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(54) Title: FUNGICIDAL PYRIMIDINE COMPOUNDS

(57) Abstract: The present invention relates to fungicidal pyrimidine compounds I, to their use and to methods for combating phytopathogenic fungi. The present invention also relates to seeds treated with at least one such compound. Furthermore the invention relates to processes for preparing compounds of formula I.



Fungicidal pyrimidine compounds

Description

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The present invention relates to fungicidal pyrimidine compounds, to their use and to methods for combating phytopathogenic fungi. The present invention also relates to seeds treated with at least one such compound. Furthermore the invention relates to processes for preparing compounds of formula I and intermediates as well as processes for the preparation of such intermediates.

WO 1998/003272 describes a process for the preparation of 4-amino-5-chloro-6-(1-fluoro-ethyl)pyrimidine compounds, which are pest controlling agents for agricultural and horticultural use. WO 1997/028133 discloses acylated 4-amino and 4-hydrazinopyrimidines and their use as pesticides. EP 665225 A1 relates to 4-phenethylamino pyrimidine derivatives useful for chemical control of noxious organisms. WO 1995/018795 relates to N-(4 pyrimidinyl)amide pesticides with a carboxy moiety instead of a methylene group as in compounds I according to the present invention.

The compounds according to the present invention differ from those described in the abovementioned publications by the specific substituent R^{a2} of the pyrimidyl moiety in position 2 and the specific ethylene linker between the phenyl ring and the amino function as defined herein.

EP 264217 A2 relates to N-(4-pyrimidinyl)arylalkylamine pesticides, inter alia disclosing N-(4-pyrimidinyl)phenylethylamines, but does not mention specifically the combination of the ethylene linker between the phenyl ring and the amino function together with the group –O-Het as defined herein.

In many cases, in particular at low application rates, the fungicidal activity of known fungicidal compounds is unsatisfactory. Based on this, it was an object of the present invention to provide compounds having improved activity and/or a broader activity spectrum against phytopathogenic fungi. This objective is achieved by the use of substituted pyrimidine compounds of formula I having good fungicidal activity against phytopathogenic harmful fungi.

Accordingly, the present invention relates to compounds of the formula I

wherein:

Ra2 is halogen, CN, NO₂, OH, SH, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-haloalkylthio, C₁-C₄-alkylsulfinyl, C₁-C₄-haloalkylsulfinyl, C₁-C₄-haloalkylsulfinyl, C₁-C₄-alkoxy-C₁-C₄-alkylsulfonyl, C₁-C₄-alkoxy-C₁-C₄-alkoxy-C₁-C₄-alkoxyl, C₂-C₄-alkynyl, C₂-C₄-haloalkenyl, C₂-C₄-haloalkynyl, C₃-C₈-cycloalkyl, C₃-C₈-cycloalkyloxy, C₃-C₈-cycloalkyl-C₁-C₄-alkyl, NR^AR^B, C(=O)R', C(=NOR")R"" or C(=NH)-O-R"";

- R^{a5}, R^{a6} independently of each other are hydrogen, halogen, CN, NO₂, OH, SH, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-haloalkylsulfinyl, C₁-C₄-alkylsulfonyl, C₁-C₄-haloalkylsulfonyl, C₁-C₄-alkylsulfonyl, C₁-C₄-alkoxy-C₁-C₄-alkoxy-C₁-C₄-alkoxy-C₁-C₄-alkoxy, C₂-C₄-alkenyl, C₂-C₄-alkynyl, C₂-C₄-haloalkenyl, C₂-C₄-haloalkynyl, C₃-C₈-cycloalkyl, C₃-C₈-cycloalkyl-C₁-C₄-alkyl, NR^AR^B, C(=O)R', C(=NOR'')R''' or C(=NH)-O-R''';
 - R^A, R^B independently of one another are hydrogen, C₁-C₄-alkyl, C₂-C₄-alkenyl, C₂-C₄-alkynyl, phenyl, benzyl, C₃-C₈-cycloalkyl, C₃-C₈-cycloalkenyl or C(=O)-R';
 - R' is hydrogen, OH, NH₂, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_2 - C_4 -alkenyl, C_2 - C_4 -alkynyl, C_1 - C_4 -alkoxy, C_1 - C_4 -alkylamino or di(C_1 - C_4 -alkyl)amino;
- 15 R" is hydrogen, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_2 - C_4 -alkenyl, C_2 - C_4 -alkynyl or C_1 - C_4 -alkoxy- C_1 - C_4 -alkyl,
 - R" is hydrogen or C₁-C₄-alkyl;

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- 20 R is hydrogen, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkoxy, C_1 - C_4 -alkoxy- C_1 - C_4 -alkoxy- C_1 - C_4 -alkyl, C_2 - C_4 -alkyl, C_2 - C_4 -haloalkenyl, C_2 - C_4 -haloalkenyl, C_2 - C_4 -haloalkynyl, C_1 - C_4 -hal
- 25 n indicates the number of substituents R^b on the phenyl ring and n is 0, 1, 2, 3 or 4;
 - R^b is halogen, CN, NO₂, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₂-C₄-alkenyl, C₂-C₄-alkynyl, C₂-C₄-alkynyl, NR^AR^B, C(=NOR")R"" or C(=NH)-O-R"",
- it being possible for n = 2, 3 or 4 that R^b are identical or different;
 - Het is a 5- or 6-membered heteroaryl, wherein the ring member atoms of the heteroaryl include besides carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S and wherein the heteroaryl is unsubstituted or carries 1, 2, 3 or 4 identical or different groups R°:
- is halogen, CN, NO₂, C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy, C₁-C₆-alkylthio, C₁-C₆-haloalkylthio, C₁-C₆-alkylsulfinyl, C₁-C₆-haloalkylsulfinyl, C₁-C₆-alkylsulfonyl, C₁-C₆-alkylsulfonyl, C₁-C₆-alkoxy-C₁-C₄-alkyl, C₁-C₆-alkoxy-C₁-C₄-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl, NR^AR^B, C(=O)R', C(=NOR'')R''', C(=NH)-O-R''', C₃-C₈-cycloalkyl, C₃-C₈-cycloalkyl-C₁-C₄-alkyl, phenyl, phenyl-C₁-C₄-alkyl, phenoxy, phenoxy-C₁-C₄-alkyl or a 5- or 6-membered heteroaryl, wherein the ring member atoms of the heteroaryl include besides carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S, and wherein the

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aforementioned cyclic radicals are unsubstituted or carry 1, 2, 3 or 4 identical or different substituents R^d:

Rd is halogen, CN, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy or C₁-C₄-haloalkoxy;

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or two radicals R^c that are bound to adjacent ring member atoms of the Het group form together with said ring member atoms a fused 5-, 6- or 7-membered saturated, partially unsaturated or aromatic carbocycle or heterocycle, wherein the ring member atoms of the fused heterocycle include besides carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S, and wherein the fused carbocycle or heterocycle is unsubstituted or carries 1, 2,

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Re is halogen, CN, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy or C₁-C₄-haloalkoxy;

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and the N-oxides and the agriculturally acceptable salts thereof.

3 or 4 identical or different radicals groups Re:

The present invention furthermore relates to processes for preparing the compounds I. The present invention furthermore relates to intermediates such as compounds of formulae II and III.

The compounds of the present invention are useful for combating harmful fungi. Therefore the present invention furthermore relates to a method for combating harmful fungi, which process comprises treating the fungi or the materials, plants, the soil or seeds to be protected against fungal attack, with an effective amount of at least one compound of formula I or of an Noxide or an agriculturally acceptable salt thereof.

Furthermore, the present invention also relates to seed comprising a compound of formula I, or an N-oxide or an agriculturally acceptable salt thereof, in an amount of from 0.1 g to 10 kg per 100 kg of seed.

Depending on the substitution pattern, the compounds of formula I and their N-oxides may have one or more centers of chirality, in which case they are present as pure enantiomers or pure diastereomers or as enantiomer or diastereomer mixtures. Both, the pure enantiomers or diastereomers and their mixtures are subject matter of the present invention.

Agriculturally useful salts of the compounds I encompass especially the salts of those cations or the acid addition salts of those acids whose cations and anions, respectively, have no adverse effect on the fungicidal action of the compounds I. Suitable cations are thus in particular the ions of the alkali metals, preferably sodium and potassium, of the alkaline earth metals, preferably calcium, magnesium and barium, of the transition metals, preferably manganese, copper, zinc and iron, and also the ammonium ion which, if desired, may carry one to four C_1 - C_4 -alkyl substituents and/or one phenyl or benzyl substituent, preferably diisopropylammonium, tetramethylammonium, tetrabutylammonium, trimethylbenzylammonium, furthermore phosphonium ions, sulfonium ions, preferably tri(C_1 - C_4 -alkyl)sulfonium, and sulfoxonium ions, preferably tri(C_1 - C_4 -alkyl)sulfoxonium.

Anions of useful acid addition salts are primarily chloride, bromide, fluoride, hydrogensulfate, sulfate, dihydrogenphosphate, hydrogenphosphate, phosphate, nitrate, bicarbonate, carbonate, hexafluorosilicate, hexafluorophosphate, benzoate, and the anions of C₁-C₄-alkanoic acids,

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preferably formate, acetate, propionate and butyrate. They can be formed by reacting a compound I with an acid of the corresponding anion, preferably of hydrochloric acid, hydrobromic acid, sulfuric acid, phosphoric acid or nitric acid.

The compounds of formula I can be present in atropisomers arising from restricted rotation about a single bond of asymmetric groups. They also form part of the subject matter of the present invention.

In repect of the variables, the embodiments of the intermediates correspond to the embodiments of the compounds of formula I.

The term "compounds I" refers to compounds of formula I. Likewise, this terminology applies to all sub-formulae, e. g. "compounds I.A1" refers to compounds of the formula I.A1 or "compounds II" refers to compounds of the formula II, etc..

The inventive compounds I can be prepared by various routes in analogy to prior art processes and, advantageously, by the synthesis shown in the following schemes and in the experimental part of this application.

A 4-halopyrimidine compound II, wherein Hal is halogen, preferably CI or F, can be reacted with a suitable phenethyl amine compound III as shown in Scheme 1:

Scheme 1

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Generally, this reaction is carried out at temperatures of from 0 to 200°C, preferably from 50 to 170°C, preferably in an inert organic solvent and preferably in presence of a base or a catalyst or a combination of a base and a catalyst (e.g. NaF, KF, LiF, NaBr, KBr, LiBr, NaI, KI, LiI and ionic liquids, such as imidazolium catalysts).

Suitable solvents are aromatic hydrocarbons such as toluene, o-, m- and p-xylene; halogenated hydro-carbons such as chlorobenzene, dichlorobenzene; ethers such as dioxane, anisole and tetra-hydrofuran (THF); nitriles such as acetonitrile and propionitrile; ketones, such as acetone, methyl ethyl ketone, diethyl ketone and tert.-butyl methyl ketone; alcohols such as ethanol, n-propanol, isopropanol, n-butanol and tert.-butanol; and also dimethyl sulfoxide (DMSO), dimethylformamide (DMF), dimethyl acetamide, N-methyl-2-pyrrolidone (NMP), N-ethyl-2-pyrrolidone (NEP) and acetic acid ethyl ester, preferably DMSO, DMF, dimethyl acetamide, NMP, or NEP. Particular preference is given to NMP. It is also possible to use mixtures of the solvents mentioned.

Suitable bases are, in general, inorganic compounds, such as alkali metal and alkaline earth metal hydroxides such as lithium hydroxide, sodium hydroxide, potassium hydroxide and calcium hydroxide; alkali metal and alkaline earth metal oxides such as lithium oxide, sodium oxide, potassium oxide and calcium oxide; alkali metal and alkaline earth metal phosphates such as lithium phosphate, sodium phosphate, potassium phosphate and calcium phosphate; alkali metal amides such as lithium amide, sodium amide and potassium amide; alkali metal and alkaline earth metal hydrides lithium hydride, sodium hydride, potassium hydride and calcium

hydride; alkali metal and alkaline earth metal carbonates such as lithium carbonate, potassium carbonate and calcium carbonate, caesium carbonate; moreover organic bases, for example tertiary amines such as trimethyl-amine (TMA), triethylamine (TEA), tributylamine (TBA), diisopropylethylamine (DIPEA) and N-methyl-2-pyrrolidone (NMP), pyridine, substituted pyridines such as collidine, lutidine and 4 dimethylaminopyridine (DMAP), and also bicyclic amines. Preference is given to sodium hydride, potassium hydride, lithium carbonate, potassium carbonate, caesium carbonate, TEA, TBA and DIPEA, in particular DIPEA. The bases are generally employed in equimolar amounts, in excess or, if appropriate, as solvent. The amount of base is typically 1.1 to 5.0 molar equivalents relative to 1 mole of compounds II.

The starting materials are generally reacted with one another in equimolar amounts. In terms of yields, it may be advantageous to employ an excess of compounds III, based on 1.1 to 2.5 equivalents, preferred 1.1 to 1.5 equivalents of compounds II.

The compounds II are known from the literature or are commercially available or they can be prepared for example in analogy to methods described in: Heterocycles (2009) 78(7), 1627-1665; New J. Chem. (1994) 18(6), 701-8; WO 2005/095357; Science of Synthesis (2004) 16, 379-572; WO 2008/156726; WO 2006/072831; Organic Reactions (Hoboken, NJ, United States) (2000), 56; or Targets in Heterocyclic Systems (2008) 12, 59-84.

The phenethyl amine compounds III are known from the literature or are commercially available or they can be prepared for example in analogy to methods described in: WO 2007/046809; WO 2011/025505; or WO 2010/025451.

Otherwise compounds III can be synthesized in analogy to WO 2011/053835; GB 2059955; WO 2007/020227; WO 2008/046598; WO 2011/053835; Eur. J. Med. Chem. (2009), 44(5), 2246-2251; or J. Med. Chem. (2007), 50(20), 5003-5011. Phenethylamines III are commercially available or can be prepared as outlined in Scheme 2:

Scheme 2

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By addition of cyanide, a carbonyl compound AD-1 can be transformed into its cyano hydrine (see e.g. Chemistry A Eur. J. (2011), 17(44), 12276-12279; Eur. J. Org. Chem. (2002), (19), 3243-3249; Synlett (2003), (3), 353-356; Chirality (2009), 21(9), 836-842; or J. Org. Chem. (2008), 73(18), 7373-7375). Reduction of the nitrile group provides compounds AD-3. Depending on the reaction conditions, the nitrile in AD-3 can be reduced and the hydroxyl group be removed in one step to furnish compounds III (see e.g. Justus Liebigs Annalen der Chemie (1949), 564, 49-54, Justus Liebigs Annalen der Chemie (1957), 605, 200-11, J. Chem. Soc. (1959), 1780-2; or WO 2007/020381).

Other conditions allow to preserve the hydroxyl group while selectively reducing the nitrile (see e.g. Archiv der Pharmazie (Weinheim, Germany, 2011), 344(6), 372-385; J. Am. Chem. Soc. (1948), 70, 3738-40, J. Am. Chem. Soc. (1933), 55, 2593-7; Tetrahedron (2001), 57(40), 8573-8580, Chem. Pharm. Bull. (2003), 51(6), 702-709).

It may be advantageous to couple AD-1 with a heterocycle Het-LG prior to the abovementioned reactions as shown in Scheme 2.

Phenethylamine compounds III can also be prepared by reductive amination of aldehyde compounds AD-4 as described in Scheme 3.

Scheme 3

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This conversion can be achieved using ammonia and a reducing agent or a metal organic compound or a cyanide source (see e.g. J. Am. Chem. Soc. (2011), 133(33), 12914-12917; Acta Pharmaceutica Suecica (1976), 13(1), 65-74; J. Med. Chem.(1976), 19(6), 763-6; or J. Am. Chem. Soc. (1952), 74, 4611-15).

Furthermore, substituted benzyl nitriles AD-9, which are available from benzyl halides AD-8, can be used as intermediates for the preparation of compounds III according to scheme 4 by way of reduction with an appropriate reducing agent (e.g. LiAlH₄, PhSiH₃ or H₂ and a catalyst) as shown in Scheme 4 (Tetrahedron (2011), 67(42), 8183-8186; WO 2011/088181; Eur. J. Inorg. Chem. (2011), 2011(22), 3381-3386; or WO 2008/124757):

Scheme 4

Hal O-Het
$$\sim$$
 O-Het \sim O

Compounds I and intermediates, wherein R is hydrogen, can be converted to tertiary substituted amines by conventional processes such as alkylation. Examples of suitable alkylating agents include alkyl halides, such as alkyl chloride, alkyl bromide or alkyl iodide, examples being methyl chloride, methyl bromide or methyl iodide, or dialkyl sulfates such as dimethyl sulfate or diethyl sulfate. The reaction with the alkylating agent is carried out advantageously in the presence of a solvent. Solvents used for these reactions are - depending on the temperature range - aliphatic, cycloaliphatic or aromatic hydrocarbons such as hexane, cyclohexane, toluene, xylene, chlorinated aliphatic and aromatic hydrocarbons such as DCM, chlorobenzene, open-chain dialkyl ethers such as diethyl ether, di-n-propyl ether, MTBE, cyclic ethers such as THF, 1,4-dioxane, glycol ethers such as dimethyl glycol ether, and also DMSO, DMF, dimethyl acetamide, NMP, NEP and acetic acid ethyl ester, preferably DMF, DMSO, NMP or NEP, or mixtures of these solvents.

If individual compounds I cannot be obtained by the routes described above, they can be prepared by derivatization of other compounds I.

The N-oxides may be prepared from the compounds I according to conventional oxidation methods, e. g. by treating compounds I with an organic peracid such as metachloroperbenzoic acid (cf. WO 03/64572 or J. Med. Chem. 1995, 38(11), 1892-1903,); or with inorganic oxidizing

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agents such as hydrogen peroxide (cf. J. Heterocyc. Chem. 1981, 18 (7), 1305-1308) or oxone (cf. J. Am. Chem. Soc. 2001, 123 (25), 5962-5973). The oxidation may lead to pure mono-Noxides or to a mixture of different N-oxides, which can be separated by conventional methods such as chromatography.

If the synthesis yields mixtures of isomers, a separation is generally not necessarily required since in some cases the individual isomers can be interconverted during work-up for use or during application (e. g. under the action of light, acids or bases). Such conversions may also take place after use, e. g. in the treatment of plants in the treated plant, or in the harmful fungus to be controlled.

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In the definitions of the variables given above, collective terms are used which are generally representative for the substituents in question. The term "C_n-C_m" indicates the number of carbon atoms possible in each case in the substituent or substituent moiety in question.

The term "halogen" refers to fluorine, chlorine, bromine and iodine.

The term ${}^{\circ}C_1$ -C₄-alkyl ${}^{\circ}$ refers to a straight-chained or branched saturated hydrocarbon group having 1 to 4 carbon atoms, for example methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, and 1,1-dimethylethyl. Likewise, the term ${}^{\circ}C_1$ -C₆-alkyl ${}^{\circ}$ refers to a straight-chained or branched saturated hydrocarbon group having 1 to 6 carbon atoms.

The term " C_1 - C_4 -haloalkyl" refers to a straight-chained or branched alkyl group having 1 to 4 carbon atoms (as defined above), wherein some or all of the hydrogen atoms in these groups may be replaced by halogen atoms as mentioned above, for example chloromethyl, bromomethyl, dichloromethyl, trichloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, chlorofluoromethyl, 1-chloroethyl, 1-bromoethyl, 1-fluoroethyl, 2,2-difluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2-chloro-2,2-difluoroethyl, 2,2-difluoroethyl, 2,2,2-trichloroethyl and pentafluoroethyl, 2-fluoropropyl, 3-fluoropropyl, 2,2-difluoropropyl, 2,3-difluoropropyl, 2,3-difluoropropyl, 3-difluoropropyl, 3-fluoropropyl, 2-bromopropyl, 3-bromopropyl, 3,3,3-trichloropropyl, CH₂- C_2 F₅, CF₂- C_2 F₅, CF(CF₃)₂, 1-(fluoromethyl)-2-fluoroethyl, 1-(chloromethyl)-2-bromoethyl, 4-fluorobutyl, 4-chlorobutyl, 4-bromobutyl or nonafluorobutyl. Likewise, the term " C_1 - C_6 -haloalkyl" refers to a straight-chained or branched alkyl group having 1 to 6 carbon atoms.

The term $"C_1-C_4$ -hydroxyalkyl" refers to a straight-chained or branched alkyl group having 2 to 4 carbon atoms (as defined above), wherein one hydrogen atom in these groups may be replaced by one hydroxy group, for example hydroxymethyl, 2-hydroxyethyl, 3-hydroxy-n-propyl, or 4-hydroxy-n-butyl.

The term " C_1 - C_4 -alkoxy" refers to a straight-chain or branched alkyl group having 1 to 4 carbon atoms (as defined above) which is bonded via an oxygen, at any position in the alkyl group, for example methoxy, ethoxy, n-propoxy, 1-methylethoxy, butoxy, 1-methyl \neg propoxy, 2-methylpropoxy or 1,1-dimethylethoxy. Likewise, the term " C_1 - C_6 -alkoxy" refers to a straight-chain or branched alkyl group having 1 to 6 carbon atoms.

The term "C₁-C₄-haloalkoxy" refers to a C₁-C₄-alkoxy group as defined above, wherein some or all of the hydrogen atoms may be replaced by halogen atoms as mentioned above, for example, OCH₂F, OCHF₂, OCF₃, OCH₂Cl, OCHCl₂, OCCl₃, chlorofluoromethoxy, dichlorofluoromethoxy, chlorodifluoromethoxy, 2-fluoroethoxy, 2-chloroethoxy, 2-bromoethoxy,

2-iodoethoxy, 2,2-difluoroethoxy, 2,2,2-trifluoroethoxy, 2-chloro-2-fluoroethoxy, 2-chloro-2,2-difluoroethoxy, 2,2-dichloro-2-fluoroethoxy, 2,2,2-trichloroethoxy, C_2F_5 , 2-fluoropropoxy, 3-fluoropropoxy, 2,3-difluoropropoxy, 2-chloropropoxy, 3-chloropropoxy, 2,3-dichloropropoxy, 2-bromopropoxy, 3-bromopropoxy, 3,3,3-trichloropropoxy, C_2F_5 , $C_2F_$

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The term $"C_1-C_4$ -alkoxy- C_1-C_4 -alkyl" refers to alkyl having 1 to 4 carbon atoms (as defined above), wherein one hydrogen atom of the alkyl radical is replaced by a C_1-C_4 -alkoxy group (as defined above). Likewise, the term $"C_1-C_6$ -alkoxy- C_1-C_4 -alkyl" refers to alkyl having 1 to 4 carbon atoms (as defined above), wherein one hydrogen atom of the alkyl radical is replaced by a C_1-C_6 -alkoxy group (as defined above).

The term ${}^{\circ}C_1$ - C_4 -alkoxy- C_1 - C_4 -alkoxy" refers to an alkoxy radical having 1 to 4 carbon atoms (as defined above), wherein one hydrogen atom of this alkoxy radical is replaced by a C_1 - C_4 -alkoxy group (as defined above). Likewise, the term ${}^{\circ}C_1$ - C_6 -alkoxy- C_1 - C_4 -alkoxy" refers to alkoxy having 1 to 4 carbon atoms (as defined above), wherein one hydrogen atom of the alkyl radical is replaced by a C_1 - C_6 -alkoxy group (as defined above).

The term $"C_1-C_4$ -haloalkoxy- C_1-C_4 -alkyl" refers to alkyl having 1 to 4 carbon atoms (as defined above), wherein one hydrogen atom of the alkyl radical is replaced by a C_1-C_4 -haloalkoxy group (as defined above). Likewise, the term $"C_1-C_6$ -haloalkoxy- C_1-C_4 -alkyl" refers to alkyl having 1 to 4 carbon atoms (as defined above), wherein one hydrogen atom of the alkyl radical is replaced by a C_1-C_6 -alkoxy group (as defined above).

The term " C_1 - C_4 -alkylthio" as used herein refers to straight-chain or branched alkyl groups having 1 to 4 carbon atoms (as defined above) bonded via a sulfur atom, at any position in the alkyl group, for example methylthio, ethylthio, propylthio, isopropylthio, and n butylthio. Likewise, the term " C_1 - C_6 -alkylthio" as used herein refers to straight-chain or branched alkyl groups having 1 to 6 carbon atoms (as defined above) bonded via a sulfur atom. Accordingly, the terms " C_1 - C_4 -haloalkylthio" and " C_1 - C_6 -haloalkylthio" as used herein refer to straight-chain or branched haloalkyl groups having 1 to 4 or 1 to 6 carbon atoms (as defined above) bonded through a sulfur atom, at any position in the haloalkyl group.

The terms $"C_1-C_4$ -alkylsulfinyl" or $"C_1-C_6$ -alkylsulfinyl" refer to straight-chain or branched alkyl groups having 1 to 4 or 1 to 6 carbon atoms (as defined above) bonded through a -S(=O)-moiety, at any position in the alkyl group, for example methylsulfinyl and ethylsulfinyl, and the like. Accordingly, the terms $"C_1-C_4$ -haloalkylsulfinyl" and $"C_1-C_6$ -haloalkylsulfinyl", respectively, refer to straight-chain or branched haloalkyl groups having 1 to 4 and 1 to 6 carbon atoms (as defined above), respectively, bonded through a -S(=O)- moiety, at any position in the haloalkyl group.

The terms $"C_1-C_4$ -alkylsulfonyl" and $"C_1-C_6$ -alkylsulfonyl", respectively, refer to straight-chain or branched alkyl groups having 1 to 4 and 1 to 6 carbon atoms (as defined above), respectively, bonded through a $-S(=O)_2$ - moiety, at any position in the alkyl group, for example methylsulfonyl. Accordingly, the terms $"C_1-C_4$ -haloalkylsulfonyl" and $"C_1-C_6$ -haloalkylsulfonyl", respectively, refer to straight-chain or branched haloalkyl groups having 1 to 4 and 1 to 6 carbon

atoms (as defined above), respectively, bonded through a -S(=O)₂- moiety, at any position in the haloalkyl group.

The term " C_1 - C_4 -alkylamino" refers to an amino radical carrying one C_1 - C_4 -alkyl group (as defined above) as substituent, for example methylamino, ethylamino, propylamino, 1-methylethylamino, butylamino, 1-methylpropylamino, 2-methylpropylamino, 1,1-dimethylethylamino and the like. Likewise, the term " C_1 - C_6 -alkylamino" refers to an amino radical carrying one C_1 - C_6 -alkyl group (as defined above) as substituent.

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The term "di(C_1 - C_4 -alkyl)amino" refers to an amino radical carrying two identical or different C_1 - C_4 -alkyl groups (as defined above) as substituents, for example dimethylamino, diethylamino, di-n-propylamino, diisopropylamino, N-ethyl-N-methylamino, N-(n-propyl)-N-methylamino, N-(isopropyl)-N methylamino, N-(n-butyl)-N-methylamino, N-(n-pentyl)-N-methylamino, N-(2-butyl)-N methylamino, N-(isobutyl)-N-methylamino, and the like. Likewise, the term "di(C_1 - C_6 -alkyl)amino" refers to an amino radical carrying two identical or different C_1 - C_6 -alkyl groups (as defined above) as substituents.

The term " $(C_1-C_4$ -alkoxy)carbonyl" refers to a C_1-C_4 -alkoxy radical (as defined above) which is attached via a carbonyl group.

The term " $di(C_1-C_4-alkyl)$ aminocarbonyl" refers to a $di(C_1-C_4)$ alkylamino radical as defined above which is attached via a carbonyl group.

The term "phenoxy" and refers to a phenyl radical which is attached via an oxygen atom. Likewise, the term "phenoxy- C_1 - C_4 -alkyl" and refers to a phenoxy radical which is attached via a C_1 - C_4 -alkyl group (as defined above).

The term "C₂-C₄-alkenyl" refers to a straight-chain or branched unsaturated hydrocarbon radical having 2 to 4 carbon atoms and a double bond in any position, such as ethenyl, 1-propenyl, 2-propenyl (allyl), 1-methylethenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl, 1-methyl-2-propenyl, 2-methyl-2-propenyl. Likewise, the term "C₂-C₆-alkenyl" refers to a straight-chain or branched unsaturated hydrocarbon radical having 2 to 6 carbon atoms and a double bond in any position.

The term " C_2 - C_4 -alkynyl" refers to a straight-chain or branched unsaturated hydrocarbon radical having 2 to 4 carbon atoms and containing at least one triple bond, such as ethynyl, 1-propynyl, 2-propynyl, 1-butynyl, 2-butynyl, 3-butynyl, 1-methyl-2-propynyl. Likewise, the term " C_2 - C_6 -alkynyl" refers to a straight-chain or branched unsaturated hydrocarbon radical having 2 to 6 carbon atoms and at least one triple bond.

The term " C_3 - C_8 -cycloalkyl" refers to monocyclic saturated hydrocarbon radicals having 3 to 8 carbon ring members, such as cyclopropyl (C_3H_5), cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl or cyclooctyl.

The term " C_3 - C_8 -cycloalkyl- C_1 - C_4 -alkyl" refers to an alkyl radical having 1 to 4 carbon atoms (as defined above), wherein one hydrogen atom of the alkyl radical is replaced by a C_3 - C_8 -cycloalkyl group (as defined above).

The term "C₃-C₈-cycloalkyloxy" refers to a cycloalkyl radical having 3 to 8 carbon atoms (as defined above), which is bonded via an oxygen.

The term "saturated or partially unsaturated 3-, 4- 5-, 6- or 7-membered carbocycle" is to be understood as meaning both saturated or partially unsaturated carbocycles having 3, 4, 5, 6 or 7 ring members. Examples include cyclopropyl, cyclopentyl, cyclopentenyl, cyclopentadienyl, cyclohexyl, cyclohexenyl, cyclohexadienyl, cycloheptyl, cycloheptyl, cycloheptadienyl, and the

like.

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The term "saturated or partially unsaturated 3-, 4-, 5-, 6-, or 7-membered heterocycle, wherein the ring member atoms of the heterocycle include besides carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S", is to be understood as meaning both saturated and partially unsaturated heterocycles, e.g.:

- a 3- or 4-membered saturated heterocycle which contains 1 or 2 heteroatoms from the group consisting of N, O and S as ring members such as oxirane, aziridine, thiirane, oxetane, azetidine, thiethane, [1,2]dioxetane, [1,2]dithietane, [1,2]diazetidine; or
- a 5- or 6-membered saturated or partially unsaturated heterocycle which contains 1, 2 or 3 heteroatoms from the group consisting of N, O and S as ring members such as 2-tetrahydrofuranyl, 3-tetrahydrofuranyl, 2-tetrahydrothienyl, 3-tetrahydrothienyl, 2-pyrrolidinyl, 3-pyrrolidinyl, 3-isoxazolidinyl, 4-isoxazolidinyl, 5-isoxazolidinyl, 3-isothiazolidinyl, 4-isothiazolidinyl, 5-isothiazolidinyl, 4-pyrazolidinyl, 5-pyrazolidinyl, 2-oxazolidinyl, 4-oxazolidinyl, 5-oxazolidinyl, 2-thiazolidinyl, 4-thiazolidinyl, 5-thiazolidinyl, 2-imidazolidinyl, 4-imidazolidinyl, 1,2,4-oxadiazolidin-3-yl, 1,2,4-oxadiazolidin-5-yl, 1,2,4-
- thiadiazolidin-3-yl, 1,2,4-thiadiazolidin-5-yl, 1,2,4-triazolidin-3-yl, 1,3,4-oxadiazolidin-2-yl, 1,3,4-thiadiazolidin-2-yl, 1,3,4-triazolidin-2-yl, 2,3-dihydrofur-2-yl, 2,3-dihydrofur-3-yl, 2,4-dihydrofur-3-yl, 2,3-dihydrothien-3-yl, 2,4-dihydrothien-3-yl, 2,4-dihydrothien-3-yl, 2-pyrrolin-2-yl, 2-pyrrolin-3-yl, 3-pyrrolin-2-yl, 3-pyrrolin-3-yl, 3-pyrrolin-3-y
- 20 2-isoxazolin-3-yl, 3-isoxazolin-3-yl, 4-isoxazolin-3-yl, 2-isoxazolin-4-yl, 3-isoxazolin-4-yl, 4-isoxazolin-4-yl, 2-isoxazolin-5-yl, 3-isoxazolin-5-yl, 4-isoxazolin-5-yl, 2-isothiazolin-3-yl, 3-isothiazolin-3-yl, 4-isothiazolin-3-yl, 2-isothiazolin-4-yl, 3-isothiazolin-4-yl, 4-isothiazolin-4-yl, 4-i
 - yl, 2-isothiazolin-5-yl, 3-isothiazolin-5-yl, 4-isothiazolin-5-yl, 2,3-dihydropyrazol-1-yl, 2,3-dihydropyrazol-2-yl, 2,3-dihydropyrazol-3-yl, 2,3-dihydropyrazol-4-yl, 2,3-dihydropyrazol-
- 5-yl, 3,4-dihydropyrazol-1-yl, 3,4-dihydropyrazol-3-yl, 3,4-dihydropyrazol-4-yl, 3,4-dihydropyrazol-5-yl, 4,5-dihydropyrazol-1-yl, 4,5-dihydropyrazol-3-yl, 4,5-dihydropyrazol-4-yl, 4,5-dihydropyrazol-5-yl, 2,3-dihydrooxazol-2-yl, 2,3-dihydrooxazol-3-yl, 2,3-dihydrooxazol-4-yl, 2,3-dihydrooxazol-5-yl, 3,4-dihydrooxazol-2-yl, 3,4-dihydrooxazol-3-yl, 3,4-dihydrooxazol-4-yl, 3,4-dihydrooxazol-5-yl, 3,4-dihydrooxazol-2-yl, 3,4-dihydrooxazol-3-yl, 3,4-di-
- hydrooxazol-4-yl, 2-piperidinyl, 3-piperidinyl, 4-piperidinyl, 1,3-dioxan-5-yl, 2-tetrahydropyranyl, 4-tetrahydropyranyl, 2-tetrahydrothienyl, 3-hexahydropyridazinyl, 4-hexahydropyrimidinyl, 4-hexahydropyrimidinyl, 5-hexahydropyrimidinyl, 2-piperazinyl, 1,3,5-hexahydrotriazin-2-yl and 1,2,4-hexahydrotriazin-3-yl and also the corresponding -ylidene radicals; and
- a 7-membered saturated or partially unsaturated heterocycle such as tetra- and hexahydroazepinyl, such as 2,3,4,5-tetrahydro[1H]azepin-1-, -2-, -3-, -4-, -5-, -6- or -7-yl, 3,4,5,6-tetrahydro[2H]azepin-2-, -3-, -4-, -5-, -6- or -7-yl, 2,3,4,7-tetrahydro-[1H]azepin-1-, -2-, -3-, -4-, -5-, -6- or -7-yl, 2,3,6,7-tetrahydro[1H]azepin-1-, -2-, -3-, -4-, -5-, -6- or -7-yl, hexahydroazepin-1-, -2-, -3- or -4-yl, tetra- and hexahydrooxepinyl such as 2,3,4,5-tetrahydro[1H]oxepin-2-, -3-, -4-, -5-, -6- or -7-yl, 2,3,6,7-tetrahydro[1H]oxepin-2-, -3-, -4-, -5-, -6- or -7-yl, hexahydroazepin-1-, -2-, -3- or -4-yl, tetra- and hexahydro-1,3-diazepinyl, tetra
 - and hexahydro-1,4-diazepinyl, tetra- and hexahydro-1,3-diazepinyl, tetra- and hexahydro-1,4-diazepinyl, tetra- and hexahydro-1,3-oxazepinyl, tetra- and hexahydro-1,4-dioxepinyl and

the corresponding -ylidene radicals; and

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The term "5-or 6--membered heteroaryl, wherein the ring member atoms of the heteroaryl include besides carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S", refers to, for example,

- a 5-membered heteroaryl such as pyrrol-1-yl, pyrrol-2-yl, pyrrol-3-yl, thien-2-yl, thien-3-yl, furan-2-yl, furan-3-yl, pyrazol-1-yl, pyrazol-3-yl, pyrazol-5-yl, imidazol-5-yl, imidazol-5-yl, imidazol-5-yl, imidazol-5-yl, oxazol-4-yl, oxazol-5-yl, isoxazol-3-yl, isoxazol-3-yl, isoxazol-5-yl, thiazol-2-yl, thiazol-5-yl, thiazol-5-yl, isothiazol-3-yl, isothiazol-3-yl, isothiazol-5-yl, 1,2,4-triazolyl-1-yl, 1,2,4-triazol-3-yl, 1,2,4-triazol-5-yl, or
 - a 6-membered heteroaryl, such as pyridin-2-yl, pyridin-3-yl, pyridin-4-yl, pyridazin-3-yl, pyridazin-4-yl, pyrimidin-2-yl, pyrimidin-5-yl, pyrimidin-5-yl, pyrizin-2-yl and 1,3,5-triazin-2-yl and 1,2,4-triazin-3-yl.

The term "two radicals R^c that are bound to adjacent ring member atoms form together with said ring member atoms a fused cycle" refers to a condensed bicyclic ring system, wherein 5- or 6-membered heteroaryl carries a fused-on 5-, 6- or 7-membered carbocyclic or heterocyclic ring it being possible that these rings are saturated or partially saturated or aromatic.

The term "one or two CH₂ groups of the abovementioned cycles may be respectively replaced by one or two C(=O) or C(=S) groups" refers to an exchange of carbon atoms from a saturated or partially unsaturated 3-, 4-, 5-, 6- or 7-membered carbocycle or a saturated or partially unsaturated 3-, 4-, 5-, 6- or 7-membered heterocycle, resulting in cycles such as cyclopropanone, cyclopentanone, cyclopropanethione, cyclopentanethione, 5-oxazolone, cyclohexane-1,4-dione, cyclohexane-1,4-dione or cyclohex-2-ene-1,4-dithione.

In this application, CH₃ shall also be understood as Me, CH₂CH₃ shall also be understood as Et, OCH₃ shall also be understood as OMe OCH₂OCH₃ shall also be understood as OMeOMe, CH₂OCH₃ shall also be understood as MeOMe, COOCH₃ shall also be understood as COOMe and COOC₂H₅ shall also be understood as COOEt.

As regards the fungicidal activity of the compounds I, preference is given to those compounds I and where applicable also to compounds of all sub-formulae provided herein, for example formulae I.A1 and I.A2 and to the intermediates such as compounds II and III wherein the substituents and variables (e.g. R^{a2}, R^{a5}, R^{a6}, R, R^A, R^B, R^D, Het, n, R^a, R^b, R^c, R^d, R^e, R', R'' and R''') have independently of each other or more preferably in combination including the combination the following meanings including also each combination of meanings for any subset of substituents and variables:

One embodiment relates to compounds I, wherein R^{a2} is halogen, CN, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkoxy, C_1 - C_4 -alkylthio, C_1 - C_4 -haloalkylthio, C_2 - C_4 -alkynyl, C_3 - C_8 -cycloalkyl, C_3 - C_8 -cycloalkyloxy or $(C_1$ - C_4 -alkoxy)carbonyl; preferably halogen, CN, C_1 - C_2 -alkyl, C_1 - C_2 -alkoxy, C_1 - C_2 -alkoxy- C_1 - C_2 - C_1 - C_1 - C_2 - C_1 -

According to a further emodiment, R^{a2} is selected from CN, CH₃, CF₃, OCH₃, COOCH₃, OCH₂CH₃ and CH₂OCH₃, more preferably from CN and CH₃.

According to a further emodiment, R^{a2} is C_2 -alkyl, C_2 -haloalkyl, C_2 -alkoxy, or C_2 -haloalkoxy.

According to a further emodiment, R^{a2} is selected from CN, CH₃, CF₃, OCH₃, COOCH₃, OCH₂CH₃ and CH₂OCH₃, more preferably from CN and CH₃.

Preferably, R^A, R^B in radicals R^{a2}, R^{a5} and R^{a6} independently of one another preferably are hydrogen or C₁-C₄-alkyl.

Preferably, R' in radicals R^{a2} , R^{a5} and R^{a6} , which may the same or different, are hydrogen, NH₂, C₁-C₄-alkyl or C₁-C₄-alkoxy.

Preferably, R'' in radicals R^{a2} , R^{a5} and R^{a6} , which may the same or different, are hydrogen, C_1 - C_4 -alkyl.

Preferably, R''' in radicals R^{a2} , R^{a5} and R^{a6} , which may the same or different, are hydrogen or C_1 - C_4 -alkyl.

According to a further embodiment, R^{a5} and R^{a6} independently of each other are halogen, CN, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy,

- C₁-C₄-alkylthio, C₁-C₄-haloalkylthio, C₂-C₄-alkenyl, C₂-C₄-alkynyl, C₃-C₈-cycloalkyl, C₃-C₈-cycloalkyloxy or (C₁-C₄-alkoxy)carbonyl, more preferably hydrogen, halogen, CN, C₁-C₂-alkyl, C₁-C₂-alkoxy, C₁-C₂-alkoxy-C₁-C₂-alkoxy-C₁-C₂-alkoxy or (C₁-C₂-alkoxy)carbonyl, it being possible that one of both, R^{a5} or R^{a6}, can in addition be hydrogen; even more preferably F, Cl, CH₃, CH₂CH₃, CF₃, CHFCH₃, CN, OCH₃, OCH₂OCH₃, CH₂OCH₃,
- 20 COOCH₃ and COOC₂H₅, it being possible that one of both, R^{a5} or R^{a6}, can in addition be hydrogen.

According to a further embodiment, R^{a5} and R^{a6} independently of each other are halogen, CN, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -alkoxy, C_1 - C_4 -alkoxy- C_1 - C_4 -alkoxy or (C_1 - C_4 -alkoxy)carbonyl, and it being possible that one of both, R^{a5} or R^{a6} , can in addition be hydrogen.

Further preferred embodiments relate to compounds I wherein R^{a2}, R^{a5} and R^{a6} independently of each other are in each case one of the following groups I-1 to I-12 in Table I, groups II-1 to II-13 in Table II and groups III-1 to III-13 in Table III, respectively:

30 Table I:

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No.	R ^{a2}
I-1	F
I-2	CI
I-3	CH ₃ (Me)
1-4	CH ₂ CH ₃ (Et)
I-5	CF ₃
I-6	CHFCH₃

No.	R ^{a2}
I-7	CN
I-8	OCH ₃ (OMe)
I-9	OCH ₂ OCH ₃
	(OMeOMe)
I-10	CH ₂ OCH ₃
	(MeOMe)

No.	R ^{a2}
I-11	COOCH ₃
	(COOMe)
I-12	COOC ₂ H ₅
	(COOEt)

Table II:

No.	R ^{a5}
II-1	H*
II-2	F
II-3	CI
11-4	Ме

No.	R ^{a5}
II-5	Et
II-6	CF ₃
II-7	CHFCH ₃
II-8	CN

No.	R ^{a5}
II-9	OMe
II-10	OMeOMe
II-11	MeOMe
II-12	COOMe

II-13 COOEt

Table III:

No.	R ^{a6}
III-1	H*
III-2	F
III-3	Cl
111-4	Me
III-5	Et

No.	R ^{a6}
III-6	CF ₃
III-7	CHFCH ₃
III-8	CN
III-9	OMe
III-10	OMeOMe

No.	R ^{a6}
III-11	MeOMe
III-12	COOMe
III-13	COOEt

Preferably, R^A, R^B in radical R independently of one another preferably are hydrogen or C₁-C₄-alkyl.

Preferably, R' in radical R is hydrogen, OH, NH₂, C₁-C₄-alkyl or C₁-C₄-alkoxy.

In the compounds I according to the invention, R is preferably hydrogen, C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -alkoxy- C_1 - C_4 -alkyl, C_2 - C_4 -alkenyl, C_2 - C_4 -alkynyl, CN, CH₂CN or CH₂-O-C(=O)R', wherein R' is hydrogen, C_1 - C_4 -alkyl or C_1 - C_4 -alkoxy; more preferably R is hydrogen, C_1 - C_4 -alkyl, C_1 - C_4 -alkyl, C_1 - C_4 -alkyl, C_1 - C_4 -alkyl, in particular R is hydrogen.

Another preferred embodiment relates to compounds I wherein R is CH₃.

According to a further embodiment n is 0, R is hydrogen, the moiety O-Het is bound in paraposition to the phenylring, which compounds are of formula I.A1:

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According to a further embodiment n is 0, R is CH₃, the moiety O-Het is bound in paraposition to the phenylring, which compounds are of formula I.A2:

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Preferably, R^A , R^B in radicals R^b and/or R^c , independently of one another preferably are hydrogen or C_1 - C_4 -alkyl.

Preferably, R' in radical R^c is hydrogen, NH_2 , C_1 - C_4 -alkyl or C_1 - C_4 -alkoxy.

Preferably, R" in radicals R^b and/or R^c , which may the same or different, are hydrogen, C_1 - C_4 -alkyl.

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Preferably, R''' in radicals R^b and/or R^c, which may the same or different, are hydrogen or C₁-C₄-alkyl.

In the compounds I according to the invention, R^b is preferably selected from the group consisting of halogen, CN, NO₂, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy and C₁-C₄-alkoxy-C₁-C₄-alkyl; more preferably R^b is halogen, CN, C₁-C₄-alkyl, C₁-C₄-haloalkyl or

C₁-C₄-alkoxy; most preferably R^b is halogen, CN, CH₃, CF₃ or OCH₃.

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According to a further embodiment, n is 1, 2, 3 or 4 and R^b is selected from the group of halogen, CN, NO₂, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy and C₁-C₄-alkoxy-C₁-C₄-alkyl.

In the compounds I according to the invention, n is preferably 0. According to a further embodiment, n is preferably 1. According to a further embodiment, n is preferably 2. According to a further embodiment, n is preferably 3.

One embodiment of the invention relates to compounds I, in which Het is a 6-membered heteroaryl, wherein the ring member atoms of the heteroaryl include besides carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S, and wherin the 6-membered heteroaryl is unsubstituted or carries 1, 2, 3 or 4 identical or different groups R^c.

If Het is a 6-membered heteroaryl, in one embodiment, Het carries at least one nitrogen as ring member atom. Preference is given to compounds I, in which Het is a pyridyl radical that is selected from pyridin-2-yl, pyridin-3-yl and pyridin-4-yl, and wherein the aforementioned pyridyl radicals are unsubstituted or carry 1, 2, 3 or 4 identical or different substituents R^c. More preferably, Het is pyridin-2-yl, which is unsubstituted or carries one or two radicals R^c.

Preference is given to compounds I, in which Het is a pyrimidinyl radical that is selected from pyrimidin-2-yl, pyrimidin-4-yl, pyrimidin-5-yl and pyrimidin-6-yl, and wherein the aformentioned pyrimidinyl radicals are unsubstituted or carry 1, 2 or 3 identical or different substituents R^c.

If Het is a 5-membered heteroaryl, in another embodiment of the invention, Het carries two heteroatoms as ring member atoms. Preference is given to compounds I, in which Het is a pyrazolyl radical that is selected from pyrazol-3-yl, pyrazol-4-yl and pyrazol-5-yl, and wherein the aforementioned pyrazolyl radicals are unsubstituted or carry 1, 2 or 3 identical or different substituents R^c. Preference is given to compounds I, in which Het is an isoxazolyl radical that is selected from isoxazol-3-yl, isoxazol-4-yl and isoxazol-5-yl, and wherein the aforementioned isoxazolyl radicals are unsubstituted or carry 1 or 2 identical or different substituents Rc. Preference is given to compounds I, in which Het is an isothiazolyl radical that is selected from isothiazol-3-yl, isothiazol-4-yl and isothiazol-5-yl, and wherein the aforementioned isothiazolyl radicals are unsubstituted or carry 1 or 2 identical or different substituents Rc. Preference is given to compounds I, in which Het is an imidazolyl radical that is selected from imidazol-2-yl, imidazol-4-yl and imidazol-5-yl, and wherein the aforementioned imidazolyl radicals are unsubstituted or carry 1, 2 or 3 identical or different substituents Rc. Preference is given to compounds I, in which Het is an oxazolyl radical that is selected from oxazol-2-yl, oxazol-4-yl and oxazol-5-yl, and wherein the aforementioned oxazolyl radicals are unsubstituted or carry 1 or 2 identical or different substituents Rc. Preference is given to compounds I, in which Het is a thiazolyl radical that is selected from thiazol-2-yl, thiazol-4-yl and thiazol-5-yl, and wherein the aforementioned thiazolyl radicals are unsubstituted or carry 1 or 2 identical or different substituents Rc.

Preferred embodiments of the invention relate to compounds I, in which the group Het is one of the following radicals H-1 to H-38:

WO 2013/113778		
No.	Het	
H-1	CF ₃	
H-2	#—(CF ₃	
H-3	$\#$ — $N=$ — CF_3	
H-4	# CF ₃	
H-5	F ₃ C	
H-6	CN # N	
H-7	# CN	
H-8	# N CN	
H-9	# N CN	
H-10	# CO ₂ CH ₃	
H-11	# CF ₃	
H-12	# N+ O-	

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No.	Het
H-13	F F Z
	#\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\
H-14	CI N
H-15	# CI
H-16	# N CI
H-17	# N CI
H-18	CI CF ₃
H-19	#_N_CF_3 S_CI
H-20	#\sum_CI
H-21	CI CN
H-22	#\CF ₃ N\N
H-23	N N CI
H-24	$H_3C \xrightarrow{N} CH_3$

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No.	Het
H-36	# CI CI

No.	Het
H-37	F N CI

No.	Het
H-38	# N CI

, in which # indicates the point of attachment.

One embodiment of the invention relates to compounds I, wherein Het carries 1, 2 or 3 radicals R^c. Another embodiment relates to compounds I, wherein Het carries 1 or 2 radicals R^c. A further embodiment relates to compounds I, wherein Het carries one radical R^c. A further embodiment relates to compounds I, wherein Het carries two radicals R^c. A further embodiment relates to compounds I, wherein Het is unsubstituted.

In a further embodiment, two radicals R^c that are bound to adjacent ring member atoms of the Het group do not form together with said ring member atoms any fused cycle.

Preferably, R^c is halogen, CN, C_1 - C_6 -alkyl, C_1 - C_6 -haloalkyl, C_1 - C_6 -alkoxy, C_1 - C_6 -haloalkoxy, C_1 - C_6 -alkoxy- C_1 - C_4 -alkyl, C(=O)R', C(=NOR'')R''', C_3 - C_8 -cycloalkyl, C_1 - C_4 -alkyl- C_3 - C_8 -cycloalkyl, phenoxy, phenoxy- C_1 - C_4 -alkyl or a 5- or 6-membered heteroaryl, wherein the ring member atoms of the heteroaryl include besides carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S, and wherein the aforementioned cyclic radicals are unsubstituted or carry 1, 2, 3 or 4 identical or different substituents R^d .

In one embodiment, R^c is halogen and selected from fluorine, chlorine, bromine and iodine and selected from fluorine and chlorine and in particular, R^c is chlorine.

In another embodiment, R^c is CN.

In a further embodiment, R^c is C₁-C₄-alkyl and selected from methyl, ethyl, n-propyl, i-propyl, n-butyl, 1-methyl-propyl, 2-methyl-propyl and 1,1-dimethylethyl, and selected from methyl, ethyl, n-propyl and i-propyl, and in particular, R^c is methyl.

In a further embodiment, R^c is C_1 - C_4 -haloalkyl and selected from C_1 -haloalkyl, C_2 -haloalkyl, C_3 -haloalkyl and C_4 -haloalkyl. More preferably, R^c is C_1 -haloalkyl and selected from fluormethyl, difluormethyl, trifluormethyl, chlormethyl, dichlormethyl and trichlormethyl, and in particular, R^c is trifluormethyl.

In a further embodiment, R^c is C_1 - C_4 -alkoxy and selected from methoxy, ethoxy, n-propyloxy, i-propyloxy, n-butyloxy, 1-methyl-propyloxy, 2-methyl-propyloxy and 1,1-dimethylethyloxy and in particular from methoxy and ethoxy.

In a further embodiment, R^c is C_1 - C_4 -haloalkoxy and specifically halomethoxy, such as difluormethoxy, trifluormethoxy, dichlormethoxy and trichlormethoxy, and haloethoxy, such as 2,2-difluorethoxy, 2,2,2-trifluorethoxy, 2,2-dichlorethoxy and 2,2,2-trichlorethoxy, and halo-n-propoxy, halo-i-propoxy, halo-n-butoxy, halo-1-methyl-propoxy, halo-2-methyl-propoxy or halo-1,1-dimethylethoxy.

In a further embodiment, R^c is C₃-C₈-cycloalkyl, and in particular, R^c is cyclopropyl.

In a further embodiment, R^c is phenyl.

In a further embodiment, R^c is phenoxy.

In a further embodiment, R^c is phenoxy-C₁-C₄-alkyl and selected from phenoxymethyl, 1-phenoxy-ethyl and 2-phenoxyethyl.

If R^c is present, one embodiment relates to compounds I, wherein R^c carries 1, 2, 3 or 4

radicals R^d, preferably 1, 2 or 3 radicals R^d, and more preferably 1 or 2 radicals R^d. In a paricularly preffered embodiment, R^c carries one radical R^d. In another particularly preferred embodiment, R^c carries two radicals R^d. In a further particularly preferred embodiment the group R^c carries 3 radicals R^d.

In one embodiment, R^d is halogen and selected from fluorine, chlorine, bromine and iodine and specifically from fluorine and chlorine and in particular, R^c is chlorine.

In another embodiment, Rd is CN.

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In a further embodiment, R^d is C_1 - C_4 -alkyl and selected from methyl, ethyl, n-propyl, i-propyl, n-butyl, 1-methyl-propyl, 2-methyl-propyl and 1,1-dimethylethyl, and preferably selected from methyl, ethyl, n-propyl and i-propyl and in particular, R^d is methyl.

In a further embodiment, R^d is C_1 - C_4 -haloalkyl and selected from C_1 -haloalkyl, C_2 -haloalkyl, C_3 -haloalkyl and C_4 -haloalkyl. More preferably, R^c is C_1 -haloalkyl and selected from fluormethyl, difluormethyl, trifluormethyl, chlormethyl, dichlormethyl and trichlormethyl, and in particular, R^d is trifluormethyl.

In a further embodiment, R^d is C_1 - C_4 -alkoxy and selected from methoxy, ethoxy, n-propyloxy, i-propyloxy, n-butyloxy, 1-methyl-propyloxy, 2-methyl-propyloxy and 1,1-dimethylethyloxy and in particular from methoxy and ethoxy.

According to a further embodiment, the present invention relates to compounds of formula I, wherein:

- R^{a2} is halogen, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkoxy, C_1 - C_4 -alkylthio, C_1 - C_4 -haloalkylthio or C_2 - C_4 -alkynylthio;
- R^{a5}, R^{a6} independently of each other are hydrogen, halogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy or C(=O)R';R' is hydrogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkyl, C₁
- n indicates the number of substituents R^b on the phenyl ring and n is 0 or 1;R^b is halogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy or C₁-C₄-haloalkoxy;
- Het is a pyridinyl, which is unsubstituted or carries 1 or 2 identical or different groups R^c : R^c is halogen, C_1 - C_6 -alkyl, C_1 - C_6 -haloalkyl, C_1 - C_6 -alkoxy or C_1 - C_6 -haloalkoxy; and the N-oxides and the agriculturally acceptable salts thereof.

A skilled person will readily understand that the preferences given in connection with compounds of formula I also apply for formulae I.A1 and I.A2 as defined herein.

The compounds I and the compositions according to the invention, respectively, are suitable as fungicides. They are distinguished by an outstanding effectiveness against a broad spectrum of phytopathogenic fungi, including soil-borne fungi, which derive especially from the classes of the Plasmodiophoromycetes, Peronosporomycetes (syn. Oomycetes), Chytridiomycetes, Zygomycetes, Ascomycetes, Basidiomycetes and Deuteromycetes (syn. Fungi imperfecti).

Some are systemically effective and they can be used in crop protection as foliar fungicides, fungicides for seed dressing and soil fungicides. Moreover, they are suitable for controlling harmful fungi, which inter alia occur in wood or roots of plants.

The compounds I and the compositions according to the invention are particularly important

in the control of a multitude of phytopathogenic fungi on various cultivated plants, such as cereals, e. g. wheat, rye, barley, triticale, oats or rice; beet, e. g. sugar beet or fodder beet; fruits, such as pomes, stone fruits or soft fruits, e. g. apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries, blackberries or gooseberries; leguminous plants, such as lentils, peas, alfalfa or soybeans; oil plants, such as rape, mustard, olives, sunflowers, coconut, cocoa beans, castor oil plants, oil palms, ground nuts or soybeans; cucurbits, such as squashes, cucumber or melons; fiber plants, such as cotton, flax, hemp or jute; citrus fruit, such as oranges, lemons, grapefruits or mandarins; vegetables, such as spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, cucurbits or paprika; lauraceous plants, such as avocados, cinnamon or camphor; energy and raw material plants, such as corn, soybean, rape, sugar cane or oil palm; corn; tobacco; nuts; coffee; tea; bananas; vines (table grapes and grape juice grape vines); hop; turf; sweet leaf (also called Stevia); natural rubber plants or ornamental and forestry plants, such as flowers, shrubs, broad-leaved trees or evergreens, e. g. conifers; and on the plant propagation material, such as seeds, and the crop material of these plants.

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Preferably, compounds I and compositions thereof, respectively are used for controlling a multitude of fungi on field crops, such as potatoes sugar beets, tobacco, wheat, rye, barley, oats, rice, corn, cotton, soybeans, rape, legumes, sunflowers, coffee or sugar cane; fruits; vines; ornamentals; or vegetables, such as cucumbers, tomatoes, beans or squashes.

The term "plant propagation material" is to be understood to denote all the generative parts of the plant such as seeds and vegetative plant material such as cuttings and tubers (e. g. potatoes), which can be used for the multiplication of the plant. This includes seeds, roots, fruits, tubers, bulbs, rhizomes, shoots, sprouts and other parts of plants, including seedlings and young plants, which are to be transplanted after germination or after emergence from soil. These young plants may also be protected before transplantation by a total or partial treatment by immersion or pouring.

Preferably, treatment of plant propagation materials with compounds I and compositions thereof, respectively, is used for controlling a multitude of fungi on cereals, such as wheat, rye, barley and oats; rice, corn, cotton and soybeans.

The term "cultivated plants" is to be understood as including plants which have been modified by breeding, mutagenesis or genetic engineering including but not limiting to agricultural biotech products on the market or in development (cf. http://www.bio.org/speeches/pubs/er/agri_products.asp). Genetically modified plants are plants, which genetic material has been so modified by the use of recombinant DNA techniques that under natural circumstances cannot readily be obtained by cross breeding, mutations or natural recombination. Typically, one or more genes have been integrated into the genetic material of a genetically modified plant in order to improve certain properties of the plant. Such genetic modifications also include but are not limited to targeted post-translational modification of protein(s), oligo- or polypeptides e. g. by glycosylation or polymer additions such as prenylated, acetylated or farnesylated moieties or PEG moieties.

The compounds I and compositions thereof, respectively, are particularly suitable for controlling the following plant diseases:

Albugo spp. (white rust) on ornamentals, vegetables (e. g. A. candida) and sunflowers (e. g. A. tragopogonis); Alternaria spp. (Alternaria leaf spot) on vegetables, rape (A. brassicola or

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brassicae), sugar beets (A. tenuis), fruits, rice, soybeans, potatoes (e. g. A. solani or A. alternata), tomatoes (e. g. A. solani or A. alternata) and wheat; Aphanomyces spp. on sugar beets and vegetables; Ascochyta spp. on cereals and vegetables, e. q. A. tritici (anthracnose) on wheat and A. hordei on barley; Bipolaris and Drechslera spp. (teleomorph: Cochliobolus spp.), e. g. Southern leaf blight (D. maydis) or Northern leaf blight (B. zeicola) on corn, e. g. spot blotch (B. sorokiniana) on cereals and e.g. B. oryzae on rice and turfs; Blumeria (formerly Erysiphe) graminis (powdery mildew) on cereals (e. g. on wheat or barley); Botrytis cinerea (teleomorph: Botryotinia fuckeliana: grey mold) on fruits and berries (e. g. strawberries). vegetables (e. g. lettuce, carrots, celery and cabbages), rape, flowers, vines, forestry plants and wheat; Bremia lactucae (downy mildew) on lettuce; Ceratocystis (syn. Ophiostoma) spp. (rot or wilt) on broad-leaved trees and evergreens, e. g. C. ulmi (Dutch elm disease) on elms; Cercospora spp. (Cercospora leaf spots) on corn (e.g. Gray leaf spot: C. zeae-maydis), rice, sugar beets (e. g. C. beticola), sugar cane, vegetables, coffee, soybeans (e. g. C. sojina or C. kikuchii) and rice; Cladosporium spp. on tomatoes (e. g. C. fulvum: leaf mold) and cereals, e. g. C. herbarum (black ear) on wheat; Claviceps purpurea (ergot) on cereals; Cochliobolus (anamorph: Helminthosporium of Bipolaris) spp. (leaf spots) on corn (C. carbonum), cereals (e. g. C. sativus, anamorph: B. sorokiniana) and rice (e. g. C. miyabeanus, anamorph: H. oryzae); Colletotrichum (teleomorph: Glomerella) spp. (anthracnose) on cotton (e. g. C. gossypii), corn (e. g. C. graminicola: Anthracnose stalk rot), soft fruits, potatoes (e. g. C. coccodes: black dot), beans (e. q. C. lindemuthianum) and soybeans (e. q. C. truncatum or C. gloeosporioides); Corticium spp., e. g. C. sasakii (sheath blight) on rice; Corynespora cassiicola (leaf spots) on soybeans and ornamentals; Cycloconium spp., e. g. C. oleaginum on olive trees; Cylindrocarpon spp. (e. g. fruit tree canker or young vine decline, teleomorph: Nectria or Neonectria spp.) on fruit trees, vines (e. g. C. liriodendri, teleomorph: Neonectria liriodendri: Black Foot Disease) and ornamentals; Dematophora (teleomorph: Rosellinia) necatrix (root and stem rot) on soybeans; Diaporthe spp., e. g. D. phaseolorum (damping off) on soybeans; Drechslera (syn. Helminthosporium, teleomorph: Pyrenophora) spp. on corn, cereals, such as barley (e. q. D. teres, net blotch) and wheat (e. q. D. tritici-repentis: tan spot), rice and turf; Esca (dieback, apoplexy) on vines, caused by Formitiporia (syn. Phellinus) punctata, F. mediterranea, Phaeomoniella chlamydospora (earlier Phaeoacremonium chlamydosporum), Phaeoacremonium aleophilum and/or Botryosphaeria obtusa; Elsinoe spp. on pome fruits (E. pyri), soft fruits (E. veneta: anthracnose) and vines (E. ampelina: anthracnose); Entyloma oryzae (leaf smut) on rice; Epicoccum spp. (black mold) on wheat; Erysiphe spp. (powdery mildew) on sugar beets (E. betae), vegetables (e. g. E. pisi), such as cucurbits (e. g. E. cichoracearum), cabbages, rape (e. g. E. cruciferarum); Eutypa lata (Eutypa canker or dieback, anamorph: Cytosporina lata, syn. Libertella blepharis) on fruit trees, vines and ornamental woods; Exserohilum (syn. Helminthosporium) spp. on corn (e. g. E. turcicum); Fusarium (teleomorph: Gibberella) spp. (wilt, root or stem rot) on various plants, such as F. graminearum or F. culmorum (root rot, scab or head blight) on cereals (e.g. wheat or barley), F. oxysporum on tomatoes, F. solani on soybeans and F. verticillioides on corn; Gaeumannomyces graminis (take-all) on cereals (e. g. wheat or barley) and corn; Gibberella spp. on cereals (e. g. G. zeae) and rice (e. g. G. fujikuroi: Bakanae disease); Glomerella cingulata on vines, pome fruits and

other plants and G. gossypii on cotton; Grainstaining complex on rice; Guignardia bidwellii

(black rot) on vines; Gymnosporangium spp. on rosaceous plants and junipers, e. g. G. sabinae

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(rust) on pears; Helminthosporium spp. (syn. Drechslera, teleomorph: Cochliobolus) on corn, cereals and rice; Hemileia spp., e. g. H. vastatrix (coffee leaf rust) on coffee; Isariopsis clavispora (syn. Cladosporium vitis) on vines; Macrophomina phaseolina (syn. phaseoli) (root and stem rot) on soybeans and cotton; Microdochium (syn. Fusarium) nivale (pink snow mold) on cereals (e.g. wheat or barley); Microsphaera diffusa (powdery mildew) on soybeans; Monilinia spp., e. g. M. laxa, M. fructicola and M. fructigena (bloom and twig blight, brown rot) on stone fruits and other rosaceous plants; Mycosphaerella spp. on cereals, bananas, soft fruits and ground nuts, such as e. g. M. graminicola (anamorph: Septoria tritici, Septoria blotch) on wheat or M. fijiensis (black Sigatoka disease) on bananas; Peronospora spp. (downy mildew) on cabbage (e. g. P. brassicae), rape (e. g. P. parasitica), onions (e. g. P. destructor), tobacco (P. tabacina) and soybeans (e. g. P. manshurica); Phakopsora pachyrhizi and P. meibomiae (soybean rust) on soybeans; Phialophora spp. e. g. on vines (e. g. P. tracheiphila and P. tetraspora) and soybeans (e. g. P. gregata: stem rot); Phoma lingam (root and stem rot) on rape and cabbage and P. betae (root rot, leaf spot and damping-off) on sugar beets; Phomopsis spp. on sunflowers, vines (e. g. P. viticola: can and leaf spot) and soybeans (e. g. stem rot: P. phaseoli, teleomorph: Diaporthe phaseolorum); Physoderma maydis (brown spots) on corn; Phytophthora spp. (wilt, root, leaf, fruit and stem root) on various plants, such as paprika and cucurbits (e. g. P. capsici), soybeans (e. g. P. megasperma, syn. P. sojae), potatoes and tomatoes (e. g. P. infestans: late blight) and broad-leaved trees (e. g. P. ramorum: sudden oak death); Plasmodiophora brassicae (club root) on cabbage, rape, radish and other plants; Plasmopara spp., e. g. P. viticola (grapevine downy mildew) on vines and P. halstedii on sunflowers; Podosphaera spp. (powdery mildew) on rosaceous plants, hop, pome and soft fruits, e. g. P. leucotricha on apples; Polymyxa spp., e. g. on cereals, such as barley and wheat (P. graminis) and sugar beets (P. betae) and thereby transmitted viral diseases;

Pseudocercosporella herpotrichoides (eyespot, teleomorph: Tapesia yallundae) on cereals, e. g. wheat or barley; Pseudoperonospora (downy mildew) on various plants, e. g. P. cubensis on cucurbits or P. humili on hop; Pseudopezicula tracheiphila (red fire disease or ,rotbrenner', anamorph: Phialophora) on vines; Puccinia spp. (rusts) on various plants, e. g. P. triticina (brown or leaf rust), P. striiformis (stripe or yellow rust), P. hordei (dwarf rust), P. graminis (stem or black rust) or P. recondita (brown or leaf rust) on cereals, such as e. g. wheat, barley or rye, P. kuehnii (orange rust) on sugar cane and P. asparagi on asparagus; Pyrenophora (anamorph: Drechslera) tritici-repentis (tan spot) on wheat or P. teres (net blotch) on barley; Pyricularia spp., e. g. P. oryzae (teleomorph: Magnaporthe grisea, rice blast) on rice and P. grisea on turf and cereals; Pythium spp. (damping-off) on turf, rice, corn, wheat, cotton, rape, sunflowers, soybeans, sugar beets, vegetables and various other plants (e. g. P. ultimum or P. aphanidermatum); Ramularia spp., e. g. R. collo-cygni (Ramularia leaf spots, Physiological leaf spots) on barley and R. beticola on sugar beets; Rhizoctonia spp. on cotton, rice, potatoes, turf, corn, rape, potatoes, sugar beets, vegetables and various other plants, e. g. R. solani (root and stem rot) on soybeans, R. solani (sheath blight) on rice or R. cerealis (Rhizoctonia spring blight) on wheat or barley; Rhizopus stolonifer (black mold, soft rot) on strawberries, carrots, cabbage, vines and tomatoes; Rhynchosporium secalis (scald) on barley, rye and triticale; Sarocladium oryzae and S. attenuatum (sheath rot) on rice; Sclerotinia spp. (stem rot or white mold) on vegetables and field crops, such as rape, sunflowers (e.g. S. sclerotiorum) and soybeans (e.g.

S. rolfsii or S. sclerotiorum); Septoria spp. on various plants, e. g. S. glycines (brown spot) on

soybeans, S. tritici (Septoria blotch) on wheat and S. (syn. Stagonospora) nodorum (Stagonospora blotch) on cereals; Uncinula (syn. Erysiphe) necator (powdery mildew, anamorph: Oidium tuckeri) on vines; Setospaeria spp. (leaf blight) on corn (e. g. S. turcicum, syn. Helminthosporium turcicum) and turf; Sphacelotheca spp. (smut) on corn, (e. g. S. reiliana: head smut), sorghum und sugar cane; Sphaerotheca fuliginea (powdery mildew) on cucurbits; Spongospora subterranea (powdery scab) on potatoes and thereby transmitted viral diseases; Stagonospora spp. on cereals, e. g. S. nodorum (Stagonospora blotch, teleomorph: Leptosphaeria [syn. Phaeosphaeria] nodorum) on wheat; Synchytrium endobioticum on potatoes (potato wart disease); Taphrina spp., e. g. T. deformans (leaf curl disease) on peaches and T. pruni (plum pocket) on plums; Thielaviopsis spp. (black root rot) on tobacco, pome fruits, vegetables, soybeans and cotton, e. g. T. basicola (syn. Chalara elegans); Tilletia spp. (common bunt or stinking smut) on cereals, such as e. g. T. tritici (syn. T. caries, wheat bunt) and T. controversa (dwarf bunt) on wheat; Typhula incarnata (grey snow mold) on barley or wheat; Urocystis spp., e. g. U. occulta (stem smut) on rye; Uromyces spp. (rust) on vegetables, such as beans (e. g. U. appendiculatus, syn. U. phaseoli) and sugar beets (e. g. U. betae); Ustilago spp. (loose smut) on cereals (e. g. U. nuda and U. avaenae), corn (e. g. U. maydis: corn smut) and sugar cane; Venturia spp. (scab) on apples (e.g. V. inaequalis) and pears; and Verticillium spp. (wilt) on various plants, such as fruits and ornamentals, vines, soft fruits, vegetables and field crops, e. g. V. dahliae on strawberries, rape, potatoes and tomatoes.

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The compounds I and compositions thereof, respectively, are also suitable for controlling harmful fungi in the protection of stored products or harvest and in the protection of materials. The term "protection of materials" is to be understood to denote the protection of technical and non-living materials, such as adhesives, glues, wood, paper and paperboard, textiles, leather, paint dispersions, plastics, colling lubricants, fiber or fabrics, against the infestation and destruction by harmful microorganisms, such as fungi and bacteria. As to the protection of wood and other materials, the particular attention is paid to the following harmful fungi: Ascomycetes such as Ophiostoma spp., Ceratocystis spp., Aureobasidium pullulans, Sclerophoma spp., Chaetomium spp., Humicola spp., Petriella spp., Trichurus spp.; Basidiomycetes such as Coniophora spp., Coriolus spp., Gloeophyllum spp., Lentinus spp., Pleurotus spp., Poria spp., Serpula spp. and Tyromyces spp., Deuteromycetes such as Aspergillus spp., Cladosporium spp., Penicillium spp., Trichorma spp., Alternaria spp., Paecilomyces spp. and Zygomycetes such as Mucor spp., and in addition in the protection of stored products and harvest the following yeast fungi are worthy of note: Candida spp. and Saccharomyces cerevisae.

The compounds I and compositions thereof, resepectively, may be used for improving the health of a plant. The invention also relates to a method for improving plant health by treating a plant, its propagation material and/or the locus where the plant is growing or is to grow with an effective amount of compounds I and compositions thereof, respectively.

The term "plant health" is to be understood to denote a condition of the plant and/or its products which is determined by several indicators alone or in combination with each other such as yield (e. g. increased biomass and/or increased content of valuable ingredients), plant vigor (e. g. improved plant growth and/or greener leaves ("greening effect")), quality (e. g. improved content or composition of certain ingredients) and tolerance to abiotic and/or biotic stress. The above identified indicators for the health condition of a plant may be interdependent or may

result from each other.

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The compounds of the formula (I) can be present in different crystal modifications whose biological activity may differ. They are likewise subject matter of the present invention.

The compounds I are employed as such or in form of compositions by treating the fungi or the plants, plant propagation materials, such as seeds, soil, surfaces, materials or rooms to be protected from fungal attack with a fungicidally effective amount of the active substances. The application can be carried out both before and after the infection of the plants, plant propagation materials, such as seeds, soil, surfaces, materials or rooms by the fungi.

Plant propagation materials may be treated with compounds I as such or a composition comprising at least one compound I prophylactically either at or before planting or transplanting.

The invention also relates to agrochemical compositions comprising an auxiliary and at least one compound I according to the invention.

An agrochemical composition comprises a fungicidally effective amount of a compound I. The term "effective amount" denotes an amount of the composition or of the compounds I, which is sufficient for controlling harmful fungi on cultivated plants or in the protection of materials and which does not result in a substantial damage to the treated plants. Such an amount can vary in a broad range and is dependent on various factors, such as the fungal species to be controlled, the treated cultivated plant or material, the climatic conditions and the specific compound I used.

The compounds I, their N-oxides and salts can be converted into customary types of agrochemical compositions, e. g. solutions, emulsions, suspensions, dusts, powders, pastes, granules, pressings, capsules, and mixtures thereof. Examples for composition types are suspensions (e.g. SC, OD, FS), emulsifiable concentrates (e.g. EC), emulsions (e.g. EW, EO, ES, ME), capsules (e.g. CS, ZC), pastes, pastilles, wettable powders or dusts (e.g. WP, SP, WS, DP, DS), pressings (e.g. BR, TB, DT), granules (e.g. WG, SG, GR, FG, GG, MG), insecticidal articles (e.g. LN), as well as gel formulations for the treatment of plant propagation materials such as seeds (e.g. GF). These and further compositions types are defined in the "Catalogue of pesticide formulation types and international coding system", Technical Monograph No. 2, 6th Ed. May 2008, CropLife International.

The compositions are prepared in a known manner, such as described by Mollet and Grubemann, Formulation technology, Wiley VCH, Weinheim, 2001; or Knowles, New developments in crop protection product formulation, Agrow Reports DS243, T&F Informa, London, 2005.

Examples for suitable auxiliaries are solvents, liquid carriers, solid carriers or fillers, surfactants, dispersants, emulsifiers, wetters, adjuvants, solubilizers, penetration enhancers, protective colloids, adhesion agents, thickeners, humectants, repellents, attractants, feeding stimulants, compatibilizers, bactericides, anti-freezing agents, anti-foaming agents, colorants, tackifiers and binders.

Suitable solvents and liquid carriers are water and organic solvents, such as mineral oil fractions of medium to high boiling point, e.g. kerosene, diesel oil; oils of vegetable or animal origin; aliphatic, cyclic and aromatic hydrocarbons, e. g. toluene, paraffin, tetrahydronaphthalene, alkylated naphthalenes; alcohols, e.g. ethanol, propanol, butanol,

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benzylalcohol, cyclohexanol; glycols; dimethyl sulfoxide (DMSO); ketones, e.g. cyclohexanone; esters, e.g. lactates, carbonates, fatty acid esters, gamma-butyrolactone; fatty acids; phosphonates; amines; amides, e.g. N-methylpyrrolidone, fatty acid dimethylamides; and mixtures thereof.

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Suitable solid carriers or fillers are mineral earths, e.g. silicates, silica gels, talc, kaolins, limestone, lime, chalk, clays, dolomite, diatomaceous earth, bentonite, calcium sulfate, magnesium sulfate, magnesium oxide; polysaccharide powders, e.g. cellulose, starch; fertilizers, e.g. ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas; products of vegetable origin, e.g. cereal meal, tree bark meal, wood meal, nutshell meal, and mixtures thereof.

Suitable surfactants are surface-active compounds, such as anionic, cationic, nonionic and amphoteric surfactants, block polymers, polyelectrolytes, and mixtures thereof. Such surfactants can be used as emusifier, dispersant, solubilizer, wetter, penetration enhancer, protective colloid, or adjuvant. Examples of surfactants are listed in McCutcheon's, Vol.1: Emulsifiers & Detergents, McCutcheon's Directories, Glen Rock, USA, 2008 (International Ed. or North American Ed.).

Suitable anionic surfactants are alkali, alkaline earth or ammonium salts of sulfonates, sulfates, phosphates, carboxylates, and mixtures thereof. Examples of sulfonates are alkylarylsulfonates, diphenylsulfonates, alpha-olefin sulfonates, lignine sulfonates, sulfonates of fatty acids and oils, sulfonates of ethoxylated alkylphenols, sulfonates of alkoxylated arylphenols, sulfonates of condensed naphthalenes, sulfonates of dodecyl- and tridecylbenzenes, sulfonates of naphthalenes and alkylnaphthalenes, sulfosuccinates or sulfosuccinamates. Examples of sulfates are sulfates of fatty acids and oils, of ethoxylated alkylphenols, of alcohols, of ethoxylated alcohols, or of fatty acid esters. Examples of phosphates are phosphate esters. Examples of carboxylates are alkyl carboxylates, and carboxylated alcohol or alkylphenol ethoxylates.

Suitable nonionic surfactants are alkoxylates, N-subsituted fatty acid amides, amine oxides, esters, sugar-based surfactants, polymeric surfactants, and mixtures thereof. Examples of alkoxylates are compounds such as alcohols, alkylphenols, amines, amides, arylphenols, fatty acids or fatty acid esters which have been alkoxylated with 1 to 50 equivalents. Ethylene oxide and/or propylene oxide may be employed for the alkoxylation, preferably ethylene oxide. Examples of N-substituted fatty acid amides are fatty acid glucamides or fatty acid alkanolamides. Examples of esters are fatty acid esters, glycerol esters or monoglycerides. Examples of sugar-based surfactants are sorbitans, ethoxylated sorbitans, sucrose and glucose esters or alkylpolyglucosides. Examples of polymeric surfactants are home- or copolymers of vinylpyrrolidone, vinylalcohols, or vinylacetate.

Suitable cationic surfactants are quaternary surfactants, for example quaternary ammonium compounds with one or two hydrophobic groups, or salts of long-chain primary amines. Suitable amphoteric surfactants are alkylbetains and imidazolines. Suitable block polymers are block polymers of the A-B or A-B-A type comprising blocks of polyethylene oxide and polypropylene oxide, or of the A-B-C type comprising alkanol, polyethylene oxide and polypropylene oxide. Suitable polyelectrolytes are polyacids or polybases. Examples of polyacids are alkali salts of polyacrylic acid or polyacid comb polymers. Examples of polybases are polyvinylamines or polyethyleneamines.

Suitable adjuvants are compounds, which have a neglectable or even no pesticidal activity themselves, and which improve the biological performance of the compound I on the target. Examples are surfactants, mineral or vegetable oils, and other auxilaries. Further examples are listed by Knowles, Adjuvants and additives, Agrow Reports DS256, T&F Informa UK, 2006, chapter 5.

Suitable thickeners are polysaccharides (e.g. xanthan gum, carboxymethylcellulose), anorganic clays (organically modified or unmodified), polycarboxylates, and silicates.

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Suitable bactericides are bronopol and isothiazolinone derivatives such as alkylisothiazolinones and benzisothiazolinones.

Suitable anti-freezing agents are ethylene glycol, propylene glycol, urea and glycerin.

Suitable anti-foaming agents are silicones, long chain alcohols, and salts of fatty acids.

Suitable colorants (e.g. in red, blue, or green) are pigments of low water solubility and water-soluble dyes. Examples are inorganic colorants (e.g. iron oxide, titan oxide, iron hexacyanoferrate) and organic colorants (e.g. alizarin-, azo- and phthalocyanine colorants).

Suitable tackifiers or binders are polyvinylpyrrolidons, polyvinylacetates, polyvinyl alcohols, polyacrylates, biological or synthetic waxes, and cellulose ethers.

The agrochemical compositions generally comprise between 0.01 and 95%, preferably between 0.1 and 90%, and most preferably between 0.5 and 75%, by weight of active substance. The active substances are employed in a purity of from 90% to 100%, preferably from 95% to 100% (according to NMR spectrum).

Water-soluble concentrates (LS), Suspoemulsions (SE), flowable concentrates (FS), powders for dry treatment (DS), water-dispersible powders for slurry treatment (WS), water-soluble powders (SS), emulsions (ES), emulsifiable concentrates (EC) and gels (GF) are usually employed for the purposes of treatment of plant propagation materials, particularly seeds. The compositions in question give, after two-to-tenfold dilution, active substance concentrations of from 0.01 to 60% by weight, preferably from 0.1 to 40%, in the ready-to-use preparations. Application can be carried out before or during sowing. Methods for applying or treating compound I and compositions thereof, respectively, on to plant propagation material, especially seeds include dressing, coating, pelleting, dusting, soaking and in-furrow application methods of the propagation material. Preferably, compound I or the compositions thereof, respectively, are applied on to the plant propagation material by a method such that germination is not induced, e. g. by seed dressing, pelleting, coating and dusting.

When employed in plant protection, the amounts of active substances applied are, depending on the kind of effect desired, from 0.001 to 2 kg per ha, preferably from 0.005 to 2 kg per ha, more preferably from 0.05 to 0.9 kg per ha, in particular from 0.1 to 0.75 kg per ha.

In treatment of plant propagation materials such as seeds, e. g. by dusting, coating or drenching seed, amounts of active substance of from 0.1 to 1000 g, preferably from 1 to 1000 g and most preferably from 5 to 100 g, per 100 kilogram of plant propagation material (preferably seed) are generally required.

When used in the protection of materials or stored products, the amount of active substance applied depends on the kind of application area and on the desired effect. Amounts customarily applied in the protection of materials are 0.001 g to 2 kg, preferably 0.005 g to 1 kg, of active substance per cubic meter of treated material.

Various types of oils, wetters, adjuvants, fertilizer, or micronutrients, and other pesticides (e.g. herbicides, insecticides, fungicides, growth regulators, safeners) may be added to the active substances or the compositions comprising them as premix or, if appropriate not until immediately prior to use (tank mix). These agents can be admixed with the compositions according to the invention in a weight ratio of 1:100 to 100:1, preferably 1:10 to 10:1.

The user applies the composition according to the invention usually from a predosage device, a knapsack sprayer, a spray tank, a spray plane, or an irrigation system. Usually, the agrochemical composition is made up with water, buffer, and/or further auxiliaries to the desired application concentration and the ready-to-use spray liquor or the agrochemical composition according to the invention is thus obtained. Usually, 20 to 2000 liters, preferably 50 to 400 liters, of the ready-to-use spray liquor are applied per hectare of agricultural useful area.

According to one embodiment, individual components of the composition according to the invention such as parts of a kit or parts of a binary or ternary mixture may be mixed by the user himself in a spray tank and further auxiliaries may be added, if appropriate.

Mixing the compounds I or the compositions comprising them in the use form as fungicides with other fungicides results in many cases in an expansion of the fungicidal spectrum of activity being obtained or in a prevention of fungicide resistance development. Furthermore, in many cases, synergistic effects are obtained.

The following list of active substances, in conjunction with which the compounds I can be used, is intended to illustrate the possible combinations but does not limit them:

A) Respiration inhibitors

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- Inhibitors of complex III at Qo site (e.g. strobilurins): azoxystrobin, coumethoxystrobin, coumoxystrobin, dimoxystrobin, enestroburin, fenaminstrobin, fenoxystrobin/flufenoxystrobin, fluoxastrobin, kresoxim-methyl, metominostrobin, orysastrobin, picoxystrobin, pyraclostrobin, pyrametostrobin, pyraoxystrobin, trifloxystrobin, 2-[2-(2,5-dimethyl-phenoxymethyl)-phenyl]-3-methoxy-acrylic acid methyl ester and 2-(2-(3-(2,6-di-chlorophenyl)-1-methyl-allylideneaminooxymethyl)-phenyl)-2-methoxyimino-N-methyl-acetamide, pyribencarb, triclopyricarb/chlorodincarb, famoxadone, fenamidone;
- inhibitors of complex III at Qi site: cyazofamid, amisulbrom, [(3S,6S,7R,8R)-8-benz-yl-3-[(3-acetoxy-4-methoxy-pyridine-2-carbonyl)amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate, [(3S,6S,7R,8R)-8-benzyl-3-[[3-(acetoxymethoxy)-4-methoxy-pyridine-2-carbonyl]amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate, [(3S,6S,7R,8R)-8-benzyl-3-[(3-isobutoxycarbonyloxy-4-methoxy-pyridine-2-carbonyl)amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate, [(3S,6S,7R,8R)-8-benzyl-3-[[3-(1,3-benzodioxol-5-ylmethoxy)-4-methoxy-pyridine-2-carbonyl]amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate;
- inhibitors of complex II (e. g. carboxamides): benodanil, bixafen, boscalid, carboxin, fenfuram, fluopyram, flutolanil, fluxapyroxad, furametpyr, isopyrazam, mepronil, oxycarboxin, penflufen, penthiopyrad, sedaxane, tecloftalam, thifluzamide, N-(4'-trifluoromethylthiobiphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-(2-(1,3,3-trimethyl-butyl)-phenyl)-1,3-dimethyl-5-fluoro-1H-pyrazole-4-carboxamide, N-[9-(dichloromethylene)-1,2,3,4-tetrahydro-1,4-methanonaphthalen-5-yl]-3-(difluoromethyl)-1-

methyl-1H-pyrazole-4-carboxamide;

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- other respiration inhibitors (e.g. complex I, uncouplers): diflumetorim, (5,8-difluoro-quinazolin-4-yl)-{2-[2-fluoro-4-(4-trifluoromethylpyridin-2-yloxy)-phenyl]-ethyl}-amine; nitrophenyl derivates: binapacryl, dinobuton, dinocap, fluazinam; ferimzone; organometal compounds: fentin salts, such as fentin-acetate, fentin chloride or fentin hydroxide; ametoctradin; and silthiofam;
- B) Sterol biosynthesis inhibitors (SBI fungicides)
 - C14 demethylase inhibitors (DMI fungicides): triazoles: azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole, diniconazole-M, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imibenconazole, ipconazole, metconazole, myclobutanil, oxpoconazole, paclobutrazole, penconazole, propiconazole, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triticonazole, uniconazole; imidazoles: imazalil, pefurazoate, prochloraz, triflumizol; pyrimidines, pyridines and piperazines: fenarimol, nuarimol, pyrifenox, triforine;
 - Delta14-reductase inhibitors: aldimorph, dodemorph, dodemorph-acetate, fenpropimorph, tridemorph, fenpropidin, piperalin, spiroxamine;
 - Inhibitors of 3-keto reductase: fenhexamid;
- C) Nucleic acid synthesis inhibitors
 - phenylamides or acyl amino acid fungicides: benalaxyl, benalaxyl-M, kiralaxyl, metalaxyl-M (mefenoxam), ofurace, oxadixyl;
 - others: hymexazole, octhilinone, oxolinic acid, bupirimate, 5-fluorocytosine, 5-fluoro-2-(p-tolylmethoxy)pyrimidin-4-amine, 5-fluoro-2-(4-fluorophenylmethoxy)pyrimidin-4-amine;
- 25 D) Inhibitors of cell division and cytoskeleton
 - tubulin inhibitors, such as benzimidazoles, thiophanates: benomyl, carbendazim, fuberidazole, thiabendazole, thiophanate-methyl; triazolopyrimidines: 5-chloro-7-(4-methylpiperidin-1-yl)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine
 - other cell division inhibitors: diethofencarb, ethaboxam, pencycuron, fluopicolide, zoxamide, metrafenone, pyriofenone;
 - E) Inhibitors of amino acid and protein synthesis
 - methionine synthesis inhibitors (anilino-pyrimidines): cyprodinil, mepanipyrim, pyrimethanil;
 - protein synthesis inhibitors: blasticidin-S, kasugamycin, kasugamycin hydrochloridehydrate, mildiomycin, streptomycin, oxytetracyclin, polyoxine, validamycin A;
 - F) Signal transduction inhibitors
 - MAP / histidine kinase inhibitors: fluoroimid, iprodione, procymidone, vinclozolin, fenpiclonil, fludioxonil;
 - G protein inhibitors: quinoxyfen;
- 40 G) Lipid and membrane synthesis inhibitors
 - Phospholipid biosynthesis inhibitors: edifenphos, iprobenfos, pyrazophos, isoprothiolane;
 - lipid peroxidation: dicloran, quintozene, tecnazene, tolclofos-methyl, biphenyl, chloroneb, etridiazole;

- phospholipid biosynthesis and cell wall deposition: dimethomorph, flumorph, mandipropamid, pyrimorph, benthiavalicarb, iprovalicarb, valifenalate and N-(1-(4-cyano-phenyl)ethanesulfonyl)-but-2-yl) carbamic acid-(4-fluorophenyl) ester;
- compounds affecting cell membrane permeability and fatty acides: propamocarb, propamocarb-hydrochlorid

H)Inhibitors with Multi Site Action

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- inorganic active substances: Bordeaux mixture, copper acetate, copper hydroxide, copper oxychloride, basic copper sulfate, sulfur;
- thio- and dithiocarbamates: ferbam, mancozeb, maneb, metam, metiram, propineb, thiram, zineb, ziram;
- organochlorine compounds (e.g. phthalimides, sulfamides, chloronitriles): anilazine, chlorothalonil, captafol, captan, folpet, dichlofluanid, dichlorophen, flusulfamide, hexachlorobenzene, pentachlorphenole and its salts, phthalide, tolylfluanid, N-(4-chloro-2-nitro-phenyl)-N-ethyl-4-methyl-benzenesulfonamide;
- guanidines and others: guanidine, dodine, dodine free base, guazatine, guazatine-acetate, iminoctadine, iminoctadine-triacetate, iminoctadine-tris(albesilate), dithianon;
- I) Cell wall synthesis inhibitors
 - inhibitors of glucan synthesis: validamycin, polyoxin B; melanin synthesis inhibitors: pyroquilon, tricyclazole, carpropamid, dicyclomet, fenoxanil;
- 20 J) Plant defence inducers
 - acibenzolar-S-methyl, probenazole, isotianil, tiadinil, prohexadione-calcium; phosphonates: fosetyl, fosetyl-aluminum, phosphorous acid and its salts;
 - K) Unknown mode of action
- bronopol, chinomethionat, cyflufenamid, cymoxanil, dazomet, debacarb, diclo-25 mezine, difenzoquat, difenzoquat-methylsulfate, diphenylamin, fenpyrazamine, flumetover, flusulfamide, flutianil, methasulfocarb, nitrapyrin, nitrothal-isopropyl, oxincopper, proquinazid, tebufloquin, tecloftalam, triazoxide, 2-butoxy-6-iodo-3-propylchromen-4-one, N-(cyclopropylmethoxyimino-(6-difluoro-methoxy-2,3-difluorophenyl)-methyl)-2-phenyl acetamide, N'-(4-(4-chloro-3-trifluoromethyl-phenoxy)-2,5-30 dimethyl-phenyl)-N-ethyl-N-methyl formamidine, N'-(4-(4-fluoro-3-trifluoromethylphenoxy)-2,5-dimethyl-phenyl)-N-ethyl-N-methyl formamidine, N'-(2-methyl-5trifluoromethyl-4-(3-trimethylsilanyl-propoxy)-phenyl)-N-ethyl-N-methyl formamidine, N'-(5difluoromethyl-2-methyl-4-(3-trimethylsilanyl-propoxy)-phenyl)-N-ethyl-N-methyl formamidine, 2-{1-[2-(5-methyl-3-trifluoromethyl-pyrazole-1-yl)-acetyl]-piperidin-4-yl}-35 thiazole-4-carboxylic acid methyl-(1,2,3,4-tetrahydro-naphthalen-1-yl)-amide, 2-{1-[2-(5methyl-3-trifluoromethyl-pyrazole-1-yl)-acetyl]-piperidin-4-yl}-thiazole-4-carboxylic acid methyl-(R)-1,2,3,4-tetrahydro-naphthalen-1-yl-amide, 1-[4-[4-[5-(2,6-difluorophenyl)-4,5-dihydro-3-isoxazolyl]-2-thiazolyl]-1-piperidinyl]-2-[5-methyl-3-(trifluoromethyl)-1H-pyrazol-1-yl]ethanone, methoxy-acetic acid 40 6-tert-butyl-8-fluoro-2,3-dimethyl-quinolin-4-yl ester, N-Methyl-2-{1-[(5-methyl-3-trifluoromethyl-1H-pyrazol-1-yl)-acetyl]-piperidin-4-yl}-N-[(1R)-1,2,3,4-tetrahydronaphthalen-1-yl]-4-thiazolecarboxamide, 3-[5-(4-methylphenyl)-2,3-dimethyl-isoxazolidin-3-yl]-pyridine, 3-[5-(4-chloro-phenyl)-2,3-dimethyl-isoxazolidin-3-yl]-pyridine (pyrisoxazole), N-(6-methoxypyridin-3-yl) cyclopropanecarboxylic acid amide, 5-chloro-1-(4,6-dimethoxy-pyrimidin-2-

- yl)-2-methyl-1H-benzoimidazole, 2-(4-chloro-phenyl)-N-[4-(3,4-dimethoxy-phenyl)-isoxazol-5-yl]-2-prop-2-ynyloxy-acetamide;
- Antifungal biocontrol agents, plant bioactivators: Ampelomyces quisqualis (e.g. AQ 10® L) 5 from Intrachem Bio GmbH & Co. KG, Germany), Aspergillus flavus (e.g. AFLAGUARD® from Syngenta, CH), Aureobasidium pullulans (e.g. BOTECTOR® from bio-ferm GmbH, Germany), Bacillus pumilus (e.g. NRRL Accession No. B-30087 in SONATA® and BALLAD® Plus from AgraQuest Inc., USA), Bacillus subtilis (e.g. isolate NRRL-Nr. B-21661 in RHAPSODY®, SERENADE® MAX and SERENADE® ASO from AgraQuest 10 Inc., USA), Bacillus subtilis var. amyloliquefaciens FZB24 (e.g. TAEGRO® from Novozyme Biologicals, Inc., USA), Candida oleophila I-82 (e.g. ASPIRE® from Ecogen Inc., USA), Candida saitoana (e.g. BIOCURE® (in mixture with lysozyme) and BIOCOAT® from Micro Flo Company, USA (BASF SE) and Arysta), Chitosan (e.g. ARMOUR-ZEN from BotriZen Ltd., NZ), Clonostachys rosea f. catenulata, also named 15 Gliocladium catenulatum (e.g. isolate J1446: PRESTOP® from Verdera, Finland), Conjothyrium minitans (e.g. CONTANS® from Prophyta, Germany), Cryphonectria parasitica (e.g. Endothia parasitica from CNICM, France), Cryptococcus albidus (e.g. YIELD PLUS® from Anchor Bio-Technologies, South Africa), Fusarium oxysporum (e.g. BIOFOX® from S.I.A.P.A., Italy, FUSACLEAN® from Natural Plant Protection, France), 20 Metschnikowia fructicola (e.g. SHEMER® from Agrogreen, Israel), Microdochium dimerum (e.g. ANTIBOT® from Agrauxine, France), Phlebiopsis gigantea (e.g. ROTSOP® from Verdera, Finland), Pseudozyma flocculosa (e.g. SPORODEX® from Plant Products Co. Ltd., Canada), Pythium oligandrum DV74 (e.g. POLYVERSUM® from Remeslo SSRO, Biopreparaty, Czech Rep.), Reynoutria sachlinensis (e.g. REGALIA® from Marrone 25 BioInnovations, USA), Talaromyces flavus V117b (e.g. PROTUS® from Prophyta, Germany), Trichoderma asperellum SKT-1 (e.g. ECO-HOPE® from Kumiai Chemical Industry Co., Ltd., Japan), T. atroviride LC52 (e.g. SENTINEL® from Agrimm Technologies Ltd, NZ), T. harzianum T-22 (e.g. PLANTSHIELD® der Firma BioWorks Inc., USA), T. harzianum TH 35 (e.g. ROOT PRO® from Mycontrol Ltd., Israel), T. 30 harzianum T-39 (e.g. TRICHODEX® and TRICHODERMA 2000® from Mycontrol Ltd., Israel and Makhteshim Ltd., Israel), T. harzianum and T. viride (e.g. TRICHOPEL from Agrimm Technologies Ltd, NZ), T. harzianum ICC012 and T. viride ICC080 (e.g. REMEDIER® WP from Isagro Ricerca, Italy), T. polysporum and T. harzianum (e.g. BINAB® from BINAB Bio-Innovation AB, Sweden), T. stromaticum (e.g. TRICOVAB® from 35 C.E.P.L.A.C., Brazil), T. virens GL-21 (e.g. SOILGARD® from Certis LLC, USA), T. viride (e.g. TRIECO® from Ecosense Labs. (India) Pvt. Ltd., Indien, BIO-CURE® F from T. Stanes & Co. Ltd., Indien), T. viride TV1 (e.g. T. viride TV1 from Agribiotec srl, Italy),
 - M) Growth regulators

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abscisic acid, amidochlor, ancymidol, 6-benzylaminopurine, brassinolide, butralin, chlormequat (chlormequat chloride), choline chloride, cyclanilide, daminozide, dikegulac, dimethipin, 2,6-dimethylpuridine, ethephon, flumetralin, flurprimidol, fluthiacet, forchlorfenuron, gibberellic acid, inabenfide, indole-3-acetic acid, maleic hydrazide, mefluidide, mepiquat (mepiquat chloride), naphthaleneacetic acid, N-6-benzyladenine,

Ulocladium oudemansii HRU3 (e.g. BOTRY-ZEN® from Botry-Zen Ltd, NZ);

paclobutrazol, prohexadione (prohexadione-calcium), prohydrojasmon, thidiazuron, triapenthenol, tributyl phosphorotrithioate, 2,3,5-tri-iodobenzoic acid, trinexapac-ethyl and uniconazole;

N) Herbicides

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- acetamides: acetochlor, alachlor, butachlor, dimethachlor, dimethenamid, flufenacet, mefenacet, metolachlor, metazachlor, napropamide, naproanilide, pethoxamid, pretilachlor, propachlor, thenylchlor;
 - amino acid derivatives: bilanafos, glyphosate, glufosinate, sulfosate;
- aryloxyphenoxypropionates: clodinafop, cyhalofop-butyl, fenoxaprop, fluazifop, haloxyfop, metamifop, propaquizafop, quizalofop, quizalofop-P-tefuryl;
 - Bipyridyls: diquat, paraquat;
- (thio)carbamates: asulam, butylate, carbetamide, desmedipham, dimepiperate, eptam (EPTC), esprocarb, molinate, orbencarb, phenmedipham, prosulfocarb, pyributicarb, thiobencarb, triallate;
- cyclohexanediones: butroxydim, clethodim, cycloxydim, profoxydim, sethoxydim, tepraloxydim, tralkoxydim;
- dinitroanilines: benfluralin, ethalfluralin, oryzalin, pendimethalin, prodiamine, trifluralin;
- diphenyl ethers: acifluorfen, aclonifen, bifenox, diclofop, ethoxyfen, fomesafen, lactofen, oxyfluorfen;
 - hydroxybenzonitriles: bomoxynil, dichlobenil, ioxynil;
- imidazolinones: imazamethabenz, imazamox, imazapic, imazapyr, imazaquin, imazethapyr;
- phenoxy acetic acids: clomeprop, 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4-DB, dichlorprop, MCPA, MCPA-thioethyl, MCPB, Mecoprop;
 - pyrazines: chloridazon, flufenpyr-ethyl, fluthiacet, norflurazon, pyridate;
- pyridines: aminopyralid, clopyralid, diflufenican, dithiopyr, fluridone, fluroxypyr, picloram, picolinafen, thiazopyr;
- sulfonyl ureas: amidosulfuron, azimsulfuron, bensulfuron, chlorimuron-ethyl, chlorsulfuron, cinosulfuron, cyclosulfamuron, ethoxysulfuron, flazasulfuron, flucetosulfuron, flupyrsulfuron, foramsulfuron, halosulfuron, imazosulfuron, iodosulfuron, mesosulfuron, metazosulfuron, metsulfuron-methyl, nicosulfuron, oxasulfuron, primisulfuron, prosulfuron, pyrazosulfuron, rimsulfuron, sulfometuron, sulfosulfuron, thifensulfuron, triasulfuron, tribenuron, trifloxysulfuron, triflusulfuron, tritosulfuron, 1-((2-chloro-6-propyl-imidazo[1,2-b]pyridazin-3-yl)sulfonyl)-3-(4,6-dimethoxy-pyrimidin-2-yl)urea;
- triazines: ametryn, atrazine, cyanazine, dimethametryn, ethiozin, hexazinone, metamitron, metribuzin, prometryn, simazine, terbuthylazine, terbutryn, triaziflam;
- ureas: chlorotoluron, daimuron, diuron, fluometuron, isoproturon, linuron, methabenzthiazuron,tebuthiuron;
- other acetolactate synthase inhibitors: bispyribac-sodium, cloransulam-methyl, diclosulam, florasulam, flucarbazone, flumetsulam, metosulam, ortho-sulfamuron, penoxsulam, propoxycarbazone, pyribambenz-propyl, pyribenzoxim, pyriftalid, pyriminobac-methyl, pyrimisulfan, pyrithiobac, pyroxasulfone, pyroxsulam;

- others: amicarbazone, aminotriazole, anilofos, beflubutamid, benazolin, bencarbazone, benfluresate, benzofenap, bentazone, benzobicyclon, bicyclopyrone, bromacil, bromobutide, butafenacil, butamifos, cafenstrole, carfentrazone, cinidon-ethyl, chlorthal, cinmethylin, clomazone, cumyluron, cyprosulfamide, dicamba, difenzoguat, diflufenzopyr, Drechslera monoceras, endothal, ethofumesate, etobenzanid, fenoxasulfone, fentrazamide, flumiclorac-pentyl, flumioxazin, flupoxam, flurochloridone, flurtamone, indanofan, isoxaben, isoxaflutole, lenacil, propanil, propyzamide, quinclorac, quinmerac, mesotrione, methyl arsonic acid, naptalam, oxadiargyl, oxadiazon, oxaziclomefone, pentoxazone, pinoxaden, pyraclonil, pyraflufen-ethyl, pyrasulfotole, pyrazoxyfen, pyrazolynate, quinoclamine, saflufenacil, sulcotrione, sulfentrazone, terbacil, tefuryltrione, tembotrione, thiencarbazone, topramezone, (3-[2-chloro-4-fluoro-5-(3methyl-2.6-dioxo-4-trifluoromethyl-3.6-dihydro-2H-pyrimidin-1-vl)-phenoxyl-pyridin-2vloxy)-acetic acid ethyl ester, 6-amino-5-chloro-2-cyclopropyl-pyrimidine-4-carboxylic acid methyl ester, 6-chloro-3-(2-cyclopropyl-6-methyl-phenoxy)-pyridazin-4-ol, 4-amino-3chloro-6-(4-chloro-phenyl)-5-fluoro-pyridine-2-carboxylic acid, 4-amino-3-chloro-6-(4chloro-2-fluoro-3-methoxy-phenyl)-pyridine-2-carboxylic acid methyl ester, and 4-amino-3chloro-6-(4-chloro-3-dimethylamino-2-fluoro-phenyl)-pyridine-2-carboxylic acid methyl ester.

O) Insecticides

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- organo(thio)phosphates: acephate, azamethiphos, azinphos-methyl, chlorpyrifos, chlorpyrifos-methyl, chlorfenvinphos, diazinon, dichlorvos, dicrotophos, dimethoate, disulfoton, ethion, fenitrothion, fenthion, isoxathion, malathion, methamidophos, methidathion, methyl-parathion, mevinphos, monocrotophos, oxydemeton-methyl, paraoxon, parathion, phenthoate, phosalone, phosmet, phosphamidon, phorate, phoxim, pirimiphos-methyl, profenofos, prothiofos, sulprophos, tetrachlorvinphos, terbufos, triazophos, trichlorfon;

- carbamates: alanycarb, aldicarb, bendiocarb, benfuracarb, carbaryl, carbofuran, carbosulfan, fenoxycarb, furathiocarb, methiocarb, methomyl, oxamyl, pirimicarb, propoxur, thiodicarb, triazamate;
- pyrethroids: allethrin, bifenthrin, cyfluthrin, cyhalothrin, cyphenothrin, cypermethrin, alpha-cypermethrin, beta-cypermethrin, zeta-cypermethrin, deltamethrin, esfenvalerate, etofenprox, fenpropathrin, fenvalerate, imiprothrin, lambda-cyhalothrin, permethrin, prallethrin, pyrethrin I and II, resmethrin, silafluofen, tau-fluvalinate, tefluthrin, tetramethrin, tralomethrin, transfluthrin, profluthrin, dimefluthrin;
- insect growth regulators: a) chitin synthesis inhibitors: benzoylureas: chlorfluazuron, cyramazin, diflubenzuron, flucycloxuron, flufenoxuron, hexaflumuron, lufenuron, novaluron, teflubenzuron, triflumuron; buprofezin, diofenolan, hexythiazox, etoxazole, clofentazine; b) ecdysone antagonists: halofenozide, methoxyfenozide, tebufenozide, azadirachtin; c) juvenoids: pyriproxyfen, methoprene, fenoxycarb; d) lipid biosynthesis inhibitors: spirodiclofen, spiromesifen, spirotetramat;
- nicotinic receptor agonists/antagonists compounds: clothianidin, dinotefuran, imidacloprid, thiamethoxam, nitenpyram, acetamiprid, thiacloprid, 1-(2-chloro-thiazol-5-ylmethyl)-2-nitrimino-3,5-dimethyl-[1,3,5]triazinane;
 - GABA antagonist compounds: endosulfan, ethiprole, fipronil, vaniliprole,

pyrafluprole, pyriprole, 5-amino-1-(2,6-dichloro-4-methyl-phenyl)-4-sulfinamoyl-1H-pyrazole-3-carbothioic acid amide;

- macrocyclic lactone insecticides: abamectin, emamectin, milbemectin, lepimectin, spinosad, spinetoram;
- mitochondrial electron transport inhibitor (METI) I acaricides: fenazaquin, pyridaben, tebufenpyrad, tolfenpyrad, flufenerim;
 - METI II and III compounds: acequinocyl, fluacyprim, hydramethylnon;
 - Uncouplers: chlorfenapyr;

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- oxidative phosphorylation inhibitors: cyhexatin, diafenthiuron, fenbutatin oxide, propargite;
 - moulting disruptor compounds: cryomazine;
 - mixed function oxidase inhibitors: piperonyl butoxide;
 - sodium channel blockers: indoxacarb, metaflumizone;
- others: benclothiaz, bifenazate, cartap, flonicamid, pyridalyl, pymetrozine, sulfur, thiocyclam, flubendiamide, chlorantraniliprole, cyazypyr (HGW86), cyenopyrafen, flupyrazofos, cyflumetofen, amidoflumet, imicyafos, bistrifluron, pyrifluquinazon and 1,1'-[(3S,4R,4aR,6S,6aS,12R,12aS,12bS)-4-[[(2-cyclopropylacetyl)oxy]methyl]-1,3,4,4a,5,6,6a,12,12a,12b-decahydro-12-hydroxy-4,6a,12b-trimethyl-11-oxo-9-(3-pyridinyl)-2H,11H-naphtho[2,1-b]pyrano[3,4-e]pyran-3,6-diyl] cyclopropaneacetic acid ester.

The present invention furthermore relates to agrochemical compositions comprising a mixture of at least one compound I (component 1) and at least one further active substance useful for plant protection, e. g. selected from the groups A) to O) (component 2), in particular one further fungicide, e. g. one or more fungicide from the groups A) to L), as described above, and if desired one suitable solvent or solid carrier. Those mixtures are of particular interest, since many of them at the same application rate show higher efficiencies against harmful fungi. Furthermore, combating harmful fungi with a mixture of compounds I and at least one fungicide from groups A) to L), as described above, is more efficient than combating those fungi with individual compounds I or individual fungicides from groups A) to L). By applying compounds I together with at least one active substance from groups A) to O) a synergistic effect can be obtained, i.e. more then simple addition of the individual effects is obtained (synergistic mixtures).

This can be obtained by applying the compounds I and at least one further active substance simultaneously, either jointly (e. g. as tank-mix) or separately, or in succession, wherein the time interval between the individual applications is selected to ensure that the active substance applied first still occurs at the site of action in a sufficient amount at the time of application of the further active substance(s). The order of application is not essential for working of the present invention.

In binary mixtures, i.e. compositions according to the invention comprising one compound I (component 1) and one further active substance (component 2), e. g. one active substance from groups A) to O), the weight ratio of component 1 and component 2 generally depends from the properties of the active substances used, usually it is in the range of from 1:100 to 100:1, regularly in the range of from 1:50 to 50:1, preferably in the range of from 1:20 to 20:1, more

preferably in the range of from 1:10 to 10:1 and in particular in the range of from 1:3 to 3:1.

In ternary mixtures, i.e. compositions according to the invention comprising one compound I (component 1) and a first further active substance (component 2) and a second further active substance (component 3), e. g. two active substances from groups A) to O), the weight ratio of component 1 and component 2 depends from the properties of the active substances used, preferably it is in the range of from 1:50 to 50:1 and particularly in the range of from 1:10 to 10:1, and the weight ratio of component 1 and component 3 preferably is in the range of from 1:50 to 50:1 and particularly in the range of from 1:10 to 10:1.

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Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group A) (component 2) and particularly selected from azoxystrobin, dimoxystrobin, fluoxastrobin, kresoxim-methyl, orysastrobin, picoxystrobin, pyraclostrobin, trifloxystrobin; famoxadone, fenamidone; bixafen, boscalid, fluopyram, fluxapyroxad, isopyrazam, penflufen, penthiopyrad, sedaxane; ametoctradin, cyazofamid, fluazinam, fentin salts, such as fentin acetate.

Preference is given to mixtures comprising a compound I (component 1) and at least one active substance selected from group B) (component 2) and particularly selected from cyproconazole, difenoconazole, epoxiconazole, fluquinconazole, flusilazole, flutriafol, metconazole, myclobutanil, penconazole, propiconazole, prothioconazole, triadimenol, tebuconazole, tetraconazole, triticonazole, prochloraz, fenarimol, triforine; dodemorph, fenpropimorph, tridemorph, fenpropidin, spiroxamine; fenhexamid.

Preference is given to mixtures comprising a compound I (component 1) and at least one active substance selected from group C) (component 2) and particularly selected from metalaxyl, (metalaxyl-M) mefenoxam, ofurace.

Preference is given to mixtures comprising a compound I (component 1) and at least one active substance selected from group D) (component 2) and particularly selected from benomyl, carbendazim, thiophanate-methyl, ethaboxam, fluopicolide, zoxamide, metrafenone, pyriofenone.

Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group E) (component 2) and particularly selected from cyprodinil, mepanipyrim, pyrimethanil.

Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group F) (component 2) and particularly selected from iprodione, fludioxonil, vinclozolin, quinoxyfen.

Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group G) (component 2) and particularly selected from dimethomorph, flumorph, iprovalicarb, benthiavalicarb, mandipropamid, propamocarb.

Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group H) (component 2) and particularly selected from copper acetate, copper hydroxide, copper oxychloride, copper sulfate, sulfur, mancozeb, metiram, propineb, thiram, captafol, folpet, chlorothalonil, dichlofluanid, dithianon.

Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group I) (component 2) and particularly selected from carpropamid and fenoxanil.

Preference is also given to mixtures comprising a compound I (component 1) and at least

one active substance selected from group J) (component 2) and particularly selected from acibenzolar-S-methyl, probenazole, tiadinil, fosetyl, fosetyl-aluminium, H₃PO₃ and salts thereof.

Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group K) (component 2) and particularly selected from cymoxanil, proquinazid and N-methyl-2-{1-[(5-methyl-3-trifluoromethyl-1H-pyrazol-1-yl)-acetyl]-piperidin-4-yl}-N-[(1R)-1,2,3,4-tetrahydronaphthalen-1-yl]-4-thiazolecarboxamide.

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Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group L) (component 2) and particularly selected from Bacillus subtilis strain NRRL No. B-21661, Bacillus pumilus strain NRRL No. B-30087 and Ulocladium oudemansii.

Accordingly, the present invention furthermore relates to compositions comprising one compound I (component 1) and one further active substance (component 2), which further active substance is selected from the column "Component 2" of the lines D-1 to D-370 of Table D.

A further embodiment relates to the compositions D-1 to D-370 listed in Table D, where a row of Table D corresponds in each case to a fungicidal composition comprising one of the in the present specification individualized compounds of formula I (component 1) and the respective further active substance from groups A) to O) (component 2) stated in the row in question. Preferably, the compositions described comprise the active substances in synergistically effective amounts.

<u>Table D:</u> Composition comprising one individualized compound I and one further active substance from groups A) to O)

Mixture	Component 1	Component 2
D-1	one individualized compound I	Azoxystrobin
D-2	one individualized compound I	Coumethoxystrobin
D-3	one individualized compound I	Coumoxystrobin
D-4	one individualized compound I	Dimoxystrobin
D-5	one individualized compound I	Enestroburin
D-6	one individualized compound I	Fenaminstrobin
D-7	one individualized compound I	Fenoxystrobin/Flufenoxystrobin
D-8	one individualized compound I	Fluoxastrobin
D-9	one individualized compound I	Kresoxim-methyl
D-10	one individualized compound I	Metominostrobin
D-11	one individualized compound I	Orysastrobin
D-12	one individualized compound I	Picoxystrobin
D-13	one individualized compound I	Pyraclostrobin
D-14	one individualized compound I	Pyrametostrobin
D-15	one individualized compound I	Pyraoxystrobin
D-16	one individualized compound I	Pyribencarb
D-17	one individualized compound I	Trifloxystrobin
D-18	one individualized compound I	Triclopyricarb/Chlorodincarb

Mixture	Component 1	Component 2
D-19		2-[2-(2,5-dimethyl-phenoxymethyl)-
	one individualized compound I	phenyl]-3-methoxy-acrylic acid methyl
		ester
		2-(2-(3-(2,6-dichlorophenyl)-1-methyl-
D-20	one individualized compound I	allylideneaminooxymethyl)-phenyl)-
		2-methoxyimino-N-methyl-acetamide
D-21	one individualized compound I	Benalaxyl
D-22	one individualized compound I	Benalaxyl-M
D-23	one individualized compound l	Benodanil
D-24	one individualized compound I	Benzovindiflupyr
D-25	one individualized compound I	Bixafen
D-26	one individualized compound I	Boscalid
D-27	one individualized compound I	Carboxin
D-28	one individualized compound I	Fenfuram
D-29	one individualized compound I	Fenhexamid
D-30	one individualized compound I	Flutolanil
D-31	one individualized compound I	Fluxapyroxad
D-32	one individualized compound I	Furametpyr
D-33	one individualized compound I	Isopyrazam
D-34	one individualized compound I	Isotianil
D-35	one individualized compound I	Kiralaxyl
D-36	one individualized compound I	Mepronil
D-37	one individualized compound I	Metalaxyl
D-38	one individualized compound I	Metalaxyl-M
D-39	one individualized compound I	Ofurace
D-40	one individualized compound I	Oxadixyl
D-41	one individualized compound I	Oxycarboxin
D-42	one individualized compound I	Penflufen
D-43	one individualized compound I	Penthiopyrad
D-44	one individualized compound I	Sedaxane
D-45	one individualized compound I	Tecloftalam
D-46	one individualized compound I	Thifluzamide
D-47	one individualized compound I	Tiadinil
D 40	one individualized compound I	2-Amino-4-methyl-thiazole-5-carboxylic
D-48		acid anilide
	one individualized compound I	N-(4'-trifluoromethylthiobiphenyl-2-yl)-
D-49		3-difluoromethyl-1-methyl-1H-pyrazole-
		4-carboxamide
		N-(2-(1,3,3-trimethyl-butyl)-phenyl)-
D-50	one individualized compound I	1,3-dimethyl-5-fluoro-1H-pyrazole-
		4-carboxamide

Mixture	Component 1	Component 2
D-51		3-(difluoromethyl)-1-methyl-N-(1,1,3-tri-
	one individualized compound I	methylindan-4-yl)pyrazole-4-carbox-
		amide
D-52		3-(trifluoromethyl)-1-methyl-N-(1,1,3-tri-
	one individualized compound I	methylindan-4-yl)pyrazole-4-carbox-
		amide
D-53	one individualized compound I	1,3-dimethyl-N-(1,1,3-trimethylindan-
D-00		4-yl)pyrazole-4-carboxamide
	one individualized compound I	3-(trifluoromethyl)-1,5-dimethyl-
D-54		N-(1,1,3-trimethylindan-4-yl)pyrazole-
		4-carboxamide
		3-(difluoromethyl)-1,5-dimethyl-
D-55	one individualized compound I	N-(1,1,3-trimethylindan-4-yl)pyrazole-
		4-carboxamide
D-56	one individualized compound I	1,3,5-trimethyl-N-(1,1,3-trimethylindan-
D-30	one marviadanzea compodna i	4-yl)pyrazole-4-carboxamide
D-57	one individualized compound I	Dimethomorph
D-58	one individualized compound I	Flumorph
D-59	one individualized compound I	Pyrimorph
D-60	one individualized compound I	Flumetover
D-61	one individualized compound I	Fluopicolide
D-62	one individualized compound I	Fluopyram
D-63	one individualized compound I	Zoxamide
D-64	one individualized compound I	Carpropamid
D-65	one individualized compound I	Diclocymet
D-66	one individualized compound I	Mandipropamid
D-67	one individualized compound I	Oxytetracyclin
D-68	one individualized compound I	Silthiofam
D-69	one individualized compound I	N-(6-methoxy-pyridin-3-yl)
D-03		cyclopropanecarboxylic acid amide
D-70	one individualized compound I	Azaconazole
D-71	one individualized compound I	Bitertanol
D-72	one individualized compound I	Bromuconazole
D-73	one individualized compound I	Cyproconazole
D-74	one individualized compound I	Difenoconazole
D-75	one individualized compound I	Diniconazole
D-76	one individualized compound I	Diniconazole-M
D-77	one individualized compound I	Epoxiconazole
D-78	one individualized compound I	Fenbuconazole
D-79	one individualized compound I	Fluquinconazole
D-80	one individualized compound I	Flusilazole
D-81	one individualized compound I	Flutriafol

Mixture	Component 1	Component 2		
D-82	one individualized compound I	Hexaconazol		
D-83	one individualized compound I	Imibenconazole		
D-84	one individualized compound I	Ipconazole		
D-85	one individualized compound I	Metconazole		
D-86	one individualized compound I	Myclobutanil		
D-87	one individualized compound I	Oxpoconazol		
D-88	one individualized compound I	Paclobutrazol		
D-89	one individualized compound I	Penconazole		
D-90	one individualized compound I	Propiconazole		
D-91	one individualized compound I	Prothioconazole		
D-92	one individualized compound I	Simeconazole		
D-93	one individualized compound I	Tebuconazole		
D-94	one individualized compound I	Tetraconazole		
D-95	one individualized compound I	Triadimefon		
D-96	one individualized compound I	Triadimenol		
D-97	one individualized compound I	Triticonazole		
D-98	one individualized compound I	Uniconazole		
		1-[rel-(2S;3R)-3-(2-chlorophenyl)-		
D-99	one individualized compound I	2-(2,4-difluorophenyl)-oxiranylmethyl]-		
		5-thiocyanato-1H-[1,2,4]triazole,		
		2-[rel-(2S;3R)-3-(2-chlorophenyl)-		
D-100	one individualized compound l	2-(2,4-difluorophenyl)-oxiranylmethyl]-		
		2H-[1,2,4]triazole-3-thiol		
D-101	one individualized compound I	Cyazofamid		
D-102	one individualized compound I	Amisulbrom		
D-103	one individualized compound I	Imazalil		
D-104	one individualized compound I	Imazalil-sulfate		
D-105	one individualized compound I	Pefurazoate		
D-106	one individualized compound I	Prochloraz		
D-107	one individualized compound I	Triflumizole		
D-108	one individualized compound I	Benomyl		
D-109	one individualized compound I	Carbendazim		
D-110	one individualized compound I	Fuberidazole		
D-111	one individualized compound I	Thiabendazole		
D-112	one individualized compound I	Ethaboxam		
D-113	one individualized compound I	Etridiazole		
D-114	one individualized compound I	Hymexazole		
		2-(4-Chloro-phenyl)-N-[4-(3,4-dimeth-		
D-115	one individualized compound I	oxy-phenyl)-isoxazol-5-yl]-2-prop-2-yn-		
		yloxy-acetamide		
D-116	one individualized compound I	Fluazinam		
D-117	one individualized compound I	Pyrifenox		

Mixture	Component 1	Component 2		
D 440		3-[5-(4-Chloro-phenyl)-2,3-dimethyl-is-		
D-118	one individualized compound l	oxazolidin-3-yl]-pyridine (Pyrisoxazole)		
D 110	and individualized compared I	3-[5-(4-Methyl-phenyl)-2,3-dimethyl-		
D-119	one individualized compound l	isoxazolidin-3-yl]-pyridine		
D-120	one individualized compound I	Bupirimate		
D-121	one individualized compound I	Cyprodinil		
D-122	one individualized compound I	5-Fluorocytosine		
D-123	one individualized compound l	5-Fluoro-2-(p-tolylmethoxy)pyrimidin-		
D-123	one marvidualized compound i	4-amine		
D-124	one individualized compound I	5-Fluoro-2-(4-fluorophenylmethoxy)-		
D-124	one marvidualized compound i	pyrimidin-4-amine		
D-125	one individualized compound I	Diflumetorim		
		(5,8-Difluoroquinazolin-4-yl)-{2-[2-fluo-		
D-126	one individualized compound I	ro-4-(4-trifluoromethylpyridin-2-yloxy)-		
		phenyl]-ethyl}-amine		
D-127	one individualized compound I	Fenarimol		
D-128	one individualized compound I	Ferimzone		
D-129	one individualized compound I	Mepanipyrim		
D-130	one individualized compound I	Nitrapyrin		
D-131	one individualized compound I	Nuarimol		
D-132	one individualized compound I	Pyrimethanil		
D-133	one individualized compound I	Triforine		
D-134	one individualized compound I	Fenpiclonil		
D-135	one individualized compound I	Fludioxonil		
D-136	one individualized compound I	Aldimorph		
D-137	one individualized compound I	Dodemorph		
D-138	one individualized compound I	Dodemorph-acetate		
D-139	one individualized compound I	Fenpropimorph		
D-140	one individualized compound I	Tridemorph		
D-141	one individualized compound I	Fenpropidin		
D-142	one individualized compound I	Fluoroimid		
D-143	one individualized compound I	Iprodione		
D-144	one individualized compound I	Procymidone		
D-145	one individualized compound I	Vinclozolin		
D-146	one individualized compound I	Famoxadone		
D-147	one individualized compound I	Fenamidone		
D-148	one individualized compound I	Flutianil		
D-149	one individualized compound I	Octhilinone		
D-150	one individualized compound I	Probenazole		
D-151	one individualized compound I	Fenpyrazamine		
D-152	one individualized compound I	Acibenzolar-S-methyl		
D-153	one individualized compound I	Ametoctradin		

Mixture	Component 1	Component 2	
D-154	one individualized compound I	Amisulbrom	
		[(3S,6S,7R,8R)-8-benzyl-3-[(3-isobuty-	
D-155	one individualized compound I	ryloxymethoxy-4-methoxypyridine-	
D-133	one individualized compound I	2-carbonyl)amino]-6-methyl-4,9-dioxo-	
		[1,5]dioxonan-7-yl] 2-methylpropanoate	
		[(3S,6S,7R,8R)-8-benzyl-3-[(3-acetoxy-	
D-156	one individualized compound l	4-methoxy-pyridine-2-carbonyl)amino]-	
D-130	one marvidualized compound i	6-methyl-4,9-dioxo-1,5-dioxonan-7-yl]	
		2-methylpropanoate	
		[(3S,6S,7R,8R)-8-benzyl-3-[[3-(acet-	
D-157	one individualized compound l	oxymethoxy)-4-methoxy-pyridine-	
D-137	one marvidualized compound i	2-carbonyl]amino]-6-methyl-4,9-dioxo-	
		1,5-dioxonan-7-yl] 2-methylpropanoate	
		[(3S,6S,7R,8R)-8-benzyl-3-[(3-isobut-	
D-158	one individualized compound l	oxycarbonyloxy-4-methoxy-pyridine-	
D-130	one marvidualized compodita i	2-carbonyl)amino]-6-methyl-4,9-dioxo-	
		1,5-dioxonan-7-yl] 2-methylpropanoate	
		[(3S,6S,7R,8R)-8-benzyl-3-[[3-(1,3-ben-	
		zodioxol-5-ylmethoxy)-4-methoxy-pyri-	
D-159	one individualized compound I	dine-2-carbonyl]amino]-6-methyl-4,9-di-	
		oxo-1,5-dioxonan-7-yl] 2-methyl-	
		propanoate	
		(3S,6S,7R,8R)-3-[[(3-hydroxy-4-meth-	
D-160	one individualized compound I	oxy-2-pyridinyl)carbonyl]amino]-	
D 100	one marriadanzoa compodna i	6-methyl-4,9-dioxo-8-(phenylmethyl)-	
		1,5-dioxonan-7-yl 2-methylpropanoate	
D-161	one individualized compound I	Anilazin	
D-162	one individualized compound I	Blasticidin-S	
D-163	one individualized compound I	Captafol	
D-164	one individualized compound I	Captan	
D-165	one individualized compound I	Chinomethionat	
D-166	one individualized compound I	Dazomet	
D-167	one individualized compound I	Debacarb	
D-168	one individualized compound I	Diclomezine	
D-169	one individualized compound I	Difenzoquat,	
D-170	one individualized compound I	Difenzoquat-methylsulfate	
D-171	one individualized compound I	Fenoxanil	
D-172	one individualized compound I	Folpet	
D-173	one individualized compound I	Oxolinsäure	
D-174	one individualized compound I	Piperalin	
D-175	one individualized compound I	Proquinazid	
D-176	one individualized compound I	Pyroquilon	

Mixture	Component 1	Component 2		
D-177	one individualized compound I	Quinoxyfen		
D-178	one individualized compound I	Triazoxid		
D-179	one individualized compound I	Tricyclazole		
D 400		2-Butoxy-6-iodo-3-propyl-chromen-4-		
D-180	one individualized compound I	one		
D 404		5-Chloro-1-(4,6-dimethoxy-pyrimidin-2-		
D-181	one individualized compound I	yl)-2-methyl-1H-benzoimidazole		
		5-Chloro-7-(4-methyl-piperidin-1-yl)-		
D-182	one individualized compound I	6-(2,4,6-trifluoro-phenyl)-[1,2,4]tri-		
		azolo[1,5-a]pyrimidine		
D-183	one individualized compound I	Ferbam		
D-184	one individualized compound I	Mancozeb		
D-185	one individualized compound I	Maneb		
D-186	one individualized compound I	Metam		
D-187	one individualized compound I	Methasulphocarb		
D-188	one individualized compound I	Metiram		
D-189	one individualized compound I	Propineb		
D-190	one individualized compound I	Thiram		
D-191	one individualized compound I	Zineb		
D-192	one individualized compound I	Ziram		
D-193	one individualized compound I	Diethofencarb		
D-194	one individualized compound I	Benthiavalicarb		
D-195	one individualized compound I	Iprovalicarb		
D-196	one individualized compound I	Propamocarb		
D-197	one individualized compound I	Propamocarb hydrochlorid		
D-198	one individualized compound I	Valifenalate		
		N-(1-(1-(4-cyanophenyl)ethanesulfon-		
D-199	one individualized compound I	yl)-but-2-yl) carbamic acid-(4-fluoro-		
		phenyl) ester		
D-200	one individualized compound I	Dodine		
D-201	one individualized compound I	Dodine free base		
D-202	one individualized compound I	Guazatine		
D-203	one individualized compound I	Guazatine-acetate		
D-204	one individualized compound I	Iminoctadine		
D-205	one individualized compound I	Iminoctadine-triacetate		
D-206	one individualized compound I	Iminoctadine-tris(albesilate)		
D-207	one individualized compound I	Kasugamycin		
D-208	one individualized compound I	Kasugamycin-hydrochloride-hydrate		
D-209	one individualized compound I	Polyoxine		
D-210	one individualized compound I	Streptomycin		
D-211	one individualized compound I	Validamycin A		
D-212	one individualized compound I	Binapacryl		

Mixture	Component 1	Component 2		
D-213	one individualized compound I	Dicloran		
D-214	one individualized compound I	Dinobuton		
D-215	one individualized compound I	Dinocap		
D-216	one individualized compound I	Nitrothal-isopropyl		
D-217	one individualized compound I	Tecnazen		
D-218	one individualized compound I	Fentin salts		
D-219	one individualized compound I	Dithianon		
		2,6-dimethyl-1H,5H-[1,4]dithiino		
D-220	one individualized compound I	[2,3-c:5,6-c']dipyrrole-		
		1,3,5,7(2H,6H)-tetraone		
D-221	one individualized compound I	Isoprothiolane		
D-222	one individualized compound I	Edifenphos		
D-223	one individualized compound I	Fosetyl, Fosetyl-aluminium		
D-224	one individualized compound I	Iprobenfos		
D 205		Phosphorous acid (H ₃ PO ₃) and		
D-225	one individualized compound I	derivatives		
D-226	one individualized compound I	Pyrazophos		
D-227	one individualized compound I	Tolclofos-methyl		
D-228	one individualized compound I	Chlorothalonil		
D-229	one individualized compound I	Dichlofluanid		
D-230	one individualized compound I	Dichlorophen		
D-231	one individualized compound I	Flusulfamide		
D-232	one individualized compound I	Hexachlorbenzene		
D-233	one individualized compound I	Pencycuron		
D-234	one individualized compound I	Pentachlorophenol and salts		
D-235	one individualized compound I	Phthalide		
D-236	one individualized compound I	Quintozene		
D-237	one individualized compound I	Thiophanate Methyl		
D-238	one individualized compound I	Tolylfluanid		
D-239	and individualized compound I	N-(4-chloro-2-nitro-phenyl)-N-ethyl-		
D-239	one individualized compound I	4-methyl-benzenesulfonamide		
D-240	one individualized compound I	Bordeaux mixture		
D-241	one individualized compound I	Copper acetate		
D-242	one individualized compound I	Copper hydroxide		
D-243	one individualized compound I	Copper oxychloride		
D-244	one individualized compound I	basic Copper sulfate		
D-245	one individualized compound I	Sulfur		
D-246	one individualized compound I	Biphenyl		
D-247	one individualized compound I	Bronopol		
D-248	one individualized compound I	Cyflufenamid		
D-249	one individualized compound I	Cymoxanil		
D-250	one individualized compound I	Diphenylamin		

Mixture	Component 1	Component 2	
D-251	one individualized compound I	Metrafenone	
D-252	one individualized compound I	Pyriofenone	
D-253	one individualized compound I	Mildiomycin	
D-254	one individualized compound I	Oxin-copper	
D-255	one individualized compound I	Oxathiapiprolin	
D-256	one individualized compound I	Prohexadione calcium	
D-257	one individualized compound I	Spiroxamine	
D-258	one individualized compound I	Tebufloquin	
D-259	one individualized compound I	Tolylfluanid	
		N-(Cyclopropylmethoxyimino-(6-	
D-260	one individualized compound I	difluoromethoxy-2,3-difluoro-phenyl)-	
		methyl)-2-phenyl acetamide	
		N'-(4-(4-chloro-3-trifluoromethyl-	
D-261	one individualized compound I	phenoxy)-2,5-dimethyl-phenyl)-N-ethyl-	
		N-methyl formamidine	
		N'-(4-(4-fluoro-3-trifluoromethyl-	
D-262	one individualized compound I	phenoxy)-2,5-dimethyl-phenyl)-N-ethyl-	
		N-methyl formamidine	
		N'-(2-methyl-5-trifluoromethyl-4-(3-tri-	
D-263	one individualized compound I	methylsilanyl-propoxy)-phenyl)-N-ethyl-	
		N-methyl formamidine	
		N'-(5-difluoromethyl-2-methyl-4-(3-tri-	
D-264	one individualized compound I	methylsilanyl-propoxy)-phenyl)-N-ethyl-	
		N-methyl formamidine	
D-265	one individualized compound I	Methoxy-acetic acid 6-tert-butyl-8-	
	·	fluoro-2,3-dimethyl-quinolin-4-yl ester	
D-266	one individualized compound I	Bacillus subtilis NRRL No. B-21661	
D-267	one individualized compound I	Bacillus pumilus NRRL No. B-30087	
D-268	one individualized compound I	Ulocladium oudemansii	
D-269	one individualized compound I	Carbaryl	
D-270	one individualized compound I	Carbofuran	
D-271	one individualized compound I	Carbosulfan	
D-272	one individualized compound I	Methomylthiodicarb	
D-273	one individualized compound I	Bifenthrin	
D-274	one individualized compound I	Cyfluthrin	
D-275	one individualized compound I	Cypermethrin	
D-276	one individualized compound I	alpha-Cypermethrin	
D-277	one individualized compound I	zeta-Cypermethrin	
D-278	one individualized compound I	Deltamethrin	
D-279	one individualized compound I	Esfenvalerate	
D-280	one individualized compound I	Lambda-cyhalothrin	
D-281	one individualized compound I	Permethrin	

Mixture	Component 1	Component 2		
D-282	one individualized compound I	Tefluthrin		
D-283	one individualized compound I	Diflubenzuron		
D-284	one individualized compound I	Flufenoxuron		
D-285	one individualized compound I	Lufenuron		
D-286	one individualized compound I	Teflubenzuron		
D-287	one individualized compound I	Spirotetramate		
D-288	one individualized compound I	Clothianidin		
D-289	one individualized compound I	Dinotefuran		
D-290	one individualized compound I	Imidacloprid		
D-291	one individualized compound I	Thiamethoxam		
D-292	one individualized compound I	Flupyradifurone		
D-293	one individualized compound I	Acetamiprid		
D-294	one individualized compound I	Thiacloprid		
D-295	one individualized compound I	Endosulfan		
D-296	one individualized compound I	Fipronil		
D-297	one individualized compound I	Abamectin		
D-298	one individualized compound I	Emamectin		
D-299	one individualized compound I	Spinosad		
D-300	one individualized compound I	Spinetoram		
D-301	one individualized compound I	Hydramethylnon		
D-302	one individualized compound I	Chlorfenapyr		
D-303	one individualized compound I	Fenbutatin oxide		
D-304	one individualized compound I	Indoxacarb		
D-305	one individualized compound I	Metaflumizone		
D-306	one individualized compound I	Flonicamid		
D-307	one individualized compound I	Lubendiamide		
D-308	one individualized compound I	Chlorantraniliprole		
D-309	one individualized compound I	Cyazypyr (HGW86)		
D-310	one individualized compound I	Cyflumetofen		
D-311	one individualized compound I	Acetochlor		
D-312	one individualized compound I	Dimethenamid		
D-313	one individualized compound I	metolachlor		
D-314	one individualized compound I	Metazachlor		
D-315	one individualized compound I	Glyphosate		
D-316	one individualized compound I	Glufosinate		
D-317	one individualized compound I	Sulfosate		
D-318	one individualized compound I	Clodinafop		
D-319	one individualized compound I	Fenoxaprop		
D-320	one individualized compound I	Fluazifop		
D-321	one individualized compound I	Haloxyfop		
D-322	one individualized compound I	Paraquat		
D-323	one individualized compound I	Phenmedipham		

Mixture	Component 1	Component 2			
D-324	one individualized compound I	Clethodim			
D-325	one individualized compound I	Cycloxydim			
D-326	one individualized compound I	Profoxydim			
D-327	one individualized compound I	Sethoxydim			
D-328	one individualized compound I	Tepraloxydim			
D-329	one individualized compound I	Pendimethalin			
D-330	one individualized compound I	Prodiamine			
D-331	one individualized compound I	Trifluralin			
D-332	one individualized compound I	Acifluorfen			
D-333	one individualized compound I	Bromoxynil			
D-334	one individualized compound I	Imazamethabenz			
D-335	one individualized compound I	Imazamox			
D-336	one individualized compound I	Imazapic			
D-337	one individualized compound I	Imazapyr			
D-338	one individualized compound I	Imazaquin			
D-339	one individualized compound I	Imazethapyr			
D-340	one individualized compound I	2,4-Dichlorophenoxyacetic acid (2,4-D)			
D-341	one individualized compound I	Chloridazon			
D-342	one individualized compound I	Clopyralid			
D-343	one individualized compound I	Fluroxypyr			
D-344	one individualized compound I	Picloram			
D-345	one individualized compound I	Picolinafen			
D-346	one individualized compound I	Bensulfuron			
D-347	one individualized compound I	Chlorimuron-ethyl			
D-348	one individualized compound I	Cyclosulfamuron			
D-349	one individualized compound I	lodosulfuron			
D-350	one individualized compound I	Mesosulfuron			
D-351	one individualized compound I	Metsulfuron-methyl			
D-352	one individualized compound I	Nicosulfuron			
D-353	one individualized compound I	Rimsulfuron			
D-354	one individualized compound I	Triflusulfuron			
D-355	one individualized compound I	Atrazine			
D-356	one individualized compound I	Hexazinone			
D-357	one individualized compound I	Diuron			
D-358	one individualized compound I	Florasulam			
D-359	one individualized compound I	Pyroxasulfone			
D-360	one individualized compound I	Bentazone			
D-361	one individualized compound I	Cinidon-ethyl			
D-362	one individualized compound I	Cinmethylin			
D-363	one individualized compound I	Dicamba			
D-364	one individualized compound I	Diflufenzopyr			
D-365	one individualized compound I	Quinclorac			

Mixture	Component 1	Component 2		
D-366	one individualized compound l	Quinmerac		
D-367	one individualized compound I	Mesotrione		
D-368	one individualized compound l	Saflufenacil		
D-369	one individualized compound I	Topramezone		
		1,1'-[(3S,4R,4aR,6S,6aS,12R,12aS,		
		12bS)-4-[[(2-cyclopropylacetyl)oxy]me-		
		thyl]-1,3,4,4a,5,6,6a,12,12a,12b-deca-		
D-370	one individualized compound I			
		11-oxo-9-(3-pyridinyl)-2H,11H-naph-		
		tho[2,1-b]pyrano[3,4-e]pyran-3,6-diyl]		
		cyclopropaneacetic acid ester		

The active substances referred to as component 2, their preparation and their activity against harmful fungi is known (cf.: http://www.alanwood.net/pesticides/); these substances are commercially available. The compounds described by IUPAC nomenclature, their preparation and their fungicidal activity are also known (cf. Can. J. Plant Sci. 48(6), 587-94, 1968; EP-A 141 317; EP-A 152 031; EP-A 226 917; EP-A 243 970; EP-A 256 503; EP-A 428 941; EP-A 532 022; EP-A 1 028 125; EP-A 1 035 122; EP-A 1 201 648; EP-A 1 122 244, JP 2002316902; DE 19650197; DE 10021412; DE 102005009458; US 3,296,272; US 3,325,503; WO 98/46608; WO 99/14187; WO 99/24413; WO 99/27783; WO 00/29404; WO 00/46148; WO 00/65913; WO 01/54501; WO 01/56358; WO 02/22583; WO 02/40431; WO 03/10149; WO 03/11853; WO 03/14103; WO 03/16286; WO 03/53145; WO 03/61388; WO 03/66609; WO 03/74491; WO 04/49804; WO 04/83193; WO 05/120234; WO 05/123689; WO 05/123690; WO 05/63721; WO 05/87772; WO 05/87773; WO 06/15866; WO 06/87325; WO 06/87343; WO 07/82098; WO 07/90624, WO 11/028657).

The mixtures of active substances can be prepared as compositions comprising besides the active ingridients at least one inert ingredient by usual means, e. g. by the means given for the compositions of compounds I.

Concerning usual ingredients of such compositions reference is made to the explanations given for the compositions containing compounds I.

The mixtures of active substances according to the present invention are suitable as fungicides, as are the compounds of formula I. They are distinguished by an outstanding effectiveness against a broad spectrum of phytopathogenic fungi, especially from the classes of the Ascomycetes, Basidiomycetes, Deuteromycetes and Peronosporomycetes (syn. Oomycetes). In addition, it is refered to the explanations regarding the fungicidal activity of the compounds and the compositions containing compounds I, respectively.

Synthesis examples

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With appropriate modification of the starting materials, the procedures given in the synthesis examples below were used to obtain further compounds I. The compounds produced in this manner are listed in Table V below including corresponding physical data. 2-(2-Chloro-4-hydroxyphenyl)ethylamine-*tert*-butyl carbamate was prepared as described in WO 2004026305

A1. 2-(2-Fluoro-4-methoxyphenyl)ethylamine hydrochloride was prepared from 2-fluoro-4-methoxybenzaldehyde as described in US 20110054173 A1.

Example 1: Preparation of 2-(2-fluoro-4-hydroxyphenyl)ethylamine-tert-butyl carbamate

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2-(2-Fluoro-4-methoxyphenyl)ethylamine hydrochloride (270 g, 1.6 mol) was carefully added portionwise to 48% HBr (1.5 L) and stirred for 4 h at 140°C. The reaction solution was reduced in vacuo, then acetonitrile (1 L) was added to the residue and was evaporated to dryness. The crude product was stirred in diisopropylether and recovered by filtration to afford 222 g (940 mmol, 59%) of desired phenol. The purified phenol was dissolved in dichloromethane (DCM, 1.5 L) to which was added triethylamine (275 mL), *tert*-butyloxycarbonyl anhydride (215 g, 990 mmol) in a solution of DCM (500 mL), and was stirred for 30 min at room temperature. The reaction solution was washed with water, dried over Na₂SO₄, then concentrated in vacuo. The residue was purified by flash silica column chromatography (4:1 cyclohexane: MTBE) to afford 220 g (860 mmol, 92%) of the desired product.

Example 2: Preparation of 2-[4-[[2-(trifluoromethyl)-4-pyridyl]oxy]phenyl]ethanamine hydrochloride

To a solution of N-*tert*-butyloxycarbonyl-protected tyramine (130 g, 550 mmol), potassium carbonate (76 g, 550 mmol), and catalytic amounts of potassium iodide in N-methyl pyrrolidone (NMP, 400 mL) that was stirred for 10 minutes at room temperature was added 4-chloro-2-trifluoromethylpyridine (100 g, 550 mmol). The reaction mixture was then heated to 160 °C for 6 h, cooled, poured into water and extracted with methyl-*tert*-butylether (MTBE, 3x). The combined organic layers were washed with succesivly with 3 N NaOH and water, dried over Na₂SO₄, and reduced in vacuo. The crude residue was purified by flash silica gel column chromatography to afford a 48% (102 g, 265 mmol) yield of N-tert-butyloxycarbonyl-protected 2-[4-[[2-(trifluoromethyl)-4-pyridyl]oxy]phenyl]ethanamine. To a solution of this material in dioxane (200 mL) was added 4 M HCl in dioxane (250 mL). The solution was left overnight to stir at room temperature, which resulted in precipitation of 2-[4-[[2-(trifluoromethyl)-4-pyridyl]oxy]phenyl]ethanamine hydrochloride. The reaction solution was evaporated and the residue was stirred with pentane and filtered to provide 100% (37 g, 104 mmol) of the desired amine hydrochloride.

Example 3: Preparation of 6-(1-fluoroethyl)-N-[2-[2-fluoro-4-[[2-(trifluoromethyl)-4-pyridyl]oxy]phenyl]ethyl]-2-methyl-pyrimidin-4-amine (V-6)

To a solution of 2-[2-fluoro-4-[[2-(trifluoromethyl)-4-pyridyl]oxy]phenyl]ethanamine hydrochloride (311 mg, 0.83 mmol) in N-methyl-2-pyrrolidone (4 mL) was added diisopropylethylamine (0.66 mL, 3.78 mmol). The solution was stirred for 5 min at room temperature at which time 4-chloro-6-(1-fluoroethyl)- 2-methyl-pyrimidine (120 mg, 0.69 mmol) was added. The reaction mixture was stirred at 80°C overnight and was then allowed to cool to room temperature. Water was added and the mixture was extracted with MTBE (3x). The combined organic layers were washed with water, dried over Na₂SO₄, and concentrated in

vacuo. The residue was purified by flash silica column chromatography to provide 100 mg (0.21 mmol, 30%) of the light yellow oily product.

The compounds listed in Table V have been prepared in an analogous manner.

Table V: Compounds V-1 to V-28 of formula I.A1 as defined above

ex. no	Ra2	R ^{a5}	R ^{a6}	(R ^b) _n *	Het	HPLC	m.p. (°C)
						R _t (min)	
V-1	CH ₃	Н	Н	o-F; n = 1	H-1	3,012	99
V-2	CF ₃	Н	Н	o-F; n = 1	H-1	4	
V-3	CH ₃	COOEt	Н	n = 0	H-2	1,018	
V-4	CH ₃	OCH ₃	Н	n = 0	H-2	0,958	105
V-5	CH ₃	OCH ₃	Н	o-F; n = 1	H-2	2,777	
V-6	CH ₃	Н	CHFCH ₃	o-F; n = 1	H-2	0,963	
V-7	CH ₃	Н	CHFCH ₃	n = 0	H-2	0,954	
V-8	OCH ₃	Н	Н	o-F; n = 1	H-2	1,006	
V-9	CH ₃	CI	Н	o-F; n = 1	H-2	0,96	135
V-10	CH ₃	OCH ₃	Н	n = 0	H-1	2,946	127
V-11	CH ₃	OCH ₃	Н	o-F; n = 1	H-1	3,008	
V-12	OCH ₃	CI	OCH ₃	n = 0	H-1	1,417	
V-13	OCH ₃	CI	OCH ₃	o-F; n = 1	H-2		
V-14	OCH ₃	CI	OCH ₃	n = 0	H-2	1,389	
V-15	CH ₃	CI	CH ₃	o-F; n = 1	H-1	1,029	
V-16	CH ₃	CI	CH ₃	o-F; n = 1	H-2	0,971	108
V-17	CH ₃	CI	CI	o-F; n = 1	H-1	1,432	124
V-18	CH ₃	CI	CI	o-F; n = 1	H-2	1,375	
V-19	CH ₃	COOEt	CH ₂ CH ₃	o-F; n = 1	H-1	1,101	
V-20	CH ₃	COOEt	CH ₂ CH ₃	o-F; n = 1	H-2	1,04	
V-21	CF ₃	OCH ₃	Н	o-F; n = 1	H-1	1,356	
V-22	OCH ₃	Н	Н	o-F; n = 1	H-1	1,004	
V-23	OCH ₃	F	Н	o-F; n = 1	H-2	0,995	
V-24	CI	CI	OCH ₃	o-F; n = 1	H-1	1,462	
V-25	CH ₃	CH ₃	CI	o-F; n = 1	H-1	1,172	106
V-26	OCH ₃	Н	Н	m-OCH ₃ ; n = 1	H-2	0,938	
V-27	CH ₃	CI	H	n = 0	H-1	_	
V-27 V-28	CH ₃	CI	H	n = 0	H-16	0,963	
V-20	СП3		⊓	11 – 0	מו-ח	0,963	

^{*} The position of R^b on the phenyl ring is defined relative to the CR^1R^2 -moiety bound to the phenyl ring as being in ortho (o-) or meta (m-) position. n = 0 indicates that no substituent R^b is present on the phenyl ring. m.p. = melting point (°C). HPLC-2: HPLC-column Kinetex XB C18 1,7 μ (50 x 2,1 mm); eluent: acetonitrile / water + 0.1% TFA (gradient from 5:95 to 100 : 0 in 1.5 min at 60°C, flow gradient from 0.8 to 1.0 ml/min in 1.5 min). MS: Quadrupol Electrospray lonisation, 80 V (positive mode).

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Biological examples for fungicidal activity

The fungicidal action of the compounds I was demonstrated by the following experiments:

A. Glass house trials

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The spray solutions were prepared in several steps: The stock solution were prepared: a mixture of acetone and/or dimethylsulfoxide and the wetting agent/emulsifier Wettol, which is based on ethoxylated alkylphenoles, in a relation (volume) solvent-emulsifier of 99 to 1 was added to 25 mg of the compound to give a total of 5 ml. Water was then added to total volume of 100 ml.

This stock solution was diluted with the described solvent-emulsifier-water mixture to the given concentration.

After the final cultivation period, the extent of fungal attack on the leaves was visually assessed as % diseased leaf area.

Use example 1: Preventative control of leaf blotch on wheat caused by Septoria tritici

Leaves of pot-grown wheat seedling were sprayed to run-off with an aqueous suspension of the active compound or their mixture, prepared as described. The plants were allowed to air-dry. At the following day the plants were inoculated with an aqueous spore suspension of *Septoria tritici*. Then the trial plants were immediately transferred to a humid chamber at 18 to 22°C and a relative humidity close to 100%. After 4 days the plants were transferred to a chamber with 18 to 22°C and a relative humidity close to 70% and kept there for 4 weeks.

In this test, the plants which had been treated with 250 ppm of the active compound V-1, V-4, V-5, V-6, V-7, V-8, V-10, V-11, V-12, V-14, V-15, V-19, V-20, V-22, V-23, V-24 or V-25 showed a diseased leaf area of at most 10%, whereas the untreated plants showed 80% diseased leaf area.

Use example 2: Control of late blight on tomatoes caused by Phytophthora infestans

Young seedlings of tomato plants were grown in pots. These plants were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient or their mixture mentioned in the table below. The next day, the treated plants were inoculated with an aqueous suspension of sporangia of *Phytophthora infestans*. After inoculation, the trial plants were immediately transferred to a humid chamber and kept for 6 days at 18 to 20°C and a relative humidity close to 100%.

In this test, the plants which had been treated with 250 ppm of the active compound V-5, V-7, V-10, V-15, V-25, V-27 or V-28 showed a diseased leaf area of at most 15%, whereas the untreated plants showed 80% diseased leaf area.

Use example 3: Protective control of soy bean rust on soy beans caused by *Phakopsora pachyrhizi* Leaves of pot-grown soybean seedlings were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient or their mixture as described below. The plants were allowed to air-dry. The trial plants were cultivated for 1 day in a greenhouse chamber at 23 to 27°C and a relative humidity between 60 and 80%. Then the plants were inoculated with spores of *Phakopsora pachyrhizi*. To ensure the success the artificial inoculation, the plants were transferred to a humid chamber with a relative humidity of about 95% and 20 to 24°C for 24 h. The trial plants

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were cultivated for fourteen days in a greenhouse chamber at 23 to 27°C and a relative humidity between 60 and 80%.

In this test, the plants which had been treated with 250 ppm of the active compound V-1, V-5, V-6, V-7, V-8, V-10, V-11, V-12, V-15, V-16, V-19, V-20, V-25 or V-26 showed a diseased leaf area of at most 15%, whereas the untreated plants showed 90% diseased leaf area.

Use example 4: Preventative control of brown rust on wheat caused by Puccinia recondita

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The first two developed leaves of pot-grown wheat seedling were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient or their mixture as described below. The next day the plants were inoculated with spores of *Puccinia recondita*. To ensure the success the artificial inoculation, the plants were transferred to a humid chamber without light and a relative humidity of 95 to 99% and 20 to

24°C for 24 h. Then the trial plants were cultivated for 6 days in a greenhouse chamber at 20 to 24°C and a relative humidity between 65 and 70 %.

In this test, the plants which had been treated with 250 ppm of the active compound V-2, V-10, V-11, V-15 or V-25 showed a diseased leaf area of at most 15%, whereas the untreated plants showed 90% diseased leaf area.

Use example 5: Preventative control of brown rust on wheat caused by Puccinia recondita

The first two developed leaves of pot-grown wheat seedling were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient or their mixture as described below. Seven days later the plants were inoculated with spores of *Puccinia recondita*. To ensure the success the artificial inoculation, the plants were transferred to a humid chamber without light and a relative humidity of 95 to 99% and 20 to 24°C for 24 h. Then the trial plants were cultivated for 6 days in a greenhouse chamber at 20 to 24°C and a relative humidity between 65 and 70 %.

In this test, the plants which had been treated with 250 ppm of the active compound V-1, V-2, V-5, V-6, V-7, V-8, V-9, V-13, V-15 or V-16 showed a diseased leaf area of at most 10%, whereas the untreated plants showed 80% diseased leaf area.

30 Use Example 6: Control of powdery mildew on wheat caused by *Blumeria graminis* f. sp. *tritici*The first fully developed leaves of pot grown wheat were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient or their mixture mentioned in the table below. Seven days later the treated plants were inoculated with spores of *Blumeria graminis* f. sp. *tritici* (= syn. *Erysiphe garminis* f. sp. *tritici*) by shaking heavily infestated stock plants over the

35 treated pots. The they were kept in the greenhouse for 7 days at 21 to 23°C and a relative humidity between 40 to 70%.

In this test, the plants which had been treated with 250 ppm of the active compound V-2, V-5, V-6, V-9 or V-13 showed a diseased leaf area of at most 10%, whereas the untreated plants showed 80% diseased leaf area.

Use example 7: Protective control of powdery mildew on cucumber

Cucumber seedlings were grown in pots to the 2 leaf stage. The plants were sprayed to runoff with an agueous suspension, containing the concentration of active ingredient or their mixture mentioned in the table below. The next day the treated plants were inoculated with an aqueous spore suspension of cucumber powdery mildew (*Sphaerotheca fuliginea*). Then the trial plants were cultivated for 8 days in a greenhouse at temperatures between 20 and 24°C and a relative humidity between 60 and 80%.

In this test, the plants which had been treated with 250 ppm of the active compound V-3, V-5, V-6, V-7, V-8, V-9, V-11, V-15, V-16, V-17, V-18 or V-20 showed a diseased leaf area of at most 10%, whereas the untreated plants showed 90% diseased leaf area.

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Use example 8: Fungicidal control of grape downy mildew caused by *Plasmopara viticola*Grape cuttings were grown in pots to the 4 to 5 leaf stage. These plants were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient or their mixture mentioned in the table below. The plants were allowed to air-dry. The next day they were inoculated with an aqueous spore suspension of *Plasmopara viticola* by spraying it at the lower leaf-side. Then the trial plants were immediately transferred for 24 h to a humid chamber with 22 to 24°C and a relative humidity close to 100%. For a period of 5 days, cultivation followed in a greenhouse at 20 to 25°C and a relative humidity about 50 to 80%. To stimulate the outbreak of the disease symptoms, the plants were transferred to a humid chamber again for 24 hours. Then the extent of fungal attack on the lower leaf surface was visually assessed as % diseased leaf area.

In this test, the plants which had been treated with 250 ppm of the active compound V-1, V-3, V-5, V-6, V-9, V-10, V-11, V-13 or V-21 showed a diseased leaf area of at most 10%, whereas the untreated plants showed 90% diseased leaf area.

We claim:

1. Compounds of formula I

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wherein:

is halogen, CN, NO₂, OH, SH, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkyl, C₁-C₄-alkylsulfinyl, C₁-C₄-haloalkylsulfinyl, C₁-C₄-haloalkylsulfinyl, C₁-C₄-haloalkylsulfonyl, C₁-C₄-alkylsulfonyl, C₁-C₄-alkoxy-C₁-C₄-alkoxy-C₁-C₄-alkoxy-C₁-C₄-alkoxy-C₁-C₄-alkoxy, C₂-C₄-alkenyl, C₂-C₄-alkynyl, C₂-C₄-haloalkenyl, C₂-C₄-haloalkyloxyl, C₃-C₈-cycloalkyl-C₁-C₄-alkyl, NR^AR^B, C(=O)R', C(=NOR'')R''' or C(=NH)-O-R''';

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Ra5, Ra6 independently of each other are hydrogen, halogen, CN, NO₂, OH, SH, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-haloalkylsulfinyl, C₁-C₄-alkylsulfonyl, C₁-C₄-alkylsulfonyl, C₁-C₄-alkoxy-C₁-C₄-alkyl, C₁-C₄-alkoxy-C₁-C₄-alkoxy, C₂-C₄-alkenyl, C₂-C₄-alkynyl, C₂-C₄-haloalkenyl, C₂-C₄-haloalkyloxyl, C₃-C₈-cycloalkyl, NRAB, C(=O)R', C(=NOR")R" or C(=NH)-O-R";

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 R^A , R^B independently of one another are hydrogen, C_1 - C_4 -alkyl, C_2 - C_4 -alkenyl, C_2 - C_4 -alkynyl, phenyl, benzyl, C_3 - C_8 -cycloalkyl, C_3 - C_8 -cycloalkenyl or $\mathsf{C}(=\mathsf{O})$ - R' ;

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R' is hydrogen, OH, NH₂, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₂-C₄-alkenyl, C₂-C₄-alkynyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylamino or di(C₁-C₄-alkyl)amino;

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R" is hydrogen, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_2 - C_4 -alkenyl, C_2 - C_4 -alkynyl or C_1 - C_4 -alkoxy- C_1 - C_4 -alkyl,

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R''' is hydrogen or C₁-C₄-alkyl;

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R is hydrogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkoxy-C₁-C₄-alkyl, C₁-C₄-alkyl, C₂-C₄-alkyl, C₂-C₄-alkynyl, C₂-C₄-haloalkenyl, C₂-C₄-haloalkynyl, CN, CH₂CN, NR^AR^B or CH₂-O-C(=O)R';

- n indicates the number of substituents R^b on the phenyl ring and n is 0, 1, 2, 3 or 4;
- R^b is halogen, CN, NO₂, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₂-C₄-alkenyl, C₂-C₄-haloalkenyl, C₂-C₄-alkynyl, C₂-C₄-haloalkynyl, NR^AR^B, C(=NOR")R"" or C(=NH)-O-R"", it being possible for n = 2, 3 or 4 that R^b are identical or different;

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- Het is a 5- or 6-membered heteroaryl, wherein the ring member atoms of the heteroaryl include besides carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S and wherein the heteroaryl is unsubstituted or carries 1, 2, 3 or 4 identical or different groups R°:
 - R° is halogen, CN, NO₂, C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkylthio, C₁-C₆-alkylsulfinyl, C₁-C₆-haloalkylsulfinyl, C₁-C₆-haloalkylsulfinyl, C₁-C₆-haloalkylsulfonyl, C₁-C₆-alkoxy-C₁-C₄-alkyl, C₁-C₆-alkoxy-C₁-C₄-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl, NR^AR^B, C(=O)R', C(=NOR")R"'', C(=NH)-O-R"'', C₃-C₈-cycloalkyl, C₃-C₈-cycloalkyl-C₁-C₄-alkyl, phenyl, phenyl-C₁-C₄-alkyl, phenoxy, phenoxy-C₁-C₄-alkyl or a 5- or 6-membered heteroaryl, wherein the ring member atoms of the heteroaryl include besides carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S, and wherein the aforementioned cyclic radicals are unsubstituted or carry 1, 2, 3 or 4 identical or different substituents R^d:
 - R^d is halogen, CN, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy or C₁-C₄-haloalkoxy;

or two radicals R^c that are bound to adjacent ring member atoms of the Het group form together with said ring member atoms a fused 5-, 6- or 7-membered saturated, partially unsaturated or aromatic carbocycle or heterocycle, wherein the ring member atoms of the fused heterocycle include besides carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S, and wherein the fused carbocycle or heterocycle is unsubstituted or carries 1, 2, 3 or 4 identical or different radicals groups R^e:

Re is halogen, CN, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy or C₁-C₄-haloalkoxy;

and the N-oxides and the agriculturally acceptable salts thereof.

2. Compounds according to claim 1, wherein R^{a2} is halogen, CN, C₁-C₂-alkyl, C₁-C₂-alkoxy, C₁-C₂-alkoxy-C₁-C₂-alkyl, C₁-C₂-alkoxy-C₁-C₂-alkoxy or (C₁-C₂-alkoxy)carbonyl.

3. Compounds according to claim 1 or 2, wherein R is hydrogen.

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- 4. Compounds according to any of claims 1 to 3, wherein n is 0 or 1 and R^b is selected from the group of halogen, CN, NO₂, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkyl, C₁-C₄-alkoxy and C₁-C₄-alkoxy-C₁-C₄-alkyl.
- 5. Compounds according to any of claims 1 to 4, wherein Het is selected from pyrimidin-2-yl, pyrimidin-3-yl, pyrimidin-4-yl, pyridin-2-yl, pyridin-3-yl, thiazol-2-yl, pyrazin-2-yl, pyridazin-3-yl, 1,3,5-triazin-2-yl, and 1,2,4-triazin-3-yl.
- 6. Compounds according to any of claims 1 to 5, wherein Het carries 1 or 2 radicals R^c which are selected from F, Cl, Br, CN, C₁-C₂-alkylsulfonyl, C₁-C₂-alkoxycarbonyl, aminocarbonyl, C₁-C₂-alkylaminocarbonyl, di(C₁-C₂-alkyl)aminocarbonyl, C₁-C₂-alkoxy, CF₃, CHF₂, OCF₃ and OCHF₂.
- 7. A process for preparing compounds I as defined in claim 1, which comprises reacting a compound of formula II

wherein R^{a2}, R^{a5} and R^{a6} are as defined in claim 1 and Hal is fluorine, chlorine or bromine, with a compound of formula III

$$(R^b)_n$$

wherein R, R^b, n and Het are as defined in claim 1 in the presence of a base or a catalyst or a combination of a base and a catalyst and in the presence of a solvent.

- 25 8. An agrochemical composition which comprises an auxiliary and at least one compound of formula I or an N-oxide or an agriculturally acceptable salt thereof, according to any of claims 1 to 6.
- 9. An agrochemical composition according to claim 8 comprising at least one further active substance.
 - 10. A method for combating phytopathogenic harmful fungi, which process comprises treating the fungi or the materials, plants, the soil or seeds to be protected against fungal attack,

with an effective amount of at least one compound of formula I of an or an N-oxide or an agriculturally acceptable salt thereof, as defined in any of claims 1 to 6.

11. The use of compounds of formula I, their N-oxides and their agriculturally acceptable salts, as defined in any of claims 1 to 6 for combating phytopathogenic harmful fungi.

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12. Seed comprising a compound of formula I, or an N-oxide or an agriculturally acceptable salt thereof, as defined in any of claims 1 to 6, in an amount of from 0.1 g to 10 kg per 100 kg of seed.

INTERNATIONAL SEARCH REPORT

International application No PCT/EP2013/051838

a. classification of subject matter INV. C07D239/42 C07D4 C07D401/12 C07D403/12 C07D417/12 A01N43/54 A01P3/00 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 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 practicable, search terms used) EPO-Internal, WPI Data, CHEM ABS Data, BEILSTEIN Data C. DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. Category' EP 0 264 217 A2 (UBE INDUSTRIES [JP]; INST 1-12 Χ PHYSICAL & CHEM RES [JP]) 20 April 1988 (1988-04-20) cited in the application the whole document EP 0 665 225 A1 (UBE INDUSTRIES [JP]) Υ 1-12 2 August 1995 (1995-08-02) cited in the application the whole document EP 0 519 211 A1 (HOECHST AG [DE]) 1-12 γ 23 December 1992 (1992-12-23) the whole document X See patent family annex. Further documents are listed in the continuation of Box C. Special categories of cited documents "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 "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive 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 step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be special reason (as specified) considered to involve an inventive step when the document is combined with one or more other such documents, such combination "O" document referring to an oral disclosure, use, exhibition or other being obvious to a person skilled in the art "P" document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 7 March 2013 17/04/2013 Name and mailing address of the ISA/ Authorized officer European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016 Fink, Dieter

INTERNATIONAL SEARCH REPORT

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