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Terminally perfluorinated long-chain alkanethiols

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Abstract

This paper describes the synthesis of a series of alkanethiols containing perfluorinated terminal segments: $F(CF_2)_m(CH_2)_nSH$, where $m = 1$, $n = 9$–15; $m = 2$, $n = 11$–14; $m = 3$, $n = 10$–13; and $m = 4$, $n = 9$–12. Fluorinated alkyl iodides of the general formula $F(CF_2)_m(CH_2)_nI$, where $m = 1$–4 and $n = 0$ or 1, were added to long-chain ω-olefins that were functionalized at the α-terminus with a thioacetate group. The reactions proceeded in good yields under free radical conditions. Reduction of the resulting secondary iodides gave long-chain alkanethioacetates with perfluoroalkyl terminal segments. These intermediates were readily transformed into the corresponding terminally perfluorinated alkanethiols by acidic deprotection. The product thiols should find use in the generation of well-defined fluorinated interfaces using the self-assembled monolayer (SAM) technique.

1. Introduction

The synthesis of specifically fluorinated long-chain α,ω-functionalized hydrocarbons remains a challenging problem for interfacial scientists. The generation of organized thin films from these molecules offers the opportunity to study fundamental properties of fluorinated interfaces, such as wetting, adhesion, and friction. The ability to control the identities of the α and ω functionalities using organic synthesis permits atomic-level control over the structure and composition of interfaces formed from these molecules by either Langmuir–Blodgett or self-assembly techniques [1,2]. Organic synthesis thus provides a convenient tool for fine-tuning the interfacial properties of thin films.

A variety of methods have been used to introduce perfluorinated segments of different lengths into aliphatic organic molecules [3–21]. Brace investigated the radical addition of iodoperfluoroalkanes to a variety of terminal vinylic alkenes [3,4]. His approach was based on initial studies by Haszeldine [22], Park et al. [23], and Moore [24], who used ultraviolet light for initiation. These reactions typically required several days for completion. By employing azo or peroxy radical initiators, however, Brace was able to achieve high yields of coupling within hours. Brace proposed that the coupling proceeds via the formation of a perfluoroalkyl radical, which attacks the terminal carbon of the olefinic group [5]. Reduction of the resultant fluorinated secondary iodide with zinc or lithium aluminum hydride provided a variety of perfluoroalkylated compounds in excellent yields.

Cloux and Kovats modified Brace's approach by exploring the addition of 2,2,2-trifluoroethyl iodide to terminal alkenes [25]. This approach is preferred for the synthesis of perfluoromethyl-terminated species because liquid 2,2,2-trifluoroethyl iodide is much easier to handle than gaseous trifluoromethyl iodide. Although formation of the 2,2,2-trifluoroethyl radical is slower than that of the corresponding perfluorinated moieties, the coupling was observed to occur upon the addition of successive portions of radical initiator. Furthermore, the yields obtained by Cloux and Kovats were satisfactory, but generally lower than those obtained by Brace.

We have targeted the synthesis of terminally perfluorinated alkanethiols for the generation of well defined fluorinated interfaces via self assembly on gold [26–31]. To this end, we have developed a synthetic strategy that relies heavily on the methods established by Brace and Cloux and Kovats, but with a new twist: the radical addition of fluorinated alkyl iodides to ω-olefins that are functionalized at the α-terminus with a thioacetate group. Herein, we describe this new approach and illustrate its efficacy by synthesizing a wide range of terminally perfluorinated alkanethiols that possess varying chain lengths and degrees of fluorination.

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2. Experimental

2.1. General information

Partially fluorinated and perfluorinated alkyl iodides were purchased from Aldrich Chemical Co. and used as received. Long-chain hydrocarbon starting materials, also purchased from Aldrich, were either used as received or modified before use via known literature procedures. Organic solvents were dried by passage through activated alumina and degassed by the freeze-pump-thaw method immediately before use. Reactions were monitored by thin-layer chromatography (TLC) using Whatman F_{254} precoated silica gel plates (0.25 mm thickness). Silica gel (EM Sciences; 63–200 μm or 35–70 μm) and reagent grade solvents were used for column chromatography. Nuclear magnetic resonance spectra (NMR) were recorded on a General Electric QE-300 spectrometer (^{1}H: 300 MHz; ^{13}C: 75.5 MHz). Elemental analyses were performed by National Chemical Consulting. High resolution mass spectra were obtained at Rice University on a Finniganmat MAT 95 mass spectrometer operating in the EI mode.

2.2. ω-Alkenyl-1-thioacetates **1** (general procedure)

Potassium thioacetate (86.0 mmol) was dissolved in 100 ml of absolute ethanol (previously degassed) under argon. To the stirred solution, the ω-alkenyl bromide (43.0 mmol) was added dropwise over 10 min. Stirring was continued, and the mixture was heated to reflux for 6 h under argon. After cooling, 150 ml of water was added, and the mixture was extracted with hexane (3 × 100 ml). The combined organic layers were washed with brine (1 × 100 ml) and dried over $MgSO_4$. The solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica gel (hexane / diethyl ether = 9 / 1) affording the ω-alkenyl-1 thioacetate in ca. 95% yield.

7-*Octenyl*-1-*thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.90$–5.73 (m, 1H), 5.03–4.91 (m, 2H), 2.86 (t, $J = 7.4$ Hz, 2H), 2.33 (s, 3H), 2.02 (m, 2H), 1.55 (m, 2H), 1.40–1.29 (m, 6H).

8-*Nonenyl*-1-*thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.89–5.71 (m, 1H), 5.01–4.89 (m, 2H), 2.87 (t, $J = 7.4$ Hz, 2H), 2.33 (s, 3H), 2.03 (m, 2H), 1.52 (m, 2H), 1.39–1.27 (m, 8H).

9-*Decenyl*-1-*thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.88$–5.71 (m, 1H), 5.01–4.90 (m, 2H), 2.85 (t, $J = 7.4$ Hz, 2H), 2.32 (s, 3H), 2.03 (m, 2H), 1.53 (m, 2H), 1.39–1.28 (m, 10H).

10-*Undecenyl*-1-*thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.88$–5.71 (m, 1H), 5.02–4.89 (m, 2H), 2.85 (t, $J = 7.4$ Hz, 2H), 2.35 (s, 3H), 2.05 (m, 2H), 1.56 (m, 2H), 1.39–1.28 (m, 12H).

11-*Dodecenyl*-1-*thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.88$–5.71 (m, 1H), 5.03–4.89 (m, 2H), 2.86 (t, $J = 7.4$ Hz, 2H), 2.33 (s, 3H), 2.03 (m, 2H), 1.55 (m, 2H), 1.38–1.25 (m, 14H).

12-*Tridecenyl*-1-*thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.88$–5.72 (m, 1H), 5.01–4.90 (m, 2H), 2.86 (t, $J = 7.4$ Hz, 2H), 2.32 (s, 3H), 2.03 (m, 2H), 1.56 (m, 2H), 1.38–1.23 (m, 16H).

2.3. Terminally perfluorinated alkyl thioacetates **3** (general procedure)

The ω-alkenyl thioacetate (65.0 mmol) and fluorinated iodide R_FI (71.5 mmol) were placed in a 50 ml Schlenk flask, and the radical initiator AIBN (2 mol%) was added under a flow of argon. The flask was closed, evacuated until the reaction mixture started to effervesce, and refilled with argon; this process was repeated at least two additional times. The flask was sealed under vacuum, and the stirred reaction mixture was heated to 90°C. After 3 h, the flask was cooled to room temperature, and another portion of AIBN (2 mol%) was added under a flow of argon as described above. The stirred solution was again heated to 90°C, and the entire process was repeated at least two additional times; 3 h passed between the additions of AIBN. The progress of the reaction was monitored by ^{1}H NMR spectroscopy of small aliquots collected between the additions. The flask was cooled to room temperature, and the crude iodothioacetate **2** was used in the next step without further purification.

2.4. Reduction method A1

$NaBH_4$ (200 mmol) was dissolved in 200 ml of dimethyl formamide (DMF, previously degassed) and cooled to 0°C. The crude iodothioacetate **2**, dissolved in 50 ml of DMF, was added slowly to the stirred solution. After stirring for 15 min, the solution was allowed to warm to room temperature. After stirring for 3 h, 100 ml of ice-water was added, and the mixture was stirred until effervescence ceased. The solution was carefully neutralized with conc. HCl and extracted with hexane (3 × 100 ml). The combined organic phases were washed with water (2 × 100 ml), dried over $MgSO_4$, and evaporated to dryness. The residue was dissolved in 50 ml of CH_2Cl_2 and cooled to ca. −10°C (ice / salt bath). Ozone was bubbled through the solution for 10–20 min; the duration varied directly with the amount of olefinic starting material remaining in the crude reaction mixture. After bubbling argon through the solution for 10 min, the solvent was evaporated at room temperature under vacuum. A portion of DMF (100 ml) was added to the flask, and a solution of $NaBH_4$ (2 molar excess) in 50 ml of DMF was added dropwise to the stirred solution at 0°C. The mixture was allowed to warm to room temperature and stirred for 3 h under argon. Ice-water (100 ml) was added. The mixture was neutralized with conc. HCl and extracted with hexane (3 × 100 ml). The combined organic layers were washed with water (1 × 100 ml) and dried over

$MgSO_4$. The solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica gel (hexane / diethyl ether = 50 / 1). Typical overall yields for the radical addition, dehalogenation, and purification were 20–30%.

2.5. Reduction method A2

The crude iodothioacetate **2** was dissolved in 130 ml of glacial acetic acid (HOAc). Zinc dust (195 mmol) was added at room temperature under argon. Compounds that were insoluble in glacial acetic acid were dissolved in a minimum amount of dry THF and then added to the Zn / HOAc slurry. The mixture was stirred for 16 h and then filtered through Celite. The filtrate was evaporated to dryness and redissolved in hexane (ca. 100 ml). The solution was washed with water (2 × 100 ml), saturated aqueous $NaHCO_3$ solution (1 × 100 ml), and brine (1 × 100 ml), and then dried over $MgSO_4$. Removal of the solvent afforded the crude thioacetate **3**, which was often contaminated with a small amount of olefinic starting material **1**. Crude thioacetate **3** was dissolved in 50 ml of toluene, and N-methyl-α-phenyl nitrone (30.0 mmol) was added. After refluxing for 48 h, the reaction mixture was diluted with diethyl ether (100 ml) and washed with water (3 × 100 ml). The organic phase was dried with $MgSO_4$, and evaporated to dryness by rotary evaporation. The residue was purified by chromatography on silica gel (hexane / diethyl ether = 50 / 1). Typical overall yields for the radical addition, dehalogenation, and purification ranged from 56–66%.

10,10,10-*Trifluorodecyl thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.85$ (t, $J = 7.4$ Hz, 2H), 2.34 (s, 3H), 2.17–1.99 (m, 2H), 1.58–1.47 (m, 4H), 1.39–1.27 (m, 10H).

11,11,11-*Trifluoroundecyl thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.86$ (t, $J = 7.4$ Hz, 2H), 2.33 (s, 3 H), 2.17–1.99 (m, 2H), 1.60–1.50 (m, 4H), 1.39–1.25 (m, 12H).

12,12,12-*Trifluorododecyl thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.85$ (t, $J = 7.4$ Hz, 2H), 2.34 (s, 3H), 2.18–1.99 (m, 2H), 1.61–1.50 (m, 4H), 1.39–1.28 (m, 14H).

13,13,13-*Trifluorotridecyl thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.85$ (t, $J = 7.4$ Hz, 2H), 2.35 (s, 3H), 2.16–1.98 (m, 2H), 1.59–1.49 (m, 4H), 1.39–1.26 (m, 16H).

12,12,13,13,13-*Pentafluorotridecyl thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.85$ (t, $J = 7.4$ Hz, 2H), 2.35 (s, 3H), 2.12–1.91 (m, 2H), 1.59–1.50 (m, 4H), 1.39–1.26 (m, 14H).

11,11,12,12,13,13,13-*Heptafluorotridecyl thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.84$ (t, $J = 7.4$ Hz, 2H), 2.30 (s, 3H), 2.10–1.92 (m, 2H), 1.59–1.49 (m, 4H), 1.40–1.24 (m, 12H).

10,10,11,11,12,12,13,13,13-*Nonafluorotridecyl thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.85$ (t, $J = 7.3$ Hz, 2H), 2.31 (s, 3H), 2.15–1.91 (m, 2H), 1.63–1.50 (m, 4H), 1.41–1.22 (m, 10H).

14,14,14-*Trifluorotetradecyl thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.85$ (t, $J = 7.4$ Hz, 2H), 2.31 (s, 3H), 2.13–1.96 (m, 2H), 1.60–1.48 (m, 4H), 1.38–1.23 (m, 18H).

13,13,14,14,14-*Pentafluorotetradecyl thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.86$ (t, $J = 7.4$ Hz, 2H), 2.35 (s, 3H) 2.11–1.91 (m, 2H), 1.59–1.49 (m, 4H), 1.39–1.25 (m, 16H).

12,12,13,13,14,14,14-*Heptafluorotetradecyl thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.85$ (t, $J = 7.4$ Hz, 2H), 2.35 (s, 3H), 2.13–1.93 (m, 2H), 1.59–1.49 (m, 4H), 1.39–1.26 (m, 14H).

15,15,15-*Trifluoropentadecyl thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.81$ (t, $J = 7.2$ Hz, 2H), 2.27 (s, 3H), 2.09–1.94 (m, 2H), 1.56–1.49 (m, 4H), 1.33–1.20 (m, 20H).

14,14,15,15,16,16,16-*Heptafluorohexadecyl thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.83$ (t, $J = 7.2$ Hz, 2H), 2.29 (s, 3H), 2.09–1.91 (m, 2H), 1.61–1.48 (m, 4H), 1.38–1.22 (m, 18H).

15,15,16,16,16-*Pentafluorohexadecyl thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.83$ (t, $J = 7.2$ Hz, 2H), 2.29 (s, 3H), 2.06–1.88 (m, 2H), 1.60–1.48 (m, 4H), 1.37–1.22 (m, 20H).

13,13,14,14,15,15,15-*Heptafluoropentadecyl thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.84$ (t, $J = 7.3$ Hz, 2H), 2.30 (s, 3H), 2.13–1.90 (m, 2H), 1.66–1.50 (m, 4H), 1.42–1.19 (m, 16H).

2.6. Terminally perfluorinated alkanethiols **4** (general procedure)

The terminally perfluorinated alkyl thioacetates **3** or **9** (15.0 mmol) was dissolved in 100 ml of absolute ethanol (previously degassed) under argon. To the solution, 40 ml conc. HCl were added, and the stirred mixture was heated under reflux at 90°C for 13 h. The reaction mixture was diluted with 30 ml of water and extracted with hexane (3 × 100 ml). The combined organic layers were washed with water (2 × 100 ml), dried over $MgSO_4$, and evaporated to dryness by rotary evaporation. The crude product was purified by chromatography on silica gel (hexane) to give the terminally perfluorinated alkanethiol in ca. 95% yield.

10,10,10-*Trifluorodecanethiol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.52$ (q, $J = 7.2$ Hz, 2H), 2.13–1.96 (m, 2H), 1.67–1.47 (m, 4H), 1.36–1.25 (m, 11H). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 127.25$ (q, $^1J_{CF} = 276$ Hz), 34.03, 33.50 (q, $^2J_{CF} = 28$ Hz), 29.11 (3C), 28.95, 28.25, 24.61, 21.81. *Anal*. Calc. for $C_{10}H_{19}F_3S$: C, 52.61; H, 8.39. Found: C, 52.80; H, 7.98.

11,11,11-*Trifluoroundecanethiol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.52$ (q, $J = 7.2$ Hz, 2H), 2.13–1.95 (m, 2H), 1.67–1.48 (m, 4H), 1.36–1.25 (m, 13H). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 127.18$ (q, $^1J_{CF} = 276$ Hz),

34.02, 33.50 (q, $^2J_{CF} = 28$ Hz), 29.36 (2C), 29.25, 29.13, 28.63, 28.30, 24.48, 21.78. *Anal*. Calc. for $C_{11}H_{21}F_3S$: C, 54.52 H; 8.73. Found: C, 54.73; H, 8.35.

12,12,12-*Trifluorododecanethiol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.52$ (q, $J = 7.2$ Hz, 2H), 2.13–1.96 (m, 2H), 1.67–1.47 (m, 4H), 1.36–1.25 (m, 15H). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 127.25$ (q, $^1J_{CF} = 277$ Hz), 33.98–33.60 (q, $^2J_{CF} = 28$ Hz), 29.39 (2C), 29.26, 29.10, 28.98, 28.60, 28.28, 24.48, 21.75. *Anal*. Calc. for $C_{12}H_{23}F_3S$: C, 56.22; H, 9.04. Found: C, 56.37; H, 9.01.

13,13,13-*Trifluorotridecanethiol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.52$ (q, $J = 7.2$ Hz, 2 H), 2.11–1.96 (m, 2H), 1.62–1.47 (m, 4H), 1.35–1.23 (m, 17H), ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 127.11$ (q, $^1J_{CF} = 276$ Hz), 34.00, 33.55 (q, $^2J_{CF} = 28$ Hz), 29.42 (3C), 29.26, 29.07, 28.98, 28.58, 28.25, 24.31, 21.71. *Anal*. Calc. for $C_{13}H_{25}F_3S$: C, 57.75; H, 9.32. Found: C, 57.45; H, 9.34.

12,12,13,13,13-*Pentafluorotridecanethiol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.52$ (q, $J = 7.2$ Hz, 2H), 2.08–1.92 (m, 2H), 1.63–1.41 (m, 4H), 1.35–1.23 (m, 15H). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 119.02$ (tq, $^1J_{CF} = 249$ Hz, $^2J_{CF} = 37$ Hz), 115.79 (qt, $^1J_{CF} = 249$ Hz, $^2J_{CF} = 37$ Hz), 34.09, 30.62 (t, $^2J_{CF} = 22$ Hz), 29.46 (3C), 29.34, 29.18, 29.07, 28.35, 24.47, 20.19. *Anal*. Calc. for $C_{13}H_{23}F_5S$: C, 50.96; H, 7.57. Found: C, 51.15; H, 7.62.

11,11,12,12,13,13,13-*Heptafluorotridecanethiol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.51$ (q, $J = 7.2$ Hz, 2H), 2.11–1.93 (m, 2H), 1.66–1.53 (m, 4H), 1.40–1.22 (m, 13H). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 117.87$ (qt, $^1J_{CF} = 287$ Hz, $^2J_{CF} = 34$ Hz), 117.72 (tt, $^1J_{CF} = 252$ Hz, $^2J_{CF} = 31$ Hz), 108.86 (ttq, $^1J_{CF} = 267$ Hz, $^2J_{CF} = 37$ Hz), 33.97, 30.54 (t, $^2J_{CF} = 22$ Hz), 29.34 (2C), 29.24, 29.13, 29.02, 28.29, 24.57, 19.98. *Anal*. Calc. for $C_{13}H_{21}F_7S$: C, 45.61; H, 6.18. Found: C, 45.73; H, 6.10.

10,10,11,11,12,12,13,13,13-*Nonafluorotridecanethiol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.50$ (q, $J = 7.2$ Hz, 2H), 2.13–1.92 (m, 2 H), 1.65–1.52 (m, 4H), 1.42–1.19 (m, 11H). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 118.30$ (tt, $^1J_{CF} = 255$ Hz, $^2J_{CF} = 32$ Hz), 117.42 (qt, $^1J_{CF} = 286$ Hz, $^2J_{CF} = 34$ Hz), 113.65–100.74 (ttq; ttt, 2C), 33.98, 30.76 (t, $^2J_{CF} = 22$ Hz), 29.22, 29.13, 29.05, 28.94, 28.29, 24.60, 20.04. *Anal*. Calc. for $C_{13}H_{19}F_9S$: C, 41.27; H, 5.06. Found: C, 41.38; H, 4.96.

14,14,14-*Trifluorotetradecanethiol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.48$ (q, $J = 7.2$ Hz, 2H), 2.11–1.95 (m, 2H), 1.62–1.46 (m, 4H), 1.34–1.23 (m, 19H). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 127.15$ (q, $^1J_{CF} = 276$ Hz), 34.03, 33.46 (q, $^2J_{CF} = 29$ Hz), 29.50 (4C), 29.31, 29.13, 29.03, 28.65, 28.32, 24.49, 21.77. *Anal*. Calc. for $C_{14}H_{27}F_3S$: C, 59.12; H, 9.57. Found: C, 59.50; H, 9.90.

13,13,14,14,14-*Pentafluorotetradecanethiol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.52$ (q, $J = 7.2$ Hz, 2H), 2.08–1.92 (m, 2H), 1.63–1.41 (m, 4H), 1.35–1.23 (m, 17H). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 119.09$ (tq, $^1J_{CF} = 285$ Hz, $^2J_{CF} = 37$ Hz), 115.62 (qt, $^1J_{CF} = 252$ Hz, $^2J_{CF} = 37$ Hz), 33.95, 30.41 (t, $^2J_{CF} = 22$ Hz), 29.37 (4C), 29.22, 29.04, 28.91, 28.20, 24.29, 20.03. *Anal*. Calc. for $C_{14}H_{25}F_5S$: C, 52.48; H, 7.86. Found: C, 52.40; H, 7.77.

12,12,13,13,14,14,14-*Heptafluorotetradecanethiol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.52$ (q, $J = 7.2$ Hz, 2H), 2.17–1.94 (m, 2H), 1.66–1.44 (m, 4H), 1.37–1.21 (m, 15H). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 117.86$ (qt, $^1J_{CF} = 287$ Hz, $^2J_{CF} = 37$ Hz), 117.67 (tt, $^1J_{CF} = 252$ Hz, $^2J_{CF} = 31$ Hz), 108.85 (ttq, $^1J_{CF} = 263$ Hz, $^2J_{CF} = 37$ Hz), 34.01, 30.47 (t, $^2J_{CF} = 22$ Hz), 29.39 (3C), 29.28, 29.13, 28.99, 28.28, 24.42, 19.93. *Anal*. Calc. for $C_{14}H_{23}F_7S$: C, 47.18; H, 6.50. Found: 47.36; H, 6.39.

11,11,12,12,13,13,14,14,14-*Nonafluorotetradecanethiol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.50$ (q, $J = 7.2$ Hz, 2H), 2.14–1.91 (m, 2H), 1.66–1.50 (m, 4H), 1.43–1.21 (m, 13H). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 118.32$ (tt, $^1J_{CF} = 254$ Hz, $^2J_{CF} = 32$ Hz), 117.46 (qt, $^1J_{CF} = 288$ Hz, $^2J_{CF} = 34$ Hz), 113.61–100.67 (ttq; ttt, 2C), 34.05, 30.78 (t, $^2J_{CF} = 23$ Hz), 29.41, 29.30, 29.20, 29.09, 29.04, 28.36, 24.62, 20.07. HRMS Calc. for $C_{14}H_{21}F_9S$: 392.1220. Found; 392.1219(4).

15,15,15-*Trifluoropentadecanethiol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.50$ (q, $J = 7.2$ Hz, 2H), 2.12–1.96 (m, 2H), 1.64–1.48 (m, 4H), 1.38–1.22 (m, 21H). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 127.27$ (q, $^1J_{CF} = 276$ Hz), 34.05, 33.71 (q, $^2J_{CF} = 28$ Hz), 29.58 (4C), 29.53, 29.35, 29.17, 29.07, 28.69, 28.37, 24.63, 21.82. *Anal*. Calc. for $C_{15}H_{29}F_3S$: C, 60.37; H, 9.79. Found: C, 59.90; H, 9.89.

14,14,15,15,15-*Pentafluoropentadecanethiol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.51$ (q, $J = 7.2$ Hz, 2H), 2.08–1.90 (m, 2H), 1.65–1.52 (m, 4H), 1.35–1.23 (m, 19H). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 119.20$ (tq, $^1J_{CF} = 285$ Hz, $^2J_{CF} = 37$ Hz), 115.53 (qt, $^1J_{CF} = 252$ Hz, $^2J_{CF} = 37$ Hz), 34.01, 30.60 (t, $^2J_{CF} = 22$ Hz), 29.48 (5 C), 29.31, 29.14, 29.03, 28.33, 24.59, 20.16. A satisfactory analysis was not obtained. HRMS Calc for $C_{15}H_{27}F_5S$; 334.1754. Found: 334.1750(3).

13,13,14,14,15,15,15-*Heptafluoropentadecanethiol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.51$ (q, $J = 7.2$ Hz, 2H), 2.13–1.92 (m, 2H), 1.69–1.53 (m, 4H), 1.45–1.20 (m, 17H). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 117.91$ (qt, $^1J_{CF} = 288$ Hz, $^2J_{CF} = 33$ Hz), 117.77 (tt, $^1J_{CF} = 252$ Hz, $^2J_{CF} = 29$ Hz), 108.67 (ttq, $^1J_{CF} = 264$ Hz, $^2J_{CF} = 37$ Hz), 34.05, 30.59 (t, $^2J_{CF} = 22$ Hz), 29.49 (4C), 29.35, 29.19, 29.07, 28.34, 24.62, 20.03. *Anal*. Calc. for $C_{15}H_{25}F_7S$: C, 48.64; H, 6.80. Found: C, 48.94; H, 6.67.

12,12,13,13,14,14,15,15,15-*Nonafluoropentadecanethiol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.50$ (q, $J = 7.2$ Hz, 2H), 2.16–1.93 (m, 2H), 1.66–1.50 (m, 4H), 1.42–1.20 (m, 15 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 118.33$ (tt, $^1J_{CF} = 253$ Hz, $^2J_{CF} = 30$ Hz), 117.41 (qt, $^1J_{CF} = 293$ Hz, $^2J_{CF} = 32$ Hz), 113.06–100.77) (ttq; ttt, 2C), 34.02, 30.77 (t, $^2J_{CF} = 22$ Hz), 29.45 (3C), 29.34, 29.20, 29.06, 28.36, 24.63, 20.05. *Anal*. Calc. for $C_{15}H_{23}F_9S$: C, 44.33; H, 5.70. Found: C, 43.93; H, 5.85.

16,16,16-*Trifluorohexadecanethiol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.50$ (q, $J = 7.2$ Hz, 2H), 2.11–1.95 (m, 2H),

1.63–1.47 (m, 4H), 1.36–1.22 (m, 23H). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 127.26$ (q, $^1J_{CF} = 276$ Hz), 34.05, 33.70 (q, $^2J_{CF} = 28$ Hz), 29.70 (5C), 29.54, 29.35, 29.17, 29.07, 28.68, 28.37, 24.63, 21.82. *Anal*. Calc. for $C_{16}H_{31}F_3S$: C, 61.50; H, 10.00. Found C, 61.86; H, 9.81.

15,15,16,16,16-*Pentafluorohexadecanethiol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.50$ (q, $J = 7.2$ Hz, 2H), 2.07–1.90 (m, 2H), 1.64–1.51 (m, 4H), 1.36–1.21 (m, 21H). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 119.24$ (tq, $^1J_{CF} = 285$ Hz, $^2J_{CF} = 36$ Hz), 115.82 (qt, $^1J_{CF} = 251$ Hz, $^2J_{CF} = 37$ Hz), 34.05, 30.27 (t, $^2J_{CF} = 22$ Hz), 29.58 (5C), 29.53, 29.36, 29.18, 29.07, 28.37, 24.62, 20.20. *Anal*. Calc. for $C_{16}H_{29}F_5S$: C, 55.15; H, 8.39. Found: C, 55.55; H, 8.30.

14,14,15,15,16,16,16-*Heptafluorohexadecanethiol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.51$ (q, $J = 7.2$ Hz, 2H), 2.11–1.93 (m, 2H), 1.64–1.53 (m, 4H), 1.38–1.22 (m, 19H). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 117.90$ (qt, $^1J_{CF} = 287$ Hz, $^2J_{CF} = 34$ Hz), 117.77 (tt, $^1J_{CF} = 252$ Hz, $^2J_{CF} = 31$ Hz), 108.90 (ttq, $^1J_{CF} = 263$ Hz, $^2J_{CF} = 37$ Hz), 34.05, 30.59 (t, $^2J_{CF} = 22$ Hz), 29.55 (4C), 29.51, 29.36, 29.20, 29.07, 28.37, 24.65, 20.02. *Anal*. Calc. for $C_{16}H_{27}F_7S$: C, 49.99; H, 7.08. Found: C, 49.61; H, 6.89.

13,13,14,14,15,15,16,16,16-*Nonafluorohexadecanethiol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.50$ (q, $J = 7.2$ Hz, 2H), 2.14–1.92 (m, 2H), 1.64–1.51 (m, 4H), 1.42–1.22 (m, 17H). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 118.31$ (tt, $^1J_{CF} = 253$ Hz, $^2J_{CF} = 31$ Hz), 117.42 (qt, $^1J_{CF} = 288$ Hz, $^2J_{CF} = 31$ Hz), 113.24–100.77 (ttq; ttt, 2C), 34.04, 30.77 (t, $^2J_{CF} = 22$ Hz), 29.49 (4C), 29.34, 29.20, 29.07, 28.36, 24.63, 20.04. *Anal*. Calc. for $C_{16}H_{25}F_9S$: C, 45.71; H, 5.99. Found: C, 45.82; H, 5.72.

2.7. *Terminally perfluorinated alcohols* **6** *(general procedure)*

The radical addition of R_FI (55.0 mmol) to the ω-alkenol acetate, ω-alkenoic methyl ester, or ω-alkenol (50.0 mmol) in the presence of AIBN was performed as described above for coupling with the ω-alkyl thioacetate. The crude secondary iodide **5** was dissolved in 100 ml of glacial acetic acid. Zinc dust (150 mmol) was added at room temperature under argon. Compounds that were insoluble in glacial acetic acid were dissolved in a minimum amount of dry THF and then added to the Zn / HOAc slurry. The mixture was stirred for 16 h and then filtered through Celite. The filtrate was evaporated to dryness and redissolved in diethyl ether (ca. 100 ml). The solution was washed with water (2 × 100 ml), saturated aqueous $NaHCO_3$ solution (1 × 100 ml), and brine (1 × 100 ml), and then dried over $MgSO_4$. Removal of the solvent afforded the crude terminally fluorinated acetate, ester, or alcohol. If analysis by ^{1}H NMR showed contamination by the olefinic starting material, the fluorinated alcohol was treated with N-methyl-α-phenyl nitrone as described above. Contaminated acetate and ester products, however, were dissolved in 100 ml of CH_2Cl_2 and cooled to ca. −10°C (ice / salt bath). Ozone was bubbled through the solution for 20 min. After bubbling argon through the solution for 10 min, the solvent was evaporated at room temperature under vacuum. The residues were dissolved in 50 ml of THF and added over 5 min to a slurry of $LiAlH_4$ in THF at 0°C under argon. The mixture was refluxed under argon for 2 h. After cooling to 0°C, water was added dropwise until the evolution of hydrogen ceased. The mixture was acidified with 2N HCl and extracted with diethyl ether (3 × 100 ml). The solution was washed with water (2 × 100 ml), saturated aqueous $NaHCO_3$ solution (1 × 100 ml), and brine (1 × 100 ml), and then dried over $MgSO_4$. Removal of the solvent by rotary evaporation afforded the crude alcohol **6**, which was purified by chromatography on silica gel (hexane / diethyl ether = 2 / 1. Typical overall yields for the radical addition, dehalogenation, and purification were 60–85%.

13,13,13-*Trifluoro*-1-*tridecanol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.61$ (t, $J = 6.6$ Hz, 2H), 2.12–1.95 (m, 2H), 1.65 (br s, OH), 1.58–1.47 (m, 4H), 1.36–1.22 (m, 16H).

14,14,15,15,15-*Pentafluoro*-1-*pentadecanol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.62$ (t, $J = 6.6$ Hz, 2H), 2.07–1.88 (m, 2H), 1.60–1.51 (m, 5H), 1.36–1.22 (m, 18H).

11,11,12,12,13,13,14,14,14-*Nonafluoro*-1-*tetradecanol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.62$ (t, $J = 6.6$ Hz, 2 H), 2.14–1.93 (m, 2H), 1.63–1.51 (m, 5H), 1.41–1.21 (m, 12H).

12,12,13,13,14,14,15,15,15-*Nonafluoro*-1-*pentadecanol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.62$ (t, $J = 6.6$ Hz, 2H), 2.15–1.94 (m, 2H), 1.64–1.51 (m, 5H), 1.41–1.20 (m, 14H).

13,13,14,14,15,15,16,16,16-*Nonafluoro*-1-*hexadecanol*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.61$ (t, $J = 6.6$ Hz, 2H), 2.06–1.87 (m, 2H), 1.62–1.51 (m, 5H), 1.35–1.22 (m, 16H).

2.8. *Terminally perfluorinated alkyl thioacetates* **3** *from fluorinated alcohols* **6** *(general procedure)*

To a stirred solution of alcohol **6** (2.83 mmol) in 50 ml of hexane at room temperature were added triethylamine (8.49 mmol) and methanesulfonyl chloride (5.66 mmol). After stirring for 2 h, 50 ml of water was added. The phases were separated, the organic layer was washed with water (1 × 100 ml) and brine (1 × 100 ml), dried with $MgSO_4$, and evaporated to dryness. The crude mesylate was dissolved in 50 ml of absolute ethanol. Under argon, potassium thioacetate (5.66 mmol) was added. The mixture was warmed to 60°C for 2 h under argon. After cooling to room temperature, 150 ml of water was added, and the mixture was extracted with hexane (3 × 100 ml). The combined organic layers were washed with brine (1 × 100 ml) and dried over $MgSO_4$. The solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica gel (hexane / diethyl ether = 9 / 1) affording the terminally perfluorinated thioacetate **3** in ca. 90% yield.

14,14,15,15,15-*Pentafluoropentadecyl thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.85$ (t, $J = 7.2$ Hz, 2H),

2.31 (s, 3H), 2.08–190 (m, 2H), 1.61–1.50 (m, 4H), 1.40–1.22 (m, 18H).

11,11,12,12,13,13,14,14,14-*Nonafluorotetradecyl thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.84$ (t, $J = 7.4$ Hz, 2H), 2.30 (s, 3H), 2.15–1.90 (m, 2H), 1.61–1.48 (m, 4H), 1.40–1.20 (m, 12H).

12,12,13,13,14,14,15,15,15-*Nonafluoropentadecyl thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.83$ (t, $J = 7.4$ Hz, 2H), 2.29 (s, 3H), 2.13–1.93 (m, 2H), 1.64–1.49 (m, 4H), 1.42–1.20 (m, 14H).

13,13,14,14,15,15,16,16,16-*Nonafluorohexadecyl thioacetate*. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.84$ (t, $J = 7.4$ Hz, 2H), 2.30 (s, 3H), 2.10–1.89 (m, 2H), 1.62–1.48 (m, 4H), 1.41–1.22 (m, 16H).

2.9. 13,13,13-Trifluorotridecyl iodide (7)

To a stirred solution of 8.10 g (32.0 mmol) of alcohol **6** in 100 ml of hexane at room temperature were added 13.3 ml (96.0 mmol) of triethylamine and 4.93 ml (64.0 mmol) methanesulfonyl chloride. After stirring for 2 h, 200 ml of water was added. The phases were separated, the organic layer was washed with water (1 × 100 ml) and brine (1 × 100 ml), dried with $MgSO_4$, and evaporated to dryness. The crude mesylate was then dissolved in 500 ml of acetone. Potassium iodide (16.6 g; 100 mmol) was added, and the mixture was refluxed for 12 h. After cooling, 200 ml of water was added, and the mixture was extracted with hexane (2 × 250 ml). The combined organic layers were washed with brine (1 × 250 ml), dried with $MgSO_4$, and evaporated to dryness by rotary evaporation. Kugelrohr distillation of the crude product gave 10.5 g (29.0 mmol; 90% yield) of iodide **7**. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.18$ (t, $J = 7.2$ Hz, 2H), 2.12–1.96 (m, 2H), 1.85–1.76 (quint, $J = 7.2$ Hz, 2H), 1.58–1.48 (m, 2H), 1.39–1.22 (m, 16H).

2.10. 16,16,16-Trifluoro-1-hexadecene (8)

To a solution of 4.13 g (11.0 mmol) of iodide **7** in 150 ml anhydrous THF were added 11.0 ml of a 0.100 M solution (1.10 mmol) of $LiCuCl_4$ in THF. The mixture was cooled to −30°C under argon. A 1 M solution of allylmagnesium bromide in diethyl ether (33 ml; 33.0 mmol) was added slowly over 5 min, during which a color change from orange to dark brown was observed. The reaction mixture was warmed to room temperature and stirred for 14 h. After the addition of 50 ml of a saturated aqueous solution of NH_4Cl and 50 ml of water, the mixture was extracted with diethyl ether (3 × 100 ml). The combined organic layers were washed with brine (1 × 100 ml), dried with $MgSO_4$, and evaporated to dryness by rotary evaporation. Kugelrohr distillation of the crude product gave 2.56 g (9.19 mmol; 81% yield) of alkene **8**. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.87$–5.74 (m, 1H), 5.01–4.90 (m, 2H), 2.12–1.96 (m, 4H), 1.58–1.49 (m, 2H), 1.36–1.22 (m, 20H).

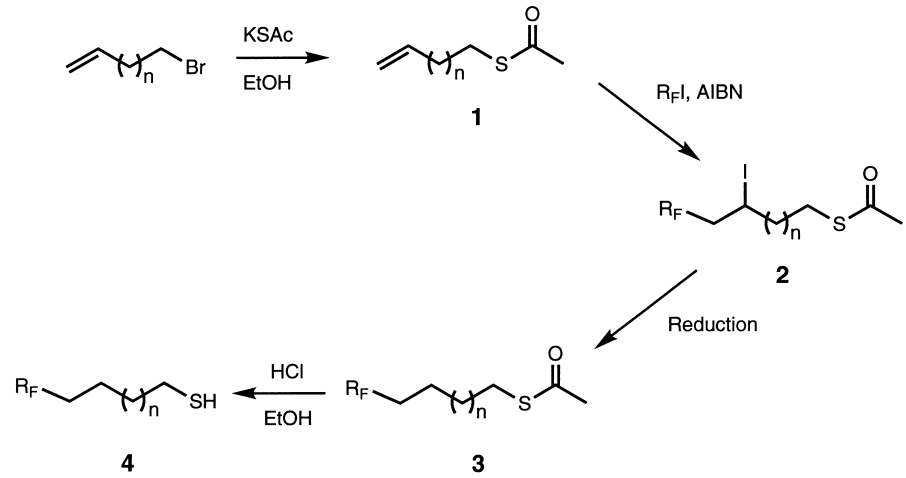
2.11. 16,16,16-Trifluorohexadecyl thioacetate (9)

A mixture of alkene **8** (2.50 g; 8.98 mmol), thioacetic acid (2.67 g; 35.1 mmol) and AIBN (0.06 g; 0.4 mmol) were combined in a small quartz tube under argon. The reaction mixture was irradiated for 1 h with a 450 W mercury high pressure lamp at a distance of 2 in. The resulting solution was poured into 100 ml of diethyl ether. Water (50 ml) was added; solid $NaHCO_3$ was then added in portions until the evolution of CO_2 ceased. The mixture was then extracted with diethyl ether (2 × 100 ml). The organic layers were washed with brine (1 × 100 ml), dried with $MgSO_4$, and evaporated to dryness by rotary evaporation. The crude product was chromatographed on silica gel using hexane as eluent to give 1.50 g (4.23 mmol; 47% yield) of thioacetate **9**. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.84$ (t, $J = 7.2$ Hz, 2H), 2.30 (s, 3H), 2.12–1.95 (m, 2H), 1.59–1.47 (m, 4H), 1.35–1.22 (m, 22H).

3. Results and discussion

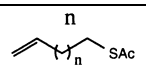
The key step in our synthetic approach involves the radical addition of fluorinated alkyl iodides to terminally unsaturated alkyl thioacetates (Scheme 1). To obtain the trifluoromethyl- and pentafluoroethyl-terminated thiols, we used 2,2,2-trifluoroethyl iodide and 2,2,3,3,3-pentafluoropropyl iodide, respectively, instead of trifluoromethyl iodide and perfluoroethyl iodide, respectively, because the latter two are gases and are thus more difficult to handle. For the synthesis of more highly fluorinated thiols, however, we used the corresponding perfluorinated alkyl iodides because they are liquids at room temperature. As shown in Scheme 1, we prepared the ω-unsaturated alkyl thioacetates **1** in excellent yields from ω-unsaturated bromides by nucleophilic displacement with potassium thioacetate.

Secondary iodides **2** were generated by the reaction of ω-alkenylthioacetates **1** with fluorinated alkyl iodides (R_FI, Table 1) in the presence of the radical initiator 2,2′-azobisisobutyronitrile (AIBN) under oxygen-free conditions. Dehalogenation of the crude iodides **2** with $NaBH_4$ in DMF according to the method of Val'pin et al. [32] yielded the terminally fluorinated alkyl thioacetates **3**. Small amounts of olefinic starting material and variable amounts of fluorinated olefins, which apparently formed as elimination by-products during the dehalogenation reaction, could not be readily separated from the desired products by distillation or chromatography. We therefore treated the product mixture with ozone followed by a reductive workup with $NaBH_4$ to convert the olefins to more polar alcohols, which could be readily separated by chromatography on silica gel. Unfortunately, partial oxidation of the thioacetate group by exposure to excess ozone often led to low yields of the pure thioacetates (Table 1; Method A1). When, however, we performed the dehalogenation reaction using zinc dust in acetic acid, we circumvented the formation of



Scheme 1. Synthesis of terminally perfluorinated alkanethiols via radical addition of R_FI to ω-alkenyl thioacetates (method A).

Table 1
Summary of the syntheses of fluorinated thiol **4**

Entry	Thiol **4**	n 	R_FI	Method	Overall % yield	n_D^{20} of **4**
1	$F(CF_2)_1(CH_2)_9SH$	5	$F(CF_2)_1CH_2I$	A1	18	1.4220
2	$F(CF_2)_1(CH_2)_{10}SH$	6	$F(CF_2)_1CH_2I$	A1	18	1.4246
3	$F(CF_2)_1(CH_2)_{11}SH$	7	$F(CF_2)_1CH_2I$	A1	18	1.4355
4	$F(CF_2)_1(CH_2)_{12}SH$	8	$F(CF_2)_1CH_2I$	A1	18	1.4327
5	$F(CF_2)_1(CH_2)_{13}SH$	9	$F(CF_2)_1CH_2I$	A1	16	1.4340
6	$F(CF_2)_1(CH_2)_{14}SH$	10	$F(CF_2)_1CH_2I$	A2	60	1.4360
7	$F(CF_2)_1(CH_2)_{15}SH$	[a]	$F(CF_2)_1CH_2I$	C	21	1.4373
8	$F(CF_2)_2(CH_2)_{11}SH$	7	$F(CF_2)_2CH_2I$	A1	26	1.4180
9	$F(CF_2)_2(CH_2)_{12}SH$	8	$F(CF_2)_2CH_2I$	A1	21	1.4205
10	$F(CF_2)_2(CH_2)_{13}SH$	$COOCH_3$ (9)	$F(CF_2)_2CH_2I$	B	39	1.4246
11	$F(CF_2)_2(CH_2)_{14}SH$	10	$F(CF_2)_2CH_2I$	A2	51	[b]
12	$F(CF_2)_3(CH_2)_{10}SH$	7	$F(CF_2)_3I$	A1	24	1.4023
13	$F(CF_2)_3(CH_2)_{11}SH$	8	$F(CF_2)_3I$	A1	24	1.4077
14	$F(CF_2)_3(CH_2)_{12}SH$	9	$F(CF_2)_3I$	A2	60	1.4083
15	$F(CF_2)_3(CH_2)_{13}SH$	10	$F(CF_2)_3I$	A2	58	1.4113
16	$F(CF_2)_4(CH_2)_9SH$	6	$F(CF_2)_4I$	A2	63	1.3880
17	$F(CF_2)_4(CH_2)_{10}SH$	OAc (8), OH	$F(CF_2)_4I$	B	59	1.3942
18	$F(CF_2)_4(CH_2)_{11}SH$	$COOCH_3$ (9)	$F(CF_2)_4I$	B	57	1.3972
19	$F(CF_2)_4(CH_2)_{12}SH$		$F(CF_2)_4I$	B	58	1.4011

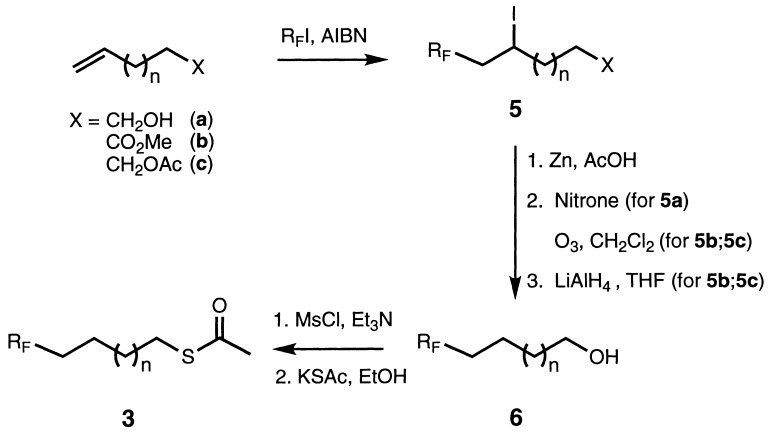
[a] Availability of starting fragments dictated an entirely different strategy (Method C; see text).
[b] At 20 °C, the product thiol is a solid (m.p.: 27°C).

unsaturated by-products. Furthermore, we could readily remove any excess olefinic starting material by reaction with N-methyl-α-phenyl nitrone [33] in refluxing toluene followed by distillation or chromatography (Table 1: Method A2).

Acidic deprotection of the thioacetates **3** afforded the terminally fluorinated alkanethiols **4**. Deprotection under acidic conditions generally gave better yields than deprotection under basic conditions, which typically led to the formation of disulfides as by-products.

We briefly compared our new approach involving the radical coupling of fluorinated alkyl iodides with ω-unsaturated thioacetates (Scheme 1; Table 1: Methods A1 and A2) to that of an analogous 'Brace-based' approach [4,6] involving the radical coupling of fluorinated alkyl iodides to ω-unsaturated acetates, alcohols, and esters (Scheme 2; Table 1; Method B). Using the latter [34], the crude secondary iodides **5** were dehalogenated with zinc dust in acetic acid. Ozonolysis of the crude product was used to destroy any olefinic starting material, and the appropriate reductive workup afforded the terminally fluorinated alcohols **6**. These alcohols were then transformed into the thioacetates **3** via mesylation and subsequent treatment with potassium thioacetate. Acidic deprotection gave the fluorinated thiols **4**.

The synthesis of $F(CF_2)_4(CH_2)_9SH$ (entry 16 in Table 1) utilized our Method A2 to generate the target compound in 63% overall yield. The synthesis of $F(CF_2)_4(CH_2)_{10}SH$,



Scheme 2. Synthesis of terminally perfluorinated alkanethiols via method B.

$F(CF_2)_4(CH_2)_{11}SH$, and $F(CF_2)_4(CH_2)_{12}SH$ (entries 17–19, respectively) utilized 'Brace-based' Method B to generate the targeted compounds in ca. 58% yield. This brief comparison thus suggests that the overall yields obtained using our approach are comparable to those obtained using an approach based on Brace's methods.

Due to the poor availability of a suitable terminally unsaturated 14-carbon starting material, the synthesis of $F(CF_2)_1(CH_2)_{15}SH$ required a strategy different from those outlined above (see Scheme 3, Table 1: Method C). In this example, we utilized Brace's method of radical addition to provide the primary alcohol **6** with $n = 8$. This intermediate was converted to the primary iodide **7** via mesylation and nucleophilic displacement of the mesylate with potassium iodide. Treatment of iodide **7** with allylmagnesium bromide in the presence of lithium tetrachlorocuprate [35] gave olefin **8** in good yield. Photochemical addition of thioacetic acid [36,37] to the terminal double bond yielded thioacetate **9**, which was hydrolyzed under acidic conditions to yield the targeted thiol.

4. Summary

We synthesized 19 new terminally fluorinated alkanethiols having the following chain lengths and specifically fluorinated terminal segments: $F(CF_2)_m(CH_2)_nSH$, where $m = 1$, $n = 9$–15; $m = 2$, $n = 11$–14; $m = 3$, $n = 10$–13; and $m = 4$, $n = 9$–12. Radical addition of $F(CF_2)_1CH_2I$, $F(CF_2)_2CH_2I$, $F(CF_2)_3I$ and $F(CF_2)_4I$ to ω-alkenylthioacetates provided a short and convenient synthetic route to this important class of compounds. Due to the inherently poor solubility of long-chain perfluorocarbons, the present strategy offers a distinct advantage over analogous 'Brace-based' synthetic strategies that necessarily require extensive post-functionalization of the fluorocarbon intermediates. Furthermore, the demonstrated ability of performing radical additions of fluorinated iodides to alkenes in the presence of thioacetate moieties should prove to be a useful tool in other areas of fluorocarbon chemistry.

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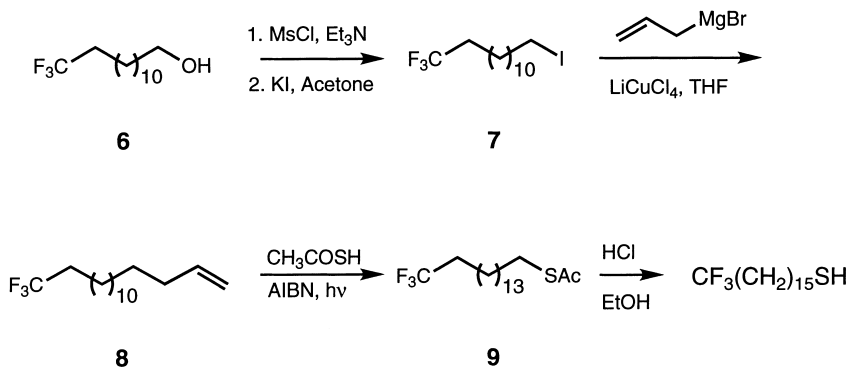

Scheme 3. Synthesis of $F(CF_2)_1(CH_2)_{15}SH$ via method C.

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