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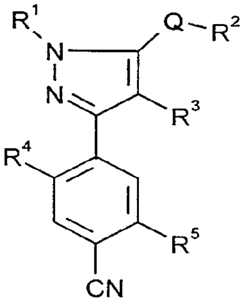
(54) **3-CYANOARYL-PYRAZOLES ET LEUR UTILISATION COMME HERBICIDES**
(54) **3-CYANOARYL PYRAZOLES AND USE THEREOF AS HERBICIDES**



(I)

(57) L'invention concerne de nouveaux 3-cyanoaryl-pyrazoles de formule générale (I), dans laquelle Q représente oxygène (O), soufre (S), SO ou SO$_2$; R^1 représente hydrogène ou l'un des radicaux suivants éventuellement substitués: alkyle, alcényle, alcynyle, cycloalkyle ou cycloalkylalkyle; R^2 représente hydrogène ou l'un des radicaux suivants éventuellement substitués: alkyle, alcényle, alcynyle, cycloalkyle ou cycloalkylalkyle; R^3 représente hydrogène, halogène ou alkyle éventuellement substitué; R^4 représente hydrogène ou halogène; et R^5 représente hydrogène, hydroxy, mercapto, amino, hydroxyamino, halogène ou l'un des radicaux suivants: -Q-R^6, -NH-R^6, -NH-O-R^6, -NH-SO$_2$-R^6, -N(SO$_2$-R^6)$_2$, -CQ^1-R^6, -CQ^1-Q^2-R^6,

(57) The invention relates to novel 3-cyanoaryl pyrazoles of the general formula (I) in which Q is oxygen (O), sulphur (S), SO or SO$_2$, R^1 is hydrogen or possibly substituted alkyl, alkenyl, alkinyl, cycloalkyl or cycloalkyl alkyl, R^2 is hydrogen or possibly substituted alkyl, alkenyl, alkinyl, cycloalkyl or cycloalkyl alkyl, R^3 is hydrogen, halogen or possibly substitued alkyl, R^4 is hydrogen or halogen, and R^5 is hydrogen, hydroxy, mercapto, amino, hydroxyamino, halogen or one of the radicals -Q-R^6, -NH-R^6, -NH-O-R^6, -NH-SO$_2$-R^6, -N(SO$_2$-R^6)$_2$, -CQ^1-R^6, -CQ^1-Q^2-R^6, -CQ^1-NH-R^6, -Q^2-CQ^1-R^6, -NH-CQ^1-R^6, -N(SO$_2$-R^6)(CQ^1-R^6),

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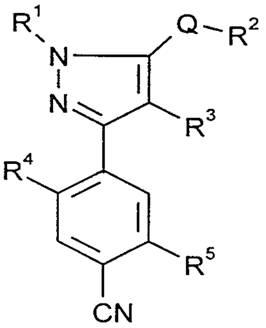
-CQ^1-NH-R^6, -Q^2-CQ^1-R^6, -NH-CQ^1-R^6, -N(SO$_2$-R^6)(CQ^1-R^6), -Q^2-CQ^1-Q^2-R^6, -NH-CQ^1-Q^2-R^6 ou -Q^2-CQ^1-NH-R^6, où Q^1 et Q^2 représente oxygène ou soufre, et R^6 représente l'un des radicaux suivants éventuellement substitués: alkyle, alcényle, alcynyle, cycloalkyle, cycloalkylalkyle, aryle, arylalkyle, hétérocyclyle ou hétérocyclylalkyle; les composés 1-méthyl-3-(4-cyano-2-fluorophényl)-4-chloro-5-difluorométhoxy-pyrazole, 1-méthyl-3-(4-cyano-2-fluorophényl)-4-bromo-5-difluorométhoxy-pyrazole, 1-méthyl-3-(4-cyano-2-fluoro-5-nitrophényl)-4-chloro-5-difluorométhoxy-pyrazole, 1-méthyl-3-(4-cyano-2-fluoro-5-éthylsulfonylaminophényl)-4-chloro-5-difluorométhoxy-pyrazole, 1-méthyl-3-(4-cyano-2-fluoro-5-éthoxycarbonylméthoxyphényl)-4-chloro-5-difluorométhoxy-pyrazole, 1-méthyl-3-(4-cyano-2-chlorophényl)-4-chloro-5-difluorométhoxy-pyrazole, 1-méthyl-3-(4-cyano-2-fluoro-5-méthylthiophényl)-4-chloro-5-difluorométhoxy-pyrazole, 1-méthyl-3-(4-cyano-2-fluoro-5-aminophényl)-4-chloro-5-difluorométhoxy-pyrazole, 1-méthyl-3-(4-cyano-2-fluoro-5-hydroxyphényl)-4-chloro-5-difluorométhoxy-pyrazole, 1-méthyl-3-(4-cyano-2-fluoro-5-chlorophényl)-4-chloro-5-difluorométhoxy-pyrazole, 1-méthyl-3-(4-cyano-2-fluoro-5-aminosulfonylphényl)-4-chloro-5-difluorométhoxy-pyrazole et 1-méthyl-3-(4-cyano-2-fluoro-5-fluorosulfonylphényl)-4-chloro-5-difluorométhoxy-pyrazole étant exclus par renonciation. L'invention concerne également un procédé pour la production desdits composés, de nouveaux produits intermédiaires et l'utilisation des 3-cyanoarylpyrazoles comme herbicides.

-Q^2-CQ^1-Q^2-R^6, -NH-CQ^1-Q^2-R^6 or -Q^2-CQ^1-NH-R^6 where Q^1 and Q^2 are oxygen or sulphur and R^6 is possibly substituted alkyl, alkenyl, alkinyl, cycloalkyl, cycloalkyl alkyl, aryl, arylalkyl, heterocyclyl or heterocyclyl alkyl, where the compounds 1-methyl-3-(4-cyano-2-fluoro-phenyl)-4-chloro-5-difluoro methoxy pyrazol, 1-methyl-3-(4-cyano-2-fluoro-phenyl)-4-bromo-5-difluoro methoxy pyrazol, 1-methyl-3-(4-cyano-2-fluoro-5-nitro-phenyl)-4-chloro-5-difluoro methoxy pyrazol, 1-methyl-3-(4-cyano-2-fluoro-5-ethyl sulphonylamino-phenyl)-4-chloro-5-difluoro methoxy pyrazol, 1-methyl-3-(4-cyano-2-fluoro-5-ethoxy carbonyl methoxy-phenyl)-4-chloro-5-difluoro methoxy pyrazol, 1-methyl-3-(4-cyano-2-chloro-phenyl)-4-chloro-5-difluoro methoxy pyrazol, 1-methyl-3-(4-cyano-2-chloro-5-methylthio-phenyl)-4-chloro-5-difluoro methoxy pyrazol, 1-methyl-3-(4-cyano-2-fluoro-5-amino-phenyl)-4-chloro-5-difluoro methoxy pyrazol, 1-methyl-3-(4-cyano-2-fluoro-5-hydroxy-phenyl)-4-chloro-5-difluoro methoxy pyrazol, 1-methyl-3-(4-cyano-2-fluoro-5-chloro-phenyl)-4-chloro-5-difluoro methoxy pyrazol, 1-methyl-3-(4-cyano-2-fluoro-5-aminosulphonyl-phenyl)-4-chloro-5-difluoro methoxy pyrazol and 1-methyl-3-(4-cyano-2-fluoro-5-fluoro-sulphonyl-phenyl)-4-chloro-5-difluoro methoxy pyrazol are excepted by disclaimer; process for their production, novel intermediate products and the use of the 3-cyanoaryl pyrazoles as herbicides.

3-Cyanoaryl-pyrazoles

Abstract

The invention relates to novel 3-cyanoaryl-pyrazoles of the general formula (I)



(I),

in which

Q represents oxygen (O), sulphur (S), SO or SO_2,

R^1 represents hydrogen or represents alkyl, alkenyl, alkinyl, cycloalkyl or cycloalkylalkyl, each of which is optionally substituted,

R^2 represents hydrogen or represents alkyl, alkenyl, alkinyl, cycloalkyl or cycloalkylalkyl, each of which is optionally substituted,

R^3 represents hydrogen, halogen or optionally substituted alkyl,

R^4 represents hydrogen or halogen and

R^5 represents hydrogen, hydroxyl, mercapto, amino, hydroxyamino, halogen, or represents one of the radicals $-Q-R^6$, $-NH-R^6$, $-NH-O-R^6$, $-NH-SO_2-R^6$, $-N(SO_2-R^6)_2$, $-CQ^1-R^6$, $-CQ^1-Q^2-R^6$, $-CQ^1-NH-R^6$, $-Q^2-CQ^1-R^6$, $-NH-CQ^1-R^6$, $-N(SO_2-R^6)(CQ^1-R^6)$, $-Q^2-CQ^1-Q^2-R^6$, $-NH-CQ^1-Q^2-R^6$ or $-Q^2-CQ^1-NH-R^6$,

where Q^1 and Q^2 each represent oxygen or sulphur and R^6 represents alkyl, alkenyl, alkinyl, cycloalkyl, cycloalkylalkyl, aryl, arylalkyl, heterocyclyl or heterocyclylalkyl, each of which is optionally substituted,

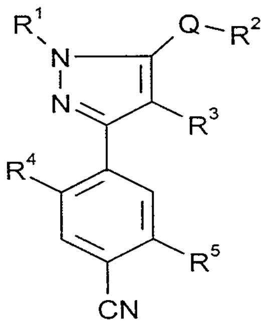
except for the compounds 1-methyl-3-(4-cyano-2-fluoro-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-phenyl)-4-bromo-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-nitro-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-ethylsulphonylamino-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-ethoxycarbonylmethoxy-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-chloro-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-methylthio-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-amino-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-hydroxy-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-chloro-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-aminosulphonyl-phenyl)-4-chloro-5-difluoromethoxy-pyrazole and 1-methyl-3-(4-cyano-2-fluoro-5-fluorosulphonyl-phenyl)-4-chloro-5-difluoromethoxy-pyrazole which are excluded by disclaimer, to processes for their preparation, to novel intermediates and to the use of the 3-cyanoarylpyrazoles as herbicides.

3-Cyanoaryl-pyrazoles

The invention relates to novel 3-cyanoaryl-pyrazoles, to processes for their preparation, to novel intermediates and to their use as herbicides.

It is known that certain substituted 3-aryl-pyrazoles have herbicidal properties (cf. EP 361114, EP 447055, WO 92/02509, WO 92/06962, WO 94/26109, WO 95/33728, WO 96/01255). However, the herbicidal activity and the crop plant safety of these compounds is not always entirely satisfactory.

This invention, accordingly, provides the novel 3-cyanoaryl-pyrazoles of the general formula (I)



(I),

in which

Q represents oxygen (O), sulphur (S), SO or SO_2,

R^1 represents hydrogen or represents alkyl, alkenyl, alkinyl, cycloalkyl or cycloalkylalkyl, each of which is optionally substituted,

R^2 represents hydrogen or represents alkyl, alkenyl, alkinyl, cycloalkyl or cycloalkylalkyl, each of which is optionally substituted,

R^3 represents hydrogen, halogen or optionally substituted alkyl,

R^4 represents hydrogen or halogen and

R^5 represents hydrogen, hydroxyl, mercapto, amino, hydroxyamino, halogen, or represents one of the radicals $-Q-R^6$, $-NH-R^6$, $-NH-O-R^6$, $-NH-SO_2-R^6$, $-N(SO_2-R^6)_2$, $-CQ^1-R^6$, $-CQ^1-Q^2-R^6$, $-CQ^1-NH-R^6$, $-Q^2-CQ^1-R^6$, $-NH-CQ^1-R^6$, $-N(SO_2-R^6)(CQ^1-R^6)$, $-Q^2-CQ^1-Q^2-R^6$, $-NH-CQ^1-Q^2-R^6$ or $-Q^2-CQ^1-NH-R^6$,

where Q^1 and Q^2 each represent oxygen or sulphur and R^6 represents alkyl, alkenyl, alkinyl, cycloalkyl, cycloalkylalkyl, aryl, arylalkyl, heterocyclyl or heterocyclylalkyl, each of which is optionally substituted,

except for the compounds 1-methyl-3-(4-cyano-2-fluoro-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-phenyl)-4-bromo-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-nitro-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-ethylsulphonylamino-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-ethoxycarbonylmethoxy-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-chloro-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-methylthio-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-amino-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-hydroxy-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-chloro-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-aminosulphonyl-phenyl)-4-chloro-5-difluoromethoxy-pyrazole and 1-methyl-3-(4-cyano-2-fluoro-5-fluorosulphonyl-phenyl)-4-chloro-5-difluoromethoxy-pyrazole (known from WO 96/01255), which are excluded by disclaimer.

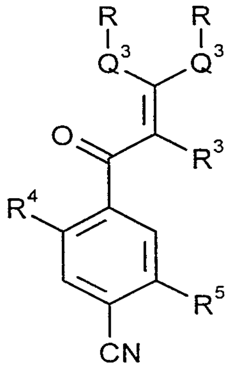
The novel 3-cyanoaryl-pyrazoles of the general formula (I) are obtained when hydrazine or derivatives thereof of the general formula (II)

$$H_2N-NH-R^1 \qquad (II),$$

in which

R^1 is as defined above

are reacted with cyanoarylcarbonyl compounds of the general formula (III)



(III),

in which

R^3, R^4 and R^5 are each as defined above,

Q^3 represents oxygen or sulphur and

R represents hydrogen or alkyl, preferably represents hydrogen or C_1-C_6-alkyl,

- and/or, if appropriate, tautomers of the compounds of the formula (III) -,

if appropriate in the presence of a diluent,

and, if appropriate, further conversions within the scope of the above definition of the substituents are carried out by customary methods on the resulting compounds of the formula (I).

The compounds of the general formula (I) can be converted by customary methods into other compounds of the general formula (I) in accordance with the above definition of the substituents, for example by customary alkylations, acylations or sulphonylations (for example R^2: H → CH_3, CHF_2, C_2H_5, $CH_2CH{=}CH_2$; R^5: OH → OCH_3, OC_2H_5,

$OCHF_2$, $OCH_2CH=CH_2$, $OCOCH_3$; SH → SCH_3, SC_2H_5; NH_2 → NHC_3H_7, $NHCOCH_3$, $NHSO_2CH_3$), by sulphurizations (for example QR^2: OH → SH), by oxidations (for example S → SO, SO_2) or by electrophilic or nucleophilic substitutions (for example R^3: H → Cl, Br; R^5: F → OH, SH, NH_2) - cf. also the Preparation Examples.

The novel 3-cyanoaryl-pyrazoles of the general formula (I) have strong herbicidal activity.

In the definitions, the saturated or unsaturated hydrocarbon radicals, such as alkyl, alkenyl or alkinyl, are in each case straight-chain or branched.

Halogen generally represents fluorine, chlorine, bromine or iodine, preferably represents fluorine, chlorine or bromine and in particular represents fluorine or chlorine.

The invention preferably provides compounds of the formula (I)

in which

Q represents oxygen (O), sulphur (S), SO or SO_2,

R^1 represents hydrogen, represents optionally cyano-, halogen- or C_1-C_4-alkoxy-substituted alkyl having 1 to 6 carbon atoms, represents alkenyl or alkinyl having in each case 2 to 6 carbon atoms and being in each case optionally substituted by halogen, or represents cycloalkyl or cycloalkylalkyl having in each case 3 to 6 carbon atoms in the cycloalkyl group and, if appropriate, 1 to 4 carbon atoms in the alkyl moiety and being in each case optionally substituted by cyano, halogen or C_1-C_4-alkyl,

R^2 represents hydrogen, represents optionally cyano-, halogen-, C_1-C_4-alkoxy- or C_1-C_4-alkylthio-substituted alkyl having 1 to 6 carbon atoms, represents alkenyl or alkinyl having in each case 2 to 6 carbon atoms and being in each case optionally substituted by halogen, or represents cycloalkyl or cycloalkylalkyl having in each case 3 to 6 carbon atoms in the cycloalkyl group and, if appropriate, 1 to 4 carbon atoms in the alkyl moiety and being in each case optionally substituted by cyano, halogen or C_1-C_4-alkyl,

R^3 represents hydrogen, halogen or optionally cyano-, halogen-, C_1-C_4-alkoxy- or C_1-C_4-alkylthio-substituted alkyl having 1 to 6 carbon atoms,

R^4 represents hydrogen or halogen and

R^5 represents hydrogen, hydroxyl, mercapto, amino, hydroxyamino, halogen, or represents one of the radicals $-Q-R^6$, $-NH-R^6$, $-NH-O-R^6$, $-NH-SO_2-R^6$, $-N(SO_2-R^6)_2$, $-CQ^1-R^6$, $-CQ^1-Q^2-R^6$, $-CQ^1-NH-R^6$, $-Q^2-CQ^1-R^6$, $-NH-CQ^1-R^6$, $-N(SO_2-R^6)(CQ^1-R^6)$, $-Q^2-CQ^1-Q^2-R^6$, $-NH-CQ^1-Q^2-R^6$ or $-Q^2-CQ^1-NH-R^6$,

where Q^1 and Q^2 each represent oxygen or sulphur and R^6 represents optionally cyano-, halogen-, C_1-C_4-alkoxy-, C_1-C_4-alkylthio-, C_1-C_4-alkyl-carbonyl-, C_1-C_4-alkoxy-carbonyl- or C_1-C_4-alkylamino-carbonyl-substituted alkyl having 1 to 6 carbon atoms, represents alkenyl or alkinyl having in each case 2 to 6 carbon atoms and being in each case optionally substituted by cyano, carboxyl, halogen, C_1-C_4-alkyl-carbonyl, C_1-C_4-alkoxy-carbonyl or C_1-C_4-alkylamino-carbonyl, represents cycloalkyl or cycloalkylalkyl having in each case 3 to 6 carbon atoms in the cycloalkyl group and, if appropriate, 1 to 4 carbon atoms in the alkyl moiety and being in each case optionally substituted by cyano, carboxyl, halogen, C_1-C_4-alkyl-carbonyl or C_1-C_4-alkoxy-carbonyl, represents aryl or arylalkyl having in each case 6 or 10 carbon atoms in the aryl group and, if appropriate, 1 to 4 carbon atoms in the alkyl moiety and being in each case optionally substituted by hydroxyl, mercapto, amino, cyano, carboxyl, carbamoyl, thiocarbamoyl, C_1-C_4-alkyl, C_1-C_4-halogenoalkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkoxy, C_1-C_4-alkylthio, C_1-C_4-halogenoalkylthio, C_1-C_4-alkylsulphinyl, C_1-C_4-alkylsulphonyl, C_1-C_4-alkylamino or dimethylamino, or represents heterocyclyl or heterocyclylalkyl having 2 to 6 carbon atoms and 1 to 3 nitrogen atoms and/or 1 or 2 oxygen atoms and/or one sulphur atom in the heterocyclyl group and, if appropriate, 1 to 4 carbon atoms in the alkyl moiety and being in each case optionally substituted by hydroxyl, mercapto, amino, cyano, carboxyl, carbamoyl, thiocarbamoyl, C_1-C_4-alkyl, C_1-C_4-halogenoalkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkoxy, C_1-C_4-alkylthio, C_1-C_4-halogenoalkylthio, C_1-C_4-alkylsulphinyl, C_1-C_4-alkylsulphonyl, C_1-C_4-alkylamino or dimethylamino,

except for the compounds 1-methyl-3-(4-cyano-2-fluoro-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-phenyl)-4-bromo-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-nitro-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-ethylsulphonylamino-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-ethoxycarbonylmethoxy-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-chloro-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-methylthio-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-amino-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-hydroxy-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-chloro-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-aminosulphonyl-phenyl)-4-chloro-5-difluoromethoxy-pyrazole and 1-methyl-3-(4-cyano-2-fluoro-5-fluorosulphonyl-phenyl)-4-chloro-5-difluoromethoxy-pyrazole (known from WO 96/01255), which are excluded by disclaimer.

The invention in particular relates to compounds of the formula (I)

in which

Q represents oxygen (O), sulphur (S), SO or SO_2,

R^1 represents hydrogen, represents methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, each of which is optionally substituted by cyano, fluorine, chlorine, methoxy or ethoxy, represents propenyl, butenyl, propinyl or butinyl, each of which is optionally substituted by fluorine, chlorine or bromine, or represents cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclopropylmethyl, cyclobutylmethyl, cyclopentylmethyl or cyclohexylmethyl, each of which is optionally substituted by cyano, fluorine, chlorine, bromine, methyl or ethyl,

R^2 represents hydrogen, represents methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, each of which is optionally substituted by cyano, fluorine, chlorine, methoxy, ethoxy, methylthio or ethylthio, represents propenyl, butenyl, propinyl or butinyl, each of which is optionally substituted by fluorine, chlorine or bromine, or represents cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclopropylmethyl, cyclobutylmethyl, cyclopentylmethyl or cyclohexylmethyl, each of which is optionally substituted by cyano, fluorine, chlorine, bromine, methyl or ethyl,

R^3 represents hydrogen, fluorine, chlorine, bromine, or represents optionally cyano-, fluorine-, chlorine-, methoxy-, ethoxy-, methylthio- or ethylthio-substituted methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl,

R^4 represents hydrogen or fluorine, chlorine or bromine and

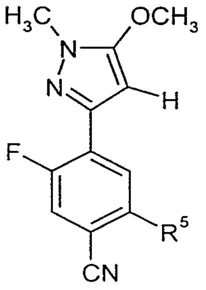
R^5 represents hydroxyl, mercapto, amino, fluorine, chlorine, bromine or represents one of the radicals $-Q-R^6$, $-NH-R^6$, $-NH-O-R^6$, $-NH-SO_2-R^6$, $-N(SO_2-R^6)_2$, $-CQ^1-R^6$, $-CQ^1-Q^2-R^6$, $-CQ^1-NH-R^6$, $-Q^2-CQ^1-R^6$, $-NH-CQ^1-R^6$, $-N(SO_2-R^6)(CQ^1-R^6)$, $-Q^2-CQ^1-Q^2-R^6$, $-NH-CQ^1-Q^2-R^6$ or $-Q^2-CQ^1-NH-R^6$,

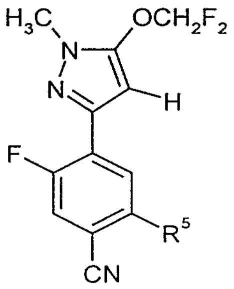
where Q^1 and Q^2 each represent oxygen or sulphur and R^6 represents methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, each of which is optionally substituted by cyano, fluorine, chlorine, methoxy, ethoxy, methylthio, ethylthio, acetyl, propionyl, methoxycarbonyl, ethoxycarbonyl, methylaminocarbonyl or ethylaminocarbonyl, represents propenyl, butenyl, propinyl or butinyl, each of which is optionally substituted by cyano, carboxyl, fluorine, chlorine, bromine, acetyl, propionyl, n- or i-butyroyl, methoxycarbonyl, ethoxycarbonyl, n- or i-propoxycarbonyl, methylaminocarbonyl, ethylaminocarbonyl, n- or i-propylaminocarbonyl, represents cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclopropylmethyl, cyclobutylmethyl, cyclopentylmethyl or cyclohexylmethyl, each of which is optionally substituted by cyano, carboxyl, fluorine, chlorine, bromine, acetyl, propionyl, methoxycarbonyl or ethoxycarbonyl, represents phenyl, benzyl or phenylethyl, each of which is optionally substituted by hydroxyl, mercapto, amino, cyano, carboxyl, carbamoyl, thiocarbamoyl, methyl, ethyl, trifluoromethyl, methoxy, ethoxy, difluoromethoxy, trifluoromethoxy, methylthio, ethylthio, difluoromethylthio, trifluoromethylthio, methylsulphinyl, ethylsulphinyl, methylsulphonyl, methylamino, ethylamino or dimethylamino, or represents heterocyclyl or heterocyclylalkyl selected from the group consisting of oxiranyl, oxetanyl, furyl, tetrahydrofuryl, dioxolanyl, thienyl, tetrahydrothienyl, pyrrolyl, pyrazolyl, imidazolyl, triazolyl, oxazolyl, isoxazolyl, thiazolyl, isothiazolyl, oxadiazolyl, thiadiazolyl, pyridinyl, pyrimidinyl, triazinyl, pyrazolylmethyl, furylmethyl, thienylmethyl, oxazolylmethyl, isoxazolylmethyl, thiazolylmethyl, pyridinylmethyl, pyrimidinylmethyl, each of which is optionally substituted by hydroxyl, mercapto, amino, cyano, carboxyl, carbamoyl, thiocarbamoyl, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, difluoromethyl, dichloromethyl, trifluoromethyl, trichloromethyl, chlorodifluoromethyl, fluorodichloromethyl, methoxy, ethoxy, difluoromethoxy, trifluoromethoxy, methylthio, ethylthio, difluoromethylthio, trifluoromethylthio, methylsulphinyl, ethylsulphinyl, methylsulphonyl, ethylsulphonyl, methylamino, ethylamino or dimethylamino,

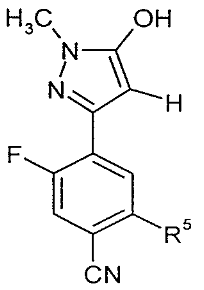
except for the compounds 1-methyl-3-(4-cyano-2-fluoro-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-phenyl)-4-bromo-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-nitro-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-ethylsulphonylamino-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-ethoxycarbonylmethoxy-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-chloro-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-methylthio-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-amino-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-

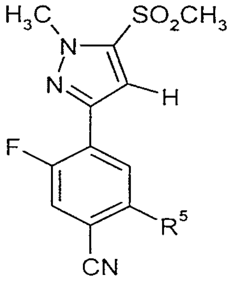
2-fluoro-5-hydroxy-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-chloro-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-aminosulphonyl-phenyl)-4-chloro-5-difluoromethoxy-pyrazole and 1-methyl-3-(4-cyano-2-fluoro-5-fluorosulphonyl-phenyl)-4-chloro-5-difluoromethoxy-pyrazole (known from WO 96/01255), which are excluded by disclaimer.

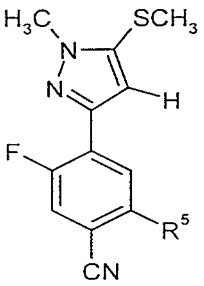
Very particular preference is given to 3-cyanoaryl-pyrazoles of the formulae

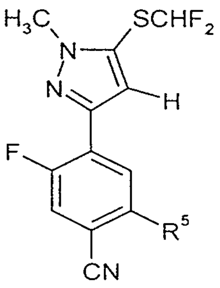


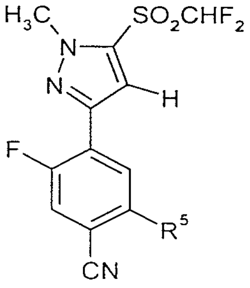


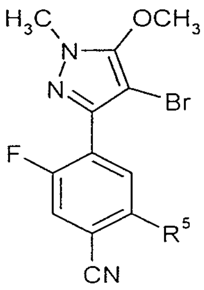


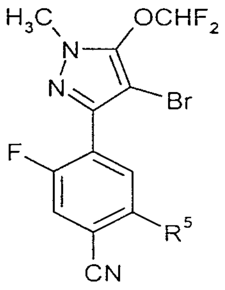


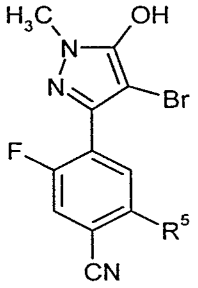








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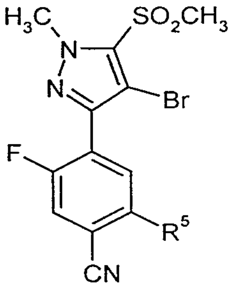
N
Br
F
R5
CN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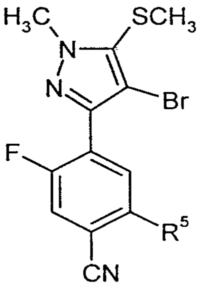
CN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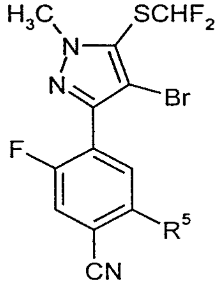
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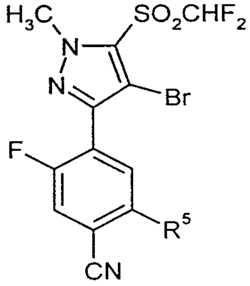
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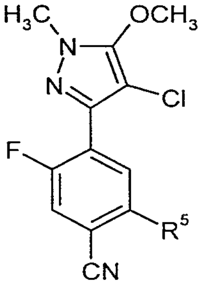
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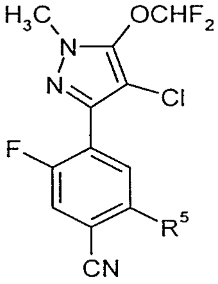
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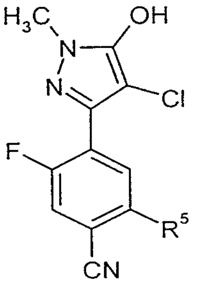
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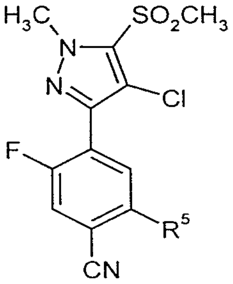
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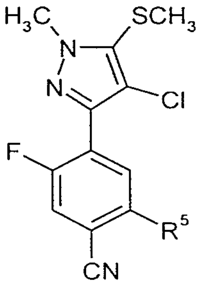
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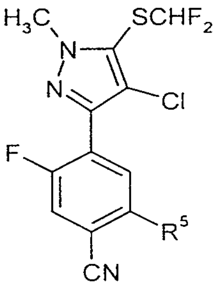
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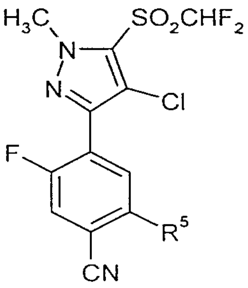
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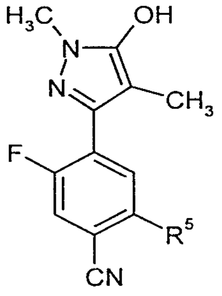
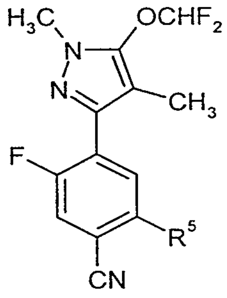
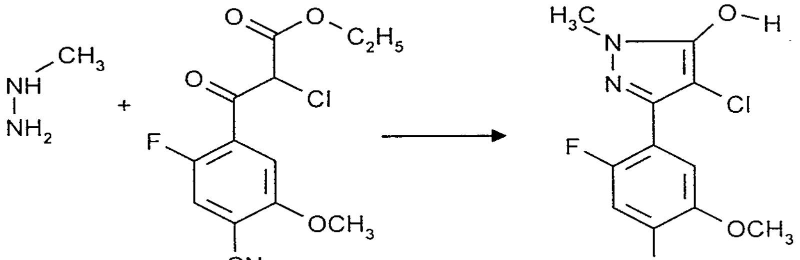




where in each case R^5 is as defined above.

The abovementioned general or preferred radical definitions apply both to the end products of the formula (I) and, correspondingly, to the starting materials or intermediates required in each case for the preparation. These radical definitions can be combined with one another as desired, i.e. including combinations between the preferred ranges stated.

Using, for example, methylhydrazine and ethyl 2-chloro-2-(4-cyano-2-fluoro-5-methoxy-benzoyl)-acetate as starting materials, the course of the reaction in the process (a) according to the invention can be illustrated by the following equation:



The formula (II) provides a general definition of the hydrazine derivatives to be used as starting materials in the process according to the invention for preparing compounds of the formula (I). In the formula (II), R^1 preferably and in particular has those meanings which have already been mentioned above, in connection with the description of compounds of the formula (I) according to the invention, as being preferred and as being particularly preferred, respectively, for R^1.

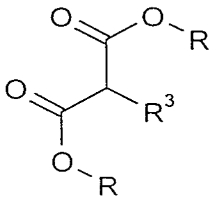
The starting materials of the formula (II) are known chemicals for synthesis.

The formula (III) provides a general definition of the cyanoarylcarbonylacetic acid derivatives further to be used as starting materials in the process (a) according to the invention. In the formula (III), R^3, R^4 and R^5 each preferably and in particular have those meanings which have already been mentioned above, in connection with the description of the compounds of the formula (I) according to the invention, as being preferred and as being particularly preferred, respectively, for R^3, R^4 and R^5;

R preferably represents hydrogen or alkyl having 1 to 4 carbon atoms, in particular hydrogen, methyl or ethyl.

Except for the compound ethyl 2-(4-cyano-2-fluoro-benzoyl)-acetate - alias ethyl 3-(4-cyano-2-fluoro-phenyl)-3-oxo-propionate (cf. WO 96/01255) -, the starting materials of the formula (III) have hitherto not been disclosed in the literature; except for ethyl 2-(4-cyano-2-fluoro-benzoyl)-acetate, they form, as novel substances, part of the subject matter of the present application.

The novel cyanoarylcarbonyl compounds of the formula (III) in which Q^3 represents oxygen are obtained when malonic acid or derivatives thereof of the general formula (IV)



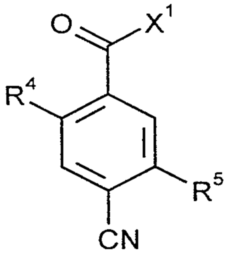
(IV).

in which

R and R^3 are each as defined above

- or salts of compounds of the formula (IV) -

are reacted with cyanobenzoyl halides of the general formula (V)



(V),

in which

R^4 and R^5 are each as defined above and

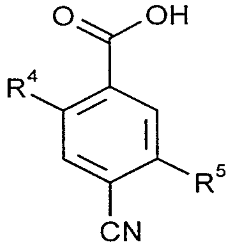
X^1 represents halogen,

if appropriate in the presence of an acid acceptor, such as, for example, triethylamine, if appropriate in the presence of a reaction auxiliary, such as, for example, magnesium chloride and if appropriate in the presence of a diluent, such as, for example, acetonitrile, at temperatures between -20°C and +50°C, and are worked up in a customary manner (cf. the Preparation Examples).

The malonic acid derivatives of the formula (IV) required as intermediates are known organic chemicals for synthesis.

Except for the compounds 4-cyano-3-methoxy-benzoyl chloride (cf. Arch. Pharm. 323 (1990), 507-512; EP 166609) and 4-cyano-2-fluoro-benzoyl chloride (cf. WO 96/01255), the cyanobenzoyl halides of the formula (V) which are further required as intermediates are hitherto not known from the literature; except for 4-cyano-3-methoxy-benzoyl chloride and 4-cyano-2-fluoro-benzoyl chloride, they form, as novel substances, part of the subject matter of the present application.

The novel cyanobenzoyl halides of the formula (V) are obtained when cyanobenzoic acids of the general formula (VI)



(VI),

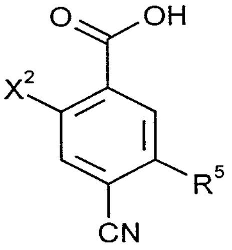
in which

R^4 and R^5 are each as defined above

are reacted with halogenating agents, such as, for example, phosgene (or its dimer or trimer) or thionyl chloride, if appropriate in the presence of a reaction auxiliary, such as, for example, N,N-dimethylformamide, and if appropriate in the presence of a diluent, such as, for example, carbon tetrachloride, at temperatures between 0°C and 120°C (cf. the Preparation Examples).

The cyanobenzoic acids of the formula (VI) required as intermediates are known and/or can be prepared by processes known per se (cf. Arch. Pharm. 323 (1990), 507-512; Collect. Czech. Chem. Commun. 40 (1975), 3009-3019; Chem. Pharm. Bull. 27 (1979), 3039-3048; J. Chem Soc., Perkin Trans. I 1994, 1679-1684; Tetrahedron Lett. 31 (1990), 7223-7226; EP 166609; EP 351856; WO 93/15078).

Hitherto not known from the literature and, as novel substances, part of the subject matter of the present application, are the compounds of the general formula (VIa)



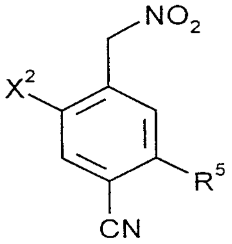
(VIa),

in which

R^5 is as defined above and

X^2 represents halogen, in particular represents fluorine or chlorine.

The novel cyanobenzoic acids of the formula (VIa) are obtained when nitromethylbenzonitriles of the general formula (VII)



(VII),

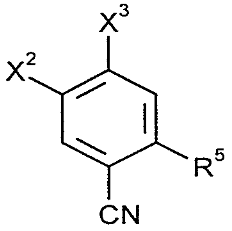
in which

R^5 and X^2 are each as defined above

are reacted with oxidizing agents, such as, for example, potassium permanganate, if appropriate in the presence of a diluent, such as, for example, acetone, at temperatures between 0°C and 50°C (cf. the Preparation Examples; cf. also J. Chem. Soc. 1949, 3374).

The nitromethylbenzonitriles of the formula (VII) are hitherto not known from the literature; they form, as novel substances, part of the subject matter of the present application.

The novel compounds of the formula (VII) are obtained when halogenobenzonitriles of the general formula (VIII)



(VIII),

in which

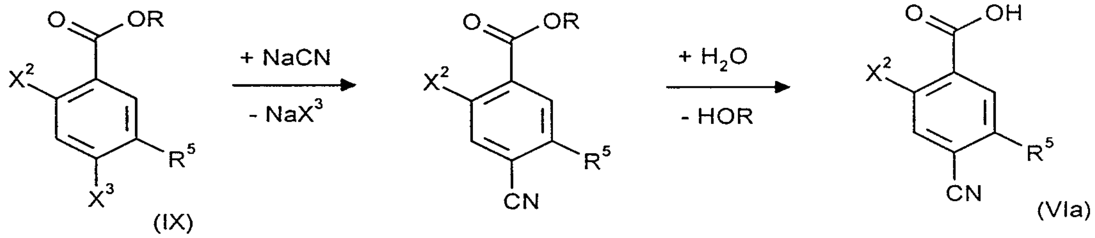
R^5 and X^2 are each as defined above and

X^3 represents halogen, in particular represents fluorine or chlorine

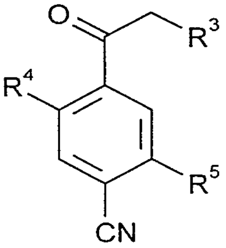
are reacted with nitromethane in the presence of an acid acceptor, such as, for example 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) and, if appropriate, in the presence of a diluent, such as, for example, ethyl acetate, at temperatures between -20°C and +40°C (cf. the Preparation Examples).

The intermediates of the formula (VIII) are known and/or can be prepared by known methods (cf. EP 191185, EP 433124, EP 431373, EP 497239, EP 557949, EP 566268, EP 635486).

The cyanobenzoic acids of the formula (VIa) can also be prepared starting from known halogenated benzoic esters of the formula (IX) - cf. J. Chem. Eng. Data 13 (1968), 587-588; cited in C.A. 69:106150 - according to the following equation (R: alkyl, in particular methyl or ethyl; X^3: halogen, in particular fluorine or chlorine):



The novel cyanoarylcarbonyl compounds of the formula (III) in which Q^3 represents sulphur are obtained when cyanoarylketones of the general formula (X)



(X),

in which

R^3, R^4 and R^5 are each as defined above

are reacted with carbon disulphide (CS_2) in the presence of an acid acceptor, such as, for example, potassium t-butoxide, and in the presence of a diluent, such as, for example, tetrahydrofuran and, if appropriate, subsequently - preferably without intermediate isolation - with an alkylating agent, such as, for example, methyl iodide, at temperatures between -30°C and +30°C (cf. the Preparation Examples).

The starting materials of the formula (III) obtained in this manner can be reacted, if appropriate without intermediate isolation, with hydrazine derivatives of the formula (II) in accordance with the process according to the invention to give the active compounds of the formula (I).

The intermediates of the formula (X) are known and/or can be prepared by known processes (cf. Chem. Pharm. Bull. 33 (1985), 1360-1366; EP166609; EP 628550; WO

94/05153; Preparation Examples).

Suitable diluents for carrying out the process according to the invention for the preparation of the novel compounds of the formula (I) are in particular organic solvents. These include, in particular, aliphatic, alicyclic or aromatic, optionally halogenated hydrocarbons, such as, for example, benzine, benzene, toluene, xylene, chlorobenzene, dichlorobenzene, petroleum ether, hexane, cyclohexane, dichloromethane, chloroform, carbon tetrachloride; ethers, such as diethyl ether, diisopropyl ether, dioxane, tetrahydrofuran or ethylene glycol dimethyl ether or ethylene glycol diethyl ether; ketones, such as acetone, butanone or methyl isobutyl ketone; carboxylic acids, such as, for example, acetic acid or propionic acid, nitriles, such as acetonitrile, propionitrile or butyronitrile; amides, such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-formanilide, N-methyl-pyrrolidone or hexamethylphosphoric triamide; esters such as methyl acetate or ethyl acetate, sulphoxides, such as dimethyl sulphoxide, alcohols, such as methanol, ethanol, n- or i-propanol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monomethyl ether or diethylene glycol monoethyl ether.

When carrying out the process according to the invention, the reaction temperatures can be varied within a relatively wide range. In general, the reaction is carried out at temperatures between 0°C and 150°C, preferably between 20°C and 120°C.

The process according to the invention is generally carried out under atmospheric pressure. However, it is also possible to carry out the process according to the invention under elevated or reduced pressure - in general between 0.1 bar and 10 bar.

When carrying out the process according to the invention, the starting materials are generally employed in approximately equimolar amounts. However, it is also possible to employ a relatively large excess of one of the components. The reaction is generally carried out in a suitable diluent and the reaction mixture is generally stirred for a number of hours at the temperature required. Work-up is carried out by customary methods (cf. the Preparation Examples).

The active compounds according to the invention can be used as defoliants, desiccants, haulm killers and, especially, as weed killers. By weeds in the broadest sense, there are to be understood all plants which grow in locations where they are not wanted. Whether the substances according to the invention act as total or selective herbicides depends essentially on the amount used.

The active compounds according to the invention can be used, for example, in connection with the following plants:

Dicotyledonous weeds of the genera: Sinapis, Lepidium, Galium, Stellaria, Matricaria, Anthemis, Galinsoga, Chenopodium, Urtica, Senecio, Amaranthus, Protulaca, Xanthium, Convolvulus, Ipomoea, Polygonum, Sesbania, Ambrosia, Cirsium, Carduus, Sonchus, Solanum, Rorippa, Rotala, Lindernia, Lamium, Veronica, Abutilon, Emex, Datura, Viola, Galeopsis, Papaver, Centaurea, Trifolium, Ranunculus and Taraxacum.

Dicotyledonous crops of the genera: Gossypium, Glycine, Beta, Daucus, Phaseolus, Pisum, Solanum, Linum, Ipomoea, Vicia, Nicotiana, Lycopersicon, Arachis, Brassica, Lactuca, Cucumis and Cucurbita.

Monocotyledonous weeds of the genera: Echinochloa, Setaria, Panicum, Digitaria, Phleum, Poa, Festuca, Eleusine, Brachiaria, Lolium, Bromus, Avena, Cyperus, Sorghum, Agropyron, Cynodon, Monochoria, Fimbristylis, Sagittaria, Eleocharis, Scirpus, Paspalum, Ischaemum, Sphenoclea, Dactyloctenium, Agrostis, Alopecurus and Apera.

Monocotyledonous crops of the genera: Oryza, Zea, Triticum, Hordeum, Avena, Secale, Sorghum, Panicum, Saccharum, Ananas, Asparagus and Allium.

However, the use of the active compounds according to the invention is in no way restricted to these genera, but also extends in the same manner to other plants.

The compounds are suitable, depending on the concentration, for the total control of weeds, for example on industrial terrain and railway tracks, and on paths and squares with or without tree plantings. Equally, the compounds can be employed for the control of weeds in perennial crops for example forests, decorative tree plantings, orchards, vineyards, citrus groves, nut orchards, banana plantations, coffee plantations, tea plantations, rubber plantations, oil palm plantations, cocoa plantations, soft fruit plantings and hop fields, in lawns, turf and pasture land, and for the selective control of weeds in annual cultures.

The compounds of the formula (I) according to the invention are suitable in particular for the selective control of monocotyledonous and dicotyledonous weeds in monocotyledonous and dicotyledonous crops, both pre-emergence and post-emergence.

The active compounds can be converted into the customary formulations, such as solutions, emulsions, wettable powders, suspensions, powders, dusting agents, pastes, soluble powders, granules, suspo-emulsion concentrates, natural and synthetic materials impregnated with active compound, and very fine capsules in polymeric substances.

These formulations are produced in a known manner, for example by mixing the active compounds with extenders, that is liquid solvents and/or solid carriers, optionally with the use of surface-active agents, that is emulsifying agents and/or dispersing agents and/or foam-forming agents.

If the extender used is water, it is also possible to employ for example organic solvents as auxiliary solvents. Suitable liquid solvents are essentially the following: aromatics, such as xylene, toluene or alkylnaphthalenes, chlorinated aromatics and chlorinated aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, for example petroleum fractions, mineral and vegetable oils, alcohols, such as butanol or glycol and also their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strongly polar solvents such as dimethylformamide and dimethyl sulphoxide, and also water.

Suitable solid carriers are: for example ammonium salts and ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals such as finely divided silica, alumina and silicates; suitable solid carriers for granules are: for example crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, and also synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks; suitable emulsifying and/or foam-forming agents are: for example, nonionic and anionic emulsifiers, such as polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkylsulphonates, alkyl sulphates, arylsulphonates as well as protein hydrolysates; suitable dispersing agents are: for example lignin-sulphite waste liquors and methylcellulose.

Tackifiers such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latexes, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, as well as natural phospholipids, such as cephalins and lecithins, and synthetic phospholipids, can be used in the formulations. Other possible additives are mineral and vegetable oils.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic dyes, such as alizarin dyes, azo dyes and metal phthalocyanine dyes, and trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The formulations in general contain between 0.1 and 95 per cent by weight of active compound, preferably between 0.5 and 90%.

For the control of weeds, the active compounds according to the invention, as such or in the form of their formulations, can also be used as mixtures with known herbicides, finished formulations or tank mixes being possible.

Possible components for the mixtures are known herbicides, for example acetochlor, acifluorfen(-sodium), aclonifen, alachlor, alloxydim(-sodium), ametryne, amidochlor, amidosulphuron, asulam, atrazine, azimsulphuron, benazolin, benfuresate, bensulphuron(-methyl), bentazon, benzofenap, benzoylprop(-ethyl), bialaphos, bifenox, bromobutide, bromofenoxim, bromoxynil, butachlor, butylate, cafenstrole, carbetamide, chlomethoxyfen, chloramben, chloridazon, chlorimuron(-ethyl), chlornitrofen, chlorsulphuron, chlortoluron, cinmethylin, cinosulphuron, clethodim, clodinafop(-propargyl), clomazone, clopyralid, clopyrasulphuron, cloransulam(-methyl), cumyluron, cyanazine, cycloate, cyclosulphamuron, cycloxydim, cyhalofop(-butyl), 2,4-D, 2,4-DB, 2,4-DP, desmedipham, diallate, dicamba, diclofop(-methyl), difenzoquat, diflufenican, dimefuron, dimepiperate, dimethachlor, dimethametryn, dimethenamid, dinitramine, diphenamid, diquat, dithiopyr, diuron, dymrom, EPTC, esprocarb, ethalfluralin, ethametsulphuron(-methyl), ethofumesate, ethoxyfen, etobenzanid, fenoxapropethyl, flamprop(-isopropyl), flamprop(-isopropyl-L), flamprop(-methyl), flazusulphuron, fluazifop(-butyl), flumetsulam, flumiclorac(-pentyl), flumioxazin, flumipropyn, fluometuron, fluorochloridone, fluoroglycofen(-ethyl), flupoxam, flupropacil, flurenol, fluridone, fluroxypyr, flurprimidol, flurtamone, fomesafen, glufosinate(-ammonium), glyphosate(-isopropylammonium), halosafen, haloxyfop(-ethoxyethyl), hexazinone, imazamethabenz(-methyl), imazamethapyr, imazamox, imazapyr, imazaquin, imazethapyr, imazosulphuron, ioxynil, isopropalin, isoproturon, isoxaben, isoxaflutole, isoxapyrifop, lactofen, lenacil, linuron, MCPA, MCPP, mefenacet, metamitron, metazachlor, methabenzthiazuron, metobenzuron, metobromuron, metolachlor, metosulam, metoxuron, metsulphuron(-methyl), metribuzin, molinate, monolinuron, naproanilide, napropamide, neburon, nicosulphuron, norflurazon orbencarb, oryzalin, oxadiazon, oxyfluorfen, paraquat, pendimethalin, phenmedipham, piperophos, pretilachlor, primisulphuron(-methyl), prometryn, propachlor, propanil, propaquizafop, propyzamide, prosulphocarb, prosulphuron, pyrazolate, pyrazosulphuron(-ethyl), pyrazoxyfen, pyributicarb, pyridate, pyrithiobac(-sodium), quinchlorac, quinmerac, quizalofop(-ethyl), quizalofop(-p-terfuryl), rimsulphuron, sethoxydim, simazine, simetryn, sulcotrione, sulphentrazone, sulphometuron(-methyl), sulphosate, tebutam, tebuthiuron, terbuthylazine, terbutryn, thenylchlor, thiafluamide, thiazopyr, thidiazimin, thifensulphuron(-methyl), thiobencarb, tiocarbazil, tralkoxydim, triallate, triasulphuron, tribenuron(-methyl), triclopyr, tridiphane, trifluralin and triflusulphuron.

Mixtures with other known active compounds, such as fungicides, insecticides, acaricides, nematicides, bird repellents, plant nutrients and agents which improve soil structure, are also possible.

The active compounds can be used as such, in the form of their formulations or in the use forms prepared therefrom by further dilution, such as ready-to-use solutions, suspension, emulsions, powders, pastes and granules. They are used in the customary manner, for example by watering, spraying, atomizing or scattering.

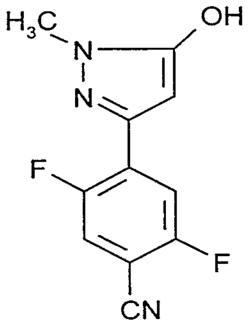
The active compounds according to the invention can be applied either before or after emergence of the plants. They can also be incorporated into the soil before sowing.

The amount of active compound used can vary within a relatively wide range. It depends essentially on the nature of the desired effect. In general, the amounts used are between 1 g and 10 kg of active compound per hectare of soil surface, preferably between 5 g and 5 kg per ha.

The preparation and the use of the active compounds according to the invention can be seen from the examples below.

Preparation Examples:

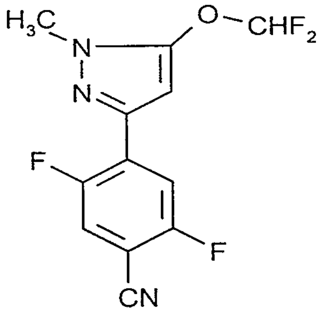
Example 1



171 g (0.676 mol) of ethyl 2-(4-cyano-2,5-difluoro-benzoyl)-acetate are initially charged in 300 ml of acetic acid and, at an internal temperature of about 40°C, admixed dropwise with 36.3 g (0.80 mol) of methylhydrazine. The mixture is subsequently heated at 90°C to 100°C for about 90 minutes, and a bright yellow solid precipitates out. The mixture is allowed to cool slowly and then poured into about 2 litres of ice-water. The solid product is isolated by filtration with suction, washed with water and dried under water pump vacuum. It is then stirred with 600 ml of dichloromethane, filtered off with suction and once more dried under water pump vacuum.

This gives 125 g (79% of theory) of 3-(4-cyano-2,5-difluoro-phenyl)-5-hydroxy-1-methyl-1H-pyrazole of melting point 198°C.

Example 2

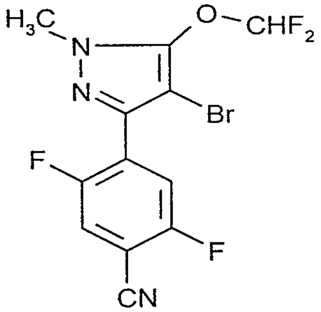


A mixture of 47 g (0.20 mol) of 3-(4-cyano-2,5-difluoro-phenyl)-5-hydroxy-1-methyl-1H-pyrazole and 350 ml of N,N-dimethyl-formamide is admixed with 55 g of potassium carbonate and heated at 50°C for about 60 minutes. At an internal temperature between 60°C and 70°C, 100 g (1.16 mol) of chlorodifluoromethane are then introduced over a period of about 6 hours. The mixture is subsequently concentrated under water pump vacuum and the residue is taken up in 500 ml of water. The aqueous suspension is acidified with 2N hydrochloric acid and extracted with dichloromethane. The organic phase is washed with water, dried with magnesium sulphate and filtered. The filtrate is concentrated under water pump vacuum and the residue is digested four times with 500 ml of hot hexane in each case. From the combined hexane fractions, the solvent is carefully distilled off under water pump vacuum.

This gives 24.6 g (43% of theory) of 3-(4-cyano-2,5-difluoro-phenyl)-5-difluoromethoxy-1-methyl-1H-pyrazole of melting point 80°C.

From the extraction residue, which is virtually insoluble in hexane, the isomeric compound 3-(4-cyano-2,5-difluoro-phenyl)-2-difluoromethyl-1-methyl-pyrazol-5-one of melting point 128°C can be isolated by column chromatography (using dichloromethane over silica gel).

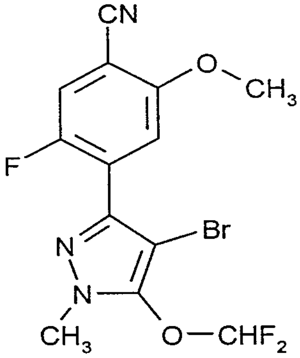
Example 3



At room temperature (approximately 20°C) a solution of 1.9 g (12 mmol) of bromine in 5 ml of dichloromethane is added with stirring to a solution of 2.85 g (10 mmol) of 3-(4-cyano-2,5-difluoro-phenyl)-2-difluoro-methyl-1-methyl-pyrazol-5-one in 20 ml of dichloromethane. The mixture is stirred at about 20°C for 3 hours, diluted with 20 ml of dichloromethane, washed with saturated aqueous sodium bicarbonate solution and with saturated aqueous sodium chloride solution, dried with magnesium sulphate and filtered. The solvent is carefully distilled off from the filtrate under water pump vacuum.

This gives 3.5 g (96% of theory) of 4-bromo-3-(4-cyano-2,5-difluoro-phenyl)-5-difluoromethoxy-1-methyl-1H-pyrazole of melting point 79°C.

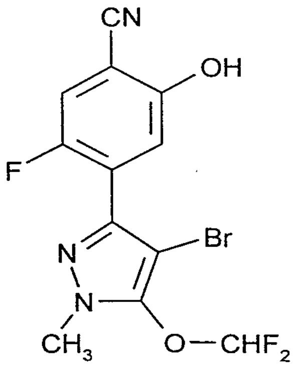
Example 4



1.5 g (4 mmol) of 4-bromo-3-(4-cyano-2,5-difluoro-phenyl)-1-methyl-5-difluoromethoxy-1H-pyrazole are added to a solution of 0.5 g (6 mmol) of sodium methoxide in 40 ml of acetonitrile. The mixture is stirred at room temperature (approximately 20°C) for 16 hours, poured into water and acidified with hydrochloric acid, and the precipitated solid is filtered off, washed with water and dried under water pump vacuum.

This gives 1.1 g (75% of theory) of 4-bromo-3-(4-cyano-2-fluoro-5-methoxy-phenyl)-1-methyl-5-difluoromethoxy-1H-pyrazole of melting point 155°C.

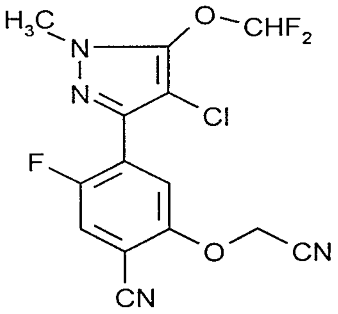
Example 5



At room temperature (approximately 20°C), 150 ml (0.15 mol) of a 1-molar solution of boron tribromide in dichloromethane are added to a solution of 18.8 g (0.05 mol) of 4-bromo-3-(4-cyano-2-fluoro-5-methoxy-phenyl)-1-methyl-5-difluoromethoxy-1H-pyrazole in 100 ml of dichloromethane. The reaction mixture is stirred at room temperature for 16 hours and then admixed with water and dichloromethane. The organic phase is separated off and washed successively with water, saturated sodium bicarbonate solution and sodium chloride solution, dried over magnesium sulphate and freed from the solvent under water pump vacuum. The resulting crude product is purified by column chromatography using dichloromethane as mobile phase.

This give 8.3 g (46% of theory) of 4-bromo-3-(4-cyano-2-fluoro-5-hydroxy-phenyl)-1-methyl-5-difluoromethoxy-1H-pyrazole of melting point 129°C).

Example 6

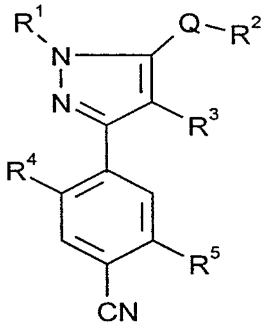


2.8 g 20 mmol) of potassium carbonate and 1.0 g (8 mmol) of bromoacetonitrile are added to a solution of 1.9 g (6.0 mmol) of 4-chloro-3-(4-cyano-2-fluoro-5-hydroxyphenyl)-5-difluoromethoxy-1-methyl-1H-pyrazole in 50 ml of acetonitrile. The reaction mixture is stirred at room temperature (approximately 20°C) for about 16 minutes and then concentrated under water pump vacuum. The residue is admixed with 50 ml of water, acidified with 2N hydrochloric acid and extracted with dichloromethane. The organic phase is washed with saturated aqueous sodium bicarbonate solution and with saturated aqueous sodium chloride solution, dried with magnesium sulphate and filtered. The filtrate is concentrated under water pump vacuum and the crude product which is obtained as residue is purified by column chromatography (dichloromethane, silica gel).

This gives 1.0 g (47% of theory) of 5-(4-chloro-5-difluoromethoxy-1-methyl-1H-pyrazol-3-yl)-2-cyano-4-fluoro-phenoxyacetonitrile of melting point 104°C.

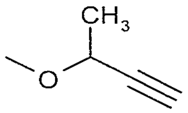
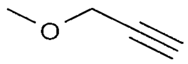
By the methods of Preparation Examples 1 to 6, and in accordance with the general description of the preparation process according to the invention, it is also possible to prepare, for example, the compounds of the formula (I) listed in Table 1 below.

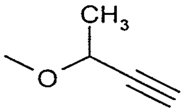
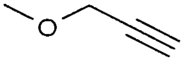
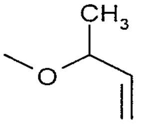
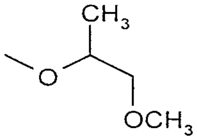
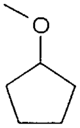
3-Cyanoaryl-pyrazoles

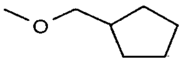
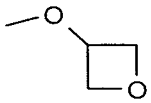
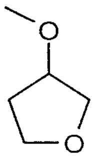
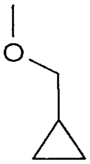
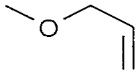


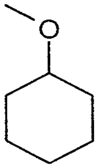
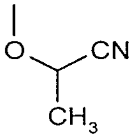
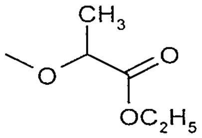
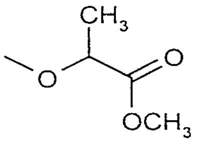
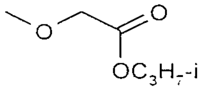
(I)

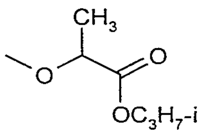
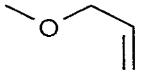
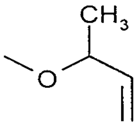
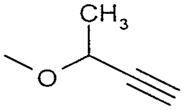
Table 1: Examples of compounds of the formula (I)

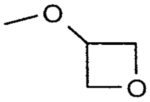
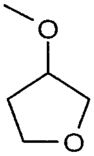
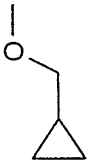
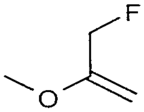
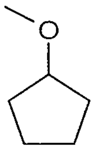
Ex. No.	Q	R^1	R^2	R^3	R^4	R^5	Melting point (°C)
7	O	CH_3	CHF_2	Cl	F	F	77
8	O	CH_3	CHF_2	Cl	F	OC_2H_5	80
9	O	CH_3	CHF_2	CH_3	F		55
10	O	CH_3	CHF_2	Br	F	OC_2H_5	94
11	O	CH_3	CHF_2	Br	F	OC_3H_7-i	93
12	O	CH_3	CHF_2	Br	F		96
13	O	CH_3	CHF_2	Br	F	$NHSO_2CH_3$	138
14	O	CH_3	H	CH_3	F	F	171
15	O	CH_3	CHF_2	CH_3	F	F	104
16	O	CH_3	CHF_2	CH_3	F	$O(CH_2)_2OCH_3$	42

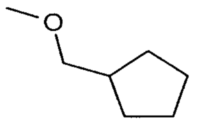
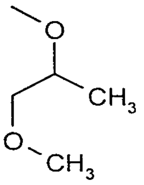
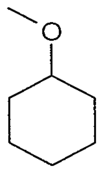
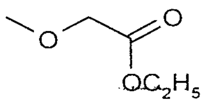
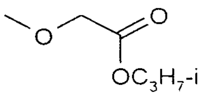
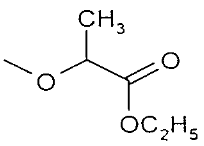
Ex. No.	**Q**	**R^1**	**R^2**	**R^3**	**R^4**	**R^5**	**Melting point (°C)**
17	O	CH_3	CHF_2	Cl	F		70
18	O	CH_3	CHF_2	Cl	F	OCH_3	150
19	O	CH_3	CHF_2	Cl	F	$O(CH_2)_2OCH_3$	43
20	O	CH_3	CHF_2	Cl	F	OC_3H_7-i	48
21	O	CH_3	CHF_2	Cl	F	OCH_2CF_3	99
22	O	CH_3	CHF_2	Cl	F		90
23	O	CH_3	CHF_2	Cl	F		47
24	O	CH_3	CHF_2	Cl	F		26
25	O	CH_3	CHF_2	Cl	F	$OCH_2C_6H_5$	88
26	O	CH_3	CHF_2	Cl	F		(amor-phous)

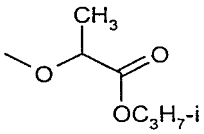
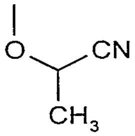
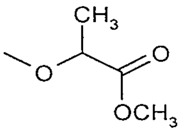
Ex. No.	**Q**	**R^1**	**R^2**	**R^3**	**R^4**	**R^5**	**Melting point (°C)**
27	O	CH_3	CHF_2	Cl	F		(amorphous)
28	O	CH_3	CHF_2	Cl	F		100
29	O	CH_3	CHF_2	Cl	F		75
30	O	CH_3	CHF_2	Cl	F		82
31	O	CH_3	CHF_2	Cl	F	$OCH(CH_2F)_2$	60
32	O	CH_3	CHF_2	Cl	F	OC_3H_7-n	46
33	O	CH_3	CHF_2	Cl	F	$O(C_2H_4O)_2CH_3$	(amorphous)
34	O	CH_3	CHF_2	Cl	F		46

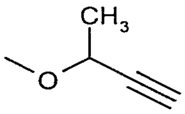
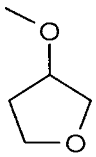
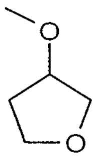
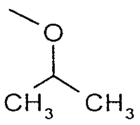
Ex. No.	Q	R^1	R^2	R^3	R^4	R^5	Melting point (°C)
35	O	CH_3	CHF_2	Cl	F		(amorphous)
36	O	CH_3	CHF_2	Cl	F		76
37	S	CH_3	CH_3	H	F	F	116
38	O	CH_3	CHF_2	Cl	F	OCH_2CH_2F	78
39	O	CH_3	CHF_2	Cl	F	OCH_2COOCH_3	110
40	O	CH_3	CHF_2	Cl	F		44
41	O	CH_3	CHF_2	Cl	F		113
42	O	CH_3	CHF_2	Cl	F	OCH_2CHF_2	73
43	O	CH_3	CHF_2	Cl	F		115

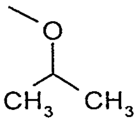
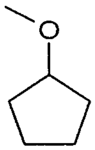
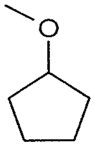
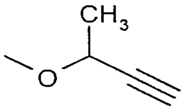
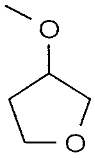
Ex. No.	Q	R^1	R^2	R^3	R^4	R^5	Melting point (°C)
44	O	CH_3	CHF_2	Cl	F		56
45	O	CH_3	CHF_2	Cl	F	$N(SO_2CH_3)_2$	175
46	O	CH_3	CHF_2	Cl	F	$NHSO_2CH_3$	139
47	S	CH_3	CH_3	Br	F	F	100
48	O	CH_3	CHF_2	Br	F	OC_3H_7-n	71
49	O	CH_3	CHF_2	Br	F		46
50	O	CH_3	CHF_2	Br	F		69
51	O	CH_3	CHF_2	Br	F		70
52	O	CH_3	CHF_2	Br	F	$O(CH_2)_2OCH_3$	36
53	O	CH_3	CHF_2	Br	F	$O(C_2H_4O)_2CH_3$	33
54	O	CH_3	CHF_2	Br	F	OCH_2CF_3	109
55	O	CH_3	CHF_2	Br	F	$OCH(CH_2F)_2$	98

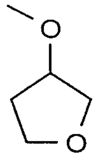
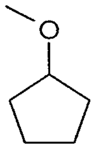
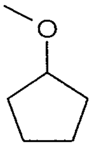
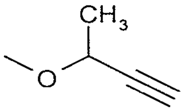
Ex. No.	Q	R^1	R^2	R^3	R^4	R^5	Melting point (°C)
56	O	CH_3	CHF_2	Br	F	$OCH_2C_6H_5$	75
57	O	CH_3	CHF_2	Br	F		122
58	O	CH_3	CHF_2	Br	F		100
59	O	CH_3	CHF_2	Br	F		103
60	O	CH_3	CHF_2	Br	F		83
61	O	CH_3	CHF_2	Br	F		40

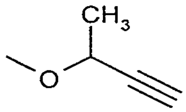
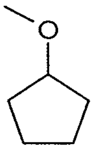
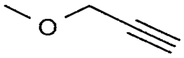
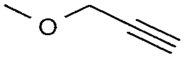
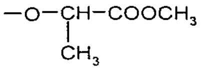
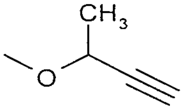
Ex. No.	**Q**	**R^1**	**R^2**	**R^3**	**R^4**	**R^5**	**Melting point (°C)**
62	O	CH_3	CHF_2	Br	F		40
63	O	CH_3	CHF_2	Br	F		35
64	O	CH_3	CHF_2	Br	F		(amor-phous)
65	O	CH_3	CHF_2	Br	F	$NHSO_2C_2H_5$	95
66	O	CH_3	CHF_2	Br	F		111
67	O	CH_3	CHF_2	Br	F		86
68	O	CH_3	CHF_2	Br	F		98

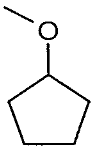
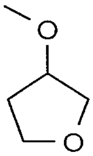
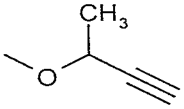
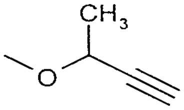
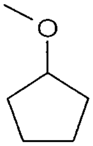
Ex. No.	Q	R^1	R^2	R^3	R^4	R^5	Melting point (°C)
69	O	CH_3	CHF_2	Br	F	OCH_2CHF_2	88
70	O	CH_3	CHF_2	Br	F	OCH_2CH_2F	89
71	O	CH_3	CHF_2	Br	F	OCH_2CN	108
72	O	CH_3	CHF_2	Br	F		56
73	O	CH_3	CHF_2	Br	F	OCH_2COOCH_3	89
74	O	CH_3	CHF_2	Br	F		74
75	O	CH_3	CHF_2	Br	F		104
76	O	CH_3	CHF_2	Br	F	$-N(SO_2CH_3)_2$	64
77	O	CH_3	CHF_2	Br	F	$-N(SO_2CH_3)-$ (COC_6H_5)	58
78	O	CH_3	CHF_2	Cl	F	$-N(SO_2CH_3)-$ (COC_6H_5)	60
79	S	CH_3	H	H	F	F	137
80	S	CH_3	CHF_2	H	F	F	104
81	S	CH_3	CH_3	Br	F	$O(CH_2)_2OCH_3$	99
82	SO_2	CH_3	CH_3	Br	F	F	176

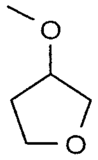
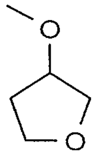
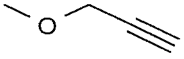
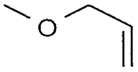
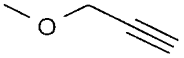
Ex. No.	**Q**	**R^1**	**R^2**	**R^3**	**R^4**	**R^5**	**Melting point (°C)**
83	S	CH_3	CHF_2	Br	F	F	100
84	SO_2	CH_3	CH_3	Br	F	$O(CH_2)_2OCH_3$	153
85	S	CH_3	CHF_2	Br	F		
86	S	CH_3	CHF_2	Br	F	$O(CH_2)_2OCH_3$	88
87	S	CH_3	CH_3	H	F	F	118
88	S	CH_3	CF_3	H	F	F	67
89	S	CH_3	CHF_2	Br	F		105
90	SO_2	CH_3	CH_3	Br	F		131
91	S	CH_3	CHF_2	Br	F		125

Ex. No.	**Q**	**R^1**	**R^2**	**R^3**	**R^4**	**R^5**	**Melting point (°C)**
92	SO_2	CH_3	CH_3	Br	F		
93	S	CH_3	CHF_2	Br	F		105
94	SO_2	CH_3	CH_3	Br	F		123
95	S	CH_3	CH_3	Cl	F	F	75
96	S	CH_3	CH_3	Br	F		101
97	SO_2	CH_3	CH_3	Br	F	F	176
98	S	CH_3	CF_3	H	F	F	67
99	S	CH_3	CHF_2	Br	F		105

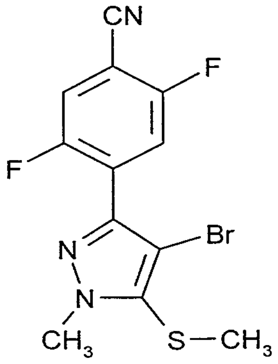
Ex. No.	**Q**	**R^1**	**R^2**	**R^3**	**R^4**	**R^5**	**Melting point (°C)**
100	SO_2	CH_3	CH_3	Br	F		131
101	S	CH_3	CHF_2	Br	F	$OCH(CH_3)_2$	125
102	S	CH_3	CHF_2	Br	F		105
103	SO_2	CH_3	CH_3	Br	F	$OCH(CH_3)_2$	182
104	SO_2	CH_3	CH_3	H	F		123
105	S	CH_3	CH_3	Cl	F	F	75
106	S	CH_3	CH_3	Br	F		101
107	S	CH_3	CHF_2	Cl	F	F	57

Ex. No.	**Q**	**R^1**	**R^2**	**R^3**	**R^4**	**R^5**	**Melting point (°C)**
108	SO_2	CH_3	CH_3	Br	F		76
109	SO_2	CH_3	CH_3	Br	F	OCH_3	195
110	SO_2	CH_3	CH_3	Br	F		117
111	SO_2	CH_3	CH_3	Br	F		130
112	S	CH_3	CHF_2	Cl	F		82
113	SO_2	CH_3	CH_3	Cl	F	F	151
114	SO_2	CH_3	CH_3	Br	F	$-OCH_2CH_2F$	139
115	SO_2	CH_3	CH_3	Br	F	 $-O-\underset{CH_3}{CH}-COOCH_3$	97
116	SO_2	CH_3	CH_3	Br	F	$-NHSO_2CH_3$	185
117	S	CH_3	CH_2F	H	F	F	129
118	SO_2	CH_3	CH_2F	Cl	F	F	79
119	SO_2	CH_3	CH_3	Cl	F		140

Ex. No.	**Q**	**R^1**	**R^2**	**R^3**	**R^4**	**R^5**	**Melting point (°C)**
120	SO_2	CH_3	CH_3	Cl	F		107
121	S	CH_3	CH_2F	Br	F	F	58
122	S	CH_3	CHF_2	Cl	F		116
123	S	CH_3	CHF_2	Cl	F	$-OCH_2CH_2OCH_3$	(amorphous)
124	S	CH_3	CHF_2	Cl	F		42
125	S	CH_3	CH_2F	Br	F		88
126	S	CH_3	CHF_2	Cl	F	$OCH(CH_3)_2$	105
127	S	CH_3	CHF_2	Cl	F		78

Ex. No.	**Q**	**R^1**	**R^2**	**R^3**	**R^4**	**R^5**	**Melting point (°C)**
128	S	CH_3	CHF_2	Cl	F	$-OCH_2CH_2F$	85
129	SO_2	CH_3	CH_2F	Br	F	F	145
130	S	CH_3	CH_2F	Br	F		146
131	SO_2	CH_3	CH_2F	Br	F		166
132	S	CH_3	CH_2F	Br	F	$-OCH(CH_3)_2$	122
133	S	CH_3	CH_2F	Br	F	$-OCH_2CH_2OCH_3$	54
134	SO_2	CH_3	CH_2F	Br	F	$-OCH_2CH_2OCH_3$	122
135	S	CH_3	CH_2F	Br	F	$-OCH_2CH_2F$	115
136	S	CH_3	CH_2F	Br	F		129
137	S	CH_3	CH_2F	Br	F		97
138	SO_2	CH_3	CH_2F	Br	F		146

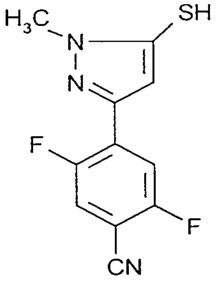
The compound listed in Table 1 as Example 47 can be prepared, for example, as follows:



At room temperature (approximately 20°C), a solution of 4.2 g (26 mmol) of bromine in 10 ml of dichloromethane is added with stirring to a solution of 6.0 g (23 mmol) of 3-(4-cyano-2,5-difluoro-phenyl)-1-methyl-5-methylmercapto-1H-pyrazole in 80 ml of dichloromethane. The reaction mixture is stirred at room temperature for about 60 minutes, diluted with 20 ml of dichloromethane and washed successively with dilute sodium hydrogen sulphite solution, saturated sodium bicarbonate solution and sodium chloride solution, dried over magnesium sulphate and freed from solvent under water pump vacuum.

This gives 7.0 g (88.5% of theory) of 4-bromo-3-(4-cyano-2,5-difluoro-phenyl)-1-methyl-5-methylmercapto-1H-pyrazole as a crystalline solid of melting point 100°C.

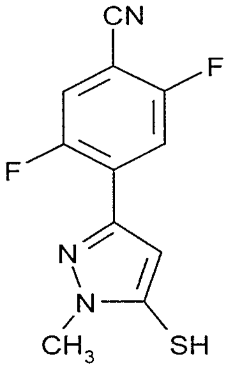
The compound listed in Table 1 as Example 79 can be prepared, for example, as follows:



A mixture of 2.4 g (10 mmol) of 3-(4-cyano-2,5-difluoro-phenyl)-5-hydroxy-1-methyl-1H-pyrazole, 6.7 g (30 mmol) of phosphorus(V) sulphide and 50 ml of xylene is heated under reflux for 9 hours. The mixture is subsequently concentrated under water pump vacuum and the residue is stirred with 50 ml of 2N aqueous sodium hydroxide solution. The mixture is then filtered and the filtrate is acidified with 2N hydrochloric acid. The crystalline product which is obtained is isolated by filtration with suction.

This gives 1.6 g (64% of theory) of 3-(4-cyano-2,5-difluoro-phenyl)-1-methyl-5-mercapto-1H-pyrazole of melting point 137°C.

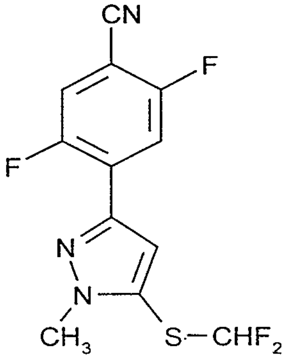
The compound listed in Table 1 as Example 79 can also be prepared, for example, as follows:



At -20°C, a solution of 10.9 g (0.06 mol) of 1-(2,5-difluoro-4-cyano-phenyl)-ethanone in 50 ml of tetrahydrofuran is added dropwise over a period of about 30 minutes to a suspension of 13.5 g (0.12 mol) of potassium t-butoxide in 100 ml of tetrahydrofuran. The mixture is stirred at -20°C for approximately 30 minutes and then admixed with 4.6 g (0.06 mol) of carbon disulphide (CS_2). After a further 30 minutes, 7.3 g (0.12 mol) of acetic acid and 5.6 g (0.12 mol) of methylhydrazine are added successively, and the reaction mixture is allowed to warm to room temperature over a period of 2 hours. The reaction mixture is then poured into 250 ml of ice-water and washed with dichloromethane. The aqueous phase is adjusted to pH 1 using hydrochloric acid and extracted repeatedly with dichloromethane. The extracts from the hydrochloric-acid solution are washed with sodium chloride solution, dried over magnesium sulphate and freed from the solvent under water pump vacuum.

This gives 5.6 g (37% of theory) of 3-(4-cyano-2,5-difluoro-phenyl)-1-methyl-5-mercapto-1H-pyrazole as a crystalline yellow solid of melting point 137°C.

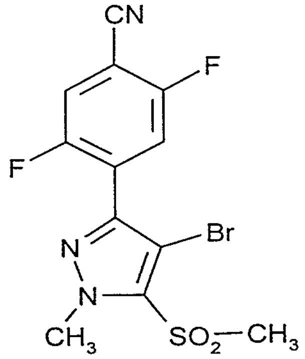
The compound listed in Table 1 as <u>Example 80</u> can be prepared, for example, as follows:



A solution of 5 g (0.02 mol) of 3-(4-cyano-2,5-difluoro-phenyl)-5-mercapto-1-methyl-1H-pyrazole in 80 ml of N,N-dimethyl-formamide is admixed with 8.3 g (0.06 mol) of potassium carbonate and heated to 50°C. At this temperature, about 10.4 g (0.12 mol) of chlorodifluoromethane are introduced over a period of 3 hours. After the reaction has ended, the predominant part of the solvent is removed under water pump vacuum and the residue is taken up in 50 ml of water. The aqueous suspension is acidified using 2N hydrochloric acid and extracted with dichloromethane. The organic phase is washed with water, dried over magnesium sulphate and freed from the solvent under water pump vacuum.

This gives 5.2 g (86% of theory) of 3-(4-cyano-2,5-difluoro-phenyl)-5-difluoromethylmercapto-1-methyl-1H-pyrazole of melting point 104°C.

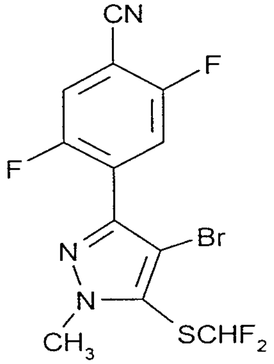
The compound listed in Table 1 as <u>Example 82</u> can be prepared, for example, as follows:



At -5°C, a suspension of 9.9 g (40 mmol) of 70% strength 3-chloro-perbenzoic acid in 130 ml of dichloromethane is added with stirring to a solution of 5.5 g (16 mmol) of 4-bromo-3-(4-cyano-2,5-difluoro-phenyl)-1-methyl-5-methylmercapto-1H-pyrazole in 100 ml of dichloromethane. The reaction mixture is stirred at room temperature (approximately 20°C) for 16 hours, the precipitated solid is filtered off and the filtrate is washed successively with saturated. sodium thiosulphate solution, saturated sodium bicarbonate solution and saturated sodium chloride solution, dried over magnesium sulphate and freed from the solvent under water pump vacuum.

This gives 5.5 g (91% of theory) of 4-bromo-3-(4-cyano-2,5-difluoro-phenyl)-1-methyl-5-methylsulphonyl-1H-pyrazole as a crystalline solid of melting point 176°C.

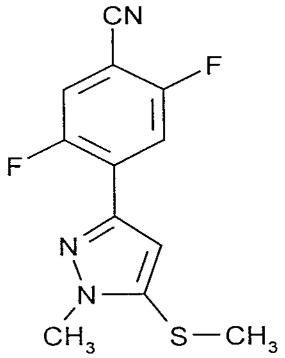
The compound listed in Table 1 as Example 83 can be prepared, for example, as follows:



At room temperature (approximately 20°C), a solution of 4.8 g (30 mmol) of bromine in 15 ml of dichloromethane is added with stirring to a solution of 5.1 g (17 mmol) of 3-(4-cyano-2,5-difluoro-phenyl)-5-difluoro-methylmercapto-1H-methyl-1H-pyrazole in 20 ml of dichloromethane. The reaction mixture is heated under reflux for 18 hours, diluted with 20 ml of dichloromethane and washed successively with dilute sodium hydrogen sulphite solution, saturated sodium bicarbonate solution and sodium chloride solution, dried over magnesium sulphate and freed from the solvent under water pump vacuum.

This gives 5.8 g (90% of theory) of 4-bromo-3-(4-cyano-2,5-difluoro-phenyl)-5-difluoromethylmercapto-1-methyl-1H-pyrazole as a crystalline solid of melting point 100°C.

The compound listed in Table 1 as Example 87 can be prepared, for example, as follows:

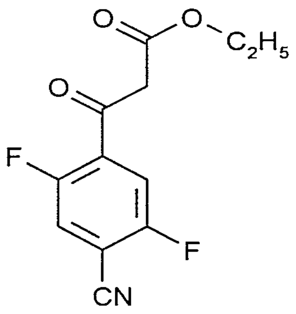


At room temperature (approximately 20°C), 2.5 g (55 mmol) of methylhydrazine are added to a solution of 6.2 g (22 mmol) of 1-(4-cyano-2,5-difluoro-phenyl)-3,3-bis-(methylthio)-2-propen-1-one in 60 ml of acetonitrile. The reaction mixture is heated under reflux for 90 minutes and then poured into ice-water. The precipitated solid is filtered off with suction, washed with water and dried under reduced pressure.

This gives 5.0 g (86% of theory) of 3-(4-cyano-2,5-difluoro-phenyl)-1-methyl-5-methylmercapto-1H-pyrazole of melting point 118°C.

Starting materials of the formula (III):

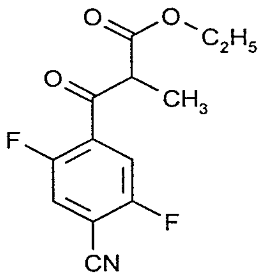
Example (III-1)



At 10°C to 15°C, 147 g (1.46 mol) of triethylamine and 170 g (1.80 mol) of magnesium chloride (anhydrous) are added successively to a mixture of 251 g (1.48 mol) of potassium monoethyl malonate in 2 litres of acetonitrile. The mixture is stirred at room temperature (approximately 20°C) for about 150 minutes, then cooled to -10°C to -5°C and, at this temperature, admixed successively with 145 g (0.72 mol) of 4-cyano-2,5-difluoro-benzoyl chloride and 14.7 g (0.146 mol) of triethylamine. The reaction mixture is then stirred at room temperature for approximately 18 hours and subsequently concentrated. The residue is admixed with 1.2 litres of toluene and then with 1 litre of 13% strength hydrochloric acid. The mixture is stirred at room temperature for 3 hours, the precipitated solid is filtered off and the organic phase is separated off from the filtrate. The organic phase is washed with 13% strength hydrochloric acid and then with water, dried with magnesium sulphate and filtered. The solvent is carefully distilled off from the filtrate under water pump vacuum.

This gives 173 g (95% of theory) of ethyl 3-(4-cyano-2,5-difluoro-phenyl)-3-oxo-propionate of melting point 44°C as a bright yellow, solid residue.

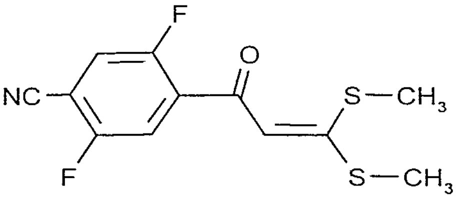
Example (III-2)



Using the method of Example (III-1) and potassium monoethylmethyl malonate instead of potassium monoethyl malonate, the compound ethyl 3-(4-cyano-2,5-difluoro-phenyl)-2-methyl-3-oxo-propionate is obtained in 93.6% yield as a yellow liquid.

^1H NMR ($CDCl_3$, d, ppm): 1.20 (t, 3H), 1.50 (d, 3H), 4.17 (q, 2H), 4.32 (q, 1H), 7.48 (dd, 1H), 7.73 (dd, 1H).

Example (III-3)

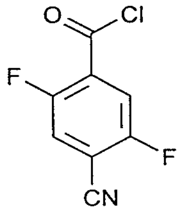


At -20°C, a solution of 10.9 g (0.06 mol) of 1-(4-cyano-2,5-difluoro-phenyl)-ethanone in 50 ml of tetrahydrofuran is added dropwise over a period of 0.5 hours to a suspension of 13.5 g (0.12 mol) of potassium t-butoxide in 100 ml of tetrahydrofuran. The mixture is stirred at -20°C for about 30 minutes and then admixed with 4.6 g (0.06 mol) of carbon disulphide (CS_2). After a further 30 minutes, 17.0 g (0.12 mol) of methyl iodide are added, and the reaction mixture is allowed to warm to room temperature over a period of 2 hours. The reaction mixture is poured into 500 ml of ice-water, adjusted to pH 1 using hydrochloric acid and extracted with 1500 ml of ethyl acetate. The organic phase is washed with sodium chloride solution, dried over magnesium sulphate and freed from the solvent under water pump vacuum. The crude product which is obtained as a residue is stirred with approximately 20 ml of acetonitrile and the precipitated solid is filtered off and dried.

This gives 6.9 g (40% of theory) of 1-(4-cyano-2,5-difluoro-phenyl)-3,3-bis-(methylthio)-2-propen-1-one as a crystalline bright yellow solid of melting point 188°C.

Starting materials of the formula (V):

Example (V-1)



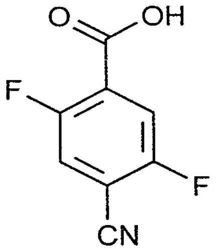
6.7 g (56 mmol) of thionyl chloride are added dropwise to a mixture of 3.4 g (19 mmol) of 4-cyano-2,5-difluoro-benzoic acid, 30 ml of carbon tetrachloride and a drop of N,N-dimethyl-formamide. The reaction mixture is then heated under reflux for approximately 6 hours. After the evolution of gas has ceased, the mixture is allowed to cool and filtered. The volatile components are then carefully distilled off from the filtrate under water pump vacuum.

This gives 3.6 g (95.5% of theory) of 4-cyano-2,5-difluoro-benzoyl chloride as a yellow liquid.

^{1}H NMR ($CDCl_3$, d, ppm): 7.95 (dd, 1H), 7.54 (dd, 1H).

Starting materials of the formula (VI):

Example (VI-1)

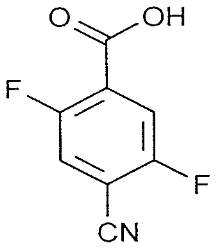


At at most 40°C, a solution of 5.74 g (29 mmol) of 2,5-difluoro-4-nitromethyl-benzonitrile in 30 ml of acetone is added dropwise to a suspension of 8.0 g (50 mmol) of potassium permanganate (ground finely in a mortar) in 100 ml of acetone. The reaction mixture is then stirred at room temperature (approximately 20°C) for about 16 hours and subsequently acidified using 2N hydrochloric acid. The precipitated manganese dioxide is removed by filtration and the filtrate is concentrated under water pump vacuum. The residue is taken up in ethyl acetate, washed with water, dried with magnesium sulphate and filtered. The filtrate is concentrated and the residue is stirred with a little dichloromethane and filtered off with suction.

This gives 3.4 g (64% of theory) of 4-cyano-2.5-difluoro-benzoic acid as a crystalline product of melting point 159°C.

^{1}H NMR (DMSO-D$_6$, d, ppm): 7.92 (dd, 1H), 8.15 (dd, 1H), 14.10 (s broad, 1H).

Example (VI-2)



Step 1

A mixture of 9.5 g (50 mmol) of methyl 2,4,5-trifluoro-benzoate, 2.7 g (55 mmol) of sodium cyanide and 100 ml of N,N-dimethyl-formamide is stirred at approximately 25°C for 3 days and subsequently filtered through activated carbon. The filtrate is concentrated using water pump vacuum and the residue is recrystallized from cyclohexane/ethyl acetate (Vol.: 9:1).

This gives 4.0 g (41% of theory) of methyl 4-cyano-2,5-difluoro-benzoate of melting point 60°C.

Step 2

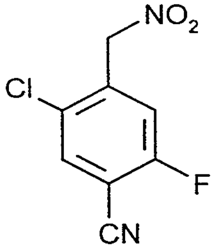
A mixture of 0.83 g (4.4 mmol) of methyl 4-cyano-2,5-difluoro-benzoate, 0.49 g (4.4 mmol) of potassium t-butoxide, 50 ml of diethyl ether and 10 ml of water is stirred at approximately 23°C for 12 hours. The mixture is subsequently acidified using conc. hydrochloric acid, and the organic phase is separated off, dried over sodium sulphate and filtered. The solvent is carefully distilled off from the filtrate under water pump vacuum.

This gives 0.50 g (62% of theory) of 4-cyano-2,5-difluoro-benzoic acid as a crystalline product of melting point 159°C.

By the method of Example (VI-1) or (VI-2), it is also possible to prepare, for example, the compounds 5-chloro-4-cyano-2-fluoro-benzoic acid (melting point: 147°C) and 2-chloro-4-cyano-5-fluoro-benzoic acid (melting point: 163°C).

Starting materials of the formula (VII):

Example (VII-1)



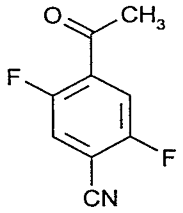
3.7 g (60 mmol) of nitromethane are initially charged together with 80 ml of ethyl acetate and 18.2 g (120 mmol) of diazabicycloundecene (DBU), and the mixture is cooled to -10°C. A solution of 8.7 g (50 mmol) of 5-chloro-2,4-difluoro-benzonitrile in 50 ml of ethyl acetate is then added dropwise, and the reaction mixture is stirred in an ice bath for about 15 hours and subsequently acidified using 2N hydrochloric acid. The organic phase is separated off, shaken with saturated aqueous sodium chloride solution, dried with magnesium sulphate and filtered. The solvent is carefully distilled off from the filtrate under water pump vacuum.

This gives 9.7 g (73.6% pure, i.e. 67% of theory) of 5-chloro-2-fluoro-4-nitromethyl-benzonitrile as an amorphous residue which can be employed without any further purification for the next reaction step.

By the method of Example (VII-1), it is also possible to prepare, for example, the compounds 2,5-difluoro-4-nitromethyl-benzonitrile (melting point: 100°C) and 2-chloro-5-fluoro-4-nitromethyl-benzonitrile (melting point: 35°C).

Starting materials of the formula (X):

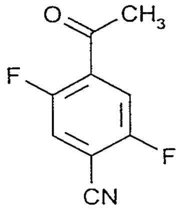
Example (X-1)



5.16 g (24 mmol) of 2,5-difluoro-4-(1-nitro-ethyl)-benzonitrile are dissolved in 50 ml of acetic acid, and the mixture is heated under reflux for 8 hours and, after cooling, introduced into about 200 ml of water. The mixture is then extracted with dichloromethane and the organic phase is washed successively with water, saturated sodium bicarbonate solution and with saturated sodium chloride solution, dried with magnesium sulphate and filtered. The filtrate is concentrated under water pump vacuum and the residue is extracted repeatedly with hot n-hexane. The solvent is carefully distilled off from the combined extract solutions under water pump vacuum.

This gives 2.72 g (62% of theory) of 1-(2,5-difluoro-4-cyano-phenyl)-ethanone as a colourless crystalline residue of melting point 42°C.

Example (X-2)



5.4 g (0.11 mol) of sodium cyanide (ground) in 200 ml of N,N-dimethyl-formamide are stirred with 17.4 g (0.10 mol) of 2,4,5-trifluoro-acetophenone at 25°C for 12 hours. The mixture is filtered off with suction, the filtrate is filtered through activated carbon and the solvent is carefully distilled off from the filtrate under water pump vacuum.

This gives 10.4 g (57% of theory) of 1-(2,5-difluoro-4-cyano-phenyl)-ethanone as an amorphous residue.

IR spectrum: 1698 cm^{-1} (CO), 2240 cm^{-1} (CN).

Use Examples:

Example A

Pre-emergence Test

Solvent: 5 parts by weight of acetone
Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent, the stated amount of emulsifier is added and the concentrate is diluted with water to the desired concentration.

Seeds of the test plants are sown in normal soil. After about 24 hours, the soil is sprayed with the preparation of active compound in such a way as to apply the particular amounts of active compound desired per unit area. The concentration of the spray series is chosen so that the particular amounts of active compound desired are applied in 1000 l of water/ha.

After three weeks, the degree of damage to the plants is rated in % damage in comparison to the development of the untreated control.

The figures denote:

0% = no effect (like untreated control)
100% = total destruction

In this test, at application rates of 60 and 125 g/ha, for example the compounds of Preparation Examples 3, 4, 7, 8, 10, 11, 12, 13 and 14 exhibit very strong activity against weeds such as Digitaria (80-100%), Setaria (70-100%), Amaranthus (100%), Datura (90-100%) and Solanum (100%), and some of them are tolerated well by crop plants, such as, for example, maize (5%), soya (0-30%) and cotton (0-30%).

Example B

Post-emergence Test

Solvent:	5 parts by weight of acetone
Emulsifier:	1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent, the stated amount of emulsifier is added and the concentrate is diluted with water to the desired concentration.

Test plants which have a height of 5-15 cm are sprayed with the preparation of active compound in such a way as to apply the particular amounts of active compound desired per unit area. The concentration of the spray liquor is chosen so that the particular amounts of active compound desired are applied in 1000 l of water/ha.

After three weeks, the degree of damage to the plants is rated in % damage in comparison to the development of the untreated control.

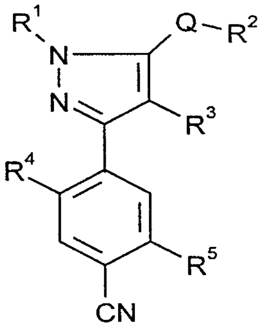
The figures denote:

0% = no effect (like untreated control)
100% = total destruction

In this test, at application rates of 20 and 60 g/ha, for example the compounds of Preparation Examples 3, 4, 7, 8, 10, 11, 12, 13 and 15 show very strong activity against weeds such as Abutilon (100%), Chenopodium (95-100%), Solanum (100%), Digitaria (70-100%) and Setaria (80-100%).

Patent Claims

1. 3-Cyanoaryl-pyrazoles of the general formula (I)



(I),

characterized in that

Q represents oxygen (O), sulphur (S), SO or SO_2,

R^1 represents hydrogen or represents alkyl, alkenyl, alkinyl, cycloalkyl or cycloalkylalkyl, each of which is optionally substituted,

R^2 represents hydrogen or represents alkyl, alkenyl, alkinyl, cycloalkyl or cycloalkylalkyl, each of which is optionally substituted,

R^3 represents hydrogen, halogen or optionally substituted alkyl,

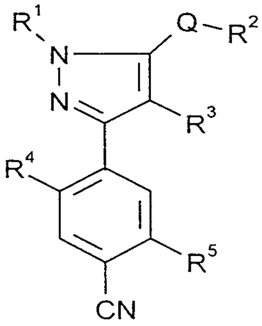
R^4 represents hydrogen or halogen and

R^5 represents hydrogen, hydroxyl, mercapto, amino, hydroxyamino, halogen, or represents one of the radicals $-Q-R^6$, $-NH-R^6$, $-NH-O-R^6$, $-NH-SO_2-R^6$, $-N(SO_2-R^6)_2$, $-CQ^1-R^6$, $-CQ^1-Q^2-R^6$, $-CQ^1-NH-R^6$, $-Q^2-CQ^1-R^6$, $-NH-CQ^1-R^6$, $-N(SO_2-R^6)(CQ^1-R^6)$, $-Q^2-CQ^1-Q^2-R^6$, $-NH-CQ^1-Q^2-R^6$ or $-Q^2-CQ^1-NH-R^6$,

where Q^1 and Q^2 each represent oxygen or sulphur and R^6 represents alkyl, alkenyl, alkinyl, cycloalkyl, cycloalkylalkyl, aryl, arylalkyl, heterocyclyl or heterocyclylalkyl, each of which is optionally substituted,

except for the compounds 1-methyl-3-(4-cyano-2-fluoro-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-phenyl)-4-bromo-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-nitro-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-ethylsulphonylamino-phenyl)-4-chloro-5-difluoromethoxy-pyrazole,1-methyl-3-(4-cyano-2-fluoro-5-ethoxycarbonylmethoxy-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-chloro-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-methylthio-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-amino-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-hydroxy-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-chloro-phenyl)-4-chloro-5-difluoromethoxy-pyrazole, 1-methyl-3-(4-cyano-2-fluoro-5-aminosulphonyl-phenyl)-4-chloro-5-difluoromethoxy-pyrazole and 1-methyl-3-(4-cyano-2-fluoro-5-fluorosulphonyl-phenyl)-4-chloro-5-difluoromethoxy-pyrazole.

2. Process for preparing 3-cyanoaryl-pyrazoles of the general formula (I)



(I).

in which

R^1, R^2, R^3, R^4, R^5 and Q are each as defined in Claim 1,

characterized in that

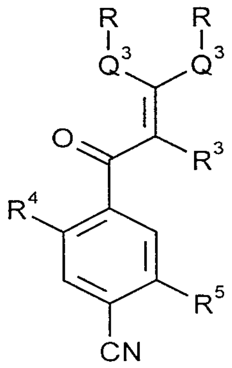
hydrazine or derivatives thereof of the general formula (II)

$$H_2N\text{-}NH\text{-}R^1 \qquad (II),$$

in which

R^1 is as defined above,

are reacted with cyanoarylcarbonyl compounds of the general formula (III)



(III),

in which

R^3, R^4 and R^5 are each as defined above,

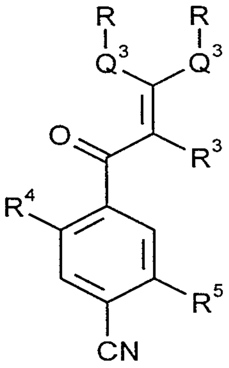
Q^3 represents oxygen or sulphur and

R represents hydrogen or alkyl,

- and/or, if appropriate, tautomers of the compounds of the formula (III) -

and, if appropriate, further conversions within the scope of the above definition of the substituents are carried out by customary methods on the resulting compounds of the formula (I).

3. Cyanoaryl compounds of the general formula (III)



(III),

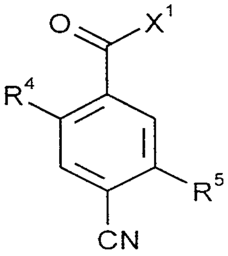
in which

R^3, R^4 and R^5 are each as defined in Claim 1 and

Q^3 represents oxygen or sulphur and

R represents hydrogen or alkyl.

4. Cyanobenzoyl halides of the general formula (V)



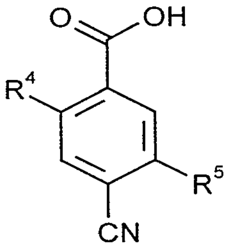
(V).

in which

R^4 and R^5 are each as defined in Claim 1 and

X^1 represents halogen.

5. 4-Cyanobenzoic acids of the general formula (VIa)

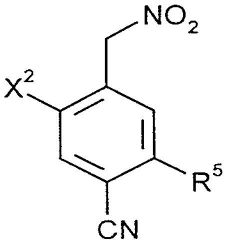


(VIa),

in which

R^4 and R^5 are each as defined in Claim 1,

6. Nitromethylbenzonitriles of the general formula (VII)



(VII),

in which

R^5 is as defined in Claim 1 and

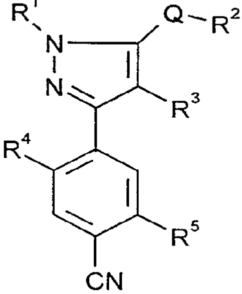
X^2 represents halogen.

7. Herbicidal compositions, characterized in that they contain at least one 3-cyanoarylpyrazole of the general formula (I) according to Claim 1.

8. Method for controlling undesirable plants, characterized in that 3-cyanoarylpyrazoles of the general formula (I) according to Claim 1 are allowed to act on undesirable plants and/or their habitat.

9. Use of 3-cyanoarylpyrazoles of the general formula (I) according to Claim 1 for controlling undesirable plants.

10. Process for preparing herbicidal compositions, characterized in that 3-cyanoarylpyrazoles of the general formula (I) according to Claim 1 are mixed with extenders and/or surface-active substances.



(I)