

# One-pot synthesis and UV-Visible absorption studies of novel tricyclic heterocycle tethered Xanthene-1,8-diones

THIRUMAL YEMPALA<sup>a</sup>, BALASUBRAMANIAN SRIDHAR<sup>b</sup> and SRINIVAS KANTEVARI<sup>a,\*</sup>

<sup>a</sup>CPC Division (Organic Chemistry Division-II), CSIR-Indian Institute of Chemical Technology, Hyderabad 500 007, India

<sup>b</sup>Centre for X-ray Crystallography, CSIR-Indian Institute of Chemical Technology, Hyderabad 500 007, India  
e-mail: kantevari@yahoo.com; kantevari@gmail.com

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**Abstract.** A series of new tricyclic heterocyclic xanthene-1,8-diones tethered with chromophoric dibenzo [*b,d*]furan, dibenzo [*b,d*]thiophene and 9-methyl-9*H*-carbazoles were synthesized through one-pot condensation of dibenzo [*b,d*]furan-2-carbaldehyde, dibenzo [*b,d*] thiophene-2-carbaldehyde and 9-methyl-9*H*-carbazole-3-carbaldehyde with cyclic 1,3-dicarbonyls in the presence of recyclable PPA-SiO<sub>2</sub> catalyst under solvent-free conditions. Further, UV-Visible absorption properties of all the synthesized compounds were investigated in CHCl<sub>3</sub>, THF and acetonitrile.

**Keywords.** Xanthenediones; Dibenzo [*b,d*]furan; 9-Methyl carbazole; Dibenzo [*b,d*]thiophene; One-pot synthesis; UV-Visible absorption studies.

## 1. Introduction

In recent years xanthene derivatives have attracted scientists world over due to their promising applications in medicinal and material chemistry.<sup>1–5</sup> Among this class, xanthenediones play a vital role as the key structural unit in a variety of natural products exhibiting several biological activities.<sup>3–5</sup> Due to the presence of in-built pyran ring architecture and their extended conjugation with aromatic groups, xanthenediones exhibit applications in optoelectronic materials. They form an important component in laser dyes<sup>6</sup> and are used in laser technologies<sup>7</sup> for photodynamic therapy. Xanthenediones are also used as pH sensitive fluorescent materials for visualization of biomolecules.<sup>8</sup> In view of the importance of xanthenediones, we would like to extend the conjugation within the xanthenedione moiety by replacing the simple/substituted phenyl groups with tricyclic heterocycles.

For the past decade, tricyclic systems such as dibenzofuran, dibenzothiophene and carbazole with planar architecture<sup>9a</sup> have got significant interest in the area of materials, dyes, photochemistry, and light-emitting diodes. They also act as ideal conjugated units for the construction of organic semiconductors. Among these three heterocycles, dibenzofuran has been used as an effective organic material for phosphorescent organic

light-emitting diodes and electron-transport materials or electron-transport-type host materials because of its high triplet energy and strong electron-withdrawing oxygen linkage in its molecular structure.<sup>9b–c</sup> Moreover, all these heterocycles dibenzofuran, carbazole and benzothiophene are naturally abundant with more pronounced anti-bacterial, anti-depressant, and anti-tuberculosis activities.<sup>10a–d</sup>

## 2. Experimental

### 2.1 General remarks

Melting points were measured with a Fischer-Johns melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets and absorptions are reported in cm<sup>–1</sup>. NMR spectra were recorded on 300 (Bruker) and 500 MHz (Varian) spectrometers in appropriate solvents using TMS as internal standard and the chemical shifts are shown in  $\delta$  scales. <sup>13</sup>C NMR spectra were recorded on 75 MHz spectrometers. High-resolution mass spectra were obtained by using ESI-QTOF mass spectrometry. All the experiments were monitored by analytical thin layer chromatography (TLC) performed on silica gel GF254 pre-coated plates. After elution, the plate was visualized under UV illumination at 254 nm for UV active materials. Silica gel finer than 200 mesh was used for column chromatography. Yields refer to chromatographically and

\*For correspondence

spectroscopically homogeneous materials, unless otherwise stated. Appropriate names for all the new compounds were given with the help of ChemBioOffice 12.0; 2010. All the photophysical properties for these compounds were recorded with JASCO 500 UV Spectrophotometer. All the graphs were drawn using Origin software version 7.0. The solvents for column elution were purchased commercially and for UV-visible studies the solvents were purchased from Sigma Aldrich.

## 2.2 General procedure for the synthesis of aldehydes 2a, 2b and 2c

All these aldehydes were synthesized according to the procedure described in literature.<sup>11a</sup> Analytical data is in agreement with the literature data for dibenzo[*b,d*]furan-2-carbaldehyde (**2a**),<sup>11a</sup> 9-methyl-9H-carbazole-3-carbaldehydes (**2b**)<sup>11a</sup> and dibenzo[*b,d*]thiophene-2-carbaldehyde (**2c**).<sup>9</sup>

**Spectral data of compound 2c:** Light yellow solid; yield: 60%; M.p. 61–63°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 10.13 (s, 1 H), 8.59 (t, *J* = 0.7 & 1.3 Hz, 1 H), 8.27–8.13 (m, 1 H), 8.00–7.90 (m, 2 H), 7.89–7.82 (m, 1 H), 7.55–7.43 (m, 2 H).

## 2.3 General procedure for the synthesis of Xanthenediones

A mixture of aldehyde (1 mmol), diketone (2 mmol) and PPA-SiO<sub>2</sub> (20 mol%) were heated at 125°C with stirring for the time specified in table 2. After completion, the reaction mixture was cooled to room temperature, and dichloromethane was added and the catalyst was filtered off. The filtrate thus obtained was concentrated under vacuum. Recrystallization of crude mass in CHCl<sub>3</sub>: hexane (1:5) yielded pure xanthenediones **6**, **7** & **8** as crystalline solids.

**2.3a 9-(Dibenzo[*b,d*]furan-2-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (6a):** Yellow solid; yield: 364 mg (95%); M.p. 198–200°C. IR (KBr): 2925, 1672, 1621, 1478, 1430, 1359, 1200, 1176, 1129, 1010, 956, 755 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.95 (d, *J* = 7.7 Hz, 1 H), 7.86 (d, *J* = 1.5 Hz, 1 H), 7.45 (d, *J* = 8.1 Hz, 1 H), 7.40–7.32 (m, 2 H), 7.31–7.22 (m, 2 H), 4.91 (s, 1 H), 2.74–2.50 (m, 4 H), 2.40–2.23 (m, 4 H), 2.11–1.94 (m, 4 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 196.6, 163.8, 156.4, 154.9, 139.1, 127.4, 126.8, 123.9, 123.6, 122.4, 120.8, 120.7, 117.1, 111.4, 111.1, 36.9, 31.6, 27.1, 20.2. HRMS (ESI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>21</sub>O<sub>4</sub>: 385.1439; found: 385.1446.

**2.3b 9-(Dibenzo[*b,d*]furan-2-yl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (7a):** White solid; yield: 404 mg (92%); M.p. 190–195°C. IR (KBr): 2955, 2927, 1661, 1622, 1448, 1431, 1360, 1200, 1166, 1138, 1002, 746 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.94 (d, *J* = 6.9 Hz, 1 H), 7.88 (d, *J* = 1.7 Hz, 1 H), 7.46 (d, *J* = 8.1 Hz, 1 H), 7.41–7.31 (m, 2 H), 7.29–7.22 (m, 2 H), 4.86 (s, 1 H), 2.48 (s, 4 H), 2.25–2.10 (m, 4 H), 1.12 (s, 6 H), 1.01 (s, 6 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 196.4, 162.1, 156.4, 154.8, 138.8, 127.2, 126.7, 123.5, 122.4, 120.8, 115.8, 111.3, 111.0, 50.7, 40.8, 31.7, 29.2, 27.2. HRMS (ESI): *m/z* [M+Na]<sup>+</sup> calcd for C<sub>29</sub>H<sub>28</sub>O<sub>4</sub>Na: 463.1885; found: 463.1887.

**2.3c 9-(Dibenzo[*b,d*]furan-2-yl)-3,6-diisopropyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (8a):** Pale yellow solid; yield: 439 mg (94%); M.p. 200–205°C. IR (KBr): 2960, 2874, 1674, 1623, 1476, 1448, 1371, 1353, 1243, 1189, 1136, 1023, 989, 841, 761 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.00–7.91 (m, 1 H), 7.88–7.78 (dd, *J* = 8.8 Hz & 1.7 Hz, 1 H), 7.46 (d, *J* = 7.9 Hz, 1 H), 7.42–7.31 (m, 2 H), 7.30–7.21 (m, 2 H), 4.87 (d, *J* = 3.0 Hz, 1 H), 2.71–2.27 (m, 6 H), 2.17–1.80 (m, 4 H), 1.70–1.52 (m, 2 H), 1.04–0.90 (m, 12 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 196.9, 163.5, 156.3, 154.8, 138.9, 127.4, 126.7, 124.2, 123.8, 122.3, 120.8, 116.6, 116.3, 111.3, 111.0, 41.3, 40.8, 38.7, 31.7, 30.8, 19.4. HRMS (ESI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>31</sub>H<sub>33</sub>O<sub>4</sub>: 469.2378; found: 469.2361.

**2.3d 9-(9-Methyl-9H-carbazol-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (6b):** White solid; yield: 361 mg (91%); M.p. 190–195°C. IR (KBr): 2926, 1734, 1668, 1622, 1432, 1358, 1201, 1177, 1131, 1009, 959, 765, 700 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.04 (d, *J* = 8.3 Hz, 1 H), 7.85 (s, 1 H), 7.41 (d, *J* = 8.3 Hz, 1 H), 7.34 (t, *J* = 8.3 Hz, 1 H), 7.28–7.22 (m, 1 H), 7.21–7.16 (d, *J* = 8.3 Hz, 1 H), 7.12 (t, *J* = 7.2 Hz, 1 H), 4.92 (s, 1 H), 3.77 (s, 3 H), 2.74–2.51 (m, 4 H), 2.45–2.26 (m, 4 H), 2.06–1.97 (m, 4 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 196.8, 163.6, 141.2, 135.4, 126.6, 125.4, 122.7, 122.5, 120.4, 119.9, 118.5, 117.5, 108.2, 107.9, 37.0, 31.5, 29.0, 27.2, 20.3. HRMS (ESI): *m/z* [M+Na]<sup>+</sup> calcd for C<sub>26</sub>H<sub>23</sub>O<sub>3</sub>NNa: 420.1575; found: 420.1570.

**2.3e 3,3,6,6-Tetramethyl-9-(9-methyl-9H-carbazol-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (7b):** Brown solid; yield: 421 mg (93%); M.p. 220–223°C. IR (KBr): 3324, 2968, 2918, 1701, 1612, 1598, 1513, 1452, 1283, 1164, 1127, 1015, 836, 694 cm<sup>-1</sup>.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.02 (d, *J* = 7.7 Hz, 1 H), 7.86 (s, 1 H), 7.46–7.29 (m, 2 H), 7.28–7.17 (m, 2 H), 7.11 (t, *J* = 8.1 Hz, 1 H), 4.87 (s, 1 H), 3.79 (s, 3 H), 2.48 (s, 4 H), 2.28–2.07 (m, 4 H), 1.12 (s, 6 H), 1.00 (s, 6 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 196.5, 161.8, 141.1, 139.81, 135.17, 126.6, 125.2, 122.7, 120.2, 119.8, 118.4, 116.2, 108.2, 107.8, 50.7, 40.8, 32.2, 31.6, 29.2, 27.3. HRMS (ESI): *m/z* [M+Na]<sup>+</sup> calcd for C<sub>30</sub>H<sub>31</sub>O<sub>3</sub>NNa: 476.2201; found: 476.2196.

2.3f 3,6-Diisopropyl-9-(9-methyl-9H-carbazol-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (**8b**): Black solid; yield: 442 mg (92%); M.p. 120–124°C. IR (KBr): 2958, 1662, 1492, 1471, 1370, 1186, 1138, 744 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.08–8.00 (m, 1 H), 7.85–7.75 (m, 1 H), 7.45–7.29 (m, 2 H), 7.27–7.07 (m, 3 H), 4.87 (d, *J* = 4.1 Hz, 1 H), 3.78 (s, 3 H), 2.84–2.21 (m, 6 H), 2.16–1.75 (m, 4 H), 1.69–1.49 (m, 2 H), 1.02–0.86 (m, 12 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 197.0, 163.9, 141.2, 138.0, 133.9, 126.7, 126.6, 125.3, 120.4, 120.3, 119.8, 118.4, 117.1, 108.2, 107.9, 41.5, 40.9, 38.8, 31.8, 31.1, 29.7, 19.4. HRMS (ESI): *m/z* [M+Na]<sup>+</sup> calcd for C<sub>32</sub>H<sub>35</sub>O<sub>3</sub>NNa: 504.2514; found: 504.2525.

2.3g 9-(Dibenzo[*b,d*]thiophen-2-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (**6c**): White solid; yield: 372 mg (93%); M.p. 210–213°C. IR (KBr): 2926, 1734, 1668, 1622, 1432, 1358, 1201, 1177, 1131, 1009, 959, 765, 700 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.20–8.14 (m, 1 H), 8.06 (d, *J* = 1.5 Hz, 1 H), 7.78–7.71 (m, 1 H), 7.69–7.63 (m, 1 H), 7.42–7.32 (m, 2 H), 7.31–7.26 (m, 1 H), 4.93 (s, 1 H), 2.74–2.49 (m, 4 H), 2.40–2.22 (m, 4 H), 2.11–1.91 (m, 4 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 196.5, 163.9, 140.9, 139.6, 137.4, 135.4, 129.9, 127.1, 126.3, 124.0, 122.5, 122.3, 121.6, 116.8, 36.8, 31.6, 27.0, 20.2. HRMS (ESI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>21</sub>O<sub>3</sub>S: 401.1211; found: 401.1206.

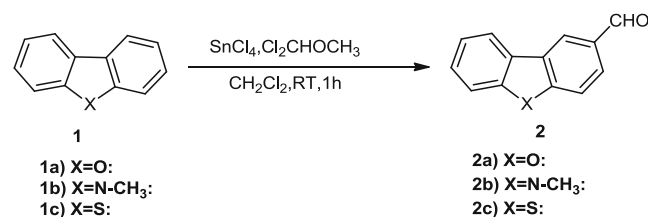
2.3h 9-(Dibenzo[*b,d*]thiophen-2-yl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (**7c**): Pale yellow solid; yield: 414 mg (91%); M.p. 200–204°C. IR (KBr): 2957, 2916, 1656, 1621, 1464, 1429, 1359, 1200, 1165, 1136, 1003, 763, 735 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.19 (m, 1 H), 8.07 (d, *J* = 1.3 Hz, 1 H), 7.80–7.70 (m, 1 H), 7.69–7.62 (d, *J* = 8.3 Hz, 1 H), 7.42–7.26 (m, 3 H), 4.88 (s, 1 H), 2.48 (s, 4 H), 2.25–2.08 (ab d, 4 H), 1.12 (s, 6 H), 1.00 (s, 6 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 196.4, 162.2, 140.6, 139.6, 135.4, 129.4, 127.1, 126.3, 124.0, 122.6, 122.3, 121.7, 121.6, 115.6, 50.6, 40.8, 31.8, 29.2, 27.2. HRMS (ESI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>29</sub>H<sub>29</sub>O<sub>3</sub>S: 457.1837; found: 457.1845.

2.3i 9-(Dibenzo[*b,d*]thiophen-2-yl)-3,6-diisopropyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (**8c**): Brick red solid; yield: 454 mg (94%); M.p. 80–85°C. IR (KBr): 2958, 1670, 1624, 1466, 1430, 1368, 1185, 1137, 819, 762, 733 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.16 (s, 1 H), 8.05 (d, *J* = 10.7 Hz, 1 H), 7.74 (d, *J* = 8.1 Hz, 1 H), 7.69–7.63 (m, 1 H), 7.46–7.17 (m, 3 H), 4.88 (s, 1 H), 2.73–2.20 (m, 6 H), 2.17–1.76 (m, 4 H), 1.68–1.42 (m, 2 H), 1.04–0.75 (m, 12 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 196.8, 164.2, 140.7, 139.6, 137.5, 135.4, 129.1, 127.1, 127.0, 126.3, 124.0, 122.5, 122.3, 121.7, 121.6, 116.1, 41.3, 40.8, 38.7, 31.7, 31.0, 19.4. HRMS (ESI): *m/z* [M+Na]<sup>+</sup> calcd for C<sub>31</sub>H<sub>32</sub>O<sub>2</sub>SNa: 507.1969; found: 507.1995.

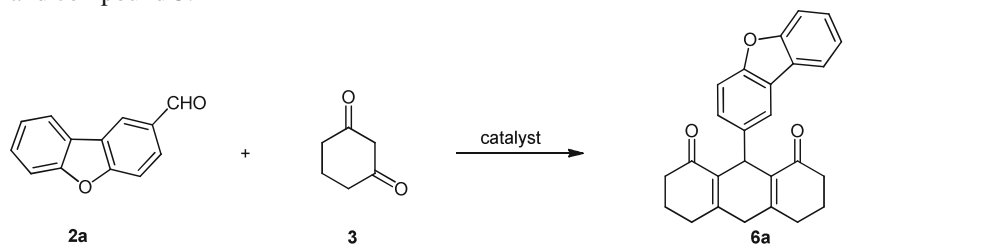
### 3. Results and Discussion

Inspired by the applications of dibenzo[*b,d*]furan (**1a**), 9-methyl-9H-carbazole (**1b**), dibenzo[*b,d*]thiophene (**1c**), and xanthenediones we envisaged to combine xanthenedione and tricyclic heterocycles in one molecular frame to examine their photophysical properties. In continuation of our work,<sup>11</sup> we herein describe an efficient one-pot synthesis of dibenzofuran, dibenzothiophene and 9-methyl-9H-carbazoles embedded xanthene-1,8-diones through the condensation of respective aldehydes with active cyclic 1,3-dicarbonyl in presence of PPA-SiO<sub>2</sub> catalyst. UV-Visible absorption properties are evaluated for these new derivatives.

Initiating the study, dibenzo[*b,d*]furan-2-carbaldehyde (**2a**), 9-methyl-9H-carbazole-3-carbaldehyde (**2b**) and dibenzo[*b,d*]thiophene-2-carbaldehyde (**2c**) required were synthesized using formylation conditions developed in our laboratory (scheme 1).<sup>11a</sup> For example, the reaction dibenzo[*b,d*]furan with α,α-dichloromethyl methyl ether and SnCl<sub>4</sub> at room temperature in dichloromethane gave the required dibenzo[*b,d*]furan-2-carbaldehyde (**2a**) in 84% yield. Similarly 9-methyl-9H-carbazole and dibenzo[*b,d*]thiophene was formylated to obtain 9-methyl-9H-carbazole-3-carbaldehyde (**2b**) and dibenzo[*b,d*]thiophene-2-carbaldehyde (**2c**) respectively in 80% and 60% yields. All the aldehydes **2a–c** was fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectral analysis and are in agreement with reported data.<sup>9,11a</sup>



**Scheme 1.** Preparation of tricyclic heterocyclic aldehydes **2a–c**.

**Table 1.** Optimization of reaction conditions for a selective reaction between aldehyde **2a** and compound **3**.


S. No	Catalyst	mol%	Temp (°C)	Time (h)	Yield (%) <sup>b</sup>
1	CH <sub>3</sub> SO <sub>3</sub> H	100	30	12	46
2	<i>p</i> -TSA	20	125	6	70
3	Montmorillonite-K10	20	125	12	50
4	HClO <sub>4</sub> -SiO <sub>2</sub>	20	125	6	66
5	H <sub>2</sub> SO <sub>4</sub> -SiO <sub>2</sub>	20	125	6	78
6	InCl <sub>3</sub> ·3H <sub>2</sub> O	20	125	12	63
7	FeCl <sub>3</sub> ·6H <sub>2</sub> O	20	125	12	53
8	LiBr	20	125	12	41
9	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·7H <sub>2</sub> O	20	125	12	54
10	SnCl <sub>2</sub> ·2H <sub>2</sub> O	20	30	12	26
11	SnCl <sub>2</sub> ·2H <sub>2</sub> O	20	125	6	45
12	K <sub>5</sub> CoW <sub>12</sub> O <sub>40</sub> ·3H <sub>2</sub> O	20	125	12	38
13	PPA-SiO <sub>2</sub>	20	100	6	62
14	PPA-SiO <sub>2</sub>	30	125	4	86
15	PPA-SiO <sub>2</sub>	20	125	1.5	95

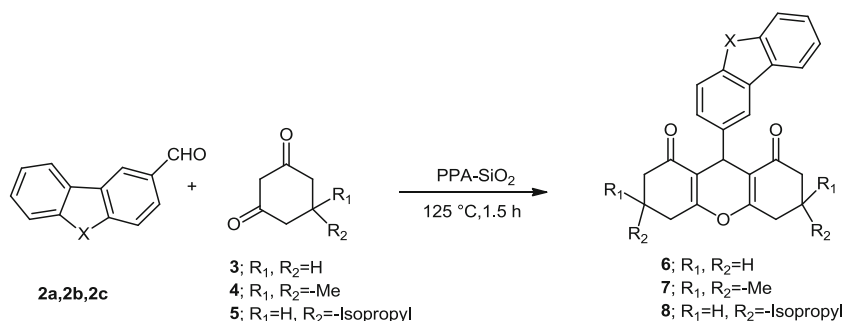
(a) Dibenzo[*b, d*]furan-2-carbaldehyde (**2a**) (1 mmol), 1,3-cyclohexane dione **3** (2 mmol), and catalyst were mixed and conducted the reaction.

(b) Isolated yields of **6a**

With the required aldehydes **2a–c** in hand, we now focused on the synthesis of new xanthenedione derivatives through the condensation of aldehydes **2a–c** with different cyclic diketones [1,3-cyclohexanedione (**3**), dimedone (**4**) and 5-isopropyl 1,3-cyclohexanedione (**5**)] in presence of various catalysts and solvents. Initial efforts were focused on the reaction of aldehyde **2a** and 1,3-cyclohexanedione (**3**) with different catalysts InCl<sub>3</sub>·3H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O, LiBr, Fe<sub>2</sub>SO<sub>4</sub>·7H<sub>2</sub>O, SnCl<sub>2</sub>·2H<sub>2</sub>O and K<sub>5</sub>CoW<sub>12</sub>O<sub>40</sub>·3H<sub>2</sub>O CH<sub>3</sub>SO<sub>3</sub>H, *p*-TSA, montmorillonite-K10, HClO<sub>4</sub>-SiO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>-SiO<sub>2</sub>. The

yields of isolated product xanthenedione **6a** along with reaction temperatures and catalysts used are shown in table 1. Among the catalysts screened, the reaction with 20 mol% of PPA-SiO<sub>2</sub> catalyst under solvent-free conditions proceeded efficiently and smoothly in shorter reaction time (1.5 h) at 125°C to give the xanthenedione derivative **6a** in very good yield in 95% (table 1, entry 15).

In order to investigate the general applicability and versatility of this procedure for the synthesis of variety of substituted xanthenedione derivatives, condensation

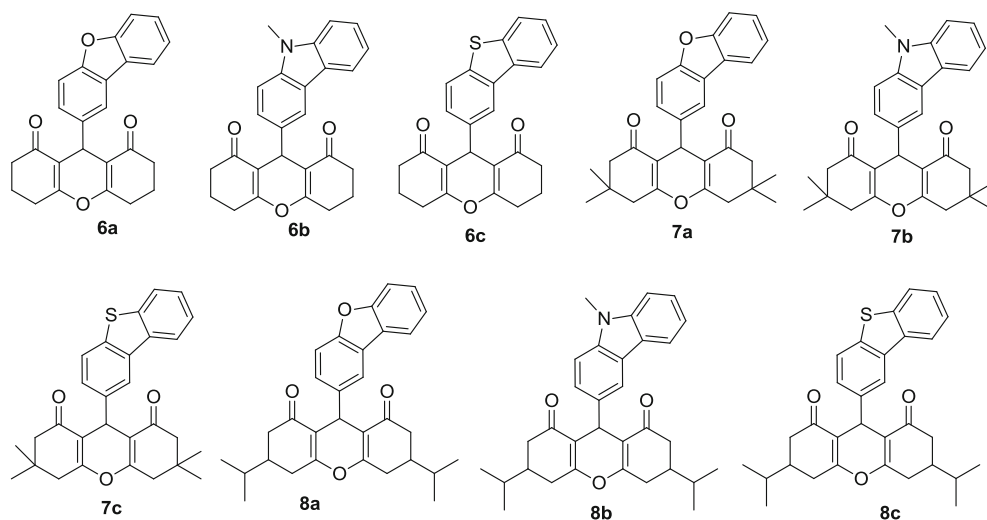
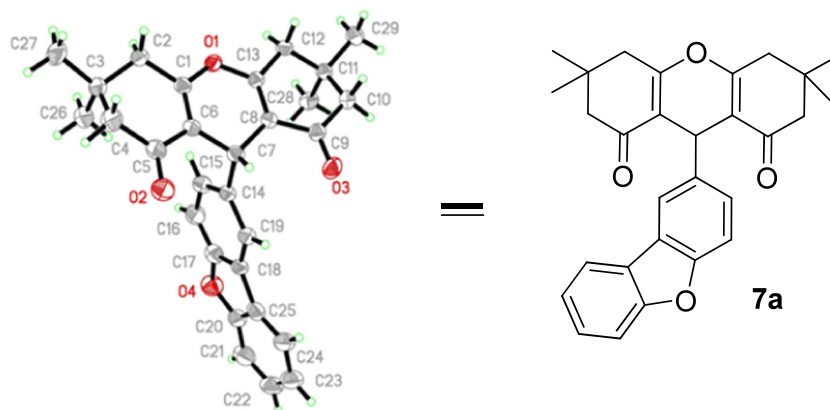
**Scheme 2.** Synthesis of tricyclic heterocycle tethered xanthenediones **6a–c**, **7a–c** and **8a–c**.

**Table 2.** Synthesis of novel dibenzo[*b, d*]furan, dibenzo[*b, d*]thiophene, 9-methyl-9*H*-carbazole embedded xanthene-1,8-diones **6a-c**, **7a-c** and **8a-c** with recyclable PPA-SiO<sub>2</sub> catalyst.

S.No	Aldehyde	diketone	Product <sup>a</sup>	Reaction time (h)	Yield (%) <sup>b</sup>
1	2a	3	6a	1.5	95
2	2a	4	7a	2	92
3	2a	5	8a	1.5	94
4	2b	3	6b	1.5	91
5	2b	4	7b	1.5	93
6	2b	5	8b	2	92
7	2c	3	6c	1.5	93
8	2c	4	7c	2	91
9	2c	5	8c	2	94

a) All the reactions were performed without solvent at 125°C.

b) Yields of isolated products.

**Figure 1.** Structures of xanthenedione derivatives **6**, **7** and **8**.**Figure 2.** ORTEP diagram of compound **7a**.

of aldehydes **2a**, **2b** and **2c** with activated methylene compounds such as cyclohexane-1,3-dione (**3**); 5,5-dimethyl cyclohexane-1,3-dione (**4**); 5-isopropylcyclo

hexane-1,3-dione (**5**) were examined (scheme 2). All these reactions proceeded to yield the corresponding xanthenediones **6a-c**, **7a-c** and **8a-c** in very good yields



**Table 3.** Comparison of absorption properties of compounds **6a–c**, **7a–c** and **8a–c**.

S. No	Product	$\lambda_{\max}(\text{nm})\{\epsilon_{\max}(\text{L mole}^{-1} \text{cm}^{-1})\}$		
		In $\text{CHCl}_3$	In THF	In $\text{CH}_3\text{-CN}$
1	6a	287.5(29373)	288.5(36398)	287(17437)
2	7a	290.5(28880)	289.5(29807)	288(26259)
3	8a	289.5(19660)	289(25702)	287(20634)
4	6b	297.5(12824)	293.5(14715)	292(11495)
5	7b	289.5(20296)	293(25158)	291.5(24707)
6	8b	297.5(14221)	293(20512)	292(8442)
7	6c	290.5(21491)	286.5(17261)	285(17270)
8	7c	291(16719)	286.5(22569)	285(13889)
9	8c	289.5(25673)	286(23000)	286(14000)
10 <sup>a</sup>	9	—	302(17000)	294(5300)

a) Product **9** refers to the xanthenedione derivative formed from benzaldehyde and dimedone.

~90–95% (table 2). All the products (figure 1) thus obtained were fully characterized by IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and Mass spectral analysis.

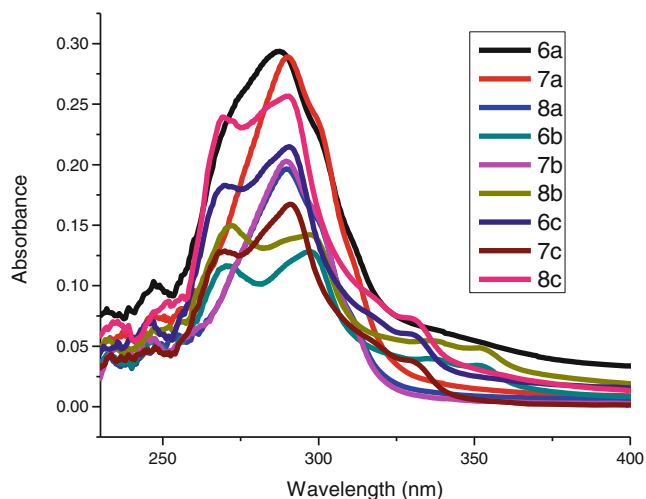
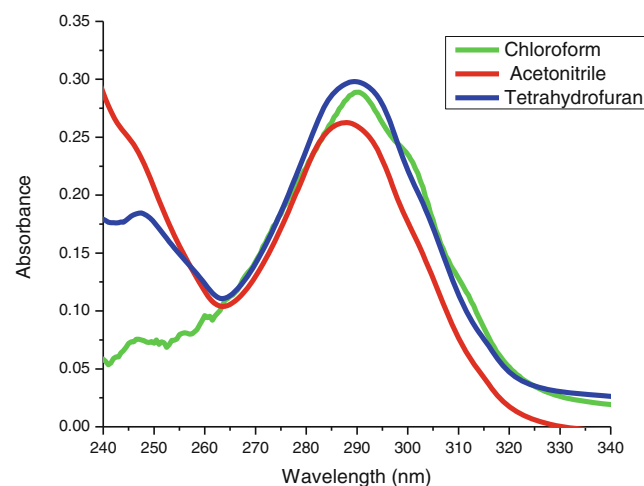
The structure of xanthenedione **7a** was confirmed from its single-crystal X-ray crystallographic analysis (figure 2).

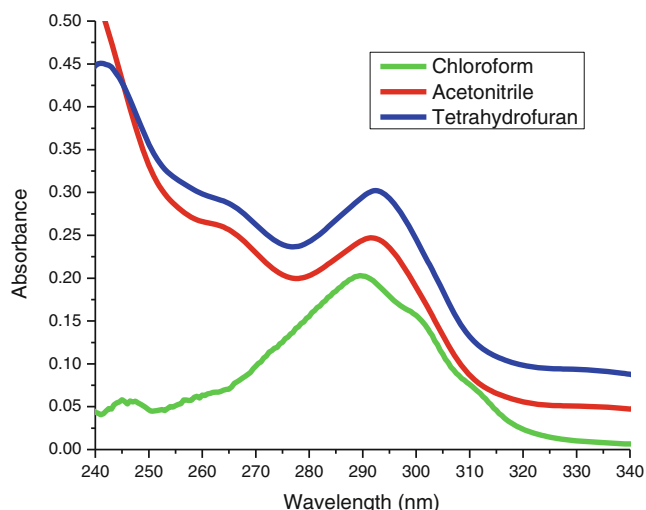
The possible application of these newly synthesized xanthenedione derivatives were investigated for their optical behaviour due to extended conjugation with in-built pyran ring system. The properties of the newly synthesized xanthenediones **6a–c**, **7a–c** and **8a–c** were investigated using JASCO UV-Visible absorption spectrophotometer in dilute solutions of chloroform at a concentration of  $10^{-5}$  moles/lit. The data obtained was summarized in table 3. All the xanthenedione derivatives **6a–c**, **7a–c** and **8a–c** exhibited similar absorption spectra with comparable molar absorptivities at an absorption maxima ( $\lambda_{\max}$ ) in the region of 287–291 nm in chloroform (figure 3). This absorption bands could

be assigned due to the excitation of  $\pi$  electrons existing in the xanthenedione derivatives **6a–c**, **7a–c** and **8a–c**.

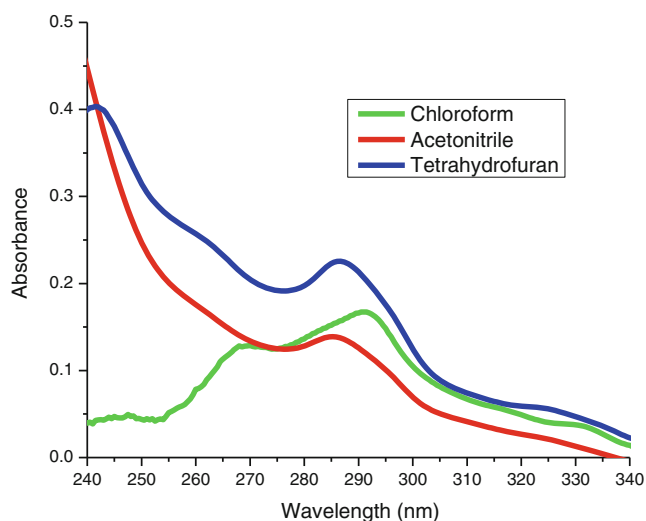
Further to study the effect of solvent on the UV-Visible absorption properties of xanthenediones, investigations were carried out using various solvents like tetrahydrofuran and acetonitrile and the results were correlated with the absorption properties in chloroform (figure 4–6 and table 3). Among these xanthenediones evaluated, compounds having dibenzo[*b, d*]furan **6a**, **7a** and **8a** has shown greater molar extinction coefficient than that of the other xanthenedione derivatives **6b–c**, **7b–c**, and **8b–c**. Moreover observation of the figures 3–5, revealed that the xanthenedione derivative **6a**, **7a** and **8a** did not exhibit any solvatochromism. Almost all the compounds have shown greater  $\epsilon_{\max}$  in tetrahydrofuran solvent compared to other solvents used.

When correlated with the known xanthenedione **9**<sup>12</sup> having phenyl ring (i.e., xanthenedione derived from benzaldehyde and dimedone, figure 7), the newly

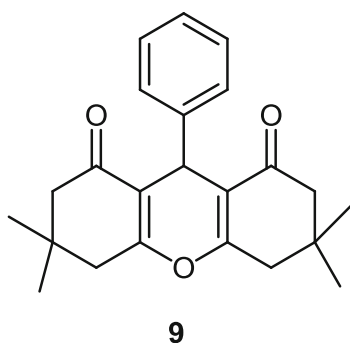
**Figure 3.** Absorption Spectrum of **6a–c**, **7a–c** and **8a–c** in  $\text{CHCl}_3$  at a concentration of  $10^{-5}$  M.**Figure 4.** Absorption Spectrum of **7a** in THF,  $\text{CH}_3\text{-CN}$  and  $\text{CHCl}_3$ .



**Figure 5.** Absorption Spectrum of **7b** in THF, CH<sub>3</sub>-CN and CHCl<sub>3</sub>.



**Figure 6.** Absorption Spectrum of **7c** in THF, CH<sub>3</sub>-CN and CHCl<sub>3</sub>.



**Figure 7.** Structure of xanthenedione derivative **9** derived from benzaldehyde and dimedone.

synthesized xanthenedione derivatives **6a-c**, **7a-c** and **8a-c** showed higher molar extinction values ( $\epsilon_{\max}$ ) and lower absorption wavelengths ( $\lambda_{\max}$ ). The lowering in the absorption wavelengths may be due to the interference of the non-bonded electrons present on the heteroatom with the extending  $\pi$  bonded conjugated electrons which results in increasing the energy gap ( $E_g$ ) between HOMO and LUMO.<sup>13</sup>

#### 4. Conclusions

We have described an efficient one-pot synthesis of novel dibenzofuran, carbazole and dibenzothiophene embodied xanthenediones (**6a-c**, **7a-c** and **8a-c**) through the condensation of respective aldehydes with cyclic 1,3-diketones in the presence of PPA-SiO<sub>2</sub> catalyst (20 mol%). Absorption spectra of all the newly synthesized xanthenediones **6a-c**, **7a-c** and **8a-c** suggested that the new compounds have greater molar extinction coefficient values when compared to the xanthenedione formed from benzaldehyde and dimedone.

#### Supplementary Information

CCDC 849770 contains Crystallographic data for the compound **7a**. This data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/datarequest/cif>. Scanned copies of <sup>1</sup>H, <sup>13</sup>C and ESI-HRMS spectra of **6a-c**, **7a-c** and **8a-c** are given in electronic supporting information available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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