Synthesis of neoflavones by Suzuki arylation of 4-substituted coumarins

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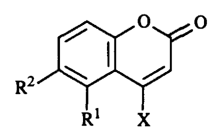
Palladium-catalysed coupling of the 4-chloro- or 4-bromo-coumarins 1–4 with arylboronic acids 5–13 under the Suzuki reaction conditions constitutes an efficient access to 4-arylcoumarins. These 4-arylcoumarins can also be obtained in good yields (70–97%) by treatment of 4-trifluoromethylsulfonyloxycoumarins 35–38 with arylboronic acids under modified Suzuki reaction conditions, involving the use of copper(I) iodide as a co-catalyst.

Introduction

Neoflavonoid, a term first introduced by Ollis,[1] describes a group of natural products with a 4-arylchromane skeleton, the 4-arylcoumarins (4-aryl-2*H*-1-benzopyran-2-ones) being the major structural type of neoflavonoids. They are found in plants belonging to the families *Guttiferae*, *Rubiaceae*, *Leguminosae*, *Passifloraceae* and *Compositae*. A number of studies have been devoted to their isolation and synthesis.[2] The most frequently used method of synthesis is the acid catalysed condensation of a phenolic component with a β-keto ester (the von Pechmann reaction). Although generally convenient, this method suffers from drastically reduced yields when the number of substituents on the B-ring increases. Direct arylation at C-4 of the preformed coumarin ring constitutes an attractive alternative route to these compounds.[3] Recently, Wattanasin used a palladium-catalysed coupling reaction of arylstannanes with 4-trifluoromethylsulfonyloxy-2*H*-1-benzopyran-2-one to prepare 4-(4-fluorophenyl)coumarin and 4-(3-pyridyl)coumarin.[4] An analogous preparation of 4-phenylcoumarin by palladium-catalysed cross-coupling reaction of 4-trifluoromethylsulfonyloxycoumarin with sodium tetraphenylborate proceeded in moderate yield.[5] More recently, the coupling reaction between 4-trimethylstannylcoumarins and aryl iodides or aryl trifluoromethanesulfonates (triflates) was reported as an efficient alternative for the synthesis of 4-arylcoumarins.[6] In the course of our investigation of the synthesis of 4-arylcoumarins by the metal-mediated ligand coupling approach, we decided to investigate the scope of the palladium-catalysed route to 4-arylcoumarins. As an alternative to the use of arylstannanes as the nucleophilic component, arylboronic acids are versatile reagents, which can be conveniently prepared with a wide variety of functional groups. These acids have been found to be an ideal reagent in the synthesis of various functionalised biaryls due to the regio- and stereo-specificity of the palladium-catalysed cross-coupling reaction of these reagents with organic electrophiles.[7] In the field of flavonoid chemistry, this type of aryl–aryl coupling was successfully used by Muller *et al.* in a synthesis of the natural product ginkgetin,[8] and the aryl–vinyl coupling in a new synthesis of isoflavone derivatives by Suzuki and co-workers[9] and by Yokoe *et al.*[10] We now describe that coumarins substituted with a 4-halogeno or a 4-trifluoromethylsulfonyloxy group can undergo aryl–vinyl coupling with arylboronic acids to afford the corresponding neoflavonoids.

Results and discussion

Since aryl bromides undergo the cross-coupling reaction very easily, the synthesis of 4-bromo-2*H*-1-benzopyran-2-ones was attempted by transformation of the hydroxy group of 4-hydroxycoumarins into a halogenated derivative. 4-Bromo-2*H*-1-benzopyran-2-one **1** was prepared in 59% yield by the method

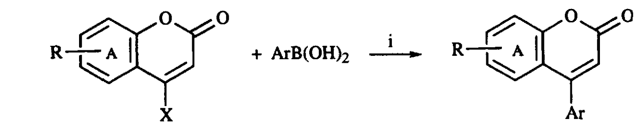


1 X = Br, R^1 = H, R^2 = H
2 X = Cl, R^1 = H, R^2 = H
3 X = Cl, R^1 = MeO, R^2 = H
4 X = Cl, R^1 = H, R^2 = MeO

of Tschesche *et al.*[11] Phosphorus oxybromide (prepared *in situ* by the reaction of phosphorus pentabromide with anhydrous formic acid) reacted with 4-hydroxycoumarin in the absence of solvent at high temperatures. Due to the difficulties encountered in preparing 4-bromocoumarin, the alternative substrate 4-chlorocoumarin **2** was synthesised. Exchange of the 4-hydroxy group with a chlorine atom was achieved by using triphenylphosphine in dry carbon tetrachloride.[12] 4-Chloro-2*H*-1-benzopyran-2-one **2** was obtained in 61% yield, and the 4-chloro-5-methoxy-2*H*-1-benzopyran-2-one **3** and 4-chloro-6-methoxy-2*H*-1-benzopyran-2-one 4 were similarly prepared in 89 and 59% yield respectively.

The boronic acids (Table 1) were prepared by treatment of the appropriate aryllithium with triisopropyl borate to form the arylboronic ester. Subsequent hydrolysis of the ester gave the boronic acid. Triisopropyl borate was chosen as the transmetallating agent as it had been found that this borate gave consistently high yields of pure arylboronic acids.[13] When the trimethyl or tributyl borate esters were used instead of triisopropyl borate, the arylboronic acid component was contaminated with di- and tri-arylboron species. These impurities had a detrimental effect on the yield of the cross-coupling reaction.

Both 4-bromo-2*H*-1-benzopyran-2-one **1** and 4-chloro-2*H*-1-benzopyran-2-one **2** underwent the Suzuki coupling reaction with arylboronic acids (Scheme 1 and Table 2). The 4-halogenocoumarin was treated with the arylboronic acid in the

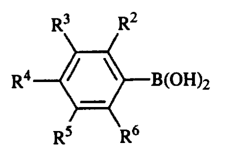


1–4 **5–13** **14–34**

Scheme 1 *Reagents:* i, $Pd(PPh_3)_4$, Na_2CO_3, C_6H_6–H_2O–EtOH

presence of 4% tetrakis(triphenylphosphine)palladium(0) in benzene. Aqueous sodium carbonate (2 equiv.) was added to catalyse the reaction. The reaction proved equally effective with either 4-bromo- or 4-chloro-2*H*-1-benzopyran-2-one. The nature of the aryl group introduced at the 4-position had very little effect on the overall yield. There was no evidence of substitution at the *ortho* position having an effect on the reaction as 4-(2-methoxyphenyl)-2*H*-1-benzopyran-2-one **17** was formed in 92% yield and 4-(2,4-dimethoxyphenyl)-2*H*-1-benzopyran-2-one **19** was formed in 88% yield. It is interesting to note that the position of the methoxy group in monomethoxy-substituted arylboronic acids did not have a large effect on the yields of the corresponding arylated products, although of the three reagents, 2-methoxyphenylboronic acid **8** gave the highest yield.

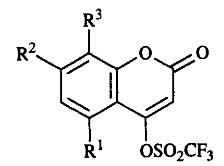
Table 1 Arylboronic acids used in the present study



Compound	R^2	R^3	R^4	R^5	R^6
5	H	H	H	H	H
6	H	H	MeO	H	H
7	H	H	Me	H	H
8	MeO	H	H	H	H
9	H	MeO	H	H	H
10	MeO	H	MeO	H	H
11	MeO	H	H	MeO	H
12	H	MeO	MeO	H	H
13	H	O–CH_2–O		H	H

4-Methoxyphenylboronic acid **6** was found to give the lowest yield (81%) of arylated product. Good yields were also obtained with 3,4-methylenedioxyphenylboronic acid **13** (72% of arylated product) and with 3,4-dimethoxyphenylboronic acid **12** (78% of arylated product). These substitution patterns in the B-ring are prevalent in many naturally occurring 4-arylcoumarins. Finally the reaction was found to be 100% regiospecific in the ipso-substitution of the arylboronic acid. Due to the success of the reaction using 4-chloro-2*H*-1-benzopyran-2-one **2** as substrate, the scope of the reaction was extended to include the A-ring methoxy-substituted 4-chloro-2*H*-1-benzopyran-2-ones. With 4-chloro-6-methoxy-2*H*-1-benzopyran-2-one the arylated product was obtained in nearly quantitative yield. The yields in the arylation of 4-chloro-5-methoxy-2*H*-1-benzopyran-2-one were slightly lower and this may be due to a steric effect caused by the 5-methoxy group. Unfortunately, attempts to prepare 4-chloro-5,7-dimethoxy-2*H*-1-benzopyran-2-one in a similar manner have all failed and the synthesis of 4-aryl-5,7-dimethoxy-2*H*-1-benzopyran-2-ones could not be attempted in this way.

Although not so widespread, coupling of trifluoromethylsulfonyloxy derivatives with organoboron compounds has become increasingly used.[14] As 4-hydroxycoumarins with various patterns of substitution in the A-ring can be easily obtained, we turned our attention to the synthesis of the triflate derivatives of 4-hydroxycoumarins and to their reaction under the conditions of the Suzuki coupling. The 4-trifluoromethylsulfonyloxycoumarins **35–38** were prepared in 80–98%

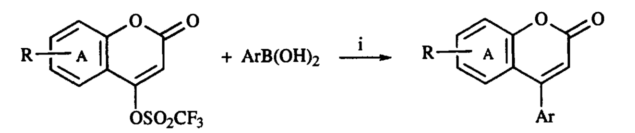


35 $R^1 = R^2 = R^3 = H$
36 R^1 = MeO, $R^2 = R^3 = H$
37 $R^1 = R^2$ = MeO, R^3 = H
38 R^1 = H, $R^2 = R^3$ = MeO

Table 2 Palladium-catalysed arylation reactions of 4-halocoumarins with arylboronic acids

Substrate	$ArB(OH)_2$	Product	*t*/h	Yield (%)	Ar
Unsubstituted A-ring					
2	**5**	**14**	20	88	Ph
1	**6**	**15**	18	81	$4\text{-}MeOC_6H_4$
1	**7**	**16**	20	84	$4\text{-}MeC_6H_4$
2	**8**	**17**	20	92	$2\text{-}MeOC_6H_4$
1	**9**	**18**	22	91	$3\text{-}MeOC_6H_4$
2	**10**	**19**	22	88	$2,4\text{-}(MeO)_2C_6H_3$
2	**11**	**20**	21	76	$2,5\text{-}(MeO)_2C_6H_3$
1	**12**	**21**	22	78	$3,4\text{-}(MeO)_2C_6H_3$
1	**13**	**22**	20	72	$3,4\text{-}(OCH_2O)C_6H_3$
5-*MeO substituted*					
3	**5**	**23**	20	79	Ph
3	**6**	**24**	16	80	$4\text{-}MeOC_6H_4$
3	**7**	**25**	22	65	$4\text{-}MeC_6H_4$
3	**8**	**26**	23	82	$2\text{-}MeOC_6H_4$
3	**9**	**27**	21	79	$3\text{-}MeOC_6H_4$
3	**11**	**28**	21	86	$2,5\text{-}(MeO)_2C_6H_3$
6-*MeO substituted*					
4	**5**	**29**	22	87	Ph
4	**6**	**30**	22	93	$4\text{-}MeOC_6H_4$
4	**7**	**31**	20	92	$4\text{-}MeC_6H_4$
4	**10**	**32**	20	91	$2,4\text{-}(MeO)_2C_6H_3$
4	**12**	**33**	20	91	$3,4\text{-}(MeO)_2C_6H_3$
4	**13**	**34**	22	95	$3,4\text{-}(OCH_2O)C_6H_3$

yield by treatment of the corresponding 4-hydroxycoumarins with triflic anhydride. In a first series of experiments, the 4-trifluoromethylsulfonyloxycoumarin **35** was treated with phenylboronic acid **5** in the presence of tetrakis(triphenylphosphine)palladium(0) and lithium chloride in benzene–ethanol at 85–90 °C. With 2 equiv. of lithium chloride under aqueous conditions, a moderate yield of **14** was observed (56%). Under anhydrous conditions, the amount of lithium chloride played a significant role. After 23 h at 85 °C, the use of 1.1 equiv. of lithium chloride led to 34% of **14**. With 2 equiv. 68% of **14** was obtained, but with 3.3 equiv. a complex mixture resulted with no formation of **14**. In view of the beneficial effect of co-catalytic copper(I) iodide on the Stille reaction,[15–17] we decided to investigate its influence in the Suzuki coupling reaction (Scheme 2 and Table 3). We were



35–38 **5–13** **14, 23, 39–51**

Scheme 2 *Reagents:* $Pd(PPh_3)_4$–CuI, Na_2CO_3, C_6H_6–EtOH

pleased to note that the palladium-catalysed coupling of the triflate derivative **35** with phenylboronic acid **5** in the presence of 1.1 equiv. of copper(I) iodide led to a significant improvement of the yield of **14**. Indeed, under aqueous conditions, after 20 h at 85 °C, the 4-phenylcoumarin **14** was isolated in 75% yield instead of 56%. Eventually a yield of 80% was reached under anhydrous conditions. The reaction was then extended to the synthesis of the A-ring-substituted 4-trifluoromethylsulfonyloxycoumarins **36–38**. A variety of 4-arylcoumarins was then synthesised under the copper co-catalysed conditions, in yields ranging from 71 to 97%. The reactivity of the boronic acids followed the patterns observed with the 4-halogeno derivatives.

In summary, the palladium-catalysed cross-coupling of arylboronic acids with 4-substituted coumarins provides a new and effective route to 4-aryl-2*H*-1-benzopyran-2-ones, which does not involve the use of toxic tin derivatives. Arylboronic acids with substitution patterns prevalent in nature were easily

Table 3 Pd/Cu-catalysed arylation reactions of 4-trifluoromethylsulfonyloxycoumarins with arylboronic acids[a]

Substrate	$ArB(OH)_2$	Product	Yield (%)	Ar
Unsubstituted A-ring				
35	**5**	**14**	80	Ph
5-MeO substituted				
36	**5**	**23**	77	Ph
5,7-(MeO)$_2$ disubstituted				
37	**5**	**39**	93	Ph
37	**6**	**40**	93	$4-MeOC_6H_4$
37	**7**	**41**	79	$4-MeC_6H_4$
37	**8**	**42**	92	$2-MeOC_6H_4$
37	**9**	**43**	96	$3-MeOC_6H_4$
37	**10**	**44**	87	$2,4-(MeO)_2C_6H_3$
37	**11**	**45**	71	$2,5-(MeO)_2C_6H_3$
37	**12**	**46**	92	$3,4-(MeO)_2C_6H_3$
37	**13**	**47**	85	$3,4-(OCH_2O)C_6H_3$
7,8-(MeO)$_2$ disubstituted				
38	**5**	**48**	71	Ph
38	**6**	**49**	97	$4-MeOC_6H_4$
38	**7**	**50**	88	$4-MeC_6H_4$
38	**8**	**51**	90	$2-MeOC_6H_4$

[a] All reactions were performed over a 20 h reaction time.

synthesised, and undergo the cross-coupling reaction in excellent yields. The copper-co-catalysed system involving the 4-trifluoromethylsulfonyloxy derivatives allows the entry into 4-arylcoumarins substituted in the A- and B-rings in good yields. To the best of our knowledge, this constitutes the first report of copper(I) salt catalysis improving noticeably the yield of the Suzuki reaction. It must be noted that, in our case, the catalytic effect influenced the overall yield but did not alter significantly the kinetics of the reaction, as reactions were performed at 85 °C for about 20–25 h in both (catalysed and non-catalysed) systems. From a mechanistic point of view, it is known that the presence of free phosphine plays a key inhibitor role to limit the efficiency of the Suzuki aryl coupling.[18] The effect of the copper(I) iodide may be therefore explained by its influence as a scavenger of free phosphine ligand, similarly to the Stille coupling. In the latter system, the presence of free phosphine was shown to inhibit the transmetallation step and this effect was suppressed by copper(I) co-catalysis.[16]

Experimental

Mps were determined on a Reichert-Jung Thermovar apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1710 or a Mattson Galaxy Series FTIR 3000 spectrometer. ^1H NMR spectra were recorded at either 60 MHz (JEOL JNM-PMX 60) or 270 MHz (JEOL JNM-GX 270). ^{13}C NMR spectra were recorded at 67.8 MHz (JEOL JNM-PMX270). Tetramethylsilane was used as the internal standard in all NMR spectra recorded. All *J* values are given in Hz. Mass spectra were recorded on a VG Analytical 770 mass spectrometer with attached INCOS 2400 data system in the EI mode. Separations by column chromatography (CC) and flash chromatography (FC) were performed using Merck Kieselgel 60 (70–230 mesh ASTM) and 60 (230–400 mesh ASTM) respectively. Ether refers to diethyl ether, and light petroleum to the fraction boiling in the range 40–60 °C.

Preparation of arylboronic acids

The arylboronic acids were prepared by reaction of the appropriate aryllithium with triisopropyl borate following the procedure of Thompson and Gaudino[13] in the case of phenylboronic acid **5**,[19] 4-methoxyphenylboronic acid **6**,[19] 4-methylphenylboronic acid **7**,[19] 2-methoxyphenylboronic acid **8**,[13] 3-methoxyphenylboronic acid **9**,[20] 2,4-dimethoxyphenylboronic acid **10**,[21] 3,4-dimethoxyphenylboronic acid **12**[22] and 3,4-methylenedioxyphenylboronic acid **13**.[23] 2,5-Dimethoxyphenylboronic acid **11**[24] was similarly prepared by reaction of 1-lithio-2,5-dimethoxybenzene with trimethyl borate.

Preparation of the halogenocoumarins

Literature procedures were used for the synthesis of 4-bromo-2*H*-1-benzopyran-2-one **1**,[11] 4-chloro-2*H*-1-benzopyran-2-one **2**[25] and 4-chloro-6-methoxy-2*H*-1-benzopyran-2-one 4.[26]

4-Chloro-5-methoxy-2*H*-1-benzopyran-2-one 3. A mixture of 4-hydroxy-5-methoxy-2*H*-1-benzopyran-2-one (1.1 g, 6 mmol) and triphenylphosphine (2.26 g, 8.6 mmol) in dry carbon tetrachloride (8 cm^3) was heated at reflux for 6 h, cooled and left to stir overnight at room temperature. The mixture was diluted with chloroform (50 cm^3), washed with water (3 × 30 cm^3) and dried ($MgSO_4$). Removal of the solvent followed by column chromatography ($CHCl_3$) afforded compound **3**, as a solid (1.08 g, 89%) which was recrystallised from ethanol as needles, mp 151–153 °C; ν_{max}(KBr)/cm^{-1} 1718, 1600, 1474, 1286, 1199 and 1093; δ_H(270 MHz, $CDCl_3$) 3.93 (3 H, s, 5-OMe), 6.45 (1 H, s, 3-H), 6.78 (1 H, d, *J* 8.1, 6-H), 6.95 (1 H, d, *J* 8.2, 8-H) and 7.47 (1 H, t, *J* 8.2, 7-H); δ_C($CDCl_3$) 56.18 (5-OMe), 107.07 (C-8), 108.07 (C-10), 109.68 (C-6), 115.61 (C-3), 133.15 (C-7), 148.56 (C-4), 154.65 (C-9), 157.40 (C-5) and 158.83 (C-2); *m/z* 212 (M + 2, 36), 210 (M^+, 100), 182 (71), 167 (61), 139 (16), 111 (14), 75 (23), 62 (18), 50 (17) and 39 (20) (Found: C, 57.18; H, 3.30; Cl, 17.13. $C_{10}H_7ClO_3$ requires C, 57.03; H, 3.35; Cl, 16.83%).

Preparation of the 4-trifluoromethylsulfonyloxycoumarins

General procedure. A solution of the appropriate 4-hydroxy-2*H*-1-benzopyran-2-one (1 equiv.) and triethylamine (1.3 equiv.) in dry CH_2Cl_2 (10 cm^3 per g) at 0 °C was treated with trifluoromethanesulfonic anhydride (1.3 equiv.) over 10 min. After stirring for 2 h, the mixture was diluted with 50% ether–light petroleum (25 cm^3 per g) and filtered through a short pad of silica. Distillation of the solvent yielded the 4-trifluoromethylsulfonyloxy-2*H*-1-benzopyran-2-one.

4-Trifluoromethylsulfonyloxy-2*H*-1-benzopyran-2-one 35. Yield 97%, mp 60–61 °C (lit.,[4] mp 59–60 °C).

5-Methoxy-4-trifluoromethylsulfonyloxy-2*H*-1-benzopyran-2-one 36. Yield 80%, needles from ethanol, mp 117–119 °C; ν_{max}(KBr)/cm^{-1} 1742, 1608, 1424, 1215 and 1041; δ_H(270 MHz, [$^2H_6$]DMSO–$CDCl_3$) 3.97 (3 H, s, 5-OMe), 6.24 (1 H, s, 3-H), 6.84 (1 H, d, *J* 8.6, 6-H), 7.02 (1 H, d, *J* 7.5, 8-H) and 7.58 (1 H, t, *J* 8.4, 7-H); δ_C([$^2H_6$]DMSO–$CDCl_3$) 55.91 (5-OMe), 104.96 (C-10), 106.99 (C-3), 107.06 (C-6), 109.77 (C-8), 118 (CF_3, q, *J* 321), 134.32 (C-7), 154.90 (C-9), 156.10 (C-5), 156.21 (C-2) and 159.67 (C-4); *m/z* 325 (M + 1, 13), 324 (M^+, 100), 283 (6), 217 (3), 163 (M – CO – SO_2CF_3, 53), 133 (11) and 107 (12) (Found: C, 41.00; H, 2.19; S, 9.89; F, 16.92. $C_{11}H_7F_3O_6S$ requires C, 40.75; H, 2.18; S, 9.89; F, 17.58%).

5,7-Dimethoxy-4-trifluoromethylsulfonyloxy-2*H*-1-benzopyran-2-one 37. Yield 84%, needles from ethanol, mp 140–142 °C; ν_{max}(KBr)/cm^{-1} 1732, 1608, 1456, 1359, 1131 and 905; δ_H(270 MHz, $CDCl_3$) 3.89 (3 H, s, 7-OMe), 3.92 (3 H, s, 5-OMe), 6.05 (1 H, s, 3-H), 6.37 (1 H, d, *J* 2.2, 6-H) and 6.50 (1 H, d, *J* 2.4, 8-H); δ_C($CDCl_3$) 55.87 (5-OMe), 56.59 (7-OMe), 93.73 (C-8), 96.03 (C-6), 99.11 (C-10), 103.37 (C-3), 118.53 (CF_3, q, *J* 321), 156.06 (C-9), 157.18 (C-2), 158.15 (C-5), 160.28 (C-4) and 164.96 (C-7); *m/z* 355 (M + 1, 16), 354 (M^+, 100), 193 (M – CO – SO_2CF_3, 90), 165 (26) and 69 (60) (Found: C, 40.57; H, 2.62; S, 9.00; F, 16.49. $C_{12}H_9F_3O_7S$ requires C, 40.68; H, 2.56; S, 9.05; F, 16.09%).

7,8-Dimethoxy-4-trifluoromethylsulfonyloxy-2*H*-1-benzopyran-2-one 38. Yield 98%, needles from ethanol, mp 90–92 °C; ν_{max}(KBr)/cm^{-1} 1743, 1608, 1299 and 1095; δ_H(270 MHz, $CDCl_3$) 3.99 (3 H, s, 7-OMe), 4.0 (3 H, s, 8-OMe), 6.34 (1 H, s, 3-H), 6.99 (1 H, d, *J* 9, 6-H) and 7.55 (1 H, d, *J* 9, 5-H); δ_C($CDCl_3$) 61.57 (8-OMe), 65.53 (7-OMe), 102.89 (C-3), 108.20 (C-10), 109.12 (C-6), 116.02 (CF_3, q, *J* 321), 117.69 (C-5), 136.50 (C-8), 147 (C-9), 157.30 (C-7)*, 157.34 (C-2)* and 159.58 (C-4) (* assignments may be reversed); *m/z* 355 (M + 1, 15), 354 (M^+, 100), 339 (6), 227 (12), 193 (M – CO – SO_2CF_3, 99), 150 (10) and 137 (6) (Found: C, 40.43; H, 2.51; S, 8.76; F, 15.80. $C_{12}H_9F_3O_7S$ requires C, 40.68; H, 2.56; S, 9.05; F, 16.09%).

Coupling of halogenocoumarins with arylboronic acids

General procedure. The required 4-halogenocoumarin **1–4** (0.4–0.8 mmol, 1 equiv.) in the presence of 4 mol% of tetrakis(triphenylphosphine)palladium(0) was stirred at room temperature under nitrogen for 30 min in dry benzene (10 cm^3) and sodium carbonate (1 cm^3 of a 2 mol dm^{-3} aqueous solution). Arylboronic acid **5–13** (3 equiv.) in dry ethanol was added and the mixture was stirred for 30 min. The reaction mixture was heated under reflux for the time indicated, cooled and 30% hydrogen peroxide was added to oxidise excess arylboronic acid. The reaction mixture was diluted with chloroform (50 cm^3), washed with water (3 × 30 cm^3) and saturated aqueous sodium hydrogen carbonate (3 × 30 cm^3). The aqueous layers were combined and further extracted with chloroform (3 × 40 cm^3). The organic extracts were combined, dried (Na_2SO_4) and the solvent evaporated. The residue was purified by preparative layer chromatography (PLC), using the indicated solvent system to give the corresponding 4-aryl-2*H*-1-benzopyran-2-one **14–34**.

4-Phenyl-2*H*-1-benzopyran-2-one 14. PLC (CH_2Cl_2), yield 88%, needles from ethanol, mp 100–102 °C (lit.,[27] mp 104 °C).

4-(4-Methoxyphenyl)-2*H*-1-benzopyran-2-one 15. PLC ($CHCl_3$–MeOH, 99:1), yield 81%, needles from ethanol, mp 128–131 °C; ν_{max}(KBr)/cm^{-1} 3422, 1729, 1605, 1512 and 1247; δ_H(270 MHz, $CDCl_3$) 3.89 (3 H, s, 4′-OMe), 6.35 (1 H, s, 3-H), 7.05 (2 H, d, *J* 9, 3′- and 5′-H), 7.21–7.27 (1 H, m, 6-H), 7.38–7.44 (3 H, m, 8-, 2′- and 6′-H) and 7.51–7.58 (2 H, m, 5- and 7-H); δ_C($CDCl_3$) 55.49 (4′-OMe), 114.36 (C-3′ and C-5′), 114.63 (C-3), 117.38 (C-8), 119.16 (C-10), 124.14 (C-6), 126.06 (C-5), 127.46 (C-1′), 130.01 (C-2′ and C-6′), 131.86 (C-7), 154.26 (C-9), 155.39 (C-4), 160.87 (C-2) and 160.99 (C-4′); *m/z* 253 (M + 1, 17), 252 (M^+, 98), 237 (8), 224 (100), 209 (74), 181 (36), 152 (71), 126 (16) and 63 (23) (Found: C, 76.18; H, 4.81. $C_{16}H_{12}O_3$ requires C, 76.18; H, 4.79%).

4-(4-Methylphenyl)-2*H*-1-benzopyran-2-one 16. PLC ($CHCl_3$), yield 84%, needles from ethanol, mp 109–111 °C (lit.,[28] mp 105–106 °C).

4-(2-Methoxyphenyl)-2*H*-1-benzopyran-2-one 17. PLC (CH_2Cl_2), yield 92%, needles from ethanol–water, mp 81–83 °C; ν_{max}(KBr)/cm^{-1} 3435, 1723, 1579, 1433, 1260 and 1021; δ_H(270 MHz, $CDCl_3$) 3.75 (3 H, s, 2′-OMe), 6.37 (1 H, s, 3-H) and 7.03–7.53 (8 H, m, Ar-H); δ_C($CDCl_3$) 55.49 (2′-OMe), 111.18 (C-3′), 116.21 (C-3), 116.93 (C-8), 119.43 (C-10), 120.91 (C-5′), 123.90 (C-6), 124.12 (C-1′), 127.22 (C-5), 130.04 (C-7), 131.04 (C-4′), 131.51 (C-6′), 153.67 (C-9), 153.78 (C-4), 156.39 (C-2′) and 161.09 (C-2); *m/z* 253 (M + 1, 23), 252 (M^+, 94), 221 (100), 210 (54), 181 (33), 165 (39), 152 (58) and 76 (21) (Found: C, 76.56; H, 4.83. $C_{16}H_{12}O_3$ requires C, 76.18; H, 4.79%).

4-(3-Methoxyphenyl)-2*H*-1-benzopyran-2-one 18. PLC ($CHCl_3$), yield 91%, plates from ethanol, mp 152–154 °C; ν_{max}(KBr)/cm^{-1} 3442, 1719 (CO), 1596, 1471, 1224 and 1035; δ_H(270 MHz, $CDCl_3$) 3.86 (3 H, s, 3′-OMe), 6.38 (1 H, s, 3-H) and 6.96–7.58 (8 H, m, Ar-H); δ_C($CDCl_3$) 55.50 (3′-OMe), 114.11 (C-2′), 115.09 (C-3 and C-4′), 117.29 (C-8), 118.94 (C-10), 120.74 (C-6′), 124.19 (C-6), 127.03 (C-5), 130.01 (C-5′), 131.94 (C-7), 136.45 (C-1′), 154.15 (C-9), 155.54 (C-4), 159.81 (C-3′) and 160.75 (C-2); *m/z* 253 (M + 1, 23), 252 (M^+, 100), 224 (M – CO, 82), 221 (M – OMe, 51), 181 (26), 165 (23), 152 (46), 126 (10) and 63 (14) (Found: C, 76.34; H, 4.77. $C_{16}H_{12}O_3$ requires C, 76.18; H, 4.79%).

4-(2,4-Dimethoxyphenyl)-2*H*-1-benzopyran-2-one 19. PLC (CH_2Cl_2), yield 88%, needles from ethanol, mp 132–134 °C; ν_{max}(KBr)/cm^{-1} 3433, 1727, 1606, 1504, 1364 and 1212; δ_H(270 MHz, $CDCl_3$) 3.73 (3 H, s, 2′-OMe), 3.88 (3 H, s, 4′-OMe), 6.35 (1 H, s, 3-H), 6.59–6.63 (2 H, m, 3′- and 5′-H), 7.13–7.52 (5 H, m, 5-, 6-, 7-, 8- and 6′-H); δ_C($CDCl_3$) 55.49 (2′-OMe)*, 55.54 (4′-OMe)*, 98.82 (C-3′), 104.81 (C-5′), 116.20 (C-3), 116.82 (C-10), 116.89 (C-8), 119.68 (C-1′), 123.79 (C-6), 127.33 (C-5), 130.86 (C-7), 131.38 (C-6′), 153.59 (C-9), 153.68 (C-4), 157.66 (C-2′), 161.23 (C-2) and 162.17 (C-4′) (* assignments may be reversed); *m/z* 283 (M + 1, 18), 282 (M^+, 100), 254 (16), 251 (83), 220 (48), 225 (13), 211 (14), 196 (12), 168 (24), 152 (24), 139 (26) and 63 (13) (Found: C, 72.58; H, 5.13. $C_{17}H_{14}O_4$ requires C, 72.33; H, 4.99%).

4-(2,5-Dimethoxyphenyl)-2*H*-1-benzopyran-2-one 20. PLC ($CHCl_3$–MeOH, 99:1), yield 76%, needles from ethanol, mp 130–132 °C; ν_{max}(KBr)/cm^{-1} 3428, 1713, 1607, 1499, 1230 and 1023; δ_H(270 MHz, $CDCl_3$) 3.70 (3 H, s, 2′-OMe), 3.80 (3 H, s, 5′-OMe), 6.37 (1 H, s, 3-H) and 6.79–7.54 (7 H, m, Ar-H); δ_C($CDCl_3$) 55.84 (2′-OMe)*, 56.09 (5′-OMe)*, 112.45 (C-3′), 115.57 (C-4′)**, 115.77 (C-6′)**, 116.20 (C-3), 116.93 (C-8), 119.28 (C-10), 123.95 (C-6), 124.82 (C-1′), 127.24 (C-5), 131.57 (C-7), 150.47 (C-9), 153.54 (C-4), 153.67 (C-2′ and C-5′) and 161.01 (C-2) (* and ** assignments may be reversed); *m/z* 283 (M + 1, 12), 282 (M^+, 59), 251 (100), 208 (15), 168 (21), 152 (25), 139 (21), 63 (13) and 28 (17) (Found: C, 72.19; H, 5.03. $C_{17}H_{14}O_4$ requires C, 72.33; H, 4.99%).

4-(3,4-Dimethoxyphenyl)-2*H*-1-benzopyran-2-one 21. PLC

($CHCl_3$–MeOH, 99:1), yield 78%, needles from ethanol, mp 145–146 °C; ν_{max}(KBr)/cm^{-1} 3422, 1732, 1518, 1450, 1255 and 1140; δ_H(270 MHz, $CDCl_3$) 3.93 (3 H, s, 3′-OMe), 3.97 (3 H, s, 4′-OMe), 6.37 (1 H, s, 3-H), 6.97 (1 H, d, *J* 1.8, 2′-H), 7.01 (1 H, d, *J* 8.2, 5′-H), 7.07 (1 H, dd, *J* 8.2 and 1.8, 6′-H), 7.22–7.42 (2 H, m, 6- and 8-H) and 7.52–7.62 (2 H, m, 5- and 7-H); δ_C($CDCl_3$) 56.06 (3′-OMe)*, 56.11 (4′-OMe)*, 111.25 (C-2′), 111.55 (C-5′), 114.69 (C-3), 117.37 (C-8), 119.11 (C-10), 121.39 (C-6′), 124.16 (C-6), 127.02 (C-5), 127.66 (C-1′), 131.87 (C-7), 149.16 (C-3′), 150.30 (C-4′), 154.22 (C-9), 155.43 (C-4) and 160.90 (C-2) (* assignments may be reversed); *m/z* 283 (M + 1, 20), 282 (M$^+$, 100), 267 (16), 254 (29), 239 (36), 168 (39), 152 (33), 139 (52), 76 (57), 70 (44), 63 (90), 51 (40) and 28 (58) (Found: C, 72.07; H, 5.12. $C_{17}H_{14}O_4$ requires C, 72.33; H, 4.99%).

4-(3,4-Methylenedioxyphenyl)-2*H*-1-benzopyran-2-one 22. PLC (CH_2Cl_2), yield 72%, leaves from chloroform–methanol, mp 188–190 °C; ν_{max}(KBr)/cm^{-1} 3440, 1718 (CO), 1604, 1446 and 1252; δ_H(270 MHz, $CDCl_3$) 6.07 (2 H, s, OCH_2O), 6.24 (1 H, s, 3-H), 6.92–6.95 (3 H, m, 2′-, 5′- and 6′-H), 7.21–7.41 (2 H, m, 6- and 8-H) and 7.51–7.59 (2 H, m, 5- and 7-H); δ_C($CDCl_3$) 101.67 (OCH_2O), 108.78 (C-2′), 108.89 (C-5′), 114.82 (C-3), 117.35 (C-8), 118.98 (C-10), 122.63 (C-6′), 124.15 (C-6), 126.93 (C-5), 128.85 (C-1′), 131.90 (C-7), 148.08 (C-3′), 148.94 (C-4′), 154.16 (C-9), 155.18 (C-4) and 160.80 (C-2); *m/z* 266 (M$^+$, 60), 238 (M − CO, 55), 152 (37), 87 (38), 76 (100), 63 (85), 51 (22) and 28 (26) (Found: C, 72.33; H, 3.82. $C_{16}H_{10}O_4$ requires C, 72.18; H, 3.79%).

5-Methoxy-4-phenyl-2*H*-1-benzopyran-2-one 23. PLC (CH_2Cl_2), yield 79%, needles from ethanol, mp 97–99 °C (lit.,[29] mp 92–94 °C).

5-Methoxy-4-(4-methoxyphenyl)-2*H*-1-benzopyran-2-one 24. PLC ($CHCl_3$), yield 80%, needles from ethanol, mp 140–142 °C; ν_{max}(KBr)/cm^{-1} 1723, 1599, 1473, 1248 and 1090; δ_H($CDCl_3$) 3.52 (3 H, s, 5-OMe), 3.87 (3 H, s, 4′-OMe), 6.16 (1 H, s, 3-H), 6.68 (1 H, dd, *J* 8.4 and 0.9, 6-H), 6.89–6.94 (2 H, m, 3′- and 5′-H), 7.01 (1 H, dd, *J* 8.4 and 1.1, 8-H), 7.20–7.25 (2 H, m, 2′- and 6′-H) and 7.46 (1 H, t, *J* 8.4, 7-H); δ_C($CDCl_3$) 55.32 (5-OMe), 55.58 (4′-OMe), 106.68 (C-8), 109.32 (C-10), 109.97 (C-6), 112.78 (C-3′ and C-5′), 115.79 (C-3), 128.68 (C-2′ and C-6′), 131.95 (C-1′), 132.24 (C-7), 155.16 (C-9), 155.47 (C-4), 157.36 (C-5), 159.60 (C-4′) and 160.62 (C-2); *m/z* 283 (M + 1, 21), 282 (M$^+$, 100), 267 (11), 254 (75), 239 (39), 211 (12), 196 (11), 168 (14), 152 (14), 138 (22), 63 (11) and 39 (13) (Found: C, 72.08; H, 4.94. $C_{17}H_{14}O_4$ requires C, 72.33; H, 4.99%).

5-Methoxy-4-(4-methylphenyl)-2*H*-1-benzopyran-2-one 25. PLC (CH_2Cl_2), yield 65%, needles from ethanol, mp 140–142 °C; ν_{max}(KBr)/cm^{-1} 1714, 1600, 1467, 1258, 1199 and 1098; δ_H($CDCl_3$) 2.41 (3 H, s, Ar-CH_3), 3.48 (3 H, s, 5-OMe), 6.15 (1 H, s, 3-H), 6.68 (1 H, dd, *J* 8.4 and 1.1, 6-H), 7.0 (1 H, dd, *J* 8.4 and 1.1, 8-H), 7.14–7.18 (4 H, m, B-ring) and 7.45 (1 H, t, *J* 8.4, 7-H); δ_C($CDCl_3$) 21.26 (Ar-CH_3), 55.47 (5-OMe), 106.64 (C-8), 109.25 (C-10), 109.87 (C-6), 115.83 (C-3), 127.05 (C-2′ and C-6′), 128.01 (C-3′ and C-5′), 132.20 (C-7), 136.68 (C-4′), 137.84 (C-1′), 155.36 (C-9), 155.47 (C-4), 157.31 (C-5) and 160.53 (C-2); *m/z* 267 (M + 1, 23), 266 (M$^+$, 100), 251 (31), 238 (80), 223 (36), 208 (26), 195 (19), 165 (28), 152 (32), 132 (16), 115 (15), 76 (16) and 39 (33) (Found: C, 76.39; H, 5.28. $C_{17}H_{14}O_3$ requires C, 76.68; H, 5.30%).

5-Methoxy-4-(2-methoxyphenyl)-2*H*-1-benzopyran-2-one 26. PLC ($CHCl_3$), yield 82%, needles from ethanol, mp 86–88 °C; ν_{max}(KBr)/cm^{-1} 1714, 1605, 1471, 1257 and 1099; δ_H($CDCl_3$) 3.44 (3 H, s, 5-OMe), 3.71 (3 H, s, 2′-OMe), 6.17 (1 H, s, 3-H), 6.63 (1 H, dd, *J* 8.4 and 1.1, 6-H), 6.90 (1 H, dd, *J* 8.4 and 0.9, 8-H), 6.96–7.02 (2 H, m, 3′- and 5′-H), 7.13 (1 H, dd, *J* 7.5 and 1.8, 6′-H), 7.34–7.40 (1 H, m, 4′-H) and 7.42 (1 H, t, *J* 8.2, 7-H); δ_C($CDCl_3$) 55.39 (5-OMe), 55.76 (2′-OMe), 106.42 (C-8), 109.57 (C-3′), 109.82 (C-6), 110.24 (C-10), 115.86 (C-3), 120.12 (C-5′), 127.88 (C-6′), 129.45 (C-1′), 129.56 (C-4′), 131.79 (C-7), 152.99 (C-4), 154.91 (C-9), 156.41 (C-5), 157.59 (C-2′) and 160.85 (C-2); *m/z* 283 (M + 1, 20), 282 (M$^+$, 100), 251 (80), 240 (24), 223 (11), 208 (22), 196 (11), 180 (13), 168 (14), 152 (16) and 139 (18) (Found: C, 72.22; H, 5.21. $C_{17}H_{14}O_4$ requires C, 72.33; H, 4.99%).

5-Methoxy-4-(3-methoxyphenyl)-2*H*-1-benzopyran-2-one 27. PLC ($CHCl_3$), yield 79%, leaves from ethanol, mp 89–91 °C; ν_{max}(KBr)/cm^{-1} 1713, 1597, 1479, 1220 and 1096; δ_H($CDCl_3$) 3.49 (3 H, s, 5-OMe), 3.83 (3 H, s, 3′-OMe), 6.18 (1 H, s, 3-H), 6.68 (1 H, dd, *J* 8.2 and 0.9, 6-H), 6.81–6.95 (3 H, m, 2′-, 4′- and 6′-H), 7.01 (1 H, dd, *J* 8.2 and 0.9, 8-H), 7.30 (1 H, t, *J* 8.1, 5′-H) and 7.47 (1 H, t, *J* 8.2, 7-H); δ_C($CDCl_3$) 55.34 (5-OMe), 55.63 (3′-OMe), 106.71 (C-8), 109.22 (C-10), 109.90 (C-6), 112.70 (C-2′), 113.49 (C-4′), 115.85 (C-3), 119.62 (C-6′), 128.54 (C-5′), 132.38 (C-7), 140.99 (C-1′), 155.16 (C-9), 155.36 (C-4), 157.29 (C-5), 158.84 (C-3′) and 160.50 (C-2); *m/z* 283 (M + 1, 19), 282 (M$^+$, 100), 267 (23), 254 (38), 239 (23), 224 (10), 208 (13), 168 (11), 152 (11) and 139 (16) (Found: C, 72.02; H, 4.94. $C_{17}H_{14}O_4$ requires C, 72.33; H, 4.99%).

5-Methoxy-4-(2,5-dimethoxyphenyl)-2*H*-1-benzopyran-2-one 28. PLC (CH_2Cl_2), yield 86%, needles from ethanol, mp 126–127.5 °C; ν_{max}(KBr)/cm^{-1} 1714, 1601, 1466, 1284 and 1101; δ_H($CDCl_3$) 3.47 (3 H, s, 5-OMe), 3.66 (3 H, s, 2′-OMe), 3.79 (3 H, s, 5′-OMe), 6.17 (1 H, s, 3-H), 6.64 (1 H, dd, *J* 8.2 and 0.9, 6-H), 6.72 (1 H, d, *J* 2.9, 6′-H), 6.81 (1 H, d, *J* 8.8, 3′-H), 6.88 (1 H, dd, *J* 8.8 and 2.9, 4′-H), 6.97–7.01 (1 H, m, 8-H) and 7.43 (1 H, t, *J* 8.2, 7-H); δ_C($CDCl_3$) 55.74 (5-OMe), 55.95 (2 × OMe), 106.36 (C-8), 109.76 (C-6), 110.06 (C-10), 110.58 (C-3′), 113.55 (C-4′), 114.20 (C-6′), 115.85 (C-3), 130.15 (C-1′), 131.84 (C-7), 150.57 (C-2′), 152.63 (C-4), 153.07 (C-5′), 154.87 (C-9), 157.53 (C-5) and 160.76 (C-2); *m/z* 313 (M + 1, 21), 312 (M$^+$, 97), 281 (100), 266 (28), 238 (19), 195 (9) and 127 (8) (Found: C, 69.12; H, 5.27. $C_{18}H_{16}O_5$ requires C, 69.22; H, 5.16%).

6-Methoxy-4-phenyl-2*H*-1-benzopyran-2-one 29. PLC (CH_2Cl_2), yield 87%, needles from ethanol, mp 149–151.5 °C (lit.,[30] mp 151 °C).

6-Methoxy-4-(4-methoxyphenyl)-2*H*-1-benzopyran-2-one 30. PLC (CH_2Cl_2), yield 93%, needles from ethanol, mp 143–145 °C; ν_{max}(KBr)/cm^{-1} 1709, 1566, 1432, 1238 and 1175; δ_H($CDCl_3$) 3.74 (3 H, s, 6-OMe), 3.89 (3 H, s, 4′-OMe), 6.34 (1 H, s, 3-H), 6.99 (1 H, d, *J* 2.9, 5-H), 7.04 (2 H, d, *J* 8.8, 3′- and 5′-H), 7.12 (1 H, dd, *J* 9 and 2.9, 7-H), 7.32 (1 H, d, *J* 9, 8-H) and 7.41 (2 H, d, *J* 9, 2′- and 6′-H); δ_C($CDCl_3$) 55.44 (4′-OMe), 55.79 (6-OMe), 109.93 (C-5), 114.38 (C-3′ and C-5′), 115.03 (C-3), 118.22 (C-7), 118.92 (C-8), 119.57 (C-10), 127.49 (C-1′), 129.83 (C-2′ and C-6′), 148.58 (C-9), 155.05 (C-4), 155.82 (C-6), 160.82 (C-4′) and 161.15 (C-2); *m/z* 283 (M + 1, 19), 282 (M$^+$, 100), 254 (53), 239 (33), 211 (15), 168 (13), 152 (13) and 139 (16) (Found: C, 72.09; H, 4.88. $C_{17}H_{14}O_4$ requires C, 72.33; H, 4.99%).

6-Methoxy-4-(4-methylphenyl)-2*H*-1-benzopyran-2-one 31. PLC (CH_2Cl_2), yield 92%, pale yellow needles from ethanol, mp 128–130 °C; ν_{max}(KBr)/cm^{-1} 1713, 1558, 1440, 1181 and 1038; δ_H($CDCl_3$) 2.45 (3 H, s, Ar-CH_3), 3.74 (3 H, s, 6-OMe), 6.36 (1 H, s, 3-H), 6.97 (1 H, d, *J* 2.9, 5-H), 7.12 (1 H, dd, *J* 9 and 2.9, 7-H), 7.26–7.34 (3 H, m, 8-, 3′- and 5′-H) and 7.36 (2 H, d, *J* 8.6, 2′- and 6′-H); δ_C($CDCl_3$) 21.37 (Ar-CH_3), 55.77 (6-OMe), 109.90 (C-5), 115.28 (C-3), 118.18 (C-7), 118.98 (C-8), 119.49 (C-10), 128.28 (C-2′ and C-6′), 129.60 (C-3′ and C-5′), 132.23 (C-1′), 139.91 (C-4′), 148.55 (C-9), 155.42 (C-4), 155.82 (C-6) and 161.07 (C-2); *m/z* 267 (M + 1, 19), 266 (100), 251 (25), 238 (50), 223 (13), 195 (18), 165 (17), 152 (24) and 28 (17) (Found: C, 76.96; H, 5.44. $C_{17}H_{14}O_3$ requires C, 76.68; H, 5.30%).

6-Methoxy-4-(2,4-dimethoxyphenyl)-2*H*-1-benzopyran-2-one 32. PLC (CH_2Cl_2), yield 91%, needles from ethanol, mp 148–150 °C; ν_{max}(KBr)/cm^{-1} 1719, 1615, 1424, 1214 and 1034; δ_H($CDCl_3$) 3.71 (3 H, s, 2′-OMe), 3.74 (3 H, s, 6-OMe), 3.89 (3 H, s, 4′-OMe), 6.35 (1 H, s, 3-H), 6.59–6.63 (2 H, m, 3′- and 5′-H), 6.68 (1 H, d, *J* 2.9, 5-H), 7.07 (1 H, dd, *J* 9 and 2.9, 7-H), 7.15 (1 H, dd, *J* 7.5 and 1.1, 6′-H) and 7.29 (1 H, d, *J* 9, 8-H); δ_C($CDCl_3$) 55.51 (2′-OMe)*, 55.55 (4′-OMe)*, 55.74 (6-OMe), 98.73 (C-3′), 104.86 (C-5′), 110.09 (C-5), 116.63 (C-3), 116.79 (C-10), 117.76 (C-7), 118.69 (C-8), 120.20 (C-1′), 130.86 (C-6′), 148.17 (C-9), 153.28 (C-4), 155.65 (C-6), 157.61 (C-2′), 161.41 (C-2) and 162.17 (C-4′) (* assignments may be reversed); *m*/*z* 313 (M + 1, 21), 312 (M^+, 100), 281 (73), 270 (31), 183 (8) and 28 (17) (Found: C, 69.49; H, 5.46. $C_{18}H_{16}O_5$ requires C, 69.22; H, 5.16%).

6-Methoxy-4-(3,4-dimethoxyphenyl)-2*H*-1-benzopyran-2-one 33. PLC ($CHCl_3$–MeOH, 99:1), yield 91%, needles from chloroform–hexane, mp 148–150 °C; ν_{max}(KBr)/cm^{-1} 1704, 1520, 1428, 1255 and 1027; δ_H($CDCl_3$) 3.76 (3 H, s, 6-OMe), 3.92 (3 H, s, 4′-OMe), 3.97 (3 H, s, 3′-OMe), 6.38 (1 H, s, 3-H), 6.97 (1 H, d, *J* 1.8, 2′-H), 7.0–7.06 (3 H, m, 5-, 5′- and 6′-H), 7.09 (1 H, dd, *J* 9 and 2.9, 7-H) and 7.30 (1 H, d, *J* 9, 8-H); δ_C($CDCl_3$) 55.79 (6-OMe), 56.04 (3′-OMe)*, 56.11 (4′-OMe)*, 109.75 (C-2′), 111.26 (C-5′), 111.41 (C-5), 115.09 (C-3), 118.29 (C-7), 119.11 (C-8), 119.50 (C-10), 121.26 (C-6′), 127.71 (C-1′), 148.58 (C-9), 149.15 (C-3′), 150.25 (C-4′), 155.11 (C-4), 155.84 (C-6) and 161.14 (C-2) (* assignments may be reversed); *m*/*z* 313 (M + 1, 18), 312 (M^+, 100), 284 (17) and 269 (13) (Found: C, 69.42; H, 5.10. $C_{18}H_{16}O_5$ requires C, 69.22; H, 5.16%).

6-Methoxy-4-(3,4-methylenedioxyphenyl)-2*H*-1-benzopyran-2-one 34. PLC (CH_2Cl_2), yield 95%, needles from chloroform–hexane, mp 193–196 °C; ν_{max}(KBr)/cm^{-1} 1703, 1566, 1504, 1440, 1281 and 1039; δ_H($CDCl_3$) 3.77 (3 H, s, 6-OMe), 6.08 (2 H, s, OCH_2O), 6.33 (1 H, s, 3-H), 6.92–6.96 (3 H, m, 2′-, 5′- and 6′-H), 7.0 (1 H, d, *J* 2.9, 5-H), 7.12 (1 H, dd, *J* 9 and 2.9, 7-H) and 7.32 (1 H, d, *J* 9, 8-H); δ_C($CDCl_3$) 55.84 (6-OMe), 101.69 (OCH_2O), 108.76 (C-2′), 108.83 (C-5′), 109.95 (C-5), 115.29 (C-3), 118.24 (C-7), 118.92 (C-8), 119.44 (C-10), 122.51 (C-6′), 128.92 (C-1′), 148.15 (C-3′), 148.53 (C-4′), 148.96 (C-9), 154.91 (C-4), 155.85 (C-6) and 161.01 (C-2); *m*/*z* 297 (M + 1, 20), 296 (M^+, 100), 268 (63), 223 (11) and 139 (20) (Found: C, 68.58; H, 4.08. $C_{17}H_{12}O_5$ requires C, 68.92; H, 4.08%).

Coupling of 4-trifluoromethylsulfonyloxycoumarins with arylboronic acids

General procedure. A mixture of 4-trifluoromethylsulfonyloxycoumarin (0.2–0.5 mmol, 1 equiv.), tetrakis(triphenylphosphine)palladium(0) (0.04 equiv.), copper(I) iodide (1.1 equiv.), sodium carbonate (7 equiv.) and dry benzene (10 cm^3) was stirred for 30 min under N_2 and a solution of the arylboronic acid (3 equiv.) in dry ethanol (3 cm^3) was added. The reaction was heated at reflux for 20 h, cooled and hydrogen peroxide (1 cm^3 of an aqueous 30% w/v solution) was added to oxidise unreacted boronic acid. The mixture was diluted with chloroform (40 cm^3), washed with water (3 × 40 cm^3), saturated aqueous sodium hydrogen carbonate (3 × 40 cm^3) and the aqueous layers were re-extracted with chloroform (3 × 40 cm^3). The combined organic layers were dried ($MgSO_4$), and then concentrated to dryness under reduced pressure. The residue was purified by preparative layer chromatography (PLC) yielding the desired product.

5,7-Dimethoxy-4-phenyl-2*H*-1-benzopyran-2-one 39. PLC (CH_2Cl_2), yield 93%, needles from ethanol, mp 167–169 °C (lit.,[31] mp 167–168 °C).

5,7-Dimethoxy-4-(4-methoxyphenyl)-2*H*-1-benzopyran-2-one 40. PLC (CH_2Cl_2), yield 93%, needles from ethanol–water, mp 154–156 °C (lit.,[32] mp 151–152 °C).

5,7-Dimethoxy-4-(4-methylphenyl)-2*H*-1-benzopyran-2-one 41. PLC (CH_2Cl_2), yield 79%, plates from ethanol–water, mp 131–133 °C; ν_{max}(KBr)/cm^{-1} 1714, 1614, 1470, 1351, 1109 and 948; δ_H(270 MHz, [$^2H_6$]DMSO–$CDCl_3$) 2.41 (3 H, s, 4′-CH_3), 3.46 (3 H, s, 5-OMe), 3.88 (3 H, s, 7-OMe), 5.98 (1 H, s, 3-H), 6.24 (1 H, d, *J* 2.4, 6-H), 6.52 (1 H, d, *J* 2.4, 8-H) and 7.17 (4 H, s, Ar′-H); δ_C([$^2H_6$]DMSO–$CDCl_3$) 20.88 (4′-CH_3), 55.62 (5-OMe), 55.88 (7-OMe), 93.76 (C-8), 95.86 (C-6), 102.53 (C-10), 111.80 (C-3), 127.08 (C-2′ and C-6′), 127.81 (C-3′ and C-5′), 136.40 (C-1′), 137.27 (C-4′), 155.24 (C-4), 156.57 (C-9), 158.02 (C-5), 159.54 (C-2) and 163.18 (C-7); *m*/*z* 297 (M + 1, 19), 296 (M^+, 100), 268 (M − CO, 94), 253 (24), 238 (10), 225 (3), 210 (6), 182 (4) and 154 (4) (Found: C, 72.76; H, 5.48. $C_{18}H_{16}O_4$ requires: C, 72.96; H, 5.44%).

5,7-Dimethoxy-4-(2-methoxyphenyl)-2*H*-1-benzopyran-2-one 42. PLC (CH_2Cl_2), yield 92%, needles from ethanol–water, mp 120–122 °C; ν_{max}(KBr)/cm^{-1} 1705, 1618, 1431, 1333, 1158 and 1110; δ_H(270 MHz, $CDCl_3$) 3.41 (3 H, s, 5-OMe), 3.71 (3 H, s, 2′-OMe), 3.85 (3 H, s, 7-OMe), 6.0 (1 H, s, 3-H), 6.20 (1 H, d, *J* 2.4, 6-H), 6.50 (1 H, d, *J* 2.4, 8-H), 6.88 (1 H, d, *J* 8.2, 3′-H), 6.98 (1 H, td, *J* 7.5 and 1, 5′-H), 7.12 (1 H, dd, *J* 7.3 and 1.5, 6′-H) and 7.35 (1 H, ddd, *J* 7.5, 1.8 and 0.7, 4′-H); δ_C($CDCl_3$) 55.41 (5-OMe), 55.61 (2′-OMe), 55.69 (7-OMe), 93.35 (C-8), 95.58 (C-6), 104.10 (C-10), 109.57 (C-3), 112.62 (C-3′), 120.10 (C-5′), 127.97 (C-6′), 129.47 (C-4′), 129.56 (C-1′), 153.18 (C-4), 156.40 (C-9), 156.63 (C-5), 158.46 (C-2′), 161.28 (C-2) and 162.95 (C-7); *m*/*z* 313 (M + 1, 33), 312 (M^+, 100), 281 (37), 270 (29), 255 (10) and 226 (5) (Found: C, 68.94; H, 5.07. $C_{18}H_{16}O_5$ requires: C, 69.22; H, 5.16%).

5,7-Dimethoxy-4-(3-methoxyphenyl)-2*H*-1-benzopyran-2-one 43. PLC (CH_2Cl_2), yield 96%, needles from ethanol–water, mp 115–116 °C; ν_{max}(KBr)/cm^{-1} 1712, 1596, 1432, 1388, 1235 and 1110; δ_H(270 MHz, $CDCl_3$) 3.45 (3 H, s, 5-OMe), 3.82 (3 H, s, 3′-OMe), 3.87 (3 H, s, 7-OMe), 6.01 (1 H, s, 3-H), 6.23 (1 H, d, *J* 2.4, 6-H), 6.52 (1 H, d, *J* 2.4, 8-H), 6.93 (3 H, m, 4′-, 5′- and 6′-H) and 7.28 (1 H, t, *J* 7.9, 2′-H); δ_C($CDCl_3$) 55.31 (5-OMe)*, 55.49 (3′-OMe)*, 55.77 (7-OMe), 93.53 (C-8), 95.77 (C-6), 104.5 (C-10), 112.54 (C-3), 112.73 (C-2′), 113.43 (C-4′), 119.67 (C-6′), 128.44 (C-5′), 141.08 (C-1′), 155.44 (C-4), 157.13 (C-9), 158.19 (C-5), 158.76 (C-2), 160.90 (C-7) and 163.67 (C-3′) (* assignments may be reversed); *m*/*z* 313 (M + 1, 19), 312 (M^+, 100), 297 (1), 284 (M − CO, 78), 269 (22), 254 (1) and 223 (1) (Found: C, 68.94; H, 5.07. $C_{18}H_{16}O_5$ requires: C, 69.22; H, 5.16%).

5,7-Dimethoxy-4-(2,4-dimethoxyphenyl)-2*H*-1-benzopyran-2-one 44. PLC (CH_2Cl_2), yield 87%, needles from ethanol–water, mp 152–154 °C; ν_{max}(KBr)/cm^{-1} 1728, 1597, 1148 and 1050; δ_H(270 MHz, $CDCl_3$) 3.46 (3 H, s, 5-OMe), 3.68 (3 H, s, 2′-OMe), 3.85 (3 H, s, 4′-OMe), 3.86 (3 H, s, 7-OMe), 5.99 (1 H, s, 3-H), 6.21 (1 H, d, *J* 2.4, 5-H), 6.46 (1 H, d, *J* 2.4, 3′-H), 6.49 (1 H, d, *J* 2.4, 8-H), 6.51 (1 H, dd, *J* 7 and 2.4, 5′-H) and 7.05 (1 H, d, *J* 8.1, 6′-H); δ_C($CDCl_3$) 55.34 (5-OMe)*, 55.44 (2′-OMe)*, 55.60 (4′-OMe)**, 55.69 (7-OMe)**, 93.31 (C-8), 95.57 (C-6), 97.83 (C-3′), 103.21 (C-5′), 104.80 (C-10), 112.72 (C-3), 122.49 (C-1′), 128.50 (C-6′), 153.04 (C-4), 156.63 (C-9), 157.70 (C-5), 158.56 (C-2′), 161.15 (C-2), 161.32 (C-4′) and 162.84 (C-7) (* and ** assignments may be reversed); *m*/*z* 343 (M + 1, 20), 342 (M^+, 100), 327 (1), 311 (50), 300 (41), 283 (11), 268 (10), 256 (8) and 240 (11) (Found: C, 66.66; H, 5.29. $C_{19}H_{18}O_6$ requires: C, 66.44; H, 5.29%).

5,7-Dimethoxy-4-(2,5-dimethoxyphenyl)-2*H*-1-benzopyran-2-one 45. PLC (CH_2Cl_2), yield 71%, needles from ethanol–water, mp 244–246 °C; ν_{max}(KBr)/cm^{-1} 1710, 1619, 1234 and 1045; δ_H(270 MHz, $CDCl_3$) 3.52 (3 H, s, 5-OMe), 3.66 (3 H, s, 2′-OMe), 3.79 (3 H, s, 5′-OMe), 3.86 (3 H, s, 7-OMe), 6.01 (1 H, s, 3-H), 6.20 (1 H, d, *J* 2.4, 6-H), 6.49 (1 H, d, *J* 2.4, 8-H), 6.71 (1 H, d, *J* 2.9, 6′-H), 6.79 (1 H, d, *J* 8.8, 3′-H) and 6.85–6.89 (1 H, dd, *J* 9 and 2.9, 4′-H); δ_C($CDCl_3$) 55.58 (5-OMe), 55.74 (2′-OMe and 5′-OMe)*, 55.76 (7-OMe)*, 93.30 (C-8), 95.54 (C-6), 104.36 (C-10), 110.64 (C-3′), 112.57 (C-4′), 113.52 (C-6′), 114.22 (C-3), 130.22 (C-1′), 150.58 (C-2′), 152.81 (C-4), 153.08 (C-5′), 156.61 (C-9), 158.41 (C-5), 161.18 (C-2) and 162.98 (C-7) (* assignments may be reversed); *m*/*z* 343 (M + 1, 20), 342 (M^+, 100), 311 (99), 296 (10), 268 (14), 240 (8), 178 (10) and 153 (28) (Found: C, 66.67; H, 5.24. $C_{19}H_{18}O_6$ requires C, 66.66; H, 5.3%).

5,7-Dimethoxy-4-(3,4-dimethoxyphenyl)-2*H*-1-benzopyran-2-one 46. PLC ($CHCl_3$–MeOH–H_2O, 25:1:0.1), yield 92%, needles from ethanol–water, mp 167–168 °C (lit.,[32] mp 169–170 °C).

5,7-Dimethoxy-4-(3,4-methylenedioxyphenyl)-2*H*-1-benzopyran-2-one 47. PLC (CH_2Cl_2), yield 85%, plates from chloroform–hexane, mp 194–198 °C (lit.,[33] mp 194–195 °C).

7,8-Dimethoxy-4-phenyl-2*H*-1-benzopyran-2-one 48. PLC ($CHCl_3$–MeOH–H_2O, 25:1:0.1), yield 71%, needles from ethanol, mp 120–122 °C; ν_{max}(KBr)/cm^{-1} 1715, 1605, 1297 and 1103; δ_H(270 MHz, $CDCl_3$) 3.95 (3 H, s, 7-OMe), 4.02 (3 H, s, 8-OMe), 6.23 (1 H, s, 3-H), 6.81 (1 H, d, *J* 9, 6-H), 7.18 (1 H, d, *J* 9, 5-H) and 7.45–7.53 (5 H, m, Ar′-H); δ_C($CDCl_3$) 56.29 (7-OMe), 61.48 (8-OMe), 107.92 (C-3), 112.18 (C-6), 113.69 (C-10), 122.16 (C-5), 128.32 (C-2′ and C-6′), 128.70 (C-3′ and C-5′), 129.54 (C-4′), 135.47 (C-8), 136.30 (C-1′), 148.26 (C-9), 155.40 (C-4), 155.90 (C-7) and 160.58 (C-2); *m/z* 283 (M + 1, 19), 282 (M^+, 100), 267 (8), 254 (M − CO, 16), 239 (31), 211 (3), 183 (3), 168 (10) and 139 (14) (Found: C, 72.52; H, 4.88. $C_{17}H_{14}O_4$ requires C, 72.33; H, 4.99%).

7,8-Dimethoxy-4-(4-methoxyphenyl)-2*H*-1-benzopyran-2-one 49. PLC ($CHCl_3$–MeOH–H_2O, 25:1:0.1), yield 97%, needles from ethanol, mp 138–139 °C; ν_{max}(KBr)/cm^{-1} 1727, 1608, 1295 and 1112; δ_H(270 MHz, $CDCl_3$) 3.89 (3 H, s, 4′-OMe), 3.95 (3 H, s, 7-OMe), 4.01 (3 H, s, 8-OMe), 6.20 (1 H, s, 3-H), 6.83 (1 H, d, *J* 9.2, 6-H), 7.03 (2 H, d, *J* 8.8, 3′- and 5′-H), 7.25 (1 H, d, *J* 9, 5-H) and 7.39 (2 H, d, *J* 8.8, 2′- and 6′-H); δ_C(67.80 MHz, $CDCl_3$) 55.49 (4′-OMe), 56.35 (7-OMe), 61.53 (8-OMe), 107.91 (C-3), 111.73 (C-6), 113.92 (C-3′ and C-5′), 114.23 (C-10), 122.21 (C-5), 127.76 (C-1′), 129.89 (C-2′ and C-6′), 136.41 (C-8), 148.38 (C-9), 155.34 (C-4), 155.61 (C-7), 160.74 (C-4′) and 160.80 (C-2); *m/z* 313 (M + 1, 20), 312 (M^+, 100), 297 (5), 284 (M − CO, 23), 269 (22), 226 (3), 213 (6), 198 (5), 155 (6) and 135 (7) (Found: C, 69.28; H, 5.15. $C_{18}H_{16}O_5$ requires C, 69.23; H, 5.16%).

7,8-Dimethoxy-4-(4-methylphenyl)-2*H*-1-benzopyran-2-one 50. PLC (CH_2Cl_2), yield 88%, needles from ethanol–water, mp 131–134 °C; ν_{max}(KBr)/cm^{-1} 1734, 1609, 1295 and 1101; δ_H(270 MHz, $CDCl_3$) 2.45 (3 H, s, 4′-CH_3), 3.95 (3 H, s, 7-OMe), 4.02 (3 H, s, 8-OMe), 6.21 (1 H, s, 3-H), 6.81 (1 H, d, *J* 9, 6-H), 7.21 (1 H, d, *J* 9, 5-H) and 7.33 (4 H, s, Ar′-H); δ_C($CDCl_3$) 21.33 (4′-Me), 61.51 (7-OMe), 66.34 (8-OMe), 107.89 (C-3), 111.98 (C-6), 113.84 (C-10), 122.19 (C-5), 128.31 (C-2′ and C-6′), 129.45 (C-3′ and C-5′), 132.60 (C-1′), 136.38 (C-8), 139.76 (C-4′), 148.32 (C-9), 155.37 (C-4), 155.98 (C-7) and 160.71 (C-2); *m/z* 297 (M + 1, 21), 296 (M^+, 100), 281 (9), 268 (M − CO, 17), 253 (28), 225 (4), 182 (8), 165 (6), 153 (10) and 139 (6) (Found: C, 72.65; H, 5.45. $C_{18}H_{16}O_4$ requires C, 72.96; H, 5.44%).

7,8-Dimethoxy-4-(2-methoxyphenyl)-2*H*-1-benzopyran-2-one 51. PLC ($CHCl_3$–MeOH–H_2O, 25:1:0.1), yield 90%, plates from ethanol–water, mp 130–132 °C; ν_{max}(KBr)/cm^{-1} 1712, 1602, 1298 and 1106; δ_H(270 MHz, $CDCl_3$) 3.76 (3 H, s, 2′-OMe), 3.93 (3 H, s, 7-OMe), 4.02 (3 H, s, 8-OMe), 6.22 (1 H, s, 3-H), 6.76 (1 H, d, *J* 9, 6-H), 6.90 (1 H, d, *J* 9, 5-H), 7.06 (2 H, m, 3′- and 5′-H), 7.21 (1 H, dd, *J* 7.5 and 1.7, 6′-H) and 7.47 (1 H, ddd, *J* 7.5, 1.8 and 0.7, 4′-H); δ_C($CDCl_3$) 55.70 (2′-OMe), 56.44 (7-OMe), 61.64 (8-OMe), 108.02 (C-3), 111.32 (C-6), 112.02 (C-3′), 114.37 (C-10), 120.99 (C-5′), 122.43 (C-5), 124.54 (C-1′), 130.16 (C-6′), 131.03 (C-4′), 136.22 (C-8), 148.03 (C-9), 154.01 (C-4), 155.33 (C-7), 156.48 (C-2′) and 161.05 (C-2); *m/z* 313 (M + 1, 20), 312 (M^+, 100), 297 (3), 281 (22), 270 (28), 255 (6), 238 (3), 226 (3) and 155 (6) (Found: C, 69.52; H, 5.15. $C_{18}H_{16}O_5$ requires C, 69.23; H, 5.16%).

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