

A convenient general synthesis of 3-substituted 2*H*-chromene derivatives

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Reactions of 2-hydroxybenzaldehydes and 2-hydroxy-1-naphthaldehydes with various activated alkenes under Baylis–Hillman conditions have been shown to proceed with regioselective cyclisation to afford the corresponding 3-substituted chromene derivatives. In some cases competitive dimerisation of the alkene component was observed, and direct dimerisation in the absence of the aldehyde has been explored.

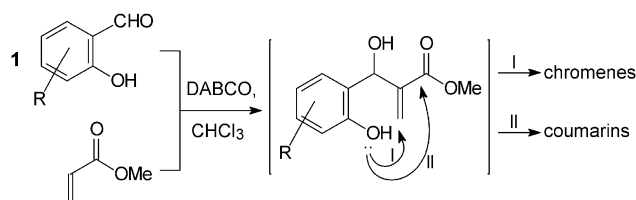
Introduction

Many naturally-occurring pharmacologically active compounds contain the 2*H*-1-benzopyran (2*H*-chromene) nucleus. Notable amongst these are the 2,2-dimethylchromene derivatives isolated from propolis, a resinous product known for over 2000 years for its healing properties.¹ Calanolide F, isolated from *Calophyllum tesmannii*,² also contains the 2,2-dimethylchromene moiety and exhibits anti-HIV activity, while synthetic analogues have been shown to possess antihypertensive³ and anti-ischaemic⁴ activity.

Various protocols have been developed for the synthesis of 2*H*-chromenes,⁵ and new methods of accessing these important compounds continue to be reported. These include: the intramolecular cyclisation of Wittig intermediates;⁶ the microwave-assisted reaction of salicylaldehyde with enamines;⁷ the iodine-catalysed cyclocondensation of 2-hydroxybenzaldehydes with 2,2-dimethoxypropane⁸ and ring-closing olefin metathesis.⁹ In a preliminary communication¹⁰ we recently described a novel and convenient synthesis of 3-acyl-2*H*-chromenes involving the Baylis–Hillman reaction of 2-hydroxybenzaldehydes with methyl vinyl ketone (MVK) in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO). DeBoer¹¹ has prepared 2*H*-chromenes by reacting salicylaldehyde (as the phenoxide ion) with activated alkenes in an approach which presumably involves conjugate addition, followed by an aldol-type cyclisation. However, there is ample evidence, which will be reported elsewhere,¹² that the DABCO-catalysed reactions follow a Baylis–Hillman pathway.^{13,14}

Results and discussion

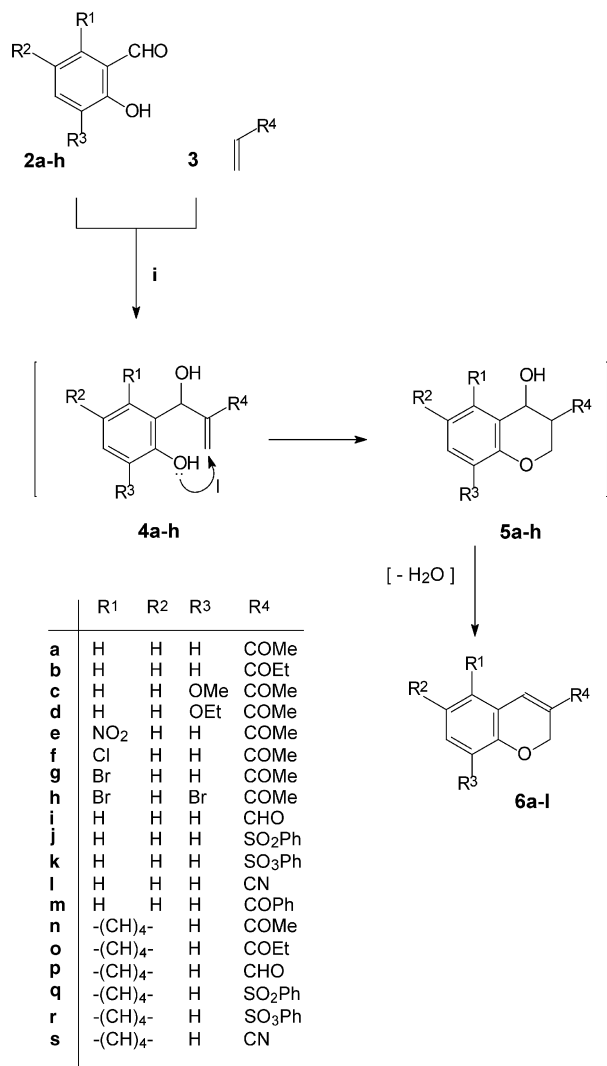
Previous attempts to prepare 2*H*-chromenes chemoselectively via the cyclisation of 2-hydroxybenzaldehyde-derived Baylis–Hillman products had proved unsuccessful affording, instead, complex mixtures of coumarin and chromene derivatives (Scheme 1).¹⁵ Thus, while conjugate addition involving attack of



Scheme 1

the phenolic oxygen at the vinylic centre (path I) provides access to chromene derivatives, nucleophilic substitution at the acyl centre of the ester group (path II) leads to coumarin derivatives. Inhibition of the latter pathway was successfully achieved by replacing the acrylic esters used in the initial study¹⁵ with vinyl ketones ($R^4 = \text{COMe}, \text{COEt}$; Scheme 2), while careful optimisation of the reaction conditions permitted isolation of chromene derivatives in up to 87% yield.¹⁰ After examining various solvent systems for the reaction of salicylaldehyde with MVK, it was found that use of a vigorously stirred, heterogeneous mixture of chloroform and water, as the solvent system, and use of 0.8 equivalents of DABCO gave the best result; further improvement in the yield was achieved by adding more MVK at intervals during the course of the reaction.¹⁰ The generality of the Baylis–Hillman approach to chromenes has subsequently been demonstrated by extending: i, the range of activated alkenes to include acrylaldehyde, acrylonitrile, phenyl vinyl sulfone and phenyl ethenesulfonate and ii, the range of 2-hydroxybenzaldehyde substrates to include 2-hydroxy-1-naphthaldehyde.

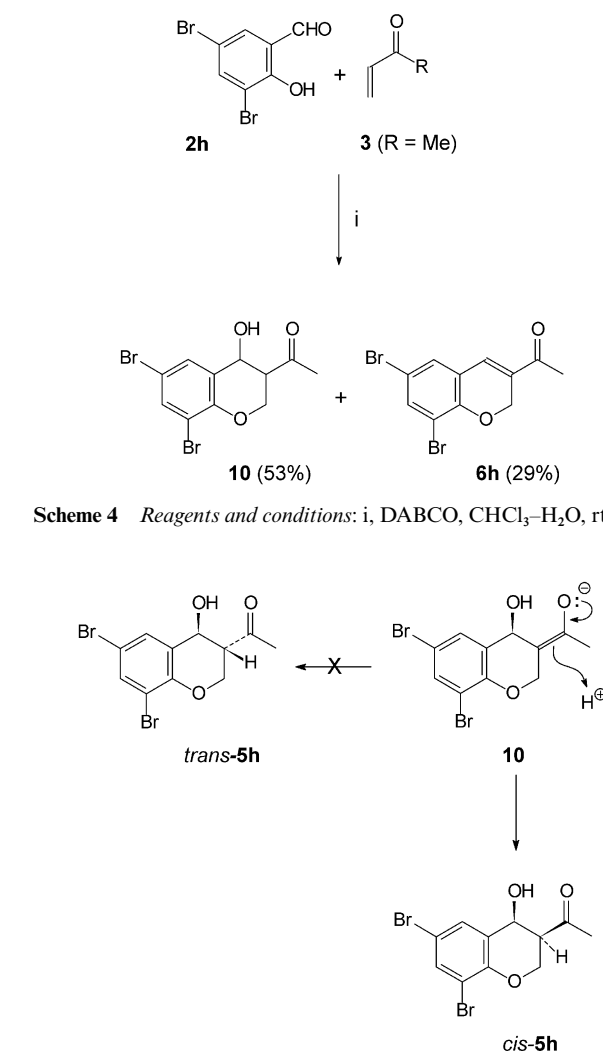
Treatment of salicylaldehyde **2a** ($R^1 = R^2 = R^3 = \text{H}$; Scheme 2) with acrylaldehyde, phenyl vinyl sulfone, phenyl ethenesulfonate and acrylonitrile under the established conditions afforded the 3-substituted chromenes **6i–l**, respectively, in yields ranging from 54 to 70%. Use of phenyl vinyl ketone **8**, however, gave 3-benzoyl-2*H*-chromene **6m** in disappointingly low yield (10%), the major product being the ketone dimer **9a** (Scheme 3), while reaction of 2-hydroxy-3,5-dinitrobenzaldehyde **2t** with MVK gave none of the expected chromene but afforded, instead, the MVK dimer **9b** as the sole product. Electron-withdrawing substituents are expected to activate the aldehyde to nucleophilic attack by a zwitterionic intermediate in the rate-determining step of the Baylis–Hillman reaction¹⁶ but, in the case of 2-hydroxy-3,5-dinitrobenzaldehyde **2t**, none of the expected product was obtained. The *ortho*- and *para*-nitro substituents presumably enhance the acidity of the phenolic hydroxy group to the extent that protonation of DABCO occurs with consequent inhibition of its catalytic activity. In the reaction of 3,5-dibromo-2-hydroxybenzaldehyde **2h** with MVK, the chroman-4-ol **5h** was isolated in 53% yield together with the expected chromene **6h** (29%; Scheme 4), a result which is clearly consistent with the addition–elimination sequence proposed in Scheme 2. Although the chroman-4-ol **5h** contains two stereogenic centres, the apparent absence of signal doubling in both the ¹H- and ¹³C NMR spectra suggests the presence of only one diastereomer (as an enantiomeric pair), formulated



Scheme 2 Reagents and conditions: i, DABCO, CHCl₃-H₂O, rt.

as the *cis*-isomer *cis*-**5h** (Fig. 1) on the basis of the small vicinal coupling ($J_{3,4} = 3.5$ Hz) between the 3- and 4-methine protons. In a *trans*-diequatorial arrangement of the 3- and 4-substituents, the methine protons would be diaxial and could be expected to exhibit much larger coupling constants. The observed stereochemistry is attributed to protonation at the less hindered face of the enolate intermediate **10**.

Reaction of 2-hydroxy-1-naphthaldehyde **2n** (instead of salicylaldehyde) with the series of activated alkenes **3** afforded

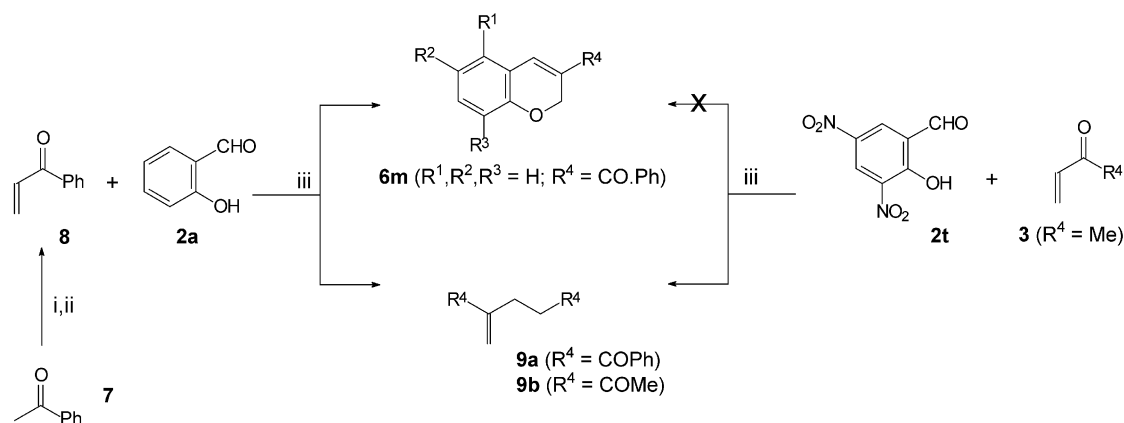


Scheme 4 Reagents and conditions: i, DABCO, CHCl₃-H₂O, rt, 7 d.

Fig. 1 Diastereofacial selectivity during enolate protonation (showing one enantiomeric series).

the corresponding 3-substituted benzo[*f*]chromenes **6n-s** in yields ranging from 17 to 67% (Table 1); in some cases, the benzochromanol precursors **5q-s** were isolated in low yields (2–4%) together with the corresponding benzo[*f*]chromenes **6**.

In an earlier study in our laboratories, Robinson^{13,15} had isolated the 4-substituted chromane **13** (Scheme 5) from a reaction between salicylaldehyde and methyl acrylate under Baylis–Hillman conditions. The formation of this product was attributed to *in situ* conjugate addition of the “Baylis–Hillman

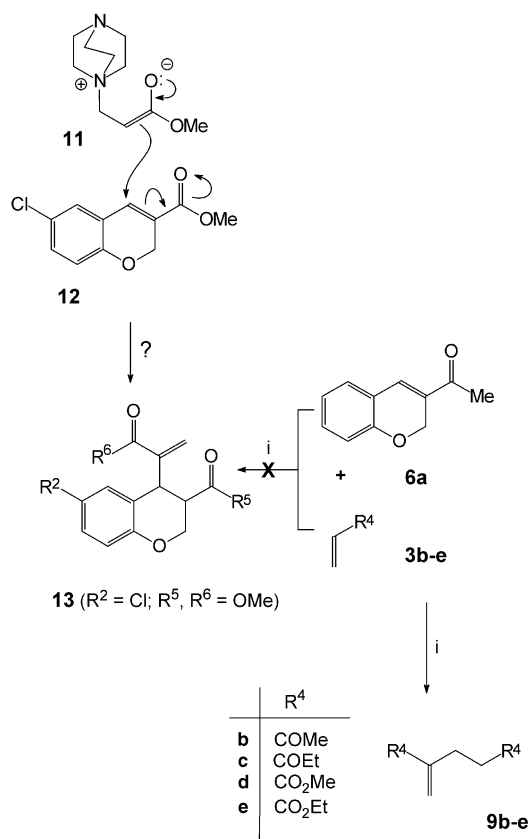


Scheme 3 Reagents and conditions: i, HCHO, Me₂NH₂Cl, HCl, EtOH, reflux, 2 h; ii, heat; iii, DABCO, CHCl₃-H₂O, rt, 7 d.

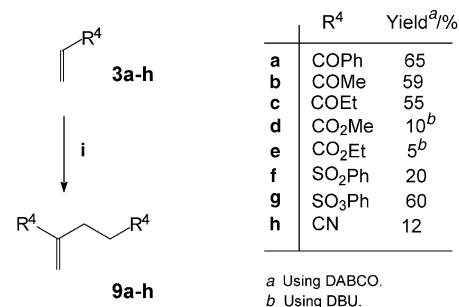
Table 1 Data for 3-substituted chromene derivatives **6a–s** (Scheme 2)

| Compd. | R ¹ | R ² | R ³ | R ⁴ | Yield ^a (%) | Found | HRMS data: <i>m/z</i> , <i>M</i> ⁺ | |
|-----------|----------------------|-----------------|----------------|--------------------|------------------------|----------|---|----------|
| | | | | | | | Mol. formula | Required |
| 6a | H | H | H | COMe | 81 | 174.0671 | C ₁₁ H ₁₀ O ₂ | 174.0681 |
| 6b | H | H | H | COEt | 83 | 188.0835 | C ₁₂ H ₁₂ O ₂ | 188.0837 |
| 6c | H | H | OMe | COMe | 79 | 204.0788 | C ₁₂ H ₁₂ O ₃ | 204.0786 |
| 6d | H | H | OEt | COMe | 84 | 218.0945 | C ₁₃ H ₁₄ O ₃ | 218.0943 |
| 6e | H | NO ₂ | H | COMe | 54 | 219.0516 | C ₁₁ H ₉ NO ₄ | 219.0532 |
| 6f | H | Cl | H | COMe | 56 | 208.0296 | C ₁₁ H ₉ ³⁵ ClO ₂ | 208.0291 |
| 6g | H | Br | H | COMe | 87 | 251.9795 | C ₁₁ H ₉ ⁷⁹ BrO ₂ | 251.9786 |
| 6h | H | Br | Br | COMe | 29(53) ^b | 329.8881 | C ₁₁ H ₈ O ₂ ⁷⁹ Br ₂ | 329.8891 |
| 6i | H | H | H | CHO | 54 | 160.0532 | C ₁₀ H ₈ O ₂ | 160.0524 |
| 6j | H | H | H | SO ₂ Ph | 70 | 272.0510 | C ₁₅ H ₁₂ O ₃ S | 272.0506 |
| 6k | H | H | H | SO ₂ Ph | 60 | 288.0444 | C ₁₅ H ₁₂ O ₄ S | 288.0455 |
| 6l | H | H | H | CN | 65 | 157.0520 | C ₁₀ H ₇ NO | 157.0527 |
| 6m | H | H | H | COPh | 10 ^c | 236.0835 | C ₁₆ H ₁₂ O ₂ | 236.0837 |
| 6n | -(CH) ₄ - | | H | COMe | 67 | 224.0832 | C ₁₅ H ₁₂ O ₂ | 224.0837 |
| 6o | -(CH) ₄ - | | H | COEt | 58 | 238.0994 | C ₁₆ H ₁₄ O ₂ | 238.1005 |
| 6p | -(CH) ₄ - | | H | CHO | 17 | 210.0678 | C ₁₄ H ₁₀ O ₂ | 210.0681 |
| 6q | -(CH) ₄ - | | H | SO ₂ Ph | 20(2) ^b | 322.0674 | C ₁₉ H ₁₄ O ₃ S | 322.0664 |
| 6r | -(CH) ₄ - | | H | SO ₂ Ph | 61(4) ^b | 338.0617 | C ₁₉ H ₁₄ O ₄ S | 338.0613 |
| 6s | -(CH) ₄ - | | H | CN | 50(2) ^b | 207.0675 | C ₁₄ H ₉ NO | 207.0684 |

^a Chromatographed material. ^b Yield of corresponding chroman-4-ol intermediate. ^c The dimer **9a** was isolated as the major product (65%; see Scheme 3).

**Scheme 5** Reagents and conditions: i, DABCO, CHCl₃, rt.

zwitterion" **11** to methyl 6-chlorochromene-3-carboxylate **12**, the latter acting as a Michael acceptor. In an attempt to demonstrate such transformations, 3-acetyl-2*H*-chromene **6a** was treated with several activated alkenes **3b–e** in the presence of DABCO but, in each case, the sole product was the corresponding alkene dimer **9** (Scheme 5). Dimerisation of activated alkenes in the presence of DABCO has been reported by Drewes *et al.*¹⁷ and Basavaia *et al.*¹⁸ while other researchers have effected similar dimerisation using phosphine¹⁹ and rhodium complex²⁰ catalysts. The formation of such dimers as competition products in our own studies prompted further examination of this reaction using the activated alkenes **3a–h** as

**Scheme 6** Reagents and conditions: i, DABCO or DBU, CHCl₃.

substrates (Scheme 6). The dimeric products **9a–h** were obtained in low to moderate yields, methyl and ethyl acrylate requiring the use of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)²¹ to effect dimerisation, albeit in very low yield (10% and 5% respectively).

In summary, it is evident that the application of Baylis–Hillman methodology provides convenient, general and relatively efficient access to 3-substituted 2*H*-chromenes, and that the alkene dimers, observed in some cases as competition products, can generally be obtained by direct dimerisation using an appropriate catalyst.

Experimental

Melting points were determined using a Kofler hot-stage apparatus and are uncorrected. NMR spectra were recorded on Bruker AMX400 or AVANCE 400 MHz spectrometers at 303 K in CDCl₃ or DMSO-*d*₆, and calibrated using solvent signals. Infrared spectra were recorded on a Perkin Elmer FT-IR spectrum 2000 spectrometer, using hexachlorobutadiene or nujol mulls, thin films or NaCl discs. Low-resolution (EI) mass spectra were obtained on a Finnigan-Mat GCQ mass spectrometer and high-resolution (EI) mass spectra on a VG70-SEQ double-focusing magnetic sector spectrometer (Cape Technikon Mass Spectrometry unit). Elemental (HRMS) analytical and other data for the chromene derivatives **6a–s** are detailed in Table 1. The general synthetic procedures are illustrated by the following examples.

3-Acetyl-2*H*-chromene **6a**

A mixture of salicylaldehyde **2a** (1.0 cm³, 9.6 mmol), methyl vinyl ketone (1.2 cm³, 14 mmol) and DABCO (0.86 g, 7.7 mmol)

in CHCl_3 (1.0 cm^3) and H_2O (1.0 cm^3) was stirred vigorously under N_2 in a stoppered flask at room temperature. After stirring the reaction mixture for 24 hours, additional methyl vinyl ketone (0.4 cm^3 , 5 mmol) and DABCO (0.29 g, 2.6 mmol) were added and stirring was continued for 24 hours before adding further quantities of methyl vinyl ketone (0.20 cm^3 , 2.4 mmol) and DABCO (0.10 g, 0.85 mmol) and stirring for a further 72 hours. Flash chromatography of the resulting mixture [on silica; elution with hexane–EtOAc (4 : 1)] afforded, as yellow crystals, 3-acetyl-2H-chromene **6a**, mp 39–40 °C (lit.¹¹ 50–53 °C); ν_{max} (hexachlorobutadiene $\text{mull}/\text{cm}^{-1}$) 1655 (CO); δ_{H} (400 MHz; CDCl_3) 2.39 (3H, s, CH_3), 4.99 (2H, s, CH_2), 6.83 (1H, d, J 7.1, ArH), 6.95–7.23 (3H, series of multiplets, ArH) and 7.29 (1H, s, 4-H); δ_{C} (100 MHz; CDCl_3) 25.0 (CH_3), 64.2 (CH_2), 116.3, 120.7, 121.8, 129.1, 130.8, 132.4, 133.9 and 155.6 (ArC and C=CH) and 195.9 (CO); m/z 174 (M^+ , 62%) and 131 (100).

3-Acetyl-6,8-dibromochroman-4-ol **5h** and 3-acetyl-6,8-dibromo-2H-chromene **6h**

3,5-Dibromo-2-hydroxybenzaldehyde **2h** (1.0 g, 3.6 mmol) was reacted with methyl vinyl ketone (0.44 cm^3 , 5.4 mmol) and DABCO (0.32 g, 2.9 mmol) in chloroform (1.0 cm^3) and water (1.0 cm^3) following the general procedure. Work-up and flash chromatography gave two products:

i) **3-Acetyl-6,8-dibromo-2H-chromene 6h**. Yellow crystals, mp 74–75 °C; ν_{max} (hexachlorobutadiene $\text{mull}/\text{cm}^{-1}$) 1666 (CO); δ_{H} (400 MHz; CDCl_3) 2.40 (3H, s, CH_3), 5.10 (2H, s, CH_2), 7.16 (1H, s, 4-H), 7.23 (1H, d, J 2.2, ArH) and 7.58 (1H, d, J 2.2, ArH); δ_{C} (100 MHz; CDCl_3) 25.2 (CH_3), 65.3 (CH_2), 111.2, 113.5, 123.2, 130.5, 131.5, 132.1, 137.4 and 151.4 (ArC and CH=C) and 195.3 (CO); m/z 332 (M^+ , 64.3%) and 289 (100).

ii) **3-Acetyl-6,8-dibromochroman-4-ol 5h**. Pale yellow crystals, mp 132–134 °C (Found: M^+ , 347.8990. $\text{C}_{11}\text{H}_{10}\text{O}_3^{79}\text{Br}_2$ requires: M , 347.8997); ν_{max} (hexachlorobutadiene $\text{mull}/\text{cm}^{-1}$) 3444 (OH) and 1696 (CO); δ_{H} (400 MHz; CDCl_3) 2.34 (3H, s, CH_3), 3.02 (1H, d, J 5.3, OH), 3.04 (1H, m, 3-H), 4.43 (1H, dd, J 11.4 and 13.8, 2-H), 4.60 (1H, dd, J 3.5 and 11.4, 2-H), 5.04 (1H, m, 4-H), 7.44 (1H, s, ArH) and 7.60 (1H, s, ArH); δ_{C} (100 MHz; CDCl_3) 29.0 (CH_3), 50.6 (CH), 63.2 (CH_2), 64.2 (CH), 111.7, 112.9, 126.1, 131.8, 135.7 and 150.1 (ArC) and 206.8 (CO); m/z 350 (M^+ , 30%) and 289 (100).

3-Benzoyl-2H-chromene **6m** and 1,5-diphenyl-2-methylene-pentane-1,5-dione **9a**

Salicylaldehyde **2a** (1.0 cm^3 , 9.6 mmol) was reacted with phenyl vinyl ketone **8**²² (1.9 g, 14 mmol) and DABCO (0.86 g, 7.7 mmol) in chloroform (1.0 cm^3) and water (1.0 cm^3) following the general procedure. Work-up and flash chromatography gave two products:

i) **3-Benzoyl-2H-chromene 6m**. Yellow oil; ν_{max} (hexachlorobutadiene $\text{mull}/\text{cm}^{-1}$) 1750 (CO); δ_{H} (400 MHz; CDCl_3) 5.16 (2H, s, CH_2), 6.91–7.73 (10H, series of multiplets, ArH and 4-H); δ_{C} (100 MHz; CDCl_3) 65.3 (CH_2), 116.4, 121.0, 121.8, 128.4, 129.0, 129.3, 129.8, 132.0, 132.5, 137.0, 137.6 and 155.6 (ArC and C=CH) and 194.1 (CO); m/z 236 (M^+ , 24.0%) and 105 (100).

ii) **1,5-Diphenyl-2-methylene-pentane-1,5-dione 9a**. White crystals, mp 52 °C (lit.²⁴ 57–58 °C); ν_{max} (in chloroform/ cm^{-1}) 1684 and 1650 (2 \times CO); δ_{H} (400 MHz; CDCl_3) 2.91 (2H, t, J 7.2, CH_2), 3.24 (2H, t, J 2.2, CH_2), 5.67 and 5.96 (2H, 2 \times s, C=CH₂) and 7.40–7.98 (10H, series of multiplets, ArH); δ_{C} (100 MHz; CDCl_3) 27.3 (CH_2), 37.2 (CH_2), 127.3, 128.1, 128.2, 128.6, 129.5, 132.2, 133.1, 136.7, 137.7 and 146.7 (ArC and C=CH₂), 198.1 (CO) and 199.2 (CO).

3-Phenylsulfonyl-3,4-dihydro-2H-benzo[*f*]chromen-4-ol **5q** and 3-phenylsulfonyl-2H-benzo[*f*]chromene **6q**

A mixture of 2-hydroxy-1-naphthaldehyde **2n** (1.0 g, 5.8 mmol), phenyl vinyl sulfone (1.5 g, 8.7 mmol) and DABCO (0.52 g, 4.7 mmol) in CHCl_3 (1.0 cm^3) and water (1.0 cm^3) was stirred vigorously at room temperature under N_2 . After stirring for 24 hours, phenyl vinyl sulfone (0.5 g, 2.9 mmol) and DABCO (0.17 g, 1.6 mmol) were added and stirring was continued for 72 hours; thereafter, additional phenyl vinyl sulfone (0.25 g, 1.5 mmol) and DABCO (0.06 g, 0.5 mmol) were added and stirring was continued for a further 72 hours. Flash chromatography of the resulting mixture [on silica; elution with hexane–EtOAc (4 : 1)] afforded two products:

i) **3-Phenylsulfonyl-2H-benzo[*f*]chromene 6q**. Dark yellow crystals, mp 186–188 °C; ν_{max} (chloroform/ cm^{-1}) 3020 (C=C–H) and 2918 (CH_2); δ_{H} (400 MHz; CDCl_3) 4.97 (2H, d, J 0.8, CH_2), 7.10 (1H, d, J 8.8, ArH), 7.21–7.80 (10H, series of multiplets, ArH) and 7.88 (1H, s, 4-H); δ_{C} (100 MHz; CDCl_3) 63.1 (CH_2), 113.4, 117.2, 121.3, 124.8, 127.8, 128.1, 128.3, 128.8, 129.3, 129.5, 130.7, 133.6, 133.7, 139.7 and 153.6 (ArC and C=CH); m/z 322 (M^+ , 66%) and 180 (100).

ii) **3-Phenylsulfonyl-3,4-dihydro-2H-benzo[*f*]chromen-4-ol 5q**. An oil, (Found: M^+ , 340.0769. $\text{C}_{19}\text{H}_{16}\text{O}_4\text{S}$ requires: M , 340.0779); ν_{max} (hexachlorobutadiene $\text{mull}/\text{cm}^{-1}$) 3023 (OH); δ_{H} (400 MHz; CDCl_3) 3.28 (1H, d, J 3.5, OH), 3.63 (1H, dt, J 3.0 and 11.8, 3-H), 4.55 (1H, m, 2-H), 4.65 (1H, t, J 11.8, 2-H), 5.83 (1H, s, 4-H), 7.00 (1H, d, J 9.0, ArH), 7.37–8.07 (10H, series of multiplets, ArH); δ_{C} (100 MHz; CDCl_3) 59.0 (CH_2), 59.5 (CH), 63.2 (CH), 113.5, 118.2, 121.8, 124.2, 127.6, 128.5, 128.6, 129.3, 129.6, 131.3, 132.3, 134.5, 138.6 and 151.5 (ArC); m/z 340 (M^+ , 90%) and 169 (100).

3-Methyleneheptane-2,6-dione **9b**

A mixture of methyl vinyl ketone (1.0 cm^3 , 12 mmol) and DABCO (0.45 g, 4.0 mmol) in chloroform (1.0 cm^3) was stirred at room temperature in a stoppered reaction flask for 7 days. The resulting mixture was purified by flash chromatography [elution with hexane–EtOAc (3 : 2)] to afford, as a dark yellow oil, 3-methyleneheptane-2,6-dione **9b**, ν_{max} (thin film/ cm^{-1}) 1709 and 1670 (CO); δ_{H} (400 MHz; CDCl_3) 2.02 (3H, s, CH_3), 2.22 (3H, s, CH_3), 2.43 (2H, m, CH_2), 2.47 (2H, m, CH_2), 5.73 and 5.93 (2H, 2 \times s, C=CH₂); δ_{C} (100 MHz; CDCl_3) 25.0 (CH_3), 25.6 (CH_2), 29.6 (CH_2), 42.2 (CH_3), 125.9 (C=C₂), 147.5 (C=C₂), 199.2 (CO) and 207.5 (CO).

Compounds **6a**, **6c**, **6f** and **6g**,²³ **6i**,¹¹ **6l**,²³ **6m**,¹¹ **9a**,²⁴ **9b**,²⁵ **9c**,²⁶ **9d** and **9e**²⁷ and **9h**¹⁸ have also been reported by other researchers; compounds **6b**, **6d**, **6e** and **6h** were reported in our preliminary communication.¹⁰ Analytical data for the other, new chromene derivatives **6** and dimeric products **9** are as follows.

3-Phenylsulfonyl-2H-chromene **6j**

White crystals, mp 122–123 °C; ν_{max} (hexachlorobutadiene $\text{mull}/\text{cm}^{-1}$) 3077 and 3058 (C=C–H) and 1311 (S=O); δ_{H} (400 MHz; CDCl_3) 4.85 (2H, s, CH_2), 6.68 (1H, d, J 16.6, ArH) and 6.81–7.92 (9H, series of multiplets, ArH and 4-H); δ_{C} (100 MHz; CDCl_3) 63.11 (CH_2), 116.3, 119.9, 122.3, 127.9, 129.4, 129.5, 131.1, 132.6, 132.8, 133.8, 139.3 and 154.1 (ArC and CH=C); m/z 272 (M^+ , 91%) and 131 (100).

Phenyl 2H-chromene-3-sulfonate **6k**

White crystals, mp 82–84 °C; ν_{max} (hexachlorobutadiene $\text{mull}/\text{cm}^{-1}$) 3065 (C=C–H), 2922 (CH_2) and 1487 (S=O); δ_{H} (400 MHz; CDCl_3) 5.21 (2H, d, J 1.0, CH_2), 6.92 (1H, d, J 8.1, ArH) and 6.97–7.37 (9H, series of multiplets, ArH and 4-H); δ_{C} (100 MHz; CDCl_3) 63.3 (CH_2), 116.7, 119.7, 122.3, 122.5,

125.1, 127.4, 129.6, 129.9, 133.3, 135.8, 149.4 and 154.7 (ArC and C=CH); m/z 288 (M^+ , 69%) and 131 (100).

3-Acetyl-2H-benzof[*f*]chromene 6n

Yellow crystals, mp 122–124 °C; ν_{\max} (hexachlorobutadiene mull/cm⁻¹) 1660 (CO); δ_{H} (400 MHz; CDCl₃) 2.51 (3H, s, CH₃), 5.09 (2H, s, CH₂), 7.10 (1H, d, *J* 8.6, ArH), 7.41–7.99 (6H, series of multiplets, ArH) and 8.01 (1H, s, 4-H); δ_{C} (100 MHz; CDCl₃) 25.1 (CH₃), 64.0 (CH₂), 113.9, 117.6, 120.9, 124.4, 127.7, 128.4, 128.9, 129.4, 130.1, 130.8, 133.2 and 155.2 (ArC and C=C) and 195.6 (CO); m/z 224 (M^+ , 63%) and 181 (100).

3-Propanoyl-2H-benzof[*f*]chromene 6o

Yellow crystals, mp 88–90 °C; ν_{\max} (chloroform/cm⁻¹) 1654 (CO); δ_{H} (400 MHz; CDCl₃) 1.22 (3H, t, *J* 7.2, CH₃), 2.89 (2H, q, *J* 7.2, CH₂), 5.10 (2H, s, CH₂), 7.10 (1H, d, *J* 8.8, ArH), 7.42–7.99 (5H, series of multiplets, ArH) and 8.02 (1H, s, 4-H); δ_{C} (100 MHz; CDCl₃) 8.6 (CH₃), 30.4 (CH₂), 64.3 (CH₂), 114.0, 117.6, 120.9, 124.3, 127.6, 127.9, 128.8, 128.9, 129.4, 130.8, 133.0 and 155.1 (ArC and C=CH) and 198.6 (CO); m/z 238 (M^+ , 95%) and 181 (100).

2H-Benzof[*f*]chromene-3-carbaldehyde 6p

Yellow crystals, mp 144–146 °C; ν_{\max} (chloroform/cm⁻¹) 1630 (CO); δ_{H} (400 MHz; CDCl₃) 5.1 (2H, s, CH₂), 7.10 (1H, d, *J* 8.6, ArH), 7.41–7.80 (4H, series of multiplets, ArH), 7.95 (1H, s, 4-H), 8.00 (1H, d, *J* 8.6, ArH) and 9.7 (1H, s, CHO); δ_{C} (100 MHz; CDCl₃) 63.2 (CH₂), 114.0, 117.7, 121.0, 124.6, 128.1, 129.0, 129.4, 129.5, 131.1, 130.7, 134.2 and 137.6 (ArC and C=CH) and 189.5 (CO); m/z 210 (M^+ , 65.5%) and 181 (100).

Phenyl 4-hydroxy-3,4-dihydro-2H-benzof[*f*]chromene-3-sulfonate 5r and phenyl 2H-benzof[*f*]chromene-3-sulfonate 6r

2-Hydroxy-1-naphthaldehyde (0.5 g, 2.9 mmol) was reacted with phenyl ethenesulfonate (0.80 g, 4.4 mmol) and DABCO (0.26 g, 2.3 mmol) in CHCl₃ (1.0 cm³) and water (1.0 cm³) following the general procedure. Work-up and flash chromatography gave two products:

i) Phenyl 2H-benzof[*f*]chromene-3-sulfonate 6r. Yellow crystals, mp 164–166 °C; ν_{\max} (chloroform/cm⁻¹) 3022 (C=C–H) and 2923 (CH₂); δ_{H} (400 MHz; CDCl₃) 5.06 (2H, s, CH₂), 7.10 (1H, d, *J* 8.8, ArH), 7.21–7.80 (10H, series of multiplets, ArH) and 7.88 (1H, s, 4-H); δ_{C} (100 MHz; CDCl₃) 63.2 (CH₂), 113.2, 117.3, 121.3, 122.0, 122.3, 124.9, 127.4, 128.2, 128.8, 129.5, 129.9, 130.6, 132.4, 134.2, 149.4 and 154.4 (ArC and C=CH); m/z 338 (M^+ , 100%) and 181 (91.7).

ii) Phenyl 4-hydroxy-3,4-dihydro-2H-benzof[*f*]chromene-3-sulfonate 5r. An oil (Found: M^+ , 356.0722. C₁₉H₁₆O₅S requires: *M*, 356.0718); ν_{\max} (chloroform/cm⁻¹) 3329 (OH); δ_{H} (400 MHz; CDCl₃) 2.74 (1H, d, *J* 4.4, OH), 4.02 (1H, q, *J* 3.5, 3-H), 4.60 (1H, dd, *J* 3.5 and 11.3, 2-H), 4.80 (1H, dd, *J* 3.5 and 11.3, 2-H), 5.93 (1H, m, 4-H), 7.11 (1H, d, *J* 9.2, ArH) and 7.19–8.12 (11H, series of multiplets, ArH); δ_{C} (100 MHz; CDCl₃) 60.6 (CH), 60.8 (CH₂), 61.3 (CH), 112.9, 118.5, 121.9, 122.3, 124.3, 127.4, 127.6, 128.9, 129.8, 130.0, 131.2, 132.2, 148.8 and 152.2 (ArC); m/z 356 (M^+ , 59%) and 198 (100).

3-Cyano-3,4-dihydro-2H-benzof[*f*]chromen-4-ol 5s and 3-cyano-2H-benzof[*f*]chromene 6s

2-Hydroxy-1-naphthaldehyde (1.0 g, 5.8 mmol) was reacted with acrylonitrile (0.57 cm³, 8.7 mmol) and DABCO (0.52 g, 4.7 mmol) in CHCl₃ (1.0 cm³) and water (1.0 cm³) following the general procedure. Work-up and flash chromatography afforded two products:

i) 3-Cyano-2H-benzof[*f*]chromene 6s. Yellow crystals, mp 120–122 °C; ν_{\max} (hexachlorobutadiene mull/cm⁻¹) 2210 (CN); δ_{H} (400 MHz; CDCl₃) 4.88 (2H, s, CH₂), 7.09 (1H, d, *J* 8.8, ArH), 7.43–7.80 (4H, series of multiplets, ArH), 7.85 (1H, s, 4-H) and 7.86 (1H, d, *J* 8.8, ArH); δ_{C} (100 MHz; CDCl₃) 64.2 (CH₂), 100.3, 113.8, 117.0, 117.3, 121.0, 124.8, 128.2, 128.9, 129.5, 129.9, 133.5 and 135.3 (ArC) and 154.0 (CN); m/z 207 (M^+ , 73%) and 206 (100).

ii) 3-Cyano-3,4-dihydro-2H-benzof[*f*]chromen-4-ol 5s. An oil (Found: M^+ , 225.0788. C₁₄H₁₁NO₂ requires: *M*, 225.0790); ν_{\max} (hexachlorobutadiene mull/cm⁻¹) 3421 (OH) and 2249 (CN); δ_{H} (400 MHz; CDCl₃) 2.75 (1H, br s, OH), 3.28 (1H, dt, *J* 11.8 and 3.6, 3-H), 4.42 (1H, m, 2-H), 4.53 (1H, dd, *J* 10.6 and 3.6, 2-H), 5.5 (1H, d, *J* 1.6, 4-H), 7.05 (1H, d, *J* 9.0, ArH), 7.41–7.79 (4H, series of multiplets, ArH) and 8.02 (1H, d, *J* 8.5, ArH); δ_{C} (100 MHz; CDCl₃) 32.3 (CH), 59.7 (CH), 60.7 (CH₂), 112.4, 116.8, 118.4, 121.6, 124.4, 127.8, 128.8, 129.4, 131.5 and 132.2 (ArC) and 151.6 (CN); m/z 225 (M^+ , 66%) and 172 (100).

2,4-Bis(phenylsulfonyl)but-1-ene 9f

A colourless oil (Found: M^+ – PhSO₂, 195.04830. C₁₆H₁₆O₄S₂ requires: *M* – PhSO₂, 195.04798); ν_{\max} (thin film/cm⁻¹) 3038 (C=C–H) and 2929 (CH₂); δ_{H} (400 MHz; CDCl₃) 2.64 (2H, m, CH₂), 3.32 (2H, m, CH₂), 5.80 and 6.38 (2H, 2 × s, C=CH₂) and 7.49–7.88 (10H, series of multiplets, ArH); δ_{C} (100 MHz; CDCl₃) 23.6 (CH₂), 54.4 (CH₂), 126.2, 128.1, 128.2, 129.4, 129.5, 133.9, 134.0, 137.8, 138.4 and 146.7 (ArC and C=CH₂).

Diphenyl but-1-ene-2,4-disulfonate 9g

A colourless oil (Found: M^+ , 368.03881. C₁₆H₁₆O₆S₂ requires: *M*, 368.03883); ν_{\max} (thin film/cm⁻¹) 2922 (CH₂) and 1588 (C=CH₂); δ_{H} (400 MHz; CDCl₃) 3.21 (2H, m, CH₂), 3.63 (2H, m, CH₂), 6.01 and 6.02 (2H, 2 × s, C=CH₂) and 7.18–7.43 (10H, series of multiplets, ArH); δ_{C} (100 MHz; CDCl₃) 25.8 (CH₂), 48.6 (CH₂), 121.8, 121.9, 127.5, 130.0, 130.1, 130.2, 130.3, 141.1, 148.9 and 149.1 (ArC and C=CH₂).

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