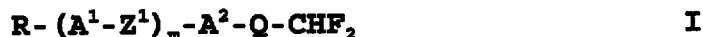


Description

The invention relates to difluoromethyl compounds of the formula I



5 in which

R

is halogen, -CN, -NCS, a straight-chain alkyl or alkenyl radical having 1 to 15 carbon atoms, in which one or more CH₂ groups in these radicals, independently of one another, can each also be replaced by -O-, -S-, , -CO-, -CO-O-, O-CO- or -O-CO-O- in such a manner that oxygen atoms are not directly linked to one another, or a straight-chain perfluoroalkyl radical, in which one or more fluorine atoms can also be replaced by H,

10

15

A¹ and A², independently of one another, are each a

(a) trans-1,4-cyclohexylene radical in which one or more non-adjacent CH₂ groups can also be replaced by -O- and/or -S-,

20

(b) 1,4-phenylene radical in which one or two CH groups can also be replaced by N,

(c) radical from the group consisting of 1,4-cyclohexenylene, 1,4-bicyclo[2.2.2]octylene, piperidine-1,4-diyl, naphthalene-2,6-diyl, decahydronaphthalene-2,6-diyl and 1,2,3,4-tetrahydronaphthalene-2,6-diyl,

25

in which the radicals (a) and (b) can be substituted by CN or fluorine,

30

Z¹

independently of one another are each -CO-O-, O-CO-, -CH₂O-, -OCH₂-, -CH₂CH₂-, -CH=CH-, -C≡C- or a single bond,

m

is 1, 2 or 3 and

Q

is alkylene having 2 to 6 carbon atoms in which a CH₂ group can also be replaced by -O-, -S-, -CO-O- or -O-CO-, -O-, -S-, -CH₂-, -CO-O-, -O-CO- or a single bond,

35

with the proviso that Q is alkylene having 2 to 6 carbon atoms in which one CH₂ group can also be replaced by -O-, -S-, -CO-O- or -O-CO-, -S-, -CH₂-, -CO-O-, -O-CO- or a single bond, provided R-(A¹-Z¹)_n-A²- is alkoxy---OOC--

5 or F₂HCO--COO--OOC--.

The invention furthermore relates to the use of these compounds as components of liquid-crystalline media and liquid crystal and electrooptical display elements containing the liquid-crystalline media according to the
10 invention.

The compounds of the formula I can be used as components of liquid-crystalline media, in particular for displays based on the principle of the twisted cell, the guest-host effect, the effect of the deformation of
15 aligned phases or the effect of dynamic scattering.

The object of the invention was to find new stable liquid-crystalline or mesogenic compounds which are suitable as components of liquid-crystalline media and in particular simultaneously have a comparably low
20 viscosity and a relatively high dielectric anisotropy.

It has now been found that compounds of the formula I are highly suitable as components of liquid-crystalline media. In particular, they have comparably low viscosities. With their aid, it is possible to obtain
25 stable liquid-crystalline media having a broad mesophase range and advantageous values for optical and dielectric anisotropy.

Compounds which have liquid-crystalline properties and a terminally bound OCHF₂ group are already
30 known. On the one hand, crystal structure investigations have been carried out with Schiff bases [S.V. Sereda et al. in Kristallografiya, 32 (5), 1165 (1987) and ibid. 33 (1) 118 (1988)]. On the other hand, V.V. Titov et al. have described in Mol. Cryst. Liq. Cryst. 47 (1-2), 1
35 (1978) benzoic esters which carry an OCHF₂ group in the para position. However, the known compounds are unstable or unusable in commercial displays. Furthermore,

EP-A-0,255,236 discloses compounds having fluorine-containing side chains. However, the compounds described there always carry a chiral wing group and therefore owing to their structure have tilted smectic mesophases and are intended for the use in ferroelectric liquid crystal mixtures. This means that they have entirely different properties and their intended use is different from that of the compounds according to the invention.

By providing the compounds of the formula I, very generally the range of liquid-crystalline substances which are suitable under various aspects relating to their application for the preparation of liquid-crystalline mixtures is furthermore considerably widened.

The compounds of the formula I have a wide application range. Depending on the selection of the substituents, these compounds can serve as basis materials of which liquid-crystalline media are predominantly composed; however, it is also possible to add liquid-crystalline basis materials from other classes of compounds to the compounds of the formula I, in order to effect, for example, dielectric and/or optical anisotropy of such a dielectric and/or to optimize its threshold voltage and/or its viscosity.

The compounds of the formula I are colourless in their pure state and form liquid-crystalline mesophases in a temperature range favourable for electrooptical use. They are chemically and thermally stable and resistant to light.

The invention accordingly relates to the compounds of the formula I and the use of these compounds as components of liquid-crystalline media. The invention further relates to liquid-crystalline media containing at least one compound of the formula I and to liquid crystal display elements, in particular electrooptical display elements containing this type of media.

For the sake of simplicity, in what follows X is Q-CHF₂, Cyc a 1,4-cyclohexylene radical, Che a 1,4-cyclohexenylene radical, Dio a 1,3-dioxane-2,5-diyl radical, Dit a 1,3-dithiane-2,5-diyl radical, Phe a 1,4-phenylene

radical, Pyd a pyridine-2,5-diyl radical, Pyr a pyrimidine-2,5-diyl radical, Pip a piperidine-1,4-diyl radical, Nap a naphthalene-2,6-diyl radical, Dec and Tet a decahydronaphthalene radical and a 1,2,3,4-tetrahydronaphthalene radical and Bi a bicyclo[2.2.2]octylene radical in which Cyc and/or Phe can be unsubstituted or monosubstituted or disubstituted by F or CN.

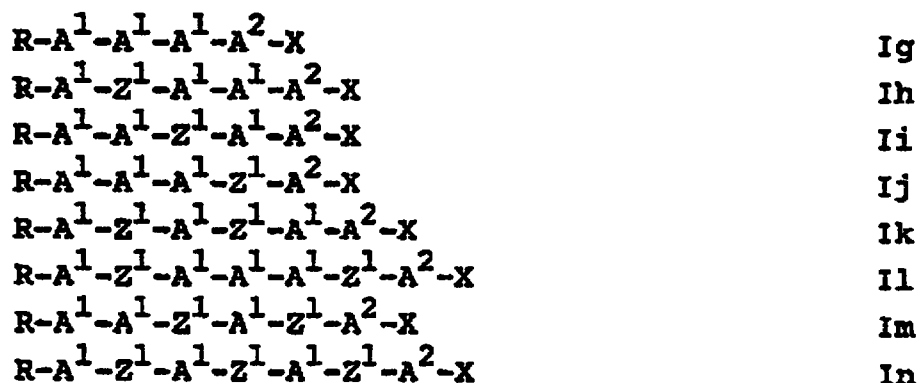
The compounds of the formula I accordingly comprise compounds having two rings of the partial formulae Ia and Ib:



Compounds having three rings of the partial formulae Ic to If:



and compounds having four rings of the partial formulae Ig to In:



Of these, in particular those of the partial formulae Ia, Ib, Ic, Id, Ie, If, Ii and Il are preferred.

The preferred compounds of the partial formula Ia

comprise those of the partial formulae Iaa to Iah:

R-Phe-Phe-X	Iaa
R-Phe-Cyc-X	Iab
R-Dio-Phe-X	Iac
R-Pyr-Phe-X	Iad
R-Pyd-Phe-X	Iae
R-Cyc-Phe-X	Iaf
R-Cyc-Cyc-X	Iag
R-Che-Phe-X	Iah

Of these, those of the formulae Iaa, Iab, Iac, Iad, Iaf and Iag are particularly preferred.

5 The preferred compounds of the partial formula Ib comprise those of the partial formulae Iba to Ibm:

R-Phe-CH ₂ CH ₂ -Phe-X	Iba
R-Phe-OCH ₂ -Phe-X	Ibb
R-Cyc-CH ₂ CH ₂ -Phe-X	Ibc
R-Cyc-CH ₂ -CH ₂ -Cyc-X	Ibd
R-Cyc-COO-Phe-X	Ibe
R-Cyc-COO-Cyc-X	Ibf
R-A ¹ -CH ₂ CH ₂ -Phe-X	Ibg
R-A ¹ -CH ₂ CH ₂ -Cyc-X	Ibh
R-A ¹ -CH ₂ O-Phe-X	Ibi
R-A ¹ -OCH ₂ -Phe-X	Ibj
R-A ¹ -COO-Phe-X	Ibk
R-A ¹ -OOC-Phe-X	Ibl
R-Che-CH ₂ CH ₂ -Phe-X	Ibm

The preferred compounds of the partial formula Ic comprise those of the partial formulae Ica to Icq:

R-Phe-Phe-Phe-X	Ica
R-Phe-Phe-Cyc-X	Icb
R-Phe-Dio-Phe-X	Icc
R-Cyc-Cyc-Phe-X	Icd

R-Phe-Cyc-Phe-X	Ice
R-Cyc-Cyc-Cyc-X	Icf
R-Pyd-Phe-Phe-X	Icg
R-Pyr-Phe-Phe-X	Ich
R-Phe-Pyr-Phe-X	Ici
R-Cyc-Pyr-Phe-X	Icj
R-Cyc-Phe-Phe-X	Ick
R-Cyc-Phe-Cyc-X	Icl
R-Dio-Phe-Phe-X	Icm
R-Che-Phe-Phe-X	Icn
R-Phe-Che-Phe-X	Ico
R-Che-Cyc-Phe-X	Icp
R-Cyc-Che-Phe-X	Icq

Of these, those of the formulae Ica, Icc, Icd, Ice, Ici and Icj are particularly preferred.

5 The preferred compounds of the partial formula Id comprise those of the partial formulae Ida to Idn:

R-Phe-Z ¹ -Phe-Z ¹ -Phe-X	Ida
R-Phe-Z ¹ -Phe-Z ¹ -Cyc-X	Idb
R-Phe-Z ¹ -Dio-Z ¹ -Phe-X	Idc
R-Cyc-Z ¹ -Cyc-Z ¹ -Phe-X	Idd
R-Cyc-Z ¹ -Cyc-Z ¹ -Cyc-X	Ide
R-Pyd-Z ¹ -Phe-Z ¹ -Phe-X	Idf
R-Phe-Z ¹ -Pyd-Z ¹ -Phe-X	Idg
R-Pyr-Z ¹ -Phe-Z ¹ -Phe-X	Idh
R-Phe-Z ¹ -Pyr-Z ¹ -Phe-X	Idi
R-Phe-Z ¹ -Cyc-Z ¹ -Phe-X	Idj
R-Cyc-Z ¹ -Phe-Z ¹ -Cyc-X	Idk
R-Cyc-Z ¹ -Phe-Z ¹ -Phe-X	Idl
R-Dio-Z ¹ -Phe-Z ¹ -Phe-X	Idm
R-Che-Z ¹ -Phe-Z ¹ -Phe-X	Idn

The preferred compounds of the partial formula Ie comprise those of the partial formulae Iea to Iem:

R-Pyr-Z ¹ -Phe-Phe-X	Iea
R-Dio-Z ¹ -Phe-Phe-X	Ieb
R-Phe-Z ¹ -Phe-Phe-X	Iec
R-Cyc-Z ¹ -Phe-Phe-X	Ied
R-Cyc-Z ¹ -Phe-Cyc-X	Iee
R-Phe-Z ¹ -Cyc-Phe-X	Ief
R-Cyc-Z ¹ -Cyc-Phe-X	Ieg
R-Cyc-Z ¹ -Cyc-Cyc-X	Ieh
R-Phe-Z ¹ -Dio-Phe-X	Iei
R-Pyd-Z ¹ -Phe-Phe-X	Iej
R-Phe-Z ¹ -Pyr-Phe-X	Iek
R-Cyc-Z ¹ -Pyr-Phe-X	Iel
R-Phe-Z ¹ -Che-Phe-X	Iem

The preferred compounds of the partial formula If comprise those of the partial formulae Ifa to Ifr:

R-Pyr-Phe-Z ¹ -Phe-X	Ifa
R-Pyr-Phe-OCH ₂ -Phe-X	Ifb
R-Phe-Phe-Z ¹ -Phe-X	Ifc
R-Phe-Phe-OOC-Phe-X	Ifd
R-Phe-Phe-Z ¹ -Cyc-X	Ife
R-Cyc-Cyc-Z ¹ -Phe-X	Iff
R-Cyc-Cyc-Z ¹ -Cyc-X	Ifg
R-Cyc-Cyc-CH ₂ CH ₂ -Phe-X	Ifh
R-Pyd-Phe-Z ¹ -Phe-X	Ifi
R-Dio-Phe-Z ¹ -Phe-X	Ifj
R-Phe-Cyc-Z ¹ -Phe-X	Ifk
R-Phe-Cyc-Z ¹ -Cyc-X	Ifl
R-Phe-Pyd-Z ¹ -Phe-X	Ifm
R-Che-Phe-Z ¹ -Phe-X	Ifn
R-Phe-Che-Z ¹ -Phe-X	lfo

R-Cyc-Phe-Z ¹ -Phe-X	Ifp
R-Cyc-Phe-OOC-Phe-X	Ifq
R-Cyc-Phe-Z ¹ -Cyc-X	Ifr

5 The preferred compounds of the partial formulae Ig to In comprise those of the partial formulae Io to Iy:

R-Cyc-Phe-Cyc-Phe-X	Io
R-Cyc-Cyc-Phe-Phe-X	Ip
R -Cyc-Phe-Phe-Cyc-X	Iq
R-A ¹ -CH ₂ O-A ¹ -A ¹ -Phe-X	Ir
R-Cyc-Cyc-Z ¹ -A ¹ -Phe-X	Is
R-Cyc-Cyc-Z ¹ -Y ¹ -Cyc-X	It
R-A ¹ -A ¹ -A ¹ -CH ₂ CH ₂ -Phe-X	Iu
R-Phe-Z ¹ -Phe-Z ¹ -Dio-Phe-X	Iv
R-Phe-Z ¹ -Phe-Phe-Z ¹ -Phe-X	Iw
R-A ¹ -COO-A ¹ -COO-A ¹ -Phe-X	Ix
R-A ¹ -A ¹ -COO-A ¹ -Z ¹ -Phe-X	Iy

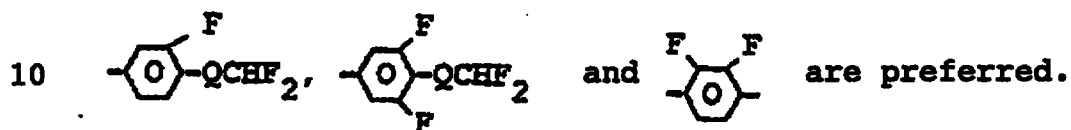
In the compounds of the formulae above and below, X is preferably Q-CHF₂ in which Q is alkylene having 2 to 4 carbon atoms and in which a CH₂ group can also be replaced by -O-, -CO-O- or -O-CO-. Furthermore, Q is preferably a single bond, -O-, -S-, -CH₂- and -CO-O-; -O- and -S- are particularly preferred.

If Q is a single bond, those compounds of the formula I are preferred in which X is bound to a cycloaliphatic ring. If Q is -O- or -S-, those compounds of the formula I are preferred in which X is bound to an aromatic ring.

R is preferably alkyl, furthermore alkoxy. Furthermore R is preferably a perfluoroalkyl radical in which fluorine can also be partially replaced by hydrogen. In particular those radicals R of the general formula -CH₂-C_nF_{2n+1} and C_pF_{2p+1} where n is equal to 1 to 14 and p is equal to 1 to 15 are preferred. A¹ and/or A² are preferably Phe, Cyc, Che, Pyr or Dio. Particularly preferably, A¹ and A² are Phe or Cyc. Furthermore, those compounds of the formula I are preferred in which, in addition to Phe and/or Cyc, a further ring selected from the group consisting of Che, Pip, Pyr, Pyd, Dio, Dit, Bi,

Nap, Dec or Tet is present.

Compounds of the formula I and of all partial formulae in which A¹ and/or A² are 1,4-phenylene which is monosubstituted or disubstituted by F or monosubstituted by CN are also preferred. These are in particular 2-fluoro-1,4-phenylene, 3-fluoro-1,4-phenylene and 2,3-difluoro-1,4-phenylene and 2-cyano-1,4-phenylene and 3-cyano-1,4-phenylene. Of the F-substituted 1,4-phenylene radicals, in particular



If a radical (a) is substituted by F or CN,



is preferred.

15 Z¹ is preferably a single bond, -CO-O-, -O-CO- and -CH₂CH₂-, the second preference being -CH₂O- and -OCH₂-. Compounds which contain no more than one and at most two linking groups Z¹ (Z¹ not being a single bond) are particularly preferred.

m is preferably 1 or 2.

20 If R is halogen, R is preferably F, Cl, Br, furthermore also I.

If R is an alkyl radical and/or an alkoxy radical, it is straight-chain and has preferably 2, 3, 4, 5, 6 or 7 carbon atoms and is accordingly preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl, ethoxy, propoxy, butoxy, pentoxy, hexoxy or heptoxy, furthermore methyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, methoxy, octoxy, nonoxy, decoxy, undecoxy, dodecoxy, tridecoxy or tetradeoxy.

30 Oxaalkyl is preferably straight-chain 2-oxapropyl (= methoxymethyl), 2- (= ethoxymethyl) or 3-oxabutyl (= 2-methoxyethyl), 2-, 3- or 4-oxapentyl, 2-, 3-, 4- or 5-oxahexyl, 2-, 3-, 4-, 5- or 6-oxaheptyl, 2-, 3-, 4-, 5-,

6- or 7-oxaocetyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl, 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl.

If R is an alkyl radical in which one CH₂ group has been replaced by -CH=CH-, it is straight-chain and preferably has 2 to 10 carbon atoms. Accordingly, it is in particular vinyl, prop-1- or prop-2-enyl, but-1-, -2- or but-3-enyl, pent-1-, -2-, -3- or pent-4-enyl, hex-1-, -2-, -3-, -4- or hex-5-enyl, hept-1-, -2-, -3-, -4-, -5- or hept-6-enyl, oct-1-, -2-, -3-, -4-, -5-, -6- or oct-7-enyl, non-1-, -2-, -3-, -4-, -5-, -6-, -7- or non-8-enyl, dec-1-, -2-, -3-, -4-, -5-, -6-, -7-, -8- or dec-9-enyl.

If R is an alkyl radical in which one CH₂ group has been replaced by -O- and one by -CO-, these groups are preferably adjacent. Thus, they contain an acyloxy group -CO-O- or an oxycarbonyl group -O-CO-. Preferably, they have 2 to 6 carbon atoms. Accordingly, they are in particular acetyloxy, propionyloxy, butyryloxy, pentanoyloxy, hexanoyloxy, acetyloxymethyl, propionyloxymethyl, butyryloxymethyl, pentanoyloxymethyl, 2-acetyloxyethyl, 2-propionyloxyethyl, 2-butyryloxyethyl, 3-acetyloxypropyl, 3-propionyloxypropyl, 4-acetyloxybutyl, methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, butoxycarbonyl, pentoxycarbonyl, methoxycarbonylmethyl, ethoxycarbonylmethyl, propoxycarbonylmethyl, butoxycarbonylmethyl, 2-(methoxycarbonyl)ethyl, 2-(ethoxycarbonyl)ethyl, 2-(propoxycarbonyl)ethyl, 3-(methoxycarbonyl)propyl, 3-(ethoxycarbonyl)propyl, 4-(methoxycarbonyl)butyl.

If R is an alkyl radical in which one CH₂ group has been replaced by -CH=CH- and one adjacent CH₂ group by CO or CO-O or O-CO-, it preferably has 4 to 13 carbon atoms. Accordingly, it is in particular acryloyloxy-methyl, 2-acryloyloxyethyl, 3-acryloyloxypropyl, 4-acryloyloxybutyl, 5-acryloyloxypropyl, 6-acryloyloxyhexyl, 7-acryloyloxyheptyl, 8-acryloyloxyoctyl, 9-acryloyloxyoctyl, 9-acryloyloxynonyl, 10-acryloyloxydecyl, methacryloyloxymethyl, 2-methacryloyloxyethyl, 3-methacryloyloxypropyl, 4-methacryloyloxybutyl, 5-meth-

acryloyloxypropyl, 6-methacryloyloxyhexyl, 7-methacryloyloxyheptyl, 8-methacryloyloxyoctyl, 9-methacryloyloxynonyl.

5 Compounds of the formula I which have wing groups R suitable for polymerization reactions are suitable for the preparation of liquid-crystalline polymers.

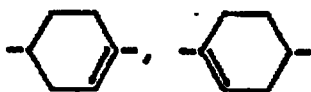
Compounds of the formula I which have S_A phases are suitable, for example, for thermally addressed displays.

10 Compounds of the formula I which have wing groups R suitable for polycondensations are suitable for the preparation of liquid-crystalline polycondensation products.

15 Of these compounds of the formula I and the subformulae, those are preferred in which at least one of the radicals contained therein has one of the preferred meanings mentioned.

20 In the compounds of the formula I, those stereoisomers are preferred in which the rings Cyc and piperidine are trans-1,4-disubstituted. Those of the abovementioned formulae which contain one or several groups Pyd, Pyr and/or Dio each comprise the two isomers in the 2,5-position.

25 The 1,4-cyclohexenylene group preferably has the following structures:



30 The compounds of the formula I are prepared by methods known per se, such as are described in the literature (for example in the standard works such as Houben-Weyl, Methoden der Organischen Chemie (Methods of Organic Chemistry), Georg-Thieme Verlag, Stuttgart Vol. IX, p. 867 ff.) under reaction conditions which are known and suitable for the reactions mentioned. It is also possible to make use of variations which are known per se and not mentioned in more detail at this point.

35 The aryldifluoromethyl ethers according to the invention can be prepared, for example, by reacting

hydroxyaryl compounds with chlorodifluoromethane under reaction conditions which are suitable for the Reimer-Tiemann reaction between phenols and chloroform [T.G. Miller, J.W. Thanassi, J. Org. Chem. 25, 2009 (1960)].

5 The etherification can be carried out in known manner in aprotic, strongly polar solvents (JP-OS 59/157,041) and in aqueous or even in almost anhydrous media, for example, by carrying out the formation of
10 alcohol in aqueous-organic phase (for example tetrahydrofuran/water), but removing most of the water azeotropically before the actual etherification.

 Difluoroalkylaryl ethers according to the invention can, for example, also be prepared, for example, by reacting the corresponding nitro- or fluorobenzenes which
15 additionally carry at least one electron-withdrawing substituent directly with alkali metal difluoroalkoxy compounds, in which F or NO₂ is substituted by the difluoroalkoxy radical [J.P. Idoux et al., J.Org. Chem. 50, 1976 (1985)].

20 Difluoromethyl compounds of the formula I can be prepared, for example, by reacting aldehydes with dialkylaminosulfur trifluoride, for example DAST (diethylamino sulfurtrifluoride) [W.J. Middleton, J.Org. Chem. 40, 574 (1975)].

25 Difluoromethylthio compounds can be prepared by the same method as difluoromethoxy compounds (for example according to L.N. Sedova et al., Zh. Org. Khim. 6, (1970) 568).

30 If desired, the starting materials can also be formed in situ in such a manner that they are not isolated from the reaction mixture but immediately reacted further to give the compounds of the formula I.

 Thus, the compounds of the formula I can be prepared by reducing a compound which otherwise corresponds to the formula I, but contains one or more
35 reducible groups and/or C-C bonds instead of the hydrogen atoms.

 Suitable reducible groups are preferably carbonyl groups, in particular keto groups, furthermore, for

example, free or esterified hydroxyl groups or aromati-
cally bound halogen atoms. Preferred starting materials
for the reduction have the formula I, but can contain a
cyclohexene ring or cyclohexanone ring instead of a
cyclohexane ring and/or a $-\text{CH}=\text{CH}-$ group instead of a
5 $-\text{CH}_2\text{CH}_2-$ group and/or a $-\text{CO}-$ group instead of a $-\text{CH}_2-$
group and/or a free or functionally (for example in the
form of its p-toluenesulfonate) modified OH group instead
of a hydrogen atom.

10 The reduction can be carried out, for example, by
catalytic hydrogenation at temperatures between about 0°
and about 200° and pressures between about 1 and 200 bar
in an inert solvent, for example an alcohol such as
methanol, ethanol or isopropanol, an ether such as
15 tetrahydrofuran (THF) or dioxane, an ester such as ethyl
acetate, a carboxylic acid such as acetic acid or a
hydrocarbon such as cyclohexane. Suitable catalysts are
advantageously noble metals such as Pt or Pd, which can
be used in the form of oxides (for example PtO_2 , PdO) on
20 a support (for example Pd on carbon, calcium carbonate or
strontium carbonate) or in finely divided form.

Ketones can also be reduced by the methods of
Clemmensen (using zinc, amalgamated zinc or tin and
hydrochloric acid, advantageously in aqueous-alcoholic
25 solution or in heterogeneous phase using water/toluene at
temperatures between about 80 and 120°) or Wolff-Kishner
(using hydrazine, advantageously in the presence of
alkali such as KOH or NaOH in a high-boiling solvent such
as diethylene glycol or triethylene glycol at tempera-
30 tures between about 100 and 200°) to give the correspond-
ing compounds of the formula I containing alkyl groups
and/or $-\text{CH}_2\text{CH}_2-$ bridges.

Another possibility are reductions using complex
hydrides. For example, arylsulfonyloxy groups can be
35 removed reductively using LiAlH_4 , in particular p-
toluenesulfonyloxymethyl groups can be reduced to methyl
groups, advantageously in an inert solvent such as
diethyl ether or THF at temperatures between about 0 and
 100° . Double bonds can be hydrogenated using NaBH_4 or

tributyltin hydride in methanol.

Compounds of the formula I which otherwise correspond to the formula I, but have 1,4-cyclohexenylene radicals instead of 1,4-phenylene radicals, can be oxidized, for example, with DDQ (dichlorodicyanobenzoquinone) in a suitable solvent.

Esters of the formula I can also be obtained by esterification of the corresponding carboxylic acids (or their reactive derivatives) with alcohols or phenols (or their reactive derivatives) or by the DCC method (DCC = dicyclohexylcarbodiimide).

The corresponding carboxylic acids and alcohols or phenols are known or can be prepared in analogy to known processes.

Thiophenols can be prepared, for example, by reacting the corresponding benzene derivatives with chlorosulfonic acid and then reducing the product, for example using zinc/dilute hydrochloric acid, or reacting the corresponding phenol derivatives with dimethylcarbamoyl chloride and then rearranging the product, as described in DE 3,434,335.

Suitable reactive derivatives of the carboxylic acids mentioned are in particular acid halides, in particular the chlorides and bromides, furthermore the anhydrides, for example even mixed anhydrides, azides or esters, in particular alkyl esters having 1-4 carbon atoms in the alkyl group.

Suitable reactive derivatives of the alcohols and phenols mentioned are in particular the corresponding metal alcoholates or phenolates, preferably of an alkali metal such as sodium or potassium.

The esterification is advantageously carried out in the presence of an inert solvent. Very suitable for this purpose are in particular ethers such as, for example, diethyl ether, di-n-butyl ether, THF, dioxane or anisole, ketones such as, for example, acetone, butanone or cyclohexanone, amides such as, for example, DMF or hexamethylphosphoric triamide, hydrocarbons such as, for example, benzene, toluene or xylene, halogenated hydro-

carbons such as, for example, carbon tetrachloride, dichloromethane or tetrachloroethylene and sulfoxides such as, for example, dimethyl sulfoxide or sulfolane.

In a further process for the preparation of the compounds of the formula I, an aryl halide is reacted with an olefin in the presence of a tertiary amine and a palladium catalyst (cf. R.F. Heck, Acc. Chem. Res. 12 (1979) 146). Examples of suitable aryl halides are chlorides, bromides and iodides, in particular bromides and iodides. The tertiary amines which are necessary for the successful completion of the coupling reaction, such as, for example, triethylamine, are also suitable as solvents. Examples of suitable palladium catalysts are palladium salts, in particular Pd(II) acetate, in combination with organic phosphorus(III) compounds such as, for example, triarylphosphanes. This reaction can be carried out in the presence or absence of an inert solvent at temperatures between about 0° and 150°, preferably between 20° and 100°; examples of suitable solvents are nitriles such as acetonitrile or hydrocarbons such as benzene or toluene. Many of the aryl halides and olefins used as starting materials are commercially available or can be prepared by processes known from the literature, for example by halogenation of the corresponding parent compounds or by elimination reactions of the corresponding alcohols or halides.

For example, stilbene derivatives can be prepared in this manner. The stilbenes can also be prepared by reaction of a 4-substituted benzaldehyde with the corresponding phosphorus ylide according to Wittig. However, it is also possible to prepare tolans of the formula I by using monosubstituted acetylene instead of the olefin (Synthesis 627 (1980) or Tetrahedron Lett. 27, 1171 (1986)).

Furthermore, aromatics can be coupled by reacting aryl halides with aryltin compounds. Preferably, these reactions are carried out with the addition of a catalyst such as, for example, a palladium(0) complex in inert solvents such as hydrocarbons at high temperatures, for

example in boiling xylene, under a protective gas.

Couplings of alkyinyl compounds with aryl halides can be carried out analogously to the process described by A.O. King, E. Negishi, F.J. Villani and A. Silveira in J.Org.Chem. 43, 358 (1978).

Tolans of the formula I can also be prepared via the Fritsch-Buttenberg-Wiechell rearrangement (Ann. 279, 319, 332, 1984), in which 1,1-diaryl-2-halogenoethylenes are rearranged to diarylacetylenes in the presence of strong bases.

Tolanes of the formula I can also be prepared by bromination of the corresponding stilbenes, followed by dehydrohalogenation. It is possible to use the variations of this reaction which are known per se but not mentioned here in more detail.

Nitriles of the formula I can be prepared by dehydrating the corresponding amides, for example those which have a CONH₂ group instead of the radical CN. The amides are obtainable, for example, from the corresponding esters or acid halides by reaction with ammonia. Examples of suitable dehydrating agents are inorganic acid chlorides such as SOCl₂, PCl₃, PCl₅, POCl₃, SO₂Cl₂, COCl₂, furthermore P₂O₅, P₂S₅, AlCl₃ (for example as double salt with NaCl), aromatic sulfonic acids and sulfonyl halides. This reaction can be carried out in the presence or absence of an inert solvent at temperatures between about 0° and 150°; examples of suitable solvents are bases such as pyridine or triethylamine, aromatic hydrocarbons such as benzene, toluene or xylene or amides such as DMF.

The abovementioned nitriles of the formula I can also be prepared by reacting the corresponding acid halides, preferably the chlorides, with sulfamide, advantageously in an inert solvent such as, for example, tetramethylene sulfone at temperatures between about 80° and 150°, preferably at 120°. After conventional work-up, the nitriles can be isolated directly.

Ethers of the formula I are available by etherification of the corresponding hydroxy compounds,

preferably of the corresponding phenols, in which the hydroxy compound is advantageously first converted into a corresponding metal derivative, for example converted into a corresponding alkali metal alcoholate or alkali metal phenolate by treatment with NaH, NaNH₂, NaOH, KOH, Na₂CO₃ or K₂CO₃. This derivative can then be reacted with the corresponding alkyl halide, alkyl sulfonate or dialkyl sulfate, advantageously in an inert solvent such as, for example, acetone, 1,2-dimethoxyethane, DMF or dimethyl sulfoxide or even with an excess of aqueous or aqueous-alcoholic NaOH or KOH at temperatures between about 20° and 100°.

The nitriles of the formula I can also be prepared by reacting the corresponding chlorine, bromine or iodine compounds of the formula I with a cyanide, preferably with a metal cyanide such as, for example, NaCN, KCN or Cu₂(CN)₂, for example in the presence of pyridine in an inert solvent such as, for example, DMF or N-methylpyrrolidone at temperatures between 20° and 200°.

Compounds of the formula I in which A¹ is substituted by at least one F atom and/or one CN group can also be obtained from the corresponding diazonium salts by exchange of the diazonium group for a fluorine atom or for a CN group, for example by the methods of Schiemann or Sandmeyer.

Dioxane derivatives or dithiane derivatives of the formula I are advantageously prepared by reaction of the corresponding aldehyde (or of one of its reactive derivatives) with a suitable 1,3-diol (or one of its reactive derivatives) or a suitable 1,3-dithiol, preferably in the presence of an inert solvent such as, for example, benzene or toluene and/or a catalyst, for example a strong acid such as sulfuric acid, benzenesulfonic acid or p-toluenesulfonic acid, at temperatures between about 20° and about 150°, preferably between 80° and 120°. Suitable reactive derivatives of the starting materials are primarily acetals.

Some of the aldehydes and 1,3-diols or 1,3-dithiols mentioned and their reactive derivatives are

known and others can be prepared without difficulties by standard processes of organic chemistry from compounds known from the literature. For example, the aldehydes are available by oxidation of the corresponding alcohols or
5 by reduction of nitriles or the corresponding carboxylic acids or their derivatives, the diols by reduction of the corresponding diesters and the dithiols by reaction of the corresponding dihalides with NaSH.

The liquid-crystalline media according to the
10 invention preferably contain, in addition to one or more compounds according to the invention, as further components 2 to 40, in particular 4 to 30 components. Very particularly preferably, these media contain, in addition to one or more compounds according to the invention, 7 to
15 25 components. These further components are preferably selected from nematic or nematogenic (monotropic or isotropic) substances, in particular substances from the classes of azoxybenzenes, benzylideneanilines, biphenyls, terphenyls, phenyl or cyclohexyl benzoates, phenyl or
20 cyclohexyl cyclohexanecarboxylates, phenyl or cyclohexyl cyclohexylbenzoates, phenyl or cyclohexyl cyclohexylcyclohexanecarboxylates, cyclohexylphenyl benzoates, cyclohexylphenyl cyclohexanecarboxylates, cyclohexylphenyl cyclohexylcyclohexanecarboxylates, phenylcyclohexanes,
25 cyclohexylbiphenyls, phenylcyclohexylcyclohexanes, cyclohexylcyclohexanes, cyclohexylcyclohexenes, cyclohexylcyclohexylcyclohexenes, 1,4-bis-cyclohexylbenzenes, 4,4'-bis-cyclohexylbiphenyls, phenyl- or cyclohexylpyrimidines, phenyl- or cyclohexylpyridines, phenyl- or cyclohexyldioxanes, phenyl- or cyclohexyl-1,3-dithianes, 1,2-diphenylethanes, 1,2-dicyclohexylethanes, 1-phenyl-2-cyclohexylethanes, 1-cyclohexyl-2-(4-phenylcyclohexyl)ethanes, 1-cyclohexyl-2-biphenylethanes, 1-phenyl-2-cyclohexylphenylethanes, halogenated or un-
30 halogenated stilbenes, benzyl phenyl ethers, tolanes and substituted cinnamic acids. The 1,4-phenylene groups in these compounds can also be fluorinated.

The most important compounds which are suitable as further components of media according to the invention

can be characterized by formulae 1, 2, 3, 4 and 5:

$R'-L-E-R''$	1
$R'-L-COO-E-R''$	2
$R'-L-OOC-E-R''$	3
$R'-L-CH_2CH_2-E-R''$	4
$R'-L-C\equiv C-E-R''$	5

In the formulae 1, 2, 3, 4 and 5, L and E, which can be identical or different, are each, independently of one another, a divalent radical from the group consisting of -Phe-, -Cyc-, -Phe-Phe-, -Phe-Cyc-, -Cyc-Cyc-, -Pyr-, -Dio-, -G-Phe- and -G-Cyc- and their mirror images, in which Phe is unsubstituted or fluorine-substituted 1,4-phenylene, Cyc is trans-1,4-cyclohexylene or 1,4-cyclohexenylene, Pyr is pyrimidine-2,5-diyl or pyridine-2,5-diyl, Dio is 1,3-dioxane-2,5-diyl and G is 2-(trans-1,4-cyclohexyl)ethyl, pyrimidine-2,5-diyl, pyridine-2,5-diyl or 1,3-dioxane-2,5-diyl.

Preferably, one of the radicals L and E is Cyc, Phe or Pyr. E is preferably Cyc, Phe or Phe-Cyc. Preferably, the media according to the invention contain one or more components selected from the compounds of the formulae 1, 2, 3, 4 and 5, in which L and E are selected from the group consisting of Cyc, Phe and Pyr and simultaneously one or more components are selected from the compounds of the formulae 1, 2, 3, 4 and 5, in which one of the radicals L and E is selected from the group consisting of Cyc, Phe and Pyr and the other radical is selected from the group consisting of -Phe-Phe-, -Phe-Cyc-, -Cyc-Cyc-, -G-Phe- and -G-Cyc-, and possibly one or more components are selected from the compounds of the formulae 1, 2, 3, 4 and 5, in which the radicals L and E are selected from the group consisting of -Phe-Cyc-, -Cyc-Cyc-, -G-Phe- and -G-Cyc-.

R' and R'' in the compounds of the partial formulae 1a, 2a, 3a, 4a and 5a are each, independently of one another, alkyl, alkenyl, alkoxy, alkenyloxy or

alkanoyloxy having up to 8 carbon atoms. In most of these compounds, R' and R" are different from one another and one of these radicals is in most cases alkyl or alkenyl. In the compounds of the partial formulae 1b, 2b, 3b, 4b and 5b, R" is -CN, -CF₃, F, Cl or -NCS; in these formulae, R has the meaning mentioned in the compounds of the partial formulae 1a to 5a and is preferably alkyl or alkenyl. However, other variations of the substituents intended for the compounds of the formulae 1, 2, 3, 4 and 5 are common. Many of these substances or even mixtures thereof are commercially available. All these substances are available by methods known from the literature or analogously to those methods.

The media according to the invention preferably contain, in addition to the components from the group of compounds 1a, 2a, 3a, 4a and 5a (group 1), also components from the group of compounds 1b, 2b, 3b, 4b and 5b (group 2), the relative proportions of which are preferably as follows:

Group 1: 20 to 90%, in particular 30 to 90%,
Group 2: 10 to 80%, in particular 10 to 50%,
the sum of the relative proportions of the compounds according to the invention and the compounds from groups 1 and 2 adding up to 100%.

The media according to the invention preferably contain 1 to 40%, in particular preferably 5 to 30%, of compounds according to the invention. Further preference is given to media containing more than 40%, in particular 45 to 90%, of compounds according to the invention. The media preferably contain three, four or five compounds according to the invention.

The media according to the invention are prepared in a manner customary per se. As a rule, the components are dissolved in one another, advantageously at elevated temperature. By means of suitable additives, the liquid-crystalline phases according to the invention can be modified in such a manner that they can be used in all previously known types of liquid crystal display elements. This type of additive is known to one skilled in

the art and has been described in detail in the literature (H. Kelker/R. Hatz, Handbook of Liquid Crystals, Verlag Chemie, Weinheim, 1980). For example, pleochroitic dyes to prepare coloured guest-host systems or substances to change the dielectric anisotropy, the viscosity and/or the orientation of the nematic phases can be added.

The examples which follow are intended to illustrate the invention without limiting it. Above and below, percentages are by weight. All temperatures are given in degrees centigrade. m.p. denotes melting point and c.p. = clear point. Furthermore, C denotes crystalline state, N nematic phase, S smectic phase and I isotropic phase. The data between these symbols represent the transition temperatures. An denotes optical anisotropy (589 nm, 20°C) and viscosity (mm²/sec) was determined at 20°C.

"Usual work-up" means: if desired, water is added, the product is extracted with methylene chloride, diethyl ether or toluene, the organic phase is separated off, dried, evaporated, and the product is purified by distillation under reduced pressure or crystallization and/or chromatography. The following abbreviations are used:

DAST	diethylaminosulfur trifluoride
25 DCC	dicyclohexylcarbodiimide
DDQ	dichlorodicyanobenzoquinone
DIBALH	diisobutylaluminum hydride
KOT	potassium t-butoxide
THF	tetrahydrofuran
30 pTSOH	p-toluenesulfonic acid

Example 1

4-Difluoromethoxy-4'-octoxy-biphenyl

A mixture of 20 g of 4-hydroxy-4'-octyloxy-biphenyl, 13.6 g of NaOH, 100 ml of water and 150 ml of dioxane is heated to 70°C with stirring. 10 g of chlorodifluoromethane are passed into the cooled two-phase mixture with vigorous stirring. The reaction mixture is poured into water, and the product is extracted with

petroleum ether. The organic phase is dried over Na_2SO_4 , evaporated, and the residue is filtered through a short silica gel column using petroleum ether as eluent. The product is recrystallized from acetonitrile. Colourless crystals are obtained. m.p.: 104°C , c.p.: 20°C (extrapolated), $A_n = 0.093$, viscosity: 17

The following were prepared analogously:

- 4-difluoromethoxy-4'-methoxy-biphenyl
- 4-difluoromethoxy-4'-ethoxy-biphenyl
- 10 4-difluoromethoxy-4'-propoxy-biphenyl
- 4-difluoromethoxy-4'-butoxy-biphenyl, m.p.: 122°C , $A_n = 0.146$
- 4-difluoromethoxy-4'-pentoxy-biphenyl
- 4-difluoromethoxy-4'-hexoxy-biphenyl
- 15 4-difluoromethoxy-4'-heptoxy-biphenyl
- 4-difluoromethoxy-4'-nonoxy-biphenyl
- 4-difluoromethoxy-4'-decoxy-biphenyl
- 4-difluoromethoxy-4'-methyl-biphenyl
- 4-difluoromethoxy-4'-ethyl-biphenyl
- 20 1-(4-difluoromethoxyphenyl)-4-ethyl-bicyclo[2.2.2]octane
- 4-difluoromethoxy-4'-propyl-biphenyl, m.p.: 84°C , c.p. (extrapolated): -30°C viscosity: 6
- 4-difluoromethoxy-4'-butyl-biphenyl
- 4-difluoromethoxy-4'-pentyl-biphenyl
- 25 4-difluoromethoxy-4'-hexyl-biphenyl
- 4-difluoromethoxy-4'-heptyl-biphenyl
- 4-difluoromethoxy-4'-nonyl-biphenyl
- 4-difluoromethoxy-4'-decyl-biphenyl
- 1-propyl-3-(4-difluoromethoxyphenyl-4'-yl)-cyclobutane
- 30 6-(4-difluoromethoxyphenyl)-2-methyl-naphthalene
- 6-(4-difluoromethoxyphenyl)-2-methyl-1,2,3,4-tetrahydro-naphthalene
- difluoromethoxy-4-(trans-4-ethylcyclohexyl)-benzene
- difluoromethoxy-4-(trans-4-propylcyclohexyl)-benzene
- 35 m.p.: -15°C , c.p.: -40°C (extrapolated), $A_n = 0.035$, viscosity: 5;
- difluoromethoxy-4-(trans-4-butylcyclohexyl)-benzene

m.p.: 8°C, c.p.: -30°C (extrapolated), $\Delta n = 0.043$,
viscosity: 6;

difluoromethoxy-4-(trans-4-pentylcyclohexyl)-benzene

m.p.: 1°C, c.p.: -17°C, $\Delta n = 0.058$, viscosity: 7;

- 5 difluoromethoxy-4-(trans-4-hexylcyclohexyl)-benzene
difluoromethoxy-4-(trans-4-heptylcyclohexyl)-benzene
difluoromethoxy-4-(trans-4-octylcyclohexyl)-benzene
difluoromethoxy-4-(trans-4-nonylcyclohexyl)-benzene
difluoromethoxy-4-(trans-4-decylcyclohexyl)-benzene
- 10 4-difluoromethoxy-2',3'-difluoro-4'-methoxy-biphenyl
4-difluoromethoxy-2',3'-difluoro-4'-ethoxy-biphenyl
4-difluoromethoxy-2',3'-difluoro-4'-propoxy-biphenyl
4-difluoromethoxy-2',3'-difluoro-4'-butoxy-biphenyl
4-difluoromethoxy-2',3'-difluoro-4'-pentoxy-biphenyl
- 15 4-difluoromethoxy-2',3'-difluoro-4'-hexoxy-biphenyl
4-difluoromethoxy-2',3'-difluoro-4'-heptoxy-biphenyl
4-difluoromethoxy-2',3'-difluoro-4'-octoxy-biphenyl
4-difluoromethoxy-2',3'-difluoro-4'-nonoxy-biphenyl
4-difluoromethoxy-2',3'-difluoro-4'-decoxy-biphenyl
- 20 4-difluoromethoxy-2',3'-difluoro-4'-methyl-biphenyl
4-difluoromethoxy-2',3'-difluoro-4'-ethyl-biphenyl
4-difluoromethoxy-2',3'-difluoro-4'-propyl-biphenyl
4-difluoromethoxy-2',3'-difluoro-4'-butyl-biphenyl
4-difluoromethoxy-2',3'-difluoro-4'-pentyl-biphenyl
- 25 4-difluoromethoxy-2',3'-difluoro-4'-hexyl-biphenyl
4-difluoromethoxy-2',3'-difluoro-4'-heptyl-biphenyl
4-difluoromethoxy-2',3'-difluoro-4'-octyl-biphenyl
4-difluoromethoxy-2',3'-difluoro-4'-nonyl-biphenyl
4-difluoromethoxy-2',3'-difluoro-4'-decyl-biphenyl
- 30 4-difluoromethoxy-4'-cyano-3'-fluorobiphenyl
- 4-difluoromethoxy-4'-methyl-terphenyl
4-difluoromethoxy-4'-ethyl-terphenyl
4-difluoromethoxy-4'-propyl-terphenyl
4-difluoromethoxy-4'-butyl-terphenyl
- 35 4-difluoromethoxy-4'-pentyl-terphenyl, m.p.: 223°C, c.p.:
241°C

- 4-difluoromethoxy-4'-hexyl-terphenyl
4-difluoromethoxy-4'-heptyl-terphenyl
4-difluoromethoxy-4'-octyl-terphenyl
4-difluoromethoxy-4'-nonyl-terphenyl
5 4-difluoromethoxy-4'-decyl-terphenyl
- 4-difluoromethoxy-4'-(trans-4-methylcyclohexyl)-biphenyl
4-difluoromethoxy-4'-(trans-4-ethylcyclohexyl)-biphenyl
4-difluoromethoxy-4'-(trans-4-propylcyclohexyl)-biphenyl,
m.p.: 82°C, c.p.: 169.4°C, $\Delta n = 0.174$
10 4-difluoromethoxy-4'-(trans-4-butylcyclohexyl)-biphenyl
4-difluoromethoxy-4'-(trans-4-pentylcyclohexyl)-biphenyl,
m.p.: 67°C, c.p.: 161.8°C, $\Delta n = 0.115$
4-difluoromethoxy-4'-(trans-4-hexylcyclohexyl)-biphenyl
4-difluoromethoxy-4'-(trans-4-heptylcyclohexyl)-biphenyl
15 4-difluoromethoxy-4'-(trans-4-octylcyclohexyl)-biphenyl
4-difluoromethoxy-4'-(trans-4-nonylcyclohexyl)-biphenyl
- 4-difluoromethoxy-4'-(trans-4-decylcyclohexyl)-biphenyl
4-methyl-4'-(4-difluoromethoxyphenyl)-trans,trans-bicyclohexyl
20 4-trifluoromethyl-4'-(4-difluoromethoxyphenyl)-trans,
trans-bicyclohexyl
4-ethyl-4'-(4-difluoromethoxyphenyl)-trans,trans-bicyclohexyl
4-propyl-4'-(4-difluoromethoxyphenyl)-trans,trans-bi-
25 cyclohexyl, m.p.: 39°C, c.p.: 148.6°C, $\Delta n = 0.088$,
viscosity: 16
4-isopropyl-4'-(4-difluoromethoxyphenyl)-trans,trans-bicyclohexyl
4-butyl-4'-(4-difluoromethoxyphenyl)-trans,trans-bicyclo-
30 hexyl
4-methoxyethyl-4'-(4-difluoromethoxyphenyl)-trans,trans-bicyclohexyl
4-pentyl-4'-(4-difluoromethoxyphenyl)-trans,trans-bi-
cyclohexyl
35 4-hexyl-4'-(4-difluoromethoxyphenyl)-trans,trans-bicyclohexyl
4-heptyl-4'-(4-difluoromethoxyphenyl)-trans,trans-bi-

- cyclohexyl
4-octyl-4'-(4-difluoromethoxyphenyl)-trans,trans-bicyclo-
hexyl
4-nonyl-4'-(4-difluoromethoxyphenyl)-trans,trans-bicyclo-
5 hexyl
4-decyl-4'-(4-difluoromethoxyphenyl)-trans,trans-bicyclo-
hexyl
- 1-(4-difluoromethoxyphenyl)-4-(trans-4-methylcyclohexyl)-
cyclohexene
10 1-(4-difluoromethoxyphenyl)-4-(trans-4-ethylcyclohexyl)-
cyclohexene
1-(4-difluoromethoxyphenyl)-4-(trans-4-propylcyclohexyl)-
cyclohexene
1-(4-difluoromethoxyphenyl)-4-(trans-4-butylcyclohexyl)-
15 cyclohexene
1-(4-difluoromethoxyphenyl)-4-(trans-4-pentylcyclohexyl)-
cyclohexene
1-(4-difluoromethoxyphenyl)-4-(trans-4-hexylcyclohexyl)-
cyclohexene
20 1-(4-difluoromethoxyphenyl)-4-(trans-4-heptylcyclohexyl)-
cyclohexene
1-(4-difluoromethoxyphenyl)-4-(trans-4-octylcyclohexyl)-
cyclohexene
1-(4-difluoromethoxyphenyl)-4-(trans-4-nonylcyclohexyl)-
25 cyclohexene
1-(4-difluoromethoxyphenyl)-4-(trans-4-decylcyclohexyl)-
cyclohexene
1-(4-difluoromethoxyphenyl)-trans-4-(1-methylcyclohexen-
4-yl)-cyclohexane
30 1-(4-difluoromethoxyphenyl)-trans-4-(1-ethylcyclohexen-4-
yl)-cyclohexane
1-(4-difluoromethoxyphenyl)-trans-4-(1-propylcyclohexen-
4-yl)-cyclohexane
1-(4-difluoromethoxyphenyl)-trans-4-(1-butylcyclohexen-4-
35 yl)-cyclohexane
1-(4-difluoromethoxyphenyl)-trans-4-(1-pentylcyclohexen-
4-yl)-cyclohexane

- 1-(4-difluoromethoxyphenyl)-trans-4-(1-hexylcyclohexen-4-yl)-cyclohexane
1-(4-difluoromethoxyphenyl)-trans-4-(1-heptylcyclohexen-4-yl)-cyclohexane
5 1-(4-difluoromethoxyphenyl)-trans-4-(1-octylcyclohexen-4-yl)-cyclohexane
1-(4-difluoromethoxyphenyl)-trans-4-(1-nonylcyclohexen-4-yl)-cyclohexane
1-(4-difluoromethoxyphenyl)-trans-4-(1-decylcyclohexen-4-yl)-cyclohexane
10

4-methyl-4'-(3-fluoro-4-difluoromethoxyphenyl)-trans, trans-bicyclohexyl
4-ethyl-4'-(3-fluoro-4-difluoromethoxyphenyl)-trans, trans-bicyclohexyl
15 4-propyl-4'-(3,5-difluoro-4-difluoromethoxyphenyl)-trans,trans-bicyclohexyl

4-propyl-4'-(3-fluoro-4-difluoromethoxyphenyl)-trans, trans-bicyclohexyl, m.p.: 33°C, c.p.: 144°C, $n_D^{20} = 0.106$
4-butyl-4'-(3-fluoro-4-difluoromethoxyphenyl)-trans, trans-bicyclohexyl
20 4-pentyl-4'-(3-fluoro-4-difluoromethoxyphenyl)-trans, trans-bicyclohexyl
4-hexyl-4'-(3-fluoro-4-difluoromethoxyphenyl)-trans, trans-bicyclohexyl
25 4-heptyl-4'-(3-fluoro-4-difluoromethoxyphenyl)-trans, trans-bicyclohexyl
4-octyl-4'-(3-fluoro-4-difluoromethoxyphenyl)-trans, trans-bicyclohexyl
4-nonyl-4'-(3-fluoro-4-difluoromethoxyphenyl)-trans, trans-bicyclohexyl
30 4-decyl-4'-(3-fluoro-4-difluoromethoxyphenyl)-trans, trans-bicyclohexyl

The following were prepared analogously from the corresponding thiols:

- 35 4-difluoromethylthio-4'-methyl-biphenyl
4-difluoromethylthio-4'-ethyl-biphenyl
4-difluoromethylthio-4'-propyl-biphenyl

- 4-difluoromethylthio-4'-butyl-biphenyl
4-difluoromethylthio-4'-pentyl-biphenyl
4-difluoromethylthio-4'-hexyl-biphenyl
4-difluoromethylthio-4'-heptyl-biphenyl
5 4-difluoromethylthio-4'-octyl-biphenyl
4-difluoromethylthio-4'-nonyl-biphenyl
4-difluoromethylthio-4'-decyl-biphenyl
- difluoromethylthio-4-(trans-4-methylcyclohexyl)-benzene
difluoromethylthio-4-(trans-4-ethylcyclohexyl)-benzene
10 difluoromethylthio-4-(trans-4-propylcyclohexyl)-benzene
difluoromethylthio-4-(trans-4-butylcyclohexyl)-benzene
difluoromethylthio-4-(trans-4-pentylcyclohexyl)-benzene
difluoromethylthio-4-(trans-4-hexylcyclohexyl)-benzene
difluoromethylthio-4-(trans-4-heptylcyclohexyl)-benzene
15 difluoromethylthio-4-(trans-4-octylcyclohexyl)-benzene
difluoromethylthio-4-(trans-4-nonylcyclohexyl)-benzene
difluoromethylthio-4-(trans-4-decylcyclohexyl)-benzene
4-difluoromethylthio-4'-(trans-4-methylcyclohexyl)-
biphenyl
20 4-difluoromethylthio-4'-(trans-4-ethylcyclohexyl)-bi-
phenyl
4-difluoromethylthio-4'-(trans-4-propylcyclohexyl)-
biphenyl
4-difluoromethylthio-4'-(trans-4-butylcyclohexyl)-bi-
25 phenyl
4-difluoromethylthio-4'-(trans-4-pentylcyclohexyl)-
biphenyl
4-difluoromethylthio-4'-(trans-4-hexylcyclohexyl)-bi-
phenyl
30 4-difluoromethylthio-4'-(trans-4-heptylcyclohexyl)-
biphenyl
4-difluoromethylthio-4'-(trans-4-octylcyclohexyl)-bi-
phenyl
4-difluoromethylthio-4'-(trans-4-nonylcyclohexyl)-bi-
35 phenyl
4-difluoromethylthio-4'-(trans-4-decylcyclohexyl)-bi-
phenyl

Example 2

Difluoromethoxy-(5-propyl-1,3-dioxan-2-yl)-benzene

17.2 g of p-difluoromethoxybenzaldehyde
(commercially available from Fluorochem. Ltd. (GB)),
5 10.4 g of ethylpropanediol and 0.2 g of p-TsOH are heated
to boiling for 2 hours in 100 ml of toluene. After
evaporation of the solvent, the mixture is worked up as
usual.

The following were prepared analogously:

10 difluoromethoxy-(5-ethyl-1,3-dioxan-2-yl)-benzene
difluoromethoxy-(5-butyl-1,3-dioxan-2-yl)-benzene
difluoromethoxy-(5-pentyl-1,3-dioxan-2-yl)-benzene
difluoromethoxy-(5-hexyl-1,3-dioxan-2-yl)-benzene
difluoromethoxy-(5-heptyl-1,3-dioxan-2-yl)-benzene
15 difluoromethoxy-(5-octyl-1,3-dioxan-2-yl)-benzene
difluoromethoxy-(5-nonyl-1,3-dioxan-2-yl)-benzene
difluoromethoxy-(5-decyl-1,3-dioxan-2-yl)-benzene

difluoromethoxy-4-[5-(trans-4-methylcyclohexyl)-1,3-
dioxan-2-yl]-benzene
20 difluoromethoxy-4-[5-(trans-4-ethylcyclohexyl)-1,3-
dioxan-2-yl]-benzene
difluoromethoxy-4-[5-(trans-4-propylcyclohexyl)-1,3-
dioxan-2-yl]-benzene
difluoromethoxy-4-[5-(trans-4-butylcyclohexyl)-1,3-
25 dioxan-2-yl]-benzene
difluoromethoxy-4-[5-(trans-4-pentylcyclohexyl)-1,3-
dioxan-2-yl]-benzene
difluoromethoxy-4-[5-(trans-4-hexylcyclohexyl)-1,3-
dioxan-2-yl]-benzene
30 difluoromethoxy-4-[5-(trans-4-heptylcyclohexyl)-1,3-
dioxan-2-yl]-benzene
difluoromethoxy-4-[5-(trans-4-octylcyclohexyl)-1,3-
dioxan-2-yl]-benzene
difluoromethoxy-4-[5-(trans-4-nonylcyclohexyl)-1,3-
35 dioxan-2-yl]-benzene
difluoromethoxy-4-[5-(trans-4-decylcyclohexyl)-1,3-
dioxan-2-yl]-benzene

Example 3

Difluoromethoxy-4-(5-heptyl-1,3-pyrimidin-2-yl)-benzene

A mixture of 22.2 g of p-difluoromethoxybenzimidamide hydrochloride (available from the nitrile via the corresponding ethyl benzimidate hydrochloride) and 31.8 g of heptylmalonedialdehyde bis(diethyl) acetal is stirred at 150°C for 15 hours. After cooling, the mixture is worked up as usual. m.p.: 26°C, c.p.: 32°C, An: 0.112, viscosity: 16.

The following were prepared analogously:

difluoromethoxy-4-(5-methyl-1,3-pyrimidin-2-yl)-benzene
difluoromethoxy-4-(5-ethyl-1,3-pyrimidin-2-yl)-benzene
difluoromethoxy-4-(5-propyl-1,3-pyrimidin-2-yl)-benzene,
m.p.: 41°C, c.p. (extrapolated): 0°C, An = 0.150, viscosity: 14

difluoromethoxy-4-(5-butyl-1,3-pyrimidin-2-yl)-benzene
difluoromethoxy-4-(5-pentyl-1,3-pyrimidin-2-yl)-benzene,
m.p.: 21°C, c.p.: 26°C, An: 0.13, viscosity: 14

difluoromethoxy-4-(5-hexyl-1,3-pyrimidin-2-yl)-benzene
difluoromethoxy-4-(5-octyl-1,3-pyrimidin-2-yl)-benzene
difluoromethoxy-4-(5-nonyl-1,3-pyrimidin-2-yl)-benzene
difluoromethoxy-4-(5-decyl-1,3-pyrimidin-2-yl)-benzene
difluoromethoxy-4-(5-methoxy-1,3-pyrimidin-2-yl)-benzene
difluoromethoxy-4-(5-ethoxy-1,3-pyrimidin-2-yl)-benzene
difluoromethoxy-4-(5-propoxy-1,3-pyrimidin-2-yl)-benzene
difluoromethoxy-4-(5-butoxy-1,3-pyrimidin-2-yl)-benzene
difluoromethoxy-4-(5-pentoxo-1,3-pyrimidin-2-yl)-benzene
difluoromethoxy-4-(5-hexoxy-1,3-pyrimidin-2-yl)-benzene
difluoromethoxy-4-(5-heptoxy-1,3-pyrimidin-2-yl)-benzene
difluoromethoxy-4-(5-octoxy-1,3-pyrimidin-2-yl)-benzene
difluoromethoxy-4-(5-nonoxo-1,3-pyrimidin-2-yl)-benzene
difluoromethoxy-4-(5-decoxy-1,3-pyrimidin-2-yl)-benzene

difluoromethoxy-4-[5-(trans-4-methylcyclohexyl)-1,3-pyrimidin-2-yl]-benzene
difluoromethoxy-4-[5-(trans-4-ethylcyclohexyl)-1,3-pyrimidin-2-yl]-benzene
difluoromethoxy-4-[5-(trans-4-propylcyclohexyl)-1,3-pyrimidin-2-yl]-benzene

- difluoromethoxy-4-[5-(trans-4-butylcyclohexyl)-1,3-pyrimidin-2-yl]-benzene
difluoromethoxy-4-[5-(trans-4-pentylcyclohexyl)-1,3-pyrimidin-2-yl]-benzene
5 difluoromethoxy-4-[5-(trans-4-hexylcyclohexyl)-1,3-pyrimidin-2-yl]-benzene
difluoromethoxy-4-[5-(trans-4-heptylcyclohexyl)-1,3-pyrimidin-2-yl]-benzene
difluoromethoxy-4-[5-(trans-4-octylcyclohexyl)-1,3-pyrimidin-2-yl]-benzene
10 difluoromethoxy-4-[5-(trans-4-nonylcyclohexyl)-1,3-pyrimidin-2-yl]-benzene
difluoromethoxy-4-[5-(trans-4-decylcyclohexyl)-1,3-pyrimidin-2-yl]-benzene
15 difluoromethoxy-4-[5-(2-(trans-4-methylcyclohexyl)-ethyl)-1,3-pyrimidin-2-yl]-benzene
difluoromethoxy-4-[5-(2-(trans-4-ethylcyclohexyl)-ethyl)-1,3-pyrimidin-2-yl]-benzene
difluoromethoxy-4-[5-(2-(trans-4-propylcyclohexyl)-ethyl)-1,3-pyrimidin-2-yl]-benzene
20 difluoromethoxy-4-[5-(2-(trans-4-butylcyclohexyl)-ethyl)-1,3-pyrimidin-2-yl]-benzene
difluoromethoxy-4-[5-(2-(trans-4-pentylcyclohexyl)-ethyl)-1,3-pyrimidin-2-yl]-benzene
25 difluoromethoxy-4-[5-(2-(trans-4-hexylcyclohexyl)-ethyl)-1,3-pyrimidin-2-yl]-benzene

difluoromethoxy-4-[5-(2-(trans-4-heptylcyclohexyl)-ethyl)-1,3-pyrimidin-2-yl]-benzene
difluoromethoxy-4-[5-(2-(trans-4-octylcyclohexyl)-ethyl)-1,3-pyrimidin-2-yl]-benzene
30 difluoromethoxy-4-[5-(2-(trans-4-nonylcyclohexyl)-ethyl)-1,3-pyrimidin-2-yl]-benzene
difluoromethoxy-4-[5-(2-(trans-4-decylcyclohexyl)-ethyl)-1,3-pyrimidin-2-yl]-benzene
35 Using 4-mercaptobenzonitrile (available from 4-cyanophenol by reaction with dimethylcarbamoyl chloride and thermal rearrangement), the following were prepared analogously:

- difluoromethylthio-4-(5-methyl-1,3-pyrimidin-2-yl)-
benzene
- difluoromethylthio-4-(5-ethyl-1,3-pyrimidin-2-yl)-benzene
- difluoromethylthio-4-(5-propyl-1,3-pyrimidin-2-yl)-
5 benzene
- difluoromethylthio-4-(5-butyl-1,3-pyrimidin-2-yl)-benzene
- difluoromethylthio-4-(5-pentyl-1,3-pyrimidin-2-yl)-
benzene
- difluoromethylthio-4-(5-hexyl-1,3-pyrimidin-2-yl)-benzene
- 10 difluoromethylthio-4-(5-heptyl-1,3-pyrimidin-2-yl)-
benzene
- difluoromethylthio-4-(5-octyl-1,3-pyrimidin-2-yl)-benzene
- difluoromethylthio-4-(5-nonyl-1,3-pyrimidin-2-yl)-benzene
- difluoromethylthio-4-(5-decyl-1,3-pyrimidin-2-yl)-benzene
- 15 difluoromethylthio-4-(5-methoxy-1,3-pyrimidin-2-yl)-
benzene
- difluoromethylthio-4-(5-ethoxy-1,3-pyrimidin-2-yl)-
benzene
- difluoromethylthio-4-(5-propoxy-1,3-pyrimidin-2-yl)-
20 benzene
- difluoromethylthio-4-(5-butoxy-1,3-pyrimidin-2-yl)-
benzene
- difluoromethylthio-4-(5-pentoxy-1,3-pyrimidin-2-yl)-
benzene
- 25 difluoromethylthio-4-(5-hexoxy-1,3-pyrimidin-2-yl)-
benzene
- difluoromethylthio-4-(5-heptoxy-1,3-pyrimidin-2-yl)-
benzene
- difluoromethylthio-4-(5-octoxy-1,3-pyrimidin-2-yl)-
30 benzene
- difluoromethylthio-4-(5-nonoxo-1,3-pyrimidin-2-yl)-
benzene
- difluoromethylthio-4-(5-decoxy-1,3-pyrimidin-2-yl)-
benzene
- 35 difluoromethoxy-4-(5-methylpyridin-2-yl)-benzene
- difluoromethoxy-4-(5-ethylpyridin-2-yl)-benzene
- difluoromethoxy-4-(5-propylpyridin-2-yl)-benzene
- difluoromethoxy-4-(5-butylpyridin-2-yl)-benzene

- difluoromethoxy-4-(5-pentylpyridin-2-yl)-benzene
difluoromethoxy-4-(5-hexylpyridin-2-yl)-benzene
difluoromethoxy-4-(5-heptylpyridin-2-yl)-benzene
difluoromethoxy-4-(5-octylpyridin-2-yl)-benzene
5 difluoromethoxy-2-fluoro-4-(2-octylpyridin-5-yl)-benzene
difluoromethoxy-4-(5-nonylpyridin-2-yl)-benzene
difluoromethoxy-4-(5-decylpyridin-2-yl)-benzene
difluoromethoxy-4-(5-methoxypyridin-2-yl)-benzene
difluoromethoxy-4-(5-ethoxypyridin-2-yl)-benzene
10 difluoromethoxy-4-(5-propoxypyridin-2-yl)-benzene
difluoromethoxy-4-(5-butoxypyridin-2-yl)-benzene
difluoromethoxy-4-(5-pentoxypyridin-2-yl)-benzene
difluoromethoxy-4-(5-hexoxypyridin-2-yl)-benzene
difluoromethoxy-4-(5-heptoxypyridin-2-yl)-benzene
15 difluoromethoxy-4-(5-octoxypyridin-2-yl)-benzene
difluoromethoxy-2-fluoro-4-(2-octoxypyridin-5-yl)-benzene
difluoromethoxy-4-(5-nonoxypyridin-2-yl)-benzene
difluoromethoxy-4-(5-decoxypyridin-2-yl)-benzene
4-difluoromethoxy-4'-(5-methyl-1,3-pyrimidin-2-yl)-
20 biphenyl
4-difluoromethoxy-4'-(5-ethyl-1,3-pyrimidin-2-yl)-
biphenyl
4-difluoromethoxy-4'-(5-propyl-1,3-pyrimidin-2-yl)-
biphenyl
25 4-difluoromethoxy-4'-(5-butyl-1,3-pyrimidin-2-yl)-
biphenyl
4-difluoromethoxy-4'-(5-pentyl-1,3-pyrimidin-2-yl)-
biphenyl
4-difluoromethoxy-4'-(5-hexyl-1,3-pyrimidin-2-yl)-
30 biphenyl
4-difluoromethoxy-4'-(5-heptyl-1,3-pyrimidin-2-yl)-
biphenyl
4-difluoromethoxy-4'-(5-octyl-1,3-pyrimidin-2-yl)-
biphenyl
35 4-difluoromethoxy-4'-(5-nonyl-1,3-pyrimidin-2-yl)-
biphenyl
4-difluoromethoxy-4'-(5-decyl-1,3-pyrimidin-2-yl)-
biphenyl

Example 4

4-Benzyloxy-difluoromethoxy-benzene

A mixture of 40.0 g of hydroquinone monobenzyl ether, 40 g of NaOH, 200 ml of water and 300 ml of dioxane are heated to 70°C with stirring. 35.5 g of chlorodifluoromethane are passed into the cooled mixture with vigorous stirring. The reaction mixture is poured into water, and the product is extracted with petroleum ether. The organic phase is dried over Na₂SO₄, evaporated, and the residue is chromatographed through a short silica gel column, using petroleum ether/ethyl acetate 8:2 as eluent. A colourless liquid is obtained.

Example 5

a) Hydroquinone monodifluoromethyl ether

A solution of 25.0 g of the product from Example 4 in 100 ml of THF is hydrogenated at room temperature and atmospheric pressure, using 8 g of Pd/C (5% Pd) as catalyst. The catalyst is filtered off, and the filtrate is evaporated.

b) 4-Difluoromethoxyphenyl trans-4-pentylcyclohexanecarboxylate

A solution of 10.3 g of DCC in 50 ml of dichloromethane is added dropwise to a solution maintained at 0°C of 9.92 g of trans-4-pentylcyclohexanecarboxylic acid, 8.11 g of hydroquinone monodifluoromethyl ether and 611 mg of 4-dimethylaminopyridine in 100 ml of dichloromethane. After stirring at room temperature for 18 hours, the precipitate formed is filtered off, and the filtrate is evaporated. The residue is chromatographed through a silica gel column, using petroleum ether/ethyl acetate 9:1 as eluent. Colourless crystals, m.p.: 54°C, c.p.: 30°C, An = 0.061, viscosity: 16 are obtained.

The following are prepared analogously:

4-difluoromethoxyphenyl trans-4-ethylcyclohexanecarboxylate

4-difluoromethoxyphenyl trans-4-propylcyclohexanecarboxylate, m.p.: 54°C, c.p.: 0°C, An = 0.052, viscosity: 10

- 4-difluoromethoxyphenyl trans-4-butylcyclohexanecarboxy-
late
- 4-difluoromethoxyphenyl trans-4-hexylcyclohexanecarboxy-
late
- 5 4-difluoromethoxyphenyl trans-4-heptylcyclohexanecarboxy-
late
- 4-difluoromethoxyphenyl trans-4-octylcyclohexanecarboxy-
late
- 4-difluoromethoxyphenyl trans-4-nonylcyclohexanecarboxy-
10 late
- 4-difluoromethoxyphenyl trans-4-decylcyclohexanecarboxy-
late
- 4-difluoromethoxybiphenyl-4'-yl trans-4-methylcyclohex-
anehexanecarboxylate
- 15 4-difluoromethoxybiphenyl-4'-yl trans-4-ethylcyclohexane-
carboxylate
- 4-difluoromethoxybiphenyl-4'-yl trans-4-propylcyclohex-
anehexanecarboxylate
- 4-difluoromethoxybiphenyl-4'-yl trans-4-butylcyclohexane-
20 carboxylate
- 4-difluoromethoxybiphenyl-4'-yl trans-4-pentylcyclohexan-
ecarboxylate
- 4-difluoromethoxybiphenyl-4'-yl trans-4-hexylcyclohexane-
carboxylate
- 25 4-difluoromethoxybiphenyl-4'-yl trans-4-heptylcyclohexane-
carboxylate
- 4-difluoromethoxybiphenyl-4'-yl trans-4-octylcyclohexane-
carboxylate
- 4-difluoromethoxybiphenyl-4'-yl trans-4-nonylcyclohexane-
30 carboxylate
- 4-difluoromethoxybiphenyl-4'-yl trans-4-decylcyclohexane-
carboxylate
- 4-difluoromethoxyphenyl-4'-methyl trans,trans-bicyclo-
hexane-4-carboxylate
- 35 4-difluoromethoxyphenyl-4'-ethyl trans,trans-bicyclo-
hexane-4-carboxylate
- 4-difluoromethoxyphenyl-4'-propyl trans,trans-bicyclo-

	hexane-4-carboxylate	
	4-difluoromethoxyphenyl-4'-butyl	trans,trans-bicyclo-
	hexane-4-carboxylate	
	4-difluoromethoxyphenyl-4'-pentyl	trans,trans-bicyclo-
5	hexane-4-carboxylate, m.p.: 61°C, c.p.: 196.9°C, An = 0.089	
	4-difluoromethoxyphenyl-4'-hexyl	trans,trans-bicyclo-
	hexane-4-carboxylate	
	4-difluoromethoxyphenyl-4'-heptyl	trans,trans-bicyclo-
10	hexane-4-carboxylate	
	4-difluoromethoxyphenyl-4'-octyl	trans,trans-bicyclo-
	hexane-4-carboxylate	
	4-difluoromethoxyphenyl-4'-nonyl	trans,trans-bicyclo-
	hexane-4-carboxylate	
15	4-difluoromethoxyphenyl-4'-decyl	trans,trans-bicyclo-
	hexane-4-carboxylate	
Using 4-difluoromethylthiophenol (obtainable by esterification of 4-hydroxybenzenesulfonic acid (Aldrich) with acetic acid, conversion to the sulfonyl chloride, reduction to the thiol using zinc/hydrochloric acid, etherification analogously to Example 1) and alkaline ether cleavage), the following were prepared analogously:		
20	4-difluoromethylthiophenyl	trans-4-methylcyclohexane-carboxylate
25	4-difluoromethylthiophenyl	trans-4-ethylcyclohexane-carboxylate
	4-difluoromethylthiophenyl	trans-4-propylcyclohexane-carboxylate
	4-difluoromethylthiophenyl	trans-4-butylcyclohexane-
30	carboxylate	
	4-difluoromethylthiophenyl	trans-4-pentylcyclohexane-
	carboxylate	
	4-difluoromethylthiophenyl	trans-4-hexylcyclohexane-
	carboxylate	
35	4-difluoromethylthiophenyl	trans-4-heptylcyclohexane-
	carboxylate	
	4-difluoromethylthiophenyl	trans-4-octylcyclohexane-
	carboxylate	
	4-difluoromethylthiophenyl	trans-4-nonylcyclohexane-

- carboxylate
4-difluoromethylthiophenyl trans-4-decylcyclohexane-
carboxylate
3-fluoro-4-difluoromethylthiophenyl-4'-methyl trans,
5 trans-bicyclohexane-4-carboxylate
3-fluoro-4-difluoromethylthiophenyl-4'-ethyl trans,
trans-bicyclohexane-4-carboxylate
3-fluoro-4-difluoromethylthiophenyl-4'-propyl trans,
trans-bicyclohexane-4-carboxylate
10 3-fluoro-4-difluoromethylthiophenyl-4'-butyl trans,
trans-bicyclohexane-4-carboxylate
3-fluoro-4-difluoromethylthiophenyl-4'-pentyl trans,
trans-bicyclohexane-4-carboxylate
3-fluoro-4-difluoromethylthiophenyl-4'-hexyl trans,
15 trans-bicyclohexane-4-carboxylate
3-fluoro-4-difluoromethylthiophenyl-4'-heptyl trans,
trans-bicyclohexane-4-carboxylate
3-fluoro-4-difluoromethylthiophenyl-4'-octyl trans,
trans-bicyclohexane-4-carboxylate
20 3-fluoro-4-difluoromethylthiophenyl-4'-nonyl trans,
trans-bicyclohexane-4-carboxylate
3-fluoro-4-difluoromethylthiophenyl-4'-decyl trans,
trans-bicyclohexane-4-carboxylate
- 2,3-difluoro-4-difluoromethylthiophenyl trans-4-methyl-
25 cyclohexanebenzoate
2,3-difluoro-4-difluoromethylthiophenyl trans-4-ethyl-
cyclohexanebenzoate
2,3-difluoro-4-difluoromethylthiophenyl trans-4-propyl-
cyclohexanebenzoate
30 2,3-difluoro-4-difluoromethylthiophenyl trans-4-butyl-
cyclohexanebenzoate
2,3-difluoro-4-difluoromethylthiophenyl trans-4-pentyl-
cyclohexanebenzoate
2,3-difluoro-4-difluoromethylthiophenyl trans-4-hexyl-
35 cyclohexanebenzoate
2,3-difluoro-4-difluoromethylthiophenyl trans-4-heptyl-
cyclohexanebenzoate
2,3-difluoro-4-difluoromethylthiophenyl trans-4-octyl-

cyclohexanebenzoate
2,3-difluoro-4-difluoromethylthiophenyl trans-4-nonyl-
cyclohexanebenzoate
2,3-difluoro-4-difluoromethylthiophenyl trans-4-decyl-
5 cyclohexanebenzoate

Example 6

a) 4-[2-(4-Benzyloxyphenyl)ethenyl]-4'-pentyl trans,
trans-bicyclohexyl

49.6 g of 4-benzyloxybenzaldehyde and 25.9 g of
10 KOT are added to a suspension of 147.1 g of 4'-pentyl
trans,trans-bicyclohexyl-4-methyltriphenylphosphonium
iodide in 1 l of THF with ice-cooling. The mixture is
stirred for 1h at 5°C 2 N HCl is then added, until the
aqueous phase is neutral, and water is added until the
15 precipitate has been dissolved. The organic phase is
separated off, dried over Na₂SO₄ and evaporated. The
residue is chromatographed through a silica gel column,
using petroleum ether/ethyl acetate 95:5 as eluent.
Colorless crystals are obtained.

20 b) 4-[2-(4-Hydroxyphenyl)ethyl]-4'-pentyl trans,trans-
bicyclohexyl

A solution of 34.6 g of product 6a in 200 ml of
THF is hydrogenated at room temperature and atmospheric
pressure, using 10 g of Pd/C (5% Pd) as catalyst. The
25 catalyst is filtered off, and the filtrate is evaporated.
A grey crystalline solid is obtained;

c) 4-[2-(4-Difluoromethoxyphenyl)ethyl]-4'-pentyl trans,
trans-bicyclohexyl

The product 6b is converted to the difluoro-
30 methoxy compound analogously to Example 1, m.p.: 24°C,
c.p.: 149.9°C, An = 0.097, viscosity: 21.

d) The phosphonium iodide from 6 a) is reacted directly
with 4-difluoromethoxybenzaldehyde, as described in 6 a),
and hydrogenated analogously to 6 b).

35 The following are prepared analogously:

4-[2-(4-difluoromethoxyphenyl)ethyl]-4'-ethyl trans,
trans-bicyclohexyl

4-[2-(4-difluoromethoxyphenyl)ethyl]-4'-propyl trans,

- trans-bicyclohexyl
4-[2-(4-difluoromethoxyphenyl)ethyl]-4'-butyl trans,
trans-bicyclohexyl
4-[2-(4-difluoromethoxyphenyl)ethyl]-4'-hexyl trans,
5 trans-bicyclohexyl
4-[2-(4-difluoromethoxyphenyl)ethyl]-4'-heptyl trans,
trans-bicyclohexyl
4-[2-(4-difluoromethoxyphenyl)ethyl]-4'-octyl trans,
trans-bicyclohexyl
10 4-[2-(4-difluoromethoxyphenyl)ethyl]-4'-nonyl trans,
trans-bicyclohexyl
4-[2-(4-difluoromethoxyphenyl)ethyl]-4'-decyl trans,
trans-bicyclohexyl
- 4-[2-(2,3-difluoro-4-difluoromethoxyphenyl)ethyl]-4'-
15 methyl trans,trans-bicyclohexyl
4-[2-(2,3-difluoro-4-difluoromethoxyphenyl)ethyl]-4'-
ethyl trans,trans-bicyclohexyl
4-[2-(2,3-difluoro-4-difluoromethoxyphenyl)ethyl]-4'-
propyl trans,trans-bicyclohexyl, 81 N 128 I
20 4-[2-(2,3-difluoro-4-difluoromethoxyphenyl)ethyl]-4'-
butyl trans,trans-bicyclohexyl
4-[2-(2,3-difluoro-4-difluoromethoxyphenyl)ethyl]-4'-
pentyl trans,trans-bicyclohexyl
4-[2-(2,3-difluoro-4-difluoromethoxyphenyl)ethyl]-4'-
25 hexyl trans,trans-bicyclohexyl
4-[2-(2,3-difluoro-4-difluoromethoxyphenyl)ethyl]-4'-
heptyl trans,trans-bicyclohexyl
4-[2-(2,3-difluoro-4-difluoromethoxyphenyl)ethyl]-4'-
octyl trans,trans-bicyclohexyl
30 4-[2-(2,3-difluoro-4-difluoromethoxyphenyl)ethyl]-4'-
nonyl trans,trans-bicyclohexyl
4-[2-(2,3-difluoro-4-difluoromethoxyphenyl)ethyl]-4'-
decyl trans,trans-bicyclohexyl
- 4-[2-(trans-4-methylcyclohexyl)ethyl]-4'-difluoro-
35 methoxybiphenyl
4-[2-(trans-4-ethylcyclohexyl)ethyl]-4'-difluoromethoxy-
biphenyl

- 4-[2-(trans-4-propylcyclohexyl)ethyl]-4'-difluoromethoxybiphenyl
- 4-[2-(trans-4-butylcyclohexyl)ethyl]-4'-difluoromethoxybiphenyl
- 5 4-[2-(trans-4-pentylcyclohexyl)ethyl]-4'-difluoromethoxybiphenyl
- 4-[2-(trans-4-hexylcyclohexyl)ethyl]-4'-difluoromethoxybiphenyl
- 10 4-[2-(trans-4-heptylcyclohexyl)ethyl]-4'-difluoromethoxybiphenyl
- 4-[2-(trans-4-octylcyclohexyl)ethyl]-4'-difluoromethoxybiphenyl
- 4-[2-(trans-4-nonylcyclohexyl)ethyl]-4'-difluoromethoxybiphenyl
- 15 4-[2-(trans-4-decylcyclohexyl)ethyl]-4'-difluoromethoxybiphenyl
-
- 4-difluoromethoxy-[2-(trans-4-methylcyclohexyl)ethyl]-benzene
- 4-difluoromethoxy-[2-(trans-4-ethylcyclohexyl)ethyl]-benzene, m.p.: -37°C, c.p. (extrapolated): -60°C, $A_n = 0.033$, viscosity: 6
- 4-difluoromethoxy-[2-(trans-4-propylcyclohexyl)ethyl]-benzene, m.p.: -2°C, c.p.: -14.5°C, $A_n = 0.042$, viscosity: 6
- 25 4-difluoromethoxy-[2-(trans-4-butylcyclohexyl)ethyl]-benzene
- 4-difluoromethoxy-[2-(trans-4-pentylcyclohexyl)ethyl]-benzene, m.p.: 4°C, c.p.: 5.1°C, $A_n = 0.065$, viscosity: 7
- 4-difluoromethoxy-[2-(trans-4-hexylcyclohexyl)ethyl]-benzene
- 30 4-difluoromethoxy-[2-(trans-4-heptylcyclohexyl)ethyl]-benzene, m.p.: 30°C, c.p.: 16.9°C, $A_n = 0.065$, viscosity: 8
- 4-difluoromethoxy-[2-(trans-4-octylcyclohexyl)ethyl]-benzene
- 35 4-difluoromethoxy-[2-(trans-4-nonylcyclohexyl)ethyl]-benzene
- 4-difluoromethoxy-[2-(trans-4-decylcyclohexyl)ethyl]-benzene

benzene

Example 7

a) 4-(1H,1H-Difluoroethoxy)-benzaldehyde

16.4 g of 2,2-difluoroethanol are added to a suspension of 3.3 g of sodium hydride in 100 ml of 1,3-dimethyl-2-imidazolidinone, and the mixture is stirred at 30°C for 2 hours. It is cooled to 0-10°C, and 12.4 g of 4-fluorobenzaldehyde are added. The mixture is stirred at 5°C for 2 hours and at 90°C for 4 hours. After cooling, the reaction mixture is poured into 200 ml of 5% HCl, and the product is extracted with ether. The organic phase is dried over Na₂SO₄, evaporated, and the residue is distilled. A colourless liquid is obtained.

b) 4-{2-[4-(1H,1H-Difluoroethoxy)-phenyl]-ethenyl}-4'-pentyl trans,trans-bicyclohexyl

17.1 g of the product 7a and 9.3 g of KOT are added to a suspension of 53 g of 4'-pentyltrans,trans-bicyclohexyl-4-methyltriphenylphosphonium iodide in 250 ml of THF with ice-cooling. The mixture is stirred at 5°C for 1 hour. 2 N HCl is then added until the aqueous phase is neutral, and water is added until the precipitate has been dissolved. The organic phase is separated off, dried over Na₂SO₄, and evaporated. The residue is chromatographed through a silica gel column, using petroleum ether/ethyl acetate 9:1 as eluent. Colourless crystals are obtained.

The following are prepared analogously:

- 4-{2-[4-(1H,1H-difluoroethoxy)-phenyl]-ethenyl}-4'-ethyl trans,trans-bicyclohexyl
- 4-{2-[4-(1H,1H-difluoroethoxy)-phenyl]-ethenyl}-4'-propyl trans,trans-bicyclohexyl
- 4-{2-[4-(1H,1H-difluoroethoxy)-phenyl]-ethenyl}-4'-butyl trans,trans-bicyclohexyl
- 4-{2-[4-(1H,1H-difluoroethoxy)-phenyl]-ethenyl}-4'-hexyl trans,trans-bicyclohexyl
- 4-{2-[4-(1H,1H-difluoroethoxy)-phenyl]-ethenyl}-4'-heptyl trans,trans-bicyclohexyl
- 4-{2-[4-(1H,1H-difluoroethoxy)-phenyl]-ethenyl}-4'-octyl

- trans,trans-bicyclohexyl
4-{2-[4-(1H,1H-difluoroethoxy)-phenyl]-ethenyl}-4'-nonyl
trans,trans-bicyclohexyl
4-{2-[4-(1H,1H-difluoroethoxy)-phenyl]-ethenyl}-4'-decyl
5 trans,trans-bicyclohexyl
- 4-difluoromethoxy-[2-(trans-4-methoxycyclohexyl)-ethenyl]-benzene
4-difluoromethoxy-[2-(trans-4-ethoxycyclohexyl)-ethenyl]-benzene
10 4-difluoromethoxy-[2-(trans-4-propoxycyclohexyl)-ethenyl]-benzene
4-difluoromethoxy-[2-(trans-4-butoxycyclohexyl)-ethenyl]-benzene
4-difluoromethoxy-[2-(trans-4-pentoxycyclohexyl)-ethenyl]-benzene
15 4-difluoromethoxy-[2-(trans-4-hexoxycyclohexyl)-ethenyl]-benzene
4-difluoromethoxy-[2-(trans-4-heptoxycyclohexyl)-ethenyl]-benzene
20 4-difluoromethoxy-[2-(trans-4-octoxycyclohexyl)-ethenyl]-benzene
4-difluoromethoxy-[2-(trans-4-nonoxycyclohexyl)-ethenyl]-benzene
4-difluoromethoxy-[2-(trans-4-decoxycyclohexyl)-ethenyl]-benzene
25 benzene

Example 8

- 4-{2-[4-1H,1H-Difluoroethoxy)-phenyl]-ethyl}-4'-pentyl
trans,trans-bicyclohexyl
- 10 g of Pd/C (5% Pd) are added to a solution of
30 16.8 g of product 7b in 150 ml of ethyl acetate, and the mixture is hydrogenated at room temperature and atmospheric pressure. The catalyst is filtered off, the filtrate is evaporated, and the residue is recrystallized from ethanol. Colourless crystals are obtained.
- 35 The following are prepared analogously:
4-{2-[4-1H,1H-difluoroethoxy)-phenyl]-ethyl}-4'-ethyl
trans,trans-bicyclohexyl

- 4-{2-[4-1H,1H-difluoroethoxy)-phenyl]-ethyl}-4'-propyl
trans,trans-bicyclohexyl
4-{2-[4-1H,1H-difluoroethoxy)-phenyl]-ethyl}-4'-butyl
trans,trans-bicyclohexyl
5 4-{2-[4-1H,1H-difluoroethoxy)-phenyl]-ethyl}-4'-hexyl
trans,trans-bicyclohexyl
4-{2-[4-1H,1H-difluoroethoxy)-phenyl]-ethyl}-4'-heptyl
trans,trans-bicyclohexyl
4-{2-[4-1H,1H-difluoroethoxy)-phenyl]-ethyl}-4'-octyl
10 trans,trans-bicyclohexyl
4-{2-[4-1H,1H-difluoroethoxy)-phenyl]-ethyl}-4'-nonyl
trans,trans-bicyclohexyl
4-{2-[4-1H,1H-difluoroethoxy)-phenyl]-ethyl}-4'-decyl
trans,trans-bicyclohexyl

15 Example 9

- a) 3-[4-(trans-4-Propylcyclohexyl)-phenyl]-propanoic
acid

A solution of 12.6 g of 3-[4-(trans-4-propyl-
cyclohexyl)-phenyl]-propenoic acid (obtained by condensa-
20 tion of 4-(trans-4-propylcyclohexyl)-benzaldehyde with
malonic acid in pyridine) in 120 ml of ethyl acetate is
hydrogenated at room temperature and atmospheric pres-
sure, using 4 g of Pd/C (5% Pd) as catalyst. The catalyst
is filtered off, and the filtrate is evaporated. Colour-
25 less crystals are obtained.

- b) 3-[4-(trans-4-Propylcyclohexyl)-phenyl]-propanol

A solution of 11.3 g of product 9a in 50 ml of
THF is added dropwise to a suspension maintained at 0°C
of 1.52 g of lithium alanate in 200 ml of THF. After
30 stirring at room temperature for 2 hours, the reaction
mixture is poured into water and acidified with 13% HCl.
The mixture is extracted with ether, the organic phase is
dried and evaporated. Colourless crystals are obtained.

- c) 3-[4-(trans-4-Propylcyclohexyl)-phenyl]-propanol

35 A solution of 7.2 g of dimethyl sulfoxide in
12 ml of dichloromethane is added dropwise to a solution
maintained at -75°C of 5.7 g of oxalyl chloride in 80 ml
of dichloromethane, and the mixture is stirred for 5

minutes. A solution of 10.3 g of product 9b in 20 ml of dichloromethane is then added dropwise, and the mixture is stirred for another 15 minutes. 28 ml of triethylamine are then added, the mixture is allowed to reach 0°C, and 100 ml of water and 200 ml of ether are added. The organic phase is separated off, washed with water and saturated NaCl solution, dried over Na₂SO₄ and evaporated. The residue is chromatographed through a silica gel column, using petroleum ether/ethyl acetate 8:2 as eluent. A colourless oil is obtained.

d) 1-(3,3-Difluoropropyl)-4-(trans-4-propylcyclohexyl)-benzene

A solution of 4.1 g of DAST in 50 ml of hexane is added dropwise to a solution of 7.9 g of product 9c in 100 ml of hexane, and the mixture is stirred at room temperature for 2 hours. 100 ml of water are added, and the organic phase is separated off, dried over Na₂SO₄ and evaporated. The residue is chromatographed through a silica gel column, using petroleum ether as eluent, and is distilled in a kugelrohr apparatus. A colourless liquid is obtained. m.p.: 12°C, c.p.: -60°C (extrapolated), $n_D^{20} = 0.032$, viscosity: 11.

The following are prepared analogously:

1-(3,3-difluoropropyl)-4-(trans-4-ethylcyclohexyl)-benzene

1-(3,3-difluoropropyl)-4-(trans-4-butylcyclohexyl)-benzene

1-(3,3-difluoropropyl)-4-(trans-4-pentylcyclohexyl)-benzene

1-(3,3-difluoropropyl)-4-(trans-4-hexylcyclohexyl)-benzene

1-(3,3-difluoropropyl)-4-(trans-4-heptylcyclohexyl)-benzene

1-(3,3-difluoropropyl)-4-(trans-4-octylcyclohexyl)-benzene

1-(3,3-difluoropropyl)-4-(trans-4-nonylcyclohexyl)-benzene

1-(3,3-difluoropropyl)-4-(trans-4-decylcyclohexyl)-benzene

Example 10

1H,1H-Difluoroethyl 4'-pentyl-trans,trans-bicyclohexane-4-carboxylate

5 A mixture of 36.5 g of 4'-pentyl-trans,trans-bicyclohexane-4-carboxylic acid and 50 ml of thionyl chloride is heated to boiling for 1 hour. Excess thionyl chloride is distilled off, 50 ml of toluene are added to the residue, and the mixture is transferred to a dropping funnel. This solution is added dropwise to a solution of
10 11.9 g of 2,2-difluoroethanol and 43.3 ml of pyridine in 100 ml of toluene. The reaction mixture is heated to boiling for 1 hour and then left to stand at room temperature for 18 hours. 100 ml of 2 N HCl are added, and the organic phase is separated off. The organic phase is
15 washed twice with water, dried over Na₂SO₄ and evaporated. The residue is taken up in 50 ml of THF and 50 ml of 5% aqueous ammonia, and the mixture is stirred for 1 hour. It is extracted with petroleum ether, the organic phase is dried over Na₂SO₄ and evaporated. The residue is
20 recrystallized from acetonitrile. Colourless crystals are obtained.

The following are prepared analogously:

- 1H,1H-difluoroethyl 4'-ethyl-trans,trans-bicyclohexane-4-carboxylate
- 25 1H,1H-difluoroethyl 4'-propyl-trans,trans-bicyclohexane-4-carboxylate
- 1H,1H-difluoroethyl 4'-butyl-trans,trans-bicyclohexane-4-carboxylate
- 1H,1H-difluoroethyl 4'-hexyl-trans,trans-bicyclohexane-4-carboxylate
- 30 1H,1H-difluoroethyl 4'-heptyl-trans,trans-bicyclohexane-4-carboxylate
- 1H,1H-difluoroethyl 4'-octyl-trans,trans-bicyclohexane-4-carboxylate
- 35 1H,1H-difluoroethyl 4'-nonyl-trans,trans-bicyclohexane-4-carboxylate
- 1H,1H-difluoroethyl 4'-decyl-trans,trans-bicyclohexane-4-carboxylate

- 1H,1H-difluoroethyl trans-4-(4-methylphenyl)-cyclohexane-carboxylate
- 1H,1H-difluoroethyl trans-4-(4-ethylphenyl)-cyclohexane-carboxylate
- 5 1H,1H-difluoroethyl trans-4-(4-propylphenyl)-cyclohexane-carboxylate
- 1H,1H-difluoroethyl trans-4-(4-butylphenyl)-cyclohexane-carboxylate
- 1H,1H-difluoroethyl trans-4-(4-pentylphenyl)-cyclohexane-carboxylate
- 10 1H,1H-difluoroethyl trans-4-(4-hexylphenyl)-cyclohexane-carboxylate
- 1H,1H-difluoroethyl trans-4-(4-heptylphenyl)-cyclohexane-carboxylate
- 15 1H,1H-difluoroethyl trans-4-(4-octylphenyl)-cyclohexane-carboxylate
- 1H,1H-difluoroethyl trans-4-(4-nonylphenyl)-cyclohexane-carboxylate
- 1H,1H-difluoroethyl trans-4-(4-decylphenyl)-cyclohexane-carboxylate
- 20 1H,1H-difluoroethyl trans-4-(4-methoxyphenyl)-cyclohexanecarboxylate
- 1H,1H-difluoroethyl trans-4-(4-ethoxyphenyl)-cyclohexane-carboxylate
- 25 1H,1H-difluoroethyl trans-4-(4-propoxyphenyl)-cyclohexanecarboxylate
- 1H,1H-difluoroethyl trans-4-(4-butoxyphenyl)-cyclohexane-carboxylate
- 1H,1H-difluoroethyl trans-4-(4-pentoxyphenyl)-cyclohexanecarboxylate
- 30 1H,1H-difluoroethyl trans-4-(3-fluoro-4-pentoxyphenyl)-cyclohexanecarboxylate
- 1H,1H-difluoroethyl trans-4-(4-hexoxyphenyl)-cyclohexane-carboxylate
- 35 1H,1H-difluoroethyl trans-4-(4-heptoxyphenyl)-cyclohexanecarboxylate
- 1H,1H-difluoroethyl trans-4-(4-octoxyphenyl)-cyclohexane-carboxylate
- 1H,1H-difluoroethyl trans-4-(4-nonoxyphehyl)-cyclohexane-

carboxylate

1H,1H-difluoroethyl trans-4-(4-decoxyphenyl)-cyclohexane-carboxylate

- 1H,1H-difluoroethyl-4-(trans-4-ethylcyclohexyl)-benzoate
5 1H,1H-difluoroethyl-4-(trans-4-propylcyclohexyl)-benzoate
1H,1H-difluoroethyl-4-(trans-4-butylcyclohexyl)-benzoate
1H,1H-difluoroethyl-4-(trans-4-pentylcyclohexyl)-benzoate
1H,1H-difluoroethyl-4-(trans-4-hexylcyclohexyl)-benzoate
1H,1H-difluoroethyl-4-(trans-4-heptylcyclohexyl)-benzoate
10 1H,1H-difluoroethyl-4-(trans-4-octylcyclohexyl)-benzoate
1H,1H-difluoroethyl-4-(trans-4-nonylcyclohexyl)-benzoate
1H,1H-difluoroethyl-4-(trans-4-decylcyclohexyl)-benzoate

Example 11

- a) 4-(trans-4-Formylcyclohexyl)-4'-pentylbiphenyl
15 112 ml of a 20% solution of DIBALH in hexane are added dropwise to a solution of 33.2 g of 4-(trans-4-cyanocyclohexyl)-4'-pentylbiphenyl in 1 l of pentane, and the mixture is stirred for 18 hours. Water is then added dropwise until the evolution of gas subsides and then 200
20 ml of 25% sulfuric acid are added dropwise. The organic phase is separated off, dried over Na₂SO₄ and evaporated. Colourless deliquescent crystals are obtained.
- b) 4-(trans-4-Difluoromethylcyclohexyl)-4'-pentylbiphenyl
25 A solution of 6.9 g of DAST in 10 ml of dichloromethane is added dropwise to a solution of 18.0 g of product 11a in 30 ml of dichloromethane at room temperature, and the mixture is stirred for 18 hours. 150 ml of water are added, the organic phase is separated off,
30 dried over Na₂SO₄ and evaporated. The residue is chromatographed through a silica gel column, using petroleum ether/ethyl acetate 95:5. Colourless crystals are obtained.

The following are prepared analogously:

- 35 4-(trans-4-difluoromethylcyclohexyl)-4'-ethylbiphenyl
4-(trans-4-difluoromethylcyclohexyl)-2',3'-difluoro-4'-propylbiphenyl

- 4-(trans-4-difluoromethylcyclohexyl)-4'-propylbiphenyl
4-(trans-4-difluoromethylcyclohexyl)-4'-butylbiphenyl
4-(trans-4-difluoromethylcyclohexyl)-4'-hexylbiphenyl
4-(trans-4-difluoromethylcyclohexyl)-4'-heptylbiphenyl
5 4-(trans-4-difluoromethylcyclohexyl)-4'-octylbiphenyl
4-(trans-4-difluoromethylcyclohexyl)-4'-nonylbiphenyl
4-(trans-4-difluoromethylcyclohexyl)-4'-decylbiphenyl
4-(trans-4-difluoromethylcyclohexyl)-4'-methoxybiphenyl
4-(trans-4-difluoromethylcyclohexyl)-4'-ethoxybiphenyl
10 4-(trans-4-difluoromethylcyclohexyl)-3'-cyano-4'-ethoxy-
biphenyl
4-(trans-4-difluoromethylcyclohexyl)-4'-propoxybiphenyl
4-(trans-4-difluoromethylcyclohexyl)-4'-butoxybiphenyl
4-(trans-4-difluoromethylcyclohexyl)-4'-pentoxybiphenyl
15 4-(trans-4-difluoromethylcyclohexyl)-4'-hexoxybiphenyl
4-(trans-4-difluoromethylcyclohexyl)-4'-heptoxybiphenyl
4-(trans-4-difluoromethylcyclohexyl)-4'-octoxybiphenyl
4-(trans-4-difluoromethylcyclohexyl)-4'-nonoxybiphenyl
4-(trans-4-difluoromethylcyclohexyl)-4'-decoxybiphenyl

20 Example 12

a) 4'-Propyl-trans,trans-bicyclohexane-4-carboxaldehyde

A solution of 59.6 g of 4-hydroxymethyl-4'-propyl-trans,trans-bicyclohexyl in 200 ml of dichloromethane is added dropwise to a suspension of 82.0 g of PCC in 400 ml of dichloromethane. After stirring for 2 hours, 200 ml of ether are added. The mixture is filtered, and the residue is washed with ether. The filtrate is evaporated, and the residue is chromatographed through a short silica gel column, using toluene as eluent. A colourless oil is obtained.

30 b) 4-Difluoromethyl-4'-propyl-trans,trans-bicyclohexyl

A solution of 2.7 ml of DAST in 30 ml of hexane is added dropwise to a solution of 4.9 g of product 12a in 100 ml of hexane at room temperature, and the mixture is stirred for 18 hours. 100 ml of water are added, the organic phase is separated off, dried over Na₂SO₄ and evaporated. The residue is chromatographed through a silica gel column, using petroleum ether as eluent: a colourless liquid is obtained. m.p.: 19°C, c.p.: 17°C, An

= 0.003, viscosity: 10.

The following are prepared analogously:

- 4-difluoromethyl-4'-ethyl-trans,trans-bicyclohexyl
- 4-difluoromethyl-4'-butyl-trans,trans-bicyclohexyl
- 5 4-difluoromethyl-4'-pentyl-trans,trans-bicyclohexyl
- m.p.: 29°C, c.p.: 32.1°C, $\Delta n = 0.0$, viscosity: 14
- 4-difluoromethyl-4'-hexyl-trans,trans-bicyclohexyl
- 4-difluoromethyl-4'-heptyl-trans,trans-bicyclohexyl
- 4-difluoromethyl-4'-octyl-trans,trans-bicyclohexyl
- 10 4-difluoromethyl-4'-nonyl-trans,trans-bicyclohexyl
- 4-difluoromethyl-4'-decyl-trans,trans-bicyclohexyl

Example 13

a) 1-Difluoromethoxy-4-iodobenzene

- 100 g (0.455 mol) of 4-iodophenol and 54.6 g
15 (1.365 mol) of sodium hydroxide are added to a mixture of
300 ml of THF and 30 ml of water. After stirring for
about 1/2 hour, the mixture is evaporated in a rotary
evaporator; this is repeated after the addition of 200 ml
of toluene. The residue is taken up in 400 ml of THF. The
20 mixture is cooled to 0°C, 47.1 g (0.545 mol) of chloro-
difluoromethane are introduced, and the mixture is then
stirred for 1 hour. It is then stirred at about +5°C for
18 hours. The solution above the resulting slurry-like
precipitate was decanted off. It was evaporated in a
25 rotary evaporator, and the residue was chromatographed
through a silica gel column, using petroleum ether as
eluent.

The following were prepared analogously:

- 1-difluoromethoxy-4-bromobenzene
- 30 1-difluoromethoxy-2-fluoro-4-bromobenzene
- b) 4-Difluoromethoxy-4'-(trans-4-pentylcyclohexyl)-tolan
- A solution of 15.3 g of 4-(trans-4-pentylcyclo-
hexyl)phenylacetylene (available from the acetophenone by
dehydration, using PCl_5/KOT), 16.2 g of difluoromethoxy-
35 4-iodobenzene, 100 ml of triethylamine, 0.085 g of bis-
(triphenylphosphine)dichloropalladium and 0.11 g of
copper(I) iodide is stirred at room temperature for 3
hours. The cloudy mixture is stirred into dilute

hydrochloric acid (500 ml of water + 200 ml of 37% hydrochloric acid), extracted with t-butyl methyl ether and worked up as usual. m.p.: 62°C, c.p.: 203.1°C

The following were prepared analogously:

- 5 4-difluoromethoxy-4'-(trans-4-methylcyclohexyl)-tolan
4-difluoromethoxy-4'-(trans-4-ethylcyclohexyl)-tolan
4-difluoromethoxy-4'-(trans-4-propylcyclohexyl)-tolan,
m.p.: 87°C, c.p.: 212°C
4-difluoromethoxy-4'-(trans-4-butylcyclohexyl)-tolan
- 10 4-difluoromethoxy-4'-(trans-4-pentylcyclohexyl)-tolan
4-difluoromethoxy-4'-(trans-4-hexylcyclohexyl)-tolan
4-difluoromethoxy-4'-(trans-4-heptylcyclohexyl)-tolan
4-difluoromethoxy-4'-(trans-4-octylcyclohexyl)-tolan
4-difluoromethoxy-4'-(trans-4-nonylcyclohexyl)-tolan
- 15 4-difluoromethoxy-4'-(trans-4-decylcyclohexyl)-tolan
- 4-difluoromethoxy-4'-[2-(trans-4-methylcyclohexyl)-ethyl]-tolan
4-difluoromethoxy-4'-[2-(trans-4-ethylcyclohexyl)-ethyl]-tolan
- 20 4-difluoromethoxy-4'-[2-(trans-4-propylcyclohexyl)-ethyl]-tolan
4-difluoromethoxy-4'-[2-(trans-4-butylcyclohexyl)-ethyl]-tolan
4-difluoromethoxy-4'-[2-(trans-4-pentylcyclohexyl)-ethyl]-tolan
- 25 4-difluoromethoxy-4'-[2-(trans-4-hexylcyclohexyl)-ethyl]-tolan
4-difluoromethoxy-4'-[2-(trans-4-heptylcyclohexyl)-ethyl]-tolan
- 30 4-difluoromethoxy-4'-[2-(trans-4-octylcyclohexyl)-ethyl]-tolan
4-difluoromethoxy-4'-[2-(trans-4-nonylcyclohexyl)-ethyl]-tolan
4-difluoromethoxy-4'-[2-(trans-4-decylcyclohexyl)-ethyl]-tolan
- 35 4-difluoromethoxy-4'-methyl-tolan
4-difluoromethoxy-4'-ethyl-tolan

4-difluoromethoxy-4'-propyl-tolan

m.p.: 50°C, c.p. (extrapolated): 10°C, viscosity: 7

4-difluoromethoxy-4'-butyl-tolan

4-difluoromethoxy-4'-pentyl-tolan

5 4-difluoromethoxy-4'-hexyl-tolan

4-difluoromethoxy-4'-heptyl-tolan

4-difluoromethoxy-4'-octyl-tolan

4-difluoromethoxy-4'-nonyl-tolan

4-difluoromethoxy-4'-decyl-tolan

10 Using 4-(difluoromethylthio)-iodobenzene
(obtainable by chlorosulfonation of iodobenzene, reduction to the 4-mercaptoiodobenzene, using zinc in dilute hydrochloric acid, and etherification analogously to Example 1), the following were prepared analogously:

15 4-difluoromethylthio-4'-(trans-4-methylcyclohexyl)-tolan

4-difluoromethylthio-4'-(trans-4-ethylcyclohexyl)-tolan

4-difluoromethylthio-4'-(trans-4-propylcyclohexyl)-tolan

4-difluoromethylthio-4'-(trans-4-butylcyclohexyl)-tolan

4-difluoromethylthio-4'-(trans-4-pentylcyclohexyl)-tolan

20 4-difluoromethylthio-4'-(trans-4-hexylcyclohexyl)-tolan

4-difluoromethylthio-4'-(trans-4-heptylcyclohexyl)-tolan

4-difluoromethylthio-4'-(trans-4-octylcyclohexyl)-tolan

4-difluoromethylthio-4'-(trans-4-nonylcyclohexyl)-tolan

4-difluoromethylthio-4'-(trans-4-decylcyclohexyl)-tolan

25 Example 14

4-(2,2-Difluoroethyl)-4'-pentyl-trans,trans-bicyclohexyl

13 g of 4-(2-oxoethyl)-4'-pentyl-trans,trans-bicyclohexyl (available from bicyclohexanecarboxylic acid, reduction to the alcohol, conversion to the nitrile and conversion to the aldehyde with DIBALH) are dissolved in 100 ml of hexane. At room temperature, a solution of 6.2 ml of DAST in 100 ml of hexane is added dropwise, and stirring of the mixture at room temperature is continued for 10 hours. It is then worked up as usual. m.p.: -1°C,
35 c.p.: 82°C, $\eta_{sp}/c = 0.040$, viscosity: 11

The following were prepared analogously:

4-(2,2-difluoroethyl)-4'-methyl-trans,trans-bicyclohexyl

4-(2,2-difluoroethyl)-4'-ethyl-trans,trans-bicyclohexyl

- 4-(2,2-difluoroethyl)-4'-propyl-trans,trans-bicyclohexyl
4-(2,2-difluoroethyl)-4'-butyl-trans,trans-bicyclohexyl
4-(2,2-difluoroethyl)-4'-hexyl-trans,trans-bicyclohexyl
4-(2,2-difluoroethyl)-4'-heptyl-trans,trans-bicyclohexyl
5 4-(2,2-difluoroethyl)-4'-octyl-trans,trans-bicyclohexyl
4-(2,2-difluoroethyl)-4'-nonyl-trans,trans-bicyclohexyl
4-(2,2-difluoroethyl)-4'-decyl-trans,trans-bicyclohexyl

Example 15

- 1-(4-Ethoxyphenyl)-2-(4'-difluoromethoxyphenyl)-ethene
10 22.2 g of 4-ethoxystyrene, 33.5 g of 4-(difluoro-
methoxy)bromobenzene (available from 4-bromophenol
analogously to Example 1)), 0.67 g of palladium(II)
acetate, 20.8 ml of triethylamine and 1.83 g of tri-o-
15 tolylphosphine are heated to boiling in 225 ml of aceto-
nitrile for 24 hours. After cooling to 0°C, the crystals
are filtered off with suction and washed with aceto-
nitrile and water. m.p.: 177°C

The following were prepared analogously:

- 1-(4-methoxyphenyl)-2-(4'-difluoromethoxyphenyl)-ethene
20 1-(4-propoxyphenyl)-2-(4'-difluoromethoxyphenyl)-ethene
1-(4-butoxyphenyl)-2-(4'-difluoromethoxyphenyl)-ethene
1-(4-pentoxyphenyl)-2-(4'-difluoromethoxyphenyl)-ethene
1-(4-hexoxyphenyl)-2-(4'-difluoromethoxyphenyl)-ethene
1-(4-heptoxyphenyl)-2-(4'-difluoromethoxyphenyl)-ethene
25 1-(4-octoxyphenyl)-2-(4'-difluoromethoxyphenyl)-ethene
1-(4-nonoxyphenyl)-2-(4'-difluoromethoxyphenyl)-ethene
1-(4-decoxyphenyl)-2-(4'-difluoromethoxyphenyl)-ethene

1-[4-(trans-4-methylcyclohexyl)-phenyl]-2-(4'-difluoro-
methoxyphenyl)-ethene
30 1-[4-(trans-4-ethylcyclohexyl)-phenyl]-2-(4'-difluoro-
methoxyphenyl)-ethene
1-[4-(trans-4-propylcyclohexyl)-phenyl]-2-(4'-difluoro-
methoxyphenyl)-ethene
1-[4-(trans-4-butylcyclohexyl)-phenyl]-2-(4'-difluoro-
35 methoxyphenyl)-ethene
1-[4-(trans-4-pentylcyclohexyl)-phenyl]-2-(4'-difluoro-
methoxyphenyl)-ethene

- 1-[4-(trans-4-hexylcyclohexyl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethene
1-[4-(trans-4-heptylcyclohexyl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethene
5 1-[4-(trans-4-octylcyclohexyl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethene
1-[4-(trans-4-nonylcyclohexyl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethene
1-[4-(trans-4-decylcyclohexyl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethene
10

1-[4-(5-methyl-1,3-pyrimidin-2-yl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethene
1-[4-(5-ethyl-1,3-pyrimidin-2-yl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethene
15 1-[4-(5-propyl-1,3-pyrimidin-2-yl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethene
1-[4-(5-butyl-1,3-pyrimidin-2-yl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethene
1-[4-(5-pentyl-1,3-pyrimidin-2-yl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethene
20 1-[4-(5-hexyl-1,3-pyrimidin-2-yl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethene
1-[4-(5-heptyl-1,3-pyrimidin-2-yl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethene
25 1-[4-(5-octyl-1,3-pyrimidin-2-yl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethene
1-[4-(5-nonyl-1,3-pyrimidin-2-yl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethene
1-[4-(5-decyl-1,3-pyrimidin-2-yl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethene
30

Example 16

1-(4-Ethoxyphenyl)-2-(4'-difluoromethoxyphenyl)-ethane

- 19.7 g of 1-(4-ethoxyphenyl)-2-(4'-difluoromethoxyphenyl)-ethene are hydrogenated in 150 ml of THF
35 analogously to Example 6b, using 6 g of Pd/C (5% Pd) as catalyst. m.p.: 37°C, $\Delta n = 0.103$, viscosity: 8

The following were prepared analogously:

- 1-(4-methoxyphenyl)-2-(4'-difluoromethoxyphenyl)-ethane
1-(4-propoxyphenyl)-2-(4'-difluoromethoxyphenyl)-ethane
1-(4-butoxyphenyl)-2-(4'-difluoromethoxyphenyl)-ethane
1-(4-pentoxyphenyl)-2-(4'-difluoromethoxyphenyl)-ethane
5 1-(4-hexoxyphenyl)-2-(4'-difluoromethoxyphenyl)-ethane
1-(4-heptoxyphenyl)-2-(4'-difluoromethoxyphenyl)-ethane
1-(4-octoxyphenyl)-2-(4'-difluoromethoxyphenyl)-ethane
1-(4-nonoxyphenyl)-2-(4'-difluoromethoxyphenyl)-ethane
1-(4-decoxyphenyl)-2-(4'-difluoromethoxyphenyl)-ethane
- 10 1-(4-methylphenyl)-2-(4-difluoromethoxybiphenyl-4'-yl)-
ethane
1-(4-ethylphenyl)-2-(4-difluoromethoxybiphenyl-4'-yl)-
ethane
1-(4-propylphenyl)-2-(4-difluoromethoxybiphenyl-4'-yl)-
15 ethane
1-(4-butylphenyl)-2-(4-difluoromethoxybiphenyl-4'-yl)-
ethane
1-(4-pentylphenyl)-2-(4-difluoromethoxybiphenyl-4'-yl)-
ethane
- 20 1-(4-hexylphenyl)-2-(4-difluoromethoxybiphenyl-4'-yl)-
ethane
1-(4-heptylphenyl)-2-(4-difluoromethoxybiphenyl-4'-yl)-
ethane
1-(4-octylphenyl)-2-(4-difluoromethoxybiphenyl-4'-yl)-
25 ethane
1-(4-nonylphenyl)-2-(4-difluoromethoxybiphenyl-4'-yl)-
ethane
1-(4-decylphenyl)-2-(4-difluoromethoxybiphenyl-4'-yl)-
ethane
- 30 1-(4-methoxyphenyl)-2-(4-difluoromethoxybiphenyl-4'-yl)-
ethane
1-(4-ethoxyphenyl)-2-(4-difluoromethoxybiphenyl-4'-yl)-
ethane, m.p.: 153°, c.p. (extrapolated): 110°, Δn : 0.118
1-(4-propoxyphenyl)-2-(4-difluoromethoxybiphenyl-4'-yl)-
35 ethane
1-(4-butoxyphenyl)-2-(4-difluoromethoxybiphenyl-4'-yl)-
ethane

- 1-(4-pentoxyphenyl)-2-(4-difluoromethoxybiphenyl-4'-yl)-ethane
1-(4-hexoxyphenyl)-2-(4-difluoromethoxybiphenyl-4'-yl)-ethane
5 1-(4-heptoxyphenyl)-2-(4-difluoromethoxybiphenyl-4'-yl)-ethane
1-(4-octoxyphenyl)-2-(4-difluoromethoxybiphenyl-4'-yl)-ethane
10 1-(4-nonoxyphenyl)-2-(4-difluoromethoxybiphenyl-4'-yl)-ethane
1-(4-decoxyphenyl)-2-(4-difluoromethoxybiphenyl-4'-yl)-ethane
- 1-[4-(trans-4-methylcyclohexyl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethane
15 1-[4-(trans-4-ethylcyclohexyl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethane
1-[4-(trans-4-propylcyclohexyl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethane, m.p.: 51°C, c.p.: 79.6°C, $\Delta n = 0.125$
20 1-[4-(trans-4-butylcyclohexyl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethane
1-[4-(trans-4-pentylcyclohexyl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethane, m.p.: 32°C, c.p.: 90.2°C, $\Delta n = 0.123$
25 1-[4-(trans-4-hexylcyclohexyl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethane
1-[4-(trans-4-heptylcyclohexyl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethane
1-[4-(trans-4-octylcyclohexyl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethane
30 1-[4-(trans-4-nonylcyclohexyl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethane
1-[4-(trans-4-decylcyclohexyl)-phenyl]-2-(4'-difluoromethoxyphenyl)-ethane
- 35 1-[4-(trans-4-methylcyclohexyl)-phenyl]-2-(4'-difluoromethylthiophenyl)-ethane
1-[4-(trans-4-ethylcyclohexyl)-phenyl]-2-(4'-difluoro-

- methylthiophenyl)-ethane
1-[4-(trans-4-propylcyclohexyl)-phenyl]-2-(4'-difluoro-
methylthiophenyl)-ethane
1-[4-(trans-4-butylcyclohexyl)-phenyl]-2-(4'-difluoro-
5 methylthiophenyl)-ethane
1-[4-(trans-4-pentylcyclohexyl)-phenyl]-2-(4'-difluoro-
methylthiophenyl)-ethane
1-[4-(trans-4-hexylcyclohexyl)-phenyl]-2-(4'-difluoro-
methylthiophenyl)-ethane
10 1-[4-(trans-4-heptylcyclohexyl)-phenyl]-2-(4'-difluoro-
methylthiophenyl)-ethane
1-[4-(trans-4-octylcyclohexyl)-phenyl]-2-(4'-difluoro-
methylthiophenyl)-ethane
1-[4-(trans-4-nonylcyclohexyl)-phenyl]-2-(4'-difluoro-
15 methylthiophenyl)-ethane
1-[4-(trans-4-decylcyclohexyl)-phenyl]-2-(4'-difluoro-
methylthiophenyl)-ethane

1-[4-(5-methyl-1,3-pyrimidin-2-yl)-phenyl]-2-(4'-di-
fluoromethoxyphenyl)-ethane
20 1-[4-(5-ethyl-1,3-pyrimidin-2-yl)-phenyl]-2-(4'-difluoro-
methoxyphenyl)-ethane
1-[4-(5-propyl-1,3-pyrimidin-2-yl)-phenyl]-2-(4'-di-
fluoromethoxyphenyl)-ethane
1-[4-(5-butyl-1,3-pyrimidin-2-yl)-phenyl]-2-(4'-difluoro-
25 methoxyphenyl)-ethane
1-[4-(5-pentyl-1,3-pyrimidin-2-yl)-phenyl]-2-(4'-di-
fluoromethoxyphenyl)-ethane
1-[4-(5-hexyl-1,3-pyrimidin-2-yl)-phenyl]-2-(4'-difluoro-
methoxyphenyl)-ethane
30 1-[4-(5-heptyl-1,3-pyrimidin-2-yl)-phenyl]-2-(4'-di-
fluoromethoxyphenyl)-ethane
1-[4-(5-octyl-1,3-pyrimidin-2-yl)-phenyl]-2-(4'-difluoro-
methoxyphenyl)-ethane
1-[4-(5-nonyl-1,3-pyrimidin-2-yl)-phenyl]-2-(4'-difluoro-
35 methoxyphenyl)-ethane
1-[4-(5-decyl-1,3-pyrimidin-2-yl)-phenyl]-2-(4'-difluoro-
methoxyphenyl)-ethane

Example 17

4-(trans-4-Propylcyclohexyl)-phenyl 4-difluoromethoxybenzoate

4-Difluoromethoxybenzoic acid (available by
5 etherification of the phenolic OH group of p-hydroxybenzyl alcohol analogously to Example 1, followed by oxidation with potassium permanganate) is esterified, as described in Example 5b), with 4-(trans-4-propylcyclohexyl)-phenol by the DCC method. m.p.: 104°C, c.p.:
10 193.5°C.

The following were prepared analogously:

	4-(trans-4-methylcyclohexyl)-phenyl	4-difluoromethoxybenzoate
	4-(trans-4-ethylcyclohexyl)-phenyl	4-difluoromethoxybenzoate
15	4-(trans-4-butylcyclohexyl)-phenyl	4-difluoromethoxybenzoate
	4-(trans-4-pentylcyclohexyl)-phenyl	4-difluoromethoxybenzoate
20	4-(trans-4-hexylcyclohexyl)-phenyl	4-difluoromethoxybenzoate
	4-(trans-4-heptylcyclohexyl)-phenyl	4-difluoromethoxybenzoate
	4-(trans-4-nonylcyclohexyl)-phenyl	4-difluoromethoxybenzoate
25	4-(trans-4-octylcyclohexyl)-phenyl	4-difluoromethoxybenzoate
	4-(trans-4-decylcyclohexyl)-phenyl	4-difluoromethoxybenzoate
30	4-methylphenyl-4-difluoromethoxybenzoate	
	4-ethylphenyl-4-difluoromethoxybenzoate	
	4-propylphenyl-4-difluoromethoxybenzoate	
	4-butylphenyl-4-difluoromethoxybenzoate	
	4-pentylphenyl-4-difluoromethoxybenzoate	
35	4-hexylphenyl-4-difluoromethoxybenzoate	
	4-heptylphenyl-4-difluoromethoxybenzoate	
	4-octylphenyl-4-difluoromethoxybenzoate	
	4-nonylphenyl-4-difluoromethoxybenzoate	

4-decylphenyl-4-difluoromethoxybenzoate

- 4'-methylbiphenyl-4-yl 4-difluoromethoxybenzoate
4'-ethylbiphenyl-4-yl 4-difluoromethoxybenzoate
4'-propylbiphenyl-4-yl 4-difluoromethoxybenzoate
5 4'-butylbiphenyl-4-yl 4-difluoromethoxybenzoate
4'-pentylbiphenyl-4-yl 4-difluoromethoxybenzoate
4'-hexylbiphenyl-4-yl 4-difluoromethoxybenzoate
4'-heptylbiphenyl-4-yl 4-difluoromethoxybenzoate
4'-octylbiphenyl-4-yl 4-difluoromethoxybenzoate
10 4'-nonylbiphenyl-4-yl 4-difluoromethoxybenzoate
4'-decylbiphenyl-4-yl 4-difluoromethoxybenzoate

Using 4-difluoromethylthiobenzoic acid (available from p-toluenesulfonic acid by oxidation to give the carboxylic acid, esterification, conversion to the sulfonyl chloride, reduction, using zinc/hydrochloric acid, etherification analogously to Example 1 and liberation of the acid), the following are obtained analogously:

- | | | |
|----|---|-------------------|
| 20 | 4-(trans-4-methylcyclohexyl)-phenyl
thiobenzoate | 4-difluoromethyl- |
| | 4-(trans-4-ethylcyclohexyl)-phenyl
thiobenzoate | 4-difluoromethyl- |
| | 4-(trans-4-propylcyclohexyl)-phenyl
thiobenzoate | 4-difluoromethyl- |
| 25 | 4-(trans-4-butylcyclohexyl)-phenyl
thiobenzoate | 4-difluoromethyl- |
| | 4-(trans-4-pentylcyclohexyl)-phenyl
thiobenzoate | 4-difluoromethyl- |
| | 4-(trans-4-hexylcyclohexyl)-phenyl
thiobenzoate | 4-difluoromethyl- |
| 30 | 4-(trans-4-heptylcyclohexyl)-phenyl
thiobenzoate | 4-difluoromethyl- |
| | 4-(trans-4-octylcyclohexyl)-phenyl
thiobenzoate | 4-difluoromethyl- |
| 35 | 4-(trans-4-nonylcyclohexyl)-phenyl
thiobenzoate | 4-difluoromethyl- |
| | 4-(trans-4-decylcyclohexyl)-phenyl
thiobenzoate | 4-difluoromethyl- |

The following examples refer to liquid-crystalline phases according to the invention.

Example A:

A liquid-crystalline phase consisting of:

- 5 10% of p-trans-4-propylcyclohexylbenzonitrile
 10% of p-trans-4-butylcyclohexylbenzonitrile
 10% of p-trans-4-pentylcyclohexylbenzonitrile
 20% of difluoromethoxy-4-(trans-4-pentylcyclohexyl)-
 benzene
- 10 10% of trans-1-p-ethoxyphenyl-4-propylcyclohexane
 8% of trans-1-p-butoxyphenyl-4-propylcyclohexane
 5% of 4'-p-propylphenyl trans-4-(trans-4-propylcyclo-
 hexyl)-cyclohexanecarboxylate
 5% of 4'-p-pentylphenyl trans-4-(trans-4-propylcyclo-
15 hexyl)-cyclohexanecarboxylate
 5% of 4'-p-propylphenyl trans-4-(trans-4-butylcyclo-
 hexyl)-cyclohexanecarboxylate
 5% of 4'-p-pentylphenyl trans-4-(trans-4-butylcyclo-
 hexyl)-cyclohexanecarboxylate
- 20 4% of 4-(trans-4-propylcyclohexyl)-2'-fluoro-4'-(trans-
 4-propylcyclohexyl)-biphenyl
 4% of 2-fluoro-4-(trans-4-pentylcyclohexyl)-4'-(trans-4-
 propylcyclohexyl)biphenyl
 and
- 25 4% of 4-(trans-4-pentylcyclohexyl)-2'-fluoro-4'-(trans-
 4-pentylcyclohexyl)-biphenyl
- has a melting point of -18.8°C, a clear point of 78°C and
a viscosity of 16 mm²/s at 20°C.

Example B:

- 30 A liquid-crystalline phase consisting of
 15% of difluoromethoxy-4-(trans-4-propylcyclohexyl)-
 benzene
 17% of difluoromethoxy-4-(trans-4-pentylcyclohexyl)-
 benzene
- 35 13% of difluoromethoxy-4-(trans-4-heptylcyclohexyl)-
 benzene
 10% of trans-1-p-methoxyphenyl-4-propylcyclohexane

10% of trans-1-p-ethoxyphenyl-4-propylcyclohexane
5% of trans-1-p-butoxyphenyl-4-propylcyclohexane
5% of 4-(trans-4-propylcyclohexyl)-2'-fluoro-4'-(trans-4-propylcyclohexyl)-biphenyl
5 5% of 2-fluoro-4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-biphenyl
5% of 4-(trans-4-pentylcyclohexyl)-2'-fluoro-4'-(trans-4-pentylcyclohexyl)-biphenyl
5% of 4,4'-bis-(trans-4-propylcyclohexyl)-biphenyl
10 5% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-biphenyl
and
5% of 4,4'-bis-(trans-4-pentylcyclohexyl)-biphenyl
has a melting point of -20.8°C, a clear point of 72°C and
15 a viscosity of 12 mm²/s at 20°C.

Example C:

A liquid-crystalline phase consisting of
16% of p-trans-4-propylcyclohexyl-benzonitrile
4% of p-trans-4-pentylcyclohexyl-benzonitrile
20 18% of 1-(3,3-difluoropropyl)-4-(trans-4-propylcyclohexyl)-benzene
10% of trans-1-p-methoxyphenyl-4-propylcyclohexane
10% of trans-1-p-ethoxyphenyl-4-propylcyclohexane
11% of 4-ethyl-4'-(trans-4-propylcyclohexyl)-biphenyl
25 11% of 4-ethyl-4'-(trans-4-pentylcyclohexyl)-biphenyl
3% of 4-(trans-4-propylcyclohexyl)-2'-fluoro-4'-(trans-4-propylcyclohexyl)-biphenyl
4% of 2-fluoro-4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-biphenyl
30 3% of 4-(trans-4-pentylcyclohexyl)-2'-fluoro-4'-(trans-4-pentylcyclohexyl)-biphenyl
3% of 4,4'-bis-(trans-4-propylcyclohexyl)-biphenyl
4% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-biphenyl and
35 3% of 4,4'-bis-(trans-4-pentylcyclohexyl)-biphenyl
has a melting point of -10.3°C, a clear point of 91°C and
a viscosity of 17 mm²/s at 20°C.

Example D:

A liquid-crystalline phase consisting of
 24% of p-trans-4-propylcyclohexyl-benzonitrile
 36% of p-trans-4-pentylcyclohexyl-benzonitrile
 5 25% of p-trans-4-heptylcyclohexyl-benzonitrile
 15% of 4-cyano-4'-(trans-4-pentylcyclohexyl)-biphenyl
 has a clear point of 71°C, a Δn of 0.140 and a viscosity
 of 28.

10 This phase is mixed with 10% of one of the
 following compounds I according to the invention. The
 values of this phase according to the invention obtained
 are summarized in Table 1 below.

Compounds I

- 1 4-difluoromethoxy-4'-octoxy-biphenyl
- 15 2 difluoromethoxy-4-(trans-4-propylcyclohexyl)-benzene
- 3 difluoromethoxy-4-(trans-4-pentylcyclohexyl)-benzene
- 4 4-[2-(4-difluoromethoxyphenyl)-ethyl]-4'-pentyl-
trans,trans-bicyclohexyl
- 5 difluoromethoxy-4-(5-heptyl-1,3-pyrimidin-2-yl)-
20 benzene
- 6 4-difluoromethoxy-4'-(trans-4-pentylcyclohexyl)-
biphenyl

Table 1

	I	c.p. [°C]	Δn	Viscosity
25	1	65.4	0.1349	26.8
	2	60.2	0.1291	23.8
	3	61.8	0.1313	24.5
	4	76.7	0.1353	27.4
30	5	63.7	0.1368	26.7
	6	76.1	0.1411	28.2

Example E:

A liquid-crystalline phase consisting of
 22% of trans-1-p-ethylphenyl-4-propylcyclohexane
 35 20% of trans-1-p-methoxyphenyl-4-propylcyclohexane
 15% of trans-1-p-ethoxyphenyl-4-propylcyclohexane
 19% of 4-ethyl-4'-(trans-4-propylcyclohexyl)-biphenyl

14% of 4-ethyl-4'-(trans-4-pentylcyclohexyl)-biphenyl

5% of 4-(trans-4-propylcyclohexyl)-4'-(trans-4-propyl-
cyclohexyl)-biphenyl

5% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propyl-
cyclohexyl)-biphenyl

5

has a clear point of 72°C, a Δn of 0.1131 and a viscosity
of 11.

This phase is mixed with 10% of one of the
following compounds I according to the invention. The
10 values of this phase according to the invention obtained
are summarized in Table 2 below.

Compounds I

7 4-difluoromethoxyphenyl trans-4-pentyl-cyclohexane-
carboxylate

15 8 4-difluoromethoxyphenyl 4'-pentyl-trans,trans-bi-
cyclohexane-4-carboxylate

Table 2

	I	c.p. [°C]	Δn	Viscosity
20	7	67.8	0.1080	11,9
	8	82.7	0.1108	12.6



Patent Claims:

1. Difluoromethyl compounds of the formula I



in which

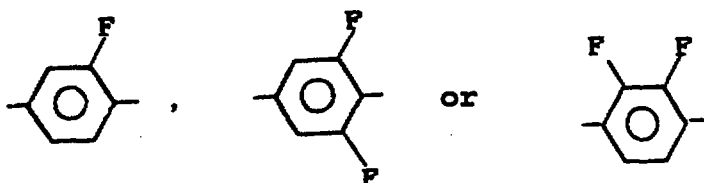
- 5 R is halogen, -CN, -NCS, a straight-chain alkyl or alkenyl radical having 1 to 15 carbon atoms, in which one or more CH₂ groups in these radicals, independently of one another, can each also be replaced by -O-, -S-, ,
10 -CO-, -CO-O-, -O-CO- or -O-CO-O- in such a manner that oxygen atoms are not directly linked to one another, or a straight-chain perfluoroalkyl radical, in which one or more fluorine atoms can also be replaced by H,
15 A¹ and A², independently of one another, are each a
 (a) trans-1,4-cyclohexylene radical in which one or more non-adjacent CH₂ groups can also be replaced by -O- and/or -S-,
 (b) 1,4-phenylene radical in which one or
20 two CH groups can also be replaced by N,
 (c) radical from the group consisting of 1,4-cyclohexenylene, 1,4-bicyclo[2,2,2]-octylene, piperidine-1,4-diyl, naphthalene-2,6-diyl, decahydronaphthalene-
25 2,6-diyl and 1,2,3,4-tetrahydronaphthalene-2,6-diyl,
 in which the radicals (a) and (b) can be substituted by CN or fluorine,
 Z¹ independently of one another are each -CO-O,
30 -O-CO-, -CH₂O-, -OCH₂-, -CH₂CH₂-,
 -CH=CH-, -C≡C- or a single bond,
 m is 1, 2 or 3 and
 Q is alkylene having 2 to 6 carbon atoms in which a CH₂ group can also be replaced by
35 -O-, -S-, -CO-O- or -O-CO-, -O-, -S-, -CH₂-,
 -CO-O-, -O-CO- or a single bond,



with the proviso that Q is alkylene having 2 to 6 carbon atoms in which one CH₂ group can also be replaced by -O-, -S-, -CO-O- or -O-CO-, -S-, -CH₂-, -CO-O-, -O-CO- or a single bond, provided R-(A¹-Z¹)_m-A²- is alkoxy--OOC--

5 or F₂HCO--COO--OOC-.

2. Difluoromethyl compounds of the formula I according to Claim 1, characterized in that A² is



3. Difluoromethyl compounds of the formula I according to Claim 1 or 2, characterized in that R is a
10 straight-chain alkyl radical having 2 to 7 carbon atoms.

4. Difluoromethyl compounds of the formula I according to at least one of Claims 1, 2 or 3, characterized in that Q is -O-.

15 5. Use of the compounds of the formula I as components of liquid-crystalline media.

6. Liquid-crystalline medium containing at least two liquid-crystalline components, characterized in that it contains at least one compound of the formula I.

20 7. Liquid crystal display element, characterized in that it contains a liquid-crystalline medium according to Claim 6.

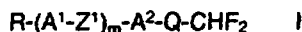
8. Electrooptical display element, characterized in that it contains a liquid-crystalline medium according to
25 Claim 6 as dielectric.



[As printed]

Claims

1. Difluoromethyl compounds of the formula I



in which

R

is halogen, -CN, -NCS, a straight-chain alkyl or alkenyl radical having 1 to 15 carbon atoms, in which one or more CH₂ groups in these radicals, independently of one another, can each also be replaced by -O-, -S-,



-CO-, -CO-O-, -O-CO- or -O-CO-O- in such a manner that oxygen atoms are not directly linked to one another, or a straight-chain perfluoroalkyl radical, in which one or more fluorine atoms can also be replaced by H,

A¹ and A²,

independently of one another, are each a

(a) trans-1,4-cyclohexylene radical in which one or more non-adjacent CH₂ groups can also be replaced by -O- and/or -S-,

(b) 1,4-phenylene radical in which one or two CH groups can also be replaced by N,

(c) radical from the group consisting of 1,4-cyclohexenylene, 1,4-bicyclo[2.2.2]octylene, piperidine-1,4-diyl, naphthalene-2,6-diyl, decahydronaphthalene-2,6-diyl and 1,2,3,4-tetrahydronaphthalene-2,6-diyl,

in which the radicals (a) and (b) can be substituted by CN or fluorine,

Z¹

independently of one another are each -CO-O-, -O-CO-, -CH₂O-, -OCH₂-, -CH₂CH₂-, -CH=CH-, -C≡C- or a single bond,

m

is 1, 2 or 3 and

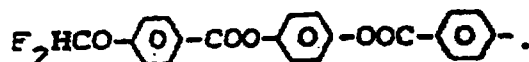
Q

is alkylene having 2 to 6 carbon atoms in which a CH₂ group can also be replaced by -O-, -S-, -CO-O- or -O-CO-, -O-, -S-, -CH₂-, -CO-O-, -O-CO- or a single bond,

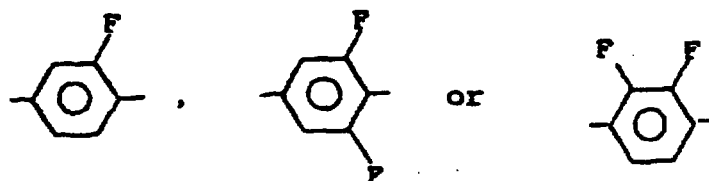
with the proviso that Q is alkylene having 2 to 6 carbon atoms in which one CH₂ group can also be replaced by -O-, -S-, -CO-O- or -O-CO-, -S-, -CH₂-, -CO-O-, -O-CO- or a single bond, provided R-(A¹-Z¹)_m-A²- is alkoxy-



or



2. Difluoromethyl compounds of the formula I according to Claim 1, characterized in that A² is



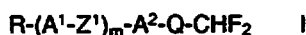


3. Difluoromethyl compounds of the formula I according to Claim 1 or 2, characterized in that R is a straight-chain alkyl radical having 2 to 7 carbon atoms.
4. Difluoromethyl compounds of the formula I according to at least one of Claims 1, 2 or 3, characterized in that Q is -O-.
5. Use of the compounds of the formula I as components of liquid-crystalline media.
6. Liquid-crystalline medium containing at least two liquid-crystalline components, characterized in that it contains at least one compound of the formula I.
7. Liquid crystal display element, characterized in that it contains a liquid-crystalline medium according to Claim 6.
8. Electrooptical display element, characterized in that it contains a liquid-crystalline medium according to Claim 6 as dielectric.

[As printed]

Revendications

1. Composés difluorométhylés de formule I



dans laquelle

R représente un halogène, un groupe -CN, -NCS, un groupe alkyle ou alcényle à chaîne droite ou ramifiée en C1-C15 dans lequel un ou plusieurs groupes CH₂ peuvent être remplacés, indépendamment les uns des autres, par -O-, -S-,



-CO-, -CO-O-, -O-CO- ou -O-CO-O- en sorte qu'il n'y ait pas de liaison directe entre des atomes d'oxygène, ou un groupe perfluoralkyle à chaîne droite dans lequel le fluor peut être remplacé partiellement par H,

A¹ et A² représentent chacun, indépendamment l'un de l'autre,

(a) un groupe trans-1,4-cyclohexylène dans lequel un ou plusieurs groupes CH₂ non voisins peuvent être remplacés par -O- et/ou -S-,

(b) un groupe 1,4-phénylène dans lequel un ou deux groupes CH peuvent être remplacés par N,

(c) un groupe choisi parmi les groupes 1,4-cyclohexénylène, 1,4-bicyclo(2,2,2)-octylène, pipéridine-1,4-diyle, naphthalène-2,6-diyle, décahydronaphtalène-2,6-diyle et 1,2,3,4-tétrahydronaphtalène-2,6-diyle,

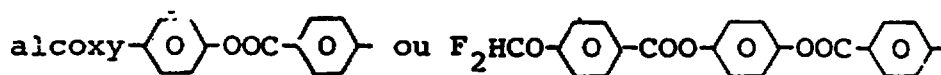
les groupes (a) et (b) peuvent être substitués par CN ou le fluor,

chacun des symboles Z¹ représente, indépendamment, -CO-O-, -O-CO-, -CH₂O-, -OCH₂-, -CH₂CH₂-, -CH=CH-, -C≡C- ou une liaison simple,

m est égal à 1, 2 ou 3,

Q représente un groupe alkylène en C2-C6 dans lequel un groupe CH₂ peut être remplacé par -O-, -S-, -CO-O- ou -O-CO-, un pont -O-, -S-, -CH₂-, -CO-O-, -O-CO- ou une liaison simple,

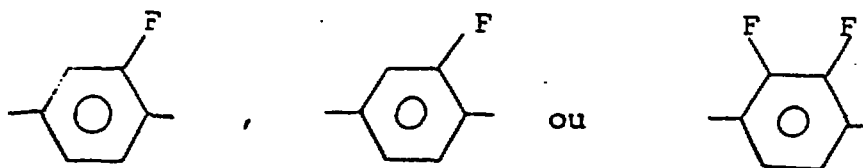
sous réserve que Q représente un groupe alkylène en C2-C6 dans lequel un groupe CH₂ peut être remplacé par -O-, -S-, -CO-O- ou -O-CO-, un pont -S-, -CH₂-, -CO-O-, -O-CO- ou une liaison simple lorsque R-(A¹-Z¹)_m-A² représente un groupe





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2. Composés difluorométhylés de formule I de la revendication 1, caractérisés en ce que A² représente



3. Composés difluorométhylés de formule I selon revendication 1 ou 2, caractérisés en ce que R représente un groupe alkyle à chaîne droite en C2-C7.
4. Composés difluorométhylés de formule I selon au moins une des revendications 1, 2 ou 3, caractérisés en ce que Q représente -O-.
5. Utilisation des composés de formule I en tant que composants de milieux à cristaux liquides.
6. Milieu à cristaux liquides à au moins deux composants à cristaux liquides, caractérisé en ce qu'il contient au moins un composé de formule I.
7. Élément d'affichage à cristaux liquides, caractérisé en ce qu'il contient un milieu à cristaux liquides selon revendication 6.
8. Élément d'affichage électro-optique caractérisé en ce qu'il contient en tant que diélectrique un milieu à cristaux liquides selon revendication 6.