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ScienceDirect
Journal of Fluorine Chemistry 128 (2007) 789–796
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/fluor

Amphiphilic perfluoroalkylated sulfones and sulfonate betaines

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Received 31 January 2007; received in revised form 19 February 2007; accepted 19 February 2007
Available online 23 February 2007

Abstract

Two types of perfluoro alkyl-containing amphiphilic sulfones **7–9** and **13–15**, respectively, and sulfonate betaines **23–32** were prepared using 2-[(perfluoroalkyl)methyl]oxiranes (**1–3**, $R_F = C_4F_9$, C_6F_{13}, C_8F_{17}) or 3-(perfluoroalkyl)propyl iodides (**16** and **17**, $R_F = C_6F_{13}$, C_8F_{17}) as the starting compounds. The overall yields of two-step syntheses were above 90%. The compounds **7–9** were prepared by the reaction of oxiranes **1–3** with 2-sulfanylethan-l-ol and subsequent oxidation of intermediate sulfides. Similarly, the amphiphiles **13–15** were obtained by analogous reaction of oxiranes **1–3** with thiomorpholine and subsequent oxidation of the sulfur atom in the morpholine ring. In the syntheses of betaines **23–32**, the starting compounds **1–3** or **16** and **17** were first reacted with dimethylamine followed by the ring-opening reaction of the intermediate fluoroalkyl(dimethyl)amines with propane-1,3- or butane-1,4-sultones.

Keywords: Perfluoroalkylated amphiphiles; Sulfones; Sulfonate betaines; Epoxide ring-opening; Sulfide oxidation

1. Introduction

Polyfluoroalkylated amphiphiles as a special class of surfactants are composed of hydrophilic moiety and both hydrophobic and lipophobic fluorinated chain. These compounds display remarkable surface properties that destine them for the use e.g., in biomedicinal area [1–4], as special detergents for cleaning [5–7], foaming agents and foam stabilizers [8–10], in material science and microelectronics [11].

Our aim has been the preparation of fluorinated amphiphiles containing strongly hydrophilic moiety as sulfone or sulfonic betaine groups. Perfluoroalkylated sulfones were applied in the synthesis of [2-(perfluorooctyl)ethyl]sulfonylethoxycarbonyl protecting group [12], as precursors of fluoroalkylated surfactants [13] and foaming agents [14]. Acrylates bearing fluoroalkyl and sulfone groups were reported for textile and oil repellents [15] in polymeric form or as hydrophilic medicinal prosthetic materials [16]. Among 1,1-dioxothiomorpholine derivatives, only one compound possessing perfluoroalkanesulfonyl moiety has been reported [17], which was prepared by the reaction of the corresponding sulfonamide with divinyl sulfone.

We would like to report here efficient syntheses of new perfluoroalkylated amphiphiles: one series of them is possessing sulfone (**7–9** and **13–15**) and the second sulfonic betaine hydrophilic groups (**23–32**).

2. Results and discussion

2.1. Perfluoroalkylated amphiphiles containing sulfone hydrophilic moiety

Two-step syntheses have been employed to prepare the target compounds. The first step was the reaction of (2-[(perfluoroalkyl)methyl]oxiranes (**1–3**, $R_F = C_4F_9$, C_6F_{13}, C_8F_{17}) with nucleophiles, by which the 2-hydroxy-3-(perfluoroalkyl)methyl moiety was introduced to the products (Scheme 1). In the synthesis of the first type of amphiphiles, the oxiranes **1–3** were reacted with 2-sulfanylethan-1-ol to afford sulfides **4–6**. The epoxide ring opening proceeded with the complete regioselectivity at the less substituted carbon atom [18,19]. The second step was oxidation at the sulfur atom. The oxidation can be carried out by hydrogen peroxide in acetic acid [14], peroxyacetic acid [12] or 3-chloroperoxybenzoic acid [20]. The oxidation of the intermediate sulfides **4–6** using 30% hydrogen peroxide was our method of choice (Scheme 1). The yields of the target products **7–9** were almost quantitative.

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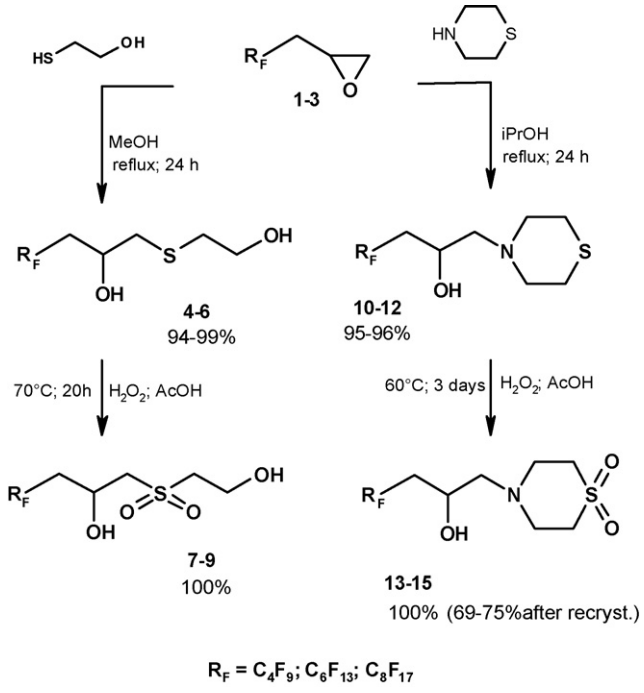
doi:10.1016/j.jfluchem.2007.02.011

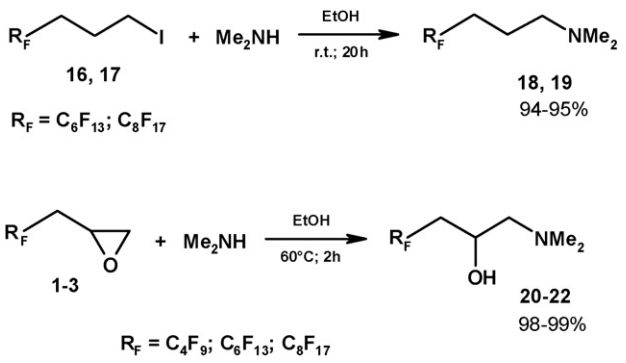


Scheme 1.

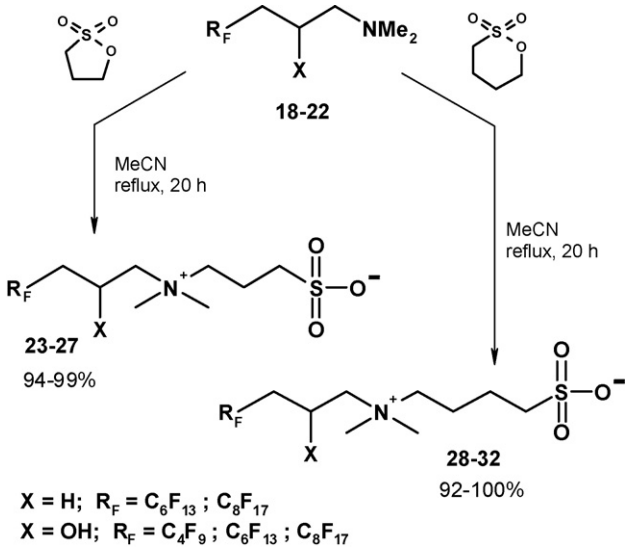
In an analogous way, the amphiphiles **13–15** were prepared (Scheme 1). The reaction of the oxiranes **1–3** with thiomorpholine proceeded with the complete regioselectivity at the more nucleophilic nitrogen atom [21] in approx. 95% yields. The same oxidation as above afforded the target products **13–15** in almost quantitative yields.

2.2. *Perfluoroalkylated amphiphiles containing sulfonic betaine hydrophilic moiety*

Sulfonic betaines can be prepared by several general methods. They include the reaction of tertiary amines with α,ω-dibromoalkanes and sodium sulfite [22], with sultones [8,22–25] or 2-chloroethane-sulfonates [24] and sulfonation of allyl(trialkyl)ammonium salts [26]. Some perfluoroalkylated sulfonic betaines bearing the propane-l,3-diyl spacer between the sulfonate group and quarternary nitrogen atom were prepared by the reaction of perfluoroalkylated amines with propane-1,3-sultone [8,27]. Perfluoroalkylated sulfonic betaines bearing the butane-1,4-diyl spacer between the groups have not yet been reported.



Scheme 2.



Scheme 3.

Our intermediates in the synthesis of sulfonic betaines **23–32** were dimethyl(polyfluoroalkyl)amines **18–22** possessing a three-carbon spacer between the perfluoroalkyl chain and tertiary nitrogen (Scheme 2). The spacer in these compounds is non-hydroxylated (**18** and **19**), or hydroxylated (**20–22**). The (polyfluoroalkyl)amines possessing the non-hydroxylated spacer can be prepared by the reaction of 3-(perfluorooctyl)-propyl iodide with dimethylamine [28] or by the reduction of the dimethylamide of 3-(perfluorooctyl)propanoic acid using $LiAlH_4$ [29].

The tertiary amines **18** and **19** we prepared by the reaction of 3-(perfluoroalkyl)propyl iodides **16** and **17** with dimethylamine in ethanol. The new tertiary amines **20–22** bearing hydroxylated spacer were obtained by the reaction of perfluoroalkylated epoxides **1–3** with dimethylamine according to Ref. [30] (Scheme 2).

8The intermediate tertiary fluoroalkyl amines **18–22** were reacted with excess propane-1,3- or butane-1,4-sultone in dry acetonitrile. The target products, sulfonate betaines **23–32** precipitated gradually from the reaction solution as white solid in yields of 92–100%. The reactions of amines **20–22** bearing hydroxylated spacer took place at the nitrogen nucleophilic center with complete regioselectivity (Scheme 3).

3. Conclusions

Two series of new perfluoroalkylated amphiphiles were prepared by simple procedures from commercially available starting compounds in overall yields above 90%. The compounds **7–9** and **13–15** in the first series possess sulfonic hydrophilic group, while the amphiphiles **23–32** in the second series possess sulfonic betaine hydrophilic group.

4. Experimental

4.1. General comments and chemicals

NMR spectra were recorded on a Varian Gemini 300 HC (FT, ^{1}H at 300 MHz, ^{13}C at 75 MHz, ^{19}F at 281 MHz) instrument using TMS and $CFCl_3$ as the internal standards. Chemical shifts are quoted in ppm (δ-scale; s-singlet, bs-broad singlet, d-doublet, t-triplet, q-quadruplet, m-multiplet), coupling constants J in Hz, solvents $CDCl_3$, acetone-d_6, CD_3OD.

The chemicals used were as follows: 2-sulfanylethanol, thiomorpholine, dimethylamine (33% in absolute ethanol), 3-(perfluorohexyl)propyl iodide, 3-(perfluorooctyl)propyl iodide, propane-1,3-sultone, butane-1,4-sultone (all Aldrich), silica gel (60–100 μm, Merck). Acetic acid and hydrogen peroxide (30%) were purchased from Penta. Polyfluoroalkylated epoxides were prepared according to the literature procedure [31]. All solvents were purchased from Penta and dried according to standard procedures.

4.2. General procedure for preparation of sulfanyls 4–6

2-[(Perfluoroalkyl)methyl]oxiranes **1**–**3** and 2-sulfanylethanol (1:1 mole equivalents) were dissolved in dry methanol and refluxed overnight while stirring. The solvent was then evaporated and a crude product was purified using column chromatography on silica gel (hexane/acetone 1:1). Products **4**–**6** were obtained as colourless liquids or waxy solids in yields of 94–99%.

4.2.1. 2-(2-Hydroxy-4,4,5,5,6,6,7,7,7-nonafluoroheptylsulfanyl)ethanol (4)

1,2-Epoxy-4,4,5,5,6,6,7,7,7-nonafluoroheptane (**1**, 1.66 g, 6 mmol), 2-sulfanylethanol (0.47 g, 6 mmol), MeOH (2 mL). Yield of **4**: 2.02 g (94%) as colourless liquid.

^{1}H NMR ($CDCl_3$): 2.15–2.50 (m, 2H, CH_2R_F), 2.60–2.87 (m, 4H, CH_2SCH_2), 3.36 (m, 1H, OH), 3.76 (t, 2H, CH_2O, $^{3}J_{HH}$ = 5.5 Hz), 3.97 (m, 1H, OH), 4.22 (m, 1H, CHO); ^{13}C NMR ($CDCl_3$): 35.6 (s, 1C, CH_2S), 36.6 (t, 1C, CH_2–R_F, $^{2}J_{CF}$ = 20.8 Hz), 40.0 (s, 1C, CH_2S), 61.3 (s, 1C, CH_2O), 64.4 (s, 1C, CHO), 105.0–125.0 (m, 4C, 3× CF_2 and 1× CF_3); ^{19}F NMR ($CDCl_3$): −81.3 (t, 3F, CF_3, $^{3}J_{FF}$ = 9.8 Hz), −113.2 (m, 2F, CH_2–CF_2), −124.7 (m, 2F, CF_2), −126.1 (m, 2F, CF_2). Anal. Calcd. for $C_9H_{11}F_9O_2S$: C, 30.52; H, 3.13. Found: C, 30.47; H, 3.21.

4.2.2. 2-(2-Hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononylsulfanyl)ethanol (5)

1,2-Epoxy-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononane (**2**, 2.335 g, 6.2 mmol), 2-sulfanylethanol (0.485 g, 6.2 mmol), MeOH (2 mL). Yield of **5**: 2.807 g (99%) as colourless liquid.

^{1}H NMR ($CDCl_3$): 2.10–2.50 (m, 2H, CH_2R_F), 2.61–2.90 (m, 4H, CH_2SCH_2), 3.77 (t, 2H, CH_2O, $^{3}J_{H0H}$ = 5.8 Hz), 3.97 (m, 1H, OH), 4.22 (m, 1H, CHO); ^{13}C NMR ($CDCl_3$): 35.7 (s, 1C, CH_2S), 36.7 (t, 1C, CH_2R_F, $^{2}J_{CF}$ = 21.0 Hz), 40.1 (s, 1C, CH_2S), 61.3 (s, 1C, CH_2O), 64.5 (s, 1C, CHO), 105.0–125.0 (m, 6C, 5× CF_2 and 1× CF_3); ^{19}F NMR ($CDCl_3$): −81.2 (t, 3F, CF_3, $^{3}J_{FF}$ = 9.8 Hz), −113.1 (m, 2F, CH_2–CF_2), −122.1 (m, 2F, CF_2), −123.2 (m, 2F, CF_2), −123.9 (m, 2F, CF_2), −116.5 (m, 2F, CF_2). Anal. Calcd. for $C_{11}H_{11}F_{13}O_2S$: C, 29.09; H, 2.44. Found: C, 29.12; H, 2.50.

4.2.3. 2-(2-Hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoroundecylsulfanyl)ethanol (6)

1,2-Epoxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoroundecane (**3**, 3.290 g, 6.9 mmol), 2-sulfanylethanol (0.540 g, 6.9 mmol), MeOH (3 mL). Yield of **6**: 3.680 g (96%) as white waxy solid.

^{1}H NMR ($CDCl_3$): 2.10–2.58 (m, 2H, CH_2R_F), 2.59–2.95 (m, 4H, CH_2SCH_2), 3.34 (m, 2H, OH), 3.79 (m, 2H, CH_2O), 4.26 (m, 1H, CHO); ^{13}C NMR ($CDCl_3$): 35.7 (s, 1C, CH_2S), 36.8 (t, 1C, CH_2–R_F, $^{2}J_{CF}$ = 20.5 Hz), 40.0 (s, 1C, CH_2S), 61.4 (s, 1C, CH_2O), 64.4 (s, 1C, CHO), 105.0–125.0 (m, 8C, 7× CF_2 and 1× CF_3); ^{19}F NMR ($CDCl_3$): −80.8 (t, 3F, CF_3, $^{3}J_{FF}$ = 9.2Hz), −112.9 (m, 2F, CH_2–CF_2), −121.6 (m, 2F, CF_2), −122.0 (m, 4F, 2× CF_2), −123.6 (m, 2F, CF_2), −126.1 (m, 2F, CF_2). Anal. Calcd. for $C_{13}H_{11}F_{17}O_2S$: C, 28.17; H, 2.00. Found: C, 27.98; H, 2.10.

4.3. General procedure for preparation of sulfones 7–9

2-[2-Hydroxy-3-(perfluoroalkyl)propylsulfanyl]ethanol (**4**–**6**) was dissolved in glacial acetic acid and excess of hydrogen peroxide (30%) was added. Reaction mixture was stirred overnight at 70 °C. The mixture was then evaporated to dryness (residual water and AcOH were removed by co-evaporation with toluene) and products **7**–**9** were obtained as white solids in quantitative yields.

4.3.1. 2-(2-Hydroxy-4,4,5,5,6,6,7,7,7-nonafluoroheptylsulfonyl)ethanol (7)

2-(2-Hydroxy-4,4,5,5,6,6,7,7,7-nonafluoroheptylsulfanyl)ethanol (**4**, 400 mg, 1.13 mmol), AcOH (2 mL), H_2O_2 (30%, 2 mL, 19.5 mmol). Yield of **7**: 438 mg (100%) as white solid.

^{1}H NMR (acetone-d_6): 2.40–2.80 (m, 2H, CH_2R_F), 2.85–3.50 (m, 4H, $CH_2SO_2CH_2$), 4.00 (m, 2H, CH_2O), 4.75 (m, 1H, CHO); ^{13}C NMR (acetone-d_6): 38.5 (t, 1C, CH_2–R_F, $^{2}J_{CF}$ = 20.1 Hz), 57.4 (s, 1C, CH_2SO_2), 58.6 (s, 1C, CH_2SO_2), 61.4 (s, 1C, CH_2O), 62.3 (s, 1C, CHO), 105.0–125.0 (m, 4C, 3× CF_2 and 1× CF_3); ^{19}F NMR (acetone-d_6): −76.9 (t, 3F, CF_3, $^{3}J_{FF}$ = 9.8 Hz), −108.0 (m, 2F, CH_2–CF_2), −120.0 (m, 2F, CF_2), −121.4 (m, 2F, CF_2). Anal. Calcd. for $C_9H_{11}F_9O_4S$: C, 27.99; H, 2.87. Found: C, 27.86; H, 2.95.

4.3.2. 2-(2-Hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononylsulfonyl)ethanol (8)

2-(2-Hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononylsulfanyl)ethanol (**5**, 460 mg, 1 mmol), AcOH (2 mL), H_2O_2 (30%, 2 mL, 19.5 mmol). Yield of **8**: 489 mg (100%) as white solid. ^{1}H NMR (acetone-d_6): 2.35–2.88 (m, 2H, CH_2R_F), 3.20–3.75 (m, 4H, $CH_2SO_2CH_2$), 4.23 (t, 2H, CH_2O, $^{3}J_{HH}$ = 5.6 Hz), 4.35–4.60 (m, 2H, 2× OH), 4.75 (m, 1H, CHO); ^{13}C NMR (acetone-d_6): 38.5 (t, 1C, CH_2–R_F, $^{2}J_{CF}$ = 20.2 Hz), 57.4 (s, 1C, CH_2SO_2), 58.6 (s, 1C, CH_2SO_2), 61.4 (s, 1C, CH_2O), 62.3 (s,

1C, CHO), 105.0–125.0 (m, 6C, 5× CF_2 and 1× CF_3); ^{19}F NMR (acetone-d_6): −76.3 (t, 3F, CF_3, $^3J_{FF}$ = 9.8 Hz), −106.4 (m, 2F, CH_2–CF_2), −114.9 (m, 2F, CF_2), −115.9 (m, 2F, CF_2), −116.5 (m, 2F, CF_2), −119.0 (m, 2F, CF_2). Anal. Calcd. for $C_{11}H_{11}F_{13}O_4S$: C, 27.17; H, 2.28. Found: C, 27.13; H, 2.36.

4.3.3. 2-(2-Hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoroundecylsulfonyl)ethanol (**9**)

2-(2-Hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoroundecylsulfanyl)ethanol (**6**, 594 mg, 1.07 mmol), AcOH (2 mL), H_2O_2 (30%, 2 mL, 19.5 mmol). Yield of **9**: 625 mg (100%) as white solid. ^1H NMR (acetone-d_6): 2.40–2.86 (m, 2H, CH_2R_F), 3.20–3.75 (m, 4H, $CH_2SO_2CH_2$), 4.06 (t, 2H, CH_2O, $^3J_{HH}$ = 5.9 Hz), 4.75 (m, 1H CHO); ^{13}C NMR (acetone-d_6): 38.5 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 20.4 Hz), 57.4 (s, 1C, CH_2SO_2), 58.6 (s, 1C, CH_2SO_2), 61.9 (s, 1C, CH_2O), 62.2 (s, 1C, CHO), 105.0–125.0 (m, 8C, 7× CF_2 and 1× CF_3); ^{19}F NMR (acetone-d_6): −76.5 (t, 3F, CF_3, $^3J_{FF}$ = 9.8 Hz), −108.1 (m, 2F, CH_2–CF_2), −117.0 (m, 2F, CF_2), −117.3 (m, 4F, 2× CF_2), −118.0 (m, 2F, CF_2), −119.1 (m, 2F, CF_2), −121.6 (m, 2F, CF_2). Anal. Calcd. for $C_{13}H_{11}F_{17}O_4S$: C, 26.63; H, 1.89. Found: C, 26.54; H, 1.91.

4.4. General procedure for preparation of thiomorpholine derivatives **10–12**

2-[(Perfluoroalkyl)methyl]oxirane **1–3** and thiomorpholine (1:1 mole equivalents) were dissolved in dry propan-2-ol and refluxed overnight while stirring. The solvent was then evaporated and crude product was purified using column chromatography on silica gel (petroleum ether/acetone 4:1). Products **10–12** were obtained as yellowish waxy solids in yields of 95–96%.

4.4.1. N-(2-Hydroxy-4,4,5,5,6,6,7,7,7-nonafluoroheptyl)thiomorpholine (**10**)

l,2-Epoxy-4,4,5,5,6,6,7,7,7-nonafluoroheptane (**1**, 1621 mg, 5.87 mmol), thiomorpholine (606 mg, 5.87 mmol), iPrOH (10 mL). Yield of **10**: 646 mg (96%) as yellowish waxy solid.

^1H NMR ($CDCl_3$): 1.96–2.42 (m, 2H, CH_2R_F), 2.24–2.75 (m, 8H, $N(CH_2CH_2)_2S$), 2.85–3.00 (m, 2H, CH_2N), 4.11 (m, 1H, CHO); ^{13}C NMR ($CDCl_3$): 28.0 (s, 2C, CH_2SCH_2), 35.9 (t, 1C, CH_2–RF, $^2J_{CF}$ = 20.7 Hz), 55.1 (s, 2C, $N(CH_2)_2$), 60.1 (s, 1C, CHO), 64.4 (s, 1C, CH_2N), 105.0–125.0 (m, 4C, 3× CF_2 and 1× CF_3); ^{19}F NMR ($CDCl_3$): −81.6 (t, 3F, CF_3, $^3J_{FF}$ = 9.8 Hz), −113.2 (m, 2F, CH_2–CF_2), −125.2 (m, 2F, CF_2), −126.6 (m, 2F, CF_2). Anal. Calcd. for $C_{11}H_{14}F_9NOS$: C, 34.83; H, 3.72; N, 3.69. Found: C, 34.85; H, 3.85; N, 3.71.

4.4.2. N-(2-Hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)thiomorpholine (**11**)

l,2-Epoxy-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononane (**2**, 2068 mg, 5.5 mmol), thiomorpholine (567 mg, 5.5 mmol), iPrOH (10 mL). Yield of **11**: 2600 mg (95%) as yellowish waxy solid.

^1H NMR ($CDCl_3$): 1.93–2.40 (m, 2H, CH_2R_F), 2.22–2.75 (m, 8H, $N(CH_2CH_2)_2S$), 2.86–3.05 (m, 2H, CH_2N), 4.08 (m, 1H, CHO); ^{13}C NMR ($CDCl_3$): 28.0 (s, 2C, CH_2SCH_2), 35.8 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 20.7 Hz), 55.1 (s, 2C, $N(CH_2)_2$), 60.2 (s, 1C, CHO), 64.3 (s, 1C, CH_2N), 105.0–125.0 (m, 6C, 5× CF_2 and 1× CF_3); ^{19}F NMR ($CDCl_3$): −81.5 (t, 3F, CF_3, $^3J_{FF}$ = 9.9 Hz), −113.5 (m, 2F, CH_2CF_2), −122.4 (m, 2F, CF_2), −123.3 (m, 2F, CF_2), −123.9 (m, 2F, CF_2), −126.7 (m, 2F, CF_2). Anal. Calcd. for $C_{13}H_{14}F_{13}NOS$: C, 32.58; H, 2.94; N, 3.34. Found: C, 32.44; H, 3.02; N, 3.36.

4.4.3. N-(2-Hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)thiomorpholine (**12**)

l,2-Epoxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecane (**3**, 2695 mg, 5.66 mmol), thiomorpholine (584 mg, 5.66 mmol), iPrOH (10 mL). Yield of **12**: 3147 mg (96%) as yellowish waxy solid.

^1H NMR ($CDCl_3$): 1.98–2.40 (m, 2H, CH_2R_F), 2.27–2.83 (m, 8H, $N(CH_2CH_2)_2S$), 2.84–2.97 (m, 2H, CH_2N), 4.14 (m, 1H, CHO); ^{13}C NMR ($CDCl_3$): 28.1 (s, 2C, CH_2SCH_2), 35.8 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 20.7 Hz), 55.1 (s, 2C, $N(CH_2)_2$), 60.1 (s, 1C, CHO), 64.4 (s, 1C, CH_2N), 105.0–125.0 (m, 8C, 7× CF_2 and 1× CF_3); ^{19}F NMR ($CDCl_3$): −81.4 (t, 3F, CF_3, $^3J_{FF}$ = 9.9 Hz), −113.0 (m, 2F, CH_2CF_2), −122.2 (m, 2F, CF_2), −122.4 (m, 4F, 2× CF_2), −123.3 (m, 2F, CF_2), −123.8 (m, 2F, CF_2), −126.7 (m, 2F, CF_2). Anal. Calcd. for $C_{15}H_{14}F_{17}NOS$: C, 31.10; H, 2.44; N, 2.42. Found: C, 31.01; H, 2.57; N, 2.41.

4.5. General procedure for preparation of sulfonyls **13-15**

N-[2-Hydroxy-3-(perfluoroalkyl)propyl]thiomorpholine (**10–12**) was dissolved in glacial acetic acid and excess hydrogen peroxide (30%) was added. Reaction mixture was stirred at 60 °C over weekend. The mixture was then evaporated to dryness (residual water and AcOH were removed by co-evaporation with toluene) and products **13–15** were obtained as white semisolid mass in the quantitative yields. After recrystallization (acetone–diethyl ether), 1,1-dioxothiomorpholines **13–15** were obtained as white solids in 69–75% yields.

4.5.1. 1,1-Dioxo-4-(2-hydroxy-4,4,5,5,6,6,7,7,7-nonafluoroheptyl)thiomorpholine (**13**)

N-(2-Hydroxy-4,4,5,5,6,6,7,7,7-nonafluoroheptyl)thiomorpholine (**10**, 620 mg, 1.63 mmol), AcOH (16 mL), H_2O_2 (30%, 1 mL, 9.75 mmol). Yield of **13**: 672 mg (100%) as white semisolid mass; after recrystallization 494 mg (73%) as white solid.

^1H NMR (acetone-d_6): 2.42–2.74 (m, 2H, CH_2R_F), 3.28–3.51 (m, 2H, CH_2N), 3.90–4.74 (m, 8H, $N(CH_2CH_2)_2SO_2$), 5.07 (m, 1H, CHO); ^{13}C NMR (acetone-d_6): 36.2 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 19.8 Hz), 46.7 (s, 2C, $N(CH_2)_2$), 47.1 (s, 2C, $(CH_2)_2SO_2$), 61.3 (s, 1C, CHO), 63.4 (s, 1C, CH_2N), 105.0–125.0 (m, 4C, 3× CF_2 and 1× CF_3); ^{19}F NMR (acetone-d_6): −81.0 (t, 3F, CF_3, $^3J_{FF}$ = 9.8 Hz), −112.1 (m, 2F, CH_2–CF_2), −124.1 (m, 2F, CF_2), −125.6 (m, 2F, CF_2). Anal. Calcd. for $C_{15}H_{14}F_9NO_3S$: C, 32.12; H, 3.43; N, 3.41. Found: C, 32.23; H, 3.55; N, 3.37.

*4.5.2. 1,1-Dioxo-4-(2-hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)thiomorpholine (**14**)*

N-(2-Hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)thiomorpholine (**11**, 356 mg, 0.74 mmol), AcOH (12 mL), H_2O_2 (30%, 0.5 mL, 4.87 mmol). Yield of **14**: 379 mg (100%) as white semisolid mass; after recrystallization 262 mg (69%) as white solid.

^{1}H NMR (acetone-d_6): 2.40–2.70 (m, 2H, CH_2R_F), 3.26–3.53 (m, 2H, CH_2N), 3.90–4.75 (m, 8H, $N(CH_2CH_2)_2SO_2$), 5.05 (m, 1H, CHO); ^{13}C NMR (acetone-d_6): 36.1 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 19.8 Hz), 46.7 (s, 2C, $N(CH_2)_2$), 47.1 (s, 2C, $(CH_2)_2SO_2$), 61.3 (s, 1C, CHO), 63.3 (s, 1C, CH_2N), 105.0–125.0 (m, 6C, 5× CF_2 and 1× CF_3); ^{19}F NMR (acetone-d_6): −80.9 (t, 3F, CF_3, $^3J_{FF}$ = 9.8 Hz), −112.7 (m, 2F, CH_2CF_2), −121.6 (m, 2F, CF_2), −122.3 (m, 2F, CF_2), −122.9 (m, 2F, CF_2), −125.7 (m, 2F, CF_2). Anal. Calcd. for $C_{13}H_{14}F_{13}NO_3S$: C, 30.54; H, 2.76; N, 2.74. Found: C, 30.47; H, 2.80; N, 2.69.

*4.5.3. 1,1-Dioxo-4-(2-hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)thiomorpholine (**15**)*

N-(2-Hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)thiomorpholine (**12**, 290 mg, 0.50 mmol), AcOH (12 mL), H_2O_2 (30%, 0.5 mL, 4.87 mmol). Yield of **15**: 305 mg (100%) as white semisolid mass; after recrystallization 230 mg (75%) as white solid.

^{1}H NMR (acetone-d_6): 2.39–2.68 (m, 2H, CH_2R_F), 3.24–3.45 (m, 2H, CH_2N), 3.84–4.70 (m, 8H, $N(CH_2CH_2)_2SO_2$), 5.04 (m, 1H, CHO); ^{13}C NMR (acetone-d_6): 36.2 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 19.9 Hz), 46.7 (s, 2C, $N(CH_2)_2$), 47.0 (s, 2C, $(CH_2)_2SO_2$), 61.4 (s, 1C, CHO), 63.4 (s, 1C, CH_2N), 105.0–125.0 (m, 8C, 7× $CF_2$and 1× CF_3); ^{19}F NMR (acetone-d_6): −81.0 (t, 3F, CF_3, $^3J_{FF}$ = 9.8 Hz), −112.4 (m, 2F, CH_2CF_2), −121.6 (m, 2F, CF_2), −121.9 (m, 4F, 2× CF_2), −122.7 (m, 2F, CF_2), −123.0 (m, 2F, CF_2), −125.9 (m, 2F, CF_2). Anal. Calcd. for $C_{15}H_{14}F_{17}NO_3S$: C, 29.47; H, 2.31; N, 2.29. Found: C, 29.36; H, 2.36; N, 2.24.

*4.6. General procedure for preparation of amines **18** and **19***

3-(Perfluoroalkyl)propyl iodide (**16** or **17**) was dissolved in solution of dimethylamine in dry ethanol (5.6 M) and reaction mixture was stirred overnight at RT. Diethyl ether (75 mL) was added and the mixture was extracted with saturated solution of Na_2CO_3 (50 mL). The aqueous layer was extracted with diethyl ether (75 mL), the combined organic fractions were extracted with water (2 × 30 mL), brine (30 mL) and dried over $MgSO_4$. After evaporation, products **18** or **19** were obtained as yellowish oily liquids in yields of 94–95%. Amines **18** and **19** were used in syntheses without further purification.

*4.6.1. Dimethyl-(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)amine (**18**)*

4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononyl iodide (**16**, 976 mg, 2 mmol), Me_2NH (5.6 M in abs. EtOH, 7 mL, 39.2 mmol). Yield of **18**: 770 mg (95%) as yellowish oil.

^{1}H NMR ($CDCl_3$): 1.64–1.79 (m, 2H, CH_2), 1.94–2.24 (m, 2H, CH_2R_F), 2.18 (s, 6H, $N(CH_3)_2$), 2.29 (t, 2H, CH_2N, $^3J_{HH}$ = 6.7 Hz); ^{13}C NMR ($CDCl_3$): 18.4 (s, 1C, CH_2), 28.7 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 21.9 Hz), 45.1 (s, 2C, $N(CH_3)_2$), 58.4 (s, 1C, CH_2N), 105.0–125.0 (m, 6C, 5× CF_2 and 1× CF_3); ^{19}F NMR ($CDCl_3$): −81.4 (t, 3F, CF_3, $^3J_{FF}$ = 7.8 Hz), −114.8 (m, 2F, CH_2F_2), −122.4 (m, 2F, CF_2), −123.4 (m, 2F, CF_2), −123.9 (m, 2F, CF_2), −126.7 (m, 2F, CF_2). Anal. Calcd. for $C_{11}H_{12}F_{13}N$: C, 32.61; H, 2.99; N, 3.46. Found: C, 32.55; H, 3.03; N, 3.40.

*4.6.2. Dimethyl-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)amine (**19**)*

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecyl iodide (**17**, 2030 mg, 3.45 mmol), Me_2NH (5.6 M in abs. EtOH, 15 mL, 84 mmol). Yield of **19**: 1636 mg (94%) as yellowish oil. ^{1}H NMR ($CDCl_3$): 1.66–1.79 (m, 2H, CH_2), 1.95–2.24 (m, 2H, CH_2R_F), 2.19 (s, 6H, $N(CH_3)_2$), 2.30 (t, 2H, CH_2N, $^3J_{HH}$ = 7.0 Hz); ^{13}C NMR ($CDCl_3$): 18.4 (s, 1C, CH_2), 28.7 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 22.1 Hz), 45.1 (s, 2C, $N(CH_3)_2$), 58.4 (s, 1C, CH_2N), 105.0–125.0 (m, 8C, 7× CF_2 and 1× CF_3); ^{19}F NMR ($CDCl_3$): −81.5 (t, 3F, CF_3, $^3J_{FF}$ = 9.8 Hz), −114.8 (m, 2F, CH_2CF_2), −122.2 (m, 2F, CF_2), −122.4 (m, 4F, 2× CF_2), −123.2 (m, 2F, CF_2), −123.9 (m, 2F, CF_2), −126.7 (m, 2F, CF_2). Anal. Calcd. for $C_{13}H_{12}F_{17}N$: C, 30.91; H, 3.39; N, 2.77. Found: C, 30.85; H, 2.42; N, 2.78.

*4.7. General procedure for preparation of amines **20–22***

2-[(Perfluoroalkyl)methyl]oxirane (**1**–**3**) was dissolved in solution of dimethylamine in dry ethanol (5.6 M) and the reaction mixture was stirred in a pressure tube at 60 °C for 2 h. After evaporation, products **20**–**22** were obtained as yellowish oily liquids or waxy solid in yields of 98–100%. Amines **20**–**22** were used in syntheses without further purification.

*4.7.1. Dimethyl(2-hydroxy-4,4,5,5,6,6,7,7,7-nonafluoroheptyl)amine (**20**)*

l,2-Epoxy-4,4,5,5,6,6,7,7,7-nonafluoroheptane (**1**, 1594 mg, 5.77 mmol), Me_2NH (5.6 M in abs. EtOH, 10 mL, 56 mmol). Yield of **20**: 1816 mg (98%) as yellowish oil.

^{1}H NMR ($CDCl_3$): 1.96–2.43 (m, 4H, CH_2R_F and CH_2N), 2.28 (s, 6H, $N(CH_3)_2$), 4.10 (m, 1H, CHO), 4.13 (bs, 1H, OH); ^{13}C NMR ($CDCl_3$): 36.0 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 20.9 Hz), 45.2 (s, 2C, $N(CH_3)_2$), 60.9 (s, 1C, CHO), 65.1 (s, 1C, CH_2N), 105.0–125.0 (m, 4C, 3× CF_2 and 1× CF_3); ^{19}F NMR ($CDCl_3$): −81.6 (t, 3F, CF_3, $^3J_{FF}$ = 9.8 Hz), −113.1 (m, 2F, CH_2–CF_2), −125.0 (m, 2F, CF_2), −126.4 (m, 2F, CF_2). Anal. Calcd. for $C_9H_{12}F_9NO$: C, 33.66; H, 3.77; N, 4.36. Found: C, 33.54; H, 3.85; N, 4.40.

*4.7.2. Dimethyl(2-hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)amine (**21**)*

l,2-Epoxy-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononane (**2**, 1695 mg, 4.50 mmol), Me_2NH (5.6 M in abs. EtOH, 10 mL, 56 mmol). Yield of **21**: 1879 mg (99%) as yellowish oil.

^{1}H NMR ($CDCl_3$): 1.97–2.43 (m, 4H, CH_2R_F and CH_2N), 2.29 (s, 6H, $N(CH_3)_2$), 3.80 (bs, 1H, OH), 4.12 (m, 1H, CHO); ^{13}C NMR ($CDCl_3$): 36.1 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 20.9 Hz), 45.3 (s, 2C, $N(CH_3)_2$), 60.9 (s, 1C, CHO), 65.1 (s, 1C, CH_2N), 105.0–125.0 (m, 6C, 5× CF_2 and 1× CF_3); ^{19}F NMR ($CDCl_3$): −81.4 (t, 3F, CF_3, $^3J_{FF}$ = 10.4 Hz), −112.9 (m, 2F, CH_2CF_2), −122.3 (m, 2F, CF_2), −123.4 (m, 2F, CF_2), −124.1 (m, 2F, CF_2), −126.7 (m, 2F, CF_2). Anal. Calcd. for $C_{11}H_{12}F_{13}NO$: C, 31.37; H, 2.87; N, 3.33. Found: C, 31.45; H, 2.93; N, 3.36.

*4.7.3. Dimethyl(2-hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)amine (**22**)*

l,2-Epoxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecane (**3**, 1320 mg, 2.77 mmol), Me_2NH (5.6 M in abs. EtOH, 10 mL, 56 mmol). Yield of **22**:1445 mg (100%) as yellowish waxy solid.

^{1}H NMR ($CDCl_3$): 1.97–2.44 (m, 4H, CH_2R_F and CH_2N), 2.29 (s, 6H, $N(CH_3)_2$), 3.53 (bs, 1H, OH), 4.12 (m, 1H, CHO); ^{13}C NMR ($CDCl_3$): 36.1 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 20.9 Hz), 45.3 (s, 2C, $N(CH_3)_2$), 60.9 (s, 1C, CHO), 65.1 (s, 1C, CH_2N), 105.0–125.0 (m, 8C, 7× CF_2 and 1× CF_3); ^{19}F NMR ($CDCl_3$): −81.4 (t, 3F, CF_3, $^3J_{FF}$ = 9.8 Hz), −112.9 (m, 2F, CH_2CF_2), −122.1 (m, 2F, CF_2), −122.4 (m, 4F, 2× CF_2), −123.2 (m, 2F, CF_2), −124.1 (m, 2F, CF_2), −126.6 (m, 2F, CF_2). Anal. Calcd. for $C_{13}H_{12}F_{17}NO$: C, 29.96; H, 2.32; N, 2.39. Found: C, 29.89; H, 2.41; N, 2.77.

*4.8. General procedure for preparation of sulfonate betaines **23–32***

Dimethyl(polyfluoroalkyl)amine (**18–22**) and propane-l,3-sultone or butane-1,4-sultone resp. (1:3 mole equivalents) were dissolved in anhydrous acetonitrile and reaction mixture was refluxed overnight while stirring. Sulfonate betaines gradually precipitated from the reaction mixture as white solids. After cooling down, ethyl acetate (30 mL) was added and the liquid removed by filtration. Precipitate was washed on filter with ethyl acetate (100 mL), diethyl ether (50 mL) and dried. Sulfonate betaines **23–32** were obtained as white solids in yields of 92–100%.

*4.8.1. 3-[Dimethyl(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)ammonium]propanesulfonate (**23**)*

Dimethyl(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)amine (**18**, 531 mg, 1.31 mmol), propane-1,3-sultone (480 mg; 3.93 mmol), MeCN (5 mL). Yield of **23**: 656 mg (95%) as white solid.

^{1}H NMR (CD_3OD): 2.06–2.30 (m, 4H, 2× CH_2), 2.30–2.46 (m, 2H, CH_2R_F), 2.88 (t, 2H, $CH_2SO_3^-$, $^3J_{HH}$ = 6.9 Hz), 3.14 (s, 6H, 2× CH_3), 3.45 (m, 2H, CH_2N), 3.57 (m, 2H, CH_2N); ^{13}C NMR (CD_3OD): 15.4 (s, 1C, CH_2), 19.6 (s, 1C, CH_2), 28.5 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 23.5 Hz), 48.6 (s, 1C, $CH_2SO_3^-$), 51.3 (s, 2C, CH_3), 64.0 (s, 1C, CH_2N), 64.3 (s, 1C, CH_2N), 105.0–125.0 (m, 6C, 5× CF_2 and 1× CF_3); ^{19}F NMR (CD_3OD): −80.7 (t, 3F, CF_3, $^3J_{FF}$ = 10.4 Hz), −113.5 (m, 2F, CH_2CF_2), −121.2 (m, 2F, CF_2), −122.2 (m, 2F, CF_2), −122.8 (m, 2F, CF_2), −125.6 (m, 2F, CF_2). Anal. Calcd. for $C_{14}H_{18}F_{13}NO_3S$: C, 31.89; H, 3.44; N, 2.66. Found: C, 31.88; H, 3.49; N, 2.68.

*4.8.2. 3-[Dimethyl(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)ammonium]propanesulfonate (**24**)*

Dimethyl(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)amine (**19**, 527mg, 1.04 mmol), propane-1,3-sultone (382 mg, 3.13 mmol), MeCN (5 mL). Yield of **24**: 651 mg (99%) as white solid.

^{1}H NMR (CD_3OD): 2.06–2.30 (m, 4H, 2× CH_2), 2.30–2.47 (m, 2H, CH_2R_F), 2.89 (t, 2H, $CH_2SO_3^-$, $^3J_{HH}$ = 6.7 Hz), 3.14 (s, 6H, 2× CH_3), 3.46 (m, 2H, CH_2N), 3.58 (m, 2H, CH_2N); ^{13}C NMR (CD_3OD): 15.4 (s, 1C, CH_2), 19.6 (s, 1C, CH_2), 28.5 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 22 Hz), 48.7 (s, 1C, $CH_2SO_3^-$), 51.3 (s, 2C, CH_3), 64.0 (s, 1C, CH_2N), 64.3 (s, 1C, CH_2N), 105.0–125.0 (m, 8C, 7× CF_2 and 1× CF_3); ^{19}F NMR (CD_3OD): −80.7 (t, 3F, CF_3, $^3J_{FF}$ = 10.4 Hz), −113.5 (m, 2F, CH_2CF_2), −121.0 (m, 2F, CF_2), −121.2 (m, 4F, 2× CF_2), −122.0 (m, 2F, CF_2), −122.8 (m, 2F, CF_2), −125.6 (m, 2F, CF_2). Anal. Calcd. for $C_{16}H_{18}F_{17}NO_3S$: C, 30.63; H, 2.89; N, 2.23. Found: C, 30.57; H, 2.92; N, 2.25.

*4.8.3. 3-[Dimethyl(2-hydroxy-4,4,5,5,6,6,7,7,7-nonafluoroheptyl)ammonium]propanesulfonate (**25**)*

Dimethyl(2-hydroxy-4,4,5,5,6,6,7,7,7-nonafluoroheptyl)amine (**20**, 810 mg, 2.52 mmol), propane-1,3-sultone (924 mg, 7.56 mmol), MeCN (10 mL). Yield of **25**: 1050 mg (94%) as white solid.

^{1}H NMR (CD_3OD): 2.10–2.34 (m, 2H, CH_2), 2.34–2.58 (m, 2H, CH_2R_F), 2.88 (t, 2H, $CH_2SO_3^-$, $^3J_{HH}$ = 6.47 Hz), 3.23 (s, 3H, CH_3), 3.25 (s, 3H, CH_3), 3.36–3.74 (m, 4H, CH_2NCH_2), 4.74 (m, 1H, CHO); ^{13}C NMR (CD_3OD): 20.1 (s, 1C, CH_2), 36.9 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 20.1 Hz), 48.7 (s, 1C, $CH_2SO_3^-$), 52.2 (s, 1C, CH_3), 52.9 (s, 1C, CH_3), 61.6 (s, 1C, CHO), 65.9 (s, 1C, CH_2N), 68.4 (s, 1C, CH_2N), 105.0–125.0 (m, 4C, 3× CF_2 and 1× CF_3); ^{19}F NMR (CD_3OD): −80.9 (t, 3F, CF_3, $^3J_{FF}$ = 8.6 Hz), −112.0 (m, 2F, CH_2–CF_2), −123.9 (m, 2F, CF_2), −125.4 (m, 2F, CF_2). Anal. Calcd. for $C_{12}H_{18}F_9NO_4S$: C, 32.51; H, 4.09; N, 3.16. Found: C, 32.49; H, 4.11; N, 3.16.

*4.8.4. 3-[Dimethyl(2-hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)ammonium]propanesulfonate (**26**)*

Dimethyl(2-hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)amine (**21**, 1075 mg, 2.55 mmol), propane-1,3-sultone (936 mg, 7.66 mmol), MeCN (10 mL). Yield of **26**: 1307 mg (94%) as white solid.

^{1}H NMR (CD_3OD): 2.12–2.34 (m, 2H, CH_2), 2.34–2.57 (m, 2H, CH_2R_F), 2.88 (t, 2H, $CH_2SO_3^-$, $^3J_{HH}$ = 6.3 Hz), 3.23 (s, 3H, CH_3), 3.25 (s, 3H, CH_3), 3.36–3.72 (m, 4H, CH_2NCH_2), 4.74 (m, 1H, CHO); ^{13}C NMR (CD_3OD): 20.0 (s, 1C, CH_2), 37.0 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 19.9 Hz), 48.7 (s, 1C, $CH_2SO_3^-$), 52.2 (s, 1C, CH_3), 52.9 (s, 1C, CH_3), 61.6 (s, 1C, CHO), 65.9 (s, 1C, CH_2N), 68.4 (s, 1C, CH_2N), 105.0–125.0 (m, 6C, 5× CF_2 and 1× CF_3); ^{19}F NMR (CD_3OD): −80.7 (t, 3F, CF_3, $^3J_{FF}$ = 10.4 Hz), −111.3 (m, 2F, CH_2CF_2), −121.1 (m, 2F, CF_2), −122.2 (m, 2F, CF_2), −122.9 (m, 2F, CF_2), −125.6 (m,

2F, CF_2). Anal. Calcd. for $C_{14}H_{18}F_{13}NO_4S$: C, 30.95; H, 3.34; N, 2.58. Found: C, 30.89; H, 3.39; N, 2.60.

*4.8.5. 3-[Dimethyl(2-hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)-ammonium]propanesulfonate (**27**)*

Dimethyl(2-hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)amine (**22**, 1402 mg, 2.72 mmol), propane-1,3-sultone (999 mg, 8.18 mmol), MeCN (10 mL). Yield of **27**: 1693 mg (97%) as white solid.

^{1}H NMR (CD_3OD): 2.12–2.34 (m, 2H, CH_2), 2.34–2.56 (m, 2H, CH_2RF), 2.87 (t, 2H, $CH_2SO_3^-$, $^3J_{HH}$ = 6.2 Hz), 3.22 (s, 3H, CH_3), 3.24 (s, 3H, CH_3), 3.36–3.71 (m, 4H, CH_2NCH_2), 4.73 (m, 1H, CHO); ^{13}C NMR (CD_3OD): 20.0 (s, 1C, CH_2), 37.0 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 19.0 Hz), 48.6 (s, 1C, $CH_2SO_3^-$), 52.2 (s, 1C, CH_3), 52.9 (s, 1C, CH_3), 61.6 (s, 1C, CHO), 66.0 (s, 1C, CH_2N), 68.4 (s, 1C, CH_2N), 105.0–125.0 (m, 8C, 7× CF_2 and 1× CF_3); ^{19}F NMR (CD_3OD): −80.7 (t, 3F, CF_3, $^3J_{FF}$ = 10.4 Hz), −111.9 (m, 2F, CH_2CF_2, −120.8 (m, 2F, CF_2), −121.2 (m, 4F, 2× CF_2), −122.0 (m, 2F, CF_2), −122.9 (m, 2F, CF_2), −125.6 (m, 2F, CF_2). Anal. Calcd. for $C_{16}H_{18}F_{17}NO_4S$: C, 29.87; H, 2.82; N, 2.18. Found: C, 29.90; H, 2.84; N, 2.18.

*4.8.6. 4-[Dimethyl(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)ammonium]butanesulfonate (**28**)*

Dimethyl(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)amine (**18**, 598 mg, 1.47 mmol), butane-1,4-sultone (600 mg, 4.41 mmol), MeCN (5 mL). Yield of **28**: 729 mg (92%) as white solid.

^{1}H NMR (CD_3OD): 1.77–1.90 (m, 2H, CH_2), 1.90–2.04 (m, 2H, CH_2), 2.04–2.20 (m, 2H, CH_2), 2.21–2.45 (m, 2H, CH_2R_F), 2.89 (t, 2H, $CH_2SO_3^-$, $^3J_{HH}$ = 7.0 Hz), 3.12 (s, 3H, CH_3), 3.35–3.47 (m, 4H, CH_2NCH_2); ^{13}C NMR (CD_3OD): 15.4 (s, 1C, CH_2), 22.2 (s, 1C, CH_2), 22.9 (s, 1C, CH_2), 28.5 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 21.9 Hz), 51.1 (s, 1C, $CH_2SO_3^-$), 51.2 (s, 2C, CH_3), 63.9 (s, 1C, CH_2N), 65.4 (s, 1C, CH_2N), 105.0–125.0 (m, 6C, 5× CF_2 and 1× CF_3); ^{19}F NMR (CD_3OD): −80.7 (t, 3F, CF_3, $^3J_{FF}$ = 9.8 Hz), −113.5 (m, 2F, CH_2CF_2), −121.2 (m, 2F, CF_2), −122.2 (m, 2F, CF_2), −122.8 (m, 2F, CF_2), −125.6 (m, 2F, CF_2). Anal. Calcd. for $C_{15}H_{20}F_{13}NO_3S$: C, 33.28; H, 3.72; N, 2.59. Found: C, 33.26; H, 3.78; N, 2.60.

*4.8.7. 4-[Dimethyl(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)ammonium]butanesulfonate (**29**)*

Dimethyl(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)amine (**19**) (602 mg; 1.19 mmol), 1,4-butanesultone (487 mg; 3.57 mmol), MeCN (5 mL). Yield of **29**: 725 mg (95%) as white solid.

^{1}H NMR (CD_3OD): 1.78–1.90 (m, 2H, CH_2), 1.90–2.05 (m, 2H, CH_2), 2.05–2.20 (m, 2H, CH_2), 2.20-2.46 (m, 2H, CH_2R_F), 2.88 (t, 2H, $CH_2SO_3^-$, $^3J_{HH}$ = 7.0 Hz), 3.11 (s, 3H, CH_3), 3.34–3.45 (m, 4H, CH_2NCH_2); ^{13}C NMR (CD_3OD): 15.4 (s, 1C, CH_2), 22.2 (s, 1C, CH_2), 22.9 (s, 1C, CH_2), 28.6 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 22.0 Hz), 51.0 (s, 1C, $CH_2SO_3^-$), 52.1 (s, 2C, CH_3), 64.0 (s, 1C, CH_2N), 65.4 (s, 1C, CH_2N), 105.0–125.0 (m, 8C, 7× CF_2 and 1× CF_3); ^{19}F NMR (CD_3OD): −80.6 (t, 3F, CF_3, $^3J_{FF}$ = 10.4 Hz), −113.5 (m, 2F, CH_2CF_2), −120.9 (m, 2F, CF_2), −121.2 (m, 4F, 2× CF_2), −122.0 (m, 2F, CF_2), −122.8 (m, 2F, CF_2), −125.6 (m, 2F, CF_2). Anal. Calcd. for $C_{17}H_{20}F_{17}NO_3S$: C, 31.84; H, 3.14; N, 2.18. Found: C, 31.87; H, 3.14; N, 2.14.

*4.8.8. 4-[Dimethyl(2-hydroxy-4,4,5,5,6,6,7,7,7-nonafluoroheptyl)ammonium]butanesulfonate (**30**)*

Dimethyl(2-hydroxy-4,4,5,5,6,6,7,7,7-nonafluoroheptyl)amine (**20**, 762 mg, 2.37 mmol), butane-1,4-sultone (970 mg, 7.12 mmol), MeCN (5 mL). Yield of **30**: 1009 mg (93%) as white solid.

^{1}H NMR (CD_3OD): 1.76–1.90 (m, 2H, CH_2), 1.90–2.12 (m, 2H, CH_2), 2.32–2.54 (m, 2H, CH_2R_F), 2.88 (t, 2H, $CH_2SO_3^-$, $^3J_{HH}$ = 7.2 Hz), 3.19 (s, 3H, CH_3), 3.22 (s, 3H, CH_3), 3.33–3.62 (m, 4H, CH_2NCH_2), 4.69 (m, 1H, CHO); ^{13}C NMR (CD_3OD): 22.4 (s, 1C, CH_2), 23.0 (s, 1C, CH_2), 36.9 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 20.5 Hz), 51.3 (s, 1C, $CH_2SO_3^-$), 52.2 (s, 1C, CH_3), 52.8 (s, 1C, CH_3), 61.6 (s, 1C, CHO), 66.9 (s, 1C, CH_2N), 68.3 (s, 1C, CH_2N), 105.0–125.0 (m, 4C, 3× CF_2 and 1× CF_3); ^{19}F NMR (CD_3OD): −81.1 (t, 3F, CF_3, $^3J_{FF}$ = 9.8 Hz), −112.7 (m, 2F, CH_2–CF_2), −124.1 (m, 2F, CF_2), −125.6 (m, 2F, CF_2). Anal. Calcd. for $C_{13}H_{20}F_9NO_4S$: C, 34.14; H, 4.41; N, 3.06. Found: C, 34.00; H, 4.53; N, 3.10.

*4.8.9. 4-[Dimethyl(2-hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)ammonium]butanesulfonate (**31**)*

Dimethyl(2-hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)amine (**21**, 612 mg, 1.45 mmol), butane-1,4-sultone (592 mg, 4.35 mmol), MeCN (5 mL). Yield of **31**: 805 mg (99%) as white solid.

^{1}H NMR (CD_3OD): 1.76–1.91 (m, 2H, CH_2), 1.91–2.12 (m, 2H, CH_2), 2.32–2.55 (m, 2H, CH_2R_F), 2.88 (t, 2H, $CH_2SO_3^-$, $^3J_{HH}$ = 7.2 Hz), 3.19 (s, 3H, CH_3), 3.22 (s, 3H, CH_3), 3.33–3.60 (m, 4H, CH_2NCH_2), 4.71 (m, 1H, CHO); ^{13}C NMR (CD_3OD): 22.2 (s, 1C, CH_2), 22.8 (s, 1C, CH_2), 36.9 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 20.5 Hz), 51.1 (s, 1C, $CH_2SO_3^-$), 52.1 (s, 1C, CH_3), 52.7 (s, 1C, CH_3), 61.5 (s, 1C, CHO), 66.8 (s, 1C, CH_2N), 68.2 (s, 1C, CH_2N), 105.0–125.0 (m, 6C, 5× CF_2 and 1× CF_3); ^{19}F NMR (CD_3OD): −80.8 (t, 3F, CF_3, $^3J_{FF}$ = 9.8 Hz), −112.5 (m, 2F, CH_2CF_2), −121.2 (m, 2F, CF_2), −122.3 (m, 2F, CF_2), −123.1 (m, 2F, CF_2), −125.8 (m, 2F, CF_2). Anal. Calcd. for $C_{15}H_{20}F_{13}NO_4S$: C, 32.32; H, 3.62; N, 2.51. Found: C, 32.03; H, 3.71; N, 2.61.

*4.8.10. 4-[N,N-Dimethyl(2-hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)-ammonium]butanesulfonate (**32**)*

Dimethyl(2-hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)amine (**22**, 670 mg, 1.28 mmol), butane-1,4-sultone (526 mg, 3.86 mmol), MeCN (5 mL). Yield of **32**: 746 mg (100%) as white solid.

^{1}H NMR (CD_3OD): 1.76–1.90 (m, 2H, CH_2), 1.90–2.10 (m, 2H, CH_2), 2.34–2.54 (m, 2H, CH_2R_F), 2.88 (t, 2H, $CH_2SO_3^-$, $^3J_{HH}$ = 7.2 Hz), 3.19 (s, 3H, CH_3), 3.22 (s, 3H, CH_3), 3.30–3.63

(m, 4H, CH_2NCH_2), 4.70 (m, 1H, CHO); ^{13}C NMR (CD_3OD): 22.2 (s, 1C, CH_2), 22.9 (s, 1C, CH_2), 36.9 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 20.4 Hz), 51.1 (s, 1C, $CH_2SO_3^-$), 52.1 (s, 1C, CH_3), 52.8 (s, 1C, CH_3), 61.6 (s, 1C, CHO), 66.8 (s, 1C, CH_2N), 68.3 (s, 1C, CH_2N), 105.0–125.0 (m, 8C, 7× CF_2 and 1× CF_3); ^{19}F NMR (CD_3OD): −80.6 (t, 3F, CF_3, $^3J_{FF}$ = 10.4 Hz), −112.3 (m, 2F, CH_2CF_2), −120.8 (m, 2F, CF_2), −121.2 (m, 4F, 2× CF_2), −122.0 (m, 2F, CF_2), −122.9 (m, 2F, CF_2), −125.5 (m, 2F, CF_2). Anal. Calcd. for $C_{17}H_{20}F_{17}NO_4S$: C, 31.06; H, 3.07; N, 2.13. Found: C, 30.87; H, 3.21; N, 2.13.

Acknowledgements

The research was supported by the Ministry of Education (Project MSM 6046137301) and the Grant Agency of the Academy of Sciences (Project KJB 401280501) of the Czech Republic.

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