

# HClO<sub>4</sub>–SiO<sub>2</sub>-catalyzed synthesis of 12-aryl-12*H*-benzo[*i*][1,3]dioxolo[4,5-*b*]xanthene-6,11-diones and 10-aryl-6,7,8,10-tetrahydro-7,7-dimethyl-9*H*-[1,3]dioxolo[4,5-*b*]xanthen-9-ones

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Received: 17 January 2010 / Accepted: 16 May 2010 / Published online: 16 June 2010  
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**Abstract** Three-component one-pot synthesis of some novel 12-aryl-12*H*-benzo[*i*][1,3]dioxolo[4,5-*b*]xanthene-6,11-diones involving treatment of 3,4-methylenedioxyphenol, aldehydes, and 2-hydroxy-1,4-naphthoquinone in presence of HClO<sub>4</sub>–SiO<sub>2</sub> was achieved, and this reaction was extended to preparation of 10-aryl-6,7,8,10-tetrahydro-7,7-dimethyl-9*H*-[1,3]dioxolo[4,5-*b*]xanthen-9-ones by three-component reaction of 3,4-methylenedioxyphenol, aldehydes, and dimedone.

**Keywords** Benzo[*i*][1,3]dioxolo[4,5-*b*]xanthene · HClO<sub>4</sub>–SiO<sub>2</sub> · Acidity · Catalysis · Solvent-free

## Introduction

Natural compounds possessing the 1,3-dioxolo[4,5-*b*]benzopyran moiety have attracted interest due to their potent anti-inflammatory activity. A variety of 1,3-dioxolo[4,5-*b*]benzopyran derivatives have been isolated from a variety of plants [1, 2]. Synthesis of xanthenes and benzoxanthenes with therapeutic and pharmacological properties such as antibacterial [3], antiviral [4], and anti-inflammatory activities [5] is currently of great interest. Many procedures have been developed for synthesis of xanthenes and benzoxanthenes, which include trapping of benzynes by phenols [6], cyclocondensation between aromatic *o*-hydroxyaldehydes and 2-tetralone [7], cyclodehydrations [8], and intramolecular phenyl carbonyl reaction of aldehydes with  $\beta$ -naphthol [9]. Furthermore,

syntheses of benzoxanthenes and their related products include the reaction of  $\beta$ -naphthol with formamide [10], carbon monoxide [11], 2-naphthol-1-methanol [12], aldehydes, and cyclic 1,3-dicarbonyl compounds [13].

In recent years, 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 cases, the catalyst can be recovered easily and reused. Silica-supported perchloric acid (HClO<sub>4</sub>–SiO<sub>2</sub>) has been used as an efficient heterogeneous catalyst for many organic transformations because of its low cost, ease of preparation, catalyst recycling, and ease of handling [14–19].

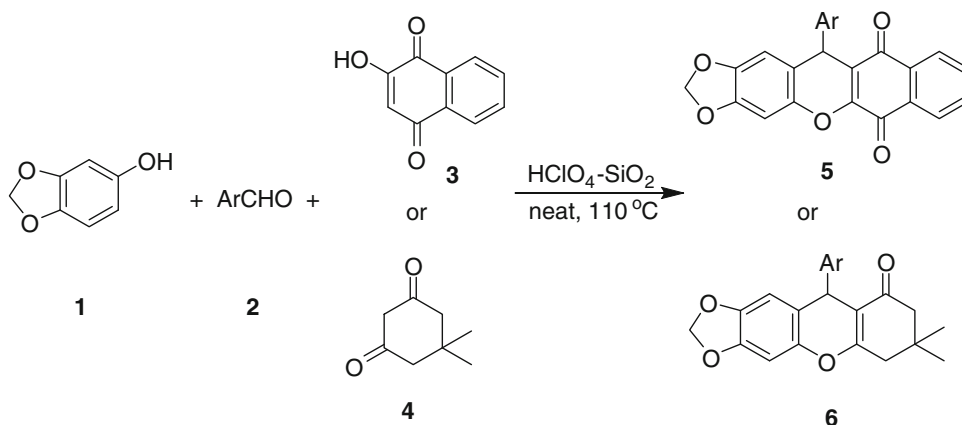
In this paper, we report an HClO<sub>4</sub>–SiO<sub>2</sub>-catalyzed, simple and efficient synthesis of 12-aryl-12*H*-benzo[*i*]-[1,3]dioxolo[4,5-*b*]xanthene-6,11-diones under solvent-free conditions. During our study, we also observed formation of 10-aryl-6,7,8,10-tetrahydro-7,7-dimethyl-9*H*-[1,3]dioxolo[4,5-*b*]xanthen-9-ones in excellent yields by one-pot condensation of 3,4-methylenedioxyphenol with aromatic aldehydes and dimedone in the presence of HClO<sub>4</sub>–SiO<sub>2</sub> (Scheme 1).

## Results and discussion

We started to study this condensation reaction by examining the amount of catalysts for the reaction involving 3,4-methylenedioxyphenol, benzaldehyde, and 2-hydroxy-1,4-naphthoquinone to afford the product 12-phenyl-12*H*-benzo[*i*][1,3]dioxolo[4,5-*b*]xanthene-6,11-dione at 110 °C under solvent-free conditions. As can be seen from Table 1, the best result was obtained with 5 mol% HClO<sub>4</sub>–SiO<sub>2</sub> under solvent-free conditions and gave the product in high yield.

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Scheme 1

**Table 1** Optimization of catalyst amount for synthesis of 12-phenyl-12H-[1,3]dioxolo[4,5-*b*]benzo[*i*]xanthene-6,11-dione

Entry	HClO <sub>4</sub> -SiO <sub>2</sub> (mol%)	Time (h)	Yield (%) <sup>a</sup>
1	0	5	<10
2	1	3	42
3	2	2	59
4	3	2	66
5	4	1.5	75
6	5	1.5	87
7	6	1.5	85
8	7	1.5	87
9	8	1.5	86

Reaction conditions: 3,4-methylenedioxyphenol (1 mmol), benzaldehyde (1 mmol), 2-hydroxy-1,4-naphthoquinone (1 mmol); 110 °C; neat

<sup>a</sup> Isolated yield

Based on the optimized reaction conditions, a range of 12-aryl-12H-benzo[*i*][1,3]dioxolo[4,5-*b*]xanthene-6,11-diones **5** were synthesized by reaction of a variety of aldehydes, 3,4-methylenedioxyphenol, and 2-hydroxy-1,4-naphthoquinone under solvent-free conditions. The reaction proceeded at 110 °C within 1–2 h in excellent yield after addition of the acid catalyst HClO<sub>4</sub>-SiO<sub>2</sub>. As indicated in Table 2, in all cases the reaction gives the product in good yields with high selectivity, and prevents problems associated with solvent use such as cost, handling, safety, and pollution. All of the products **5** exhibited a singlet in their <sup>1</sup>H spectra at  $\delta = 5.03$ – $5.52$  ppm for H-12, two singlets at  $\delta = 5.98$ – $6.05$  ppm for –OCH<sub>2</sub>O–, a distinguishing peak at  $\delta = 35.61$ – $38.35$  ppm for C-12 in their <sup>13</sup>C nuclear magnetic resonance (NMR) spectra, and a distinguishing peak at  $\delta = 98.42$ – $99.06$  ppm for C-2. There were two overlapping doublets at  $\delta = 7.98$ – $8.15$  ppm, which probably arise from the protons peri to the quinone C=O. The resonances of two nonequivalent carbonyl groups in the <sup>13</sup>C NMR spectra of **5** appeared at  $\delta = 177.92$ – $178.35$  ppm.

**Table 2** Preparation of 12-aryl-12H-benzo[*i*][1,3]dioxolo[4,5-*b*]xanthene-6,11-diones catalyzed by HClO<sub>4</sub>-SiO<sub>2</sub>

Entry	R	Time (h)	Product	Yield (%) <sup>a</sup>
1	C <sub>6</sub> H <sub>5</sub>	1.5	<b>5a</b>	87 (85, 88, 82) <sup>b</sup>
2	4-Cl-C <sub>6</sub> H <sub>4</sub>	1.5	<b>5b</b>	84
3	4-MeO-C <sub>6</sub> H <sub>4</sub>	1	<b>5c</b>	86
4	4-Me-C <sub>6</sub> H <sub>4</sub>	1	<b>5d</b>	90
5	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	2	<b>5e</b>	82
6	3-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	2	<b>5f</b>	87
7	3,4-Cl <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	1.5	<b>5g</b>	88
8	2-F-C <sub>6</sub> H <sub>4</sub>	1	<b>5h</b>	89

Reaction conditions: 3,4-methylenedioxyphenol (1 mmol), aldehyde (1 mmol), 2-hydroxy-1,4-naphthoquinone (1 mmol), HClO<sub>4</sub>-SiO<sub>2</sub> (0.05 mmol); 110 °C; neat

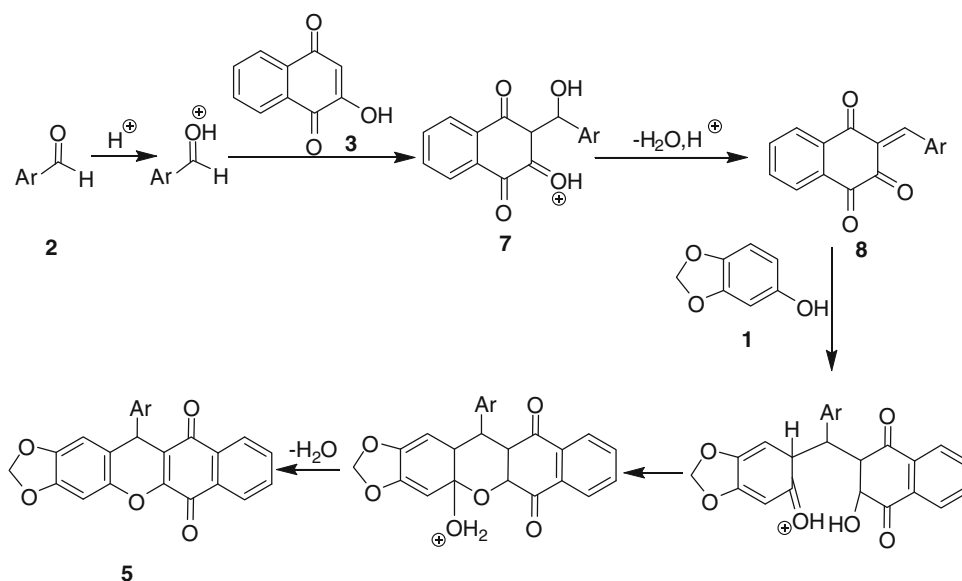
<sup>a</sup> Isolated yield

<sup>b</sup> Yields after three times of catalyst recovery

In these experiments, the reaction mixture was isolated with CHCl<sub>3</sub> and the remaining catalyst was dried at 50 °C for 1 h and then reloaded with fresh reagents for further runs. Apparently, recycling of the catalyst is possible for three successive times without significant loss of activity (Table 2, entry 1). Finally, it should be mentioned that, when reactions were carried out in the absence of catalyst for a long period of time (5 h), the yields of products were low (<10%).

A tentative mechanism for this transformation is proposed in Scheme 2. It is conceivable that HClO<sub>4</sub>-SiO<sub>2</sub> catalyzes the formation of a carbocation in a reversible reaction with the aromatic aldehyde. The higher reactivity of the carbocation compared with the carbonyl species is utilized to facilitate Knoevenagel condensation between arylaldehyde **2** and 2-hydroxy-1,4-naphthoquinone **3** via intermediate **7**, and after dehydration olefin **8** is produced. Subsequent Michael-type addition of 3,4-methylenedioxyphenol **1** to the olefin followed by cyclization and dehydration affords the corresponding products **5a**–**5h**.

Scheme 2

**Table 3** Comparison of the effect of catalysts in synthesis of 12-phenyl-12*H*-benzo[*i*][1,3]dioxolo[4,5-*b*]xanthene-6,11-dione

Entry	Catalyst	Yield (%) <sup>a</sup>
1	H <sub>2</sub> SO <sub>4</sub>	<10
2	NaHSO <sub>4</sub>	55
3	NH <sub>2</sub> SO <sub>3</sub> H	78
4	AlCl <sub>3</sub>	69
5	I <sub>2</sub>	72
6	HClO <sub>4</sub> -SiO <sub>2</sub>	87

Reaction conditions: 3,4-methylenedioxyphenol (1 mmol), benzaldehyde (1 mmol), 2-hydroxy-1,4-naphthoquinone (1 mmol), catalyst (0.05 mmol); 110 °C; neat

<sup>a</sup> Isolated yield

To emphasize the effect of the catalyst, the model reaction of 3,4-methylenedioxyphenol, benzaldehyde, and 2-hydroxy-1,4-naphthoquinone was described, and different catalysts were applied for the reaction. All reactions were run under the same conditions, and similar amounts of catalysts (0.05 mol%) were used. As shown in Table 3, satisfactory results were obtained only with HClO<sub>4</sub>-SiO<sub>2</sub>.

Encouraged by these results, we were delighted to observe that the present protocol could safely be extended to the condensation reaction of 3,4-methylenedioxyphenol with aromatic aldehydes and dimedone under the same conditions. 10-Aryl-6,7,8,10-tetrahydro-7,7-dimethyl-9*H*-[1,3]dioxolo[4,5-*b*]xanthene-9-ones were obtained in excellent yields (Table 4).

In conclusion, we have developed a simple, efficient, and green protocol for synthesis of 12-aryl-12*H*-benzo[*i*][1,3]dioxolo[4,5-*b*]xanthene-6,11-diones and 10-aryl-6,7,8,10-tetrahydro-7,7-dimethyl-9*H*-[1,3]dioxolo[4,5-*b*]xanthene-9-ones using HClO<sub>4</sub>-SiO<sub>2</sub> under solvent-free conditions.

**Table 4** Preparation of 10-aryl-6,7,8,10-tetrahydro-7,7-dimethyl-9*H*-[1,3]dioxolo[4,5-*b*]xanthene-9-ones catalyzed by HClO<sub>4</sub>-SiO<sub>2</sub>

Entry	R	Time (h)	Product	Melting point (Lit)	Yield (%) <sup>a</sup>
1	C <sub>6</sub> H <sub>5</sub>	1	<b>6a</b>	188–190 (190–192 [20])	90
2	2,4-Cl <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	1	<b>6b</b>	218–219 (214–215 [20])	89
4	2-Me-C <sub>6</sub> H <sub>4</sub>	1	<b>6c</b>	174–176 (176–178 [20])	88
5	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	1.5	<b>6d</b>	208–209 (201–202 [20])	89
6	3-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	2	<b>6e</b>	162–163 (156–158 [20])	86

Reaction conditions: 3,4-methylenedioxyphenol (1 mmol), aldehyde (1 mmol), dimedone (1 mmol), HClO<sub>4</sub>-SiO<sub>2</sub> (0.05 mmol); 110 °C; neat

<sup>a</sup> Isolated yield

Short reaction times, simple work-up in isolation of the products in good yields with high purity, mild reaction conditions, and recyclability of catalyst are features of this new procedure.

## Experimental

NMR spectra were determined on an Avance 400 FT-NMR spectrometer in CDCl<sub>3</sub> or dimethyl sulfoxide (DMSO)-*d*<sub>6</sub> and are expressed in  $\delta$  values relative to tetramethylsilane; coupling constants (*J*) are measured in Hz. Infrared (IR) spectra were determined on an FTS-40 infrared spectrometer. Elemental analyses were recorded on a Vario-III

elemental analyzer. Melting points were determined on a XT-4 binocular microscope. Commercially available reagents were used throughout without further purification unless otherwise stated.

#### Preparation of the $\text{HClO}_4\text{-SiO}_2$ catalyst

$\text{HClO}_4$  (1.8 g, 12.5 mmol, as 70% aqueous solution) was added to a suspension of  $\text{SiO}_2$  (230–400 mesh, 23.7 g) in 70.0  $\text{cm}^3$   $\text{Et}_2\text{O}$ . The mixture was concentrated and the residue was heated at 100 °C for 72 h under vacuum to furnish  $\text{HClO}_4\text{-SiO}_2$  (0.5 mmol/g) as a free-flowing powder (50 mg = 0.025 mmol of  $\text{HClO}_4$ ).

#### General procedure for preparation of **5** and **6**

A mixture of 3,4-methylenedioxyphenol (1 mmol), aldehyde (1 mmol), 2-hydroxy-1,4-naphthoquinone or dimedone (1 mmol), and  $\text{HClO}_4\text{-SiO}_2$  (100 mg, 0.05 mmol) was heated at 110 °C for an appropriate time and monitored by thin-layer chromatography (TLC) until the final conversion. After cooling, the reaction mixture was washed with  $\text{CHCl}_3$  and filtered to recover the catalyst. The solvent was evaporated and the crude product purified by silica gel column chromatography using  $\text{CHCl}_3$  as eluent to afford the pure product.

#### 12-Phenyl-12H-benzo[*i*][1,3]dioxolo[4,5-*b*]xanthene-6,11-dione (**5a**, $\text{C}_{24}\text{H}_{14}\text{O}_5$ )

Maroon powder, m.p.: 242–243 °C; IR (KBr):  $\bar{\nu}$  = 1,706, 1,642, 1,607, 1,577, 1,504, 1,481, 1,374, 1,290, 1,188, 1,141, 1,031, 913  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  = 8.15 (d, 1H,  $J$  = 7.6 Hz), 8.12 (d, 1H,  $J$  = 7.6 Hz), 8.04–7.70 (m, 2H), 8.44–7.13 (m, 6H), 6.61 (s, 1H), 6.05 (s, 1H), 5.99 (s, 1H), 5.52 (s, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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 ppm.

#### 12-(4-Chlorophenyl)-12H-benzo[*i*][1,3]dioxolo[4,5-*b*]xanthene-6,11-dione (**5b**, $\text{C}_{24}\text{H}_{13}\text{ClO}_5$ )

Maroon powder, m.p.: 229–230 °C; IR (KBr):  $\bar{\nu}$  = 2,903, 1,701, 1,646, 1,606, 1,502, 1,481, 1,371, 1,288, 1,242, 1,183, 1,143, 1,035, 935, 909, 776  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  = 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) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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 ppm.

#### 12-(4-Methoxyphenyl)-12H-benzo[*i*][1,3]dioxolo[4,5-*b*]xanthene-6,11-dione (**5c**, $\text{C}_{25}\text{H}_{16}\text{O}_6$ )

Maroon powder, m.p.: 201–202 °C; IR (KBr):  $\bar{\nu}$  = 2,982, 1,736, 1,700, 1,645, 1,606, 1,511, 1,479, 1,372, 1,287, 1,255, 1,139, 1,037, 910, 834  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,

$\text{DMSO-}d_6$ ):  $\delta$  = 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) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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 ppm.

#### 12-(4-Methylphenyl)-12H-benzo[*i*][1,3]dioxolo[4,5-*b*]xanthene-6,11-dione (**5d**, $\text{C}_{25}\text{H}_{16}\text{O}_5$ )

Orange powder, m.p.: 215–216 °C; IR (KBr):  $\bar{\nu}$  = 2,932, 1,700, 1,644, 1,575, 1,480, 1,373, 1,288, 1,234, 1,186, 1,142, 1,037, 912, 769  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  = 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) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  = 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 ppm.

#### 12-(4-Nitrophenyl)-12H-benzo[*i*][1,3]dioxolo[4,5-*b*]xanthene-6,11-dione (**5e**, $\text{C}_{27}\text{H}_{13}\text{NO}_7$ )

Maroon powder, m.p.: 219–220 °C; IR (KBr):  $\bar{\nu}$  = 2,991, 1,694, 1,645, 1,604, 1,576, 1,518, 1,481, 1,375, 1,349, 1,290, 1,235, 1,187, 1,144, 1,036, 914, 834  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  = 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) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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 ppm.

#### 12-(3-Nitrophenyl)-12H-benzo[*i*][1,3]dioxolo[4,5-*b*]xanthene-6,11-dione (**5f**, $\text{C}_{27}\text{H}_{13}\text{NO}_7$ )

Orange powder, m.p.: 232–233 °C; IR (KBr):  $\bar{\nu}$  = 2,894, 1,700, 1,644, 1,604, 1,575, 1,528, 1,482, 1,374, 1,350, 1,289, 1,233, 1,188, 1,144, 1,039, 937, 774, 731  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  = 8.19–8.15 (m, 2H), 8.15–7.98 (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) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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 ppm.

#### 12-(3,4-Dichlorophenyl)-12H-benzo[*i*][1,3]dioxolo[4,5-*b*]xanthene-6,11-dione (**5g**, $\text{C}_{24}\text{H}_{12}\text{Cl}_2\text{O}_5$ )

Orange powder, m.p.: 227–228 °C; IR (KBr):  $\bar{\nu}$  = 2,975, 1,694, 1,644, 1,608, 1,503, 1,480, 1,374, 1,291, 1,238, 1,144, 1,037, 915, 863  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):

$\delta = 8.13$  (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) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 178.14$ , 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 ppm.

*12-(4-Fluorophenyl)-12H-benzo[i][1,3]dioxolo[4,5-b]xanthene-6,11-dione* (**5h**, C<sub>24</sub>H<sub>13</sub>FO<sub>5</sub>)

Maroon powder, m.p.: 251–252 °C; IR (KBr):  $\bar{\nu} = 2,930$ , 1,701, 1,646, 1,605, 1,502, 1,480, 1,373, 1,288, 1,186, 1,143, 1,035, 935, 909 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 8.14$  (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) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 178.22$ , 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 ppm.

**Acknowledgments** We are pleased to acknowledge the financial support from Xinxiang Medical University.

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