Studies on Sulfinatodehalogenation. Part 30.† Synthesis of 3-Perfluoroalkylated Coumarins, Thiocoumarins and 2-Quinolones by Direct Perfluoroalkylation with Perfluoroalkyl Iodides and Sodium Hydroxymethanesulfinate

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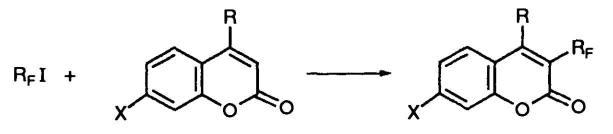
Coumarins react with perfluoroalkyl iodides in the presence of sodium hydroxymethanesulfinate (Rongalite) to give 3-perfluoroalkylcoumarins selectively in good yields and under mild conditions. The same results were obtained when thiocoumarin and 2-quinolones were used in place of coumarins and the corresponding C-3 substituted perfluoroalkyl thiocoumarins and 2-quinolones were prepared readily. A free-radical mechanism was proposed for the reaction.

Interest in perfluoroalkyl-containing compounds is rapidly increasing owing to both their unique properties and their use as starting materials for the preparation of fluorine-containing dyes, drugs and insecticides *etc.* Thus, the development of methods for the introduction of perfluoroalkyl groups into organic molecules has been much investigated.[1-3] Although perfluoroalkylated coumarins, known for their utility as fluorescent and laser dyes,[4,5] have been the subject of much study, few 4-trifluoromethylcoumarins have been synthesised because of the limited availability of starting materials.[6,7] Here we report a facile synthesis of 3-perfluoroalkylated coumarins, thiocoumarins and 2-quinolones by direct perfluoroalkylation with perfluoroalkyl iodides in the presence of sodium hydroxymethanesulfinate (Rongalite).‡

Because of the high electronegativity of fluorine, scope for electrophilic perfluoroalkylations of aromatic compounds *via* perfluoroalkyl cationic intermediates is very limited.[8] Thus, generally, free-radical reactions have been used for the introduction of perfluoroalkyl groups. Rongalite, recently used by us as a new sulfinatodehalogenation reagent is able to convert perfluoroalkyl iodides or bromides into their corresponding sodium sulfinates through a free-radical process.[9] With the generation of perfluoroalkyl radicals, the R_FI–Rongalite system has been employed for the perfluoroalkylation of olefins and some nitrogen-containing heteroaromatics.[10,11] Further studies showed that the R_F radical thus formed could also react with coumarin, thiocoumarin, 2-quinolone and their derivatives to yield the corresponding perfluoroalkylated products.



1 2 3

a $R_F = F(CF_2)_6$
b $R_F = F(CF_2)_7$
c $R_F = F(CF_2)_8$
d $R_F = Cl(CF_2)_4$
e $R_F = Cl(CF_2)_6$
f $R_F = Cl(CF_2)_8$

g R = X = H
h R = Me, X = OH
j R = Me, X = NEt_2

ag $R_F = F(CF_2)_6$, R = X = H
bg $R_F = F(CF_2)_7$, R = X = H
cg $R_F = F(CF_2)_8$, R = X = H
dg $R_F = Cl(CF_2)_4$, R = X = H
eg $R_F = Cl(CF_2)_6$, R = X = H
fg $R_F = Cl(CF_2)_8$, R = X = H
ah $R_F = F(CF_2)_6$, R = Me, X = OH
eh $R_F = Cl(CF_2)_6$, R = Me, X = OH
ej $R_F = Cl(CF_2)_6$, R = Me, X = NEt_2

Scheme 1 *Reagents and conditions:* $HOCH_2SO_2Na$, $NaHCO_3$, MeCN–H_2O, 70–75 °C

Table 1 Reaction of R_FI with coumarins

Entry	R_FI	Coumarin	Product	Yield (%)[a]
1	**1a**	**2g**	**3ag**	63
2	**1b**	**2g**	**3bg**	70
3	**1c**	**2g**	**3cg**	78
4	**1d**	**2g**	**3dg**	63
5	**1e**	**2g**	**3eg**	67
6	**1f**	**2g**	**3fg**	72
7	**1a**	**2h**	**3ah**	59
8	**1e**	**2h**	**3eh**	57
9	**1e**	**2j**	**3ej**	42

[a] Isolated yield based on **1**.

Results and Discussion

Using acetonitrile as co-solvent, perfluoroalkyl iodides **1** reacted readily at 70–75 °C with coumarin **2g** in an aqueous solution of Rongalite to give 3-perfluoroalkylcoumarins **3** as the major products (Scheme 1). Addition of sodium hydrogen carbonate to the reaction mixture kept the medium slightly basic and prevented decomposition of the Rongalite. The results are listed in Table 1.

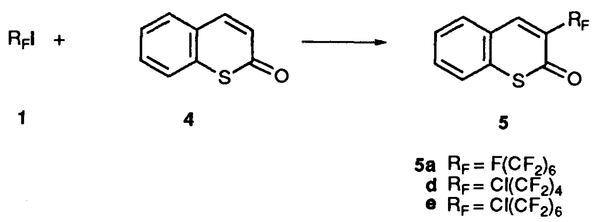
As shown in Table 1, the yields of perfluoroalkylation changed only slightly with different R_F groups, but were influenced more significantly by the presence of certain substituents on the coumarin ring (entries 7–9). Compared with their unsubstituted analogues, the reactions of 7-hydroxy-4-methylcoumarin **2h** and 7-diethylamino-4-methylcoumarin **2j** with **1** under similar conditions were somewhat complicated with lower isolated yields. The OH and NEt_2 groups are strongly electron donating, but the perfluoroalkylation still took place at C-3 in preference to other positions, indicating a satisfying regioselectivity of this reaction.

Replacing Rongalite by other sulfinatodehalogenating agents as initiator, gave different results. In the presence of sodium dithionate,[12] **1** was converted into the corresponding sodium sulfinates completely at room temperature without the formation of **3**. When thiourea dioxide[13] was used, compounds **3** were obtained in low yields together with some by-products

† Part 29, B.-N. Huang and F.-H. Wu, *J. Fluorine Chem.*, in the press.
‡ Part of the work was published as a communication in *J. Chem. Soc., Chem. Commun.*, 1990, 1781. Soon afterward, M. Matsui, K. Shibata, H. Muramatsu, H. Sawada and M. Nakayama (*Synlett.*, 1991, 113) reported similar results using bis(perfluoroalkanoyl)peroxides as perfluoroalkylation reagents.

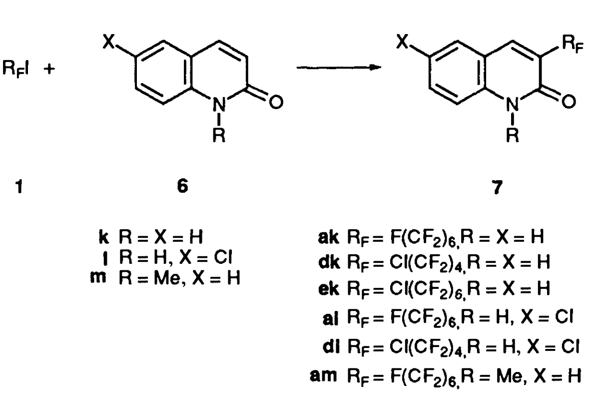
such as R_FSO_2Na and R_FH. Besides acetonitrile, DMF and ethanol could also be used as co-solvent, but more R_FH was formed when ethanol was used.

In a similar way, thiocoumarin **4** reacted with **1** in the presence of Rongalite to yield the corresponding C-3 perfluoroalkylthiocoumarins in moderate yields (Scheme 2). The results are listed in Table 2.



Scheme 2 *Reagents and conditions:* $HOCH_2SO_2Na$, $NaHCO_3$, $MeCN-H_2O$, 70–75 °C

Considering the structural similarity between 2-quinolone **6** and coumarin, the reaction of **6** and **1** under similar conditions was performed and the same results as above were obtained (Scheme 3). Again the perfluoroalkylation took place,



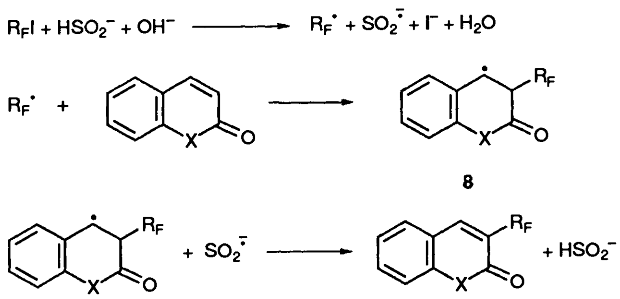
Scheme 3 *Reagents and conditions:* $HOCH_2SO_2Na$, $NaHCO_3$, $MeCN-H_2O$, 70–75 °C

predominantly, at position 3, resulting in the formation of the corresponding 3-perfluoroalkyl-2-quinolones. The presence of substituents on the aromatic ring or at the N atom did not influence the regioselectivity of this reaction (Table 2, entries 7–9).

The results obtained from the above reactions may be explained in terms of the following radical mechanism:

$$HOCH_2SO_2^- \longrightarrow HSO_2^- + CH_2O$$

$$R_FI + HSO_2^- + OH^- \longrightarrow R_F^{\bullet} + SO_2^{\bullet-} + I^- + H_2O$$



The HSO_2^- anion generated from the dissociation of Rongalite reacts with **1** and OH^- to form $SO_2^{\bullet-}$ and the corresponding R_F radicals, which then react with coumarins to form a benzylic radical intermediate **8**. Abstraction of hydrogen from **8** by $SO_2^{\bullet-}$ results in the formation of the title products with the regeneration of HSO_2^-. The intermediate **8**, resulting from attack of R_F at the 3-position, is more stable than others because it is stabilised by benzylic delocalisation, and thus its formation is favoured kinetically in the reaction system. This might explain the regioselectivity of this reaction.

Table 2 Reaction of R_FI with thiocoumarin and 2-quinolones

Entry	R_FI	Substrate	Product	Yield (%)[a]
1	**1a**	**4**	**5a**	53
2	**1d**	**4**	**5d**	58
3	**1e**	**4**	**5e**	60
4	**1a**	**6k**	**7ak**	62
5	**1d**	**6k**	**7dk**	55
6	**1e**	**6k**	**7ek**	58
7	**1a**	**6l**	**7al**	52
8	**1d**	**6l**	**7dl**	47
9	**1a**	**6m**	**7am**	42

[a] Isolated yield based on **1**.

In conclusion, direct perfluoroalkylation of coumarin and its analogues has been achieved with good regioselectivity. The reaction is believed to proceed through a free-radical process.

Experimental

M.p.s are uncorrected. IR spectra were taken on a Shimadzu-440 spectrometer with solid samples as KBr pellets and liquid samples as films. ^1H NMR spectra were recorded on Varian EM-360A (60 MHz) and XL-200 (200 MHz) spectrometers with internal TMS reference. ^{19}F NMR spectra were recorded on a Varian EM-360L spectrometer at 56.4 MHz with external CF_3CO_2H reference. *J* Values are recorded in Hz. The values reported were $\delta_F = \delta_{TFA} + 76.8$ ppm, positive for upfield shifts. The mass spectra were taken on a Finnigan GC–MS-4021 mass spectrometer. Silica gel (10–40 μm) was used for column chromatography. All chemicals were used directly without further purification.

General Procedure.—A mixture of **1a** (10 mmol), **2g** (15–20 mmol), Rongalite (2.3 g) and $NaHCO_3$ (1.3 g) in MeCN (5 cm^3) and water (10 cm^3) was stirred at 70–75 °C for 5 h. After cooling, the resulting mixture was extracted with diethyl ether and the extract washed with water and dried (Na_2SO_4). Isolation by column chromatography of the crude product on silica gel with light petroleum–benzene as eluent gave the title compound **3ag** as colourless needles after recrystallisation from light petroleum.

3-*Tridecafluorohexylcoumarin* **3ag**. M.p. 93–94 °C (Found: C, 38.7; H, 0.9; F, 53.75. Calc. for $C_{15}H_5F_{13}O_2$: C, 38.81; H, 1.08; F, 53.21%); ν_{max}/cm^{-1} 3060, 1740, 1630, 1615, 1575, 1460 and 1200; δ_H($CDCl_3$) 8.15 (1 H, s, 4-H) and 7.70–7.25 (4 H, m); δ_F($CDCl_3$) 81.0 (3 F, t), 111.3 (2 F, t), 121.8 (6 F, m) and 126.3 (2 F, m); *m/z* (%) 464 (M^+, 15), 445 ($M^+ - F$, 6), 196 (13), 195 ($M^+ - C_5F_{11}$, 100) and 69 (CF_3^+, 8).

3-*Pentadecafluoroheptylcoumarin* **3bg**. M.p. 99–100 °C (Found: C, 37.0; H, 0.9; F, 55.6. Calc. for $C_{16}H_5F_{15}O_2$: C, 37.37; H, 0.98; F, 55.42%); ν_{max}/cm^{-1} 3050, 1740, 1630, 1615, 1580, 1460, 1240 and 1200; δ_H(200 MHz, $CDCl_3$) 8.16 (1 H, s, 4-H), 7.74–7.64 (2 H, m) and 7.43–7.36 (2 H, m); δ_F($CDCl_3$) 80.7 (3 F, t), 110.9 (2 F, t), 121.4 (8 F, m) and 126.0 (2 F, m); *m/z* (%) 514 (M^+, 14), 495 ($M^+ - F$, 8), 196 (13), 195 ($M^+ - C_6F_{13}$, 100) and 69 (CF_3^+, 12).

3-*Heptadecafluorooctylcoumarin* **3cg**. M.p. 107–108 °C (Found: C, 35.9; H, 0.7; F, 58.0. Calc. for $C_{17}H_5F_{17}O_2$: C, 36.19; H, 0.89; F, 57.24%); ν_{max}/cm^{-1} 3050, 1740, 1630, 1615, 1575, 1460 and 1200; δ_H($CDCl_3$) 8.13 (1 H, s) and 7.70–7.25 (4 H, m); δ_F($CDCl_3$) 80.8 (3 F, t), 110.7 (2 F, t), 121.2 (10 F, m) and 125.8 (2 F, m); *m/z* (%) 565 (6), 564 (M^+, 18), 545 (9), 195 ($M^+ - C_7F_{15}$, 100) and 69 (CF_3^+, 11).

3-(4-*Chlorooctafluorobutyl*)*coumarin* **3dg**. M.p. 73–74 °C

(Found: C, 40.9; H, 1.1; F, 40.55. Calc. for $C_{13}H_5ClF_8O_2$: 41.02; H, 1.32; F, 39.93%); ν_{max}/cm^{-1} 3050, 1738, 1625, 1600, 1575, 1458 and 1200; $\delta_H(CDCl_3)$ 8.20 (1 H, s, 4-H) and 7.80–7.30 (4 H, m); $\delta_F(CDCl_3)$ 67.7 (2 F, t), 110.8 (2 F, t) and 119.8 (4 F, m); *m/z* (%) 382 (6), 381 (4), 380 (M^+, 17), 345 ($M^+ - Cl$, 11) and 195 ($M^+ - ClC_3F_6$, 100).

3-(6-*Chlorododecafluorohexyl*)*coumarin* **3eg**. M.p. 86–87 °C (Found: C, 37.4; H, 0.8; F, 48.05. Calc. for $C_{15}H_5ClF_{12}O_2$: C, 37.48; H, 1.05; F, 47.43%); ν_{max}/cm^{-1} 3050, 1735, 1630, 1610, 1575, 1458 and 1200; $\delta_H(CDCl_3)$ 8.16 (1 H, s, 4-H) and 7.70–7.30 (4 H, m); $\delta_F(CDCl_3)$ 68.0 (2 F, t), 111.0 (2 F, t) and 120.6 (8 F, m); *m/z* (%) 482 (3), 481 (2), 480 (M^+, 7), 445 ($M^+ - Cl$, 5) and 196 ($M^+ - ClC_5F_{10} + 1$, 100).

3-(8-*Chlorohexadecafluorooctyl*)*coumarin* **3fg**. M.p. 106–107 °C (Found: C, 34.85; H, 0.65; F, 52.87. Calc. for $C_{17}H_5ClF_{16}O_2$: C, 35.16; H, 0.87; F, 52.35%); ν_{max}/cm^{-1} 3050, 1738, 1630, 1610, 1572, 1458 and 1200; $\delta_H(CDCl_3)$ 8.25 (1 H, s, 4-H) and 7.80–7.35 (4 H, m); $\delta_F(CDCl_3)$ 69.0 (2 F, t), 111.6 (2 F, t) and 121.8 (12 F, m); *m/z* (%) 582 (3), 581 (2), 580 (M^+, 7), 545 ($M^+ - Cl$, 4) and 196 ($M^+ - ClC_7F_{14}$, 100).

7-*Hydroxy*-4-*methyl*-3-*tridecafluorohexylcoumarin* **3ah**. M.p. 146–147 °C (Found: C, 38.7; H, 1.1; F, 50.35. Calc. for $C_{16}H_7F_{13}O_3$: C, 38.88; H, 1.42; F, 49.97%); ν_{max}/cm^{-1} 3360, 1700, 1620, 1555, 1450 and 1200; δ_H[200 MHz, $(CD_3)_2CO$] 7.25 (1 H, d, $^3J_{HH}$ 9, 5-H), 6.28 (1 H, dd, $^3J_{HH}$ 9, $^4J_{HH}$ 2.5, 6-H), 6.10 (1 H, d, $^4J_{HH}$ 2.5, 8-H) and 2.03 (3 H, t, J_{HF} 2.7); δ_F[$(CD_3)_2CO$] 81.5 (3 F, t), 103.0 (2 F, t), 120.7 (2 F, m), 122.8 (2 F, m) and 126.5 (2 F, m); *m/z* (%) 495 ($M^+ + 1$, 55), 494 (M^+, 15), 475 ($M^+ - F$, 9), 225 ($M^+ - C_5F_{11}$, 100) and 69 (CF_3^+, 36).

3-(6-*Chlorododecafluorohexyl*)-7-*hydroxy*-4-*methylcoumarin* **3eh**. M.p. 165–167 °C (Found: C, 37.6; H, 1.2; F, 44.3. Calc. for $C_{16}H_7ClF_{12}O_3$: C, 37.63; H, 1.38; F, 44.64%); ν_{max}/cm^{-1} 3350, 1690, 1620, 1598, 1550, 1450, 1210 and 1145; δ_H[200 MHz, $(CD_3)_2CO$] 7.27 (1 H, d, $^3J_{HH}$ 9, 5-H), 6.29 (1 H, dd, $^3J_{HH}$ 9, $^4J_{HH}$ 2.5, 6-H), 6.12 (1 H, d, $^4J_{HH}$ 2.5, 8-H) and 2.05 (3 H, t, J_{HF} 2.7); δ_F[$(CD_3)_2CO$] 69.7 (2 F, t), 103.2 (2 F, t) and 121.0 (8 F, m); *m/z* (%) 512 (3), 511 (2), 510 (M^+, 8), 475 ($M^+ - Cl$, 6) and 225 ($M^+ - ClC_5F_{10}$, 100).

3-(6-*Chlorododecafluorohexyl*)-7-*diethylamino*-4-*methylcoumarin* **3ej**. M.p. 109–110 °C (Found: C, 42.75; H, 2.6; F, 39.8; N, 2.35. Calc. for $C_{20}H_{16}ClF_{12}NO_2$: C, 42.46; H, 2.85; F, 40.32; N, 2.47%); ν_{max}/cm^{-1} 2960, 1710, 1625, 1575, 1520, 1415, 1200 and 1155; δ_H(200 MHz, $CDCl_3$) 7.54 (1 H, d, $^3J_{HH}$ 9, 5-H), 6.59 (1 H, dd, $^3J_{HH}$ 9, $^4J_{HH}$ 2.5, 6-H), 6.42 (1 H, d, $^4J_{HH}$ 2.5, 8-H), 3.42 (4 H, q, $^3J_{HH}$ 7, CH_2), 2.52 (3 H, t, J_{HF} 2.7, 4-CH_3) and 1.21 (6 H, t, $^3J_{HH}$ 7, CH_3); $\delta_F(CDCl_3)$ 69.6 (2 F, t), 102.6 (2 F, t) and 121.5 (8 F, m); *m/z* (%) 567 (41), 566 (28), 565 (M^+, 89), 552 (37), 550 ($M^+ - CH_3$, 100), 546 (14), 530 ($M^+ - Cl$, 38) and 280 ($M^+ - ClC_5F_{10}$, 74).

3-*Tridecafluorohexylthiocoumarin* **5a**. M.p. 48–50 °C (Found: C, 37.6; H, 0.8; F, 50.8; S, 6.7. Calc. for $C_{15}H_5F_{13}OS$: 37.51; H, 1.05; F, 51.43; S, 6.68%); ν_{max}/cm^{-1} 1645, 1595, 1550, 1200 and 1140; δ_H[200 MHz, $(CD_3)_2CO$] 8.58 (1 H, s, 4-H), 8.18 (1 H, d, $^3J_{HH}$ 9, 5-H) and 7.84–7.58 (3 H, m); δ_F[$(CD_3)_2CO$] 81.5 (3 F, t), 109.4 (2 F, t), 120.8–123.0 (6 F, m) and 126.6 (2 F, m); *m/z* (%) 481 (13), 480 (M^+, 42), 461 ($M^+ - F$, 13), 452 (27), 211 ($M^+ - C_5F_{11}$, 12), 183 (100) and 69 (CF_3^+, 12).

3-(4-*Chlorooctafluorobutyl*)*thiocoumarin* **5d**. M.p. 71–72 °C (Found: C, 39.4; H, 1.1; F, 38.2; S, 8.1. Calc. for $C_{13}H_5ClF_8OS$: C, 39.36; H, 1.27; F, 38.31; S, 8.08%); ν_{max}/cm^{-1} 1645, 1610, 1590, 1550 and 1200; $\delta_H(CDCl_3)$ 8.18 (1 H, s, 4-H) and 7.95–7.50 (4 H, m); $\delta_F(CDCl_3)$ 66.8 (2 F, t), 108.8 (2 F, t) and 118.8 (4 F, m); *m/z* (%) 398 (9), 397 (4), 396 (M^+, 25), 361 ($M^+ - Cl$, 13), 211 ($M^+ - ClC_3F_6$, 11) and 183 (100).

3-(6-*Chlorododecafluorohexyl*)*thiocoumarin* **5e**. (Found: C, 36.1; H, 0.75; F, 45.6; S, 6.5. Calc. for $C_{15}H_5ClF_{12}OS$: C, 36.27; H, 1.01; F, 45.90; S, 6.46%); ν_{max}/cm^{-1} 1645, 1595, 1550, 1200 and 1140; $\delta_H(CDCl_3)$ 8.20 (1 H, s, 4-H) and 7.95–7.50 (4 H, m); $\delta_F(CDCl_3)$ 67.0 (2 F, t), 108.8 (2 F, t) and 119.0–121.0 (8 F, m); *m/z* (%) 498 (5), 496 (M^+, 13), 461 ($M^+ - Cl$, 8), 211 ($M^+ - ClC_5F_{10}$, 5) and 183 (100).

3-*Tridecafluorohexyl*-2-*quinolone* **7ak**. M.p. 183–184 °C (Found: C, 39.2; H, 1.3; F, 52.65; N, 3.5. Calc. for $C_{15}H_6F_{13}NO$: C, 38.90; H, 1.30; F, 53; N, 3.02%); ν_{max}/cm^{-1} 1670, 1575, 1500, 1438, 1360, 1200 and 1140; δ_H[200 MHz, $(CD_3)_2CO$] 8.50 (1 H, s, 4-H), 7.95 (1 H, d, $^3J_{HH}$ 9, 5-H), 7.74 (1 H, t, $^3J_{HH}$ 9, 7-H), 7.53 (1 H, d, $^3J_{HH}$ 9, 8-H) and 7.35 (1 H, t, $^3J_{HH}$ 9, 6-H); δ_F[$(CD_3)_2CO$] 81.6 (3 F, t), 110.1 (2 F, t), 120.5–123.0 (6 F, m) and 126.4 (2 F, m); *m/z* (%) 464 (4), 463 (M^+, 19), 444 (6), 194 ($M^+ - C_5F_{11}$, 100), 176 (15), 146 (14) and 69 (CF_3^+, 10).

3-(4-*Chlorooctafluorobutyl*)-2-*quinolone* **7dk**. M.p. 198–200 °C (Found: C, 40.9; H, 1.45; F, 39.9; N, 3.7. Calc. for $C_{13}H_6ClF_8NO$: C, 41.13; H, 1.59; F, 40.03; N, 3.69%); ν_{max}/cm^{-1} 3035, 1670, 1570, 1500, 1435 and 1190; δ_H[200 MHz, $(CD_3)_2CO$] 8.48 (1 H, s), 7.92 (1 H, d), 7.72 (1 H, t), 7.51 (1 H, d) and 7.33 (1 H, t); δ_F[$(CD_3)_2CO$] 68.6 (2 F, t), 110.3 (2 F, t), 120.2 (2 F, m) and 121.5 (2 F, m); *m/z* (%) 381 (11), 380 (3), 379 (M^+, 31), 361 (19), 344 ($M^+ - Cl$, 15), 194 ($M^+ - ClC_3F_6$, 100), 176 (57) and 146 (21).

3-(6-*Chlorododecafluorohexyl*)-2-*quinolone* **7ek**. M.p. 203–204 °C (Found: C, 37.7; H, 1.1; F, 47.0; N, 2.8. Calc. for $C_{15}H_6ClF_{12}NO$: C, 37.56; H, 1.26; F, 47.53; N, 2.92%); ν_{max}/cm^{-1} 1670, 1625, 1575, 1500, 1440, 1200 and 1150; $\delta_H(CDCl_3)$ 8.46 (1 H, s), 7.90 (1 H, d), 7.70 (1 H, t), 7.49 (1 H, d) and 7.30 (1 H, t); $\delta_F(CDCl_3)$ 69.0 (2 F, t), 110.2 (2 F, t) and 120.8–121.8 (8 F, m); *m/z* (%) 481 (13), 480 (13), 479 (M^+, 33), 444 ($M^+ - Cl$, 13), 194 ($M^+ - ClC_5F_{10}$, 100), 176 (10) and 146 (13).

6-*Chloro*-3-*tridecafluorohexyl*-2-*quinolone* **7al**. M.p. 217–218 °C (Found: C, 36.6; H, 0.9; F, 49.7; N, 2.9. Calc. for $C_{15}H_5ClF_{13}NO$: C, 36.20; H, 1.01; F, 49.63; N, 2.81%); ν_{max}/cm^{-1} 1600, 1480, 1415, 1358, 1200 and 1140; δ_H[200 MHz, $(CD_3)_2CO$] 8.52 (1 H, s, 4-H), 8.03 (1 H, d, $^4J_{HH}$ 2.5, 5-H), 7.74 (1 H, dd, $^3J_{HH}$ 9, $^4J_{HH}$ 2.5 Hz, 7-H) and 7.56 (1 H, d, $^3J_{HH}$ 9, 8-H); δ_F[$(CD_3)_2CO$] 81.6 (3 F, t), 110.5 (2 F, t), 120.7–123.2 (6 F, m) and 126.6 (2 F, m); *m/z* (%) 498 (18), 496 (M^+, 42), 477 (12), 228 ($M^+ - C_5F_{11}$, 100), 180 (17), 69 (CF_3^+, 19) and 44 (20).

6-*Chloro*-3-(4-*chlorooctafluorobutyl*)-2-*quinolone* **7dl**. M.p. 223–224 °C (Found: C, 37.95; H, 1.0; F, 36.4; N, 3.2. Calc. for $C_{13}H_5Cl_2F_8NO$: C, 37.71; H, 1.22; F, 36.70; N, 3.38%); ν_{max}/cm^{-1} 1600, 1420, 1360, 1200 and 1140; δ_H[200 MHz, $(CD_3)_2CO$] 8.52 (1 H, s, 4-H), 8.02 (1 H, d, $^4J_{HH}$ 2.5, 5-H), 7.74 (1 H, dd, $^3J_{HH}$ 9, $^4J_{HH}$ 2.5, 7-H) and 7.56 (1 H, d, $^3J_{HH}$ 9, 8-H); δ_F[$(CD_3)_2CO$] 68.8 (2 F, t), 110.5 (2 F, t) and 120.3 (4 F, m); *m/z* (%) 415 (20), 414 (11), 413 (M^+, 36), 378 ($M^+ - Cl$, 13), 230 (36), 228 ($M^+ - ClC_3F_6$, 100) and 180 (22).

2-*Methyl*-3-*tridecafluorohexyl*-2-*quinolone* **7am**. M.p. 103–104 °C (Found: C, 40.5; H, 1.7; F, 51.2; N, 2.9. Calc. for $C_{16}H_8F_{13}NO$: C, 40.27; H, 1.69; F, 51.75; N, 2.94%); ν_{max}/cm^{-1} 1660, 1600, 1570, 1460, 1200 and 1140; δ_H(200 MHz; $CDCl_3$) 8.14 (1 H, s, 4-H), 7.72 (2 H, m), 7.46–7.30 (2 H, m) and 3.78 (3 H, s, CH_3); $\delta_F(CDCl_3)$ 80.0 (3 F, t), 109.5 (2 F, t), 119.3–121.8 (6 F, m) and 125.4 (2 F, m); *m/z* (%) 478 (7), 477 (M^+, 33), 458 ($M^+ - F$, 11), 209 (12), 208 ($M^+ - C_5F_{11}$, 100) and 69 (CF_3^+, 5).

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