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Aryllead Mediated Synthesis of Isoflavanone and Isoflavone Derivatives

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Dedicated to Professor Sir Derek Barton on the occasion of his 75th birthday

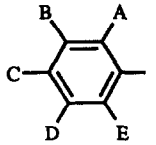
Abstract: The reaction of aryllead (IV) triacetates with 3-(phenylthio)-chroman-4-one and 2-*p*-methoxyphenyl-3-(phenylthio)-chroman-4-one derivatives was carried out in chloroform in presence of pyridine to afford moderate to quantitative yields of the corresponding hindered 3-aryl-3-phenylthiochroman-4-one derivatives. Removal of the phenylthio group by oxidation with dimethyldioxirane led to the corresponding isoflavones and 2-*p*-methoxyphenylisoflavones, and by reduction with a large excess of nickel boride to the isoflavanones and 2-(4'-anisyl)-isoflavanones respectively. In the 2-*p*-methoxyphenyl series the nickel boride reduction of the compounds bearing *ortho*-substituted 3-aryl groups gave the chalcones which were recyclised under basic catalysis.

Isoflavonoids, a group of compounds mostly found in the *Leguminoseae* family, have important phytoalexin properties.[1] They also are important biogenetic intermediates in the biosynthesis of different benzopyran derived heterocyclic systems, some of them showing biological activities such as, *e.g.* the insecticidal rotenoids. The isoflavonoid skeleton is also found in a number of biologically active biflavonoids presenting a 3-8' bond between two flavone ring systems. Two major approaches to the synthesis of the isoflavonoid rings are known : cyclisation of the pyran ring on a preformed complete skeleton or coupling of the two preformed ring systems. Among the latter, the organobismuth mediated ligand coupling route to isoflavonoids is high yielding but limited by the very narrow range of substituted arylbismuth derivatives.[2,3] We would like now to report a general selective synthesis of isoflavanones and isoflavones from a common intermediate prepared by arylation of 3-phenylthiochroman-4-one derivatives with aryllead (IV) triacetates.[4]

The arylthio group can be easily introduced on a ketonic substrate by a variety of methods,[5] among them either the reaction of a ketone enolate on diaryldisulfides or the reaction of an α-haloketone or α-alkyl- or aryl-sulfonyloxyketone on sodium arylthiolate. The latter reaction enables the activation of base-sensitive ketones such as chroman-4-ones. Ketones **7** (R^1=H or CH_3O, R^2=H) were prepared by reaction of sodium phenylthiolate with the corresponding α-bromoketones[6] and ketone **7** (R^1=H, R^2=2) by reaction on 2-*p*-methoxyphenyl-3-mesyloxychroman-4-one.[7] Although arylsulfides are easily oxidised by lead tetraacetate[8], the reaction of these α-phenylthioketones with variously substituted electron-rich aryllead triacetates

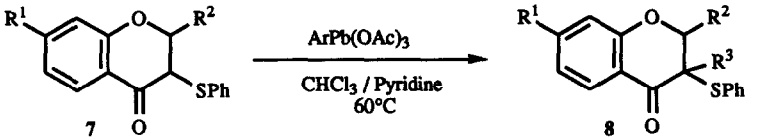
[$R^3Pb(OAc)_3$ / pyridine / anhydrous chloroform / 60°C] afforded moderate to quantitative yields of the sterically hindered α-aryl β-ketosulfides in the two series (**7**, R^2=H or R^2=2). For example, arylation of the mixture of 2,3-*cis*- and 2,3-*trans*-2-*p*-methoxyphenyl-3-phenylthiochroman-4-one[7] **7** (R^1=H, R^2=2) with 2,4,6-trimethoxyphenyllead triacetate led to the corresponding 2,3-diaryl derivative **8** (R^1=H, R^2=2, R^3=4) in 99% yield. The 270MHz ^{1}H-NMR and ^{13}C-NMR spectra of this product indicated the presence of a single isomer. In the chromanone series (**7**, R^2=H), a small percentage of α-acetoxylated chromanone was also observed with the more sterically hindered aryllead reagents.

Table 1 : Structure of the Aryl Groups R^2 and R^3 :



Ar	A	B	C	D	E
1	H	H	H	H	H
2	H	H	OCH_3	H	H
3	OCH_3	H	OCH_3	H	H
4	OCH_3	H	OCH_3	H	OCH_3
5	H	H	CH_3	H	H
6	H	OCH_2O		H	H

Table 2 : Arylation of α-Phenylthioketones with Aryllead Triacetates

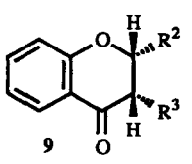


7		$ArPb(OAc)_3$	R'n Time	% of Products	
R^1	R^2	Ar	(h)	8, R^3=Ar	8, R^3=OAc
H	H	1	8	93	-
H	H	2	8	69	-
H	H	3	8	60	5
H	H	4	8	59	8
CH_3O	H	1	8	58	-
CH_3O	H	2	8	85	-
CH_3O	H	3	8	63	5
CH_3O	H	4	8	50	10
H	2	1	2	82	-
H	2	2	2	90	-
H	2	3	1	93	-
H	2	4	1	99	-
H	2	5	3	90	-
H	2	6	3	97	-

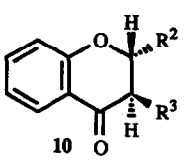
The interest in the activation of a carbonyl group by an α-arylthio substituent lies in the derivatives which can be obtained. Reduction leads to the ketone, whereas oxidation to the sulfoxide followed by thermal extrusion leads to α,β-unsaturated ketones. Unfortunately, all our attempts of reduction with classical reagents met with failure. Eventually, we discovered that even the more sterically hindered 2-*p*-methoxyphenyl-3-aryl-3-phenylthiochroman-4-ones could be mildly deprotected by using a large excess of nickel boride[9] ($NiCl_2$, 24 eq; $NaBH_4$, 20 eq; EtOH, H_2O, reflux). Although 14 equivalents are sufficient for complete sulfide removal,

best yields were obtained in both series (**8**, R^2=H or R^2=2) with 20 equivalents of nickel boride (Table 3). In the 2-substituted series (**8**, R^2=2), when the aryl group R^3 is not substituted on the *ortho* positions, the 2,3-*cis*-2-*p*-methoxyphenylisoflavanone was obtained either as only the *cis* isomer **9** or as a *ca.* 4/1 mixture of *cis*/*trans* isomers **9** and **10**. But when these *ortho* positions are substituted as in the 2-*p*-methoxyphenyl-3-phenylthioisoflavanones **8** (R^2=2, R^3=3 and R^2=2, R^3=4), that deprotection procedure led to the chalcones **11**, which were easily recyclised to the 2,3-*trans*-2-anisylisoflavanones **10**, using 1.5% aqueous sodium hydroxide in ethanol[10].

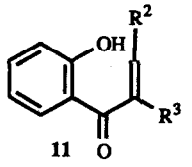
Table 3 : Desulfurisation of 3-Aryl-3-phenylthioflavanones **8** (R^1 = H) with Nickel Boride[a,b]



9



10

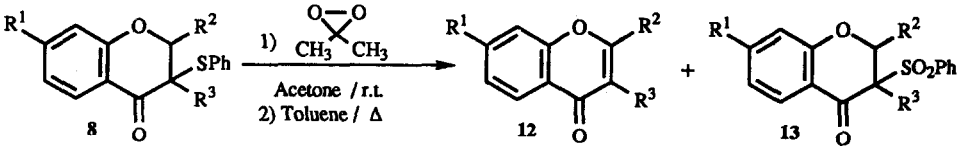


11

R^2	R^3	Rn time (h)	**9**	**10**[b]	**11**
H	2	6	69		
H	3	6	98		
H	4	8	71		
2	1	24	74		
2	2	18	72	15	
2	3	9	-	- (38)	62
2	4	6	-	- (44)	70
2	5	3	58	trace	
2	6	16	70	17	

a - **8** was added to a mixture of $NiCl_2$, $6H_2O$ (24 equiv.), $NaBH_4$ (20 equiv.), ethanol and water and stirred under reflux for the time indicated to give **10** and **11**.
b - The yields reported in brackets are for the cyclisation of **11** , which were stirred in a mixture of 1.5% aqueous sodium hydroxide in ethanol for 48h at room temperature.

Table 4 : Synthesis of Isoflavone Derivatives by Oxidation of **8** with Dimethyldioxirane (DMDO) and Thermal Elimination.



R^1	R^2	R^3	DMDO (eq)	**12** (%)	**13** (%)
H	H	1	1.2	38	35
H	H	2	1	65	-
H	H	2	2	26	34
H	H	3	1	85	-
H	H	4	2	82	-
CH_3O	H	1	1	52	-
CH_3O	H	2	1.2	67	15
CH_3O	H	2	1	33	-
H	2	4	2	61	-
H	2	6	2	41	-

On the other hand, oxidation of the sterically hindered 3-aryl 3-phenylthiochroman-4-ones **8** (R^2=H or 2) with classical oxidants ($NaIO_4$, MCPBA or H_2O_2) gave very poor yields of the sulfoxides. However, 3-phenylthio compounds were smoothly oxidised by dimethyldioxirane[11] (DMDO) in acetone at room temperature (Table 4). In the case of the 3-phenyl derivative, the sulfone was obtained with 1.2 equivalents of DMDO, but oxidation of **8** (R^2=H, R^3=2) with 2 equivalents of dimethyldioxirane led to 34% of the sulfone. The intermediate sulfoxides were not isolated but led to the corresponding isoflavones by refluxing in toluene. In the case of the very hindered 3-(2',4',6'-trimethoxyphenyl) derivative, only the sulfoxide was obtained, even with 2 equivalents of DMDO. Thermal elimination in toluene under reflux afforded the isoflavone in 83% yield from the sulfide. In the 2-anisylisoflavanone series, oxidation of **8** (R^2=2) with dimethyldioxirane led to the 2,3-diarylchromone derivatives, the intermediate sulfoxides remaining undetected.

This route using arylation of a common α-phenylthiocarbonyl intermediate with aryllead reagents offers a direct, efficient and selective entry into the synthesis of isoflavanones and isoflavones and their derivatives. Moreover, for the synthesis of the naturally occurring isoflavonoids, this method is more general than the recently described phenylations of 3-hydroxymethylene- and 3-ethyloxalyl-chroman-4-one with various pentavalent triphenylbismuth derivatives[2] or of 3-phenylsulfonylchroman-4-ones with triphenylbismuth carbonate[3]. These latter methods suffer from the limited range of available polyalkoxyphenylbismuth derivatives as opposed to the wide range of easily accessible polyalkoxyphenyllead derivatives.

Experimental

Melting points were determined on a Reichert-Jung Thermovar apparatus and are uncorrected. 60 MHz ^1H NMR spectra were recorded on a Jeol JNM-PMX-60 spectrometer. 270 MHz ^1H NMR and 67.8 MHz ^{13}C NMR spectra were recorded on a Jeol JNM-GX 270 FT NMR spectrometer. Tetramethylsilane was used as the internal standard in all NMR spectra recorded. J values are given in Herz. Infra-red spectra were recorded on a Mattson Galaxy Series FT-IR 3000. Ultra-violet spectra were recorded on a Philips PU 8720 UV/VIS scanning spectrophotometer. 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 were performed using Merck Kieselgel 60 (Art. 7734). Merck Kieselgel $PF_{254+336}$ was used for preparative layer chromatography. All solvents were purified and dried by standard techniques. Ether refers to diethyl ether. The aryllead reagents were prepared as previously reported.[12]

3-Phenylthio-2,3-dihydro-(4H)-benzopyran-4-one : 3-Bromo-2,3-dihydro-(*4H*)-benzopyran-4-one[6b] (3g) was treated with sodium thiophenolate [from thiophenol (1.48g) and sodium hydride (0.39g of an 80% suspension in oil)] in THF (50cm^3) under argon for 40 min. Work-up followed by flash column chromatography [eluant: hexane–ethyl acetate–methanol, 5:1:0.1] yielded 3-phenylthio-2,3-dihydro-(*4H*)-benzopyran-4-one (1.69g, 64%) as plates, m.p. 51-54°C (ethanol) (Found: C, 70.1; H, 4.84; S, 12.4. $C_{15}H_{12}O_2S$ requires: C, 70.31; H, 4.69; S, 12.5%); ν_{max}(KBr)/cm^{-1} 1688, 1603, 1323, 1306; λ_{max} (CH_3CN)/nm 323(4267), 253(13400); δ_H 7.94-6.94(9H, m, Ar-H), 4.64(1H, dd, J 11.91 and 3.85, $H_{2A \text{ or } 2B}$), 4.54(1H, dd, J 11.9 and 6.41, $H_{2B \text{ or } 2A}$), 4.05(1H, dd, J 6.41 and 3.85, H-3); *m/z* 256(M^+), 147, 136, 135, 121, 109.

3-Bromo-7-methoxy-2,3-dihydro-(4H)-benzopyran-4-one : A mixture of 7-methoxy-2,3-dihydro-(*4H*)-benzopyran-4-one[13] (0.4g) and copper(II) bromide (0.84g) in chloroform (2cm^3) and ethyl acetate (2cm^3) was vigorously stirred under reflux for 3h. Filtration, evaporation of the solvents and column chromatography [eluant: dichloromethane–ethyl acetate, 10:1] gave 3-bromo-7-methoxy-2,3-dihydro-(*4H*)-benzopyran-4-one as a solid (0.43g, 74%), m.p. 93-97°C, [petroleum ether] (Found: C, 46.49; H, 3.51. $C_{10}H_9BrO_3$ requires: C, 46.71; H, 3.5%); δ_H 7.93(1H, d, J 9.8, H-5), 6.69(1H, dd, J 9.8 and 2.88, H-6), 6.5(1H, d, J 2.88, H-8), 4.64(3H, s, OCH_2, H-3), 3.88(3H, s, OCH_3); *m/z* 256(M^+), 177, 150, 122, 107, 79.

7-Methoxy-3-phenylthio-2,3-dihydro-(4H)-benzopyran-4-one : Prepared as above, (62%); white plates, m.p. 70-72°C (Found: C, 67.21; H, 5.12; S, 11.16. $C_{16}H_{14}O_3S$ requires: C, 67.13; H, 4.9; S, 11.19%); ν_{max}(KBr)/cm^{-1} 1674, 1616, 1260; λ_{max}(CH_3CN)/nm 314(8597), 274(14333); δ_H 7.85(1H, d, J 8.8, H-5), 7.54-7.5(2H, m, H-3', H-5'),

7.33-7.26(3H, m, H-2', H-4', H-6'), 6.61(1H, dd, J 8.8 and 2.38, H-6), 6.4(1H, d, J 2.38, H-8), 4.63-4.46(2H, ddd, J 11.72, 6.41 and 3.84, OCH_2), 4.01(1H, dd, J 6.41 and 4.03, H-3); δ_C 186.87(C-4), 166.17(C-7), 162.83(C-9), 133.17(C-3', C-5'), 132.05(C-1'), 129.6(C-2', C-6'), 129.06(C-5), 128.22(C-4'), 113.76(C-10), 110.52(C-6), 100.57(C-8), 70.66(C-2), 51.28(C-3), 45.3(OCH_3); *m/z* 286(M^+), 177, 150, 136, 135, 122, 107.

Arylation of 3-Phenylthio-2,3-dihydro-*(4H)*-benzopyran-4-one Derivatives.

General Procedure : A mixture of the 3-phenylthiochroman-4-one derivative (1eq), pyridine (3.3eq) and aryllead (IV) triacetate (1.1eq) in chloroform ($1cm^3$ per 0.6mmol of substrate) was stirred at 60°C for 1-8 h (Table 2). The reaction mixture was diluted with chloroform ($100cm^3$) and washed with 6% H_2SO_4 aqueous solution ($100cm^3$). The organic layer was filtered through Celite, dried (Na_2SO_4) and concentrated. The residue was purified by chromatography with the indicated solvent system (CC=column chromatography, PLC=plate layer chromatography).

3-Phenyl-3-phenylthio-2,3-dihydro-(4H)-benzopyran-4-one : [eluant: ether–hexane, 3:1], (93%); needles, m.p. 129-131°C (ethanol) (Found: C, 75.61; H, 4.74; S, 9.82. $C_{21}H_{16}O_2S$ requires: C, 75.9; H, 4.82; S, 9.64%); ν_{max}(KBr)/cm^{-1} 1682, 1603, 1304; λ_{max}(CH_3CN)/nm 325(3726), 259(11770), 226(21762); δ_H 7.96(1H, dd, J 7.97 and 1.74, H-5), 7.53-7.49(2H, m, H-3", H-5"), 7.44-7.37(1H, m, H-7), 7.33-7.13(8H, m, Ar-H), 7.02-6.96(1H, m, H-6), 6.86(1H, d, J 8.43, H-8), 4.85(1H, d, J 12.28, $H_{2A\ or\ 2B}$), 4.64(1H, d, J 12.28, $H_{2B\ or\ 2A}$); δ_C 188.77(C-4), 160.44(C-9), 136.68(C-3", C-5"), 135.94(C-7), 134.34(C-1"), 129.38(C-5), 128.63 (C-2", C-6"), 128.49(C-3', C-5'), 128.41(C-4'), 128.36(C-4"), 128.01(C-2', C-6'), 121.69(C-6), 120.09(C-10), 117.53(C-8), 72.68(C-2), 61.22(C-3), (C-1' was not observed); *m/z* 332(M^+), 223, 212, 121, 103, 92, 77.

3-(4-Methoxyphenyl)-3-phenylthio-2,3-dihydro-(4H)-benzopyran-4-one : [eluant: hexane–ethyl acetate, 2:1], (69%); yellow solid, m.p. 158-162°C; ν_{max}(KBr)/cm^{-1} 1672, 1636, 1601, 1304, 1287; λ_{max}(CH_3CN)/nm 331(6171), 256(17433); δ_H 7.95(1H, dd, J 8.06 and 1.47, H-5), 7.53-7.14(8H, m, Ar-H), 7.05-6.83(1H, m, H-6), 6.83-6.74(3H, m, J 6.96 and 2.2, H-8, H-3', H-5'), 4.82(1H, d, J 12.46, $H_{2A\ or\ 2B}$), 4.62(1H, d, J 12.45, $H_{2B\ or\ 2A}$), 3.76(3H, s, OCH_3); δ_C 188.88(C-4), 160.41(C-9), 159.59(C-4'), 136.68(C-3", C-5"), 136.15(C-1"), 135.84(C-7), 129.31(C-2", C-6"), 129.2(C-5), 128.62(C-2', C-6'), 128.38(C-4"), 126.13(C-1'), 121.64(C-6), 120.11(C-10), 117.48(C-8), 113.91(C-3', C-5'), 72.79(C-2), 60.84(C-3), 55.24(OCH_3); *m/z* 362(M^+), 253, 121, 109, 92.

3-(2,4-Dimethoxyphenyl)-3-phenylthio-2,3-dihydro-(4H)-benzopyran-4-one : [eluant: hexane–ether, 2:1], (60%); needles, m.p. 139-141°C (methanol) (Found: C, 70.4; H, 5.28; S, 7.98. $C_{23}H_{20}O_4S$ requires: C, 70.41; H, 5.1; S, 8.16%); ν_{max}(KBr)/cm^{-1} 1684, 1605, 1306, 1289; λ_{max}(CH_3CN)/nm 320(4750), 277(6395); δ_H 7.96(1H, d, J 8.61, H-6'), 7.94(1H, dd, J 7.87 and 1.65, H-5), 7.49-7.43(1H, m, H-7), 7.34-7.3(2H, m, H-3", H-5"), 7.26-7.11(3H, m, H-2", H-4", H-6"), 7.06-7(1H, m, J 8.24, 7.88 and 1.1, H-6), 6.97-6.93(1H, distorted dd, J 8.25, H-8), 6.57(1H, dd, J 8.61 and 2.38, H-5'), 6.47(1H, d, J 2.56, H-3'), 4.91(1H, d, J 12.27, $H_{2A\ or\ 2B}$), 4.24(1H, d, J 12.09, $H_{2B\ or\ 2A}$), 3.81(3H, s, 4'-OCH_3), 3.63(3H, s, 2'-OCH_3); δ_C 185.73(C-4), 161.22(C-9), 159.73(C-4'), 157.94(C-2'), 135.13 (C-3", C-5"), 134.99(C-7), 131.97(C-5), 130.55(C-1"), 128.52(C-6'), 128.38(C-2", C-6"), 128.28(C-4"), 121.53(C-6), 120.49(C-10), 117.45(C-8), 116.55(C-1'), 104.81(C-5'), 100.16(C-3'), 72.6(C-2), 62.86(C-3), 55.58(2'-OCH_3), 55.41(4'-OCH_3); *m/z* 392(M^+), 283, 163, 121, 109.

3-Phenylthio-3-(2,4,6-trimethoxyphenyl)-2,3-dihydro-(4H)-benzopyran-4-one : [eluant: hexane–ether–methanol, 3:1:0.1], (59%); needles, m.p. 138-140°C (ethanol) (Found: C, 68.37; H, 5.46; S, 7.85. $C_{24}H_{22}O_5S$ requires: C, 68.25; H, 5.21; S, 7.58%); ν_{max}(KBr)/cm^{-1} 1713, 1607, 1290; λ_{max}(CH_3CN)/nm 308(3263), 244(18412); δ_H 7.73(1H, dd, J 7.7 and 1.74, H-5), 7.4-7.37(2H, m, H-3", H-5"), 7.3-7.11(4H, m, H-7, H-2", H-4", H-6"), 6.94-6.88(1H, m, J 8.24 and 7.7, H-6), 6.76-6.72(1H, m, H-8), 5.94(2H, s, H-3', H-5'), 5.54(1H, d, J 11.72, $H_{2A\ or\ 2B}$), 4.31(1H, d, J 11.72, $H_{2B\ or\ 2A}$), 3.74(3H, s, 4'-OCH_3), 3.48(6H, s, 2'-OCH_3, 6'-OCH_3); δ_C 191.63(C-4), 161.07 (C-9), 160.16(C-4'), 160(C-2', C-6'), 137.46(C-3", C-5"), 133.87(C-7), 131(C-1"), 128.57(C-5), 127.97 (C-2", C-6"), 127.68(C-4"), 122.19(C-10), 120.9(C-6), 116.55(C-8), 104.71(C-1'), 91.74(C-3', C-5'), 73.99(C-2), 61.47(C-3), 55.51(2'-OCH_3, 6'-OCH_3), 55.17(4'-OCH_3); *m/z* 422(M^+), 313, 193, 121, 109.

7-Methoxy-3-phenyl-3-phenylthio-2,3-dihydro-(4H)-benzopyran-4-one : [eluant: hexane–ethyl acetate, 2:1], (58%); needles, m.p. 118-121°C (methanol-benzene) (Found: C, 73.16; H, 5.09; S, 8.6. $C_{22}H_{18}O_3S$ requires: C, 72.93; H, 4.97; S, 8.84%); ν_{max}(KBr)/cm^{-1} 1678, 1613, 1254; λ_{max}(CH_3CN)/nm 314(7831), 278(14392); δ_H 7.88(1H, d, J 8.97, H-5), 7.53-7.12(10H, m, Ar-H), 6.53(1H, dd, J 8.79 and 2.38, H-6), 6.28(1H, d, J 2.38, H-8), 4.83(1H, d, J 12.09, $H_{2A\ or\ 2B}$), 4.63(1H, d, J 12.27, $H_{2B\ or\ 2A}$), 3.75(3H, s, 7-OCH_3); δ_C 187.71(C-4), 165.99(C-7), 162.48(C-9), 136.67(C-3", C-5"), 134.75(C-1"), 130.01(C-5), 129.56(C-1'), 129.28(C-4"), 128.58(C-2", C-6"), 128.41(C-2', C-6'), 128.28(C-4'), 127.89(C-3', C-5'), 113.81(C-10), 110.44(C-6), 100.27(C-8), 72.95(C-2), 60.8 (C-3), 55.58(7-OCH_3); *m/z* 362(M^+), 253, 212, 151, 109, 103.

7-Methoxy-3-(4-methoxyphenyl)-3-phenylthio-2,3-dihydro-(4H)-benzopyran-4-one : [eluant: hexane–ethyl acetate–methanol, 5:1:0.2], (85%); needles, m.p. 97-99°C (methanol) (Found: C, 70.63; H, 5.3; S, 8.1. $C_{23}H_{20}O_4S$ requires: C, 70.41; H, 5.1; S, 8.16%); ν_{max}(KBr)/cm^{-1} 1687, 1674, 1611, 1250; λ_{max}(CH_3CN)/nm 314(9359),

277(17330), 232(23613); δ_H 7.88(1H, d, J 8.79, H-5), 7.41-7.15(5H, m, Ar-H), 7.43(2H, dd, J 6.78 and 2.2, H-2', H-6'), 6.81(2H, dd, J 6.78 and 2.2, H-3', H-5'), 6.54(1H, dd, J 8.79 and 2.38, H-6), 6.28(1H, d, J 2.38, H-8), 4.79(1H, d, J 12.09, $H_{2A \text{ or } 2B}$), 4.61(1H, d, J 12.09, $H_{2B \text{ or } 2A}$), 3.76-3.75(6H, 2s, 4'-OCH_3, 7-OCH_3); δ_C 187.87 (C-4), 165.96(C-7), 162.42(C-9), 159.46(C-4'), 136.68(C-3", C-5"), 130.02(C-5), 129.77(C-1"), 129.22(C-4"), 129.15(C-2', C-6'), 128.6(C-2",C-6"), 126.48(C-1'), 114.55(C-10), 113.81(C-3', C-5'), 110.39(C-6), 100.25(C-8), 73.02(C-2), 60.42(C-3), 55.6(7-OCH_3), 55.22(4'-OCH_3); *m/z* 392(M^+), 283, 255, 151, 133, 122, 109.

3-(2,4-Dimethoxyphenyl)-7-methoxy-3-phenylthio-2,3-dihydro-(4H)-benzopyran-4-one : CC [eluant: hexane–ethyl acetate–methanol, 5:1:0.2], (63%); plates, m.p. 132-133°C (Found: C, 67.88; H, 5.51; S, 7.14. $C_{24}H_{22}O_5S$ requires: C, 68.25; H, 5.21; S, 7.58%); ν_{max}(KBr)/cm^{-1} 1688, 1672, 1607, 1250; λ_{max}(CH_3CN)/nm 312(9346), 273(16095); δ_H 7.94(1H, d, J 8.61, H-6'), 7.86(1H, d, J 8.8, H-5), 7.37-7.29(2H, m, H-3", H-5"), 7.27-7.11(3H, m, H-2", H-4", H-6"), 6.61-6.53(2H, m, J 2.38, H-6, H-5'), 6.47(1H, d, J 2.38, H-8), 6.4(1H, d, J 2.38, H-3'), 4.95(1H, d, J 12.09, $H_{2A \text{ or } 2B}$), 4.22(1H, d, J 12.09, $H_{2B \text{ or } 2A}$), 3.83(3H, s, 7-OCH_3), 3.81(3H, s, 4'-OCH_3), 3.63(3H, s, 2'-OCH_3); δ_C 185.15(C-4), 165.33(C-7), 161.72(C-9), 161.2(C-4'), 158.15(C-2'), 135.21(C-3", C-5"), 132.08 (C-6'), 130.91(C-1"), 129.96(C-5), 128.35(C-2", C-6"), 128.47(C-4"), 116.97(C-1'), 114.55(C-10), 109.95(C-6), 104.87(C-5'), 100.54(C-8), 100.27(C-3'), 72.94(C-2), 62.73(C-3), 55.62(7-OCH_3), 55.57(2'-OCH_3), 55.41 (4'-OCH_3); *m/z* 422(M^+), 313, 285, 151.

7-Methoxy-3-phenylthio-3-(2,4,6-trimethoxyphenyl)-2,3-dihydro-(4H)-benzopyran-4-one : CC [eluant: ether–hexane, 3:1], (50%); needles, m.p. 143-145°C (ethanol) (Found: C, 66.07; H, 5.44; S, 7.4. $C_{25}H_{24}O_6S$ requires: C, 66.37; H, 5.31; S, 7.08%); ν_{max}(KBr)/cm^{-1} 1692, 1613, 1250; λ_{max}(CH_3CN)/nm 266(16037), 304(6841); δ_H 7.67(1H, d, J 8.79, H-5), 7.4-7.37(2H, m, H-3", H-5"), 7.27-7.13(3H, m, H-2", H-4", H-6"), 6.47(1H, dd, J 8.79 and 2.38, H-6), 6.22(1H, d, J 2.38, H-8), 5.96(2H, s, H-3', H-5'), 5.48(1H, d, J 11.54, $H_{2A \text{ or } 2B}$), 4.33(1H, d, J 11.54, $H_{2B \text{ or } 2A}$), 3.74(3H, s, 7-OCH_3), 3.73(3H, s, 4'-OCH_3), 3.49(6H, s, 2'-OCH_3, 6'-OCH_3); δ_C 190.35(C-4), 164.33 (C-7), 161.82(C-9), 160.98(C-2', C-6'), 160.61(C-4'), 137.35(C-3", C-5"), 131.23(C-1"), 129.14(C-5), 128.47 (C-4"), 127.92(C-2", C-6"), 115.6(C-10), 109.19(C-6), 105.09(C-1'), 99.92(C-8), 91.84(C-3', C-5'), 74.3(C-2), 61.33(C-3), 55.54(2'-OCH_3, 6'-OCH_3), 55.39(7-OCH_3), 55.17(4'-OCH_3); *m/z* 452(M^+), 343, 285, 193, 151, 135, 109.

2-(4-Methoxyphenyl)-3-phenyl-3-phenylthio-2,3-dihydro-(4H)-benzopyran-4-one : [eluant: hexane–ether–chloroform, 3:1:1], (82%); colorless plates, m.p. 133-136°C (Found: C, 76.64; H, 5.07; S, 7.34. $C_{28}H_{22}O_3S$ requires: C, 76.69; H, 5.06; S, 7.31%); ν_{max}(KBr)/cm^{-1} 1680, 1607, 1462, 1300; δ_H 7.96(1H, dd, J 8.24 and 1.83, H-5), 7.56(1H, distorted ddd, J 8.71 and 1.84, H-7), 7.38-7.34(2H, m, H-6, H-8), 7.28-7.23(3H, m, H-2", H-4", H-6"), 7.17-7.04(7H, m, H-3", H-5", H-2'", H-3'", H-4'", H-5'", H-6'"), 6.91(2H, d, J 8.61, H-2', H-6'), 6.73(2H, d, J 8.79, H-3', H-5'), 5.53(1H, s, H-2), 3.79(3H, s, OCH_3); δ_C 186.67(C-4), 160.01(C-9), 159.67(C-4'), 135.5(C-5), 135.2(C-3", C-5"), 134.89(C-1'"), 130.7(C-3'", C-5'"), 129.67(C-1"), 129.42(C-2'", C-6'"), 128.66(C-4'"), 128.57 (C-2', C-6'), 128.44(C-4"), 127.89(C-2", C-6", C-7), 126.42(C-1'), 121.94(C-6), 120.61(C-10), 117.72(C-8), 112.7(C-3', C-5'), 86.67(C-2), 69.8(C-3), 55.2(OCH_3); *m/z* 438(M^+), 329, 229, 209, 165, 121.

2-(4-Methoxyphenyl)-3-(4-methoxyphenyl)-3-phenylthio-2,3-dihydro-(4H)-benzopyran-4-one : [eluant: hexane–ether, 1:1], (90%); colorless plates, m.p. 177-179°C (Found: C, 74.64; H, 5.38; S, 6.97. $C_{29}H_{24}O_4S$ requires: C, 74.34; H, 5.16; S, 6.84%); ν_{max}(KBr)/cm^{-1} 1684, 1605, 1579, 1511; δ_H 7.95(1H, dd, J 8.3 and 1.69, H-5), 7.54(1H, distorted ddd, J 8.02 and 1.69, H-7), 7.4(2H, d, J 9, H-2', H-6'), 7.17-7.04(7H, m, H-6, H-8, H-2", H-3", H-4", H-5", H-6"), 6.94(2H, d, J 8.72, H-2'", H-6'"), 6.78(2H, d, J 9, H-3', H-5'), 5.49(1H, s, H-2), 3.79(3H, s, 4'"-OCH_3), 3.78(3H, s, 4'-OCH_3); δ_C 186.9(C-4), 160.03(C-9), 159.7(C-4'), 159.1(C-4'"), 135.43(C-5), 135.16(C-3", C-5"), 131.89(C-2'", C-6'"), 129.83(C-1"), 129.56(C-2', C-6'), 128.6(C-7), 128.57(C-4"), 128.41(C-2", C-6"), 126.81 (C-1'"), 126.61(C-1'), 121.88(C-6), 120.63(C-10), 117.7(C-8), 113.26(C-3'", C-5'"), 112.77(C-3', C-5'), 86.73(C-2), 69.14(C-3), 55.27(4'"-OCH_3), 55.22(4'-OCH_3); *m/z* 468(M^+), 359, 239, 229, 121.

2-(4-Methoxyphenyl)-3-(4-methylphenyl)-3-phenylthio-2,3-dihydro-(4H)-benzopyran-4-one : [eluant: hexane–ethyl acetate, 4:1], (90%); colorless plates, m.p. 195-197°C (Found: C, 76.72; H, 5.27; S, 7.39. $C_{29}H_{24}O_3S$ requires: C, 76.97; H, 5.35; S, 7.08%); ν_{max}(KBr)/cm^{-1} 1682, 1605, 1515, 1462; λ_{max}(CH_3OH)/nm 213(80058), 254(22332), 325(6851); δ_H 7.95(1H, dd, J 8.25 and 1.83, H-5), 7.54(1H, distorted ddd, J 8.61 and 1.83, H-7), 7.23(2H, d, J 8.61, H-2', H-6'), 7.17-7.01(9H, m, H-6, H-8, H-3', H-5', H-2", H-3", H-4", H-5", H-6"), 6.92(2H, d, J 8.79, H-2'", H-6'"), 6.72(2H, d, J 8.79, H-3'", H-5'"), 5.52(1H, s, H-2), 3.79(3H, s, OCH_3), 2.32(3H, s, CH_3); δ_C 186.83(C-4), 159.98(C-9), 159.6(C-4'), 137.54(C-4'"), 135.43(C-5), 135.18(C-3", C-5"), 131.76(C-1'"), 130.51 (C-2'", C-6'"), 129.8(C-1"), 129.48(C-3'", C-5'"), 128.61(C-2", C-4", C-7), 128.39(C-2', C-6', C-4"), 126.54(C-1'), 121.86(C-6), 120.6(C-10), 117.68(C-8), 112.67(C-3', C-5'), 86.6(C-2), 69.55(C-3), 55.19(OCH_3), 21.1(CH_3); *m/z* 452(M^+), 343, 229, 223, 121.

2-[4-Methoxyphenyl]-3-[3,4-methylenedioxyphenyl]-3-phenylthio-2,3-dihydro-(4H)-benzopyran-4-one : [eluant: chloroform], (97%); pale yellow plates, m.p. 184-187°C (Found: C, 72.23; H, 4.73; S, 6.76. $C_{29}H_{22}O_5S$ requires: C, 72.18; H, 4.6; S, 6.64%); ν_{max}(KBr)/cm^{-1} 1683, 1606, 1515, 1297; λ_{max}(CH_3CN)/nm 197(165896), 324(11462); δ_H 7.94(1H, dd, J 1.65 and 8.25, H-5), 7.65(1H, distorted ddd, J 8.06 and 1.65, H-7), 7.21-7.04(7H, m, H-6, H-8, H-2", H-3", H-4", H-5", H-6"), 6.99(2H, d, J 8.79, H-2', H-6'), 6.9-6.84(2H, m, H-2'", H-6'"), 6.76(2H, d,

J 8.8 , H-3', H-5'), 6.69(1H, d, J 8.24, H-5'"), 5.96(1H, d, J 1.37, OCH_2O), 5.92(1H, d, J 1.37, OCH_2O), 5.49(1H, s, H-2), 3.8(3H, s, OCH_3); δ_C 186.67(C-4), 159.97(C-9), 159.75(C-4'), 147.34(C-3'"), 147.17(C-4'"), 135.53(C-5), 135.29(C-3", C-5"), 129.6(C-2', C-6'), 129.42(C-1"), 128.77(C-7), 128.66(C-4"), 128.57(C-2", C-6"), 128.49(C-1'"), 126.5(C-1'), 124.66(C-6'"), 121.92(C-6), 120.53(C-10), 117.7(C-8), 112.81(C-3', C-5'), 111.04(C-2'"), 107.63(C-5'"), 101.17 (OCH_2O), 86.6(C-2), 69.65(C-3), 55.22(OCH_3); *m/z* 482(M^+), 373, 253, 229, 195.

2-[4-Methoxyphenyl]-3-[2,4-dimethoxyphenyl]-3-phenylthio-2,3-dihydro-(4H)-benzopyran-4-one : [eluant: hexane–ether–chloroform, 3:2:2], (93%); pale yellow plates, m.p. 138-140°C (HRMS Found: $M^{\cdot+}$ 498.1464. $C_{30}H_{26}O_5S$ requires: $M^{\cdot+}$ 498.1494); ν_{max}(KBr)/cm^{-1} 1689, 1609, 1461; λ_{max}(CH_3OH)/nm 213(58022), 324 (4484); δ_H 7.9(1H, dd, J 8.06 and 1.83, H-5), 7.53(1H, distorted ddd, J 8.7 and 1.83, H-7), 7.52(2H, d, J 8.61, H-2', H-6'), 7.18-6.95(8H, m, H-6, H-8, H-2", H-3", H-4", H-5", H-6", H-6'"), 6.73(2H, d, J 8.79, H-3', H-5'), 6.54(1H, d, J 2.56, H-3'"), 6.4(1H, dd, J 8.7 and 2.56, H-5'"), 6.03(1H, s, H-2), 3.82(3H, s, 4'-OCH_3), 3.78(3H, s, 4'"-OCH_3), 3.7(3H, s, 2'"-OCH_3); δ_C 184.75(C-4), 160.99(C-9), 159.91(C-4'), 159.35(C-4'"), 157.61(C-2'"), 135.49(C-3", C-5"), 134.86(C-5), 133.53(C-6'"), 130.34(C-1"), 129.09(C-2', C-6'), 128.47(C-7), 128.39(C-2", C-6"), 128.2(C-4"), 127.52(C-1'), 121.59(C-6), 120.17(C-10), 117.65(C-8), 117.22(C-1'"), 112.54(C-3', C-5'), 104.76(C-5'"), 100.16 (C-3'"), 82.3(C-2), 68.76(C-3), 55.76(OCH_3), 55.35(OCH_3), 55.12(OCH_3); *m/z* 498(M^+), 389, 254, 239, 121.

2-(4-Methoxyphenyl)-3-(2,4,6-trimethoxyphenyl)-3-phenylthio-2,3-dihydro-(4H)-benzopyran-4-one : [eluant: hexane–chloroform–ethyl acetate, 2:1:1], (99%); pale yellow plates, m.p. 209-212°C (HRMS Found: $M^{\cdot+}$ 528.1675. $C_{31}H_{28}O_6S$ requires: $M^{\cdot+}$ 528.1599); ν_{max}(KBr)/cm^{-1} 1678, 1606, 1583, 1460; λ_{max}(CH_3OH)/nm 216(60105), 322(3643); δ_H 7.73(1H, dd, J 8.3 and 1.7, H-5), 7.42(2H, d, J 8.25, H-2', H-6'), 7.29(1H, distorted ddd, J 8.5 and 1.6, H-7), 7.25-7.22(2H, m, H-2", H-6"), 7-6.83(5H, m, H-6, H-8, H-3", H-4", H-5"), 6.81-6.78(2H, d, J 8.8, H-3', H-5'), 6.18(1H, d, J 2.4, H-5'"), 5.92(1H, d, J 2.4, H-3'"), 5.7(1H, s, H-2), 3.79(3H, s, 4'-OCH_3), 3.78(3H, s, 4'"-OCH_3), 3.6(3H, s, 6'"-OCH_3), 3.14(3H, s, 2'"-OCH_3); δ_C 186.58(C-4), 161.36(C-9), 161.25(C-4'), 159.93 (C-4'"), 159.51(C-2'"), 158.14(C-6'"), 136.87(C-3", C-5"), 134.19(C-5), 132.44(C-1"), 129.96(C-2', C-6'), 129.04 (C-1'), 128.15(C-7), 128(C-4"), 127.63(C-2", C-6"), 122.25(C-10), 121.44(C-6), 117.61(C-8), 112.38(C-3', C-5'), 107.87(C-1'"), 92.83(C-3'"), 92.68(C-5'"), 84.36(C-2), 67.33(C-3), 55.89(4'-OCH_3), 55.4(2'"-OCH_3, 6'"-OCH_3), 54.95(4'"-OCH_3); *m/z* 528(M^+), 419, 300, 284, 121.

Preparation of Isoflavones via Desulfurisation of 3-Aryl-3-phenylthio-2,3-dihydro-(4H)-benzopyran-4-ones Using Dimethyldioxirane. *General Procedure* :

Freshly distilled dimethyldioxirane (1-2eq) solution in acetone was added to a solution of the 3-aryl-3-phenylthiochroman-4-one (1eq) in acetone (1cm^3 per 0.2mmol substrate) and the resulting mixture was stirred at room temperature for 15 min. The solvent was evaporated. The solution of the crude sulfoxide in toluene was refluxed for 2h and concentrated. The residue was purified by column chromatography on silica gel using the indicated solvent system.

Reaction of 3-phenyl-3-phenylthiochroman-4-one : [eluant: ethyl acetate–hexane, 3:1], 3-phenyl-3-phenylsulfonylchroman-4-one as a waxy solid (35%) (Found: HRMS 364.0706. $C_{21}H_{16}O_4S$ requires: 364.0769), δ_H 8.06-7.88(1H, dd, H-5), 7.84-6.8(13H, m, Ar-H), 5.57(1H, d, J 12, $H_{2A\ or\ 2B}$), 5.18(1H, d, J 12, $H_{2B\ or\ 2A}$); *m/z* 364, 223, 120, 103, 92, and isoflavone as a solid (38%), m.p. 131-132°C (lit [14] 131-132°C).

4'-Methoxyisoflavone : [eluant: (i) hexane–ethyl acetate, 2:1 (ii) chloroform–ethyl acetate–hexane, 10:1:1], (65%); needles, m.p. 123-125°C (ethanol) (Found: C, 76.35; H, 4.91. $C_{16}H_{12}O_3$ requires: C, 76.19; H, 4.76%) (lit.[14] 140-141°C); δ_H 8.3(1H, dd, J 7.97 and 1.75, H-5), 7.99(1H, s, H-2), 7.69-7.63(1H, m, H-7), 7.52-7.25(4H, m, Ar-H), 6.97(2H, d, J 8.98, H-3', H-5'), 3.83(3H, s, OCH_3); δ_C 176.45(C-4), 159.59(C-9), 156.15(C-4'), 152.52(C-2), 133.5(C-7), 130.09(C-2', C-6'), 126.35(C-5), 125.12(C-6), 124.95(C-3), 124.47(C-1'), 124.08(C-10), 118.02(C-3', C-5'), 113.97(C-8), 55.32(4'-OCH_3).

2',4'-Dimethoxyisoflavone : [eluant: (i) hexane–ethyl acetate, 2:1 (ii) hexane–ether, 1:1], (85%); needles, m.p. 156-158°C (ethanol) (lit.[14] 157-158°C).

2',4',6'-Trimethoxyisoflavone : [eluant: hexane–ethyl acetate, 2:1], (82%); pale yellow needles, m.p. 212-215°C (ethanol) (Found: C, 68.9; H, 5.23. $C_{18}H_{16}O_5$ requires: C, 69.23; H, 5.13%); ν_{max}(KBr)/cm^{-1} 1694, 1607, 1501, 1482, 1466, 1291; δ_H 8.38-8.16(1H, dd, H-5), 7.81(1H, s, H-2), 7.64-7.2(3H, m, Ar-H), 6.24(2H, s, H-3', H-5'), 3.86(3H, s, 4'-OCH_3), 3.72(6H, s, 2'-OCH_3, 6'-OCH_3); *m/z* 312(M^+), 281, 191, 121, 92.

7-Methoxyisoflavone : [eluant: ether–hexane, 3:1], 52%; m.p. 156-157°C (lit.[15] 157-158°C).

4',7-Dimethoxyisoflavone : [eluant: (i) hexane–ethyl acetate–methanol, 5:1:0.2 (ii) dichloromethane–ethyl acetate, 10:1], (67%); needles, m.p. 159-162°C (ethanol) (lit.[15] 159°C). 4',7-Dimethoxy-3-phenylsulfonylisoflavanone was also obtained as an oil (15%); δ_H 7.85(1H, d, J 9, H-5), 7.76-6.26(11H, m, Ar-H), 5.48(1H, d, J 12, $H_{2A\ or\ 2B}$), 5.12(1H, d, J 12, $H_{2B\ or\ 2A}$), 3.8(6H, s, 4'-OCH_3, 7-OCH_3).

2',4',7-Trimethoxyisoflavone : [eluant: (i) hexane–ethyl acetate, 2:1 (ii) dichloromethane–ethyl acetate, 10:1], (33%); needles, m.p. 136-138°C (ethanol) (lit.[16] 148-149°C) (Found: HRMS 312.0995. $C_{18}H_{16}O_5$ requires: 312.0998); δ_H 8.14(1H, d, *J* 8.65, H-5), 7.81(1H, s, H-2), 7.3-6.4(5H, m, Ar-H), 3.87(3H, s, 7-OCH_3), 3.8(3H, s, 4'-OCH_3), 3.74(3H, s, 2'-OCH_3); *m/z* 312(M^+), 311, 281, 162, 161, 151, 150.

2-(4-Methoxyphenyl)-3-(3,4-methylenedioxyphenyl)-(4H)-benzopyran-4-one : [eluant: hexane–acetone, 3:2]; (41%), pale yellow plates, m.p. 160-162°C(methanol) (HRMS Found: $M^{\cdot+}$ 372.0929. $C_{23}H_{16}O_5$ requires: $M^{\cdot+}$ 372.0993); ν_{max}(KBr)/cm^{-1} 2360, 1640, 1613, 1470; δ_H 8.27(1H, dd, *J* 8.06 and 1.74, H-5), 7.68(1H, distorted ddd, *J* 7.74 and 1.74, H-7), 7.51(1H, dd, *J* 7.87 and 1.81, H-8), 7.44-7.38(1H, m, H-6), 7.41(2H, d, *J* 8.98, H-2', H-6'), 6.82(2H, d, *J* 8.98, H-3', H-5'), 6.77(1H, d, *J* 7.79, H-5"), 6.77(1H, d, *J* 1.65, H-2"), 6.66(1H, dd, *J* 7.79 and 1.65, H-6"), 5.97(2H, s, OCH_2O), 3.82(3H, s, OCH_3); δ_C 177.49(C-4), 160.96(C-9), 155.95(C-4'), 147.64(C-3"), 147.07(C-4"), 133.52(C-5), 131.15(C-2', C-6'), 126.83(C-1"), 126.37(C-7), 125.5(C-1'), 124.95(C-6"), 124.85(C-6), 123.43(C-3), 121.69(C-10), 117.86(C-8), 113.62(C-3', C-5'), 111.66(C-2"), 108.54(C-5"), 101.03(OCH_2O), 55.33 (OCH_3) (C-2 could not be found); *m/z* 372(M^+), 357, 341, 252, 237, 171.

2-(4-Methoxyphenyl)-3-(2,4,6-trimethoxyphenyl)-(4H)-benzopyran-4-one : [eluant: hexane–ether–chloroform, 1:2:1], (61%); colorless plates, m.p. 150-152°C (ethyl acetate–petroleum ether) (HRMS Found: $M^{\cdot+}$ 418.1365. $C_{25}H_{22}O_6$ requires: $M^{\cdot+}$ 418.1410); ν_{max}(KBr)/cm^{-1} 1625, 1610, 1514, 1467; δ_H 8.31(1H, dd, *J* 7.97 and 1.65, H-5), 7.64(1H, distorted ddd, *J* 7.7 and 1.65, H-7), 7.47-7.36(2H, m, H-6, H-8), 7.1(2H, d, *J* 8.8, H-2', H-6'), 6.73(2H, d, *J* 8.79, H-3', H-5'), 6.01(2H, s, H-3", H-5"), 3.79(3H, s, 6"-OCH_3), 3.75(3H, s, 2"-OCH_3), 3.64(6H, s, 4'-OCH_3, 4"-OCH_3); δ_C 177.67(C-4), 162.94(C-9), 158.84(C-4'), 158.57(C-4"), 158.51(C-6'), 156.82(C-2"), 133.03(C-5), 130.93(C-2', C-6'), 126.05(C-7), 125.8(C-1'), 124.47(C-6), 123.92(C-3), 118.03(C-8, C-10), 112.86(C-3', C-5'), 105.27(C-1"), 90.34(C-3", C-5"), 56.01(4'-OCH_3, 4"-OCH_3), 55.35(OCH_3), 55.02(OCH_3); *m/z* 418(M^+), 387, 298, 209, 92.

Preparation of Isoflavanones via Desulfurisation of 3-Aryl-3-phenylthio chroman-4-one Derivatives Using Nickel Boride.

General Procedure : 3-Aryl-3-phenylthio chroman-4-one (1eq) and nickel chloride hexahydrate (24eq) in ethanol (150cm^3 per 0.2mmol substrate) were stirred under nitrogen and treated dropwise with a solution of sodium borohydride (20eq) in water (1cm^3 per 2mmol substrate). The formation of a black precipitate was observed. The mixture was then heated under reflux until reaction completion as indicated by tlc. The mixture was filtered through Celite and the solid washed with ethanol. The combined filtrates were evaporated and the residue extracted with ether. The ether solution was dried ($MgSO_4$) and concentrated to give the product directly or after column chromatography.

4'-Methoxyisoflavanone : (69%); needles, m.p. 98-99°C (methanol) (lit.[17] 98-99°C).

2',4'-Dimethoxyisoflavanone : (98%); needles, m.p. 78-80°C, (methanol) (HRMS: Found 284.0994. $C_{17}H_{16}O_4$ requires: 284.1049); δ_H 7.98(1H, dd, *J* 7.79 and 1.74, H-5), 7.52-7.45(1H, m, H-7), 7.07-6.98(3H, m, Ar-H), 6.5-6.45(2H, m, H-3', H-5'), 4.66-4.46(2H, m, OCH_2), 4.29(1H, dd, *J* 12.09 and 5.49, H-3), 3.8(3H, s, 4'-OCH_3), 3.76(3H, s, 2'-OCH_3); δ_C 192.84(C-4), 161.85(C-9), 160.58(C-2'), 158.39(C-4'), 135.61(C-7), 130.74(C-6'), 127.65(C-5), 121.61(C-10), 121.34(C-6), 117.81(C-8), 115.72(C-1'), 104.62(C-5'), 99.16(C-3'), 70.86(C-2), 55.51(2'-OCH_3), 55.38(4'-OCH_3), 47.93(C-3); *m/z* 284, 164, 149.

2',4',6'-Trimethoxyisoflavanone : (71%); needles, m.p. 170-173°C (methanol–hexane) (Found: C, 68.50; H, 5.95. $C_{18}H_{18}O_5$ requires: C, 68.79; H, 5.73%); δ_H 8-7.97(1H, dd, *J* 7.97 and 1.56, H-5), 7.5-7.43(1H, m, H-7), 7.26-6.97(2H, m, H-6, H-8), 6.16(2H, s, H-3', H-5'), 4.78-4.61(2H, m, OCH_2), 4.38-4.33(1H, m, H-3), 3.81(3H, s, 4'-OCH_3), 3.73(6H, s, 2'-OCH_3, 6'-OCH_3); δ_C 192.95(C-4), 161.9(C-9), 161.06(C-4'), 159.21(C-2', C-6'), 135.15(C-7), 127.67(C-5), 121.52(C-10), 121.13(C-6), 117.75(C-8), 104.1(C-1'), 91.22(C-3', C-5'), 69.65(C-2), 55.76(2'-OCH_3, 6'-OCH_3), 55.38(4'-OCH_3), 43.48(C-3); *m/z* 314 , 194, 179, 28.

2,3-cis-2-(4-Methoxyphenyl)-3-phenyl-2,3-dihydro-(4H)-benzopyran-4-one : [eluant: hexane–ether–chloroform, 3:1:1], (74%), colorless needles, m.p. 140-141°C (Found: C, 79.93; H, 5.4. $C_{22}H_{18}O_3$ requires: C, 79.98; H, 5.49); ν_{max}(KBr)/cm^{-1} 1686, 1605, 1516, 1462; λ_{max}(CH_3CN)/nm 195(73264), 216(48934), 251(15364), 321(4975); δ_H 8.03(1H, dd, *J* 7.88 and 1.65, H-5), 7.59(1H, distorted ddd, *J* 7.52 and 1.65, H-7), 7.18-7.01(7H, m, H-6, H-8, H-2', H-6', H-3", H-4", H-5"), 6.91-6.88(2H, m, H-2", H-6"), 6.76(2H, d, *J* 8.8, H-3', H-5'), 5.75(1H, d, *J* 3.48, H-2), 3.89(1H, d, *J* 3.48, H-3), 3.75(3H, s, OCH_3); δ_C 192.74(C-4), 161.74(C-9), 159.24(C-4'), 136.4(C-5), 133.27 (C-1"), 129.48(C-3", C-5"), 128.88(C-1'), 128.35(C-2', C-6'), 128(C-7), 127.86(C-4"), 127.51(C-2", C-6"), 121.94(C-6), 120.93(C-10), 118.25(C-8), 113.46(C-3', C-5'), 82.16(C-2), 58.48(C-3), 55.17(OCH_3); *m/z* 330 (M^+), 210, 195, 165, 152.

2-(4-Methoxyphenyl)-3-(4-methylphenyl)-2,3-dihydro-(4H)-benzopyran-4-one : [eluant: hexane–chloroform–ethyl acetate, 5:1:1], (58%); colorless plates, m.p. 158-159°C (Found: C, 79.96; H, 5.82. $C_{23}H_{20}O_3$ requires: C,

80.21; H, 5.85); ν_{max}(KBr)/cm^{-1} 1692, 1604, 1518, 1462; λ_{max}(CH_3OH)/nm 218, 254, 322; δ_H 8.02(1H, dd, J 7.88 and 1.83, H-5), 7.58(1H, distorted ddd, J 7.78 and 1.83, H-7), 7.18-7.09(2H, m, H-6, H-8), 7.07(2H, d, J 8.97, H-2', H-6'), 6.92(2H, d, J 7.88, H-2", H-6"), 6.8(2H, d, J 6.96, H-3", H-5"), 6.77(2H, d, J 8.97, H-3', H-5'), 5.73(1H, d, J 3.3, H-2), 3.87(1H, d, J 3.3, H-3), 3.76(3H, s, OCH_3), 2.22(3H, s, CH_3); δ_C 192.87(C-4), 161.72(C-9), 159.24(C-4'), 137.14(C-4"), 136.3(C-5), 130.18(C-1"), 129.33(C-2", C-6"), 129.11(C-2', C-6'), 129.04(C-1'), 128(C-7), 127.57 (C-3", C-5"), 122.02(C-6), 120.91(C-10), 118.21(C-8), 113.51(C-3', C-5'), 82.14(C-2), 58.05(C-3), 55.19(OCH_3), 21.05(CH_3); *m/z* 344(M^+), 224, 209, 165, 121.

2-(4-Methoxyphenyl)-3-(4-methoxyphenyl)-2,3-dihydro-(4H)-benzopyran-4-one : inseparable 83:17 mixture of 2,3-cis and 2,3-trans isomers [eluant: hexane–ether, 2:1], (87%); colorless plates, m.p. 139-142°C (Found: C, 76.57; H, 5.9. $C_{23}H_{20}O_4$ requires: C, 76.65; H, 5.6%); ν_{max}(KBr)/cm^{-1} 1692, 1614, 1519, 1465; δ_H 8.04[0.83H(cis), dd, J 7.83 and 1.65, H-5], 8[0.17H(trans), dd, J 7.4 and 1.57, H-5], 7.58[0.83H(cis), distorted ddd, J 7.74 and 1.65, H-7], 7.52[0.17H(trans), distorted ddd, J 8.24 and 1.57, H-7], 7.18-7.11(2H, m, H-6, H-8), 7.07(2H, d, J 8.79, H-2', H-6'), 6.92[0.34H(trans), d, J 8.79, H-2", H-6"], 6.85[1.66H(cis), d, J 9.24, H-2", H-6"], 6.79(2H, d, J 8.79, H-3', H-5'), 6.67(2H, d, J 8.79, H-3", H-5"), 5.71[0.83H(cis), d, J 3.3, H-2], 5.5[0.17H(trans), d, J 11.64, H-2], 4.12[0.17H (trans), d, J 11.64, H-3], 3.84[0.83H(cis), d, J 3.3, H-3], 3.76[2.49H(cis), s, 4'-OCH_3], 3.75[0.51H(trans), s, 4'-OCH_3], 3.73[0.51H(trans), s, 4"-OCH_3], 3.69[2.49H(cis), s, 4"-OCH_3]; δ_C 193.12(trans C-4), 192.87(cis C-4), 161.69(cis C-9), 161.18(trans C-9), 159.59(trans C-4'), 159.27(cis C-4'), 158.91(cis C-4"), 158.67(trans C-4"), 136.3(cis C-5), 136.11(trans C-5), 130.59(trans C-2', C-6'), 130.53(cis C-2', C-6'), 130.1(trans C-1"), 129.04(cis C-1"), 128.47(trans C-7), 128(cis C-7), 127.6(C-2", C-6"), 127.03(trans C-1'), 125.34(cis C-1'), 122.03(cis C-6), 121.6(trans C-6), 121.02(cis C-10), 120.9(trans C-10), 118.21(cis C-8), 118.06(trans C-8), 114.03(trans C-3', C-5'), 113.83(cis C-3', C-5'), 113.76(trans C-3", C-5"), 113.53(cis C-3", C-5"), 84.56(trans C-2), 82.22(cis C-2), 58.67(trans C-3), 57.64(cis C-3), 55.13(4'-OCH_3, 4"-OCH_3); *m/z* 360(M^+), 253, 240, 225, 209.

2-(2,4-Dimethoxyphenyl)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one : [eluant: hexane–chloroform–ethyl acetate, 2:1:1], (62%); yellow plates, m.p. 135-137°C (Found: C, 73.9; H, 5.82. $C_{24}H_{22}O_5$ requires: C, 73.83; H, 5.68%); ν_{max}(KBr)/cm^{-1} 3479, 1628, 1602, 1506, 1264; λ_{max}(CH_3OH)/nm 207, 234, 264; δ_H 11.84(1H, s, OH), 7.83(1H, dd, J 7.78 and 1.68, H-6'), 7.43(1H, distorted ddd, J 7.88 and 1.68, H-4'), 7.15(2H, d, J 8.44, H-2, H-6), 7.13(1H, d, J 8.72, H-6"), 7.02(1H, s, H-β), 7(1H, dd, J 8.02 and 0.99, H-3'), 6.8(1H, distorted ddd, J 7.6 and 0.99, H-5'), 6.75(2H, d, J 9, H-3, H-5), 6.5-6.46(2H, m, H-3", H-5"), 3.83(3H, s, OCH_3), 3.78(3H, s, OCH_3), 3.6(3H, s, OCH_3); δ_C 203.04(CO), 162.59(C-4), 161.31(C-2'), 160.01(C-4"), 158.13(C-2"), 138.74(C-β), 135.42(C-6'), 134.74(C-α), 132.82(C-4'), 132.03(C-6"), 131.59(C-2, C-6), 127.76(C-1), 119.91(C-1'), 118.92(C-1"), 118.27 (C-5'), 117.97(C-3'), 113.73(C-3, C-5), 105.39(C-5"), 99.11(C-3"), 55.54(4-OCH_3), 55.39(4"-OCH_3), 55.25 (6"-OCH_3); *m/z* 390(M^+), 283, 254, 239, 121.

1-(2-Hydroxyphenyl)-3-(4-methoxyphenyl)-2-(2,4,6-trimethoxyphenyl)prop-2-en-1-one : [eluant: hexane–chloroform–ether, 2:1:1], (70%); yellow plates, m.p. 149-151°C (Found: C, 71; H, 5.76. $C_{25}H_{24}O_6$ requires: C, 71.42; H, 5.75%; HRMS Found: $M^{\cdot+}$ 420.1620. $C_{25}H_{24}O_6$ requires/ $M^{\cdot+}$ 420.1566); ν_{max}(KBr)/cm^{-1} 3482, 1624, 1603, 1582, 1155; λ_{max}(CH_3OH)/nm 206, 209, 234, 266; δ_H 11.71(1H, s, OH), 7.8(1H, dd, J 8.16 and 1.77, H-6'), 7.4(1H, distorted ddd, J 8.53 and 1.77, H-4'), 7.16(2H, d, J 8.72, H-2, H-6), 7.15(1H, s, H-β), 6.98(1H, dd, J 8.43 and 0.98, H-3'), 6.76(1H, distorted ddd, J 8.2 and 0.98, H-5'), 6.74(2H, d, J 9, H-3, H-5), 6.13(2H, s, H-3", H-5"), 3.84(3H, s, 4-OCH_3), 3.78(3H, s, 4"-OCH_3), 3.53(6H, s, 2"'-OCH_3, 6"-OCH_3); δ_C 203.2(CO), 162.13(C-4), 161.68 (C-2'), 159.95(C-4"), 158.53(C-2", C-6"), 140.41(C-β), 135.07(C-6'), 132.54(C-4'), 130.77(C-2, C-6), 130.31(C-α), 129.07(C-1), 120.03(C-1'), 118.14(C-5'), 117.75(C-3'), 113.43(C-3, C-5), 108.05(C-1"), 91.17(C-3", C-5"), 55.68 (2"-OCH_3, 6"-OCH_3), 55.35(4'-OCH_3), 55.22(4"-OCH_3); *m/z* 420(M^+), 284, 269, 168, 121.

2-(4-Methoxyphenyl)-3-(3,4-methylenedioxyphenyl)-2,3-dihydro-(4H)-benzopyran-4-one : inseparable 4:1 mixture of 2,3-cis and trans isomers, [eluant: petroleum ether–ethyl acetate, 3:1], (87%); colorless plates, m.p. 136-139°C (Found: C, 73.71; H, 4.82. $C_{23}H_{18}O_5$ requires: C, 73.79; H, 4.85%); ν_{max}(KBr)/cm^{-1} 1688, 1611, 1513, 1469; δ_H 8.01[0.8H(cis), dd, J 8.7 and 1.65, H-5], 7.97[0.2H(trans), dd, J 7.88 and 1.83, H-5], 7.58[0.8H(cis), distorted ddd, J 7.79 and 1.65, H-7], 7.52[0.2H(trans), distorted ddd, J 8.25 and 1.83, H-7], 7.21-7.03(2H, m, H-6, H-8), 7.11(2H, d, J 8.8, H-2', H-6'), 6.8(2H, d, J 8.8, H-3', H-5'), 6.64[0.2H(trans), d, J 7.87, H-5"], 6.57[0.8H (cis), d, J 8.06, H-5"], 6.51[0.2H(trans), d, J 1.84, H-2"], 6.46[0.8H(cis), d, J 1.83, H-2"], 6.45[0.2H(trans), dd, J 7.88 and 1.84, H-6"], 6.39[0.8H(cis), dd, J 8.06 and 1.83, H-6"], 5.89[0.2H(trans), d, J 1.47, OCH_2O], 5.88[0.2H(trans), d, J 1.47, OCH_2O], 5.86[0.8H(cis), d, J 1.46, OCH_2O], 5.83[0.8H(cis), d, J 1.46, OCH_2O], 5.7[0.8H(cis), d, J 3.39, H-2], 5.48[0.2H(trans), d, J 11.72, H-2], 4.1[0.2H(trans), d, J 11.72, H-3], 3.81[0.8H(cis), d, J 3.39, H-3], 3.77[2.4H(cis), s, OCH_3], 3.76[0.6H(trans), s, OCH_3]; δ_C 192.96(trans C-4), 192.54(cis C-4), 161.58(cis C-9),161.15(trans C-9), 159.63(trans C-4'), 159.27(cis C-4'), 147.69(trans C-3"), 147.52(cis C-3"), 146.9(cis C-4"), 146.74(trans C-4"), 136.45(cis C-5), 136.22(trans C-5), 129.85(trans C-1"), 128.87(cis C-1"), 128.5(trans C-7), 128.03(cis C-7), 127.64(cis C-2', C-6'), 127.51(trans C-2', C-6'), 126.8(cis and trans C-1'), 123.24(C-6"), 122.16(cis C-6), 121.65(trans C-6), 120.88(trans C-10), 120.69(cis C-10), 118.29(cis C-8), 118.07(trans C-8), 113.79(trans C-3', C-5'), 113.57(cis C-3', C-5'), 109.55(C-2"), 108.4(trans C-5"), 108.27(cis C-5"), 100.98(trans OCH_2O), 100.92(cis OCH_2O), 84.47(trans C-2), 82.09(cis C-2), 59.08(trans C-3), 57.93(cis C-3), 55.2(4'-OCH_3); *m/z* 374(M^+), 254, 239, 181, 152.

2,3-trans-2-(4-Methoxyphenyl)-3-(2,4-dimethoxyphenyl)-2,3-dihydro-(4H)-benzopyran-4-one : [eluant: hexane–chloroform–ether, 3:1:1], (38%); colorless plates, m.p. 105.5-107.5°C (Found: C, 73.53; H, 5.55. $C_{24}H_{22}O_5$ requires: C, 73.83; H, 5.68%); ν_{max}(KBr)/cm^{-1} 1692, 1613, 1587, 1514, 1462; λ_{max}(CH_3OH)/nm 207, 234, 264, 322; δ_H 8(1H, dd, J 7.79 and 1.74, H-5), 7.5(1H, distorted ddd, J 7.74 and 1.74, H-7), 7.18(2H, d, J 8.61, H-2', H-6'), 7.06(2H, m, H-6, H-8), 6.77(2H, d, J 8.8, H-3', H-5'), 6.68(1H, d, J 8.42, H-6"), 6.37(1H, d, J 2.38, H-3"), 6.3(1H, dd, J 8.34 and 2.38, H-5"), 5.71(1H, d, J 12.27, H-2), 4.24(1H, d, J 12.28, H-3), 3.76(3H, s, 4'-OCH_3), 3.73(3H, s, 4"-OCH_3), 3.66(3H, s, 2'"-OCH_3); δ_C 193.03(C-4), 161.42(C-9), 160.2(C-4'), 159.43(C-4"), 157.96 (C-2"), 135.67(C-5), 132.1(C-6"), 130.58(C-1'), 128.38(C-2', C-6'), 127.62(C-7), 121.45(C-6), 121.12(C-10), 118(C-8), 116.14(C-1"), 113.49(C-3', C-5'), 104.56(C-5"), 99.08(C-3"), 83.06(C-2), 56.2(C-3), 55.44(4'-OCH_3), 55.23(4"-OCH_3), 55.2(2"-OCH_3); *m/z* 390(M^+), 270, 255, 227, 121.

2,3-trans-2-(4-Methoxyphenyl)-3-(2,4,6-trimethoxyphenyl)-2,3-dihydro-(4H)benzopyran-4-one : [eluant: hexane–chloroform–ethyl acetate, 3:1:1], (44%); pale yellow plates, m.p. 148-151°C (HRMS Found: $M^{\cdot+}$ 420.1598. $C_{25}H_{24}O_6$ requires: $M^{\cdot+}$ 420.1566); ν_{max}(KBr)/cm^{-1} 1694, 1607, 1462; λ_{max}(CH_3OH)/nm 206; δ_H 8.01(1H, dd, J 8.06 and 1.83, H-5), 7.48(1H, distorted ddd, J 7.79 and 1.83, H-7), 7.22(2H, d, J 8.61, H-2', H-6'), 7.05(2H, m, H-6, H-8), 6.75(2H, d, J 8.79, H-3', H-5'), 6(2H, br s, H-3", H-5"), 5.78(1H, d, J 12.28, H-2), 4.75(1H, d, J 12.46, H-3), 3.76(3H, s, 4'-OCH_3), 3.74(3H, s, 4"-OCH_3), 3.6(6H, br s, 2"-OCH_3, 6"-OCH_3); δ_C 193.45(C-4), 161.8(C-9), 160.77(C-4', C-4"), 159.47(C-6"), 158.93(C-2"), 135.27(C-5), 130.9(C-1'), 128.58(C-2', C-6'), 127.64(C-7), 121.24(C-10, C-6), 117.95(C-8), 113.16(C-3', C-5'), 104.76(C-1"), 91.17(C-3", C-5"), 82.6(C-2), 55.68(C-3, 4'-OCH_3), 55.22(4"-OCH_3), 49.72(2"-OCH_3, 6"-OCH_3); *m/z* 420(M^+), 300, 285, 168, 121.

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