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Liquid crystals based on hypervalent sulfur fluorides Part 4. [1] Pentafluorosulfanyl alkanes and olefins

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Abstract

New liquid crystals with a pentafluorosulfanyl function as their polar terminal group were prepared and fully characterized. The synthetic key step was the triethyl borane-catalyzed addition of SF_5Br to a suitable olefin precursor, followed by dehydrobromination. The most interesting characteristic of the new materials is their combination of high polarity ($\Delta\varepsilon$) with very low birefringence (Δn), which is of particular importance for LCDs for mobile applications.

Keywords: Cholestane derivatives; Hypervalent compounds; Liquid crystals; Mesogens; Steroids; Sulfur fluorides

1. Introduction

In the recent few years liquid crystal displays (LCD) have become an integral part of our daily life [2]. The nematic liquid crystalline material in the "heart" of all LCD devices is required to keep functioning for tenths of thousands of hours under sometimes rather extreme environmental conditions without noticable deterioration [3]. In particular for high-resolution active matrix LCDs the liquid crystal has also to show a very low ability to solvate and mobilize ionic impurities by coordinative complexation [4]. These stringent requirements can currently only be met by the so-called super fluorinated materials (SFM), which do not contain any heteroatoms except fluorine and oxygen [5]. The main functions of the fluorine substitution in this type of materials are the modulation of the mesophases and the achievement of a strong dielectric anisotropy ($\Delta\varepsilon$) [2,6].

Many LCD applications require a very high dielectric anisotropy ($\Delta\varepsilon$) of the liquid crystal, which is often difficult to achieve with conventional fluorinated materials deriving their molecular dipole moment (μ) from the dipoles of several polar carbon–fluorine bonds [7]. The current benchmark for the maximum achievable polarity for commercially used liquid crystals is set by the trifluoromethyl group (e.g., **1**). In order to further increase $\Delta\varepsilon$ we started several years ago to investigate the potential of polar groups based on hypervalent sulfur fluorides, such as the pentafluorosulfanyl [1,8] and the *trans*-trifluoromethyltetrafluorosulfuranyl group [1]. The SF_5 group shows a chemical and photochemical stability similar to the CF_3 group [9], but its group dipole moment is significantly higher, rendering it a kind of "super-CF_3" function. The ion affinity of the pentafluorosulfanyl group is weak enough to make it compatible with current active matrix LCD technology [10].

The design of polar liquid crystals becomes a particular challenge, when the combination of high dielectric anisotropy ($\Delta\varepsilon$) with very low birefringence (Δn) is required. The main application for this type of materials are LCDs for mobile devices, such as cellular phones, personal digital assistants (PDA) or video games. Here, the state of the art are materials with a terminal trifluoromethyl group (**2**) or longer perfluoroalkyl groups [2]. In order to extend the range of $\Delta\varepsilon$ for liquid crystals with very low birefringence we selected materials with pentafluorosulfanyl vinyl (**3**), methylene (**4**), ethyl (**5**) and difluoromethyl functions (**6**) as our target compounds (Scheme 1).

With few exceptions [11], so far mostly aromatic SF_5 derivatives have been used as structural motifs in materials

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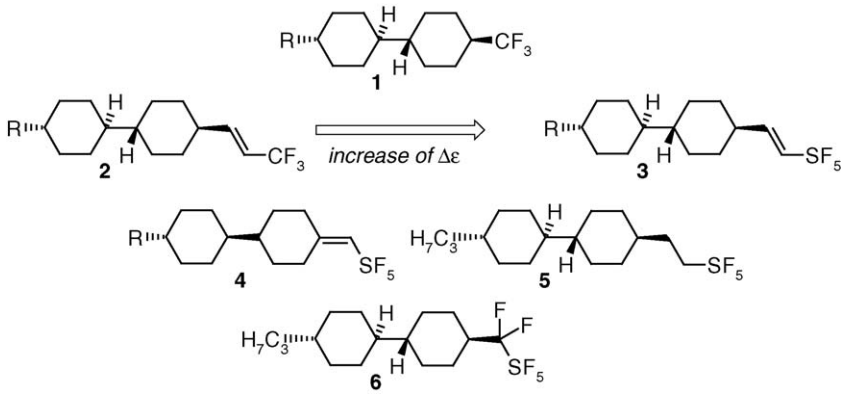
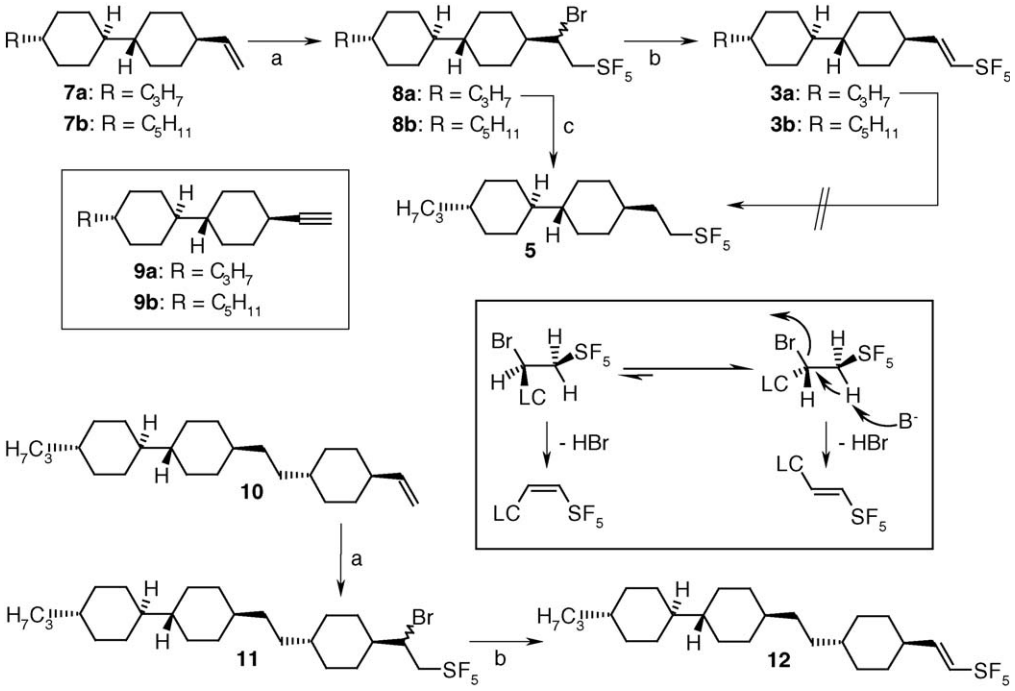


Scheme 1. Liquid crystals **3**–**6** with a terminal pentafluorosulfanyl group are combining high dielectric anisotropy (Δε) with very low birefringence (Δ*n*).

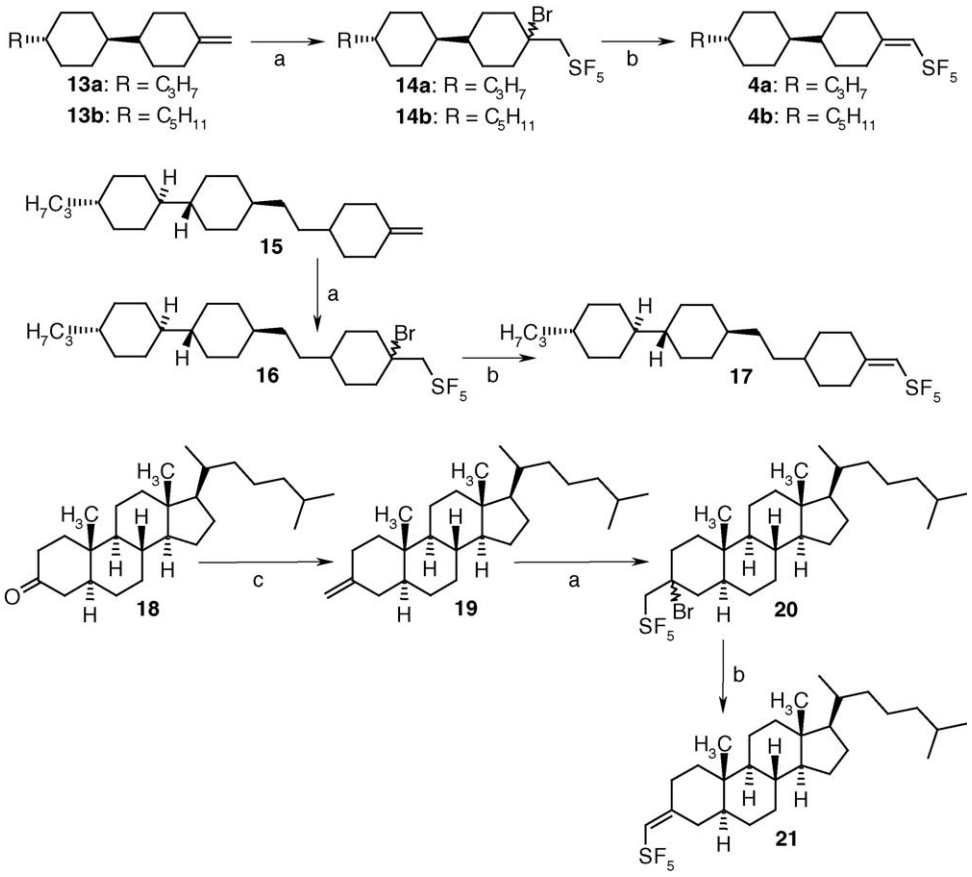
sciences, due to the commercial availability of several pentafluorosulfanyl derivatives. Pentafluorosulfanyl arenes are readily available from aromatic disulfides or sulfenyl chlorides by oxidative fluorination with silver difluoride [9,12] or – on a larger scale – by selective direct fluorination [13]. The most commonly used access to pentafluorosulfanyl alkanes and olefins is much less convenient, requiring the addition of SF_5Cl (bp −21 °C) or SF_5Br (bp 3.1 °C) to carbon–carbon double bonds [14]. Both reagents are highly toxic gases [15], which are not commercially available on a regular basis.

2. Results and discussion

With regard to their addition to carbon–carbon double bonds, the pentafluorosulfanyl halides SF_5Cl and SF_5Br show a similar but slightly higher reactivity than perfluoroalkyl bromides and iodides. The uncatalyzed addition proceeds from around room temperature upwards [14a–d], but the onset of the exothermic reaction is sometimes unpredictable. A smooth reaction of SF_5Br can be induced by catalytic amounts of triethyl borane at −20 °C [14e]. Application of this general procedure to our liquid crystal precursors (**7**, **10**, **13**, **15** and **19**)

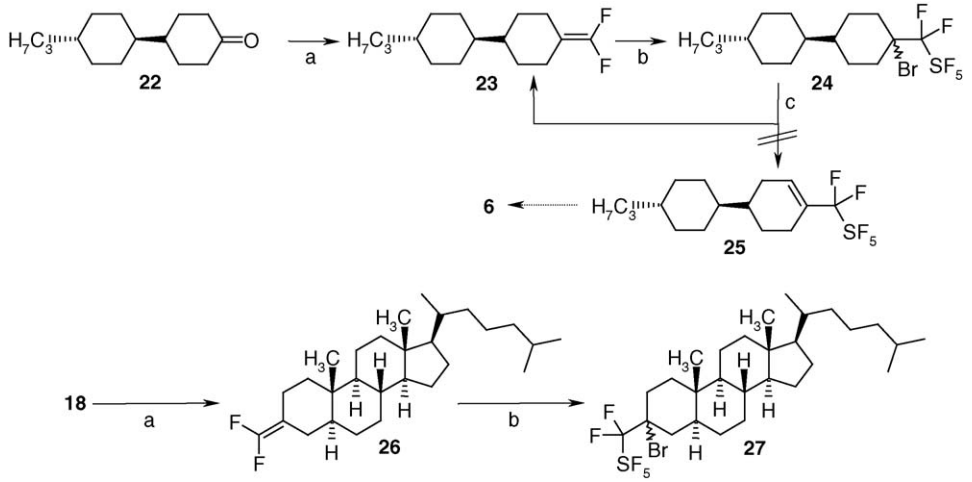


Scheme 2. Syntheses of the liquid crystals **3**, **5** and **12**: (a) SF_5Br, BEt_3 (0.15 equiv.), *n*-heptane; −40 to −20 °C, 2 h (**8a**: 85%, **8b**: 87%, **11**: 83%). (b) KOH powder, *n*-heptane; 35 °C, 18 h (**3a**: 74%, **3b**: 84%, **12**: 97%). (c) (1) *tert*-BuLi, *n*-pentane; −78 °C, 18 h; (2) EtOH; −60 °C to room temperature (16%, GC yield). If the dehydrohalogenation of **8** is carried out at higher temperature (65 °C), significant quantities of the corresponding acetylene derivative **9** (*upper box*) are formed: **3a/9a**: 66%/19%; **3b/9b**: 69%/18%. The *E*-selectivity of the dehydrobromination can be explained by the elimination with the bulky liquid crystal (LC) and the SF_5 groups in the sterically favorable *anti* conformation (*lower box*).



Scheme 3. Syntheses of the liquid crystals **4**, **17** and **21**: (a) SF_5Br, BEt_3 (0.15 equiv.), *n*-heptane; −40 to −20 °C (**14a**: 87%, **14b**: 76%, **16**: 87%, **20**: 77%). (b) KOH powder, *n*-heptane; 65 °C, 18 h (**4a**: 87%, **4b**: 89%, **17**: 96%, **21**: 81%). (c) $Ph_3PCH_3^+Br^-$, KO*t*Bu, THF; 0 °C to room temperature, 3 h (75%).

furnished the corresponding addition products not only in good yields but also with a surprisingly high regioselectivity. In all cases the terminal β-bromo pentafluorosulfanyl alkanes were obtained exclusively (Schemes 2 and 3). The dehydrohalogenation of the primary addition products **8** and **11** with potassium hydroxide powder at 35 °C in *n*-heptane furnished pure *E*-olefins. For the reaction of compounds **14**, **16** and **20** an elevated temperature of 65 °C was necessary. Interestingly, when the dehydrohalogenation of **8** was tried also at 65 °C, the formation of significant quantities of **9** was observed. This unexpected reactivity indicates a pseudohalide-like reactivity of the SF_5 group, allowing a second dehydropentafluorosulfanylation step from the primarily formed product **3**. In the case of the cholestane derivative **20** a 10:1 *Z*/*E*-isomer mixture of the



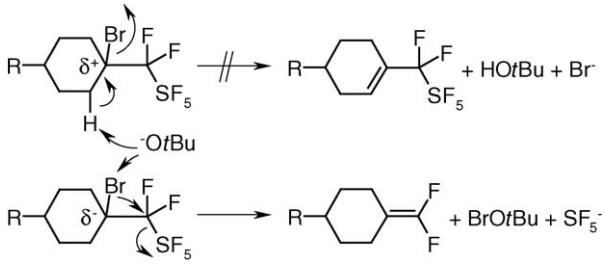
Scheme 4. Syntheses of the liquid crystal precursors **24** and **27**: (a) CF_2Br_2, $P(NMe_2)_3$, dioxane/THF 4:1; 5 °C to room temperature, 18 h (**23**: 89%, **26**: 64%). (b) SF_5Br, BEt_3 (0.15 equiv.), *n*-heptane; −40 to −20 °C (**24**: 79%, **27**: 82%). (c) KO*t*Bu, THF, 35 °C (yield of **23** not determined).

crude dehydrobromination product **21** was obtained. Crystallization from ethanol/*n*-heptane 1:1 yielded pure *Z*-isomer.

Unexpectedly, all attempts to reduce any of the SF_5 olefins to the corresponding alkanes failed completely. Under the conditions of catalytic hydrogenation neither with heterogeneous palladium, rhodium or platinum catalysts, nor with Wilkonson's catalyst any reactivity of **3a** was observed. Increasing the temperature to 100 °C and the hydrogen pressure to 100 bar resulted only in reductive decomposition of the SF_5 group. Also other reductive agents, acting by different mechanisms, such as diimine [16], Hantztsch's 1,4-dihydropyridine [17], sodium borohydride [18] or triethyl silane/trifluoroacetic acid [19] were tried without success. A possible reason for this surprising lack of reactivity of the double bond is the combination of steric bulkiness and the strongly negative (−I) inductive effect of the SF_5 group.

As an alternative access to pentafluorosulfanyl ethyl derivatives such as **5**, the hydrodebromination of **8a** was attempted—also with limited success. Reducing agents such as tri-*n*-butyl tin hydride [20], $NaBH_4$ [21] and magnesium [22] showed no reactivity at all. The use of zinc [23] and $LiAlH_4$ [24] resulted only in the reduction of the SF_5 group. *n*-Butyl lithium [22] acted only as a base but did not cause bromine lithium exchange. Finally, a partial success was achieved using *tert*-butyl lithium [25] in *n*-pentane at −78 °C, followed by addition of ethanol. Here, the formation of 16% of the reduced target compound **5** was achieved, unfortunately accompanied by 20% of starting material **8a** and 48% of **7a** as the dehydropentafluorosulfanylation product of **8a** (Scheme 2).

The addition of SF_5Br to difluoromethylene derivatives [26] **23** and **26** succeeded smoothly as for the other olefins (Scheme 4). Also here, perfect regioselectivity was found. On the other hand, all attempts for the subsequent dehydrobromination of **24** gave either no reaction at all or – using KO*t*Bu as a stronger base – the difluoromethylene starting material **23** as the unexpected reaction



Scheme 5. Proposed mechanism for the base-induced reversion of the SF_5Br addition in **24** → **23** (*bottom*), compared to the dehydrobromination of **14** → **4** (*top*).

product. A possible explanation for this unusual reaction path is the combined inductive effect of the two β-fluorine atoms and the SF_5 substituent which is destabilizing any transient positive charge at the β-carbon during the "normal" dehydrohalogenation (Scheme 5). On the other hand, if the bromine is attacked by a nucleophile, a stabilized transient negative charge is generated during the formal "Br-SF_5" elimination.

Crystallization of the liquid crystal **3a** from ethanol furnished needles suitable for X-ray structure analysis [27] (Fig. 1). Like for the aromatic SF_5 derivatives [8b,28], the C–S–F_{eq} angle is with ca. 91.4° resp. ca. 93.9° larger than the 90° found for the basic system SF_6. Therefore, the equatorial fluorine atoms are – along with the axial fluorine – contributing significantly to the molecular dipole moment (μ) and thus also to the dielectric anisotropy ($\Delta\varepsilon$) of the liquid crystal [7]. The packing of **3a** at −100 °C shows a clear segregation of the fluorophobic hydrocarbon moiety of the mesogenic core structure and the fluorophilic SF_5 groups into a layered arrangement, possibly preforming the smectic phase observed at higher temperatures.

The mesogenic properties [30] of all the newly synthesized liquid crystals (Table 1) are quite typical for bicyclohexyl

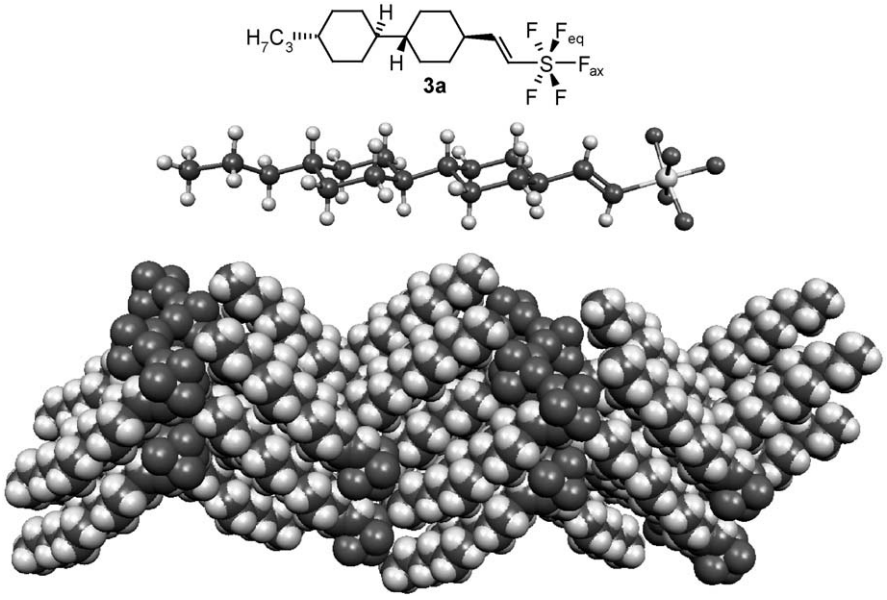
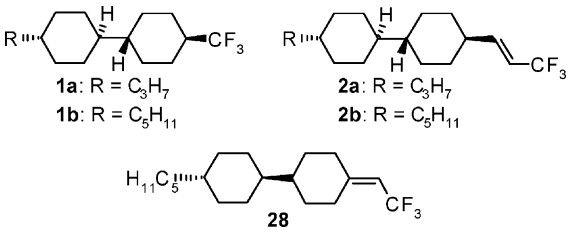


Fig. 1. Crystal structure of the pentafluorosulfanyl vinyl substituted liquid crystal **3a** [27,29]: the molecular unit (*middle*) and packing (*bottom*). Selected bond lengths and angles: C–S 178.2(3) pm; S–F_{eq} 158.3(2), 158.7(2), 158.7(2) and 158.8(2) pm; S–F_{ax} 159.8(2) pm; C–S–F_{eq} 91.31°, 91.53°, 93.83° and 94.10°.

Table 1
The physical properties of the new SF_5 substituted liquid crystals (**3a/b**, **4a/b**, **12**, **17**, **21**) in comparison to some of their CF_3 analogues (**1a/b**, **2a/b**, **28**) [30]



No.	Phase sequence	$T_{NI,virt}$	$\Delta\varepsilon_{virt}$	Δn_{virt}
1a	C 19 S_H? (8) S_B? 41 I	−44.4	6.8	0.0594
1b	C 35 S_G? (33) I	−22.0	5.3	0.0510
2a	C 60 S_B 61 I	5.6	6.2[a]	0.0510[a]
2b	C 59 N (57.2) I	18.8	7.9	0.0710
3a	C 51 S_G? 65 I	8.3	10.5	0.0704
3b	C 58 S_B 89 I	24.5	9.9	0.0707
4a	C 41 I	−93.8	6.3	0.0633
4b	C 37 I	−78.9	5.8	0.0654
12	C 145 S_B 173 N 194.1 I	168.4	10.1	0.0641
17	C 68 S_B 115 I	79.5	4.3	0.0567
21	C 123 I	–	–	–
28	C 21 I	−78.9	3.4	0.0581

The phase transition temperatures and the virtual clearing points ($T_{NI,virt}$) are cited in °C. C: crystalline, S_B: smectic B, S_G: smectic G, N: nematic, I: isotropic. In the cases marked by a question mark the mesophase assignment is not clear. Values in parentheses denote monotropic phase transitions.
[a] Extrapolated from Merck mixture N.

systems, i.e., they show a strong tendency to form smectic phases. Their birefringences (Δn) are rather low, although slightly higher than for **1**, which is due to the insertion of the polarizable vinyl group. Compared to their trifluoromethyl analogues (**2a/b** and **28**), the extrapolated clearing points ($T_{NI,virt}$) of **3a/b** and **4b** are several degrees higher. This effect has already been found for aromatic SF_5 systems [8b], and it is presumably caused by the larger size of the SF_5 group compared to CF_3. Most important, the dielectric anisotropies ($\Delta\varepsilon$) of **3a/b** and **4b** are about two to four units higher than for **2a/b** and **28**. In particular, compound **12** has a very favourable combination of high clearing point ($T_{NI,virt}$), high $\Delta\varepsilon$ and low Δn.

The SF_5 methylene systems **4** and **17** have generally much lower clearing temperatures and dielectric anisotropies than their SF_5 vinyl analogues. This is caused by the geometry of these compounds, which have a kink in their otherwise elongated shape, reducing the clearing point. Since the SF_5 group is oriented in an oblique angle relative to the long molecular axis, the director of the nematic phase and the molecular dipole moment μ are misaligned, which is reducing $\Delta\varepsilon$ in spite of the high absolute value of μ [7].

The cholestane derivative **21** shows no mesophase in the neat state, but it induces a cholesteric phase in a nematic host mixture with a helical twisting power (HTP) of 7.7 μm^{-1} [30].

3. Conclusion

Using the pentafluorosulfanyl group, a new class of liquid crystals became available, combining high dielectric anisotropy ($\Delta\varepsilon$) with low birefringence (Δn). The pentafluorosulfanyl group is so far the most polar terminal group for liquid crystals which is still compatible with current active matrix LCD technology. The compounds show a remarkable chemical stability, just like their trifluoromethyl analogues. The synthetic key step – the addition of SF_5Br to a carbon–carbon double bond – was extended to 1,1-difluoroolefins, giving access to a variety of potentially useful intermediates. The primary pentafluorosulfanyl β-bromo alkanes as well as the corresponding olefins were found to be surprisingly resistant towards all kinds of reducing agents.

4. Experimental

4.1. General remarks

Caution: When handling SF_5Br, adequate safety precautions have to be taken. The reactive and highly toxic gas (bp 3.1 °C) [15] should be handled only under a well-ventilated hood. Even under normal ambient illumination photochemical dissociation into bromine and extremely toxic S_2F_{10} occurs, which is easily visible by the emerging brown color. After completion of the addition reaction the apparatus should be purged with nitrogen, and the exhaust gas washed and hydrolyzed with KOH solution. The SF_5Br was purchased from Air Products & Chemicals. The precursor **19** was synthesized according to Ref. [31], **26** in analogy to Ref. [26].

4.2. Addition of SF_5Br to olefins and difluoroolefins

4.2.1. Representative procedure for 4-[1-bromo-2-(pentafluoro-λ^6-sulfanyl)ethyl]-4′-propyl-1,1′-bicyclohexyl (8a)

A solution of **7a** (7.03 g, 30.0 mmol) in *n*-heptane (120 mL) was treated at a temperature between −40 and −30 °C with

BEt_3 (1 M in *n*-hexane; 4.5 mL, 4.5 mmol). Then SF_5Br (10.6 g, 51.2 mmol) was condensed into the reaction vessel. The end of the reaction was indicated by a yellow or orange coloration of the reaction mixture. The completion was verified by the addition of a small quantity of BEt_3 (1 M in *n*-hexane; 0.4–0.5 mL): if no discoloration occurred, the addition was considered complete. The mixture was stirred for additional 2 h between −30 and −20 °C, then allowed to warm up to room temperature. The mixture was poured into ice-cold saturated aqueous $NaHCO_3$ solution, and the organic phase was separated and extracted with aqueous $NaHCO_3$ until the color disappeared. The aqueous phase was extracted three times with *n*-heptane. The combined organic extracts were dried over Na_2SO_4 and evaporated to dryness. The crude product was purified by chromatography (silica gel; *n*-heptane) and subsequent crystallization from ethanol: yield 85% (98.1% purity by HPLC), colorless solid, mp 47–48 °C (EtOH); IR (KBr): 2934 (s), 2850 (s), 1453 (m), 1432 (w), 1210 (vw), 1011 (vw), 978 (w), 956 (w), 937 (w), 909 (m), 875 (vs), 856 (vs), 814 (vs), 790 (m), 784 (m), 708 (vw), 638 (vw), 606 (vw), 587 (m), 571 (w), 566 (w), 559 cm^{-1} (w); ^1H NMR (500 MHz, $CDCl_3$, 303 K): $\delta = 4.40$ (td, $J = 6.3$ Hz, $J = 3.0$ Hz, 1H), 4.12 (m, 2H), 1.90–1.53 (m, 9H), 1.50–0.55 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): $\delta = 75.9$ (quint, $J = 13.0$ Hz), 53.2, 43.3, 43.2, 42.9, 39.8, 37.6, 33.5, 31.4, 30.1, 29.3, 29.1, 27.6, 20.0, 14.4; ^{19}F NMR (235 MHz, $CDCl_3$, 300 K): $\delta = 84.7$ (m, 1F, SF_{ax}; overlapped by quintet with $J = 146.1$ Hz), 67.0 (m, 4F, SF_{eq}; overlapped by doublet with $J = 146.1$ Hz); MS (EI, 70 eV, 180 °C): *m/z* (%) = 440 (5) [M^+], 207 (5), 127 (11), 125 (78), 108 (5), 89 (6), 96 (100), 43 (51); HRMS for [M^+]($C_{17}H_{30}BrF_5S$): calcd. 440.1172, found 440.1174.

4.2.2. 4-[1-Bromo-2-(pentafluoro-λ⁶-sulfanyl)ethyl]-4′-pentyl-1,1′-bicyclohexyl (**8b**)

Yield 87% (98.9% purity by HPLC), colorless solid, mp 38–39 °C (EtOH); IR (KBr): 2925 (s), 2848 (s), 1468 (w), 1450 (w), 1416 (w), 1217 (vw), 1172 (vw), 1053 (vw), 917 (m), 878 (vs), 863 (s), 847 (s), 813 (vs), 790 (w), 712 (w), 629 (w), 600 (m), 573 (vw), 558 cm^{-1} (w); ^1H NMR (500 MHz, $CDCl_3$, 303 K): $\delta = 4.41$ (td, $J = 6.3$ Hz, $J = 3.0$ Hz, 1H), 4.12 (m, 2H), 1.85–1.65 (m, 8H), 1.59 (mc, 1H), 1.38–1.18 (m, 8H), 1.17–0.80 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): $\delta = 75.9$ (quint, $J = 13.0$ Hz), 53.2, 43.3, 43.2, 42.9, 37.9, 37.4, 33.6, 32.2, 31.4, 30.1, 29.4, 29.2, 27.6, 26.6, 22.7, 14.1; ^{19}F NMR (235 MHz, $CDCl_3$, 300 K): $\delta = 81.1$ (m, 1F, SF_{ax}; overlapped by quintet with $J = 146.2$ Hz), 63.4 (m, 4F, SF_{eq}; overlapped by doublet with $J = 146.1$ Hz); MS (EI, 70 eV, 160 °C): *m/z* (%) = 468 (8) [M^+], 235 (10), 153 (65), 127 (8), 69 (100), 43 (21); HRMS for [M^+]($C_{19}H_{34}BrF_5S$): calcd. 468.1485, found 468.1490.

4.2.3. 4-{2-[4-[1-Bromo-2-(pentafluoro-λ⁶-sulfanyl)ethyl]cyclohexyl]ethyl}-4′-propyl-1,1′-bicyclohexyl (**11**)

Yield 83% (98.4% purity by HPLC), colorless solid, mp 135 °C (*i*-PrOH/*n*-heptane 1:1); IR (KBr): 2917 (s), 2848 (s), 1447 (m), 1380 (vw), 1311 (vw), 1203 (vw), 1171 (vw), 888 (vs), 864 (s), 841 (s), 819 (vs), 725 (vw), 659 (vw), 618 (w), 594 (w), 581 (m), 571 (w), 563 cm^{-1} (w); ^1H NMR (500 MHz, $CDCl_3$, 303 K): $\delta = 4.41$ (td, $J = 6.0$ Hz, $J = 2.9$ Hz, 1H), 4.12 (m, 2H), 1.87–1.78 (m, 2H), 1.75–1.65 (m, 10H), 1.60 (mc, 1H), 1.40–1.23 (m, 4H), 1.22–0.80 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): $\delta = 76.3$ (quint, $J = 13.0$ Hz), 53.4, 43.9, 43.7, 40.2, 38.6, 38.1, 38.0, 35.1, 34.7, 34.1, 32.9, 32.7, 31.8, 30.1, 27.7, 20.4, 14.8; ^{19}F NMR (235 MHz, $CDCl_3$, 300 K): $\delta = 84.1$ (m, 1F, SF_{ax}; overlapped by quintet with $J = 146.4$ Hz), 66.4 (m, 4F, SF_{eq}; overlapped by doublet with $J = 146.4$ Hz); MS (EI, 70 eV, 220 °C): *m/z* (%) = 550 (16) [M^+], 424 (8), 345 (5), 207 (6), 125 (70), 108 (6), 96 (79), 69 (100), 43 (10), 29 (7); HRMS for [M^+]($C_{25}H_{44}BrF_5S$): calcd. 550.22673, found 550.22670.

4.2.4. 4-Bromo-4-[(pentafluoro-λ⁶-sulfanyl)methyl]-4′-propyl-1,1′-bicyclohexyl (**14a**)

Yield 61% (97.2% purity by HPLC), colorless solid, mp 30–31 °C (*i*-PrOH/EtOH 1:1); IR (KBr): 2949 (s), 2922 (s), 2851 (m), 1465 (w), 1441 (m), 1146 (w), 1066 (w), 1053 (w), 978 (w), 955 (w), 941 (w), 930 (m), 853 (vs), 821 (vs), 779 (w), 690 (w), 636 (s), 596 (m), 566 (w), 500 cm^{-1} (w); ^1H NMR (500 MHz, $CDCl_3$, 303 K): $\delta = 4.21$ (quint, $J = 8.8$ Hz, 2H), 2.40–2.09 (m, 2H), 1.87–1.51 (m, 10H), 1.35–0.84 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): $\delta = 83.3$ (quint, $J = 11.0$ Hz), 69.4, 42.9, 41.8, 39.7, 39.0, 37.6, 33.4, 30.0, 26.4, 20.0, 14.4; ^{19}F NMR (235 MHz, $CDCl_3$, 300 K): $\delta = 84.4$ (m, 1F, SF_{ax}; overlapped by quintet with $J = 144.9$ Hz), 70.1 (m, 4F, SF_{eq}; overlapped by doublet with $J = 145.9$ Hz); MS (EI, 70 eV, 200 °C): *m/z* (%) = 347 (27) [M^+–Br], 219 (23), 125 (38), 111 (30), 95 (41), 83 (52), 79 (38), 69 (77), 43 (88), 41 (100); HRMS for [M^+–Br]($C_{16}H_{28}F_5S$): calcd. 347.1832, found 347.1837.

4.2.5. 4-Bromo-4-[(pentafluoro-λ⁶-sulfanyl)methyl]-4′-pentyl-1,1′-bicyclohexyl (**14b**)

Yield 76% (82.9% purity by HPLC), colorless solid, mp 35 °C (*i*-PrOH/EtOH 1:1); IR (KBr): 2956 (m), 2923 (s), 2851 (m), 1653 (vw), 1443 (w), 1060 (w), 929 (w), 871 (s), 845 (vs), 838 (vs), 823 (s), 725 (vw), 691 (vw), 637 (w), 596 (w), 563 (vw), 504 cm^{-1} (vw); ^1H NMR (500 MHz, $CDCl_3$, 303 K): $\delta = 4.21$ (quint, $J = 8.9$ Hz, 2H), 2.20–2.12 (m, 2H), 1.87–1.55 (m, 9H), 1.49–0.80 (m, 19H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): $\delta = 83.3$ (quint, $J = 10.9$ Hz), 69.4, 42.8, 41.8, 39.0, 37.8, 37.4, 33.4, 32.2, 30.0, 26.6, 26.4, 22.7, 14.1; ^{19}F NMR (235 MHz, $CDCl_3$, 300 K): $\delta = 81.9$ (m, 1F, SF_{ax}; overlapped by quintet with $J = 145.8$ Hz), 67.6 (m, 4F, SF_{eq}; overlapped by doublet with $J = 145.8$ Hz); MS (EI, 70 eV, 180 °C): *m/z* (%) = 375 (35) [M^+–Br], 247 (14), 153 (17), 111 (30), 97 (96), 82 (100), 69 (50), 55 (58), 43 (33); HRMS for [M^+–Br]($C_{18}H_{32}F_5S$): calcd. 375.2145, found 375.2151.

4.2.6. 4-{2-[4-Bromo-4-[(pentafluoro-λ⁶-sulfanyl)methyl]cyclohexyl]ethyl}-4′-propyl-1,1′-bicyclohexyl (**16**)

Yield 87% (97.2% purity by HPLC), colorless solid, mp 125 °C (*i*-PrOH/*n*-heptane 1:1); IR (KBr): 2952 (m), 2913 (s),

2847 (m), 1653 (vw), 1457 (w), 1444 (m), 957 (w), 944 (w), 915 (m), 866 (vs), 855 (m), 824 (m-s), 807 (s), 690 (vw), 636 (m), 598 (w), 564 cm^{-1} (w); ^1H NMR: $\delta = 4.22$ (quint, $J = 8.7$ Hz, 2H), 2.23–2.01 (m, 3H), 1.89–1.65 (m, 11H), 1.54–1.46 (m, 2H), 1.37–0.80 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): $\delta = 83.7$ (quint, $J = 10.7$ Hz), 69.7, 43.9, 40.2, 39.2, 38.6, 38.1, 36.9, 35.0, 34.3, 34.1, 30.5, 29.8, 20.4, 14.8; ^{19}F NMR: $\delta = 85.7$ (m, 1F, SF_{ax}; overlapped by quintet with $J = 145.9$ Hz), 71.4 (m, 4F, SF_{eq}; overlapped by doublet with $J = 145.9$ Hz); MS (EI, 70 eV, 180 °C): *m/z* (%) = 538 (2) [M^+], 457 (29), 330 (25), 220 (12), 203 (24), 125 (56), 111 (25), 108 (8), 95 (62), 89 (10), 83 (71), 69 (100), 55 (69), 43 (12); HRMS for [M^+]($C_{24}H_{42}BrF_5S$): calcd. 536.2111, found 536.2100.

4.2.7. 3-Bromo-3-[(pentafluoro-λ⁶-sulfanyl)methyl]-5α-cholestane (**20**)

Yield 77% (98.8% purity by HPLC), colorless solid, mp 102 °C (*i*-PrOH/*n*-heptane 1:1); $[\alpha]_D^{20} = +27.2°$ (*i*-PrOH, 0.0106 g mL^{-1}); IR (KBr): 2960 (s), 2931 (s), 2870 (s), 1468 (m), 1444 (m), 1426 (w), 1386 (m), 1369 (m), 1334 (vw), 1307 (vw), 1293 (vw), 1244 (w), 1161 (m), 1117 (w), 1033 (w), 979 (m), 963 (m), 931 (m), 902 (m), 874 (vs), 849 (vs), 819 (vs), 788 (m), 732 (w), 699 (w), 641 (s), 624 (w), 600 (m), 572 (w), 565 cm^{-1} (w); ^1H NMR (500 MHz, $CDCl_3$, 303 K): $\delta = 4.25$ (quint, $J = 8.6$ Hz, 2H), 2.09–1.95 (m, 3H), 1.86–1.67 (m, 6H), 1.60–1.48 (m, 4H), 1.40–1.23 (m, 8H), 1.17–0.95 (m, 10H), 0.90 (d, $J = 6.5$ Hz, 3H), 0.89 (d, $J = 6.5$ Hz, 3H), 0.87 (d, $J = 6.5$ Hz, 3H), 0.76 (s, 3H), 0.66 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): $\delta = 82.9$ (quint, $J = 10.3$ Hz), 71.0, 56.4, 56.3, 53.6, 42.7, 42.6, 41.2, 39.9, 39.5, 36.2, 35.8, 35.7, 35.4, 35.2, 35.0, 31.7, 28.3, 28.0, 27.8, 24.2, 23.9, 22.8, 22.6, 21.0, 18.7, 12.4, 12.1; ^{19}F NMR (235 MHz, $CDCl_3$, 300 K): $\delta = 85.5$ (m, 1F, SF_{ax}; overlapped by quintet with $J = 145.8$ Hz), 70.9 (m, 4F, SF_{eq}; overlapped by doublet with $J = 145.8$ Hz); MS (EI, 70 eV, 200 °C): *m/z* (%) = 590 (76) [M^+], 575 (18), 435 (100), 421 (20), 385 (9), 384 (32), 369 (25), 357 (13), 229 (51), 121 (47), 106 (50), 95 (87), 89 (8), 81 (71), 71 (29), 57 (62), 43 (97); HRMS for [M^+]($C_{28}H_{48}BrF_5S$): calcd. 590.2580, found 590.2577.

4.2.8. 4-Bromo-4-[difluoro(pentafluoro-λ⁶-sulfanyl)methyl]-4′-propyl-1,1′-bicyclohexyl (**24**)

Yield 79% (93.3% purity by HPLC), colorless solid, mp 21–22 °C; IR (KBr): 2956 (m), 2926 (s), 2852 (s), 1449 (m), 1379 (vw), 1258 (vw), 1202 (m), 1153 (m), 1130 (w), 1108 (w), 1086 (vw), 1054 (vw), 977 (vw), 877–860 (vs), 802 (s), 775 (m), 760 (s), 724 (vw), 670 (w), 596 (s), 574 cm^{-1} (w); ^1H NMR (500 MHz, $CDCl_3$, 303 K): $\delta = 2.29–2.20$ (m, 2H), 1.97–1.52 (m, 10H), 1.38–0.80 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): $\delta = 131.1$, 97.3, 42.8, 41.8, 39.8, 37.6, 33.4, 31.0, 30.0, 25.2, 20.1, 14.4; ^{19}F NMR (235 MHz, $CDCl_3$, 300 K): $\delta = 71.3$ (quint, $J = 145.9$ Hz, 1F, SF_{ax}), 47.0 (dt, $J = 145.9$ Hz, $J = 17.6$ Hz, 4F, SF_{eq}), −83.0 (br. s, 2F, CF_2); MS (EI, 70 eV, 180 °C): *m/z* (%) = 462 (1) [M^+], 383 (6), 125 (92), 111 (20), 83 (65), 69 (100), 55 (36), 43 (15); HRMS for [M^+]($C_{16}H_{26}BrF_7S$): calcd. 462.0827, found 462.0832.

4.2.9. 3-Bromo-3-[difluoro(pentafluoro-λ⁶-sulfanyl)methyl]-5α-cholestane (**27**)

Yield 82% (99.0% purity by HPLC), colorless solid, mp 150 °C (*i*-PrOH/*n*-heptane 1:1); $[\alpha]_D^{20} = +24.5°$ (*n*-heptane, 0.0106 g mL^{-1}); IR (KBr): 2959 (s), 2936 (s), 2870 (m), 1468 (m), 1444 (w), 1387 (w), 1372 (w), 1198 (w), 1156 (m), 1133 (w), 975 (w), 956 (w), 929 (w), 877 (vs), 866 (vs), 836 (m), 795 (w), 766 (s), 730 (w), 670 (w), 595 (m), 571 cm^{-1} (w); ^1H NMR (500 MHz, $CDCl_3$, 303 K): $\delta = 2.10–2.05$ (m, 2H), 1.90 (mc, 1H), 1.87–1.67 (m, 6H), 1.60–1.47 (m, 4H), 1.40–1.21 (m, 8H), 1.17–0.95 (m, 10H), 0.91 (d, $J = 6.5$ Hz, 3H), 0.87 (d, $J = 6.5$ Hz, 3H), 0.86 (d, $J = 6.6$ Hz, 3H), 0.79 (s, 3H), 0.66 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): $\delta = 130.8$, 56.4, 56.3, 53.6, 42.6, 41.2, 39.9, 39.5, 36.2, 35.8, 35.5, 35.4, 33.8, 31.7, 28.2, 28.0, 27.8, 24.2, 23.9, 22.8, 22.6, 21.0, 18.7, 12.4, 12.1; ^{19}F NMR (235 MHz, $CDCl_3$, 300 K): $\delta = 70.6$ (quint, $J = 145.7$ Hz, 1H, SF_{ax}), 46.4 (dt, $J = 145.7$, $J = 17.5$ Hz, 4F, SF_{eq}), −83.0 (br. s, 2F, CF_2); MS (EI, 70 eV, 220 °C): *m/z* (%) = 626 (49) [M^+], 611 (12), 471 (100), 457 (24), 420 (56), 405 (27), 265 (88), 169 (19), 156 (22), 123 (47), 109 (46), 81 (58), 69 (41), 55 (55), 43 (40); HRMS for [M^+]($C_{28}H_{46}BrF_7S$): calcd. 626.2392, found 626.2393.

4.3. Dehydrobromination of β-bromo pentafluorosulfanyl alkanes

4.3.1. Representative procedure for 4-[E-2-(pentafluoro-λ⁶-sulfanyl)vinyl]-4′-propyl-1,1′-bicyclohexyl (**3a**)

A solution of **8a** (3.38 g, 7.66 mmol) in *n*-heptane (100 mL) was treated with KOH powder (4.49 g, 80.0 mmol) and stirred at 35 °C for 18 h. The KOH powder is filtered off, the solvent evaporated to dryness and the crude product purified by chromatography (silica gel; *n*-heptane) and subsequent crystallization from ethanol: yield 74% (99.4% purity by HPLC), colorless solid, mp 51 °C (EtOH), smectic G 65 °C, isotropic; IR (KBr): 2952 (m), 2927 (s), 2851 (s), 1650 (w), 1443 (m), 1186 (w), 976 (m), 960 (m), 915 (s), 891 (vs), 867 (vs), 849–838 (vs), 797 (m), 739 (w), 717 (m), 649 (m), 629 (m), 596 (m), 572 (m), 561 cm^{-1} (w); ^1H NMR (500 MHz, $CDCl_3$, 303 K): $\delta = 6.47–6.28$ (m, 2H), 2.03 (mc, 1H), 1.84–1.67 (m, 8H), 1.34–0.84 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): $\delta = 143.9$, 139.1, 43.3, 42.6, 39.8, 39.6, 37.6, 33.5, 31.9, 30.0, 29.3, 20.0, 14.4; ^{19}F NMR (235 MHz, $CDCl_3$, 300 K): $\delta = 84.4$ (m, 1F, SF_{ax}; overlapped by quintet with $J = 149.9$ Hz), 62.8 (m, 4F, SF_{eq}; overlapped by doublet with $J = 149.9$ Hz); MS (EI, 70 eV, 140 °C): *m/z* (%) = 360 (29) [M^+], 317 (8), 276 (6), 262 (5), 123 (29), 109 (22), 95 (14), 83 (67), 69 (100), 55 (51), 41 (53); HRMS for [M^+]($C_{17}H_{29}F_5S$): calcd. 360.1910, found 360.1900.

For **3a**, **3b** and **12** the dehydrobromination was conducted at 35 °C, for **4**, **17** and **21** at 65 °C.

4.3.2. 4-[E-2-(Pentafluoro-λ⁶-sulfanyl)vinyl]-4′-pentyl-1,1′-bicyclohexyl (**3b**)

Yield 84% (99.8% purity by HPLC), colorless solid, mp 58 °C (EtOH), smectic B 89 °C, isotropic; IR (KBr): 2920 (s), 2849 (s), 1655 (w), 1468 (m), 1443 (m), 1221 (vw), 977 (m),

915 (s), 833 (vs), 824 (vs), 774 (w), 745 (m), 722 (w), 664 (vw), 651 (vw), 633 (m), 600 (m), 579 (m), 572 cm^{-1} (w); ^1H NMR (500 MHz, $CDCl_3$, 303 K): δ = 6.46–6.29 (m, 2H), 2.02 (mc, 1H), 1.83–1.65 (m, 8H), 1.32–0.82 (m, 22H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ = 143.9, 139.1, 43.3, 42.6, 39.6, 37.9, 37.4, 33.6, 32.2, 31.9, 30.0, 29.3, 26.6, 22.7, 14.1; ^{19}F NMR (235 MHz, $CDCl_3$, 300 K): δ = 85.8 (m, 1F, SF_{ax}; overlapped by quintet with J = 149.9 Hz), 64.1 (m, 4F, SF_{eq}; overlapped by doublet with J = 149.9 Hz); MS (EI, 70 eV, 220 °C): m/z (%) = 388 (22) [M^+], 317 (8), 276 (7), 262 (6), 151 (22), 109 (23), 97 (83), 83 (100), 69 (58), 55 (78), 41 (59); HRMS for [M^+]($C_{19}H_{33}F_5S$): calcd. 388.2223, found 388.2210.

4.3.3. 4-{2-[4-[E-2-(Pentafluoro-λ⁶-sulfanyl)vinyl]cyclohexyl]ethyl}-4′-propyl-1,1′-bicyclohexyl (**12**)

Yield 97% (99.8% purity by HPLC), colorless solid, mp 145 °C (*i*-PrOH/*n*-heptane 1:1), smectic B 173 °C, nematic 194 °C, isotropic; IR (KBr): 2919 (s), 2849 (s), 1653 (w), 1448 (m), 1381 (w), 968 (m), 912 (s), 832 (vs), 795 (w), 746 (w), 722 (w), 664 (vw), 650 (w), 609 (w), 600 (m), 570 cm^{-1} (w); ^1H NMR (500 MHz, $CDCl_3$, 303 K): δ = 6.45–6.30 (m, 2H), 2.04 (mc, 1H), 1.82–1.68 (m, 12H), 1.32–1.26 (m, 2H), 1.40–0.80 (m, 26H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ = 143.9, 139.0, 43.5, 39.9, 39.6, 38.2, 37.7, 37.3, 34.7, 34.5, 33.7, 33.7, 32.5, 31.6, 30.1, 20.1, 14.4; ^{19}F NMR (235 MHz, $CDCl_3$, 300 K): δ = 83.3 (m, 1F, SF_{ax}; overlapped by quintet with J = 149.9 Hz), 61.6 (m, 4F, SF_{eq}; overlapped by doublet with J = 149.9 Hz); MS (EI, 70 eV, 220 °C): m/z (%) = 470 (30) [M^+], 345 (6), 220 (38), 205 (8), 191 (5), 125 (39), 109 (21), 96 (60), 83 (75), 69 (100), 55 (58), 40 (77); HRMS for [M^+]($C_{25}H_{43}F_5S$): calcd. 470.3006, found 470.3012.

4.3.4. 4-[(Pentafluoro-λ⁶-sulfanyl)methylene]-4′-propyl-1,1′-bicyclohexyl (**4a**)

Yield 87% (99.8% purity by HPLC), colorless solid, mp 41 °C (*i*-PrOH/*n*-heptane 1:1); IR (KBr): 2955 (s), 2925 (s), 2850 (s), 1655 (m), 1465 (m), 1444 (s), 1430 (w), 975 (m), 929 (m), 900 (s), 841 (vs), 827 (vs), 790 (s), 782 (s), 726 (s), 648 (s), 597 (m), 572 (m), 566 cm^{-1} (m); ^1H NMR (500 MHz, $CDCl_3$, 303 K): δ = 6.13 (quint, J = 8.9 Hz, 1H), 3.08 (mc, 1H), 2.25–2.09 (m, 2H), 1.99–1.85 (m, 3H), 1.77–1.69 (m, 4H), 1.35–0.79 (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ = 149.7, 132.5 (quint, J = 17.3 Hz), 43.0, 42.9, 40.1, 37.9, 36.2, 33.8, 31.8, 30.8, 30.5, 20.4, 14.7; ^{19}F NMR (235 MHz, $CDCl_3$, 300 K): δ = 86.4 (m, 1F, SF_{ax}; overlapped by quintet with J = 149.5 Hz), 66.0 (dd, J = 149.5 Hz, J = 8.9 Hz, 4F, SF_{eq}); MS (EI, 70 eV, 180 °C): m/z (%) = 346 (40) [M^+], 303 (6), 219 (7), 123 (33), 103 (14), 95 (18), 83 (63), 79 (13), 69 (100), 55 (43), 41 (41); HRMS for [M^+]($C_{16}H_{27}F_5S$): calcd. 346.1754, found 346.1756.

4.3.5. 4-[(Pentafluoro-λ⁶-sulfanyl)methylene]-4′-pentyl-1,1′-bicyclohexyl (**4b**)

Yield 89% (99.8% purity by HPLC), colorless solid, mp 37 °C (*i*-PrOH/*n*-heptane 1:1); IR (KBr): 2957 (s), 2919 (s), 2850 (s), 1657 (m), 1468 (m), 1445 (s), 1382 (w), 1351 (w), 1167 (w), 1154 (w), 1138 (w), 929 (s), 904 (vs), 870 (vs), 847–826 (vs), 782 (s), 726 (s), 678 (w), 647 (s), 598 (s), 573 (m), 566 cm^{-1} (m); ^1H NMR (500 MHz, $CDCl_3$, 303 K): δ = 6.13 (quint, J = 9.0 Hz, 1H), 3.08 (mc, 1H), 2.23–2.10 (m, 2H), 1.97–1.87 (m, 3H), 1.77–1.69 (m, 4H), 1.32–0.80 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ = 149.7, 132.5 (quint, J = 17.2 Hz), 43.0, 42.9, 38.2, 37.8, 36.2, 33.9, 32.6, 31.8, 30.8, 30.5, 27.0, 23.1, 14.4; ^{19}F NMR (235 MHz, $CDCl_3$, 300 K): δ = 84.5 (m, 1F, SF_{ax}; overlapped by quintet with J = 149.5 Hz), 64.1 (dd, J = 149.5 Hz, J = 9.0 Hz, 4F, SF_{eq}); MS (EI, 70 eV, 180 °C): m/z (%) = 374 (81) [M^+], 318 (5), 303 (12), 289 (7), 262 (8), 248 (5), 247 (11), 191 (7), 151 (32), 137 (12), 111 (19), 97 (79), 83 (100), 71 (17), 69 (55), 55 (66), 49 (19), 43 (28); HRMS for [M^+]($C_{18}H_{31}F_5S$): calcd. 374.2067, found 374.2070.

4.3.6. 4-{2-[4-[(Pentafluoro-λ⁶-sulfanyl)methylene]cyclohexyl]ethyl}-4′-propyl-1,1′-bicyclohexyl (**17**)

Yield 96% (99.4% purity by HPLC), colorless solid, mp 68 °C (*i*-PrOH/*n*-heptane 1:1), smectic B 115 °C, isotropic; IR (KBr): 3017 (w), 2952 (s), 2923 (s), 2848 (s), 1658 (w), 1443 (m), 1435 (m), 1376 (w), 1222 (vw), 1158 (w), 1138 (vw), 960 (w), 937 (w), 926 (m), 884 (vs), 852 (s), 822 (vs), 787 (s), 722 (s), 675 (w), 644 (s), 597 (s), 573 (m), 568 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, 303 K): δ = 6.14 (quint, J = 8.9 Hz, 1H), 3.03 (mc, 1H), 2.22–2.10 (m, 2H), 1.96–1.89 (m, 3H), 1.75–1.68 (m, 8H), 1.42 (mc, 1H), 1.32–0.80 (m, 25H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ = 149.3, 132.2, 43.5, 39.9, 38.2, 37.7, 37.2, 35.5, 34.8, 34.3, 33.7, 33.4, 33.2, 30.1, 30.1, 29.9, 20.1, 14.4; ^{19}F NMR (235 MHz, $CDCl_3$, 300 K): δ = 84.4 (m, 1F, SF_{ax}; overlapped by quintet with J = 149.6 Hz), 64.0 (dd, J = 149.6 Hz, J = 8.9 Hz, 4F, SF_{eq}); MS (EI, 70 eV, 240 °C): m/z (%) = 456 (8) [M^+], 330 (12), 329 (24), 203 (15), 191 (7), 125 (54), 96 (47), 83 (72), 69 (100), 55 (58); HRMS for [M^+]($C_{24}H_{41}F_5S$): calcd. 456.2849, found 456.2855.

4.3.7. 3-[Z-(Pentafluoro-λ⁶-sulfanyl)methylene]-5α-cholestane (**21**)

Yield 81% (96.2% purity by HPLC), colorless solid, mp 123 °C (EtOH/*n*-heptane 1:1); $[\alpha]_D^{20}$ = +44.2° (*n*-heptane, 0.01016 g mL^{-1}); IR (KBr): 2950 (s), 2913 (s), 2866 (s), 1644 (w), 1469 (m), 1445 (m), 1384 (w), 1147 (w), 1033 (w), 929 (m), 879 (vs), 844 (s), 832 (vs), 794 (m), 778 (m), 723 (s), 642 (m), 627 (w), 594 (m), 575 (w), 568 cm^{-1} (w); ^1H NMR (500 MHz, $CDCl_3$, 303 K): δ = 6.10 (quint, J = 8.6 Hz, 1H), 2.68 (mc, 1H), 2.32 (mc, 1H), 2.05 (mc, 1H), 1.98–1.78 (m, 4H), 1.68 (mc, 1H), 1.59–1.42 (m, 3H), 1.40–0.95 (m, 20H), 0.90 (s, 3H), 0.89 (s, 3H), 0.87 (d, J = 6.6 Hz, 3H), 0.85 (d, J = 6.6 Hz, 3H), 0.66 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ = 149.5, 132.2 (quint, J = 17.0 Hz), 56.8, 56.7, 54.5, 47.4, 43.0, 40.3, 40.2, 39.9, 36.6, 36.3, 36.2, 35.8, 33.1, 32.3, 32.1, 29.3, 28.6, 28.4, 24.6, 24.2, 23.2, 22.9, 21.6, 19.1, 12.5, 12.3; ^{19}F NMR (235 MHz, $CDCl_3$, 300 K): δ = 88.5 (m, 1F, SF_{ax}; overlapped by quintet with J = 149.7 Hz), 68.0 (dd, J = 149.7 Hz, J = 8.6 Hz, 4F, SF_{eq}); MS (EI, 70 eV, 180 °C): $m/$

z (%) = 510 (80) [M^+], 495 (16), 370 (10), 355 (100), 341 (18), 287 (14), 122 (21), 109 (23), 95 (30), 81 (27), 69 (23), 57 (21), 43 (27); HRMS for [M^+]($C_{28}H_{47}F_5S$): calcd. 510.3319, found 510.3331.

4.4. Hydrodebromination of **8a** with tert-butyl lithium

A solution of **8a** (1.48 g, 3.35 mmol) in *n*-pentane (30 mL) was cooled to −78 °C. *tert*-Butyl Lithium (15% solution in *n*-pentane; 4.3 mL, 6.8 mmol) was added dropwise, and the mixture was stirred for 18 h between −78 and −60 °C. After careful addition of ethanol (5 mL), the mixture was allowed to warm up to room temperature and poured into ice water (100 mL). The organic layer was separated and the aqueous phase extracted three times with *n*-heptane. The combined organic phases were dried over Na_2SO_4 and evaporated to dryness. The composition of the crude product was determined by GC–MS (column: Factor Four VF5 ms; temperature profile: 100–320 °C at 8 °C min^{-1}; pressure: 1 bar; split: 50 mL min^{-1}; injector temperature: 280 °C; injected sample volume: 1 μL):

4-Propyl-4′-vinyl-1,1′-bicyclohexyl (**7a**): t_R = 13.1 min; 48% GC yield; MS (EI, 70 eV): *m*/*z* (%) = 234 (39) [M^+], 205 (17), 150 (12), 136 (11), 123 (24), 109 (59), 95 (43), 81 (65), 69 (100), 55 (60), 41 (50), 29 (8), 27 (16).

4-[2-(Pentafluoro-λ^6-sulfanyl)ethyl]-4′-propyl-1,1′-bicyclohexyl (**5**): t_R = 16.6 min; 16% GC yield; MS (EI, 70 eV): *m*/*z* (%) = 362 (11) [M^+], 236 (9), 125 (83), 109 (14), 95 (10), 83 (63), 69 (100), 55 (32), 41 (19).

4-[1-Bromo-2-(pentafluoro-λ^6-sulfanyl)ethyl]-4′-propyl-1,1′-bicyclohexyl (**8a**): t_R = 19.6 min; 20% GC yield; MS see above.

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