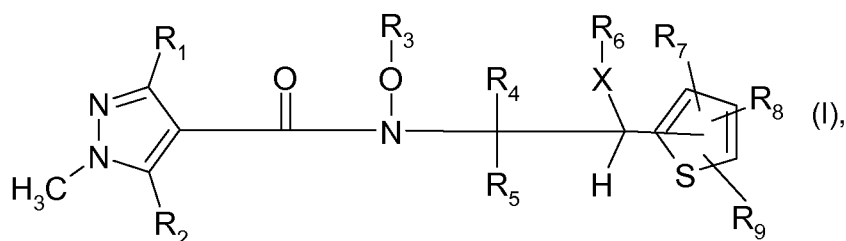


Novel Microbiocides

The present invention relates to novel microbiocidally 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.

Thienyl ethyl amides and their use as fungicides are described for example in WO2008/151828. It has been found that novel thienyl ethyl amides with a specific substitution pattern have microbiocidal activity.

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



wherein

R₁ is C₁-C₄alkyl or C₁-C₄haloalkyl;

R₂ is hydrogen, fluoro or chloro;

R₃ is hydrogen or C₁-C₄alkyl;

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

X is oxygen, sulfur or absent;

R₆ is C₁-C₄alkyl or C₁-C₄haloalkyl if X is oxygen or sulfur, or is hydrogen if X is absent;

R₇, R₈ and R₉, independently from each other, are hydrogen, halogen or $\equiv$ R₁₀; with the proviso that at least one of R₇, R₈ and R₉ is different from hydrogen;

R₁₀ is hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl or C₁-C₄alkoxyalkyl;

and agronomically acceptable salts/isomers/structural

isomers/stereoisomers/diastereoisomers/enantiomers/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 and alkynyl radicals are derived from the

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alkyl radicals mentioned. 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. Haloalkyl groups preferably have a chain length of from 1 to 4 carbon atoms. Halonalkyl 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. Structural isomers are, for example, regioisomers, enantiomers or diastereoisomers.

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

- a) R₁ is difluoromethyl, trifluoromethyl or methyl;
- b) R₂ is hydrogen or fluoro;
- d) R₃ is hydrogen, methyl or ethyl;
- e) R₄ is hydrogen or methyl;
- f) R₅ is hydrogen or methyl;
- g) R₆ is methyl;
- h) X is oxygen;
- i) X is absent and R₆ is hydrogen;
- j) R₇, R₈ and R₉ independently of each other, are hydrogen, chloro or bromo; with the proviso that at least one of R₇, R₈ and R₉ is different from hydrogen.

Especially preferred compounds of formula I are those, wherein

R₁ is difluoromethyl or trifluoromethyl;

R₂ is hydrogen;

R₃ is methyl;

R₄ is hydrogen;

R₅ is methyl;

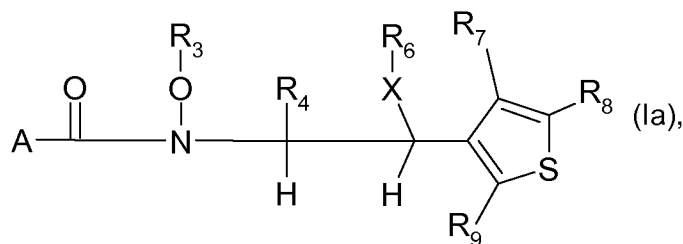
X is absent and R₆ is hydrogen; or

X is oxygen and R₆ is methyl;

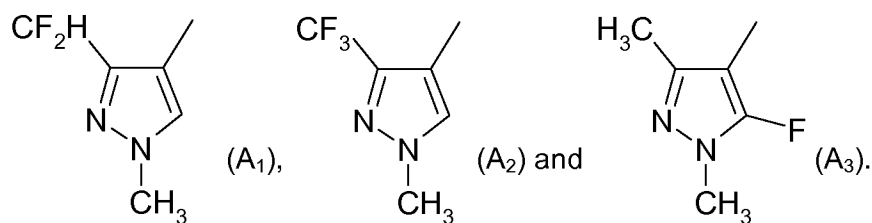
R₇, R₈ and R₉ independently of each other, are hydrogen or chloro; with the proviso that at least one of R₇, R₈ and R₉ is different from hydrogen.

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

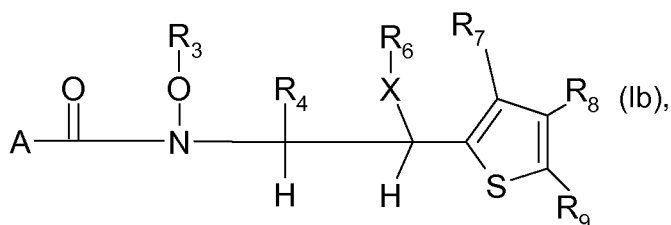


wherein A is selected from the groups consisting of A₁,

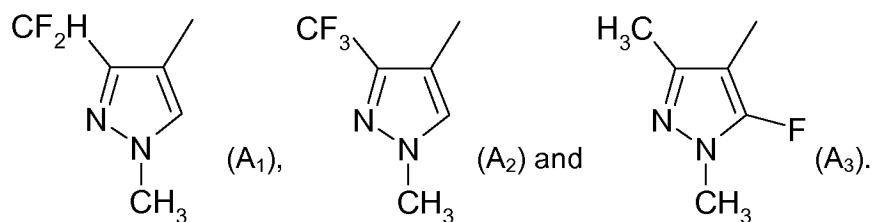


and R₃, R₄, R₆, R₇, R₈, R₉ and X are as defined under formula I above.

A further preferred group of compounds of formula I is represented by the compounds of formula Ib:



wherein A is selected from the groups consisting of A₁,



and R₃, R₄, R₆, R₇, R₈, R₉ and X are as defined under formula I above.

In preferred compounds of formula Ia and Ib, independently from each other,

a) R₃ is hydrogen, methyl or ethyl;

b) R₄ is hydrogen or methyl;

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- c) R₆ is methyl;
- d) X is oxygen;
- e) X is absent and R₆ is hydrogen;
- f) R₇, R₈ and R₉ independently of each other, are hydrogen, chloro or bromo; with the proviso that at least one of R₇, R₈ and R₉ is different from hydrogen.

Especially preferred compounds of formula Ia and Ib are those, wherein

R₃ is methyl;

R₄ is hydrogen;

X is absent and R₆ is hydrogen; or

X is oxygen and R₆ is methyl;

R₇, R₈ and R₉ independently of each other, are hydrogen or chloro; with the proviso that at least one of R₇, R₈ and R₉ is different from hydrogen.

In another preferred group of compounds of formula I, the substituents have the following meanings:

R₁ is C₁-C₄haloalkyl;

R₂ is hydrogen or fluoro;

R₃ is hydrogen or C₁-C₄alkyl;

R₄ hydrogen or C₁-C₄alkyl;

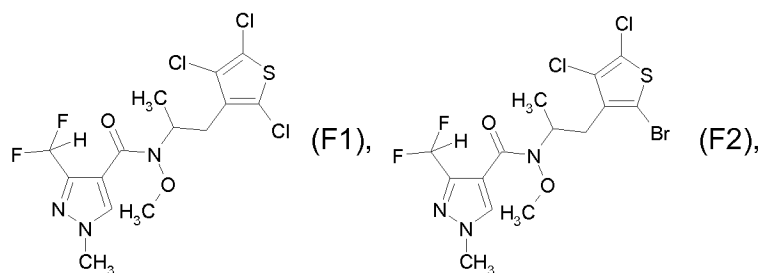
R₅ is hydrogen;

X is oxygen or absent;

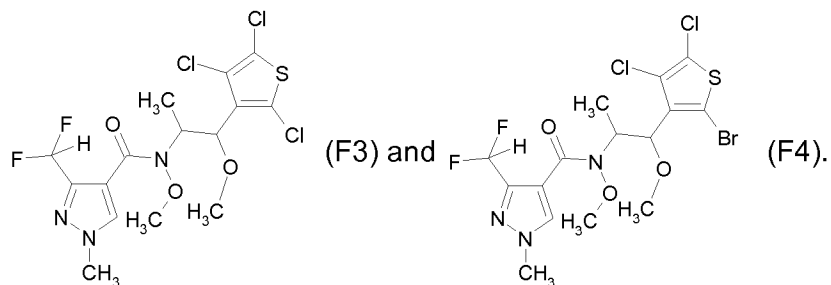
R₆ is C₁-C₄alkyl if X is oxygen, or is hydrogen if X is absent; and

R₇, R₈ and R₉, independently from each other, are hydrogen or halogen.

Other especially preferred compounds are selected from the group consisting of the compounds of formulae F1, F2, F3 and F4:

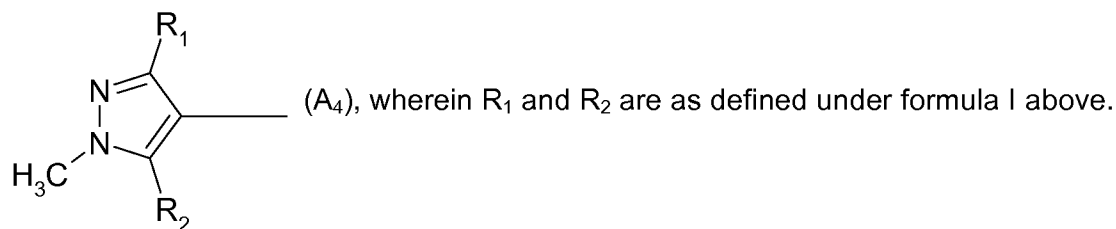


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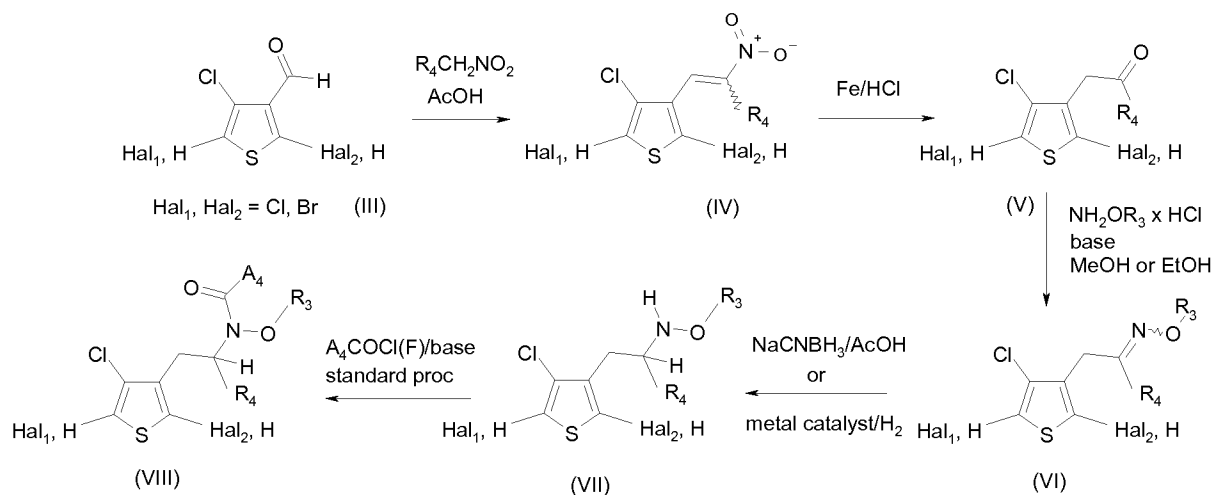


Compounds of formula I may be prepared according to the general synthesis pathways described in Schemes 1-6. In Schemes 1, and 3-5, X is absent and R₆ is hydrogen.

A₄ represents the group:

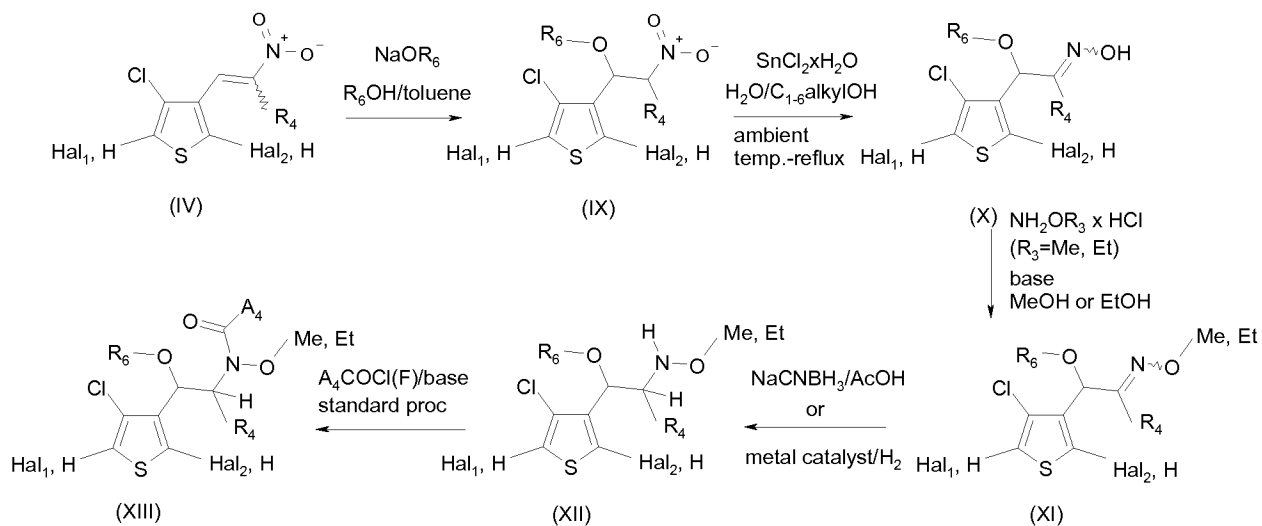


Scheme 1:

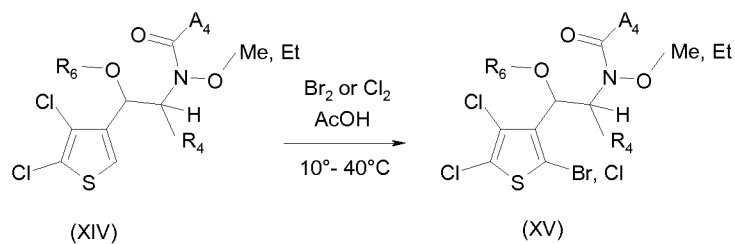


Scheme 2:

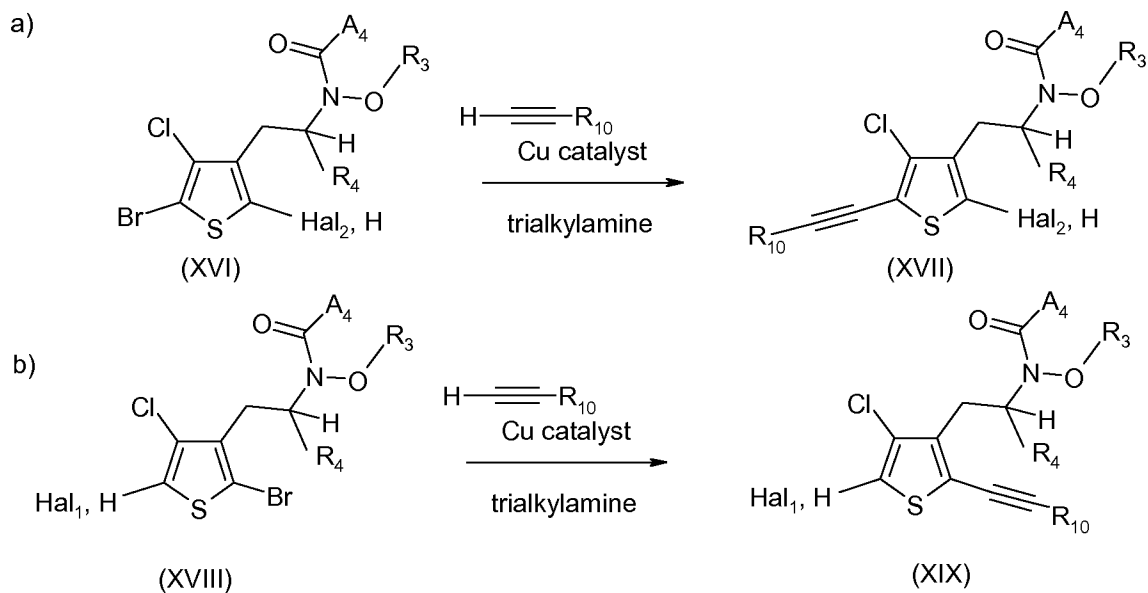
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Scheme 3:

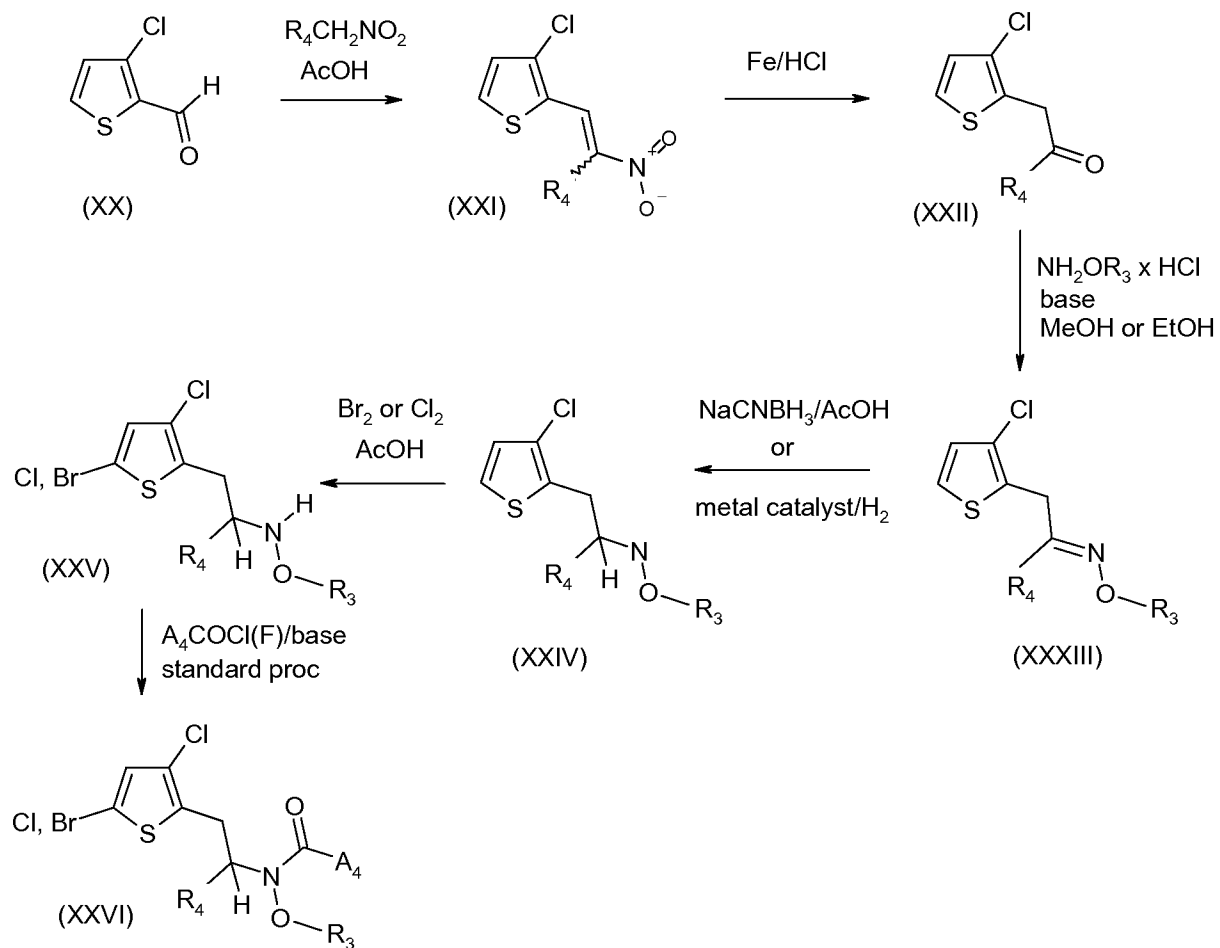


Scheme 4:



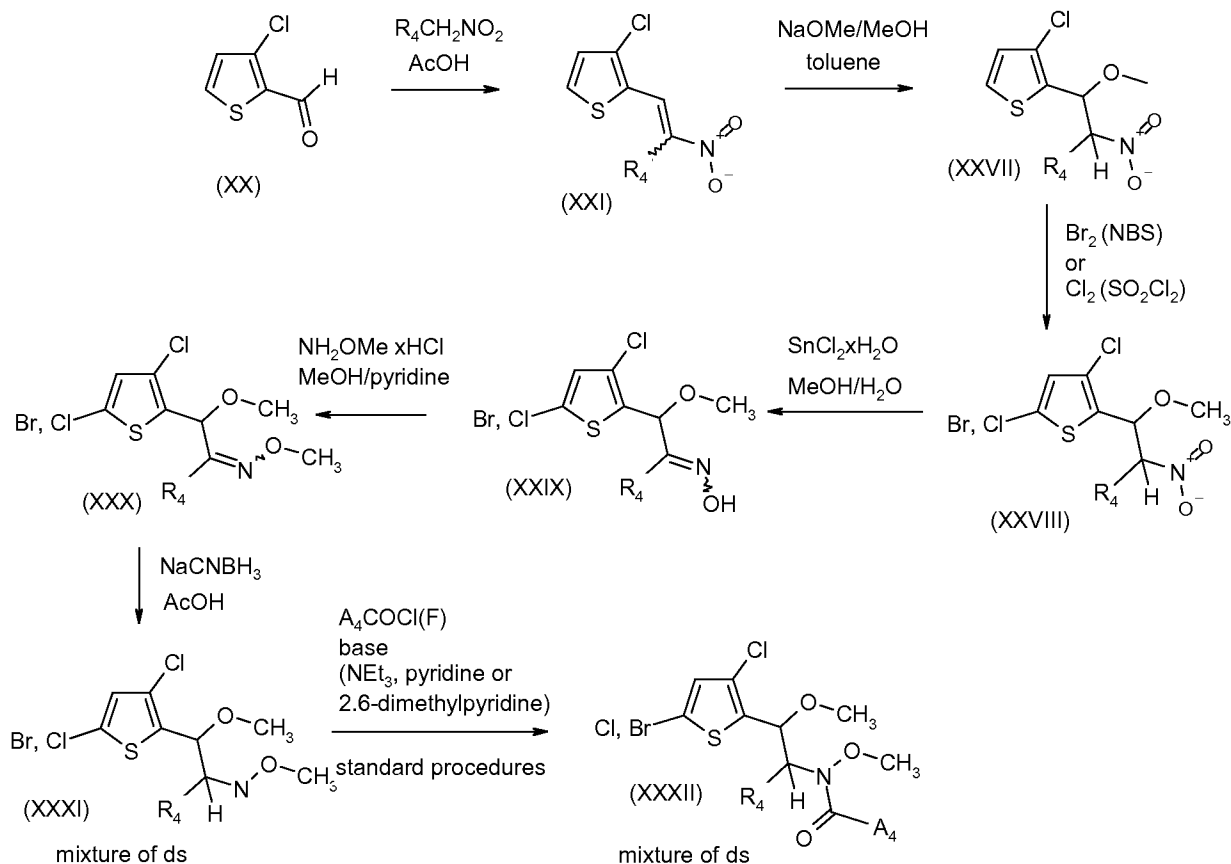
Scheme 5:

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Scheme 6:

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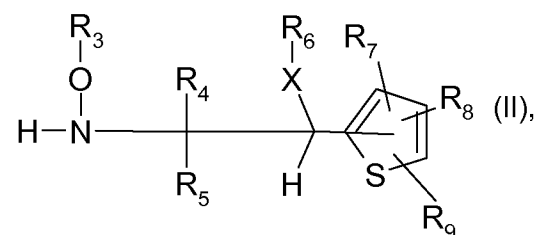


The reactions to give compounds of formula I are advantageously carried out in aprotic inert organic solvents. Such solvents are hydrocarbons such as benzene, toluene, xylene or cyclohexane, chlorinated hydrocarbons such as dichloromethane, trichloromethane, tetrachloromethane or chlorobenzene, ethers 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 $-20^{\circ}C$ and $+120^{\circ}C$. 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

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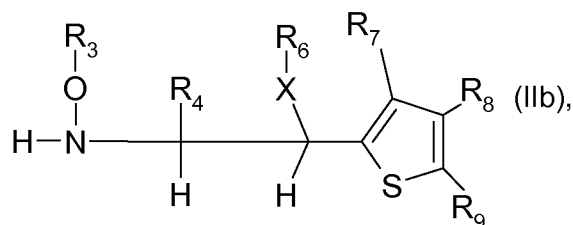
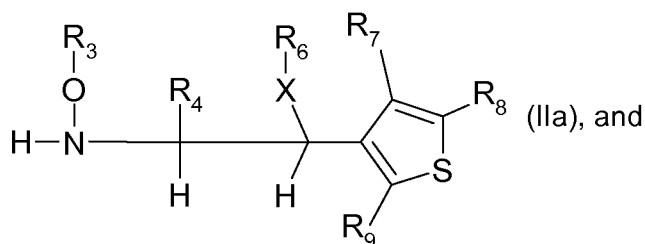
bases. The bases can be used as such or else with catalytic amounts of a phase-transfer catalyst, for example a crown ether, in particular 18-crown-6, or a tetraalkylammonium salt.

The intermediates of formula II



wherein R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 and X are as defined under formula I above, are especially developed for the preparation of the compounds of formula I and therefore constitute a further object of the present invention.

Preferred intermediates of formula II are represented by the compounds of formula IIa and IIb:



wherein R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 and X are as defined under formula I above. The preferred substituent definitions for the compounds of formula I are also valid for the compounds of formula II, IIa and IIb.

The compounds I and, where appropriate, the tautomers thereof, 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.

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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.). Furthermore, the novel compounds of formula I are effective against phytopathogenic bacteria and viruses (e.g. against *Xanthomonas* spp,

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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

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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.

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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

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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 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

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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

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prevent any future infection, or to reduce or slow the increase or spread of any future infection.

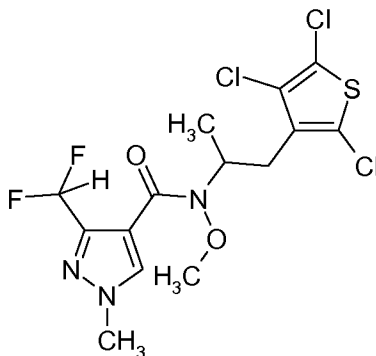
According to the present invention there is provided the use of a compound of formula (I) in the manufacture of a medicament for use in the treatment and/or prevention of microbial infection in an animal. There is also provided the use of a compound of formula (I) as a pharmaceutical agent. There is 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 non-limiting Examples illustrate the above-described invention in greater detail without limiting it.

Preparation examples:

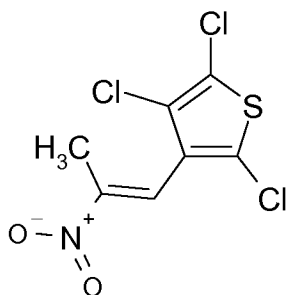
Example P1: Preparation of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid methoxy-[1-methyl-2-(2,4,5-trichlorothiophen-3-yl)ethyl]amide (compound No. 1.001):



In a sulfonation flask, 171 mg (0.62 mmol) of the amine prepared in example P2c) and 94 mg (0.93 mmol) triethylamine were dissolved in 10 ml of methylenechloride. Then a mixture of 139 mg (0.72 mmol) 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid chloride and 10 ml methylenechloride was slowly added at ambient temperature under stirring. After stirring for 24h at ambient temperature, the solvent was evaporated in a water jet vacuum and the residue purified by column chromatography over silicagel (eluent: ethylacetate/heptane 1:2). The resulting oil (254 mg) was further purified by recrystallisation from heptane. Yield: 198 mg (74% of theory) white crystals; m.p. 70-72°C.

Example P2: Preparation of O-methyl-N-[1-methyl-2-(2,4,5-trichlorothiophen-3-yl)ethyl]hydroxyl amine (compound No. 7.001):

a) Preparation of 2,3,5-trichloro-4-((E/Z)-2-nitropropenyl)thiophene

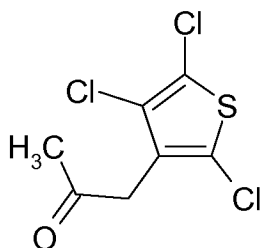


A mixture containing 15.1 g (0.07 mol) 2,4,5-trichlorothiophene-3-carbaldehyde, 36 g (0.48 mol) nitroethane, 12.9 g (0.167 mol) sodiumacetate and 100ml of acetic acid was heated for

- 18 -

6h under stirring at a temperature of 85°C. After cooling the mixture was diluted with 600 ml of tert. butylmethylether and the organic phase 5 times washed with water. After drying and evaporation of the solvent, the residue was purified by column chromatography (eluent: tert.butylmethylether/heptane 1:50 – 1:10). Yield: 10.9g (57% of theory) of a brownish oil. $^1\text{H-NMR}$ (CDCl_3): 2.25/s/3H, 7.61/s/1H (E or Z isomer)

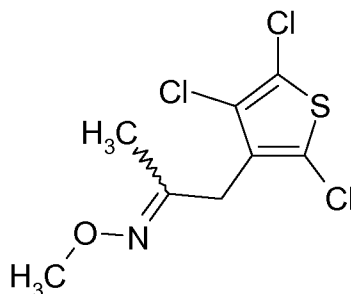
b) Preparation of 1-(2,4,5-trichlorothiophene-3-yl)propan-2-one



In a sulfonation flask 0.5g (1.83 mmol) of 2,3,5-trichloro-4-((E/Z)-2-nitropropenyl)thiophene was dissolved in a mixture of 2ml of water and 6ml of methanol. Then 0.23g (4.1 mmol) Fe powder was added and after stirring for 30 seconds, 1.2 ml of concentrated aqueous hydrogen chloride was added. After stirring for 1h at ambient temperature again 231 mg Fe powder and 1.2 ml of concentrated aqueous hydrogen chloride solution was added and the mixture stirred for 2 hours at a temperature of 75°C. After again adding the same amounts of Fe powder and hydrogen chloride solution the mixture was stirred for further 5 hours at a temperature of 75°C. Thin layer chromatography showed complete disappearance of starting material and the mixture was then diluted with 120 ml of ethylacetate. The resulting mixture was then treated 3 times with water, separating, drying of the organic phase and evaporation of the solvent in a water jet vacuum, the crude material was obtained. The raw material was purified by column chromatography (eluent: ethylacetate/heptane 1:4). Yield: 349mg (78% of theory) of a slightly brownish oil. $^1\text{HNMR}$ (CDCl_3): 2.23/s/3H, 3.71/s/2H.

c) Preparation of 1-(2,4,5-trichlorothiophene-3-yl)propan-2-one O-methyl oxime (E/Z isomer mixture):

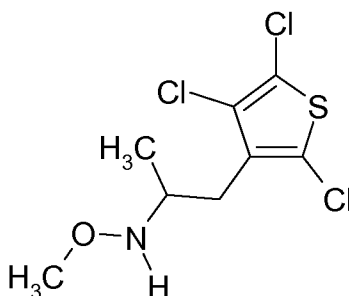
- 19 -



In a sulfonation flask, 306 mg (1.26 mmol) of propane-2-one was dissolved in 4 ml of methanol. Then 131 mg (1.57 mmol) of O-methylhydroxylamine hydrochloride and shortly afterwards 125 mg (1.57 mmol) of pyridine was added. The resulting mixture was stirred for 16 hours at ambient temperature and then diluted with 75 ml of ethylacetate. The organic phase was washed 3 times with water, dried over sodiumsulfate and the solvent was evaporated in a water jet vacuum giving the crude material. The raw material (343 mg of an orange oil) was an E/Z mixture of sufficient purity for further chemical transformations.

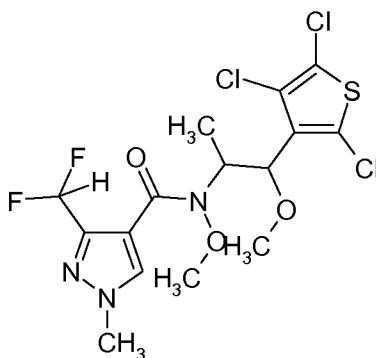
¹HNMR (CDCl₃): 1.70/d/3H minor isomer, 1.79/s/3H, major isomer, 3.49/s/2H major isomer, 3.70/s/2H minor isomer, 3.87/s/3H major isomer, 3.89/s/3H minor isomer.

d) Preparation of O-methyl-N-[1-methyl-2-(2,4,5-trichlorothiophene-3-yl)ethyl]hydroxylamine (compound No. 7.001)



In a sulfonation flask 299 mg (1.1 mmol) 1-(2,4,5-trichlorothiophene-3-yl)propan-2-one O-methyl oxime were dissolved in 3.5 ml acetic acid and the resulting mixture was cooled to a temperature of 15°C. Then 138 mg (2.2 mmol) sodiumcyanoborohydride was added and the reaction mixture was stirred for 7 hours at ambient temperature. The mixture was then carefully diluted with 20 ml of water and the pH was adjusted to ca.10 by slowly adding 16 ml of 4N sodiumhydroxide solution. The mixture was extracted 3 times with ethylacetate and the combined organic phase was washed 2 times with water. After drying and evaporation of the solvent, the residue was purified by column chromatography (eluent: ethylacetate/heptane 1:9). Yield: 304 mg (100 % of theory) of a colourless liquid (NMR-data see table 9).

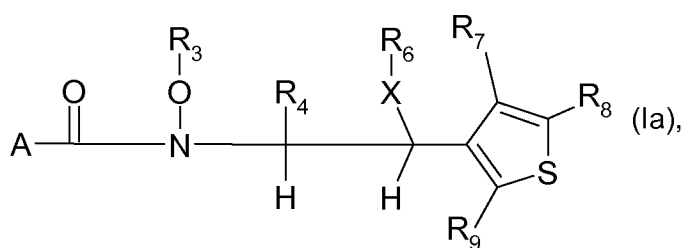
Example P3: Preparation of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid methoxy-[2-methoxy-1-methyl-2-(2,4,5-trichlorothiophene-3-yl)ethyl]amide (compound No. 1.016):



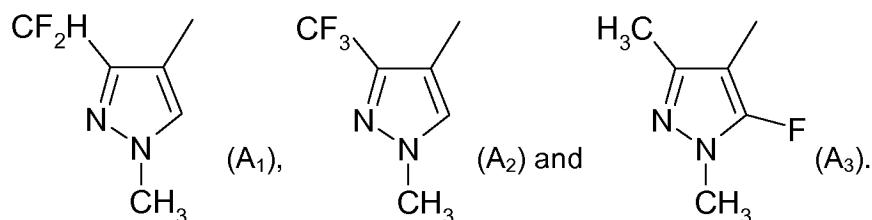
In a sulfonation flask, 257 mg (0.6 mmol) of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid methoxy-[2-methoxy-1-methyl-2-(4,5-dichlorothiophen-3-yl)ethyl]amide (compound 1.037), prepared according to methodology outlined in Scheme 2, was dissolved in 2.5 ml acetic acid. Then 1.02g of an acetic acid solution containing 5% chlorine (0.72mmol) was added slowly under cooling (ice bath). The mixture was stirred for 16h and then again 0.26g of a 5% chlorine containing acetic acid solution was added and stirring continued for 72h. Then the mixture was diluted with 12 ml of water and a slightly basic pH was adjusted by adding 14 ml of a 4N aqueous sodium hydroxide solution. The water phase was then extracted 3 times with ethylacetate. After drying of the organic phase and distilling off the solvent in a water jet vacuum, the crude product was obtained (270 mg oil). The crude material was purified by column chromatography over silicagel (eluent: ethylacetate/heptanes/methylenechloride 1:1:1). Yield: 179 mg (64% of theory) white crystals; m.p. 113-116°C, diastereomer-ratio 18 : 1.

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 is given in Table 9.



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



Each of Tables 1 to 3, which follow the Table Y below, comprises 37 compounds of the formula (Ia) in which R₄, R₅, R₇, X, R₇, R₈ and R₉ 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” is methyl, “Et” is ethyl.

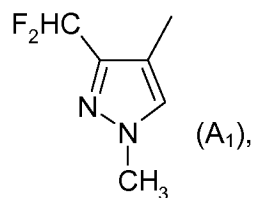
Table Y: chemical designations of the substituents of the compounds of formula Ia and Ib:

Cpd No.	R ₃	R ₄	R ₆	X	R ₇	R ₈	R ₉
Y.001	Me	Me	H	absent	Cl	Cl	Cl
Y.002	Me	Me	H	absent	Cl	H	Cl
Y.003	Me	Me	H	absent	H	Cl	Cl
Y.004	Me	Me	H	absent	Cl	Cl	Br
Y.005	Me	Me	H	absent	Cl	H	Br
Y.006	Me	Me	H	absent	H	Cl	Br
Y.007	Me	Me	H	absent	H	Cl	H
Y.008	Me	Me	H	absent	Cl	H	H
Y.009	Me	Me	H	absent	Cl	Br	Cl
Y.010	Me	H	H	absent	Cl	Cl	Cl
Y.011	Me	H	H	absent	Cl	Cl	Br
Y.012	H	Me	H	absent	Cl	Cl	Cl
Y.013	H	Me	H	absent	Cl	Cl	Br
Y.014	i-Pr	Me	H	absent	Cl	Cl	Cl

Cpd No.	R ₃	R ₄	R ₆	X	R ₇	R ₈	R ₉
Y.015	i-Pr	Me	H	absent	Cl	Cl	Br
Y.016	Me	Me	Me	O	Cl	Cl	Cl
Y.017	Me	Me	Me	O	Cl	H	Cl
Y.018	Me	Me	Me	O	H	Cl	Cl
Y.019	Me	Me	Me	O	Cl	Cl	Br
Y.020	Me	Me	Me	O	Cl	H	Br
Y.021	Me	Me	Me	O	H	Cl	Br
Y.022	Me	Me	Me	O	H	Cl	H
Y.023	Me	Me	Me	O	Cl	H	H
Y.024	Me	Me	Me	O	Cl	Br	Cl
Y.025	Me	H	Me	O	Cl	Cl	Cl
Y.026	Me	H	Me	O	Cl	Cl	Br
Y.027	H	Me	Me	O	Cl	Cl	Cl
Y.028	H	Me	Me	O	Cl	Cl	Br
Y.029	i-Pr	Me	Me	O	Cl	Cl	Cl
Y.030	i-Pr	Me	Me	O	Cl	Cl	Br
Y.031	Me	Me	Me	absent	Cl	Cl	C≡CMe
Y.032	Me	Me	Me	absent	Cl	Cl	C≡C-t-Bu
Y.033	Me	Me	Me	O	Cl	Cl	C≡CMe
Y.034	Me	Me	Me	O	Cl	Cl	C≡C-t-Bu
Y.035	Me	H	Me	O	Cl	Cl	C≡C-t-Bu
Y.036	Me	Me	H	absent	Cl	Cl	H
Y.037	Me	Me	Me	O	Cl	Cl	H

Table 1 provides 37 compounds of formula (Ia), wherein A is A₁

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and R₃, R₄, R₆, X, R₇, R₈ and R₉ are as defined in Table Y.

For example, compound 1.001 has the following structure:

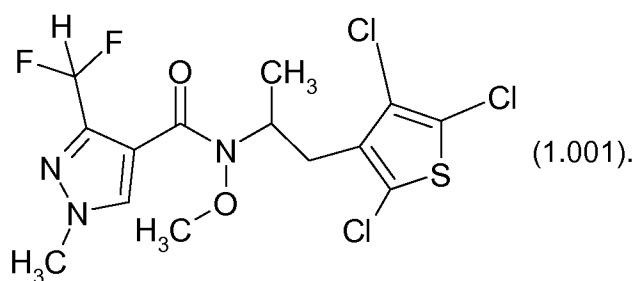
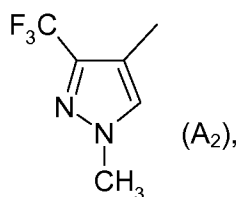


Table 2 provides 37 compounds of formula (Ia), wherein A is A₂



and R₃, R₄, R₆, X, R₇, R₈ and R₉ are as defined in Table Y.

For example, compound 2.002 has the following structure:

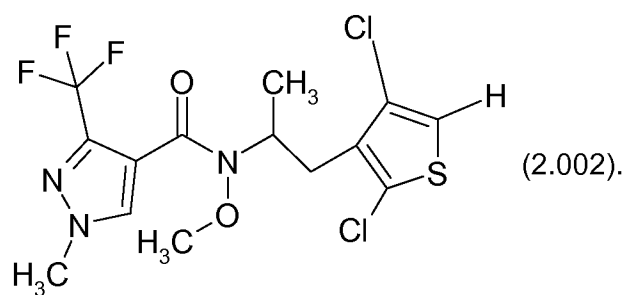
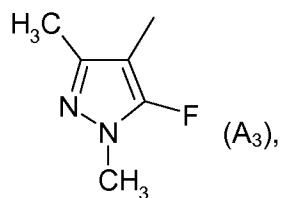


Table 3 provides 37 compounds of formula (Ia), wherein A is A₃

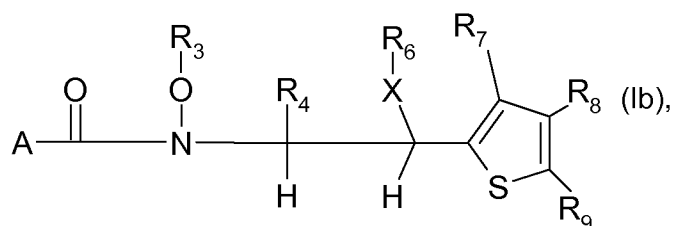


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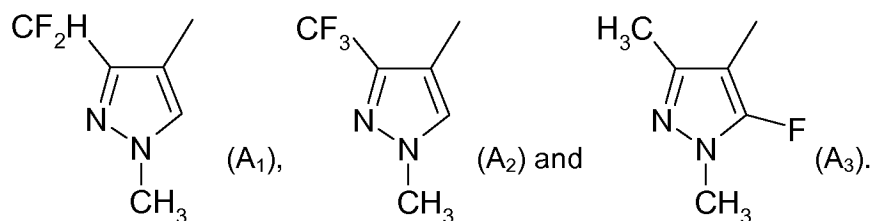
and R₃, R₄, R₆, X, R₇, R₈ and R₉ are as defined in Table Y.

Tables 4 to 6: Compounds of formula Ib:

The invention was further illustrated by the preferred individual compounds of formula (Ia) listed below in Tables 4 to 6. Characterising data are given in Table 9.

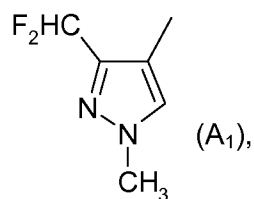


In the compounds of formula Ib, A is selected from the groups consisting of A₁,



Each of Tables 4 to 6, which follow the Table Y below, comprises 37 compounds of the formula (Ib) in which R₄, R₅, R₇, X, R₇, R₈ and R₉ have the values given in Table Y and A has the value given in the relevant Table 4 to 6. Thus Table 4 corresponds to Table Y when Y is 4 and A has the value given under the Table 4 heading, Table 5 corresponds to Table Y when Y is 5 and A has the value given under the Table 5 heading, and so on for Table 6.

Table 4 provides 37 compounds of formula (Ib), wherein A is A₁



and R₃, R₄, R₆, X, R₇, R₈ and R₉ are as defined in Table Y.

For example, compound 4.001 has the following structure:

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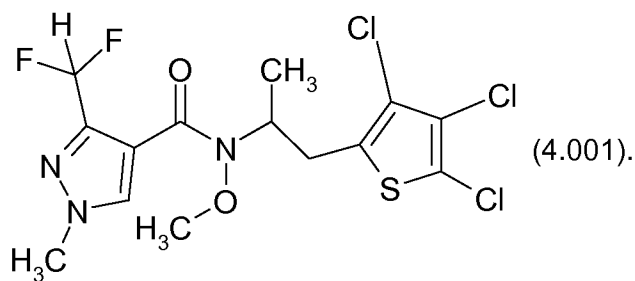
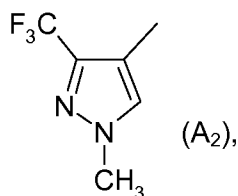


Table 5 provides 37 compounds of formula (Ib), wherein A is A₂



and R₃, R₄, R₆, X, R₇, R₈ and R₉ are as defined in Table Y.

For example, compound 5.002 has the following structure:

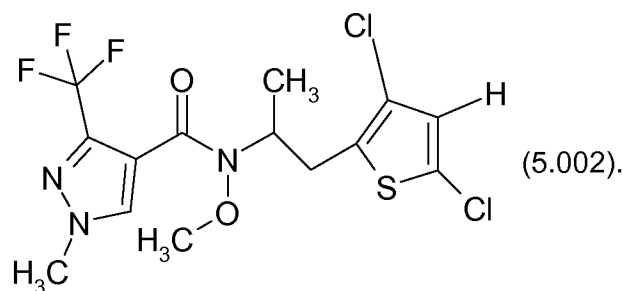
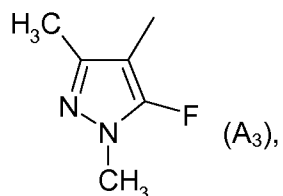


Table 6 provides 37 compounds of formula (Ib), wherein A is A₃



and R₃, R₄, R₆, X, R₇, R₈ and R₉ are as defined in Table Y.

Tables 7-8: chemical designations of the substituents of the compounds of formula IIa and IIb (amine intermediates):

Cpd No.	R ₃	R ₄	R ₆	X	R ₇	R ₈	R ₉
Z.001	Me	Me	H	absent	Cl	Cl	Cl

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Cpd No.	R ₃	R ₄	R ₆	X	R ₇	R ₈	R ₉
Z.002	Me	Me	H	absent	Cl	H	Cl
Z.003	Me	Me	H	absent	H	Cl	Cl
Z.004	Me	Me	H	absent	Cl	Cl	Br
Z.005	Me	Me	H	absent	Cl	H	Br
Z.006	Me	Me	H	absent	H	Cl	Br
Z.007	Me	Me	H	absent	H	Cl	H
Z.008	Me	Me	H	absent	Cl	H	H
Z.009	Me	Me	H	absent	Cl	Br	Cl
Z.010	Me	H	H	absent	Cl	Cl	Cl
Z.011	Me	H	H	absent	Cl	Cl	Br
Z.012	H	Me	H	absent	Cl	Cl	Cl
Z.013	H	Me	H	absent	Cl	Cl	Br
Z.014	i-Pr	Me	H	absent	Cl	Cl	Cl
Z.015	i-Pr	Me	H	absent	Cl	Cl	Br
Z.016	Me	Me	Me	O	Cl	Cl	Cl
Z.017	Me	Me	Me	O	Cl	H	Cl
Z.018	Me	Me	Me	O	H	Cl	Cl
Z.019	Me	Me	Me	O	Cl	Cl	Br
Z.020	Me	Me	Me	O	Cl	H	Br
Z.021	Me	Me	Me	O	H	Cl	Br
Z.022	Me	Me	Me	O	H	Cl	H
Z.023	Me	Me	Me	O	Cl	H	H
Z.024	Me	Me	Me	O	Cl	Br	Cl
Z.025	Me	H	Me	O	Cl	Cl	Cl
Z.026	Me	H	Me	O	Cl	Cl	Br
Z.027	H	Me	Me	O	Cl	Cl	Cl
Z.028	H	Me	Me	O	Cl	Cl	Br

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Cpd No.	R ₃	R ₄	R ₆	X	R ₇	R ₈	R ₉
Z.029	i-Pr	Me	Me	O	Cl	Cl	Cl
Z.030	i-Pr	Me	Me	O	Cl	Cl	Br
Z.031	Me	Me	Me	absent	Cl	Cl	H
Z.032	Me	Me	Me	O	Cl	Cl	H

Table 7 (Z = 7) describes 32 compounds (amine intermediates) of formula (IIa) – physical data are given in Table 9:

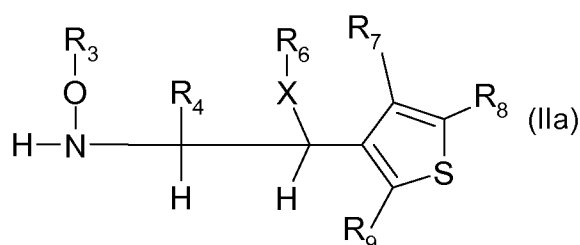


Table 8 (Z = 8) describes 32 compounds (amine intermediates) of formula (IIb) – physical data are given in Table 9:

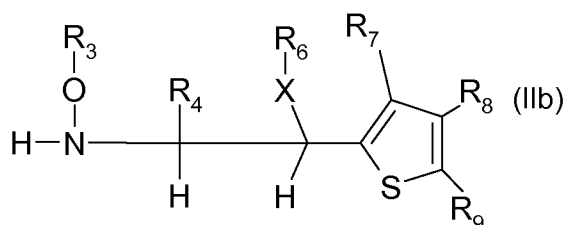


Table 9 : Characterising data:

Table 9 shows selected melting point and selected NMR data for compounds of Tables 1 to 8. 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 9 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.

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S = singlet	br = broad
d = doublet	dd = doublet of doublets
t = triplet	q = quartet
m = multiplet	ppm = parts per million

LC/MS Method A: ZQ Mass Spectrometer from Waters (Single quadrupole mass spectrometer) Instrument Parameter:

Ionisation method: Electrospray

Polarity: positive (negative) ions

Capillary (kV) 3.00, Cone (V) 30.00 (AIDA: 45V), Extractor (V) 2.00, Source Temperature (°C) 100, Desolvation Temperature (°C) 250, Cone Gas Flow (L/Hr) 50, Desolvation Gas Flow (L/Hr) 400

Mass range: 100 to 900 Da (LC8 apolar: 150 – 1000 Da)

HP 1100 HPLC from Agilent: solvent degasser, quaternary pump (ZCQ) / binary pump (ZDQ), heated column compartment and diode-array detector.

Column: Phenomenex Gemini C18, 3 µm particle size, 110 Angström, 30 x 3 mm,

Temp: 60 °C

DAD Wavelength range (nm): 200 to 500

Solvent Gradient:

A = water + 0.05 % HCOOH

B= Acetonitril/Methanol (4:1, v:v) + 0.04 % HCOOH

Time	A%	B%	Flow (ml/min)
0.00	95.0	5.0	1.700
2.00	0.0	100.0	1.700
2.80	0.0	100.0	1.700
2.90	95.0	5.0	1.700
3.00	95.0	5.0	1.700

Table 9 :

Cpd No.	¹ H-NMR data: (ppm/multiplicity/number of Hs)	MS [M+H] ⁺	m.p. (°C)	LCMS data (ret-time [min]) Method A
1.001			70-72	

Cpd No.	¹ H-NMR data: (ppm/multiplicity/number of Hs)	MS [M+H] ⁺	m.p. (°C)	LCMS data (ret-time [min]) Method A
1.004		478		2.04
1.012			147-149	
1.016			113-116	
1.019		508	110-115 (pure ds1) 98-110 (ds mix)	1.93
1.036			84-89	
1.037			80-83 (ds1) 106-110 (ds2)	
2.001			94-96	
2.016			101-106	
2.019		526	oil	2.02
2.036			71-74 (pure ds)	
2.037		526/528 [M] ⁺		2.02 (ds mix)
3.001			111-113	
3.016			112-117	
3.018			amorph	
3.019			112-116	
3.036			107-109	
3.037		410 [M] ⁺		1.77
4.001			amorph	
4.005			amorph	

Cpd No.	¹ H-NMR data: (ppm/multiplicity/number of Hs)	MS [M+H] ⁺	m.p. (°C)	LCMS data (ret-time [min]) Method A
4.016	1.49 (s/3H), 3.34 (s/3H), 3.64 (s/3H), 3.98 (s/3H), 4.60 (m/1H), 4.85 (dxd/1H), 7.19 (t/1H), 7.75 (s, 1H)			
4.017				
4.020	1.49 (d/3H), 3.32 (s/3H), 3.63 (s/3H), 3.97 (s/3H), 4.59 (m/1H), 4.86 (dxd/1H), 6.80 (s/1H), 7.18 (t/1H), 7.75 (s/1H)			
7.001	1.3(d/3H), 2.58(m/1H), 2.91(m/1H), 3.35(m/1H), 3.56(s/3H), 5.45 (m(br), 1H)			
7.012			123-126	
7.016				
7.031	1.09 (d/3H), 2.59 (m/1H), 2.85 (m, 1H), 3.57 (s/3H), 5.30 (s(broad)/1H), 6.92 (s/1H)			
7.032			oil	
8.001			oil	
8.017			oil	

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 1-6	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 1-6	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

Components	F-3.1	F-3.2	F-3.3	F-3.4
compound of Tables 1-6	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

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Components	F-4.1	F-4.2	F-4.3	F-4.4
compound of Tables 1-6	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 1-6	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 1-6	25%	50%	75%
sodium lignin sulfonate	5%	5%	-
sodium lauryl sulfate	3%	-	5%
sodium diisobutylphenylene sulfonate	-	6%	10%
octylphenolpolyethylene glycol ether (7 to 8 mol ethylenoxy units)	-	2%	-
highly dispersed silicic acid	5%	10%	10%
kaolin	62%	27%	-

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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 1-6	40 %
propylene glycol	5 %
copolymer butanol PO/EO	2 %
tristyrenephenol 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:

Example B-1: 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.

Compound 1.001, 1.004, 1.012, 1.016, 1.019, 1.036, 1.037 (diastereoisomer pair 1), 1.037 (diastereoisomer pair 2), 2.016, 2.036, 2.037, 3.001, 3.016, 3.019, 3.036 and 3.037 show very good activity in this test ($\geq 80\%$ inhibition).

Example B-2: Preventive 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.

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Compound 1.001, 1.004, 1.016, 1.019, 1.036, 1.037 (diastereoisomer pair 1), 1.037 (diastereoisomer pair 2), 2.036, 3.001, 3.016 and 3.019 show very good activity in this test ($\geq 80\%$ inhibition).

Example B-3: 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 1.001, 1.004, 1.016, 1.019, 1.036, 1.037 (diastereoisomer pair 2), and 3.001 show very good activity in this test ($\geq 80\%$ inhibition).

Example B-4: Preventive action against *Phaeosphaeria nodorum* (Glume blotch) on wheat

Wheat leaf segments were placed on agar in a multiwell plate (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.

Compound 1.001, 1.012, 1.016, 1.019, 1.036, 2.037 and 3.001 show very good activity in this test ($\geq 80\%$ inhibition).

Example B-5: 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.

Compound 1.001, 1.012, 1.016, 1.019, 1.036, 1.037 (diastereoisomer pair 1), 2.016, 2.037, 3.001, 3.016 and 3.037 show very good activity in this test ($\geq 80\%$ inhibition).

Example B-6: Action against *Botryotinia fuckeliana*/liquid culture (Gray mould)

Conidia of the fungus from cryogenic storage were directly mixed into nutrient broth. After placing a (DMSO) solution (0.02% active ingredient) of the test compounds 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 3-4 days.

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Compound 1.001, 1.004, 1.012, 1.016, 1.019, 1.036, 1.037 (diastereoisomer pair 1), 1.037 (diastereoisomer pair 2), 2.016, 2.036, 2.037, 3.001, 3.016, 3.019, 3.036 and 3.037 show very good activity in this test ($\geq 80\%$ inhibition).

Example B-7: Action against *Mycosphaerella arachidis* / liquid culture (early leaf spot)

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 (0.02% 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.

Compound 1.001, 1.004, 1.012, 1.016, 1.019, 1.036, 1.037 (diastereoisomer pair 1), 1.037 (diastereoisomer pair 2), 2.016, 2.036, 2.037, 3.001, 3.016, 3.019, 3.036 and 3.037 show very good activity in this test ($\geq 80\%$ inhibition).

Example B-8: Action against *Fusarium culmorum* / wheat / spikelet preventive (Head blight):

Wheat spikelets were placed on agar in multiwell plates (24-well format) and sprayed with test solutions. After drying, the spikelets were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was assessed 6 dpi (days after inoculation) as preventative fungicidal activity.

Compounds 1.001, 1.004, 1.016, 1.019, 1.037, 2.016, 3.001 and 3.019 show very good activity in this test ($\geq 80\%$ inhibition).

Example B-9: Action against *Gibberella zeae* (*Fusarium graminearum*) / wheat / spikelet preventive (Head blight):

Wheat spikelets were placed on agar in multiwell plates (24-well format) and sprayed with test solutions. After drying, the spikelets were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was assessed 6 dpi (days after inoculation) as preventative fungicidal activity.

Compounds 1.001, 1.004, 1.016, 1.019 and 2.016, show very good activity in this test ($\geq 80\%$ inhibition).

Example B10: Action against *Mycosphaerella graminicola* (*Septoria tritici*) / liquid culture (Septoria blotch):

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 into a microtiter plate (96-

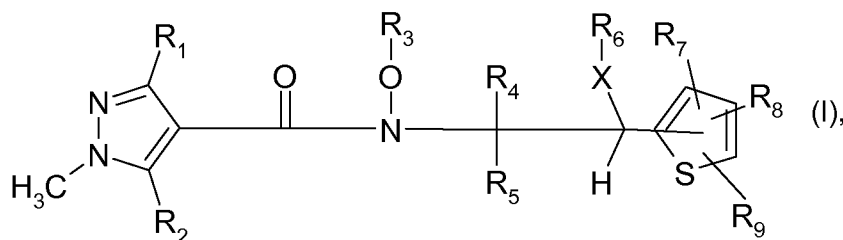
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well format) the nutrient broth containing the fungal spores was added. The test plates were incubated at 24 C and the inhibition of growth was measured photometrically after 4 days.

Compound 1.001, 1.004, 1.012, 1.016, 1.019, 1.036, 1.037 (diastereoisomer pair 1), 1.037 (diastereoisomer pair 2), 2.016, 2.036, 2.037, 3.001, 3.016, 3.019, 3.036 and 3.037 show very good activity in this test ($\geq 80\%$ inhibition).

WHAT IS CLAIMED IS:

1. A compound of formula I



wherein

R₁ is C₁-C₄alkyl or C₁-C₄haloalkyl;

R₂ is hydrogen, fluoro or chloro;

R₃ is hydrogen or C₁-C₄alkyl;

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

X is oxygen, sulfur or absent;

R₆ is C₁-C₄alkyl or C₁-C₄haloalkyl if X is oxygen or sulfur, or is hydrogen if X is absent;

R₇, R₈ and R₉, independently from each other, are hydrogen, halogen or ≡R₁₀; with the proviso that at least one of R₇, R₈ and R₉ is different from hydrogen; and

R₁₀ is hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl or C₁-C₄alkoxyalkyl;

and agronomically acceptable salts/isomers/structural

isomers/stereoisomers/diastereoisomers/enantiomers/tautomers and N-oxides of those compounds.

2. A compound according to claim 1, wherein R₁ is difluoromethyl, trifluoromethyl or methyl.

3. A compound according to claim 1, wherein R₂ is hydrogen or fluoro.

4. A compound according to claim 1, wherein R₃ is hydrogen, methyl or ethyl.

5. A compound according to claim 1, wherein R₄ is hydrogen or methyl.

6. A compound according to claim 1, wherein R₅ is hydrogen or methyl.

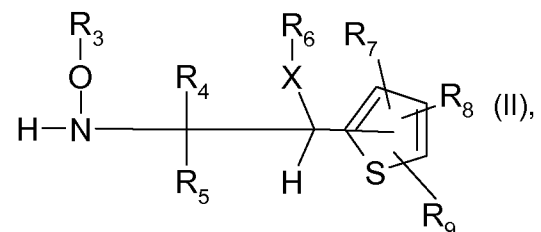
7. A compound according to claim 1, wherein R₆ is methyl.

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8. A compound according to claim 1, wherein X is oxygen.

9. A compound according to claim 1, wherein X is absent and R₆ is hydrogen.

10. A compound of formula II



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

11. 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.

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