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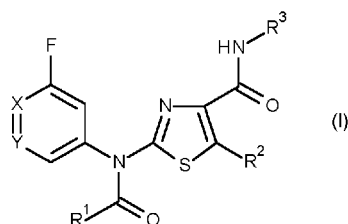
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(54) Title: MICROBIOCIDAL 2-ACYLAMINO-THIAZOLE-4-CARBOXAMIDE DERIVATIVES



(57) Abstract: Compounds of the formula (I) wherein the substituents are as defined in claim 1, useful as pesticides, and especially fungicides.

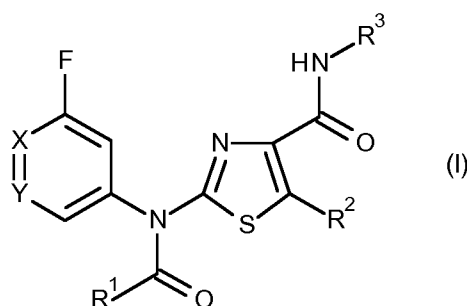


MICROBIOCIDAL 2-ACYLAMINO-THIAZOLE-4-CARBOXAMIDE DERIVATIVES

The present invention relates to microbiocidal thiazole derivatives, e.g., as active ingredients, which have microbiocidal activity, in particular fungicidal activity. The invention also relates to the preparation of these thiazole derivatives, to agrochemical compositions which comprise at least one of the thiazole derivatives and to uses of the thiazole derivatives or compositions thereof in agriculture or horticulture for controlling or preventing the infestation of plants, harvested food crops, seeds or non-living materials by phytopathogenic microorganisms, preferably fungi.

WO 2010/012793 and WO 2017/207362 describe thiazole derivatives as pesticidal agents.

According to the present invention, there is provided a compound of formula (I):



wherein

Y is C-F, C-H or N;

R¹ is hydrogen, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆hydroxyalkyl, C₁-C₆alkoxyC₁-C₆alkyl, C₃-C₈cycloalkyl, C₁-C₆alkoxyC₁-C₃alkoxy, C₁-C₆alkoxycarbonyl, C₁-C₆alkoxycarbonylC₁-C₄alkyl, C₁-C₆alkoxycarbonyloxyC₁-C₄alkyl, C₁-C₆alkylcarbonyloxyC₁-C₄alkyl, C₂-C₆alkenyloxy, C₂-C₆alkynyloxy, C₁-C₆alkylsulfanyl, di(C₁-C₆alkyl)amino, phenyl, phenylC₁-C₃alkyl, phenylC₁-C₃alkoxyC₁-C₃alkyl, phenoxy, or heteroaryl wherein the heteroaryl is a 5- or 6-membered aromatic monocyclic ring comprising 1 or 2 heteroatoms individually selected from nitrogen, oxygen and sulfur;

R² is hydrogen, halogen, cyano, C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄haloalkyl, or HC(O)NH-

R³ is C₁-C₈alkyl, C₁-C₈haloalkyl, C₁-C₈alkoxy, C₃-C₈cycloalkyl, C₃-C₈cycloalkylC₁-C₂alkyl (wherein the cycloalkyl groups are optionally substituted with 1 to 3 groups represented by R⁴), phenyl, phenylC₁-C₂alkyl, heteroaryl, heteroarylC₁-C₂alkyl, wherein the heteroaryl is a 5- or 6-membered aromatic monocyclic ring comprising 1, 2, 3 or 4 heteroatoms individually selected from nitrogen, oxygen and sulfur, heterocyclyl, heterocyclylC₁-C₂alkyl, wherein the heterocyclyl is a 4-, 5- or 6-membered non-aromatic monocyclic ring comprising 1, 2 or 3 heteroatoms individually selected from nitrogen, oxygen and sulfur, or a 5- to 10-membered non-aromatic spirocyclic carbobi- or carbetri-cyclyl ring system optionally comprising 1, 2, 3, 4 or 5 heteroatoms individually selected from nitrogen, oxygen and sulfur, and wherein said spirocyclic carbobi- or carbetri-cyclyl ring systems are each optionally bonded to the rest of the molecule through a C₁-C₂alkylene linker;

R⁴ is halogen, C₁-C₄alkyl, C₁-C₄alkoxy, or C₁-C₄haloalkyl;

X is N or C-H;

or a salt or an N-oxide thereof.

- 5 Wherein the compound of formula (I) is not 2-(N-acetyl-3-fluoro-anilino)-N-isopropyl-5-methyl-thiazole-4-carboxamide or 2-(N-acetyl-3-fluoro-anilino)-5-methyl-N-sec-butyl-thiazole-4-carboxamide.

Surprisingly, it has been found that the novel compounds of formula (I) have, for practical purposes, a very advantageous level of biological activity for protecting plants against diseases that are
10 caused by fungi.

Further to this, it has been found that that the novel compounds of formula (I) wherein R¹ is hydrogen, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆hydroxyalkyl, C₁-C₆alkoxyC₁-C₆alkyl, C₃-C₆cycloalkyl, C₁-C₆alkoxyC₁-C₃alkoxy, C₁-C₆alkoxycarbonyl, C₁-C₆alkoxycarbonylC₁-C₄alkyl, C₁-C₆alkoxycarbonyloxyC₁-C₄alkyl, C₁-C₆alkylcarbonyloxyC₁-C₄alkyl, C₂-C₆alkenyloxy, C₂-C₆alkynyloxy, C₁-C₆alkylsulfanyl, di(C₁-C₆alkyl)amino, phenyl, phenylC₁-C₃alkyl, phenylC₁-C₃alkoxyC₁-C₃alkyl, phenoxy, or heteroaryl, wherein the heteroaryl is a 5- or 6-membered aromatic monocyclic ring comprising 1 or 2 heteroatoms individually selected from nitrogen, oxygen and sulfur, in particular when R¹ is hydrogen, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆alkoxyC₁-C₆alkyl, C₃-C₆cycloalkyl, C₁-C₆alkoxyC₁-C₃alkoxy, C₁-C₆alkoxycarbonyl, C₁-C₆alkoxycarbonylC₁-C₄alkyl, C₂-C₆alkenyloxy, C₂-C₆alkynyloxy, C₁-C₆alkylsulfanyl, phenyl, phenoxy, or heteroaryl, wherein the heteroaryl is a 5- or 6-membered aromatic monocyclic ring comprising 1 or 2 heteroatoms individually selected from nitrogen, oxygen and sulfur, may show improved solubility properties (in particular in non-polar solvents), and/or photostability properties when compared to their corresponding free amine, which are known for
25 example from WO 2017/207362.

According to a second aspect of the invention, there is provided an agrochemical composition comprising a fungicidally effective amount of a compound of formula (I) according to the present invention. Such an agricultural composition may further comprise at least one additional active ingredient
30 and/or an agrochemically-acceptable diluent or carrier.

According to a third aspect of the invention, there is provided a method of controlling or preventing infestation of useful plants by phytopathogenic microorganisms, wherein a fungicidally effective amount of a compound of formula (I), or a composition comprising this compound as active ingredient, is applied
35 to the plants, to parts thereof or the locus thereof.

According to a fourth aspect of the invention, there is provided the use of a compound of formula (I) as a fungicide. According to this particular aspect of the invention, the use may or may not include methods for the treatment of the human or animal body by surgery or therapy.

Where substituents are indicated as being "optionally substituted", this means that they may or may not carry one or more identical or different substituents, e.g., one, two or three R⁴ substituents. For example, C₁-C₈alkyl substituted by 1, 2 or 3 halogens, may include, but not be limited to, -CH₂Cl, -CHCl₂, -CCl₃, -CH₂F, -CHF₂, -CF₃, -CH₂CF₃ or -CF₂CH₃ groups. As another example, C₁-C₆alkoxy substituted by 1, 2 or 3 halogens, may include, but not limited to, CH₂ClO-, CHCl₂O-, CCl₃O-, CH₂FO-, CHF₂O-, CF₃O-, CF₃CH₂O- or CH₃CF₂O- groups.

As used herein, the term "cyano" means a -CN group.

As used herein, the term "halogen" refers to fluorine (fluoro), chlorine (chloro), bromine (bromo) or iodine (iodo).

As used herein, the term "C₁-C₈alkyl" refers to a straight or branched hydrocarbon chain radical consisting solely of carbon and hydrogen atoms, containing no unsaturation, having from one to eight carbon atoms, and which is attached to the rest of the molecule by a single bond. "C₁-C₆alkyl", "C₁-C₄alkyl" and "C₁-C₃alkyl" are to be construed accordingly. Examples of C₁-C₈alkyl include, but are not limited to, methyl, ethyl, n-propyl, and the isomers thereof, for example, iso-propyl. A "C₁-C₆alkylene" group refers to the corresponding definition of C₁-C₆alkyl, except that such radical is attached to the rest of the molecule by two single bonds. The term "C₁-C₂alkylene" is to be construed accordingly. Examples of C₁-C₆alkylene, include, but are not limited to, -CH₂-, -CH₂CH₂- and -(CH₂)₃-.

As used herein, the term "C₁-C₈hydroxyalkyl" refers a C₁-C₈alkyl radical as generally defined above substituted by one or more hydroxy groups. Examples of C₁-C₆hydroxyalkyl include but are not limited to 1-hydroxyethyl.

As used herein, the term "C₁-C₈haloalkyl" refers a C₁-C₈alkyl radical as generally defined above substituted by one or more of the same or different halogen atoms. Examples of C₁-C₈haloalkyl include, but are not limited to trifluoromethyl.

As used herein, the term "C₁-C₈alkoxy" refers to a radical of the formula -OR_a where R_a is a C₁-C₈alkyl radical as generally defined above. The terms "C₁-C₆alkoxy", "C₁-C₄alkoxy" and "C₁-C₃alkoxy" are to be construed accordingly. Examples of C₁-C₈alkoxy include, but are not limited to, methoxy, ethoxy, 1-methylethoxy (iso-propoxy), and propoxy.

As used herein, the term "C₂-C₆alkenyl" refers to a straight or branched hydrocarbon chain radical group consisting solely of carbon and hydrogen atoms, containing at least one double bond that can be of either the (E)- or (Z)-configuration, having from two to six carbon atoms, which is attached to the rest of the molecule by a single bond. The term "C₂-C₃alkenyl" is to be construed accordingly. Examples of C₂-C₆alkenyl include, but are not limited to, ethenyl (vinyl), prop-1-enyl, prop-2-enyl (allyl), but-1-enyl.

As used herein, the term "C₂-C₆alkenyloxy" refers to a radical of the formula -OR_a where R_a is a C₂-C₆alkenyl radical as generally defined above.

As used herein, the term "C₂-C₆alkynyl" refers to a straight or branched hydrocarbon chain radical group consisting solely of carbon and hydrogen atoms, containing at least one triple bond, having from two to six carbon atoms, and which is attached to the rest of the molecule by a single bond. The term "C₂-C₃alkynyl" is to be construed accordingly. Examples of C₂-C₆alkynyl include, but are not limited to, ethynyl, prop-1-ynyl, but-1-ynyl.

As used herein, the term "C₂-C₆alkynyloxy" refers to a radical of the formula -OR_a where R_a is a C₂-C₆alkynyl radical as generally defined above.

As used herein, the term "C₁-C₆alkoxyC₁-C₆alkyl" refers to a radical of the formula R_bOR_a- wherein R_b is a C₁-C₆alkyl radical as generally defined above, and R_a is a C₁-C₆alkylene radical as generally defined above.

As used herein, the term "C₁-C₆alkoxyC₁-C₃alkoxy" refers to a radical of the formula R_bOR_aO- wherein R_b is a C₁-C₆alkyl radical as generally defined above, and R_a is a C₁-C₃alkyl radical as generally defined above.

As used herein, the term "C₁-C₆alkoxycarbonyl" refers to a radical of the formula R_aOC(O)-, wherein R_a is a C₁-C₆alkyl radical as generally defined above.

As used herein, the term "C₁-C₆alkoxycarbonylC₁-C₄alkyl" refers to a radical of the formula R_aOC(O)R_b-, wherein R_a is a C₁-C₆alkyl radical as generally defined above, and R_b is a C₁-C₄alkylene radical as generally defined above.

As used herein, the term "C₁-C₆alkoxycarbonyloxyC₁-C₄alkyl" refers to a radical of the formula R_aOCO₂R_b-, wherein R_a is a C₁-C₆alkyl radical as generally defined above, and R_b is a C₁-C₄alkylene radical as generally defined above. Examples of C₁-C₆alkoxycarbonyloxyC₁-C₄alkyl include, but are not limited to 1-methoxycarbonyloxy-ethyl and 1-methoxycarbonyloxy-methyl.

As used herein, the term "C₁-C₆alkylcarbonyloxyC₁-C₄alkyl" refers to a radical of the formula R_aCO₂R_b-, wherein R_a is a C₁-C₆alkyl radical as generally defined above, and R_b is a C₁-C₄alkylene radical as generally defined above. Examples of C₁-C₆alkylcarbonyloxyC₁-C₄alkyl include, but are not limited to 1-methylcarbonyloxy-methyl.

As used herein, the term "C₁-C₆alkylsulfanyl" refers to a radical of the formula R_aS-, wherein R_a is a C₁-C₆alkyl radical as generally defined above.

As used herein, the term "di(C₁-C₆alkyl)amino" refers to a radical of the formula (R_a)(R_b)N-, wherein R_a and R_b are each individually a C₁-C₆alkyl radical as generally defined above. Examples of di(C₁-C₆alkyl)amino include, but are not limited to dimethylamino and diethylamino.

As used herein, the term "C₃-C₈cycloalkyl" refers to a radical which is a monocyclic saturated ring system and which contains 3 to 8 carbon atoms. The terms "C₃-C₆cycloalkyl", "C₃-C₄cycloalkyl" are to be construed accordingly. Examples of C₃-C₆cycloalkyl include, but are not limited to, cyclopropyl, 1-methylcyclopropyl, 2-methylcyclopropyl, cyclobutyl, 1-methylcyclobutyl, 1,1-dimethylcyclobutyl, 2-methylcyclobutyl, and 2,2-dimethylcyclobutyl.

As used herein, the term "C₃-C₈cycloalkylC₁-C₂alkyl" refers to a C₃-C₈cycloalkyl ring attached to the rest of the molecule by a C₁-C₂alkylene linker as defined above.

As used herein, the term "phenylC₁-C₃alkyl" refers to a phenyl ring attached to the rest of the molecule by a C₁-C₃alkylene linker as defined above.

As used herein, the term "phenylC₁-C₃alkoxyC₁-C₃alkyl" refers to a radical of the formula R_cR_bOR_a-, wherein R_a and R_b is each independently a C₁-C₃alkylene radical as generally defined above and R_c is a phenyl ring. Examples of phenylC₁-C₃alkoxyC₁-C₃alkyl include, but are not limited to benzyloxymethyl and 1-benzyloxyethyl.

As used herein, the term "heteroaryl" refers to a 5- or 6-membered aromatic monocyclic ring radical which comprises 1, 2, 3 or 4 heteroatoms individually selected from nitrogen, oxygen and sulfur.

Examples of heteroaryl include, but are not limited to, furanyl, pyrrolyl, thienyl, pyrazolyl, imidazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, triazolyl, tetrazolyl, pyrazinyl, pyridazinyl, pyrimidyl or pyridyl.

As used herein, the term "heteroarylC₁-C₂alkyl" refers to a heteroaryl ring attached to the rest of the molecule by a C₁-C₂alkylene linker as defined above.

5 As used herein, the term "heterocyclyl" refers to a stable 4-, 5- or 6-membered non-aromatic monocyclic ring which comprises 1, 2 or 3 heteroatoms, wherein the heteroatoms are individually selected from nitrogen, oxygen and sulfur. The heterocyclyl radical may be bonded to the rest of the molecule *via* a carbon atom or heteroatom. Examples of heterocyclyl include, but are not limited to, aziridinyl, azetidiny, oxetanyl, thietanyl, tetrahydrofuryl, pyrrolidinyl, pyrazolidinyl, imidazolidinyl, 10 piperidinyl, piperazinyl, morpholinyl, dioxolanyl, dithiolanyl and thiazolidinyl.

As used herein, the term "heterocyclylC₁-C₂alkyl" refers to a heterocyclyl ring attached to the rest of the molecule by a C₁-C₂alkylene linker as defined above.

As used herein, a "spirocyclic carbobi- or carbetri-cyclyl ring" is a non-aromatic bicyclic ring system comprising two rings joined together at one carbon atom, i.e., sharing one carbon atom.

15 Examples of a spirocyclic carbobi- or carbetri-cyclyl ring system include, but are not limited to, spiro[3.3]heptanyl, spiro[3.4]octanyl, spiro[4.5]decanyl, spiro[cyclobutan-1,2'-indanyl], or spiro[cyclopentane-1,2'-tetralinyl].

The presence of one or more possible asymmetric carbon atoms in a compound of formula (I) 20 means that the compounds may occur in optically isomeric forms, i.e., enantiomeric or diastereomeric forms. Also, atropisomers may occur as a result of restricted rotation about a single bond. Formula (I) is intended to include all those possible isomeric forms and mixtures thereof. The present invention includes all those possible isomeric forms and mixtures thereof for a compound of formula (I). Likewise, formula (I) is intended to include all possible tautomers. The present invention includes all possible 25 tautomeric forms for a compound of formula (I).

In each case, the compounds of formula (I) according to the invention are in free form, in oxidized form as an N-oxide, or in salt form, e.g., an agronomically usable salt form.

N-oxides are oxidized forms of tertiary amines or oxidized forms of nitrogen-containing heteroaromatic compounds. They are described for instance in the book "Heterocyclic N-oxides" by A. 30 Albini and S. Pietra, CRC Press, Boca Raton (1991).

The following list provides definitions, including preferred definitions, for substituents R¹, R², R³, R⁴, X and Y with reference to compounds of formula (I). For any one of these substituents, any of the definitions given below may be combined with any definition of any other substituent given below or 35 elsewhere in this document.

Y is C-F, C-H or N. In one embodiment, Y is C-F. In another embodiment, Y is C-H. In a further embodiment, Y is N.

40 R¹ is hydrogen, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆hydroxyalkyl, C₁-C₆alkoxyC₁-C₆alkyl, C₃-C₆cycloalkyl, C₁-C₆alkoxyC₁-C₃alkoxy, C₁-C₆alkoxycarbonyl, C₁-C₆alkoxycarbonylC₁-

C₄alkyl, C₁-C₆alkoxycarbonyloxyC₁-C₄alkyl, C₁-C₆alkylcarbonyloxyC₁-C₄alkyl, C₂-C₆alkenyloxy, C₂-C₆alkynyloxy, C₁-C₆alkylsulfanyl, di(C₁-C₆alkyl)amino, phenyl, phenylC₁-C₃alkyl, phenylC₁-C₃alkoxyC₁-C₃alkyl, phenoxy, or heteroaryl, wherein the heteroaryl is a 5- or 6-membered aromatic monocyclic ring comprising 1 or 2 heteroatoms individually selected from nitrogen, oxygen and sulfur.

5

Preferably, R¹ is hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄haloalkyl, C₁-C₄hydroxyalkyl, C₁-C₃alkoxyC₁-C₄alkyl, C₃-C₆cycloalkyl, C₁-C₄alkoxyC₁-C₃alkoxy, C₁-C₃alkoxycarbonyl, C₁-C₃alkoxycarbonylC₁-C₄alkyl, C₁-C₄alkoxycarbonyloxyC₁-C₃alkyl, C₁-C₄alkylcarbonyloxyC₁-C₃alkyl, C₃-C₅alkynyloxy, C₁-C₄alkylsulfanyl, di(C₁-C₄alkyl)amino, phenyl, phenylC₁-C₃alkyl, phenylC₁-C₃alkoxyC₁-C₃alkyl, phenoxy, or heteroaryl, wherein the heteroaryl is a 5- or 6-membered aromatic monocyclic ring comprising 1 or 2 heteroatoms individually selected from nitrogen, oxygen and sulfur.

More preferably, R¹ is hydrogen, C₁-C₃alkyl, C₁-C₃alkoxy, C₁-C₃haloalkyl, C₁-C₃hydroxyalkyl, methoxyC₁-C₄alkyl, C₃-C₄cycloalkyl, C₁-C₂alkoxyC₁-C₂alkoxy, C₁-C₃alkoxycarbonyl, methoxycarbonylC₁-C₃alkyl, C₁-C₂alkoxycarbonyloxyC₁-C₂alkyl, C₁-C₂alkylcarbonyloxyC₁-C₂alkyl, C₃-C₄alkynyloxy, C₁-C₃alkylsulfanyl, diethylamino, phenyl, benzyl, phenoxy, benzyloxyC₁-C₂alkyl, or heteroaryl, wherein the heteroaryl is a 5- or 6-membered aromatic monocyclic ring comprising a single heteroatom selected from oxygen and sulfur.

Even more preferably, R¹ is hydrogen, methyl, ethyl, methoxy, ethoxy, fluoromethyl, chloromethyl, bromomethyl, 2,2,2-trifluoroethyl, 1-hydroxyethyl, methoxymethyl, 1-methoxyethyl, 1-ethoxymethyl, 1-methoxy-1-methylethyl, cyclopropyl, methoxyethoxy, ethoxycarbonyl, 2-methoxy-2-oxo-ethyl, 2-methoxy-oxo-ethyl, 2-methoxy-oxo-propyl, propargyloxy, 1-methoxycarbonyloxy-ethyl, 1-ethoxycarbonyloxy-ethyl, 1-methylcarbonyloxy-ethyl, methylcarbonyloxymethyl, methylsulfanyl, ethylsulfanyl, isopropylsulfanyl, diethylamino, phenyl, benzyl, phenoxy, benzyloxymethyl, 1-benzyloxyethyl, 2-furanyl, or 2-thiophenyl.

More preferably still, R¹ is hydrogen, methyl, ethyl, methoxy, ethoxy, fluoromethyl, 2,2,2-trifluoroethyl, 1-hydroxyethyl, 1-ethoxymethyl, cyclopropyl, methoxyethoxy, 2-methoxy-2-oxo-ethyl, 2-methoxy-oxo-ethyl, 2-methoxy-oxo-propyl, propargyloxy, 1-methoxycarbonyloxy-ethyl, 1-ethoxycarbonyloxy-ethyl, 1-methylcarbonyloxy-ethyl, methylcarbonyloxymethyl, isopropylsulfanyl, diethylamino, phenyl, benzyl, phenoxy, benzyloxymethyl, 1-benzyloxyethyl, 2-furanyl, or 2-thiophenyl.

In a particular set of embodiments, R¹ is hydrogen, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆alkoxyC₁-C₆alkyl, C₃-C₆cycloalkyl, C₁-C₆alkoxyC₁-C₃alkoxy, C₁-C₆alkoxycarbonyl, C₁-C₆alkoxycarbonylC₁-C₄alkyl, C₂-C₆alkenyloxy, C₂-C₆alkynyloxy, C₁-C₆alkylsulfanyl, phenyl, phenoxy, or heteroaryl, wherein the heteroaryl is a 5- or 6-membered aromatic monocyclic ring comprising 1 or 2 heteroatoms individually selected from nitrogen, oxygen and sulfur.

Preferably, R¹ is hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄haloalkyl, C₁-C₃alkoxyC₁-C₄alkyl, C₃-C₆cycloalkyl, C₁-C₄alkoxyC₁-C₃alkoxy, C₁-C₃alkoxycarbonyl, C₁-C₃alkoxycarbonylC₁-C₄alkyl, C₃-C₅alkynyloxy, C₁-C₄alkylsulfanyl, phenyl, phenoxy, or heteroaryl, wherein the heteroaryl is a 5- or 6-

membered aromatic monocyclic ring comprising 1 or 2 heteroatoms individually selected from nitrogen, oxygen and sulfur.

More preferably, R¹ is hydrogen, C₁-C₃alkyl, C₁-C₃alkoxy, C₁-C₃haloalkyl, methoxyc₁-C₄alkyl, C₃-C₄cycloalkyl, C₁-C₂alkoxyc₁-C₂alkoxy, C₁-C₃alkoxycarbonyl, methoxycarbonylc₁-C₃alkyl, C₃-C₄alkynyloxy, C₁-C₃alkylsulfanyl, phenyl, phenoxy, or heteroaryl, wherein the heteroaryl is a 5- or 6-membered aromatic monocyclic ring comprising a single heteroatom selected from oxygen and sulfur.

Even more preferably, R¹ is hydrogen, methyl, ethyl, methoxy, ethoxy, fluoromethyl, chloromethyl, bromomethyl, 2,2,2-trifluoroethyl, methoxymethyl, 1-methoxyethyl, 1-methoxy-1-methylethyl, cyclopropyl, methoxyethoxy, ethoxycarbonyl, 2-methoxy-2-oxo-ethyl, 2-methoxy-oxo-ethyl, 2-methoxy-oxo-propyl, propargyloxy, methylsulfanyl, ethylsulfanyl, isopropylsulfanyl, phenyl, phenoxy, 2-furanyl, or 2-thiophenyl.

More preferably still, R¹ is hydrogen, methyl, ethyl, methoxy, ethoxy, fluoromethyl, 2,2,2-trifluoroethyl, cyclopropyl, methoxyethoxy, 2-methoxy-2-oxo-ethyl, 2-methoxy-oxo-ethyl, 2-methoxy-oxo-propyl, propargyloxy, isopropylsulfanyl, phenyl, phenoxy, 2-furanyl, or 2-thiophenyl.

R² is hydrogen, halogen, cyano, C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄haloalkyl, or HC(O)NH-. Preferably, R² is hydrogen, halogen, C₁-C₃alkyl, C₁-C₃alkoxy, C₁-C₂haloalkyl, or HC(O)NH-, more preferably halogen, C₁-C₂alkyl, C₁-C₂alkoxy, or HC(O)NH-. Even more preferably, R² is chloro, bromo, methyl, methoxy, or HC(O)NH-. Even more preferably, R² is methyl or HC(O)NH-, and most preferably methyl.

R³ is C₁-C₈alkyl, C₁-C₈haloalkyl, C₁-C₈alkoxy, C₃-C₈cycloalkyl, C₃-C₈cycloalkylc₁-C₂alkyl (wherein the cycloalkyl groups are optionally substituted with 1 to 3 groups represented by R⁴), phenyl, phenylc₁-C₂alkyl, heteroaryl, heteroarylc₁-C₂alkyl, wherein the heteroaryl is a 5- or 6-membered aromatic monocyclic ring comprising 1, 2, 3 or 4 heteroatoms individually selected from nitrogen, oxygen and sulfur, heterocyclyl, heterocyclylc₁-C₂alkyl, wherein the heterocyclyl is a 4-, 5- or 6-membered non-aromatic monocyclic ring comprising 1, 2 or 3 heteroatoms individually selected from nitrogen, oxygen and sulfur, or a 5- to 10-membered non-aromatic spirocyclic carbobi- or carbotri-cyclyl ring system optionally comprising 1, 2, 3, 4 or 5 heteroatoms individually selected from nitrogen, oxygen and sulfur, and wherein said spirocyclic carbobi- or carbotri-cyclyl ring systems are each optionally bonded to the rest of the molecule through a C₁-C₂alkylene linker.

Preferably, R³ is C₁-C₆alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₃-C₆cycloalkyl, C₃-C₆cycloalkylc₁-C₂alkyl (wherein the cycloalkyl groups are optionally substituted with 1 to 3 groups represented by R⁴), phenyl, heteroaryl, heteroarylc₁-C₂alkyl, wherein the heteroaryl is a 5- or 6-membered aromatic monocyclic ring comprising 1, 2 or 3 heteroatoms individually selected from nitrogen, oxygen and sulfur, heterocyclyl, heterocyclylc₁-C₂alkyl, wherein the heterocyclyl is a 4-, 5- or 6-membered non-aromatic monocyclic ring comprising 1, 2 or 3 heteroatoms individually selected from nitrogen, oxygen and sulfur, or a 5- to 12-membered non-aromatic spirocyclic carbobi- or carbotri-cyclyl ring system optionally comprising 1, 2 or 3 heteroatoms individually selected from nitrogen, oxygen and sulfur, and wherein said spirocyclic carbobi- or carbotri-cyclyl ring systems are each optionally bonded to the rest of the molecule through a C₁-C₂alkylene linker.

More preferably, R^3 is C_1 - C_4 alkyl, C_1 - C_3 alkoxy, C_3 - C_6 cycloalkyl, C_3 - C_6 cycloalkyl- C_1 - C_2 alkyl (wherein the cycloalkyl groups are optionally substituted with 1 to 3 groups represented by R^4), phenyl, heteroaryl wherein the heteroaryl is a 5- or 6-membered aromatic monocyclic ring comprising 1, 2 or 3 heteroatoms individually selected from nitrogen, oxygen and sulfur, heterocyclyl wherein the
 5 heterocyclyl is a 4-, 5- or 6-membered non-aromatic monocyclic ring comprising 1, 2 or 3 heteroatoms individually selected from nitrogen, oxygen and sulfur, or a 5- to 12-membered non-aromatic spirocyclic carbobi- or carbetri-cyclyl ring system optionally comprising a single heteroatom selected from nitrogen, oxygen and sulfur.

Even more preferably, R^3 is C_3 - C_6 cycloalkyl, wherein the cycloalkyl groups are optionally
 10 substituted with 1 or 2 groups represented by R^4 , or R^3 is a 6- to 10-membered non-aromatic spirocyclic carbobi-cyclyl ring system.

More preferably still, R^3 is C_3 - C_4 cycloalkyl, wherein the cycloalkyl groups are optionally substituted with 1 or 2 groups represented by R^4 , or R^3 is a 6- to 8-membered non-aromatic spirocyclic carbobi-cyclyl ring system.

15 Even more preferably still, R^3 is cyclobutyl, 2,2-dimethylcyclobutyl or spiro[3.4]octanyl, and most preferably, cyclobutyl, 2,2-dimethylcyclobutyl, or spiro[3.4]octan-3-yl.

R^4 is halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, or C_1 - C_4 haloalkyl. Preferably, R^4 is halogen, C_1 - C_3 alkyl, C_1 - C_3 alkoxy, C_1 - C_2 haloalkyl, more preferably, halogen, C_1 - C_3 alkyl, C_1 - C_3 alkoxy, or C_1 - C_3 haloalkyl. Even more preferably, R^4 is C_1 - C_3 alkyl, more preferably still, methyl, ethyl or isopropyl, and most preferably
 20 R^4 is methyl.

X is N or C-H. In one embodiment, X is N. In another embodiment, X is C-H.

In a compound of formula (I) according to the present invention, preferably:

25 R^1 is hydrogen, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkyl, C_1 - C_6 hydroxyalkyl, C_1 - C_6 alkoxy- C_1 - C_6 alkyl, C_3 - C_6 cycloalkyl, C_1 - C_6 alkoxy- C_1 - C_3 alkoxy, C_1 - C_6 alkoxycarbonyl, C_1 - C_6 alkoxycarbonyl- C_1 - C_4 alkyl, C_1 - C_6 alkoxycarbonyloxy- C_1 - C_4 alkyl, C_1 - C_6 alkylcarbonyloxy- C_1 - C_4 alkyl, C_2 - C_6 alkenyloxy, C_2 - C_6 alkynyloxy, C_1 - C_6 alkylsulfanyl, di(C_1 - C_6 alkyl)amino, phenyl, phenyl- C_1 - C_3 alkyl, phenyl- C_1 - C_3 alkoxy- C_1 - C_3 alkyl, phenoxy, or heteroaryl, wherein the heteroaryl is a 5- or 6-membered aromatic monocyclic ring
 30 comprising 1 or 2 heteroatoms individually selected from nitrogen, oxygen and sulfur;

R^2 is methyl;

R^3 is C_1 - C_8 alkyl, C_1 - C_8 haloalkyl, C_1 - C_8 alkoxy, C_3 - C_8 cycloalkyl, C_3 - C_8 cycloalkyl- C_1 - C_2 alkyl (wherein the cycloalkyl groups are optionally substituted with 1 to 3 groups represented by R^4), phenyl, phenyl- C_1 - C_2 alkyl, heteroaryl, heteroaryl- C_1 - C_2 alkyl, wherein the heteroaryl is a 5- or 6-membered
 35 aromatic monocyclic ring comprising 1, 2, 3 or 4 heteroatoms individually selected from nitrogen, oxygen and sulfur, heterocyclyl, heterocyclyl- C_1 - C_2 alkyl, wherein the heterocyclyl is a 4-, 5- or 6-membered non-aromatic monocyclic ring comprising 1, 2 or 3 heteroatoms individually selected from nitrogen, oxygen and sulfur, or a 5- to 10-membered non-aromatic spirocyclic carbobi- or carbetri-cyclyl ring system optionally comprising 1, 2, 3, 4 or 5 heteroatoms individually selected from nitrogen, oxygen and sulfur,
 40 and wherein said spirocyclic carbobi- or carbetri-cyclyl ring systems are each optionally bonded to the rest of the molecule through a C_1 - C_2 alkylene linker;

R⁴ is halogen, C₁-C₄alkyl, C₁-C₄alkoxy, or C₁-C₄haloalkyl;

X is C N; and

Y is C-F.

5 More preferably, R¹ is hydrogen, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆hydroxyalkyl, C₁-C₆alkoxyC₁-C₆alkyl, C₃-C₆cycloalkyl, C₁-C₆alkoxyC₁-C₃alkoxy, C₁-C₆alkoxycarbonyl, C₁-C₆alkoxycarbonylC₁-C₄alkyl, C₁-C₆alkoxycarbonyloxyC₁-C₄alkyl, C₁-C₆alkylcarbonyloxyC₁-C₄alkyl, C₂-C₆alkynyloxy, C₁-C₆alkylsulfanyl, di(C₁-C₆alkyl)amino, phenyl, phenylC₁-C₃alkyl, phenylC₁-C₃alkoxyC₁-C₃alkyl, phenoxy, or heteroaryl, wherein the heteroaryl is a 5- or 6-membered aromatic monocyclic ring
10 comprising 1 or 2 heteroatoms individually selected from nitrogen, oxygen and sulfur;

R² is methyl;

R³ is C₃-C₈cycloalkyl, wherein the cycloalkyl groups are optionally substituted with 1 to 3 groups represented by R⁴, or R³ is a 5- to 10-membered non-aromatic spirocyclic carbobicyclic ring system optionally comprising 1, 2, 3, 4 or 5 heteroatoms individually selected from nitrogen, oxygen and sulfur,
15 and wherein said spirocyclic carbobi- or carbetri-cyclic ring systems are each optionally bonded to the rest of the molecule through a C₁-C₂alkylene linker;

X is N; and

Y is C-F.

20 Even more preferably, R¹ hydrogen, C₁-C₃alkyl, C₁-C₃alkoxy, C₁-C₃haloalkyl, C₁-C₃hydroxyalkyl, methoxyC₁-C₄alkyl, C₃-C₄cycloalkyl, C₁-C₂alkoxyC₁-C₂alkoxy, C₁-C₃alkoxycarbonyl, methoxycarbonylC₁-C₃alkyl, C₁-C₂alkoxycarbonyloxyC₁-C₂alkyl, C₁-C₂alkylcarbonyloxyC₁-C₂alkyl, C₃-C₄alkynyloxy, C₁-C₃alkylsulfanyl, diethylamino, phenyl, benzyl, phenoxy, benzyloxyC₁-C₂alkyl, or heteroaryl, wherein the heteroaryl is a 5- or 6-membered aromatic monocyclic ring comprising a single
25 heteroatom selected from oxygen and sulfur;

R² is methyl;

R³ is cyclobutyl, 2,2-dimethylcyclobutyl, or spiro[3.4]octan-3-yl;

X is N; and

Y is C-F.

30

More preferably still, R¹ is hydrogen, methyl, ethyl, methoxy, ethoxy, fluoromethyl, chloromethyl, bromomethyl, 2,2,2-trifluoroethyl, 1-hydroxyethyl, methoxymethyl, 1-methoxyethyl, 1-ethoxymethyl, 1-methoxy-1-methylethyl, cyclopropyl, methoxyethoxy, ethoxycarbonyl, 2-methoxy-2-oxo-ethyl, 2-methoxy-oxo-ethyl, 2-methoxy-oxo-propyl, propargyloxy, 1-methoxycarbonyloxy-ethyl, 1-ethoxycarbonyloxy-ethyl, 1-methylcarbonyloxy-ethyl, methylcarbonyloxy-methyl, methylsulfanyl, ethylsulfanyl, isopropylsulfanyl, diethylamino, phenyl, benzyl, phenoxy, benzyloxymethyl, 1-benzyloxyethyl, 2-furanyl, or 2-thiophenyl;

R² is methyl;

R³ is cyclobutyl, 2,2-dimethylcyclobutyl, or spiro[3.4]octan-3-yl;

40

X is N; and

Y is C-F.

In a particular set of embodiments, in a compound of formula (I) according to the present invention, preferably:

R^1 is hydrogen, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy C_1 - C_6 alkyl, C_3 -
 5 C_6 cycloalkyl, C_1 - C_6 alkoxy C_1 - C_3 alkoxy, C_1 - C_6 alkoxycarbonyl, C_1 - C_6 alkoxycarbonyl C_1 - C_4 alkyl, C_2 -
 C_6 alkenyloxy, C_2 - C_6 alkynyloxy, C_1 - C_6 alkylsulfanyl, phenyl, phenoxy, or heteroaryl, wherein the
 heteroaryl is a 5- or 6-membered aromatic monocyclic ring comprising 1 or 2 heteroatoms individually
 selected from nitrogen, oxygen and sulfur;

R^2 is methyl;

10 R^3 is C_1 - C_8 alkyl, C_1 - C_8 haloalkyl, C_1 - C_8 alkoxy, C_3 - C_8 cycloalkyl, C_3 - C_8 cycloalkyl C_1 - C_2 alkyl
 (wherein the cycloalkyl groups are optionally substituted with 1 to 3 groups represented by R^4), phenyl,
 phenyl C_1 - C_2 alkyl, heteroaryl, heteroaryl C_1 - C_2 alkyl, wherein the heteroaryl is a 5- or 6-membered
 aromatic monocyclic ring comprising 1, 2, 3 or 4 heteroatoms individually selected from nitrogen, oxygen
 and sulfur, heterocyclyl, heterocyclyl C_1 - C_2 alkyl, wherein the heterocyclyl is a 4-, 5- or 6-membered non-
 15 aromatic monocyclic ring comprising 1, 2 or 3 heteroatoms individually selected from nitrogen, oxygen
 and sulfur, or a 5- to 10-membered non-aromatic spirocyclic carbobi- or carbetri-cyclyl ring system
 optionally comprising 1, 2, 3, 4 or 5 heteroatoms individually selected from nitrogen, oxygen and sulfur,
 and wherein said spirocyclic carbobi- or carbetri-cyclyl ring systems are each optionally bonded to the
 rest of the molecule through a C_1 - C_2 alkylene linker;

20 R^4 is halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, or C_1 - C_4 haloalkyl;

X is C N; and

Y is C-F.

More preferably, R^1 is hydrogen, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy C_1 -
 25 C_6 alkyl, C_3 - C_6 cycloalkyl, C_1 - C_6 alkoxy C_1 - C_3 alkoxy, C_1 - C_6 alkoxycarbonyl, C_1 - C_6 alkoxycarbonyl C_1 -
 C_4 alkyl, C_2 - C_6 alkynyloxy, C_1 - C_6 alkylsulfanyl, phenyl, phenoxy, or heteroaryl, wherein the heteroaryl is a
 5- or 6-membered aromatic monocyclic ring comprising 1 or 2 heteroatoms individually selected from
 nitrogen, oxygen and sulfur;

R^2 is methyl;

30 R^3 is C_3 - C_8 cycloalkyl, wherein the cycloalkyl groups are optionally substituted with 1 to 3 groups
 represented by R^4 , or R^3 is a 5- to 10-membered non-aromatic spirocyclic carbobicyclyl ring system
 optionally comprising 1, 2, 3, 4 or 5 heteroatoms individually selected from nitrogen, oxygen and sulfur,
 and wherein said spirocyclic carbobi- or carbetri-cyclyl ring systems are each optionally bonded to the
 rest of the molecule through a C_1 - C_2 alkylene linker;

35 X is N; and

Y is C-F.

Even more preferably, R^1 hydrogen, C_1 - C_3 alkyl, C_1 - C_3 alkoxy, C_1 - C_3 haloalkyl, methoxy C_1 -
 C_4 alkyl, C_3 - C_4 cycloalkyl, C_1 - C_2 alkoxy C_1 - C_2 alkoxy, C_1 - C_3 alkoxycarbonyl, methoxycarbonyl C_1 - C_3 alkyl,
 40 C_3 - C_4 alkynyloxy, C_1 - C_3 alkylsulfanyl, phenyl, phenoxy, heteroaryl, wherein the heteroaryl is a 5- or 6-
 membered aromatic monocyclic ring comprising a single heteroatom selected from oxygen and sulfur;

R² is methyl;

R³ is cyclobutyl, 2,2-dimethylcyclobutyl, or spiro[3.4]octan-3-yl;

X is N; and

Y is C-F.

5

More preferably still, R¹ is hydrogen, methyl, ethyl, methoxy, ethoxy, fluoromethyl, chloromethyl, bromomethyl, 2,2,2-trifluoroethyl, methoxymethyl, 1-methoxyethyl, 1-methoxy-1-methylethyl, cyclopropyl, methoxyethoxy, ethoxycarbonyl, 2-methoxy-2-oxo-ethyl, 2-methoxy-oxo-ethyl, 2-methoxy-oxo-propyl, propargyloxy, methylsulfanyl, ethylsulfanyl, isopropylsulfanyl, phenyl, phenoxy, 2-furanyl, or

10 2-thiophenyl;

R² is methyl;

R³ is cyclobutyl, 2,2-dimethylcyclobutyl, or spiro[3.4]octan-3-yl;

X is N; and

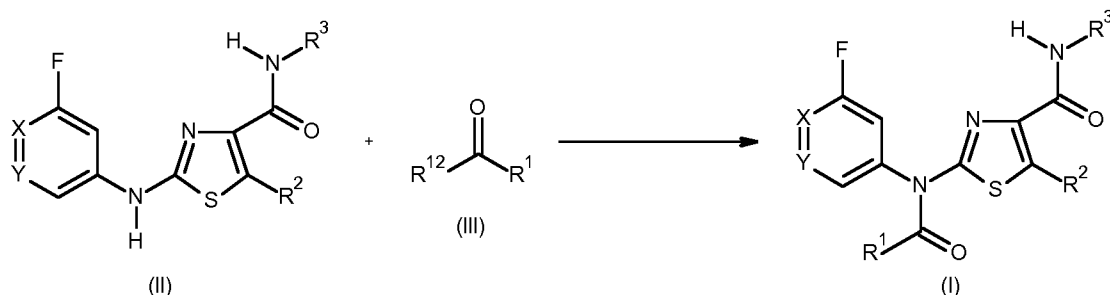
Y is C-F.

15

Compounds of the present invention can be made as shown in the following schemes, in which, unless otherwise stated, the definition of each variable is as defined above for a compound of formula (I).

The compounds of formula (I) according to the invention, wherein R¹, R², R³, X and Y are as defined for formula (I), can be obtained by transformation of a compound of formula (II), wherein R², R³, X and Y are as defined for formula (I), with a compound of formula (III), wherein R¹ is as defined for formula (I) and R¹² is halogen, preferably chloro, either by thermal heating, or with the aid of a base. This is shown in Scheme 1 below.

Scheme 1

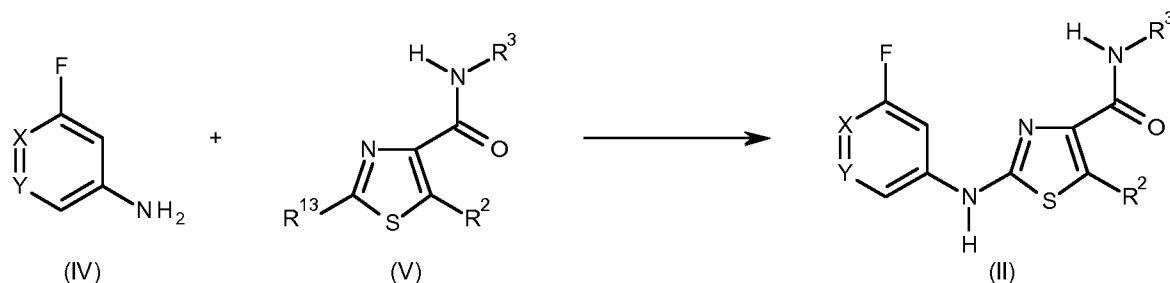


The compounds of formula (II), wherein R², R³, X and Y are as defined for formula (I), can be obtained by transformation of a compound of formula (IV), wherein X and Y are as defined for formula (I), with a compound of formula (V), wherein R² and R³ are as defined for formula (I) and R¹³ is halogen, preferably bromo, either by thermal heating, or with the aid of a base or under the conditions of the

30 transition metal catalysed Buchwald-Hartwig amination. This is shown in Scheme 2 below.

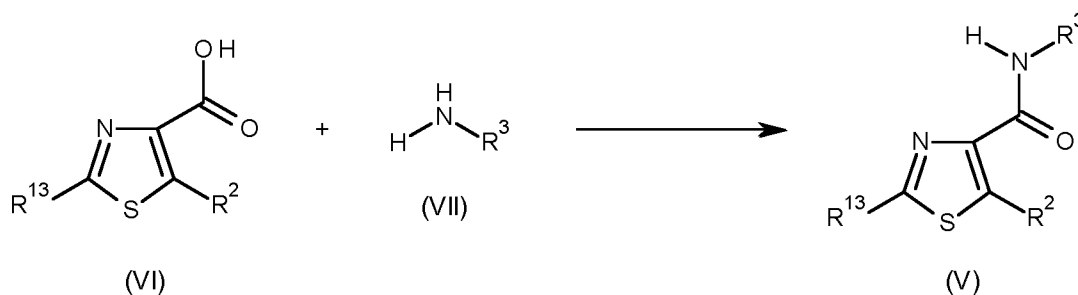
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Scheme 2



The compounds of formula (V), wherein R^2 and R^3 are as defined for formula (I) and R^{13} is halogen, preferably bromo, can be obtained by transformation of a compound of formula (VI), wherein R^2 is as defined for formula (I) and R^{13} is halogen, preferably bromo, and a compound of formula (VII), wherein R^3 is as defined for formula (I), either *via* an intermediate acid chloride or directly with a peptide coupling agent. This is shown in Scheme 3 below.

Scheme 3



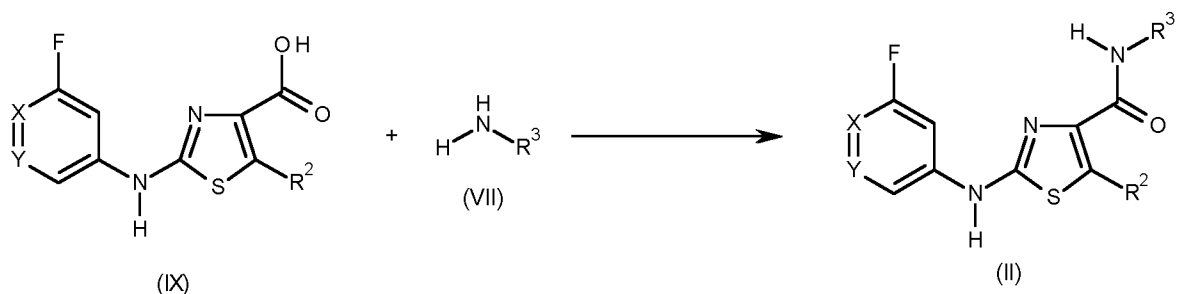
The compounds of formula (VI), wherein R^2 is as defined for formula (I) and R^{13} is halogen, preferably bromo, can be obtained by transformation of a compound of formula (VIII), wherein R^2 is as defined for formula (I), R^{13} is halogen, preferably bromo, and R^{14} is C_1 - C_6 alkyl, and a base. This is shown in Scheme 4 below.

Scheme 4



Alternatively, the compounds of formula (II), wherein R^2 , R^3 , X and Y are as defined for formula (I), can be obtained by transformation of a compound of formula (IX), wherein R^2 , X and Y are as defined for formula (I), with a compound of formula (VII), wherein R^3 is as defined for formula (I), either *via* an intermediate acid chloride or directly with an peptide coupling agent. This is shown in Scheme 5 below.

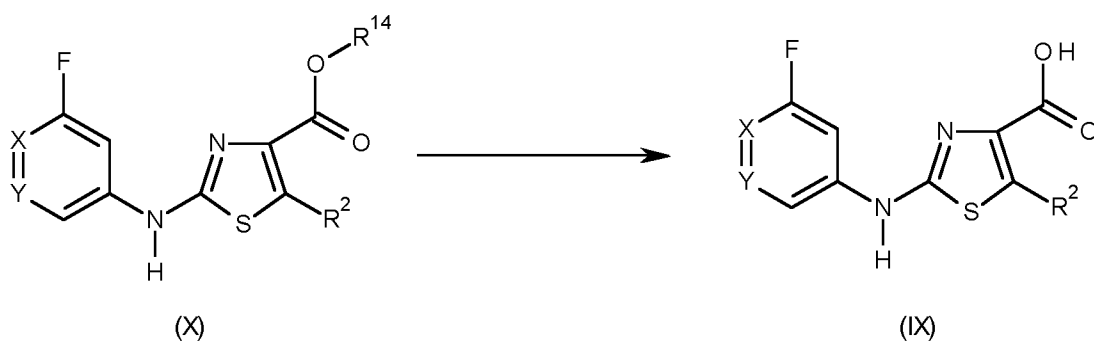
Scheme 5



The compounds of formula (IX), wherein R², X and Y are as defined for formula (I), can be obtained by transformation of a compound of formula (X), wherein R², X and Y are as defined for formula (I) and

5 R¹⁴ is C₁-C₆alkyl, with a base. This is shown in Scheme 6 below.

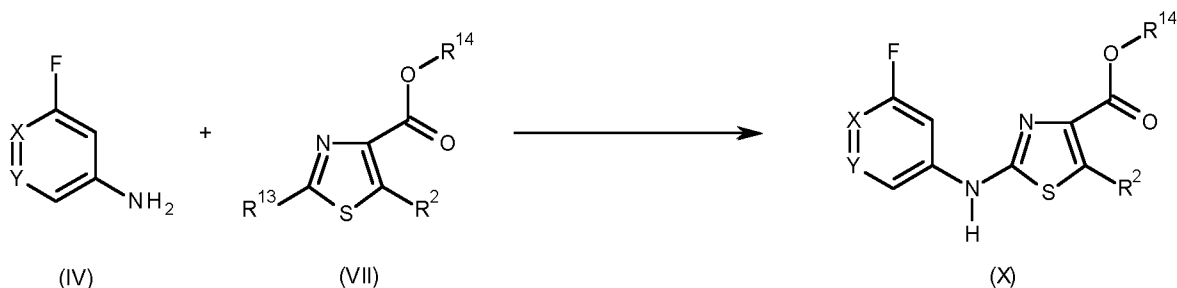
Scheme 6



The compounds of formula (X), wherein R², X, and Y are as defined for formula (I) and R¹⁴ is C₁-C₆alkyl, can be obtained by transformation of a compound of formula (IV), wherein X and Y are as defined for formula (I), with a compound of formula (VII), wherein R² is as defined for formula (I), R¹² is halogen, preferably bromo, and R¹³ is C₁-C₆alkyl, either by thermal heating, or with the aid of a base or under the conditions of the transition metal catalysed Buchwald-Hartwig amination. This is shown in

15

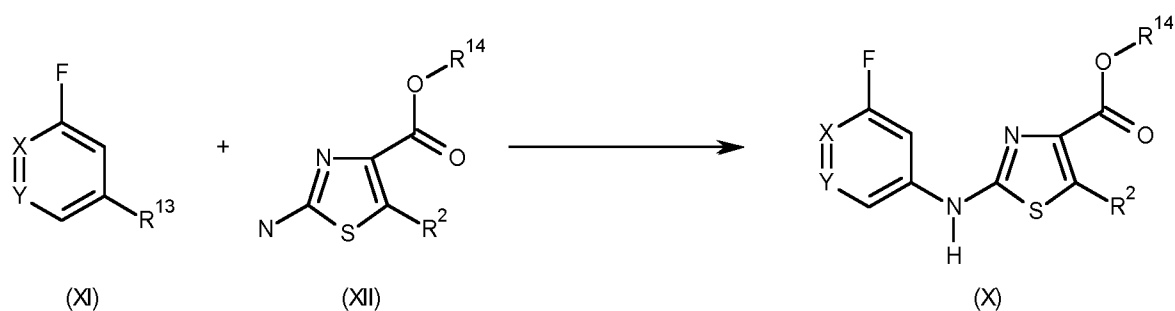
Scheme 7



Alternatively, the compounds of formula (X), wherein R², X and Y are as defined for formula (I) and R¹⁴ is C₁-C₆alkyl, can be obtained by transformation of a compound of formula (XI), wherein X and Y are as defined for formula (I) and R¹³ is halogen, preferably bromo or iodo, with a compound of formula (XII), wherein R² is as defined for formula (I) and R¹⁴ is C₁-C₆alkyl, under the conditions of the transition metal catalysed Buchwald-Hartwig amination. This is shown in Scheme 8 below.

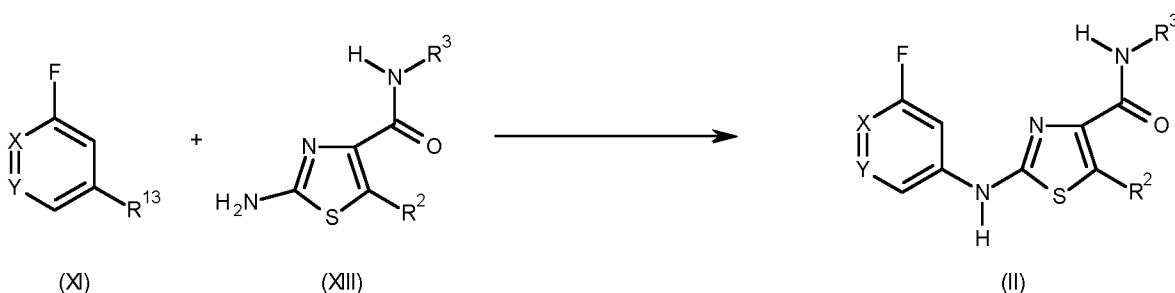
20

Scheme 8



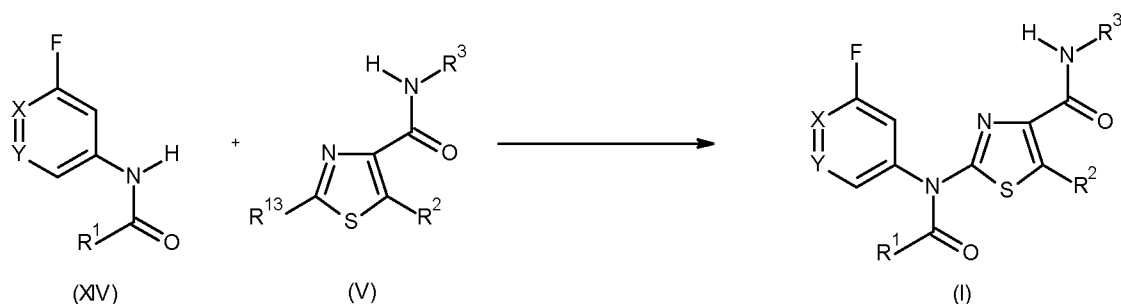
Alternatively, the compounds of formula (II), wherein R², R³, X and Y are as defined for formula (I), can be obtained by transformation of a compound of formula (XI), wherein X and Y are as defined for formula (I) and R¹³ is halogen, preferably bromo or iodo, with a compound of formula (XIII), wherein R² and R³ are as defined for formula (I), either by thermal heating, or with the aid of a base or under the conditions of the transition metal catalysed Buchwald-Hartwig amination. This is shown in Scheme 9 below.

10 Scheme 9



Alternatively, the compounds of formula (I) according to the invention, wherein R¹, R², R³, X and Y are as defined for formula (I), can be obtained by transformation of a compound of formula (V), wherein R² and R³ are as defined for formula (I) and R¹³ is halogen, preferably bromo, with a compound of formula (XIV), wherein R¹, X and Y are as defined for formula (I) either by thermal heating, or with the aid of a base or under the conditions of the transition metal catalysed Buchwald-Hartwig amination. This is shown in Scheme 10 below.

Scheme 10

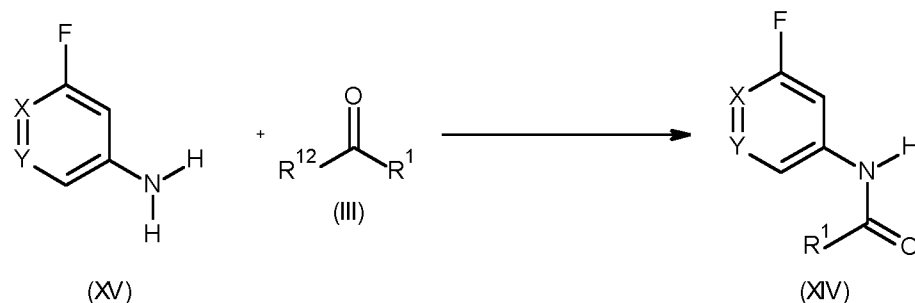


20

The compounds of formula (XIV), wherein R¹, X and Y are as defined for formula (I), can be obtained by transformation of a compound of formula (XV), wherein X and Y are as defined for formula

(I), with a compound of formula (III), wherein R^1 is as defined for formula (I) and R^{12} is halogen, preferably chloro, either by thermal heating, or with the aid of a base. This is shown in Scheme 11 below.

Scheme 11

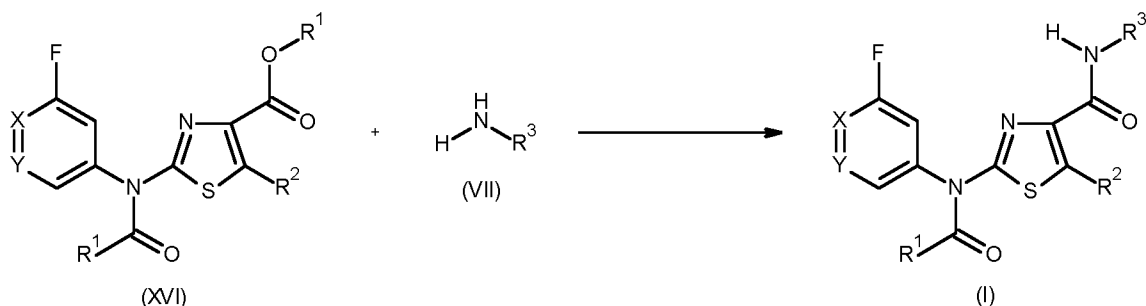


5

Alternatively, the compounds of formula (I), wherein R^1 , R^2 , R^3 , X and Y are as defined for formula (I), can be obtained by transformation of a compound of formula (XVI), wherein R^1 , R^2 , X and Y are as defined for formula (I), with a compound of formula (VII), wherein R^3 is as defined for formula (I), either by thermal heating, or with the aid of a base. This is shown in Scheme 12 below.

10

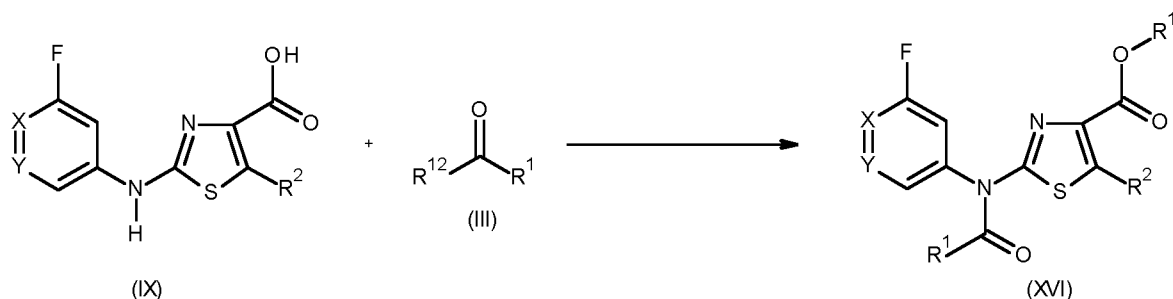
Scheme 12



The compounds of formula (XVI), wherein R^1 , R^2 , X and Y are as defined for formula (I), can be obtained by transformation of a compound of formula (IX), wherein R^2 , X and Y are as defined for formula (I), with a compound of formula (III), wherein R^1 is as defined for formula (I) and R^{12} is halogen, preferably chloro, either by thermal heating, or with the aid of a base. This is shown in Scheme 13 below.

15

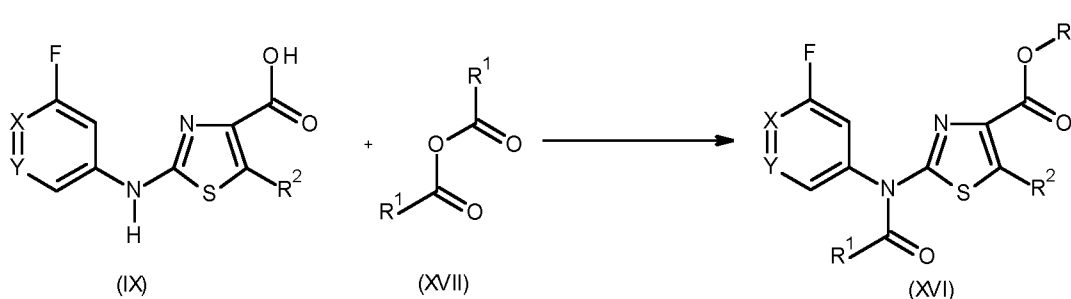
Scheme 13



20

Alternatively, the compounds of formula (XVI), wherein R^1 , R^2 , X and Y are as defined for formula (I), can be obtained by transformation of a compound of formula (IX), wherein R^2 , X and Y are as defined for formula (I), with a compound of formula (XVII), wherein R^1 is as defined for formula (I), either by thermal heating, or with the aid of a base. This is shown in Scheme 14 below.

Scheme 14



Surprisingly, it has now been found that the novel compounds of formula (I) have, for practical purposes, a very advantageous level of biological activity for protecting plants against diseases that are caused by fungi.

The compounds of formula (I) can be used in the agricultural sector and related fields of use, e.g., as active ingredients for controlling plant pests or on non-living materials for control of spoilage microorganisms or organisms potentially harmful to man. The novel compounds are distinguished by excellent activity at low rates of application, by being well tolerated by plants and by being environmentally safe. They have very useful curative, preventive and systemic properties and may be used for protecting numerous cultivated plants. The compounds of formula (I) can be used to inhibit or destroy the pests that occur on plants or parts of plants (fruit, blossoms, leaves, stems, tubers, roots) of different crops of useful plants, while at the same time protecting also those parts of the plants that grow later, e.g., from phytopathogenic microorganisms.

The present invention further relates to a method for controlling or preventing infestation of plants or plant propagation material and/or harvested food crops susceptible to microbial attack by treating plants or plant propagation material and/or harvested food crops wherein an effective amount a compound of formula (I) is applied to the plants, to parts thereof or the locus thereof.

It is also possible to use the compounds of formula (I) as fungicide. The term "fungicide" as used herein means a compound that controls, modifies, or prevents the growth of fungi. The term "fungicidally effective amount" means the quantity of such a compound or combination of such compounds that is capable of producing an effect on the growth of fungi. Controlling or modifying effects include all deviation from natural development, such as killing, retardation and the like, and prevention includes barrier or other defensive formation in or on a plant to prevent fungal infection.

It is also possible to use compounds of formula (I) as dressing agents for the treatment of plant propagation material, e.g., seed, such as fruits, tubers or grains, or plant cuttings (e.g., rice), for the protection against fungal infections, as well as against phytopathogenic fungi occurring in the soil. The propagation material can be treated with a composition comprising a compound of formula (I) before planting: seed, e.g., can be dressed before being sown.

The active ingredients according to the invention can also be applied to grains (coating), either by impregnating the seeds in a liquid formulation or by coating them with a solid formulation. The composition can also be applied to the planting site when the propagation material is being planted, e.g., to the seed furrow during sowing. The invention relates also to such methods of treating plant propagation material and to the plant propagation material so treated.

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

In addition, the invention could be used to protect non-living materials from fungal attack, e.g.,
5 lumber, wall boards and paint.

The compounds of formula (I) may be, for example, effective against fungi and fungal vectors of disease as well as phytopathogenic bacteria and viruses. These fungi and fungal vectors of disease as well as phytopathogenic bacteria and viruses are for example:

- 10 *Absidia corymbifera*, *Alternaria* spp, *Aphanomyces* spp, *Ascochyta* spp, *Aspergillus* spp. including *A. flavus*, *A. fumigatus*, *A. nidulans*, *A. niger*, *A. terrus*, *Aureobasidium* spp. including *A. pullulans*, *Blastomyces dermatitidis*, *Blumeria graminis*, *Bremia lactucae*, *Botryosphaeria* spp. including *B. dothidea*, *B. obtusa*, *Botrytis* spp. including *B. cinerea*, *Candida* spp. including *C. albicans*, *C. glabrata*, *C. krusei*, *C. lusitaniae*, *C. parapsilosis*, *C. tropicalis*, *Cephaloascus fragrans*, *Ceratocystis* spp,
- 15 *Cercospora* spp. including *C. arachidicola*, *Cercosporidium personatum*, *Cladosporium* spp, *Claviceps purpurea*, *Coccidioides immitis*, *Cochliobolus* spp, *Colletotrichum* spp. including *C. musae*, *Cryptococcus neoformans*, *Diaporthe* spp, *Didymella* spp, *Drechslera* spp, *Elsinoe* spp, *Epidermophyton* spp, *Erwinia amylovora*, *Erysiphe* spp. including *E. cichoracearum*, *Eutypa lata*, *Fusarium* spp. including *F. culmorum*, *F. graminearum*, *F. langsethiae*, *F. moniliforme*, *F. oxysporum*,
- 20 *F. proliferatum*, *F. subglutinans*, *F. solani*, *Gaeumannomyces graminis*, *Gibberella fujikuroi*, *Gloeodes pomigena*, *Gloeosporium musarum*, *Glomerella cingulate*, *Guignardia bidwellii*, *Gymnosporangium juniperi-virginianae*, *Helminthosporium* spp, *Hemileia* spp, *Histoplasma* spp. including *H. capsulatum*, *Laetisaria fuciformis*, *Leptographium lindbergi*, *Leveillula taurica*, *Lophodermium seditiosum*, *Microdochium nivale*, *Microsporum* spp, *Monilinia* spp, *Mucor* spp, *Mycosphaerella* spp. including *M.*
- 25 *graminicola*, *M. pomi*, *Oncobasidium theobromaeon*, *Ophiostoma piceae*, *Paracoccidioides* spp, *Penicillium* spp. including *P. digitatum*, *P. italicum*, *Petriellidium* spp, *Peronosclerospora* spp. Including *P. maydis*, *P. philippinensis* and *P. sorghi*, *Peronospora* spp, *Phaeosphaeria nodorum*, *Phakopsora pachyrhizi*, *Phellinus igniarius*, *Phialophora* spp, *Phoma* spp, *Phomopsis viticola*, *Phytophthora* spp. including *P. infestans*, *Plasmopara* spp. including *P. halstedii*, *P. viticola*, *Pleospora* spp., *Podosphaera*
- 30 spp. including *P. leucotricha*, *Polomyxa graminis*, *Polomyxa betae*, *Pseudocercospora herpotrichoides*, *Pseudomonas* spp, *Pseudoperonospora* spp. including *P. cubensis*, *P. humuli*, *Pseudopeziza tracheiphila*, *Puccinia* Spp. including *P. hordei*, *P. recondita*, *P. striiformis*, *P. triticina*, *Pyrenopeziza* spp, *Pyrenophora* spp, *Pyricularia* spp. including *P. oryzae*, *Pythium* spp. including *P. ultimum*, *Ramularia* spp, *Rhizoctonia* spp, *Rhizomucor pusillus*, *Rhizopus arrhizus*, *Rhynchosporium*
- 35 spp, *Scedosporium* spp. including *S. apiospermum* and *S. prolificans*, *Schizothyrium pomi*, *Sclerotinia* spp, *Sclerotium* spp, *Septoria* spp, including *S. nodorum*, *S. tritici*, *Sphaerotheca macularis*, *Sphaerotheca fusca* (*Sphaerotheca fuliginea*), *Sporothrix* spp, *Stagonospora nodorum*, *Stemphylium* spp., *Stereum hirsutum*, *Thanatephorus cucumeris*, *Thielaviopsis basicola*, *Tilletia* spp, *Trichoderma* spp., including *T. harzianum*, *T. pseudokoningii*, *T. viride*, *Trichophyton* spp, *Typhula* spp, *Uncinula*
- 40 *necator*, *Urocystis* spp, *Ustilago* spp, *Venturia* spp. including *V. inaequalis*, *Verticillium* spp, and *Xanthomonas* spp.

Within the scope of present invention, target crops and/or useful plants to be protected typically comprise perennial and annual crops, such as berry plants for example blackberries, blueberries, cranberries, raspberries and strawberries; cereals for example barley, maize (corn), millet, oats, rice, 5 rye, sorghum tritcale and wheat; fibre plants for example cotton, flax, hemp, jute and sisal; field crops for example sugar and fodder beet, coffee, hops, mustard, oilseed rape (canola), poppy, sugar cane, sunflower, tea and tobacco; fruit trees for example apple, apricot, avocado, banana, cherry, citrus, nectarine, peach, pear and plum; grasses for example Bermuda grass, bluegrass, bentgrass, centipede grass, fescue, ryegrass, St. Augustine grass and Zoysia grass; herbs such as basil, borage, chives, 10 coriander, lavender, lovage, mint, oregano, parsley, rosemary, sage and thyme; legumes for example beans, lentils, peas and soya beans; nuts for example almond, cashew, ground nut, hazelnut, peanut, pecan, pistachio and walnut; palms for example oil palm; ornamentals for example flowers, shrubs and trees; other trees, for example cacao, coconut, olive and rubber; vegetables for example asparagus, aubergine, broccoli, cabbage, carrot, cucumber, garlic, lettuce, marrow, melon, okra, onion, pepper, 15 potato, pumpkin, rhubarb, spinach and tomato; and vines for example grapes.

The term "useful plants" is to be understood as including also useful plants that have been rendered tolerant to herbicides like bromoxynil or classes of herbicides (such as, for example, HPPD inhibitors, ALS inhibitors, for example primisulfuron, prosulfuron and trifloxysulfuron, EPSPS (5-enol-pyrovyl-shikimate-3-phosphate-synthase) inhibitors, GS (glutamine synthetase) inhibitors or PPO 20 (protoporphyrinogen-oxidase) inhibitors) as a result of conventional methods of breeding or genetic engineering. An example of a crop that has been rendered tolerant to imidazolinones, e.g. imazamox, by conventional methods of breeding (mutagenesis) is Clearfield® summer rape (Canola). Examples of crops that have been rendered tolerant to herbicides or classes of herbicides by genetic engineering methods include glyphosate- and glufosinate-resistant maize varieties commercially available under the 25 trade names RoundupReady®, Herculex I® and LibertyLink®.

The term "useful plants" is to be understood as including also useful plants which have been so transformed by the use of recombinant DNA techniques that they are capable of synthesising one or more selectively acting toxins, such as are known, for example, from toxin-producing bacteria, especially 30 those of the genus *Bacillus*.

Examples of such plants are: YieldGard® (maize variety that expresses a CryIA(b) toxin); YieldGard Rootworm® (maize variety that expresses a CryIIIB(b1) toxin); YieldGard Plus® (maize variety that expresses a CryIA(b) and a CryIIIB(b1) toxin); Starlink® (maize variety that expresses a 35 Cry9(c) toxin); Herculex I® (maize variety that expresses a CryIF(a2) toxin and the enzyme phosphinothricine N-acetyltransferase (PAT) to achieve tolerance to the herbicide glufosinate ammonium); NuCOTN 33B® (cotton variety that expresses a CryIA(c) toxin); Bollgard I® (cotton variety that expresses a CryIA(c) toxin); Bollgard II® (cotton variety that expresses a CryIA(c) and a CryIIA(b) toxin); VIPCOT® (cotton variety that expresses a VIP toxin); NewLeaf® (potato variety that expresses

a CryIIIA toxin); NatureGard® Agrisure® GT Advantage (GA21 glyphosate-tolerant trait), Agrisure® CB Advantage (Bt11 corn borer (CB) trait), Agrisure® RW (corn rootworm trait) and Protecta®.

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

Toxins that can be expressed by such transgenic plants include, for example, insecticidal proteins from *Bacillus cereus* or *Bacillus popilliae*; or insecticidal proteins from *Bacillus thuringiensis*, such as δ -endotoxins, e.g. Cry1Ab, Cry1Ac, Cry1F, Cry1Fa2, Cry2Ab, Cry3A, Cry3Bb1 or Cry9C, or vegetative insecticidal proteins (Vip), e.g. Vip1, Vip2, Vip3 or Vip3A; or insecticidal proteins of bacteria colonising nematodes, for example *Photorhabdus* spp. or *Xenorhabdus* spp., such as *Photorhabdus luminescens*, *Xenorhabdus nematophilus*; toxins produced by animals, such as scorpion toxins, arachnid toxins, wasp toxins and other insect-specific neurotoxins; toxins produced by fungi, such as *Streptomyces* toxins, plant lectins, such as pea lectins, barley lectins or snowdrop lectins; agglutinins; proteinase inhibitors, such as trypsin inhibitors, serine protease inhibitors, patatin, cystatin, papain inhibitors; ribosome-inactivating proteins (RIP), such as ricin, maize-RIP, abrin, luffin, saporin or bryodin; steroid metabolism enzymes, such as 3-hydroxysteroidoxidase, ecdysteroid-UDP-glycosyl-transferase, cholesterol oxidases, ecdysone inhibitors, HMG-COA-reductase, ion channel blockers, such as blockers of sodium or calcium channels, juvenile hormone esterase, diuretic hormone receptors, stilbene synthase, bibenzyl synthase, chitinases and glucanases.

In the context of the present invention there are to be understood by δ -endotoxins, for example Cry1Ab, Cry1Ac, Cry1F, Cry1Fa2, Cry2Ab, Cry3A, Cry3Bb1 or Cry9C, or vegetative insecticidal proteins (Vip), for example Vip1, Vip2, Vip3 or Vip3A, expressly also hybrid toxins, truncated toxins and modified toxins. Hybrid toxins are produced recombinantly by a new combination of different domains of those proteins (see, for example, WO 02/15701). Truncated toxins, for example a truncated Cry1Ab, are known. In the case of modified toxins, one or more amino acids of the naturally occurring toxin are replaced. In such amino acid replacements, preferably non-naturally present protease recognition sequences are inserted into the toxin, such as, for example, in the case of Cry3A055, a cathepsin-G-recognition sequence is inserted into a Cry3A toxin (see WO 03/018810).

Examples of such toxins or transgenic plants capable of synthesising such toxins are disclosed, for example, in EP-A-0 374 753, WO 93/07278, WO 95/34656, EP-A-0 427 529, EP-A-451 878 and WO 03/052073.

The processes for the preparation of such transgenic plants are generally known to the person skilled in the art and are described, for example, in the publications mentioned above. CryI-type deoxyribonucleic acids and their preparation are known, for example, from WO 95/34656, EP-A-0 367 474, EP-A-0 401 979 and WO 90/13651.

The toxin contained in the transgenic plants imparts to the plants tolerance to harmful insects. Such insects can occur in any taxonomic group of insects, but are especially commonly found in the beetles (Coleoptera), two-winged insects (Diptera) and butterflies (Lepidoptera).

5 Transgenic plants containing one or more genes that code for an insecticidal resistance and express one or more toxins are known and some of them are commercially available. Examples of such plants are: YieldGard® (maize variety that expresses a Cry1Ab toxin); YieldGard Rootworm® (maize variety that expresses a Cry3Bb1 toxin); YieldGard Plus® (maize variety that expresses a Cry1Ab and a Cry3Bb1 toxin); Starlink® (maize variety that expresses a Cry9C toxin); Herculex I® (maize variety
10 that expresses a Cry1Fa2 toxin and the enzyme phosphinothricine N-acetyltransferase (PAT) to achieve tolerance to the herbicide glufosinate ammonium); NuCOTN 33B® (cotton variety that expresses a Cry1Ac toxin); Bollgard I® (cotton variety that expresses a Cry1Ac toxin); Bollgard II® (cotton variety that expresses a Cry1Ac and a Cry2Ab toxin); VipCot® (cotton variety that expresses a Vip3A and a Cry1Ab toxin); NewLeaf® (potato variety that expresses a Cry3A toxin); NatureGard®, Agrisure® GT
15 Advantage (GA21 glyphosate-tolerant trait), Agrisure® CB Advantage (Bt11 corn borer (CB) trait) and Protecta®.

Further examples of such transgenic crops are:

20 1. **Bt11 Maize** from Syngenta Seeds SAS, Chemin de l'Hobit 27, F-31 790 St. Sauveur, France, registration number C/FR/96/05/10. Genetically modified *Zea mays* which has been rendered resistant to attack by the European corn borer (*Ostrinia nubilalis* and *Sesamia nonagrioides*) by transgenic expression of a truncated Cry1Ab toxin. Bt11 maize also transgenically expresses the enzyme PAT to achieve tolerance to the herbicide glufosinate ammonium.

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2. **Bt176 Maize** from Syngenta Seeds SAS, Chemin de l'Hobit 27, F-31 790 St. Sauveur, France, registration number C/FR/96/05/10. Genetically modified *Zea mays* which has been rendered resistant to attack by the European corn borer (*Ostrinia nubilalis* and *Sesamia nonagrioides*) by transgenic expression of a Cry1Ab toxin. Bt176 maize also transgenically expresses the enzyme PAT to achieve
30 tolerance to the herbicide glufosinate ammonium.

3. **MIR604 Maize** from Syngenta Seeds SAS, Chemin de l'Hobit 27, F-31 790 St. Sauveur, France, registration number C/FR/96/05/10. Maize which has been rendered insect-resistant by transgenic expression of a modified Cry3A toxin. This toxin is Cry3A055 modified by insertion of a cathepsin-G-
35 protease recognition sequence. The preparation of such transgenic maize plants is described in WO 03/018810.

4. **MON 863 Maize** from Monsanto Europe S.A. 270-272 Avenue de Tervuren, B-1150 Brussels, Belgium, registration number C/DE/02/9. MON 863 expresses a Cry3Bb1 toxin and has resistance to
40 certain Coleoptera insects.

5. **IPC 531 Cotton** from Monsanto Europe S.A. 270-272 Avenue de Tervuren, B-1150 Brussels, Belgium, registration number C/ES/96/02.
- 5 6. **1507 Maize** from Pioneer Overseas Corporation, Avenue Tedesco, 7 B-1160 Brussels, Belgium, registration number C/NL/00/10. Genetically modified maize for the expression of the protein Cry1F for achieving resistance to certain Lepidoptera insects and of the PAT protein for achieving tolerance to the herbicide glufosinate ammonium.
- 10 7. **NK603 × MON 810 Maize** from Monsanto Europe S.A. 270-272 Avenue de Tervuren, B-1150 Brussels, Belgium, registration number C/GB/02/M3/03. Consists of conventionally bred hybrid maize varieties by crossing the genetically modified varieties NK603 and MON 810. NK603 × MON 810 Maize transgenically expresses the protein CP4 EPSPS, obtained from *Agrobacterium sp.* strain CP4, which imparts tolerance to the herbicide Roundup® (contains glyphosate), and also a Cry1Ab toxin obtained
15 from *Bacillus thuringiensis subsp. kurstaki* which brings about tolerance to certain Lepidoptera, include the European corn borer.

The term "locus" as used herein means fields in or on which plants are growing, or where seeds of cultivated plants are sown, or where seed will be placed into the soil. It includes soil, seeds, and
20 seedlings, as well as established vegetation.

The term "plants" refers to all physical parts of a plant, including seeds, seedlings, saplings, roots, tubers, stems, stalks, foliage, and fruits.

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

30 Pesticidal agents referred to herein using their common name are known, for example, from "The Pesticide Manual", 15th Ed., British Crop Protection Council 2009.

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

Suitable carriers and adjuvants, e.g., for agricultural use, can be solid or liquid and are substances useful in formulation technology, e.g. natural or regenerated mineral substances, solvents, dispersants, wetting agents, tackifiers, thickeners, binders or fertilizers. Such carriers are for example described in WO 97/33890.

5 The compounds of formula (I) are normally used in the form of compositions and can be applied to the crop area or plant to be treated, simultaneously or in succession with further compounds. These further compounds can be, e.g., fertilizers or micronutrient donors or other preparations, which influence the growth of plants. They can also be selective herbicides or non-selective herbicides as well as insecticides, fungicides, bactericides, nematocides, molluscicides or mixtures of several of these
10 preparations, if desired together with further carriers, surfactants or application promoting adjuvants customarily employed in the art of formulation.

The compounds of formula (I) may be used in the form of (fungicidal) compositions for controlling or protecting against phytopathogenic microorganisms, comprising as active ingredient at least one compound of formula (I) or of at least one preferred individual compound as above-defined, in free form
15 or in agrochemically usable salt form, and at least one of the above-mentioned adjuvants.

The invention provides a composition, preferably a fungicidal composition, comprising at least one compound formula (I) an agriculturally acceptable carrier and optionally an adjuvant. An agricultural acceptable carrier is for example a carrier that is suitable for agricultural use. Agricultural carriers are well known in the art. Preferably, said composition may comprise at least one or more pesticidally active
20 compounds, for example an additional fungicidal active ingredient in addition to the compound of formula (I).

The compound of formula (I) may be the sole active ingredient of a composition or it may be admixed with one or more additional active ingredients such as a pesticide, fungicide, synergist, herbicide or plant growth regulator where appropriate. An additional active ingredient may, in some
25 cases, result in unexpected synergistic activities.

Examples of suitable additional active ingredients include the following acycloamino acid fungicides, aliphatic nitrogen fungicides, amide fungicides, anilide fungicides, antibiotic fungicides, aromatic fungicides, arsenical fungicides, aryl phenyl ketone fungicides, benzamide fungicides, benzanilide fungicides, benzimidazole fungicides, benzothiazole fungicides, botanical fungicides,
30 bridged diphenyl fungicides, carbamate fungicides, carbanilate fungicides, conazole fungicides, copper fungicides, dicarboximide fungicides, dinitrophenol fungicides, dithiocarbamate fungicides, dithiolane fungicides, furamide fungicides, furanilide fungicides, hydrazide fungicides, imidazole fungicides, mercury fungicides, morpholine fungicides, organophosphorous fungicides, organotin fungicides, oxathiin fungicides, oxazole fungicides, phenylsulfamide fungicides, polysulfide fungicides, pyrazole
35 fungicides, pyridine fungicides, pyrimidine fungicides, pyrrole fungicides, quaternary ammonium fungicides, quinoline fungicides, quinone fungicides, quinoxaline fungicides, strobilurin fungicides, sulfonanilide fungicides, thiadiazole fungicides, thiazole fungicides, thiazolidine fungicides, thiocarbamate fungicides, thiophene fungicides, triazine fungicides, triazole fungicides, triazolopyrimidine fungicides, urea fungicides, valinamide fungicides, and zinc fungicides.

40 Examples of suitable additional active ingredients also include the following: petroleum oils, 1,1-bis(4-chlorophenyl)-2-ethoxyethanol, 2,4-dichlorophenyl benzenesulfonate, 2-fluoro-N-methyl-N-1-

naphthylacetamide, 4-chlorophenyl phenyl sulfone, acetoprole, aldoxycarb, amidithion, amidothioate, amiton, amiton hydrogen oxalate, amitraz, aramite, arsenous oxide, azobenzene, azothoate, benomyl, benoxafos, benzyl benzoate, bixafen, brofenvalerate, bromocyclen, bromophos, bromopropylate, buprofezin, butocarboxim, butoxycarboxim, butylpyridaben, calcium polysulfide, camphechlor, 5 carbanolate, carbophenothion, cymiazole, chinomethionat, chlorbenside, chlordimeform, chlordimeform hydrochloride, chlorfenethol, chlorfenson, chlorfensulfide, chlorobenzilate, chloromebuform, chloromethiuron, chloropropylate, chlorthiophos, cinerin I, cinerin II, cinerins, closantel, coumaphos, crotamiton, crotoxyphos, cufraneb, cyanthoate, DCPM, DDT, demephion, demephion-O, demephion-S, demeton-methyl, demeton-O, demeton-O-methyl, demeton-S, demeton-S-methyl, demeton-S- 10 methylsulfon, dichlofluanid, dichlorvos, dicliphos, dienochlor, dimefox, dinex, dinex-diclexine, dinocap-4, dinocap-6, dinocron, dinopenton, dinosulfon, dinoterbon, dioxathion, diphenyl sulfone, disulfiram, DNOC, dofenapyn, doramectin, endothion, eprinomectin, ethoate-methyl, etrimfos, fenazaflor, fenbutatin oxide, fenothiocarb, fenpyrad, fenpyroximate, fenpyrazamine, fenson, fentrifanil, flubenzimine, flucycloxuron, fluenetil, fluorbenside, FMC 1137, formetanate, formetanate hydrochloride, 15 formparanate, gamma-HCH, glyodin, halfenprox, hexadecyl cyclopropanecarboxylate, isocarbophos, jasmolin I, jasmolin II, jodfenphos, lindane, malonoben, mecarbam, mephosfolan, mesulfen, methacrifos, methyl bromide, metolcarb, mexacarbate, milbemycin oxime, mipafox, monocrotophos, morphothion, moxidectin, naled, 4-chloro-2-(2-chloro-2-methyl-propyl)-5-[(6-iodo-3-pyridyl)methoxy]pyridazin-3-one, nifluridide, nikkomycins, nitrilacarb, nitrilacarb 1:1 zinc chloride 20 complex, omethoate, oxydeprofos, oxydisulfoton, pp'-DDT, parathion, permethrin, phenkapton, phosalone, phosfolan, phosphamidon, polychloroterpenes, polynactins, proclonol, promacyl, propoxur, prothidathion, prothoate, pyrethrin I, pyrethrin II, pyrethrins, pyridaphenthion, pyrimitate, quinalphos, quintiofos, R-1492, phosglycin, rotenone, schradan, sebufos, selamectin, sophamide, SSI-121, sulfiram, sulfluramid, sulfotep, sulfur, diflovidazin, tau-fluvalinate, TEPP, terbam, tetradifon, tetrasul, thiafenox, 25 thiocarboxime, thiofanox, thiometon, thioquinox, thuringiensin, triamiphos, triarathene, triazophos, triazuron, trifenofos, trinactin, vamidothion, vanilprole, bethoxazin, copper dioctanoate, copper sulfate, cybutryne, dichlone, dichlorophen, endothal, fentin, hydrated lime, nabam, quinoxamine, quinonamid, simazine, triphenyltin acetate, triphenyltin hydroxide, crufomate, piperazine, thiophanate, chloralose, fenthion, pyridin-4-amine, strychnine, 1-hydroxy-1H-pyridine-2-thione, 4-(quinoxalin-2-ylamino)benzenesulfonamide, 8-hydroxyquinoline sulfate, bronopol, copper hydroxide, cresol, 30 dipyrithione, dodicin, fenaminosulf, formaldehyde, hydrargaphen, kasugamycin, kasugamycin hydrochloride hydrate, nickel bis(dimethyldithiocarbamate), nitrapyrin, oclothilone, oxolinic acid, oxytetracycline, potassium hydroxyquinoline sulfate, probenazole, streptomycin, streptomycin sesquisulfate, tecloftalam, thiomersal, Adoxophyes orana GV, Agrobacterium radiobacter, Amblyseius spp., Anagrapta falcifera NPV, Anagrus atomus, Aphelinus abdominalis, Aphidius colemani, 35 Aphidoletes aphidimyza, Autographa californica NPV, Bacillus sphaericus Neide, Beauveria brongniartii, Chrysoperla carnea, Cryptolaemus montrouzieri, Cydia pomonella GV, Dacnusa sibirica, Diglyphus isaea, Encarsia formosa, Eretmocerus eremicus, Heterorhabditis bacteriophora and H. megidis, Hippodamia convergens, Leptomastix dactylopii, Macrolophus caliginosus, Mamestra brassicae NPV, 40 Metaphycus helvolus, Metarhizium anisopliae var. acridum, Metarhizium anisopliae var. anisopliae, Neodiprion sertifer NPV and N. lecontei NPV, Orius spp., Paecilomyces fumosoroseus, Phytoseiulus

persimilis, Steinernema bibionis, Steinernema carpocapsae, Steinernema feltiae, Steinernema glaseri, Steinernema riobrave, Steinernema riobravus, Steinernema scapterisci, Steinernema spp., Trichogramma spp., Typhlodromus occidentalis, Verticillium lecanii, apholate, bisazir, busulfan, dimatif, hemel, hempa, metepa, methiotepa, methyl apholate, morzid, penfluron, tepa, thiohempa, thiotepa, 5 tretamine, uredepa, (E)-dec-5-en-1-yl acetate with (E)-dec-5-en-1-ol, (E)-tridec-4-en-1-yl acetate, (E)-6-methylhept-2-en-4-ol, (E,Z)-tetradeca-4,10-dien-1-yl acetate, (Z)-dodec-7-en-1-yl acetate, (Z)-hexadec-11-enal, (Z)-hexadec-11-en-1-yl acetate, (Z)-hexadec-13-en-11-yn-1-yl acetate, (Z)-icos-13-en-10-one, (Z)-tetradec-7-en-1-al, (Z)-tetradec-9-en-1-ol, (Z)-tetradec-9-en-1-yl acetate, (7E,9Z)-dodeca-7,9-dien-1-yl acetate, (9Z,11E)-tetradeca-9,11-dien-1-yl acetate, (9Z,12E)-tetradeca-9,12-dien-1-yl acetate, 14-10 methyloctadec-1-ene, 4-methylnonan-5-ol with 4-methylnonan-5-one, alpha-multistriatin, brevicomin, codlure, codlemone, cuelure, disparlure, dodec-8-en-1-yl acetate, dodec-9-en-1-yl acetate, dodeca-8,10-dien-1-yl acetate, dominicalure, ethyl 4-methyloctanoate, eugenol, frontalin, grandlure, grandlure I, grandlure II, grandlure III, grandlure IV, hexalure, ipsdienol, ipsenol, japonilure, lineatin, litlure, looplure, medlure, megatomoic acid, methyl eugenol, muscalure, octadeca-2,13-dien-1-yl acetate, octadeca-15 3,13-dien-1-yl acetate, orfuralure, oryctalure, ostramone, siglure, sordidin, sulcatol, tetradec-11-en-1-yl acetate, trimedlure, trimedlure A, trimedlure B₁, trimedlure B₂, trimedlure C, trunc-call, 2-(octylthio)-ethanol, butopyronoxyl, butoxy(polypropylene glycol), dibutyl adipate, dibutyl phthalate, dibutyl succinate, diethyltoluamide, dimethyl carbate, dimethyl phthalate, ethyl hexanediol, hexamide, methoquin-butyl, methylneodecanamide, oxamate, picaridin, 1-dichloro-1-nitroethane, 1,1-dichloro-2,2-20 bis(4-ethylphenyl)ethane, 1,2-dichloropropane with 1,3-dichloropropene, 1-bromo-2-chloroethane, 2,2,2-trichloro-1-(3,4-dichlorophenyl)ethyl acetate, 2,2-dichlorovinyl 2-ethylsulfinylethyl methyl phosphate, 2-(1,3-dithiolan-2-yl)phenyl dimethylcarbamate, 2-(2-butoxyethoxy)ethyl thiocyanate, 2-(4,5-dimethyl-1,3-dioxolan-2-yl)phenyl methylcarbamate, 2-(4-chloro-3,5-xylyloxy)ethanol, 2-chlorovinyl diethyl phosphate, 2-imidazolidone, 2-isovalerylindan-1,3-dione, 2-methyl(prop-2-ynyl)aminophenyl 25 methylcarbamate, 2-thiocyanatoethyl laurate, 3-bromo-1-chloroprop-1-ene, 3-methyl-1-phenylpyrazol-5-yl dimethylcarbamate, 4-methyl(prop-2-ynyl)amino-3,5-xylyl methylcarbamate, 5,5-dimethyl-3-oxocyclohex-1-enyl dimethylcarbamate, acethion, acrylonitrile, aldrin, allosamidin, allyxycarb, alpha-ecdysone, aluminium phosphide, aminocarb, anabasine, athidathion, azamethiphos, Bacillus thuringiensis delta endotoxins, barium hexafluorosilicate, barium polysulfide, barthrin, Bayer 22/190, 30 Bayer 22408, beta-cyfluthrin, beta-cypermethrin, bioethanomethrin, biopermethrin, bis(2-chloroethyl) ether, borax, bromfenvinfos, bromo-DDT, bufencarb, butacarb, butathiofos, butonate, calcium arsenate, calcium cyanide, carbon disulfide, carbon tetrachloride, cartap hydrochloride, cevadine, chlorbicyclen, chlordane, chlordecone, chloroform, chloropicrin, chlorphoxim, chlorprazophos, cis-resmethrin, cismethrin, clocythrion, copper acetoarsenite, copper arsenate, copper oleate, coumithoate, cryolite, CS 35 708, cyanofenphos, cyanophos, cyclethrin, cythioate, d-tetramethrin, DAEP, dazomet, decarbofuran, diamidafos, dicapthon, dichlofenthion, dicresyl, dicyclanil, dieldrin, diethyl 5-methylpyrazol-3-yl phosphate, dilor, dimefluthrin, dimetan, dimethrin, dimethylvinphos, dimetilan, dinoprop, dinosam, dinoseb, diofenolan, dioxabenzofos, dithicrofos, DSP, ecdysterone, EI 1642, EMPC, EPBP, etaphos, ethiofencarb, ethyl formate, ethylene dibromide, ethylene dichloride, ethylene oxide, EXD, fenchlorphos, 40 fenethacarb, fenitrothion, fenoxacrim, fenpirithrin, fensulfothion, fenthion-ethyl, flucofuron, fosmethilan, fospirate, fosthietan, furathiocarb, furethrin, guazatine, guazatine acetates, sodium tetrathiocarbonate,

halfenprox, HCH, HEOD, heptachlor, heterophos, HHDN, hydrogen cyanide, hyquincarb, IPSP, isazofos, isobenzan, isodrin, isofenphos, isolane, isoprothiolane, isoxathion, juvenile hormone I, juvenile hormone II, juvenile hormone III, kelevan, kinoprene, lead arsenate, leptophos, lirimfos, lythidathion, m-cumenyl methylcarbamate, magnesium phosphide, mazidox, mecarphon, menazon, mercurous chloride, mesulfenfos, metam, metam-potassium, metam-sodium, methanesulfonyl fluoride, methocrotophos, methoprene, methothrin, methoxychlor, methyl isothiocyanate, methylchloroform, methylene chloride, metoxadiazone, mirex, naftalofos, naphthalene, NC-170, nicotine, nicotine sulfate, nithiazine, nornicotine, O-5-dichloro-4-iodophenyl O-ethyl ethylphosphonothioate, O,O-diethyl O-4-methyl-2-oxo-2H-chromen-7-yl phosphorothioate, O,O-diethyl O-6-methyl-2-propylpyrimidin-4-yl phosphorothioate, O,O,O',O'-tetrapropyl dithiopyrophosphate, oleic acid, para-dichlorobenzene, parathion-methyl, pentachlorophenol, pentachlorophenyl laurate, PH 60-38, phenkapton, phosnichlor, phosphine, phoxim-methyl, pirimetaphos, polychlorodicyclopentadiene isomers, potassium arsenite, potassium thiocyanate, precocene I, precocene II, precocene III, primidophos, profluthrin, promecarb, prothiofos, pyrazophos, pyresmethrin, quassia, quinalphos-methyl, quinothion, rafoxanide, resmethrin, rotenone, kadethrin, ryania, ryanodine, sabadilla), schradan, sebufos, SI-0009, thiapronil, sodium arsenite, sodium cyanide, sodium fluoride, sodium hexafluorosilicate, sodium pentachlorophenoxide, sodium selenate, sodium thiocyanate, sulcofuron, sulcofuron-sodium, sulfuryl fluoride, sulprofos, tar oils, tazimcarb, TDE, tebupirimfos, temephos, terallethrin, tetrachloroethane, thicofos, thiocyclam, thiocyclam hydrogen oxalate, thionazin, thiosultap, thiosultap-sodium, tralomethrin, transpermethrin, triazamate, trichlormetaphos-3, trichloronat, trimethacarb, tolprocarb, triclopyricarb, triprene, veratridine, veratrine, XMC, zetamethrin, zinc phosphide, zolaprofos, and meperfluthrin, tetramethylfluthrin, bis(tributyltin) oxide, bromoacetamide, ferric phosphate, niclosamide-olamine, tributyltin oxide, pyrimorph, trifenmorph, 1,2-dibromo-3-chloropropane, 1,3-dichloropropene, 3,4-dichlorotetrahydrothiophene 1,1-dioxide, 3-(4-chlorophenyl)-5-methylrhodanine, 5-methyl-6-thioxo-1,3,5-thiadiazinan-3-ylacetic acid, 6-isopentenylaminopurine, benclotiaz, cytokinins, DCIP, furfural, isamidofos, kinetin, Myrothecium verrucaria composition, tetrachlorothiophene, xlenols, zeatin, potassium ethylxanthate, acibenzolar, acibenzolar-S-methyl, Reynoutria sachalinensis extract, alpha-chlorohydrin, antu, barium carbonate, bisthiosemi, brodifacoum, bromadiolone, bromethalin, chlorophacinone, cholecalciferol, coumachlor, coumafuryl, coumatetralyl, crimidine, difenacoum, difethialone, diphacinone, ergocalciferol, flocoumafen, fluoroacetamide, flupropadine, flupropadine hydrochloride, norbormide, phosacetim, phosphorus, pindone, pyrinuron, scilliroside, sodium fluoroacetate, thallium sulfate, warfarin, 2-(2-butoxyethoxy)ethyl piperonylate, 5-(1,3-benzodioxol-5-yl)-3-hexylcyclohex-2-enone, farnesol with nerolidol, verbutin, MGK 264, piperonyl butoxide, piprotal, propyl isomer, S421, sesamex, sesasmolin, sulfoxide, anthraquinone, copper naphthenate, copper oxychloride, dicyclopentadiene, thiram, zinc naphthenate, ziram, imanin, ribavirin, mercuric oxide, thiophanate-methyl, azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, furametpyr, hexaconazole, imazalil, imibenconazole, ipconazole, metconazole, myclobutanil, paclobutrazole, pefurazoate, penconazole, prothioconazole, pyrifenoxy, prochloraz, propiconazole, pyrisoxazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triflumizole, triticonazole, ancymidol, fenarimol, nuarimol, bupirimate, dimethirimol, ethirimol, dodemorph, fenpropidine, fenpropimorph, spiroxamine, tridemorph, cyprodinil, mepanipyrim,

pyrimethanil, fenpiclonil, fludioxonil, benalaxyl, furalaxyl, metalaxyl, R-metalaxyl, ofurace, oxadixyl, carbendazim, debacarb, fuberidazole, thiabendazole, chlozolate, dichlozoline, myclozoline, procymidone, vinclozoline, boscalid, carboxin, fenfuram, flutolanil, mepronil, oxycarboxin, penthiopyrad, thifluzamide, dodine, iminocadine, azoxystrobin, dimoxystrobin, enestroburin, fenaminstrobin,

5 flufenoxystrobin, fluoxastrobin, kresoxim-methyl, metominostrobin, trifloxystrobin, orysastrobin, picoxystrobin, pyraclostrobin, pyrametostrobin, pyraoxystrobin, ferbam, mancozeb, maneb, metiram, propineb, zineb, captan, fluoroimide, folpet, tolylfluanid, bordeaux mixture, copper oxide, mancopper, oxine-copper, nitrothal-isopropyl, edifenphos, iprobenphos, phosdiphen, tolclofos-methyl, anilazine, benthialdicarb, blasticidin-S, chloroneb, chlorothalonil, cyflufenamid, cymoxanil, diclocymet,

10 diclomezine, dicloran, diethofencarb, dimethomorph, flumorph, dithianon, ethaboxam, etridiazole, famoxadone, fenamidone, fenoxanil, ferimzone, fluazinam, fluopicolide, flusulfamide, fluxapyroxad, fenhexamid, fosetyl-aluminium, hymexazol, iprovalicarb, cyazofamid, methasulfocarb, metrafenone, pencycuron, phthalide, polyoxins, propamocarb, pyribencarb, proquinazid, pyroquilon, pyriofenone, quinoxifen, quintozene, tiadinil, triazoxide, tricyclazole, triforine, validamycin, valifenalate, zoxamide,

15 mandipropamid, isopyrazam, sedaxane, benzovindiflupyr, pydiflumetofen, 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (3',4',5'-trifluoro-biphenyl-2-yl)-amide, isoflucypram, isotianil, dipymetitrone, 6-ethyl-5,7-dioxo-pyrrolo[4,5][1,4]dithiino[1,2-c]isothiazole-3-carbonitrile, 2-(difluoromethyl)-N-[3-ethyl-1,1-dimethyl-indan-4-yl]pyridine-3-carboxamide, 4-(2,6-difluorophenyl)-6-methyl-5-phenyl-pyridazine-3-carbonitrile, (R)-3-(difluoromethyl)-1-methyl-N-[1,1,3-trimethylindan-4-yl]pyrazole-4-carboxamide,

20 4-(2-bromo-4-fluoro-phenyl)-N-(2-chloro-6-fluoro-phenyl)-2,5-dimethyl-pyrazol-3-amine, 4-(2-bromo-4-fluorophenyl)-N-(2-chloro-6-fluorophenyl)-1,3-dimethyl-1H-pyrazol-5-amine, fluindapyr, coumethoxystrobin (jiaxiangjunzhi), lvbenmixianan, dichlobentiazox, mandestrobin, 3-(4,4-difluoro-3,4-dihydro-3,3-dimethylisoquinolin-1-yl)quinolone, 2-[2-fluoro-6-[(8-fluoro-2-methyl-3-quinolyl)oxy]phenyl]propan-2-ol, oxathiapiprolin, tert-butyl N-[6-[[[(1-methyltetrazol-5-yl)-phenyl-methylene]amino]oxymethyl]-2-pyridyl]carbamate,

25 pyraziflumid, inpyrfluxam, trolprocarb, mefentrifluconazole, ipfentrifluconazole, 2-(difluoromethyl)-N-[(3R)-3-ethyl-1,1-dimethyl-indan-4-yl]pyridine-3-carboxamide, N'-(2,5-dimethyl-4-phenoxy-phenyl)-N-ethyl-N-methyl-formamidine, N'-[4-(4,5-dichlorothiazol-2-yl)oxy-2,5-dimethyl-phenyl]-N-ethyl-N-methyl-formamidine, [2-[3-[2-[1-[2-[3,5-bis(difluoromethyl)pyrazol-1-yl]acetyl]-4-piperidyl]thiazol-4-yl]-4,5-dihydroisoxazol-5-yl]-3-chloro-phenyl]

30 methanesulfonate, but-3-ynyl N-[6-[[[(1-methyltetrazol-5-yl)-phenyl-methylene]amino]oxymethyl]-2-pyridyl]carbamate, methyl N-[[5-[4-(2,4-dimethylphenyl)triazol-2-yl]-2-methyl-phenyl]methyl]carbamate, 3-chloro-6-methyl-5-phenyl-4-(2,4,6-trifluorophenyl)pyridazine, pyridachlometyl, 3-(difluoromethyl)-1-methyl-N-[1,1,3-trimethylindan-4-yl]pyrazole-4-carboxamide, 1-[2-[[1-(4-chlorophenyl)pyrazol-3-yl]oxymethyl]-3-methyl-phenyl]-4-methyl-tetrazol-5-one, 1-methyl-4-[3-

35 methyl-2-[[2-methyl-4-(3,4,5-trimethylpyrazol-1-yl)phenoxy]methyl]phenyl]tetrazol-5-one, aminopyrifin, ametocetradin, amisulbrom, penflufen, (Z,2E)-5-[1-(4-chlorophenyl)pyrazol-3-yl]oxy-2-methoxyimino-N,3-dimethyl-pent-3-enamide, florylpicoxamid, fempicoxamid, tebufloquin, ipflufenquin, quinfumelin, isofetamid, N-[2-[2,4-dichloro-phenoxy]phenyl]-3-(difluoromethyl)-1-methyl-pyrazole-4-carboxamide, N-[2-[2-chloro-4-(trifluoromethyl)phenoxy]phenyl]-3-(difluoromethyl)-1-methyl-pyrazole-4-carboxamide,

40 benzothiostrobin, phenamacril, 5-amino-1,3,4-thiadiazole-2-thiol zinc salt (2:1), fluopyram, flutianil, fluopimomide, pyrapropoyne, picarbutrazox, 2-(difluoromethyl)-N-(3-ethyl-1,1-dimethyl-indan-4-

yl)pyridine-3-carboxamide, 2-(difluoromethyl)-N-((3R)-1,1,3-trimethylindan-4-yl)pyridine-3-carboxamide, 4-[[6-[2-(2,4-difluorophenyl)-1,1-difluoro-2-hydroxy-3-(1,2,4-triazol-1-yl)propyl]-3-pyridyl]oxy]benzonitrile, metyltetraprole, 2-(difluoromethyl)-N-((3R)-1,1,3-trimethylindan-4-yl)pyridine-3-carboxamide, α -(1,1-dimethylethyl)- α -[4'-(trifluoromethoxy)[1,1'-biphenyl]-4-yl]-5-pyrimidinemethanol, fluoxapiprolin, enoxastrobin, 4-[[6-[2-(2,4-difluorophenyl)-1,1-difluoro-2-hydroxy-3-(1,2,4-triazol-1-yl)propyl]-3-pyridyl]oxy] benzonitrile, 4-[[6-[2-(2,4-difluorophenyl)-1,1-difluoro-2-hydroxy-3-(5-sulfanyl-1,2,4-triazol-1-yl)propyl]-3-pyridyl]oxy] benzonitrile, 4-[[6-[2-(2,4-difluorophenyl)-1,1-difluoro-2-hydroxy-3-(5-thioxo-4H-1,2,4-triazol-1-yl)propyl]-3-pyridyl]oxy]benzonitrile, trinexapac, coumoxystrobin, zhongshengmycin, thiodiazole copper, zinc thiazole, amectotractin, iprodione, N-methoxy-N-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]cyclopropanecarboxamide, N,2-dimethoxy-N-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]propanamide, N-ethyl-2-methyl-N-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]propanamide, 1-methoxy-3-methyl-1-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]urea, 1,3-dimethoxy-1-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]urea, 3-ethyl-1-methoxy-1-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]urea, N-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]propanamide, 4,4-dimethyl-2-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]isoxazolidin-3-one, 5,5-dimethyl-2-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]isoxazolidin-3-one, ethyl 1-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]pyrazole-4-carboxylate, N,N-dimethyl-1-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]-1,2,4-triazol-3-amine, which may be prepared from the methods described in WO 2017/055473, WO 2017/055469, WO 2017/093348 and WO 2017/118689, 2-[6-(4-chlorophenoxy)-2-(trifluoromethyl)-3-pyridyl]-1-(1,2,4-triazol-1-yl)propan-2-ol (this compound may be prepared from the methods described in WO 2017/029179), 2-[6-(4-bromophenoxy)-2-(trifluoromethyl)-3-pyridyl]-1-(1,2,4-triazol-1-yl)propan-2-ol (this compound may be prepared from the methods described in WO 2017/029179), 3-[2-(1-chlorocyclopropyl)-3-(2-fluorophenyl)-2-hydroxy-propyl]imidazole-4-carbonitrile (this compound may be prepared from the methods described in WO 2016/156290), 3-[2-(1-chlorocyclopropyl)-3-(3-chloro-2-fluoro-phenyl)-2-hydroxy-propyl]imidazole-4-carbonitrile (this compound may be prepared from the methods described in WO 2016/156290), (4-phenoxyphenyl)methyl 2-amino-6-methyl-pyridine-3-carboxylate (this compound may be prepared from the methods described in WO 2014/006945), 2,6-Dimethyl-1H,5H-[1,4]dithiino[2,3-c:5,6-c']dipyrrole-1,3,5,7(2H,6H)-tetrone (this compound may be prepared from the methods described in WO 2011/138281), N-methyl-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzenecarbothioamide, N-methyl-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzamide, (Z,2E)-5-[1-(2,4-dichlorophenyl)pyrazol-3-yl]oxy-2-methoxyimino-N,3-dimethyl-pent-3-enamide (this compound may be prepared from the methods described in WO 2018/153707), N'-(2-chloro-5-methyl-4-phenoxy-phenyl)-N-ethyl-N-methyl-formamidine, N'-[2-chloro-4-(2-fluorophenoxy)-5-methyl-phenyl]-N-ethyl-N-methyl-formamidine (this compound may be prepared from the methods described in WO 2016/202742), 2-(difluoromethyl)-N-[(3S)-3-ethyl-1,1-dimethyl-indan-4-yl]pyridine-3-carboxamide (this compound may be prepared from the methods described in WO 2014/095675).

The compounds of the invention may also be used in combination with anthelmintic agents. Such anthelmintic agents include, compounds selected from the macrocyclic lactone class of

compounds such as ivermectin, avermectin, abamectin, emamectin, eprinomectin, doramectin, selamectin, moxidectin, nemadectin and milbemycin derivatives as described in EP-357460, EP-444964 and EP-594291. Additional anthelmintic agents include semisynthetic and biosynthetic avermectin/milbemycin derivatives such as those described in US-5015630, WO-9415944 and WO-9522552. Additional anthelmintic agents include the benzimidazoles such as albendazole, cambendazole, fenbendazole, flubendazole, mebendazole, oxfendazole, oxibendazole, parbendazole, and other members of the class. Additional anthelmintic agents include imidazothiazoles and tetrahydropyrimidines such as tetramisole, levamisole, pyrantel pamoate, oxantel or morantel. Additional anthelmintic agents include flukicides, such as triclabendazole and clorsulon and the cestocides, such as praziquantel and epsiprantel.

The compounds of the invention may be used in combination with derivatives and analogues of the paraherquamide/marcfortine class of anthelmintic agents, as well as the antiparasitic oxazolines such as those disclosed in US-5478855, US- 4639771 and DE-19520936.

The compounds of the invention may be used in combination with derivatives and analogues of the general class of dioxomorpholine antiparasitic agents as described in WO-9615121 and also with anthelmintic active cyclic depsipeptides such as those described in WO-9611945, WO-9319053, WO-9325543, EP-626375, EP-382173, WO-9419334, EP-382173, and EP-503538.

The compounds of the invention may be used in combination with other ectoparasiticides; for example, fipronil; pyrethroids; organophosphates; insect growth regulators such as lufenuron; ecdysone agonists such as tebufenozide and the like; neonicotinoids such as imidacloprid and the like.

The compounds of the invention may be used in combination with terpene alkaloids, for example those described in WO 95/19363 or WO 04/72086, particularly the compounds disclosed therein.

Other examples of such biologically active compounds that the compounds of the invention may be used in combination with include but are not restricted to the following:

Organophosphates: acephate, azamethiphos, azinphos-ethyl, azinphos- methyl, bromophos, bromophos-ethyl, cadusafos, chlorethoxyphos, chlorpyrifos, chlorfenvinphos, chlormephos, demeton, demeton-S-methyl, demeton-S-methyl sulphone, dialifos, diazinon, dichlorvos, dicrotophos, dimethoate, disulfoton, ethion, ethoprophos, etrimfos, famphur, fenamiphos, fenitrothion, fensulfothion, fenthion, flupyrzofos, fonofos, formothion, fosthiazate, heptenophos, isazophos, isothioate, isoxathion, malathion, methacriphos, methamidophos, methidathion, methyl- parathion, mevinphos, monocrotophos, naled, omethoate, oxydemeton-methyl, paraoxon, parathion, parathion-methyl, phenthoate, phosalone, phosfolan, phosphocarb, phosmet, phosphamidon, phorate, phoxim, pirimiphos, pirimiphos- methyl, profenofos, propaphos, proetamphos, prothiofos, pyraclofos, pyridapenthion, quinalphos, sulprophos, temephos, terbufos, tebupirimfos, tetrachlorvinphos, thimeton, triazophos, trichlorfon, vamidothion.

Carbamates: alanycarb, aldicarb, 2-sec-butylphenyl methylcarbamate, benfuracarb, carbaryl, carbofuran, carbosulfan, cloethocarb, ethiofencarb, fenoxycarb, fenthioncarb, furathiocarb, HCN-801, isoprocarb, indoxacarb, methiocarb, methomyl, 5-methyl-m-cumenylbutyryl(methyl)carbamate, oxamyl, pirimicarb, propoxur, thiodicarb, thiofanox, triazamate, UC-51717.

Pyrethroids: acrinathin, allethrin, alphametrin, 5-benzyl-3-furylmethyl (E) -

(1 R)-cis-2,2-dimethyl-3-(2-oxothiolan-3-ylidenemethyl)cyclopropanecarboxylate, bifenthrin, beta -cyfluthrin, cyfluthrin, a-cypermethrin, beta -cypermethrin, bioallethrin, bioallethrin((S)-cyclopentylisomer), bioresmethrin, bifenthrin, NCI-85193, cycloprothrin, cyhalothrin, cythithrin, cyphenothrin, deltamethrin, empenthrin, esfenvalerate, ethofenprox, fenfluthrin, fenpropathrin, fenvalerate, flucythrinate, flumethrin, fluvalinate (D isomer), imiprothrin, cyhalothrin, lambda-cyhalothrin, permethrin, phenothrin, prallethrin, pyrethrins (natural products), resmethrin, tetramethrin, transfluthrin, theta-cypermethrin, silafluofen, t-fluvalinate, tefluthrin, tralomethrin, Zeta-cypermethrin.

Arthropod growth regulators: a) chitin synthesis inhibitors: benzoylureas: chlorfluazuron, diflubenzuron, fluazuron, flucycloxuron, flufenoxuron, hexaflumuron, lufenuron, novaluron, teflubenzuron, triflumuron, buprofezin, diofenolan, hexythiazox, etoxazole, chlorfentazine; b) ecdysone antagonists: halofenozide, methoxyfenozide, tebufenozide; c) juvenoids: pyriproxyfen, methoprene (including S-methoprene), fenoxycarb; d) lipid biosynthesis inhibitors: spiroadicofen.

Other antiparasitics: acequinocyl, amitraz, AKD-1022, ANS-118, azadirachtin, *Bacillus thuringiensis*, bensultap, bifenazate, binapacryl, bromopropylate, BTG-504, BTG-505, camphechlor, cartap, chlorobenzilate, chlordimeform, chlorfenapyr, chromafenozide, clothianidine, cyromazine, diacloden, diafenthiuron, DBI-3204, dinactin, dihydroxymethyl-dihydroxypyrrolidine, dinobuton, dinocap, endosulfan, ethiprole, ethofenprox, fenazaquin, flumite, MTI- 800, fenpyroximate, fluacrypyrim, flubenzimine, flubrocycythrinate, flufenzine, flufenprox, fluproxyfen, halofenprox, hydramethylnon, IKI-220, kanemite, NC-196, neem guard, nidinorterfuran, nitenpyram, SD-35651, WL-108477, pirydaryl, propargite, protrifenbute, pymethroline, pyridaben, pyrimidifen, NC-1111, R-195, RH-0345, RH-2485, RYI-210, S-1283, S-1833, SI-8601, silafluofen, silomadin, spinosad, tebufenpyrad, tetradifon, tetranactin, thiacloprid, thiocyclam, thiamethoxam, tolfenpyrad, triazamate, triethoxyspinosyn, trinactin, verbutin, vertalec, YI-5301.

Biological agents: *Bacillus thuringiensis* ssp aizawai, kurstaki, *Bacillus thuringiensis* delta endotoxin, baculovirus, entomopathogenic bacteria, virus and fungi.

Bactericides: chlortetracycline, oxytetracycline, streptomycin.

Other biological agents: enrofloxacin, febantel, penethamate, moloxicam, cefalexin, kanamycin, pimobendan, clenbuterol, omeprazole, tiamulin, benazepril, pyriprole, cefquinome, florfenicol, buserelin, cefovecin, tulathromycin, ceftiofur, carprofen, metaflumizone, praziquantel, triclabendazole.

Another aspect of invention is related to the use of a compound of formula (I) or of a preferred individual compound as above-defined, of a composition comprising at least one compound of formula (I) or at least one preferred individual compound as above-defined, or of a fungicidal or insecticidal mixture comprising at least one compound of formula (I) or at least one preferred individual compound as above-defined, in admixture with other fungicides or insecticides as described above, for controlling or preventing infestation of plants, e.g. useful plants such as crop plants, propagation material thereof, e.g. seeds, harvested crops, e.g., harvested food crops, or non-living materials by insects or by phytopathogenic microorganisms, preferably fungal organisms.

A further aspect of invention is related to a method of controlling or preventing an infestation of plants, e.g., useful plants such as crop plants, propagation material thereof, e.g. seeds, harvested crops, e.g. harvested food crops, or of non-living materials by insects or by phytopathogenic or spoilage microorganisms or organisms potentially harmful to man, especially fungal organisms, which comprises

the application of a compound of formula (I) or of a preferred individual compound as above-defined as active ingredient to the plants, to parts of the plants or to the locus thereof, to the propagation material thereof, or to any part of the non-living materials.

Controlling or preventing means reducing infestation by insects or by phytopathogenic or spoilage microorganisms or organisms potentially harmful to man, especially fungal organisms, to such a level that an improvement is demonstrated.

A preferred method of controlling or preventing an infestation of crop plants by phytopathogenic microorganisms, especially fungal organisms, or insects which comprises the application of a compound of formula (I), or an agrochemical composition which contains at least one of said compounds, is foliar application. The frequency of application and the rate of application will depend on the risk of infestation by the corresponding pathogen or insect. However, the compounds of formula (I) can also penetrate the plant through the roots via the soil (systemic action) by drenching the locus of the plant with a liquid formulation, or by applying the compounds in solid form to the soil, e.g., in granular form (soil application). In crops of water rice such granulates can be applied to the flooded rice field. The compounds of formula (I) may also be applied to seeds (coating) by impregnating the seeds or tubers either with a liquid formulation of the fungicide or coating them with a solid formulation.

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

Advantageous rates of application are normally from 5g to 2kg of active ingredient (a.i.) per hectare (ha), preferably from 10g to 1kg a.i./ha, most preferably from 20g to 600g a.i./ha. When used as seed drenching agent, convenient dosages are from 10mg to 1g of active substance per kg of seeds.

When the combinations of the present invention are used for treating seed, rates of 0.001 to 50 g of a compound of formula (I) per kg of seed, preferably from 0.01 to 10g per kg of seed are generally sufficient.

The compositions of the invention may be employed in any conventional form, for example in the form of a twin pack, a powder for dry seed treatment (DS), an emulsion for seed treatment (ES), a flowable concentrate for seed treatment (FS), a solution for seed treatment (LS), a water dispersible powder for seed treatment (WS), a capsule suspension for seed treatment (CF), a gel for seed treatment (GF), an emulsion concentrate (EC), a suspension concentrate (SC), a suspo-emulsion (SE), a capsule suspension (CS), a water dispersible granule (WG), an emulsifiable granule (EG), an emulsion, water in oil (EO), an emulsion, oil in water (EW), a micro-emulsion (ME), an oil dispersion (OD), an oil miscible flowable (OF), an oil miscible liquid (OL), a soluble concentrate (SL), an ultra-low volume suspension (SU), an ultra-low volume liquid (UL), a technical concentrate (TK), a dispersible concentrate (DC), a wettable powder (WP) or any technically feasible formulation in combination with agriculturally acceptable adjuvants.

Such compositions may be produced in conventional manner, e.g., by mixing the active ingredients with appropriate formulation inerts (diluent, solvents, fillers and optionally other formulating ingredients such as surfactants, biocides, anti-freeze, stickers, thickeners and compounds that provide adjuvancy effects). Also conventional slow release formulations may be employed where long lasting

efficacy is intended. Particularly formulations to be applied in spraying forms, such as water dispersible concentrates (e.g. EC, SC, DC, OD, SE, EW, EO and the like), wettable powders and granules, may contain surfactants such as wetting and dispersing agents and other compounds that provide adjuvancy effects, e.g. the condensation product of formaldehyde with naphthalene sulphonate, an alkylarylsulphonate, a lignin sulphonate, a fatty alkyl sulphate, and ethoxylated alkylphenol and an ethoxylated fatty alcohol.

A seed dressing formulation is applied in a manner known per se to the seeds employing the combination of the invention and a diluent in suitable seed dressing formulation form, e.g., as an aqueous suspension or in a dry powder form having good adherence to the seeds. Such seed dressing formulations are known in the art. Seed dressing formulations may contain the single active ingredients or the combination of active ingredients in encapsulated form, e.g. as slow release capsules or microcapsules.

In general, the formulations include from 0.01 to 90% by weight of active agent, from 0 to 20% agriculturally acceptable surfactant and 10 to 99.99% solid or liquid formulation inerts and adjuvant(s), the active agent consisting of at least the compound of formula (I) together with component (B) and (C), and optionally other active agents, particularly microbiocides or conservatives or the like. Concentrated forms of compositions generally contain in between about 2 and 80%, preferably between about 5 and 70% by weight of active agent. Application forms of formulation may for example contain from 0.01 to 20% by weight, preferably from 0.01 to 5% by weight of active agent. Whereas commercial products will preferably be formulated as concentrates, the end user will normally employ diluted formulations.

Table 1 below illustrates examples of individual compounds of formula (I) according to the invention.

Table 1: Individual compounds of formula (I) according to the invention

Cpd No.	X	Y	R ²	R ¹	Cpd No.	X	Y	R ²	R ¹
1	CH	CH	Cl	H	411	N	CH	Cl	CH ₂ OCH ₃
2	CH	CH	Cl	CH ₃	412	N	CH	Cl	CH(CH ₃)OCH ₃
3	CH	CH	Cl	CH ₂ CH ₃	413	N	CH	Cl	C(CH ₃) ₂ OCH ₃
4	CH	CH	Cl	OCH ₃	414	N	CH	Cl	CH ₂ F
5	CH	CH	Cl	OCH ₂ CH ₃	415	N	CH	Cl	CH ₂ Cl
6	CH	CH	Cl	CH ₂ OCH ₃	416	N	CH	Cl	CH ₂ Br
7	CH	CH	Cl	CH(CH ₃)OCH ₃	417	N	CH	Cl	CH ₂ CF ₃
8	CH	CH	Cl	C(CH ₃) ₂ OCH ₃	418	N	CH	Cl	CH ₂ CO ₂ CH ₃
9	CH	CH	Cl	CH ₂ F	419	N	CH	Cl	CH ₂ CH ₂ CO ₂ CH ₃
10	CH	CH	Cl	CH ₂ Cl	420	N	CH	Cl	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃
11	CH	CH	Cl	CH ₂ Br	421	N	CH	Cl	cyclopropyl
12	CH	CH	Cl	CH ₂ CF ₃	422	N	CH	Cl	CO ₂ CH ₃
13	CH	CH	Cl	CH ₂ CO ₂ CH ₃	423	N	CH	Cl	CO ₂ CH ₂ CH ₃
14	CH	CH	Cl	CH ₂ CH ₂ CO ₂ CH ₃	424	N	CH	Cl	Ph

Cpd No.	X	Y	R ²	R ¹	Cpd No.	X	Y	R ²	R ¹
15	CH	CH	Cl	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃	425	N	CH	Cl	2-furanyl
16	CH	CH	Cl	cyclopropyl	426	N	CH	Cl	2-thiophenyl
17	CH	CH	Cl	CO ₂ CH ₃	427	N	CH	Cl	OPh
18	CH	CH	Cl	CO ₂ CH ₂ CH ₃	428	N	CH	Cl	OCH ₂ CCH
19	CH	CH	Cl	Ph	429	N	CH	Cl	OCH ₂ CH ₂ OCH ₃
20	CH	CH	Cl	2-furanyl	430	N	CH	Cl	SCH ₃
21	CH	CH	Cl	2-thiophenyl	431	N	CH	Cl	SCH ₂ CH ₃
22	CH	CH	Cl	OPh	432	N	CH	Cl	SCH(CH ₃) ₂
23	CH	CH	Cl	OCH ₂ CCH	433	N	CH	Br	H
24	CH	CH	Cl	OCH ₂ CH ₂ OCH ₃	434	N	CH	Br	CH ₃
25	CH	CH	Cl	SCH ₃	435	N	CH	Br	CH ₂ CH ₃
26	CH	CH	Cl	SCH ₂ CH ₃	436	N	CH	Br	OCH ₃
27	CH	CH	Cl	SCH(CH ₃) ₂	437	N	CH	Br	OCH ₂ CH ₃
28	CH	CH	Br	H	438	N	CH	Br	CH ₂ OCH ₃
29	CH	CH	Br	CH ₃	439	N	CH	Br	CH(CH ₃)OCH ₃
30	CH	CH	Br	CH ₂ CH ₃	440	N	CH	Br	C(CH ₃) ₂ OCH ₃
31	CH	CH	Br	OCH ₃	441	N	CH	Br	CH ₂ F
32	CH	CH	Br	OCH ₂ CH ₃	442	N	CH	Br	CH ₂ Cl
33	CH	CH	Br	CH ₂ OCH ₃	443	N	CH	Br	CH ₂ Br
34	CH	CH	Br	CH(CH ₃)OCH ₃	444	N	CH	Br	CH ₂ CF ₃
35	CH	CH	Br	C(CH ₃) ₂ OCH ₃	445	N	CH	Br	CH ₂ CO ₂ CH ₃
36	CH	CH	Br	CH ₂ F	446	N	CH	Br	CH ₂ CH ₂ CO ₂ CH ₃
37	CH	CH	Br	CH ₂ Cl	447	N	CH	Br	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃
38	CH	CH	Br	CH ₂ Br	448	N	CH	Br	cyclopropyl
39	CH	CH	Br	CH ₂ CF ₃	449	N	CH	Br	CO ₂ CH ₃
40	CH	CH	Br	CH ₂ CO ₂ CH ₃	450	N	CH	Br	CO ₂ CH ₂ CH ₃
41	CH	CH	Br	CH ₂ CH ₂ CO ₂ CH ₃	451	N	CH	Br	Ph
42	CH	CH	Br	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃	452	N	CH	Br	2-furanyl
43	CH	CH	Br	cyclopropyl	453	N	CH	Br	2-thiophenyl
44	CH	CH	Br	CO ₂ CH ₃	454	N	CH	Br	OPh
45	CH	CH	Br	CO ₂ CH ₂ CH ₃	455	N	CH	Br	OCH ₂ CCH
46	CH	CH	Br	Ph	456	N	CH	Br	OCH ₂ CH ₂ OCH ₃
47	CH	CH	Br	2-furanyl	457	N	CH	Br	SCH ₃
48	CH	CH	Br	2-thiophenyl	458	N	CH	Br	SCH ₂ CH ₃
49	CH	CH	Br	OPh	459	N	CH	Br	SCH(CH ₃) ₂
50	CH	CH	Br	OCH ₂ CCH	460	N	CH	CH ₃	H
51	CH	CH	Br	OCH ₂ CH ₂ OCH ₃	461	N	CH	CH ₃	CH ₃
52	CH	CH	Br	SCH ₃	462	N	CH	CH ₃	CH ₂ CH ₃
53	CH	CH	Br	SCH ₂ CH ₃	463	N	CH	CH ₃	OCH ₃
54	CH	CH	Br	SCH(CH ₃) ₂	464	N	CH	CH ₃	OCH ₂ CH ₃
55	CH	CH	CH ₃	H	465	N	CH	CH ₃	CH ₂ OCH ₃
56	CH	CH	CH ₃	CH ₃	466	N	CH	CH ₃	CH(CH ₃)OCH ₃
57	CH	CH	CH ₃	CH ₂ CH ₃	467	N	CH	CH ₃	C(CH ₃) ₂ OCH ₃
58	CH	CH	CH ₃	OCH ₃	468	N	CH	CH ₃	CH ₂ F
59	CH	CH	CH ₃	OCH ₂ CH ₃	469	N	CH	CH ₃	CH ₂ Cl

Cpd No.	X	Y	R ²	R ¹	Cpd No.	X	Y	R ²	R ¹
60	CH	CH	CH ₃	CH ₂ OCH ₃	470	N	CH	CH ₃	CH ₂ Br
61	CH	CH	CH ₃	CH(CH ₃)OCH ₃	471	N	CH	CH ₃	CH ₂ CF ₃
62	CH	CH	CH ₃	C(CH ₃) ₂ OCH ₃	472	N	CH	CH ₃	CH ₂ CO ₂ CH ₃
63	CH	CH	CH ₃	CH ₂ F	473	N	CH	CH ₃	CH ₂ CH ₂ CO ₂ CH ₃
64	CH	CH	CH ₃	CH ₂ Cl	474	N	CH	CH ₃	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃
65	CH	CH	CH ₃	CH ₂ Br	475	N	CH	CH ₃	cyclopropyl
66	CH	CH	CH ₃	CH ₂ CF ₃	476	N	CH	CH ₃	CO ₂ CH ₃
67	CH	CH	CH ₃	CH ₂ CO ₂ CH ₃	477	N	CH	CH ₃	CO ₂ CH ₂ CH ₃
68	CH	CH	CH ₃	CH ₂ CH ₂ CO ₂ CH ₃	478	N	CH	CH ₃	Ph
69	CH	CH	CH ₃	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃	479	N	CH	CH ₃	2-furanyl
70	CH	CH	CH ₃	cyclopropyl	480	N	CH	CH ₃	2-thiophenyl
71	CH	CH	CH ₃	CO ₂ CH ₃	481	N	CH	CH ₃	OPh
72	CH	CH	CH ₃	CO ₂ CH ₂ CH ₃	482	N	CH	CH ₃	OCH ₂ CCH
73	CH	CH	CH ₃	Ph	483	N	CH	CH ₃	OCH ₂ CH ₂ OCH ₃
74	CH	CH	CH ₃	2-furanyl	484	N	CH	CH ₃	SCH ₃
75	CH	CH	CH ₃	2-thiophenyl	485	N	CH	CH ₃	SCH ₂ CH ₃
76	CH	CH	CH ₃	OPh	486	N	CH	CH ₃	SCH(CH ₃) ₂
77	CH	CH	CH ₃	OCH ₂ CCH	487	N	CH	OCH ₃	H
78	CH	CH	CH ₃	OCH ₂ CH ₂ OCH ₃	488	N	CH	OCH ₃	CH ₃
79	CH	CH	CH ₃	SCH ₃	489	N	CH	OCH ₃	CH ₂ CH ₃
80	CH	CH	CH ₃	SCH ₂ CH ₃	490	N	CH	OCH ₃	OCH ₃
81	CH	CH	CH ₃	SCH(CH ₃) ₂	491	N	CH	OCH ₃	OCH ₂ CH ₃
82	CH	CH	OCH ₃	H	492	N	CH	OCH ₃	CH ₂ OCH ₃
83	CH	CH	OCH ₃	CH ₃	493	N	CH	OCH ₃	CH(CH ₃)OCH ₃
84	CH	CH	OCH ₃	CH ₂ CH ₃	494	N	CH	OCH ₃	C(CH ₃) ₂ OCH ₃
85	CH	CH	OCH ₃	OCH ₃	495	N	CH	OCH ₃	CH ₂ F
86	CH	CH	OCH ₃	OCH ₂ CH ₃	496	N	CH	OCH ₃	CH ₂ Cl
87	CH	CH	OCH ₃	CH ₂ OCH ₃	497	N	CH	OCH ₃	CH ₂ Br
88	CH	CH	OCH ₃	CH(CH ₃)OCH ₃	498	N	CH	OCH ₃	CH ₂ CF ₃
89	CH	CH	OCH ₃	C(CH ₃) ₂ OCH ₃	499	N	CH	OCH ₃	CH ₂ CO ₂ CH ₃
90	CH	CH	OCH ₃	CH ₂ F	500	N	CH	OCH ₃	CH ₂ CH ₂ CO ₂ CH ₃
91	CH	CH	OCH ₃	CH ₂ Cl	501	N	CH	OCH ₃	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃
92	CH	CH	OCH ₃	CH ₂ Br	502	N	CH	OCH ₃	cyclopropyl
93	CH	CH	OCH ₃	CH ₂ CF ₃	503	N	CH	OCH ₃	CO ₂ CH ₃
94	CH	CH	OCH ₃	CH ₂ CO ₂ CH ₃	504	N	CH	OCH ₃	CO ₂ CH ₂ CH ₃
95	CH	CH	OCH ₃	CH ₂ CH ₂ CO ₂ CH ₃	505	N	CH	OCH ₃	Ph
96	CH	CH	OCH ₃	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃	506	N	CH	OCH ₃	2-furanyl
97	CH	CH	OCH ₃	cyclopropyl	507	N	CH	OCH ₃	2-thiophenyl
98	CH	CH	OCH ₃	CO ₂ CH ₃	508	N	CH	OCH ₃	OPh
99	CH	CH	OCH ₃	CO ₂ CH ₂ CH ₃	509	N	CH	OCH ₃	OCH ₂ CCH
100	CH	CH	OCH ₃	Ph	510	N	CH	OCH ₃	OCH ₂ CH ₂ OCH ₃
101	CH	CH	OCH ₃	2-furanyl	511	N	CH	OCH ₃	SCH ₃
102	CH	CH	OCH ₃	2-thiophenyl	512	N	CH	OCH ₃	SCH ₂ CH ₃
103	CH	CH	OCH ₃	OPh	513	N	CH	OCH ₃	SCH(CH ₃) ₂
104	CH	CH	OCH ₃	OCH ₂ CCH	514	N	CH	NHCHO	H

Cpd No.	X	Y	R ²	R ¹	Cpd No.	X	Y	R ²	R ¹
105	CH	CH	OCH ₃	OCH ₂ CH ₂ OCH ₃	515	N	CH	NHCHO	CH ₃
106	CH	CH	OCH ₃	SCH ₃	516	N	CH	NHCHO	CH ₂ CH ₃
107	CH	CH	OCH ₃	SCH ₂ CH ₃	517	N	CH	NHCHO	OCH ₃
108	CH	CH	OCH ₃	SCH(CH ₃) ₂	518	N	CH	NHCHO	OCH ₂ CH ₃
109	CH	CH	NHCHO	H	519	N	CH	NHCHO	CH ₂ OCH ₃
110	CH	CH	NHCHO	CH ₃	520	N	CH	NHCHO	CH(CH ₃)OCH ₃
111	CH	CH	NHCHO	CH ₂ CH ₃	521	N	CH	NHCHO	C(CH ₃) ₂ OCH ₃
112	CH	CH	NHCHO	OCH ₃	522	N	CH	NHCHO	CH ₂ F
113	CH	CH	NHCHO	OCH ₂ CH ₃	523	N	CH	NHCHO	CH ₂ Cl
114	CH	CH	NHCHO	CH ₂ OCH ₃	524	N	CH	NHCHO	CH ₂ Br
115	CH	CH	NHCHO	CH(CH ₃)OCH ₃	525	N	CH	NHCHO	CH ₂ CF ₃
116	CH	CH	NHCHO	C(CH ₃) ₂ OCH ₃	526	N	CH	NHCHO	CH ₂ CO ₂ CH ₃
117	CH	CH	NHCHO	CH ₂ F	527	N	CH	NHCHO	CH ₂ CH ₂ CO ₂ CH ₃
118	CH	CH	NHCHO	CH ₂ Cl	528	N	CH	NHCHO	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃
119	CH	CH	NHCHO	CH ₂ Br	529	N	CH	NHCHO	cyclopropyl
120	CH	CH	NHCHO	CH ₂ CF ₃	530	N	CH	NHCHO	CO ₂ CH ₃
121	CH	CH	NHCHO	CH ₂ CO ₂ CH ₃	531	N	CH	NHCHO	CO ₂ CH ₂ CH ₃
122	CH	CH	NHCHO	CH ₂ CH ₂ CO ₂ CH ₃	532	N	CH	NHCHO	Ph
123	CH	CH	NHCHO	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃	533	N	CH	NHCHO	2-furanyl
124	CH	CH	NHCHO	cyclopropyl	534	N	CH	NHCHO	2-thiophenyl
125	CH	CH	NHCHO	CO ₂ CH ₃	535	N	CH	NHCHO	OPh
126	CH	CH	NHCHO	CO ₂ CH ₂ CH ₃	536	N	CH	NHCHO	OCH ₂ CCH
127	CH	CH	NHCHO	Ph	537	N	CH	NHCHO	OCH ₂ CH ₂ OCH ₃
128	CH	CH	NHCHO	2-furanyl	538	N	CH	NHCHO	SCH ₃
129	CH	CH	NHCHO	2-thiophenyl	539	N	CH	NHCHO	SCH ₂ CH ₃
130	CH	CH	NHCHO	OPh	540	N	CH	NHCHO	SCH(CH ₃) ₂
131	CH	CH	NHCHO	OCH ₂ CCH	541	N	CF	Cl	H
132	CH	CH	NHCHO	OCH ₂ CH ₂ OCH ₃	542	N	CF	Cl	CH ₃
133	CH	CH	NHCHO	SCH ₃	543	N	CF	Cl	CH ₂ CH ₃
134	CH	CH	NHCHO	SCH ₂ CH ₃	544	N	CF	Cl	OCH ₃
135	CH	CH	NHCHO	SCH(CH ₃) ₂	545	N	CF	Cl	OCH ₂ CH ₃
136	CH	CF	Cl	H	546	N	CF	Cl	CH ₂ OCH ₃
137	CH	CF	Cl	CH ₃	547	N	CF	Cl	CH(CH ₃)OCH ₃
138	CH	CF	Cl	CH ₂ CH ₃	548	N	CF	Cl	C(CH ₃) ₂ OCH ₃
139	CH	CF	Cl	OCH ₃	549	N	CF	Cl	CH ₂ F
140	CH	CF	Cl	OCH ₂ CH ₃	550	N	CF	Cl	CH ₂ Cl
141	CH	CF	Cl	CH ₂ OCH ₃	551	N	CF	Cl	CH ₂ Br
142	CH	CF	Cl	CH(CH ₃)OCH ₃	552	N	CF	Cl	CH ₂ CF ₃
143	CH	CF	Cl	C(CH ₃) ₂ OCH ₃	553	N	CF	Cl	CH ₂ CO ₂ CH ₃
144	CH	CF	Cl	CH ₂ F	554	N	CF	Cl	CH ₂ CH ₂ CO ₂ CH ₃
145	CH	CF	Cl	CH ₂ Cl	555	N	CF	Cl	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃
146	CH	CF	Cl	CH ₂ Br	556	N	CF	Cl	cyclopropyl
147	CH	CF	Cl	CH ₂ CF ₃	557	N	CF	Cl	CO ₂ CH ₃
148	CH	CF	Cl	CH ₂ CO ₂ CH ₃	558	N	CF	Cl	CO ₂ CH ₂ CH ₃
149	CH	CF	Cl	CH ₂ CH ₂ CO ₂ CH ₃	559	N	CF	Cl	Ph

Cpd No.	X	Y	R ²	R ¹	Cpd No.	X	Y	R ²	R ¹
150	CH	CF	Cl	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃	560	N	CF	Cl	2-furanyl
151	CH	CF	Cl	cyclopropyl	561	N	CF	Cl	2-thiophenyl
152	CH	CF	Cl	CO ₂ CH ₃	562	N	CF	Cl	OPh
153	CH	CF	Cl	CO ₂ CH ₂ CH ₃	563	N	CF	Cl	OCH ₂ CCH
154	CH	CF	Cl	Ph	564	N	CF	Cl	OCH ₂ CH ₂ OCH ₃
155	CH	CF	Cl	2-furanyl	565	N	CF	Cl	SCH ₃
156	CH	CF	Cl	2-thiophenyl	566	N	CF	Cl	SCH ₂ CH ₃
157	CH	CF	Cl	OPh	567	N	CF	Cl	SCH(CH ₃) ₂
158	CH	CF	Cl	OCH ₂ CCH	568	N	CF	Br	H
159	CH	CF	Cl	OCH ₂ CH ₂ OCH ₃	569	N	CF	Br	CH ₃
160	CH	CF	Cl	SCH ₃	570	N	CF	Br	CH ₂ CH ₃
161	CH	CF	Cl	SCH ₂ CH ₃	571	N	CF	Br	OCH ₃
162	CH	CF	Cl	SCH(CH ₃) ₂	572	N	CF	Br	OCH ₂ CH ₃
163	CH	CF	Br	H	573	N	CF	Br	CH ₂ OCH ₃
164	CH	CF	Br	CH ₃	574	N	CF	Br	CH(CH ₃)OCH ₃
165	CH	CF	Br	CH ₂ CH ₃	575	N	CF	Br	C(CH ₃) ₂ OCH ₃
166	CH	CF	Br	OCH ₃	576	N	CF	Br	CH ₂ F
167	CH	CF	Br	OCH ₂ CH ₃	577	N	CF	Br	CH ₂ Cl
168	CH	CF	Br	CH ₂ OCH ₃	578	N	CF	Br	CH ₂ Br
169	CH	CF	Br	CH(CH ₃)OCH ₃	579	N	CF	Br	CH ₂ CF ₃
170	CH	CF	Br	C(CH ₃) ₂ OCH ₃	580	N	CF	Br	CH ₂ CO ₂ CH ₃
171	CH	CF	Br	CH ₂ F	581	N	CF	Br	CH ₂ CH ₂ CO ₂ CH ₃
172	CH	CF	Br	CH ₂ Cl	582	N	CF	Br	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃
173	CH	CF	Br	CH ₂ Br	583	N	CF	Br	cyclopropyl
174	CH	CF	Br	CH ₂ CF ₃	584	N	CF	Br	CO ₂ CH ₃
175	CH	CF	Br	CH ₂ CO ₂ CH ₃	585	N	CF	Br	CO ₂ CH ₂ CH ₃
176	CH	CF	Br	CH ₂ CH ₂ CO ₂ CH ₃	586	N	CF	Br	Ph
177	CH	CF	Br	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃	587	N	CF	Br	2-furanyl
178	CH	CF	Br	cyclopropyl	588	N	CF	Br	2-thiophenyl
179	CH	CF	Br	CO ₂ CH ₃	589	N	CF	Br	OPh
180	CH	CF	Br	CO ₂ CH ₂ CH ₃	590	N	CF	Br	OCH ₂ CCH
181	CH	CF	Br	Ph	591	N	CF	Br	OCH ₂ CH ₂ OCH ₃
182	CH	CF	Br	2-furanyl	592	N	CF	Br	SCH ₃
183	CH	CF	Br	2-thiophenyl	593	N	CF	Br	SCH ₂ CH ₃
184	CH	CF	Br	OPh	594	N	CF	Br	SCH(CH ₃) ₂
185	CH	CF	Br	OCH ₂ CCH	595	N	CF	CH ₃	H
186	CH	CF	Br	OCH ₂ CH ₂ OCH ₃	596	N	CF	CH ₃	CH ₃
187	CH	CF	Br	SCH ₃	597	N	CF	CH ₃	CH ₂ CH ₃
188	CH	CF	Br	SCH ₂ CH ₃	598	N	CF	CH ₃	OCH ₃
189	CH	CF	Br	SCH(CH ₃) ₂	599	N	CF	CH ₃	OCH ₂ CH ₃
190	CH	CF	CH ₃	H	600	N	CF	CH ₃	CH ₂ OCH ₃
191	CH	CF	CH ₃	CH ₃	601	N	CF	CH ₃	CH(CH ₃)OCH ₃
192	CH	CF	CH ₃	CH ₂ CH ₃	602	N	CF	CH ₃	C(CH ₃) ₂ OCH ₃
193	CH	CF	CH ₃	OCH ₃	603	N	CF	CH ₃	CH ₂ F
194	CH	CF	CH ₃	OCH ₂ CH ₃	604	N	CF	CH ₃	CH ₂ Cl

Cpd No.	X	Y	R ²	R ¹	Cpd No.	X	Y	R ²	R ¹
195	CH	CF	CH ₃	CH ₂ OCH ₃	605	N	CF	CH ₃	CH ₂ Br
196	CH	CF	CH ₃	CH(CH ₃)OCH ₃	606	N	CF	CH ₃	CH ₂ CF ₃
197	CH	CF	CH ₃	C(CH ₃) ₂ OCH ₃	607	N	CF	CH ₃	CH ₂ CO ₂ CH ₃
198	CH	CF	CH ₃	CH ₂ F	608	N	CF	CH ₃	CH ₂ CH ₂ CO ₂ CH ₃
199	CH	CF	CH ₃	CH ₂ Cl	609	N	CF	CH ₃	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃
200	CH	CF	CH ₃	CH ₂ Br	610	N	CF	CH ₃	cyclopropyl
201	CH	CF	CH ₃	CH ₂ CF ₃	611	N	CF	CH ₃	CO ₂ CH ₃
202	CH	CF	CH ₃	CH ₂ CO ₂ CH ₃	612	N	CF	CH ₃	CO ₂ CH ₂ CH ₃
203	CH	CF	CH ₃	CH ₂ CH ₂ CO ₂ CH ₃	613	N	CF	CH ₃	Ph
204	CH	CF	CH ₃	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃	614	N	CF	CH ₃	2-furanyl
205	CH	CF	CH ₃	cyclopropyl	615	N	CF	CH ₃	2-thiophenyl
206	CH	CF	CH ₃	CO ₂ CH ₃	616	N	CF	CH ₃	OPh
207	CH	CF	CH ₃	CO ₂ CH ₂ CH ₃	617	N	CF	CH ₃	OCH ₂ CCH
208	CH	CF	CH ₃	Ph	618	N	CF	CH ₃	OCH ₂ CH ₂ OCH ₃
209	CH	CF	CH ₃	2-furanyl	619	N	CF	CH ₃	SCH ₃
210	CH	CF	CH ₃	2-thiophenyl	620	N	CF	CH ₃	SCH ₂ CH ₃
211	CH	CF	CH ₃	OPh	621	N	CF	CH ₃	SCH(CH ₃) ₂
212	CH	CF	CH ₃	OCH ₂ CCH	622	N	CF	OCH ₃	H
213	CH	CF	CH ₃	OCH ₂ CH ₂ OCH ₃	623	N	CF	OCH ₃	CH ₃
214	CH	CF	CH ₃	SCH ₃	624	N	CF	OCH ₃	CH ₂ CH ₃
215	CH	CF	CH ₃	SCH ₂ CH ₃	625	N	CF	OCH ₃	OCH ₃
216	CH	CF	CH ₃	SCH(CH ₃) ₂	626	N	CF	OCH ₃	OCH ₂ CH ₃
217	CH	CF	OCH ₃	H	627	N	CF	OCH ₃	CH ₂ OCH ₃
218	CH	CF	OCH ₃	CH ₃	628	N	CF	OCH ₃	CH(CH ₃)OCH ₃
219	CH	CF	OCH ₃	CH ₂ CH ₃	629	N	CF	OCH ₃	C(CH ₃) ₂ OCH ₃
220	CH	CF	OCH ₃	OCH ₃	630	N	CF	OCH ₃	CH ₂ F
221	CH	CF	OCH ₃	OCH ₂ CH ₃	631	N	CF	OCH ₃	CH ₂ Cl
222	CH	CF	OCH ₃	CH ₂ OCH ₃	632	N	CF	OCH ₃	CH ₂ Br
223	CH	CF	OCH ₃	CH(CH ₃)OCH ₃	633	N	CF	OCH ₃	CH ₂ CF ₃
224	CH	CF	OCH ₃	C(CH ₃) ₂ OCH ₃	634	N	CF	OCH ₃	CH ₂ CO ₂ CH ₃
225	CH	CF	OCH ₃	CH ₂ F	635	N	CF	OCH ₃	CH ₂ CH ₂ CO ₂ CH ₃
226	CH	CF	OCH ₃	CH ₂ Cl	636	N	CF	OCH ₃	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃
227	CH	CF	OCH ₃	CH ₂ Br	637	N	CF	OCH ₃	cyclopropyl
228	CH	CF	OCH ₃	CH ₂ CF ₃	638	N	CF	OCH ₃	CO ₂ CH ₃
229	CH	CF	OCH ₃	CH ₂ CO ₂ CH ₃	639	N	CF	OCH ₃	CO ₂ CH ₂ CH ₃
230	CH	CF	OCH ₃	CH ₂ CH ₂ CO ₂ CH ₃	640	N	CF	OCH ₃	Ph
231	CH	CF	OCH ₃	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃	641	N	CF	OCH ₃	2-furanyl
232	CH	CF	OCH ₃	cyclopropyl	642	N	CF	OCH ₃	2-thiophenyl
233	CH	CF	OCH ₃	CO ₂ CH ₃	643	N	CF	OCH ₃	OPh
234	CH	CF	OCH ₃	CO ₂ CH ₂ CH ₃	644	N	CF	OCH ₃	OCH ₂ CCH
235	CH	CF	OCH ₃	Ph	645	N	CF	OCH ₃	OCH ₂ CH ₂ OCH ₃
236	CH	CF	OCH ₃	2-furanyl	646	N	CF	OCH ₃	SCH ₃
237	CH	CF	OCH ₃	2-thiophenyl	647	N	CF	OCH ₃	SCH ₂ CH ₃
238	CH	CF	OCH ₃	OPh	648	N	CF	OCH ₃	SCH(CH ₃) ₂
239	CH	CF	OCH ₃	OCH ₂ CCH	649	N	CF	NHCHO	H

Cpd No.	X	Y	R ²	R ¹	Cpd No.	X	Y	R ²	R ¹
240	CH	CF	OCH ₃	OCH ₂ CH ₂ OCH ₃	650	N	CF	NHCHO	CH ₃
241	CH	CF	OCH ₃	SCH ₃	651	N	CF	NHCHO	CH ₂ CH ₃
242	CH	CF	OCH ₃	SCH ₂ CH ₃	652	N	CF	NHCHO	OCH ₃
243	CH	CF	OCH ₃	SCH(CH ₃) ₂	653	N	CF	NHCHO	OCH ₂ CH ₃
244	CH	CF	NHCHO	H	654	N	CF	NHCHO	CH ₂ OCH ₃
245	CH	CF	NHCHO	CH ₃	655	N	CF	NHCHO	CH(CH ₃)OCH ₃
246	CH	CF	NHCHO	CH ₂ CH ₃	656	N	CF	NHCHO	C(CH ₃) ₂ OCH ₃
247	CH	CF	NHCHO	OCH ₃	657	N	CF	NHCHO	CH ₂ F
248	CH	CF	NHCHO	OCH ₂ CH ₃	658	N	CF	NHCHO	CH ₂ Cl
249	CH	CF	NHCHO	CH ₂ OCH ₃	659	N	CF	NHCHO	CH ₂ Br
250	CH	CF	NHCHO	CH(CH ₃)OCH ₃	660	N	CF	NHCHO	CH ₂ CF ₃
251	CH	CF	NHCHO	C(CH ₃) ₂ OCH ₃	661	N	CF	NHCHO	CH ₂ CO ₂ CH ₃
252	CH	CF	NHCHO	CH ₂ F	662	N	CF	NHCHO	CH ₂ CH ₂ CO ₂ CH ₃
253	CH	CF	NHCHO	CH ₂ Cl	663	N	CF	NHCHO	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃
254	CH	CF	NHCHO	CH ₂ Br	664	N	CF	NHCHO	cyclopropyl
255	CH	CF	NHCHO	CH ₂ CF ₃	665	N	CF	NHCHO	CO ₂ CH ₃
256	CH	CF	NHCHO	CH ₂ CO ₂ CH ₃	666	N	CF	NHCHO	CO ₂ CH ₂ CH ₃
257	CH	CF	NHCHO	CH ₂ CH ₂ CO ₂ CH ₃	667	N	CF	NHCHO	Ph
258	CH	CF	NHCHO	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃	668	N	CF	NHCHO	2-furanyl
259	CH	CF	NHCHO	cyclopropyl	669	N	CF	NHCHO	2-thiophenyl
260	CH	CF	NHCHO	CO ₂ CH ₃	670	N	CF	NHCHO	OPh
261	CH	CF	NHCHO	CO ₂ CH ₂ CH ₃	671	N	CF	NHCHO	OCH ₂ CCH
262	CH	CF	NHCHO	Ph	672	N	CF	NHCHO	OCH ₂ CH ₂ OCH ₃
263	CH	CF	NHCHO	2-furanyl	673	N	CF	NHCHO	SCH ₃
264	CH	CF	NHCHO	2-thiophenyl	674	N	CF	NHCHO	SCH ₂ CH ₃
265	CH	CF	NHCHO	OPh	675	N	CF	NHCHO	SCH(CH ₃) ₂
266	CH	CF	NHCHO	OCH ₂ CCH	676	N	N	Cl	H
267	CH	CF	NHCHO	OCH ₂ CH ₂ OCH ₃	677	N	N	Cl	CH ₃
268	CH	CF	NHCHO	SCH ₃	678	N	N	Cl	CH ₂ CH ₃
269	CH	CF	NHCHO	SCH ₂ CH ₃	679	N	N	Cl	OCH ₃
270	CH	CF	NHCHO	SCH(CH ₃) ₂	680	N	N	Cl	OCH ₂ CH ₃
271	CH	N	Cl	H	681	N	N	Cl	CH ₂ OCH ₃
272	CH	N	Cl	CH ₃	682	N	N	Cl	CH(CH ₃)OCH ₃
273	CH	N	Cl	CH ₂ CH ₃	683	N	N	Cl	C(CH ₃) ₂ OCH ₃
274	CH	N	Cl	OCH ₃	684	N	N	Cl	CH ₂ F
275	CH	N	Cl	OCH ₂ CH ₃	685	N	N	Cl	CH ₂ Cl
276	CH	N	Cl	CH ₂ OCH ₃	686	N	N	Cl	CH ₂ Br
277	CH	N	Cl	CH(CH ₃)OCH ₃	687	N	N	Cl	CH ₂ CF ₃
278	CH	N	Cl	C(CH ₃) ₂ OCH ₃	688	N	N	Cl	CH ₂ CO ₂ CH ₃
279	CH	N	Cl	CH ₂ F	689	N	N	Cl	CH ₂ CH ₂ CO ₂ CH ₃
280	CH	N	Cl	CH ₂ Cl	690	N	N	Cl	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃
281	CH	N	Cl	CH ₂ Br	691	N	N	Cl	cyclopropyl
282	CH	N	Cl	CH ₂ CF ₃	692	N	N	Cl	CO ₂ CH ₃
283	CH	N	Cl	CH ₂ CO ₂ CH ₃	693	N	N	Cl	CO ₂ CH ₂ CH ₃
284	CH	N	Cl	CH ₂ CH ₂ CO ₂ CH ₃	694	N	N	Cl	Ph

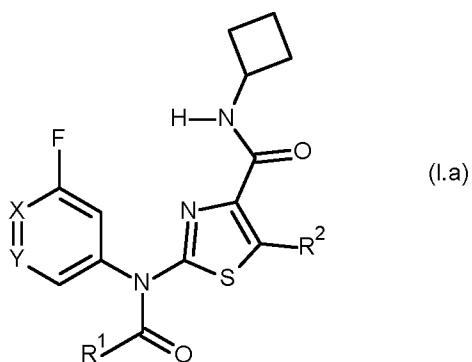
Cpd No.	X	Y	R ²	R ¹	Cpd No.	X	Y	R ²	R ¹
285	CH	N	Cl	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃	695	N	N	Cl	2-furanyl
286	CH	N	Cl	cyclopropyl	696	N	N	Cl	2-thiophenyl
287	CH	N	Cl	CO ₂ CH ₃	697	N	N	Cl	OPh
288	CH	N	Cl	CO ₂ CH ₂ CH ₃	698	N	N	Cl	OCH ₂ CCH
289	CH	N	Cl	Ph	699	N	N	Cl	OCH ₂ CH ₂ OCH ₃
290	CH	N	Cl	2-furanyl	700	N	N	Cl	SCH ₃
291	CH	N	Cl	2-thiophenyl	701	N	N	Cl	SCH ₂ CH ₃
292	CH	N	Cl	OPh	702	N	N	Cl	SCH(CH ₃) ₂
293	CH	N	Cl	OCH ₂ CCH	703	N	N	Br	H
294	CH	N	Cl	OCH ₂ CH ₂ OCH ₃	704	N	N	Br	CH ₃
295	CH	N	Cl	SCH ₃	705	N	N	Br	CH ₂ CH ₃
296	CH	N	Cl	SCH ₂ CH ₃	706	N	N	Br	OCH ₃
297	CH	N	Cl	SCH(CH ₃) ₂	707	N	N	Br	OCH ₂ CH ₃
298	CH	N	Br	H	708	N	N	Br	CH ₂ OCH ₃
299	CH	N	Br	CH ₃	709	N	N	Br	CH(CH ₃)OCH ₃
300	CH	N	Br	CH ₂ CH ₃	710	N	N	Br	C(CH ₃) ₂ OCH ₃
301	CH	N	Br	OCH ₃	711	N	N	Br	CH ₂ F
302	CH	N	Br	OCH ₂ CH ₃	712	N	N	Br	CH ₂ Cl
303	CH	N	Br	CH ₂ OCH ₃	713	N	N	Br	CH ₂ Br
304	CH	N	Br	CH(CH ₃)OCH ₃	714	N	N	Br	CH ₂ CF ₃
305	CH	N	Br	C(CH ₃) ₂ OCH ₃	715	N	N	Br	CH ₂ CO ₂ CH ₃
306	CH	N	Br	CH ₂ F	716	N	N	Br	CH ₂ CH ₂ CO ₂ CH ₃
307	CH	N	Br	CH ₂ Cl	717	N	N	Br	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃
308	CH	N	Br	CH ₂ Br	718	N	N	Br	cyclopropyl
309	CH	N	Br	CH ₂ CF ₃	719	N	N	Br	CO ₂ CH ₃
310	CH	N	Br	CH ₂ CO ₂ CH ₃	720	N	N	Br	CO ₂ CH ₂ CH ₃
311	CH	N	Br	CH ₂ CH ₂ CO ₂ CH ₃	721	N	N	Br	Ph
312	CH	N	Br	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃	722	N	N	Br	2-furanyl
313	CH	N	Br	cyclopropyl	723	N	N	Br	2-thiophenyl
314	CH	N	Br	CO ₂ CH ₃	724	N	N	Br	OPh
315	CH	N	Br	CO ₂ CH ₂ CH ₃	725	N	N	Br	OCH ₂ CCH
316	CH	N	Br	Ph	726	N	N	Br	OCH ₂ CH ₂ OCH ₃
317	CH	N	Br	2-furanyl	727	N	N	Br	SCH ₃
318	CH	N	Br	2-thiophenyl	728	N	N	Br	SCH ₂ CH ₃
319	CH	N	Br	OPh	729	N	N	Br	SCH(CH ₃) ₂
320	CH	N	Br	OCH ₂ CCH	730	N	N	CH ₃	H
321	CH	N	Br	OCH ₂ CH ₂ OCH ₃	731	N	N	CH ₃	CH ₃
322	CH	N	Br	SCH ₃	732	N	N	CH ₃	CH ₂ CH ₃
323	CH	N	Br	SCH ₂ CH ₃	733	N	N	CH ₃	OCH ₃
324	CH	N	Br	SCH(CH ₃) ₂	734	N	N	CH ₃	OCH ₂ CH ₃
325	CH	N	CH ₃	H	735	N	N	CH ₃	CH ₂ OCH ₃
326	CH	N	CH ₃	CH ₃	736	N	N	CH ₃	CH(CH ₃)OCH ₃
327	CH	N	CH ₃	CH ₂ CH ₃	737	N	N	CH ₃	C(CH ₃) ₂ OCH ₃
328	CH	N	CH ₃	OCH ₃	738	N	N	CH ₃	CH ₂ F
329	CH	N	CH ₃	OCH ₂ CH ₃	739	N	N	CH ₃	CH ₂ Cl

Cpd No.	X	Y	R ²	R ¹	Cpd No.	X	Y	R ²	R ¹
330	CH	N	CH ₃	CH ₂ OCH ₃	740	N	N	CH ₃	CH ₂ Br
331	CH	N	CH ₃	CH(CH ₃)OCH ₃	741	N	N	CH ₃	CH ₂ CF ₃
332	CH	N	CH ₃	C(CH ₃) ₂ OCH ₃	742	N	N	CH ₃	CH ₂ CO ₂ CH ₃
333	CH	N	CH ₃	CH ₂ F	743	N	N	CH ₃	CH ₂ CH ₂ CO ₂ CH ₃
334	CH	N	CH ₃	CH ₂ Cl	744	N	N	CH ₃	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃
335	CH	N	CH ₃	CH ₂ Br	745	N	N	CH ₃	cyclopropyl
336	CH	N	CH ₃	CH ₂ CF ₃	746	N	N	CH ₃	CO ₂ CH ₃
337	CH	N	CH ₃	CH ₂ CO ₂ CH ₃	747	N	N	CH ₃	CO ₂ CH ₂ CH ₃
338	CH	N	CH ₃	CH ₂ CH ₂ CO ₂ CH ₃	748	N	N	CH ₃	Ph
339	CH	N	CH ₃	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃	749	N	N	CH ₃	2-furanyl
340	CH	N	CH ₃	cyclopropyl	750	N	N	CH ₃	2-thiophenyl
341	CH	N	CH ₃	CO ₂ CH ₃	751	N	N	CH ₃	OPh
342	CH	N	CH ₃	CO ₂ CH ₂ CH ₃	752	N	N	CH ₃	OCH ₂ CCH
343	CH	N	CH ₃	Ph	753	N	N	CH ₃	OCH ₂ CH ₂ OCH ₃
344	CH	N	CH ₃	2-furanyl	754	N	N	CH ₃	SCH ₃
345	CH	N	CH ₃	2-thiophenyl	755	N	N	CH ₃	SCH ₂ CH ₃
346	CH	N	CH ₃	OPh	756	N	N	CH ₃	SCH(CH ₃) ₂
347	CH	N	CH ₃	OCH ₂ CCH	757	N	N	OCH ₃	H
348	CH	N	CH ₃	OCH ₂ CH ₂ OCH ₃	758	N	N	OCH ₃	CH ₃
349	CH	N	CH ₃	SCH ₃	759	N	N	OCH ₃	CH ₂ CH ₃
350	CH	N	CH ₃	SCH ₂ CH ₃	760	N	N	OCH ₃	OCH ₃
351	CH	N	CH ₃	SCH(CH ₃) ₂	761	N	N	OCH ₃	OCH ₂ CH ₃
352	CH	N	OCH ₃	H	762	N	N	OCH ₃	CH ₂ OCH ₃
353	CH	N	OCH ₃	CH ₃	763	N	N	OCH ₃	CH(CH ₃)OCH ₃
354	CH	N	OCH ₃	CH ₂ CH ₃	764	N	N	OCH ₃	C(CH ₃) ₂ OCH ₃
355	CH	N	OCH ₃	OCH ₃	765	N	N	OCH ₃	CH ₂ F
356	CH	N	OCH ₃	OCH ₂ CH ₃	766	N	N	OCH ₃	CH ₂ Cl
357	CH	N	OCH ₃	CH ₂ OCH ₃	767	N	N	OCH ₃	CH ₂ Br
358	CH	N	OCH ₃	CH(CH ₃)OCH ₃	768	N	N	OCH ₃	CH ₂ CF ₃
359	CH	N	OCH ₃	C(CH ₃) ₂ OCH ₃	769	N	N	OCH ₃	CH ₂ CO ₂ CH ₃
360	CH	N	OCH ₃	CH ₂ F	770	N	N	OCH ₃	CH ₂ CH ₂ CO ₂ CH ₃
361	CH	N	OCH ₃	CH ₂ Cl	771	N	N	OCH ₃	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃
362	CH	N	OCH ₃	CH ₂ Br	772	N	N	OCH ₃	cyclopropyl
363	CH	N	OCH ₃	CH ₂ CF ₃	773	N	N	OCH ₃	CO ₂ CH ₃
364	CH	N	OCH ₃	CH ₂ CO ₂ CH ₃	774	N	N	OCH ₃	CO ₂ CH ₂ CH ₃
365	CH	N	OCH ₃	CH ₂ CH ₂ CO ₂ CH ₃	775	N	N	OCH ₃	Ph
366	CH	N	OCH ₃	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃	776	N	N	OCH ₃	2-furanyl
367	CH	N	OCH ₃	cyclopropyl	777	N	N	OCH ₃	2-thiophenyl
368	CH	N	OCH ₃	CO ₂ CH ₃	778	N	N	OCH ₃	OPh
369	CH	N	OCH ₃	CO ₂ CH ₂ CH ₃	779	N	N	OCH ₃	OCH ₂ CCH
370	CH	N	OCH ₃	Ph	780	N	N	OCH ₃	OCH ₂ CH ₂ OCH ₃
371	CH	N	OCH ₃	2-furanyl	781	N	N	OCH ₃	SCH ₃
372	CH	N	OCH ₃	2-thiophenyl	782	N	N	OCH ₃	SCH ₂ CH ₃
373	CH	N	OCH ₃	OPh	783	N	N	OCH ₃	SCH(CH ₃) ₂
374	CH	N	OCH ₃	OCH ₂ CCH	784	N	N	NHCHO	H

Cpd No.	X	Y	R ²	R ¹	Cpd No.	X	Y	R ²	R ¹
375	CH	N	OCH ₃	OCH ₂ CH ₂ OCH ₃	785	N	N	NHCHO	CH ₃
376	CH	N	OCH ₃	SCH ₃	786	N	N	NHCHO	CH ₂ CH ₃
377	CH	N	OCH ₃	SCH ₂ CH ₃	787	N	N	NHCHO	OCH ₃
378	CH	N	OCH ₃	SCH(CH ₃) ₂	788	N	N	NHCHO	OCH ₂ CH ₃
379	CH	N	NHCHO	H	789	N	N	NHCHO	CH ₂ OCH ₃
380	CH	N	NHCHO	CH ₃	790	N	N	NHCHO	CH(CH ₃)OCH ₃
381	CH	N	NHCHO	CH ₂ CH ₃	791	N	N	NHCHO	C(CH ₃) ₂ OCH ₃
382	CH	N	NHCHO	OCH ₃	792	N	N	NHCHO	CH ₂ F
383	CH	N	NHCHO	OCH ₂ CH ₃	793	N	N	NHCHO	CH ₂ Cl
384	CH	N	NHCHO	CH ₂ OCH ₃	794	N	N	NHCHO	CH ₂ Br
385	CH	N	NHCHO	CH(CH ₃)OCH ₃	795	N	N	NHCHO	CH ₂ CF ₃
386	CH	N	NHCHO	C(CH ₃) ₂ OCH ₃	796	N	N	NHCHO	CH ₂ CO ₂ CH ₃
387	CH	N	NHCHO	CH ₂ F	797	N	N	NHCHO	CH ₂ CH ₂ CO ₂ CH ₃
388	CH	N	NHCHO	CH ₂ Cl	798	N	N	NHCHO	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃
389	CH	N	NHCHO	CH ₂ Br	799	N	N	NHCHO	cyclopropyl
390	CH	N	NHCHO	CH ₂ CF ₃	800	N	N	NHCHO	CO ₂ CH ₃
391	CH	N	NHCHO	CH ₂ CO ₂ CH ₃	801	N	N	NHCHO	CO ₂ CH ₂ CH ₃
392	CH	N	NHCHO	CH ₂ CH ₂ CO ₂ CH ₃	802	N	N	NHCHO	Ph
393	CH	N	NHCHO	CH ₂ CH ₂ CH ₂ CO ₂ CH ₃	803	N	N	NHCHO	2-furanyl
394	CH	N	NHCHO	cyclopropyl	804	N	N	NHCHO	2-thiophenyl
395	CH	N	NHCHO	CO ₂ CH ₃	805	N	N	NHCHO	OPh
396	CH	N	NHCHO	CO ₂ CH ₂ CH ₃	806	N	N	NHCHO	OCH ₂ CCH
397	CH	N	NHCHO	Ph	807	N	N	NHCHO	OCH ₂ CH ₂ OCH ₃
398	CH	N	NHCHO	2-furanyl	808	N	N	NHCHO	SCH ₃
399	CH	N	NHCHO	2-thiophenyl	809	N	N	NHCHO	SCH ₂ CH ₃
400	CH	N	NHCHO	OPh	810	N	N	NHCHO	SCH(CH ₃) ₂
401	CH	N	NHCHO	OCH ₂ CCH	811	N	CF	CH ₃	CH(CH ₃)OCO ₂ CH ₃
402	CH	N	NHCHO	OCH ₂ CH ₂ OCH ₃	812	N	CF	CH ₃	CH(CH ₃)OCO ₂ CH ₂ CH ₃
403	CH	N	NHCHO	SCH ₃	813	N	CF	CH ₃	CH(CH ₃)OC(O)CH ₃
404	CH	N	NHCHO	SCH ₂ CH ₃	814	N	CF	CH ₃	CH(CH ₃)OH
405	CH	N	NHCHO	SCH(CH ₃) ₂	815	N	CF	CH ₃	CH ₂ OCH ₂ CH ₃
406	N	CH	Cl	H	816	N	CF	CH ₃	CH ₂ OC(O)CH ₃
407	N	CH	Cl	CH ₃	817	N	CF	CH ₃	CH ₂ (C ₆ H ₅)
408	N	CH	Cl	CH ₂ CH ₃	818	N	CF	CH ₃	CH ₂ OCH ₂ (C ₆ H ₅)
409	N	CH	Cl	OCH ₃	819	N	CF	CH ₃	CH(CH ₃)OCH ₂ (C ₆ H ₅)
410	N	CH	Cl	OCH ₂ CH ₃	820	N	CF	CH ₃	N(CH ₂ CH ₃) ₂

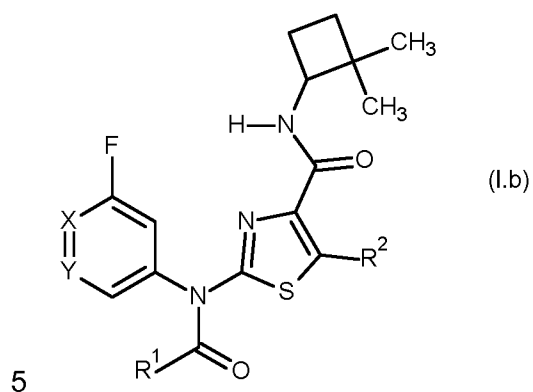
wherein

a) 820 compounds of formula (I.a):



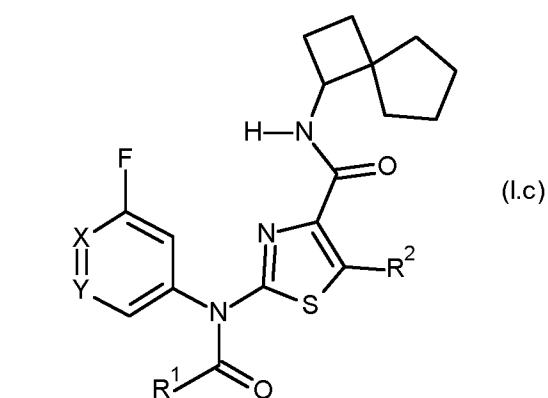
wherein R¹, R², X and Y are as defined in Table 1.

b) 820 compounds of formula (I.b):



wherein R¹, R², X and Y are as defined in Table 1.

c) 820 compounds of formula (I.c):



wherein R¹, R², X and Y are as defined in Table 1.

Formulation Examples

Wettable powders

active ingredient [compound of formula (I)]
sodium lignosulfonate
sodium lauryl sulfate

a)	b)	c)
25 %	50 %	75 %
5 %	5 %	-
3 %	-	5 %

sodium diisobutyl naphthalenesulfonate	-	6 %	10 %
phenol polyethylene glycol ether (7-8 mol of ethylene oxide)	-	2 %	-
highly dispersed silicic acid	5 %	10 %	10 %
Kaolin	62 %	27 %	-

The active ingredient is thoroughly mixed with the adjuvants and the mixture is thoroughly ground in a suitable mill, affording wettable powders that can be diluted with water to give suspensions of the desired concentration.

5

<u>Powders for dry seed treatment</u>	a)	b)	c)
active ingredient [compound of formula (I)]	25 %	50 %	75 %
light mineral oil	5 %	5 %	5 %
highly dispersed silicic acid	5 %	5 %	-
Kaolin	65 %	40 %	-
Talcum	-		20 %

The active ingredient is thoroughly mixed with the adjuvants and the mixture is thoroughly ground in a suitable mill, affording powders that can be used directly for seed treatment.

Emulsifiable concentrate

active ingredient [compound of formula (I)]	10 %
octylphenol polyethylene glycol ether (4-5 mol of ethylene oxide)	3 %
calcium dodecylbenzenesulfonate	3 %
castor oil polyglycol ether (35 mol of ethylene oxide)	4 %
Cyclohexanone	30 %
xylene mixture	50 %

10

Emulsions of any required dilution, which can be used in plant protection, can be obtained from this concentrate by dilution with water.

<u>Dusts</u>	a)	b)	c)
Active ingredient [compound of formula (I)]	5 %	6 %	4 %
talcum	95 %	-	-
Kaolin	-	94 %	-
mineral filler	-	-	96 %

15 Ready-for-use dusts are obtained by mixing the active ingredient with the carrier and grinding the mixture in a suitable mill. Such powders can also be used for dry dressings for seed.

Extruder granules

Active ingredient [compound of formula (I)]	15 %
sodium lignosulfonate	2 %
carboxymethylcellulose	1 %
Kaolin	82 %

The active ingredient is mixed and ground with the adjuvants, and the mixture is moistened with water. The mixture is extruded and then dried in a stream of air.

Coated granules

Active ingredient [compound of formula (I)]	8 %
polyethylene glycol (mol. wt. 200)	3 %
Kaolin	89 %

5

The finely ground active ingredient is uniformly applied, in a mixer, to the kaolin moistened with polyethylene glycol. Non-dusty coated granules are obtained in this manner.

Suspension concentrate

active ingredient [compound of formula (I)]	40 %
propylene glycol	10 %
nonylphenol polyethylene glycol ether (15 mol of ethylene oxide)	6 %
Sodium lignosulfonate	10 %
carboxymethylcellulose	1 %
silicone oil (in the form of a 75 % emulsion in water)	1 %
Water	32 %

10

The finely ground active ingredient is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired dilution can be obtained by dilution with water. Using such dilutions, living plants as well as plant propagation material can be treated and protected against infestation by microorganisms, by spraying, pouring or immersion.

15

Flowable concentrate for seed treatment

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

The finely ground active ingredient is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired dilution can be obtained by dilution with water. Using such dilutions, living plants as well as plant propagation material can be treated and protected against infestation by microorganisms, by spraying, pouring or immersion.

5

Slow Release Capsule Suspension

28 parts of a combination of the compound of formula (I) are mixed with 2 parts of an aromatic solvent and 7 parts of toluene diisocyanate/polymethylene-polyphenylisocyanate-mixture (8:1). This mixture is emulsified in a mixture of 1.2 parts of polyvinyl alcohol, 0.05 parts of a defoamer and 51.6 parts of water until the desired particle size is achieved. To this emulsion a mixture of 2.8 parts 1,6-diaminohexane in 5.3 parts of water is added. The mixture is agitated until the polymerization reaction is completed.

The obtained capsule suspension is stabilized by adding 0.25 parts of a thickener and 3 parts of a dispersing agent. The capsule suspension formulation contains 28% of the active ingredients. The medium capsule diameter is 8-15 microns.

The resulting formulation is applied to seeds as an aqueous suspension in an apparatus suitable for that purpose.

Examples

The Examples which follow serve to illustrate the invention. The compounds of the invention can be distinguished from known compounds by virtue of greater efficacy at low application rates, which can be verified by the person skilled in the art using the experimental procedures outlined in the Examples, using lower application rates if necessary, for example 50 ppm, 12.5 ppm, 6 ppm, 3 ppm, 1.5 ppm, 0.8 ppm or 0.2 ppm.

Compounds of formula (I) may possess any number of benefits including, *inter alia*, advantageous levels of biological activity for protecting plants against diseases that are caused by fungi or superior properties for use as agrochemical active ingredients (for example, greater biological activity, an advantageous spectrum of activity, an increased safety profile (including improved crop tolerance), improved physico-chemical properties, or increased biodegradability).

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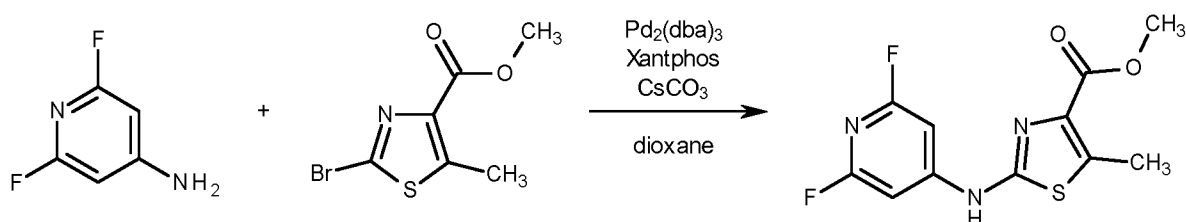
List of Abbreviations

°C	= degrees Celsius
CDCl ₃	= chloroform-d
d	= doublet
35 Pd ₂ (dba) ₃	= Tris(dibenzylideneacetone)dipalladium(0)
DIPEA	= N,N-diisopropylethylamine
DMF	= dimethylformamide
HATU	= 1-[Bis(dimethylamino)methylene]-1H-1,2,3-triazolo[4,5-b]pyridinium 3-oxid hexafluorophosphate
40 m	= multiplet
MHz	= mega hertz

mp	= melting point
N	= normal
ppm	= parts per million
q	= quartet
5 s	= singlet
t	= triplet
THF	= tetrahydrofuran
Xantphos	= 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene

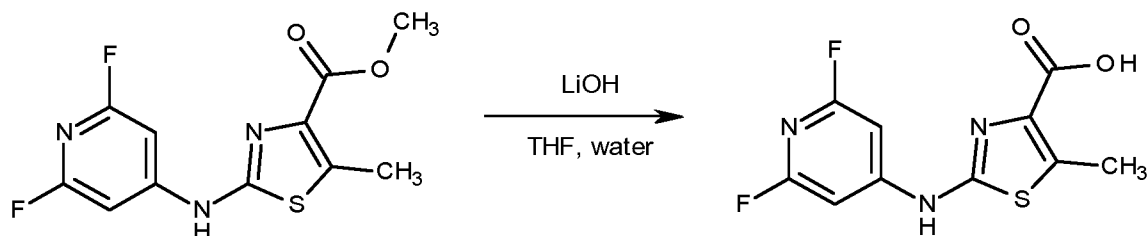
- 10 **Example 1:** This example illustrates the preparation of 2-[acetyl-(2,6-difluoro-4-pyridyl)amino]-N-(2,2-dimethylcyclobutyl)-5-methyl-thiazole-4-carboxamide (Compound I.b.596)

a) Preparation of methyl 2-[(2,6-difluoro-4-pyridyl)amino]-5-methyl-thiazole-4-carboxylate



- 15 Under Argon atmosphere, Xantphos (0.2 equiv.), Pd₂(dba)₃ (0.1 equiv.) and cesium carbonate (2 equiv.) were added to a degassed, stirred mixture of methyl 2-bromo-5-methyl-thiazole-4-carboxylate (4.6 g, 18.5 mmol, 1 equiv.) and 2,6-difluoropyridin-4-amine (1 equiv.) in 1,4-dioxane (660 mL). The reaction was heated to reflux and stirred for 4 h before allowing the temperature to cool to room temperature. The mixture was diluted with ethyl acetate and filtered over Celite, and the resulting filtrate
- 20 was concentrated using a rotatory evaporator. Purification by column chromatography on silica gel (eluent mixtures cyclohexane/ethyl acetate) afforded the desired methyl 2-[(2,6-difluoro-4-pyridyl)amino]-5-methyl-thiazole-4-carboxylate (1.8 g, 6.31 mmol). ¹H-NMR (400 MHz, CDCl₃): δ = 2.73 (s, 3H), 3.94 (s, 3H), 6.75 (s, 1H).

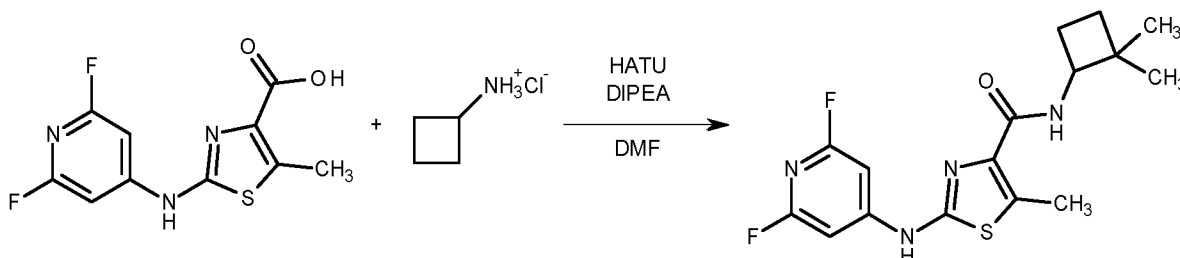
25 b) Preparation of 2-[(2,6-difluoro-4-pyridyl)amino]-5-methyl-thiazole-4-carboxylic acid



- Lithium hydroxide monohydrate (4 equiv.) was added to a solution of 2-[(2,6-difluoro-4-pyridyl)amino]-5-methyl-thiazole-4-carboxylic acid (1.8 g, 6.31 mmol) in a mixture of tetrahydrofuran (35 mL) and water (12 mL). The reaction mixture was stirred 16 h at room temperature, then the solvents
- 30 were removed in vacuo. The residue was diluted with ethyl acetate and water, then 2 N hydrochloric acid was slowly added until a pH of 3 - 4 was reached. The formed precipitate was isolated by filtration

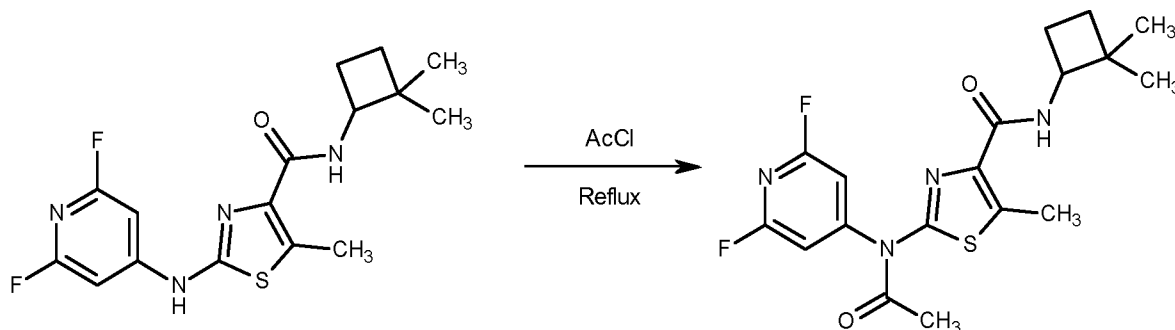
and washed twice with water, giving the desired product 2-[(2,6-difluoro-4-pyridyl)amino]-5-methyl-thiazole-4-carboxylic acid (1.55 g, 5.71 mmol). ¹H-NMR (400 MHz, (CD₃)₂SO): δ = 2.69 (s, 3H), 7.30 (s, 2H), 11.35 (bs, 1H), 12.90 (bs, 1H).

- 5 c) Preparation of 2-[(2,6-difluoro-4-pyridyl)amino]-N-(2,2-dimethylcyclobutyl)-5-methyl-thiazole-4-carboxamide



- (2,2-dimethylcyclobutyl) ammonium chloride (1.1 equiv.), HATU (1.1 equiv.), and DIPEA (2.6 equiv.), were added in sequence to a DMF solution (9.2 mL) of 2-[(2,6-difluoro-4-pyridyl)amino]-5-methyl-thiazole-4-carboxylic acid (250 mg, 0.92 mmol, 1 equiv.). The resulting solution was stirred at room temperature for 1 h until consumption of starting material (LCMS control). Then a saturated NaHCO₃ solution was added to the mixture and the solution extracted three times with ethyl acetate. The organic phases were combined, dried over sodium sulphate and the volatiles removed by rotatory evaporator. Purification by column chromatography on silica gel (eluent: mixtures of cyclohexane/ethyl acetate) gave the desired product 2-[(2,6-difluoro-4-pyridyl)amino]-N-(2,2-dimethylcyclobutyl)-5-methyl-thiazole-4-carboxamide (280 mg, 86% yield). ¹H-NMR (400 MHz, CDCl₃): δ = 1.17 (s, 3H), 1.20 (s, 3H), 1.50 – 1.75 (m, 2H), 1.86 – 1.92 (m, 1H), 2.29 – 2.36 (m, 1H), 2.79 (s, 3H), 4.25 – 4.31 (m, 1H), 6.87 (s, 2H), 7.32 (d, 1H), 7.67 (s, 1H).

- 20 d) 2-[acetyl-(2,6-difluoro-4-pyridyl)amino]-N-(2,2-dimethylcyclobutyl)-5-methyl-thiazole-4-carboxamide (Compound I.b.596)



- A mixture of 2-[(2,6-difluoro-4-pyridyl)amino]-N-(2,2-dimethylcyclobutyl)-5-methyl-thiazole-4-carboxamide (1.9 g, 5.4 mmol) in acetyl chloride (20 ml) was stirred under reflux for 3 days. The reaction was then allowed to cool to room temperature and the volatiles removed by rotatory evaporator. Purification of the crude material obtained by column chromatography on silica gel (eluent: mixtures of cyclohexane/ethyl acetate) gave the desired product 2-[acetyl-(2,6-difluoro-4-pyridyl)amino]-N-(2,2-dimethylcyclobutyl)-5-methyl-thiazole-4-carboxamide (1.57 g, 3.98 mmol, 74% yield). ¹H-NMR (400

MHz, CDCl₃): δ = 0.92 (s, 3H), 1.12 (s, 3H), 1.48 – 1.75 (m, 3H), 2.10-2.30 (m, 1H), 2.17 (s, 3H), 2.79 (s, 3H), 4.25 – 4.31 (m, 1H), 6.87 (s, 2H), 7.32 (d, 1H).

Throughout this description, temperatures are given in degrees Celsius (°C) and “m.p.” means melting point. LC/MS means Liquid Chromatography Mass Spectrometry and the description of the apparatus and the method is:

Method A: ACQUITY UPLC from Waters, Waters UPLC HSS T3, 1.8 μm particle size, 30 x 2.1 mm column, 0.85 mL/min., 60 °C, H₂O/MeOH 95:5 + 0.05% HCOOH (90%) / CH₃CN + 0.05% HCOOH (10%) – 1.2 min. – CH₃CN + 0.05% HCOOH (100%) – 0.30 min., ACQUITY SQD Mass Spectrometer from Waters, ionization method: electrospray (ESI), Polarity: positive ions, Capillary (kV) 3.00, Cone (V) 30.00, Extractor (V) 2.00, Source Temperature (°C) 150, Desolvation Temperature (°C) 350, Cone Gas Flow (L/Hr) 0, Desolvation Gas Flow (L/Hr) 650).

Method B: ACQUITY UPLC from Waters, Waters UPLC HSS T3, 1.8 μm particle size, 30 x 2.1 mm column, 0.85 mL/min., 60 °C, H₂O/MeOH 95:5 + 0.05% HCOOH (90%) / CH₃CN + 0.05% HCOOH (10%) – 2.7 min. – CH₃CN + 0.05% HCOOH (100%) – 0.30 min., ACQUITY SQD Mass Spectrometer from Waters, ionization method: electrospray (ESI), Polarity: positive ions, Capillary (kV) 3.00, Cone (V) 30.00, Extractor (V) 2.00, Source Temperature (°C) 150, Desolvation Temperature (°C) 350, Cone Gas Flow (L/Hr) 0, Desolvation Gas Flow (L/Hr) 650).

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Method C: MS: ZQ Mass Spectrometer from Waters (Single quadrupole mass spectrometer)
Instrument Parameter: Ionisation method: Electrospray Polarity: positive (negative) ions Capillary (kV) 3.00, Cone (V) 30.00, Extractor (V) 2.00, Gas Temperature (°C) 350, Drying Gas Flow (mL/min) 9.8, Neb press 45 psig, Mass range: 90 to 1000 Da.

HPLC: HP 1100 HPLC from Agilent: solvent degasser, quaternary pump (ZCQ) / binary pump (ZDQ), heated column compartment and diode-array detector. Column: porpshell 120 C18, 2.7 μm particle size, 120 Angström, 4.6 x 50 mm, Temp: 30 °C. DAD Wavelength range (nm): 190 to 400 Solvent Gradient: A = water + 0.1 % HCOOH. B= Acetonitrile+ 0.08% HCOOH. Mobile phase:

Time (min)	A%	B%	Flow (ml/min)
0	85	15	0.6
4	5	95	0.6
10	5	95	0.6

30 **Method D:** Mass Spectrometer as method C.

HPLC: Shimadzu LC-20A. Column: Dikma, DiamonsilC18(2) (5 μm, 150*4.6mm).

Mobile phase A: H₂O (add 0.1% TFA); Mobile phase B: ACN (add 0.1% TFA). Flow: 1.0ml/min.

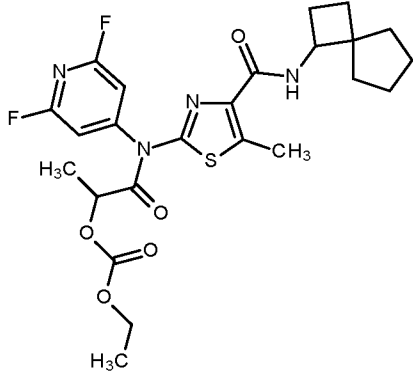
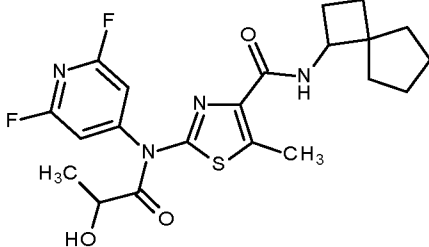
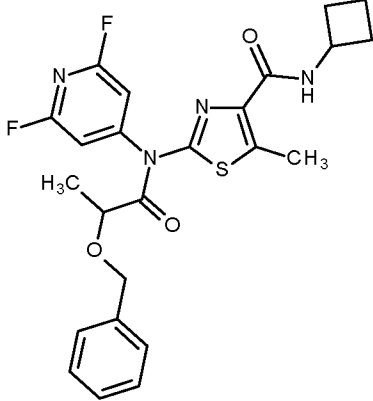
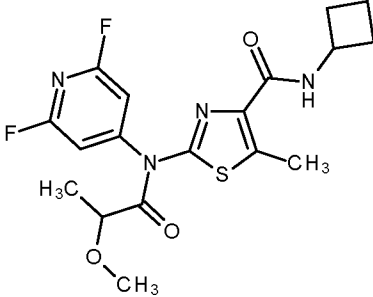
Detection: UV@254nm. Oven Temperature: 40 °C. Mobile Phase:

Time (mins)	A%	B%
0	90	10
15	0	100

25	0	100
27	90	10
35	90	10

Table 2: Melting point and LC/MS data (R_t = Retention time) for selected compounds of Table 1.

No.	Compound Name	Structure	Mp (°C)	LC/MS
I.c.813	[2-[(2,6-difluoro-4-pyridyl)-[5-methyl-4-(spiro[3.4]octan-3-ylcarbamoyl)thiazol-2-yl]amino]-1-methyl-2-oxo-ethyl] acetate			R_t = 5.10 min (C); MS: m/z = 493 (M+1)
I.a.812	[2-[[4-(cyclobutylcarbamoyl)-5-methyl-thiazol-2-yl]-(2,6-difluoro-4-pyridyl)amino]-1-methyl-2-oxo-ethyl] ethyl carbonate		105 - 106	R_t = 15.33 min (D); MS: m/z = 469 (M+1)
I.c.811	[2-[(2,6-difluoro-4-pyridyl)-[5-methyl-4-(spiro[3.4]octan-3-ylcarbamoyl)thiazol-2-yl]amino]-1-methyl-2-oxo-ethyl] methyl carbonate			R_t = 5.18 min (C); MS: m/z = 509 (M+1)

No.	Compound Name	Structure	Mp (°C)	LC/MS
I.c.812	[2-[(2,6-difluoro-4-pyridyl)-[5-methyl-4-(spiro[3.4]octan-3-ylcarbamoyl)thiazol-2-yl]amino]-1-methyl-2-oxoethyl] ethyl carbonate		106 - 108	R _t = 5.41 min (C); MS: m/z = 523 (M+1)
I.c.814	2-[(2,6-difluoro-4-pyridyl)-(2-hydroxypropanoyl)amino]-5-methyl-N-spiro[3.4]octan-3-yl-thiazole-4-carboxamide		101 - 103	R _t = 5.15 min (C); MS: m/z = 451 (M+1)
I.a.819	2-[2-benzoyloxypropanoyl-(2,6-difluoro-4-pyridyl)amino]-N-cyclobutyl-5-methyl-thiazole-4-carboxamide		98 - 100	R _t = 5.10 min (C); MS: m/z = 497 (M+1)
I.a.601	N-cyclobutyl-2-[(2,6-difluoro-4-pyridyl)-(2-methoxypropanoyl)amino]-5-methyl-thiazole-4-carboxamide		128 - 130	R _t = 13.80 min (D); MS: m/z = 411 (M+1)

No.	Compound Name	Structure	Mp (°C)	LC/MS
I.b.816	[2-[(2,6-difluoro-4-pyridyl)-[4-[(2,2-dimethylcyclobutyl)carbonyl]-5-methyl-thiazol-2-yl]amino]-2-oxo-ethyl] acetate		65.5 – 67.2	R _t = 1.10 min (A); MS: m/z = 453 (M+1)
I.b.817	2-[(2,6-difluoro-4-pyridyl)-(2-phenylacetyl)amino]-N-(2,2-dimethylcyclobutyl)-5-methyl-thiazole-4-carboxamide			R _t = 1.23 min (A); MS: m/z = 471 (M+1)
I.c.596	2-[acetyl-(2,6-difluoro-4-pyridyl)amino]-5-methoxy-N-spiro[3.4]octan-3-yl-thiazole-4-carboxamide		199 - 200	R _t = 1.06 min (A); MS: m/z = 437 (M+1)
I.c.600	2-[(2,6-difluoro-4-pyridyl)-(2-methoxyacetyl)amino]-5-methyl-N-spiro[3.4]octan-3-yl-thiazole-4-carboxamide			R _t = 15.94 min (D); MS: m/z = 451 (M+1)
I.a.600	N-cyclobutyl-2-[(2,6-difluoro-4-pyridyl)-(2-methoxyacetyl)amino]-5-methyl-thiazole-4-carboxamide			R _t = 13.64 min (D); MS: m/z = 398 (M+1)

No.	Compound Name	Structure	Mp (°C)	LC/MS
I.a.596	2-[acetyl-(2,6-difluoro-4-pyridyl)amino]-N-cyclobutyl-5-methyl-thiazole-4-carboxamide		174 - 175	R _t = 13.92 min (D); MS: m/z = 367 (M+1)
I.b.818	2-[(2-benzyloxyacetyl)-(2,6-difluoro-4-pyridyl)amino]-N-(2,2-dimethylcyclobutyl)-5-methyl-thiazole-4-carboxamide		182.9 - 187.1	R _t = 1.22 min (A); MS: m/z = 501 (M+1)
I.b.815	2-[(2-ethoxyacetyl)-(2,6-difluoro-4-pyridyl)amino]-N-(2,2-dimethylcyclobutyl)-5-methyl-thiazole-4-carboxamide		146.1 - 147.6	R _t = 1.14 min (A); MS: m/z = 439 (M+1)
I.b.820	2-[diethylcarbamoyl-(2,6-difluoro-4-pyridyl)amino]-N-(2,2-dimethylcyclobutyl)-5-methyl-thiazole-4-carboxamide			R _t = 1.19 min (A); MS: m/z = 452 (M+1)
I.b.604	2-[(2-chloroacetyl)-(2,6-difluoro-4-pyridyl)amino]-N-(2,2-dimethylcyclobutyl)-5-methyl-thiazole-4-carboxamide		155.6 - 157.1	R _t = 1.11 min (A); MS: m/z = 429/431 (M+1)

No.	Compound Name	Structure	Mp (°C)	LC/MS
I.b.607	methyl 3-[(2,6-difluoro-4-pyridyl)-[4-[(2,2-dimethyl cyclobutyl)carbamoyl]-5-methyl-thiazol-2-yl]amino]-3-oxo-propanoate			R _t = 1.09 min (A); MS: m/z = 453 (M+1)
I.b.614	2-[(2,6-difluoro-4-pyridyl)-(furan-2-carbonyl)amino]-N-(2,2-dimethyl cyclobutyl)-5-methyl-thiazole-4-carboxamide		166 - 172	R _t = 1.15 min (A); MS: m/z = 447 (M+1)
I.b.609	methyl 5-[(2,6-difluoro-4-pyridyl)-[4-[(2,2-dimethyl cyclobutyl)carbamoyl]-5-methyl-thiazol-2-yl] amino]-5-oxo-pentanoate		175 - 178	R _t = 1.12 min (A); MS: m/z = 481 (M+1)
I.b.606	2-[(2,6-difluoro-4-pyridyl)-(3,3,3-trifluoropropanoyl)amino]-N-(2,2-dimethyl cyclobutyl)-5-methyl-thiazole-4-carboxamide		157 - 163	R _t = 1.15 min (A); MS: m/z = 463 (M+1)
I.b.621	S-isopropyl N-(2,6-difluoro-4-pyridyl)-N-[4-[(2,2-dimethyl cyclobutyl)carbamoyl]-5-methyl-thiazol-2-yl]carbamothioate		155 - 158	R _t = 1.28 min (A); MS: m/z = 455 (M+1)

No.	Compound Name	Structure	Mp (°C)	LC/MS
I.b.608	methyl 4-[(2,6-difluoro-4-pyridyl)-[4-[(2,2-dimethyl cyclobutyl)carbamoyl]-5-methyl-thiazol-2-yl]amino]-4-oxo-butanoate		160 - 163	R _t = 1.11 min (A); MS: m/z = 467 (M+1)
I.b.610	2-[cyclopropane carbonyl-(2,6-difluoro-4-pyridyl)amino]-N-(2,2-dimethyl cyclobutyl)-5-methyl-thiazole-4-carboxamide		165 - 170	R _t = 1.16 min (A); MS: m/z = 421 (M+1)
I.b.617	prop-2-ynyl N-(2,6-difluoro-4-pyridyl)-N-[4-[(2,2-dimethyl cyclobutyl)carbamoyl]-5-methyl-thiazol-2-yl]carbamate		129 - 131	R _t = 1.14 min (A); MS: m/z = 435 (M+1)
I.b.616	phenyl N-(2,6-difluoro-4-pyridyl)-N-[4-[(2,2-dimethylcyclobutyl)carbamoyl]-5-methyl-thiazol-2-yl]carbamate		138 - 140	R _t = 1.23 min (A); MS: m/z = 473 (M+1)
I.b.603	2-[(2,6-difluoro-4-pyridyl)-(2-fluoroacetyl)amino]-N-(2,2-dimethyl cyclobutyl)-5-methyl-thiazole-4-carboxamide		158 - 162	R _t = 1.09 min (A); MS: m/z = 413 (M+1)

No.	Compound Name	Structure	Mp (°C)	LC/MS
I.b.618	2-methoxyethyl N-(2,6-difluoro-4-pyridyl)-N-[4-[(2,2-dimethylcyclobutyl)carbonyl]-5-methyl-thiazol-2-yl]carbamate			R _t = 1.14 min (A); MS: m/z = 455 (M+1)
I.b.600	2-[(2,6-difluoro-4-pyridyl)-(2-methoxyacetyl)amino]-N-(2,2-dimethyl cyclobutyl)-5-methyl-thiazole-4-carboxamide		102 - 108	R _t = 1.08 min (A); MS: m/z = 425 (M+1)
I.b.599	ethyl N-(2,6-difluoro-4-pyridyl)-N-[4-[(2,2-dimethylcyclobutyl)carbonyl]-5-methyl-thiazol-2-yl]carbamate			R _t = 1.16 min (A); MS: m/z = 425 (M+1)
I.b.615	2-[(2,6-difluoro-4-pyridyl)-(thiophene-2-carbonyl)amino]-N-(2,2-dimethyl cyclobutyl)-5-methyl-thiazole-4-carboxamide		178 - 185	R _t = 1.19 min (A); MS: m/z = 463 (M+1)
I.b.598	methyl N-(2,6-difluoro-4-pyridyl)-N-[4-[(2,2-dimethylcyclobutyl)carbonyl]-5-methyl-thiazol-2-yl]carbamate			R _t = 1.14 min (A); MS: m/z = 411 (M+1)
I.b.595	2-[(2,6-difluoro-4-pyridyl)-formyl-amino]-N-(2,2-dimethyl cyclobutyl)-5-methyl-thiazole-4-carboxamide		132 - 135	R _t = 1.09 min (A); MS: m/z = 381 (M+1)

No.	Compound Name	Structure	Mp (°C)	LC/MS
I.b.612	ethyl 2-[(2,6-difluoro-4-pyridyl)-[4-[(2,2-dimethylcyclobutyl)carbamoyl]-5-methyl-thiazol-2-yl]amino]-2-oxo-acetate		159 - 161	R _t = 1.17 min (A); MS: m/z = 453 (M+1)
I.b.613	2-[benzoyl-(2,6-difluoro-4-pyridyl) amino]-N-(2,2-dimethylcyclobutyl)-5-methyl-thiazole-4-carboxamide		142 - 151	R _t = 1.19 min (A); MS: m/z = 457 (M+1)
I.b.596	2-[acetyl-(2,6-difluoro-4-pyridyl)amino]-N-(2,2-dimethyl cyclobutyl)-5-methyl-thiazole-4-carboxamide		141 - 145	R _t = 1.09 min (A); MS: m/z = 395 (M+1)
I.c.596	2-[acetyl-(2,6-difluoro-4-pyridyl)amino]-5-methyl-N-spiro[3.4] octan-3-yl-thiazole-4-carboxamide			R _t = 1.15 min (A); MS: m/z = 421 (M+1)

Surprisingly, it has been found that that the novel compounds of formula (I) i.e. wherein R¹ is hydrogen, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆alkoxyC₁-C₆alkyl, C₃-C₆cycloalkyl, C₁-C₆alkoxyC₁-C₃alkoxy, C₁-C₆alkoxycarbonyl, C₁-C₆alkoxycarbonylC₁-C₄alkyl, C₂-C₆alkenyloxy, C₂-C₆alkynyloxy, C₁-C₆alkylsulfanyl, phenyl, phenoxy, or heteroaryl, wherein the heteroaryl is a 5- or 6-membered aromatic monocyclic ring comprising 1 or 2 heteroatoms individually selected from nitrogen, oxygen and sulfur, may show improved solubility (in particular in non-polar solvents) and/or photostability properties when compared to their corresponding free amine, which are known from WO 2017/207362.

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Throughout the following description, LogP means logarithm of the partition coefficient, ppm means parts per million, and T₅₀ represents the half-time of the compound under irradiation conditions.

The methods used for these measurements are presented below.

Partition coefficient

Octanol-water partition coefficients (presented as LogP) were measured by an HPLC method using reverse phase mini-columns coated with octanol. The partition coefficient P is directly proportional to the HPLC retention factor. The general principles of this method have been described for example in *J. Pharm. Sci.*, 67 (1978) 1364-7.

A Waters HPLC system (model 1525 binary pump; 2707 autosampler with thermostat and model 2298 photodiode array detector) was used with Hichrom mini-columns and an aqueous mobile phase containing 20mM phosphate buffers adjusted to pH7, saturated with 1-octanol (Aldrich, HPLC grade). Mini-columns used were HiRPB stationary phase, either 4.6 mm internal diameter by 4 mm length or 2 mm internal diameter x 10 mm length. Anisole (Aldrich, 99%+ purity, LogP 2.11) was used as the primary reference to calibrate the system.

Photostability

Photostability tests were carried out by irradiation of thin-film deposits of compounds and formulations on glass surfaces, using a filtered xenon lamp system (Atlas Suntest) which reproduces the spectrum and intensity of sunlight. The spectral output power of the Suntest was set to 750W/m², which is the typical daily maximum irradiance level at noon (UK, midsummer).

Test compounds were typically dissolved in HPLC grade methanol to give 1 g/L stock solutions. Alternatively, formulated compounds were suspended in water at the same concentration. 2µL droplets of test solutions were spotted onto microscope cover slips in a 3D printed holder, allowed to dry then irradiated in the Suntest for varying times. Cover slips were then removed from the Suntest and placed in 4 dram vials; 1mL of wash solvent (typically 30:70 acetonitrile: 0.2% aqueous formic acid) was added, and the vials shaken to extract compounds into solution. Solutions were analysed by reverse phase HPLC, typically using a Waters UPLC system with Photodiode Array (PDA) and Waters columns (BEH C18, 100 x 2.1mm x 1.7µm) using mixed aqueous:acetonitrile mobile phase, acidified with 0.2% formic acid. Peak detection was at the optimum wavelength for each candidate compound and PDA peak areas were used for quantification. Plots of % loss versus time were used to estimate T₅₀ values, being the time taken for first 50% loss of test compound.

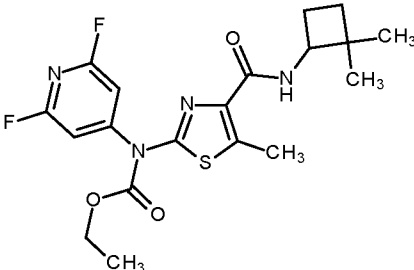
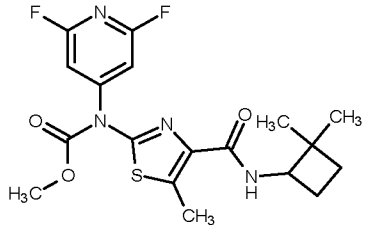
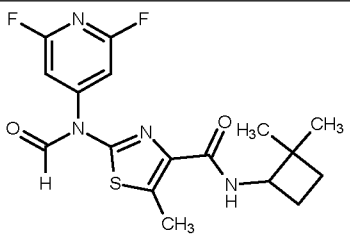
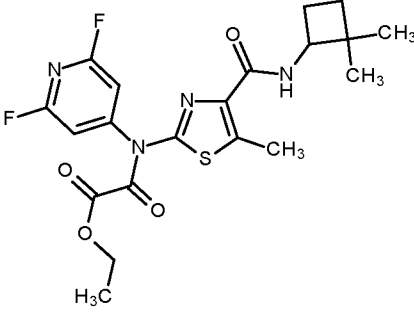
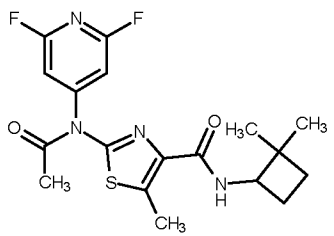
Solubility

Saturated solutions of test compounds were prepared in either aqueous buffer solutions (10 mM mixed phosphate, pH 7.20) or in heptane. Typically 1 mg of test compound in a 2 dram vial with 1mL of buffer or heptane was left overnight (20 hours) on a roller shaker after an initial 20 minute period in a sonic bath. Saturated samples were then filtered through Millex-HV 0.45 micron syringe driven filters (aqueous or non-aqueous version dependent on solvent). Aqueous samples were then analysed by direct injection on LCMS, and peak areas using PDA detection were compared with standards of known concentration; heptane samples were first dried and redissolved in an LC compatible solvent, typically 30:70 acetonitrile: 0.2% formic acid. Protocol variations included pre-saturation of the filters for compounds expected to have very low solubility, and centrifugation of the saturated samples for oils.

Table 3 below illustrates surprising physical chemistry properties (partition coefficient LogP, Solubility in heptane and/or photostability) with respect to the prior art compounds of WO2017/207362.

Table 3

No.	Compound Name	Structure	LogP	Solubility in water (ppm)	Solubility in heptane (ppm)	Photostability T ₅₀ (h)
E-0	2-[(2,6-difluoro-4-pyridyl)amino]-N-(2,2-dimethylcyclobutyl)-5-methyl-thiazole-4-carboxamide		5.08	0.70	4.1	3.5
I.b.607	methyl 3-[(2,6-difluoro-4-pyridyl)-[4-[(2,2-dimethylcyclobutyl)carbamoyl]-5-methyl-thiazol-2-yl]amino]-3-oxo-propanoate		3.59	12	224	4.4
I.b.614	2-[(2,6-difluoro-4-pyridyl)-(furan-2-carbonyl) amino]-N-(2,2-dimethylcyclobutyl)-5-methyl-thiazole-4-carboxamide		4.61	0.054	98	14
I.b.616	phenyl N-(2,6-difluoro-4-pyridyl)-N-[4-[(2,2-dimethylcyclobutyl)carbamoyl]-5-methyl-thiazol-2-yl]carbamate		5.34	0.10	673	18
I.b.600	2-[(2,6-difluoro-4-pyridyl)-(2-methoxyacetyl) amino]-N-(2,2-dimethylcyclobutyl)-5-methyl-thiazole-4-carboxamide		3.35	18	859	2.8

No.	Compound Name	Structure	LogP	Solubility in water (ppm)	Solubility in heptane (ppm)	Photostability T ₅₀ (h)
I.b.599	ethyl N-(2,6-difluoro-4-pyridyl)-N-[4-[(2,2-dimethylcyclobutyl)carbamoyl]-5-methyl-thiazol-2-yl] carbamate		4.58	1.0	>1300	11
I.b.598	methyl N-(2,6-difluoro-4-pyridyl)-N-[4-[(2,2-dimethylcyclobutyl)carbamoyl]-5-methyl-thiazol-2-yl]carbamate		4.21	1.4	1155	6.2
I.b.595	2-[(2,6-difluoro-4-pyridyl)-formyl-amino]-N-(2,2-dimethylcyclobutyl)-5-methyl-thiazole-4-carboxamide		3.61	2.5	193	2.8
I.b.612	ethyl 2-[(2,6-difluoro-4-pyridyl)-[4-[(2,2-dimethylcyclobutyl)carbamoyl]-5-methyl-thiazol-2-yl]amino]-2-oxo-acetate		4.34	nd	379	5.5
I.b.596	2-[acetyl-(2,6-difluoro-4-pyridyl) amino]-N-(2,2-dimethylcyclobutyl)-5-methyl-thiazole-4-carboxamide		3.80	3.7	619	5.5

Biological Examples

Example B1: *Alternaria solani* / tomato / leaf disc (early blight)

Tomato leaf disks cv. Baby are placed on agar in multiwell plates (24-well format) and sprayed with the formulated test compound diluted in water. The leaf disks are inoculated with a spore suspension of the fungus 2 days after application. The inoculated leaf disks are incubated at 23 °C / 21°C (day/night) and 80% rh under a light regime of 12/12 h (light/dark) in a climate cabinet and the activity of a compound is assessed as percent disease control compared to untreated when an appropriate level of disease damage appears on untreated check disk leaf disks (5 - 7 days after application).

The following compounds gave at least 80% control of *Alternaria solani* at 200 ppm when compared to untreated control under the same conditions, which showed extensive disease development: I.b.595, I.b.596, I.b.600, I.b.603, I.b.604, I.b.606, I.b.607, I.b.608, I.b.612, I.b.613, I.b.617, I.b.815, I.b.816, I.b.817, I.b.818, I.c.812, I.c.813.

Example B2: *Botryotinia fuckeliana* (*Botrytis cinerea*) / liquid culture (Gray mould)

Conidia of the fungus from cryogenic storage are directly mixed into nutrient broth (Vogels broth). After placing a (DMSO) solution of test compound into a microtiter plate (96-well format), the nutrient broth containing the fungal spores is added. The test plates are incubated at 24 °C and the inhibition of growth is determined photometrically 3-4 days after application.

The following compounds gave at least 80% control of *Botryotinia fuckeliana* at 20 ppm when compared to untreated control under the same conditions, which showed extensive disease development: I.b.595, I.b.596, I.b.600, I.b.612, I.b.613, I.b.815, I.b.818.

Example B3: *Glomerella lagenarium* (*Colletotrichum lagenarium*) / liquid culture (Anthracnose)

Conidia of the fungus from cryogenic storage are directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of test compound into a microtiter plate (96-well format), the nutrient broth containing the fungal spores is added. The test plates are incubated at 24 °C and the inhibition of growth is measured photometrically 3-4 days after application.

The following compounds gave at least 80% control of *Glomerella lagenarium* at 20 ppm when compared to untreated control under the same conditions, which showed extensive disease development: I.b.595, I.b.596, I.b.600, I.b.603, I.b.604, I.b.606, I.b.607, I.b.608, I.b.612, I.b.613, I.b.815, I.b.816, I.b.817, I.b.818, I.b.820, I.c.600, I.c.811, I.c.812, I.c.813, I.c.814.

Example B4: *Blumeria graminis f. sp. tritici* (*Erysiphe graminis f. sp. tritici*) / wheat / leaf disc preventative (Powdery mildew on wheat)

Wheat leaf segments cv. Kanzler are placed on agar in a multiwell plate (24-well format) and sprayed with the formulated test compound diluted in water. The leaf disks are inoculated by shaking powdery mildew infected plants above the test plates 1 day after application. The inoculated leaf disks are incubated at 20 °C and 60% rh under a light regime of 24 h darkness followed by 12 h light / 12 h darkness in a climate chamber and the activity of a compound is assessed as percent disease control compared to untreated when an appropriate level of disease damage appears on untreated check leaf segments (6 - 8 days after application).

The following compounds gave at least 80% control of *Blumeria graminis* f. sp. *tritici* at 200 ppm when compared to untreated control under the same conditions, which showed extensive disease development: I.a.596, I.a.600, I.a.601, I.a.812, I.b.595, I.b.596, I.b.598, I.b.599, I.b.600, I.b.603, I.b.604, I.b.606, I.b.607, I.b.608, I.b.610, I.b.612, I.b.613, I.b.614, I.b.615, I.b.616, I.b.617, I.b.618, I.b.815, I.b.816, I.b.817, I.b.818, I.b.820, I.c.596, I.c.600, I.c.811, I.c.812, I.c.813, I.c.814.

Example B5: *Fusarium culmorum* / wheat / spikelet preventative (Head blight)

Wheat spikelets cv. Monsun are placed on agar in multiwell plates (24-well format) and sprayed with the formulated test compound diluted in water. The spikelets are inoculated with a spore suspension of the fungus 1 day after application. The inoculated spikelets are incubated at 20 °C and 60% rh under a light regime of 72 h semi darkness followed by 12 h light / 12 h darkness in a climate chamber and the activity of a compound is assessed as percent disease control compared to untreated when an appropriate level of disease damage appears on untreated check spikelets (6 - 8 days after application).

The following compounds gave at least 80% control of *Fusarium culmorum* at 200 ppm when compared to untreated control under the same conditions, which showed extensive disease development: I.b.600.

Example B6: *Gibberella zeae* (*Fusarium graminearum*) / wheat / spikelet preventative (Head blight)

Wheat spikelets cv. Monsun are placed on agar in multiwell plates (24-well format) and sprayed with the formulated test compound diluted in water. One day after application, the spikelets are inoculated with a spore suspension of the fungus. The inoculated test leaf disks are incubated at 20 °C and 60% rh under a light regime of 72 h semi darkness followed by 12 h light / 12 h darkness in a climate chamber, the activity of a compound is assessed as percent disease control compared to untreated when an appropriate level of disease damage appears on untreated check spikelets (6 - 8 days after application).

The following compounds gave at least 80% control of *Gibberella zeae* at 200 ppm when compared to untreated control under the same conditions, which showed extensive disease development: I.b.607.

Example B7: *Phaeosphaeria nodorum* (*Septoria nodorum*) / wheat / leaf disc preventative (Glume blotch)

Wheat leaf segments cv. Kanzler are placed on agar in a multiwell plate (24-well format) and sprayed with the formulated test compound diluted in water. The leaf disks are inoculated with a spore suspension of the fungus 2 days after application. The inoculated test leaf disks are incubated at 20 °C and 75% rh under a light regime of 12 h light / 12 h darkness in a climate cabinet and the activity of a compound is assessed as percent disease control compared to untreated when an appropriate level of disease damage appears in untreated check leaf disks (5 - 7 days after application).

The following compounds gave at least 80% control of *Phaeosphaeria nodorum* at 200 ppm when compared to untreated control under the same conditions, which showed extensive disease development: I.b.603, I.b.604, I.b.607, I.a.812.

Example B8: *Monographella nivalis* (*Microdochium nivale*) / liquid culture (foot rot cereals)

Conidia of the fungus from cryogenic storage are directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of test compound into a microtiter plate (96-well format), the nutrient broth containing the fungal spores is added. The test plates are incubated at 24 °C and the inhibition of growth is determined photometrically 4-5 days after application.

The following compounds gave at least 80% control of *Monographella nivalis* at 20 ppm when compared to untreated control under the same conditions, which showed extensive disease development: I.a.600, I.b.595, I.b.596, I.b.600, I.b.603, I.b.604, I.b.606, I.b.607, I.b.608, I.b.612, I.b.613, I.b.615, I.b.616, I.b.817, I.b.618, I.b.815, I.b.816, I.b.818, I.b.820, I.c.600, I.c.811, I.c.812, I.c.813, I.c.814.

5 **Example B9: *Mycosphaerella arachidis* (*Cercospora arachidicola*) / liquid culture (early leaf spot)**

Conidia of the fungus from cryogenic storage are directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of test compound into a microtiter plate (96-well format), the nutrient broth containing the fungal spores is added. The test plates are incubated at 24 °C and the inhibition of growth is determined photometrically 4-5 days after application.

- 10 The following compounds gave at least 80% control of *Mycosphaerella arachidis* at 20 ppm when compared to untreated control under the same conditions, which showed extensive disease development: I.b.595, I.b.600, I.b.603, I.b.604, I.b.606, I.b.607, I.b.612, I.b.816, I.c.812.

Example B10: *Phakopsora pachyrhizi* / soybean / preventative (soybean rust)

Soybean leaf disks are placed on water agar in multiwell plates (24-well format) and sprayed with the formulated test compound diluted in water. One day after application leaf discs are inoculated by spraying a spore suspension on the lower leaf surface. After an incubation period in a climate cabinet of 24-36 hours in darkness at 20 °C and 75% rh leaf disc are kept at 20 °C with 12 h light/day and 75% rh. The activity of a compound is assessed as percent disease control compared to untreated when an appropriate level of disease damage appears in untreated check leaf disks (12 - 14 days after

- 20 application).

The following compounds gave at least 80% control of *Phakopsora pachyrhizi* at 200 ppm when compared to untreated control under the same conditions, which showed extensive disease development: I.a.601, I.b.595, I.b.600, I.b.603, I.b.604, I.b.612, I.b.613, I.b.815, I.b.816, I.b.818.

Example B11: *Plasmopara viticola* / grape / leaf disc preventative (late blight)

- 25 Grape vine leaf disks are placed on water agar in multiwell plates (24-well format) and sprayed with the formulated test compound diluted in water. The leaf disks are inoculated with a spore suspension of the fungus 1 day after application. The inoculated leaf disks are incubated at 19 °C and 80% rh under a light regime of 12 h light / 12 h darkness in a climate cabinet and the activity of a compound is assessed as percent disease control compared to untreated when an appropriate level of disease damage appears
- 30 in untreated check leaf disks (6 - 8 days after application).

The following compounds gave at least 80% control of *Plasmopara viticola* at 200 ppm when compared to untreated control under the same conditions, which showed extensive disease development: I.b.603, I.b.607.

Example B12: *Puccinia recondita f. sp. tritici* / wheat / leaf disc curative (Brown rust)

- 35 Wheat leaf segments cv. Kanzler are placed on agar in multiwell plates (24-well format). The leaf segments are inoculated with a spore suspension of the fungus. Plates are stored in darkness at 19 °C and 75% rh. The formulated test compound diluted in water is applied 1 day after inoculation. The leaf segments are incubated at 19 °C and 75% rh under a light regime of 12 h light / 12 h darkness in a climate cabinet and the activity of a compound is assessed as percent disease control compared to

untreated when an appropriate level of disease damage appears in untreated check leaf segments (6 - 8 days after application).

The following compounds gave at least 80% control of *Puccinia recondita* f. sp. *tritici* at 200 ppm when compared to untreated control under the same conditions, which showed extensive disease development: I.b.595, I.b.600, I.b.603, I.b.604, I.b.606, I.b.607, I.b.608, I.b.612, I.b.618, I.b.815, I.b.816, I.b.818.

Example B13: *Puccinia recondita* f. sp. *tritici* / wheat / leaf disc preventative (Brown rust)

Wheat leaf segments cv. Kanzler are placed on agar in multiwell plates (24-well format) and sprayed with the formulated test compound diluted in water. The leaf disks are inoculated with a spore suspension of the fungus 1 day after application. The inoculated leaf segments are incubated at 19 °C and 75% rh under a light regime of 12 h light / 12 h darkness in a climate cabinet and the activity of a compound is assessed as percent disease control compared to untreated when an appropriate level of disease damage appears in untreated check leaf segments (7 - 9 days after application).

The following compounds gave at least 80% control of *Puccinia recondita* f. sp. *tritici* at 200 ppm when compared to untreated control under the same conditions, which showed extensive disease development: I.a.596, I.a.600, I.a.601, I.a.812, I.b.595, I.b.596, I.b.600, I.b.603, I.b.604, I.b.606, I.b.607, I.b.608, I.b.612, I.b.613, I.b.614, I.b.618, I.b.815, I.b.816, I.b.817, I.b.818, I.c.600, I.c.811, I.c.812, I.c.813, I.c.814.

Example B14: *Magnaporthe grisea* (*Pyricularia oryzae*) / rice / leaf disc preventative (Rice Blast)

Rice leaf segments cv. Ballila are placed on agar in a multiwell plate (24-well format) and sprayed with the formulated test compound diluted in water. The leaf segments are inoculated with a spore suspension of the fungus 2 days after application. The inoculated leaf segments are incubated at 22 °C and 80% rh under a light regime of 24 h darkness followed by 12 h light / 12 h darkness in a climate cabinet and the activity of a compound is assessed as percent disease control compared to untreated when an appropriate level of disease damage appears in untreated check leaf segments (5 - 7 days after application).

The following compounds gave at least 80% control of *Magnaporthe grisea* at 200 ppm when compared to untreated control under the same conditions, which showed extensive disease development: I.a.596, I.a.600, I.a.601, I.a.812, I.b.595, I.b.596, I.b.598, I.b.600, I.b.603, I.b.604, I.b.606, I.b.607, I.b.608, I.b.612, I.b.613, I.b.614, I.b.615, I.b.616, I.b.617, I.b.618, I.b.815, I.b.816, I.b.817, I.b.818, I.b.820, I.c.596, I.c.598, I.c.600, I.c.811, I.c.812, I.c.813, I.c.814.

Example B15: *Pyrenophora teres* / barley / leaf disc preventative (Net blotch)

Barley leaf segments cv. Hasso are placed on agar in a multiwell plate (24-well format) and sprayed with the formulated test compound diluted in water. The leaf segments are inoculated with a spore suspension of the fungus 2 days after application. The inoculated leaf segments are incubated at 20 °C and 65% rh under a light regime of 12 h light / 12 h darkness in a climate cabinet and the activity of a compound is assessed as disease control compared to untreated when an appropriate level of disease damage appears in untreated check leaf segments (5 - 7 days after application).

The following compounds gave at least 80% control of Pyrenophora teres at 200 ppm when compared to untreated control under the same conditions, which showed extensive disease development: I.a.600, I.b.595, I.b.596, I.b.600, I.b.603, I.b.604, I.b.607, I.b.608, I.b.612, I.b.613, I.b.617, I.b.815, I.b.816, I.b.818, I.c.596, I.c.600, I.c.811, I.c.812, I.c.813.

5 **Example B16: Sclerotinia sclerotiorum** / liquid culture (cottony rot)

Mycelia fragments of a newly grown liquid culture of the fungus are directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of test compound into a microtiter plate (96-well format) the nutrient broth containing the fungal material is added. The test plates are incubated at 24 °C and the inhibition of growth is determined photometrically 3-4 days after application.

- 10 The following compounds gave at least 80% control of Sclerotinia sclerotiorum at 20 ppm when compared to untreated control under the same conditions, which showed extensive disease development: I.b.607, I.b.612.

Example B17: Mycosphaerella graminicola (*Septoria tritici*) / liquid culture (Septoria blotch)

- 15 Conidia of the fungus from cryogenic storage are directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of test compound into a microtiter plate (96-well format), the nutrient broth containing the fungal spores is added. The test plates are incubated at 24 °C and the inhibition of growth is determined photometrically 4-5 days after application.

- The following compounds gave at least 80% control of Mycosphaerella graminicola at 20 ppm when compared to untreated control under the same conditions, which showed extensive disease
20 development: I.b.595, I.b.596, I.b.600, I.b.603, I.b.604, I.b.606, I.b.607, I.b.612, I.b.815, I.b.816, I.b.817, I.b.818, I.c.811, I.c.812, I.c.813, I.c.814.

C₄alkylcarbonyloxyC₁-C₃alkyl, C₃-C₅alkynyloxy, C₁-C₄alkylsulfanyl, di(C₁-C₄alkyl)amino, phenyl, phenylC₁-C₃alkyl, phenylC₁-C₃alkoxyC₁-C₃alkyl, phenoxy, or heteroaryl, wherein the heteroaryl is a 5- or 6-membered aromatic monocyclic ring comprising 1 or 2 heteroatoms individually selected from nitrogen, oxygen and sulfur.

5

3. The compound according to claim 1 or claim 2, wherein R¹ is hydrogen, C₁-C₃alkyl, C₁-C₃alkoxy, C₁-C₃haloalkyl, C₁-C₃hydroxyalkyl, methoxyC₁-C₄alkyl, C₃-C₄cycloalkyl, C₁-C₂alkoxyC₁-C₂alkoxy, C₁-C₃alkoxycarbonyl, methoxycarbonylC₁-C₃alkyl, C₁-C₂alkoxycarbonyloxyC₁-C₂alkyl, C₁-C₂alkylcarbonyloxyC₁-C₂alkyl, C₃-C₄alkynyloxy, C₁-C₃alkylsulfanyl, diethylamino, phenyl, benzyl, phenoxy, benzyloxyC₁-C₂alkyl, or heteroaryl, wherein the heteroaryl is a 5- or 6-membered aromatic monocyclic ring comprising a single heteroatom selected from oxygen and sulfur.

4. The compound according to any one of claims 1 to 3, wherein R¹ is hydrogen, methyl, ethyl, methoxy, ethoxy, fluoromethyl, chloromethyl, bromomethyl, 2,2,2-trifluoroethyl, 1-hydroxyethyl, methoxymethyl, 1-methoxyethyl, 1-ethoxymethyl, 1-methoxy-1-methylethyl, cyclopropyl, methoxyethoxy, ethoxycarbonyl, 2-methoxy-2-oxo-ethyl, 2-methoxy-oxo-ethyl, 2-methoxy-oxo-propyl, propargyloxy, 1-methoxycarbonyloxy-ethyl, 1-ethoxycarbonyloxy-ethyl, 1-methylcarbonyloxy-ethyl, methylcarbonyloxymethyl, methylsulfanyl, ethylsulfanyl, isopropylsulfanyl, diethylamino, phenyl, benzyl, phenoxy, benzyloxymethyl, 1-benzyloxyethyl, 2-furanyl, or 2-thiophenyl.

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5. The compound according to any one of claims 1 to 4, wherein R² is halogen, C₁-C₂alkyl, C₁-C₂alkoxy or HC(O)NH-.

6. The compound according to any one of claims 1 to 5, wherein R² is methyl.

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7. The compound according to any one of claims 1 to 6, wherein R³ is C₁-C₄alkyl, C₁-C₃alkoxy, C₃-C₆cycloalkyl, C₃-C₆cycloalkylC₁-C₂alkyl (wherein the cycloalkyl groups are optionally substituted with 1 to 3 groups represented by R⁴), phenyl, heteroaryl wherein the heteroaryl is a 5- or 6-membered aromatic monocyclic ring comprising 1, 2 or 3 heteroatoms individually selected from nitrogen, oxygen and sulfur, heterocyclyl wherein the heterocyclyl is a 4-, 5- or 6-membered non-aromatic monocyclic ring comprising 1, 2 or 3 heteroatoms individually selected from nitrogen, oxygen and sulfur, or a 5- to 12-membered non-aromatic spirocyclic carbobi- or carbetri-cyclyl ring system optionally comprising a single heteroatom selected from nitrogen, oxygen and sulfur.

8. The compound according to any one of claims 1 to 7, wherein R³ is C₃-C₄cycloalkyl, wherein the cycloalkyl groups are optionally substituted with 1 or 2 groups represented by R⁴, or R³ is a 6- to 8-membered non-aromatic spirocyclic carbobi-cyclyl ring system.

9. The compound according to any one of claims 1 to 8, wherein X is N.

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10. The compound according to any one of claims 1 to 9, wherein Y is C-F.

11. The compound according to any one of claims 1 to 10, wherein R³ is cyclobutyl, 2,2-dimethylcyclobutyl or spiro[3.4]octanyl.

5 12. An agrochemical composition comprising a fungicidally effective amount of a compound of formula (I) according to any one of claims 1 to 11.

13. The composition according to claim 12, further comprising at least one additional active ingredient and/or an agrochemically-acceptable diluent or carrier.

10

14. A method of controlling or preventing infestation of useful plants by phytopathogenic microorganisms, wherein a fungicidally effective amount of a compound of formula (I) according to any of claims 1 to 11, or a composition comprising this compound as active ingredient, is applied to the plants, to parts thereof or the locus thereof.

15

15. Use of a compound of formula (I) according to any one of claims 1 to 11 as a fungicide.