## An Efficient Synthesis of 14-Aryl or Alkyl-14*H*-dibenzo[*a*. *j*]xanthenes Using Reusable HBF<sub>4</sub>-SiO<sub>2</sub> Catalyst Under Thermal and Solvent-Free Conditions

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A simple and convenient procedure for the synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a.j*]xanthene derivatives is described through a one-pot condensation of  $\beta$ -naphthol with various aryl or alkyl aldehydes in the presence of HBF<sub>4</sub>-SiO<sub>2</sub> as the catalyst under thermal and solvent-free conditions.

Keywords: Xanthene; HBF<sub>4</sub>-SiO<sub>2</sub>; Aldehyde;  $\beta$ -Naphthol; Solvent-free; One-pot condensation.

The synthesis of xanthenes, especially enzoxanthenes, has emerged as a powerful tool in organic synthesis due to their wide range of biological and therapeutic properties such as antibacterial,<sup>1</sup> antiviral<sup>2</sup> and antiinflammatory activities,<sup>3</sup> as well as in photodynamic therapy<sup>4</sup> and for antagonism of the paralyzing action of zoxazolamine.<sup>5,6</sup> Furthermore, due to their useful spectroscopic properties, they are used as dyes,<sup>7,8</sup> in laser technologies,<sup>9</sup> and in fluorescent materials for visualization of biomolecules.<sup>10</sup> Thus, the synthesis of benzoxanthene derivatives currently is of great interest. Various methods have been reported for the synthesis of benzoxanthenes, including (a) dehydration of bis-(2-hydroxy-1-naphthyl)methane using POCl<sub>3</sub><sup>11</sup> or by boiling acetic acid diester of bis(2-hydroxy-1-naphthyl)methane,  $^{12}$  (b) condensation of  $\beta$ -naphthol with aliphatic and aromatic aldehydes in the presence of hydrochloric acid or phosphoric acid<sup>13</sup> and also sulfuric acid<sup>14</sup> in acetic acid as solvent. However, all these methods have many disadvantages such as low yields, the need for a prolonged reaction time, the use of toxic organic solvents, excess reagents, and harsh reaction conditions. Because of these drawbacks, the reaction has been improved by mixing β-naphthol with aldehydes in the presence of a catalyst, such as p-toluenesulfonic acid,<sup>15,16</sup> sulfamic acid,<sup>17</sup> I<sub>2</sub>,<sup>18</sup> Amberlyst-15,<sup>19</sup> silica sulfuric acid,<sup>20</sup> Al(HSO<sub>4</sub>)<sub>3</sub>,<sup>21</sup> NaHSO<sub>4</sub>,<sup>22</sup> Selectfluor<sup>TM</sup>,<sup>23</sup> K<sub>5</sub>CoW<sub>12</sub>O<sub>40</sub>·3H<sub>2</sub>O<sup>24</sup> and hetero polyacid.<sup>25</sup> Although some of these methods have convenient protocols with good to high yields, the majority of these methods suffer at least from one of the following disadvantages: harsh

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reaction conditions, long reaction time, tedious experimental procedures, the use of toxic solvents and catalysts. Hence, a practical and more efficient method for the synthesis of dibenzoxanthene derivatives would still be of interest. Over the last few years, there has been a considerable growth in interest in the use of solid-phase reagents in organic synthesis because of their ease of handing, enhanced reaction rates, greater selectivity, simple workup and recoverablity of catalysts.<sup>26</sup> Among the various heterogeneous catalysts, particularly, silica-supported reagents have advantages of low cost, ease of preparation, and catalyst recycling.<sup>27</sup> Herein we demonstrate tetrafluorooric acid adsorbed on silica gel (HBF<sub>4</sub>-SiO<sub>2</sub>)<sup>28</sup> as an inexpensive, highly efficient, heterogeneous, and reusable catalyst for the preparation of 14-aryl or alkyl-14*H*-dibenzo[*a.j*]xanthene derivatives by the condensation reaction of various aryl or alkyl aldehydes with β-naphthol under thermal and solvent-free conditions (Scheme I). The present method not only affords the products in excellent yields but also avoids the problems associated with catalyst cost, handing, safety and pollution.

Scheme I



In the first instance, the catalytic effect of HBF<sub>4</sub>-SiO<sub>2</sub> on the condensation reaction of benzaldehyde **1a** (1.0 mmol) and  $\beta$ -naphthol **2** (2.0 mmol) under solvent-free conditions was investigated. After many studies on the above condensation, we found that when less than 3 mol % of HBF<sub>4</sub>-SiO<sub>2</sub> was applied, lower yields of the corresponding product (Table 1, entries 2-7) resulted, whereas use of more than 3 mol % did not improve the yield (Table 1, entries 10 and 11). When attempts were made to carry out this reaction for 3 h in the absence of HBF<sub>4</sub>-SiO<sub>2</sub>, the substrate was recovered almost quantitatively (Table 1, entry 1).

Next, for optimization of temperature, the reaction was performed using benzaldehyde **1a** (1.0 mmol) and  $\beta$ -naphthol **2** (2.0 mmol) in the presence of HBF<sub>4</sub>-SiO<sub>2</sub> (3 mol %) under thermal solvent-free conditions. As can be seen from Table 1 (entry 8), the shorter time and excellent yield (94%) for 14*H*-phenyldibenzo[*a*. *j*]xanthene (**3a**) were achieved at 125 °C.

Based on the above results, we also conducted the same reactions using aldehydes 1b-1l and 2 in the presence of HBF<sub>4</sub>-SiO<sub>2</sub> under similar conditions. As expected, both aromatic aldehydes containing electron-donating as well as electron-withdrawing groups, and aliphatic aldehyde were utilized in the present case to form the corresponding benzoxanthenes **3** in high yields (Table 2). In addition, as seen from Table 2, the aromatic aldehydes with electron donating groups are generally more reactive than their corresponding benzaldehydes with electron withdrawing groups and give the desired product in a short reaction time; however, the substituent character seemed to result in no obvious effect on the reaction yields.

In view of a greener chemistry, efficient recovery and reuse of the catalyst is highly desirable. Thus the recovery and reusability of HBF<sub>4</sub>-SiO<sub>2</sub> was investigated. After the reaction was completed, ethyl acetate was added until the solid crude product was dissolved. Then, HBF<sub>4</sub>-SiO<sub>2</sub> as the catalyst was isolated from the mixture of the reaction by simple filtration and reused again after washing with ethyl acetate. The reusability of HBF<sub>4</sub>-SiO<sub>2</sub> was examined efficiently without any activation by using benzaldehyde (**1a**) as a model substrate in the above experimental procedure. The recovered HBF<sub>4</sub>-SiO<sub>2</sub> was reused directly for three consecutive condensation reactions of benzaldehyde (**1a**) with  $\beta$ -naphthol (**2**) affording 92%, 90%, 88% yields in 32 min, 35 min, 38 min, respectively.

In conclusion, we have developed a simple, convenient and effective method for easy one-pot synthesis of

 Table 1. Preparation of 14*H*-phenyldibenzo[*a. j*]xanthene (3a) under solvent-free conditions

Entry	$\mathrm{HBF}_4 ext{-}\mathrm{SiO}_2$	Temperature (°C)	Time (min)	Yield <sup>a</sup> (%)
1	None	125 °C	180	_
2	0.01 mmol	50 °C	30	45
3	0.01 mmol	80 °C	30	70
4	0.01 mmol	100 °C	30	77
5	0.01 mmol	125 °C	30	80
6	0.01 mmol	125 °C	40	80
7	0.02 mmol	125 °C	30	85
8	0.03 mmol	125 °C	30	94
9	0.03 mmol	125 °C	40	94
10	0.04 mmol	125 °C	40	94
11	0.05 mmol	125 °C	40	94

<sup>a</sup> Yield refers to the pure isolated product.

Table 2. Synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a*. *j*]xanthenes<sup>a</sup>

Entry	R (aldehyde)	Time (min)	Product	Yield <sup>b</sup> (%)
1	$C_{6}H_{5}(1a)$	30	3a	94
2	$4-CH_{3}C_{6}H_{4}(1b)$	25	3b	92
3	$4-CH_{3}OC_{6}H_{4}(1c)$	22	3c	92
4	2,5-(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (1d)	20	3d	91
5	$4-HOC_{6}H_{4}(1e)$	18	3e	88
6	$4-NO_2C_6H_4$ (1f)	40	3f	94
7	$2-NO_2C_6H_4$ (1g)	37	3g	95
8	$4-ClC_{6}H_{4}(1h)$	28	3h	93
9	3-ClC <sub>6</sub> H <sub>4</sub> (1i)	31	3i	94
10	$2,4-Cl_2C_6H_3(1j)$	34	3j	88
11	$3-FC_{6}H_{4}(1\mathbf{k})$	30	3k	90
12	$CH_3CH_2$ (11)	32	31	89

<sup>a</sup> Aldehyde (1.0 mmol), β-napthol (2.0 mmol); HBF<sub>4</sub>-SiO<sub>2</sub> (0.03 mmol).

<sup>b</sup> Yield refers to the pure isolated products.

14-aryl or alkyl-14*H*-dibenzo[*a. j*]xanthene derivatives by the condensation of various aldehydes with  $\beta$ -naphthol using silica-supported fluoroboric acid as a heterogeneous catalyst under thermal and solvent-free conditions. This methodology offers very attractive features such as reduced reaction times, higher yields, economic viability of catalyst, and mild nature of silica-supported fluoroboric acid. This simple procedure combined with ease of recovery and reuse of catalyst make this method economic, benign and a waste-free chemical process for the synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a. j*]xanthenes.

## **EXPERIMENTAL SECTION**

Melting points were determined on an X<sub>4</sub> melting

point apparatus and are uncorrected. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded on a Bruker Avance (400 MHz) spectrometer using CDCl<sub>3</sub> as the solvent and TMS as an internal standard. FT-IR spectra were taken on a Perkin-Elmer SP One FT-IR spectrophotometer. Microanalyses were performed with a PE 2400 elemental analyzer. Mass spectra (EI, 70 eV) were recorded on an HP5989B mass spectrometer. All reagents were purchased from commercial sources and were used without further purification.

## Preparation of HBF<sub>4</sub>-SiO<sub>2</sub>

 $HBF_4$  (1.65 g, as a 40% aq solution) was added to the suspension of silica gel (13.35 g, 230-400 mesh) in Et<sub>2</sub>O (40 mL). The mixture was concentrated and the residue was dried under vacuum at 100 °C for 72 h to afford HBF<sub>4</sub>-SiO<sub>2</sub> (0.5 mmol/g) as a free-flowing powder.

## General Procedure for the Synthesis of 14-Aryl or Alkyl-14*H*-dibenzo[*a.j*]xanthenes

To a mixture of aldehyde (1.0 mmol) and  $\beta$ -naphthol (2.0 mmol), HBF<sub>4</sub>-SiO<sub>2</sub> (60 mg, 0.03 mmol) was added and the mixture was heated in an oil bath at 125 °C for the appropriate time (Table 2). After completion of the reaction, as monitored by TLC, the reaction mixture was cooled to 25 °C, and ethyl acetate (30 mL) was added until the solid crude product was dissolved. Then, the heterogeneous catalyst was isolated from the mixture of the reaction by simple filtration and washing with ethyl acetate (2 × 5 mL). The filtrated organic solution was concentrated to afford crude product, which was recrystallized from ethyl alcohol to give pure product.

## 14-Phenyl-14*H*-dibenzo[*a*. *j*]xanthene (3a)

Pale yellow solid, mp 182-183 °C (lit.<sup>14</sup> mp 183 °C); <sup>1</sup>H NMR:  $\delta = 8.40$  (d, J = 8.4 Hz, 2H), 7.82 (d, J = 7.9 Hz, 2H), 7.79 (d, J = 8.8 Hz, 2H), 7.58 (t, J = 7.7 Hz, 2H), 7.53 (d, J = 7.5 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H), 7.41 (t, J = 7.5Hz, 2H), 7.15 (t, J = 7.5 Hz, 2H), 7.00 (t, J = 7.5 Hz, 1H), 6.49 (s, 1H); <sup>13</sup>C NMR:  $\delta = 148.7$ , 145.0, 131.3, 131.0, 128.8, 128.5, 128.1, 126.8, 126.5, 126.3, 124.2, 122.6, 117.9, 117.4, 38.2; IR (KBr): v = 3068, 3020, 2885, 1620, 1590, 1512, 1488, 1457, 1402, 1252, 1080, 1025, 965, 825, 745, 700 cm<sup>-1</sup>; EI-MS: m/z (%) = 358 (M<sup>+</sup>); Anal. Calcd for C<sub>27</sub>H<sub>18</sub>O: C, 90.47; H, 5.06. Found: C, 90.41; H, 5.14.

## 14-(4-Methylphenyl)-14*H*-dibenzo[*a*. *j*]xanthene (3b)

Yellow solid, Mp 227-228 °C (lit.<sup>14</sup> mp 228 °C); <sup>1</sup>H NMR:  $\delta = 8.38$  (d, J = 8.5 Hz, 2H), 7.82 (d, J = 8.8 Hz, 2H), 7.78 (d, J = 8.8 Hz, 2H), 7.57 (t, J = 8.5 Hz, 2H), 7.49 (d, J =8.8 Hz, 2H), 7.45-7.37 (m, 4H), 6.94 (d, J = 7.8 Hz, 2H), 6.45 (s, 1H), 2.12 (s, 3H); <sup>13</sup>C NMR:  $\delta$  = 147.9, 147.7, 142.6, 135.8, 130.7, 128.8, 128.5, 127.6, 126.7, 124.4, 123.3, 117.5, 117.3, 117.1, 37.2, 20.3; IR (KBr): v = 3070, 2915, 1624, 1598, 1515, 1465, 1436, 1404, 1260, 1125, 1088, 968, 840, 815, 786, 745 cm<sup>-1</sup>; EI-MS: *m/z* (%) = 372 (M<sup>+</sup>); Anal. Calcd for C<sub>28</sub>H<sub>20</sub>O: C, 90.29; H, 5.41. Found: C, 90.37; H, 5.48.

## 14-(4-Methoxyphenyl)-14*H*-dibenzo[*a*. *j*]xanthene (3c)

Yellow solid, mp 204-206 °C (lit.<sup>16</sup> mp 205 °C); <sup>1</sup>H NMR:  $\delta = 8.42$  (d, J = 8.9 Hz, 2H), 7.83 (d, J = 8.8 Hz, 2H), 7.76 (d, J = 8.8 Hz, 2H), 7.58 (t, J = 8.5 Hz, 2H), 7.50 (d, J =8.8 Hz, 2H), 7.44-7.36 (m, 4H), 6.71 (d, J = 8.9 Hz, 2H), 6.51 (s, 1H), 3.70 (s, 3H); <sup>13</sup>C NMR:  $\delta = 158.4$ , 149.0, 137.8, 134.2, 131.4, 130.8, 129.2, 129.1, 127.1, 124.5, 123.2, 118.4, 117.8, 114.5, 54.1, 37.4; IR (KBr): v = 3040, 2915, 1617, 1580, 1515, 1465, 1436, 1404, 1250, 1125, 1088, 968, 825, 805, 745 cm<sup>-1</sup>; EI-MS: m/z (%) = 388 (M<sup>+</sup>); Anal. Calcd for C<sub>28</sub>H<sub>20</sub>O<sub>2</sub>: C, 86.57; H, 5.19. Found: C, 86.45; H, 5.27.

## 14-(2,5-Dimethoxyphenyl)-14*H*-dibenzo[*a*. *j*]xanthene (3d)

Yellow solid, mp 169-171 °C (lit.<sup>21</sup> mp 169 °C); <sup>1</sup>H NMR:  $\delta = 8.60$  (d, J = 8.5 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.8 Hz, 2H), 7.57 (t, J = 7.5 Hz, 2H), 7.49 (d, J =8.8 Hz, 2H), 7.46 (t, J = 7.4 Hz, 2H), 6.89 (s, 1H), 6.85 (s, 1H), 6.77 (d, J = 9.0 Hz, 1H), 6.47 (d, J = 6.0 Hz, 1H), 4.25 (s, 3H), 3.46 (s, 3H); <sup>13</sup>C NMR:  $\delta = 154.0$ , 148.7, 148.2, 135.5, 132.0, 129.8, 129.7, 128.7, 128.4, 126.7, 124.3, 123.5, 118.2, 117.0, 111.8, 111.4, 56.0, 55.1, 30.6; IR (KBr): v = 2926, 2832, 1620, 1595, 1460, 1432, 1405, 1255, 1208, 1175, 1044, 966, 850, 815, 800, 745, 701 cm<sup>-1</sup>; EI-MS: m/z (%) = 418 (M<sup>+</sup>); Anal. Calcd for C<sub>29</sub>H<sub>22</sub>O<sub>3</sub>: C, 83.23; H, 5.30. Found: C, 83.31; H, 5.36.

## 14-(4-Hydroxyphenyl)-14*H*-dibenzo[*a*, *j*]xanthene (3e)

Pink solid, mp 140-141 °C (lit.<sup>23</sup> mp 140 °C); <sup>1</sup>H NMR:  $\delta$  = 8.35-6.55 (m, 16H), 6.45 (s, 1H), 4.98 (br s, 1H); <sup>13</sup>C NMR:  $\delta$  = 154.1, 149.0, 137.7, 131.7, 131.5, 129.7, 129.2, 129.0, 127.3, 124.7, 123.2, 118.5, 117.8, 115.8, 37.6; IR (KBr):  $\nu$  = 3405, 1595, 1512, 1400, 1250, 1244, 816, 750, 695 cm<sup>-1</sup>; EI-MS: *m/z* (%) = 374 (M<sup>+</sup>); Anal. Calcd for C<sub>27</sub>H<sub>18</sub>O<sub>2</sub>: C, 86.61; H, 4.85. Found: C, 86.55; H, 4.80.

## 14-(4-Nitrophenyl)-14*H*-dibenzo[*a*. *j*]xanthene (3f)

Yellow solid, mp 311-313 °C (lit.<sup>16</sup> mp 312 °C); <sup>1</sup>H NMR:  $\delta = 8.30$  (d, J = 8.5 Hz, 2H), 7.98 (d, J = 8.7 Hz, 2H), 7.85 (d, J = 4.0 Hz, 2H), 7.82 (d, J = 5.5 Hz, 2H), 7.66 (d, J = 8.7 Hz, 2H), 7.61 (t, J = 5.5 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H), 7.45 (t, J = 7.9 Hz, 2H), 6.60 (s, 1H); <sup>13</sup>C NMR:  $\delta = 152.5$ , 148.0, 145.8, 135.1, 130.9, 130.7, 129.7, 128.6, 127.3, 124.7, 123.5, 123.0, 117.8, 116.2, 36.5; IR (KBr):  $\nu = 3065$ , 2930, 1622, 1590, 1520, 1458, 1401, 1342, 1200, 1141, 1108, 1015, 965, 850, 828, 810, 743 cm<sup>-1</sup>; EI-MS: m/z (%) = 403 (M<sup>+</sup>); Anal. Calcd for C<sub>27</sub>H<sub>17</sub>NO<sub>3</sub>: C, 80.38; H, 4.25; N, 3.47. Found: C, 80.30; H, 4.35; N, 3.55.

#### 14-(2-Nitrophenyl)-14*H*-dibenzo[*a*. *j*]xanthene (3g)

Yellow solid, mp 292-293 °C (lit.<sup>17</sup> mp 293 °C); <sup>1</sup>H NMR:  $\delta = 8.59$ -7.15 (m, 16H), 7.54 (s, 1H); <sup>13</sup>C NMR:  $\delta =$ 150.1, 147.8, 141.3, 134.5, 132.7, 132.0, 130.5, 129.8, 129.6, 129.2, 128.1, 127.6, 125.5, 125.1, 124.5, 122.9, 118.5, 118.1, 33.1; IR (KBr): v = 3402, 3056, 2928, 1615, 1594, 1524, 1352, 1243, 1140, 815, 750 cm<sup>-1</sup>; EI-MS: *m/z* (%) = 403 (M<sup>+</sup>); Anal. Calcd for C<sub>27</sub>H<sub>17</sub>NO<sub>3</sub>: C, 80.38; H, 4.25; N, 3.47. Found: C, 80.26; H, 4.32; N, 3.57.

## 14-(4-Chlorophenyl)-14*H*-dibenzo[*a*. *j*]xanthene (3h)

Brown solid, mp 287-288 °C (lit.<sup>16</sup> mp 289 °C); <sup>1</sup>H NMR:  $\delta = 8.45$  (d, J = 8.5 Hz, 2H), 8.01 (d, J = 8.7 Hz, 2H), 7.88 (d, J = 4.0 Hz, 2H), 7.84 (d, J = 5.5 Hz, 2H), 7.69 (d, J = 8.7 Hz, 2H), 7.64 (t, J = 5.5 Hz, 2H), 7.55 (d, J = 8.8 Hz, 2H), 7.50 (t, J = 7.9 Hz, 2H), 7.46 (s, 1H); <sup>13</sup>C NMR:  $\delta =$ 156.0, 147.8, 132.8, 131.2, 129.3, 128.8, 128.3, 127.0, 126.8, 126.5, 124.7, 119.3, 118.2, 117.8, 33.5; IR (KBr): v =3050, 2925, 1620, 1595, 1456, 1431, 1396, 1242, 1060, 960, 824, 778, 695 cm<sup>-1</sup>; EI-MS: m/z (%) = 392 (M<sup>+</sup>); Anal. Calcd for C<sub>27</sub>H<sub>17</sub>ClO: C, 82.54; H, 4.36. Found: C, 82.46; H, 4.44.

## 14-(3-Chlorophenyl)-14H-dibenzo[a. j]xanthene (3i)

Brown solid, mp 172-173 °C (lit.<sup>21</sup> mp 173 °C); <sup>1</sup>H NMR:  $\delta = 8.30$  (d, J = 8.4 Hz, 2H), 7.86 (d, J = 8.6 Hz, 2H), 7.76 (d, J = 9.0 Hz, 2H), 7.60 (t, J = 7.0 Hz, 2H), 7.50 (d, J =8.9 Hz, 2H), 7.48-7.43 (m, 4H), 7.10 (t, J = 8.0 Hz, 1H), 6.96 (d, J = 8.7 Hz, 1H), 6.45 (1H, s); <sup>13</sup>C NMR:  $\delta = 148.5$ , 146.8, 134.5, 131.2, 131.0, 129.7, 129.1, 128.8, 128.2, 127.1, 126.8, 126.4, 124.5, 122.4, 118.1, 116.4, 37.8; IR (KBr): v = 3053, 2926, 1622, 1590, 1508, 1455, 1430, 1398, 1245, 1064, 959, 815, 775, 745, 690 cm<sup>-1</sup>; EI-MS: m/z (%) = 392 (M<sup>+</sup>); Anal. Calcd for C<sub>27</sub>H<sub>17</sub>ClO: C, 82.54; H, 4.36. Found: C, 82.48; H, 4.42.

# 14-(2,4-Dichlorophenyl)-14*H*-dibenzo[*a*. *j*]xanthene (3j)

Brown solid, mp 227-228 °C (lit.<sup>22</sup> mp 228 °C); <sup>1</sup>H NMR:  $\delta = 8.65$  (d, J = 8.5 Hz, 2H), 7.82 (d, J = 7.9 Hz, 2H), 7.80 (d, J = 8.7 Hz, 2H), 7.63 (t, J = 7.5 Hz, 2H), 7.48 (d, J = 8.7 Hz, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.31 (d, J = 8.6 Hz, 1H), 7.27 (s, 1H), 6.88 (d, J = 6.8 Hz, 1H), 6.75 (s, 1H); <sup>13</sup>C NMR:  $\delta = 148.8$ , 142.2, 132.9, 132.5, 131.6, 130.8, 130.5, 129.4, 129.1, 128.8, 128.5, 127.1, 124.4, 123.2, 117.9, 117.5, 34.2; IR (KBr): v = 3055, 2922, 1620, 1590, 1560, 1515, 1458, 1406, 1242, 1210, 1140, 1101, 1042, 962, 865, 838, 810, 742, 700 cm<sup>-1</sup>; EI-MS: m/z (%) = 427 (M<sup>+</sup>); Anal. Calcd for C<sub>27</sub>H<sub>16</sub>Cl<sub>2</sub>O: C, 75.89; H, 3.77. Found: C, 75.96; H, 3.84.

### 14-(3-Fluorophenyl)-14*H*-dibenzo[*a*. *j*]xanthene (3k)

Brown solid, mp 258-260 °C (lit.<sup>23</sup> mp 259 °C); <sup>1</sup>H NMR:  $\delta = 8.38$  (d, J = 8.6 Hz, 2H), 7.89 (d, J = 8.6 Hz, 2H), 7.78 (d, J = 8.9 Hz, 2H), 7.63 (t, J = 7.0 Hz, 2H), 7.53 (d, J =8.9 Hz, 2H), 7.50-7.45 (m, 4H), 7.13 (t, J = 8.0 Hz, 1H), 6.73 (d, J = 8.7 Hz, 1H), 6.50 (1H, s); <sup>13</sup>C NMR:  $\delta = 165.0$ , 161.5, 149.3, 148.0 ( $J_{C-F} = 6.3$  Hz), 147.9, 131.7 ( $J_{C-F} =$ 19.4 Hz), 131.5, 130.2 and 130.1 ( $J_{C-F} = 8.2$  Hz), 129.4, 129.3, 127.5, 124.8, 124.4 and 124.1 ( $J_{C-F} = 2.8$  Hz), 122.8, 118.2, 117.1, 115.8 and 115.6 ( $J_{C-F} = 21.5$  Hz), 114.0 and 113.7 ( $J_{C-F} = 21.5$  Hz), 38.2; IR (KBr): v = 3155, 2925, 1621, 1594, 1550, 1456, 1404, 1241, 1208, 1104, 1068, 967, 818, 749, 698 cm<sup>-1</sup>. EI-MS: m/z (%) = 376 (M<sup>+</sup>); Anal. Calcd for C<sub>27</sub>H<sub>17</sub>FO<sub>3</sub>: C, 86.15; H, 4.55. Found: C, 86.06; H, 4.46.

## 14-Ethyl-14*H*-dibenzo[*a*. *j*]xanthene (31)

Pale yellow solid, mp 151-152 °C (lit.<sup>14</sup> mp 152 °C); <sup>1</sup>H NMR:  $\delta = 8.25$  (d, J = 8.0 Hz, 2H), 7.89-7.71 (m, 4H), 7.60-7.50 (m, 2H), 7.43-7.33 (m, 4H), 5.41 (t, J = 7.2 Hz, 1H), 2.26 (m, 2H), 0.87 (t, J = 7.5 Hz, 3H); <sup>13</sup>C NMR:  $\delta =$ 142.4, 137.1, 131.8, 130.2, 128.5, 128.1, 126.5, 126.3, 124.4, 117.2, 37.8, 23.5, 14.3; IR (KBr): v = 3050, 2923,1622, 1591, 1560, 1516, 1457, 1386, 1240, 1210, 1140, 1100, 1045, 965, 828, 810, 745, 696 cm<sup>-1</sup>; EI-MS: *m/z* (%) = 310 (M<sup>+</sup>); Anal. Calcd for C<sub>23</sub>H<sub>18</sub>O: C, 89.00; H, 5.85. Found: C, 89.12; H, 5.93.

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