Liquid Crystals Based on Hypervalent Sulfur Fluorides: Exploring the Steric Effects of *ortho*-Fluorine Substituents[‡]

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Liquid crystals that have *ortho*-fluorinated pentafluoro-λ^6-sulfanyl terminal groups are the most polar materials that are still compatible with current active matrix LCD technology. The synthesis of the first examples of this class of substance has been achieved by direct fluorination. The physico-chemical characterization, supported by DFT calculations, revealed some surprising features of these new compounds: the bulky SF_5 group is easily deformed and responds in a quite unusual way to the steric strain exerted by its *ortho* substituents.

Introduction

More than 40 years after their initial synthesis and characterization,[1] the chemistry of compounds that have a pentafluoro-λ^6-sulfanyl substituent is currently experiencing a renaissance.[2,3] The combination of high polarity and lipophilicity ("polar hydrophobicity"),[4] which is unique to the SF_5 group, renders it an attractive building block not only for biomedical applications[5] but also for materials sciences.[6] The use of a pentafluoro-λ^6-sulfanyl group offers some advantages,[7] particularly in liquid crystals, because it is the most polar terminal group that is still compatible with active matrix LCD (liquid crystal display) technology.[8] For this application it is imperative that the polar function does not coordinate to cations, thereby mobilizing ubiquitous ionic impurities in the liquid crystal and other peripheral display components.[8b] Nevertheless, there is a need for even more polar liquid crystalline materials for LCDs with lower power consumption particularly in mobile devices, such as notebook PCs, cellular phones and PDAs (personal digital assistants).

The molecular dipole moment (μ) and the dielectric anisotropy ($\Delta\varepsilon$) of liquid crystals is usually increased by flanking the polar terminal group by one or two *ortho*-fluorine substituents on the aromatic moiety.[7] Thus, for the liquid crystal **1**, addition of two *ortho*-fluorine atoms (**2**) increases the dielectric anisotropy by 8.5 units (Scheme 1 and Table 1).

In our previous communication[7a] we pointed out that the pentafluoro-λ^6-sulfanyl group is easily deformed, resulting in significant changes in its dipole moment. Therefore, the effect of *ortho*-fluorination on the sterically demanding pentafluoro-λ^6-sulfanyl group might be quantitatively as well as qualitatively different to the effect on the smaller trifluoromethyl group for which the simple addition of local dipole moments leads to an observed increase in $\Delta\varepsilon$ of 8.5 units.

Results and Discussion

Synthesis and Characterization of Liquid Crystals

In order to obtain experimental evidence on how the pentafluoro-λ^6-sulfanyl group responds to steric pressure from *ortho* substituents, the liquid crystal **4** was selected as a target compound. The material **5** was also chosen because the combination of an *ortho*-fluoro(pentafluoro-λ^6-sulfanyl)-phenyl group with a difluorooxymethylene bridge in the mesogenic core structure promised some attractive features, such as high dielectric anisotropy ($\Delta\varepsilon$) and also a broad nematic phase range.[7c] Liquid crystals are a particularly convenient tool for the experimental determination of the mode of sterically induced deformation of the SF_5 group because even relatively small changes in the molecular dipole moment translate into noticeable changes in dielectric anisotropy.[9]

In his first paper on pentafluoro-λ^6-sulfanyl compounds[1a] Sheppard pointed out that the synthesis of *ortho*-substituted aromatic SF_5 derivatives would be problematic as a result of strong steric interactions with the bulky SF_5 group. More than 40 years later Thrasher and co-workers succeeded in the first synthesis of *ortho*-fluoro(pentafluoro-

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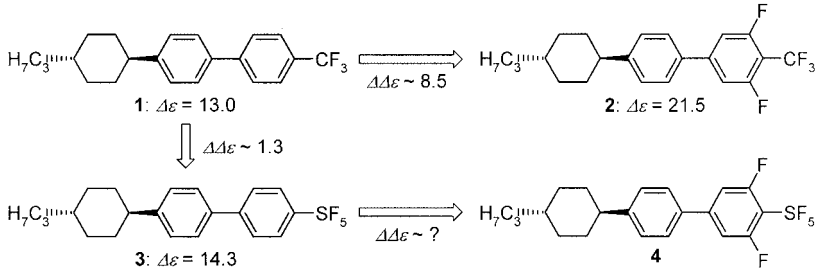
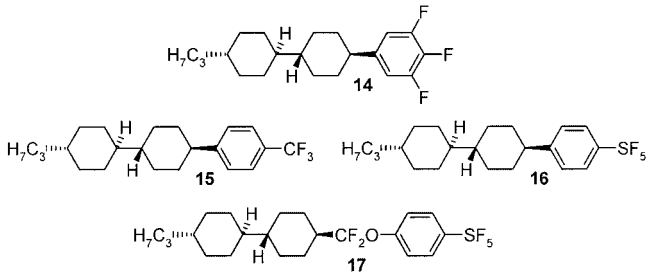


Scheme 1. Increase in the dielectric anisotropies ($\Delta\varepsilon$) of liquid crystals induced by the replacement of CF_3 by the SF_5 group (**1** → **3**) and by difluorination of the *ortho* positions of the polar terminal group (**1** → **2**).

Table 1. The physical properties of the liquid crystals **1**–**5** and **14**–**17** for comparison.[a]



Compound	Phase sequence	$\Delta\varepsilon_{virt}$	Δn_{virt}	$T_{NI,virt}$
1	C 134 I	13.0	0.165	109.5
2	C 86 I	21.5	0.149	47.1
3	C 109 N (87.8) I	14.3	0.154	94.6
4	C 103 I	21.4	0.132	49.6
5	C 50 N 101.9 I	14.3	0.080	87.6
14	C 66 N 94.1 I	9.7	0.075	74.7
15	C 133 I	9.5	0.091	112.2
16	C 121 I	11.7	0.093	95.5
17	C 67 N 116.5 I	11.8	0.080	108.2

[a] The virtual electrooptical parameters ($\Delta\varepsilon_{virt}$, Δn_{virt}) and clearing points ($T_{NI,virt}$) were extrapolated from the mixture ZLI-4792 (Merck)[12] (C = crystalline, N = nematic, I = isotropic; the phase transition temperatures are given in °C, numbers in parentheses denote monotropic phase transitions.).

λ^6-sulfanyl)benzene derivatives[3] and were also able to perform a variety of nucleophilic replacement reactions on the *ortho*-fluorine atom with even more sterically demanding substituents. However, the resulting derivatives did not have the right substitution pattern for the synthesis of liquid crystals.

As the starting point for our syntheses (Scheme 2), we chose the direct fluorination[10] of the suitably fluorinated bis(4-nitrophenyl) disulfides **7a** and **7b**, which were synthesized from **6a** and **6b**, respectively.[11] The *ortho*-fluorinated (pentafluoro-λ^6-sulfanyl)benzenes **8a** and **8b** were obtained in rather low but reproducible yields (9% and 4.6%, respectively). These nitro compounds were catalytically hydrogenated to the amines **9a** and **9b** in high yields without complications. Also the subsequent Sandmeyer reaction furnished the bromides **10a** and **10b** with no indication of instability in any of the reaction intermediates, even under quite harsh and strongly acidic conditions. The monofluoro compound **10a** was converted into the corresponding phenol **11**, although we did not succeed in obtaining an analytically pure sample. Nevertheless, subjecting the crude phenol to oxidative phenoxydifluorodesulfuration in the presence of the ketene dithioketal **12**[7c] yielded 7% of the liquid crystal **5** which was isolated and purified by chromatography and subsequent crystallization.

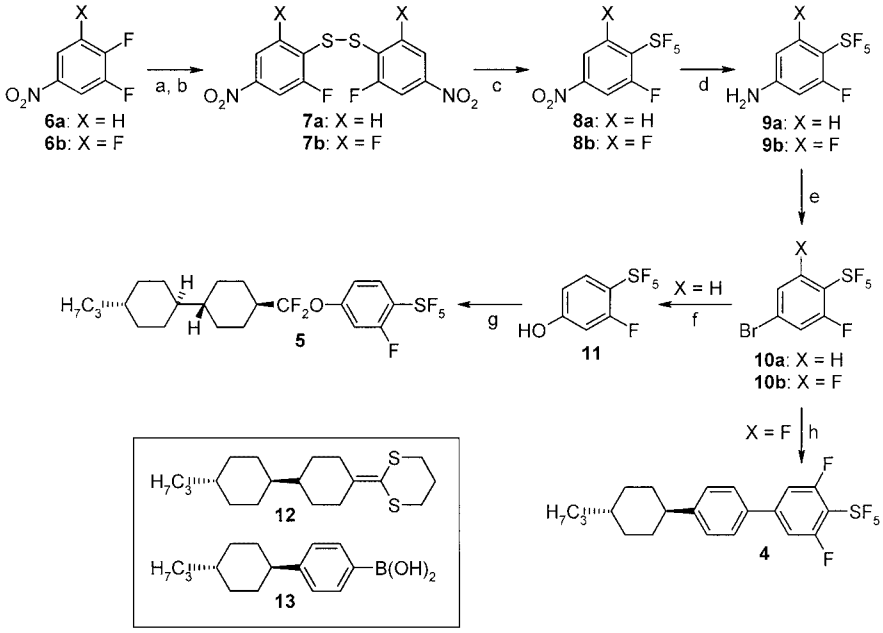
An attempt to convert the bromide **10b** into the corresponding phenol failed completely to furnish even an impure product. Also, Suzuki coupling of **10b** with the boronic acid **13** produced an untypically[7a] low yield (16%) of the liquid crystal **4**.

These new compounds were all characterized by ^1H and ^{19}F NMR spectroscopy and by EI mass spectrometry. Some of the intermediates contained minor by-products resulting from over-fluorination. In these cases the compounds were used without further purification in the subsequent reaction steps. The purities were determined by HPLC and are noted in the Exp. Sect.

In conclusion, it seems that in some cases the yields of the synthetic conversions of *ortho*-fluoro(pentafluoro-λ^6-sulfanyl)arenes decrease with an increasing number of fluorine substituents. On the other hand, none of the isolated and purified reaction products shows any sign of instability.

The "virtual" parameters,[12] which were used to characterize the new liquid crystals **4** and **5** (Table 1), reflect the contribution of a given compound to the anisotropic characteristics of a liquid crystal mixture. They play an important role in the application-oriented evaluation of new compounds as they allow electrooptic, viscoelastic and mesogenic properties to be compared even if they do not form a thermodynamically stable mesophase.

Like its trifluoromethyl analogue **2**, compound **4** does not exhibit any mesophase. It shows a slightly higher virtual clearing point which may be attributed to the larger steric bulk of the SF_5 group. Compared with the simple pentafluoro-λ^6-sulfanyl derivative **3** the dielectric anisotropy ($\Delta\varepsilon_{virt}$) of its *ortho*-difluoro analogue is increased by only about 7 units and has nearly the same dielectric anisotropy as its trifluoromethyl analogue **2**. This means that the contribution of the SF_5 group to the overall dipole moment and dielectric anisotropy of **4** is the same as that of the CF_3 group in **2**, whereas usually (e.g., for the pair **15** and **16**) $\Delta\varepsilon$ is about 2 units higher for the SF_5 compound.



Scheme 2. Synthesis of the liquid crystals **4** and **5**; reagents and conditions: a) $Na_2S·9H_2O$, DMSO, room temp. → 50 °C; b) $NaBO_4·3H_2O$, HOAc, room temp. (**7a**: 63%, **7b**: 77%); c) 10% F_2/N_2, CH_3CN, –3 → 0 °C (**8a**: 9%, **8b**: 4.6%); d) cat. Raney Ni, H_2, THF, room temp., 1 bar (**9a**: 95%, **9b**: 95%); e) 1. $NaNO_2$, 47% HBr, 0–5 °C; 2. CuBr, 85 °C (**10a**: 51%, **10b**: 49%). f) 1. *t*BuLi, Et_2O, –70 °C; 2. $B(OMe)_3$; 3. HOAc, H_2SO_4, 30% H_2O_2, –20 → 35 °C (crude product used for next step); g) 1. **12**, CF_3SO_3H, CH_2Cl_2, 0 °C (5 min) → room temp. (30 min) → –70 °C; 2. **11**, NEt_3, CH_2Cl_2, –70 °C; 3. $NEt_3·3HF$, –70 °C; 4. Br_2, CH_2Cl_2, –70 → –10 °C (7%); h) **13**, $NaBO_2·8H_2O$, H_2O, THF, cat. $Pd(PPh_3)_4$, reflux, 18 h (16%).

The general tendency of SF_5-substituted liquid crystals not to form thermodynamically stable mesophases is shared by their CF_3 analogues. These materials have found some limited practical applications[8a] owing to their high polarity, but in general, liquid crystals with a broad nematic phase, such as **14**, are much more versatile and have a wide range of applications. In our previous communication[7c] we showed that the ability of liquid crystals to form a nematic phase can be effectively promoted by the insertion of a difluorooxymethylene bridge into the mesogenic core structure. This design principle also works for the material **17** in which a broad nematic phase (relative to **16**) is induced by the CF_2O bridge, along with an increase in the virtual clearing point of about 13 °C. The *ortho*-fluorine substituent in **5** leads to a further increase in $\Delta\varepsilon$ of 2.5 units (compared with **17**) and retains a broad nematic phase range. The observed drop in the virtual clearing points (**5** vs. **17**, as well as **4** vs. **3**) is a normal effect of *ortho*-fluorination of any polar terminal group[8] and can be seen, in terms of practical applications, as the price to pay for increased polarity.

Quantum Chemical Calculations

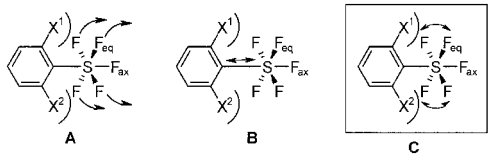
Intuitively, it may be expected that the repulsive interactions of the *ortho*-fluorine atoms "push" the equatorial fluorine atoms away from the aromatic moiety rendering the pentafluoro-λ^6-sulfanyl group as a whole more polar, thereby exceeding the effect of the simple addition of lateral carbon–fluorine dipole moments. In our previous communication[7a] we showed that the molecular dipole moment is increased by about 0.3 D per degree of deformation, requiring less than 1 kcal mol^{-1} in terms of steric strain. In contrast to the experimental results, this would mean that the gain in the molecular dipole moment (μ) and the dielectric anisotropy ($\Delta\varepsilon$) for SF_5-substituted liquid crystals should be much higher than for their otherwise similar CF_3 analogues. Alternatively, the steric strain might be relieved by the elongation of the carbon–sulfur bond.

Nevertheless, quantum chemical calculations [geometry optimization at the B3LYP/6-31+G(d) level of theory][9] indicate that the SF_5 group copes with the repulsive steric interactions with *ortho*-fluoro substituents (Table 2) in a different way: the equatorial fluorine atoms are neither pushed "forward" by the *ortho* substituents (**A**) nor is the carbon–sulfur bond elongated (**B**); instead they are pushed apart allowing the *ortho*-fluorine atom to "squeeze" in between (**C**). The C–S–F_{eq} angle (for the monofluorinated model system the averaged value of 92.34° for the two relevant angles has to be considered) is even reduced by the *ortho*-fluorination. Of these three deformation modes, only for **A** could an extraordinary increase in the molecular dipole moment or the dielectric anisotropy be expected to occur.

Together with the experimental evidence, the molecular modelling results indicate that *ortho*-difluorination (**4** vs. **3**) distorts the SF_5 group by mode **C** (Table 2), that is, by enlarging the F_{eq}–S–F_{eq} angle. A concomitant reduction of the C–S–F_{eq} angle leads to the observed decrease in the polarity of the SF_5 group in the liquid crystal **4**.

For *ortho*-monofluorinated SF_5 derivatives this effect is not observed experimentally: compound **5** shows the expected increase in $\Delta\varepsilon$ induced by its *ortho*-fluorine substitu-

Table 2. Results of the quantum chemical calculations (geometry optimization) performed at the B3LYP/6-31+G(d) level of theory.[a]

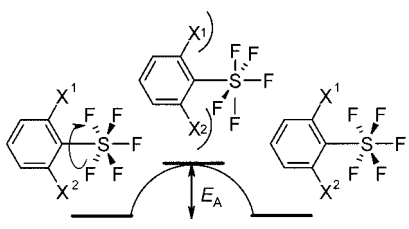


	18	19	20
C–S [Å]	1.838	1.835	1.837
S–F_{ax} [Å]	1.633	1.631	1.630
S–F_{eq} (*o*-H) [Å]	1.642	1.642	–
S–F_{eq} (*o*-F) [Å]	–	1.632	1.632
C–S–F_{eq} (*o*-H) [°]	92.57	91.97	–
C–S–F_{eq} (*o*-F) [°]	–	92.70	92.11
F_{eq}–S–F_{eq} (*o*-H) [°]	89.82	89.39	–
F_{eq}–S–F_{eq} (*o*-F) [°]	–	90.74	90.32
μ [D]	4.65	5.16	5.44

[a] The calculations (geometry optimization at the B3LYP/6-31+G(d) level of theory)[13] indicate that the pentafluoro-λ^6-sulfanyl group responds to the repulsive interactions with the *ortho* substituents X^1 and X^2 by widening the F_{eq}–S–F_{eq} angle as a result of the partial insertion of the *ortho*-fluorine atom. Note that, in contrast to the calculations reported here, the only reported experimental value for the dipole moment of (pentafluoro-λ^6-sulfanyl)-benzene (**18**) is 3.44 D.[1]

ent relative to **17**. The quantum chemical calculations on the model system **19** indicate that only the equatorial fluorine atoms on the side of the *ortho*-fluorine atom are pushed apart. At the same time they are also pushed forward by about 0.1°. On the side of the *ortho*-hydrogen atom, the C–S–F_{eq} angle is slightly reduced, resulting in an overall tilt of the plane formed by the equatorial fluorine atoms. The effects on the two sides of the SF_5 group seem to cancel each other and so the group dipole moment is not significantly changed.

In addition the dynamics of the molecular rotation of the SF_5 group around the central carbon–sulfur bond is affected by the steric hindrance of the *ortho*-fluorine atoms. In the transition state of this rotation (Scheme 3) two of the equatorial fluorine atoms have to "pass" the aromatic *ortho* substituents. Calculations at the B3LYP/6-311+G(2d,p)// B3LYP/6-31+G(d) level of theory indicate that the relative energies of these transition states are elevated by *ortho*-fluorination. Whereas the rotational barrier of (pentafluoro-λ^6-sulfanyl)benzene (**18**) is only 1.8 kcal mol^{-1}, it is 4.4 kcal mol^{-1} for **19** (one *ortho*-fluorine atom) and



Scheme 3. The activation barriers, E_A, for the rotation of the SF_5 group around the central C–S bond: **18**: 1.8 kcal mol^{-1}; **19**: 4.4 kcal mol^{-1}; **20**: 7.8 kcal mol^{-1}.[13]

7.8 kcal mol^{-1} for **20** (two *ortho*-fluorine atoms). During the transition, the "passing" equatorial fluorine atoms are pushed "forward" by about 0.8° by the aromatic *ortho*-hydrogen atoms and by about 1.5° by the *ortho*-fluorine atoms.

Conclusions

For the first time we have been able to synthesize liquid crystals with a polar pentafluoro-λ^6-sulfanyl group and additional *ortho*-fluorine substituents. These materials were used in combination with quantum chemical calculations to determine how the bulky SF_5 group responds to steric pressure, and how the dynamics of its rotation are affected. The polarity of a terminal SF_5 group can be enhanced significantly by *ortho*-monofluorination (**5**). Introduction of a second *ortho*-fluorine atom (**4**) leads to a sterically induced deformation of the SF_5 group which reduces its polarity to about that of the more "conventional" CF_3 group. In spite of this limitation, use of the pentafluoro-λ^6-sulfanyl group has allowed the design of liquid crystals with the most polar terminal functions that are still compatible with active matrix LCD technology. The unique combination of high polarity, low polarizability and chemical stability renders the SF_5 group an interesting structural feature not only for polymers and functional materials in molecular electronics, but also in medicinal chemistry.

Experimental Section

General: The starting materials **6a** and **6b** are commercially available from Apollo Scientific. They were converted into the corresponding disulfides **7a** and **7b** according to methods previously reported.[11] ***Caution:*** Working with elemental fluorine is potentially hazardous! The fluorination reactions were carried out under a well-ventilated hood in a 1-L PFA bottle with PTFE and PFA tubing. Even traces of non-fluorine-resistant organic compounds, such as lubricants, can combust spontaneously. Before and after operation the apparatus was purged with dry nitrogen. Excess fluorine and hydrofluoric acid were scrubbed in a column filled with a mixture of granulated charcoal and aluminium oxide pearls. The acetonitrile used as the reaction solvent (Merck KGaA, DNA synthesis grade) contained less than 10 ppm of water. Interruption of the fluorination for several hours overnight did not reduce the reaction yields.

8a: A solution of **7a** (35.0 g, 101.6 mmol) in dry acetonitrile (500 mL) was cooled to –3 °C. A stream of 10% F_2/N_2 was bubbled into the vigorously stirred solution at a rate of 200 mL min^{-1} at a temperature between –3 and 0 °C for approximately 32 h under GC-MS control (the samples were injected into the GC apparatus without prior aqueous work-up, in order to avoid extraction of water-soluble intermediates). After completion of the reaction, the apparatus was purged with nitrogen and the solution was concentrated to dryness. The residue was dissolved in CH_2Cl_2 (400 mL) and stirred with ice/water (500 mL). The organic layer was separated and washed three times with 10% aqueous NaOH and twice with water. The solution was dried with Na_2SO_4 and the solvent evaporated to dryness. The residue (25.1 g) was distilled in a Kugelrohr apparatus (b.p. 120 °C/0.1 mbar) to furnish 13.4 g of a crude

product, which was purified by chromatography (silica gel; toluene/*n*-heptane, 3:2) and distilled again (b.p. 102 °C/0.1 mbar) to yield the product **8a** (4.9 g, 9%) as a yellow oil, m.p. 11 °C (92% purity by GC, over-fluorinated by-product). ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): δ = 8.00 (dd, J = 9.8, J = 6.9 Hz, 1 H), 8.08–8.15 (m, 2 H) ppm. ^{19}F NMR (235 MHz, $CDCl_3$, 300 K; standard $CFCl_3$): δ = –103.1 (m_c, 1 F, Ar-F), 66.8 (dd, J = 150.9, J = 25.2 Hz, 4 F, SF_{eq}), 77.2 (quint, J = 150.9 Hz, 1 F, SF_{ax}; an additional, insufficiently resolved fine structure is underlying the quint) ppm. MS (EI, 70 eV): *m*/*z* (%) = 267 [M^+] (100), 248 (30), 221 (24), 113 (58), 101 (16), 94 (31), 93 (31), 89 (45). HRMS for [M^+] ($C_6H_3F_6NO_2S$): calcd. 266.9789; found 266.9796.

8b: Starting from **7b** (35.0 g, 92.0 mmol) the same procedure as that in the synthesis of **8a** was applied. The final Kugelrohr distillation (b.p. 85 °C/0.1 mbar) furnished **8b** (2.4 g, 4.6%) as a yellow oil (79% purity by GC, over-fluorinated by-product). ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): δ = 7.92 (d, J = 8.3 Hz, 2 H) ppm. ^{19}F NMR (235 MHz, $CDCl_3$, 300 K; standard $CFCl_3$): δ = –98.2 to –97.7 (m, 2 F, Ar-F), 71.6–75.7 (m, 5 F, SF_5; the SF_{ax} quint with an additional, insufficiently resolved fine structure is overlapping a complex SF_{eq} signal group) ppm. MS (EI, 70 eV): *m*/*z* (%) = 285 [M^+] (100), 266 (38), 239 (13), 131 (39), 119 (25), 112 (34), 99 (16), 89 (49), 83 (23), 81 (42), 69 (18), 65 (90), 62 (22). HRMS for [M^+] ($C_6H_2F_7NO_2S$): calcd. 284.9694; found 284.9690.

9a: A solution of **8a** (4.5 g, 15.5 mmol) in THF (30 mL) was hydrogenated in the presence of Raney nickel (0.2 g, THF wet) at room temp. and ambient pressure. The mixture was filtered through Celite and the solvents were evaporated to dryness to furnish **9a** (3.5 g, 95%) as an off-white solid, m.p. 56.5 °C (93% purity by HPLC). ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): δ = 4.10 (br. s, 2 H, NH_2), 6.32–6.41 (m, 2 H), 7.47 (t, J = 8.5 Hz, 1 H) ppm. ^{19}F NMR (235 MHz, $CDCl_3$, 300 K; standard $CFCl_3$): δ = –107.8 to –108.3 (m_c, 1 F, Ar-F), 69.9 (dd, J = 150.9, J = 23.5 Hz, 4 F, SF_{eq}), 85.1 (quint, J = 150.9 Hz, 1 F, SF_{ax}; an additional, insufficiently resolved fine structure is underlying the quint) ppm. MS (EI, 70 eV): *m*/*z* (%) = 237 (100) [M^+], 128 (27), 129 (70), 110 (51), 102 (13), 101 (14), 90 (12), 89 (14), 83 (48). HRMS for [M^+] ($C_6H_5F_6NS$): calcd. 237.0047; found 237.0044.

9b: Starting from **8b** (2.0 g, 7.0 mmol) the same procedure as that in the synthesis of **9a** was applied. The yield of **9b** was 1.7 g (95%). The crude product was used without further purification in the next step. ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): δ = 3.22 (br. s, 2 H, NH_2), 6.19 (d, J = 11.7 Hz, 2 H) ppm. ^{19}F NMR (235 MHz, $CDCl_3$, 300 K; standard $CFCl_3$): δ = –107.3 to –106.7 (m, 2 F, Ar-F), 73.3–74.5 (m, 4 F, SF_{eq}), 77.8–82.0 (m, 1 F, SF_{ax}) ppm. MS (EI, 70 eV): *m*/*z* (%) = 255 (100) [M^+], 236 (14), 205 (12), 165 (13), 147 (55), 128 (51), 119 (17), 101 (61), 89 (15).

10a: A mixture of **9a** (3.2 g, 13.5 mmol) and 23% HBr (40 mL) was cooled to 0 °C, and a solution of $NaNO_2$ (1.2 g, 17.4 mmol) in water (7 mL) was added dropwise, keeping the temperature between 0 and 2 °C. After the completion of the diazotization reaction (30 min), urea (50 mg) was added in order to destroy excess nitrous acid. Then, a solution of CuBr (4.3 g, 30 mmol) in 47% HBr (15 mL) was added at 0–5 °C. The strongly foaming mixture was heated to 85 °C for 1 h. When the evolution of nitrogen had ceased, it was cooled to room temp., poured into ice/water and extracted with *n*-pentane. The aqueous phase was extracted twice with *n*-pentane, and the combined organic phases were washed with water and saturated aqueous $NaHCO_3$ solution, dried with Na_2SO_4 and the solvents evaporated to dryness. The residue was purified by chromatography (silica gel; *n*-pentane) to yield **10a** (2.1 g, 51%) as a colorless oil (94% purity by GC). ^{1}H NMR (300 MHz, [D_6]DMSO, 303 K): δ = 7.67 (d, J = 8.8 Hz, 1 H, Ar-H), 7.92–7.98 (m, 2 H, Ar-H) ppm. ^{19}F NMR (235 MHz, $CDCl_3$, 300 K; standard $CFCl_3$): δ = –104.9 to –104.4 (m_c, 1 F, Ar-F), 66.8 (ddd, J = 151.9, J = 24.6, J = 3.5 Hz, 4 F, SF_{eq}), 86.1 (quint, J = 151.9 Hz, 1 F, SF_{ax}; an additional, insufficiently resolved fine structure is underlying the quint) ppm. MS (EI, 70 eV): *m*/*z* (%) = 300/302 (100) [M^+], 281/283 (18), 192/194 (40), 173/175 (18), 113 (78), 94 (60), 93 (25), 89 (34), 74 (18).

10b: Starting from **9b** (1.5 g, 3.2 mmol) the same procedure as that in the synthesis of **10a** was applied. The yield of **10b** was 510 mg (49%) as a colorless oil (70% purity by GC, containing 14% of over-fluorinated by-product). ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): δ = 7.25 (d, J = 7.6 Hz, 2 H, overlap with solvent signal) ppm. ^{19}F NMR (235 MHz, $CDCl_3$, 300 K; standard $CFCl_3$): δ = –105.0 to –104.5 (m, 2 F, Ar-F), 71.0–72.1 (m, 4 F, SF_{eq}), 73.0–76.8 (m, 1 F, SF_{ax}) ppm. MS (EI, 70 eV): *m*/*z* (%) = 318/320 (100) [M^+], 299/301 (18), 228/230 (13), 210/212 (53), 191/193 (15), 149 (16), 131 (65), 130 (20), 112 (68), 89 (40), 81 (36).

11: A solution of **10a** (2.0 g, 6.6 mmol) in diethyl ether (50 mL) was cooled to –70 °C, and *tert*-butyllithium (9.0 mL of a 15% solution in *n*-pentane, 13.3 mmol; ***Caution:*** ignites spontaneously on contact with air!) was added dropwise. After stirring at –70 °C for 30 min, trimethyl borate (0.8 mL, 7.2 mmol) was added, and after 30 min the temperature was allowed to rise to –20 °C. Then, acetic acid (0.4 mL, 7.0 mmol), 96% H_2SO_4 (0.3 mL, 5.6 mmol), 30% hydrogen peroxide (1.3 mL, 13 mmol) and water (5 mL) were added. After warming the mixture to 35 °C over 2 h, it was cooled to room temp. and the organic phase was separated. The aqueous phase was extracted a second time with diethyl ether. The combined organic phases were concentrated to dryness, and the residue was co-evaporated three times with methanol and subsequently dried in vacuo. The crude phenol **11** (1.3 g, 81%) was used in the next reaction step without further purification.

4: A mixture of **10b** (450 mg, 1.41 mmol), $NaBO_2 \cdot 8H_2O$ (300 mg), water (5.0 mL), $PdCl_2(PPh_3)_2$ (50 mg) and hydrazine hydrate (50 μL) was stirred at room temp. for 15 min. Then, **13** (400 mg, 1.63 mmol) was added, and the mixture was heated at reflux under nitrogen for 18 h. After cooling, the solution was diluted with *tert*-butyl methyl ether (100 mL), and water (20 mL) was added. The organic layer was separated, washed with brine, dried with Na_2SO_4 and the solvents were evaporated to dryness. The residue was subjected to chromatography through a short silica gel column (*n*-heptane). According to HPLC analysis, the purity of the eluate was 90.4% with 9.3% of over-fluorinated by-product. The product fraction was purified by preparative HPLC (RP-18 phase; acetonitrile) and crystallized from *n*-heptane at –70 °C to yield **4** (110 mg, 16%) as colorless crystals (purity 99.9% by HPLC), m.p. 103 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): δ = 0.91 (t, J = 7.0 Hz, 3 H), 0.99–1.56 (m, 9 H), 1.87–1.94 (m, 4 H), 2.53 (m_c, 1 H), 7.22 (d, J = 10.8 Hz, 2 H, Ar-H; overlap with solvent signal), 7.33 (d, J = 8.4 Hz, 2 H, Ar-H), 7.48 (d, J = 8.4 Hz, 2 H, Ar-H) ppm. ^{19}F NMR (235 MHz, $CDCl_3$, 300 K; standard $CFCl_3$): δ = –105.6 to –105.0 (m, 2 F, Ar-F), 72.7–73.7 (m, 4 F, SF_{eq}), 77.3–79.8 (m, 1 F, SF_{ax}) ppm. MS (EI, 70 eV): *m*/*z* (%) = 440 (100) [M^+], 355 (29), 342 (95), 329 (50), 228 (14), 215 (13), 202 (17), 86 (16).

5: A solution of **12** (1.2 g, 3.6 mmol) in CH_2Cl_2 (30 mL) was treated dropwise at 0 °C with triflic acid (320 μL, 3.65 mmol). After 10 min, the mixture was allowed to warm to room temp., stirred for 30 min and then cooled to –70 °C. A solution of **11** (1.3 g of crude product, ca. 5.5 mmol) and NEt_3 (800 μL, 5.77 mmol) in CH_2Cl_2 (10 mL) was added dropwise, followed after 30 min at –70 °C first by $NEt_3 \cdot 3HF$ (3.0 mL, 18.6 mmol) and then by bro-

mine (1.0 mL, 19.5 mmol) in CH_2Cl_2 (10 mL). The orange mixture was stirred at –70 °C for 1 h, and then it was allowed to warm to –10 °C and poured into ice-cold 2 N NaOH. The organic phase was separated and the aqueous phase was extracted again with CH_2Cl_2. The combined organic phases were dried with Na_2SO_4, filtered and the solvents evaporated to dryness. The tar-like crude product was twice subjected to chromatography through a short silica gel column using *n*-heptane as eluent and crystallized from *n*-heptane at –20 °C to yield **5** (120 mg, 7%) as colorless crystals, m.p. 50 °C, nematic to 101.9 °C, isotropic (purity 99.0% by HPLC). ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): δ = 0.87 (t, J = 7.2 Hz, 3 H), 0.90–1.42 (m, 15 H), 1.69–1.87 (m, 6 H), 1.95–2.08 (m, 3 H), 7.00–7.06 (m, 2 H, Ar-H), 7.70 (t, J = 8.3 Hz, 1 H, Ar-H) ppm. ^{19}F NMR (235 MHz, $CDCl_3$, 300 K; standard $CFCl_3$): δ = –105.6 to –105.1 (m, 1 F, Ar-F), –79.2 (d, J = 8.6 Hz, 2 F, CF_2O), 68.4 (ddd, J = 150.8, J = 24.6, J = 3.4 Hz, 4 F, SF_{eq}), 81.5 (quint, J = 150.8 Hz, 1 F, SF_{ax}; an additional, insufficiently resolved fine structure is underlying the quint) ppm. MS (EI, 70 eV): *m/z* (%) = 494 (22) [M^+], 475 (9), 256 (34), 125 (45), 111 (26), 83 (67), 69 (100).

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