

## Microwave-assisted solvent-free synthesis of 14-aryl/alkyl-14H-dibenzo[*a,j*]xanthenes and tetrahydrobenzo[*a*]xanthen-11-ones catalyzed by nano silica phosphoric acid

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### ABSTRACT

Nano silica phosphoric acid (nano SPA) was applied as a catalyst for synthesis of 14-aryl/alkyl-14H-dibenzo[*a,j*]xanthenes and tetrahydrobenzo[*a*]xanthen-11-ones in microwave oven under solvent free conditions. High efficiency, easy availability and reusability are some advantages of this catalyst.

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## 1. Introduction

Multi-component reactions (MCRs) are special types of synthetically useful organic reactions in which three or more different starting materials react to form a product in one pot procedure<sup>1</sup>. Such reactions are atom-efficient processes by incorporating the essential parts of the starting materials into the final product. MCRs are powerful tools in the modern drug discovery process and allow the fast, automated, and high through put generation of organic compounds<sup>2</sup>.

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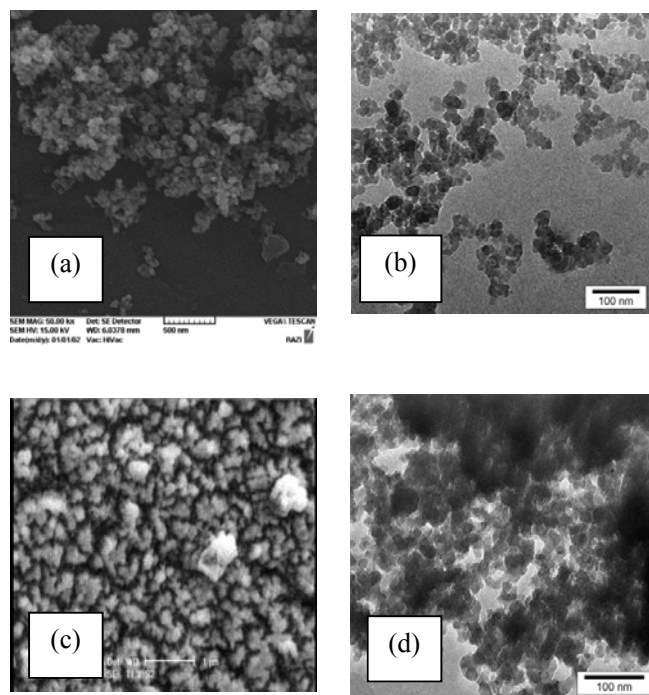
14-Aryl/alkyl-14*H*-dibenzo[*a,j*]xanthenes and tetrahydrobenzo[*a*]xanthen-11-ones are produced *via* multi-component reactions in the presence of an acidic catalyst. These compounds have important biological and pharmaceutical activities such as antibacterial and anti-inflammatory ones<sup>3</sup>. The best procedure for synthesis of 14-aryl/alkyl-14*H*-dibenzo[*a,j*]xanthene is the mixing of 2-naphthol with aldehydes in the presence of a catalyst. This procedure have been catalyzed with silica sulfuric acid<sup>4,5</sup>, Dowex-50W<sup>6</sup>, sulfamic acid<sup>7</sup>, HClO<sub>4</sub>-SiO<sub>2</sub><sup>8</sup>, cyanuric chloride<sup>9</sup>, BF<sub>3</sub>·SiO<sub>2</sub><sup>10</sup> and InCl<sub>3</sub><sup>11</sup>.

Tetrahydrobenzo[*a*]xanthenes-11-ones as benzoxanthene derivatives could be synthesized *via* one pot condensation of 2-naphthol, aldehydes and 1,3-diketones in the presence of an acidic catalyst. According to literature, this protocol was catalyzed by strontium triflate<sup>12</sup>, proline triflate<sup>13</sup>, p-toluenesulfonic acid<sup>14</sup>, ammonium fluoride<sup>15</sup> and NaHSO<sub>4</sub>·SiO<sub>2</sub><sup>16</sup>. Silica phosphoric acid (SPA) is an efficient and reusable acidic catalyst. Previously, this catalyst was applied for coupling of thiols<sup>17</sup> and synthesis of biginelli products<sup>18</sup>.

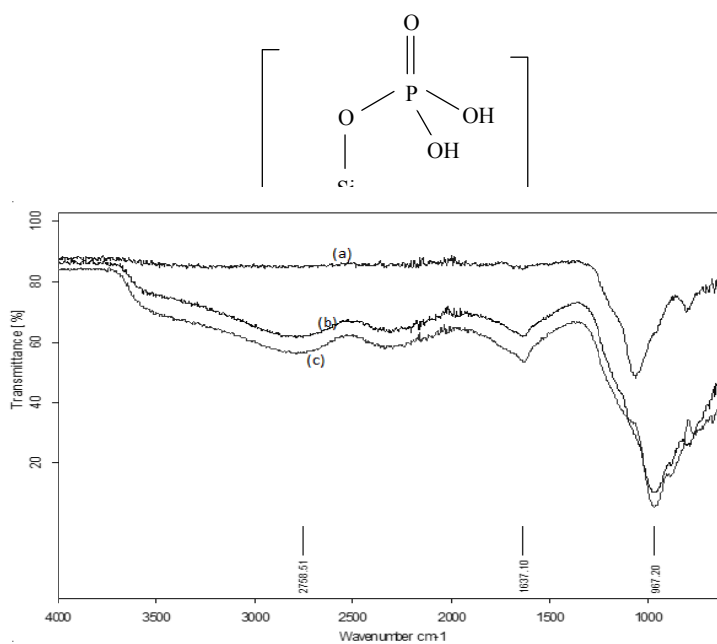
## 2. Results and Discussion

Silica phosphoric acid was prepared by reaction of silica chloride with dry phosphoric acid. It is noted that, silica chloride was prepared *via* reaction of silica gel and thionyl chloride. By using nano silica gel instead of silica gel, according to above pathway, nano silica phosphoric acid (nano-SPA) was prepared. The particle size of nano-SiO<sub>2</sub> and nano-SPA were measured by SEM and TEM imaging (Fig. 1).

The acid capacity of nano-SPA is 10.32 mmol.g<sup>-1</sup> and was determined by titration of 0.2 g of catalyst with standard solution of NaOH. The FT-IR (ATR) spectra of silica chloride, nano-SPA and H<sub>3</sub>PO<sub>4</sub>·SiO<sub>2</sub> were shown in figure 2. In all ATR spectra, the Si-O-H and Si-O-Si stretching bonds are appeared in 900 until 1100 cm<sup>-1</sup>. In silica chloride spectrum, the Si-Cl stretching bond is appeared in 700 cm<sup>-1</sup>. In ATR spectra of nano-SPA and H<sub>3</sub>PO<sub>4</sub>·SiO<sub>2</sub>, the P-O-H, P=O, P-O stretching bonds are appeared 910-1040, 1637 and 2400-2800 cm<sup>-1</sup> respectively. According to above data, we suggested one structure for nano-SPA with PO<sub>3</sub>H<sub>2</sub> on silica gel (Scheme 1).



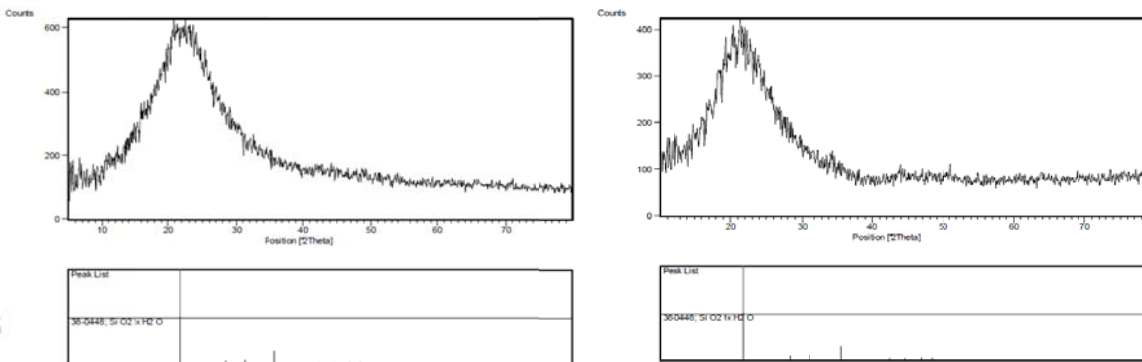
**Fig. 1.** a) SEM image of nano-SiO<sub>2</sub>, b) TEM image of nano-SiO<sub>2</sub>, c) SEM image of nano-SPA, b) TEM image of nano-SPA.



Scheme 1

Fig. 2. ATR of a) silica chloride, b) nano-SPA and c)  $\text{H}_3\text{PO}_4.\text{SiO}_2$ 

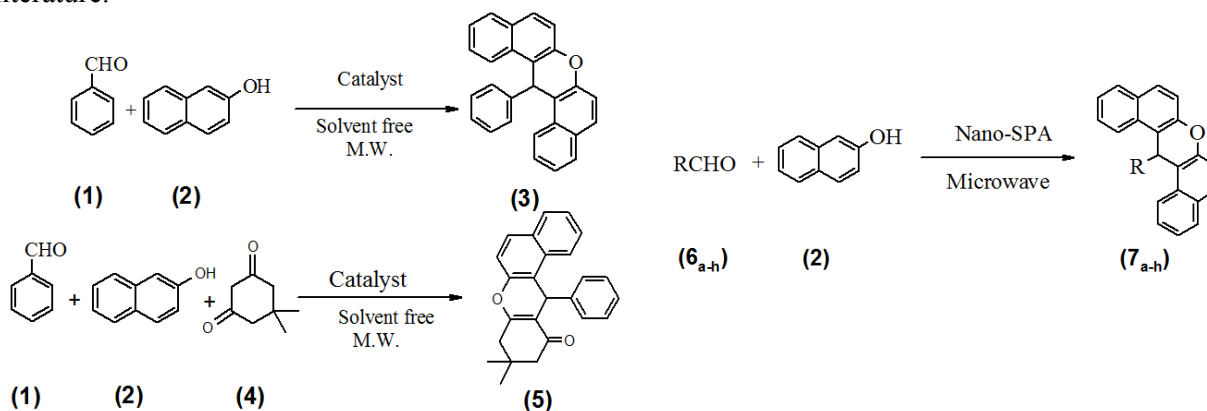
The X-ray diffraction (XRD) patterns of nano- $\text{SiO}_2$  and nano-SPA are shown in figure 3. Nano- $\text{SiO}_2$  XRD pattern has a strong peak in  $2\theta$  value of  $21.8024^\circ$  and FWHM equal to 1771 and nano-SPA XRD pattern has a strong broad peak in  $21.718$  and FWHM equal to 2.3616. According to scherrer's formula, the broadening of peaks implies the decrease in crystalline size of nano-SPA.

Fig. 3. X-ray diffraction (XRD) pattern of a) nano- $\text{SiO}_2$  and b) nano-SPA

In continuation of our investigations on the application of solid acids in organic synthesis,<sup>19-22</sup> we have investigated the synthesis of 14-aryl/alkyl-14*H*-dibenzo[*a,j*]xanthenes and tetrahydrobenzo[*a*]xanthen-11-one in the presence of nano-SPA as an acid catalyst. Model reactions were examined to optimize the reaction conditions in microwave (Scheme 2). Reactions in the presence of various amount of catalysts and various time of irradiation in microwave oven revealed that the best yield of products were obtained in 8 minutes irradiation using 0.04 g of SPA or 0.02 g of nano-SPA (Table 1, Entries 5 and 9).

To examine the reusability of nano-SPA in a microwave condition, after each run, the product was dissolved in  $\text{CHCl}_3$  and filtered. The catalyst was washed with acetone and reused. Treatment with acetone removes the tar from the catalyst surface more efficiently (Table 1, Entries 10 and 11). The catalyst was reusable although a gradual decline was observed in its activity. All products were

known and characterized by FT-IR,  $^1\text{H-NMR}$ , and the physical properties of those reported in the literature.



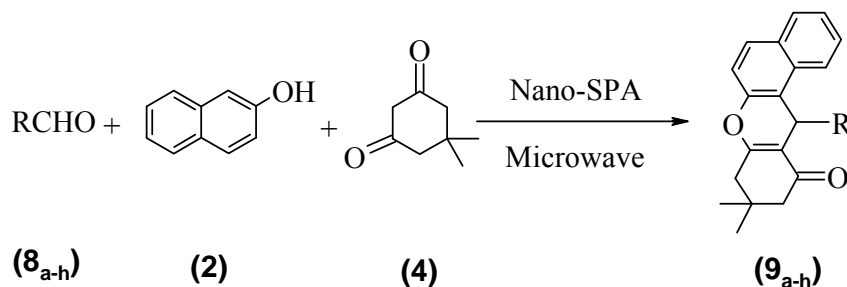
**Table 1.** Optimization of the reaction conditions for preparation of (3) and (5) in microwave oven under solvent free conditions

Entry	Catalyst (g)	Compound (3)	Compound (5)
		Time (min)/ Yield (%) <sup>a</sup>	Time (min)/ Yield (%) <sup>b</sup>
1	SPA (0.02)	12/57	12/62
2	SPA (0.03)	12/72	12/70
3	SPA (0.04)	12/80	12/78
4	SPA (0.05)	12/91	12/92
5	SPA (0.04)	8/90	8/90
6	SPA (0.04)	6/81	5/80
7	nano-SPA (0.04)	6/95	5/96
8	nano-SPA (0.03)	6/94	8/95
9	nano-SPA (0.02)	6/95	6/95
10	nano-SPA (0.02), 2 <sup>nd</sup> run	6/75	6/70
11	nano-SPA (0.02), 3 <sup>rd</sup> run	6/60	6/50

<sup>a</sup>The molar ratio of 2-naphthol : benzaldehyde is 2:1

<sup>b</sup>The molar ratio of 2-naphthol : benzaldehyde : dimedone is 1:1:1

According to the obtained best condition, we have applied 2-naphthol and various aldehydes: a) for the synthesis of 14-aryl/alkyl-14H-dibenzo[*a,j*]xanthene derivatives (Scheme 3 and Table 2) and b) with dimedone for the synthesis of tetrahydrobenzo[*a*]xanthen-11-one (Scheme 4 and Table 3).



**Table 2.** Synthesis of 14-aryl/alkyl-14H-dibenzo[*a,j*]xanthenes (7<sub>a-h</sub>) in the presence of nano-SPA under solvent-free conditions and microwave irradiation for 6 min.

Entry	R	Yield (%) <sup>b</sup>	M.P. (°C)	
			Found	Reported <sup>Ref</sup>
7 <sub>a</sub>	C <sub>6</sub> H <sub>5</sub>	90	183-184	185 <sup>9</sup>
7 <sub>b</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	92	288-289	289-290 <sup>9</sup>
7 <sub>c</sub>	4-MeC <sub>6</sub> H <sub>4</sub>	88	225-227	227-229 <sup>9</sup>
7 <sub>d</sub>	(CH <sub>3</sub> ) <sub>2</sub> CH-	70	155-156	156-157 <sup>8</sup>
7 <sub>e</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> -	75	150-152	152-154 <sup>7</sup>
7 <sub>f</sub>	4-OHC <sub>6</sub> H <sub>4</sub>	85	130-131	133-134 <sup>10</sup>
7 <sub>g</sub>	3,4(OMe) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	80	194-195	198-199 <sup>8</sup>
7 <sub>h</sub>	2,4(Cl) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	90	250-251	251-252 <sup>7</sup>

<sup>a</sup>The ratio of 2-naphthol (mmole): aldehydes (mmole): nano SPA (g) is 1:1:0.02.

<sup>b</sup> Isolated yield.

**Table 3.** Synthesis of tetrahydrobenzo[*a*]xanthen-11-ones (**9<sub>a-h</sub>**) in the presence of nano-SPA under solvent-free conditions and microwave irradiation for 6 min

Entry	R	Yield (%) <sup>b</sup>	Mp (°C)	
			Found	Reported <sup>Ref</sup>
<b>9<sub>a</sub></b>	C <sub>6</sub> H <sub>5</sub>	88	150-151	151-153 <sup>12</sup>
<b>9<sub>b</sub></b>	4-BrC <sub>6</sub> H <sub>4</sub>	96	181-183	186-187 <sup>12</sup>
<b>9<sub>c</sub></b>	4-OHC <sub>6</sub> H <sub>4</sub>	96	148-1149	150-151 <sup>15</sup>
<b>9<sub>d</sub></b>	4-ClC <sub>6</sub> H <sub>4</sub>	96	178-180	180-182 <sup>15</sup>
<b>9<sub>e</sub></b>	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	95	181-182	183-185 <sup>12</sup>
<b>9<sub>f</sub></b>	4-MeOC <sub>6</sub> H <sub>4</sub>	84	206-207	204-205 <sup>15</sup>
<b>9<sub>g</sub></b>	3-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	94	164-166	168-170 <sup>12</sup>
<b>9<sub>h</sub></b>	3-BrC <sub>6</sub> H <sub>4</sub>	93	173-174	175-176 <sup>15</sup>

<sup>a</sup>The ratio of 2-naphthol (mmole): aldehydes (mmole):dimedone (mmole): nano-SPA (g) is 1:1:1:0.02 .

<sup>b</sup> Isolated yield.

### 3. Conclusions

We have demonstrated a simple method for the synthesis of tetrahydrobenzo[*a*]xanthen-11-ones and 14-aryl/alkyl-14*H*-dibenzo[*a,j*]xanthenes using nano-SPA as eco-friendly and efficient catalyst. Short reaction times, high yields, a clean process, simple methodology, easy work-up and green conditions are advantages of these protocols.

### Acknowledgements

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### Experimental

#### Materials and Methods

The materials were purchased from Merck Company and were used without any additional purification. Products were characterized by FT-IR, <sup>1</sup>H-NMR and comparison of their physical properties with those reported in the literature. FT-IR (ATR) spectra were run on a Bruker, Eqinox 55 spectrometer. A Bruker (DRX-400 Avance) NMR was used to record the <sup>1</sup>H NMR spectra. The SEM and TEM of nano particles were determined with a VEGA/TESCAN scanning electron microscope and Leo 912AB OMEGA transmission electron microscopy, respectively. The X-ray diffraction (XRD) patterns of materials were recorded by employing a Philips Xpert MPD diffract meter equipped with a Cu K $\alpha$  anode ( $\lambda = 1.54 \text{ \AA}$ ) in the  $2\theta$  range from 5 to 80°.

#### *Typical procedures for the preparation 14-aryl/alkyl-14H-dibenzo[*a,j*]xanthenes under microwave condition in the presence of nano-SPA*

In a 5 ml microwave reactor vessel, a mixture of of 2-naphthol (2 mmol), aldehyde (1 mmol) and nano-SPA (0.02 g) was irradiated in microwave oven for 6 minutes. After completion of the reaction, the product was dissolved in hot ethanol and filtered to recover the catalyst. The solvent of filtrate was evaporated to obtain the product. The crude product was recrystallized from ethanol.

#### *Typical procedures for the preparation of tetrahydrobenzo[*a*]xanthenes-11-one under microwave condition in the presence of nano-SPA*

In a 5 ml microwave reactor vessel, a mixture of 2-naphthol (1 mmol), aldehyde (1 mmol), 1,3-diketone (1.2 mmol), and nano-SPA (0.02 g) was irradiated in microwave oven for 6 min. After completion of the reaction, the product was dissolved in hot ethanol and filtered to recover the catalyst. The solvent of filtrate was evaporated to obtain the product. The crude product was recrystallized from ethanol.

### Selected spectroscopic data

**14-Phenyl-14H-dibenzo[*a,j*]xanthenes (Table 2, Entry 7<sub>a</sub>):** White solid, FT-IR:  $\bar{\nu}$  (KBr) = 3020, 2900, 1621, 1592, 1513, 1403, 1252, 827, 803, 766, 744, 700  $\text{cm}^{-1}$ ,  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 6.3 (s, 1H), 6.8 (t,  $J$  = 7.2 Hz, 1H), 6.9 (t,  $J$  = 7.2 Hz, 2H), 7.2 (t,  $J$  = 7.2 Hz, 2H), 7.3 (d,  $J$  = 8.8 Hz, 2H), 7.36 (d,  $J$  = 8 Hz, 2H), 7.4 (d,  $J$  = 7.2 Hz, 2H), 7.6 (d,  $J$  = 9.2 Hz, 2H), 7.63 (d,  $J$  = 8 Hz, 2H), 8.2 (d,  $J$  = 8.4 Hz, 2H) ppm.

**14-(4-Chlorophenyl)-14H-dibenzo[*a,j*]xanthenes (Table 2, Entry 7<sub>b</sub>):** White solid, FT-IR:  $\bar{\nu}$  (KBr) = 3068, 2900, 1621, 1591, 1514, 1484, 1400, 1239, 831, 806, 777, 740, 711  $\text{cm}^{-1}$ ,  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 6.27 (s, 1H), 6.9 (d,  $J$  = 8.4 Hz, 1H), 7.3-7.2 (m, 6H), 7.4 (t,  $J$  = 7.2 Hz, 2H), 7.6 (d,  $J$  = 9.2 Hz, 2H), 7.66 (d,  $J$  = 8 Hz, 2H), 8.1 (d,  $J$  = 8.4 Hz, 2H) ppm.

**14-(4-Tolyl)-14H-dibenzo[*a,j*]xanthene (Table 2, Entry 7<sub>c</sub>):** White solid, FT-IR:  $\bar{\nu}$  (KBr) = 3020, 2900, 1621, 1591, 1509, 1458, 1430, 1248, 809, 740  $\text{cm}^{-1}$ ,  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2 (s, 3H), 6.27 (s, 1H), 6.77 (d,  $J$  = 8 Hz, 2H), 7.3 (m, 4H), 7.3 (d,  $J$  = 8.8 Hz, 2H), 7.4 (t,  $J$  = 7.2 Hz, 2H), 7.6 (d,  $J$  = 8.8 Hz, 2H), 7.64 (d,  $J$  = 8 Hz, 2H), 8.2 (d,  $J$  = 8.4 Hz, 2H) ppm.

**14- Isopropyl-14H-dibenzo[*a,j*]xanthene (Table 2, Entry 7<sub>d</sub>):** White solid, FT- IR:  $\bar{\nu}$  (KBr) = 3020, 2900, 1619, 1589, 1514, 1457, 1433, 1236, 816, 738  $\text{cm}^{-1}$ ,  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.647 (d, 6H), 1.2 (m, 1H), 5.2 (s, 1H), 7.2 (s br, 4H), 7.4 (s br, 2H), 7.6 (d,  $J$  = 8 Hz, 2H), 7.68 (d,  $J$  = 6.4 Hz, 2H), 8.1 (d,  $J$  = 6 Hz, 2H) ppm

**14-Propyl-14H-dibenzo[*a,j*]xanthenes (Table 3, Entry 7<sub>e</sub>):** White solid, FT- IR:  $\bar{\nu}$  (KBr) 3060, 2953, 2867, 1621, 1590, 1516, 1468, 1397, 1242, 813, 747  $\text{cm}^{-1}$ ,  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.4 (s br, 3H), 0.8 (s br, 2H), 1.8 (m, 2H), 5.2 (s, 1H), 7.1 (d,  $J$  = 8.8 Hz, 2H), 7.28 (t,  $J$  = 7.6 Hz, 2H), 7.4 (t,  $J$  = 7.6 Hz, 2H), 7.6 (d,  $J$  = 8.8 Hz, 2H), 7.7 (d,  $J$  = 8 Hz, 2H), 8 (d,  $J$  = 8.4 Hz, 2H) ppm.

**14-(4-Hydroxyphenyl)-14H-dibenzo[*a,j*]xanthenes (Table 2, Entry 7<sub>f</sub>):** White solid, FT- IR:  $\bar{\nu}$  (KBr) = 3403, 3058, 2920, 1620, 1593, 1512, 1457, 1432, 1401, 1245, 1175, 1064, 1038, 962, 817, 746, 609  $\text{cm}^{-1}$ ,  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 6.23 (s, 1H), 6.40 (d,  $J$  = 8.0 Hz, 2H), 7.17 (d,  $J$  = 8.4 Hz, 2H), 7.19 (t,  $J$  = 7.6 Hz, 2H), 7.27 (d,  $J$  = 8.8 Hz, 2H), 7.38 (t,  $J$  = 7.5 Hz, 2H), 7.58 (d,  $J$  = 8.8 Hz, 2H), 7.63 (d,  $J$  = 8.0 Hz, 2H), 8.17 (d,  $J$  = 8.4 Hz, 2H) ppm.

**14-(3,4-Dimethoxyphenyl)-14H-dibenzo[*a,j*]xanthenes (Table 2, Entry 7<sub>g</sub>):** White solid, FT- IR:  $\bar{\nu}$  (KBr) = 3064, 2932, 2832, 1622, 1592, 1514, 1457, 1433, 1401, 1239, 1140, 1072, 1020, 961, 859, 819, 748  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 3.49 (s, 6H), 6.26 (s, 1H), 6.46 (d,  $J$  = 8.0 Hz, 1H), 6.72 (s, 1H), 6.93 (d,  $J$  = 8.0 Hz, 1H), 7.22-7.70 (m, 12H), 8.21 (d,  $J$  = 6.0 Hz, 2H) ppm

**14-(2,4-Dichlorophenyl)-14H-dibenzo[*a,j*]xanthenes (Table 2, Entry 7<sub>h</sub>):** White solid, FT- IR:  $\bar{\nu}$  (KBr) = 3059, 2920, 1620, 1592, 1515, 1464, 1403, 1247, 1142, 1103, 1041, 960, 863, 836, 808, 743, 699, 608  $\text{cm}^{-1}$   $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 6.57 (s, 1H), 6.71 (d,  $J$  = 6.8 Hz, 1H), 7.05-7.50 (m, 10H), 7.63 (t,  $J$  = 7.5 Hz, 2H), 8.46 (d,  $J$  = 8.5 Hz, 2H) ppm.

**9, 9-Dimethyl-12-phenyl-8, 9, 10, 12-tetrahydrobenzo[*a*]xanthen-11-one (Table 3, Entry 9<sub>a</sub>):** White solid, FT- IR:  $\bar{\nu}$  (KBr) = 3053, 2957, 2891, 1649, 1620, 1596, 1469, 1452, 1372, 1241, 1226, 1184, 1032, 837, 747, 723, 697  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.97 (s, 3H), 1.13 (s, 3H), 2.25 (d,  $J$  = 16 Hz, 1H,  $\text{COCH}_2$ ), 2.32 (d,  $J$  = 16.4 Hz, 1H,  $\text{COCH}_2$ ), 2.58 (s, 2H), 5.71 (s, 1H), 7.06 (t,  $J$  = 7.6 Hz, 1H), 7.18 (t,  $J$  = 8 Hz, 2H), 7.32-7.46 (m, 5H), 7.77 (d,  $J$  = 8.4 Hz, 1H), 7.79 (d,  $J$  = 6.4 Hz, 1H), 8.00 (d,  $J$  = 8.4 Hz, 1H) ppm.

**12(4-Bromophenyl)-9, 9-dimethyl-8, 9, 10, 12-tetrahydrobenzo[*a*]xanthen-11-one (Table 3, Entry 9<sub>b</sub>):** White solid, FT- IR:  $\bar{\nu}$  (KBr) 2966, 2876, 1640, 1622, 1593, 1484, 1372, 1274, 1220, 1174, 1071, 1010, 837, 811, 756  $\text{cm}^{-1}$ ,  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.97 (s, 3H), 1.13 (s, 3H), 2.25 (d,  $J$  = 16.4 Hz, 1H,  $\text{COCH}_2$ ), 2.32 (d,  $J$  = 16 Hz, 1H,  $\text{COCH}_2$ ), 2.58 (s, 2H), 5.67 (s, 1H), 7.22 (d,

$J=7.2$  Hz, 2H), 7.29 (d,  $J=7.2$  Hz, 2H), 7.33 (d,  $J=9.2$  Hz, 1H), 7.40 (t,  $J=7.6$  Hz, 1H), 7.45 (t,  $J=7.6$  Hz, 1H), 7.78 (d,  $J=7.2$  Hz, 1H), 7.80 (d,  $J=6.8$  Hz, 1H), 7.91 (d,  $J=8$  Hz, 1H) ppm.

**12-(4-hydroxyphenyl)-9, 9-dimethyl-8, 9, 10, 12-tetrahydrobenzo[*a*]xanthen-11-one (Table 3, Entry 9<sub>c</sub>):** White solid, FT- IR:  $\bar{\nu}$  (KBr) = 3610, 3141-3440, 3029, 2952, 2891, 1649, 1615, 1595, 1510, 1466, 1371, 1234, 1227, 1174, 1014, 837, 818, 747  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.99 (s, 3H), 1.14 (s, 3H), 2.31 (d,  $J=16.4$  Hz, 1H,  $\text{COCH}_2$ ), 2.35 (d,  $J=16$  Hz, 1H,  $\text{COCH}_2$ ), 2.48 (s, 1H), 2.59 (s, 2H), 5.65 (s, 1H), 6.62 (d,  $J=8.5$  Hz, 2H), 7.19 (d,  $J=8.6$  Hz, 2H), 7.39 (d,  $J=6.8$  Hz, 1H), 7.45 (t,  $J=8.4$  Hz, 1H), 7.47 (t,  $J=8.4$  Hz, 1H), 7.78 (d,  $J=8.8$  Hz, 1H), 7.80 (d,  $J=6.9$  Hz, 1H), 8.0 (d,  $J=8.4$  Hz, 1H) ppm.

**12-(4-chlorophenyl)-9, 9-dimethyl-8, 9, 10, 12-tetrahydrobenzo[*a*]xanthen-11-one (Table 3, Entry 9<sub>d</sub>):** White solid, FT- IR:  $\bar{\nu}$  (KBr) = 2957, 2884, 1644, 1622, 1596, 1487, 1469, 1372, 1234, 1221, 1141, 1088, 1013, 845, 838, 750  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.97 (s, 3H), 1.13 (s, 3H), 2.25 (d,  $J=16.4$  Hz, 1H,  $\text{COCH}_2$ ), 2.32 (d,  $J=16$  Hz, 1H,  $\text{COCH}_2$ ), 2.58 (s, 2H), 5.69 (s, 1H), 7.14 (d,  $J=8.4$  Hz, 2H), 7.28 (d,  $J=8.4$  Hz, 2H), 7.33 (d,  $J=8.8$  Hz, 1H), 7.40 (td,  $J=6.8$  and 1.2 Hz, 1H), 7.45 (td,  $J=6.8$  and 1.2 Hz, 1H), 7.78 (d,  $J=8.8$  Hz, 1H), 7.8 (d,  $J=5.6$  Hz, 1H), 7.91 (d,  $J=8.4$  Hz, 1H).

**9,9-Dimethyl-12-(4-nitrophenyl)-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (Table 3, Entry 9<sub>e</sub>):** Yellow solid; FT- IR:  $\bar{\nu}$  (KBr) = 2956, 1643, 1622, 1594, 1477, 1513, 1477, 1376, 1342, 1244, 1221, 1183, 1031, 850, 830, 751  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.95 (s, 3H), 1.14 (s, 3H), 2.25 (d,  $J=16.4$  Hz, 1H,  $\text{COCH}_2$ ), 2.34 (d,  $J=16$  Hz, 1H,  $\text{COCH}_2$ ), 2.61 (s, 2H), 5.82 (s, 1H), 7.36 (d,  $J=9.2$  Hz, 1H), 7.39-7.47 (m, 2H), 7.52 (d,  $J=8.8$  Hz, 2H), 7.81-7.85 (m, 3H), 8.05 (d,  $J=8.4$  Hz, 2H) ppm.

**12-(4-methoxyphenyl)-9, 9-dimethyl-8, 9, 10, 12-tetrahydrobenzo[*a*]xanthen-11-one (Table 3, Entry 9<sub>f</sub>):** White solid, FT- IR:  $\bar{\nu}$  (KBr) 2957, 2898, 1644, 1611, 1594, 1509, 1460, 1371, 1245, 1249, 1223, 1164, 1027, 1025, 833, 812, 747  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.98 (s, 3H), 1.12 (s, 3H), 2.25 (d,  $J=16$  Hz, 1H,  $\text{COCH}_2$ ), 2.32 (d,  $J=16.4$  Hz, 1H,  $\text{COCH}_2$ ), 2.57 (s, 2H), 3.69 (s, 3H), 5.66 (s, 1H), 6.71 (d,  $J=8.4$  Hz, 2H), 7.20-7.27 (m, 2H), 7.32 (d,  $J=8.8$  Hz, 1H), 7.38 (t,  $J=8$  Hz, 1H), 7.44 (t,  $J=8$  Hz, 1H), 7.76 (d,  $J=9.2$  Hz, 1H), 7.78 (d,  $J=9.2$  Hz, 1H), 7.99 (d,  $J=8.4$  Hz, 1H) ppm.

**9,9-Dimethyl-12-(3-nitrophenyl)-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (Table 3, Entry 9<sub>g</sub>):** Yellow solid; FT- IR:  $\bar{\nu}$  (KBr) 2969, 2891, 1645, 1622, 1594, 1465, 1536, 1477, 1371, 1355, 1249, 1218, 1174, 1024, 830, 806, 779, 689, 741  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.96 (s, 3H), 1.14 (s, 3H), 2.25 (d,  $J=16.4$  Hz, 1H,  $\text{COCH}_2$ ), 2.34 (d,  $J=16$  Hz, 1H,  $\text{COCH}_2$ ), 2.62 (s, 2H), 5.82 (s, 1H), 7.36-7.48 (m, 4H), 7.81-7.84 (m, 3H), 7.78 (d,  $J=8.4$  Hz, 1H), 7.94 (d,  $J=8$  Hz, 1H), 8.12 (s, 1H) ppm.

**12-(3-Bromophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (Table 3, Entry 9<sub>h</sub>):** White solid, FT- IR:  $\bar{\nu}$  (KBr) 2958, 2891, 1646, 1622, 1594, 1470, 1432, 1370, 1282, 1218, 1175, 1076, 1024, 805, 879, 775, 692, 744  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.99 (s, 3H), 1.13 (s, 3H), 2.26 (d,  $J=16.4$  Hz, 1H,  $\text{COCH}_2$ ), 2.32 (d,  $J=16$  Hz, 1H,  $\text{COCH}_2$ ), 2.59 (s, 2H), 5.68 (s, 1H), 7.06 (t,  $J=8$  Hz, 1H), 7.20 (d,  $J=8.4$  Hz, 1H), 7.34 (d,  $J=8.4$  Hz, 2H), 7.39-7.42 (m, 2H), 7.47 (t,  $J=8$  Hz, 1H), 7.79 (d,  $J=5.2$  Hz, 1H), 7.81 (d,  $J=6.4$  Hz, 1H), 7.92 (d,  $J=8.4$  Hz, 1H) ppm.

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