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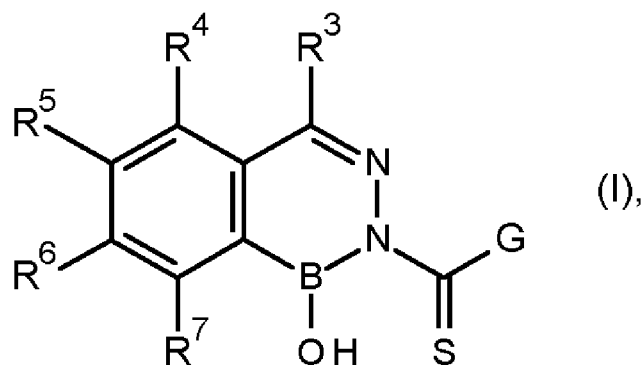
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(54) Title: FUNGICIDES COMPRISING BORON



(57) Abstract: Compounds of formula (I), are as defined in the claims, and their use in compositions and methods for the control and/or prevention of microbial infection, particularly fungal infection, in plants and to processes for the preparation of these compounds.

FUNGICIDES COMPRISING BORON

The present invention relates to novel microbiocidally active, in particular fungicidally active, diazaborines moiety containing compounds their use in compositions and methods for the control and/or prevention of microbial infection, particularly fungal infection, in plants or plant propagation material, harvested food crops by phytopathogenic microorganisms, preferably fungi and to processes for the preparation of these compounds. Preferably these compounds are used in agriculture or horticulture for controlling or preventing infestation of plants by phytopathogenic microorganisms, preferably fungi.

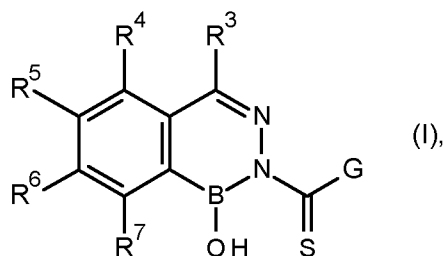
The incidence of serious microbial infections, particularly fungal infections, either systemic or topical, continues to increase for plants.

Fungicides are compounds, of natural or synthetic origin, which act to protect plants against damage caused by fungi. Current methods of agriculture rely heavily on the use of fungicides. In fact, some crops cannot be grown usefully without the use of fungicides. Using fungicides allows a grower to increase the yield of the crop and consequently, increase the value of the crop. Numerous fungicidal agents have been developed. However, the treatment of fungal infestations continues to be a major problem. Furthermore, fungicide resistance has become a serious problem, rendering these agents ineffective for some agricultural uses. As such, a need exists for the development of new fungicidal compounds with improved antifungal properties. It has been found that novel diazaborines with a specific substitution pattern are novel and have improved microbiocidal activity.

Fungicidally active Diazaborines are described in CHEMISTRY & BIODIVERSITY – Vol. 5 (2008), 2415-2422.

It has been found that novel Diazaborines with a specific substitution pattern are novel and have microbiocidal activity.

According to the present invention there is provided a method for controlling or preventing infestation preferably fungal 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 with an effective amount of a diazaborine of general formula (I)

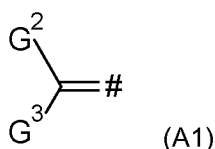


wherein

G = N(R¹R²), SCH₃

R^1 is H, C_1 - C_8 alkyl or C_1 - C_8 alkyl substituted by one to five Z, C_1 - C_8 alkenyl or C_1 - C_8 alkenyl substituted by one to five Z, C_3 - C_{10} cycloalkyl or C_3 - C_{10} cycloalkyl substituted by one to five Y, aryl- C_1 - C_4 alkylene- or aryl- C_1 - C_4 alkylene- wherein the aryl moiety is substituted by one to five Y, heterocyclyl- C_1 - C_4 alkylene- or heterocyclyl- C_1 - C_4 alkylene- wherein the heterocyclyl moiety is substituted by one to five Y, aryl-(W)- or aryl-(W)- wherein the aryl moiety is substituted by one to five Y, heterocyclyl-(W)- or heterocyclyl-(W)- wherein the heterocyclyl moiety is substituted by one to five Y, aryl or aryl substituted by one to five Y, heterocyclyl or heterocyclyl substituted by one to five Y, C_1 - C_8 alkylaminocarbonyl- C_1 - C_4 alkylene, C_1 - C_8 haloalkylaminocarbonyl- C_1 - C_4 alkylene, C_3 - C_8 cycloalkylaminocarbonyl- C_1 - C_4 alkylene, C_1 - C_8 alkylaminocarbonyl-, C_1 - C_8 haloalkylaminocarbonyl, C_3 - C_8 cycloalkylaminocarbonyl, C_1 - C_6 alkyl-O-N=CH-, C_1 - C_6 haloalkyl-O-N=CH-;

R^2 is hydrogen, C_1 - C_6 alkyl, C_1 - C_6 alkoxy-, C_1 - C_6 alkylcarbonyl-, or C_1 - C_6 alkoxycarbonyl-; or when $G=N(R^2 R^1)$, R^1 and R^2 together can also form a ring or can represent group A1



G^2 is $O(R^8)$, $N(R^9)(R^{10})$ or $S(R^{11})$;

G^3 is $N(R^{12})(R^{13})$ or $S(R^{14})$;

R^3 = H, halogen, cyano, nitro, formyl, C_1 - C_6 alkyl, C_1 - C_6 alkenyl, C_1 - C_6 alkynyl and aryl

R^4 , R^5 , R^6 and R^7 is independently hydrogen, halogen, cyano, nitro, hydroxy, amino, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_1 - C_6 alkenyl, C_1 - C_6 alkynyl or two neighbored substituents R^4 , R^5 , R^6 and R^7 form a -O- C_1 - C_4 alkyl-O- ring together with the carbon atoms to which they are attached;

each Z is independently halogen, cyano, nitro, hydroxy, amino, C_1 - C_8 alkylamino, $(C_1$ - C_8 alkyl)₂amino, C_1 - C_8 alkylcarbonylamino, C_1 - C_8 haloalkylcarbonylamino, C_1 - C_8 alkoxy-, C_1 - C_8 haloalkoxy-, aryloxy or aryloxy substituted by one to five M, C_1 - C_8 alkylcarbonyl-, C_1 - C_8 alkoxycarbonyl-, mercapto, C_1 - C_8 alkylthio-, C_1 - C_8 haloalkylthio-, C_1 - C_8 alkylsulfinyl-, C_1 - C_8 haloalkylsulfinyl-, C_1 - C_8 alkylsulfonyl-, C_1 - C_8 haloalkylsulfonyl-, aryl- C_1 - C_4 alkylthio or aryl- C_1 - C_4 alkylthio wherein the aryl moiety is substituted by one to five M; C_3 - C_7 aliphatic and aromatic carbocycle or C_3 - C_7 aliphatic and aromatic carbocycle wherein the carbocycle is substituted by one to five M, 3 to 7 membered heterocycles containing 1-3 heteroatoms selected from N, O, S, wherein the heterocycle can be optionally substituted by M;

each Y is independently halogen, cyano, nitro, oxo, hydroxy, C_1 - C_8 alkyl, C_1 - C_8 haloalkyl, C_1 - C_8 cyanoalkyl, C_2 - C_8 alkenyl, C_2 - C_8 haloalkenyl, C_2 - C_8 alkynyl, C_2 - C_8 haloalkynyl, C_3 - C_{10} cycloalkyl, C_1 - C_8 alkoxy-, C_1 - C_8 haloalkoxy-, mercapto, C_1 - C_8 alkylthio-, C_1 - C_8 haloalkylthio-, C_1 - C_8 alkylsulfinyl-, C_1 - C_8 haloalkylsulfinyl-, C_1 - C_8 alkylsulfonyl-, C_1 - C_8 haloalkylsulfonyl-, C_1 - C_8 alkylaminosulfonyl, $(C_1$ - C_8 alkyl)₂aminosulfonyl-, C_1 - C_8 alkylcarbonyl-, C_1 - C_8 alkoxycarbonyl-, aryl or aryl substituted by one to

five M, heterocyclyl or heterocyclyl substituted by one to five M, aryl-C₁-C₄alkylene or aryl-C₁-C₄alkylene wherein the aryl moiety is substituted by one to five M, heterocyclyl-C₁-C₄alkylene or heterocyclyl-C₁-C₄alkylene wherein the heterocyclyl moiety is substituted by one to five M, aryloxy or aryloxy substituted by one to five M, aryloxy-C₁-C₄alkylene or aryloxy-C₁-C₄alkylene wherein the aryl moiety is substituted by one to five M;

each M is independently halogen, cyano, nitro, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy-, or C₁-C₄haloalkoxy, substituted or unsubstituted aralkyl -;

R⁸, R¹¹ and R¹⁴ are independently C₁-C₄ alkyl;

R⁹, R¹⁰, R¹², and R¹³ are independently hydrogen or C₁-C₄ alkyl;

W is hydrogen or C₁-C₄ alkyl

and agronomically acceptable salts, stereoisomers, diastereoisomers, enantiomers, tautomers, atropisomers and N-oxides of those compounds.

The present invention accordingly further relates to the use of diazaborine derivatives according to formula (I) and salts thereof for controlling or preventing infestation of plants or plant propagation material, the application of diazaborine derivatives according to formula (I) to useful plants, the application of diazaborine derivatives according to formula (I) to the locus of useful plants or the application of diazaborine derivatives according to formula (I) to plant propagation material of useful plants a compound of formula (I).

The present invention accordingly further relates to the use of diazaborine derivatives according to formula (I) and salts thereof for controlling or preventing infestation of plants or plant propagation material by treating plants or plant propagation material with an effective amount of an diazaborine of general formula (I).

The present invention accordingly further relates to the method of controlling phytopathogenic diseases on useful plants or plant propagation material thereof, which comprises applying to said plant or plant propagation material a fungicidally effective amount of a compound of formula (I). Preferably the method method of controlling phytopathogenic diseases on useful plants or plant propagation material thereof, which comprises applying to said plant or plant propagation material a fungicidally effective amount of a compound of formula (I), wherein plant propagation material of useful plants are seeds of useful plants.

The present invention accordingly further relates to the method for controlling or preventing infestation of plants or plant propagation material by treating plants or plant propagation material with an effective amount of an diazaborine of general formula (I).

The present invention accordingly further relates to the method of controlling phytopathogenic diseases on useful plants or plant propagation material thereof, which comprises applying to said plant propagation material a fungicidally effective amount of a compound of formula (I).

Accordingly the present invention also relates to a method of protecting plant propagation material and organs that grow at a later point in time against damage phytopathogenic diseases, which method comprises applying to said propagation material a fungicidally effective amount of a compound of formula I.

In a further aspect of the invention, the invention provides a plant propagation material protecting composition comprising a compound of formula I, together with a suitable carrier therefore.

In a further aspect of the invention, the invention provides a method of controlling phytopathogenic diseases on useful plants or plant propagation material thereof, which comprises applying to said plant propagation material a fungicidally effective amount of a plant propagation material protecting composition comprising a compound of formula (I) as defined in claim 1, together with a suitable carrier therefore.

A preferred embodiment of this aspect of the invention is a plant propagation material protecting composition comprising a compound of formula I, together with a suitable carrier therefor, wherein said plant propagation material protecting composition comprises additionally a colouring agent.

In yet a further aspect of the invention, the invention provides plant propagation material treated with a plant propagation material protecting composition comprising a compound of formula I, together with a suitable carrier therefor.

A preferred embodiment of this aspect of the invention is plant propagation material treated with a plant propagation material protecting composition comprising a compound of formula I, together with a suitable carrier therefor, wherein said plant propagation material protecting composition comprises additionally a colouring agent.

A method of controlling or preventing pest damage in a growing plant said method comprising applying onto the plant propagation material, before planting or sowing thereof a compound of formula (I).

A method of controlling or preventing pest damage in a growing plant or growing plant tissue said method comprising: applying onto the plant propagation material, before planting or sowing thereof a fungicidal effective amount of a compound of formula (I).

A method of controlling or preventing fungal diseases in a growing plant or growing plant tissue said method comprising: applying onto the plant propagation material before planting or sowing thereof a fungicidal effective amount of a compound of formula (I).

In a preferred embodiment the plant propagation material is a seed or a tuber. In a further preferred embodiment the plant propagation material is a seed. In a further preferred embodiment the plant propagation material is a tuber. Preferably the seeds and tubers (stem tubers and root tubers) according to this application are alive. Preferably the seeds and tubers according to this application are able to germinate

In a further aspect of the invention, the invention provides a method of controlling or preventing pest damage in a growing plant said method comprising applying onto the seed, before planting or sowing thereof a compound of formula (I).

In a further aspect of the invention, the invention provides a method of controlling or preventing pest damage in a growing plant or growing plant tissue said method comprising: applying onto the seed, before planting or sowing thereof a fungicidal effective amount of a compound of formula (I).

In a further aspect of the invention, the invention provides a method of controlling or preventing fungal diseases in a growing plant or growing plant tissue said method comprising: applying onto the seed before planting or sowing thereof a fungicidal effective amount of a compound of formula (I).

In a further aspect of the invention, the invention provides a method of protecting plant propagation material and organs that grow at a later point in time against damage by phytopathogenic diseases, which method comprises applying to said propagation material a fungicidally effective amount of a compound of formula (I).

In a further aspect of the invention, the invention provides a plant propagation material comprising a compound of formula (I). Preferably the plant propagation material comprising a fungicidal effective amount of a compound of formula (I).

In a further aspect of the invention, the invention provides a plant propagation material comprising a compound of formula (I) and comprises additionally a colouring agent.

In a further aspect of the invention, the invention provides a coated plant propagation material coated with a compound of formula (I).

In a further aspect of the invention, the invention provides a combination of a plant propagation material and a compound of formula (I).

In a further aspect of the invention, the invention provides a coated plant propagation material coated with a coating comprising a compound of formula (I) as defined in claim 1.

In a further aspect of the invention, the invention provides a plant propagation material comprising an outer coating characterized that the outer coating comprises a compound according to formula (I), preferably a seed comprising an outer coating characterized that the outer coating comprises a compound according to formula (I).

In a further aspect of the invention, the invention provides a composition comprising a plant propagation material and a compound of formula (I).

In a further aspect of the invention, the invention provides a composition comprising a plant propagation material and a compound of formula and further comprising a seed grow medium.

In a further aspect of the invention, the invention provides a plant which results from the germination of a coated seed wherein the coating comprises a compound of formula (I).

In a further aspect of the invention, the invention provides a coated plant propagation material wherein the coating comprises a compound of formula (I).

In a further aspect of the invention, the invention provides a coated plant propagation material according to the preceding paragraph, wherein the said material is a seed.

In a further aspect of the invention, the invention provides the combination of a plant propagation material and a composition comprising a compound of formula (I).

In a further aspect of the invention, the invention provides the combination according to the preceding paragraph wherein the said material is a seed.

In a further aspect of the invention, the invention provides the combination according to one of the two preceding paragraphs, further comprising a plant growth and/or seed germination medium.

In a further aspect of the invention, the invention provides a plant which results from the germination and/or growth of the coated plant propagation material wherein the coating comprises a compound of formula (I).

In a further aspect of the invention, the invention provides a plant which results from the germination and/or growth of the coated plant propagation material wherein the coating comprises a compound of formula (I) and wherein the coated plant propagation material is a seed. Preferably the coated plant propagation material is a seed.

In a further aspect of the invention, the invention relates to the use of a compound of formula (I) according to claim 1, in the preparation of a composition for coating a plant propagation material for

the prevention or control of plant pathogenic fungi.

The compounds of formula I are applied by treating plant propagation material with a fungicidally effective amount of a compound of formula I. Preferably, compounds of formula I are applied by adhering compounds of formula I to plant propagation material in a fungicidally effective amount.

A preferred application method is seed treatment.

The method according to the invention is especially suitable to increase the yield and/or quality of useful plants, such as crop yield of crop plants.

The invention covers all agronomically acceptable salts, isomers, structural isomers, stereoisomers, diastereoisomers, enantiomers, tautomers, atropisomers and N-oxides of those compounds. The compounds of formula (I) may exist in different geometric or optical isomeric forms or in different tautomeric forms. One or more centres of chirality may be present, in which case compounds of the formula (I) may be present as pure enantiomers, mixtures of enantiomers, pure diastereomers or mixtures of diastereomers. There may be double bonds present in the molecule, such as C=C or C=N bonds, in which case compounds of formula (I) may exist as single isomers or mixtures of isomers. Centres of tautomerisation may be present. This invention covers all such isomers and tautomers and mixtures thereof in all proportions as well as isotopic forms such as deuterated compounds. Also atropisomerism may occur as a result of a restricted rotation about a single bond.

Suitable salts of the compounds of formula (I) include acid addition salts such as those with an inorganic acid such as hydrochloric, hydrobromic, sulphuric, nitric or phosphoric acid, or an organic carboxylic acid such as oxalic, tartaric, lactic, butyric, toluic, hexanoic or phthalic acid, or a sulphonic acid such as methane, benzene or toluene sulphonic acid. Other examples of organic carboxylic acids include haloacids such as trifluoroacetic acid.

N-oxides are oxidised forms of tertiary amines or oxidised forms of nitrogen containing heteroaromatic compounds. They are described in many books for example in "Heterocyclic N-oxides" by Angelo Albini and Silvio Pietra, CRC Press, Boca Raton, Florida, 1991.

In the context of the present specification the term "aryl" refers to a ring system which may be mono-, bi- or tricyclic. Examples of such rings include phenyl, naphthalenyl, anthracenyl, indenyl or phenanthrenyl. A preferred aryl group is phenyl.

The term "heteroaryl" refers to an aromatic ring system containing at least one heteroatom and consisting either of a single ring or of two or more fused rings. Preferably, single rings will contain up to three and bicyclic systems up to four heteroatoms which will preferably be chosen from nitrogen, oxygen and sulfur. Examples of such groups include pyridyl, pyridazinyl, pyrimidinyl, pyrazinyl, furanyl,

thiophenyl, oxazolyl, isoxazolyl, oxadiazolyl, thiazolyl, isothiazolyl, thiadiazolyl, pyrrolyl, pyrazolyl, imidazolyl, triazolyl and tetrazolyl. A preferred heteroaryl group is pyridine. Examples of bicyclic groups are benzothiophenyl, benzimidazolyl, benzothiadiazolyl, quinolinyl, cinnolinyl and quinoxalinyl.

The term "heterocyclyl" is defined to include heteroaryl and in addition their unsaturated or partially unsaturated analogues such as 4,5,6,7-tetrahydro-benzothiophenyl, 9H-fluorenyl, 3,4-dihydro-2H-benzo-1,4-dioxepinyl, 2,3-dihydro-benzofuranyl, piperidinyl, 1,3-dioxolanyl, 1,3-dioxanyl, 4,5-dihydro-isoxazolyl, tetrahydrofuranyl and morpholinyl.

The alkyl groups, the alkenyl groups, the alkynyl groups and the alkoxy groups in the compound of formula (I) are either linear or branched or they are perhalogenated and forming haloalkyl groups, haloalkenyl groups, haloalkynyl groups or haloalkoxy groups. Halogen signifies preferably F, Cl, Br, I, and more preferred halogen signifies F or Cl. A oxo substituent is =O, thus a oxygen atom doubly bonded to carbon or another element. The term "oxo substituent" thus embraces aldehydes, carboxylic acids, ketones, sulfonic acids, amides and esters.

The preferred substituents of the substituted alkyl groups, the substituted alkenyl groups, the substituted alkynyl groups, the substituted alkoxy groups, substituted aryl groups and / or the aromatic heterocycle groups in the compound of formula (I) are selected from the following substituents F, Cl, Br, I, -OH, -CN, nitro, a oxo substituent, -C₁₋₄alkoxy, -C₁₋₄ alkylthio, C₁₋₄alkyl, C₂₋₄alkenyl, C₂₋₄alkenyl, C₂₋₄alkynyl, -C(O)H, -C(O)(C₁₋₄ alkyl), -C(O)(C₁₋₄ alkoxy), -C(O)NH₂, -C(O)NH(C₁₋₄ alkyl), -C(O)N(C₁₋₄ alkyl)(C₁₋₄ alkyl), -OC(O)NH(C₁₋₄ alkyl), -OC(O)N(C₁₋₄ alkyl)(C₁₋₄ alkyl), -NHC(O)(C₁₋₄ alkyl), -NHC(O)(C₁₋₄ alkoxy), -N(C₁₋₄ alkyl)C(O)(C₁₋₄ alkyl), -N(C₁₋₄ alkyl)C(O)(C₁₋₄ alkoxy), -OC(O)(C₁₋₄ alkyl), -OC(O)(C₁₋₄ alkoxy), -Si(C₁₋₄ alkyl)₃, -Si(C₁₋₄ alkoxy)₃, C₆₋₁₀aryl, C₆₋₁₀aryloxy, C₆₋₁₀arylthio, C₆₋₁₀heteroaryl, -(C₁₋₈ - perhaloalkyl), arylC₂₋₆alkynyl, -C₂₋₆alkenyl, heteroarylC₂₋₆alkynyl, -C₂₋₆alkenyl, C₃₋₈cycloalkyl, -NR⁸R⁹ where R⁸ and R⁹ are independently H, -C₁₋₄alkyl -C₂₋₄alkenyl, -C₂₋₄alkynyl or combine with the interjacent nitrogen to form a five- or six-membered ring which may comprise one or two or three heteroatoms (one or two N, O or S atoms in addition to the interjacent nitrogen atom), in which case the heterocyclic ring is unsubstituted or the heterocyclic ring is substituted by one or two oxo substituent, C₁₋₄ alkyl groups, -C₂₋₄alkenyl or substituted -C₂₋₄alkenyl, -C₂₋₄alkynyl or substituted -C₂₋₄alkynyl, -C(O)H, -C(O)(C₁₋₄ alkyl), -C(O)(C₁₋₄ alkoxy), -C(O)NH₂, -C(O)NH(C₁₋₄ alkyl), -C(O)N(C₁₋₄ alkyl)(C₁₋₄ alkyl), -OC(O)NH(C₁₋₄ alkyl), -OC(O)N(C₁₋₄ alkyl)(C₁₋₄ alkyl), -NHC(O)(C₁₋₄ alkyl), -NHC(O)(C₁₋₄ alkoxy), -N(C₁₋₄ alkyl)C(O)(C₁₋₄ alkyl), -N(C₁₋₄ alkyl)C(O)(C₁₋₄ alkoxy), -OC(O)(C₁₋₄ alkyl), -OC(O)(C₁₋₄ alkoxy), -Si(C₁₋₄ alkyl)₃, -Si(C₁₋₄ alkoxy)₃, C₆₋₁₀aryl, C₆₋₁₀aryloxy, C₆₋₁₀arylthio, C₆₋₁₀heteroaryl, -(C₁₋₈ - perhaloalkyl), arylC₁₋₄alkynyl, -C₁₋₆alkynyl, wherein all the alkyl, alkenyl, alkynyl, alkoxy, aryl, aryloxy, arylthio or heteroaryl groups are either substituted or unsubstituted, preferably these substituents of the substituted groups bear only one further substituent, more preferably these substituents of the substituted groups are not further substituted.

The more preferred substituents of the substituted alkyl groups, alkenyl groups, the alkynyl groups and the alkoxy are selected from the following substituents -OH, CN, F, Cl, C₁₋₄alkoxy, -C₁₋₄alkoxy, -C₁₋₄

alkylthio, C₁₋₄alkyl, C₂₋₄alkenyl, C₂₋₄alkenyl, C₂₋₄alkynyl, C₆₋₁₀aryl, -C₁₋₄alkylamino. The alkyl groups are branched or linear. The most preferred alkyl groups are methyl, ethyl, propyl, iso-propyl, n-butyl, t-butyl (1,1-dimethylethyl), sec-butyl (1-methylpropyl), iso-butyl (2-methylpropyl), pentyl, iso-pentyl (3-methylbutyl, isoamyl), 1-methylpentyl, 1-ethylpentyl, hexyl, heptyl, or octyl. Preferred alkenyl groups are ethenyl, propenyl (1-propenyl, 2-propenyl), butenyl (1-butenyl, 2-butenyl, 3-butenyl, 2-methylpropen-1-yl, 2-methylpropen-2-yl), pentenyl (pent-1-enyl, pent-2-enyl, pent-3-enyl, 2-methylbut-1-enyl, 3-methylbut-1-enyl, 2-methylbut-2-enyl, 3-methylbut-2-enyl, 2-methylbut-3-enyl, 3-methylbut-3-enyl, 1,2-dimethylprop-2-enyl, 1,1-dimethylprop-2-enyl). Preferred alkynyl groups are ethynyl, propynyl (prop-1-ynyl or prop-2-ynyl (propargyl)), butyl (but-1-ynyl, but-2-ynyl, but-3-ynyl), pentynyl (pent-1-ynyl, pent-2-ynyl, pent-3-ynyl, pent-4-ynyl, 3-methylbut-1-ynyl, 2-methylbut-3-ynyl, 1-methylbut-3-ynyl). The most preferred alkyl groups and the most preferred alkoxy groups are methyl, ethyl, propyl, t-butyl, methoxy and ethoxy groups. Methyl, ethyl and methoxy groups are very particularly preferred.

Preferably the alkyl groups in the compound of formula (I) and/or the alkoxy groups in the compound of formula (I) bear not more than two further substituents, more preferably the alkyl groups in the compound of formula (I) and/or the alkoxy groups in the compound of formula (I) bear not more than one further substituent, most preferred the alkyl groups in the compound of formula (I) and/or the alkoxy groups in the compound of formula (I) are not further substituted.

The aryl and hetero aryl groups are either substituted or unsubstituted 5- membered or 6-membered aromatic monocyclic which may contain one or two heteroatoms selected from N or S or unsubstituted or substituted 9-membered aromatic bicyclic ring system which may contain one or two heteroatoms selected from N or S.

The aryl groups and heteroaryl groups are preferably unsubstituted or substituted 5- membered or 6-membered aromatic monocyclic ring system which may contain one or two heteroatoms selected from N or S wherein the substituents are selected from the group consisting of halogen, hydroxy, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄alkylthio, C₁-C₄alkoxy-C₁-C₄alkyl, C₁-C₄haloalkoxy, C₁-C₄alkoximino and C₁-C₄alkylendioxy groups, more preferably phenyl, pyridyl, thiophene, imidazole or pyrrol groups.

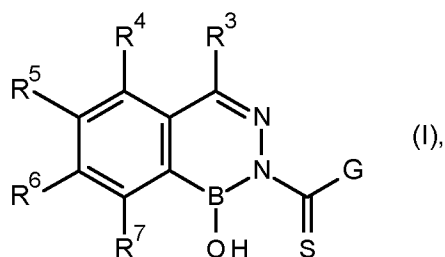
The preferred substituents of the substituted aryl groups and heteroaryl groups in the compound of formula (I) are selected from the group consisting of halogen, hydroxy, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄alkylthio, C₁-C₄alkoxy-C₁-C₄alkyl, C₁-C₄haloalkoxy, C₁-C₄alkoximino and C₁-C₄alkylendioxy;; more preferred substituents of the substituted aryl groups or heteroaryl groups in the compound of formula (I) are selected from the following substituents F, Cl, CF₃, CN, -OH, nitro, -C₁₋₄alkyl, -C₁₋₄alkoxy, -C(O)(C₁₋₄alkoxy), -C(O)H, -C(O)(C₁₋₄Alkyl) wherein the alkyl groups are either substituted or unsubstituted.

The most preferred substituents of the substituted aryl groups in the compound of formula (I) are selected from the following substituents, F, Cl, -C₁₋₄Alkyl, C₁₋₄alkoxy, -CN, -C(O)(C₁₋₄alkoxy), -

C(O)(C₁₋₄ Alkyl) and preferably F, Cl are the even more preferred substituents of the substituted aryl groups in the compound of formula (I).

In particularly preferred embodiments for the methods and compounds of the invention, the preferred groups for X, R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ in any combination thereof, are as set out below.

In a further aspect the present invention relates to compounds of formula (I)

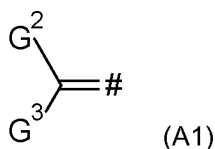


wherein

G = N(R¹R²), SCH₃

R¹ is H, C₁-C₈alkyl or C₁-C₈alkyl substituted by one to five Z, C₁-C₈alkenyl or C₁-C₈alkenyl substituted by one to five Z, C₃-C₁₀cycloalkyl or C₃-C₁₀cycloalkyl substituted by one to five Y, aryl-C₁-C₄alkylene- or aryl-C₁-C₄alkylene- wherein the aryl moiety is substituted by one to five Y, heterocyclyl-C₁-C₄alkylene- or heterocyclyl-C₁-C₄alkylene- wherein the heterocyclyl moiety is substituted by one to five Y, aryl- (W)- or aryl-(W)- wherein the aryl moiety is substituted by one to five Y, heterocyclyl- (W)- or heterocyclyl-(W)- wherein the heterocyclyl moiety is substituted by one to five Y, aryl or aryl substituted by one to five Y, heterocyclyl or heterocyclyl substituted by one to five Y, C₁-C₈alkylaminocarbonyl-C₁-C₄ alkylene, C₁-C₈haloalkylaminocarbonyl-C₁-C₄ alkylene, C₃-C₈cycloalkylaminocarbonyl-C₁-C₄ alkylene, C₁-C₈alkylaminocarbonyl-, C₁-C₈haloalkylaminocarbonyl, C₃-C₈cycloalkylaminocarbonyl, C₁-C₆alkyl-O-N=CH-, C₁-C₆haloalkyl-O-N=CH-;

R² is hydrogen, C₁-C₆alkyl, C₁-C₆alkoxy-, C₁-C₆alkylcarbonyl-, or C₁-C₆alkoxycarbonyl-; or when G=N(R² R¹), R¹ and R² together can also form a ring or can represent group A1



G² is O(R⁸), N(R⁹)(R¹⁰) or S(R¹¹);

G³ is N(R¹²)(R¹³) or S(R¹⁴);

R³ = H, halogen, cyano, nitro, formyl, C₁-C₆alkyl, alkenyl, alkynyl and aryl

R⁴, R⁵, R⁶ and R⁷ is independently hydrogen halogen, cyano, nitro, hydroxy, amino, alkyl, haloalkyl, alkoxy, haloalkoxy, alkenyl, alkynyl, provided that at least one of R⁴, R⁵, R⁶ and R⁷ is not a hydrogen; or or two neighboured substituents R⁴, R⁵, R⁶ and R⁷ form a -O- C₁-C₄alkyl-O- ring together with the carbon atoms to which they are attached;

each Z is independently halogen, cyano, nitro, hydroxy, amino, C₁-C₈alkylamino, (C₁-C₈alkyl)₂amino, C₁-C₈alkylcarbonylamino, C₁-C₈haloalkylcarbonylamino, C₁-C₈alkoxy-, C₁-C₈haloalkoxy-, aryloxy or aryloxy substituted by one to five M, C₁-C₈alkylcarbonyl-, C₁-C₈alkoxycarbonyl-, mercapto, C₁-C₈alkylthio-, C₁-C₈haloalkylthio-, C₁-C₈alkylsulfinyl-, C₁-C₈haloalkylsulfinyl-, C₁-C₈alkylsulfonyl-, C₁-C₈haloalkylsulfonyl-, aryl-C₁-C₄alkylthio or aryl-C₁-C₄alkylthio wherein the aryl moiety is substituted by one to five M; C₃-C₇ aliphatic and aromatic carbocycle or C₃-C₇ aliphatic and aromatic carbocycle wherein the carbocycle is substituted by one to five M, 3 to 7 membered heterocycles containing 1-3 heteroatoms selected from N, O, S, wherein the heterocycle can be optionally substituted by M;

each Y is independently halogen, cyano, nitro, oxo, hydroxy, C₁-C₈alkyl, C₁-C₈haloalkyl, C₁-C₈cyanoalkyl, C₂-C₈alkenyl, C₂-C₈haloalkenyl, C₂-C₈alkynyl, C₂-C₈haloalkynyl, C₃-C₁₀cycloalkyl, C₁-C₈alkoxy-, C₁-C₈haloalkoxy-, mercapto, C₁-C₈alkylthio-, C₁-C₈haloalkylthio-, C₁-C₈alkylsulfinyl-, C₁-C₈haloalkylsulfinyl-, C₁-C₈alkylsulfonyl-, C₁-C₈haloalkylsulfonyl-, C₁-C₈alkylaminosulfonyl, (C₁-C₈alkyl)₂aminosulfonyl-, C₁-C₈alkylcarbonyl-, C₁-C₈alkoxycarbonyl-, aryl or aryl substituted by one to five M, heterocyclyl or heterocyclyl substituted by one to five M, aryl-C₁-C₄alkylene or aryl-C₁-C₄alkylene wherein the aryl moiety is substituted by one to five M, heterocyclyl-C₁-C₄alkylene or heterocyclyl-C₁-C₄alkylene wherein the heterocyclyl moiety is substituted by one to five M, aryloxy or aryloxy substituted by one to five M, aryloxy-C₁-C₄alkylene or aryloxy-C₁-C₄alkylene wherein the aryl moiety is substituted by one to five M;

each M is independently halogen, cyano, nitro, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy-, or C₁-C₄haloalkoxy, substituted or unsubstituted alkyl -;

R⁸, R¹¹ and R¹⁴ are independently C₁-C₄ alkyl;

R⁹, R¹⁰, R¹², and R¹³ are independently hydrogen or C₁-C₄ alkyl;

W is hydrogen or C₁-C₄ alkyl

and agronomically acceptable salts, stereoisomers, diastereoisomers, enantiomers, tautomers, atropisomers and N-oxides of those compounds.

In a preferred embodiment G= N(R¹R²),

In an other preferred embodiment SCH₃

In a preferred embodiment R¹ is H, C₁-C₈alkyl or C₁-C₈alkyl substituted by one to five Z, C₁-C₈alkenyl or C₁-C₈alkenyl substituted by one to five Z, C₃-C₁₀cycloalkyl or C₃-C₁₀cycloalkyl substituted by one to five Y, aryl-C₁-C₄alkylene- or aryl-C₁-C₄alkylene- wherein the aryl moiety is substituted by one to five Y, heterocyclyl-C₁-C₄alkylene-.

or heterocyclyl-C₁-C₄alkylene- wherein the heterocyclyl moiety is substituted by one to five Y, aryl-(W)- or aryl-(W)- wherein the aryl moiety is substituted by one to five Y, heterocyclyl-(W)- or heterocyclyl-(W)- wherein the heterocyclyl moiety is substituted by one to five Y, aryl or aryl substituted by one to five Y; heterocyclyl or heterocyclyl substituted by one to five Y, C₁-C₈alkylaminocarbonyl-C₁-C₄ alkylene, C₁-C₈haloalkylaminocarbonyl-C₁-C₄ alkylene, C₃-C₈cycloalkyl-

aminocarbonyl-C₁-C₄ alkylene, C₁-C₈alkylaminocarbonyl-, C₁-C₈haloalkylaminocarbonyl, C₃-C₈cycloalkyl-aminocarbonyl, C₁-C₆alkyl-O-N=CH-, C₁-C₆haloalkyl-O-N=CH-;

In a further preferred embodiment R¹ is H, C₁-C₈alkyl or C₁-C₈alkyl substituted by one to five Z, C₁-C₈alkenyl or C₁-C₈alkenyl substituted by one to five Z, C₃-C₁₀cycloalkyl or C₃-C₁₀cycloalkyl substituted by one to five Y, aryl-C₁-C₄alkylene- or aryl-C₁-C₄alkylene- wherein the aryl moiety is substituted by one to five Y, heterocyclyl-C₁-C₄alkylene-.

In a further preferred embodiment R¹ is or heterocyclyl-C₁-C₄alkylene- wherein the heterocyclyl moiety is substituted by one to five Y, aryl- (W)- or aryl-(W)- wherein the aryl moiety is substituted by one to five Y, heterocyclyl- (W)- or heterocyclyl-(W)- wherein the heterocyclyl moiety is substituted by one to five Y, aryl or aryl substituted by one to five Y; heterocyclyl or heterocyclyl substituted by one to five Y, C₁-C₈alkylaminocarbonyl-C₁-C₄ alkylene, C₁-C₈haloalkylaminocarbonyl-C₁-C₄ alkylene, C₃-C₈cycloalkyl-aminocarbonyl-C₁-C₄ alkylene, C₁-C₈alkylaminocarbonyl-, C₁-C₈haloalkylaminocarbonyl, C₃-C₈cycloalkyl-aminocarbonyl, C₁-C₆alkyl-O-N=CH-, C₁-C₆haloalkyl-O-N=CH-;

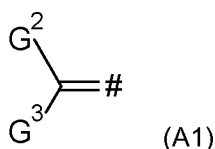
In a further preferred embodiment R¹ is heterocyclyl or heterocyclyl substituted by one to five Y,

In a further preferred embodiment R¹ is C₁-C₈alkylaminocarbonyl-C₁-C₄ alkylene, C₁-C₈haloalkylaminocarbonyl-C₁-C₄ alkylene, C₃-C₈cycloalkyl-aminocarbonyl-C₁-C₄ alkylene, C₁-C₈alkylaminocarbonyl-, C₁-C₈haloalkylaminocarbonyl, C₃-C₈cycloalkyl-aminocarbonyl, C₁-C₆alkyl-O-N=CH-, C₁-C₆haloalkyl-O-N=CH-;

In a preferred embodiment R² is hydrogen, C₁-C₆alkyl, C₁-C₆alkoxy-, C₁-C₆alkylcarbonyl-, or C₁-C₆alkoxycarbonyl-;

In a more preferred embodiment R² is hydrogen

In a preferred embodiment R² is when G=N(R² R¹), R¹ and R² together can also form a ring or can represent group A1



G² is O(R⁸), N(R⁹)(R¹⁰) or S(R¹¹);

G³ is N(R¹²)(R¹³) or S(R¹⁴);

In a preferred embodiment R³= H, halogen, C₁-C₆alkyl, aryl

In a further preferred embodiment R³= H, halogen, C₁-C₆alkyl, preferably H, CH₃

In a preferred embodiment R⁴, R⁵, R⁶ and R⁷ is independently hydrogen halogen, cyano, nitro, hydroxy, amino, alkyl, haloalkyl, alkoxy, haloalkoxy, alkenyl, alkynyl, provided that at least one of R⁴, R⁵, R⁶ and R⁷ is not a hydrogen;

In a further preferred embodiment

Preferably each Z is independently halogen, cyano, nitro, hydroxy, amino, C₁-C₈alkylamino, (C₁-C₈alkyl)₂amino, C₁-C₈alkylcarbonylamino, C₁-C₈haloalkylcarbonylamino, C₁-C₈alkoxy-, C₁-C₈haloalkoxy-, aryloxy or aryloxy substituted by one to five M, C₁-C₈alkylcarbonyl-, C₁-C₈alkoxycarbonyl-, C₃-C₇ aliphatic and aromatic carbocycle or C₃-C₇ aliphatic and aromatic carbocycle wherein the carbocycle is substituted by one to five M, 3 to 7 membered heterocycles containing 1-3 heteroatoms selected from N, O, S, wherein the heterocycle can be optionally substituted by M;

Further preferred are each Y each Y is independently halogen, cyano, nitro, oxo, hydroxy, C₁-C₈alkyl, C₁-C₈haloalkyl, C₁-C₈cyanoalkyl, C₂-C₈alkenyl, C₂-C₈haloalkenyl, C₂-C₈alkynyl, C₂-C₈haloalkynyl, C₃-C₁₀cycloalkyl, C₁-C₈alkoxy-, C₁-C₈haloalkoxy-, mercapto, C₁-C₈alkylthio-, C₁-C₈haloalkylthio-, C₁-C₈alkylsulfanyl-, C₁-C₈haloalkylsulfanyl-, C₁-C₈alkylsulfonyl-, C₁-C₈haloalkylsulfonyl-, C₁-C₈alkylaminosulfonyl-, (C₁-C₈alkyl)₂aminosulfonyl-, C₁-C₈alkylcarbonyl-, C₁-C₈alkoxycarbonyl-, aryl or aryl substituted by one to five M,

Further preferred are each Y is independently heterocyclyl or heterocyclyl substituted by one to five M, aryl-C₁-C₄alkylene or aryl-C₁-C₄alkylene wherein the aryl moiety is substituted by one to five M, heterocyclyl-C₁-C₄alkylene or heterocyclyl-C₁-C₄alkylene wherein the heterocyclyl moiety is substituted by one to five M, aryloxy or aryloxy substituted by one to five M, aryloxy-C₁-C₄alkylene or aryloxy-C₁-C₄alkylene wherein the aryl moiety is substituted by one to five M;

By preference each M is independently halogen, cyano, nitro, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy-, or C₁-C₄haloalkoxy,

More preferred

R⁸, R¹¹ and R¹⁴ are independently C₁-C₄ alkyl;

R⁹, R¹⁰, R¹², and R¹³ are independently hydrogen or C₁-C₄ alkyl;

W is hydrogen or C₁-C₄ alkyl

In a preferred embodiment

G= N(R¹R²) or SCH₃;

R¹ is C₁-C₄alkyl or C₁-C₄alkenyl each branched or linear and each optionally substituted by halogen, hydroxyl, phenyl, thiophen hydroxycyclohexyl, pyridyl, 2-(1,3-benzodioxol-5-yl); 2-benzylsulfanyl, ([1',3']dioxolan-2'-yl)-, tetrahydrofuranyl, 3-pyrrolidin-1-yl, 1,3-benzodioxol-5-yl;

Or phenyl or benzyl each optionally substituted by halogen, C₁-C₄alkoxy, 4-Methanesulfonyl-2-oxotetrahydrothiophen-3-yl;

or C₁-C₄alkoxy-C₁-C₄alkyl, C₁-C₆cycloalkyl, 6-ethoxycarbonylcyclohex-3-en-1-yl,

R² is hydrogen;

R³= H, CH₃;

R⁴, R⁵, R⁶ and R⁷ is independently hydrogen Cl, F, NO₂, OH, C₁-C₄alkoxy, or two neighbored substituents R⁴, R⁵, R⁶ and R⁷ form a -O-C₁-C₄alkyl-O- ring together with the carbon atoms to which they are attached

In a more preferred embodiment

$G = N(R^1R^2)$ or SCH_3 ;

R^1 is CH_3 , 2-methoxy-1-ethyl, 4-methoxy-1-benzyl, cyclobutyl, phenyl, H, allyl, benzyl, 3,3,3-trifluoropropyl-, (1-hydroxycyclohexyl)methyl, 2-oxotetrahydrothiophen-3-yl, 6-ethoxycarbonylcyclohex-3-en-1-yl, 2-(1,3-benzodioxol-5-yl)ethyl, 2-benzylsulfanylethyl, 4-Methanesulfonyl-benzyl, sec-Butyl, Butan-1-ol-2-yl, 2-([1',3']dioxolan-2'-yl)-eth-1-yl-, tetrahydrofuran-2-ylmeth-yl-, 3-pyrrolidin-1-ylpropyl, (pyrid-3-yl)-methyl-, 2-fluorobenzyl, 1-phenyl-eth-1-yl-, 2-phenyl-eth-1-yl-, 2-(thiophen-2'-yl)-eth-1-yl-,

R^2 is hydrogen;

$R^3 = H, CH_3$;

R^4, R^5, R^6 and R^7 is independently hydrogen Cl, F, NO_2 , OH, OMe, or two neighboured substituents R^4, R^5, R^6 and R^7 form a $-O-CH_2-O-$ ring together with the carbon atoms to which they are attached

In a other more preferred embodiment

$G = SCH_3$;

$R^3 = H, CH_3$;

R^4, R^5, R^6 and R^7 is independently hydrogen Cl, F, NO_2 , OH, C_1-C_4 alkoxy, or two neighboured substituents R^4, R^5, R^6 and R^7 form a $-O-C_1-C_4$ alkyl-O- ring together with the carbon atoms to which they are attached

In a even more preferred embodiment

$G = SCH_3$;

$R^3 = H, CH_3$;

R^4, R^5, R^6 and R^7 is independently hydrogen Cl, F, NO_2 , OH, OMe, or two neighboured substituents R^4, R^5, R^6 and R^7 form a $-O-CH_2-O-$ ring together with the carbon atoms to which they are attached

In an other more preferred embodiment

$G = N(R^1R^2)$;

R^1 is C_1-C_4 alkyl or C_1-C_4 alkenyl each branched or linear and each optionally substituted by halogen, hydroxyl, phenyl, thiophen hydroxycyclohexyl, pyridyl, 2-(1,3-benzodioxol-5-yl); 2-benzylsulfanyl, ([1',3']dioxolan-2'-yl)-, tetrahydrofuranyl, 3-pyrrolidin-1-yl, 1,3-benzodioxol-5-yl;

Or phenyl or benzyl each optionally substituted by halogen, C_1-C_4 alkoxy, 4-Methanesulfonyl-2-oxotetrahydrothiophen-3-yl;

or C_1-C_4 alkoxy- C_1-C_4 alkyl, C_1-C_6 cycloalkyl, 6-ethoxycarbonylcyclohex-3-en-1-yl,

R^2 is hydrogen;

$R^3 = H, CH_3$;

R^4, R^5, R^6 and R^7 is independently hydrogen Cl, F, NO_2 , OH, C_1-C_4 alkoxy, or two neighboured substituents R^4, R^5, R^6 and R^7 form a $-O-C_1-C_4$ alkyl-O- ring together with the carbon atoms to which they are attached

In an other even more preferred embodiment

$G = N(R^1R^2)$;

R^1 is CH_3 , 2-methoxy-1-ethyl, 4-methoxy-1-benzyl, cyclobutyl, phenyl, H, allyl, benzyl, 3,3,3-trifluoropropyl-, (1-hydroxycyclohexyl)methyl, 2-oxotetrahydrothiophen-3-yl, 6-ethoxycarbonylcyclohex-3-en-1-yl, 2-(1,3-benzodioxol-5-yl)ethyl, 2-benzylsulfanylethyl, 4-Methanesulfonyl-benzyl, sec-Butyl, Butan-1-ol-2-yl, 2-([1',3']dioxolan-2'-yl)-eth-1-yl-, tetrahydrofuran-2-ylmeth-yl-, 3-pyrrolidin-1-ylpropyl, (pyrid-3-yl)-methyl-, 2-fluorobenzyl, 1-phenyl-eth-1-yl-, 2-phenyl-eth-1-yl-, 2-(thiophen-2'-yl)-eth-1-yl-,

R^2 is hydrogen;

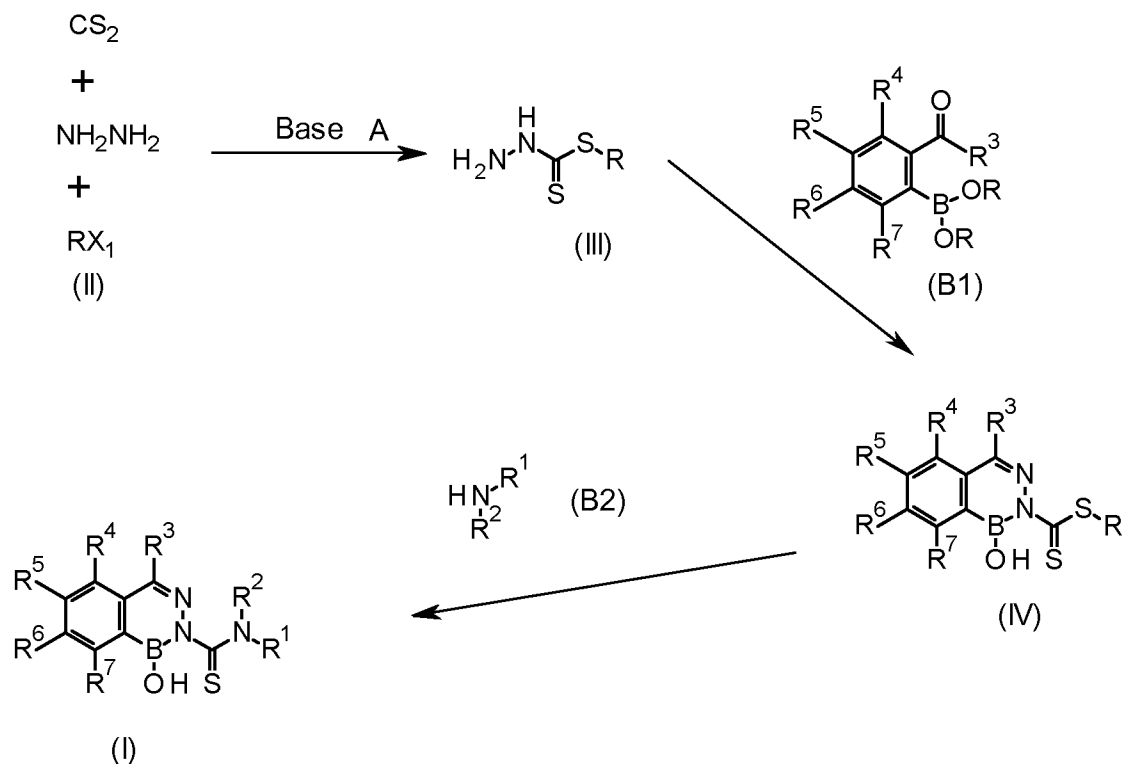
$R^3 = H, CH_3$;

R^4, R^5, R^6 and R^7 is independently hydrogen Cl, F, NO_2 , OH, OMe, or two neighbored substituents R^4, R^5, R^6 and R^7 form a -O-CH₂-O- ring together with the carbon atoms to which they are attached

The compounds of the invention may be made by a variety of methods. For example, the compounds of formula (I) may be prepared according to Chemistry and Biodiversity, (Vol 5), 2008, 2415-2422 or may be prepared according to the procedure illustrated in scheme 1

In all compounds shown in the schemes below $X_1, R^1, R^2, R^3, R^4, R^5, R^6$ and R^7 are as defined above.

Scheme 1



Compounds of formula (III) are commercially available but can also be prepared by state of the art methodologies from compounds of formula (II). In formula (II), X_1 is a halogen and $R = R^1$; when R^1 is as defined above. When R is a methyl group in formula (II) the reaction with with carbon

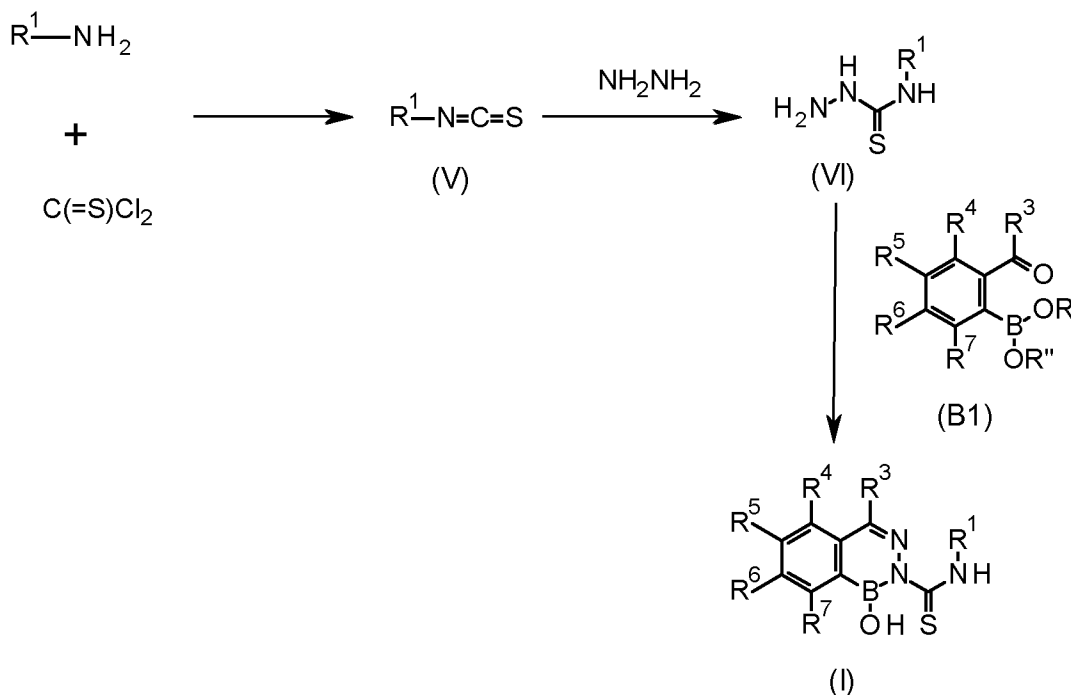
disulfide and hydrazine hydrate in presence of a suitable base example potassium hydroxide in a protic solvent such as water or any alcohol at temperature 0°C to 35°C provides compounds of formula (III) (See: Bioorg. Med. Chem. Lett, 22(15); 2012; 4934-4938, US6545172, US5861526).

Compounds of formula (IV) can be obtained by the condensation of compounds of formula (III) wherein R is R¹ as defined above with compounds of formula (B1), which is commercially available or can also be prepared by the state of the art methodologies, in suitable protic solvent such as water or in solvent combination of water with alcoholic solvents such as methanol, ethanol or isopropanol in presence or acids such as formic acid or acetic acid at a temperature between 0°C and 100°C.

Compounds of formula (I) can be obtained by the reaction of the compounds of formula (IV) with suitable nucleophilic amines optionally in the presence of an organic or inorganic base such as Hunigs base, triethylamine or DBU in protic solvents such as ethanol or water at temperatures ranging from 0°C to reflux temperature of the solvents used.

Scheme 2 illustrates an alternative method for the preparation of compounds of formula (I)

Scheme-2

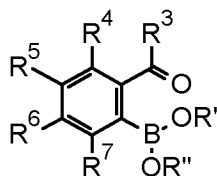


Compounds of formula (V) (-isothiocyanates) can be obtained by the reaction of primary amines with thiophosgene by state of the art methodologies. Substituted thiosemicarbazide Compounds of formula (VI), can be obtained by the reaction of isocyanates of formula (V) with hydrazine.

Compounds of formula (I) can be obtained by the condensation of thiosemicarbazide of formula (VI) with boron derivatives of formula (B1) in a suitable protic solvent such as water or in

solvent combination of water with alcoholic solvents such as methanol, ethanol or isopropanol in presence or acids such as formic acid or acetic acid at temperatures ranging from 0°C to 100°C. However, using the synthetic method in scheme 2 leads to the compounds of formula (I) with R² is H.

Description for the compounds of formula (B1)



(B1)

R³, R⁴, R⁵, R⁶, R⁷ are as defined for formula (I). R' and R'' are each members independently selected from H, alkyl such as methyl, ethyl, propyl, isopropyl, butyl, t-butyl or phenyl or benzyl. Also, R' and R'' together with the atoms to which they are attached form a cyclic unit comprising more than one heteroatoms such as substituted or unsubstituted dioxaborolane, substituted or unsubstituted dioxaborinane or substituted or unsubstituted dioxaboropane or MIDA boronates.

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

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

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

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

The methods according to the instant invention are particularly effective to protect useful plants or plant propagation material thereof against phytopathogenic fungi belonging to the following classes:

Ascomycetes (e.g. the genus *Cochliobolus*, *Colletotrichum*, *Fusarium*, *Gaeumannomyces*, *Giberella*, *Monographella*, *Microdochium*, *Penicillium*, *Phoma*, *Pyricularia*, *Magnaporthe*, *Septoria*, *Pseudocercospora*, *Tapesia* and *Thielaviopsis*); Basidiomycetes (e.g. the genus *Phakopsora*, *Puccinia*, *Rhizoctonia*, *Thanatephorus*, *Sphacelotheca*, *Tilletia*, *Typhula* and *Ustilago*); Fungi imperfecti (also known as Deuteromycetes; e.g. the genus *Ascochyta*, *Diplodia*, *Erysiphe*, *Fusarium*, *Helminthosporium*, *Phomopsis*, *Pyrenophora* and *Verticillium*); Oomycetes (e.g. *Aphanomyces*, *Peronospora*, *Peronosclerospora*, *Phytophthora*, *Plasmopara*, *Pseudoperonospora*, *Pythium*); and Zygomycetes (e.g. the genus *Rhizopus*).

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

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

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

Examples of such plants are: YieldGard® (maize variety that expresses a CryIA(b) toxin); YieldGard Rootworm® (maize variety that expresses a CryIIIB(b1) toxin); YieldGard Plus® (maize variety that expresses a CryIA(b) and a CryIIIB(b1) toxin); Starlink® (maize variety that expresses a Cry9(c) toxin); Herculex I® (maize variety that expresses a CryIF(a2) toxin and the enzyme phosphinothricine

N-acetyltransferase (PAT) to achieve tolerance to the herbicide glufosinate ammonium); NuCOTN 33B® (cotton variety that expresses a CryIA(c) toxin); Bollgard I® (cotton variety that expresses a CryIA(c) toxin); Bollgard II® (cotton variety that expresses a CryIA(c) and a CryIIA(b) toxin); VIPCOT® (cotton variety that expresses a VIP toxin); NewLeaf® (potato variety that expresses a CryIIIA toxin); NatureGard® Agrisure® GT Advantage (GA21 glyphosate-tolerant trait), Agrisure® CB Advantage (Bt11 corn borer (CB) trait), Agrisure® RW (corn rootworm trait) and Protecta®.

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

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

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

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

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

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

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

Further examples of such transgenic crops are:

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.
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.
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.

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 term “locus” of a useful plant as used herein is intended to embrace the place on which the useful plants are growing, where the plant propagation materials of the useful plants are sown or where the plant propagation materials of the useful plants will be placed into the soil. An example for such a locus is a field, on which crop plants are growing.

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

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

Therefore the invention also relates to compositions for controlling and protecting against phytopathogenic microorganisms, comprising a compound of formula (I) and an inert carrier, and to a

method of controlling or preventing infestation of useful plants by phytopathogenic microorganisms, wherein a composition, comprising a compound of formula (I) as active ingredient and an inert carrier, is applied to the plants, to parts thereof or the locus thereof.

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

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

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

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

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

The activity of the compositions according to the invention can be broadened considerably, and adapted to prevailing circumstances, by adding other insecticidally, acaricidally and/or fungicidally active ingredients. The mixtures of the compounds of formula (I) with other insecticidally, acaricidally and/or fungicidally active ingredients may also have further surprising advantages which can also be described, in a wider sense, as synergistic activity. For example, better tolerance by plants, reduced phytotoxicity, insects can be controlled in their different development stages or better behaviour during their production, for example during grinding or mixing, during their storage or during their use.

Suitable additions to active ingredients here are, for example, representatives of the following classes of active ingredients: organophosphorus compounds, nitrophenol derivatives, thioureas, juvenile hormones, formamidines, benzophenone derivatives, ureas, pyrrole derivatives, carbamates, pyrethroids, chlorinated hydrocarbons, acylureas, pyridylmethyleamino derivatives, macrolides, neonicotinoids and *Bacillus thuringiensis* preparations.

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 one specific compound listed in Table 1 (compounds 1 to 116) of the present invention"):

an adjuvant selected from the group of substances consisting of petroleum oils (alternative name) (628) + TX,

an acaricide selected from the group of substances consisting of 1,1-bis(4-chlorophenyl)-2-ethoxyethanol (IUPAC name) (910) + TX, 2,4-dichlorophenyl benzenesulfonate (IUPAC/Chemical Abstracts name) (1059) + TX, 2-fluoro-*N*-methyl-*N*-1-naphthylacetamide (IUPAC name) (1295) + TX, 4-chlorophenyl phenyl sulfone (IUPAC name) (981) + TX, abamectin (1) + TX, acequinocyl (3) + TX, acetoprole [CCN] + TX, acrinathrin (9) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, alpha-cypermethrin (202) + TX, amidithion (870) + TX, amidoflumet [CCN] + TX, amidothioate (872) + TX, amiton (875) + TX, amiton hydrogen oxalate (875) + TX, amitraz (24) + TX, aramite (881) + TX, arsenous oxide (882) + TX, AVI 382 (compound code) + TX, AZ 60541 (compound code) + TX, azinphos-ethyl (44) + TX, azinphos-methyl (45) + TX, azobenzene (IUPAC name) (888) + TX, azocyclotin (46) + TX, azothoate (889) + TX, benomyl (62) + TX, benoxafos (alternative name) [CCN] + TX, benzoximate (71) + TX, benzyl benzoate (IUPAC name) [CCN] + TX, bifenazate (74) + TX, bifenthrin (76) + TX, binapacryl (907) + TX, brofenvalerate (alternative name) + TX, bromocyclen (918) + TX, bromophos (920) + TX, bromophos-ethyl (921) + TX, bromopropylate (94) + TX, buprofezin (99) + TX, butocarboxim (103) + TX, butoxycarboxim (104) + TX, butylpyridaben (alternative name) + TX, calcium polysulfide (IUPAC name) (111) + TX, camphechlor (941) + TX, carbanolate (943) + TX, carbaryl (115) + TX, carbofuran (118) + TX, carbophenothion (947) + TX, CGA 50'439 (development code) (125) + TX, chinomethionat (126) + TX, chlordbenside (959) + TX, chlordimeform (964) + TX, chlordimeform hydrochloride (964) + TX, chlorfenapyr (130) + TX, chlorfenethol (968) + TX, chlorfenson (970) + TX, chlorfensulphide (971) + TX, chlorfenvinphos (131) + TX, chlorobenzilate (975) + TX, chloromebuform (977) + TX, chloromethiuron (978) + TX, chloropropylate (983) + TX, chlorpyrifos (145) + TX, chlorpyrifos-methyl (146) + TX, chlorthiophos (994) + TX, cinerin I (696) + TX, cinerin II (696) + TX, cinerins (696) + TX, clofentezine (158) + TX, closantel (alternative name) [CCN] + TX, coumaphos (174) + TX, crotamiton (alternative

name) [CCN] + TX, crotoxyphos (1010) + TX, cufraneb (1013) + TX, cyanthoate (1020) + TX, cyflumetofen (CAS Reg. No.: 400882-07-7) + TX, cyhalothrin (196) + TX, cyhexatin (199) + TX, cypermethrin (201) + TX, DCPM (1032) + TX, DDT (219) + TX, demephion (1037) + TX, demephion-O (1037) + TX, demephion-S (1037) + TX, demeton (1038) + TX, demeton-methyl (224) + TX, demeton-O (1038) + TX, demeton-O-methyl (224) + TX, demeton-S (1038) + TX, demeton-S-methyl (224) + TX, demeton-S-methylsulphon (1039) + TX, diafenthiuron (226) + TX, dialifos (1042) + TX, diazinon (227) + TX, dichlofluanid (230) + TX, dichlorvos (236) + TX, dicliphos (alternative name) + TX, dicofol (242) + TX, dicrotophos (243) + TX, dienochlor (1071) + TX, dimefox (1081) + TX, dimethoate (262) + TX, dinactin (alternative name) (653) + TX, dinex (1089) + TX, dinex-diclexine (1089) + TX, dinobuton (269) + TX, dinocap (270) + TX, dinocap-4 [CCN] + TX, dinocap-6 [CCN] + TX, dinocton (1090) + TX, dinopenton (1092) + TX, dinosulfon (1097) + TX, dinoterbon (1098) + TX, dioxathion (1102) + TX, diphenyl sulfone (IUPAC name) (1103) + TX, disulfiram (alternative name) [CCN] + TX, disulfoton (278) + TX, DNOC (282) + TX, dofenapyn (1113) + TX, doramectin (alternative name) [CCN] + TX, endosulfan (294) + TX, endothion (1121) + TX, EPN (297) + TX, eprinomectin (alternative name) [CCN] + TX, ethion (309) + TX, ethoate-methyl (1134) + TX, etoxazole (320) + TX, etrimfos (1142) + TX, fenazaflor (1147) + TX, fenazaquin (328) + TX, fenbutatin oxide (330) + TX, fenothiocarb (337) + TX, fenpropathrin (342) + TX, fenpyrad (alternative name) + TX, fenpyroximate (345) + TX, fenson (1157) + TX, fentrifanil (1161) + TX, fenvalerate (349) + TX, fipronil (354) + TX, fluacrypyrim (360) + TX, fluazuron (1166) + TX, flubenzimine (1167) + TX, flucycloxuron (366) + TX, flucythrinate (367) + TX, fluenetil (1169) + TX, flufenoxuron (370) + TX, flumethrin (372) + TX, fluorbenside (1174) + TX, fluvalinate (1184) + TX, FMC 1137 (development code) (1185) + TX, formetanate (405) + TX, formetanate hydrochloride (405) + TX, formothion (1192) + TX, formparanate (1193) + TX, gamma-HCH (430) + TX, glyodin (1205) + TX, halfenprox (424) + TX, heptenophos (432) + TX, hexadecyl cyclopropanecarboxylate (IUPAC/Chemical Abstracts name) (1216) + TX, hexythiazox (441) + TX, iodomethane (IUPAC name) (542) + TX, isocarbophos (alternative name) (473) + TX, isopropyl O-(methoxyaminothiophosphoryl)salicylate (IUPAC name) (473) + TX, ivermectin (alternative name) [CCN] + TX, jasmolin I (696) + TX, jasmolin II (696) + TX, jodfenphos (1248) + TX, lindane (430) + TX, lufenuron (490) + TX, malathion (492) + TX, malonoben (1254) + TX, mecarbam (502) + TX, mephosfolan (1261) + TX, mesulfen (alternative name) [CCN] + TX, methacrifos (1266) + TX, methamidophos (527) + TX, methidathion (529) + TX, methiocarb (530) + TX, methomyl (531) + TX, methyl bromide (537) + TX, metolcarb (550) + TX, mevinphos (556) + TX, mexacarbate (1290) + TX, milbemectin (557) + TX, milbemycin oxime (alternative name) [CCN] + TX, mipafox (1293) + TX, monocrotophos (561) + TX, morphothion (1300) + TX, moxidectin (alternative name) [CCN] + TX, naled (567) + TX, NC-184 (compound code) + TX, NC-512 (compound code) + TX, nifluridide (1309) + TX, nikkomycins (alternative name) [CCN] + TX, nitrilacarb (1313) + TX, nitrilacarb 1:1 zinc chloride complex (1313) + TX, NNI-0101 (compound code) + TX, NNI-0250 (compound code) + TX, omethoate (594) + TX, oxamyl (602) + TX, oxydeprofos (1324) + TX, oxydisulfoton (1325) + TX, pp'-DDT (219) + TX, parathion (615) + TX, permethrin (626) + TX, petroleum oils (alternative name) (628) + TX, phenkapton (1330) + TX, phenthoate (631) + TX, phorate (636) + TX, phosalone (637) + TX, phosfolan (1338) + TX,

phosmet (638) + TX, phosphamidon (639) + TX, phoxim (642) + TX, pirimiphos-methyl (652) + TX, polychloroterpenes (traditional name) (1347) + TX, polynactins (alternative name) (653) + TX, proclonol (1350) + TX, profenofos (662) + TX, promacyl (1354) + TX, propargite (671) + TX, propetamphos (673) + TX, propoxur (678) + TX, prothidathion (1360) + TX, prothoate (1362) + TX, pyrethrin I (696) + TX, pyrethrin II (696) + TX, pyrethrins (696) + TX, pyridaben (699) + TX, pyridaphenthion (701) + TX, pyrimidifen (706) + TX, pyrimitate (1370) + TX, quinalphos (711) + TX, quintiofos (1381) + TX, R-1492 (development code) (1382) + TX, RA-17 (development code) (1383) + TX, rotenone (722) + TX, schradan (1389) + TX, sebufos (alternative name) + TX, selamectin (alternative name) [CCN] + TX, SI-0009 (compound code) + TX, sophamide (1402) + TX, spirodiclofen (738) + TX, spiromesifen (739) + TX, SSI-121 (development code) (1404) + TX, sulfiram (alternative name) [CCN] + TX, sulfluramid (750) + TX, sulfotep (753) + TX, sulphur (754) + TX, SZI-121 (development code) (757) + TX, tau-fluvalinate (398) + TX, tebufenpyrad (763) + TX, TEPP (1417) + TX, terbam (alternative name) + TX, tetrachlorvinphos (777) + TX, tetradifon (786) + TX, tetranactin (alternative name) (653) + TX, tetrasul (1425) + TX, thiafenox (alternative name) + TX, thiocarboxime (1431) + TX, thiofanox (800) + TX, thiometon (801) + TX, thioquinox (1436) + TX, thuringiensin (alternative name) [CCN] + TX, triamiphos (1441) + TX, triarathene (1443) + TX, triazophos (820) + TX, triazuron (alternative name) + TX, trichlorfon (824) + TX, trifenofos (1455) + TX, trinactin (alternative name) (653) + TX, vamidothion (847) + TX, vaniliprole [CCN] and YI-5302 (compound code) + TX,

an algicide selected from the group of substances consisting of bethoxazin [CCN] + TX, copper dioctanoate (IUPAC name) (170) + TX, copper sulfate (172) + TX, cybutryne [CCN] + TX, dichlone (1052) + TX, dichlorophen (232) + TX, endothal (295) + TX, fentin (347) + TX, hydrated lime [CCN] + TX, nabam (566) + TX, quinoclamine (714) + TX, quinonamid (1379) + TX, simazine (730) + TX, triphenyltin acetate (IUPAC name) (347) and triphenyltin hydroxide (IUPAC name) (347) + TX,

an anthelmintic selected from the group of substances consisting of abamectin (1) + TX, crufomate (1011) + TX, doramectin (alternative name) [CCN] + TX, emamectin (291) + TX, emamectin benzoate (291) + TX, eprinomectin (alternative name) [CCN] + TX, ivermectin (alternative name) [CCN] + TX, milbemycin oxime (alternative name) [CCN] + TX, moxidectin (alternative name) [CCN] + TX, piperazine [CCN] + TX, selamectin (alternative name) [CCN] + TX, spinosad (737) and thiophanate (1435) + TX,

an avicide selected from the group of substances consisting of chloralose (127) + TX, endrin (1122) + TX, fenthion (346) + TX, pyridin-4-amine (IUPAC name) (23) and strychnine (745) + TX,

a bactericide selected from the group of substances consisting of 1-hydroxy-1*H*-pyridine-2-thione (IUPAC name) (1222) + TX, 4-(quinoxalin-2-ylamino)benzenesulfonamide (IUPAC name) (748) + TX, 8-hydroxyquinoline sulfate (446) + TX, bronopol (97) + TX, copper dioctanoate (IUPAC name) (170) + TX, copper hydroxide (IUPAC name) (169) + TX, cresol [CCN] + TX, dichlorophen (232) + TX, dipyrithione (1105) + TX, dodicin (1112) + TX, fenaminosulf (1144) + TX, formaldehyde (404) + TX, hydrargaphen (alternative name) [CCN] + TX, kasugamycin (483) + TX, kasugamycin hydrochloride hydrate (483) + TX, nickel bis(dimethyldithiocarbamate) (IUPAC name) (1308) + TX, nitrapyrin (580) + TX, octhilinone (590) + TX, oxolinic acid (606) + TX, oxytetracycline (611) + TX,

potassium hydroxyquinoline sulfate (446) + TX, probenazole (658) + TX, streptomycin (744) + TX, streptomycin sesquisulfate (744) + TX, tecloftalam (766) + TX, and thiomersal (alternative name) [CCN] + TX,

a biological agent selected from the group of substances consisting of *Adoxophyes orana* GV (alternative name) (12) + TX, *Agrobacterium radiobacter* (alternative name) (13) + TX, *Amblyseius* spp. (alternative name) (19) + TX, *Anagrapha falcifera* NPV (alternative name) (28) + TX, *Anagrus atomus* (alternative name) (29) + TX, *Aphelinus abdominalis* (alternative name) (33) + TX, *Aphidius colemani* (alternative name) (34) + TX, *Aphidoletes aphidimyza* (alternative name) (35) + TX, *Autographa californica* NPV (alternative name) (38) + TX, *Bacillus firmus* (alternative name) (48) + TX, *Bacillus sphaericus* Neide (scientific name) (49) + TX, *Bacillus thuringiensis* Berliner (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *aizawai* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *israelensis* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *japonensis* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *kurstaki* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *tenebrionis* (scientific name) (51) + TX, *Beauveria bassiana* (alternative name) (53) + TX, *Beauveria brongniartii* (alternative name) (54) + TX, *Chrysoperla carnea* (alternative name) (151) + TX, *Cryptolaemus montrouzieri* (alternative name) (178) + TX, *Cydia pomonella* GV (alternative name) (191) + TX, *Dacnusa sibirica* (alternative name) (212) + TX, *Diglyphus isaea* (alternative name) (254) + TX, *Encarsia formosa* (scientific name) (293) + TX, *Eretmocerus eremicus* (alternative name) (300) + TX, *Helicoverpa zea* NPV (alternative name) (431) + TX, *Heterorhabditis bacteriophora* and *H. megidis* (alternative name) (433) + TX, *Hippodamia convergens* (alternative name) (442) + TX, *Leptomastix dactylopii* (alternative name) (488) + TX, *Macrolophus caliginosus* (alternative name) (491) + TX, *Mamestra brassicae* NPV (alternative name) (494) + TX, *Metaphycus helvolus* (alternative name) (522) + TX, *Metarhizium anisopliae* var. *acridum* (scientific name) (523) + TX, *Metarhizium anisopliae* var. *anisopliae* (scientific name) (523) + TX, *Neodiprion sertifer* NPV and *N. lecontei* NPV (alternative name) (575) + TX, *Orius* spp. (alternative name) (596) + TX, *Paecilomyces fumosoroseus* (alternative name) (613) + TX, *Phytoseiulus persimilis* (alternative name) (644) + TX, *Spodoptera exigua* multicapsid nuclear polyhedrosis virus (scientific name) (741) + TX, *Steinernema bibionis* (alternative name) (742) + TX, *Steinernema carpocapsae* (alternative name) (742) + TX, *Steinernema feltiae* (alternative name) (742) + TX, *Steinernema glaseri* (alternative name) (742) + TX, *Steinernema riobrave* (alternative name) (742) + TX, *Steinernema riobris* (alternative name) (742) + TX, *Steinernema scapterisci* (alternative name) (742) + TX, *Steinernema* spp. (alternative name) (742) + TX, *Trichogramma* spp. (alternative name) (826) + TX, *Typhlodromus occidentalis* (alternative name) (844) and *Verticillium lecanii* (alternative name) (848) + TX,

a soil sterilant selected from the group of substances consisting of iodomethane (IUPAC name) (542) and methyl bromide (537) + TX,

a chemosterilant selected from the group of substances consisting of apholate [CCN] + TX, bisazir (alternative name) [CCN] + TX, busulfan (alternative name) [CCN] + TX, diflubenzuron (250) + TX, dimatif (alternative name) [CCN] + TX, hemel [CCN] + TX, hempa [CCN] + TX, metepa [CCN] + TX, methiotepa [CCN] + TX, methyl apholate [CCN] + TX, morzid [CCN] + TX, penfluron (alternative name) [CCN] + TX, tepa [CCN] + TX, thiohempa (alternative name) [CCN] + TX,

thiotepa (alternative name) [CCN] + TX, tretamine (alternative name) [CCN] and uredepa (alternative name) [CCN] + TX,

an insect pheromone selected from the group of substances consisting of (*E*)-dec-5-en-1-yl acetate with (*E*)-dec-5-en-1-ol (IUPAC name) (222) + TX, (*E*)-tridec-4-en-1-yl acetate (IUPAC name) (829) + TX, (*E*)-6-methylhept-2-en-4-ol (IUPAC name) (541) + TX, (*E,Z*)-tetradeca-4,10-dien-1-yl acetate (IUPAC name) (779) + TX, (*Z*)-dodec-7-en-1-yl acetate (IUPAC name) (285) + TX, (*Z*)-hexadec-11-enal (IUPAC name) (436) + TX, (*Z*)-hexadec-11-en-1-yl acetate (IUPAC name) (437) + TX, (*Z*)-hexadec-13-en-11-yn-1-yl acetate (IUPAC name) (438) + TX, (*Z*)-icos-13-en-10-one (IUPAC name) (448) + TX, (*Z*)-tetradec-7-en-1-al (IUPAC name) (782) + TX, (*Z*)-tetradec-9-en-1-ol (IUPAC name) (783) + TX, (*Z*)-tetradec-9-en-1-yl acetate (IUPAC name) (784) + TX, (7*E*,9*Z*)-dodeca-7,9-dien-1-yl acetate (IUPAC name) (283) + TX, (9*Z*,11*E*)-tetradeca-9,11-dien-1-yl acetate (IUPAC name) (780) + TX, (9*Z*,12*E*)-tetradeca-9,12-dien-1-yl acetate (IUPAC name) (781) + TX, 14-methyloctadec-1-ene (IUPAC name) (545) + TX, 4-methylnonan-5-ol with 4-methylnonan-5-one (IUPAC name) (544) + TX, alpha-multistriatin (alternative name) [CCN] + TX, brevicomin (alternative name) [CCN] + TX, codlure (alternative name) [CCN] + TX, codlemone (alternative name) (167) + TX, cuelure (alternative name) (179) + TX, disparlure (277) + TX, dodec-8-en-1-yl acetate (IUPAC name) (286) + TX, dodec-9-en-1-yl acetate (IUPAC name) (287) + TX, dodeca-8 + TX, 10-dien-1-yl acetate (IUPAC name) (284) + TX, dominicalure (alternative name) [CCN] + TX, ethyl 4-methyloctanoate (IUPAC name) (317) + TX, eugenol (alternative name) [CCN] + TX, frontalinal (alternative name) [CCN] + TX, gossyplure (alternative name) (420) + TX, grandlure (421) + TX, grandlure I (alternative name) (421) + TX, grandlure II (alternative name) (421) + TX, grandlure III (alternative name) (421) + TX, grandlure IV (alternative name) (421) + TX, hexalure [CCN] + TX, ipsdienol (alternative name) [CCN] + TX, ipsenol (alternative name) [CCN] + TX, japonilure (alternative name) (481) + TX, lineatin (alternative name) [CCN] + TX, litlure (alternative name) [CCN] + TX, looplure (alternative name) [CCN] + TX, medlure [CCN] + TX, megatomoic acid (alternative name) [CCN] + TX, methyl eugenol (alternative name) (540) + TX, muscalure (563) + TX, octadeca-2,13-dien-1-yl acetate (IUPAC name) (588) + TX, octadeca-3,13-dien-1-yl acetate (IUPAC name) (589) + TX, orfralure (alternative name) [CCN] + TX, oryctalure (alternative name) (317) + TX, ostramone (alternative name) [CCN] + TX, siglure [CCN] + TX, sordidin (alternative name) (736) + TX, sulcatol (alternative name) [CCN] + TX, tetradec-11-en-1-yl acetate (IUPAC name) (785) + TX, trimedlure (839) + TX, trimedlure A (alternative name) (839) + TX, trimedlure B₁ (alternative name) (839) + TX, trimedlure B₂ (alternative name) (839) + TX, trimedlure C (alternative name) (839) and trunc-call (alternative name) [CCN] + TX,

an insect repellent selected from the group of substances consisting of 2-(octylthio)ethanol (IUPAC name) (591) + TX, butopyronoxyl (933) + TX, butoxy(polypropylene glycol) (936) + TX, dibutyl adipate (IUPAC name) (1046) + TX, dibutyl phthalate (1047) + TX, dibutyl succinate (IUPAC name) (1048) + TX, diethyltoluamide [CCN] + TX, dimethyl carbate [CCN] + TX, dimethyl phthalate [CCN] + TX, ethyl hexanediol (1137) + TX, hexamide [CCN] + TX, methoquin-butyl (1276) + TX, methylneodecanamide [CCN] + TX, oxamate [CCN] and picaridin [CCN] + TX,

an insecticide selected from the group of substances consisting of 1-dichloro-1-nitroethane (IUPAC/Chemical Abstracts name) (1058) + TX, 1,1-dichloro-2,2-bis(4-ethylphenyl)ethane (IUPAC

name) (1056), + TX, 1,2-dichloropropane (IUPAC/Chemical Abstracts name) (1062) + TX, 1,2-dichloropropane with 1,3-dichloropropene (IUPAC name) (1063) + TX, 1-bromo-2-chloroethane (IUPAC/Chemical Abstracts name) (916) + TX, 2,2,2-trichloro-1-(3,4-dichlorophenyl)ethyl acetate (IUPAC name) (1451) + TX, 2,2-dichlorovinyl 2-ethylsulphinyloethyl methyl phosphate (IUPAC name) (1066) + TX, 2-(1,3-dithiolan-2-yl)phenyl dimethylcarbamate (IUPAC/Chemical Abstracts name) (1109) + TX, 2-(2-butoxyethoxy)ethyl thiocyanate (IUPAC/Chemical Abstracts name) (935) + TX, 2-(4,5-dimethyl-1,3-dioxolan-2-yl)phenyl methylcarbamate (IUPAC/Chemical Abstracts name) (1084) + TX, 2-(4-chloro-3,5-xylyloxy)ethanol (IUPAC name) (986) + TX, 2-chlorovinyl diethyl phosphate (IUPAC name) (984) + TX, 2-imidazolidone (IUPAC name) (1225) + TX, 2-isovalerylindan-1,3-dione (IUPAC name) (1246) + TX, 2-methyl(prop-2-ynyl)aminophenyl methylcarbamate (IUPAC name) (1284) + TX, 2-thiocyanatoethyl laurate (IUPAC name) (1433) + TX, 3-bromo-1-chloroprop-1-ene (IUPAC name) (917) + TX, 3-methyl-1-phenylpyrazol-5-yl dimethylcarbamate (IUPAC name) (1283) + TX, 4-methyl(prop-2-ynyl)amino-3,5-xylyl methylcarbamate (IUPAC name) (1285) + TX, 5,5-dimethyl-3-oxocyclohex-1-enyl dimethylcarbamate (IUPAC name) (1085) + TX, abamectin (1) + TX, acephate (2) + TX, acetamiprid (4) + TX, acethion (alternative name) [CCN] + TX, acetoprole [CCN] + TX, acrinathrin (9) + TX, acrylonitrile (IUPAC name) (861) + TX, alanycarb (15) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, aldrin (864) + TX, allethrin (17) + TX, allosamidin (alternative name) [CCN] + TX, allyxycarb (866) + TX, alpha-cypermethrin (202) + TX, alpha-ecdysone (alternative name) [CCN] + TX, aluminium phosphide (640) + TX, amidithion (870) + TX, amidothioate (872) + TX, aminocarb (873) + TX, amiton (875) + TX, amiton hydrogen oxalate (875) + TX, amitraz (24) + TX, anabasine (877) + TX, athidathion (883) + TX, AVI 382 (compound code) + TX, AZ 60541 (compound code) + TX, azadirachtin (alternative name) (41) + TX, azamethiphos (42) + TX, azinphos-ethyl (44) + TX, azinphos-methyl (45) + TX, azothoate (889) + TX, *Bacillus thuringiensis* delta endotoxins (alternative name) (52) + TX, barium hexafluorosilicate (alternative name) [CCN] + TX, barium polysulfide (IUPAC/Chemical Abstracts name) (892) + TX, barthrin [CCN] + TX, Bayer 22/190 (development code) (893) + TX, Bayer 22408 (development code) (894) + TX, bendiocarb (58) + TX, benfuracarb (60) + TX, bensultap (66) + TX, beta-cyfluthrin (194) + TX, beta-cypermethrin (203) + TX, bifenthrin (76) + TX, bioallethrin (78) + TX, bioallethrin S-cyclopentenyl isomer (alternative name) (79) + TX, bioethanomethrin [CCN] + TX, biopermethrin (908) + TX, bioresmethrin (80) + TX, bis(2-chloroethyl) ether (IUPAC name) (909) + TX, bistrifluron (83) + TX, borax (86) + TX, brofenvalerate (alternative name) + TX, bromfenvinfos (914) + TX, bromocyclen (918) + TX, bromo-DDT (alternative name) [CCN] + TX, bromophos (920) + TX, bromophos-ethyl (921) + TX, bufencarb (924) + TX, buprofezin (99) + TX, butacarb (926) + TX, butathiofos (927) + TX, butocarboxim (103) + TX, butonate (932) + TX, butoxycarboxim (104) + TX, butylpyridaben (alternative name) + TX, cadusafos (109) + TX, calcium arsenate [CCN] + TX, calcium cyanide (444) + TX, calcium polysulfide (IUPAC name) (111) + TX, camphechlor (941) + TX, carbanolate (943) + TX, carbaryl (115) + TX, carbofuran (118) + TX, carbon disulfide (IUPAC/Chemical Abstracts name) (945) + TX, carbon tetrachloride (IUPAC name) (946) + TX, carbophenothion (947) + TX, carbosulfan (119) + TX, cartap (123) + TX, cartap hydrochloride (123) + TX, cevadine (alternative name) (725) + TX, chlorbicyclen (960) + TX, chlordane (128) + TX, chlordecone (963) + TX, chlordimeform (964) + TX, chlordimeform

hydrochloride (964) + TX, chlorethoxyfos (129) + TX, chlorfenapyr (130) + TX, chlorfenvinphos (131) + TX, chlorfluazuron (132) + TX, chlormephos (136) + TX, chloroform [CCN] + TX, chloropicrin (141) + TX, chlorphoxim (989) + TX, chlorprazophos (990) + TX, chlorpyrifos (145) + TX, chlorpyrifos-methyl (146) + TX, chlorthiophos (994) + TX, chromafenozide (150) + TX, cinerin I (696) + TX, cinerin II (696) + TX, cinerins (696) + TX, cis-resmethrin (alternative name) + TX, cismethrin (80) + TX, clocythrin (alternative name) + TX, cloethocarb (999) + TX, closantel (alternative name) [CCN] + TX, clothianidin (165) + TX, copper acetoarsenite [CCN] + TX, copper arsenate [CCN] + TX, copper oleate [CCN] + TX, coumaphos (174) + TX, coumithoate (1006) + TX, crotamiton (alternative name) [CCN] + TX, crotoxyphos (1010) + TX, crufomate (1011) + TX, cryolite (alternative name) (177) + TX, CS 708 (development code) (1012) + TX, cyanofenphos (1019) + TX, cyanophos (184) + TX, cyanthoate (1020) + TX, cyclethrin [CCN] + TX, cycloprothrin (188) + TX, cyfluthrin (193) + TX, cyhalothrin (196) + TX, cypermethrin (201) + TX, cyphenothrin (206) + TX, cyromazine (209) + TX, cythioate (alternative name) [CCN] + TX, *d*-limonene (alternative name) [CCN] + TX, *d*-tetramethrin (alternative name) (788) + TX, DAEP (1031) + TX, dazomet (216) + TX, DDT (219) + TX, decarbofuran (1034) + TX, deltamethrin (223) + TX, demephion (1037) + TX, demephion-O (1037) + TX, demephion-S (1037) + TX, demeton (1038) + TX, demeton-methyl (224) + TX, demeton-O (1038) + TX, demeton-O-methyl (224) + TX, demeton-S (1038) + TX, demeton-S-methyl (224) + TX, demeton-S-methylsulphon (1039) + TX, diafenthiuron (226) + TX, dialifos (1042) + TX, diamidafos (1044) + TX, diazinon (227) + TX, dicapthon (1050) + TX, dichlofenthion (1051) + TX, dichlorvos (236) + TX, dicliphos (alternative name) + TX, dicresyl (alternative name) [CCN] + TX, dicrotophos (243) + TX, dicyclanil (244) + TX, dieldrin (1070) + TX, diethyl 5-methylpyrazol-3-yl phosphate (IUPAC name) (1076) + TX, diflubenzuron (250) + TX, dilor (alternative name) [CCN] + TX, dimefluthrin [CCN] + TX, dimefox (1081) + TX, dimetan (1085) + TX, dimethoate (262) + TX, dimethrin (1083) + TX, dimethylvinphos (265) + TX, dimetilan (1086) + TX, dinex (1089) + TX, dinex-diclexine (1089) + TX, dinoprop (1093) + TX, dinosam (1094) + TX, dinoseb (1095) + TX, dinotefuran (271) + TX, diofenolan (1099) + TX, dioxabenzofos (1100) + TX, dioxacarb (1101) + TX, dioxathion (1102) + TX, disulfoton (278) + TX, dithicrofos (1108) + TX, DNOC (282) + TX, doramectin (alternative name) [CCN] + TX, DSP (1115) + TX, ecdysterone (alternative name) [CCN] + TX, EI 1642 (development code) (1118) + TX, emamectin (291) + TX, emamectin benzoate (291) + TX, EMPC (1120) + TX, empenthrin (292) + TX, endosulfan (294) + TX, endothion (1121) + TX, endrin (1122) + TX, EPBP (1123) + TX, EPN (297) + TX, epofenonane (1124) + TX, eprinomectin (alternative name) [CCN] + TX, esfenvalerate (302) + TX, etaphos (alternative name) [CCN] + TX, ethiofencarb (308) + TX, ethion (309) + TX, ethiprole (310) + TX, ethoate-methyl (1134) + TX, ethoprophos (312) + TX, ethyl formate (IUPAC name) [CCN] + TX, ethyl-DDD (alternative name) (1056) + TX, ethylene dibromide (316) + TX, ethylene dichloride (chemical name) (1136) + TX, ethylene oxide [CCN] + TX, etofenprox (319) + TX, etrimfos (1142) + TX, EXD (1143) + TX, famphur (323) + TX, fenamiphos (326) + TX, fenazaflor (1147) + TX, fenchlorphos (1148) + TX, fenethacarb (1149) + TX, fenfluthrin (1150) + TX, fenitrothion (335) + TX, fenobucarb (336) + TX, fenoxacrim (1153) + TX, fenoxycarb (340) + TX, fenpirithrin (1155) + TX, fenpropathrin (342) + TX, fenpyrad (alternative name) + TX, fensulfothion (1158) + TX, fenthion (346) + TX, fenthion-ethyl

[CCN] + TX, fenvalerate (349) + TX, fipronil (354) + TX, flonicamid (358) + TX, flubendiamide (CAS. Reg. No.: 272451-65-7) + TX, flucofuron (1168) + TX, flucycloxuron (366) + TX, flucythrinate (367) + TX, fluenetil (1169) + TX, flufenimerim [CCN] + TX, flufenoxuron (370) + TX, flufenprox (1171) + TX, flumethrin (372) + TX, fluvalinate (1184) + TX, FMC 1137 (development code) (1185) + TX, fonofos (1191) + TX, formetanate (405) + TX, formetanate hydrochloride (405) + TX, formothion (1192) + TX, formparanate (1193) + TX, fosmethilan (1194) + TX, fospirate (1195) + TX, fosthiazate (408) + TX, fosthietan (1196) + TX, furathiocarb (412) + TX, furethrin (1200) + TX, gamma-cyhalothrin (197) + TX, gamma-HCH (430) + TX, guazatine (422) + TX, guazatine acetates (422) + TX, GY-81 (development code) (423) + TX, halfenprox (424) + TX, halofenozide (425) + TX, HCH (430) + TX, HEOD (1070) + TX, heptachlor (1211) + TX, heptenophos (432) + TX, heterophos [CCN] + TX, hexaflumuron (439) + TX, HHDN (864) + TX, hydramethylnon (443) + TX, hydrogen cyanide (444) + TX, hydroprene (445) + TX, hyquincarb (1223) + TX, imidacloprid (458) + TX, imiprothrin (460) + TX, indoxacarb (465) + TX, iodomethane (IUPAC name) (542) + TX, IPSP (1229) + TX, isazofos (1231) + TX, isobenzan (1232) + TX, isocarbophos (alternative name) (473) + TX, isodrin (1235) + TX, isofenphos (1236) + TX, isolane (1237) + TX, isoprocab (472) + TX, isopropyl O-(methoxy-aminothiophosphoryl)salicylate (IUPAC name) (473) + TX, isoprothiolane (474) + TX, isothioate (1244) + TX, isoxathion (480) + TX, ivermectin (alternative name) [CCN] + TX, jasmolin I (696) + TX, jasmolin II (696) + TX, jodfenphos (1248) + TX, juvenile hormone I (alternative name) [CCN] + TX, juvenile hormone II (alternative name) [CCN] + TX, juvenile hormone III (alternative name) [CCN] + TX, kelevan (1249) + TX, kinoprene (484) + TX, lambda-cyhalothrin (198) + TX, lead arsenate [CCN] + TX, lepimectin (CCN) + TX, leptophos (1250) + TX, lindane (430) + TX, lirimfos (1251) + TX, lufenuron (490) + TX, lythidathion (1253) + TX, *m*-cumenyl methylcarbamate (IUPAC name) (1014) + TX, magnesium phosphide (IUPAC name) (640) + TX, malathion (492) + TX, malonoben (1254) + TX, mazidox (1255) + TX, mecarbam (502) + TX, mecarphon (1258) + TX, menazon (1260) + TX, mephosfolan (1261) + TX, mercurous chloride (513) + TX, mesulfenfos (1263) + TX, metaflumizone (CCN) + TX, metam (519) + TX, metam-potassium (alternative name) (519) + TX, metam-sodium (519) + TX, methacrifos (1266) + TX, methamidophos (527) + TX, methanesulphonyl fluoride (IUPAC/Chemical Abstracts name) (1268) + TX, methidathion (529) + TX, methiocarb (530) + TX, methocrotophos (1273) + TX, methomyl (531) + TX, methoprene (532) + TX, methoquin-butyl (1276) + TX, methothrin (alternative name) (533) + TX, methoxychlor (534) + TX, methoxyfenozide (535) + TX, methyl bromide (537) + TX, methyl isothiocyanate (543) + TX, methylchloroform (alternative name) [CCN] + TX, methylene chloride [CCN] + TX, metofluthrin [CCN] + TX, metolcarb (550) + TX, metoxadiazone (1288) + TX, mevinphos (556) + TX, mexacarbate (1290) + TX, milbemectin (557) + TX, milbemycin oxime (alternative name) [CCN] + TX, mipafox (1293) + TX, mirex (1294) + TX, monocrotophos (561) + TX, morphothion (1300) + TX, moxidectin (alternative name) [CCN] + TX, naftalofos (alternative name) [CCN] + TX, naled (567) + TX, naphthalene (IUPAC/Chemical Abstracts name) (1303) + TX, NC-170 (development code) (1306) + TX, NC-184 (compound code) + TX, nicotine (578) + TX, nicotine sulfate (578) + TX, nifluridide (1309) + TX, nitenpyram (579) + TX, nithiazine (1311) + TX, nitrilacarb (1313) + TX, nitrilacarb 1:1 zinc chloride complex (1313) + TX, NNI-0101 (compound code) + TX, NNI-0250

(compound code) + TX, nornicotine (traditional name) (1319) + TX, novaluron (585) + TX, noviflumuron (586) + TX, O-5-dichloro-4-iodophenyl O-ethyl ethylphosphonothioate (IUPAC name) (1057) + TX, O,O-diethyl O-4-methyl-2-oxo-2*H*-chromen-7-yl phosphorothioate (IUPAC name) (1074) + TX, O,O-diethyl O-6-methyl-2-propylpyrimidin-4-yl phosphorothioate (IUPAC name) (1075) + TX, O,O,O',O'-tetrapropyl dithiopyrophosphate (IUPAC name) (1424) + TX, oleic acid (IUPAC name) (593) + TX, omethoate (594) + TX, oxamyl (602) + TX, oxydemeton-methyl (609) + TX, oxydeprofos (1324) + TX, oxydisulfoton (1325) + TX, pp'-DDT (219) + TX, para-dichlorobenzene [CCN] + TX, parathion (615) + TX, parathion-methyl (616) + TX, penfluron (alternative name) [CCN] + TX, pentachlorophenol (623) + TX, pentachlorophenyl laurate (IUPAC name) (623) + TX, permethrin (626) + TX, petroleum oils (alternative name) (628) + TX, PH 60-38 (development code) (1328) + TX, phenkapton (1330) + TX, phenothrin (630) + TX, phenthoate (631) + TX, phorate (636) + TX, phosalone (637) + TX, phosfolan (1338) + TX, phosmet (638) + TX, phosnichlor (1339) + TX, phosphamidon (639) + TX, phosphine (IUPAC name) (640) + TX, phoxim (642) + TX, phoxim-methyl (1340) + TX, pirimetaphos (1344) + TX, pirimicarb (651) + TX, pirimiphos-ethyl (1345) + TX, pirimiphos-methyl (652) + TX, polychlorodicyclopentadiene isomers (IUPAC name) (1346) + TX, polychloroterpenes (traditional name) (1347) + TX, potassium arsenite [CCN] + TX, potassium thiocyanate [CCN] + TX, prallethrin (655) + TX, precocene I (alternative name) [CCN] + TX, precocene II (alternative name) [CCN] + TX, precocene III (alternative name) [CCN] + TX, primidophos (1349) + TX, profenofos (662) + TX, profluthrin [CCN] + TX, promacyl (1354) + TX, promecarb (1355) + TX, propaphos (1356) + TX, propetamphos (673) + TX, propoxur (678) + TX, prothidathion (1360) + TX, prothiofos (686) + TX, prothoate (1362) + TX, protrifenbute [CCN] + TX, pymetrozine (688) + TX, pyraclofos (689) + TX, pyrazophos (693) + TX, pyresmethrin (1367) + TX, pyrethrin I (696) + TX, pyrethrin II (696) + TX, pyrethrins (696) + TX, pyridaben (699) + TX, pyridalyl (700) + TX, pyridaphenthion (701) + TX, pyrimidifen (706) + TX, pyrimitate (1370) + TX, pyriproxyfen (708) + TX, quassia (alternative name) [CCN] + TX, quinalphos (711) + TX, quinalphos-methyl (1376) + TX, quinotion (1380) + TX, quintiofos (1381) + TX, R-1492 (development code) (1382) + TX, rafoxanide (alternative name) [CCN] + TX, resmethrin (719) + TX, rotenone (722) + TX, RU 15525 (development code) (723) + TX, RU 25475 (development code) (1386) + TX, ryania (alternative name) (1387) + TX, ryanodine (traditional name) (1387) + TX, sabadilla (alternative name) (725) + TX, schradan (1389) + TX, sebufos (alternative name) + TX, selamectin (alternative name) [CCN] + TX, SI-0009 (compound code) + TX, SI-0205 (compound code) + TX, SI-0404 (compound code) + TX, SI-0405 (compound code) + TX, silafluofen (728) + TX, SN 72129 (development code) (1397) + TX, sodium arsenite [CCN] + TX, sodium cyanide (444) + TX, sodium fluoride (IUPAC/Chemical Abstracts name) (1399) + TX, sodium hexafluorosilicate (1400) + TX, sodium pentachlorophenoxide (623) + TX, sodium selenate (IUPAC name) (1401) + TX, sodium thiocyanate [CCN] + TX, sophamide (1402) + TX, spinosad (737) + TX, spiromesifen (739) + TX, spirotetmat (CCN) + TX, sulcofuron (746) + TX, sulcofuron-sodium (746) + TX, sulfluramid (750) + TX, sulfotep (753) + TX, sulphuryl fluoride (756) + TX, sulprofos (1408) + TX, tar oils (alternative name) (758) + TX, tau-fluvalinate (398) + TX, tazimcarb (1412) + TX, TDE (1414) + TX, tebufenozide (762) + TX, tebufenpyrad (763) + TX, tebupirimfos (764) + TX, teflubenzuron (768) + TX, tefluthrin (769) + TX, temephos (770) + TX, TEPP (1417) + TX,

terallethrin (1418) + TX, terbam (alternative name) + TX, terbufos (773) + TX, tetrachloroethane [CCN] + TX, tetrachlorvinphos (777) + TX, tetramethrin (787) + TX, theta-cypermethrin (204) + TX, thiacloprid (791) + TX, thiafenox (alternative name) + TX, thiamethoxam (792) + TX, thicrofos (1428) + TX, thiocarboxime (1431) + TX, thiocyclam (798) + TX, thiocyclam hydrogen oxalate (798) + TX, thiodicarb (799) + TX, thiofanox (800) + TX, thiometon (801) + TX, thionazin (1434) + TX, thiosultap (803) + TX, thiosultap-sodium (803) + TX, thuringiensin (alternative name) [CCN] + TX, tolfenpyrad (809) + TX, tralomethrin (812) + TX, transfluthrin (813) + TX, transpermethrin (1440) + TX, triamiphos (1441) + TX, triazamate (818) + TX, triazophos (820) + TX, triazuron (alternative name) + TX, trichlorfon (824) + TX, trichlormetaphos-3 (alternative name) [CCN] + TX, trichloronat (1452) + TX, trifenofos (1455) + TX, triflumuron (835) + TX, trimethacarb (840) + TX, triprene (1459) + TX, vamidothion (847) + TX, vaniliprole [CCN] + TX, veratridine (alternative name) (725) + TX, veratrine (alternative name) (725) + TX, XMC (853) + TX, xylylcarb (854) + TX, YI-5302 (compound code) + TX, zeta-cypermethrin (205) + TX, zetamethrin (alternative name) + TX, zinc phosphide (640) + TX, zolaprofos (1469) and ZXI 8901 (development code) (858) + TX, cyantraniliprole [736994-63-19] + TX, chlorantraniliprole [500008-45-7] + TX, cyenopyrafen [560121-52-0] + TX, cyflumetofen [400882-07-7] + TX, pyrifluquinazon [337458-27-2] + TX, spinetoram [187166-40-1 + 187166-15-0] + TX, spirotetramat [203313-25-1] + TX, sulfoxaflor [946578-00-3] + TX, flufiprole [704886-18-0] + TX, meperfluthrin [915288-13-0] + TX, tetramethylfluthrin [84937-88-2] + TX, a molluscicide selected from the group of substances consisting of bis(tributyltin) oxide (IUPAC name) (913) + TX, bromoacetamide [CCN] + TX, calcium arsenate [CCN] + TX, cloethocarb (999) + TX, copper acetoarsenite [CCN] + TX, copper sulfate (172) + TX, fentin (347) + TX, ferric phosphate (IUPAC name) (352) + TX, metaldehyde (518) + TX, methiocarb (530) + TX, niclosamide (576) + TX, niclosamide-olamine (576) + TX, pentachlorophenol (623) + TX, sodium pentachlorophenoxide (623) + TX, tazimcarb (1412) + TX, thiodicarb (799) + TX, tributyltin oxide (913) + TX, trifenmorph (1454) + TX, trimethacarb (840) + TX, triphenyltin acetate (IUPAC name) (347) and triphenyltin hydroxide (IUPAC name) (347) + TX, pyriprole [394730-71-3] + TX, a nematicide selected from the group of substances consisting of AKD-3088 (compound code) + TX, 1,2-dibromo-3-chloropropane (IUPAC/Chemical Abstracts name) (1045) + TX, 1,2-dichloropropane (IUPAC/ Chemical Abstracts name) (1062) + TX, 1,2-dichloropropane with 1,3-dichloropropene (IUPAC name) (1063) + TX, 1,3-dichloropropene (233) + TX, 3,4-dichlorotetrahydrothiophene 1,1-dioxide (IUPAC/Chemical Abstracts name) (1065) + TX, 3-(4-chlorophenyl)-5-methylrhodanine (IUPAC name) (980) + TX, 5-methyl-6-thioxo-1,3,5-thiadiazinan-3-ylacetic acid (IUPAC name) (1286) + TX, 6-isopentenylaminopurine (alternative name) (210) + TX, abamectin (1) + TX, acetoprole [CCN] + TX, alanycarb (15) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, AZ 60541 (compound code) + TX, benclonthiaz [CCN] + TX, benomyl (62) + TX, butylpyridaben (alternative name) + TX, cadusafos (109) + TX, carbofuran (118) + TX, carbon disulfide (945) + TX, carbosulfan (119) + TX, chloropicrin (141) + TX, chlorpyrifos (145) + TX, cloethocarb (999) + TX, cytokinins (alternative name) (210) + TX, dazomet (216) + TX, DBCP (1045) + TX, DCIP (218) + TX, diamidafos (1044) + TX, dichlofenthion (1051) + TX, dicliphos (alternative name) + TX, dimethoate (262) + TX, doramectin (alternative name) [CCN] + TX, emamectin (291) + TX, emamectin benzoate (291) + TX, eprinomectin (alternative name) [CCN] + TX, ethoprophos (312) +

TX, ethylene dibromide (316) + TX, fenamiphos (326) + TX, fenpyrad (alternative name) + TX, fensulfothion (1158) + TX, fosthiazate (408) + TX, fosthietan (1196) + TX, furfural (alternative name) [CCN] + TX, GY-81 (development code) (423) + TX, heterophos [CCN] + TX, iodomethane (IUPAC name) (542) + TX, isamidofos (1230) + TX, isazofos (1231) + TX, ivermectin (alternative name) [CCN] + TX, kinetin (alternative name) (210) + TX, mecarphon (1258) + TX, metam (519) + TX, metam-potassium (alternative name) (519) + TX, metam-sodium (519) + TX, methyl bromide (537) + TX, methyl isothiocyanate (543) + TX, milbemycin oxime (alternative name) [CCN] + TX, moxidectin (alternative name) [CCN] + TX, *Myrothecium verrucaria* composition (alternative name) (565) + TX, NC-184 (compound code) + TX, oxamyl (602) + TX, phorate (636) + TX, phosphamidon (639) + TX, phosphocarb [CCN] + TX, sebufos (alternative name) + TX, selamectin (alternative name) [CCN] + TX, spinosad (737) + TX, terbam (alternative name) + TX, terbufos (773) + TX, tetrachlorothiophene (IUPAC/ Chemical Abstracts name) (1422) + TX, thiafenox (alternative name) + TX, thionazin (1434) + TX, triazophos (820) + TX, triazuron (alternative name) + TX, xlenols [CCN] + TX, YI-5302 (compound code) and zeatin (alternative name) (210) + TX, fluensulfone [318290-98-1] + TX,

a nitrification inhibitor selected from the group of substances consisting of potassium ethylxanthate [CCN] and nitrapyrin (580) + TX,

a plant activator selected from the group of substances consisting of acibenzolar (6) + TX, acibenzolar-S-methyl (6) + TX, probenazole (658) and *Reynoutria sachalinensis* extract (alternative name) (720) + TX,

a rodenticide selected from the group of substances consisting of 2-isovalerylindan-1,3-dione (IUPAC name) (1246) + TX, 4-(quinoxalin-2-ylamino)benzenesulfonamide (IUPAC name) (748) + TX, alpha-chlorohydrin [CCN] + TX, aluminium phosphide (640) + TX, antu (880) + TX, arsenous oxide (882) + TX, barium carbonate (891) + TX, bisthiosemi (912) + TX, brodifacoum (89) + TX, bromadiolone (91) + TX, bromethalin (92) + TX, calcium cyanide (444) + TX, chloralose (127) + TX, chlorophacinone (140) + TX, cholecalciferol (alternative name) (850) + TX, coumachlor (1004) + TX, coumafuryl (1005) + TX, coumatetralyl (175) + TX, crimidine (1009) + TX, difenacoum (246) + TX, difethialone (249) + TX, diphacinone (273) + TX, ergocalciferol (301) + TX, flocoumafen (357) + TX, fluoroacetamide (379) + TX, flupropadine (1183) + TX, flupropadine hydrochloride (1183) + TX, gamma-HCH (430) + TX, HCH (430) + TX, hydrogen cyanide (444) + TX, iodomethane (IUPAC name) (542) + TX, lindane (430) + TX, magnesium phosphide (IUPAC name) (640) + TX, methyl bromide (537) + TX, norbormide (1318) + TX, phosacetim (1336) + TX, phosphine (IUPAC name) (640) + TX, phosphorus [CCN] + TX, pindone (1341) + TX, potassium arsenite [CCN] + TX, pyrinuron (1371) + TX, scilliroside (1390) + TX, sodium arsenite [CCN] + TX, sodium cyanide (444) + TX, sodium fluoroacetate (735) + TX, strychnine (745) + TX, thallium sulfate [CCN] + TX, warfarin (851) and zinc phosphide (640) + TX,

a synergist selected from the group of substances consisting of 2-(2-butoxyethoxy)ethyl piperonylate (IUPAC name) (934) + TX, 5-(1,3-benzodioxol-5-yl)-3-hexylcyclohex-2-enone (IUPAC name) (903) + TX, farnesol with nerolidol (alternative name) (324) + TX, MB-599 (development code) (498) + TX, MGK 264 (development code) (296) + TX, piperonyl butoxide (649) + TX, piprotal (1343) + TX,

propyl isomer (1358) + TX, S421 (development code) (724) + TX, sesamex (1393) + TX, sesasmolin (1394) and sulfoxide (1406) + TX,

an animal repellent selected from the group of substances consisting of anthraquinone (32) + TX, chloralose (127) + TX, copper naphthenate [CCN] + TX, copper oxychloride (171) + TX, diazinon (227) + TX, dicyclopentadiene (chemical name) (1069) + TX, guazatine (422) + TX, guazatine acetates (422) + TX, methiocarb (530) + TX, pyridin-4-amine (IUPAC name) (23) + TX, thiram (804) + TX, trimethacarb (840) + TX, zinc naphthenate [CCN] and ziram (856) + TX,

a virucide selected from the group of substances consisting of imanin (alternative name) [CCN] and ribavirin (alternative name) [CCN] + TX,

a wound protectant selected from the group of substances consisting of mercuric oxide (512) + TX, octhilinone (590) and thiophanate-methyl (802) + TX,

and biologically active compounds selected from the group consisting of azaconazole (60207-31-0) + TX, bitertanol [70585-36-3] + TX, bromuconazole [116255-48-2] + TX, cyproconazole [94361-06-5] + TX, difenoconazole [119446-68-3] + TX, diniconazole [83657-24-3] + TX, epoxiconazole [106325-08-0] + TX, fenbuconazole [114369-43-6] + TX, fluquinconazole [136426-54-5] + TX, flusilazole [85509-19-9] + TX, flutriafol [76674-21-0] + TX, hexaconazole [79983-71-4] + TX, imazalil [35554-44-0] + TX, imibenconazole [86598-92-7] + TX, ipconazole [125225-28-7] + TX, metconazole [125116-23-6] + TX, myclobutanil [88671-89-0] + TX, pefurazoate [101903-30-4] + TX, penconazole [66246-88-6] + TX, prothioconazole [178928-70-6] + TX, pyrifenoxy [88283-41-4] + TX, prochloraz [67747-09-5] + TX, propiconazole [60207-90-1] + TX, simeconazole [149508-90-7] + TX, tebuconazole [107534-96-3] + TX, tetraconazole [112281-77-3] + TX, triadimefon [43121-43-3] + TX, triadimenol [55219-65-3] + TX, triflumizole [99387-89-0] + TX, triticonazole [131983-72-7] + TX, ancymidol [12771-68-5] + TX, fenarimol [60168-88-9] + TX, nuarimol [63284-71-9] + TX, bupirimate [41483-43-6] + TX, dimethirimol [5221-53-4] + TX, ethirimol [23947-60-6] + TX, dodemorph [1593-77-7] + TX, fenpropidine [67306-00-7] + TX, fenpropimorph [67564-91-4] + TX, spiroxamine [118134-30-8] + TX, tridemorph [81412-43-3] + TX, cyprodinil [121552-61-2] + TX, mepanipyrin [110235-47-7] + TX, pyrimethanil [53112-28-0] + TX, fenpiclonil [74738-17-3] + TX, fludioxonil [131341-86-1] + TX, benalaxyl [71626-11-4] + TX, furalaxyl [57646-30-7] + TX, metalaxyl [57837-19-1] + TX, R-metalaxyl [70630-17-0] + TX, ofurace [58810-48-3] + TX, oxadixyl [77732-09-3] + TX, benomyl [17804-35-2] + TX, carbendazim [10605-21-7] + TX, debacarb [62732-91-6] + TX, fuberidazole [3878-19-1] + TX, thiabendazole [148-79-8] + TX, chlozolinate [84332-86-5] + TX, dichlozoline [24201-58-9] + TX, iprodione [36734-19-7] + TX, myclozoline [54864-61-8] + TX, procymidone [32809-16-8] + TX, vinclozoline [50471-44-8] + TX, boscalid [188425-85-6] + TX, carboxin [5234-68-4] + TX, fenfuram [24691-80-3] + TX, flutolanil [66332-96-5] + TX, mepronil [55814-41-0] + TX, oxycarboxin [5259-88-1] + TX, penthiopyrad [183675-82-3] + TX, thifluzamide [130000-40-7] + TX, guazatine [108173-90-6] + TX, dodine [2439-10-3] [112-65-2] (free base) + TX, iminoctadine [13516-27-3] + TX, azoxystrobin [131860-33-8] + TX, dimoxystrobin [149961-52-4] + TX, enestroburin {Proc. BCPC, Int. Congr., Glasgow, 2003, 1, 93} + TX, fluoxastrobin [361377-29-9] + TX, kresoxim-methyl [143390-89-0] + TX, metominostrobin [133408-50-1] + TX, trifloxystrobin [141517-21-7] + TX, orysastrobin [248593-16-0] + TX, picoxystrobin [117428-22-5] + TX, pyraclostrobin [175013-18-0] + TX, ferbam [14484-64-1] + TX,

mancozeb [8018-01-7] + TX, maneb [12427-38-2] + TX, metiram [9006-42-2] + TX, propineb [12071-83-9] + TX, thiram [137-26-8] + TX, zineb [12122-67-7] + TX, ziram [137-30-4] + TX, captafol [2425-06-1] + TX, captan [133-06-2] + TX, dichlofluanid [1085-98-9] + TX, fluoroimide [41205-21-4] + TX, folpet [133-07-3] + TX, tolylfluanid [731-27-1] + TX, bordeaux mixture [8011-63-0] + TX, copperhydroxid [20427-59-2] + TX, copperoxychlorid [1332-40-7] + TX, coppersulfat [7758-98-7] + TX, copperoxid [1317-39-1] + TX, mancopper [53988-93-5] + TX, oxine-copper [10380-28-6] + TX, dinocap [131-72-6] + TX, nitrothal-isopropyl [10552-74-6] + TX, edifenphos [17109-49-8] + TX, iprobenphos [26087-47-8] + TX, isoprothiolane [50512-35-1] + TX, phosdiphen [36519-00-3] + TX, pyrazophos [13457-18-6] + TX, tolclofos-methyl [57018-04-9] + TX, acibenzo-lar-S-methyl [135158-54-2] + TX, anilazine [101-05-3] + TX, benthiavalicarb [413615-35-7] + TX, blasticidin-S [2079-00-7] + TX, chinomethionat [2439-01-2] + TX, chloroneb [2675-77-6] + TX, chlorothalonil [1897-45-6] + TX, cyflufenamid [180409-60-3] + TX, cymoxanil [57966-95-7] + TX, dichlone [117-80-6] + TX, diclocymet [139920-32-4] + TX, diclomezine [62865-36-5] + TX, dicloran [99-30-9] + TX, diethofencarb [87130-20-9] + TX, dimethomorph [110488-70-5] + TX, SYP-LI90 (Flumorph) [211867-47-9] + TX, dithianon [3347-22-6] + TX, ethaboxam [162650-77-3] + TX, etridiazole [2593-15-9] + TX, famoxadone [131807-57-3] + TX, fenamidone [161326-34-7] + TX, fenoxanil [115852-48-7] + TX, fentin [668-34-8] + TX, ferimzone [89269-64-7] + TX, fluazinam [79622-59-6] + TX, fluopicolide [239110-15-7] + TX, flusulfamide [106917-52-6] + TX, fenhexamid [126833-17-8] + TX, fosetyl-aluminium [39148-24-8] + TX, hymexazol [10004-44-1] + TX, iprovalicarb [140923-17-7] + TX, IKF-916 (Cyazofamid) [120116-88-3] + TX, kasugamycin [6980-18-3] + TX, methasulfocarb [66952-49-6] + TX, metrafenone [220899-03-6] + TX, pencycuron [66063-05-6] + TX, phthalide [27355-22-2] + TX, polyoxins [11113-80-7] + TX, probenazole [27605-76-1] + TX, propamocarb [25606-41-1] + TX, proquinazid [189278-12-4] + TX, pyroquilon [57369-32-1] + TX, quinoxifen [124495-18-7] + TX, quintozone [82-68-8] + TX, sulphur [7704-34-9] + TX, tiadinil [223580-51-6] + TX, triazoxide [72459-58-6] + TX, tricyclazole [41814-78-2] + TX, triforine [26644-46-2] + TX, validamycin [37248-47-8] + TX, zoxamide (RH7281) [156052-68-5] + TX, mandipropamid [374726-62-2] + TX, isopyrazam [881685-58-1] + TX, sedaxane [874967-67-6] + TX, 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (9-dichloromethylene-1,2,3,4-tetrahydro-1,4-methano-naphthalen-5-yl)-amide (disclosed in WO 2007/048556) + TX, 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid [2-(2,4-dichlorophenyl)-2-methoxy-1-methyl-ethyl]-amide (disclosed in WO 2008/148570) + TX, 1-[4-[4-[(5S)5-(2,6-difluorophenyl)-4,5-dihydro-1,2-oxazol-3-yl]-1,3-thiazol-2-yl]piperidin-1-yl]-2-[5-methyl-3-(trifluoromethyl)-1H-pyrazol-1-yl]ethanone + TX, 1-[4-[4-[5-(2,6-difluorophenyl)-4,5-dihydro-1,2-oxazol-3-yl]-1,3-thiazol-2-yl]piperidin-1-yl]-2-[5-methyl-3-(trifluoromethyl)-1H-pyrazol-1-yl]ethanone [1003318-67-9], both disclosed in WO 2010/123791, WO 2008/013925, WO 2008/013622 and WO 2011/051243 page 20) + TX, 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (3',4',5'-trifluoro-biphenyl-2-yl)-amide (disclosed in WO 2006/087343) + TX, 1-methyl-2-(2,4,5-trichloro-thiophen-3-yl)-ethyl + TX, (S)-[3-(4-Chloro-2-fluoro-phenyl)-5-(2,4-difluoro-phenyl)-isoxazol-4-yl]-pyridin-3-yl-methanol + TX, 3-(4-Chloro-2-fluoro-phenyl)-5-(2,4-difluoro-phenyl)-isoxazol-4-yl]-pyridin-3-yl-methanol + TX, (3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (3',4'-dichloro-5-fluoro-1,1'-biphenyl-2-yl)-amide (bixafen) + TX, (N-[2-[3-Chloro-5-(trifluoromethyl)pyridin-2-yl]ethyl]-2-(trifluoromethyl)benzamid (fluopyram) + TX, N-[2-(1,3-

dimethylbutyl)phenyl]-5-fluoro-1,3-dimethyl-1H-pyrazole-4-carboxamide (Penflufen) + TX, 1-[4-[4-[5-(2,6-difluorophenyl)-4,5-dihydro-3-isoxazolyl]-2-thiazolyl]-1-piperidinyl]-2-[5-methyl-3-(trifluoromethyl)-1H-pyrazol-1-yl]ethanone (CAS Reg.-No.: 1003318-67-9, oxathiapiprolin) + TX and 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (3',4',5'-trifluoro-biphenyl-2-yl)-amide (disclosed in WO 2006/087343) + TX, flupyradifurone (CAS registry number 951659-40-8) + TX, afidopyropen (CAS registry number 915972-17-7) + TX, pasteuria penetrans and TX, pasteuria spp. + TX, bacillus firmus + TX, bacillus cereus + TX, bacillus subtilis + TX and pasteuria penetrans + TX..

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.

The active ingredient mixture of the compound of formula I or a compound selected from the Table 1 and an active ingredient as described above 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 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 understood to include, on the one hand, ratios by weight and also, on the other hand, molar ratios.

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 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 of formula I or a compound selected from the Tables 2 to 33 and A1 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 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 the compound of formula I or a compound selected from the Tables 2 to 33 and A1 and the active ingredients as described above is not essential for working the present invention.

The compositions 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.

The application methods for the compositions, that is the methods of controlling pests of the abovementioned type, such as spraying, atomizing, dusting, brushing on, dressing, scattering or pouring - which are to be selected to suit the intended aims of the prevailing circumstances - and the use of the compositions for controlling pests of the abovementioned type are other subjects of the invention. Typical rates of concentration are between 0.1 and 1000 ppm, preferably between 0.1 and 500 ppm, of active ingredient. The rate of application per hectare is generally 1 to 2000 g of active ingredient per hectare, in particular 10 to 1000 g/ha, preferably 10 to 600 g/ha.

A preferred method of application in the field of crop protection is application to the foliage of the plants (foliar application), it being possible to select frequency and rate of application to match the danger of infestation with the pest in question. Alternatively, the active ingredient can reach the plants via the root system (systemic action), by drenching the locus of the plants with a liquid composition or by incorporating the active ingredient in solid form into the locus of the plants, for example into the soil, for example in the form of granules (soil application). In the case of paddy rice crops, such granules can be metered into the flooded paddy-field.

The compositions 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.

The application methods for the compositions, that is the methods of controlling pests of the abovementioned type, such as spraying, atomizing, dusting, brushing on, dressing, scattering or pouring - which are to be selected to suit the intended aims of the prevailing circumstances - and the use of the compositions for controlling pests of the abovementioned type are other subjects of the invention. Typical rates of concentration are between 0.1 and 1000 ppm, preferably between 0.1 and 500 ppm, of active ingredient. The rate of application per hectare is generally 1 to 2000 g of active ingredient per hectare, in particular 10 to 1000 g/ha, preferably 10 to 600 g/ha.

A preferred method of application in the field of crop protection is application to the foliage of the plants (foliar application), it being possible to select frequency and rate of application to match the danger of infestation with the pest in question. Alternatively, the active ingredient can reach the plants via the root system (systemic action), by drenching the locus of the plants with a liquid composition or by incorporating the active ingredient in solid form into the locus of the plants, for example into the soil, for example in the form of granules (soil application). In the case of paddy rice crops, such granules can be metered into the flooded paddy-field.

The compositions according to the invention are also suitable for the protection of plant propagation material, for example seeds, such as fruit, tubers or kernels, or nursery plants, against pests of the abovementioned type. The propagation material can be treated with the compositions prior to planting, for example seed can be treated prior to sowing. Alternatively, the compositions can be applied to seed kernels (coating), either by soaking the kernels in a liquid composition or by applying a layer of a solid composition. It is also possible to apply the compositions when the propagation material is planted to the site of application, for example into the seed furrow during drilling. These treatment methods for plant propagation material and the plant propagation material thus treated are further subjects of the invention.

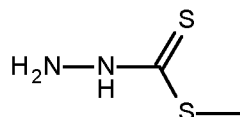
The following non-limiting examples illustrate the above-described invention in greater detail without limiting it. The compounds of the invention can be distinguished from known compounds by virtue of

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 100ppm, 50 ppm, 12.5 ppm, 6 ppm, 3 ppm, 1.5 ppm or 0.8 ppm.

Preparation examples:

The following examples describe synthesis of compounds of formula (I) and intermediates thereof.

Example-1: Preparation of methyl *N*-aminocarbamodithioate (A)

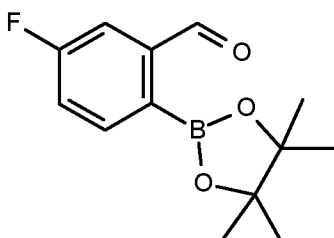


To a solution of hydrazine hydrate (5 g, 154.46 mmol) in ethanol (100 mL) and triethylamine (21.7 mL, 154.467 mmol) maintained at 0 °C, was added drop wise methanedithione (11.8 g, 154.467 mmol) carefully (exothermic reaction). After 10 min iodomethane (21.92 g, 154.467 mmol) was added. The resulting reaction mass was stirred at ambient temperature for 24h under a nitrogen atmosphere. The solvent was carefully evaporated. The resulting crude product mixture was dissolved in water and extracted with ethyl acetate. The organic layer was separated, dried over sodium sulphate, filtered and concentrated under reduced pressure to afford 8.9g (12.19 g of theory) of methyl *N*-aminocarbamodithioate. The obtained product was directly used for the next reaction without any further purification.

¹H NMR (400 MHz, CDCl₃): 2.75 (s, 3H)

MS [M+H]⁺: 122.9

Example-2: Preparation of 5-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (B)

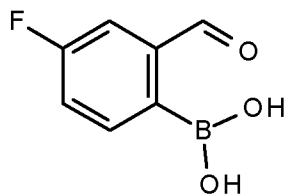


2-bromo-5-fluoro-benzaldehyde (10 g, 49.26 mmol) was dissolved DME (200 mL) and the solution was degassed by bubbling nitrogen through the reaction mixture for 15 min. Then bis(pinacolato)diboron (18.763 g, 73.88 mmol), potassium acetate (14.65 g, 147.78 mmol) and [1,1'-bis(diphenylphosphino)ferrocene] (1.8 g, 2.46 mmol) were added and the reaction vessel was heated to 80 °C for 2h. Reaction mass was then cooled to ambient temperature and water (50 mL) was added. The organic layer was collected separately and aqueous layer was extracted with ethylacetate. Combined organic layer were washed with water (3X 50 mL), dried over sodiumsulphate, filtered and concentrated under reduced pressure. Crude product was purified by flash column chromatography using 40% ethyl acetate in cyclohexane to afford 9.8 g (79% of theory) of 5-fluoro-2-(4,4,5,5-

tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde as a solid.

^1H NMR (400 MHz, CDCl_3): δ 1.37 (s, 12H), 7.271 (td, J = 8, 2.4 Hz, 1H), 7.65 (dd, J = 9.6, 2.4 Hz, 1H), 7.93 (dd, J = 8.4, 6 Hz, 1H), 10.65 (s, 1H).

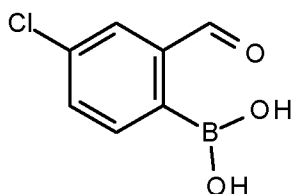
Example-3: Preparation of (4-fluoro-2-formyl-phenyl)boronic acid (C)



5-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (**B**), (8.0 g, 31.99 mmol), was dissolved in a mixture of THF/Water (4:1 ratio). Then sodium periodate (20.73 g, 95.96 mmol) was added at room temperature. After stirring at ambient temperature for 2h 2N HCL (20 mL) was added and then the reaction mass was stirred for 24h. Ethyl acetate was added and organic layer was collected dried over sodium sulphate, filtered concentrated under reduced pressure to afford 4.8 g (89% of theory) of (4-fluoro-2-formyl-phenyl)boronic acid in form of solid.

^1H NMR (400 MHz, CDCl_3): δ 7.156 (s, 2H), 7.408 (dd, J = 8, 2.4 Hz, 1H), 7.616 (dd, J = 8.8, 2.4 Hz, 1H), 8.305 (dd, J = 8.4, 6 Hz, 1H), 9.897 (s, 1H).

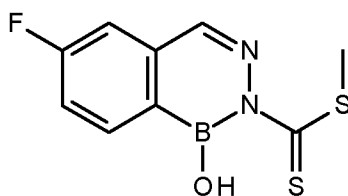
Example-4: Preparation of (4-chloro-2-formyl-phenyl)boronic acid (D)



5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (335 mg, 1.257 mmol) was dissolved in a mixture of acetonitrile/1NHCl (4:1 ratio) and added benzenboronic acid, polymer-supported (2.4 g). Then the reaction mass was stirred at room temperature for 24h, filtered and concentrated under reduced pressure to afford 216 mg (79.4% of theory) of (4-chloro-2-formyl-phenyl)boronic acid in form of solid.

^1H NMR (400 MHz, DMSO-d_6): δ 7.617 (d, J = 8 Hz, 1H), 7.688 (dd, J = 8, 2.4 Hz, 1H), 7.887 (d, J = 2.4 Hz, 1H), 8.356 (s, 2H), 10.329 (s, 1H).

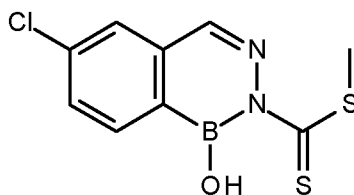
Example-5: Preparation of methyl 6-fluoro-1-hydroxy-2,3,1-benzodiazaborinine-2-carbodithioate (E)



(4-fluoro-2-formyl-phenyl)boronic acid (**C**), (3.0 g, 17.86 mmol), was dissolved in a mixture of water (40 mL) and THF (10 mL) and methyl *N*-aminocarbamodithioate (**A**), (4.36 g, 35.73 mmol), prepared as described in example 1, and formic acid (68 μ L, 1.78 mmol) were added. Then the reaction mixture was heated to reflux temperature for 24h. The reaction mixture was cooled to ambient temperature and then cyclohexane was added. The desired compound precipitated and the solid mass was filtered, washed with cyclohexane and dried under high vacuum, to afford 2.4 g (53.3% of theory) of methyl 6-fluoro-1-hydroxy-2,3,1-benzodiazaborinine-2-carbodithioate in form of a solid. Mp 152-154°C.

MS [M+H]: 255

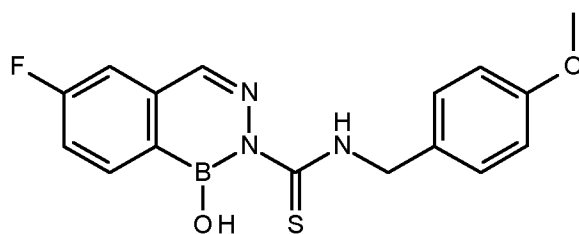
Example-6: Preparation of methyl 6-chloro-1-hydroxy-2,3,1-benzodiazaborinine-2-carbodithioate (**F**)



(4-chloro-2-formyl-phenyl)boronic acid (**D**), (4.0 g, 21.69 mmol), was dissolved in a mixture of water (48 mL) and THF (12 mL) and methyl *N*-aminocarbamodithioate (3.71 g, 30.37 mmol), prepared as described in example 1, and formic acid (41.3 μ L, 1.08 mmol) were added. The reaction mixture was heated to reflux for 24h, cooled to ambient temperature and cyclohexane was added. The desired compound precipitated and the solid mass was filtered washed with cyclohexane and dried to afford 4.62 g (78.7% of theory) of methyl 6-chloro-1-hydroxy-2,3,1-benzodiazaborinine-2-carbodithioate

MS [M+H]: 271

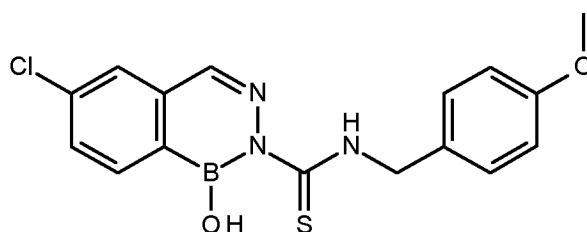
Example-7: Preparation of 6-fluoro-1-hydroxy-N-[(4-methoxyphenyl)methyl]-2,3,1-benzodiazaborinine-2-carbothioamide



6-fluoro-1-hydroxy-2,3,1-benzodiazaborinine-2-carbodithioate (**E**) (42 mg, 0.15 mmol), was dissolved in ethanol (2 mL) added 4-methoxybenzylamine (259 mg, 0.18 mmol) was added. Then reaction mixture was heated to 80°C for 24h. The solvent was evaporated and crude product was recrystallized from ethanol to afford 9 mg (17% of theory) of 6-fluoro-1-hydroxy-N-[(4-methoxyphenyl)methyl]-2,3,1-benzodiazaborinine-2-carbothioamide.

¹H NMR (400 MHz, DMSO-d₆): δ 3.729 (s, 3H), 4.805(dd, J= 6.4, 2Hz, 2H), 6.905(dd, J=6.8,2.4Hz, 2H), 7.335(dd, 6.8, 2Hz, 2H), 7.583 (td, J=18, 2.8Hz, 1H), 7.7645(dd, J= 9.2, 2.4Hz, 1H), 8.165(dd, J=8.4, 6.4Hz, 1H),10.527(s, 1H), 10.803(m, 1H)

Example-8: Preparation of 6-chloro-1-hydroxy-N-[(4-methoxyphenyl)methyl]-2,3,1-benzodiazaborinine-2-carbothioamide



Methyl 6-chloro-1-hydroxy-2,3,1-benzodiazaborinine-2-carbodithioate (**F**), (50 mg, 0.18 mmol), was dissolved in ethanol (2 mL) and 4-methoxybenzylamine (31 mg, 0.22 mmol) was added. The reaction mixture was heated to 80°C for 24h. The solvent was evaporated and the crude product recrystallized from ethanol to afford 11 mg (16.6% of theory) of 6-chloro-1-hydroxy-N-[(4-methoxyphenyl)methyl]-2,3,1-benzodiazaborinine-2-carbothioamide.

MS [M-H]: 358.1

Example-9: Preparation of 6-fluoro-1-hydroxy-N-(methoxymethyl)-2,3,1-benzodiazaborinine-2-carbothioamide

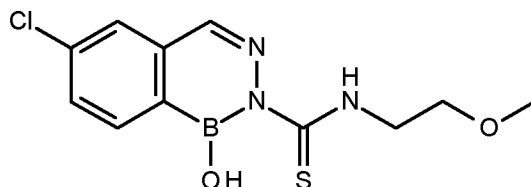


Methyl 6-fluoro-1-hydroxy-2,3,1-benzodiazaborinine-2-carbodithioate (**E**), (150 mg, 0.59 mmol), was dissolved in ethyl alcohol (2 mL) and 2-methoxyethylamine (72.6 µL, 0.82 mmol) was added. The reaction mixture was heated to 80°C for 24h. The solvent was evaporated and the crude product mixture was dissolved in ethyl acetate and washed with water. The organic layer was separated, dried over sodium sulphate, filtered and concentrated under reduced pressure to afford 46mg (25% of theory) of 6-fluoro-1-hydroxy-N-(methoxymethyl)-2,3,1-benzodiazaborinine-2-

carbothioamide

^1H NMR (400 MHz, CD_3OD): δ 3.4 (s, 3H), 3.65(t, J = 10.4, 5.2 Hz, 2H), 3.89(t, J =10.8, 5.2 Hz, 2H), 7.15(td, J = 11.6, 8.4 Hz, 1H), 7.27 (dd, J =10, 2.4 Hz, 1H), 7.385(dd, J = 8, 6 Hz, 1H), 7.385(dd, J =8, 6 Hz, 1H), 7.984(s, 1H).

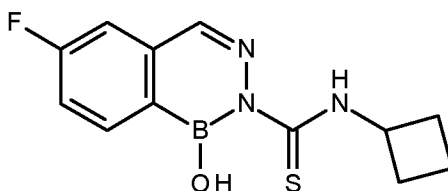
Example-10: Preparation of 6-chloro-1-hydroxy-N-(methoxymethyl)-2,3,1-benzodiazaborinine-2-carbothioamide



Methyl 6-chloro-1-hydroxy-2,3,1-benzodiazaborinine-2-carbodithioate (F), (150 mg, 0.55 mmol), was dissolved in ethanol (2 mL) and 2-methoxyethylamine (72.6 μL , 0.82 mmol) was added. The reaction mixture was heated to 80 $^{\circ}\text{C}$ for 24h. The solvent was evaporated and the crude product mixture was dissolved in ethyl acetate and washed with water. Organic layer was separated, dried over sodium sulphate, filtered and concentrated under reduced pressure to afford 98mg (59.3% of theory) of 6-chloro-1-hydroxy-N-(methoxymethyl)-2,3,1-benzodiazaborinine-2-carbothioamide.

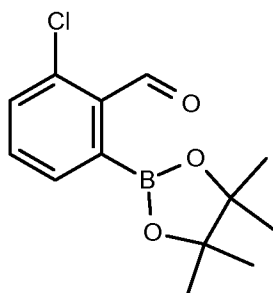
^1H NMR (400 MHz, CD_3OD): δ 3.4 (s, 3H), 3.65(t, J = 10.4, 5.2 Hz, 2H), 3.89(t, J =10.8, 5.6 Hz, 2H), 7.34(d, J = 8 Hz, 1H), 7.44 (dd, J =8, 2 Hz, 1H), 7.52 (d, J = 1.6 Hz, 1H), 7.971 (s, 1H).

Example-11: Preparation of N-cyclobutyl-6-fluoro-1-hydroxy-2,3,1-benzodiazaborinine-2-carbothioamide



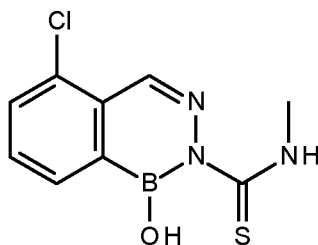
Methyl 6-fluoro-1-hydroxy-2,3,1-benzodiazaborinine-2-carbodithioate (E), (150 mg, 0.59 mmol), was dissolved in ethanol (2 mL) and cyclobutylamine (72 μL , 0.82 mmol) was added. The reaction mixture was heated to 80 $^{\circ}\text{C}$ for 24h. The solvent was evaporated and the crude product mixture was dissolved in ethyl acetate and washed with dilute HCl (solution pH adjusted to 6). The organic layer was separated, dried over sodium sulphate, filtered and concentrated under reduced pressure to afford 82 mg (50.3% of theory) of N-cyclobutyl-6-fluoro-1-hydroxy-2,3,1-benzodiazaborinine-2-carbothioamide

^1H NMR (400 MHz, DMSO-d_6): δ 1.72-1.76 (m, 2H), 2.22-2.32 (m, 4H), 4.70-4.72(m, 1H), 7.58 (td, J =17.6, 8.8, Hz, 1H), 7.77 (dd, J =9.6, 2.8 Hz, 1H), 8.161(dd, J = 8, 6 Hz, 1H), 8.293(s, 1H), 10.29(d, J =7Hz, 1H), 10.505 (s, 1H)

Example-12: Preparation of 2-chloro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzaldehyde (G)

To a solution of 2-bromo-6-chloro-benzaldehyde (0.5 g) in DME (10 mL) were added bispinacolato diboron (0.809 g) and potassium acetate (0.670 g) and the solution was degassed by bubbling nitrogen through the reaction mixture for 15 min. Then [1,1'-Bis(diphenyl phosphino)ferrocene]palladium(II) dichloride dichloromethane adduct (0.094 g), was added into the reaction mixture and heated at 80°C for 4 hrs. The reaction mass was cooled to ambient temperature and diluted with water. The aqueous layer was extracted with ethyl acetate, organic layer was separated and dried over sodiumsulphate, filtered and concentrated under reduced pressure. Crude product was purified by flash column chromatography using 40% ethyl acetate in cyclohexane to yield 0.32 g (52.7% of theory) of 2-chloro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde as a solid compound.

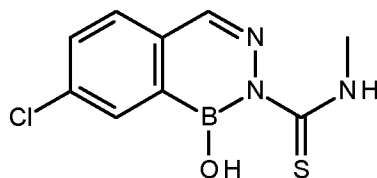
^1H NMR (400 MHz, CDCl_3) δ ppm 1.348 (s, 12 H) 7.370 (d, $J = 7.2$ Hz, 1H) 7.433 (m, 1 H) 7.723 (m, 1 H) 10.31 (s, 1H)

Example-13: Preparation of 5-chloro-1-hydroxy-N-methyl-2,3,1-benzodiazaborinine-2-carbothioamide

To a solution of 2-chloro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (G), (0.08 g, 0.3002 mmol), in water (2 mL) were added formic acid (0.1 mL) and 1-amino-3-methyl-thiourea (0.037 g, 0.3602 mmol). The reaction mass was stirred at 100°C for 2 hr. The reaction mixture was cooled to ambient temperature and then cyclohexane was added. The desired compound precipitated and the solid mass was filtered, washed with cyclohexane and dried to afford 50 mg (65% of theory) of 5-chloro-1-hydroxy-N-methyl-2,3,1-benzodiazaborinine-2-carbothioamide as white solid.

LC-MS $[\text{M}+\text{H}]$: 254.1 (RT; 1.12-1.19)

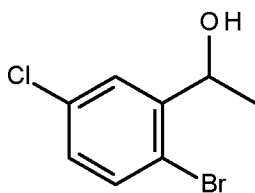
Example-14: Preparation of 7-chloro-1-hydroxy-N-methyl-2,3,1-benzodiazaborinine-2-carbothioamide



To a solution of 5-chloro-2-formyl-phenyl)boronic acid (0.1 g, 0.5 mmol), in water(2 mL) were added formic acid (0.1 mL) and 1-amino-3-methyl-thiourea (0.06 g , 0.5 mmol). The reaction mass was stirred at 100°C for 2 hr. The reaction mixture was cooled to ambient temperature and then cyclohexane was added. The desired compound precipitated and the solid mass was filtered, washed with cyclohexane and dried to afford 90 mg (70% of theory) of 7-chloro-1-hydroxy-N-methyl-2,3,1-benzodiazaborinine-2-carbothioamide.

MS [M-H]: 251.9 (RT: 1.43-1.46)

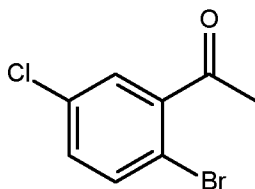
Example-14: Preparation of 1-(2-bromo-5-chloro-phenyl)ethanol, (H):



To a solution of 2-bromo-5-chloro-benzaldehyde (5 g) in anhydrous THF (40 mL) was added Methyl magnesium bromide (8.7 ml of 3 M solution in diethylether) maintained at 0-5°C. Reaction mass was allowed to stirr at ambient temperature for 6 h. Reaction mixture was quenched by dropwise addition of saturated aqueous solution of ammoniumchloride and stirred for 10 mins. The aqueous layer was extracted with ethyl acetate, organic layer was separated and dried over sodiumsulphate, filtered and concentrated under reduced pressure. Crude product was purified by flash column chromatography using 40% ethyl acetate in cyclohexane to afford 4.8 g (89% of theory) of (2-bromo-5-chloro-phenyl) ethanol as a gummy mass.

¹H NMR (400 MHz, DMSO-*d*₆) δ ppm 1.28-1.33 (d, 3 H *J*=6.4 Hz) 4.81-4.92 (m, 1 H) 5.56-5.59 (d, 1 H, *J*=4 Hz) 7.24-7.34 (m, 1 H) 7.56-7.58 (m, 2 H)

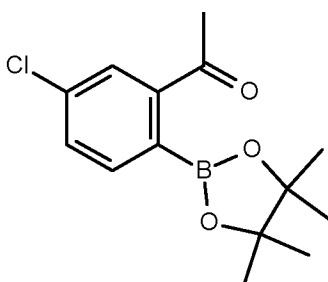
Example-15: Preparation of 1-(2-bromo-5-chloro-phenyl)ethanone (I):



To a solution of 1-(2-bromo-5-chloro-phenyl) ethanol (H), (5.1 g) in dichloromethane (50 mL) was added Dess-Martin Periodinane (10 g) slowly at 0-5°C. The reaction mass was allowed to stir at ambient temperature for 3 h. The reaction mixture was diluted with 50 mL of dichloromethane and then a 1:1:1 mixture of saturated aqueous sodium thiosulfate solution (35 mL), a saturated aqueous sodiumbicarbonate solution (35 mL), and water (35 mL) was added slowly. The resulting biphasic mixture was stirred for 1 h, resulting in two clear layers. The organic layer was collected separately and the aqueous layer was extracted with dichloromethane (3X25 ml). The combined organic layer were washed with water, dried over sodiumsulphate, filtered and concentrated under reduced pressure. Crude product was purified by flash column chromatography using 10% ethyl acetate in cyclohexane to afford 3.5 g (69% of theory) of 1-(2-bromo-5-chloro-phenyl)ethanone as a off white solid.

¹H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 2.62 – 2.68 (s, 1 H) 7.25-7.27 (m, 1 H) 7.42-7.40 (d, 1 H *J*=2.4 Hz) 7.52-7.54 (d, *J*=8.4 Hz, 1 H)

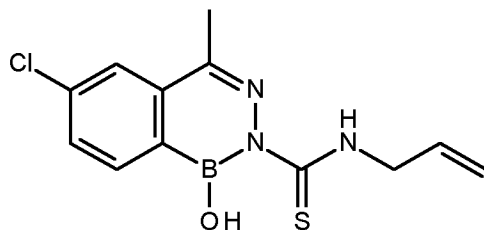
Example-15: Preparation of 1-[5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]ethanone (J):



To a solution of 1-(2-bromo-5-chloro-phenyl) ethanone (I), (2.5 g) in DME (10 mL) were added bispinacolato diboron (4.1 g) and potassium acetate (2.5 g) and the solution was degassed by bubbling nitrogen through the reaction mixture for 15 min. Then [1,1'-Bis(diphenyl phosphino)ferrocene]palladium(II) dichloride dichloromethane adduct (0.44 g), was added into the reaction mixture and heated at 80°C for 4 hrs. The reaction mass was cooled to ambient temperature and diluted with water. The aqueous layer was extracted with ethyl acetate, organic layer was separated and dried over sodiumsulphate, filtered and concentrated under reduced pressure. Crude product was purified by flash column chromatography using 30% ethyl acetate in cyclohexane to afford 2.4 g (79% of theory) of 1-[5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl]ethanone as a solid) as white solid.

¹H NMR (400 MHz, CDCl₃) δ ppm 1.42 (s, 12 H) 7.43-7.45 (d, 1 H *J*=8 Hz) 7.52-7.49 (m, 1 H) 7.76-7.763 (d, *J*=2.4 Hz, 1 H)

Example-16: Preparation of N-allyl-6-chloro-1-hydroxy-4-methyl-2,3,1-benzodiazaborinine-2-carbothioamide

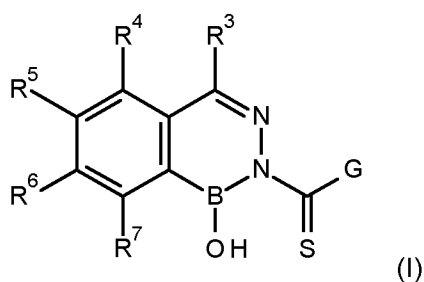


To a solution of 1-[5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]ethanone (J), (0.2 g), dissolved in a mixture of water (4 mL) and THF (1 mL) were added 1-allyl-3-amino-thiourea (0.93g) and formic acid (0.1 ml) were added. The reaction mixture was heated to reflux for 24h, cooled to ambient temperature and cyclohexane was added. The desired compound precipitated and the solid mass was filtered washed with cyclohexane and dried to afford 0.16 g (60% of theory) of N-allyl-6-chloro-1-hydroxy-4-methyl-2,3,1-benzodiazaborinine-2-carbothioamide as white solid.

LC-MS- M+H- 294 (RT;2.44-2.54)

The following Table 1 illustrates the invention

Table 1: Compounds of formula (I)



Cpd No.	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	R ⁷	G
1	Methyl	H	H	H	F	H	H	NR ¹ R ²
2	Methyl	H	H	H	Cl	H	H	NR ¹ R ²
3	-	-	H	H	Cl	H	H	SCH ₃
4	2-methylthoxy-1-ethyl	H	H	H	F	H	H	NR ¹ R ²
5	2-methylthoxy-1-ethyl	H	H	H	Cl	H	H	NR ¹ R ²
6	4-methylthoxy-1-benzyl	H	H	H	Cl	H	H	NR ¹ R ²
7	4-methylthoxy-1-benzyl	H	H	H	F	H	H	NR ¹ R ²
8	Cyclobutyl	H	H	H	F	H	H	NR ¹ R ²
9	-	-	H	H	F	H	H	SCH ₃
10	Phenyl	H	H	H	F	H	H	NR ¹ R ²
11	Phenyl	H	H	H	Cl	H	H	NR ¹ R ²
12	Phenyl	H	H	H	H	H	H	NR ¹ R ²
13	H	H	H	H	F	H	H	NR ¹ R ²
14	H	H	H	H	Cl	H	H	NR ¹ R ²
15	H	H	H	H	H	H	H	NR ¹ R ²

16	Allyl	H	H	H	F	H	H	NR ¹ R ²
17	Allyl	H	H	H	Cl	H	H	NR ¹ R ²
18	Allyl	H	H	H	H	H	H	NR ¹ R ²
19	Methyl	H	Methyl	H	Cl	H	H	NR ¹ R ²
20	Allyl	H	Methyl	H	Cl	H	H	NR ¹ R ²
21	Benzyl	H	Methyl	H	Cl	H	H	NR ¹ R ²
22	3,3,3-trifluoro-propyl-	H	H	H	Cl	H	H	NR ¹ R ²
23	(1-hydroxycyclohexyl)methylthyl	H	H	H	Cl	H	H	NR ¹ R ²
24	2-oxotetrahydrothiophen-3-yl	H	H	H	Cl	H	H	NR ¹ R ²
25	6-ethoxycarbonylcyclohex-3-en-1-yl	H	H	H	Cl	H	H	NR ¹ R ²
26	2-(1,3-benzodioxol-5-yl)ethyl	H	H	H	Cl	H	H	NR ¹ R ²
27	2-benzylsulfanylethyl	H	H	H	Cl	H	H	NR ¹ R ²
28	4-Methylthanesulfonyl-benzyl	H	H	H	Cl	H	H	NR ¹ R ²
29	sec-Butyl	H	H	H	Cl	H	H	NR ¹ R ²
30	Butan-1-ol-2-yl	H	H	H	Cl	H	H	NR ¹ R ²
31	2-([1',3']dioxolan-2'-yl)-eth-1-yl-	H	H	H	Cl	H	H	NR ¹ R ²
32	tetrahydrofuran-2-ylmethylth-yl-	H	H	H	Cl	H	H	NR ¹ R ²
33	3-pyrrolidin-1-ylpropyl	H	H	H	Cl	H	H	NR ¹ R ²
34	(pyrid-3-yl)-methylthyl-	H	H	H	Cl	H	H	NR ¹ R ²
35	Benzyl	H	H	H	Cl	H	H	NR ¹ R ²
36	2-fluorobenzyl	H	H	H	Cl	H	H	NR ¹ R ²
37	1-phenyl-eth-1-yl-	H	H	H	Cl	H	H	NR ¹ R ²
38	2-phenyl-eth-1-yl-	H	H	H	Cl	H	H	NR ¹ R ²
39	2-(thiophen-2'-yl)-eth-1-yl-	H	H	H	Cl	H	H	NR ¹ R ²
40	2-Acetylamino-ethyl	H	H	H	Cl	H	H	NR ¹ R ²
41	4-Pyrazol-1-yl-benzyl	H	H	H	Cl	H	H	NR ¹ R ²
42	2-(1H-indol-3-yl)ethyl	H	H	H	Cl	H	H	NR ¹ R ²
43	2-Methylthylsulfanyl-ethyl	H	H	H	Cl	H	H	NR ¹ R ²
44	2-Piperidin-1-yl-benzyl	H	H	H	Cl	H	H	NR ¹ R ²
45	(6-Chloro-pyridin-3-yl)-methylthyl	H	H	H	Cl	H	H	NR ¹ R ²
46	2-(4-benzylpiperazin-1-yl)ethyl	H	H	H	Cl	H	H	NR ¹ R ²
47	1H-benzimidazol-2-ylmethylthyl	H	H	H	F	H	H	NR ¹ R ²
48	3,3,3-trifluoro-propyl-	H	H	H	F	H	H	NR ¹ R ²
49	6-ethoxycarbonylcyclohex-3-en-1-yl	H	H	H	F	H	H	NR ¹ R ²
50	2-(1,3-benzodioxol-5-yl)ethyl	H	H	H	F	H	H	NR ¹ R ²
51	2-benzylsulfanylethyl	H	H	H	F	H	H	NR ¹ R ²
52	4-Methylthanesulfonyl-benzyl	H	H	H	F	H	H	NR ¹ R ²
53	sec-Butyl	H	H	H	F	H	H	NR ¹ R ²
54	Butan-1-ol-2-yl	H	H	H	F	H	H	NR ¹ R ²

55	2-([1',3']dioxolan-2'-yl)-eth-1-yl-	H	H	H	F	H	H	NR ¹ R ²
56	tetrahydrofuran-2-ylmethylthyl-	H	H	H	F	H	H	NR ¹ R ²
57	2-methylthyl-cyclohex-1-yl-	H	H	H	F	H	H	NR ¹ R ²
58	(pyrid-3-yl)-methylthyl-	H	H	H	F	H	H	NR ¹ R ²
59	3-(1-piperidyl)propyl	H	H	H	F	H	H	NR ¹ R ²
60	Benzyl	H	H	H	F	H	H	NR ¹ R ²
61	2-fluorobenzyl	H	H	H	F	H	H	NR ¹ R ²
62	1-phenyl-eth-1-yl-	H	H	H	F	H	H	NR ¹ R ²
63	2-phenyl-eth-1-yl-	H	H	H	F	H	H	NR ¹ R ²
64	2-(thiophen-2'-yl)-eth-1-yl-	H	H	H	F	H	H	NR ¹ R ²
65	2-Phenoxy-ethyl	H	H	H	F	H	H	NR ¹ R ²
66	3-chlorobenzyl-	H	H	H	F	H	H	NR ¹ R ²
67	2-Acetylamino-ethyl	H	H	H	F	H	H	NR ¹ R ²
68	4-Pyrazol-1-yl-benzyl	H	H	H	F	H	H	NR ¹ R ²
69	2-(1H-indol-3-yl)ethyl	H	H	H	F	H	H	NR ¹ R ²
70	2-trifluoromethylthyl-benzyl-	H	H	H	F	H	H	NR ¹ R ²
71	2-Methylthylsulfanyl-ethyl	H	H	H	F	H	H	NR ¹ R ²
72	2-Piperidin-1-yl-benzyl	H	H	H	F	H	H	NR ¹ R ²
73	4-Phenoxy-benzyl	H	H	H	F	H	H	NR ¹ R ²
74	1-Benzyl-pyrrolidin-3-yl	H	H	H	F	H	H	NR ¹ R ²
75	2-(4-benzylpiperazin-1-yl)ethyl	H	H	H	F	H	H	NR ¹ R ²
76	Furan-2-yl-methylthyl	H	H	H	F	H	H	NR ¹ R ²
77	Methyl	H	H	H	H	H	H	NR ¹ R ²
78	Benzyl	H	H	H	H	H	H	NR ¹ R ²
79	Methyl	H	Methyl	H	H	H	H	NR ¹ R ²
80	Benzyl	H	Methyl	H	H	H	H	NR ¹ R ²
81	Allyl	H	Methyl	H	H	H	H	NR ¹ R ²
82	H	H	Methyl	H	H	H	H	NR ¹ R ²
83	Phenyl	H	Methyl	H	H	H	H	NR ¹ R ²
84	Allyl	H	Methyl	H	F	H	H	NR ¹ R ²
85	Benzyl	H	Methyl	H	F	H	H	NR ¹ R ²
86	Methyl	H	Methyl	H	F	H	H	NR ¹ R ²
87	Phenyl	H	H	Cl	H	H	H	NR ¹ R ²
88	Methyl	-	H	H	H	Cl	H	SCH ₃
89	Methyl	H	H	H	H	F	H	NR ¹ R ²
90	H	H	H	F	H	H	H	NR ¹ R ²
91	Phenyl	H	H	H	H	F	H	NR ¹ R ²
92	-	-	H	Cl	H	H	H	SCH ₃
93	Methyl	H	H	H	-O-CH ₂ -O-		H	NR ¹ R ²
94	-	-	H	H	-O-CH ₂ -O-		H	SCH ₃

95	H	H	H	H	OH	H	H	NR ¹ R ²
96	Methyl	H	H	H	Cl	OMethyl	H	NR ¹ R ²
97	Methyl	H	H	H	H	Cl	H	NR ¹ R ²
98	Methyl	H	H	F	H	H	H	NR ¹ R ²
99	Methyl	H	H	Cl	H	H	H	NR ¹ R ²
100	Allyl	H	H	H	NO ₂	OMethyl	H	NR ¹ R ²
101	Allyl	H	H	H	Cl	OMethyl	H	NR ¹ R ²
102	H	H	H	H	H	F	H	NR ¹ R ²
103	-	H	H	H	NO ₂	OMethyl	H	SCH ₃
104	Methyl	H	H	H	H	H	F	NR ¹ R ²
105	H	H	H	H	OMethyl	H	H	NR ¹ R ²
106	Phenyl	H	H	H	H	Cl	H	NR ¹ R ²
107	Methyl	H	H	H	H	OMethyl	H	NR ¹ R ²
108	Phenyl	H	H	H	H	OMethyl	H	NR ¹ R ²
109	-	-	H	H	H	F	H	SCH ₃
110	Phenyl	H	H	F	H	H	H	NR ¹ R ²
111	Methyl	H	H	H	OMethyl	H	H	NR ¹ R ²
112	Phenyl	H	H	H	OMethyl	H	H	NR ¹ R ²
113	H	H	H	Cl	H	H	H	NR ¹ R ²
114	Phenyl	H	H	H	-O-CH ₂ -O-		H	NR ¹ R ²
115	Methyl	-	H	H	H	OMethyl	H	SCH ₃
116	Methyl	H	H	H	OH	H	H	NR ¹ R ²

Table 2 : Characterising data:

Table 3 shows selected melting point and selected NMR data for compounds of Table 1. CDCl₃/D₂O and DMSO are used as solvents for NMR 400 MHz measurements. No attempt is made to list all characterising data in all cases.

In Table 3 and throughout the description that follows, temperatures are given in degrees Celsius; "NMR" means nuclear magnetic resonance spectrum; MS stands for mass spectrum; "%" is percent by weight, unless corresponding concentrations are indicated in other units. The following abbreviations are used throughout this description:

m.p. = melting point

b.p.= boiling point.

S = singlet

br = broad

d = doublet

dd = doublet of doublets

t = triplet

q = quartet

m = multiplet

ppm = parts per million

The following LC-MS method was used to characterize the compounds:

Method A

ACQUITY SQD Mass Spectrometer from Waters (Single quadrupole mass spectrometer)

Ionisation method: Electrospray

Polarity: positive ions

Capillary (kV) 3.00, Cone (V) 20.00, Extractor (V) 3.00, Source Temperature (°C) 150, Desolvation

Temperature (°C) 400, Cone Gas Flow (L/Hr) 60, Desolvation Gas Flow (L/Hr) 700

Mass range: 100 to 800 Da

DAD Wavelength range (nm): 210 to 400

Method Waters ACQUITY UPLC with the following HPLC gradient conditions

(Solvent A: Water/Methanol 9:1, 0.1% formic acid and Solvent B: Acetonitrile, 0.1% formic acid)

Time (minutes)	A (%)	B (%)	Flow rate (ml/min)
0	100	0	0.75
2.5	0	100	0.75
2.8	0	100	0.75
3.0	100	0	0.75

Type of column: Waters ACQUITY UPLC HSS T3; Column length: 30 mm; Internal diameter of column: 2.1 mm; Particle Size: 1.8 micron; Temperature: 60°C.

And

Method B

Mass Spectrometer : 6410 Triple Quadrupole Mass Spectrometer from Agilent Technologies

HPLC : Agilent 1200 Series HPLC

Optimized Mass Parameter :-

Ionisation method : Electrospray (ESI)

Polarity : positive and Negative Polarity Switch

Scan Type : MS2 Scan

Capillary (kV) : 4.00

Fragmentor (V) : 100.00

Gas Temperature (°C) : 350

Gas Flow (L/min) : 11

Nebulizer Gas (psi) : 35

Mass range : 110 to 1000 Da

DAD Wavelength range (nm): 190 to 400

Optimized Chromatographic parameter :-

Gradient conditions

(Solvent A: Water, 0.1% formic acid and Solvent B: Acetonitrile, 0.1% formic acid)

Time (minutes)	A (%)	B (%)	Flow rate (ml/min)
0	90	10	1.8
2.0	0	100	1.8
3.0	0	100	1.8
3.2	90	10	1.8
4.0	90	10	1.8

Column : Waters Xterra MS C18
 Column length : 30 mm
 Internal diameter of column : 4.6 mm
 Particle Size : 3.5 μ
 Temperature : Room Temperature

The characteristic values obtained for each compound were the retention time ("R_t", recorded in minutes) and the molecular ion as listed in Table 3.

Table 3: Physical data of compounds of formula I:

Cpd No.	m.p. (°C)	MS [M+H] ⁺	R _t (min)	¹ H-NMR data: ppm (multiplicity/number of Hs)
1	168 - 170			
2	168 - 170			
3	158 - 160			
4	130 - 132			
5	144 - 146			
6	145 - 147	359.92	2.06	
7	133 - 135	343.97	1.94	
8	148 - 150			
9	156 - 158			
10	152 - 154	300	1.73	¹ H NMR (400 MHz, CDCl ₃): δ 7.32-7.42 (m, 3H), 7.44-7.48 (m, 2H), 7.56-7.58 (m, 2H), 7.99 (s, 1H), 8.31 (dd, J = 6.0, 8.4 Hz, 1H), 10.62 (s, 1H), 11.16 (s, 1H).
11	203 - 205			
12	157 - 159	282	1.63	¹ H NMR (400 MHz, CDCl ₃): δ 7.32-7.35 (m, 1H), 7.44-7.48 (m, 2H), 7.57-7.59 (m, 2H), 7.66-7.77 (m, 3H), 8.04 (s, 1H), 8.30-8.32 (m, 1H), 10.68 (s, 1H), 11.23 (s, 1H).
13	188 - 190	224	1.05	¹ H NMR (400 MHz, CDCl ₃): δ 6.87 (bs, 1H), 7.29 (dd, J = 2.4, 8.8 Hz, 1H), 7.38 (dt, J = 2.4, 8.8 Hz, 1H), 7.93 (s, 1H), 8.28 (dd, J = 5.6, 8.4

				Hz, 1H), 8.89 (bs, 1H), 10.40 (s, 1H).
14	188 - 190			
15	184 - 186	206	0.64	¹ H NMR (400 MHz, CDCl ₃): δ 6.86 (bs, 1H), 7.62-7.75 (m, 3H), 7.97 (s, 1H), 8.27 (d, J = 6.8 Hz, 1H), 8.93 (bs, 1H), 10.45 (s, 1H).
16		264	1.55	¹ H NMR (400 MHz, CDCl ₃): δ 4.35-4.38 (m, 2H), 5.27-5.37 (m, 2H), 5.99 (dd, J = 10.0, 17.2 Hz, 1H), 7.28 (dd, J = 2.4, 8.4 Hz, 1H), 7.36 (dt, J = 2.4, 6.6 Hz, 1H), 7.92 (s, 1H), 8.27 (dd, J = 6.0, 8.4 Hz, 1H), 9.57 (s, 1H), 10.55 (s, 1H).
17	136 - 138			
18		246	1.39	¹ H NMR (400 MHz, CDCl ₃): δ 4.35-4.39 (m, 2H), 5.27-5.37 (m, 2H), 5.99 (dd, J = 10.4, 17.2 Hz, 1H), 7.62-7.72 (m, 3H), 7.96 (s, 1H), 8.26-8.28 (m, 1H), 9.64 (s, 1H), 10.59 (s, 1H).
19	158 - 160			
20	96 - 98			
21	117 - 119			
22		335.88	2	
23		351.98	2.01	
24		339.89	1.82	
25		391.96	2.22	
26		387.94	2.11	
27		389.92	2.21	
28		409.07	1.74	
29		295.98	2.13	
30		311.95	1.72	
31		339.93	1.83	
32		323.94	1.92	
33		350.98	1.15	
34		330.92	1.33	
35		329.95	2.08	
36		347.92	2.09	
37		343.94	2.17	
38		343.94	2.17	
39		349.88	2.12	
40		324.95	1.43	

41		395.95	1.99	
42		382.93	2.05	
43		313.91	1.96	
44		413	2.5	
45		364.88	1.9	
46		442.01	1.33	
47		353.97	1.15	
48		319.9	1.85	
49		376	2.09	
50		371.97	1.98	
51		373.94	2.09	
52		391.93	1.61	
53		280.01	1.99	
54		295.99	1.58	
55		323.98	1.68	
56		307.97	1.78	
57		320	2.22	
58		314.96	1.18	
59		349.03	1.08	
60		313.96	1.95	
61		331.94	1.96	
62		327.95	2.04	
63		327.96	2.05	
64		333.92	2	
65		343.98	2	
66		347.91	2.05	
67		308.98	1.29	
68		379.96	1.87	
69		366.98	1.93	
70		381.94	20.9	
71		297.95	1.82	
72		397.03	2.37	
73		405.96	2.21	
74		382.99	1.19	
75		426.05	1.22	
76		303.95	1.82	
77	108 - 109	220	1.19	1H NMR (400 MHz, CDCl ₃): δ 3.25 (d, J = 4.8 Hz, 3H), 7.61-7.73 (m, 3H), 7.94 (s, 1H), 8.26 (d, J = 7.2 Hz, 1H), 9.58 (bs, 1H), 10.62 (s, 1H).

78	155 - 156	296	1.69	¹ H NMR (400 MHz, CDCl ₃): δ 4.92 (d, J = 5.2 Hz, 2H), 7.32-7.41 (m, 4H), 7.61-7.74 (m, 3H), 7.92 (s, 1H), 8.28 (d, J = 7.2 Hz, 1H), 9.79 (bs, 1H), 10.62 (s, 1H).
79		234.1	2.13	¹ H NMR (400 MHz, CDCl ₃): δ 2.59 (s, 3H), 3.26 (d, J = 4.8 Hz, 3H), 7.63-7.67 (m, 1H), 7.69-7.74 (m, 1H), 7.77 (d, J = 7.6 Hz, 1H), 8.29 (d, J = 6.8 Hz, 1H), 9.68 (bs, 1H), 10.58 (s, 1H).
80		310.1	2.42	¹ H NMR (400 MHz, CDCl ₃): δ 2.54 (s, 3H), 4.94 (d, J = 5.6 Hz, 2H), 7.30-7.39 (m, 5H), 7.64-7.73 (m, 2H), 7.75-7.73 (m, 1H), 8.29 (d, J = 8.29 Hz, 1H), 9.94 (bs, 1H), 10.57 (s, 1H).
81		260	2.29	¹ H NMR (400 MHz, CDCl ₃): δ 2.59 (s, 3H), 4.36-4.39 (m, 2H), 5.25-5.36 (m, 2H), 6.00 (dd, J = 10.0, 17.2 Hz, 1H), 7.64-7.76 (m, 3H), 8.27-8.29 (m, 1H), 9.75 (bs, 1H), 10.55 (s, 1H).
82	175 - 176	220	1.89	¹ H NMR (400 MHz, CDCl ₃): δ 2.58 (s, 3H), 6.79 (bs, 1H), 7.65-7.77 (m, 3H), 8.27-8.29 (m, 1H), 9.03 (bs, 1H), 10.39 (s, 1H).
83	60 - 62	296	2.37	¹ H NMR (400 MHz, CDCl ₃): δ 2.65 (s, 3H), 7.33-7.83 (m, 8H), 8.32 (m, 1H), 10.64 (s, 1H), 11.34 (s, 1H).
84	112 - 113	276	2.35	¹ H NMR (400 MHz, CDCl ₃): δ 2.56 (s, 3H), 4.35-4.39 (m, 2H), 5.26-5.35 (m, 2H), 5.92-6.05 (m, 1H), 7.25-7.41 (m, 2H), 8.28 (dd, J = 6.0, 8.8 Hz, 1H), 9.81 (bs, 1H), 10.51 (s, 1H).
85	143 - 144	327.9	2.46	¹ H NMR (400 MHz, CDCl ₃): δ 2.51 (s, 3H), 4.98 (d, J = 5.6 Hz, 2H), 7.32-7.42 (m, 7H), 8.29 (dd, J = 6.0, 8.4 Hz, 1H), 9.87 (bs, 1H), 10.53 (s, 1H).
86	197 - 198	251.9	2.19	¹ H NMR (400 MHz, CDCl ₃): δ 2.56 (s, 3H), 3.26 (d, J = 4.8 Hz, 2H), 7.33-7.42 (m, 2H), 8.29 (dd, J = 6.4, 8.4 Hz, 1H), 9.63 (bs, 1H), 10.54 (s, 1H).
87	184-186	316.1	1.62-1.7	
88	149-151	270.9	1.82-1.84	
89	190-192			
90	300-300	224	0.79-0.83	
91	209-211	300.1	1.66-1.72	

92	140-142	271.1	1.76-1.8	
93	236-238	264	1.99-2.04	
94	181-183	280.9	1.67-1.69	
95	300-300			
96	213-215	283.9	1.50-1.54	
97	194-196			
98	200-202	238	1.13-1.16	
99	200-202	254.1	1.12-1.19	
100	243-245	320.9	1.54-1.56	
101	149-151	309.8	1.67-1.71	
102	250-250			
103	229-231	294.9	1.35-1.37	
104	181-183	238	1.05-1.08	
105	194-196	236	1.04-1.08	
106	189-191			
107	147-149	250	2.01-2.06	
108	157-159	312	1.63-1.70	
109	125-127			
110	190-192	300	1.63-1.66	
111	178-179	250	1.31-1.33	
112	176-178	312	1.68-1.72	
113	302-304	240	0.75-0.86	
114	241-243	326	1.65-1.69	
115	138-140	267	1.63-1.68	
116	198-200			

Formulation examples for compounds of formula (I):

Example F-1.1 to F-1.2: Emulsifiable concentrates

Components	F-2.1	F-2.2
A compound selected from the Tables 2 to 2400	25%	50%
calciumdodecylbenzenesulfonate	5%	6%
castoroilpolyethyleneglycolether		
(36molethylenoxyunits)	5%	-
tributylphenolpolyethyleneglycolether		
(30molethylenoxyunits)	-	
cyclohexanone	-	20%
xylene mixture	65%	20%

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

Example F-2: Emulsifiable concentrate

Components	F-2
A compound selected from the Tables 2 to 2400	10%
octylphenolpolyethyleneglycolether (4 to 5 mol ethylenoxy units)	3%
Calcium dodecylbenzenesulfonate	3%
Castoroilpolyglycolether (36 mol ethylenoxy units)	4%
cyclohexanone	30%
xylene mixture	50%

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

Examples F-3.1 to F-3.4: Solutions

Components	F-3.1	F-3.2	F-3.3	F-3.4
A compound selected from the Tables 2 to 2400	80%	10%	5%	95%
propylene glycol monomethyl ether	20%	-	-	-
polyethylene glycol (relative molecular mass: 400 atomic mass units)	-	70%	-	-
N-methylpyrrolid-2-one	-	20%	-	-
epoxidised coconut oil	-	-	1%	5%
benzin (boiling range: 160-190°)	-	-	94%	-
The solutions are suitable for use in the form of microdrops.				

Examples F-4.1 to F-4.4: Granulates

Components	F-4.1	F-4.2	F-4.3	F-4.4
A compound selected from the Tables 2 to 2400	5%	10%	8%	21%
Kaolin	94%	-	79%	54%
highly dispersed silicic acid	1%	-	13%	7%
Attapulgate	-	90%	-	18%

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

Examples F-5.1 and F-5.2: Dusts

Components	F-5.1	F-5.2
A compound selected from the Tables 2 to 2400	2%	5%
highly dispersed silicic acid	1%	5%

Talcum	97%	-
Kaolin	-	90%

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

Examples F-6.1 to F-6.3: Wettable powders

Components	F-6.1	F-6.2	F-6.3
A compound selected from the Tables 2 to 2400	25%	50%	75%
sodium lignin sulfonate	5%	5%	-
sodium lauryl sulphate	3%	-	5%
sodium diisobutylphenylene sulfonate	6%	10%	-
octylphenolpolyethylene glycol ether (7 to 8 mol ethylenoxy units)	2%	-	-
highly dispersed silicic acid	5%	10%	10%
Kaolin	62%	27%	-

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

Example F7: Flowable concentrate for seed treatment

Components	F-7
A compound selected from the Tables 2 to 2400	40 %
propylene glycol	5 %
copolymer butanol PO/EO	2 %
tristyrenephenole with 10-20 moles EO	2 %
1,2-benzisothiazolin-3-one (in the form of a 20% solution in water)	0.5 %
monoazo-pigment calcium salt	5 %
Silicone oil (in the form of a 75 % emulsion in water)	0.2 %
Water	45.3 %

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

BIOLOGICAL EXAMPLES: FUNGICIDAL ACTION:

Table 4: Activity against different phytopathogenic fungi in %

Compound	Rate ppm	PYTULT	COLLAG	MONNIV	RHISOL	PUCREC	FUSCUL
Compd No. 17	200	100	100	100	70	70	70
	20	100	100	50	0	0	0
Compd No. 18	200	100	100	100	20	0	20
	20	100	0	0	0	0	0

Table 5: Activity against different phytopathogenic fungi in %

Compound	Rate ppm	PYTULT	COLLAG	MONNIV	RHISOL	PUCREC	GAEGRA
Compd No. 14	200	100	100	100	100	50	100
	20	100	100	70	0	0	100
Compd No. 15	200	100	100	100	100	0	100
	20	100	0	0	0	0	0

Table 6: Activity against different phytopathogenic fungi in %

Compound	Rate ppm	PYTULT	COLLAG	MONNIV	RHISOL	PUCREC	PLAVIT
Compd No. 10	200	100	100	100	50	20	50
	20	100	70	0	20	0	20
Compd No.11	200	100	100	100	0	90	100
	20	100	100	70	0	0	50
Compd No. 12	200	100	100	100	0	0	20
	20	100	50	0	0	0	20

The test procedures are detailed below; in the above table the abbreviations gives test results against the following agriculturally relevant pathogens as follows:

PYTULT = *Pythium ultimum*

COLLAG = *Colletotrichum lagenarium*

MONNIV = *Monographella nivalis*

RHISOL = *Rhizoctonia solanis*

PUCREC = *Puccinia recondita*

FUSCUL = *Fusarium culmorum*

GAEGRA = *Gäumannomyces graminis*

PLAVIT = *Plasmopara viticola*

The compounds which gave >80% disease control at 200 ppm in various tests when compared to untreated control under the same conditions, which show extensive disease development are specified below

1 *Phytophthora infestans* / tomato / leaf disc preventative (late blight)

Tomato leaf disks were placed on water agar in multiwell plates (24-well format) and sprayed with the formulated test compound diluted in water at an application rate of 200ppm. The leaf disks were inoculated with a spore suspension of the fungus 1 day after application. The inoculated leaf disks were incubated at 16°C and 75% relative humidity under a light regime of 24 h darkness followed by 12/12 h (light/dark) in a climate cabinet and the activity of a compound was assessed as percent disease control compared to untreated when an appropriate level of disease damage appears in untreated check leaf disks.

The compound 3 at 200 ppm give at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development

2 *Plasmopara viticola* / grape / leaf disc preventative (late blight)

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

The following compounds 11, 19 and 31 at 200 ppm give at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development.

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

Wheat leaf segments cultivated variety (cv) Kanzler were placed on agar in 24-well plates and sprayed with formulated test compound diluted in water at an application rate of 200ppm. The leaf disks were inoculated with a spore suspension of the fungus 1 day after application. The inoculated leaf segments were incubated at 19°C and 75% relative humidity under a light regime of 12/12 h (light/dark) in a climate cabinet and the activity of a compound was assessed as percent disease control compared to untreated when an appropriate level of disease damage appears in untreated check leaf segments (7 – 9 days after application).

The compounds 3, 11 and 97 at 200 ppm give at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development.

4 *Alternaria solani* / tomato / leaf disc (early blight)

Tomato leaf disks cultivated variety (cv.) Baby were placed on agar in multiwell plates (24-well format) and sprayed with the formulated test compound diluted in water at an application rate of 200ppm. The leaf disks were inoculated with a spore suspension of the fungus 2 days after application. The inoculated leaf disks were incubated at 23°C/21°C (day/night) and 80% relative humidity under a light regime of 12/12 h (light/dark) in a climate cabinet and the activity of a compound was assessed as

percent disease control compared to untreated when an appropriate level of disease damage appears on untreated check disk leaf disks (5 – 7 days after application).

The compound 105 at 200 ppm give at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development

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

Rice leaf segments cv. Ballila were placed on agar in multiwell plate (24-well format) and sprayed with the formulated test compound diluted in water at an application rate of 200ppm. The leaf segments were inoculated with a spore suspension of the fungus 2 days after application. The inoculated leaf segments were incubated at 22°C and 80% rh under a light regime of 24 h darkness followed by 12/12 h (light/dark) in a climate cabinet and the activity of a compound was assessed as percent disease control compared to untreated when an appropriate level of disease damage appears in untreated check leaf segments (5 – 7 days after application).

The Compound 94 at 200 ppm give at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development.

6 *Pythium ultimum* / liquid culture (seedling damping off)

Mycelia fragments and oospores of a newly grown liquid culture of the fungus were directly mixed into nutrient broth (potato dextrose broth). After placing a DMSO solution of test compound into a 96-well format microtiter plate at an application rate of 200ppm, the nutrient broth containing the fungal mycelia/spore mixture was added. The test plates were incubated at 24°C and the inhibition of growth was determined photometrically 2-3 days after application.

The compounds 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 87, 88, 89, 90, 91, 92, 93, 94, 96, 97, 98, 99, 100, 101, 102, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113 and 115 at 200 ppm give at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development.

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

Conidia of the fungus from cryogenic storage were directly mixed into nutrient broth (Vogels broth). After placing a DMSO solution of test compound into a 96-well microtiter plate at an application rate of 200ppm, the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was determined photometrically 3-4 days after application.

The following compounds 1, 2, 3, 4, 5, 6, 7, 8, 9, 11, 12, 13, 14, 15, 17, 18, 34, 60, 77, 78, 79, 88, 89, 96, 97, 101, 105, 108, 110 and 111 at 200 ppm give at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development.

8 *Glomerella lagenarium* (*Colletotrichum lagenarium*) / liquid culture (Anthracnose) :

Conidia of the fungus from cryogenic storage were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a DMSO solution of test compound into a 96-well microtiter plate at an application rate of 200ppm, the nutrient broth containing the fungal spores was added. The test plates

were incubated at 24°C and the inhibition of growth was measured photometrically 3-4 days after application.

The following compounds 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 17, 18, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 51, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 85, 89, 97, 107, 109 and 116 at 200 ppm give at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development.

9 *Mycosphaerella arachidis* (*Cercospora arachidicola*) / liquid culture (early leaf spot):

Conidia of the fungus from cryogenic storage were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a DMSO solution of test compound into a 96-well microtiter plate at an application rate of 200ppm, the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was determined photometrically 4-5 days after application.

The Compounds 1, 2, 3, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 17, 18, 37, 77, 78, 87, 88, 90, 91, 92, 94, 96, 97, 98, 99, 101, 102, 105, 106, 108, 109, 110, 111, 112, 113, 115 and 116 at 200 ppm give at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development

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

Conidia of the fungus from cryogenic storage were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a DMSO solution of test compound into a 96-well microtiter plate at an application rate of 200ppm, the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was determined photometrically 4-5 days after application.

The following compounds 1, 2, 3, 4, 5, 7, 8, 9, 10, 11, 12, 13, 14, 15, 17, 18, 22, 24, 29, 30, 31, 32, 34, 35, 37, 39, 40, 42, 43, 44, 45, 48, 49, 51, 53, 54, 55, 56, 58, 60, 61, 62, 64, 66, 67, 69, 71, 75, 76, 77, 78, 88, 90, 99, 102, 105, 111, 113 and 115 at 200 ppm give at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development.

11 *Gaeumannomyces graminis* / liquid culture (Take-all of cereals):

Mycelial fragments of the fungus from cryogenic storage were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a DMSO solution of test compound into a 96-well microtiter plate at an application rate of 200ppm, the nutrient broth Cp.33, containing the fungal spores is added. The test plates were incubated at 24°C and the inhibition of growth was determined photometrically 4-5 days after application.

The following compounds 1, 2, 3, 5, 8, 9, 10, 11, 12, 13, 14, 15, 17, 18, 19, 20, 21, 29, 31, 32, 37, 43, 51, 53, 54, 55, 56, 60, 61, 62, 64, 66, 71, 73, 76, 77, 78, 85, 86, 87, 88, 92, 94, 98, 99, 102, 106, 110 and 111 at 200 ppm give at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development.

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

Conidia of the fungus from cryogenic storage were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a DMSO solution of test compound into a 96-well microtiter plate at an application rate of 200ppm, the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was determined photometrically 4-5 days after application.

The following compounds 1, 2, 3, 4, 5, 7, 8, 9, 10, 11, 12, 13, 14, 15, 17, 18, 24, 30, 31, 32, 37, 42, 43, 48, 49, 53, 54, 55, 56, 57, 58, 60, 61, 62, 63, 64, 66, 71, 73, 75, 76, 77, 78, 87, 88, 89, 90, 91, 92, 94, 97, 98, 99, 101, 102, 105, 106, 107, 108, 109, 110, 111, 113 and 115 at 200 ppm give at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development.

13 *Fusarium culmorum* / liquid culture (Head blight):

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

The following compounds 2, 3 and 14 at 200 ppm give at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development

14 *Thanatephorus cucumeris* (*Rhizoctonia solani*) / liquid culture (foot rot, damping-off):

Mycelia fragments of a newly grown liquid culture of the fungus were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a DMSO solution of the test compounds into a 96-well microtiter plate at an application rate of 200ppm, the nutrient broth containing the fungal material was added. The test plates were incubated at 24°C and the inhibition of growth was determined photometrically 3-4 days after application.

The following compounds 2, 9, 12, 13, 14, 15, 77, 78, 88, 90, 99, 102, 108, 110, 113 and 116 at 200 ppm give at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development

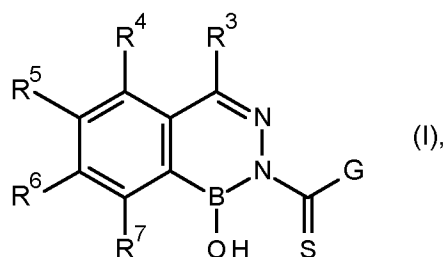
15 *Sclerotinia sclerotiorum* / liquid culture (cottony rot) :

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

The following compounds 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 17, 18, 19, 21, 22, 23, 24, 27, 28, 29, 30, 31, 32, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 48, 49, 53, 54, 55, 56, 57, 58, 61, 62, 63, 64, 65, 66, 67, 69, 71, 72, 73, 74, 75, 76, 77, 78, 87, 89, 91, 92, 97, 98, 99, 102, 105, 109, 111 and 113 at 200 ppm give at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development.

Claims:

1. A method for controlling or preventing fungal 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 with an effective amount of an diazaborine of general formula (I)

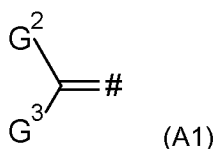


wherein

G = N(R¹R²), SCH₃

R¹ is H, C₁-C₈alkyl or C₁-C₈alkyl substituted by one to five Z, C₁-C₈alkenyl or C₁-C₈alkenyl substituted by one to five Z, C₃-C₁₀cycloalkyl or C₃-C₁₀cycloalkyl substituted by one to five Y, aryl-C₁-C₄alkylene- or aryl-C₁-C₄alkylene- wherein the aryl moiety is substituted by one to five Y, heterocyclyl-C₁-C₄alkylene- or heterocyclyl-C₁-C₄alkylene- wherein the heterocyclyl moiety is substituted by one to five Y, aryl-(W)- or aryl-(W)- wherein the aryl moiety is substituted by one to five Y, heterocyclyl-(W)- or heterocyclyl-(W)- wherein the heterocyclyl moiety is substituted by one to five Y, aryl or aryl substituted by one to five Y, heterocyclyl or heterocyclyl substituted by one to five Y, C₁-C₈alkylaminocarbonyl-C₁-C₄ alkylene, C₁-C₈haloalkylaminocarbonyl-C₁-C₄ alkylene, C₃-C₈cycloalkylaminocarbonyl-C₁-C₄ alkylene, C₁-C₈alkylaminocarbonyl-, C₁-C₈haloalkylaminocarbonyl, C₃-C₈cycloalkylaminocarbonyl, C₁-C₆alkyl-O-N=CH-, C₁-C₆haloalkyl-O-N=CH-;

R² is hydrogen, C₁-C₆alkyl, C₁-C₆alkoxy-, C₁-C₆alkylcarbonyl-, or C₁-C₆alkoxycarbonyl-; or when G=N(R² R¹), R¹ and R² together can also form a ring or can represent group A1



G² is O(R⁸), N(R⁹)(R¹⁰) or S(R¹¹);

G³ is N(R¹²)(R¹³) or S(R¹⁴);

R³ = H, halogen, cyano, nitro, formyl, C₁-C₆alkyl, alkenyl, alkynyl and aryl

R⁴, R⁵, R⁶ and R⁷ is independently hydrogen, halogen, cyano, nitro, hydroxy, amino, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkenyl, C₁-C₆alkynyl or two neighbored substituents R⁴, R⁵, R⁶ and R⁷ form a -O- C₁-C₄alkyl-O- ring together with the carbon atoms to which they are attached;

each Z is independently halogen, cyano, nitro, hydroxy, amino, C₁-C₈alkylamino, (C₁-C₈alkyl)₂amino, C₁-C₈alkylcarbonylamino, C₁-C₈haloalkylcarbonylamino, C₁-C₈alkoxy-, C₁-C₈haloalkoxy-, aryloxy or aryloxy substituted by one to five M, C₁-C₈alkylcarbonyl-, C₁-C₈alkoxycarbonyl-, mercapto, C₁-C₈alkylthio-, C₁-C₈haloalkylthio-, C₁-C₈alkylsulfinyl-, C₁-C₈haloalkylsulfinyl-, C₁-C₈alkylsulfonyl-, C₁-C₈haloalkylsulfonyl-, aryl-C₁-C₄alkylthio or aryl-C₁-C₄alkylthio wherein the aryl moiety is substituted by one to five M; C₃-C₇ aliphatic and aromatic carbocycle or C₃-C₇ aliphatic and aromatic carbocycle wherein the carbocycle is substituted by one to five M, 3 to 7 membered heterocycles containing 1-3 heteroatoms selected from N, O, S, wherein the heterocycle can be optionally substituted by M;

each Y is independently halogen, cyano, nitro, oxo, hydroxy, C₁-C₈alkyl, C₁-C₈haloalkyl, C₁-C₈cyanoalkyl, C₂-C₈alkenyl, C₂-C₈haloalkenyl, C₂-C₈alkynyl, C₂-C₈haloalkynyl, C₃-C₁₀cycloalkyl, C₁-C₈alkoxy-, C₁-C₈haloalkoxy-, mercapto, C₁-C₈alkylthio-, C₁-C₈haloalkylthio-, C₁-C₈alkylsulfinyl-, C₁-C₈haloalkylsulfinyl-, C₁-C₈alkylsulfonyl-, C₁-C₈haloalkylsulfonyl-, C₁-C₈alkylaminosulfonyl-, (C₁-C₈alkyl)₂aminosulfonyl-, C₁-C₈alkylcarbonyl-, C₁-C₈alkoxycarbonyl-, aryl or aryl substituted by one to five M, heterocyclyl or heterocyclyl substituted by one to five M, aryl-C₁-C₄alkylene or aryl-C₁-C₄alkylene wherein the aryl moiety is substituted by one to five M, heterocyclyl-C₁-C₄alkylene or heterocyclyl-C₁-C₄alkylene wherein the heterocyclyl moiety is substituted by one to five M, aryloxy or aryloxy substituted by one to five M, aryloxy-C₁-C₄alkylene or aryloxy-C₁-C₄alkylene wherein the aryl moiety is substituted by one to five M;

each M is independently halogen, cyano, nitro, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy-, or C₁-C₄haloalkoxy, substituted or unsubstituted aralkyl -;

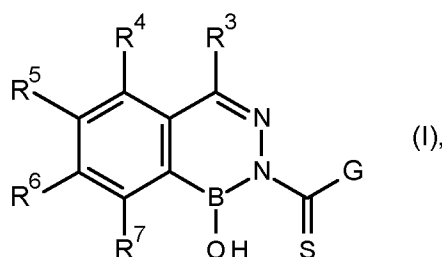
R⁸, R¹¹ and R¹⁴ are independently C₁-C₄ alkyl;

R⁹, R¹⁰, R¹², and R¹³ are independently hydrogen or C₁-C₄ alkyl;

W is hydrogen or C₁-C₄ alkyl

and agronomically acceptable salts, stereoisomers, diastereoisomers, enantiomers, tautomers, atropisomers and N-oxides of those compounds.

2. Compounds of formula (I) compounds of formula (I)



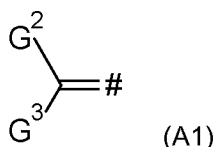
wherein

G = N(R¹R²), SCH₃

R¹ is H, C₁-C₈alkyl or C₁-C₈alkyl substituted by one to five Z, C₁-C₈alkenyl or C₁-C₈alkenyl substituted by one to five Z, C₃-C₁₀cycloalkyl or C₃-C₁₀cycloalkyl substituted by one to five Y, aryl-C₁-C₄alkylene- or aryl-C₁-C₄alkylene- wherein the aryl moiety is substituted by one to five Y, heterocyclyl-C₁-

C₄alkylene- or heterocyclyl-C₁-C₄alkylene- wherein the heterocyclyl moiety is substituted by one to five Y, aryl- (W)- or aryl-(W)- wherein the aryl moiety is substituted by one to five Y, heterocyclyl- (W)- or heterocyclyl-(W)- wherein the heterocyclyl moiety is substituted by one to five Y, aryl or aryl substituted by one to five Y, heterocyclyl or heterocyclyl substituted by one to five Y, C₁-C₈alkylaminocarbonyl-C₁-C₄ alkylene, C₁-C₈haloalkylaminocarbonyl-C₁-C₄ alkylene, C₃-C₈cycloalkylaminocarbonyl-C₁-C₄ alkylene, C₁-C₈alkylaminocarbonyl-, C₁-C₈haloalkylaminocarbonyl-, C₃-C₈cycloalkylaminocarbonyl-, C₁-C₆alkyl-O-N=CH-, C₁-C₆haloalkyl-O-N=CH-;

R² is hydrogen, C₁-C₆alkyl, C₁-C₆alkoxy-, C₁-C₆alkylcarbonyl-, or C₁-C₆alkoxycarbonyl-; or when G=N(R² R¹), R¹ and R² together can also form a ring or can represent group A1



G² is O(R⁸), N(R⁹)(R¹⁰) or S(R¹¹);

G³ is N(R¹²)(R¹³) or S(R¹⁴);

R³= H, halogen, C₁-C₆alkyl, aryl

R⁴, R⁵, R⁶ and R⁷ is independently halogen, cyano, nitro, hydroxy, amino, alkyl, haloalkyl, alkoxy, haloalkoxy, alkenyl, alkynyl, provided that at least one of R⁴, R⁵, R⁶ and R⁷ is not a hydrogen; or two neighbored substituents R⁴, R⁵, R⁶ and R⁷ form a -O- C₁-C₄alkyl-O- ring together with the carbon atoms to which they are attached;

each Z is independently halogen, cyano, nitro, hydroxy, amino, C₁-C₈alkylamino, (C₁-C₈alkyl)₂amino, C₁-C₈alkylcarbonylamino, C₁-C₈haloalkylcarbonylamino, C₁-C₈alkoxy-, C₁-C₈haloalkoxy-, aryloxy or aryloxy substituted by one to five M, C₁-C₈alkylcarbonyl-, C₁-C₈alkoxycarbonyl-, mercapto, C₁-C₈alkylthio-, C₁-C₈haloalkylthio-, C₁-C₈alkylsulfinyl-, C₁-C₈haloalkylsulfinyl-, C₁-C₈alkylsulfonyl-, C₁-C₈haloalkylsulfonyl-, aryl-C₁-C₄alkylthio or aryl-C₁-C₄alkylthio wherein the aryl moiety is substituted by one to five M; C₃-C₇ aliphatic and aromatic carbocycle or C₃-C₇ aliphatic and aromatic carbocycle wherein the carbocycle is substituted by one to five M, 3 to 7 membered heterocycles containing 1-3 heteroatoms selected from N, O, S, wherein the heterocycle can be optionally substituted by M;

each Y is independently halogen, cyano, nitro, oxo, hydroxy, C₁-C₈alkyl, C₁-C₈haloalkyl, C₁-C₈cyanoalkyl, C₂-C₈alkenyl, C₂-C₈haloalkenyl, C₂-C₈alkynyl, C₂-C₈haloalkynyl, C₃-C₁₀cycloalkyl, C₁-C₈alkoxy-, C₁-C₈haloalkoxy-, mercapto, C₁-C₈alkylthio-, C₁-C₈haloalkylthio-, C₁-C₈alkylsulfinyl-, C₁-C₈haloalkylsulfinyl-, C₁-C₈alkylsulfonyl-, C₁-C₈haloalkylsulfonyl-, C₁-C₈alkylaminosulfonyl-, (C₁-C₈alkyl)₂aminosulfonyl-, C₁-C₈alkylcarbonyl-, C₁-C₈alkoxycarbonyl-, aryl or aryl substituted by one to five M, heterocyclyl or heterocyclyl substituted by one to five M, aryl-C₁-C₄alkylene or aryl-C₁-C₄alkylene wherein the aryl moiety is substituted by one to five M, heterocyclyl-C₁-C₄alkylene or heterocyclyl-C₁-C₄alkylene wherein the heterocyclyl moiety is substituted by one to five M, aryloxy or

aryloxy substituted by one to five M, aryloxy-C₁-C₄alkylene or aryloxy-C₁-C₄alkylene wherein the aryl moiety is substituted by one to five M;

each M is independently halogen, cyano, nitro, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy-, or C₁-C₄haloalkoxy, substituted or unsubstituted aralkyl -;

R⁸, R¹¹ and R¹⁴ are independently C₁-C₄ alkyl;

R⁹, R¹⁰, R¹², and R¹³ are independently hydrogen or C₁-C₄ alkyl;

W is hydrogen or C₁-C₄ alkyl

and agronomically acceptable salts, stereoisomers, diastereoisomers, enantiomers, tautomers, atropisomers and N-oxides of those compounds.

3. Compounds of formula (I) according to claim 1 or 2 characterized in that

G= N(R¹R²),

4. Compounds of formula (I) according to claim 1 or 2 characterized in that

R¹ is H, C₁-C₈alkyl or C₁-C₈alkyl substituted by one to five Z, C₁-C₈alkenyl or C₁-C₈alkenyl substituted by one to five Z, C₃-C₁₀cycloalkyl or C₃-C₁₀cycloalkyl substituted by one to five Y, aryl-C₁-C₄alkylene- or aryl-C₁-C₄alkylene- wherein the aryl moiety is substituted by one to five Y, heterocycl-C₁-C₄alkylene-

or heterocycl-C₁-C₄alkylene- wherein the heterocycl moiety is substituted by one to five Y, aryl-(W)- or aryl-(W)- wherein the aryl moiety is substituted by one to five Y, heterocycl-(W)- or heterocycl-(W)- wherein the heterocycl moiety is substituted by one to five Y, aryl or aryl substituted by one to five Y, heterocycl or heterocycl substituted by one to five Y, C₁-C₈alkylaminocarbonyl-C₁-C₄ alkylene, C₁-C₈haloalkylaminocarbonyl-C₁-C₄ alkylene, C₃-C₈cycloalkylaminocarbonyl-C₁-C₄ alkylene, C₁-C₈alkylaminocarbonyl-, C₁-C₈haloalkylaminocarbonyl, C₃-C₈cycloalkylaminocarbonyl, C₁-C₆alkyl-O-N=CH-, C₁-C₆haloalkyl-O-N=CH-;

5. Compounds of formula (I) according to claim 1 characterized in that the

R² is hydrogen, C₁-C₆alkyl, C₁-C₆alkoxy-, C₁-C₆alkylcarbonyl-, or C₁-C₆alkoxycarbonyl-;

6. Compounds of formula (I) according to claim 1 characterized in that

R³= H, halogen, C₁-C₆alkyl, aryl

7. Compounds of formula (I) according to claim 1 characterized in that

R³= H, halogen, C₁-C₆alkyl

8. A method of controlling or preventing infestation of useful plants by phytopathogenic

microorganisms, wherein a compound of formula (I) as defined in claim 1 or 2 or a composition comprising a compound of formula (I) as defined in claim 1 or 2 as active ingredient, is applied to the plants, to parts thereof or the locus thereof.

9. A composition for controlling and protecting against phytopathogenic microorganisms, comprising a compound of formula (I) as defined in claim 1 or 2 and at least one auxiliary.
10. A method of controlling phytopathogenic diseases on useful plants or plant propagation material thereof, which comprises applying to said plant propagation material a fungicidally effective amount of a plant propagation material protecting composition comprising a compound of formula (I) as defined in claim 1 or 2, together with a suitable carrier therefor.
11. A composition comprising a fungicidally effective amount of a compound of formula (I) as defined in claim 1 or 2, optionally comprising at least one additional active ingredient.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2014/057457

A. CLASSIFICATION OF SUBJECT MATTER

INV. A01P3/00 A01N43/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JUSTIN W. HICKS ET AL: "Synthesis, Characterization, and Antifungal Activity of Boron-Containing Thiosemicarbazones", CHEMISTRY & BIODIVERSITY, vol. 5, no. 11, 1 November 2008 (2008-11-01), pages 2415-2422, XP055086930, ISSN: 1612-1872, DOI: 10.1002/cbdv.200890206 table 2 ----- -/--	1-11



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier 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

26 May 2014

Date of mailing of the international search report

03/06/2014

Name and mailing address of the ISA/

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Authorized officer

Davies, Maxwell

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/057457

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ALISON M. IRVING ET AL: "Synthesis and antifungal and antibacterial bioactivity of cyclic diamines containing boronate esters", NEW JOURNAL OF CHEMISTRY, vol. 27, no. 10, 1 January 2003 (2003-01-01), page 1419, XP055120162, ISSN: 1144-0546, DOI: 10.1039/b304500e the whole document -----	1-11