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A New Synthetic Route to Fluorine-containing Thiochromones

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ABSTRACT

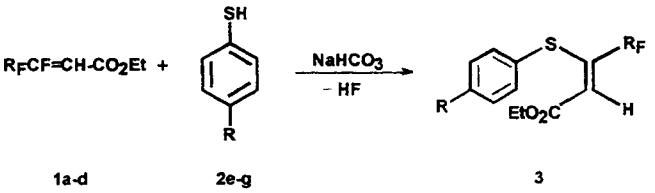
The Michael-addition of polyfluoroalkenoates with thiophenols in acetonitrile in the presence of $NaHCO_3$ yielded the corresponding addition products, which were further treated with polyphosphoric acid (PPA) to give a series of new fluorine-containing thiochromones in good yields.

INTRODUCTION

In our previous synthetic studies on fluorine-containing heterocyclic compounds directed toward the development of biologically active substances, we have prepared some polycyclic derivatives of fluorine-containing quinolines [1] and chromones [2], which bear a common six-membered heterocyclic ring with a 2-polyfluoroalkyl substituent. As sulfur analogues, thiochromones have also been investigated extensively by various workers because of their potential biological activity [3–6]. Probably due to the lack of suitable fluorine-containing building blocks, reports on the synthesis of fluoroalkyl substituted thiochromones are quite limited [7]. In our previous studies [1,2,8], we have found that, in the presence of triethylamine, polyfluoroalkenoates generated in situ from ethyl 2,2-dihydropolyfluoroalkanoates reacted readily with *N*, *O*, and *C*-nucleophiles to give the corresponding adducts in high yields. However, when thiophenols were used as nucleophiles, the reaction proved to be difficult to control and always resulted in a complex mixture, presumably due to the enhanced nucleophilicity of thiophenols in the presence of excess triethylamine. It was therefore necessary to prepare first the dehydrofluorination products, polyfluoroalkenoates, which were then subjected to Michael-addition with thiophenols and subsequent acid catalyzed intramolecular cyclization. By the addition-cyclization procedure, some fluoroalkyl substituted thiochromones were synthesized, and the results are reported herein.

RESULTS AND DISCUSSION

Among various bases tested for the Michael-addition of thiophenols to polyfluoroalkenoates, it was found that either $NaHCO_3$ or K_2CO_3 was the reagent of choice, whereas with triethylamine, pyridine or other organic bases, a complex reaction mixture resulted. In the presence of $NaHCO_3$, thiophenols reacted with ethyl polyfluoroalkenoates readily under mild conditions to give the corresponding addition products, thioethers, in good yields. Only *Z*-isomers were obtained in all cases. Their structures were established by ^1H NMR and ^{19}F NMR spectroscopy [9].



1a-d 2e-g 3

a, $R_F = F(CF_2)_3$; b, $R_F = Cl(CF_2)_3$; c, $R_F = F(CF_2)_5$; d, $R_F = Cl(CF_2)_5$; e, R = H; f, R = Cl; g, $R = CH_3$.

Temperature has a profound effect on the reaction. The optimum temperature for the reaction

Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

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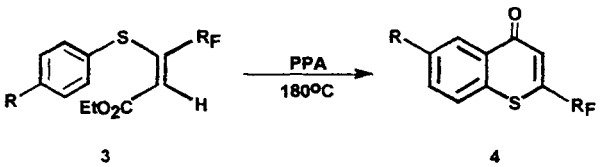
TABLE 1 Synthesis of Fluoroalkylated Thiochromones

Polyfluoroalkenoates	ArSH	R	Isolated Yield[a] (%) Thioether		Thiochromone	
1b	2e	H	3be	91	4be	67
1c	2e	H	3ce	81	4ce	70
1d	2e	H	3de	88	4de	76
1b	2f	Cl	3bf	89	4bf	76
1c	2f	Cl	3cf	83	4cf	72
1d	2f	Cl	3df	84	4df	71
1a	2g	CH_3	3ag	82	4ag	68
1b	2g	CH_3	3bg	91	4bg	77
1c	2g	CH_3	3cg	84	4cg	73
1d	2g	CH_3	3dg	87	4dg	79
1c	2h	CH_3	3ch	86	4ch	76
1d	2h	CH_3	3dh	86	4dh	73
1a	5		6a	83	7a	79
1b	5		6b	88	7b	84
1c	5		6c	81	7c	84

[a]Isolated yield after chromatography.

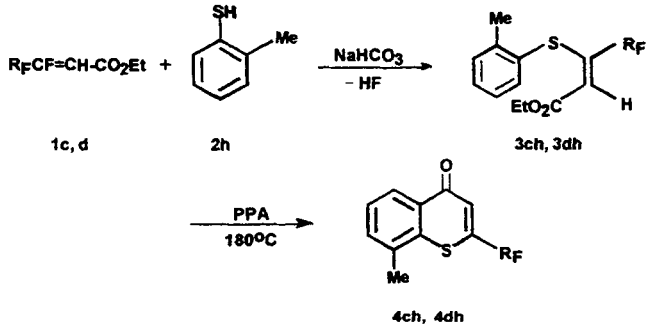
was found to be about 40°C. A lower temperature required a prolonged reaction time, and a higher temperature led to a complicated reaction mixture.

When the fluoroalkylated thioethers were treated with polyphosphoric acid (PPA) at 180°C for 8 to 10 hours, the intramolecular cyclization products, 2-(*F*-alkyl)thiochromones, were obtained in good yields. The detailed results are shown in Table 1.



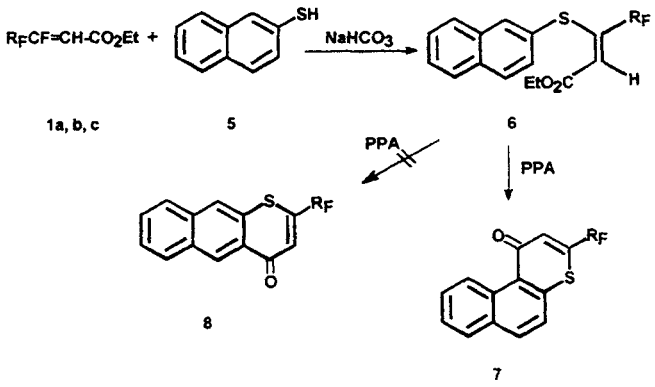
3 4

Different from the case of the reaction of an aromatic *N*- nucleophile, such as *O*-toluidine [1] to **1**, the presence of an ortho-substituent does not show steric hindrance in the addition and cyclization reaction of a thiopenol. Thus, when *O*-thiocresol was used, the addition-cyclization reaction proceeded smoothly and gave the expected products in good yields.



1c, d 2h 3ch, 3dh 4ch, 4dh

Under the same conditions, β-thionaphthol reacted with each polyfluoroalkenoate to give the corresponding polycyclic product that was shown to possess the thia-phenanthrene structure **7**, rather than the isomeric thia-anthracene structure **8**, by its 600 MHz ^{1}H NMR spectrum.



1a, b, c 5 6 8 7

Taking **7a** as an example, due to the deshielding effect of the carbonyl group, in its 600 MHz ^{1}H NMR spectra, the C_{10}-H showed a doublet at δ 10.00 (J = 8.7 Hz). Also, through a series of decoupling experiments, the other proton chemical shifts were assigned as follows: C_2-H, 7.45 (s); C_5-H, 8.04 (d, J = 8.7 Hz); C_6-H, 7.56 (d, J = 8.8 Hz); C_7-H, 7.91 (d, J = 7.8 Hz); C_8-H, 7.68 (dd, J_1 = 7.7 Hz, J_2 = 7.1 Hz); and C_9-H, 7.78 (dd, J_1 = 7.1 Hz, J_2 = 8.6 Hz).

In conclusion, we have developed a convenient new route to the preparation of 2-fluoroalkylated thiochromones starting from polyfluoroalkenoates.

EXPERIMENTAL

All melting points were uncorrected. The IR spectra were measured with an IR-440 spectrometer, using liquid films. The ^{1}H NMR spectra were recorded on a Varian EM-360A (60 MHz), AMX-600 (600 MHz) spectrometer using TMS as internal standard, and ^{19}F NMR spectra were recorded on a Varian EM-360I (56.4 MHz) spectrometer using TFA as an external standard. The ^{19}F chemical shifts are positive for upfield shifts, and the values reported are related to δ $CFCl_3$ (δ $CFCl_3$ = δ TFA + 76.8). Mass spectra were taken on a GC-MS 4021 spectrometer, and HRMS spectra were taken on a Finnigan MAT-8430 spectrometer. The column chromatography was performed using silica gel H, particle size 10–40 μm.

Preparations of Thioethers

Typical Procedure. A mixture of polyfluoroalkenoate (4 mmol), thiophenol (5 mmol), $NaHCO_3$ (10 mmol), and CH_3CN (5 mL) was stirred at 40°C for 6 hours. The mixture was then diluted with water and extracted with ether (30 mL × 3). The ethereal layer was combined and washed with saturated NaCl solution. After removal of the solvent, the residue was purified by column chromatogra-

phy using petroleum ether/ethyl acetate (100:1) as eluant to give the thioether.

Compound **3be**. ^{1}H NMR ($CDCl_3$) δ: 1.21 (3H, t, J = 6.8 Hz, CH_2CH_3), 4.09 (2H, q, J = 6.8 Hz, CH_2CH_3), 6.81 (1H, s, =CH), 7.38 (5H, m, Ar-H). ^{19}F NMR ($CDCl_3$) δ: 66.2 (2F, s, CF_2Cl), 105.9 (2F, s, $=CCF_2$), 117.0 (2F, s, other CF_2). IR ν_{max}: 1740 (C=O), 1100–1220 (C-F) cm^{-1}.

Compound **3ce**. ^{1}H NMR ($CDCl_3$) δ: 1.21 (3H, t, J = 6.8 Hz, CH_2CH_3), 4.09 (2H, q, J = 6.8 Hz, CH_2CH_3), 6.80 (1H, s, =CH), 7.37 (5H, m, Ar-H). ^{19}F NMR ($CDCl_3$) δ: 80.2 (3F, s, CF_3), 106.7 (2F, s, $=CCF_2$), 119.8–125.3 (6F, m, other 3 × CF_2). IR ν_{max}: 1740 (C=O), 1100–1260 (C-F) cm^{-1}.

Compound **3de**. ^{1}H NMR ($CDCl_3$) δ: 1.19 (3H, t, J = 6.8 Hz, CH_2CH_3), 4.08 (2H, q, J = 6.8 Hz, CH_2CH_3), 6.80 (1H, s, =CH), 7.35 (5H, m, Ar-H). ^{19}F NMR ($CDCl_3$) δ: 67.0 (2F, s, CF_2Cl), 106.6 (2F, s, $=CCF_2$), 119.2 (6F, m, other 3 × CF_2). IR ν_{max}: 1740 (C=O), 1100–1240 (C-F) cm^{-1}.

Compound **3bf**. ^{1}H NMR ($CDCl_3$) δ: 1.26 (3H, t, J = 6.8 Hz, CH_2CH_3), 4.17 (2H, q, J = 6.8 Hz, CH_2CH_3), 6.86 (1H, s, =CH), 7.35 (4H, s, Ar-H). ^{19}F NMR ($CDCl_3$) δ: 66.2 (2F, s, CF_2Cl), 105.7 (2F, s, $=CCF_2$), 117.9 (2F, s, other CF_2). IR ν_{max}: 1740 (C=O), 1100–1220 (C-F) cm^{-1}.

Compound **3cf**. ^{1}H NMR ($CDCl_3$) δ: 1.24 (3H, t, J = 6.8 Hz, CH_2CH_3), 4.16 (2H, q, J = 6.8 Hz, CH_2CH_3), 6.83 (1H, s, =CH), 7.33 (4H, s, Ar-H). ^{19}F NMR ($CDCl_3$) δ: 80.2 (3F, s, CF_3), 106.6 (2F, s, $=CCF_2$), 119.9–125.6 (6F, m, other 3 × CF_2). IR ν_{max}: 1740 (C=O), 1100–1270 (C-F) cm^{-1}.

Compound **3d**. ^{1}H NMR ($CDCl_3$) δ: 1.25 (3H, t, J = 6.8 Hz, CH_2CH_3), 4.16 (2H, q, J = 6.8 Hz, CH_2CH_3), 6.83 (1H, s, =CH), 7.33 (4H, s, Ar-H). ^{19}F NMR ($CDCl_3$) δ: 67.1 (2F, s, CF_2Cl), 106.4 (2F, s, $=CCF_2$), 119.5 (6F, m, other 3 × CF_2). IR ν_{max}: 1740 (C=O), 1100–1240 (C-F) cm^{-1}.

Compound **3ag**. ^{1}H NMR ($CDCl_3$) δ: 1.22 (3H, t, J = 6.8 Hz, CH_2CH_3), 2.31 (3H, s, Ar-CH_3), 4.20 (2H, q, J = 6.8 Hz, CH_2CH_3), 6.77 (1H, s, =CH), 7.28 (4H, AB, J_{AB} = 8 Hz, Ar-H). ^{19}F NMR ($CDCl_3$) δ: 79.9 (3F, s, CF_3), 105.7 (2F, s, $=CCF_2$), 121.3 (2F, s, other CF_2). IR ν_{max}: 1740 (C=O), 1120–1240 (C-F) cm^{-1}.

Compound **3bg**. ^{1}H NMR ($CDCl_3$) δ: 1.22 (3H, t, J = 6.8 Hz, CH_2CH_3), 2.32 (3H, s, Ar-CH_3), 4.21 (2H, q, J = 6.8 Hz, CH_2CH_3), 6.75 (1H, s, =CH), 7.22 (4H, AB, J_{AB} = 8 Hz, Ar-H). ^{19}F NMR ($CFCl_3$) δ: 66.1 (2F, s, CF_2Cl), 105.6 (2F, s, $=CCF_2$), 117.8 (2F, s, other CF_2). IR ν_{max}: 1740 (C=O), 1120–1200 (C-F) cm^{-1}.

Compound **3cg**. ^{1}H NMR ($CDCl_3$) δ: 1.21 (3H, t, J = 6.8 Hz, CH_2CH_3), 2.30 (3H, s, Ar-CH_3), 4.09 (2H, q, J = 6.8 Hz, CH_2CH_3), 6.73 (1H, s, =CH), 7.22 (4H, AB, J_{AB} = 8 Hz, Ar-H). ^{19}F NMR ($CDCl_3$) δ: 80.1 (3F, s, CF_3), 106.5 (2F, s, $=CCF_2$), 119.8–125.6 (6F, m, other 3 × CF_2). IR ν_{max}: 1740 (C=O), 1120–1270 (C-F) cm^{-1}.

Compound **3dg**. ^{1}H NMR ($CDCl_3$) δ: 1.22 (3H, t, J = 6.8 Hz, CH_2CH_3), 2.33 (3H, s, Ar-CH_3), 4.10 (2H, q, J = 6.8 Hz, CH_2CH_3), 6.76 (1H, s, =CH), 7.24 (4H, AB, J_{AB} = 8 Hz, Ar-H). ^{19}F NMR ($CDCl_3$) δ: 67.3 (2F, s, CF_2Cl), 106.5 (2F, s, $=CCF_2$), 119.5 (6F, m, other 3 × CF_2). IR ν_{max}: 1740 (C=O), 1100–1240 (C-F) cm^{-1}. Anal.: Found: C, 39.98; H, 2.57; F, 38.17; S, 12.21%. $C_{17}H_{13}ClF_{10}O_2S$ requires: C, 40.29; H, 2.59; F, 37.49; S, 12.65%.

Compound **3bh**. ^{1}H NMR ($CDCl_3$) δ: 1.18 (3H, t, J = 6.8 Hz, CH_2CH_3), 2.43 (3H, s, Ar-CH_3), 4.04 (2H, q, J = 6.8 Hz, CH_2CH_3), 6.75 (1H, s, =CH), 7.32 (4H, m, Ar-H). ^{19}F NMR ($CDCl_3$) δ: 67.2 (2F, s, CF_2Cl), 106.9 (2F, s, $=CCF_2$), 119.7 (6F, m, other 3 × CF_2). IR ν_{max}: 1735 (C=O), 1120–1200 (C-F) cm^{-1}.

Compound **3ch**. ^{1}H NMR ($CDCl_3$) δ: 1.23 (3H, t, J = 6.8 Hz, CH_2CH_3), 2.47 (3H, s, Ar-CH_3), 4.05 (2H, q, J = 6.8 Hz, CH_2CH_3), 6.75 (1H, s, =CH), 7.23 (4H, m, Ar-H). ^{19}F NMR ($CDCl_3$) δ: 80.1 (3F, s, CF_3), 106.8 (2F, s, $=CCF_2$), 119.8–125.4 (6F, m, other 3 × CF_2). IR ν_{max}: 1735 (C=O), 1100–1260 (C-F) cm^{-1}. m/z: 506 (M^+), 433 (M-CO_2Et), 123 (ArS^+). HRMS: calcd. for $C_{17}H_{13}ClF_{10}O_2S$, 506.0165. Found: 506.0142.

Compound **6a**. ^{1}H NMR ($CDCl_3$) δ: 1.13 (3H, t, J = 6.8 Hz, CH_2CH_3), 4.04 (2H, q, J = 6.8 Hz, CH_2CH_3), 6.85 (1H, s, =CH), 7.29–7.91 (7H, m, Ar-H). ^{19}F NMR ($CDCl_3$) δ: 79.9 (3F, s, CF_3), 105.6 (2F, s, $=CCF_2$), 121.6 (2F, s, other CF_2). IR ν_{max}: 1735 (C=O), 1120–1240 (C-F) cm^{-1}.

Compound **6b**. ^{1}H NMR ($CDCl_3$) δ: 1.13 (3H, t, J = 6.8 Hz, CH_2CH_3), 4.03 (2H, q, J = 6.8 Hz, CH_2CH_3), 6.86 (1H, s, =CH), 7.26–7.94 (7H, m, Ar-H). ^{19}F NMR ($CDCl_3$) δ: 66.1 (2F, s, CF_2Cl), 105.8 (2F, s, $=CCF_2$), 117.8 (2F, s, other CF_2). IR ν_{max}: 1735 (C=O), 1120–1200 (C-F) cm^{-1}.

Compound **6c**. ^{1}H NMR ($CDCl_3$) δ: 1.11 (3H, t, J = 6.8 Hz, CH_2CH_3), 4.02 (2H, q, J = 6.8 Hz, CH_2CH_3), 6.87 (1H, s, =CH), 7.29–7.94 (7H, m, Ar-H). ^{19}F NMR ($CDCl_3$) δ: 80.1 (3F, s, CF_3), 106.8 (2F, s, $=CCF_2$), 119.6–125.2 (6F, m, other 3 × CF_2). IR ν_{max}: 1735 (C=O), 1140–1240 (C-F) cm^{-1}. m/z: 526 (M^+), 453 (M^+-CO_2Et), 159 (ArS^+). HRMS: calcd. for $C_{20}H_{13}F_{11}O_2S$, 526.0461. Found: 526.0491; diff. −3.0 μm.

Preparation of 2-(F-alkyl)substituted Thiochromones

Typical Procedure. The thioether (1 g) and polyphosphoric acid (PPA) (20 g) were stirred together at 180°C for 8–10 hours. After cooling to 100°C, the mixture was poured into ice water and neutralized with aqueous 2 N NaOH and then 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 (100:1) as eluant gave the pure product thiochromones.

Compound **4be**. Mp 59–61°C. ^{1}H NMR ($CDCl_3$) δ: 7.30 (1H, s, C_3-H), 7.69 (3H, m, H at $C_{6,7,8}$), 8.51 (1H, d, J = 6 Hz, C_5-H). ^{19}F NMR ($CDCl_3$) δ: 66.3 (2F, s, CF_2Cl), 108.6 (2F, s, $ArCF_2$), 119.1 (2F, s, other CF_2). IR ν_{max}: 1640 (C=O), 1590 (C=C), 1120–1200 (C-F) cm^{-1}. m/z: 346 (M^+), 311 (M^+-Cl), 183 (M^+-C_2F_4Cl-CO). Anal.: Found: C, 41.43; H, 1.27; F, 32.81; S, 9.11%. $C_{12}H_5ClF_6OS$, requires: C, 41.58; H, 1.45; F, 32.88; S, 9.25%.

Compound **4ce**. Mp 98–100°C. ^{1}H NMR ($CDCl_3$) δ: 7.34 (1H, s, C_3-H), 7.72 (3H, m, H at $C_{6,7,8}$), 8.52 (1H, d, J = 6 Hz, C_5-H). ^{19}F NMR ($CDCl_3$) δ: 80.0 (3F, s, CF_3), 109.2 (2F, s, $ArCF_2$), 121.1–125.7 (6F, m, other 3 × CF_2). IR ν_{max}: 1640 (C=O), 1590 (C=C), 1100–1240 (C-F) cm^{-1}. Anal.: Found: C, 39.10; H, 0.79; F, 48.32; S, 7.65%. C14$H_5F_{11}OS$, requires: C, 39.08; H, 1.17; F, 48.57; S, 7.45%.

Compound **4de**. Mp 76–78°C. ^{1}H NMR ($CDCl_3$) δ: 7.26 (1H, s, C_3-H), 7.65 (3H, m, H at $C_{6,7,8}$), 8.48 (TH, d, J = 6 Hz, C_5-H). ^{19}F NMR ($CDCl_3$) δ: 67.1 (2F, s, CF_2Cl), 109.2 (2F, s, $ArCF_2$), 120.0 (6F, ms, other 3 × CF_2). IR ν_{max}: 1635 (C=O), 1590 (C=C), 1140–1210 (C-F) cm^{-1}. m/z: 446 (M^+), 411 (M^+-Cl), 383 (M^+-CO-Cl), 183 (M^+-C_4F_8Cl-CO). HRMS: calcd. for $C_{14}H_5ClF_{10}OS$, 445.9590. Found: 445.9612.

Compound **4bf**. Mp 80–82°C. ^{1}H NMR ($CDCl_3$) δ: 7.33 (1H, s, C_3-H), 7.66 (2H, s, C_7-H, C_8-H), 8.51 (1H, s, C_5-H). ^{19}F NMR ($CDCl_3$) δ: 66.3 (2F, s, CF_2Cl), 108.7 (2F, s, $ArCF_2$), 119.2 (2F, s, other CF_2). IR ν_{max}: 1640 (C=O), 1580 (C=C), 1100–1190 (C-F) cm^{-1}. Anal.: Found: C, 37.56; H, 0.77; F, 30.48; S, 8.73%. $C_{12}H_4Cl_2F_6OS$, requires: C, 37.82; H, 1.06; F, 29.91; S, 8.41%.

Compound **4cf**. Mp 97–99°C. ^{1}H NMR ($CDCl_3$) δ: 7.33 (1H, s, C_3-H), 7.67 (2H, s, C_7-H, C_8-H), 8.51 (1H, s, C_5-H). ^{19}F NMR ($CDCl_3$) δ: 80.1 (3F, s, CF_3), 109.4 (2F, s, $ArCF_2$), 121.3–125.6 (6F, m, other 3 × CF_2). IR ν_{max}: 1635 (C=O), 1590 (C=C), 1100–1250 (C-F) cm^{-1}. m/z: 464 (M^+), 445 (M^+-F), 417 (M^+-F-CO), 217 (M^+-C_4F_9-CO). Anal.: Found: C, 36.11; H, 0.59; F, 44.82; S, 7.01%. $C_{14}H_4ClF_{11}OS$, requires: C, 36.19; H, 0.87; F, 44.97; S, 6.90%.

Compound **4df**. Mp 108–110°C. ^{1}H NMR ($CDCl_3$) δ: 7.32 (1H, s, C_3-H), 7.66 (2H, s, C_7-H, C_8-H), 8.48 (1H, s, C_5-H). ^{19}F NMR ($CDCl_3$) δ: 67.2 (2F, s, CF_2Cl), 109.2 (2F, s, $ArCF_2$), 120.1 (6F, m, other 3 × CF_2). IR ν_{max}: 1640 (C=O), 1590 (C=C), 1140–1210 (C-F) cm^{-1}. Anal.: Found: C, 34.85; H, 0.67; F, 39.84; S, 6.81%. $C_{14}H_4Cl_2F_{10}OS$, requires: C, 34.95; H, 0.84; F, 39.59; S, 6.66%.

Compound **4ag**. Mp 112–114°C. ^{1}H NMR ($CDCl_3$) δ: 2.52 (3H, s, $ArCH_3$), 7.29 (1H, s, C_3-H), 7.57 (2H, s, C_7-H, C_8-H), 8.34 (1H, s, C_5-H). ^{19}F NMR ($CDCl_3$) δ: 78.9 (3F, s, CF_3), 107.9 (2F, s, $ArCF_2$), 122.6 (2F, s, other CF_2). IR ν_{max}: 1640 (C=O), 1605 (C=C), 1100–1200 (C-F) cm^{-1}. Anal.: Found: C, 50.82; H, 1.42; F, 34.81; S, 8.38%. $C_{16}H_7F_7OS$, requires: C, 50.54; H, 1.86; F, 34.97; S, 8.43%.

Compound **4bg**. Mp 86–88°C. ^{1}H NMR ($CDCl_3$) δ: 2.51 (3H, s, $ArCH_3$), 7.29 (1H, s, C_3-H), 7.56 (2H, s, C_7-H, C_8-H), 8.34 (1H, s, C_5-H). ^{19}F NMR ($CDCl_3$) δ: 66.4 (2F, s, CF_2Cl), 108.5 (2F, s, $ArCF_2$), 119.2 (2F, s, other CF_2). IR ν_{max}: 1640 (C=O), 1610 (C=C), 1100–1200 (C-F) cm^{-1}. Anal.: Found: C, 43.29; H, 1.55; F, 31.54; S, 8.98%. $C_{13}H_7ClF_6OS$, requires: C, 43.29; H, 1.91; F, 31.60; S, 8.89%.

Compound **4cg**. Mp 83–85°C. ^{1}H NMR ($CDCl_3$) δ: 2.50 (3H, s, $ArCH_3$), 7.29 (1H, s, C_3-H), 7.54 (2H, s, C_7-H, C_8-H), 8.30 (1H, s, C_5-H). ^{19}F NMR ($CDCl_3$) δ: 80.2 (3F, s, CF_3), 109.4 (2F, s, $ArCF_2$), 120.9–124.6 (6F, m, other 3 × CF_2). IR ν_{max}: 1640 (C=O), 1600 (C=C), 1100–1240 (C-F) cm^{-1}. Anal.: Found: C, 40.75; H, 1.31; F, 47.14; S, 7.34%. $C_{15}H_7F_{11}OS$, requires: C, 40.55; H, 1.59; F, 47.04; S, 7.22%.

Compound **4dg**. Mp 76–78°C. ^{1}H NMR ($CDCl_3$) δ: 2.51 (3H, s, $ArCH_3$), 7.28 (1H, s, C_3-H), 7.54 (2H, s, C_7-H, C_8-H), 8.32 (1H, s, C_5-H). ^{19}F NMR ($CDCl_3$) δ: 66.8 (2F, s, CF_2Cl), 108.8 (2F, s, $ArCF_2$), 119.6 (6F, m, other 3 × CF_2). IR ν_{max}: 1640 (C=O), 1605 (C=C), 1100–1200 (C-F) cm^{-1}. Anal.: Found: C, 39.10; H, 1.15; F, 41.38; S, 7.26%. $C_{15}H_7ClF_{10}OS$, requires: C, 39.11; H, 1.53; F, 41.24; S, 6.96%.

Compound **4ch**. Mp 89–91°C. ^{1}H NMR ($CDCl_3$) δ: 2.56 (3H, s, $ArCH_3$), 7.31 (1H, s, C_3-H), 7.50–8.37 (3H, m, H at $C_{5,6,7}$). ^{19}F NMR ($CDCl_3$) δ: 80.1 (3F, s, CF_3), 109.2 (2F, s, $ArCF_2$), 121.1–125.5 (6F, m, other 3 × CF_2). IR ν_{max}: 1640 (C=O), 1590 (C=C), 1100–1240 (C-F) cm^{-1}. m/z: 444 (M^+), 425 (M^+-F), 197 (M^+-C_4F_9-CO). Anal.: Found: C, 40.52; H, 1.11; F, 46.98; S, 7.29%. $C_{15}H_7F_{11}OS$, requires: C, 40.55; H, 1.59; F, 47.04; S, 7.22%.

Compound **4dh**. Mp 115–116°C. ^{1}H NMR ($CDCl_3$) δ: 2.57 (3H, s, $ArCH_3$), 7.33 (1H, s, C_3-H), 7.52–8.40 (3H, m, H at $C_{5,6,7}$). ^{19}F NMR ($CDCl_3$) δ: 66.9 (2F, s, CF_2Cl), 109.2 (2F, s, $ArCF_2$), 120.0 (6F, m, other 3 × CF_2). IR ν_{max}: 1640 (C=O), 1590 (C=C),

1100–1210 (C-F) cm^{-1}. Anal.: Found: C, 39.43; H, 1.15; F, 41.15; S, 7.20%. $C_{15}H_7ClF_{10}OS$, requires: C, 39.11; H, 1.53; F, 41.24; S, 6.96%.

Compound **7a**. 3-Heptafluoropropyl-1-H-naphtho[2,1-b]thiopyran-1-one. Mp 99–101°C. ^{19}F NMR ($CDCl_3$) δ: 78.9 (3F, s, CF_3), 107.8 (2F, s, $ArCF_2$), 122.6 (2F, s, other CF_2). IR ν_{max}: 1625 (C=O), 1590 (C=C), 1110–1230 (C-F) cm^{-1}. Anal.: Found: C, 50.82; H, 1.42; F, 34.89; S, 8.38%. $C_{16}H_7F_7OS$, requires: C, 50.54; H, 1.86; F, 34.97; S, 8.43%.

Compound **7b**. Mp 93–95°C. ^1H NMR ($CDCl_3$) δ: 7.45 (1H, s, C_2-H), 7.58–8.09 (5H, m, all other Ar-H), 9.99 (1H, d, J = 8.8 Hz, C_{10}-H). ^{19}F NMR ($CDCl_3$) δ: 66.2 (2F, s, CF_2Cl), 108.5 (2F, s, $ArCF_2$), 119.2 (2F, s, other CF_2). IR ν_{max}: 1625 (C=O), 1590 (C=C), 1100–1190 (C-F) cm^{-1}. *m/z*: 396 (M^+), 361 (M^+-Cl), 233 (M^+-C_2F_4Cl-CO). Anal.: Found: C, 48.26; H, 1.61; F, 29.49; S, 8.24%. $C_{16}H_7ClF_6OS$, requires: C, 48.44; H, 1.78; F, 28.73; S, 8.08%.

Compound **7c**. Mp 94–97°C. ^1H NMR ($CDCl_3$) δ: 7.47 (1H, s, C_2-H), 7.61–8.13 (5H, m, all other Ar-H), 10.02 (1H, d, J = 8.8 Hz, C_{10}-H). ^{19}F NMR ($CDCl_3$) δ: 79.8 (3F, s, CF_3), 109.2 (2F, s, $ArCF_2$), 121.1–125.3 (6F, m, other 3 × CF_2). IR ν_{max}: 1625 (C=O), 1590 (C=C), 1100–1240 (C-F) cm^{-1}. *m/z*: 480 (M^+), 46 (M^+-F), 233 (M^+-C_4F_9-CO). HRMS: calcd for $C_{18}H_7F_{11}OS$, 480.0042. Found: 480.0063.

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