Dithianylium Salts as Versatile Reagents for Organofluorine Chemistry: Fluorodesulfuration in the Presence of Various *O*- and *N*-Nucleophiles

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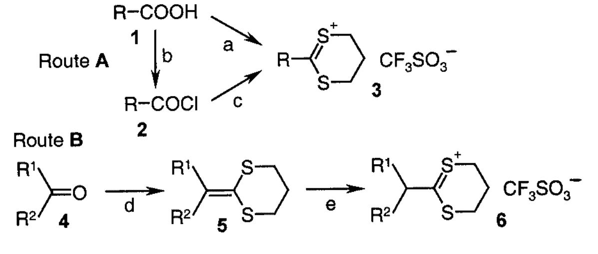
Dithianylium salts in combination with oxidative fluorodesulfuration chemistry act as a versatile new class of α,α-difluoroalkylation reagents, allowing for the first time the convenient synthesis of complex α,α-difluoroethers or α-fluoroacetals. Even relatively fragile species, such as α,α-difluoroalkyl azides or peroxides, can be obtained under very mild reaction conditions.

Introduction

As part of our search for a reliable synthetic route to difluorooxymethylene-linked liquid crystals,[1] we found that the oxidative alkoxydifluorodesulfuration[2] of aromatic or aliphatic dithianylium salts can serve as a synthetic equivalent to electrophilic α,α-difluoroalkylation under very mild reaction conditions.[3] Based on these initial results, it is now our aim to undertake a systematic study of the scope and viability of dithianylium salts[4] as reagents for the synthesis of fluorine-containing organic molecules.

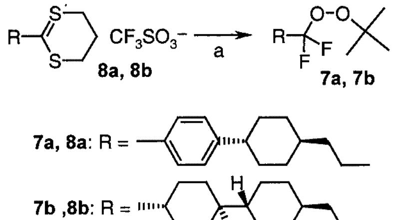
In our previous communication[3] we reported that acidic hydroxy compounds, such as phenols or β-halogenated aliphatic alcohols, can be converted into, for example, their difluorobenzyl or cyclohexyldifluoromethyl ethers. The dithianylium salts may be prepared either by condensation of carboxylic acids with propane-1,3-dithiol in the presence of trifluoromethanesulfonic acid with azeotropic removal of water,[3] or as a milder variant, by condensation of an acid chloride[5] with propanedithiol in the presence of trifluoromethanesulfonic acid and acetic anhydride as a dehydrating agent (Scheme 1, Route A). Aliphatic dithianylium salts are also accessible by protonation of the corresponding ketenedithioketals with trifluoromethanesulfonic acid (Route B).[4e] This route (with R^1 = alkyl and R^2 = H) is especially useful for the generation of linear alkyl dithianylium salts in situ, many of which are non-crystalline.



Scheme 1. General methods for the preparation of dithianylium triflates [R = aryl, (cyclo)alkyl; R^1 = alkyl; R^2 = H, alkyl]: a) 1. $HS(CH_2)_3SH$, CF_3SO_3H, toluene/isooctane (1:1), reflux, azeotropic removal of water; 2. precipitation with Et_2O (typical yield 70−95%); b) $SOCl_2$, reflux; c) 1. $HS(CH_2)_3SH$, CF_3SO_3H, 0 °C; 2. Ac_2O; 3. precipitation with Et_2O (typical yield 70−95%); d) 1. 2-trimethylsilyl-1,3-dithiane, *n*BuLi, THF, −20 °C; 2. **4**, THF, −20 °C → room temp.; e) CF_3SO_3H, CH_2Cl_2, 0 °C (product is usually not isolated but converted in situ)

Results and Discussion

In order to probe and extend the scope of the α,α-difluoroalkylation reaction, we focused our attention on a number of *O*- and *N*-nucleophiles. The oxidative fluorodesulfuration reaction sequence was applied to *tert*-butyl hydroperoxide, a compound which also bears a sufficiently acidic proton. Treatment of a solution of an aromatic or aliphatic dithianylium salt at −78 °C in dichloromethane first with *tert*-butyl hydroperoxide and triethylamine, then with triethylamine tris(hydrofluoride) and finally with the inexpensive electrophilic brominating agent 1,3-dibromo-5,5-dimethylhydantoin (DBH) afforded the desired peroxides (e.g. **7a**, **7b**; Scheme 2) in moderate to high yields. To



Scheme 2. a) 1. *tert*-BuOOH (90% solution in toluene), NEt_3, −70 °C; 2. NEt_3·3HF; 3. DBH, CH_2Cl_2, −78 °C → −10 °C (**7a**: 78%, **7b**: 26%)

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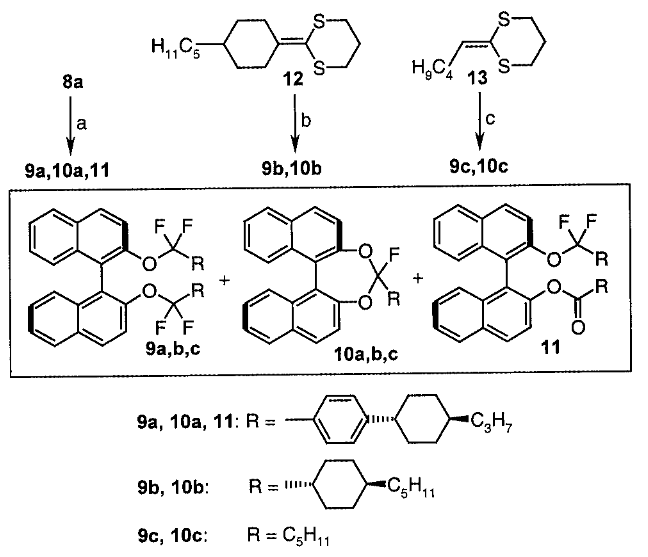
the best of our knowledge, this is the first synthetic route to more complex organic structures containing an α,α-difluoroperoxide moiety.[6]

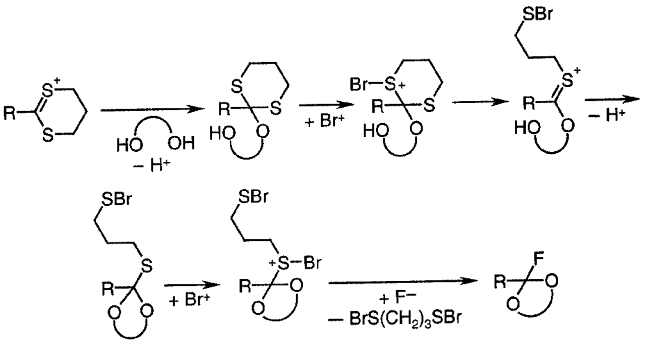
The reaction of dithianylium salts with bivalent *O*-nucleophiles gave an unexpected result: in addition to the desired bis(α,α-difluoroethers) the formation of significant amounts of cyclic α-fluoroketals and of a partial hydrolysis product containing one α,α-difluoroether group and one ester group was observed. When we attempted to synthesise bis(α,α-difluoroethers) such as **9a** from (*S*)-1,1′-bis(2-naphthol), we found that 15−20% of the cyclic side-products **10** (Scheme 3) was always formed in addition to the target compound. All synthesised derivatives of **10a−c** are thermally very stable compounds with high melting points. Due to their limited solubility in most organic solvents, they may be readily isolated from the reaction mixture.



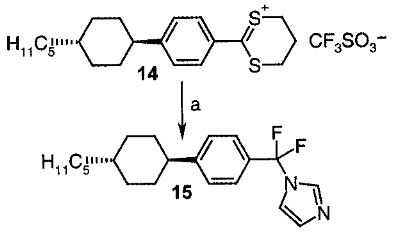
Scheme 3. a) 1. (*S*)-1,1′-Bis(2-naphthol), NEt_3, CH_2Cl_2, −65 °C; 2. NEt_3·3HF; 3. DBH, CH_2Cl_2, −65 °C → −20 °C (**9a**: not determined; **10a**: 11%; **11**: not determined); b) 1. CF_3SO_3H, CH_2Cl_2, 0 °C (40 min) → room temp. (50 min) → −70 °C; 2. (*S*)-1,1′-bis(2-naphthol), NEt_3, CH_2Cl_2, −70 °C; 3. NEt_3·3HF; 4. DBH, CH_2Cl_2, −70 °C → −20 °C (**9b**: 20%; **10b**: 3.5%); c) 1. CF_3SO_3H, CH_2Cl_2, 0 °C (30 min) → −70 °C; 2. (*S*)-1,1′-bis(2-naphthol), NEt_3, CH_2Cl_2, −70 °C; 3. NEt_3·3HF; 4. DBH, CH_2Cl_2, −70 °C → −20 °C (**9c**: not determined; **10c**: 16%)

For the formation of aliphatic derivatives, the dithianylium salts were generated in situ by protonation of the corresponding ketenedithioketals **12** and **13**.[7] In the case of the cyclohexane derivative **12**, equilibration of the initially formed mixture of *cis* and *trans* dithianylium salts by leaving for some time at room temperature, led to the exclusive formation of the thermodynamically preferred *trans*-**12**·H^+. This may be converted in a subsequent fluorodesulfuration reaction to pure *trans*-**10b**.[3] A tentative mechanism explaining the formation of cyclic α-fluoroacetals is depicted in Scheme 4.

Under the same general conditions dithianylium salts can also be used for the difluoroalkylation of *N*-nucleophiles (Scheme 5).[8] The reaction of the salt **14** with imidazole yields 14% of **15**.

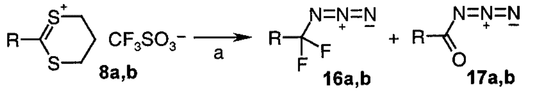


Scheme 4. Tentative mechanism for the formation of cyclic α-fluoroacetals from dithianylium salts and diols



Scheme 5. a) 1. Imidazole, NEt_3, CH_2Cl_2, −70 °C; 2. NEt_3·HF; 3. DBH, CH_2Cl_2, −70 °C → −20 °C (14%)

Trimethylsilyl-protected nitrogen nucleophiles also undergo analogous reactions with good results (Scheme 6), provided the nucleophile is liberated by treatment with tetrabutylammonium fluoride. The major by-product of this reaction is the corresponding carboxylic acid azide as a partial hydrolysis product.



Scheme 6. a) 1. Me_3SiN_3, CH_2Cl_2, −0 °C; 2. Bu_4NF, THF, 0 °C; 3. NEt_3·3HF, −70 °C; 3. DBH, −70 °C → −20 °C [**16a**: 89%, R = 4-(*trans*-4-propylcyclohexyl)phenyl; **17b**: 16%, R = *trans*-*trans*-4′-propylbicyclohex-4-yl; the yields of **17a** and **17b** were not determined]

To date, only a few examples of higher fluorinated α,α-difluoroazides[8b,9] have been reported in the literature. Whilst there is one example of the preparation of α,α-difluorobenzyl azides,[10] the procedure described in this paper is the first generally applicable method for the preparation of complex benzylic as well as aliphatic α,α-difluoroazides.

Conclusion

Dithianylium salts are a versatile new class of α,α-difluoroalkylation reagents, allowing for the first time the synthesis of structurally complex derivatives of relatively fragile species such as α,α-difluoroalkyl azides or peroxides under very mild reaction conditions. Cyclic α-fluoroacetals are also available in preparatively useful yields by reaction with acidic diols. Many such compounds are of interest as pharmaceuticals, agrochemicals and advanced materials, or as key intermediates in their synthesis.

Experimental Section

General Procedures: The melting points, mesophase transitions and decomposition temperatures were determined by differential scanning calorimetry (DSC). The types of the mesophases were identified by optical polarisation microscopy.

7a: *tert*-Butyl hydroperoxide (3.25 mL, 16.3 mmol) was cooled to −78 °C. After addition of CH_2Cl_2 (50 mL) and NEt_3 (2.96 mL, 21.3 mmol) the mixture was allowed to warm up under continuous stirring until a homogeneous suspension was obtained. After cooling to −78 °C again, a solution of **8a** (5.00 g, 10.7 mmol) in CH_2Cl_2 (50 mL) was added dropwise, followed after 90 min by $NEt_3·3HF$ (8.8 mL, 53.4 mmol). Then, a suspension of DBH (15.3 g, 53.4 mmol) in CH_2Cl_2 (50 mL) was added in several small portions within 30 min. After 1 h, the orange-coloured suspension was allowed to warm up to −10 °C and was then poured into 100 mL of a saturated aqueous $NaHCO_3$ solution. The organic layer was separated, and the aqueous phase was extracted three times with CH_2Cl_2. The combined organic extracts were washed with brine and dried over Na_2SO_4. The solution was filtered through silica gel and evaporated to dryness. The product was purified by chromatography with *n*-heptane/ethyl acetate (30:1) on silica gel. Yield: 2.84 g (78%) of a colourless oil. M.p. 20 °C. ^1H NMR (250 MHz, $CDCl_3$, 303 K): δ = 7.50 (d, *J* = 5.3 Hz, 2 H, ar-*H*), 7.25 (d, *J* = 5.3 Hz, 2 H, ar-*H*), 2.58−2.43 (m, 1 H), 1.93−1.83 (m, 4 H), 1.53−0.97 (m, 18 H), 1.35 (s, 9 H, *tert*-C_4H9; part of previous multiplet), 0.90 (t, *J* = 5.1 Hz, 3 H, $CH_2CH_2CH_3$) ppm. ^{19}F NMR (280 MHz, $CDCl_3$, 303 K): δ = −77.0 (s, 2F, CF_2O) ppm. MS (EI): *m*/*z* (%) = 340 (10) [M^+], 251 (100) [$M^+ - C_4H_9O_2$], 201 (10), 127 (18), 91 (9), 73 (10), 57 (37). HR-MS (EI): $C_{20}H_{30}F_2O_2$ [M^+]: calcd. 340.221387; found 340.220759. $C_{16}H_{21}F_2$ [$M^+ - C_4H_9O_2$]: calcd. 251.161132; found 251.160790.

7b: Peroxide **7b** was synthesised by the same general method as described for **7a**, starting from **8b** (10 g, 22.0 mmol). The crude product was purified by chromatography with *n*-heptane/ethyl acetate (100:1) on silica gel. Yield: 2.19 g (26%) of a colourless solid. M.p. 61 °C. ^1H NMR (250 MHz, $CDCl_3$, 303 K): δ = 2.00−1.65 (m, 4 H), 1.30 (s, 9 H, *tert*-C_4H_9), 1.25−0.85 (m, 23 H) ppm. ^{19}F NMR (280 MHz, $CDCl_3$, 303 K): δ = −85.8 (d, *J* = 8 Hz, 2F, CF_2O) ppm. MS (EI): *m*/*z* (%) = 346 (0.1) [M^+], 254 (3), 125 (7), 83 (19), 69 (27), 57 (100). HR-MS (EI): $C_{20}H_{36}F_2O_2$: calcd. 346.268337; found 346.268822.

10a: NEt_3 (10.7 mL, 76.8 mmol) and a solution of **8a** (16.4 g, 34.9 mmol) in 80 mL of CH_2Cl_2 were added successively within 1 h to a solution of (*S*)-1,1′-bis(2-naphthol) (10.0 g, 34.9 mmol) in 120 mL of CH_2Cl_2 at −65 °C. After 1 h, $NEt_3·3HF$ (25 mL, 150 mmol) was added, followed by the addition of a suspension of DBH (30.0 g, 105 mmol) in 50 mL of CH_2Cl_2 in several small portions over 90 min. After 1 h, the mixture was allowed to warm up to −20 °C and poured into an ice-cold mixture of 500 mL of 1 N NaOH and 50 mL of 39% aqueous $NaHSO_3$ solution. The organic layer was separated and the aqueous phase extracted three times with CH_2Cl_2. The combined organic extracts were washed with brine, dried over Na_2SO_4 and the solvents evaporated to dryness. The crude product was filtered through a short silica gel column (*n*-heptane/ethyl acetate, 10:1). After evaporation of the solvent, the yellowish foamy crude product was triturated with methyl *tert*-butyl ether to furnish a colourless solid which was washed with cold methyl *tert*-butyl ether. A further purification was achieved by two recrystallizations from THF/*n*-hexane. Yield: 2.06 g (11%) of colourless fine needles. M.p. 228 °C. ^1H NMR (250 MHz, $CDCl_3$, 303 K): δ = 7.98 (d, *J* = 5.7 Hz, 1 H, ar-*H*), 7.93 (d, *J* = 5.3 Hz, 1 H, ar-*H*), 7.85 (d, *J* = 5.3 Hz, 1 H, ar-*H*), 7.73(d, *J* = 5.7 Hz, 1 H, ar-*H*), 7.59−7.40 (m, 7 H, ar-*H*), 7.33−7.16 (m, 4 H, ar-*H*), 6.95 (d, *J* = 7.0 Hz, 1 H, ar-*H*), 2.03−2.40 (m, 1 H), 1.94−1.81 (m, 4 H), 1.52−0.97 (m, 9 H), 0.90 (t, *J* = 5.1 Hz, 3 H, $CH_2CH_2CH_3$) ppm. ^{19}F NMR (280 MHz, $CDCl_3$, 303 K): δ = −66.4 [s, 1F, $CF(OR)_2$] ppm. MS (EI): *m*/*z* (%) = 516 (100) [M^+], 268 (66), 239 (35). HR-MS (EI): $C_{36}H_{33}FO_2$: calcd. 516.246459; found 516.247609. $[\alpha]_D^{20}$ = +25.9 (*c* = 1.0, $CHCl_3$).

9b and 10b: A solution of **11**[7] (10.0 g, 37.0 mmol) in 50 mL of CH_2Cl_2 was treated dropwise at 0 °C with CF_3SO_3H (3.24 mL, 37.0 mmol). After 40 min, the mixture was allowed to warm up and stirred at room temp. for 50 min. Then, it was cooled to −70 °C, and a solution of NEt_3 (5.12 mL, 37.0 mmol) and (*S*)-1,1′-bis(2-naphthol) (4.76 g, 16.6 mmol) in 30 mL of CH_2Cl_2 was added dropwise. After 90 min, $NEt_3·3HF$ (25.0 mL, 155 mmol) was added, followed by a suspension of DBH (52.9 g, 185 mmol) in 80 mL of CH_2Cl_2. After stirring at −70 °C for 1 h, the yellow suspension was allowed to warm up to −20 °C and poured into an ice-cold mixture of 1 L of 1 N NaOH and 100 mL of 39% aqueous $NaHSO_3$ solution. The organic layer was separated and the aqueous phase extracted three times with CH_2Cl_2. The combined organic extracts were washed with brine, dried over Na_2SO_4 and the solvents evaporated to dryness. The residue was filtered through a short silica gel column (*n*-heptane/ethyl acetate, 50:1). The resulting crude product was purified by preparative HPLC (LiChrospher 100 RP-18, CH_3CN/methyl *tert*-butyl ether, 4:1). The first elution peak (1.31 g) furnished 890 mg (3.5%) of **10b** as colourless crystals (purity 99.8% by HPLC; m.p. 143 °C) after crystallization from *n*-pentane. The second elution peak yielded 5.16 g (20%) of **9b** as a yellowish oil.

10b: ^1H NMR (250 MHz, $CDCl_3$, 303 K): δ = 7.95−7.88 (m, 4 H, ar-*H*), 7.53−7.38 (m, 6 H, ar-*H*), 7.33−7.25 (m, 2 H, ar-*H*), 2.35−2.26 (m, 1 H), 2.13−1.66 (m, 4 H), 1.57−1.12 (m, 11 H), 1.23−1.02 (m, 5 H) ppm. ^{19}F NMR (280 MHz, $CDCl_3$, 303 K): δ = −86.5 [d, *J* = 18.9 Hz, 1F, $CF(OR)_2$] ppm. MS (EI): *m*/*z* (%) = 468 (100) [M^+], 420 (42), 297 (15), 286 (22), 268 (95), 239 (80). $[\alpha]_D^{20}$ = +268.7 (*c* = 1.0, $CHCl_3$).

9b: ^1H NMR (250 MHz, $CDCl_3$, 303 K): δ = 7.93−7.84 (m, 4 H, ar-*H*), 7.67 (d, *J* = 7.5 Hz, 2 H, ar-*H*), 7.45−7.37 (m, 2 H, ar-*H*), 7.30−7.23 (m, 4 H, ar-*H*), 1.60−0.38 (m, 42 H) ppm. ^{19}F NMR (280 MHz, $CDCl_3$, 303 K): δ = −75.8 (d, *J* = 7.5 Hz, 4F, CF_2O) ppm. MS (EI): *m*/*z* (%) = 690 (100) [M^+], 420 (9), 285 (22), 268 (39), 239 (7).

10c: Compound **10c** was synthesised by the same general method as **10b**, starting from **13**[7] (10.6 g, 53.1 mmol) and (*S*)-1,1′-bis(2-naphthol) (6.84 g, 23.9 mmol). The crude product was filtered through a short silica gel column (*n*-heptane/ethyl acetate, 50:1), crystallised twice from *n*-heptane at 4 °C, filtered a second time over silica gel (toluene) and crystallised from *n*-heptane. Yield: 3.36 g (16.4%) of colourless crystals. M.p. 138 °C. ^1H NMR (250 MHz, $CDCl_3$, 303 K): δ = 7.94−7.89 (m, 4 H, ar-*H*), 7.55−7.40 (m, 6 H, ar-*H*), 7.34−7.23 (m, 2 H, ar-*H*), 2.16−2.03 (m, 2 H, $CFCH_2$), 1.84−1.63 (m, 2 H, CH_2), 1.38−1.28 (m, 4 H, CH_2), 0.91 (m, 3 H, CH_3) ppm. ^{19}F NMR (280 MHz, $CDCl_3$, 303 K): δ = −75.3 [t, *J* = 15.6 Hz, 1F, $CF(OR)_2$] ppm. MS (EI): *m*/*z* (%) = 386 (100) [M^+], 268 (77), 239 (68), 134 (19), 119 (25). HR-MS (EI): $C_{26}H_{23}FO_2$: calcd. 386.168208; found 386.168810. $[\alpha]_D^{20}$ = +437.8 (*c* = 1.0, $CHCl_3$).

15: A solution of **14**[3] (10.0 g, 20.1 mmol) in 100 mL of CH_2Cl_2 was added dropwise to a mixture of imidazole (2.07 g, 30.2 mmol) and NEt_3 (5.02 mL, 36.2 mmol) in 20 mL of CH_2Cl_2. After 15 min at room temp., the mixture was cooled to −70 °C and first NEt_3·3HF (16.8 mL, 101 mmol) and then within 30 min a suspension of DBH (28.8 g, 101 mmol) in 40 mL of CH_2Cl_2 were added in several small portions. After stirring for 105 min at −70 °C the mixture was allowed to warm up to −20 °C and then poured into 500 mL of ice-cold 1 N aqueous NaOH. The organic layer was separated, washed twice with brine and dried over Na_2SO_4. The solvent was removed in vacuo, the crude product chromatographed on silica gel (*n*-heptane/ethyl acetate, 7:1) and crystallised from *n*-pentane at −20 °C. Yield: 972 mg (14%) of a yellowish solid. M.p. 45 °C. ^1H NMR (250 MHz, $CDCl_3$, 303 K): δ = 7.56 (s, 1 H, imidazole-2-*H*), 7.47 (d, *J* = 5.7 Hz, 2 H, ar-*H*), 7.33 (d, *J* = 5.7 Hz, 2 H, ar-*H*), 7.10−7.07 (m, 2 H, imidazole-4,5-*H*), 2.60−2.49 (m, 1 H), 1.94−1.75 (m, 4 H), 1.57−0.97 (m, 13 H), 0.90 (t, *J* = 5.1 Hz, 3 H, CH_3) ppm. ^{19}F NMR (280 MHz, $CDCl_3$, 303 K): δ = −71.8 (s, 2F, CF_2N) ppm. MS (EI): *m*/*z* (%) = 346 (12) [M^+], 279 (100) [$M^+ - C_3H_3N_2$], 153 (11), 127 (25). HR-MS (EI): $C_{21}H_{28}F_2N_2$: calcd. 346.222056; found 346.223183.

16a: Trimethylsilyl azide (5.24 mL, 40 mmol) was added at 0 °C to a solution of **8a** (12.5 g, 26.7 mmol) in 100 mL of CH_2Cl_2, followed by the dropwise addition of tetrabutylammonium fluoride (1 M in THF; 40.0 mL, 40.0 mmol). The mixture was stirred for 1 h at 0 °C and then cooled to −70 °C. NEt_3·3HF (22.2 mL, 133 mmol) was then added, followed by a suspension of DBH (38.1 g, 133 mmol) in 50 mL of CH_2Cl_2 over a period of 45 min. After 90 min at −70 °C the mixture was allowed to warm to −20 °C and poured into an ice-cold mixture of 500 mL of 1 N NaOH and 50 mL of 39% aqueous $NaHSO_3$ solution. The organic phase was separated, neutralised by addition of 1 N NaOH and extracted three times with CH_2Cl_2. The combined organic extracts were washed with water and brine, dried over Na_2SO_4 and evaporated to dryness. The crude product was chromatographed over silica gel (*n*-hexane/ethyl acetate, 50:1) and crystallised twice from *n*-pentane at −78 °C. Yield: 6.44 g (89%) of colourless crystals. Mesophase sequence: Crystalline 44 °C, nematic > 80 dec. ^1H NMR (250 MHz, $CDCl_3$, 303 K): δ = 7.50 (d, *J* = 5.7 Hz, 2 H, ar-*H*), 7.27 (d, *J* = 5.7 Hz, 2 H, ar-*H*), 2.55−2.44 (m, 1 H), 1.92−1.83 (m, 4 H), 1.52−0.93 (m, 12 H) ppm. ^{19}F NMR (280 MHz, $CDCl_3$, 303 K): δ = −67.9 (s, 2F, CF_2O) ppm. MS (EI): *m*/*z* (%) = 293 (45) [M^+], 251 (100) [$M^+ - N_3$], 195 (15), 153 (21), 127 (18). HR-MS (EI): $C_{16}H_{21}F_2N_3$: calcd. 293.170354; found 293.170746. IR (KBr): strongest absorptions at $\tilde{\nu}$ = 2923, 2130 and 1310 cm^{-1}.

16b: The azide **16b** was synthesised by the same general method as **16a**, starting from **8b** (12.7 g, 26.7 mmol). The crude product was purified by chromatography with *n*-heptane/ethyl acetate (100:1) over silica gel. Yield: 1.33 g (16%) of a nematic oil. Crystalline 8 °C, smectic 13 °C, nematic 61.1 °C, isotropic > 160 °C dec. ^1H NMR (250 MHz, $CDCl_3$, 303 K): δ = 1.93−1.62 (m, 4 H), 1.35−0.75 (m, 23 H) ppm. ^{19}F NMR (280 MHz, $CDCl_3$, 303 K): δ = −81.3 (d, *J* = 9.7 Hz, 2F, CF_2O) ppm. MS (EI): *m*/*z* (%) = 299 (0.1) [M^+], 271 (28) [$M^+ - N_2$], 242 (27), 229 (22), 188 (26), 174 (100), 161 (47), 148 (27), 125 (25). HR-MS (EI): $C_{16}H_{27}F_2N_3$: calcd. 299.217305; found 299.217803. $C_{16}H_{27}F_2N$: calcd. 271.211157; found 271.211036.

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