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Journal of Fluorine Chemistry 120 (2003) 85–91
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/jfluchem

Organofluorine compounds and fluorinating agents Part 28. New perfluoroalkyl substituted chiral mesogens☆

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Received 21 September 2002; received in revised form 7 November 2002; accepted 12 November 2002

Abstract

The perfluorohexyl-aryl-thioethers **3** and **4**, building blocks for the synthesis of the chiral target mesogens **12–15**, were prepared by dithionite-mediated *S*-perfluoroalkylation of the *p*-substituted thiophenols **1** and **2**. The phenolic HO– group of **3** was *O*-glucosylated with pentaacetyl-D-glucopyranose to **5** followed by deacetylation forming the tetrol **6** and by acetalizing with 4-(4-perfluorohexylsulfanyl-benzoyloxy)-benzaldehyde-dimethylacetal (**8**) generating the dihydroxy-intermediate **9**. The latter contains two perfluorohexylthio chains. Alternatively, the dimethylacetal **8** was linked to *p*-octylphenyl-β-D-glucopyranoside (**10**) giving the mixed octyl/perfluorohexyl substituted *p*-octylphenyl-4,6-*O*-[4′-(4″-perfluorohexylsulfanyl)-benzoyloxy]-benzylidene-β-D-glucopyranoside (**11**). Compound **8** was obtained via esterification of **4** with *p*-hydroxy-benzaldehyde to 4-(4-perfluorohexylsulfanyl-benzoyloxy)-benzaldehyde (**7**). Finally, the diols **9** and **11** were dehydroxylated to **12** and **13** followed by hydrogenation yielding **14** and **15**, respectively. Tetrol **6**, diols **9**, **11** and the non-amphiphilic compounds **7**, **12–15** are thermotropic liquid crystals.

Keywords: Fluorinated compounds; Perfluoroalkylation; Carbohydrates; Liquid crystals

1. Introduction

In the last two decades interest in carbohydrate-derived liquid crystals increased greatly (for reviews see [2–6]). The introduction of perfluoroalkyl chains has a remarkable effect on the stabilization of mesophases, especially on those formed by amphiphilic mesogens [7]. This is due to the higher stiffness combined with loss of conformational freedom of perfluoroalkyl chains compared with alkyl chains. Furthermore, the intramolecular contrast between the polar head group and the hydrophobic chain is higher in amphiphiles when an alkyl chain is replaced by a perfluoroalkyl chain of same length. This usually leads to higher clearing points of the corresponding perfluoroalkylated thermotropic amphiphiles. Recently, a review was published discussing these effects in detail [8].

In 1996, Vill et al. [9] described an efficient pathway to synthesize chiral non-amphiphilic carbohydrate-derived liquid crystals starting with a Ferrier reaction. The reported synthesis strategy is not practicable to build up similar structures with perfluoroalkyl chains in place of alkyl chains, because the lower nucleophilicity of fluorinated building blocks (e.g. perfluorohexylpropyl-phenylether) prevents the first synthesis step. However, perfluoroalkylated non-amphiphilic liquid crystals based on carbohydrates are easily accessible via radical perfluoroalkylation of unsaturated precursors [10]. Radical initiated perfluoroalkylations of unsaturated compounds and of thiols are well-established methods to introduce perfluoroalkyl chains in organic substrates (see [11–14] and papers cited therein).

2. Results and discussion

2.1. Synthesis

Aromatic building blocks are often used in liquid crystals. Recently, first examples of liquid crystals were described in which fluoroalkyl aromatics are linked to carbohydrates [15]. Our strategy to prepare further new perfluoroalkyl substituted mesogens uses as the key step a radical *S*-perfluoroalkylation mediated by sodium dithionite. The thiophenols **1** and **2** formed with 1-iodo-perfluorohexane the thioethers **3** and **4** in yields of 43 and 78%, respectively. 4-Perfluoroalkylsulfanyl-phenol **3** was subsequently gluco-

☆ For Part 27, see [1].

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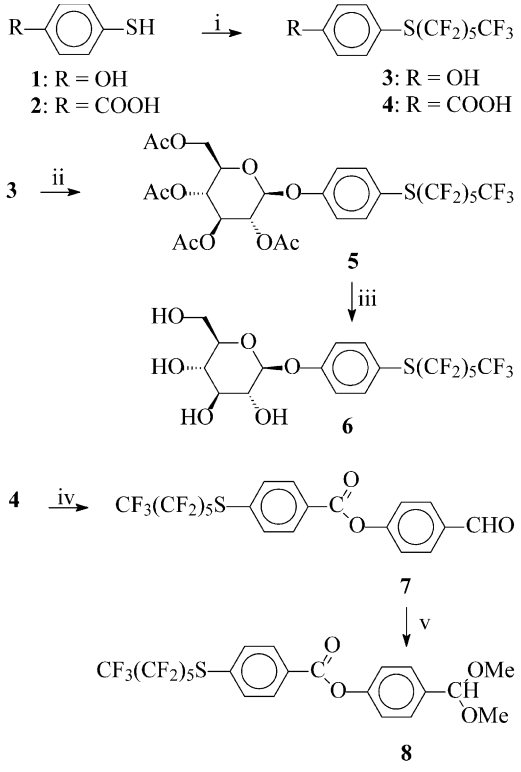
0022-1139/02/$ – see front matter
PII: S0022-1139(02)00310-X



i: $C_6F_{13}I/Na_2S_2O_4/NaHCO_3$, DMF/$H_2O$, 1.5 h, 0°C to 20°C;
ii: 1,2,3,4,6-Penta-*O*-acetyl-ß-D-glucopyranose, BF_3xEt_2O, CH_2Cl_2, 16 h, 0°C to 20°C;
iii: NaOMe/MeOH, 3 h, 20°C; iv: *p*-Hydroxybenzaldehyde, DMAP, CH_2Cl_2, 20°C, 4 days;
v: Trimethyl-orthoformate, MeOH, H^+-resin, 4 h, reflux.

Scheme 1.

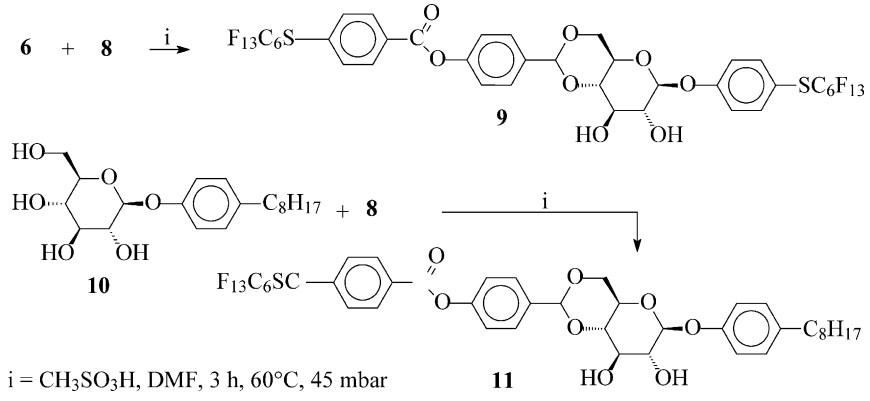
sylated with glucose pentaacetate in a boron trifluoride catalyzed reaction analogously to [16] and the resulting β-glucoside **5** was deprotected analogously to [17] yielding the amphiphile **6** (Scheme 1). Furthermore, perfluoroalkylsulfanyl-benzoic acid **4** was treated with *p*-hydroxy-benzaldehyde and 4-(dimethylamino)-pyridine in dichloromethane yielding aldehyde **7** followed by acetalizing with methanol in the presence of trimethyl orthoformate giving dimethyl acetal **8** (Scheme 1).

Compound **6** was connected with dimethylacetal **8** by a transacetalizing reaction catalyzed by methanesulfonic acid. The resulting dihydroxy derivative **9** contains two perfluoroalkyl chains. In the same manner the non-fluorinated amphiphile **10** [18] was connected with dimethylacetal **8** yielding the mixed alkyl/perfluoroalkyl substituted derivative **11** (Scheme 2).

To obtain the non-amphiphilic target products **12** and **13**, the dihydroxy derivatives **9** and **11** were dehydroxylated by application of a modified method of Garegg and Samuelsson [19] (Scheme 3). Thus, the diols **9** and **11** were treated for 3 h with PPh_3, triiodoimidazole and imidazole in dry xylene at 130 °C. The isolation of the pure products **12** and **13** required a separation by flash chromatography.

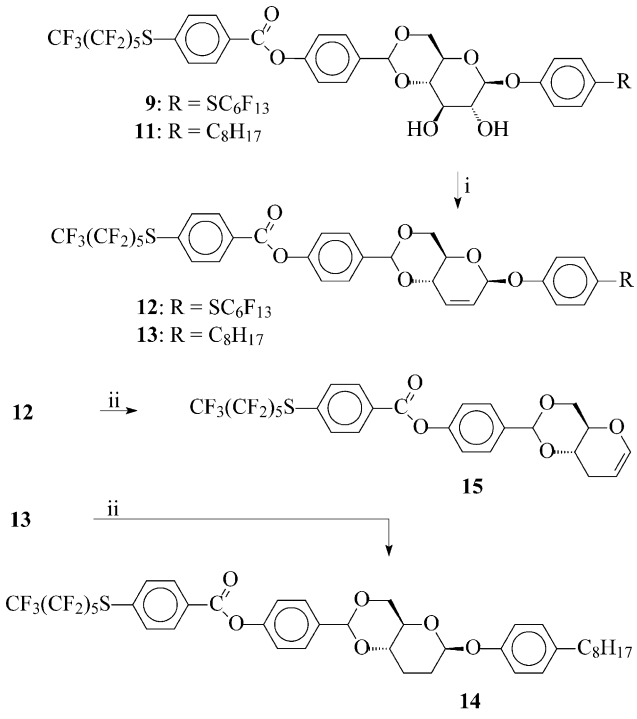
The structures of the compounds **9**, **11–13** are supported by ^1H, ^{13}C, and ^{19}F NMR spectra including correlation spectra. It is noteworthy that compound **9** is insoluble in all relevant solvents at room temperature. Therefore, the NMR spectra of this compound were recorded at 40 °C, however, the optical rotation was not measured.

The unsaturated compounds **12** and **13** were finally treated with dihydrogen and palladium on charcoal to hydrogenate the C=C double bond (Scheme 3). These hydrogenations gave a surprise. Whereas the mixed alkyl/perfluoroalkyl derivative **13** yielded the expected saturated product **14**, compound **12** reacted in a different way. In this case, a reductive cleavage of the glycosidic bond occurs accompanied by migration of the double bond yielding 3-deoxyglucal **15**. The structure of the latter is supported by NMR spectroscopic data. Thus, the C-1 signal of **15** shows a significant downfield shift compared to starting material **12** (**12**: $\delta = 96.3$ ppm; **15**: $\delta = 143.1$ ppm). Furthermore, a second CH_2 group is found at 26.3 ppm (DEPT spectrum) and the ^{19}F NMR spectrum of **15** shows only the characteristic signals of one SC_6F_{13} group. The SCF_2-fluoro signal is easily assigned. Whereas compound **12** shows two multiplets of SCF_2 groupings at $\delta = -85.8$ and -87.1 ppm, the



i = CH_3SO_3H, DMF, 3 h, 60°C, 45 mbar

Scheme 2.



i: PPh_3/triiodoimidazole/imidazole, xylene, 3 h, 130°C, argon;
ii: H_2, Pd/C (10%), ethanol/ethyl acetate (1:1 v/v)

Scheme 3.

^{19}F NMR spectrum of compound **15** shows only the signal at $\delta = -85.8$ ppm.

2.2. Thermal behavior

The thermotropic liquid crystalline properties of the tetrol **6**, the diols **9**, **11** and the non-amphiphilic mesogens **7**, **12**–**15** were investigated by polarizing microscopy and by DSC measurements (transition temperatures given in Table 1 are DSC data). The textures observed under the polarizing microscope allowed an assignment of the phase type. All mesogens except compound **6** show a very colorful fan-like texture, which is typical for *smectic* A phases. The texture of compound **6** is less colored, however, likewise, a *smectic* A phase type. The non-amphiphilic mesogen **12** showed under certain circumstances polymorphism. When the isotropic melt of **12** was cooled down, a fan-shaped texture (*smectic* A phase) as well as a striated fan-shaped texture (chiral *smectic* C^* phase) were observed.

However, the appearance of the striated fan-shaped texture varies depending on the cooling rate, i.e. the slower the sample is cooled down, the higher is this transition point. DSC measurements indicate that compound **12** gradually decomposes in the corresponding temperature range (Table 1), i.e. the *smectic* C^* phase is probably induced by any reaction products. A further phenomenon was observed in the case of liquid crystals **11** and **13**. Whereas on heating of **11** and **13** the transition temperatures of polarizing microscopic investigation and DSC measurements are easily detectable, the behavior on cooling down is quite different. The liquid crystalline textures can certainly be observed under the polarizing microscope, but the DSC measurements show no energetic effects on cooling of their melts (Table 1).

A further result is noteworthy. Compared to the other mesogens, the enthalpy value for the transition *smectic* A/isotropic liquid of compound **14** is significantly higher than the transition crystalline/*smectic* A (Table 1).

3. Experimental

The reactions were followed by thin layer chromatography using pre-coated aluminum sheets (silica gel 60, F 254,

Table 1
Thermal data of the mesogens **6**, **7**, **9**, and **11**–**15** based on DSC measurements

No.	Transition temperatures	Enthalpies (J/g)	Comments
6	$cr \xrightarrow{168\,^\circ C} S_A \xrightarrow{226\,^\circ C} i$	$\Delta H_{cr\rightarrow S_A} = 45.93$	Decomposition while melting
7	$cr \underset{54\,^\circ C}{\overset{74\,^\circ C}{\rightleftharpoons}} S_A \underset{110\,^\circ C}{\overset{114\,^\circ C}{\rightleftharpoons}} i$	$\Delta H_{cr\rightarrow S_A} = 45.06$, $\Delta H_{S_A\rightarrow i} = 4.84$	
9	$cr \underset{138\,^\circ C}{\overset{179\,^\circ C}{\rightleftharpoons}} S_A \underset{200\,^\circ C}{\overset{213\,^\circ C}{\rightleftharpoons}} i$	$\Delta H_{cr\rightarrow S_A} = 30.57$, $\Delta H_{S_A\rightarrow i} = 2.42$	
11	$cr \xrightarrow{150\,^\circ C} S_A \xrightarrow{229\,^\circ C} i$	$\Delta H_{cr\rightarrow S_A} = 32.46$, $\Delta H_{S_A\rightarrow i} = 6.37$	Reentrance of lc-phase only under microscope, no recrystallization
12	$cr \xrightarrow{168\,^\circ C} S_A \underset{176\,^\circ C}{\overset{186\,^\circ C}{\rightleftharpoons}} i$; $128\,^\circ C$ / $160\,^\circ C$; $(S_C^*?)$	$\Delta H_{cr\rightarrow S_A} = 45.22$, $\Delta H_{S_A\rightarrow i} = 7.25$	Annotations (see text)
13	$cr \underset{112\,^\circ C}{\overset{147\,^\circ C}{\rightleftharpoons}} S_A \underset{204\,^\circ C}{\overset{211\,^\circ C}{\rightleftharpoons}} i$	$\Delta H_{cr\rightarrow S_A} = 39.30$, $\Delta H_{S_A\rightarrow i} = 15.26$	No DSC-values for cooling
14	$cr_1 \xrightarrow{42\,^\circ C} cr_2 \xrightarrow{170\,^\circ C} S_A \underset{185\,^\circ C}{\overset{195\,^\circ C}{\rightleftharpoons}} i$	$\Delta H_{cr_1\rightarrow cr_2} = 12.91$, $\Delta H_{cr_2\rightarrow S_A} = 4.84$, $\Delta H_{SA\rightarrow i} = 64.23$	No recrystallization
15	$cr \underset{110\,^\circ C}{\overset{136\,^\circ C}{\rightleftharpoons}} S_A \underset{157\,^\circ C}{\overset{160\,^\circ C}{\rightleftharpoons}} i$	$\Delta H_{cr\rightarrow S_A} = 61.02$, $\Delta H_{S_A\rightarrow i} = 6.05$	

Merck); detection was affected by observation under UV irradiation (254 nm) or spraying with 10% methanolic sulfuric acid solution and subsequent thermal treatment. Silica gel 60 (0.062–0.2 mm, Merck) and silica gel 60 (40–63 μm, Merck), respectively, were used for column chromatographic separations. All solvents were purified and dried using standard procedures [20]. Melting points were determined with a Leitz Laborlux 12 Pol microscope equipped with a Mettler FP 90 hot stage. Optical rotations were measured on a polarimeter Polar LμP (IBZ Meßtechnik) and the NMR spectra were recorded on a Bruker AC-250 and a Bruker ARX-300 using TMS and CCl_3F as internal standards, respectively. Chemicals: 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (Fluka), 1-iodo-perfluorohexane (Fluka), sodium dithionite (Fluka), 4-mercaptophenol (Aldrich), 4-mercaptobenzoic acid (Fluka), 4-(dimethylamino)-pyridine (Fluka), triphenylphosphine (Fluka), dicyclohexyl carbodiimide (Fluka), trimethylorthoformate (Fluka), Amberlite IR-120 (Fluka), Amberlite IRA-400 (Fluka).

3.1. 4-(Perfluorohexylsulfanyl)-phenol (3)

To a stirred and cooled solution of 4-mercaptophenol (**1**) (5.0 g, 40 mmol) in DMF (100 ml) saturated aq. $NaHCO_3$-solution (100 ml) and 1-iodo-perfluorohexane (17.3 ml, 77.6 mmol) were added. Then sodium dithionite (6.97 g, 40 mmol) was added in small portions under a inert gas atmosphere. After completion of the reaction (tlc-control heptane/EtOAc 5:1 (v/v), **3**: $R_F = 0.26$) the reaction mixture was diluted with diethyl ether (200 ml), washed with brine (100 ml) and water (100 ml), dried (Na_2SO_4) and concentrated under reduced pressure.

The residue was purified by column chromatography (heptane/EtOAc 5:1 (v/v), $R_F = 0.26$) followed by sublimation at 150 °C bath temperature and pressure <1 mmHg yielding 7.69 g (43%) of **3**; mp 28–30 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.52 (m, 2H, Ph), 7.86 (m, 2H, Ph), 5.24 (s, 1H, –OH); ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) = 158.2 (s, C_q), 139.4 (s, C_t), 116.5 (s, C_t); ^{19}F NMR (235 MHz, $CDCl_3$): δ (ppm) = −80.5 (m, CF_3), −87.5 (s, SCF_2), −119.0, −121.2, −122.5, −125.9 (4s, $4CF_2$); $m/z = 444$ $[M]^+$; HRMS 443.98135.

$C_{12}H_5F_{13}OS$ (443.99): Calcd. C: 32.45%, H: 1.13%, S: 7.22%; found C: 32.43%, H: 1.40%, S: 7.08%.

3.2. 4-(Perfluorohexylsulfanyl)-benzoic acid (4)

To a stirred mixture of 4-mercaptobenzoic acid (**2**) (1.23 g, 8.0 mmol) in DMF (80 ml) and saturated aq. $NaHCO_3$-solution (80 ml) 1-iodo-perfluorohexane (3.47 ml, 16 mmol) and sodium dithionite (1.39 g, 8.0 mmol) were added. The stirring was continued at room temperature for approximately 2 h. After complete conversion (tlc-control, eluent EtOAc/toluene 1:1 (v/v)), the reaction mixture was diluted with brine (50 ml) and acidified with concentrated hydrochloric acid to slight acidic reaction (pH 6). This solution was extracted three times with diethyl ether (50 ml each). The combined organic phases were washed with water (20 ml), dried (Na_2SO_4) and concentrated under reduced pressure. The residue was recrystallized from aq. MeOH yielding 2.96 g (78%) of **4**. Colorless crystals; mp 184 °C.

^{1}H NMR (300 MHz, Me_2SO-d_6): δ (ppm) = 13.35 (br, 1H, COOH), 8.04 (m, 2H, Ph), 7.02 (m, 2H, Ph); ^{13}C NMR (63 MHz, Me_2SO-d_6): δ (ppm) = 164.2 (s, COOH), 134.9 (s), 131.5 (s), 128.2 (s), 124.2 (m); ^{19}F NMR (235 MHz, Me_2SO-d_6): δ (ppm) = −80.5 (s, CF_3), −86.5 (m, SCF_2), −119.4, −121.7, −123.1, −126.4 (4s, $4CF_2$).

$C_{13}H_5F_{13}O_2S$ (472.22): Calcd. C: 33.07%, H: 1.07%, S: 6.79%; found C: 32.92%, H: 1.07%, S: 7.02%.

3.3. (4-Perfluorohexylsulfanyl-phenyl)-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (5)

To a solution of compound **3** (3.5 g, 7.88 mmol) and 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (6.0 g, 15.37 mmol) in dry dichloromethane (18 ml) an ethereal solution of boron trifluoride (1.0 ml) was added at 0 °C under inert gas atmosphere. This mixture was allowed to warm up to room temperature and then was stirred for 24 h. After completion of the reaction (tlc-control), the solution was poured onto saturated aq. $NaHCO_3$ solution (50 ml) with stirring. The organic phase was separated and the aqueous phase was extracted with dichloromethane (50 ml). The combined organic extracts were washed with water, dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography (eluent heptane/EtOAc 5:1 (v/v), **5**: $R_F = 0.05$) and recrystallized from aqueous ethanol yielding 4.02 g (66%) of **5**. White crystals; mp 111–112 °C; $[\alpha]_D^{23}$: −15.1° ($CHCl_3$, $c = 0.98$).

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.58 (m, 2H, Ph), 7.01 (m, 2H, Ph), 5.29 (m, 2H, H-1, H-2), 5.16 (m, 2H, H-3, H-4), 4.28 (dd, 1H, $^2J_{6a/6b} = 12.3$ Hz, $^3J_{5/6a} = 5.4$ Hz, H-6a), 4.16 (dd, 1H, $^3J_{5/6b} = 2.5$ Hz, H-6b), 3.89 (ddd, 1H, $^3J_{4/5} = 8.0$ Hz, H-5), 2.04 (m, 12H, CH_3); ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) = 170.5, 170.2, 169.4, 169.2 (4s, C=O), 158.9 (s, Ph-C_q), 139.1 (s, Ph-C_t), 117.5 (s, Ph-C_t), 116.3 (m, Ph-C_q), 98.2 (s, C-1), 72.5, 72.2, 71.0, 68.1 (4s, C-2, C-3, C-4, C-5), 61.9 (s, C-6), 20.6 (s, CH_3); ^{19}F NMR (235 MHz, $CDCl_3$): δ (ppm) = −80.5 (t, $^3J_{F/F} = 9.5$ Hz, CF_3), −87.2 (t, $^3J_{F/F} = 13.0$ Hz, SCF_2), −119.0 (s, CF_2), −121.2 (s, CF_2), −122.5 (s, CF_2), −125.9 (s, CF_2).

$C_{26}H_{23}F_{13}O_{10}S$ (774.50): Calcd. C: 40.32%, H: 2.99%, S: 4.14%; found C: 40.53%, H: 3.16%, S: 4.44%.

3.4. p-Perfluorohexylsulfanyl-phenyl-β-D-glucopyranoside (6)

Compound **5** (4.52 g, 5.8 mmol) was dissolved in dry MeOH (100 ml) followed by addition of 1% methanolic sodium methoxide (10 ml). After stirring for 3 h at room

temperature the reaction was finished. Then an acidic ion exchanger resin (Amberlite IR-120; 5.0 g) was added and stirring was continued for further 10 min. After filtration, the solution was concentrated under reduced pressure. Then methanol was added in such an amount that the resulting crude product dissolved at room temperature. After that acetonitrile was added (about double the volume of MeOH) and the resulting clear solution was concentrated at room temperature at normal pressure until crystals of the pure product precipitate (3.43 g, 97%). Thermotropic behavior: mp 169 °C, S_A-phase, cp 226 °C; $[\alpha]_D^{25}$: −37.3° (MeOH, $c = 1.12$).

^{1}H NMR (250 MHz, CD_3OD): δ (ppm) = 7.60 (m, 2H, Ph), 7.18 (m, 2H, Ph), 4.97 (m, 1H, H-1), 3.89 (m, 1H), 3.68 (m, 1H), 3.45 (m, 4H); ^{13}C NMR (63 MHz, CD_3OD): δ (ppm) = 164.7 (s, Ph-C_q), 143.1 (s, Ph-C_t), 121.6 (s, Ph-C_t), 118.4 (s, Ph-C_q), 104.6 (s, C-1), 81.2, 80.8, 77.7, 74.1 (4s, C-2, C-3, C-4, C-5), 65.3 (s, C-6); ^{19}F NMR (235 MHz, CD_3OD): δ (ppm) = −79.8 (t, $^3J_{F/F} = 10.5$ Hz, CF_3), −86.3 (t, $^3J_{F/F} = 14.0$ Hz, SCF_2), −117.7 (s, CF_2), −119.8 (s, CF_2), −121.2 (s, CF_2), −124.7 (s, CF_2).

$C_{18}H_{15}F_{13}O_6S$ (606.35): Calcd. C: 35.66%, H: 2.49%, S: 5.29%; found C: 36.05%, H: 2.39%, S: 5.46%.

3.5. 4-(4-Perfluorohexylsulfanyl-benzoyloxy)-benzaldehyde (7)

Compound **4** (1.416 g, 3.0 mmol) was dissolved in dry dichloromethane (70 ml). Then 4-hydroxy-benzaldehyde (0.366 g, 3.0 mmol), 4-(dimethylamino)-pyridine (0.36 g, 0.3 mmol) and dicyclohexyl carbodiimide (0.927 g, 4.5 mmol) were added. This reaction mixture was stirred at room temperature and exclusion of moisture for about 72 h (tlc-control, heptane/EtOAc 5:1 (v/v), $R_F = 0.36$). The precipitated dicyclohexylurea was removed by filtration, the filtrate was concentrated under reduced pressure and the solid residue was recrystallized from isopropanol yielding 1.5 g (60%) of compound **7** as colorless needles. Thermotropic behavior: mp 72 °C, S_A-phase, cp 120 °C.

^{1}H NMR (300 MHz, Me_2SO-d_6): δ (ppm) = 10.04 (s, 1H, –CHO), 8.26 (m, 2H, Ph), 8.04 (m, 2H, Ph), 7.96 (m, 2H, Ph), 7.58 (m, 2H, Ph); ^{13}C NMR (75 MHz, Me_2SO-d_6): δ (ppm) = 191.8 (s, C_q), 163.1 (s, C_q), 154.9 (s, C_q), 137.2 (s, C_t), 134.1 (s, C_q), 131.3 (s, C_q), 131.0 (s, C_t), 130.9 (s, C_t), 122.7 (s, C_t), 99.3 (s, C_t); ^{19}F NMR (235 MHz, Me_2SO-d_6): δ (ppm) = −80.4 (t, $^3J_{F,F} = 10.0$ Hz, CF_3), −86.2 (t, $^3J_{F,F} = 12.0$ Hz, SCF_2), −119.1, −121.4, −122.7, −125.9 (4 m, $4CF_2$); IR (KBr, cm^{-1}) 1746.5 (C=O); 1698.3 (C=O).

$C_{20}H_9F_{13}O_3S$ (576.33): Calcd. C: 41.68%, H: 1.57%, S: 5.56%; found C: 41.74%, H: 1.76%, S: 5.62%.

3.6. 4-(4-Perfluorohexylsufanyl-benzoyloxy)-benzaldehyde-dimethylacetal (8)

Aldehyde **7** (1.4 g, 2.43 mmol) was dissolved in dry MeOH (120 ml) followed by addition of trimethylorthoformate (0.31 ml, 2.8 mmol) and an acidic ion exchanger resin (Amberlite IR-120, 0.5 g). This mixture was refluxed for 4 h under exclusion of moisture. After completion of the reaction (tlc-control) the resin was removed by filtration and the filtrate was neutralized by a basic ion exchanger resin (Amberlite IRA-400, 0.3 g). After 5 min the solution was concentrated under reduced pressure and crude product was recrystallized from isopropanol yielding 1.49 g (98.4%) of **8**; colorless crystals; mp 60 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 8.23 (m, 2H, Ph), 7.82 (m, 2H, Ph), 7.53 (m, 2H, Ph), 7.22 (m, 2H, Ph), 5.43 (s, 1H, acetal-H), 3.34 (s, 6H, CH_3); ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) = 190.9 (s, C_q), 164.0 (s, C_q), 150.7 (s, C_q), 137.1 (s, C_t), 130.9 (s, C_t), 128.1 (s, C_t), 121.3 (s, C_t), 102.5 (s, acetal-C), 52.7 (s, CH_3); ^{19}F NMR (235 MHz, $CDCl_3$): δ (ppm) = −85.7 (t, $^3J_{F,F} = 11.0$ Hz, CF_3), −91.0 (t, $^3J_{F,F} = 12.0$ Hz, SCF_2), −123.9, −126.3, −127.7, −131.0 (4m, $4CF_2$); IR (KBr, cm^{-1}) 1740.7 (C=O).

$C_{22}H_{15}F_{13}O_4S$ (622.40): Calcd. C: 42.46%, H: 2.43%, S: 5.15%; found C: 42.48%, H: 2.40%, S: 5.35%.

3.7. (4-Perfluorohexylsulfanyl-phenyl)-(R)-4,6-O-[4′-(4-perfluorohexylsulfanyl)-benzoyloxyl]-benzylidene-β-D-glucopyranoside (9)

Dimethylacetal **8** (3.5 g, 5.62 mmol) and compound **6** (3.5 g, 5.77 mmol) were dissolved in dry DMF (150 ml). Subsequently, methanesulfonic acid (1 ml) was added. This mixture was attached to a rotary evaporator and kept there for 3 h at 60 °C bath temperature and 45 mbar. After completion of the reaction (tlc-control), saturated aq. $NaHCO_3$ solution (200 ml) was added and the product was extracted by ethyl acetate (twice 100 ml). The combined organic phases were dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash chromatography using an eluent gradient (1 l of toluene/EtOAc 10:1 (v/v), 2 l toluene/EtOAc 1:1 (v/v) ($R_F = 0.38$ at toluene/EtOAc 1:1 (v/v)) yielding 3.47 g, (53.0%) of **9**. Colorless crystals; mp 151.5 °C, S_A-phase, cp 225 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.22 (m, 2H, Ph), 7.79 (m, 2H, Ph), 7.59 (m, 4H, Ph), 7.24 (m, 2H, Ph), 7.09 (m, 2H, Ph), 5.60 (s, 1H, acetal-H), 5.08 (d, $^3J_{1/2} = 7.7$ Hz, 1H, H-1), 4.40 (dd, $^3J_{3/4} = 4.4$ Hz, $^3J_{4/5} = 10.5$ Hz, 1H, H-4), 3.94–3.72 (m, 3H, H-2, H-3, H-6a), 3.69–3.57 (m, 2H, H-5, H-6b); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 163.9 (s, C_q), 159.3 (s, Ph-C_q), 151.6 (s, Ph-C_q), 139.2 (s, Ph-C_t), 137.0 (s, Ph-C_t), 135.0 (s, Ph-C_q), 132.1 (s, Ph-C_q), 130.9, 127.8, 121.5, 117.8 (4s, Ph-C_t), 101.5, 100.9 (2s, acetal-C, C-1), 80.3, 74.5, 73.5, 66.9 (4s, C-2, C-3, C-4, C-5), 68.6 (s, C-6); ^{19}F NMR (235 MHz, $CDCl_3$): δ (ppm) = −80.5 (s, CF_3), −85.8 (m, SCF_2), −87.1 (m, SCF_2), −118.8 (m, CF_2), −121.2 (s, CF_2), −122.5 (s, CF_2), −125.8 (s, CF_2).

$C_{38}H_{22}F_{26}O_8S_2$ (1164.67): Calcd. C: 39.19%, H: 1.90%, S: 5.51%; found C: 39.16%, H: 1.91%, S: 5.55%.

3.8. *p*-Octylphenyl-(R)-4,6-O-[4′-(4-perfluorohexylsulfanyl)-benzoyloxy]-benzylidene-β-D-glucopyranoside (**11**)

A mixture of *p*-octylphenyl-β-D-glucopyranoside [16] (1.5 g, 8.15 mmol) and compound **8** (2.5 g, 4.01 mmol) was dissolved in dry DMF (75 ml). Then methanesulfonic acid (0.75 ml) was added and the mixture was treated as described for compound **9**. An amount of 1.2 g (32%) of colorless crystals **11** were isolated, mp 150 °C, S_A-phase, cp 229 °C; $[\alpha]_D^{24}$: −11.8° ($CHCl_3$, $c = 1.09$).

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 8.22 (m, 2H, Ph), 7.79 (m, 2H, Ph), 7.58 (m, 2H, Ph), 7.22 (m, 2H, Ph), 7.09 (m, 2H, Ph), 6.96 (m, 2H, Ph), 5.58 (s, 1H, acetal-H), 4.98 (d, $^3J_{1/2} = 7.6$ Hz, 1H, H-1), 4.38 (dd, $^3J_{3/4} = 4.6$ Hz, $^3J_{4/5} = 10.5$ Hz, 1H, H-4), 3.94–3.73 (m, 3H, H-2, H-3 H-6a), 3.69–3.52 (m, 2H, H-5, H-6b), 2.99 (br, 1H, OH), 2.82 (br, 1H, OH), 2.55 (t, 2H, Ph-CH_2), 1.59–1.26 (m, 12H, CH_2), 0.87 (t, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 164.2 (s, C_q), 155.0 (s, Ph-C_q), 151.4 (s, Ph-C_q), 138.1 (s, Ph-C_q), 137.2 (s, Ph-C_t), 135.1 (s, Ph-C_q), 131.9 (s, Ph-C_q), 131.0, 129.6, 127.9, 121.5, 116.8 (5s, Ph-C_t), 101.6 (s, C-1), 101.4 (s, acetal-C), 80.4, 74.6, 73.3, 66.6 (4s, C-2, C-3, C-4, C-5), 68.8 (s, C-6), 35.3 (s, Ph-$\underline{C}H_2$), 32.0, 31.8, 29.6, 29.4, 29.4, 22.8 (6s, CH_2), 14.3 (s, CH_3); ^{19}F NMR (235 MHz, $CDCl_3$); δ (ppm) = −80.5 (s, CF_3), −85.8 (m, SCF_2), −118.8 (m, CF_2), −121.1 (s, CF_2), −122.5 (s, CF_2), −125.8 (s, CF_2).

$C_{40}H_{39}F_{13}O_8S$ (926.78): Calcd. C: 51.84%, H: 4.24%, S: 3.46%; found C: 51.63%, H: 4.19%, S: 3.61%.

3.9. (4-Perfluorohexylsulfanyl-phenyl)-(R)-4,6-O-[4′-(4-perfluorohexylsulfanyl)-benzoyloxy]-benzylidene-2,3-dideoxy-β-D-erythro-hex-2-enopyranoside (**12**)

A mixture of compound **9** (700 mg, 0.6 mmol), triphenylphosphine (630 mg, 2.42 mmol), triiodoimidazole [19] (431 mg, 0.97 mmol) and imidazole (83 mg, 1.23 mmol) in dry xylene (25 ml) was stirred for 3 h at 130 °C under argon atmosphere. After completion of the reaction (tlc-control, eluent toluene $R_F = 0.36$), this mixture was cooled down to room temperature, diluted with toluene (25 ml), and decanted into a beaker containing saturated aq. $NaHCO_3$-solution (150 ml). The residue was dissolved in a small volume acetone and the solution was also added to the beaker. After stirring for 10 min and filtration, the organic phase was successively washed with 5% aq. $Na_2S_2O_3$-solution, saturated aq. $NaHCO_3$-solution and water and then dried (Na_2SO_4). Then the solution was concentrated under reduced pressure and the crude product was purified by flash chromatography (eluent toluene $R_F = 0.36$). After recrystallization from toluene, colorless crystals of **12** (384 mg, 56.5%) were obtained; mp 168 °C, S_A-phase, cp 186 °C, $[\alpha]_D^{22}$ +7.4° ($CHCl_3$, $c = 1.09$).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.23 (m, 2H, Ph), 7.80 (m, 2H, Ph), 7.58 (m, 4H, Ph), 7.24 (m, 2H, Ph), 7.12 (m, 2H, Ph), 6.31 (d, $^3J_{2/3} = 10.2$ Hz, 1H, H-2 or H-3), 6.00 (m, 1H, H-1), 5.85 (dd, 1H, H-2 or H-3), 5.66 (s, 1H, acetal-H), 4.64–4.35 (m, 2H, H-4, H-6a), 3.91 (m, 2H, H-5, H-6b); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 164.1 (s, C_q), 159.3 (s, Ph-C_q), 151.4 (s, Ph-C_q), 139.3 (s, Ph-C_t), 137.2 (s, Ph-C_t), 135.3 (s, Ph-C_q), 132.7 (s, Ph-C_q), 132.0, 126.7 (2s, C-2, C-3), 131.0 (s, Ph-C_t), 127.8 (s, Ph-C_t), 121.6, 117.5 (2s, Ph-C_t), 101.6 (s, acetal-C), 96.3 (s, C-1), 74.7, 71.2 (2s, C-4, C-5), 69.0 (s, C-6); ^{19}F NMR (235 MHz, $CDCl_3$): δ (ppm) = −80.5 (s, CF_3), −85.8 (m, SCF_2), −87.1 (m, SCF_2), −118.8 (m, CF_2), −121.2 (s, CF_2), −122.5 (s, CF_2), −125.8 (s, CF_2).

$C_{38}H_{20}F_{26}O_6S_2$ (1130.65): Calcd. C: 40.37%, H: 1.78%, S: 5.67%; found C: 40.56%, H: 1.78%, S: 5.73%.

3.10. (4-Octylphenyl)-(R)-4,6-O-[4′-(4-perfluorohexylsulfanyl)-benzoyloxy]-benzylidene-2,3-dideoxy-β-D-erythro-hex-2-enopyranoside (**13**)

A mixture of **11** (0.9 g, 0.971 mmol), triphenylphosphine (1.008 g, 3.8 mmol), triiodoimidazole (0.69 g, 1.55 mmol) and imidazole (0.133 g, 1.96 mmol) was treated as described for compound **12** giving 0.456 g (52.6%) colorless crystals of compound **13**. Thermotropic properties: mp 150 °C, S_A-phase, cp 214 °C, $[\alpha]_D^{22}$: +17.9° ($CHCl_3$, $c = 1.00$).

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 8.23 (m, 2H, Ph), 7.80 (m, 2H, Ph), 7.58 (m, 2H, Ph), 7.23 (m, 2H, Ph), 7.10 (m, 2H, Ph), 7.00 (m, 2H, Ph), 6.25 (d, $^3J_{2/3} = 10.1$ Hz, 1H, H-2 or H-3), 5.93 (m, 1H, H-1), 5.85 (dd, 1H, H-2 or H-3), 5.65 (s, 1H, acetal-H), 4.45–4.35 (m, 2H, H-4, H-6a), 3.91 (m, 2H, H-5, H-6b), 2.55 (t, 2H, α-CH_2), 1.55–1.27 (m, 12H, CH_2), 0.88 (t, 3H, CH_3); ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) = 163.9 (s, C_q), 154.8 (s, Ph-C_q), 151.2 (s, Ph-C_q), 137.3 (s, Ph-C_q), 137.1 (s, Ph-C_t), 135.3 (s, Ph-C_q), 131.8 (s, Ph-C_q), 131.7, 127.6 (2s, C-2, C-3), 129.3 (s, Ph-C_t), 127.5 (s, Ph-C_t), 121.4, 116.7 (2s, Ph-C_t), 101.4 (s, acetal-C), 97.0 (s, C-1), 74.8, 70.9 (2s, C-4, C-5), 69.1 (s, C-6), 35.2, 31.9, 31.7, 29.5, 29.3, 22.7 (6s, CH_2), 14.1 (s, CH_3); ^{19}F NMR (235 MHz, $CDCl_3$): δ (ppm) = −80.5 (s, CF_3), −85.8 (m, SCF_2), −118.8 (m, CF_2), −121.1 (s, CF_2), −122.5 (s, CF_2), −125.8 (s, CF_2).

$C_{40}H_{37}F_{13}O_6S$ (892.77): Calcd. C: 53.81%, H: 4.18%, S: 3.59%; found C: 53.58%, H: 4.21%, S: 3.64%.

3.11. (4-Octylphenyl)-(R)-4,6-O-[4′-(4-perfluorhexylsulfanyl)-benzoyloxy]-benzylidene-2,3-dideoxy-β-D-erythro-hexopyranoside (**14**)

The olefin **13** (300 mg, 0.336 mmol) was dissolved in ethanol/EtOAc (1:1 (v/v), 10 ml). An amount of 20 mg of palladium on charcoal (10%) was added. Under a hydrogen atmosphere (1 atm) hydrogenation was carried out at room temperature overnight. After filtration, the charcoal was washed with ethanol and ethyl acetate. The combined organic phases were concentrated under reduced pressure and the residue was purified by column chromatography

(eluent toluene $R_F = 0.33$). Compound **14** was recrystallized from a small volume toluene yielding 0.284 g (95%) of colorless crystals; mp 170 °C, S_A-phase, cp 195 °C, $[\alpha]_D^{24}$: −4.7° ($CHCl_3$, $c = 1.12$).

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 8.24 (m, 2H, Ph), 7.81 (m, 2H, Ph), 7.59 (m, 2H, Ph), 7.23 (m, 2H, Ph), 7.10 (m, 2H, Ph), 6.94 (m, 2H, Ph), 5.60 (s, 1H, acetal-H), 5.22 (dd, $^3J_{1/2a} = 2.1$ Hz, $^3J_{1/2b} = 9.8$ Hz, 1H, H-1), 4.33 (dd, $^3J_{3/4} = 4.6$ Hz, $^3J_{4/5} = 10.5$ Hz, lH, H-4), 3.83 (dd, 1H, H-6a), 3.02 (m, 2H, H-5, H-6b), 2.33 (t, 2H, α-CH_2), 2.22, 1.90 (2 m, 2 × 2H, H-2, H-3), 1.60–1.28 (m, 12H, CH_2), 0.88 (t, 3H, CH_3); ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) = 163.9 (s, C_q), 154.8 (s, Ph-C_q), 151.1 (s, Ph-C_q), 137.1 (s, Ph-C_t), 135.6 (s, Ph-C_q), 131.8 (s, Ph-C_q), 130.8, 129.3 (2s, Ph-C_t), 127.6 (s, Ph-C_t), 121.4, 116.3 (2s, Ph-C_t), 101.1 (s, acetal-C), 99.7 (s, C-1), 77.3 (s, C-4), 70.7 (s, C-5), 69.3 (s, C-6), 35.2, 31.9, 31.7 (3s, CH_2), 30.5 (s, C-2 or C-3), 29.5, 29.3 (2s, CH_2), 27.5 (s, C-2 or C-3), 22.7 (s, CH_2), 14.1 (s, CH_3); ^{19}F NMR (235 MHz, $CDCl_3$): δ (ppm) = −80.5 (s, CF_3), −85.8 (m, SCF_2), −118.8 (m, CF_2), −121.1 (s, CF_2), −122.5 (s, CF_2), −125.8 (s, CF_2).

$C_{40}H_{39}F_{13}O_6S$ (894.79): Calcd. C: 53.69%, H: 4.39%, S: 3.58%; found C: 53.31%, H: 4.30%, S: 3.62%.

*3.12. 3-Deoxy-(R)-4,6-O-[4′-(4-perfluorohexylsulfanyl)-benzoyloxy]-benzylidene-D-glucal (**15**)*

The olefin **12** (300 mg, 0.265 mmol) was hydrogenated as described for compound **13** (eluent toluene $R_F = 0.34$) yielding 0.136 g (75%) of colorless crystals after recrystallization from a small volume toluene; mp 136 °C, S_A-phase, cp 160 °C; $[\alpha]_D^{26}$: +17.7° ($CHC1_3$, $c = 1.09$).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.22 (m, 2H, Ph), 7.79 (m, 2H, Ph), 7.58 (m, 2H, Ph), 7.22 (m, 2H, Ph), 6.33 (m, 1H, H-1), 5.64 (s, 1H, acetal-H), 4.73 (m, 1H, H-2), 4.40 (m, 1H, H-6a), 3.93 (m, 1H, H-4), 3.83–3.74 (m, 2H, H-5, H-6b), 2.30 (m, 2H, H-3); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 163.9 (s, C_q), 151.1 (s, Ph-C_q), 143.1 (s, C-1), 137.1 (s, Ph-C_t), 135.5 (s, Ph-C_q), 131.9 (s, Ph-C_q), 130.8, 127.6, 121.4 (3s, Ph-C_t), 101.0 (s, acetal-C), 98.7 (s, C-2), 75.1, 69.9 (2s, C-4, C-5), 68.9 (s, C-6), 26.3 (s, C-3); ^{19}F NMR (235 MHz, $CDCl_3$): δ (ppm) = −80.5 (s, CF_3); −85.8 (m, SCF_2), −118.8 (m, CF_2), −121.1 (s, CF_2), −122.5 (s, CF_2), −125.8 (s, CF_2); MS-CI (isobutane) $m/z = 689$ $[M + H]^+$.

$C_{26}H_{17}F_{13}O_5S$ (688.46): Calcd. C: 45.36%, H: 2.49%, S: 4.66%; found C: 45.64%, H: 2.15%, S: 4.79%.

Acknowledgements

The authors are grateful to Prof. Dr. Manfred Michalik (IfOK Rostock) for recording the NMR spectra, Prof. Dr. Christoph Schick (Universität Rostock, FB Physik) for DSC measurements, and Angela Niemann for technical assistance.

References

[1] C. Hager, R. Miethchen, H. Reinke, J. Prakt. Chem. 342 (2000) 414–420.
[2] H. Prade, R. Miethchen, V. Vill, J. Prakt. Chem. 237 (1995) 427–440.
[3] C.M. Paleos, D. Tsiourvas, Angew. Chem. (Int. Ed. Engl.) 134 (1995) 1696–1712.
[4] J.W. Goodby, M.J. Watson, G. MacKenzie, S.M. Kelly, S. Bachir, P. Bault, P. Gode, G. Goethals, P. Martin, G. Ronco, P. Villa, Liq. Cryst. 25 (1998) 139–147.
[5] J.W. Goodby, G.H. Mehl, I.M. Saez, R.P. Tuftin, G. Mackenzie, R. Auzely-Velty, T. Benvegnu, D. Plusquellec, Chem. Commun. (1998) 2057–2070.
[6] M. Veber, E. Cheylan, S. Czernecki, J. Xie, Liq. Cryst. 21 (1996) 197–201.
[7] M. Hein, R. Miethchen, D. Schwäbisch, C. Schick, Liq. Cryst. 27 (2000) 163–168.
[8] R. Miethchen, M. Hein, Carbohydr. Res. 327 (2000) 169–183.
[9] V. Vill, H.W. Tunger, M.V. Minden, J. Mater. Chem. 6 (1996) 739–745.
[10] M. Hein, R. Miethchen, Eur. J. Org. Chem. (1999) 2429–2432.
[11] W.Y. Huang, J. Fluorine Chem. 58 (1992) 1–8.
[12] W.Y. Huang, F.H. Wu, Isr. J. Chem. 39 (1999) 167–170.
[13] C. Zur, R. Miethchen, Eur. J. Org. Chem. (1998) 531–539.
[14] M. Hein, R. Miethchen, D. Schwäbisch, J. Fluorine Chem. 98 (1999) 55–60.
[15] H.L. Nguyen, J. Dedier, H.T. Nguyen, J.C. Rouillon, G. Sigaud, Liq. Cryst. 26 (1999) 1637–1644.
[16] E. Smits, J.B.F.N. Engberts, R.M. Kellog, H.A. van Doren, J. Chem. Soc., Perkin Trans. 1 (1996) 2858–2873.
[17] G. Zemplén, A. Gerecs, I. Hadácsy, Ber. Dtsch. Chem. Ges. 69 (1936) 1827–1829.
[18] E. Smits, J.B.F.N. Engberts, R.M. Kellog, H.A. van Doren, Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A 260 (1995) 185–200.
[19] P.J. Garegg, B. Samuelsson, Synthesis (1979) 813–814.
[20] J. Leonhard, B. Lygo, G. Procter, Praxis der Organischen Chemie, VCH Verlag, Weinheim, 1996.