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Synthesis of neoflavenes by ligand coupling reactions with aryllead triacetates

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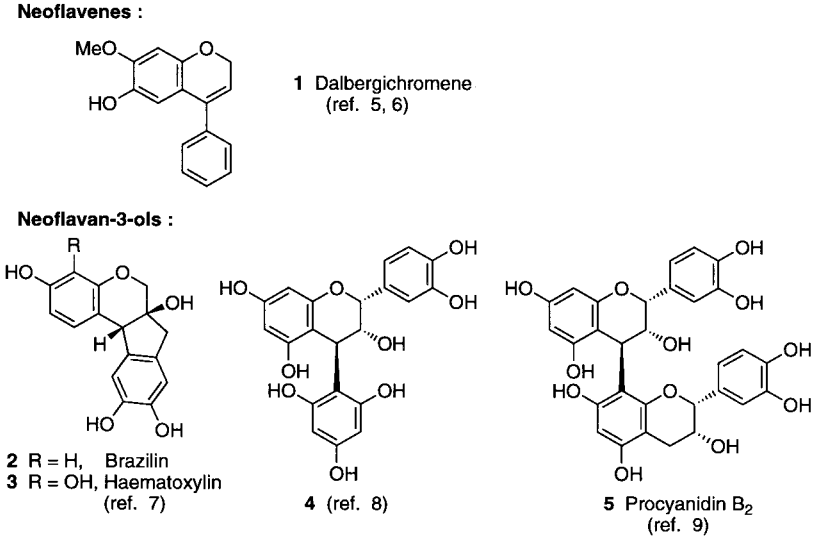
Abstract—The reaction of 4-methoxycarbonylchroman-3-one with aryllead triacetates gave the 4-aryl derivatives after 3-4 h reaction times in moderate to good yields. Unexpectedly, 2,4-diarylated derivatives were also obtained after longer reaction times. The activating methyl ester group proved difficult to remove by standard decarboxylation procedures. 4-Benzyloxycarbonylchroman-3-ones were therefore prepared and reacted with aryllead triacetates to afford the corresponding 4-aryl derivatives. These were subsequently decarboxylated, reduced and dehydrated to afford neoflavenes in modest overall yields.

1. Introduction

The neoflavene [4-arylchromene or (4-aryl-2*H*-1-benzopyran)] skeleton is one of the five main structural types found in the group of neoflavonoid derivatives.[1,2] Neoflavenes are thought to be important intermediates in the biosynthetic transformation of dalbergiquinols or dalbergiones into 4-arylcoumarins, and a few representatives have been isolated from *Dalbergia* and *Machaerium* genera of the *Leguminosae* family.[3–6] The related 4-aryl-3-hydroxychroman skeleton is also found in members of the homoflavonoid family, such as in brazilin **2**, isolated from *Cesalpinia sappan* and haematoxylin **3**, isolated from *Haematoxylon campechianum*.[7] Other examples of 3-hydroxy-4-arylchroman structures are observed in the 4-arylflavan-3-ol **4** isolated from the South African plant *Nelia*



Scheme 1.

Keywords: arylation; α,γ-diarylation; neoflavonoids; organolead reagents.
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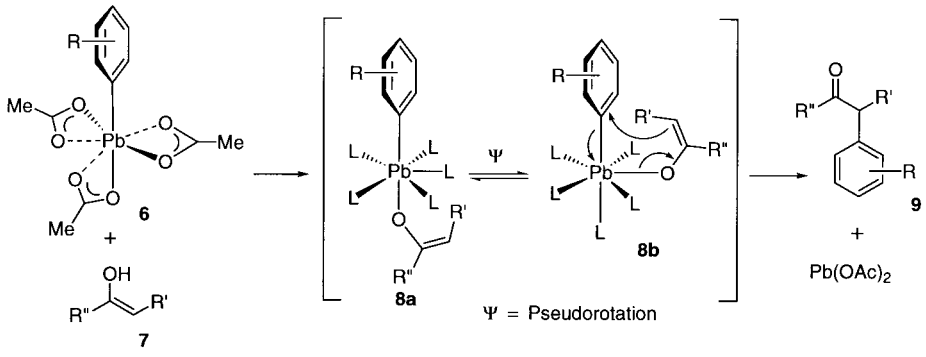
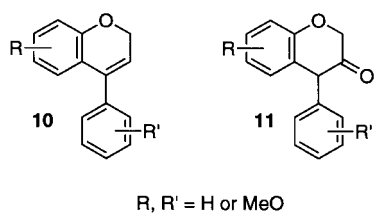


Scheme 2.

meyeri,[8] and in the more complex proanthocyanidin dimers derived from catechin and epicatechin such as procyanidin B_2 **5**[9–11] (Scheme 1).

In principle, formation of an aryl link to the C-4 can be obtained either by electrophilic arylation at a benzylic cation generated on C-4, or by reaction of a benzylic anion on C-4 with an aryl cation equivalent. The former approach has been the most generally applied in the synthesis of 4-arylchroman derivatives.[9–11] The latter system can be realised by the ligand coupling reactions of a nucleophilic species with aryllead triacetates, a reaction which was discovered and extensively exploited by Pinhey and his group.[12–15] In recent years, we have applied this ligand coupling procedure to the synthesis of a number of isoflavonoid derivatives.[15–21] We have observed that the highest yields are obtained in the reaction of C-3 chroman anions with the more electron-rich aryllead triacetates, such as 2,4,6-trimethoxyphenyllead triacetate. Aryllead triacetates, which act as the active aryl cationic species, are prepared either by direct oxidation of the parent arene with lead tetraacetate, or by an indirect sequence involving metalation of the arene, followed by metal–lead exchange reaction. The ligand coupling reaction occurs selectively on the *ipso*-carbon substituted by the lead group and does not involve the intermediacy of free radical species.[12–15] Although no intermediates have ever been detected with these organolead reagents, it is likely that various topoisomers of the short-lived intermediates are involved in the reaction pathway. In the first step, the aryllead triacetate **6** (R=H or MeO) undergoes a ligand exchange with the enolic substrate **7** (R′=acyl, R″=alkyl in the case of β-dicarbonyl compounds) to afford the species **8a** in which the aryl substituent and the enolic moiety possess a *trans*-diaxial configuration. Then thermal pseudorotation (Ψ) of the enolic group leads to the *cis*-conformer **8b**, in which the enolic group occupies an equatorial position. In this favourable transition state, overlap between the two π-systems of the aryl and enolic groups makes the ligand coupling process possible leading to ketone **9**. This non-synchronous concerted elimination is triggered by the development of a partial positive charge on the aryl group. Formally an oxidative activation of the aromatic ring is associated with the change of oxidation state from Pb(IV) to Pb(II) being the driving force of the reaction[15] (Scheme 2).



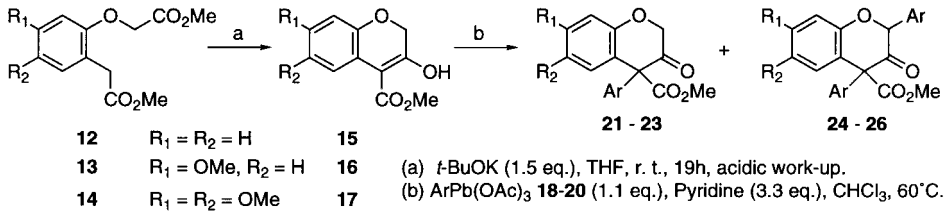
Scheme 3.

2. Results and discussion

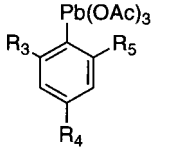
We therefore decided to extend the application of this ligand coupling reaction to the synthesis of neoflavenes **10**, as this would constitute an attractive approach toward the selective synthesis of structurally complex proanthocyanidin dimers. In this paper, we describe the synthesis of 4-arylchroman-3-ones **11**, and their elaboration into 4-arylchromenes or neoflavenes (Schemes 3 and 4). The key step is the ligand coupling reaction between the aryllead(IV) triacetates and a suitably activated chroman-3-one moiety. Previous work had shown that conversion of ketones into β-ketoesters was a convenient means of activating them for reaction with aryllead(IV) triacetates.[22]

Therefore, methyl β-ketoesters **15**–**17** were chosen as suitable substrates and were obtained in 62–81% yields by Dieckmann condensation of the diesters **12**–**14** with potassium *tert*-butoxide in tetrahydrofuran. This condensation led directly to the 4-methoxycarbonyl-2*H*-1-benzopyran-3(4*H*)-one structure, with the required activating ester group at the 4-position.

A series of arylation reactions was carried out on the methyl β-keto ester **15** with 1.1 molar equivalent of the aryllead(IV) triacetates **18**–**20** and 3 molar equivalents of pyridine in dry chloroform at 60°C. The arylation reactions with the lead reagents **19** and **20** were complete within 3–4 h and afforded the arylated products in good yields. Even the bulky 2,4,6-trimethoxyphenyl group was transferred in an impressive 83% yield in the reaction of **15** with aryllead triacetate **20**. However, the reaction involving the less reactive 4-methoxyphenyllead triacetate gave only moderate yields of the aryl derivatives after 4 h (60–65%) (Table 1). Thus, the more electron-rich aryl groups of the aryllead(IV) triacetates **19** and **20** are transferred in higher yields than the 4-methoxyphenyl group of **18**, a reactivity pattern which is in good agreement with our previous findings.[16–21]



Scheme 4.



	R_3	R_4	R_5
18	H	OMe	H
19	OMe	OMe	H
20	OMe	OMe	OMe

In an attempt to increase the yield of the 4-methoxyphenyl derivative **21**, the reaction of the methyl β-keto ester **15** with 4-methoxyphenyllead(IV) triacetate **18** was performed for 12 rather than 3 h at 60°C. Under these conditions, two products were obtained: the expected monoaryl product **21** in a poor 40% yield and an unexpected product of diarylation **24**, 4-methoxycarbonyl-2-(4-methoxyphenyl)-4-(4-methoxyphenyl)-2*H*-1-benzopyran-3(4*H*)-one, in 38% yield. Therefore under long enough reaction times, the 2-position is reactive enough for γ-arylation to take place. In contrast, when chroman-3-one, prepared by acid-catalyzed hydrolysis of **15** and in situ decarboxylation (10% aqueous H_2SO_4 under reflux, 82% yield), was treated with various aryllead triacetates under the same reaction conditions, no 2-aryl nor 4-aryl product was formed. Under these conditions, either one of the two possible enolic forms of the ketone leading to the corresponding intermediate enoxylead derivatives is not formed.

The influence of the reaction time on the outcome of the arylation was then studied with the two other lead reagents **19** and **20**. When β-ketoester **15** was treated with **19** and **20** for 12 h at 60°C, the yields of the monoaryl derivatives were again lower than after 3 h. However, only the 2,4-dimethoxyphenyl reagent **19** led to the diaryl product **25**, and none of the diaryl product **26** was detected in the reaction with **20**. In order to obtain this product **26** (which contains two bulky 2,4,6-trimethoxyphenyl groups), arylation of the monoaryl product **23** with the aryllead triacetate **20** was carried out at 60°C for 12 h. Under these conditions, **26** was isolated in 16% yield, with recovery of **23** in 83% yield. Similarly, reaction of the C-4 monoaryl derivatives **21** and **22** with their corresponding aryllead triacetates **18** and **19** led to the diaryl derivatives in better yields. However, even after 12 h the monoaryl substrate was still isolated from each reaction.

These results show that the reactivity pattern of aryllead triacetates is reversed in the case of α-aryloxyketones; the less electron-rich and the less sterically-hindered 4-methoxyphenyl group is transferred in higher yields. Such a pattern was already observed in the reaction of non-activated benzofuran-2-ones with aryllead triacetates.[22,23]

Unfortunately, all the decarboxylation methods which were attempted to decarboxylate the methyl esters **21**–**23** failed or gave intractable mixtures. The failure of these methods confirmed the unsuitability of the β-methoxycarbonyl group for the α-arylation of ketones, not because of its inability to activate α-arylation, but due to its difficulty in removal, an observation which we had also noted with the ethoxycarbonyl group in the isoflavone and benzofuranone series.[17,22] We therefore turned our attention to an alternative activating group, the benzyloxycarbonyl group, which was successfully used in lead mediated arylations by Suginome et al.[24] and was removed in high yields by palladium catalysed hydrogenolysis. The 4-benzyloxycarbonyl-2*H*-1-benzopyran-3(4*H*)-ones **27**–**29** were prepared in 78–82% yields after 9 to 24 h by the 4-dimethylaminopyridine catalysed transesterification of their corresponding 4-methoxycarbonyl derivatives **15**–**17** with benzyl alcohol in refluxing toluene, following the procedure of Taber et al.[25] Treatment of these esters with aryllead triacetates under the same reaction conditions as with the methyl esters proceeded in higher

Table 1. Structure of the 4-aryl-2*H*-1-benzopyrane derivatives **21**–**26** and **30**–**59**

R^1	R^2	Substituents on 4-Ar	Me esters		Benzyl esters	Ketones	3-Hydroxy	Neoflavenes
			4-aryl	2,4-diaryl				
H	H	4′-MeO	**21**	**24**	**30**		**42**	**51**
H	H	2′,4′-$(MeO)_2$	**22**	**25**	**31**		**43**	**52**
H	H	2′,4′,6′-$(MeO)_3$	**23**	**26**	**32**	**39**	**44**	**53**
OMe	H	4′-MeO			**33**		**45**	**54**
OMe	H	2′,4′-$(MeO)_2$			**34**		**46**	**55**
OMe	H	2′,4′,6′-$(MeO)_3$			**35**	**40**	**47**	**56**
OMe	OMe	4′-MeO			**36**		**48**	**57**
OMe	OMe	2′,4′-$(MeO)_2$			**37**		**49**	**58**
OMe	OMe	2′,4′,6′-$(MeO)_3$			**38**	**41**	**50**	**59**

Table 2. Reaction of aryllead(IV) triacetates with β-keto esters

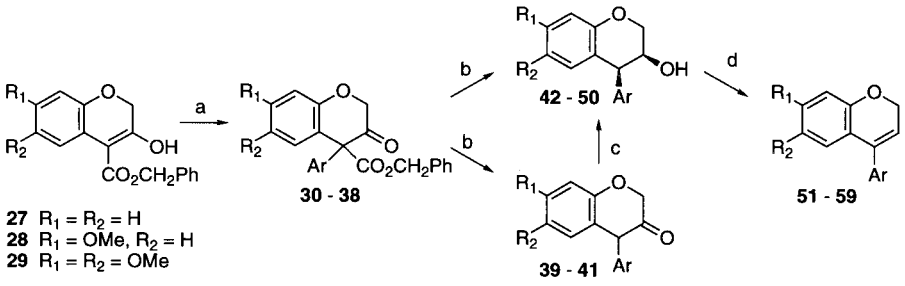
Substrate	$ArPb(OAc)_3$[a]	Time (h)	Products, (%)
Methyl esters			
15	**18**	4	**21**, (65)
15	**18**	12	**21**, (40); **24**, (36)
15	**19**	3	**22**, (86)
15	**19**	12	**22**, (43); **25**, (38)
15	**19**[b]	12	**22**, (36); **25**, (30)
15	**20**	3	**23**, (83)
15	**20**	12	**23**, (71)
21	**18**	12	**21**, (14); **24**, (46)
22	**19**	12	**22**, (46); **25**, (21)
23	**20**	12	23, (83); 26, (16)
Benzyl esters			
27	**18**	3	**30**, (74)
27	**19**	2.5	**31**, (87)
27	**20**	2.5	**32**, (92)
28	**18**	3	**33**, (70)
28	**19**	2.5	**34**, (80)
28	**20**	2.5	**35**, (81)
29	**18**	3	**36**, (55)
29	**19**	2.5	**37**, (63)
29	**20**	2.5	**38**, (72)

[a] All reactions were performed with 1.1 mol equiv. of the lead reagent and 3.3 mol equiv. of pyridine, unless otherwise reported.
[b] 2.2 mol equiv. of the lead reagent and 6.6 mol equiv. of pyridine were used.

yields than for the equivalent methyl β-keto ester series. The arylations also appeared to require slightly shorter reaction times. Again, no difficulties occurred in the introduction of the bulky 2,4,6-trimethoxyphenyl group. The highest yield observed for each of the substrates was for the reaction with 2,4,6-trimethoxyphenyllead(IV) triacetate **20**, which afforded products **32**, **35** and **38** in 72, 81 and 92% yields, respectively (Table 2, Scheme 5).

The benzyloxycarbonyl group was then conveniently removed from the compounds **30**–**38** by palladium catalysed hydrogenolysis, using 10% palladium on charcoal in methanol under a hydrogen atmosphere. Each of the starting benzyl esters was hydrogenated for three days and high yields were obtained in all cases (Table 3). When the 4-aryl group was the 2,4,6-trimethoxyphenyl group, the expected ketones **39**–**41** were obtained in 75–79% yields. However, when the 4-aryl group was the 4-methoxyphenyl group or the 2,4-dimethoxyphenyl group, the debenzylation product underwent further reduction to give the corresponding 4-(4-methoxyphenyl)- or 4-(2,4-dimethoxyphenyl)-3,4-dihydro-2*H*-1-benzopyran-3-ols in 76-91% yields, respectively. The 4-(2,4,6-trimethoxyphenyl)-2*H*-1-benzopyran-3(4*H*)-ones **39**–**41** were then reduced by sodium borohydride in THF and water at room temperature for 1 h to give the corresponding 4-(2,4,6-trimethoxyphenyl)-3,4-dihydro-2*H*-1-benzopyran-3-ol derivatives in 89–91% yields. ^{1}H NMR analysis of alcohols **42**–**50** indicated the presence of only one detectable isomer in all cases. The *J* values for the H_3–H_4 coupling constants were all in the range 4.2–4.95 Hz. Assignment of the C_3–C_4 relative stereochemistry in these conformationally flexible systems cannot be definitively drawn from these values, which are compatible with an axial–equatorial relationship as well as with an equatorial–equatorial one between the coupled H_3–H_4 protons. However, mechanistic arguments would be in favour of the 3,4-cis isomers. Indeed, approach of the ketone by the reducing agent (Pd/H_2 or $NaBH_4$) will be favoured on the less congested face of the pyran ring opposite from the 4-aryl substituent. The last step in the synthetic pathway towards 4-aryl-2*H*-1-benzopyrans was the dehydration of the 4-aryl-3,4-dihydro-2*H*-1-benzopyran-3-ols **42**–**50** obtained either in one or two steps from β-keto esters **30**–**38**. Attempts to employ acid-catalysed dehydration led either to recovery of the starting alcohol (*p*-toluenesulfonic acid in toluene under reflux) or to intractable mixtures (10% HCl or 10% H_2SO_4 under reflux). Successful dehydration was eventually realised by treating the 4-aryl-3,4-dihydro-2*H*-1-benzopyran-3-ols with phosphorus oxychloride (26 equiv.) in dry pyridine, following the procedure of Dauben and Boswell.[26,27] The 4-aryl-2*H*-1-benzopyrans **51**–**59** were obtained in relatively modest yields (33–50%), although, after each reaction, no trace of the starting material was found. The low yields of these reactions could possibly be attributed to competing polymerisation reaction of these diarylethylene type derivatives.

In conclusion, the aryllead triacetate mediated arylation of conveniently activated 3-oxochromane derivatives affords an easy and efficient synthesis of 4-arylchroman-3-one derivatives. This sequence should be useful for the synthesis of proanthocyanidin structures from 3-oxoflavanes. Moreover, an α,γ-diarylation was observed for the first time in



Scheme 5.

Table 3. Yields of the debenzylation, reduction and dehydration steps

Aryl β-keto-esters	Debenzylation, (%)	$NaBH_4$ reduction, (%)	Dehydration, (%)
30	**42**, (82)		**51**, (38)
31	**43**, (91)		**52**, (38)
32	**39**, (79)	**44**, (93)	**53**, (41)
33	**45**, (83)		**54**, (50)
34	**46**, (78)		**55**, (37)
35	**40**, (75)	**47**, (89)	**56**, (43)
36	**48**, (76)		**57**, (38)
37	**49**, (89)		**58**, (44)
38	**41**, (77)	**50**, (91)	**59**, (33)

the case of aryllead triacetate mediated arylation of β-keto esters. This unexpected result could be exploited to achieve a direct entry from chroman-3-ones into the 4-arylflavan-3-one series, which are the precursors of proanthocyanidin-type dimers. Extra flexibility in the introduction of aryl groups is available with this process as the relative reaction rates allow the selective α-monoarylation followed by the second γ-arylation which could be performed with a different aryllead reagent.

3. Experimental

Melting points were determined on a Reichert–Jung Thermovar apparatus and are uncorrected. IR spectra were recorded on a Mattson Galaxy Series FTIR 3000 spectrometer. 270 MHz ^{1}H NMR and 67.8 MHz ^{13}C NMR were recorded on a Jeol JNM-GX 270 spectrometer, and 400 MHz ^{1}H NMR were recorded on a Bruker AM 400X spectrometer. Spectra were obtained in $CDCl_3$ with TMS as the internal standard and are reported in ppm. All *J* values are given in Hz. The sign '*' is used when assignments may be reversed in ^{1}H NMR attributions. In the description of the NMR data of compounds, A′ refers to atom A of the aryl group linked to C-4 and A″ to atom A of the benzyloxycarbonyl group linked to C-4. Mass spectra were determined on a VG Analytical 770 mass spectrometer with attached INCOS 2400 data system in the EI mode. Separations by column chromatography (CC), preparative thin layer chromatography (PLC) and flash chromatography (FC) were performed using Merck Kieselgel 60 (70–230 mesh ASTM), Merck Kieselgel 60 (7748) and 60 (230–400 mesh ASTM), respectively.

3.1. Methyl (2-methoxycarboxymethoxy-4-methoxyphenyl)acetate (13)

A solution of 2-hydroxy-4-methoxyphenylacetic acid[28] (20 g), methanol (150 mL) and sulfuric acid (5 g) was refluxed for 8 h. The mixture was diluted with water (100 mL) and extracted with dichloromethane (100 mL). The extract was washed with a 10% $NaHCO_3$ solution (100 mL) and water (100 mL). Distillation of the solvents under reduced pressure gave methyl (2-hydroxy-4-methoxyphenyl)acetate as a yellow oil. The crude ester was directly treated with methyl bromoacetate (10.93 mL, 116 mmol), potassium carbonate (20 g) and acetone (100 mL), under reflux for 8 h. After filtration, the solvent was distilled under reduced pressure to yield (**13**) as a yellow solid (22.13 g, 75%), mp 60–62°C, ν_{max}(KBr)/cm^{-1} 1758, 1740; δ_H (270 MHz) 3.64 (s, 2H, CH_2CO_2), 3.68 (s, 3H, CH_2CO_2*Me*), 3.78 (s, 3H, OCH_2CO_2*Me*), 3.85 (s, 3H, OMe), 4.62 (s, 2H, OCH_2), 6.33 (d, *J*=2.3 Hz, 1H, 3-H), 6.52 (dd, *J*=2.3, 8.5 Hz, 1H, 5-H), 7.10 (d, *J*=8.5 Hz, 1H, 6-H);δ_C 35.1, 51.9, 55.2, 55.4, 65.7, 99.9, 105.5, 116.2, 131.6, 156.7, 160.0, 169.1, 172.5; *m/z* 268 (M^+, 18), 236 (20), 209 (52), 151 (16), 121 (19), 91 (14), 77 (23), 45 (100), 28 (10) (Found: C, 57.97; H, 6.08. $C_{13}H_{16}O_6$ requires: C, 58.20; H, 6.01%).

3.2. Methyl (2-methoxycarbonylmethoxy-4,5-dimethoxyphenyl)acetate (14)

By the same procedure, 2-hydroxy-4,5-dimethoxyphenylacetic acid[28] afforded (**14**) as a yellow solid, 77%, mp 57–60°C; ν_{max}(KBr)/cm^{-1} 1756, 1740; δ_H (270 MHz) 3.67 (s, 2H, CH_2CO_2), 3.69 (s, 3H, CH_2CO_2*Me*), 3.78 (s, 3H, OCH_2CO_2*Me*), 3.83 (s, 3H, 5-OMe), 3.84 (s, 3H, 4-OMe), 4.61 (s, 2H, OCH_2), 6.50 (s, 1H, 3-H), 6.74 (s, 1H, 6-H); δ_C 35.0, 51.9, 52.1, 56.1, 56.3, 67.6, 99.8, 114.2, 115.7, 144.1, 148.7, 150.1, 169.5, 172.4; *m/z* 298 (M^+, 45), 239 (42), 193 (43), 151 (22), 59 (18), 45 (100), 28 (72) (Found: C, 56.28; H, 6.17. $C_{14}H_{18}O_7$ requires: C, 56.37; H, 6.08%).

3.3. General procedure for the preparation of 4-methoxycarbonyl-2*H*-1-benzopyran-3(4*H*)-ones

The diester (1 equiv.) was added to a solution of potassium *tert*-butoxide (1.5 equiv.) in THF (30 mL per 5 mmol of diester) under nitrogen. The mixture was stirred at room temperature for 19 h. The reaction mixture was then poured into ice-water (200 mL) and acidified with 5% aqueous hydrochloric acid to pH 2. The reaction mixture was extracted with chloroform (2×100 mL), dried ($MgSO_4$) and the solvent removed. The residue was purified by chromatography on silica gel and crystallised.

3.3.1. 4-Methoxycarbonyl-2*H*-1-benzopyran-3(4*H*)-one (15). CC (eluant: $CHCl_3$), 81%; needles from ethanol, mp 37–38°C (lit.,[29] mp 34.5–36.5°C); ν_{max}(KBr)/cm^{-1} 3215, 1725, 1652; δ_H (270 MHz) 3.93 (s, 3H, CO_2Me), 4.63 (s, 2H, 2-H), 6.89 (dd, *J*=1.4, 7.7 Hz, 1H, 8-H), 6.97 (dt, *J*=1.7, 7.6 Hz, 1H, 6-H), 7.06 (dt, *J*=1.7, 7.6 Hz, 1H, 7-H), 7.73 (dd, *J*=1.4, 7.9 Hz, 1H, 5-H), 12.84 (s, 1H, OH); δ_C 52.1, 65.8, 97.0, 116.3, 119.7, 125.7, 126.5, 151.2, 169.3, 170.5; *m/z* 206 (M^+, 71), 174 (100), 147 (22), 118 (78), 91 (49), 45 (20), 39 (50), 31 (26).

3.3.2. 7-Methoxy-4-methoxycarbonyl-2*H*-1-benzopyran-3(4*H*)-one (16). CC (eluant: $CHCl_3$), 67%; yellow solid

from ethanol, mp 56–58°C; ν_{max}(KBr)/cm^{-1} 3210, 1738, 1652; δ_H (270 MHz) 3.77 (s, 3H, 7-OMe), 3.93 (s, 3H, CO_2Me), 4.63 (s, 2H, 2-H), 6.48-6.57 (m, 2H, 6-H, 8-H), 7.64 (d, J=8.7 Hz, 1H, 5-H), 12.63 (s, 1H, OH); δ_C 52.1, 55.4, 66.1, 97.0, 102.3, 108.0, 112.4, 126.5, 152.5, 158.5, 167.3, 171.2; *m/z* 236 (M^+, 49), 204 (100), 177 (12), 148 (74), 120 (20), 91 (14), 77 (22), 51 (12), 28 (8) (Found: C, 60.81; H, 5.16. $C_{12}H_{12}O_5$ requires: C, 61.02; H, 5.12%).

3.3.3. 6,7-Dimethoxy-4-methoxycarbonyl-2*H*-1-benzopyran-3(4*H*)-one (17). CC (eluant: $CHCl_3$), 62%; yellow solid from ethanol, mp 109–111°C; ν_{max}(KBr)/cm^{-1} 3212, 1733, 1647; δ_H (270 MHz) 3.83 (s, 3H, 6-OMe), 3.85 (s, 3H, 7-OMe), 3.95 (s, 3H, CO_2Me), 4.60 (s, 2H, 2-H), 6.51 (s, 1H, 8-H), 7.34 (s, 1H, 5-H), 12.63 (s, 1H, OH); δ_C 52.1, 56.0, 56.7, 66.3, 96.9, 101.0, 110.1, 111.4, 143.9, 145.6, 147.6, 167.9, 171.0; *m/z* 266 (M^+, 50), 234 (100), 191 (39), 163 (38), 135 (32), 107 (30), 69 (48), 51 (32), 29 (31) (Found: C, 58.60; H, 5.38. $C_{13}H_{14}O_6$ requires: C, 58.65; H, 5.30%).

3.4. General procedure for the preparation of 4-benzyloxycarbonyl-2*H*-1-benzopyran-3(4*H*)-ones

A solution of the appropriate 4-methoxycarbonyl-2*H*-1-benzopyran-3(4*H*)-one (1 equiv.), benzyl alcohol (2 equiv.) and 4-dimethylaminopyridine (0.2 equiv.) in dry toluene (40 mL per 5 mmol of ketone) was refluxed for the specified time. The cooled solution was diluted with ether (100 mL), washed successively with 1 M aqueous H_2SO_4 solution (50 mL), 5% aqueous $NaHCO_3$ solution (50 mL) and brine (100 mL), and dried over anhydrous Na_2SO_4. Distillation under reduced pressure of the volatiles gave a residue which was purified by chromatography on silica and crystallised.

3.4.1. 4-Benzyloxycarbonyl-2*H*-1-benzopyran-3(4*H*)-one (27). Refluxed for 24 h, CC (eluant: $CHCl_3$), 82%; amorphous solid, mp 58–60°C; ν_{max} (KBr)/cm^{-1} 3190, 1722, 1642; δ_H (270 MHz) 4.63 (s, 2H, 2-H), 5.39 (s, 2H, 2′-H), 6.87-6.96 (m, 2H, 6-H, 8-H), 7.05 (app. dt, J=1.7, 7.6 Hz, 1H, 7-H), 7.34–7.43 (m, 5H, C_6H_5), 7.76 (dd, J=1.7, 7.9 Hz, 1H, 5-H), 12.86 (s, 1H, OH); δ_C 66.0, 67.1, 97.1, 116.4, 119.9, 122.3, 125.8, 126.6, 128.3, 128.6, 128.8, 135.2, 151.3, 169.8, 170.7; *m/z* 282 (M^+, 20), 174 (18), 147 (7), 118 (9), 91 (100), 65 (19), 39 (8) (Found: C, 72.33; H, 4.92. $C_{17}H_{14}O_4$ requires: C, 72.33; H, 5%).

3.4.2. 4-Benzyloxycarbonyl-7-methoxy-2*H*-1-benzopyran-3(4*H*)-one (28). Refluxed for 9 h; CC (eluant: $CHCl_3$), 78%; amorphous solid, mp 57–60°C; ν_{max} (KBr)/cm^{-1} 3126, 1734, 1650; δ_H (270 MHz) 3.74 (s, 3H, 7-OMe), 4.61 (s, 2H, 2-H), 5.37 (s, 2H, 2′-H), 6.48-6.51 (m, 2H, 6-H, 8-H), 7.36-7.41 (m, 5H, C_6H_5), 7.67 (d, J=9 Hz, 1H, 5-H), 12.64 (s, 1H, OH); δ_C 55.4, 66.1, 67.0, 97.0, 102.4, 108.0, 112.5, 126.5, 128.3, 128.5, 128.8, 135.3, 152.5, 158.5, 167.7, 170.6; *m/z* 312 (M^+, 18), 221 (31), 204 (32), 177 (15), 121 (28), 91 (100), 77 (14), 65 (18), 39 (8) (Found: C, 69.02; H, 5.09. $C_{18}H_{16}O_5$ requires: C, 69.22; H, 5.16%).

3.4.3. 4-Benzyloxycarbonyl-6,7-dimethoxy-2*H*-1-benzopyran-3(4*H*)-one (29). Refluxed for 9 h; CC (eluant: $CHCl_3$), 79%; amorphous solid, mp 103–105°C; ν_{max} (KBr)/cm^{-1} 3160, 1729, 1637; δ_H (270 MHz) 3.44 (s, 3H, 6-OMe), 3.80 (s, 3H, 7-OMe), 4.60 (s, 2H, 2-H), 5.33 (s, 2H, 2′-H), 6.48 (s, 1H, 8-H), 7.25 (s, 1H, 5-H), 7.36-7.44 (m, 5H, C_6H_5), 12.68 (s, 1H, OH); δ_C 55.8, 55.9, 66.3, 67.5, 96.9, 100.8, 109.2, 111.3, 128.8, 128.9, 134.9, 143.8, 145.2, 147.2, 168.2, 170.3; *m/z* 342 (M^+, 24), 251 (38), 234 (74), 207 (32), 151 (28), 107 (18), 91 (100), 65 (33), 28 (52) (Found: C, 66.40; H, 5.39. $C_{19}H_{18}O_6$ requires: C, 66.66; H, 5.30%).

3.5. General procedure for the arylation of 4-methoxy- and 4-benzyloxycarbonyl-2*H*-1-benzopyran-3(4*H*)-ones

Dry pyridine (3.3 equiv.) was added to a stirred mixture of the 2*H*-1-benzopyran-3(4*H*)-one (1 equiv.) and aryllead triacetate (1.1 equiv.) in dry chloroform (1 mL per 0.6 mmol of substrate). The mixture was stirred at 60°C for the time specified. The reaction mixture was diluted with chloroform (50 mL) and washed with 6% aqueous sulfuric acid (2×50 mL). The aqueous phase was washed with chloroform (2×50 mL) and the combined organic extracts were washed with water (2×50 mL), dried ($MgSO_4$), filtered and the solvent removed in vacuo. The residue was purified by chromatography on silica using the indicated solvent system.

3.5.1. 4-Methoxycarbonyl-4-(4-methoxyphenyl)-2*H*-1-benzopyran-3(4*H*)-one (21). PLC (eluant: $CHCl_3$); plates from ethanol, mp 84–86°C; ν_{max} (KBr)/cm^{-1} 1746, 1722; δ_H (270 MHz) 3.78 (3H, s, 4′-OMe), 3.80 (s, 3H, 2″-H), 4.52 (d, J=17.5 Hz, 1H, 2-H), 4.60 (d, J=17.5 Hz, 1H, 2-H), 6.85 (dd, J=2.4, 6.8 Hz, 2H, 5′-H, 3′-H), 6.96 (dd, J=2.4, 6.8 Hz, 2H, 6′-H, 2′-H), 7.02 (dd, J=1.75, 8.15 Hz, 1H, 8-H), 7.09-7.14 (m, 2H, 5-H, 6-H), 7.35 (m, 1H, 7-H); δ_C 53.8, 55.7, 67.2, 71.9, 114.3, 118.7, 124.0, 125.1, 126.9, 129.9, 130.3, 130.8, 154.9, 159.9, 170.7, 203.0; *m/z* 312 (M^+, 40), 253 (92), 225 (100), 197 (99), 181 (25), 165 (34), 152 (34), 139 (22), 91 (12), 45 (16) (Found: C, 69.29; H, 4.87. $C_{18}H_{16}O_5$ requires: C, 69.22; H, 5.16%).

3.5.2. 4-Methoxycarbonyl-4-(2,4-dimethoxyphenyl)-2*H*-1-benzopyran-3(4*H*)-one (22). PLC (eluant: Et_2O–light petroleum 8:2); needles from ethanol, mp 105–107°C; ν_{max} (KBr)/cm^{-1} 1752, 1736; δ_H (400 MHz) 3.49 (s, 3H, 2′-OMe), 3.78 (s, 3H, 4′-OMe), 3.81 (s, 3H, 2″-H), 4.48 (d, J= 17.1 Hz, 1H, 2-H), 4.80 (d, J=17.1 Hz, 1H, 2-H), 6.47 (d, J=2.5 Hz, 1H, 3′-H), 6.54 (dd, J=2.5, 8.6 Hz, 1H, 5′-H), 6.85 (dd, J=1.5, 7.75 Hz, 1H, 8-H), 6.95 (dt, J=1.2, 7.55 Hz, 1H, 6-H), 7.03 (dd, J=1.1, 8.1 Hz, 1H, 5-H), 7.17 (d, J=8.6 Hz, 1H, 6′-H), 7.21–7.27 (m, 1H, 7-H); δ_C 53.3, 55.4, 55.6, 64.4, 71.8, 100.3, 104.5, 117.5, 118.0, 123.1, 126.6, 128.8, 129.0, 130.3, 153.9, 157.5, 161.0, 168.9, 202.7; *m/z* 342 (M^+, 36), 283 (21), 255 (94), 227 (16), 152 (19), 139 (14), 91 (100), 28 (24) (Found: C, 66.49; H, 5.30. $C_{19}H_{18}O_6$ requires: C, 66.66; H, 5.30%).

3.5.3. 4-Methoxycarbonyl-4-(2,4,6-trimethoxyphenyl)-2*H*-1-benzopyran-3(4*H*)-one (23). PLC (eluant: $CHCl_3$); needles from ethanol, mp 144–146°C; ν_{max} (KBr)/cm^{-1} 1747, 1730; δ_H (270 MHz) 3.63 (s, 6H, 2′-OMe, 6′-OMe), 3.73 (s, 3H, 4′-OMe), 3.80 (s, 3H, 2″-H), 4.47 (d, J=16.7 Hz, 1H, 2-H), 4.68 (d, J=16.7 Hz, 1H, 2-H), 6.18 (s, 2H, 3′-H, 5′-H), 6.89–7.04 (m, 3H, 5-H, 6-H, 8-H),

7.19–7.26 (m, 1H, 7-H); δ_C 53.3, 55.4, 56.1, 63.0, 71.9, 92.5, 108.7, 117.4, 122.9, 127.3, 128.6, 128.9, 154.1, 158.5, 161.2, 168.6, 202.6; *m/z* 372 (M^+, 41), 313 (12), 285 (100), 255 (15), 152 (12), 139 (14), 91 (66), 69 (22), 28 (39) (Found: C, 64.64; H, 5.48. $C_{20}H_{20}O_7$ requires: C, 64.51; H, 5.41%).

3.5.4. 4-Methoxycarbonyl-2-(4-methoxyphenyl)-4-(4-methoxyphenyl)-2*H*-1-benzopyran-3(4*H*)-one (24). PLC (eluant: $CHCl_3$); amorphous powder from ethanol–water, mp 150–152°C; ν_{max} (KBr)/cm^{-1} 1745, 1734; δ_H (270 MHz) 3.72 (s, 3H, 4′-OMe), 3.76 (s, 3H, 4″-OMe), 3.78 (s, 3H, CO_2Me), 5.58 (s, 1H, 2-H), 6.62-7.30 (m, 12H, Ar-H); *m/z* 418 (M^+, 3), 390 (20), 330 (100), 180 (48), 165 (22), 151 (24), 121 (29), 91 (20) (Found: C, 72.0; H, 5.49. $C_{25}H_{22}O_6$ requires: C, 71.76; H, 5.30%).

3.5.5. 4-Methoxycarbonyl-2-(2,4-dimethoxyphenyl)-4-(2,4-dimethoxyphenyl)-2*H*-1-benzopyran-3(4*H*)-one (25). PLC (eluant: Et_2O–light petroleum 8:2); needles from ethanol, mp 169–172°C; ν_{max} (KBr)/cm^{-1} 1747, 1736; δ_H (400 MHz) 3.52 (s, 6H, 2″-OMe, 2′-OMe), 3.79 (s, 3H, 4′-OMe), 3.80 (s, 3H, 4″-OMe), 3.81 (s, 3H, CO_2Me), 5.72 (s, 1H, 2-H), 6.46 (d, *J*=2.3 Hz, 1H, 3′-H), 6.48 (d, *J*=2.3 Hz, 1H, 3″-H), 6.52 (t, *J*=2.2 Hz, 1H, 5′-H), 6.54 (t, *J*=2.2 Hz, 1H, 5″-H), 6.81 (dd, *J*=1.5, 7.75 Hz, 1H, 8-H), 6.97 (dt, *J*=1.2, 7.55 Hz, 1H, 6-H), 7.07 (dd, *J*=1.1, 8.05 Hz, 1H, 5-H), 7.17 (d, *J*=8.6 Hz, 1H, 6′-H), 7.21–7.28 (m, 1H, 7-H), 7.33 (d, *J*=8.5 Hz, 1H, 6″-H); *m/z* 478 (M^+, 5), 450 (20), 390 (100), 363 (20), 269 (18), 225 (23), 180 (55), 151 (50), 121 (38), 91 (29), 77(32) (Found: C, 67.82; H, 5.55. $C_{27}H_{26}O_8$ requires: C, 67.77; H, 5.48%).

3.5.6. 4-Methoxycarbonyl-2-(2,4,6-trimethoxyphenyl)-4-(2,4,6-trimethoxyphenyl)-2*H*-1-benzopyran-3(4*H*)-one (26). PLC (eluant: $CHCl_3$); amorphous powder from ethanol, mp 197–199°C; ν_{max} (KBr)/cm^{-1} 1744, 1734; δ_H (270 MHz) 3.66 (s, 6H, 2′-OMe, 6′-OMe), 3.73 (s, 6H, 2″-OMe, 6″-OMe), 3.76 (s, 3H, 4′-OMe), 3.80 (s, 3H, 4″-OMe), 3.81 (s, 3H, CO_2Me), 5.92 (s, 1H, 2-H), 6.15 (s, 2H, 3′-H, 5′-H), 6.19 (s, 2H, 3″-H, 5″-H), 6.78 (dd, *J*=1.45, 7.7 Hz, 1H, 8-H), 6.92-6.97 (m, 1H, 6-H), 7.10 (d, *J*=6.95 Hz, 1H, 5-H), 7.21–7.26 (m, 1H, 7-H); *m/z* 538 (M^+, 3), 510 (25), 451 (100), 299 (15), 211 (80), 181 (23), 151 (18), 121 (22), 91 (17) (Found: C, 64.61; H, 5.91. $C_{29}H_{30}O_{10}$ requires: C, 64.68; H, 5.61%).

3.5.7. 4-Benzyloxycarbonyl-4-(4-methoxyphenyl)-2*H*-1-benzopyran-3(4*H*)-one (30). PLC (eluant: $CHCl_3$); needles from ethanol, mp 124–126°C; ν_{max} (KBr)/cm^{-1} 1739, 1724; δ_H (270 MHz) 3.77 (s, 3H, 4′-OMe), 4.49 (d, *J*=17.5 Hz, 1H, 2-H), 4.57 (d, *J*=17.5 Hz, 1H, 2-H), 5.22 (d, *J*= 12.45 Hz, 1H, 2″-H), 5.29 (d, *J*=12.45 Hz, 1H, 2″-H), 6.83 (dd, *J*=2.2, 6.8 Hz, 2H, 5′-H, 3′-H), 6.90-7.10 (m, 4H, 5-H, 6-H, 2′-H, 6′-H), 7.21-7.38 (m, 6H, 7-H, C_6H_5); δ_C 55.5, 67.8, 67.9, 71.4, 113.9, 118.2, 123.6, 124.9, 126.5, 128.2, 128.4, 128.5, 129.7, 130.0, 130.5, 135.1, 154.3, 159.5, 169.1, 202.6; *m/z* 388 (M^+, 8), 297 (20), 253 (36), 225 (22), 197 (32), 181 (10), 165 (19), 152 (18), 91 (100), 28 (20) (Found: C, 74.52; H, 4.89. $C_{24}H_{20}O_5$ requires: C, 74.22; H, 5.19%).

3.5.8. 4-Benzyloxycarbonyl-4-(2,4-dimethoxyphenyl)-2*H*-1-benzopyran-3(4*H*)-one (31). PLC (eluant: Et_2O–light petroleum 8:2); rods from ethanol, mp 137–138°C; ν_{max} (KBr)/cm^{-1} 1746, 1733; δ_H (270 MHz) 3.46 (s, 3H, 2′-OMe), 3.80 (s, 3H, 4′-OMe), 4.46 (d, *J*=17.2 Hz, 1H, 2-H), 4.75 (d, *J*=17.2 Hz, 1H, 2-H), 5.22 (s, 2H, 2″-H), 6.44 (d, *J*=2.4 Hz, 1H, 3′-H), 6.46 (dd, *J*=2.4, 5.6 Hz, 1H, 5′-H), 6.84 (dd, *J*=1.45, 7.9 Hz, 1H, 8-H), 6.95 (dt, *J*=1.3, 7.5 Hz, 1H, 6-H), 7.03 (dd, *J*=1.1, 8.05 Hz, 1H, 5-H), 7.10 (d, *J*=5.6 Hz, 1H, 6′-H), 7.18–7.32 (m, 6H, 7-H, C_6H_5); δ_C 55.4, 55.6, 66.2, 67.9, 71.8, 100.3, 100.4, 117.6, 117.9, 123.2, 126.6, 127.9, 128.3, 128.5, 128.9, 129.0, 130.4, 135.0, 153.9, 157.6, 161.1, 168.3, 202.7; *m/z* 418 (M^+, 18), 327 (23), 283 (24), 255 (39), 227 (9), 152 (10), 91 (100), 65 (12), 28 (9) (Found: C, 71.57; H, 5.27. $C_{25}H_{22}O_6$ requires: C, 71.76; H, 5.30%).

3.5.9. 4-Benzyloxycarbonyl-4-(2,4,6-trimethoxyphenyl)-2*H*-1-benzopyran-3(4*H*)-one (32). PLC (eluant: $CHCl_3$); needles from ethanol, mp 156–159°C; ν_{max} (KBr)/cm^{-1} 1743, 1729; δ_H (270 MHz) 3.50 (s, 6H, 2′-OMe, 6′-OMe), 3.79 (s, 3H, 4′-OMe), 4.46 (d, *J*=16.75 Hz, 1H, 2-H), 4.65 (d, *J*= 16.75 Hz, 1H, 2-H), 5.17 (s, 2H, 2″-H), 6.15 (s, 2H, 3′-H, 5′-H), 6.91–7.04 (m, 3H, 5-H, 6-H, 8-H), 7.18–7.28 (m, 6H, 7-H, C_6H_5); δ_C 55.3, 55.9, 62.6, 67.5, 71.9, 92.4, 108.9, 117.4, 122.8, 127.5, 127.6, 127.8, 128.3, 128.5, 128.9, 135.6, 154.1, 158.6, 161.2, 168.0, 202.5; *m/z* 448 (M^+, 32), 357 (31), 313 (22), 285 (40), 181 (8), 107 (12), 91 (100), 28 (5) (Found: C, 69.48; H, 5.39. $C_{26}H_{24}O_7$ requires: C, 69.63; H, 5.39%).

3.5.10. 4-Benzyloxycarbonyl-7-methoxy-4-(4-methoxyphenyl)-2*H*-1-benzopyran-3(4*H*)-one (33). PLC (eluant: $CHCl_3$); amorphous powder from ethanol, mp 103–104°C; ν_{max} (KBr)/cm^{-1} 1748, 1736; δ_H (270 MHz) 3.78 (s, 3H, 4′-OMe),* 3.82 (s, 3H, 7-OMe),* 4.48 (d, *J*=16.6 Hz, 1H, 2-H), 4.56 (d, *J*=16.6 Hz, 1H, 2-H), 5.21 (d, *J*=12.45 Hz, 1H, 2″-H), 5.28 (d, *J*=12.45 Hz, 1H, 2″-H), 6.60 (d, *J*=8.6 Hz, 2H, 3′-H, 5′-H), 6.81–6.85 (m, 3H, 5-H, 6-H, 8-H), 6.97 (d, *J*=8.6 Hz, 2H, 2′-H, 6′-H), 7.23-7.32 (m, 5H, C_6H_5); δ_C 55.3, 55.5, 66.2, 67.8, 71.4, 103.1, 110.2, 113.9, 116.3, 127.0, 128.2, 128.4, 128.5, 130.4, 130.5, 135.1, 155.5, 159.5, 160.9, 169.8, 202.4; *m/z* 418 (M^+, 5), 327 (10), 283 (68), 255 (11), 227 (24), 139 (5), 115 (6), 91 (100), 65 (18) (Found: C, 71.49; H, 5.37. $C_{25}H_{22}O_6$ requires: C, 71.76; H, 5.30%).

3.5.11. 4-Benzyloxycarbonyl-7-methoxy-4-(2,4-dimethoxyphenyl)-2*H*-1-benzopyran-3(4*H*)-one (34). PLC (eluant: Et_2O–light petroleum 8:2); amorphous powder from ethanol, mp 124–126°C; ν_{max} (KBr)/cm^{-1} 1743, 1733; δ_H (270 MHz) 3.49 (s, 3H, 2′-OMe), 3.78 (s, 3H, 4′-OMe),* 3.80 (s, 3H, 7-OMe),* 4.46 (d, *J*=16.7 Hz, 1H, 2-H), 4.72 (d, *J*= 16.7 Hz, 1H, 2-H), 5.22 (s, 2H, 2″-H), 6.46–6.56 (m, 4H, 6-H, 8-H, 5′-H, 3′-H), 6.76 (d, *J*=8.6 Hz, 1H, 5-H), 7.10 (d, *J*=9.15 Hz, 1H, 6′-H), 7.24-7.30 (m, 5H, C_6H_5); δ_C 55.4, 55.6, 63.8, 67.7, 71.8, 100.3, 102.5, 104.4, 109.6, 118.1, 118.2, 127.9, 128.3, 128.5, 129.7, 130.3, 135.5, 155.4, 158.4, 159.9, 161.0, 168.6, 202.6; *m/z* 448 (M^+, 10), 357 (8), 313 (33), 285 (18), 257 (16), 121 (38), 91 (100), 65 (12) (Found: C, 69.62; H, 5.47. $C_{26}H_{24}O_7$ requires: C, 69.63; H, 5.39%).

3.5.12. 4-Benzyloxycarbonyl-7-methoxy-4-(2,4,6-trimethoxyphenyl)-2*H*-1-benzopyran-3(4*H*)-one (35). PLC (eluant:

$CHCl_3$); plates from ethanol, mp 151–153°C; ν_{max} (KBr)/cm^{-1} 1744, 1734; δ_H (270 MHz) 3.51 (s, 6H, 2′-OMe, 6′-OMe), 3.77 (s, 3H, 4′-OMe),* 3.79 (s, 3H, 7-OMe),* 4.47 (d, J=16.7 Hz, 1H, 2-H), 4.60 (d, J=16.7 Hz, 1H, 2-H), 5.18 (s, 2H, 2″-H), 6.14 (s, 2H, 3′-H, 5′-H), 6.57 (m, 2H, 6-H, 8-H), 6.82 (d, J=8.6 Hz, 1H, 5-H), 7.25–7.27 (m, 5H, C_6H_5); δ_C 55.4, 55.9, 62.5, 67.6, 72.1, 92.5, 102.5, 108.9, 109.5, 119.3, 127.9, 128.0, 128.4, 129.8, 135.8, 155.1, 158.6, 160.0, 161.2, 167.9, 202.5; *m/z* 478 (M^+, 18), 387 (12), 343 (69), 315 (18), 287 (5), 137 (15), 121 (46), 91 (100), 65 (10) (Found: C, 68.03; H, 5.55. $C_{27}H_{26}O_8$ requires: C, 67.77; H, 5.47%).

3.5.13. 4-Benzyloxycarbonyl-6,7-dimethoxy-4-(4-methoxyphenyl)-2*H*-1-benzopyran-3(4*H*)-one (36). PLC (eluant: $CHCl_3$); amorphous powder from ethanol–water, mp 95–98°C; ν_{max} (KBr)/cm^{-1} 1745, 1733; δ_H (270 MHz) 3.50 (3H, s, 6-OMe), 3.78 (3H, s, 4′-OMe),* 3.89 (3H, s, 7-OMe),* 4.45 (d, J=16.6 Hz, 1H, 2-H), 4.54 (d, J=16.6 Hz, 1H, 2-H), 5.15 (d, J=12.3 Hz, 1H, 2″-H), 5.35 (d, J=12.3 Hz, 1H, 2″-H), 6.29 (s, 1H, 8-H), 6.63 (s, 1H, 5-H), 6.83 (d, J=9 Hz, 2H, 3′-H, 5′-H), 6.99 (d, J=9 Hz, 2H, 2′-H, 6′-H), 7.26-7.30 (m, 5H, C6H5); δ_C 55.3, 56.1, 56.2, 66.7, 67.9, 71.5, 101.7, 111.1, 113.9, 114.4, 127.0, 128.4, 128.5, 128.6, 130.5, 135.2, 145.3, 148.7, 150.2, 159.5, 169.9, 202.3; *m/z* 448 (M^+, 18), 313 (84), 285 (12), 257 (44), 213 (12), 121 (9), 91 (100), 65 (20), 28 (45) (Found: C, 69.35; H, 5.42. $C_{26}H_{24}O_7$ requires: C, 69.63; H, 5.39%).

3.5.14. 4-Benzyloxycarbonyl-6,7-dimethoxy-4-(2,4-dimethoxyphenyl)-2*H*-1-benzopyran-3(4*H*)-one (37). PLC (eluant: Et_2O–light petroleum 8:2); plates from ethanol–water, mp 121–123°C; ν_{max} (KBr)/cm^{-1} 1744, 1733; δ_H (270 MHz) 3.51 (s, 3H, 2′-OMe), 3.58 (s, 3H, 6-OMe), 3.80 (s, 3H, 4′-OMe),* 3.86 (s, 3H, 7-OMe),* 4.43 (d, J=16.75 Hz, 1H, 2-H), 4.71 (d, J=16.75 Hz, 1H, 2-H), 5.22 (s, 2H, 2″-H), 6.34 (s, 1H, 8-H), 6.46 (m, 2H, 3′-H, 5′-H), 6.58 (s, 1H, 5-H), 7.07 (d, J=8.6 Hz, 1H, 6′-H), 7.25-7.30 (m, 5H, C6H5); δ_C 55.4, 55.7, 56.0, 56.3, 63.7, 67.7, 72.0, 100.2, 101.3, 104.5, 111.4, 116.7, 118.0, 128.0, 128.3, 128.5, 130.4, 135.1, 144.9, 148.3, 149.7, 157.9, 161.0, 168.6, 202.2; *m/z* 478 (M^+, 17), 343 (54), 315 (18), 287 (19), 151 (28), 91 (100), 65 (18), 28 (6) (Found: C, 67.91; H, 5.66. $C_{27}H_{26}O_8$ requires: C, 67.77; H, 5.47%).

3.5.15. 4-Benzyloxycarbonyl-6,7-dimethoxy-4-(2,4,6-trimethoxyphenyl)-2*H*-1-benzopyran-3(4*H*)-one (38). PLC (eluant: $CHCl_3$); amorphous solid from ether, mp 149–151°C; ν_{max} (KBr)/cm^{-1} 1745, 1731; δ_H (270 MHz) 3.52 (s, 6H, 2′-OMe, 6′-OMe), 3.62 (s, 3H, 6-OMe), 3.80 (s, 3H, 4′-OMe),* 3.85 (s, 3H, 7-OMe),* 4.47 (d, J=16.72 Hz, 1H, 2-H), 4.58 (d, J=16.72 Hz, 1H, 2-H), 5.16 (d, J=12.38 Hz, 1H, 2″-H), 5.22 (d, J=12.38 Hz, 1H, 2″-H), 6.14 (s, 2H, 3′-H, 5′-H), 6.49 (s, 1H, 8-H), 6.57 (s, 1H, 5-H), 7.26-7.27 (m, 5H, C_6H_5); δ_C 55.4, 55.9, 56.3, 62.1, 67.5, 72.3, 92.5, 101.3, 108.8, 112.0, 118.1, 127.9, 128.0, 128.4, 135.8, 144.6, 148.3, 149.2, 158.6, 161.1, 168.4, 202.4; *m/z* 508 (M^+, 14), 373 (28), 345 (10), 317 (8), 151 (16), 91 (100), 65 (12), 28 (7) (Found: C, 65.84; H, 5.69. $C_{28}H_{28}O_9$ requires: C, 66.13; H, 5.55%).

3.6. General procedure for the debenzyloxycarbonylation of 4-benzyloxycarbonyl-4-aryl-2*H*-1-benzopyran-3(4*H*)-ones

A mixture of the 4-benzyloxycarbonyl-4-aryl-2*H*-1-benzopyran-3(4*H*)-one and 10% palladium on charcoal (0.110 g per 1 mmol of ketone) in methanol (200 mL per 1 mmol of ketone) was hydrogenated at room temperature and atmospheric pressure for 3 d. The catalyst was filtered off, the filtrate was evaporated and the residue purified by chromatography on silica using the indicated solvent system.

3.6.1. 3,4-Dihydro-4-(4-methoxyphenyl)-2*H*-1-benzopyran-3-ol (42). PLC (eluant: Et_2O); plates from ethanol, mp 77–80°C; ν_{max} (KBr)/cm^{-1} 3386; δ_H (270 MHz) 1.76 (bs, 1H, 3-OH), 3.79 (s, 3H, 4′-OMe), 4.13 (m, 3H, 3-H, 2-H), 4.31 (d, J=4.25 Hz, 1H, 4-H), 6.83-6.91 (m, 5H, 5-H, 6-H, 8-H, 3′-H, 5′-H), 7.09-7.15 (m, 3H, 7-H, 2′-H, 6′-H); δ_C 46.6, 55.3, 66.0, 67.5, 114.0, 116.6, 121.0, 122.8, 128.1, 128.2, 130.9, 131.2, 154.3, 158.9; *m/z* 256 (M^+, 48), 211 (86), 197 (23), 181 (100), 168 (8), 152 (10), 115 (12), 91 (7) (Found: C, 75.01; H, 6.44. $C_{16}H_{16}O_3$ requires: C, 74.98; H, 6.29%).

3.6.2. 3,4-Dihydro-4-(2,4-dimethoxyphenyl)-2*H*-1-benzopyran-3-ol (43). PLC (eluant: Et_2O–light petroleum 6:4); needles from ethanol, mp 86–88°C; ν_{max} (KBr)/cm^{-1} 3358; δ_H (270 MHz) 2.58 (d, J=3.3 Hz, 1H, 3-OH), 3.79 (s, 3H, 4′-OMe), 3.86 (s, 3H, 2′-OMe), 4.08 (m, 2H, 2-H), 4.27 (m, 1H, 3-H), 4.80 (d, J=4.45 Hz, 1H, 4-H), 6.43 (dd, J= 2.4, 8.45 Hz, 1H, 5′-H), 6.53 (d, J=2.4 Hz, 1H, 3′-H), 6.75-6.92 (m, 4H, 5-H, 6-H, 8-H, 6′-H), 7.12-7.18 (m, 1H, 7-H); δ_C 40.0, 55.4, 55.6, 65.7, 66.8, 98.5, 104.4, 116.6, 120.6, 120.8, 122.6, 127.8, 130.8, 132.0, 154.8, 158.3, 159.9; *m/z* 286 (M^+, 23), 268 (5), 241 (12), 227 (14), 211 (100), 168 (8), 139 (6), 91 (5) (Found: C, 71.16; H, 6.41. $C_{17}H_{18}O_4$ requires: C, 71.31; H, 6.33%).

3.6.3. 4-(2,4,6-Trimethoxyphenyl)-2*H*-1-benzopyran-3(4*H*)-one (39). PLC (eluant: $CHCl_3$); needles from ethanol, mp 130–132°C; ν_{max} (KBr)/cm^{-1} 1721; δ_H (270 MHz) 3.68 (s, 6H, 2′-OMe, 6′-OMe), 3.81 (s, 3H, 4′-OMe), 4.46 (d, J=16.5 Hz, 1H, 2-H), 4.61 (d, J=16.5 Hz, 1H, 2-H), 5.14 (s, 1H, 4-H), 6.17 (s, 2H, 3′-H, 5′-H), 6.75 (m, 1H, 8-H), 6.88 (dt, J=1.3, 6.9 Hz, 1H, 6-H), 7.02 (dd, J=1.3, 8.05 Hz, 1H, 5-H), 7.12-7.18 (m, 1H, 7-H); δ_C 44.4, 55.5, 55.6 72.6, 91.2, 107.3, 117.0, 122.6, 126.1, 127.4, 127.5, 154.0, 158.7, 161.1, 208.5; *m/z* 314 (M^+, 100), 286 (82), 255 (25), 241 (17), 179 (14), 168 (18), 137 (16), 91 (18), 28 (22) (Found: C, 68.80; H, 5.80. $C_{18}H_{18}O_5$ requires: C, 68.78; H, 5.77%).

3.6.4. 3,4-Dihydro-7-methoxy-4-(4-methoxyphenyl)-2*H*-1-benzopyran-3-ol (45). PLC (eluant: Et_2O); plates from ethanol, mp 100–102°C; ν_{max} (KBr)/cm^{-1} 3307; δ_H (270 MHz) 1.68 (bs, 1H, 3-OH), 4.11 (m, 3H, 2-H, 3-H), 4.25 (d, J=4.2 Hz, 1H, 4-H), 6.43–6.46 (m, 2H, 3′-H, 5′-H), 6.77–6.90 (m, 3H, 5-H, 6-H, 8-H), 7.10 (d, J=8.45 Hz, 2H, 2′-H, 6′-H); δ_C 46.1, 55.3, 66.1, 67.5, 101.1, 108.2, 114.1, 114.8, 131.2, 131.4, 131.8, 155.2, 158.9, 159.6; *m/z* 286 (M^+, 47), 241 (100), 227 (25), 211 (98), 198 (12), 184 (8), 168 (10), 152 (8), 121 (18), 91 (6) (Found: C, 71.55; H, 6.36. $C_{17}H_{18}O_4$ requires: C, 71.31; H, 6.34%).

3.6.5. 3,4-Dihydro-7-methoxy-4-(2,4-dimethoxyphenyl)-2*H*-1-benzopyran-3-ol (46). PLC (eluant: Et_2O–light petroleum 8:2); needles from ethanol, mp 116–118°C; ν_{max} (KBr)/cm^{-1} 3515; δ_H (270 MHz) 2.58 (s, 1H, 3-OH), 3.77 (s, 3H, 4′-OMe),* 3.78 (s, 3H, 7-OMe),* 3.85 (s, 3H, 2′-OMe), 4.07 (m, 2H, 2-H), 4.24 (m, 1H, 3-H), 4.73 (d, *J*= 4.75 Hz, 1H, 4-H), 6.40-6.46 (m, 4H, 6-H, 8-H, 3′-H, 5′-H), 6.51–6.78 (m, 2H, 5-H, 6′-H); δ_C 39.5, 55.0, 55.5, 55.6, 65.9, 66.9, 98.6, 101.1, 104.5, 108.2, 114.7, 120.9, 131.4, 132.0, 155.7, 158.4, 159.5, 160.0; *m/z* 316 (M^+, 20), 298 (5), 271 (6), 257 (5), 241 (75), 198 (8), 149 (6), 121 (5), 28 (100) (Found: C, 68.08; H, 6.14. $C_{18}H_{20}O_5$ requires: C, 68.34; H, 6.37%).

3.6.6. 7-Methoxy-4-(2,4,6-trimethoxyphenyl)-2*H*-1-benzopyran-3(4*H*)-one (40). PLC (eluant: $CHCl_3$); needles from ethanol, mp 140–142°C; ν_{max} (KBr)/cm^{-1} 1718; δ_H (270 MHz) 3.69 (s, 6H, 2′-OMe, 6′-OMe), 3.76 (s, 3H, 4′-OMe),* 3.81 (s, 3H, 7-OMe),* 4.47 (d, *J*=16.55 Hz, 1H, 2-H), 4.58 (d, *J*=16.55 Hz, 1H, 2-H), 5.07 (s, 1H, 4-H), 6.16 (s, 2H, 3′-H, 5′-H), 6.48–6.58 (m, 2H, 6-H, 8-H), 6.64 (d, *J*= 8.6 Hz, 1H, 5-H); δ_C 43.7, 55.4, 55.8, 72.8, 91.2, 102.3, 108.0, 109.1, 118.0, 128.5, 154.7, 158.6, 159.2, 161.0, 208.5; *m/z* 344 (M^+, 42), 316 (18), 285 (16), 271 (13), 167 (12), 137 (13), 121 (15), 69 (10), 28 (100) (Found: C, 66.19; H, 5.65. $C_{19}H_{20}O_6$ requires: C, 66.27; H, 5.85%).

3.6.7. 3,4-Dihydro-6,7-dimethoxy-4-(4-methoxyphenyl)-2*H*-1-benzopyran-3-ol (48). PLC (eluant: Et_2O); plates from ethanol, mp 93–95°C; ν_{max} (KBr)/cm^{-1} 3493; δ_H (270 MHz) 1.69 (bs, 1H, 3-OH), 3.65 (s, 3H, 6-OMe), 3.80 (s, 3H, 4′-OMe), 3.84 (s, 3H, 7-OMe), 4.07 (m, 3H, 2-H, 3-H), 4.24 (d, *J*=4.3 Hz, 1H, 4-H), 6.33 (s, 1H, 8-H), 6.47 (s, 1H, 5-H), 6.88 (d, *J*=8.7 Hz, 2H, 3′-H, 5′-H), 7.12 (d, *J*= 8.7 Hz, 2H, 2′-H, 6′-H); δ_C 46.2, 55.2, 55.9, 56.3, 66.2, 67.3, 100.3, 112.9, 113.9, 114.0, 131.2, 131.6, 143.6, 148.4, 148.9, 158.9; *m/z* 316 (M^+, 65), 271 (100), 257 (40), 241 (79), 227 (10), 186 (10), 145 (18), 69 (25), 44 (45) (Found: C, 68.07; H, 6.51. $C_{18}H_{20}O_5$ requires: C, 68.34; H, 6.37%).

3.6.8. 3,4-Dihydro-6,7-dimethoxy-4-(2,4-dimethoxyphenyl)-2*H*-1-benzopyran-3-ol (49). PLC (eluant: Et_2O–light petroleum 8:2); needles from ethanol, mp 128–130°C; ν_{max} (KBr)/cm^{-1} 3527; δ_H (270 MHz) 2.23 (bs, 1H, 3-OH), 3.67 (s, 3H, 6-OMe), 3.79 (s, 3H, 4′-OMe), 3.85 (s, 3H, 7-OMe), 3.87 (s, 3H, 2′-OMe), 4.04 (m, 2H, 2-H), 4.25 (m, 1H, 3-H), 4.72 (d, *J*=4.95 Hz, 1H, 4-H), 6.34 (s, 1H, 8-H), 6.43 (dd, *J*=2.4, 8.45 Hz, 1H, 5′-H), 6.47 (s, 1H, 5-H), 6.52 (d, *J*=2.4 Hz, 1H, 3′-H), 6.78 (d, *J*=8.45 Hz, 1H, 6′-H); δ_C 39.7, 55.4, 55.6, 55.9, 56.4, 65.9, 66.7, 98.5, 100.4, 104.4, 112.8, 112.9, 120.6, 132.0, 143.6, 148.8, 148.9, 158.4, 159.9; *m/z* 346 (M^+, 32), 328 (4), 287 (6), 271 (100), 227 (9), 185 (7), 151 (16), 69 (16), 44 (21) (Found: C, 65.60; H, 6.55. $C_{19}H_{22}O_6$ requires: C, 65.88; H, 6.40%).

3.6.9. 6,7-Dimethoxy-4-(2,4,6-trimethoxyphenyl)-2*H*-1-benzopyran-3(4*H*)-one (41). PLC (eluant: $CHCl_3$); needles from ethanol, mp 112–114°C; ν_{max} (KBr)/cm^{-1} 1731; δ_H (270 MHz) 3.65 (s, 3H, 6-OMe), 3.71 (s, 6H, 2′-OMe, 6′-OMe), 3.82 (s, 3H, 4′-OMe),* 3.85 (s, 3H, 7-OMe),* 4.47 (d, *J*=16.7 Hz, 1H, 2-H), 4.55 (d, *J*=16.7 Hz, 1H, 2-H), 5.07 (s, 1H, 4-H), 6.17 (s, 2H, 3′-H, 5′-H), 6.28 (s, 1H, 8-H), 6.59 (s, 1H, 5-H); δ_C 43.8, 55.4, 55.8, 56.0, 56.4, 73.0, 91.3, 101.3, 107.9, 110.9, 116.8, 144.6, 147.8, 148.4, 158.9, 161.0, 208.6; *m/z* 374 (M^+, 100), 359 (22), 346 (20), 331 (18), 315 (19), 301 (25), 206 (13), 167 (12), 151 (18), 137 (12), 69 (20) (Found: C, 63.87; H, 6.10. $C_{20}H_{22}O_7$ requires: C, 64.16; H, 5.92%).

3.7. General procedure for the reduction of 4-aryl-2*H*-1-benzopyran-3(4*H*)-ones

Sodium borohydride (5 equiv.) was added to a stirred mixture of the 4-aryl-2*H*-1-benzopyran-3(4*H*)-one (1 equiv.) in THF (20 mL per 0.5 mmol of ketone) and water (4 mL per 0.5 mmol of ketone). The mixture was stirred at room temperature for 1 h and then acetone (10 mL) was added slowly. After addition of water (20 mL), the mixture was extracted with ethyl acetate (2×30 mL), washed with dilute hydrochloric acid (40 mL), brine (40 mL) and dried over anhydrous sodium sulfate. Removal of the solvent gave a solid or oil which was crystallised as indicated.

3.7.1. 3,4-Dihydro-4-(2,4,6-trimethoxyphenyl)-2*H*-1-benzopyran-3-ol (44). Needles from ethanol, mp 133–135°C; ν_{max} (KBr)/cm^{-1} 3506; δ_H (270 MHz) 3.35 (s, 3H, 4′-OMe), 3.81 (s, 6H, 2′-OMe, 6′-OMe), 3.98 (s, 1H, 3-OH), 4.15 (d, *J*=11.2 Hz, 2H, 2-H), 4.30 (m, 1H, 3-H), 4.99 (d, *J*=4.4 Hz, 1H, 4-H), 6.15 (s, 1H, 5′-H), 6.26 (s, 1H, 3′-H), 6.70–6.73 (m, 2H, 6-H, 8-H), 6.86 (d, *J*=7.9 Hz, 1H, 5-H), 7.04 (m, 1H, 7-H); δ_C 37.1, 56.0, 56.6, 67.8, 71.3, 92.3, 93.1, 109.7, 116.9, 121.0, 124.9, 127.3, 128.6, 154.7, 159.6, 159.9, 161.0; *m/z* 316 (M^+, 28), 298 (19), 267 (10), 241 (100), 226 (8), 168 (5), 91 (8), 44 (11) (Found: C, 68.10; H, 6.33. $C_{18}H_{20}O_5$ requires: C, 68.34; H, 6.37%).

3.7.2. 3,4-Dihydro-7-methoxy-4-(2,4,6-trimethoxyphenyl)-2*H*-1-benzopyran-3-ol (47). Needles from ethanol, mp 98–100°C; ν_{max} (KBr)/cm^{-1} 3505; δ_H (270 MHz) 3.42 (s, 3H, 4′-OMe),* 3.75 (s, 3H, 7-OMe),* 3.82 (s, 6H, 2′-OMe, 6′-OMe), 3.98 (s, 1H, 3-OH), 4.16 (d, *J*=11.2 Hz, 2H, 2-H), 4.31 (m, 1H, 3-H), 4.93 (d, *J*=4.6 Hz,1H, 4-H), 6.15 (s, 1H, 5′-H), 6.25 (s, 1H, 3′-H), 6.34 (dd, *J*=2.55, 8.5 Hz, 1H, 6-H), 6.45 (d, *J*=2.55 Hz, 1H, 8-H), 6.58 (d, *J*=8.5 Hz, 1H, 5-H); δ_C 36.0, 55.3, 55.4, 56.1, 67.2, 70.9, 91.7, 92.5, 101.0, 107.5, 109.2, 116.2, 128.6, 154.8, 158.6, 159.3, 159.7, 160.5; *m/z* 346 (M^+, 13), 328 (8), 271 (66), 256 (5), 227 (4), 151 (4), 121 (5), 28 (100) (Found: C, 65.93; H, 6.69. $C_{19}H_{22}O_6$ requires: C, 65.88; H, 6.40%).

3.7.3. 3,4-Dihydro-6,7-dimethoxy-4-(2,4,6-trimethoxyphenyl)-2*H*-1-benzopyran-3-ol (50). Needles from ethanol, mp 145–147°C; ν_{max} (KBr)/cm^{-1} 3497; δ_H (270 MHz) 3.42 (s, 3H, 6-OMe), 3.61 (s, 3H, 4′-OMe), 3.83 (s, 3H, 7-OMe), 3.84 (s, 3H, 6′-OMe), 3.85 (s, 3H, 2′-OMe), 3.89 (s, 1H, 3-OH), 4.12 (d, *J*=10.1 Hz, 2H, 2-H), 4.31 (m, 1H, 3-H), 4.93 (d, *J*=4.85 Hz, 1H, 4-H), 6.16 (s, 1H, 5′-H), 6.21 (s, 1H, 3′-H), 6.27 (s, 1H, 8-H), 6.48 (s, 1H, 5-H); δ_C 36.1, 55.3, 55.4, 55.8, 56.0, 56.7, 67.2, 70.7, 91.6, 92.3, 100.5, 108.8, 111.2, 114.9, 143.2, 147.9, 159.3, 159.6, 160.5; *m/z* 376 (M^+, 34), 358 (6), 301 (100), 285 (7), 257 (8), 167 (7), 121 (5), 69 (13), 44 (19)

(Found: C, 63.61; H, 6.61. $C_{20}H_{24}O_7$ requires: C, 63.82; H, 6.43%).

3.8. General procedure for the dehydration of 4-aryl-3,4-dihydro-2*H*-1-benzopyran-3-ols

A cooled (0–5°C) solution of the 4-aryl-3,4-dihydro-2*H*-1-benzopyran-3-ol (1 equiv.) in dry pyridine (7.5 mL per 1 mmol of alcohol) was treated, dropwise, with phosphorus oxychloride (26 equiv.). The mixture was stirred at 0–5°C for 2 h and then at room temperature for 24 h. Water (15 mL) was carefully added and the solution was extracted with ether (2×15 mL), washed with 10% hydrochloric acid (30 mL), water (30 mL), brine (30 mL) and dried over magnesium sulfate. After distillation of the solvent under reduced pressure, the residue was purified by chromatography on silica using the indicated solvent system.

3.8.1. 4-(4-Methoxyphenyl)-2*H*-1-benzopyran (51). PLC (eluant: Et_2O–light petroleum 2:3); pale yellow plates from ethanol, mp 89–92°C (lit.,[30] mp 92°C); ν_{max} (KBr)/cm^{-1} 1635; δ_H (270 MHz) 3.82 (s, 3H, 4′-OCH3), 4.81 (d, *J*=4.03 Hz, 2H, 2-H), 5.74 (t, *J*=4.03 Hz, 1H, 3-H), 6.84-6.93 (m, 4H, 6-H, 8-H, 3′-H, 5′-H), 7.02 (dd, *J*=1.65, 7.69 Hz, 1H, 5-H), 7.13 (m, 1H, 7-H), 7.26 (dd, *J*=2.19, 6.59 Hz, 2H, 2′-H, 6′-H); δ_C 55.4, 65.3, 113.8, 116.3, 119.3, 121.2, 124.0, 125.9, 129.2, 129.8, 130.7, 136.7, 154.9, 159.3; *m/z* 238 (M^+, 82), 237 (100), 223 (30), 207 (33), 194 (22), 165 (38), 152 (20), 139 (22), 131 (35), 119 (22), 89 (21), 28 (23).

3.8.2. 4-(2,4-Dimethoxyphenyl)-2*H*-1-benzopyran (52). PLC (eluant: Et_2O–light petroleum 1:1); plates from ethanol, mp 124–126°C; ν_{max} (KBr)/cm^{-1} 1643; δ_H (270 MHz) 3.61 (s, 3H, 2′-OMe), 3.75 (s, 3H, 4′-OMe), 4.80 (d, *J*=3.65 Hz, 2H, 2-H), 5.63 (t, *J*=3.65 Hz, 1H, 3-H), 6.41–6.45 (m, 2H, 3′-H, 5′-H), 6.63-6.76 (m, 3H, 5-H, 6-H, 8-H), 6.96–7.15 (m, 2H, 7-H, 6′-H); δ_C 55.4, 55.5, 65.6, 98.8, 104.4, 115.9, 120.0, 121.0, 121.1, 124.0, 125.8, 128.8, 131.4, 133.9, 154.0, 158.3, 160.8; *m/z* 268 (M^+, 44), 267 (46), 253 (14), 237 (73), 221 (12), 152 (12), 127 (23), 28 (100) (Found: C, 75.78; H, 6.06. $C_{17}H_{16}O_3$ requires: C, 76.10; H, 6.01%).

3.8.3. 4-(2,4,6-Trimethoxyphenyl)-2*H*-1-benzopyran (53). PLC (eluant: $CHCl_3$); needles from ethanol, mp 163–166°C; ν_{max} (KBr)/cm^{-1} 1652; δ_H (270 MHz) 3.69 (s, 6H, 2′-OMe, 6′-OMe), 3.85 (s, 3H, 4′-OMe), 4.94 (d, *J*=3.65 Hz, 2H, 2-H), 5.66 (t, *J*=3.65 Hz, 1H, 3-H), 6.19 (s, 2H, 3′-H, 5′-H), 6.58-6.84 (m, 3H, 5-H, 6-H, 8-H), 7.25 (m, 1H, 7-H); δ_C 55.4, 55.9, 65.7, 90.8, 108.9, 115.7, 120.9, 122.5, 124.1, 124.9, 128.4, 128.8, 154.2, 159.0, 160.9; *m/z* 298 (M^+, 100), 297 (26), 283 (28), 267 (96), 252 (18), 181 (10), 152 (12), 139 (12), 131 (28), 91 (11) (Found: C, 72.43; H, 6.17. $C_{18}H_{18}O_4$ requires: C, 72.47; H, 6.08%).

3.8.4. 7-Methoxy-4-(4-methoxyphenyl)-2*H*-1-benzopyran (54). PLC (eluant: Et_2O–light petroleum 2:3); amorphous powder from ethanol, mp 101–103°C (lit.,[30] mp 105°C); ν_{max} (KBr)/cm^{-1} 1636; δ_H (270 MHz) 3.78 (s, 3H, 4′-OCH3),* 3.83 (s, 3H, 7-OCH3),* 4.79 (d, *J*=4.03 Hz, 2H, 2-H), 5.60 (t, *J*=4.03 Hz, 1H, 3-H), 6.39–6.48 (m, 2H, 3′-H, 5′-H), 6.89-6.96 (m, 3H, 5-H, 6-H, 8-H), 7.26 (d, *J*=8.79 Hz, 2H, 2′-H, 6′-H); δ_C 55.3, 55.4, 65.6, 102.0, 106.9, 113.8, 116.3, 117.2, 126.8, 130.0, 130.9, 136.5, 156.2, 159.3, 160.5; *m/z* 268 (M^+, 38), 267 (34), 253 (15), 241 (21), 237 (10), 151 (22), 135 (22), 83 (30), 28 (100).

3.8.5. 7-Methoxy-4-(2,4-dimethoxyphenyl)-2*H*-1-benzopyran (55). PLC (eluant: Et_2O–light petroleum 1:1); yellow oil; ν_{max} (CH_2Cl_2)/cm^{-1} 1645; δ_H (270 MHz) 3.70 (s, 3H, 2′-OMe), 3.75 (s, 3H, 4′-OMe),* 3.83 (s, 3H, 7-OMe),* 4.87 (d, *J*=3.84 Hz, 2H, 2-H), 5.57 (t, *J*=3.84 Hz, 1H, 3-H), 6.33 (dd, *J*=2.56, 8.61 Hz, 1H, 5′-H), 6.42 (d, *J*= 2.56 Hz, 1H, 3′-H), 6.49–6.52 (m, 2H, 6-H, 8-H), 6.63 (d, *J*=8.61 Hz, 1H, 5-H), 7.08 (d, *J*=8.61 Hz, 1H, 6′-H); δ_C 55.3, 55.4, 55.5, 65.8, 98.8, 101.5, 103.9, 106.7, 117.2, 118.0, 120.1, 125.5, 131.1, 133.7, 155.2, 158.2, 160.2, 160.7; *m/z* 298 (M^+, 36), 297 (33), 283 (8), 267 (18), 241 (100), 198 (18), 161 (24), 121 (12), 43 (22).

3.8.6. 7-Methoxy-4-(2,4,6-trimethoxyphenyl)-2*H*-1-benzopyran (56). PLC (eluant: $CHCl_3$); needles from ethanol, mp 179–181°C; ν_{max} (KBr)/cm^{-1} 1652; δ_H (270 MHz) 3.69 (s, 6H, 2′-OMe, 6′-OMe), 3.74 (s, 3H, 4′-OMe),* 3.85 (s, 3H, 7-OMe),* 4.92 (d, *J*=3.65 Hz, 2H, 2-H), 5.52 (t, *J*= 3.65 Hz, 1H, 3-H), 6.19 (s, 2H, 3′-H, 5′-H), 6.30 (dd, *J*=2.55, 8.55 Hz, 1H, 6-H), 6.41 (d, *J*=2.55 Hz, 1H, 8-H), 6.51 (d, *J*=8.55 Hz, 1H, 5-H); δ_C 55.3, 55.4, 56.0, 66.0, 90.9, 101.6, 106.7, 108.3, 117.4, 119.5, 125.8, 128.7, 155.4, 159.1, 160.1, 160.9; *m/z* 328 (M^+, 100), 327 (92), 313 (18), 297 (86), 281 (22), 254 (8), 161 (18), 139 (12), 69 (32) (Found: C, 69.27; H, 6.29. $C_{19}H_{20}O_5$ requires: C, 69.50; H, 6.14%).

3.8.7. 6,7-Dimethoxy-4-(4-methoxyphenyl)-2*H*-1-benzopyran (57). PLC (eluant: Et_2O–light petroleum 2:3); yellow oil; ν_{max} (CH_2Cl_2)/cm^{-1} 1638; δ_H (270 MHz) 3.66 (s, 3H, 6-OMe), 3.79 (s, 3H, 4′-OMe),* 3.84 (s, 3H, 7-OMe),* 4.76 (d, *J*=4 Hz, 2H, 2-H), 5.66 (t, *J*=4 Hz, 1H, 3-H), 6.32 (s, 1H, 8-H), 6.43 (s, 1H, 5-H), 6.83 (d, *J*=8.8 Hz, 2H, 3′-H, 5′-H), 7.05 (d, *J*=8.8 Hz, 2H, 2′-H, 6′-H); δ_C 55.2, 55.8, 56.3, 63.6, 100.5, 113.0, 113.9, 114.0, 115.0, 129.6, 135.7, 138.0, 143.1, 148.7, 149.1, 158.1; *m/z* 298 (M^+, 100), 297 (95), 283 (32), 267 (78), 251 (21), 164 (22), 127 (20), 69 (21), 28 (18).

3.8.8. 6,7-Dimethoxy-4-(2,4-dimethoxyphenyl)-2*H*-1-benzopyran (58). PLC (eluant: Et_2O–light petroleum 1:1); amorphous powder from ethanol–water, mp 134–137°C; ν_{max} (KBr)/cm^{-1} 1644; δ_H (270 MHz) 3.64 (s, 3H, 6-OMe), 3.71 (s, 3H, 2′-OMe), 3.85 (s, 6H, 7-OMe, 4′-OMe), 4.82 (d, *J*=4 Hz, 2H, 2-H), 5.62 (t, *J*=4 Hz, 1H, 3-H), 6.30 (s, 1H, 8-H), 6.48 (s, 1H, 5-H), 6.51-6.53 (m, 2H, 3′-H, 5′-H), 7.12 (d, *J*=88 Hz, 1H, 6′-H); δ_C 55.4, 55.5, 56.0, 56.6, 65.6, 98.8, 100.5, 104.4, 109.7, 116.1, 118.3, 120.0, 130.0, 131.5, 143.2, 148.7, 149.5, 158.2, 160.8; *m/z* 328 (M^+, 89), 327 (46), 313 (28), 297 (100), 281 (8), 266 (15), 164 (19), 156 (22), 127 (18), 115 (18), 69 (23) (Found: C, 69.04; H, 6.38. $C_{19}H_{20}O_5$ requires: C, 69.50; H, 6.14%).

3.8.9. 6,7-Dimethoxy-4-(2,4,6-trimethoxyphenyl)-2*H*-1-benzopyran (59). PLC (eluant: $CHCl_3$); yellow oil; ν_{max} (CH_2Cl_2)/cm^{-1} 1653; δ_H (270 MHz) 3.62 (s, 3H, 6-OMe), 3.71 (s, 6H, 2′-OMe, 6′-OMe), 3.83 (s, 3H, 4′-OMe),* 3.86 (s, 3H, 7-OMe),* 4.87 (d, *J*=3.85 Hz, 2H, 2-H), 5.57 (t, *J*=3.85 Hz, 1H, 3-H), 6.2 (s, 3H, 8-H, 3′-H, 5′-H), 6.47 (s, 1H, 5-H); δ_C 55.4, 55.9, 56.0, 56.1, 65.8, 90.9, 100.5, 108.1,

108.7, 116.4, 119.7, 128.8, 143.2, 148.8, 149.3, 159.1, 161.0; *m/z* 358 (M^+, 52), 357 (45), 343 (31), 327 (100), 312 (20), 221 (18), 164 (18), 127 (18), 69 (19), 28 (30).

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