

Efficient Syntheses of New Polyhydroxylated 2,3-Diaryl-9H-xanthen-9-ones

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A large number of hydroxylated 2,3-diaryl-9H-xanthen-9-ones have been synthesised by two different approaches, starting either from 3-bromo-2-methyl-4H-chromen-4-one or from (*E*)-3-bromo-2-styryl-4H-chromen-4-ones. The former method involves Heck reactions between 3-bromo-2-methyl-4H-chromen-4-one and styrenes, leading to (*E*)-2-methyl-3-styryl-4H-chromen-4-ones; these condensed with benzaldehyde to give (*E,E*)-2,3-distyryl-4H-chromen-4-ones, which led to the desired 2,3-diaryl-9H-xanthen-9-ones under reflux in 1,2,4-trichlorobenzene. 3-Bromo-2-styryl-4H-chromen-4-ones were obtained either by aldol condensations between 3-bromo-2-methyl-4H-chromen-4-one and benzaldehydes, or through Baker–Venkataraman rearrangements of 2-acetylphenyl cinnamates, followed by one-pot bromination/cyclisation with phenyltrimethylammonium tribromide. The 2,3-diaryl-9H-xanthen-9-ones were obtained in one-pot transformations involving Heck reactions between (*E*)-3-

bromo-2-styryl-4H-chromen-4-ones and styrenes, followed by electrocyclisation and oxidation processes. The 2,3-diaryl-3,4-dihydro-9H-xanthene-9-one intermediates were also isolated under these conditions, and so when 5-methoxy-2-styryl-4H-chromen-4-ones were used as starting materials the 1-hydroxy-6,7-diaryl-9H-xanthene-9-ones were also observed. The second method is a general one, because it allowed the synthesis of a great number of 2,3-diaryl-9H-xanthen-9-ones with several substitution patterns, whereas the first one is limited to certain derivatives. The last step in the synthesis of hydroxylated 2,3-diaryl-9H-xanthen-9-ones was the cleavage of the hydroxy protecting groups with boron tribromide. The structures and stereochemistry of all new compounds were established by NMR studies.

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Introduction

Xanthenes constitute one of the major classes of naturally occurring oxygen-containing heterocyclic compounds containing dibenzo- γ -pyrone rings.^[1] They occur in two major plant families, *Guttiferae* and *Gentianaceae*, and also in some families of fungi and lichens.^[2,3] Natural derivatives can be hydroxylated, methoxylated or prenylated, among other possibilities; the parent compound xanthone itself is not known as a natural product.^[3,4] The presence of aryl groups on the xanthone core has only been reported for a few synthetic derivatives, and as far as we know the literature had never presented the synthesis of xanthenes featuring 2,3-diaryl moieties before our work.^[5,6]

Over the last decades these substances have been extensively studied not only because they participate in several biological functions but also as a consequence of their remarkable antifungal,^[7–9] anti-inflammatory,^[10,11] antimalarial^[12–14] and antitumour activities,^[15,16] and even as promising antioxidant agents.^[17–19] Structure–activity stud-

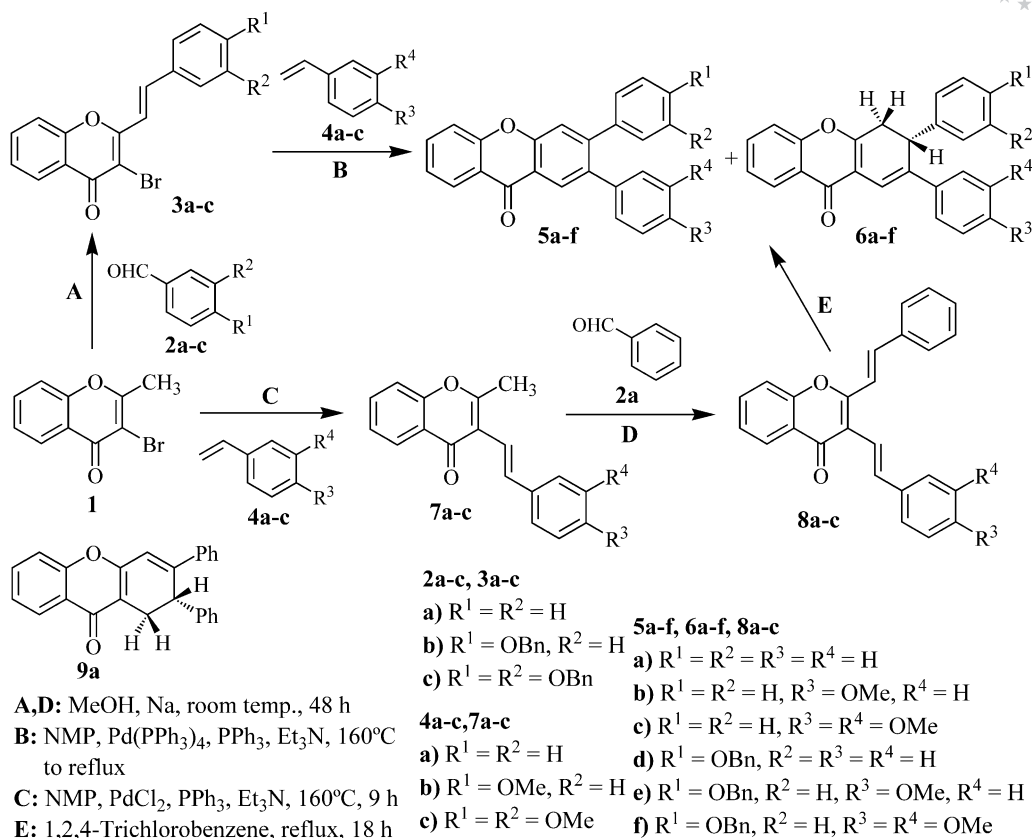
ies of phenolic compounds have revealed that features conducive to high antioxidant activity are the presence of hydroxy groups at certain positions on the skeleton, a catechol group being the most prominent moiety.^[20,21] In view of these considerations, here we report two main routes for the synthesis of polyhydroxylated 2,3-diaryl-9H-xanthen-9-ones.

There are various known methods for the synthesis of 9H-xanthen-9-ones.^[22] The classic ones involve the bonding of two benzene rings through a pyran unit. The most commonly reported are Friedel–Crafts acylations of phenolic derivatives with benzoyl chlorides and Ullmann condensation between sodium phenolates and *ortho*-halo-substituted benzoic acids for the synthesis of diaryl ethers, with both methods being followed by cyclisations of these compounds to form the heterocyclic rings. The literature also reports direct formation of the 9H-xanthen-9-one nucleus through a diaryl ester pyrolysis process or by photo-Fries or Smiles rearrangements of these intermediates, accompanied by ring closure. These classical methods require some drastic conditions, give poor yields because of the formation of several by-products and only allow the presence of certain substituents in certain positions on the 9H-xanthen-9-one core.^[22–24]

Modifications of the classical methods and several other less traditional approaches to construction of the 9H-xanthen-9-one framework have been widely described, but

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Scheme 1. Synthesis of 2,3-diaryl-9*H*-xanthen-9-ones **5a-f**.

none of them allows the synthesis of our target compounds, the 2,3-diaryl-9*H*-xanthen-9-ones.^[22] In this context, we have developed two methods for the synthesis of new polyhydroxylated 2,3-diaryl-9*H*-xanthen-9-ones, starting from 3-bromo-2-methyl-4*H*-chromen-4-one (**1**, Scheme 1) and the (*E*)-3-bromo-2-styryl-4*H*-chromen-4-ones **3a-k** (Scheme 2).

Results and Discussion

Syntheses

Our first approach to the synthesis of 2,3-diaryl-9*H*-xanthen-9-ones involved the use of the functionalised 3-bromo-2-methyl-4*H*-chromen-4-one (**1**), which was prepared from 2'-hydroxyacetophenone in a three-step sequence and in a good overall yield.^[25–26] Two methods to obtain the 2,3-diaryl-9*H*-xanthen-9-ones **5a-f** were developed (Scheme 1). In one of these, the (*E*)-3-bromo-2-styryl-4*H*-chromen-4-ones **3a-c** were prepared through base-catalysed aldol reactions between 4*H*-chromen-4-one **1** and benzaldehydes **2a-c** in methanolic solutions. The best results were achieved when 4 molar equivalents of base and reaction times of 48 h were used. Even after several attempts, the yields of (*E*)-3'-,4'-dibenzyloxy-3-bromo-2-styryl-4*H*-chromen-4-one (**3c**) never exceeded 6% and its isolation and characterisation was not possible, due to its degradation in chloroform solution.^[25] The next step consisted of Heck reactions between the (*E*)-3-bromo-2-styryl-4*H*-

chromen-4-ones **3a** and **3b** and styrenes **4a-c** in the presence of tetrakis(triphenylphosphane)palladium(0) as catalyst, directly giving the 9*H*-xanthen-9-ones **5a-f** (see Exp. Section, Table 2). Under these conditions it was also possible in each case to isolate a minor compound with lower *R_f* value, corresponding to the 2,3-diaryl-3,4-dihydro-9*H*-xanthen-9-one intermediates **6a-f**.

An alternative method for the synthesis of 2,3-diaryl-9*H*-xanthen-9-ones started with Heck reactions between 3-bromo-2-methyl-4*H*-chromen-4-one (**1**) and styrenes **4a-c** (Scheme 1). Several attempts to optimise the coupling reaction conditions were made, and the best results for the synthesis of the (*E*)-2-methyl-3-styryl-4*H*-chromen-4-ones **7a-c** were achieved with 1 molar equivalent of base, 0.1 molar equivalent of phosphane and 5 molar equivalents of styrenes **4a-c** over 9 h at 160 °C. Unlike in the coupling reaction described above, in which the best results were achieved with tetrakis(triphenylphosphane)palladium(0), here the best yields were obtained in the presence of palladium chloride as catalyst (Table 1).

The (*E,E*)-2,3-distyryl-4*H*-chromen-4-ones **8a-c** were prepared through base-catalysed aldol condensations between the (*E*)-2-methyl-3-styryl-4*H*-chromen-4-ones **7a-c** and benzaldehyde (**2a**) in the presence of 4 molar equivalents of base over 48 h at room temperature. Condensations between the (*E*)-2-methyl-3-styryl-4*H*-chromen-4-ones **7a-c** and the benzaldehydes **2b** and **2c** were unsuccessful, probably due to poor reactivity of benzyloxybenzaldehydes **2b**

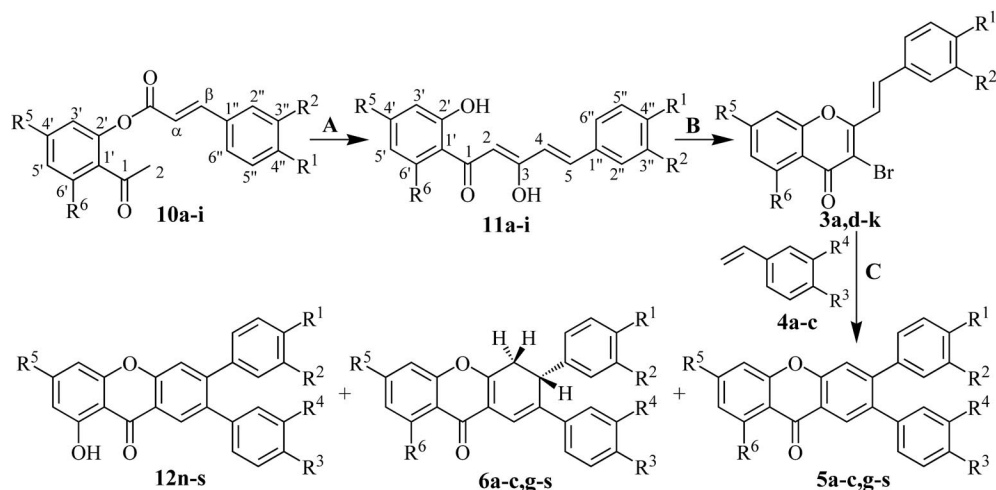
Table 1. Yields for the formation of (*E*)-2-methyl-3-styryl-4*H*-chromen-4-ones **7a–c** through Heck reactions between 3-bromo-2-methyl-4*H*-chromen-4-one (**1**) and styrenes **4a–c**.

Catalyst [equiv.]	% Yield 7a	% Yield 7b	% Yield 7c
Pd(OAc) ₂ (0.05)	46	28	17
Pd(PPh ₃) ₄ (0.05)	48	43	30
PdCl ₂ (0.05)	48	49	52

and **2c**. The 2,3-diaryl-9*H*-xanthen-9-ones **5a–c** were then obtained by heating the (*E,E*)-2,3-distyryl-4*H*-chromen-4-ones **8a–c** in 1,2,4-trichlorobenzene at reflux. In the case of the unsubstituted 2,3-distyryl-4*H*-chromen-4-one **8a**, TLC analysis of the reaction medium after a reaction time of 12 h revealed the presence of three compounds, with the

major one with the highest *R_f* value corresponding to the desired 2,3-diphenyl-9*H*-xanthen-9-one **5a**, together with two other minor compounds. Their NMR spectra showed that the minor product with high *R_f* was 2,3-diphenyl-3,4-dihydro-9*H*-xanthen-9-one (**6a**) and the other, with a lower *R_f*, was 2,3-diphenyl-1,2-dihydro-9*H*-xanthen-9-one (**9a**). After 18 h, however, only the desired 2,3-diphenyl-9*H*-xanthen-9-one (**5a**) was obtained.

In view of the lack of reactivity in some steps in the two previously described methods, we developed a third and more general method for the synthesis of 2,3-diaryl-9*H*-xanthen-9-ones, starting from the 2-acetylphenyl cinnamates **10a–i** (Scheme 2).^[27] The cinnamates **10a–i** were obtained in good yields from reactions between acetophenones and cinnamic acid derivatives. Baker–Venkataraman



A: DMSO, KOH, room temp., 2 h

B: THF, PTT, room temp., 12 h

C: NMP, Pd(PPh₃)₄, PPh₃, Et₃N, 160°C to reflux

10a–i, 11a–i

- a)** R¹ = R² = R⁵ = R⁶ = H
- b)** R¹ = OMe, R² = R⁵ = R⁶ = H
- c)** R¹ = R² = OMe, R⁵ = R⁶ = H
- d)** R¹ = R² = H, R⁵ = OMe, R⁶ = H
- e)** R¹ = R² = R⁵ = OMe, R⁶ = H
- f)** R¹ = R² = R⁵ = H, R⁶ = OMe
- g)** R¹ = R² = OMe, R⁵ = H, R⁶ = OMe
- h)** R¹ = R² = H, R⁵ = R⁶ = OMe
- i)** R¹ = R² = R⁵ = R⁶ = OMe

3a,d–k

- a)** R¹ = R² = R⁵ = R⁶ = H
- d)** R¹ = OMe, R² = R⁵ = R⁶ = H
- e)** R¹ = R² = OMe, R⁵ = R⁶ = H
- f)** R¹ = R² = H, R⁵ = OMe, R⁶ = H
- g)** R¹ = R² = R⁵ = OMe, R⁶ = H
- h)** R¹ = R² = R⁵ = H, R⁶ = OMe
- i)** R¹ = R² = OMe, R⁵ = H, R⁶ = OMe
- j)** R¹ = R² = H, R⁵ = R⁶ = OMe
- k)** R¹ = R² = R⁵ = R⁶ = OMe

5a–c,g–s, 6a–c,g–s

- a)** R¹ = R² = R³ = R⁴ = R⁵ = R⁶ = H
- b)** R¹ = R² = H, R³ = OMe, R⁴ = R⁵ = R⁶ = H
- c)** R¹ = R² = H, R³ = R⁴ = OMe, R⁵ = R⁶ = H
- g)** R¹ = OMe, R² = R³ = R⁴ = R⁵ = R⁶ = H
- h)** R¹ = OMe, R² = H, R³ = OMe, R⁴ = R⁵ = R⁶ = H
- i)** R¹ = OMe, R² = H, R³ = R⁴ = OMe, R⁵ = R⁶ = H
- j)** R¹ = R² = OMe, R³ = R⁴ = R⁵ = R⁶ = H
- k)** R¹ = R² = R³ = OMe, R⁴ = R⁵ = R⁶ = H
- l)** R¹ = R² = R³ = R⁴ = OMe, R⁵ = R⁶ = H
- m)** R¹ = R² = R³ = R⁴ = H, R⁵ = OMe, R⁶ = H
- n)** R¹ = R² = R³ = R⁴ = R⁵ = H, R⁶ = OMe
- o)** R¹ = R² = H, R³ = OMe, R⁴ = R⁵ = H, R⁶ = OMe
- p)** R¹ = R² = H, R³ = R⁴ = OMe, R⁵ = H, R⁶ = OMe
- q)** R¹ = R² = OMe, R³ = R⁴ = R⁵ = H, R⁶ = OMe
- r)** R¹ = R² = R³ = R⁴ = OMe, R⁵ = H, R⁶ = OMe
- s)** R¹ = R² = R³ = R⁴ = H, R⁵ = R⁶ = OMe

12n–s

- n)** R¹ = R² = R³ = R⁴ = R⁵ = H
- o)** R¹ = R² = H, R³ = OMe, R⁴ = R⁵ = H
- p)** R¹ = R² = H, R³ = R⁴ = OMe, R⁵ = H
- q)** R¹ = R² = OMe, R³ = R⁴ = R⁵ = H
- r)** R¹ = R² = R³ = R⁴ = OMe, R⁵ = H
- s)** R¹ = R² = R³ = R⁴ = H, R⁵ = OMe

Scheme 2. Synthesis of 2,3-diaryl-9*H*-xanthen-9-ones **5a–c**, **5g–s** and **12n–s**.

rearrangements of **10a–i** in the presence of potassium hydroxide in DMSO gave the desired 5-aryl-3-hydroxy-1-(2-hydroxyaryl)penta-2,4-dien-1-ones **11a–i** in good yields.^[28] The key step in the synthesis of the (*E*)-3-bromo-2-styryl-4*H*-chromen-4-ones **3a** and **3d–k** involves treatment of ketones **11a–i** with phenyltrimethylammonium tribromide (PTT) in THF at room temperature. The presence of this reactant promotes a one-pot transformation, involving ketone α -bromination^[29] followed by cyclisation to afford, after careful column chromatographic purification, the 3-bromo-2-styryl-4*H*-chromen-4-ones **3a** and **3d–k**.

An extensive optimisation study on Heck reactions between the (*E*)-3-bromo-2-styryl-4*H*-chromen-4-ones **3a** and **3d–k** and the styrenes **4a–c** was carried out, with investigation of the amounts of base and styrene and the reaction time and temperature. These reactions afforded the desired 2,3-diaryl-9*H*-xanthen-9-ones **5a–c** and **5g–s**, the 2,3-diaryl-3,4-dihydro-9*H*-xanthen-9-one intermediates **6a–c** and **6g–s** and also the 6,7-diaryl-1-hydroxy-9*H*-xanthen-9-ones **12n–s**, in the cases of compounds **3h–k**, each bearing a 5-methoxy group from which the methyl group was cleaved off during the reaction. The yields of each of these compounds changed according to the experimental conditions used (see Experimental Section, Table 2 and Table 3).

Table 3. Best experimental conditions (*T* in all cases: reflux temp.) for the synthesis of 2,3-diaryl-9*H*-xanthen-9-ones **5g–s**, 2,3-diaryl-3,4-dihydro-9*H*-xanthen-9-ones **6g–s** and 1-hydroxy-6,7-diaryl-9*H*-xanthen-9-ones **12n–s**.

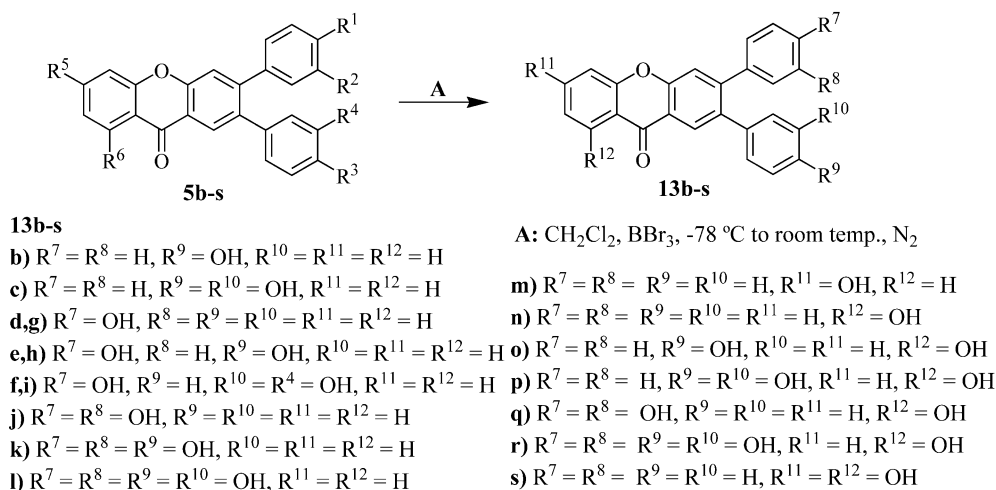
	<i>t</i> [h]	% Yield 5	% Yield 6	% Yield 12	<i>t</i> [h]	% Yield 5	% Yield 6	% Yield 12
g	9	60	11	–	6	49	43	–
h	9	62	–	–	3	46	10	–
i	9	28	–	–	3	21	4	–
j	9	62	3	–	6	41	13	–
k	9	80	–	–	6	46	21	–
l	3	70	–	–	9	55	6	–
m	6	47	17	–	3	33	21	–
n	9	58	–	–	6	47	12	12
o	9	24	–	37	3	16	43	2
p	6	22	10	3	3	22	5	2
q	9	50	–	1	6	43	17	34
r	9	43	–	11	3	31	13	5
s	6	42	–	2	3	21	46	1

Finally, to afford the desired polyhydroxylated 2,3-diaryl-9*H*-xanthen-9-ones **13b–s** it was necessary to cleave the benzyl and methyl groups of the 2,3-diaryl-9*H*-xanthen-9-ones **5b–s**. Boron tribromide in dry dichloromethane was used as deprotecting agent for simultaneous cleavage of both pro-

Table 2. Best experimental conditions for the synthesis of the 2,3-diaryl-9*H*-xanthen-9-ones **5a–f** and the 2,3-diaryl-3,4-dihydro-9*H*-xanthen-9-ones **6a–f**.

	Time [h]	Temperature [°C]	% Yield 5	% Yield 6	Time [h]	Temperature [°C]	% Yield 5	% Yield 6
a	9	160 ^[a]	56	–	9	160	54	9
b	3	160	66	14	3	160 ^[a]	58	–
c	12	160	45	–	12	160 ^[a]	44	6
d	6	reflux	51	–	3	reflux	46	11
e	6	reflux ^[a]	66	–	3	reflux	25	27
f	12	reflux	39	27	3	reflux	36	28

[a] Et₃N (4 equiv.).



Scheme 3. Cleavage of the hydroxy protecting groups.

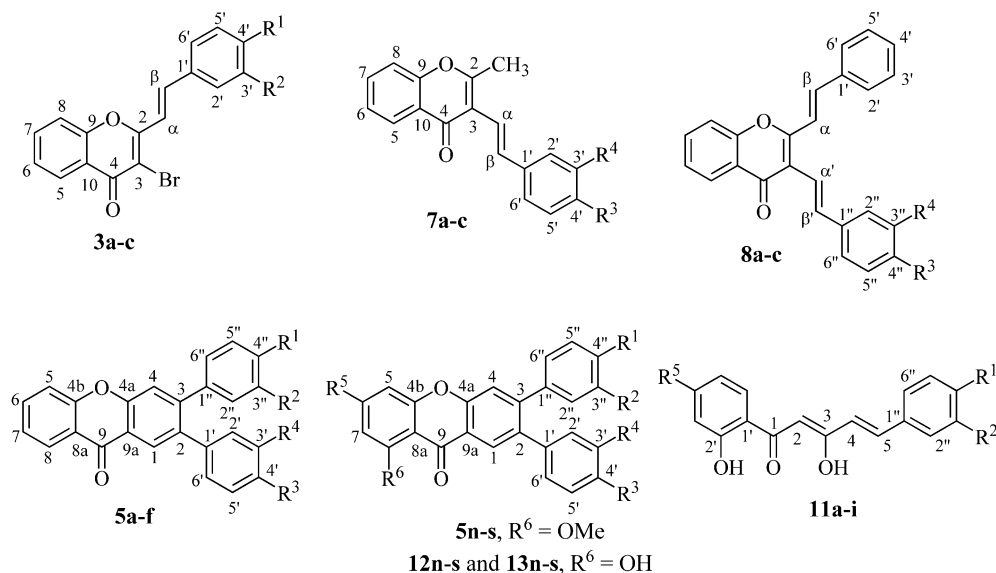


Figure 1. Structures and numbering system used for (*E*)-3-bromo-2-styryl-4*H*-chromen-4-ones **3a–c**, (*E*)-2-methyl-3-styryl-4*H*-chromen-4-ones **7a–c**, (*E,E*)-2,3-distyryl-4*H*-chromen-4-ones **8a–c**, 9*H*-xanthen-9-ones **5a–f**, **5n–s**, **12n–s** and **13n–s** and 5-aryl-3-hydroxy-1-(2-hydroxyphenyl)penta-2,4-dien-1-ones **11a–i**. (We applied the recommended IUPAC rules to establish the names of all compounds, but preferred the numbering systems indicated in Figure 1 and retained this atom numbering of each compound for reasons of better comparability of NMR data. For example, according to IUPAC nomenclature the 9*H*-xanthen-9-ones **5a–f** and **5n–s**, **12n–s** and **13n–s** must have different numbering, but we kept the same numbering for consistency of NMR signal assignments).

tecting groups.^[30,31] The polyhydroxy-2,3-diaryl-9*H*-xanthen-9-ones **13b–s** were obtained in moderate to good yields (Scheme 3, Figure 1).

Nuclear Magnetic Resonance Spectroscopy

The most important features in the ¹H NMR spectra of the 5-aryl-3-hydroxy-1-(2-hydroxyaryl)penta-2,4-dien-1-ones **11a–i** are, in each case: i) the singlets at $\delta = 6.17$ – 6.80 and 12.28 – 13.63 ppm, corresponding to 2-H and 2'-OH, respectively, and ii) a doublet at $\delta = 14.51$ – 15.01 ppm with $J \approx 1$ Hz, due to long-range coupling with the 4-H proton, corresponding to the 3-hydroxy group. The high-frequency values of the last two signals are due to the deshielding effect of the hydrogen bonds of the hydroxy protons with a carbonyl group. NOESY correlations between the signal of 2-H and those of 4-H and 6'-H (for **11a–e**), and of 4-H and 5-H with 2'',6''-H, together with the coupling constant of $J_{H4,H5} = 15$ – 16 Hz indicate that the compounds of this type have planar (*Z*)-*s*-(*Z*)-(*E*) configurations (Figure 2).

The ¹H NMR spectra of the (*E*)-3-bromo-2-styryl-4*H*-chromen-4-ones **3a–k** each revealed the presence of two doublets, corresponding to the vinylic protons α -H and β -H [$\delta = 7.20$ – 7.46 and 7.58 – 7.73 ppm, respectively] in a *trans* configuration ($J \approx 16.0$ Hz). The high-frequency values assigned to the resonances of β -H and C- β ($\delta = 138.1$ – 139.6 ppm) relative to the resonance of α -H and C- α ($\delta = 116.9$ – 119.3 ppm) are due to the mesomeric deshielding effect of the carbonyl group. HMBC spectra allowed the assignment of the quaternary carbons of the chromone moiety: C-2 and C-9 at $\delta = 156.1$ – 158.8 and 154.8 – 158.4 ppm, respectively, C-3 at $\delta = 108.9$ – 116.9 ppm and C-10 at $\delta = 107.5$ – 122.1 ppm.

An important feature in the ¹H NMR spectra of the (*E*)-2-methyl-3-styryl-4*H*-chromen-4-ones **7a–c** is the presence in each case of a singlet corresponding to the 2-CH₃ protons at $\delta = 2.61$ – 2.62 ppm, and doublets corresponding to the olefinic protons α -H ($\delta = 6.83$ – 6.97 ppm) and β -H ($\delta = 7.59$ – 7.71 ppm) in a *trans* configuration ($J = 16.3$ Hz). The difference in the chemical shifts is due to the deshielding

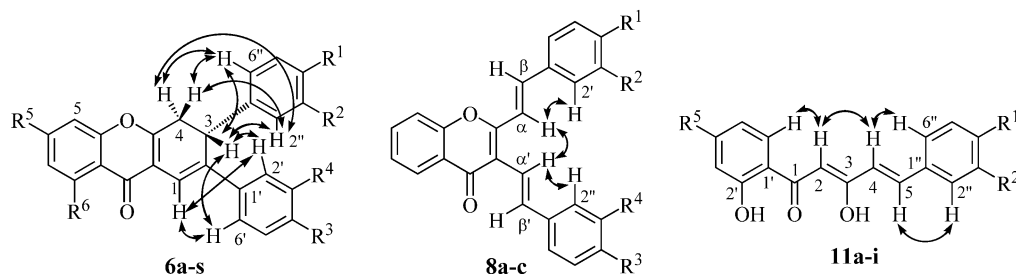


Figure 2. Main NOE cross peaks found in the NOESY spectra of the 2,3-diaryl-3,4-dihydro-9*H*-xanthen-9-ones **6a–s**, the (*E,E*)-2,3-distyryl-4*H*-chromen-4-ones **8a–c** and the 5-aryl-3-hydroxy-1-(2-hydroxyphenyl)penta-2,4-dien-1-ones **11a–i**.

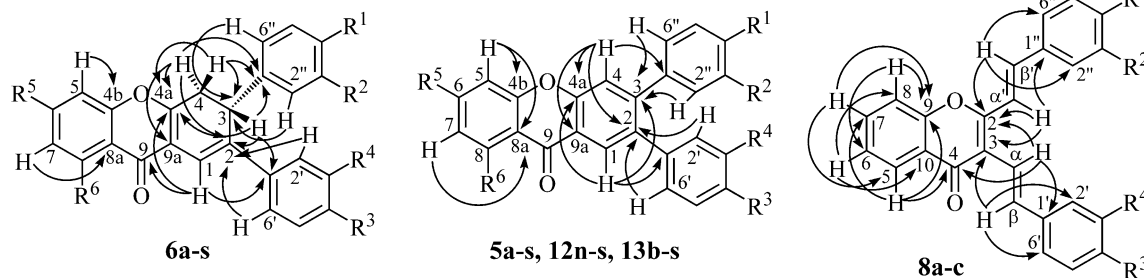


Figure 3. Important connectivities found in the HMBC spectra of the 2,3-diaryl-9*H*-xanthen-9-ones **5a-s**, **12n-s** and **13b-s**, the 2,3-diaryl-3,4-dihydro-9*H*-xanthen-9-ones **6a-s** and the (*E,E*)-2,3-distyryl-4*H*-chromen-4-ones **8a-c**.

effect of the chromone moiety, β -H being the more deshielded. NOESY correlations between the protons of the methyl group and the two protons α -H and β -H, indicate free rotation around the C-3 and C- α bonds. The ^{13}C NMR spectra of the (*E*)-2-methyl-3-styryl-4*H*-chromen-4-ones **7a-c** each present the characteristic signals corresponding to the 2-methyl carbon at $\delta = 19.3$ – 19.4 ppm, to C-2 at $\delta = 163.3$ – 163.8 ppm and to the carbonyl carbon at $\delta = 176.9$ – 177.0 ppm.

The NMR spectra of the (*E,E*)-2,3-distyryl-4*H*-chromen-4-ones **8a-c** are not easy to interpret because of the symmetry of the molecules and the fact that all the signals are in the aromatic region, except for the signals corresponding to 5-H, which each appear as a double doublet at the highest frequency value ($\delta = 8.22$ – 8.25 ppm). The assignment of the two AB spin-systems, due in each case to the resonances of α -H ($\delta = 7.37$ – 7.42 ppm), β -H ($\delta = 7.67$ – 7.71 ppm), α' -H ($\delta = 7.11$ – 7.21 ppm) and β' -H ($\delta = 7.27$ – 7.43 ppm), was made on the basis of the connectivities found in the HMBC spectra. The correlation observed in these spectra between the signal of the carbonyl carbon and the doublet at $\delta = 7.11$ – 7.21 ppm identifies α' -H (Figure 3). The coupling constants of the vinylic systems ($J \approx 16$ Hz) indicate their *trans* configurations, whereas the NOE cross peaks between the signals of α -H and α' -H, as well as those of α -H and $2',6'$ -H and also of α' -H and $2'',6''$ -H, support the conformations presented in Figure 2 for compounds **8a-c**.

In the ^1H NMR spectra of all the synthesised 2,3-diaryl-9*H*-xanthen-9-ones **5a-s**, **12n-s** and **13b-s**, the signals corresponding to 1-H and 4-H appear as singlets at $\delta = 7.91$ – 8.38 and 7.43 – 7.65 ppm, respectively; the high-frequency values of the 1-H protons are due to the anisotropic and mesomeric deshielding effects of the carbonyl groups. In the case of the xanthenes **12n-s** and **13n-s** it was also possible to identify the singlets corresponding to the resonances of the 8-hydroxy groups at $\delta = 12.48$ – 12.92 ppm. The high-frequency values of these resonances are due to intramolecular hydrogen bonding of the hydroxy protons with the carbonyl groups. For compounds **13b-n**, the signals corresponding to the proton resonance of the hydroxy groups also appear as singlets, at high-frequency values, with chemical shifts higher than 8.9 ppm.

The correlations found in the HMBC spectra provided unequivocal support for the structures of the 2,3-diaryl-9*H*-

xanthen-9-ones **5a-s**, **12n-s** and **13b-s**, allowing the assignment of the quaternary carbons of the xanthenone cores. The main connectivities are: i) 4-H and $2',6'$ -H with C-2, ii) 1-H and $2'',6''$ -H with C-3, iii) 1-H and 4-H with C-4a, iv) 5-H and 6-H with C-4b, v) 5-H and 7-H with C-8a, and vi) 4-H with carbon C-9a (Figure 3).

The ^1H NMR spectra of the 2,3-diaryl-3,4-dihydro-9*H*-xanthen-9-ones **6a-s** in each case revealed the presence of the aliphatic protons H-3 and H-4. The signal corresponding to 3-H appears as a doublet or a double doublet, at $\delta = 4.22$ – 4.31 ppm and at a higher-frequency value than that of H-4. From the coupling constants, the stereochemistry of 4_{cis} -H ($J = 8.3$ – 9.1 Hz, $\delta = 3.57$ – 3.67 ppm) and 4_{trans} -H ($J = 1.3$ – 1.6 Hz, $\delta = 2.89$ – 3.01 ppm) is related to 3-H. Another main feature in each ^1H NMR spectrum is the presence, in the aromatic region, of a singlet at $\delta = 7.44$ – 7.56 ppm corresponding to 1-H. The correlations found in the HMBC spectrum between this singlet (1-H) and the signal of the carbonyl carbon and also between the signal of 3-H with those of carbons C- $2'',6''$, supports the presence of the 3,4-dihydro-9*H*-xanthen-9-one moiety (Figure 3). This structure was also confirmed by the correlations found in the NOESY spectrum, mainly those indicating close proximity of 1-H to $2',6'$ -H, of 3-H to $2',6'$ -H and $2'',6''$ -H and of 4_{cis} -H and 4_{trans} -H to $2'',6''$ -H (Figure 3).

Conclusions

We have reported two different routes for the synthesis of hydroxylated 2,3-diaryl-9*H*-xanthen-9-ones. One of them involves Heck reactions between 3-bromo-2-methyl-4*H*-chromen-4-one and styrenes, followed by aldol condensations of the obtained compounds with benzaldehyde to gave 2,3-distyryl-4*H*-chromen-4-ones, which gave the desired 2,3-diaryl-9*H*-xanthen-9-ones after electrocycloislation and oxidation processes. In the second route, the 2,3-diaryl-9*H*-xanthen-9-ones were obtained through Heck reactions between 3-bromo-2-styryl-4*H*-chromen-4-ones and styrenes. The 3-bromo-2-styryl-4*H*-chromen-4-ones were obtained either through aldol condensations between 3-bromo-2-methyl-4*H*-chromen-4-one and benzaldehydes or through Baker–Venkataraman rearrangements of 2-acetylphenyl cinnamates followed by one-pot bromination/cycloislation

with phenyltrimethylammonium tribromide. The cleavage of the methyl and benzyl protecting groups with boron tribromide gave the desired hydroxylated 2,3-diaryl-9H-xanthen-9-ones.

Experimental Section

General Remarks: Melting points were measured in a Reichert Thermovar apparatus fitted with a microscope and are uncorrected. NMR spectra were recorded on a Bruker Avance 300 spectrometer (300.13 MHz for ^1H and 75.47 MHz for ^{13}C), in CDCl_3 as solvent if not stated otherwise. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz; the internal standard was TMS. Unequivocal ^{13}C assignments were made with the aid of 2D gHSQC and gHMBC (delays for one-bond and long-range J C/H couplings were optimised for 145 and 7 Hz, respectively) experiments. Positive-ion ESI mass spectra were acquired with a Q-TOF 2 instrument [dilution of 1 μL of the sample in chloroform solution (ca. 10^{-5} M) in 200 μL of 0.1% trifluoroacetic acid/methanol solution. Nitrogen was used as nebuliser gas and argon as collision gas. The needle voltage was set at 3000 V, with the ion source at 80 $^\circ\text{C}$ and the desolvation temperature at 150 $^\circ\text{C}$. The cone voltage was 35 V]. Other low- and high-resolution mass spectra (EI, 70 eV) were measured with VG Autospec Q and M spectrometers. Elemental analyses were obtained with a LECO 932 CHNS analyser. Preparative thin-layer chromatography was performed with Merck silica gel (60 DGF₂₅₄). Column chromatography was performed with Merck silica gel (60, 70–230 mesh). All chemicals and solvents used were obtained from commercial sources and used as received or dried by standard procedures.

Synthesis of (E)-3-Bromo-2-styryl-4H-chromen-4-ones 3a and 3b: Sodium (0.4 g, 16.7 mmol) was gradually added to dry methanol (20 mL) and the mixture was stirred until the reaction mixture had returned to room temperature. 3-Bromo-2-methyl-4H-chromen-4-one (**1**, 1.0 g, 4.2 mmol) and the appropriate benzaldehyde **2a** or **2b** (5.0 mmol) were added and the reaction mixture was allowed to stand at room temperature for 48 h. After this period, the solution was poured into ice (100 g) and water (100 mL) and the pH was adjusted to 4 with hydrochloric acid. The yellow solid was removed by filtration, taken up in dichloromethane and purified by silica gel column chromatography with dichloromethane as eluent. The solvent was removed to dryness and the residue was recrystallised from ethanol to give the (E)-3-bromo-2-styryl-4H-chromen-4-ones **3a** or **3b**.

(E)-3-Bromo-2-(2-phenylvinyl)-4H-chromen-4-one (3a): Yield 1.42 g (87%); m.p. 167–169 $^\circ\text{C}$. ^1H NMR: δ = 7.40–7.49 (m, 4 H, 6-H, 3',4',5'-H), 7.51 (d, J = 16.0 Hz, 1 H, α -H), 7.56 (d, J = 7.9 Hz, 1 H, 8-H), 7.64–7.67 (m, 2 H, 2',6'-H), 7.72 (dt, J = 7.9, 1.7 Hz, 1 H and 7-H), 7.73 (d, J = 16.0 Hz, 1 H, β -H), 8.25 (dd, J = 8.0, 1.7 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 109.8 (C-3), 117.5 (C-8), 119.2 (C- α), 122.1 (C-10), 125.4 (C-6), 126.4 (C-5), 128.1 (C-2',6'), 129.1 (C-3',5'), 130.3 (C-4'), 134.1 (C-7), 134.9 (C-1'), 139.6 (C- β), 154.9 (C-9), 158.4 (C-2), 172.8 (C-4) ppm. EI-MS: m/z (%) = 328 [$\text{M}]^+$ (^{81}Br , 22), 326 [$\text{M}]^+$ (^{79}Br , 22), 282 (10), 247 (100), 218 (12), 191 (11), 189 (12), 165 (4), 127 (24), 109 (7), 101 (3), 92 (10), 77 (9), 63 (6), 51 (4). $\text{C}_{17}\text{H}_{11}\text{BrO}_2$ (327.13): calcd. C 62.41, H 3.39; found C 62.49, H 3.42.

(E)-4'-Benzyloxy-3-bromo-2-(2-phenylvinyl)-4H-chromen-4-one (3b): This compound was shown to possess spectroscopic and analytical data identical to those previously reported.^[26]

Synthesis of the 2,3-Diaryl-9H-xanthen-9-ones 5a–f: The appropriate styrene (**4a–c**, 3 mmol for styrene **4a** and 0.8 mmol for styrenes

4b or **4c**) was added to a mixture of the appropriate 3-bromo-2-styryl-4H-chromen-4-one (**3a** or **3b**, 0.6 mmol), triphenylphosphane (15.7 mg, 0.06 mmol), tetrakis(triphenylphosphane)palladium(0) (34.7 mg, 0.03 mmol) and triethylamine (83.6 μL , 0.6 mmol) in *N*-methyl-2-pyrrolidin-1-one (10 mL). The mixture was stirred under different time and temperature conditions according to the substitution on the compounds (Table 2). The mixture was then poured into water (20 mL) and ice (10 g) and extracted with diethyl ether (4×25 mL) and dried with anhydrous sodium sulfate. The residue was concentrated, taken up in dichloromethane (5 mL) and purified by thin layer chromatography (eluent: dichloromethane/light petroleum, 7:3). The major spot with higher R_f value corresponds to the 2,3-diaryl-9H-xanthen-9-one (**5a–f**) and a minor spot with lower R_f corresponds to the 2,3-diaryl-3,4-dihydro-9H-xanthen-9-one (**6a–f**). The 2,3-diaryl-9H-xanthen-9-ones **5a–f** were recrystallised from ethanol and obtained in moderate to good yields.

2,3-Diaryl-9H-xanthen-9-ones 5a and 5b and 2,3-Diphenyl-3,4-dihydro-9H-xanthen-9-ones 6a and 6f: These compounds were shown to possess spectroscopic and analytical data identical to those previously reported.^[26]

2-(4-Methoxyphenyl)-3-phenyl-3,4-dihydro-9H-xanthen-9-one (6b): M.p. 153–156 $^\circ\text{C}$. ^1H NMR: δ = 2.99 (dd, J = 17.3, 1.3 Hz, 1 H, 4_{trans}-H), 3.64 (dd, J = 17.3, 9.0 Hz, 1 H, 4_{cis}-H), 3.77 (s, 3 H, 4'-OCH₃), 4.27 (dd, J = 9.0, 1.3 Hz, 1 H, 3-H), 6.81 (d, J = 8.9 Hz, 2 H, 3',5'-H), 7.15–7.40 (m, 7 H, 5,7,2'',3'',4'',5'',6''-H), 7.43 (d, J = 8.9 Hz, 2 H, 2',6'-H), 7.46 (s, 1 H, 1-H), 7.58 (dt, J = 7.8, 1.6 Hz, 1 H, 6-H), 8.28 (dd, J = 7.8, 1.6 Hz, 1 H, 8-H) ppm. ^{13}C NMR: δ = 36.6 (C-4), 41.6 (C-3), 55.2 (4'-OCH₃), 113.8 (C-3',5'), 114.8 (C-1), 117.0 (C-9a), 118.0 (C-5), 123.8 (C-8a), 125.0 (C-7), 126.1 (C-8), 126.8 (C-2',6'), 127.1 (C-4'), 127.3 (C-2'',6''), 128.9 (C-3'',5''), 131.5 (C-1'), 132.9 (C-6), 134.9 (C-2), 140.8 (C-1''), 155.8 (C-4b), 159.1 (C-4'), 162.0 (C-4a), 174.2 (C-9) ppm. EI-MS: m/z (%) = 380 (100) [$\text{M}]^+$, 379 (18), 378 (31), 365 (6), 347 (3), 303 (23), 287 (6), 273 (16), 260 (10), 215 (9), 202 (6), 190 (6), 165 (3), 139 (3), 121 (14), 108 (3), 92 (5), 77 (6), 65 (4), 51 (4). HRMS (EI): calcd. for $\text{C}_{26}\text{H}_{20}\text{O}_3$ [$\text{M}]^+$ 380.1412; found 380.1412.

2-(3,4-Dimethoxyphenyl)-3-phenyl-9H-xanthen-9-one (5c): M.p. 139–140 $^\circ\text{C}$. ^1H NMR: δ = 3.56 and 3.87 (2 $\times$ s, 6 H, 3',4'-OCH₃), 6.54 (d, J = 1.9 Hz, 1 H, 2'-H), 6.78–6.90 (m, 2 H, 5'H and 6'-H), 7.20–7.24 (m, 2 H, 2'',6''-H), 7.26–7.32 (m, 3 H, 3'',4'',5''-H), 7.40 (dt, J = 7.6, 1.0 Hz, 1 H, 7-H), 7.52 (d, J = 8.2 Hz, 1 H, 5-H), 7.55 (s, 1 H, 4-H), 7.74 (ddd, J = 8.2, 7.6, 1.7 Hz, 1 H, 6-H), 8.38 (dd, J = 7.6, 1.7 Hz, 1 H, 8-H), 8.39 (s, 1 H, 1-H) ppm. ^{13}C NMR: δ = 55.7 and 55.9 (3',4'-OCH₃), 110.7 (C-5'), 113.4 (C-2'), 118.0 (C-5), 119.5 (C-4), 120.7 (C-9a), 121.9 (C-8a), 122.1 (C-6'), 123.9 (C-7), 126.7 (C-8), 127.5 (C-4'), 128.7 (C-1), 128.2 (C-3'',5''), 129.5 (C-2'',6''), 132.2 (C-1'), 134.8 (C-6), 136.7 (C-2), 140.1 (C-1''), 147.6 (C-3), 148.0 and 148.1 (C-3', C-4'), 155.0 (C-4a), 156.2 (C-4b), 177.0 (C-9) ppm. EI-MS: m/z (%) = 408 [$\text{M}]^+$ (100), 393 (9), 361 (8), 333 (8), 321 (7), 292 (4), 263 (3), 204 (4), 188 (3), 167 (4), 138 (2), 77 (1). $\text{C}_{27}\text{H}_{20}\text{O}_4$ (408.45): calcd. for C 79.40, H 4.94; found C 79.64, H 4.83.

2-(3,4-Dimethoxyphenyl)-3-phenyl-3,4-dihydro-9H-xanthen-9-one (6c): Yellowish oil. ^1H NMR: δ = 3.00 (dd, J = 17.3, 1.5 Hz, 1 H, 4_{trans}-H), 3.65 (dd, J = 17.3, 9.1 Hz, 1 H, 4_{cis}-H), 3.84 (s, 6 H, 3',4'-OCH₃), 4.29 (dd, J = 9.1, 1.5 Hz, 1 H, 3-H), 6.74 (d, J = 8.4 Hz, 1 H, 5'-H), 6.96 (dd, J = 8.4, 2.2 Hz, 1 H, 6'-H), 7.09 (d, J = 2.2 Hz, 1 H, 2'-H), 7.18–7.32 (m, 5 H, 2'',3'',4'',5'',6''-H), 7.33–7.41 (m, 2 H, 5-H, 7-H), 7.46 (s, 1 H, 1-H), 7.59 (dt, J = 7.8, 1.6 Hz, 1 H, 6-H), 8.28 (dd, J = 8.0, 1.6 Hz, 1 H, 8-H) ppm. ^{13}C NMR: δ = 36.5 (C-4), 41.8 (C-3), 55.8 (3',4'-OCH₃), 108.7 (C-2'), 110.8 (C-

5'), 115.0 (C-1), 116.9 (C-9a), 117.9 (C-5), 118.2 (C-6'), 123.8 (C-8a), 125.0 (C-7), 126.1 (C-8), 127.1 (C-4'), 127.2 (C-2'',6''), 128.9 (C-3'',5''), 131.9 (C-1'), 133.0 (C-6), 135.1 (C-2), 140.9 (C-1''), 148.70 and 148.72 (C-3',4'), 155.8 (C-4b), 162.1 (C-4a), 174.2 (C-9) ppm. EI-MS: m/z = 410 [M]⁺ (100), 409 (8), 408 (20), 395 (7), 379 (4), 361 (3), 333 (15), 319 (4), 289 (4), 273 (13), 205 (5), 165 (12), 151 (6), 138 (5), 121 (9), 92 (4), 77 (5). HRMS (EI): calcd. for C₂₇H₂₂O₄ [M]⁺ 410.1518; found 410.1521.

3-(4-Benzoyloxyphenyl)-2-phenyl-9H-xanthen-9-one (5d): M.p. 182–183 °C. ¹H NMR: δ = 5.05 (s, 2 H, 4'-OCH₂C₆H₅), 6.88 (d, J = 8.7 Hz, 2 H, 3'',5''-H), 7.13 (d, J = 8.7 Hz, 2 H, 2'',6''-H), 7.18–7.27 (m, 5 H, 2',3',4',5',6'-H), 7.33–7.45 (m, 6 H, 7-H, 2,3,4,5,6-H of 4'-OCH₂C₆H₅), 7.52 (d, J = 7.9 Hz, 1 H, 5-H), 7.54 (s, 1 H, 4-H), 7.74 (dt, J = 7.9, 1.6 Hz, 1 H, 6-H), 8.35 (s, 1 H, 1-H), 8.37 (dd, J = 7.9, 1.6 Hz, 1 H, 8-H) ppm. ¹³C NMR: δ = 70.0 (4'-OCH₂C₆H₅), 114.5 (C-3'',5''), 118.0 (C-5), 119.2 (C-4), 120.4 (C-9a), 122.0 (C-8a), 123.9 (C-7), 126.76 (C-8), 126.84 (C-4'), 127.5 (C-2,6 of 4'-OCH₂C₆H₅), 128.0 (C-4 of 4'-OCH₂C₆H₅), 128.1 (C-2',6'), 128.4 (C-1), 128.6 (C-3,5 of 4'-OCH₂C₆H₅), 129.9 (C-3',5'), 130.9 (C-2'',6''), 132.4 (C-1''), 134.7 (C-6), 136.7 (C-1 of 4'-OCH₂C₆H₅), 137.0 (C-1'), 140.0 (C-2), 147.3 (C-3), 155.3 (C-4a), 156.3 (C-4b), 158.4 (C-4'), 177.0 (C-9) ppm. EI-MS: m/z (%) = 454 [M]⁺ (33), 408 (2), 363 (8), 333 (2), 305 (3), 236 (3), 91 (100), 65 (3). C₃₂H₂₂O₃ (454.52): calcd. for C 84.56, H 4.88; found C 84.29, H 4.87.

3-(4-Benzoyloxyphenyl)-2-phenyl-3,4-dihydro-9H-xanthen-9-one (6d): Yellowish oil. ¹H NMR: δ = 2.97 (dd, J = 17.4, 1.5 Hz, 1 H, 4_{trans}-H), 3.63 (dd, J = 17.4, 8.4 Hz, 1 H, 4_{cis}-H), 4.26 (brd, J = 8.4 Hz, 1 H, 3-H), 4.95 (s, 2 H, 4'-OCH₂C₆H₅), 6.85 (d, J = 8.7 Hz, 2 H, 3'',5''-H), 7.22 (d, J = 8.7 Hz, 2 H, 2'',6''-H), 7.24–7.41 (m, 10 H, 5,7,3',4',5'-H, 2,3,4,5,6-H of 4'-OCH₂C₆H₅), 7.46 (m, 2 H, 2',6'-H), 7.54 (s, 1 H, 1-H), 7.59 (dt, J = 7.8, 1.6 Hz, 1 H, 6-H), 8.28 (dd, J = 7.9, 1.6 Hz, 1 H, 8-H) ppm. ¹³C NMR: δ = 36.8 (C-4), 40.9 (C-3), 69.9 (4'-OCH₂C₆H₅), 115.1 (C-3'',5''), 116.5 (C-1), 116.8 (C-9a), 118.0 (C-5), 123.9 (C-8a), 125.0 (C-7), 125.6 (C-2',6'), 126.2 (C-8), 127.49 (C-2,6 of 4'-OCH₂C₆H₅), 127.52 (C-4'), 127.9 (C-4 of 4'-OCH₂C₆H₅), 128.41, 128.44 and 128.5 (C-3',5', C-2'',6', C-3,5 of 4'-OCH₂C₆H₅), 132.8 (C-1''), 133.0 (C-6), 135.6 (C-2), 136.8 (C-1 of 4'-OCH₂C₆H₅), 139.1 (C-1'), 155.8 (C-4b), 157.9 (C-4'), 162.6 (C-4a), 174.2 (C-9) ppm. EI-MS: m/z (%) = 456 [M]⁺ (59), 455 (11), 454 (9), 379 (4), 365 (20), 289 (5), 272 (13), 215 (5), 121 (4), 92 (11), 91 (100), 77 (3), 65 (8). HRMS (EI): calcd. for C₃₂H₂₄O₃ [M]⁺ 456.1725; found 456.1725.

3-(4-Benzoyloxyphenyl)-2-(4-methoxyphenyl)-9H-xanthen-9-one (5e): M.p. 140–142 °C. ¹H NMR: δ = 3.81 (s, 3 H, 4'-OCH₃), 5.06 (s, 2 H, 4'-OCH₂C₆H₅), 6.80 (d, J = 8.8 Hz, 2 H, 3',5'-H), 6.90 (d, J = 8.8 Hz, 2 H, 3'',5''-H), 7.11 (d, J = 8.8 Hz, 2 H, 2',6'-H), 7.15 (d, J = 8.8 Hz, 2 H, 2'',6''-H), 7.34–7.46 (m, 6 H, 7-H, 4'-OCH₂C₆H₅), 7.520 (d, J = 7.8 Hz, 1 H, 5-H), 7.522 (s, 1 H, 4-H), 7.74 (dt, J = 7.8, 1.6 Hz, 1 H, 6-H), 8.32 (s, 1 H, 1-H), 8.37 (dd, J = 8.0, 1.6 Hz, 1 H, 8-H) ppm. ¹³C NMR: δ = 55.2 (4'-OCH₃), 70.0 (4'-OCH₂C₆H₅), 113.6 (C-3',5'), 114.5 (C-3'',5''), 118.0 (C-5), 119.2 (C-4), 120.4 (C-9a), 122.0 (C-8a), 123.9 (C-7), 126.8 (C-8), 127.6 (C-2,6 of 4'-OCH₂C₆H₅), 128.1 (C-4 of 4'-OCH₂C₆H₅), 128.2 (C-1), 128.6 (C-3,5 of 4'-OCH₂C₆H₅), 130.9 (C-2'',6''), 131.0 (C-2',6'), 132.4 (C-1'), 132.6 (C-1''), 134.7 (C-6), 136.65 (C-2), 136.72 (C-1 of 4'-OCH₂C₆H₅), 147.3 (C-3), 155.1 (C-4a), 156.3 (C-4b), 158.3 (C-4'), 158.6 (C-4'), 177.1 (C-9) ppm. EI-MS: m/z (%) = 484 [M]⁺ (61), 394 (15), 393 (23), 91 (100), 85 (6). C₃₃H₂₄O₄ (484.54): calcd. for C 81.80, H 4.99; found C 82.02, H 5.06.

3-(4-Benzoyloxyphenyl)-2-(4-methoxyphenyl)-3,4-dihydro-9H-xanthen-9-one (6e): Yellowish oil. ¹H NMR: δ = 2.95 (dd, J = 17.3,

1.4 Hz, 1 H, 4_{trans}-H), 3.60 (dd, J = 17.3, 8.4 Hz, 1 H, 4_{cis}-H), 3.77 (s, 3 H, 4'-OCH₃), 4.22 (brd, J = 8.4 Hz, 1 H, 3-H), 4.94 (s, 2 H, 4'-OCH₂C₆H₅), 6.81 (d, J = 8.9 Hz, 1 H, 3',5'-H), 6.84 (d, J = 8.7 Hz, 2 H, 3'',5''-H), 7.20 (d, J = 8.7 Hz, 2 H, 2'',6''-H), 7.28–7.39 (m, 7 H, 5-H, 7-H, 2,3,4,5,6-H of 4'-OCH₂C₆H₅), 7.43 (s, 1 H, 1-H), 7.43 (d, J = 8.9 Hz, 2 H, 2',6'-H), 7.58 (dt, J = 7.8, 1.6 Hz, 1 H, 6-H), 8.27 (dd, J = 8.0, 1.6 Hz, 1 H, 8-H) ppm. ¹³C NMR: δ = 36.7 (C-4), 40.8 (C-3), 55.2 (4'-OCH₃), 69.8 (4'-OCH₂C₆H₅), 113.8 (C-3',5'), 114.5 (C-1), 115.0 (C-3'',5''), 116.9 (C-9a), 117.9 (C-5), 123.8 (C-8a), 124.9 (C-7), 126.1 (C-8), 126.8 (C-2',6'), 127.4 (C-2,6 of 4'-OCH₂C₆H₅), 127.9 (C-4 of 4'-OCH₂C₆H₅), 128.3 (C-2'',6''), 128.5 (C-3,5 of 4'-OCH₂C₆H₅), 131.5 (C-1'), 132.87 (C-6), 132.90 (C-1''), 135.2 (C-2), 136.8 (C-1 of 4'-OCH₂C₆H₅), 155.8 (C-4b), 157.9 (C-4'), 155.9 (C-4'), 162.1 (C-4a), 174.2 (C-9) ppm. EI-MS: m/z (%) = 486 [M]⁺ (44), 485 (7), 484 (9), 408 (6), 395 (15), 364 (3), 302 (5), 213 (3), 135 (33), 121 (8), 92 (14), 91 (100), 77 (7), 65 (9). HRMS (EI): calcd. for C₃₃H₂₆O₄ [M]⁺ 486.1831; found 486.1829.

3-(4-Benzoyloxyphenyl)-2-(3,4-dimethoxyphenyl)-9H-xanthen-9-one (5f): M.p. 188–189 °C. ¹H NMR: δ = 3.61 (s, 3 H, 4'-OCH₃), 3.89 (s, 3 H, 3'-OCH₃), 5.06 (s, 2 H, 4'-OCH₂C₆H₅), 6.59 (d, J = 1.8 Hz, 1 H, 2'-H), 6.79–6.86 (m, 2 H, 5'-H, 6'-H), 6.90 (d, J = 8.8 Hz, 2 H, 3'',5''-H), 7.15 (d, J = 8.8 Hz, 2 H, 2'',6''-H), 7.31–7.46 (m, 6 H, 7-H, 4'-OCH₂C₆H₅), 7.52 (d, J = 7.9 Hz, 1 H, 5-H), 7.53 (s, 1 H, 4-H), 7.75 (dt, J = 7.9, 1.8 Hz, 1 H, 6-H), 8.36 (s, 1 H, 1-H), 8.38 (dd, J = 8.2, 1.8 Hz, 1 H, 8-H) ppm. ¹³C NMR: δ = 55.6 (4'-OCH₃), 55.8 (3'-OCH₃), 69.9 (4'-OCH₂C₆H₅), 110.8 (C-5'), 113.4 (C-2'), 114.6 (C-3'',5''), 118.0 (C-5), 119.2 (C-4), 120.4 (C-9a), 121.9 (C-8a), 122.2 (C-6'), 123.9 (C-7), 126.8 (C-8), 127.4 (C-2,6 of 4'-OCH₂C₆H₅), 127.9 (C-1), 128.0 (C-4 of 4'-OCH₂C₆H₅), 128.6 (C-3,5 of 4'-OCH₂C₆H₅), 130.8 (C-2'',6''), 132.5 (C-1'), 132.7 (C-1''), 134.7 (C-6), 136.7 (C-2, C-1 of 4'-OCH₂C₆H₅), 147.3 (C-3), 148.0 (C-3'), 148.2 (C-4'), 155.1 (C-4a), 156.3 (C-4b), 158.3 (C-4'), 177.0 (C-9) ppm. EI-MS: m/z (%) = 514 [M]⁺ (11), 388 (11), 166 (11), 165 (13), 91 (100), 77 (3), 65 (5). HRMS (EI): calcd. for C₃₄H₂₆O₅ [M]⁺ 514.1780; found 514.1785.

Synthesis of the (E)-2-Methyl-3-styryl-4H-chromen-4-ones 7a–c:

The appropriate styrene (**4a–c**, 2.5 mmol) was added to a mixture of 3-bromo-2-methyl-4H-chromen-4-one (**1**, 0.12 g, 0.5 mmol), triphenylphosphane (13.1 mg, 0.05 mmol), palladium chloride (4.4 mg, 0.025 mmol) and triethylamine (69.7 μ L, 0.5 mmol) in *N*-methyl-2-pyrrolidin-1-one (5 mL). The mixture was stirred at 160 °C for 9 h. It was then poured into water (15 mL) and ice (10 g), extracted with diethyl ether (4 $\times$ 25 mL) and dried with anhydrous sodium sulfate. The residue was concentrated, taken up in dichloromethane (10 mL) and purified by thin layer chromatography (eluent: dichloromethane/light petroleum 7:3). The obtained (E)-2-methyl-3-styryl-4H-chromen-4-ones (**7a–c**) were recrystallised from ethanol and obtained in moderate to good yields.

(E)-2-Methyl-3-(2-phenylvinyl)-4H-chromen-4-one (7a): Yield 6.30 mg (48%); m.p. 136–137 °C. ¹H NMR: δ = 2.62 (s, 3 H, 2-CH₃), 6.97 (d, J = 16.3 Hz, 1 H, α -H), 7.24–7.29 (m, 1 H, 4'-H), 7.36 (d, J = 7.7 Hz, 2 H, 3',5'-H), 7.38 (ddd, J = 8.0, 7.9, 1.0 Hz, 2 H, 6-H), 7.41 (d, J = 8.2 Hz, 1 H, 8-H), 7.53 (dd, J = 7.7, 1.5 Hz, 2 H, 2',6'-H), 7.63 (ddd, J = 8.2, 8.0, 1.6 Hz, 1 H, 7-H), 7.71 (d, J = 16.3 Hz, 1 H, β -H), 8.25 (dd, J = 7.9, 1.6 Hz, 1 H, 5-H) ppm. ¹³C NMR: δ = 19.3 (2-CH₃), 117.5 (C-8), 118.5 (C-3), 119.4 (C-a), 123.4 (C-10), 124.8 (C-6), 126.1 (C-5), 126.4 (C-2',6'), 127.7 (C-4'), 128.6 (C-3',5'), 133.1 (C-7), 134.2 (C- β), 137.9 (C-1'), 155.2 (C-9), 163.8 (C-2), 176.9 (C-4) ppm. EI-MS: m/z (%) = 262 [M]⁺ (100), 247 (39), 233 (7), 218 (5), 202 (3), 191 (5), 185 (63), 141 (27), 121 (14), 115 (21), 102 (3), 92 (11), 77 (8), 63 (10), 51 (6). C₁₈H₁₄O₂ (262.30): calcd. for C 82.42, H 5.38; found C 82.31, H 5.46.

(E)-3-[2-(4-Methoxyphenyl)vinyl]-2-methyl-4H-chromen-4-one (7b): Yield 71.6 mg (49%); m.p. 89–91 °C. ^1H NMR: δ = 2.61 (s, 3 H, 2-CH₃), 3.83 (s, 3 H, 4'-OCH₃), 6.83 (d, J = 16.3 Hz, 1 H, α -H), 6.90 (d, J = 8.7 Hz, 2 H, 3',5'-H), 7.35–7.43 (m, 2 H, 6-H, 8-H), 7.47 (d, J = 8.7 Hz, 2 H, 2',6'-H), 7.60–7.67 (m, 1 H, 7-H), 7.64 (d, J = 16.3 Hz, 1 H, β -H), 8.25 (dd, J = 8.1, 0.9 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 19.3 (2-CH₃), 55.3 (4'-OCH₃), 114.0 (C-3',5'), 117.3 (C-8), 117.5 (C- α), 118.7 (C-3), 123.4 (C-10), 124.8 (C-6), 126.1 (C-5), 127.7 (C-2',6'), 130.7 (C-1'), 133.1 (C-7), 133.8 (C- β), 155.3 (C-9), 159.3 (C-4'), 163.3 (C-2), 177.0 (C-4) ppm. EI-MS: m/z (%) = 292 [M]⁺ (31), 277 (14), 211 (8), 197 (10), 183 (11), 169 (13), 155 (17), 141 (19), 127 (24), 125 (10), 113 (28), 111 (16), 99 (34), 97 (27), 85 (96), 83 (20), 71 (100), 69 (18). HRMS (EI): calcd. for C₁₉H₁₆O₃ [M]⁺ 292.1099; found 292.1091.

(E)-3-[2-(3,4-Dimethoxyphenyl)vinyl]-2-methyl-4H-chromen-4-one (7c): Yield 83.8 mg (52%); m.p. 117–118 °C. ^1H NMR: δ = 2.61 (s, 3 H, 2-CH₃), 3.90 and 3.93 (2 $\times$ s, 6 H, 3',4'-OCH₃), 6.77–6.92 (m, 1 H, 5'-H), 6.84 (d, J = 16.3 Hz, 1 H, α -H), 7.06–7.07 (m, 2 H, 2',6'-H), 7.35–7.41 (m, 2 H, 6-H, 8-H), 7.59 (d, J = 16.3 Hz, 1 H, β -H), 7.59–7.65 (m, 1 H, 7-H), 8.24 (dd, J = 7.7, 1.2 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 19.4 (2-CH₃), 55.8 and 55.9 (3',4'-OCH₃), 109.0 (C-2'), 111.0 (C-5'), 117.5 (C-8, C- α), 118.6 (C-3), 119.4 (C-6'), 123.2 (C-10), 124.7 (C-6), 126.0 (C-5), 130.9 (C-1'), 133.1 (C-7), 134.0 (C- β), 148.8 and 148.9 (C-3',4'), 155.2 (C-9), 163.3 (C-2), 176.9 (C-4) ppm. EI-MS: m/z (%) = 322 [M]⁺ (100), 307 (30), 292 (6), 276 (6), 263 (6), 247 (7), 235 (9), 221 (3), 202 (3), 185 (17), 161 (9), 144 (5), 138 (7), 121 (10), 115 (15), 92 (13), 77 (7), 63 (9), 51 (6). C₂₀H₁₈O₄ (322.35): calcd. for C 74.52, H 5.63; found C 74.36, H 5.86.

Synthesis of the (E,E)-2,3-Distyryl-4H-chromen-4-ones 8a–c: Sodium (0.4 g, 16.7 mmol) was gradually added to dry methanol (20 mL) and the mixture was stirred until the reaction mixture had reached room temperature. The appropriate (E)-2-methyl-3-styryl-4H-chromen-4-one (7a–c, 4.2 mmol) and benzaldehyde (2a, 0.53 g, 5.0 mmol) were added and the reaction mixture was allowed to stand at room temperature for 48 h. After this period, the solution was poured into ice (30 g) and water (50 mL) and the pH was adjusted to 4 with hydrochloric acid. The yellow solid was removed by filtration, taken up in dichloromethane (10 mL) and purified by thin layer chromatography with dichloromethane as eluent. The solvent was evaporated to dryness and the residue were recrystallised from ethanol to give the (E,E)-2,3-distyryl-4H-chromen-4-ones 8a–c.

(E,E)-2,3-Bis(2-phenylvinyl)-4H-chromen-4-one (8a): Yield 0.78 g (53%); m.p. 160–162 °C. ^1H NMR: δ = 7.21 (d, J = 15.8 Hz, 1 H, α' -H), 7.29 (tt, J = 7.2, 1.7 Hz, 1 H, 4'-H), 7.33–7.43 (m, 6 H, 6-H, 3',5',3'',4'',5''-H), 7.37 (d, J = 15.7 Hz, 1 H, α -H), 7.43 (d, J = 15.8 Hz, 1 H, β' -H), 7.50 (d, J = 8.1 Hz, 1 H, 8-H), 7.54–7.59 (m, 4 H, 2',6',2'',6''-H), 7.65 (dt, J = 8.1, 1.7 Hz, 1 H, 7-H), 7.67 (d, J = 15.7 Hz, 1 H, β -H), 8.22 (dd, J = 7.9, 1.7 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 117.5 (C-8), 118.5 (C- α), 119.0 (C-3), 119.1 (C- α'), 123.1 (C-10), 124.7 (C-6), 126.0 (C-5), 126.7 (C-2',6'), 127.7 (C-2'',6''), 127.9 (C-4'), 128.6 (C-3',5'), 129.0 (C-3'',5''), 129.7 (C-4''), 133.5 (C-7), 135.5 (C-1'), 136.1 (C- β'), 137.1 (C- β), 137.5 (C-1'), 154.9 (C-9), 158.0 (C-2), 177.5 (C-4) ppm. EI-MS: m/z (%) = 350 [M]⁺ (58), 273 (100), 259 (4), 228 (9), 215 (7), 202 (8), 152 (6), 121 (8), 115 (11), 92 (8), 77 (13), 63 (7), 51 (7). C₂₅H₁₈O₂ (350.41): calcd. for C 85.69, H 5.18; found C 85.44, H 5.34.

2,3-Diphenyl-1,2-dihydro-9H-xanthen-9-one (9a): Yellowish oil. ^1H NMR: δ = 3.19 (dd, J = 16.8, 8.4 Hz, 1 H, 1_{cis}-H), 3.45 (dd, J = 16.8, 2.0 Hz, 1 H, 1_{trans}-H), 4.33 (brd, J = 8.4 Hz, 1 H, 2-H), 7.02 (s, 1 H, 4-H), 7.15–7.23 (m, 3 H, 3',4',5'-H), 7.25–7.27 (m, 2 H,

2',6'-H), 7.32–7.41 (m, 4 H, 7,3',4'',5''-H), 7.48 (d, J = 8.4 Hz, 1 H, 5-H), 7.50–7.53 (m, 2 H, 2'',6''-H), 7.60–7.66 (m, 1 H, 6-H), 8.16 (dd, J = 8.1, 1.1 Hz, 1 H, 8-H) ppm. ^{13}C NMR: δ = 28.2 (C-1), 41.5 (C-2), 111.5 (C-9a), 118.4 (C-4), 124.1 (C-8a), 124.7 (C-7), 125.7 (C-8), 126.8 (C-2'',6''), 127.0 (C-4'), 127.2 (C-2',6'), 128.8 (C-3',5', C-3'',5''), 129.3 (C-4''), 133.0 (C-6), 138.1 (C-1'), 140.7 (C-1'), 150.6 (C-3), 155.6 (C-4a), 159.6 (C-4b), 176.7 (C-9) ppm. EI-MS: m/z (%) = 350 [M]⁺ (84), 349 (52), 274 (55), 273 (100), 261 (14), 228 (10), 215 (12), 202 (8), 189 (6), 152 (10), 139 (7), 121 (12), 115 (11), 105 (33), 92 (8), 91 (6), 77 (23), 63 (7), 51 (12). HRMS (EI): calcd. for C₂₅H₁₈O₂ [M]⁺ 350.1307; found 350.1306.

(E,E)-2-[2-(4-Methoxyphenyl)vinyl]-3-(2-phenylvinyl)-4H-chromen-4-one (8b): Yield 1.07 g (67%); m.p. 163–164 °C. ^1H NMR: δ = 3.85 (s, 3 H, 4'-OCH₃), 6.93 (d, J = 8.8 Hz, 2 H, 3',5'-H), 7.11 (d, J = 16.4 Hz, 1 H, α' -H), 7.36 (d, J = 16.4 Hz, 1 H, β' -H), 7.36–7.42 (m, 4 H, 6-H, 3',4',5'-H), 7.42 (d, J = 16.0 Hz, 1 H, α -H), 7.52 (d, J = 8.8 Hz, 2 H, 2'',6''-H), 7.51–7.52 (m, 1 H, 8-H), 7.60 (dd, J = 7.9, 1.7 Hz, 2 H, 2',6'-H), 7.68 (dt, J = 7.8, 1.6 Hz, 1 H, 7-H), 7.70 (d, J = 16.0 Hz, 1 H, β -H), 8.25 (dd, J = 8.0, 1.6 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 55.3 (4'-OCH₃), 114.1 (5'', C-3''), 116.9 (C- α'), 117.5 (C-8), 118.8 (C- α), 119.5 (C-3), 123.1 (C-10), 124.7 (C-6), 126.1 (C-5), 127.7 (C-2',6'), 128.0 (C-2'',6''), 129.0 (C-3',5'), 129.4 (C-4'), 130.4 (C-1'), 133.5 (C-7), 135.6 (C-1'), 135.8 (C- β'), 136.8 (C- β), 155.1 (C-9), 157.7 (C-2), 159.6 (C-4'), 177.7 (C-4) ppm. EI-MS: m/z (%) = 380 [M]⁺ (100), 303 (65), 289 (6), 273 (41), 260 (11), 215 (13), 202 (7), 190 (6), 151 (7), 121 (48), 115 (7), 92 (9), 77 (9), 63 (6), 51 (4). C₂₆H₂₀O₃ (380.44): calcd. for C 82.08, H 5.30; found C 82.05, H 4.99.

(E,E)-2-[2-(3,4-Dimethoxyphenyl)vinyl]-3-(2-phenylvinyl)-4H-chromen-4-one (8c): Yield 1.19 g (69%); m.p. 128–130 °C. ^1H NMR: δ = 3.93 and 3.96 (s, 6 H, 3',4'-OCH₃), 6.89 (d, J = 8.2 Hz, 1 H, 5''-H), 7.11 (dd, J = 8.2, 1.9 Hz, 1 H, 6''-H), 7.13 (d, J = 16.1 Hz, 1 H, α' -H), 7.14 (d, J = 1.9 Hz, 1 H, 2''-H), 7.27 (d, J = 16.1 Hz, 1 H, β' -H), 7.38–7.42 (m, 4 H, 6,3',4',5'-H), 7.42 (d, J = 15.8 Hz, 1 H, α -H), 7.54 (d, J = 8.0 Hz, 1 H, 8-H), 7.61 (d, J = 7.3 Hz, 2 H, 2',6'-H), 7.69 (dt, J = 8.0, 1.5 Hz, 1 H, 7-H), 7.71 (d, J = 15.8 Hz, 1 H, β -H), 8.25 (dd, J = 8.0, 1.5 Hz, 1 H, 5-H) ppm. ^{13}C NMR: δ = 55.9 (3'',4''-OCH₃), 109.1 (C-2''), 111.1 (C-5''), 117.2 (C- α'), 117.6 (C-8), 118.9 (C- α), 119.6 (C-3), 120.0 (C-6'), 123.1 (C-10), 124.7 (C-6), 126.1 (C-5), 127.6 (C-2',6'), 129.0 (C-3',5'), 129.6 (C-4'), 130.7 (C-1'), 133.6 (C-7), 135.6 (C-1'), 136.1 (C- β'), 136.8 (C- β), 149.1 (C-3''), 149.2 (C-4''), 155.1 (C-9), 157.8 (C-2), 177.7 (C-4) ppm. EI-MS: m/z (%) = 410 [M]⁺ (100), 333 (29), 317 (6), 289 (3), 273 (27), 261 (4), 215 (6), 202 (10), 189 (5), 151 (31), 138 (10), 121 (11), 92 (10), 77 (8), 63 (5), 51 (5). C₂₇H₂₂O₄ (410.46): calcd. for C 79.01, H 5.40; found C 78.75, H 5.55.

Synthesis of the 2-Acetylphenyl (E)-Cinnamates 10a–i. Method 1: Cinnamoyl chloride (1.9 g, 11.4 mmol) was added to a solution of the appropriate acetophenone (5.7 mmol) in dry pyridine (150 mL). The solution was stirred under nitrogen at room temperature for 2 h. After that period, the solution was poured into ice (100 g) and water (100 mL), and the pH was adjusted to 4 with dilute hydrochloric acid. The mixture was vigorously stirred for 15 min, the precipitate was removed and dissolved in chloroform (100 mL), and the organic layer was washed with water (3 $\times$ 100 mL). The solvent was evaporated to dryness, and the residue was purified by silica gel column chromatography with dichloromethane as eluent. The solvent was removed to dryness in each case, and the residue was recrystallised from ethanol to give the desired 2-acetylphenyl (E)-cinnamate 10a, 10d, 10f or 10h in good yield.

2-Acetylphenyl (E)-3-Phenylacrylate (10a): This compound showed spectroscopic and analytical data identical to those previously reported.^[32]

2-Acetyl-5-methoxyphenyl (E)-3-Phenylacrylate (10d): Yield 1.47 g (87%); m.p. 97–99 °C. ^1H NMR: δ = 2.53 (s, 3 H, 2-CH₃), 3.86 (s, 3 H, 4'-OCH₃), 6.69 (d, J = 16.0 Hz, 1 H, α -H), 6.69 (d, J = 2.5 Hz, 1 H, 3'-H), 6.85 (dd, J = 8.8, 2.5 Hz, 1 H, 5'-H), 7.42–7.44 (m, 3 H, 3'',4'',5''-H), 7.59–7.62 (m, 2 H, 2'',6''-H), 7.88 (d, J = 8.8 Hz, 1 H, 6'-H), 7.91 (d, J = 16.0 Hz, 1 H, β -H) ppm. ^{13}C NMR: δ = 29.5 (2-CH₃), 55.7 (4'-OCH₃), 109.1 (C-3'), 111.9 (C-5'), 116.8 (C- α), 123.5 (C-1'), 128.4 (C-2'',6''), 128.9 (C-3'',5''), 130.8 (C-4''), 132.3 (C-6'), 134.0 (C-1''), 147.3 (C- β), 151.4 (C-2'), 163.7 (C-4'), 165.1 (C=O), 195.8 (C-1) ppm. ESI-MS: m/z (%) = 297 [M + H]⁺ (8), 319 [M + Na]⁺ (100), 335 [M + K]⁺ (13), 615 [2M + Na]⁺ (43). C₁₈H₁₆O₄ (296.32): calcd. for C 72.96, H 5.44; found C 72.84, H 5.57.

2-Acetyl-3-methoxyphenyl (E)-3-Phenylacrylate (10f): Yield 1.43 g (85%); m.p. 101–102 °C. ^1H NMR: δ = 2.52 (s, 3 H, 2-CH₃), 3.87 (s, 3 H, 6'-OCH₃), 6.58 (d, J = 16.0 Hz, 1 H, α -H), 6.81 (dd, J = 8.3, 0.7 Hz, 1 H, 3'-H), 6.85 (d, J = 8.3 Hz, 1 H, 5'-H), 7.38 (t, J = 8.3 Hz, 1 H, 4'-H), 7.40–7.42 (m, 3 H, 3'',4'',5''-H), 7.55–7.58 (m, 2 H, 2'',6''-H), 7.83 (d, J = 16.0 Hz, 1 H, β -H) ppm. ^{13}C NMR: δ = 31.7 (2-CH₃), 55.9 (6'-OCH₃), 108.6 (C-5'), 115.1 (C-3'), 116.6 (C- α), 124.5 (C-1'), 128.4 (C-2'',6''), 128.9 (C-3'',5''), 130.8 (C-4''), 130.9 (C-4'), 134.0 (C-1''), 147.2 (C- β), 147.6 (C-2'), 157.3 (C-6'), 165.1 (C=O), 200.7 (C-1) ppm. ESI-MS: m/z (%) = 297 [M + H]⁺ (6), 319 [M + Na]⁺ (100), 335 [M + K]⁺ (16), 615 [2M + Na]⁺ (89). C₁₈H₁₆O₄ (296.32): calcd. for C 72.96, H 5.44; found C 73.36, H 5.47.

2-Acetyl-3,5-dimethoxyphenyl (E)-3-Phenylacrylate (10h): Yield 1.75 g (94%); m.p. 97–98 °C. ^1H NMR: δ = 2.49 (s, 3 H, 2-CH₃), 3.82 (s, 3 H, 4'-OCH₃), 3.86 (s, 3 H, 6'-OCH₃), 6.31 (d, J = 2.2 Hz, 1 H, 3'-H), 6.39 (d, J = 2.2 Hz, 1 H, 5'-H), 6.59 (d, J = 16.0 Hz, 1 H, α -H), 7.40–7.42 (m, 3 H, 3'',4'',5''-H), 7.56–7.59 (m, 2 H, 2'',6''-H), 7.83 (d, J = 16.0 Hz, 1 H, β -H) ppm. ^{13}C NMR: δ = 31.9 (2-CH₃), 55.6 (4'-OCH₃), 55.9 (6'-OCH₃), 96.5 (C-5'), 99.9 (C-3'), 116.7 (C- α), 117.3 (C-1'), 128.4 (C-2'',6''), 128.9 (C-3'',5''), 130.7 (C-4''), 134.0 (C-1''), 147.1 (C- β), 149.5 (C-2'), 159.1 (C-6'), 162.2 (C-4'), 165.2 (C=O), 199.5 (C-1) ppm. ESI-MS: m/z (%) = 327 [M + H]⁺ (14), 349 [M + Na]⁺ (73), 365 [M + K]⁺ (12), 675 [2M + Na]⁺ (100). C₁₉H₁₈O₅ (326.34): calcd. for C 69.93, H 5.56; found C 69.81, H 5.62.

Method 2: The appropriate cinnamic acid (16.8 mmol) and phosphorus oxychloride (4.2 mL, 45.9 mmol) were added to a solution of the appropriate acetophenone (8.6 mmol) in dry pyridine (100 mL). The solution was stirred at 60 °C for 2 h, and after that the solution was poured into ice (50 g) and water (100 mL) and the pH was adjusted to 4 with hydrochloric acid. The precipitate was removed by filtration, the residue was dissolved with chloroform (100 mL), and the organic layer was washed with water (3 $\times$ 100 mL). The solvent was evaporated, and the residue was purified by silica gel column chromatography with light petroleum/dichloromethane 3:7 as eluent. The solvent was removed to dryness in each case, and the residue was recrystallised from ethanol to give the desired 2-acetylphenyl (E)-cinnamates **10b**, **10c**, **10e**, **10g** or **10i** in good yield.

2-Acetylphenyl (E)-2-(4-Methoxyphenyl)acrylate (10b): This compound showed spectroscopic and analytical data identical to those previously reported.^[32]

2-Acetylphenyl (E)-2-(3,4-Dimethoxyphenyl)acrylate (10c): Yield 1.96 g (70%); m.p. 97–99 °C. ^1H NMR: δ = 2.58 (s, 3 H, 2-CH₃), 3.94 (s, 6 H, 3'',4''-OCH₃), 6.55 (d, J = 16.0 Hz, 1 H, α -H), 6.90 (d, J = 8.3 Hz, 1 H, 5'-H), 7.13 (d, J = 1.9 Hz, 1 H, 2''-H), 7.18 (dd, J = 8.3, 1.9 Hz, 1 H, 6''-H), 7.19 (dd, J = 7.9, 1.2 Hz, 1 H, 3'-H), 7.35 (dt, J = 7.9, 1.2 Hz, 1 H, 5'-H), 7.57 (dt, J = 7.9, 1.7 Hz,

1 H, 4'-H), 7.85 (dd, J = 7.9, 1.7 Hz, 1 H, 6'-H), 7.85 (d, J = 16.0 Hz, 1 H, β -H) ppm. ^{13}C NMR: δ = 29.8 (2-CH₃), 55.9 and 56.0 (3'',4''-OCH₃), 109.6 (C-2''), 110.9 (C-5'), 114.2 (C- α), 123.3 (C-6''), 123.8 (C-3'), 126.0 (C-5'), 126.9 (C-1''), 130.1 (C-6'), 131.4 (C-1'), 133.3 (C-4'), 147.3 (C- β), 149.2 (C-2', C-3'), 151.6 (C-4''), 165.5 (C=O), 197.9 (C-1) ppm. ESI-MS: m/z (%) = 349 [M + Na]⁺ (100), 365 [M + K]⁺ (17), 675 [2M + Na]⁺ (86). C₁₉H₁₈O₅ (326.34): calcd. for C 69.93, H 5.56; found C 69.56, H 5.69.

2-Acetyl-5-methoxyphenyl (E)-2-(3,4-Dimethoxyphenyl)acrylate (10e): Yield 2.05 g (67%); m.p. 142–143 °C. ^1H NMR: δ = 2.53 (s, 3 H, 2-CH₃), 3.87 (s, 3 H, 4'-OCH₃), 3.94 (s, 6 H, 3'',4''-OCH₃), 6.56 (d, J = 15.9 Hz, 1 H, α -H), 6.68 (d, J = 2.5 Hz, 1 H, 3'-H), 6.85 (dd, J = 8.8, 2.5 Hz, 1 H, 5'-H), 6.90 (d, J = 8.3 Hz, 1 H, 5''-H), 7.13 (d, J = 1.9 Hz, 1 H, 2''-H), 7.18 (dd, J = 8.3, 1.9 Hz, 1 H, 6''-H), 7.85 (d, J = 15.9 Hz, 1 H, β -H), 7.88 (d, J = 8.8 Hz, 1 H, 6'-H) ppm. ^{13}C NMR: δ = 29.6 (2-CH₃), 55.7 (4'-OCH₃), 55.9 and 56.0 (3'',4''-OCH₃), 109.1 (C-3'), 109.7 (C-2''), 110.9 (C-5'), 111.8 (C-5'), 114.4 (C- α), 123.3 (C-6''), 123.6 (C-1'), 127.0 (C-1''), 132.3 (C-6'), 147.3 (C- β), 149.2 (C-3''), 151.50 and 151.54 (C-2', C-4''), 163.7 (C-4'), 165.4 (C=O), 195.9 (C-1) ppm. ESI-MS: m/z (%) = 379 [M + Na]⁺ (92), 395 [M + K]⁺ (15), 735 [2M + Na]⁺ (100), 751 [2M + K]⁺ (4), 1091 [3M + Na]⁺ (4). C₂₀H₂₀O₆ (356.37): calcd. for C 67.41, H 5.66; found C 67.32, H 5.94.

2-Acetyl-3-methoxyphenyl (E)-2-(3,4-Dimethoxyphenyl)acrylate (10g): Yield 1.96 g (64%); m.p. 86–88 °C. ^1H NMR: δ = 2.52 (s, 3 H, 2-CH₃), 3.88 (s, 3 H, 6'-OCH₃), 3.93 and 3.94 (2 $\times$ s, 6 H, 3'',4''-OCH₃), 6.45 (d, J = 15.8 Hz, 1 H, α -H), 6.81 (dd, J = 8.3, 0.7 Hz, 1 H, 3'-H), 6.85 (d, J = 8.4 Hz, 1 H, 5'-H), 6.89 (d, J = 8.3 Hz, 1 H, 5''-H), 7.10 (d, J = 2.0 Hz, 1 H, 2''-H), 7.15 (dd, J = 8.3, 2.0 Hz, 1 H, 6''-H), 7.38 (dd, J = 8.4, 8.3 Hz, 1 H, 4'-H), 7.78 (d, J = 15.8 Hz, 1 H, β -H) ppm. ^{13}C NMR: δ = 31.7 (2-CH₃), 55.9 and 56.0 (6',3'',4''-OCH₃), 108.6 (C-5'), 109.6 (C-2''), 110.9 (C-5''), 114.2 (C- α), 115.2 (C-3'), 123.3 (C-6''), 124.6 (C-1'), 127.0 (C-1''), 130.9 (C-4'), 147.1 (C- β), 147.7 (C-2'), 149.2 (C-3''), 151.5 (C-4''), 157.3 (C-6'), 165.3 (C=O), 200.9 (C-1) ppm. ESI-MS: m/z (%) = 357 [M + H]⁺ (15), 379 [M + Na]⁺ (53), 395 [M + K]⁺ (11), 753 [2M + Na]⁺ (31). C₂₀H₂₀O₆ (356.37): calcd. for C 67.41, H 5.66; found C 67.55, H 5.74.

2-Acetyl-3,5-dimethoxyphenyl (E)-2-(3,4-Dimethoxyphenyl)acrylate (10i): Yield 1.66 g (50%); m.p. 140–142 °C. ^1H NMR: δ = 2.49 (s, 3 H, 2-CH₃), 3.82 (s, 3 H, 4'-OCH₃), 3.85 (s, 3 H, 6'-OCH₃), 3.93 (s, 6 H, 3'',4''-OCH₃), 6.31 (d, J = 2.2 Hz, 1 H, 3'-H), 6.38 (d, J = 2.2 Hz, 1 H, 5'-H), 6.46 (d, J = 15.9 Hz, 1 H, α -H), 6.88 (d, J = 8.3 Hz, 1 H, 5''-H), 7.10 (d, J = 2.0 Hz, 1 H, 2''-H), 7.15 (dd, J = 8.3, 2.0 Hz, 1 H, 6''-H), 7.78 (d, J = 15.9 Hz, 1 H, β -H) ppm. ^{13}C NMR: δ = 31.8 (2-CH₃), 55.6 (4'-OCH₃), 55.8 (3'',4''-OCH₃), 55.9 (6'-OCH₃), 96.4 (C-5'), 100.0 (C-3'), 109.6 (C-2''), 110.9 (C-5''), 114.3 (C- α), 117.3 (C-1'), 123.2 (C-6''), 127.0 (C-1''), 147.0 (C- β), 149.1 (C-3''), 149.6 (C-2'), 151.4 (C-4''), 159.0 (C-6'), 162.1 (C-4'), 165.4 (C=O), 199.6 (C-1) ppm. ESI-MS: m/z (%) = 387 [M + H]⁺ (6), 409 [M + Na]⁺ (89), 425 [M + K]⁺ (12), 795 [2M + Na]⁺ (100), 811 [2M + K]⁺ (5). C₂₁H₂₂O₇ (386.40): calcd. for C 65.28, H 5.74; found C 65.60, H 5.71.

Synthesis of the 5-Aryl-3-hydroxy-1-(2-hydroxyphenyl)penta-2,4-dien-1-ones 11a–i: Potassium hydroxide (powder, 1.4 g, 25 mmol) was added to a solution of the appropriate 2-acetylphenyl cinnamate (**10a–i**, 5 mmol) in dimethyl sulfoxide (30 mL). The solution was stirred at room temperature for 2 h. After that period, the solution was poured into ice (50 g) and water (100 mL), and the pH was adjusted to 4 with dilute hydrochloric acid. The obtained solid was removed by filtration, dissolved in chloroform (80 mL) and washed with water (2 $\times$ 100 mL). The solvent was evaporated to

dryness in each case, and the residue was recrystallised from ethanol to give the expected 5-aryl-3-hydroxy-1-(2-hydroxyphenyl)-2,4-pentadien-1-one (**11a-i**) in good yield.

5-Aryl-3-hydroxy-1-(2-hydroxyphenyl)penta-2,4-dien-1-ones 11a and 11b: These compounds showed spectroscopic and analytical data identical to those previously reported.^[32]

3-Hydroxy-1-(2-hydroxyphenyl)-5-(3,4-dimethoxyphenyl)penta-2,4-dien-1-one (11c): Yield 1.19 g (73%); m.p. 136–138 °C. ¹H NMR: δ = 3.93 (s, 3 H, 4'-OCH₃), 3.95 (s, 3 H, 3''-OCH₃), 6.31 (s, 1 H, 2-H), 6.47 (brd, J = 15.8 Hz, 1 H, 4-H), 6.89 (ddd, J = 8.3, 8.1, 1.0 Hz, 1 H, 5'-H), 6.89 (d, J = 8.3 Hz, 1 H, 5''-H), 6.99 (dd, J = 7.7, 1.0 Hz, 1 H, 3'-H), 7.08 (d, J = 1.9 Hz, 1 H, 2''-H), 7.15 (dd, J = 8.3, 1.9 Hz, 1 H, 6''-H), 7.45 (ddd, J = 8.1, 7.7, 1.5 Hz, 1 H, 4'-H), 7.61 (d, J = 15.8 Hz, 1 H, 5-H), 7.70 (dd, J = 8.3, 1.5 Hz, 1 H, 6'-H), 12.28 (s, 1 H, 2'-OH), 14.74 (d, J = 0.8 Hz, 1 H, 3-OH) ppm. ¹³C NMR: δ = 55.9 (3''-OCH₃), 56.0 (4'-OCH₃), 96.5 (C-2), 109.5 (C-2''), 111.1 (C-5'), 118.7 (C-3'), 118.9 (C-5'), 119.1 (C-1'), 119.8 (C-4), 122.6 (C-6''), 127.9 (C-1'), 128.4 (C-6'), 135.6 (C-4'), 139.9 (C-5), 149.2 (C-3'), 151.1 (C-4'), 162.5 (C-2'), 175.0 (C-3), 195.6 (C-1) ppm. ESI-MS: m/z (%) = 327 [M + H]⁺ (35), 349 [M + Na]⁺ (25). C₁₉H₁₈O₅ (326.34): calcd. for C 69.93, H 5.56; found C 69.54, H 5.74%.

3-Hydroxy-1-(2-hydroxy-4-methoxyphenyl)-5-phenylpenta-2,4-dien-1-one (11d): Yield 1.20 g (81%); m.p. 125–127 °C. ¹H NMR: δ = 3.82 (s, 3 H, 4'-OCH₃), 6.18 (s, 1 H, 2-H), 6.43 (brs, 1 H, 3'-H), 6.45 (dd, J = 8.7, 2.5 Hz, 1 H, 5'-H), 6.56 (dd, J = 15.9, 0.9 Hz, 1 H, 4-H), 7.35–7.41 (m, 3 H, 3'', 4'', 5''-H), 7.52–7.55 (m, 2 H, 2'', 6''-H), 7.59 (d, J = 8.7 Hz, 1 H, 6'-H), 7.59 (d, J = 15.9 Hz, 1 H, 5-H), 12.70 (s, 1 H, 2'-OH), 14.51 (d, J = 0.9 Hz, 1 H, 3-OH) ppm. ¹³C NMR: δ = 55.5 (4'-OCH₃), 96.8 (C-2), 101.2 (C-3'), 107.9 (C-5'), 112.7 (C-1'), 122.3 (C-4), 127.9 (C-2'', 6''), 128.9 (C-3'', 5''), 129.8 (C-4''), 130.1 (C-6'), 135.1 (C-1''), 139.0 (C-5), 165.4 (C-4'), 165.8 (C-2'), 173.0 (C-3), 194.6 (C-1) ppm. ESI-MS: m/z (%) = 297 [M + H]⁺ (15), 319 [M + Na]⁺ (17). C₁₈H₁₆O₄ (296.32): calcd. for C 72.96, H 5.44; found C 72.74, H 5.47.

5-(3,4-Dimethoxyphenyl)-3-hydroxy-1-(2-hydroxy-4-methoxyphenyl)penta-2,4-dien-1-one (11e): Yield 1.21 g (68%); m.p. 149–151 °C. ¹H NMR: δ = 3.84 (s, 3 H, 4'-OCH₃), 3.93 (s, 3 H, 4''-OCH₃), 3.95 (s, 3 H, 3''-OCH₃), 6.18 (s, 1 H, 2-H), 6.44 (brs, 1 H, 3'-H), 6.45 (dd, J = 15.4, 1.0 Hz, 1 H, 4-H), 6.44–6.47 (m, 1 H, 5'-H), 6.89 (d, J = 8.3 Hz, 1 H, 5''-H), 7.07 (d, J = 1.9 Hz, 1 H, 2''-H), 7.14 (dd, J = 8.3, 1.9 Hz, 1 H, 6''-H), 7.56 (d, J = 15.4 Hz, 1 H, 5-H), 7.59–7.62 (m, 1 H, 6'-H), 12.74 (s, 1 H, 2'-OH), 14.59 (d, J = 1.0 Hz, 1 H, 3-OH) ppm. ¹³C NMR: δ = 55.5 (4'-OCH₃), 55.9 (3''-OCH₃), 56.0 (4''-OCH₃), 96.2 (C-2), 101.2 (C-3'), 107.8 (C-5'), 109.5 (C-2''), 111.1 (C-5'), 112.7 (C-1'), 120.1 (C-4), 122.4 (C-6''), 128.1 (C-1''), 130.0 (C-6'), 139.1 (C-5), 149.2 (C-3'), 150.8 (C-4''), 165.3 (C-2'), 165.7 (C-4'), 173.6 (C-3), 194.3 (C-1) ppm. ESI-MS: m/z (%) = 357 [M + H]⁺ (18), 379 [M + Na]⁺ (27), 735 [2M + Na]⁺ (7). C₂₀H₂₀O₆ (356.37): calcd. for C 67.41, H 5.66; found C 67.85, H 5.78.

3-Hydroxy-1-(2-hydroxy-6-methoxyphenyl)-5-phenylpenta-2,4-dien-1-one (11f): Yield 1.38 g (93%); m.p. 123–125 °C. ¹H NMR: δ = 3.93 (s, 3 H, 6'-OCH₃), 6.42 (dd, J = 8.2, 0.7 Hz, 1 H, 5'-H), 6.59 (dd, J = 15.8, 1.1 Hz, 1 H, 4-H), 6.60 (dd, J = 8.4, 0.7 Hz, 1 H, 3'-H), 6.80 (s, 1 H, 2-H), 7.32 (dd, J = 8.4, 8.2 Hz, 1 H, 4'-H), 7.36–7.42 (m, 3 H, 3'', 4'', 5''-H), 7.55–7.58 (m, 2 H, 2'', 6''-H), 7.63 (d, J = 15.8 Hz, 1 H, 5-H), 12.73 (s, 1 H, 2'-OH), 14.88 (d, J = 1.1 Hz, 1 H, 3-OH) ppm. ¹³C NMR: δ = 55.8 (6'-OCH₃), 101.7 (C-5'), 103.8 (C-2), 110.6 (C-1'), 111.1 (C-3'), 122.9 (C-4), 127.9 (C-2'', 6''), 128.9 (C-3'', 5''), 129.9 (C-4''), 135.1 (C-4'), 135.2 (C-1''), 139.2 (C-5), 160.3 (C-6'), 164.1 (C-2'), 174.3 (C-3), 195.2 (C-

1) ppm. ESI-MS: m/z (%) = 397 [M + H]⁺ (22), 319 [M + Na]⁺ (18). C₁₈H₁₆O₄ (296.32): calcd. for C 72.96, H 5.44; found C 72.86, H 5.44.

5-(3,4-Dimethoxyphenyl)-3-hydroxy-1-(2-hydroxy-6-methoxyphenyl)penta-2,4-dien-1-one (11g): Yield 1.16 g (65%); m.p. 123–125 °C. ¹H NMR: δ = 3.929, 3.932 and 3.95 (3 × s, 9 H, 6', 3'', 4''-OCH₃), 6.41 (d, J = 8.2 Hz, 1 H, 5'-H), 6.45 (brd, J = 15.0 Hz, 1 H, 4-H), 6.59 (dd, J = 8.3, 0.8 Hz, 1 H, 3'-H), 6.77 (s, 1 H, 2-H), 6.88 (d, J = 8.3 Hz, 1 H, 5''-H), 7.08 (d, J = 1.9 Hz, 1 H, 2''-H), 7.15 (dd, J = 8.3, 1.9 Hz, 1 H, 6''-H), 7.31 (dd, J = 8.3, 8.2 Hz, 1 H, 4'-H), 7.59 (d, J = 15.0 Hz, 1 H, 5-H), 12.76 (s, 1 H, 2'-OH), 15.01 (d, J = 1.0 Hz, 1 H 3-OH) ppm. ¹³C NMR: δ = 55.85, 55.91 and 56.0 (6', 3'', 4''-OCH₃), 101.6 (C-5'), 103.3 (C-2), 109.7 (C-2''), 110.6 (C-1'), 111.1 (C-3', C-5'), 120.6 (C-4), 122.4 (C-6''), 128.2 (C-1''), 134.9 (C-4'), 139.4 (C-5), 149.2 (C-3'), 150.9 (C-4''), 160.2 (C-6'), 164.0 (C-2'), 175.0 (C-3), 194.7 (C-1) ppm. ESI-MS: m/z (%) = 357 [M + H]⁺ (16), 379 [M + Na]⁺ (21). C₂₀H₂₀O₆ (356.37): calcd. for C 67.41, H 5.66; found C 67.29, H 5.71.

3-Hydroxy-1-(2-hydroxy-4,6-dimethoxyphenyl)-5-phenylpenta-2,4-dien-1-one (11h): Yield 1.30 g (80%); m.p. 127–128 °C. ¹H NMR: δ = 3.81 (s, 3 H, 4'-OCH₃), 3.89 (s, 3 H, 6'-OCH₃), 5.95 (d, J = 2.4 Hz, 1 H, 5'-H), 6.08 (d, J = 2.4 Hz, 1 H, 3'-H), 6.57 (dd, J = 15.9, 1.2 Hz, 1 H, 4-H), 6.75 (s, 1 H, 2-H), 7.34–7.42 (m, 3 H, 3'', 4'', 5''-H), 7.53–7.56 (m, 2 H, 2'', 6''-H), 7.57 (d, J = 15.9 Hz, 1 H, 5-H), 13.62 (s, 1 H, 2'-OH), 14.73 (d, J = 1.2 Hz, 1 H, 3-OH) ppm. ¹³C NMR: δ = 55.5 (4'-OCH₃), 55.6 (6'-OCH₃), 91.3 (C-5'), 94.0 (C-3'), 103.0 (C-2), 104.6 (C-1'), 123.2 (C-4), 127.8 (C-2'', 6''), 128.8 (C-3'', 5''), 129.6 (C-4''), 135.3 (C-1''), 138.3 (C-5), 161.8 (C-6'), 165.5 (C-4'), 167.2 (C-2'), 173.1 (C-3), 193.9 (C-1) ppm. ESI-MS: m/z (%) = 326 [M + H]⁺ (21), 349 [M + Na]⁺ (21), 675 [2M + Na]⁺ (6). C₁₉H₁₈O₅ (326.34): calcd. for C 69.93, H 5.56; found C 70.33, H 5.55.

5-(3,4-Dimethoxyphenyl)-3-hydroxy-1-(2-hydroxy-4,6-dimethoxyphenyl)penta-2,4-dien-1-one (11i): Yield 1.49 g (77%); m.p. 148–150 °C. ¹H NMR: δ = 3.929, 3.932 and 3.95 (3 × s, 9 H, 6', 3'', 4''-OCH₃), 6.41 (d, J = 8.2 Hz, 1 H, 5'-H), 6.45 (d, J = 15.0 Hz, 1 H, 4-H), 6.59 (dd, J = 8.2, 0.8 Hz, 1 H, 3'-H), 6.77 (s, 1 H, 2-H), 6.88 (d, J = 8.3 Hz, 1 H, 5''-H), 7.08 (d, J = 1.9 Hz, 1 H, 2''-H), 7.15 (dd, J = 8.3, 1.9 Hz, 1 H, 6''-H), 7.31 (t, J = 8.2 Hz, 1 H, 4'-H), 7.59 (d, J = 15.0 Hz, 1 H, 5-H), 12.76 (s, 1 H, 2'-OH), 15.01 (d, J = 1.0 Hz, 1 H, 3-OH) ppm. ¹³C NMR: δ = 55.5 (4'-OCH₃), 55.6, 55.8 and 55.9 (6', 3'', 4''-OCH₃), 91.3 (C-5'), 94.0 (C-3'), 102.5 (C-2), 104.6 (C-1'), 109.6 (C-2''), 111.0 (C-5'), 120.9 (C-4), 122.2 (C-6''), 128.3 (C-1''), 138.5 (C-5), 149.1 (C-3'), 150.6 (C-4''), 161.8 (C-6'), 165.4 (C-4'), 167.1 (C-2'), 173.7 (C-3), 193.6 (C-1) ppm. ESI-MS: m/z (%) = 387 [M + H]⁺ (29), 409 [M + Na]⁺ (38), 795 [2M + Na]⁺ (11). C₂₁H₂₂O₇ (386.40): calcd. for C 65.28, H 5.74; found C 65.56, H 5.83.

Synthesis of the 3-Bromo-2-styryl-4H-chromen-4-ones 3a and 3d-k: Phenyltrimethylammonium tribromide (PTT, 2.1 g, 5.5 mmol) was added to a THF (60 mL) solution of the appropriate 5-aryl-3-hydroxy-1-(2-hydroxyphenyl)penta-2,4-dien-1-one (**11a-i**, 5 mmol). The reaction mixture was stirred and allowed to stand at room temperature for 12 h. After that period, the solution was poured into ice (50 g) and water (80 mL) and stirred for 20 min, and the obtained yellow solid was removed by filtration. The residue was taken up in chloroform (50 mL) and washed with water (3 × 50 mL). The solvent was removed to dryness and the residue was purified by silica gel column chromatography with dichloromethane as eluent. The obtained residue was recrystallised from ethanol to give the 3-bromo-2-styryl-4H-chromen-4-one (**3a** or **3d-k**).

(E)-3-Bromo-2-[2-(4-methoxyphenyl)vinyl]-4H-chromen-4-one (3d): Yield 0.95 g (53%); m.p. 149–151 °C. ¹H NMR: δ = 3.86 (s, 3 H, 4'-OCH₃), 6.94 (d, J = 8.8 Hz, 2 H, 3',5'-H), 7.33 (d, J = 15.9 Hz, 1 H, α -H), 7.40 (ddd, J = 8.5, 8.4, 0.7 Hz, 1 H, 6-H), 7.52 (d, J = 8.0 Hz, 1 H, 8-H), 7.59 (d, J = 8.8 Hz, 2 H, 2',6'-H), 7.66 (d, J = 15.9 Hz, 1 H, β -H), 7.69 (ddd, J = 8.4, 8.0, 1.6 Hz, 1 H, 7-H), 8.22 (dd, J = 8.5, 1.6 Hz, 1 H, 5-H) ppm. ¹³C NMR: δ = 55.4 (4'-OCH₃), 108.9 (C-3), 114.5 (C-3',5'), 116.7 (C- α), 117.4 (C-8), 122.0 (C-10), 125.2 (C-6), 126.3 (C-5), 127.6 (C-1'), 129.8 (C-2',6'), 133.9 (C-7), 139.3 (C- β), 154.8 (C-9), 158.8 (C-2), 161.4 (C-4'), 172.7 (C-4) ppm. ESI-MS: m/z (%) = 357 [M + H]⁺ (⁷⁹Br, 65), 359 [M + H]⁺ (⁸¹Br, 66), 379 [M + Na]⁺ (⁷⁹Br, 29), 381 [M + Na]⁺ (⁸¹Br, 89), 735 [2M + Na]⁺ (⁷⁹Br, 19), 737 [2M + Na]⁺ (⁸¹Br, 40). C₁₈H₁₃BrO₃ (357.20): calcd. for C 60.52, H 3.67; found C 60.14, H 3.66.

(E)-3-Bromo-2-[2-(3,4-dimethoxyphenyl)vinyl]-4H-chromen-4-one (3e): This compound showed spectroscopic and analytical data identical to those previously reported.^[27]

(E)-3-Bromo-7-methoxy-2-(2-phenylvinyl)-4H-chromen-4-one (3f): Yield 1.73 g (97%); m.p. 174–176 °C. ¹H NMR: δ = 3.95 (s, 3 H, 7-OCH₃), 6.93 (d, J = 2.4 Hz, 1 H, 8-H), 6.97 (dd, J = 8.8, 2.4 Hz, 1 H, 6-H), 7.40–7.45 (m, 3 H, 3',4',5'-H), 7.46 (d, J = 16.0 Hz, 1 H, α -H), 7.63–7.66 (m, 2 H, 2',6'-H), 7.67 (d, J = 16.0 Hz, 1 H, β -H), 8.13 (d, J = 8.8 Hz, 1 H, 5-H) ppm. ¹³C NMR: δ = 55.9 (7-OCH₃), 99.7 (C-8), 109.9 (C-3), 114.7 (C-6), 115.9 (C-10), 119.3 (C- α), 127.7 (C-5), 128.0 (C-2',6'), 129.0 (C-3',5'), 130.2 (C-4'), 135.0 (C-1'), 138.9 (C- β), 156.6 (C-9), 157.9 (C-2), 164.4 (C-7), 172.1 (C-4) ppm. ESI-MS: m/z (%) = 357 [M + H]⁺ (⁷⁹Br, 97), 359 [M + H]⁺ (⁸¹Br, 96), 379 [M + Na]⁺ (⁷⁹Br, 39), 381 [M + Na]⁺ (⁸¹Br, 83), 395 [M + K]⁺ (⁷⁹Br, 10), 397 [M + K]⁺ (⁸¹Br, 13), 735 [2M + Na]⁺ (⁷⁹Br, 50), 737 [2M + Na]⁺ (⁸¹Br, 98). C₁₈H₁₃BrO₃ (357.20): calcd. for C 60.52, H 3.67; found C 60.43, H 4.12.

(E)-3-Bromo-2-[2-(3,4-dimethoxyphenyl)vinyl]-7-methoxy-4H-chromen-4-one (3g): Yield 1.25 g (60%); m.p. 195–197 °C. ¹H NMR: δ = 3.937 and 3.943 (2 $\times$ s, 6 H, 7,4'-OCH₃), 3.97 (s, 3 H, 3'-OCH₃), 6.90 (d, J = 2.3 Hz, 1 H, 8-H), 6.91 (d, J = 8.3 Hz, 1 H, 5'-H), 6.95 (dd, J = 8.8, 2.3 Hz, 1 H, 6-H), 7.12 (d, J = 1.9 Hz, 1 H, 2'-H), 7.21 (dd, J = 8.3, 1.9 Hz, 1 H, 6'-H), 7.28 (d, J = 15.9 Hz, 1 H, α -H), 7.60 (d, J = 15.9 Hz, 1 H, β -H), 8.11 (d, J = 8.8 Hz, 1 H, 5-H) ppm. ¹³C NMR: δ = 55.86, 55.92 and 56.0 (7,3',4'-OCH₃), 99.7 (C-8), 109.1 (C-3), 109.6 (C-2'), 111.1 (C-5'), 114.5 (C-6), 115.9 (C-10), 116.9 (C- α), 122.4 (C-6'), 127.7 (C-5), 128.0 (C-1'), 138.9 (C- β), 149.3 (C-3'), 151.1 (C-4'), 156.5 (C-9), 158.3 (C-2), 164.3 (C-7), 172.0 (C-4) ppm. ESI-MS: m/z (%) = 417 [M + H]⁺ (⁷⁹Br, 34), 419 [M + H]⁺ (⁸¹Br, 33), 439 [M + Na]⁺ (⁷⁹Br, 13), 441 [M + Na]⁺ (⁸¹Br, 13), 855 [2M + Na]⁺ (⁷⁹Br, 13), 857 [2M + Na]⁺ (⁸¹Br, 25). C₂₀H₁₇BrO₅ (417.25): calcd. for C 57.57, H 4.11; found C 57.76, H 4.18.

(E)-3-Bromo-5-methoxy-2-(2-phenylvinyl)-4H-chromen-4-one (3h): Yield 1.50 g (84%); m.p. 172–173 °C. ¹H NMR: δ = 3.97 (s, 3 H, 5-OCH₃), 6.82 (dd, J = 8.4, 0.9 Hz, 1 H, 6-H), 7.10 (dd, J = 8.4, 0.9 Hz, 1 H, 8-H), 7.42 (d, J = 16.0 Hz, 1 H, α -H), 7.40–7.45 (m, 3 H, 3',4',5'-H), 7.58 (t, J = 8.4 Hz, 1 H, 7-H), 7.63 (d, J = 16.0 Hz, 1 H, β -H), 7.62–7.64 (m, 2 H, 2',6'-H) ppm. ¹³C NMR: δ = 56.4 (5-OCH₃), 106.5 (C-6), 109.4 (C-8), 111.4 (C-3), 112.7 (C-10), 119.1 (C- α), 127.9 (C-2',6'), 129.0 (C-3',5'), 130.1 (C-4'), 134.1 (C-7), 134.9 (C-1'), 138.8 (C- β), 156.5 (C-9), 156.8 (C-2), 159.7 (C-5), 171.7 (C-4) ppm. ESI-MS: m/z (%) = 357 [M + H]⁺ (⁷⁹Br, 83), 359 [M + H]⁺ (⁸¹Br, 80), 379 [M + Na]⁺ (⁷⁹Br, 28), 381 [M + Na]⁺ (⁸¹Br, 28), 735 [2M + Na]⁺ (⁷⁹Br, 51), 737 [2M + Na]⁺ (⁸¹Br, 100), 1091 [3M + Na]⁺ (⁷⁹Br, 4), 1093 [3M + Na]⁺ (⁸¹Br, 11). C₁₈H₁₃BrO₃ (357.20): calcd. for C 60.52, H 3.67; found C 60.77, H 3.69.

(E)-3-Bromo-2-[2-(3,4-dimethoxyphenyl)vinyl]-5-methoxy-4H-chromen-4-one (3i): Yield 1.21 g (58%); m.p. 190–192 °C. ¹H NMR: δ = 3.94 (s, 3 H, 4'-OCH₃), 3.977 (s, 3 H, 3'-OCH₃), 3.982 (s, 3 H, 5-OCH₃), 6.82 (d, J = 8.2 Hz, 1 H, 6-H), 6.91 (d, J = 8.3 Hz, 1 H, 5'-H), 7.10 (d, J = 8.4 Hz, 1 H, 8-H), 7.13 (d, J = 1.7 Hz, 1 H, 2'-H), 7.22 (dd, J = 8.3, 1.7 Hz, 1 H, 6'-H), 7.27 (d, J = 15.8 Hz, 1 H, α -H), 7.576 (dd, J = 8.4, 8.2 Hz, 1 H, 7-H), 7.578 (d, J = 15.8 Hz, 1 H, β -H) ppm. ¹³C NMR: δ = 56.0 (4'-OCH₃), 56.3 and 56.5 (5,3'-OCH₃), 106.5 (C-6), 109.4 (C-8), 109.6 (C-2'), 110.6 (C-3), 111.1 (C-5'), 112.8 (C-10), 116.9 (C- α), 122.4 (C-6'), 128.1 (C-1'), 133.9 (C-7), 138.8 (C- β), 149.3 (C-3'), 151.0 (C-4'), 156.8 (C-9), 156.9 (C-2), 159.7 (C-5), 171.8 (C-4) ppm. ESI-MS: m/z (%) = 417 [M + H]⁺ (⁷⁹Br, 26), 419 [M + H]⁺ (⁸¹Br, 25), 439 [M + Na]⁺ (⁷⁹Br, 13), 441 [M + Na]⁺ (⁸¹Br, 13), 855 [2M + Na]⁺ (⁷⁹Br, 15), 857 [2M + Na]⁺ (⁸¹Br, 30). C₂₀H₁₇BrO₅ (417.25): calcd. for C 57.57, H 4.11; found C 57.27, H 4.21.

(E)-3-Bromo-5,7-dimethoxy-2-(2-phenylvinyl)-4H-chromen-4-one (3j): Yield 0.95 g (49%); m.p. 181–183 °C. ¹H NMR: δ = 3.928 and 3.931 (2 $\times$ s, 6 H, 5,7-OCH₃), 6.36 (d, J = 2.3 Hz, 1 H, 6-H), 6.53 (d, J = 2.3 Hz, 1 H, 8-H), 7.40 (d, J = 16.0 Hz, 1 H, α -H), 7.41–7.44 (m, 3 H, 3',4',5'-H), 7.59 (d, J = 16.0 Hz, 1 H, β -H), 7.61–7.64 (m, 2 H, 2',6'-H) ppm. ¹³C NMR: δ = 55.8 and 56.4 (5,7-OCH₃), 92.2 (C-8), 96.3 (C-6), 107.6 (C-10), 111.6 (C-3), 119.2 (C- α), 127.9 (C-2',6'), 129.0 (C-3',5'), 130.0 (C-4'), 135.1 (C-1'), 138.2 (C- β), 156.1 (C-2), 158.4 (C-9), 160.9 (C-5), 164.3 (C-7), 171.0 (C-4) ppm. ESI-MS: m/z (%) = 387 [M + H]⁺ (⁷⁹Br, 33), 389 [M + H]⁺ (⁸¹Br, 33), 409 [M + Na]⁺ (⁷⁹Br, 8), 411 [M + Na]⁺ (⁸¹Br, 8), 795 [2M + Na]⁺ (⁷⁹Br, 18), 797 [2M + Na]⁺ (⁸¹Br, 35). C₁₉H₁₅BrO₄ (387.22): calcd. for C 58.93, H 3.90; found C 58.77, H 4.07.

(E)-3-Bromo-2-[2-(3,4-dimethoxyphenyl)vinyl]-5,7-dimethoxy-4H-chromen-4-one (3k): Yield 0.67 g (30%); m.p. 208–210 °C. ¹H NMR: δ = 3.91 (s, 3 H, 5-OCH₃), 3.92 (s, 3 H, 7-OCH₃), 3.94 (s, 3 H, 4'-OCH₃), 3.96 (s, 3 H, 3'-OCH₃), 6.33 (d, J = 2.3 Hz, 1 H, 6-H), 6.50 (d, J = 2.3 Hz, 1 H, 8-H), 6.90 (d, J = 8.5 Hz, 1 H, 5'-H), 7.10 (d, J = 1.9 Hz, 1 H, 2'-H), 7.19 (dd, J = 8.5, 1.9 Hz, 1 H, 6'-H), 7.20 (d, J = 15.9 Hz, 1 H, α -H), 7.50 (d, J = 15.9 Hz, 1 H, β -H) ppm. ¹³C NMR: δ = 55.8 (7-OCH₃), 55.9 (3'-OCH₃), 56.0 (4'-OCH₃), 56.3 (5-OCH₃), 92.1 (C-8), 96.2 (C-6), 107.5 (C-10), 109.6 (C-2'), 110.8 (C-3), 111.1 (C-5'), 116.9 (C- α), 122.2 (C-6'), 128.1 (C-1'), 138.1 (C- β), 149.2 (C-3'), 150.9 (C-4'), 156.4 (C-2), 158.4 (C-9), 160.8 (C-5), 164.2 (C-7), 170.9 (C-4) ppm. ESI-MS: m/z (%) = 447 [M + H]⁺ (⁷⁹Br, 46), 449 [M + H]⁺ (⁸¹Br, 21), 469 [M + Na]⁺ (⁷⁹Br, 16), 471 [M + Na]⁺ (⁸¹Br, 16), 915 [2M + Na]⁺ (⁷⁹Br, 19), 917 [2M + Na]⁺ (⁸¹Br, 38). C₂₁H₁₉BrO₆ (447.28): calcd. for C 56.39, H 4.28; found C 56.27, H 4.36.

Synthesis of the Methoxylated 2,3-Diaryl-9H-xanthen-9-ones 5g–s:

The appropriate styrene (**4a–c**, 1.6 mmol for styrene **4a** and 0.8 mmol for styrenes **4b** and **4c**) was added to a mixture of the appropriate 3-bromo-2-styryl-4H-chromen-4-one (**3d–k**, 0.4 mmol), triphenylphosphane (10.5 mg, 0.04 mmol), tetrakis(triphenylphosphane)palladium(0) (23.1 mg, 0.02 mmol) and triethylamine (55.8 μ L, 0.4 mmol) in *N*-methyl-2-pyrrolidin-1-one (6 mL). The mixture was stirred under different time and temperature conditions according to the substitution of the compounds (Table 3). The mixture was then poured into water (20 mL) and ice (10 g) and extracted with diethyl ether (4 $\times$ 25 mL) and dried with anhydrous sodium sulfate. The solvent was removed to dryness and the residue was taken up in dichloromethane (5 mL) and purified by thin layer chromatography (eluent: dichloromethane/light petroleum 7:3). The major spot with higher *R_f* value corresponds to the methoxylated 2,3-diaryl-9H-xanthen-9-one (**5g–s**) and the minor spot with lower *R_f* corresponds to the 2,3-diaryl-3,4-dihydro-9H-

xanthen-9-one (**6g-s**). In the cases of the (*E*)-3-bromo-5-methoxy-2-styryl-4*H*-chromen-4-ones **5n-s**, it was also possible to isolate the 6,7-diaryl-1-hydroxy-9*H*-xanthen-9-ones **12n-s**. The obtained methoxylated 2,3-diaryl-9*H*-xanthen-9-ones were recrystallised from ethanol and obtained in moderate to good yields (Table 3).

3-(4-Methoxyphenyl)-2-phenyl-9*H*-xanthen-9-one (5g): M.p. 150–153 °C. ¹H NMR: δ = 3.80 (s, 3 H, 4'-OCH₃), 6.80 (d, *J* = 8.8 Hz, 2 H, 3'',5''-H), 7.13 (d, *J* = 8.8 Hz, 2 H, 2'',6''-H), 7.17–7.20 (m, 2 H, 2',6'-H), 7.23–7.27 (m, 3 H, 3',4',5'-H), 7.39 (ddd, *J* = 7.7, 7.6, 0.9 Hz, 1 H, 7-H), 7.51 (d, *J* = 8.5 Hz, 1 H, 5-H), 7.53 (s, 1 H, 4-H), 7.73 (ddd, *J* = 8.5, 7.6, 1.7 Hz, 1 H, 6-H), 8.34 (s, 1 H, 1-H), 8.37 (dd, *J* = 7.7, 1.7 Hz, 1 H, 8-H) ppm. ¹³C NMR: δ = 55.2 (4'-OCH₃), 113.6 (C-3'',5''), 118.0 (C-5), 119.2 (C-4), 120.4 (C-9a), 122.0 (C-8a), 123.9 (C-7), 126.7 (C-8), 126.8 (C-4'), 128.1 (C-3',5'), 128.4 (C-1), 129.9 (C-2',6'), 130.8 (C-2'',6''), 132.1 (C-1'), 134.7 (C-6), 137.0 (C-2), 140.1 (C-1'), 147.3 (C-3), 155.3 (C-4a), 156.3 (C-4b), 159.1 (C-4''), 177.0 (C-9) ppm. EI-MS: *m/z* (%) = 378 [M]⁺ (100), 377 (23), 363 (10), 347 (23), 335 (11), 334 (13), 305 (10), 276 (6). C₂₆H₁₈O₃ (378.42): calcd. for C 82.52, H 4.79; found C 82.24, H 5.03.

3-(4-Methoxyphenyl)-2-phenyl-3,4-dihydro-9*H*-xanthen-9-one (6g): Yellowish oil. ¹H NMR: δ = 2.96 (dd, *J* = 17.3, 1.3 Hz, 1 H, 4_{trans}-H), 3.61 (dd, *J* = 17.3, 8.8 Hz, 1 H, 4_{cis}-H), 3.70 (s, 3 H, 4'-OCH₃), 4.25 (dd, *J* = 8.8, 1.3 Hz, 1 H, 3-H), 6.76 (d, *J* = 8.7 Hz, 2 H, 3'',5''-H), 7.21 (d, *J* = 8.7 Hz, 2 H, 2'',6''-H), 7.23–7.29 (m, 3 H, 3',4',5'-H), 7.33 (d, *J* = 8.5 Hz, 1 H, 5-H), 7.36 (ddd, *J* = 8.2, 7.9, 1.0 Hz, 1 H, 7-H), 7.46–7.49 (m, 2 H, 2'',6''-H), 7.54 (s, 1 H, 1-H), 7.58 (ddd, *J* = 8.5, 8.2, 1.6 Hz, 1 H, 6-H), 8.27 (dd, *J* = 7.9, 1.6 Hz, 1 H, 8-H) ppm. ¹³C NMR: δ = 36.8 (C-4), 40.8 (C-3), 55.1 (4'-OCH₃), 114.2 (C-3'',5''), 116.4 (C-1), 116.8 (C-9a), 118.0 (C-5), 123.8 (C-8a), 125.0 (C-7), 125.6 (C-2',6'), 126.1 (C-8), 127.5 (C-4'), 128.3 (C-2'',6''), 128.4 (C-3',5'), 132.5 (C-1'), 133.0 (C-6), 135.6 (C-2), 139.0 (C-1'), 155.8 (C-4b), 158.6 (C-4''), 162.6 (C-4a), 174.2 (C-9) ppm. EI-MS: *m/z* (%) = 380 [M]⁺ (14), 379 (29), 378 (100), 377 (30), 363 (16), 347 (24), 335 (13), 334 (14), 333 (11), 305 (11), 276 (8), 215 (6), 135 (7), 105 (5). HRMS (EI): calcd. for C₂₆H₁₈O₃ [M]⁺ 378.1256; found 378.1244.

2,3-Bis(4-methoxyphenyl)-9*H*-xanthen-9-one (5h): M.p. 164–166 °C. ¹H NMR: δ = 3.807 and 3.813 (s, 6 H, 4',4''-OCH₃), 6.80 (d, *J* = 8.8 Hz, 2 H, 3',5'-H), 6.82 (d, *J* = 8.8 Hz, 2 H, 3'',5''-H), 7.11 (d, *J* = 8.8 Hz, 2 H, 2',6'-H), 7.14 (d, *J* = 8.8 Hz, 2 H, 2'',6''-H), 7.40 (ddd, *J* = 7.8, 7.6, 1.0 Hz, 1 H, 7-H), 7.52 (d, *J* = 7.8 Hz, 1 H, 5-H), 7.52 (s, 1 H, 4-H), 7.74 (ddd, *J* = 7.8, 7.6, 1.7 Hz, 1 H, 6-H), 8.32 (s, 1 H, 1-H), 8.37 (dd, *J* = 7.8, 1.7 Hz, 1 H, 8-H) ppm. ¹³C NMR: δ = 55.19 and 55.21 (4',4''-OCH₃), 113.5 and 113.6 (C-3',5', C-3'',5''), 118.0 (C-5), 119.2 (C-4), 120.4 (C-9a), 122.0 (C-8a), 123.9 (C-7), 126.8 (C-8), 128.1 (C-1), 130.8 and 131.0 (C-2',6', C-2'',6''), 132.35 and 132.43 (C-1', C-1''), 134.7 (C-6), 136.6 (C-2), 147.3 (C-3), 155.1 (C-4a), 156.3 (C-4b), 158.5 (C-4'), 159.1 (C-4''), 177.0 (C-9) ppm. EI-MS: *m/z* (%) = 408 [M]⁺ (100), 407 (8), 393 (14), 377 (19), 365 (8), 350 (12), 334 (6), 333 (6), 321 (10). C₂₇H₂₀O₄ (408.45): calcd. for C 79.40, H 4.94; found C 79.12, H 5.03.

2,3-Bis(4-methoxyphenyl)-3,4-dihydro-9*H*-xanthen-9-one (6h): Yellowish oil. ¹H NMR: δ = 2.96 (dd, *J* = 17.3, 1.5 Hz, 1 H, 4_{trans}-H), 3.62 (dd, *J* = 17.3, 8.3 Hz, 1 H, 4_{cis}-H), 3.72 (s, 3 H, 4'-OCH₃), 3.79 (s, 3 H, 4''-OCH₃), 4.24 (brd, *J* = 8.3 Hz, 1 H, 3-H), 6.77 (d, *J* = 8.7 Hz, 2 H, 3'',5''-H), 6.83 (d, *J* = 8.9 Hz, 2 H, 3',5'-H), 7.21 (d, *J* = 8.7 Hz, 2 H, 2'',6''-H), 7.36 (d, *J* = 8.1 Hz, 1 H, 5-H), 7.39 (ddd, *J* = 7.8, 7.7, 1.1 Hz, 1 H, 7-H), 7.44 (s, 1 H, 1-H), 7.44 (d, *J* = 8.9 Hz, 2 H, 2',6'-H), 7.60 (ddd, *J* = 8.1, 7.7, 1.7 Hz, 1 H, 6-H), 8.29 (dd, *J* = 7.8, 1.7 Hz, 1 H, 8-H) ppm. ¹³C NMR: δ = 36.8 (C-

4), 40.9 (C-3), 55.1 (4''-OCH₃), 55.3 (4'-OCH₃), 113.8 (C-3',5'), 114.2 (C-3'',5''), 114.6 (C-1), 117.0 (C-9a), 118.0 (C-5), 123.9 (C-8a), 125.0 (C-7), 126.2 (C-8), 126.9 (C-2',6'), 128.4 (C-2'',6''), 131.6 (C-1'), 132.7 (C-1''), 132.9 (C-6), 135.3 (C-2), 155.9 (C-4b), 158.6 (C-4''), 159.1 (C-4'), 162.1 (C-4a), 174.2 (C-9) ppm. EI-MS: *m/z* (%) = 410 [M]⁺ (21), 409 (24), 408 (100), 393 (11), 377 (13), 365 (6), 350 (8), 321 (6), 303 (11), 121 (6). HRMS (EI): calcd. for C₂₇H₂₂O₄ [M]⁺ 410.1518; found 410.1526.

2-(3,4-Dimethoxyphenyl)-3-(4-methoxyphenyl)-9*H*-xanthen-9-one (5i): M.p. 155–156 °C. ¹H NMR: δ = 3.63 (s, 3 H, 4'-OCH₃), 3.81 (s, 3 H, 4''-OCH₃), 3.89 (s, 3 H, 3'-OCH₃), 6.60 (d, *J* = 1.7 Hz, 1 H, 2'-H), 6.83 (d, *J* = 8.6 Hz, 2 H, 3'',5''-H), 6.79–6.85 (m, 2 H, 5',6'-H), 7.15 (d, *J* = 8.6 Hz, 2 H, 2'',6''-H), 7.41 (ddd, *J* = 8.0, 7.7, 1.1 Hz, 1 H, 7-H), 7.52 (d, *J* = 8.0 Hz, 1 H, 5-H), 7.53 (s, 1 H, 4-H), 7.75 (ddd, *J* = 8.0, 7.7, 1.7 Hz, 1 H, 6-H), 8.36 (s, 1 H, 1-H), 8.38 (dd, *J* = 8.0, 1.7 Hz, 1 H, 8-H) ppm. ¹³C NMR: δ = 55.3 (4'-OCH₃), 55.6 (4''-OCH₃), 55.8 (3'-OCH₃), 110.8 (C-5'), 113.3 (C-2'), 113.6 (C-3'',5''), 118.0 (C-5), 119.2 (C-4), 120.4 (C-9a), 121.9 (C-8a), 122.2 (C-6'), 123.9 (C-7), 126.8 (C-8), 127.9 (C-1), 130.7 (C-2'',6''), 132.4 (C-1'), 132.6 (C-1''), 134.7 (C-6), 136.7 (C-2), 147.3 (C-3), 147.9 and 148.2 (C-3', C-4'), 155.1 (C-4a), 156.3 (C-4b), 159.1 (C-4''), 177.0 (C-9) ppm. EI-MS: *m/z* (%) = 438 [M]⁺ (100), 423 (8), 407 (9). C₂₈H₂₂O₅ (438.47): calcd. for C 76.70, H 5.06; found C 76.47, H 4.93.

2-(3,4-Dimethoxyphenyl)-3-(4-methoxyphenyl)-3,4-dihydro-9*H*-xanthen-9-one (6i): Yellowish oil. ¹H NMR: δ = 2.96 (dd, *J* = 17.3, 1.6 Hz, 1 H, 4_{trans}-H), 3.62 (dd, *J* = 17.3, 8.8 Hz, 1 H, 4_{cis}-H), 3.71 (s, 3 H, 4'-OCH₃), 3.84 and 3.86 (2 × s, 6 H, 3',4'-OCH₃), 4.24 (brd, *J* = 8.8 Hz, 1 H, 3-H), 6.75 (d, *J* = 8.5 Hz, 1 H, 5'-H), 6.77 (d, *J* = 8.7 Hz, 2 H, 3'',5''-H), 6.97 (dd, *J* = 8.5, 2.2 Hz, 1 H, 6'-H), 7.10 (d, *J* = 2.2 Hz, 1 H, 2'-H), 7.21 (d, *J* = 8.7 Hz, 2 H, 2'',6''-H), 7.35 (dd, *J* = 8.3, 1.0 Hz, 1 H, 5-H), 7.38 (ddd, *J* = 7.8, 7.7, 1.0 Hz, 1 H, 7-H), 7.44 (s, 1 H, 1-H), 7.59 (ddd, *J* = 8.3, 7.7, 1.7 Hz, 1 H, 6-H), 8.29 (dd, *J* = 7.8, 1.7 Hz, 1 H, 8-H) ppm. ¹³C NMR: δ = 36.7 (C-4), 41.1 (C-3), 55.1 (4'-OCH₃), 55.81 and 55.82 (3',4'-OCH₃), 108.7 (C-2'), 110.8 (C-5'), 114.2 (C-3'',5''), 114.8 (C-1), 116.9 (C-9a), 118.0 (C-5), 118.2 (C-6'), 123.8 (C-8a), 125.0 (C-7), 126.1 (C-8), 128.3 (C-2'',6''), 132.0 (C-1'), 132.8 (C-1''), 132.9 (C-6), 135.5 (C-2), 148.7 and 148.8 (C-3', C-4'), 155.8 (C-4b), 158.6 (C-4''), 162.2 (C-4a), 174.2 (C-9) ppm. EI-MS: *m/z* (%) = 440 [M]⁺ (100), 439 (29), 438 (53), 423 (11), 391 (8), 333 (10), 303 (13), 165 (47), 151 (14), 121 (8), 86 (8), 84 (13). HRMS (EI): calcd. for C₂₈H₂₄O₅ [M]⁺ 440.1624; found 440.1623.

3-(3,4-Dimethoxyphenyl)-2-phenyl-9*H*-xanthen-9-one (5j): M.p. 212–214 °C. ¹H NMR: δ = 3.52 (s, 3 H, 3''-OCH₃), 3.89 (s, 3 H, 4''-OCH₃), 6.56 (d, *J* = 2.0 Hz, 1 H, 2''-H), 6.83 (d, *J* = 8.3 Hz, 1 H, 5''-H), 6.92 (dd, *J* = 8.3, 2.0 Hz, 1 H, 6''-H), 7.18–7.21 (m, 2 H, 2',6'-H), 7.24–7.28 (m, 3 H, 3',4',5'-H), 7.40 (ddd, *J* = 7.8, 7.6, 1.0 Hz, 1 H, 7-H), 7.52 (d, *J* = 8.0 Hz, 1 H, 5-H), 7.58 (s, 1 H, 4-H), 7.74 (ddd, *J* = 8.0, 7.6, 1.7 Hz, 1 H, 6-H), 8.35 (s, 1 H, 1-H), 8.37 (dd, *J* = 7.8, 1.7 Hz, 1 H, 8-H) ppm. ¹³C NMR: δ = 55.5 (3''-OCH₃), 55.8 (4''-OCH₃), 110.7 (C-5''), 113.3 (C-2''), 117.9 (C-5), 119.0 (C-4), 120.4 (C-9a), 121.89 (C-6''), 121.93 (C-8a), 123.9 (C-7), 126.7 (C-8), 126.8 (C-4'), 128.1 (C-3',5'), 128.3 (C-1), 129.8 (C-2',6'), 132.2 (C-1''), 134.7 (C-6), 137.0 (C-2), 140.2 (C-1'), 147.2 (C-3), 148.1 and 148.6 (C-3'', C-4''), 155.3 (C-4a), 156.2 (C-4b), 176.9 (C-9) ppm. EI-MS: *m/z* (%) = 408 [M]⁺ (100), 393 (15), 377 814, 361 (13), 350 (10), 333 (15), 321 (10), 305 (8), 292 (6). C₂₇H₂₀O₄ (408.45): calcd. for C 79.40, H 4.94; found C 79.07, H 4.91.

3-(3,4-Dimethoxyphenyl)-2-phenyl-3,4-dihydro-9*H*-xanthen-9-one (6j): Yellowish oil. ¹H NMR: δ = 2.99 (dd, *J* = 17.3, 1.5 Hz, 1 H,

4-*trans*-H), 3.63 (dd, $J = 17.3$, 8.9 Hz, 1 H, 4-*cis*-H), 3.77 (s, 3 H, 3'-*OCH*₃), 3.79 (s, 3 H, 4'-*OCH*₃), 4.25 (dd, $J = 8.9$, 1.5 Hz, 1 H, 3-H), 6.71 (d, $J = 8.2$ Hz, 1 H, 5'-H), 6.82 (d, $J = 2.0$ Hz, 1 H, 2'-H), 6.85 (dd, $J = 8.2$, 2.0 Hz, 1 H, 6'-H), 7.22–7.32 (m, 3 H, 3',4',5'-H), 7.36 (d, $J = 8.0$ Hz, 1 H, 5-H), 7.38 (ddd, $J = 7.8$, 7.7, 1.3 Hz, 1 H, 7-H), 7.47–7.50 (m, 2 H, 2',6'-H), 7.54 (s, 1 H, 1-H), 7.60 (ddd, $J = 8.0$, 7.7, 1.6 Hz, 1 H, 6-H), 8.28 (dd, $J = 7.8$, 1.6 Hz, 1 H, 8-H) ppm. ¹³C NMR: $\delta = 37.0$ (C-4), 41.3 (C-3), 55.7 and 55.8 (3',4'-*OCH*₃), 110.3 (C-2'), 111.4 (C-5'), 116.6 (C-1), 116.7 (C-9a), 118.0 (C-5), 119.2 (C-6'), 123.8 (C-8a), 125.0 (C-7), 125.6 (C-2',6'), 126.1 (C-8), 127.5 (C-4'), 128.4 (C-3',5'), 132.99 and 133.01 (C-6, C-1'), 135.6 (C-2), 139.1 (C-1'), 148.0 (C-4'), 149.1 (C-3'), 155.8 (C-4b), 162.6 (C-4a), 174.1 (C-9) ppm. EI-MS: m/z (%) = 410 [M]⁺ (100), 409 (53), 408 (73), 395 (18), 393 (19), 379 (10), 377 (12), 361 (18), 334 (16), 333 (46), 321 (11), 299 (31), 273 (27), 215 (10), 202 (8), 165 (12), 151 (11), 105 (14), 86 (17), 84 (26). HRMS (EI): calcd. for C₂₇H₂₂O₄ [M]⁺ 410.1518; found 410.1515.

3-(3,4-Dimethoxyphenyl)-2-(4-methoxyphenyl)-9H-xanthen-9-one (5k) and 3-(3,4-Dimethoxyphenyl)-2-(4-methoxyphenyl)-3,4-dihydro-9H-xanthen-9-one (6k): These compounds showed spectroscopic and analytical data identical to those previously reported.^[27]

2,3-Bis(3,4-dimethoxyphenyl)-9H-xanthen-9-one (5l): M.p. 171–173 °C. ¹H NMR: $\delta = 3.63$ and 3.66 (2 × s, 6 H, 4',4''-*OCH*₃), 3.88 and 3.89 (2 × s, 6 H, 3',3''-*OCH*₃), 6.63 (brs, 2 H, 2'-H, 2''-H), 6.80–6.89 (m, 4 H, 5'-H, 6'-H, 5''-H, 6''-H), 7.41 (dd, $J = 8.2$, 7.7 Hz, 1 H, 7-H), 7.52 (d, $J = 8.1$ Hz, 1 H, 5-H), 7.56 (s, 1 H, 4-H), 7.75 (ddd, $J = 8.1$, 7.7, 1.6 Hz, 1 H, 6-H), 8.36 (s, 1 H, 1-H), 8.38 (dd, $J = 8.2$, 1.6 Hz, 1 H, 8-H) ppm. ¹³C NMR: $\delta = 55.69$ and 55.71 (4',4''-*OCH*₃), 55.8 (3',3''-*OCH*₃), 110.8 (C-5', C-5''), 113.0 (C-2'), 113.2 (C-2''), 118.0 (C-5), 119.1 (C-4), 120.4 (C-9a), 121.9 (C-6', C-6''), 122.2 (C-8a), 123.9 (C-7), 126.7 (C-8), 128.0 (C-1), 132.5 and 132.7 (C-1', C-1''), 134.8 (C-6), 136.7 (C-2), 147.3 (C-3), 148.0, 148.3 and 148.6 (C-3', C-4', C-3'' and C-4''), 155.1 (C-4a), 156.3 (C-4b), 177.0 (C-9) ppm. EI-MS: m/z (%) = 468 [M]⁺ (100), 453 (10), 379 (5), 97 (6). C₂₉H₂₄O₆ (468.50): calcd. for C 74.35, H 5.16; found C 74.25, H 5.22.

2,3-Bis(3,4-dimethoxyphenyl)-3,4-dihydro-9H-xanthen-9-one (6l): Yellowish oil. ¹H NMR: $\delta = 2.98$ (dd, $J = 17.3$, 1.5 Hz, 1 H, 4-*trans*-H), 3.63 (dd, $J = 17.3$, 8.3 Hz, 1 H, 4-*cis*-H), 3.77 and 3.79 (2 × s, 6 H, 4',4''-*OCH*₃), 3.85 and 3.86 (2 × s, 6 H, 3',3''-*OCH*₃), 4.23 (br d, $J = 8.3$ Hz, 1 H, 3-H), 6.72 (d, $J = 8.0$ Hz, 1 H, 5'-H), 6.76 (d, $J = 8.4$ Hz, 1 H, 5'-H), 6.83 (d, $J = 2.0$ Hz, 1 H, 2'-H), 6.85 (dd, $J = 8.0$, 2.0 Hz, 1 H, 6'-H), 6.98 (dd, $J = 8.4$, 2.1 Hz, 1 H, 6'-H), 7.11 (d, $J = 2.1$ Hz, 1 H, 2'-H), 7.36 (dd, $J = 8.5$, 1.0 Hz, 1 H, 5-H), 7.38 (dt, $J = 7.7$, 1.0 Hz, 1 H, 7-H), 7.45 (s, 1 H, 1-H), 7.60 (ddd, $J = 8.5$, 7.7, 1.7 Hz, 1 H, 6-H), 8.28 (dd, $J = 7.7$, 1.7 Hz, 1 H, 8-H) ppm. ¹³C NMR: $\delta = 36.7$ (C-4), 41.5 (C-3), 55.7, 55.77 and 55.80 (3',4',3'',4''-*OCH*₃), 108.7 (C-2'), 110.2 (C-2''), 110.8 (C-5'), 111.4 (C-5''), 114.9 (C-1), 116.8 (C-9a), 117.9 (C-5), 118.2 (C-6'), 119.1 (C-6''), 123.7 (C-8a), 125.0 (C-7), 126.1 (C-8), 132.0 (C-1'), 133.0 (C-6), 133.2 (C-1''), 135.4 (C-2), 148.0, 148.7 and 149.1 (C-3', C-4', C-3'' and C-4''), 155.8 (C-4b), 162.3 (C-4a), 174.1 (C-9) ppm. EI-MS: m/z (%) = 470 [M]⁺ (78), 469 (28), 468 (100), 455 (7), 453 (10), 421 (7), 333 (16), 332 (7), 84 (7). HRMS (EI): calcd. for C₂₉H₂₆O₆ [M]⁺ 470.1729; found 470.1739.

6-Methoxy-2,3-diphenyl-9H-xanthen-9-one (5m): M.p. 151–153 °C. ¹H NMR: $\delta = 3.95$ (s, 3 H, 6-*OCH*₃), 6.91 (d, $J = 2.4$ Hz, 1 H, 5-H), 6.96 (dd, $J = 8.9$, 2.4 Hz, 1 H, 7-H), 7.15–7.28 (m, 10 H, 2,3-*C*₆H₅), 7.52 (s, 1 H, 4-H), 8.28 (d, $J = 8.9$ Hz, 1 H, 8-H), 8.36 (s, 1 H, 1-H) ppm. ¹³C NMR: $\delta = 55.8$ (6-*OCH*₃), 100.2 (C-5), 113.3 (C-7), 115.9 (C-8a), 119.3 (C-4), 120.8 (C-9a), 126.8 (C-4'), 127.5 (C-4''), 128.0 (C-3',5'), 128.1 (C-3'',5''), 128.3 (C-1, C-8), 129.6

(C-2',6'), 129.9 (C-2',6'), 137.0 (C-2), 139.88 and 139.94 (C-1', C-1''), 147.0 (C-3), 155.2 (C-4a), 158.2 (C-4b), 165.0 (C-6), 176.0 (C-9) ppm. EI-MS: m/z (%) = 378 [M]⁺ (100), 377 (63), 363 (13), 335 (7), 334 (16), 277 (5), 276 (7), 228 (5), 226 (5). C₂₆H₁₈O₃ (378.42): calcd. for C 82.52, H 4.79; found C 82.56, H 4.92.

6-Methoxy-2,3-diphenyl-3,4-dihydro-9H-xanthen-9-one (6m): Yellowish oil. ¹H NMR: $\delta = 2.96$ (dd, $J = 17.3$, 1.5 Hz, 1 H, 4-*trans*-H), 3.64 (dd, $J = 17.3$, 9.0 Hz, 1 H, 4-*cis*-H), 3.85 (s, 3 H, 6-*OCH*₃), 4.28 (dd, $J = 9.0$, 1.5 Hz, 1 H, 3-H), 6.74 (d, $J = 2.4$ Hz, 1 H, 5-H), 6.95 (dd, $J = 8.9$, 2.4 Hz, 1 H, 7-H), 7.18–7.32 (m, 8 H, 3',4',5'-H, 3-*C*₆H₅), 7.45–7.48 (m, 2 H, 2',6'-H), 7.54 (s, 1 H, 1-H), 8.18 (d, $J = 8.9$ Hz, 1 H, 8-H) ppm. ¹³C NMR: $\delta = 36.6$ (C-4), 41.7 (C-3), 55.7 (6-*OCH*₃), 100.4 (C-5), 114.2 (C-7), 116.6 (C-9a), 116.9 (C-1), 117.7 (C-8a), 125.6 (C-2',6'), 127.1 (C-4'), 127.3 (C-2'',6''), 127.46 and 127.49 (C-8, C-4''), 128.4 (C-3',5'), 128.9 (C-3'',5''), 135.0 (C-2), 139.1 (C-1'), 140.8 (C-1''), 157.5 (C-4b), 161.8 (C-4a), 163.5 (C-6), 173.8 (C-9) ppm. EI-MS: m/z (%) = 380 [M]⁺ (8), 379 (20), 378 (100), 377 (51), 363 (11), 334 (11), 303 (8). HRMS (EI): calcd. for C₂₆H₂₀O₃ [M]⁺ 380.1412; found 380.1444.

1-Methoxy-6,7-diphenyl-9H-xanthen-9-one (5n): M.p. 203–205 °C. ¹H NMR: $\delta = 4.04$ (s, 3 H, 8-*OCH*₃), 6.82 (dd, $J = 8.4$, 0.7 Hz, 1 H, 7-H), 7.07 (dd, $J = 8.4$, 0.7 Hz, 1 H, 5-H), 7.14–7.27 (m, 10 H, 2,3-*C*₆H₅), 7.47 (s, 1 H, 4-H), 7.61 (t, $J = 8.4$ Hz, 1 H, 6-H), 8.33 (s, 1 H, 1-H) ppm. ¹³C NMR: $\delta = 56.4$ (8-*OCH*₃), 105.4 (C-7), 110.0 (C-5), 112.6 (C-8a), 118.9 (C-4), 121.8 (C-9a), 126.7 (C-4'), 127.4 (C-4''), 127.9 (C-3',5'), 128.0 (C-3'',5''), 128.4 (C-1), 129.6 (C-2',6'), 129.9 (C-2',6'), 134.8 (C-6), 136.8 (C-2), 139.9 (C-1', C-1''), 146.9 (C-3), 154.1 (C-4a), 158.2 (C-4b), 160.7 (C-8), 176.3 (C-9) ppm. EI-MS: m/z (%) = 378 [M]⁺ (100), 377 (23), 361 (10), 360 (8), 350 (9), 349 (60), 347 (10), 333 (13), 332 (42), 301 (6), 289 (8), 276 (6). C₂₆H₁₈O₃ (378.42): calcd. for C 82.52, H 4.79; found C 82.27, H 4.73.

1-Methoxy-6,7-diphenyl-7,8-dihydro-9H-xanthen-9-one (6n): M.p. 169–172 °C. ¹H NMR: $\delta = 2.91$ (dd, $J = 17.3$, 1.5 Hz, 1 H, 4-*trans*-H), 3.59 (dd, $J = 17.3$, 9.1 Hz, 1 H, 4-*cis*-H), 3.98 (s, 3 H, 8-*OCH*₃), 4.27 (dd, $J = 9.1$, 1.5 Hz, 1 H, 3-H), 6.77 (d, $J = 8.3$ Hz, 1 H, 7-H), 6.89 (d, $J = 8.3$ Hz, 1 H, 5-H), 7.17–7.31 (m, 8 H, 3',4',5'-H, 3-*C*₆H₅), 7.45 (t, $J = 8.3$ Hz, 1 H, 6-H), 7.44–7.47 (m, 2 H, 2',6'-H), 7.55 (s, 1 H, 1-H) ppm. ¹³C NMR: $\delta = 36.2$ (C-4), 41.7 (C-3), 56.3 (8-*OCH*₃), 106.3 (C-7), 110.1 (C-5), 114.4 (C-8a), 117.0 (C-1), 117.8 (C-9a), 125.8 (C-2',6'), 127.1 and 127.4 (C-4', C-4''), 127.3 (C-2',6''), 128.4 (C-3',5'), 128.9 (C-3'',5''), 133.0 (C-6), 134.8 (C-2), 139.2 (C-1'), 140.8 (C-1''), 157.8 (C-4b), 160.09 and 161.13 (C-8, C-4a), 173.9 (C-9) ppm. EI-MS: m/z (%) = 380 [M]⁺ (58), 379 (28), 378 (100), 377 (28), 363 (13), 362 (11), 361 (23), 360 (11), 350 (14), 349 (69), 347 (15), 333 (20), 332 (46), 303 (17), 301 (11), 289 (21), 288 (14), 285 (14), 266 (27), 261 (10), 226 (9), 215 (8). HRMS (EI): calcd. for C₂₆H₂₀O₃ [M]⁺ 380.1412; found 380.1418.

1-Hydroxy-6,7-diphenyl-9H-xanthen-9-one (12n): M.p. 160–162 °C. ¹H NMR: $\delta = 6.79$ (dd, $J = 8.4$, 0.6 Hz, 1 H, 7-H), 6.91 (dd, $J = 8.4$, 0.6 Hz, 1 H, 5-H), 7.12–7.16 (m, 2 H, 2',6'-H), 7.17–7.20 (m, 2 H, 2'',6''-H), 7.22–7.28 (m, 6 H, 3',4',5'-H, 3'',4'',5''-H), 7.49 (s, 1 H, 4-H), 7.57 (t, $J = 8.4$ Hz, 1 H, 6-H), 8.26 (s, 1 H, 1-H), 12.67 (s, 1 H, 8-*OH*) ppm. ¹³C NMR: $\delta = 107.0$ (C-5), 109.0 (C-8a), 110.5 (C-7), 119.3 (C-4, C-9a), 127.0 and 127.5 (C-4', C-4''), 127.7 (C-1), 128.0 and 128.1 (C-3',5', C-3'',5''), 129.5 (C-2',6'), 129.8 (C-2',6'), 133.7 (C-6), 137.2 (C-2), 139.5 and 139.6 (C-1', C-1''), 148.4 (C-3), 155.1 (C-4a), 156.3 (C-4b), 161.9 (C-8), 182.0 (C-9) ppm. EI-MS: m/z (%) = 378 [M]⁺ (100), 365 (16), 363 (40), 349 (12), 289 (6), 228 (6). HRMS (EI): calcd. for C₂₅H₁₆O₃ [M]⁺ 364.1099; found 364.1102.

1-Methoxy-7-(4-methoxyphenyl)-6-phenyl-9H-xanthen-9-one (5o): M.p. 192–194 °C. ^1H NMR: δ = 3.79 (s, 3 H, 4'-OCH₃), 4.04 (s, 3 H, 8-OCH₃), 6.78 (d, J = 8.8 Hz, 2 H, 3',5'-H), 6.82 (d, J = 8.3 Hz, 1 H, 7-H), 7.08 (d, J = 8.8 Hz, 2 H, 2',6'-H), 7.08 (dd, J = 8.3, 0.8 Hz, 1 H, 5-H), 7.18–7.21 (m, 2 H, 2'',6''-H), 7.27–7.29 (m, 3 H, 3'',4'',5''-H), 7.46 (s, 1 H, 4-H), 7.62 (t, J = 8.3 Hz, 1 H, 6-H), 8.30 (s, 1 H, 1-H) ppm. ^{13}C NMR: δ = 55.2 (4'-OCH₃), 56.5 (8-OCH₃), 105.4 (C-7), 110.1 (C-5), 112.6 (C-8a), 113.4 (C-3',5'), 118.9 (C-4), 121.9 (C-9a), 127.4 (C-4''), 128.1 (C-3'',5''), 128.2 (C-1), 129.6 (C-2'',6''), 131.0 (C-2',6'), 132.4 (C-1'), 134.8 (C-6), 136.5 (C-2), 140.2 (C-1''), 146.9 (C-3), 153.9 (C-4a), 158.2 (C-4b), 158.5 (C-4'), 160.8 (C-8), 176.4 (C-9) ppm. EI-MS: m/z (%) = 408 [M]⁺ (100), 407 (23), 391 (14), 390 (9), 380 (10), 379 (41), 363 (14), 362 (32), 347 (10), 346 (6), 305 (5). C₂₇H₂₀O₄ (408.45): calcd. for C 79.40, H 4.94; found C 79.42, H 4.91.

1-Methoxy-7-(4-methoxyphenyl)-6-phenyl-7,8-dihydro-9H-xanthen-9-one (6o): M.p. 168–170 °C. ^1H NMR: δ = 2.89 (dd, J = 17.3, 1.5 Hz, 1 H, 4_{trans}-H), 3.58 (dd, J = 17.3, 8.5 Hz, 1 H, 4_{cis}-H), 3.76 (s, 3 H, 4'-OCH₃), 3.98 (s, 3 H, 8-OCH₃), 4.24 (brd, J = 8.5 Hz, 1 H, 3-H), 6.76 (d, J = 8.4 Hz, 1 H, 7-H), 6.80 (d, J = 8.9 Hz, 2 H, 3',5'-H), 6.89 (dd, J = 8.4, 0.7 Hz, 1 H, 5-H), 7.17–7.30 (m, 5 H, 3-C₆H₅), 7.40 (d, J = 8.9 Hz, 2 H, 2',6'-H), 7.44 (t, J = 8.4 Hz, 1 H, 6-H), 7.45 (s, 1 H, 1-H) ppm. ^{13}C NMR: δ = 36.1 (C-4), 41.7 (C-3), 55.2 (8-OCH₃), 56.3 (8-OCH₃), 106.2 (C-7), 110.1 (C-5), 113.8 (C-3',5'), 114.4 (C-8a), 115.1 (C-1), 117.9 (C-9a), 126.8 (C-2',6'), 127.0 (C-4''), 127.3 (C-2'',6''), 128.9 (C-3'',5''), 131.7 (C-1'), 132.9 (C-6), 134.4 (C-2), 140.9 (C-1''), 157.8 (C-4b), 159.0 (C-4'), 159.6 (C-4a), 160.1 (C-8), 173.9 (C-9) ppm. EI-MS: m/z (%) = 410 [M]⁺ (10), 409 (28), 408 (100), 407 (34), 391 (21), 390 (15), 380 (18), 379 (62), 363 (26), 362 (43), 347 (16), 305 (9), 153 (10), 152 (13), 137 (14), 121 (21), 99 (16), 78 (9). HRMS (EI): calcd. for C₂₇H₂₂O₄ [M]⁺ 410.1518; found 410.1505.

1-Hydroxy-7-(4-methoxyphenyl)-6-phenyl-9H-xanthen-9-one (12o): M.p. 126–128 °C. ^1H NMR: δ = 3.79 (s, 3 H, 4'-OCH₃), 6.77 (d, J = 8.8 Hz, 2 H, 3',5'-H), 6.81 (dd, J = 8.4, 0.7 Hz, 1 H, 7-H), 6.93 (dd, J = 8.4, 0.7 Hz, 1 H, 5-H), 7.07 (d, J = 8.8 Hz, 2 H, 2',6'-H), 7.18–7.21 (m, 2 H, 2'',6''-H), 7.26–7.30 (m, 3 H, 3'',4'',5''-H), 7.49 (s, 1 H, 4-H), 7.59 (t, J = 8.4 Hz, 1 H, 6-H), 8.25 (s, 1 H, 1-H), 12.70 (s, 1 H, 8-OH) ppm. ^{13}C NMR: δ = 55.2 (4'-OCH₃), 107.0 (C-5), 109.0 (C-8a), 110.5 (C-7), 113.5 (C-3',5'), 119.35 (C-4), 119.38 (C-9a), 127.3 (C-4''), 127.7 (C-1), 128.2 (C-3'',5''), 129.5 (C-2'',6''), 131.0 (C-2',6'), 131.9 (C-1'), 136.7 (C-6), 136.9 (C-2), 139.8 (C-1''), 148.4 (C-3), 155.0 (C-4a), 156.4 (C-4b), 158.7 (C-4'), 161.9 (C-8) 182.1 (C-9) ppm. EI-MS: m/z (%) = 394 [M]⁺ (100), 393 (15), 395 (25), 379 (15), 363 (15), 351 (10), 129 (17), 125 (11), 123 (10), 111 (17), 97 (22), 96 (13), 86 (14), 84 (16), 83 (21), 73 (12), 69 (12). HRMS (EI): calcd. for C₂₇H₂₂O₄ [M]⁺ 394.1205; found 394.1204.

7-(3,4-Dimethoxyphenyl)-1-methoxy-6-phenyl-9H-xanthen-9-one (5p): M.p. 189–190 °C. ^1H NMR: δ = 3.55 (s, 3 H, 3'-OCH₃), 3.87 (s, 3 H, 4'-OCH₃), 4.04 (s, 3 H, 8-OCH₃), 6.53 (d, J = 1.9 Hz, 1 H, 2'-H), 6.80 (d, J = 8.3 Hz, 1 H, 5'-H), 6.83 (dd, J = 8.6, 0.9 Hz, 1 H, 7-H), 6.85 (dd, J = 8.3, 1.9 Hz, 1 H, 6'-H), 7.09 (dd, J = 8.6, 0.9 Hz, 1 H, 5-H), 7.19–7.22 (m, 2 H, 2'',6''-H), 7.27–7.31 (m, 3 H, 3'',4'',5''-H), 7.47 (s, 1 H, 4-H), 7.62 (t, J = 8.6 Hz, 1 H, 6-H), 8.35 (s, 1 H, 1-H) ppm. ^{13}C NMR: δ = 55.5 (3'-OCH₃), 55.8 (4'-OCH₃), 56.5 (8-OCH₃), 105.4 (C-7), 110.1 (C-5), 110.7 (C-5'), 112.6 (C-8a), 113.5 (C-2'), 118.8 (C-4), 121.9 (C-9a), 122.1 (C-6'), 127.4 (C-4''), 128.0 (C-1), 128.2 (C-3'',5''), 129.5 (C-2'',6''), 132.4 (C-1'), 134.8 (C-6), 136.5 (C-2), 140.3 (C-1''), 146.9 (C-3), 147.9 and 148.0 (C-3', C-4'), 154.0 (C-4a), 158.2 (C-4b), 160.8 (C-8), 176.4 (C-9) ppm. EI-MS: m/z = 438 [M]⁺ (100), 424 (7), 423 (25),

408 (6), 395 (13), 391 (12), 380 (6), 363 (6), 351 (8). C₂₈H₂₂O₅ (438.47): calcd. for C 76.70, H 5.06; found C 76.73, H 5.27.

7-(3,4-Dimethoxyphenyl)-1-methoxy-6-phenyl-3,4-dihydro-9H-xanthen-9-one (6p): Yellowish oil. ^1H NMR: δ = 2.91 (dd, J = 17.3, 1.4 Hz, 1 H, 4_{trans}-H), 3.60 (dd, J = 17.3, 9.1 Hz, 1 H, 4_{cis}-H), 3.82 and 3.84 (2 × s, 6 H, 3',4'-OCH₃), 3.99 (s, 3 H, 8-OCH₃), 4.25 (dd, J = 9.1, 1.4 Hz, 1 H, 3-H), 6.75 (d, J = 8.4 Hz, 1 H, 5'-H), 6.78 (dd, J = 8.4, 0.7 Hz, 1 H, 7-H), 6.90 (dd, J = 8.4, 0.7 Hz, 1 H, 5-H), 6.95 (dd, J = 8.4, 2.1 Hz, 1 H, 6'-H), 7.07 (d, J = 2.1 Hz, 1 H, 2'-H), 7.18–7.31 (m, 5 H, 3-C₆H₅), 7.46 (s, 1 H, 1-H), 7.46 (t, J = 8.4 Hz, 1 H, 6-H) ppm. ^{13}C NMR: δ = 36.1 (C-4), 41.9 (C-3), 55.74 and 55.84 (3',4'-OCH₃), 56.4 (8-OCH₃), 106.3 (C-7), 108.7 (C-2'), 110.1 (C-5), 110.8 (C-5'), 114.5 (C-8a), 115.4 (C-1), 117.9 (C-9a), 118.2 (C-6'), 127.1 (C-4''), 127.3 (C-2'',6''), 128.9 (C-3'',5''), 133.2 (C-1'), 133.0 (C-6), 135.6 (C-2), 141.1 (C-1''), 148.7 and 148.8 (C-3', C-4'), 157.9 (C-4b), 159.7 (C-4a), 160.2 (C-8), 174.0 (C-9) ppm. EI-MS: m/z (%) = 440 [M]⁺ (22), 439 (24), 408 (100), 423 (20), 395 (10), 391 (9), 363 (8). HRMS (EI): calcd. for C₂₈H₂₄O₅ [M]⁺ 440.1624; found 440.1615.

7-(3,4-Dimethoxyphenyl)-1-hydroxy-6-phenyl-9H-xanthen-9-one (12p): M.p. 186–188 °C. ^1H NMR: δ = 3.56 (s, 3 H, 4'-OCH₃), 3.88 (s, 3 H, 3'-OCH₃), 6.52 (d, J = 1.9 Hz, 1 H, 2'-H), 6.80 (d, J = 8.2 Hz, 1 H, 5'-H), 6.82 (d, J = 8.3 Hz, 1 H, 7-H), 6.84 (dd, J = 8.2, 1.9 Hz, 1 H, 6'-H), 6.95 (dd, J = 8.3, 0.7 Hz, 1 H, 5-H), 7.20–7.24 (m, 2 H, 2'',6''-H), 7.28–7.32 (m, 3 H, 3'',4'',5''-H), 7.52 (s, 1 H, 4-H), 7.61 (t, J = 8.3 Hz, 1 H, 6-H), 8.30 (s, 1 H, 1-H), 12.69 (s, 1 H, 8-OH) ppm. ^{13}C NMR: δ = 55.5 (4'-OCH₃), 55.7 (3'-OCH₃), 107.0 (C-5), 109.0 (C-8a), 110.5 (C-7), 110.7 (C-5'), 113.3 (C-2'), 119.3 (C-4), 119.4 (C-9a), 122.1 (C-6'), 127.0 (C-1), 127.7 (C-4''), 128.2 (C-3'',5''), 129.4 (C-2'',6''), 132.0 (C-1'), 136.7 (C-6), 136.9 (C-2), 139.9 (C-1''), 148.09 and 148.12 (C-3',4'), 148.4 (C-3), 155.0 (C-4a), 156.4 (C-4b), 161.9 (C-8) 182.1 (C-9) ppm. EI-MS: m/z (%) = 424 [M]⁺ (100), 409 (20), 381 (10), 377 (14), 363 (10), 349 (13), 337 (10), 139 (10), 137 (14), 125 (12), 111 (16), 110 (13), 97 (19), 96 (13), 86 (13), 84 (19), 83 (15), 81 (16), 73 (12), 69 (17). C₂₇H₂₀O₅ (424.45): calcd. for C 76.40, H 4.75; found C 76.11, H 4.75.

6-(3,4-Dimethoxyphenyl)-1-methoxy-7-phenyl-9H-xanthen-9-one (5q): M.p. 188–190 °C. ^1H NMR: δ = 3.52 (s, 3 H, 3'-OCH₃), 3.88 (s, 3 H, 4'-OCH₃), 4.04 (s, 3 H, 8-OCH₃), 6.54 (d, J = 2.0 Hz, 1 H, 2'-H), 6.82 (d, J = 8.4 Hz, 2 H, 5'-H, 7-H), 6.90 (dd, J = 8.4, 2.0 Hz, 1 H, 6'-H), 7.09 (dd, J = 8.4, 0.8 Hz, 1 H, 5-H), 7.17–7.20 (m, 2 H, 2',6'-H), 7.23–7.27 (m, 3 H, 3',4',5'-H), 7.50 (s, 1 H, 4-H), 7.62 (t, J = 8.4 Hz, 1 H, 6-H), 8.31 (s, 1 H, 1-H) ppm. ^{13}C NMR: δ = 55.5 (3'-OCH₃), 55.8 (4'-OCH₃), 56.5 (8-OCH₃), 105.5 (C-7), 110.0 (C-5), 110.7 (C-5'), 112.6 (C-8a), 113.3 (C-2'), 118.3 (C-4), 121.6 (C-9a), 121.8 (C-6'), 126.7 (C-4'), 128.1 (C-3',5'), 128.4 (C-1), 129.9 (C-2',6'), 132.3 (C-1''), 134.6 (C-6), 136.8 (C-2), 140.4 (C-1'), 146.6 (C-3), 148.1 and 148.5 (C-3'', C-4''), 154.2 (C-4a), 158.2 (C-4b), 160.8 (C-8), 176.3 (C-9) ppm. EI-MS: m/z (%) = 438 [M]⁺ (100), 437 (19), 422 (5), 421 (18), 420 (8), 410 (8), 409 (35), 393 (13), 392 (20), 377 (6), 376 (5), 361 (6), 333 (5). C₂₈H₂₂O₅ (438.47): calcd. for C 76.70, H 5.06; found C 76.66, H 5.11.

6-(3,4-Dimethoxyphenyl)-1-methoxy-7-phenyl-7,8-dihydro-9H-xanthen-9-one (6q): Yellowish oil. ^1H NMR: δ = 2.91 (dd, J = 17.3, 1.4 Hz, 1 H, 4_{trans}-H), 3.58 (dd, J = 17.3, 8.6 Hz, 1 H, 4_{cis}-H), 3.76 (s, 3 H, 3'-OCH₃), 3.80 (s, 3 H, 4'-OCH₃), 3.99 (s, 3 H, 8-OCH₃), 4.22 (dd, J = 8.6, 1.4 Hz, 1 H, 3-H), 6.72 (d, J = 8.2 Hz, 1 H, 5'-H), 6.79 (d, J = 8.4 Hz, 1 H, 7-H), 6.81 (d, J = 2.0 Hz, 1 H, 2'-H), 6.84 (dd, J = 8.2, 2.0 Hz, 1 H, 6'-H), 6.92 (dd, J = 8.4, 0.7 Hz, 1 H, 5-H), 7.19–7.31 (m, 3 H, 3',4',5'-H), 7.46 (d, J = 8.4 Hz, 2 H, 2',6'-H), 7.47 (t, J = 8.4 Hz, 1 H, 6-H), 7.53 (s, 1 H, 1-H) ppm.

^{13}C NMR: δ = 36.5 (C-4), 41.5 (C-3), 55.78 and 55.82 (3',4'-OCH₃), 56.4 (8-OCH₃), 106.3 (C-7), 110.2 (C-5), 110.3 (C-2''), 111.4 (C-5''), 114.4 (C-8a), 116.9 (C-1), 117.7 (C-9a), 119.3 (C-6''), 125.6 (C-2',6'), 127.4 (C-4'), 128.5 (C-3',5'), 133.1 (C-6), 133.2 (C-1''), 135.2 (C-2), 139.4 (C-1'), 148.0 (C-4''), 149.1 (C-3'), 157.9 (C-4b), 160.2 (C-8), 160.3 (C-4a), 174.0 (C-9) ppm. EI-MS: m/z (%) = 440 [M]⁺ (18), 439 (23), 438 (100), 437 (23), 421 (24) 420 (11), 410 (10), 409 (42), 393 (18), 392 (25), 361 (8), 151 (8), 137 (9). HRMS (EI): calcd. for C₂₈H₂₄O₅ [M]⁺ 440.1624; found 440.1627.

6-(3,4-Dimethoxyphenyl)-1-hydroxy-7-phenyl-9H-xanthen-9-one (12q): M.p. 165–167 °C. ^1H NMR: δ = 3.53 (s, 3 H, 3'-OCH₃), 3.89 (s, 3 H, 4'-OCH₃), 6.55 (d, J = 2.0 Hz, 1 H, 2''-H), 6.83 (dd, J = 8.4, 0.7 Hz, 1 H, 7-H), 6.84 (d, J = 8.3 Hz, 1 H, 5''-H), 6.92 (dd, J = 8.3, 2.0 Hz, 1 H, 6''-H), 6.97 (dd, J = 8.4, 0.7 Hz, 1 H, 5-H), 7.17–7.20 (m, 2 H, 2',6'-H), 7.25–7.30 (m, 3 H, 3',4',5'-H), 7.56 (s, 1 H, 4-H), 7.61 (t, J = 8.4 Hz, 1 H, 6-H), 8.28 (s, 1 H, 1-H), 12.71 (s, 1 H, 8-OH) ppm. ^{13}C NMR: δ = 55.6 (3'-OCH₃), 55.8 (4'-OCH₃), 107.0 (C-5), 109.1 (C-8a), 110.6 (C-7), 110.8 (C-5''), 113.3 (C-2''), 118.8 (C-4), 119.2 (C-9a), 1220 (C-6''), 127.0 (C-4'), 127.6 (C-1), 128.2 (C-3',5'), 129.8 (C-2',6'), 132.0 (C-1''), 136.7 (C-6), 137.2 (C-2), 140.0 (C-1'), 148.1 (C-3), 148.2 (C-3''), 148.8 (C-4''), 155.4 (C-4a), 156.4 (C-4b), 162.0 (C-8), 182.1 (C-9) ppm. EI-MS: m/z (%) = 424 [M]⁺ (100), 409 (12), 393 (12), 377 (11), 350 (8), 349 (13), 337 (8), 84 (10). HRMS (EI): calcd. for C₂₇H₂₀O₅ [M]⁺ 424.1311; found 424.1312.

6,7-Bis(3,4-dimethoxyphenyl)-1-methoxy-9H-xanthen-9-one (5r): M.p. 187–188 °C. ^1H NMR: δ = 3.62 and 3.65 (2 × s, 6 H, 4',4''-OCH₃), 3.88 and 3.89 (2 × s, 6 H, 3',3''-OCH₃), 4.04 (s, 3 H, 8-OCH₃), 6.65–6.66 (m, 2 H, 2'-H, 2''-H), 6.79–6.84 (m, 5 H, 7-H, 5'-H, 6'-H, 5''-H, 6''-H), 7.09 (dd, J = 8.4, 0.7 Hz, 1 H, 5-H), 7.48 (s, 1 H, 4-H), 7.62 (t, J = 8.4 Hz, 1 H, 6-H), 8.32 (s, 1 H, 1-H) ppm. ^{13}C NMR: δ = 55.7 (4',4''-OCH₃), 55.8 (3',3''-OCH₃), 56.5 (8-OCH₃), 105.5 (C-7), 110.0 (C-5), 110.76 and 110.80 (C-5', C-5''), 112.6 (C-8a), 113.0 and 113.3 (C-2', C-2''), 118.4 (C-4), 121.7 (C-9a), 121.9 and 122.2 (C-6', C-6''), 128.1 (C-1), 132.7 and 132.9 (C-1', C-1''), 134.8 (C-6), 136.5 (C-2), 146.7 (C-3), 147.9, 148.3 and 148.5 (C-3', C-4', C-3'', C-4''), 154.0 (C-4a), 158.2 (C-4b), 160.8 (C-8), 176.3 (C-9) ppm. EI-MS: m/z (%) = 498 [M]⁺ (100), 497 (16), 481 (15), 480 (7), 470 (9), 469 (26), 453 (9), 452 (15), 409 (5), 406 (5), 361 (6), 141 (9), 99 (7), 86 (9), 84 (14), 78 (8). C₃₀H₂₆O₇ (498.52): calcd. for C 72.28, H 5.26; found C 72.33, H 5.24.

6,7-Bis(3,4-dimethoxyphenyl)-1-methoxy-7,8-dihydro-9H-xanthen-9-one (6r): Yellowish oil. ^1H NMR: δ = 2.90 (dd, J = 17.3, 1.3 Hz, 1 H, 4_{trans}-H), 3.57 (dd, J = 17.3, 8.3 Hz, 1 H, 4_{cis}-H), 3.76, 3.80, 3.85 and 3.85 (4 × s, 12 H, 3',4',3'',4''-OCH₃), 3.99 (s, 3 H, 8-OCH₃), 4.20 (brd, J = 8.3 Hz, 1 H, 3-H), 6.72 (d, J = 8.2 Hz, 1 H, 5''-H), 6.76 (d, J = 8.5 Hz, 1 H, 5'-H), 6.79 (d, J = 8.5 Hz, 1 H, 7-H), 6.82 (d, J = 2.0 Hz, 1 H, 2''-H), 6.84 (dd, J = 8.2, 2.0 Hz, 1 H, 6''-H), 6.92 (dd, J = 8.7, 0.7 Hz, 1 H, 5-H), 6.96 (dd, J = 8.5, 2.1 Hz, 1 H, 6'-H), 7.08 (d, J = 2.1 Hz, 1 H, 2'-H), 7.44 (s, 1 H, 1-H), 7.47 (dd, J = 8.7, 8.5 Hz, 1 H, 6-H) ppm. ^{13}C NMR: δ = 36.4 (C-4), 41.6 (C-3), 55.78, 55.82 and 55.85 (3',4',3'',4''-OCH₃), 56.4 (8-OCH₃), 106.3 (C-7), 108.8 (C-2'), 110.16 (C-5), 110.24 (C-2''), 110.9 (C-5'), 111.4 (C-5''), 114.4 (C-8a), 115.3 (C-1), 117.8 (C-9a), 118.2 (C-6'), 119.2 (C-6''), 132.3 (C-1'), 133.0 (C-6), 133.5 (C-1''), 135.0 (C-2), 148.0, 148.7, 148.8 and 149.1 (C-3', C-4', C-3'', C-4''), 157.9 (C-4b), 159.9 (C-4a), 160.2 (C-8), 174.0 (C-9) ppm. EI-MS: m/z (%) = 500 [M]⁺ (21), 499 (24), 498 (100), 497 (12), 481 (13), 469 (21), 452 (12), 363 (7). HRMS (EI): calcd. for C₃₀H₂₈O₇ [M]⁺ 500.1835; found 500.1837.

6,7-Bis(3,4-dimethoxyphenyl)-1-hydroxy-9H-xanthen-9-one (12r): M.p. 164–166 °C. ^1H NMR: δ = 3.63 and 3.66 (2 × s, 6 H, 4',4''-

OCH₃), 3.88 and 3.89 (2 × s, 6 H, 3',3''-OCH₃), 6.64–6.66 (m, 2 H, 2'-H, 2''-H), 6.79–6.88 (m, 5 H, 7-H, 5'-H, 6'-H, 5''-H, 6''-H), 6.94 (dd, J = 8.4, 0.6 Hz, 1 H, 5'-H), 7.52 (s, 1 H, 4-H), 7.60 (t, J = 8.4 Hz, 1 H, 6-H), 8.26 (s, 1 H, 1-H), 12.70 (s, 1 H, 8-OH) ppm. ^{13}C NMR: δ = 55.68 and 55.71 (4',4''-OCH₃), 55.8 (3',3''-OCH₃), 107.0 (C-5), 109.0 (C-8a), 110.5 (C-7), 110.77 and 110.81 (C-5', C-5''), 112.9 and 113.1 (C-2', C-2''), 118.4 (C-4), 119.1 (C-9a), 121.9 and 122.1 (C-6', C-6''), 127.1 (C-1), 132.2 and 132.4 (C-1', C-1''), 136.7 (C-6), 136.9 (C-2), 148.11, 148.13, 148.36, 148.38 and 148.7 (C-3, C-3', C-4', C-3'', C-4''), 155.1 (C-4a), 156.3 (C-4b), 161.9 (C-8), 182.0 (C-9) ppm. EI-MS: m/z (%) = 484 [M]⁺ (100), 469 (9), 185 (12), 129 (19), 111 (10), 97 (16), 83 (13), 73 (20), 71 (10), 69 (13), 60 (12). HRMS (EI): calcd. for C₂₉H₂₄O₇ [M]⁺ 484.1522; found 484.1523.

1,3-Dimethoxy-6,7-diphenyl-9H-xanthen-9-one (5s): M.p. 209–210 °C. ^1H NMR: δ = 3.93 (s, 3 H, 6-OCH₃), 4.00 (s, 3 H, 8-OCH₃), 6.37 (d, J = 2.3 Hz, 1 H, 7-H), 6.53 (d, J = 2.3 Hz, 1 H, 5-H), 7.14–7.27 (m, 10 H, 2,3-C₆H₅), 7.43 (s, 1 H, 4-H), 8.32 (s, 1 H, 1-H) ppm. ^{13}C NMR: δ = 55.8 (6-OCH₃), 56.4 (8-OCH₃), 92.9 (C-5), 95.2 (C-7), 107.4 (C-8a), 118.4 (C-4), 122.0 (C-9a), 126.7 (C-4'), 127.4 (C-4''), 128.0 (C-3',5'), 128.1 (C-3'',5''), 128.4 (C-1), 129.6 (C-2',6'), 130.0 (C-2',6''), 136.8 (C-2), 140.05 and 140.08 (C-1', C-1''), 146.4 (C-3), 154.1 (C-4a), 159.9 (C-4b), 162.0 (C-8), 164.9 (C-6), 175.2 (C-9) ppm. EI-MS: m/z (%) = 408 [M]⁺ (100), 407 (40), 394 (5), 391 (13), 390 (8), 380 (14), 379 (66), 378 (15), 377 (39), 363 (13), 362 (27), 336 (7), 334 (14), 333 (13), 276 (6), 226 (5), 215 (8), 189 (5). C₂₇H₂₀O₄ (408.45): calcd. for C 79.40, H 4.94; found C 79.22, H 5.00.

1,3-Dimethoxy-6,7-diphenyl-7,8-dihydro-9H-xanthen-9-one (6s): M.p. 189–191 °C. ^1H NMR: δ = 2.90 (dd, J = 17.2, 1.4 Hz, 1 H, 4_{trans}-H), 3.61 (dd, J = 17.2, 8.9 Hz, 1 H, 4_{cis}-H), 3.86 (s, 3 H, 6-OCH₃), 3.98 (s, 3 H, 8-OCH₃), 4.28 (brd, J = 8.9 Hz, 1 H, 3-H), 6.36 and 6.37 (AB, J = 2.6 Hz, 2 H, 5-H, 7-H), 7.21–7.33 (m, 8 H, 3',4',5'-H, 3-C₆H₅), 7.46–7.49 (m, 2 H, 2',6'-H), 7.56 (s, 1 H, 1-H) ppm. ^{13}C NMR: δ = 36.2 (C-4), 41.8 (C-3), 55.6 (6-OCH₃), 56.3 (8-OCH₃), 92.8 (C-5), 96.0 (C-7), 109.1 (C-8a), 117.2 (C-1), 117.6 (C-9a), 125.6 (C-2',6'), 127.1 and 127.3 (C-4', C-4''), 127.4 (C-2'',6''), 128.4 (C-3',5'), 128.9 (C-3'',5''), 134.6 (C-2), 139.3 (C-1'), 140.9 (C-1''), 159.39 and 159.43 (C-4a, C-4b), 161.3 (C-8), 163.4 (C-6), 173.3 (C-9) ppm. EI-MS: m/z (%) = 410 [M]⁺ (17), 409 (29), 408 (100), 407 (45), 395 (15), 394 (45), 393 (23), 391 (20), 390 (10), 380 (23), 379 (82), 378 (24), 377 (49), 365 (13), 364 (12), 363 (21), 362 (32), 334 (19), 333 (20), 289 (11), 228 (11), 215 (12), 105 (11). HRMS (EI): calcd. for C₂₇H₂₂O₄ [M]⁺ 410.1518; found 410.1510.

1-Hydroxy-3-methoxy-6,7-diphenyl-9H-xanthen-9-one (12s): M.p. 197–200 °C. ^1H NMR: δ = 3.91 (s, 3 H, 6-OCH₃), 6.38 (d, J = 2.2 Hz, 1 H, 7-H), 6.46 (d, J = 2.2 Hz, 1 H, 5-H), 7.14–7.20 (m, 4 H, 2',6'-H, 2'',6''-H), 7.22–7.29 (m, 6 H, 3',4',5'-H, 3'',4'',5''-H), 7.49 (s, 1 H, 4-H), 8.27 (s, 1 H, 1-H), 12.91 (s, 1 H, 8-OH) ppm. ^{13}C NMR: δ = 55.8 (6-OCH₃), 93.0 (C-5), 97.1 (C-7), 104.0 (C-8a), 119.1 (C-4), 119.5 (C-9a), 127.0 and 127.7 (C-4', C-4''), 127.5 (C-1), 128.0 and 128.2 (C-3',5', C-3'',5''), 129.6 and 129.9 (C-2',6', C-2'',6''), 137.2 (C-2), 139.67 and 139.74 (C-1', C-1''), 147.8 (C-3), 155.1 (C-4a), 157.8 (C-4b), 163.6 (C-8), 166.7 (C-6), 180.6 (C-9) ppm. EI-MS: m/z (%) = 394 [M]⁺ (100), 393 (31), 365 (16), 350 (6). HRMS (EI): calcd. for C₂₆H₁₈O₄ [M]⁺ 394.1205; found 394.1209.

Synthesis of the Hydroxylated 2,3-Diaryl-9H-xanthen-9-ones 13b–s: A solution of the appropriate 2,3-diaryl-9H-xanthen-9-one (5b–s) in recently distilled dichloromethane (3 mL) was cooled to –78 °C and placed under nitrogen. A solution of boron tribromide in dichloromethane (0.1 M, 2.5 equiv. for each methyl group to be

cleaved) was gradually added. The reaction mixture was stirred and left at room temperature for a period of time according to the substitution of the compounds (one hour for each group to be cleaved). After that period, the solution was poured into water (20 mL) and vigorously stirred until the formation of a yellow precipitate. The solid was washed abundantly with water (4×50 mL) and then with light petroleum (4×20 mL) to afford the hydroxylated 2,3-diaryl-9H-xanthen-9-one (**13b-s**) in good yields.

2-(4-Hydroxyphenyl)-3-phenyl-9H-xanthen-9-one (13b): Reaction time 1 h, 72% yield; m.p. 241–242 °C. ^1H NMR ($[\text{D}_6]\text{DMSO}$): δ = 6.66 (d, J = 8.5 Hz, 2 H, 3',5'-H), 6.95 (d, J = 8.5 Hz, 2 H, 2',6'-H), 7.22–7.25 (m, 2 H, 2'',6''-H), 7.32–7.34 (m, 3 H, 3'',4'',5''-H), 7.52 (t, J = 7.7 Hz, 1 H, 7-H), 7.64 (s, 1 H, 4-H), 7.69 (d, J = 8.1 Hz, 1 H, 5-H), 7.91 (ddd, J = 8.1, 7.7, 1.6 Hz, 1 H, 6-H), 8.06 (s, 1 H, 1-H), 8.23 (dd, J = 7.7, 1.6 Hz, 1 H, 8-H), 9.53 (s, 1 H, 4'-OH) ppm. ^{13}C NMR ($[\text{D}_6]\text{DMSO}$): δ = 115.1 (C-3',5'), 118.3 (C-5), 119.5 (C-4), 120.1 (C-9a), 121.2 (C-8a), 124.5 (C-7), 126.1 (C-8), 127.0 (C-1), 127.7 (C-4''), 128.3 (C-3'',5''), 129.4 (C-2'',6''), 130.0 (C-1'), 130.7 (C-2',6'), 135.6 (C-6), 136.7 (C-2), 139.5 (C-1''), 147.2 (C-3), 154.4 (C-4a), 155.8 (C-4b), 156.5 (C-4'), 175.8 (C-9) ppm. EI-MS: m/z (%) = 364 $[\text{M}]^{+}$ (100), 349 (3), 335 (4), 305 (5), 276 (3), 244 (3), 213 (3), 173 (4), 138 (2), 77 (2). HRMS (EI): calcd. for $\text{C}_{25}\text{H}_{16}\text{O}_3$ $[\text{M}]^{+}$ 364.1099; found 364.1100.

2-(3,4-Dihydroxyphenyl)-3-phenyl-9H-xanthen-9-one (13c): Reaction time 2 h, 80% yield; m.p. 171–173 °C. ^1H NMR ($[\text{D}_6]\text{DMSO}$): δ = 6.37 (dd, J = 8.1, 2.0 Hz, 1 H, 6'-H), 6.58 (d, J = 2.0 Hz, 1 H, 2'-H), 6.63 (d, J = 8.1 Hz, 1 H, 5'-H), 7.24–7.30 (m, 2 H, 2'',6''-H), 7.33–7.36 (m, 3 H, 3'',4'',5''-H), 7.50 (dt, J = 7.7, 0.5 Hz, 1 H, 7-H), 7.60 (s, 1 H, 4-H), 7.67 (d, J = 8.2 Hz, 1 H, 5-H), 7.89 (ddd, J = 8.2, 7.7, 1.4 Hz, 1 H, 6-H), 8.03 (s, 1 H, 1-H), 8.22 (dd, J = 7.7, 1.4 Hz, 1 H, 8-H), 8.94 and 8.99 (2 $\times$ brs, 2 H, 3',4'-OH) ppm. ^{13}C NMR ($[\text{D}_6]\text{DMSO}$): δ = 115.5 (C-5'), 117.0 (C-2'), 118.3 (C-5), 119.4 (C-4), 120.0 (C-9a), 120.8 (C-6'), 121.2 (C-8a), 124.5 (C-7), 126.1 (C-8), 127.0 (C-1), 127.7 (C-4''), 128.2 (C-3'',5''), 129.3 (C-2'',6''), 130.7 (C-1'), 135.6 (C-6), 136.9 (C-2), 139.6 (C-1''), 144.6 (C-3'), 145.0 (C-4'), 147.0 (C-3), 154.3 (C-4a), 155.8 (C-4b), 175.8 (C-9) ppm. EI-MS: m/z (%) = 380 $[\text{M}]^{+}$ (100), 363 (5), 333 (12), 321 (3), 305 (6), 292 (2), 276 (4), 263 (2), 239 (2), 213 (2), 181 (2), 167 (8), 152 (2), 138 (4), 121 (2), 77 (2). HRMS (EI): calcd. for $\text{C}_{25}\text{H}_{16}\text{O}_4$ $[\text{M}]^{+}$ 380.1049; found 380.1035.

3-(4-Hydroxyphenyl)-2-phenyl-9H-xanthen-9-one (13d, 13g): Reaction time 24 h, 69% yield when obtained from compound **5d**; 1 h, 82% when obtained from compound **5g**; m.p. 244–245 °C. ^1H NMR (500 MHz, $[\text{D}_6]\text{DMSO}$): δ = 6.69 (d, J = 8.6 Hz, 2 H, 3'',5''-H), 7.05 (d, J = 8.6 Hz, 2 H, 2'',6''-H), 7.19 (dd, J = 7.8, 1.5 Hz, 2 H, 2',6'-H), 7.30–7.35 (m, 3 H, 3',4',5'-H), 7.53 (ddd, J = 7.7, 7.6, 0.9 Hz, 1 H, 7-H), 7.65 (s, 1 H, 4-H), 7.71 (d, J = 8.1 Hz, 1 H, 5-H), 7.92 (ddd, J = 8.1, 7.6, 1.6 Hz, 1 H, 6-H), 8.08 (s, 1 H, 1-H), 8.24 (dd, J = 7.7, 1.6 Hz, 1 H, 8-H), 9.67 (s, 1 H, 4'-OH) ppm. ^{13}C NMR (500 MHz, $[\text{D}_6]\text{DMSO}$): δ = 115.1 (C-3'',5''), 118.3 (C-5), 119.1 (C-4), 119.6 (C-9a), 121.3 (C-8a), 124.5 (C-7), 126.1 (C-8), 127.0 (C-4'), 127.4 (C-1), 128.3 (C-3',5'), 129.5 (C-2',6'), 129.7 (C-1''), 130.8 (C-2'',6''), 135.6 (C-6), 136.5 (C-2), 139.9 (C-1'), 147.4 (C-3), 154.8 (C-4a), 155.8 (C-4b), 157.2 (C-4''), 175.7 (C-9) ppm. EI-MS: m/z (%) = 364 $[\text{M}]^{+}$ (100), 347 (7), 335 (4), 305 (6), 289 (4), 276 (3), 244 (4), 213 (4), 173 (5), 138 (2), 84 (4), 66 (4). $\text{C}_{25}\text{H}_{16}\text{O}_3$ (364.39): calcd. for C 82.40, H 4.43; found C 82.50, H 4.43.

2,3-Bis(4-hydroxyphenyl)-9H-xanthen-9-one (13e, 13h): Reaction time 24 h, 82% yield when obtained from compound **5e**; 2 h, 94% when obtained from compound **5h**; m.p. 231–233 °C. ^1H NMR (500 MHz, $[\text{D}_6]\text{DMSO}$): δ = 6.68 (d, J = 8.7 Hz, 2 H, 3',5'-H), 6.69

(d, J = 8.6 Hz, 2 H, 3'',5''-H), 6.94 (d, J = 8.7 Hz, 2 H, 2',6'-H), 7.02 (d, J = 8.6 Hz, 2 H, 2'',6''-H), 7.47 (t, J = 7.8 Hz, 1 H, 7-H), 7.51 (s, 1 H, 4-H), 7.63 (d, J = 8.0 Hz, 1 H, 5-H), 7.87 (ddd, J = 8.0, 7.8, 1.6 Hz, 1 H, 6-H), 7.98 (s, 1 H, 1-H), 8.19 (dd, J = 7.8, 1.6 Hz, 1 H, 8-H), 9.51 and 9.64 (2 $\times$ s, 2 H, 4',4''-OH) ppm. ^{13}C NMR (500 MHz, $[\text{D}_6]\text{DMSO}$): δ = 115.1 (C-3',5', C-3'',5''), 118.2 (C-5), 118.9 (C-4), 119.5 (C-9a), 121.2 (C-8a), 124.4 (C-7), 126.0 (C-8), 127.0 (C-1), 130.0 (C-1''), 130.4 (C-1'), 130.6 (C-2',6'), 130.7 (C-2'',6''), 135.6 (C-6), 136.6 (C-2), 147.3 (C-3), 154.4 (C-4a), 155.7 (C-4b), 156.4 (C-4'), 157.1 (C-4''), 175.7 (C-9) ppm. EI-MS: m/z (%) = 380 $[\text{M}]^{+}$ (43), 363 (2), 321 (1), 305 (1), 264 (2), 236 (3), 174 (100), 158 (70), 144 (28), 131 (48), 121 (30), 115 (26), 105 (54), 91 (27), 77 (64), 65 (20), 53 (22), 51 (24). $\text{C}_{25}\text{H}_{16}\text{O}_4$ (380.39): calcd. for C 78.94, H 4.24; found C 78.95, H 4.23.

3-(4-Hydroxyphenyl)-2-(3,4-dihydroxyphenyl)-9H-xanthen-9-one (13f, 13i): Reaction time 24 h, 92% yield when obtained from compound **5f**, 3 h, 80% when obtained from compound **5i**; m.p. 260–261 °C. ^1H NMR ($[\text{D}_6]\text{DMSO}$): δ = 6.41 (dd, J = 8.1, 2.1 Hz, 1 H, 6'-H), 6.58 (d, J = 2.1 Hz, 1 H, 2'-H), 6.65 (d, J = 8.1 Hz, 1 H, 5'-H), 6.71 (d, J = 8.6 Hz, 2 H, 3'',5''-H), 7.08 (d, J = 8.6 Hz, 2 H, 2'',6''-H), 7.51 (dd, J = 7.7, 7.4 Hz, 1 H, 7-H), 7.58 (s, 1 H, 4-H), 7.70 (d, J = 7.9 Hz, 1 H, 5-H), 7.90 (ddd, J = 7.9, 7.4, 1.6 Hz, 1 H, 6-H), 8.00 (s, 1 H, 1-H), 8.23 (dd, J = 7.7, 1.6 Hz, 1 H, 8-H), 8.95 (s, 1 H, 4'-OH), 9.01 (s, 1 H, 3'-OH), 9.65 (s, 1 H, 4''-OH) ppm. ^{13}C NMR ($[\text{D}_6]\text{DMSO}$): δ = 115.1 (C-3'',5''), 115.5 (C-5'), 116.9 (C-2'), 118.3 (C-5), 118.9 (C-4), 119.5 (C-9a), 120.6 (C-6'), 121.3 (C-8a), 124.4 (C-7), 126.1 (C-8), 127.0 (C-1), 130.0 (C-1''), 130.6 (C-2'',6''), 131.1 (C-1'), 135.6 (C-6), 136.8 (C-2), 144.5 (C-4'), 145.0 (C-3'), 147.3 (C-3), 154.4 (C-4a), 155.8 (C-4b), 157.2 (C-4''), 175.8 (C-9) ppm. EI-MS: m/z (%) = 396 $[\text{M}]^{+}$ (100), 380 (7), 349 (7), 175 (5), 105 (1), 78 (15), 77 (5), 63 (21). $\text{C}_{25}\text{H}_{16}\text{O}_5$ (396.39): calcd. for C 75.75, H 4.07; found C 75.34, H 4.06.

3-(3,4-Dihydroxyphenyl)-2-phenyl-9H-xanthen-9-one (13j): Reaction time 2 h, 80% yield; m.p. 244–246 °C. ^1H NMR ($[\text{D}_6]\text{DMSO}$): δ = 6.48 (dd, J = 8.1, 1.9 Hz, 1 H, 6''-H), 6.62 (d, J = 1.9 Hz, 1 H, 2''-H), 6.65 (d, J = 8.1 Hz, 1 H, 5''-H), 7.18–7.21 (m, 2 H, 2',6'-H), 7.28–7.35 (m, 3 H, 3',4',5'-H), 7.51 (dd, J = 7.9, 7.5 Hz, 1 H, 7-H), 7.55 (s, 1 H, 4-H), 7.68 (d, J = 8.1 Hz, 1 H, 5-H), 7.90 (ddd, J = 8.1, 7.5, 1.0 Hz, 1 H, 6-H), 8.05 (s, 1 H, 1-H), 8.22 (dd, J = 7.9, 1.1 Hz, 1 H, 8-H), 8.97 (s, 1 H, 4''-OH), 9.16 (s, 1 H, 3''-OH) ppm. ^{13}C NMR ($[\text{D}_6]\text{DMSO}$): δ = 115.4 (C-5''), 116.9 (C-2''), 118.3 (C-5), 119.0 (C-4), 119.6 (C-9a), 120.9 (C-6''), 121.3 (C-8a), 124.5 (C-7), 126.1 (C-8), 127.0 (C-4'), 127.4 (C-1), 128.3 (C-3',5'), 129.4 (C-2',6'), 130.3 (C-1''), 135.6 (C-6), 136.5 (C-2), 140.0 (C-1'), 145.0 (C-3''), 145.4 (C-4''), 147.7 (C-3), 154.7 (C-4a), 155.8 (C-4b), 175.7 (C-9) ppm. EI-MS: m/z (%) = 380 $[\text{M}]^{+}$ (100), 379 (17), 363 (16), 334 (12), 333 (15), 167 (13), 129 (17), 115 (11), 111 (16), 105 (17), 97 (23), 96 (12), 95 (16), 85 (16), 84 (48), 83 (27), 77 (12), 73 (18), 71 (21), 69 (31), 66 (35), 60 (29). HRMS (EI): calcd. for $\text{C}_{25}\text{H}_{16}\text{O}_4$ $[\text{M}]^{+}$ 380.1049; found 380.1048.

3-(3,4-Dihydroxyphenyl)-2-(4-hydroxyphenyl)-9H-xanthen-9-one (13k): Reaction time 3 h, 94% yield. This compound showed spectroscopic and analytical data identical to those previously reported.^[27]

2,3-Bis(3,4-dihydroxyphenyl)-9H-xanthen-9-one (13l): Reaction time 4 h, 70% yield; m.p. > 340 °C, dec. at 265 °C. ^1H NMR ($[\text{D}_6]\text{DMSO}$): δ = 6.42 (dd, J = 8.1, 2.1 Hz, 1 H, 6''-H), 6.53 (dd, J = 8.0, 2.2 Hz, 1 H, 6'-H), 6.61 (d, J = 2.1 Hz, 1 H, 2''-H), 6.65 (d, J = 2.2 Hz, 1 H, 2'-H), 6.66 (d, J = 8.0 Hz, 1 H, 5'-H), 6.68 (d, J = 8.1 Hz, 1 H, 5''-H), 7.50 (dt, J = 7.7, 0.8 Hz, 1 H, 7-H), 7.50 (s, 1 H, 4-H), 7.69 (d, J = 8.0 Hz, 1 H, 5-H), 7.89 (ddd, J = 8.0, 7.7, 1.7 Hz, 1 H, 6-H), 7.98 (s, 1 H, 1-H), 8.22 (dd, J = 7.7, 1.7 Hz, 1

H, 8-H), 8.95, 8.98 and 9.14 ($3 \times s$, 4 H, 3',4',3'',4''-OH) ppm. ^{13}C NMR ($[\text{D}_6]\text{DMSO}$): δ = 115.4 and 115.5 (C-5', C-5''), 116.8 (C-2', C-2''), 118.3 (C-5), 118.9 (C-4), 119.4 (C-9a), 120.6 (C-6'), 120.7 (C-6''), 121.3 (C-8a), 124.4 (C-7), 126.1 (C-8), 127.0 (C-1), 130.7 (C-1'), 131.1 (C-1''), 135.5 (C-6), 136.8 (C-3), 144.5 (C-4'), 144.9 (C-3', C-3''), 145.3 (C-4'), 147.6 (C-2), 154.3 (C-4a), 155.8 (C-4b), 175.8 (C-9) ppm. EI-MS: m/z (%) = 412 $[\text{M}]^+$ (79), 396 (17), 395 (16), 365 (15), 213 (26), 199 (17), 185 (30), 171 (25), 157 (20), 151 (18), 147 (17), 143 (22), 141 (17), 139 (19), 137 (22), 135 (20), 133 (20), 129 (43), 125 (31), 123 (31), 121 (30), 115 (23), 112 (32), 111 (60), 98 (96), 97 (89), 83 (100), 69 (30), 67 (33). HRMS (EI): calcd. for $\text{C}_{25}\text{H}_{16}\text{O}_6$ $[\text{M}]^+$ 412.0947; found 412.0955.

6-Hydroxy-2,3-diphenyl-9H-xanthen-9-one (13m): Reaction time 72 h, 37% yield. ^1H NMR ($[\text{D}_6]\text{DMSO}$): δ = 6.91 (d, J = 2.1 Hz, 1 H, 5-H), 6.94 (dd, J = 8.7, 2.1 Hz, 1 H, 7-H), 7.13–7.16 (m, 2 H, 2',6'-H), 7.20–7.23 (m, 2 H, 2'',6''-H), 7.26–7.31 (m, 6 H, 3',4',5'-H, 3'',4'',5''-H), 7.63 (s, 1 H, 4-H), 8.07 (s, 1 H, 1-H), 8.08 (d, J = 8.7 Hz, 1 H, 8-H), 11.04 (s, 1 H, 6-OH) ppm. ^{13}C NMR ($[\text{D}_6]\text{DMSO}$): δ = 102.8 (C-5), 114.1 (C-7), 114.3 (C-8a), 119.4 (C-4), 120.2 (C-9a), 127.0 (C-4'), 127.4 (C-1), 127.7 (C-4''), 128.1 (C-8), 128.2 (C-3',5', C-3'',5''), 129.4 (C-2',6'), 129.5 (C-2'',6''), 136.4 (C-2), 139.3 (C-1'), 139.7 (C-1''), 146.5 (C-3), 154.7 (C-4a), 157.8 (C-4b), 164.1 (C-6), 174.5 (C-9) ppm.

1-Hydroxy-6,7-diphenyl-9H-xanthen-9-one (12n, 13n): Reaction time 1 h, 63% yield, see spectroscopic characterisation above. Also occurs as a by-product in the synthesis of 1-hydroxy-6,7-diphenyl-9H-xanthen-9-one (5n).

1-Hydroxy-7-(4-hydroxyphenyl)-6-phenyl-9H-xanthen-9-one (13o): Reaction time 2 h, 90% yield; m.p. 130–133 °C. ^1H NMR ($[\text{D}_6]\text{DMSO}$): δ = 6.63 (d, J = 8.4 Hz, 2 H, 3',5'-H), 6.79 (d, J = 8.4 Hz, 1 H, 7-H), 6.87 (d, J = 8.4 Hz, 2 H, 2',6'-H), 7.00 (d, J = 8.3 Hz, 1 H, 5-H), 7.15–7.18 (m, 2 H, 2'',6''-H), 7.29–7.31 (m, 3 H, 3',4',5''-H), 7.49 (s, 1 H, 4-H), 7.70 (dd, J = 8.4, 8.3 Hz, 1 H, 6-H), 7.91 (s, 1 H, 1-H), 12.49 (s, 1 H, 8-OH) ppm. ^{13}C NMR ($[\text{D}_6]\text{DMSO}$): δ = 107.6 (C-5), 108.6 (C-8a), 110.6 (C-7), 115.4 (C-3',5'), 118.9 (C-9a), 119.5 (C-4), 126.5 (C-1), 128.1 (C-4'), 128.5 (C-3'',5''), 129.6 (C-2',6'), 130.1 (C-1'), 130.9 (C-2',6'), 137.1 (C-2), 137.8 (C-6), 139.6 (C-1''), 148.2 (C-3), 154.6 (C-4a), 156.1 (C-4b), 156.8 (C-4'), 161.2 (C-8), 181.6 (C-9) ppm. EI-MS: m/z (%) = 380 $[\text{M}]^+$ (100), 379 (20), 351 (6). HRMS (EI): calcd. for $\text{C}_{25}\text{H}_{16}\text{O}_4$ $[\text{M}]^+$ 380.1049; found 380.1046.

7-(3,4-Dihydroxyphenyl)-1-hydroxy-6-phenyl-9H-xanthen-9-one (13p): Reaction time 3 h, 83% yield; m.p. 222–224 °C. ^1H NMR ($[\text{D}_6]\text{DMSO}$): δ = 6.32 (dd, J = 8.1, 2.1 Hz, 1 H, 6'-H), 6.54 (d, J = 2.1 Hz, 1 H, 2'-H), 6.60 (d, J = 8.1 Hz, 1 H, 5'-H), 6.79 (d, J = 8.3 Hz, 1 H, 7-H), 7.01 (d, J = 8.3 Hz, 1 H, 5-H), 7.17–7.20 (m, 2 H, 2'',6''-H), 7.30–7.32 (m, 3 H, 3',4',5''-H), 7.48 (s, 1 H, 4-H), 7.70 (t, J = 8.3 Hz, 1 H, 6-H), 7.91 (s, 1 H, 1-H), 12.48 (s, 1 H, 8-OH) ppm. ^{13}C NMR ($[\text{D}_6]\text{DMSO}$): δ = 107.8 (C-5), 108.7 (C-8a), 110.7 (C-7), 115.8 (C-5'), 117.3 (C-2'), 118.9 (C-9a), 119.6 (C-4), 121.2 (C-6'), 126.6 (C-1), 128.3 (C-4'), 128.7 (C-3'',5''), 129.6 (C-2'',6''), 130.9 (C-1'), 137.4 (C-2), 138.0 (C-6), 139.7 (C-1''), 145.0 (C-4'), 145.3 (C-3'), 148.3 (C-3), 154.7 (C-4a), 156.2 (C-4b), 161.2 (C-8), 181.7 (C-9) ppm. EI-MS: m/z (%) = 396 $[\text{M}]^+$ (100), 380 (15), 379 (15), 349 (16), 213 (27), 199 (18), 185 (19), 171 (24), 157 (20), 147 (40), 143 (25), 137 (28), 129 (40), 125 (32), 123 (29), 121 (34), 111 (48), 98 (77), 97 (98), 96 (45), 95 (53), 85 (36), 83 (77), 81 (47), 73 (40), 67 (29). HRMS (EI): calcd. for $\text{C}_{25}\text{H}_{16}\text{O}_5$ $[\text{M}]^+$ 396.0998; found 396.0996.

6-(3,4-Dihydroxyphenyl)-1-hydroxy-7-phenyl-9H-xanthen-9-one (13q): Reaction time 3 h, 71% yield; m.p. 205–207 °C. ^1H NMR ($[\text{D}_6]\text{DMSO}$): δ = 6.47 (dd, J = 8.2, 2.2 Hz, 1 H, 6''-H), 6.61 (d, J

= 2.2 Hz, 1 H, 2''-H), 6.65 (d, J = 8.2 Hz, 1 H, 5''-H), 6.84 (dd, J = 8.2, 0.6 Hz, 1 H, 7-H), 7.09 (d, J = 8.2 Hz, 1 H, 5-H), 7.17–7.20 (m, 2 H, 2',6'-H), 7.28–7.36 (m, 3 H, 3',4',5'-H), 7.54 (s, 1 H, 4-H), 7.75 (t, J = 8.2 Hz, 1 H, 6-H), 8.01 (s, 1 H, 1-H), 8.99 and 9.20 ($2 \times \text{brs}$, 2 H, 3'',4''-OH), 12.59 (s, 1 H, 8-OH) ppm. ^{13}C NMR ($[\text{D}_6]\text{DMSO}$): δ = 107.4 (C-5), 108.4 (C-8a), 110.4 (C-7), 115.5 (C-5'), 116.9 (C-2''), 118.3 (C-9a), 118.8 (C-4), 120.9 (C-6''), 126.7 (C-1), 127.1 (C-4'), 128.3 (C-3',5'), 129.3 (C-2',6'), 130.1 (C-1''), 136.7 (C-2), 137.5 (C-6), 139.8 (C-1'), 145.0 (C-3''), 145.5 (C-4'), 148.6 (C-3), 154.8 (C-4a), 155.9 (C-4b), 161.0 (C-8), 181.4 (C-9) ppm. EI-MS: m/z (%) = 396 $[\text{M}]^+$ (100), 395 (7), 380 (9), 379 (9), 349 (7). HRMS (EI): calcd. for $\text{C}_{25}\text{H}_{16}\text{O}_5$ $[\text{M}]^+$ 396.0998; found 396.1003.

1-Hydroxy-6,7-bis(3,4-dihydroxyphenyl)-9H-xanthen-9-one (13r): Reaction time 5 h, 90% yield; m.p. > 340 °C, dec. at 305 °C. ^1H NMR ($[\text{D}_6]\text{DMSO}$): δ = 6.42 (dd, J = 8.0, 2.1 Hz, 1 H, 6'-H), 6.52 (dd, J = 8.2, 2.2 Hz, 1 H, 6''-H), 6.60 (d, J = 2.1 Hz, 1 H, 2'-H), 6.65 (d, J = 2.2 Hz, 1 H, 2''-H), 6.66 (d, J = 8.0 Hz, 1 H, 5'-H), 6.68 (d, J = 8.2 Hz, 1 H, 5''-H), 6.84 (dd, J = 8.4, 0.7 Hz, 1 H, 7-H), 7.09 (dd, J = 8.4, 0.7 Hz, 1 H, 5-H), 7.49 (s, 1 H, 4-H), 7.74 (t, J = 8.4 Hz, 1 H, 6-H), 7.95 (s, 1 H, 1-H), 8.95 (s, 1 H, 4'-OH), 8.98 (s, 1 H, 4''-OH), 9.00 and 9.17 ($2 \times s$, 2 H, 3',3''-OH), 12.63 (s, 1 H, 8-OH) ppm. ^{13}C NMR ($[\text{D}_6]\text{DMSO}$): δ = 107.4 (C-5), 108.4 (C-8a), 110.3 (C-7), 115.46 and 115.53 (C-5', C-5''), 116.8 (C-2', C-2''), 118.2 (C-9a), 118.7 (C-4), 120.5 (C-6'), 120.7 (C-6''), 126.3 (C-1), 130.5 (C-1'), 130.9 (C-1''), 137.0 (C-2), 137.4 (C-6), 144.6 (C-4'), 144.9 and 145.0 (C-3', C-3''), 145.4 (C-4''), 148.5 (C-3), 154.4 (C-4a), 156.0 (C-4b), 161.0 (C-8), 181.5 (C-9) ppm. EI-MS: m/z (%) = 428 $[\text{M}]^+$ (100), 396 (24), 381 (18), 213 (24), 191 (21), 185 (30), 129 (43), 125 (25), 123 (27), 121 (27), 115 (20), 112 (32), 111 (46), 107 (25), 105 (24), 98 (75), 97 (92), 95 (43), 85 (33), 83 (83), 81 (37), 73 (34), 71 (36), 67 (30). HRMS (EI): calcd. for $\text{C}_{25}\text{H}_{16}\text{O}_7$ $[\text{M}]^+$ 428.0896; found 428.0888.

1,3-Dihydroxy-6,7-diphenyl-9H-xanthen-9-one (13s): Reaction time 120 h, 60% yield. ^1H NMR ($[\text{D}_6]\text{DMSO}$): δ = 6.24 (d, J = 1.9 Hz, 1 H, 7-H), 6.43 (d, J = 1.9 Hz, 1 H, 5-H), 7.13–7.31 (m, 10 H, 2,3-C₆H₅), 7.61 (s, 1 H, 4-H), 8.02 (s, 1 H, 1-H), 11.23 (brs, 1 H, 6-OH), 12.80 (s, 1 H, 8-OH) ppm. ^{13}C NMR ($[\text{D}_6]\text{DMSO}$): δ = 94.3 (C-5), 98.3 (C-7), 102.4 (C-8a), 118.9 (C-4), 119.2 (C-9a), 126.6 (C-1), 127.2 (C-4'), 127.9 (C-4''), 128.3 (C-3',5', C-3'',5''), 129.5 (C-2'',6''), 129.6 (C-2',6'), 136.6 (C-2), 139.2 (C-1'), 139.5 (C-1''), 147.3 (C-3), 154.5 (C-4a), 157.6 (C-4b), 162.9 (C-8), 166.0 (C-6), 179.4 (C-9) ppm. EI-MS: m/z (%) = 380 $[\text{M}]^+$ (100), 379 (35), 365 (7), 228 (5), 84 (10), 66 (11). HRMS (EI): calcd. for $\text{C}_{25}\text{H}_{16}\text{O}_4$ $[\text{M}]^+$ 380.1049; found 380.1045.

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