

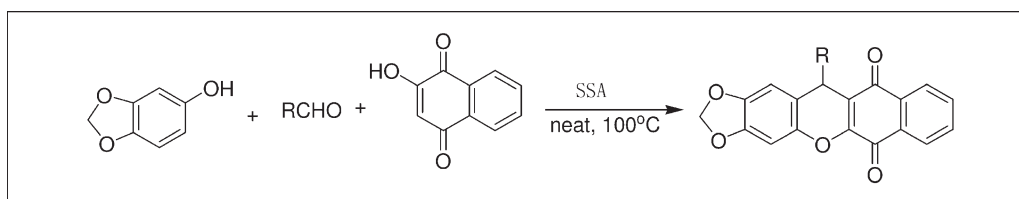
Liqiang Wu,<sup>a,\*</sup> Shujun Chao,<sup>b</sup> and Fulin Yan<sup>a</sup><sup>a</sup>School of Pharmacy, Xinxiang Medical University, Xinxiang, Henan 453003, People's Republic of China<sup>b</sup>Department of Chemistry, Xinxiang Medical University, Xinxiang, Henan 453003, People's Republic of China

\*E-mail: wliq870@163.com

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Some novel 12-aryl-12*H*-benzo[*i*][1,3]-dioxolo[4,5-*b*]xanthene-6,11-diones can be rapidly and efficiently synthesized in excellent yields by condensing a variety of aldehydes with 3,4-methylenedioxyphenol and 2-hydroxy-1,4-naphthoquinone in the presence of a catalytic amount of silica sulfuric acid under solvent-free conditions. The simple experimental procedure, solvent-free reaction conditions, utilization of an inexpensive and readily available catalyst, short period of conversion, and excellent yields are the advantages of the present method. Furthermore, the catalyst can be recycled and reused three times without significant loss of activity. The structures of the novel compounds are confirmed by IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, MS, and elemental analysis.

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## INTRODUCTION

Xanthenes and benzoxanthenes have recently received great attention because of their wide range of therapeutic and biological properties, such as antibacterial [1], antiviral [2], and anti-inflammatory activities [3]. Furthermore, these compounds show useful spectroscopic properties and are used as dyes [4], in laser technologies [5], and in fluorescent materials for visualization of biomolecules [6]. A number of xanthene dyes are extracted naturally from soil and plants, such as *Indigofera longracemosa* [7]. Thus, the development of new and simple synthetic methods for the efficient preparation of new xanthenes is therefore an interesting challenge. 1,3-Dioxolo[4,5-*b*]benzopyrans and their derivatives are very important group of heterocyclic tricyclic systems, which are widely found in natural products and have potent anti-inflammatory activity [8,9].

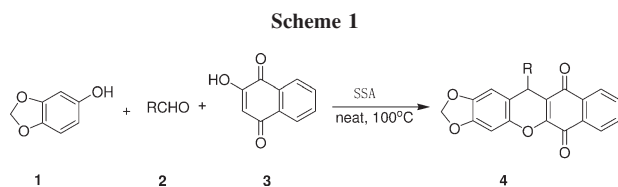
In recent years, the use of heterogeneous catalysts has received considerable interest in various disciplines including organic synthesis. They are advantageous over their homogeneous counterparts due to the prime advantage that in most of the cases, the catalyst can be recovered easily and reused. Silica sulfuric acid (SSA) has been used as efficient heterogeneous catalysts for many organic transformations because of their low cost,

ease of preparation, catalyst recycling, and ease of handling [10]. Herein, we wish to report a facile, three-component one-pot synthesis of novel 12-aryl-12*H*-benzo[*i*][1,3]-dioxolo[4,5-*b*]xanthene-6,11-diones (**4a–h**), which have not been published before, from the condensation of 3,4-methylenedioxyphenol (**1**), aldehydes (**2**), and 2-hydroxy-1,4-naphthoquinone (**3**) in the presence of a catalytic amount of SSA under solvent-free conditions (Scheme 1).

## RESULTS AND DISCUSSION

Initially, to optimize the reaction temperature, the reaction of 3,4-methylenedioxyphenol (**1**, 1 mmol) with benzaldehyde (**2a**, 1 mmol) and 2-hydroxy-1,4-naphthoquinone (**3**, 1 mmol) was studied under solvent-free conditions in the presence of 5 mol % SSA at different temperatures. The results are summarized in Table 1. As shown in Table 1, the reaction at 100°C proceeded in highest yield.

Next, the study set out to determine optimal amount of SSA, the reaction was carried out by varying amount of the catalyst (Table 2). Maximum yield was obtained with 0.05 equiv SSA. Further increase in the amount of



the catalyst in the mentioned reaction did not have any significant effect on the product yield.

Based on the optimized reaction conditions, a variety of aldehydes reacted smoothly with 3,4-methylenedioxyphenol and 2-hydroxy-1,4-naphthoquinone in the presence of 0.05 equiv of SSA at 100°C under solvent-free conditions to furnish the corresponding 12-aryl-12*H*-benzo[*i*][1,3]-dioxolo[4,5-*b*]xanthene-6,11-diones in high yields. The reactions were rapid and in most cases, 12-aryl-12*H*-benzo[*i*][1,3]-dioxolo[4,5-*b*]xanthene-6,11-diones formation was complete in 2.5 h with excellent yields (Table 3). The structures of the products were established from their spectral properties (IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and elemental analysis). All of the products **4** exhibited a singlet in their <sup>1</sup>H spectra at  $\delta = 5.03$ – $5.52$  for H-12, two singlet in their <sup>1</sup>H spectra at  $\delta = 5.98$ – $6.05$  ppm for OCH<sub>2</sub>O, a distinguishing peak at  $\delta = 35.61$ – $38.35$  for C-12 in their <sup>13</sup>C-NMR spectra, and a distinguishing peak at  $\delta = 98.42$ – $99.06$  for C-2 in their <sup>13</sup>C-NMR spectra. There were two overlapping doublets at  $\delta = 7.98$ – $8.15$ , which probably arise from the protons peri to the quinone C=O. The resonances of two nonequivalent carbonyl groups in their <sup>13</sup>C-NMR spectrum of **4** appeared at  $\delta = 177.92$ – $178.35$ . In these experiments, the catalyst was isolated by filtration and could be recycled up to three times without significant loss of activity (entry 1). When this reaction was carried out with aliphatic aldehyde such as butanal or pentanal, thin-layer chromatography (TLC) and <sup>1</sup>H-NMR spectra of the reaction mixture showed a combination of starting materials and numerous products, the yield of the expected product was very poor (entries 9 and 10).

**Table 1**

Temperature optimization for the synthesis of 12-phenyl-12*H*-benzo[*i*][1,3]-dioxolo[4,5-*b*]xanthene-6, 11-dione.

Entry	Temperature (°C)	Time (h)	Yield (%) <sup>a</sup>
1	25	5	<10
2	50	5	22
3	80	2	65
4	90	2	69
5	100	1.5	86
6	110	1.5	86
7	120	1.5	85

<sup>a</sup> Isolated yield.

**Table 2**

The amounts of catalyst optimization for the synthesis of 12-phenyl-12*H*-benzo[*i*][1,3]-dioxolo[4,5-*b*]xanthene-6, 11-dione<sup>a</sup>.

Entry	SSA (mol %)	Time (h)	Yield (%) <sup>b</sup>
1	0	5	8
2	1	3	49
3	2	2	62
4	3	2	69
5	4	1.5	74
6	5	1.5	86
7	6	1.5	85
8	7	1.5	86
9	8	1.5	84

<sup>a</sup> Reaction conditions: 3,4-methylenedioxyphenol (1 mmol); benzaldehyde (1 mmol); 2-hydroxy-1,4-naphthoquinone (1 mmol); 100°C; neat.

<sup>b</sup> Isolated yield.

A tentative mechanism for this transformation is proposed in Scheme 2. It is conceivable that SSA catalyses the formation of carbocation **5** in a reversible reaction with the aromatic aldehyde. The higher reactivity of the carbocation compared with the carbonyl species is used to facilitate Knoevenagel condensation between arylaldehyde **2** and 2-hydroxy-1,4-naphthoquinone **3**, *via* intermediate **6** and after dehydration, olefin **7** is produced. Subsequent Michael-type addition of 3,4-methylenedioxyphenol **1** to the olefin followed by cyclization and dehydration to afford the corresponding products **4a–4h**.

To emphasize the effect of catalyst, the model reaction of 3,4-methylenedioxyphenol, benzaldehyde, and 2-hydroxy-1,4-naphthoquinone was described and different catalysts, which have been reported recently for synthesis of benzoxanthenes [11], were subjected to the reaction. All the reactions were run in the same conditions

**Table 3**

Preparation of 12-aryl-12*H*-benzo[*i*][1,3]-dioxolo[4,5-*b*]xanthene-6, 11-diones catalyzed by SSA<sup>a</sup>.

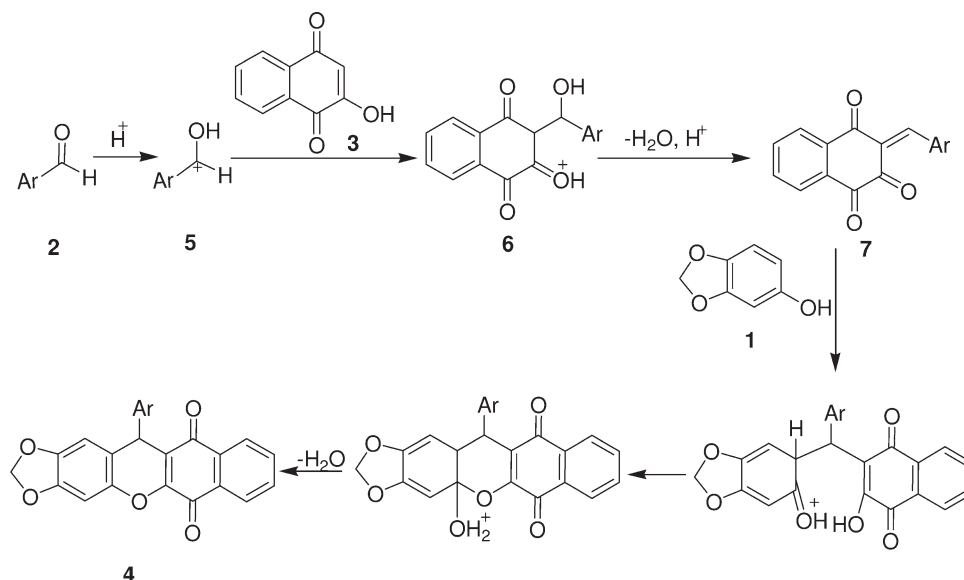
Entry	R	Time (H)	Product	Yield (%) <sup>b</sup>
1	C <sub>6</sub> H <sub>5</sub>	1.5	<b>4a</b>	86 (84,82,79) <sup>c</sup>
2	4-Cl-C <sub>6</sub> H <sub>4</sub>	2	<b>4b</b>	88
3	4-MeO-C <sub>6</sub> H <sub>4</sub>	1.5	<b>4c</b>	84
4	4-Me-C <sub>6</sub> H <sub>4</sub>	1.5	<b>4d</b>	91
5	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	2	<b>4e</b>	82
6	3-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	2	<b>4f</b>	89
7	3,4-Cl <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	2.5	<b>4g</b>	82
8	2-F-C <sub>6</sub> H <sub>4</sub>	2	<b>4h</b>	87
9	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub>	4	<b>4i</b>	0
10	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub>	4	<b>4j</b>	0

<sup>a</sup> Reaction conditions: 3,4-methylenedioxyphenol (1 mmol); aldehyde (1 mmol); 2-hydroxy-1,4-naphthoquinone (1 mmol); SSA (20 mg); 100°C; neat.

<sup>b</sup> Isolated yield.

<sup>c</sup> Yields after three times of catalyst recovery.

Scheme 2



and similar amounts of catalyst (5 mol %) were used. As can be seen in Table 4, satisfactory results were obtained only with SSA (entry 12).

In conclusion, we have developed a convenient and efficient method for the synthesis of 12-aryl-12*H*-benzo[*i*][1,3]-dioxolo[4,5-*b*]xanthene-6,11-diones by single-pot condensation of 3,4-methylenedioxyphenol with aldehydes and 2-hydroxy-1,4-naphthoquinone in the presence of SSA. The simple experimental procedure, solvent-free reaction conditions, utilization of an inexpensive and readily available catalyst, short period of conversion, and excellent yields are the advantages of the present method.

## EXPERIMENTAL

NMR spectra were determined on Bruker AV-400 instrument at room temperature using TMS as internal standard, coupling constants (*J*) were measured in Hz; IR spectra were determined on FTS-40 infrared spectrometer; elemental analysis were performed by a Vario-III elemental analyzer; mass spectra were taken on a macro mass spectrometer (Waters) by electrospray method; melting points were determined on a XT-4 binocular microscope and were uncorrected; commercially available reagents were used throughout without further purification unless otherwise stated.

**Preparation of SSA.** A 500-mL suction flask was used. It was equipped with a constant pressure-dropping funnel containing chlorosulfonic acid (23.3 g, 0.2 mol) and gas inlet tube for conducting HCl gas over an adsorbing solution. Into it were charged 60.0 g of silica gel. Chlorosulfonic acid was added dropwise over a period of 30 min at room temperature. HCl gas evolved from the reaction vessel immediately. After the addition was complete, the mixture was shaken for 30 min. A white solid of 76.0 g was obtained.

**General procedure for the preparation of 4.** To a mixture of 3,4-methylenedioxyphenol (1 mmol), aldehyde (1 mmol), and 2-hydroxy-1,4-naphthoquinone (1 mmol), SSA (20 mg, 0.05 mmol) was added. The mixture was stirred at 100°C for 1.5–2.5 h. After completion of the reaction (TLC), CHCl<sub>3</sub> (20 mL) was added, and the solid catalyst was removed by filtration. The solvent was evaporated and the crude product was purified by silica gel column chromatography using CHCl<sub>3</sub> as eluent.

**12-Phenyl-12*H*-benzo[*i*][1,3]-dioxolo[4,5-*b*]xanthene-6, 11-dione (4a).** Marron powder, m.p. 242–243°C; IR (KBr)  $\nu$ : 1706, 1642, 1607, 1577, 1504, 1481, 1374, 1290, 1188, 1141, 1031, 913 cm<sup>-1</sup>; <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$ : 8.15 (d, 1H, *J* = 7.6 Hz), 8.12 (d, 1H, *J* = 7.6 Hz), 8.04–7.70 (m, 2H),

Table 4

Effect of catalyst on the reaction of 3,4-methylenedioxyphenol, benzaldehyde, and 2-hydroxy-1,4-naphthoquinone<sup>a</sup>.

Entry	Catalyst	Time (h)	Yield (%) <sup>b</sup>
1	H <sub>14</sub> [NaP <sub>5</sub> W <sub>30</sub> O <sub>110</sub> ]	1	84
2	KAl(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	1	70
3	Sulfamic acid	2	62
4	Dowex-50W	1	76
5	BF <sub>3</sub> ·SiO <sub>2</sub>	0.5	84
6	I <sub>2</sub>	2	82
7	LiBr	1.5	70
8	Cyanuric chloride	2	76
9	Ce(SO <sub>4</sub> ) <sub>2</sub>	2	72
10	Al(HSO <sub>4</sub> ) <sub>3</sub>	2.5	69
11	Silica chloride	2	78
12	SSA	1.5	86

<sup>a</sup> Reaction conditions: 3,4-methylenedioxyphenol (1 mmol); benzaldehyde (1 mmol); 2-hydroxy-1,4-naphthoquinone (1 mmol); catalyst (0.05 mmol); 100°C; neat.

<sup>b</sup> Isolated yield.

7.44–7.13 (m, 6H), 6.61 (s, 1H), 6.05 (s, 1H), 5.99 (s, 1H), 5.52 (s, 1H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 178.12, 178.10, 158.09, 147.39, 145.56, 142.89, 135.63, 135.12, 132.91, 131.98, 131.38, 130.66, 130.46, 130.17, 130.02, 129.56, 128.24, 127.24, 124.62, 115.70, 107.77, 101.82, 98.42, 35.61; MS (ESI)  $m/z$  383 ( $M + 1$ ); Anal. Calcd. for  $\text{C}_{24}\text{H}_{14}\text{O}_5$ : C 75.39, H 3.69; Found: C 75.52, H 3.51.

**12-(4-Chlorophenyl)-12H-benzo[i][1,3]-dioxolo[4,5-b]-xanthene-6, 11-dione (4b).** Marron powder, m.p. 229–230°C; IR (KBr)  $\nu$ : 2903, 1701, 1646, 1606, 1502, 1481, 1371, 1288, 1242, 1183, 1143, 1035, 935, 909, 776  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ , 400 MHz)  $\delta$ : 8.14 (d, 1H,  $J = 7.6$  Hz), 7.99 (d, 1H,  $J = 7.6$  Hz), 7.90–7.68 (m, 2H), 7.35–7.13 (m, 5H), 6.82 (s, 1H), 6.05 (s, 1H), 5.99 (s, 1H), 5.12 (s, 1H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 178.21, 178.14, 157.59, 147.51, 145.77, 143.37, 142.88, 135.15, 132.73, 131.38, 130.65, 129.99, 129.57, 129.42, 128.72, 126.71, 124.59, 115.93, 114.85, 110.18, 108.06, 101.92, 98.54, 37.80; MS (ESI)  $m/z$  417 ( $M + 1$ ); Anal. Calcd. for  $\text{C}_{24}\text{H}_{13}\text{ClO}_5$ : C 69.16, H 3.14; Found: C 69.32, H 3.01.

**12-(4-Methoxyphenyl)-12H-benzo[i][1,3]-dioxolo[4,5-b]-xanthene-6, 11-dione (4c).** Marron powder, m.p. 201–202°C; IR (KBr)  $\nu$ : 2982, 1736, 1700, 1645, 1606, 1511, 1479, 1372, 1287, 1255, 1139, 1037, 910, 834  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ , 400 MHz)  $\delta$ : 8.13 (d, 1H,  $J = 8.0$  Hz), 7.98 (d, 1H,  $J = 7.6$  Hz), 7.89–7.67 (m, 2H), 7.21–7.12 (m, 3H), 6.80–6.78 (m, 3H), 6.04 (s, 1H), 5.99 (s, 1H), 5.03 (s, 1H), 3.67 (s, 3H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 178.35, 178.31, 158.39, 157.29, 147.24, 145.63, 143.42, 136.79, 135.07, 131.16, 130.90, 129.98, 129.33, 129.18, 124.49, 116.83, 115.58, 113.91, 108.18, 101.80, 98.41, 55.22, 37.48; MS (ESI)  $m/z$  413 ( $M + 1$ ); Anal. Calcd. for  $\text{C}_{25}\text{H}_{16}\text{O}_6$ : C 72.81, H 3.91; Found: C 72.92, H 3.82.

**12-(4-Methylphenyl)-12H-benzo[i][1,3]-dioxolo[4,5-b]-xanthene-6, 11-dione (4d).** Orange powder, m.p. 215–216°C; IR (KBr)  $\nu$ : 2932, 1700, 1644, 1575, 1480, 1373, 1288, 1234, 1186, 1142, 1037, 912, 769  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ , 400 MHz)  $\delta$ : 8.14 (d, 1H,  $J = 7.6$  Hz), 7.98 (d, 1H,  $J = 7.6$  Hz), 7.91–7.88 (m, 1H), 7.71–7.68 (m, 1H), 7.19–7.03 (m, 5H), 6.81 (s, 1H), 6.04 (s, 1H), 5.98 (s, 1H), 5.05 (s, 1H), 2.20 (s, 3H);  $^{13}\text{C-NMR}$  ( $\text{DMSO-}d_6$ , 100 MHz)  $\delta$ : 178.24, 178.05, 157.51, 147.24, 145.42, 143.16, 142.66, 136.10, 135.46, 131.78, 130.71, 130.66, 129.44, 128.84, 127.90, 124.77, 117.32, 114.78, 108.22, 102.23, 98.99, 37.65, 20.95; MS (ESI)  $m/z$  397 ( $M + 1$ ); Anal. Calcd. for  $\text{C}_{25}\text{H}_{16}\text{O}_5$ : C 75.75, H 4.07; Found: C 75.84, H 4.01.

**12-(4-Nitrophenyl)-12H-benzo[i][1,3]-dioxolo[4,5-b]-xanthene-6, 11-dione (4e).** Marron powder, m.p. 219–220°C; IR (KBr)  $\nu$ : 2991, 1694, 1645, 1604, 1576, 1518, 1481, 1375, 1349, 1290, 1235, 1187, 1144, 1036, 914, 834  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ , 400 MHz)  $\delta$ : 8.17 (d, 1H,  $J = 8.0$  Hz), 8.12–8.10 (m, 2H), 8.00 (d, 1H,  $J = 7.6$  Hz), 7.92–7.88 (m, 1H), 7.74–7.70 (m, 1H), 7.64–7.62 (m, 2H), 7.18 (s, 1H), 6.86 (s, 1H), 6.06 (s, 1H), 6.00 (s, 1H), 5.30 (s, 1H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 178.08, 177.92, 158.07, 151.29, 147.92, 146.72, 146.01, 143.33, 135.29, 131.71, 130.33, 130.00, 129.55, 129.31, 129.20, 124.75, 123.94, 123.63, 114.75, 113.87, 107.91, 102.09, 98.78, 38.35; MS (ESI)  $m/z$  428 ( $M + 1$ ); Anal. Calcd. for  $\text{C}_{27}\text{H}_{13}\text{NO}_7$ : C 67.45, H 3.07, N 3.28; Found: C 67.32, H 3.14, N 3.20.

**12-(3-Nitrophenyl)-12H-benzo[i][1,3]-dioxolo[4,5-b]-xanthene-6, 11-dione (4f).** Orange powder, m.p. 232–233°C; IR (KBr)  $\nu$ : 2894, 1700, 1644, 1604, 1575, 1528, 1482, 1374, 1350, 1289,

1233, 1188, 1144, 1039, 937, 774, 731  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ , 400 MHz)  $\delta$ : 8.19–8.15 (m, 2H), 8.13–7.98 (m, 2H), 7.90–7.531 (m, 4H), 7.16 (s, 1H), 6.86 (s, 1H), 6.05 (s, 1H), 6.00 (s, 1H), 5.32 (s, 1H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 178.01, 177.99, 157.97, 148.48, 147.89, 146.30, 146.01, 143.36, 135.29, 134.77, 131.67, 130.38, 130.05, 129.53, 129.44, 124.86, 123.13, 122.16, 114.81, 113.93, 107.94, 102.07, 98.84, 38.27; MS (ESI)  $m/z$  428 ( $M + 1$ ); Anal. Calcd. for  $\text{C}_{27}\text{H}_{13}\text{NO}_7$ : C 67.45, H 3.07, N 3.28; Found: C 67.38, H 3.02, N 3.34.

**12-(3,4-Dichlorophenyl)-12H-benzo[i][1,3]-dioxolo[4,5-b]-xanthene-6, 11-dione (4g).** Orange powder, m.p. 227–228°C; IR (KBr)  $\nu$ : 2975, 1694, 1644, 1608, 1503, 1480, 1374, 1291, 1238, 1144, 1037, 915, 863  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 8.13 (d, 1H,  $J = 7.6$  Hz), 8.09 (d, 1H,  $J = 7.6$  Hz), 7.81–7.78 (m, 1H), 7.64–7.60 (m, 1H), 7.34–7.18 (m, 3H), 6.85 (s, 1H), 6.51 (s, 1H), 6.02 (s, 1H), 5.99 (s, 1H), 5.13 (s, 1H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 178.14, 178.03, 157.76, 147.75, 145.92, 144.46, 143.35, 135.19, 132.63, 131.54, 131.08, 130.50, 130.45, 130.11, 130.04, 129.48, 127.78, 124.69, 115.19, 114.25, 107.97, 102.01, 98.66, 37.71; MS (ESI)  $m/z$  451 ( $M + 1$ ); Anal. Calcd. for  $\text{C}_{24}\text{H}_{12}\text{Cl}_2\text{O}_5$ : C 63.88, H 2.68; Found: C 64.02, H 2.52.

**12-(4-Fluorophenyl)-12H-benzo[i][1,3]-dioxolo[4,5-b]-xanthene-6, 11-dione (4h).** Marron powder, m.p. 251–252°C; IR (KBr)  $\nu$ : 2930, 1701, 1646, 1605, 1502, 1480, 1373, 1288, 1186, 1143, 1035, 935, 909  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ , 400 MHz)  $\delta$ : 8.14 (d, 1H,  $J = 7.6$  Hz), 7.99 (d, 1H,  $J = 7.6$  Hz), 7.90–7.86 (m, 1H), 7.71–7.67 (m, 1H), 7.36–7.03 (m, 5H), 6.82 (s, 1H), 6.05 (s, 1H), 5.99 (s, 1H), 5.12 (s, 1H);  $^{13}\text{C-NMR}$  ( $\text{DMSO-}d_6$ , 100 MHz)  $\delta$ : 178.22, 177.97, 157.61, 147.39, 145.51, 143.19, 141.71, 135.40, 131.82, 130.77, 130.65, 130.03, 129.95, 128.80, 124.80, 116.91, 115.65, 115.43, 114.46, 108.19, 102.29, 99.06, 37.29; MS (ESI)  $m/z$  401 ( $M + 1$ ); Anal. Calcd. for  $\text{C}_{24}\text{H}_{13}\text{FO}_5$ : C 72.00, H 3.27; Found: C 72.15, H 3.18.

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