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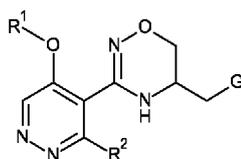
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(54) Title: MICROBIOCIDAL PYRIDAZINE DIHYDROOXADIAZINE DERIVATIVES



(I)

(57) Abstract: A compound of formula (I) wherein R¹, R², and G are as defined in claim 1, useful as pesticides, especially as fungicides.



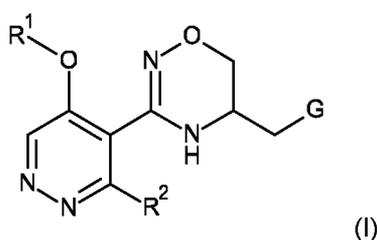
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MICROBIOCIDAL PYRIDAZINE DIHYDROOXADIAZINE DERIVATIVES

The present invention relates to pyridazine dihydrooxadiazines, as active ingredients, which have microbiocidal activity, and in particular, fungicidal activity. The invention also relates to agrochemical compositions which comprise at least one of the pyridazine 5,6-dihydro-4H-1,2,4-oxadiazine derivatives, to processes of preparation of these compounds and to uses of the pyridazine 5,6-dihydro-4H-1,2,4-oxadiazine derivatives or compositions in agriculture or horticulture for controlling or preventing infestation of plants, harvested food crops, seeds or non-living materials by phytopathogenic microorganisms, preferably fungi.

Many plant protection compounds have been developed to prevent or reduce plant disease caused by micro-organisms, for instance, by fungi. For example, WO 2020/109391 discloses pyridazine (thio)amide derivatives. WO 2020/127780 discloses pyridazine oxadiazine derivatives.

The present invention therefore provides, in a first aspect, compounds of formula (I)



or an agrochemically acceptable salt, stereoisomer, enantiomer, or N-oxide thereof, wherein:

R¹ is phenyl unsubstituted or substituted with:

- a single substituent selected from hydroxyl, nitro, halogen, mercapto, amino, cyano, NHMe, N(Me)₂, C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₂fluoroalkyl, C₁-C₄alkoxy, C₁-C₂fluoroalkoxy, C₃-C₄alkenyloxy, C₃-C₄alkenyloxy, C₃-C₆cycloalkyl, C₃-C₆cycloalkyloxy, C₃-C₆cycloalkylC₁-C₂alkyloxy, C₁-C₃alkylsulfanyl, and C₁-C₃alkylsulfonyl; or
- 1, 2 or 3 substituents independently selected from hydroxyl, halogen, mercapto, amino, cyano, methyl, ethyl, propyl, *iso*-propyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl, methoxy, ethoxy, propoxy, *iso*-propoxy, *tert*-butoxy, allyloxy, prop-2-ynoxy, prop-1-ynoxy, methylsulfanyl, methylsulfonyl, difluoromethoxy, trifluoromethoxy, and cyclopropyl; or
- R¹ is a 5- or 6-membered monocyclic heteroaryl ring comprising 1, 2 or 3 heteroatoms each independently selected from N, O and S, with the proviso that no more than one is O or S; wherein said heteroaryl ring is unsubstituted or substituted with:
 - a single substituent selected from hydroxyl, nitro, halogen, mercapto, amino, cyano, NHMe, N(Me)₂, C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₂fluoroalkyl, C₁-C₄alkoxy, C₁-C₂fluoroalkoxy, C₃-C₄alkenyloxy, C₃-C₄alkenyloxy, C₃-C₆cycloalkyl, C₃-C₆cycloalkyloxy, C₃-C₆cycloalkylC₁-C₂alkyloxy, C₁-C₃alkylsulfanyl, and C₁-C₃alkylsulfonyl; or
 - 1 or 2 substituents independently selected from hydroxyl, halogen, mercapto, amino, cyano, methyl, ethyl, propyl, *iso*-propyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl, methoxy, ethoxy,

propoxy, *iso*-propoxy, *tert*-butoxy, allyloxy, prop-2-ynoxy, prop-1-ynoxy, methylsulfanyl, methylsulfonyl, difluoromethoxy, trifluoromethoxy, and cyclopropyl;

R² is hydrogen, hydroxyl, nitro, halogen, mercapto, amino, cyano, C₁-C₆alkyl, C₁-C₂fluoroalkyl, C₃-C₅alkenyl, C₃-C₅alkynyl, C₁-C₃alkoxyC₂-C₃alkyl, C₃-C₆cycloalkyl, or C₃-C₆cycloalkylC₁₋₂alkyl, C₁-C₄alkoxy, C₁-C₂fluoroalkoxy, C₃-C₅alkenyloxy, C₃-C₅alkenyloxy, C₃-C₆cycloalkyl, C₃-C₆cycloalkyloxy, C₃-C₆cycloalkylC₁₋₂alkyloxy, C₁-C₄alkylamino, di-C₁-C₄alkylamino, C₃-C₅alkenylamino, C₃-C₅alkynylamino, C₁-C₃alkylsulfanyl, or C₁-C₃alkylsulfonyl; or

R² is phenyl, phenylC₁₋₂alkyl, heteroaryl, heteroarylC₁₋₂alkyl, heterocyclyl, heterocyclylC₁₋₂alkyl, C₃-C₆cycloalkyl, or C₃-C₆cycloalkylC₁₋₂alkyl; wherein the heteroaryl moiety is a 5- or 6-membered monocyclic aromatic ring which comprises 1, 2, or 3 heteroatoms independently selected from N, O and S, with the proviso that no more than one is O or S; wherein the heterocyclyl moiety is a 4- to 6-membered non-aromatic ring which comprises 1 or 2 heteroatoms independently selected from N, O and S, with the proviso that no more than one is O or S; and wherein any of said cycloalkyl, phenyl, heteroaryl and heterocyclyl moieties are unsubstituted or substituted with:

- a single substituent selected from hydroxyl, nitro, halogen, mercapto, amino, cyano, NHMe, N(Me)₂, C₁-C₄alkyl, C₂-C₃alkenyl, C₂-C₃alkynyl, C₁-C₂fluoroalkyl, C₁-C₄alkoxy, C₁-C₂fluoroalkoxy, allyloxy, prop-2-ynoxy, prop-1-ynoxy, C₃-C₆cycloalkyl, C₁-C₃alkylsulfanyl, and C₁-C₃alkylsulfonyl; or

- 1 or 2 substituents independently selected from hydroxyl, halogen, mercapto, amino, cyano, methyl, ethyl, propyl, *iso*-propyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl, methoxy, ethoxy, methylsulfanyl, methylsulfonyl, difluoromethoxy, trifluoromethoxy, and cyclopropyl;

G is selected from G-1, G-2, G-3, and G-4, wherein:

G-1 is phenyl or phenoxy, wherein said phenyl or phenoxy is unsubstituted or substituted with:

- a single substituent selected from hydroxyl, nitro, halogen, mercapto, amino, cyano, NHMe, N(Me)₂, C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₂fluoroalkyl, C₁-C₄alkoxy, C₁-C₂fluoroalkoxy, C₃-C₄alkenyloxy, C₃-C₄alkenyloxy, C₃-C₆cycloalkyl, C₃-C₆cycloalkyloxy, C₃-C₆cycloalkylC₁₋₂alkyloxy, C₁-C₃alkylsulfanyl, and C₁-C₃alkylsulfonyl; or

- 1 or 2 substituents independently selected from hydroxyl, halogen, mercapto, amino, cyano, methyl, ethyl, propyl, *iso*-propyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl, methoxy, ethoxy, propoxy, *iso*-propoxy, *tert*-butoxy, allyloxy, prop-2-ynoxy, prop-1-ynoxy, methylsulfanyl, methylsulfonyl, difluoromethoxy, trifluoromethoxy, and cyclopropyl;

- G-2 is a 5- or 6-membered monocyclic heteroaryl or heteroaryl-oxy; wherein said heteroaryl comprises 1, 2 or 3 heteroatoms each independently selected from N, O and S with the proviso that no more than one is O or S; and wherein said heteroaryl or heteroaryl-oxy is unsubstituted or substituted with:

- a single substituent selected from hydroxyl, nitro, halogen, mercapto, amino, cyano, NHMe, N(Me)₂, C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₂fluoroalkyl, C₁-C₄alkoxy, C₁-C₂fluoroalkoxy, C₃-C₄alkenyloxy, C₃-C₄alkenyloxy, C₃-C₆cycloalkyl, C₃-C₆cycloalkyloxy, C₃-C₆cycloalkylC₁₋₂alkyloxy, C₁-C₃alkylsulfanyl, and C₁-C₃alkylsulfonyl; or

- 1 or 2 substituents independently selected from hydroxyl, halogen, mercapto, amino, cyano, methyl, ethyl, propyl, *iso*-propyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl, methoxy, ethoxy, propoxy, *iso*-propoxy, *tert*-butoxy, allyloxy, prop-2-ynoxy, prop-1-ynoxy, methylsulfanyl, methylsulfonyl, difluoromethoxy, trifluoromethoxy, and cyclopropyl;

5 G-3 is a 9- or 10-membered heterobicyclic ring system comprising 1, 2 or 3 heteroatoms each independently selected from N, O and S with the proviso that no more than one is O or S; wherein said heterobicyclic ring system is saturated, partially unsaturated, or aromatic; and wherein said heterobicyclic ring system is unsubstituted or substituted with a single substituent selected from hydroxyl, nitro, halogen, mercapto, amino, cyano, NHMe, N(Me)₂, C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₂fluoroalkyl, C₁-
10 C₄alkoxy, C₁-C₂fluoroalkoxy, C₃-C₄alkenyloxy, C₃-C₄alkenyloxy, C₃-C₆cycloalkyl, C₃-C₆cycloalkyloxy, C₃-C₆cycloalkylC₁-C₂alkyloxy, C₁-C₃alkylsulfanyl, and C₁-C₃alkylsulfonyl;

G-4 is a 9- or 10-membered carbobicyclic ring system; wherein said carbobicyclic ring system is saturated, partially unsaturated, or aromatic; and wherein said carbobicyclic ring system is unsubstituted or substituted with a single substituent selected from hydroxyl, nitro, halogen, mercapto, amino, cyano, NHMe, N(Me)₂,
15 C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₂fluoroalkyl, C₁-C₄alkoxy, C₁-C₂fluoroalkoxy, C₃-C₄alkenyloxy, C₃-C₄alkenyloxy, C₃-C₆cycloalkyl, C₃-C₆cycloalkyloxy, C₃-C₆cycloalkylC₁-C₂alkyloxy, C₁-C₃alkylsulfanyl, and C₁-C₃alkylsulfonyl.

The present invention also provides a method of preparation of compounds of formula (I) as well as intermediate compounds useful in the preparation of compounds of formula (I).

20 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 caused by fungi.

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). Such an agricultural composition may further comprise at least one additional active ingredient and/or an agrochemically-acceptable diluent or carrier.

25 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 to the plants, to parts thereof or the locus thereof.

30 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 exclude methods for the treatment of the human or animal body by surgery or therapy.

According to a fifth aspect, the present invention makes available a plant propagation material, such as a seed, comprising, or treated with, or adhered thereto, a compound of formula (I) or a composition comprising such a compound.

35 As used herein, the term "hydroxyl" or "hydroxy" means an -OH group.

As used herein, the term "mercapto" means an -SH group.

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

As used herein, amino means an -NH₂ group.

As used herein, nitro means an -NO₂ group.

As used herein, oxo means an =O group (eg, as in a carbonyl (C=O) group).

As used herein, the term "halogen" or "halo" refers to fluorine (fluoro), chlorine (chloro), bromine (bromo)
5 or iodine (iodo), preferably fluorine, chlorine or bromine. This also applies, correspondingly, to halogen in
combination with other meanings, such as haloalkyl.

As used herein, the term "C₁-C₆alkyl" refers to a straight or branched hydrocarbon chain radical consisting
solely of carbon and hydrogen atoms, containing no unsaturation, having from one to six carbon atoms,
and which is attached to the rest of the molecule by a single bond. C₁-C₄alkyl should be construed
10 accordingly. Examples of C₁-C₆alkyl include, but are not limited to, methyl, ethyl, *iso*-propyl.

As used herein, the term "C₂-C₄alkenyl" refers to a straight or branched hydrocarbon chain radical group
consisting solely of carbon and hydrogen atoms, containing at least one double bond that may be of either
the (*E*) or (*Z*) configuration, having two or four carbon atoms, which is attached to the rest of the molecule
by a single bond. Examples of C₂-C₄alkenyl include, but are not limited to, vinyl (ethenyl), prop-1-enyl, allyl
15 (prop-2-enyl).

As used herein, the term "C₂-C₄alkynyl" 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 or four
carbon atoms, and which is attached to the rest of the molecule by a single bond. Examples of C₂-C₄alkynyl
include, but are not limited to, prop-1-ynyl and propargyl (prop-2-ynyl).

20 As used herein, the term "C₁-C₂fluoroalkyl" refers to a C₁-C₂alkyl radical as generally defined above
substituted by one or more fluorine atoms. Examples of C₁-C₂fluoroalkyl include, but are not limited to
difluoromethyl and trifluoromethyl.

As used herein, the term "C₁-C₄alkoxy" refers to a radical of the formula R_aO- where R_a is a C₁-C₄alkyl
radical as generally defined above. Examples of C₁-C₄alkoxy include, but are not limited to, methoxy,
25 ethoxy, *iso*-propoxy.

As used herein, the term "C₁-C₂fluoroalkoxy" refers to a C₁-C₂alkoxy radical as generally defined above
substituted by one or more fluorine atoms. Examples of C₁-C₂fluoroalkoxy include, but are not limited to
difluoromethoxy or trifluoromethoxy.

30 As used herein, the term "C₃-C₆cycloalkyl" refers to a stable, monocyclic ring radical which is saturated and
contains 3 to 6 carbon atoms.

As used herein, the term "C₃-C₄alkenyloxy" refers to a radical of the formula R_aO- where R_a is a C₃-C₄alkenyl
radical as generally defined above. Examples of C₃-C₄alkenyloxy include, but are not limited to allyloxy.

As used herein, the term "C₃-C₄alkynyloxy" refers to a radical of the formula R_aO- where R_a is a C₃-C₄alkynyl
radical as generally defined above. Examples of C₃-C₄alkynyloxy include, but are not limited to propargyloxy

35 As used herein, the term "C₃-C₆cycloalkoxy" refers to a radical of the formula R_aO- where R_a is a
C₃-C₆cycloalkyl radical as generally defined above. Examples of C₃-C₆cycloalkoxy include, but are not
limited to cyclopropoxy.

As used herein, the term "C₃-C₆cycloalkylC₁-C₂alkyl" refers to a radical of the formula R_aO- where R_a is a C₃-C₆cycloalkylC₁-C₂alkyl radical as generally defined above. Examples of C₃-C₆cycloalkyl C₁-C₂alkyloxy include, but are not limited to cyclopropylmethyl.

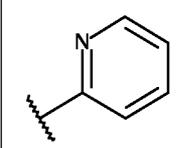
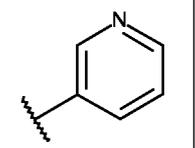
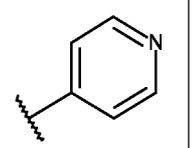
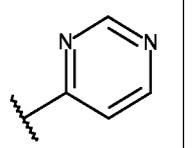
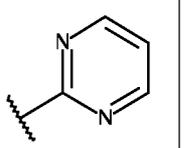
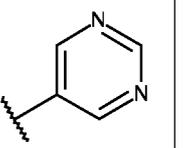
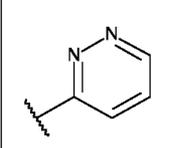
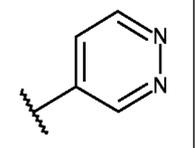
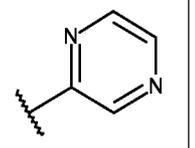
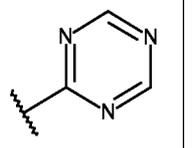
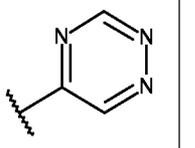
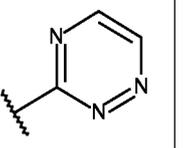
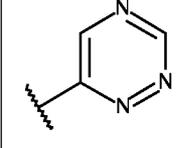
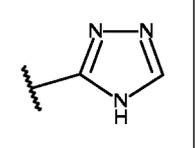
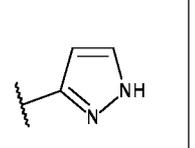
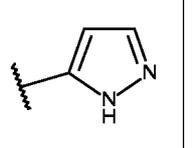
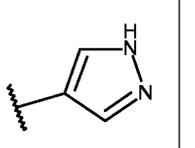
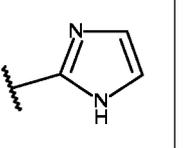
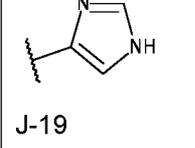
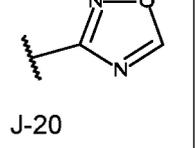
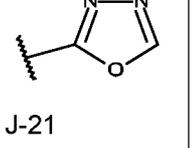
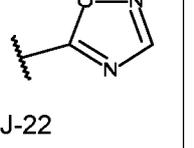
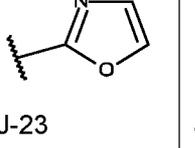
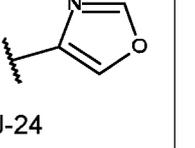
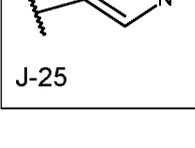
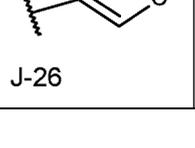
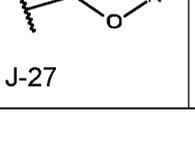
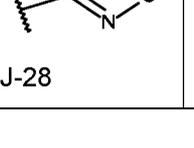
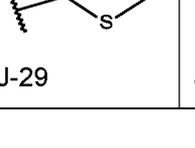
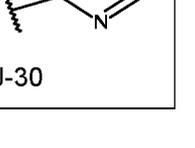
As used herein, the term "C₃-C₆cycloalkylC₁-C₂alkyloxy" refers to a radical of the formula R_aO- where R_a is a C₃-C₆cycloalkylC₁-C₂alkyl radical as generally defined above. Examples of C₃-C₆cycloalkyl C₁-C₂alkyloxy include, but are not limited to cyclohexylmethoxy.

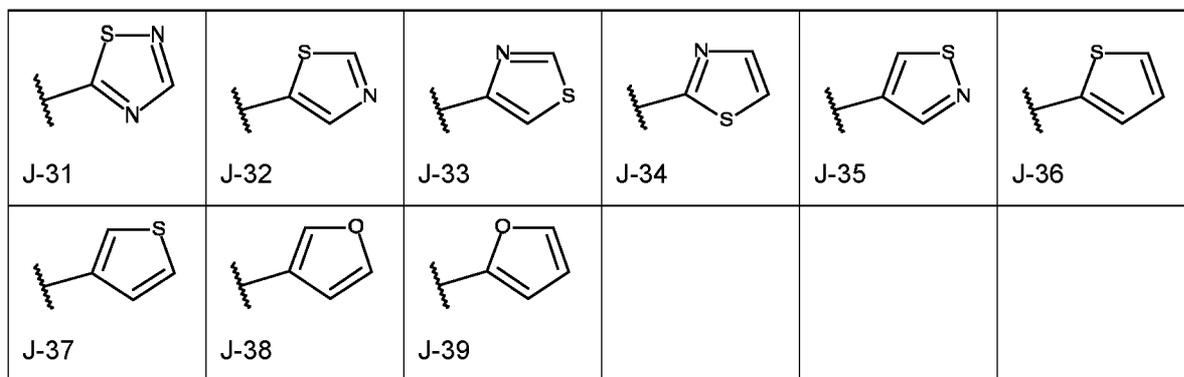
As used herein, the term "C₁-C₃alkylsulfanyl" refers to a radical of the formula -SR_a wherein R_a is a C₁-C₃alkyl radical as generally defined above.

As used herein, the term "C₁-C₃alkylsulfonyl" refers to a radical of the formula -S(O)₂R_a wherein R_a is a C₁-C₃alkyl radical as generally defined above.

The term "heteroaryl" as used herein refers to a 5- or 6-membered aromatic monocyclic ring having 1 to 3 heteroatoms independently selected from N, O and S. Examples of heteroaryls include J-1 to J-43 shown in Table J below. The staggered line in heteroaryls J-1 to J-39 represents the point of attachment to the rest of the compound. Preferred heteroaryls include pyridinyl, pyrimidinyl, pyridazinyl, pyrazinyl, and thiazolyl; preferably pyridinyl, and thiazolyl.

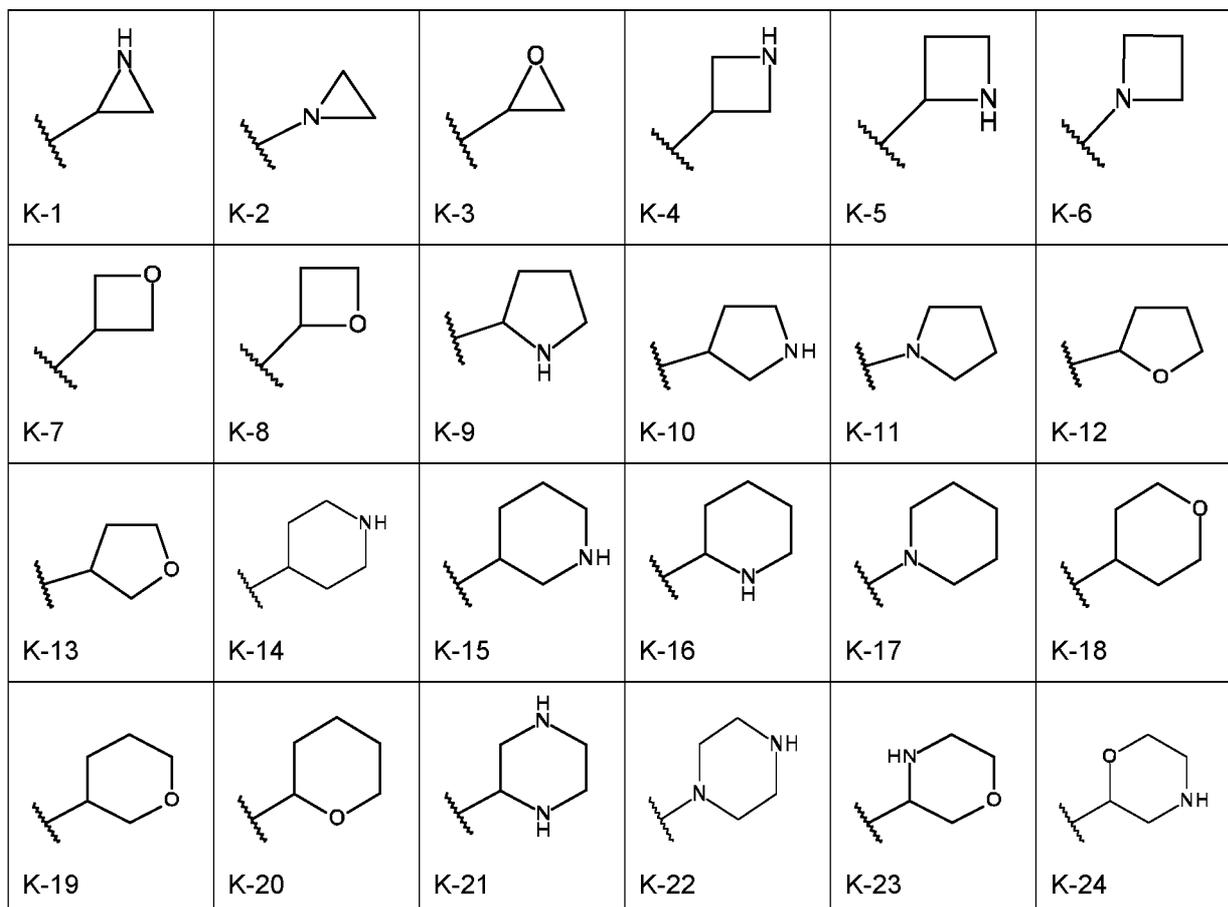
Table J: Heteroaryl J-1 to J-39:

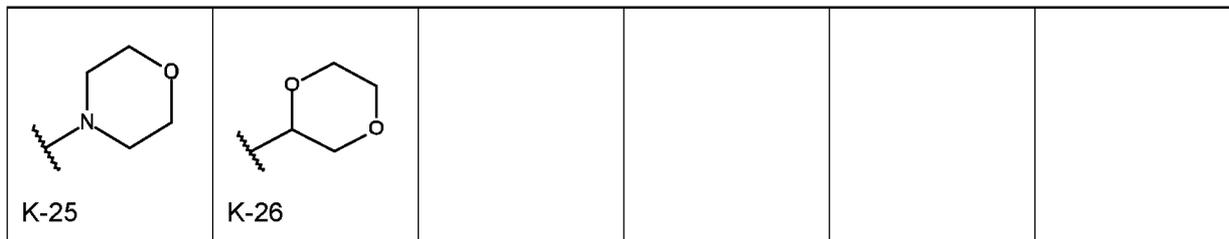
 J-1	 J-2	 J-3	 J-4	 J-5	 J-6
 J-7	 J-8	 J-9	 J-10	 J-11	 J-12
 J-13	 J-14	 J-15	 J-16	 J-17	 J-18
 J-19	 J-20	 J-21	 J-22	 J-23	 J-24
 J-25	 J-26	 J-27	 J-28	 J-29	 J-30



The term "heterocyclyl" as used herein refers to a 3-, 4-, 5-, and 6-membered saturated monocyclic rings having 1 or 2 heteroatoms independently selected from nitrogen and oxygen. Examples of heterocyclyls include K-1 to K-26 shown in Table K below. The staggered line in heterocyclyls K-1 to K-26 represents the point of attachment to the rest of the compound. Some of the heterocyclyls shown below contain an asymmetric carbon, which means that compounds containing them may occur in chiral isomeric forms, i.e., enantiomeric or diastereomeric forms. Preferred heterocyclyls include pyrrolidinyl, piperidinyl, piperazinyl, and tetrahydropyranyl; preferably pyrrolidinyl, piperazinyl, and tetrahydropyranyl.

Table K: heterocyclyl K-1 to K-26:





The term "optionally substituted" as used herein means that the group referenced is either unsubstituted or is substituted by a designated substituent, for example, phenyl is optionally substituted with 1 or 2 halo atoms" means phenyl substituted with 1 halo atom and phenyl substituted with 2 halo atoms. The term
5 "optionally substituted" can be used interchangeably with "unsubstituted or substituted".

As used herein, the term "controlling" refers to reducing the number of pests, eliminating pests and/or preventing further pest damage such that damage to a plant or to a plant derived product is reduced.

As used herein, the term "pest" refers to insects, and molluscs that are found in agriculture, horticulture, forestry, the storage of products of vegetable origin (such as fruit, grain, and timber); and those pests
10 associated with the damage of man-made structures. The term pest encompasses all stages in the life cycle of the pest.

As used herein, the term "effective amount" refers to the amount of the compound, or a salt thereof, which, upon single or multiple applications provides the desired effect.

An effective amount is readily determined by the skilled person in the art, by the use of known techniques
15 and by observing results obtained under analogous circumstances. In determining the effective amount, a number of factors are considered including, but not limited to the type of plant or derived product to be applied; the pest to be controlled & its lifecycle; the particular compound applied; the type of application; and other relevant circumstances.

As used herein, the term "room temperature" or "RT" or "rt" or "ambient temperature" refer to a temperature
20 of about 15° C to about 35° C. For example, rt can refer to a temperature of about 20° C to about 30° C.

The staggered line as used herein, for example in heteroaryls shown in Table J and heterocyclyls shown in Table K, represent the point of connection / attachment to the rest of the compound.

The presence of one or more possible asymmetric carbon atoms in a compound of Formula (I) means that the compounds may occur in chiral isomeric forms, i.e., enantiomeric or diastereomeric forms. Also,
25 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 (including lactam-lactim tautomerism and keto-enol tautomerism) where present. The present invention includes all possible tautomeric forms for a compound of Formula (I).

30 Compounds of formula (I) which have at least one basic centre can form, for example, acid addition salts, for example with strong inorganic acids such as mineral acids, for example perchloric acid, sulfuric acid, nitric acid, nitrous acid, a phosphorus acid or a hydrohalic acid, with strong organic carboxylic acids, such as C₁-C₄alkanecarboxylic acids which are unsubstituted or substituted, for example by halogen, for example

acetic acid, such as saturated or unsaturated dicarboxylic acids, for example oxalic acid, malonic acid, succinic acid, maleic acid, fumaric acid or phthalic acid, such as hydroxycarboxylic acids, for example ascorbic acid, lactic acid, malic acid, tartaric acid or citric acid, or such as benzoic acid, or with organic sulfonic acids, such as C₁-C₄alkane- or arylsulfonic acids which are unsubstituted or substituted, for example by halogen, for example methane- or p-toluenesulfonic acid. Compounds of Formula (I) which have at least one acidic group can form, for example, salts with bases, for example mineral salts, such as alkali metal or alkaline earth metal salts, for example sodium, potassium or magnesium salts, or salts with ammonia or an organic amine, such as morpholine, piperidine, pyrrolidine, a mono-, di- or tri-lower-alkylamine, for example ethyl-, diethyl-, triethyl- or dimethylpropylamine, or a mono-, di- or trihydroxy-lower-alkylamine, for example mono-, di- or triethanolamine.

The compounds of formula (I) according to the invention also include hydrates which may be formed during the salt formation.

In each case, the compounds of formula (I) according to the invention are in free form, in oxidized form as an N-oxide, in covalently hydrated form, or in salt form, e.g., an agronomically usable or agrochemically acceptable 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. Albini and S. Pietra, CRC Press, Boca Raton 1991.

The following lists provide definitions, including preferred definitions, for substituents R¹, R², and G with reference to the compounds of Formula (I) of the present invention. 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 elsewhere in this document.

In an embodiment of each aspect of the invention, R¹ is:

A. phenyl, pyridine, pyrazine, pyrimidine, or pyridazine, wherein said phenyl, pyridine, pyrazine, pyrimidine, or pyridazine is unsubstituted or substituted with a one or two substituents, for instance a single substituent, independently selected hydroxyl, halogen, mercapto, amino, nitro, cyano, methyl, ethyl, propyl, *iso*-propyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl, methoxy, ethoxy, allyloxy, prop-2-ynoxy, prop-1-ynoxy, *iso*-propoxy, *tert*-butoxy, propynoxy, NHMe, N(Me)₂, methylsulfanyl, methylsulfonyl, difluoromethoxy, trifluoromethoxy, cyclopropyl, cyclobutyl, and cyclopropyloxy; or

B. phenyl, pyridine, pyrazine, pyrimidine, or pyridazine, wherein said phenyl, pyridine, pyrazine, pyrimidine, or pyridazine is unsubstituted or substituted with a one or two substituents, for instance a single substituent, independently selected from hydroxyl, halogen, mercapto, amino, cyano, methyl, ethyl, propyl, *iso*-propyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl, methoxy, ethoxy, propoxy, *iso*-propoxy, *tert*-butoxy, allyloxy, prop-2-ynoxy, prop-1-ynoxy, methylsulfanyl, methylsulfonyl, difluoromethoxy, trifluoromethoxy, and cyclopropyl; or

C. phenyl, pyridine, pyrazine, pyrimidine or pyridazine, wherein said phenyl, pyridine, pyrazine, pyrimidine or pyridazine is unsubstituted or substituted with a one or two substituents, for instance one substituent, independently selected from hydroxyl, chloro, fluoro, cyano, methyl, difluoromethyl, trifluoromethyl, methoxy, allyloxy, propargyloxy, difluoromethoxy, trifluoromethoxy, cyclopropyl, and cyclopropyloxy; or

D. pyridine, pyrazine, pyrimidine or pyridazine, wherein said pyridine, pyrazine, pyrimidine or pyridazine is unsubstituted or substituted with a one or two substituents, for instance one substituent, independently selected from hydroxyl, chloro, fluoro, cyano, methyl, difluoromethyl, trifluoromethyl, methoxy, allyloxy, propargyloxy, difluoromethoxy, trifluoromethoxy, cyclopropyl, and cyclopropyloxy; or

5 E. phenyl substituted with a one or two substituents, for instance one substituent, independently selected from hydroxyl, chloro, fluoro, cyano, methyl, difluoromethyl, trifluoromethyl, methoxy, allyloxy, propargyloxy, difluoromethoxy, trifluoromethoxy, cyclopropyl, and cyclopropyloxy; or

F. phenyl substituted with a single substituent selected from hydroxyl, chloro, fluoro, cyano, methyl, difluoromethyl, trifluoromethyl, methoxy, allyloxy, propargyloxy, difluoromethoxy, trifluoromethoxy, cyclopropyl, and cyclopropyloxy; or

G. 2-fluoro-3-cyclopropylphenyl, 2-fluoro-3-methylphenyl, 2-fluorophenyl, 3-(difluoromethoxy)phenyl, 3-(trifluoromethoxy)phenyl, 2-(trifluoromethyl)pyridin-4-yl, 3-ethoxyphenyl, 3-ethylphenyl, 3-ethynylphenyl, 3-fluorophenyl, 4-(difluoromethoxy)phenyl, 4-(trifluoromethoxy)phenyl, 4-chlorophenyl, 4-cyanophenyl, 4-ethoxyphenyl, 4-ethylphenyl, 4-fluorophenyl, 3-methoxyphenyl, 3,4-dichlorophenyl, 3,4-difluorophenyl, 3,4-dimethoxyphenyl, 3,5-dichlorophenyl, 3,5-difluorophenyl, 3-cyanophenyl, 3,4-difluorophenyl, 3,4-dimethoxyphenyl, 3,5-dichlorophenyl, 3,5-difluorophenyl, 3-cyanophenyl, 2-methylpyrimidin-4-yl, 2-(trifluoromethyl)pyridin-4-yl, 3-(trifluoromethyl)pyridin-2-yl, 3-methoxypyridin-2-yl, 3-methylpyridin-2-yl, 2-chloropyridin-3-yl, 2-chloropyridin-4-yl, 2-cyanopyridin-3-yl, 2-fluoropyridin-3-yl, 2-methoxypyridin-4-yl, 2-methylpyridin-3-yl, 5-(trifluoromethyl)pyridin-3-yl, 5-chloropyridin-3-yl, 5-cyanopyridin-3-yl, 5-cyclopropylpyridin-3-yl, 5-methylpyridin-3-yl, 5-pyridazin-4-yl, 6-(trifluoromethyl)pyridin-3-yl, 6-chloropyridin-2-yl, 6-cyanopyridin-3-yl, 6-cyclopropylpyridin-2-yl, 6-methoxypyridin-3-yl, 6-methyl-2-pyridyl, 6-methylpyridazin-3-yl, 6-methylpyridin-2-yl, 6-methylpyridin-3-yl, pyridin-3-yl, pyridin-4-yl, or phenyl; or

H. 3-cyclopropyl-2-fluorophenyl, 3-(trifluoromethyl)phenyl, 3-chloro-2-fluorophenyl, 3-chlorophenyl, 5-cyanopyridin-3-yl, 3-methylphenyl, phenyl, 3-cyclopropylphenyl, 3-(difluoromethyl)phenyl, 3-(difluoromethoxy)phenyl, 3-(trifluoromethyl)-2-fluorophenyl, 3-methoxyphenyl, or 2,3-difluorophenyl; or

I. phenyl, 3-(trifluoromethyl)phenyl, 3-methoxyphenyl, 3-cyclopropylphenyl, 3-cyclopropyl-2-fluorophenyl, or 5-cyanopyridin-3-yl; or

J. 3-cyclopropylphenyl.

30

For example, in an embodiment of each aspect of the invention, R¹ is:

A. phenyl unsubstituted or substituted with a 1 or 2 substituents, each independently selected from hydroxyl, halogen, mercapto, amino, nitro, cyano, methyl, ethyl, propyl, *iso*-propyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl, methoxy, ethoxy, allyloxy, prop-2-yloxy, prop-1-yloxy, *iso*-propoxy, *tert*-butoxy, propynoxy, NHMe, N(Me)₂, methylsulfanyl, methylsulfonyl, difluoromethoxy, trifluoromethoxy, cyclopropyl, cyclobutyl, and cyclopropyloxy; or

B. phenyl unsubstituted or substituted with 1 or 2 substituents, each independently selected from hydroxyl, halogen, cyano, methyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl methoxy, ethoxy, allyloxy, prop-2-yloxy, prop-1-yloxy, difluoromethoxy, trifluoromethoxy, and cyclopropyl; or

40 C. phenyl unsubstituted or substituted with 1 or 2 substituents. each independently selected selected from chloro, fluoro, cyano, methyl, methoxy, difluoromethoxy, and cyclopropyl; or

D. phenyl unsubstituted or substituted with 1 or 2 substituents, each independently selected selected from fluoro, chloro, cyano, methyl, and cyclopropyl; or

E. phenyl unsubstituted or substituted with a single substituent selected from fluoro, chloro, methyl, and cyclopropyl.

5

Also for example, in an embodiment of each aspect of the invention, R¹ is:

A. a 5- or 6-membered monocyclic heteroaryl ring comprising 1, 2 or 3 heteroatoms which may be the same or different, independently selected from N, O and S, with the proviso that no more than one is O or S; wherein said heteroaryl ring is unsubstituted or substituted with 1 or 2 substituents, each independently
10 selected from hydroxyl, halogen, mercapto, amino, nitro, cyano, methyl, ethyl, propyl, *iso*-propyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl, methoxy, ethoxy, allyloxy, prop-2-ynoxy, prop-1-ynoxy, *iso*-propoxy, *tert*-butoxy, propynoxy, NHMe, N(Me)₂, methylsulfanyl, methylsulfonyl, difluoromethoxy, trifluoromethoxy, and cyclopropyl; or

B. pyridine, pyrimidine, or pyridazine, wherein said pyridine, pyrimidine, or pyridazine, is unsubstituted
15 or substituted with 1 or 2 substituents, independently selected from hydroxyl, halogen, mercapto, amino, cyano, methyl, ethyl, propyl, *iso*-propyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl, methoxy, ethoxy, propoxy, *iso*-propoxy, *tert*-butoxy, allyloxy, prop-2-ynoxy, prop-1-ynoxy, methylsulfanyl, methylsulfonyl, difluoromethoxy, trifluoromethoxy, and cyclopropyl; or

C. pyridine substituted with 1 or 2 substituents, each independently selected from hydroxyl, halogen,
20 cyano, methyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl, methoxy, ethoxy, allyloxy, prop-2-ynoxy, prop-1-ynoxy, difluoromethoxy, and cyclopropyl; or

D. pyridine substituted with a single substituent selected from chloro, fluoro, cyano, methyl, methoxy, difluoromethoxy, and cyclopropyl; or

E. pyridine substituted with a single substituent selected from chloro, cyano, methyl, and cyclopropyl.

25

In an embodiment of each aspect of the invention, R² is:

A. hydrogen, hydroxyl, halogen, mercapto, amino, cyano, C₁-C₄-alkyl, C₂-C₄-alkenyl, C₂-C₄-alkynyl, C₁-C₄-alkoxy, C₁-C₄-fluoroalkyl, C₁-C₄-fluoroalkoxy, or C₃-C₄-cycloalkyl; or

B. hydrogen, hydroxyl, halogen, amino, cyano, C₁-C₄-alkyl, C₁-C₄-alkoxy, C₃-C₄-cycloalkyl, C₂-C₄-alkenyl, C₁-C₄-alkylethynyl, C₃-C₄-cycloalkylethynyl, or C₂-C₄-alkenyloxy; or

C. hydrogen, hydroxy, chloro, methyl, ethyl, isopropyl, methoxy, cyclopropyl, isoprenyl, 2-cyclopropylethynyl, 2-methylallyloxy, or isopropoxy; or

D. hydrogen, hydroxyl, halogen, mercapto, amino, cyano, methyl, ethyl, propyl, *iso*-propyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl, methoxy, ethoxy, allyloxy, prop-2-ynoxy, prop-1-ynoxy, *iso*-propoxy, propynoxy, NHMe, N(Me)₂, methylsulfanyl, methylsulfonyl, difluoromethoxy, trifluoromethoxy, cyclopropyl, cyclobutyl, or cyclopropyloxy; or

E. hydrogen, hydroxyl, halogen, amino, cyano, methyl, ethyl, propyl, *iso*-propyl, vinyl, ethynyl, methoxy, ethoxy, difluoromethoxy, or cyclopropyl; or

F. hydrogen, hydroxyl, fluoro, chloro, bromo, cyano, methyl, ethyl, propyl, *iso*-propyl, or cyclopropyl; or

G. hydrogen, hydroxy, cyano, mercaptyl, fluoro, chloro, methyl, or ethyl; or

H. hydrogen, hydroxyl, chloro, cyano, methyl, ethyl, methoxy, or cyclopropyl; or

40

I. hydrogen, methyl, ethyl, or cyclopropyl.

In an embodiment of each aspect of the invention, G is G-1:

- 5 A. phenyl or phenoxy unsubstituted or substituted with 1 or 2 substituents each independently selected from hydroxyl, halogen, mercapto, amino, cyano, methyl, ethyl, propyl, *iso*-propyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl, methoxy, ethoxy, propoxy, *iso*-propoxy, *tert*-butoxy, allyloxy, prop-2-ynoxy, prop-1-ynoxy, methylsulfanyl, methylsulfonyl, difluoromethoxy, trifluoromethoxy, and cyclopropyl; or
- 10 B. phenyl or phenoxy unsubstituted or substituted with 1 or 2 substituents, each independently selected from hydroxyl, halogen, cyano, methyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl, methoxy, ethoxy, allyloxy, prop-2-ynoxy, prop-1-ynoxy, difluoromethoxy, trifluoromethoxy, and cyclopropyl; or
- C. phenyl unsubstituted or substituted with 1, 2 or 3 substituents, for instance 2 or 3 substituents, each independently selected from chloro, fluoro, bromo, methyl, methoxy, and cyclopropyl; or
- D. phenyl substituted with 1 or 2 substituents, for instance one substituent, each independently selected from chloro and methyl; or
- 15 E. 2,4-dichlorophenyl.

In an embodiment of each aspect of the invention, G is G-2:

- 20 A. pyridine, pyrimidine, pyridazine, pyridine-oxy, pyrimidine-oxy, pyridazine-oxy, wherein said pyridine, pyrimidine, or pyridazine ring is unsubstituted or substituted with 1 or 2 substituents, each independently selected from hydroxyl, halogen, mercapto, amino, cyano, methyl, ethyl, propyl, *iso*-propyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl, methoxy, ethoxy, propoxy, *iso*-propoxy, *tert*-butoxy, allyloxy, prop-2-ynoxy, prop-1-ynoxy, methylsulfanyl, methylsulfonyl, difluoromethoxy, trifluoromethoxy, and cyclopropyl; or
- 25 B. pyridine unsubstituted or substituted with 1 or 2 substituents, each independently selected from hydroxyl, halogen, cyano, methyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl methoxy, ethoxy, allyloxy, prop-2-ynoxy, prop-1-ynoxy, difluoromethoxy, and cyclopropyl; or
- C. pyrimidine, or pyridazine, wherein said pyrimidine or pyridazine is unsubstituted or substituted with 1 or 2 substituents, each independently selected from hydroxyl, halogen, cyano, methyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl methoxy, ethoxy, allyloxy, prop-2-ynoxy, prop-1-ynoxy, difluoromethoxy, and cyclopropyl; or
- 30 D. pyridine unsubstituted or substituted with 1 or 2 substituents, each independently selected from chloro, fluoro, cyano, methyl, and methoxy; or
- E. pyridine or pyridine-oxy, unsubstituted or substituted with a single substituent selected from chloro and methyl.

35 In an embodiment of each aspect of the invention, G is G-3:

- A. chroman-4-yl, isochroman-4-yl, 4H-chromen-4-yl, 2,3-dihydrobenzofuran-2-yl, 2,3-dihydrobenzofuran-3-yl, 1,3-benzodioxol-5-yl, benzothiazol-2-yl, benzothiazol-5-yl, benzothiazol-6-yl, benzooxazol-2-yl, benzooxazol-5-yl, benzooxazol-6-yl, benzofuran-2-yl, benzofuran-3-yl, benzofuran-5-yl, benzofuran-6-yl, benzothiophen-2-yl, benzothiophen-3-yl, benzothiophen-5-yl, or benzothiophen-6-yl

unsubstituted or substituted with 1 or 2 substituents, for instance a single substituent, each independently selected from chloro, fluoro, cyano, methyl, and methoxy; or

B. chroman-4-yl, isochroman-4-yl, 4H-chromen-4-yl, 2,3-dihydrobenzofuran-2-yl, 2,3-dihydrobenzofuran-3-yl, 1,3-benzodioxol-5-yl, benzothiazol-2-yl, benzothiazol-5-yl, benzothiazol-6-yl, 5 benzooxazol-2-yl, benzofuran-2-yl, benzofuran-3-yl, benzothiophen-2-yl, or benzothiophen-3-yl, unsubstituted or substituted with a single substituent selected from chloro, fluoro, cyano, methyl, and methoxy

C. chroman-4-yl, isochroman-4-yl, 4H-chromen-4-yl, 2,3-dihydrobenzofuran-2-yl, or 2,3-dihydrobenzofuran-3-yl unsubstituted or substituted with a single substituent selected from chloro, fluoro, 10 cyano, methyl, and methoxy; or

D. 1,3-benzodioxol-5-yl, benzothiazol-2-yl, benzothiazol-5-yl, benzothiazol-6-yl, benzooxazol-2-yl, benzofuran-2-yl, benzofuran-3-yl, benzothiophen-2-yl, or benzothiophen-3-yl.

In an embodiment of each aspect of the invention, G is G-4:

15 A. naphthalen-2-yl, tetralin-1-yl, tetralin-2-yl, tetralin-6-yl, indan-1-yl, indan-2-yl, or indan-5-yl unsubstituted or substituted with 1 or 2 substituents, for instance a single substituent, each independently selected from chloro, fluoro, cyano, methyl, and methoxy; or

B. tetralin-1-yl, tetralin-2-yl, indan-1-yl, or indan-2-yl, or unsubstituted or substituted with one or two substituents, for instance a single substituent, each independently selected from chloro, fluoro, cyano, 20 methyl, and methoxy.

For instance, in each aspect of the invention, G is

A. 2,4-dimethylphenyl, 2,4-dichlorophenyl, 4-bromo-2-methylphenyl, 4-bromo-2-chlorophenyl, 2,6-dichloro-3-pyridyl, 4,6-dichloro-3-pyridyl, 3,5-dichloro-2-pyridyl, 3,4-dimethylphenyl, 2-chloro-4-methylphenyl, 2-methyl-4-bromophenyl, 2-methyl-4-chlorophenyl, or 2,4-difluorophenyl; or 25

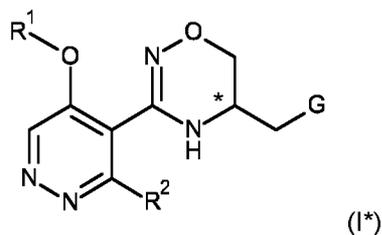
B. 2,4-dimethylphenyl, 2,4-dichlorophenyl, 4-bromo-2-methylphenyl, 4-bromo-2-chlorophenyl, 2,6-dichloro-3-pyridyl, 4,6-dichloro-3-pyridyl, 3,5-dichloro-2-pyridyl, 3,4-dimethylphenyl, 2-chloro-4-methylphenyl, 2-methyl-4-bromophenyl, or 2-methyl-4-chlorophenyl; or

C. 2,4-dimethylphenyl, 2,4-dichlorophenyl, 4-bromo-2-methylphenyl, 4-bromo-2-chlorophenyl, 3,4-dimethylphenyl, 2-chloro-4-methylphenyl, 2-methyl-4-bromophenyl, 2-methyl-4-chlorophenyl, or 2,4-difluorophenyl; or 30

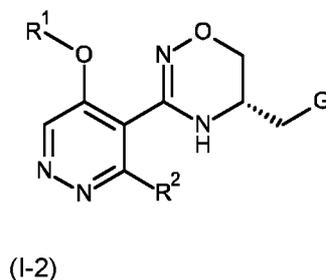
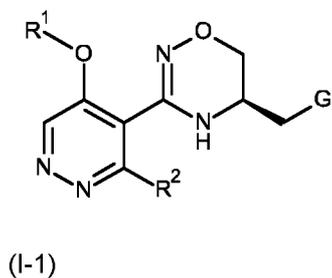
D. 2,6-dichloro-3-pyridyl, 4,6-dichloro-3-pyridyl, or 3,5-dichloro-2-pyridyl; or

E. 2,4-dichlorophenyl.

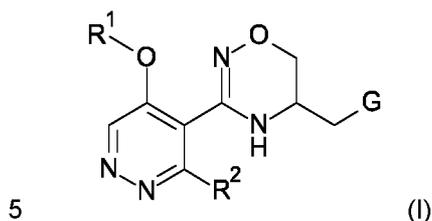
35 The compound of the formula (I) may comprise a stereogenic centre, shown with an asterisk in formula (I*), wherein R^1 , R^2 and G are as defined in the first aspect, each with the corresponding embodiments as described above.



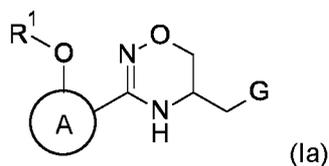
The compounds of the present invention may be enantiomers of the compound of Formula (I) as represented by formula (I-1) or formula (I-2):



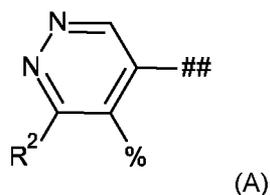
The compounds of formula (I)



can be prepared by those skilled in the art as shown in the following schemes 1 to 32, wherein G, R¹ and R² are as defined above. Compounds of formula (I) may be depicted with formula (Ia) below:



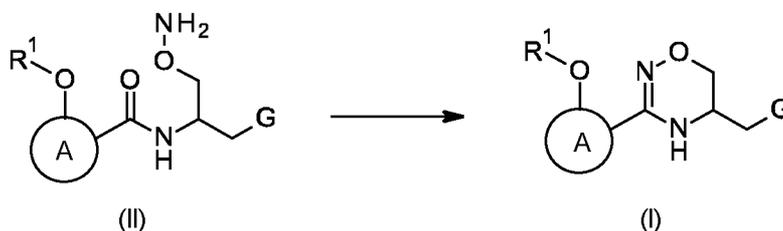
10 wherein G and R¹ are as defined above for a compound of formula (I), and wherein (A) represents the



15 wherein ## marks the bond to the -O-R¹ moiety, % marks the bond to the -5,6-dihydro-4H-1,2,4-oxadiazin-3-yl moiety, and R² is as defined above for a compound of formula (I), unless otherwise stated. The same definition of (A) applies to certain intermediate compounds shown in Schemes 1 to 32, in particular to compounds of formula (I), (II), (III), (IV), (VIII), (IX), (X), (XI), (XIII), (XIV), (XV), (XVI), (XVII), (XVIII), (XIX), (XX), (XXI), (XXII), (XXIV), (XXV), (XXVI), (XXVII), (XXVIII), (XXIX), (XXX), (XXXI), (XXXII), (XXXIII), and

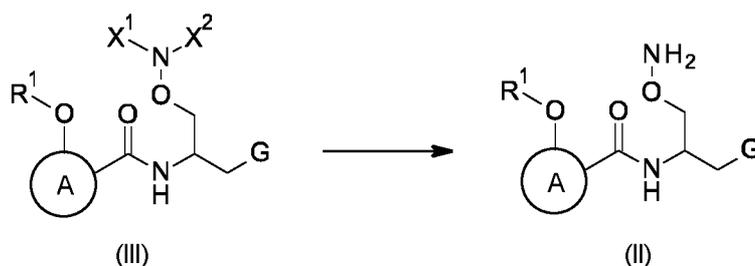
(XXXIV). Certain stereogenic centers have been left unspecified for the clarity and are not intended to limit the teaching of the schemes in any way.

As shown below in Scheme 1, compounds of formula (I), wherein G and R¹ are as defined for compounds of formula (I), can be obtained by intramolecular cyclization of compounds of formula (II), wherein G and R¹ are as defined for compounds of formula (I), using a chlorinating agent, for example by using POCl₃, PCl₅, (COCl)₂ or SOCl₂ in the optional presence of dimethylformamide, preferably at temperatures between 0°C and 80°C, more preferable between 25°C and 60°C, in an appropriate solvent or mixture of solvent (e.g. dichloromethane, dimethylformamide, 2-methyltetrahydrofuran, tetrahydrofuran, diethyl ether, toluene, ethyl acetate). For examples, see Heterocycles **2016**, 92, 2166-2200 or CN114437077.



Scheme 1

As shown below in Scheme 2, compounds of formula (II), wherein G and R¹ are as defined for compounds of formula (I), may be obtained by amine deprotection of compounds of formula (III), wherein G and R¹ are as defined for compounds of formula (I), and wherein X¹ is H and X² is a protective group, or X¹ and X² are identical or different protective groups, or X¹ and X² form a protective group together with the nitrogen they are attached to. Examples of protective groups include, for instance, *tert*-butyloxycarbonyl, benzylcarbonyl, 9-fluorenylmethylcarbonyl, trifluoroacetyl, benzyl, triphenylmethyl, benzyldienyl, *p*-toluenesulfonyl, phthalimide, or succinimide. Protective groups can be removed using standard techniques; see *Greene's Protective Groups in Organic Synthesis*, 4th Ed., Wiley-Interscience.

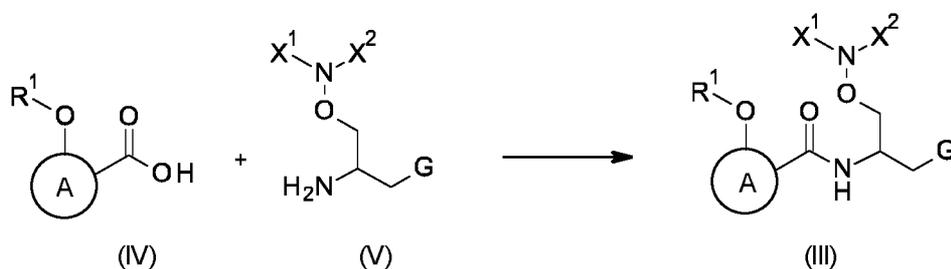


Scheme 2

As shown below in Scheme 3, compounds of formula (III), wherein G and R¹ are as defined for compounds of formula (I), and wherein X¹ and X² are as defined for compounds of formula (III) in Scheme 2, may be obtained by amide coupling transformation with compounds of formula (IV) wherein G is as defined for compounds of formula (I), and amine compounds of formula (V), wherein is as defined for compounds of formula (I), and wherein X¹ and X² are as defined for compounds of formula (III) in Scheme 2, by activating the carboxylic acid function of the compounds of formula (IV), a process that usually takes place by converting the -OH of the carboxylic acid into a good leaving group, such as a chloride group, for example by using (COCl)₂ or SOCl₂, prior to treatment with the compounds of formula (IV), preferably in a suitable

solvent (e.g., N-methylpyrrolidone, acetonitrile, dimethylacetamide, dichloromethane or tetrahydrofuran), preferably at temperatures between 25 °C and 60 °C, and optionally in the presence of a base, such as triethylamine or *N,N*-diisopropylethylamine.

Alternatively, compounds of formula (III) may be obtained under conditions described in the literature for an amide coupling, using an amidation coupling reagent, such as 1-propanephosphonic acid cyclic anhydride (T3P), in a suitable solvent (e.g., acetonitrile), optionally in the presence of a base (e.g., triethylamine or *N,N*-diisopropylethylamine). For examples, see *Chem. Soc. Rev.* **2009**, 38, 606 and *Chem. Soc. Rev.* **2011**, 40, 5084.



Scheme 3

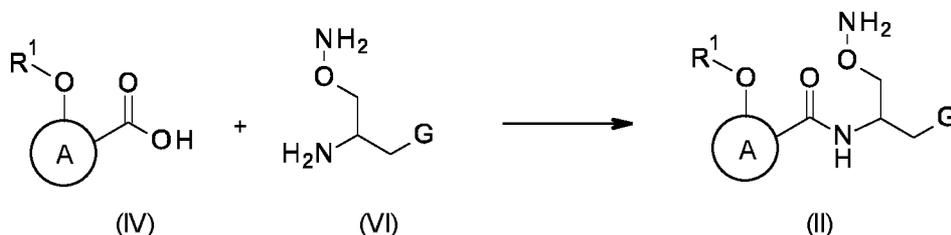
10

As shown below in Scheme 4, compounds of formula (II), wherein G and R¹ are as defined for compounds of formula (I), may also be obtained by amide coupling transformation with compounds of formula (IV), wherein R¹ is as defined for compounds of formula (I), and amine compounds of formula (VI), wherein G is as defined for compounds of formula (I), by activating the carboxylic acid function of the compounds of formula (IV), a process that usually takes place by converting the -OH of the carboxylic acid into a good leaving group, such as a chloride group, for example by using (COCl)₂ or SOCl₂, prior to treatment with the compounds of formula (IV), preferably in a suitable solvent (e.g., N-methylpyrrolidone, acetonitrile, dimethylacetamide, dichloromethane, or tetrahydrofuran), preferably at temperatures between 25 °C and 60 °C, and optionally in the presence of a base, such as triethylamine or *N,N*-diisopropylethylamine.

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Alternatively, compounds of formula (II) may be obtained under conditions described in the literature for an amide coupling, using an amidation coupling reagent, such as 1-propanephosphonic acid cyclic anhydride (T3P), in suitable solvent (e.g., acetonitrile), optionally in the presence of a base (e.g., triethylamine or *N,N*-diisopropylethylamine). For examples, see *Chem. Soc. Rev.* **2009**, 38, 606 and *Chem. Soc. Rev.* **2011**, 40, 5084.

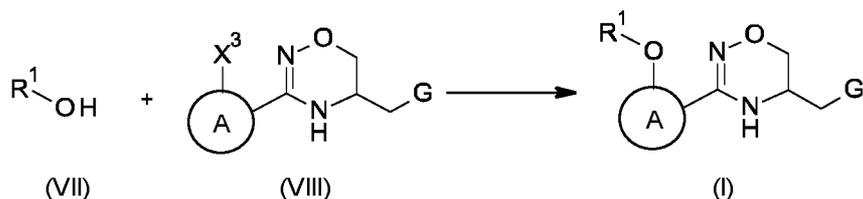


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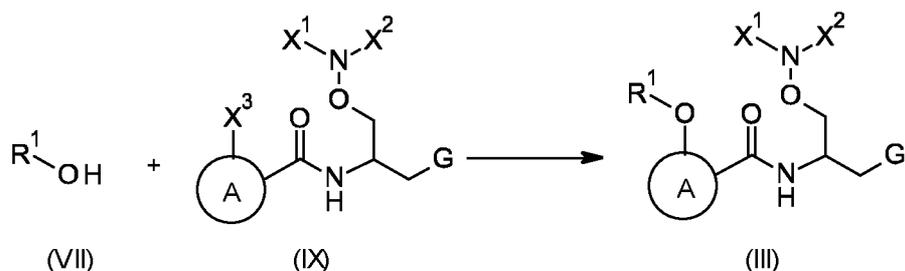
Scheme 4

As shown below in Schemes 5a, 5b and 5c respectively, compounds of formula (I), (III) or (II), as defined in Schemes 1, 2, 3 and 4 above, may also be prepared by reacting nucleophilic compounds of formula (VII), wherein R¹ is as defined for compounds of formula (I), with electrophilic compounds of formula (VIII), (IX)

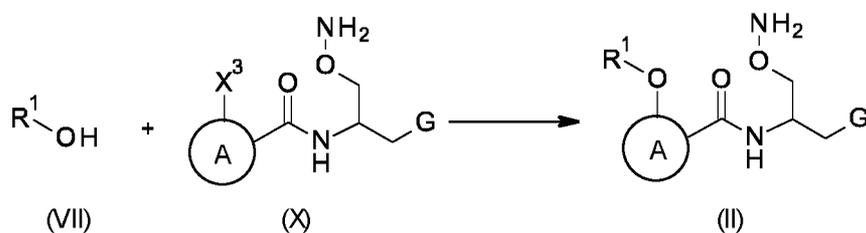
or (X) respectively, wherein G is as defined for compounds of formula (I), wherein X¹ and X² are as defined for compounds of formula (III) in Scheme 2, and X³ is a suitable leaving group, such as fluoro, chloro, bromo, iodo, BF₃K, B(OH)₂, or B(pinacol), in the presence of a base (e.g., KO-*t*-Bu, K₃PO₄, K₂CO₃, triethylamine, or Cs₂CO₃), in a suitable solvent (e.g., *N*-methylpyrrolidone, dimethylacetamide, acetonitrile, tetrahydrofuran, 2-methyl tetrahydrofuran, sulfolane, or dimethylsulfoxide) at temperatures between 10 °C and 90 °C, and preferably using a metal catalyst complex (e.g., Cu or Pd). For related examples, see *Eur. J. Org. Chem.* **2011**, *18*, 3353; *J. Org. Chem.* **2009**, *74*, 7951; *Tetrahedron Lett.*, **2012**, *53*, 5318. Compounds of formula (VII) are either known or commercially available.



Scheme 5a

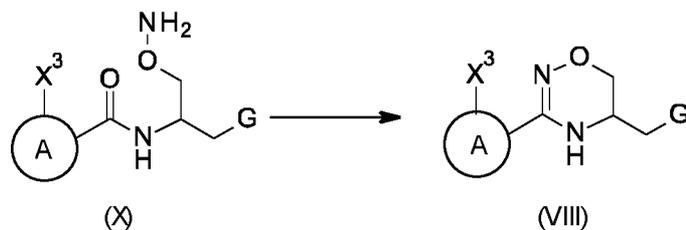


Scheme 5b



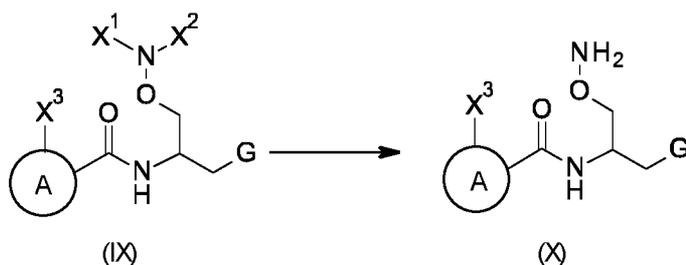
Scheme 5c

As shown below in Scheme 6, compounds of formula (VIII) wherein G is as defined for compounds of formula (I), and X³ is a suitable leaving group, such as fluoro, chloro, bromo, iodo, BF₃K, B(OH)₂, or B(pinacol), can be obtained by intramolecular cyclization of compounds of formula (X), wherein G is as defined for compounds of formula (I), and X³ is as defined for compound of formula (VIII), using a chlorinating agent, for example POCl₃, PCl₅, (COCl)₂, or SOCl₂, optionally in the presence of dimethylformamide, preferably at temperatures between 0 °C and 80 °C, more preferably between 25 °C and 60 °C, in an appropriate solvent or mixture of solvents (e.g. dichloromethane, dimethylformamide, 2-methyltetrahydrofuran, tetrahydrofuran, diethyl ether, toluene, ethyl acetate). For examples, see *Chem. Soc. Rev.* **2009**, *38*, 606 and *Chem. Soc. Rev.* **2011**, *40*, 5084.



Scheme 6

As shown below in Scheme 7, compounds of formula (X), wherein G is as defined for compounds of formula (I), and X³ is a suitable leaving group, such as fluoro, chloro, bromo, iodo, BF₃K, B(OH)₂, or B(pinacol), may be obtained by amine deprotection of compounds of formula (IX), wherein G is as defined for compounds of formula (I), and X³ is as defined for compound of formula (X), and wherein X¹ and X² are as defined for compounds of formula (III) in connection with Scheme 2. Protective groups can be removed using standard techniques; see *Greene's Protective Groups in Organic Synthesis*, 4th Ed., Wiley-Interscience.

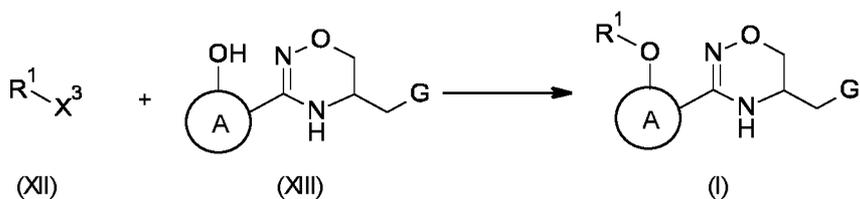


Scheme 7

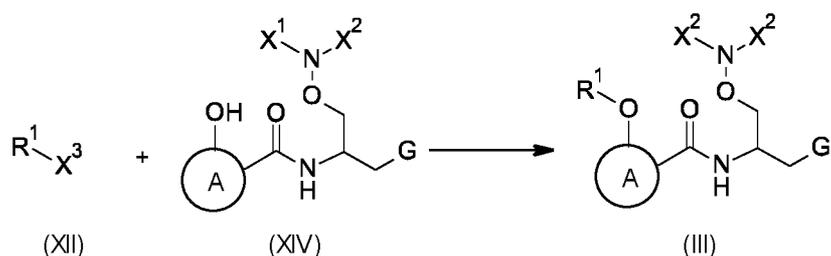
As shown below in Scheme 8, compounds of formula (IX), wherein G is as defined for compounds of formula (I), X¹ and X² are as defined for compounds of formula (III) in connection with Scheme 2, and X³ is a suitable leaving group such as fluoro, chloro, bromo, iodo, BF₃K, B(OH)₂ or B(pinacol), may be prepared by an amide coupling transformation with compounds of formula (XI), wherein X³ is as defined for compounds of formula (IX), and amine compounds of formula (V), wherein G is as defined for compounds of formula (I), X¹ and X² are as defined for compounds of formula (III) in connection with Scheme 2, by activating the carboxylic acid function of the compounds of formula (XI), a process that usually takes place by converting the -OH of the carboxylic acid into a good leaving group, such as a chloride group, for example by using (COCl)₂ or SOCl₂, prior to treatment with the compounds of formula (V), preferably in a suitable solvent (e.g., N-methylpyrrolidone dimethylacetamide, dichloromethane or tetrahydrofuran), preferably at temperatures between 25 °C and 60 °C, and optionally in the presence of a base such as triethylamine or *N,N*-diisopropylethylamine.

Alternatively, compounds of formula (IX) may be obtained under conditions described in the literature for an amide coupling, using an amidation coupling reagent such as 1-propanephosphonic acid cyclic anhydride (T3P) in suitable solvent (e.g., acetonitrile), optionally in the presence of a base (e.g., triethylamine or *N,N*-diisopropylethylamine). For examples, see: *Chem. Soc. Rev.* **2009**, *38*, 606 and *Chem. Soc. Rev.* **2011**, *40*, 5084.

Compounds of formula (V) are either known, commercially available or readily available to experts in the field.

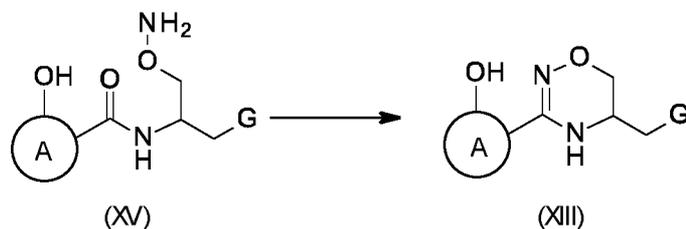


Scheme 10a



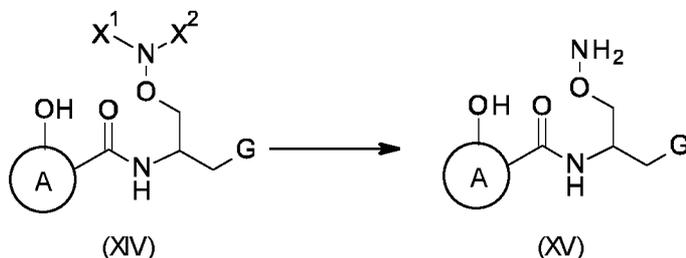
Scheme 10b

- 5 As shown below in Scheme 11, compounds of formula (XIII), wherein G is as defined for compounds of formula (I), can be obtained by intramolecular cyclization of compounds of formula (XV), wherein G is as defined for compounds of formula (I), using a chlorinating agent, for example by using POCl₃, PCl₅, (COCl)₂ or SOCl₂, optionally in the presence of dimethylformamide, preferably at temperatures between 0 °C and 80 °C, more preferably between 25 °C and 60 °C, in an appropriate solvent or mixture of solvents (e.g. dichloromethane, dimethylformamide, 2-methyltetrahydrofuran, tetrahydrofuran, diethyl ether, toluene, ethyl acetate). For examples, see *Chem. Soc. Rev.* **2009**, 38, 606 and *Chem. Soc. Rev.* **2011**, 40, 5084.
- 10



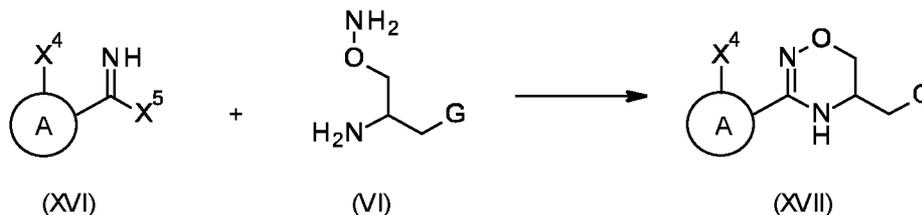
Scheme 11

- 15 As shown below in Scheme 12, compounds of formula (XV) wherein G is as defined for compounds of formula (I), may be obtained by amine deprotection of compounds of formula (XIV), wherein G is as defined for compounds of formula (I), and X¹ and X² are as defined for compounds of formula (III) in Scheme 2. Protective groups can be removed using standard techniques, see *Greene's Protective Groups in Organic Synthesis*, 4th Ed., Wiley-Interscience.



Scheme 12

As shown below in Scheme 13, compounds of formula (XVII), wherein G is as defined for compounds of formula (I), and X⁴ is OH or OR¹, with R¹ as defined for compounds of formula (I), may be obtained by coupling of compounds of formula (VI), wherein G is as defined for compounds of formula (I), with compounds of formula (XVI), wherein X⁴ is OH or OR¹, with R¹ as defined for compounds of formula (I), and X⁵ is C₁-C₄-alkoxy, such as methoxy or ethoxy. The subsequent cyclization may be achieved using an acid, typically acetic acid at temperatures between 20°C and 120°C, preferably between 80°C and 120°C. For related examples, see: *Heterocycles* **2016**, 92, 2166 and WO 2017/031325. Compounds of formula (VI) are known or can be readily accessed by experts in the field.



Scheme 13

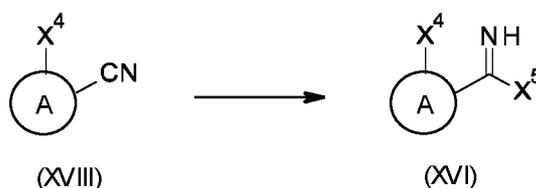
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As shown below in Scheme 14, compounds of formula (XVI), wherein X⁴ is OH or OR¹, with R¹ as defined for compounds of formula (I), and X⁵ is C₁-C₄-alkoxy, such as methoxy or ethoxy, may be obtained by reaction of a compound of formula (XVIII) using an alkoxide, typically in solution in the corresponding alcohol (e.g. sodium methoxide, sodium methoxide or potassium *tert*-butoxide) or an excess of an alcohol, such as methanol or ethanol, and an alkali metal at temperatures between -30°C to 20°C.

15

Alternatively, compounds of formula (XVI) may be obtained by hydrolysing compounds of formula (XVIII) in the presence of an acid, preferably but not limited to hydrochloric acid, in a suitable solvent or mixture of solvents, such as methanol, ethanol, dichloromethane, or 1,4-dioxane at temperatures between -30°C to 40°C. For related examples, see: WO2012178015, JP2014037370 or *Angew. Chem. Int. Ed.* **2020**, 59, 23306.

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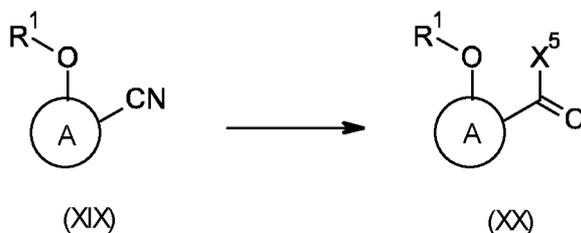


Scheme 14

As shown below in Scheme 15, compounds of formula (XX), wherein R¹ is as defined for compounds of formula (I), and X⁵ is C₁-C₄-alkoxy, such as methoxy or ethoxy, may be prepared by reaction of a compound of formula (XIX), wherein R¹ is as defined for compounds of formula (I), in aqueous solvent or mixture of solvents, such as *iso*-propanol or ethanol, optionally in an alkaline media, at temperatures between 60°C and 110°C. For related examples, see: *J. Med. Chem.* **2012**, 55, 10118.

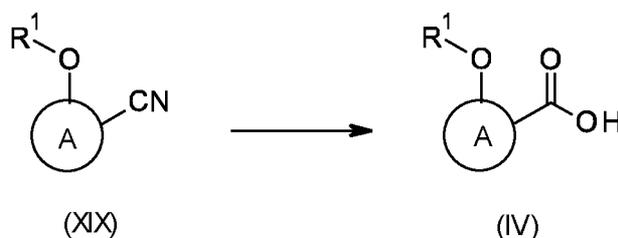
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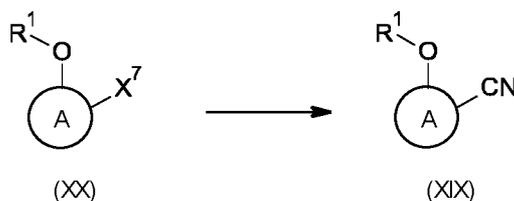
Scheme 15

As shown below in Scheme 15a, compounds of formula (IV), wherein R¹ is as defined for compounds of formula (I), may be prepared by hydrolysis of compounds of formula (XIX), wherein R¹ is as defined for compounds of formula (I), in an aqueous solvent mixture of solvents, such as tetrahydrofuran, optionally in an alkaline media, at temperatures between 60°C and 110°C. For related examples, see: *J. Med. Chem.* **2012**, *55*, 10118.



Scheme 15a

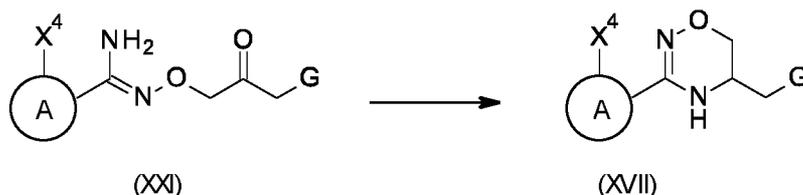
Compounds of formula (XIX), wherein R¹ is as defined for compounds of formula (I), are known or, as shown below in Scheme 16, may be obtained from compounds of formula (XX), wherein R¹ is as defined for compounds of formula (I), and X⁷ is chloro, bromo, iodo, or O-trifluoromethanesulfonyl, at temperatures between 50°C and 120°C, preferably between 80°C and 110°C, using a metal source, such as XPhos Pd G1, in the presence of a cyanide source, such as potassium ferrocyanide, copper cyanide, zinc cyanide, or potassium cyanide, and of a base (e.g., KOAc), in a suitable solvent or mixture of solvents (e.g., dioxane, water, toluene, tetrahydrofuran, 2-methyl-tetrahydrofuran, xylene). For related examples, see: *J. Org. Chem.* **2018**, *83*, 4922 and *Org. Lett.* **2006**, *8*, 1189. Compounds of formula (XX) are either known or can be readily prepared by experts in the field.



Scheme 16

As shown below in Scheme 17, compounds of formula (XVII), wherein G is as defined for compounds of formula (I), X⁴ is OH or OR¹, with R¹ as defined for compounds of formula (I), may be obtained by cyclization of compounds of formula (XXI), wherein G is as defined for compounds of formula (I), and X⁴ is as defined for compounds of formula (XVII), using an acid, e.g. acetic acid, either neat or in an appropriate solvent, such as methanol or ethanol, at temperatures between 20°C to 75°C, followed by a reduction in the

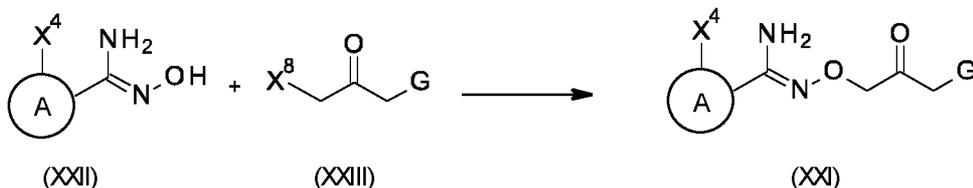
presence of a hydride (e.g. sodium cyanoborohydride, sodium borohydride, sodium triacetoxyborohydride or lithium borohydride) in a solvent or mixture of solvents, such as tetrahydrofuran, toluene, or methanol. For related example, see: WO2016201168.



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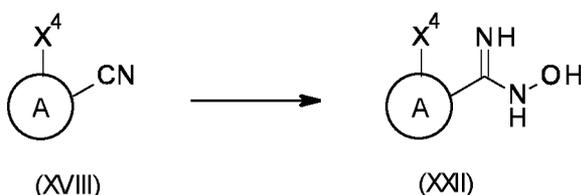
Scheme 17

As shown below in Scheme 18, compounds of formula (XXI), wherein G is as defined for compounds of formula (I), and X⁴ is OH or OR¹, with R¹ as defined for compounds of formula (I), can be obtained by reaction of a compound of formula (XXIII), wherein G is as defined for compounds of formula (I), and X⁸ is a leaving group, such as chloro, bromo, iodo, mesyl, tosyl, or O-trifluoromethanesulfonyl, with compounds of formula (XXII), wherein X⁴ is OH or OR¹, with R¹ as defined for compounds of formula (I), in the optional presence of a base (e.g. pyridine, triethylamine, potassium carbonate, sodium carbonate) in a suitable solvent or mixture of solvents, such as benzene, toluene, tetrahydrofuran, chloroform, acetonitrile, or 2-methyl-tetrahydrofuran, at temperatures between 0°C and 110°C, more preferably between 20°C and 80°C. For related examples, see: *J. Med. Chem.* **2011**, *54*, 8407; WO2002051811 or WO2010078867. Compounds of formula (XXIII) are either known or readily available to experts in the field.



Scheme 18

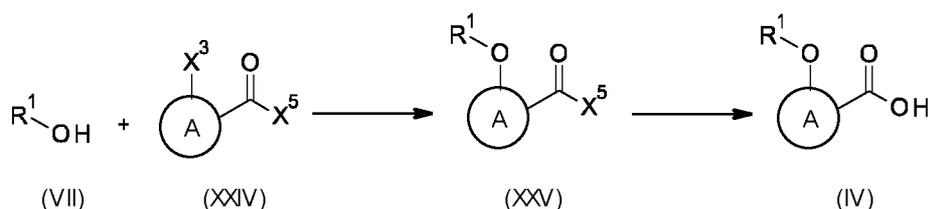
As shown below in Scheme 19, compounds of formula (XXII), wherein X⁴ is OH or OR¹, with R¹ as defined for compounds of formula (I), may be prepared by reaction of a compound of formula (XVIII) using hydroxyamine or an hydroxyamine salt, such as hydrochloride, in the optional presence of a base (e.g. potassium or sodium carbonate) in a suitable solvent or mixture of solvents, for example methanol, ethanol, 2-methyl-2-butanol, water, or 1-butyl-3-methylimidazolium acetate. For related examples, see: *Org. Biomol. Chem.* **2014**, *12*, 8036; WO2016143655 or WO2019224743. Compounds of formula (XVIII) are either known, commercially available or easily obtained by experts in the field. Compounds of formula (XXII) may also be known.



Scheme 19

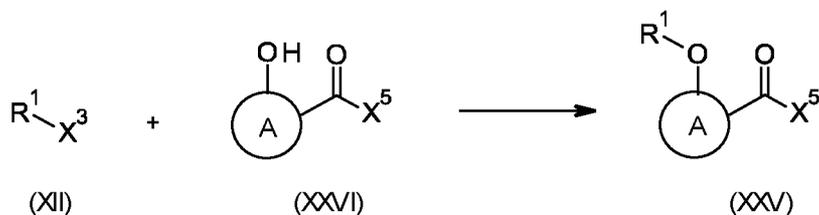
As shown below in Scheme 20, compounds of formula (XXV), wherein R¹ is as defined for compounds of formula (I), and X⁵ is C₁-C₄-alkoxy, for instance methoxy or ethoxy, may be prepared by reacting nucleophilic compounds of formula (VII), wherein R¹ is as defined for compounds of formula (I), with electrophilic compounds of formula (XXIV), wherein X⁵ is C₁-C₄-alkoxy, such as methoxy or ethoxy, and X³ is a suitable leaving group, such as fluoro, chloro, bromo, iodo, BF₃K, B(OH)₂, or B(pinacol), in the presence of a base (e.g., KO-*t*-Bu, K₃PO₄, K₂CO₃, triethylamine, or Cs₂CO₃) in a suitable solvent or mixture of solvents (e.g., N-methylpyrrolidone, dimethylacetamide, acetonitrile, tetrahydrofuran, 2-methyl tetrahydrofuran, sulfolane, or dimethylsulfoxide), at temperatures between 20°C and 110°C, and preferably using a metal catalyst complex (e.g., Cu or Pd). For related examples, see *Eur. J. Org. Chem.* **2011**, *18*, 3353; *J. Org. Chem.* **2009**, *74*, 7951; *Tetrahedron Lett.* **2012**, *53*, 5318; WO2008110313 and WO2012136604. Compounds of formula (VII) are either known or commercially available.

Compounds of formula (IV), wherein R¹ is as defined for compounds of formula (I), can then be obtained by ester hydrolysis of compounds of formula (XXV), wherein X⁵ is C₁-C₄-alkoxy, for instance methoxy or ethoxy, using an alkali hydroxide, such as lithium, sodium, potassium, or barium hydroxide, in a suitable solvent or mixture of solvents (e.g. methanol, acetonitrile, ethanol, water, tetrahydrofuran, or 2-methyl-tetrahydrofuran), at temperatures between 0°C and 80°C. Alternatively, the ester can be cleaved in acidic conditions using, for instance, hydrochloric acid. For related examples, see: WO2021086879 or *Org. Biomol. Chem.* **2015**, *13*, 7928.



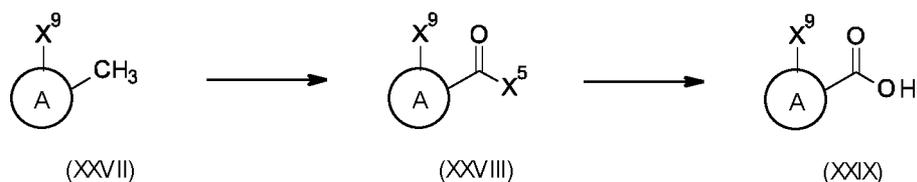
Scheme 20

As shown below in Scheme 21, compounds of formula (XXV), wherein R¹ is as defined for compounds of formula (I), and X⁵ is C₁-C₄-alkoxy, such as methoxy or ethoxy, may also be prepared by reacting nucleophilic compounds of formula (XXVI), wherein X⁵ is C₁-C₄-alkoxy, such as methoxy or ethoxy, with electrophilic compounds of formula (XII), wherein R¹ is as defined for compounds of formula (I), and X³ is a suitable leaving group, such as chloro, bromo, iodo, BF₃K, B(OH)₂, or B(pinacol), in a suitable solvent (e.g., dichloromethane, 1,2-dichloromethane, acetonitrile, tetrahydrofuran, 2-methyl tetrahydrofuran, N-methylpyrrolidone, or dimethylacetamide) at temperatures between 40°C and 80°C and using a metal source (e.g., Cu(OAc)₂), and preferably in the presence of an oxidant, such as O₂, or a suitable palladium pre-catalyst, such as RockPhos Pd G3, in the presence of a base (e.g., K₃PO₄) and suitable solvent (e.g., dimethyl ether or toluene) at temperatures between 20°C and 80°C. For related examples, see *Org. Lett.* **2003**, *5*, 1381; *Tetrahedron Lett.* **1998**, *39*, 2933; *Tetrahedron Lett.* **2003**, *44*, 3863 and *Org. Lett.* **2013**, *15*, 2876. Compounds of formula (XII) are either known or commercially available.



Scheme 21

As shown below in Scheme 22, compounds of formula (XXIX), wherein X⁹ is OH or halogen, may be obtained from compounds of formula (XXVIII) by hydrolysis in a similar manner as described for the conversion of compounds of formula (XXVI) into compounds of formula (XXV) in Scheme 21. Compounds of formula (XXVIII), wherein X⁵ is C₁-C₄-alkoxy, such as methoxy or ethoxy, and X⁹ is OH or halogen, may be obtained from compounds of formula (XXVII), wherein X⁹ is OH or halogen, via an oxidation method using a suitable oxidant, such as KMnO₄ or a cobalt(II) salt and trihydroxyisocyanuric acid (THICA) in a suitable solvent (e.g., acetic acid) at temperatures between 25°C and 200°C. For related examples, see: *Can. J. Chem.* **1978**, *56*, 1273 and WO2021160470. Compounds of formula (XXVII) are known or can be prepared as described in *Bulletin de la Societe Chimique de France* **1972**, *8*, 3198.

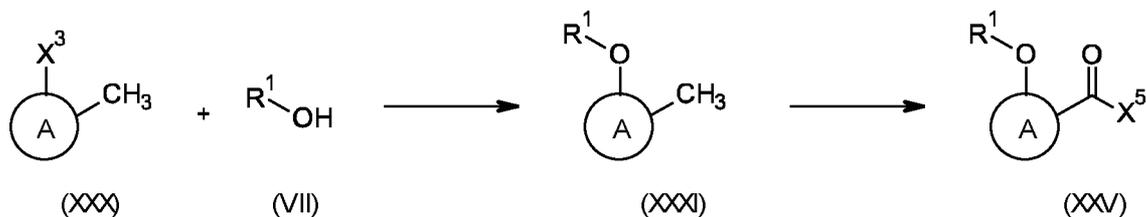


Scheme 22

As shown below in Scheme 23, compounds of formula (XXV), wherein X⁵ is C₁-C₄-alkoxy, such as methoxy or ethoxy, may be obtained from compounds of formula (XXXI) via an oxidation method using a suitable oxidant, such as KMnO₄ or a suitable cobalt(II) salt and trihydroxyisocyanuric acid (THICA) in a suitable solvent (e.g., acetic acid) at temperatures between 25°C and 200°C. For related examples, see: *Can. J. Chem.* **1978**, *56*, 1273 and WO 2021/160470. Compounds of formula (XXV) may be prepared as described in *Bulletin de la Societe Chimique de France* **1972**, *8*, 3198.

Furthermore, compounds of formula (XXXI), may be prepared by reacting nucleophilic compounds of formula (VII), wherein R¹ is as defined for compounds of formula (I), with electrophilic compounds of formula (XXX), wherein X³ is a suitable leaving group such as fluoro, chloro, bromo, iodo, BF₃K, B(OH)₂ or B(pinacol), in the presence of base (e.g., KO-*t*-Bu, K₃PO₄, K₂CO₃, triethylamine, or Cs₂CO₃), in a suitable solvent (e.g., N-methylpyrrolidone, dimethylacetamide, acetonitrile, tetrahydrofuran, 2-methyl tetrahydrofuran, sulfolane, dimethylsulfoxide) at temperatures between 25°C and 120°C, and optionally using a metal catalyst and ligand complex (e.g., CuI, *N,N*-dimethylglycine). For related examples, see *Eur. J. Org. Chem.* **2011**, *18*, 3353; *J. Org. Chem.* **2009**, *74*, 7951; *Tetrahedron Lett.* **2012**, *53*, 5318; WO2008110313 and WO 2012/136604. Compounds of formula (XXX) are either known or commercially available.

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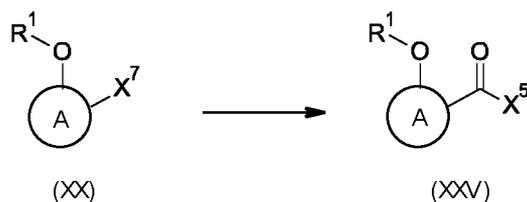


Scheme 23

As shown below in Scheme 24, compounds of formula (XXV), wherein R¹ is as defined for compounds of formula (I), and X⁵ is OH or C₁-C₄-alkoxy, may also be obtained from compounds of formula (XX) wherein R¹ is as defined for compounds of formula (I), and X⁷ is chloro, bromo, iodo, or trifluoromethanesulfonyl-O-

5 , at temperatures between 20°C and 130°C, preferably between 70°C and 110°C, using a metal source such as XPhos Pd G1 in a pressure vessel, typically a stainless steel autoclave, loaded with carbon monoxide, at a pressure typically between 1 to 50 bar, preferably between 5 to 15 bar, in the presence of an organic base, for instance triethylamine or diisopropylethylamine, and an appropriate solvent (e.g.,

10 methanol or ethanol). For related examples, see: *J. Med. Chem.* **2014**, *57*, 2692 and *Adv. Synth. Catal.* **2006**, *348*, 1255.

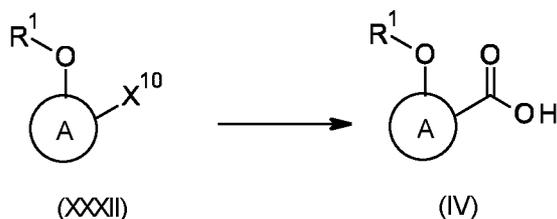


Scheme 24

Alternatively, as shown below in Scheme 25, compounds of formula (IV), wherein R¹ is as defined for compounds of formula (I), may also be obtained by reacting a compound of formula (XXXII) wherein R¹ is as defined for compounds of formula (I), and X¹⁰ is chloro, bromo or iodo, with a lithium reagent (e.g., n-

15 butyl lithium, sec-butyl lithium, tert-butyl lithium or lithium diisopropylamine) at temperatures between -78°C and -30°C in an appropriate solvent, for instance hexane, diethyl ether or tetrahydrofuran, followed by the addition of carbon dioxide. For related examples, see: *J. Am. Chem. Soc.* **2018**, *140*, 9140 and *J. Am.*

20 *Chem. Soc.* **2021**, *143*, 1539.

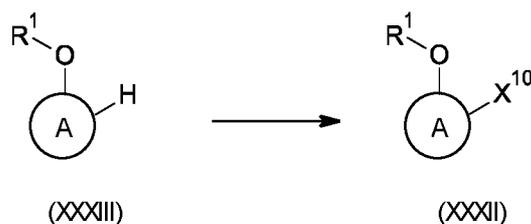


Scheme 25

As shown below in Scheme 26, compounds of formula (XXXII), wherein R¹ is as defined for compounds of formula (I), and X¹⁰ is chloro, bromo or iodo, are either known or may be prepared by reacting a compound of formula (XXXIII), wherein R¹ is as defined for compounds of formula (I), with an electrophilic halogen reagent like bromine, dibromohydantoin, N-bromo-, or N-chloro-succinimide, at temperatures between -

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78°C and 10°C, optionally with a base, typically lithium diisopropylamine or *n*-butyl lithium, in a suitable solvent (e.g., chloroform, 2-methyltetrahydrofuran or dimethylformamide). For related examples, see: *Tetrahedron Lett.* **2003**, 44, 823; *J. Am. Chem. Soc.* **2010**, 132, 8858 and *Synthesis* **2005**, 16, 2782.

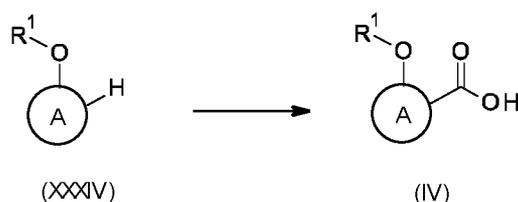


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Scheme 26

As shown below in Scheme 27, compounds of formula (IV), wherein R¹ is as defined for compounds of formula (I), may also be prepared by reacting a compound of formula (XXXIV), wherein R¹ is as defined for compounds of formula (I), at temperatures between -78°C and 10°C with a base, typically lithium diisopropylamine or *n*-butyl lithium, in the presence or not of a catalyst (e.g., potassium tert-butoxide), in a suitable solvent (e.g., diethyl ether, cyclopentyl methyl ether, methyl tert-butyl ether or tetrahydrofuran) followed by the addition of carbon dioxide. Compounds of formula (XXXIV) are either known, commercially available or readily prepared by experts in the field. For related examples, see: *Bioorg. Med. Chem.* **2004**, 12, 5579; *J. Am. Chem. Soc.* **2010**, 132, 8858 and *Synthesis* **2005**, 16, 2782.

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Scheme 27

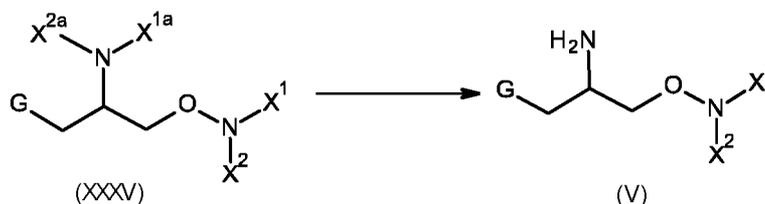
As shown below in Scheme 28, compounds of formula (V) may be obtained by treatment of compound of formula (XXXV), wherein X¹ is H and X² is a protective group, or X¹ and X² are identical or different protective groups, or X¹ and X² form a protective group together with the nitrogen they are attached to, and wherein X¹ᵃ is H and X²ᵃ is a protective group, or X¹ᵃ and X²ᵃ are identical or different protective groups, or X¹ᵃ and X²ᵃ form a protective group together with the nitrogen they are attached to; and X² is different from X²ᵃ. X¹ and X¹ᵃ may both be hydrogen. Also, if X¹ and X² on the one hand, and X¹ᵃ and X²ᵃ on the other hand, form a protective group together with the nitrogen they are attached to, said protective groups shall be different. Examples of protective groups include, for instance, *tert*-butyloxycarbonyl, benzylcarbonyl, 9-fluorenylmethylcarbonyl, trifluoroacetyl, benzyl, triphenylmethyl, benzylidene, *p*-toluenesulfonyl, phthalimide, or succinimide.

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Treatment of compound of formula (XXXV) is performed, with an acid (e.g., hydrochloric acid, trifluoroacetic acid), optionally in a suitable solvent or mixture of solvents, for instance dichloromethane, tetrahydrofuran, 2-methyltetrahydrofuran or diethyl ether at temperatures between 0°C and 50°C. For related examples, see: *ChemBioChem.* **2009**, 10, 323 and *Org. Process Res. Dev.* **2002**, 6, 520. Compounds of formula (XXXV) are either known or readily available to experts in the field.

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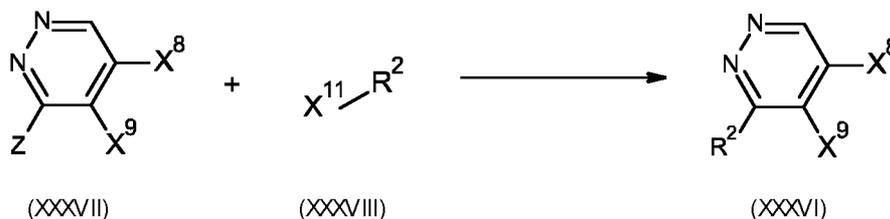
Scheme 28

As shown below in Scheme 29, compounds of formula (XXXVI), wherein X^8 is OH, halogen, $O-R^1$, with R^1 as defined for compound of formula (I), X^9 is halogen, methyl, trifluoromethanesulfonyl-O-, cyano, COOH, or $-C(O)C_1-C_4$ alkoxy, and R^2 is as described below, are prepared by reacting a compound of formula (XXXVII), wherein X^8 and X^9 are as defined for compounds of formula (XXXVI), and Z is as described below, with a reagent R^2-X^{11} of formula (XXXVIII). Compounds of formula R^2-X^{11} (XXXVIII) and suitable reaction conditions for various substituents R^2 and Z are as described below.

For example, compounds of formula (XXXVI), wherein R^2 is cyano, C_1-C_6 alkyl, C_3-C_5 alkenyl, C_3-C_5 alkynyl, C_1-C_3 alkoxy C_2-C_3 alkyl, C_3-C_6 cycloalkyl, C_3-C_6 cycloalkyl C_{1-2} alkyl, cycloalkyl, phenyl, heteroaryl or heterocyclyl, can be prepared by reacting a compound of formula (XXXVII), wherein Z is chloro, bromo, or iodo, with a suitable cross-coupling reagent of formula (XXXVIII), wherein R^2 is cyano, C_1-C_6 alkyl, C_3-C_5 alkenyl, C_3-C_5 alkynyl, C_1-C_3 alkoxy C_2-C_3 alkyl, C_3-C_6 cycloalkyl, C_3-C_6 cycloalkyl C_{1-2} alkyl, cycloalkyl, phenyl, heteroaryl, or heterocyclyl, and X^{11} is a metal, a metalloid (e.g. Zn(CN), cyclopropylMgBr, MeZnCl, or AlMe₃), or an organometaloid (e.g. trimethylboroxine) reagent, preferably in the presence of a suitable metal (e.g. CuBr) or catalyst complex (e.g., 1,1'-bis(diphenylphosphino)ferrocene-palladium(II)dichloride), optionally in the presence of a base (e.g. K₂CO₃), and in an inert solvent, such as toluene or 2-methyl tetrahydrofuran, at temperatures between 25°C and reflux temperature. For examples, see *J. Org. Chem.* **1987**, 52, 3847; WO 2006/045514; WO 2004/080998.

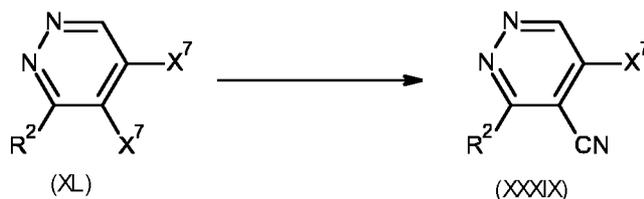
Compounds of formula (XXXVI), wherein R^2 is C_1-C_4 alkoxy, C_3-C_4 alkenyloxy, C_3-C_4 alkynyloxy, phenoxy, heteroaryloxy, or C_3-C_6 cycloalkyloxy, can be prepared by treatment of compounds of formula (XXXVII), wherein Z is suitable leaving group, such as halogen, with a suitable nucleophilic compound of formula (XXXVIII), wherein R^2 is C_1-C_6 alkyl, C_3-C_4 alkenyl, C_3-C_4 alkynyl, C_1-C_3 alkoxy C_2-C_3 alkyl, C_3-C_6 cycloalkyl, C_3-C_6 cycloalkyl C_{1-2} alkyl, phenyl, heteroaryl, or C_3-C_6 cycloalkyl, and X^{11} is selected from -OH, NH, SH, or C_1-C_4 alkylamino, in the presence of a base, such as NaH, KO-*t*-Bu, K₃PO₄, K₂CO₃, triethylamine, or Cs₂CO₃, optionally in the presence of an additional solvent (e.g. N-methylpyrrolidone, dimethylacetamide, acetonitrile, tetrahydrofuran, 2-methyl tetrahydrofuran, sulfolane, or dimethylsulfoxide), at temperatures between 25°C and reflux temperature. For related examples, see: F. Terrier, *Modern Nucleophilic Aromatic Substitution*, Wiley-VCH, Weinheim, 2013.

Compounds of formula (XXXVI), wherein R^2 is C_1-C_4 -alkoxy, C_3-C_4 alkenyloxy, C_3-C_4 alkynyloxy, C_1-C_2 fluoroalkoxy, or C_3-C_6 cycloalkyloxy, are readily accessed from compounds of formula (XXXVII), wherein Z is OH or SH, using a suitable alkylating reagent of formula (XXXVIII), such as a C_1-C_6 alkylhalide, C_3-C_5 alkenylhalide, C_3-C_5 alkynylhalide, C_1-C_3 alkoxy C_2-C_3 alkyl C_3-C_5 alkenyl, C_3-C_5 alkynylhalide, C_1-C_3 alkoxy C_2-C_3 alkylhalide, C_3-C_6 cycloalkylhalide, and C_3-C_6 cycloalkyl C_{1-2} alkylhalide or reagents such as ClF₂COOH and Me₂SO₄, via known conditions described in the literature.



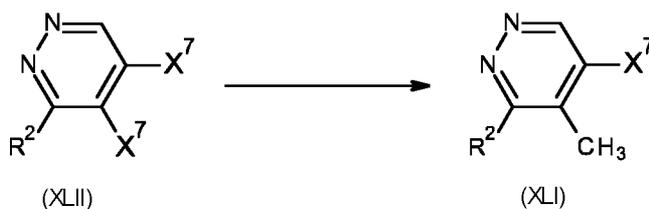
Scheme 29

As shown below in Scheme 30, related compounds of formula (XXXIX), wherein X⁷ is chloro, bromo, or iodo, are prepared by reaction of a compound of formula (XL), wherein X⁷ are identically selected from chloro, bromo, and iodo, with a cyanide salt, such as sodium or potassium cyanide, optionally in the presence of a copper salt (eg. copper cyanide), in a suitable solvent or solvent mixtures (e.g., dimethylformamide, tetrahydrofuran, 2-methyl-tetrahydrofuran), at temperatures between 50°C and 120°C, preferably between 80°C and 100°C. For related examples, see: WO199507264.



Scheme 30

As shown below in Scheme 31, related compounds of formula (XLI), wherein X⁷ is chloro, bromo, or iodo, are prepared by reaction of a compound of formula (XLII), wherein X⁷ are identically selected from chloro, bromo, and iodo, with a methyl magnesium halide, wherein halide is bromide or chloride, in the optional presence of a copper salt (e.g., copper iodide, copper cyanide, copper chloride, copper acetate), in a suitable solvent or solvent mixtures (eg. diethyl ether, cyclopentyl methyl ether, tetrahydrofuran, 2-methyl-tetrahydrofuran, tert-butyl methyl ether), at temperatures between from -20°C to 10°C. For related examples see: WO199507264.



Scheme 31

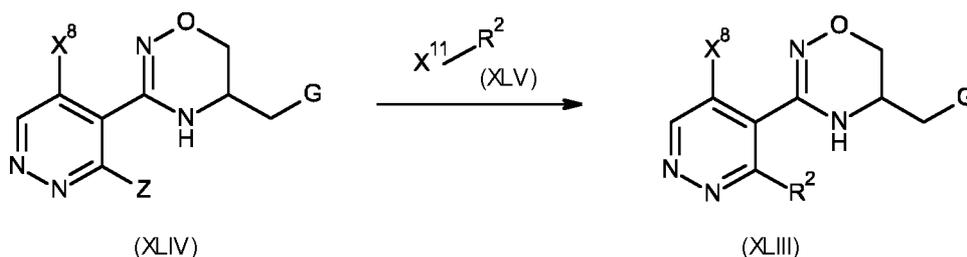
As shown below in Scheme 32, compounds of formula (XLIII), wherein X⁸ is OH, O-R¹, or halogen, wherein R¹ is as defined for compound of formula (I), and R² is as described below, are prepared by reacting a compound of formula (XLIV), wherein X⁸ and R¹ are as defined for compounds of formula (XLIII), and Z is as described below, with a reagent R²-X¹¹ of formula (XLV). Compounds of formula R²-X¹¹ (XLV) and suitable reaction conditions for various substituents R² and Z are as described below.

For example, compounds of formula (XLIII), wherein R² is cyano, C₁-C₆alkyl, C₃-C₅alkenyl, C₃-C₅alkynyl, C₁-C₃alkoxyC₂-C₃alkyl, C₃-C₆cycloalkyl, C₃-C₆cycloalkylC₁₋₂alkyl, cycloalkyl, phenyl, heteroaryl or

heterocyclyl, and wherein X^8 is as generally defined for compounds of formula (XLIII) above, can be prepared by reacting a compound of formula (XLIV), wherein Z is chloro, bromo, or iodo, with a suitable cross-coupling reagent of formula (XLV), wherein R^2 is cyano, C_1 - C_6 alkyl, C_3 - C_5 alkenyl, C_3 - C_5 alkynyl, C_1 - C_3 alkoxy C_2 - C_3 alkyl, C_3 - C_6 cycloalkyl, C_3 - C_6 cycloalkyl C_{1-2} alkyl, cycloalkyl, phenyl, heteroaryl or heterocyclyl, and X^{11} is a metal, a metalloid (e.g. Zn(CN), cyclopropylMgBr, MeZnCl, AlMe₃), or an organometalloid (e.g. trimethylboroxine) reagent, preferably in the presence of a suitable metal (e.g. CuBr) or catalyst complex (e.g., 1,1'-bis(diphenylphosphino)ferrocene-palladium(II)dichloride), optionally in the presence of a base (e.g. K₂CO₃), and in an inert solvent, such as toluene or 2-methyl tetrahydrofuran, at temperatures between 25°C and reflux temperature. For examples, see *J. Org. Chem.* **1987**, 52, 3847; WO 2006/045514; WO 2004/080998.

Compounds of formula (XLIII), wherein R^2 is C_1 - C_4 alkoxy, C_3 - C_4 alkenyloxy, C_3 - C_4 alkynyloxy, phenoxy, heteroaryloxy, or C_3 - C_6 cycloalkyloxy, are prepared by treatment of compounds of formula (XLIV), wherein Z is a suitable leaving group, such as halogen, with a suitable nucleophilic compound of formula (XLV), wherein R^2 is C_1 - C_6 alkyl, C_3 - C_4 alkenyl, C_3 - C_4 alkynyl, C_1 - C_3 alkoxy C_2 - C_3 alkyl, C_3 - C_6 cycloalkyl, C_3 - C_6 cycloalkyl C_{1-2} alkyl, phenyl, heteroaryl, or C_3 - C_6 cycloalkyl, and X^{11} is selected from -OH, NH, SH, or C_1 - C_4 alkylamino, in the presence of a base, such as NaH, KO-*t*-Bu, K₃PO₄, K₂CO₃, triethylamine, or Cs₂CO₃, optionally in the presence of an additional solvent (e.g. N-methylpyrrolidone, dimethylacetamide, acetonitrile, tetrahydrofuran, 2-methyl tetrahydrofuran, sulfolane, dimethylsulfoxide), at temperatures between 25°C and reflux temperature. For related examples, see: F. Terrier, *Modern Nucleophilic Aromatic Substitution*, Wiley-VCH, Weinheim, 2013.

Additionally, compounds of formula (XLIII), wherein R^2 is C_1 - C_4 -alkoxy, C_3 - C_4 alkenyloxy, C_3 - C_4 alkynyloxy, C_1 - C_2 fluoroalkoxy, or C_3 - C_6 cycloalkyloxy, are readily accessed from compounds of formula (XLIV), wherein Z is OH or SH, using a suitable alkylating reagent of formula (XLV), wherein R^2 is C_1 - C_6 alkyl, C_3 - C_4 alkenyl, C_3 - C_4 alkynyl, C_1 - C_3 alkoxy C_2 - C_3 alkyl, C_3 - C_6 cycloalkyl, C_3 - C_6 cycloalkyl C_{1-2} alkyl, phenyl, heteroaryl, or C_3 - C_6 cycloalkyl, and X^{11} is a suitable leaving group, such as chloro, bromo, iodo, trifluoromethanesulfonyl-O-, and methanesulfonyl-O- or known reagents, such as ClF₂COOH and Me₂SO₄, via known conditions described in the literature.



Scheme 32

Depending on the choice of the reaction conditions and starting materials which are suitable in each case, it is possible, for example, in one reaction step only to replace one substituent by another substituent according to the invention, or a plurality of substituents can be replaced by other substituents according to the invention in the same reaction step.

Salts of compounds of formula (I) may be prepared in a manner known *per se*. Thus, for example, acid addition salts of compounds of formula (I) are obtained by treatment with a suitable acid or a suitable ion exchanger reagent and salts with bases are obtained by treatment with a suitable base or with a suitable ion exchanger reagent. All other compounds mentioned in schemes 1 to 16 are readily prepared by those skilled in the art or are commercially available.

Salts of compounds of formula (I) can be converted in the customary manner into the free compounds (I), acid addition salts, for example, by treatment with a suitable basic compound or with a suitable ion exchanger reagent and salts with bases, for example, by treatment with a suitable acid or with a suitable ion exchanger reagent.

Salts of compounds of formula (I) can be converted in a manner known *per se* into other salts of compounds of formula (I), acid addition salts, for example, into other acid addition salts, for example by treatment of a salt of inorganic acid such as hydrochloride with a suitable metal salt such as a sodium, barium or silver salt, of an acid, for example with silver acetate, in a suitable solvent in which an inorganic salt which forms, for example silver chloride, is insoluble and thus precipitates from the reaction mixture.

Depending on the procedure or the reaction conditions, the compounds of formula (I), which have salt-forming properties, can be obtained in free form or in the form of salts.

The compounds of formula (I) and, where appropriate, the tautomer's thereof, in each case in free form or in salt form, can be present in the form of one of the isomers which are possible or as a mixture of these, for example in the form of pure isomers, such as antipodes and/or diastereomers, or as isomer mixtures, such as enantiomer mixtures, for example racemates, or diastereomer mixtures, depending on the number, absolute and relative configuration of asymmetric carbon atoms which occur in the molecule and/or depending on the configuration of non-aromatic double bonds which occur in the molecule, the invention relates to the pure isomers and also to all isomer mixtures which are possible and is to be understood in each case in this sense hereinabove and herein below, even when stereochemical details are not mentioned specifically in each case.

Diastereomeric mixtures or racemic mixtures of compounds of formula (I), in free form or in salt form, which can be obtained depending on which starting materials and procedures have been chosen can be separated in a known manner into the pure diastereomers or racemates on the basis of the physicochemical differences of the components, for example by fractional crystallization, distillation and/or chromatography.

Enantiomeric mixtures, such as racemates, which can be obtained in a similar manner can be resolved into the optical antipodes by known methods, for example by recrystallization from an optically active solvent, by chromatography on chiral adsorbents, for example high-performance liquid chromatography (HPLC) on acetyl cellulose, with the aid of suitable microorganisms, by cleavage with specific, immobilized enzymes, via the formation of inclusion compounds, for example using chiral crown ethers, where only one enantiomer is complexed, or by conversion into diastereomeric salts, for example by reacting a basic end-product racemate with an optically active acid, such as a carboxylic acid, for example camphor, tartaric or malic acid, or sulfonic acid, for example camphorsulfonic acid, and separating the diastereomer mixture which can be obtained in this manner, for example by fractional crystallization based on their differing

solubilities, to give the diastereomers, from which the desired enantiomer can be set free by the action of suitable agents, for example basic agents.

Pure diastereomers or enantiomers can be obtained according to the invention not only by separating suitable isomer mixtures, but also by generally known methods of diastereoselective or enantioselective synthesis, for example by carrying out the process according to the invention with starting materials of a suitable stereochemistry.

It is advantageous to isolate or synthesize in each case the biologically more effective isomer, for example enantiomer or diastereomer, or isomer mixture, for example enantiomer mixture or diastereomer mixture, if the individual components have a different biological activity.

As an example, compounds with more than one asymmetric carbon atoms may exist in diastereomeric forms which can be optionally separated using for example supercritical fluid chromatography (SFC) chromatography with chiral columns. Such diastereomers can show a different fungicidal activity profile, but all isomers and diastereomers form part of this invention.

The compounds of formula (I) and, where appropriate, the tautomers thereof, in each case in free form or in salt form, can, if appropriate, also be obtained in the form of hydrates and/or include other solvents, for example those which may have been used for the crystallization of compounds which are present in solid form.

As already indicated, surprisingly, it has now been found that the compounds of formula (I) of the present invention 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 the 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 can 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 also protecting 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 compounds of formula (I) as a fungicide. The term "fungicide" as used herein means a compound that controls, modifies, or prevents the growth of fungi. The term "fungicidally effective amount" where used 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 may also be 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, 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, for example, can be dressed before being sown. The active compounds of formula (I) 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, for example, 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 of formula (I) 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. lumber, wall boards and paint.

The compounds of formula (I) are 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:

Absidia corymbifera, Alternaria spp, Aphanomyces spp, Ascochyta spp, Aspergillus spp. including A. flavus, A. fumigatus, A. nidulans, A. niger, A. terreus, 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, 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, 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, Microsporium spp, Monilinia spp, Mucor spp, Mycosphaerella spp. including M. 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 spp. including P. leucotricha, Polymyxa graminis, Polymyxa 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 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 necator, Urocystis spp, Ustilago spp, Venturia spp. including V. inaequalis, Verticillium spp, and Xanthomonas spp.

10 The compounds of formula (I) may be used for example on turf, ornamentals, such as flowers, shrubs, broad-leaved trees or evergreens, for example conifers, as well as for tree injection, pest management and the like.

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, rye, sorghum triticale 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, 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, potato, pumpkin, rhubarb, spinach and tomato; and vines for example grapes.

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

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

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

Further, 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, WO93/07278, WO95/34656, 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.

- 5 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).

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:

10 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 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

15 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 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.
- 25 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 tolerance to the herbicide glufosinate ammonium.
- 30 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-protease recognition sequence. The preparation of such transgenic maize plants is described in WO 03/018810.
- 35 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 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.

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.

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 from *Bacillus thuringiensis subsp. kurstaki* which brings about tolerance to certain Lepidoptera, include the European corn borer.

The compounds of formula (I) may be used in controlling or preventing phytopathogenic diseases, especially caused by phytopathogenic fungi, such as *Botrytis cinerea* on Rosaceae, Vitaceae, Solanaceae, Cucurbitaceae, and Fabaceae; *Glomerella lagenarium* on Cucurbitaceae; *Blumeria graminis* on Poaceae, such as wheat.

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 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 or tubers, for example potatoes. There can 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 can be protected before transplantation by a total or partial treatment by immersion. Preferably “plant propagation material” is understood to denote seeds.

The compounds of formula (I) 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 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 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 Suspension concentrates are aqueous formulations in which finely divided solid particles of the active compound are suspended. Such formulations include anti-settling agents and dispersing agents and may further include a wetting agent to enhance activity as well an anti-foam and a crystal growth inhibitor. In use, these concentrates are diluted in water and normally applied as a spray to the area to be treated. The amount of active ingredient may range from 0.5% to 95% of the concentrate.
- 10 Wettable powders are in the form of finely divided particles which disperse readily in water or other liquid carriers. The particles contain the active ingredient retained in a solid matrix. Typical solid matrices include fuller's earth, kaolin clays, silicas and other readily wet organic or inorganic solids. Wettable powders normally contain from 5% to 95% of the active ingredient plus a small amount of wetting, dispersing or emulsifying agent.
- 15 Emulsifiable concentrates are homogeneous liquid compositions dispersible in water or other liquid and may consist entirely of the active compound with a liquid or solid emulsifying agent, or may also contain a liquid carrier, such as xylene, heavy aromatic naphthas, isophorone and other non-volatile organic solvents. In use, these concentrates are dispersed in water or other liquid and normally applied as a spray to the area to be treated. The amount of active ingredient may range from 0.5% to 95% of the concentrate.
- 20 Granular formulations include both extrudates and relatively coarse particles and are usually applied without dilution to the area in which treatment is required. Typical carriers for granular Formulations include sand, fuller's earth, attapulgite clay, bentonite clays, montmorillonite clay, vermiculite, perlite, calcium carbonate, brick, pumice, pyrophyllite, kaolin, dolomite, plaster, wood flour, ground corn cobs, ground peanut hulls, sugars, sodium chloride, sodium sulphate, sodium silicate, sodium borate, magnesia, mica,
- 25 iron oxide, zinc oxide, titanium oxide, antimony oxide, cryolite, gypsum, diatomaceous earth, calcium sulphate and other organic or inorganic materials which absorb or which can be coated with the active compound. Granular formulations normally contain 5% to 25% of active ingredients which may include surface-active agents such as heavy aromatic naphthas, kerosene and other petroleum fractions, or vegetable oils; and/or stickers such as dextrans, glue or synthetic resins.
- 30 Dusts are free-flowing admixtures of the active ingredient with finely divided solids such as talc, clays, flours and other organic and inorganic solids which act as dispersants and carriers.

Microcapsules are typically droplets or granules of the active ingredient enclosed in an inert porous shell which allows escape of the enclosed material to the surroundings at controlled rates. Encapsulated droplets are typically 1 to 50 microns in diameter. The enclosed liquid typically constitutes 50 to 95% of the weight

35 of the capsule and may include solvent in addition to the active compound. Encapsulated granules are generally porous granules with porous membranes sealing the granule pore openings, retaining the active species in liquid form inside the granule pores. Granules typically range from 1 millimetre to 1 centimetre and preferably 1 to 2 millimetres in diameter. Granules are formed by extrusion, agglomeration or prilling, or are naturally occurring. Examples of such materials are vermiculite, sintered clay, kaolin, attapulgite clay,

sawdust and granular carbon. Shell or membrane materials include natural and synthetic rubbers, cellulosic materials, styrene-butadiene copolymers, polyacrylonitriles, polyacrylates, polyesters, polyamides, polyureas, polyurethanes and starch xanthates.

Other useful formulations for agrochemical applications include simple solutions of the active ingredient in a solvent in which it is completely soluble at the desired concentration, such as acetone, alkylated naphthalenes, xylene and other organic solvents. Pressurised sprayers, wherein the active ingredient is dispersed in finely-divided form as a result of vaporisation of a low boiling dispersant solvent carrier, may also be used.

Suitable agricultural adjuvants and carriers that are useful in formulating the compositions of the invention in the formulation types described above are well known to those skilled in the art.

Liquid carriers that can be employed include, for example, water, toluene, xylene, petroleum naphtha, crop oil, acetone, methyl ethyl ketone, cyclohexanone, acetic anhydride, acetonitrile, acetophenone, amyl acetate, 2-butanone, chlorobenzene, cyclohexane, cyclohexanol, alkyl acetates, diacetonolcohol, 1,2-dichloropropane, diethanolamine, p-diethylbenzene, diethylene glycol, diethylene glycol abietate, diethylene glycol butyl ether, diethylene glycol ethyl ether, diethylene glycol methyl ether, N,N-dimethyl formamide, dimethyl sulfoxide, 1,4-dioxane, dipropylene glycol, dipropylene glycol methyl ether, dipropylene glycol dibenzoate, diproxitol, alkyl pyrrolidinone, ethyl acetate, 2-ethyl hexanol, ethylene carbonate, 1,1,1-trichloroethane, 2-heptanone, alpha pinene, d-limonene, ethylene glycol, ethylene glycol butyl ether, ethylene glycol methyl ether, gamma-butyrolactone, glycerol, glycerol diacetate, glycerol monoacetate, glycerol triacetate, hexadecane, hexylene glycol, isoamyl acetate, isobornyl acetate, isooctane, isophorone, isopropyl benzene, isopropyl myristate, lactic acid, laurylamine, mesityl oxide, methoxy-propanol, methyl isoamyl ketone, methyl isobutyl ketone, methyl laurate, methyl octanoate, methyl oleate, methylene chloride, m-xylene, n-hexane, n-octylamine, octadecanoic acid, octyl amine acetate, oleic acid, oleylamine, o-xylene, phenol, polyethylene glycol (PEG400), propionic acid, propylene glycol, propylene glycol monomethyl ether, p-xylene, toluene, triethyl phosphate, triethylene glycol, xylene sulfonic acid, paraffin, mineral oil, trichloroethylene, perchloroethylene, ethyl acetate, amyl acetate, butyl acetate, methanol, ethanol, isopropanol, and higher molecular weight alcohols such as amyl alcohol, tetrahydrofurfuryl alcohol, hexanol, octanol, etc., ethylene glycol, propylene glycol, glycerine and N-methyl-2-pyrrolidinone. Water is generally the carrier of choice for the dilution of concentrates.

Suitable solid carriers include, for example, talc, titanium dioxide, pyrophyllite clay, silica, attapulgite clay, kieselguhr, chalk, diatomaceous earth, lime, calcium carbonate, bentonite clay, fuller's earth, cotton seed hulls, wheat flour, soybean flour, pumice, wood flour, walnut shell flour and lignin.

A broad range of surface-active agents are advantageously employed in both said liquid and solid compositions, especially those designed to be diluted with carrier before application. These agents, when used, normally comprise from 0.1% to 15% by weight of the formulation. They can be anionic, cationic, non-ionic or polymeric in character and can be employed as emulsifying agents, wetting agents, suspending agents or for other purposes. Typical surface active agents include salts of alkyl sulfates, such as diethanolammonium lauryl sulphate; alkylarylsulfonate salts, such as calcium dodecylbenzenesulfonate; alkylphenol-alkylene oxide addition products, such as nonylphenol-C.sub. 18 ethoxylate; alcohol-alkylene oxide addition products, such as tridecyl alcohol-C.sub. 16 ethoxylate; soaps, such as sodium stearate;

alkylnaphthalenesulfonate salts, such as sodium dibutylnaphthalenesulfonate; dialkyl esters of sulfosuccinate salts, such as sodium di(2-ethylhexyl) sulfosuccinate; sorbitol esters, such as sorbitol oleate; quaternary amines, such as lauryl trimethylammonium chloride; polyethylene glycol esters of fatty acids, such as polyethylene glycol stearate; block copolymers of ethylene oxide and propylene oxide; and salts of
5 mono and dialkyl phosphate esters.

Other adjuvants commonly utilized in agricultural compositions include crystallisation inhibitors, viscosity modifiers, suspending agents, spray droplet modifiers, pigments, antioxidants, foaming agents, anti-foaming agents, light-blocking agents, compatibilizing agents, antifoam agents, sequestering agents, neutralising agents and buffers, corrosion inhibitors, dyes, odorants, spreading agents, penetration aids,
10 micronutrients, emollients, lubricants and sticking agents.

In addition, further, other biocidally active ingredients or compositions may be combined with the compositions of the invention and used in the methods of the invention and applied simultaneously or sequentially with the compositions of the invention. When applied simultaneously, these further active ingredients may be formulated together with the compositions of the invention or mixed in, for example, the
15 spray tank. These further biocidally active ingredients may be fungicides, herbicides, insecticides, bactericides, acaricides, nematocides and/or plant growth regulators.

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

In addition, the compositions of the invention may also be applied with one or more systemically acquired
20 resistance inducers ("SAR" inducer). SAR inducers are known and described in, for example, United States Patent No. US 6,919,298 and include, for example, salicylates and the commercial SAR inducer acibenzolar-S-methyl.

The compounds of Formula (I) are normally used in the form of agrochemical compositions and can be applied to the crop area or plant to be treated, simultaneously or in succession with further compounds.
25 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 preparations, if desired together with further carriers, surfactants or application promoting adjuvants customarily employed in the art of formulation.

30 The compounds of Formula (I) may be used in the form of 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 defined herein, in free form or in agrochemically usable salt form, and at least one of the above-mentioned adjuvants.

The invention therefore provides a composition, preferably a fungicidal composition, comprising at least
35 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 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 cases, result in unexpected synergistic activities.

5 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, bridged diphenyl fungicides, carbamate fungicides, carbanilate fungicides, conazole fungicides, copper fungicides, dicarboximide
10 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 fungicides, pyridine fungicides, pyrimidine fungicides, pyrrole fungicides, quaternary ammonium fungicides, quinoline fungicides, quinone fungicides,
15 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.

Specific examples of suitable additional active ingredients also include a compound selected from the group
20 of substances consisting of petroleum oils, 1,1-bis(4-chloro-phenyl)-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, benoxa-fos, benzyl benzoate, bixafen, brofenvalerate, bromo-cylen, bromophos, bromopropylate, buprofezin, butocarboxim, butoxycarboxim, butylpyridaben, calcium
25 polysulfide, camphechlor, carbanolate, carbophenothion, cymiazole, chino-methionat, 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-methylsulfon, dichlofluanid, dichlorvos, dicliphos, dienochlor, dimefox, dinex, dinex-diclexine, dinocap-4, dinocap-6, dinocron, dino-penton, dinosulfon, dinoterbon, dioxathion, diphenyl sulfone, disulfiram, DNOC, dofenapyn, doramectin, endothion, eprinomectin, ethoate-methyl, etrimfos, fenazaflor, fenbutatin oxide, fenothiocarb, fenpyrad, fen-pyroximate, fenpyrazamine, fenson, fentrifanil, flubenzimine, flucycloxuron, fluenetil, fluorbenside, FMC 1137, formetanate, formetanate hydrochloride, formparanate, gamma-HCH,
35 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 complex, omethoate, oxydeprofos, oxydisulfoton, pp'-DDT, parathion,
40 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, thiocarboxime, thiofanox, thiometon, thioquinox, thuringiensin, triamiphos, triarathene, triazophos, triazuron, trifenofos, trinactin, vamidothion, vaniliprole, bethoxazin, copper dioctanoate, copper sulfate, cybutryne, dichlone, dichlorophen, endothal, fentin, hydrated lime, nabam, quinoclamine, 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, dipyrithione, dodicin, fenaminosulf, formaldehyde, hydrargaphen, kasugamycin, kasugamycin hydrochloride hydrate, nickel bis(dimethyldithiocarbamate), nitrapyrin, octhilinone, oxolinic acid, oxytetracycline, potassium hydroxyquinoline sulfate, probenazole, streptomycin, streptomycin sesquisulfate, tecloftalam, thiomersal, Adoxophyes orana GV, Agrobacterium radiobacter, Amblyseius spp., Anagrapha falcifera NPV, Anagrus atomus, Aphelinus abdominalis, Aphidius colemani, 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, 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 riobravis, 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, 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-yl acetate, (Z)-tetradec-9-en-1-yl acetate, (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-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, frontaline, grandlure, grandlure I, grandlure II, grandlure III, grandlure IV, hexalure, ipsdienol, ipsenol, japonilure, lineatin, lilture, looplure, medlure, megatomoic acid, methyl eugenol, muscalure, octadeca-2,13-dien-1-yl acetate, octadeca-3,13-dien-1-yl acetate, orfralure, 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-bis(4-ethylphenyl)-ethane, 1,2-dichloropropane with 1,3-dichloropropene, 1-bromo-2-chloroethane, 2,2,2-trichloro-1-(3,4-dichloro-phenyl)ethyl acetate, 2,2-dichlorovinyl 2-ethylsulfinyethyl 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 methylcarbamate, 2-thiocyanatoethyl laurate, 3-bromo-1-chloroprop-1-ene, 3-methyl-1-phenylpyrazol-5-yl dimethyl-carbamate, 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, 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, clocythrin, copper acetoarsenite, copper arsenate, copper oleate, coumithoate, cryolite, CS 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, 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, thicrofos, 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, meperfluthrin, tetramethylfluthrin, bis(tributyltin) oxide, bromoacetamide, ferric phosphate, niclosamide-olamine, tributyltin oxide, pyrimorph, trifenmorph, 1,2-dibromo-3-chloropropane, 1,3-dichloropropene, 3,4-

dichlorotetrahydrothio-phenone 1,1-dioxide, 3-(4-chlorophenyl)-5-methylrhodanine, 5-methyl-6-thioxo-1,3,5-thiadiazinan-3-ylacetic acid, 6-isopentenylaminopurine, anisiflupurin, benclonthiaz, cytokinins, DCIP, furfural, isamidofos, kinetin, Myrothecium verrucaria composition, tetrachlorothiophene, xylenols, 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 fluoro-acetate, thallium sulfate, warfarin, 2-(2-butoxyethoxy)-ethyl piperonylate, 5-(1,3-benzodioxol-5-yl)-3-hexylcyclohex-2-enone, famesol 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, chloroinconazide, mercuric oxide, thiophanate-methyl, azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, furametpyr, hexaconazole, imazalil, imiben-conazole, ipconazole, metconazole, myclobutanil, paclobutrazole, pefurazoate, penconazole, prothioconazole, pyrifenoxy, prochloraz, propiconazole, pyrisoxazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadime-nol, triflumizole, triticonazole, ancymidol, fenarimol, nuarimol, bupirimate, dimethirimol, ethirimol, dodemorph, fenpropidin, fenpropimorph, spiroxamine, tridemorph, cyprodinil, mepanipyrim, pyrimethanil, fenpiclonil, fludioxonil, benalaxyl, furalaxyl, meta-laxyl, R-metalaxyl, ofurace, oxadixyl, carbendazim, debacarb, fuberidazole, thiaben-dazole, chlozolinate, dichlozoline, myclozoline, procymidone, vinclozoline, boscalid, carboxin, fenfuram, flutolanil, mepronil, oxycarboxin, penthiopyrad, thifluzamide, dodine, iminoctadine, azoxystrobin, dimoxystrobin, enestroburin, fenaminstrobin, flufenoxystrobin, fluoxastrobin, kresoxim-methyl, metomi-nostrobin, trifloxystrobin, orysastrobin, picoxystrobin, pyraclostrobin, pyrametostrobin, pyraoxystrobin, ferbam, mancozeb, maneb, metiram, propineb, zineb, captafol, captan, fluoroimide, folpet, tolylfluanid, bordeaux mixture, copper oxide, mancozeb, oxine-copper, nitrothal-isopropyl, edifenphos, iprobenphos, phosdiphen, tolclofos-methyl, anilazine, benthiavalicarb, blasticidin-S, chloroneb, chloro-tha-lo-nil, cyflufenamid, cymoxanil, cyclobutrifluram, diclocymet, diclomezine, dicloran, diethofencarb, dimetho-morph, flumorph, dithianon, ethaboxam, etridiazole, famoxa-done, fenamidone, fenoxanil, ferimzone, fluazinam, flumetylsulfurim, fluopicolide, fluoxytioconazole, flusulfamide, fluxapyroxad, fenhexamid, fos-etyl-aluminium, hymexazol, iprovalicarb, cyazofamid, methasulfo-carb, metrafenone, pencycuron, phthalide, polyoxins, propamocarb, pyribencarb, proquinazid, pyroquilon, pyriofenone, quinoxifen, quintozone, tiadinil, triazoxide, tricyclazole, triforine, validamycin, valifenalate, zoxamide, mandipropamid, flubeneteram, isopyrazam, sedaxane, benzovindiflupyr, pydiflumetofen, 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (3',4',5'-trifluoro-biphenyl-2-yl)-amide, isoflucypram, isotianil, dipymetitron, 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, 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), lvenmixianan, 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, 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]methanesulfonate, but-3-ynyl N-[6-[[[(Z)-(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-methyl-2-[[2-methyl-4-(3,4,5-trimethylpyrazol-1-yl)phenoxy]methyl]phenyl]tetrazol-5-one, aminopyrifen, ametocradin, amisulbrom, penflufen, (Z,2E)-5-[1-(4-chlorophenyl)pyrazol-3-yl]oxy-2-methoxyimino-N,3-dimethyl-pent-3-enamide, florylpicoxamid, fempicoxamid, metaryl picoxamid, tebufloquin, ipflufenquin, quinofumelin, isofetamid, ethyl 1-[[4-[[2-(trifluoromethyl)-1,3-dioxolan-2-yl]methoxy]phenyl]methyl]pyrazole-3-carboxylate (may be prepared from the methods described in WO 2020/056090), ethyl 1-[[4-(Z)-2-ethoxy-3,3,3-trifluoro-prop-1-enoxy]phenyl]methyl]pyrazole-3-carboxylate (may be prepared from the methods described in WO 2020/056090), methyl N-[[4-[1-(4-cyclopropyl-2,6-difluoro-phenyl)pyrazol-4-yl]-2-methyl-phenyl]methyl]carbamate (may be prepared from the methods described in WO 2020/097012), methyl N-[[4-[1-(2,6-difluoro-4-isopropyl-phenyl)pyrazol-4-yl]-2-methyl-phenyl]methyl]carbamate (may be prepared from the methods described in WO 2020/097012), 6-chloro-3-(3-cyclopropyl-2-fluoro-phenoxy)-N-[2-(2,4-dimethylphenyl)-2,2-difluoro-ethyl]-5-methyl-pyridazine-4-carboxamide (may be prepared from the methods described in WO 2020/109391), 6-chloro-N-[2-(2-chloro-4-methyl-phenyl)-2,2-difluoro-ethyl]-3-(3-cyclopropyl-2-fluoro-phenoxy)-5-methyl-pyridazine-4-carboxamide (may be prepared from the methods described in WO 2020/109391), 6-chloro-3-(3-cyclopropyl-2-fluoro-phenoxy)-N-[2-(3,4-dimethylphenyl)-2,2-difluoro-ethyl]-5-methyl-pyridazine-4-carboxamide (may be prepared from the methods described in WO 2020/109391), 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, benzothiofostrobil, phenamacril, 5-amino-1,3,4-thiadiazole-2-thiol zinc salt (2:1), fluopyram, flufenoxadiazam, 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]benzotrile, 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, methyl (Z)-3-methoxy-2-[2-methyl-5-[4-(trifluoromethyl)triazol-2-yl]phenoxy]prop-2-enoate, methyl (Z)-3-methoxy-2-[2-methyl-5-(4-propyltriazol-2-yl)phenoxy]prop-2-enoate, methyl (Z)-2-[5-(3-isopropylpyrazol-1-yl)-2-methyl-phenoxy]-3-methoxy-prop-2-enoate, methyl (Z)-3-methoxy-2-[2-methyl-5-(3-propylpyrazol-1-yl)phenoxy]prop-2-enoate, methyl (Z)-3-methoxy-2-[2-methyl-5-[3-(trifluoromethyl)pyrazol-1-yl]phenoxy]prop-2-enoate (these compounds may be prepared from the methods described in WO2020/079111), methyl (Z)-2-(5-cyclohexyl-2-methyl-phenoxy)-3-

methoxy-prop-2-enoate, methyl (Z)-2-(5-cyclopentyl-2-methyl-phenoxy)-3-methoxy-prop-2-enoate (these compounds may be prepared from the methods described in WO2020/193387), 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, 5
trinexapac, coumoxystrobin, zhongshengmycin, thiodiazole copper, zinc thiazole, amectotractin, iprodione, seboctylamine, N'-[5-bromo-2-methyl-6-[(1S)-1-methyl-2-propoxy-ethoxy]-3-pyridyl]-N-ethyl-N-methyl-formamidine, N'-[5-bromo-2-methyl-6-[(1R)-1-methyl-2-propoxy-ethoxy]-3-pyridyl]-N-ethyl-N-methyl-formamidine, N'-[5-bromo-2-methyl-6-(1-methyl-2-propoxy-ethoxy)-3-pyridyl]-N-ethyl-N-methyl-10
formamidine, N'-[5-chloro-2-methyl-6-(1-methyl-2-propoxy-ethoxy)-3-pyridyl]-N-ethyl-N-methyl-formamidine, N'-[5-bromo-2-methyl-6-(1-methyl-2-propoxy-ethoxy)-3-pyridyl]-N-isopropyl-N-methyl-formamidine (these compounds may be prepared from the methods described in WO2015/155075); N'-[5-bromo-2-methyl-6-(2-propoxypropoxy)-3-pyridyl]-N-ethyl-N-methyl-formamidine (this compound may be prepared from the methods described in IPCOM000249876D); N-isopropyl-N'-[5-methoxy-2-methyl-4-15
(2,2,2-trifluoro-1-hydroxy-1-phenyl-ethyl)phenyl]-N-methyl-formamidine, N'-[4-(1-cyclopropyl-2,2,2-trifluoro-1-hydroxy-ethyl)-5-methoxy-2-methyl-phenyl]-N-isopropyl-N-methyl-formamidine (these compounds may be prepared from the methods described in WO2018/228896); N-ethyl-N'-[5-methoxy-2-methyl-4-[(2-trifluoromethyl)oxetan-2-yl]phenyl]-N-methyl-formamidine, N-ethyl-N'-[5-methoxy-2-methyl-4-[(2-trifluoromethyl)tetrahydrofuran-2-yl]phenyl]-N-methyl-formamidine (these compounds may be prepared from the methods described in WO2019/110427); N-[(1R)-1-benzyl-3-chloro-1-methyl-but-3-enyl]-8-fluoro-20
quinoline-3-carboxamide, N-[(1S)-1-benzyl-3-chloro-1-methyl-but-3-enyl]-8-fluoro-quinoline-3-carboxamide, N-[(1R)-1-benzyl-3,3,3-trifluoro-1-methyl-propyl]-8-fluoro-quinoline-3-carboxamide, N-[(1S)-1-benzyl-3,3,3-trifluoro-1-methyl-propyl]-8-fluoro-quinoline-3-carboxamide, N-[(1R)-1-benzyl-1,3-dimethyl-butyl]-7,8-difluoro-quinoline-3-carboxamide, N-[(1S)-1-benzyl-1,3-dimethyl-butyl]-7,8-difluoro-quinoline-3-25
carboxamide, 8-fluoro-N-[(1R)-1-[(3-fluorophenyl)methyl]-1,3-dimethyl-butyl]quinoline-3-carboxamide, 8-fluoro-N-[(1S)-1-[(3-fluorophenyl)methyl]-1,3-dimethyl-butyl]quinoline-3-carboxamide, N-[(1R)-1-benzyl-1,3-dimethyl-butyl]-8-fluoro-quinoline-3-carboxamide, N-[(1S)-1-benzyl-1,3-dimethyl-butyl]-8-fluoro-quinoline-3-carboxamide, N-((1R)-1-benzyl-3-chloro-1-methyl-but-3-enyl)-8-fluoro-quinoline-3-30
carboxamide, N-((1S)-1-benzyl-3-chloro-1-methyl-but-3-enyl)-8-fluoro-quinoline-3-carboxamide (these compounds may be prepared from the methods described in WO2017/153380); 1-(6,7-dimethylpyrazolo[1,5-a]pyridin-3-yl)-4,4,5-trifluoro-3,3-dimethyl-isoquinoline, 1-(6,7-dimethylpyrazolo[1,5-a]pyridin-3-yl)-4,4,6-trifluoro-3,3-dimethyl-isoquinoline, 4,4-difluoro-3,3-dimethyl-1-(6-methylpyrazolo[1,5-a]pyridin-3-yl)isoquinoline, 4,4-difluoro-3,3-dimethyl-1-(7-methylpyrazolo[1,5-a]pyridin-3-yl)isoquinoline, 1-(6-chloro-7-methyl-pyrazolo[1,5-a]pyridin-3-yl)-4,4-difluoro-3,3-dimethyl-isoquinoline (these compounds may be prepared from the methods described in WO2017/025510); 1-(4,5-dimethylbenzimidazol-1-yl)-4,4,5-trifluoro-3,3-dimethyl-isoquinoline, 1-(4,5-dimethylbenzimidazol-1-yl)-4,4-difluoro-3,3-dimethyl-isoquinoline, 6-chloro-4,4-difluoro-3,3-dimethyl-1-(4-methylbenzimidazol-1-yl)isoquinoline, 4,4-difluoro-1-(5-fluoro-4-methyl-benzimidazol-1-yl)-3,3-dimethyl-isoquinoline, 3-(4,4-difluoro-3,3-dimethyl-1-isoquinolyl)-7,8-dihydro-6H-cyclopenta[e]benzimidazole (these compounds may be prepared from the methods described in WO2016/156085); 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-

y]]phenyl]]methyl]]propanamide, N-ethyl-2-methyl-N-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]]phenyl]]methyl]]propanamide,
 y]]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-
 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 (these compounds may be prepared from the methods described in
 10 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
 15 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
 20 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-
 25 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); (5-methyl-2-pyridyl)-[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]]phenyl]methanone, (3-methylisoxazol-5-yl)-[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]]phenyl]methanone (these compounds may be prepared from the methods described in WO
 30 2017/220485); 2-oxo-N-propyl-2-[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]]phenyl]acetamide (this compound may be prepared from the methods described in WO 2018/065414); ethyl 1-[[5-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]-2-thienyl]]methyl]]pyrazole-4-carboxylate (this compound may be prepared from the methods described in WO 2018/158365); 2,2-difluoro-N-methyl-2-[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]]phenyl]acetamide, N-[(E)-methoxyiminomethyl]-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzamide, N-[(Z)-methoxyiminomethyl]-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzamide, N-[N-methoxy-C-methyl-carbonimidoyl]-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzamide (these
 35 compounds may be prepared from the methods described in WO 2018/202428).

The following mixtures of the compounds of Formula (I) with active ingredients are preferred. The abbreviation "TX" means one compound selected from the group consisting of the compounds as
 40 represented in Tables A-1 to A-13, a compound 1.1 listed in Table T1 (below):

a compound selected from the group of substances consisting of petroleum oils + TX, 1,1-bis(4-chloro-phenyl)-2-ethoxyethanol + TX, 2,4-dichlorophenyl benzenesulfonate + TX, 2-fluoro-N-methyl-N-1-naphthylacetamide + TX, 4-chlorophenyl phenyl sulfone + TX, acetoprole + TX, aldoxycarb + TX, amidithion + TX, amidothioate + TX, amiton + TX, amiton hydrogen oxalate + TX, amitraz + TX, aramite + TX, arsenous oxide + TX, azobenzene + TX, azothoate + TX, benomyl + TX, benoxa-fos + TX, benzyl benzoate + TX, bixafen + TX, brofenvalerate + TX, bromo-cyclen + TX, bromophos + TX, bromopropylate + TX, buprofezin + TX, butocarboxim + TX, butoxycarboxim + TX, butylpyridaben + TX, calcium polysulfide + TX, camphechlor + TX, carbanolate + TX, carbophenothion + TX, cymiazole + TX, chino-methionat + TX, chlorbenside + TX, chlordimeform + TX, chlordimeform hydrochloride + TX, chlorfenethol + TX, chlorfenson + TX, chlorfensulfide + TX, chlorobenzilate + TX, chloromebuform + TX, chloromethiuron + TX, chloropropylate + TX, chlorthiophos + TX, cinerin I + TX, cinerin II + TX, cinerins + TX, closantel + TX, coumaphos + TX, crotamiton + TX, crotoxyphos + TX, cufraneb + TX, cyanthoate + TX, DCPM + TX, DDT + TX, demephion + TX, demephion-O + TX, demephion-S + TX, demeton-methyl + TX, demeton-O + TX, demeton-O-methyl + TX, demeton-S + TX, demeton-S-methyl + TX, demeton-S-methylsulfon + TX, dichlofluanid + TX, dichlorvos + TX, dicliphos + TX, dienochlor + TX, dimefox + TX, dinex + TX, dinex-diclexine + TX, dinocap-4 + TX, dinocap-6 + TX, dinocton + TX, dino-penton + TX, dinosulfon + TX, dinoterbon + TX, dioxathion + TX, diphenyl sulfone + TX, disulfiram + TX, DNOC + TX, dofenapyn + TX, doramectin + TX, endothion + TX, eprinomectin + TX, ethoate-methyl + TX, etrimfos + TX, fenazaflor + TX, fenbutatin oxide + TX, fenothiocarb + TX, fenpyrad + TX, fen-pyroximate + TX, fenpyrazamine + TX, fenson + TX, fentrifanil + TX, flubenzimine + TX, flucycloxiuron + TX, fluenetil + TX, fluorbenside + TX, FMC 1137 + TX, formetanate + TX, formetanate hydrochloride + TX, formparanate + TX, gamma-HCH + TX, glyodin + TX, halfenprox + TX, hexadecyl cyclopropanecarboxylate + TX, isocarbophos + TX, jasmolin I + TX, jasmolin II + TX, jodfenphos + TX, lindane + TX, malonoben + TX, mecarbarn + TX, mephosfolan + TX, mesulfen + TX, methacrifos + TX, methyl bromide + TX, metolcarb + TX, mexacarbate + TX, milbemycin oxime + TX, mipafox + TX, monocrotophos + TX, morphothion + TX, moxidectin + TX, naled + TX, 4-chloro-2-(2-chloro-2-methyl-propyl)-5-[(6-iodo-3-pyridyl)methoxy]pyridazin-3-one + TX, nifluridide + TX, nikkomyocins + TX, nitrilacarb + TX, nitrilacarb 1:1 zinc chloride complex + TX, omethoate + TX, oxydeprofos + TX, oxydisulfoton + TX, pp'-DDT + TX, parathion + TX, permethrin + TX, phenkapton + TX, phosalone + TX, phosfolan + TX, phosphamidon + TX, polychloroterpenes + TX, polynactins + TX, proclonol + TX, promacyl + TX, propoxur + TX, prothidathion + TX, prothoate + TX, pyrethrin I + TX, pyrethrin II + TX, pyrethrins + TX, pyridaphenthion + TX, pyrimitate + TX, quinalphos + TX, quintiofos + TX, R-1492 + TX, phosglycin + TX, rotenone + TX, schradan + TX, sebufos + TX, selamectin + TX, sophamide + TX, SSI-121 + TX, sulfiram + TX, sulfluramid + TX, sulfotep + TX, sulfur + TX, diflovidazin + TX, tau-fluvalinate + TX, TEPP + TX, terbarn + TX, tetradifon + TX, tetrasul + TX, thiafenox + TX, thiocarboxime + TX, thiofanox + TX, thiometon + TX, thioquinox + TX, thuringiensin + TX, triamiphos + TX, triarathene + TX, triazophos + TX, triazuron + TX, trifenofos + TX, trinactin + TX, vamidothion + TX, vaniliprole + TX, bethoxazin + TX, copper dioctanoate + TX, copper sulfate + TX, cybutryne + TX, dichlone + TX, dichlorophen + TX, endothal + TX, fentin + TX, hydrated lime + TX, nabarn + TX, quinoclamine + TX, quinonamid + TX, simazine + TX, triphenyltin acetate + TX, triphenyltin hydroxide + TX, crufomate + TX, piperazine + TX, thiophanate + TX, chloralose + TX, fenthion + TX, pyridin-4-amine + TX, strychnine + TX, 1-hydroxy-1H-pyridine-2-thione + TX, 4-(quinoxalin-2-ylamino)benzenesulfonamide + TX, 8-hydroxyquinoline sulfate + TX, bronopol + TX,

copper hydroxide + TX, cresol + TX, dipyrithione + TX, dodicin + TX, fenaminosulf + TX, formaldehyde + TX, hydrargaphen + TX, kasugamycin + TX, kasugamycin hydrochloride hydrate + TX, nickel bis(dimethylthiocarbamate) + TX, nitrapyrin + TX, octhilinone + TX, oxolinic acid + TX, oxytetracycline + TX, potassium hydroxyquinoline sulfate + TX, probenazole + TX, streptomycin + TX, streptomycin sesquisulfate + TX, tecloftalam + TX, thiomersal + TX, Adoxophyes orana GV + TX, Agrobacterium radiobacter + TX, Amblyseius spp. + TX, Anagrapha falcifera NPV + TX, Anagrus atomus + TX, Aphelinus abdominalis + TX, Aphidius colemani + TX, Aphidoletes aphidimyza + TX, Autographa californica NPV + TX, Bacillus sphaericus Neide + TX, Beauveria brongniartii + TX, Chrysoperla carnea + TX, Cryptolaemus montrouzieri + TX, Cydia pomonella GV + TX, Dacnusa sibirica + TX, Diglyphus isaea + TX, Encarsia formosa + TX, Eretmocerus eremicus + TX, Heterorhabditis bacteriophora and H. megidis + TX, Hippodamia convergens + TX, Leptomastix dactylopii + TX, Macrolophus caliginosus + TX, Mamestra brassicae NPV + TX, Metaphycus helvolus + TX, Metarhizium anisopliae var. acridum + TX, Metarhizium anisopliae var. anisopliae + TX, Neodiprion sertifer NPV and N. lecontei NPV + TX, Orius spp. + TX, Paecilomyces fumosoroseus + TX, Phytoseiulus persimilis + TX, Steinernema bibionis + TX, Steinernema carpocapsae + TX, Steinernema feltiae + TX, Steinernema glaseri + TX, Steinernema riobrave + TX, Steinernema riobravis + TX, Steinernema scapterisci + TX, Steinernema spp. + TX, Trichogramma spp. + TX, Typhlodromus occidentalis + TX, Verticillium lecanii + TX, apholate + TX, bisazir + TX, busulfan + TX, dimatif + TX, hemel + TX, hempa + TX, metepa + TX, methiotepa + TX, methyl apholate + TX, morzid + TX, penfluron + TX, tepa + TX, thiohempa + TX, thiotepa + TX, tretamine + TX, uredepa + TX, (E)-dec-5-en-1-yl acetate with (E)-dec-5-en-1-ol + TX, (E)-tridec-4-en-1-yl acetate + TX, (E)-6-methylhept-2-en-4-ol + TX, (E,Z)-tetradeca-4,10-dien-1-yl acetate + TX, (Z)-dodec-7-en-1-yl acetate + TX, (Z)-hexadec-11-enal + TX, (Z)-hexadec-11-en-1-yl acetate + TX, (Z)-hexadec-13-en-11-yn-1-yl acetate + TX, (Z)-icos-13-en-10-one + TX, (Z)-tetradec-7-en-1-yl acetate + TX, (Z)-tetradec-9-en-1-yl acetate + TX, (7E,9Z)-dodeca-7,9-dien-1-yl acetate + TX, (9Z,11E)-tetradeca-9,11-dien-1-yl acetate + TX, (9Z,12E)-tetradeca-9,12-dien-1-yl acetate + TX, 14-methyloctadec-1-ene + TX, 4-methylnonan-5-ol with 4-methylnonan-5-one + TX, alpha-multistriatin + TX, brevicomin + TX, codlelure + TX, codlemone + TX, cuelelure + TX, disparlure + TX, dodec-8-en-1-yl acetate + TX, dodec-9-en-1-yl acetate + TX, dodeca-8 + TX, 10-dien-1-yl acetate + TX, dominicalure + TX, ethyl 4-methyloctanoate + TX, eugenol + TX, frontaline + TX, grandlure + TX, grandlure I + TX, grandlure II + TX, grandlure III + TX, grandlure IV + TX, hexalure + TX, ipsdienol + TX, ipsenol + TX, japonilure + TX, lineatin + TX, lilture + TX, looplure + TX, medlure + TX, megatomoic acid + TX, methyl eugenol + TX, muscalure + TX, octadeca-2,13-dien-1-yl acetate + TX, octadeca-3,13-dien-1-yl acetate + TX, orfralure + TX, oryctalure + TX, ostramone + TX, siglure + TX, sordidin + TX, sulcatol + TX, tetradec-11-en-1-yl acetate + TX, trimedlure + TX, trimedlure A + TX, trimedlure B₁ + TX, trimedlure B₂ + TX, trimedlure C + TX, trunc-call + TX, 2-(octylthio)-ethanol + TX, butopyronoxyl + TX, butoxy(polypropylene glycol) + TX, dibutyl adipate + TX, dibutyl phthalate + TX, dibutyl succinate + TX, diethyltoluamide + TX, dimethyl carbate + TX, dimethyl phthalate + TX, ethyl hexanediol + TX, hexamide + TX, methoquin-butyl + TX, methylneodecanamide + TX, oxamate + TX, picaridin + TX, 1,1-dichloro-1-nitroethane + TX, 1,1-dichloro-2,2-bis(4-ethylphenyl)-ethane + TX, 1,2-dichloropropane with 1,3-dichloropropene + TX, 1-bromo-2-chloroethane + TX, 2,2,2-trichloro-1-(3,4-dichloro-phenyl)ethyl acetate + TX, 2,2-dichlorovinyl 2-ethylsulfinylethyl methyl phosphate + TX, 2-(1,3-dithiolan-2-yl)phenyl dimethylcarbamate + TX, 2-(2-butoxyethoxy)ethyl thiocyanate + TX, 2-(4,5-dimethyl-1,3-dioxolan-2-

yl)phenyl methylcarbamate + TX, 2-(4-chloro-3,5-xilyloxy)ethanol + TX, 2-chlorovinyl diethyl phosphate + TX, 2-imidazolidone + TX, 2-isovalerylindan-1,3-dione + TX, 2-methyl(prop-2-ynyl)aminophenyl methylcarbamate + TX, 2-thiocyanatoethyl laurate + TX, 3-bromo-1-chloroprop-1-ene + TX, 3-methyl-1-phenylpyrazol-5-yl dimethyl-carbamate + TX, 4-methyl(prop-2-ynyl)amino-3,5-xylol methylcarbamate + TX, 5,5-dimethyl-3-oxocyclohex-1-enyl dimethylcarbamate + TX, acethion + TX, acrylonitrile + TX, aldrin + TX, allosamidin + TX, allyxycarb + TX, alpha-ecdysone + TX, aluminium phosphide + TX, aminocarb + TX, anabasine + TX, athidathion + TX, azamethiphos + TX, *Bacillus thuringiensis* delta endotoxins + TX, barium hexafluorosilicate + TX, barium polysulfide + TX, barthrin + TX, Bayer 22/190 + TX, Bayer 22408 + TX, beta-cyfluthrin + TX, beta-cypermethrin + TX, bioethanomethrin + TX, biopermethrin + TX, bis(2-chloroethyl) ether + TX, borax + TX, bromfenvinfos + TX, bromo-DDT + TX, bufencarb + TX, butacarb + TX, butathiofos + TX, butonate + TX, calcium arsenate + TX, calcium cyanide + TX, carbon disulfide + TX, carbon tetrachloride + TX, cartap hydrochloride + TX, cevadine + TX, chlorbicyclen + TX, chlordane + TX, chlordecone + TX, chloroform + TX, chloropicrin + TX, chlorphoxim + TX, chlorprazophos + TX, cis-resmethrin + TX, cismethrin + TX, clocythrion + TX, copper acetoarsenite + TX, copper arsenate + TX, copper oleate + TX, coumithoate + TX, cryolite + TX, CS 708 + TX, cyanofenphos + TX, cyanophos + TX, cyclethrin + TX, cythioate + TX, d-tetramethrin + TX, DAEP + TX, dazomet + TX, decarbofuran + TX, diamidafos + TX, dicapthon + TX, dichlofenthion + TX, dicresyl + TX, dicyclanil + TX, dieldrin + TX, diethyl 5-methylpyrazol-3-yl phosphate + TX, dilor + TX, dimefluthrin + TX, dimetan + TX, dimethrin + TX, dimethylvinphos + TX, dimetilan + TX, dinoprop + TX, dinosam + TX, dinoseb + TX, diofenolan + TX, dioxabenzofos + TX, dithicrofos + TX, DSP + TX, ecdysterone + TX, EI 1642 + TX, EMPC + TX, EPBP + TX, etaphos + TX, ethiofencarb + TX, ethyl formate + TX, ethylene dibromide + TX, ethylene dichloride + TX, ethylene oxide + TX, EXD + TX, fenchlorphos + TX, fenethacarb + TX, fenitrothion + TX, fenoxacrim + TX, fenpirithrin + TX, fensulfothion + TX, fenthion-ethyl + TX, flucofuron + TX, fosmethilan + TX, fospirate + TX, fosthietan + TX, furathiocarb + TX, furethrin + TX, guazatine + TX, guazatine acetates + TX, sodium tetrathiocarbonate + TX, halfenprox + TX, HCH + TX, HEOD + TX, heptachlor + TX, heterophos + TX, HHDN + TX, hydrogen cyanide + TX, hyquincarb + TX, IPSP + TX, isazofos + TX, isobenzan + TX, isodrin + TX, isofenphos + TX, isolane + TX, isoprothiolane + TX, isoxathion + TX, juvenile hormone I + TX, juvenile hormone II + TX, juvenile hormone III + TX, kelevan + TX, kinoprene + TX, lead arsenate + TX, leptophos + TX, lirimfos + TX, lythidathion + TX, m-cumenyl methylcarbamate + TX, magnesium phosphide + TX, mazidox + TX, mecarphon + TX, menazon + TX, mercurous chloride + TX, mesulfenfos + TX, metam + TX, metam-potassium + TX, metam-sodium + TX, methanesulfonyl fluoride + TX, methocrotophos + TX, methoprene + TX, methothrin + TX, methoxychlor + TX, methyl isothiocyanate + TX, methylchloroform + TX, methylene chloride + TX, metoxadiazone + TX, mirex + TX, naftalofos + TX, naphthalene + TX, NC-170 + TX, nicotine + TX, nicotine sulfate + TX, nithiazine + TX, normicotine + TX, O-5-dichloro-4-iodophenyl O-ethyl ethylphosphonothioate + TX, O,O-diethyl O-4-methyl-2-oxo-2H-chromen-7-yl phosphorothioate + TX, O,O-diethyl O-6-methyl-2-propylpyrimidin-4-yl phosphorothioate + TX, O,O,O',O'-tetrapropyl dithiopyrophosphate + TX, oleic acid + TX, para-dichlorobenzene + TX, parathion-methyl + TX, pentachlorophenol + TX, pentachlorophenyl laurate + TX, PH 60-38 + TX, phenkapton + TX, phosnichlor + TX, phosphine + TX, phoxim-methyl + TX, pirimetaphos + TX, polychlorodicyclopentadiene isomers + TX, potassium arsenite + TX, potassium thiocyanate + TX, precocene I + TX, precocene II + TX, precocene III + TX, primidophos + TX, profluthrin + TX, promecarb + TX, prothiofos + TX, pyrazophos + TX, pyresmethrin

+ TX, quassia + TX, quinalphos-methyl + TX, quinothion + TX, rafoxanide + TX, resmethrin + TX, rotenone + TX, kadethrin + TX, ryania + TX, ryanodine + TX, sabadilla + TX, schradan + TX, sebufos + TX, SI-0009 + TX, thiapronil + TX, sodium arsenite + TX, sodium cyanide + TX, sodium fluoride + TX, sodium hexafluorosilicate + TX, sodium pentachlorophenoxide + TX, sodium selenate + TX, sodium thiocyanate + TX, sulcofuron + TX, sulcofuron-sodium + TX, sulfuryl fluoride + TX, sulprofos + TX, tar oils + TX, tazimcarb + TX, TDE + TX, tebufos + TX, temephos + TX, terallethrin + TX, tetrachloroethane + TX, thicofos + TX, thiocyclam + TX, thiocyclam hydrogen oxalate + TX, thionazin + TX, thiosultap + TX, thiosultap-sodium + TX, tralomethrin + TX, transpermethrin + TX, triazamate + TX, trichlormetaphos-3 + TX, trichloronat + TX, trimethacarb + TX, tolprocarb + TX, triclopyricarb + TX, triprene + TX, veratridine + TX, veratrine + TX, XMC + TX, zetamethrin + TX, zinc phosphide + TX, zolaprofos + TX, meperfluthrin + TX, tetramethylfluthrin + TX, bis(tributyltin) oxide + TX, bromoacetamide + TX, ferric phosphate + TX, niclosamide-olamine + TX, tributyltin oxide + TX, pyrimorph + TX, trifenmorph + TX, 1,2-dibromo-3-chloropropane + TX, 1,3-dichloropropene + TX, 3,4-dichlorotetrahydrothio-phene 1,1-dioxide + TX, 3-(4-chlorophenyl)-5-methylrhodanine + TX, 5-methyl-6-thioxo-1,3,5-thiadiazinan-3-ylacetic acid + TX, 6-isopentenylaminopurine + TX, anisiflupurin + TX, benclotiaz + TX, cytokinins + TX, DCIP + TX, furfural + TX, isamidofos + TX, kinetin + TX, Myrothecium verrucaria composition + TX, tetrachlorothiophene + TX, xylenols + TX, zeatin + TX, potassium ethylxanthate + TX, acibenzolar + TX, acibenzolar-S-methyl + TX, Reynoutria sachalinensis extract + TX, alpha-chlorohydrin + TX, antu + TX, barium carbonate + TX, bithiosemi + TX, brodifacoum + TX, bromadiolone + TX, bromethalin + TX, chlorophacinone + TX, cholecalciferol + TX, coumachlor + TX, coumafuryl + TX, coumatetralyl + TX, crimidine + TX, difenacoum + TX, difethialone + TX, diphacinone + TX, ergocalciferol + TX, flocoumafen + TX, fluoroacetamide + TX, flupropradine + TX, flupropradine hydrochloride + TX, norbormide + TX, phosacetim + TX, phosphorus + TX, pindone + TX, pyrinuron + TX, scilliroside + TX, -sodium fluoroacetate + TX, thallium sulfate + TX, warfarin + TX, -2-(2-butoxyethoxy)ethyl piperonylate + TX, 5-(1,3-benzodioxol-5-yl)-3-hexylcyclohex-2-enone + TX, farnesol with nerolidol + TX, verbutin + TX, MGK 264 + TX, piperonyl butoxide + TX, piprotal + TX, propyl isomer + TX, S421 + TX, sesamex + TX, sesasmolin + TX, sulfoxide + TX, anthraquinone + TX, copper naphthenate + TX, copper oxychloride + TX, dicyclopentadiene + TX, thiram + TX, zinc naphthenate + TX, ziram + TX, imanin + TX, ribavirin + TX, chloroinconazole + TX, mercuric oxide + TX, thiophanate-methyl + TX, azaconazole + TX, bitertanol + TX, bromuconazole + TX, cyproconazole + TX, difenoconazole + TX, diniconazole -+ TX, epoxiconazole + TX, fenbuconazole + TX, fluquinconazole + TX, flusilazole + TX, flutriafol + TX, furametpyr + TX, hexaconazole + TX, imazalil- + TX, imiben-conazole + TX, ipconazole + TX, metconazole + TX, myclobutanil + TX, paclobutrazole + TX, pefurazoate + TX, penconazole + TX, prothioconazole + TX, pyrifenox + TX, prochloraz + TX, propiconazole + TX, pyrisoxazole + TX, -simeconazole + TX, tebuconazole + TX, tetraconazole + TX, triadimefon + TX, triadimenol + TX, triflumizole + TX, triticonazole + TX, ancymidol + TX, fenarimol + TX, nuarimol + TX, bupirimate + TX, dimethirimol + TX, ethirimol + TX, dodemorph + TX, fenpropidin + TX, fenpropimorph + TX, spiroxamine + TX, tridemorph + TX, cyprodinil + TX, mepanipyrim + TX, pyrimethanil + TX, fenciclonil + TX, fludioxonil + TX, benalaxyl + TX, furalaxyl + TX, metalaxyl + TX, R-metalaxyl + TX, ofurace + TX, oxadixyl + TX, carbendazim + TX, debacarb + TX, fuberidazole -+ TX, thiabendazole + TX, chlozolinate + TX, dichlozoline + TX, myclozoline- + TX, procymidone + TX, vinclozoline + TX, boscalid + TX, carboxin + TX, fenfuram + TX, flutolanil + TX, mepronil + TX, oxycarboxin + TX, penthiopyrad + TX, thifluzamide + TX, dodine + TX,

iminocadine + TX, azoxystrobin + TX, dimoxystrobin + TX, enestroburin + TX, fenaminstrobin + TX, flufenoxystrobin + TX, fluoxastrobin + TX, kresoxim--methyl + TX, metominostrobin + TX, trifloxystrobin + TX, orysastrobin + TX, picoxystrobin + TX, pyraclostrobin + TX, pyrametostrobin + TX, pyraoxystrobin + TX, ferbam + TX, mancozeb + TX, maneb + TX, metiram + TX, propineb + TX, zineb + TX, captafol + TX, 5 captan + TX, fluoroimide + TX, folpet + TX, tolylfluanid + TX, bordeaux mixture + TX, copper oxide + TX, mancopper + TX, oxine-copper + TX, nitrothal-isopropyl + TX, edifenphos + TX, iprobenphos + TX, phosdiphen + TX, tolclofos-methyl + TX, anilazine + TX, benthiavalicarb + TX, blasticidin-S + TX, chloroneb + TX, chloro-tha-lonil + TX, cyflufenamid + TX, cymoxanil + TX, cyclobutrifluram + TX, diclocymet + TX, diclomezine + TX, dicloran + TX, diethofencarb + TX, dimethomorph + TX, flumorph + TX, dithianon + TX, ethaboxam + TX, etridiazole + TX, famoxadone + TX, fenamidone + TX, fenoxanil + TX, ferimzone + TX, fluazinam + TX, flumetylsulfurim + TX, fluopicolide + TX, fluoxytioconazole + TX, flusulfamide + TX, fluxapyroxad + TX, -fenhexamid + TX, fosetyl-aluminium + TX, hymexazol + TX, iprovalicarb + TX, cyazofamid + TX, methasulfocarb + TX, metrafenone + TX, pencycuron + TX, phthalide + TX, polyoxins + TX, propamocarb + TX, pyribencarb + TX, proquinazid + TX, pyroquilon + TX, pyriofenone + TX, quinoxyfen + TX, 15 + TX, quintozene + TX, tiadinil + TX, triazoxide + TX, tricyclazole + TX, triforine + TX, validamycin + TX, valifenalate + TX, zoxamide + TX, mandipropamid + TX, flubeneteram + TX, isopyrazam + TX, sedaxane + TX, benzovindiflupyr + TX, pydiflumetofen + TX, 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (3',4',5'-trifluoro-biphenyl-2-yl)-amide + TX, isoflucypram + TX, isotianil + TX, dipymetrone + TX, 6-ethyl-5,7-dioxo-pyrrolo[4,5][1,4]dithiino[1,2-c]isothiazole-3-carbonitrile + TX, 2-(difluoromethyl)-N-[3-ethyl-1,1-dimethyl-indan-4-yl]pyridine-3-carboxamide + TX, 4-(2,6-difluorophenyl)-6-methyl-5-phenyl-pyridazine-3-carbonitrile + TX, (R)-3-(difluoromethyl)-1-methyl-N-[1,1,3-trimethylindan-4-yl]pyrazole-4-carboxamide + TX, 4-(2-bromo-4-fluoro-phenyl)-N-(2-chloro-6-fluoro-phenyl)-2,5-dimethyl-pyrazol-3-amine + TX, 4-(2-bromo-4-fluorophenyl)-N-(2-chloro-6-fluorophenyl)-1,3-dimethyl-1H-pyrazol-5-amine + TX, fluindapyr + TX, coumethoxystrobin (jiaxiangjunzhi) + TX, lvbenmixianan + TX, dichlobentiazox + TX, 25 mandestrobin + TX, 3-(4,4-difluoro-3,4-dihydro-3,3-dimethylisoquinolin-1-yl)quinolone + TX, 2-[2-fluoro-6-[(8-fluoro-2-methyl-3-quinolyl)oxy]phenyl]propan-2-ol + TX, oxathiapiprolin + TX, tert-butyl N-[6-[[[(1-methyltetrazol-5-yl)-phenyl-methylene]amino]oxymethyl]-2-pyridyl]carbamate + TX, pyraziflumid + TX, inpyrfluxam + TX, trolprocarb + TX, mefentrifluconazole + TX, ipfentrifluconazole + TX, 2-(difluoromethyl)-N-[(3R)-3-ethyl-1,1-dimethyl-indan-4-yl]pyridine-3-carboxamide + TX, N'-(2,5-dimethyl-4-phenoxy-phenyl)-N-ethyl-N-methyl-formamidine + TX, N'-[4-(4,5-dichlorothiazol-2-yl)oxy-2,5-dimethyl-phenyl]-N-ethyl-N-methyl-formamidine + TX, [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]methanesulfonate + TX, but-3-ynyl N-[6-[[[(Z)-[(1-methyltetrazol-5-yl)-phenyl-methylene]amino]oxymethyl]-2-pyridyl]carbamate + TX, methyl N-[[5-[4-(2,4-dimethylphenyl)triazol-2-yl]-2-methyl-phenyl]methyl]carbamate + TX, 3-chloro-6-methyl-5-phenyl-4-(2,4,6-trifluorophenyl)pyridazine + TX, pyridachlometyl + TX, 3-(difluoromethyl)-1-methyl-N-[1,1,3-trimethylindan-4-yl]pyrazole-4-carboxamide + TX, 1-[2-[[1-(4-chlorophenyl)pyrazol-3-yl]oxymethyl]-3-methyl-phenyl]-4-methyl-tetrazol-5-one + TX, 1-methyl-4-[3-methyl-2-[[2-methyl-4-(3,4,5-trimethylpyrazol-1-yl)phenoxy]methyl]phenyl]tetrazol-5-one + TX, aminopyrifen + TX, ametocradin + TX, amisulbrom + TX, penflufen + TX, (Z,E)-5-[1-(4-chlorophenyl)pyrazol-3-yl]oxy-2-methoxyimino-N,3-dimethyl-pent-3-enamide + TX, florylpicoxamid + TX, fempicoxamid + TX, metarylpicoxamid + TX, tebufloquin + TX, 40 ipflufenoquin + TX, quinofumelin + TX, isofetamid + TX, ethyl 1-[[4-[[2-(trifluoromethyl)-1,3-dioxolan-2-

yl]methoxy]phenyl]methyl]pyrazole-3-carboxylate + TX (may be prepared from the methods described in WO 2020/056090), ethyl 1-[[4-[(Z)-2-ethoxy-3,3,3-trifluoro-prop-1-enoxy]phenyl]methyl]pyrazole-3-carboxylate + TX (may be prepared from the methods described in WO 2020/056090), methyl N-[[4-[1-(4-cyclopropyl-2,6-difluoro-phenyl)pyrazol-4-yl]-2-methyl-phenyl]methyl]carbamate + TX (may be prepared from the methods described in WO 2020/097012), methyl N-[[4-[1-(2,6-difluoro-4-isopropyl-phenyl)pyrazol-4-yl]-2-methyl-phenyl]methyl]carbamate + TX (may be prepared from the methods described in WO 2020/097012), 6-chloro-3-(3-cyclopropyl-2-fluoro-phenoxy)-N-[2-(2,4-dimethylphenyl)-2,2-difluoro-ethyl]-5-methyl-pyridazine-4-carboxamide + TX (may be prepared from the methods described in WO 2020/109391), 6-chloro-N-[2-(2-chloro-4-methyl-phenyl)-2,2-difluoro-ethyl]-3-(3-cyclopropyl-2-fluoro-phenoxy)-5-methyl-pyridazine-4-carboxamide + TX (may be prepared from the methods described in WO 2020/109391), 6-chloro-3-(3-cyclopropyl-2-fluoro-phenoxy)-N-[2-(3,4-dimethylphenyl)-2,2-difluoro-ethyl]-5-methyl-pyridazine-4-carboxamide + TX (may be prepared from the methods described in WO 2020/109391), N-[2-[2,4-dichloro-phenoxy]phenyl]-3-(difluoromethyl)-1-methyl-pyrazole-4-carboxamide + TX, N-[2-[2-chloro-4-(trifluoromethyl)phenoxy]phenyl]-3-(difluoromethyl)-1-methyl-pyrazole-4-carboxamide + TX, benzothiostrubin + TX, phenamacril + TX, 5-amino-1,3,4-thiadiazole-2-thiol zinc salt (2:1) + TX, fluopyram + TX, flufenoxadiazam + TX, flutianil + TX, fluopimomide + TX, pyrapropoyne + TX, picarbutrazox + TX, 2-(difluoromethyl)-N-(3-ethyl-1,1-dimethyl-indan-4-yl)pyridine-3-carboxamide + TX, 2-(difluoromethyl) - N- ((3R) - 1, 1, 3- trimethylindan- 4- yl) pyridine- 3- carboxamide + TX, 4-[[6-[2-(2,4-difluorophenyl)-1,1-difluoro-2-hydroxy-3-(1,2,4-triazol-1-yl)propyl]-3-pyridyl]oxy]benzotrile + TX, metyltetraprole + TX, 2- (difluoromethyl) - N- ((3R) - 1, 1, 3- trimethylindan- 4- yl) pyridine- 3- carboxamide + TX, α - (1, 1- dimethylethyl) - α - [4'- (trifluoromethoxy) [1, 1'- biphenyl] - 4- yl] -5- pyrimidinemethanol + TX, fluoxapiprolin + TX, enoxastrobin + TX, methyl (Z)-3-methoxy-2-[2-methyl-5-[4-(trifluoromethyl)triazol-2-yl]phenoxy]prop-2-enoate + TX, methyl (Z)-3-methoxy-2-[2-methyl-5-(4-propyltriazol-2-yl)phenoxy]prop-2-enoate + TX, methyl (Z)-2-[5-(3-isopropylpyrazol-1-yl)-2-methyl-phenoxy]-3-methoxy-prop-2-enoate + TX, methyl (Z)-3-methoxy-2-[2-methyl-5-(3-propylpyrazol-1-yl)phenoxy]prop-2-enoate + TX, methyl (Z)-3-methoxy-2-[2-methyl-5-[3-(trifluoromethyl)pyrazol-1-yl]phenoxy]prop-2-enoate + TX (these compounds may be prepared from the methods described in WO2020/079111), methyl (Z)-2-(5-cyclohexyl-2-methyl-phenoxy)-3-methoxy-prop-2-enoate + TX, methyl (Z)-2-(5-cyclopentyl-2-methyl-phenoxy)-3-methoxy-prop-2-enoate + TX (these compounds may be prepared from the methods described in WO2020/193387), 4-[[6-[2-(2,4-difluorophenyl)-1,1-difluoro-2-hydroxy-3-(1,2,4-triazol-1-yl)propyl]-3-pyridyl]oxy] benzonitrile + TX, 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 + TX, 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 + TX, trinexapac + TX, coumoxystrobin + TX, zhongshengmycin + TX, thiodiazole copper + TX, zinc thiazole + TX, amectotractin + TX, iprodione + TX, seboctylamine + TX; N'-[5-bromo-2-methyl-6-[(1S)-1-methyl-2-propoxy-ethoxy]-3-pyridyl]-N-ethyl-N-methyl-formamidine + TX, N'-[5-bromo-2-methyl-6-[(1R)-1-methyl-2-propoxy-ethoxy]-3-pyridyl]-N-ethyl-N-methyl-formamidine + TX, N'-[5-bromo-2-methyl-6-(1-methyl-2-propoxy-ethoxy)-3-pyridyl]-N-ethyl-N-methyl-formamidine + TX, N'-[5-chloro-2-methyl-6-(1-methyl-2-propoxy-ethoxy)-3-pyridyl]-N-ethyl-N-methyl-formamidine + TX, N'-[5-bromo-2-methyl-6-(1-methyl-2-propoxy-ethoxy)-3-pyridyl]-N-isopropyl-N-methyl-formamidine + TX (these compounds may be prepared from the methods described in WO2015/155075); N'-[5-bromo-2-methyl-6-(2-propoxypropoxy)-3-pyridyl]-N-ethyl-N-methyl-formamidine + TX (this compound may be prepared from

the methods described in IPCOM000249876D); N-isopropyl-N'-[5-methoxy-2-methyl-4-(2,2,2-trifluoro-1-hydroxy-1-phenyl-ethyl)phenyl]-N-methyl-formamidine + TX, N'-[4-(1-cyclopropyl-2,2,2-trifluoro-1-hydroxy-ethyl)-5-methoxy-2-methyl-phenyl]-N-isopropyl-N-methyl-formamidine + TX (these compounds may be prepared from the methods described in WO2018/228896); N-ethyl-N'-[5-methoxy-2-methyl-4-[(2-trifluoromethyl)oxetan-2-yl]phenyl]-N-methyl-formamidine + TX, N-ethyl-N'-[5-methoxy-2-methyl-4-[(2-trifluoromethyl)tetrahydrofuran-2-yl]phenyl]-N-methyl-formamidine + TX (these compounds may be prepared from the methods described in WO2019/110427); N-[(1R)-1-benzyl-3-chloro-1-methyl-but-3-enyl]-8-fluoro-quinoline-3-carboxamide + TX, N-[(1S)-1-benzyl-3-chloro-1-methyl-but-3-enyl]-8-fluoro-quinoline-3-carboxamide + TX, N-[(1R)-1-benzyl-3,3,3-trifluoro-1-methyl-propyl]-8-fluoro-quinoline-3-carboxamide + TX, N-[(1S)-1-benzyl-3,3,3-trifluoro-1-methyl-propyl]-8-fluoro-quinoline-3-carboxamide + TX, N-[(1R)-1-benzyl-1,3-dimethyl-butyl]-7,8-difluoro-quinoline-3-carboxamide + TX, N-[(1S)-1-benzyl-1,3-dimethyl-butyl]-7,8-difluoro-quinoline-3-carboxamide + TX, 8-fluoro-N-[(1R)-1-[(3-fluorophenyl)methyl]-1,3-dimethyl-butyl]quinoline-3-carboxamide + TX, 8-fluoro-N-[(1S)-1-[(3-fluorophenyl)methyl]-1,3-dimethyl-butyl]quinoline-3-carboxamide + TX, N-[(1R)-1-benzyl-1,3-dimethyl-butyl]-8-fluoro-quinoline-3-carboxamide + TX, N-[(1S)-1-benzyl-1,3-dimethyl-butyl]-8-fluoro-quinoline-3-carboxamide + TX, N-[(1R)-1-benzyl-3-chloro-1-methyl-but-3-enyl]-8-fluoro-quinoline-3-carboxamide + TX, N-[(1S)-1-benzyl-3-chloro-1-methyl-but-3-enyl]-8-fluoro-quinoline-3-carboxamide + TX (these compounds may be prepared from the methods described in WO2017/153380); 1-(6,7-dimethylpyrazolo[1,5-a]pyridin-3-yl)-4,4,5-trifluoro-3,3-dimethyl-isoquinoline + TX, 1-(6,7-dimethylpyrazolo[1,5-a]pyridin-3-yl)-4,4,6-trifluoro-3,3-dimethyl-isoquinoline + TX, 4,4-difluoro-3,3-dimethyl-1-(6-methylpyrazolo[1,5-a]pyridin-3-yl)isoquinoline + TX, 4,4-difluoro-3,3-dimethyl-1-(7-methylpyrazolo[1,5-a]pyridin-3-yl)isoquinoline + TX, 1-(6-chloro-7-methylpyrazolo[1,5-a]pyridin-3-yl)-4,4-difluoro-3,3-dimethyl-isoquinoline + TX (these compounds may be prepared from the methods described in WO2017/025510); 1-(4,5-dimethylbenzimidazol-1-yl)-4,4,5-trifluoro-3,3-dimethyl-isoquinoline + TX, 1-(4,5-dimethylbenzimidazol-1-yl)-4,4-difluoro-3,3-dimethyl-isoquinoline + TX, 6-chloro-4,4-difluoro-3,3-dimethyl-1-(4-methylbenzimidazol-1-yl)isoquinoline + TX, 4,4-difluoro-1-(5-fluoro-4-methyl-benzimidazol-1-yl)-3,3-dimethyl-isoquinoline + TX, 3-(4,4-difluoro-3,3-dimethyl-1-isoquinolyl)-7,8-dihydro-6H-cyclopenta[e]benzimidazole + TX (these compounds may be prepared from the methods described in WO2016/156085); N-methoxy-N-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]cyclopropanecarboxamide + TX, N,2-dimethoxy-N-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]propanamide + TX, N-ethyl-2-methyl-N-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]propanamide + TX, 1-methoxy-3-methyl-1-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]urea + TX, 1,3-dimethoxy-1-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]urea + TX, 3-ethyl-1-methoxy-1-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]urea + TX, N-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]propanamide + TX, 4,4-dimethyl-2-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]isoxazolidin-3-one + TX, 5,5-dimethyl-2-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]isoxazolidin-3-one + TX, ethyl 1-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]pyrazole-4-carboxylate + TX, N,N-dimethyl-1-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]-1,2,4-triazol-3-amine + TX. The compounds in this paragraph 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 + TX (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 + TX (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 + TX (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 + TX (this compound may be prepared from the methods described in WO 2016/156290); (4-phenoxyphenyl)methyl 2-amino-6-methyl-pyridine-3-carboxylate + TX (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 + TX (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 + TX; N-methyl-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzamide + TX; (Z,2E)-5-[1-(2,4-dichlorophenyl)pyrazol-3-yl]oxy-2-methoxyimino-N,3-dimethyl-pent-3-enamide + TX (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 + TX; N'-[2-chloro-4-(2-fluorophenoxy)-5-methyl-phenyl]-N-ethyl-N-methyl-formamidine + TX (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 + TX (this compound may be prepared from the methods described in WO 2014/095675); (5-methyl-2-pyridyl)-[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methanone + TX, (3-methylisoxazol-5-yl)-[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methanone + TX (these compounds may be prepared from the methods described in WO 2017/220485); 2-oxo-N-propyl-2-[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]acetamide + TX (this compound may be prepared from the methods described in WO 2018/065414); ethyl 1-[[5-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]-2-thienyl]methyl]pyrazole-4-carboxylate + TX (this compound may be prepared from the methods described in WO 2018/158365); 2,2-difluoro-N-methyl-2-[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]acetamide + TX, N-[(E)-methoxyiminomethyl]-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzamide + TX, N-[(Z)-methoxyiminomethyl]-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzamide + TX, N-[N-methoxy-C-methyl-carbonimidoyl]-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzamide + TX (these compounds may be prepared from the methods described in WO 2018/202428).

The references in brackets behind the active ingredients, e.g. [3878-19-1] refer to the Chemical Abstracts Registry number. The above described mixing partners are known. Where the active ingredients are included in "The Pesticide Manual" [The Pesticide Manual - A World Compendium; Thirteenth Edition; Editor: C. D. S. Tomlin; The British Crop Protection Council], they are described therein under the entry number given in round brackets hereinabove for the particular compound; for example, the compound "abamectin" is described under entry number (1). Where "[CCN]" is added hereinabove to the particular compound, the compound in question is included in the "Compendium of Pesticide Common Names", which is accessible on the internet [A. Wood; Compendium of Pesticide Common Names, Copyright © 1995-2004]; for example, the compound "acetoprole" is described under the internet address <http://www.alanwood.net/pesticides/acetoprole.html>.

Most of the active ingredients described above are referred to hereinabove by a so-called "common name", the relevant "ISO common name" or another "common name" being used in individual cases. If the designation is not a "common name", the nature of the designation used instead is given in round brackets for the particular compound; in that case, the IUPAC name, the IUPAC/Chemical Abstracts name, a

"chemical name", a "traditional name", a "compound name" or a "development code" is used or, if neither one of those designations nor a "common name" is used, an "alternative name" is employed. "CAS Reg. No" means the Chemical Abstracts Registry Number.

5 The active ingredient mixture of the compounds of formula (I) selected from one compound as represented in Tables A-1 to A-13 (below), or compound 1.1 listed in Table T1 (below), is preferably in a mixing ratio of from 100:1 to 1:6000, especially from 50:1 to 1:50, more especially in a ratio of from 20:1 to 1:20, even more especially from 10:1 to 1:10, very especially from 5:1 and 1:5, special preference being given to a ratio of from 2:1 to 1:2, and a ratio of from 4:1 to 2:1 being likewise preferred, above all in a ratio of 1:1, or 5:1, or 5:2, or 5:3, or 5:4, or 4:1, or 4:2, or 4:3, or 3:1, or 3:2, or 2:1, or 1:5, or 2:5, or 3:5, or 4:5, or 1:4, or 10 2:4, or 3:4, or 1:3, or 2:3, or 1:2, or 1:600, or 1:300, or 1:150, or 1:35, or 2:35, or 4:35, or 1:75, or 2:75, or 4:75, or 1:6000, or 1:3000, or 1:1500, or 1:350, or 2:350, or 4:350, or 1:750, or 2:750, or 4:750. Those mixing ratios are by weight.

The mixtures as described above can be used in a method for controlling pests, which comprises applying a composition comprising a mixture as described above to the pests or their environment, with the exception 15 of a method for treatment of the human or animal body by surgery or therapy and diagnostic methods practised on the human or animal body.

The mixtures comprising a compound as represented in Tables A-1 to A-13 (below), or compound 1.1 listed in Table T1 (below), and one or more active ingredients as described above can be applied, for example, in a single "ready-mix" form, in a combined spray mixture composed from separate formulations of the 20 single active ingredient components, such as a "tank-mix", and in a combined use of the single active ingredients when applied in a sequential manner, i.e. one after the other with a reasonably short period, such as a few hours or days. The order of applying a compound as represented in in Tables A-1 to A-13 (below), or compound 1.1 listed in Table T1 (below) and the active ingredient(s) as described above, is not essential for working the present invention.

25 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 30 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 35 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 96/15121 and also with anthelmintic active cyclic depsipeptides such as those described in WO 96/11945, WO 93/19053, WO 93/25543, EP 0 626 375, EP 0 382 173, WO 94/19334, EP 0 382 173, and EP 0 503 538.

5 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 International Patent Application Publication Numbers WO 95/19363 or WO 04/72086,
10 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-
15 methyl, demeton-S-methyl sulphone, dialifos, diazinon, dichlorvos, dicrotophos, dimethoate, disulfoton, ethion, ethoprophos, etrimfos, famphur, fenamiphos, fenitrothion, fensulfothion, fenthion, flupyrazofos, 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,
20 phosphocarb, phosmet, phosphamidon, phorate, phoxim, pirimiphos, pirimiphos-methyl, profenofos, propaphos, proetamphos, prothiofos, pyraclofos, pyridapenthion, quinalphos, sulprophos, temephos, terbufos, tebutirimfos, tetrachlorvinphos, thimeton, triazophos, trichlorfon, vamidothion.

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

Pyrethroids: acrinathin, allethrin, alphamethrin, 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,
30 cycloprothrin, cyhalothrin, cythithrin, cyphenothrin, deltamethrin, empenethrin, 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.

35 Arthropod growth regulators: a) chitin synthesis inhibitors: benzoylureas: chlorfluazuron, diflubenzuron, fluazuron, flucyclohexuron, 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: spiroadiclofen.

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, flubrocycytrinate, flufenzine, flufenprox, fluproxyfen, halofenprox, hydramethylnon, IKI-220, kanemite, NC-196, neem guard, nidinorterfuran, nitenpyram, SD-35651, WL-108477, pirydaryl, propargite, protrifenbute, pymethrozone, pyridaben, pyrimidifen, NC-1111, R-195, RH-0345, RH-2485, RYI-210, S-1283, S-1833, SI-8601, silafluofen, silomadine, spinosad, tebufenpyrad, tetradifon, tetranactin, thiachlopid, 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, praziquarantel, triclabendazole.

The compositions according to the invention can also comprise further solid or liquid auxiliaries, such as stabilizers, for example unepoxidized or epoxidized vegetable oils (for example epoxidized coconut oil, rapeseed oil or soya oil), antifoams, for example silicone oil, preservatives, viscosity regulators, binders and/or tackifiers, fertilizers or other active ingredients for achieving specific effects, for example bactericides, fungicides, nematocides, plant activators, molluscicides or herbicides.

The compositions according to the invention are prepared in a manner known per se, in the absence of auxiliaries for example by grinding, screening and/or compressing a solid active ingredient and in the presence of at least one auxiliary for example by intimately mixing and/or grinding the active ingredient with the auxiliary (auxiliaries). These processes for the preparation of the compositions and the use of the compounds (I) for the preparation of these compositions are also a subject of the invention.

Another aspect of the invention is related to the use of a compound of Formula (I) or of a preferred individual compound as defined herein, 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 the 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 or spoilage by phytopathogenic 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.

The term "g a.i./ha" as used herein refer to the application rate given in gram [g] of active ingredient [a.i.] per unit of surface [ha]. The unit hectare (symbol ha) is the metric unit of area that equals a square with 100 m side (1 hm²) or 10,000 square meters. Hectare is a commonly used unit of area in the metric system.

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.

Suitably, a composition comprising a compound of formula (I) according to the present invention is applied either preventative, meaning prior to disease development or curative, meaning after disease development.

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) optionally together with 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.

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

The compounds according to the following Tables A-1 to A-13 below can be prepared following the methods described above. The examples which follow are intended to illustrate the invention and show preferred compounds of formula (I), wherein R¹ is as defined in Tables A-1 to A-13; and R² and G are as defined in Table G below.

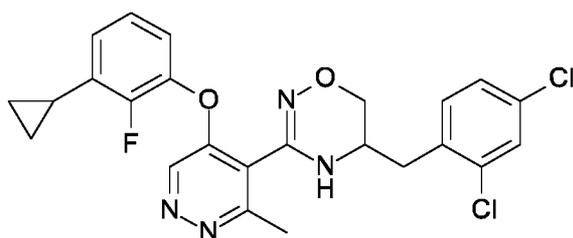
Table G

No.	G	R ²	No.	G	R ²
1	2,4-dimethylphenyl	methyl	25	2,4-dimethylphenyl	ethyl
2	2,4-dichlorophenyl	methyl	26	2,4-dichlorophenyl	ethyl
3	4-bromo-2-methylphenyl	methyl	27	4-bromo-2-methylphenyl	ethyl
4	4-bromo-2-chlorophenyl	methyl	28	4-bromo-2-chlorophenyl	ethyl
5	2,6-dichloro-3-pyridyl	methyl	29	2,6-dichloro-3-pyridyl	ethyl
6	4,6-dichloro-3-pyridyl	methyl	30	4,6-dichloro-3-pyridyl	ethyl

No.	G	R ²	No.	G	R ²
7	3,5-dichloro-2-pyridyl	methyl	31	3,5-dichloro-2-pyridyl	ethyl
8	3,4-dimethylphenyl	methyl	32	3,4-dimethylphenyl	ethyl
9	2-chloro-4-methylphenyl	methyl	33	2-chloro-4-methylphenyl	ethyl
10	2-methyl-4-bromophenyl	methyl	34	2-methyl-4-bromophenyl	ethyl
11	2-methyl-4-chlorophenyl	methyl	35	2-methyl-4-chlorophenyl	ethyl
12	2,4-difluorophenyl	methyl	36	2,4-difluorophenyl	ethyl
13	2,4-dimethylphenyl	hydrogen	37	2,4-dimethylphenyl	cyclopropyl
14	2,4-dichlorophenyl	hydrogen	38	2,4-dichlorophenyl	cyclopropyl
15	4-bromo-2-methylphenyl	hydrogen	39	4-bromo-2-methylphenyl	cyclopropyl
16	4-bromo-2-chlorophenyl	hydrogen	40	4-bromo-2-chlorophenyl	cyclopropyl
17	2,6-dichloro-3-pyridyl	hydrogen	41	2,6-dichloro-3-pyridyl	cyclopropyl
18	4,6-dichloro-3-pyridyl	hydrogen	42	4,6-dichloro-3-pyridyl	cyclopropyl
19	3,5-dichloro-2-pyridyl	hydrogen	43	3,5-dichloro-2-pyridyl	cyclopropyl
20	3,4-dimethylphenyl	hydrogen	44	3,4-dimethylphenyl	cyclopropyl
21	2-chloro-4-methylphenyl	hydrogen	45	2-chloro-4-methylphenyl	cyclopropyl
22	2-methyl-4-bromophenyl	hydrogen	46	2-methyl-4-bromophenyl	cyclopropyl
23	2-methyl-4-chlorophenyl	hydrogen	47	2-methyl-4-chlorophenyl	cyclopropyl
24	2,4-difluorophenyl	hydrogen	48	2,4-difluorophenyl	cyclopropyl

Table A-1: This table provides 48 compounds A-1.01 and A-1.48 of formula (I) wherein R¹ is 3-cyclopropyl-2-fluorophenyl and substituents R² and G are as defined in Table G above.

As an example, compound A-1.02 is:



(A-1.02)

5

Table A-2: This table provides 48 compounds A-2.01 and A-2.48 of formula (I) wherein R¹ is 3-(trifluoromethyl)phenyl and substituents R² and G are as defined in Table G above.

Table A-3: This table provides 48 compounds A-3.01 and A-3.48 of formula (I) wherein R¹ is 3-chloro-2-fluorophenyl and substituents R² and G are as defined in Table G above.

10 **Table A-4:** This table provides 48 compounds A-4.01 and A-4.48 of formula (I) wherein R¹ is 3-chlorophenyl and substituents R² and G are as defined in Table G above.

Table A-5: This table provides 48 compounds A-5.01 and A-5.48 of formula (I) wherein R¹ is 5-cyanopyridin-3-yl and substituents R² and G are as defined in Table G above.

Table A-6: This table provides 48 compounds A-6.01 and A-6.48 of formula (I) wherein R¹ is 3-methylphenyl and substituents R² and G are as defined in Table G above.

Table A-7: This table provides 48 compounds A-7.01 and A-7.48 of formula (I) wherein R¹ is phenyl and substituents R² and G are as defined in Table G above.

5 Table A-8: This table provides 48 compounds A-8.01 and A-8.48 of formula (I) wherein R¹ is 3-cyclopropylphenyl and substituents R² and G are as defined in Table G above.

Table A-9: This table provides 48 compounds A-9.01 and A-9.48 of formula (I) wherein R¹ is 3-(difluoromethyl)phenyl and substituents R² and G are as defined in Table G above.

10 Table A-10: This table provides 48 compounds A-10.01 and A-10.48 of formula (I) wherein R¹ is 3-(difluoromethoxy)phenyl, R² is methyl and substituents R² and G are as defined in Table G above.

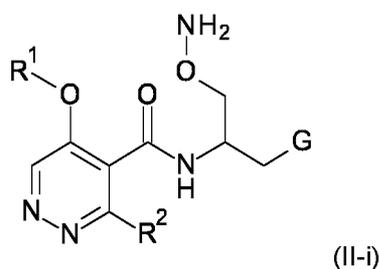
Table A-11: This table provides 48 compounds A-11k.01 and A-11.48 of formula (I) wherein R¹ is 3-(trifluoromethyl)-2-fluorophenyl and substituents R² and G are as defined in Table G above.

Table A-12: This table provides 48 compounds A-12.01 and A-12.48 of formula (I) wherein R¹ is 3-methoxyphenyl and substituents R² and G are as defined in Table G above.

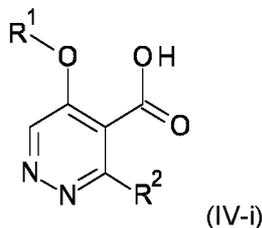
15 Table A-13: This table provides 48 compounds A-13.01 and A-13.48 of formula (I) wherein R¹ is 2,3-difluorophenyl and substituents R² and G are as defined in Table G above

Also made available are certain intermediate compounds of formulae (II-i), (IV-i), (VIII-i), (X-i), (XIII-i), (XX-i), (XXI-i), (XXXVI-i), and (XLIV-i), some of which are novel. For example:

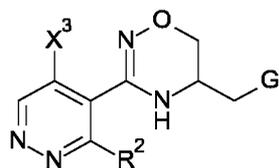
20 - A compound of formula (II-i), wherein R¹, R² and G are as defined for compounds of formula (I); such as wherein R¹ is as defined in Tables A-1 to A-13 above, and R² and G are as defined in Table G above:



- A compound of formula (IV-i), wherein R¹ and R² are as defined for compounds of formula (I); such as wherein R¹ is as defined in Tables A-1 to A-13 above, and R² is as defined in Table G above:

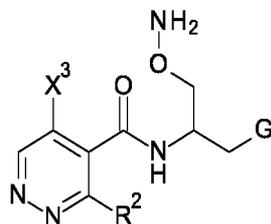


25 - A compound of formula (VIII-i), wherein R² and G are as defined for compounds of formula (I), and X³ is a suitable leaving group such as fluoro, chloro, bromo, iodo, BF₃K, B(OH)₂ or B(pinacol); such as wherein R² and G are as defined in Table G above:



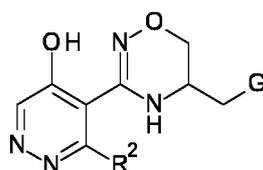
(VIII-i)

- A compound of formula (X-i), wherein R² and G are as defined for compounds of formula (I), and X³ is a suitable leaving group such as fluoro, chloro, bromo, iodo, BF₃K, B(OH)₂ or B(pinacol); such as wherein R² and G are as defined in Table G above:



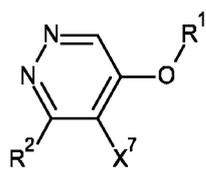
(X-i)

- A compound of formula (XIII-i), wherein R² and G are as defined for compounds of formula (I); such as wherein R² and G are as defined in Table G above:



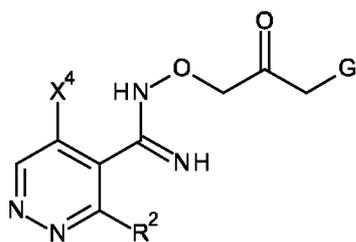
(XIII-i)

- A compound of formula (XX-i), wherein R¹ and R² are as defined for compounds of formula (I), and X⁷ is chloro, bromo, iodo or O-trifluoromethanesulfonyl; such as wherein R¹ is as defined in Tables A-1 to A-13 above, and R² is as defined in Table G above:



(XX-i)

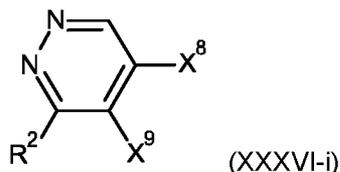
- A compound of formula (XXI-i), wherein R² and G are as defined for compounds of formula (I), and X⁴ is OH, halogen, or OR¹, with R¹ as defined for compounds of formula (I); such as wherein R¹ is as defined in Tables A-1 to A-13 above, and R² and G are as defined in Table G above:



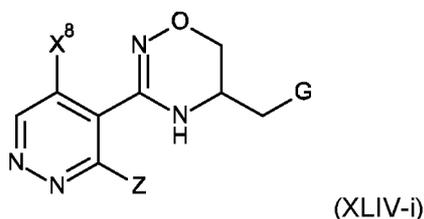
(XXI-i)

- A compound of formula (XXXVI-i), wherein R² is as defined for compounds of formula (I), X⁸ is OH, halogen, or O-R¹, with R¹ as defined for compounds of formula (I), and X⁹ is halogen, methyl,

trifluoromethanesulfonyl-O-, cyano, COOH, or -C(O)C₁-C₄alkoxy; such as wherein R¹ is as defined in Tables A-1 to A-13 above, and R² and G are as defined in Table G above:



5 - A compound of formula (XLIV-i), wherein G is as defined for compounds of formula (I), Z is OH, SH, chloro, bromo, or iodo, and X⁸ is OH, halogen, or O-R¹, with R¹ as defined for compounds of formula (I); such as wherein R¹ is as defined in Tables A-1 to A-13 above, and G are as defined in Table G above:



EXAMPLES

10 The Examples which follow serve to illustrate the invention and are not meant in any way to limit 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 a person skilled in the art using the experimental procedures outlined in the Examples, using lower application rates, if necessary, for example 60 ppm, 20
15 ppm or 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-
20 chemical properties, or increased biodegradability).

Throughout this description, temperatures are given in degrees Celsius (°C) and "m.p." means melting point. LC/MS or LC-MS or LCMS means Liquid Chromatography Mass Spectroscopy and the description of the apparatus, and the methods is as follows.

Unless indicated otherwise, ¹H NMR and ¹⁹F NMR measurements were recorded on a Bruker 400MHz
25 spectrometer, chemical shifts are given in ppm relevant to a TMS (¹H) and CFCI₃ (¹⁹F) standard. Spectra measured in deuterated solvents as indicated. The following abbreviations are used: s = singlet; br s = broad singlet; d = doublet; br d = broad doublet; dd = double doublet; dt = double triplet; t = triplet, tt = triple triplet, q = quartet, quin = quintuplet, sept = septet; m = multiplet.

Either one of the LCMS methods below was used to characterize the compounds. The characteristic LCMS values obtained for each compound were the retention time ("Rt", recorded in minutes) and the measured molecular ion (M+H)⁺ or (M-H)⁻.

Method B (LCMS): Spectra were recorded on a Mass Spectrometer 6410 Triple Quadruple Mass Spectrometer from Agilent Technologies equipped with an electrospray source (Positive and Negative Polarity Switch, Capillary (kV) 7.00, Scan Type MS2 Scan, Fragmentor (V) 120.00, Gas Temperature (°C) 350, Gas Flow (L/min) 11, Nebulizer Gas (psi) 40, Mass range : 110 to 650 Da) and an Agilent 1200 Series HPLC: DAD Wavelength: 254 nm, Column : KINETEX EVO C18, Column length : 50 mm, Internal diameter of column : 4.6 mm, Particle Size : 2.6 µm, Column oven temperature : 40 °C

10 Gradient conditions:

Solvent A: Water with 0.1% formic acid : Acetonitrile : 95 : 5 v/v

Solvent B: Acetonitrile with 0.1% formic acid

	Time (minutes)	A (%)	B (%)	Flow rate (ml/min)
	0	90	10	1.8
15	0.9	0	100	1.8
	1.8	0	100	1.8
	2.2	90	10	1.8
	2.5	90	10	1.8

Where necessary, enantiomerically pure final compounds may be obtained from racemic materials as appropriate via standard physical separation techniques, such as reverse phase chiral chromatography, or through stereoselective synthetic techniques, eg, by using chiral starting materials.

Method C (LCMS): Spectra were recorded on a Mass Spectrometer Acquity QDA Mass Spectrometer from Waters equipped with an electrospray source (Positive and Negative Polarity Switch, Capillary (kV) 0.8, Cone Voltage (V) 25.00, Full Scan, Source Temperature (°C) 120, Desolvation Gas Flow (L/Hr) 1000, Desolvation Temperature (°C) 600, Gas Flow @ Cone (L/Hr) 50, Mass range : 110 to 850 Da) and HPLC: DAD Wavelength range: 230 to 400 nm, a column Acquity UPLC HSS T3 C18 Column length : 30 mm, Internal diameter of column : 2.1 mm, Particle Size : 1.8 µm, Column oven temperature : 40 °C

30 Gradient conditions:

Solvent A: Water with 0.1% formic acid: Acetonitrile: 95: 5 v/v

30 Solvent B: Acetonitrile with 0.05% formic acid

	Time (minutes)	A (%)	B (%)	Flow rate (ml/min)
	0	90	10	0.6
	0.2	90	10	0.6
	0.3	50	50	0.6
35	0.6	0	100	0.6
	1.3	0	100	0.6
	1.4	90	10	0.6
	1.6	90	10	0.6

Where necessary, enantiomerically pure final compounds may be obtained from racemic materials as appropriate via standard physical separation techniques, such as reverse phase chiral chromatography, or through stereoselective synthetic techniques, eg, by using chiral starting materials.

Method D (LCMS): Spectra were recorded on a Mass Spectrometer Acquity SDQ Mass Spectrometer from Waters equipped with an electrospray source (Positive and Negative Polarity Switch, Capillary (kV) 3.0, Full Scan, Cone voltage (V) 41.0, Source Temperature (°C) 150, Desolvation Temperature (°C) 500, Gas Flow @ Cone (L/Hr) 50, Mass range : 110 to 800 Da) and HPLC 'H' class: DAD Wavelength range: 210 to 400 nm, a column Acquity UPLC HSS T3 C18 Column length : 30 mm, Internal diameter of column : 2.1 mm, Particle Size : 1.8 µm, Column oven temperature : 40 °C

10 Gradient conditions:

Solvent A: Water with 0.1% formic acid: Acetonitrile: 95: 5 v/v

Solvent B: Acetonitrile with 0.05% formic acid

Time (minutes)	A (%)	B (%)	Flow rate (ml/min)
0	90	10	0.6
15 0.2	90	10	0.6
0.3	50	50	0.6
0.6	0	100	0.6
1.3	0	100	0.6
1.4	90	10	0.6
20 1.6	90	10	0.6

Where necessary, enantiomerically pure final compounds may be obtained from racemic materials as appropriate via standard physical separation techniques, such as reverse phase chiral chromatography, or through stereoselective synthetic techniques, eg, by using chiral starting materials.

Formulation Examples

	a)	b)	c)
25 <u>Wettable powders</u>			
active ingredients	25 %	50 %	75 %
sodium lignosulfonate	5 %	5 %	-
sodium lauryl sulfate	3 %	-	5 %
sodium diisobutyl naphthalenesulfonate	-	6 %	10 %
30 phenol polyethylene glycol ether (7-8 mol of ethylene oxide)	-	2 %	-
highly dispersed silicic acid	5 %	10 %	10 %
Kaolin	62 %	27 %	-

The combination 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.

	a)	b)	c)
35 <u>Powders for dry seed treatment</u>			
active ingredients	25 %	50 %	75 %
light mineral oil	5 %	5 %	5 %
highly dispersed silicic acid	5 %	5 %	-

Kaolin	65 %	40 %	-
Talcum	-	-	20 %

The combination 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.

5	<u>Emulsifiable concentrate</u>		
	active ingredients	10 %	
	octylphenol polyethylene glycol ether (4-5 mol of ethylene oxide)		3 %
	calcium dodecylbenzene sulfonate	3 %	
	castor oil polyglycol ether (35 mol of ethylene oxide)	4 %	
10	Cyclohexanone	30 %	
	xylene mixture	50 %	

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)
15	Active ingredients	5 %	6 %	4 %
	Talcum	95 %	-	-
	Kaolin	-	94 %	-
	mineral filler	-	-	96 %

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

	<u>Extruder granules</u>	
	Active ingredients	15 %
	sodium lignosulfonate	2 %
	carboxymethylcellulose	1 %
25	Kaolin	82 %

The combination 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.

	<u>Coated granules</u>	
	Active ingredients	8%
30	polyethylene glycol (mol. wt. 200)	3 %
	Kaolin	89 %

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

	<u>Suspension concentrate</u>	
35	active ingredients	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 %

The finely ground combination 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.

Flowable concentrate for seed treatment

active ingredients	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 combination is intimately mixed with the adjuvants, giving a flowable concentrate from which solutions of any desired dilution can be obtained by dilution with water, that can be used directly for seed treatment. 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.

Slow Release Capsule Suspension

28 parts of the combination 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 polyvinylalcohol, 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.

Formulation types include 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), a soluble granule (SG) or any technically feasible formulation in combination with agriculturally acceptable adjuvants.

Abbreviations

Abbreviations used in synthesis schemes and preparatory examples

ACN	Acetonitrile (or MeCN)
DCM	dichloromethane
DMSO	dimethyl sulfoxide
DMSO- <i>d</i> ⁶	deuterated dimethylsulfoxide
Et ₃ N	Triethylamine (or TEA)
EtOAc	ethyl acetate
HATU	O-(7-Aza-1-benzotriazolyl)-N,N,N',N'-tetramethyluronium-hexafluorophosphat
MeOH	methanol
THF	tetrahydrofuran
equiv.	equivalent
h	hour(s)
LC/MS or LC-MS	liquid chromatography mass spectrometry
M	molar
MHz	megahertz
min	minutes
NMR	nuclear magnetic resonance
ppm	parts per million
RT	room temperature
R _t	retention time
TLC	thin layer chromatography

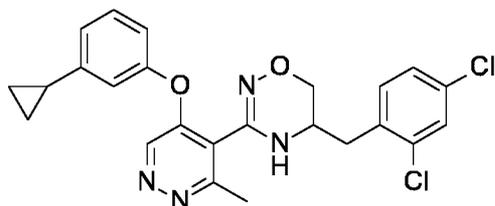
PREPARATION EXAMPLES

5 The following examples further illustrate, but do not limit, the invention. Those skilled in the art will promptly recognize appropriate variations from the procedures both as to reactants and as to reaction conditions and techniques.

10 Unless indicated otherwise, ¹H NMR spectra are recorded at 400 MHz and ¹⁹F NMR spectra are recorded at 377 MHz, and chemical shifts are recorded in ppm. The following abbreviations are used: s = singlet; br s = broad singlet; d = doublet; br d = broad doublet; dd = double doublet; dt = double triplet; t = triplet, tt = triple triplet, q = quartet, quin = quintuplet, sept = septet; m = multiplet.

Throughout this description, temperatures are given in degrees Celsius (°C). "MP" means melting point. "R_t" means retention time. LC/MS means Liquid Chromatography Mass Spectrometry. LC/MS apparatus and methods are:

15 **Example P1:** 3-[5-(3-cyclopropylphenoxy)-3-methyl-pyridazin-4-yl]-5-[(2,4-dichlorophenyl)methyl]-5,6-dihydro-4H-1,2,4-oxadiazine (Compound 1.1 of Table T1)



(Compound 1.1 of Table T1)

a) Preparation of 5-bromo-4-(3-cyclopropylphenoxy)-1H-pyridazin-6-one

To a mixture of 4,5-dibromopyridazin-3-ol (10 g, 37.4 mmol), 3-cyclopropylphenol (41.16 mmol) were taken in DMSO (80 mL) in a round bottom flask, cesium carbonate (93.5 mmol) was added and purged with a stream of Nitrogen for 10 minutes. Copper(I) iodide (1.87 mmol) and *N,N*-dimethylglycine (5.61 mmol) were added and the reaction mixture was purged another 5 minutes with Nitrogen. The reaction mixture was then heated at 110 °C for 5 hours. The progress of the reaction was monitored by TLC and LCMS. The mixture was diluted with EtOAc, quenched with water and extracted with EtOAc. The organic layer was washed with water, brine, dried over sodium sulfate, filtered and evaporated under reduced pressure to obtain the crude. The crude material was purified by combiflash column chromatography (cyclohexane/EtOAc). The desired fractions were evaporated and the obtained solid was triturated with tert-butyl methyl ether to get pure 5-bromo-4-(3-cyclopropylphenoxy)-1H-pyridazin-6-one (6.1 g, 50%) as a white solid.

LCMS (method D): retention time 1.02 min, *m/z* 307, 309 [M+H]⁺.

¹H NMR (400 MHz, CDCl₃) δ ppm 11.82 (br s, 1H), 7.44 (s, 1H), 7.34 (t, 1H), 7.03 (d, 1H), 6.89 (ddd, 1H), 6.83 (t, 1H), 1.90 - 1.97 (m, 1H), 1.02 - 1.08 (m, 2H), 0.71 - 0.77 (m, 2H).

b) Preparation of methyl 4-(3-cyclopropylphenoxy)-6-oxo-1H-pyridazine-5-carboxylate

A 50 mL autoclave vessel was charged with 5-bromo-4-(3-cyclopropylphenoxy)-1H-pyridazin-6-one (3.0 g, 9.8 mmol), TEA (20 mmol), MeOH (30 mL) and Pd(dppf)Cl₂.CH₂Cl₂ (0.98 mmol). The reactor was flushed twice with carbon monoxide and loaded with 15 bar. The reaction mass was heated to 90 °C. After 5 hours, the reaction mass was cooled to 25 °C, the pressure was released and the reaction mixture was flushed with nitrogen. The reaction mass was discharged to a clean conical flask. The reaction mass was diluted with water, extracted twice with EtOAc. The combined organic layers were washed with brine, dried over sodium sulfate, filtered and concentrated under reduced pressure to get crude which was washed with pentane to get methyl 4-(3-cyclopropylphenoxy)-6-oxo-1H-pyridazine-5-carboxylate (1.4 g, 45% yield).

LCMS (method C): retention time 0.98 min, *m/z* 287 [M+H]⁺.

¹H NMR (400 MHz, CDCl₃) δ ppm 11.16 - 11.34 (m, 1H), 7.56 (s, 1H), 7.32 (t, 1H), 7.01 (d, 1H), 6.90 (ddd, 1H), 6.81 (t, 1H), 3.88 (s, 3H), 1.89 - 1.96 (m, 1H), 0.98 - 1.11 (m, 2H), 0.68 - 0.78 (m, 2H).

c) Preparation of methyl 3-chloro-5-(3-cyclopropylphenoxy)pyridazine-4-carboxylate

A round bottom flask was charged with methyl 5-(3-cyclopropylphenoxy)-2-methyl-3-oxo-pyridazine-4-carboxylate (0.8 g, 2.65 mmol) and phosphorous oxychloride (53.11 mmol) was added slowly under stirring. The reaction mixture was heated at 75 °C for 2 hours. The resulted yellow oil was allowed to cool to room temperature, diluted with EtOAc, and slowly poured on water (50 mL) in a conical flask with gentle shaking.

The organic layer was separated, washed with water, dried over sodium sulphate and evaporated to get methyl 3-chloro-5-(3-cyclopropylphenoxy)pyridazine-4-carboxylate (750 mg, 85% mass, 78% yield) which was used as such in next step without purification.

LCMS (method 2): retention time 1.08 min, m/z 305, 307 [M+H]⁺.

5 d) Preparation of methyl 5-(3-cyclopropylphenoxy)-3-methyl-pyridazine-4-carboxylate

To a solution of methyl 3-chloro-5-(3-cyclopropylphenoxy)pyridazine-4-carboxylate (1.75 g, 5.74 mmol) in 2-methyl-THF (35 mL) was added potassium carbonate (11.5 mmol), Pd(dppf)Cl₂.CH₂Cl₂ (0.287 mmol) and trimethylboroxine (11.5 mmol). The reaction mixture was stirred at 95°C for 3 hrs and progress was confirmed by TLC and LCMS. Reaction mass was diluted with water and extracted with EtOAc, organic
10 layer was washed with brine, dried over sodium sulphate and evaporated to get crude which was purified by Combiflash (cyclohexane/EtOAc) to afford methyl 5-(3-cyclopropylphenoxy)-3-methyl-pyridazine-4-carboxylate (1.2g, 72% Yield)

LCMS (method D): retention time 1.07 min, m/z 285 [M+H]⁺.

¹H NMR (400 MHz, CDCl₃) δ ppm 8.71 (s, 1H), 7.33 (t, 1H), 7.02 (d, 1H), 6.89 (ddd, 1H), 6.81 (t, 1H), 3.97
15 (s, 3H), 2.76 (s, 3H), 1.84 - 2.00 (m, 1H), 0.97 - 1.09 (m, 2H), 0.69 - 0.75 (m, 1H), 0.66 - 0.78 (m, 1H).

e) Preparation of 5-(3-cyclopropylphenoxy)-3-methyl-pyridazine-4-carboxylic acid

To a stirred solution of methyl 5-(3-cyclopropylphenoxy)-3-methyl-pyridazine-4-carboxylate (0.65 g, 2.3 mmol) in 3:1 THF/water (20 mL) was added barium hydroxide octahydrate (6.9 mmol). The mixture was stirred at room temperature for 4 hours. The progress of the reaction was confirmed by TLC and LCMS.
20 The reaction mixture was acidified with a 1N HCl, and extracted with EtOAc twice, obtained organic layer was dried over anhydrous sodium sulphate and concentrated under reduced pressure to afford 5-(3-cyclopropylphenoxy)-3-methyl-pyridazine-4-carboxylic acid (0.423 g, 65% Yield).

LCMS (method C): retention time 0.18 min, m/z 271 [M+H]⁺.

25 f) Preparation of 5-(3-cyclopropylphenoxy)-N-[1-[(2,4-dichlorophenyl)methyl]-2-(1,3-dioxoisindolin-2-yl)oxy-ethyl]-3-methyl-pyridazine-4-carboxamide

To a mixture of 5-(3-cyclopropylphenoxy)-3-methyl-pyridazine-4-carboxylic acid (300 mg, 1.11 mmol) and 2-[2-amino-3-(2,4-dichlorophenyl)propoxy]isoindoline-1,3-dione 2,2,2-trifluoroacetic acid (1.33 mmol) in dimethylformamide (3 mL) was added *N*-ethyl-*N*-isopropyl-propan-2-amine (2.77 mmol) and HATU (1.22 mmol) were added. The resulting light-yellow solution was stirred at room temperature for 16 hours. The
30 progress of the reaction was monitored by LCMS. The reaction mixture was diluted with water and extracted with EtOAc. The combined organic layers were washed using a saturated solution of sodium carbonate and brine, dried over sodium sulphate, filtered and concentrated under reduced pressure to get the crude material which was purified by Combiflash chromatography (cyclohexane/EtOAc) to afford 5-(3-cyclopropylphenoxy)-N-[1-[(2,4-dichlorophenyl)methyl]-2-(1,3-dioxoisindolin-2-yl)oxy-ethyl]-3-methyl-
35 pyridazine-4-carboxamide (0.7 g, 70 mass%, 70% Yield).

LCMS (method B): retention time 1.67 min, m/z 617 [M+H]⁺.

g) Preparation of N-[1-(aminooxymethyl)-2-(2,4-dichlorophenyl)ethyl]-5-(3-cyclopropylphenoxy)-3-methyl-pyridazine-4-carboxamide

To a solution of 5-(3-cyclopropylphenoxy)-N-[1-[(2,4-dichlorophenyl)methyl]-2-(1,3-dioxoisindolin-2-yl)oxy-ethyl]-3-methyl-pyridazine-4-carboxamide (300 mg, 0.485 mmol) in THF (9 mL) was added
 5 hydrazine monohydrate (0.971 mmol, 97 mass%) and the mixture was stirred at room temperature for 30 min. After that, a solid precipitated out. The solid was filtered off and the filtrate was concentrated to afford N-[1-(aminooxymethyl)-2-(2,4-dichlorophenyl)ethyl]-5-(3-cyclopropylphenoxy)-3-methyl-pyridazine-4-carboxamide (260mg, 90 mass%, 98% yield) which was used directly in the next step.

LCMS (method C): retention time 1.21 min, m/z 487, 489 [M+H]⁺.

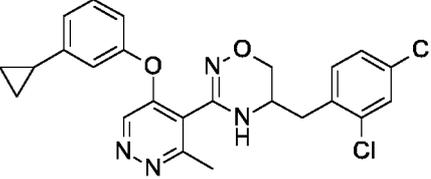
10 g) 3-[5-(3-cyclopropylphenoxy)-3-methyl-pyridazin-4-yl]-5-[(2,4-dichlorophenyl)methyl]-5,6-dihydro-4H-1,2,4-oxadiazine

To a solution of N-[1-(aminooxymethyl)-2-(2,4-dichlorophenyl)ethyl]-5-(3-cyclopropylphenoxy)-3-methyl-pyridazine-4-carboxamide (140 mg, 0.287 mmol) in DCM (5 mL) was added phosphorous pentachloride (0.488 mmol). The mixture was stirred at 45 °C for 2 hours. The progress of the reaction was monitored by
 15 TLC and LCMS. The reaction mixture was then cooled down to room temperature and slowly quenched with a saturated solution of sodium bicarbonate sat. NaHCO₃ solution, diluted with water and extracted with EtOAc twice. Combined organic layers were dried over sodium sulfate, filtered and concentrated under reduced pressure to get crude. The crude material was initially purified by Combiflash (cyclohexane/EtOAc), followed by preparative HPLC to afford 3-[5-(3-cyclopropylphenoxy)-3-methyl-pyridazin-4-yl]-5-[(2,4-dichlorophenyl)methyl]-5,6-dihydro-4H-1,2,4-oxadiazine (25 mg, 18%).
 20

LCMS (method C): retention time 1.25 min, m/z 469, 471 [M+H]⁺.

¹H NMR (400 MHz, CDCl₃) δ ppm 8.60 (s, 1H), 7.31 - 7.43 (m, 2H), 7.16 (d, 1H), 7.04 (dd, 2H), 6.83 - 6.91 (m, 1H), 6.80 (s, 1H), 4.97 (br s, 1H), 3.92 - 4.05 (m, 3H), 3.03 - 3.17 (m, 2H), 2.80 (s, 3H), 1.82 - 2.04 (m, 1H), 0.98 - 1.11 (m, 2H), 0.68 - 0.78 (m, 2H).

25 Table T1: Physical data of compounds of formula (I) - * [M+H]⁺ measured

Entry	Name	Structure	Rt (min)	Mass charge*	Method
1.1	3-[6-(3-cyclopropylphenoxy)pyrazolo[1,5-a]pyrimidin-7-yl]-5-[(2,4-dichlorophenyl)methyl]-5,6-dihydro-4H-1,2,4-oxadiazine		1.25	469	C

Entry	Name	Structure	Rt (min)	Mass charge*	Method
1.2	3-[5-(3-cyclopropyl-2-fluorophenoxy)-3-isopropoxy-pyridazin-4-yl]-5-[(2,4-dichlorophenyl)methyl]-5,6-dihydro-4H-1,2,4-oxadiazine		1.28	531	C
1.3	3-[5-(3-cyclopropylphenoxy)-3-isopropoxy-pyridazin-4-yl]-5-[(2,4-dimethylphenyl)methyl]-5,6-dihydro-4H-1,2,4-oxadiazine		1.27	473	C
1.4	3-[5-(3-cyclopropylphenoxy)-3-methoxy-pyridazin-4-yl]-5-[(2,4-dichlorophenyl)methyl]-5,6-dihydro-4H-1,2,4-oxadiazine		1.25	485	C
1.5	3-[5-(3-cyclopropylphenoxy)-3-(2-methylallyloxy)pyridazin-4-yl]-5-[(2,4-dichlorophenyl)methyl]-5,6-dihydro-4H-1,2,4-oxadiazine		1.30	525	C
1.6	3-[5-(3-cyclopropylphenoxy)pyridazin-4-yl]-5-[(2,4-dichlorophenyl)methyl]-5,6-dihydro-4H-1,2,4-oxadiazine		1.22	455	C

BIOLOGICAL EXAMPLES AND TEST METHODS:

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).

General description of test methods

Leaf disks or leaf segments of various plant species are cut from plants grown in a greenhouse. The cut leaf disks or segments are placed in multiwell plates (24-well format) onto water agar. The leaf disks are sprayed with a test solution before (preventative) or after (curative) inoculation. Compounds to be tested are prepared as DMSO solutions (max. 10 mg/mL) which are diluted to the appropriate concentration with 0.025% Tween20 just before spraying. The inoculated leaf disks or segments are incubated under defined conditions (temperature, relative humidity, light, etc.) according to the respective test system. A single evaluation of disease level is carried out 3 to 14 days after inoculation, depending on the pathosystem. Percent disease control relative to the untreated check leaf disks or segments is then calculated.

Mycelia fragments or conidia suspensions of a fungus prepared either freshly from liquid cultures of the fungus or from cryogenic storage, are directly mixed into nutrient broth. DMSO solutions of the test compound (max. 10 mg/mL) are diluted with 0.025% Tween20 by a factor of 50 and 10 µL of this solution is pipetted into a microtiter plate (96-well format). The nutrient broth containing the fungal spores/mycelia fragments is then added to give an end concentration of the tested compound. The test plates are incubated in the dark at 24 °C and 96% relative humidity. The inhibition of fungal growth is determined photometrically after 2 to 7 days, depending on the pathosystem, and percent antifungal activity relative to the untreated check is calculated.

Example B1: *Botryotinia fuckeliana* syn. *Botrytis cinerea* (Gray mould of grapevine)

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 from Table T1 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:

1.1, 1.2, 1.3, 1.4, 1.5, 1.6

Example B2: *Glomerella lagenarium* syn *Colletotrichum lagenarium* (Anthracnose of cucurbits)

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 from Table T1 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:

1.1, 1.2, 1.3, 1.4, 1.5, 1.6

5 **Example B3: *Blumeria graminis* f. sp. *tritici* (Powdery mildew on wheat)**

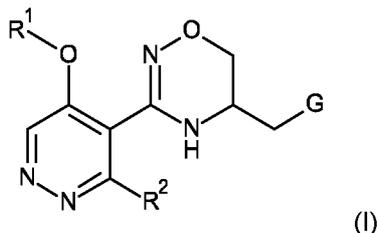
10 Wheat leaf segments cv. Kanzler are placed on agar in a multiwell plate (24-well format) and sprayed with the formulated test compound diluted in water. The leaf disks are inoculated by shaking powdery mildew infected plants above the test plates 1 day after application. The inoculated leaf disks 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).

15 The following compounds from Table T1 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:

1.1, 1.2

CLAIMS

1. A compound of formula (I)



5 or an agrochemically acceptable salt, stereoisomer, enantiomer, or N-oxide of the compound of formula (I), wherein:

R¹ is phenyl unsubstituted or substituted with:

- a single substituent selected from hydroxyl, nitro, halogen, mercapto, amino, cyano, NHMe, N(Me)₂, C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₂fluoroalkyl, C₁-C₄alkoxy, C₁-C₂fluoroalkoxy, C₃-C₄alkenyloxy, C₃-C₄alkenyloxy, C₃-C₆cycloalkyl, C₃-C₆cycloalkyloxy, C₃-C₆cycloalkylC₁-C₂alkyloxy, C₁-C₃alkylsulfanyl, and C₁-C₃alkylsulfonyl; or

- 1, 2 or 3 substituents independently selected from hydroxyl, halogen, mercapto, amino, cyano, methyl, ethyl, propyl, *iso*-propyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl, methoxy, ethoxy, propoxy, *iso*-propoxy, *tert*-butoxy, allyloxy, prop-2-ynoxy, prop-1-ynoxy, methylsulfanyl, methylsulfonyl, difluoromethoxy, trifluoromethoxy, and cyclopropyl; or

R¹ is a 5- or 6-membered monocyclic heteroaryl ring comprising 1, 2 or 3 heteroatoms each independently selected from N, O and S, with the proviso that no more than one is O or S; wherein said heteroaryl ring is unsubstituted or substituted with:

- a single substituent selected from hydroxyl, nitro, halogen, mercapto, amino, cyano, NHMe, N(Me)₂, C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₂fluoroalkyl, C₁-C₄alkoxy, C₁-C₂fluoroalkoxy, C₃-C₄alkenyloxy, C₃-C₄alkenyloxy, C₃-C₆cycloalkyl, C₃-C₆cycloalkyloxy, C₃-C₆cycloalkylC₁-C₂alkyloxy, C₁-C₃alkylsulfanyl, and C₁-C₃alkylsulfonyl; or

- 1 or 2 substituents independently selected from hydroxyl, halogen, mercapto, amino, cyano, methyl, ethyl, propyl, *iso*-propyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl, methoxy, ethoxy, propoxy, *iso*-propoxy, *tert*-butoxy, allyloxy, prop-2-ynoxy, prop-1-ynoxy, methylsulfanyl, methylsulfonyl, difluoromethoxy, trifluoromethoxy, and cyclopropyl;

R² is hydrogen, hydroxyl, nitro, halogen, mercapto, amino, cyano, C₁-C₆alkyl, C₁-C₂fluoroalkyl, C₃-C₅alkenyl, C₃-C₅alkynyl, C₁-C₃alkoxyC₂-C₃alkyl, C₃-C₆cycloalkyl, or C₃-C₆cycloalkylC₁₋₂alkyl, C₁-C₄alkoxy, C₁-C₂fluoroalkoxy, C₃-C₅alkenyloxy, C₃-C₅alkenyloxy, C₃-C₆cycloalkyl, C₃-C₆cycloalkyloxy, C₃-C₆cycloalkylC₁-C₂alkyloxy, C₁-C₄alkylamino, di-C₁-C₄alkylamino, C₃-C₅alkenylamino, C₃-C₅alkynylamino, C₁-C₃alkylsulfanyl, or C₁-C₃alkylsulfonyl; or

R² is phenyl, phenylC₁-C₂alkyl, heteroaryl, heteroarylC₁-C₂alkyl, heterocyclyl, heterocyclylC₁-C₂alkyl, C₃-C₆cycloalkyl, or C₃-C₆cycloalkylC₁₋₂alkyl; wherein the heteroaryl moiety is a 5- or 6-membered monocyclic aromatic ring which comprises 1, 2, or 3 heteroatoms independently selected from N, O and S, with the proviso that no more than one is O or S; wherein the heterocyclyl moiety is a 4- to 6-membered non-aromatic ring which comprises 1 or 2 heteroatoms independently selected from N, O and S, with the proviso that no more than one is O or S; and wherein any of said cycloalkyl, phenyl, heteroaryl and heterocyclyl moieties are unsubstituted or substituted with:

- a single substituent selected from hydroxyl, nitro, halogen, mercapto, amino, cyano, NHMe, N(Me)₂, C₁-C₄alkyl, C₂-C₃alkenyl, C₂-C₃alkynyl, C₁-C₂fluoroalkyl, C₁-C₄alkoxy, C₁-C₂fluoroalkoxy, allyloxy, prop-2-ynoxy, prop-1-ynoxy, C₃-C₆cycloalkyl, C₁-C₃alkylsulfanyl, and C₁-C₃alkylsulfonyl; or

- 1 or 2 substituents independently selected from hydroxyl, halogen, mercapto, amino, cyano, methyl, ethyl, propyl, *iso*-propyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl, methoxy, ethoxy, methylsulfanyl, methylsulfonyl, difluoromethoxy, trifluoromethoxy, and cyclopropyl;

G is selected from G-1, G-2, G-3, and G-4, wherein:

G-1 is phenyl or phenoxy, wherein said phenyl or phenoxy is unsubstituted or substituted with:

- a single substituent selected from hydroxyl, nitro, halogen, mercapto, amino, cyano, NHMe, N(Me)₂, C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₂fluoroalkyl, C₁-C₄alkoxy, C₁-C₂fluoroalkoxy, C₃-C₄alkenyloxy, C₃-C₄alkenyloxy, C₃-C₆cycloalkyl, C₃-C₆cycloalkyloxy, C₃-C₆cycloalkylC₁-C₂alkyloxy, C₁-C₃alkylsulfanyl, and C₁-C₃alkylsulfonyl; or

- 1 or 2 substituents independently selected from hydroxyl, halogen, mercapto, amino, cyano, methyl, ethyl, propyl, *iso*-propyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl, methoxy, ethoxy, propoxy, *iso*-propoxy, *tert*-butoxy, allyloxy, prop-2-ynoxy, prop-1-ynoxy, methylsulfanyl, methylsulfonyl, difluoromethoxy, trifluoromethoxy, and cyclopropyl;

G-2 is a 5- or 6-membered monocyclic heteroaryl or heteroaryl-oxy; wherein said heteroaryl comprises 1, 2 or 3 heteroatoms each independently selected from N, O and S, with the proviso that no more than one is O or S; and wherein said heteroaryl or heteroaryl-oxy is unsubstituted or substituted with:

- a single substituent selected from hydroxyl, nitro, halogen, mercapto, amino, cyano, NHMe, N(Me)₂, C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₂fluoroalkyl, C₁-C₄alkoxy, C₁-C₂fluoroalkoxy, C₃-C₄alkenyloxy, C₃-C₄alkenyloxy, C₃-C₆cycloalkyl, C₃-C₆cycloalkyloxy, C₃-C₆cycloalkylC₁-C₂alkyloxy, C₁-C₃alkylsulfanyl, and C₁-C₃alkylsulfonyl; or

- 1 or 2 substituents independently selected from hydroxyl, halogen, mercapto, amino, cyano, methyl, ethyl, propyl, *iso*-propyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl, methoxy, ethoxy, propoxy, *iso*-propoxy, *tert*-butoxy, allyloxy, prop-2-ynoxy, prop-1-ynoxy, methylsulfanyl, methylsulfonyl, difluoromethoxy, trifluoromethoxy, and cyclopropyl;

G-3 is a 9- or 10-membered heterobicyclic ring system comprising 1, 2 or 3 heteroatoms each independently selected from N, O and S, with the proviso that no more than one is O or S; wherein said heterobicyclic ring system is saturated, partially unsaturated, or aromatic; and wherein said

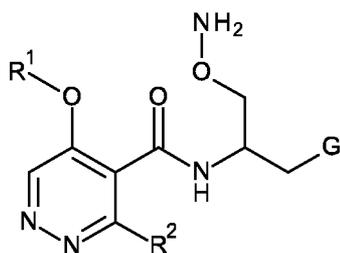
heterobicyclic ring system is unsubstituted or substituted with a single substituent selected from hydroxyl, nitro, halogen, mercapto, amino, cyano, NHMe, N(Me)₂, C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₂fluoroalkyl, C₁-C₄alkoxy, C₁-C₂fluoroalkoxy, C₃-C₄alkenyloxy, C₃-C₄alkenyloxy, C₃-C₆cycloalkyl, C₃-C₆cycloalkyloxy, C₃-C₆cycloalkylC₁-C₂alkyloxy, C₁-C₃alkylsulfanyl, and C₁-C₃alkylsulfonyl;

G-4 is a 9- or 10-membered carbobicyclic ring system; wherein said carbobicyclic ring system is saturated, partially unsaturated, or aromatic; and wherein said carbobicyclic ring system is unsubstituted or substituted with a single substituent selected from hydroxyl, nitro, halogen, mercapto, amino, cyano, NHMe, N(Me)₂, C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₂fluoroalkyl, C₁-C₄alkoxy, C₁-C₂fluoroalkoxy, C₃-C₄alkenyloxy, C₃-C₄alkenyloxy, C₃-C₆cycloalkyl, C₃-C₆cycloalkyloxy, C₃-C₆cycloalkylC₁-C₂alkyloxy, C₁-C₃alkylsulfanyl, and C₁-C₃alkylsulfonyl.

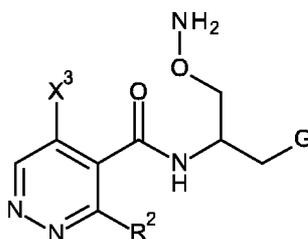
2. The compound according to claim 1, wherein R¹ is phenyl, pyridine, pyrazine, pyrimidine, or pyridazine, wherein said phenyl, pyridine, pyrazine, pyrimidine, or pyridazine is unsubstituted or substituted with a one or two substituents, for instance a single substituent, independently selected hydroxyl, halogen, mercapto, amino, nitro, cyano, methyl, ethyl, propyl, *iso*-propyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl, methoxy, ethoxy, allyloxy, prop-2-yloxy, prop-1-yloxy, *iso*-propoxy, *tert*-butoxy, propynoxy, NHMe, N(Me)₂, methylsulfanyl, methylsulfonyl, difluoromethoxy, trifluoromethoxy, cyclopropyl, cyclobutyl, and cyclopropyloxy.
3. The compound according to claim 1 or claim 2, wherein R¹ is 3-cyclopropyl-2-fluorophenyl, 3-(trifluoromethyl)phenyl, 3-chloro-2-fluorophenyl, 3-chlorophenyl, 5-cyanopyridin-3-yl, 3-methylphenyl, phenyl, 3-cyclopropylphenyl, 3-(difluoromethyl)phenyl, 3-(difluoromethoxy)phenyl, 3-(trifluoromethyl)-2-fluorophenyl, 3-methoxyphenyl, or 2,3-difluorophenyl.
4. The compound according to any one of claims 1 to 3, wherein R² is hydrogen, hydroxyl, halogen, mercapto, amino, cyano, C₁-C₄-alkyl, C₂-C₄-alkenyl, C₂-C₄-alkynyl, C₁-C₄-alkoxy, C₁-C₄-fluoroalkyl, C₁-C₄-fluoroalkoxy, or C₃-C₄-cycloalkyl.
5. The compound according to any one of claims 1 to 4, wherein R² is hydrogen, methyl, ethyl, or cyclopropyl.
6. The compound according to any one of claims 1 to 5, wherein G is phenyl or phenoxy unsubstituted or substituted with 1 or 2 substituents each independently selected from hydroxyl, halogen, mercapto, amino, cyano, methyl, ethyl, propyl, *iso*-propyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl, methoxy, ethoxy, propoxy, *iso*-propoxy, *tert*-butoxy, allyloxy, prop-2-yloxy, prop-1-yloxy, methylsulfanyl, methylsulfonyl, difluoromethoxy, trifluoromethoxy, and cyclopropyl; or

wherein G is pyridine unsubstituted or substituted with 1 or 2 substituents, each independently selected from hydroxyl, halogen, cyano, methyl, vinyl, ethynyl, difluoromethyl, trifluoromethyl methoxy, ethoxy, allyloxy, prop-2-ynoxy, prop-1-ynoxy, difluoromethoxy, and cyclopropyl.

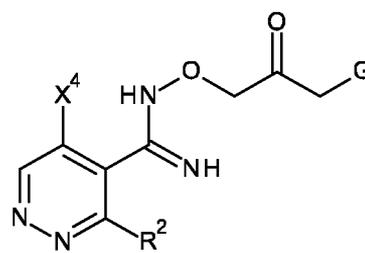
- 5 7. The compound according to any one of claims 1 to 6, wherein G is 2,4-dimethylphenyl, 2,4-dichlorophenyl, 4-bromo-2-methylphenyl, 4-bromo-2-chlorophenyl, 2,6-dichloro-3-pyridyl, 4,6-dichloro-3-pyridyl, 3,5-dichloro-2-pyridyl, 3,4-dimethylphenyl, 2-chloro-4-methylphenyl, 2-methyl-4-bromophenyl, 2-methyl-4-chlorophenyl, or 2,4-difluorophenyl.
- 10 8. An agrochemical composition comprising a fungicidally effective amount of a compound according to any one of claims 1 to 7.
9. The composition according to claim 8, further comprising at least one additional active ingredient and/or an agrochemically-acceptable diluent or carrier.
- 15 10. A method of controlling or preventing infestation of useful plants by phytopathogenic microorganisms, wherein a fungicidally effective amount of a compound according to any of claims 1 to 7, or a composition as defined in claim 8 or 9, is applied to the plants, to parts thereof or the locus thereof.
- 20 11. Use of a compound according to any one of claims 1 to 7 as a fungicide.
12. A plant propagation material, such as a seed, comprising, or treated with or adhered thereto, a compound as defined in any one of claims 1 to 7, or a composition as defined in claim 8 or 9.
- 25 13. A compound of the formula (II-i), (X-i), or (XXI-i):



(II-i)



(X-i)



(XXI-i)

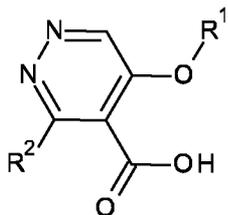
wherein

X³ is a leaving group selected from fluoro, chloro, bromo, iodo, BF₃K, B(OH)₂ and B(pinacol);

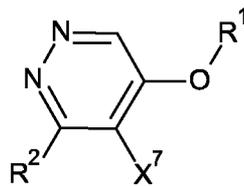
X⁴ is OH, halogen, or OR¹; and

R¹, R² and G are as defined in any one of claims 1 to 7.

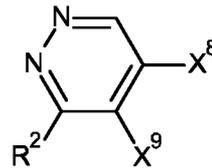
14. A compound of the formula (IV-i), (XX-i), or (XXXVI-i):



(IV-i)



(XX-i)

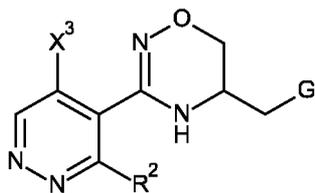


(XXXVI-i)

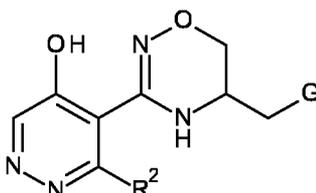
wherein

- 5 X⁷ is chloro, bromo, iodo, or O-trifluoromethanesulfonyl;
 X⁸ is OH, halogen, or O-R¹;
 X⁹ is halogen, methyl, trifluoromethanesulfonyl-O-, cyano, COOH, or -C(O)C₁-C₄alkoxy; and
 R¹ and R² are as defined in any one of claims 1 to 5.

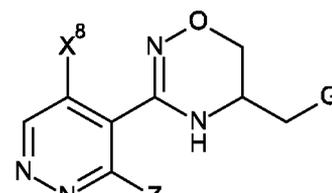
- 10 15. A compound of the formula (VIII-i), (XV-i), or (XLIV-i):



(VIII-i)



(XIII-i)



(XLIV-i)

wherein

- X³ is a leaving group selected from fluoro, chloro, bromo, iodo, BF₃K, B(OH)₂ and B(pinacol);
 X⁸ is OH, halogen, or O-R¹;
 Z is OH, SH, chloro, bromo, or iodo; and
 15 R¹, R² and G are as defined in any one of claims 1 to 7.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/086003

A. CLASSIFICATION OF SUBJECT MATTER INV. C07D237/14 A01N43/88 C07D237/16 C07D237/24 C07D413/04 ADD.				
According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED				
Minimum documentation searched (classification system followed by classification symbols) C07D A01N				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, CHEM ABS Data, WPI Data				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	WO 2013/004984 A1 (CT NAC INVESTIGACIONES ONCOLOGICAS CNIO [ES] ET AL.) 10 January 2013 (2013-01-10) synthesis intermediate I-09 and its synthesis precursor; page 70 -----	14		
X	EP 1 426 365 B9 (MITSUI CHEMICALS AGRO INC [JP]) 21 October 2009 (2009-10-21) page 174; example 3.1; compounds 3,4-dichloro-3-(2-methylphenoxy)pyridazine ----- -/--	14		
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;"> <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. </td> <td style="width: 50%; border: none;"> <input checked="" type="checkbox"/> See patent family annex. </td> </tr> </table>			<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.	<input checked="" type="checkbox"/> See patent family annex.
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.	<input checked="" type="checkbox"/> See patent family annex.			
* Special categories of cited documents :				
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;"> "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 50%; border: none;"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family </td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family			
Date of the actual completion of the international search <p style="text-align: center;">1 March 2024</p>		Date of mailing of the international search report <p style="text-align: center;">20/03/2024</p>		
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer <p style="text-align: center;">Brandstetter, T</p>		

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/086003

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>WISE DEAN S. ET AL: "The synthesis of novel dipyridazinothiazine ring systems", JOURNAL OF HETEROCYCLIC CHEMISTRY, vol. 11, no. 6, 1 December 1974 (1974-12-01), pages 1001-1009, XP093135379, US ISSN: 0022-152X, DOI: 10.1002/jhet.5570110627 4,5-dichloropyridazine; page 1002; compound 6</p> <p>-----</p>	14
X	<p>JOJIMA TERUOMI ET AL: "Syntheses of Pyridazine Derivatives as Herbicides", AGRICULTURAL AND BIOLOGICAL CHEMISTRY; AGRICULTURAL AND BIOLOGICAL CHEMISTRY, AGRICULTURAL CHEMICAL SOCIETY OF JAPAN, JP, vol. 32, no. 11, 1 January 1968 (1968-01-01), pages 1376-1381, XP009552328, ISSN: 0002-1369, DOI: 10.1080/00021369.1968.10859237 page 1379; compounds Xa, Xb</p> <p>-----</p>	14
X	<p>KANG YOUNG-JIN ET AL: "Functionalization of 4,5-dihalopyridazin-6-ones using 1-(1,1-dibromo-2-oxopropyl) derivatives", JOURNAL OF HETEROCYCLIC CHEMISTRY, vol. 35, no. 3, 1 May 1998 (1998-05-01), pages 595-600, XP093135676, US ISSN: 0022-152X, DOI: 10.1002/jhet.5570350317 scheme I; page 595; compounds 3g, 3h scheme II; page 596; compounds 6a, 6b, 6c, 6d, 6e, 6f, 6g, 6h</p> <p>-----</p>	14
X	<p>WO 2009/127544 A1 (HOFFMANN LA ROCHE [CH]; BERTHEL STEVEN JOSEPH [US] ET AL.) 22 October 2009 (2009-10-22) 4-chloro-5-phenoxy-2H-pyridazin-3-one; page 108, line 13 corresponding intermediates in the preparation of intermediates 21-36, 41-48, 54, 58, 66, 68, 76-78, 84, 88, 89, 92, 93, 96, 97 and 102 2-[5-chloro-6-oxo-2-(5-chloro-6-oxo-1,6-dihydro-pyridazin-4-yloxy)-benzotrile]; page 130, lines 18-19</p> <p>-----</p> <p style="text-align: center;">-/--</p>	14

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/086003

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE Registry [Online] Chemical Abstracts Service; 12 January 2014 (2014-01-12), Anonymous: "5-(2-Aminophenoxy)-4-chloro-3(2H)-pyridaz inone", XP093135825, retrieved from STN Database accession no. 1516980-56-5 abstract</p> <p>-----</p>	14
X	<p>DATABASE Registry [Online] Chemical Abstracts Service; 8 January 2014 (2014-01-08), Anonymous: "5-(3-aminophenoxy)-4-chloro-3(2H)-pyridaz inone", XP093135827, retrieved from STN Database accession no. 1514160-71-4 abstract</p> <p>-----</p>	14
X	<p>DATABASE Registry [Online] Chemical Abstracts Serrvice; 20 December 2013 (2013-12-20), Anonymous: "5-(4-aminophenoxy)-4-chloro-3(2H)-pyridaz inone", XP093135829, retrieved from STN Database accession no. 1499520-16-9 abstract</p> <p>-----</p>	14
X	<p>WO 2021/245083 A1 (BAYER AG [DE]) 9 December 2021 (2021-12-09) claims 1, 7, 8 page 2, line 3 page 406; compounds I-028 page 389, line 33</p> <p>-----</p>	1-15
X	<p>WO 2020/127780 A1 (BAYER AG [DE]) 25 June 2020 (2020-06-25) cited in the application claim 14</p> <p>-----</p>	12
X,P	<p>WO 2023/089049 A2 (SYNGENTA CROP PROTECTION AG [CH]) 25 May 2023 (2023-05-25) products of examples 3e, 4a, 5b, 6b, 7b, 8b, 9b, 10b, 11b, 12b, 13c, 15a, 16a and 17a; starting material in example 13a page 1, line 7</p> <p>-----</p>	12, 14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2023/086003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2013004984	A1	10-01-2013	NONE
<hr/>			
EP 1426365	B9	21-10-2009	CA 2457575 A1 27-02-2003
			CN 1543455 A 03-11-2004
			EP 1426365 A1 09-06-2004
			ES 2330089 T3 04-12-2009
			JP WO2003016286 A1 02-12-2004
			KR 20040050061 A 14-06-2004
			KR 20080097494 A 05-11-2008
			TW I254708 B 11-05-2006
			US 2005037925 A1 17-02-2005
			US 2010041555 A1 18-02-2010
			WO 03016286 A1 27-02-2003
<hr/>			
WO 2009127544	A1	22-10-2009	AR 071323 A1 09-06-2010
			AU 2009237792 A1 22-10-2009
			BR PI0911476 A2 19-03-2019
			CA 2720559 A1 22-10-2009
			CN 102007116 A 06-04-2011
			EP 2268633 A1 05-01-2011
			IL 207349 A 31-08-2014
			JP 5301655 B2 25-09-2013
			JP 2011516592 A 26-05-2011
			KR 20100124328 A 26-11-2010
			PE 20091725 A1 13-11-2009
			TW 200944517 A 01-11-2009
			US 2009264434 A1 22-10-2009
			WO 2009127544 A1 22-10-2009
<hr/>			
WO 2021245083	A1	09-12-2021	BR 112022024405 A2 31-01-2023
			CN 116157397 A 23-05-2023
			EP 4161914 A1 12-04-2023
			JP 2023529643 A 11-07-2023
			US 2023295138 A1 21-09-2023
			WO 2021245083 A1 09-12-2021
<hr/>			
WO 2020127780	A1	25-06-2020	AR 117461 A1 04-08-2021
			CA 3124013 A1 25-06-2020
			CL 2021001661 A1 03-12-2021
			CN 113454079 A 28-09-2021
			CO 2021007995 A2 30-06-2021
			EA 202191668 A1 10-11-2021
			EC SP21044312 A 30-07-2021
			EP 3898620 A1 27-10-2021
			JP 2022514651 A 14-02-2022
			KR 20210106492 A 30-08-2021
			TW 202039468 A 01-11-2020
			US 2023064576 A1 02-03-2023
			UY 38524 A 31-07-2020
			WO 2020127780 A1 25-06-2020
<hr/>			
WO 2023089049	A2	25-05-2023	NONE
<hr/>			