

# Synthesis of C-ring substituted xanthenes from the [4 + 2] cycloaddition reaction of vinylchromones and acyclic enamines

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A novel approach to the synthesis of C-ring substituted xanthenes utilising the [4 + 2] cycloaddition reactions of enamines with aromatically substituted vinylchromones has been developed. 1-Methyl-, 1-ethyl-, 2-methyl- and 2-ethyl-substituted xanthenes are obtained in a one-pot synthesis from the reaction of pyrrolidine enamines derived from acetone, butan-2-one, propanal and butanal respectively, when taken as solvent incorporating a catalytic amount of pyrrolidine. Some 1-methylidene- and 1-methylidene-2-methyl-substituted tetrahydroxanthenes were also obtained and these compounds are proposed to be intermediates in the reaction, since they undergo facile conversion to 1-methyl- and 1,2-dimethyl-xanthenes. Further evidence for the proposed reaction pathway was obtained from the isolation of a 1-pyrrolidino-2,2-dimethyl substituted tetrahydroxanthone from the reaction between a vinylchromone and the pyrrolidine enamine of 2-methylpropanal.

## Introduction

The xanthenes are a large group of natural products with varied biological activities.<sup>1</sup> General synthetic approaches to xanthenes have been reviewed<sup>2,3</sup> and several syntheses of alkyl-substituted xanthone natural products have been reported in the literature.<sup>4</sup> 2-Vinylchromones have often been used as starting materials for synthesis of xanthenes<sup>5,6</sup> and Letcher<sup>7,8</sup> has recently reported the effective use of the Diels–Alder reactions of 2-vinylchromones and pre-formed cycloalkylenamines in the synthesis of cycloalkano[a]xanthenes. In continuation of these studies we herein report a modified procedure employing 2-vinylchromones (**1a–1k**) and enamines which are obtained *in situ* from the corresponding alkyl ketones or aldehydes in the presence of a catalytic amount of pyrrolidine, to synthesise 1-methyl- (**2a–2j**), 2-methyl- (**8a**), 1,2-dimethyl- (**7a**), 1-ethyl- (**5b**, **5f** and **5i**) and 2-ethyl- (**9b**) substituted xanthenes in a one-pot process.

## Results and discussion

The synthesis of 1-methyl-3-phenylxanthone (**2a**) was achieved in good yield by refluxing 2-styrylchromone (**1a**) and 2-pyrrolidinoprop-1-ene, which was generated *in situ* from acetone (taken as solvent) and a catalytic quantity of pyrrolidine (Scheme 1). The structure of **2a**—in particular the location of the methyl substituent at the 1-position of the xanthone C-ring—was rigorously established by 2D-NMR, which also resulted in unambiguous <sup>1</sup>H and <sup>13</sup>C NMR assignments for all resonances (see Tables 1 and 2). Several other xanthenes which are variously substituted at the 3-position and in the xanthone A-ring (**2b–2j**) were obtained in similar yields by this procedure. NMR spectra of these compounds (Tables 1 and 2) have been assigned by analogy with compound **2a**: in all cases the methyl group was found to be substituted at the 1-position.

An additional kind of reaction product incorporating a methylidene group substituted on a tetrahydroxanthone

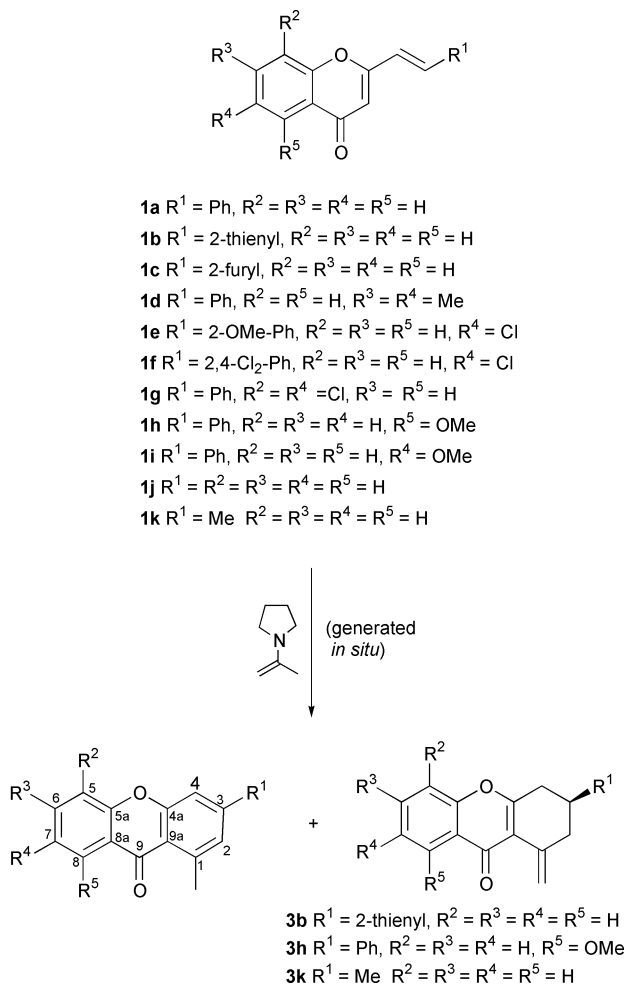
nucleus was also isolated in low yield from the reaction of compounds **1b** and **1h** (yielding **3b** and **3h** respectively). This class of product is believed to be the precursor to the fully aromatised 1-methylxanthenes (**2a–2j**) - *via* migration of the exocyclic double bond and oxidation of the C-ring (Fig. 1) (facile dehydrogenation of di- and tetrahydroxanthenes has been observed previously).<sup>6</sup> Indeed, the 1-methylidene-tetrahydroxanthone **3k** was the only product isolated from the reaction of vinylchromone **1k**. 1-Methyl-3-arylxanthenes **2b** and **2h** were readily obtained by treating the corresponding 1-methylidene-tetrahydroxanthone side-products **3b** and **3h** with strong acid; the conversion was followed by observing the disappearance in the <sup>1</sup>H NMR spectrum of the *exo*-methylene signals at  $\delta_{\text{H}}$  6.7 and 5.3 ppm (the large difference in the observed chemical shift of the two alkene protons arises because of the proximity of one member of the pair to the carbonyl group, which is consistent with the location of this substituent at the 1-position) and the appearance of a methyl singlet at  $\delta_{\text{H}}$  3.0 ppm.

It was anticipated that if butan-2-one was used as the solvent in place of acetone, with pyrrolidine as catalyst, then 2-styrylchromone (**1a**) would yield the corresponding 1,2-dimethyl-substituted xanthone directly. Somewhat surprisingly, this reaction instead yielded the 1-methylidene-2-methyltetrahydroxanthone **4a** in moderate yield (Scheme 2). As previously, the structure of **4a** was rigorously characterized by 2D-NMR and, in particular, it was possible to unambiguously confirm the location of the methylidene group at the 1-position and the methyl group at the 2-position (see Tables 3 and 4 for complete <sup>1</sup>H and <sup>13</sup>C NMR assignments). As noted above, compound **4a** probably represents the initial product of elimination of pyrrolidine from the Diels–Alder adduct (Fig. 1), which in this case has failed to undergo subsequent rearrangement and aromatisation under the conditions of the reaction. This finding was quite general and tetrahydroxanthenes **4b**, **4c**, **4f**, **4i** and **4k** were obtained from chromones **1b**, **1c**, **1f**, **1i** and **1k** respectively, in comparable yields. NMR assignments of **4b**, **4c**, **4f**, **4i** and **4k** (Tables 3 and 4) were made by analogy with **4a**, and were consistent with 1-methylidene- and 2-methyl-substitution of the xanthone C-ring in all cases.

The 1-methylidene-2-methyltetrahydroxanthone **4a** could easily be converted to the desired 1,2-dimethylxanthone **7a**

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- 2a** R<sup>1</sup> = Ph, R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = R<sup>5</sup> = H  
**2b** R<sup>1</sup> = 2-thienyl, R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = R<sup>5</sup> = H  
**2c** R<sup>1</sup> = 2-furyl, R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = R<sup>5</sup> = H  
**2d** R<sup>1</sup> = Ph, R<sup>2</sup> = R<sup>5</sup> = H, R<sup>3</sup> = R<sup>4</sup> = Me  
**2e** R<sup>1</sup> = 2-OMe-Ph, R<sup>2</sup> = R<sup>3</sup> = R<sup>5</sup> = H, R<sup>4</sup> = Cl  
**2f** R<sup>1</sup> = 2,4-Cl<sub>2</sub>-Ph, R<sup>2</sup> = R<sup>3</sup> = R<sup>5</sup> = H, R<sup>4</sup> = Cl  
**2g** R<sup>1</sup> = Ph, R<sup>2</sup> = R<sup>4</sup> = Cl, R<sup>3</sup> = R<sup>5</sup> = H  
**2h** R<sup>1</sup> = Ph, R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H, R<sup>5</sup> = OMe  
**2i** R<sup>1</sup> = Ph, R<sup>2</sup> = R<sup>3</sup> = R<sup>5</sup> = H, R<sup>4</sup> = OMe  
**2j** R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = R<sup>5</sup> = H

Scheme 1

(fully assigned by 2D-NMR) by treatment with strong acid (Scheme 3). Quenching the reaction after a short period of time also yielded 1,2-dimethyl-3-phenyl-3,4-dihydroxanthene-9-one **6a** as a minor product. Treatment of **6a** with acid gave **7a** in almost quantitative yields, thus establishing its status as a reaction intermediate, and confirming that aromatisation of the xanthone C-ring occurs by conversion of an exocyclic to an endocyclic double bond. Logically, this endocyclic diene must then undergo oxidation to the resulting xanthone (Fig. 1), although this was not explicitly demonstrated.

1-Ethyl-substituted xanthenes (Scheme 2) were also recorded as minor side-products from the reaction of vinylchromone substrates **1b**, **1f** and **1i** with the pyrrolidine enamine of butan-2-one. It is known that more than one isomer may sometimes be produced during enamine formation with acyclic ketones;<sup>9</sup> we propose that although the (*E*)-isomer of 2-pyrrolidinobut-2-ene is the major component of this reaction, small amounts of the terminal methylene isomer (2-pyrrolidinobut-1-ene) are also formed. The isolation of 1-ethyl-substituted xanthenes **5b**, **5f** and **5i** requires that this less substituted enamine must also be generated in significant quantities under the conditions of

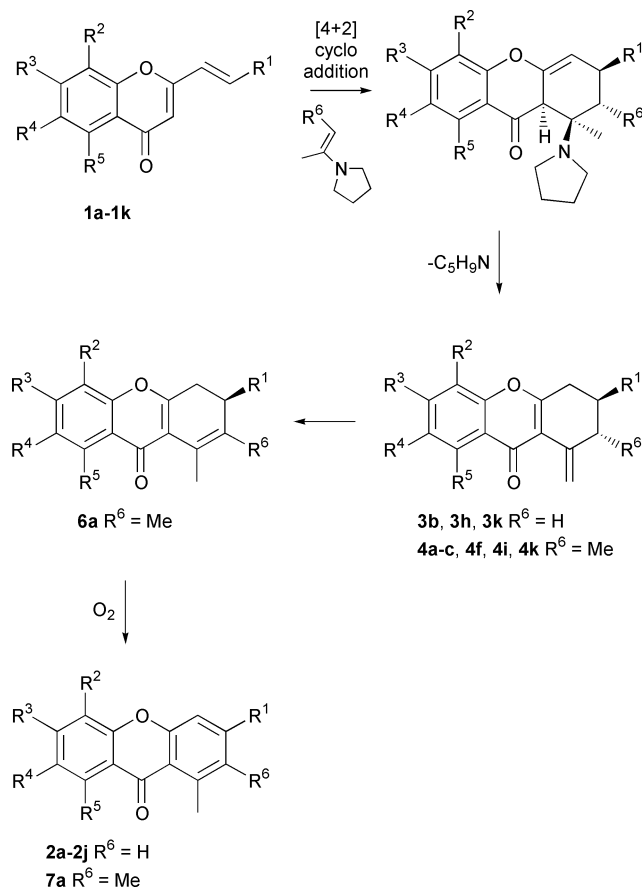
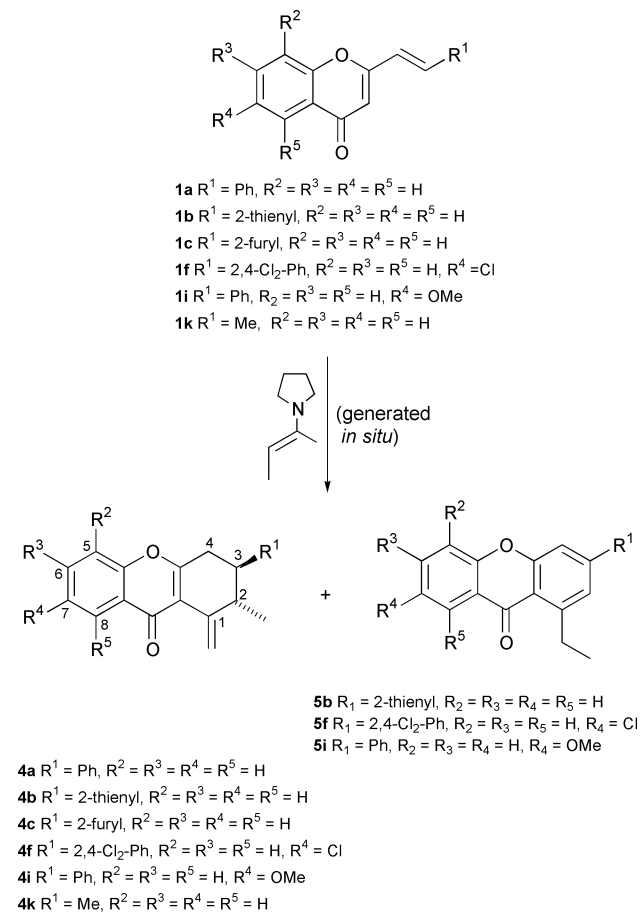


Fig. 1 Proposed mechanism involved in the formation of 1-methyl- and 1,2-dimethyl-substituted xanthenes from vinylchromones and acyclic ketones in the presence of pyrrolidine.



Scheme 2

**Table 1** <sup>1</sup>H NMR assignments for 1-methylxanthenes **2a–2j**<sup>a</sup>

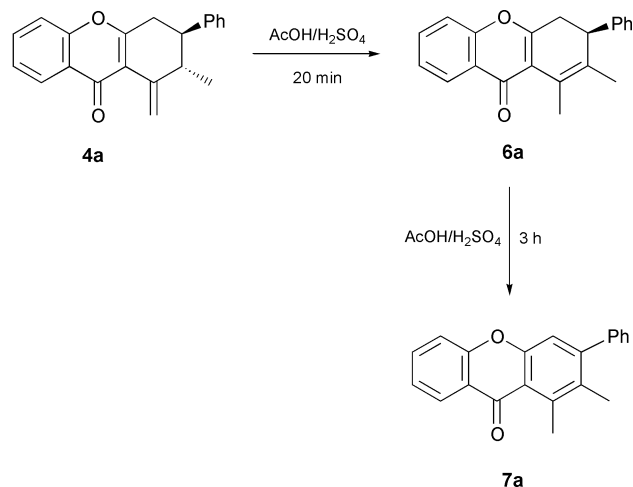
Atom	<b>2a</b>	<b>2b</b>	<b>2c</b>	<b>2d</b>	<b>2e</b>	<b>2f</b>	<b>2g</b>	<b>2h</b>	<b>2i</b>	<b>2j</b>
2	7.33 (d, <i>J</i> = 1.6 Hz)	7.33 (d, <i>J</i> = 1.5 Hz)	7.31 (d, <i>J</i> = 1.1 Hz)	7.35 (s)	7.31 (d, <i>J</i> = 0.9 Hz)	7.34 (d, <i>J</i> = 1.7 Hz)	7.39 (d, <i>J</i> = 1.4 Hz)	7.32 (d, <i>J</i> = 1.4 Hz)	7.34 (d, <i>J</i> = 1.2 Hz)	7.31 <sup>b</sup> (dd, <i>J</i> = 8.3, 1.5 Hz)
3	—	—	—	—	—	—	—	—	—	7.53 (dd, <i>J</i> = 8.3, 7.5 Hz)
4	7.51 (d, <i>J</i> = 1.6 Hz)	7.51 (d, <i>J</i> = 1.5 Hz)	7.51 (d, <i>J</i> = 1.1 Hz)	7.58 (s)	7.53 (d, <i>J</i> = 0.9 Hz)	7.53 (d, <i>J</i> = 1.7 Hz)	7.61 (d, <i>J</i> = 1.4 Hz)	7.47 (d, <i>J</i> = 1.4 Hz)	7.52 (d, <i>J</i> = 1.2 Hz)	7.11 <sup>b</sup> (dd, <i>J</i> = 7.5, 1.5 Hz)
5	7.44 (d, <i>J</i> = 7.5 Hz)	7.40 (d, <i>J</i> = 8.5 Hz)	7.37 (d, <i>J</i> = 8.0 Hz)	7.35 (br s)	7.39 (d, <i>J</i> = 8.8 Hz)	7.39 (d, <i>J</i> = 8.9 Hz)	—	7.02 <sup>b</sup> (dd, <i>J</i> = 8.3, 0.8 Hz)	7.38 (d, <i>J</i> = 9.0 Hz)	7.42 (d, <i>J</i> = 8.1 Hz)
6	7.66 (ddd, <i>J</i> = 7.5, 7.5, 1.5 Hz)	7.66 (ddd, <i>J</i> = 8.5, 7.5, 1.6 Hz)	7.63 (ddd, <i>J</i> = 8.0, 7.5, 1.5 Hz)	—	7.61 (dd, <i>J</i> = 8.8, 2.6 Hz)	7.62 (dd, <i>J</i> = 8.9, 2.6 Hz)	7.69 (d, <i>J</i> = 2.1 Hz)	7.57 (dd, <i>J</i> = 8.3, 8.3 Hz)	7.29 (dd, <i>J</i> = 9.0, 1.8 Hz)	7.67 (ddd, <i>J</i> = 8.1, 7.2, 1.6 Hz)
7	7.33 (dd, <i>J</i> = 7.5, 7.5 Hz)	7.33 (dd, <i>J</i> = 7.5, 7.5 Hz)	7.29 (dd, <i>J</i> = 8.0, 7.5 Hz)	—	—	—	—	6.78 <sup>b</sup> (dd, <i>J</i> = 8.3, 0.8 Hz)	—	7.33 (dd, <i>J</i> = 8.0, 7.2 Hz)
8	8.27 (dd, <i>J</i> = 7.5, 1.5 Hz)	8.25 (dd, <i>J</i> = 7.5, 1.6 Hz)	8.22 (dd, <i>J</i> = 8.0, 1.5 Hz)	7.92 (s)	8.24 (d, <i>J</i> = 2.6 Hz)	8.21 (d, <i>J</i> = 2.6 Hz)	8.11 (d, <i>J</i> = 2.1 Hz)	—	7.67 (d, <i>J</i> = 1.8 Hz)	8.27 (dd, <i>J</i> = 8.0, 1.6 Hz)
1-Me	2.97 (3H, s)	2.95 (3H, s)	2.91 (3H, s)	2.99 (3H, s)	2.97 (3H, s)	2.96 (3H, s)	2.95 (3H, s)	2.98 (3H, s)	3.00 (3H, s)	2.93 (3H, s)
2'	7.67 (dd, <i>J</i> = 7.5, 1.5 Hz)	—	—	7.69 (d, <i>J</i> = 7.6 Hz)	—	—	7.68 (d, <i>J</i> = 7.8 Hz)	7.68 (dd, <i>J</i> = 7.5, 1.7 Hz)	7.68 (d, <i>J</i> = 8.0 Hz)	—
3'	7.49 (dd, <i>J</i> = 7.5, 7.5 Hz)	7.48 <sup>b</sup> (dd, <i>J</i> = 3.7, 1.0 Hz)	6.82 (d, <i>J</i> = 3.4 Hz)	7.50 (d, <i>J</i> = 7.5, 7.5 Hz)	7.02 (d, <i>J</i> = 8.0 Hz)	7.17 (s)	7.49 (dd, <i>J</i> = 7.8, 7.8 Hz)	7.49 (dd, <i>J</i> = 7.5, 7.5 Hz)	7.49 (dd, <i>J</i> = 8.0, 7.5 Hz)	—
4'	7.42 (dddd, <i>J</i> = 7.5, 7.5, 1.5, 1.5 Hz)	7.13 (dd, <i>J</i> = 4.9, 3.7 Hz)	6.52 (dd, <i>J</i> = 3.4, 1.5 Hz)	7.43 (dd, <i>J</i> = 7.5, 7.5 Hz)	7.39 (dd, <i>J</i> = 8.0, 7.5 Hz)	—	7.46 (dd, <i>J</i> = 7.8, 7.8 Hz)	7.42 (dddd, <i>J</i> = 7.5, 7.5, 1.7, 1.7 Hz)	7.43 (dd, <i>J</i> = 7.5, 7.5 Hz)	—
5'	7.49 (dd, <i>J</i> = 7.5, 7.5 Hz)	7.39 <sup>b</sup> (dd, <i>J</i> = 4.9, 1.0 Hz)	7.52 (d, <i>J</i> = 1.5 Hz)	7.50 (d, <i>J</i> = 7.5, 7.5 Hz)	7.07 (dd, <i>J</i> = 7.5, 7.5 Hz)	7.40 <sup>b</sup> (d, <i>J</i> = 8.5 Hz)	7.49 (dd, <i>J</i> = 7.8, 7.8 Hz)	7.49 (dd, <i>J</i> = 7.5, 7.5 Hz)	7.49 (dd, <i>J</i> = 8.0, 7.5 Hz)	—
6'	7.67 (dd, <i>J</i> = 7.5, 1.5 Hz)	—	—	7.69 (d, <i>J</i> = 7.6 Hz)	7.38 (d, <i>J</i> = 7.5 Hz)	7.35 <sup>b</sup> (d, <i>J</i> = 8.5 Hz)	7.68 (d, <i>J</i> = 7.8 Hz)	7.68 (dd, <i>J</i> = 7.5, 1.7 Hz)	7.68 (d, <i>J</i> = 8.0 Hz)	—
Others	—	—	—	2.51 <sup>b</sup> (3H, s) 6-Me; 2.42 <sup>b</sup> (3H, s) 7-Me	3.86 (3H, s) 2'-OMe	—	—	4.03 (3H, s) 8-OMe	3.91 (3H, s) 7-OMe	—

<sup>a</sup> Splitting pattern and coupling in Hz indicated in parentheses. <sup>b</sup> Interchangeable within column.

**Table 2**  $^{13}\text{C}$  NMR assignments for 1-methylxanthenes **2a–2j**<sup>a</sup>

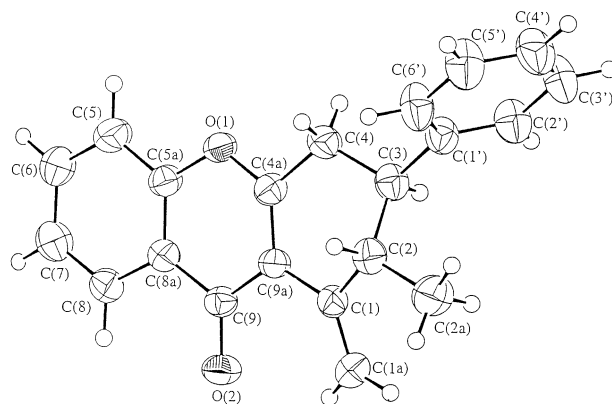
Atom	2a	2b	2c	2d	2e	2f	2g	2h	2i	2j
1 (C)	142.5	142.7	142.5	142.3	141.6	142.3	142.7	142.4	142.3	142.1
2 (CH)	125.6	128.4 <sup>b</sup>	121.8	125.4	126.1 <sup>c</sup>	128.1	124.9	125.8	125.5	126.7 <sup>b</sup>
3 (C)	146.4	142.1	135.2	146.1	144.7	144.0	147.1	145.9	146.2	133.7 (CH) <sup>b</sup>
4 (CH)	114.0	112.1	112.2	114.1	116.8 <sup>d</sup>	116.9	114.2	113.4	114.0	116.1
4a (C)	157.9	157.9	157.9	157.8	157.2	157.1	157.4	157.5	157.9	157.6
5a (C)	155.4	155.3	155.3	152.1	156.5	153.8	149.7	156.8	155.9	155.4
5 (CH)	117.4	117.3	117.3	123.6	119.2 <sup>d</sup>	119.3	123.4 (C)	109.6 <sup>b</sup>	124.3	117.5
6 (CH)	134.3	134.2	134.1	132.8 (C) <sup>b</sup>	134.3	134.6	134.1	134.4	105.9 <sup>b</sup>	134.4
7 (CH)	123.7	123.7	123.6	126.4 (C) <sup>b</sup>	129.4 (C) <sup>b</sup>	129.7 (C) <sup>c</sup>	123.4 (C)	105.2 <sup>b</sup>	150.2 (C)	123.7
8 (CH)	126.7	126.6	126.6	136.5	121.0 <sup>c</sup>	126.2	126.3	160.7 (C)	118.9 <sup>b</sup>	126.8
8a (C)	122.9	122.9	122.9	122.4	123.8	123.7	124.5	120.2 <sup>c</sup>	123.2	122.8
9 (C)	178.6	178.2	178.2	179.1	177.5	177.5	176.6	178.6	178.5	178.8
9a (C)	119.0	118.9	118.9	118.8	118.5	Nr	118.2	118.4 <sup>c</sup>	118.5	120.3
1-Me (CH <sub>3</sub> )	23.5	23.4	23.5	23.5	23.4	23.4	23.4	23.7	23.5	23.3
1' (C)	139.1	—	—	139.3	130.7 <sup>b</sup>	134.9 (C) <sup>b</sup>	138.6	139.3	139.2	—
2' (CH)	127.3	139.2 (C)	152.1 (C)	127.3	153.9 (C)	127.7 (C) <sup>b</sup>	127.3	127.3	127.3	—
3' (CH)	129.0	125.2 <sup>b</sup>	110.2 <sup>b</sup>	129.0	111.4	127.4 <sup>c</sup>	129.1	129.0	129.0	—
4' (CH)	128.6	124.0 <sup>b</sup>	108.3 <sup>b</sup>	128.5	129.9 <sup>c</sup>	133.1 (C) <sup>b</sup>	128.9	128.5	128.6	—
5' (CH)	129.0	126.9 <sup>b</sup>	143.6	129.0	128.5 <sup>c</sup>	130.1 <sup>c</sup>	129.1	129.0	129.0	—
6' (CH)	127.3	—	—	127.3	128.6 <sup>c</sup>	131.8 <sup>c</sup>	127.3	127.3	127.3	—
Others				20.9 (CH <sub>3</sub> ) <sup>c</sup> 6-Me 15.6 (CH <sub>3</sub> ) <sup>c</sup> 7-Me	55.6 (CH <sub>3</sub> ) 2'-OMe			56.4 (CH <sub>3</sub> ) 8-OMe	55.9 (CH <sub>3</sub> ) 7-OMe	

<sup>a</sup> Multiplicity determined from DEPT. <sup>bcd</sup> Interchangeable within column; Nr = not resolved.



reaction when pyrrolidine is employed as catalyst because this is the only way to account for formation of such xanthenes if a Diels–Alder process is invoked (*cf.* Fig. 1).

The X-ray structure of the 1-methylidene-2-methyltetrahydroxanthone **4a** (Fig. 2) indicated a *trans* geometry between the aromatic 3-substituent and the 2-methyl group (and also showed that the *exo*-methylene group is not co-planar with respect to the chromone system). This relative stereochemistry for **4a** can be explained by assuming that [4 + 2] inverse electron demand cycloaddition of the (*E*)-isomer of the enamine derived from pyrrolidine and methyl ethyl ketone over the diene system of the chromone **1a** occurs regioselectively such that the pyrrolidine is located at the 1-position in the initial addition product (as already indicated) and from an *endo* transition state, which would account for the *trans* stereochemistry observed between the 3-R- and the 2-methyl substituents in the newly formed ring. An alternative mechanism, which cannot be ruled out on the basis of our results, is that of a stepwise 1,6-conjugate addition of the enamine to the vinylchromone, resulting in a six-membered ring in which the 3-R- and 2-methyl substituents adopt the thermodynamically more stable *trans* configuration.

**Fig. 2** ORTEP diagram for **4a**.

Thus, 1-methylxanthenes and 1,2-dimethylxanthenes can be synthesized in good to moderate yields in one or two steps respectively from the reaction of vinylchromones and acyclic ketones in the presence of a catalytic amount of pyrrolidine (1-ethyl-substituted xanthenes are obtained as side-products in a few cases). A slight modification to this strategy was required in order to synthesise 2-methyl- and 2-ethyl-xanthenes. Since the regioselectivity and stereoselectivity in the [4 + 2] cycloaddition reaction of enamine and vinylchromone is expected to remain fixed (as discussed above), the synthesis of 2-alkylxanthenes is only possible from an enamine in which the pyrrolidine group is located at the end of the alkyl chain *i.e.* enamines generated from aldehydes rather than ketones should give 2-alkyl-substituted xanthenes. This was indeed found to be the case and two examples of this reaction, using propanal and butanal as solvent in the presence of a catalytic amount of pyrrolidine, for the formation of 2-methyl- and 2-ethyl-xanthenes **8a** and **9b** respectively, are shown in Scheme 4. An extension of this procedure was used to further confirm the reaction mechanism proposed in Fig. 1. Thus, when 2-styrylchromone (**1a**) is treated with the pyrrolidine enamine of 2-methylpropanal (Scheme 4) elimination of pyrrolidine from the predicted Diels–Alder adduct should be impossible since there are no hydrogens available  $\alpha$  to the nitrogen atom to participate in this reaction (the 2-position

**Table 3** <sup>1</sup>H NMR assignments for 1-methylenexanthones **3b**, **3h**, **3k**, **4a–c**, **4f**, **4i** and **4k**<sup>a</sup>

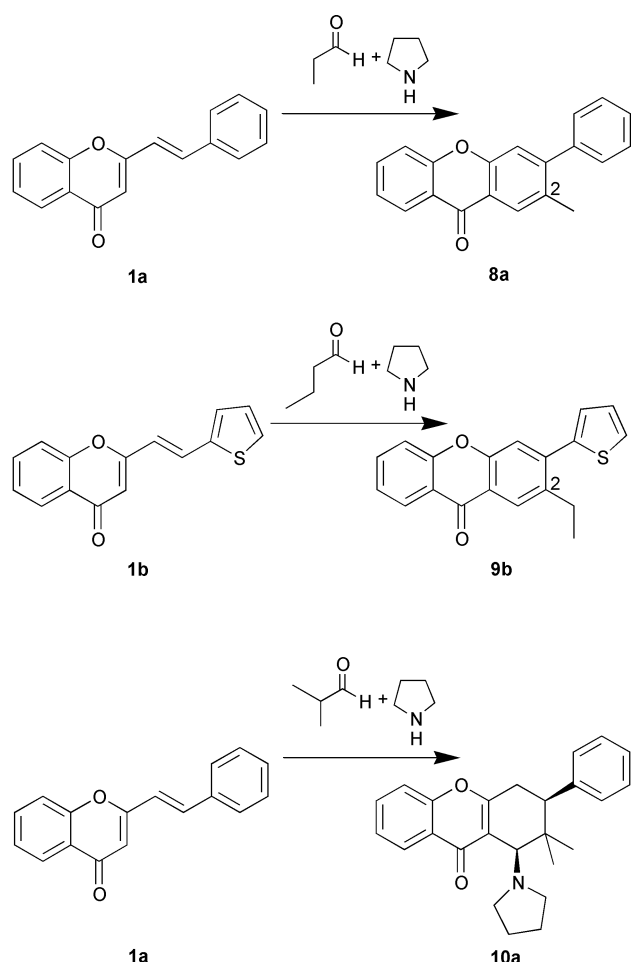
Atom	<b>3b</b>	<b>3h</b>	<b>3k</b>	<b>4a</b>	<b>4b</b>	<b>4c</b>	<b>4f</b>	<b>4i</b>	<b>4k</b>
2 $\alpha$	2.85 (dd, $J = 14.0$ , 1.9 Hz)	2.70–2.65 (2H, m)	2.51 (dd, $J = 18.7$ , 5.2 Hz)	—	—	—	—	—	—
2 $\beta$	2.68 (dddd, $J = 14.0$ , 11.7, 1.7, 1.7 Hz)		2.48 (dd, $J = 18.7$ , 8.6 Hz)	2.62 (dq, $J = 8.1$ , 6.8 Hz)	2.69 (dq, $J = 6.6$ , 6.9 Hz)	2.80 (dq, $J = 6.6$ , 7.1 Hz)	2.68 (dq, $J = 6.8$ , 6.9 Hz)	2.62 (dq, $J = 6.8$ , 6.8 Hz)	2.24 (dq, $J = 6.1$ , 6.9 Hz)
3 $\alpha$	3.52 (m)	3.20 (m)	2.30 (m)	2.90 (ddd, $J = 8.1$ , 7.9, 6.6 Hz)	3.29 (m)	3.10 (ddd, $J = 7.1$ , 6.7, 6.6 Hz)	3.52 (ddd, $J = 6.8$ , 6.5, 6.1 Hz)	2.89 (ddd, $J = 8.0$ , 6.8, 6.8 Hz)	1.93 (ddd, $J = 6.1$ , 6.1, 4.2 Hz)
4 $\alpha$	3.19 (ddd, $J = 17.6$ , 5.4, 1.5 Hz)	3.05–2.90 (2H, m)	2.88 (dd, $J = 18.4$ , 3.8 Hz)	3.16 (dd, $J = 18.8$ , 6.6 Hz)	3.32 (m)	3.14 <sup>b</sup> (dd, $J = 18.2$ , 7.1 Hz)	3.22 (dd, $J = 19.8$ , 6.5 Hz)	3.15 (dd, $J = 18.7$ , 6.8 Hz)	3.03 (dd, $J = 18.6$ , 6.1 Hz)
4 $\beta$	3.04 (dd, $J = 17.6$ , 10.1 Hz)		2.82 (dd, $J = 18.4$ , 9.3 Hz)	3.04 (dd, $J = 18.8$ , 7.9 Hz)	3.07 (dd, $J = 18.1$ , 7.0 Hz)	3.11 <sup>b</sup> (dd, $J = 18.2$ , 6.7 Hz)	2.92 (dd, $J = 19.8$ , 6.1 Hz)	3.02 (dd, $J = 18.7$ , 8.0 Hz)	2.47 (dd, $J = 18.6$ , 4.2 Hz)
5	7.39 (m)	6.92 <sup>b</sup> (dd, $J = 8.3$ , 1.0 Hz)	7.36 (m)	7.38 (dd, $J = 8.5$ , 1.3 Hz)	7.36 (m)	7.36 (d, $J = 8.7$ Hz)	7.36 (d, $J = 8.7$ Hz)	7.31 (d, $J = 8.7$ Hz)	7.37 (d, $J = 8.3$ Hz)
6	7.62 (ddd, $J = 7.4$ , 7.4, 1.8 Hz)	7.50 (dd, $J = 8.3$ , 8.3 Hz)	7.59 (ddd, $J = 8.4$ , 7.5, 1.7 Hz)	7.62 (ddd, $J = 8.5$ , 7.0, 1.5 Hz)	7.61 (ddd, $J = 8.4$ , 7.6, 1.6 Hz)	7.60 (ddd, $J = 8.7$ , 7.2, 1.5 Hz)	7.58 (d, $J = 8.7$ Hz)	7.21 (dd, $J = 8.7$ , 2.0 Hz)	7.60 (ddd, $J = 8.3$ , 7.3, 1.6 Hz)
7	7.39 (m)	6.79 <sup>b</sup> (dd, $J = 8.3$ , 1.0 Hz)	7.36 (m)	7.38 (ddd, $J = 8.2$ , 7.0, 1.3 Hz)	7.36 (m)	7.35 (dd, $J = 8.2$ , 7.2 Hz)	—	—	7.35 (dd, $J = 7.8$ , 7.3 Hz)
8	8.24 (dd, $J = 8.3$ , 1.8 Hz)	—	8.22 (dd, $J = 8.4$ , 1.7 Hz)	8.27 (dd, $J = 8.2$ , 1.5 Hz)	8.24 (dd, $J = 8.4$ , 1.6 Hz)	8.23 (dd, $J = 8.2$ , 1.5 Hz)	8.23 (s)	7.63 (d, $J = 2.0$ Hz)	8.24 (dd, $J = 7.8$ , 1.6 Hz)
1-CH <sub>2</sub> (a) <sup>c</sup>	6.74 (t, $J = 1.8$ Hz)	6.73 (d, $J = 2.2$ Hz)	6.63 (s)	6.63 (s)	6.71 (s)	6.66 (d, $J = 1.6$ Hz)	6.61 (s)	6.64 (s)	6.62 (d, $J = 2.0$ Hz)
1-CH <sub>2</sub> (b)	5.35 (s)	5.28 (s)	5.27 (d, $J = 1.9$ Hz)	5.36 (s)	5.39 (d, $J = 0.9$ Hz)	5.37 (s)	5.36 (s)	5.36 (s)	5.35 (s)
2'	—	7.30 (m)	—	7.21 (dd, $J = 7.7$ , 3.1 Hz)	—	—	—	7.20 (d, $J = 7.4$ Hz)	—
3'	6.93 (dd, $J = 3.6$ , 1.0 Hz)	7.30 (m)	—	7.33 (dd, $J = 7.7$ , 7.7 Hz)	6.87 (dd, $J = 3.2$ , 1.1 Hz)	6.10 (d, $J = 3.2$ Hz)	7.43 (s)	7.33 (dd, $J = 7.4$ , 7.4 Hz)	—
4'	6.98 (dd, $J = 5.1$ , 3.6 Hz)	7.36 (dd, $J = 7.2$ , 7.2 Hz)	—	7.25 (dddd, $J = 7.7$ , 7.7, 1.3, 1.3 Hz)	6.90 (dd, $J = 5.0$ , 3.2 Hz)	6.26 (dd, $J = 3.2$ , 1.8 Hz)	—	7.24 (dd, $J = 7.4$ , 7.4 Hz)	—
5'	7.21 (dd, $J = 5.1$ , 1.0 Hz)	7.30 (m)	—	7.33 (dd, $J = 7.7$ , 7.7 Hz)	7.15 (dd, $J = 5.0$ , 1.1 Hz)	7.32 (d, $J = 1.8$ Hz)	7.20 <sup>b</sup> (d, $J = 8.1$ Hz)	7.33 (dd, $J = 7.4$ , 7.4 Hz)	—
6'	—	7.30 (m)	—	7.21 (dd, $J = 7.1$ , 1.3 Hz)	—	—	7.11 <sup>b</sup> (d, $J = 8.1$ Hz)	7.20 (d, $J = 7.4$ Hz)	—
Others	—	4.00 (3H, s) 8-OMe	1.09 (3H, d, $J = 6.1$ Hz) 3-Me	1.06 (3H, d, $J = 6.8$ Hz) 2-Me	1.17 (3H, d, $J = 6.9$ Hz) 2-Me	1.15 (3H, d, $J = 7.1$ Hz) 2-Me	1.16 (3H, d, $J = 6.9$ Hz) 2-Me	3.90 (3H, s) 7-OMe 1.06 (3H, d, $J = 6.8$ Hz) 2-Me	1.14 (3H, d, $J = 6.9$ Hz) 2-Me 1.03 (3H, d, $J = 6.2$ Hz) 3-Me

<sup>a</sup> Splitting pattern and coupling in Hz indicated in parentheses. <sup>b</sup> Interchangeable within column. <sup>c</sup> 1-CH<sub>2</sub> (a) next to C=O.

**Table 4**  $^{13}\text{C}$  NMR assignments for 1-methylidenexanthones **3b**, **3h**, **3k**, **4a–c**, **4f**, **4i** and **4k**<sup>a</sup>

Atom	<b>3b</b>	<b>3h</b>	<b>3k</b>	<b>4a</b>	<b>4b</b>	<b>4c</b>	<b>4f</b>	<b>4i</b>	<b>4k</b>
1 (C)	134.9	135.4	135.7	139.4	138.7	138.8	138.3	139.6	139.1
2 (CH)	42.2 (CH <sub>2</sub> )	41.6 (CH <sub>2</sub> )	42.1 (CH <sub>2</sub> )	41.3	40.2	40.1 <sup>b</sup>	40.7 <sup>b</sup>	41.4	43.2
3 (CH)	34.5	39.2	28.0	45.4	43.1	38.1 <sup>b</sup>	40.2 <sup>b</sup>	45.5	32.2
4 (CH <sub>2</sub> )	37.9	36.9	37.7	35.6	35.2	31.4	33.4	35.6	33.9
4a (C)	164.6	163.3	165.8	164.1	163.2	163.3	163.7	164.0	163.9
5a (C)	154.7	156.8	154.8	154.8	154.8	154.8	153.4	156.7	155.0
5 (CH)	117.4	109.6 <sup>b</sup>	117.4	117.4	117.4	117.4	119.4	123.2	117.4
6 (CH)	133.2	133.1	132.9	133.1	133.1	133.1	133.7	105.6 <sup>b</sup>	132.9
7 (CH)	124.9	106.2 <sup>b</sup>	124.7	124.8	124.8	124.8	120.3 (C)	149.7 (C)	124.7
8 (CH)	126.4	160.2 (C)	126.3	126.4	126.4	126.4	126.1	118.9 <sup>b</sup>	126.5
8a (C)	124.0	124.6	124.8	124.1	124.6	124.0	125.2	124.6	124.2
9 (C)	176.4	176.4	176.5	176.3	176.4	176.5	175.3	176.2	176.7
9a (C)	116.6	117.4	117.5	117.0	116.3	116.0	117.0	116.3	114.6
1-CH <sub>2</sub>	116.5	116.0	115.5	115.0	116.2	115.7	116.8	114.8	115.6
1' (C)	—	143.8	—	143.8	—	—	139.8 <sup>d</sup>	143.8	—
2' (CH)	147.4 (C)	126.7	—	127.3	147.3 (C)	156.3 (C)	133.2 <sup>d</sup> (C)	127.4	—
3' (CH)	126.8 <sup>a</sup>	128.7	—	128.7	126.6 <sup>b</sup>	110.1 <sup>b</sup>	129.8 <sup>c</sup>	128.7	—
4' (CH)	123.5 <sup>a</sup>	126.9	—	126.8	124.1 <sup>b</sup>	105.7 <sup>b</sup>	131.1 <sup>d</sup> (C)	126.8	—
5' (CH)	123.2 <sup>a</sup>	128.7	—	128.7	123.6 <sup>b</sup>	141.3	128.6 <sup>c</sup> (CH)	128.7	—
6' (CH)	—	126.7	—	127.3	—	—	127.5 <sup>c</sup> (CH)	127.4	—
Others	—	56.4 (CH <sub>3</sub> ) 8-OMe	20.9 (CH <sub>3</sub> ) 3-Me	17.5 (CH <sub>3</sub> ) 2-Me	18.5 (CH <sub>3</sub> ) 2-Me	18.4 (CH <sub>3</sub> ) 2-Me	18.4 (CH <sub>3</sub> ) 2-Me	55.9 (CH <sub>3</sub> ) 7-OMe; 17.6 (CH <sub>3</sub> ) 2-Me	20.3 (CH <sub>3</sub> ) 3-Me; 18.8 (CH <sub>3</sub> ) 2-Me

<sup>a</sup> Multiplicity determined from DEPT. <sup>bcd</sup> Interchangeable within column.

**Scheme 4**

of the dihydroxanthone nucleus is “blocked” by the presence of two methyl groups). The tetrahydroxanthone product of this reaction (**10a**), which was obtained in good yield, did indeed retain the pyrrolidine group at the 1-position and is believed to be derived from this proposed intermediate by double bond rearrangement.

## Experimental

### General

$^1\text{H}$  NMR (500, 300 and 270 MHz) and  $^{13}\text{C}$  NMR (125, 75 and 67.5 MHz) spectra were recorded on JEOL or Bruker spectrometers in  $\text{CDCl}_3$  and were referenced to tetramethylsilane; chemical shifts are reported in ppm ( $\delta$ ),  $^1\text{H}$ – $^1\text{H}$  coupling constants ( $J$ ) are given in Hz, and multiplicities in  $^{13}\text{C}$  spectra were determined from DEPT and are reported as C, CH, CH<sub>2</sub> and CH<sub>3</sub>. Mass spectra and accurate mass measurements were recorded on a Finnigan MAT-95 instrument using the EI mode with a direct inlet system and operating at 70 eV. Infrared spectra were recorded for KBr discs. All melting points were determined with a Kofler hotstage microscope apparatus and are uncorrected. Column chromatography was carried out using Merck Kieselgel 60 (70–230 mesh) and *n*-hexane–diethyl ether (9 : 1 v/v) as the mobile phase; thin layer chromatography was performed on precoated silica gel 60 GF<sub>254</sub> (E. Merck 7730) plates (20 cm<sup>2</sup>) which had been activated at 120 °C for 3 hours.

### Substituted vinylchromones (1a–1k)

All the aromatically 2-substituted vinylchromones (**1a–1i**) were prepared from cyclization of the corresponding  $\alpha,\beta$ -unsaturated 1,3-diketones<sup>10</sup> in acid in almost quantitative yields (the  $\alpha,\beta$ -unsaturated 1,3-diketones were in turn synthesised by the Baker–Venkatraman reaction of esters prepared from 2-hydroxyacetophenones and appropriately substituted acryloyl chlorides).<sup>11</sup> Chromones **1j** and **1k**, for which there is no aromatic substituent at the 2-position of the chromone, were prepared by the procedure of Hercouet *et al.*<sup>12</sup>

### 1-Methyl-3-phenyl-9H-xanthene-9-one (2a)

(*E*)-2-Styryl-4-chromone (**1a**) (0.2 g, 0.80 mmol) was refluxed in acetone (25 ml) with a drop of pyrrolidine for 4 h. The product mixture was rotary evaporated and the resulting gum was subjected to column chromatography yielding 1-methyl-3-phenyl-9H-xanthene-9-one (**2a**) ( $R_f$  = 0.85) as colourless needles (0.18 g, 76%) (mp 154–155 °C, EtOH).  $\nu_{\text{max}}/\text{cm}^{-1}$  1665, 1656, 1620, 1606, 1552 (HRMS: found  $M^+$ , 286.0989.  $\text{C}_{20}\text{H}_{14}\text{O}_2$  requires  $M$ , 286.0994);  $m/z$  286 ( $M^+$ , 100%), 285 (24), 257 (13);  $\delta_{\text{H}}$  see Table 1;  $\delta_{\text{C}}$  see Table 2.

**1-Methyl-3-(2'-thienyl)-9H-xanthen-9-one (2b) and 1-methylidene-1,2,3,4-tetrahydro-3-(2'-thienyl)-9H-xanthen-9-one (3b)**

(*E*)-2-[2'-(2'-Thienyl)ethenyl]-4-chromone (**1b**) (0.2 g, 0.78 mmol) was refluxed in acetone (25 ml) with a drop of pyrrolidine for 2 h. The product mixture was rotary evaporated and the resulting gum was subjected to column chromatography yielding two products: (i) 1-methyl-3-(2'-thienyl)-9H-xanthen-9-one (**2b**) ( $R_f = 0.80$ ) was obtained as colourless needles (0.16 g, 70%) (mp 145–146 °C, EtOH).  $\nu_{\max}/\text{cm}^{-1}$  1654, 1618, 1608, 1560 (HRMS: found  $M^+$ , 292.0553.  $C_{18}H_{12}O_2S$  requires  $M$ , 292.0558),  $m/z$  292 ( $M^+$ , 100%), 291 (23), 263 (8);  $\delta_H$  see Table 1;  $\delta_C$  see Table 2; (ii) 1-methylidene-1,2,3,4-tetrahydro-3-(2'-thienyl)-9H-xanthen-9-one (**3b**) ( $R_f = 0.50$ ) was also obtained as a colourless oil (0.05 g, 21%).  $\nu_{\max}/\text{cm}^{-1}$  1654, 1637, 1560, 1508 (HRMS: found  $M^+$ , 294.0715.  $C_{18}H_{14}SO_2$  requires  $M$ , 294.0715),  $m/z$  294 ( $M^+$ , 100%), 293 (53), 279 (69);  $\delta_H$  see Table 3;  $\delta_C$  see Table 4. Treatment of **3b** with refluxing AcOH containing a drop of  $H_2SO_4$  resulted in quantitative conversion into **2b**.

**1-Methyl-3-(2'-furyl)-9H-xanthen-9-one (2c)**

(*E*)-2-[2'-(2'-Furyl)ethenyl]-4-chromone (**1c**) (0.2 g, 0.84 mmol) was refluxed in acetone (25 ml) with a drop of pyrrolidine for 4 h. The product mixture was rotary evaporated and the resulting gum was subjected to column chromatography yielding 1-methyl-3-(2'-furyl)-9H-xanthen-9-one (**2c**) ( $R_f = 0.70$ ) as colourless needles (0.13 g, 56%) (mp 144–145 °C, EtOH).  $\nu_{\max}/\text{cm}^{-1}$  1655, 1624, 1610, 1559, 1555 (HRMS: found  $M^+$ , 276.0781.  $C_{18}H_{12}O_3$  requires  $M$ , 276.0786),  $m/z$  276 ( $M^+$ , 100%), 275 (24), 247 (13);  $\delta_H$  see Table 1;  $\delta_C$  see Table 2.

**1,6,7-Trimethyl-3-phenyl-9H-xanthen-9-one (2d)**

(*E*)-2-Styryl-6,7-dimethyl-4-chromone (**1d**) (0.2 g, 0.72 mmol) was refluxed in acetone (25 ml) with a drop of pyrrolidine for 4 h. The product mixture was rotary evaporated and the resulting gum was subjected to column chromatography [elution with *n*-hexane–diethyl ether (9:1 v/v)] yielding 1,6,7-trimethyl-3-phenyl-9H-xanthen-9-one (**2d**) ( $R_f = 0.85$ ) as pinkish needles (0.17 g, 75%) (mp 157–158 °C, EtOH).  $\nu_{\max}/\text{cm}^{-1}$  1656, 1605, 1562 (HRMS: found  $M^+$ , 314.1306.  $C_{22}H_{18}O_2$  requires  $M$ , 314.1301),  $m/z$  314 ( $M^+$ , 100%), 313 (22), 299 (12), 285 (5);  $\delta_H$  see Table 1;  $\delta_C$  see Table 2.

**1-Methyl-3-(2'-methoxyphenyl)-7-chloro-9H-xanthen-9-one (2e)**

(*E*)-2-[2'-(2'-Methoxyphenyl)ethenyl]-6-chloro-4-chromone (**1e**) (0.2 g, 0.64 mmol) was refluxed in acetone (25 ml) with a drop of pyrrolidine for 8 h. The product mixture was rotary evaporated and the resulting gum was subjected to column chromatography yielding 1-methyl-3-(2'-methoxyphenyl)-7-chloro-9H-xanthen-9-one (**2e**) ( $R_f = 0.65$ ) as colourless needles (0.14 g, 63%) (mp 123–124 °C, EtOH).  $\nu_{\max}/\text{cm}^{-1}$  1647, 1620, 1599, 1558 (HRMS: found  $M^+$ , 350.0708.  $C_{21}H_{15}O_3Cl$  requires  $M$ , 350.0710),  $m/z$  352/350 ( $M^+$ , 42/100%), 337/335 (23/32), 321 (6);  $\delta_H$  see Table 1;  $\delta_C$  see Table 2.

**1-Methyl-3-(2',4'-dichlorophenyl)-7-chloro-9H-xanthen-9-one (2f)**

(*E*)-2-[2'-(2',4'-Dichlorophenyl)ethenyl]-6-chloro-4-chromone (**1f**) (0.23 g, 0.64 mmol) was refluxed in acetone (25 ml) with a drop of pyrrolidine for 24 h. The product mixture was rotary evaporated and the resulting gum was subjected to column chromatography [elution with *n*-hexane–diethyl ether (9:1 v/v)] yielding 1-methyl-3-(2',4'-dichlorophenyl)-7-chloro-9H-xanthen-9-one (**2f**) ( $R_f = 0.75$ ) as colourless needles (0.144 g, 58%) (mp 200–201 °C, 95% EtOH– $CHCl_3$ ).  $\nu_{\max}/\text{cm}^{-1}$  1650, 1626, 1611, 1556 (HRMS: found  $M^+$ , 387.9820.  $C_{20}H_{11}O_2Cl_3$  requires  $M$ , 387.9824),  $m/z$  394/392/390/388 ( $M^+$ , 4/35/100/

99%), 357/355/353 (1/7/9), 291/289 (2/6);  $\delta_H$  see Table 1;  $\delta_C$  see Table 2.

**1-Methyl-3-phenyl-5,7-dichloro-9H-xanthen-9-one (2g)**

(*E*)-6,8-Dichloro-2-styryl-4-chromone (**1g**) (0.2 g, 0.63 mmol) was refluxed in acetone (25 ml) with a drop of pyrrolidine for 24 h. The product mixture was rotary evaporated and the resulting gum was subjected to column chromatography yielding 1-methyl-3-phenyl-5,7-dichloro-9H-xanthen-9-one (**2g**) ( $R_f = 0.90$ ) as colourless needles (0.13 g, 57%) (mp 195–196 °C, 95% EtOH– $CHCl_3$ ).  $\nu_{\max}/\text{cm}^{-1}$  1660, 1623, 1607 (HRMS: found  $M^+$ , 354.0212.  $C_{20}H_{12}O_2Cl_2$  requires  $M$ , 354.0214),  $m/z$  358/356/354 ( $M^+$ , 12/66/100%), 321/319 (3/10);  $\delta_H$  see Table 1;  $\delta_C$  see Table 2.

**1-Methyl-3-phenyl-8-methoxy-9H-xanthen-9-one (2h) and 1-methylidene-1,2,3,4-tetrahydro-3-phenyl-8-methoxy-9H-xanthen-9-one (3h)**

(*E*)-2-Styryl-5-methoxy-4-chromone (**1h**) (0.2 g, 0.72 mmol) was refluxed in acetone (25 ml) with a drop of pyrrolidine for 28 h. The product mixture was rotary evaporated and the resulting gum was subjected to column chromatography yielding two products: (i) 1-methyl-3-phenyl-8-methoxy-9H-xanthen-9-one (**2h**) ( $R_f = 0.90$ ) was obtained as colourless needles (0.13 g, 59%) (mp 200–201 °C, EtOH).  $\nu_{\max}/\text{cm}^{-1}$  1653, 1607, 1551 (HRMS: found  $M^+$ , 316.1103.  $C_{21}H_{16}O_3$  requires  $M$ , 316.1099);  $m/z$  316 ( $M^+$ , 48%), 298 (100), 270 (11);  $\delta_H$  see Table 1;  $\delta_C$  see Table 2; (ii) 1-methylidene-1,2,3,4-tetrahydro-3-phenyl-8-methoxy-9H-xanthen-9-one (**3h**) ( $R_f = 0.70$ ) was also obtained as colourless needles (0.055 g, 24%) (mp 174–175 °C, 95% EtOH– $CHCl_3$ ) (HRMS: found  $M^+$ , 318.1256.  $C_{21}H_{18}O_3$  requires  $M$ , 318.1256),  $m/z$  318 ( $M^+$ , 100%), 317 (29), 303 (42), 227 (40);  $\delta_H$  see Table 3;  $\delta_C$  see Table 4. Treatment of **3h** with refluxing AcOH containing a drop of  $H_2SO_4$  resulted in quantitative conversion into **2h**.

**1-Methyl-3-phenyl-7-methoxy-9H-xanthen-9-one (2i)**

(*E*)-2-Styryl-6-methoxy-4-chromone (**1i**) (0.2 g, 0.72 mmol) was refluxed in acetone (25 ml) with a drop of pyrrolidine for 20 h. The product mixture was rotary evaporated and the resulting gum was subjected to column chromatography yielding 1-methyl-3-phenyl-7-methoxy-9H-xanthen-9-one (**2i**) ( $R_f = 0.85$ ) as colourless needles (0.14 g, 63%) (mp 144–145 °C, 95% EtOH– $CHCl_3$ ).  $\nu_{\max}/\text{cm}^{-1}$  1653, 1647, 1616, 1597 (HRMS: found  $M^+$ , 316.1098.  $C_{21}H_{16}O_3$  requires  $M$ , 316.1099);  $m/z$  316 ( $M^+$ , 100%), 315 (24), 301 (20), 245 (11), 158 (5);  $\delta_H$  see Table 1;  $\delta_C$  see Table 2.

**1-Methyl-9H-xanthen-9-one (2j)**

2-Ethenyl-4-chromone (**1j**) (0.082 g, 0.47 mmol) was refluxed in acetone (25 ml) with a drop of pyrrolidine for 48 h. The product mixture was rotary evaporated and the resulting gum was subjected to column chromatography yielding 1-methyl-9H-xanthen-9-one (**2j**) ( $R_f = 0.60$ ) as colourless needles (0.038 g, 58%) (mp 100–101 °C, EtOH).  $\nu_{\max}/\text{cm}^{-1}$  1653, 1646, 1616, 1597, 1560, 1543, 1508 (HRMS: found  $M^+$ , 210.0678.  $C_{14}H_{10}O_2$  requires  $M$ , 210.0681),  $m/z$  210 ( $M^+$ , 100%), 209 (56), 181 (23), 152 (10), 105 (6);  $\delta_H$  see Table 1;  $\delta_C$  see Table 2.

**(3*R/S*)-1-Methylidene-1,2,3,4-tetrahydro-3-methyl-9H-xanthen-9-one (3k)**

(*E*)-2-(Prop-1'-enyl)-4-chromone (**1k**) (0.2 g, 1.07 mmol) was refluxed in acetone (25 ml) with a drop of pyrrolidine for 15 h. The product mixture was rotary evaporated and the resulting gum was subjected to column chromatography yielding (3*R/S*)-1-methylidene-1,2,3,4-tetrahydro-3-methyl-9H-xanthen-9-one (**3k**) ( $R_f = 0.70$ ) as a yellow oil (0.092 g, 58%).  $\nu_{\max}/\text{cm}^{-1}$  1645, 1630, 1610, 1562 (HRMS: found  $M^+$ , 226.0990.  $C_{15}H_{14}O_2$

requires  $M$ , 226.0993),  $m/z$  226 ( $M^+$ , 64%), 225 (50), 211 (100);  $\delta_H$  see Table 3;  $\delta_C$  see Table 4.

**(2*S*/R,3*R*/S)-1-Methylidene-1,2,3,4-tetrahydro-2-methyl-3-phenyl-9*H*-xanthen-9-one (4a)**

(*E*)-2-Styryl-4-chromone (**1a**) (0.2 g, 0.80 mmol) was refluxed in butan-2-one (25 ml) with a drop of pyrrolidine for 70 min. The product mixture was rotary evaporated and the resulting gum was subjected to column chromatography yielding (2*S*/R,3*R*/S)-1-methylidene-1,2,3,4-tetrahydro-2-methyl-3-phenyl-9*H*-xanthen-9-one (**4a**) ( $R_f = 0.65$ ) as a colourless oil (0.11 g, 55%).  $\nu_{\max}/\text{cm}^{-1}$  1643, 1614 (HRMS: found  $M^+$ , 302.1307.  $C_{21}H_{18}O_2$  requires  $M$ , 302.1306),  $m/z$  302 ( $M^+$ , 100%), 301 (19), 287 (77), 273 (22), 211 (53);  $\delta_H$  see Table 3;  $\delta_C$  see Table 4.

**(2*S*/R,3*R*/S)-1-Methylidene-1,2,3,4-tetrahydro-2-methyl-3-(2'-thienyl)-9*H*-xanthen-9-one (4b) and 1-ethyl-3-(2'-thienyl)-9*H*-xanthen-9-one (5b)**

(*E*)-2-[2'-(2'-Thienyl)ethenyl]-4-chromone (**1b**) (0.2 g, 0.78 mmol) was refluxed in butan-2-one (25 ml) with a drop of pyrrolidine for 6 h. The product mixture was rotary evaporated and the resulting gum was subjected to column chromatography yielding two products: (i) (2*S*/R,3*R*/S)-1-methylidene-1,2,3,4-tetrahydro-2-methyl-3-(2'-thienyl)-9*H*-xanthen-9-one (**4b**) ( $R_f = 0.55$ ) was obtained as a yellowish oil (0.097 g, 40%).  $\nu_{\max}/\text{cm}^{-1}$  1647, 1632, 1612 (HRMS: found  $M^+$ , 308.0875.  $C_{19}H_{16}SO_2$  requires  $M$ , 308.0871),  $m/z$  308 ( $M^+$ , 100%), 293 (61), 279 (17), 211 (45);  $\delta_H$  see Table 3;  $\delta_C$  see Table 4; (ii) 1-ethyl-3-(2'-thienyl)-9*H*-xanthen-9-one (**5b**) ( $R_f = 0.83$ ) was obtained as colourless needles (0.036 g, 15%) (mp 113–114 °C, 95% EtOH-CHCl<sub>3</sub>).  $\nu_{\max}/\text{cm}^{-1}$  1655, 1619, 1605 (HRMS: found  $M^+$ , 306.0713.  $C_{19}H_{14}SO_2$  requires  $M$ , 306.0715),  $m/z$  306 ( $M^+$ , 100%), 305 (41), 289 (62), 278 (15);  $\delta_H$  8.27 (1H, dd,  $J = 7.9$ , 1.6 Hz, H-8), 7.67 (1H, ddd,  $J = 8.8$ , 7.5, 1.6 Hz, H-6), 7.56 (1H, d,  $J = 1.6$  Hz, H-4), 7.51 (1H, dd,  $J = 3.7$ , 0.8 Hz, H-3'), 7.43 (1H, d,  $J = 8.8$  Hz, H-5), 7.42 (1H, dd,  $J = 5.0$ , 0.8 Hz, H-5'), 7.39 (1H, d,  $J = 1.6$  Hz, H-2), 7.35 (1H, dd,  $J = 7.9$ , 7.5 Hz, H-7), 7.14 (1H, dd,  $J = 5.0$ , 3.7 Hz, H-4'), 3.42 (2H, q,  $J = 7.3$  Hz, 1-CH<sub>2</sub>CH<sub>3</sub>), 1.35 (3H, t,  $J = 7.3$  Hz, 1-CH<sub>2</sub>CH<sub>3</sub>);  $\delta_C$  178.2 (s, C-9), 158.2 (C, C-4a), 155.3 (C, C-5a), 149.0 (C, C-1), 142.5 (C, C-3), 139.5 (C, C-2'), 134.3 (CH, C-6), 128.4 (CH, C-2), 127.0 (CH, C-3'/4'/5'), 126.8 (CH, C-8), 125.2 (CH, C-3'/4'/5'), 123.7 (CH, C-7), 122.9 (C, C-8a), 122.8 (CH, C-3'/4'/5'), 118.9 (C-9a), 117.3 (CH, C-5), 112.4 (CH, C-4), 28.9 (CH<sub>2</sub>, 1-CH<sub>2</sub>-CH<sub>3</sub>), 15.7 (CH<sub>3</sub>, 1-CH<sub>2</sub>CH<sub>3</sub>).

**(2*S*/R,3*R*/S)-1-Methylidene-1,2,3,4-tetrahydro-2-methyl-3-(2'-furyl)-9*H*-xanthen-9-one (4c)**

(*E*)-2-[2'-(2'-Furyl)ethenyl]-4-chromone (**1c**) (0.2 g, 0.84 mmol) was refluxed in butan-2-one (25 ml) with a drop of pyrrolidine for 2 h. The product mixture was rotary evaporated and the resulting gum was subjected to column chromatography yielding (2*S*/R,3*R*/S)-1-methylidene-1,2,3,4-tetrahydro-2-methyl-3-(2'-furyl)-9*H*-xanthen-9-one (**4c**) ( $R_f = 0.60$ ) as a yellowish oil (0.11 g, 46%) (HRMS: found  $M^+$ , 292.0943.  $C_{19}H_{16}O_3$  requires  $M$ , 292.1099),  $m/z$  292 ( $M^+$ , 100%), 263 (7), 213 (68);  $\delta_H$  see Table 3;  $\delta_C$  see Table 4.

**(2*S*/R,3*R*/S)-1-Methylidene-1,2,3,4-tetrahydro-2-methyl-3-(2',4'-dichlorophenyl)-7-chloro-9*H*-xanthen-9-one (4f) and 1-ethyl-3-(2',4'-dichlorophenyl)-7-chloro-9*H*-xanthen-9-one (5f)**

(*E*)-2-[2'-(2',4'-Dichlorophenyl)ethenyl]-6-chloro-4-chromone (**1f**) (0.23 g, 0.64 mmol) was refluxed in butan-2-one (25 ml) with a drop of pyrrolidine for 30 h. The product mixture was rotary evaporated and the resulting gum was subjected to column chromatography yielding two products: (i) (2*S*/R,3*R*/S)-1-methylidene-1,2,3,4-tetrahydro-2-methyl-3-(2',4'-dichlorophenyl)-7-chloro-9*H*-xanthen-9-one (**4f**) ( $R_f = 0.55$ ) was

obtained as white needles (0.093 g, 36%) (mp 134–135 °C, 95% EtOH-CHCl<sub>3</sub>).  $\nu_{\max}/\text{cm}^{-1}$  1647, 1618 (HRMS: found  $M^+$ , 404.0133.  $C_{21}H_{15}O_2Cl_3$  requires  $M$ , 404.0138),  $m/z$  410/408/406/404 ( $M^+$ , 3/27/78/81%), 395/393/391/389 (1/6/50/54), 247/245 (34/100);  $\delta_H$  see Table 3;  $\delta_C$  see Table 4; (ii) 1-ethyl-3-(2',4'-dichlorophenyl)-7-chloro-9*H*-xanthen-9-one (**5f**) ( $R_f = 0.70$ ) was obtained as colourless needles (0.033 g, 13%) (mp 167–168 °C, 95% EtOH-CHCl<sub>3</sub>).  $\nu_{\max}/\text{cm}^{-1}$  1649, 1610 (HRMS: found  $M^+$ , 401.9983.  $C_{21}H_{13}O_2Cl_3$  requires  $M$ , 401.9981),  $m/z$  408/406/404/402 ( $M^+$ , 4/33/98/100%), 391/389/387/385 (2/21/50/48);  $\delta_H$  8.25 (1H, d,  $J = 2.0$  Hz, H-8), 7.62 (1H, dd,  $J = 8.8$ , 2.0 Hz, H-6), 7.53 (1H, d,  $J = 1.8$  Hz, H-4), 7.40 (2H, m, H-5'/6'), 7.39 (1H, d,  $J = 8.8$  Hz, H-5'), 7.34 (1H, d,  $J = 1.8$  Hz, H-2), 7.21 (1H, s, H-3'), 3.43 (2H, q,  $J = 7.3$  Hz, 1-CH<sub>2</sub>CH<sub>3</sub>), 1.33 (3H, t,  $J = 7.3$  Hz, 1-CH<sub>2</sub>CH<sub>3</sub>);  $\delta_C$  177.0 (C, C-9), 157.3 (C, C-4a), 153.6 (C, C-5a), 148.4 (C, C-1), 144.2 (C, C-3), 137.2 (C, C-2'/4'), 134.9 (C, C-1'), 134.6 (CH, C-6), 133.1 (C, C-2'/4'), 131.8 (CH, C-5'/6'), 130.1 (CH, C-5'/6'), 129.6 (C, C-7), 127.5 (CH, C-2), 126.7 (CH, C-3'), 126.2 (CH, C-8), 123.7 (C, C-8a), 119.2 (CH, C-5), 118.6 (C, C-9a), 117.0 (CH, C-4), 28.7 (CH<sub>2</sub>, 1-CH<sub>2</sub>CH<sub>3</sub>), 15.5 (CH<sub>3</sub>, 1-CH<sub>2</sub>CH<sub>3</sub>).

**(2*S*/R,3*R*/S)-1-Methylidene-1,2,3,4-tetrahydro-2-methyl-3-phenyl-7-methoxy-9*H*-xanthen-9-one (4i) and 1-ethyl-3-phenyl-7-methoxy-9*H*-xanthen-9-one (5i)**

(*E*)-2-Styryl-6-methoxy-4-chromone (**1i**) (0.2 g, 0.72 mmol) was refluxed in butan-2-one (25 ml) with a drop of pyrrolidine for 3 days. The product mixture was rotary evaporated and the resulting gum was subjected to column chromatography yielding two products: (i) (2*S*/R,3*R*/S)-1-methylidene-1,2,3,4-tetrahydro-2-methyl-3-phenyl-7-methoxy-9*H*-xanthen-9-one (**4i**) ( $R_f = 0.55$ ) was obtained as colourless needles (0.088 g, 37%) (mp 200–201 °C, 95% EtOH).  $\nu_{\max}/\text{cm}^{-1}$  1645, 1605, 1597, 1561 (HRMS: found  $M^+$ , 332.1404.  $C_{22}H_{20}O_3$  requires  $M$ , 332.1410),  $m/z$  332 ( $M^+$ , 100%), 331 (18), 317 (74), 241 (46);  $\delta_H$  see Table 3;  $\delta_C$  see Table 4; (ii) 1-ethyl-3-phenyl-7-methoxy-9*H*-xanthen-9-one (**5i**) ( $R_f = 0.75$ ) was obtained as colourless needles (0.037 g, 16%) (mp 144–145 °C, 95% EtOH).  $\nu_{\max}/\text{cm}^{-1}$  1654, 1608 (HRMS: found  $M^+$ , 330.1252.  $C_{22}H_{18}O_3$  requires  $M$ , 330.1256),  $m/z$  330 ( $M^+$ , 100%), 329 (29), 313 (37);  $\delta_H$  7.69 (2H, dd,  $J = 8.0$ , 1.5 Hz, H-2'/6'), 7.69 (1H, d,  $J = 1.8$  Hz, H-8), 7.54 (1H, d,  $J = 1.1$  Hz, H-4), 7.50 (2H, dd,  $J = 8.0$ , 7.5 Hz, H-3'/5'), 7.43 (1H, dd,  $J = 7.5$ , 7.5 Hz, H-4'), 7.38 (1H, d,  $J = 8.9$  Hz, H-5), 7.38 (1H, d,  $J = 1.1$  Hz, H-2), 7.29 (1H, d,  $J = 8.9$  Hz, H-6), 3.91 (3H, s, 7-OMe), 3.45 (2H, q,  $J = 7.4$  Hz, 1-CH<sub>2</sub>CH<sub>3</sub>), 1.37 (3H, t,  $J = 7.4$  Hz, 1-CH<sub>2</sub>CH<sub>3</sub>);  $\delta_C$  178.0 (C, C-9), 158.1 (C, C-4a), 155.9 (C, C-5a), 150.1 (C, C-7), 148.6 (C, C-1), 146.4 (C, C-3), 139.3 (C, C-1'), 129.0 (CH, C-3'/5'), 128.6 (CH, C-4'), 127.4 (CH, C-2'/6'), 124.4 (CH, C-2), 124.2 (CH, C-5), 123.2 (CH, C-8a), 118.8, (CH, C-8/6), 117.9 (C, C-9a), 114.1 (CH, C-4), 105.9 (CH, C-6/8), 55.8 (CH<sub>3</sub>, 7-OMe), 29.0 (CH<sub>2</sub>, 1-CH<sub>2</sub>-CH<sub>3</sub>), 15.9 (CH<sub>3</sub>, 1-CH<sub>2</sub>CH<sub>3</sub>).

**(2*S*/R,3*R*/S)-1-Methylidene-1,2,3,4-tetrahydro-2,3-dimethyl-9*H*-xanthen-9-one (4k)**

(*E*)-2-(Prop-1'-enyl)-4-chromone (**1k**) (0.2 g, 1.07 mmol) was refluxed in butan-2-one (25 ml) with a drop of pyrrolidine for 6 h. The product mixture was rotary evaporated and the resulting gum was subjected to column chromatography yielding (2*S*/R,3*R*/S)-1-methylidene-1,2,3,4-tetrahydro-2,3-dimethyl-9*H*-xanthen-9-one (**4k**) ( $R_f = 0.65$ ) as a colourless oil (0.12 g, 48%).  $\nu_{\max}/\text{cm}^{-1}$  1645, 1615, 1597 (HRMS: found  $M^+$ , 240.1146.  $C_{16}H_{16}O_2$  requires  $M$ , 240.1150),  $m/z$  240 ( $M^+$ , 49%), 239 (12), 225 (100);  $\delta_H$  see Table 3;  $\delta_C$  see Table 4.

**1,2-Dimethyl-3-phenyl-9*H*-xanthen-9-one (7a) and 1,2-dimethyl-3-phenyl-3,4-dihydro-9*H*-xanthen-9-one (6a)**

Compound **4a** (0.175 g, 0.57 mmol) was dissolved in AcOH–



H<sub>2</sub>SO<sub>4</sub> and heated at 100 °C for 3 h. The reaction was neutralized with NaOH (4 M, 20 ml) and extracted with CHCl<sub>3</sub>. The product mixture was rotary evaporated and the resulting gum was subjected to column chromatography yielding 1,2-dimethyl-3-phenyl-9*H*-xanthen-9-one (**7a**) (*R*<sub>f</sub> = 0.84) as colourless needles (0.086 g, 89%) (mp 129–130 °C, 95% EtOH–CHCl<sub>3</sub>).  $\nu_{\max}/\text{cm}^{-1}$  1653, 1646, 1616, 1597 (HRMS: found *M*<sup>+</sup>, 300.113. C<sub>21</sub>H<sub>16</sub>O<sub>2</sub> requires *M*, 300.1151), *m/z* 300 (*M*<sup>+</sup>, 61%), 299 (100), 285 (7), 255 (9), 142 (8);  $\delta_{\text{H}}$  8.31 (1H, dd, *J* = 8.0, 1.5 Hz, H-8), 7.67 (1H, ddd, *J* = 8.5, 7.0, 1.5 Hz, H-6), 7.46 (2H, dd, *J* = 7.5, 7.5 Hz, H-3'/5'), 7.41 (1H, dd, *J* = 7.5, 7.5 Hz, H-4'), 7.35 (1H, ddd, *J* = 8.0, 7.0, 1.0 Hz, H-7), 7.34 (2H, d, *J* = 7.5 Hz, H-2'/6'), 7.25 (1H, s, H-4), 2.98 (3H, s, 1-Me), 2.24 (3H, s, 2-Me);  $\delta_{\text{C}}$  178.0 (C, C-9), 155.3 (C, C-4a and C-5a), 148.7 (C, C-3), 141.3 (C, C-1'), 140.8 (C, C-1), 134.1 (CH, C-6), 130.9 (C, C-2), 128.9 (CH, C-2'/6'), 128.3 (CH, C-3'/5'), 127.6 (CH, C-4'), 126.9 (CH, C-8), 123.5 (CH, C-7), 123.2 (C, C-8a), 119.2 (C, C-9a), 117.3 (CH, C-5), 116.6 (CH, C-4), 18.2 (CH<sub>3</sub>, 1-Me), 17.3 (CH<sub>3</sub>, 2-Me). Quenching the reaction after 20 min produced a gum (after rotary evaporation) which was subjected to column chromatography yielding in addition to **7a**, 1,2-dimethyl-3-phenyl-3,4-dihydro-9*H*-xanthen-9-one (**6a**) (*R*<sub>f</sub> = 0.54) as an oil (0.02 g).  $\nu_{\max}/\text{cm}^{-1}$  1654, 1608, 1560 (HRMS: *M*<sup>+</sup>, 302.1307. C<sub>21</sub>H<sub>18</sub>O<sub>2</sub> requires *M*, 302.1307), *m/z* 302 (*M*<sup>+</sup>, 58%), 301 (20), 287 (100);  $\delta_{\text{H}}$  8.21 (1H, dd, *J* = 8.0, 1.5 Hz, H-8), 7.53 (1H, ddd, *J* = 8.5, 7.0, 1.5 Hz, H-6), 7.33 (1H, ddd, *J* = 8.0, 7.0, 1.0 Hz, H-7), 7.27 (1H, dd, *J* = 8.5, 1.0 Hz, H-5), 7.23 (2H, dd, *J* = 7.5, 7.5 Hz, H-3'/5'), 7.17 (3H, m, H-2'/4'/6'), 3.51 (1H, br d, *J* = 8.2 Hz, H-3), 3.36 (1H, dd, *J* = 16.6, 8.2 Hz, H-4 $\beta$ ), 2.81 (1H, dd, *J* = 16.6, 2.6 Hz, H-4 $\alpha$ ), 2.36 (3H, d, *J* = 0.9 Hz, 1-Me), 1.81 (3H, d, *J* = 0.7 Hz, 2-Me);  $\delta_{\text{C}}$  175.4 (C, C-9), 163.3 (C, C-4a), 155.2 (C, C-5a), 140.9 (C, C-1'), 132.5 (CH, C-6), 129.6 (C, C-1/2), 128.7 (CH, C-3'/5'), 127.8 (CH, C-2'/6'), 126.9 (CH, C-4'), 126.2 (CH, C-8), 125.8 (C, C-2/1), 125.2 (C, C-8a), 124.7 (CH, C-7), 118.5 (C, C-9a), 117.5 (CH, C-5), 45.0 (CH, C-3), 36.1 (CH<sub>2</sub>, C-4), 18.4 (CH<sub>3</sub>, 1-Me), 16.3 (CH<sub>3</sub>, 2-Me). Treatment of **6a** with refluxing AcOH containing a drop of H<sub>2</sub>SO<sub>4</sub> resulted in quantitative conversion to **7a**.

### 2-Methyl-3-phenyl-9*H*-xanthen-9-one (**8a**)

(*E*)-2-Styryl-4-chromone (**1a**) (0.2 g, 0.80 mmol) was refluxed in propanal (25 ml) with a drop of pyrrolidine for 4 days. The product mixture was rotary evaporated and the resulting gum was subjected to column chromatography yielding 2-methyl-3-phenyl-9*H*-xanthen-9-one (**8a**) (*R*<sub>f</sub> = 0.64) as colourless needles (0.027 g, 12%) (mp 86–87 °C, 95% EtOH–CHCl<sub>3</sub>).  $\nu_{\max}/\text{cm}^{-1}$  1655, 1611 (HRMS: found *M*<sup>+</sup>, 286.0980. C<sub>20</sub>H<sub>14</sub>O<sub>2</sub> requires *M*, 286.0994), *m/z* 286 (*M*<sup>+</sup>, 100%), 285 (16), 271 (34);  $\delta_{\text{H}}$  8.36 (1H, dd, *J* = 8.0, 1.5 Hz, H-8), 8.21 (1H, s, H-1), 7.71 (1H, ddd, *J* = 8.5, 7.5, 1.5 Hz, H-6), 7.47 (2H, dd, *J* = 7.5, 7.5 Hz, H-3'/5'), 7.46 (1H, dd, *J* = 8.5, 1.0 Hz, H-5), 7.42 (1H, dd, *J* = 7.5, 7.5 Hz, H-4'), 7.38 (1H, s, H-4), 7.37 (3H, m, H-2'/6'/7), 2.36 (3H, s, 2-Me);  $\delta_{\text{C}}$  177.0 (C, C-9), 156.4 (C, C-4a and C-7), 154.4 (C, C-5a), 149.3 (C, C-3), 140.3 (C, C-1'), 134.6 (CH, C-6), 131.9 (C, C-2), 128.8 (CH, C-2'/6'), 128.4 (CH, C-3'/5'), 127.8 (CH, C-1), 127.5 (CH, C-4'), 126.8 (CH, C-8), 123.8 (CH, C-7), 122.0 (C, C-8a), 120.6 (C, C-9a), 118.7 (CH, C-4), 118.0 (CH, C-5), 20.1 (CH<sub>3</sub>, 2-Me).

### 2-Ethyl-3-(2'-thienyl)-9*H*-xanthen-9-one (**9b**)

(*E*)-2-[2'-(2'-Thienyl)ethenyl]-4-chromone (**1b**) (0.2 g, 0.78 mmol) was refluxed in butanal (25 ml) with a drop of pyrrolidine for 4 days. The product mixture was rotary evaporated and the resulting gum was subjected to column chromatography yielding 2-ethyl-3-(2'-thienyl)-9*H*-xanthen-9-one (**9b**) (*R*<sub>f</sub> = 0.54) as a yellowish oil (0.036 g, 15%).  $\nu_{\max}/\text{cm}^{-1}$  1648, 1597, 1518 (HRMS: found *M*<sup>+</sup>, 306.0718. C<sub>19</sub>H<sub>14</sub>SO<sub>2</sub> requires *M*, 306.0715), *m/z* 306 (*M*<sup>+</sup>, 94%), 291 (100), 273 (15), 261 (15),

247 (19);  $\delta_{\text{H}}$  8.37 (1H, dd, *J* = 8.0, 1.5 Hz, H-8), 8.26 (1H, s, H-1), 7.74 (1H, ddd, *J* = 8.5, 7.0, 1.5 Hz, H-6), 7.55 (1H, s, H-4), 7.50 (1H, dd, *J* = 8.5, 1.0 Hz, H-5), 7.46 (1H, dd, *J* = 5.0, 1.2 Hz, H-5'), 7.39 (1H, ddd, *J* = 8.0, 7.0, 1.0 Hz, H-7), 7.20 (1H, dd, *J* = 3.5, 1.2 Hz, H-3'), 7.16 (1H, dd, *J* = 5.0, 3.5 Hz, H-4'), 2.90 (2H, q, *J* = 7.5 Hz, 1-CH<sub>2</sub>CH<sub>3</sub>), 1.27 (3H, t, *J* = 7.5 Hz, 1-CH<sub>2</sub>CH<sub>3</sub>);  $\delta_{\text{C}}$  177.0 (C, C-9), 156.4 (C, C-4a), 154.0 (C, C-5a), 141.1 (C, C-2/2'/3), 140.9 (C, C-2/2'/3), 138.5 (C, C-2/2'/3), 134.8 (CH, C-6), 127.4 (CH, C-1), 127.4 (CH, C-3'/4'/5'), 126.8 (CH, C-8), 126.6 (CH, C-3'/4'/5'), 126.6 (CH, C-3'/4'/5'), 123.8 (CH, C-7), 122.0 (C, C-8a), 121.0 (C, C-9a), 119.7 (CH, C-4), 118.0 (CH, C-5), 29.2 (CH<sub>2</sub>, 2-CH<sub>2</sub>CH<sub>3</sub>), 15.4 (CH<sub>3</sub>, 2-CH<sub>2</sub>-CH<sub>3</sub>).

### (1*R*/3*R*/5*S*)-1-Pyrrolidino-1,2,3,4-tetrahydro-2,2-dimethyl-3-phenyl-9*H*-xanthen-9-one (**10a**)

(*E*)-2-Styryl-4-chromone (**1a**) (0.43 g, 1.73 mmol) and freshly prepared 2-methyl-1-pyrrolidinoprop-1-ene (5.46 g, 43.7 mmol) in EtOH (95%, 25 ml) were refluxed for 24 h. The product mixture was rotary evaporated and the resulting gum was subjected to column chromatography yielding (1*R*/3*R*/5*S*)-1-pyrrolidino-1,2,3,4-tetrahydro-2,2-dimethyl-3-phenyl-9*H*-xanthen-9-one (**10a**) as yellow crystals (0.42 g, 65%) (mp 148–150 °C, 95% EtOH–CHCl<sub>3</sub>).  $\nu_{\max}/\text{cm}^{-1}$  1635 (Found C, 80.06; H, 7.33; N, 3.72%. C<sub>25</sub>H<sub>27</sub>NO<sub>2</sub> requires C, 80.40; H, 7.29; N, 3.75%); *m/z* 373 (*M*<sup>+</sup>, 19%), 305 (20), 304 (88), 302 (20), 242 (17), 241 (100);  $\delta_{\text{H}}$  8.24 (1H, dd, *J* = 7.8, 1.7 Hz, H-8), 7.64 (1H, m, H-6), 7.43–7.24 (7H, m, H-5/7/2'/6'/3'/5'/4'), 3.77 (1H, s, H-1), 3.36 (1H, dd, *J* = 12.2, 6.4 Hz, H-3), 3.12 (1H, dd, *J* = 19.0, 12.2 Hz, H-4), 2.91–2.87 (2H, m), 2.81 (1H, dd, *J* = 19.0, 6.4 Hz, H-4), 2.74–2.71 (2H, m), 1.74–1.68 (4H, m), 0.86 (3H, s, 2-Me), 0.81 (3H, s, 2-Me);  $\delta_{\text{C}}$  178.0 (C, C-9), 164.1 (C, C-4a), 155.9 (C, C-5a), 140.9 (C, C-1'), 133.2 (CH, 129.3 (CH, C-3' and 5'), 128.0 (CH, C-2' and 6'), 126.7 (CH), 126.1 (CH), 124.7 (CH), 123.3 (C), 118.8 (C), 117.7 (CH), 62.7 (CH, C-1), 53.3 (CH<sub>2</sub>, pyrrolidine), 53.3 (CH<sub>2</sub>, pyrrolidine), 43.2 (CH, C-3), 32.1 (CH<sub>2</sub>, C-4), 25.1 (CH<sub>3</sub>, 2-Me), 24.2 (CH<sub>2</sub>, pyrrolidine), 24.2 (CH<sub>2</sub>, pyrrolidine), 19.8 (CH<sub>3</sub>, 2-Me).

### Crystal data for **4a**

A colourless crystal of dimensions 0.30 × 0.15 × 0.10 mm mounted on a glass fibre. C<sub>21</sub>H<sub>18</sub>O<sub>2</sub>, *M* = 302.37. Monoclinic, *a* = 14.408(2), *b* = 7.933(2), *c* = 14.544(2) Å,  $\beta$  = 107.88(2)°, *V* = 1594.0(5) Å<sup>3</sup>, *F*<sub>000</sub> = 640,  $\lambda$  = 0.710 73 Å, *T* = 301.2 K, space group *P*2<sub>1</sub>/*n* (no. 14), *Z* = 4, *D*<sub>c</sub> = 1.260 g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha)$  = 0.08 m<sup>-1</sup>. Data collected on a MAR diffractometer with a 300 mm image plate. A total of 22412 reflections was measured, of which 2946 were unique (*R*<sub>int</sub> = 0.067). Final least-squares refinement for 208 parameters using 1661 reflections gave *R* = 0.071, *wR* = 0.097 and GOF = 1.99. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.<sup>13</sup> CCDC reference number 2071476. See <http://www.rsc.org/suppdata/p1/b0/b004422i/> for crystallographic files in .cif format.

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