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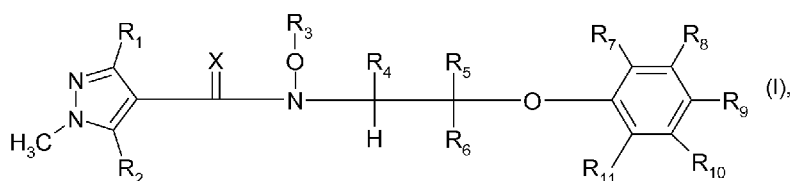
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(54) Title: N-HYDROXY-L-METHYL-LH-PYRAZOLE-4-CARBOXAMIDE DERIVATIVES AND THEIR USE AS MICROBIOCIDES



(57) Abstract: Compounds of formula (I) in which the substituents are as defined in claim 1, are suitable for use as microbiocides.

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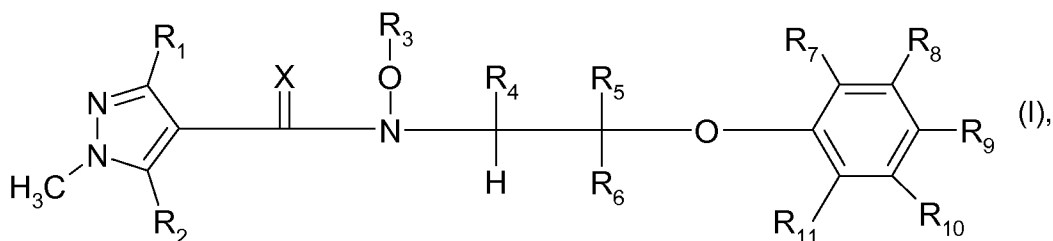
N-HYDROXY-I-METHYL-1H-PYRAZOLE-4-CARBOXAMIDE DERIVATIVES AND THEIR USE AS MICROBIOCIDES

The present invention relates to novel microbicidally active, in particular fungicidally active, carboxamides. It further relates to intermediates used in the preparation of these compounds, to compositions which comprise these compounds and to their use in agriculture or horticulture for controlling or preventing infestation of plants by phytopathogenic microorganisms, preferably fungi.

Fungicidally active carboxamides are described, for example, in EP 1787981 and EP 1792901.

It has been found that novel carboxamides with a specific substitution pattern have microbicidal activity.

The present invention accordingly relates to N-alkoxycarboxamides of formula I



wherein

R₁ is C₁-C₄alkyl or C₁-C₄haloalkyl;

R₂ is hydrogen or halogen;

X is oxygen or sulfur;

R₃ is hydrogen, C₁-C₄alkyl or C₁-C₄halogenalkyl;

R₄, R₅ and R₆ are, independently from each other, hydrogen, halogen, C₁-C₄alkyl or C₁-C₄haloalkyl;

R₇, R₈, R₉, R₁₀ and R₁₁ are, independently from each other, hydrogen, halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy or phenoxy; wherein phenoxy in turn may be mono- di- or trisubstituted by substituents selected from the group consisting of halogen, C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄-halogenalkyl, cyano, nitro, C₁-C₄-halogenalkoxy, C₁-C₄-alkylthio, C₁-C₄-alkylsulphinyl and C₁-C₄-alkylsulphonyl, or are phenyl, which in turn may be

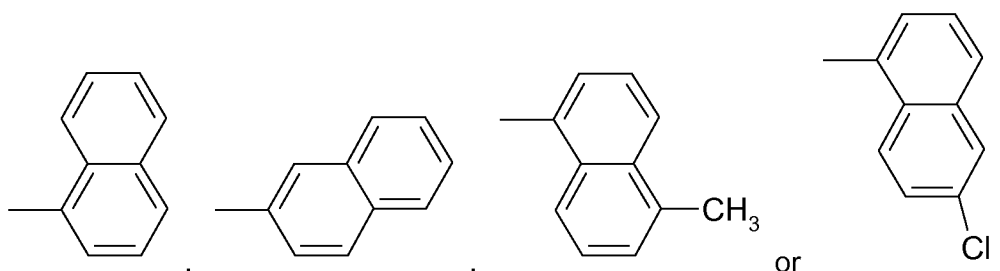
mono- di- or trisubstituted by substituents selected from the group consisting of halogen, C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄-halogenalkyl, cyano, nitro, C₁-C₄-halogenalkoxy and C₁-C₄-alkylthio;

or R₇ and R₈, or R₈ and R₉, or R₉ and R₁₀ or R₁₀ and R₁₁ together form together with the carbon atoms to which they are attached, a 6-membered aromatic ring which can be mono- di- or trisubstituted by substituents selected from the group consisting of halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy and C₁-C₄haloalkoxy; and agronomically acceptable salts/isomers/structural isomers/stereoisomers/diastereoisomers/enantio-mers/tautomers and N-oxides of those compounds.

The alkyl groups occurring in the definitions of the substituents can be straight-chain or branched and are, for example, methyl, ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, *n*-hexyl, *iso*-propyl, *n*-butyl, *sec*-butyl, *iso*-butyl or *tert*-butyl. Alkoxy, alkenyl and alkynyl radicals are derived from the alkyl radicals mentioned. The alkenyl and alkynyl groups can be mono- or di-unsaturated. The cycloalkyl groups occurring in the definitions of the substituents are, for example, cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl. Halogen is generally fluorine, chlorine, bromine or iodine, preferably fluorine, bromine or chlorine. This also applies, correspondingly, to halogen in combination with other meanings, such as halogenalkyl or halogenalkoxy. Haloalkyl groups preferably have a chain length of from 1 to 4 carbon atoms. Haloalkyl is, for example, fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, 2,2,2-trifluoroethyl, 2-fluoroethyl, 2-chloroethyl, pentafluoroethyl, 1,1-difluoro-2,2,2-trichloroethyl, 2,2,3,3-tetrafluoroethyl and 2,2,2-trichloroethyl; preferably trichloromethyl, difluorochloromethyl, difluoromethyl, trifluoromethyl and dichlorofluoromethyl. Alkoxy is, for example, methoxy, ethoxy, propoxy, *i*-propoxy, *n*-butoxy, isobutoxy, *sec*-butoxy and *tert*-butoxy; preferably methoxy and ethoxy. Halogenalkoxy is, for example, fluoromethoxy, difluoromethoxy, trifluoromethoxy, 2,2,2-trifluoroethoxy, 1,1,2,2-tetrafluoroethoxy, 2-fluoroethoxy, 2-chloroethoxy, 2,2-difluoroethoxy and 2,2,2-trichloroethoxy; preferably difluoromethoxy, 2-chloroethoxy and trifluoromethoxy.

Examples of bicyclic groups formed by the substituents at the phenyl ring (R₇ and R₈, or R₈ and R₉, or R₉ and R₁₀ or R₁₀ and R₁₁ together form together with the carbon atoms to which they are attached, a 6-membered aromatic ring which can be mono- di- or trisubstituted by substituents selected from the group consisting of halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy and C₁-C₄haloalkoxy) are

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In preferred compounds of formula I, independently from each other,

- a) R_1 is difluoromethyl, trifluoromethyl or methyl;
- b) R_2 is hydrogen or fluoro;
- c) R_3 is hydrogen, methyl or ethyl;
- d) R_4 is hydrogen or methyl;
- e) R_5 is hydrogen or methyl;
- f) R_6 is hydrogen or methyl;
- g) X is oxygen;
- h) R_7 is hydrogen, chloro, bromo or methyl;
- i) R_8 is hydrogen;
- j) R_9 is hydrogen, chloro, bromo, methyl, tert butyl, phenoxy substituted by halogen or phenyl substituted by halogen;
- k) R_{10} is hydrogen;
- l) R_{11} is hydrogen, chloro, bromo or methyl;
- m) R_8 and R_9 , together form together with the carbon atoms to which they are attached, a 6-membered aromatic ring which can be mono- di- or trisubstituted by chloro;

Especially preferred compounds of formula I are those, wherein

- a) R_1 is difluoromethyl, trifluoromethyl or methyl;
- b) R_2 is hydrogen or fluoro;
- c) R_3 is hydrogen, methyl or ethyl;
- d) R_4 is hydrogen or methyl;
- e) R_5 is hydrogen or methyl;
- f) R_6 is hydrogen or methyl;
- g) X is oxygen;
- h) R_7 is chloro or bromo;

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- i) R₈ is hydrogen;
- j) R₉ is chloro, bromo, methyl, tert butyl, phenoxy substituted by halogen or phenyl substituted by halogen;
- k) R₁₀ is hydrogen;
- l) R₁₁ chloro, bromo or methyl;
- m) R₈ and R₉, together form together with the carbon atoms to which they are attached, a 6-membered aromatic ring which can be mono- di- or trisubstituted by chloro;

In a preferred group of compounds of formula I,

R₁ is C₁-C₄haloalkyl;

R₂ is hydrogen or halogen;

X is oxygen or sulfur;

R₃ is C₁-C₄alkyl;

R₄ is hydrogen or C₁-C₄alkyl;

R₅ and R₆ are hydrogen;

R₇ and R₉, are, independently from each other, hydrogen, halogen or C₁-C₄alkyl; and

R₈ and R₁₀ are hydrogen and

R₁₁ is halogen or C₁-C₄alkyl.

In a further preferred group of compounds of formula I,

R₁ is C₁-C₄haloalkyl;

R₂ is hydrogen or halogen;

X is oxygen;

R₃ is C₁-C₄alkyl;

R₄ is hydrogen or C₁-C₄alkyl;

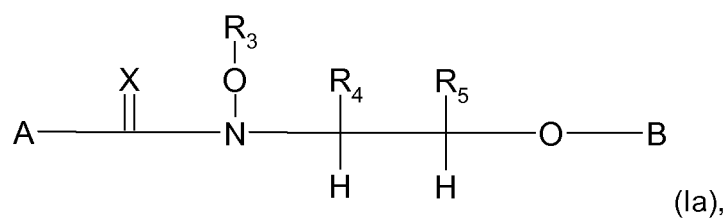
R₅ and R₆ are hydrogen;

R₇ and R₉, are, independently from each other, hydrogen, halogen or C₁-C₄alkyl; and

R₈ and R₁₀ are hydrogen.

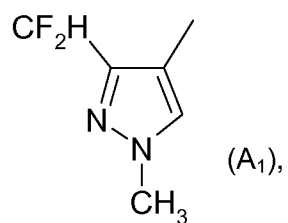
A preferred group of compounds of formula I is represented by the compounds of formula Ia

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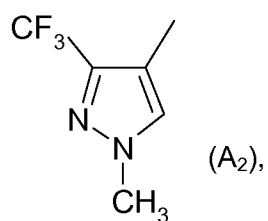


wherein

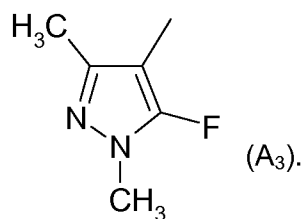
In the compounds of formula 1a, A is selected from the groups consisting of A₁,



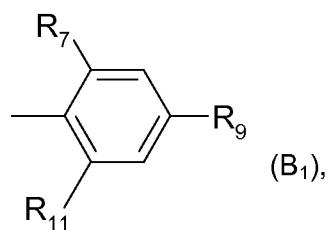
A₂,



and A₃,

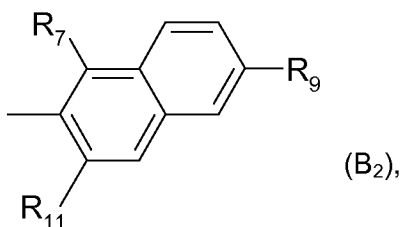


B is selected from the groups consisting of B₁,



and B₂,

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X is oxygen or sulfur;

R₃ is C₁-C₄alkyl;

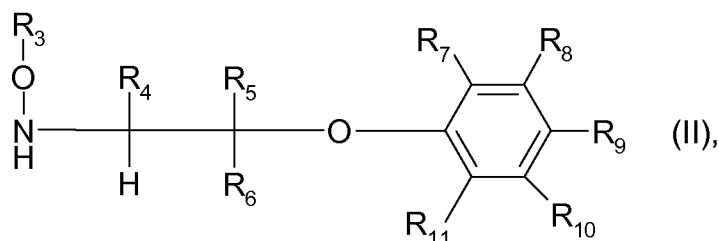
R₄ is hydrogen or C₁-C₄alkyl;

R₅ is hydrogen;

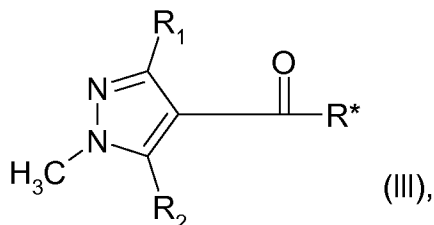
R₇ and R₉, are, independently from each other, hydrogen, halogen or C₁-C₄alkyl; and

R₁₁ is halogen or C₁-C₄alkyl.

Compounds of formula I may be prepared by reacting a compound of formula II



in which R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀ and R₁₁ are as defined under formula I; with a compound of formula III



in which R₁ and R₂ are as defined under formula I, and R* is halogen, hydroxy or C₁₋₆ alkoxy, preferably chloro.

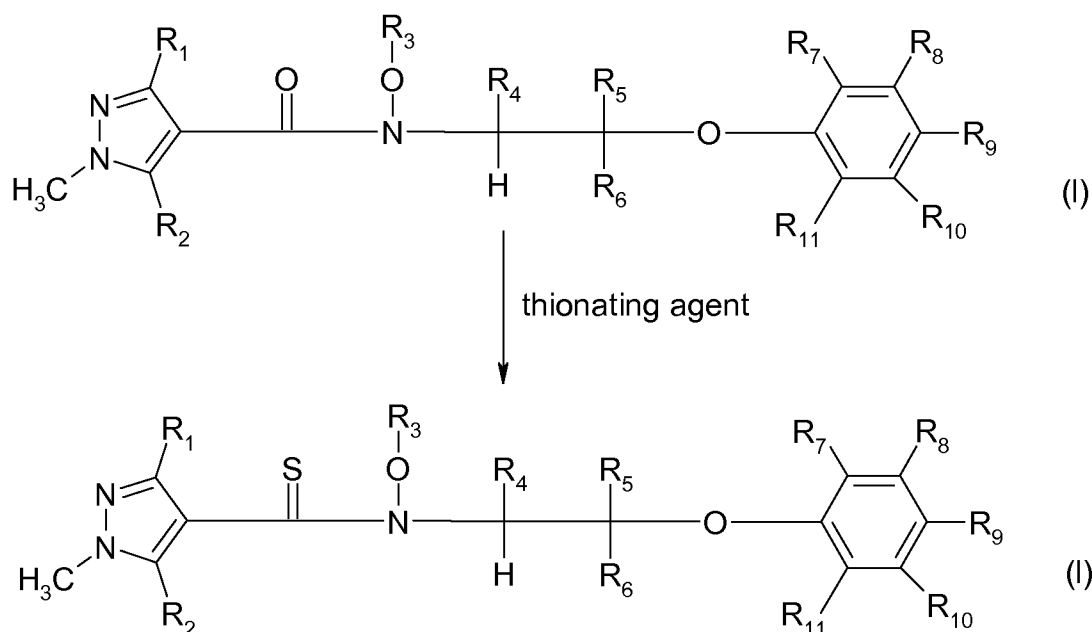
The reactions to give compounds of formula I are advantageously carried out in aprotic inert organic solvents. Such solvents are hydrocarbons such as benzene, toluene, xylene or cyclohexane, chlorinated hydrocarbons such as dichloromethane, trichloromethane,

tetrachloromethane or chlorobenzene, ethers such as diethyl ether, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, tetrahydrofuran or dioxane, nitriles such as acetonitrile or propionitrile, amides such as N,N-dimethylformamide, diethylformamide or N-methylpyrrolidinone. The reaction temperatures are advantageously between -20°C and +120°C. In general, the reactions are slightly exothermic and, as a rule, they can be carried out at ambient temperature. To shorten the reaction time, or else to start the reaction, the mixture may be heated briefly to the boiling point of the reaction mixture. The reaction times can also be shortened by adding a few drops of base as reaction catalyst. Suitable bases are, in particular, tertiary amines such as trimethylamine, triethylamine, quinuclidine, 1,4-diazabicyclo[2.2.2]octane, 1,5-diazabicyclo[4.3.0]non-5-ene or 1,5-diazabicyclo-[5.4.0]undec-7-ene. However, inorganic bases such as hydrides, e.g. sodium hydride or calcium hydride, hydroxides, e.g. sodium hydroxide or potassium hydroxide, carbonates such as sodium carbonate and potassium carbonate, or hydrogen carbonates such as potassium hydrogen carbonate and sodium hydrogen carbonate may also be used as bases. The bases can be used as such or else with catalytic amounts of a phase-transfer catalyst, for example a crown ether, in particular 18-crown-6, or a tetraalkylammonium salt.

When R* is hydroxy, a coupling agent, such as benzotriazol-1-yloxytris(dimethylamino) phosphoniumhexafluorophosphate, bis-(2-oxo-3-oxazolidinyl)-phosphinic acid chloride (BOP-Cl), N,N'-dicyclohexylcarbodiimide (DCC) or 1,1'-carbonyl-diimidazole (CDI), may be used.

Compounds of formula I in which R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀ and R₁₁ are as defined under formula I and X is sulfur; may be prepared by reacting a compound of formula I in which R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀ and R₁₁ are as defined under formula I and X is oxygen in the presence of a thionating agent.

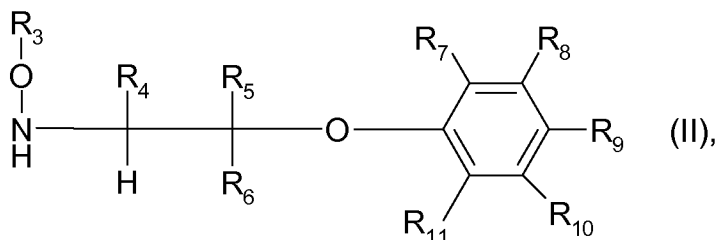
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Suitable thionating agents include sulphur, hydrogensulfide, sodium sulphide, ammonium sulphide, boron trisulfide, phosphorous pentasulfide or Lawesson's reagent in the presence or in the absence of a base such as an inorganic and organic base. Suitable bases include metal carbonates such as sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, triethylamine, Hunig base, pyridine, picoline, lutidine or quinoline. Suitable solvents include inert organic solvents such as optionally halogenated aliphatic, alicyclic or aromatic hydrocarbons, such as petroleum ether, hexane, heptane, cyclohexane, benzene, toluene, xylene, chlorobenzene, dichlorobenzene, dichloromethane, chloroform, carbon tetrachloride, dichloroethane; ethers, such as diethylether, diisopropylether, methyl t-butylether, dioxane, THF, 1,2-dimethoxyethane, 1,2-diethoxyethane or sulfolane.

The reaction temperature can be varied from 0°C to 150°C, preferably from 20°C to 130°C.

The intermediates of the formula II

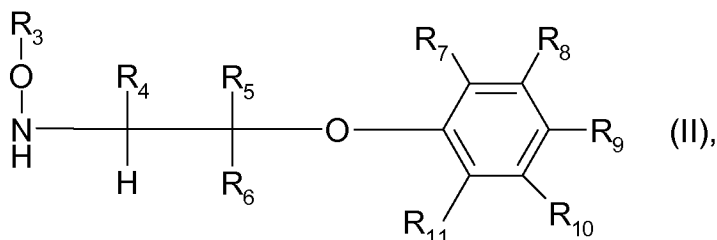


wherein R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 , R_{10} , and R_{11} are as defined under formula I, preferably wherein R_4 is C_1 - C_4 alkyl; are novel and were developed specifically for the preparation of the compounds of the formula I. Accordingly, these intermediates of the formula II also form a part of the subject-matter of the present invention.

The preferred substituent definitions for the compounds of formula I are also valid for the compound of formula II. Thus, preferred compounds of formula II are for example those, wherein, independently from each other,

- a) R_3 is hydrogen, methyl or ethyl; especially preferred methyl;
- b) R_4 is hydrogen, methyl or ethyl; especially preferred methyl
- c) R_5 is hydrogen or methyl;
- d) R_6 is hydrogen or methyl;
- e) R_8 and R_{10} are hydrogen;
- f) R_7 , R_9 and R_{11} is hydrogen, chloro, bromo or methyl;
- g) R_8 and R_9 , together form together with the carbon atoms to which they are attached, a 6-membered aromatic ring which can be mono- di- or trisubstituted by chloro.

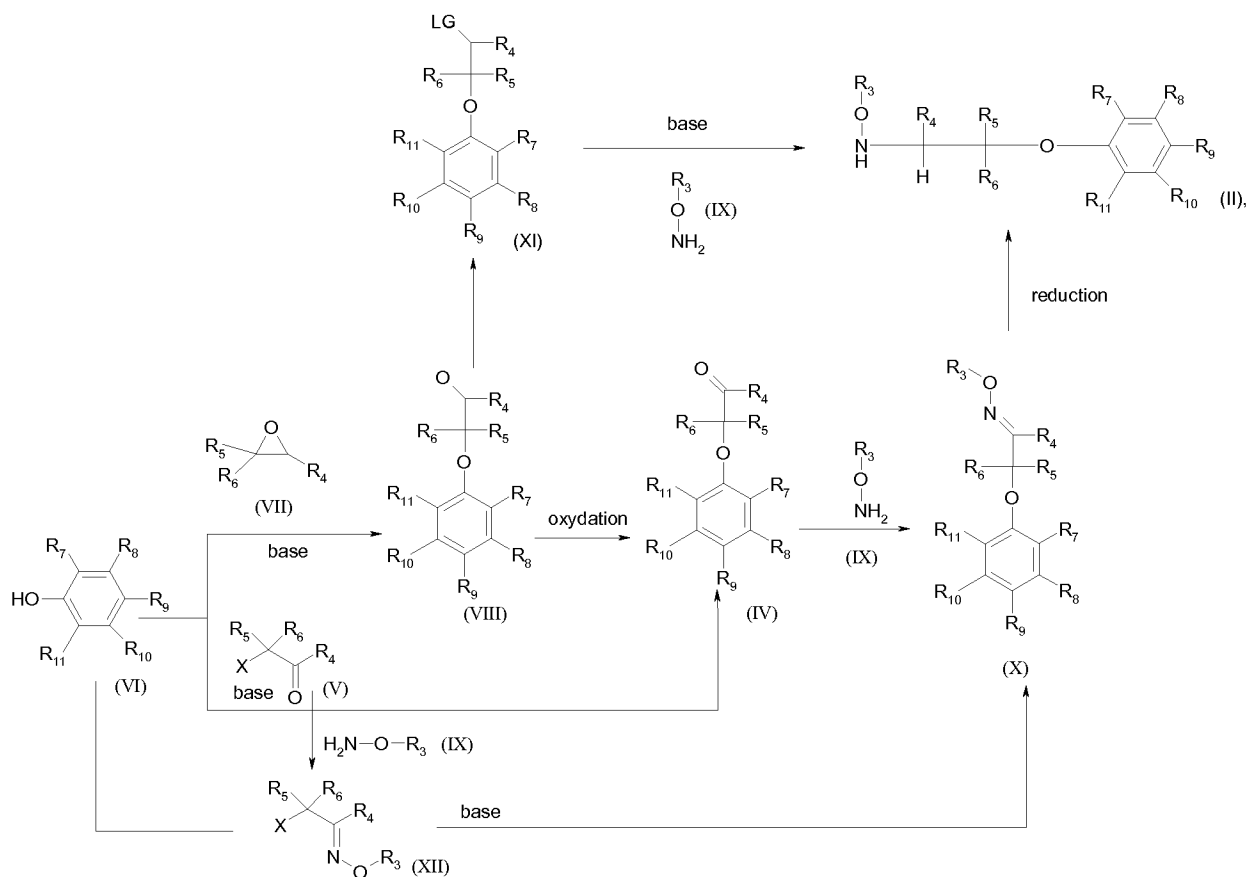
Intermediates of formula II



wherein R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 , R_{10} and R_{11} are as defined under formula I may be prepared as described in reaction scheme 1.

Scheme 1:

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Intermediates of formula IV, in which $R_4, R_5, R_6, R_7, R_8, R_9, R_{10}$ and R_{11} are as defined under formula II can be prepared by a Williamson reaction of a hydroxy derivative of formula VI, in which R_7, R_8, R_9, R_{10} and R_{11} are as defined under formula II, with a α -halogen carbonyl compound of formula V, in which R_4, R_5 and R_6 are as defined under formula II and X is halogen, preferably chloro. Said alkylation reaction may be performed in the presence of a base. Suitable bases include metal hydroxides and/or carbonates such as lithium hydroxide, cesium carbonate, potassium carbonate, potassium hydroxide, sodium hydroxide or metal hydrides, such as sodium hydride and lithium hydride or cesiumfluoride. Suitable solvents include ketones, such as acetone and methyl ethyl ketone, and other solvents, such as N,N-dimethylformamide, dimethylacetamide and nitriles, such as acetonitrile and propionitrile. The reaction temperature can vary within wide limits, but typically is from ambient temperature to the boiling point of the reaction mixture.

O-alkoxy oxime derivatives of formula X may be prepared by oximation of ketones of formula IV with O-alkyl hydroxylamine derivatives of formula IX or a salt thereof.

Suitable solvents carrying out the oximation step are hydrocarbons such as benzene, toluene, xylene or cyclohexane, chlorinated hydrocarbons such as dichloromethane, trichloromethane, tetrachloromethane or chlorobenzene, ethers such as diethyl ether, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, tetrahydrofuran or dioxane, nitriles such as acetonitrile or propionitrile, amides such as N,N-dimethylformamide, diethylformamide, N-methylpyrrolidinone, alcohols such as methanol, ethanol, water or mixtures thereof. The reaction temperatures are advantageously between -20°C and +120°C. In general, the reactions can be carried out at ambient temperature. Suitable bases are, in particular pyridine, tertiary amines such as trimethylamine, triethylamine, huenigs base, quinuclidine, 1,4-diazabicyclo[2.2.2]octane, 1,5-diazabicyclo[4.3.0]non-5-ene or 1,5-diazabicyclo[5.4.0]undec-7-ene. However, inorganic bases such as hydroxides, e.g. sodium hydroxide or potassium hydroxide, carbonates such as sodium carbonate and potassium carbonate, or hydrogen carbonates such as potassium hydrogen carbonate and sodium hydrogen carbonate may also be used. Alternatively O-alkoxy oxime derivatives of formula X may be prepared by Williamson reaction of a hydroxy derivative of formula VI, in which R₇, R₈, R₉, R₁₀ and R₁₁ are as defined under formula II, with a α -halogen carbonyl compound of formula XII, in which R₃, R₄, R₅ and R₆ are as defined under formula II and X is halogen, preferably chloro. Said compounds of formula XII may be prepared by oximation of ketones of formula V with O-alkyl hydroxylamine derivatives of formula IX or a salt thereof.

O-Alkylhydroxylamines of formula II may be prepared by the reduction of O-alkoxy oxime derivatives of formula X, in the presence of a 1-10 equivalents of hydride reducing reagent such as sodium or tetrabutyl cyanoborohydride or sodium triacetoxyborohydride. The reaction can be performed in protic solvents, such as alcohols methanol, ethanol, isopropanol, tert-butanol and the like. An acid catalyst such as HCl or p-toluenesulfonic acid can be added portionwise in order to maintain a pH of 3-5 as determined by pH-meter or indicator dye, such as bromocresol green or methyl orange. The reaction can also be performed directly in an acidic solvent such as acetic acid. The reaction temperature typically lies in the range of -5°C to 60°C.

Alcohols of formula VIII in which R₄, R₅, R₆, R₇, R₈, R₉, R₁₀ and R₁₁ are as defined under formula II, are available by ring opening of an epoxyde of formula VII, in which R₄, R₅ and R₆ are as defined under formula II, while using the hydroxy derivative of formula VI. The ring opening reaction may be performed in the presence of a catalyst. Suitable

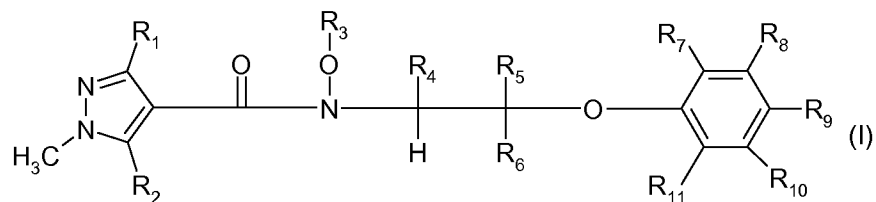
catalysts include bases, such as amines like pyridine, tri-ethanolamine and the like, or metal hydroxides and/or carbonates such as lithium hydroxide, cesium carbonate, potassium carbonate, potassium hydroxide, sodium hydroxide or metal hydrides, such as sodium hydride and lithium hydride or cesiumfluoride as well as Lewis acids, such as tetramethylammoniumchlorid. Suitable solvents include alcohols, such as ethanol, isopropanol, tert-butanol and the like, ketones, such as acetone and methyl ethyl ketone, and other solvents, such as N,N-dimethylformamide, dimethylacetamide and nitriles, such as acetonitrile and propionitrile. The reaction temperature can vary within wide limits, but typically is from ambient temperature to the boiling point of the reaction mixture.

The ketone intermediates of formula IV may then be prepared by oxidizing the corresponding alcohols of formula VIII. Advantageous oxidation procedures can be based on sulphur based oxidation agents (in the literature referred to, for example, as Swern-oxidation or Pfitzner-Moffat-oxidation), metal based oxidation agents or hydrogen peroxide in the presence of metal catalysts, such as Na_2WO_4 (c.f. e.g. R. Noyori, *Bull. Chem. Soc. Jpn.* 1999, 72, 2287-2306).

An alternative access to the compounds of formula II is the transformation of the compounds of formula VIII into compounds of formula XI, in which R_4 , R_5 , R_6 , R_7 , R_8 , R_9 , R_{10} and R_{11} are as defined under formula II and LG stands for a leaving group, by standard methods. Typical leaving groups are chloride, bromide, iodide, (methylsulfonyl)oxy or [(4-methylphenyl)sulfonyl]oxy. Conversion of alcohols to halides is described in: March, J. *Advanced Organic Chemistry*; J. Wiley & Sons: New York, (1992); 4th Ed, pp 498-499). The conversion of compounds of formula XI, into compounds of formula II may be achieved by nucleophilic substitution with O-alkyl hydroxylamine derivatives of formula IX or a salt thereof. In such a reaction, the leaving group LG is displaced in the presence of an acid acceptor, which can be a tertiary amine, such as triethylamine, an alkoxyde, such as tertiary-butoxyde, or a carbonate, such as potassium or cesium carbonate. The displacements can be carried out in polar aprotic solvents, such as dimethylformamide or dimethylsulfoxide, ether solvents, such as tetrahydrofurane or dioxane, or protic solvents, such as methanol or ethanol. Reaction temperature typically lies in the range of from 20°C to 150°C.

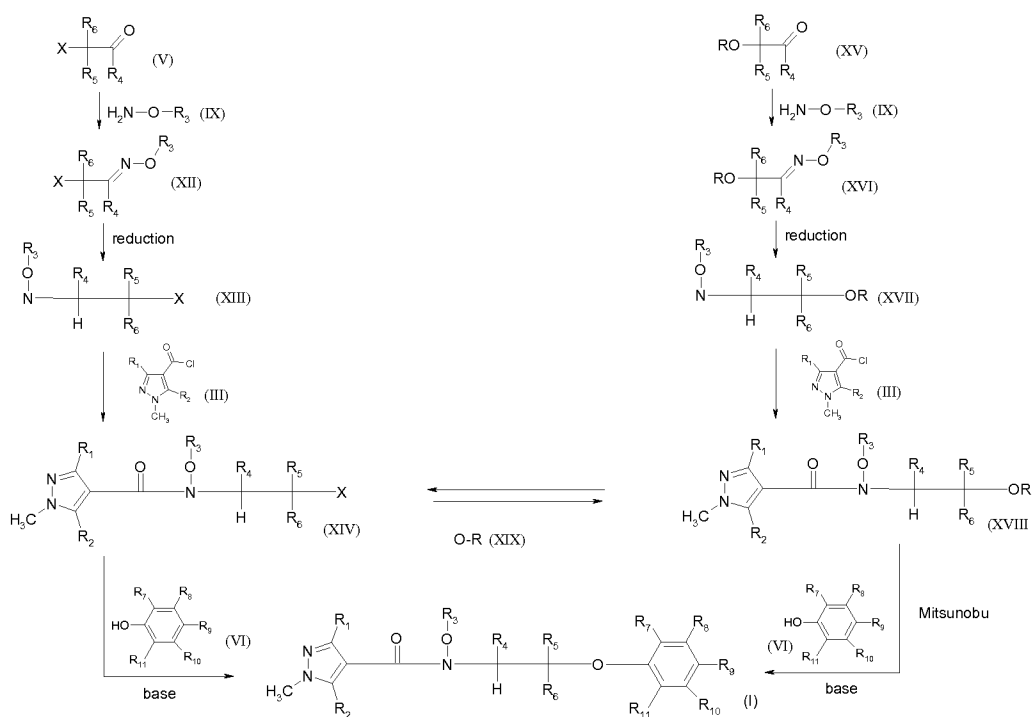
Compounds of formula I

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may be prepared alternatively as described in reaction scheme 2.

Scheme 2:



O-alkoxy oxime derivatives of formula XII or XVI, in which R_3 , R_4 , R_5 and R_6 are as defined under formula II, R is H or a common hydroxy protecting group and X is halogen, preferably chloro, may be prepared by oximation of oxo compounds of formula V or XV with O-alkyl hydroxylamine derivatives of formula IX or a salt thereof. Reduction of O-alkoxy oxime derivatives of formula XII or XVI into O-Alkylhydroxylamines of formula XIII or XVII can be carried out as described in reaction scheme 1. O-Alkylhydroxylamines of formula XIII or XVII may be coupled to compounds of formula III to obtain compounds of formula XIV or XVIII as described for the preparation of compounds of formula I. Compounds of formula XVIII, in which R is still a hydroxy protecting group, can be deprotected according to methods known in the art.

Williamson reaction of a hydroxy derivative of formula VI, in which R₇, R₈, R₉, R₁₀ and R₁₁ are as defined under formula II, with a α -halogen carbonyl compound of formula XIV in which R₁, R₂, R₃, R₄, R₅ and R₆ are as defined under formula I and X stands for a halogen afford compounds of formula I, using the same conditions as described in reaction scheme 1.

Alternatively compounds of formula I, can be directly prepared as described by Mitsunobu (O. Mitsunobu, *Synthesis*, 1981, 1-28) from a compound of formula XVIII, in which R₁, R₂, R₃, R₄, R₅ and R₆ are as defined under formula I and R stands for a hydrogen and a hydroxy derivative of formula VI, in which R₇, R₈, R₉, R₁₀ and R₁₁ are as defined under formula II in the presence of 1-2 equivalents of triphenylphosphine and 1-2 equivalents dialkylazodicarboxylate, such as diethylazodicarboxylate or diisopropylazodicarboxylate. The reaction is generally run in an inert solvent, such as tetrahydrofuran or dichloromethane, at a temperature range of 0°C to 80°C.

Yet another access to the compound of formula XIV is the transformation of compounds of formula XVIII by standard conversion methods of alcohols to halides, as described in: March, J. *Advanced Organic Chemistry*; J. Wiley & Sons: New York, (1992); 4th Ed, pp 498-499).

The preparation of compounds of formula XVIII from compounds of formula XIV may be achieved by nucleophilic substitution with a compound of formula XIX in which R is preferably acetate. The esters can be cleaved according to methods known in the art.

The compounds of the formula V, VI, VII, IX, XV and XIX, wherein the substituents as described above, are known. Some of them are commercially available or can be prepared according to methods known in the art.

The compounds of formula III, wherein the substituents as described above, are known and partially commercially available. They can be prepared analogously as described, for example, in WO 00/09482, WO 02/38542, WO 2004/018438, EP-0-589-301, WO 93/11117 and Arch. Pharm. Res. 2000, 23(4), 315-323.

For preparing all further compounds of the formula I functionalized according to the definitions of R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁ and X there are a large number of suitable known standard methods, such as alkylation, halogenation, acylation, amidation,

oximation, oxidation and reduction. The choice of the preparation methods which are suitable are depending on the properties (reactivity) of the substituents in the intermediates.

The compounds I can, if appropriate, also be obtained in the form of hydrates and/or include other solvents, for example those which may have been used for the crystallization of compounds which are present in solid form.

It has now been found that the compounds of formula I according to the invention have, for practical purposes, a very advantageous spectrum of activities for protecting useful plants against diseases that are caused by phytopathogenic microorganisms, such as fungi, bacteria or viruses.

The invention relates to a method of controlling or preventing infestation of useful plants by phytopathogenic microorganisms, wherein a compound of formula I is applied as active ingredient to the plants, to parts thereof or the locus thereof. The compounds of formula I according to the invention are distinguished by excellent activity at low rates of application, by being well tolerated by plants and by being environmentally safe. They have very useful curative, preventive and systemic properties and are used for protecting numerous useful plants. The compounds of formula I can be used to inhibit or destroy the diseases that occur on plants or parts of plants (fruit, blossoms, leaves, stems, tubers, roots) of different crops of useful plants, while at the same time protecting also those parts of the plants that grow later e.g. from phytopathogenic microorganisms.

It is also possible to use compounds of formula I as dressing agents for the treatment of plant propagation material, in particular of seeds (fruit, tubers, grains) and plant cuttings (e.g. rice), for the protection against fungal infections as well as against phytopathogenic fungi occurring in the soil.

Furthermore the compounds of formula I according to the invention may be used for controlling fungi in related areas, for example in the protection of technical materials, including wood and wood related technical products, in food storage or in hygiene management.

The compounds of formula I are, for example, effective against the phytopathogenic fungi of the following classes: Fungi imperfecti (e.g. *Botrytis*, *Pyricularia*, *Helminthosporium*, *Fusarium*, *Septoria*, *Cercospora* and *Alternaria*) and Basidiomycetes (e.g. *Rhizoctonia*, *Hemileia*, *Puccinia*). Additionally, they are also effective against the Ascomycetes classes (e.g. *Venturia* and *Erysiphe*, *Podosphaera*, *Monilinia*, *Uncinula*) and of the Oomycetes classes (e.g. *Phytophthora*, *Pythium*, *Plasmopara*). Outstanding activity has been observed against powdery mildew (*Erysiphe* spp.). Therefore, the invention preferably relates to a method of controlling or preventing infestation of useful plants by powdery mildew. Furthermore, the novel compounds of formula I are effective against phytopathogenic bacteria and viruses (e.g. against *Xanthomonas* spp, *Pseudomonas* spp, *Erwinia amylovora* as well as against the tobacco mosaic virus). Good activity has been observed against Asian soybean rust (*Phakopsora pachyrhizi*).

Within the scope of the invention, useful plants to be protected typically comprise the following species of plants: cereal (wheat, barley, rye, oat, rice, maize, sorghum and related species); beet (sugar beet and fodder beet); pomes, drupes and soft fruit (apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries and blackberries); leguminous plants (beans, lentils, peas, soybeans); oil plants (rape, mustard, poppy, olives, sunflowers, coconut, castor oil plants, cocoa beans, groundnuts); cucumber plants (pumpkins, cucumbers, melons); fibre plants (cotton, flax, hemp, jute); citrus fruit (oranges, lemons, grapefruit, mandarins); vegetables (spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, paprika); lauraceae (avocado, cinnamomum, camphor) or plants such as tobacco, nuts, coffee, eggplants, sugar cane, tea, pepper, vines, hops, bananas and natural rubber plants, as well as ornamentals.

The term "useful plants" is to be understood as including also useful plants that have been rendered tolerant to herbicides like bromoxynil or classes of herbicides (such as, for example, HPPD inhibitors, ALS inhibitors, for example primisulfuron, prosulfuron and trifloxysulfuron, EPSPS (5-enol-pyrovyl-shikimate-3-phosphate-synthase) inhibitors, GS (glutamine synthetase) inhibitors or PPO (protoporphyrinogen-oxidase) inhibitors) as a result of conventional methods of breeding or genetic engineering. An example of a crop that has been rendered tolerant to imidazolinones, e.g. imazamox, by conventional methods of breeding (mutagenesis) is Clearfield® summer rape (Canola). Examples of crops that have been rendered tolerant to herbicides or classes of herbicides by genetic engineering

methods include glyphosate- and glufosinate-resistant maize varieties commercially available under the trade names RoundupReady®, Herculex I® and LibertyLink®.

The term "useful plants" is to be understood as including also useful plants which have been so transformed by the use of recombinant DNA techniques that they are capable of synthesising one or more selectively acting toxins, such as are known, for example, from toxin-producing bacteria, especially those of the genus *Bacillus*.

Examples of such plants are: YieldGard® (maize variety that expresses a CryIA(b) toxin); YieldGard Rootworm® (maize variety that expresses a CryIIIB(b1) toxin); YieldGard Plus® (maize variety that expresses a CryIA(b) and a CryIIIB(b1) toxin); Starlink® (maize variety that expresses a Cry9(c) toxin); Herculex I® (maize variety that expresses a CryIF(a2) toxin and the enzyme phosphinothricine N-acetyltransferase (PAT) to achieve tolerance to the herbicide glufosinate ammonium); NuCOTN 33B® (cotton variety that expresses a CryIA(c) toxin); Bollgard I® (cotton variety that expresses a CryIA(c) toxin); Bollgard II® (cotton variety that expresses a CryIA(c) and a CryIIA(b) toxin); VIPCOT® (cotton variety that expresses a VIP toxin); NewLeaf® (potato variety that expresses a CryIIIA toxin); Nature-Gard® Agrisure® GT Advantage (GA21 glyphosate-tolerant trait), Agrisure® CB Advantage (Bt11 corn borer (CB) trait), Agrisure® RW (corn rootworm trait) and Protecta®.

The term "useful plants" is to be understood as including also useful plants which have been so transformed by the use of recombinant DNA techniques that they are capable of synthesising antipathogenic substances having a selective action, such as, for example, the so-called "pathogenesis-related proteins" (PRPs, see e.g. EP-A-0 392 225). Examples of such antipathogenic substances and transgenic plants capable of synthesising such antipathogenic substances are known, for example, from EP-A-0 392 225, WO 95/33818, and EP-A-0 353 191. The methods of producing such transgenic plants are generally known to the person skilled in the art and are described, for example, in the publications mentioned above.

The term "locus" of a useful plant as used herein is intended to embrace the place on which the useful plants are growing, where the plant propagation materials of the useful plants are

sown or where the plant propagation materials of the useful plants will be placed into the soil. An example for such a locus is a field, on which crop plants are growing.

The term "plant propagation material" is understood to denote generative parts of the plant, such as seeds, which can be used for the multiplication of the latter, and vegetative material, such as cuttings or tubers, for example potatoes. There may be mentioned for example seeds (in the strict sense), roots, fruits, tubers, bulbs, rhizomes and parts of plants. Germinated plants and young plants which are to be transplanted after germination or after emergence from the soil, may also be mentioned. These young plants may be protected before transplantation by a total or partial treatment by immersion. Preferably "plant propagation material" is understood to denote seeds.

The compounds of formula I can be used in unmodified form or, preferably, together with carriers and adjuvants conventionally employed in the art of formulation.

Therefore the invention also relates to compositions for controlling and protecting against phytopathogenic microorganisms, comprising a compound of formula I and an inert carrier, and to a method of controlling or preventing infestation of useful plants by phytopathogenic microorganisms, wherein a composition, comprising a compound of formula I as active ingredient and an inert carrier, is applied to the plants, to parts thereof or the locus thereof.

To this end compounds of formula I and inert carriers are conveniently formulated in known manner to emulsifiable concentrates, coatable pastes, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granulates, and also encapsulations e.g. in polymeric substances. As with the type of the compositions, the methods of application, such as spraying, atomising, dusting, scattering, coating or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances. The compositions may also contain further adjuvants such as stabilizers, antifoams, viscosity regulators, binders or tackifiers as well as fertilizers, micronutrient donors or other formulations for obtaining special effects.

Suitable carriers and adjuvants can be solid or liquid and are substances useful in formulation technology, e.g. natural or regenerated mineral substances, solvents, dispersants,

wetting agents, tackifiers, thickeners, binders or fertilizers. Such carriers are for example described in WO 97/33890.

The compounds of formula I or compositions, comprising a compound of formula I as active ingredient and an inert carrier, can be applied to the locus of the plant or plant to be treated, simultaneously or in succession with further compounds. These further compounds can be e.g. fertilizers or micronutrient donors or other preparations which influence the growth of plants. They can also be selective herbicides as well as insecticides, fungicides, bactericides, nematocides, molluscicides or mixtures of several of these preparations, if desired together with further carriers, surfactants or application promoting adjuvants customarily employed in the art of formulation.

A preferred method of applying a compound of formula I, or a composition, comprising a compound of formula I as active ingredient and an inert carrier, is foliar application. The frequency of application and the rate of application will depend on the risk of infestation by the corresponding pathogen. However, the compounds of formula I can also penetrate the plant through the roots via the soil (systemic action) by drenching the locus of the plant with a liquid formulation, or by applying the compounds in solid form to the soil, e.g. in granular form (soil application). In crops of water rice such granulates can be applied to the flooded rice field. The compounds of formula I may also be applied to seeds (coating) by impregnating the seeds or tubers either with a liquid formulation of the fungicide or coating them with a solid formulation.

A formulation, i.e. a composition comprising the compound of formula I and, if desired, a solid or liquid adjuvant, is prepared in a known manner, typically by intimately mixing and/or grinding the compound with extenders, for example solvents, solid carriers and, optionally, surface-active compounds (surfactants).

The agrochemical formulations will usually contain from 0.1 to 99% by weight, preferably from 0.1 to 95% by weight, of the compound of formula I, 99.9 to 1% by weight, preferably 99.8 to 5% by weight, of a solid or liquid adjuvant, and from 0 to 25% by weight, preferably from 0.1 to 25% by weight, of a surfactant.

Whereas it is preferred to formulate commercial products as concentrates, the end user will normally use dilute formulations.

Advantageous rates of application are normally from 5g to 2kg of active ingredient (a.i.) per hectare (ha), preferably from 10g to 1kg a.i./ha, most preferably from 20g to 600g a.i./ha. When used as seed drenching agent, convenient rates of application are from 10mg to 1g of active substance per kg of seeds. The rate of application for the desired action can be determined by experiments. It depends for example on the type of action, the developmental stage of the useful plant, and on the application (location, timing, application method) and can, owing to these parameters, vary within wide limits.

Surprisingly, it has now been found that the compounds of formula I can also be used in methods of protecting crops of useful plants against attack by phytopathogenic organisms as well as the treatment of crops of useful plants infested by phytopathogenic organisms comprising administering a combination of glyphosate and at least one compound of formula I to the plant or locus thereof, wherein the plant is resistant or sensitive to glyphosate.

Said methods may provide unexpectedly improved control of diseases compared to using the compounds of formula I in the absence of glyphosate. Said methods may be effective at enhancing the control of disease by compounds of formula I. While the mixture of glyphosate and at least one compound of formula I may increase the disease spectrum controlled, at least in part, by the compound of formula I, an increase in the activity of the compound of formula I on disease species already known to be controlled to some degree by the compound of formula I can also be the effect observed.

Said methods are particularly effective against the phytopathogenic organisms of the kingdom *Fungi*, phylum *Basidiomycot*, class *Uredinomycetes*, subclass *Urediniomycetidae* and the order *Uredinales* (commonly referred to as rusts). Species of rusts having a particularly large impact on agriculture include those of the family *Phakopsoraceae*, particularly those of the genus *Phakopsora*, for example *Phakopsora pachyrhizi*, which is also referred to as Asian soybean rust, and those of the family *Pucciniaceae*, particularly those of the genus *Puccinia* such as *Puccinia graminis*, also known as stem rust or black

rust, which is a problem disease in cereal crops and *Puccinia recondita*, also known as brown rust.

An embodiment of said method is a method of protecting crops of useful plants against attack by a phytopathogenic organism and/or the treatment of crops of useful plants infested by a phytopathogenic organism, said method comprising simultaneously applying glyphosate, including salts or esters thereof, and at least one compound of formula I, which has activity against the phytopathogenic organism to at least one member selected from the group consisting of the plant, a part of the plant and the locus of the plant.

The compounds of formula (I), or a pharmaceutical salt thereof, described above may also have an advantageous spectrum of activity for the treatment and/or prevention of microbial infection in an animal. "Animal" can be any animal, for example, insect, mammal, reptile, fish, amphibian, preferably mammal, most preferably human. "Treatment" means the use on an animal which has microbial infection in order to reduce or slow or stop the increase or spread of the infection, or to reduce the infection or to cure the infection. "Prevention" means the use on an animal which has no apparent signs of microbial infection in order to prevent any future infection, or to reduce or slow the increase or spread of any future infection.

According to the present invention there is provided the use of a compound of formula (I) in the manufacture of a medicament for use in the treatment and/or prevention of microbial infection in an animal. There is also provided the use of a compound of formula (I) as a pharmaceutical agent. There is also provided the use of a compound of formula (I) as an antimicrobial agent in the treatment of an animal. According to the present invention there is also provided a pharmaceutical composition comprising as an active ingredient a compound of formula (I), or a pharmaceutically acceptable salt thereof, and a pharmaceutically acceptable diluent or carrier. This composition can be used for the treatment and/or prevention of antimicrobial infection in an animal. This pharmaceutical composition can be in a form suitable for oral administration, such as tablet, lozenges, hard capsules, aqueous suspensions, oily suspensions, emulsions dispersible powders, dispersible granules, syrups and elixirs. Alternatively this pharmaceutical composition can be in a form suitable for topical application, such as a spray, a cream or lotion. Alternatively this pharmaceutical composition can be in a form suitable for parenteral administration, for example injection.

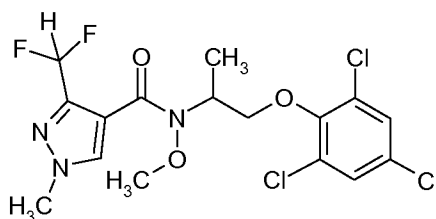
Alternatively this pharmaceutical composition can be in inhalable form, such as an aerosol spray.

The compounds of formula (I) may be effective against various microbial species able to cause a microbial infection in an animal. Examples of such microbial species are those causing Aspergillosis such as *Aspergillus fumigatus*, *A. flavus*, *A. terreus*, *A. nidulans* and *A. niger*; those causing Blastomycosis such as *Blastomyces dermatitidis*; those causing Candidiasis such as *Candida albicans*, *C. glabrata*, *C. tropicalis*, *C. parapsilosis*, *C. krusei* and *C. lusitanae*; those causing Coccidioidomycosis such as *Coccidioides immitis*; those causing Cryptococcosis such as *Cryptococcus neoformans*; those causing Histoplasmosis such as *Histoplasma capsulatum* and those causing Zygomycosis such as *Absidia corymbifera*, *Rhizomucor pusillus* and *Rhizopus arrhizus*. Further examples are *Fusarium* Spp such as *Fusarium oxysporum* and *Fusarium solani* and *Scedosporium* Spp such as *Scedosporium apiospermum* and *Scedosporium prolificans*. Still further examples are *Microsporum* Spp, *Trichophyton* Spp, *Epidermophyton* Spp, *Mucor* Spp, *Sporothrix* Spp, *Phialophora* Spp, *Cladosporium* Spp, *Petriellidium* spp, *Paracoccidioides* Spp and *Histoplasma* Spp.

The following preparatory examples illustrate the above-described invention in greater detail without limiting it.

Preparation examples:

Example P1: Preparation of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid methoxy-[1-methyl-2-(2,4,6-trichloro-phenoxy)-ethyl]-amide (compound 1.003):



A solution of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carbonyl chloride (680 mg; 3.5 mmol) in dichloromethane (5ml) was added dropwise to a stirred solution of O-Methyl-N-[1-methyl-2-(2,4,6-trichloro-phenoxy)-ethyl]-hydroxylamine (1000 mg; 3.5 mmol), prepared as described in example P7c and triethylamine (1.0 ml; 7.0 mmol) in dichloromethane (20ml) at 0°C. The reaction mixture was stirred for 4 hours at ambient temperature. The reaction

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mixture was washed with 1M NaOH (20ml), 1M HCl (20ml) brine (20ml) and then dried over Na₂SO₄. After removal of the solvent the residue (1.5g) was purified by flash chromatography over silica gel (eluant: c-hexane/ethyl acetate 8:2).

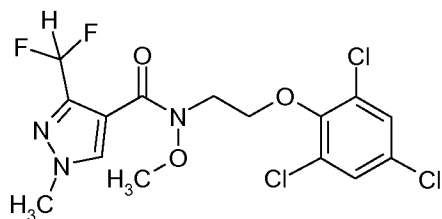
0.80 g (53.0 % of theory) of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid methoxy-[1-methyl-2-(2,4,6-trichloro-phenoxy)-ethyl]-amide (compound 1.003) was obtained in form of a resin.

¹H NMR: (CDCl₃, 400MHz):

1.46-1.48(d,3H); 3.80(s,3H); 3.88(s,3H); 4.02-4.06(dd,1H); 4.27-4.31(dd,1H); 4.83-4.91(m,1H); 7.10-7.37(t,1H,CHF₂); 7.29(s,2H,Ar-H); 7.92(s,1H, Pyr-H).

MS [M+H]⁺ 442/444/446.

Example P2: Preparation of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid methoxy-[2-(2,4,6-trichloro-phenoxy)-ethyl]-amide (compound 1.032):



A solution of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carbonyl chloride (1.08 g; 5.54 mmol) in dichloromethane (5ml) was added dropwise to a stirred solution of O-methyl-N-[2-(2,4,6-trichloro-phenoxy)-ethyl]-hydroxylamine (1.50 g; 5.54 mmol), prepared as described in example P8c, triethylamine (1.5 ml; 11.1 mmol) in dichloromethane (10ml) at 0°C. The reaction mixture was stirred for 15 hours over night at ambient temperature. The reaction mixture was directly purified by flash chromatography over silica gel (eluant: c-hexane/ethyl acetate 6:4).

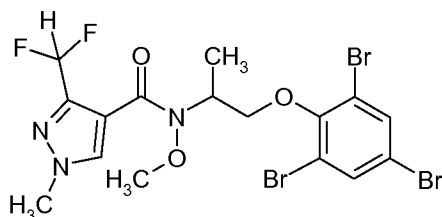
1.69 g (71.0 % of theory) of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid methoxy-[1-2-(2,4,6-trichloro-phenoxy)-ethyl]-amide (compound 1.032) was obtained in form of a resin.

¹H NMR: (CDCl₃, 400MHz):

3.78(s,3H); 3.99(s,3H); 4.15-4.19(dd,2H); 4.23-4.26(dd,1H); 7.15-7.43(t,1H,CHF₂); 7.29(s,2H,Ar-H); 7.95(s,1H, Pyr-H).

MS [M+H]⁺ 428/430/432.

Example P3: Preparation of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid methoxy-[1-methyl-2-(2,4,6-tribromo-phenoxy)-ethyl]-amide (compound 1.026):



A mixture of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (2-chloro-1-methyl-ethyl)-methoxy-amide (1.0 g; 3.6 mmol), prepared as described in example P5, 2,4,6-tribromophenol (1.2g; 3.6 mmol), sodium iodide (0.27g; 1.8 mmol) and anhydrous potassium carbonate (0.75g; 5.4mol) in acetonitrile (10ml) was stirred for 16 hours at 70°C. The reaction mixture was cooled to ambient temperature. After removal of the solvent the residue was purified by reversed phase chromatography (eluant: acetonitrile/water).

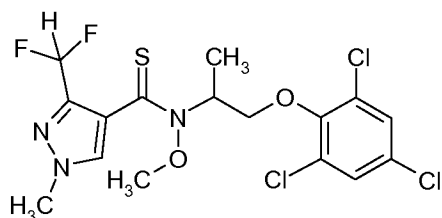
0.28 g (14.0 % of theory) of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid methoxy-[1-methyl-2-(2,4,6-tribromo-phenoxy)-ethyl]-amide was obtained in form of a resin.

^1H NMR: (CDCl_3 , 400MHz):

1.48-1.50(d,3H); 3.81(s,3H); 3.98(s,3H); 3.99-4.03(dd,1H); 4.28-4.32(dd,1H); 4.84-4.92(m,1H); 7.10-7.37(t,1H,CHF₂); 7.64(s,2H,Ar-H); 7.92(s,1H, Pyr-H).

MS $[\text{M}+\text{H}]^+$ 574/576/578/580.

Example P4: Preparation of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carbothioic acid methoxy-[1-methyl-2-(2,4,6-trichloro-phenoxy)-ethyl]-amide (compound 1.072):



Lawesson reagent (182 mg; 0.45 mmol) was added to a stirred solution of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid methoxy-[1-methyl-2-(2,4,6-trichloro-phenoxy)-ethyl]-amide (200 mg; 0.45 mmol), prepared as described in example P1 in toluene (10ml) at 20°C. The reaction mixture was stirred for 3 days at 60°C. The reaction mixture was purified directly by flash chromatography over silica gel (eluant: c-hexane/ethyl acetate 9:1 to 7:3).

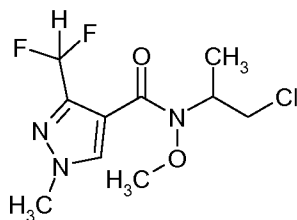
0.02 g (9.6 % of theory) of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carbothioic acid methoxy-[1-methyl-2-(2,4,6-trichloro-phenoxy)-ethyl]-amide (compound 1.072) was obtained in form of a resin.

^1H NMR: (CDCl_3 , 400MHz):

1.58-1.60(d,3H); 3.81(s,3H); 3.88(s,3H); 4.10-4.16(dd,1H); 4.24-4.30(dd,1H); 5.09-4.18(m,1H); 6.65-6.93(t,1H,CHF₂); 7.24(s,2H,Ar-H); 8.12(s,1H, Pyr-H).

MS $[\text{M}+\text{H}]^+$ 458/460/462.

Example P5: Preparation of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (2-chloro-1 methyl-ethyl)-methoxy-amide:



A solution of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carbonyl chloride (13.0 g; 67 mmol) in dichloromethane (20ml) was added dropwise to a stirred mixture of N-(2-Chloro-1-methyl-ethyl)-O-methyl-hydroxylamine hydrochloride (10.7 g; 67 mmol), prepared as described in example P9b, and triethylamine (37 ml; 268 mmol) in dichloromethane (130ml) at 0°C. The reaction mixture was stirred for 3 hours at ambient temperature. The reaction mixture was washed with 1M HCl (50ml), brine (100ml) and then dried over Na_2SO_4 . After removal of the solvent the residue was purified by flash chromatography over silica gel (eluant: c-hexane/ethyl acetate 1:1).

16.0 g (85.0 % of theory) of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (2-chloro-1 methyl-ethyl)-methoxy-amide was obtained in form of a resin.

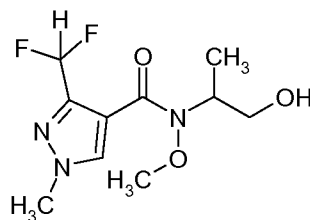
^1H NMR: (CDCl_3 , 400MHz):

1.42-1.45(d,3H); 3.60-3.64(dd,1H); 3.75(s,3H); 3.81-3.86(dd,1H); 3.98(s,3H); 4.66-4.75(m,1H); 7.08-7.35(t,1H,CHF₂); 7.90(s,1H, Pyr-H).

MS $[\text{M}+\text{H}]^+$ 282/284.

Example P6: Preparation of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (2-hydroxy-1-methyl-ethyl)-methoxy-amide:

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A solution of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carbonyl chloride (3.70 g; 19.0 mmol) in dichloromethane (5ml) was added dropwise to a stirred solution of 2-methoxyamino-propan-1-ol (2.00 g; 19.0 mmol), prepared as described in example P10b, triethylamine (3.2 ml; 23.0 mmol) in dichloromethane (30ml) at 0°C. The reaction mixture was stirred for 15 hours over night at ambient temperature. The reaction mixture was poured onto water (180ml) and extracted with dichloromethane (3x60ml). The combined organic layers were washed with brine, dried over MgSO₄ and filtered. After removal of the solvent the residue (4.20g) was purified by flash chromatography over silica gel (eluant: ethyl acetate). 0.20 g (4.0 % of theory) of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (2-hydroxy-1-methyl-ethyl)-methoxy-amide was obtained in form of a resin.

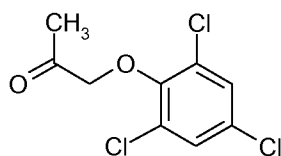
¹H NMR: (CDCl₃, 400MHz):

1.31-1.33(d,3H); 2.63(sbr, 1H,OH); 3.72(s,3H); 3.74-3.83(m,2H); 3.99(s,3H); 4.42-4.56(m,1H); 7.06-7.35(t,1H,CHF₂); 7.90(s,1H, Pyr-H).

MS [M+H]⁺ 264.

Example P7: Preparation of O-Methyl-N-[1-methyl-2-(2,4,6-trichloro-phenoxy)-ethyl]-hydroxylamine:

a) Preparation of 1-(2,4,6-trichloro-phenoxy)-propan-2-one:



A mixture of 2,4,6-trichlorophenol (245g; 1.24mol) and anhydrous potassium carbonate (342g; 2.5mol) in DMF (1.5l) was treated with 1-chloroacetone (99ml; 1.24mol) at 25°C. The reaction mixture was stirred for 3 hours at ambient temperature and poured onto water (3l). The mixture was extracted with ethyl acetate (3x400ml). The combined ethyl acetate layers were washed with brine, dried over MgSO₄ and filtered under reduced pressure.

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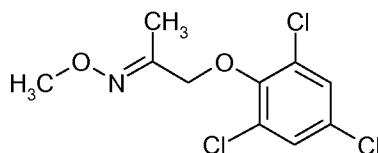
The solvent volume was reduced and 400ml c-hexane was added. The resulting precipate was filtered off and dried. 235 g (74.8 % of theory) of 1-(2,4,6-trichloro-phenoxy)-propan-2-one was obtained in form of a beige solid (mp. 69-73°C).

^1H NMR: (CDCl_3 , 400MHz):

2.42(s,3H); 4.50(s,2H); 7.34(s,2H,Ar-H).

MS $[\text{M}+\text{H}]^+$ 253/255/257.

b) Preparation of 1-(2,4,6-trichloro-phenoxy)-propan-2-one O-methyl-oxime:



A solution of 1-(2,4,6-trichloro-phenoxy)-propan-2-one (5.0 g, 19.7 mmole) in methanol (50 ml) was treated with pyridine (2.0 ml, 24 mmol) followed by O-methyl hydroxylamine hydrochloride (2.0 g, 24 mmol). The resulting mixture was stirred at 23°C for 1 hour. The reaction mixture was poured onto water (100ml). The resulting precipate was filtered off, washed with water (100ml) and dried in the vacuum oven.

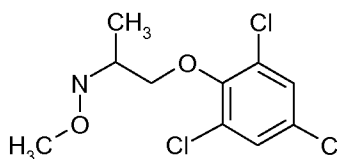
5.49 g (99 % of theory) of 1-(2,4,6-trichloro-phenoxy)-propan-2-one O-methyl-oxime was obtained in form of a beige solid (mp. 70-74°C). The compound was used in the next step without further purification.

^1H NMR: (CDCl_3 , 400MHz):

2.11(s,3H);3.83(s,3H);4.50(s,3H); 7.32(s,2H,ArH).

MS $[\text{M}+\text{H}]^+$ 282/284/286.

c) Preparation of O-methyl-N-[1-methyl-2-(2,4,6,-trichloro-phenoxy)-ethyl]-hydroxylamine:



A solution of 1-(2,4,6-trichloro-phenoxy)-propan-2-one O-methyl-oxime (5.0 g, 17.7 mmol) in acetic acid (50 ml) was treated at 10°C with sodium cyanoborohydride (2.9g, 35.0 mmol) added in small portions over 10 minutes and the resulting solution was stirred at 24 °C for 4

hours. The solvent was evaporated under reduced pressure (co-evaporation with toluene twice) and the residue was slurried with water and pH was adjusted to 9 with 1M NaOH. The aqueous phase was extracted with dichloromethane (2x100 ml), washed with brine and dried over anhydrous Na₂SO₄. 5.06 g (100.0 % of theory) of O-methyl-N-[1-methyl-2-(2,4,6-trichloro-phenoxy)-ethyl]-hydroxylamine was obtained in form of a clear liquid. The crude was used in example P1 without further purification.

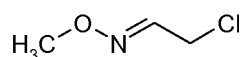
¹H NMR: (CDCl₃, 400MHz):

1.21-1.23(d,3H);3.38-3.48(m,1H);3.56(s,3H);3.98-4.02(d,2H),6.10(s_{br},1H); 7.31(s,2H,Ar-H).

MS [M+H]⁺ 284/286/288.

Example P8: Preparation of O-methyl-N-[2-(2,4,6-trichloro-phenoxy)-ethyl]-hydroxylamine:

a) Preparation of chloro-acetaldehyde O-methyl-oxime:

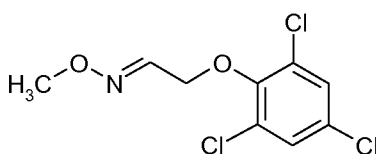


A solution of chloro-acetaldehyde 55% in water (15.0 ml, 128 mmole) was treated with O-methyl hydroxylamine hydrochloride (14.2 g, 170 mmol). The resulting mixture was stirred at 23°C over night for 16 hour. The reaction mixture was poured onto water (100ml), extracted with ether (2x50ml). The combined organic layers were washed with brine, dried over MgSO₄, filtered and dried under reduced pressure (200mbar; 30°C). 15.0 g (>100 % of theory*) of chloro-acetaldehyde O-methyl-oxime was obtained in form of a liquid as an E/Z-mixture. The volatile compound* (containing ether) was used in the next step without further purification.

¹H NMR: (CDCl₃, 400MHz):

3.86+3.92(2s,3H);4.09-4.11+4.22-4.25(2d,2H);6.80-6.82+7.39-7.43(2t,1H).

b) Preparation of (2,4,6-trichloro-phenoxy)-acetaldehyde O-methyl-oxime:



A solution of chloro-acetaldehyde O-methyl-oxime (12.0g; 112mmol) in DMF (20ml) was added dropwise to a stirred mixture of 2,4,6-trichlorophenol (22.1g; 112mmol) and anhydrous potassium carbonate (31g; 224mol) in DMF at 25°C. The reaction mixture was

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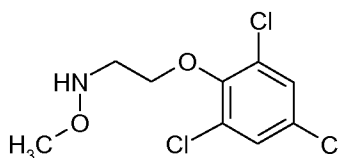
stirred for 3 hours at ambient temperature and poured onto water (200ml). The mixture was extracted with ethyl acetate (3x400ml). The combined ethyl acetate layers were washed with brine, dried over MgSO_4 , filtered and the solvent was evaporated. 19.51 g (65.0 % of theory) of (2,4,6-trichloro-phenoxy)-acetaldehyde O-methyl-oxime was obtained in form of a beige solid (mp. 50-56°C) as an E/Z-mixture.

^1H NMR: (CDCl_3 , 400MHz):

3.87+3.89(2s,3H); 4.62-4.65+4.83-4.85(2d,2H); 7.17-7.19+7.64-7.67(2t,1H); 7.30(s,2H,Ar-H).

MS $[\text{M}+\text{H}]^+$ 268/270/272.

c) Preparation of O-methyl-N-[2-(2,4,6-trichloro-phenoxy)-ethyl]-hydroxylamine:



A solution of (2,4,6-trichloro-phenoxy)-acetaldehyde O-methyl-oxime (13.4 g, 50.0 mmol) in acetic acid (40 ml) was treated at 10°C with sodium cyanoborohydride (6.3g, 100.0 mmol) added in small portions over 15 minutes and the resulting solution was stirred at 24 °C for 3 hours. The solvent was evaporated under reduced pressure (co-evaporation with toluene twice) and the residue was slurried with water and pH was adjusted to 9 with 1M NaOH. The aqueous phase was extracted with dichloromethane (2x100 ml), washed with brine and dried over anhydrous Na_2SO_4 . 14.0 g (quantitative yield) of O-methyl-N-[2-(2,4,6-trichloro-phenoxy)-ethyl]-hydroxylamine was obtained in form of a yellow liquid. The crude intermediate was used in example P2 without further purification.

^1H NMR: (CDCl_3 , 400MHz):

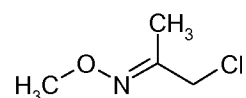
3.31-3.33(t,2H); 3.55(s,3H); 4.18-4.20(s,3H); 6.10(s_{br},1H); 7.31(s,2H,Ar-H).

MS $[\text{M}+\text{H}]^+$ 270/272/274.

Example P9: Preparation of N-(2-chloro-1-methyl-ethyl)-O-methyl-hydroxylamine hydrochloride:

a) Preparation of 1-chloro-propan-2-one O-methyl-oxime:

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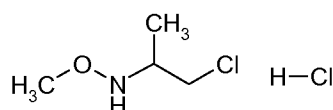
A stirred solution of chloroacetone (13.0 ml, 163 mmole) in water (150ml) was treated with O-methyl hydroxylamine hydrochloride (14.3 g, 171 mmol). The resulting mixture was stirred at 23°C for 2 hours. The reaction mixture was poured onto water (180ml), extracted with dichloromethane (3x50ml). The combined organic layers were dried over sodium sulphate, filtered and evaporated carefully under reduced pressure at (500mbar; 35°C).

22.3 g (>100 % of theory*) of 1-chloro-propan-2-one O-methyl-oxime was obtained in form of a liquid. The volatile compound* (containing dichloromethane) was used in the next step without further purification.

¹H NMR: (CDCl₃, 400MHz):

1.95(s,3H);3.88(s,3H);4.08(s,2H).

b) Preparation of N-(2-chloro-1-methyl-ethyl)-O-methyl-hydroxylamine hydrochloride:



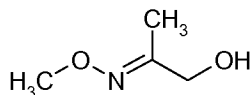
A solution of 1-chloro-propan-2-one O-methyl-oxime (17.5 g, 144 mmol) in acetic acid (250 ml) was treated at 10°C with sodium cyanoborohydride (18.1g, 288 mmol) added in small portions over 30 minutes and the resulting solution was stirred at 24 °C for 5 hours. The solvent was evaporated under reduced pressure (co-evaporation of N-(2-Chloro-1-methyl-ethyl)-O-methyl-hydroxylamine). This distillate was treated with 35% hydrochloric acid (10ml). The solution was evaporated under reduced pressure (co-evaporation with toluene and ethanol). The oil was triturated in ether to form the hydrochloride salt. After filtration, the product was dried at 30°C under vacuum. 14.5 g (81.0 % of theory) of N-(2-chloro-1-methyl-ethyl)-O-methyl-hydroxylamine hydrochloride was obtained in form of a white solid (mp. 80-94°C).

¹H NMR: (DMSO, 400MHz):

1.24-1.26(d,3H);3.71-3.79(m,1H);3.84(s,3H);3.87-3.88(d,2H).

MS [M+H]⁺ 284/286/288.

Example P10: Preparation of 2-methoxyamino-propan-1-ol:

a) Preparation of 1-hydroxy-propan-2-one O-methyl-oxime:

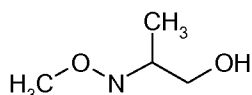
A stirred solution of hydroxyacetone (10.0 ml, 146 mmole) in methanol (150ml) was treated pyridine (36 ml, 440 mmol), followed by O-methyl hydroxylamine hydrochloride (37.0 g, 440 mmol). The resulting mixture was stirred at 23°C for 17 hours over night. Methanol was partially removed by distillation under reduced pressure at 200mbar, 35°C. The resulting reaction mixture was poured onto water (400ml), extracted with dichloromethane (3x150ml). The combined organic layers were dried over sodium sulphate, filtered and evaporated carefully under reduced pressure at (100mbar; 40°C).

10.8 g (72 % of theory) of 1-hydroxy-propan-2-one O-methyl-oxime was obtained in form of a liquid as an E/Z-mixture. The intermediate was used in the next step without further purification.

^1H NMR: (CDCl_3 , 400MHz):

1.78+1.86(2s,3H);3.06(s,1H,OH);3.71+3.76(2s,3H);4.06+4.28(2s,2H).

MS $[\text{M}+\text{H}]^+$ 104.

b) Preparation of 2-methoxyamino-propan-1-ol:

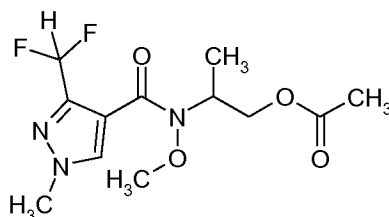
A solution of 1-hydroxy-propan-2-one O-methyl-oxime (10.5 g, 102 mmol) in acetic acid (200 ml) was treated at 10°C with sodium cyanoborohydride (7.2g, 115 mmol) added in small portions over 15 minutes and the resulting solution was stirred at 24 °C for 3.5 hours. The solvent was evaporated under reduced pressure to remove most of the acetic acid. The reaction mixture was poured onto water (200ml), extracted with dichloromethane (3x100 ml), washed with brine and dried over anhydrous Na_2SO_4 . 9.9 g 93 % of theory) of 2-methoxyamino-propan-1-ol was obtained in form of a yellow liquid. The crude intermediate (containing traces of pyridine and acetic acid) was used in example P6 without further purification.

^1H NMR: (CDCl_3 , 400MHz):

1.13-1.15(d,3H); 3.25-3.29(m,1H); 3.61-3.69(m,2H); 3.70(s,3H); 3.78-3.85(m,2H).

MS $[\text{M}+\text{H}]^+$ 106.

Example P11: Preparation of acetic acid 2-[(3-difluoromethyl-1-methyl-1H-pyrazole-4-carbonyl)-methoxy-amino]-propyl ester:



A mixture of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (2-chloro-1 methyl-ethyl)-methoxy-amide (1.0 g; 3.6 mmol), prepared as described in example P5, potassium acetate (0.7 g; 7.2 mmol) and sodium iodide (0.27 g; 1.8 mmol) in DMF (10ml) was reacted under microwave irradiation at 80°C for 5 minutes, at 100°C for 5 minutes and at 120°C for another 5 minutes.

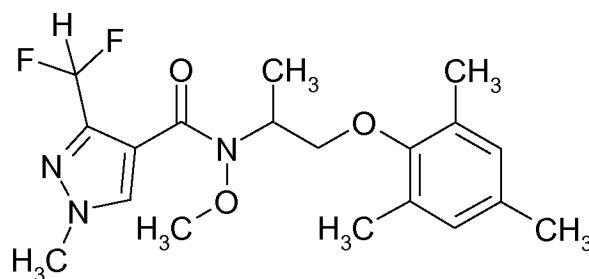
The reaction mixture was poured onto water (50ml) and extracted with dichloromethane (3x30ml). The combined organic layers were washed with brine, dried over MgSO₄ and filtered. After removal of the solvent the residue (1.15g) was purified by reversed phase chromatography (eluant: acetonitrile/water). 0.80 g (73.0 % of theory) of acetic acid 2-[(3-difluoromethyl-1-methyl-1H-pyrazole-4-carbonyl)-methoxy-amino]-propyl ester was obtained in form of a resin.

¹H NMR: (CDCl₃, 400MHz):

1.31-1.33(d,3H); 1.99(s,3H); 3.73(s,3H); 3.98(s,3H); 4.18-4.27(2dd,2H); 4.75-4.85(m,1H); 7.10-7.37(t,1H,CHF₂); 7.87(s,1H, Pyr-H).

MS [M+H]⁺ 306.

Example P12: Preparation of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid methoxy-[1-methyl-2-(2,4,6-trimethyl-phenoxy)-ethyl]-amide (compound No. 1.023):



To a mixture of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (2-hydroxy-1-methyl-ethyl)-methoxy-amide (0.2 g; 0.76 mmol), prepared as described in example P6, 2,4,6-trimethylphenol (0.1 g; 0.76 mmol) and diisopropylazodicarboxylate (0.15ml; 0.76 mmol) in THF (4ml) a solution of triphenylphosphine (0.20g; 0.76 mmol) in THF (2ml) was added at a temperature of 5°C. The reaction mixture was stirred for 2 hours at ambient temperature.

After removal of the solvent the residue (1.15g) was purified by flash master column chromatography (eluant gradient: 99:1 to 1:99 cyclohexane/ethylacetate). 0.08 g (27.0 % of theory) of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid methoxy-[1-methyl-2-(2,4,6-trimethyl-phenoxy)-ethyl]-amide (compound No. 1.023) was obtained in form of a resin.

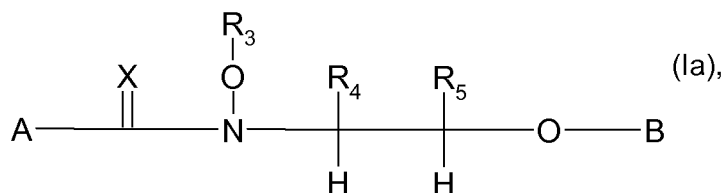
^1H NMR: (CDCl_3 , 400MHz):

1.47-1.49(d,3H); 2.21(s,9H); 3.71-3.78(dd,1H); 3.79(s,3H); 3.98(s,3H); 4.01-4.06(dd,1H); 4.27-4.33(dd,1H); 6.79(s,2H,Ar-H); 7.09-7.34(t,1H, CHF_2); 7.89(s,1H, Pyr-H).

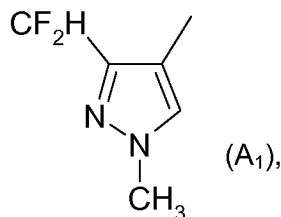
MS $[\text{M}+\text{H}]^+$ 382.

Tables 1 to 3: Compounds of formula Ia:

The invention was further illustrated by the preferred individual compounds of formula (Ia) listed below in Tables 1 to 3. Characterising data are given in Table 4.

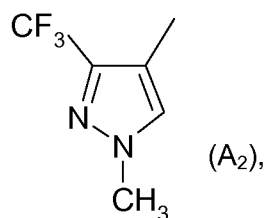
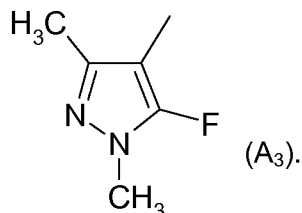


In the compounds of formula Ia, A is selected from the groups consisting of A₁,

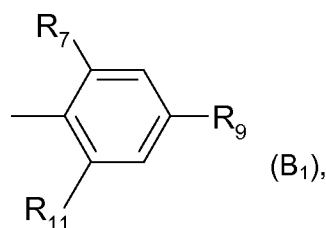
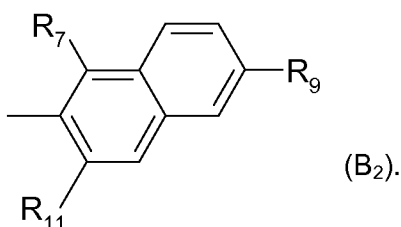


A₂,

- 34 -

and A₃,

In the compounds of formula Ia, B is selected from the groups consisting of B₁,

and B₂,

Each of Tables 1 to 3, which follow the Table Y below, comprises 100 compounds of the formula (Ia) in which X, R₃, R₄, R₅, B, R₇, R₉ and R₁₁ have the values given in Table Y and A has the value given in the relevant Table 1 to 3. Thus Table 1 corresponds to Table Y when Y is 1 and A has the value given under the Table 1 heading, Table 2 corresponds to Table Y when Y is 2 and A has the value given under the Table 2 heading, and so on for Table 3.

In Tables 1 to 3 below “Me” signifies methyl, “Et” signifies ethyl and “t-Bu” signifies tertiary butyl.

Table Y:

Cpd No.	X	R ₃	R ₄	R ₅	B	R ₇	R ₉	R ₁₁
Y.001	O	Me	Me	H	B1	H	Cl	H
Y.002	O	Me	Me	H	B1	Cl	H	Cl
Y.003	O	Me	Me	H	B1	Cl	Cl	Cl
Y.004	O	Me	Me	H	B1	Cl	Br	Cl
Y.005	O	Me	Me	H	B1	Cl	I	Cl
Y.006	O	Me	Me	H	B1	Cl	Me	Cl
Y.007	O	Me	Me	H	B1	Cl	CF ₃	Cl
Y.008	O	Me	Me	H	B1	Cl	C≡CH	Cl
Y.009	O	Me	Me	H	B1	Cl	t-Bu	Cl
Y.010	O	Me	Me	H	B1	Cl	CH=NOCH ₃	Cl
Y.011	O	Me	Me	H	B1	H	4-Cl-phenyl	H
Y.012	O	Me	Me	H	B1	Cl	4-Cl-phenyl	H
Y.013	O	Me	Me	H	B1	Cl	4-Cl-phenyl	Cl
Y.014	O	Me	Me	H	B1	H	4-Cl-phenoxy	H
Y.015	O	Me	Me	H	B1	Cl	4-Cl-phenoxy	H
Y.016	O	Me	Me	H	B1	Cl	4-Cl-phenoxy	Cl
Y.017	O	Me	Me	H	B1	Me	Cl	H
Y.018	O	Me	Me	H	B1	Me	H	Cl
Y.019	O	Me	Me	H	B1	Me	Cl	Cl
Y.020	O	Me	Me	H	B1	Me	Br	Cl
Y.021	O	Me	Me	H	B1	Me	I	Cl
Y.022	O	Me	Me	H	B1	Me	Me	Cl
Y.023	O	Me	Me	H	B1	Me	Me	Me
Y.024	O	Me	Me	H	B1	H	Br	H
Y.025	O	Me	Me	H	B1	Br	Br	H

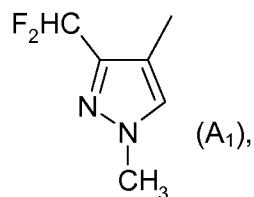
Cpd No.	X	R ₃	R ₄	R ₅	B	R ₇	R ₉	R ₁₁
Y.026	O	Me	Me	H	B1	Br	Br	Br
Y.027	O	CHF ₃	Me	H	B1	Cl	Cl	Cl
Y.028	O	CHF ₃	Me	H	B1	Me	Me	Me
Y.029	O	CHF ₃	Me	H	B1	Br	Br	Br
Y.030	O	CHF ₃	Me	H	B1	Cl	4-Cl-phenyl	Cl
Y.031	O	CHF ₃	Me	H	B1	Cl	4-Cl-phenoxy	Cl
Y.032	O	Me	H	H	B1	Cl	Cl	Cl
Y.033	O	Me	H	H	B1	Cl	Br	Cl
Y.034	O	Me	H	H	B1	Cl	Me	Cl
Y.035	O	Me	H	H	B1	Me	Me	Me
Y.036	O	Me	H	H	B1	Br	Br	Br
Y.037	O	Me	Et	H	B1	Cl	Cl	Cl
Y.038	O	Me	Et	H	B1	Me	Me	Me
Y.039	O	Me	Et	H	B1	Br	Br	Br
Y.040	O	Me	Me	Me	B1	Cl	Cl	Cl
Y.041	O	Me	Me	Me	B1	Cl	Br	Cl
Y.042	O	Me	Me	Me	B1	Me	Me	Me
Y.043	O	Me	Me	Me	B1	Br	Br	Br
Y.044	O	Me	Me	Me	B1	Cl	4-Cl-phenyl	Cl
Y.045	O	Me	Me	Me	B1	Cl	4-Cl-phenoxy	Cl
Y.046	O	Me	Me	Et	B1	Cl	Cl	Cl
Y.047	O	Me	Me	Et	B1	Cl	Br	Cl
Y.048	O	Me	Me	Et	B1	Me	Me	Me
Y.049	O	Me	Me	Et	B1	Br	Br	Br
Y.050	O	Me	Me	Et	B1	Cl	4-Cl-phenyl	Cl

Cpd No.	X	R ₃	R ₄	R ₅	B	R ₇	R ₉	R ₁₁
Y.051	O	Me	Me	H	B2	Cl	H	Cl
Y.052	O	Me	Me	H	B2	Cl	Cl	Cl
Y.053	O	Me	Me	H	B2	Cl	Br	Cl
Y.054	O	Me	Me	H	B2	Cl	Me	Cl
Y.055	O	Me	Me	H	B2	Br	H	Br
Y.056	O	Me	Me	H	B2	Br	Cl	Br
Y.057	O	Me	Me	H	B2	Br	Br	Br
Y.058	O	Me	Me	H	B2	Br	Me	Br
Y.059	O	Me	Me	H	B2	Me	H	Me
Y.060	O	Me	Me	H	B2	Me	Cl	Me
Y.061	O	Me	Me	H	B2	Me	Br	Me
Y.062	O	Me	Me	H	B2	Me	Me	Me
Y.063	O	Me	H	H	B2	Cl	H	Cl
Y.064	O	Me	H	H	B2	Cl	Cl	Cl
Y.065	O	Me	H	H	B2	Br	H	Br
Y.066	O	Me	H	H	B2	Me	H	Me
Y.067	O	Me	Me	Me	B2	Cl	H	Cl
Y.068	O	Me	Me	Me	B2	Cl	Cl	Cl
Y.069	O	Me	Me	Me	B2	Br	H	Br
Y.070	S	Me	Me	H	B1	H	Cl	H
Y.071	S	Me	Me	H	B1	Cl	H	Cl
Y.072	S	Me	Me	H	B1	Cl	Cl	Cl
Y.073	S	Me	Me	H	B1	Cl	Br	Cl
Y.074	S	Me	Me	H	B1	Cl	Me	Cl
Y.075	S	Me	Me	H	B1	Cl	4-Cl-phenyl	Cl

Cpd No.	X	R ₃	R ₄	R ₅	B	R ₇	R ₉	R ₁₁
Y.076	S	Me	Me	H	B1	Me	Me	Me
Y.077	S	Me	Me	H	B1	Br	Br	Br
Y.078	S	Me	H	H	B1	Cl	Cl	Cl
Y.079	S	Me	H	H	B1	Me	Me	Me
Y.080	S	Me	H	H	B1	Br	Br	Br
Y.081	S	Me	Me	Me	B1	Cl	Cl	Cl
Y.082	S	Me	Me	Me	B1	Me	Me	Me
Y.083	S	Me	Me	Me	B1	Br	Br	Br
Y.084	S	Me	Me	Et	B1	Cl	Cl	Cl
Y.085	S	Me	Me	Et	B1	Cl	Br	Cl
Y.086	S	Me	Me	Et	B1	Me	Me	Me
Y.087	S	Me	Me	H	B2	Cl	H	Cl
Y.088	S	Me	Me	H	B2	Cl	Cl	Cl
Y.089	S	Me	Me	H	B2	Br	H	Br
Y.090	S	Me	Me	H	B2	Br	Br	Br
Y.091	S	Me	Me	H	B2	Me	H	Me
Y.092	S	Me	Me	H	B2	Me	Me	Me
Y.093	S	Me	Me	Me	B2	Cl	H	Cl
Y.094	S	Me	Me	Me	B2	Cl	Cl	Cl
Y.095	S	Me	Me	Me	B2	Br	H	Br
Y.096	S	Me	Me	Me	B2	Br	Br	Br
Y.097	S	Me	Me	Me	B2	Me	H	Me
Y.098	S	Me	Me	Me	B2	Me	Me	Me
Y.099	S	Me	Me	Et	B2	Cl	H	Cl
Y.100	S	Me	Me	Et	B2	Br	H	Br

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Table 1 provides 100 compounds of formula (Ia), wherein A is A₁



X, R₃, R₄, R₅, R₇, R₉ and R₁₁ are as defined in Table Y and B is selected from the groups consisting B₁ and B₂. For example, compound 1.003 has the following structure:

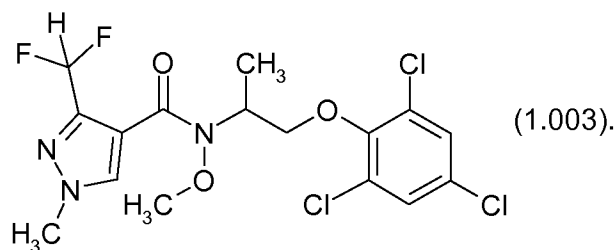
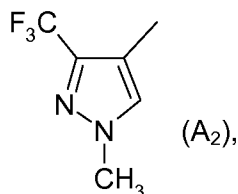


Table 2 provides 100 compounds of formula (Ia), wherein A is A₂



X, R₃, R₄, R₅, R₇, R₉ and R₁₁ are as defined in Table Y and B is selected from the groups consisting B₁ and B₂. For example, compound 2.051 has the following structure:

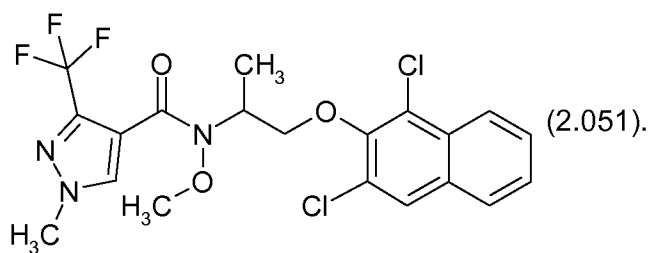
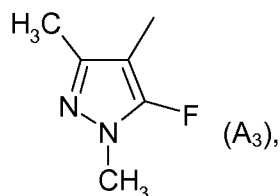


Table 3 provides 100 compounds of formula (Ia), wherein A is A₃

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X, R₃, R₄, R₅, R₇, R₉ and R₁₁ are as defined in Table Y and B is selected from the groups consisting B₁ and B₂. For example, compound 3.055 has the following structure:

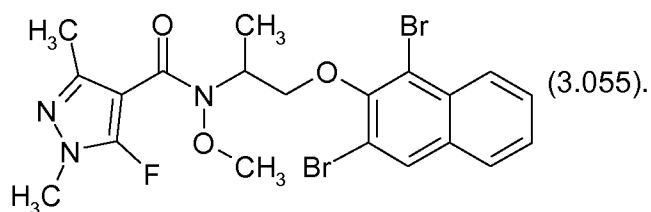


Table 4 : Characterising data:

Table 4 shows selected melting point and selected NMR data for compounds of Table 1 to 3. CDCl₃ is used as the solvent for NMR measurements, unless otherwise stated. If a mixture of solvents is present, this is indicated as, for example: CDCl₃/d₆-DMSO). No attempt is made to list all characterising data in all cases.

In Table 4 and throughout the description that follows, temperatures are given in degrees Celsius; "NMR" means nuclear magnetic resonance spectrum; MS stands for mass spectrum; "%" is percent by weight, unless corresponding concentrations are indicated in other units. The following abbreviations are used throughout this description:

m.p. = melting point

b.p.= boiling point.

S = singlet

br = broad

d = doublet

dd = doublet of doublets

t = triplet

q = quartet

m = multiplet

ppm = parts per million

Table 4:

Cpd No.	¹ H-NMR data: ppm (multiplicity/number of Hs)	MS [M+H] ⁺	m.p. (°C)	LCMS data
1.002	1.46-1.48 (d,3H); 3.82 (s,3H); 3.98 (s,3H); 4.04-4.07 (dd,1H); 4.30-4.34 (dd,1H); 4.85-4.93 (m,1H); 6.98-7.02 (m,1H,Ar-H); 7.11-7.38 (t,1H,CHF ₂); 7.26-7.29 (m,2H,Ar-H); 7.94 (s,1H, Pyr-H).	408/410/412	resin	1.87 min; 408

Cpd No.	¹ H-NMR data: ppm (multiplicity/number of Hs)	MS [M+H] ⁺	m.p. (°C)	LCMS data
1.003	1.46-1.48(d,3H); 3.80(s,3H); 3.88(s,3H); 4.02-4.06(dd,1H); 4.27-4.31(dd,1H); 4.83-4.91(m,1H); 7.10-7.37(t,1H,CHF ₂); 7.29(s,2H,Ar-H); 7.92(s,1H, Pyr-H).	442/444/446	resin	
1.023	1.47-1.49(d,3H); 2.21(s,9H); 3.71-3.78(dd,1H); 3.79(s,3H); 3.98(s,3H); 4.01-4.06(dd,1H); 4.27-4.33(dd,1H); 6.79(s,2H,Ar-H); 7.09-7.34(t,1H,CHF ₂); 7.89(s,1H, Pyr-H).	382.	resin	
1.026	1.48-1.50 (d,3H); 3.81 (s,3H); 3.98 (s,3H); 3.99-4.03 (dd,1H); 4.28-4.32 (dd,1H); 4.84-4.92 (m,1H); 7.10-7.37 (t,1H); 7.64 (s, 2H); 7.92 (s,1H, Pyr-H).	574/576/578/580	resin	
1.032	3.78(s,3H); 3.99(s,3H); 4.15-4.19(dd,2H); 4.23-4.26(dd,1H); 7.15-7.43(t,1H,CHF ₂); 7.29(s,2H,Ar-H); 7.95(s,1H, Pyr-H).	428/430/432	resin	
1.051	1.5(d,3H); 3.85(s,3H); 3.98(s,3H); 4.15(m,1H); 4.41(m,1H); 4.98(m,1H); 7.25(t,1H); 7.51(m,1H); 7.59(m,1H); 7.74(d,1H); 7.83(s,1H); 7.95(s, 1H); 8.18(d,1H)	458/460	resin	2.09 min; 458
1.055	1.54(d,3H); 3.87(s,3H); 3.99(s,3H); 4.11(m,1H); 4.42(m,1H); 4.99(m,1H); 7.27(t,1H); 7.49(m,1H); 7.6(m,1H); 7.72(d,1H); 7.98(s,1H); 8.07(s,1H); 8.18(d,1H)	548/550	resin	2.12 min; 548
1.072	1.58-1.60(d,3H); 3.81(s,3H); 3.88(s,3H); 4.10-4.16(dd,1H); 4.24-4.30(dd,1H); 5.09-4.18(m,1H); 6.65-6.93(t,1H,CHF ₂); 7.24(s,2H,Ar-H); 8.12(s,1H, Pyr-H)	458/460/462	resin	2.11 min; 460
2.051	1.47(d,3H); 3.81(s,3H); 3.98(s,3H); 4.06(m,1H); 4.42(m,1H); 4.86(m,1H); 7.51(m,1H); 7.59(m,1H); 7.74(d,1H); 7.83(s,1H); 7.87(s,1H); 8.19(d,1H)	476/478	resin	2.14 min; 476
2.055	1.49(d,3H); 3.82(s,3H); 3.97(s,3H); 4.02(m,1H); 4.43(m,1H); 4.88(m,1H); 7.5(m,1H); 7.6(m,1H); 7.72(d,1H); 7.88(s,1H); 8.08(s,1H); 8.19(d,1H)	566/568	resin	2.18 min; 566
3.051	1.52(d,3H); 2.35(s,3H); 3.7(s,3H); 3.8(s,3H); 4.07(m,1H); 4.4(m,1H); 4.8(m,1H); 7.51(m,1H); 7.6(m,1H); 7.72(d,1H); 7.82(s,1H); 8.19(d,1H)	440/442	resin	2.05 min; 440
3.055	1.57(d,3H); 2.35(s,3H); 3.7(s,3H); 3.8(s,3H); 4.03(m,1H); 4.41(m,1H); 4.85(m,1H); 7.5(m,1H); 7.6(m,1H); 7.74(m,1H); 8.08(s,1H); 8.19(d,1H)	530/532	resin	2.09 min; 530

Formulation examples for compounds of formula I:

Example F-1.1 to F-1.2: Emulsifiable concentrates

Components	F-1.1 F-1.2	
compound of Tables 1-3	25%	50%
calcium dodecylbenzenesulfonate	5%	6%
castor oil polyethylene glycol ether (36 mol ethylenoxy units)	5%	-
tributylphenolpolyethylene glycol ether (30 mol ethylenoxy units)	-	4%
cyclohexanone	-	20%
xylene mixture	65%	20%

Emulsions of any desired concentration can be prepared by diluting such concentrates with water.

Example F-2: Emulsifiable concentrate

Components	F-2
compound of Tables 1-3	10%
octylphenolpolyethylene glycol ether (4 to 5 mol ethylenoxy units)	3%
calcium dodecylbenzenesulfonate	3%
castor oil polyglycol ether (36 mol ethylenoxy units)	4%
cyclohexanone	30%
xylene mixture	50%

Emulsions of any desired concentration can be prepared by diluting such concentrates with water.

Examples F-3.1 to F-3.4: Solutions

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Components	F-3.1	F-3.2	F-3.3	F-3.4
compound of Tables 1-3	80%	10%	5%	95%
propylene glycol monomethyl ether	20%	-	-	-
polyethylene glycol (relative molecular mass: 400 atomic mass units)	-	70%	-	-
N-methylpyrrolid-2-one	-	20%	-	-
epoxidised coconut oil	-	-	1%	5%
benzin (boiling range: 160-190°)	-	-	94%	-

The solutions are suitable for use in the form of microdrops.

Examples F-4.1 to F-4.4: Granulates

Components	F-4.1	F-4.2	F-4.3	F-4.4
compound of Tables 1-3	5%	10%	8%	21%
kaolin	94%	-	79%	54%
highly dispersed silicic acid	1%	-	13%	7%
attapulgit	-	90%	-	18%

The novel compound is dissolved in dichloromethane, the solution is sprayed onto the carrier and the solvent is then removed by distillation under vacuum.

Examples F-5.1 and F-5.2: Dusts

Components	F-5.1	F-5.2
compound of Tables 1-3	2%	5%
highly dispersed silicic acid	1%	5%
talcum	97%	-
kaolin	-	90%

Ready for use dusts are obtained by intimately mixing all components.

Examples F-6.1 to F-6.3: Wettable powders

Components	F-6.1	F-6.2	F-6.3
compound of Tables 1-3	25%	50%	75%
sodium lignin sulfonate	5%	5%	-
sodium lauryl sulfate	3%	-	5%
sodium diisobutyl naphthalene sulfonate	-	6%	10%
octylphenolpolyethylene glycol ether (7 to 8 mol ethylenoxy units)	-	2%	-
highly dispersed silicic acid	5%	10%	10%
kaolin	62%	27%	-

All components are mixed and the mixture is thoroughly ground in a suitable mill to give wettable powders which can be diluted with water to suspensions of any desired concentration.

Example F7: Flowable concentrate for seed treatment

compound of Tables 1-3	40 %
propylene glycol	5 %
copolymer butanol PO/EO	2 %
tristyrenephenole with 10-20 moles EO	2 %
1,2-benzisothiazolin-3-one (in the form of a 20% solution in water)	0.5 %
monoazo-pigment calcium salt	5 %
Silicone oil (in the form of a 75 % emulsion in water)	0.2 %
Water	45.3 %

The finely ground active ingredient is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired dilution can be obtained by dilution with water. Using such dilutions, living plants as well as plant propagation material

can be treated and protected against infestation by microorganisms, by spraying, pouring or immersion.

BIOLOGICAL EXAMPLES: FUNGICIDAL ACTION:

Example B-1: Action against *Botrytis cinerea* – fungal growth assay

Conidia of the fungus from cryogenic storage was directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of the test compounds (0.002% active ingredient) into a microtiter plate (96-well format) the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was measured photometrically after 3-4 days. The activity of a compound was expressed as fungal growth inhibition (0 = no growth inhibition, ratings of 80 % to 99 % mean good to very good inhibition, 100 % = complete inhibition). Compounds 1.003, 1.051 and 1.055 show very good activity in this test ($\geq 80\%$ inhibition).

Example B-2: Action against *Mycosphaerella arachidis* (early leaf spot of groundnut; *Cercospora arachidicola* [anamorph]) – fungal growth assay

Conidia of the fungus from cryogenic storage were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of the test compounds (0.002% active ingredient) into a microtiter plate (96-well format) the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was measured photometrically after 6-7 days. The activity of a compound was expressed as fungal growth inhibition (0 = no growth inhibition, ratings of 80 % to 99 % mean good to very good inhibition, 100 % = complete inhibition). Compounds 1.003, 1.051, 1.055, 2.051 and 2.055 show very good activity in this test ($\geq 80\%$ inhibition).

Example B-3: Action against *Septoria tritici* – fungal growth assay

Conidia of the fungus from cryogenic storage were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of the test compounds (0.002% active ingredient) into a microtiter plate (96-well format) the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was determined photometrically after 72 hrs. The activity of a compound was

expressed as fungal growth inhibition (0 = no growth inhibition, ratings of 80 % to 99 % mean good to very good inhibition, 100 % = complete inhibition).

Compounds 1.003, 1.051, 1.055, 2.051 and 2.055 show very good activity in this test ($\geq$ 80% inhibition).

Example B-4: Action against *Monographella nivalis* (anamorph: *Fusarium nivale*, *Microdochium nivale*; Snow mould) – fungal growth assay

Conidia of the fungus from cryogenic storage were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a DMSO-solution of the test compounds (0.002% active ingredient) into a microtiter plate (96-well format) the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was measured photometrically after 72 hrs (0 = no growth inhibition, ratings of 80 % to 99 % mean good to very good inhibition, 100 % = complete inhibition).

Compounds 1.003, 1.051, 1.055, 2.051 and 2.055 show very good activity in this test ($\geq$ 80% inhibition).

Example B-5: Action against *Rhizoctonia solani* – fungal growth assay

Mycelial fragments of a newly grown liquid culture of the fungus were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of the test compounds (0.002% active ingredient) into a microtiter plate (96-well format) the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was measured photometrically after 3-4 days. The activity of a compound was expressed as fungal growth inhibition (0 = no growth inhibition, ratings of 80 % to 99 % mean good to very good inhibition, 100 % = complete inhibition).

Compound 1.003 shows very good activity in this test ($\geq$ 80% inhibition).

Example B-6: Action against *Erysiphe graminis* f.sp. *tritici* (wheat powdery mildew)

Wheat leaf segments were placed on agar in multiwell plates (24-well format) and sprayed with test solutions (0.02% active ingredient). After drying, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was assessed 7 days after inoculation as preventive fungicidal activity.

Compounds 1.003 and 1.055 show very good activity in this test ($\geq$ 80% inhibition).

Example B-7: Protective action against *Puccinia recondita* (brown rust) on wheat

Wheat leaf segments were placed on agar in multiwell plates (24-well format) and sprayed with test solutions (0.02% active ingredient). After drying, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was assessed 8 days after inoculation as preventive fungicidal activity.

Compounds 1.003, 1.051, 1.055, 2.051 and 2.055 show very good activity in this test ($\geq$ 80% inhibition).

Example B-8: Curative action against *Puccinia recondita* (brown rust) on wheat

Wheat leaf segments were placed on agar in multiwell plates (24-well format) and inoculated with a spore suspension of the fungus. One day after inoculation the leaf segments were sprayed with test solutions (0.02% active ingredient). After appropriate incubation the activity of a compound was assessed 8 days after inoculation as curative fungicidal activity.

Compound 1.003 shows very good activity in this test ($\geq$ 80% inhibition).

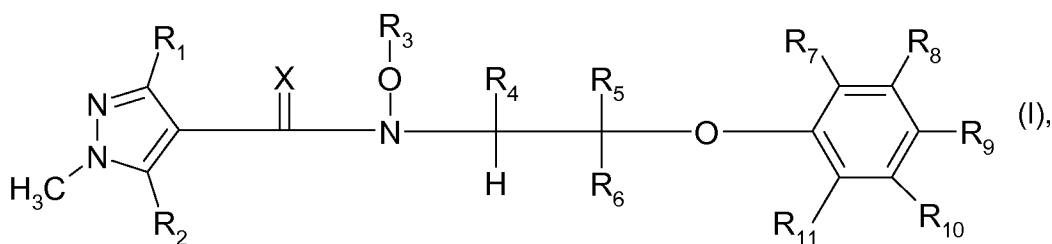
Example B-9: Action against *Pyrenophora teres* (net blotch) on barley

Barley leaf segments were placed on agar in multiwell plates (24-well format) and sprayed with test solutions (0.02% active ingredient). After drying, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was assessed 4 days after inoculation as preventive fungicidal activity.

Compounds 1.003, 1.051, 1.055, 2.051 and 2.055 show very good activity in this test ($\geq$ 80% inhibition).

WHAT IS CLAIMED IS:

1. Compounds of formula I



wherein

R₁ is C₁-C₄alkyl or C₁-C₄haloalkyl;

R₂ is hydrogen or halogen;

X is oxygen or sulfur;

R₃ is hydrogen, C₁-C₄alkyl or C₁-C₄halogenalkyl;

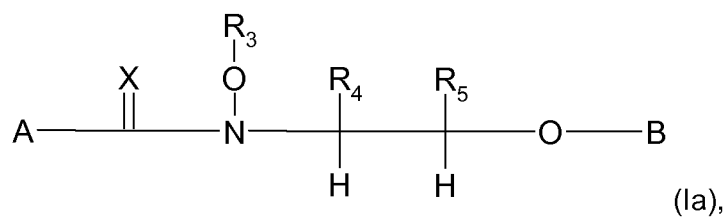
R₄, R₅ and R₆ are, independently from each other, hydrogen, halogen, C₁-C₄alkyl or C₁-C₄haloalkyl;

R₇, R₈, R₉, R₁₀ and R₁₁ are, independently from each other, hydrogen, halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy or phenoxy; wherein phenoxy in turn may be mono- di- or trisubstituted by substituents selected from the group consisting of halogen, C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄-halogenalkyl, cyano, nitro, C₁-C₄-halogenalkoxy, C₁-C₄-alkylthio, C₁-C₄-alkylsulphinyl and C₁-C₄-alkylsulphonyl, or are phenyl, which in turn may be mono- di- or trisubstituted by substituents selected from the group consisting of halogen, C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄-halogenalkyl, cyano, nitro, C₁-C₄-halogenalkoxy and C₁-C₄-alkylthio;

or R₇ and R₈, or R₈ and R₉, or R₉ and R₁₀ or R₁₀ and R₁₁ together form together with the carbon atoms to which they are attached, a 6-membered aromatic ring which can be mono- di- or trisubstituted by substituents selected from the group consisting of halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy and C₁-C₄haloalkoxy; and agronomically acceptable salts/isomers/structural isomers/stereoisomers/diastereoisomers/enantio-mers/tautomers and N-oxides of those compounds.

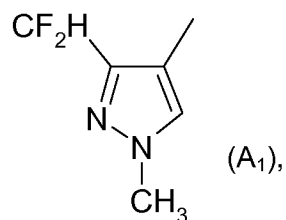
2. A compound of formula I according to claim 1, wherein R₁ is difluoromethyl, trifluoromethyl or methyl.
3. A compound of formula I according to claim 1, wherein R₂ is hydrogen or fluoro.
4. A compound of formula I according to claim 1, wherein R₃ is hydrogen, methyl or ethyl.
5. A compound of formula I according to claim 1, wherein R₇ is hydrogen, chloro, bromo or methyl.
6. A compound of formula I according to claim 1, wherein R₈ is hydrogen.
7. A compound of formula I according to claim 1, wherein R₉ is hydrogen, chloro, bromo, methyl, tert. butyl, phenoxy substituted by halogen or phenyl substituted by halogen.
8. A compound of formula I according to claim 1, wherein R₁₀ is hydrogen.
9. A compound of formula I according to claim 1, wherein R₁₁ is hydrogen, chloro, bromo or methyl.
10. A compound of formula I according to claim 1, wherein R₈ and R₉, together form together with the carbon atoms to which they are attached, a 6-membered aromatic ring which can be mono- di- or trisubstituted by chloro.
11. A compound of formula I according to claim 1, wherein
R₁ is C₁-C₄haloalkyl;
R₂ is hydrogen or halogen;
X is oxygen or sulfur;
R₃ is C₁-C₄alkyl;
R₄ is hydrogen or C₁-C₄alkyl;
R₅ and R₆ are hydrogen;
R₇ and R₉, are, independently from each other, hydrogen, halogen or C₁-C₄alkyl; and
R₈ and R₁₀ are hydrogen and
R₁₁ is halogen or C₁-C₄alkyl.

12. A compound of formula I according to claim 1 represented by the compounds of formula Ia

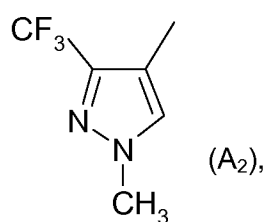


wherein

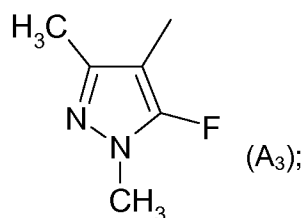
A is selected from the groups consisting of A₁,



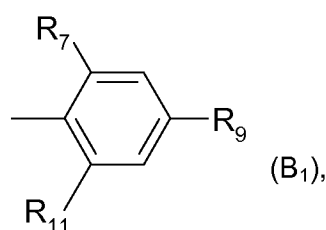
A₂,



and A₃,

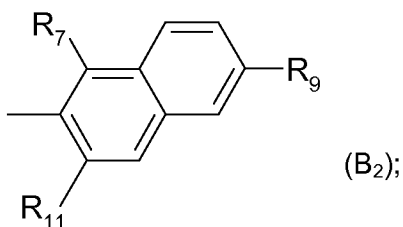


B is selected from the groups consisting of B₁,



and B₂,

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X is oxygen or sulfur;

R₃ is C₁-C₄alkyl;

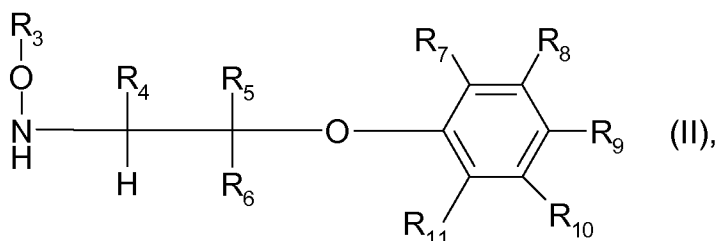
R₄ is hydrogen or C₁-C₄alkyl;

R₅ is hydrogen;

R₇ and R₉, are, independently from each other, hydrogen, halogen or C₁-C₄alkyl; and

R₁₁ is halogen or C₁-C₄alkyl.

13. A compound formula II



wherein R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀ and R₁₁ are as defined under formula I in claim 1.

14. A method of controlling or preventing infestation of useful plants by phytopathogenic microorganisms, wherein a compound of formula I according to claim 1 or a composition, comprising this compound as active ingredient, is applied to the plants, to parts thereof or the locus thereof.

15. A composition for controlling and protecting against phytopathogenic microorganisms, comprising a compound of formula I according to claim 1 and an inert carrier.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2010/053396

A. CLASSIFICATION OF SUBJECT MATTER INV. C07D231/14 C07D231/16 A01N43/56 C07C239/12 C07C239/20 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C07D A01N C07C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, CHEM ABS Data, WPI Data, BEILSTEIN Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 159 584 A2 (BASF AG [DE]) 30 October 1985 (1985-10-30) page 4; compound (VI) page 5; example 1a) page 8; compounds 54,55 page 9; compounds 65-67	13
X	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; 1992, IWAMURA, HAJIME ET AL: "Preparation of alkoxyamines as insecticides." XP002592577 retrieved from STN Database accession no. 1992:101157 the abstract and the compound with the Registry-Number [136588-97-1] ---	13
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 20 July 2010		Date of mailing of the international search report 06/08/2010
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Fink, Dieter

INTERNATIONAL SEARCH REPORT

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