A facile synthesis of fluoroalkylated chromones and their analogues from 2,2-dihydropolyfluoroalkanoates

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(Received December 1, 1992; accepted April 8, 1993)

Abstract

Fluoroalkylated chromones and their analogues have been prepared in good yield by the Michael addition reactions of 2,2-dihydropolyfluoroalkanoates with phenols in the presence of triethylamine, followed by acid-catalyzed intramolecular ring-closure.

Introduction

The development of new and more efficient methods for the synthesis of fluorine-containing heteroaromatic compounds continue to arouse considerable interest due to their unique biological activities [1–5]. Chromone is a very useful heterocyclic system [6] and some fluorinated chromones have been prepared for medicinal research [7, 8]. Reported preparations of 2-(*F*-alkyl)-substituted chromones have been based on the Claisen condensation reactions of *o*-hydroxyacetophenones with polyfluoroalkanoates followed by ring-closure [9, 10]. We have recently reported a convenient method for the synthesis of 2-(*F*-alkyl)-substituted quinolines [11] by the reaction of 2,2-dihydropolyfluoroalkanoates with aromatic amines. In the present paper, the results of the reaction of 2,2-dihydropolyfluoroalkanoates with phenols are reported, providing a new synthetic route to 2-(*F*-alkyl)-substituted chromones and their analogues.

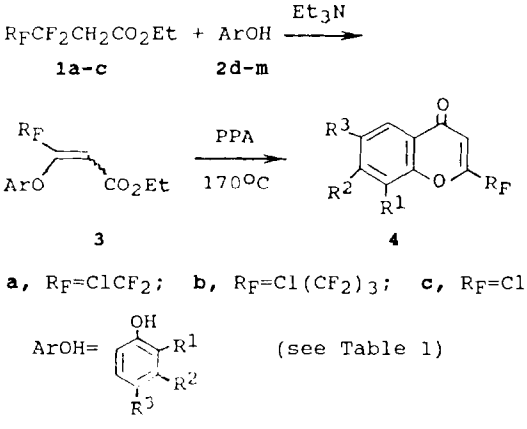
Results and discussions

As starting materials, 2,2-dihydropolyfluoroalkanoates were readily prepared through the sodium dithionite-initiated addition reaction of a polyfluoroalkyl iodide (R_FI) to ethyl vinyl ether followed by oxidation and esterification [12]. In a similar manner to aromatic amines, phenols **2** reacted with 2,2-dihydropolyfluoroalkanoates **1** in acetonitrile at 60 °C in the presence of triethylamine to give enol ethers **3** in high yield. Only the *Z*-isomer was obtained in the case of *p*-nitrophenol, *p*-bromophenol and 2,4-dichlorophenol, whilst other phenols produced a mixture of *E*- and *Z*-isomers as observed from their ^1H and ^{19}F NMR spectra.

$$R_FCF_2CH_2CO_2Et \xrightarrow[-HF]{Et_3N} R_FCF{=}CHCO_2Et \xrightarrow{ArOH}$$

$$R_fCFCH_2CO_2Et \xrightarrow[-HF]{Et_3N} R_FC{=}CHCO_2Et$$
$$\quad OAr \qquad\qquad\qquad\quad OAr$$

Cyclization of the fluorinated enol ethers **3** in polyphosphoric acid (PPA) at 170 °C for *c.* 10 h gave the corresponding 2-(*F*-alkyl)-substituted chromones **4** in good yield. The detailed results are listed in Table 1.



When a *meta*-substituted phenol such as *m*-cresol was used, cyclization gave two isomers in a ratio of nearly 1:1, namely 2-(*F*-alkyl)-5-methyl chromone (**4ck1**) and 2-(*F*-alkyl)-7-methyl chromone (**4ck2**). The two isomers were separated by column chromatography and their structures were assigned on the basis of ^1H NMR spectroscopy. The ^1H NMR absorption of compound

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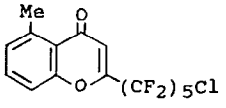
SSDI 0022-1139(93)02913-Y

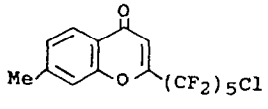
TABLE 1. Synthesis of 2-(*F*-alkyl)-substituted chromones

Fluorinated esters	Ar–OH				Isolated yield[a] (%)	
		R_1	R_2	R_3	Enol ether (**3**)[b]	Chromone (**4**)
1b	**2d**	H	H	H	**3bd**, 92	**4bd**, 81
1c	**2d**	H	H	H	**3cd**, 92	**4cd**, 75
1b	**2e**	H	H	Br	**3be**, 93	**4be**, 90
1b	**2f**	H	H	NO_2	**3bf**, 92	**4bf**, 58
1c	**2f**	H	H	NO_2	**3cf**, 90	**4cf**, 64
1a	**2g**	H	H	Me	**3ag**, 93	**4ag**, 86
1c	**2g**	H	H	Me	**3cg**, 84	**4cg**, 83
1b	**2h**	H	H	Ph	**3bh**, 88	**4bh**, 85
1c	**2h**	H	H	Ph	**3ch**, 84	**4ch**, 80
1a	**2j**	Cl	H	Cl	**3aj**, 91	**4aj**, 78
1b	**2j**	Cl	H	Cl	**3bj**, 90	**4bj**, 71
1c	**2k**	H	Me	H	**3ck**, 92	**4ck**, 92[c]
1a	**2m**	Me	H	H	**3am**, 91	**4am**, 81
1c	**2m**	Me	H	H	**3cm**, 88	**4cm**, 80

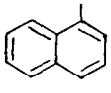
[a]Isolated yield after chromatography. All new compounds exhibited correct spectral and elemental analytical data.
[b]A mixture of *E*- and *Z*-isomers.
[c]Total yield of two isomers **4ck1** and **4ck2** in a ratio of 1:1.

4ck1 showed a multiplet at δ 7.03–7.58 ppm for three aromatic protons at positions 6, 7 and 8, while that of compound **4ck2** showed a singlet at δ 7.28 ppm for the aromatic proton at position 8 and an AB pattern centered at δ 8.60 ppm (J_{AB} = 8.0 Hz) for the other two aromatic protons at positions 5 and 6.

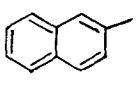




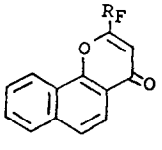
α-Naphthol and β-naphthol underwent similar reactions to give the corresponding enol ethers **5b** and **7a, b** corresponding to **3**, Ar =



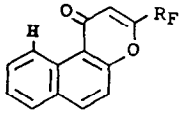
and



respectively, which were also converted to cyclization products (**6b** and **8a, b**) in overall yields of 80%–90%. Interestingly, cyclization of the derivatives (**7a, b**) of β-naphthol occurred only at position 1 [13] to give the compounds **8a** and **8b**, respectively. The ^{1}H NMR absorptions of compounds **8a** and **8b** showed a doublet at δ 9.85–10.00 ppm for the aromatic proton at position 10 due to the deshielding effect of the carbonyl group.



6b, $R_F = Cl(CF_2)_3$



8a, $R_F = ClCF_2$;
8b, $R_F = Cl(CF_2)_3$

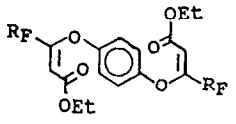
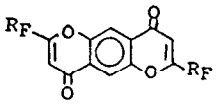
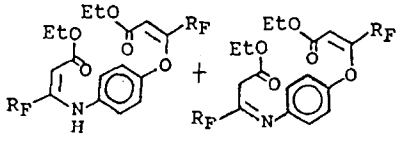
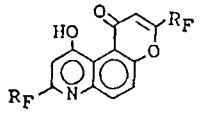
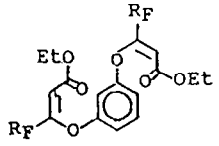
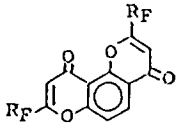
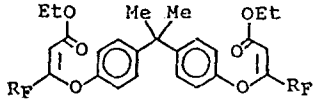
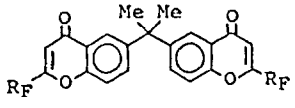
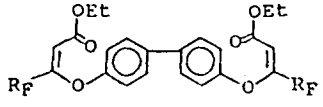
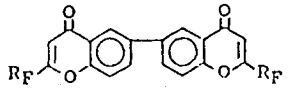
Under the same conditions, bifunctional nucleophiles such as hydroquinone, *p*-aminophenol, resorcinol, 4,4′-biphenol and 4,4′-dihydroxydiphenylpropane reacted with 2 equiv. of 2,2-dihydropolyfluoroalkanoates to give the corresponding polycyclic products (Table 2). Interestingly, cyclization reactions for *p*-aminophenol and resorcinol gave compound **12b** and **14b**, respectively, with an angular structure, while hydroquinone gave the linear product. These structures were also established by the ^{1}H NMR spectra. For example, the ^{1}H NMR absorptions of compounds **12b** and **14b** all showed a typical AB pattern for two aromatic protons.

In summary, we have developed a new, efficient synthetic procedure for the preparation of 2-(*F*-alkyl)-substituted chromones and their analogues such as bichromones and bischromones, starting from readily available 2,2-dihydropolyfluoroalkanoates.

Experimental

All melting points were uncorrected. IR spectra were measured with an IR-440 spectrometer, using liquid films. ^{1}H NMR spectra were recorded on a Varian EM-360A (60 MHz) spectrometer using TMS as internal or external standard and ^{19}F NMR spectra were recorded on a Varian EM-360L (56.4 MHz) spectrometer using TFA as external standard. The ^{19}F chemical shifts (in ppm) are positive for upfield shifts and the values reported are related to δ $CFCl_3$ (δ $CFCl_3 = \delta$ TFA + 76.8). Mass spectra were taken on a GC–MS 4021 spectrometer. The column chromatography was performed using silica gel H, particle size 10–40 μm.

TABLE 2. Synthesis of fluoroalkylated polycyclic chromones

Phenols	R_F	Product structures and isolated yield[a]	
Hydroquinone			
	$Cl(CF_2)_3$	(**9b**) 90%	(**10b**) 85%
p-Aminophenol			
	$Cl(CF_2)_3$	(**11b**) 80%	(**12b**) 86%
Resorcinol			
	$Cl(CF_2)_3$	(**13b**) 88%	(**14b**) 71%
4,4′-Dihydroxy-diphenylpropane[b]			
	$ClCF_2$	(**15a**) 81%	(**16a**) 81%
	$Cl(CF_2)_5$	(**15c**) 93%	(**16c**) 70%
4,4′-Biphenol[b]			
	$ClCF_2$	(**17a**) 86%	(**18a**) 70%
	$Cl(CF_2)_3$	(**17b**) 85%	(**18b**) 76%

[a]Overall yield after chromatography.
[b]Cyclization reactions carried out at 230 °C.

Preparations of enol ethers

A typical procedure was as follows. A mixture consisting of 2,2-dihydropolyfluoroalkanoate (5 mmol), phenol (6 mmol), Et_3N (20 mmol) and CH_3CN (5 mmol) was stirred at 60 °C for 5 h. The mixture was then extracted with ether and the ethereal layer washed with saturated NaCl solution. After removal of the solvent, the residue was purified by column chromatography using petroleum ether/ethyl acetate (20:1) as eluant to give the enol ether as an oily liquid.

Compound **3bd**: ^1H NMR (CCl_4) δ: 0.75–1.23 (3H, m, CH_2CH_3); 3.60–4.15 (2H, m, CH_2CH_3); 5.28, 6.07 (1H, olefinic proton for *E*- and *Z*-isomers); 6.82–7.33 (5H, m, Ar–H) ppm. ^{19}F NMR (CCl_4) δ: 67.1 (2F, s, CF_2Cl); 112.0, 114.8 (2F, $C{=}CCF_2$ for *E*- and *Z*-isomers); 118.8, 119.8 (2F, CF_2 for *E*- and *Z*-isomers) ppm. IR $\nu_{max.}$ (cm^{-1}): 1735 (C=O); 1660 (C=C); 1590 (Ar); 1120–1220 (C–F). MS *m/z*: 376 (M^+); 331 ($M^+ - OEt$); 191 ($M^+ - C_3F_6Cl$). (Analysis: Found: C, 44.42; H, 2.83; F, 30.34%. $C_{14}H_{11}ClF_6O_3$ requires: C, 44.64; H, 2.94; F, 30.26%).

Compound **3cd**: ^1H NMR (CCl_4) δ: 0.71–1.18 (3H, m, CH_2CH_3); 3.54–4.15 (2H, m, CH_2CH_3); 5.26, 6.05 (1H, olefinic proton for *E*- and *Z*-isomers); 6.79–7.03 (5H, m, Ar–H) ppm. ^{19}F NMR (CCl_4) δ: 67.1 (2F, s, CF_2Cl); 112.7, 115.5 (2F, $C{=}CCF_2$) for *E*- and *Z*-isomers); 119.5–120.0 (6F, m, other $3\times CF_2$) ppm. IR $\nu_{max.}$ (cm^{-1}): 1730 (C=O); 1660 (C=C); 1600 (Ar); 1120–1220 (C–F). (Analysis: Found: C, 40.10; H, 2.33; F, 39.79%. $C_{16}H_{11}ClF_{10}O_3$ requires: C, 40.31; H, 2.33; F, 39.85%).

Compound **3be**: ^1H NMR ($CDCl_3$) δ: 0.94–1.48 (3H, m, CH_2CH_3); 3.84–4.20 (2H, m, CH_2CH_3); 6.38 (1H, s, olefinic proton); 6.82–7.51 (4H, AB pattern, $J_{AB}=8.0$ Hz, Ar–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 66.7 (2F, s, CF_2Cl); 113.3 (2F, s, $C{=}CCF_2$); 120.3 (2F, other CF_2) ppm. IR $\nu_{max.}$ (cm^{-1}): 1735 (C=O); 1670 (C=C); 1590 (Ar); 1130–1220 (C–F). MS *m/z*: 456 ($M^+ + 2$); 454

(M^+); 409 ($M^+ - OEt$); 269 ($M^+ - C_3F_6Cl$). (Analysis: Found: C, 37.37; H, 2.13; F, 25.17%. $C_{14}H_{10}BrClF_6O_3$ requires: C, 36.91; H, 2.21; F, 25.12%).

Compound **3bf**: ^1H NMR (CCl_4) δ: 0.91–1.15 (3H, t, CH_2CH_3, $^3J_{H-H}=6.9$ Hz); 3.78–4.14 (2H, q, CH_2CH_3, $^3J_{H-H}=6.9$ Hz); 6.29 (1H, s, olefinic proton); 6.93–8.25 (AB pattern, 4H for Ar–H; $J_{AB}=8.0$ Hz) ppm. ^{19}F NMR (CCl_4) δ: 66.5 (2F, s, CF_2Cl); 113.8 (2F, s, $C=CCF_2$); 118.8 (2F, s, other CF_2) ppm. IR $\nu_{max.}$ (cm^{-1}): 1730 (C=O); 1670 (C=C); 1620 (Ar); 1120–1200 (C–F). MS *m/z*: 442 ($M^+ + 1$); 421 (M^+); 376 ($M^+ - OEt$); 330 ($M^+ - NO_2 - OEt$); 236 ($M^+ - C_3F_6Cl$). (Analysis: Found: C, 39.40; H, 2.09; N, 3.20; F, 26.41%. $C_{14}H_{10}ClF_6NO_5$ requires: C, 39.88; H, 2.39; N, 3.32; F, 27.03%).

Compound **3cf**: ^1H NMR (CCl_4) δ: 0.92–1.15 (3H, t, CH_2CH_3, $^3J_{H-H}=6.9$ Hz); 3.78–4.13 (2H, q, CH_2CH_3, $^3J_{H-H}=6.9$ Hz); 6.28 (1H, s, olefinic proton); 6.93–8.22 (AB pattern, 4H for Ar–H; $J_{AB}=8.0$ Hz) ppm. ^{19}F NMR (CCl_4) δ: 67.1 (2F, s, CF_2Cl); 114.9 (2F, s, $C=CCF_2$); 119.3–120.5 (6F, m, other $3\times CF_2$) ppm. IR $\nu_{max.}$ (cm^{-1}): 1730 (C=O); 1670 (C=C); 1620, 1600 (Ar); 1120–1230 (C–F). (Analysis: Found: C, 36.72; H, 1.96; N, 2.79; F, 37.17%. $C_{16}H_{10}ClF_{10}NO_5$ requires: C, 36.84; H, 1.93; N, 2.68; F, 36.42%).

Compound **3ag**: ^1H NMR (CCl_4) δ: 0.70–1.21 (3H, m, CH_2CH_3); 2.20 (3H, s, Ar–CH_3); 3.55–4.16 (2H, m, CH_2CH_3); 5.01, 6.00 (1H, olefinic proton for *E*- and *Z*-isomers); 6.46–7.18 (4H, m, Ar–H) ppm. ^{19}F NMR (CCl_4) δ: 54.8, 57.6 (2F, CF_2Cl for *E*- and *Z*-isomers) ppm. IR $\nu_{max.}$ (cm^{-1}): 1735 (C=O); 1670 (C=C); 1610, 1600 (Ar); 1110–1200 (C–F). (Analysis: Found: C, 53.62; H, 4.56; F, 12.75%). $C_{13}H_{13}ClF_2O_3$ requires: C, 53.71; H, 4.51; F, 13.07%).

Compound **3cg**: ^1H NMR ($CDCl_3$) δ: 0.92–1.37 (3H, m, CH_2CH_3); 2.32 (3H, s, Ar–CH_3); 3.78–4.35 (2H, m, CH_2CH_3); 5.46, 6.22 (1H, olefinic proton for *E*- and *Z*-isomers); 7.82–8.28 (4H, m, Ar–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 67.2 (2F, s, CF_2Cl); 112.2, 114.9 (2F, $C=CCF_2$ for *E*- and *Z*-isomers); 119.6–120.8 (6F, m, other $3\times CF_2$) ppm. IR $\nu_{max.}$ (cm^{-1}): 1740 (C=O); 1670 (C=C); 1610 (Ar); 1110–1220 (C–F). MS *m/z*: 490 (M^+); 445 ($M^+ - OEt$); 205 ($M^+ - C_5F_{10}Cl$). (Analysis: Found: C, 40.80; H, 2.95; F, 39.33%. $C_{17}H_{13}ClF_{10}O_3$ requires: C, 41.61; H, 2.67; F, 38.71%).

Compound **3bh**: ^1H NMR (CCl_4) δ: 0.86–1.31 (3H, m, CH_2CH_3); 3.71–4.26 (2H, m, CH_2CH_3); 5.42, 6.14 (1H, olefinic proton for *E*- and *Z*-isomers); 6.94–7.65 (9H, m, Ar–H) ppm. ^{19}F NMR (CCl_4) δ: 66.4 (2F, s, CF_2Cl); 112.2, 115.1 (2F, $C=CCF_2$ for *E*- and *Z*-isomers); 119.1, 120.2 (2F, CF_2 for *E*- and *Z*-isomers) ppm. IR $\nu_{max.}$ (cm^{-1}): 1730 (C=O); 1670 (C=C); 1610 (Ar); 1120–1290 (C–F). (Analysis: Found: C, 52.89; H, 2.03; F, 28.70%. $C_{20}H_{15}ClF_6O_3$ requires: C, 53.16; H, 2.23; F, 28.03%).

Compound **3ch**: ^1H NMR (CCl_4) δ: 0.83–1.29 (3H, m, CH_2CH_3); 3.68–4.22 (2H, m, CH_2CH_3); 5.40, 6.11 (1H, olefinic proton for *E*- and *Z*-isomers); 6.90–7.61 (9H, m, Ar–H) ppm. ^{19}F NMR (CCl_4) δ: 67.0 (2F, s, CF_2Cl); 112.0, 114.8 (2F, $C=CCF_2$ for *E*- and *Z*-isomers); 119.2–120.1 (6F, m, other $3\times CF_2$) ppm. IR $\nu_{max.}$ (cm^{-1}) 1730 (C=O); 1660 (C=C); 1600 (Ar); 1120–1240 (C–F). MS *m/z*: 552 (M^+); 507 ($M^+ - OEt$). (Analysis: Found: C, 47.00; H, 2.53; F, 34.50%. $C_{22}H_{15}ClF_{10}O_3$ requires: C, 47.80; H, 2.74; F, 34.37%).

Compound **3aj**: ^1H NMR ($CDCl_3$) δ: 0.99–1.40 (3H, m, CH_2CH_3); 3.88–4.25 (2H, m, CH_2CH_3); 5.06, 6.26 (1H, olefinic proton for *E*- and *Z*-isomers); 6.86–7.49 (3H, m, Ar–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 55.3, 58.4 (2F, CF_2Cl for *E*- and *Z*-isomers) ppm. IR $\nu_{max.}$ (cm^{-1}): 1730 (C=O); 1670 (C=C); 1590 (Ar); 1100–1200 (C–F). MS *m/z*: 345 ($M^+ + 1$); 344 (M^+); 299 ($M^+ - OEt$); 259 ($M^+ - CF_2Cl$). (Analysis: Found: C, 41.49; H, 2.44; F, 10.96%. $C_{12}H_9ClF_2O_3$ requires: C, 41.71; H, 2.63; F, 11.00%).

Compound **3bj**: ^1H NMR ($CDCl_3$) δ: 0.92–1.15 (3H, t, CH_2CH_3, $^3J_{H-H}=6.9$ Hz); 3.73–4.08 (2H, q, CH_2CH_3, $^3J_{H-H}=6.9$ Hz); 6.14 (1H, olefinic proton); 6.73–7.40 (3H, m, Ar–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 66.5 (2F, s, CF_2Cl); 114.1 (2F, s, $C=CCF_2$); 119.1 (2F, s, other CF_2) ppm. IR $\nu_{max.}$ (cm^{-1}): 1730 (C=O); 1670 (C=C); 1590 (Ar); 1120–1200 (C–F). MS *m/z*: 444 (M^+); 409 ($M^+ - Cl$); 399 ($M^+ - OEt$); 374 ($M^+ - 2Cl$); 259 ($M^+ - C_3F_6Cl$). (Analysis: Found: C, 37.46; H, 1.87; F, 25.10%. $C_{14}H_9ClF_6O_3$ requires: C, 37.74; H, 2.04; F, 25.58%).

Compound **3ck**: ^1H NMR (CCl_4) δ: 0.76–1.23 (3H, m, CH_2CH_3); 2.21 (3H, s, Ar–CH_3); 3.59–4.18 (2H, m, CH_2CH_3); 5.28, 6.03 (1H, olefinic proton for *E*- and *Z*-isomers); 6.60–7.20 (4H, m, Ar–H) ppm. ^{19}F NMR (CCl_4) δ: 67.3 (2F, s, CF_2Cl); 111.3, 114.1 (2F, $C=CCF_2$ for *E*- and *Z*-isomers); 119.7–120.6 (6F, m, other $3\times CF_2$) ppm. IR $\nu_{max.}$ (cm^{-1}): 1730 (C=O); 1670 (C=C); 1620, 1600 (Ar); 1100–1200 (C–F). MS *m/z*: 490 (M^+); 445 ($M^+ - OEt$); 205 ($M^+ - C_5F_{10}Cl$). (Analysis: Found: C, 41.47; H, 2.61; F, 38.57%. $C_{17}H_{13}ClF_{10}O_3$ requires: C, 41.61; H, 2.67; F, 38.71%).

Compound **3am**: ^1H NMR ($CDCl_3$) δ: 0.88–1.38 (3H, m, CH_2CH_3); 2.25, 2.35 (3H, d, Ar–CH_3 for *E*- and *Z*-isomers); 3.73–4.38 (2H, m, CH_2CH_3); 5.13, 6.15 (1H, olefinic proton for *E*- and *Z*-isomers); 6.96–7.30 (4H, m, Ar–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 55.2, 58.5 (2F, $C=CCF_2$ for *E*- and *Z*-isomers) ppm. IR $\nu_{max.}$ (cm^{-1}): 1730 (C=O); 1660 (C=C); 1600 (Ar); 1100–1210 (C–F). (Analysis: Found: C, 53.60; H, 4.37; F, 13.07%. $C_{13}H_{13}ClF_2O_3$ requires: C, 53.71; H, 4.51; F, 13.09%).

Compound **3cm**: ^1H NMR (CCl_4) δ: 0.76–1.25 (3H, m, CH_2CH_3); 2.13, 2.16 (3H, d, Ar–CH_3 for *E*- and *Z*-isomers); 3.55–4.21 (2H, m, CH_2CH_3); 5.10, 5.98 (1H, olefinic proton for *E*- and *Z*-isomers); 6.75–7.11 (4H,

m, Ar–H) ppm. ^{19}F NMR (CCl_4) δ: 67.1 (2F, s, CF_2Cl); 112.0, 115.4 (2F, C=CCF_2 for *E*- and *Z*-isomers); 119.5–120.3 (6F, m, other 3×CF_2) ppm. IR $\nu_{max.}$ (cm^{-1}): 1740 (C=O); 1660 (C=C); 1590 (Ar); 1140–1210 (C–F). MS *m/z*: 490 (M^+); 445 ($M^+ - OEt$); 205 ($M^+ - C_5F_{10}Cl$). (Analysis: Found: C, 42.02; H, 2.38; F, 38.23%. $C_{17}H_{13}ClF_{10}O_3$ requires: C, 41.61; H, 2.67; F, 38.71%).

Compound **5b**: ^{1}H NMR ($CDCl_3$) δ: 0.55–1.32 (3H, m, CH_2CH_3); 3.55–4.32 (2H, m, CH_2CH_3); 5.93, 6.33 (1H, olefinic proton for *E*- and *Z*-isomers); 6.90–8.33 (7H, m, Ar–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 66.5 (2F, s, CF_2Cl); 110.9, 114.3 (2F, C=CCF_2) for *E*- and *Z*-isomers); 117.8, 119.1 (2F, CF_2 for *E*- and *Z*-isomers) ppm. IR $\nu_{max.}$ (cm^{-1}): 1730 (C=O); 1660 (C=C); 1600 (Ar); 1100–1220 (C–F). MS *m/z*: 426 (M^+); 381 ($M^+ - OEt$). (Analysis: Found: C, 50.33; H, 3.22; F, 26.84%. $C_{18}H_{13}ClF_6O_3$ requires: C, 50.66; H, 3.07; F, 26.71%).

Compound **7a**: ^{1}H NMR ($CDCl_3$) δ: 0.64–1.23 (3H, m, CH_2CH_3); 3.57–4.16 (2H, m, CH_2CH_3); 5.26, 6.27 (1H, olefinic proton for *E*- and *Z*-isomers); 7.20–7.78 (7H, m, Ar–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 55.3, 57.9 (2F, CF_2Cl for *E*- and *Z*-isomers) ppm. IR $\nu_{max.}$ (cm^{-1}): 1730 (C=O); 1660 (C=C); 1600 (Ar); 1140–1240 (C–F). MS *m/z*: 326 (M^+); 281 ($M^+ - OEt$); 241 ($M^+ - CF_2Cl$). (Analysis: Found: C, 58.59; H, 4.59; F, 11.64%. $C_{16}H_{13}ClF_2O_3$ requires: C, 58.82; H, 4.01; F, 11.63%).

Compound **7b**: ^{1}H NMR ($CDCl_3$) δ: 0.82–1.23 (3H, m, CH_2CH_3); 3.70–43.23 (2H, m, CH_2CH_3); 5.50, 6.32 (1H, olefinic proton for *E*- and *Z*-isomers); 7.26–7.78 (7H m, m, Ar–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 66.5 (2F, s, CF_2Cl); 111.4, 114.0 (2F, C=CCF_2 for *E*- and *Z*-isomers); 118.0, 119.0 (2F, CF_2 for *E*- and *Z*-isomers) ppm. IR $\nu_{max.}$ (cm^{-1}): 1730 (C=O); 1660 (C=C); 1600 (Ar); 1120–1220 (C–F). MS *m/z*: 426 (M^+); 381 ($M^+ - OEt$); 241 ($M^+ - C_3F_6Cl$). (Analysis: Found: C, 50.92; H, 2.83; F, 26.91%. $C_{18}H_{13}ClF_6O_3$ requires: C, 50.66; H, 3.07; F, 26.71%).

Compound **9b**: ^{1}H NMR ($CDCl_3$) δ: 0.95–1.22 (6H, m, 2×CH_2CH_3); 3.82–4.23 (4H, m, 2×CH_2CH_3); 5.41, 6.22 (2H, olefinic proton for *E*- and *Z*-isomers); 6.96, 7.06 (4H, d, Ar–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 66.8 (4F, s, 2×CF_2Cl); 111.5, 118.0 (4F, 2×C=CCF_2 for *E*- and *Z*-isomers); 118.4, 119.5 (4F, 2×CF_2 for *E*- and *Z*-isomers) ppm. IR $\nu_{max.}$ (cm^{-1}): 1730 (C=O); 1660 (C=C); 1600 (Ar); 1120–1220 (C–F). MS *m/z*: 674 (M^+); 629 ($M^+ - OEt$); 583 ($M^+ - OEt - EtOH$). (Analysis: Found: C, 39.42; H, 2.45; F, 34.24%. $C_{22}H_{16}Cl_2F_{12}O_6$ requires: C, 39.13; H, 2.39; F, 33.76%).

Compound **11b**: ^{1}H NMR ($CDCl_3$) δ: 0.90–1.32 (6H, m, 2×CH_2CH_3); 3.40 (s, CH_2CO in imine); 3.81–4.30 (4H, m, 2×CH_2CH_3); 5.35, 5.41, 6.18 (olefinic proton); 6.70–7.20 (4H, m, Ar–H); 9.32 (NH in enamine) ppm. ^{19}F NMR ($CDCl_3$) δ: 66.6 (4F, s, 2×CF_2Cl); 102.0, 107.3, 114.3 (4F, N=CCF_2 and C=CCF_2); 119.0 (4F, s, other 2×CF_2) ppm. IR $\nu_{max.}$ (cm^{-1}): 3300 (NH); 1730 (C=O); 1670 (C=N); 1660 (C=C); 1620 (Ar); 1100–1280 (C–F). MS *m/z*: 674 ($M^+ + 1$); 673 (M^+); 628 ($M^+ - OEt$); 582 ($M^+ - OEt - EtOH$); 488 ($M^+ - C_3F_6Cl$); 442 ($M^+ - EtOH - C_3F_6Cl$). (Analysis: Found: C, 39.04; H, 2.82; N, 2.12; F, 33.82%. $C_{22}H_{17}Cl_2F_{12}NO_5$ requires: C, 39.19; H, 2.54; N, 2.08; F, 33.81%).

Compound **13b**: ^{1}H NMR ($CDCl_3$) δ: 0.87–1.28 (6H, m, 2×CH_2CH_3); 3.72–4.12 (4H, m, 2×CH_2CH_3); 5.40, 6.14 (2H, olefinic proton for *E*-and *Z*-isomers); 6.56–7.43 (4H, m, Ar–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 66.5 (4F, s, 2×CF_2Cl); 111.4, 114.3 (4F, 2×C=CCF_2 for *E*- and *Z*-isomers); 118.2, 119.2 (4F, other 2×CF_2 for *E*- and *Z*-isomers) ppm. IR $\nu_{max.}$ (cm^{-1}): 1740 (C=O); 1670 (C=C); 1620, 1600 (Ar); 1110–1240 (C–F). MS *m/z*: 674 (M^+); 629 ($M^+ - OEt$); 583 ($M^+ - OEt - EtOH$). (Analysis: Found: C, 39.34; H, 2.27; F, 34.52%. $C_{22}H_{16}Cl_2F_{12}O_6$ requires: C, 39.13; H, 2.39; F, 33.76%).

Compound **15a**: ^{1}H NMR ($CDCl_3$) δ: 0.88–1.40 (6H, m, 2×CH_2CH_3); 1.61 (6H, s, 2×CH_3); 3.66–4.29 (4H, m, 2×CH_2CH_3); 5.26, 6.19 (2H, 2×olefinic proton for *E*- and *Z*-isomers); 6.90–7.31 (8H, m, Ar–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 55.4, 58.2 (4F, 2×CF_2Cl for *E*- and *Z*-isomers) ppm. IR $\nu_{max.}$ (cm^{-1}): 1730 (C=O); 1660 (C=C); 1600 (Ar); 1130–1240 (C–F). MS *m/z*: 592 (M^+); 577 ($M^+ - CH_3$). (Analysis: Found: C, 54.10; H, 4.19; F, 13.03%. $C_{27}H_{26}Cl_2F_4O_6$ requires: C, 54.65; H, 4.42; F, 12.81%).

Compound **15c**: ^{1}H NMR (CCl_4) δ: 0.82–1.12 (6H, m, 2×CH_2CH_3); 1.59 (6H, s, 2×CH_3); 3.69–4.26 (4H, m, 2×CH_2CH_3); 5.40, 6.11 (2H, 2×olefinic proton for *E*- and *Z*-isomers); 6.90–7.29 (8H, m, Ar–H) ppm. ^{19}F NMR (CCl_4) δ: 67.1 (4F, s, 2×CF_2Cl); 112.0, 114.9 (4F, 2×C=CCF_2 for *E*- and *Z*-isomers); 118.2–121.0 (12F, m, other 2×3×CF_2) ppm. IR $\nu_{max.}$ (cm^{-1}): 1740 (C=O); 1670 (C=C); 1610 (Ar); 1110–1220 (C–F). (Analysis: Found: C, 42.48; H, 2.36; F, 38.02%. $C_{35}H_{26}Cl_2F_{20}O_6$ requires: C, 42.32; H, 2.64; F, 38.25%).

Compound **17a**: ^{1}H NMR (CCl_4) δ: 0.87–1.35 (6H, m, 2×CH_2CH_3); 3.75–4.20 (4H, m, 2×CH_2CH_3); 5.17, 6.16 (2H, 2×olefinic proton for *E*- and *Z*-isomers); 5.98–7.63 (8H, m, Ar–H) ppm. ^{19}F NMR (CCl_4) δ: 55.6, 58.1 (4F, s, 2×CF_2Cl for *E*- and *Z*-isomers) ppm. IR $\nu_{max.}$ (cm^{-1}): 1730 (C=O); 1660 (C=C); 1110–1240 (C–F). MS *m/z*: 551 (M^+); 505 ($M^+ - EtOH$); 459 ($M^+ - 2EtOH$). (Analysis: Found: C, 52.07; H, 3.37; F, 13.77%. $C_{24}H_{20}Cl_2F_4O_6$ requires: C, 52.59; H, 3.66; F, 13.78%).

Compound **17b**: ^{1}H NMR (CCl_4) δ: 0.82–1.32 (6H, m, 2×CH_2CH_3); 3.65–4.18 (4H, m, 2×CH_2CH_3); 5.44, 6.19 (2H, 2×olefinic proton for *E*- and *Z*-isomers); 6.93–7.61 (8H, m, Ar–H) ppm. ^{19}F NMR (CCl_4) δ: 66.6 Z(4F, s, 2×CF_2Cl); 111.4, 114.2 (4F, 2×C=CCF_2 for *E*- and *Z*-isomers); 118.1, 119.1 (4F, other 2×CF_2 for

E- and *Z*-isomers) ppm. IR $\nu_{max.}$ (cm^{-1}): 1740 (C=O); 1670 (C=C); 1600 (Ar); 1120–1210 (C–F). (Analysis: Found: C, 44.56; H, 2.47; F, 30.15%. $C_{28}H_{20}Cl_2F_{12}O_6$ requires: C, 44.76; H, 2.68; F, 30.34%).

Preparation of 2-(F-alkyl)-substituted chromones

A typical procedure was as follows. Enol ether (1 g) and polyphosphoric acid (PPA) (20 g) were stirred together at 170 °C for 10 h. After cooling to room temperature, the mixture was neutralized with aqueous 3 N NaOH and extracted with ether. The organic layer was washed with saturated NaCl solution. Removal of the solvent followed by column chromatography using petroleum ether/ethyl acetate (20:1) as eluant gave the pure fluoroalkylated chromones.

Compound **4bd**: M.p. 63–65 °C. ^1H NMR ($CDCl_3$) δ: 6.77 (1H, s, olefinic proton); 7.48–8.29 (4H, m, Ar–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 66.9 (2F, s, CF_2Cl); 116.1 (2F, s, $C=CCF_2$); 119.8 (2F, s, other CF_2) ppm. IR $\nu_{max.}$ (cm^{-1}): 1670 (C=O); 1640 (C=C); 1600 (Ar); 1100–1220 (C–F). MS *m/z*: 330 (M^+); 295 ($M^+ - Cl$); 267 ($M^+ - CO - Cl$); 167 ($M^+ - C_2F_4Cl - CO$). (Analysis: Found: C, 43.62; H, 1.59; F, 33.95%. $C_{12}H_5ClF_6O_2$ requires: C, 43.59; H, 1.52; F, 34.48%).

Compound **4cd**: M.p. 42–44 °C. ^1H NMR (CCl_4) δ: 6.60 (1H, s, olefinic proton); 7.23–8.15 (4H, m, Ar–H) ppm. ^{19}F NMR (CCl_4) δ: 66.9 (2F, s, CF_2Cl); 116.9 (2F, s, $C=CCF_2$); 119.4–121.3 (6F, m, other $3\times CF_2$) ppm. IR $\nu_{max.}$ (cm^{-1}): 1680 (C=O); 1660 (C=C); 1600 (Ar); 1120–1220 (C–F). MS *m/z*: 430 (M^+); 195 ($M^+ - C_4F_8Cl$); 167 ($M^+ - C_4F_8Cl - CO$). (Analysis: Found: C, 39.07; H, 1.16; F, 43.90%. $C_{14}H_5ClF_{10}O_2$ requires: C, 39.05; H, 1.17; F, 44.12%).

Compound **4be**: M.p. 60–62 °C. ^1H NMR (CCl_4) δ: 6.63 (1H, s, olefinic proton); 7.27–7.86 (2H, AB pattern, C_7–H, C_8–H, $J_{AB}=9.0$ Hz); 8.21 (1H, s, C_5–H) ppm. ^{19}F NMR (CCl_4) δ: 67.0 (2F, s, CF_2Cl); 116.1 (2F, s, $C=CCF_2$); 119.8 (2F, s, other CF_2) ppm. IR $\nu_{max.}$ (cm^{-1}): 1670 (C=O); 1640 (C=C); 1600 (Ar); 1120–1220 (C–F). MS *m/z*: 410 ($M^+ + 2$); 408 (M^+); 247 ($M^+ - C_2F_4Cl - CO$). (Analysis: Found: C, 35.17; H, 1.12; F, 27.03%. $C_{12}H_4BrClF_6O_2$ requires: C, 35.20; H, 0.98; F, 27.84%).

Compound **4bf**: M.p. 70–72 °C. ^1H NMR (CCl_4) δ: 6.72 (1H, s, olefinic proton); 7.59–8.63 (2H, AB pattern, C_7–H, C_8–H, $J_{AB}=9.0$ Hz); 8.87 (1H, s, C_5–H) ppm. ^{19}F NMR (CCl_4) δ: 66.8 (2F, s, CF_2Cl); 118.9 (2F, s, $C=CCF_2$); 120.4 (2F, other CF_2) ppm. IR $\nu_{max.}$ (cm^{-1}): 1680 (C=O); 1650 (C=C); 1620 (Ar); 1120–1200 (C–F). MS *m/z*: 375 (M^+); 345 ($M^+ - NO$); 329 ($M^+ - NO_2$); 166 ($M^+ - C_2F_4Cl - CO$). (Analysis: Found: C, 39.11; H, 1.34; N, 3.60; F, 30.20%. $C_{14}H_{10}ClF_6NO_5$ requires: C, 38.37; H, 1.07; N, 3.73; F, 30.35%).

Compound **4cf**: M.p. 99–101 °C. ^1H NMR ($CDCl_3$) δ: 6.86 (1H, s, olefinic proton); 7.66–8.21 (2H, AB pattern, C_7–H, C_8–H, $J_{AB}=9.0$ Hz); 9.07 (1H, s, C_5–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 67.3 (2F, s, CF_2Cl); 116.8 (2F, s, $C=CCF_2$); 119.1–121.1 (6F, m, other $3\times CF_2$) ppm. IR $\nu_{max.}$ (cm^{-1}): 1670 (C=O); 1640 (C=C); 1620, 1590 (Ar); 1130–1210 (C–F). (Analysis: Found: C, 35.49; H, 1.23; N, 3.13; F, 39.04%. $C_{14}H_4ClF_{10}NO_4$ requires: C, 35.35; H, 0.85; N, 2.94; F, 39.94%).

Compound **4ag**: M.p. 74–76 °C. ^1H NMR (CCl_4) δ: 2.42 (3H, s, Ar–CH_3); 6.52 (1H, s, olefinic proton); 7.38 (2H, s, C_7–H, C_8–H); 7.85 (1H, s, C_5–H) ppm. ^{19}F NMR (CCl_4) δ: 59.1 (2F, s, CF_2Cl) ppm. IR $\nu_{max.}$ (cm^{-1}): 1670 (C=O); 1640 (C=C); 1620 (Ar); 1130–1220 (C–F). MS *m/z*: 244 (M^+); 209 ($M^+ - Cl$); 181 ($M^+ - Cl - CO$). (Analysis: Found: C, 53.50; H, 2.79; F, 15.92%. $C_{11}H_7ClF_2O_2$ requires: C, 54.00; H, 2.88; F, 15.53%).

Compound **4cg**: M.p. 63–65 °C. ^1H NMR (CCl_4) δ: 2.45 (3H, s, Ar–CH_3); 6.61 (1H, s, olefinic proton); 7.41 (2H, s, C_7–H, C_8–H); 7.93 (1H, s, C_5–H) ppm. ^{19}F NMR (CCl_4) δ: 66.9 (2F, s, CF_2Cl); 116.9 (2F, s, $C=CCF_2$); 119.1–121.2 (6F, m, other $3\times CF_2$) ppm. IR $\nu_{max.}$ (cm^{-1}): 1670 (C=O); 1640 (C=C); 1620 (Ar); 1120–1220 (C–F). (Analysis: Found: C, 40.55; H, 1.57; F, 42.25%. $C_{15}H_7ClF_{10}O_2$ requires: C, 40.52; H, 1.59; F, 42.73%).

Compound **4bh**: M.p. 102–104 °C. ^1H NMR ($CDCl_3$) δ: 6.87 (1H, s, olefinic proton); 7.52–8.19 (7H, m, Ar–H); 8.52 (1H, s, C_5–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 66.9 (2F, s, CF_2Cl); 116.2 (2F, s, $C=CCF_2$); 119.9 (2F, s, other CF_2) ppm. IR $\nu_{max.}$ (cm^{-1}): 1670 (C=O); 1620 (Ar); 1120–1220 (C–F). MS *m/z*: 406 (M^+); 243 ($M^+ - C_2F_4Cl - CO$). (Analysis: Found: C, 52.89; H, 2.03; F, 28.70%. $C_{18}H_9ClF_6O_2$ requires: C, 53.16; H, 2.23; F, 28.03%).

Compound **4ch**: M.p. 128–130 °C. ^1H NMR ($CDCl_3$) δ: 6.82 (1H, s, olefinic proton); 7.46–8.15 (7H, m, Ar–H); 8.47 (1H, s, C_5–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 67.2 (2F, s, CF_2Cl); 116.7 (2F, s, $C=CCF_2$); 119.1–121.2 (6F, m, other $3\times CF_2$) ppm. IR $\nu_{max.}$ (cm^{-1}): 1670 (C=O); 1620 (Ar); 1140–1220 (C–F). MS *m/z*: 506 (M^+); 243 ($M^+ - C_4F_8Cl - CO$). (Analysis: Found: C, 47.11; H, 1.61; F, 38.35%. $C_{20}H_9ClF_{10}O_2$ requires: C, 47.40; H, 1.79; F, 37.49%).

Compound **4aj**: M.p. 65–67 °C. ^1H NMR (CCl_4) δ: 6.63 (1H, s, olefinic proton); 7.76 (1H, s, C_7–H); 8.00 (1H, s, C_5–H) ppm. ^{19}F NMR (CCl_4) δ: 58.9 (2F, s, CF_2Cl) ppm. IR $\nu_{max.}$ (cm^{-1}): 1680 (C=O); 1640 (C=C); 1600 (Ar); 1120–1220 (C–F). MS *m/z*: 298 (M^+); 263 ($M^+ - Cl$); 235 ($M^+ - CO - Cl$). (Analysis: Found: C, 40.20; H, 1.12; F, 12.68%. $C_{10}H_3Cl_3F_2O_2$ requires: C, 40.10; H, 1.01; F, 12.69%).

Compound **4bj**: M.p. 54–56 °C. ^1H NMR ($CDCl_3$) δ: 6.81 (1H, s, olefinic proton); 7.81 (1H, s, C_7–H); 8.09 (1H, s, C_5–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 66.9 (2F, s, CF_2Cl); 116.0 (2F, s, $C=CCF_2$); 119.7 (2F, s,

other CF_2) ppm. IR $\nu_{max.}$ (cm^{-1}): 1670 (C=O); 1600 (Ar); 1120–1200 (C–F). (Analysis: Found: C, 36.42; H, 0.94; F, 28.60%. $C_{12}H_3Cl_3F_6O_2$ requires: C, 36.08; H, 0.76; F, 28.53%).

Compound **4ck1**: M.p. 41–43 °C. ^1H NMR (CCl_4) δ: 2.72 (3H, s, Ar–CH_3); 6.54 (1H, s, olefinic proton); 7.03–7.58 (3H, m, Ar–H) ppm. ^{19}F NMR (CCl_4) δ: 67.1 (2F, s, CF_2Cl); 117.3 (2F, s, C=CCF_2); 119.4–121.5 (6F, m, other 3×CF_2) ppm. IR $\nu_{max.}$ (cm^{-1}): 1670 (C=O); 1610 (Ar); 1120–1220 (C–F). MS *m/z*: 444 (M^+); 181 ($M^+ - C_4F_8Cl - CO$). (Analysis: Found: C, 40.35; H, 1.69; F, 42.73%. $C_{15}H_7ClF_{10}O_2$ requires: C, 40.52; H, 1.59; F, 42.73%).

Compound **4ck2**: M.p. 70–72 °C. ^1H NMR (CCl_4) δ: 2.43 (3H, s, Ar–CH_3); 6.58 (1H, s, olefinic proton); 7.15–8.06 (2H, AB pattern, C_5–H, C_6–H, J_{AB}=8.0 Hz); 7.28 (1H, s, C_8–H) ppm. ^{19}F NMR (CCl_4) δ: 66.9 (2F, s CF_2Cl); 116.8 (2F, s, C=CCF_2); 119.3–121.4 (6F, m, other 3×CF_2) ppm. IR $\nu_{max.}$ (cm^{-1}): 1670 (C=O); 1610 (Ar); 1120–1220 (C–F). MS *m/z*: 444 (M^+); 181 ($M^+ - C_4F_8Cl - CO$). (Analysis: Found: C, 40.81; H, 1.45; F, 42.97%. $C_{15}H_7ClF_{10}O_2$ requires: C, 40.52; H, 1.59; F, 42.73%).

Compound **4am**: M.p. 52–54 °C. ^1H NMR ($CDCl_3$) δ: 2.52 (3H, s, Ar–CH_3); 6.74 (1H, s, olefinic proton); 7.32–8.19 (3H, m, Ar–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 59.1 (2F, s, CF_2Cl) ppm. IR $\nu_{max.}$ (cm^{-1}): 1670 (C=O); 1610, 1600 (Ar); 1130–1230 (C–F). (Analysis: Found: C, 53.66; H, 3.06; F, 15.17%. $C_{11}H_7ClF_2O_2$ requires: C, 54.00; H, 2.88; F, 15.53%).

Compound **4cm**: M.p. 51–53 °C. ^1H NMR (CCl_4) δ: 2.40 (3H, s, Ar–CH_3); 6.61 (1H, s, olefinic proton); 7.15–8.01 (3H, m, Ar–H) ppm. ^{19}F NMR (CCl_4) δ: 67.2 (2F, s, CF_2Cl); 116.9 (2F, s, C=CCF_2); 119.1–121.5 (6F, m, other 3×CF_2) ppm. IR $\nu_{max.}$ (cm^{-1}): 1670 (C=O); 1640 (C=C); 1610, 1590 (Ar); 1110–1220 (C–F). MS *m/z*: 444 (M^+); 409 ($M^+ - Cl$); 209 ($M^+ - C_4F_8Cl$); 181 ($M^+ - C_4F_8Cl - CO$). (Analysis: Found: C, 40.66; H, 1.29; F, 42.11%. $C_{15}H_7ClF_{10}O_2$ requires: C, 40.52; H, 1.59; F, 42.73%).

Compound **6b**: M.p. 130–132 °C. ^1H NMR ($CDCl_3$) δ: 6.89 (1H, s, olefinic proton); 7.60–8.58 (6H, m, Ar–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 66.8 (2F, s, CF_2Cl); 116.1 (2F, s, C=CCF_2); 120.1 (2F, s, other CF_2) ppm. IR $\nu_{max.}$ (cm^{-1}): 1660 (C=O); 1600 (Ar); 1120–1200 (C–F). MS *m/z*: 380 (M^+); 345 ($M^+ - Cl$); 217 ($M^+ - C_2F_4Cl$). (Analysis: Found: C, 50.45; H, 1.79; F, 29.87%. $C_{16}H_7ClF_6O_2$ requires: C, 50.48; H, 1.85; F, 29.94%).

Compound **8a**: M.p. 102–104 °C. ^1H NMR (CCl_4) δ: 6.62 (1H, s, olefinic proton); 7.30–8.05 (5H, m, other Ar–H); 9.75–9.88 (1H, d, $^3J_{H-H}$=7.8 Hz, C_{10}–H) ppm. ^{19}F NMR (CCl_4) δ: 58.7 (2F, s, CF_2Cl) ppm. IR $\nu_{max.}$ (cm^{-1}): 1670 (C=O); 1640 (C=C); 1600 (Ar); 1130–1240 (C–F). MS *m/z*: 280 (M^+); 245 ($M^+ - Cl$); 217 ($M^+ - CO - Cl$). (Analysis: Found: C, 59.61; H, 2.62; F, 13.13%. $C_{14}H_7ClF_2O_2$ requires: C, 59.91; H, 2.51; F, 13.54%).

Compound **8b**: M.p. 100–102 °C. ^1H NMR ($CDCl_3$) δ: 6.99 (1H, s, olefinic proton); 7.50–8.30 (5H, m, other Ar–H); 9.92–10.05 (1H, d, C_{10}–H, $^3J_{H-H}$=7.8 Hz) ppm. ^{19}F NMR ($CDCl_3$) δ: 66.8 (2F, s, CF_2Cl); 116.1 (2F, s, C=CCF_2); 120.0 (2F, s, other CF_2) ppm. IR $\nu_{max.}$ (cm^{-1}): 1670 (C=O); 1640 (C=C); 1590 (Ar); 1120–1190 (C–F). MS *m/z*: 380 (M^+); 217 ($M^+ - C_2F_4Cl - CO$). (Analysis: Found: C, 50.62; H, 1.76; F, 29.92%. $C_{16}H_7ClF_6O_2$ requires: C, 50.48; H, 1.85; F, 29.94%).

Compound **10b**: M.p. 188–190 °C. ^1H NMR ($CDCl_3$) δ: 6.91 (2H, s, 2×olefinic proton); 7.85 (2H, s, 2×Ar–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 66.8 (4F, s, 2×CF_2Cl); 115.6 (4F, s, 2×C=CCF_2); 119.6 (4F, s, other 2×CF_2) ppm. IR $\nu_{max.}$ (cm^{-1}): 1670 (C=O); 1650 (C=C); 1600 (Ar); 1120–1200 (C–F). MS *m/z*: 583 ($M^+ + 1$); 582 (M^+); 547 ($M^+ - Cl$); 419 ($M^+ - C_2F_4Cl - CO$); 256 ($M^+ - 2\times C_2F_4Cl - 2CO$). (Analysis: Found: C, 37.06; H, 0.54; F, 39.09%. $C_{18}H_4Cl_2F_{12}O_4$ requires: C, 37.08; H, 0.69; F, 39.10%).

Compound **12b**: M.p. 147–149 °C. ^1H NMR ($CDCl_3$) δ: 7.11, 7.39 (2H, olefinic protons); 7.77–8.64 (2H, AB pattern, Ar–H, J_{AB}=9.0 Hz) ppm. ^{19}F NMR ($CDCl_3$) δ: 66.8, 67.3 (4F, 2×CF_2Cl); 112.8, 115.8 (4F, N=CCF_2), C=CCF_2); 119.2–119.5 (4F, d, other 2×CF_2) ppm. IR $\nu_{max.}$ (cm^{-1}): 1670 (C=O); 1630 (C=C); 1600 (Ar); 1120–1220 (C–F). MS *m/z*: 581 (M^+); 446 ($M^+ - C_2F_4Cl$); 418 ($M^+ - C_2F_4Cl - CO$); 283 ($M^+ - 2\times C_2F_4Cl - CO$). (Analysis: Found: C, 37.16; H, 0.74; N, 2.31; F, 37.54%). $C_{18}H_5Cl_2F_{12}NO_3$ requires: C, 37.14; H, 0.87; N, 2.41; F, 39.16%).

Compound **14b**: M.p. 136–138 °C. ^1H NMR ($CDCl_3$) δ: 6.82 (1H, s, C_9–H); 6.93 (1H, s, C_3–H); 7.55–8.66 (2H, AB pattern, AR–H, J_{AB}=9.0 Hz) ppm. ^{19}F NMR ($CDCl_3$) δ: 67.2 (4F, s, 2×CF_2Cl); 116.3 (4F, s, 2×C=CCF_2); 119.9 (4F, s, other 2×CF_2) ppm. IR $\nu_{max.}$ (cm^{-1}): 1670 (C=O); 1650 (C=C); 1600 (Ar); 1100–1220 (C–F). MS *m/z*: 582 (M^+); 419 ($M^+ - C_2F_4Cl - CO$). (Analysis: Found: C, 37.53; H, 0.55; F, 39.22%. $C_{18}H_4Cl_2F_{12}O_4$ requires: C, 37.08; H, 0.69; F, 39.10%).

*Preparation of fluoroalkylated bichromones **18a, b** and bischromones **16a, c***

A typical procedure was as follows: Enol ether (1 g) (**17a, b** or **15a, c**) and PPA (25 g) were stirred together at 230 °C for 10 h. After cooling to room temperature, the mixture was neutralized with aqueous 3 N NaOH and extracted with $CHCl_3$. The organic layer was washed with saturated NaCl solution. Removal of the solvent followed by column chromatography using $CHCl_3$ as eluant gave the pure fluoroalkylated bichromones **18a, b** or bischromones **16a, c**, respectively.

Compound **16a**: M.p. 87–89 °C. ^{1}H NMR ($CDCl_3$) δ: 1.82 (6H, s, 2×CH_3); 6.72 (2H, s, 2×olefinic proton); 7.50 (4H, s, other Ar–H); 8.22 (2H, s, C_5–H, $C_{5'}$–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 59.2 (4F, s, 2×CF_2Cl) ppm. IR $\nu_{max.}$ (cm^{-1}): 1670 (C=O); 1620 (Ar); 1150–1240 (C–F). MS *m/z*: 500 (M^+); 485 ($M^+ - CH_3$). (Analysis: Found: C, 55.45; H, 2.43; F, 14.47%. $C_{23}H_{14}Cl_2F_4O_4$ requires: C, 55.11; H, 2.82; F, 15.16%).

Compound **16c**: M.p. 120–122 °C. ^{1}H NMR ($CDCl_3$) δ: 1.86 (6H, s, 2×CH_3); 6.85 (2H, s, 2×olefinic proton); 7.54 (4H, s, other Ar–H); 8.28 (2H, s, C_5–H, $C_{5'}$–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 67.0 (4F, s, 2×CF_2Cl); 117.1 (4F, s, 2×C=CCF_2); 119.6–121.4 (12F, m, other 2×3×CF_2) ppm. IR $\nu_{max.}$ (cm^{-1}): 1670 (C=O); 1610 (Ar); 1110–1220 (C–F). (Analysis: Found: C, 41.39; H, 1.28; F, 41.62%. $C_{31}H_{14}Cl_2F_{20}O_4$ requires: C, 41.31; H, 1.57; F, 41.69%).

Compound **18a**: M.p. 234–236 °C. ^{1}H NMR ($CDCl_3$) δ: 6.72 (2H, s, 2×olefinic proton); 7.63–8.20 (4H, AB pattern, other Ar–H, J_{AB}=9.0 Hz); 8.51 (2H, s, C_5–H, $C_{5'}$–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 66.8 (4F, s, 2×CF_2Cl) ppm. IR $\nu_{max.}$ (cm^{-1}): 1670 (C=O); 1610 (Ar); 1140–1230 (C–F). MS *m/z*: 458 (M^+); 395 ($M^+ - Cl - CO$). (Analysis: Found: C, 52.01; H, 1.85; F, 15.61%. $C_{20}H_8Cl_2F_4O_2$ requires: C, 52.31; H, 1.76; F, 16.55%).

Compound **18b**: M.p. 203–205 °C. ^{1}H NMR ($CDCl_3$) δ: 6.83 (2H, s, 2×olefinic proton); 7.61–8.20 (4H, AB pattern, other Ar–H, J_{AB}=9.0 Hz); 8.51 (2H, s, C_5–H, $C_{5'}$–H) ppm. ^{19}F NMR ($CDCl_3$) δ: 66.8 (4F, s, 2×CF_2Cl); 116.3 (4F, s, 2×C=CCF_2); 120.1 (4F, s, other 2×CF_2) ppm. IR $\nu_{max.}$ (cm^{-1}): 1670 (C=O); 1610 (Ar); 1110–1210 (C–F). (Analysis: Found: C, 43.56; H, 1.09; F, 34.23%. $C_{24}H_8Cl_2F_{12}O_4$ requires: C, 43.73; H, 1.22; F, 34.85%).

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