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Silica supported boron trifluoride nanoparticles (BF_3-SiO_2 NPs): An efficient and reusable catalyst for one-pot synthesis of benzo[*a*]xanthene-11-one derivatives

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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 (BF_3-SiO_2 NPs) as a mild solid acid catalyst in improved yields.

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*]xanthen-11-ones has been reported in the presence of TCCA [10], SSA [11], $InCl_3$ [12], $HClO_4$-SiO_2 [13], PWA [14], Ph_3CCl [15], HY Zeolite [16], $CeCl_3.7H_2O$ [17] and $Sr(OTf)_2$ [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.

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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 BF_3-SiO_2 NPs catalyst.

In this work, BF_3-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 BF_3-SiO_2 NPs (Scheme 1).

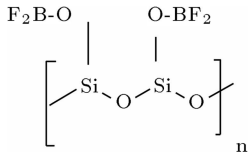
The dimensions of nanoparticles were observed with SEM. The size of commercial BF_3-SiO_2 nanoparticles is about 30-40 nm (Figure 1).

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 BF_3-SiO_2 NPs was compared

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_3CCl ((7 mol))	110°C/-	50	89	15
7	HY zeolite (0.02)	80°C/-	60	93	16
8	$CeCl_3.7H_2O$ ((3))	50°C/MeOH	120	90	17
9	$Sr(OTf)_2$ ((10))	80°C/$ClCH_2CH_2Cl$	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_2O	20	80	-
17	37% BF_3-SiO_2 NPs (0.08)	Reflux/CH_2Cl_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 BF_3-SiO_2 NPs.

with some other catalysts, such as 1,3,5-trichloro-2,4,6-triazinetrion, silica sulfuric acid, $InCl_3$, $HClO_4$-SiO_2 and $Sr(OTf)_2$. According to obtained data, TCCA and SSA have less yield. $InCl_3$ 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 BF_3-SiO_2 NPs, a model reaction was carried out at 80°C under solvent free condition (Table 1, entry 10-14). 37% BF_3-SiO_2 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

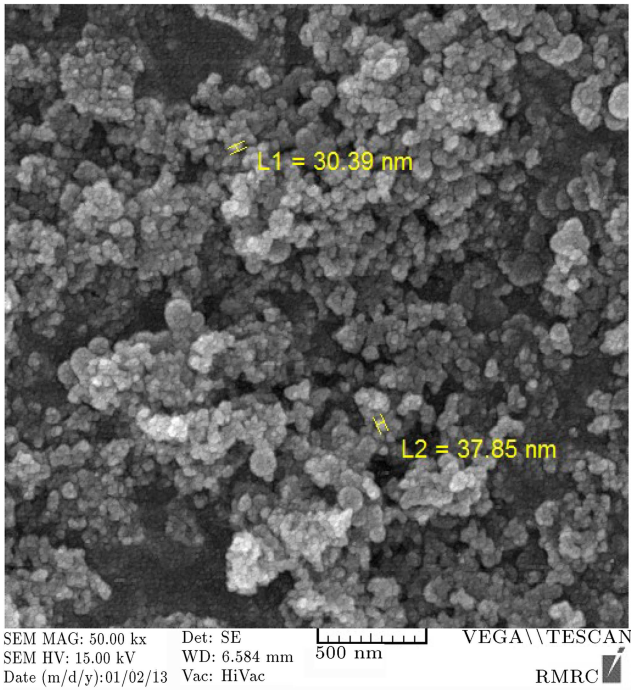


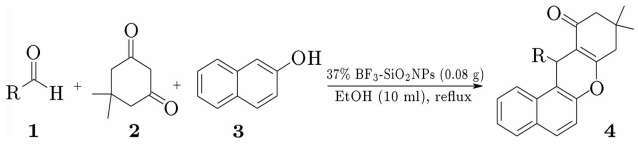
Figure 1. The SEM image of BF_3-SiO_2 NPs.

filtered and recrystallized from hot ethanol, catalyst was separated and washed with $CHCl_3$ 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 BF_3-SiO_2 NPs.

Entry	*R*	Product	Time/min	Yield%[a]	m.p./°C	
					Found	Reported[Ref.]
1	C_6H_5	**4a**	15	92	149-151	150-151[10]
2	3-$NO_2C_6H_4$	**4b**	20	95	170-172	168-170[12]
3	4-ClC_6H_4	**4c**	15	86	180-182	180-182[12]
4	2-ClC_6H_4	**4d**	20	89	178-180	179-180[12]
5	4-FCH_4	**4e**	15	95	184-187	185-186[14]
6	4-$MeOC_6H_4$	**4f**	20	92	202-204	204-205[12]
7	4-OHC_6H_4	**4g**	20	83	222-224	223-225[12]
8	3-OHC_6H_4	**4h**	20	89	242-244	240-241[12]
9	5-Br-2-OHC_6H_3	**4i**	20	87	270-272	266-268[12]
10	2,4-ClC_6H_3	**4j**	20	96	179-181	178-180[12]
11	2-$MeOC_6H_4$	**4k**	20	92	162-164	167-168[10]
12	4-MeC_6H_4	**4l**	30	82	177-179	176-178[12]
13	5-NO_2-2-OHC_6H_3	**4m**	15	91	264-266	263-265[12]
14	2-OH-3-$MeOC_6H_3$	**4n**	20	87	211-213	213-215[12]
15	2-$NO_2C_6H_4$	**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% BF_3-SiO_2 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.

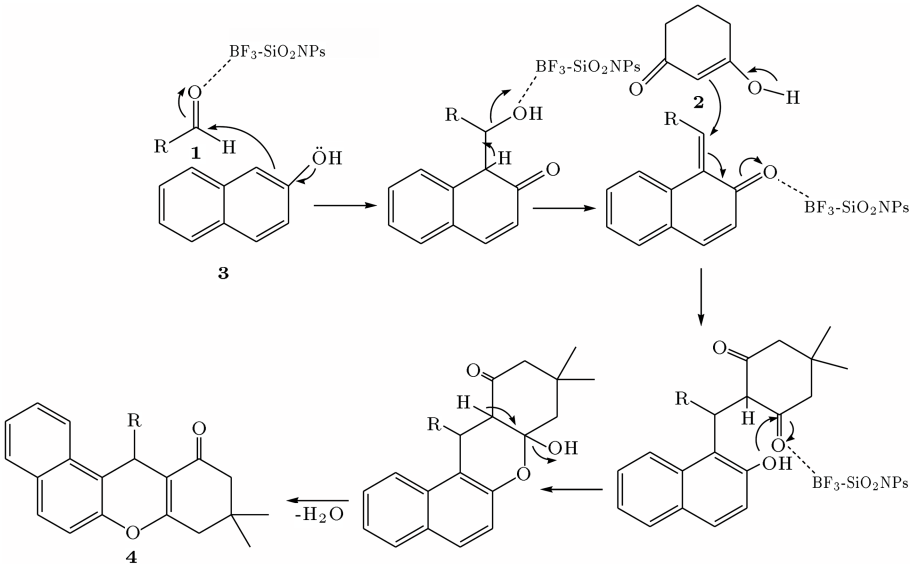
Compounds **4a-q** were characterized by their ^1H, ^{13}C NMR and IR spectroscopy [10,12,14,17]. A mechanistic route is suggested for the generation of benzo[*a*]xanthene-11-ones, similar to that shown in previous literature [12], from the reaction of aldehydes, dimedone and 2-naphthol in the presence of BF_3-SiO_2 nanoparticles and BF_3-SiO_2 is shown as the catalyst in this proposed mechanism (Scheme 3). In the first step, Lewis acid sites of F_3-SiO_2 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, BF_3-SiO_2 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 ^{13}C 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 BF3.OEt2 (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 BF3-SiO2) 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 BF_3-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; ^{1}H 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; ^{1}H 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; ^{1}H 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; ^{1}H 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; ^{1}H 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, $J = 16.2$, 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; ^{1}H 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; ^{1}H 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),3.97(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; ^{1}H 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; ^{1}H 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; ^{1}H 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, $J = 6.8$, 1H), 5.93 (s, 1H), 2.60 (s, 2H), 2.37 (2, $J = 16.2$ 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; ^{1}H 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; ^{1}H 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; ^{1}H 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, $J = 8.6$, 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; ^{1}H 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; ^{1}H 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, $J = 17.4$, 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; ^{1}H 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; ^{1}H 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, $J = 16.4$, 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.

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Biography

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