Supplementary Material

Liquid Crystals Carrying Stereodefined Vicinal Difluoro- and Trifluoro-Alkyl Motifs

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Experimental Methods

General methods

Dichloromethane and methanol were distilled from calcium hydride. Tetrahydrofuran was distilled from sodium wire. All other commercial reagents and solvents were purchased in synthetic quality and were used as supplied. Reactions were conducted in oven-dried glassware under nitrogen atmosphere with magnetic stirring. Reactions were

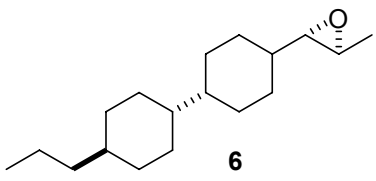
monitored by thin-layer chromatography using Merck Kieselgel 60 plates; visualisation was achieved by inspection under short-wave UV light followed by staining with potassium permanganate or phosphomolybdic acid dip. Flash chromatography was performed using Merck Kieselgel 60 silica gel; eluting solvents are quoted as volume/volume mixtures.

Melting points were determined using a Griffin melting point apparatus and are uncorrected. Infrared spectra were recorded as thin films on sodium chloride plates using a Perkin-Elmer Spectrum GX FT-IR instrument. Nuclear magnetic resonance spectra were recorded using a Bruker AV-500, a Bruker AV-400, a Bruker AV-300 or a Varian Unity Plus 300 instrument.

The starting materials olefin **5** and aldehyde **9** were obtained from Merck. Merck KGaA, Liquid Crystals Division, Frankfurter Str. 250 D-64271 Darmstadt, Germany.

Preparation of Liquid crystal *rac*-3.

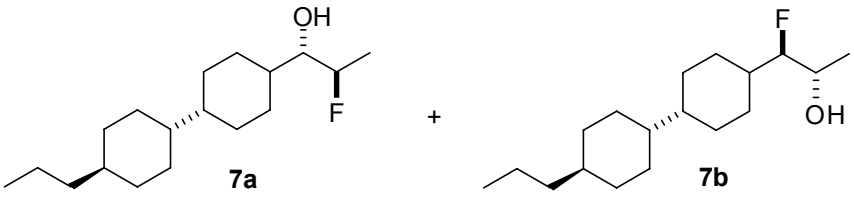
The preparation of *rac*-**3** described below outlines in detail the method by separation and purification of both diastereoisomers of intermediates **7** and **8**. This allowed individual characterisation of the purified diastereoisomers. For practical purposes this separation is not necessary (see Scheme 1 in text).



6

Preparation of epoxide 6:A solution of **5** (24.8 g, 100 mmol) and 3-chloro perbenzoic acid (27.1 g, 110 mmol; 70% purity) in CH_2Cl_2 (120 ml) was stirred at 0°C for 2 h. Then, after

addition of 10% w/w aqueous solution of Na_2SO_3 (50 ml) the mixture was stirred for further 20 min at 0°C. The organic layer was separated, washed twice with saturated aqueous $NaHCO_3$ (100 ml each) and evaporated to dryness. The crude product was recrystallized from *n*-pentane at 0°C to give **6** (20.3 g, 77%) as colourless crystals (99.6% purity by HPLC). ^1H NMR (500 MHz, $CDCl_3$, 303 K): δ_H = 2.83-2.76 (mc, 1H), 2.42-2.39 (mc, 1H), 1.93-1.87 (m, 1H), 1.79-1.65 (m, 7H), 1.58-1.53 (m, 1H), 1.36-1.22 (m, 5H), 1.18-0.80 (m, 16H); IR (KBr): ν_{max}/cm^{-1} = 2999 (m), 2952 (s), 2908 (s), 2849 (s), 1477 (w), 1465 (w), 1441 (m), 1375 (w), 1222 (w), 1130 (w), 1057 (w), 1011 (w), 996 (m), 917 (w), 856 (m), 720 (w), 677 (w), 490 (w), 433 (w); MS (EI, 70 eV): *m/z* (%) = 218 (100), 190 (19), 175 (12), 135 (11), 123 (15), 109 (18), 95 (47), 81 (44), 69 (46), 55 (44).

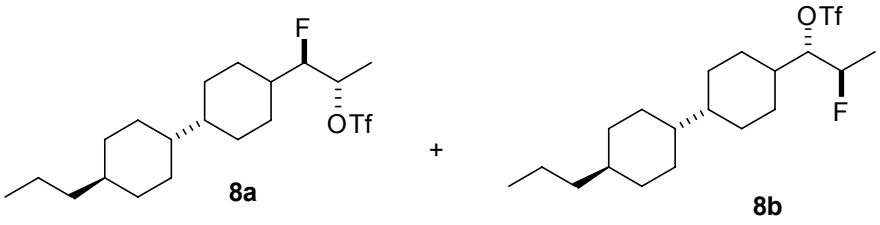


Prepapration of fluorohydrins 7a and **7b**: A solution of epoxide **6** (10.0 g, 38 mmol) in CH_2Cl_2 (50 ml) was treated with 65% HF-pyridine (11.4 ml, 76 mmol) at –5°C for 4 h. The mixture was poured into an excess of 5% (w/v) aqueous $NaHCO_3$ in order to neutralize the hydrofluoric acid. The organic layer was separated, washed with aqueous NH_4Cl solution, dried over Na_2SO_4 and evaporated to dryness. The residue was purified by chromatography (silica gel; *n*-heptane/ethyl acetate 7:1), furnishing the two isomers **7a** (fraction 1: 2.7 g, 25%; 99.4% purity by HPLC) and **7b**

(fraction 2: 3.0 g, 28%; 93.0% purity by HPLC) as colourless crystals.

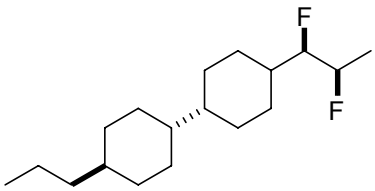
7a: ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ_H = 4.84-4.59 (mc, 1H, C*H*F), 3.57-3.46 (mc, 1H, C*H*OH), 2.07-2.05 (m, 1H), 1.85-1.50 (m, 6H), 1.40-0.80 (m, 16H); ^{19}F NMR (235 Hz, $CDCl_3$, 300 K): δ_F = -181.65 (mc); MS (EI, 70 eV): *m/z* (%) = 237 (100), 219 (28), 137 (12), 123 (24), 109 (18), 95 (35), 81 (36), 79 (11), 69 (36), 67 (21), 55 (31).

7b: ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ_H = 4.24-4.00 (mc, 1H, C*H*F), 3.96-3.84 (mc, 1H, C*H*OH), 2.06-1.68 (m, 9H), 2.07-1.97 (m, 1H), 1.82-1.45 (m, 9H), 1.37-0.80 (m, 21H); ^{19}F NMR (235 Hz, $CDCl_3$, 300 K): δ_F = -205.57 (dt, *J* = 48.3 Hz, *J* = 18.6 Hz); MS (EI, 70 eV): *m/z* (%) = 266 (18), 246 (23), 240 (52), 206 (14), 125 (34), 114 (20), 95 (36), 83 (48), 81 (48), 69 (77), 55 (51), 45 (100).



Preparation of triflates 8a: A solution of **7a** (2.0 g, 7.0 mmol) in CH_2Cl_2 (50 ml) was treated with pyridine (0.82 ml) at -40°C. After 5 min, triflic anhydride (2.18 g, 7.7 mmol) was added dropwise. The mixture was stirred for 1 h at -40°C, then it was allowed to warm up to room temperature and stirred for additional 4 h. Cold *n*-heptane was added, and the precipitate was filtered off and discarded. The filtrate was evaporated to dryness to furnish crude **8a** (2.5 g, 80%; 93% purity by HPLC) as a colourless solid.

8b: An anlogous procedure was applied to **7b** (2.6 g, 9.1 mmol), yielding **8b** (2.6 g, 74%; 91% purity by HPLC) as colourless crystals. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ_H = 5.19-5.04 (mc, 1H), 4.46-4.23 (mc, 1H), 2.08-2.01 (m, 1H), 1.83-1.43 (m, 11H), 1.35-0.80 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ_C = 118.9 (quart, *J* = 319.4 Hz, SO_2CF_3), 98.9, 96.0, 86.6, 86.2, 43.4 (d, *J* = 27.3 Hz), 40.2, 39.4 (d, *J* = 19.1 Hz), 38.0, 33.9, 30.4, 29.4 (d, *J* = 17.0 Hz), 28.8 (dd, *J* = 17.3 Hz, *J* = 6.2 Hz), 20.4, 15.1 (d, *J* = 6.7 Hz), 14.8; ^{19}F NMR (235 Hz, $CDCl_3$, 300 K): δ_F = -73.48 (s, 3F, SO_2CF_3), -199.57 (mc, 1F); MS (EI, 70 eV): *m/z* (%) = 416 (3.6)[M^+], 270 (6), 207 (6), 125 (100), 95 (11), 83 (57), 69 (85), 55 (30).



Liquid crystal *rac*-**3**: A solution of triflate **8a** (7.2 g, 16 mmol; 93% purity by HPLC) in THF (250 ml) was treated at 0°C dropwise via a syringe with tetrabutyl ammonium fluoride (1 M solution in THF; 17.6 ml, 17.6 mmol). The reaction was monitored by TLC for 2 h until the starting material was consumed. Then, the mixture was diluted with brine, extracted twice with methyl *tert*-butyl ether (30 ml each), and the solvent was evaporated. The crude product was purified by chromatography (silica gel; *n*-heptane/ethyl acetate 25:1) to furnish *rac*-**3** (1.70 g, 37%; 99.5% purity by HPLC) as colourless crystals. Starting from **8b** (2.2 g, 5.3 mmol) the analogous procedure yielded 0.40 g (27%) of *rac*-**3**. For mesophases and electrooptical properties see Table 1. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ_H = 4.93-4.62 (mc, 1H), 4.18-3.85 (mc, 1H), 2.00-1.90 (m, 1H), 1.83-1.63 (m, 8H), 1.47-1.23 (m, 5H), 1.17-0.68 (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ_C = 98.1 (dd, *J* = 178.9 Hz, *J* = 19 Hz), 88.2 (dd, *J* = 173.4 Hz, *J* = 20.8 Hz), 43.1 (d, *J* = 25.4 Hz), 39.8, 38.4 (dd, *J* = 19.7 Hz, *J* = 4.2 Hz), 37.6, 33.5, 30.0, 29.2 (d, *J* = 18.0 Hz), 28.7 (d, *J* = 6.4 Hz), 28.1 (d, *J* = 4.0 Hz), 20.0, 16.4 (dd, *J* = 23.2 Hz, *J* = 7.2 Hz), 14.4; ^{19}F NMR (235 Hz, $CDCl_3$, 300 K): δ_F = -191.02 (mc, 1F), -202.50 (mc, 1F); MS (EI, 70 eV): *m/z* (%) = 286 (44)[M^+], 160 (37), 125 (73), 83 (69), 81 (60), 69 (100), 67 (23), 55 (45).

HRMS(EI) calc for $C_{18}H_{32}F_2$ (M^+)286.2478 found (M^+)286.2471.

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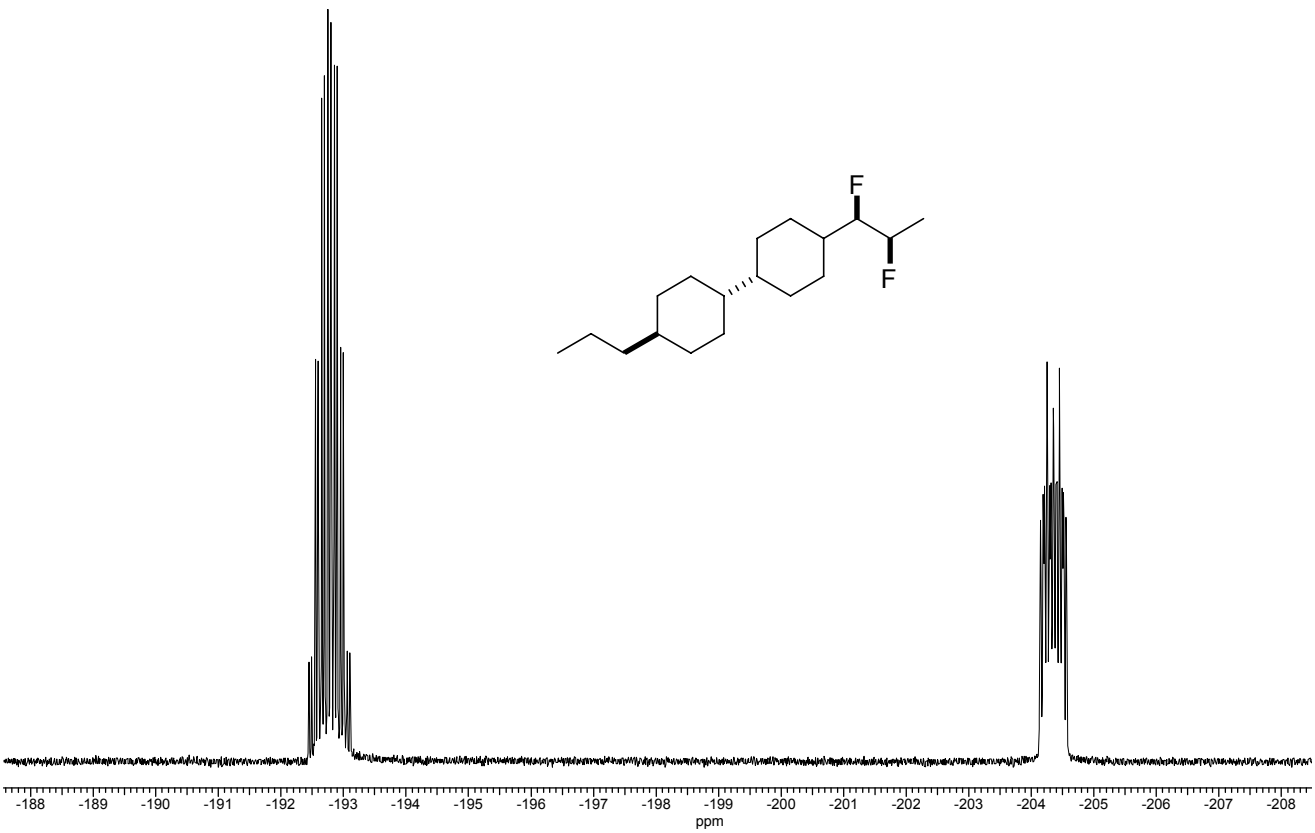
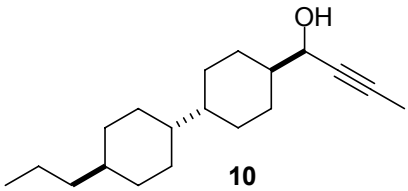


^{19}F-NMR or rac-**3** showing both fluorine signals and a single diastereoisomer.

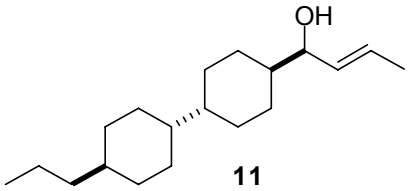
Preparation of Liquid crystal *rac*-4.



10

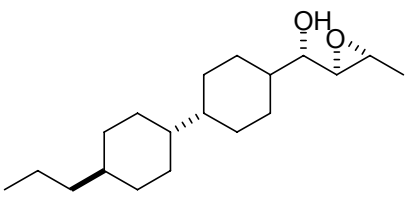
Preparation of 10: Propyne gas (4.3 g, 93 mmol) was bubbled through a solution of *n*-butyl lithium (15% in *n*-hexane; 58 ml) in THF (100 ml) at –78°C for 30 min. $CeCl_3$ (pearls – 10 mesh; 25.2 g, 101 mmol) was placed in a three-neck flask and heated in vacuo to 140°C for 2 h. After cooling down, dry THF was added to form a suspension which was cooled to –78°C. To this solution, the previously prepared propynyl lithium solution was added at -78°C over 1 h. Then, a cooled (-78°C) solution of the propylbicyclohexyl carbaldehyde **9** in THF (200 ml) was added dropwise over 2 h, and stirring was continued until TLC monitoring (*n*-hexane/ethyl acetate 3:1) indicated complete consumption of the starting material. After addition of saturated aqueous NH_4Cl the mixture was allowed to warm up to room temperature. It was extracted with methyl *tert*-butyl ether, and the extract was washed with water and brine, dried over $MgSO_4$ and concentrated to dryness. The residue was filtered in through a short dad of silica gel (*n*-heptane/ethyl acetate 5:1) to furnish the alcohol **10** (7.0 g, 27%; 99% purity by HPLC) as a colourless solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ_H = 4.10 (br. m, 1H), 1.95-1.53 (m, 12H), 1.51-0.82 (m, 19H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ_C = 81.4, 79.2, 67.3, 44.4, 43.2, 43.1, 39.7, 37.5, 3.4, 30.0, 29.2, 28.6, 28.1, 19.9, 14.2, 3.4; MS (EI, 70 eV): *m/z* (%)

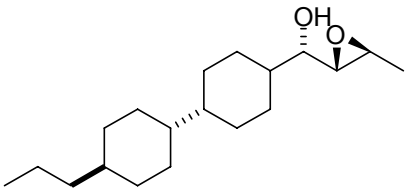
= 276 (3)[M^+], 258 (9), 207 (37), 151 (15), 137 (14), 125 (30), 111 (35), 97 (36), 83 (74), 69 (100), 55 (59).



11

Preparation of allylic alcohol 11: Propargylic alcohol **10** (12.0 g, 43 mmol) in THF (25 ml) was added dropwise to a suspension of $LiAlH_4$ (4.04 g, 106 mmol) in THF (50 ml) at 0°C over a period of 10 min. The mixture was refluxed for 18 h until GC-MS analysis indicated the full consumption of the starting material. The reaction was quenched by careful addtion (under ice-cooling) with water (3 ml). The precipitated solid was washed with methyl *tert*-butyl ether. The organic extracts were collected and evaporated to dryness. The crude product was purified by chromatography (silica gel; *n*-heptane/ethyl acetate 6:1) to yield **11** as a colourless solid (7.0 g, 59%). ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ_H = 5.66-5.57 (m, 1H), 5.52-5.44 (m, 1H), 3.74 (br. t, *J* = 6.8 Hz, 1H), 1.94-1.89 (m, 1H), 1.80-1.65 (m, 10H), 1.40-1.25 (m, 4H), 1.16-1.10 (m, 3H), 1.05-0.80 (m, 13H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ_C = 132.7, 127.3, 77.8, 43.8, 43.3, 43.2, 39.7, 33.5, 30.0, 29.6, 29.5, 28.8, 19.9, 17.6, 14.3; MS (EI, 70 eV): *m/z* (%) = 278 (23)[M^+], 260 (17), 207 (13), 125 (13), 111 (13), 83 (35), 71 (100), 55 (31).

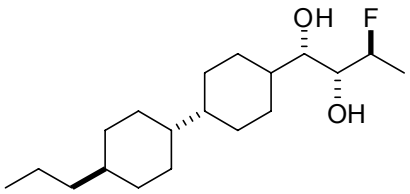


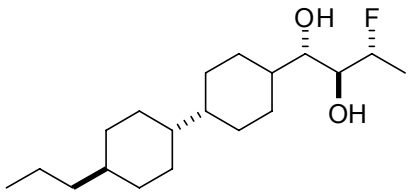


12a	:	**12b**
3	:	1

Preparation of epoxides 12a and **12b**: A solution of allylic aclohol **11** (7.0 g, 25 mmol) and 3-chloro perbenzoic acid (6.9 g, 28 mmol; 70% purity) in CH_2Cl_2 (25 ml) was stirred at 0°C for 2 h. Then, after addition of 10% (w/v) aqueous solution of Na_2SO_3 (50 ml) the mixture was stirred for additional 20 min at 0°C. The organic layer was separated, washed twice with saturated aqueous $NaHCO_3$ (20 ml each), dried over $MgSO_4$ and evaporated to dryness. The crude product was recrystallized from *n*-pentane at 0°C to give a mixture of **12a** and **12b** (7.0 g, 95%) as a 3:1 mixture as colourless crystals. It is assumed that the major isomer is the syn isomer **12a** following from from our previous studies and the well known Henbest effect.

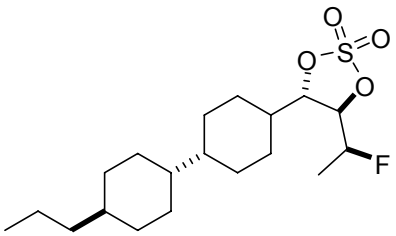
^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ_H = 3.58 (mc, 1H), 3.15-3.05 (m, 2H), 2.94 (mc, 1H), 2.78-2.72 (m, 2H), 2.00-0.80 (m, 2 x 31H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ_C= 75.5, 72.2, 61.3, 60.4, 52.9, 50.8, 43.2, 43.1, 42.2, 41.6, 39.7, 37.5, 35.5, 29.9, 29.6, 29.5, 29.4, 28.8, 28.7, 28.4, 19.9, 17.0, 14.2; MS (EI, 70 eV): *m/z* (%) = 294 (2)[M^+], 276 (10), 206 (12), 151 (20), 135 (10), 123 (33), 109 (43), 95 (50), 88 (20), 81 (73), 69 (100), 58 (28), 55 (73).



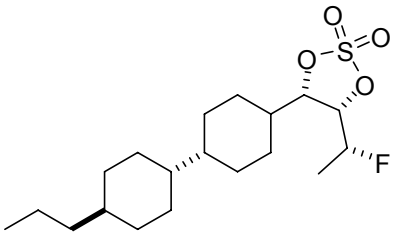


13a	:	**13b**
3	:	1

Fluorohydrins 13a and **13b**: The 3 : 1 diastereoisomeric mixture of expoxides **12a** and **12b** (7.0 g, 24 mmol) in CH_2Cl_2 (100 ml) was treated with 65% HF-pyridine (4.4 ml) at –5°C for 4 h. The reaction mixture was poured into an excess of 5% (w/v) aqueous $NaHCO_3$ in order to neutralize the HF. The organic layer was separated, washed with aqueous NH_4Cl, dried over $MgSO_4$ and evaporated to dryness. The crude product was chromatographed over silica gel (*n*-heptane/ethyl acetate 3:1) to yield 6.0 g (79%) of a 3 : 1 mixture of **13a** and **13b** as a colourless solid. ^1H NMR (500 MHz, $CDCl_3$, 303 K): δ_H = 4.82-4.53 (m, 2 x 1H), 4.06-3.38 (m, 2 x 2H), 2.4-0.75 (m, 2 x 32H); ^{19}F NMR (235 Hz, $CDCl_3$, 300 K): δ_F = -181.86 (mc, 1F), -183.05 (mc, 1F).



14a



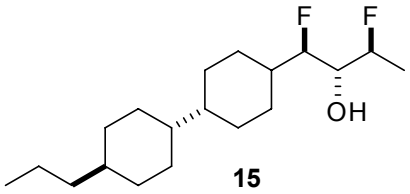
14b

Cyclic sulfates 14a and **14b**: The 3 : 1 mixture of fluorohydrin diastereoisomers **13a** and **13b** (3.15 g, 10 mmol) in CH_2Cl_2 (50 ml) was treated with pyridine (1.2 ml) at room temperature. After cooling down to 0°C, $SOCl_2$ (0.87 ml, 12 mmol) was added dropwise via a syringe. The mixture was stirred at 0°C for 30 min, then saturated aqueous $NaHCO_3$ as added. The separated organic layer was dried over $MgSO_4$, and the solvent was removed. The crude cyclic sulfite was dissolved in acetonitrile (20 ml). First $NaIO_4$ (5.36 g, 25 mmol) was added, followed by a catalytic quantity of $RuCl_3 \cdot 3H_2O$ (20 mg) and water (18 ml). The heterogeneous mixture was stirred vigorously at 0°C until no starting material was detectable by TLC (4 h). After addition of diethyl ether (20 ml), the organic layer was separated, washed with 5% (w/v) aqueous $NaHCO_3$, dried over $MgSO_4$, filtered over a pad of silica gel and evaporated to dryness. The crude product was chromatographed over silica gel (*n*-heptane/ethyl acetate 8:1) to obtain the two diastereomers **14a** (0.8 g, 21%) and **14b** (1.2 g, 32%) as colourless solids. For preparative purposes a sample of **14a** was used contaminated with **14b** (~10%)

14a: ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ_H = 4.75 (dt, *J* = 44.0 Hz, *J* = 7.0 Hz, 1H), 4.60-4.54 (m, 2H), 1.97 (d, *J* = 15.0 Hz, 1H), 1.86-1.65 (m, 10H), 1.48 (dd, *J* = 28.2 Hz, *J*

= 7.9 Hz, 3H), 1.33-0.80 (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ_C = 88.4 (d, *J* = 172.7 Hz), 88.3, 83.4 (d, *J* = 29.8 Hz), 43.3 (d, *J* = 19.2 Hz), 40.9, 40.1, 38.0, 33.8, 30.4, 29.4, 29.0 (d, *J* = 13.3 Hz), 27.8, 20.4, 17.3 (d, *J* = 21.7 Hz), 14.8; ^{19}F NMR (235 Hz, $CDCl_3$, 300 K): δ_F = -186.21 (mc, 1F); MS (EI, 70 eV): *m/z* (%) = 376 (20)[M^+], 278 (14), 153 (19), 125 (85), 95 (14), 83 (78), 69 (100), 55 (27).

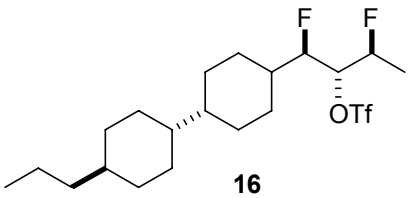
14b: ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ_H = 5.06 (dt, *J* = 45.8 Hz, *J* = 8.5 Hz, 1H), 4.78-3.72 (m, 2H), 2.02 (d, *J* = 15.0 Hz, 1H), 1.92-1.66 (m, 10H), 1.53 (dd, *J* = 28.0 Hz, *J* = 7.0 Hz, 3H), 1.33-0.80 (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ_C = 89.8, 85.8 (d, *J* = 170.6 Hz), 85.1 (d, *J* = 31.6 Hz), 43.3 (d, *J* = 25.7 Hz), 40.7, 38.0, 37.2, 33.9, 30.4, 30.1, 28.9, 20.4, 18.1 (d, *J* = 21.9 Hz), 14.8; ^{19}F NMR (235 Hz, $CDCl_3$, 300 K): δ_F = -182.07 (mc, 1F); MS (EI, 70 eV): *m/z* (%) = 376 (42)[M^+], 278 (15), 153 (17), 125 (80), 95 (17), 83 (71), 69 (100), 55 (47).



15

15: A solution of **14a** (1.20 g, 3.19 mmol) in acetonitrile (50 ml) was cooled to 0°C and the treated via a syringe with tetrabutyl ammonium fluoride (1 M solution in THF; 3.73 ml, 3.73 mmol). The reaction was monitored by TLC (silica gel; *n*-heptane/ethyl acetate 4:1) for 1 h, until the starting material was consumed. Then, the solvent was

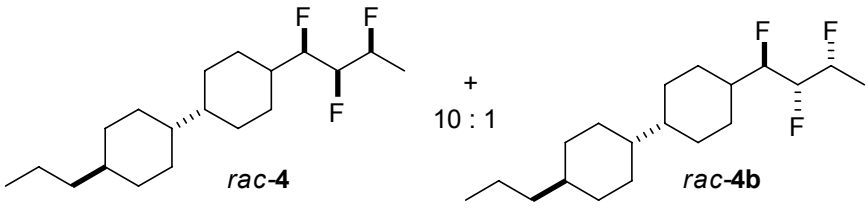
evaporated and the residue dissolved in THF (30 ml). Sulfuric acid 98% (330 µl) was added, and the mixture was stirred for 12 h at room temperature. After the addition of saturated aqueous $NaHCO_3$, the solution was extracted twice with methyl *tert*-butyl ether (30 ml each) and the combined organic phases were evaporated to dryness. The crude product was purified by chromatography (silica gel; *n*-heptane/ethyl acetate 10:1) to furnish **15** (500 mg, 50%) as a colourless solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ_H = 5.00-4.75 (m, 2 x 1H), 4.37-3.99 (m, 2 x 1H), 3.65-3.47 (m, 2 x 1H), 2.10-1.63 (m, 2 x 10H), 1.47-0.80 (m, 2 x 21H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ_C = 95.9 (dd, *J* = 171.4 Hz, *J* = 6.8 Hz), 94.5 (d, *J* = 171.4 Hz), 90.5 (d, *J* = 160.1 Hz), 89.1 (d, *J* = 167.6 Hz), 43.2 (d, *J* = 21.1 Hz), 42.6, 39.7, 38.6 (d, *J* = 19.6 Hz), 38.2 (d, *J* = 18.9 Hz), 37.5, 33.4, 31.9, 31.7, 29.9-28.9 (m), 26.6, 26.0 (d, *J* = 4.5 Hz), 25.1 (d, *J* = 4.5 Hz), 22.5, 19.9, 16.9 (d, *J* = 22.7 Hz), 14.2, 13.9; ^{19}F NMR (235 Hz, $CDCl_3$, 300 K): δ_F = -184.31 (mc, 1F), -195.70 (mc, 1F), -202.18 (mc, 1F), -204.64 (mc, 1F); MS (EI, 70 eV): *m/z* (%) = 316 (8)[M^+], 298 (10), 276 (30), 269 (13), 249 (98), 125 (59), 123 (59) 109 (23), 95 (47), 83 (75), 81 (78), 69 (100), 55 (62).



16

Triflate 16: A mixture of **15** (500 mg, 1.58 mmol) in CH_2Cl_2 (20 ml) was treated with pyridine (200 µl) at -40°C. After

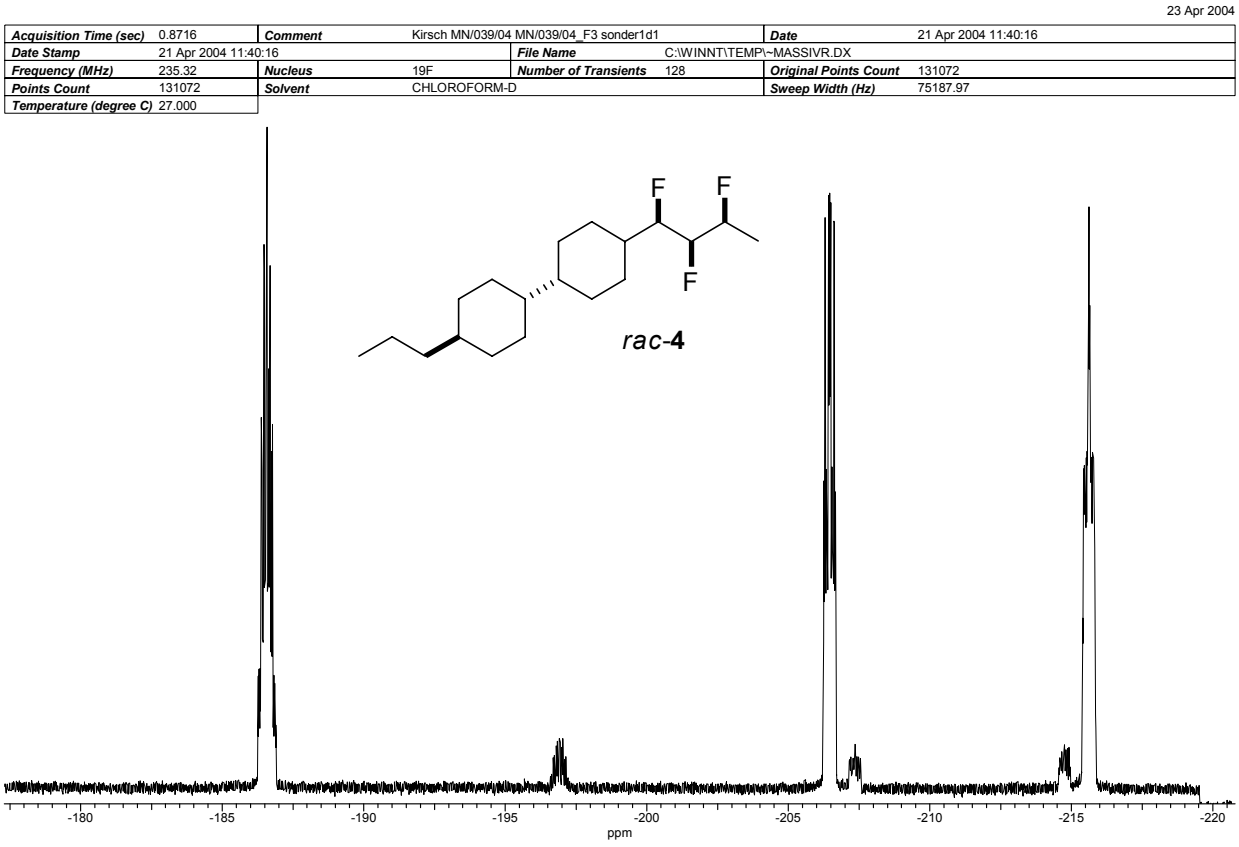
5 min, triflic anhydride (300 µl, 2.0 mmol) was added dropwise. The mixture was stirred for 2 h at -40°C, then cold *n*-heptane (10 ml) was added, and the precipitate was filtered off and discarded. The filtrate was evaporated to dryness to furnish **16** (260 mg, 37%), a material which was used directly without purification.



rac-**4** *rac*-**4b**

Liquid crystal *rac*-**4**: The preparation of **16** (520 mg, 1.16 mmol) in THF (20 ml) was treated at 0°C dropwise *via* a syringe with tetrabutylammonium fluoride (1 M solution in THF; 1.16 ml, 1.16 mmol). The reaction was monitored by TLC until the starting material was consumed (~45 min). Then, the mixture was diluted with saturated aqueous NH_4Cl solution, extracted twice with methyl *tert*-butyl ether (30 ml each), and the solvent was evaporated. The product was purified by chromatography (silica gel; *n*-heptane/ethyl acetate 25:1) to furnish *rac*-**4** (40 mg, 11%; 90% purity by HPLC, 10% impurity was diastereoisomer **4b** - see ^{19}F-NMR) as colourless crystals. The available quantity and the purity of the product was insufficient to determine mesophase sequence and transition temperatures. For virtual clearing point and electrooptical properties see Table 1. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ_H = 4.90-4.63 (m, 1H), 4.54-4.00 (m, 2H), 2.06-1.95 (m, 1H), 1.76-1.57 (m, 8H), 1.47-0.75 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ_C = 43.0 (d, *J* = 24.7 Hz), 39.6, 37.9 (d, *J* = 16.4 Hz), 37.5, 33.4, 31.7,

30.0 (d, *J* = 20.5 Hz), 28.9 (d, *J* = 14.6 Hz), 28.2 (d, *J* = 7.1 Hz), 22.5, 19.9, 17.0 (d, *J* = 22.3 Hz), 14.2, 13.9; ^{19}F NMR (235 Hz, $CDCl_3$, 300 K): δ_F = -187.07 (mc, 1F), -207.00 (mc, 1F), -216.08 (mc, 1F); MS (EI, 70 eV): *m/z* (%) = 318 (2)[M^+], 192 (12), 125 (43), 113 (11), 91 (12), 83 (83), 81 (68), 69 (100), 55 (67).



^{19}F-NMR of *rac*-**4** showing a 10% contamination of isomer *rac*-**4b**