



Silica supported boron trifluoride nanoparticles ($\text{BF}_3\text{-SiO}_2$ NPs): An efficient and reusable catalyst for one-pot synthesis of benzo[*a*]xanthene-11-one derivatives

B. Sadeghi*

Department of Chemistry, Yazd Branch, Islamic Azad University, Yazd, P.O. Box 89195-155, Iran.

Received 17 November 2012; received in revised form 30 June 2013; accepted 14 January 2014

KEYWORDS

Silica supported boron trifluoride nanoparticles;
 Dimedone;
 2-naphthol;
 Aromatic aldehydes;
 Xanthenes.

Abstract. An efficient and convenient synthesis of benzo[*a*]xanthene-11-one derivatives has been achieved by a one-pot, three-component reaction of various aromatic aldehydes with 2-naphthol and dimedone in the presence of Silica supported boron trifluoride nanoparticles ($\text{BF}_3\text{-SiO}_2$ NPs) as a mild solid acid catalyst in improved yields.

© 2014 Sharif University of Technology. All rights reserved.

1. Introduction

Recently, multi-component, one-pot syntheses have become one of the most attractive reactions due to their vast applications. Xanthene and benzoxanthene synthesis are widely applied in pharmaceutical chemistry for important biological properties, including antiviral [1], anti-inflammatory [2] and antibacterial [3] activities. These are being used as antagonists for paralyzing action of zoxazolamine [4] and in photodynamic therapy [5,6]. Furthermore, these compounds can be used as dyes [7], in laser technologies [8] and as pH sensitive fluorescent materials for visualization of biomolecules [9]. The synthesis of benzo[*a*]xanthene-11-ones has been reported in the presence of TCCA [10], SSA [11], InCl_3 [12], $\text{HClO}_4\text{-SiO}_2$ [13], PWA [14], Ph_3CCl [15], HY Zeolite [16], $\text{CeCl}_3\cdot 7\text{H}_2\text{O}$ [17] and $\text{Sr}(\text{OTf})_2$ [18]. In this work, application of a solid phase acidic green nano catalyst has been investigated for synthesis of benzo[*a*]xanthene-11-one derivatives.

2. Results and discussion

In continuation of previous research into the use of solid acids in organic synthesis [19,20], synthesis of benzo[*a*]xanthene-11-one derivatives has been investigated by three-component condensation of aldehydes **1**, dimedone **2** and 2-naphthol **3**, in the presence of a $\text{BF}_3\text{-SiO}_2$ NPs catalyst.

In this work, $\text{BF}_3\text{-SiO}_2$ nanoparticles were prepared via adsorption method. Since boron trifluoride is a liquid and reacts with the moisture to form HF, the supported form is preferable and used effectively as a catalyst. Solid supported catalysts have improved activity and selectivity than liquid form. Based on previous results [21], the following structure has been suggested for $\text{BF}_3\text{-SiO}_2$ NPs (Scheme 1).

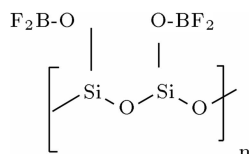
The dimensions of nanoparticles were observed with SEM. The size of commercial $\text{BF}_3\text{-SiO}_2$ nanoparticles is about 30-40 nm (Figure 1).

To optimize the reaction conditions, the study was initiated by using benzaldehyde, dimedone and 2-naphthol as a model substrates for the preparation of **4a**. The efficiency of $\text{BF}_3\text{-SiO}_2$ NPs was compared

*. E-mail address: sadeghi@iauyazd.ac.ir

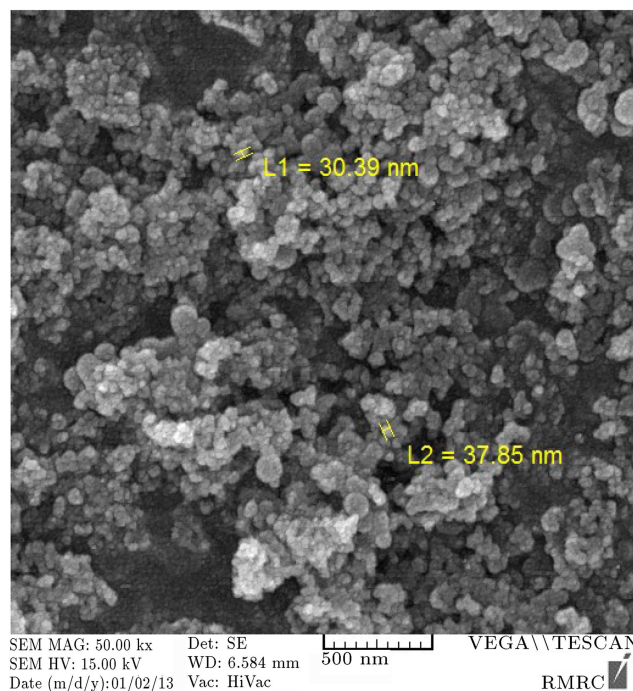
Table 1. Synthesis of 12-phenyl-9,9-dimethyl-8,9, 10,12-tetrahydrobenzo [a]xanthen-11-one under various condition.

Entry	Catalyst (mol%)(g)	Cond./Sol.	Time (min)	Yield ^a (%)	Ref.
1	TCCA ((5))	110°C/-	40	80	10
2	SSA (0.08)	80°C/-	60	83	11
3	InCl ₃ ((30))	120°C/-	30	84	12
4	HClO ₄ -SiO ₂ ((5))	80°C/-	72	89	13
5	PWA ((5))	60°C/-	70	86	14
6	Ph ₃ CCl ((7 mol))	110°C/-	50	89	15
7	HY zeolite (0.02)	80°C/-	60	93	16
8	CeCl ₃ .7H ₂ O ((3))	50°C/MeOH	120	90	17
9	Sr(OTf) ₂ ((10))	80°C/ClCH ₂ CH ₂ Cl	300	85	18
10	28% BF ₃ -SiO ₂ NPs (0.1)	80°C/-	20	47	-
11	33% BF ₃ -SiO ₂ NPs (0.1)	80°C/-	20	54	-
12	37% BF ₃ -SiO ₂ NPs (0.04)	80°C/-	20	72	-
13	37% BF ₃ -SiO ₂ NPs (0.08)	80°C/-	20	85	-
14	37% BF ₃ -SiO ₂ NPs (0.1)	80°C/-	20	85	-
15	37% BF ₃ -SiO ₂ NPs (0.08)	Reflux/EtOH	20	92	-
16	37% BF ₃ -SiO ₂ NPs (0.08)	Reflux/H ₂ O	20	80	-
17	37% BF ₃ -SiO ₂ NPs (0.08)	Reflux/CH ₂ Cl ₂	20	85	-
18	37% BF ₃ -SiO ₂ NPs (0.08), 2nd run	Reflux/EtOH	20	88	-
19	37% BF ₃ -SiO ₂ NPs (0.08), 3rd run	Reflux/EtOH	20	85	-

^a: Isolated yield.**Scheme 1.** Structure for BF₃-SiO₂ NPs.

with some other catalysts, such as 1,3,5-trichloro-2,4,6-triazinetrion, silica sulfuric acid, InCl₃, HClO₄-SiO₂ and Sr(OTf)₂. According to obtained data, TCCA and SSA have less yield. InCl₃ was applied (30 mol%) and showed harsh reaction conditions, and Sr(OTf)₂ had long reaction time. These results clearly show the advantages of this methodology over other protic or Lewis acid catalyzed benzo[a]xanthene-11-one synthesis, such as low consumption of the catalyst and short reaction time.

In order to determine the optimum quantity of BF₃-SiO₂ NPs, a model reaction was carried out at 80°C under solvent free condition (Table 1, entry 10-14). 37% BF₃-SiO₂ NPs (0.08 g) gave an excellent yield in 20 min (Table 1, entry 13). The above reaction was also examined in various solvents. The best results were obtained when EtOH was used as a solvent at reflux (Table 1, entry 15). An interesting feature of this approach is that the catalyst can be regenerated at the end of the reaction and can be used multiple times without losing its activity. To recover the catalyst, after completion of the reaction, the mixture was

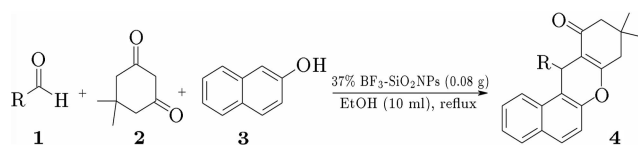
**Figure 1.** The SEM image of BF₃-SiO₂ NPs.

filtered and recrystallized from hot ethanol, catalyst was separated and washed with CHCl₃ and then the solid residue was dried. This process was repeated for two cycles and the yield of product **4a** did not change significantly (Table 1, entries 18 and 19).

Table 2. The synthesis of benzo[*a*]xanthene-11-one derivatives catalyzed by BF₃-SiO₂ NPs.

Entry	<i>R</i>	Product	Time/min	Yield% ^a	m.p./°C	
					Found	Reported ^[Ref.]
1	C ₆ H ₅	4a	15	92	149-151	150-151 ^[10]
2	3-NO ₂ C ₆ H ₄	4b	20	95	170-172	168-170 ^[12]
3	4-ClC ₆ H ₄	4c	15	86	180-182	180-182 ^[12]
4	2-ClC ₆ H ₄	4d	20	89	178-180	179-180 ^[12]
5	4-FCH ₃	4e	15	95	184-187	185-186 ^[14]
6	4-MeOC ₆ H ₄	4f	20	92	202-204	204-205 ^[12]
7	4-OHC ₆ H ₄	4g	20	83	222-224	223-225 ^[12]
8	3-OHC ₆ H ₄	4h	20	89	242-244	240-241 ^[12]
9	5-Br-2-OHC ₆ H ₃	4i	20	87	270-272	266-268 ^[12]
10	2,4-ClC ₆ H ₃	4j	20	96	179-181	178-180 ^[12]
11	2-MeOC ₆ H ₄	4k	20	92	162-164	167-168 ^[10]
12	4-MeC ₆ H ₄	4l	30	82	177-179	176-178 ^[12]
13	5-NO ₂ -2-OHC ₆ H ₃	4m	15	91	264-266	263-265 ^[12]
14	2-OH-3-MeOC ₆ H ₃	4n	20	87	211-213	213-215 ^[12]
15	2-NO ₂ C ₆ H ₄	4o	15	85	221-223	220-222 ^[10]
16	2-thienyl	4p	20	75	182-184	183-184 ^[17]
17	n-propyl	4q	25	78	oil	Oil ^[14]

^a: Yield refer to the pure isolated products.

**Scheme 2.** Synthesis of benzo[*a*]xanthene-11-one derivatives.

To study the scope of the reaction, a series of aromatic aldehydes, dimedone and 2-naphthol catalysed by 37% BF₃-SiO₂ NPs were examined (Scheme 2). The results are shown in Table 2. In all cases, aromatic aldehyde substituted with either electron-donating or electron-withdrawing groups underwent the reaction smoothly and gave products in good to excellent yields.

Compounds **4a-q** were characterized by their ¹H, ¹³C NMR and IR spectroscopy [10,12,14,17]. A mechanistic route is suggested for the generation of benzo[*a*]xanthene-11-ones, similar to that shown in previous literature [12], from the reaction of aldehydes, dimedone and 2-naphthol in the presence of BF₃-SiO₂ nanoparticles and BF₃-SiO₂ is shown as the catalyst in this proposed mechanism (Scheme 3). In the first step, Lewis acid sites of F₃-SiO₂ are coordinated to the oxygen of the carbonyl group, hence, the reactivity of the carbonyl group increases. Then a nucleophilic attack of 2-naphthol to the activated carbonyl groups proceeds the reaction forward. Subsequent Michael addition of the ortho-quinone methides with dimedone

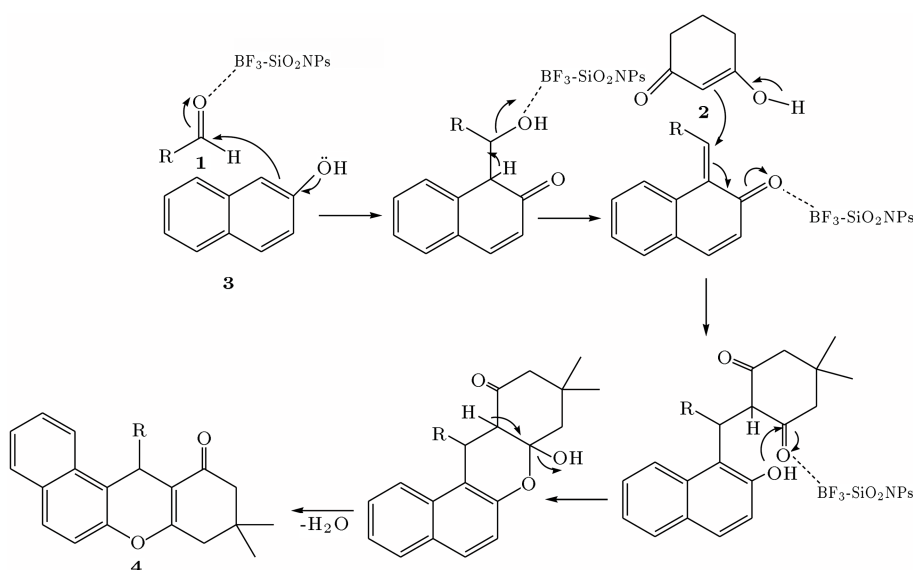
and followed by addition of the phenolic hydroxyl group to the activated carbonyl of ketone provides cyclic hemiketal which on dehydration afforded **4**.

3. Conclusions

In summary, BF₃-SiO₂ NPs has been prepared as a new catalyst and it has been shown that it has advantages in the preparation of benzo[*a*]xanthene-11-ones. These advantages include shorter reaction times, simple work-up, and excellent yields. As a significant conclusion, the solid phase acidic catalyst was re-usable for a number of times without appreciable loss of activity. Also, the present method does not involve any hazardous organic solvent, and, therefore, this procedure could be classified as green chemistry.

4. Materials and methods

Chemicals and apparatus. The chemicals for this work were purchased from Fluka (Buchs, Switzerland) and were used without further purification. Melting points were determined with an Electrothermal 9100 apparatus. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ¹H and ¹³C NMR spectra were recorded on a Bruker DRX-300 Avance spectrometer. The morphology of the catalyst was observed using an SEM model VEGA//TESCAN with an accelerating voltage of 15 kV.



Scheme 3. Plausible mechanism for the formation of benzo[a]xanthenes-11-one derivatives.

4.1. Preparation of nanoparticles silica supported boron trifluoride

The reagent was prepared by stirring a mixture of 0.6 g $\text{BF}_3\cdot\text{OEt}_2$ (4.2 mmol) and 0.4 g of nano silica gel in 5 ml of ethanol for 1 h at room temperature. The slurry was dried slowly on a rotary evaporator at 40°C . The obtained solid (37% NPs $\text{BF}_3\text{-SiO}_2$) was dried at an ambient temperature for 2 h and then stored in a dry container for at least 3 months. The dimensions of nanoparticles were observed with SEM (Figure 1). The sizes of nanoparticles are between 30-40 nm.

4.2. General procedure

37% NPs $\text{BF}_3\text{-SiO}_2$ (0.08 g) was added to a stirred mixture of the aromatic aldehyde (1 mmol), dimedone (1 mmol) and 2-naphthol in EtOH (10 mL). The reaction mixture was then refluxed for an appropriate time (Table 2). The progress of the reaction was followed by TLC (*n*-hexane:ethylacetate, 3:1). After completion of the reaction, the mixture was filtered to remove the catalyst. After evaporation of the solvent, the crude product was recrystallized to afford the pure product.

4.3. Spectral data of the products

4.3.1. 9,9-dimethyl-12-phenyl-8,9,10,12-tetrahydrobenzo[a]xanthene-11-one (4a)

White solid; IR (KBr, cm^{-1}): 3057, 2946, 1653, 1376, 1231, 1169; ^1H NMR (300 MHz, CDCl_3): δ 7.96 (d, $J = 8.1$ Hz, 1H), 7.73-7.78 (m, 2H), 7.02-7.42 (m, 8H), 5.70 (s, 1H), 2.57 (s, 2H), 2.32 (d, $J = 16.2$ Hz, 1H), 2.26 (d, $J = 16.2$ Hz, 1H), 1.11 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 198.8, 163.4, 147.7, 144.6, 131.3, 131.1, 128.9, 128.5, 128.2, 128.0, 126.9, 126.2, 124.8, 123.6, 117.5, 117.0, 112.9, 50.8, 41.2, 34.6, 32.3, 29.2, 27.1.

4.3.2. 9,9-dimethyl-12-(3-nitrophenyl)-8,9,10,12-tetrahydrobenzo[a]xanthene-11-one (4b)

White solid; IR (KBr, cm^{-1}): 3067, 2955, 1647, 1535, 1374, 1227, 1174; ^1H NMR (300 MHz, CDCl_3): δ 8.09 (s, 1H), 7.82-7.96 (m, 5H), 7.35-7.48 (m, 4H), 5.81 (s, 1H), 2.63 (s, 2H), 2.41 (d, $J = 16.2$ Hz, 1H), 2.24 (d, $J = 16.2$ Hz, 1H), 1.14 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 196.7, 164.2, 146.9, 145.7, 145.6, 132.9, 131.2, 130.8, 129.5, 129.0, 128.4, 126.3, 125.4, 123.8, 123.3, 121.5, 117.6, 115.8, 113.6, 51.2, 43.4, 35.7, 32.2, 29.2, 27.2.

4.3.3. 12-(4-chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthene-11-one (4c)

White solid; IR (KBr, cm^{-1}): 3051, 2963, 1645, 1478, 1225, 1146; ^1H NMR (300 MHz, CDCl_3): δ 7.88 (d, $J = 8.1$ Hz, 1H), 7.76-7.78 (m, 2H), 7.13-7.45 (m, 7H), 5.67 (s, 1H), 2.57 (s, 2H), 2.32 (d, $J = 16.2$, 1H), 2.26 (d, $J = 16.2$ Hz, 1H), 1.12 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 197.2, 165.8, 151.6, 146.7, 142.1, 134.2, 131.2, 129.6, 129.2, 128.4, 127.3, 125.6, 123.6, 123.2, 117.2, 114.7, 50.9, 42.9, 37.3, 34.5, 29.7, 27.2.

4.3.4. 12-(2-chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthene-11-one (4d)

White solid; IR (KBr, cm^{-1}): 3073, 2936, 1648, 1467, 1229, 1179; ^1H NMR (300 MHz, CDCl_3): δ 8.24 (d, $J = 8.4$ Hz, 1H), 7.76-7.79 (m, 2H), 7.23-7.49 (m, 5H), 6.98-7.075 (m, 2H), 5.67 (s, 1H), 2.57 (s, 2H), 2.32 (d, $J = 16.2$, 1H), 2.24 (d, $J = 16.2$ Hz, 1H), 1.13 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 196.2, 164.8, 147.6, 142.7, 132.1, 131.6, 131.4, 131.1, 129.8, 129.0, 128.3, 127.6, 127.0, 126.2, 124.2, 123.8, 117.3, 117.0, 114.7, 50.7, 41.9, 32.3, 32.1, 29.3, 27.1.

4.3.5. 12-(4-fluorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]-xanthene-11-one (**4e**)

White solid; IR (KBr, cm^{-1}): 3059, 2933, 1649, 1465, 1227, 1184; ^1H NMR (300 MHz, CDCl_3): δ 7.92 (d, $J = 8.4$ Hz, 1H), 7.75-7.78 (m, 2H), 7.27-7.43 (m, 5H), 6.87 (t, $J = 8.4$ Hz, 2H), 5.68 (s, 1H), 2.53 (s, 2H), 2.32 (d, $J = 16.2$ Hz, 1H), 2.24 (d, $J = 16.2$ Hz, 1H), 1.10 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 197.2, 164.1, 147.6, 140.7, 131.5, 131.2, 129.6, 129.2, 128.4, 127.3, 125.6, 123.6, 117.2, 117.5, 115.9, 115.0, 114.2, 51.0, 41.9, 34.3, 32.5, 29.5, 27.2.

4.3.6. 12-(4-methoxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]-xanthene-11-one (**4f**)

White solid; IR (KBr, cm^{-1}): 3056, 2945, 1643, 1229, 1172; ^1H NMR (300 MHz, CDCl_3): δ 7.98 (d, $J = 8.1$ Hz, 1H), 7.73-7.77 (m, 2H), 7.22-7.46 (m, 5H), 6.71 (d, $J = 8.4$ Hz, 2H), 5.71 (s, 1H), 3.64 (s, 3H), 2.55 (s, 2H), 2.34 (d, $J = 16.2$ Hz, 1H), 2.26 (d, $J = 16.2$ Hz, 1H), 1.16 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 196.4, 163.7, 154.7, 143.2, 136.0, 131.4, 130.7, 130.2, 128.3, 126.1, 126.0, 125.9, 123.8, 122.1, 117.2, 116.8, 116.9, 113.3, 112.5, 51.9, 49.2, 40.0, 32.4, 32.0, 27.9, 26.0.

4.3.7. 12-(4-hydroxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]-xanthene-11-one (**4g**)

White solid; IR (KBr, cm^{-1}): 3409, 3053, 2951, 1640, 1575, 1222, 1173; ^1H NMR (300 MHz, CDCl_3): δ 7.99 (d, $J = 8.1$ Hz, 1H), 7.74-7.78 (m, 2H), 7.15-7.45 (m, 5H), 6.68 (d, $J = 8.4$ Hz, 2H), 5.69 (s, 1H), 5.64 (s, 1H), 2.56 (s, 2H), 2.36 (d, $J = 16.2$ Hz, 1H), 2.32 (d, $J = 16.2$ Hz, 1H), 1.12 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 198.3, 164.5, 154.3, 146.4, 134.6, 131.7, 131.3, 129.2, 128.6, 128.3, 126.5, 123.9, 123.2, 117.8, 117.0, 115.2, 114.9, 51.2, 41.3, 34.7, 32.2, 29.1, 27.0.

4.3.8. 12-(3-hydroxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]-xanthene-11-one (**4h**)

White solid; IR (KBr, cm^{-1}): 3405, 2956, 1638, 1589, 1227, 1170; ^1H NMR (300 MHz, CDCl_3): δ 7.98 (d, $J = 8.1$ Hz, 1H), 7.73-7.79 (m, 2H), 7.30-7.45 (m, 3H), 7.02 (t, $J = 7.8$ Hz, 1H), 6.93 (s, 1H), 6.81 (d, $J = 7.5$ Hz, 1H), 6.54 (d, $J = 6.2$ Hz, 1H), 5.67 (s, 1H), 5.41 (s, 1H), 2.56 (s, 2H), 2.34 (d, $J = 16.2$ Hz, 1H), 2.31 (d, $J = 16.2$ Hz, 1H), 1.11 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 198.2, 164.5, 148.2, 147.5, 146.3, 132.2, 131.5, 130.9, 129.7, 129.0, 128.7, 127.5, 125.1, 123.4, 123.0, 121.7, 117.0, 115.9, 114.2, 50.7, 41.3, 34.9, 31.9, 29.2, 27.0.

4.3.9. 12-(5-bromo-2-hydroxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]-xanthene-11-one (**4i**)

White solid; IR (KBr, cm^{-1}): 3275, 2963, 1624, 1227, 1143; ^1H NMR (300 MHz, CDCl_3): δ 7.80-7.84 (m,

2H), 7.24-7.58 (m, 4H), 7.10 (d, $J = 6.0$ Hz, 1H), 6.92 (d, $J = 8.4$ Hz, 1H), 6.65 (s, 1H), 5.74 (s, 1H), 4.75 (s, 1H), 2.70 (d, $J = 16.8$ Hz, 1H), 2.61 (d, $J = 16.8$ Hz, 1H), 2.45 (d, $J = 16.2$ Hz, 1H), 2.36 (d, $J = 16.2$ Hz, 1H), 1.13 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 199.8, 167.3, 151.9, 147.7, 134.8, 133.9, 131.6, 131.0, 130.6, 129.5, 128.3, 128.0, 125.2, 123.0, 121.9, 120.8, 116.4, 113.9, 113.1, 51.4, 41.5, 32.9, 29.7, 28.8, 27.3.

4.3.10. 12-(2,4-dichlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]-xanthene-11-one (**4j**)

White solid; IR (KBr, cm^{-1}): 3068, 2984, 1652, 1229, 1147; ^1H NMR (300 MHz, CDCl_3): δ 8.09 (d, $J = 8.4$ Hz, 1H), 7.71-7.76 (m, 2H), 7.36-7.49 (m, 2H), 7.21-7.29 (m, 3H), 7.04 (d, $J = 6.8$ Hz, 1H), 5.93 (s, 1H), 2.60 (s, 2H), 2.37 (d, $J = 16.2$ Hz, 1H), 2.26 (d, $J = 16.2$ Hz, 1H), 1.14 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 196.9, 164.7, 147.6, 140.2, 133.6, 132.8, 132.6, 131.9, 131.2, 130.1, 129.3, 128.4, 127.5, 127.0, 125.3, 123.9, 117.0, 115.8, 114.3, 50.2, 41.6, 32.6, 32.1, 29.0, 27.2.

4.3.11. 12-(2-methoxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]-xanthene-11-one (**4k**)

White solid; IR (KBr, cm^{-1}): 3072, 2928, 1645, 1235, 1184; ^1H NMR (300 MHz, CDCl_3): δ 8.31 (d, $J = 8.4$ Hz, 1H), 7.68-7.74 (m, 2H), 7.25-7.45 (m, 4H), 7.05 (t, $J = 7.2$ Hz, 1H), 6.77-6.83 (m, 2H), 5.94 (s, 1H), 3.94 (s, 3H), 2.58 (s, 2H), 2.31 (d, $J = 16.2$ Hz, 1H), 2.22 (d, $J = 16.2$ Hz, 1H), 1.14 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 198.3, 164.2, 156.3, 148.4, 133.2, 131.9, 131.0, 130.5, 128.2, 128.1, 127.4, 126.7, 124.3, 121.9, 120.6, 118.2, 116.9, 112.9, 111.0, 59.1, 50.8, 41.6, 32.5, 32.2, 29.4, 27.0.

4.3.12. 9,9-dimethyl-12-p-tolyl-8,9,10,12-tetrahydrobenzo[a]-xanthene-11-one (**4l**)

White solid; IR (KBr, cm^{-1}): 3067, 2965, 1643, 1378, 1221, 1018; ^1H NMR (300 MHz, CDCl_3): δ 7.99 (d, $J = 8.4$ Hz, 1H), 7.64-7.79 (m, 2H), 7.38-7.40 (m, 1H), 7.30-7.34 (m, 2H), 7.14-7.25 (m, 2H), 7.03 (d, $J = 8.0$ Hz, 2H), 4.79 (s, 1H), 2.55 (s, 2H), 2.45 (d, $J = 16.3$ Hz, 1H), 2.21 (d, $J = 16.3$ Hz, 1H), 2.16 (s, 3H), 1.10 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 196.2, 164.1, 153.2, 146.3, 141.2, 134.5, 133.6, 130.2, 128.6, 127.8, 127.2, 126.5, 125.9, 123.9, 122.5, 117.2, 116.0, 115.9, 113.1, 49.5, 40.2, 33.1, 31.0, 28.4, 26.0, 19.4.

4.3.13. 12-(5-nitro-2-hydroxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]-xanthene-11-one (**4m**)

White solid; IR (KBr, cm^{-1}): 3372, 2927, 1631, 1513, 1342, 1219, 1110; ^1H NMR (300 MHz, CDCl_3): δ 10.98 (s, 1H), 7.82-7.94 (m, 3H), 7.35-7.51 (m, 5H), 7.09 (d, $J = 8.6$ Hz, 1H), 5.68 (s, 1H), 2.76 (d, $J = 17.7$ Hz,

1H), 2.63 (d, $J = 17.7$ Hz, 1H), 2.45 (d, $J = 17.2$ Hz, 1H), 2.40 (d, 17.2 Hz, 1H), 1.19 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 199.3, 167.5, 159.2, 147.9, 143.0, 132.9, 131.7, 130.4, 130.1, 129.0, 127.7, 125.6, 125.1, 124.3, 122.6, 119.2, 116.2, 114.8, 112.0, 51.9, 41.5, 32.4, 29.1, 28.1, 27.0.

4.3.14. 12-(2-hydroxy-3-methoxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]-xanthene-11-one (**4n**)

White solid; IR (KBr, cm^{-1}): 3198, 3065, 2964, 1643, 1225, 1109; ^1H NMR (300 MHz, CDCl_3): δ 8.64 (s, 1H), 7.74–7.85 (m, 3H), 7.22–7.39 (m, 3H), 6.57–6.59 (m, 2H), 6.36 (d, $J = 4.5$ Hz, 1H), 5.83 (s, 1H), 3.89 (s, 3H), 2.59 (s, 2H), 2.41 (d, $J = 16.2$ Hz, 1H), 2.33 (d, $J = 16.2$ Hz, 1H), 1.13 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 198.6, 164.3, 147.9, 147.3, 142.2, 133.7, 131.3, 131.2, 128.9, 128.1, 127.5, 125.1, 123.8, 121.2, 120.0, 117.5, 116.7, 114.0, 109.0, 56.2, 50.2, 41.5, 32.6, 29.0, 28.2, 27.3.

4.3.15. 9,9-dimethyl-12-(2-nitrophenyl)-8,9,10,12-tetrahydrobenzo[a]-xanthene-11-one (**4o**)

Pale yellow solid; IR (KBr, cm^{-1}): 3074, 2985, 1674, 1534, 1369, 1228, 1143; ^1H NMR (300 MHz, CDCl_3): δ 8.56 (d, $J = 8.1$ Hz, 1H), 7.71–7.81 (m, 3H), 7.03–7.38 (m, 6H), 6.59 (s, 1H), 2.60 (d, $J = 17.4$ Hz, 1H), 2.52 (d, $J = 17.4$ Hz, 1H), 2.31 (d, $J = 16.2$ Hz, 1H), 2.22 (d, $J = 16.2$ Hz, 1H), 1.11 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 196.6, 164.5, 149.2, 142.3, 132.9, 131.4, 131.1, 131.0, 129.7, 129.1, 128.3, 127.4, 127.2, 126.4, 124.2, 123.9, 117.6, 117.0, 113.2, 50.4, 41.4, 34.9, 31.9, 29.4, 27.2.

4.3.16. 9,9-dimethyl-12-(thiophen-2-yl)-8,9,10,12-tetrahydrobenzo[a]-xanthene-11-one (**4p**)

White solid; IR (KBr, cm^{-1}): 3087, 2953, 1677, 1362, 1212, 1177; ^1H NMR (300 MHz, CDCl_3): δ 7.74–7.78 (m, 2H), 7.65 (d, $J = 8.5$ Hz, 1H), 7.28–7.39 (m, 3H), 7.19–7.25 (m, 1H), 7.09–7.16 (m, 2H), 5.57 (s, 1H), 3.65 (s, 2H), 2.46 (s, 2H), 1.25 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 196.5, 164.3, 148.4, 148.1, 131.5, 129.2, 128.6, 127.1, 126.4, 125.0, 124.9, 124.2, 123.4, 117.3, 117.2, 114.0, 51.0, 41.2, 32.4, 29.4, 29.2, 27.1.

4.3.17. 9,9-dimethyl-12-propyl-8,9,10,12-tetrahydrobenzo[a]-xanthene-11-one (**4q**)

Colorless liquid; IR (KBr, cm^{-1}): 3072, 2949, 2913, 1627, 1467, 1395, 1226, 1146; ^1H NMR (300 MHz, CDCl_3): δ 8.3 (d, $J = 8.8$ Hz, 1H), 7.83 (d, $J = 8.8$ Hz, 1H), 7.71 (d, $J = 8.8$ Hz, 1H), 7.55 (d, $J = 7.6$ Hz, 1H), 7.45 (d, $J = 7.6$ Hz, 1H), 7.2 (d, $J = 8.8$ Hz, 1H), 4.76 (t, $J = 4.4$ Hz, 1H), 2.54 (d, $J = 17.6$ Hz, 2H), 2.40 (d, $J = 16.4$ Hz, 2H), 1.77–1.83 (m, 2H), 1.22 (s, 3H), 1.15 (s, 3H), 0.89–0.98 (m, 2H), 0.76 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 197.7, 166.3, 148.4, 145.0,

131.5, 131.2, 128.6, 128.1, 124.3, 123.7, 118.4, 116.7, 112.7, 51.1, 41.5, 37.3, 32.3, 29.9, 28.0, 27.3, 18.5, 14.2.

Acknowledgements

The research Council of the Islamic Azad University of Yazd is gratefully acknowledged for its financial support of this work.

References

1. Jamison, J.M., Krabill, K., Hatwalkar, A., Jamison, E. and Tsai, C.C. "Potentiation of the antiviral activity of poly r(A-U) by Xanthene dyes", *Cell. Biol. Int. Rep.*, **14**, pp. 1075–1084 (1990).
2. Poupelin, J.P., Saint-Ruf, G., Foussard-Blanpin, O., Narcisse, G., Uchida-Ernouf, G. and Lacroix, R. "Synthesis and antiinflammatory properties of bis(2-hydroxy-1-naphthyl)methane derivatives. I. Monosubstituted derivatives", *Eur. J. Med. Chem.*, **13**, pp. 67–71 (1978).
3. Qiao, Y.F., Okazaki, T., Ando, T. and Mizoue, K. "Isolation and characterization of a new pyrano [4,3':6,7] naphtho [1,2-b] xanthene antibiotic FD-594", *J. Antibiotics*, **51**, pp. 282–287 (1998).
4. Saint-Ruf, G., Hieu, H.T. and Poupelin, J.P. "The effect of dibenzoxanthenes on the paralyzing action of zoxazolamine", *Naturwissenschaften*, **62**, pp. 584–585 (1975).
5. Ion, R.M. "PDT- a photosensitization or a photocatalytic process", *Progr. Catal.*, **2**, pp. 55–76 (1997).
6. Ion, R.M., Frackowiak, D., Planner, A. and Wiktorowicz, K. "The incorporation of various porphyrins into human blood cells", *Acta Biochim. Pol.*, **45**, pp. 833–845 (1998).
7. Banerjee, A. and Mukherjee, A.K. "Chemical aspects of santalin as a histological stain", *Stain Technol.*, **56**, pp. 83–85 (1981).
8. Ahmad, M., King, T.A., Ko, D.-K., Cha, B.H. and Lee, J. "Performance and photostability of xanthene and pyrromethene laser dyes in sol-gel phases", *J. Phys. D: Appl. Phys.*, **35**, pp. 1473–1476 (2002).
9. Knight, C.G. and Stephens, T. "Xanthene-dye-labelled phosphatidylethanolamines as probes of interfacial pH. Studies in phospholipid vesicles", *Biochem. J.*, **258**, pp. 683–687 (1989).
10. Maleki, B., Gholizadeh, M. and Sepehr, Z. "1,3,5-trichloro-2,4,6-triazinetriol: A versatile heterocycle for the one-pot synthesis of 14-aryl- or alkyl-14H-dibenzo [a, j] xanthene, 1,8-dioxooctahydroxanthene and 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthene-11-one derivatives under solvent-free conditions", *Bull. Korean Chem. Soc.*, **32**, pp. 1697–1701 (2011).
11. Nazeruddin, G.M., Pandharpatte, M.S. and Mulani, K.B. "Heterogeneous catalyst: Silica sulfuric acid catalyzed synthesis of 9,10-dihydro-12-aryl-8H-benzo[a]xanthene-11(12H)-one derivatives under

- solvent-free conditions", *Indian J. Chem.*, **50B**, pp. 1532-1537 (2011).
12. Nandi, G.C., Samai, S., Kumar, R. and Singh, M.S. "An efficient one-pot synthesis of tetrahydrobenzo[a]xanthene-11-one and diazabenzo[a]anthracene-9,11-dione derivatives under solvent free condition", *Tetrahedron*, **65**, pp. 7129-7134 (2009).
 13. Mo, L.P. and Chen, H.L. "One-pot, three-component condensation of aldehydes, 2-naphthol and 1,3-dicarbonyl compounds", *J. Chin. Chem. Soc.*, **57**, pp. 157-161 (2010).
 14. Wang, H.J., Ren, X.Q., Zhang, Y.Y. and Zhang, Z.H. "Synthesis 12-aryl or 12-alkyl-8,9,10,12-tetrahydrobenzo[a]xanthene-11-one derivatives catalyzed by dodecatungstophosphoric Acid", *J. Braz. Chem. Soc.*, **20**, pp. 1939-1943 (2009).
 15. Khazaei, A., Zolfigol, M.A., Moosavi-Zare, A.R., Zare, A., Khojasteh, M., Asgari, Z., Khakyzadeh, V. and Khalafi-Nezhad, A. "Organocatalyst trityl chloride efficiently promoted the solvent-free synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]-xanthene-11-ones by in situ formation of carbocationic system in neutral media", *Catal. Commun.*, **20**, pp. 54-57 (2012).
 16. Rama, V., Kanagaraj, K. and Pitchumani, K. "A multicomponent, solvent-free, one-pot synthesis of benzoxanthenones catalyzed by HY zeolite: their antimicrobial and cell imaging studies", *Tetrahedron Lett.*, **53**, pp. 1018-1024 (2012).
 17. Kidwai, M., Jahan, A. and Mishra, N.K. "A novel method for the synthesis of tetrahydrobenzo[a]-xanthene-11-one derivatives using cerium (III) chloride as a highly efficient catalyst", *C. R. Chimie*, **15**, pp. 324-330 (2012).
 18. Li, J., Tang, W., Lu, L., Su, W. "Strontium triflate catalyzed one-pot condensation of β -naphthol, aldehydes and cyclic 1,3-dicarbonyl compounds", *Tetrahedron Lett.*, **49**, pp. 7117-7120 (2008).
 19. Sadeghi, B., Mirjalili, B.F., Bidaki, S. and Ghasemkhani, M. "SbCl₅.SiO₂: an efficient alternative for one-pot synthesis of 1,2,4,5-tetrasubstituted imidazoles in solvent or under solvent-free condition", *J. Iran. Chem. Soc.*, **8**, pp. 648-652 (2011).
 20. Sadeghi, B., Hassanabadi, A. and Bidaki, S. "Synthesis of nanoparticles silica sulfuric acid (NPs SiO₂-OSO₃H): a solid phase acidic catalyst for one-pot synthesis of 4H-chromene derivatives", *J. Chem. Res.*, **35**, pp. 666-668 (2011).
 21. Mirjalili, B.F., Bamoniri, A. and Akbari, A. "One-pot synthesis of 3,4-dihydropyrimidin-2(1H)-ones (thiones) promoted by nano-BF₃.SiO₂", *J. Iran. Chem. Soc.*, **8**, pp. 135-140 (2011).

Biography

Bahareh Sadeghi was born in Tehran, Iran, in 1978. She received her BS degree in Applied Chemistry from the Islamic Azad University, Shahreza, Iran, in 1999, her MS degree in Organic Chemistry from Mazandaran University, Iran, in 2003, and her PhD from the Islamic Azad University, Science and Research Campus, Tehran, Iran, in 2008. She is currently faculty member of the Islamic Azad University, Yazd, Iran. Her research interests include applications of solvent-free conditions, new solid-supported reagents, especially nano silica-based resins, study of methodology in organic chemistry, and green chemistry.