

Description

The present invention is concerned with novel compounds, their manufacture, liquid crystalline mixtures, especially mixtures having a chiral tilted smectic phase, which contain such compounds and with their use for electro-optical purposes.

Liquid crystals are suitable as dielectrics in indicating devices, since their optical properties can be influenced by an electric potential. Suitable electro-optical devices are well-known to the person skilled in the art. Examples of such devices are cells having dynamic scattering, DAP cells (deformation of aligned phases), TN cells (twisted-nematic) and STN cells (super twisted-nematic) having a twisted nematic structure, guest/host cells, phase change cells having a cholesteric-nematic phase transition and SBE cells (super birefringence effect).

Further, electro-optical devices based on chiral tilted smectic liquid crystals are proposed in Appl. Phys. Lett. 36, 899 (1980) and in Recent Developments in Condensed Matter Physics 4, 309 (1981). In this case the ferroelectric properties of these materials are made use of. As the tilted smectic phases there are suitable, for example, smectic C, F, G, H, I and K phases. There are generally preferred smectic C phases which, in particular, permit high response speeds. The chiral tilted phases are usually denoted by S_C^* , S_F^* etc., with the asterisk indicating the chirality.

Ferroelectric liquid crystals should have a good stability towards chemical and thermal influences and towards electrical fields. Further, they should have a suitable mesophase over a broad temperature range, low viscosity and especially a sufficiently high spontaneous polarization.

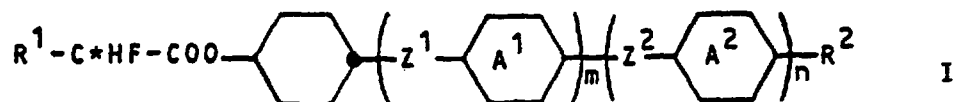
Compounds which can come into consideration for the aforementioned purpose are, for example, the phenyl esters of branched α -chlorinated aliphatic carboxylic acids which are specifically disclosed in GB-A-2 182 037 or in WO-A-8 705 017.

As ferroelectric liquid crystals there are primarily suitable mixtures consisting of one or more optically active dopants and a liquid crystal material which can consist of one or more components and which as a rule should have a tilted smectic phase. The optically active dopants need not themselves be smectic, but in the liquid crystal material they should produce a chiral tilted smectic phase and should induce a high spontaneous

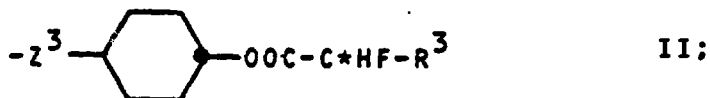
polarization. In order to achieve a high spontaneous polarization in the mixture and/or in order that the amount of optically active dopants can be held relatively low, dopants which already in small amounts are capable of inducing a high spontaneous polarization are desired.

On the other hand, the pitch of the liquid crystal should be distinctly greater than the plate separation of the cell which is used and should typically amount to at least about 10 μm in order to obtain bistable displays which switch well. Optically active dopants for ferro-electric liquid crystals should therefore preferably induce in the mixture a chiral tilted smectic phase having a high spontaneous polarization but a comparatively small twisting (i.e. with a large pitch).

The invention is concerned with optically active compounds of the general formula



wherein m stands for the number 1 and R^2 signifies an unsubstituted or halogen-substituted alkyl or alkenyl group in which optionally one methylene group is replaced by oxygen and/or optionally one methylene group is replaced by an ester group $-\text{COO}-$ or $-\text{OOC}-$; or m stands for the number 0 or 1 and R^2 denotes a group of the general formula



R^1 and R^3 each independently represent an alkyl or alkenyl group in which optionally one methylene group is replaced by oxygen; Z^1 , Z^2 and Z^3 each independently signify a single covalent bond, $-\text{CH}_2\text{O}-$, $-\text{OCH}_2-$, $-\text{CH}_2\text{CH}_2-$, $-\text{COO}-$ or $-\text{OOC}-$; n stands for the number 0 or 1; rings A^1 and A^2 each independently signify unsubstituted or halogen-, cyano- and/or methyl-substituted 1,4-phenylene in which optionally 1 CH group or 2 CH groups is/are replaced by nitrogen; and C^* denotes a chiral carbon

atom; with the proviso that simultaneously R¹ does not signify an alkyl group, m and n do not signify the number 1. Z¹ does not signify the group -CH₂CH₂- or -CH₂O- and ring A¹, Z², ring A² and R² together do not signify 4-(5-alkyl-2-pyrimidinyl)-phenyl.

The compounds in accordance with the invention are colourless, have a good solubility in usual liquid crystal materials and as a rule themselves have liquid crystalline properties. Although the chiral α -fluorocarboxylic acid residue is attached to a saturated group, the compounds of formula I induce an amazingly high spontaneous polarization in tilted smectic phases. However, on the other hand surprisingly only a comparatively small twisting is induced in mixtures. In contrast to α -fluorocarboxylic acid phenyl esters, the present α -fluorocarboxylic acid cyclohexyl esters have, moreover, a very good stability.

The term "unsubstituted or halogen-, cyano- and/or methyl-substituted 1,4-phenylene in which optionally 1 CH group or 2 CH groups is/are replaced by oxygen" embraces in the scope of the present invention groups such as 1,4-phenylene, fluoro-1,4-phenylene, chloro-1,4-phenylene, bromo-1,4-phenylene, cyano-1,4-phenylene, 2,3-dicyano-1,4-phenylene, 2,3-difluoro-1,4-phenylene, methyl-1,4-phenylene, pyridine-2,5-diyl, pyrimidine-2,5-diyl, pyrazine-2,5-diyl, pyridazine-3,6-diyl and the like.

The term "halogen" embraces fluorine, chlorine, bromine and iodine, especially fluorine, chlorine and bromine.

The term "unsubstituted or halogen-substituted alkyl or alkenyl group in which optionally one methylene group is replaced by oxygen and/or optionally one methylene group is replaced by an ester group -COO- or -OOC-" embraces unsubstituted or halogen (especially fluorine or chlorine)-substituted alkyl, alkenyl, alkoxy, alkenyloxy, alkoxyalkyl, alkoxyalkoxycarbonyl, alkenyloxyalkoxycarbonyl, alkanoyloxy, alkenoyloxy, alkoxyalkoxyalkoxycarbonyl, alkoxyalkanoxyloxy groups and the like, especially alkyl, alkenyl, alkoxy, alkenyloxy, alkoxyalkoxycarbonyl, alkenyloxyalkoxycarbonyl, alkanoyloxy, alkenoyloxy, 2-fluoroalkyl, 2-chloroalkyl, 2-fluoroalkoxy, 2-chloroalkoxy, 2-fluoroalkoxyalkoxycarbonyl, 2-chloroalkoxyalkoxycarbonyl, 2-fluoroalkanoxyloxy and 2-chloroalkanoxyloxy. An optionally present oxygen atom and an optionally present ester group can additionally form a carbonate group; they are, however, preferably not immediately adjacent. The groups can be straight-chain or branched (e.g. n-alkyl, n-alkoxy, isoalkyl, isoalkoxy) and can have the location of the radical in the 1-position (insofar as not expressly indicated the location of the radical

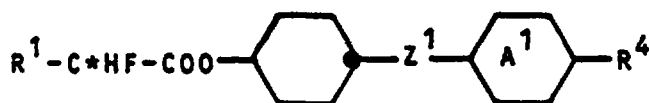
hereinafter is in each case in the 1-position) or in the chain, e.g. in the 2-position (such as 2-alkyl, 2-alkoxy, 2-alkoxycarbonyl). The groups preferably have a maximum of 15 carbon atoms, for example 2-15 carbon atoms. Examples of preferred groups are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, isopropyl, isobutyl, 2-butyl, 2-octyl, 2-methylbutyl, 3-methylpentyl, vinyl, 1-propenyl, 1-butenyl, 1-pentenyl, allyl, 2-butenyl, 2-pentenyl, 3-butenyl, 3-pentenyl, 4-pentenyl, 5-hexenyl, 6-heptenyl, methoxy, ethoxy, propyloxy, butyloxy, pentyloxy, hexyloxy, heptyloxy, octyloxy, nonyloxy, decyloxy, isopropyloxy, isobutyloxy, 2-butyloxy, 2-octyloxy, 2-methylbutyloxy, 3-methylpentyloxy, allyloxy, 2E-butenyloxy, 3-butenyloxy, 4-pentenyl, 5-hexenyloxy, 6-heptenyloxy, 2-fluoro-1-propyloxy, 2-chloro-1-propyloxy, 2-fluoro-1-butyloxy, 2-chloro-1-butyloxy, 2-fluoropropanoyloxy, 2-chloropropanoyloxy, 2-fluorobutanoyloxy, 2-chlorobutanoyloxy, 2-fluoropentanoyloxy, 2-chloropentanoyloxy, 2-fluorohexanoyloxy, 2-chlorohexanoyloxy, 2-fluoroheptanoyloxy, 2-chloroheptanoyloxy, 2-fluorooctanoyloxy, 2-chlorooctanoyloxy, 2-octyloxycarbonyl and the like.

The term "alkyl or alkenyl group in which optionally one methylene group is replaced by oxygen" embraces alkyl, alkenyl, alkoxy, alkenyloxy, alkoxyalkyl, alkenyloxyalkyl and alkoxyalkenyl, especially alkyl, alkenyl, alkoxyalkyl and alkenyloxyalkyl. The groups can be straight-chain or branched and can have the location of the radical in the 1-position or in the chain. The groups preferably have about 1-15 carbon atoms, especially about 3-15 carbon atoms. Examples of preferred groups are the examples given above for alkyl, alkenyl etc. In general, straight-chain residues are preferred, especially the straight-chain residues which have the location of the radical in the 1-position or 2-position.

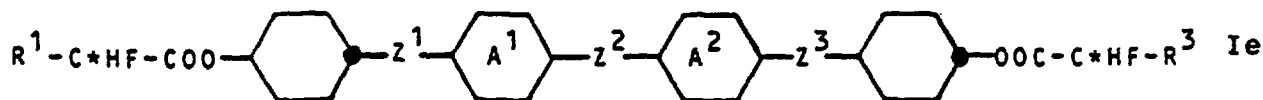
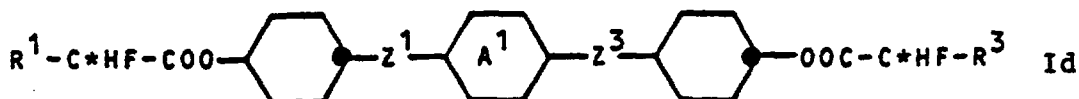
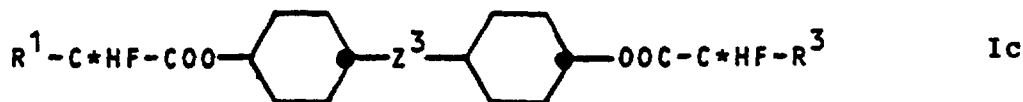
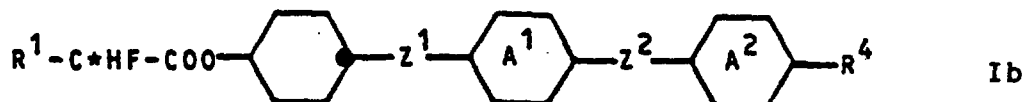
When n in formula I above signifies the number 1, m conveniently stands for the number 1 (m = 0, n = 1 embraces the same compounds as m = 1, n = 0).

If R² signifies a group of formula II, then the two α-fluorocarboxylic acid residues preferably have the same configuration at the α-C atom.

Formula I above therefore embraces optically active compounds of the general formulae



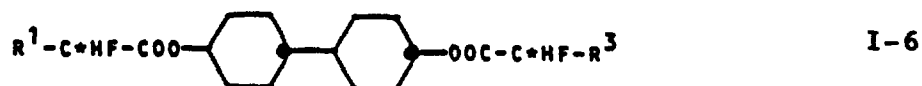
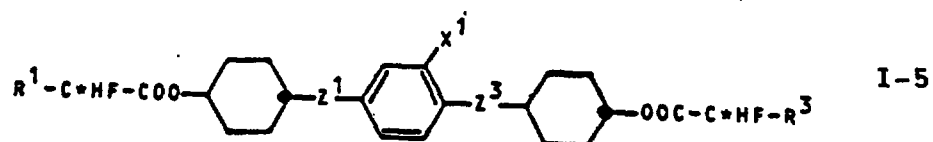
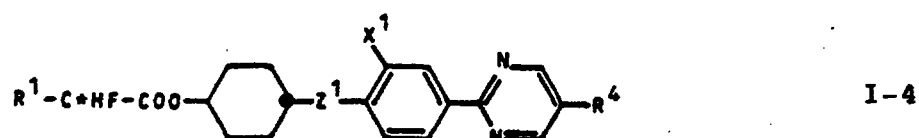
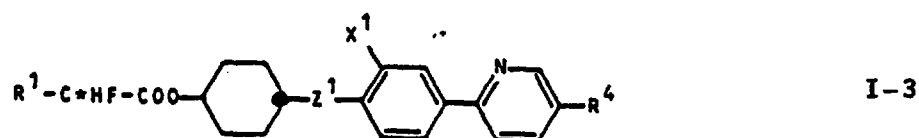
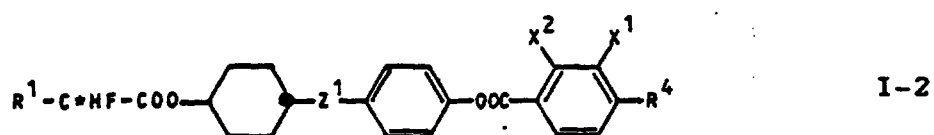
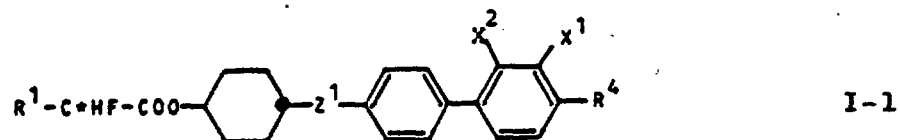
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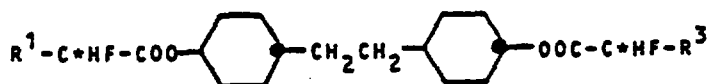


wherein R^1 , R^3 , Z^1 , Z^2 , Z^3 , C^* and rings A^1 and A^2 have the above significances; R^4 denotes an unsubstituted or halogen-substituted alkyl or alkenyl group in which optionally one methylene group is replaced by oxygen and/or optionally one methylene group is replaced by an ester group $-COO-$ or $-OOC-$; with the proviso that in formula Ib simultaneously R^1 does not signify an alkyl group, Z^1 does not signify the group $-\text{CH}_2\text{CH}_2-$ or $-\text{CH}_2\text{O}-$ and ring A^1 , Z^2 , ring A^2 and R^4 together do not signify 4-(5-alkyl-2-pyrimidinyl)-phenyl.

Preferably, rings A^1 and A^2 in formulae I, Ia, Ib, Id and Ie each independently signify 1,4-phenylene, fluoro-1,4-phenylene, chloro-1,4-phenylene, bromo-1,4-phenylene, cyano-1,4-phenylene, 2,3-difluoro-1,4-phenylene, pyridine-2,5-diyl or pyrimidine-2,5-diyl. Of the compounds of formulae I, Ib and Ie there are generally especially preferred those in which one or both of rings A^1 and A^2 signifies 1,4-phenylene, pyrimidine-2,5-diyl, fluoro-1,4-phenylene, chloro-1,4-phenylene, 2,3-difluoro-1,4-phenylene and/or cyano-1,4-phenylene, especially 1,4-phenylene. As a rule there are especially preferred those compounds of formulae I and Ia-Ie in which one of rings A^1 and A^2 signifies 1,4-phenylene, fluoro-1,4-phenylene or 2,3-difluoro-1,4-phenylene and the other of rings A^1 and A^2 signifies 1,4-phenylene or pyrimidine-2,5-diyl.

Examples of preferred groups of compounds in accordance with the invention are the optically active compounds of the general formulae





I-7

wherein R^1 , R^3 , R^4 , Z^1 , Z^3 and C^* have the above significances; X^1 and X^2 signify hydrogen, fluorine, chlorine, bromine, cyano or methyl; with the proviso that in formula I-4 X^1 denotes fluorine, chlorine, bromine, cyano or methyl when Z^1 represents $-CH_2CH_2-$ or $-CH_2O-$.

Z^1 in each of formulae I, Ia, Ib, Id, Ie and I-1 to I-5 above preferably signifies a single covalent bond, $-CH_2O-$, $-CH_2CH_2-$ or $-COO-$. Z^3 in each of formulae II, Id, Ie and I-5 above preferably signifies a single covalent bond, $-OCH_2-$, $-CH_2CH_2-$ or $-OOC-$. Z^2 in formulae I, Ib and Ie above preferably signifies a single covalent bond, $-COO-$ or $-OOC-$. Further, in formulae I-1 and I-2 at least one of the substituents X^1 and X^2 preferably stands for hydrogen or fluorine; as a rule there are especially preferred those compounds in which X^1 signifies hydrogen, fluorine, chlorine, bromine or cyano and X^2 signifies hydrogen as well as those compounds in which X^1 signifies hydrogen or fluorine and X^2 signifies fluorine.

Preferred residues R^1 in formulae I, Ia to Ie and I-1 to I-7 are alkyl, alkenyl, alkoxyalkyl and alkenyloxyalkyl, especially alkyl. The residues R^1 can be straight-chain or branched and generally have a maximum of 15 carbon atoms, preferably 3-15 carbon atoms and particularly 3-8 carbon atoms. Examples of preferred residues R^1 are propyl, isopropyl, butyl, 2-butyl, pentyl, 2-pentyl, allyl, 3-butenyl, 4-pentenyl, alkoxy-methyl such as methoxymethyl or ethoxymethyl, alkenyloxy-methyl such as allyloxymethyl or (3-butenyl)oxymethyl, 1-alkoxyethyl such as 1-methoxyethyl or 1-ethoxyethyl, 1-alkenyloxyethyl such as 1-allyloxyethyl or 1-(3-butenyl)oxyethyl, 2-alkoxyethyl such as 2-methoxyethyl or 2-ethoxyethyl, 2-alkenyloxyethyl such as 2-allyloxyethyl or 2-(3-butenyl)oxyethyl and the like.

Preferred residues R^3 in formulae II, Ic, Id, Ie and I-4 to I-7 above are alkyl, alkenyl, alkoxyalkyl and

alkenyloxyalkyl, especially alkyl. The residues R^3 can be straight-chain or branched and generally have a maximum of 15 carbon atoms, preferably 3-15 carbon atoms and particularly 3-8 carbon atoms. Examples of preferred residues for R^3 are the residues given above for R^1 . R^1 and R^3 can be different or preferably also have the same significance.

If desired, chiral residues R^1 and, respectively, R^3 can preferably also be present in optically active form. Preferably, that configuration which increases the spontaneous polarization of the compound is chosen.

Especially preferred residues R^1 and R^3 are 1-alkyl and 2-alkyl (= 1-methylalkyl). 2-Alkyl residues preferably have the S-configuration when the adjacent group $-C^*HF-$ has the S-form and the R-configuration when the adjacent group $-C^*HF-$ has the R-form.

R^2 in formula I above signifies a residue R^4 or a group of formula II. In formula II R^3 and Z^3 preferably have one of the preferred significances given above.

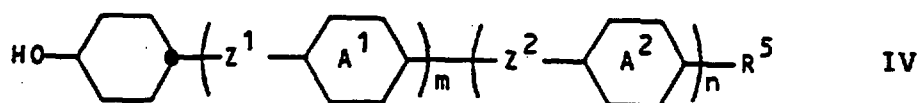
Preferred residues R^4 in the above formulae Ia, Ib, I-1, I-2, I-3 and I-4 (and, respectively, preferred residues R^2 in formula I) are alkyl, alkenyl, alkoxy, alkenyloxy, haloalkoxy (preferably 2-fluoroalkoxy or 2-chloroalkoxy), alkoxycarbonyl and haloalkanoyloxy (preferably 2-fluoroalkanoyloxy or 2-chloroalkanoyloxy), especially alkyl, alkenyl, alkoxy, alkenyloxy and 2-chloroalkoxy. The residues R^4 can be straight-chain or branched and preferably have a maximum of 15, for example 2-15, carbon atoms and particularly about 3-10 carbon atoms. Examples of preferred residues R^4 are the groups referred to earlier. Especially preferred residues R^4 are alkenyl, alkenyloxy and particularly alkyl and alkoxy.

The compounds of formula I can be manufactured in accordance with the invention by esterifying an optically active α -fluorocarboxylic acid of the general formula

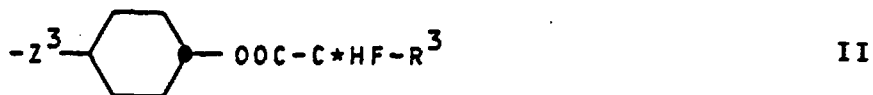


III

and a cyclohexanol derivative of the general formula



wherein m stands for the number 1 and R⁵ denotes an unsubstituted or halogen-substituted alkyl or alkenyl group in which optionally one methylene group is replaced by oxygen and/or optionally one methylene group is replaced by an ester group -COO- or -OOC-; or m stands for the number 0 or 1 and R⁵ denotes a group of the general formula



or



R¹ and R³ each independently represent an alkyl or alkenyl group in which optionally one methylene group is replaced by oxygen; Z¹, Z² and Z³ each independently signify a single covalent bond, -CH₂O-, -OCH₂-, -CH₂CH₂-, -COO- or -OOC-; n stands for the number 0 or 1; rings A¹ and A² each independently signify unsubstituted or halogen-, cyano- and/or methyl-substituted 1,4-phenylene in which optionally 1 CH group or 2 CH groups is/are replaced by nitrogen; and C* denotes a chiral carbon atom; with the proviso that simultaneously R¹ does not signify an alkyl group, m and n do not signify the number 1, Z¹ does not signify the group -CH₂CH₂- or -CH₂O- and ring A¹, Z², ring A² and R⁵ together do not signify 4-(5-alkyl-2-pyrimidinyl)-phenyl, or suitable derivatives of these compounds.

The esterification of the compounds of formulae III and IV or suitable derivatives of these compounds can be effected in a manner known per se according to methods which are described in standard works (e.g. Houben-Weyl,

Methoden der Organischen Chemie, Georg Thieme Verlag, Stuttgart).

The starting materials of formula IV are known or are analogues of known compounds and can be prepared according to methods which are known to the person skilled in the art. In particular, such cyclohexanol derivatives have already been used for the manufacture of other liquid crystal components.

The optically active α -fluorocarboxylic acids of formula III are also known or are analogues of known compounds and can be prepared according to known methods. For example, they can be obtained from the racemic α -fluorocarboxylic acids by conventional racemate resolution, e.g. with ephedrine. Further, racemic and optically active α -fluorocarboxylic acids can be prepared, for example, from α -hydroxycarboxylic acid esters by reaction with diethylaminosulphur trifluoride and subsequent hydrolysis of the ester group. Such methods and starting materials are likewise known from standard works such as Houben-Weyl, Methoden der Organischen Chemie, Georg Thieme Verlag, Stuttgart).

Moreover, α -fluorocarboxylic acids are especially readily accessible by reacting amino acids such as norleucine, isoleucine, valine, serine, threonine and the like with sodium nitrite and pyridine hydrofluoride according to the method described in Helv. Chim. Acta 64, 2528 (1981). (Where inversion at the α -C atom is desired, there can e.g. firstly be prepared in an analogous manner the α -hydroxy acid, this can then be converted into the mesylate using methyl chloride and the mesylate can be converted into the α -fluorocarboxylic acid using potassium fluoride.) In the case of α -amino acids which do not have a further functional group, such as leucine, isoleucine and valine, this leads directly to the desired α -fluorocarboxylic acids. In the case of hydroxy- α -amino acids, such as serine and threonine, there are obtained in this manner hydroxy- α -fluorocarboxylic acids and, by subsequent esterification of the carboxy group (e.g. with diazomethane), hydroxy- α -fluorocarboxylic acid esters. These can be converted into alkoxy- or alkenyloxy-substituted α -fluorocarboxylic acids, for example by etherification with an alkyl bromide or alkenyl bromide and subsequent hydrolysis of the ester group. Further, the hydroxy- α -fluorocarboxylic acid esters can e.g. be converted by oxidation with pyridinium chlorochromate into formyl-substituted α -fluorocarboxylic acid esters and these can be converted into homologous formyl-substituted α -fluorocarboxylic acid esters by reaction with methoxy-triphenylphosphonium chloride and subsequent hydrolysis of the enol ether (this

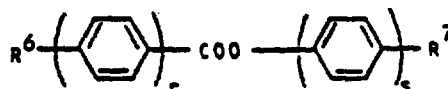
chain-lengthening reaction can be repeated once or several times if desired). The formyl-substituted α -fluorocarboxylic acid esters can be converted into alkoxy- or alkenyloxy-substituted α -fluorocarboxylic acids e.g. by reduction with sodium borohydride, etherification of the hydroxy group with an alkyl bromide or alkenyl bromide and hydrolysis of the ester group. Alternatively, the formyl-substituted α -fluorocarboxylic acids can be converted into α -fluorocarboxylic acid esters of formula III in which R^1 signifies alkyl or alkenyl by a Wittig reaction with an alkyl-triphenylphosphonium bromide, optional catalytic hydrogenation of the double bond and by subsequent hydrolysis of the ester group.

The compounds of formula I can be used as chiral dopants in liquid crystalline mixtures. The invention is therefore also concerned with a liquid crystalline mixture having at least 2 components, which is characterized in that at least one component is an optically active compound of formula I. Conveniently, the mixture contains a liquid crystal material having a nematic, cholesteric or smectic phase and one or more optically active compounds of formula I.

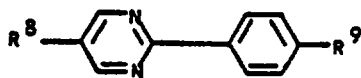
Mixtures having a chiral tilted smectic phase, especially those having a S_C^* phase, are preferred. These mixtures preferably contain a liquid crystal material having a tilted smectic phase (especially a smectic C phase) and one or more optically active compounds of formula I.

The amount of compounds of formula I in the mixtures in accordance with the invention can vary in a wide range and can be, for example, about 0.5-40 wt.%. In general, the preferred concentration depends mainly on the desired values of the spontaneous polarization and the pitch. In general, a range of about 3-20 wt.% is preferred and a range of about 5-15 wt.% is especially preferred.

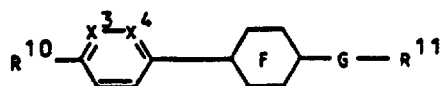
As further components there come into consideration usual liquid crystal materials. The mixtures in accordance with the invention preferably contain, in addition to one or more compounds of formula I, one or more of the compounds of the following general formulae



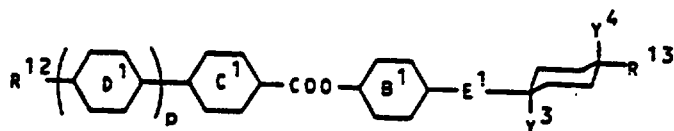
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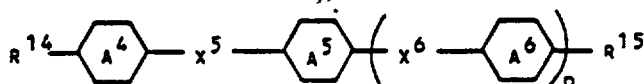
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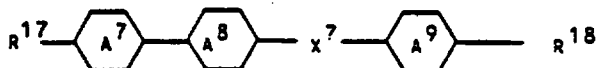
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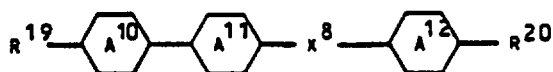
IX



X



XI



XII

wherein R⁶ and R⁷ signify alkyl, alkoxy, alkanoyl, alkanoyloxy, alkoxy carbonyl or alkoxy carbonyloxy with up to 18 carbon atoms; r and s each independently signify 1 or 2; R⁸ and R⁹ represent alkyl or alkoxy with 1-18 carbon atoms; X³ stands for CH and X⁴ stands for N or X³ stands for N and X⁴ stands for CH; G signifies a single covalent bond, trans-1,4-cyclohexylene, cis-4-cyano-trans-1,4-cyclohexylene or 1,4-phenylene which is optionally substituted with halogen or methyl; ring F represents trans-1,4-cyclo-

hexylene, 1,4-phenylene which is optionally substituted with halogen or methyl or, when G signifies a single covalent bond, also cis-4-cyano-trans-1,4-cyclohexylene; R¹⁰ and R¹¹ each denote an optionally halogen-substituted alkyl or alkenyl group in which optionally one CH₂ group or two non-adjacent CH₂ groups is/are replaced by -O-, -COO- and/or -OOC-; p stands for the number 0 or 1; E¹ signifies a single covalent bond, -CH₂-CH₂-, -OCH₂-, -COO- or -OOC-; rings B¹, C¹ and D¹ denote 1,4-phenylene which is optionally substituted with cyano, halogen or lower alkyl; Y³ and Y⁴ signify hydrogen or one of the substituents Y³ and Y⁴ also signifies cyano; R¹² and R¹³ each independently represent optionally halogen-substituted C₁-C₁₈-alkyl or optionally halogen-substituted C₂-C₁₈-alkenyl in which optionally one CH₂ group or two non-adjacent CH₂ groups is/are replaced by oxygen; X⁵ represents a single covalent bond, -COO- or -OOC- and X⁶ represents a single covalent bond, -COO-, -OOC-, -CH₂CH₂-, -OCH₂- or -CH₂O-; rings A⁴, A⁵ and A⁶ each independently signify unsubstituted or cyano-, halogen- or lower alkyl-substituted 1,4-phenylene or one of the rings also signifies pyrimidine-2,5-diyl or pyrazine-2,5-diyl and/or, when p stands for the number 1, one of the rings also signifies trans-1,4-cyclohexylene or trans-m-dioxane-2,5-diyl; R¹⁴ signifies an optionally halogen-substituted alkenyl group with up to 18 carbon atoms in which optionally 1 CH₂ group or 2 non-adjacent CH₂ groups is/are replaced by -O-, -CO-, -COO- or -OOC- and/or optionally one C-C single bond is replaced by a C-C double bond; R¹⁵ signifies an optionally halogen-substituted alkyl group with up to 18 carbon atoms in which optionally 1 CH₂ group or 2 non-adjacent CH₂ groups is/are replaced by -O-, -CO-, -COO- or -OOC- and/or optionally one C-C single bond is replaced by a C-C double bond; X⁷ denotes a single covalent bond, -COO-, -OOC-, -CH₂CH₂-, -OCH₂- or -CH₂O-; one of rings A⁷, A⁸ and A⁹ represents pyrimidine-2,5-diyl, one of rings A⁷, A⁸ and A⁹ represents unsubstituted or cyano-, halogen- or lower alkyl-substituted 1,4-phenylene and one of rings A⁷, A⁸ and A⁹ represents trans-1,4-cyclohexylene or unsubstituted or cyano-, halogen- or lower alkyl-substituted 1,4-phenylene; and R¹⁷ and R¹⁸ each independently signify an optionally halogen-substituted alkyl group with up to 18 carbon atoms in which optionally 1 CH₂ group or 2 non-adjacent CH₂ groups is/are replaced by -O-, -CO-, -COO- and/or -OOC-; X⁸ denotes a single covalent bond, -COO-, -OOC-, -CH₂CH₂-, -OCH₂- or -CH₂O-; one of rings A¹⁰, A¹¹ and A¹²

represents trans-m-dioxane-2,5-diyl and the other two of rings A10, A11 and A12 each independently represent unsubstituted or cyano-, halogen- or lower alkyl-substituted 1,4-phenylene; R19 and R20 each independently signify an optionally halogen-substituted alkyl group with up to 18 carbon atoms in which optionally 1 CH2 group or 2 non-adjacent CH2 groups is/are replaced by -O-, -CO-, -COO- and/or -OOC-.

The manufacture of the liquid crystalline mixtures and of the electro-optical devices can be effected in a manner known per se.

The invention is illustrated in more detail by the following Examples. Optical antipodes have in each case the same phase transition temperatures and induce absolutely the same spontaneous polarization values and twisting values, but with opposite signs. The abbreviations used for the characterization of the phase transitions have the following significances:

C stands for crystalline
S stands for smectic
SA, SB etc. stand for smectic A, B etc.
SC*, SF* etc. stand for chiral smectic C, F etc.
Ch stands for cholesteric
N stands for nematic
I stands for isotropic.

Example 1

0.16 g of (S)-2-fluorohexanoic acid (S- α -fluorocaproic acid), 0.52 g of trans-4-(4'-decyl-4-biphenyl)-cyclohexanol and 0.02 g of 4-(dimethylamino)pyridine were dissolved in 50 ml of dichloromethane and the solution was treated portionwise within 10 minutes while stirring with 0.35 g of N,N'-dicyclohexylcarbodiimide. The mixture was stirred at room temperature overnight and then filtered. The filtrate was diluted with dichloromethane, washed twice with 50 ml of saturated sodium carbonate solution each time and then with water, dried over magnesium sulphate, filtered and subsequently concentrated. The crude product obtained was purified by chromatography on silica gel with hexane/ethyl acetate (vol. 9:1). The trans-4-(4'-decyl-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate was recrystallized from methanol; m.p. (C-S) -80°C, transition S-S -26°C, cl.p. (S-I) 144.5°C.

The trans-4-(4'-decyl-4-biphenyl)cyclohexanol used as the starting material was prepared as follows:

(a) A suspension of 10 g of 4-(4'-cyano-4-biphenyl)cyclohexanone, 30 ml of diethyl ether and 270 ml of methanol was treated portionwise at 0°C with 1.8 g of sodium borohydride. After 3 hours the reaction mixture was made acid (pH 1-2) with 25% hydrochloric acid. The reaction mixture was extracted three times with 50 ml of dichloromethane each time. The combined organic phases were washed twice with 500 ml of water each time and subsequently dried over magnesium sulphate, filtered and concentrated. Recrystallization from methanol gave 3.5 g of trans-4-(4'-cyano-4-biphenyl)cyclohexanol.

(b) A solution of 3.0 g of trans-4-(4'-cyano-4-biphenyl)cyclohexanol, 1.1 ml of 3,4-dihydro-2H-pyran in 30 ml of dichloromethane was treated at 0°C with a solution of 0.007 g of bistrimethylsilyl sulphate in 2 ml of dichloromethane. The reaction mixture was stirred at 0°C for a further 30 minutes and then washed once with sodium carbonate solution and twice with water and subsequently dried over magnesium sulphate, filtered and concentrated. The crude product was purified by chromatography on silica gel with toluene/ethyl acetate (vol. 9:1). Recrystallization from ethyl acetate at -20°C gave 1.75 g of pure trans-4-(4'-cyano-4-biphenyl)cyclohexyl tetrahydropyranyl ether.

(c) A solution of nonylmagnesium bromide (8.3 mmol) in 30 ml of diethyl ether was treated at 0°C with a solution of 1.5 g of trans-4-(4'-cyano-4-biphenyl)cyclohexyl tetrahydropyranyl ether in 15 ml of tetrahydrofuran. The reaction mixture was heated at slight reflux overnight and then treated with dilute sodium carbonate solution. The organic phase was separated and the aqueous phase was back-extracted three times with 50 ml of diethyl ether each time. The combined organic phases were washed once with dilute sodium carbonate solution and twice with water and then dried over magnesium sulphate, filtered and concentrated. The residue was purified by chromatography on silica gel with toluene/ethyl acetate (vol. 9:1). The trans-4-(4-decanoyl-4-biphenyl)cyclohexyl tetrahydropyranyl ether (1.8 g) obtained was used in the next step without further purification.

(d) A mixture of 1.8 g of trans-4-(4-decanoyl-4-biphenyl)cyclohexyl tetrahydropyranyl ether, 0.2 g of palladium/carbon (5%), 20 ml of toluene and 2 ml of ethanol was stirred for 16 hours while conducting hydrogen through the mixture. Subsequently, the inorganic material was filtered off and the filtrate was concentrated. The residue was purified by chromatography on silica gel with

toluene/ethyl acetate (vol. 9:1). The trans-4-(4'-decyl-4-biphenyl)cyclohexyl tetrahydropyranyl ether (1.2 g) obtained was used in the next step without further purification.

(e) A solution of 1.2 g of trans-4-(4'-decyl-4-biphenyl)cyclohexyl tetrahydropyranyl ether in 40 ml of methanol and 2 ml of diethyl ether was treated with a solution of 7.3 mg of bistrimethylsilyl sulphate in 2 ml of dichloromethane. The reaction mixture was stirred at room temperature for 2 hours and then treated with 0.2 ml of pyridine. Subsequently, the reaction mixture was concentrated and the residue was then taken up in 50 ml of dichloromethane, washed twice with water, dried over magnesium sulphate, filtered and again concentrated. The residue was purified by chromatography on silica gel with toluene/ethyl acetate (vol. 9:1). Recrystallization from methanol gave 0.5 g of trans-4-(4'-decyl-4-biphenyl)-cyclohexanol.

The following compounds can be manufactured in an analogous manner:

trans-4-(4'-Methyl-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-ethyl-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-propyl-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-butyl-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-pentyl-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-hexyl-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-heptyl-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-octyl-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-nonyl-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-methoxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-ethoxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-propyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-butyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-pentyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-hexyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;

trans-4-(4'-octyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-nonyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-decyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(3'-fluoro-4'-methoxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(3'-fluoro-4'-ethoxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(3'-fluoro-4'-propyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(3'-fluoro-4'-butyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(3'-fluoro-4'-pentyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(3'-fluoro-4'-hexyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(3'-fluoro-4'-heptyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(3'-fluoro-4'-octyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(3'-fluoro-4'-nonyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(3'-fluoro-4'-decyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2',3'-difluoro-4'-methoxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2',3'-difluoro-4'-ethoxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2',3'-difluoro-4'-propyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2',3'-difluoro-4'-butyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2',3'-difluoro-4'-pentyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2',3'-difluoro-4'-hexyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2',3'-difluoro-4'-heptyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2',3'-difluoro-4'-octyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2',3'-difluoro-4'-nonyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2',3'-difluoro-4'-decyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(3'-chloro-4'-methoxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(3'-chloro-4'-ethoxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(3'-chloro-4'-propyloxy-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(3'-chloro-4'-butyloxy-4-biphenyl)cyclohexyl

(S)-2-fluorohexanoate;
trans-4-(3'-chloro-4'-pentyloxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-chloro-4'-hexyloxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-chloro-4'-heptyloxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-chloro-4'-octyloxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-chloro-4'-nonyloxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-chloro-4'-decyloxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-bromo-4'-methoxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-bromo-4'-ethoxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-bromo-4'-propyloxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-bromo-4'-butyloxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-bromo-4'-pentyloxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-bromo-4'-hexyloxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-bromo-4'-heptyloxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-bromo-4'-octyloxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-bromo-4'-nonyloxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-bromo-4'-decyloxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-cyano-4'-methoxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-cyano-4'-ethoxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-cyano-4'-propyloxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-cyano-4'-butyloxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-cyano-4'-pentyloxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-cyano-4'-hexyloxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-cyano-4'-heptyloxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-cyano-4'-octyloxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-cyano-4'-nonyloxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(3'-cyano-4'-decyloxy-4-biphenyl) cyclohexyl
(S)-2-fluorohexanoate;

trans-4-(2-[4'-methyl-4-biphenyl]ethyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(2-[4'-ethyl-4-biphenyl]ethyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(2-[4'-propyl-4-biphenyl]ethyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(2-[4'-butyl-4-biphenyl]ethyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(2-[4'-pentyl-4-biphenyl]ethyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(2-[4'-hexyl-4-biphenyl]ethyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(2-[4'-heptyl-4-biphenyl]ethyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(2-[4'-octyl-4-biphenyl]ethyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(2-[4'-nonyl-4-biphenyl]ethyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(2-[4'-decyl-4-biphenyl]ethyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(2-[4'-methoxy-4-biphenyl]ethyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(2-[4'-ethoxy-4-biphenyl]ethyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(2-[4'-propyloxy-4-biphenyl]ethyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(2-[4'-butyloxy-4-biphenyl]ethyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(2-[4'-pentyloxy-4-biphenyl]ethyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(2-[4'-hexyloxy-4-biphenyl]ethyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(2-[4'-heptyloxy-4-biphenyl]ethyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(2-[4'-octyloxy-4-biphenyl]ethyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(2-[4'-nonyloxy-4-biphenyl]ethyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(2-[4'-decyloxy-4-biphenyl]ethyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(2-[4'-undecyloxy-4-biphenyl]ethyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(2-[4'-dodecyloxy-4-biphenyl]ethyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(2-[3'-fluoro-4'-methoxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-fluoro-4'-ethoxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-fluoro-4'-propyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-fluoro-4'-butyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-fluoro-4'-pentyloxy-4-biphenyl]ethyl)-

cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-fluoro-4'-hexyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-fluoro-4'-heptyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-fluoro-4'-octyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-fluoro-4'-nonyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-fluoro-4'-decyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-fluoro-4'-undecyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-fluoro-4'-dodecyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-chloro-4'-methoxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-chloro-4'-ethoxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-chloro-4'-propyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-chloro-4'-butyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-chloro-4'-pentyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-chloro-4'-hexyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-chloro-4'-heptyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-chloro-4'-octyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-chloro-4'-nonyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-chloro-4'-decyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-bromo-4'-methoxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-bromo-4'-ethoxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-bromo-4'-propyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-bromo-4'-butyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-bromo-4'-pentyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-bromo-4'-hexyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-bromo-4'-heptyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-bromo-4'-octyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-bromo-4'-nonyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;

trans-4-(2-[3'-bromo-4'-decyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-cyano-4'-methoxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-cyano-4'-ethoxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-cyano-4'-propyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-cyano-4'-butyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-cyano-4'-pentyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-cyano-4'-hexyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-cyano-4'-heptyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-cyano-4'-octyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-cyano-4'-nonyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[3'-cyano-4'-decyloxy-4-biphenyl]ethyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-[2-(4'-[(S)-2-octyloxy]-4-biphenyl)ethyl]-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-[2-(3'-fluoro-4'-[(S)-2-octyloxy]-4-biphenyl)-
ethyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[2-(3'-chloro-4'-[(S)-2-octyloxy]-4-biphenyl)-
ethyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[2-(3'-bromo-4'-[(S)-2-octyloxy]-4-biphenyl)-
ethyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[2-(3'-cyano-4'-[(S)-2-octyloxy]-4-biphenyl)-
ethyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[2-(4'-[(R)-2-octyloxy]-4-biphenyl)ethyl]-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-[2-(3'-fluoro-4'-[(R)-2-octyloxy]-4-biphenyl)-
ethyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[2-(3'-chloro-4'-[(R)-2-octyloxy]-4-biphenyl)-
ethyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[2-(3'-bromo-4'-[(R)-2-octyloxy]-4-biphenyl)-
ethyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[2-(3'-cyano-4'-[(R)-2-octyloxy]-4-biphenyl)-
ethyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[2-(4'-[(S)-2-chloro-1-propyloxy]-4-biphenyl)-
ethyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[2-(4'-[(S)-2-chloro-1-propyloxy]-4-biphenyl)-
ethyl]cyclohexyl (R)-2-fluorohexanoate;
trans-4-[2-(4'-[(R)-2-chloro-1-propyloxy]-4-biphenyl)-
ethyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[2-(4'-[(R)-2-chloro-1-propyloxy]-4-biphenyl)-
ethyl]cyclohexyl (R)-2-fluorohexanoate;
trans-4-(4-methoxyphenyl)cyclohexyl (S)-2-fluoro-
hexanoate;
trans-4-(4-ethoxyphenyl)cyclohexyl (S)-2-fluoro-

hexanoate;
trans-4-(4-propyloxyphenyl)cyclohexyl (S)-2-fluoro-
hexanoate;
trans-4-(4-butyloxyphenyl)cyclohexyl (S)-2-fluoro-
hexanoate;
trans-4-(4-pentyloxyphenyl)cyclohexyl (S)-2-fluoro-
hexanoate;
trans-4-(4-hexyloxyphenyl)cyclohexyl (S)-2-fluoro-
hexanoate;
trans-4-(4-heptyloxyphenyl)cyclohexyl (S)-2-fluoro-
hexanoate;
trans-4-(4-octyloxyphenyl)cyclohexyl (S)-2-fluoro-
hexanoate;
trans-4-(4-nonyloxyphenyl)cyclohexyl (S)-2-fluoro-
hexanoate;
trans-4-(4-decyloxyphenyl)cyclohexyl (S)-2-fluoro-
hexanoate, m.p. (C-I) 42.5°C, cl.p. (S_B-I) 41°C;
trans-4-(4-undecyloxyphenyl)cyclohexyl (S)-2-fluoro-
hexanoate;
trans-4-(4-dodecyloxyphenyl)cyclohexyl (S)-2-fluoro-
hexanoate.

The compounds listed hereinafter are manufactured in an analogous manner by esterifying trans-4-[4-(5-alkyl-2-pyrimidinyl)phenyl]cyclohexanols; the starting materials were obtained by reducing 4-(4-cyanophenyl)cyclohexanone with sodium borohydride and reacting the resulting trans-4-(4-cyanophenyl)cyclohexanol in an analogous manner to Z. Naturforschung 34b, 1535 (1979):

trans-4-[4-(5-Methyl-2-pyrimidinyl)phenyl]cyclohexyl
(S)-2-fluorohexanoate;
trans-4-[4-(5-ethyl-2-pyrimidinyl)phenyl]cyclohexyl
(S)-2-fluorohexanoate;
trans-4-[4-(5-propyl-2-pyrimidinyl)phenyl]cyclohexyl
(S)-2-fluorohexanoate;
trans-4-[4-(5-butyl-2-pyrimidinyl)phenyl]cyclohexyl
(S)-2-fluorohexanoate;
trans-4-[4-(5-pentyl-2-pyrimidinyl)phenyl]cyclohexyl
(S)-2-fluorohexanoate;
trans-4-[4-(5-hexyl-2-pyrimidinyl)phenyl]cyclohexyl
(S)-2-fluorohexanoate, m.p. (C-S_B) 34°C, transition
(S_B-S_A) 98°C, cl.p. (S_A-I) 137°C;
trans-4-[4-(5-heptyl-2-pyrimidinyl)phenyl]cyclohexyl
(S)-2-fluorohexanoate, m.p. (C-S_B) 53°C, transition
(S_B-S_A) 101°C, cl.p. (S_A-I) 143°C;
trans-4-[4-(5-octyl-2-pyrimidinyl)phenyl]cyclohexyl
(S)-2-fluorohexanoate, m.p. (C-S_B) 41°C, transition
(S_B-S_A) 109°C, cl.p. (S_A-I) 143°C;
trans-4-[4-(5-nonyl-2-pyrimidinyl)phenyl]cyclohexyl
(S)-2-fluorohexanoate, m.p. (C-S_B) 49°C, transition
(S_B-S_A) 113°C, cl.p. (S_A-I) 145°C;
trans-4-[4-(5-decyl-2-pyrimidinyl)phenyl]cyclohexyl

(S)-2-fluorohexanoate, m.p. (C-S_B) 48°C, transition (S_B-S_A) 116°C, cl.p. (S_A-I) 145°C;
trans-4-[4-(5-methyl-2-pyrimidinyl)phenyl]cyclohexyl
(2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-[4-(5-ethyl-2-pyrimidinyl)phenyl]cyclohexyl
(2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-[4-(5-propyl-2-pyrimidinyl)phenyl]cyclohexyl
(2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-[4-(5-butyl-2-pyrimidinyl)phenyl]cyclohexyl
(2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-[4-(5-pentyl-2-pyrimidinyl)phenyl]cyclohexyl
(2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-[4-(5-hexyl-2-pyrimidinyl)phenyl]cyclohexyl
(2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-[4-(5-heptyl-2-pyrimidinyl)phenyl]cyclohexyl
(2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-[4-(5-octyl-2-pyrimidinyl)phenyl]cyclohexyl
(2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-[4-(5-nonyl-2-pyrimidinyl)phenyl]cyclohexyl
(2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-[4-(5-decyl-2-pyrimidinyl)phenyl]cyclohexyl
(2S,3S)-2-fluoro-3-methylpentanoate.

The compounds listed hereinafter can be manufactured in an analogous manner by esterifying trans-4-(4'-alkoxy-2',3'-difluoro-4-biphenyl)cyclohexanols; the starting materials were obtained according to known methods by the etherification of 2,3-difluorophenol with an alkyl bromide, subsequent reaction with butyllithium and the monoketal of bicyclohexyl-4,4'-dione with ethylene glycol, dehydration with toluenesulphonic acid, reaction with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, hydrolysis of the ketal group and reduction of the resulting ketone with sodium borohydride to the alcohol:

trans-4-(4'-Methoxy-2',3'-difluoro-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-ethoxy-2',3'-difluoro-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-propyloxy-2',3'-difluoro-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-butyloxy-2',3'-difluoro-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-pentyloxy-2',3'-difluoro-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-hexyloxy-2',3'-difluoro-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-heptyloxy-2',3'-difluoro-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-octyloxy-2',3'-difluoro-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-nonyloxy-2',3'-difluoro-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate;

trans-4-(4'-decyloxy-2',3'-difluoro-4-biphenyl)l)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4'-methoxy-2',3'-difluoro-4-biphenyl)l)cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-(4'-ethoxy-2',3'-difluoro-4-biphenyl)l)cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-(4'-propyloxy-2',3'-difluoro-4-biphenyl)l)cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-(4'-butyloxy-2',3'-difluoro-4-biphenyl)l)cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-(4'-pentyloxy-2',3'-difluoro-4-biphenyl)l)cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-(4'-hexyloxy-2',3'-difluoro-4-biphenyl)l)cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-(4'-heptyloxy-2',3'-difluoro-4-biphenyl)l)cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-(4'-octyloxy-2',3'-difluoro-4-biphenyl)l)cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-(4'-nonyloxy-2',3'-difluoro-4-biphenyl)l)cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-(4'-decyloxy-2',3'-difluoro-4-biphenyl)l)cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate.

Example 2

0.2 g of (S)-2-fluorohexanoic acid (S- α -fluorocaproic acid), 0.5 g of trans-4-([2-bromo-4-(5-decyl-2-pyrimidinyl)phenoxy]methyl)cyclohexanol, 0.35 g of N,N'-dicyclohexylcarbodiimide, 0.02 g of 4-(dimethylamino)pyridine and 50 ml of dichloromethane were reacted in an analogous manner to Example 1. This gave 0.4 g of trans-4-([2-bromo-4-(5-decyl-2-pyrimidinyl)phenoxy]methyl)cyclohexyl (S)-2-fluorohexanoate.

The trans-4-([2-bromo-4-(5-decyl-2-pyrimidinyl)phenoxy]methyl)cyclohexanol used as the starting material was prepared as follows:

(a) A solution of 5 g of 4-(5-decyl-2-pyrimidinyl)phenol in 50 ml of dichloromethane was treated at 0°C while gassing with argon with a solution of 2.6 g of bromine in 50 ml of dichloromethane. The reaction mixture was stirred for a further 2 hours and then treated with water. The organic phase was separated and the aqueous phase was back-extracted three times with 50 ml of dichloromethane each time. The combined organic phases were washed with water, sodium hydrogen carbonate solution and again with water, dried over magnesium sulphate, filtered and subsequently concentrated. The residue was purified by chromatography on silica gel with toluene/ethyl acetate (vol. 4:1). Recrystallization from hexane gave 4.8 g of 2-bromo-4-(5-decyl-2-pyrimidinyl)phenol.

(b) A mixture of 4.8 g of 2-bromo-4-(5-decyl-2-pyrimidinyl)phenol, 3.5 g of (trans-4-hydroxycyclohexyl)methyl tosylate, 6.8 g of potassium carbonate and 100 ml of butanone was heated under slight reflux for 2 days. Subsequently, the cooled reaction mixture was poured into water and extracted three times with 50 ml of dichloromethane each time. The combined organic phases were washed with water, dried over magnesium sulphate, filtered and subsequently concentrated. The residue was purified by chromatography on silica gel with toluene/ethyl acetate (vol. 4:1). This gave 4.5 g of trans-4-([2-bromo-4-(5-decyl-2-pyrimidinyl)phenoxy]methyl)cyclohexanol.

The following compounds can be manufactured in an analogous manner:

trans-4-([2-Fluoro-4-(5-methyl-2-pyrimidinyl)phenoxy]-methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-fluoro-4-(5-ethyl-2-pyrimidinyl)phenoxy]-methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-fluoro-4-(5-propyl-2-pyrimidinyl)phenoxy]-methyl)cyclohexyl ((S)-2-fluorohexanoate;
trans-4-([2-fluoro-4-(5-butyl-2-pyrimidinyl)phenoxy]-methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-fluoro-4-(5-pentyl-2-pyrimidinyl)phenoxy]-methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-fluoro-4-(5-hexyl-2-pyrimidinyl)phenoxy]-methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-fluoro-4-(5-heptyl-2-pyrimidinyl)phenoxy]-methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-fluoro-4-(5-octyl-2-pyrimidinyl)phenoxy]-methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-fluoro-4-(5-nonyl-2-pyrimidinyl)phenoxy]-methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-fluoro-4-(5-decyl-2-pyrimidinyl)phenoxy]-methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-chloro-4-(5-methyl-2-pyrimidinyl)phenoxy]-methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-chloro-4-(5-ethyl-2-pyrimidinyl)phenoxy]-methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-chloro-4-(5-propyl-2-pyrimidinyl)phenoxy]-methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-chloro-4-(5-butyl-2-pyrimidinyl)phenoxy]-methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-chloro-4-(5-pentyl-2-pyrimidinyl)phenoxy]-methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-chloro-4-(5-hexyl-2-pyrimidinyl)phenoxy]-methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-chloro-4-(5-heptyl-2-pyrimidinyl)phenoxy]-methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-chloro-4-(5-octyl-2-pyrimidinyl)phenoxy]-methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-chloro-4-(5-nonyl-2-pyrimidinyl)phenoxy]-

methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-chloro-4-(5-decyl-2-pyrimidinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-bromo-4-(5-methyl-2-pyrimidinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-bromo-4-(5-ethyl-2-pyrimidinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-bromo-4-(5-propyl-2-pyrimidinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-bromo-4-(5-butyl-2-pyrimidinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-bromo-4-(5-pentyl-2-pyrimidinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-bromo-4-(5-hexyl-2-pyrimidinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-bromo-4-(5-heptyl-2-pyrimidinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-bromo-4-(5-octyl-2-pyrimidinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-bromo-4-(5-nonyl-2-pyrimidinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-cyano-4-(5-methyl-2-pyrimidinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-cyano-4-(5-ethyl-2-pyrimidinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-cyano-4-(5-propyl-2-pyrimidinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-cyano-4-(5-butyl-2-pyrimidinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-cyano-4-(5-pentyl-2-pyrimidinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-cyano-4-(5-hexyl-2-pyrimidinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-cyano-4-(5-heptyl-2-pyrimidinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-cyano-4-(5-octyl-2-pyrimidinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-cyano-4-(5-nonyl-2-pyrimidinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-cyano-4-(5-decyl-2-pyrimidinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([4'-methyl-4-biphenyloxy]methyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-([4'-ethyl-4-biphenyloxy]methyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-([4'-propyl-4-biphenyloxy]methyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-([4'-butyl-4-biphenyloxy]methyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-([4'-pentyl-4-biphenyloxy]methyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-([4'-hexyl-4-biphenyloxy]methyl)cyclohexyl
(S)-2-fluorohexanoate;

trans-4-([4'-heptyl-4-biphenyloxy]methyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-([4'-octyl-4-biphenyloxy]methyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-([4'-nonyl-4-biphenyloxy]methyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-([4'-decyl-4-biphenyloxy]methyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-([4'-undecyl-4-biphenyloxy]methyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-([4'-dodecyl-4-biphenyloxy]methyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-([4'-methoxy-4-biphenyloxy]methyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-([4'-ethoxy-4-biphenyloxy]methyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-([4'-propyloxy-4-biphenyloxy]methyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-([4'-butyloxy-4-biphenyloxy]methyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-([4'-pentyloxy-4-biphenyloxy]methyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-([4'-hexyloxy-4-biphenyloxy]methyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-([4'-heptyloxy-4-biphenyloxy]methyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-([4'-octyloxy-4-biphenyloxy]methyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-([4'-nonyloxy-4-biphenyloxy]methyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-([4'-decyloxy-4-biphenyloxy]methyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-([3'-fluoro-4'-octyloxy-4-biphenyloxy]methyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-([3'-chloro-4'-octyloxy-4-biphenyloxy]methyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-([3'-bromo-4'-octyloxy-4-biphenyloxy]methyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-([3'-cyano-4'-octyloxy-4-biphenyloxy]methyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-([3'-fluoro-4'-octyloxy-4-biphenyloxy]methyl)-
cyclohexyl (R)-2-fluorohexanoate;
trans-4-([3'-chloro-4'-octyloxy-4-biphenyloxy]methyl)-
cyclohexyl (R)-2-fluorohexanoate;
trans-4-([3'-bromo-4'-octyloxy-4-biphenyloxy]methyl)-
cyclohexyl (R)-2-fluorohexanoate;
trans-4-([3'-cyano-4'-octyloxy-4-biphenyloxy]methyl)-
cyclohexyl (R)-2-fluorohexanoate;
trans-4-([4'-[(S)-2-octyloxy]-4-biphenyloxy]methyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-([4'-[(S)-2-octyloxy]-4-biphenyloxy]methyl)-
cyclohexyl (R)-2-fluorohexanoate;
trans-4-([4-(5-methyl-2-pyridinyl)phenoxy]methyl)cyclo-

hexyl (S)-2-fluorohexanoate;
trans-4-([4-(5-ethyl-2-pyridinyl)phenoxy]methyl)cyclo-
hexyl (S)-2-fluorohexanoate;
trans-4-([4-(5-propyl-2-pyridinyl)phenoxy]methyl)cyclo-
hexyl (S)-2-fluorohexanoate;
trans-4-([4-(5-butyl-2-pyridinyl)phenoxy]methyl)cyclo-
hexyl (S)-2-fluorohexanoate;
trans-4-([4-(5-pentyl-2-pyridinyl)phenoxy]methyl)cyclo-
hexyl (S)-2-fluorohexanoate;
trans-4-([4-(5-hexyl-2-pyridinyl)phenoxy]methyl)cyclo-
hexyl (S)-2-fluorohexanoate;
trans-4-([4-(5-heptyl-2-pyridinyl)phenoxy]methyl)cyclo-
hexyl (S)-2-fluorohexanoate;
trans-4-([4-(5-octyl-2-pyridinyl)phenoxy]methyl)cyclo-
hexyl (S)-2-fluorohexanoate;
trans-4-([4-(5-nonyl-2-pyridinyl)phenoxy]methyl)cyclo-
hexyl (S)-2-fluorohexanoate;
trans-4-([4-(5-decyl-2-pyridinyl)phenoxy]methyl)cyclo-
hexyl (S)-2-fluorohexanoate;
trans-4-([2-fluoro-4-(5-decyl-2-pyridinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-chloro-4-(5-decyl-2-pyridinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-bromo-4-(5-decyl-2-pyridinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-([2-cyano-4-(5-decyl-2-pyridinyl)phenoxy]-
methyl)cyclohexyl (S)-2-fluorohexanoate.

Example 3

0.2 g of (S)-2-fluorohexanoic acid (S- α -fluorocaproic acid), 0.8 g of trans-4-(2-[4-(4-dodecyloxybenzoyloxy)phenyl]ethyl)cyclohexanol, 0.45 g of N,N'-dicyclohexylcarbodiimide, 3 mg of 4-(dimethylamino)pyridine and 30 ml of dichloromethane were reacted in an analogous manner to Example 1. This gave 0.6 g of trans-4-(2-[4-(4-dodecyloxybenzoyloxy)phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate.

The trans-4-(2-[4-(4-dodecyloxybenzoyloxy)phenyl]ethyl)cyclohexanol used as the starting material was prepared as follows:

(a) A mixture of 5 g of trans-4-hydroxycyclohexanecarboxaldehyde, 30 g of 4-methoxybenzyl-triphenylphosphonium bromide and 250 ml of tert.butyl methyl ether was treated with 7 g of potassium tert.butylate at 0°C while gassing with argon. The reaction mixture was stirred at room temperature for a further 2 hours and then treated with water. The reaction mixture was extracted three times with 50 ml of diethyl ether each time. The combined organic phases were washed with water, dried over magnesium sulphate, filtered and subsequently concentrated. The

residue was treated several times with hexane. The combined organic phases were again concentrated. The crude product obtained was purified by chromatography on silica gel with hexane. This gave 8 g of 1-(trans-4-hydroxycyclohexyl)-2-(4-methoxyphenyl)ethene (cis/trans mixture).

(b) A mixture of 8 g of 1-(trans-4-hydroxycyclohexyl)-2-(4-methoxyphenyl)ethene, 0.5 g of palladium/carbon (5%) and 100 ml of ethyl acetate was reacted in an analogous manner to Example 1 (d) while conducting hydrogen through the mixture. This gave 7.5 g of trans-4-(2-[4-methoxyphenyl]ethyl)cyclohexanol.

(c) A mixture of 7.5 g trans-4-(2-[4-methoxyphenyl]ethyl)-cyclohexanol and 100 ml of dichloromethane was treated at 0°C with 27 ml of a 1M solution of boron tribromide in dichloromethane. The reaction mixture was stirred at room temperature for a further 2 hours and then poured on to ice-water. The organic phase was separated and the aqueous phase was back-extracted three times with 50 ml of dichloromethane each time. The combined organic phases were washed with water, sodium hydrogen carbonate solution and again with water and then dried over magnesium sulphate, filtered and concentrated. The residue was recrystallized from hexane and gave 5.2 g of trans-4-(2-[4-hydroxyphenyl]ethyl)cyclohexanol.

(d) 0.7 g of 4-dodecyloxybenzoic acid, 0.5 g of trans-4-(2-[4-hydroxyphenyl]ethyl)cyclohexanol, 0.6 g of N,N'-dicyclohexylcarbodiimide, 4 mg of 4-(dimethylamino)pyridine and 50 ml of dichloromethane were reacted in an analogous manner to Example 1. This gave 0.8 g of trans-4-(2-[4-(4-dodecyloxybenzoyloxy)phenyl]ethyl)cyclohexanol.

The following compounds can be manufactured in an analogous manner:

trans-4-(2-[4-(4-Methoxybenzoyloxy)phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(4-ethoxybenzoyloxy)phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(4-propyloxybenzoyloxy)phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(4-butyloxybenzoyloxy)phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(4-pentyloxybenzoyloxy)phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(4-hexyloxybenzoyloxy)phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(4-heptyloxybenzoyloxy)phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(4-octyloxybenzoyloxy)phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;

trans-4-(2-[4-(4-nonyloxybenzoyloxy)phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(4-decyloxybenzoyloxy)phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(4-undecyloxybenzoyloxy)phenyl]ethyl)-cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(4-methylbenzoyloxy)phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(4-ethylbenzoyloxy)phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(4-propylbenzoyloxy)phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(4-butylbenzoyloxy)phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(4-pentylbenzoyloxy)phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(4-hexylbenzoyloxy)phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(4-heptylbenzoyloxy)phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(4-octylbenzoyloxy)phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(4-nonylbenzoyloxy)phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(4-decylbenzoyloxy)phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(2-fluoro-4-methoxybenzoyloxy)phenyl]-ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(2-fluoro-4-ethoxybenzoyloxy)phenyl]-ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(2-fluoro-4-propyloxybenzoyloxy)phenyl]-ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(2-fluoro-4-butyloxybenzoyloxy)phenyl]-ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(2-fluoro-4-pentyloxybenzoyloxy)phenyl]-ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(2-fluoro-4-hexyloxybenzoyloxy)phenyl]-ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(2-fluoro-4-heptyloxybenzoyloxy)phenyl]-ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(2-fluoro-4-octyloxybenzoyloxy)phenyl]-ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(2-fluoro-4-nonyloxybenzoyloxy)phenyl]-ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(2-fluoro-4-decyloxybenzoyloxy)phenyl]-ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(2-fluoro-4-undecyloxybenzoyloxy)phenyl]-ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(2-fluoro-4-dodecyloxybenzoyloxy)phenyl]-ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(3-fluoro-4-methoxybenzoyloxy)phenyl]-ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(3-fluoro-4-ethoxybenzoyloxy)phenyl]-

ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(3-fluoro-4-propyloxybenzoyloxy)phenyl]-
ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(3-fluoro-4-butyloxybenzoyloxy)phenyl]-
ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(3-fluoro-4-pentyloxybenzoyloxy)phenyl]-
ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(3-fluoro-4-hexyloxybenzoyloxy)phenyl]-
ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(3-fluoro-4-heptyloxybenzoyloxy)phenyl]-
ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(3-fluoro-4-octyloxybenzoyloxy)phenyl]-
ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(3-fluoro-4-nonyloxybenzoyloxy)phenyl]-
ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(3-fluoro-4-decyloxybenzoyloxy)phenyl]-
ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(3-fluoro-4-undecyloxybenzoyloxy)phenyl]-
ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(3-fluoro-4-dodecyloxybenzoyloxy)phenyl]-
ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(2-chloro-4-dodecyloxybenzoyloxy)phenyl]-
ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(3-chloro-4-dodecyloxybenzoyloxy)phenyl]-
ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(2-bromo-4-dodecyloxybenzoyloxy)phenyl]-
ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(3-bromo-4-dodecyloxybenzoyloxy)phenyl]-
ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(2-cyano-4-dodecyloxybenzoyloxy)phenyl]-
ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(3-cyano-4-dodecyloxybenzoyloxy)phenyl]-
ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(2-chloro-4-dodecyloxybenzoyloxy)phenyl]-
ethyl)cyclohexyl (R)-2-fluorohexanoate;
trans-4-(2-[4-(3-chloro-4-dodecyloxybenzoyloxy)phenyl]-
ethyl)cyclohexyl (R)-2-fluorohexanoate;
trans-4-(2-[4-(2-bromo-4-dodecyloxybenzoyloxy)phenyl]-
ethyl)cyclohexyl (R)-2-fluorohexanoate;
trans-4-(2-[4-(3-bromo-4-dodecyloxybenzoyloxy)phenyl]-
ethyl)cyclohexyl (R)-2-fluorohexanoate;
trans-4-(2-[4-(2-cyano-4-dodecyloxybenzoyloxy)phenyl]-
ethyl)cyclohexyl (R)-2-fluorohexanoate;
trans-4-(2-[4-(3-cyano-4-dodecyloxybenzoyloxy)phenyl]-
ethyl)cyclohexyl (R)-2-fluorohexanoate;
trans-4-(2-[4-(4-[(S)-2-chloro-1-propyloxy]benzoyloxy)-
phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(4-[(R)-2-chloro-1-propyloxy]benzoyloxy)-
phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(4-[(S)-2-chloro-1-propyloxy]benzoyloxy)-
phenyl]ethyl)cyclohexyl (R)-2-fluorohexanoate;
trans-4-(2-[4-(4-[(R)-2-chloro-1-propyloxy]benzoyloxy)-
phenyl]ethyl)cyclohexyl (R)-2-fluorohexanoate;

trans-4-(4-[4-methoxybenzoyloxy]phenyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(4-[4-ethoxybenzoyloxy]phenyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(4-[4-propyloxybenzoyloxy]phenyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(4-[4-butyloxybenzoyloxy]phenyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(4-[4-pentyloxybenzoyloxy]phenyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(4-[4-hexyloxybenzoyloxy]phenyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(4-[4-heptyloxybenzoyloxy]phenyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(4-[4-octyloxybenzoyloxy]phenyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(4-[4-nonyloxybenzoyloxy]phenyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(4-[4-decyloxybenzoyloxy]phenyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(4-[4-undecyloxybenzoyloxy]phenyl)cyclohexyl
(S)-2-fluorohexanoate;
trans-4-(4-[4-dodecyloxybenzoyloxy]phenyl)cyclohexyl
(S)-2-fluorohexanoate, m.p. (C-S_B) 64°C, transition
(S_B-S_A) 113°C, cl.p. (S_A-I) 159°C;
trans-4-(4-[3-fluoro-4-dodecyloxybenzoyloxy]phenyl)-
cyclohexyl (S)-2-fluorohexanoate, m.p. (C-S_C^{*}) 73°C,
cl.p. (S_C^{*}-I) 148°C;
trans-4-(4-[3-chloro-4-dodecyloxybenzoyloxy]phenyl)-
cyclohexyl (S)-2-fluorohexanoate, m.p. (C-S_C^{*}) 50°C,
cl.p. (S_C^{*}-I) 138°C;
trans-4-(4-[3-bromo-4-dodecyloxybenzoyloxy]phenyl)-
cyclohexyl (S)-2-fluorohexanoate, m.p. (C-S_C^{*}) 56°C,
cl.p. (S_C^{*}-I) 118°C;
trans-4-(4-[3-cyano-4-dodecyloxybenzoyloxy]phenyl)-
cyclohexyl (S)-2-fluorobenzoic acid;
trans-4-(4-[2,3-difluoro-4-methoxybenzoyloxy]phenyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4-[2,3-difluoro-4-ethoxybenzoyloxy]phenyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4-[2,3-difluoro-4-propyloxybenzoyloxy]phenyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4-[2,3-difluoro-4-butyloxybenzoyloxy]phenyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4-[2,3-difluoro-4-pentyloxybenzoyloxy]phenyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4-[2,3-difluoro-4-hexyloxybenzoyloxy]phenyl)-
cyclohexyl (S)-2-fluorohexanoate;
trans-4-(4-[2,3-difluoro-4-heptyloxybenzoyloxy]phenyl)-
cyclohexyl (R)-2-fluorohexanoate, m.p. (C-S_C^{*}) 82°C,
transition (S_C^{*}-S_A) 93°C, transition (S_A-Ch)
140°C, cl.p. (Ch-I) 151°C;
trans-4-(4-[2,3-difluoro-4-octyloxybenzoyloxy]phenyl)-

cyclohexyl (S)-2-fluorohexanoate, m.p. (C-S_C^{*}) 77°C,
transition (S_C^{*}-S_A) 91°C, transition (S_A-Ch)
143°C, cl.p. (Ch-I) 150°C;
trans-4-(4-[2,3-difluoro-4-nonyloxybenzoyloxy]phenyl)-
cyclohexyl (R)-2-fluorohexanoate, m.p. (C-S_C^{*}) 74°C,
transition (S_C^{*}-S_A) 87°C, transition (S_A-Ch)
145°C, cl.p. (Ch-I) 148°C;
trans-4-(4-[2,3-difluoro-4-decyloxybenzoyloxy]phenyl)-
cyclohexyl (S)-2-fluorohexanoate, m.p. (C-S_C^{*}) 72°C,
transition (S_C^{*}-S_A) 84°C, transition (S_A-Ch)
147°C, cl.p. (Ch-I) 148°C;
trans-4-(4-[2,3-difluoro-4-undecyloxybenzoyloxy]-
phenyl)cyclohexyl (S)-2-fluorohexanoate, m.p. (C-S_A)
78°C, transition (S_C^{*}-S_A) 77°C, cl.p. (S_A-I) 147°C;
trans-4-(4-[2,3-difluoro-4-dodecyloxybenzoyloxy]-
phenyl)cyclohexyl (S)-2-fluorohexanoate, m.p. (C-S_C^{*})
73°C, transition (S_C^{*}-S_A) 74°C, cl.p. (S_A-I) 147°C;
trans-4-(4-[2,3-difluoro-4-methoxybenzoyloxy]phenyl)-
cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-(4-[2,3-difluoro-4-ethoxybenzoyloxy]phenyl)-
cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-(4-[2,3-difluoro-4-propyloxybenzoyloxy]phenyl)-
cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-(4-[2,3-difluoro-4-butyloxybenzoyloxy]phenyl)-
cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-(4-[2,3-difluoro-4-pentyloxybenzoyloxy]phenyl)-
cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-(4-[2,3-difluoro-4-hexyloxybenzoyloxy]phenyl)-
cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-(4-[2,3-difluoro-4-heptyloxybenzoyloxy]phenyl)-
cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-(4-[2,3-difluoro-4-octyloxybenzoyloxy]phenyl)-
cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-(4-[2,3-difluoro-4-nonyloxybenzoyloxy]phenyl)-
cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-(4-[2,3-difluoro-4-decyloxybenzoyloxy]phenyl)-
cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-(4-[2,3-difluoro-4-undecyloxybenzoyloxy]phenyl)-
cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-(4-[2,3-difluoro-4-dodecyloxybenzoyloxy]phenyl)-
cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-[(4-[4-methoxybenzoyloxy]phenoxy)methyl]cyclo-
hexyl (S)-2-fluorohexanoate;
trans-4-[(4-[4-ethoxybenzoyloxy]phenoxy)methyl]cyclo-
hexyl (S)-2-fluorohexanoate;
trans-4-[(4-[4-propyloxybenzoyloxy]phenoxy)methyl]cyclo-
hexyl (S)-2-fluorohexanoate;
trans-4-[(4-[4-butyloxybenzoyloxy]phenoxy)methyl]cyclo-
hexyl (S)-2-fluorohexanoate;
trans-4-[(4-[4-pentyloxybenzoyloxy]phenoxy)methyl]cyclo-
hexyl (S)-2-fluorohexanoate;
trans-4-[(4-[4-hexyloxybenzoyloxy]phenoxy)methyl]cyclo-
hexyl (S)-2-fluorohexanoate;

trans-4-[(4-[4-heptyloxybenzoyloxy]phenoxy)methyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[(4-[4-octyloxybenzoyloxy]phenoxy)methyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[(4-[4-nonyloxybenzoyloxy]phenoxy)methyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[(4-[4-decyloxybenzoyloxy]phenoxy)methyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[(4-[4-undecyloxybenzoyloxy]phenoxy)methyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[(4-[4-dodecyloxybenzoyloxy]phenoxy)methyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[(4-[3-fluoro-4-dodecyloxybenzoyloxy]phenoxy)methyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[(4-[3-chloro-4-dodecyloxybenzoyloxy]phenoxy)methyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[(4-[3-bromo-4-dodecyloxybenzoyloxy]phenoxy)methyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[(4-[3-cyano-4-dodecyloxybenzoyloxy]phenoxy)methyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[(4-[2,3-difluoro-4-methoxybenzoyloxy]phenoxy)methyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[(4-[2,3-difluoro-4-ethoxybenzoyloxy]phenoxy)methyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[(4-[2,3-difluoro-4-propyloxybenzoyloxy]phenoxy)methyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[(4-[2,3-difluoro-4-butyloxybenzoyloxy]phenoxy)methyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[(4-[2,3-difluoro-4-pentyloxybenzoyloxy]phenoxy)methyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[(4-[2,3-difluoro-4-hexyloxybenzoyloxy]phenoxy)methyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[(4-[2,3-difluoro-4-heptyloxybenzoyloxy]phenoxy)methyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[(4-[2,3-difluoro-4-octyloxybenzoyloxy]phenoxy)methyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[(4-[2,3-difluoro-4-nonyloxybenzoyloxy]phenoxy)methyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[(4-[2,3-difluoro-4-decyloxybenzoyloxy]phenoxy)methyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[(4-[2,3-difluoro-4-undecyloxybenzoyloxy]phenoxy)methyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[(4-[2,3-difluoro-4-dodecyloxybenzoyloxy]phenoxy)methyl]cyclohexyl (S)-2-fluorohexanoate.

Example 4

0.23 g of (S)-2-fluorohexanoic acid (S- α -fluorocaproic acid), 0.24 g of trans-4-(4-[(trans-4-hydroxycyclohexyl)methoxy]phenyl)cyclohexanol, 0.29 g of N,N'-dicyclohexylcarbodiimide, 0.02 g of 4-(dimethylamino)pyridine and 20 ml of dichloromethane were reacted in an analogous manner to Example 1. This gave 0.2 g of

trans-4-(4-[(trans-4-[(S)-2-fluorohexanoyloxy]cyclohexyl)-methoxy]phenyl)cyclohexyl (S)-2-fluorohexanoate; m.p. (C-S) < 25°C, transition (S-S_A) 67°C, cl.p. (S_A-I) 88.9°C.

The trans-4-(4-[(trans-4-hydroxycyclohexyl)methoxy]phenyl)cyclohexanol used as the starting material was prepared as follows:

(a) A mixture of 1.0 g of 4-(4-hydroxyphenyl)cyclohexanone, 1.4 g of (trans-4-hydroxycyclohexyl)methyl tosylate, 1.5 g of potassium carbonate and 60 ml of absolute butanone was heated under reflux for 2 days. Subsequently, the cooled reaction mixture was poured into water and extracted three times with 50 ml of dichloromethane each time. The combined organic phases were washed with water, dried over magnesium sulphate, filtered and subsequently concentrated. The residue was purified by chromatography on silica gel with toluene/ethyl acetate (vol. 5:1). This gave 1.0 g of 4-(4-[(trans-4-hydroxycyclohexyl)methoxy]phenyl)cyclohexanone.

(b) 1.0 g of 4-(4-[(trans-4-hydroxycyclohexyl)methoxy]phenyl)cyclohexanone, 0.12 g of sodium borohydride, 20 ml of methanol and 2 ml of diethyl ether were reacted in an analogous manner to Example 1 (a). The crude product was purified by chromatography on silica gel with dichloromethane/methanol (vol. 19:1). This gave 0.24 g of trans-4-(4-[(trans-4-hydroxycyclohexyl)methoxy]phenyl)cyclohexanol.

The following compounds can be manufactured in an analogous manner:

trans-4-(4-[(trans-4-[(S)-2-Fluoropropanoyloxy]cyclohexyl)methoxy]phenyl)cyclohexyl (S)-2-fluoropropanoate;
trans-4-(4-[(trans-4-[(S)-2-fluorobutanoyloxy]cyclohexyl)methoxy]phenyl)cyclohexyl (S)-2-fluorobutanoate;
trans-4-(4-[(trans-4-[(S)-2-fluoropentanoyloxy]cyclohexyl)methoxy]phenyl)cyclohexyl (S)-2-fluoropentanoate;
trans-4-(4-[(trans-4-[(S)-2-fluoroheptanoyloxy]cyclohexyl)methoxy]phenyl)cyclohexyl (S)-2-fluoroheptanoate;
trans-4-(4-[(trans-4-[(S)-2-fluorooctanoyloxy]cyclohexyl)methoxy]phenyl)cyclohexyl (S)-2-fluorooctanoate;
trans-4-(4-[(trans-4-[(S)-2-fluorononanoyloxy]cyclohexyl)methoxy]phenyl)cyclohexyl (S)-2-fluorononanoate;
trans-4-(4-[(trans-4-[(S)-2-fluorodecanoyloxy]cyclohexyl)methoxy]phenyl)cyclohexyl (S)-2-fluorodecanoate;
trans-4-(4-[(trans-4-[(R)-2-fluoropropanoyloxy]cyclohexyl)methoxy]phenyl)cyclohexyl (R)-2-fluoropropanoate;
trans-4-(4-[(trans-4-[(R)-2-fluorobutanoyloxy]cyclohexyl)methoxy]phenyl)cyclohexyl (R)-2-fluorobutanoate;
trans-4-(4-[(trans-4-[(R)-2-fluoropentanoyloxy]cyclohexyl)methoxy]phenyl)cyclohexyl (R)-2-fluoropentanoate;

trans-4-(4-[(trans-4-[(R)-2-fluorohexanoyloxy]cyclohexyl)methoxy]phenyl)cyclohexyl (R)-2-fluorohexanoate;
trans-4-(4-[(trans-4-[(R)-2-fluoroheptanoyloxy]cyclohexyl)methoxy]phenyl)cyclohexyl (R)-2-fluoroheptanoate;
trans-4-(4-[(trans-4-[(R)-2-fluorooctanoyloxy]cyclohexyl)methoxy]phenyl)cyclohexyl (R)-2-fluorooctanoate;
trans-4-(4-[(trans-4-[(R)-2-fluorononanoyloxy]cyclohexyl)methoxy]phenyl)cyclohexyl (R)-2-fluorononanoate;
trans-4-(4-[(trans-4-[(R)-2-fluorodecanoyloxy]cyclohexyl)methoxy]phenyl)cyclohexyl (R)-2-fluorodecanoate;
trans-4-(2-[4-(trans-4-[(S)-2-fluoropropanoyloxy]cyclohexyl)phenyl]ethyl)cyclohexyl (S)-2-fluoropropanoate;
trans-4-(2-[4-(trans-4-[(S)-2-fluorobutanoyloxy]cyclohexyl)phenyl]ethyl)cyclohexyl (S)-2-fluorobutanoate;
trans-4-(2-[4-(trans-4-[(S)-2-fluoropentanoyloxy]cyclohexyl)phenyl]ethyl)cyclohexyl (S)-2-fluoropentanoate;
trans-4-(2-[4-(trans-4-[(S)-2-fluorohexanoyloxy]cyclohexyl)phenyl]ethyl)cyclohexyl (S)-2-fluorohexanoate;
trans-4-(2-[4-(trans-4-[(S)-2-fluoroheptanoyloxy]cyclohexyl)phenyl]ethyl)cyclohexyl (S)-2-fluoroheptanoate;
trans-4-(2-[4-(trans-4-[(S)-2-fluorooctanoyloxy]cyclohexyl)phenyl]ethyl)cyclohexyl (S)-2-fluorooctanoate;
trans-4-(2-[4-(trans-4-[(S)-2-fluorononanoyloxy]cyclohexyl)phenyl]ethyl)cyclohexyl (S)-2-fluorononanoate;
trans-4-(2-[4-(trans-4-[(S)-2-fluorodecanoyloxy]cyclohexyl)phenyl]ethyl)cyclohexyl (S)-2-fluorodecanoate;
trans-4, trans-4'-di[(S)-2-fluoropropanoyloxy]bicyclohexyl;
trans-4, trans-4'-di[(S)-2-fluorobutanoyloxy]bicyclohexyl;
trans-4, trans-4'-di[(S)-2-fluoropentanoyloxy]bicyclohexyl;
trans-4, trans-4'-di[(S)-2-fluorohexanoyloxy]bicyclohexyl, m.p. (C-I) 38.1°C, transition (S-S) 18.8°C, cl.p. (S-I) 22.3°C;
trans-4, trans-4'-di[(S)-2-fluoroheptanoyloxy]bicyclohexyl;
trans-4, trans-4'-di[(S)-2-fluorooctanoyloxy]bicyclohexyl;
trans-4, trans-4'-di[(S)-2-fluorononanoyloxy]bicyclohexyl;
trans-4, trans-4'-di[(S)-2-fluorodecanoyloxy]bicyclohexyl;
trans-4, trans-4'-di[(R)-2-fluoropropanoyloxy]bicyclohexyl;
trans-4, trans-4'-di[(R)-2-fluorobutanoyloxy]bicyclohexyl;
trans-4, trans-4'-di[(R)-2-fluoropentanoyloxy]bicyclohexyl;
trans-4, trans-4'-di[(R)-2-fluorohexanoyloxy]bicyclohexyl;
trans-4, trans-4'-di[(R)-2-fluoroheptanoyloxy]bicyclohexyl;

trans-4, trans-4'-di[(R)-2-fluorooctanoyloxy]bicyclohexyl;
trans-4, trans-4'-di[(R)-2-fluorononanoyloxy]bicyclohexyl;
trans-4, trans-4'-di[(R)-2-fluorodecanoyloxy]bicyclohexyl;
1,4-bis(trans-4-[(S)-2-fluoropropanoyloxy]cyclohexyl)-benzene;
1,4-bis(trans-4-[(S)-2-fluorobutanoyloxy]cyclohexyl)-benzene;
1,4-bis(trans-4-[(S)-2-fluoropentanoyloxy]cyclohexyl)-benzene;
1,4-bis(trans-4-[(S)-2-fluorohexanoyloxy]cyclohexyl)-benzene;
1,4-bis(trans-4-[(S)-2-fluoroheptanoyloxy]cyclohexyl)-benzene;
1,4-bis(trans-4-[(S)-2-fluorooctanoyloxy]cyclohexyl)-benzene;
1,4-bis(trans-4-[(S)-2-fluorononanoyloxy]cyclohexyl)-benzene;
1,4-bis(trans-4-[(S)-2-fluorodecanoyloxy]cyclohexyl)-benzene;
2-fluoro-1,4-bis(trans-4-[(S)-2-fluoropropanoyloxy]cyclohexyl)benzene;
2-fluoro-1,4-bis(trans-4-[(S)-2-fluorobutanoyloxy]cyclohexyl)benzene;
2-fluoro-1,4-bis(trans-4-[(S)-2-fluoropentanoyloxy]cyclohexyl)benzene;
2-fluoro-1,4-bis(trans-4-[(S)-2-fluorohexanoyloxy]cyclohexyl)benzene;
2-fluoro-1,4-bis(trans-4-[(S)-2-fluoroheptanoyloxy]cyclohexyl)benzene;
2-fluoro-1,4-bis(trans-4-[(S)-2-fluorooctanoyloxy]cyclohexyl)benzene;
2-fluoro-1,4-bis(trans-4-[(S)-2-fluorononanoyloxy]cyclohexyl)benzene;
2-fluoro-1,4-bis(trans-4-[(S)-2-fluorodecanoyloxy]cyclohexyl)benzene;
2-chloro-1,4-bis(trans-4-[(S)-2-fluoropropanoyloxy]cyclohexyl)benzene;
2-chloro-1,4-bis(trans-4-[(S)-2-fluorobutanoyloxy]cyclohexyl)benzene;
2-chloro-1,4-bis(trans-4-[(S)-2-fluoropentanoyloxy]cyclohexyl)benzene;
2-chloro-1,4-bis(trans-4-[(S)-2-fluorohexanoyloxy]cyclohexyl)benzene;
2-chloro-1,4-bis(trans-4-[(S)-2-fluoroheptanoyloxy]cyclohexyl)benzene;
2-chloro-1,4-bis(trans-4-[(S)-2-fluorooctanoyloxy]cyclohexyl)benzene;
2-chloro-1,4-bis(trans-4-[(S)-2-fluorononanoyloxy]cyclohexyl)benzene;
2-chloro-1,4-bis(trans-4-[(S)-2-fluorodecanoyloxy]cyclohexyl)benzene;

cyclohexyl)benzene;
2-bromo-1,4-bis(trans-4-[(S)-2-fluoropropanoyloxy]-
cyclohexyl)benzene;
2-bromo-1,4-bis(trans-4-[(S)-2-fluorobutanoyloxy]-
cyclohexyl)benzene;
2-bromo-1,4-bis(trans-4-[(S)-2-fluoropentanoyloxy]-
cyclohexyl)benzene;
2-bromo-1,4-bis(trans-4-[(S)-2-fluorohexanoyloxy]-
cyclohexyl)benzene;
2-bromo-1,4-bis(trans-4-[(S)-2-fluoroheptanoyloxy]-
cyclohexyl)benzene;
2-bromo-1,4-bis(trans-4-[(S)-2-fluorooctanoyloxy]-
cyclohexyl)benzene;
2-bromo-1,4-bis(trans-4-[(S)-2-fluorononanoyloxy]-
cyclohexyl)benzene;
2-bromo-1,4-bis(trans-4-[(S)-2-fluorodecanoyloxy]-
cyclohexyl)benzene;
2-cyano-1,4-bis(trans-4-[(S)-2-fluoropropanoyloxy]-
cyclohexyl)benzene;
2-cyano-1,4-bis(trans-4-[(S)-2-fluorobutanoyloxy]-
cyclohexyl)benzene;
2-cyano-1,4-bis(trans-4-[(S)-2-fluoropentanoyloxy]-
cyclohexyl)benzene;
2-cyano-1,4-bis(trans-4-[(S)-2-fluorohexanoyloxy]-
cyclohexyl)benzene;
2-cyano-1,4-bis(trans-4-[(S)-2-fluoroheptanoyloxy]-
cyclohexyl)benzene;
2-cyano-1,4-bis(trans-4-[(S)-2-fluorooctanoyloxy]-
cyclohexyl)benzene;
2-cyano-1,4-bis(trans-4-[(S)-2-fluorononanoyloxy]-
cyclohexyl)benzene;
2-cyano-1,4-bis(trans-4-[(S)-2-fluorodecanoyloxy]-
cyclohexyl)benzene;
1,4-bis(trans-4-[(R)-2-fluoropropanoyloxy]cyclohexyl)-
benzene;
1,4-bis(trans-4-[(R)-2-fluorobutanoyloxy]cyclohexyl)-
benzene;
1,4-bis(trans-4-[(R)-2-fluoropentanoyloxy]cyclohexyl)-
benzene;
1,4-bis(trans-4-[(R)-2-fluorohexanoyloxy]cyclohexyl)-
benzene;
1,4-bis(trans-4-[(R)-2-fluoroheptanoyloxy]cyclohexyl)-
benzene;
1,4-bis(trans-4-[(R)-2-fluorooctanoyloxy]cyclohexyl)-
benzene;
1,4-bis(trans-4-[(R)-2-fluorononanoyloxy]cyclohexyl)-
benzene;
1,4-bis(trans-4-[(R)-2-fluorodecanoyloxy]cyclohexyl)-
benzene;
1,4-bis[(trans-4-[(S)-2-fluoropropanoyloxy]cyclohexyl)-
methoxy]benzene;
1,4-bis[(trans-4-[(S)-2-fluorobutanoyloxy]cyclohexyl)-
methoxy]benzene;

1,4-bis[(trans-4-[(S)-2-fluoropentanoyloxy]cyclohexyl)-methoxy]benzene;
1,4-bis[(trans-4-[(S)-2-fluorohexanoyloxy]cyclohexyl)-methoxy]benzene;
1,4-bis[(trans-4-[(S)-2-fluoroheptanoyloxy]cyclohexyl)-methoxy]benzene;
1,4-bis[(trans-4-[(S)-2-fluorooctanoyloxy]cyclohexyl)-methoxy]benzene;
1,4-bis[(trans-4-[(S)-2-fluorononanoyloxy]cyclohexyl)-methoxy]benzene;
1,4-bis[(trans-4-[(S)-2-fluorodecanoyloxy]cyclohexyl)-methoxy]benzene;
1,4-bis[(trans-4-[(R)-2-fluoropropanoyloxy]cyclohexyl)-methoxy]benzene;
1,4-bis[(trans-4-[(R)-2-fluorobutanoyloxy]cyclohexyl)-methoxy]benzene;
1,4-bis[(trans-4-[(R)-2-fluoropentanoyloxy]cyclohexyl)-methoxy]benzene;
1,4-bis[(trans-4-[(R)-2-fluorohexanoyloxy]cyclohexyl)-methoxy]benzene;
1,4-bis[(trans-4-[(R)-2-fluoroheptanoyloxy]cyclohexyl)-methoxy]benzene;
1,4-bis[(trans-4-[(R)-2-fluorooctanoyloxy]cyclohexyl)-methoxy]benzene;
1,4-bis[(trans-4-[(R)-2-fluorononanoyloxy]cyclohexyl)-methoxy]benzene;
1,4-bis[(trans-4-[(R)-2-fluorodecanoyloxy]cyclohexyl)-methoxy]benzene;
2-fluoro-1,4-bis[(trans-4-[(S)-2-fluorohexanoyloxy]cyclohexyl)methoxy]benzene;
2-chloro-1,4-bis[(trans-4-[(S)-2-fluorohexanoyloxy]cyclohexyl)methoxy]benzene;
2-bromo-1,4-bis[(trans-4-[(S)-2-fluorohexanoyloxy]cyclohexyl)methoxy]benzene;
2-cyano-1,4-bis[(trans-4-[(S)-2-fluorohexanoyloxy]cyclohexyl)methoxy]benzene;
1,4-bis[2-(trans-4-[(S)-2-fluoropropanoyloxy]cyclohexyl)ethyl]benzene;
1,4-bis[2-(trans-4-[(S)-2-fluorobutanoyloxy]cyclohexyl)ethyl]benzene;
1,4-bis[2-(trans-4-[(S)-2-fluoropentanoyloxy]cyclohexyl)ethyl]benzene;
1,4-bis[2-(trans-4-[(S)-2-fluorohexanoyloxy]cyclohexyl)ethyl]benzene;
1,4-bis[2-(trans-4-[(S)-2-fluoroheptanoyloxy]cyclohexyl)ethyl]benzene;
1,4-bis[2-(trans-4-[(S)-2-fluorooctanoyloxy]cyclohexyl)ethyl]benzene;
1,4-bis[2-(trans-4-[(S)-2-fluorononanoyloxy]cyclohexyl)ethyl]benzene;
1,4-bis[2-(trans-4-[(S)-2-fluorodecanoyloxy]cyclohexyl)ethyl]benzene;
1,4-bis[2-(trans-4-[(R)-2-fluoropropanoyloxy]cyclo-

hexyl)ethyl]benzene;
1,4-bis[2-(trans-4-[(R)-2-fluorobutanoyloxy]cyclohexyl)ethyl]benzene;
1,4-bis[2-(trans-4-[(R)-2-fluoropentanoyloxy]cyclohexyl)ethyl]benzene;
1,4-bis[2-(trans-4-[(R)-2-fluorohexanoyloxy]cyclohexyl)ethyl]benzene;
1,4-bis[2-(trans-4-[(R)-2-fluoroheptanoyloxy]cyclohexyl)ethyl]benzene;
1,4-bis[2-(trans-4-[(R)-2-fluorooctanoyloxy]cyclohexyl)ethyl]benzene;
1,4-bis[2-(trans-4-[(R)-2-fluorononanoyloxy]cyclohexyl)ethyl]benzene;
1,4-bis[2-(trans-4-[(R)-2-fluorodecanoyloxy]cyclohexyl)ethyl]benzene;
trans-4-(4-[(trans-4-[(2S,3S)-2-fluoro-3-methylpentanoyloxy]cyclohexyl)methoxy]phenyl)cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4-(2-[4-(trans-4-[(2S,3S)-2-fluoro-3-methylpentanoyloxy]cyclohexyl)phenyl]ethyl)cyclohexyl (2S,3S)-2-fluoro-3-methylpentanoate;
trans-4, trans-4'-di[(2S,3S)-2-fluoro-3-methylpentanoyloxy]bicyclohexyl;
1,4-bis(trans-4-[(2S,3S)-2-fluoro-3-methylpentanoyloxy]cyclohexyl)benzene;
1,4-bis[(trans-4-[(2S,3S)-2-fluoro-3-methylpentanoyloxy]cyclohexyl)methoxy]benzene;
1,4-bis[2-(trans-4-[(2S,3S)-2-fluoro-3-methylpentanoyloxy]cyclohexyl)ethyl]benzene.

Example 5

0.2 g of (S)-2-fluorohexanoic acid (S- α -fluorocaproic acid), 0.7 g of trans-4-(4'-[(R)-2-octyl]oxycarbonyl-4-biphenyl)cyclohexanol, 0.45 g of N,N'-dicyclohexylcarbodiimide, 3 mg of 4-(dimethylamino)pyridine and 30 ml of dichloromethane were reacted in an analogous manner to Example 1. This gave 0.5 g of trans-4-(4'-[(R)-2-octyl]oxycarbonyl-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate; m.p. (C-S_A) 34°C, cl.p. (S_A-I) 41°C.

The trans-4-(4'-[(R)-2-octyl]oxycarbonyl-4-biphenyl)cyclohexanol used as the starting material was prepared as follows:

(a) A mixture of 20 g of 4-(4'-amido-4-biphenyl)cyclohexanone, 200 ml of 50% sulphuric acid and 400 ml of acetic acid was heated to a temperature of 115°C overnight. The cooled reaction mixture was poured on to ice-water and the white precipitate was filtered off. The filter residue was washed with water and subsequently recrystallized from ethanol. This gave 9.9 g of 4-(4'-

-carboxy-4-biphenyl)cyclohexanone.

(b) A mixture of 2 g of 4-(4'-carboxy-4-biphenyl)cyclohexanone, 0.9 g of R-(-)-2-octanol, 2.0 g of N,N'-dicyclohexylcarbodiimide, 1 mg of 4-(dimethylamino)pyridine and 80 ml of dichloromethane was reacted in an analogous manner to Example 1. The residue was purified by chromatography on silica gel with hexane/ethyl acetate (vol. 7:3). This gave 1.5 g of 4-(4'-[(R)-2-octyl]oxycarbonyl-4-biphenyl)cyclohexanone.

(c) A suspension of 0.14 g of sodium borohydride in 10 ml of 1,2-dimethoxyethane was treated at 0°C with a solution of 4-(4'-[(R)-2-octyl]oxycarbonyl-4-biphenyl)cyclohexanone in 10 ml of 1,2-dimethoxyethane. The reaction mixture was stirred at room temperature for a further 30 minutes and then treated with 25% hydrochloric acid. The reaction mixture was extracted three times with 50 ml of diethyl ether each time. The combined organic phases were washed with sodium hydrogen carbonate solution and several times with water and subsequently dried over magnesium sulphate, filtered and concentrated. The residue was recrystallized twice from hexane and gave 0.8 g of trans-4-(4'-[(R)-2-octyl]oxycarbonyl-4-biphenyl)cyclohexanol.

The following compounds can be manufactured in an analogous manner:

trans-4-(4'-[(R)-2-Octyl]oxycarbonyl-4-biphenyl)cyclohexyl (S)-2-fluoropropanoate;
trans-4-(4'-[(R)-2-octyl]oxycarbonyl-4-biphenyl)cyclohexyl (S)-2-fluorobutanoate;
trans-4-(4'-[(R)-2-octyl]oxycarbonyl-4-biphenyl)cyclohexyl (S)-2-fluoropentanoate;
trans-4-(4'-[(R)-2-octyl]oxycarbonyl-4-biphenyl)cyclohexyl (S)-2-fluoroheptanoate;
trans-4-(4'-[(R)-2-octyl]oxycarbonyl-4-biphenyl)cyclohexyl (S)-2-fluorooctanoate;
trans-4-(4'-[(R)-2-octyl]oxycarbonyl-4-biphenyl)cyclohexyl (S)-2-fluorononanoate;
trans-4-(4'-[(R)-2-octyl]oxycarbonyl-4-biphenyl)cyclohexyl (S)-2-fluorodecanoate;
trans-4-[2-(4'-[(R)-2-octyl]oxycarbonyl-4-biphenyl)-ethyl]cyclohexyl (S)-2-fluoropropanoate;
trans-4-[2-(4'-[(R)-2-octyl]oxycarbonyl-4-biphenyl)-ethyl]cyclohexyl (S)-2-fluorobutanoate;
trans-4-[2-(4'-[(R)-2-octyl]oxycarbonyl-4-biphenyl)-ethyl]cyclohexyl (S)-2-fluoropentanoate;
trans-4-[2-(4'-[(R)-2-octyl]oxycarbonyl-4-biphenyl)-ethyl]cyclohexyl (S)-2-fluorohexanoate;
trans-4-[2-(4'-[(R)-2-octyl]oxycarbonyl-4-biphenyl)-ethyl]cyclohexyl (S)-2-fluoroheptanoate;

trans-4-[2-(4'-[(R)-2-octyloxy]oxycarbonyl-4-biphenyl)-ethyl]cyclohexyl (S)-2-fluorooctanoate;
trans-4-[2-(4'-[(R)-2-octyloxy]oxycarbonyl-4-biphenyl)-ethyl]cyclohexyl (S)-2-fluorononanoate;
trans-4-[2-(4'-[(R)-2-octyloxy]oxycarbonyl-4-biphenyl)-ethyl]cyclohexyl (S)-2-fluorodecanoate.

Example 6

The use of the compounds of formula I in tilted smectic phases is illustrated by the mixtures set forth in Table I and by Mixture M-3. The percentages signify wt.% of the respective components in the total mixture. The optically active dopants of formula I which are denoted by D and the additional components denoted by C are the following compounds:

- C-1 = 4-dodecyloxy-2-fluorobenzoic acid 4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,
- C-2 = 4-dodecyloxy-2-fluorobenzoic acid 4-[(trans-4-pentylcyclohexyl)methoxy]phenyl ester,
- C-3 = 4-dodecyloxybenzoic acid 4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,
- C-4 = 4-decyloxybenzoic acid 4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,
- C-5 = 4-undecyloxybenzoic acid 4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,
- C-6 = 2-(4-hexyloxyphenyl)-5-nonylpyrimidine,
- C-7 = 2-(4-nonyloxyphenyl)-5-nonylpyrimidine,
- C-8 = 2-(4-nonyloxyphenyl)-5-heptylpyrimidine,
- C-9 = 2-(4-octyloxyphenyl)-5-heptylpyrimidine,
- C-10 = 2-(4-heptyloxyphenyl)-5-heptylpyrimidine,
- C-11 = 2-(4-hexyloxyphenyl)-5-heptylpyrimidine,
- C-12 = 2-(4-decyloxyphenyl)-5-decylpyrimidine,
- C-13 = 2-(4-hexyloxyphenyl)-5-decylpyrimidine,
- D-1 = trans-4-(4'-decyl-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate,
- D-2 = trans-4-(4-[(trans-4-[(S)-2-fluorohexanoyloxy]cyclohexyl)methoxy]phenyl)cyclohexyl (S)-2-fluorohexanoate.

Table 1

	M-1	M-2
C-1	16.32%	14.44%
C-2	4.57%	5.42%
C-3	5.86%	5.23%
C-4	5.25%	5.23%
C-5	3.30%	4.87%

C-6	12.11%	12.09%
C-7	21.79%	20.58%
C-8	2.78%	2.53%
C-9	7.59%	6.23%
C-10	4.92%	5.60%
C-11	-	4.51%
C-12	3.58%	-
C-13	3.63%	3.52%
D-1	8.30%	-
D-2	-	9.75%

The melting points of the mixtures are difficult to determine. Crystallization or highly ordered smectic phases could not, however, be observed upon cooling to just below 0°C. The mixtures in accordance with Table 1 have the following properties:

Mixture M-1

M.p. <0°C, transitions S_C^* - S_A 46.8°C, S_A -Ch 72.1°C, cl.p. (Ch-I) 89.2%.

Mixture M-2

M.p. <0°C, transitions S_C^* - S_A 18.3°C, S_A -Ch 70.7°C, cl.p. (Ch-I) 86.1°C.

Mixture M-3

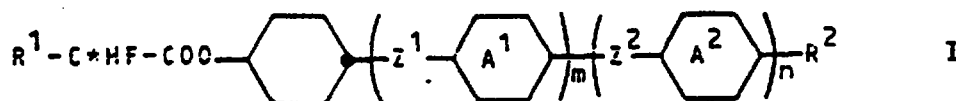
3.53 wt. %	trans-5-hexyl-2-(4'-octyloxy-4-biphenyl)-1,3-dioxane,
3.53 wt. %	trans-5-heptyl-2-(4'-heptyloxy-4-biphenyl)-1,3-dioxane,
8.25 wt. %	trans-5-heptyl-2-(4'-octyloxy-4-biphenyl)-1,3-dioxane,
8.20 wt. %	trans-5-nonyl-2-(4'-octyloxy-4-biphenyl)-1,3-dioxane,
5.99 wt. %	2-(4-hexyloxyphenyl)-5-octylpyrimidine,
12.73 wt. %	2-(4-hexyloxyphenyl)-5-nonylpyrimidine,
7.72 wt. %	2-(4-octyloxyphenyl)-5-heptylpyrimidine,
4.22 wt. %	2-(4-nonyloxyphenyl)-5-heptylpyrimidine,
5.89 wt. %	2-(4-nonyloxyphenyl)-5-octylpyrimidine,
25.44 wt. %	2-(4-nonyloxyphenyl)-5-nonylpyrimidine,
5.00 wt. %	trans-4-(4-decyl-4-biphenyl)cyclohexyl (S)-2-fluorohexanoate,
9.50 wt. %	trans-4-[4-(2,3-difluoro-4-dodecyloxybenzoyloxy)phenyl]cyclohexyl (S)-2-fluorohexanoate,



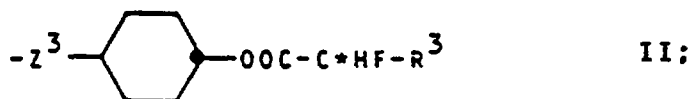
m.p. < 0°C, transitions $S_C^*-S_A$ 61.1°C, S_A-Ch 83.7°C; c.l.p. (Ch-I) 94.7°C; pitch 9 μ m. The mixture had a response time of 90 μ s at 25°C in a cell according to Appl. Phys. 36, 899 (1980) utilizing a plate separation of 2 μ m and a potential of 20 V (square wave, peak to peak).

Claims

1. Optically active compounds of the general formula



wherein m stands for the number 1 and R^2 signifies an unsubstituted or halogen-substituted alkyl or alkenyl group in which optionally one methylene group is replaced by oxygen and/or optionally one methylene group is replaced by an ester group -COO- or -OOC-; or m stands for the number 0 or 1 and R^2 denotes a group of the general formula



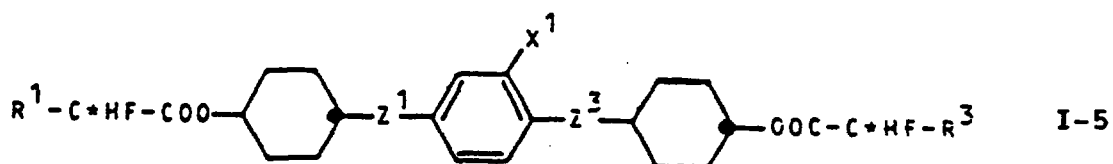
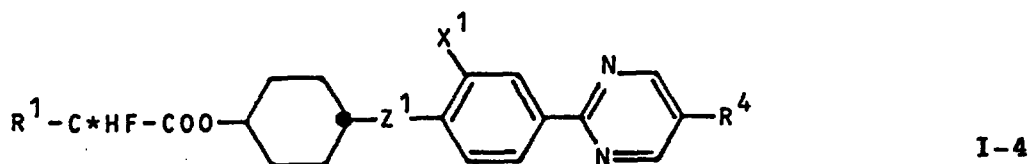
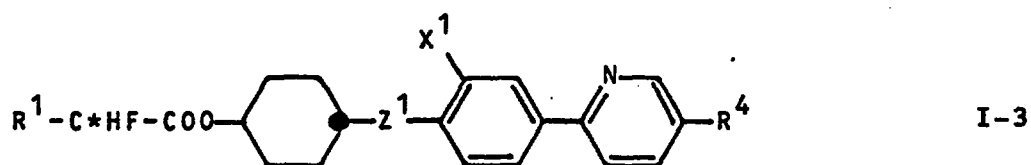
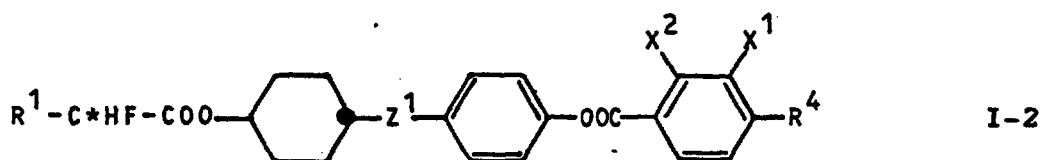
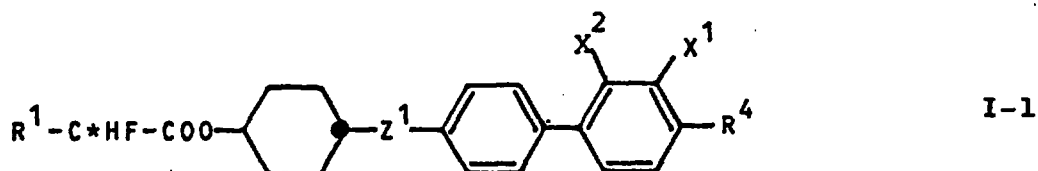
R^1 and R^3 each independently represent an alkyl or alkenyl group in which optionally one methylene group is replaced by oxygen; Z^1 , Z^2 and Z^3 each independently signify a single covalent bond, -CH₂O-, -OCH₂-, -CH₂CH₂-, -COO- or -OOC-; n stands for the number 0 or 1; rings A^1 and A^2 each independently signify unsubstituted or halogen-, cyano- and/or methyl-substituted 1,4-phenylene in which optionally 1 CH group or 2 CH groups is/are replaced by nitrogen; and C^* denotes a chiral carbon atom; with the proviso that simultaneously R^1 does not signify an alkyl group, m and n do not signify the number 1, Z^1 does not signify the group -CH₂CH₂- or -CH₂O- and ring A^1 , Z^2 , ring A^2 and R^2 together do not signify 4-(5-alkyl-2-pyrimidinyl)-phenyl.

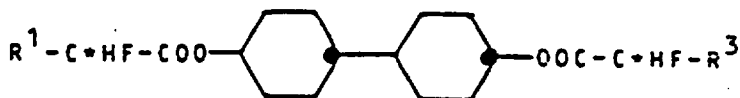
2. Compounds according to claim 1, characterized in



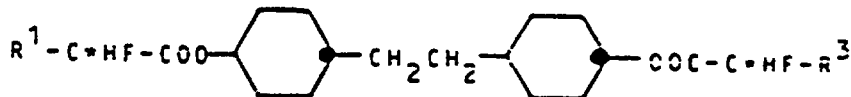
that rings A¹ and A² each independently signify 1,4-phenylene, fluoro-1,4-phenylene, chloro-1,4-phenylene, bromo-1,4-phenylene, cyano-1,4-phenylene, 2,3-difluoro-1,4-phenylene, pyridine-2,5-diyl or pyrimidine-2,5-diyl.

3. Compounds according to claim 1 or 2, characterized by the general formulae





I-6



I-7

wherein R^1 , R^3 , Z^1 , Z^3 and C^* have the significances given in claim 1; R^4 represents an unsubstituted or halogen-substituted alkyl or alkenyl group in which optionally one methylene group is replaced by oxygen and/or optionally one methylene group is replaced by the ester group $-COO-$ or $-OOC-$, X^1 and X^2 signify hydrogen, fluorine, chlorine, bromine, cyano or methyl; with the proviso that in formula I-4 X^1 denotes fluorine, chlorine, bromine, cyano or methyl when Z^1 represents $-CH_2CH_2-$ or $-CH_2O-$.

4. Compounds according to any one of claims 1 to 3, characterized in that Z^1 signifies a single covalent bond, $-CH_2O-$, $-CH_2CH_2-$ or $-COO-$ and Z^3 signifies a single covalent bond, $-OCH_2-$, $-CH_2CH_2-$ or $-OOC-$.

5. Compounds according to any one of claims 1 to 4, characterized in that R^1 signifies alkyl, alkenyl, alkoxyalkyl or alkenyloxyalkyl with up to 15 carbon atoms, preferably C_3-C_{15} -alkyl.

6. Compounds according to any one of claims 1 to 5, characterized in that R^2 denotes a group of formula II and R^3 signifies alkyl, alkenyl, alkoxyalkyl or alkenyloxyalkyl with up to 15 carbon atoms.

7. Compounds according to any one of claims 1 to 5, characterized in that R^2 denotes a residue R^4 and R^4 signifies alkyl, alkenyl, alkoxy, alkenyloxy, haloalkoxy, alkoxy carbonyl or haloalkanoyloxy with up to 15 carbon atoms.

8. A process for the manufacture of compounds of formula I defined in claim 1, characterized by esterifying an optically active α -fluorocarboxylic acid of the



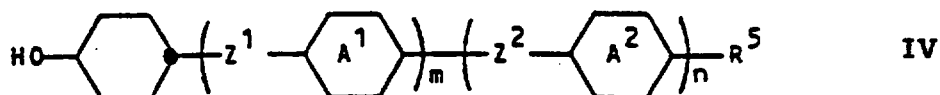
- 47 -

general formula

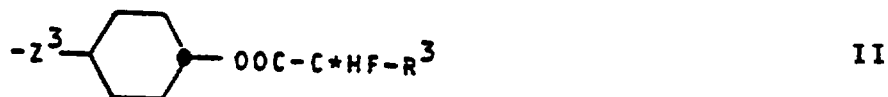


III

and a cyclohexanol derivative of the general formula



wherein m stands for the number 1 and R^5 denotes an unsubstituted or halogen-substituted alkyl or alkenyl group in which optionally one methylene group is replaced by oxygen and/or optionally one methylene group is replaced by an ester group $-COO-$ or $-OOC-$; or m stands for the number 0 or 1 and R^5 denotes a group of the general formula



or



R^1 and R^3 each independently represent an alkyl or alkenyl group in which optionally one methylene group is replaced by oxygen; Z^1 , Z^2 and Z^3 each independently signify a single covalent bond, $-CH_2O-$, $-OCH_2-$, $-CH_2CH_2-$, $-COO-$ or $-OOC-$; n stands for the number 0 or 1; rings A^1 and A^2 each independently signify unsubstituted or halogen-, cyano- and/or methyl-substituted 1,4-phenylene in which optionally 1 CH group or 2 CH groups is/are replaced by nitrogen; and C^* denotes a chiral carbon atom; with the proviso that simultaneously R^1 does not signify an alkyl group, m and n do not signify the number 1, Z^1 does not signify the group $-CH_2CH_2-$



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or $-\text{CH}_2\text{O}-$ and ring A^1 , Z^2 , ring A^2 and R^5
together do not signify 4-(5-alkyl-2-pyrimidinyl)-
phenyl.
or suitable derivatives of these compounds.

9. A liquid crystalline mixture having at least 2
components, characterized in that at least one component
is an optically active compound in accordance with any one
of claims 1 to 7.

10. The use of the compounds of formula 1 defined in
claim 1 for electro-optical purposes.