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Liquid Crystalline Compounds with 2,2-Disubstituted Cyclopropane End Groups in their Side Chains*

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Novel liquid crystalline compounds with racemic and enantiomerically pure 2,2-difluoro-, 2,2-dichloro-, 2,2-dibromo-, and 2,2-bis(trifluoromethyl)-cyclopropane-1-carboxylate end groups have been synthesized. The Ps values, tilt angles, and response times of SmC* mixtures containing 10 wt% of the novel optically active liquid crystalline compounds in a SmC base mixture were measured, and the potential of the novel compounds as chiral dopants for ferroelectric liquid crystal mixtures was estimated. The novel liquid crystalline compounds with racemic bis(trifluoromethyl)cyclopropane have a remarkably strong tendency to form smectic phases SmB and SmA. The bistrifluoromethyl derivatives exhibited only SmB and SmA phases although the corresponding compounds with 2,2-difluoro-, 2,2-dichloro-, and 2,2-dibromocyclopropane rings showed nematic or chiral nematic phases. In some cases, almost perfect substitutions of the nematic phases by the smectic phases upon changing the substituents from halogen to trifluoromethyl were observed.

Keywords: cyclopropane; trifluoromethyl; halogen; ferroelectric; synthesis

* Part 68 in the series "Cyclopropyl Building Blocks in Organic Synthesis". For part 67 see: A. Brandi, S. Cicchi, M. Brandl, S. I. Kozhushkov, A. de Meijere, *Synlett* **2001**, submitted; part 66 see: M. W. Nötzel, T. Labahn, M. Es-Sayed, A. de Meijere, *Eur. J. Org. Chem.* **2001**, submitted.

INTRODUCTION

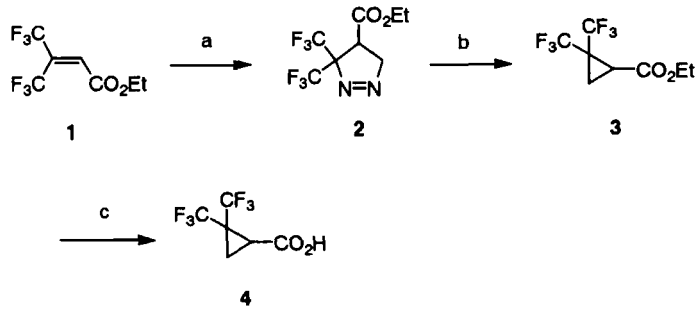
Although a huge number of liquid crystalline compounds have been synthesized until now,[1] only a small number of compounds with 2,2-disubstituted cyclopropane rings have been reported.[2] 2,2-Disubstituted cyclopropane moieties definitely have conformational characteristics which differ from those of the normal and branched alkyl chains. To estimate the potential of 2,2-disubstituted cyclopropane moieties as structural entities of liquid crystalline compounds, we have developed the synthetic methodology providing 2,2-dihalo- and 2,2-bis(trifluoromethyl)cyclopropane-1-carboxylic acids both in racemic and enantiomerically pure forms, synthesized novel liquid crystalline compounds with these structural moieties and measured their physical properties.

RESULTS AND DISCUSSION

Synthesis

2,2-Bis(trifluoromethyl)cyclopropane-1-carboxylic acid **4** was synthesized by photolysis of the pyrazoline **2** which was prepared from ethyl 3,3-bis(trifluoromethyl)acrylate **1**[3] and diazomethane, followed by hydrolysis using NaOH in aqueous ethanol (SCHEME 1). Photolysis of the pyrazoline **2** in boiling CCl_4 gave the best result. Pyrolysis of **2** at 180 °C gave a mixture of the ethyl ester **3** and two undesired isomers, i. e. ethyl 5,5,5-trifluoro-4-trifluoromethylpent-3-enoate and ethyl 1-methyl-3,3-bis(trifluoromethyl)-acrylate.

SCHEME 1

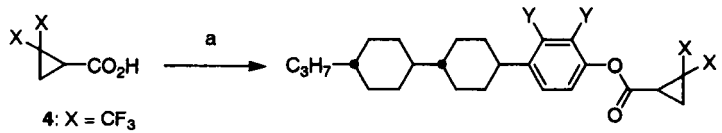


1 2 3 4

a: CH_2N_2, Et_2O, r. t., 1 h (99%). – b: hv, CCl_4, Δ, 20 h (99%). – c: NaOH, EtOH, H_2O, Δ, 3 h (86%).

2,2-Difluoro-, 2,2-dichloro-, and 2,2-dibromocyclopropane-1-carboxylic acids **5**, **6** and **7** were prepared according to procedures described in the literature.[4][5][6] The synthesized four 2,2-disubstituted cyclopropane-1-carboxylic acids **4**, **5**, **6** and **7** were transformed into liquid crystalline compounds with ester linkages **8**, **9**, **10**, **11**, **12**, **13** and **14** in racemic form by usual synthetic procedures (SCHEME 2).

SCHEME 2

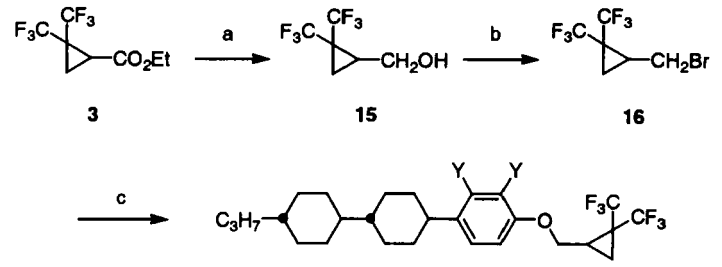


4: X = CF_3
5: X = F
6: X = Cl
7: X = Br

8: X = CF_3, Y = H (69%)
9: X = CF_3, Y = F (79%)
10: X = F, Y = H (77%)
11: X = F, Y = F (53%)
12: X = Cl, Y = H (90%)
13: X = Cl, Y = F (71%)
14: X = Br, Y = F (52%)

a: AOH, DCC, DMAP, CH_2Cl_2, r. t., 12 h, A = 4-[4-(4-propylcyclohexyl)-cyclohexyl)]phenyl, 2,3-difluoro-4-[4-(4-propylcyclohexyl)cyclohexyl)]-phenyl.

SCHEME 3



3 **15** **16**

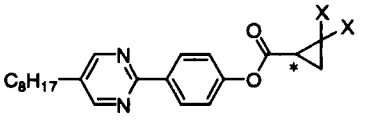
17: Y = H (21%)
18: Y = F (52%)

a: $LiAlH_4$, Et_2O, −10 °C ~ r. t., 2.5 h (69%). – b: PPh_3Br_2, Py, CH_2Cl_2, r. t., 12 h (94%). – c: AOH, K_2CO_3, EtOH, Δ, 7 h, A = 4-[4-(4-propylcyclohexyl)-cyclohexyl)]phenyl, 2,3-difluoro-4-[4-(4-propylcyclohexyl)cyclohexyl)]-phenyl.

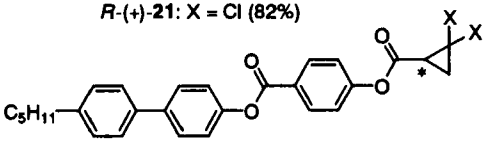
The ethyl ester **3** was reduced with $LiAlH_4$ in ether, and the primary alcohol **15** transformed to the bromide **16** by treatment with PPh_3Br_2 in a mixture of pyridine and CH_2Cl_2. The bromide **16** was substituted with the appropriate phenols under basic condition to result in the two types of liquid crystalline compounds **17** and **18** with ether linkages (SCHEME 3).

SCHEME 4

R-(–)-**4**: X = CF_3 (>95% *ee*)
S-(–)-**5**: X = F (46% or 53% *ee*)
R-(+)-**6**: X = Cl (>95% *ee*)
S-(–)-**6**: X = Cl (>95% *ee*)



R-(–)-**19**: X = CF_3 (85%)
S-(–)-**20**: X = F (25%)
R-(+)-**21**: X = Cl (82%)



R-(–)-**22**: X = CF_3 (86%)
S-(–)-**23**: X = F (95%)
S-(–)-**24**: X = Cl (68%)

a: AOH, DCC, DMAP, CH_2Cl_2, r. t., 12 h, A = 4-(5-octylpyrimid-2-yl)-phenyl, 4-(4-pentyl-1,1'-biphenyl-4'-yl)oxycarbonylphenyl.

The racemates **4** and **6** were optically resolved using *S*-(–)-1-phenylethanol (99.7% *ee*) as the chiral auxiliary. The racemates **4** and **6** were esterified with

S-(−)-1-phenylethanol (99.7% *ee*) using DCC and DMAP to give a mixture of two of diastereoisomers, which were separated by column chromatography on silica gel, then both diastereoisomeric esters were cleaved by treatment with 30% HBr in acetic acid at room temperature, to give the carboxylic acids *R*-(−)-**4**, *R*-(+)-**6** and *S*-(−)-**6** in optically active form. The enantiomeric excesses of the prepared carboxylic acids *R*-(−)-**4**, *R*-(+)-**6** and *S*-(−)-**6** were determined by Mosher's method[7] to be >95% *ee* according to the ^{1}H NMR spectra. The absolute configurations of the prepared optically active carboxylic acids were confirmed by X-ray structural analyses of the corresponding *R*-(+)-1-phenylethylamides.

Attempted optical resolutions of the racemates by crystallization of diastereomeric salts with optically active amines like *R*-(+)-1-phenylethylamine and (+)-dehydroabietylamine, were not successful and gave the carboxylic acids only with poor enantiomeric excesses (15–82% *ee*).

In case of the optical resolution of 2,2-difluorocyclopropane-1-carboxylic acid (**5**) by the previously described procedure, the hydrolysis of the diastereomeric ester with 30% HBr in acetic acid exclusively resulted in the ring-opening product 4-bromo-3,3-difluorobutyric acid. Therefore the optically active 2,2-difluorocyclopropane-1-carboxylic acid *S*-(−)-**5** was prepared by crystallization using (+)-dehydroabietylamine as the chiral resolving reagent in 46% *ee* and 53% *ee*. The optically active 2,2-disubstituted cyclopropane-1-carboxylic acids *R*-(−)-**4**, *S*-(−)-**5**, *R*-(+)-**6** and *S*-(−)-**6** were transformed into the liquid crystalline compounds *R*-(−)-**19**, *S*-(−)-**20**, *R*-(+)-**21**, *R*-(−)-**22**, *S*-(−)-**23** and *S*-(−)-**24** by usual synthetic techniques (SCHEME 4).

Physical properties of the liquid crystalline compounds in racemic forms

The phase transition temperatures, extrapolated dielectric anisotropies ($\Delta\varepsilon$) and extrapolated optical anisotropies (Δn) of the synthesized novel liquid crystalline compounds with 2,2-disubstituted cyclopropane rings in their side chains in racemic form are summarized in TABLE 1. The extrapolated values for $\Delta\varepsilon$ and Δn were obtained using a base mixture A (see Experimental).

The observed phase transition temperatures and phase sequences clearly indicate that the trifluoromethyl group has strong smectogenic characteristics. The compounds with trifluoromethyl groups in their side chains showed only SmB for the compounds **8** and **17**, and SmA for the compounds **9** and **18**, while the corresponding compounds with *n*-alkyl chains have nematic phases.[8] The 2,2-bis(trifluoromethyl)cyclopropane moiety at the terminal position of the liquid crystalline compounds may work as a hydrophobic part and the propyl group at the opposite end as a relatively hydrophilic part. Intermolecular interactions of the liquid crystalline

compounds can be influenced by these different polarities at the two termini, which induces a tendency to form layered structures in the mesomorphic states.

TABLE 1 Phase transition temperatures, extrapolated dielectric anisotropies ($\Delta\varepsilon$) and extrapolated optical anisotropies (Δn) of the liquid crystalline compounds with 2,2-disubstituted cyclopropane rings in their side chains in racemic form[1)]

Compound	Phase Transition Temperatures/°C	$\Delta\varepsilon$	Δn
8	Cr < r.t. SmB 199.9 I	−0.82	0.080
9	Cr 110.5 SmA 156.1 I	−3.22	0.080
10	Cr 99.7 SmB 199.2 N 199.6 I	–[2)]	–[2)]
11	Cr 123.0 N 176.1 I	–[2)]	–[2)]
12	Cr < r.t. SmB 178.3 I	–[2)]	–[2)]
13	Cr 121.7 N 146.0 I	−2.62[3)]	0.097[3)]
14	Cr 124.5 N 135.5 I	–[2)]	–[2)]
17	Cr 68.2 SmB 176.6 I	−1.58	–[2)]
18	Cr 75.2 SmA 130.3 I	−4.89	0.080

1) Extrapolated from mixtures of 15 wt% of the compounds and the base mixture A.
2) Miscibility was very low, < 5 wt%.
3) Extrapolated from a mixture of 10 wt% of the compound and the base mixture A.

The 2,2-bis(trifluoromethyl)cycloprop-1-ylmethoxy group apparently helped to induce the dipole moment along the short axis of the liquid crystalline molecules. The compound **17** without the fluorine substituents on the benzene ring and **18** with the fluorine substituents showed a negative $\Delta\varepsilon$ with large magnitudes of −1.58 and −4.89, respectively.

Physical properties of the liquid crystalline compounds in optically active form

Phase transition temperatures of the optically active liquid crystalline compounds *R*-(−)-**19**, *S*-(−)-**20**, *R*-(+)-**21**, *R*-(−)-**22**, *S*-(−)-**23** and *S*-(−)-**24** are summarized in Table 2. Among the biaryl derivatives, only the compound *S*-(−)-**20** with the fluorine substituents on the cyclopropane ring exhibited a monotropic SmA, while the compounds *R*-(−)-**19** and *R*-(+)-**21** with the chlorine and the trifluoromethyl substituents showed only melting points at 75 °C and 47 °C, respectively. This result indicates that the bulky substituents such as chlorine and trifluoromethyl, decrease the length to breadth ratios of the molecules, which diminishes their mesogeneity.[9] A strong tendency to

show smectic phases was found also for the bicyclohexylaryl derivatives with three rings in the mesogenic unit. The bis(trifluoromethyl) derivative *R*-(−)-**22** exhibits only an SmA phase in the range 143–187.5 °C, while the difluoride *S*-(−)-**23** shows only a nematic phase.

TABLE 2 Phase transition temperatures of the liquid crystalline compounds with optically active 2,2-disubstituted cyclopropane rings in their side chains

Compound	Phase Transition Temperatures/°C
R-(−)-**19**	Cr 75 I
S-(−)-**20**[1]	Cr 69 (SmA 50) I
R-(+)-**21**	Cr 47 I
R-(−)-**22**	Cr 143 SmA 187.5 I
S-(−)-**23**[2]	Cr 159 N* 198.7 I
S-(−)-**24**	Cr 127 (SmX 119.7) SmC* 128.2 N* 176.3 I

1) *S*-(−)-**5** with 46% *ee* was used for the preparation.
2) *S*-(−)-**5** with 53% *ee* was used for the preparation.

TABLE 3 Physical properties of SmC* mixtures containing 10 wt% of the optically active liquid crystalline compounds and the base mixture B

Compound	Transition Temperatures /°C	τ /μsec	Ps /nC cm^{-2}	θ/°	N*[1]
R-(−)-**19**	SmC* 59.0 SmA 79.6 N* 85.2 I	92	−3.0	20.7	R
S-(−)-**20**[2]	SmC* 54.7 SmA 76.1 N* 84.6 I	96	−2.8	18.3	R
R-(+)-**21**	SmC* 55.1 SmA 75.1 N* 83.2 I	100	+1.9	18.2	L
R-(−)-**22**	SmC* 72.7 SmA 79.0 N* 91.7 I	–[4]	–[4]	26.7	–[5]
S-(−)-**23**[3]	SmC* 70.4 SmA 74.7 N* 92.1 I	–[4]	–[4]	–[4]	R
S-(−)-**24**	SmC* 69.2 SmA 74.3 N* 91.6 I	–[4]	–[4]	–[4]	R

1) Helical sense of N* phase where R and L indicate right- and left-handed, respectively.
2) *S*-(−)-**5** with 46% *ee* was used for the preparation.
3) *S*-(−)-**5** with 53% *ee* was used for the preparation.
4) Due to the very small values for Ps, the switching was not observed.
5) A helical structure was not formed in the Cano-wedge cell.

All synthesized optically active compounds showed relatively small Ps values (<3.0 nC cm^{-1}) and slow switching in the applied electric field. Especially the three rings system *R*-(−)-**22**, *S*-(−)-**23** and *S*-(−)-**24** showed extremely small Ps values (~0 nC cm^{-1}) so that switching times could not be measured (TABLE 3).

TABLE 4 Dependence of helical pitches (μm) of N* mixtures containing 1 wt% of the optically active compounds with 2,2-disubstituted cyclopropane rings in ZLI-1132®

Compound	60 °C	50 °C	40 °C	30 °C	25 °C	20 °C
R-(−)-**19**	24.0	24.4	24.2	24.7	25.0	25.2
S-(−)-**20**[1)]	53	54	58	60	63	64
R-(+)-**21**	10.4	10.6	10.7	10.8	10.9	10.9
S-(−)-**23**[2)]	61	60	66	69	71	72
S-(−)-**24**	14.7	18.1	18.4	19.1	19.1	19.4

1) *S*-(−)-**5** with 46% *ee* was used for the preparation.
2) *S*-(−)-**5** with 53% *ee* was used for the preparation.

The dependences of helical pitches of N* mixtures containing 1 wt% of the synthesized optically active compounds in ZLI-1132® are summarized in Table 4. The dichlorides *R*-(+)-**21** and *S*-(−)-**24** showed the shorter pitches in the range of 10–20 μm, than the difluorides *S*-(−)-**20**, *S*-(−)-**23** and bis(trifluoromethyl) derivatives *R*-(−)-**19**. The helical pitches of all the compounds listed in Table 4 increased as temperature decreased. The compound *R*-(−)-**22** did not form a helical structure under these conditions.

CONCLUSION

Novel liquid crystalline compounds with racemic and optically active 2,2-difluoro-, 2,2-dichloro-, 2,2-dibromo-, and 2,2-bis(trifluoromethyl)cyclopropane-1-carboxylate end groups have been synthesized. The novel liquid crystalline compounds with the 2,2-bis(trifluoromethyl)cyclopropane rings have a remarkably strong tendency to form smectic phases SmB and SmA. The bis(trifluoromethyl) derivatives exhibited only SmB and SmA phases although the corresponding compounds with 2,2-difluoro-, 2,2-dichloro-, and 2,2-dibromocyclopropane rings showed nematic or chiral nematic phases. The novel compounds in optically active forms showed relatively small Ps values and slow response phenomena when doped in the SmC base mixture.

EXPERIMENTAL

Mesasurements

The nematic base mixture ZLI-1132® (N-I point 71.7 °C, $\Delta\varepsilon$ 11.0, Δn 0.132) is available from Merck GmbH. The nematic base mixture A (N-I point 74.6 °C, $\Delta\varepsilon$ −1.23) is a liquid crystal mixture consisting of 4-ethoxyphenyl 4-propylcyclohexane-1-carboxylate, 4-butoxyphenyl 4-propylcyclohexane-1-carboxylate, 4-ethoxyphenyl 4-butylcyclohexane-1-carboxylate, 4-methoxyphenyl 4-pentylcyclohexane-1-carboxylate, 4-ethoxyphenyl 4-pentylcyclohexane-1-carboxylate in a ratio of 10:16:12:12:8 in weights. Evaluation of the synthesized novel liquid crystalline compounds as chiral dopants was made for mixtures containing 10 wt% of the novel compounds in the achiral SmC mixture base mixture B (Cr 4 SmC 65 SmA 79 N 90 I) comprising of 2-(4-hexyloxyphenyl)-5-octylpyrimidine (30 wt%), 5-octyl-2-(4-octyloxyphenyl)pyrimidine (20 wt%), 2-(4-nonyloxyphenyl)-5-octylpyrimidine (10 wt%), 2-(4-decyloxyphenyl)-5-heptylpyrimidine (10 wt%), 5-octyl-2-(4'-pentyl-1,1'-biphenyl-4-yl)pyrimidine (20 wt%), and 2-(4'-hept-yl-1,1'-biphenyl-4-yl)-5-octylpyrimidine (10 wt%). 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,[10] 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.[11] 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.[12] The helical pitch in the N* phase was determined on N* mixtures containing 1 wt% of the novel compounds in the nematic mixture ZLI-1132®, by the Cano-wedge method.[13] 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.

Synthesis

General: All reactions with moisture- and air-sensitive substrates or reagents were carried out under an atmosphere of dry nitrogen. Diethyl ether was 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 mentioned. 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), 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.

4-Ethoxycarbonyl-3,3-bistrifluoromethyl-2-pyrazoline (2): To a mixture of ethyl 3,3-bistrifluoromethylacrylate **1** (236 mg, 1 mmol) and diethyl ether (4 mL), was added a solution of CH_2N_2 in diethyl ether prepared from *N*-methylnitrosourea (1.03 g, 10 mmol), 40% aqueous KOH (6.6 g, 47 mmol) in diethyl ether (8 mL) at 0 °C. The reaction mixture was stirred for 1 h and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (30 mL) eluting with pentane/diethyl ether (5:1) to yield 278 mg (99%) of **2** as a colorless oil. R_f = 0.26. – IR (Film): $\tilde{\nu}$ = 1746 cm^{-1} (C=O). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.25 (t, *J* 7.2 Hz, 3 H), 3.24 (t, *J* 8.6 Hz, 1 H), 4.14–4.28 (m, 2 H), 5.19 (dd, *J* 19.0 Hz, 8.6 Hz, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.5, 39.7, 62.7, 82.8, 98.2 (t, J_{CF} 27 Hz), 121.0 (q, J_{CF} 285 Hz), 121.6 (q, J_{CF} 285 Hz), 166.2. – MS (70 eV, EI), *m/z* (%): 279 (100), 251 (33), 233 (28), 205 (61), 185 (25), 157 (33), 137 (37), 75 (25), 69 (54). – UV (*iso*-octane): λ_{max} = 321.5 nm. – Anal. Cald for $C_8H_8F_6N_2O_2$: C, 35.54, H, 2.90, N, 10.07. Found: C, 35.08, H, 2.96, N, 10.06.

Ethyl 2,2-bis(trifluoromethyl)cyclopropane-1-carboxylate (3): A solution of **2** (3.7 g, 13.3 mmol) in CCl_4 (40 mL) in a well-washed photo reactor was irradiated with UV light from a medium pressure Hg lamp (450 W) in a quartz immersion wall for 7 h at the boiling point of the solvent. The reaction mixture was carefully distillated to give 3.29 g (99%) of **3** as a colorless oil, bp 110 °C (320 mbar). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.24 (t, *J* 7.1 Hz, 3 H), 1.54 (t, *J* 8.8 Hz, 1 H), 1.91 (t, *J* 8.8 Hz, 1 H), 2.45 (t, *J* 8.8 Hz, 1 H), 4.11–4.28 (m, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.2, 13.6, 23.3, 32.4 (t, J_{CF} 34 Hz), 62.0, 122.4 (q, J_{CF} 276 Hz), 165.4. – MS (70 eV, EI), *m/z* (%): 250 (3), 205 (100). – Anal. Cald for $C_8H_8F_6O_2$: C, 38.41, H, 3.22. Found: C, 38.15, H, 3.35.

2,2-Bis(trifluoromethyl)cyclopropane-1-carboxylic acid (4): A mixture of **3** (5.0 g, 20 mmol), NaOH (960 mg, 24 mmol), ethanol (80 mL) and water (40 mL) was stirred under reflux for 3 h. The reaction mixture was shaken with diethyl ether (30 mL) and the separated aqueous layer was acidified with 6M HCl to pH 2.0. The resulting acidic mixture was extracted with diethyl ether (3 × 20 mL) and the separated organic layer was dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by recrystallization from pentane (2 mL) to yield 3.82 g (86%) of **4** as colorless crystals, mp 39–42 °C. – ^{1}H NMR (250 MHz, $CDCl_3$):

δ = 1.65 (t, *J* 8.0 Hz, 1 H), 1.98 (t, *J* 8.0 Hz, 1 H), 2.52 (t, *J* 8.0 Hz, 1 H), 9.90 (brs, 1 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.6, 23.1, 33.2 (q, J_{CF} 36.2 Hz), 122.3 (q, J_{CF} 276 Hz), 170.9. – MS (70 eV, EI), *m/z* (%): 222 (1), 205 (15), 183 (44), 158 (80), 153 (100), 145 (17), 89 (35), 69 (33), 45 (36). – Anal. Calcd for $C_6H_4F_6O_2$: C, 32.45, H, 1.82. Found: C, 32.48, H, 1.92.

4-[*trans*-4-(*trans*-4-Propylcyclohexyl)cyclohexyl]phenyl 2,2-bis(trifluoromethyl)cyclopropane-1-carboxylate (8): A mixture of **4** (68.5 mg, 0.31 mmol), 4-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]phenol (111 mg, 0.37 mmol), DCC (96 mg, 0.47 mmol), DMAP (3.8 mg, 0.031 mmol) and CH_2Cl_2 (2 mL) was stirred at room temperature for 12 h. The precipitates were removed by filtration, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (25 mL) eluting with hexane/toluene (2:1) to yield 108 mg (69%) of **8** as a colorless solid, R_f = 0.37, Cr < r. t. SmB 199.9 I. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.88–1.45 (m, 18 H), 1.67–1.95 (m, 9 H), 2.09 (t, *J* 8.6 Hz, 1 H), 2.47–2.52 (m, 1 H), 2.75 (t, *J* 8.6 Hz, 1 H), 7.03 (d, *J* 8.5 Hz, 2 H), 7.23 (d, *J* 8.5 Hz, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.6, 14.3, 20.0, 23.4, 30.0, 30.2, 32.9 (t, J_{CF} 35 Hz), 33.5, 34.5, 37.6, 39.8, 42.8, 43.3, 44.0, 120.5 (q, J_{CF} 279 Hz), 120.6, 131.8, 146.0, 148.1, 164.3. – MS (70 eV, EI), *m/z* (%): 504 (19), 301 (26), 300 (100), 205 (8), 120 (20). – Anal. Calcd for $C_{27}H_{34}F_6O_2$: C, 64.27, H, 6.79. Found: C, 64.47, H, 7.10.

According to the method for the preparation of compound **8**, the compounds **9**, **10**, **11**, **12**, **13** and **14** were synthesized from 2,2-bis(trifluoromethyl)cyclopropane-1-carboxylic acid **4**, 2,2-difluorocyclopropane-1-carboxylic acid **5**, 2,2-dichlorocyclopropane-1-carboxylic acid **6** and 2,2-dibromocyclopropane-1-carboxylic acid **7**.

2,3-Difluoro-4-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]-phenyl 2,2-bis(trifluoromethyl)cyclopropane-1-carboxylate (9): From 99.9 mg (0.45 mmol) of **4**, 2,3-difluoro-4-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]phenol (150 mg, 0.45 mmol), DCC (120 mg, 0.58 mmol), DMAP (5.5 mg, 0.045 mmol) and CH_2Cl_2 (10 mL) was obtained 192 mg (79%) of **9**, R_f = 0.69 (pentane/diethyl ether 5:1) as colorless crystals, Cr 110.5 SmA 156.1 I. – IR (KBr): $\tilde{\nu}$ = 1783 cm^{-1} (C=O). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.87 (t, *J* 7.0 Hz, 3 H), 0.96–1.52 (m, 16 H), 1.74–1.90 (m, 9 H), 2.10 (t, *J* 7.0 Hz, 1 H), 2.74–2.81 (m, 1 H), 6.80 (t, *J* 8.7 Hz, J_{HF} 1.9 Hz, 1 H), 6.96 (t, *J* 8.7 Hz, J_{HF} 1.9 Hz, 1 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.8, 14.3, 20.0, 22.3 (t, J_{CF} 35 Hz), 22.8, 30.05, 30.08, 33.0, 33.5, 37.2, 37.6, 39.8, 42.3, 42.8, 117.2, 121.1, 124.5 (q, J_{CF} 277 Hz), 134.7, 136.2, 140.8, 147.0 (d, J_{CF} 258 Hz), 163.2. – MS (70 eV, EI), *m/z* (%): 541/540 (6/20), 521 (2), 336 (100), 205 (26), 156 (9). – Anal. Calcd for $C_{27}H_{32}F_8O_2$: C, 60.00, H, 5.97. Found: C, 60.00, H, 5.78.

4-[*trans*-4-(*trans*-4-Propylcyclohexyl)cyclohexyl]phenyl 2,2-difluorocyclopropane-1-carboxylate (10): From 80 mg (0.66 mmol) of **5**, 4-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]phenol (216 mg, 0.72 mmol), DCC (162 mg, 0.79 mmol), DMAP (8.0 mg, 0.065 mmol) and CH_2Cl_2 (10 mL) was obtained 206 mg (77%) of **10**, R_f = 0.64 (toluene) as colorless crystals, Cr 99.7 SmB 199.2 N 199.6 I. – IR (KBr): $\tilde{\nu}$ = 1754 cm^{-1} (C=O). – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.87 (t, *J* 7.0 Hz, 3 H), 0.90–1.55 (m, 16 H), 1.74–1.94 (m, 8 H), 2.20 (triple of dd, *J* 12.0 Hz, 7.8 Hz, J_{HF} 6.4 Hz, 1 H), 2.44 (t, *J* 23 Hz, 1 H), 2.65 (ddd, *J* 12.0 Hz, 7.8 Hz, J_{HF} 10.7 Hz, 1 H), 7.00 (d, *J* 8.7 Hz, 2 H), 7.20 (d, *J* 8.7 Hz, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.4, 16.8 (t, J_{CF} 11.0 Hz), 20.0, 25.6 (t, J_{CF} 11.0 Hz), 30.0, 30.2, 33.5, 34.6, 37.5, 39.7, 42.8, 43.3, 44.0, 110.6 (t, J_{CF} 289 Hz), 120.8, 127.7, 145.7, 148.2, 165.3. – MS (70 eV, EI), *m/z* (%): 405/404 (5/20), 301 (22), 300 (100), 133 (12), 120 (23), 107 (17). – Anal. Calcd for $C_{25}H_{34}F_2O_2$: C, 74.23, H, 8.47. Found: C, 74.05, H, 8.44.

2,3-Difluoro-4-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]-phenyl 2,2-difluorocyclopropane-1-carboxylate (11): From 54.9 mg (0.45 mmol) of **5**, 2,3-difluoro-4-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]phenol (150 mg, 0.45 mmol), DCC (120 mg, 0.58 mmol), DMAP (5.5 mg, 0.045 mmol) and CH_2Cl_2 (10 mL) was obtained 106 mg (53%) of **11**, R_f = 0.59 (pentane/diethyl ether 5:1) as colorless crystals, Cr 123.0 N 176.1 I. – IR (KBr): $\tilde{\nu}$ = 1757 cm^{-1} (C=O). – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.01 (t, *J* 7.1 Hz, 3 H), 1.35–1.55 (m, 16 H), 1.74–2.00 (m, 8 H), 2.22 (triple of dd, *J* 12.0 Hz, 7.8 Hz, J_{HF} 6.4 Hz, 1 H), 2.78 (ddd, *J* 12.0 Hz, 7.8 Hz, J_{HF} 10.7 Hz, 1 H), 2.68–2.79 (m, 1 H), 6.85 (dt, *J* 8.6 Hz, J_{HF} 1.9 Hz, 1 H), 6.96 (dt, *J* 8.6 Hz, J_{HF} 1.9 Hz, 1 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.4, 17.2 (t, J_{CF} 10.0 Hz), 20.0, 25.1 (t, J_{CF} 10.3 Hz), 30.03, 30.06, 33.0, 33.5, 37.2, 37.5, 39.7, 42.7, 43.3, 110.4 (t, J_{CF} 287 Hz), 117.6, 121.0, 134.4 (d, J_{CF} 12.1 Hz), 136.4, 139.7 (dd, J_{CF} 250 Hz, 15.0 Hz), 146.9 (dd, J_{CF} 250 Hz, 11.0 Hz), 164.2. – MS (70 eV, EI), *m/z* (%): 441/440 (20/76), 337 (20), 336 (100), 316 (9), 260 (62), 247 (28), 156 (35), 143 (47), 105 (63), 83 (67), 69 (98).

4-[*trans*-4-(*trans*-4-Propylcyclohexyl)cyclohexyl]phenyl 2,2-dichlorocyclopropane-1-carboxylate (12): From 503 mg (3.25 mmol) of **6**, 4-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]phenol (976 mg, 3.25 mmol), DCC (670 mg, 3.25 mmol), DMAP (40.3 mg, 0.33 mmol) and CH_2Cl_2 (20 mL) was obtained 1.27 g (90%) of **12**, R_f = 0.71 (pentane/diethyl ether 5/1) as a white solid, Cr < r. t. SmB 178.3 I. – IR (KBr): $\tilde{\nu}$ = 1760 cm^{-1} (C=O). – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.87 (t, *J* 7.0 Hz, 3 H), 1.02–1.32 (m, 16 H), 1.78–1.99 (m, 7 H), 2.00 (dd, *J* 9.7 Hz, 7.4 Hz, 1 H), 2.20 (t, *J* 7.4 Hz, 1 H), 2.45–2.58 (m, 1 H), 2.77 (dd, *J* 9.7 Hz, 7.4 Hz, 1 H), 7.02 (d, *J* 8.6 Hz, 2 H), 7.21 (d, *J* 8.6 Hz, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.4, 20.0,

26.6, 30.0, 30.2, 33.1, 33.5, 34.5, 37.5, 39.7, 42.8, 43.3, 44.0, 57.7, 120.9, 127.7, 145.8, 148.3, 165.6. – MS (70 eV, CI), *m/z* (%): 473/471 (3/6), 458/456/454 (11/67/100). – Anal. Calcd for $C_{25}H_{34}Cl_2O_2$: C, 68.64, H, 7.83. Found: C, 68.77, H, 7.62.

2,3-Difluoro-4-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]-phenyl 2,2-dichlorocyclopropane-1-carboxylate (13): From 82.4 mg (0.54 mmol) of **6**, 2,3-difluoro-4-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]-phenol (150 mg, 0.45 mmol), DCC (120 mg, 0.59 mmol), DMAP (5.5 mg, 0.045 mmol) and CH_2Cl_2 (10 mL) was obtained 150 mg (71%) of **13**, R_f = 0.74 (toluene) as colorless crystals, Cr 121.7 N 146.0 I. – IR (KBr): $\tilde{\nu}$ = 1769 cm^{-1} (C=O). – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.87 (t, *J* 7.0 Hz, 3 H), 0.96–1.44 (m, 16 H), 1.74–2.08 (m, 7 H), 2.05 (dd, *J* 9.7 Hz, 7.4 Hz, 1 H), 2.21 (t, *J* 7.4 Hz, 1 H), 2.70–2.80 (m, 1 H), 2.83 (dd, *J* 9.7 Hz, 7.4 Hz, 1 H), 6.88 (dt, *J* 6.8 Hz, J_{HF} 1.9 Hz, 1 H), 6.95 (dt, *J* 6.8 Hz, J_{HF} 1.9 Hz, 1 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.4, 20.0, 26.9, 30.01, 30.05, 32.6, 32.9, 33.5, 37.2, 37.5, 39.7, 42.7, 43.2, 57.5, 117.5, 121.0, 134.4, 136.4, 142.7 (dd, J_{CF} 252 Hz, 15.8 Hz), 149.0 (dd, J_{CF} 247 Hz, 10.5 Hz), 164.4. – MS (70 eV, EI), *m/z* (%): 474/472 (11/16), 336 (100), 156 (12), 137 (29). – Anal. Calcd for $C_{25}H_{32}Cl_2F_2O_2$: C, 63.43, H, 6.81. Found: C, 63.67, H, 6.77.

2,3-Difluoro-4-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]-phenyl 2,2-dibromocyclopropane-1-carboxylate (14): From 110 mg (0.45 mmol) of **7**, 2,3-difluoro-4-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]-phenol (151 mg, 0.45 mmol), DCC (92.8 mg, 0.45 mmol), DMAP (5.5 mg, 0.045 mmol) and CH_2Cl_2 (20 mL) was obtained 131 mg (52%) of **14**, R_f = 0.62 (pentane/diethyl ether 5:1), as colorless crystals, Cr 124.5 N 135.5 I. – IR (KBr): $\tilde{\nu}$ = 1759 cm^{-1} (C=O). – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.87 (t, *J* 7.0 Hz, 3 H), 0.90–1.49 (m, 16 H), 1.70–1.90 (m, 7 H), 2.18 (dd, *J* 9.5 Hz, 7.7 Hz, 1 H), 2.30 (t, *J* 7.7 Hz, 1 H), 2.78 (t, *J* 11.3 Hz, 1 H), 2.88 (dd, *J* 9.5 Hz, 7.7 Hz, 1 H), 6.93 (d of quintets, *J* 7.5 Hz, J_{HF} 1.7 Hz, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.4, 19.7, 20.0, 28.7, 30.03, 30.07, 32.9, 33.0, 33.5, 37.5, 37.7, 39.7, 42.7, 43.3, 117.6, 121.1, 134.7, 136.5, 141.8 (d, J_{CF} 260 Hz), 148.0 (d, J_{CF} 260 Hz), 165.0. – MS (70 eV, EI), *m/z* (%): 564/562/560 (5/10/5), 336 (100), 229/227/225 (5/12/6). – Anal. Calcd for $C_{25}H_{32}Br_2F_2O_2$: C, 53.40, H, 5.74. Found: C, 54.04, H, 5.95.

2,2-Bis(trifluoromethyl)cycloprop-1-ylmethanol (15): A solution of **3** (15 g, 60 mmol) in diethyl ether (50 mL) was added dropwise to a suspension of $LiAlH_4$ (1.48 g, 39 mmol) in diethyl ether (100 mL) at –10 °C. The resulting mixture was stirred at room temperature for 2.5 h, then cooled to 0 °C, and sat. $MgSO_4$ was added until the precipitate turned colorless. The precipitate was removed by filtration, and the filtrate was distilled to give 8.68 g (69%) of **15** as a colorless oil, bp 90–95 °C (100 mbar). – IR (Film): $\tilde{\nu}$

= 3354 cm^{-1} (OH). – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.31–1.37 (m, 1 H), 1.41–1.50 (m, 1 H), 1.63 (brs, 1 H), 1.94–2.07 (m, 1 H), 3.73–3.81 (m, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.8, 23.6 (d, J_{CF} 2.2 Hz), 30.1 (t, J_{CF} 34.0 Hz), 59.4 (d, J_{CF} 2.6 Hz), 123.2 (q, J_{CF} 274 Hz), 123.7 (q, J_{CF} 274 Hz).

2,2-Bis(trifluoromethyl)cycloprop-1-ylmethyl bromide (16): A mixture of PPh_3 (43.2 g, 165 mmol), Br_2 (26.4 g, 165 mmol) and CH_2Cl_2 (180 mL) was stirred at –40 °C for 1 h. To the resulting suspension, a mixture of **15** (23.9 g, 115 mmol), pyridine (10.2 mL, 151 mmol) and CH_2Cl_2 (15 mL) was added dropwise at –15 °C, and the reaction mixture was stirred at room temperature for 12 h. The solvent and the crude material were bulb to bulb distilled, and the product fraction was carefully redistilled to give 29.3 g (94%) of **16** as a colorless oil, bp 67 °C (100 mbar). – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.40 (t, *J* 6.8 Hz, 1 H), 1.58 (dt, *J* 6.8 Hz, J_{CF} 1.8 Hz, 1 H), 2.11–2.25 (m, 1 H), 3.42 (dd, *J* 10.9 Hz, 9.6 Hz, 1 H), 3.58 (dd, *J* 10.9 Hz, 6.7 Hz, 1 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.3, 24.1, 26.6, 33.2 (quint, J_{CF} 34.1 Hz), 123.0 (q, J_{CF} 275 Hz), 123.5 (q, J_{CF} 275 Hz). – MS (70 eV, CI), *m/z* (%): 242 (26), 225 (100), 208 (12).

1-[2,2-Bis(trifluoromethyl)cycloprop-1-ylmethylenoxy]-4-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]benzene (17): A mixture of **16** (170 mg, 0.63 mmol), 4-[4-(4-propylcyclohexyl)cyclohexyl]]phenol (190 mg, 0.63 mmol), K_2CO_3 (96 mg, 0.69 mmol) and ethanol (7 mL) was stirred at reflux for 7h. The usual work-up followed by column chromatography on silica gel (60 mL) eluting with pentane/diethyl ether (10:1) gave 65 mg (21%) of **17** as a colorless solid, R_f = 0.70 (pentane/diethyl ether 10:1), Cr 68.2 SmB 176.6 I. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.87 (t, *J* 6.9 Hz, 3 H), 0.90–1.16 (m, 9 H), 1.25–1.51 (m, 7 H), 1.74–1.90 (m, 9 H), 2.05–2.10 (m, 1 H), 2.30–2.45 (m, 1 H), 4.05–4.13 (m, 2 H), 6.81 (d, *J* 8.7 Hz, 2 H), 7.12 (d, *J* 8.7 Hz, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.4, 14.4, 20.0, 20.9, 30.1, 30.3, 30.6 (t, J_{CF} 35 Hz), 33.6, 34.8, 37.6, 39.8, 42.9, 43.4, 43.7, 64.6, 114.4, 121.2 (q, J_{CF} 275 Hz), 127.7, 140.9, 156.2. – MS (70 eV, EI), *m/z* (%): 491/490 (26/100), 323 (12), 297 (4). – Anal. Calcd for $C_{27}H_{36}F_6O$: C, 66.11, H, 7.40. Found: C, 66.28, H, 7.17.

According to the same method compound **18** was prepared from 2,3-difluoro-4-[4-(4-propylcyclohexyl)cyclohexyl]phenol.

2,3-Difluoro-1-[2,2-bis(trifluoromethyl)cycloprop-1-ylmethyl-enoxy]-4-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]benzene (18): From 170 mg (0.63 mmol) of **16**, 2,3-difluoro-4-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]phenol (212 mg, 0.63 mmol), K_2CO_3 (96 mg, 0.69 mmol) and ethanol (8 mL) was obtained 172 mg (52%) of **18**, R_f = 0.63 (pentane/diethyl ether 10:1) as colorless solid, Cr 75.2 SmA 130.3 I. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.84–1.61 (m, 7 H), 1.74–1.89 (m, 21 H),

2.16–2.22 (m, 1 H), 2.65–2.81 (m, 1 H), 4.19 (t, *J* 8.1 Hz, 1 H), 4.20 (dd, *J* 10.1 Hz, 6.5 Hz, 1 H), 6.68 (dt, *J* 10.0 Hz, J_{CF} 2.0 Hz, 1 H), 6.85 (dt, *J* 10.0 Hz, J_{CF} 2.0 Hz, 1 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.3, 14.3, 20.0, 20.7, 29.6 (t, J_{CF} 35 Hz), 30.0, 30.2, 33.2, 33.6, 37.0, 37.6, 39.8, 42.8, 43.4, 66.8, 110.5, 120.6 (t, J_{CF} 5.0 Hz), 125.3 (q, J_{CF} 275 Hz), 125.7 (q, J_{CF} 275 Hz), 129.7 (d, J_{CF} 12 Hz), 145.2 (d, J_{CF} 2.7 Hz), 147.4 (q, J_{CF} 246 Hz), 147.5 (q, J_{CF} 246 Hz). – MS (70 eV, EI), *m/z* (%): 527/526 (27/100), 507 (2), 362 (3), 346 (10), 333 (7), 156 (9), 143 (14). – Anal. Calcd for $C_{27}H_{34}F_8O$: C, 61.59, H, 6.51. Found: C, 61.80, H, 6.54.

(*R*)-(–)-4-(5-Octylpyrimid-2-yl)phenyl 2,2-bistrifluoromethylcyclopropane-1-carboxylate [(*R*)-(–)-**19**]: A mixture of (*R*)-(–)-**4** [$[\alpha]_D^{25}$ = –31.3 (*c* 1.12, $CHCl_3$), >95% *ee*, 100 mg, 0.45 mmol], 4-(5-octylpyrimid-2-yl)phenol (340 mg, 1.2 mmol), DCC (122 mg, 0.59 mmol), DMAP (5.5 mg, 0.045 mmol) and CH_2Cl_2 (7 mL) was stirred at room temperature for 12 h. The precipitates were removed by filtration, the filtrate was washed with water (10 mL), and dried over anhydrous $MgSO_4$. Column chromatography on silica gel (100 mL) eluting with pentane/diethyl ether (5:1) gave 187 mg (85%) of (*R*)-(–)-**19** as colorless crystals, R_f = 0.16, mp 75 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.84–0.90 (m, 3 H), 1.27–1.32 (m, 8 H), 1.62–1.77 (m, 5 H), 2.13 (t, *J* 6.8 Hz, 1 H), 2.62 (t, *J* 7.4 Hz, 2 H), 2.77 (t, *J* 7.9 Hz, 1 H), 7.19 (d, *J* 8.5 Hz, 2 H), 8.46 (d, *J* 8.5 Hz, 2 H), 8.61 (s, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.7, 14.0, 19.5, 22.6, 29.0, 29.1, 29.2, 30.1, 30.7, 31.7, 32.3 (quint, J_{CF} 36.2 Hz), 119.8 (q, J_{CF} 276 Hz), 121.1, 129.2, 133.1, 135.9, 151.8, 157.0, 164.0, 165.0. – MS (70 eV, EI), *m/z* (%): 488 (19), 284 (100), 185 (24). – $[\alpha]_D^{20}$ = –15.8 (*c* 1.17, $CHCl_3$). – Anal. Calcd for $C_{24}H_{26}F_6N_2O_2$: C, 59.01, H, 5.36, N, 5.73. Found: C, 59.08, H, 5.20, N, 5.57.

According to the same method, the liquid crystalline compounds (*S*)-(–)-**20**, (*R*)-(+)-**21**, (*R*)-(–)-**22**, (*S*)-(–)-**23** and (*S*)-(–)-**24** were synthesized from (*R*)-(–)-**4**, (*S*)-(–)-**5**, (*R*)-(+)-**6** and (*S*)-(–)-**6**.

(*S*)-(–)-4-(5-Octylpyrimid-2-yl)phenyl 2,2-difluorocyclopropane-1-carboxylate [(*S*)-(–)-**20**]: From 104 mg (0.85 mmol) of (*S*)-(–)-**5** (46% *ee*), 4-(5-octylpyrimid-2-yl)phenol (284 mg, 1.0 mmol), DCC (309 mg, 1.5 mmol), DMAP (10.3 mg, 0.084 mmol) and CH_2Cl_2 (10 mL) was obtained 82 mg (25%) of (*S*)-(–)-**20**, R_f = 0.14 (pentane/diethyl ether 5:1) as a colorless solid, Cr 69 (SmA 50) I. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.87 (t, *J* 7.0 Hz, 3 H), 1.20–1.32 (m, 11 H), 1.62–1.65 (m, 1 H), 1.91 (dddd, *J* 12.0 Hz, 10.6 Hz, 7.8 Hz, 5.0 Hz, 1 H), 2.20 (tdd, *J* 12.0 Hz, 7.8 Hz, 6.4 Hz, 1 H), 2.62 (t, *J* 7.7 Hz, 2 H), 2.67 (ddd, *J* 12.5 Hz, 10.6 Hz, 7.8 Hz, 1 H), 7.23 (d, *J* 8.9 Hz, 2 H), 8.45 (d, *J* 8.9 Hz, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.9, 16.8 (t, J_{CF} 11.1 Hz), 22.5, 25.5 (t, J_{CF} 12.5 Hz), 28.9, 29.0, 29.1, 30.0, 30.6, 31.6, 110.6 (dd, J_{CF} 288 Hz, 283 Hz), 121.2, 129.0, 132.9, 135.5, 152.0, 156.8,

161.4, 164.8. – MS (70 eV, EI), *m/z* (%): 388 (20), 284 (100), 199 (8), 185 (32), 158 (4), 105 (5). – $[\alpha]_D^{20} = -7.1$ (*c* 0.95, $CHCl_3$). – Anal. Calcd for $C_{22}H_{26}F_2N_2O_2$: C, 68.02, H, 6.75. Found: C, 68.31, H, 6.77.

(*R*)-(+)-4-(5-Octylpyrimid-2-yl)phenyl 2,2-dichlorocyclopropane-1-carboxylate [(*R*)-(+)-**21**]: From 154 mg (1.0 mmol) of (*R*)-(+)-**6** [$[\alpha]_D^{25}$ = +155.6 (*c* 1.27, $CHCl_3$), >95% *ee*], 4-(5-octylpyrimid-2-yl)phenol (340 mg, 1.2 mmol), DCC (247 mg, 1.2 mmol), DMAP (12.2 mg, 0.1 mmol) and CH_2Cl_2 (10 mL) was obtained 346 mg (82%) of (*R*)-(+)-**21**, R_f = 0.20 (pentane/diethyl ether 5:1), as a colorless solid, mp 47 °C. – IR (Film): $\tilde{\nu}$ = 1762 cm^{-1} (C=O). – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.85–0.90 (m, 3 H), 1.27–1.32 (m, 10 H), 1.63–1.99 (m, 2 H), 2.02 (dd, *J* 9.7 Hz, 7.4 Hz, 1 H), 2.23 (t, *J* 7.5 Hz, 1 H), 2.62 (t, *J* 7.4 Hz, 2 H), 2.81 (dd, *J* 9.7 Hz, 7.9 Hz, 1 H), 7.25 (d, *J* 8.9 Hz, 2 H), 8.46 (d, *J* 8.9 Hz, 2 H), 8.61 (s, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.0, 22.6, 26.7, 29.0, 29.1, 29.2, 30.1, 30.7, 31.7, 33.2, 57.7, 121.4, 129.2, 133.1, 135.7, 152.2, 157.0, 161.5, 165.2. – MS (70 eV, EI), *m/z* (%): 424/422/420 (1/6/10), 284 (100), 199 (5), 185 (24). – $[\alpha]_D^{20}$ = +89.05 (*c* 1.06, $CHCl_3$). – Anal. Calcd for $C_{22}H_{26}Cl_2N_2O_2$: C, 62.71, H, 6.22, N, 6.65. Found: C, 62.44, H, 6.11, N, 6.53.

(*R*)-(–)-4-Pentyl-1,1'-biphenyl-4'-yl 4-[2,2-bis(trifluoromethyl)-cyclopropanoyloxy]benzoate [(*R*)-(–)-**22**]: From 60 mg (0.27 mmol) of (*R*)-(–)-**4** [$[\alpha]_D^{25}$ = –31.3 (*c* 1.12, $CHCl_3$), >95% *ee*], 4-pentyl-1,1'-biphenyl-4'-yl 4-hydroxybenzoate (97.3 mg, 0.27 mmol), DCC (56 mg, 0.27 mmol), DMAP (3.3 mg, 0.027 mmol) and CH_2Cl_2 (5 mL) was obtained 131 mg (86%) of (*R*)-(–)-**22**, R_f = 0.39 (toluene) as a colorless solid, mp Cr 143 SmA 187.5 I. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.89–0.95 (m, 3 H), 1.33–1.39 (m, 4 H), 1.64–1.77 (m, 2 H), 1.80 (dt, *J* 5.5 Hz, J_{CF} 1.8 Hz, 1 H), 2.13 (t, *J* 5.5 Hz, 1 H), 2.66 (t, *J* 6.3 Hz, 2 H), 2.79 (t, *J* 8.6 Hz, 1 H), 7.24–7.29 (m, 6 H), 7.51 (d, *J* 8.1 Hz, 2 H), 7.64 (d, *J* 8.7 Hz, 2 H), 8.28 (d, *J* 8.7 Hz, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.8, 14.0, 22.5, 23.4, 31.1, 31.5, 33.0 (q, J_{CF} 35 Hz), 35.5, 118.5 (q, J_{CF} 275 Hz), 121.4, 121.8, 126.9, 127.7, 128.0, 128.8, 131.9, 137.6, 139.1, 142.2, 149.9, 154.1, 163.7, 164.2. – MS (70 eV, EI), *m/z* (%): 565/564 (32/100), 325 (98), 120 (90). – $[\alpha]_D^{20}$ = –6.32 (*c* 1.25, $CHCl_3$). – Anal. Calcd for $C_{30}H_{26}F_6O_4$: C, 63.83, H, 4.64. Found: C, 64.05, H, 4.57.

(*S*)-(–)-4-Pentyl-1,1'-biphenyl-4'-yl 4-(2,2-difluorocyclopropanoyloxy)benzoate [(*S*)-(–)-**23**]: From 150 mg (1.23 mmol) of (*S*)-(–)-**5** [$[\alpha]_D^{20}$ = –7.05 (*c* 0.95, $CHCl_3$), 53% *ee*], 4-pentyl-1,1'-biphenyl-4'-yl 4-hydroxybenzoate (442 mg, 1.23 mmol), DCC (304 mg, 1.48 mmol), DMAP (15 mg, 0.12 mmol) and CH_2Cl_2 (9 mL) was obtained 543 mg (95%) of (*S*)-(–)-**23**, R_f = 0.39 (toluene) as a colorless solid, Cr 159 N* 198.7 I. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.90–0.95 (m, 3 H), 1.33–1.39 (m, 4 H), 1.61–1.67

(m, 2 H), 1.87–2.01 (m, 1 H), 2.17–2.31 (m, 1 H), 2.63–2.79 (m, 3 H), 7.25–7.32 (m, 6 H), 7.52 (d, *J* 8.1 Hz, 2 H), 7.64 (d, *J* 8.7 Hz, 2 H), 8.28 (d, *J* 8.7 Hz, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.0, 17.0 (J_{CF} 11.5 Hz), 22.5, 25.6 (J_{CF} 12.5 Hz), 31.1, 31.5, 35.5, 110.5 (dd, J_{CF} 288 Hz, 283 Hz), 121.6, 121.8, 126.9, 127.4, 128.0, 128.8, 131.8, 137.5, 139.0, 142.2, 149.9, 154.3, 164.3, 164.7. – MS (70 eV, EI), *m/z* (%): 465/464 (14/48), 239 (12), 225 (100), 183 (7), 121 (96). – Anal. Calcd for $C_{28}H_{26}F_2O_4$: C, 72.40, H, 5.64. Found: C, 72.13, H, 5.87.

(*S*)-(–)-4-Pentyl-1,1'-biphenyl-4'-yl 4-(2,2-dichlorocyclopropanoyloxy)benzoate [(*S*)-(–)-24]: From 50 mg (0.32 mmol) of (*S*)-(–)-**6** [$[\alpha]_D^{25}$ = –160.7 (*c* 1.19, $CHCl_3$) >95% *ee*], 4-pentyl-1,1'-biphenyl-4'-yl 4-hydroxybenzoate (140 mg, 0.39 mmol), DCC (80.3 mg, 0.39 mmol), DMAP (4.8 mg, 0.039 mmol) and CH_2Cl_2 (7 mL) was obtained 110 mg (68%) of (*S*)-(–)-**24**, R_f = 0.48 (toluene) as a colorless solid, Cr 127 (SmX 119.7) SmC* 128.2 N* 176.3 I. – IR (Film): $\tilde{\nu}$ = 1759 cm^{-1}, 1741 (C=O). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.89–0.94 (m, 3 H), 1.33–1.38 (m, 4 H), 1.61–1.75 (m, 2 H), 2.06 (dd, *J* 9.7 Hz, 7.6 Hz, 1 H), 2.25 (t, *J* 7.6 Hz, 1 H), 2.65 (t, *J* 7.4 Hz, 2 H), 2.83 (dd, *J* 9.7 Hz, 7.6 Hz, 1 H), 7.25–7.33 (m, 6 H), 7.52 (d, *J* 8.7 Hz, 2 H), 7.63 (d, *J* 8.7 Hz, 2 H), 8.28 (d, *J* 8.7 Hz, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.0, 22.5, 26.8, 31.1, 31.5, 33.1, 35.5, 57.7, 121.7, 121.8, 126.9, 127.5, 128.0, 128.8, 131.9, 137.6, 139.1, 142.2, 149.9, 154.5, 164.3, 164.9. – MS (70 eV, EI), *m/z* (%): 500/498/496 (2/18/25), 258/256 (27/43), 121 (100). – $[\alpha]_D^{20}$ = –43.4 (*c* 1.09, $CHCl_3$). – Anal. Calcd for $C_{28}H_{26}Cl_2O_4$: C, 67.61, H, 5.27. Found: C, 67.64, H, 5.31.

Acknowledgments

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