Supplementary Material (ESI) for Chemical Communications
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Ionic strength mediated hydrophobic force switching of CF_3-terminated ethylene glycol self-assembled monolayers (SAMs) on gold

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Supplementary Information:

Sample preparation

Preparation of gold coated surfaces

The gold coated wafers (purchased from Georg Albert PVD, Heidelberg, Germany) were stored under vacuum in desiccators and cut in pieces just before SAM preparation.

Preparation of gold coated surfaces

The gold coated wafer pieces were rinsed with ethanol and dried under a nitrogen stream. They were then immersed in a 1mM solution of the synthesized molecules in DMF over night. The samples were then rinsed with ethanol and dried with nitrogen two times.

Characterisation of the SAMs

Contact angle measurements

Advancing water contact angles (deionised water) were measured with a G10 goniometer microscope (KRÜSS GmbH, Hamburg, Germany) under ambient conditions. Droplets were dispensed from a microburette. The reported values are the average of three measurements taken at different places on the surface.

XPS

X-ray Photoelectron Spectroscopy spectra were obtained using a VG Escalab II (VG Scientific Ltd., UK) and Al Kα radiation (1486.6eV). During the analysis, the pressure in the test chamber was kept around $2x10^{-10}$ mbar. The detector had a takeoff angle of 90° to the surface.

The XPS spectra were corrected for charging by referencing the aliphatic C(1s) peak for hydrocarbons to 284.6 eV. Elemental compositions of the various surfaces were

determined from the area under individual elemental peaks using sensitivity factors provided with the software as well as taking the transmission function of the analyzer into account. CasaXPS (Casa Software Ltd., UK) was the software used for the analysis. The data base for the sensitivity factors is given in D. Briggs, M. P. Seah, Practical Surface Analysis, 2nd Ed, Auger and X-Ray Photoelectron Spectroscopy, vol. 1, Wiley, 1995 and is integrated in CasaXPS. The spectra were fitted using a Gaussian peak shape. A Shirley background was subtracted for the quantitative analysis.

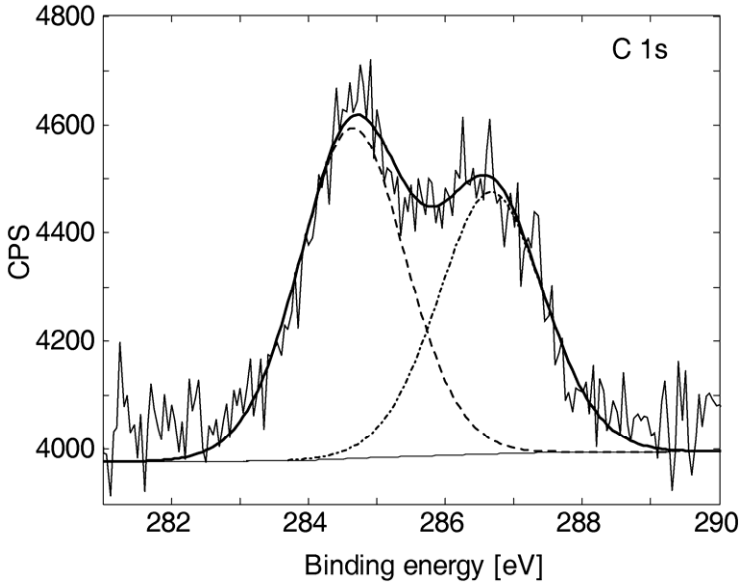


Figure 1: XPS carbon peaks for the $EG_3O(CH_2)_2CF_3$ film.

Figure 1 is an example of the fit of a single region scan for the carbon in an $EG_3O(CH_2)_2CF_3$ SAM film. The raw area was corrected by the relative sensitivities (RSF) and the transmission factors for each atom giving the atomic ratio for the three molecules. Table 1 summarizes the results.

	$EG_3O(CH_2)_2CF_3$		**$EG_3O(CH_2)_3CF_3$**		**$EG_4O(CH_2)_2CF_3$**	
	Exp.	**theor.**	**Exp.**	**theor.**	**Exp.**	**theor.**
C/O	4.2	5	3.9	5.25	3.7	4.4
C/F	4.9	6.6	4.9	7	5.2	7.3
O/F	1.2	1.3	1.3	1.3	1.4	1.6

C_{ether}/O	1.9	2	1.8	2	1.8	2
C_{ether}/F	2.2	2.67	2.3	2.67	2.6	3.33
C_{aliph}/C_{ether}	1.3	1.5	1.1	1.625	1.0	1.2
C/Au4f	0.57		0.61		0.58	

Table 1:XPS atomic ratios (experimental and theoretical) for the three synthesized molecules

Note that the theoretical values are ideal values not taking into account the attenuation of the signal from atoms closer to the substrate. Lower experimental values are therefore expected. The density of the films was determined following the method described by Herrwerth et al. (J. Am. Chem. Soc. **2003**, *125*, 9359-9366). The C/Au4f ratio was measured for a dodecanethiol (C_{12}) SAM and for an octadecanethiol SAM (C_{18}) and was found to be 0.42 and 0.54, respectively. These two values were used to determine a straight line for alkanethiol films according to ln(C/Au4f) =a* (effective molecular chain length)+b:

$$\ln(\frac{C}{Au_{4f}}) = 0.043 * (\textit{effective molecular length}) - 1.395$$

This equation was then used to determine the effective molecular length values for the three molecules as described by Herrwerth et al.. The values are given in table 2.

	$EG_3O(CH_2)_2CF_3$	$EG_3O(CH_2)_3CF_3$	$EG_4O(CH_2)_2CF_3$
Effective molecular length in nm	1.9	2.1	2.0

Table 2: Experimentally determined molecular lengths of the three synthesized molecules

The experimentally determined molecular lengths in connection with the theoretical lengths allow it to quantify the packing density of the films relative to an alkanethiol film:

	$EG_3O(CH_2)_2CF_3$	$EG_3O(CH_2)_3CF_3$	$EG_4O(CH_2)_2CF_3$
Relative coverage	77%	81%	73%.

Density (molecules/nm^2)	3.58	3.77	3.40

Table 3: Relative coverage compared to an alkanethiol SAM and density of the three films

Ellipsometry

The thickness of the SAMs was measured with an M-2000DI^{TM} spectroscopic ellipsometer (J. A. Woollam Co., Inc., USA). Measurements were done at 45, 50, 55, 60, 65, 70, and 75°. The integrated data acquisition software for the J.A. Woollam Co., Inc. spectroscopic ellipsometer is WVASE32®. The thickness of the organic films was fitted using a Cauchy model.

Ellipsometry provides another way to estimate the density of the SAMs relative to alkanethiol films. Assuming a tilt angle of 30°, the expected thickness of the organic layers can be calculated. A lower value obtained from ellipsometry then indicates a lower density. Results are given in table 4.

	$EG_3O(CH_2)_2CF_3$	$EG_3O(CH_2)_3CF_3$	$EG_4O(CH_2)_2CF_3$
Measured thickness of the organic layer	1.8 (1)nm	1.9(1)nm	2.0(1)nm
Relative coverage	81%	82%	82%

Table 4: Thickness of the organic layer of the three films

Atomic Force Microscopy

The Atomic Force Microscope used was a PicoSPM II (Molecular Imaging, AZ, USA) with an interchangeable nose scanner. It is equipped with a video system and a liquid cell. The spring constant of the tips used was 0.06 or 0.12 N/m. These tips were functionalized by covering them with 5nm of a nickel/chromium mixture and 50nm of gold via thermal evaporation. Subsequently, a dodecanethiol SAM was added by immersing the cantilevers in solution. For measurements under different ionic conditions several aqueous solutions were prepared. The most concentrated solution was obtained first by dissolving KNO_3 (Aldrich) in deionised water. Then, dilutions by a factor of 10

were prepared for the other solutions. To confirm that the tips were hydrophobic a dodecanethiol SAM sample was measured under liquid with different ionic strengths. A typical result is shown in figure 2.

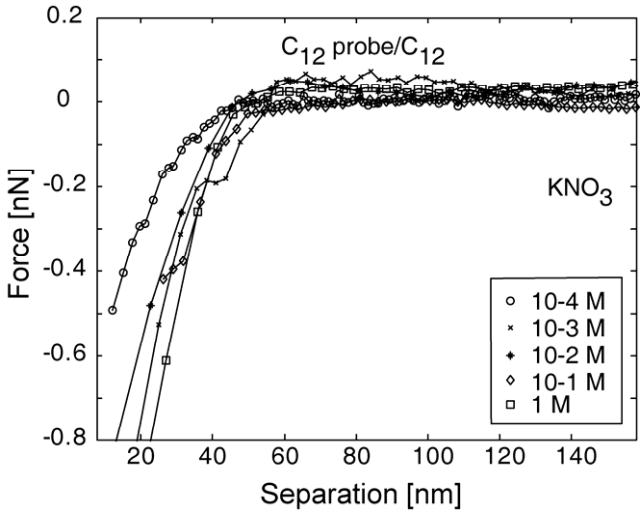


Figure 2: Force-distance curves for a dodecanethiol SAM and a functionalized tip

The observed interaction was always attractive and did not depend on the ionic strength of the environment, indicating a purely hydrophobic force and a well functionalized tip. The tip, along with the surface, was dried between each experiment. Measurements were started with the least concentrated solution and then progressed toward the most concentrated one. A home written MATLAB routine was employed to convert measured cantilever deflection versus piezo displacement curves into force distance curves.

Synthesis

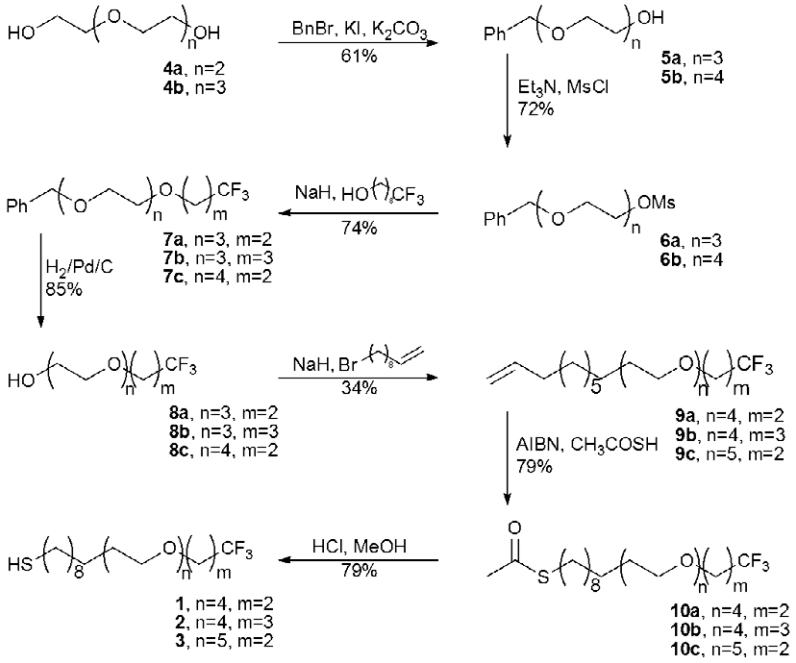
General methods

All reagents of synthetic grade were used as supplied. If further purification or drying were required the procedures used are detailed in Armarego and Perrin, "Purification of laboratory chemicals" 4th ED. Room temperature refers to 20–25 ºC. Reaction progress was monitored by thin layer chromatography (TLC) performed using Merck, Kieselgel 60 plates. Column chromatography was performed using Merck Kieselgel 60 silica gel (230 – 400 nm mesh).

Nuclear magnetic resonance (NMR) spectra were measured using a Bruker Av-300 or a Varian Unity Plus 300 operating at 300 MHz for ^{1}H NMR, 75 MHz for ^{13}C NMR, 282 MHz for ^{19}F NMR. All chemical shifts (δ) are reported in parts per million (ppm) and are quoted relative to the residual proton peak of $CDCl_3$. Coupling constants (J) are given in Hertz (Hz) and represent $^{3}J_{H,H}$ unless otherwise stated. Spectral coupling patterns are designated as follows; s: singlet; d: doublet; t: triplet; q: quartet; m: multiplet and br: broad signal.

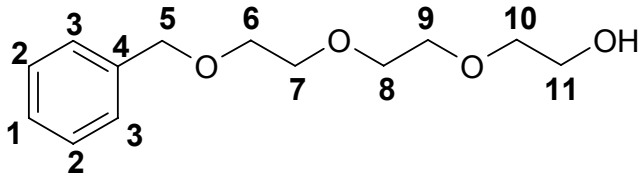
Synthesis of 11-(2-{2-[2-(3,3,3-trifluoro-propoxy)-ethoxy]-ethhoxy}-ethoxy)-undecane-1-thiol

The synthetic pathway for the trifluoroethoxy-tri(ethylene glycol) undecanthiol is the following :



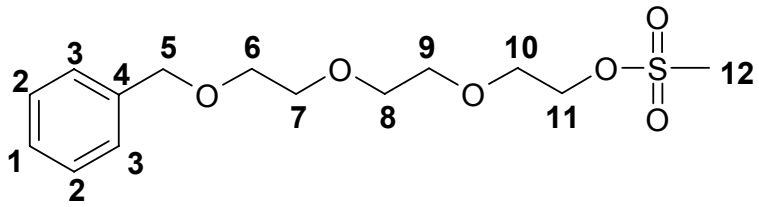
Trifluoroethoxy-tri(ethylene glycol) undecanthiol synthetic pathway

2-[2-(2-Benzyloxy-ethoxy)-ethoxy]-ethanol (**5a**)



Anhydrous potassium carbonate (0.36 mol, 50 g), potassium iodide (6 mmol, 1 g) and benzyl bromide (0.1 mol, 17.1 g) were added to a solution of triethylene glycol (**4a**) (0.2 mol, 30 g) in dry acetone (200 mL). The solution was refluxed for 71 h. The mixture was cooled to room temperature and filtered through sintered glass. After acetone removal under reduced pressure the residue was dissolved in diethyl ether (30 mL). The organic layer was washed with water (30 mL), brine (30 mL) and dried over magnesium sulfate. Diethyl ether was removed under vacuum. The product was purified over silica (eluent: cyclohexane:ethyl acetate, 4:6) and was obtained as a yellow oil (14.73g, 61% yield). $\boldsymbol{\delta_H}$ 2.59 (1H, br, **11**-O*H*), 3.58–3.76 (12H, m, **6**-H, **7**-H, **8**-H, **9**-H, **10**-H, and **11**-H), 4.5760 (2H, s, **5**-H), 7.28–7.38 (5H, m, **1**-H, **2**-H, and **3**-H); $\boldsymbol{\delta_C}$ 61.5 (1C, **11**), 69.2, 70.2, 70.4, 70.5, 72.4, 73.1 (6C, **5**, **6**, **7**, **8**, **9**, and **10**), 127.5, 127.6, 128.2 (5C, **1**, **2**, and **3**), 138.0 (1C, **4**); $\boldsymbol{\nu_{MAX}}$***(film)/cm*$^{-1}$ 699.39, 740.41 (Ar); 1099.55, 1351.10, 1454.44 (C-O-C); 2867.94 (C-H); 3030.54, 3062.98, 3087.76 (Ar); 3446.43 (O-H); ***HRMS m/z*** *(ES+)*: $[MNa]^+$ 263.1262, calculated 263.1259.

Methanesulfonic acid 2-[2-(2-benzyloxy-ethoxy)-ethoxy]-ethylester (**6a**)



Triethylamine (0.067 mol, 6.93 g) and mesyl chloride (0.061 mol, 2.69 g) were added to a solution of **5a** (0.030 mol, 7.26 g) in dichloromethane (300 mL). Then, the mixture was stirred at 0ºC under nitrogen for 2 h.

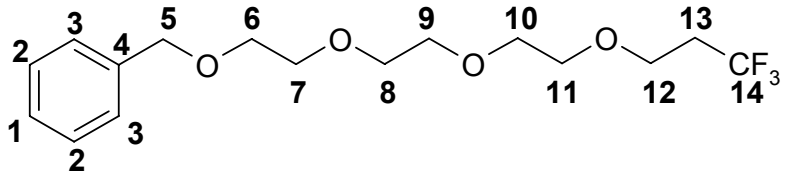
The reaction was quenched with 30 mL of water. The phases were separated. The aqueous layer was extracted with dichloromethane and the combined organic layers were washed with water and brine, and dried over $MgSO_4$.

Dichloromethane was evaporated under vacuum. The product was purified over silica (eluent: hexane:ethyl acetate, 5:5) and isolated as a pale yellow oil (7.12 g, 72% yield).

The methanesulfonic acid 2-[2-(2-benzyloxy-ethoxy)-ethoxy]-ethyl ester was stored under nitrogen. δ_H 3.04 (3H, s, **12**-H), 3.60–3.71, 3.75–3.81 (4H, m, **10**-H, and **11**-H), 4.57 (2H, s, **5**-H), 7.28–7.39 (5H, m, **1**-H, **2**-H, and **3**-H); δ_C 37.3 (1C, **12**), 60.0, 68.6, 69.1, 69.2, 70.2, 70.3, and 72.82 (7C, **5**, **6**, **7**, **8**, **9**, **10**, and **11**), 127.3, 127.4, 128.1 (5C, **1**, **2**, and **3**), 137.9 (1C, **4**); ν_{MAX}*(film)/cm*$^{-1}$ 701.12, 737.70 (Ar); 810.77 (-SO_2-); 1101.72 (C-O-C); 1175.83 (-SO_2-); 1352.91, 1454.73 (C-O-C); 2870.86 (C-H); 3029.05, 3062.76 (Ar);

HRMS m/z (*ES+)*: $[MNa]^+$ 341.1031, calculated 341.1035.

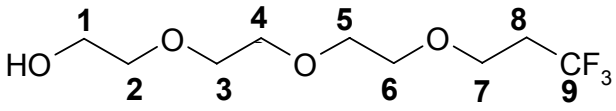
2-{2-[2-(3,3,3-trifluoro-propoxy)-ethoxy]-ethoxy}-ethoxymethyl-benzene (**7a**)



Sodium hydride (0.048 mol, 1.16 g) was added to a solution of **6a** (0.0438 mol, 5 g) in dry tetrahydrofuran (400 mL). The mixture was stirred for 30 min under nitrogen at room temperature. Methanesulfonic acid 2-[2-(2-benzyloxy-ethoxy)-ethoxy]-ethylester (0.021 mol, 6.97 g) was then added and the solution was refluxed for 26 h. After cooling, a few drops of isopropanol and water were added to hydrolyse the excess sodium hydride. Tetrahydrofuran was removed *in vacuo* and, the residue was dissolved in diethyl ether (40mL). The organic layer was washed with brine (3 times 30 mL) and dried over magnesium sulfate. The product was recovered as light brown oil (5.39 g, 74% yield). δ_H

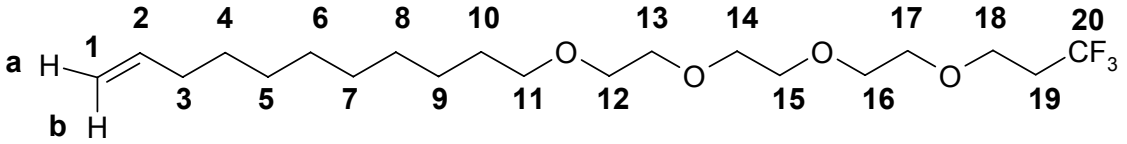
2.84 (2H, tq, $^{3}J_{H,F}$: 10.8, $^{3}J_{H,H}$: 6.8, **13**-H) 3.57–3.72 (14H, m, **6**-H, **7**-H, **8**-H, **9**-H, **10**-H, **11**-H and **12**-H), 4.55 (2H, **5**-H), 7.28–7.37 (5H, m, **1**-H, **2**-H and **3**-H); δ_C 34.4 (1C, q, $^{2}J_{C,F}$: 28.6, **13**), 64.1 (1C, q, $^{3}J_{C,F}$: 3.3, **12**), 69.4, 70.4, 70.5, 70.6, 70.7, 72.5, 73.2 (7C, **5**, **6**, **7**, **8**, **9**, **10**, and **11**), 127.6, 127. 6, 127.7, 127.8, 128.4 (5C, **1**, **2**, and **3**), 138.3 (1C, **4**); δ_F -65.2 (t, $^{1}J_{C,F}$: 10.8, **14**-F); ν_{MAX}*(film)/cm*$^{-1}$ 699.15, 739.26 (Ar); 844.84, 1004.91, 1145.02, 1256.22 (CF_3); 1351.47, 1454.58 (C-O-C); 2869.11 (C-H); 3031.19, 3064.20, 3088.41 (Ar); ***HRMS m/z*** *(ES+)*: $[MNa]^+$ 359.1454, calculated 359.1446.

2-{2-[2-(3,3,3-trifluoro-propoxy)-ethoxy]-ethoxy}-ethanol (**8a**)



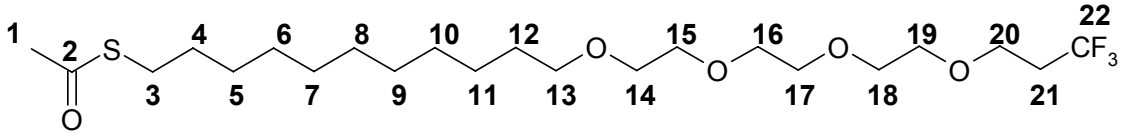
7a (0.016 mol, 5.39 g) was added to a suspension of palladium on charcoal (10% weight) (0.675 mmol, 71.8 mg of palladium) in ethanol (200 mL). The reaction mixture was left to stir for 36 hours under hydrogen pressure of 20 bar at room temperature. The solution was filtered through celite. Ethanol was evaporated under vacuum and the product was purified over silica (eluent: hexane: ethyl acetate: 60/40) to give the product as pale orange oil (3.86 g, 85% yield). δ_H 2.33 (2H, tq, $^{3}J_{H,F}$: 10.8, $^{3}J_{H,H}$: 6.8, **8**-H), 3.09 (1H, br, **1**-OH), 3.48–3.65 (14H, m, **1**-H, **2**-H, **3**-H, **4**-H, **5**-H, **6**-H, and **7**-H); δ_C 34.0 (1C, q, $^{2}J_{C,F}$: 28.2, **8**), 61.3 (1C, **1**), 63.8 (1C, q, $^{3}J_{H,H}$: 3.5, **7**), 70.0, 70.2, 70.4, 72.3 (5C, m, **2**, **3**, **4**, **5**, and **6**), 125.9 (1C, q, J: 276.8, **9**); δ_F -65.4 (s, decoupling); ν_{MAX}*(film)/cm*$^{-1}$ 837.35, 1005.63 1150.87, 1256.83 (CF_3); 1351.65, 1443.39 (C-O-C); 2879.18 (C-H); 3447.88 (O-H); ***HRMS m/z*** *(ES+)*: $[MNa]^+$ 269.0970, calculated 269.0977.

11-(2-{2-[2-(3,3,3-trifluoro-propoxy)-ethoxy]-ethoxy}-ethoxy)-undec-1-ene (**9a**)



Sodium hydroxide (20.4 mmol, 490 mg) was added to a solution of **8a** (3.86 g, 15.7 mmol) in tetrahydrofuran (350 mL) and the mixture was stirred 30 minutes. Then 11-bromoundec-1-ene (39.2 mmol, 9.14 g) was added to the solution. The mixture was refluxed for 26 hours. Then the solution was cooled and quenched with isopropanol and water. THF was removed and the organic layer was washed with water (30 mL), and brine (2 times 30 mL), and dried over magnesium sulfate. The product is purified over silica (eluent: hexane: ethyl acetate: 80/20) and isolated as colourless oil (4.45 mmol, 2.11 g, 34% yield). δ_H 1.18–1.41（12H, m, **4**-H, **5**-H, **6**-H, **7**-H, **8**-H and **9**-H, 1.51 (2H, t, $^3J_{H,H}$: 6.8, **10**-H), 1.97 (2H, q, $^3J_{H,H}$: 7.0, **3**-H), 2.35 (2H, tq, $^4J_{H,F}$: 10.8, $^3J_{H,H}$: 6.8, **18**-H), 3.38 (2H, t, $^3J_{H,H}$: 6.8, **11**-H), 3.48–3.68 (14H, m, **12**-H, **13**-H, **14**-H, **15**-H, **16**-H, **17**-H, and **18**-H), 4.86 (1H, d, $^3J_{H,H}$: 10.2, **1**-H_a), 4.92 (1H, d, $^3J_{H,H}$: 17.1, **1**-H_b), 5.72–5.88 (1H, m, **2**-H); δ_C 25.9, 28.7, 28.9, 29.2, 29.2, 29.3, 29.4 (7C, **4**, **5**, **6**, **7**, **8**, **9**, and **10**), 33. 6 (1C, **3**), 34.1 (1C, q, $^2J_{C,F}$: 28.2, **19**), 63. 9 (1C, q, $^3J_{C,F}$: 3.3, **18**), 66.4, 69.6, 69.8, 70.3, 70.4, 70.4, 71.2 (7C, **11**, **12**, **13**, **14**, **15**, **16**, and **17**), 113.9 (1C, **1**), 125.9 (1C, q, $^1J_{C,F}$: 276.5, **20**), 138.9 (1C, **2**); δ_F -65.4 (t, $^3J_{F,H}$: 10.8); ν_{MAX}*(film)/cm*$^{-1}$ 994.14, 1122.50, 1255.35 (CF_3); 1351.06, 1440.56 (C-O-C); 1640.76 ($CH=CH_2$); 2855.77, 2927.02 (C-H); 3077.05 ($=CH_2$); ***HRMS m/z*** *(ES+)*: $[MNa]^+$ 399.2720, calculated 399.2722.

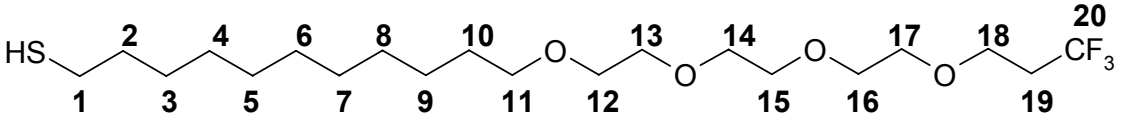
Thioacetic acid S-[10-(2-{2-[2-(3,3,3-trifluoro-propoxy)-ethoxy]-ethoxy}-ethoxy)-decyl]-ester (**10a**)



Thioacetic acid (17.8 mmol, 1.35 g) and AIBN (25 mg) were added to a solution of **9a** (4.45 mmol, 2.11 g) in methanol (50 mL). The reaction solution was plunged into a preheated oil bath and refluxed for 2 hours under nitrogen atmosphere. The mixture was concentrated under vacuum and purified by chromatography over silica giving colourless and malodorous oil (1.69 g, 79 % yield). δ_H 1.19 (1H, t, $^3J_{H,H}$: 7.1, **3**-H), 1.22–1.36 (14H,

m, **6**-H, **7**-H, **8**-H, **9**-H, **10**-H, **11**-H, and **12**-H), 1.48–1.60 (4H, m, **4**-H, and **12**-H), 2.30 (3H, s, **1**), 2.40 (2H, tq, $^{3}J_{H,F}$: 10.8, $^{3}J_{H,H}$: 6.9, **21**-H), 2.84 (2H, t, $^{3}J_{H,H}$: 7.4, **13**-H), 3.42 (2H, t, $^{3}J_{H,H}$:6.8, **20**-H), 3.54–3.65 (12H, m, **14**-H, **15**-H, **16**-H, **17**-H, **18**-H, and **19**-H); δ_C 26.0, 28.7, 29.0, 29.0, 29.4, 29.4, 29.5, 29.5 (10C, **3**, **4**, **5**, **6**, **7**, **8**, **9**, **10**, **11**, and **12**), 30.5 (1C, **1**), 34.3 (1C, q, $^{2}J_{C,F}$: 28.1, **21**), 64.0 (1C, q, $^{3}J_{C,F}$: 3.6, **20**), 66.5, 69.2, 69.9, 70.4, 70.5, 70.6, 71.4 (7C, **13**, **14**, **15**, **16**, **17**, **18**, **19**), 126.0 (1C, q, $^{1}J_{C,F}$: 276.7, **22**) ; δ_F -65.3 (3F, t, $^{3}J_{F,H}$:10.8, **22**-F); ν_{MAX}*(film)/cm*$^{-1}$ 627.49 (-S-); 840.71, 1005.10, 1135.13, 1255.84 (CF_3); 1352.92, 1442.05 (C-O-C); 1693.72 (C=O); 2856.62, 2927.34 (C-H); ***HRMS m/z*** *(ES+)*: $[MNa]^+$ 497.2526, calculated 497.2525.

11-(2-{2-[2-(3,3,3-trifluoro-propoxy)-ethoxy]-ethhoxy}-ethoxy)-undecane-1-thiol (**1**)

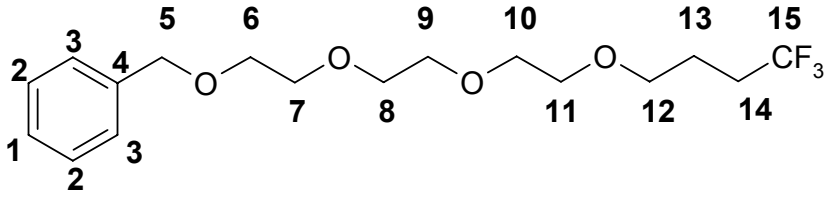


10a was dissolved in HCl/methanol solution (60 mL, 1.25 mol.L^{-1}). The mixture was refluxed overnight, concentrated and purified over silica (eluent: hexane, ethylacetate: 80/20) to give the thiol as colourless oil (2.82 mmol, 1.22 g, 79% yield). δ_H 1.24–1.39 (14H, m, **3**-H, **4**-H, **5**-H, **6**-H, **7**-H, **8**-H, and **9**-H), 1.43 (1H, s, S-H), 1.53–1.67 (4H, m, **2**-H, and **10**-H), 2.43 (2H, tq, $^{3}J_{H,F}$: 10.8, and $^{3}J_{H,H}$: 6.8, **19**-H), 2.53 (2H, dt, $^{3}J_{H,H}$: 7.10, $^{3}J_{H,H}$: 7.49, **1**-H) , 3.45 (2H, t, $^{3}J_{H,H}$: 6.9, **11**-H), 3.56–3.68 (12H, m, **12**-H, **13**-H, **14**-H, **15**-H, **16**-H, and **17**-H), 3.71 (2H, t, $^{3}J_{H,H}$: 6.8, **18**-H); δ_C 24.5, 25.9, 26.8, 28.2, 28.9, 29.4, 29.4, 29.5, 33.7, 33.9 (10C, **1**, **2**, **3**, **4**, **5**, **6**, **7**, **8**, **9**, and **10**), 34.2 (1C, q, $^{2}J_{C,F}$: 28.2, **19**), 64.0 (1C, q, $^{3}J_{C,F}$: 3.5, **18**), 69.9, 70.4, 70.5, 70.5, 71.4, (7C, **11**, **12**, **13**, **14**, **15**, **16**, and **17**), 126.0 (1C, q, $^{1}J_{C,F}$: 126.2, **20**); δ_F -65.3 (3F, t, $^{3}J_{F,H}$:10.8, **20**-F); ν_{MAX}*(film)/cm*$^{-1}$ 636.19, 657.91 (S-C); 839.33, 1005.05, 1150.29, 1255.62 (CF_3); 1350.77, 1442.24 (C-O-C); 2855.94, 2926.77 (C-H); ***HRMS m/z*** *(ES+)*: $[MNa]^+$ 455.2420, calculated 455.2419.

Synthesis of 11-(2-{2-[2-(3,3,3-trifluoro-butoxy)-ethoxy]-ethhoxy}-ethoxy)-undecane-1-thiol (2)

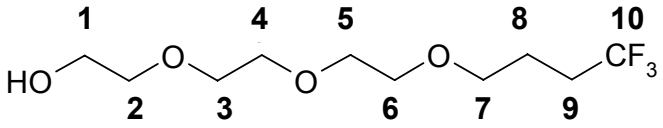
The same synthetic pathway was followed for the Trifluoropropoxy-tri(ethylene glycol) undecanethiol and the Trifluoroethoxy-tetra(ethylene glycol) undecanethiol but two starting materials change. For the trifluoropropoxy-tri(ethylene glycol) undecanethiol, trifluoropropanol was used rather than trifluoroethanol, and tetraethyleneglycol was used rather than triethylene glycol for the the Trifluoroethoxy-tetra(ethylene glycol) undecanethiol.

2-{2-[2-(3,3,3-trifluoro-butoxy)-ethoxy]-ethoxy}-ethoxymethyl-benzene (**7b**)



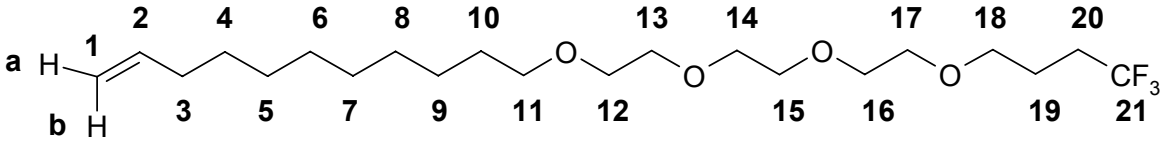
δ_H 1.74–1.89 (2H, m, **13**-H), 2.10–2.29 (2H, m, **14**-H), 3.46–3.72 (14H, m, **6**-H, **7**-H, **8**-H, **9**-H, **10**-H, **11**-H and **12**-H), 4.57 (2H, **5**-H), 7.27–7.38 (5H, m, **1**-H, **2**-H and **3**-H); δ_C 22.2 (1C, q, $^2J_{C,F}$: 2.8, **13**), 30.5 (1C, q, $^3J_{C,F}$: 29.1, **14**), 69.2, 69.3, 70.0, 70.4, 70.5, 73.0 (8C, **5**, **6**, **7**, **8**, **9**, **10**, **11** and **12**), 127.4, 127. 6, 128.2, 129.0, 132.8 (5H, **1**, **2**, and **3**), 127.2 (1C, q, $^1J_{C,F}$: 276.1, **15**), 138.1 (1C, **4**); δ_F -66.8 (t, $^1J_{C,F}$: 11.1, **14**-F); ν_{MAX}*(film)/cm*$^{-1}$ 699.13, 738.55 (Ar); 833.92, 1029.40, 1112.71, 1254.26 (CF_3); 1388.88, 1454.31 (C-O-C); 2867.81 (C-H); 3031.44, 3064.50, 3088.49 (Ar); ***HRMS m/z*** *(ES+)*: $[MNa]^+$ 373.1598, calculated 373.1603.

2-{2-[2-(3,3,3-trifluoro-butoxy)-ethoxy]-ethoxy}-ethanol (**8b**)



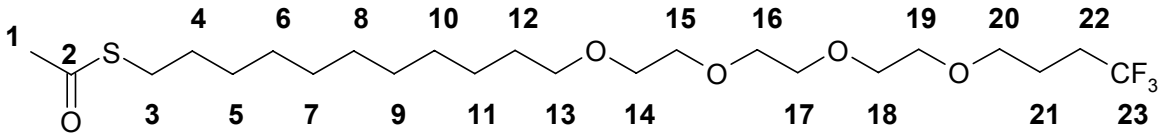
δ_H 1.72–1.84 (2H, m, **8**-H), 2.06–2.24 (2H, m, **9**-H), 2.91 (1H, br, **1**-OH), 3.43–3.73 (14H, m, **1**-H, **2**-H, **3**-H, **4**-H, **5**-H, **6**-H, and **7**-H); δ_C 22.2 (1C, q, $^2J_{C,F}$: 2.9, **8**), 30.5 (1C, q, $^2J_{C,F}$: 28.9, **9**), 61.5, 69.2, 70.0, 70.2, 70.3, 70.5, 72.4 (7C, **2**, **3**, **4**, **5**, **6**, and **7**), 125.2 (1C, q, J: 274.6, **10**); δ_F -66.9 (t, $^1J_{C,F}$: 11); ν_{MAX}*(film)/cm*$^{-1}$ 833.68, 935.36, 1157.96, 1256.07 (CF_3); 1454.83 (C-O-C); 2865.78 (C-H); 3449.62 (O-H); ***HRMS m/z*** *(ES+)*: $[MNa]^+$ 283.1128, calculated 283.1133.

11-(2-{2-[2-(3,3,3-trifluoro-propoxy)-ethoxy]-ethoxy}-ethoxy)-undec-1-ene (**9b**)



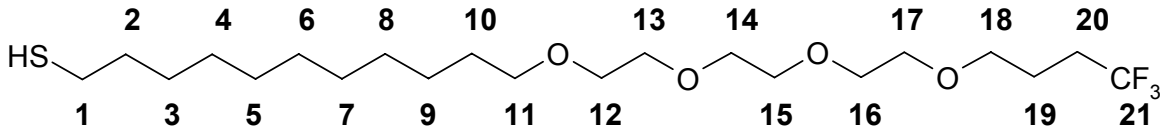
δ_H 1.22–1.40 (12H, m, **4**-H, **5**-H, **6**-H, **7**-H, **8**-H and **9**-H), 1.51–1.62 (2H, m, **10**-H), 1.76–1.88 (2H, m, **19**-H), 1.97–2.08 (2H, m, **3**-H), 2.10–2.27 (2H, m, **20**-H), 3.39–3.70 (16H, m, **11**-H, **12**-H, **13**-H, **14**-H, **15**-H, **16**-H, **17**-H, and **18**-H), 4.89–5.03 (2H, m, **1**-H_a, and **1**-H_b), 5.81 (1H, tdd, $^3J_{H,Hb}$: 16.9, $^3J_{H,Ha}$: 10.2, $^3J_{H,H}$: 6.7, **2**-H); δ_C 22.2 (1C, q, $^3J_{C,F}$: 2.7, **19**), 25.9, 28.7, 28.9, 29.3, 29.3, and 33.6 (8C, **3**, **4**, **5**, **6**, **7**, **8**, **9**, and **10**), 30.5 (1C, q, $^2J_{C,F}$: 28.9, **20**), 66.4, 69.2, 69.7, 69.9, 70.0, 70.4, 70.5, and 71.3 (8C, **11**, **12**, **13**, **14**, **15**, **16**, **17** and **18**), 113.9 (1C, **1**), 127.1 (1C, q, $^1J_{C,F}$: 276.4, **21**), 139.0 (1C, **2**); δ_F -66.9 (t, $^3J_{F,H}$: 11.0); ν_{MAX}*(film)/cm*$^{-1}$ 1031.41, 1121.92, 1254.19 (CF_3); 1351.28, 1454.61 (C-O-C); 1640.92 ($CH{=}CH_2$); 2857.53, 2927.67 (C-H); 3077.30 ($=CH_2$); ***HRMS m/z*** *(ES+)*: $[MNa]^+$ 413.2879, calculated 413.2879.

Thioacetic acid S-[10-(2-{2-[2-(3,3,3-trifluoro-propoxy)-ethoxy]-ethoxy}-ethoxy)-decyl]-ester (**10b**)



δ_H 1.21–1.31 (14 H, m, **5**-H, **6**-H, **7**-H, **8**-H, **9**-H, **10**-H, and **11**-H), 1.49–1.59 (4 H, m, **4**-H, and **12**-H), 1.75–1.86 (2H, m, **21**-H), 2.07–2.26 (2H, m, **22**-H), 2.29 (3H, s, **1**-H), 2.83 (2H, t, $^{3}J_{H,H}$: 7.3, **3**-H), 3.42 (2H, t, $^{3}J_{H,H}$: 6.8, **13**-H), 3.46–3.66 (14H, m, **14**-H, **15**-H, **16**-H, **17**-H, **18**-H, **19**-H, and **20**-H); ***δ_C*** 22.2, 26.0, 28.7, 29.0, 29.0, 29.4, 29.4, 29.5, 29.5 (10C, **3**, **4**, **5**, **6**, **7**, **8**, **9**, **10**, **11**, and **12**), 30.6 (1C, q, **23**), 34.3 (1C, q, $^{2}J_{C,F}$: 28.9, **21**), 66.5 (1C, **22**), 69.2, 69.7, 69.9, 70.1, 70.4, 70.5, and 71.4 (9C, **13**, **14**, **15**, **16**, **17**, **18**, **19**, **20**, and **21**) 127.2 (1C, q, $^{1}J_{C,F}$: 276.4, **24**), 196.0 (1C, **2**); ***δ_F*** -66.8 (3F, t, $^{3}J_{F,H}$:11.0, **24**-F); ***ν_{MAX}(film)/cm⁻¹*** 634.28 (-S-); 834.47, 994.76, 1120.09, 1254.00 (CF_3); 1351.20, 1454.90 (C-O-C); 16403.84 (C=O); 2859.49, 2935.18 (C-H); ***HRMS m/z*** *(ES+)*: $[MNa]^+$ 511.2679, calculated 511.2681.

11-(2-{2-[2-(3,3,3-trifluoro-propoxy)-ethoxy]-ethhoxy}-ethoxy)-undecane-1-thiol (**2**)

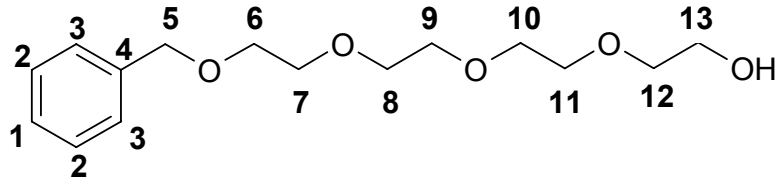


δ_H 1.15–1.37 (15H, m, **4**-H, **5**-H, **6**-H, **7**-H, **8**-H, **9**-H, and **10**-H, a triplet with $^{3}J_{H,H}$: 7.7 in the multiplet for S-H), 1.50–1.65 (4H, m, **3**-H, and **11**-H), 1.76–1.89 (2H, m, **20**-H), 2.06–2.28 (2H, m, **21**-H), 2.50 (2H, td, $^{3}J_{H,H} \approx {}^{3}J_{H,H}$ (through S atom): 7.7, **1**-H), 3.43 (2H, t, $^{3}J_{H,H}$**:** 6.7, **12**-H), 3.50 (2H, t, $^{3}J_{H,H}$**:** 6.2, **19**-H), 3.54–3.69 (12 H, m, **13**-H, **14**-H, **15**-H, **16**-H, **17**-H, and **18**-H); ***δ_C*** 22.3 (1C, q, $^{3}J_{C,F}$: 2.8), 24.6, 26.0, 28.3, 29.0, 29.4, 29.5, 29.5, 34.0 (10 C, **1**, **2**, **3**, **4**, **5**, **6**, **7**, **8**, **9**, and **10**), 30.6 (1C, q, $^{2}J_{C,F}$: 28.8, **20**), 69.3, 69.8, 70.0, 70.1, 70.5, 70.6, and 71.5 (8C, **11**, **12**, **13**, **14**, **15**, **16**, **17**, and **18**), 127.2 (1C,

q, $^{1}J_{C,F}$: 276.4, **21**) δ_F -66.8 (3F, t, $^{3}J_{F,H}$:11.0, **21**-F); ν_{MAX}*(film)/cm*$^{-1}$ 660.04 (S-C); 868.31, 1029.83, 1121.97, 1253.88 (CF_3); 1351.18, 1452.55 (C-O-C); 2859.94, 2936.20 (C-H); ***HRMS m/z*** *(ES+)*: $[MNa]^+$ 447.2750, calculated 447.2756.

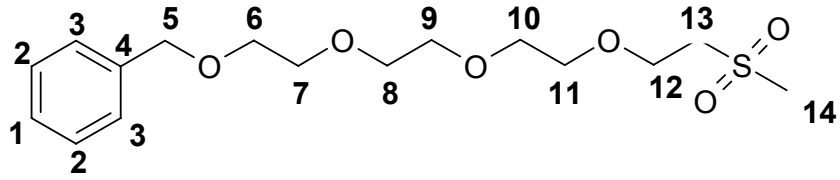
Synthesis of 11-[2-(2-{2-[2-(3,3,3-Trifluoro-propoxy)-ethoxy]-ethoxy}-ethoxy)-ethoxy]-undecane-1-thiol (3)

2-[2-(2-Benzyloxy-ethoxy)-ethoxy]-ethanol (**5b**)



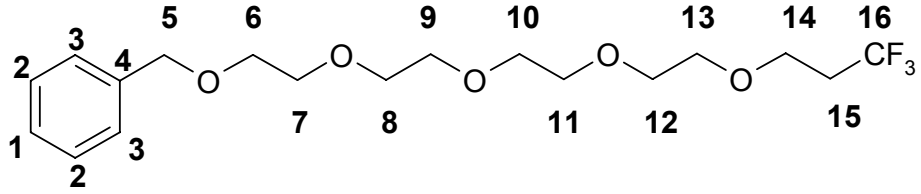
δ_H 3.03 (1H, s br, O-H), 3.56–3.73 (16H, m, **6**-H, **7**-H, **8**-H, **9**-H, **10**-H, **11**-H, **12**-H, and **13**-H), 4.58 (2H, s, **5**-H), 7.28–7.37 (5H, m, **1**-H, **2**-H, and **3**-H); δ_C 61.4, 69.2, 70.1, 70.4, 70.4, 70.6, 72.4, 73.0, and 73.3 (9C, **5**, **6**, **7**, **8**, **9**, **10**, **11**, **12**, and **13**), 127.4, 127.6, and 128.2 (5C, **1**, **2**, and **3**), 138.0 (1C, **4**); ν_{MAX}*(film)/cm*$^{-1}$ 699.21, 738.66 (Ar); 1102.20, 1357.65, 1454.22 (C-O-C); 2868.85 (C-H); 3030.15, 3063.44, 3087.58 (Ar); 3439.71 (O-H); ***HRMS m/z*** *(ES+)*: $[MNa]^+$ 307.1512, calculated 307.1521.

Methanesulfonic acid 2-[2-(2-benzyloxy-ethoxy)-ethoxy]-ethylester (**6b**)



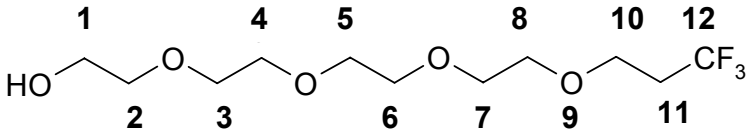
δ_H 3.02 (3H, s, **14**-H), 3.59–3.68 (12H, m, **6**-H, **7**-H, **8**-H, **9**-H, **10**-H, and **11**-H), 3.69–3.74, and 4.29–4.36 (4H, m, **12**-H, and **13**-H), 4.54 (2H, s, **5**-H), 7.27–7.35 (4H, m, **1**-H, **2**-H, and **3**-H); δ_C 37.2 (1C, **14**), 68.6, 69.1, 70.1, 70.2, 72.7 (9C, **5**, **6**, **7**, **8**, **9**, **10**, **11**, **12**, and **13**), 128.0, 128.1, 128.7 (5C, **1**, **2**, and **3**), 137.9 (1C, **4**); ν_{MAX}*(film)/cm*$^{-1}$ 700.56, 740.92 (Ar); 806.54 (-SO_2-); 1105.91 (C-O-C); 1175.21 (-SO_2-); 1352.52, 1454.84 (C-O-C); 2869.48 (C-H); 3028.98, 3062.70 (Ar);
HRMS m/z *(ES+)*: $[MNa]^+$ 385.1304, calculated 385.1297.

2-{2-[2-(3,3,3-trifluoro-propoxy)-ethoxy]-ethoxy}-ethoxymethyl-benzene (**7c**)



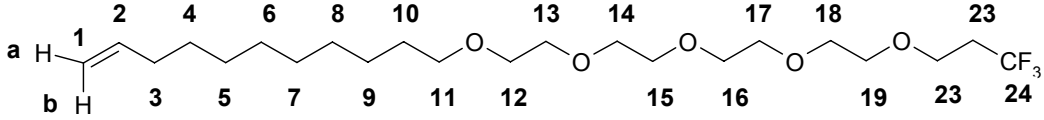
δ_H 1.79 (1H, s br, O-H), 2.42 (tq, $^3J_{H,F}$: 10.9, $^3J_{H,H}$: 6.8, **15**-H), 3.59–3.73 (18H, m, **6**-H, **7**-H, **8**-H, **9**-H, **10**-H, **11**-H, **12**-H, **13**-H, and **14**-H), 4.57 (2H, s, 5-H), 7.26–7.38 (5H, m, 1-H, 2-H, and 3-H); δ_C 34.0 (1C, q, $^2J_{C,F}$: 28.2, **15**), 63.7 (1C, q, $^3J_{C,F}$: 3.6, **14**), 69.1, 70.1, 70.2, 70.3, 70.3, and 72.8 (9C, **5**, **6**, **7**, **8**, **9**, **10**, **11**, **12**, and **13**), 125.9 (1C, $^1J_{C,F}$: 276.7, **16**), 127.2, 127.3, 128.0 (5C, **1**, **2**, and **3**), 138.0 (1C, **4**); δ_F -65.2 (t, $^1J_{C,F}$: 10.8, **16**-F); ν_{MAX}*(film)/cm*$^{-1}$ 699.20, 738.88 (Ar); 848.03, 1004.69, 1144.58, 1256.00 (CF_3); 1351.56, 1454.55 (C-O-C); 2868.64 (C-H); 3031.09, 3063.91, 3088.27 (Ar); ***HRMS m/z*** *(ES+)*: $[MNa]^+$ 403.1706, calculated 403.1708.

2-{2-[2-(3,3,3-trifluoro-propoxy)-ethoxy]-ethoxy}-ethanol (**8c**)



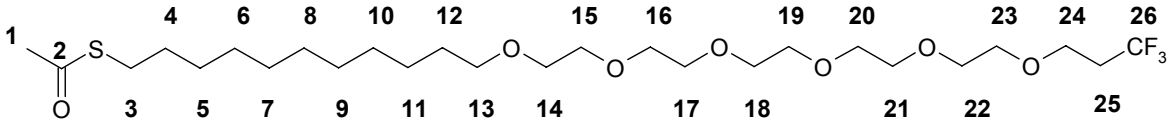
δ_H 2.43 (2H, tq, $^3J_{H,F}$: 10.8, $^3J_{H,H}$: 6.8, **11**-H), 3.59–3.76 (18H, m, **1**-H, **2**-H, **3**-H, **4**-H, **5**-H, **6**-H, **7**-H, **8**-H, **9**-H, and **10**-H); δ_C 34.0 (1C, q, $^2J_{C,F}$: 28.3, **11**), 61.3 (1C, **1**), 63.8 (1C, q, $^3J_{H,H}$: 3.5, **7**), 70.0, 70.2, 70.3, 72.3, 70.3 (7C, m, **2**, **3**, **4**, **5**, **6**, **7**, and **8**), 125.9 (1C, q, J: 276.5, **12**); δ_F -65.3 (3F, t, $^1J_{C,F}$: 10.8); ν_{MAX}*(film)/cm*$^{-1}$ 838.34, 1005.46 1146.22, 1256.74 (CF_3); 1351.14, 1443.49 (C-O-C); 2879.89 (C-H); 3458.17 (O-H); ***HRMS m/z*** *(ES+)*: $[MNa]^+$ 313.1237, calculated 313.1239.

11-(2-{2-[2-(3,3,3-trifluoro-propoxy)-ethoxy]-ethoxy}-ethoxy)-undec-1-ene (**9c**)



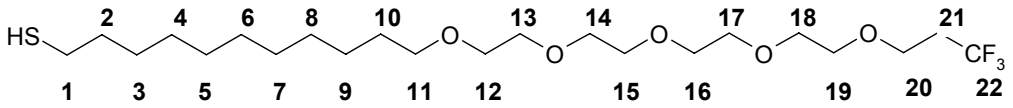
δ_H 1.21–1.41 (12H, m, **4**-H, **5**-H, **6**-H, **7**-H, **8**-H and **9**-H), 1.51–1.64 (2H, m, **10**-H), 1.95–2.14 (2H, m, **3**-H), 2.43 (2H, tq, $^4J_{H,F}$: 10.8, $^3J_{H,H}$: 6.8, **23**-H), 3.45 (2H, t, $^3J_{H,H}$: 6.8, **11**-H), 3.55–3.71 (18H, m, **12**-H, **13**-H, **14**-H, **15**-H, **16**-H, **17**-H, **18**-H, **19**-H, and **20**-H), 4.90–5.04 (2H, m, **1**-H), 5.81 (1H, tdd, $^3J_{H,Hb}$: 17,0 $^3J_{H,Ha}$: 10.2, $^3J_{H,H}$: 6.7); δ_C 26.0, 28.8, 29.0, 29.3, 29.4, 29.4, 29.5, 33.7 (8C, **3**, **4**, **5**, **6**, **7**, **8**, **9**, and **10**), 34.3 (1C, q, $^2J_{C,F}$: 28.3, **21**), 64.0 (1C, q, $^3J_{C,F}$: 3.6, **20**), 70.0, 70.4, 70.5, 70.6, 71.4 (9C, **11**, **12**, **13**, **14**, **15**, **16**, **17**, **18**, and **19**), 114.0 (1C, **1**), 126.0 (1C, q, $^1J_{C,F}$: 276.0, **22**), 139.1 (1C, **2**); δ_F -65.3 (t, $^3J_{F,H}$: 10.8); ν_{MAX}*(film)/cm*$^{-1}$ 993.09, 1121.72, 1257.73 (CF_3); 1351.03, 14250.35 (C-O-C); 1640.71 ($CH=CH_2$); 2855.94, 2926.77 (C-H); 3076.90 ($=CH_2$); ***HRMS m/z*** *(ES+)*: $[MNa]^+$ 465.2801, calculated 465.2804.

Thioacetic acid S-[10-(2-{2-[2-(3,3,3-trifluoro-propoxy)-ethoxy]-ethoxy}-ethoxy)-decyl]-ester (**10c**)



δ_H 1.23–1.30 (12H, m, 6-H, 7-H, 8-H, 9-H, 10-H, and 11-H), 1.52–1.61 (6H, m, 4-H, 5-H, and 12-H), 2.32 (3H, s, 1-H), 2.42 (2H, tq, $^{3}J_{H,F}$: 10.8, $^{3}J_{H,H}$: 6.8, 23-H), 2.86 (2H, t, $^{3}J_{H,H}$:6.8, 3-H), 3.44 (2H, t, $^{3}J_{H,H}$:6.8, 13-H), 3.54–3.73 (18, m, **14**-H, **15**-H, **16**-H, **17**-H, **18**-H, **19**-H, **20**-H, **21**-H, and **22**-H); ***δ_C*** 26.0, 28.7, 29.0, 29.0, 29.4, 29.4, 29.4, 29.5 (10C, **3**, **4**, **5**, **6**, **7**, **8**, **9**, and **10**), 34.3 (1C, q, $^{3}J_{C,F}$: 28.2, **23**), 64.0 (1C, q, $^{3}J_{C,F}$: 3.5, **22**), 69.9, 70.4, 70.5, 70.6, 71.4 (9C, **13**, **14**, **15**, **16**, **17**, **18**, **19**, **20**, and **21**), 126.0 (1C, q, $^{3}J_{C,F}$:276.9, **24**), 196.0 (1C, **2**); ***δ_F*** -65.3 (3F, t, $^{3}J_{F,H}$:10.8, **22**-F); ***ν_{MAX}(film)/cm⁻¹*** 627.84 (-S-); 841.58, 1005.04, 1135.93, 1255.78 (CF_3); 1352.96, 1441.76 (C-O-C); 1693.70 (C=O); 2856.59, 2926.82 (C-H); ***HRMS m/z (ES+)***: $[MNa]^+$ 541.2787, calculated 541.2787.

11-(2-{2-[2-(3,3,3-trifluoro-propoxy)-ethoxy]-ethhoxy}-ethoxy)-undecane-1-thiol (**3**)



δ_H 1.15–1.39 (15H, m, **4**-H, **5**-H, **6**-H, **7**-H, **8**-H, **9**-H, **10**-H, and S-H), 1.47–1.62 (4H, m, **2**-H, and **10**-H), 2.26–2.52 (4H, m, **1**-H, and **21**-H), 3.40 (2H, t, $^{3}J_{H,H}$: 6.8, **11**-H), 3.50–3.70 (18H, m, **12**-H, **13**-H, **14**-H, **15**-H, **16**-H, **17**-H, **18**-H, **19**-H, and **20**-H); ***δ_C*** 24.5, 25.9, 28.2, 28.9, 29.3, 29.4, 29.5, 32.8, 33.9, 34.0 (10C, **1**, **2**, **3**, **4**, **5**, **6**, **7**, **8**, **9**, and **10**), 34.2 (1C, q, $^{2}J_{C,F}$: 28.1, **21**), 63.9 (1C, q, $^{3}J_{C,F}$: 3.6, **20**), 69.9, 70.4, 70.4, 70.5, 71.3, (8C, **11**, **12**, **13**, **14**, **15**, **16**, **17**, and **18**), 126.0 (1C, q, $^{1}J_{C,F}$: 277.0, **22**); ***δ_F*** -65.3 (3F, t, $^{3}J_{F,H}$:10.8, **20**-F); ***ν_{MAX}(film)/cm⁻¹*** 657.73 (S-C); 842.51, 1004.91, 1148.59, 1255.80

(CF_3); 1351.01, 1439.67 (C-O-C); 2856.45, 2927.02 (C-H); ***HRMS m/z (****ES+)*: $[MNa]^+$ 499.2685, calculated 499.2681.