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Microwave-assisted clean synthesis of xanthenes and chromenes in [bmim][PF_6] and their antioxidant studies

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Abstract An efficient one-pot synthesis of xanthene and chromene derivatives by three-component reactions of aryl aldehydes, cyclic 1,3-diketones, and 2-naphthol/4-hydroxy coumarin catalyzed by ionic liquid (IL) [bmim][PF_6] under microwave irradiation is described. The present scheme provides several advantages such as short reaction time, mild reaction conditions, good yields, convenient operation, and reuse of IL. In vitro antioxidant activity was evaluated for the synthesized compounds by DPPH method. Compounds **6a, 6h, 6c, 6b, 4k**, and **4a** showed the highest antioxidant potency.

Keywords Xanthenes · Chromenes · Ionic liquid · Antioxidant activity

Introduction

Multicomponent reactions (MCRs) are chemical transformations in which several reactions are mixed into one synthetic operation to form several bonds to construct a final complex product in a time- and cost-effective way [1–3]. The primary goal of MCRs research is to synthesize heterocyclic compounds, which make up the majority of pharmaceuticals, agrochemicals, natural products, and drug-like molecules [4, 5]. In a true sense, these reactions are environmentally friendly processes by reducing the number of steps, energy consumption, and waste output [6, 7]. In recent times, microwave-assisted chemistry has been demonstrated to be

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effective at increasing the rate of MCR procedures [8, 9]. Microwave irradiation offers several unique advantages like enhanced yields, reproducibility, cleaner reactions, and being used as an alternative thermal energy source to conventional heating [10, 11]. It has been applied to a wide range of reactions like cycloaddition, organometallic reactions, and nanoparticle synthesis [12–14].

Xanthenes and chromenes are cited as active oxygen heterocycles possessing a broad spectrum of biological activity [15]. Xanthene derivatives have been found to exhibit as pH-sensitive fluorescent materials for visualization of biomolecules [16]. These compounds have also been used as dyes [17], antagonists [18], and in laser technologies [19].

On the other hand, chromenes are used as potent anti-tuberculosis agents and often appear as an important structural element in many biologically active natural compounds [20, 21]. Though various procedures were described for the preparation of xanthenes and chromenes, they have been hampered by several disadvantages like prolonged reaction time, unsatisfactory yields, harsh reaction conditions, and the requirement of excess catalysts [22].

Recently, the use of ionic liquids (ILs) earned recognition as environmentally benign green media in organic synthesis, especially those based on the 1,3-dialkylimidazolium cation have significant intrinsic characteristics over common organic solvents such as non-inflammable, reusability, low toxicity, wide liquid range, and acidic catalytic activity and so on [23, 24]. The organic reactions using ILs can be carried out in a homogeneous phase and it can be recycled in a green procedure [25].

With all of this in mind, and as part of our ongoing research devoted to the development of novel synthetic methods in heterocyclic chemistry [26–30], here we describe the microwave-assisted synthesis of xanthene and chromene derivatives by the reactions of arylaldehydes, 2-naphthol or 4-hydroxycoumarin and 1,3-cyclodiones in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]).

Results and discussion

For the synthesis of xanthenes, 4-chlorobenzaldehyde, 2-naphthol and 1, 3-cyclohexanedione were selected as model reactants in [bmim][PF_6] under conventional way in different conditions. Although the reactions were successful with moderate yield, it required prolonged reaction times. Because of the advantage of using microwave irradiation, the microwave method was applied to this reaction under solvent-free conditions. The use of microwaves afforded high yield and the reaction time fell to 15 min. In search of an optimization of reaction conditions, the model reaction was performed with different catalysts and solvents and the results are summarized in Table 1.

Apart from [bmim][PF_6], all solvents and catalysts afforded the product with a moderate yield in longer reaction times. We next investigated the amount of IL required for this reaction and the results showed that 10 mol % of [bmim][PF_6] was sufficient to catalyze the reaction. Excess or <10 mol % concentration of [bmim][PF_6] has no obvious difference in the reaction yield (Table 1).

To explore the scope and limitations of this reaction, the optimized reaction conditions (IL, MW 340 W, 40 % power, 15 min) were used for the construction of

Table 1 Synthesis of 12-(4-chlorophenyl)-9,10-dihydro-8*H*-benzo[a]xanthen-11(12*H*)-one (**4b**) in different conditions

Entry	Catalyst	Mol %	Solvent	Time	Yield (%)
1	[bmim][PF_6]	15	–	15	90
2	**[bmim][PF_6]**	**10**	**–**	**15**	**91**
3	[bmim][PF_6]	5	–	20	88
4	[bmim][PF_6]	10	EtOH	15	71
5	[bmim][PF_6]	10	DMF	15	75
6	[bmim][PF_6]	10	CH_2Cl_2	15	83
7	[bmim][PF_6]	10	CH_3CN	15	54
8	[bmim][BF_4]	5	–	20	88
9	L-Proline	5	–	15	75
10	CF_3CO_2H	5	–	15	60
11	$AlCl_3$	5	–	15	57
12	$CuCl_2$	5	–	15	31
13	–	–	–	30	–

Experimental conditions: cyclohexane-1,3-dione (1 mmol), 2-naphthol (1 mmol), 4-chlorobenzaldehyde (1 mmol) under microwave irradiation

a library from various aldehydes (Scheme 1). The reaction went along well with both electron-withdrawing and electron-donating substituted aromatic aldehydes (Table 2).

With the encouraging results from the above reaction, it was thought worthwhile to replace the 2-naphthol with 4-hydroxy coumarin in order to get some novel chromene derivatives (Scheme 2).

Moreover, compounds with the coumarin scaffold also exhibit a wide range of biological activities [31–33]. Interestingly all the substrates afford the desired chromene derivatives in good yields as shown in Table 3.

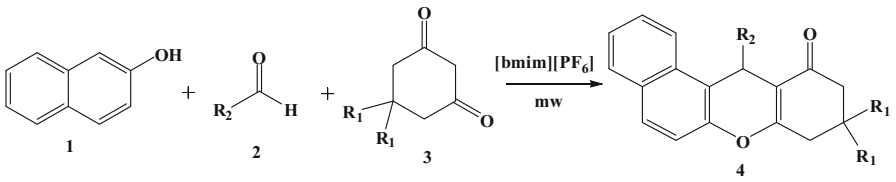
It was observed that in the absence of 2-naphthol, the [bmim][PF_6] catalyzed reaction of 1,3-cyclodione and aldehyde under the same conditions resulted to the formation of compounds **7a–i** in good yields (Scheme 3; Table 4).

With the above-mentioned results in hand, a plausible sequence of reaction pathway is depicted in Fig. 1. The interaction of 1,3-cyclodiones and aromatic aldehydes lead to the intermediate **8** catalyzed with [bmim][PF_6]. The resulting intermediate leads to **10** and **12** by *ortho* C-alkylation of 2-naphthol/4-hydroxy coumarin. Subsequently, **10** and **12** intermediate losses a molecule of H_2O by cyclodehydrogenation afforded the products **4a–k** and **6a–h**. In the absence of **1**, the second molecules of 1,3-dicarbonyl compounds attacks intermediate **8** leading to the compounds **7a–i**.

The catalytic activity of the recycled IL was also studied. To our delight, IL was recycled for five runs without an apparent loss of activity under the above-investigated conditions (Fig. 2).

DPPH radical scavenging assay

The antioxidant activities of the synthesized compounds was investigated using DPPH (2,2-diphenyl-1-picrylhydrazyl) free radical scavenging assay with respect to



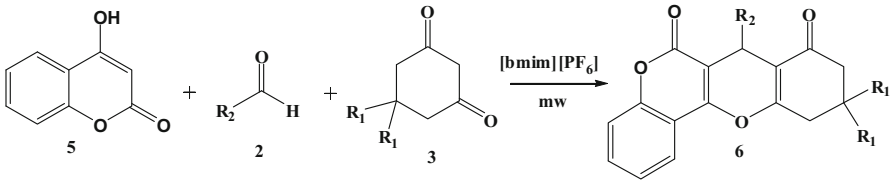
Scheme 1 [bmim][PF_6] catalyzed synthesis of benzoxanthene derivatives under microwave irradiation (**4a–k**)

Table 2 Physical data of the synthesised compounds **4a–k**

Entry	R_2	R_1	Product	Time (min)	Yield (%)	m.p (°C)	
						Found	Lit
1	3,4,5-$(OCH_3)C_6H_2$	H	**4a**	12	92	180–182	–
2	4-ClC_6H_5	H	**4b**	15	91	205–207	208–209 [34]
3	3,4-$(OCH_3)C_6H_3$	H	**4c**	15	90	182–184	–[43][a]
4	3,5-OCH_3-4-OHC_6H_2	H	**4d**	12	90	189–191	–
5	2-$OCH_2CH_3C_6H_4$	H	**4e**	17	85	194–196	–
6	4-$C_6H_5C_6H_4$	H	**4f**	15	91	225–227	–
7	3-$NO_2C_6H_4$	H	**4g**	16	87	231–233	235–236 [35]
8	2-FC_6H_4	H	**4h**	17	83	270–272	–
9	3-OHC_6H_4	H	**4i**	17	82	205–207	–
10	C_6H_5	CH_3	**4j**	16	87	190–192	189–190 [35]
11	3,5-OCH_3-4-OHC_6H_2	CH_3	**4k**	15	92	205–207	–

The reaction was carried out with **1** (1 mmol), **2** (1 mmol), **3** (1 mmol), ionic liquid (10 mol %) under microwave irradiation for the given time in the table

[a] Reported, but m.p is unavailable



Scheme 2 [bmim][PF_6] catalyzed synthesis of benzo chromene derivatives under microwave irradiation (**6a–h**)

the standard BHT (butylated hydroxy toluene). Percentage activity of the compounds was calculated using the following equation

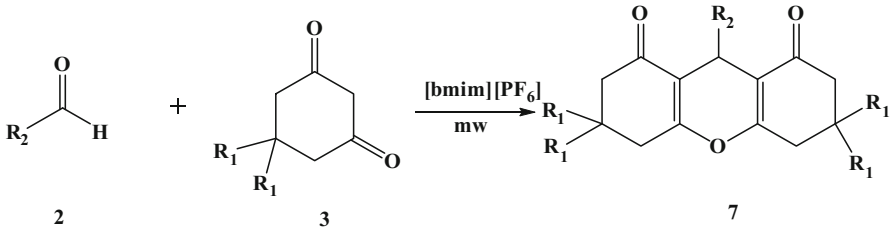
$$\text{Inhibition } (\%) = \left[1 - \left(A_{\text{sample}}/A_{\text{control}}\right)\right] \times 100$$

where A_{control} is the absorbance of the control (blank, without compound) and A_{sample} is the absorbance of the compounds. The percentage of inhibition was given

Table 3 Physical data of the synthesised compounds **6a–h**

Entry	R_2	R_1	Product	Time (min)	Yield (%)	m.p (°C)	
						Found	Lit
1	3,4,5-$(OCH_3)C_6H_2$	H	**6a**	12	92	179–181	–
2	3,4-$(OCH_3)C_6H_3$	H	**6b**	15	91	192–194	–
3	3,5-OCH_3-4-OHC_6H_2	H	**6c**	12	92	176–178	–
4	4-$C_6H_5C_6H_4$	H	**6d**	15	89	235–237	–
5	3-FC_6H_4	H	**6e**	17	86	238–240	–
6	4-OHC_6H_4	H	**6f**	17	90	178–180	180 [36]
7	3-OHC_6H_4	H	**6g**	17	88	209–211	–
8	3,5-OCH_3-4-OHC_6H_2	CH_3	**6h**	15	89	178–180	–

The reaction was carried out with **5** (1 mmol), **2** (1 mmol), **3** (1 mmol), ionic liquid (10 mol %) under microwave irradiation for the given time in the table



Scheme 3 [bmim][PF_6] catalyzed synthesis of xanthene derivatives under microwave irradiation (**7a–i**)

Table 4 Physical data of the synthesised compounds **7a–i**

Entry	R_2	R_1	Product	Time (min)	Yield (%)	m.p (°C)	
						Found	Lit
1	3,4,5-$(OCH_3)C_6H_4$	H	**7a**	10	93	182–184	–[a]
2	3,4-$(OCH_3)C_6H_4$	H	**7b**	10	91	215–217	216 [37]
3	3,5-OCH_3-4-OHC_6H_2	H	**7c**	10	91	224–226	–
4	4-$C_6H_5C_6H_4$	H	**7d**	12	92	196–198	196–198 [38]
5	4-$OC_2H_5C_6H_4$	H	**7e**	15	87	170–172	–[a]
6	3,4,5-$(OCH_3)C_6H_4$	CH_3	**7f**	10	92	186–188	187–189 [39]
7	3,4-$(OCH_3)C_6H_4$	CH_3	**7g**	10	90	173–175	170 [40]
8	$C_6H_5C_6H_4$	CH_3	**7h**	15	89	205–207	204–207 [41]
9	3-OHC_6H_4	CH_3	**7i**	15	88	230–232	223–225 [42]

The reaction was carried out with **2** (1 mmol), **3** (2 mmol), ionic liquid (10 mol %) under microwave irradiation for the given time in the table

[a] Reported, but m.p is unavailable

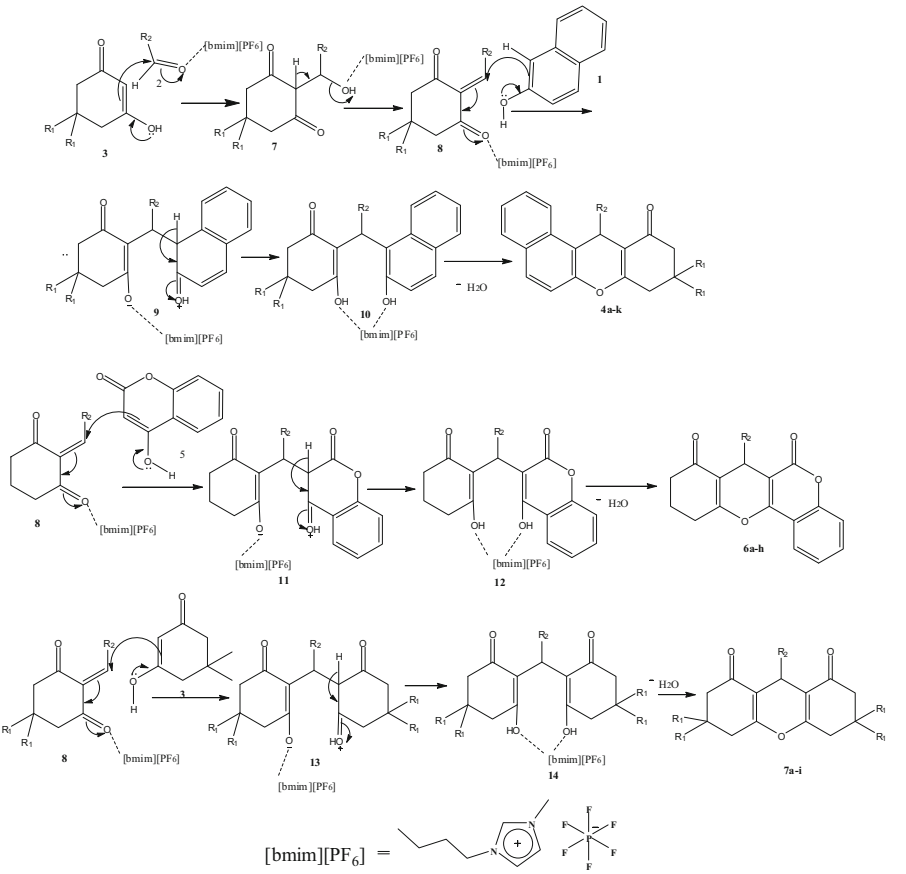


Fig. 1 Proposed mechanism for the synthesis of xanthenes and chromenes

in Table 5. The results revealed that the radical scavenging activities of benzochromenes were found more active in comparison to benzoxanthenes. Compounds **6a, 6h, 6c, 6b, 4k**, and **4a** have showed better activity at their higher concentrations.

Experimental

Solvents and reagents were commercially sourced and used without further purification. Melting points were recorded on an Elchem microprocessor-based DT apparatus in open capillary tubes and are uncorrected. IR spectra were obtained on an Avatar-330 FT-IR spectrophotometer (Thermo Nicolet) using KBr pellets. NMR spectra were recorded on a Bruker 400-MHz spectrometer with TMS as internal standard using $CDCl_3$ and DMSO-d_6. Mass analysis was performed using a Waters Micromass ZQ mass spectrometer. The microwave oven used was a synthetic microwave, CATA R catalyst microwave synthesizer with the maximum power of 850 W at 100 % power level. All reactions were carried at 40 % power level, which

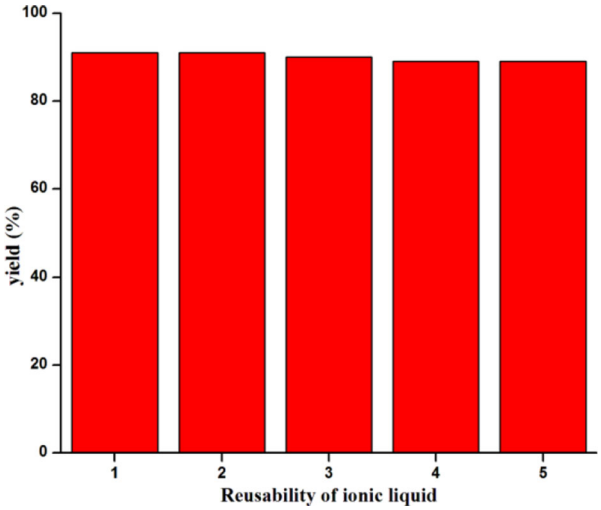


Fig. 2 Reusability of ionic liquid

Table 5 Antioxidant activity of synthesized compounds by DPPH method

Product	Inhibition (%)			Product	Inhibition (%)		
	100 μg/ml	500 μg/ml	1,000 μg/ml		100 μg/ml	500 μg/ml	1,000 μg/ml
BHT	94	96	98	**4k**	25	58	81
4a	21	54	78	**6a**	35	62	87
4b	8	15	33	**6b**	31	55	80
4c	17	52	76	**6c**	30	53	81
4d	14	40	67	**6d**	8	22	35
4e	11	35	61	**6e**	9	33	41
4f	8	21	36	**6f**	25	46	76
4g	5	17	22	**6g**	21	42	77
4h	5	16	25	**6h**	34	56	86
4i	20	51	65	**7a**	18	53	76
4j	9	31	51	**7c**	15	50	75

produces power of 340 W. TLC was performed on silica gel preparative plates (S.D. Fine-Chem) and spots were visualized in an iodine chamber.

General procedure for the synthesis of xanthene and chromene derivatives

For the synthesis of **4a–k** and **6a–h**, 2-naphthol/4-hydroxy coumarin (1 mmol), cyclic 1,3-diketones (1 mmol), aromatic aldehydes (1 mmol), [bmim][PF_6] (10 mol %) was taken and microwave irradiation at 40 % power was applied for the reaction mixture and the progress of the reaction was followed by TLC. For the synthesis of compounds **7a–i**, 1,3-diketones (2 mmol) and aromatic aldehydes (1 mmol) have taken in the same conditions. After the reaction completion, the mixture was

extracted with chloroform and the combined organic phase was evaporated and the residue was recrystallized with ethanol to afford the product. The remaining IL was dried in vacuum at 90 °C, which was used for further subsequent runs without further purification.

Spectral data of compounds **4a–k**, **6a–h,** and **7a–i**

12-(3,4,5-Trimethoxyphenyl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4a**): white solid, mp 180–182 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05 (m, 2H, CH_2), 2.46 (m, 2H, CH_2), 2.72 (m, 2H, CH_2), 3.72 (s, 9H, OCH_3), 5.7 (s, 1H, CH), 6.53 (s, 2H, ArH), 7.34 (d, $J = 8.8$ Hz, 1H, ArH), 7.4 (d, $J = 8$, 2H, ArH), 7.78 (t, $J = 7.6$ Hz, 2H, ArH), 7.97 (d, $J = 8$ Hz, 1H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.32, 27.82, 34.65, 37.14, 56.1, 60.75, 105.68, 115.56, 116.97, 117.53, 123.78, 125.05, 127.09, 128.46, 129.01, 131.53, 136.35, 140.77, 147.97, 152.99, 165.82, 197.31 ppm; DEPT-135 (100 MHz, $CDCl_3$): δ 20.27 (CH_2, C-9), 27.77 (CH_2, C-8), 34.6 (CH, C-12) 37.08 (CH_2, C-10), 56.05 (OCH_3, C-17 17′), 60.7 (OCH_3, C-18), 105.62 (CH, C-14,14′), 116.73 (CH, C-6), 123.73 (CH, C-1), 125 (CH, C-5), 127.04 (CH, C-4), 128.41 (CH, C-3), 128.95 (CH, C-2) ppm; LC–MS: m/z 416.95 (M + 1); Anal. calcd. for $C_{26}H_{24}O_5$ C, 74.98; H, 5.81, Found C, 74.28; H, 5.86.

12-(4-Chlorophenyl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4b**): white solid, mp 205–207 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05 (m, 2H, CH_2), 2.39 (m, 2H, CH_2), 2.69 (m, 2H, CH_2), 5.71 (s, 1H, CH), 7.12 (d, $J = 6.8$ Hz, 2H, ArH), 7.25 (d, $J = 6.4$ Hz, 2H, ArH), 7.34 (d, $J = 8.8$ Hz, 1H, ArH), 7.4 (d, 2H, $J = 7.6$ Hz, ArH), 7.78 (t, 2H, $J = 7.6$ Hz, ArH), 7.87 (d, 2H, $J = 8$ Hz, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.41, 27.87, 34.26, 37.16, 115.26, 117.12, 117.20, 123.63, 125.16, 127.26, 128.62, 129.24, 131.33, 131.65, 132.09, 143.65, 147.88, 165.9, 197.22 ppm; Anal. calcd. for $C_{23}H_{17}ClO_2$ C, 76.56; H, 4.75, Found C, 75.98; H, 4.25.

12-(3,4-Dimethoxyphenyl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4c**): white solid, mp 182–184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.03 (m, 2H, CH_2), 2.45 (m, 2H, CH_2), 2.75 (m, 2H, CH_2), 3.74 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3) 5.7 (s, 1H, CH), 6.64 (d, $J = 8$, 2H, ArH), 7.01 (s, 1H, ArH), 7.42 (m, 3H, ArH), 7.77 (t, $J = 7.6$ Hz, 2H, ArH), 7.95 (d, $J = 8$ Hz, 1H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.41, 27.86, 34.14, 37.19, 55.81, 55.99, 111.04, 112.25, 115.8, 117.02, 117.83, 120.5, 123.85, 125.02, 127.08, 128.48, 128.9, 131.56, 131.6, 137.99, 147.41, 147.95, 148.7, 165.6, 197.34 ppm; Anal. calcd. for $C_{25}H_{22}O_4$ C, 77.70; H, 5.74, Found C, 78.20; H, 5.71.

12-(4-Hydroxy-3,5-dimethoxyphenyl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4d**): white solid, mp 189–191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.03 (m, 2H, CH_2), 2.46 (m, 2H, CH_2), 2.71 (m, 2H, CH_2), 3.75 (s, 6H, OCH_3), 5.32 (s, 1H, OH) 5.68 (s, 1H, CH), 6.53 (s, 2H, ArH), 7.33 (m, 3H, ArH), 7.78 (m, 2H, ArH), 7.95 (m, 1H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.31, 27.15, 32.7, 36.94, 55.86, 56.05, 106.88, 111.15, 113.01, 113.72, 116.41, 116.85, 120.02, 122.43, 124.31, 132.19, 135.6, 148.13, 148.71, 152.56, 153.78, 160.76, 163.58, 196.23 ppm; Anal. calcd. for $C_{25}H_{22}O_5$ C, 74.61; H, 5.51, Found C, 73.91; H, 5.43.

12-(2-Ethoxyphenyl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4e**): white solid, mp 194–196 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.46 (t, 3H, $OCH_2\underline{CH_3}$), 2.03 (m, 2H, CH_2), 2.38 (m, 2H, CH_2), 2.72 (m, 2H, CH_2), 3.97,4.08(q, 2H, $J = 7.6$ Hz, $OC\underline{H_2}CH_3$), 5.93 (s, 1H, CH), 6.74 (d, $J = 8$ Hz, 1H, ArH), 6.8 (t, $J = 7.2$ Hz, 1H, ArH), 7.02 (t, $J = 7.6$ Hz, 1H, ArH), 7.24 (d, $J = 7.2$ Hz, 1H, ArH), 7.33 (t, $J = 7.6$ Hz 1H, ArH), 7.41 (d, $J = 7.6$ Hz, 2H, ArH), 7.72 (t, $J = 8$ Hz, 2H, ArH), 8.29 (d, $J = 8.4$ Hz, 1H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.00, 20.64, 27.95, 30.91, 37.29, 63.87, 112.12, 114.7, 118.28, 120.44, 124.22, 126.72, 127.78, 128.41, 131.40, 132.04, 132.99, 147.88, 156.31, 165.96, 197.15 ppm; Anal. calcd. for $C_{25}H_{22}O_3$ C, 81.06; H, 5.99, Found C, 80.37; H, 5.13.

12-(Biphenyl-4-yl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4f**): white solid, mp 225–227 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.04 (m, 2H, CH_2), 2.46 (m, 2H, CH_2), 2.72 (m, 2H, CH_2), 5.77 (s, 1H, CH), 6.53 (d, $J = 6.4$ Hz, 8H, ArH), 7.47 (t, $J = 7.6$ Hz, 3H, ArH), 7.78 (t, $J = 6.0$ Hz, 2H, ArH), 7.9 (d, $J = 8.4$ Hz, 1H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.43, 27.91, 34.45, 37.22, 115.62, 117.16, 117.75, 123.85, 125.08, 127.09, 127.12, 127.18, 128.55, 128.74, 128.99, 129.03, 131.52, 131.64, 139.16, 141.03, 144.26, 147.94, 165.86, 197.33 ppm; Anal. calcd. for $C_{29}H_{22}O_2$ C, 86.54; H, 5.51, Found C, 86.91; H, 5.39.

12-(3-Nitrophenyl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4g**): white solid, mp 231–233 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.07 (m, 2H, CH_2), 2.44 (m, 2H, CH_2), 2.77 (m, 2H, CH_2), 5.84 (s, 1H, CH), 7.42 (d, 4H, ArH), 7.82 (t, $J = 8.4$ Hz, 4H, ArH), 7.95 (d, $J = 7.2$ Hz, 1H, ArH), 8.08 (s, 1H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.39, 27.88, 34.85, 37.06, 114.54, 116.15, 117.30, 121.75, 123.29, 123.46, 125.33, 127.49, 128.83, 129.21, 129.81, 131.08, 131.74, 135.09, 147.13, 147.97, 148.60, 166.39, 197.15 Anal. calcd. for $C_{23}H_{17}NO_4$ C, 74.38; H, 4.61; N, 3.77, Found C, 74.18; H, 4.22; N, 4.12.

12-(2-Fluorophenyl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4h**): red solid, mp 270–272 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.17 (m, 2H, CH_2), 2.55 (m, 2H, CH_2), 2.72 (m, 2H, CH_2), 5.75 (s, 1H, CH), 6.61 (m, 2H, ArH), 7.01 (m, 2H, ArH), 7.34 (m, 1H, ArH), 7.37 (m, 3H, ArH), 7.64 (d, $J = 8.0$ Hz, 1H, ArH), 7.79 (m, 1H, ArH), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.08, 28.05, 28.28, 31.08, 36.52, 76.85, 77.16, 77.48, 115.29, 116.65, 117.65, 118.85, 121.56, 123.57, 125.41, 127.67, 128.13, 128.39, 129.07, 129.27, 131.19, 131.67, 132.83, 147.95, 153.15, 168.81, 201.21 ppm; Anal. calcd. for $C_{23}H_{17}FO_2$ C, 80.22; H, 4.98, Found C, 79.01; H, 5.13.

12-(3-Hydroxyphenyl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4i**): white solid, mp 205–207 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.86 (s, 2H, CH_2), 2.35 (s, 2H, CH_2), 2.73 (s, 2H, CH_2), 5.52 (s, 1H, CH), 6.45 (m, 1H, ArH), 6.64 (m, 1H, ArH), 6.75 (m, 1H, ArH), 6.97 (m, 1H, ArH), 7.43 (m, 3H, ArH), 7.92 (m, 3H, ArH), 9.26 (s, 1H, OH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.52, 19.90, 26.42, 26.92, 30.49, 33.81, 36.45, 56.03, 113.13, 113.26, 114.47, 115.04, 115.59, 117.07, 117.33, 118.46, 118.98, 123.17, 124.94, 127.09, 128.51, 128.95, 129.04, 130.67, 131.02, 146.46, 147.22, 156.93, 157.13, 164.75, 165.62, 196.15 ppm; Anal. calcd. for $C_{23}H_{18}O_3$ C, 80.68; H, 5.30, Found C, 79.98; H, 5.23.

9,9-Dimethyl-12-phenyl-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4j**): white solid, mp 205–207 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (s, 3H, CH_3),

1.12 (s, 3H, CH_3), 2.3 (q, $J = 8.8$ Hz, 2H, CH_2), 2.59 (s, 2H, CH_2), 5.74 (s, 1H, CH), 7.33 (m, 2H, ArH), 7.35 (m, 4H, ArH), 7.4 (m, 2H, ArH), 7.78 (m, 2H, ArH), 8.04 (d, $J = 6.8$ Hz, 1H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.39, 29.43, 32.47, 34.53, 41.57, 51.06, 114.3, 117.23, 117.73, 123.82, 125.08, 127.06, 127.13, 128.56, 128.74, 128.92, 129.02, 131.53, 131.64, 139.07, 141, 143.98, 147.88, 164.16, 197.19 ppm; Anal. calcd. for $C_{25}H_{22}O_2$ C, 84.72; H, 6.26, Found C, 85.12; H, 6.39.

12-(4-Hydroxy-3,5-dimethoxyphenyl)-9,9-dimethyl-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4k**): white solid, mp 205–207 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (s, 3H, CH_3), 1.12 (s, 3H, CH_3), 2.29 (s, 2H, CH_2), 2.56 (s, 2H, CH_2), 3.75 (s, 6H, OCH_3), 5.32 (s, 1H, OH) 5.64 (s, 1H, CH), 6.54 (s, 2H, ArH), 7.32 (m, 4H, ArH), 7.77 (m, 2H, ArH), 8 (m, 1H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.06, 27.13, 29.37, 29.44, 31.62, 32.20, 32.28, 34.50, 40.92, 41.45, 50.76, 50.93, 56.27, 56.35, 105.38, 105.53, 114.38, 115.73, 116.98, 117.63, 123.70, 124.97, 126.99, 128.41, 128.86, 131.50, 133.12, 133.47, 135.43, 136.14, 146.64, 146.73, 147.80, 162.18, 163.81, 197.07. ppm; Anal. calcd. for $C_{27}H_{26}O_5$. C, 75.33; H, 6.09, Found C, 74.37; H, 6.29.

7-(3,4,5-Trimethoxyphenyl)-10,11-dihydrochromeno[4,3-*b*]chromene-6,8(7*H*,9*H*)-dione (**6a**): white solid, mp 179–181 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.14 (m, 2H, CH_2), 2.44 (m, 2H, CH_2), 2.77 (m, 2H, CH_2), 3.76 (s, 3H, OCH_3), 3.8 (s, 6H, OCH_3), 4.95 (s, 1H, CH), 6.59 (s, 2H, ArH), 7.32 (t, $J = 8$ Hz, 2H, ArH), 7.56 (d, 1H, ArH), 7.88 (d, $J = 8.0$, 2H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.44, 27.27, 33.33, 37.03, 56.38, 60.79, 106.20, 106.73, 113.72, 116.26, 117, 122.55, 124.44, 132.41, 137.4, 138.24, 153.14, 160.85, 163.91, 196.28 ppm; Anal. calcd. for $C_{25}H_{22}O_7$ C, 69.12; H, 5.10, Found C, 69.19; H, 5.65.

7-(3,4-Dimethoxyphenyl)-10,11-dihydrochromeno[4,3-*b*]chromene-6,8(7*H*,9*H*)-dione (**6b**): white solid, mp 192–194 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.96 (m, 2H, CH_2), 2.29 (m, 2H, CH_2), 2.95 (m, 2H, CH_2), 3.95 (s, 3H, OCH_3), 4.05 (s, 3H, OCH_3), 5.10 (s, 1H, CH), 6.61 (s, 2H, ArH), 7.32 (t, $J = 8.0$ Hz, 2H, ArH), 7.56 (d, 1H, ArH), 7.86 (d, $J = 8.0$, 2H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.34, 27.20, 32.72, 36.98, 55.87, 56.06, 76.84, 77.16, 77.48, 106.89, 111.03, 112.91, 113.73, 116.42, 116.91, 120.01, 122.48, 132.26, 135.58, 148.08, 148.65, 152.57, 153.83, 160.86, 163.66, 196.38 ppm; Anal. calcd. for $C_{24}H_{20}O_6$ C, 71.28; H, 4.98, Found C, 71.39; H, 5.06.

7-(4-Hydroxy-3,5-dimethoxyphenyl)-10,11-dihydrochromeno[4,3-*b*]chromene-6,8(7*H*,9*H*)-dione (**6c**): white solid, mp 176–178 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.14 (m, 2H, CH_2), 2.45 (m, 2H, CH_2), 2.79 (m, 2H, CH_2), 3.83 (s, 6H, OCH_3), 4.93 (s, 1H, OH), 5.47 (s, 1H, CH), 6.61 (s, 2H, ArH), 7.32 (t, $J = 8.0$ Hz, 2H, ArH), 7.56 (d, 1H, ArH), 7.86 (d, $J = 8.0$, 2H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.39, 27.20, 33.12, 36.98, 56.54, 105.93, 106.78, 113.68, 116.32, 116.91, 122.5, 124.39, 132.31, 133.86, 134.24, 146.87, 152.57, 153.83, 160.82, 163.71, 196.32 ppm; Anal. calcd. for $C_{24}H_{20}O_7$ C, 68.57; H, 4.80, Found C, 69.21; H, 5.09.

7-(Biphenyl-4-yl)-10,11-dihydrochromeno[4,3-*b*]chromene-6,8(7*H*, 9*H*)-dione (**6d**): white solid, mp 235–237 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.13 (m, 2H, CH_2), 2.42 (m, 2H, CH_2), 2.88 (m, 2H, CH_2), 5.03 (s, 1H, CH), 7.29 (d, $J = 7.6$ Hz,

2H, ArH) 7.33 (d, $J = 8.0$ Hz, 3H, ArH), 7.38 (t, $J = 7.6$ Hz, 4H, ArH), 7.51 (d, $J = 6.8$ Hz, 2H, ArH), 7.56 (t, $J = 7.6$ Hz, 1H, ArH), 7.88 (d, $J = 7.6$ Hz, 2H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.37, 27.29, 33.13, 37.03, 106.82, 113.78, 116.41, 117.03, 122.58, 124.44, 127.20, 127.28, 128.76, 129.14, 132.39, 140.07, 141.06, 141.87, 152.73, 154.08, 160.83, 163.83, 196.35 ppm; Anal. calcd. for $C_{28}H_{20}O_4$ C, 79.98; H, 4.79, Found C, 80.18; H, 4.27.

7-(3-Fluorophenyl)-10,11-dihydrochromeno[4,3-*b*]chromene-6,8(7*H*,9*H*)-dione (**6e**): white solid, mp 238–240 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.17 (m, 2H, CH_2), 2.49 (m, 2H, CH_2), 2.9 (m, 2H, CH_2), 5.03 (s, 1H, CH), 7.29 (d, $J = 7.6$ Hz, 2H, ArH) 7.33 (d, $J = 8.0$ Hz, 3H, ArH), 7.38 (t, $J = 7.6$ Hz, 4H, ArH), 7.51 (d, $J = 6.8$ Hz, 2H, ArH), 7.56 (t, $J = 7.6$ Hz, 1H, ArH), 7.88 (d, $J = 7.6$ Hz, 2H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.32, 27.27, 33.24, 36.96, 106.33, 113.63, 114.08, 114.29, 115.46,115.68, 116.07, 117.06, 122.63, 124.53, 124.67, 124.7, 129.76 129.84, 132.57, 145.15, 145.21, 152.75, 154.23, 160.70, 161.74, 164, 164.19 196.19 ppm; Anal. calcd. for $C_{22}H_{15}FO_4$ C, 72.92; H, 4.17, Found C, 71.28; H, 4.29.

7-(4-Hydroxyphenyl)-10,11-dihydrochromeno[4,3-*b*]chromene-6,8(7*H*,9*H*)-dione (**6f**): white solid, mp 178–180 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.39 (m, 2H, CH_2), 2.53 (m, 2H, CH_2), 2.75 (m, 2H, CH_2), 5.55 (m, 1H, CH), 6.49 (m, 1H, ArH), 6.68 (m, 1H, ArH), 7.02 (m, 1H, ArH), 7.46 (m, 2H, ArH), 7.95 (d, $J = 8.0$ Hz, 2H, ArH), 8.02 (d, $J = 8.0$ Hz, 1H, ArH), 9.32 (s, 1H, OH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 19.91, 26.92, 33.82, 36.45, 79.16, 113.26, 114.49, 115.05, 117.06, 118.98, 123.18, 124.92, 127.08, 128.50, 128.94, 129.03, 130.68, 131.02, 146.46, 147.23, 157.16, 165.57, 196.09 ppm; Anal. calcd. for $C_{22}H_{16}O_5$ C, 73.33; H, 4.48, Found C, 72.93; H, 4.56.

7-(3-Hydroxyphenyl)-10,11-dihydrochromeno[4,3-*b*]chromene-6,8(7*H*,9*H*)-dione (**6g**): white solid, mp 209–211 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.95 (m, 2H, CH_2), 2.4 (m, 2H, CH_2), 2.81 (m, 2H, CH_2), 4.64 (s, 1H, CH), 6.56 (s, 1H, ArH), 6.67 (m, 2H, ArH), 7.03 (d, $J = 7.6$ Hz, 1H, ArH), 7.43 (m, 2H, ArH), 7.67 (m, 1H, ArH), 7.95 (d, $J = 8.0$ Hz, 1H, ArH), 9.32 (s, 1H, OH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 19.80, 21.03, 26.36, 32.57, 36.38, 105.84, 113.06, 113.78, 114.94, 115.37, 116.55, 118.84, 122.55, 124.77, 129.13, 132.77, 144.25, 151.86, 153.58, 157.08, 159.95, 164.45, 172.02, 196.09 ppm; Anal. calcd. for $C_{22}H_{16}O_5$ C, 73.33; H, 4.48, Found C, 74.02; H, 4.63.

7-(4-Hydroxy-3,5-dimethoxyphenyl)-10,10-dimethyl-10,11-dihydrochromeno[4,3-*b*]chromene 6,8(7*H*,9*H*)-dione (**6h**): white solid, mp 178–180 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.14 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 2.31 (m, 2H, CH_2), 2.69 (m, 2H, CH_2), 3.83 (s, 6H, OCH_3), 4.9 (s, 1H, OH), 5.4 (s, 1H, CH), 6.6 (s, 2H, ArH), 7.34 (m, 2H, ArH), 7.55 (m, 1H, ArH), 7.87 (m, 1H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.30, 29.42, 30.95, 32.32, 33.22, 40.89, 50.71, 56.46, 105.86, 106.91, 113.73, 115.12, 116.96, 122.42, 124.29, 132.24, 133.71, 134.13, 146.82, 152.58, 153.72, 160.75, 162.05, 196.08 ppm; Anal. calcd. for $C_{26}H_{24}O_7$ C, 69.63; H, 5.39, Found C, 69.92; H, 5.79.

9-(3,4,5-Trimethoxyphenyl)-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione (**7a**): white solid, mp 182–184 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2 (m, 4H, CH_2), 2.35 (m, 4H, CH_2), 2.64 (m, 4H, CH_2), 3.77 (s, 3H, OCH_3), 3.82 (s, 6H, OCH_3), 4.79 (s, 1H, CH), 6.52 (s, 2H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.45, 27.27, 31.54,

37.09, 56.26, 60.79, 105.73, 116.81, 117.22, 136.71, 140, 152.91, 164.19, 196.83 ppm; Anal. calcd. for $C_{22}H_{24}O_6$ C, 68.74; H, 6.29, Found C, 68.29; H, 6.19.

9-(3,4-Dimethoxyphenyl)-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione (**7b**): white solid, mp 215–217 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01 (m, 4H, CH_2), 2.37 (m, 4H, CH_2), 2.67 (m, 4H, CH_2), 3.79 (s, 6H, OCH_3), 4.77 (s, 1H, CH), 6.7 (s, 2H, ArH), 7 (s, 1H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.17, 20.34, 27.16, 30.95, 36.99, 55.79, 55.95, 60.41, 110.90, 112.66, 116.95, 119.61, 137.28, 147.53, 148.42, 163.88, 196.72 ppm; Anal. calcd. for $C_{21}H_{22}O_5$ C, 71.17; H, 6.26, Found C, 70.29; H, 6.01.

9-(4-Hydroxy-3,5-dimethoxyphenyl)-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione (**7c**): white solid, mp 224–226 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.04 (m, 4H, CH_2), 2.35 (m, 4H, CH_2), 2.59 (m, 4H, CH_2), 3.85 (s, 6H, OCH_3), 4.76 (s, 1H, OH), 5.36 (s, 1H, CH) 6.54 (s, 2H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.39, 27.18, 31.30, 37.02, 56.44, 76.73, 77.05, 77.25, 77.37, 105.55, 116.90, 133.63, 135.56, 146.65, 163.87, 196.70 ppm; Anal. calcd. for $C_{21}H_{22}O_6$ C, 68.10; H, 5.99; Found C, 69.79; H, 6.14.

9-(Biphenyl-4-yl)-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione (**7d**): white solid, mp 196–198 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.02 (m, 4H, CH_2), 2.36 (m, 4H, CH_2), 2.65 (m, 4H, CH_2), 4.85 (s, 1H, CH), 7.38 (m, 9H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.32, 27.20, 31.36, 36.99, 116.85, 126.96, 127.08, 128.61, 128.78, 139.28, 141.16, 143.49, 164.04, 196.69. ppm; Anal. calcd. for $C_{25}H_{22}O_3$ C, 81.06; H, 5.99, Found C, 80.85; H, 6.04.

9-(4-Ethoxyphenyl)-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione (**7e**): white solid, mp 170–172 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35 (t, $J = 6.8$ Hz, 3H, OCH_2CH_3), 1.98 (m, 4H, CH_2), 2.34 (m, 4H, CH_2), 2.56 (m, 4H, CH_2), 3.94 (m, 2H, OCH_2CH_3), 4.74 (s, 1H, CH), 6.74 (d, $J = 8.0$ Hz, 2H, ArH), 7.19 (d, $J = 8.0$ Hz, 2H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.03, 20.45, 27.27, 30.86, 37.11, 63.37, 76.84, 77.16, 77.47, 114.18, 117.22, 129.42, 136.69, 157.57, 163.82, 196.75 ppm; Anal. calcd. for $C_{21}H_{22}O_4$ C, 74.54; H, 6.55, Found C, 74.91; H, 6.78.

3,3,6,6-Tetramethyl-9-(3,4,5-trimethoxyphenyl)-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione (**7f**): mp 186–188 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1 (s, 6H, CH_3), 1.11 (s, 6H, CH_3), 2.23 (s, 4H, CH_2), 2.47 (s, 4H, CH_2), 3.8 (s, 9H, OCH_3), 4.7 (s, 1H, CH), 6.51 (s, 2H, ArH), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.21, 29.39, 32.21, 40.92, 50.75, 56.11, 60.73, 105.70, 115.58, 136.54, 139.75, 152.80, 162.39, 196.57 ppm; Anal. calcd. for $C_{26}H_{32}O_6$ C, 70.89; H, 7.32, Found C, 70.23; H, 7.19.

9-(3,4-Dimethoxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione (**7g**): mp 173–175 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (s, 6H, CH_3), 1.03 (s, 6H, CH_3), 2.15 (q, $J = 8.0$ Hz, 4H, CH_2), 2.39 (m, 4H, CH_2), 3.78 (s, 6H, OCH_3), 4.62 (s, 1H, CH), 6.65 (d, $J = 9.6$ Hz, 2H, ArH) 6.83 (s, 1H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.26, 29.35, 31.23, 32.20, 40.88, 50.75, 55.76, 55.88, 110.83, 112.28, 115.75, 120.11, 136.99, 147.45, 148.43, 162.18, 196.58. ppm; Anal. calcd. for $C_{25}H_{30}O_5$ C, 73.15; H, 7.37, Found C, 73.29; H, 7.96.

9-(Biphenyl-4-yl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione (**7h**): white solid, mp 205–207 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1(s, 6H, CH_3), 1.1 (s, 6H, CH_3) 2.23 (q, $J = 10.4$ Hz, 4H, CH_2), 2.48 (s, 4H, CH_2), 4.79 (s, 1H, CH),

7.27 (d, $J = 8.4$ Hz, 1H, ArH),), 7.36 (t, $J = 7.6$ Hz, 4H, ArH), 7.45 (d, $J = 8$ Hz, 2H, ArH), 7.51 (d, $J = 8$ Hz, 2H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.37, 29.29, 32.05, 40.80, 50.66, 113.29, 126.73, 129.87, 132.81, 134.04, 163.24, 196.55 ppm; Anal. calcd. for $C_{29}H_{30}O_3$ C, 81.66; H, 7.09, Found C, 81.82; H, 7.76.

9-(3-Hydroxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione (**7i**): white solid, mp 230–232 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1(s, 6H, CH_3), 1.09 (s, 6H, CH_3) 2.21 (q, $J = 8$ Hz, 4H, CH_2), 2.46 (s, 4H, CH_2), 4.73 (s, 1H, CH), 6.58 (d, $J = 8.0$ Hz, 1H, ArH),), 6.71 (d, $J = 8.0$ Hz, 4H, ArH), 7.01 (s, 1H, ArH), 7.04 (t, $J = 8.0$ Hz, 1H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.44, 29.19, 31.72, 32.26, 40.88, 50.69, 113.62, 115.61, 116.32, 119.70, 129.16, 145.55, 155.91, 162.59, 196.98 ppm; Anal. calcd. for $C_{23}H_{26}O_4$ C, 75.38; H, 7.15, Found C, 75.59; H, 7.49.

Conclusions

In summary, a convenient, green, and efficient methodology was developed to synthesize xanthene and chromene derivatives via a three-component reaction of aldehydes, 4-hydroxy coumarin/2-naphthol and 1,3-cyclohexanediones. The synthesis of variety of these compounds with better yield in reasonable reaction time is the main scope of this developed methodology. In addition, the reactions were carried out in IL, which is considerably safer, nontoxic, and reusable. Antioxidant studies of the synthesized compounds revealed that the compounds showed good-to-moderate activity.

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