

Synthesis of (perfluoroalkylsulfonyl)benzenes

Bharati Joglekar, Tomoko Miyake, Ritsu Kawase, Katsuyoshi Shibata, Hiroshige Muramatsu,
Masaki Matsui *

Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido 1-1, Gifu 501-11, Japan

Received 11 October 1994; accepted 12 February 1995

Abstract

4-Substituted (perfluoroalkylsulfonyl)benzenes have been synthesized by the oxidation of 4-substituted (perfluoroalkylthio)benzenes with hydrogen peroxide, anhydrous chromic oxide and potassium permanganate in good yields. 4-(Perfluoroalkylsulfonyl)anilines have been also prepared by the reduction of the corresponding nitrobenzenes.

Keywords: Synthesis; (Perfluoroalkylsulfonyl)benzenes; NMR spectroscopy; Mass spectrometry

1. Introduction

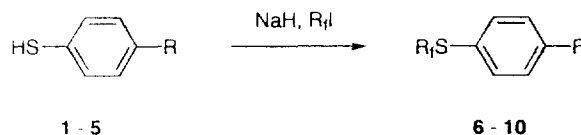
Homo- and hetero-aromatics having a perfluoroalkylthio group are synthesized by the photochemical [1–3] and phase-transfer catalyzed reactions [4] of thiols with perfluoroalkyl iodides and the *S*-perfluoroalkylation of thiolates with perfluoroalkyl iodides [5]. Yagupolskii et al. have reported a general procedure for the oxidation of the trifluoromethylthio moiety [6,7]. However, very little is known about the synthesis of (perfluoroalkylsulfonyl)aromatics. We wish to report here the synthesis of some (perfluoroalkylsulfonyl)benzenes.

2. Results and discussion

A variety of *para*-substituted (perfluoroalkylthio)benzenes **6–10** were prepared by the reaction of *para*-substituted thiophenols **1–5** with perfluoroalkyl iodides in the presence of sodium hydride in good yield (Scheme 1 and Table 1).

In order to synthesize *para*-substituted (perfluoroalkylsulfonyl)benzenes **11–15**, hydrogen peroxide (Method A), chromic oxide (Method B) and potassium permanganate (Method C) were used (Scheme 2 and Table 2). Oxidation of the electron-donating methyl and hydroxy derivatives **7a** and **8a** with hydrogen peroxide satisfactorily gave the corresponding perfluoroalkylsulfonyl derivatives **12a** and **13a**, while the corresponding oxidations of the electron-withdraw-

ing chloro and nitro derivatives **9a** and **10a** with both hydrogen peroxide and potassium permanganate were not suitable for preparing (perfluoroalkylsulfonyl)benzenes. This result may be ascribed to the presence of electron-withdrawing groups on both sides of the phenylene ring. In these cases, oxidation by chromic oxide gave the corresponding perfluoroalkylsulfonyl derivatives **14a** and **15a–c** in good yield. The *1H,1H,2H,2H*-perfluoroalkyl derivatives **10d** and **10e** were oxidized by both hydrogen peroxide and potassium permanganate to afford **15d** and **15e** in excellent yields.



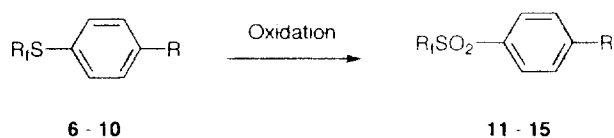
Scheme 1.

Table 1
Synthesis of (perfluoroalkylthio)benzenes

Comp.	R	R _f	Product (yield ^a , %)
1a	H	C ₄ F ₉	6a (66)
2a	CH ₃	C ₄ F ₉	7a (77)
3a	OH	C ₄ F ₉	8a (30)
4a	Cl	C ₄ F ₉	9a (83)
5a	NO ₂	C ₄ F ₉	10a (99)
5b	NO ₂	C ₆ F ₁₃	10b (93)
5c	NO ₂	C ₈ F ₁₇	10c (93)
5d	NO ₂	C ₄ F ₉ CH ₂ CH ₂	10d (90)
5e	NO ₂	C ₆ F ₁₃ CH ₂ CH ₂	10e (68)

* Corresponding author.

^a Isolated yield.



Scheme 2.

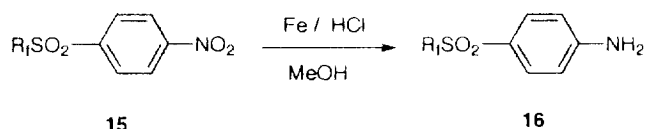
Table 2
Synthesis of (perfluoroalkylsulfonyl)benzenes

Comp.	R	R ₁	Method ^a	Product (yield ^b , %)
6a	H	C ₄ F ₉	A	11a (51)
7a	CH ₃	C ₄ F ₉	A	12a (75)
8a	OH	C ₄ F ₉	A	13a (69)
9a	Cl	C ₄ F ₉	A	14a (6 ^c)
9a	Cl	C ₄ F ₉	B	14a (87)
10a	NO ₂	C ₄ F ₉	A	no reaction
10a	NO ₂	C ₄ F ₉	B	15a (98)
10a	NO ₂	C ₄ F ₉	C	no reaction
10b	NO ₂	C ₆ F ₁₃	B	15b (90)
10c	NO ₂	C ₈ F ₁₇	B	15c (98)
10d	NO ₂	C ₄ F ₉ CH ₂ CH ₂	A	15d (83)
10d	NO ₂	C ₄ F ₉ CH ₂ CH ₂	C	15d (83)
10e	NO ₂	C ₆ F ₁₃ CH ₂ CH ₂	C	15e (95)

^a Method A: H₂O₂, 80 °C; Method B: CrO₃, 118 °C; Method C: KMnO₄, 40 °C.

^b Isolated yield.

^c 4-(Perfluorobutylsulfinyl)chlorobenzene was obtained in 31% yield.



Scheme 3.

Table 3
Synthesis of 4-(perfluoroalkylsulfonyl)anilines

Comp.	R ₁	Product (yield ^a , %)
15a	C ₄ F ₉	16a (99)
15b	C ₆ F ₁₃	16b (99)
15c	C ₈ F ₁₇	16c (99)
15d	C ₄ F ₉ CH ₂ CH ₂	16d (99)
15e	C ₆ F ₁₃ CH ₂ CH ₂	16e (98)

^a Isolated yield.

para-Substituted (perfluoroalkylsulfonyl)anilines **16** were prepared quantitatively by the reduction of the nitro groups of compound **15** (Scheme 3 and Table 3).

3. Experimental details

3.1. Instruments

Melting points were measured with a Yanagimoto micro melting point apparatus and were uncorrected. ¹H NMR spec-

tra were taken on a JEOL JNM 270 GX spectrometer in CDCl₃ using TMS as an internal standard. ¹⁹F NMR spectra were measured with a JEOL α-400 spectrometer in CDCl₃ using trifluoroacetic acid as an external standard. Mass spectra were recorded on a Shimadzu QP-1000 spectrometer by electron-impact ionization at 70 eV (unless otherwise indicated).

3.2. Synthesis of the *para*-substituted (perfluoroalkylthio)benzenes **6–10**

A general procedure consisted of adding 60% sodium hydride (34 mmol) to a DMF solution (30 ml) of thiol (30 mmol) at ambient temperature. The mixture was stirred for 2 h under a nitrogen atmosphere. To the solution was then added perfluoroalkyl iodide (34 mmol) followed by overnight stirring at ambient temperature under nitrogen. The mixture was poured into water (100 ml) and extracted with ether (100 ml × 2). After drying the extract over anhydrous sodium sulfate, the product was distilled under reduced pressure (**6a**, **7a**, **8a**, **9a**, **10d**) or recrystallized from hexane (**10a**, **10b**, **10c**, **10e**, **10f**). The corresponding physical and spectral data are given below.

(Perfluorobutylthio)benzene (**6a**): B.p. 94–96 °C/5330 Pa. ¹H NMR δ: 7.38 (t, *J* = 7.3 Hz, 1H); 7.47 (t, *J* = 7.3 Hz, 2H); 7.64 (d, *J* = 7.3 Hz, 2H) ppm. MS EI (*m/z*): 328 (M⁺, 80); 159 (72); 109 (100); 77 (52); 69 (45). Elemental analysis: Found: C, 36.48; H, 1.78%. Calc. for C₁₀H₅F₉S: C, 36.60; H, 1.54%.

4-(Perfluorobutylthio)toluene (**7a**): B.p. 105–106 °C/5330 Pa. ¹H NMR δ: 2.37 (s, 3H); 7.21 (d, *J* = 8.1 Hz, 2H); 7.52 (d, *J* = 8.1 Hz, 2H) ppm. MS EI (*m/z*): 342 (M⁺, 35); 341 (32); 123 (100); 91 (26); 77 (17); 69 (25). Elemental analysis: Found: C, 38.58; H, 2.06%. Calc. for C₁₁H₇F₉S: C, 38.61; H, 2.06%.

4-(Perfluorobutylthio)phenol (**8a**): B.p. 80–84 °C/130 Pa. ¹H NMR δ: 6.90 (d, *J* = 8.7 Hz, 2H); 7.48 (d, *J* = 8.7 Hz, 2H); 8.40 (br s, 1H) ppm. MS EI (*m/z*): 344 (M⁺, 21); 125 (100). Elemental analysis: Found: C, 35.22; H, 1.58%. Calc. for C₁₀H₅F₉OS: C, 34.90; H, 1.46%.

4-(Perfluorobutylthio)chlorobenzene (**9a**): B.p. 120–122 °C/5330 Pa. ¹H NMR δ: 7.39 (d, *J* = 8.2 Hz, 2H); 7.57 (d, *J* = 8.2 Hz, 2H) ppm. MS EI (*m/z*): 362 (M⁺, 76); 361 (79); 193 (39); 192 (39); 143 (100); 108 (48); 69 (33). Elemental analysis: Found: C, 33.39; H, 1.23%. Calc. for C₁₀H₄ClF₉S: C, 33.12; H, 1.11%.

4-(Perfluorobutylthio)nitrobenzene (**10a**): M.p. 40–42 °C. ¹H NMR δ: 7.86 (d, *J* = 8.5 Hz, 2H); 8.29 (d, *J* = 8.5 Hz, 2H) ppm. ¹⁹F NMR δ: −3.61 (3F); −8.26 (2F); −42.12 (2F); −47.80 (2F) ppm. MS EI (*m/z*): 373 (M⁺, 100); 204 (56); 124 (27); 108 (72); 69 (92). Elemental analysis: Found: C, 32.14; H, 1.23; N, 3.81%. Calc. for C₁₀H₄F₉NO₂S: C, 32.18; H, 1.08; N, 3.75%.

4-(Perfluorohexylthio)nitrobenzene (**10b**): M.p. 49–51 °C. ¹H NMR δ: 7.85 (d, *J* = 8.7 Hz, 2H); 8.28 (d, *J* = 8.7 Hz, 2H) ppm. EI MS (*m/z*): 473 (M⁺, 65); 308 (39); 276 (42);

204 (37); 125 (22); 96 (24); 95 (29); 82 (27); 81 (33); 71 (54); 69 (85). Elemental analysis: Found: C, 30.29; H, 0.87; N, 2.56%. Calc. for $C_{12}H_4F_{13}NO_2S$: C, 30.46; H, 0.85; N, 2.96%.

4-(Perfluorooctylthio)nitrobenzene (**10c**): M.p. 79–81 °C. 1H NMR δ : 7.86 (d, $J=8.9$ Hz, 2H); 8.29 (d, $J=8.9$ Hz, 2H) ppm. MS EI (m/z): 573 (M^+ , 33); 204 (100); 158 (23); 108 (47); 69 (75). Elemental analysis: Found: C, 28.83; H, 1.03; N, 2.73%. Calc. for $C_{14}H_4F_{17}NO_2S$: C, 29.33; H, 0.70; N, 2.44%.

4-(1*H*,1*H*,2*H*,2*H*-Perfluorohexylthio)nitrobenzene (**10d**): B.p. 136 °C/130 Pa. 1H NMR δ : 2.50 (tt, $J=16.5$, 8.2 Hz, 2H); 3.29 (tt, $J=8.2$, 2.4 Hz, 2H); 7.38 (d, $J=8.9$ Hz, 2H); 8.18 (d, $J=8.9$ Hz, 2H) ppm. MS EI (m/z): 401 (M^+ , 100); 371 (18); 168 (25). Elemental analysis: Found: C, 36.12; H, 2.31; N, 3.55%. Calc. for $C_{12}H_8F_9NO_2S$: C, 35.92; H, 2.01; N, 3.49%.

4-(1*H*,1*H*,2*H*,2*H*-Perfluorooctylthio)nitrobenzene (**10e**): M.p. 40–41 °C. 1H NMR δ : 2.45 (tt, $J=16.5$, 8.1 Hz, 2H); 3.27 (tt, $J=8.1$, 2.6 Hz, 2H); 7.37 (d, $J=9.0$ Hz, 2H); 8.18 (d, $J=9.0$ Hz, 2H) ppm. MS EI (m/z): 501 (M^+ , 90); 170 (52); 123 (45); 122 (23); 109 (50); 77 (32); 69 (100). Elemental analysis: Found: C, 33.81; H, 1.60; N, 3.12%. Calc. for $C_{14}H_8F_{13}NO_2S$: C, 33.55; H, 1.61; N, 2.79%.

3.3. Synthesis of the (perfluoroalkylsulfonyl)benzenes 11–15

Method A

To an acetic acid solution (15 ml) of (perfluoroalkylthio)benzene (10 mmol) was added dropwise an aqueous 30% hydrogen peroxide solution (100 mmol) at 80 °C, with stirring for 8 h. After reaction, the mixture was poured into water (100 ml). The product was extracted with ether (100 ml \times 2), washed with a 10% aqueous sodium hydrogen carbonate solution (100 ml) and brine (100 ml), and dried over anhydrous sodium sulfate. After evaporation of the solvent, the product was isolated by distillation or column chromatography.

Method B

To an acetic acid solution (50 ml) of 4-(perfluoroalkylthio)benzene (10 mmol) was added anhydrous chromic oxide (100 mol) with refluxing for 24 h. The mixture was poured into water. The resulting precipitate was filtered, washed with hot water, dried and recrystallized from hexane.

Method C

To an acetic acid solution (40 ml) of 4-(1*H*,1*H*,2*H*,2*H*-perfluoroalkylthio)benzene (4 mmol) was added an aqueous solution (75 ml) of potassium permanganate (1.58 g, 10 mmol) with stirring for 15 min at 40 °C. The mixture was poured into an aqueous sodium hydrogen sulfite solution. The resulting precipitate was filtered, washed with water, dried and recrystallized from hexane.

The physical and spectral data of the (perfluoroalkylsulfonyl)benzenes are given below.

(Perfluorobutylsulfonyl)benzene (**11a**): B.p. 141–147 °C/6000 Pa. 1H NMR δ : 7.69 (t, $J=7.6$ Hz, 2H); 7.86 (t,

$J=7.6$ Hz, 1H); 8.06 (d, $J=7.6$ Hz, 2H) ppm. ^{19}F NMR δ : -3.21 (3F); -34.02 (2F); -43.25 (2F); -48.40 (2F) ppm. MS EI (m/z): 141 ($M^+ - C_4F_9$, 35); 77 (100). MS CI (isobutane) (m/z): 361 (MH^+ , 100%). Elemental analysis: Found: C, 33.23; H, 1.38%. Calc. for $C_{10}H_5F_9O_2S$: C, 33.35; H, 1.40%.

4-(Perfluorobutylsulfonyl)toluene (**12a**): B.p. 163–165 °C/5470 Pa. 1H NMR δ : 2.52 (s, 3H); 7.47 (d, $J=8.2$ Hz, 2H); 7.92 (d, $J=8.2$ Hz, 2H) ppm. MS EI (m/z): 155 ($M^+ - C_4F_9$, 43); 91 (100); 69 (16). MS CI (isobutane) (m/z): 375 (MH^+ , 100%). Elemental analysis: Found: C, 35.28; H, 2.08%. Calc. for $C_{11}H_7F_9O_2S$: C, 35.31; H, 1.89%.

4-(Perfluorobutylsulfonyl)phenol (**13a**): M.p. 95–97 °C. 1H NMR δ : 5.90 (br s, 1H); 7.06 (d, $J=8.5$ Hz, 2H); 7.93 (d, $J=8.5$ Hz, 2H) ppm. ^{19}F NMR δ : -2.95 (3F); -34.16 (2F); -43.12 (2F); -48.23 (2F) ppm. MS EI (m/z): 157 ($M^+ - C_4F_9$, 100); 93 (74); 69 (32); 65 (58); MS CI (isobutane) (m/z): 377 (MH^+ , 100%). Elemental analysis: Found: C, 31.77; H, 1.28%. Calc. for $C_{10}H_5F_9O_3S$: C, 31.93; H, 1.34%.

4-(Perfluorobutylsulfonyl)chlorobenzene (**14a**): B.p. 101–104 °C/5330 Pa. 1H NMR δ : 7.67 (d, $J=8.8$ Hz, 2H); 7.98 (d, $J=8.8$ Hz, 2H) ppm. ^{19}F NMR δ : -3.03 (3F); -33.71 (2F); -43.10 (2F); -48.27 (2F) ppm. MS EI (m/z): 175 ($M^+ - C_4F_9$, 85); 111 (100); 69 (24). MS CI (isobutane) (m/z): 395 (MH^+ , 100%). Elemental analysis: Found: C, 30.48; H, 1.12%. Calc. for $C_{10}H_4ClF_9O_2S$: C, 30.44; H, 1.02%.

4-(Perfluorobutylsulfonyl)chlorobenzene (**14'a**): oil. 1H NMR δ : 7.62 (d, $J=8.6$ Hz, 2H); 7.75 (d, $J=8.6$ Hz, 2H) ppm. MS EI (m/z): 159 ($M^+ - C_4F_9$, 100); 131 (32); 111 (21); 69 (35). MS CI (isobutane) (m/z): 379 (MH^+ , 100%). Elemental analysis: Found: C, 31.78; H, 1.11%. Calc. for $C_{10}H_4ClF_9OS$: C, 31.72; H, 1.06%.

4-(Perfluorobutylsulfonyl)nitrobenzene (**15a**): M.p. 125–126 °C. 1H NMR δ : 8.28 (d, $J=8.5$ Hz, 2H); 8.52 (d, $J=8.5$ Hz, 2H) ppm. ^{19}F NMR δ : -2.87 (3F); -32.92 (2F); -42.90 (2F); -48.13 (2F) ppm. MS EI (m/z): 186 ($M^+ - C_4F_9$, 100); 170 (21); 122 (93); 76 (66); 50 (77). MS CI (isobutane) (m/z): 406 (MH^+ , 100%). Elemental analysis: Found: C, 29.96; H, 1.00; N, 3.43%. Calc. for $C_{10}H_4F_9NO_4S$: C, 29.64; H, 1.00; N, 3.46%.

4-(Perfluorohexylsulfonyl)nitrobenzene (**15b**): M.p. 133–135 °C. 1H NMR δ : 8.27 (d, $J=8.8$ Hz, 2H); 8.52 (d, $J=8.8$ Hz, 2H) ppm. MS EI (m/z): 186 ($M^+ - C_6F_{13}$, 100); 122 (82); 92 (29); 76 (49); 75 (38); 69 (29). MS CI (isobutane) (m/z): 506 (MH^+ , 23); 476 (34); 186 (23); 140 (45); 124 (100); 108 (39). Elemental analysis: Found: C, 28.86; H, 0.76; N, 2.57%. Calc. for $C_{12}H_4F_{13}NO_4S$: C, 28.53; H, 0.80; N, 2.77%.

4-(Perfluorooctylsulfonyl)nitrobenzene (**15c**): M.p. 155–156 °C. 1H NMR δ : 8.28 (d, $J=8.2$ Hz, 2H); 8.52 (d, $J=8.2$ Hz, 2H) ppm. MS EI (m/z): 186 ($M^+ - C_8F_{17}$, 100); 170 (17); 122 (94); 92 (23); 76 (42); 69 (38). MS CI (isobutane) (m/z): 606 (MH^+ , 100%). Elemental analysis:

Found: C, 27.93; H, 0.70; N, 2.29%. Calc. for $C_{14}H_4F_{17}NO_4S$: C, 27.78; H, 0.67; N, 2.31%.

4-(1*H*,1*H*,2*H*,2*H*-Perfluorohexylsulfonyl)nitrobenzene (**15d**): M.p. 121–123 °C. 1H NMR δ : 2.56 (tt, $J = 17.1, 8.2$ Hz, 2H); 3.40 (tt, $J = 8.2, 4.0$ Hz, 2H); 8.18 (d, $J = 8.5$ Hz, 2H); 8.49 (d, $J = 8.5$ Hz, 2H) ppm. MS EI (m/z): 433 (M^+ , 6); 186 (100); 122 (74); 77 (38). Elemental analysis: Found: C, 33.15; H, 1.59; N, 3.42%. Calc. for $C_{12}H_8F_9NO_4S$: C, 33.27; H, 1.86; N, 3.23%.

4-(1*H*,1*H*,2*H*,2*H*-Perfluorooctylsulfonyl)nitrobenzene (**15e**): M.p. 122–123 °C. 1H NMR δ : 2.65 (tt, $J = 16.0, 8.2$ Hz, 2H); 3.39 (tt, $J = 8.2, 3.8$ Hz, 2H); 8.17 (d, $J = 8.9$ Hz, 2H); 8.48 (d, $J = 8.9$ Hz, 2H) ppm. MS EI (m/z): 533 (M^+ , 5); 186 (100); 122 (72); 77 (70). Elemental analysis: Found: C, 31.74; H, 1.82; N, 2.98%. Calc. for $C_{14}H_8F_{13}NO_4S$: C, 31.53; H, 1.51; N, 2.63%.

3.4. Synthesis of 4-(Perfluoroalkylsulfonyl)anilines **16**

A general procedure involved adding iron powder (12 mmol) in small portions to a refluxing methanol solution (30 ml) of 4-(perfluoroalkylsulfonyl)nitrobenzene (2 mmol) and conc. hydrochloric acid (14 mmol). After the disappearance of the starting material, the mixture was poured into aqueous sodium hydroxide solution. The resulting precipitate was filtered, dried, and extracted using a Soxhlet extractor. The physical and spectral data of the 4-(perfluoroalkylsulfonyl)anilines are given below.

4-(Perfluorobutylsulfonyl)aniline (**16a**): M.p. 85–87 °C. 1H NMR δ : 4.52 (br s, 2H); 6.75 (d, $J = 8.8$ Hz, 2H); 7.76 (d, $J = 8.8$ Hz, 2H) ppm. ^{19}F NMR δ : -3.21 (3F); -34.60 (2F); -48.18 (2F); -48.23 (2F) ppm. MS EI (m/z): 375 (M^+ , 22); 156 (100); 140 (17); 108 (50); 92 (77); 69 (20); 65 (59). Elemental analysis: Found: C, 32.12; H, 1.57; N, 3.87%. Calc. for $C_{10}H_6F_9NO_2S$: C, 32.01; H, 1.61; N, 3.73%.

4-(Perfluorohexylsulfonyl)aniline (**16b**): M.p. 122–124 °C. 1H NMR δ : 4.56 (br s, 2H); 6.75 (d, $J = 8.9$ Hz, 2H); 7.75 (d, $J = 8.9$ Hz, 2H) ppm. ^{19}F NMR δ : -3.02 (3F); -34.38 (2F); -41.91 (2F); -43.87 (2F); -45.00 (2F); -48.39 (2F) ppm. MS EI (m/z): 475 (M^+ , 24); 156 (100); 108 (39); 92 (59); 69 (18); 65 (40). Elemental analysis: Found: C, 30.66; H, 1.24; N, 3.18%. Calc. for $C_{12}H_6F_{13}NO_2S$: C, 30.33; H, 1.27; N, 2.95%.

4-(Perfluorooctylsulfonyl)aniline (**16c**): M.p. 138–139 °C. 1H NMR δ : 4.51 (s, 2H); 6.75 (d, $J = 8.5$ Hz, 2H); 7.76

(d, $J = 8.5$ Hz, 2H) ppm. ^{19}F NMR δ : -2.99 (3F); -34.36 (2F); -42.11 (2F); -43.80 (2F); -43.96 (2F); -44.14 (2F); -44.93 (2F); -48.34 (2F) ppm. MS EI (m/z): 575 (M^+ , 2); 156 (100); 108 (46); 92 (70); 69 (47). MS CI (isobutane) (m/z): 576 (MH^+ , 20%); 126 (100%). Elemental analysis: Found: C, 29.57; H, 0.95; N, 2.48%. Calc. for $C_{14}H_6F_{17}NO_2S$: C, 29.23; H, 1.05; N, 2.43%.

4-(1*H*,1*H*,2*H*,2*H*-Perfluorohexylsulfonyl)aniline (**16d**): M.p. 179–180 °C. 1H NMR δ : 2.56 (tt, $J = 17.8, 8.4$ Hz, 2H); 3.27 (tt, $J = 8.4, 3.7$ Hz, 2H); 4.30 (br s, 2H); 6.74 (d, $J = 8.7$ Hz, 2H); 7.68 (d, $J = 8.7$ Hz, 2H) ppm. MS EI (m/z): 403 (M^+ , 64); 156 (100); 108 (69); 92 (79); 65 (59). Elemental analysis: Found: C, 35.89; H, 2.48; N, 3.41%. Calc. for $C_{12}H_{10}F_9NO_2S$: C, 35.74; H, 2.50; N, 3.47%.

4-(1*H*,1*H*,2*H*,2*H*-Perfluorooctylsulfonyl)aniline (**16e**): M.p. 164–165 °C. 1H NMR δ : 2.56 (tt, $J = 17.0, 8.4$ Hz, 2H); 3.26 (tt, $J = 8.4, 4.4$ Hz, 2H); 4.28 (br s, 2H); 6.74 (d, $J = 8.7$ Hz, 2H); 7.67 (d, $J = 8.7$ Hz, 2H) ppm. ^{19}F NMR δ : -3.51 (3F); -35.54 (1F); -35.88 (1F); -44.61 (2F); -45.61 (2F); -45.89 (2F); -48.88 (2F) ppm. MS EI (m/z): 503 (M^+ , 32); 471 (51); 140 (100); 124 (69); 92 (52). Elemental analysis: Found: C, 33.29; H, 2.00; N, 3.08%. Calc. for $C_{14}H_{10}F_{13}NO_2S$: C, 33.41; H, 2.00; N, 2.78%.

Acknowledgements

This work was partially supported by the Grant-in-Aid for Scientific Research No. 06650978 from the Ministry of Education, Science and Culture of Japan. B. Joglekar wishes to thank the Ministry of Education, Science and Culture of Japan for the award of a research fellowship.

References

- [1] V.N. Boiko, G.M. Shchupak and L.M. Yagupolskii, *J. Org. Chem. USSR*, 13 (1977) 972.
- [2] V.I. Popov, V.N. Boiko, N.V. Kondratenko, V.P. Sambur and L.M. Yagupolskii, *J. Org. Chem. USSR*, 13 (1977) 1985.
- [3] V.N. Boiko, T.A. Dawshevskaya, G.M. Shchupak and L.M. Yagupolskii, *J. Org. Chem. USSR*, 15 (1979) 347.
- [4] V.I. Popov, V.N. Boiko and L.M. Yagupolskii, *J. Fluorine Chem.*, 21 (1982) 365.
- [5] A.E. Feiring, *J. Fluorine Chem.*, 24 (1984) 191.
- [6] L.M. Yagupolskii, V.N. Kondratenko and V.P. Sambur, *Synthesis*, (1975) 721.
- [7] L.M. Yagupolskii and V.N. Boiko, *J. Gen. Chem. USSR*, 39 (1969) 179.