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Optically Active Mesogenic Dispiro[2.0.2.1]Heptane Derivatives and their Unusual Physical Properties*

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Physical properties, i.e. phase transition temperatures, response times, Ps values, tilt angles, helical twisting powers and helical twisting senses of a series of novel ferroelectric liquid crystalline compounds with non-substituted and halogen-substituted dispiro[2.0.2.1]heptyl moieties in their side chains have been measured. When mixed with an achiral SmC base mixture, the resulting SmC^* mixtures containing the novel compounds showed ferroelectricity, and the novel compounds were estimated as useful dopants for ferroelectric liquid crystal mixtures. Further unusual properties were observed with the combinations of the two diastereomeric novel compounds, for example (1*S*,3*R*,4*S*)-**4a** and (1*S*,3*R*,4*R*)-**5a**. They showed opposite signs for the Ps and the same sense for the N^* helical twisting, which clearly suggests that the direction of the Ps and helical sense of N^* must be derived from different origins.

Keywords: ferroelectric; dispiro[2.0.2.1]heptane; spontaneous polarization; helical twist

* Part 69 in the series "Cylopropyl Building Blocks in Organic Synthesis". For part 68 see: K. Miyazawa, A. de Meijere, *Mol. Cryst. Liq. Cryst.* **2001**, in press; part 67: A. Brandi, S. Cicchi, M. Brandl, S.I. Kozhushkov, A. de Meijere, *Synlett* **2001**, submitted.

INTRODUCTION

Substituted [*n*]triangulane moieties, i. e. units consisting of spiroannelated cyclopropane rings only, are predisposed to have rigid conformations[1] which are significantly different from those of the branched alkyl end groups that are commonly applied as the chiral subunits in certain liquid crystalline compounds. Although a huge number of ferroelectric liquid crystalline compounds have been reported until now,[2] only few of them contain a conformationally rigid unit such as the dispiro[2.0.2.1]heptyl moiety. We have therefore developed appropriate synthetic methods and prepared novel optically active ferroelectric liquid crystalline compounds containing dispiro-[2.0.2.1]heptyl moieties, as well as measured their physical properties to estimate the potential of the novel compounds as dopants for ferroelectric liquid crystal mixtures.

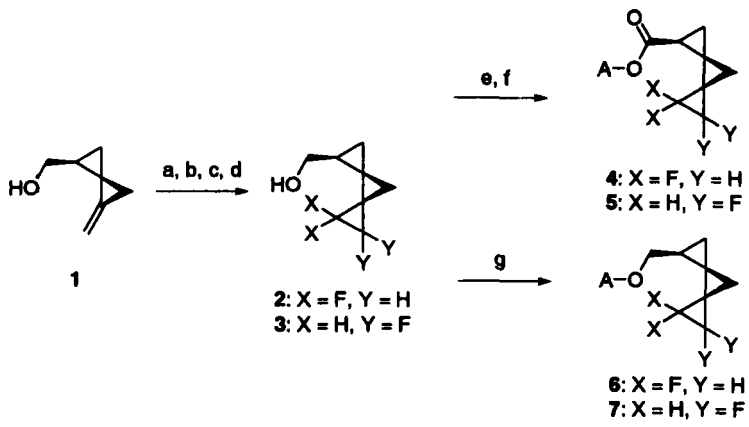
RESULTS AND DISCUSSION

Synthesis[3]

Liquid crystalline 5,5- and 6,6-difluorodispiro[2.0.2.1]heptane derivatives were synthesized using *endo*-4-methylenespiropent-1-ylmethanol **1** as the starting compound. (SCHEME 1) *endo*-4-Methylenespiropent-1-yl-methanol **1**[4] was optically resolved enzymatically with Lipase PS® (Amano Pharmaceutical Co. Ltd., *Pseudomonas* sp) to yield both enantiomers in high enantiomeric excesses (>95% *ee*), as determined applying Mosher's method[5]. The absolute configurations were confirmed by comparing the specific rotations of the optically active *exo*-dispiro[2.0.2.1]hept-1-ylmethanols, that were synthesized from the optically active *endo*-4-methylenespiropent-1-ylmethanol **1** and CH_2N_2 in the presence of $Pd(OAc)_2$[6], with those of the authentic optically active *exo*-dispiro-[2.0.2.1]hept-1-ylmethanol[1b]. The optically active (1*S*,3*R*)- and (1*R*,3*S*)-4-methylenespiropent-1-ylmethanols **1** were reacted with difluorocarbene generated from CBr_2F_2 and PPh_3 according to the method of Burton[7], to provide two diastereoisomers **2** and **3** which were separated by column chromatography. Both diastereoisomers **2** and **3** were converted to the liquid crystalline esters **4** and **5** by oxidation to the acids and subsequent

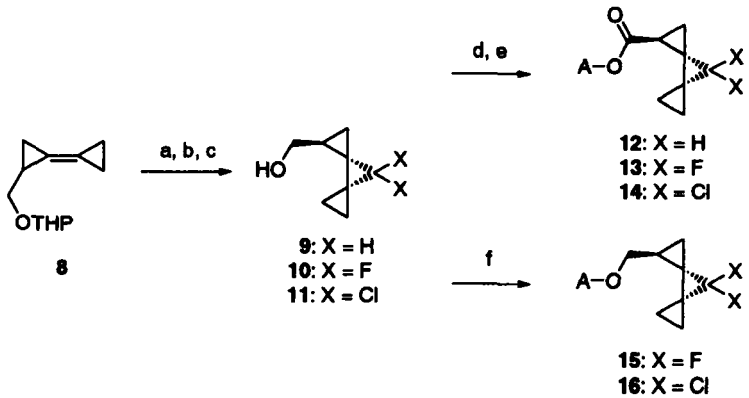
esterification, as well as to the liquid crystalline ethers **6** and **7** by Mitsunobu reactions, respectively (SCHEME 1).

SCHEME 1



a: $AcOCH{=}CH_2$, Lipase PS, Et_2O, r. t.; b: DHP, PPTS, CH_2Cl_2, r. t.; c: CBr_2F_2, PPh_3, KF, DME, r. t.; d: PPTS, MeOH, Δ.; e: CrO_3, H_2SO_4, acetone, 0 °C.; f: AOH, DCC, DMAP, CH_2Cl_2, r. t.; g: AOH, DEAD, PPh_3 THF, r. t., A = 4-(5-octylpyrimid-2-yl)phenyl, 2-(4-pentyl-1,1'-biphenyl-4'-yl)pyrimid-5-ol.

SCHEME 2



a: CH_2N_2, Et_2O, r. t., or CBr_2F_2, PPh_2, KF, DME, r. t., or $CHBr_3$, NaOH, r.t.; b: PPTS, MeOH, Δ; c: $AcOCH{=}CH_2$, Lipase PS, Et_2O, r. t.; d: CrO_3, H_2SO_4, acetone, 0 °C; e: AOH, DCC, DMAP, CH_2Cl_2, r.t.; f: AOH, DEAD, PPh_3 THF, r. t., A = 4-(5-octylpyrimid-2-yl)phenyl, 2-(4-pentyl-1,1'-biphenyl-4'-yl)pyrimid-5-ol.

Liquid crystalline non-substituted and 7,7-dihalogen-substituted dispiro-[2.0.2.1]heptane derivatives were synthesized using bicyclopropylidene-methyl tetrahydropyranyl ether **8**[8] as the starting compound. The THP ether **8** was cyclopropanated with difluoro- and dichlorocarbenes[7][9], and the THP groups were removed under acidic conditions to yield the compounds **10** and **11** in racemic forms. The carbene addition reactions were, in these cases, stereospecific and only the *endo*-configurated **10** and **11** were produced selectively. The racemate **9** was synthesized according to the literature[10][11]. The racemates were optically resolved by the enzymatic technique using Lipase PS® to give both enantiomers. The high enantiomeric excesses (>95% *ee*) of the optically active compounds **9**, **10** and **11** were determined applying Mosher's method[5], and their absolute configurations were confirmed by X-ray crystallography[12]. (SCHEME 2)

RESULTS AND DISCUSSION

Phase transition temperatures

Transition temperatures of the novel compounds with dispiro[2.0.2.1]heptyl moieties in their side chains are listed in Table 1 along with their chemical structures. Almost all the compounds prepared, except for the triaryl derivative (1*S*,3*R*,4*R*)-**7b**, did not show any mesophase. Introduction of halogen atoms, especially fluorine atoms, on the dispiro[2.0.2.1]heptyl moiety apparently increases the melting point. The large dipole moments of these molecules might be stabilizing their crystallinity.

Properties of SmC mixtures containing the novel compounds*

The transition temperatures, response times (τ), Ps values, tilt angles (Θ) and helical twisting senses of the N* phase, of SmC* mixtures containing 10 wt% of the novel compounds in the base mixture A, comprising phenylpyrimidine derivatives (see Experimental), are shown in Table 2. All the SmC* mixtures show moderate values of Ps and short response times (<149 μsec). Dihalogen substitution in the 7-position of the dispiro[2.0.2.1]-heptane moieties induces the largest Ps value and the quickest response.

Especially the twofold fluorine subsitution in the 7-position leads to the shortest response time of 41 μsec for (1*S*,3*S*)-**13a** and (1*R*,3*R*)-**13a**.

TABLE 1 Transition temperatures and chemical structures of the liquid crystalline compounds with dispiro[2.0.2.1]heptane moieties

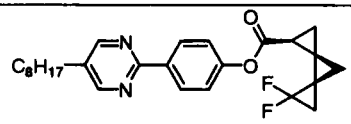
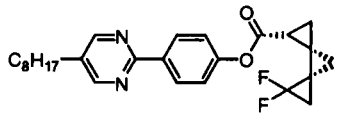
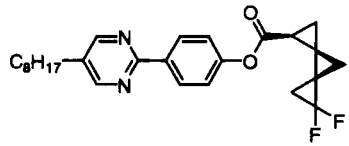
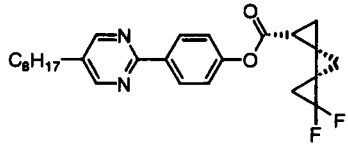
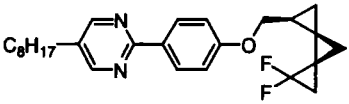
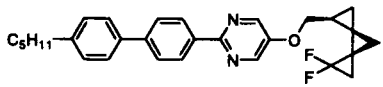
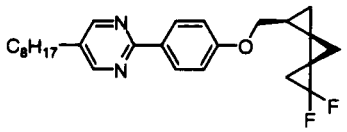
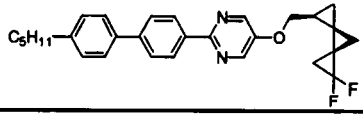
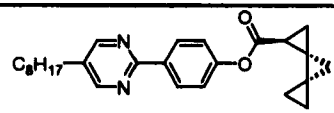
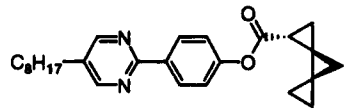
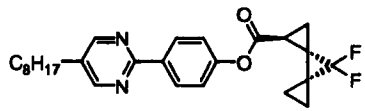
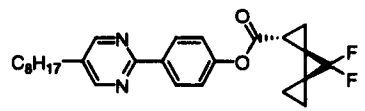
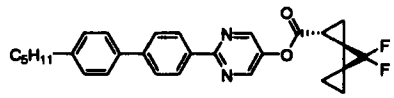
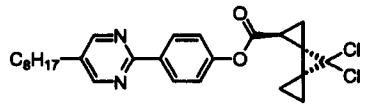
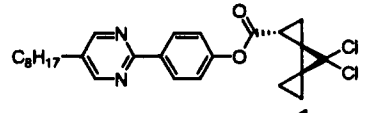
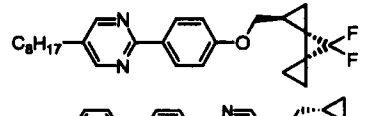
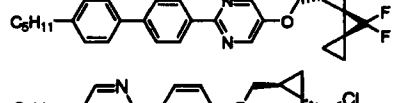
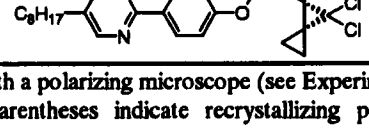
Compound	Chemical Structure	Transition tempenperatures /°C[1)2)]
(1*S*,3*R*,4*S*)-**4a**		C 104 I (75)
(1*R*,3*S*,4*R*)-**4a**		C 102 I (72)
(1*S*,3*R*,4*R*)-**5a**		C 81 I (60)
(1*R*,3*S*,4*S*)-**5a**		C 80 I (60)
(1*S*,3*R*,4*S*)-**6a**		C 77 I (60)
(1*S*,3*R*,4*S*)-**6b**		C 145 I (129)
(1*S*,3*R*,4*R*)-**7a**		C 102 I (81)
(1*S*,3*R*,4*R*)-**7b**		C 133 SmA 146.9 N* 163.8 I

TABLE 1 Continued

(1*S*,3*S*)-**12a**		C 44 I (6)
(1*R*,3*R*)-**12a**		C 44 I (10)
(1*S*,3*S*)-**13a**		C 78 I (66)
(1*R*,3*R*)-**13a**		C 79 I (65)
(1*R*,3*R*)-**13b**		C 162 I (151)
(1*S*,3*S*)-**14a**		C 70 I (51)
(1*R*,3*R*)-**14a**		C 70 I (55)
(1*S*,3*S*)-**15a**		C 76 I (50)
(1*R*,3*R*)-**15b**		C 162 I (140)
(1*S*,3*S*)-**16a**		C 102 I (60)

1) Measured with a polarizing microscope (see Experimental).
2) Values in parentheses indicate recrystallizing points during cooling process.

TABLE 2 Physical properties of SmC* mixtures containing 10 wt% of the liquid crystalline compounds with dispiro[2.0.2.1]heptane moieties

Compound	Transition temperatures /°C	τ /μsec	Ps /nC cm^{-2}	Θ /°	N*[1)]
(1*S*,3*R*,4*S*)-**4a**	SmC* 48.8 SmA 73.6 N* 83.2 I	75	+5.6	14.0	L
(1*R*,3*S*,4*R*)-**4a**	SmC* 49.2 SmA 73.0 N* 81.2 I	81	−4.7	14.0	R
(1*S*,3*R*,4*R*)-**5a**	SmC* 47.1 SmA 77.2 N* 86.2 I	68	−3.3	15.3	L
(1*R*,3*S*,4*S*)-**5a**	SmC* 46.7 SmA 76.0 N* 84.3 I	149	+3.3	16.1	R
(1*S*,3*R*,4*S*)-**6a**	SmC* 49.7 SmA 71.5 N* 80.4 I	76.5	+5.6	15.8	L
(1*S*,3*R*,4*S*)-**6b**	SmC* 69.9 SmA 72.2 N* 91.0 I	77	+15.7	27.0	L
(1*S*,3*R*,4*R*)-**7a**	SmC* 44.3 SmA 77.7 N* 84.7 I	–[2)]	~0	19.0	L
(1*S*,3*R*,4*R*)-**7b**	SmC* 59.2 SmA 84.7 N* 94.2 I	–[2)]	~0	15.3	L
(1*S*,3*S*)-**12a**	SmC* 41.3 SmA 67.2 N* 77.2 I	88	−1.9	13.0	L
(1*R*,3*R*)-**12a**	SmC* 40.1 SmA 68.8 N* 77.7 I	92	+2.3	12.2	R
(1*S*,3*S*)-**13a**	SmC* 36.4 SmA 75.1 N* 81.4 I	41	+3.0	8.6	L
(1*R*,3*R*)-**13a**	SmC* 37.0 SmA 74.9 N* 81.6 I	41	−2.9	11.7	R
(1*R*,3*R*)-**13b**	SmC* 64.8 SmA 73.7 N* 89.7 I	–[3)]	–[3)]	–[3)]	R
(1*S*,3*S*)-**14a**	SmC* 39.3 SmA 74.4 N* 83.1 I	56	+3.5	12.8	L
(1*R*,3*R*)-**14a**	SmC* 37.0 SmA 74.4 N* 82.4 I	56	−3.8	11.7	R
(1*S*,3*S*)-**15a**	SmC* 47.2 SmA 75.0 N* 84.6 I	55	+4.5	13.8	L
(1*R*,3*R*)-**15b**	SmC* 63.2 SmA 75.9 N* 90.8 I	94	−9.4	26.6	R
(1*S*,3*S*)-**16a**	SmC* 47.7 SmA 73.7 N* 83.4 I	70.5	+3.8	15.7	L

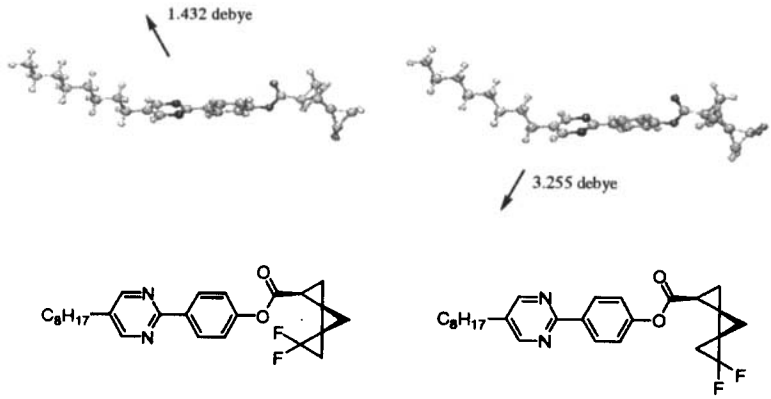
1) Helical sense of N* phase where R and L indicate right- and left handed, respectively.
2) Due to the very small value for Ps, the switching was not observed.
3) Crystallized at 20 °C.

It is noteworthy that the fluorine and chlorine substitutions in the 7-position at the central cyclopropane ring of the dispiro[2.0.2.1]heptane moieties introduce the reverse of the sign of the Ps. For instance, the non-halogenated compound (1*R*,3*R*)-**12a** shows a right-handed helical twisting sense in the N* phase which has the same direction as those of the halogenated compounds (1*R*,3*R*)-**13a** and (1*R*,3*R*)-**14a**, but shows a positive spontaneous polarization (+Ps) while the compounds (1*R*,3*R*)-**13a** and (1*R*,3*R*)-**14a** show -Ps.

An extremely interesting phenomenon is the unusual relation between the properties of the compounds (1*S*,3*R*,4*S*)-**4a** and (1*S*,3*R*,4*R*)-**5a**. They show opposite signs of the Ps values with almost the same magnitude, although both compounds show left-handed helical twisting senses in their N* phase. The only structural difference between the two diastereomeric compounds relates to the position of the two fluorine substituents. This would be a useful property, with which a SmC* mixture with an infinitive length of N* helical twisting pitch providing a homogeneous alignment in a LC cell, would easily be realized. More importantly, this result strongly suggests that the directions of Ps and helical twisting sense must be derived from different origins.

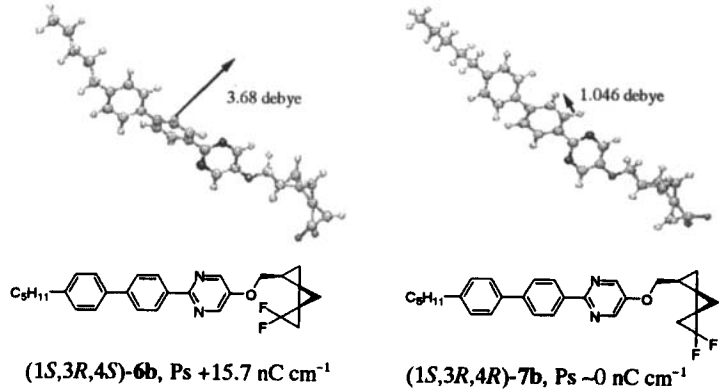
The two combinations of the compounds (1*S*,3*R*,4*S*)-**6a** and (1*S*,3*R*,4*R*)-**7a**, and (1*S*,3*R*,4*S*)-**6b** and (1*S*,3*R*,4*R*)-**7b** should also be noted. All four compounds show left-handed helical twisiting senses in their N* phase, however, only the (1*S*,3*R*,4*S*)-isomers show large value of positive Ps, namely +5.6 and +15.7 nC cm^{-1}, whereas the (1*S*,3*R*,4*R*)-isomers show Ps values close to 0.

Semiempirical molecular orbital calculations may help to understand the reason for these unusual properties of the compounds (1*S*,3*R*,4*S*)-**4a**, (1*S*,3*R*,4*R*)-**5a**, (1*S*,3*R*,4*S*)-**6a**, (1*S*,3*R*,4*R*)-**7a**, (1*S*,3*R*,4*S*)-**6b** and (1*S*,3*R*,4*R*)-**7b**. Figure 1 and 2 show the molecular shapes and overall diploe moments, while Table 3 lists the dipole components of the compounds (1*S*,3*R*,4*S*)-**4a**, (1*S*,3*R*,4*R*)-**5a**, (1*S*,3*R*,4*S*)-**6b** and (1*S*,3*R*,4*R*)-**7b** as calculated by MOPAC/AM1[13][14].



(1*S*,3*R*,4*S*)-**4a**, Ps +5.6 nC cm^{-1} (1*S*,3*R*,4*R*)-**5a**, Ps −3.3 nC cm^{-1}

FIGURE 1 Calculated molecular shapes and overall dipole moments of (1*S*,3*R*,4*S*)-**4a** and (1*S*,3*R*,4*R*)-**5a**.



(1*S*,3*R*,4*S*)-**6b**, Ps +15.7 nC cm^{-1} (1*S*,3*R*,4*R*)-**7b**, Ps ~0 nC cm^{-1}

FIGURE 2 Calculated molecular shapes and overall dipole moments of (1*S*,3*R*,4*S*)-**6b** and (1*S*,3*R*,4*R*)-**7b**.

TABLE 3 Dipole moments of the compounds (1*S*,3*R*,4*S*)-**4a**, (1*S*,3*R*,4*R*)-**5a**, (1*S*,3*R*,4*S*)-**6b** and (1*S*,3*R*,4*R*)-**7b** calculated by MOPAC/AM1

Compound	Dipole component/Debye			μ_{total}	Ps
	A	B	C	/Debye	/nC cm^{-2}
(1*S*,3*R*,4*S*)-**4a**	−0.621	0.460	−1.205	1.432	+5.6
(1*S*,3*R*,4*R*)-**5a**	−3.091	0.764	1.325	3.255	−3.3
(1*S*,3*R*,4*S*)-**6b**	1.610	2.901	−1.558	3.680	+15.7
(1*S*,3*R*,4*R*)-**7b**	−0.656	0.808	−0.095	1.046	~0

The axis A designates the long axis with the minimum moment of inertia (A-axis, long axis of rotation), while the other two axes B and C are perpendicular to the long axis. It is well known that the sponteneous polarization is connected with lateral dipole components. Comparing the Ps and the lateral dipole components B and C, it becomes clear that the magnitude and the sign of the component B cannot explain the Ps data. However, the component C shows negative sign, when the Ps is positive, and vice versa. It is about zero, when the Ps is zero. Thus we may assume that the dipole component C is responsible for producing the observed Ps. Further we may conclude that the shapes of the compounds provide the sign of the helical twisting senses, and the lateral dipole components induce the sign and the magnitude of the spontaneous polarization.

Helical pitches of the novel compounds

The temperature dependences of helical pitches of N* mixtures containing 1 wt% of the novel compounds in the nematic base mixture ZLI-1132® (E. Merck KGaA, see Experimental) are compiled in Table 4. The helical pitches and its temperature dependence was found to be strongly influenced by the chemical structures, and in general dihalogen substitution in the 7-position of the central cyclopropane ring in the dispiro[2.0.2.1]heptyl moiety makes the helical pitches shorter. It is interesting to note that the compounds (1*S*,3*R*,4*S*)-**4a** and (1*R*,3*S*,4*R*)-**4a** show the normal temperature dependence of the pitch, this is decrease with increasing temperature. However, the compounds (1*S*,3*S*)-**15a**, (1*R*,3*R*)-**15b** and (1*S*,3*S*)-**16a** exhibit the seldom inverse temperature dependences, and the compounds (1*S*,3*R*,4*R*)-**5a**, (1*R*,3*S*,4*S*)-**5a**, (1*S*,3*R*,4*R*)-**7a**, (1*S*,3*S*)-**13a**, (1*R*,3*R*)-**13a**, (1*R*,3*R*)-**13b**, (1*S*,3*S*)-**14a** and (1*R*,3*R*)-**14b** possess a nearly temperature independent pitch, a fact which has been observed in polymers below the glass transition. These anomalies need further explanation on a molecular basis.

TABLE 4 Dependence of helical pitches (μm) of N* mixtures containing 1 wt% of the liquid crystalline compounds with dispiro[2.0.2.1]heptane moieties in ZLI-1132®

Compound	60 °C	50 °C	40 °C	30 °C	25 °C	20 °C
(1*S*,3*R*,4*S*)-**4a**	22.3	24.5	26.5	28.9	29.9	30.6
(1*R*,3*S*,4*R*)-**4a**	19.7	20.7	22.4	24.2	26.1	26.8
(1*S*,3*R*,4*R*)-**5a**	30.1	30.5	30.6	30.1	29.9	29.7
(1*R*,3*S*,4*S*)-**5a**	34.7	34.7	34.6	34.2	33.7	33.5
(1*S*,3*R*,4*S*)-**6a**	–[1]	–[1]	–[1]	–[1]	–[1]	–[1]
(1*S*,3*R*,4*S*)-**6b**	–[1]	–[1]	–[1]	43.4	43.6	42.9
(1*S*,3*R*,4*R*)-**7a**	42.9	42.7	42.8	43.4	43.3	43.7
(1*S*,3*R*,4*R*)-**7b**	66.4	68.5	70.2	–[1]	–[1]	–[1]
(1*S*,3*S*)-**12a**	–[1]	–[1]	–[1]	–[1]	–[1]	–[1]
(1*R*,3*R*)-**12a**	–[1]	–[1]	–[1]	–[1]	–[1]	–[1]
(1*S*,3*S*)-**13a**	14.0	14.1	14.1	14.0	14.1	14.1
(1*R*,3*R*)-**13a**	13.4	13.4	13.4	13.4	13.5	13.5
(1*R*,3*R*)-**13b**	14.4	14.9	15.0	15.2	15.4	15.3
(1*S*,3*S*)-**14a**	15.8	16.1	16.4	16.7	16.9	16.7
(1*R*,3*R*)-**14a**	15.8	15.9	16.2	16.4	16.5	16.6
(1*S*,3*S*)-**15a**	17.9	16.2	14.5	14.5	13.3	12.5
(1*R*,3*R*)-**15b**	15.5	14.6	13.4	12.3	12.0	11.6
(1*S*,3*S*)-**16a**	20.7	20.2	18.6	17.5	16.8	16.3

1) Helical structure was not formed in the Cano-wedge cell.

CONCLUSION

The novel ferroelectric liquid crystalline compounds with dispiro[2.0.2.1]-heptyl moieties have some interesting properties. SmC* mixtures containing 10 wt% of the fluorinated compounds (1*R*,3*R*)-**13a** and (1*S*,3*S*)-**13a** in the base mixture showed the shortest response times. The two diastereomeric compounds (1*S*,3*R*,4*S*)-**4a** and (1*S*,3*R*,4*R*)-**5a** with the difluorine substitution on the terminal cyclopropane ring, exhibited the extremely strange phenomenon of non-correlating signs of the Ps and the sense of the N* phase, which strongly suggests that the sign of the Ps and the sense of the helical twisting must have different origins. Also, a reversal of the sign of the Ps was observed on going from 7,7-dihalodispiro[2.0.2.1]heptane to the non-substituted dispiro[2.0.2.1]heptane derivatives.

EXPERIMENTALS

Measurements

Evaluation of the synthesized novel liquid crystalline compounds as chiral dopants was made for mixtures containing 10 wt% of the novel compounds in an achiral SmC base mixture A comprising of 2-(4-hexyloxyphenyl)-5-octylpyrimidine (30 wt%), 2-(4-octyloxyphenyl)-5-octylpyrimidine (20 wt%), 2-(4-nonyloxyphenyl)-5-octylpyrimidine (10 wt%), 2-(4-decyloxyphenyl)-5-heptylpyrimidine (10 wt%), 2-(4'-pentyl-1,1'-biphenyl-4-yl)-5-octylpyrimidine (20 wt%), and 2-(4'-heptyl-1,1'-biphenyl-4-yl)-5-octylpyrimidine (10 wt%) (phase sequence Cr 4 SmC 65 SmA 79 N 90 I). The transition temperatures were measured with a polarizing microscope, Nikon XTP-11, in conjunction with a Mettler hot stage FP 82 and a control unit FP 80. The magunitude of Ps was measured with the triangular wave method,[15] and the sign of Ps was determined according to the convention of Lagerwall et al. with the field reversal method by optical observation of the director motion.[16] The tilt angle was determined, with crossed Nicol prisms, as one half of the rotation angle between the two maximum extinction positions, associated with the oppositely directed polarizations.[17] The helical pitch in the N* phase was determined on N* mixtures containing 1 wt% of the novel compounds in a nematic mixture ZLI-1132® (N-I point 71.7 °C, $\Delta\varepsilon$ 11.0, Δn 0.132, E. Merck KGaA), by the Cano-wedge method.[18] The helical twist sense was determined by observation of textures of a contact preparation using specimen of known twist sense as a component of the binary system. The response time was measured from the transmission characteristics, as determined with a photodiode, through crossed polarizers applying a square wave voltage. We define τ as the time from field reversal to 90% response.

Syntheses

General: All reactions with moisture- and air-sensitive substrates or reagents were carried out under an atmosphere of dry nitrogen. Diethyl ether, tetrahydrofuran and dimethoxyethane were distilled from sodium benzophenone ketyl, and dichloromethane was distilled from P_2O_5 prior to use. All other commercial reagents were used as received unless otherwise stated. All new compounds were purified by column chromatography on silica gel (silica gel 60, 0.063–0.200 mm) or recrystallization. Their chemical structures were fully confirmed by spectroscopic techniques: IR [Bruker IFS 66 (FT–IR)], ^{1}H NMR (250 MHz), ^{13}C NMR (62.9 MHz, additional DEPT), ^{19}F NMR (470 MHz), mass spectrometry (Varian MAT CH 7, MAT 731), and their molecular formulas were established by elemental analysis, which was carried out at the Mikroanalytisches Laboratorium des Instituts für Organische Chemie der Universität Göttingen.

(1*S*,3*R*,4*S*)-5,5-Difluorodispiro[2.0.2.1]hept-1-ylmethanol [(1*S*,3*R*,4*S*)-2] and (1*S*,3*R*,4*R*)-6,6-difluorodispiro[2.0.2.1]hept-1-ylmethanol [(1*S*,3*R*,4*R*)-3]: According to the method for the preparation of (1*R*,3*S*,4*R*)-**2**[3] and (1*R*,3*S*,4*S*)-**3**[3], (1*S*,3*R*,4*S*)-**2** and (1*S*,3*R*,4*R*)-**3** were synthesized. (1*S*,3*R*,4*S*)-**2**: Yellow oil (451 mg, 29%). – R_f = 0.293 (pentane/diethyl ether 1:1). – $[\alpha]_D^{25}$ = +48.7 (*c* 1.01, $CHCl_3$). (1*S*,3*R*,4*R*)-**3**: Yellow oil (555 mg, 36%). – R_f = 0.195 (pentane/diethyl ether 1:1). – $[\alpha]_D^{25}$ = +122.2 (*c* 1.14, $CHCl_3$). The ^{1}H NMR spectra of (1*S*,3*R*,4*S*)-**2** and (1*S*,3*R*,4*R*)-**3** were identical to those of (1*R*,3*S*,4*R*)-**2** and (1*R*,3*S*,4*S*)-**3**, respectively.

According to the synthesis of (1*R*,3*S*,4*R*)-5,5-difluorodispiro-[2.0.2.1]heptane-1-carboxylic acid[3], (1*S*,3*R*,4*S*)-5,5-difluorodispiro-[2.0.2.1]heptane-1-carboxylic acid, and (1*S*,3*R*,4*R*)-6,6-difluorodispiro-[2.0.2.1]heptane-1-carboxylic acid were synthesized from (1*S*,3*R*,4*S*)-**2** and (1*S*,3*R*,4*R*)-**3**, respectively.

(1*S*,3*R*,4*S*)-5,5-Difluorodispiro[2.0.2.1]heptane-1-carboxylic acid: Colorless crystals (183 mg, 74%), mp 108–110 °C. – $[\alpha]_D^{25}$ = +236 (*c* 1.00, $CHCl_3$). The ^{1}H NMR spectrum was identical to that of the (1*R*,3*S*,4*R*)-isomer.

(1*S*,3*R*,4*R*)-6,6-Difluorodispiro[2.0.2.1]heptane-1-carboxylic acid: Colorless crystals (260 mg, 79%), mp 108–110 °C. – $[\alpha]_D^{25}$ = +323.2 (*c* 1.18, $CHCl_3$). The ^{1}H NMR spectrum was identical to that of the (1*R*,3*S*,4*S*)-isomer.

(1*S*,3*R*,4*S*)-4-(5-Octylpyrimid-2-yl)phenyl 5,5-difluorodispiro-[2.0.2.1]heptane-1-carboxylate [(1*S*,3*R*,4*S*)-4a] and (1*S*,3*R*,4*R*)-4-(5-octylpyrimid-2-yl)phenyl 6,6-difluorodispiro[2.0.2.1]heptane-1-carboxylate [(1*S*,3*R*,4*R*)-5a]: The compounds (1*S*,3*R*,4*S*)-**4a** and (1*S*,3*R*,4*R*)-**5a** were synthesized from the corresponding optically active carboxylic acids, DCC and DMAP according to the synthesis of (1*R*,3*S*,4*R*)-**4a**[3] and (1*R*,3*S*,4*S*)-**5a**[3].

(1*S*,3*R*,4*S*)-**4a**: Colorless crystals (244 mg, 64%), mp 104 °C. – Anal. Calcd for $C_{26}H_{30}F_2N_2O_2$: C, 70.89, H, 6.86, N, 6.36. Found: C, 71.13, H, 7.06, N, 6.36. – $[\alpha]_D^{25}$ = +163.6 (*c* 1.05, $CHCl_3$). The ^{1}H and ^{13}C NMR, and MS spectra were identical to those of (1*R*,3*S*,4*R*)-**4a**.

(1*S*,3*R*,4*R*)-**5a**: Colorless crystals (330 mg, 65%), mp 81 °C. – Anal. Calcd for $C_{26}H_{30}F_2N_2O_2$: C, 70.89, H, 6.86, N, 6.36. Found: C, 71.04, H, 6.88, N, 6.27. – $[\alpha]_D^{25}$ = +195.7 (*c* 0.87, $CHCl_3$). The ^{1}H and ^{13}C NMR, and MS spectra were identical to those of (1*R*,3*S*,4*S*)-**5a**.

(1*S*,3*R*,4*S*)-5,5-Difluorodispiro[2.0.2.1]hept-1-ylmethyl 4-(5-octylpyrimid-2-yl)phenyl ether [(1*S*,3*R*,4*S*)-6a]: To a mixture of (1*S*,3*R*,4*S*)-**2**

(100 mg, 0.62 mmol), 4-(5-octylpyrimid-2-yl)phenol (178 mg, 0.63 mmol), PPh_3 (197 mg, 0.75 mmol) and THF (10 mL), was added DEAD (218 mg, 1.25 mmol) at 0 °C. The resulting mixture was stirred for 3.5 h, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (60 mL) eluting with benzene to yield 153 mg (58%) of (1*S*,3*R*,4*S*)-**6a** as colorless crystals, mp 77 °C. – R_f = 0.23. – IR (KBr): $\tilde{\nu}$ = 1253 cm^{-1}, 1210, 1174. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.87 (t, *J* 6.8 Hz, 3 H), 0.97 (t, *J* 4.9 Hz, 1 H), 1.13–1.70 (m, 17 H), 1.81 (quint, *J* 7.0 Hz, 1 H), 2.59 (t, *J* 7.4 Hz, 2 H), 3.97 (dd, *J* 9.9 Hz, 7.2 Hz, 1 H), 4.07 (dd, *J* 9.9 Hz, 6.6 Hz, 1 H), 6.98 (d, *J* 8.9 Hz, 2 H), 8.34 (d, *J* 8.9 Hz, 2 H), 8.56 (s, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 9.6, 9.7, 10.8, 14.0, 16.0 (t, J_{CF} 11.3 Hz), 19.3 (t, J_{CF} 11.3 Hz), 20.2, 22.6, 29.0, 29.1, 29.2, 30.1, 30.8, 31.7, 70.7, 114.5, 129.3, 130.4, 132.1, 156.9, 160.9, 162.3. – ^{19}F NMR (470 Mhz, $CDCl_3$): δ = –132.3 (dd, *J* 152 Hz, 10 Hz, 1 F), –137.6 (d, *J* 152 Hz, 1 F). – MS (70 eV, EI), *m/z* (%): 427/426 (25/92) [M^+]. – Anal. Cald for $C_{26}H_{32}F_2N_2O$: C, 73.21, H, 7.56, N, 6.57. Found: C, 73.41, H, 7.76, N, 6.49. – $[\alpha]_D^{25}$ = +73.4 (*c* 1.00, $CHCl_3$).

(1*S*,3*R*,4*S*)-**6b**, (1*S*,3*R*,4*R*)-**7a** and (1*S*,3*R*,4*R*)-**7b** were synthesized from (1*S*,3*R*,4*S*)-**2** and (1*S*,3*R*,4*R*)-**3** according to the synthesis of (1*S*,3*R*,4*S*)-**6a**.

(1*S*,3*R*,4*S*)-5,5-Difluorodispiro[2.0.2.1]hept-1-ylmethyl 2-(4'-pentyl-1,1'-biphenyl-4-yl)prymid-5-yl ether [(1*S*,3*R*,4*S*)-**6b**]: Colorless crystals (176 mg, 76%), mp 145 °C. – R_f = 0.57 (pentane/diethyl ether 5:1). – IR (KBr): $\tilde{\nu}$ = 1273 cm^{-1}. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.91 (t, *J* 6.4 Hz, 3 H), 1.01 (t, *J* 5.0 Hz, 1 H), 1.21 (t, *J* 7.5 Hz, 1 H), 1.24–1.38 (m, 4 H), 1.46–1.71 (m, 6 H), 1.83 (quint, *J* 6.9 Hz, 1 H), 2.65 (t, *J* 7.8 Hz, 2 H), 4.09 (dd, *J* 9.9 Hz, 7.0 Hz, 1 H), 4.14 (dd, *J* 9.9 Hz, 6.4 Hz, 1 H), 7.25 (d, *J* 8.3 Hz, 2 H), 7.59 (d, *J* 8.3 Hz, 2 H), 7.71 (d, *J* 8.3 Hz, 2 H), 8.40 (d, *J* 8.3 Hz, 2 H), 8.48 (s, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 9.6, 9.7, 10.8, 14.0, 16.0 (t, J_{CF} 11.2 Hz), 19.4 (t, J_{CF} 11.2 Hz), 20.3 (d, J_{CF} 3.6 Hz), 22.5, 31.1, 31.5, 35.5, 71.6, 126.9, 127.0, 127.9, 128.8, 136.0, 137.8, 142.3, 142.4, 144.0, 151.2, 157.7. – ^{19}F NMR (470 Mz, $CDCl_3$): δ = –132.5 (dd, *J* 152 Hz, 9.5 Hz, 1 F), –137.6 (dt, *J* 152 Hz, 8.9 Hz, 1 F). – MS (70 eV, EI), *m/z* (%): 461/460 (28/100) [M^+]. – Anal. Cald for $C_{29}H_{30}F_2N_2O$: C, 75.63, H, 6.57, N, 6.08. Found: C, 75.86, H, 6.57, N, 5.87. – $[\alpha]_D^{25}$ = +76.0 (*c* 0.62, $CHCl_3$).

(1*S*,3*R*,4*R*)-6,6-Difluorodispiro[2.0.2.1]hept-1-ylmethyl 4-(5-octylpyrimid-2-yl)phenyl ether [(1*S*,3*R*,4*R*)-**7a**]: Colorless crystals (176 mg, 66%), mp 102 °C. – R_f = 0.23 (pentane/diethyl ether 5:1). – IR (KBr): $\tilde{\nu}$ = 1250 cm^{-1}. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.87 (t, *J* 6.5 Hz, 3 H),

0.99 (t, *J* 4.9 Hz, 1 H), 1.01–1.33 (m, 10 H), 1.55–1.75 (m, 8 H), 2.59 (t, *J* 7.8 Hz, 2 H), 4.00 (dd, *J* 9.9 Hz, 7.4 Hz, 1 H), 4.13 (dd, *J* 9.9 Hz, 6.8 Hz, 1 H), 6.97 (d, *J* 8.9 Hz, 2 H), 8.34 (d, *J* 8.9 Hz, 2 H), 8.57 (s, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 10.0, 10.7, 14.0, 15.3 (d, J_{CF} 3.2 Hz), 16.1 (t, J_{CF} 10.8 Hz), 19.0 (t, J_{CF} 10.8 Hz), 20.4 (d, J_{CF} 3.2 Hz), 22.6, 29.0, 29.1, 29.2, 30.1, 30.8, 31.7, 70.9, 114.5 (t, J_{CF} 250 Hz), 114.5, 129.3, 130.4, 132.2, 156.9, 160.8, 162.3. – MS (70 eV, EI), *m/z* (%): 427/426 (11/49) [M^+], 185 (100). – $[\alpha]_D^{25}$ = +105.4 (*c* 1.06, $CHCl_3$).

(1*S*,3*R*,4*R*)-6,6-Difluorodispiro[2.0.2.1]hept-1-ylmethyl 2-(4'-pentyl-1,1'-biphenyl-4-yl)pyrimid-5-yl ether [(1*S*,3*R*,4*R*)-**7b**]: Colorless solid (267 mg, 92%), C 133 SmA 146.9 N* 163.8 I. – R_f = 0.63 (pentane/diethyl ether 1:1). – IR (KBr): $\tilde{\nu}$ = 1277 cm^{-1}, 1201. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.91 (t, *J* 6.8 Hz, 3 H), 1.04 (t, *J* 5.0 Hz, 1 H), 1.33–1.38 (m, 7 H), 1.53–1.75 (m, 5 H), 2.65 (t, *J* 7.3 Hz, 2 H), 4.04 (dd, *J* 9.8 Hz, 7.4 Hz, 1 H), 4.21 (dd, *J* 9.8 Hz, 6.8 Hz, 1 H), 7.27 (d, *J* 8.9 Hz, 2 H), 7.59 (d, *J* 8.5 Hz, 2 H), 7.70 (d, *J* 8.5 Hz, 2 H), 8.40 (d, *J* 8.9 Hz, 2 H), 8.47 (s, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 10.0, 10.7 (d, J_{CF} 3.2 Hz), 14.0, 15.1 (d, J_{CF} 3.3 Hz), 16.1 (t, J_{CF} 11.0 Hz), 19.3 (t, J_{CF} 11.0 Hz), 20.5 (d, J_{CF} 3.2 Hz), 22.5, 31.1, 31.5, 35.5, 71.8, 126.9, 127.0, 127.9, 128.8, 136.0, 137.8, 142.4, 142.5, 144.0, 151.2, 157.7. – ^{19}F NMR (470 MHz, $CDCl_3$): δ = –132.6 (dd, *J* 153 Hz, 10 Hz, 1 F), –138.2 (dt, *J* 153 Hz, 8.6 Hz, 1 F). – MS (70 eV, EI), *m/z* (%): 461/460 (32/100) [M^+]. – Anal. Calcd for $C_{29}H_{30}F_2N_2O$: C, 75.63, H, 6.57, N, 6.08. Found: C, 75.43, H, 6.30, N, 5.89. – $[\alpha]_D^{25}$ = +102.1 (*c* 0.83, $CHCl_3$).

2-(4'-Pentyl-1,1'-biphenyl-4-yl)pyrimid-5-yl (1*R*,3*R*)-7,7-difluorodispiro[2.0.2.1]-heptane-1-carboxylate [(1*R*,3*R*)-**13b**]: According to the synthesis of (1*R*,3*R*)-**14a**[p], the compound (1*R*,3*R*)-**13b** was prepared. Colorless solid (107 mg, 65%), mp 162 °C. – R_f = 0.38 (benzene). – IR (KBr): $\tilde{\nu}$ = 1758 cm^{-1}, 1233. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.91 (t, *J* 6.7 Hz, 3 H), 1.18–1.38 (m, 7 H), 1.58–1.77 (m, 4 H), 1.79–1.89 (m, 1 H), 2.62–2.69 (m, 3 H), 7.28 (d, *J* 8.1 Hz, 2 H), 7.59 (d, *J* 8.1 Hz, 2 H), 7.71 (d, *J* 8.5 Hz, 2 H), 8.45 (d, *J* 8.5 Hz, 2 H), 8.64 (s, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 5.0, 6.9, 14.0, 14.7, 18.7 (t, J_{CF} 11.0 Hz), 20.3, 22.5, 26.8 (t, J_{CF} 12.8 Hz), 31.1, 31.5, 35.5, 126.9, 127.1, 128.6, 128.9, 135.3, 137.6, 142.7, 143.3, 143.9, 150.0, 161.8, 169.4 (d, J_{CF} 4.4 Hz). – ^{19}F NMR (470 Mz, $CDCl_3$): δ = –137.2 (dd, *J* 146 Hz, 7.8 Hz, 1 F), –135.4 (dt, *J* 146 Hz, 8.0 Hz, 1 F). – MS (70 eV, EI), *m/z* (%): 475/474 (27/88) [M^+], 318/317 (14/100). – Anal. Cald for $C_{29}H_{28}F_2N_2O_2$: C, 73.40, H, 5.95, N, 5.90. Found: C, 73.09, H, 6.19, N, 5.95. – $[\alpha]_D^{25}$ = –56.7 (*c* 1.00, $CHCl_3$).

(1*S*,3*S*)-7,7-Difluoro[2.0.2.1]hept-1-ylmethyl 4-(5-octylpyrimid-2-yl)phenyl ether [(1*S*,3*S*)-15a]: To a mixture of (1*S*,3*S*)-**10** (120 mg, 0.75 mmol), 4-(5-octylpyrimid-2-yl)phenol (213 mg, 0.75 mmol), PPh_3 (236 mg, 0.9 mmol) and THF (10 mL), was addded dropwise DEAD (348 mg, 2 mmol) at room temperature. The resulting mixture was stirred at ambient temperature over night. The mixture was extracted with diethyl ether (30 mL), the organic layer was washed with water (2 × 20 mL) and dried over anhydrous $MgSO_4$. After removing the solvent under reduced pressure, the residue was purified by silica gel column chromatography on silica gel (60 mL) eluting with pentane/diethyl ether (5:1). Crystallization from MeOH gave 225 mg (70%) of (1*S*,3*S*)-**15a** as colorless crystals, mp 76 °C. – R_f = 0.24. – IR (KBr): $\tilde{\nu}$ = 1246 cm^{-1}, 1169. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.84–1.09 (m, 6 H), 1.19–1.31 (m, 12 H), 1.46 (dd, *J* 8.3 Hz, 5.1 Hz, 1 H), 1.57–1.65 (m, 2 H), 2.08 (ddd, *J* 11.1 Hz, 8.4 Hz, 5.6 Hz, 1 H), 2.59 (t, *J* 7.3 Hz, 2 H), 3.95 (dd, *J* 10.0 Hz, 5.7 Hz, 1 H), 3.99 (dd, *J* 10.0 Hz, 5.7 Hz, 1 H), 6.92 (d, *J* 9.0 Hz, 2 H), 8.33 (d, *J* 9.0 Hz, 2 H), 8.57 (s, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 6.0, 6.3, 10.1, 14.0, 17.8 (t, J_{CF} 11.2 Hz), 18.4, 21.9 (t , J_{CF} 11.7 Hz), 22.6, 29.0, 29.1, 29.2, 30.1, 30.7, 31.7, 67.5, 114.3, 115.1 (t, J_{CF} 290 Hz), 129.4, 130.6, 132.2, 156.9, 160.3, 162.2. – MS (70 eV, EI), *m/z* (%): 426 (96) [M^+], 185 (100). – Anal. Cald for $C_{26}H_{32}F_2N_2O$: C, 73.21, H, 7.56, N, 6.57. Found: C, 73.60, H, 7.57, N, 6.51. – $[\alpha]_D^{25}$ = +16.4 (*c* 1.05, $CHCl_3$).

According to the synthesis of (1*S*,3*S*)-**15a**, (1*R*,3*R*)-**15b** and (1*S*,3*S*)-**16a** were prepared from the corresponding optically active alcohols.

(1*R*,3*R*)-7,7-Difluorodispiro[2.0.2.1]hept-1-ylmethyl 2-(4'-pentyl-1,1'-biphenyl-4-yl)pyrimid-5-yl ether [(1*R*,3*R*)-15b]: Colorless crystals (201 mg, 70%), mp 162 °C. – R_f = 0.50 (pentane/diethyl ether 5:1). – IR (KBr): $\tilde{\nu}$ = 1280 cm^{-1}, 1251, 1135, 786. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.88–1.10 (m, 6 H), 1.21–1.38 (m, 6 H), 1.51–1.60 (m, 1 H), 1.63–1.68 (m, 2 H), 2.10–2.15 (m, 1 H), 2.65 (t, *J* 7.4 Hz, 2 H), 4.02 (dd, *J* 12.0 Hz, 6.2 Hz, 1 H), 4.04 (dd, *J* 12.0 Hz, 6.2 Hz, 1 H), 7.28 (d, *J* 8.4 Hz, 2 H), 7.58 (d, *J* 8.4 Hz, 2 H), 7.70 (d, *J* 8.4 Hz, 2 H), 8.40 (d, *J* 8.4 Hz, 2 H), 8.43 (s, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 6.1, 6.3, 10.4, 14.0, 17.6 (t, J_{CF} 11.4 Hz), 18.1, 22.1 (t, J_{CF} 11.4 Hz), 22.5, 31.1, 31.5, 35.5, 69.0 (d, J_{CF} 3.3 Hz), 114.7 (t, J_{CF} 250 Hz), 126.9, 127.0, 127.9, 128.8, 135.8, 137.8, 142.4, 142.5, 143.8, 150.8, 157.9. – MS (70 eV, EI), *m/z* (%): 461/460 (32/100) [M^+]. – Anal. Cald for $C_{29}H_{30}F_2N_2O$: C, 75.63, H, 6.57, N, 6.08. Found: C, 75.60, H, 6.74, N, 5.97. – $[\alpha]_D^{25}$ = –2.47 (*c* 0.97, $CHCl_3$).

(1*S*,3*S*)-7,7-Dichloro[2.0.2.1]hept-1-ylmethyl 4-(5-octylpyrimid-2-yl)phenyl ether [(1*S*,3*S*)-16a]: Colorless crystals (368 mg, 80%), mp 102

°C. – R_f = 0.30 (pentane/diethyl ether 5:1). – IR (KBr): $\tilde{\nu}$ = 1250 cm^{-1}, 1169, 1106. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.87 (t, *J* 5.9 Hz, 3 H), 0.99–1.05 (m, 2 H), 1.14 (t, *J* 5.5 Hz, 1 H), 1.26–1.30 (m, 13 H), 1.53–1.65 (m, 2 H), 2.15 (dq, *J* 8.6 Hz, 5.6 Hz, 1 H), 2.58 (t, *J* 7.4 Hz, 2 H), 3.95 (dd, *J* 9.8 Hz, 4.1 Hz, 1 H), 3.98 (dd, *J* 9.8 Hz, 5.7 Hz, 1 H), 6.90 (d, *J* 8.9 Hz, 2 H), 8.33 (d, *J* 8.9 Hz, 2 H), 8.56 (s, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 8.7, 8.9, 12.5, 14.0, 20.8, 22.5, 28.9, 29.0, 29.1, 29.2, 30.0, 30.7, 31.7, 32.6, 67.3, 67.5, 114.2, 129.3, 130.6, 132.1, 156.9, 160.3, 162.2. – MS (70 eV, EI), *m/z* (%): 460/458 (33/48) [M^+], 284 (100). – Anal. Cald for $C_{26}H_{32}Cl_2N_2O$: C, 67.97, H, 7.02, N, 6.10. Found: C, 67.71, H, 6.98, N, 5.97. – $[\alpha]_D^{25}$ = +60.2 (*c* 0.97, $CHCl_3$).

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