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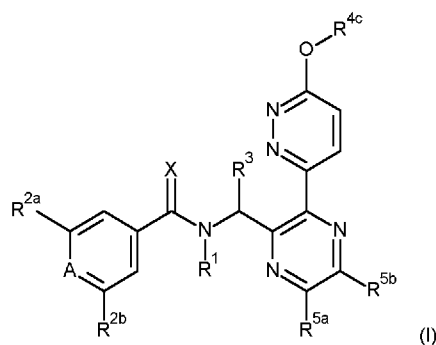
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(54) Title: PESTICIDALLY ACTIVE PYRIDAZINE COMPOUNDS

(57) Abstract: Compounds of formula (I) wherein the substituents are as defined in claim 1, and the agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of those compounds, can be used as insecticides.



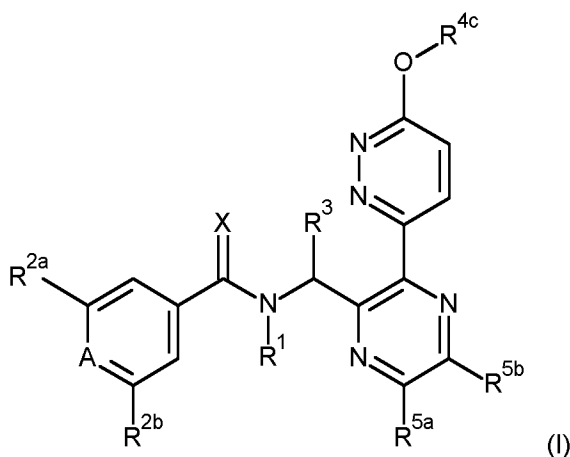
PESTICIDALLY ACTIVE PYRIDAZINE COMPOUNDS

The present invention relates to pesticidally active pyridazine compounds, e.g. as active ingredients, which have pesticidal activity. The invention also relates to preparation of these pyridazine compounds, to intermediates useful in the preparation of these pyridazine compounds, to the preparation of these intermediates, to agrochemical compositions which comprise at least one of these pyridazine compounds, to preparation of these compositions and to the use of these pyridazine compounds or compositions in agriculture or horticulture for controlling animal pests, including arthropods and in particular insects, or representatives of the order *Acarina*. In particular, pesticidally active 3-oxy pyridazine compounds are disclosed herein.

WO2021069575, WO2021068179, WO2020208036, WO2020201079, WO2020201398 and WO2020070049 describe pesticidally active pyrazine-amide compounds.

It has now surprisingly been found that certain novel pyridazine compounds have pesticidal activity.

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



wherein:

A is N or CR<sup>Y</sup>;

R<sup>1</sup> is hydrogen, C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>cyanoalkyl, aminocarbonylC<sub>1</sub>-C<sub>6</sub>alkyl, hydroxycarbonylC<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>nitroalkyl, trimethylsilaneC<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy-C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>haloalkyl, C<sub>2</sub>-C<sub>6</sub>alkenyl, C<sub>2</sub>-C<sub>6</sub>haloalkenyl, C<sub>2</sub>-C<sub>6</sub>alkynyl, C<sub>2</sub>-C<sub>6</sub>haloalkynyl, C<sub>3</sub>-C<sub>4</sub>cycloalkyl-C<sub>1</sub>-C<sub>2</sub>alkyl, C<sub>3</sub>-C<sub>4</sub>cycloalkyl-C<sub>1</sub>-C<sub>2</sub>alkyl wherein the C<sub>3</sub>-C<sub>4</sub>cycloalkyl group is substituted with 1 or 2 halogen atoms, oxetan-3-yl-CH<sub>2</sub>-, C<sub>1</sub>-C<sub>6</sub>alkylcarbonyl, C<sub>1</sub>-C<sub>6</sub>alkoxycarbonyl, phenyloxycarbonyl, benzyloxycarbonyl, benzyl, or benzyl substituted with 1 to 3 substituents independently selected from halogen, C<sub>1</sub>-C<sub>6</sub>alkoxy and C<sub>1</sub>-C<sub>6</sub>haloalkyl;

R<sup>2a</sup> and R<sup>2b</sup> are independently selected from hydrogen, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>haloalkylsufanyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, C<sub>1</sub>-C<sub>3</sub>haloalkoxy, halogen, NO<sub>2</sub>, SF<sub>5</sub>, CN, C(O)NH<sub>2</sub>, C(O)OH, C(S)NH<sub>2</sub>, C<sub>3</sub>-C<sub>6</sub>cycloalkyl, C<sub>3</sub>-C<sub>6</sub>cycloalkyl substituted with one to three substituents independently selected from R<sup>X</sup>; C<sub>3</sub>-C<sub>6</sub>cycloalkylcarbonyl, phenyl, phenyl substituted with one to three substituents independently selected from R<sup>X</sup>; heteroaryl, heteroaryl substituted with one to three substituents

independently selected from  $R^X$ ;  $OR^6$ , piperidin-2-one-1-yl, piperidin-2-one-1-yl substituted with one to two substituents independently selected from  $R^X$ ; pyridin-2-one-1-yl, pyridin-2-one-1-yl substituted with one to two substituents independently selected from  $R^X$ ; azetidin-1-yl, azetidin-1-yl substituted with one to two substituents independently selected from  $R^X$ ; pyrrolidin-1-yl, pyrrolidin-1-yl substituted with one to two substituents independently selected from  $R^X$ ;  $C_3$ - $C_6$ cycloalkyl- $C_1$ - $C_4$ alkyl,  $C_3$ - $C_6$ cycloalkyl- $C_1$ - $C_4$ alkyl substituted with one to two substituents independently selected from  $R^Z$ ;  $C_3$ - $C_6$ cycloalkyl- $C_1$ - $C_3$ alkoxy,  $C_3$ - $C_6$ cycloalkyl- $C_1$ - $C_3$ alkoxy substituted with one to two substituents independently selected from  $R^X$ ;  $C_1$ - $C_5$ cyanoalkyl,  $C_1$ - $C_5$ cyanoalkoxy,  $C_1$ - $C_4$ alkylsulfanyl,  $C_1$ - $C_4$ alkylsulfanyl substituted with one to three substituents independently selected from  $R^X$ ;  $C_1$ - $C_4$ alkylsulfonyl,  $C_1$ - $C_4$ alkylsulfonyl substituted with one to three substituents independently selected from  $R^X$ ;  $C_1$ - $C_4$ alkylsulfinyl, and  $C_1$ - $C_4$ alkylsulfinyl substituted with one to three substituents independently selected from  $R^X$ ;

$R^3$  is  $C_1$ - $C_3$ alkyl or  $C_1$ - $C_3$ haloalkyl;

$R^{4c}$  is hydrogen,  $C_1$ - $C_3$ alkyl optionally substituted with a single substituent selected from cyano,  $C_1$ - $C_3$ alkylsulfanyl,  $C_1$ - $C_3$ alkylsulfinyl,  $C_1$ - $C_3$ alkylsulfonyl, and  $-C(O)NR^{4d}R^{4e}$ ;  $C_1$ - $C_3$ haloalkyl, allyl, propargyl,  $C_3$ - $C_6$ cycloalkyl- $C_1$ - $C_4$ alkyl,  $C_1$ - $C_2$ alkoxy- $C_1$ - $C_3$ alkyl,  $-C(O)NR^{4d}R^{4e}$ ,  $-N=CR^{4f}R^{4g}$ , or benzyl optionally substituted with 1 to 3 substituents independently selected from halogen, cyano,  $C_1$ - $C_3$ alkyl,  $C_1$ - $C_3$ haloalkyl,  $C_1$ - $C_3$ alkoxy, and  $C_3$ - $C_4$ cycloalkyl; or

$R^{4c}$  is heteroaryl-methyl, where said heteroaryl group is optionally substituted with 1 to 3 substituents independently selected from halogen, cyano,  $C_1$ - $C_3$ alkyl,  $C_1$ - $C_3$ haloalkyl,  $C_1$ - $C_3$ alkoxy, and  $C_3$ - $C_4$ cycloalkyl; or

$R^{4c}$  is  $-C(O)C_1$ - $C_6$ alkyl, or  $-C(O)OC_1$ - $C_6$ alkyl, each optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, and  $C_1$ - $C_3$ alkoxy;

$R^{4d}$  and  $R^{4e}$  are independently hydrogen, or  $C_1$ - $C_5$ alkyl optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, and  $C_1$ - $C_3$ alkoxy;

$R^{4f}$  and  $R^{4g}$  are independently  $C_1$ - $C_3$ alkyl, or  $R^{4f}$  and  $R^{4g}$  form, together with the carbon atom they are attached to, a  $C_4$ - $C_6$ cycloalkyl or a 4- to 6-membered saturated heterocycle containing one oxygen atom;

$R^{5a}$  and  $R^{5b}$  are, independently of each other, selected from hydrogen, halogen,  $-CN$ ,  $C_1$ - $C_3$ alkyl,  $C_1$ - $C_3$ haloalkyl,  $C_3$ - $C_4$ cycloalkyl,  $C_1$ - $C_3$ alkoxy, and  $C_1$ - $C_3$ haloalkoxy;

$R^6$  is phenyl, benzyl, heteroaryl, or  $C_3$ - $C_6$ cycloalkyl; or

$R^6$  is phenyl, benzyl, heteroaryl, or  $C_3$ - $C_6$ cycloalkyl, each of which, independently of each other, is substituted with one to three substituents independently selected from  $R^X$ ;

$R^X$  is independently selected from halogen,  $C_1$ - $C_3$ alkyl,  $C_1$ - $C_3$ haloalkyl,  $C_1$ - $C_3$ alkoxy,  $C_1$ - $C_3$ haloalkoxy,  $NO_2$ ,  $SF_5$ ,  $CN$ ,  $-C(O)NH_2$ ,  $-C(S)NH_2$ ,  $C_1$ - $C_4$ haloalkylsulfanyl,  $C_1$ - $C_4$ haloalkylsulfinyl,  $C_1$ - $C_4$ haloalkylsulfonyl,  $C_1$ - $C_4$ alkylsulfanyl,  $C_1$ - $C_4$ alkylsulfinyl and  $C_1$ - $C_4$ alkylsulfonyl;

$R^Y$  is selected from hydrogen,  $C_1$ - $C_3$ alkyl,  $C_1$ - $C_3$ haloalkyl, hydroxy,  $C_1$ - $C_3$ alkoxy,  $C_1$ - $C_3$ haloalkoxy, halogen,  $-CN$  and cyclopropyl;

$R^Z$  is selected from oxo, halogen,  $C_1$ - $C_3$ alkyl,  $C_1$ - $C_3$ haloalkyl,  $C_1$ - $C_3$ alkoxy,  $C_1$ - $C_3$ haloalkoxy and  $CN$ ;

X is O or S;

and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers, and N-oxides of the compound of formula (I).

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

          In a second aspect, the present invention makes available a composition comprising a compound of formula (I), one or more auxiliaries and diluent, and optionally one or more other active ingredient.

10           In a third aspect, the present invention makes available a method of combating and controlling insects, acarines, nematodes or molluscs, which method comprises applying to a pest, to a locus of a pest, or to a plant susceptible to attack by a pest an insecticidally, acaricidally, nematocidally or molluscicidally effective amount of a compound of formula (I) or a composition comprising such a compound.

15           In a fourth aspect, the present invention makes available a method for the protection of plant propagation material from the attack by insects, acarines, nematodes or molluscs, which method comprises treating the propagation material, or the site where the propagation material is planted, with an effective amount of a compound of formula (I) or a composition comprising such a compound.

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

20           The present invention in a further aspect provides a method of controlling parasites in or on an animal in need thereof comprising administering an effective amount of a compound of the first aspect. The present invention further provides a method of controlling ectoparasites on an animal in need thereof comprising administering an effective amount of a compound of formula (I) as defined in the first aspect. The present invention further provides a method for preventing and/or treating diseases transmitted by ectoparasites comprising administering an effective amount of a compound of formula (I) as defined in the first aspect, to an animal in need thereof.

          Compounds of formula (I) which have at least one basic centre can form, for example, acid addition salts, for example with strong inorganic acids such as mineral acids, for example perchloric acid, sulfuric acid, nitric acid, nitrous acid, a phosphorus acid or a hydrohalic acid, with strong organic carboxylic acids, such as C<sub>1</sub>-C<sub>4</sub>alkanecarboxylic acids which are unsubstituted or substituted, for example by halogen, for example acetic acid, such as saturated or unsaturated dicarboxylic acids, for example oxalic acid, malonic acid, succinic acid, maleic acid, fumaric acid or phthalic acid, such as hydroxycarboxylic acids, for example ascorbic acid, lactic acid, malic acid, tartaric acid or citric acid, or such as benzoic acid, or with organic sulfonic acids, such as C<sub>1</sub>-C<sub>4</sub>alkane- or arylsulfonic acids which are unsubstituted or substituted, for example by halogen, for example methane- or p-toluenesulfonic acid. Compounds of formula (I) which have at least one acidic group can form, for example, salts with bases, for example mineral salts such as alkali metal or alkaline earth metal salts, for example sodium,

potassium or magnesium salts, or salts with ammonia or an organic amine, such as morpholine, piperidine, pyrrolidine, a mono-, di- or tri-lower-alkylamine, for example ethyl-, diethyl-, triethyl- or dimethylpropylamine, or a mono-, di- or trihydroxy-lower-alkylamine, for example mono-, di- or triethanolamine.

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

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

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

The term "C<sub>1</sub>-C<sub>n</sub>alkyl" as used herein refers to a saturated straight-chain or branched hydrocarbon radical attached via any of the carbon atoms having 1 to n carbon atoms, for example, any one of the radicals methyl, ethyl, n-propyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2, 2-dimethylpropyl, 1-ethylpropyl, n-hexyl, n-pentyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 15 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methylpropyl or 1-ethyl-2-methylpropyl.

The term "C<sub>1</sub>-C<sub>n</sub>haloalkyl" as used herein refers to a straight-chain or branched saturated alkyl radical attached via any of the carbon atoms having 1 to n carbon atoms (as mentioned above), where some or all of the hydrogen atoms in these radicals may be replaced by fluorine, chlorine, bromine and/or iodine, i.e., for example, any one of chloromethyl, dichloromethyl, trichloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, chlorofluoromethyl, dichlorofluoromethyl, chlorodifluoromethyl, 2-fluoroethyl, 2-chloroethyl, 2-bromoethyl, 2-iodoethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2-chloro-2-fluoroethyl, 2-chloro-2,2-difluoroethyl, 2,2-dichloro-2-fluoroethyl, 2,2,2-trichloroethyl, pentafluoroethyl, 2-fluoropropyl, 3-fluoropropyl, 2,2-difluoropropyl, 2,3-difluoropropyl, 2-chloropropyl, 3-chloropropyl, 2,3-dichloropropyl, 2-bromopropyl, 3-bromopropyl, 3,3,3-trifluoropropyl, 3,3,3-trichloropropyl, 2,2,3,3,3-pentafluoropropyl, heptafluoropropyl, 1-(fluoromethyl)-2-fluoroethyl, 1-(chloromethyl)-2-chloroethyl, 1-(bromomethyl)-2-bromoethyl, 4-fluorobutyl, 4-chlorobutyl, 4-bromobutyl or nonafluorobutyl. Accordingly, 25 a term "C<sub>1</sub>-C<sub>2</sub>fluoroalkyl" would refer to a C<sub>1</sub>-C<sub>2</sub>alkyl radical which carries 1, 2, 3, 4 or 5 fluorine atoms, for example, any one of difluoromethyl, trifluoromethyl, 1-fluoroethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 1,1,2,2-tetrafluoroethyl or pentafluoroethyl.

The term "C<sub>1</sub>-C<sub>n</sub>alkoxy" as used herein refers to a straight-chain or branched saturated alkyl radical having 1 to n carbon atoms (as mentioned above) which is attached via an oxygen atom, i.e., for 35 example, any one of the radicals methoxy, ethoxy, n-propoxy, 1-methylethoxy, n-butoxy, 1-methylpropoxy, 2-methylpropoxy or 1,1-dimethylethoxy. The term "C<sub>1</sub>-C<sub>n</sub>haloalkoxy" as used herein refers to a C<sub>1</sub>-C<sub>n</sub>alkoxy radical where one or more hydrogen atoms on the alkyl radical is replaced by the same or different halo atom(s) - examples include trifluoromethoxy, 2-fluoroethoxy, 3-fluoropropoxy, 3,3,3-trifluoropropoxy, 4-chlorobutoxy.

The term "C<sub>1</sub>-C<sub>n</sub>alkoxyC<sub>1</sub>-C<sub>m</sub>alkyl" as used herein refers to an alkoxy radical having 1 to n carbon atoms (as mentioned above) which is attached via the oxygen atom to an alkyl radical having 1 to m carbon atoms (as mentioned above), which alkyl radical is connected to the rest of the molecule.

5 The term "C<sub>1</sub>-C<sub>n</sub>cyanoalkyl" as used herein refers to a straight chain or branched saturated C<sub>1</sub>-C<sub>n</sub>alkyl radical having 1 to n carbon atoms (as mentioned above), where one of the hydrogen atoms in these radicals is replaced by a cyano group -CN: for example, cyanomethyl, 2-cyanoethyl, 2-cyanopropyl, 3-cyanopropyl, 1-(cyanomethyl)-2-ethyl, 1-(methyl)-2-cyanoethyl, 4-cyanobutyl, and the like.

10 The term "C<sub>1</sub>-C<sub>n</sub>nitroalkyl" as used herein refers to a straight chain or branched saturated C<sub>1</sub>-C<sub>n</sub>alkyl radical having 1 to n carbon atoms (as mentioned above), where one of the hydrogen atoms in these radicals is replaced by a nitro group -NO<sub>2</sub>: for example, nitromethyl, 2-nitroethyl, 2-nitropropyl, 3-nitropropyl, 1-(nitromethyl)-2-ethyl, 1-(methyl)-2-nitroethyl, 4-nitrobutyl, and the like.

The term "C<sub>3</sub>-C<sub>n</sub>cycloalkyl" as used herein refers to 3-n membered cycloalkyl groups such as cyclopropane, cyclobutane, cyclopentane and cyclohexane.

15 The term "C<sub>3</sub>-C<sub>n</sub>cycloalkylcarbonyl" as used herein refers to a 3-n membered cycloalkyl group attached to a carbonyl (C=O) group, which carbonyl group is connected to the rest of the molecule. Similarly the terms "C<sub>1</sub>-C<sub>n</sub>alkylcarbonyl", "C<sub>1</sub>-C<sub>n</sub>alkoxycarbonyl", "phenyloxycarbonyl" and "benzyloxycarbonyl" as used herein refers to an alkyl, alkoxy, phenoxy and benzyloxy group attached to a carbonyl (C=O) group, which carbonyl group is connected to the rest of the molecule.

20 The term "C<sub>3</sub>-C<sub>4</sub>cycloalkylC<sub>1</sub>-C<sub>2</sub>alkyl" as used herein refers to 3 or 4 membered cycloalkyl group with either a methylene or ethylene group, which methylene or ethylene group is connected to the rest of the molecule. In the instance the C<sub>3</sub>-C<sub>4</sub>cycloalkyl-C<sub>1</sub>-C<sub>2</sub>alkyl group is substituted, the substituent(s) can be on the cycloalkyl group and/or on the alkyl group.

25 The term "C<sub>3</sub>-C<sub>6</sub>cycloalkylC<sub>1</sub>-C<sub>4</sub>haloalkoxy" as used herein refers to a 3 to 6 membered cycloalkyl group connected to a 1 to 4 membered haloalkoxy group, which haloalkoxy group is connected to the rest of the molecule.

The term "aminocarbonylC<sub>1</sub>-C<sub>n</sub>alkyl" as used herein refers to an alkyl radical where one of the hydrogen atoms in the radical is replaced by CONH<sub>2</sub> group.

30 The term "hydroxycarbonylC<sub>1</sub>-C<sub>n</sub>alkyl" as used herein refers to an alkyl radical where one of the hydrogen atoms in the radical is replaced by COOH group.

The term "C<sub>1</sub>-C<sub>n</sub>alkylsulfanyl" as used herein refers to a C<sub>1</sub>-C<sub>n</sub>alkyl moiety linked through a sulfur atom. Similarly, the term "C<sub>1</sub>-C<sub>n</sub>haloalkylthio" or "C<sub>1</sub>-C<sub>n</sub>haloalkylsulfanyl" as used herein refers to a C<sub>1</sub>-C<sub>n</sub>haloalkyl moiety linked through a sulfur atom. Similarly, the term "C<sub>3</sub>-C<sub>n</sub>cycloalkylsulfanyl" refers to 3-n membered cycloalkyl moiety linked through a sulfur atom.

35 The term "C<sub>1</sub>-C<sub>n</sub>alkylsulfinyl" as used herein refers to a C<sub>1</sub>-C<sub>n</sub>alkyl moiety linked through the sulfur atom of the S(=O) group. Similarly, the term "C<sub>1</sub>-C<sub>n</sub>haloalkylsulfinyl" as used herein refers to a C<sub>1</sub>-C<sub>n</sub>haloalkyl moiety linked through the sulfur atom of the S(=O) group. Similarly, the term "C<sub>3</sub>-C<sub>n</sub>cycloalkylsulfinyl" refers to 3-n membered cycloalkyl moiety linked through the sulfur atom of the S(=O) group.

The term “C<sub>1</sub>-C<sub>n</sub>alkylsulfonyl” as used herein refers to a C<sub>1</sub>-C<sub>n</sub>alkyl moiety linked through the sulfur atom of the S(=O)<sub>2</sub> group. Similarly, the term “C<sub>1</sub>-C<sub>n</sub>haloalkylsulfonyl” as used herein refers to a C<sub>1</sub>-C<sub>n</sub>haloalkyl moiety linked through the sulfur atom of the S(=O)<sub>2</sub> group. Similarly, the term “C<sub>3</sub>-C<sub>n</sub>cycloalkylsulfonyl” refers to 3-n membered cycloalkyl moiety linked through the sulfur atom of the S(=O)<sub>2</sub> group

The term “trimethylsilaneC<sub>1</sub>-C<sub>n</sub>alkyl” as used herein refers to an alkyl radical where one of the hydrogen atoms in the radical is replaced by a -Si(CH<sub>3</sub>)<sub>3</sub> group.

The term “C<sub>2</sub>-C<sub>n</sub>alkenyl” as used herein refers to a straight or branched alkenyl chain having from two to n carbon atoms and one or two double bonds, for example, ethenyl, prop-1-enyl, but-2-enyl.

The term “C<sub>2</sub>-C<sub>n</sub>haloalkenyl” as used herein refers to a C<sub>2</sub>-C<sub>n</sub>alkenyl moiety substituted with one or more halo atoms which may be the same or different.

The term “C<sub>2</sub>-C<sub>n</sub>alkynyl” as used herein refers to a straight or branched alkynyl chain having from two to n carbon atoms and one triple bond, for example, ethynyl, prop-2-ynyl, but-3-ynyl.

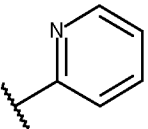
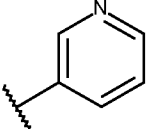
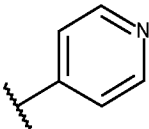
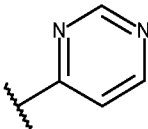
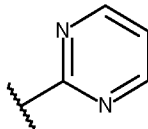
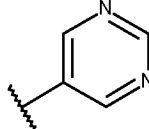
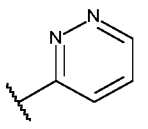
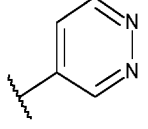
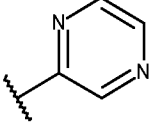
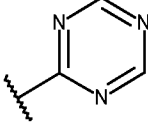
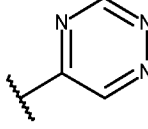
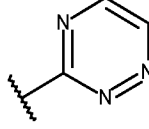
The term “C<sub>2</sub>-C<sub>n</sub>haloalkynyl” as used herein refers to a C<sub>2</sub>-C<sub>n</sub>alkynyl moiety substituted with one or more halo atoms which may be the same or different.

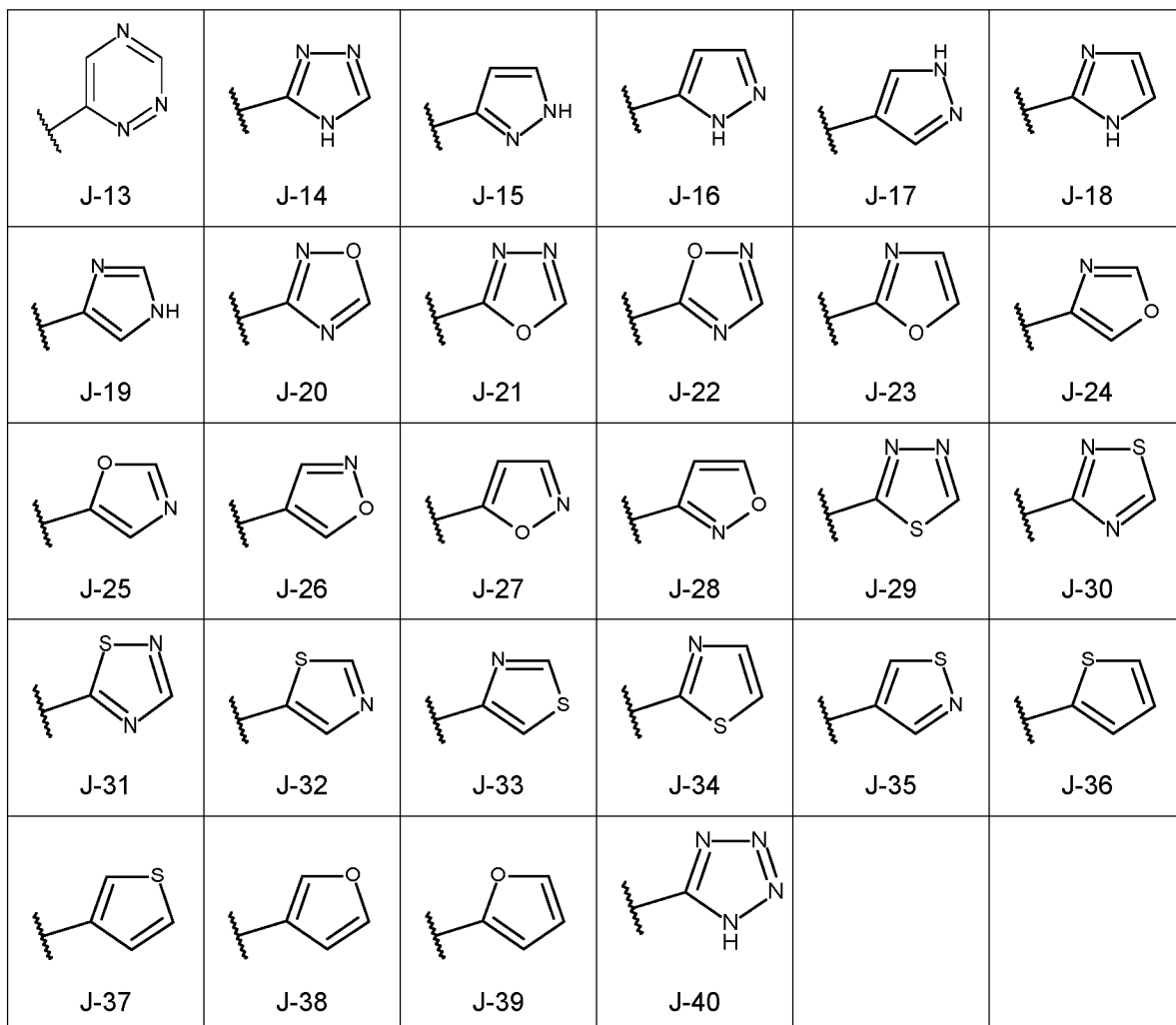
Halogen or “halo” is generally fluorine, chlorine, bromine or iodine. This also applies, correspondingly, to halogen in combination with other meanings, such as haloalkyl.

The term “heteroaryl” as used herein refers to a 5- or 6-membered aromatic monocyclic ring having 1 to 3 heteroatoms independently selected from N, O and S. Examples are heteroaryls J-1 to J-39 shown in Scheme A below. Preferred heteroaryl is pyridyl, pyrimidyl, and pyrazolyl.

The term “heteroaryl-methyl” as used herein refers to a heteroaryl connected to a methyl group, which methyl group is connected to the rest of the molecule. Examples of heteroaryl are shown in Table J below. As used herein, the term “substituted heteroaryl-methyl” refers to a heteroaryl-methyl wherein the heteroaryl group is substituted by a designated substituent. Preferred heteroaryls include J-3 (4-pyridyl) and J-5 (pyrimidin-2-yl).

Table J: Heteroaryl J-1 to J-40:

					
J-1	J-2	J-3	J-4	J-5	J-6
					
J-7	J-8	J-9	J-10	J-11	J-12



The term “optionally substituted” as used herein means that the group referenced is either unsubstituted or is substituted with a designated substituent, for example, “C<sub>3</sub>-C<sub>4</sub>cycloalkyl is optionally substituted with 1 or 2 halo atoms” means C<sub>3</sub>-C<sub>4</sub>cycloalkyl, C<sub>3</sub>-C<sub>4</sub>cycloalkyl substituted with 1 halo atom and C<sub>3</sub>-C<sub>4</sub>cycloalkyl substituted with 2 halo atoms.

The staggered line as used herein, for example, in table J above, or in group T, represent the point of connection / attachment to the rest of the compound.

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

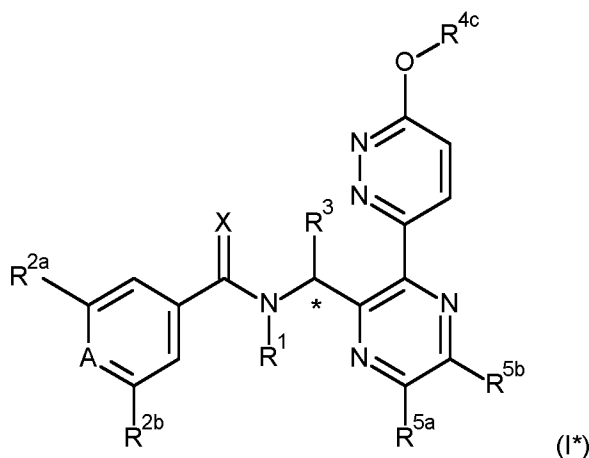
As used herein, the term “pest” refers to insects, and molluscs that are found in agriculture, horticulture, forestry, the storage of products of vegetable origin (such as fruit, grain and timber); and those pests associated with the damage of man-made structures. The term pest encompasses all stages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

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



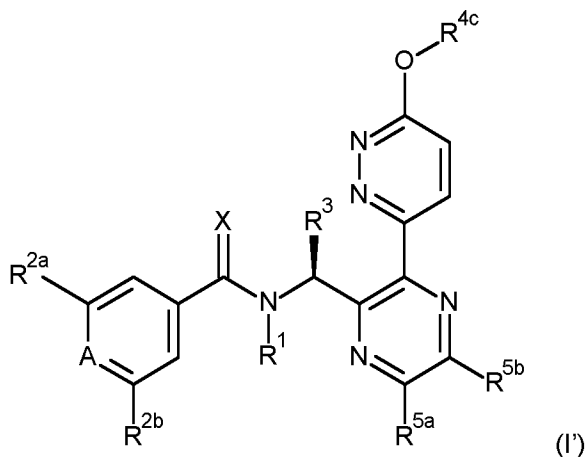
An effective amount is readily determined by the skilled person in the art, by the use of known techniques and by observing results obtained under analogous circumstances. In determining the effective amount a number of factors are considered including, but not limited to: the type of plant or derived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

As one of ordinary skill in the art will appreciate, compounds of formula (I) contain a stereogenic centre which is indicated with an asterisk in the formula (I\*) below:



where A, R<sup>1</sup>, R<sup>2a</sup>, R<sup>2b</sup>, R<sup>3</sup>, R<sup>4c</sup>, R<sup>5a</sup>, R<sup>5b</sup> and X are as defined in the first aspect.

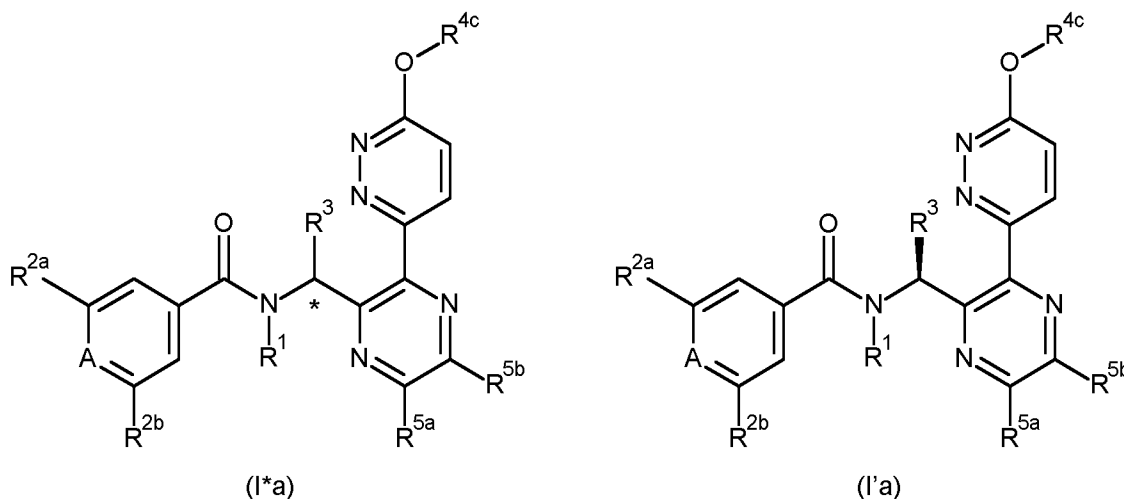
The present invention contemplates both racemates and individual enantiomers. Compounds having preferred stereochemistry are set out below:



Particularly preferred compounds of the present invention are compounds of formula (I') where A, R<sup>1</sup>, R<sup>2a</sup>, R<sup>2b</sup>, R<sup>3</sup>, R<sup>4c</sup>, R<sup>5a</sup>, R<sup>5b</sup> and X are as defined in the first aspect, and stereoisomers, enantiomers, tautomers and N-oxides of the compounds of formula (I'a), and agrochemically acceptable salts thereof.

Preferred compounds of formula (I\*) include compounds of formula (I\*a) as shown below, where X is oxygen, and A, R<sup>1</sup>, R<sup>2a</sup>, R<sup>2b</sup>, R<sup>3</sup>, R<sup>4c</sup>, R<sup>5a</sup>, and R<sup>5b</sup> are as defined in the first aspect, and stereoisomers, enantiomers, tautomers and N-oxides of the compounds of formula (I\*a), and agrochemically acceptable salts thereof.

Particularly preferred compounds of formula (I') include compounds of formula (I'a) as shown below, where X is oxygen, and A, R<sup>1</sup>, R<sup>2a</sup>, R<sup>2b</sup>, R<sup>3</sup>, R<sup>4c</sup>, R<sup>5a</sup>, and R<sup>5b</sup> are as defined in the first aspect, and stereoisomers, enantiomers, tautomers and N-oxides of the compounds of formula (I'a), and agrochemically acceptable salts thereof.



Embodiments according to the invention are provided as set out below.

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

- 10
- A. N; or
  - B. CR<sup>Y</sup>; or
  - C. CH.

In preferred embodiments of each aspect of the invention, A is CH.

15 In an embodiment of each aspect of the invention, X is:

- A. S; or
- B. O.

In preferred embodiments of each aspect of the invention, X is oxygen.

20 In an embodiment of each aspect of the invention, R<sup>1</sup> is

- A. hydrogen, C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>cyanoalkyl, aminocarbonylC<sub>1</sub>-C<sub>6</sub>alkyl, hydroxycarbonylC<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>nitroalkyl, trimethylsilaneC<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy-C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>haloalkyl, C<sub>2</sub>-C<sub>6</sub>alkenyl, C<sub>2</sub>-C<sub>6</sub>haloalkenyl, C<sub>2</sub>-C<sub>6</sub>alkynyl, C<sub>2</sub>-C<sub>6</sub>haloalkynyl, C<sub>3</sub>-C<sub>4</sub>cycloalkylC<sub>1</sub>-C<sub>2</sub>alkyl-, C<sub>3</sub>-C<sub>4</sub>cycloalkylC<sub>1</sub>-C<sub>2</sub>alkyl- wherein the C<sub>3</sub>-C<sub>4</sub>cycloalkyl group is substituted with 1 or 2 halogen atoms, oxetan-3-yl-CH<sub>2</sub>-, C<sub>1</sub>-C<sub>3</sub>alkylcarbonyl, C<sub>1</sub>-C<sub>3</sub>alkoxycarbonyl, phenyloxycarbonyl, benzyloxycarbonyl, or benzyl; or
  - B. hydrogen, C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>cyanoalkyl, aminocarbonylC<sub>1</sub>-C<sub>6</sub>alkyl, hydroxycarbonylC<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>nitroalkyl, trimethylsilaneC<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy-C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>haloalkyl, C<sub>2</sub>-C<sub>6</sub>alkenyl, C<sub>2</sub>-C<sub>6</sub>haloalkenyl, C<sub>2</sub>-C<sub>6</sub>alkynyl, C<sub>2</sub>-C<sub>6</sub>haloalkynyl, C<sub>3</sub>-C<sub>4</sub>cycloalkylC<sub>1</sub>-C<sub>2</sub>alkyl-, benzyloxycarbonyl, or benzyl; or
- 25
- 30

- C. hydrogen, C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>cyanoalkyl, aminocarbonylC<sub>1</sub>-C<sub>6</sub>alkyl, hydroxycarbonylC<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy-C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>haloalkyl, C<sub>2</sub>-C<sub>6</sub>alkenyl, C<sub>2</sub>-C<sub>6</sub>haloalkenyl, C<sub>2</sub>-C<sub>6</sub>alkynyl, C<sub>2</sub>-C<sub>6</sub>haloalkynyl, C<sub>3</sub>-C<sub>4</sub>cycloalkylC<sub>1</sub>-C<sub>2</sub>alkyl-, benzyloxycarbonyl, or benzyl; or
- 5 D. hydrogen, C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>cyanoalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy-C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>haloalkyl, C<sub>2</sub>-C<sub>6</sub>alkenyl, C<sub>2</sub>-C<sub>6</sub>haloalkenyl, C<sub>2</sub>-C<sub>6</sub>alkynyl, C<sub>2</sub>-C<sub>6</sub>haloalkynyl, C<sub>3</sub>-C<sub>4</sub>cycloalkylC<sub>1</sub>-C<sub>2</sub>alkyl-, benzyloxycarbonyl, or benzyl; or
- E. hydrogen, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>cyanoalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy-C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>2</sub>-C<sub>4</sub>alkenyl, C<sub>2</sub>-C<sub>4</sub>haloalkenyl, C<sub>2</sub>-C<sub>4</sub>alkynyl, C<sub>2</sub>-C<sub>4</sub>haloalkynyl, C<sub>3</sub>-C<sub>4</sub>cycloalkylC<sub>1</sub>-C<sub>2</sub>alkyl-, benzyloxycarbonyl, or benzyl; or
- 10 F. hydrogen, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>cyanoalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy-C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>2</sub>-C<sub>4</sub>alkenyl, C<sub>2</sub>-C<sub>4</sub>haloalkenyl, C<sub>2</sub>-C<sub>4</sub>alkynyl, C<sub>2</sub>-C<sub>4</sub>haloalkynyl, C<sub>3</sub>-C<sub>4</sub>cycloalkylC<sub>1</sub>-C<sub>2</sub>alkyl-, benzyloxycarbonyl, or benzyl; or
- G. hydrogen, methyl, ethyl, cyanomethyl, methoxymethyl, cyclopropyl-methyl, allyl, propargyl, benzyloxycarbonyl, or benzyl; or
- 15 H. hydrogen, methyl, ethyl, allyl, propargyl or cyclopropyl-methyl; or
- I. hydrogen, methyl, propargyl or cyclopropyl-methyl; or
- J. hydrogen, methyl, or cyclopropyl-methyl; or
- K. hydrogen, or methyl; or
- L. hydrogen.
- 20 In preferred embodiments of each aspect of the invention, R<sup>1</sup> is hydrogen, methyl, or cyclopropyl-methyl. More preferably, R<sup>1</sup> is hydrogen or methyl. Even more preferably, R<sup>1</sup> is hydrogen.

In an embodiment of each aspect of the invention, R<sup>2a</sup> is

- 25 A. hydrogen, halogen, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, C<sub>1</sub>-C<sub>3</sub>haloalkoxy, CN, C<sub>3</sub>-C<sub>4</sub>cycloalkyl, C<sub>3</sub>-C<sub>6</sub>cycloalkylcarbonyl, phenyl, heteroaryl selected from J-1 to J-40, each of C<sub>3</sub>-C<sub>4</sub>cycloalkyl, phenyl and heteroaryl, independently of each other, being optionally substituted with one to three substituents R<sup>x</sup>; OR<sup>6</sup>, piperidin-2-one-1-yl, pyridin-2-one-1-yl, azetidin-1-yl optionally substituted with R<sup>x</sup>; pyrrolidin-1-yl, C<sub>3</sub>-C<sub>6</sub>cycloalkylC<sub>1</sub>-C<sub>4</sub>alkyl optionally substituted with one or two substituents R<sup>Z</sup>; C<sub>3</sub>-C<sub>6</sub>cycloalkylC<sub>1</sub>-C<sub>3</sub>alkoxy optionally substituted with one or two substituents R<sup>x</sup>; C<sub>1</sub>-C<sub>5</sub>cyanoalkyl, C<sub>1</sub>-C<sub>5</sub>cyanoalkoxy, C<sub>1</sub>-C<sub>4</sub>alkylsulfanyl optionally substituted with one to three substituents R<sup>x</sup>, C<sub>1</sub>-C<sub>4</sub>alkylsulfonyl optionally substituted with one to three substituents R<sup>x</sup>, or C<sub>1</sub>-C<sub>4</sub>alkylsulfinyl optionally substituted by one to three substituents R<sup>x</sup>; or
- 30
- 35 B. hydrogen, halogen, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, C<sub>1</sub>-C<sub>3</sub>haloalkoxy, CN, C<sub>3</sub>-C<sub>4</sub>cycloalkyl, C<sub>3</sub>-C<sub>6</sub>cycloalkylcarbonyl, phenyl, or pyrazolyl, each of C<sub>3</sub>-C<sub>4</sub>cycloalkyl, phenyl, and pyrazolyl, independently of each other, being optionally substituted with one to three substituents R<sup>x</sup>; OR<sup>6</sup>, piperidin-2-one-1-yl, pyridin-2-one-1-yl, azetidin-1-yl optionally substituted with one or two substituents R<sup>x</sup>; pyrrolidin-1-yl, C<sub>3</sub>-C<sub>6</sub>cycloalkylC<sub>1</sub>-C<sub>4</sub>alkyl optionally substituted with one or two substituents R<sup>Z</sup>; C<sub>3</sub>-C<sub>6</sub>cycloalkylC<sub>1</sub>-C<sub>3</sub>alkoxy optionally substituted with R<sup>x</sup>, C<sub>1</sub>-

C<sub>5</sub>cyanoalkyl, C<sub>1</sub>-C<sub>5</sub>cyanoalkoxy, C<sub>1</sub>-C<sub>4</sub>alkylsulfanyl optionally substituted with one to three substituents R<sup>x</sup>; C<sub>1</sub>-C<sub>4</sub>alkylsulfonyl optionally substituted with one to three substituents R<sup>x</sup>, or C<sub>1</sub>-C<sub>4</sub>alkylsulfinyl optionally substituted with one to three substituents R<sup>x</sup>; or

5 C. hydrogen, halogen, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, C<sub>1</sub>-C<sub>3</sub>haloalkoxy, CN, C<sub>3</sub>-C<sub>4</sub>cycloalkyl, C<sub>3</sub>-C<sub>6</sub>cycloalkylcarbonyl, phenyl or pyrazolyl, each of C<sub>3</sub>-C<sub>4</sub>cycloalkyl, phenyl, and pyrazolyl, independently of each other, being optionally substituted with one to two substituents R<sup>x</sup>, OR<sup>6</sup>, azetidin-1-yl optionally substituted with R<sup>x</sup>, C<sub>3</sub>-C<sub>6</sub>cycloalkylC<sub>1</sub>-C<sub>4</sub>alkyl optionally substituted with one or two substituents R<sup>Z</sup>, C<sub>3</sub>-C<sub>6</sub>cycloalkylC<sub>1</sub>-C<sub>3</sub>alkoxy optionally substituted with R<sup>x</sup>, C<sub>1</sub>-C<sub>4</sub>alkylsulfanyl optionally substituted by one to three substituents R<sup>x</sup>, C<sub>1</sub>-C<sub>4</sub>alkylsulfonyl optionally substituted by one to three substituents R<sup>x</sup>, or C<sub>1</sub>-C<sub>4</sub>alkylsulfinyl optionally substituted by one to three substituents R<sup>x</sup>; or

10 D. hydrogen, halogen, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, C<sub>1</sub>-C<sub>3</sub>haloalkoxy, CN, C<sub>3</sub>-C<sub>4</sub>cycloalkyl, C<sub>3</sub>-C<sub>4</sub>cycloalkyl substituted with one to two substituents R<sup>x</sup>; C<sub>3</sub>-C<sub>6</sub>cycloalkylcarbonyl, OR<sup>6</sup>, C<sub>3</sub>-C<sub>6</sub>cycloalkylC<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>3</sub>-C<sub>6</sub>cycloalkylC<sub>1</sub>-C<sub>4</sub>alkyl substituted with one or two substituents R<sup>Z</sup>, C<sub>1</sub>-C<sub>4</sub>alkylsulfanyl, C<sub>1</sub>-C<sub>4</sub>alkylsulfanyl substituted by one to three substituents R<sup>x</sup>, C<sub>1</sub>-C<sub>4</sub>alkylsulfonyl, C<sub>1</sub>-C<sub>4</sub>alkylsulfonyl substituted by one to three substituents R<sup>x</sup>, C<sub>1</sub>-C<sub>4</sub>alkylsulfinyl, or C<sub>1</sub>-C<sub>4</sub>alkylsulfinyl substituted by one to three substituents R<sup>x</sup>; or

15 E. hydrogen, halogen, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, C<sub>1</sub>-C<sub>3</sub>haloalkoxy, CN, C<sub>3</sub>-C<sub>4</sub>cycloalkyl, C<sub>3</sub>-C<sub>4</sub>cycloalkyl substituted with one to two substituents independently selected from halogen, C<sub>1</sub>-C<sub>3</sub>alkyl and C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>3</sub>-C<sub>4</sub>cycloalkylcarbonyl, C<sub>3</sub>-C<sub>4</sub>cycloalkylmethyl, C<sub>3</sub>-C<sub>4</sub>cycloalkylmethyl substituted with one to two substituents independently selected from oxo, halogen, C<sub>1</sub>-C<sub>3</sub>alkyl, and C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>2</sub>alkylsulfanyl substituted with one to three halogens or C<sub>1</sub>-C<sub>2</sub>alkylsulfonyl substituted with one to three halogens; or

20 F. hydrogen, halogen, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, C<sub>1</sub>-C<sub>3</sub>haloalkoxy, cyclopropyl, cyclopropyl substituted with one to two substituents independently selected from halogen, methyl, and trifluoromethyl, cyclopropylcarbonyl, cyclopropylmethyl substituted with one to two substituents independently selected from oxo, halogen, and trifluoromethyl, or C<sub>1</sub>-C<sub>2</sub>alkylsulfanyl substituted with one to three halogens or C<sub>1</sub>-C<sub>2</sub>alkylsulfonyl substituted with one to three halogens; or

25 G. hydrogen, halogen, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>haloalkylsulfanyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, C<sub>1</sub>-C<sub>3</sub>haloalkoxy, CN, C<sub>3</sub>-C<sub>6</sub>cycloalkyl, C<sub>3</sub>-C<sub>6</sub>cycloalkyl substituted with one to three substituents independently selected from C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, cyano, and halogen, cyclopropylcarbonyl, C<sub>3</sub>-C<sub>6</sub>cycloalkylC<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>3</sub>-C<sub>6</sub>cycloalkylC<sub>1</sub>-C<sub>4</sub>alkyl substituted with one to five substituents independently selected from oxo, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, cyano, and halogen, C<sub>1</sub>-C<sub>5</sub>cyanoalkyl, C<sub>1</sub>-C<sub>4</sub>alkylsulfonyl, C<sub>1</sub>-C<sub>4</sub>haloalkylsulfonyl, C<sub>1</sub>-C<sub>4</sub>alkylsulfinyl, C<sub>1</sub>-C<sub>4</sub>haloalkylsulfinyl, C<sub>3</sub>-C<sub>6</sub>cycloalkylsulfanyl, C<sub>3</sub>-C<sub>6</sub>cycloalkylsulfinyl, or C<sub>3</sub>-C<sub>6</sub>cycloalkylsulfonyl; or

- H. hydrogen, halogen, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>haloalkylsulfanyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, C<sub>1</sub>-C<sub>3</sub>haloalkoxy, CN, C<sub>3</sub>-C<sub>6</sub>cycloalkyl, C<sub>3</sub>-C<sub>6</sub>cycloalkyl substituted with one or two substituents independently selected from C<sub>1</sub>-C<sub>3</sub>haloalkyl, cyano, and halogen, C<sub>3</sub>-C<sub>4</sub>cycloalkylcarbonyl, C<sub>3</sub>-C<sub>6</sub>cycloalkylC<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>3</sub>-C<sub>6</sub>cycloalkylC<sub>1</sub>-C<sub>4</sub>alkyl substituted with one to three substituents independently selected from oxo, C<sub>1</sub>-C<sub>3</sub>haloalkyl, cyano, and halogen, C<sub>1</sub>-C<sub>5</sub>cyanoalkyl, C<sub>1</sub>-C<sub>4</sub>alkylsulfonyl, C<sub>1</sub>-C<sub>4</sub>haloalkylsulfonyl, C<sub>1</sub>-C<sub>4</sub>alkylsulfinyl, C<sub>1</sub>-C<sub>4</sub>haloalkylsulfinyl, C<sub>3</sub>-C<sub>6</sub>cycloalkylsulfanyl, C<sub>3</sub>-C<sub>6</sub>cycloalkylsulfinyl, or C<sub>3</sub>-C<sub>6</sub>cycloalkylsulfonyl; or
- I. hydrogen, halogen, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>haloalkylsulfanyl, C<sub>1</sub>-C<sub>3</sub>haloalkoxy, C<sub>3</sub>-C<sub>6</sub>cycloalkyl, C<sub>3</sub>-C<sub>6</sub>cycloalkyl substituted with one or two substituents independently selected from C<sub>1</sub>-C<sub>3</sub>haloalkyl, cyano, and halogen, C<sub>3</sub>-C<sub>4</sub>cycloalkylcarbonyl, C<sub>3</sub>-C<sub>6</sub>cycloalkylC<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>3</sub>-C<sub>6</sub>cycloalkylC<sub>1</sub>-C<sub>4</sub>alkyl substituted with one to three substituents independently selected from oxo, C<sub>1</sub>-C<sub>3</sub>haloalkyl, cyano, and halogen, C<sub>1</sub>-C<sub>5</sub>cyanoalkyl, C<sub>1</sub>-C<sub>4</sub>alkylsulfonyl, C<sub>1</sub>-C<sub>4</sub>haloalkylsulfonyl, C<sub>1</sub>-C<sub>4</sub>alkylsulfinyl, C<sub>1</sub>-C<sub>4</sub>haloalkylsulfinyl, C<sub>3</sub>-C<sub>6</sub>cycloalkylsulfanyl, C<sub>3</sub>-C<sub>6</sub>cycloalkylsulfinyl, or C<sub>3</sub>-C<sub>6</sub>cycloalkylsulfonyl; or
- J. hydrogen, halogen, C<sub>3</sub>-C<sub>4</sub>cycloalkyl, C<sub>3</sub>-C<sub>4</sub>cycloalkylcarbonyl, C<sub>3</sub>-C<sub>4</sub>cycloalkyl-C<sub>1</sub>-C<sub>2</sub>alkyl optionally substituted with one to two substituents selected from oxo, halogen, C<sub>1</sub>-C<sub>3</sub>alkyl and C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>haloalkylsulfanyl, C<sub>1</sub>-C<sub>3</sub>haloalkylsulfonyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, C<sub>1</sub>-C<sub>3</sub>haloalkoxy, or CN; or
- K. halogen, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>haloalkylsulfanyl, C<sub>1</sub>-C<sub>3</sub>haloalkylsulfonyl, or C<sub>1</sub>-C<sub>3</sub>haloalkoxy; or
- L. halogen, C<sub>1</sub>-C<sub>2</sub>fluoroalkyl, C<sub>1</sub>-C<sub>2</sub>fluoroalkylsulfanyl, C<sub>1</sub>-C<sub>2</sub>fluoroalkylsulfonyl, or C<sub>1</sub>-C<sub>2</sub>fluoroalkoxy; or
- M. chlorine, fluorine, bromine, iodine, difluoromethyl, trifluoromethyl, trifluoromethylsulfanyl or trifluoromethylsulfonyl; or
- N. fluorine, chlorine, bromine, iodine, trifluoromethylsulfanyl, trifluoromethylsulfonyl or trifluoromethyl; or
- O. chlorine, bromine, iodine, trifluoromethylsulfonyl or trifluoromethyl; or
- P. chlorine, bromine, trifluoromethyl, difluoromethoxy, trifluoromethoxy, or 1-cyanocyclopropyl; or
- Q. chlorine, bromine, iodine, or trifluoromethyl; or
- R. chlorine, bromine, or difluoromethoxy; or
- S. chlorine or bromine.

In preferred embodiments of each aspect of the invention, R<sup>2a</sup> is chlorine, bromine, trifluoromethyl, or difluoromethoxy. Preferably, R<sup>2a</sup> is chlorine, bromine, or difluoromethoxy.

In an embodiment of each aspect of the invention, R<sup>2b</sup> is :

- A. hydrogen, halogen, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>3</sub>-C<sub>4</sub>cycloalkyl, cyclopropylcarbonyl, C<sub>3</sub>-C<sub>6</sub>cycloalkylC<sub>1</sub>-C<sub>4</sub>alkyl optionally substituted with one or two substituents R<sup>Z</sup>, C<sub>1</sub>-C<sub>3</sub>alkoxy, C<sub>1</sub>-C<sub>3</sub>haloalkoxy, CN, C<sub>1</sub>-C<sub>4</sub>alkylsulfanyl optionally substituted with one to three substituents R<sup>X</sup>, C<sub>1</sub>-C<sub>4</sub>alkylsulfonyl optionally substituted with one to three substituents R<sup>X</sup>, or C<sub>1</sub>-C<sub>4</sub>alkylsulfinyl optionally substituted with one to three substituents R<sup>X</sup>; or

B. hydrogen, halogen, C<sub>3</sub>-C<sub>4</sub>cycloalkyl, cyclopropylcarbonyl, C<sub>3</sub>-C<sub>4</sub>cycloalkyl-C<sub>1</sub>-C<sub>2</sub>alkyl optionally substituted with one to two substituents selected from oxo, halogen, C<sub>1</sub>-C<sub>3</sub>alkyl and C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>haloalkylsulfanyl, C<sub>1</sub>-C<sub>3</sub>haloalkylsulfonyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, C<sub>1</sub>-C<sub>3</sub>haloalkoxy, or CN; or

5 C. halogen, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>haloalkylsulfanyl, C<sub>1</sub>-C<sub>3</sub>haloalkylsulfonyl, or C<sub>1</sub>-C<sub>3</sub>haloalkoxy; or

D. halogen, C<sub>1</sub>-C<sub>2</sub>haloalkyl, C<sub>1</sub>-C<sub>2</sub>haloalkylsulfanyl, C<sub>1</sub>-C<sub>2</sub>haloalkylsulfonyl, or C<sub>1</sub>-C<sub>2</sub>haloalkoxy; or

E. fluorine, chlorine, bromine, iodine, difluoromethyl, trifluoromethyl, trifluoromethylsulfanyl, trifluoromethylsulfonyl; or

10 F. fluorine, chlorine, bromine, iodine, trifluoromethylsulfanyl, trifluoromethylsulfonyl or trifluoromethyl; or

G. chlorine, bromine, iodine, trifluoromethylsulfonyl, or trifluoromethyl; or

H. chlorine, bromine, iodine, or trifluoromethyl; or

I. chlorine, iodine, or trifluoromethyl; or

J. bromine, iodine, trifluoromethyl, trifluoromethoxy, or 1-cyanocyclopropyl; or

15 K. bromine, iodine, or trifluoromethyl; or

L. trifluoromethyl.

In preferred embodiments of each aspect of the invention, R<sup>2b</sup> is bromine, iodine, difluoromethyl, trifluoromethyl, difluoromethoxy, trifluoromethoxy, trifluoromethylsulfonyl, 1-cyano-1-methyl-ethyl, or 1-cyanocyclopropyl. Preferably, R<sup>2b</sup> is bromine, iodine, trifluoromethyl, trifluoromethoxy, or 1-cyanocyclopropyl.

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In an embodiment of each aspect of the invention,

A. R<sup>2a</sup> and R<sup>2b</sup> are independently selected from halogen, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>haloalkylsulfanyl, C<sub>1</sub>-C<sub>3</sub>haloalkylsulfonyl, and C<sub>1</sub>-C<sub>3</sub>haloalkoxy; or

25 B. R<sup>2a</sup> and R<sup>2b</sup> are independently selected from halogen, C<sub>1</sub>-C<sub>3</sub>fluoroalkyl, C<sub>1</sub>-C<sub>3</sub>fluoroalkylsulfanyl, C<sub>1</sub>-C<sub>3</sub>fluoroalkylsulfonyl, and C<sub>1</sub>-C<sub>3</sub>fluoroalkoxy; or

C. R<sup>2a</sup> and R<sup>2b</sup> are independently selected from chlorine, bromine, iodine, C<sub>1</sub>-C<sub>3</sub>fluoroalkyl, C<sub>1</sub>-C<sub>3</sub>fluoroalkylsulfonyl, and C<sub>1</sub>-C<sub>3</sub>fluoroalkoxy; or

30 D. R<sup>2a</sup> and R<sup>2b</sup> are independently selected from fluorine, chlorine, bromine, iodine, trifluoromethylsulfanyl, trifluoromethylsulfonyl, and trifluoromethyl; or

E. R<sup>2a</sup> and R<sup>2b</sup> are independently selected from chlorine, bromine, iodine, trifluoromethylsulfanyl, and trifluoromethyl; or

F. R<sup>2a</sup> and R<sup>2b</sup> are independently selected from chlorine, bromine, iodine, trifluoromethyl, difluoromethoxy, trifluoromethoxy, and 1-cyanocyclopropyl; or

35 G. R<sup>2a</sup> and R<sup>2b</sup> are differently selected from chlorine, bromine, iodine, trifluoromethylsulfonyl, and trifluoromethyl; or

H. R<sup>2a</sup> and R<sup>2b</sup> are differently selected from chlorine, bromine, iodine, trifluoromethyl, difluoromethoxy, trifluoromethoxy, and 1-cyanocyclopropyl; or

- I. R<sup>2a</sup> and R<sup>2b</sup> are differently selected from chlorine, bromine, iodine, trifluoromethyl, difluoromethoxy, and trifluoromethoxy.

In preferred embodiments of each aspect of the invention, R<sup>2a</sup> is chlorine, bromine, trifluoromethyl, or difluoromethoxy, and R<sup>2b</sup> is bromine, iodine, difluoromethyl, trifluoromethyl, difluoromethoxy, trifluoromethoxy, trifluoromethylsulfonyl, 1-cyano-1-methyl-ethyl, or 1-cyanocyclopropyl. For instance, R<sup>2a</sup> is chlorine, bromine, trifluoromethyl, or difluoromethoxy, and R<sup>2b</sup> is bromine, iodine, trifluoromethyl, trifluoromethoxy, or 1-cyanocyclopropyl. More preferably, R<sup>2a</sup> is chlorine, bromine, or difluoromethoxy, and R<sup>2b</sup> is bromine, iodine, trifluoromethyl, trifluoromethoxy, or 1-cyanocyclopropyl. Even more preferably, R<sup>2a</sup> is chlorine, bromine, or difluoromethoxy, and R<sup>2b</sup> is bromine, iodine, or trifluoromethyl, such as trifluoromethyl. For instance, R<sup>2a</sup> is chlorine, or difluoromethoxy, such as chlorine, and R<sup>2b</sup> is bromine, iodine, or trifluoromethyl, such as trifluoromethyl.

In an embodiment of each aspect of the invention, R<sup>3</sup> is

- A. C<sub>1</sub>-C<sub>3</sub>alkyl or C<sub>1</sub>-C<sub>3</sub>haloalkyl; or  
 B. methyl or trifluoromethyl; or  
 C. methyl.

In preferred embodiments of each aspect of the invention, R<sup>3</sup> is methyl.

In an embodiment of each aspect of the invention, R<sup>4c</sup> is:

- A. hydrogen; C<sub>1</sub>-C<sub>3</sub>alkyl optionally substituted with a single substituent selected from cyano, C<sub>1</sub>-C<sub>3</sub>alkylsulfanyl, C<sub>1</sub>-C<sub>3</sub>alkylsulfinyl, C<sub>1</sub>-C<sub>3</sub>alkylsulfonyl, and -C(O)NR<sup>4d</sup>R<sup>4e</sup>; C<sub>1</sub>-C<sub>3</sub>haloalkyl, allyl, propargyl, C<sub>3</sub>-C<sub>6</sub>cycloalkylC<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>2</sub>alkoxyC<sub>1</sub>-C<sub>3</sub>alkyl, -C(O)NR<sup>4d</sup>R<sup>4e</sup>, -N=CR<sup>4f</sup>R<sup>4g</sup>; or benzyl optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, and C<sub>3</sub>-C<sub>4</sub>cycloalkyl; or heteroaryl-methyl, wherein said heteroaryl is optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, and C<sub>3</sub>-C<sub>4</sub>cycloalkyl; or -C(O)C<sub>1</sub>-C<sub>6</sub>alkyl optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, and C<sub>1</sub>-C<sub>3</sub>alkoxy; or -C(O)OC<sub>1</sub>-C<sub>6</sub>alkyl optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, and C<sub>1</sub>-C<sub>3</sub>alkoxy; wherein R<sup>4d</sup> and R<sup>4e</sup> are independently hydrogen, or C<sub>1</sub>-C<sub>5</sub>alkyl optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, and C<sub>1</sub>-C<sub>3</sub>alkoxy; and wherein R<sup>4f</sup> and R<sup>4g</sup> are independently C<sub>1</sub>-C<sub>3</sub>alkyl, or R<sup>4f</sup> and R<sup>4g</sup> form, together with the carbon atom they are attached to, a C<sub>4</sub>-C<sub>6</sub>cycloalkyl or a 4- to 6-membered saturated heterocycle containing one oxygen atom; or
- B. hydrogen; C<sub>1</sub>-C<sub>3</sub>alkyl optionally substituted with a single substituent selected from cyano, -SCH<sub>3</sub>, -S(O)CH<sub>3</sub>, -SO<sub>2</sub>CH<sub>3</sub> and -C(O)NR<sup>4d</sup>R<sup>4e</sup>; C<sub>1</sub>-C<sub>3</sub>haloalkyl, allyl, propargyl, C<sub>3</sub>-C<sub>6</sub>cycloalkylC<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>2</sub>alkoxyC<sub>1</sub>-C<sub>3</sub>alkyl, -C(O)NR<sup>4d</sup>R<sup>4e</sup>; isopropylideneamino, 1-methylpropylideneamino, 1-ethylpropylideneamino, cyclobutylideneamino, cyclopentylideneamino, cyclohexylideneamino, oxetan-3-ylideneamino, tetrahydrofuran-3-

ylideneamino, tetrahydropyran-4-ylideneamino; or benzyl optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, and C<sub>3</sub>-C<sub>4</sub>cycloalkyl; or heteroaryl-methyl, wherein said heteroaryl is optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, and C<sub>3</sub>-C<sub>4</sub>cycloalkyl; or -C(O)C<sub>1</sub>-C<sub>6</sub>alkyl optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, and C<sub>1</sub>-C<sub>3</sub>alkoxy; or -C(O)OC<sub>1</sub>-C<sub>6</sub>alkyl optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, and C<sub>1</sub>-C<sub>3</sub>alkoxy; wherein R<sup>4d</sup> and R<sup>4e</sup> are independently hydrogen, or C<sub>1</sub>-C<sub>3</sub>alkyl optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, methoxy, ethoxy, propoxy, or isopropoxy; or

C. C<sub>1</sub>-C<sub>3</sub>alkyl optionally substituted with a single substituent selected from cyano, -SCH<sub>3</sub>, -S(O)CH<sub>3</sub>, -SO<sub>2</sub>CH<sub>3</sub> and -C(O)NR<sup>4d</sup>R<sup>4e</sup>; C<sub>1</sub>-C<sub>3</sub>haloalkyl, allyl, propargyl, C<sub>3</sub>-C<sub>6</sub>cycloalkylC<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>2</sub>alkoxyC<sub>1</sub>-C<sub>3</sub>alkyl, -C(O)NR<sup>4d</sup>R<sup>4e</sup>; isopropylideneamino, 1-methylpropylideneamino, 1-ethylpropylideneamino, cyclobutylideneamino, cyclopentylideneamino, cyclohexylideneamino, oxetan-3-ylideneamino, tetrahydrofuran-3-ylideneamino, tetrahydropyran-4-ylideneamino; or benzyl optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, and C<sub>3</sub>-C<sub>4</sub>cycloalkyl; or heteroaryl-methyl, wherein said heteroaryl is optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, and C<sub>3</sub>-C<sub>4</sub>cycloalkyl; or -C(O)C<sub>1</sub>-C<sub>6</sub>alkyl optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, and C<sub>1</sub>-C<sub>3</sub>alkoxy; or -C(O)OC<sub>1</sub>-C<sub>6</sub>alkyl optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, and C<sub>1</sub>-C<sub>3</sub>alkoxy; wherein R<sup>4d</sup> and R<sup>4e</sup> are independently hydrogen, or C<sub>1</sub>-C<sub>3</sub>alkyl optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, methoxy, ethoxy, propoxy, or isopropoxy; or

D. hydrogen, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, allyl, propargyl, C<sub>3</sub>-C<sub>4</sub>cycloalkylC<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>2</sub>alkoxyC<sub>1</sub>-C<sub>3</sub>alkyl, isopropylideneamino, 1-methylpropylideneamino, 1-ethylpropylideneamino, cyclobutylideneamino, cyclopentylideneamino, cyclohexylideneamino, oxetan-3-ylideneamino, tetrahydrofuran-3-ylideneamino, tetrahydropyran-4-ylideneamino, -C(O)NR<sup>4d</sup>R<sup>4e</sup>, benzyl optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, and C<sub>3</sub>-C<sub>4</sub>cycloalkyl; or heteroaryl-methyl where the heteroaryl is optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, and C<sub>3</sub>-C<sub>4</sub>cycloalkyl; -C(O)C<sub>1</sub>-C<sub>6</sub>alkyl, or -C(O)OC<sub>1</sub>-C<sub>6</sub>alkyl; wherein R<sup>4d</sup> and R<sup>4e</sup> are independently hydrogen, or C<sub>1</sub>-C<sub>3</sub>alkyl optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, methoxy, ethoxy, propoxy, or isopropoxy; or

E. hydrogen, methyl, ethyl, propyl, isopropyl, C<sub>1</sub>-C<sub>3</sub>fluoroalkyl, C<sub>1</sub>-C<sub>3</sub>chloroalkyl, C<sub>3</sub>-C<sub>4</sub>cycloalkylC<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>2</sub>alkoxyC<sub>1</sub>-C<sub>3</sub>alkyl, isopropylideneamino, 1-methylpropylideneamino, 1-ethylpropylideneamino, cyclobutylideneamino,



cyclopentylideneamino, cyclohexylideneamino, oxetan-3-ylideneamino, tetrahydrofuran-3-ylideneamino, tetrahydropyran-4-ylideneamino, benzyl optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, and C<sub>3</sub>-C<sub>4</sub>cycloalkyl; or heteroaryl-methyl where the heteroaryl group is a pyridyl or a diaziny cycle, optionally substituted with 1 or 2 substituents independently selected from halogen, cyano, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, and C<sub>3</sub>-C<sub>4</sub>cycloalkyl; or

F. hydrogen, C<sub>1</sub>-C<sub>3</sub>alkyl, cyclopropyl-C<sub>1</sub>-C<sub>2</sub>alkyl, cyclobutyl-C<sub>1</sub>-C<sub>2</sub>alkyl, isopropylideneamino, 1-methylpropylideneamino, 1-ethylpropylideneamino, cyclobutylideneamino, cyclopentylideneamino, cyclohexylideneamino, oxetan-3-ylideneamino, tetrahydrofuran-3-ylideneamino, tetrahydropyran-4-ylideneamino, pyrimidin-2-yl-methyl, 4-pyridinyl-methyl, where the pyridyl or pyrimidinyl is optionally substituted with 1 or 2 substituents independently selected from halogen, cyano, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, and C<sub>3</sub>-C<sub>4</sub>cycloalkyl; -C(O)C<sub>1</sub>-C<sub>3</sub>alkyl, or -C(O)OC<sub>1</sub>-C<sub>3</sub>alkyl; or

G. C<sub>3</sub>-C<sub>4</sub>cycloalkylC<sub>1</sub>-C<sub>4</sub>alkyl, isopropylideneamino, 1-methylpropylideneamino, cyclobutylideneamino, cyclopentylideneamino, oxetan-3-ylideneamino, tetrahydrofuran-3-ylideneamino, pyrimidin-2-yl-methyl, 4-pyridinyl-methyl; or

H. hydrogen, methyl, ethyl, cyclopropylmethyl, oxetan-3-ylideneamino, isopropylideneamino, or pyrimidin-2-ylmethyl; or

I. methyl, ethyl, cyclopropylmethyl, oxetan-3-ylideneamino, isopropylideneamino, or pyrimidin-2-ylmethyl; or

J. hydrogen, methyl, ethyl, 2,2-difluoroethyl, cyclopropylmethyl, or pyrimidin-2-ylmethyl; or

K. hydrogen, methyl, ethyl, 2,2-difluoroethyl, or cyclopropylmethyl; or

L. hydrogen, methyl, ethyl, or cyclopropylmethyl; or

M. methyl.

In an embodiment of each aspect of the invention, where R<sup>4c</sup> is -N=CR<sup>4f</sup>R<sup>4g</sup>,

A. R<sup>4f</sup> and R<sup>4g</sup> are independently selected from methyl, ethyl, propyl, and isopropyl, or R<sup>4f</sup> and R<sup>4g</sup> form, together with the carbon atom they are attached to, a cyclopropyl, cyclobutyl or cyclohexyl group, or a 4- to 6-membered saturated heterocycle containing one oxygen atom; or

B. R<sup>4f</sup> and R<sup>4g</sup> are independently selected from methyl, ethyl, and propyl, or R<sup>4f</sup> and R<sup>4g</sup> form, together with the carbon atom they are attached to, a cyclopropyl, cyclobutyl, cyclohexyl, oxetan-3-yl, tetrahydrofuran-3-yl, tetrahydropyran-3-yl, tetrahydropyran-4-yl group;

C. R<sup>4f</sup> and R<sup>4g</sup> are independently selected from methyl and ethyl, or R<sup>4f</sup> and R<sup>4g</sup> form, together with the carbon atom they are attached to, a cyclopropyl, cyclobutyl, cyclohexyl, oxetan-3-yl, tetrahydrofuran-3-yl, tetrahydropyran-4-yl group; or

D. R<sup>4f</sup> and R<sup>4g</sup> are independently selected from methyl and ethyl; or

E. R<sup>4f</sup> and R<sup>4g</sup> form, together with the carbon atom they are attached to, a cyclopropyl, cyclobutyl, cyclohexyl, oxetan-3-yl, tetrahydrofuran-3-yl, tetrahydropyran-4-yl group; or

- F. R<sup>4f</sup> and R<sup>4g</sup> are independently selected from methyl and ethyl; or R<sup>4f</sup> and R<sup>4g</sup> form, together with the carbon atom they are attached to, a cyclopropyl, cyclobutyl, or cyclohexyl group; or
- G. R<sup>4f</sup> and R<sup>4g</sup> are independently selected from methyl and ethyl; or R<sup>4f</sup> and R<sup>4g</sup> form, together with the carbon atom they are attached to, an oxetan-3-yl, tetrahydrofuran-3-yl, tetrahydropyran-4-yl group; or
- H. R<sup>4f</sup> and R<sup>4g</sup> form, together with the carbon atom they are attached to, a cyclopropyl, cyclobutyl, or cyclohexyl group; or
- I. R<sup>4f</sup> and R<sup>4g</sup> form, together with the carbon atom they are attached to, an oxetan-3-yl, tetrahydrofuran-3-yl, tetrahydropyran-4-yl group; or
- J. R<sup>4f</sup> and R<sup>4g</sup> are methyl; or R<sup>4f</sup> and R<sup>4g</sup> form, together with the carbon atom they are attached to, an oxetan-3-yl group.

In preferred embodiments of each aspect of the invention, R<sup>4c</sup> is hydrogen, methyl, ethyl, 2,2-difluoroethyl, cyclopropylmethyl, propargyl, or pyrimidin-2-ylmethyl. Preferably, R<sup>4c</sup> is hydrogen, methyl, ethyl, or cyclopropylmethyl. More preferably, R<sup>4c</sup> is hydrogen, methyl, or ethyl; such as R<sup>4c</sup> is methyl or ethyl.

In an embodiment of each aspect of the invention, R<sup>5a</sup> is

- A. hydrogen, halogen, CN, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>3</sub>-C<sub>4</sub>cycloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy or C<sub>1</sub>-C<sub>3</sub>haloalkoxy; or
- B. hydrogen, halogen, CN, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>3</sub>-C<sub>4</sub>cycloalkyl or C<sub>1</sub>-C<sub>3</sub>alkoxy; or
- C. hydrogen, halogen, CN, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl or C<sub>1</sub>-C<sub>3</sub>alkoxy; or
- D. hydrogen, halogen, CN, C<sub>1</sub>-C<sub>3</sub>alkyl or C<sub>1</sub>-C<sub>3</sub>alkoxy; or
- E. hydrogen or halogen; or
- F. hydrogen.

In an embodiment of each aspect of the invention, R<sup>5b</sup> is

- A. hydrogen, halogen, CN, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>3</sub>-C<sub>4</sub>cycloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, or C<sub>1</sub>-C<sub>3</sub>haloalkoxy; or
- B. hydrogen, halogen or C<sub>1</sub>-C<sub>3</sub>alkoxy; or
- C. hydrogen.

In preferred embodiments of each aspect of the invention, R<sup>5a</sup> and R<sup>5b</sup> are hydrogen.

In an embodiment of each aspect of the invention, R<sup>6</sup> is

- A. phenyl, benzyl, heteroaryl, or C<sub>3</sub>-C<sub>6</sub> cycloalkyl, each of which, independently of each other, is optionally substituted with one substituent selected from R<sup>x</sup>; or
- B. phenyl, benzyl, cyclopropyl or cyclopropyl substituted with one substituent selected from R<sup>x</sup>.

In an embodiment of each aspect of the invention, R<sup>x</sup> is independently selected from

- A. halogen, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, C<sub>1</sub>-C<sub>3</sub>haloalkoxy or CN; or
- B. F, Cl, Br, OCF<sub>2</sub>H, OCH<sub>3</sub> or CN.

In an embodiment of each aspect of the invention,  $R^Z$  is independently selected from

- A. oxo, halogen, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, C<sub>1</sub>-C<sub>3</sub>haloalkoxy or CN; or
- B. oxo, F, Cl, Br, OCF<sub>2</sub>H, OCH<sub>3</sub> or CN.

5 In an embodiment of each aspect of the invention,  $R^Y$  is independently selected from

- A. hydrogen, C<sub>1</sub>-C<sub>3</sub> alkyl, C<sub>1</sub>-C<sub>3</sub> haloalkyl, C<sub>1</sub>-C<sub>3</sub> alkoxy, C<sub>1</sub>-C<sub>3</sub> haloalkoxy, halogen, CN and cyclopropyl; or
- B. hydrogen, C<sub>1</sub>-C<sub>3</sub> alkyl, C<sub>1</sub>-C<sub>3</sub> haloalkyl, C<sub>1</sub>-C<sub>3</sub> alkoxy, C<sub>1</sub>-C<sub>3</sub> haloalkoxy, halogen, and cyclopropyl; or
- 10 C. hydrogen, C<sub>1</sub>-C<sub>3</sub> alkyl, C<sub>1</sub>-C<sub>3</sub> haloalkyl, and C<sub>1</sub>-C<sub>3</sub> alkoxy; or
- D. hydrogen, methyl, trifluoromethyl, and methoxy; or
- E. hydrogen.

15 The present invention, accordingly, makes available a compound of formula (I) having the substituents A, R<sup>1</sup>, R<sup>2a</sup>, R<sup>2b</sup>, R<sup>3</sup>, R<sup>4c</sup>, R<sup>5a</sup>, R<sup>5b</sup> and X as defined above in all combinations and each permutation.

Accordingly, compounds of formula (I) are made available, where, for instance, A is CH or nitrogen, preferably A is CH; X is oxygen or sulfur, preferably X is oxygen; R<sup>1</sup> is hydrogen, methyl, ethyl, allyl, propargyl or cyclopropyl-methyl, such as R<sup>1</sup> is hydrogen or methyl; R<sup>2a</sup> is halogen, C<sub>1</sub>-C<sub>2</sub>fluoroalkyl, C<sub>1</sub>-C<sub>2</sub>fluoroalkylsulfanyl, C<sub>1</sub>-C<sub>2</sub>fluoroalkylsulfonyl, or C<sub>1</sub>-C<sub>2</sub>fluoroalkoxy; R<sup>2b</sup> is fluorine, chlorine, bromine, iodine, difluoromethyl, trifluoromethyl, trifluoromethylsulfanyl, trifluoromethylsulfonyl; R<sup>3</sup> is C<sub>1</sub>-C<sub>3</sub>alkyl or C<sub>1</sub>-C<sub>3</sub>haloalkyl, such as R<sup>3</sup> is methyl or trifluoromethyl; R<sup>4c</sup> is hydrogen, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, allyl, propargyl, C<sub>3</sub>-C<sub>4</sub>cycloalkylC<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>2</sub>alkoxyC<sub>1</sub>-C<sub>3</sub>alkyl, isopropylideneamino, 1-methylpropylideneamino, 1-ethylpropylideneamino, cyclobutylideneamino, cyclopentylideneamino, cyclohexylideneamino, oxetan-3-ylideneamino, tetrahydrofuran-3-ylideneamino, tetrahydropyran-4-ylideneamino, -C(O)NR<sup>4d</sup>R<sup>4e</sup>, benzyl optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, and C<sub>3</sub>-C<sub>4</sub>cycloalkyl; or heteroaryl-methyl where the heteroaryl is optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, and C<sub>3</sub>-C<sub>4</sub>cycloalkyl; -C(O)C<sub>1</sub>-C<sub>6</sub>alkyl, or -C(O)OC<sub>1</sub>-C<sub>6</sub>alkyl; wherein R<sup>4d</sup> and R<sup>4e</sup> are independently hydrogen, or C<sub>1</sub>-C<sub>3</sub>alkyl optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, methoxy, ethoxy, propoxy, or isopropoxy; R<sup>5a</sup> is hydrogen or halogen; and R<sup>5b</sup> is hydrogen, halogen or C<sub>1</sub>-C<sub>3</sub>alkoxy, such as R<sup>5a</sup> and R<sup>5b</sup> are hydrogen.

35 Other compounds of formula (I) are made available, where, for instance, A is CH or nitrogen, preferably A is CH; X is oxygen or sulfur, preferably X is oxygen; R<sup>1</sup> is hydrogen, C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>cyanoalkyl, aminocarbonylC<sub>1</sub>-C<sub>6</sub>alkyl, hydroxycarbonylC<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>nitroalkyl, trimethylsilaneC<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy-C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>haloalkyl, C<sub>2</sub>-C<sub>6</sub>alkenyl, C<sub>2</sub>-C<sub>6</sub>haloalkenyl, C<sub>2</sub>-C<sub>6</sub>alkynyl, C<sub>2</sub>-C<sub>6</sub>haloalkynyl, C<sub>3</sub>-C<sub>4</sub>cycloalkyl-C<sub>1</sub>-C<sub>2</sub>alkyl, C<sub>3</sub>-C<sub>4</sub>cycloalkyl-C<sub>1</sub>-C<sub>2</sub>alkyl wherein the C<sub>3</sub>-C<sub>4</sub>cycloalkyl group is substituted with 1 or 2 halogen atoms, oxetan-3-yl-CH<sub>2</sub>-, C<sub>1</sub>-C<sub>6</sub>alkylcarbonyl, C<sub>1</sub>-

C<sub>6</sub>alkoxycarbonyl, phenyloxycarbonyl, benzyloxycarbonyl, benzyl, or benzyl substituted with 1 to 3 substituents independently selected from halogen, C<sub>1</sub>-C<sub>6</sub>alkoxy and C<sub>1</sub>-C<sub>6</sub>haloalkyl, such as R<sup>1</sup> is hydrogen or methyl; R<sup>2a</sup> is chlorine, bromine, trifluoromethyl, or difluoromethoxy; R<sup>2b</sup> is bromine, iodine, difluoromethyl, trifluoromethyl, difluoromethoxy, trifluoromethoxy, trifluoromethylsulfonyl, 1-cyano-1-methyl-ethyl, or 1-cyanocyclopropyl; R<sup>3</sup> is C<sub>1</sub>-C<sub>3</sub>alkyl or C<sub>1</sub>-C<sub>3</sub>haloalkyl, such as R<sup>3</sup> is methyl; R<sup>4c</sup> is heteroaryl-methyl, where said heteroaryl group is optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, and C<sub>3</sub>-C<sub>4</sub>cycloalkyl; R<sup>5a</sup> and R<sup>5b</sup> are, independently of each other, selected from hydrogen, halogen, -CN, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>3</sub>-C<sub>4</sub>cycloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, and C<sub>1</sub>-C<sub>3</sub>haloalkoxy; such as R<sup>5a</sup> and R<sup>5b</sup> are hydrogen.

Compounds of formula (I) are made available, where, A is CH or nitrogen, for instance A is CH; X is oxygen; R<sup>1</sup> is hydrogen, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>cyanoalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy-C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>2</sub>-C<sub>4</sub>alkenyl, C<sub>2</sub>-C<sub>4</sub>haloalkenyl, C<sub>2</sub>-C<sub>4</sub>alkynyl, C<sub>2</sub>-C<sub>4</sub>haloalkynyl, C<sub>3</sub>-C<sub>4</sub>cycloalkyl-C<sub>1</sub>-C<sub>2</sub>alkyl-, benzyloxycarbonyl, or benzyl; such as R<sup>1</sup> is hydrogen, methyl, ethyl, allyl, propargyl or cyclopropyl-methyl; R<sup>2a</sup> is chlorine, bromine, trifluoromethyl, or difluoromethoxy; R<sup>2b</sup> is bromine, iodine, difluoromethyl, trifluoromethyl, difluoromethoxy, trifluoromethoxy, trifluoromethylsulfonyl, 1-cyano-1-methyl-ethyl, or 1-cyanocyclopropyl; R<sup>3</sup> is C<sub>1</sub>-C<sub>3</sub>alkyl or C<sub>1</sub>-C<sub>3</sub>haloalkyl, such as R<sup>3</sup> is methyl; R<sup>4c</sup> is -C(O)C<sub>1</sub>-C<sub>6</sub>alkyl, or -C(O)OC<sub>1</sub>-C<sub>6</sub>alkyl, each optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, and C<sub>1</sub>-C<sub>3</sub>alkoxy; and R<sup>5a</sup> is hydrogen, halogen, CN, C<sub>1</sub>-C<sub>3</sub>alkyl or C<sub>1</sub>-C<sub>3</sub>alkoxy; R<sup>5b</sup> is hydrogen, halogen or C<sub>1</sub>-C<sub>3</sub>alkoxy; such as R<sup>5a</sup> and R<sup>5b</sup> are hydrogen.

Compounds of formula (I) are also made available, where A is CH or nitrogen, preferably A is CH; X is oxygen or sulfur, preferably X is oxygen; R<sup>1</sup> is hydrogen, methyl, or cyclopropyl-methyl; R<sup>2a</sup> is chlorine, bromine, trifluoromethyl, or difluoromethoxy; R<sup>2b</sup> is bromine, iodine, difluoromethyl, trifluoromethyl, difluoromethoxy, trifluoromethoxy, trifluoromethylsulfonyl, 1-cyano-1-methyl-ethyl, or 1-cyanocyclopropyl; R<sup>3</sup> is methyl; R<sup>4c</sup> is hydrogen, methyl, ethyl, 2,2-difluoroethyl, cyclopropylmethyl, propargyl, or pyrimidin-2-ylmethyl; and R<sup>5a</sup> and R<sup>5b</sup> are hydrogen.

Further compounds of formula (I) are made available, where A is nitrogen; X is oxygen or sulfur, preferably X is oxygen; R<sup>1</sup> is hydrogen, methyl, or cyclopropyl-methyl; R<sup>2a</sup> is chlorine, bromine, trifluoromethyl, or difluoromethoxy; R<sup>2b</sup> is bromine, iodine, difluoromethyl, trifluoromethyl, difluoromethoxy, trifluoromethoxy, trifluoromethylsulfonyl, 1-cyano-1-methyl-ethyl, or 1-cyanocyclopropyl; R<sup>3</sup> is methyl; R<sup>4c</sup> is hydrogen, methyl, ethyl, 2,2-difluoroethyl, cyclopropylmethyl, propargyl, or pyrimidin-2-ylmethyl; and R<sup>5a</sup> and R<sup>5b</sup> are hydrogen.

Further compounds of formula (I) are made available, where A is CH; X is oxygen; R<sup>1</sup> is hydrogen or methyl; R<sup>2a</sup> is chlorine, bromine, or difluoromethoxy, such as R<sup>2a</sup> is chlorine; R<sup>2b</sup> is bromine, iodine, or trifluoromethyl, such as R<sup>2b</sup> is trifluoromethyl; R<sup>3</sup> is methyl; R<sup>4c</sup> is hydrogen, methyl, or ethyl; and R<sup>5a</sup> and R<sup>5b</sup> are hydrogen.

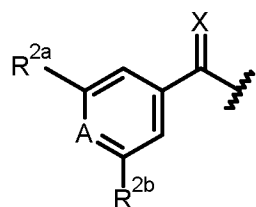
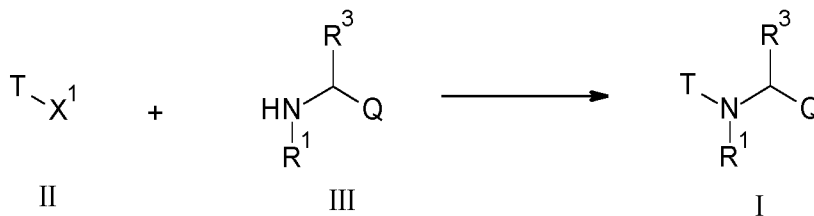
Compounds of formula (I) can be prepared by those skilled in the art following known methods. More specifically compounds of formula (I), compounds of formula (I'), and intermediates therefor, can

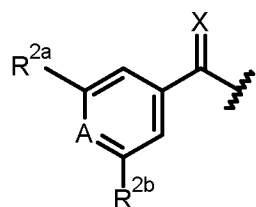
be prepared as described below in the schemes and examples. Certain stereogenic centers have been left unspecified for the clarity and are not intended to limit the teaching of the schemes in any way.

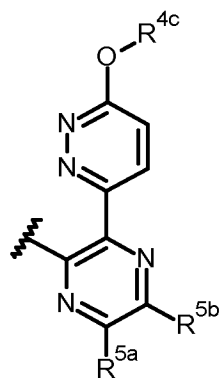
Compounds of formula (I) can be made, for example, as shown in scheme 1.

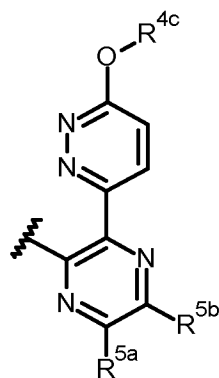
5

Scheme 1:



where T is , and A, R<sup>2a</sup>, R<sup>2b</sup> and X have the same meaning as given above for compounds of the formula (I), and

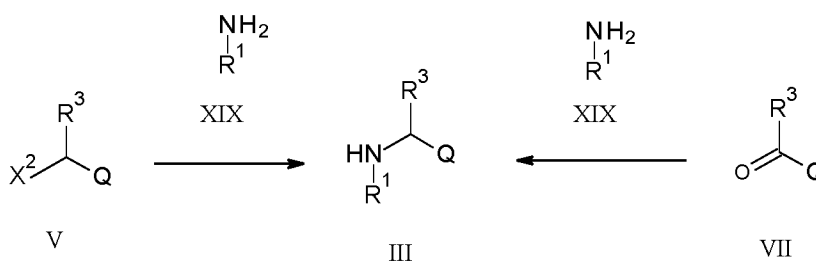


10 where Q is , and R<sup>4c</sup>, R<sup>5a</sup> and R<sup>5b</sup> have the same meaning as given above for compounds of the formula (I), and where the staggered line represents the connection to the remainder of the compounds of the formula (I), (Ia), (Ib), (Ic), (Id), (Id-1), (If), (II), (III), (IV), (IVa), (V), (VII), (VIII), (XVII) in Schemes 1 to 9.

15 Compounds of the formula (I) can be made, for example, by reaction of a compound of the formula (II), wherein X<sup>1</sup> is hydroxy or a leaving group, such as a halogen or sulfonate, for instance chloride, and wherein T has the meaning given above, with a compound of formula (III), or a salt thereof (such as a hydrohalide salt, preferably a hydrochloride or a hydrobromide salt, or a trifluoroacetic acid salt, or any other equivalent salt), wherein R<sup>1</sup> and R<sup>3</sup> have the same meaning as given above for  
 20 compounds of the formula (I), and wherein Q has the meaning given above. In the case that X<sup>1</sup> is hydroxy, it may be advantageous to carry out the reaction in the presence of a dehydration reagent, for instance a peptide coupling reagent, such as, for example, a carbodiimide or propanephosphonic acid

cyclic anhydride (T3P®). Such reactions can be conducted neat or in a solvent, preferably in a solvent, such as an organic solvent, for instance acetonitrile, tetrahydrofuran, 2-methyltetrahydrofuran, ethyl acetate, N,N-dimethylacetamide or N,N-dimethylformamide, in a temperature range of -100 to +300 °C, preferably between ambient temperature and 200 °C, with or without the presence of a catalyst, for instance an acylation catalyst, such as 4-dimethylaminopyridine (DMAP), and with or without the addition of a base, such as an inorganic base, for instance sodium, potassium or cesium carbonate, or an organic base, such as, for example, triethylamine, diisopropylethylamine or pyridine. Compounds of the formula (II) are either known, or they can be prepared by methods known to a person skilled in the art. In particular, compounds of the formula (II) wherein X<sup>1</sup> is a leaving group, such as a halogen, for instance chloride, can be formed by treatment of compounds of formula (II) wherein X<sup>1</sup> is hydroxy with, for example, oxalyl chloride or thionyl chloride, in the presence of catalytic quantities of N,N-dimethylformamide (DMF), in inert solvents such as for instance dichloromethane (DCM) or tetrahydrofuran (THF), at temperatures between 0°C to 100°C, preferably around 25°C. Such methods are known to those skilled in the art and described for example in Tetrahedron 2005, 61 (46), 10827-10852.

Scheme 2:

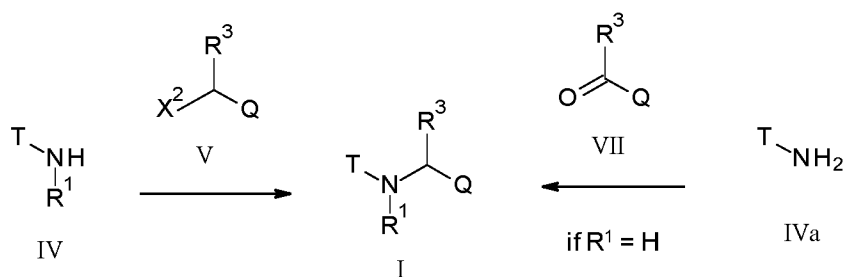


Compounds of formula (III), or a salt thereof, can be made, for example, as shown in scheme 2. Treatment of a compound of the formula (V), wherein Q has the same meaning as given above in Scheme 1, and wherein R<sup>3</sup> has the same meaning as given above for compounds of the formula (I) and X<sup>2</sup> is a leaving group, such as a halogen or sulfonate, for instance bromide, with an amine of the formula (XIX), or a salt thereof, wherein R<sup>1</sup> has the same meaning as given above for compounds of the formula I, gives compounds of the formula (III), wherein Q has the same meaning as given above in Scheme 1, and R<sup>1</sup> and R<sup>3</sup> have the same meaning as given above for compounds of the formula I. The reaction can be conducted neat or in a solvent, preferably in a solvent, such as an organic solvent, for instance acetonitrile, in a temperature range of -100 to +300 °C, preferably between ambient temperature and 200 °C, with or without the addition of a base, such as an inorganic base, for instance potassium carbonate, or an organic base, such as, for example, triethylamine.

Alternatively, treatment of a compound of the formula (VII), wherein Q has the same meaning as given above in Scheme 1, and wherein R<sup>3</sup> has the same meaning as given above for compounds of the formula (I), with an amine of the formula (XIX), or a salt thereof, wherein R<sup>1</sup> has the same meaning as given above for compounds of the formula I, gives compounds of the formula (III), wherein Q has the same meaning as given above in Scheme 1, and R<sup>1</sup> and R<sup>3</sup> have the same meaning as given above for

compounds of the formula I. This reaction is done in the presence of a reducing agent, such as for example hydrogen, or a hydride, such as sodium borohydride, with or without a catalyst, such as a hydrogenation catalyst, for example palladium on carbon, with or without the presence of an acid, such as acetic acid, or a Lewis acid, such as zinc bromide or titanium(IV) isopropoxide, in a solvent or without  
 5 a solvent, such as, for instance, methanol. The reaction can be conducted in a temperature range of -100 to +300 °C, preferably between ambient temperature and 200 °C. Such methods, and the range of conditions to perform them, for the alkylation of amines and for the reductive alkylation of amines (e.g. in the presence of NaBH(OAc)<sub>3</sub> or NaBH<sub>3</sub>CN, in a suitable solvent, preferably in acetic acid, at room temperature, analogous to WO2002/088073; or alternatively, by the use of a combination of Ti(i-OiPr)<sub>4</sub>  
 10 and NaBH<sub>4</sub> as described in Synthesis 2003 (14), 2206) are well known to a person skilled in the art. The amines of formula (XIX), or a salt thereof, wherein R<sup>1</sup> has the same meaning as given above for compounds of the formula (I), are either known, or they can be prepared by methods known to a person skilled in the art.

15 Scheme 3:

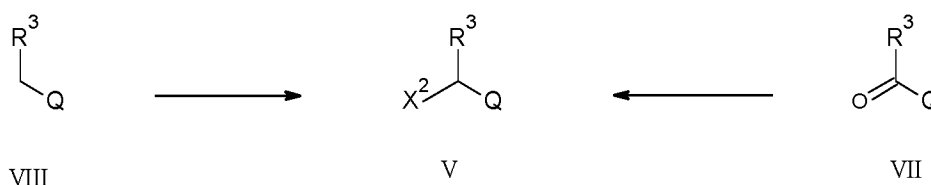


Alternatively, compounds of formula (I) can be made, for example, by reaction of compound of the formula (IV), wherein T has the same meaning as given above in Scheme 1, and R<sup>1</sup> has the same meaning as given above for compounds of the formula (I), with a compound of the formula (V), wherein  
 20 Q has the same meaning as given above in Scheme 1, and wherein R<sup>3</sup> has the same meaning as given above for compounds of the formula (I), and X<sup>2</sup> is a leaving group, such as a halogen or sulfonate, for instance chloride or bromide. The reaction can be conducted neat or in a solvent, preferably in a solvent, such as an organic solvent, for instance acetonitrile, in a temperature range of -100 to +300 °C, preferably between ambient temperature and 200 °C, with or without the addition of a base, such as an  
 25 inorganic base, for instance potassium carbonate, or an organic base, such as, for example, triethylamine. Such methods for the alkylation of amines, and the range of conditions to perform them, are well known to a person skilled in the art.

Alternatively, a compound of the formula (I) can be made by reaction of a compound of the formula (IVa), wherein T has the same meaning as given above in Scheme 1, with a compound of the  
 30 formula (VII), wherein Q has the same meaning as given above in Scheme 1, and wherein R<sup>3</sup> has the same meaning as given above for compounds of the formula (I). This reaction is done in the presence of a reducing agent, such as for example hydrogen, or a hydride, such as sodium borohydride, with or without a catalyst, such as a hydrogenation catalyst, for example palladium on carbon, with or without

the presence of an acid, such as acetic acid, or a Lewis acid, such as zinc bromide, in a solvent or without a solvent, such as, for instance, methanol. The reaction can be conducted in a temperature range of -100 to +300 °C, preferably between ambient temperature and 200 °C. Such methods for the reductive alkylation of amines, and the range of conditions to perform them, are well known to a person skilled in the art.

Scheme 4:



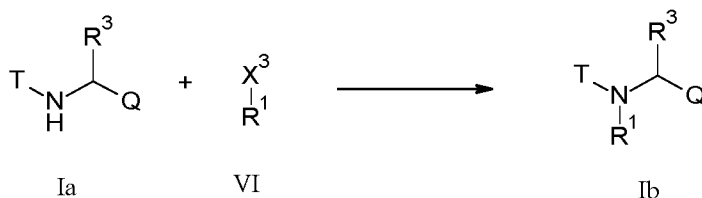
Compounds of formula (V) can be made, for example, as shown in scheme 4. Treatment of a compound of the formula (VIII) with a halogenating agent, such as chlorine or bromine or N-bromosuccinimide, for example, gives compound of the formula (V), wherein the leaving group X<sup>2</sup> is a halogen, for instance chloride or bromide. This reaction is done with or without a solvent, preferably in a solvent, with or without an additive, such as a radical starter, such as, for example, benzoyl peroxide or azoisobutyronitrile. The reaction can be done with or without exposure to visible light, or to UV light, and it can be conducted in a temperature range of -100 to +300 °C, preferably between ambient temperature and 200 °C.

Alternatively, a compound of the formula (VII) can be treated with a reducing agent, followed by reaction with a sulfonyl chloride, for instance methanesulfonyl chloride, to give a compound of the formula (V), wherein the leaving group X<sup>2</sup> is a sulfonate, for instance a mesylate. This reaction can be done in a solvent, or without a solvent, in the presence of a base, such as an inorganic base, for instance potassium carbonate, or an organic base, such as an amine base, for instance trimethylamine, or without a base, and it can be conducted in a temperature range of -100 to +300 °C, preferably between ambient temperature and 200 °C. A suitable reducing agent could be, for example, hydrogen, or a hydride, such as sodium borohydride, with or without a catalyst, such as a hydrogenation catalyst, for example palladium on carbon, with or without the presence of an acid, such as acetic acid, or a Lewis acid, such as zinc bromide, in a solvent or without a solvent, such as, for instance, methanol. The reaction can be conducted in a temperature range of -100 to +300 °C, preferably between ambient temperature and 200 °C. Such methods for the halogenation, the reduction of carbonyl compounds and the sulfonylation of alcohols, and the range of conditions to perform them, are well known to a person skilled in the art. The compounds of the formula (VII) and the compounds of formula (VIII) are either known, or they can be prepared by methods known to a person skilled in the art.

Scheme 5:

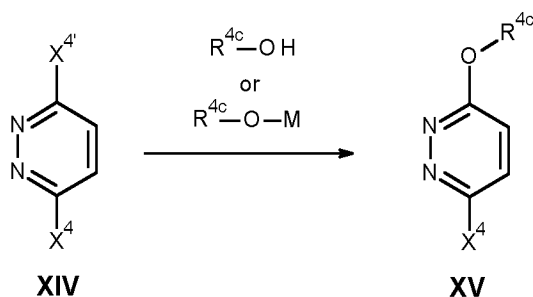


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Alternatively, compounds of formula (Ib), wherein T and Q have the same meaning as given above in Scheme 1, and R<sup>1</sup> and R<sup>3</sup> have the same meaning as given above for compounds of the formula (I), except that R<sup>1</sup> is different from hydrogen, can be made, for example, as shown in scheme 5. A compound of the formula (Ia), wherein T and Q have the same meaning as given above in Scheme 1, and R<sup>3</sup> has the same meaning as given above for compounds of the formula (I), can be reacted with a compound of the formula (VI), wherein R<sup>1</sup> has the same meaning as given above for compounds of the formula (I), except that R<sup>1</sup> is different from hydrogen, and wherein X<sup>3</sup> is a leaving group, such as a halogen or sulfonate, for instance a chloride, bromide, iodide or mesylate, to give a compound of formula (Ib). This reaction can be conducted neat or in a solvent, preferably in a solvent, such as an organic solvent, for instance acetonitrile, N,N-dimethylformamide (DMF) or N,N-dimethylacetamide (DMA), or mixtures thereof, in a temperature range of -100 to +300 °C, preferably between ambient temperature and 200 °C, with or without the addition of a base, such as an inorganic base, for instance sodium, potassium or cesium carbonate, or an organic base, such as, for example, triethylamine, diisopropylethylamine or pyridine. Such methods for the alkylation of amines, and the range of conditions to perform them, are well known to a person skilled in the art. Compounds of the formula (VI), wherein R<sup>1</sup> has the same meaning as given above for compounds of the formula (I), except that R<sup>1</sup> is different from hydrogen, and wherein X<sup>3</sup> is a leaving group, such as a halogen or sulfonate, for instance a chloride, bromide, iodide or mesylate, are either known, or they can be prepared by methods known to a person skilled in the art.

Scheme 6:



Compounds of the formula (XV), in which R<sup>4c</sup> has the same meaning as defined above for compounds of the formula (I), except that R<sup>4c</sup> is different from hydrogen, and X<sup>4</sup> is a leaving group, such as for example a halogen, a sulfonate, C<sub>1</sub>-C<sub>4</sub>-sulfanyl, C<sub>1</sub>-C<sub>4</sub>-sulfinyl or C<sub>1</sub>-C<sub>4</sub>-sulfonyl, can be made (Scheme 6) by treatment of compounds of the formula (XIV), in which X<sup>4</sup> and X<sup>4'</sup> are, independently of each other, a leaving group, such as for example a halogen, a sulfonate, C<sub>1</sub>-C<sub>4</sub>-sulfanyl, C<sub>1</sub>-C<sub>4</sub>-sulfinyl or C<sub>1</sub>-C<sub>4</sub>-sulfonyl, with a reagent of the formula R<sup>4c</sup>-OH, or a salt thereof, wherein R<sup>4c</sup> has the same

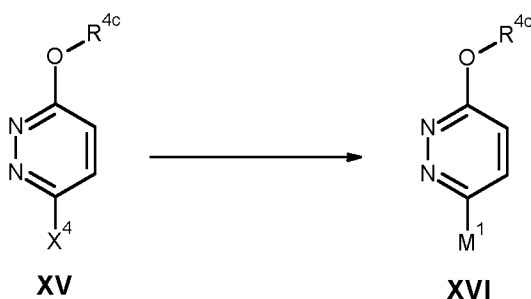
meaning as defined above for compounds of the formula (I), except that  $R^{4c}$  is different from hydrogen. This reaction can be conducted neat or in a solvent, preferably in a solvent, such as an organic solvent, for instance tetrahydrofuran, dioxane, acetonitrile, N,N-dimethylformamide (DMF) or N,N-dimethylacetamide (DMA), or mixtures thereof, in a temperature range of -100 to +300 °C, preferably  
 5 between ambient temperature and 200 °C, optionally under microwave conditions, with or without the addition of a base, such as an inorganic base, for instance alkali metal carbonates such as sodium, potassium or cesium carbonate, or alkali metal hydrides such as sodium hydride, or alkali metal hydroxides such as sodium hydroxide and potassium hydroxide, or sodium or potassium tert-butoxide, or an organic base, such as, for example, triethylamine, diisopropylethylamine or pyridine. Such  
 10 alkoxylation methods, and the range of conditions to perform them, are well known to a person skilled in the art, and described for example in Journal of Heterocyclic Chemistry (2013), 50(5), 1165-1173. Some compounds of the formula (XV) are known or even commercially available.

Examples of salts of the compound of formula  $R^{4c}$ -OH include compounds of formula  $R^{4c}$ -O-M, wherein  $R^{4c}$  has the same meaning as defined above for compounds of the formula (I), except that  $R^{4c}$   
 15 is different from hydrogen, and wherein M is, for example, sodium or potassium. Alcohols  $R^{4c}$ -OH may be used as solvent when preparing compounds of the formula (XV) with such a reagent of the formula  $R^{4c}$ -O-M, as described for example in J. Org. Chem. 1995, 60, 748-750.

Compounds of formula  $R^{4c}$ -OH, salts thereof of formula  $R^{4c}$ -O-M, and compounds of the formula (XIV) are known or even commercially available, or they can be made by known methods.

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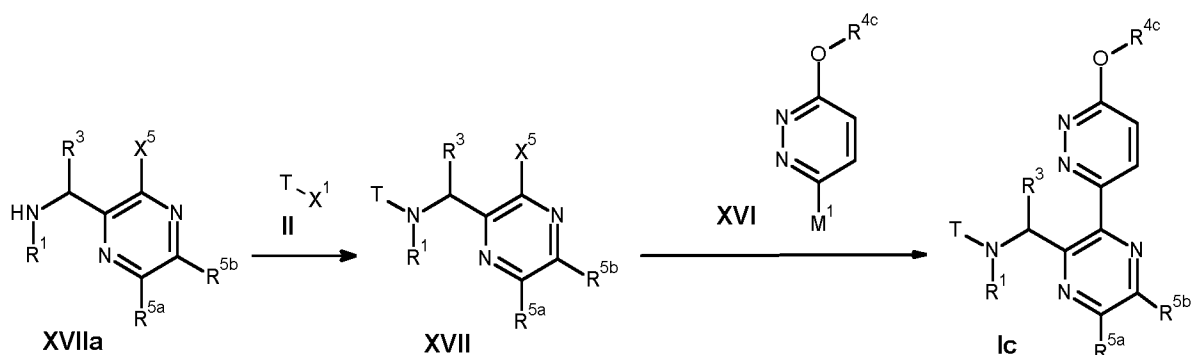
Scheme 7:



Compounds of the formula (XVI), in which  $R^{4c}$  has the same meaning as defined above for compounds of the formula (I), and  $M^1$  is a metal-containing substituent, for instance a boron substituent  
 25 or a tin substituent, such as, for example, tributylstannyl ( $M^1$  is  $-\text{SnBu}_3$ ), borono ( $M^1$  is  $-\text{B}(\text{OH})_2$ ) or a boronate such as 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl, can be made (Scheme 7) by treatment of compounds of the formula (XV), in which  $R^{4c}$  has the same meaning as defined above for compounds of the formula (I), and  $X^4$  is a leaving group, such as for example a halogen or a sulfonate, with tributyl(tributylstannyl)stannane, or with hypoboric acid, or with 4,4,5,5-tetramethyl-2-(4,4,5,5-  
 30 tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolane (also known as bis(pinacolato)diboron). The reaction can be done in the presence of a catalyst, such as a metal catalyst, for instance a palladium catalyst, for example palladium acetate, and in the presence of a ligand, such as a phosphine ligand, for example 2-dicyclohexyl-phosphino-2',4',6'-triisopropylbiphenyl (XPhos). The reaction can be done in

the presence of a base, such as an alkoxide or a carboxylate base, for instance potassium acetate. The reaction can be done neat or in a solvent, for instance in dioxane or toluene as a solvent, at a temperature between -100 °C and 200 °C, more commonly between 0 °C and 150 °C, such as, for example, at 100 °C. Some compounds of the formula (XVI) are known or even commercially available, or they can be made by known methods.

Scheme 8:

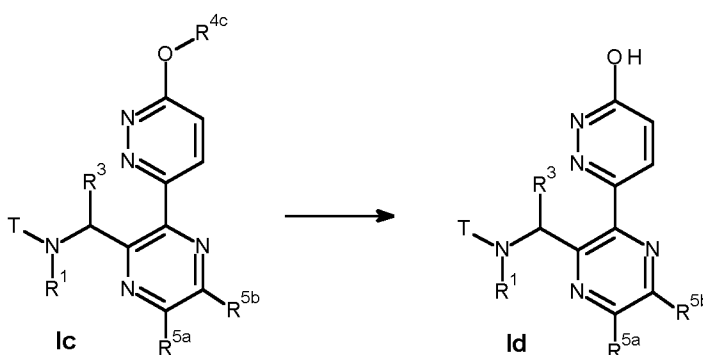


Compounds of the formula (Ic), wherein T has the same meaning as given above in Scheme 1, and wherein  $R^1$ ,  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as given above for compounds of the formula (I), can be made (Scheme 8) from compounds of the formula (XVII), wherein T has the same meaning as given above in Scheme 1, and wherein  $R^1$ ,  $R^3$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as given above for compounds of the formula (I), and in which  $X^5$  is a leaving group such as for example chlorine, bromine or iodine, by reaction with compounds of the formula (XVI), in which  $R^{4c}$  has the same meaning as defined above for compounds of the formula (I), and  $M^1$  is a metal-containing substituent which has the same meaning as given above in Scheme 7. The reaction can be done in the presence of a catalyst, such as a palladium catalyst, for instance 1,1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloride ( $PdCl_2dppf$ ), in the presence of a base, such as a carbonate base, for example cesium carbonate  $Cs_2CO_3$ , or such as a carboxylate base, for instance potassium acetate. The reaction can be done neat or in a solvent, for instance in dioxane or toluene as a solvent, at a temperature between -100 °C and 200 °C, more commonly between 0 °C and 150 °C, such as, for example, at 85 °C. Such reactions known as Suzuki-Miyaura or Stille cross-coupling reactions are familiar to a person skilled in the art.

Compounds of the formula (XVII), wherein T has the same meaning as given above in Scheme 1, and wherein  $R^1$ ,  $R^3$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as given above for compounds of the formula (I), and in which  $X^5$  is a leaving group such as for example chlorine, bromine or iodine, can be made by reacting compounds of the formula (XVIIa), or a salt thereof, wherein  $R^1$ ,  $R^3$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as given above for compounds of the formula (I), and in which  $X^5$  is a leaving group such as for example chlorine, bromine or iodine, with compounds of the formula (II), wherein T has the same meaning as given above in Scheme 1, and wherein  $X^1$  is a leaving group, such as a halogen or sulfonate, for instance chloride, under analogous conditions already described above in Scheme 1.

Compounds of the formula (XVIIa), or a salt thereof, wherein  $R^1$ ,  $R^3$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as given above for compounds of the formula (I), and in which  $X^5$  is a leaving group such as for example chlorine, bromine or iodine, are known from the literature, for instance from WO2021/170881, WO2021/037614, WO2020/208036, WO2020/201398 or WO2020/070049, or they can be made in analogy to descriptions found therein.

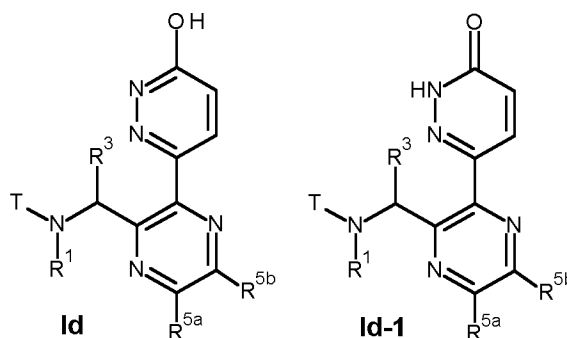
Scheme 9:



Compounds of the formula (Id), a subset of compounds of formula (I) wherein  $R^{4c}$  is hydrogen, and wherein T has the same meaning as given above in Scheme 1, and wherein  $R^1$ ,  $R^3$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as given above for compounds of the formula (I), can be made (Scheme 9) by treatment of compounds of the formula (Ic), wherein T has the same meaning as given above in Scheme 1, and wherein  $R^1$ ,  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as given above for compounds of the formula (I), preferably in this transformation  $R^{4c}$  is methyl or ethyl (even more preferably  $R^{4c}$  is methyl), with an acid such hydrochloric acid, for example in form of a solution of gaseous hydrochloric acid in an inert organic solvent (for instance dioxane), in the presence of a suitable solvent such as dichloromethane, tetrahydrofuran or dioxane, and in a temperature range of 0°C to 90°C, for instance between 40 to 60°C.

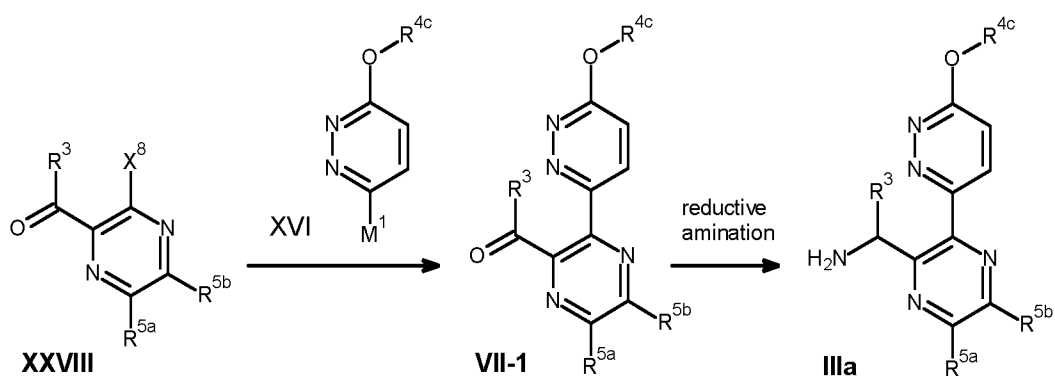
Alternatively, and when  $R^{4c}$  in (Ic) is methyl, boron tribromide ( $BBr_3$ ) may be used as a reagent for this ether cleavage (demethylation), under conditions known to a person skilled in the art.

Compounds of the formula (Id), a subset of compounds of formula (I) wherein  $R^{4c}$  is hydrogen, and wherein T has the same meaning as given above in Scheme 1, and wherein  $R^1$ ,  $R^3$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as given above for compounds of the formula (I), may exist in a different tautomeric form (Id-1):



This invention covers all such tautomers and mixtures thereof in all proportions.

Scheme 10:



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Compounds of the formula (IIIa), or a salt thereof (such as a hydrohalide salt, preferably a hydrochloride or a hydrobromide salt, or a trifluoroacetic acid salt, or any other equivalent salt), a subset of compounds of formula (III) above in which  $R^1$  is hydrogen, wherein  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I), may be made (Scheme 10) from compounds of the formula (VII-1), a subset of compounds of formula (VII), wherein  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I), by a reductive amination reaction under analogous conditions already described above in Scheme 2 (transformation VII into III).

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Compounds of the formula (VII-1), a subset of compounds of formula (VII), wherein  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I), may be made by treatment of compounds of the formula (XXVIII), wherein  $R^3$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I), and in which  $X^8$  is a leaving group, such as a halogen, for instance a chloride, bromide or iodide, with a compound of the formula (XVI), wherein  $R^{4c}$  has the same meaning as defined above for compounds of the formula (I) and  $M^1$  is a metal-containing substituent which has the same meaning as given above in Scheme 7, under similar conditions already described above in Scheme 8 (transformation XVII + XVI into Ic). Compounds of the formula (XXVIII), wherein  $R^3$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I), and in which  $X^8$  is a leaving group, such as a halogen, for instance a chloride, bromide or iodide, are known or even commercially available, or they can be made by known methods.

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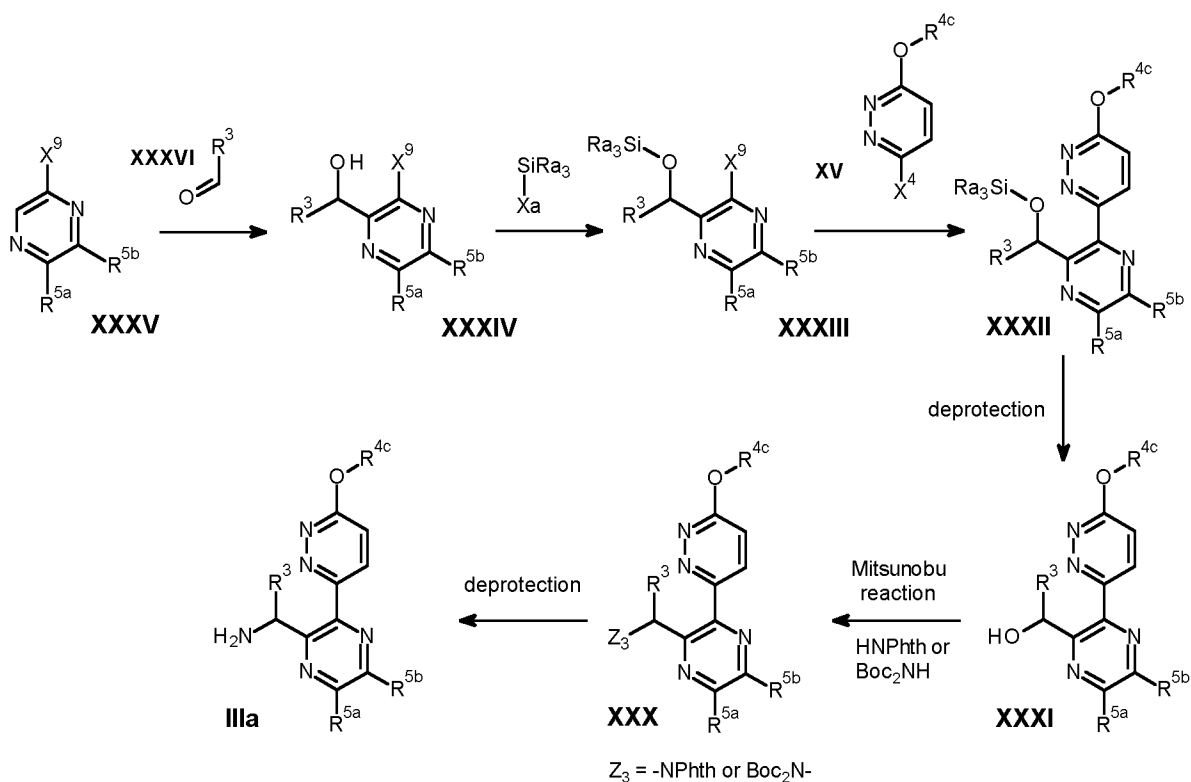
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Alternatively, compounds of the formula (VII-1), a subset of compounds of formula (VII), wherein  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I), may

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be made by oxidation of compounds of the formula (XXXI) described below (Scheme 11), wherein  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I), for example using Dess-Martin periodinane (or similar hypervalent iodine reagents), commonly conducted in chlorinated solvents, such as dichloromethane or chloroform, at temperatures between 0 and 50 °C, preferably around room temperature.

Scheme 11:



Alternatively, compounds of the formula (IIIa), or a salt thereof (such as a hydrohalide salt, preferably a hydrochloride or a hydrobromide salt, or a trifluoroacetic acid salt, or any other equivalent salt), a subset of compounds of formula (III) above in which  $R^1$  is hydrogen, wherein  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I), can be made (Scheme 14) from compounds of the formula (XXX), wherein  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I) and  $Z_3$  is -NPhth (N-phthalimide group) or -NBoc<sub>2</sub> (N-bis(*tert*-butyloxycarbonyl) group), typically by treatment with either hydrazine (preferably hydrazine hydrate or hydrazine monohydrate) in an alcohol solvent such as ethanol or isopropanol and in a temperature range of 0°C to 90°C, for instance at 80°C ( $Z_3$  is -NPhth), or with an acid such as trifluoroacetic acid or hydrochloric acid in the presence of a suitable solvent such as dichloromethane, tetrahydrofuran or dioxane ( $Z_3$  is -NBoc<sub>2</sub>), under deprotection conditions known to a person skilled in the art, and described in the literature, such as for example in: Protective Groups in Organic Synthesis, 3rd Edition Theodora W. Green (The Rowland Institute for Science) and Peter G. M. Wuts (Pharmacia and Upjohn Company), John Wiley & Sons, Inc., New York, NY. 1999, ISBN 0-471-16019-9.

Compounds of the formula (XXX), wherein  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I) and  $Z_3$  is -NPhth (N-phthalimide group) or -NBoc<sub>2</sub> (N-bis(*tert*-butoxycarbonyl) group), can be made from compounds of the formula (XXXI), wherein  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I), by a Mitsunobu reaction. Such a reaction involves treating compounds of the formula (XXXI) with an azodicarboxylate, such as diethyl azodicarboxylate or diisopropyl azodicarboxylate, in the presence of a phosphine, such as triphenylphosphine or tributylphosphine, and of an amine such as phthalimide (HNPhth) or bis(*tert*-butoxycarbonyl)amine (HNBoc<sub>2</sub>), in an inert solvent, such as for example tetrahydrofuran, and in a temperature range of -10°C to 60°C, for instance between 0°C and 30°C. Mitsunobu reactions (and conditions to perform them) are known by those skilled in the art and described for instance in *Chem. Rev.* 2009, 109, 2551-2651.

Compounds of the formula (XXXI), wherein  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I), can be made from silyl ether compounds of the formula (XXXII), wherein  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I), and in which each of the group Ra is independently C<sub>1</sub>-C<sub>4</sub>alkyl, by deprotection, for instance by treatment with fluoride, for example with tetrabutylammonium fluoride, in an inert solvent, such as for example tetrahydrofuran. The reaction can be done in a temperature range of -10°C to 80°C, for instance between 0°C and 30°C. Such deprotection reactions are known to a person skilled in the art, and described in the literature, for instance in: Protective Groups in Organic Synthesis, 3rd Edition Theodora W. Green (The Rowland Institute for Science) and Peter G. M. Wuts (Pharmacia and Upjohn Company). John Wiley & Sons, Inc., New York, NY. 1999, ISBN 0-471-16019-9.

Alternatively, compounds of the formula (XXXI), wherein  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I), may be made by reduction of compounds of the formula (VII-1) described above (Scheme 10), a subset of compounds of formula (VII), wherein  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I), for example with sodium borohydride NaBH<sub>4</sub>, under conditions known to a person skilled in the art (see for example WO2012/082997, p. 141), preferably in MeOH as solvent.

Compounds of the formula (XXXII), wherein  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I), except that  $R^{4c}$  is different from hydrogen, and in which each of the group Ra is independently C<sub>1</sub>-C<sub>4</sub>alkyl, can be made from silyl ether compounds of the formula (XXXIII), wherein  $R^3$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I),  $X^9$  is a leaving group, such as a halogen, for instance a bromide or iodide, and in which each of the group Ra is independently C<sub>1</sub>-C<sub>4</sub>alkyl, by metalation, such as by treatment with a Turbo Grignard reagent (iPrMgCl·LiCl) or with butyl lithium. Such metalations are known to a person skilled in the art, and described in the literature, for instance in Carey, Francis A. (2007), "Organometallic compounds of Group I and II metals", Advanced Organic Chemistry: Reaction and Synthesis Pt. B (Kindle ed.), Springer, ISBN 978-0-387-44899-2. The lithium- or magnesium species thus generated can be transmetalated, for instance with a zinc halide, for example zinc chloride, and subsequently coupled with compounds of the formula (XV), wherein  $R^{4c}$  has the same meaning as defined above for

compounds of the formula (I), except that  $R^{4c}$  is different from hydrogen, and  $X^4$  is a leaving group, such as a halogen, for example a bromide or iodide, in the presence of a catalyst, for instance a palladium catalyst, for example tris(dibenzylideneacetone)dipalladium(0), and of a ligand, for instance a phosphine ligand, such as for example tri(2-furyl)phosphine, in an inert solvent, such as for example tetrahydrofuran, optionally in the presence of a co-solvent such as toluene. Alternatively, (2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl) [2-(2'-amino-1,1'-biphenyl)]palladium(II) methanesulfonate (SPhos Pd G3, a stable phosphine-ligated palladium precatalyst), and related palladacycle precatalysts, can also be used as a catalyst. The reaction can be done in a temperature range of  $-100^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ , for instance between  $-78^{\circ}\text{C}$  and  $80^{\circ}\text{C}$ . This transformation is known to a person skilled in the art, for instance as Negishi cross-coupling reaction, and described in the literature, for example in: Jie Jack Li, Name Reactions, A Collection of Detailed Mechanisms and Synthetic Applications, Springer, ISBN: 978-3-030-50865-4.

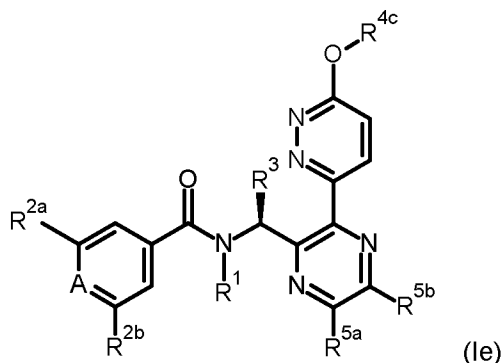
Compounds of the formula (XXXIII), wherein  $R^3$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I),  $X^9$  is a leaving group, such as a halogen, for instance a bromide or iodide, and in which each of the group  $R_a$  is independently  $C_1$ - $C_4$ alkyl, can be made from compounds of the formula (XXXIV), wherein  $R^3$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I), and  $X^9$  is a leaving group, such as a halogen, for instance a bromide or iodide, by treatment with a silylating agent of the formula  $R_{a3}Si-X_a$ , wherein  $X_a$  is a leaving group, such as for example chloride, bromide, iodide or triflate, and in which each of the group  $R_a$  is independently  $C_1$ - $C_4$ alkyl ( $R_{a3}Si$  is trialkylsilyl, for instance dimethyl-tert-butylsilyl; in compounds  $R_{a3}Si-X_a$ ,  $R_a$  is a straight or branched  $C_1$ - $C_4$ alkyl, such as methyl or tert-butyl), in the presence of a base, such as an amine base, for instance imidazole, in an inert solvent, such as for example tetrahydrofuran. The reaction can be done in a temperature range of  $0^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ , for instance between  $10^{\circ}\text{C}$  and  $80^{\circ}\text{C}$ . Such silylation reactions are known to a person skilled in the art, and described in the literature, such as for example in: Protective Groups in Organic Synthesis, 3rd Edition Theodora W. Green (The Rowland Institute for Science) and Peter G. M. Wuts (Pharmacia and Upjohn Company). John Wiley & Sons, Inc., New York, NY. 1999, ISBN 0-471-16019-9.

Compounds of the formula (XXXIV), wherein  $R^3$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I), and  $X^9$  is a leaving group, such as a halogen, for instance a bromide or iodide, can be made from compounds of the formula (XXXV), wherein  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I), and  $X^9$  is a leaving group, such as a halogen, for instance a bromide or iodide, by treatment with a base, such as a lithium amide base, for instance lithium 2,2,6,6-tetramethylpiperidide, followed by reaction of the lithiated species with aldehyde compounds of the formula (XXXVI), wherein  $R^3$  has the same meaning as given above in formula (I). This reaction can be done neat or in a solvent, for instance in an organic solvent, such as for example tetrahydrofuran as a solvent. The reaction can be done in a temperature range of  $-100^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ , for instance between  $-80^{\circ}\text{C}$  and  $0^{\circ}\text{C}$ , for example at  $0^{\circ}\text{C}$  or at  $-78^{\circ}\text{C}$ . Compounds of the formula (XXXV), wherein  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I), and  $X^9$  is a leaving group, such as a halogen, for instance a bromide or iodide, and compounds of the formula



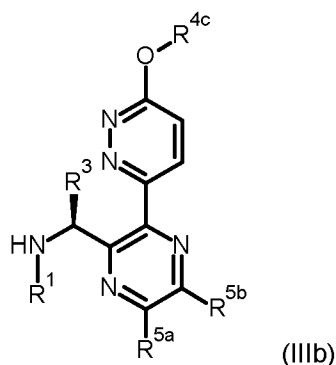
(XXXVI), wherein  $R^3$  has the same meaning as given above in formula (I), are known or even commercially available, or they can be made by known methods.

Compounds of the formula (Ie), a subset of compounds of the formula (I'), wherein A,  $R^1$ ,  $R^{2a}$ ,  $R^{2b}$ ,  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as given above for compounds of the formula (I)

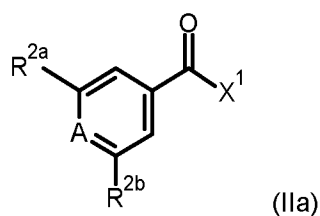


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may be prepared by reaction of an amine of the formula (IIIb), or a salt thereof



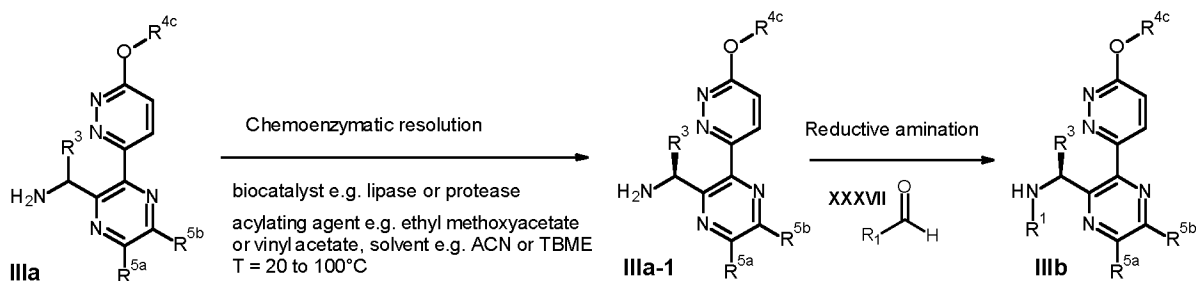
wherein  $R^1$ ,  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  are as described in formula (I), with a compound of the formula (IIa), a subset of compounds of the formula (II),



10

wherein A,  $R^{2a}$  and  $R^{2b}$  are as described in formula I and  $X^1$  is hydroxy or a leaving group, such as a halogen or a sulfonate, for instance chloride, under conditions already described in Scheme 1.

#### Scheme 12:

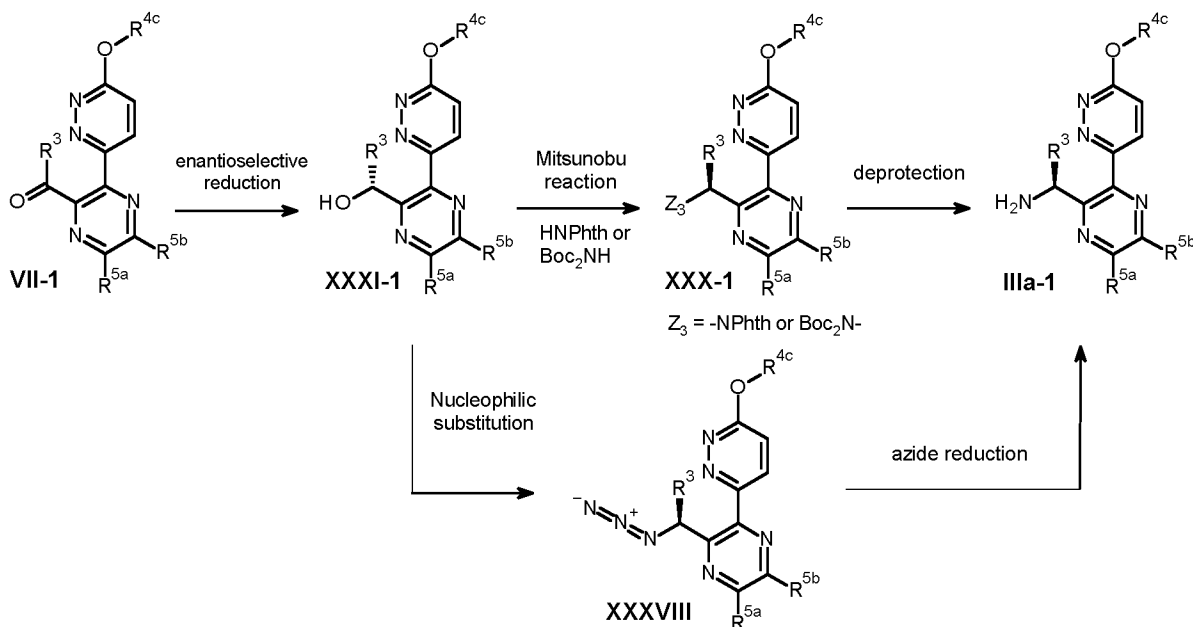


15

Compounds of formula (IIIb), or a salt thereof (such as a hydrohalide salt, preferably a hydrochloride or a hydrobromide salt, or a trifluoroacetic acid salt, or any other equivalent salt), wherein  $R^1$ ,  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I), may be made (Scheme 12) by treatment of compounds of formula (IIIa-1), or a salt thereof, wherein  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I), with compounds of formula (XXXVII), wherein  $R^1$  is as defined in formula I, by a reductive amination reaction under analogous conditions already described above in Scheme 2 (transformation VII into III).

Compounds of formula (IIIa-1), or a salt thereof, wherein  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I), may be obtained by biocatalyzed deracemization of compounds of formula (IIIa), or a salt thereof, wherein  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I). This may be done for instance using a lipase, e.g. *Candida Antarctica* lipase B or *Pseudomonas fluorescens* lipase, eventually in immobilized form (e.g. Novozym® 435) in presence of an acyl donor, e.g. ethyl methoxyacetate or vinyl acetate, in a suitable solvent such as acetonitrile or methyl tert-butyl ether at temperatures between 20 °C to 100 °C. Such processes are described for instance in *J. Org. Chem.* 2007, 72, 6918-6923 or *Adv. Synth. Catal.* 2007, 349, 1481-1488. The expected stereochemical outcome of such enzymatic deracemization are known of those skilled in the art and are documented in the literature, for instance in *J. Org. Chem.* 1991, 56, 2656-2665 or *J. Am. Chem. Soc.* 2015, 137, 3996-4009.

20 Scheme 13:



In an alternative process (Scheme 13), compounds of formula (IIIa-1), or a salt thereof, wherein  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I), may be obtained from compounds of the formula (XXX-1), wherein  $R^3$ ,  $R^{4c}$ ,  $R^{5a}$  and  $R^{5b}$  have the same meaning as defined above for compounds of the formula (I) and  $Z_3$  is -NPhth (N-phthalimide group) or -

NBoc<sub>2</sub> (N-bis(*tert*-butyloxycarbonyl) group), under deprotection conditions already described above in Scheme 11 (transformation XXX into IIIa).

Compounds of the formula (XXX-1), wherein R<sup>3</sup>, R<sup>4c</sup>, R<sup>5a</sup> and R<sup>5b</sup> have the same meaning as defined above for compounds of the formula (I) and Z<sub>3</sub> is -NPhth (N-phthalimide group) or -NBoc<sub>2</sub> (N-bis(*tert*-butyloxycarbonyl) group), may be obtained from compounds of the formula (XXXI-1), wherein  
5 R<sup>3</sup>, R<sup>4c</sup>, R<sup>5a</sup> and R<sup>5b</sup> have the same meaning as defined above for compounds of the formula (I), by a Mitsunobu reaction with phthalimide (HNPht) or bis(*tert*-butoxycarbonyl)amine (HNBoc<sub>2</sub>) under conditions already described above in Scheme 11 (transformation XXXI into XXX). Such processes are known by those skilled in the art to proceed with inversion of the stereocenter.

10 Compounds of the formula (XXXI-1), wherein R<sup>3</sup>, R<sup>4c</sup>, R<sup>5a</sup> and R<sup>5b</sup> have the same meaning as defined above for compounds of the formula (I), may be obtained by enantioselective reduction of ketones of formula (VII-1), wherein R<sup>3</sup>, R<sup>4c</sup>, R<sup>5a</sup> and R<sup>5b</sup> have the same meaning as defined above for compounds of the formula (I). Such reductions can be done using a catalyst, for instance a ruthenium or a rhodium catalyst with a chiral ligand such as RuCl[(*R,R*)-TsDPEN](mesitylene) or RuBF<sub>4</sub>[(*R,R*)-  
15 TsDPEN](*p*-cymene) in the presence of a hydrogen donor system such as for example HCOOH/Et<sub>3</sub>N or HCO<sub>2</sub>NH<sub>4</sub>. Such processes are described in the literature for instance in *J. Org. Chem.* 2017, 82, 5607.

Alternatively, compounds of formula (IIIa-1), or a salt thereof, wherein R<sup>3</sup>, R<sup>4c</sup>, R<sup>5a</sup> and R<sup>5b</sup> have the same meaning as defined above for compounds of the formula (I), may be obtained by reduction of  
20 azide compounds of formula (XXXVIII), wherein R<sup>3</sup>, R<sup>4c</sup>, R<sup>5a</sup> and R<sup>5b</sup> have the same meaning as defined above for compounds of the formula (I), by treatment with for instance triphenylphosphine (or tributylphosphine) and water (2 steps Staudinger reduction), or by hydrogenation using for example a palladium catalyst in the presence of hydrogen. Procedures and conditions for such azide reductions are well known to a person skilled in the art, and known from the literature and text books.

Compounds of formula (XXXVIII), wherein R<sup>3</sup>, R<sup>4c</sup>, R<sup>5a</sup> and R<sup>5b</sup> have the same meaning as  
25 defined above for compounds of the formula (I), may be obtained by treatment of alcohol compounds of the formula (XXXI-1), wherein R<sup>3</sup>, R<sup>4c</sup>, R<sup>5a</sup> and R<sup>5b</sup> have the same meaning as defined above for compounds of the formula (I), with an azidation reagent such as diphenyl phosphoryl azide (amongst others like sodium azide, trimethylsilyl azide or tetrabutylammonium azide), in a solvent such as toluene, tetrahydrofuran or 2-methyltetrahydrofuran, in the presence of a base such as for example 1,8-  
30 diazabicyclo(5.4.0)undec-7-ene DBU, and at temperatures preferably around room temperature. Such processes are known by those skilled in the art to proceed with inversion of the stereocenter and are described in the literature for instance in *Adv. Synth. Catal.* 2018, 360, 2157–2165.

Any of the compounds of the formula (IIIa) (substituents as defined in Scheme 10/11), formula (IIIa-1) (substituents as defined in Schemes 12/13), and formula (IIIb) (substituents as defined in  
35 Schemes 12), or (where applicable) a salt thereof, or (where applicable) a free base thereof, represent a particular subset of compounds of the formula (III) defined above in Scheme 1, hence can be used according to descriptions outlined in said Scheme 1 for the preparation of compounds of the formula (I).

Depending on the procedure or the reaction conditions, the reactants can be reacted in the presence of a base. Examples of suitable bases are alkali metal or alkaline earth metal hydroxides, alkali metal or alkaline earth metal hydrides, alkali metal or alkaline earth metal amides, alkali metal or alkaline earth metal alkoxides, alkali metal or alkaline earth metal acetates, alkali metal or alkaline earth metal carbonates, alkali metal or alkaline earth metal dialkylamides or alkali metal or alkaline earth metal alkylsilylamides, alkylamines, alkylenediamines, free or N-alkylated saturated or unsaturated cycloalkylamines, basic heterocycles, ammonium hydroxides and carbocyclic amines. Examples which may be mentioned are sodium hydroxide, sodium hydride, sodium amide, sodium methoxide, sodium acetate, sodium carbonate, potassium tert-butoxide, potassium hydroxide, potassium carbonate, potassium hydride, lithium diisopropylamide, potassium bis(trimethylsilyl)amide, calcium hydride, triethylamine, diisopropylethylamine, triethylenediamine, cyclohexylamine, N-cyclohexyl-N,N-dimethylamine, N,N-diethylaniline, pyridine, 4-(N,N-dimethylamino)pyridine, quinuclidine, N-methylmorpholine, benzyltrimethylammonium hydroxide and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

The reactants can be reacted with each other as such, i.e. without adding a solvent or diluent. In most cases, however, it is advantageous to add an inert solvent or diluent or a mixture of these. If the reaction is carried out in the presence of a base, bases which are employed in excess, such as triethylamine, pyridine, N-methylmorpholine or N,N-diethylaniline, may also act as solvents or diluents.

The reactions are advantageously carried out in a temperature range from approximately -80°C to approximately +140°C, preferably from approximately -30°C to approximately +100°C, in many cases in the range between ambient temperature and approximately +80°C.

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

Salts of compounds of formula (I) can be prepared in a manner known *per se*. Thus, for example, acid addition salts of compounds of formula (I) are obtained by treatment with a suitable acid or a suitable ion exchanger reagent and salts with bases are obtained by treatment with a suitable base or with a suitable ion exchanger reagent.

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

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

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

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

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

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

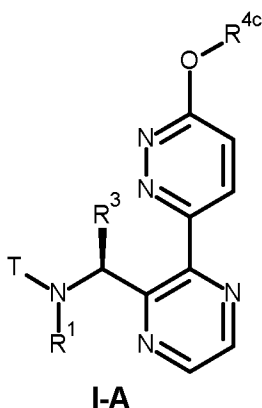
Pure diastereomers or enantiomers can be obtained according to the invention not only by separating suitable isomer mixtures, but also by generally known methods of diastereoselective or enantioselective synthesis, for example by carrying out the process according to the invention with starting materials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

N-oxides can be prepared by reacting a compound of the formula (I) with a suitable oxidizing agent, for example the H<sub>2</sub>O<sub>2</sub>/urea adduct in the presence of an acid anhydride, e.g. trifluoroacetic anhydride. Such oxidations are known from the literature, for example from *J. Med. Chem.*, 32 (12), 2561-73, 1989 or WO 2000/15615.

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

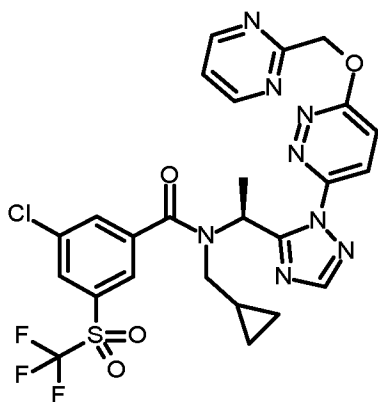
The compounds of formula (I) and, where appropriate, the tautomers thereof, in each case in free form or in salt form, can, if appropriate, also be obtained in the form of hydrates and/or include other solvents, for example those which may have been used for the crystallization of compounds which are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

- 5 The compounds of formula (I) according to the following Tables A-1 to A-21 can be prepared according to the methods described above. The examples which follow are intended to illustrate the invention and show preferred compounds of formula (I), in the form of a compound of formula (I-A).



Tables A-1 to A-21

- 10 Table A-1 provides 25 compounds A-1.001 to A-1.025 of formula I-A wherein R<sub>1</sub> is H, R<sup>3</sup> is CH<sub>3</sub>, R<sup>4c</sup> is H and T are as defined in table Z. For example, compound A-20.007 is



(A-20.007).

Table A-2 provides 25 compounds A-2.001 to A-2.025 of formula I-A wherein R<sub>1</sub> is H, R<sup>3</sup> is CH<sub>3</sub>, R<sup>4c</sup> is CH<sub>3</sub> and T are as defined in table Z.

- 15 Table A-3 provides 25 compounds A-3.001 to A-3.025 of formula I-A wherein R<sub>1</sub> is H, R<sup>3</sup> is CH<sub>3</sub>, R<sup>4c</sup> is CH<sub>2</sub>CH<sub>3</sub> and T are as defined in table Z.

Table A-4 provides 25 compounds A-4.001 to A-4.025 of formula I-A wherein R<sub>1</sub> is H, R<sup>3</sup> is CH<sub>3</sub>, R<sup>4c</sup> is CH<sub>2</sub>CHF<sub>2</sub> and T are as defined in table Z.

Table A-5 provides 25 compounds A-5.001 to A-5.025 of formula I-A wherein R<sub>1</sub> is H, R<sup>3</sup> is CH<sub>3</sub>, R<sup>4c</sup> is CH<sub>2</sub>-cyclopropyl and T are as defined in table Z.

- 20 Table A-6 provides 25 compounds A-6.001 to A-6.025 of formula I-A wherein R<sub>1</sub> is H, R<sup>3</sup> is CH<sub>3</sub>, R<sup>4c</sup> is pyrimidin-2-ylmethyl and T are as defined in table Z.

Table A-7 provides 25 compounds A-7.001 to A-7.025 of formula I-A wherein R<sub>1</sub> is H, R<sup>3</sup> is CH<sub>3</sub>, R<sup>4c</sup> is propargyl and T are as defined in table Z.

Table A-8 provides 25 compounds A-8.001 to A-8.025 of formula I-A wherein R<sub>1</sub> is CH<sub>3</sub>, R<sup>3</sup> is CH<sub>3</sub>, R<sup>4c</sup> is H and T are as defined in table Z.

5 Table A-9 provides 25 compounds A-9.001 to A-9.025 of formula I-A wherein R<sub>1</sub> is CH<sub>3</sub>, R<sup>3</sup> is CH<sub>3</sub>, R<sup>4c</sup> is CH<sub>3</sub> and T are as defined in table Z.

Table A-10 provides 25 compounds A-10.001 to A-10.025 of formula I-A wherein R<sub>1</sub> is CH<sub>3</sub>, R<sup>3</sup> is CH<sub>3</sub>, R<sup>4c</sup> is CH<sub>2</sub>CH<sub>3</sub> and T are as defined in table Z.

10 Table A-11 provides 25 compounds A-11.001 to A-11.025 of formula I-A wherein R<sub>1</sub> is CH<sub>3</sub>, R<sup>3</sup> is CH<sub>3</sub>, R<sup>4c</sup> is CH<sub>2</sub>CHF<sub>2</sub> and T are as defined in table Z.

Table A-12 provides 25 compounds A-12.001 to A-12.025 of formula I-A wherein R<sub>1</sub> is CH<sub>3</sub>, R<sup>3</sup> is CH<sub>3</sub>, R<sup>4c</sup> is CH<sub>2</sub>-cyclopropyl and T are as defined in table Z.

Table A-13 provides 25 compounds A-13.001 to A-13.025 of formula I-A wherein R<sub>1</sub> is CH<sub>3</sub>, R<sup>3</sup> is CH<sub>3</sub>, R<sup>4c</sup> is pyrimidin-2-ylmethyl and T are as defined in table Z.

15 Table A-14 provides 25 compounds A-14.001 to A-14.025 of formula I-A wherein R<sub>1</sub> is CH<sub>3</sub>, R<sup>3</sup> is CH<sub>3</sub>, R<sup>4c</sup> is propargyl and T are as defined in table Z.

Table A-15 provides 25 compounds A-15.001 to A-15.025 of formula I-A wherein R<sub>1</sub> is CH<sub>2</sub>-cyclopropyl, R<sup>3</sup> is CH<sub>3</sub>, R<sup>4c</sup> is H and T are as defined in table Z.

20 Table A-16 provides 25 compounds A-16.001 to A-16.025 of formula I-A wherein R<sub>1</sub> is CH<sub>2</sub>-cyclopropyl, R<sup>3</sup> is CH<sub>3</sub>, R<sup>4c</sup> is CH<sub>3</sub> and T are as defined in table Z.

Table A-17 provides 25 compounds A-17.001 to A-17.025 of formula I-A wherein R<sub>1</sub> is CH<sub>2</sub>-cyclopropyl, R<sup>3</sup> is CH<sub>3</sub>, R<sup>4c</sup> is CH<sub>2</sub>CH<sub>3</sub> and T are as defined in table Z.

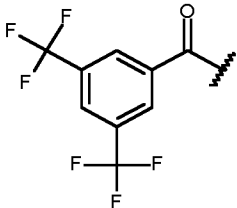
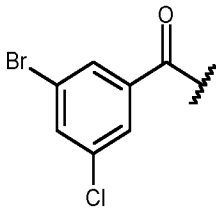
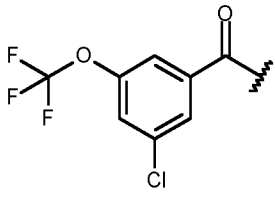
Table A-18 provides 25 compounds A-18.001 to A-18.025 of formula I-A wherein R<sub>1</sub> is CH<sub>2</sub>-cyclopropyl, R<sup>3</sup> is CH<sub>3</sub>, R<sup>4c</sup> is CH<sub>2</sub>CHF<sub>2</sub> and T are as defined in table Z.

25 Table A-19 provides 25 compounds A-19.001 to A-19.025 of formula I-A wherein R<sub>1</sub> is CH<sub>2</sub>-cyclopropyl, R<sup>3</sup> is CH<sub>3</sub>, R<sup>4c</sup> is CH<sub>2</sub>-cyclopropyl and T are as defined in table Z.

Table A-20 provides 25 compounds A-20.001 to A-20.025 of formula I-A wherein R<sub>1</sub> is CH<sub>2</sub>-cyclopropyl, R<sup>3</sup> is CH<sub>3</sub>, R<sup>4c</sup> is pyrimidin-2-ylmethyl and T are as defined in table Z.

30 Table A-21 provides 25 compounds A-21.001 to A-21.025 of formula I-A wherein R<sub>1</sub> is CH<sub>2</sub>-cyclopropyl, R<sup>3</sup> is CH<sub>3</sub>, R<sup>4c</sup> is propargyl and T are as defined in table Z.

Table Z: Substituent definitions of T

Index	T	Index	T	Index	T
1		10		19	

Index	T	Index	T	Index	T
2		11		20	
3		12		21	
4		13		22	
5		14		23	
6		15		24	
7		16		25	



Index	T	Index	T	Index	T
8		17			
9		18			

Also made available are certain intermediate compounds of formulae III-1(i), III-2(i), III'-1(i), and III'-2(i), which are novel, and are shown in Table T-III below:

Table T-III: Intermediate compounds of formulae III-1(i), III-2(i), III'-1(i), and III'-2(i)

III-1(i)	III-2(i)	III'-1(i)	III'-2(i)

5 wherein  $R^{4c}$  are as defined in any one of the Tables A-1 to A-21, and wherein  $X^-$  is an anion, i.e. the conjugate base of an acid, such as an inorganic acid, for instance hydrochloric acid, hydrobromic acid, hydrogen fluoride, hydrogen iodide, sulfuric acid, or the like, or of an organic acid, such as a carboxylic acid or a sulfonic acid, for instance trifluoroacetic acid, or methane sulfonic acid, or para-toluene sulfonic acid.

10 As one of ordinary skill in the art will appreciate, the compounds shown in Table T-III above contain a stereogenic centre. The present invention contemplates both racemates and individual enantiomers. Intermediate compounds III'-1(i) and III'-2(i) having preferred stereochemistry are set out in Table T-III.

In preferred intermediates of the formulae III-1(i) or III'-1(i),  $R^{4c}$  is hydrogen, methyl or ethyl.

The compounds of formula (I) according to the invention are preventively and/or curatively valuable active ingredients in the field of pest control, even at low rates of application, which have a very favorable biocidal spectrum and are well tolerated by warm-blooded species, fish and plants. The active ingredients according to the invention act against all or individual developmental stages of normally sensitive, but also resistant, animal pests, such as insects or representatives of the order Acarina. The insecticidal or acaricidal activity of the active ingredients according to the invention can manifest itself directly, i.e. in destruction of the pests, which takes place either immediately or only after some time has elapsed, for example during ecdysis, or indirectly, for example in a reduced oviposition and/or hatching rate.

10 Examples of the above mentioned animal pests are:

from the order *Acarina*, for example, *Acalitus* spp, *Aculus* spp, *Acaricalus* spp, *Aceria* spp, *Acarus siro*, *Amblyomma* spp., *Argas* spp., *Boophilus* spp., *Brevipalpus* spp., *Bryobia* spp, *Calipitimerus* spp., *Chorioptes* spp., *Dermanyssus gallinae*, *Dermatophagoides* spp, *Eotetranychus* spp, *Eriophyes* spp., *Hemitarsonemus* spp, *Hyalomma* spp., *Ixodes* spp., *Olygonychus* spp, *Ornithodoros* spp.,  
15 *Polyphagotarsonus latus*, *Panonychus* spp., *Phyllocoptura oleivora*, *Phytonemus* spp, *Polyphagotarsonemus* spp, *Psoroptes* spp., *Rhipicephalus* spp., *Rhizoglyphus* spp., *Sarcoptes* spp., *Steneotarsonemus* spp, *Tarsonemus* spp. and *Tetranychus* spp.;

from the order *Anoplura*, for example, *Haematopinus* spp., *Linognathus* spp., *Pediculus* spp., *Pemphigus* spp. and *Phylloxera* spp.;

20 from the order *Coleoptera*, for example, *Agriotes* spp., *Amphimallon majale*, *Anomala orientalis*, *Anthonomus* spp., *Aphodius* spp, *Astylus atromaculatus*, *Ataenius* spp, *Atomaria linearis*, *Chaetocnema tibialis*, *Cerotoma* spp, *Conoderus* spp, *Cosmopolites* spp., *Cotinis nitida*, *Curculio* spp., *Cyclocephala* spp, *Dermestes* spp., *Diabrotica* spp., *Diloboderus abderus*, *Epilachna* spp., *Eremnus* spp., *Heteronychus arator*, *Hypothenemus hampei*, *Lagria vilosa*, *Leptinotarsa decemlineata*, *Lissorhoptrus*  
25 spp., *Liogenys* spp, *Maecolaspis* spp, *Maladera castanea*, *Megascelis* spp, *Melighetes aeneus*, *Melolontha* spp., *Myochrous armatus*, *Orycaephilus* spp., *Otiorhynchus* spp., *Phyllophaga* spp, *Phlyctinus* spp., *Popillia* spp., *Psylliodes* spp., *Rhysomatus aubtilis*, *Rhizopertha* spp., *Scarabeidae*, *Sitophilus* spp., *Sitotroga* spp., *Somaticus* spp, *Sphenophorus* spp, *Sternechus subsignatus*, *Tenebrio* spp., *Tribolium* spp. and *Trogoderma* spp.;

30 from the order *Diptera*, for example, *Aedes* spp., *Anopheles* spp, *Antherigona soccata*, *Bactrocea oleae*, *Bibio hortulanus*, *Bradysia* spp, *Calliphora erythrocephala*, *Ceratitis* spp., *Chrysomyia* spp., *Culex* spp., *Cuterebra* spp., *Dacus* spp., *Delia* spp, *Drosophila melanogaster*, *Fannia* spp., *Gastrophilus* spp., *Geomyza tripunctata*, *Glossina* spp., *Hypoderma* spp., *Hyppobosca* spp., *Liriomyza* spp., *Lucilia* spp., *Melanagromyza* spp., *Musca* spp., *Oestrus* spp., *Orseolia* spp., *Oscinella*  
35 frit, *Pegomyia hyoscyami*, *Phorbia* spp., *Rhagoletis* spp, *Rivelia quadrifasciata*, *Scatella* spp, *Sciara* spp., *Stomoxys* spp., *Tabanus* spp., *Tannia* spp. and *Tipula* spp.;

from the order *Hemiptera*, for example, *Acanthocoris scabrator*, *Acrosternum* spp, *Adelphocoris lineolatus*, *Aleurodes* spp., *Amblypelta nitida*, *Bathycoelia thalassina*, *Blissus* spp, *Cimex* spp., *Clavigralla tomentosicollis*, *Creontiades* spp, *Distantiella theobroma*, *Dichelops furcatus*, *Dysdercus*

spp., Edessa spp, Euchistus spp., Eurydema pulchrum, Eurygaster spp., Halyomorpha halys, Horcias nobilellus, Leptocoris spp., Lygus spp, Margarodes spp, Murgantia histrionic, Neomegalotomus spp, Nesidiocoris tenuis, Nezara spp., Nysius simulans, Oebalus insularis, Piesma spp., Piezodorus spp, Rhodnius spp., Sahlbergella singularis, Scaptocoris castanea, Scotinophara spp., Thyanta spp ,  
 5 Triatoma spp., Vatica illudens; Acyrthosium pisum, Adalges spp, Agalliana ensigera, Agonoscena targionii, Aleurodicus spp, Aleurocanthus spp, Aleurolobus barodensis, Aleurothrixus floccosus, Aleyrodes brassicae, Amarasca biguttula, Amritodus atkinsoni, Aonidiella spp., Aphididae, Aphis spp., Aspidiotus spp., Aulacorthum solani, Bactericera cockerelli, Bemisia spp, Brachycaudus spp, Brevicoryne brassicae, Cacopsylla spp, Cavariella aegopodii Scop., Ceroplaster spp., Chrysomphalus  
 10 aonidium, Chrysomphalus dictyospermi, Cicadella spp, Cofana spectra, Cryptomyzus spp, Cicadulina spp, Coccus hesperidum, Dalbulus maidis, Dialeurodes spp, Diaphorina citri, Diuraphis noxia, Dysaphis spp, Empoasca spp., Eriosoma larigerum, Erythroneura spp., Gascardia spp., Glycaspis brimblecombei, Hyadaphis pseudobrassicae, Hyalopterus spp, Hyperomyzus pallidus, Idioscopus clypealis, Jacobiasca lybica, Laodelphax spp., Lecanium corni, Lepidosaphes spp., Lopaphis erysimi, Lyogenys maidis,  
 15 Macrosiphum spp., Mahanarva spp, Metcalfa pruinosa, Metopolophium dirhodum, Myndus crudus, Myzus spp., Neotoxoptera sp, Nephrotettix spp., Nilaparvata spp., Nippolachnus piri Mats, Odonaspis ruthae, Oregma lanigera Zehnter, Parabemisia myricae, Paratrioza cockerelli, Parlatoria spp., Pemphigus spp., Peregrinus maidis, Perkinsiella spp, Phorodon humuli, Phylloxera spp, Planococcus spp., Pseudaulacaspis spp., Pseudococcus spp., Pseudatomoscelis seriatus, Psylla spp., Pulvinaria  
 20 aethiopica, Quadraspidiotus spp., Quesada gigas, Recilia dorsalis, Rhopalosiphum spp., Saissetia spp., Scaphoideus spp., Schizaphis spp., Sitobion spp., Sogatella furcifera, Spissistilus festinus, Tarophagus Proserpina, Toxoptera spp, Trialeurodes spp, Tridiscus sporoboli, Trionymus spp, Trioza erytrae , Unaspis citri, Zyginia flammigera, Zyginidia scutellaris, ;

from the order *Hymenoptera*, for example, Acromyrmex, Arge spp, Atta spp., Cephus spp.,  
 25 Diprion spp., Diprionidae, Gilpinia polytoma, Hoplocampa spp., Lasius spp., Monomorium pharaonis, Neodiprion spp., Pogonomyrmex spp, Slenopsis invicta, Solenopsis spp. and Vespa spp.;

from the order *Isoptera*, for example, Coptotermes spp, Cornitermes cumulans, Incisitermes spp, Macrotermes spp, Mastotermes spp, Microtermes spp, Reticulitermes spp.; Solenopsis geminata

from the order *Lepidoptera*, for example, Acleris spp., Adoxophyes spp., Aegeria spp., Agrotis  
 30 spp., Alabama argillaceae, Amylois spp., Anticarsia gemmatalis, Archips spp., Argyroresthia spp, Argyrotaenia spp., Autographa spp., Bucculatrix thurberiella, Busseola fusca, Cadra cautella, Carposina nipponensis, Chilo spp., Choristoneura spp., Chrysoteuchia topiaria, Clysia ambiguella, Cnaphalocrocis spp., Cnephasia spp., Cochylis spp., Coleophora spp., Colias lesbia, Cosmophila flava, Crambus spp, Crocidolomia binotalis, Cryptophlebia leucotreta, Cydalima perspectalis, Cydia spp., Diaphania  
 35 perspectalis, Diatraea spp., Diparopsis castanea, Earias spp., Elasmopalpus lignosellus, Eldana saccharina, Ephestia spp., Epinotia spp, Estigmene acrea, Etiella zinckenella, Eucosma spp., Eupoecilia ambiguella, Euproctis spp., Euxoa spp., Feltia jaculiferia, Grapholita spp., Hedyia nubiferana, Heliothis spp., Hellula undalis, Herpetogramma spp, Hyphantria cunea, Keiferia lycopersicella, Lasmopalpus lignosellus, Leucoptera scitella, Lithocolletis spp., Lobesia botrana, Loxostege bifidalis, Lymantria spp.,

Lyonetia spp., Malacosoma spp., Mamestra brassicae, Manduca sexta, Mythimna spp, Noctua spp, Operophtera spp., Orniodes indica, Ostrinia nubilalis, Pammene spp., Pandemis spp., Panolis flammea, Papaipema nebris, Pectinophora gossypiella, Perileucoptera coffeella, Pseudaletia unipuncta, Phthorimaea operculella, Pieris rapae, Pieris spp., Plutella xylostella, Prays spp., Pseudoplusia spp,  
 5 Rachiplusia nu, Richia albicosta, Scirpophaga spp., Sesamia spp., Sparganothis spp., Spodoptera spp., Sylepta derogate, Synanthedon spp., Thaumetopoea spp., Tortrix spp., Trichoplusia ni, Tuta absoluta, and Yponomeuta spp.;

from the order *Mallophaga*, for example, Damalinae spp. and Trichodectes spp.;

from the order *Orthoptera*, for example, Blatta spp., Blattella spp., Gryllotalpa spp., Leucophaea  
 10 maderae, Locusta spp., Neocurtilla hexadactyla, Periplaneta spp. , Scapteriscus spp, and Schistocerca spp.;

from the order *Psocoptera*, for example, Liposcelis spp.;

from the order *Siphonaptera*, for example, Ceratophyllus spp., Ctenocephalides spp. and  
 Xenopsylla cheopis;

15 from the order *Thysanoptera*, for example, Calliothrips phaseoli, Frankliniella spp., Heliothrips spp, Hercinothrips spp., Parthenothrips spp, Scirtothrips aurantii, Sericothrips variabilis, Taeniothrips spp., Thrips spp;

from the order *Thysanura*, for example, Lepisma saccharina.

In a further aspect, the invention may also relate to a method of controlling damage to plant and  
 20 parts thereof by plant parasitic nematodes (Endoparasitic-, Semiendoparasitic- and Ectoparasitic nematodes), especially plant parasitic nematodes such as root knot nematodes, Meloidogyne hapla, Meloidogyne incognita, Meloidogyne javanica, Meloidogyne arenaria and other Meloidogyne species; cyst-forming nematodes, Globodera rostochiensis and other Globodera species; Heterodera avenae, Heterodera glycines, Heterodera schachtii, Heterodera trifolii, and other Heterodera species; Seed gall  
 25 nematodes, Anguina species; Stem and foliar nematodes, Aphelenchoides species; Sting nematodes, Belonolaimus longicaudatus and other Belonolaimus species; Pine nematodes, Bursaphelenchus xylophilus and other Bursaphelenchus species; Ring nematodes, Criconema species, Criconemella species, Criconemoides species, Mesocriconema species; Stem and bulb nematodes, Ditylenchus destructor, Ditylenchus dipsaci and other Ditylenchus species; Awl nematodes, Dolichodorus species;  
 30 Spiral nematodes, Helicotylenchus multicinctus and other Helicotylenchus species; Sheath and sheathoid nematodes, Hemicycliophora species and Hemicriconemoides species; Hirshmanniella species; Lance nematodes, Hoploaimus species; false rootknot nematodes, Nacobbus species; Needle nematodes, Longidorus elongatus and other Longidorus species; Pin nematodes, Pratylenchus species; Lesion nematodes, Pratylenchus neglectus, Pratylenchus penetrans, Pratylenchus curvatus,  
 35 Pratylenchus goodeyi and other Pratylenchus species; Burrowing nematodes, Radopholus similis and other Radopholus species; Reniform nematodes, Rotylenchus robustus, Rotylenchus reniformis and other Rotylenchus species; Scutellonema species; Stubby root nematodes, Trichodorus primitivus and other Trichodorus species, Paratrachodorus species; Stunt nematodes, Tylenchorhynchus claytoni, Tylenchorhynchus dubius and other Tylenchorhynchus species; Citrus nematodes, Tylenchulus

species; Dagger nematodes, Xiphinema species; and other plant parasitic nematode species, such as Subanguina spp., Hypsoperine spp., Macroposthonia spp., Melinius spp., Punctodera spp., and Quinisulcius spp..

The compounds of the invention may also have activity against the molluscs. Examples of which  
5 include, for example, Ampullariidae; Arion (*A. ater*, *A. circumscriptus*, *A. hortensis*, *A. rufus*);  
Bradybaenidae (*Bradybaena fruticum*); Cepaea (*C. hortensis*, *C. Nemoralis*); ochlodina; Deroceras (*D.*  
*agrestis*, *D. empiricorum*, *D. laeve*, *D. reticulatum*); Discus (*D. rotundatus*); Euomphalia; Galba (*G.*  
*trunculata*); Helicelia (*H. itala*, *H. obvia*); Helicidae *Helicigona arbustorum*); Helicodiscus; Helix (*H.*  
*aperta*); Limax (*L. cinereoniger*, *L. flavus*, *L. marginatus*, *L. maximus*, *L. tenellus*); Lymnaea; Milax (*M.*  
10 *gagates*, *M. marginatus*, *M. sowerbyi*); Opeas; Pomacea (*P. canaticulata*); Vallonia and Zanitoides.

The active ingredients according to the invention can be used for controlling, i.e. containing or  
destroying, pests of the abovementioned type which occur in particular on plants, especially on useful  
plants and ornamentals in agriculture, in horticulture and in forests, or on organs, such as fruits, flowers,  
foliage, stalks, tubers or roots, of such plants, and in some cases even plant organs which are formed  
15 at a later point in time remain protected against these pests.

Suitable target crops are, in particular, cereals, such as wheat, barley, rye, oats, rice, maize or  
sorghum; beet, such as sugar or fodder beet; fruit, for example pomaceous fruit, stone fruit or soft fruit,  
such as apples, pears, plums, peaches, almonds, cherries or berries, for example strawberries,  
raspberries or blackberries; leguminous crops, such as beans, lentils, peas or soya; oil crops, such as  
20 oilseed rape, mustard, poppies, olives, sunflowers, coconut, castor, cocoa or ground nuts; cucurbits,  
such as pumpkins, cucumbers or melons; fibre plants, such as cotton, flax, hemp or jute; citrus fruit,  
such as oranges, lemons, grapefruit or tangerines; vegetables, such as spinach, lettuce, asparagus,  
cabbages, carrots, onions, tomatoes, potatoes or bell peppers; Lauraceae, such as avocado,  
Cinnamomum or camphor; and also tobacco, nuts, coffee, eggplants, sugarcane, tea, pepper,  
25 grapevines, hops, the plantain family and latex plants.

The compositions and/or methods of the present invention may be also used on any ornamental  
and/or vegetable crops, including flowers, shrubs, broad-leaved trees and evergreens.

For example the invention may be used on any of the following ornamental species: *Ageratum*  
spp., *Alonsoa* spp., *Anemone* spp., *Anisodonteia capsensis*, *Anthemis* spp., *Antirrhinum* spp., *Aster*  
30 spp., *Begonia* spp. (e.g. *B. elatior*, *B. semperflorens*, *B. tubéreux*), *Bougainvillea* spp., *Brachycome* spp.,  
*Brassica* spp. (ornamental), *Calceolaria* spp., *Capsicum annuum*, *Catharanthus roseus*, *Canna* spp.,  
*Centaurea* spp., *Chrysanthemum* spp., *Cineraria* spp. (*C. maritime*), *Coreopsis* spp., *Crassula coccinea*,  
*Cuphea ignea*, *Dahlia* spp., *Delphinium* spp., *Dicentra spectabilis*, *Dorotheantus* spp., *Eustoma*  
*grandiflorum*, *Forsythia* spp., *Fuchsia* spp., *Geranium gnaphalium*, *Gerbera* spp., *Gomphrena globosa*,  
35 *Heliotropium* spp., *Helianthus* spp., *Hibiscus* spp., *Hortensia* spp., *Hydrangea* spp., *Hypoestes*  
*phyllostachya*, *Impatiens* spp. (*I. Walleriana*), *Iresines* spp., *Kalanchoe* spp., *Lantana camara*, *Lavatera*  
*trimestris*, *Leonotis leonurus*, *Lilium* spp., *Mesembryanthemum* spp., *Mimulus* spp., *Monarda* spp.,  
*Nemesia* spp., *Tagetes* spp., *Dianthus* spp. (carnation), *Canna* spp., *Oxalis* spp., *Bellis* spp.,  
*Pelargonium* spp. (*P. peltatum*, *P. Zonale*), *Viola* spp. (pansy), *Petunia* spp., *Phlox* spp., *Plecthranthus*

spp., *Poinsettia* spp., *Parthenocissus* spp. (*P. quinquefolia*, *P. tricuspidata*), *Primula* spp., *Ranunculus* spp., *Rhododendron* spp., *Rosa* spp. (rose), *Rudbeckia* spp., *Saintpaulia* spp., *Salvia* spp., *Scaevola aemola*, *Schizanthus wisetonensis*, *Sedum* spp., *Solanum* spp., *Surfinia* spp., *Tagetes* spp., *Nicotinia* spp., *Verbena* spp., *Zinnia* spp. and other bedding plants.

5 For example the invention may be used on any of the following vegetable species: *Allium* spp. (*A. sativum*, *A. cepa*, *A. oschaninii*, *A. Porrum*, *A. ascalonicum*, *A. fistulosum*), *Anthriscus cerefolium*, *Apium graveolus*, *Asparagus officinalis*, *Beta vulgaris*, *Brassica* spp. (*B. Oleracea*, *B. Pekinensis*, *B. rapa*), *Capsicum annuum*, *Cicer arietinum*, *Cichorium endivia*, *Cichorium* spp. (*C. intybus*, *C. endivia*), *Citrillus lanatus*, *Cucumis* spp. (*C. sativus*, *C. melo*), *Cucurbita* spp. (*C. pepo*, *C. maxima*), *Cyanara* spp.  
10 (*C. scolymus*, *C. cardunculus*), *Daucus carota*, *Foeniculum vulgare*, *Hypericum* spp., *Lactuca sativa*, *Lycopersicon* spp. (*L. esculentum*, *L. lycopersicum*), *Mentha* spp., *Ocimum basilicum*, *Petroselinum crispum*, *Phaseolus* spp. (*P. vulgaris*, *P. coccineus*), *Pisum sativum*, *Raphanus sativus*, *Rheum rhaponticum*, *Rosemarinus* spp., *Salvia* spp., *Scorzonera hispanica*, *Solanum melongena*, *Spinacea oleracea*, *Valerianella* spp. (*V. locusta*, *V. eriocarpa*) and *Vicia faba*.

15 Preferred ornamental species include African violet, Begonia, Dahlia, Gerbera, Hydrangea, Verbena, Rosa, Kalanchoe, Poinsettia, Aster, Centaurea, Coreopsis, Delphinium, Monarda, Phlox, Rudbeckia, Sedum, Petunia, Viola, Impatiens, Geranium, Chrysanthemum, Ranunculus, Fuchsia, Salvia, Hortensia, rosemary, sage, St. Johnswort, mint, sweet pepper, tomato and cucumber.

The active ingredients according to the invention are especially suitable for controlling *Aphis craccivora*, *Diabrotica balteata*, *Heliothis virescens*, *Myzus persicae*, *Plutella xylostella* and *Spodoptera littoralis* in cotton, vegetable, maize, rice and soya crops. The active ingredients according to the invention are further especially suitable for controlling *Mamestra* (preferably in vegetables), *Cydia pomonella* (preferably in apples), *Empoasca* (preferably in vegetables, vineyards), *Leptinotarsa* (preferably in potatoes) and *Chilo suppressalis* (preferably in rice).

25 The compounds of formula (I) are particularly suitable for control of

- a pest of the order Hemiptera, for example, one or more of the species *Bemisia tabaci*, *Aphis craccivora*, *Myzus persicae*, *Rhopalosiphum padi*, *Nilaparvata lugens*, and *Euschistus heros* (preferably in vegetables, soybeans, and sugarcane);
- a pest of the order Lepidoptera, for example, one or more of the species *Spodoptera littoralis*,  
30 *Spodoptera frugiperda*, *Plutella xylostella*, *Cnaphalocrocis medinalis*, *Cydia pomonella*, *Chrysodeixis* includes, *Chilo suppressalis*, *Elasmopalpus lignosellus*, *Pseudoplusia includens*, and *Tuta absoluta* (preferably in vegetables and corn);
- a pest of the order Thysanoptera, such as the family Thripidae, for example, one or more of *Thrips tabaci* and *Frankliniella occidentalis* (preferably in vegetables); and
- 35 • soil pests (such as of the order Coleoptera), for example, the species *Diabrotica balteata*, *Agriotes* spp. and *Leptinotarsa decemlineata* (preferably in vegetables and corn).

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, for example insecticidal proteins from *Bacillus cereus* or *Bacillus popilliae*; or insecticidal  
5 proteins from *Bacillus thuringiensis*, such as  $\delta$ -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;  
10 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  
15 esterase, diuretic hormone receptors, stilbene synthase, bibenzyl synthase, chitinases and glucanases.

In the context of the present invention there are to be understood by  $\delta$ -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  
20 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-  
25 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  
30 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  
35 beetles (Coleoptera), two-winged insects (Diptera) and moths (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:

- 10 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.
- 15 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.
- 20 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.
- 25 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.
- 30 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.
- 35 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.

Transgenic crops of insect-resistant plants are also described in BATS (Zentrum für Biosicherheit und Nachhaltigkeit, Zentrum BATS, Clarastrasse 13, 4058 Basel, Switzerland) Report 2003, (<http://bats.ch>).

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 antipathogenic substances having a selective action, such as, for example, the so-called "pathogenesis-related proteins" (PRPs, see e.g. EP-A-0 392 225). Examples of such antipathogenic substances and transgenic plants capable of synthesising such antipathogenic substances are known, for example, from EP-A-0 392 225, WO 95/33818 and EP-A-0 353 191. The methods of producing such transgenic plants are generally known to the person skilled in the art and are described, for example, in the publications mentioned above.

Crops may also be modified for enhanced resistance to fungal (for example Fusarium, Anthracnose, or Phytophthora), bacterial (for example Pseudomonas) or viral (for example potato leafroll virus, tomato spotted wilt virus, cucumber mosaic virus) pathogens.

Crops also include those that have enhanced resistance to nematodes, such as the soybean cyst nematode.

Crops that are tolerance to abiotic stress include those that have enhanced tolerance to drought, high salt, high temperature, chill, frost, or light radiation, for example through expression of NF-YB or other proteins known in the art.

Antipathogenic substances which can be expressed by such transgenic plants include, for example, ion channel blockers, such as blockers for sodium and calcium channels, for example the viral KP1, KP4 or KP6 toxins; stilbene synthases; bibenzyl synthases; chitinases; glucanases; the so-called "pathogenesis-related proteins" (PRPs; see e.g. EP-A-0 392 225); antipathogenic substances produced by microorganisms, for example peptide antibiotics or heterocyclic antibiotics (see e.g. WO 95/33818) or protein or polypeptide factors involved in plant pathogen defence (so-called "plant disease resistance genes", as described in WO 03/000906).

Further areas of use of the compositions according to the invention are the protection of stored goods and store rooms and the protection of raw materials, such as wood, textiles, floor coverings or buildings, and also in the hygiene sector, especially the protection of humans, domestic animals and productive livestock against pests of the mentioned type.

The present invention provides a compound of the first aspect for use in therapy. The present invention provides a compound of the first aspect, for use in controlling parasites in or on an animal. The present invention further provides a compound of the first aspect, for use in preventing and/or treating diseases transmitted by ectoparasites.

The present invention provides the use of a compound of the first aspect, for the manufacture of a medicament for controlling parasites in or on an animal. The present invention further provides the

use of a compound of the first aspect, for the manufacture of a medicament for controlling ectoparasites on an animal. The present invention further provides the use of a compound of the first aspect, for the manufacture of a medicament for preventing and/or treating diseases transmitted by ectoparasites.

The present invention provides the use of a compound of the first aspect, in controlling parasites  
5 in or on an animal. The present invention further provides the use of a compound of the first aspect , in controlling ectoparasites on an animal.

The term “controlling” when used in context of parasites in or on an animal refers to reducing the number of pests or parasites, eliminating pests or parasites and/or preventing further pest or parasite infestation.

10 The term “treating” when used in context of parasites in or on an animal refers to restraining, slowing, stopping or reversing the progression or severity of an existing symptom or disease.

The term “preventing” when used in context of parasites in or on an animal refers to the avoidance of a symptom or disease developing in the animal.

15 The term “animal” when used in context of parasites in or on an animal may refer to a mammal and a non-mammal, such as a bird or fish. In the case of a mammal, it may be a human or non-human mammal. Non-human mammals include, but are not limited to, livestock animals and companion animals. Livestock animals include, but are not limited to, cattle, camelids, pigs, sheep, goats and horses. Companion animals include, but are not limited to, dogs, cats and rabbits.

A “parasite” is a pest which lives in or on the host animal and benefits by deriving nutrients at  
20 the host animal's expense. An “endoparasite” is a parasite which lives in the host animal. An “ectoparasite” is a parasite which lives on the host animal. Ectoparasites include, but are not limited to, acari, insects and crustaceans (e.g. sea lice). The Acari (or Acarina) sub-class comprises ticks and mites. Ticks include, but are not limited to, members of the following genera: *Rhipicaphalus*, for example, *Rhipicaphalus (Boophilus) microplus* and *Rhipicephalus sanguineus*; *Amblyomrna*; *Dermacentor*;  
25 *Haemaphysalis*; *Hyalomma*; *Ixodes*; *Rhipicentor*; *Margaropus*; *Argas*; *Otobius*; and *Ornithodoros*. Mites include, but are not limited to, members of the following genera: *Chorioptes*, for example *Chorioptes bovis*; *Psoroptes*, for example *Psoroptes ovis*; *Cheyletiella*; *Dermanyssus*; for example *Dermanyssus gallinae*; *Ornithonyssus*; *Demodex*, for example *Demodex canis*; *Sarcoptes*, for example *Sarcoptes scabiei*; and *Psorergates*. Insects include, but are not limited to, members of the orders: Siphonaptera,  
30 Diptera, Phthiraptera, Lepidoptera, Coleoptera and Homoptera. Members of the Siphonaptera order include, but are not limited to, *Ctenocephalides felis* and *Ctenocephalides canis*. Members of the Diptera order include, but are not limited to, *Musca spp.*; bot fly, for example *Gasterophilus intestinalis* and *Oestrus ovis*; biting flies; horse flies, for example *Haematopota spp.* and *Tabanus spp.*; *haematobia*, for example *haematobia irritans*; *Stomoxys*; *Lucilia*; midges; and mosquitoes. Members of the Phthiraptera  
35 class include, but are not limited to, blood sucking lice and chewing lice, for example *Bovicola Ovis* and *Bovicola Bovis*.

The term “effective amount” when used in context of parasites in or on an animal refers to the amount or dose of the compound of the invention, or a salt thereof, which, upon single or multiple dose administration to the animal, provides the desired effect in or on the animal. The effective amount can

be readily determined by the attending diagnostician, as one skilled in the art, by the use of known techniques and by observing results obtained under analogous circumstances. In determining the effective amount a number of factors are considered by the attending diagnostician, including, but not limited to: the species of mammal; its size, age, and general health; the parasite to be controlled and the degree of infestation; the specific disease or disorder involved; the degree of involvement or the severity of the disease or disorder; the response of the individual; the particular compound administered; the mode of administration; the bioavailability characteristics of the preparation administered; the dose regimen selected; the use of concomitant medication; and other relevant circumstances.

The compounds of the invention may be administered to the animal by any route which has the desired effect including, but not limited to topically, orally, parenterally and subcutaneously. Topical administration is preferred. Formulations suitable for topical administration include, for example, solutions, emulsions and suspensions and may take the form of a pour-on, spot-on, spray-on, spray race or dip. In the alternative, the compounds of the invention may be administered by means of an ear tag or collar.

Salt forms of the compounds of the invention include both pharmaceutically acceptable salts and veterinary acceptable salts, which can be different to agrochemically acceptable salts. Pharmaceutically and veterinary acceptable salts and common methodology for preparing them are well known in the art. See, for example, Gould, P.L., "Salt selection for basic drugs", *International Journal of Pharmaceutics*, 33: 201 -217 (1986); Bastin, R.J., *et al.* "Salt Selection and Optimization Procedures for Pharmaceutical New Chemical Entities", *Organic Process Research and Development*, 4: 427-435 (2000); and Berge, S.M., *et al.*, "Pharmaceutical Salts", *Journal of Pharmaceutical Sciences*, 66: 1-19, (1977). One skilled in the art of synthesis will appreciate that the compounds of the invention are readily converted to and may be isolated as a salt, such as a hydrochloride salt, using techniques and conditions well known to one of ordinary skill in the art. In addition, one skilled in the art of synthesis will appreciate that the compounds of the invention are readily converted to and may be isolated as the corresponding free base from the corresponding salt.

The present invention also provides a method for controlling pests (such as mosquitoes and other disease vectors; see also [http://www.who.int/malaria/vector\\_control/irs/en/](http://www.who.int/malaria/vector_control/irs/en/)). In one embodiment, the method for controlling pests comprises applying the compositions of the invention to the target pests, to their locus or to a surface or substrate by brushing, rolling, spraying, spreading or dipping. By way of example, an IRS (indoor residual spraying) application of a surface such as a wall, ceiling or floor surface is contemplated by the method of the invention. In another embodiment, it is contemplated to apply such compositions to a substrate such as non-woven or a fabric material in the form of (or which can be used in the manufacture of) netting, clothing, bedding, curtains and tents.

In one embodiment, the method for controlling such pests comprises applying a pesticidally effective amount of the compositions of the invention to the target pests, to their locus, or to a surface or substrate so as to provide effective residual pesticidal activity on the surface or substrate. Such application may be made by brushing, rolling, spraying, spreading or dipping the pesticidal composition of the invention. By way of example, an IRS application of a surface such as a wall, ceiling or floor

surface is contemplated by the method of the invention so as to provide effective residual pesticidal activity on the surface. In another embodiment, it is contemplated to apply such compositions for residual control of pests on a substrate such as a fabric material in the form of (or which can be used in the manufacture of) netting, clothing, bedding, curtains and tents.

5 Substrates including non-woven, fabrics or netting to be treated may be made of natural fibres such as cotton, raffia, jute, flax, sisal, hessian, or wool, or synthetic fibres such as polyamide, polyester, polypropylene, polyacrylonitrile or the like. The polyesters are particularly suitable. The methods of textile treatment are known, e.g. WO 2008/151984, WO 2003/034823, US 5631072, WO 2005/64072, WO2006/128870, EP 1724392, WO 2005113886 or WO 2007/090739.

10 Further areas of use of the compositions according to the invention are the field of tree injection/trunk treatment for all ornamental trees as well all sort of fruit and nut trees.

In the field of tree injection/trunk treatment, the compounds according to the present invention are especially suitable against wood-boring insects from the order *Lepidoptera* as mentioned above and from the order *Coleoptera*, especially against woodborers listed in the following tables A and B:

15 Table A. Examples of exotic woodborers of economic importance.

Family	Species	Host or Crop Infested
Buprestidae	<i>Agrilus planipennis</i>	Ash
Cerambycidae	<i>Anoplura glabripennis</i>	Hardwoods
Scolytidae	<i>Xylosandrus crassiusculus</i>	Hardwoods
	<i>X. mutilatus</i>	Hardwoods
	<i>Tomicus piniperda</i>	Conifers

Table B. Examples of native woodborers of economic importance.

Family	Species	Host or Crop Infested
Buprestidae	<i>Agrilus anxius</i>	Birch
	<i>Agrilus politus</i>	Willow, Maple
	<i>Agrilus sayi</i>	Bayberry, Sweetfern
	<i>Agrilus vittaticollis</i>	Apple, Pear, Cranberry, Serviceberry, Hawthorn
	<i>Chrysobothris femorata</i>	Apple, Apricot, Beech, Boxelder, Cherry, Chestnut, Currant, Elm, Hawthorn, Hackberry, Hickory, Horsechestnut, Linden, Maple, Mountain-ash, Oak, Pecan, Pear, Peach, Persimmon, Plum, Poplar, Quince, Redbud, Serviceberry, Sycamore, Walnut, Willow
	<i>Texania campestris</i>	Basswood, Beech, Maple, Oak, Sycamore, Willow, Yellow-poplar

Family	Species	Host or Crop Infested
Cerambycidae	<i>Goes pulverulentus</i>	Beech, Elm, Nuttall, Willow, Black oak, Cherrybark oak, Water oak, Sycamore
	<i>Goes tigrinus</i>	Oak
	<i>Neoclytus acuminatus</i>	Ash, Hickory, Oak, Walnut, Birch, Beech, Maple, Eastern hophornbeam, Dogwood, Persimmon, Redbud, Holly, Hackberry, Black locust, Honeylocust, Yellow-poplar, Chestnut, Osage-orange, Sassafras, Lilac, Mountain-mahogany, Pear, Cherry, Plum, Peach, Apple, Elm, Basswood, Sweetgum
	<i>Neoptychodes trilineatus</i>	Fig, Alder, Mulberry, Willow, Netleaf hackberry
	<i>Oberea ocellata</i>	Sumac, Apple, Peach, Plum, Pear, Currant, Blackberry
	<i>Oberea tripunctata</i>	Dogwood, Viburnum, Elm, Sourwood, Blueberry, Rhododendron, Azalea, Laurel, Poplar, Willow, Mulberry
	<i>Oncideres cingulata</i>	Hickory, Pecan, Persimmon, Elm, Sourwood, Basswood, Honeylocust, Dogwood, Eucalyptus, Oak, Hackberry, Maple, Fruit trees
	<i>Saperda calcarata</i>	Poplar
Scolytidae	<i>Corthylus columbianus</i>	Maple, Oak, Yellow-poplar, Beech, Boxelder, Sycamore, Birch, Basswood, Chestnut, Elm
	<i>Dendroctonus frontalis</i>	Pine
	<i>Dryocoetes betulae</i>	Birch, Sweetgum, Wild cherry, Beech, Pear
	<i>Monarthrum fasciatum</i>	Oak, Maple, Birch, Chestnut, Sweetgum, Blackgum, Poplar, Hickory, Mimosa, Apple, Peach, Pine
	<i>Phloeotribus liminaris</i>	Peach, Cherry, Plum, Black cherry, Elm, Mulberry, Mountain-ash
	<i>Pseudopityophthorus pruinosis</i>	Oak, American beech, Black cherry, Chickasaw plum, Chestnut, Maple, Hickory, Hornbeam, Hophornbeam
Sesiidae	<i>Paranthrene simulans</i>	Oak, American chestnut
	<i>Sannina uroceriformis</i>	Persimmon
	<i>Synanthedon exitiosa</i>	Peach, Plum, Nectarine, Cherry, Apricot, Almond, Black cherry
	<i>Synanthedon pictipes</i>	Peach, Plum, Cherry, Beach, Black Cherry
	<i>Synanthedon rubrofascia</i>	Tupelo

Family	Species	Host or Crop Infested
	<i>Synanthedon scitula</i>	Dogwood, Pecan, Hickory, Oak, Chestnut, Beech, Birch, Black cherry, Elm, Mountain-ash, Viburnum, Willow, Apple, Loquat, Ninebark, Bayberry
	Vitacea polistiformis	Grape

The present invention may be also used to control any insect pests that may be present in turfgrass, including for example beetles, caterpillars, fire ants, ground pearls, millipedes, sow bugs, mites, mole crickets, scales, mealybugs, ticks, spittlebugs, southern chinch bugs and white grubs. The present invention may be used to control insect pests at various stages of their life cycle, including eggs, larvae, nymphs and adults.

In particular, the present invention may be used to control insect pests that feed on the roots of turfgrass including white grubs (such as *Cyclocephala* spp. (e.g. masked chafer, *C. lurida*), *Rhizotrogus* spp. (e.g. European chafer, *R. majalis*), *Cotinus* spp. (e.g. Green June beetle, *C. nitida*), *Popillia* spp. (e.g. Japanese beetle, *P. japonica*), *Phyllophaga* spp. (e.g. May/June beetle), *Ataenius* spp. (e.g. Black turfgrass ataenius, *A. spretulus*), *Maladera* spp. (e.g. Asiatic garden beetle, *M. castanea*) and *Tomarus* spp.), ground pearls (*Margarodes* spp.), mole crickets (tawny, southern, and short-winged; *Scapteriscus* spp., *Gryllotalpa africana*) and leatherjackets (European crane fly, *Tipula* spp.).

The present invention may also be used to control insect pests of turfgrass that are thatch dwelling, including armyworms (such as fall armyworm *Spodoptera frugiperda*, and common armyworm *Pseudaletia unipuncta*), cutworms, billbugs (*Sphenophorus* spp., such as *S. venatus verstitus* and *S. parvulus*), and sod webworms (such as *Crambus* spp. and the tropical sod webworm, *Herpetogramma phaeopteralis*).

The present invention may also be used to control insect pests of turfgrass that live above the ground and feed on the turfgrass leaves, including chinch bugs (such as southern chinch bugs, *Blissus insularis*), Bermudagrass mite (*Eriophyes cynodontiensis*), rhodesgrass mealybug (*Antonina graminis*), two-lined spittlebug (*Prospapia bicincta*), leafhoppers, cutworms (*Noctuidae* family), and greenbugs.

The present invention may also be used to control other pests of turfgrass such as red imported fire ants (*Solenopsis invicta*) that create ant mounds in turf.

In the hygiene sector, the compositions according to the invention are active against ectoparasites such as hard ticks, soft ticks, mange mites, harvest mites, flies (biting and licking), parasitic fly larvae, lice, hair lice, bird lice and fleas. Examples of such parasites are:

Of the order Anoplurida: *Haematopinus* spp., *Linognathus* spp., *Pediculus* spp. and *Phtirus* spp., *Solenopotes* spp.;

Of the order Mallophagida: *Trimenopon* spp., *Menopon* spp., *Trinoton* spp., *Bovicola* spp., *Werneckiella* spp., *Lepikentron* spp., *Damalina* spp., *Trichodectes* spp. and *Felicola* spp.;

Of the order Diptera and the suborders Nematocera and Brachycera, for example *Aedes* spp., *Anopheles* spp., *Culex* spp., *Simulium* spp., *Eusimulium* spp., *Phlebotomus* spp., *Lutzomyia* spp., *Culicoides* spp., *Chrysops* spp., *Hybomitra* spp., *Atylotus* spp., *Tabanus* spp., *Haematopota* spp.,

Philipomyia spp., Braula spp., Musca spp., Hydrotaea spp., Stomoxys spp., Haematobia spp., Morellia spp., Fannia spp., Glossina spp., Calliphora spp., Lucilia spp., Chrysomyia spp., Wohlfahrtia spp., Sarcophaga spp., Oestrus spp., Hypoderma spp., Gasterophilus spp., Hippobosca spp., Lipoptena spp. and Melophagus spp.;

5 Of the order Siphonaptera, for example Pulex spp., Ctenocephalides spp., Xenopsylla spp., Ceratophyllus spp.;

Of the order Heteroptera, for example Cimex spp., Triatoma spp., Rhodnius spp., Panstrongylus spp.;

10 Of the order Blattaria, for example Blatta orientalis, Periplaneta americana, Blattella germanica and Supella spp.;

Of the subclass Acaria (Acarida) and the orders Meta- and Meso-stigmata, for example Argas spp., Ornithodoros spp., Otobius spp., Ixodes spp., Amblyomma spp., Boophilus spp., Dermacentor spp., Haemophysalis spp., Hyalomma spp., Rhipicephalus spp., Dermanyssus spp., Raillietia spp., Pneumonyssus spp., Sternostoma spp. and Varroa spp.;

15 Of the orders Actiniedida (Prostigmata) and Acaridida (Astigmata), for example Acarapis spp., Cheyletiella spp., Ornithocheyletia spp., Myobia spp., Psorergates spp., Demodex spp., Trombicula spp., Lirophorus spp., Acarus spp., Tyrophagus spp., Caloglyphus spp., Hypodectes spp., Pterolichus spp., Psoroptes spp., Chorioptes spp., Otodectes spp., Sarcoptes spp., Notoedres spp., Knemidocoptes spp., Cytodites spp. and Laminosioptes spp.

20 The compositions according to the invention are also suitable for protecting against insect infestation in the case of materials such as wood, textiles, plastics, adhesives, glues, paints, paper and card, leather, floor coverings and buildings.

The compositions according to the invention can be used, for example, against the following pests: beetles such as Hylotrupes bajulus, Chlorophorus pilosus, Anobium punctatum, Xestobium  
25 rufovillosum, Ptilinuspecticornis, Dendrobium pertinax, Ernobius mollis, Priobium carpini, Lyctus brunneus, Lyctus africanus, Lyctus planicollis, Lyctus linearis, Lyctus pubescens, Trogoxylon aequale, Minthesrugicollis, Xyleborus spec., Tryptodendron spec., Apatte monachus, Bostrychus capucinus, Heterobostrychus brunneus, Sinoxylon spec. and Dinoderus minutus, and also hymenopterans such as Sirex juvencus, Urocerus gigas, Urocerus gigas taignus and Urocerus augur, and termites such as  
30 Kaloterms flavicollis, Cryptotermes brevis, Heterotermes indicola, Reticulitermes flavipes, Reticulitermes santonensis, Reticulitermes lucifugus, Mastotermes darwiniensis, Zootermopsis nevadensis and Coptotermes formosanus, and bristletails such as Lepisma saccharina.

The compounds of formulae (I), and (I'), or salts thereof, are especially suitable for controlling one or more pests selected from the family: Noctuidae, Plutellidae, Chrysomelidae, Thripidae,  
35 Pentatomidae, Tortricidae, Delphacidae, Aphididae, Noctuidae, Crambidae, Meloidogynidae, and Heteroderidae. In a preferred embodiment of each aspect, a compound TX (where the abbreviation "TX" means "one compound selected from the compounds defined in Tables A-1 to A-21, and Table P") controls one or more of pests selected from the family: Noctuidae, Plutellidae, Chrysomelidae, Thripidae,

Pentatomidae, Tortricidae, Delphacidae, Aphididae, Noctuidae, Crambidae, Meloidogynidae, and Heteroderidae.

The compounds of formulae (I), and (I'), or salts thereof, are especially suitable for controlling one or more of pests selected from the genus: *Spodoptera spp*, *Plutella spp*, *Frankliniella spp*, *Thrips spp*, *Euschistus spp*, *Cydia spp*, *Nilaparvata spp*, *Myzus spp*, *Aphis spp*, *Diabrotica spp*, *Rhopalosiphum spp*, *Pseudoplusia spp* and *Chilo spp*. . In a preferred embodiment of each aspect, a compound TX (where the abbreviation "TX" means "one compound selected from the compounds defined in Tables A-1 to A-21, and Table P") controls one or more of pests selected from the genus: *Spodoptera spp*, *Plutella spp*, *Frankliniella spp*, *Thrips spp*, *Euschistus spp*, *Cydia spp*, *Nilaparvata spp*, *Myzus spp*, *Aphis spp*, *Diabrotica spp*, *Rhopalosiphum spp*, *Pseudoplusia spp* and *Chilo spp*.

The compounds of formulae (I), and (I'), or salts thereof, are especially suitable for controlling one or more of *Spodoptera littoralis*, *Plutella xylostella*, *Frankliniella occidentalis*, *Thrips tabaci*, *Euschistus heros*, *Cydia pomonella*, *Nilaparvata lugens*, *Myzus persicae*, *Chrysodeixis includens*, *Aphis craccivora*, *Diabrotica balteata*, *Rhopalosiphum padi*, and *Chilo suppressalis*.

In a preferred embodiment of each aspect, a compound TX (where the abbreviation "TX" means "one compound selected from the compounds defined in Tables A-1 to A-21, and Table P") controls one or more of *Spodoptera littoralis*, *Plutella xylostella*, *Frankliniella occidentalis*, *Thrips tabaci*, *Euschistus heros*, *Cydia pomonella*, *Nilaparvata lugens*, *Myzus persicae*, *Chrysodeixis includens*, *Aphis craccivora*, *Diabrotica balteata*, *Rhopalosiphum Padi*, and *Chilo Suppressalis*, such as *Spodoptera littoralis* + TX, *Plutella xylostella* + TX; *Frankliniella occidentalis* + TX, *Thrips tabaci* + TX, *Euschistus heros* + TX, *Cydia pomonella* + TX, *Nilaparvata lugens* + TX, *Myzus persicae* + TX, *Chrysodeixis includens* + TX, *Aphis craccivora* + TX, *Diabrotica balteata* + TX, *Rhopalosiphum Padi* + TX, and *Chilo suppressalis* + TX.

In an embodiment, of each aspect, one compound from Tables A-1 to A-21, and Table P is suitable for controlling *Spodoptera littoralis*, *Plutella xylostella*, *Frankliniella occidentalis*, *Thrips tabaci*, *Euschistus heros*, *Cydia pomonella*, *Nilaparvata lugens*, *Myzus persicae*, *Chrysodeixis includens*, *Aphis craccivora*, *Diabrotica balteata*, *Rhopalosiphum padi*, and *Chilo suppressalis* in cotton, vegetable, maize, cereal, rice and soya crops.

In an embodiment, one compound from Tables A-1 to A-21, and Table P is suitable for controlling *Mamestra* (preferably in vegetables), *Cydia pomonella* (preferably in apples), *Empoasca* (preferably in vegetables, vineyards), *Leptinotarsa* (preferably in potatoes) and *Chilo suppressalis* (preferably in rice).

Compounds according to the invention may possess any number of benefits including, inter alia, advantageous levels of biological activity for protecting plants against insects or superior properties for use as agrochemical active ingredients (for example, greater biological activity, an advantageous spectrum of activity, an increased safety profile (against non-target organisms above and below ground (such as fish, birds and bees), improved physico-chemical properties, or increased biodegradability). In particular, it has been surprisingly found that certain compounds of formula (I) may show an



advantageous safety profile with respect to non-target arthropods, in particular pollinators such as honey bees, solitary bees, and bumble bees. Most particularly, *Apis mellifera*.

The compounds according to the invention can be used as pesticidal agents in unmodified form, but they are generally formulated into compositions in various ways using formulation adjuvants, such as carriers, solvents and surface-active substances. The formulations can be in various physical forms, e.g. in the form of dusting powders, gels, wettable powders, water-dispersible granules, water-dispersible tablets, effervescent pellets, emulsifiable concentrates, micro-emulsifiable concentrates, oil-in-water emulsions, oil-flowables, aqueous dispersions, oily dispersions, suspo-emulsions, capsule suspensions, emulsifiable granules, soluble liquids, water-soluble concentrates (with water or a water-miscible organic solvent as carrier), impregnated polymer films or in other forms known e.g. from the Manual on Development and Use of FAO and WHO Specifications for Pesticides, United Nations, First Edition, Second Revision (2010). Such formulations can either be used directly or diluted prior to use. The dilutions can be made, for example, with water, liquid fertilisers, micronutrients, biological organisms, oil or solvents.

The formulations can be prepared e.g. by mixing the active ingredient with the formulation adjuvants in order to obtain compositions in the form of finely divided solids, granules, solutions, dispersions or emulsions. The active ingredients can also be formulated with other adjuvants, such as finely divided solids, mineral oils, oils of vegetable or animal origin, modified oils of vegetable or animal origin, organic solvents, water, surface-active substances or combinations thereof.

The active ingredients can also be contained in very fine microcapsules. Microcapsules contain the active ingredients in a porous carrier. This enables the active ingredients to be released into the environment in controlled amounts (e.g. slow-release). Microcapsules usually have a diameter of from 0.1 to 500 microns. They contain active ingredients in an amount of about from 25 to 95 % by weight of the capsule weight. The active ingredients can be in the form of a monolithic solid, in the form of fine particles in solid or liquid dispersion or in the form of a suitable solution. The encapsulating membranes can comprise, for example, natural or synthetic rubbers, cellulose, styrene/butadiene copolymers, polyacrylonitrile, polyacrylate, polyesters, polyamides, polyureas, polyurethane or chemically modified polymers and starch xanthates or other polymers that are known to the person skilled in the art. Alternatively, very fine microcapsules can be formed in which the active ingredient is contained in the form of finely divided particles in a solid matrix of base substance, but the microcapsules are not themselves encapsulated.

The formulation adjuvants that are suitable for the preparation of the compositions according to the invention are known *per se*. As liquid carriers there may be used: water, toluene, xylene, petroleum ether, vegetable oils, acetone, methyl ethyl ketone, cyclohexanone, acid anhydrides, acetonitrile, acetophenone, amyl acetate, 2-butanone, butylene carbonate, chlorobenzene, cyclohexane, cyclohexanol, alkyl esters of acetic acid, diacetone alcohol, 1,2-dichloropropane, diethanolamine, p-diethylbenzene, diethylene glycol, diethylene glycol abietate, diethylene glycol butyl ether, diethylene glycol ethyl ether, diethylene glycol methyl ether, *N,N*-dimethylformamide, dimethyl sulfoxide, 1,4-

dioxane, dipropylene glycol, dipropylene glycol methyl ether, dipropylene glycol dibenzoate, diproxitol, alkylpyrrolidone, ethyl acetate, 2-ethylhexanol, ethylene carbonate, 1,1,1-trichloroethane, 2-heptanone, alpha-pinene, d-limonene, ethyl lactate, ethylene glycol, ethylene glycol butyl ether, ethylene glycol methyl ether, gamma-butyrolactone, glycerol, glycerol acetate, glycerol diacetate, glycerol triacetate, 5 hexadecane, hexylene glycol, isoamyl acetate, isobornyl acetate, isooctane, isophorone, isopropylbenzene, isopropyl myristate, lactic acid, laurylamine, mesityl oxide, methoxypropanol, methyl isoamyl ketone, methyl isobutyl ketone, methyl laurate, methyl octanoate, methyl oleate, methylene chloride, m-xylene, n-hexane, n-octylamine, octadecanoic acid, octylamine acetate, oleic acid, oleylamine, o-xylene, phenol, polyethylene glycol, propionic acid, propyl lactate, propylene carbonate, 10 propylene glycol, propylene glycol methyl ether, p-xylene, toluene, triethyl phosphate, triethylene glycol, xylenesulfonic acid, paraffin, mineral oil, trichloroethylene, perchloroethylene, ethyl acetate, amyl acetate, butyl acetate, propylene glycol methyl ether, diethylene glycol methyl ether, methanol, ethanol, isopropanol, and alcohols of higher molecular weight, such as amyl alcohol, tetrahydrofurfuryl alcohol, hexanol, octanol, ethylene glycol, propylene glycol, glycerol, N-methyl-2-pyrrolidone and the like.

15 Suitable solid carriers are, for example, talc, titanium dioxide, pyrophyllite clay, silica, attapulgite clay, kieselguhr, limestone, calcium carbonate, bentonite, calcium montmorillonite, cottonseed husks, wheat flour, soybean flour, pumice, wood flour, ground walnut shells, lignin and similar substances.

A large number of surface-active substances can advantageously be used in both solid and liquid formulations, especially in those formulations which can be diluted with a carrier prior to use.

20 Surface-active substances may be anionic, cationic, non-ionic or polymeric and they can be used as emulsifiers, wetting agents or suspending agents or for other purposes. Typical surface-active substances include, for example, salts of alkyl sulfates, such as diethanolammonium lauryl sulfate; salts of alkylarylsulfonates, such as calcium dodecylbenzenesulfonate; alkylphenol/alkylene oxide addition products, such as nonylphenol ethoxylate; alcohol/alkylene oxide addition products, such as 25 tridecylalcohol ethoxylate; soaps, such as sodium stearate; salts of alkylnaphthalenesulfonates, such as sodium dibutyl-naphthalenesulfonate; dialkyl esters of sulfosuccinate salts, such as sodium di(2-ethylhexyl)sulfosuccinate; sorbitol esters, such as sorbitol oleate; quaternary amines, such as lauryltrimethylammonium chloride, polyethylene glycol esters of fatty acids, such as polyethylene glycol stearate; block copolymers of ethylene oxide and propylene oxide; and salts of mono- and di- 30 alkylphosphate esters; and also further substances described e.g. in McCutcheon's Detergents and Emulsifiers Annual, MC Publishing Corp., Ridgewood New Jersey (1981).

Further adjuvants that can be used in pesticidal formulations include crystallisation inhibitors, viscosity modifiers, suspending agents, dyes, anti-oxidants, foaming agents, light absorbers, mixing auxiliaries, antifoams, complexing agents, neutralising or pH-modifying substances and buffers, 35 corrosion inhibitors, fragrances, wetting agents, take-up enhancers, micronutrients, plasticisers, glidants, lubricants, dispersants, thickeners, antifreezes, microbicides, and liquid and solid fertilisers.

The compositions according to the invention can include an additive comprising an oil of vegetable or animal origin, a mineral oil, alkyl esters of such oils or mixtures of such oils and oil derivatives. The amount of oil additive in the composition according to the invention is generally from

0.01 to 10 %, based on the mixture to be applied. For example, the oil additive can be added to a spray tank in the desired concentration after a spray mixture has been prepared. Preferred oil additives comprise mineral oils or an oil of vegetable origin, for example rapeseed oil, olive oil or sunflower oil, emulsified vegetable oil, alkyl esters of oils of vegetable origin, for example the methyl derivatives, or  
 5 an oil of animal origin, such as fish oil or beef tallow. Preferred oil additives comprise alkyl esters of C<sub>8</sub>-C<sub>22</sub> fatty acids, especially the methyl derivatives of C<sub>12</sub>-C<sub>18</sub> fatty acids, for example the methyl esters of lauric acid, palmitic acid and oleic acid (methyl laurate, methyl palmitate and methyl oleate, respectively). Many oil derivatives are known from the Compendium of Herbicide Adjuvants, 10<sup>th</sup> Edition, Southern Illinois University, 2010.

10 The inventive compositions generally comprise from 0.1 to 99 % by weight, especially from 0.1 to 95 % by weight, of compounds of the present invention and from 1 to 99.9 % by weight of a formulation adjuvant which preferably includes from 0 to 25 % by weight of a surface-active substance. Whereas commercial products may preferably be formulated as concentrates, the end user will normally employ dilute formulations.

15 The rates of application vary within wide limits and depend on the nature of the soil, the method of application, the crop plant, the pest to be controlled, the prevailing climatic conditions, and other factors governed by the method of application, the time of application and the target crop. As a general guideline compounds may be applied at a rate of from 1 to 2000 l/ha, especially from 10 to 1000 l/ha.

20 Formulation types include an emulsion concentrate (EC), a suspension concentrate (SC), a suspo-emulsion (SE), a capsule suspension (CS), a water dispersible granule (WG), an emulsifiable granule (EG), an emulsion, water in oil (EO), an emulsion, oil in water (EW), a micro-emulsion (ME), an oil dispersion (OD), an oil miscible flowable (OF), an oil miscible liquid (OL), a soluble concentrate (SL), an ultra-low volume suspension (SU), an ultra-low volume liquid (UL), a technical concentrate (TK), a dispersible concentrate (DC), a wettable powder (WP), a soluble granule (SG) or any technically feasible  
 25 formulation in combination with agriculturally acceptable adjuvants.

Preferred formulations can have the following compositions (weight %):

Emulsifiable concentrates:

active ingredient: 1 to 95 %, preferably 60 to 90 %  
 surface-active agent: 1 to 30 %, preferably 5 to 20 %  
 30 liquid carrier: 1 to 80 %, preferably 1 to 35 %

Dusts:

active ingredient: 0.1 to 10 %, preferably 0.1 to 5 %  
 solid carrier: 99.9 to 90 %, preferably 99.9 to 99 %  
 35

Suspension concentrates:

active ingredient: 5 to 75 %, preferably 10 to 50 %  
 water: 94 to 24 %, preferably 88 to 30 %  
 surface-active agent: 1 to 40 %, preferably 2 to 30 %

Wettable powders:

active ingredient: 0.5 to 90 %, preferably 1 to 80 %

surface-active agent: 0.5 to 20 %, preferably 1 to 15 %

5 solid carrier: 5 to 95 %, preferably 15 to 90 %

Granules:

active ingredient: 0.1 to 30 %, preferably 0.1 to 15 %

solid carrier: 99.5 to 70 %, preferably 97 to 85 %

10 The following combinations of a compound of formula I with another active substance in a weight ratio of 1:1 are preferred (where the abbreviation "TX" means "one compound selected from the compounds defined in the Tables A-1 to A-21, and Table P"):

(7E,9Z)-dodeca-7,9-dien-1-yl acetate + TX, (9Z,11E)-tetradeca-9,11-dien-1-yl acetate + TX, (9Z,12E)-tetradeca-9,12-dien-1-yl acetate + TX, (E)-6-methylhept-2-en-4-ol + TX, (E)-dec-5-en-1-yl acetate with (E)-dec-5-en-1-ol + TX, (E)-tridec-4-en-1-yl acetate + TX, (E,Z)-tetradeca-4,10-dien-1-yl acetate + TX, (Z)-dodec-7-en-1-yl acetate + TX, (Z)-hexadec-11-en-1-yl acetate + TX, (Z)-hexadec-11-enal + TX, (Z)-hexadec-13-en-11-yn-1-yl acetate + TX, (Z)-icos-13-en-10-one + TX, (Z)-tetradec-7-en-1-al + TX, (Z)-tetradec-9-en-1-ol + TX, (Z)-tetradec-9-en-1-yl acetate + TX, 1,2-dibromo-3-chloropropane + TX, 1,2-dichloropropane + TX, 1,2-dichloropropane with 1,3-dichloropropene + TX, 1,3-dichloropropene + TX, 14-methyloctadec-1-ene + TX, 1-hydroxy-1H-pyridine-2-thione + TX, 2-(octylthio)ethanol + TX, 2-chlorophenyl N-methylcarbamate (CPMC) + TX, 3-(4-chlorophenyl)-5-methylrhodanine + TX, 3,4-dichlorotetrahydrothiophene 1,1-dioxide + TX, 4-(quinoxalin-2-ylamino)benzenesulfonamide + TX, 4-methylnonan-5-ol with 4-methylnonan-5-one + TX, 5-methyl-6-thioxo-1,3,5-thiadiazinan-3-ylacetic acid + TX, 6-isopentenylaminopurine + TX, 8-hydroxyquinoline sulfate + TX, abamectin + TX, acequinocyl + TX, acetamiprid + TX, acetoprole + TX, acrinathrin + TX, acynonapyr + TX, Adoxophyes orana GV + TX, afidopyropen + TX, afoxalaner + TX, Agrobacterium radiobacter + TX, AKD-3088 + TX, alanycarb + TX, aldicarb + TX, aldoxycarb + TX, allethrin + TX, alpha-cypermethrin + TX, alphamethrin + TX, alpha-multistriatin + TX, Amblyseius spp. + TX, amidoflumet + TX, amino acids + TX, aminocarb + TX, Anagrapha falcifera NPV + TX, Anagrus atomus + TX, Aphelinus abdominalis + TX, Aphidius colemani + TX, Aphidoletes aphidimyza + TX, apholate + TX, Autographa californica NPV + TX, AZ 60541 + TX, azadirachtin + TX, azocyclotin + TX, Bacillus aizawai + TX, Bacillus chitosporus AQ746 (NRRL Accession No B-21 618) + TX, Bacillus firmus + TX, Bacillus kurstaki + TX, Bacillus mycooides AQ726 (NRRL Accession No. B-21664) + TX, Bacillus pumilus (NRRL Accession No B-30087) + TX, Bacillus pumilus AQ717 (NRRL Accession No. B-21662) + TX, Bacillus sp. AQ175 (ATCC Accession No. 55608) + TX, Bacillus sp. AQ177 (ATCC Accession No. 55609) + TX, Bacillus sp. AQ178 (ATCC Accession No. 53522) + TX, Bacillus sphaericus Neide + TX, Bacillus subtilis AQ153 (ATCC Accession No. 55614) + TX, Bacillus subtilis AQ30002 (NRRL Accession No. B-50421) + TX, Bacillus subtilis AQ30004 (NRRL

Accession No. B- 50455) + TX, *Bacillus subtilis* AQ713 (NRRL Accession No. B-21661) + TX,  
*Bacillus subtilis* AQ743 (NRRL Accession No. B-21665) + TX, *Bacillus subtilis* unspecified + TX,  
*Bacillus thuringiensis* AQ52 (NRRL Accession No. B-21619) + TX, *Bacillus thuringiensis* BD#32  
 (NRRL Accession No B-21530) + TX, *Bacillus thuringiensis* Berliner + TX, *Bacillus thuringiensis*  
 5 subsp. Aizawai + TX, *Bacillus thuringiensis* subsp. Israelensis + TX, *Bacillus thuringiensis* subsp.  
*Japonensis* + TX, *Bacillus thuringiensis* subsp. Kurstaki + TX, *Bacillus thuringiensis* subsp.  
*Tenebrionis* + TX, *Bacillus thuringiensis* subspec. kurstaki BMP 123 + TX, *Beauveria bassiana* +  
 TX, *Beauveria brongniartii* + TX, benclothiaz + TX, benomyl + TX, bensultap + TX, benzoximate  
 + TX, benzpyrimoxan + TX, betacyfluthrin + TX, beta-cypermethrin + TX, bethoxazin + TX,  
 10 bifenazate + TX, bifenthrin + TX, binapacryl + TX, bioallethrin + TX, bioresmethrin + TX,  
 bis(tributyltin) oxide + TX, bisazir + TX, bistrifluron + TX, brevicomin + TX, broflanilide + TX,  
 brofluthrin + TX, bromoacetamide + TX, bromophos-ethyl + TX, bronopol + TX, buprofezine +  
 TX, busulfan + TX, butocarboxim + TX, butopyronoxyl + TX, butoxy(polypropylene glycol) + TX,  
 butylpyridaben + TX, cadusafos + TX, calcium arsenate + TX, carbaryl + TX, carbofuran + TX,  
 15 carbon disulfide + TX, carbosulfan + TX, cartap + TX, CAS number: 1594624-87-9 + TX, CAS  
 number: 1922957-47-8 + TX, CAS number: 1255091-74-7 + TX, CAS number: 1365070-72-9 +  
 TX, CAS number: 1445683-71-5 + TX, CAS number: 1445684-82-1 + TX, CAS number:  
 1594626-19-3 + TX, CAS number: 1594637-65-6 + TX, CAS number: 1632218-00-8 + TX, CAS  
 number: 1808115-49-2 + TX, CAS number: 1922957-45-6 + TX, CAS number: 1922957-46-7 +  
 20 TX, CAS number: 1922957-48-9 + TX, CAS number: 1956329-03-5 + TX, CAS number:  
 1990457-52-7 + TX, CAS number: 1990457-55-0 + TX, CAS number: 1990457-57-2 + TX, CAS  
 number: 1990457-66-3 + TX, CAS number: 1990457-77-6 + TX, CAS number: 1990457-85-6 +  
 TX, CAS number: 2032403-97-5 + TX, CAS number: 2044701-44-0 + TX, CAS number:  
 2095470-94-1 + TX, CAS number: 2128706-05-6 + TX, CAS number: 2133042-31-4 + TX, CAS  
 25 number: 2133042-44-9 + TX, CAS number: 2171099-09-3 + TX, CAS number: 2220132-55-6 +  
 TX, CAS number: 2368920-61-8 + TX, CAS number: 2377084-09-6 + TX, CAS number:  
 2396747-83-2 + TX, CAS number: 2408220-91-5 + TX, CAS number: 2408220-94-8 + TX, CAS  
 number: 2415706-16-8 + TX, CAS number: 2615135-05-0 + TX, CAS number: 2719848-60-7 +  
 TX, CAS number: RNA (*Leptinotarsa decemlineata*-specific recombinant double-stranded  
 30 interfering GS2) + TX, chlorantraniliprole + TX, chlordane + TX, chlorfenapyr + TX, chloropicrin +  
 TX, chloroprallethrin + TX, chlorpyrifos + TX, chromafenozide + TX, *Chrysoperla carnea* + TX,  
 clenpirin + TX, cloethocarb + TX, clothianidin + TX, codlélure + TX, codlemone + TX, copper  
 acetoarsenite + TX, copper dioctanoate + TX, copper hydroxide + TX, copper sulfate + TX,  
 cresol + TX, crufomate + TX, *Cryptolaemus montrouzieri* + TX, cuelure + TX, cyanofenphos +  
 35 TX, cyantraniliprole + TX, cybutryne + TX, cyclaniliprole + TX, cyclobutrifluram + TX,  
 cycloprothrin + TX, cycloxaprid + TX, *Cydia pomonella* GV + TX, cyenopyrafen + TX, cyetpyrafen  
 + TX, cyflumetofen + TX, cyfluthrin + TX, cyhalodiamide + TX, cylohalothrin + TX, cypermethrin +  
 TX, cyphenothrin + TX, cyproflanilide + TX, cyromazine + TX, cytokinins + TX, *Dacnusa sibirica*  
 + TX, dazomet + TX, DBCP + TX, DCIP + TX, deltamethrin + TX, diafenthiuron + TX, dialifos +

TX, diamidafos + TX, dibrom + TX, dibutyl adipate + TX, dibutyl phthalate + TX, dibutyl succinate + TX, dichlofenthion + TX, dichlone + TX, dichlorophen + TX, dicliphos + TX, dicloromezotiaz + TX, diethyltoluamide + TX, diflubenzuron + TX, Diglyphus isaea + TX, dimatif + TX, dimethoate + TX, dimethyl carbate + TX, dimethyl phthalate + TX, dimpropyridaz + TX, dinactin + TX, dinocap + TX, dinotefuran + TX, dioxabenzofos + TX, dipyrithione + TX, disparlure + TX, D-limonene + TX, dodec-8-en-1-yl acetate + TX, dodec-9-en-1-yl acetate + TX, dodeca-8,10-dien-1-yl acetate + TX, dodicin + TX, dominicalure + TX, doramectin + TX, emamectin + TX, emamectin benzoate + TX, empenethrin + TX, Encarsia formosa + TX, endothal + TX, endrin + TX, eprinomectin + TX, epsilon - momfluorothrin + TX, epsilon-metofluthrin + TX, Eretmocerus eremicus + TX, esfenvalerate + TX, ethion + TX, ethiprole + TX, ethoprophos + TX, ethyl 4-methyloctanoate + TX, ethyl hexanediol + TX, ethylene dibromide + TX, etofenprox + TX, etoxazole + TX, etpyrafen + TX, eugenol + TX, Extract of seaweed and fermentation product derived from melasse + TX, Extract of seaweed and fermentation product derived from melasse comprising urea + TX, Extract of seaweed and fermented plant products + TX, Extract of seaweed and fermented plant products comprising phytohormones + TX, vitamins + TX, EDTA-chelated copper + TX, zinc + TX, and iron + TX, famphur + TX, fenaminosulf + TX, fenamiphos + TX, fenazaquin + TX, fenfluthrin + TX, fenitrothion + TX, fenmezoditiaz + TX, fenobucarb + TX, fenothiocarb + TX, fenoxycarb + TX, fenpropathrin + TX, fenpyrad + TX, fenpyroximate + TX, fensulfothion + TX, fenthion + TX, fentin + TX, fentinacetate + TX, fenvalerate + TX, ferric phosphate + TX, fipronil + TX, flometoquin + TX, flonicamid + TX, fluacrypyrim + TX, fluazaindolizine + TX, fluazuron + TX, flubendiamide + TX, flubenzimine + TX, fluchlordiniliprole + TX, flucitrate + TX, flucycloxuron + TX, flucythrinate + TX, fluensulfone + TX, fluensulfone [318290-98-1] + TX, flufenerim + TX, flufenprox + TX, flufiprole + TX, fluhexafon + TX, flumethrin + TX, fluopyram + TX, flupentiofenox flupyradifurone + TX, flupyrimin + TX, flupyroxystrobin + TX, fluralaner + TX, fluvalinate + TX, fluxametamide + TX, formaldehyde + TX, fosthiazate + TX, fosthietan + TX, frontalin + TX, furfural + TX, gamma-cyhalothrin + TX, Gossyplure® (1:1 mixture of the (Z,E) and (Z,Z) isomers of hexadeca-7,11-dien-1-yl-acetate) + TX, grandlure + TX, grandlure I + TX, grandlure II + TX, grandlure III + TX, grandlure IV + TX, Granulovirus + TX, guadipyr + TX, GY-81 + TX, halfenprox + TX, halofenozide + TX, Harpin + TX, Helicoverpa armigera Nucleopolyhedrovirus + TX, Helicoverpa zea NPV + TX, Helicoverpa zea Nucleopolyhedrovirus + TX, Heliothis punctigera Nucleopolyhedrovirus + TX, Heliothis virescens Nucleopolyhedrovirus + TX, hemel + TX, hempa + TX, heptafluthrin + TX, heterophos + TX, Heterorhabditis bacteriophora and H. megidis + TX, hexalure + TX, hexamide + TX, hexythiazox + TX, Hippodamia convergens + TX, hydramethylnon + TX, hydrargaphen + TX, hydrated lime + TX, imicyafos + TX, imidacloprid + TX, imiprothrin + TX, Indazapyroxamet + TX, indoxacarb + TX, iodomethane + TX, iprodione + TX, ipsdienol + TX, ipsenol + TX, isamidofos + TX, isazofos + TX, isocycloseram + TX, Isoflualanam (CAS number: 2892524-05-7) + TX, isothioate + TX, ivermectin + TX, japonilure + TX, kappa-bifenthrin + TX, kappa-tefluthrin + TX, kasugamycin + TX, kasugamycin hydrochloride hydrate + TX, kinetin + TX, lambda-cyhalothrin + TX, ledprona + TX, lepimectin + TX,

Leptomastix dactylopii + TX, lineatin + TX, litlure + TX, looplure + TX, lotilaner + TX, lufenuron + TX, Macrolophus caliginosus + TX, Mamestra brassicae NPV + TX, mecarphon + TX, medlure + TX, megatomoic acid + TX, metaflumizone + TX, metaldehyde + TX, metam + TX, metam-potassium + TX, metam-sodium + TX, Metaphycus helvolus + TX, Metarhizium anisopliae var. acridum + TX, Metarhizium anisopliae var. anisopliae + TX, Metarhizium spp. + TX, metepa + TX, methiocarb + TX, methiotepa + TX, methomyl + TX, methoquin-butyl + TX, methoxyfenozide + TX, methyl apholate + TX, methyl bromide + TX, methyl eugenol + TX, methyl isothiocyanate + TX, methylneodecanamide + TX, metofluthrin + TX, metolcarb + TX, mexacarbate + TX, milbemectin + TX, milbemycin oxime + TX, momfluorothrin + TX, morzid + TX, moxidectin + TX, muscalure + TX, Muscodor albus 620 (NRRL Accession No. 30547) + TX, Muscodor roseus A3-5 (NRRL Accession No. 30548) + TX, Myrothecium verrucaria composition + TX, nabam + TX, NC-184 + TX, Neem tree based products + TX, Neodiprion sertifer NPV and N. lecontei NPV + TX, nickel bis(dimethyldithiocarbamate) + TX, niclosamide + TX, niclosamide-olamine + TX, nicofluprole + TX, nitenpyram + TX, nithiazine + TX, nitrapyrin + TX, octadeca-2,13-dien-1-yl acetate + TX, octadeca-3,13-dien-1-yl acetate + TX, octhilinone + TX, omethoate + TX, orfralure + TX, Orius spp. + TX, oryctalure + TX, ostramone + TX, oxamate + TX, oxamyl + TX, oxazosulfyl + TX, oxolinic acid + TX, oxytetracycline + TX, Paecilomyces fumosoroseus + TX, Paecilomyces lilacinus + TX, parathion-ethyl + TX, Pasteuria nishizawae + TX, Pasteuria penetrans + TX, Pasteuria ramosa + TX, Pasteuria thornei + TX, Pasteuria usgae + TX, P-cymene + TX, penfluron + TX, pentachlorophenol + TX, permethrin + TX, phenothrin + TX, phorate + TX, phosphamidon + TX, phosphocarb + TX, Phytoseiulus persimilis + TX, picaridin + TX, piperazine + TX, piperonylbutoxide + TX, pirimicarb + TX, pirimiphos-ethyl + TX, pirimiphos-methyl + TX, Plutella xylostella Granulosis virus + TX, Plutella xylostella Nucleopolyhedrovirus + TX, Polyhedrosis virus + TX, potassium and molybdenum and EDTA-chelated manganese + TX, potassium ethylxanthate + TX, potassium hydroxyquinoline sulfate + TX, prallethrin + TX, probenazole + TX, profenofos + TX, profluthrin + TX, propargite + TX, propetamphos + TX, propoxur + TX, prothiophos + TX, protrifenbute + TX, pyflubumide + TX, pymetrozine + TX, pyraclofos + TX, pyrafluprole + TX, pyrethrum + TX, pyridaben + TX, pyridalyl + TX, pyridin-4-amine + TX, pyrifluquinazon + TX, pyrimidifen + TX, pyriminostrobin + TX, pyriprole + TX, pyriprole [394730-71-3] + TX, pyriproxifen + TX, QRD 420 (a terpenoid blend) + TX, QRD 452 (a terpenoid blend) + TX, QRD 460 (a terpenoid blend) + TX, Quillaja saponaria + TX, quinoclamine + TX, quinonamid + TX, resmethrin + TX, Rhodococcus globerulus AQ719 (NRRL Accession No B-21663) + TX, sarolaner + TX, S-bioallethrin + TX, sebufos + TX, selamectin + TX, siglure + TX, silafluofen + TX, simazine + TX, sodium pentachlorophenoxide + TX, sordidin + TX, spidoxamat + TX, spinetoram + TX, spinosad + TX, spirotetramat + TX, Spirodiclofen + TX, spiromesifen + TX, spiropidion + TX, spirotetramat + TX, Spodoptera exigua multicapsid nuclear polyhedrosis virus + TX, Spodoptera frugiperda Nucleopolyhedrovirus + TX, Steinernema bibionis + TX, Steinernema carpocapsae + TX, Steinernema feltiae + TX, Steinernema glaseri + TX, Steinernema riobrave + TX, Steinernema riobravus + TX, Steinernema scapterisci + TX,

Steinernema spp. + TX, Streptomyces galbus (NRRL Accession No. 30232) + TX, Streptomyces sp. (NRRL Accession No. B-30145) + TX, streptomycin + TX, streptomycin sesquisulfate + TX, strychnine + TX, sulcatol + TX, sulfoxaflor + TX, tazimcarb + TX, tebufenozide + TX, tebufenpyrad + TX, tebupirimiphos + TX, tecloftalam + TX, tefluthrin + TX, temephos + TX, tepa + TX, terbam + TX, terbufos + TX, terpenoid blend + TX, tetrachlorantraniliprole + TX, tetrachlorothiophene + TX, tetradec-11-en-1-yl acetate + TX, tetradiphon + TX, tetramethrin + TX, tetramethylfluthrin + TX, tetranactin + TX, tetraniliprole + TX, theta-cypermethrin + TX, thiacloprid + TX, thiafenox + TX, thiamethoxam + TX, thiocyclam + TX, thiodicarb + TX, thiofanox + TX, thiohempa + TX, thiomersal + TX, thiometon + TX, thionazin + TX, thiophanate + TX, thiosultap + TX, thiotepa + TX, tigolaner + TX, tiorantraniliprole + TX, tioazafen + TX, tolfenpyrad + TX, toxaphene + TX, tralomethrin + TX, transfluthrin + TX, tretamine + TX, triazamate + TX, triazophos + TX, triazuron + TX, tributyltin oxide + TX, trichlorfon + TX, trichloronate + TX, trichlorphon + TX, Trichogramma spp. + TX, trifenmorph + TX, trifluenfurionate + TX, triflumezopyrim + TX, trimedlure + TX, trimedlure A + TX, trimedlure B1 + TX, trimedlure B2 + TX, trimedlure C + TX, trimethacarb + TX, triphenyltin acetate + TX, triphenyltin hydroxide + TX, trunc-call + TX, tyclopyrazoflor + TX, Typhlodromus occidentalis + TX, uredepa + TX, Verticillium lecanii + TX, Verticillium spp. + TX, xyleneols + TX, YI-5302 + TX, zeatin + TX, zeta-Cypermethrin + TX;

N-[(1R)-1-benzyl-3-chloro-1-methyl-but-3-enyl]-8-fluoro-quinoline-3-carboxamide + TX, N-[(1S)-1-benzyl-3-chloro-1-methyl-but-3-enyl]-8-fluoro-quinoline-3-carboxamide + TX, N-ethyl-N'-[5-methoxy-2-methyl-4-[(2-trifluoromethyl)tetrahydrofuran-2-yl]phenyl]-N-methylformamidine (these compounds may be prepared from the methods described in WO2019/110427) + TX, (3',4',5'-trifluoro-biphenyl-2-yl)-amide + TX, (3-methylisoxazol-5-yl)-[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methanone (these compounds may be prepared from the methods described in WO 2017/220485) + TX, (4-phenoxyphenyl)methyl 2-amino-6-methyl-pyridine-3-carboxylate (this compound may be prepared from the methods described in WO 2014/006945) + TX, (5-methyl-2-pyridyl)-[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methanone + TX, (7E,9Z)-dodeca-7,9-dien-1-yl acetate + TX, (9Z,11E)-tetradeca-9,11-dien-1-yl acetate + TX, (9Z,12E)-tetradeca-9,12-dien-1-yl acetate + TX, (E)-6-methylhept-2-en-4-ol + TX, (E)-dec-5-en-1-yl acetate with (E)-dec-5-en-1-ol + TX, (E)-tridec-4-en-1-yl acetate + TX, (E,Z)-tetradeca-4,10-dien-1-yl acetate + TX, + TX, (R)-3-(difluoromethyl)-1-methyl-N-[1,1,3-trimethylindan-4-yl]pyrazole-4-carboxamide + TX, (Z)-dodec-7-en-1-yl acetate + TX, (Z)-hexadec-11-en-1-yl acetate + TX, (Z)-hexadec-11-enal + TX, (Z)-hexadec-13-en-11-yn-1-yl acetate + TX, (Z)-icos-13-en-10-one + TX, (Z)-tetradec-7-en-1-yl acetate + TX, (Z)-tetradec-9-en-1-yl acetate + TX, (Z,2E)-5-[1-(2,4-dichlorophenyl)pyrazol-3-yl]oxy-2-methoxyimino-N,3-dimethyl-pent-3-enamide (this compound may be prepared from the methods described in WO 2018/153707) + TX, (Z,2E)-5-[1-(4-chlorophenyl)pyrazol-3-yl]oxy-2-methoxyimino-N,3-dimethyl-pent-3-enamide + TX, + TX, [2-[3-[2-[1-[2-[3,5-bis(difluoromethyl)pyrazol-1-yl]acetyl]-4-piperidyl]thiazol-4-yl]-4,5-dihydroisoxazol-5-yl]-3-chloro-



phenyl] methanesulfonate + TX, 1-(4,5-dimethylbenzimidazol-1-yl)-4,4,5-trifluoro-3,3-dimethyl-isoquinoline + TX, 1-(4,5-dimethylbenzimidazol-1-yl)-4,4-difluoro-3,3-dimethyl-isoquinoline + TX, 1-(6,7-dimethylpyrazolo[1,5-a]pyridin-3-yl)-4,4,5-trifluoro-3,3-dimethyl-isoquinoline + TX, 1-(6,7-dimethylpyrazolo[1,5-a]pyridin-3-yl)-4,4,6-trifluoro-3,3-dimethyl-isoquinoline + TX, 1-(6-chloro-7-methyl-pyrazolo[1,5-a]pyridin-3-yl)-4,4-difluoro-3,3-dimethyl-isoquinoline (these compounds may be prepared from the methods described in WO2017/025510) + TX, 1,1-bis(4-chloro-phenyl)-2-ethoxyethanol + TX, 1,1-dichloro-2,2-bis(4-ethylphenyl)-ethane + TX, 1,2-dibromo-3-chloropropane + TX, 1,2-dichloropropane with 1,3-dichloropropene + TX, 1,3-dichloropropene + TX, 1,3-dimethoxy-1-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]urea + TX, 1-[2-[[1-(4-chlorophenyl)pyrazol-3-yl]oxymethyl]-3-methyl-phenyl]-4-methyl-tetrazol-5-one + TX, 10-dien-1-yl acetate + TX, 14-methyloctadec-1-ene + TX, 1-bromo-2-chloroethane + TX, 1-dichloro-1-nitroethane + TX, 1-hydroxy-1H-pyridine-2-thione + TX, 1-methoxy-3-methyl-1-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]urea + TX, 1-methyl-4-[3-methyl-2-[[2-methyl-4-(3,4,5-trimethylpyrazol-1-yl)phenoxy]methyl]phenyl]tetrazol-5-one + TX, 2-(difluoromethyl) - N-((3R) - 1 + TX, 1 + TX, 3- trimethylindan- 4- yl) pyridine- 3- carboxamide + TX, 2-(difluoromethyl) - N-((3R) - 1 + TX, 1 + TX, 3- trimethylindan- 4- yl) pyridine- 3- carboxamide + TX, 2-(1,3-dithiolan-2-yl)phenyl dimethylcarbamate + TX, 2-(2-butoxyethoxy)-ethyl piperonylate + TX, 2-(2-butoxyethoxy)ethyl thiocyanate + TX, 2-(4,5-dimethyl-1,3-dioxolan-2-yl)phenyl methylcarbamate + TX, 2-(4-chloro-3,5-xylyloxy)ethanol + TX, 2-(difluoromethyl)-N-(3-ethyl-1,1-dimethyl-indan-4-yl)pyridine-3-carboxamide + TX, 2-(difluoromethyl)-N-[(3R)-3-ethyl-1,1-dimethyl-indan-4-yl]pyridine-3-carboxamide + TX, 2-(difluoromethyl)-N-[(3S)-3-ethyl-1,1-dimethyl-indan-4-yl]pyridine-3-carboxamide (this compound may be prepared from the methods described in WO 2014/095675) + TX, 2-(difluoromethyl)-N-[3-ethyl-1,1-dimethyl-indan-4-yl]pyridine-3-carboxamide + TX, 2-(octylthio)-ethanol + TX, 2,2,2-trichloro-1-(3,4-dichloro-phenyl)ethyl acetate + TX, 2,2-dichlorovinyl 2-ethylsulfinylethyl methyl phosphate + TX, 2,2-difluoro-N-methyl-2-[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]acetamide + TX, 2,4-dichlorophenyl benzenesulfonate + TX, 2,6-Dimethyl-1H,5H-[1,4]dithiino[2,3-c:5,6-c']dipyrrole-1,3,5,7(2H,6H)-tetrone (this compound may be prepared from the methods described in WO 2011/138281) + TX, 2-[2-fluoro-6-[(8-fluoro-2-methyl-3-quinolyl)oxy]phenyl]propan-2-ol + TX, 2-[6-(4-bromophenoxy)-2-(trifluoromethyl)-3-pyridyl]-1-(1,2,4-triazol-1-yl)propan-2-ol (this compound may be prepared from the methods described in WO 2017/029179) + TX, 2-[6-(4-chlorophenoxy)-2-(trifluoromethyl)-3-pyridyl]-1-(1,2,4-triazol-1-yl)propan-2-ol (this compound may be prepared from the methods described in WO 2017/029179) + TX, 2-chlorovinyl diethyl phosphate + TX, 2-fluoro-N-methyl-N-1-naphthylacetamide + TX, 2-imidazolidone + TX, 2-isovalerylindan-1,3-dione + TX, 2-methyl(prop-2-ynyl)aminophenyl methylcarbamate + TX, 2-oxo-N-propyl-2-[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]acetamide (this compound may be prepared from the methods described in WO 2018/065414) + TX, 2-thiocyanatoethyl laurate + TX, 3-(4,4-difluoro-3,3-dimethyl-1-isoquinolyl)-7,8-dihydro-6H-cyclopenta[e]benzimidazole (these compounds may be prepared from the methods described in WO2016/156085) + TX, 3-(4,4-

5 difluoro-3,4-dihydro-3,3-dimethylisoquinolin-1-yl)quinolone + TX, 3-(4-chlorophenyl)-5-methylrhodanine + TX, 3-(difluoromethyl)-1-methyl-N-[1,1,3-trimethylindan-4-yl]pyrazole-4-carboxamide + TX, 3,4-dichlorotetrahydrothio-phenone 1,1-dioxide + TX, 3-[2-(1-chlorocyclopropyl)-3-(2-fluorophenyl)-2-hydroxy-propyl]imidazole-4-carbonitrile (this compound  
5 may be prepared from the methods described in WO 2016/156290) + TX, 3-[2-(1-chlorocyclopropyl)-3-(3-chloro-2-fluoro-phenyl)-2-hydroxy-propyl]imidazole-4-carbonitrile (this compound may be prepared from the methods described in WO 2016/156290) + TX, 3-bromo-1-chloroprop-1-ene + TX, 3-chloro-6-methyl-5-phenyl-4-(2,4,6-trifluorophenyl)pyridazine + TX, 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid + TX, 3-ethyl-1-methoxy-1-[[4-[5-  
10 (trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]urea + TX, 3-methyl-1-phenylpyrazol-5-yl dimethyl-carbamate + TX, 4-(2-bromo-4-fluorophenyl)-N-(2-chloro-6-fluorophenyl)-1 + TX, 3-dimethyl-1H-pyrazol-5-amine + TX, 4-(2,6-difluorophenyl)-6-methyl-5-phenylpyridazine-3-carbonitrile + TX, 4-(2-bromo-4-fluoro-phenyl)-N-(2-chloro-6-fluoro-phenyl)-2,5-dimethyl-pyrazol-3-amine + TX, 4-(quinoxalin-2-ylamino)benzenesulfonamide + TX, 4,4-difluoro-  
15 1-(5-fluoro-4-methyl-benzimidazol-1-yl)-3,3-dimethyl-isoquinoline + TX, 4,4-difluoro-3,3-dimethyl-1-(6-methylpyrazolo[1,5-a]pyridin-3-yl)isoquinoline + TX, 4,4-difluoro-3,3-dimethyl-1-(7-methylpyrazolo[1,5-a]pyridin-3-yl)isoquinoline + TX, 4,4-dimethyl-2-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]isoxazolidin-3-one + TX, 4-[[6-[2-(2,4-difluorophenyl)-1,1-difluoro-2-hydroxy-3-(1,2,4-triazol-1-yl)propyl]-3-pyridyl]oxy] benzonitrile + TX, 4-[[6-[2-(2,4-difluorophenyl)-  
20 1,1-difluoro-2-hydroxy-3-(5-sulfanyl-1,2,4-triazol-1-yl)propyl]-3-pyridyl]oxy] benzonitrile + TX, 4-[[6-[2-(2,4-difluorophenyl)-1,1-difluoro-2-hydroxy-3-(5-thioxo-4H-1,2,4-triazol-1-yl)propyl]-3-pyridyl]oxy] benzonitrile + TX, 4-chloro-2-(2-chloro-2-methyl-propyl)-5-[(6-iodo-3-pyridyl)methoxy]pyridazin-3-one + TX, 4-chlorophenyl phenyl sulfone + TX, 4-methyl(prop-2-ynyl)amino-3,5-xylol methylcarbamate + TX, 4-methylnonan-5-ol with 4-methylnonan-5-one + TX,  
25 5-(1,3-benzodioxol-5-yl)-3-hexylcyclohex-2-enone + TX, 5,5-dimethyl-2-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]isoxazolidin-3-one + TX, 5,5-dimethyl-3-oxocyclohex-1-enyl dimethylcarbamate + TX, 5-amino-1,3,4-thiadiazole-2-thiol zinc salt (2:1) + TX, 5-methyl-6-thioxo-1,3,5-thiadiazinan-3-ylacetic acid + TX, 6-chloro-3-(3-cyclopropyl-2-fluoro-phenoxy)-N-[2-(2,4-dimethylphenyl)-2,2-difluoro-ethyl]-5-methyl-pyridazine-4-carboxamide (may be prepared  
30 from the methods described in WO 2020/109391) + TX, 6-chloro-3-(3-cyclopropyl-2-fluoro-phenoxy)-N-[2-(3,4-dimethylphenyl)-2,2-difluoro-ethyl]-5-methyl-pyridazine-4-carboxamide (may be prepared from the methods described in WO 2020/109391) + TX, 6-chloro-4,4-difluoro-3,3-dimethyl-1-(4-methylbenzimidazol-1-yl)isoquinoline + TX, 6-chloro-N-[2-(2-chloro-4-methylphenyl)-2,2-difluoro-ethyl]-3-(3-cyclopropyl-2-fluoro-phenoxy)-5-methyl-pyridazine-4-  
35 carboxamide (may be prepared from the methods described in WO 2020/109391) + TX, 6-ethyl-5,7-dioxo-pyrrolo[4,5][1,4]dithiino[1,2-c]isothiazole-3-carbonitrile + TX, 6-isopentenylaminopurine + TX, 8-fluoro-N-[(1R)-1-[(3-fluorophenyl)methyl]-1,3-dimethyl-butyl]quinoline-3-carboxamide + TX, 8-fluoro-N-[(1S)-1-[(3-fluorophenyl)methyl]-1,3-dimethyl-butyl]quinoline-3-carboxamide + TX, 8-hydroxyquinoline sulfate + TX, acethion + TX, acetoprole + TX, acibenzolar + TX, acibenzolar-

S-methyl + TX, acrylonitrile + TX, Adoxophyes orana GV + TX, Agrobacterium radiobacter + TX, aldoxycarb + TX, aldrin + TX, allosamidin + TX, allyxycarb + TX, alpha-chlorohydrin + TX, alpha-ecdysone + TX, alpha-multistriatin + TX, aluminium phosphide + TX, Amblyseius spp. + TX, amectotractin + TX, ametoctradin + TX, amidithion + TX, amidothioate + TX, aminocarb + TX, 5 aminopyrifin + TX, amisulbrom + TX, amiton + TX, amiton hydrogen oxalate + TX, amitraz + TX, anabasine + TX, Anagrapha falcifera NPV + TX, Anagrus atomus + TX, ancymidol + TX, anilazine + TX, anisiflupurin + TX, anthraquinone + TX, antu + TX, Aphelinus abdominalis + TX, Aphidius colemani + TX, Aphidoletes aphidimyza + TX, apholate + TX, aramite + TX, arsenous oxide + TX, athidathion + TX, Autographa californica NPV + TX, azaconazole + TX, 10 azamethiphos + TX, azobenzene + TX, azothoate + TX, azoxystrobin + TX, Bacillus sphaericus Neide + TX, Bacillus thuringiensis delta endotoxins + TX, barium carbonate + TX, barium hexafluorosilicate + TX, barium polysulfide + TX, barthrin + TX, Bayer 22/190 + TX, Bayer 22408 + TX, Beauveria brongniartii + TX, benalaxyl + TX, benclothiaz + TX, benomyl + TX, benoxa-fos + TX, benthiavalicarb + TX, benzothiofostrobin + TX, benzovindiflupyr + TX, benzyl benzoate + TX, 15 beta-cyfluthrin + TX, beta-cypermethrin + TX, bethoxazin + TX, bioethanomethrin + TX, biopermethrin + TX, bis(2-chloroethyl) ether + TX, bis(tributyltin) oxide + TX, bisazir + TX, bithiosemi + TX, bitertanol + TX, bixafen + TX, blasticidin-S + TX, borax + TX, bordeaux mixture + TX, boscalid + TX, brevicomin + TX, brodifacoum + TX, brofenvalerate + TX, bromadiolone + TX, bromethalin + TX, bromfeninfos + TX, bromoacetamide + TX, bromo-cyclen + TX, bromo- 20 DDT + TX, bromophos + TX, bromopropylate + TX, bromuconazole + TX, bronopol + TX, bufencarb + TX, bupirimate + TX, buprofezin + TX, busulfan + TX, but-3-ynyl N-[6-[[[(Z)-[(1-methyltetrazol-5-yl)-phenyl-methylene]amino]oxymethyl]-2-pyridyl]carbamate + TX, butacarb + TX, butathiofos + TX, butocarboxim + TX, butonate + TX, butopyronoxyl + TX, butoxy(polypropylene glycol) + TX, butoxycarboxim + TX, butylpyridaben + TX, calcium arsenate 25 + TX, calcium cyanide + TX, calcium polysulfide + TX, camphechlor + TX, captafol + TX, captan + TX, carbanolate + TX, carbendazim + TX, carbon disulfide + TX, carbon tetrachloride + TX, carbophenothion + TX, carboxin + TX, cartap hydrochloride + TX, cevadine + TX, chino-methionat + TX, chloralose + TX, chlorbenseide + TX, chlorbicyclen + TX, chlordane + TX, chlordecone + TX, chlordimeform + TX, chlordimeform hydrochloride + TX, chlorfenethol + TX, 30 chlorfenson + TX, chlorfensulfide + TX, chlorobenzilate + TX, chloroform + TX, chloroinconazide + TX, chloromebuform + TX, chloromethiuron + TX, chloroneb + TX, chlorophacinone + TX, chloropicrin + TX, chloropropylate + TX, chloro-tha-lo-nil + TX, chlorphoxim + TX, chlorprazophos + TX, chlorthiophos + TX, chlozolate + TX, cholecalciferol + TX, Chrysoperla carnea + TX, cinerin I + TX, cinerin II + TX, cinerins + TX, cismethrin + TX, cis-resmethrin + TX, 35 clocythrins + TX, closantel + TX, codlure + TX, codlemone + TX, copper acetoarsenite + TX, copper arsenate + TX, copper dioctanoate + TX, copper hydroxide + TX, copper naphthenate + TX, copper oleate + TX, copper oxide + TX, copper oxychloride + TX, copper sulfate + TX, coumachlor + TX, coumafuryl + TX, coumaphos + TX, coumatetralyl + TX, coumethoxystrobin (jiaxiangjunzhi) + TX, coumithoate + TX, coumoxystrobin + TX, cresol + TX, crimidine + TX,

crotamiton + TX, crotoxyphos + TX, crufomate + TX, cryolite + TX, Cryptolaemus montrouzieri + TX, CS 708 + TX, cuelure + TX, cufraneb + TX, cyanofenphos + TX, cyanophos + TX, cyanthoate + TX, cyazofamid + TX, cybutryne + TX, cyclethrin + TX, cyclobutrifluram + TX, Cydia pomonella GV + TX, cyflufenamid + TX, cymiazole + TX, cymoxanil + TX, cyproconazole + TX, 5 cyprodinil + TX, cythioate + TX, cytokinins + TX, Dacnusa sibirica + TX, DAEP + TX, dazomet + TX, DCIP + TX, DCPM + TX, DDT + TX, debacarb + TX, decarbofuran + TX, demephion + TX, demephion-O + TX, demephion-S + TX, demeton-methyl + TX, demeton-O + TX, demeton-O-methyl + TX, demeton-S + TX, demeton-S-methyl + TX, demeton-S-methylsulfon + TX, diamidafos + TX, dibutyl adipate + TX, dibutyl phthalate + TX, dibutyl succinate + TX, dicapthon 10 + TX, dichlobentiazox + TX, dichlofenthion + TX, dichlofluamid + TX, dichlone + TX, dichlorophen + TX, dichlorvos + TX, dichlozoline + TX, dicliphos + TX, diclocymet + TX, diclomezine + TX, dicloran + TX, dicresyl + TX, dicyclanil + TX, dicyclopentadiene + TX, dieldrin + TX, dienochlor + TX, diethofencarb + TX, diethyl 5-methylpyrazol-3-yl phosphate + TX, diethyltoluamide + TX, difenacoum + TX, difenoconazole + TX, difethialone + TX, diflovidazin + TX, Diglyphus isaea + TX, 15 dilor + TX, dimatif + TX, dimefluthrin + TX, dimefox + TX, dimetan + TX, dimethirimol + TX, dimetho-morph + TX, dimethrin + TX, dimethyl carbate + TX, dimethyl phthalate + TX, dimethylvinphos + TX, dimetilan + TX, dimoxystrobin + TX, dinex + TX, dinex-diclexine + TX, diniconazole + TX, dinocap-4 + TX, dinocap-6 + TX, dinoceton + TX, dino-penton + TX, dinoprop + TX, dinosam + TX, dinoseb + TX, dinosulfon + TX, dinoterbon + TX, diofenolan + TX, 20 dioxabenzofos + TX, dioxathion + TX, diphacinone + TX, diphenyl sulfone + TX, dipymetitron + TX, dipyrithione + TX, disparlure + TX, disulfiram + TX, dithianon + TX, dithicrofos + TX, DNOC + TX, dodec-8-en-1-yl acetate + TX, dodec-9-en-1-yl acetate + TX, dodeca-8 + TX, dodemorph + TX, dodicin + TX, dodine + TX, dofenapyn + TX, dominicalure + TX, doramectin + TX, DSP + TX, d-tetramethrin + TX, ecdysterone + TX, edifenphos + TX, EI 1642 + TX, EMPC + TX, Encarsia 25 formosa + TX, endothal + TX, endothion + TX, enestroburin + TX, enoxastrobin + TX, EPBP + TX, epoxicon-azole + TX, eprinomectin + TX, Eretmocerus eremicus + TX, ergocalciferol + TX, etaphos + TX, ethaboxam + TX, ethiofencarb + TX, ethirimol + TX, ethoate-methyl + TX, ethyl 1-[[4-[(Z)-2-ethoxy-3,3,3-trifluoro-prop-1-enoxy]phenyl]methyl]pyrazole-3-carboxylate (may be prepared from the methods described in WO 2020/056090) + TX, ethyl 1-[[4-[[2-(trifluoromethyl)- 1,3-dioxolan-2-yl]methoxy]phenyl]methyl]pyrazole-3-carboxylate (may be prepared from the 30 methods described in WO 2020/056090) + TX, ethyl 1-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]pyrazole-4-carboxylate + TX, ethyl 1-[[5-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]-2-thienyl]methyl]pyrazole-4-carboxylate (this compound may be prepared from the methods described in WO 2018/158365) + TX, ethyl 4-methyloctanoate + TX, ethyl formate + TX, ethyl 35 hexanediol + TX, ethylene dibromide + TX, ethylene dichloride + TX, ethylene oxide + TX, etridiazole + TX, etrimfos + TX, eugenol + TX, EXD + TX, famoxa-done + TX, farnesol + TX, farnesol with nerolidol + TX, fenamidone + TX, fenaminosulf + TX, fenaminstrobin + TX, fenarimol + TX, fenazaflor + TX, fenbuconazole + TX, fenbutatin oxide + TX, fenchlorphos + TX, fenethacarb + TX, fenfuram + TX, fenhexamid + TX, fenitrothion + TX, fenothiocab + TX,

fenoxacrim + TX, fenoxanil + TX, fencpiclonil + TX, fencpicoxamid + TX, fencpirithrin + TX,  
 fenpropidin + TX, fenpropimorph + TX, fenpyrad + TX, fenpyrazamine + TX, fen-pyroximate +  
 TX, fenson + TX, fensulfothion + TX, fenthion + TX, fenthion-ethyl + TX, fentin + TX, fentrifanil +  
 TX, ferbam + TX, ferimzone + TX, ferric phosphate + TX, flocoumafen + TX, florylpicoxamid +  
 5 TX, fluazinam + TX, flubeneteram + TX, flubenzimine + TX, flucofuron + TX, flucycloxiuron + TX,  
 fludioxonil + TX, fluenetil + TX, flufenoxadiazam + TX, flufenoxystrobin + TX, fluindapyr + TX,  
 flumetylsulforim + TX, flumorph + TX, fluopicolide + TX, fluopimomide + TX, fluopyram + TX,  
 fluorbenside + TX, fluoroacetamide + TX, fluoroimide + TX, fluoxapiprolin + TX, fluoxastrobin +  
 TX, fluoxytioconazole + TX, flupropadine + TX, flupropadine hydrochloride + TX, fluquinconazole  
 10 + TX, flusilazole + TX, flusulfamide + TX, flutianil + TX, flutolanil + TX, flutriafol + TX,  
 fluxapyroxad + TX, FMC 1137 + TX, folpet + TX, formaldehyde + TX, formetanate + TX,  
 formetanate hydrochloride + TX, formparanate + TX, fosetyl-aluminium + TX, fosmethilan + TX,  
 fospirate + TX, fosthietan + TX, frontaline + TX, fuberidazole + TX, furalaxyl + TX, furametpyr +  
 TX, furathiocarb + TX, furethrin + TX, furfural + TX, gamma-HCH + TX, glyodin + TX, grandlure +  
 15 TX, grandlure I + TX, grandlure II + TX, grandlure III + TX, grandlure IV + TX, guazatine + TX,  
 guazatine acetates + TX, halfenprox + TX, HCH + TX, hemel + TX, hempa + TX, HEOD + TX,  
 heptachlor + TX, heterophos + TX, Heterorhabditis bacteriophora and H. megidis + TX,  
 hexaconazole + TX, hexadecyl cyclopropanecarboxylate + TX, hexalure + TX, hexamide + TX,  
 HHDN + TX, Hippodamia convergens + TX, hydrargaphen + TX, hydrated lime + TX, hydrogen  
 20 cyanide + TX, hymexazol + TX, hyquincarb + TX, imanin + TX, imazalil + TX, imiben-conazole +  
 TX, iminoctadine + TX, inpyrfluxam + TX, ipconazole + TX, ipfentrifluconazole + TX,  
 ipflufenquin + TX, iprobenphos + TX, iprodione + TX, iprovalicarb + TX, ipsdienol + TX, ipsenol  
 + TX, IPSP + TX, isamidofos + TX, isazofos + TX, isobenzan + TX, isocarbophos + TX, isodrin +  
 TX, isofenphos + TX, isofetamid + TX, isoflucypram + TX, isolane + TX, isoprothiolane + TX,  
 25 isopyrazam + TX, isotianil + TX, isoxathion + TX, japonilure + TX, jasmolin I + TX, jasmolin II +  
 TX, jodfenphos + TX, juvenile hormone I + TX, juvenile hormone II + TX, juvenile hormone III +  
 TX, kadethrin + TX, kasugamycin + TX, kasugamycin hydrochloride hydrate + TX, kelevan + TX,  
 kinetin + TX, kinoprene + TX, kresoxim-methyl + TX, lead arsenate + TX, Leptomastix dactylopii  
 + TX, leptophos + TX, lindane + TX, lineatin + TX, lirimfos + TX, litlure + TX, looplure + TX,  
 30 lvenmixianan + TX, lythidathion + TX, Macrolophus caliginosus + TX, magnesium phosphide +  
 TX, malonoben + TX, Mamestra brassicae NPV + TX, mancopper + TX, mancozeb + TX,  
 mandestrobin + TX, mandipropamid + TX, maneb + TX, mazidox + TX, m-cumenyl  
 methylcarbamate + TX, mecarbam + TX, mecarphon + TX, medlure + TX, mefentrifluconazole +  
 TX, megatomoic acid + TX, menazon + TX, mepanipyrim + TX, meperfluthrin + TX, mephosfolan  
 35 + TX, mepronil + TX, mercuric oxide + TX, mercurous chloride + TX, mesulfen + TX, mesulfenfos  
 + TX, meta-laxyl + TX, metam + TX, metam-potassium + TX, metam-sodium + TX, Metaphycus  
 helvolus + TX, Metarhizium anisopliae var. acridum + TX, Metarhizium anisopliae var. anisopliae  
 + TX, metarylpicoxamid + TX, metconazole + TX, metepa + TX, methacrifos + TX,  
 methanesulfonyl fluoride + TX, methasulfo-carb + TX, methiotepa + TX, methocrotophos + TX,

methoprene + TX, methoquin-butyl + TX, methothrin + TX, methoxychlor + TX, methyl (Z)-2-(5-cyclohexyl-2-methyl-phenoxy)-3-methoxy-prop-2-enoate + TX, methyl (Z)-2-(5-cyclopentyl-2-methyl-phenoxy)-3-methoxy-prop-2-enoate (these compounds may be prepared from the methods described in WO2020/193387) + TX, methyl (Z)-2-[5-(3-isopropylpyrazol-1-yl)-2-methyl-phenoxy]-3-methoxy-prop-2-enoate + TX, methyl (Z)-3-methoxy-2-[2-methyl-5-(3-propylpyrazol-1-yl)phenoxy]prop-2-enoate + TX, methyl (Z)-3-methoxy-2-[2-methyl-5-(4-propyltriazol-2-yl)phenoxy]prop-2-enoate + TX, methyl (Z)-3-methoxy-2-[2-methyl-5-[3-(trifluoromethyl)pyrazol-1-yl]phenoxy]prop-2-enoate (these compounds may be prepared from the methods described in WO2020/079111) + TX, methyl (Z)-3-methoxy-2-[2-methyl-5-[4-(trifluoromethyl)triazol-2-yl]phenoxy]prop-2-enoate + TX, methyl apholate + TX, methyl bromide + TX, methyl eugenol + TX, methyl isothiocyanate + TX, methyl N-[[4-[1-(2,6-difluoro-4-isopropyl-phenyl)pyrazol-4-yl]-2-methyl-phenyl]methyl]carbamate (may be prepared from the methods described in WO 2020/097012) + TX, methyl N-[[4-[1-(4-cyclopropyl-2,6-difluoro-phenyl)pyrazol-4-yl]-2-methyl-phenyl]methyl]carbamate (may be prepared from the methods described in WO 2020/097012) + TX, methyl N-[[5-[4-(2,4-dimethylphenyl)triazol-2-yl]-2-methyl-phenyl]methyl]carbamate + TX, methylchloroform + TX, methylene chloride + TX, methylneodecanamide + TX, metiram + TX, metolcarb + TX, metomi-nostrobin + TX, metoxadiazone + TX, metrafenone + TX, metyltetraprole + TX, MGK 264 + TX, milbemycin oxime + TX, mipafox + TX, mirex + TX, monocrotophos + TX, morphothion + TX, morzid + TX, moxidectin + TX, muscalure + TX, myclobutanil + TX, myclozoline + TX, Myrothecium verrucaria composition + TX, N-((1R)-1-benzyl-3-chloro-1-methyl-but-3-enyl)-8-fluoro-quinoline-3-carboxamide (these compounds may be prepared from the methods described in WO2017/153380) + TX, N-((1S)-1-benzyl-3-chloro-1-methyl-but-3-enyl)-8-fluoro-quinoline-3-carboxamide (these compounds may be prepared from the methods described in WO2017/153380) + TX, N'-(2,5-dimethyl-4-phenoxy-phenyl)-N-ethyl-N-methyl-formamidine + TX, N'-(2-chloro-5-methyl-4-phenoxy-phenyl)-N-ethyl-N-methyl-formamidine + TX, N,2-dimethoxy-N-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]propanamide + TX, N,N-dimethyl-1-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]-1,2,4-triazol-3-amine (THESE COMPOUNDS may be prepared from the methods described in WO 2017/055473 + TX, WO 2017/055469 + TX, WO 2017/093348 and WO 2017/118689) + TX, N-[(1R)-1-benzyl-1,3-dimethyl-butyl]-7,8-difluoro-quinoline-3-carboxamide + TX, N-[(1R)-1-benzyl-1,3-dimethyl-butyl]-8-fluoro-quinoline-3-carboxamide + TX, N-[(1R)-1-benzyl-3,3,3-trifluoro-1-methyl-propyl]-8-fluoro-quinoline-3-carboxamide + TX, N-[(1S)-1-benzyl-1,3-dimethyl-butyl]-7,8-difluoro-quinoline-3-carboxamide + TX, N-[(1S)-1-benzyl-1,3-dimethyl-butyl]-8-fluoro-quinoline-3-carboxamide + TX, N-[(1S)-1-benzyl-3,3,3-trifluoro-1-methyl-propyl]-8-fluoro-quinoline-3-carboxamide + TX, N-[(E)-methoxyiminomethyl]-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzamide + TX, N-[(Z)-methoxyiminomethyl]-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzamide + TX, N-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]propanamide + TX, N-[2-[2,4-dichloro-phenoxy]phenyl]-3-(difluoromethyl)-1-methyl-pyrazole-4-carboxamide + TX, N-[2-[2-chloro-4-(trifluoromethyl)phenoxy]phenyl]-3-(difluoromethyl)-1-methyl-pyrazole-4-carboxamide + TX, N'-[2-

chloro-4-(2-fluorophenoxy)-5-methyl-phenyl]-N-ethyl-N-methyl-formamidine (this compound may be prepared from the methods described in WO 2016/202742) + TX, N'-[4-(4,5-dichlorothiazol-2-yl)oxy-2,5-dimethyl-phenyl]-N-ethyl-N-methyl-formamidine + TX, N'-[5-bromo-2-methyl-6-(1-methyl-2-propoxy-ethoxy)-3-pyridyl]-N-ethyl-N-methyl-formamidine + TX, N'-[5-bromo-2-methyl-6-(1-methyl-2-propoxy-ethoxy)-3-pyridyl]-N-isopropyl-N-methyl-formamidine (these compounds  
5 may be prepared from the methods described in WO2015/155075) + TX, N'-[5-bromo-2-methyl-6-(2-propoxypropoxy)-3-pyridyl]-N-ethyl-N-methyl-formamidine (this compound may be prepared from the methods described in IPCOM000249876D) + TX, N'-[5-bromo-2-methyl-6-[(1R)-1-methyl-2-propoxy-ethoxy]-3-pyridyl]-N-ethyl-N-methyl-formamidine + TX, N'-[5-bromo-2-methyl-6-  
10 [(1S)-1-methyl-2-propoxy-ethoxy]-3-pyridyl]-N-ethyl-N-methyl-formamidine + TX, N'-[5-chloro-2-methyl-6-(1-methyl-2-propoxy-ethoxy)-3-pyridyl]-N-ethyl-N-methyl-formamidine + TX, N-[N-methoxy-C-methyl-carbonimidoyl]-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzamide (these compounds may be prepared from the methods described in WO 2018/202428) + TX, N'-[4-(1-cyclopropyl-2,2,2-trifluoro-1-hydroxy-ethyl)-5-methoxy-2-methyl-phenyl]-N-isopropyl-N-methyl-  
15 formamidine (these compounds may be prepared from the methods described in WO2018/228896) + TX, nabam + TX, naftalofos + TX, naled + TX, naphthalene + TX, NC-170 + TX, Neodiprion sertifer NPV and N. lecontei NPV + TX, nerolidol + TX, N-ethyl-2-methyl-N-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]propanamide + TX, N-ethyl-N'-[5-methoxy-2-methyl-4-[(2-trifluoromethyl)oxetan-2-yl]phenyl]-N-methyl-formamidine + TX, nickel  
20 bis(dimethyldithiocarbamate) + TX, niclosamide-olamine + TX, nicotine + TX, nicotine sulfate + TX, nifluridide + TX, nikkomycins + TX, N-isopropyl-N'-[5-methoxy-2-methyl-4-(2,2,2-trifluoro-1-hydroxy-1-phenyl-ethyl)phenyl]-N-methyl-formamidine + TX, nithiazine + TX, nitrapyrin + TX, nitrilacarb + TX, nitrilacarb 1:1 zinc chloride complex + TX, nitrothal-isopropyl + TX, N-methoxy-N-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]cyclopropanecarboxamide + TX, N-methyl-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzamide + TX, N-methyl-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzenecarbothioamide + TX, norbormide + TX, nuarimol + TX, O,O,O',O'-tetrapropyl dithiopyrophosphate + TX, octadeca-2,13-dien-1-yl acetate + TX, octadeca-3,13-dien-1-yl acetate + TX, octhilinone + TX, ofurace + TX, oleic acid + TX, omethoate + TX, orfralure + TX, Orius spp. + TX, oryctalure + TX, oryastrobin + TX, ostramone  
30 + TX, oxadixyl + TX, oxamate + TX, oxathiapiprolin + TX, oxine-copper + TX, oxolinic acid + TX, oxycarboxin + TX, oxydeprofos + TX, oxydisulfoton + TX, oxytetracycline + TX, paclobutrazole + TX, Paecilomyces fumosoroseus + TX, para-dichlorobenzene + TX, parathion + TX, parathion-methyl + TX, pefurazoate + TX, penconazole + TX, pencycuron + TX, penflufen + TX, penfluron + TX, pentachlorophenol + TX, pentachlorophenyl laurate + TX, penthiopyrad + TX, permethrin + TX, PH 60-38 + TX, phenamacril + TX, phenkapton + TX, phosacetim + TX, phosalone + TX,  
35 phosdiphen + TX, phosfolan + TX, phosglycin + TX, phosnichlor + TX, phosphamidon + TX, phosphine + TX, phosphorus + TX, phoxim-methyl + TX, phthalide + TX, Phytoseiulus persimilis + TX, picarbutrazox + TX, picaridin + TX, picoxystrobin + TX, pindone + TX, piperazine + TX, piperonyl butoxide + TX, piprotal + TX, pirimetaphos + TX, polychlorodicyclopentadiene isomers

+ TX, polychloroterpenes + TX, polynactins + TX, polyoxins + TX, potassium arsenite + TX, potassium ethylxanthate + TX, potassium hydroxyquinoline sulfate + TX, potassium thiocyanate + TX, pp'-DDT + TX, precocene I + TX, precocene II + TX, precocene III + TX, primidophos + TX, probenazole + TX, prochloraz + TX, proclonol + TX, procymidone + TX, profluthrin + TX, 5 promacyl + TX, promecarb + TX, propamocarb + TX, propiconazole + TX, propineb + TX, propoxur + TX, propyl isomer + TX, proquinazid + TX, prothidathion + TX, prothioconazole + TX, prothiofos + TX, prothoate + TX, pydiflumetofen + TX, pyraclostrobin + TX, pyrametostrobin + TX, pyraoxystrobin + TX, pyrapropoyne + TX, pyraziflumid + TX, pyrazophos + TX, pyresmethrin + TX, pyrethrin I + TX, pyrethrin II + TX, pyrethrins + TX, pyribencarb + TX, pyridachlometyl + 10 TX, pyridaphenthion + TX, pyridin-4-amine + TX, pyrifenox + TX, pyrimethanil + TX, pyrimitate + TX, pyrimorph + TX, pyrinuron + TX, pyriofenone + TX, pyrisoxazole + TX, pyroquilon + TX, quassia + TX, quinalphos + TX, quinalphos-methyl + TX, quinoclamine + TX, quinofumelin + TX, quinonamid + TX, quinothion + TX, quinoxifen + TX, quintiofos + TX, quintozone + TX, R-1492 + TX, rafoxanide + TX, resmethrin + TX, Reynoutria sachalinensis extract + TX, ribavirin + TX, 15 R-metalaxyl + TX, rotenone + TX, ryania + TX, ryanodine + TX, S421 + TX, sabadilla + TX, schradan + TX, scilliroside + TX, seboctylamine + TX, sebufos + TX, sedaxane + TX, selamectin + TX, sesamex + TX, sesasmolin + TX, SI-0009 + TX, siglure + TX, simazine + TX, simeconazole + TX, sodium arsenite + TX, sodium cyanide + TX, sodium fluoride + TX, sodium fluoro-acetate + TX, sodium hexafluorosilicate + TX, sodium pentachlorophenoxide + TX, sodium 20 selenate + TX, sodium tetrathiocarbonate + TX, sodium thiocyanate + TX, sophamide + TX, sordidin + TX, spiroxamine + TX, SSI-121 + TX, Steinernema bibionis + TX, Steinernema carpocapsae + TX, Steinernema feltiae + TX, Steinernema glaseri + TX, Steinernema riobrave + TX, Steinernema riobravense + TX, Steinernema scapterisci + TX, Steinernema spp. + TX, streptomycin + TX, streptomycin sesquisulfate + TX, strychnine + TX, sulcatol + TX, sulcofuron + 25 TX, sulcofuron-sodium + TX, sulfiram + TX, sulfluramid + TX, sulfotep + TX, sulfoxide + TX, sulfur + TX, sulfuryl fluoride + TX, sulprofos + TX, tar oils + TX, tau-fluvalinate + TX, tazimcarb + TX, TDE + TX, tebuconazole + TX, tebufloquin + TX, tebupirimfos + TX, tecloftalam + TX, temephos + TX, tepa + TX, TEPP + TX, terallethrin + TX, terbam + TX, tert-butyl N-[6-[[[(1-methyltetrazol-5-yl)-phenyl-methylene]amino]oxymethyl]-2-pyridyl]carbamate + TX, 30 tetrachloroethane + TX, tetrachlorothiophene + TX, tetraconazole + TX, tetradec-11-en-1-yl acetate + TX, tetradifon + TX, tetramethylfluthrin + TX, tetrasul + TX, thallium sulfate + TX, thiaben-dazole + TX, thiafenox + TX, thiapronil + TX, thicofos + TX, thifluzamide + TX, thiocarboxime + TX, thiocyclam + TX, thiocyclam hydrogen oxalate + TX, thiodiazole copper + TX, thiofanox + TX, thiohempa + TX, thiomersal + TX, thiometon + TX, thionazin + TX, 35 thiophanate + TX, thiophanate-methyl + TX, thioquinox + TX, thiosultap + TX, thiosultap-sodium + TX, thiotepa + TX, thiram + TX, thuringiensin + TX, tiadinil + TX, tolclofos-methyl + TX, tolprocarb + TX, tolylfluanid + TX, tralomethrin + TX, transpermethrin + TX, tretamine + TX, triadimefon + TX, triadime-nol + TX, triamiphos + TX, triarathene + TX, triazamate + TX, triazophos + TX, triazoxide + TX, triazuron + TX, tributyltin oxide + TX, trichlormetaphos-3 + TX,



trichloronat + TX, Trichogramma spp. + TX, triclopyricarb + TX, tricyclazole + TX, tridemorph + TX, trifenmorph + TX, trifenofos + TX, trifloxystrobin + TX, triflumizole + TX, triforine + TX, trimedlure + TX, trimedlure A + TX, trimedlure B1 + TX, trimedlure B2 + TX, trimedlure C + TX, trimethacarb + TX, trinactin + TX, trinexapac + TX, triphenyltin acetate + TX, triphenyltin hydroxide + TX, triprene + TX, triticonazole + TX, trunc-call + TX, Typhlodromus occidentalis + TX, uredepa + TX, validamycin + TX, valifenalate + TX, vamidothion + TX, vaniliprole + TX, veratridine + TX, veratrine + TX, verbutin + TX, Verticillium lecanii + TX, vinclozoline + TX, warfarin + TX, XMC + TX, xylenols + TX, zeatin + TX, zetamethrin + TX, zhongshengmycin + TX, zinc naphthenate + TX, zinc phosphide + TX, zinc thiazole + TX, zineb + TX, ziram + TX, zolaprofos + TX, zoxamide + TX,  $\alpha$ - (1 + TX, 1- dimethylethyl) -  $\alpha$ - [4'- (trifluoromethoxy) [1 + TX, 1'- biphenyl] - 4- yl] -5- pyrimidinemethanol + TX;

Typhula phacorrhiza strain 94670 + TX, Acinetobacter lwoffii + TX, Acremonium alternatum + TX, Acremonium cephalosporium + TX, Acremonium diospyri + TX, Acremonium obclavatum + TX, Adoxophyes orana granulovirus (AdoxGV) (Capex®) + TX, Agrobacterium radiobacter strain K84 (Galltrol-A®) + TX, Alternaria alternate + TX, Alternaria cassia + TX, Alternaria destruens (Smolder®) + TX, Ampelomyces quisqualis (AQ10®) + TX, Aspergillus flavus AF36 (AF36®) + TX, Aspergillus flavus NRRL 21882 (Aflaguard®) + TX, Aspergillus spp. + TX, Aureobasidium pullulans + TX, Azospirillum (MicroAZ® + TX, TAZO B®) + TX, Azotobacter + TX, Azotobacter chroococcum (Azotomeal®) + TX, Azotobacter cysts (Bionatural Blooming Blossoms®) + TX, Bacillus amyloliquefaciens + TX, Bacillus cereus + TX, Bacillus chitinosporus strain AQ746 + TX, Bacillus chitinosporus strain CM-1 + TX, Bacillus circulans + TX, Bacillus firmus (BioSafe® + TX, BioNem-WP®) in particular strain CNMC 1-1582 (e.g. VOTIVO® from BASF SE) + TX, Bacillus licheniformis strain 3086 (EcoGuard® + TX, Green Releaf®) + TX, Bacillus licheniformis strain HB-2 (Biostart™ formerly Rhizoboost®) + TX, Bacillus macerans + TX, Bacillus marismortui + TX, Bacillus megaterium + TX, Bacillus mycoides strain AQ726 + TX, Bacillus papillae (Milky Spore Powder®) + TX, Bacillus pumilus spp. + TX, Bacillus pumilus strain AQ717 + TX, Bacillus pumilus strain GB34 (Yield Shield®) + TX, Bacillus pumilus strain QST 2808 (Sonata® + TX, Ballad Plus®) + TX, Bacillus sphaericus (VectoLex®) + TX, Bacillus spp. + TX, Bacillus spp. strain AQ175 + TX, Bacillus spp. strain AQ177 + TX, Bacillus spp. strain AQ178 + TX, Bacillus subtilis strain AQ153 + TX, Bacillus subtilis strain AQ743 + TX, Bacillus subtilis strain QST 713 (CEASE® + TX, Serenade® + TX, Rhapsody®) + TX, Bacillus subtilis strain QST 714 (JAZZ®) + TX, Bacillus subtilis strain QST3002 + TX, Bacillus subtilis strain QST3004 + TX, Bacillus subtilis var. amyloliquefaciens strain FZB24 (Taegro® + TX, Rhizopro®) + TX, Bacillus thuringiensis aizawai GC 91 (Agree®) + TX, Bacillus thuringiensis Cry 2Ae + TX, Bacillus thuringiensis Cry1Ab + TX, Bacillus thuringiensis israelensis (BMP123® + TX, Aquabac® + TX, VectoBac®) + TX, Bacillus thuringiensis kurstaki (Javelin® + TX, Deliver® + TX, CryMax® + TX, Bonide® + TX, Scutella WP® + TX, Turilav WP® + TX, Astuto® + TX, Dipel WP® + TX, Biobit® + TX, Foray®) + TX, Bacillus thuringiensis kurstaki BMP 123 (Baritone®) + TX, Bacillus thuringiensis kurstaki HD-1 (Bioprotec-CAF / 3P®) + TX, Bacillus thuringiensis strain

AQ52 + TX, *Bacillus thuringiensis* strain BD#32 + TX, *Bacillus thuringiensis tenebrionis* (Novodor® + TX, BtBooster) + TX, *Bacillus thuringiensis* var. aizawai (XenTari® + TX, DiPel®) + TX, bacteria spp. (GROWMEND® + TX, GROWSWEET® + TX, Shootup®) + TX, bacteriophage of *Clavipacter michiganensis* (AgriPhage® + TX, Bakflor®) + TX, *Beauveria bassiana* (Beaugenic® + TX, Brocaril WP®) + TX, *Beauveria bassiana* GHA (Mycotrol ES® + TX, Mycotrol O® + TX, BotaniGuard®) + TX, *Beauveria brongniartii* (Engerlingspilz® + TX, Schweizer Beauveria® + TX, Melocont®) + TX, *Beauveria* spp. + TX, *Botrytis cineria* + TX, *Bradyrhizobium japonicum* (TerraMax®) + TX, *Brevibacillus brevis* + TX, *Burkholderia cepacia* (Deny® + TX, Intercept® + TX, Blue Circle®) + TX, *Burkholderia gladii* + TX, *Burkholderia gladioli* + TX, *Burkholderia* spp. + TX, Canadian thistle fungus (CBH Canadian Bioherbicide®) + TX, *Candida butyri* + TX, *Candida famata* + TX, *Candida fructus* + TX, *Candida glabrata* + TX, *Candida guilliermondii* + TX, *Candida melibiosica* + TX, *Candida oleophila* strain O + TX, *Candida parapsilosis* + TX, *Candida pelliculosa* + TX, *Candida pulcherrima* + TX, *Candida reukaufii* + TX, *Candida saitoana* (Bio-Coat® + TX, Biocure®) + TX, *Candida sake* + TX, *Candida* spp. + TX, *Candida tenuis* + TX, *Cedecea davisae* + TX, *Cellulomonas flavigena* + TX, *Chaetomium cochliodes* (Nova-Cide®) + TX, *Chaetomium globosum* (Nova-Cide®) + TX, *Chromobacterium subtsugae* strain PRAA4-1T (Grandevo®) + TX, *Cladosporium chlorocephalum* + TX, *Cladosporium cladosporioides* + TX, *Cladosporium oxysporum* + TX, *Cladosporium* spp. + TX, *Cladosporium tenuissimum* + TX, *Clonostachys rosea* (EndoFine®) + TX, *Colletotrichum acutatum* + TX, *Coniothyrium minitans* (Cotans WG®) + TX, *Coniothyrium* spp. + TX, *Cryptococcus albidus* (YIELDPLUS®) + TX, *Cryptococcus humicola* + TX, *Cryptococcus infirmominiatus* + TX, *Cryptococcus laurentii* + TX, *Cryptophlebia leucotreta* granulovirus (Cryptex®) + TX, *Cupriavidus campinensis* + TX, *Cydia pomonella* granulovirus (CYD-X® + TX, Madex® + TX, Madex® Plus + TX, Madex Max + TX, Carpovirusine® + TX, *Cylindrobasidium laeve* (Stumpout®) + TX, *Cylindrocladium* + TX, *Debaryomyces hansenii* + TX, *Drechslera hawaiiensis* + TX, *Enterobacter cloacae* + TX, *Enterobacteriaceae* + TX, *Entomophthora virulenta* (Vektor®) + TX, *Epicoccum nigrum* + TX, *Epicoccum purpurascens* + TX, *Epicoccum* spp. + TX, *Filobasidium floriforme* + TX, *Fusarium acuminatum* + TX, *Fusarium chlamydosporum* + TX, *Fusarium oxysporum* (Fusaclean® + TX, Biofox C®) + TX, *Fusarium proliferatum* + TX, *Fusarium* spp. + TX, *Galactomyces geotrichum* + TX, *Gliocladium catenulatum* (Primastop® + TX, Prestop®) + TX, *Gliocladium roseum* + TX, *Gliocladium* spp. (SoilGard®) + TX, *Gliocladium virens* (Soilgard®) + TX, *Granulovirus* (Granupom®) + TX, *Halobacillus halophilus* + TX, *Halobacillus litoralis* + TX, *Halobacillus trueperi* + TX, *Halomonas* spp. + TX, *Halomonas subglaciescola* + TX, *Halovibrio variabilis* + TX, *Hanseniaspora uvarum* + TX, *Helicoverpa armigera* nucleopolyhedrovirus (Helicovex®) + TX, *Helicoverpa zea* nuclear polyhedrosis virus (Gemstar®) + TX, *Isaria fumosorosea* (previously known as *Paecilomyces fumosoroseus* strain + TX, PFR-97® + TX, PreFeRal®) + TX, *Isoflavone formononetin* (Myconate®) + TX, *Kloeckera apiculata* + TX, *Kloeckera* spp. + TX, *Lagenidium giganteum* (Laginex®) + TX, *Lecanicillium lecanii* (formerly known as *Verticillium lecanii* (Mycotal®) conidia of strain KV01 (e.g. Vertalec®

by Koppert/Arysta) + TX, Lecanicillium longisporum (Vertiblast®) + TX, Lecanicillium muscarium  
 (Vertikil®) + TX, Lymantria Dispar nucleopolyhedrosis virus (Disparvirus®) + TX, Marinococcus  
 halophilus + TX, Meira geulakonigii + TX, Metarhizium anisopliae (Destruxin WP®) + TX,  
 Metarhizium anisopliae (Met52®) + TX, Metschnikowia fruticola (Shemer®) + TX, Metschnikowia  
 5 pulcherrima + TX, Microdochium dimerum (Antibot®) + TX, Micromonospora coerulea + TX,  
 Microsphaeropsis ochracea + TX, Muscodor albus 620 (Muscudor®) + TX, Muscodor roseus in  
 particular strain A3-5 (Accession No. NRRL 30548) + TX, Mycorrhizae spp. (AMykor® + TX, Root  
 Maximizer®) + TX, Myrothecium verrucaria strain AARC-0255 (DiTera® + TX, BROS PLUS®) +  
 TX, Ophiostoma piliferum strain D97 (Sylvanex®) + TX, Paecilomyces farinosus + TX,  
 10 Paecilomyces lilacinus strain 251 (MeloCon WG®) + TX, Paecilomyces linacinus (Biostat WP®)  
 + TX, Paenibacillus polymyxa + TX, Pantoea agglomerans (BlightBan C9-1®) + TX, Pantoea  
 spp. + TX, Pasteuria nishizawae in particular strain Pn1 (CLARIVA from Syngenta/ChemChina) +  
 TX; + TX, Pasteuria spp. (Econem®) + TX, Penicillium aurantiogriseum + TX, Penicillium billai  
 (Jumpstart® + TX, TagTeam®) + TX, Penicillium brevicompactum + TX, Penicillium frequentans  
 15 + TX, Penicillium griseofulvum + TX, Penicillium purpurogenum + TX, Penicillium spp. + TX,  
 Penicillium viridicatum + TX, Phlebiopsis gigantea (Rotstop®) + TX, phosphate solubilizing  
 bacteria (Phosphomeal®) + TX, Phytophthora cryptogea + TX, Phytophthora palmivora  
 (Devine®) + TX, Pichia anomala + TX, Pichia guilliermondii + TX, Pichia membranaefaciens +  
 TX, Pichia onychis + TX, Pichia stipites + TX, Pseudomonas aeruginosa + TX, Pseudomonas  
 20 aureofasciens (Spot-Less Biofungicide®) + TX, Pseudomonas cepacia + TX, Pseudomonas  
 chlororaphis (AtEze®) + TX, Pseudomonas corrugate + TX, Pseudomonas fluorescens strain  
 A506 (BlightBan A506®) + TX, Pseudomonas putida + TX, Pseudomonas reactans + TX,  
 Pseudomonas spp. + TX, Pseudomonas syringae (Bio-Save®) + TX, Pseudomonas viridiflava +  
 TX, Pseudomonas fluorescens (Zequanox®) + TX, Pseudozyma flocculosa strain PF-A22 UL  
 25 (Sporodex L®) + TX, Puccinia canaliculata + TX, Puccinia thlaspeos (Wood Warrior®) + TX,  
 Pythium paroecandrum + TX, Pythium oligandrum (Polygandron® + TX, Polyversum®) + TX,  
 Pythium periplocum + TX, Rhanella aquatilis + TX, Rhanella spp. + TX, Rhizobia (Dormal® + TX,  
 Vault®) + TX, Rhizoctonia + TX, Rhodococcus globerulus strain AQ719 + TX, Rhodosporidium  
 diobovatum + TX, Rhodosporidium toruloides + TX, Rhodotorula glutinis + TX, Rhodotorula  
 30 graminis + TX, Rhodotorula mucilagnosa + TX, Rhodotorula rubra + TX, Rhodotorula spp. + TX,  
 Saccharomyces cerevisiae + TX, Salinococcus roseus + TX, Sclerotinia minor + TX, Sclerotinia  
 minor (SARRITOR®) + TX, Scytalidium spp. + TX, Scytalidium uredinicola + TX, Serratia  
 marcescens + TX, Serratia plymuthica + TX, Serratia spp. + TX, Sordaria fimicola + TX,  
 Spodoptera exigua nuclear polyhedrosis virus (Spod-X® + TX, Spexit®) + TX, Spodoptera  
 35 littoralis nucleopolyhedrovirus (Littovir®) + TX, Sporobolomyces roseus + TX, Stenotrophomonas  
 maltophilia + TX, Streptomyces hygrosopicus + TX, Streptomyces albaduncus + TX,  
 Streptomyces exfoliates + TX, Streptomyces galbus + TX, Streptomyces griseoplanus + TX,  
 Streptomyces griseoviridis (Mycostop®) + TX, Streptomyces lydicus (Actinovate®) + TX,  
 Streptomyces lydicus WYEC-108 (ActinoGrow®) + TX, Streptomyces violaceus + TX, Tilletiopsis

minor + TX, Tilletiopsis spp. + TX, Trichoderma asperellum (T34 Biocontrol®) + TX, Trichoderma atroviride (Plantmate®) + TX, Trichoderma gamsii (Tenet®) + TX, Trichoderma hamatum TH 382 + TX, Trichoderma harzianum rifai (Mycostar®) + TX, Trichoderma harzianum T-22 (Trianum-P®) + TX, PlantShield HC® + TX, RootShield® + TX, Trianum-G® + TX, Trichoderma harzianum T-39 (Trichodex®) + TX, Trichoderma inhamatum + TX, Trichoderma koningii + TX, Trichoderma lignorum + TX, Trichoderma longibrachiatum + TX, Trichoderma polysporum (Binab T®) + TX, Trichoderma spp. LC 52 (Sentinel®) + TX, Trichoderma taxi + TX, Trichoderma virens + TX, Trichoderma virens (formerly Gliocladium virens GL-21) (SoilGuard®) + TX, Trichoderma viride + TX, Trichoderma viride strain ICC 080 (Remedier®) + TX, Trichosporon pullulans + TX, Trichosporon spp. + TX, Trichothecium roseum + TX, Trichothecium spp. + TX, Typhula phacorrhiza strain 94671 + TX, Ulocladium atrum + TX, Ulocladium oudemansii (Botry-Zen®) + TX, Ustilago maydis + TX, various bacteria and supplementary micronutrients (Natural II®) + TX, various fungi (Millennium Microbes®) + TX, Verticillium chlamydosporium + TX, Vip3Aa20 (VIPTera®) + TX, Virgibacillus marismortui + TX, Xanthomonas campestris pv. Poae (Camperico®) + TX, Xenorhabdus bovienii + TX, Xenorhabdus nematophilus + TX;

azadirachtin (Plasma Neem Oil® + TX, AzaGuard® + TX, MeemAzal® + TX, Molt-X® e.g. AZATIN XL from Certis, US) + TX, Botanical IGR (Neemazad® + TX, Neemix®) + TX, canola oil (Lilly Miller Vegol®) + TX, Chenopodium ambrosioides near ambrosioides (Requiem®) + TX, Chrysanthemum extract (Crisant®) + TX, essentials oils of Labiatae (Botania®) + TX, extract of neem oil (Trilogy®) + TX, extracts of clove rosemary peppermint and thyme oil (Garden insect killer®) + TX, garlic + TX, Glycinebetaine (Greenstim®) + TX, kaolin (Screen®) + TX, lemongrass oil (GreenMatch®) + TX, Melaleuca alternifolia extract (also called tea tree oil) (Timorex Gold®) + TX, mixture of clove peppermint garlic oil and mint (Soil Shot®) + TX, mixture of clove rosemary and peppermint extract (EF 400®) + TX, mixture of rosemary sesame peppermint thyme and cinnamon extracts (EF 300®) + TX, neem oil + TX, Nepeta cataria (Catnip oil) + TX, Nepeta catarina + TX, nicotine + TX, oregano oil (MossBuster®) + TX, Pedaliaceae oil (Nematon®) + TX, pine oil (Retenol®) + TX, pyrethrum + TX, Quillaja saponaria (NemaQ®) + TX, Reynoutria sachalinensis (Regalia® + TX, Sakalia®) + TX, rotenone (Eco Roten®) + TX, Rutaceae plant extract (Soleo®) + TX, soybean oil (Ortho ecosense®) + TX, storage glucan of brown algae (Laminarin®) + TX, thyme oil (AGNIQUE® MMF + TX, BugOil®+ TX) + TX;

(E,Z)-7,9-Dodecadien-1-yl acetate + TX, (E,Z,Z)-3,8,11 Tetradecatrienyl acetate + TX, (Z,Z,E)-7,11,13-Hexadecatrienal + TX, 2-Methyl-1-butanol + TX, Biolure® + TX, blackheaded fireworm pheromone (3M Sprayable Blackheaded Fireworm Pheromone®) + TX, Calcium acetate + TX, Check-Mate® + TX, Codling Moth Pheromone (Paramount dispenser-(CM)/ Isomate C-Plus®) + TX, Entostat powder (extract from palm tree) (Exosex CM®) + TX, Grape Berry Moth Pheromone (3M MEC-GBM Sprayable Pheromone®) + TX, Lavandulyl senecioate + TX, Leafroller pheromone (3M MEC – LR Sprayable Pheromone®) + TX, Muscamone (Snip7 Fly Bait® + TX, Oriental Fruit Moth Pheromone (3M oriental fruit moth sprayable pheromone®) + TX,

Peachtree Borer Pheromone (Isomate-P®) + TX, Scenturion® + TX, Starbar Premium Fly Bait® + TX, Tomato Pinworm Pheromone (3M Sprayable pheromone®) + TX;

Fopius arisanus + TX, Acerophagus papaya + TX, Adalia bipunctata (Adalia-System®) + TX, Adalia bipunctata (Adaline®) + TX, Adalia bipunctata (Aphidalia®) + TX, Ageniaspis citricola + TX, Ageniaspis fuscicollis + TX, Amblyseius andersoni (Anderline®, or Andersoni-System®) + TX, Amblyseius californicus (Amblyline®, or Spical®) + TX, Amblyseius cucumeris (Thripex®, or Bugline cucumeris®) + TX, Amblyseius fallacis (Fallacis®) + TX, Amblyseius swirskii (Bugline swirskii®, or Swirskii-Mite®) + TX, Amblyseius womersleyi (WomerMite®) + TX, Amitus hesperidum + TX, Anagrus atomus + TX, Anagrus fusciventris + TX, Anagrus kamali + TX, Anagrus loeckii + TX, Anagrus pseudococci (Citripar®) + TX, Anicetus benefices + TX, Anisopteromalus calandrae + TX, Anthocoris nemoralis (Anthocoris-System®) + TX, Aphelinus abdominalis (Apheline® + TX, Aphiline®) + TX, + TX, Aphelinus asychis + TX, Aphidius colemani (Ahipar®) + TX, Aphidius ervi (Aphelinus-System®) + TX, Aphidius ervi (Ervipar®) + TX, Aphidius gifuensis + TX, Aphidius matricariae (Ahipar-M®) + TX, Aphidoletes aphidimyza (Aphidend® + TX, Aphidoline®) + TX, Aphytis lingnanensis + TX, Aphytis melinus + TX, Aprostocetus hagenowii + TX, Atheta coriaria (Staphyline®) + TX, Bombus spp. + TX, Bombus terrestris (Beeline® + TX, Tripol®) + TX, Bombus terrestris (Natupol Beehive®) + TX, Cephalonomia stephanoderis + TX, Chilocorus nigritus + TX, Chrysoperla carnea (Chrysoline® + TX, Chrysopa®) + TX, Chrysoperla rufilabris + TX, Cirrospilus ingenuus + TX, Cirrospilus quadristriatus + TX, Citrostichus phyllocnistoides + TX, Closterocerus chamaeleon + TX, Closterocerus spp. + TX, Coccidoxenoides perminutus (Planopar®) + TX, Coccophagus cowperi + TX, Coccophagus lycimnia + TX, Cotesia flavipes + TX, Cotesia plutellae + TX, Cryptolaemus montrouzieri (Cryptobug® + TX, Cryptoline®) + TX, Cybocephalus nipponicus + TX, Dacnusa sibirica (Minusa® + TX, DacDigline® + TX, Minex®) + TX, Delphastus catalinae (Delphastus®) + TX, Delphastus pusillus + TX, Diachasmimorpha krausii + TX, Diachasmimorpha longicaudata + TX, Diaparsis jucunda + TX, Diaphorencyrtus aligarhensis + TX, Diglyphus isaea (Diminex® + TX, Miglyphus® + TX, Digline®) + TX, Diversinervus spp. + TX, Encarsia citrina + TX, Encarsia formosa (Encarsia max® + TX, Encarine® + TX, En-Strip®) + TX, Encarsia guadeloupae + TX, Encarsia haitiensis + TX, Episyrrhus balteatus (Syrphidend®) + TX, Eretmoceris siphonini + TX, Eretmoceris californicus + TX, Eretmoceris eremicus (Enermix® + TX, Ercal® + TX, Eretline e® + TX, Bemimix®) + TX, Eretmoceris hayati + TX, Eretmoceris mundus (Bemipar® + TX, Eretline m®) + TX, Eretmoceris siphonini + TX, Exochomus quadripustulatus + TX, Feltiella acarisuga (Feltiline®) + TX, Feltiella acarisuga (Spidend®) + TX, Fopius ceratitivorus + TX, Formononetin (Wirless Beehome®) + TX, Franklinothrips vespiformis (Vespop®) + TX, Galendromus occidentalis + TX, Goniozus legneri + TX, Habrobracon hebetor + TX, Harmonia axyridis (HarmoBeetle®) + TX, Heterorhabditis bacteriophora (NemaShield HB® + TX, Nemaseek® + TX, Terranem-Nam® + TX, Terranem® + TX, Larvanem® + TX, B-Green® + TX, NemAttack® + TX, Nematop®) + TX, Heterorhabditis megidis (Nemasys H® + TX, BioNem H® + TX, Exhibitline hm® + TX, Larvanem-M®) + TX, Heterorhabditis spp. (Lawn Patrol®) + TX, Hippodamia

convergens + TX, Hypoaspis aculeifer (Aculeifer-System® + TX, Entomite-A®) + TX, Hypoaspis miles (Hypoline m® + TX, Entomite-M®) + TX, Lbalia leucospoides + TX, Lecanoideus floccissimus + TX, Lemophagus errabundus + TX, Leptomastidea abnormis + TX, Leptomastix dactylopii (Leptopar®) + TX, Leptomastix epona + TX, Lindorus lophanthae + TX, Lipolexis oregmae + TX, Lucilia caesar (NatuFly®) + TX, Lysiphlebus testaceipes + TX, Macrolophus caliginosus (Mirical-N® + TX, Macroline c® + TX, Mirical®) + TX, Mesoseiulus longipes + TX, Metaphycus flavus + TX, Metaphycus lounsburyi + TX, Micromus angulatus (Milacewing®) + TX, Microterys flavus + TX, Muscidifurax raptorellus and Spalangia cameroni (Biopar®) + TX, Neodryinus typhlocybae + TX, Neoseiulus californicus + TX, Neoseiulus cucumeris (THRYPEX®) + TX, Neoseiulus fallacis + TX, Nesideocoris tenuis (NesidioBug® + TX, Nesibug®) + TX, Ophyra aenescens (Biofly®) + TX, Orius insidiosus (Thripor-I® + TX, Oriline i®) + TX, Orius laevigatus (Thripor-L® + TX, Oriline l®) + TX, Orius majusculus (Oriline m®) + TX, Orius strigicollis (Thripor-S®) + TX, Pauesia juniperorum + TX, Pediobius foveolatus + TX, Phasmarhabditis hermaphrodita (Nemaslug®) + TX, Phymastichus coffea + TX, Phytoseiulus macropilus + TX, Phytoseiulus persimilis (Spidex® + TX, Phytoline p®) + TX, Podisus maculiventris (Podisus®) + TX, Pseudacteon curvatus + TX, Pseudacteon obtusus + TX, Pseudacteon tricuspis + TX, Pseudaphycus maculipennis + TX, Pseudleptomastix mexicana + TX, Psyllaephagus pilosus + TX, Psytalia concolor (complex) + TX, Quadrastichus spp. + TX, Rhizobius lophanthae + TX, Rodolia cardinalis + TX, Rumina decollate + TX, Semielacher petiolatus + TX, Sitobion avenae (Ervibank®) + TX, Steinernema carpocapsae (Nematac C® + TX, Millenium® + TX, BioNem C® + TX, NemAttack® + TX, Nemastar® + TX, Capsanem®) + TX, Steinernema feltiae (NemaShield® + TX, Nemasys F® + TX, BioNem F® + TX, Steinernema-System® + TX, NemAttack® + TX, Nemaplus® + TX, Exhibitline sf® + TX, Scia-rid® + TX, Entonem®) + TX, Steinernema kraussei (Nemasys L® + TX, BioNem L® + TX, Exhibitline srb®) + TX, Steinernema riobrave (BioVector® + TX, BioVektor®) + TX, Steinernema scapterisci (Nematac S®) + TX, Steinernema spp. + TX, Steinernematid spp. (Guardian Nematodes®) + TX, Stethorus punctillum (Stethorus®) + TX, Tamarixia radiate + TX, Tetrastichus setifer + TX, Thripobius semiluteus + TX, Torymus sinensis + TX, Trichogramma brassicae (Tricholine b®) + TX, Trichogramma brassicae (Tricho-Strip®) + TX, Trichogramma evanescens + TX, Trichogramma minutum + TX, Trichogramma ostrinae + TX, Trichogramma platneri + TX, Trichogramma pretiosum + TX, Xanthopimpla stemmator + TX;

abscisic acid + TX, Aminomite® + TX, BioGain® + TX, bioSea® + TX, Chondrostereum purpureum (Chontrol Paste®) + TX, Colletotrichum gloeosporioides (Collego®) + TX, Copper Octanoate (Cueva®) + TX, Delta traps (Trapline d®) + TX, Erwinia amylovora (Harpin) (ProAct®) + TX, Ni-HIBIT Gold CST®) + TX, fatty acids derived from a natural by-product of extra virgin olive oil (FLIPPER®) + TX, Ferri-phosphate (Ferramol®) + TX, Funnel traps (Trapline y®) + TX, Gallex® + TX, Grower's Secret® + TX, Homo-brassonolide + TX, Iron Phosphate (Lilly Miller Worry Free Ferramol Slug & Snail Bait®) + TX, MCP hail trap (Trapline f®) + TX, Microctonus hyperodae + TX, Mycoleptodiscus terrestris (Des-X®) + TX, Nosema locustae (Semaspore

Organic Grasshopper Control®) + TX, Pheromone trap (Thripline ams®) + TX, potassium bicarbonate (MilStop®) + TX, potassium iodide + potassiumthiocyanate (Enzicur®) + TX, potassium salts of fatty acids (Sanova®) + TX, potassium silicate solution (Sil-Matrix®) + TX, Spider venom + TX, Sticky traps (Trapline YF® + TX, Rebell Amarillo®) + TX, SuffOil-X® + TX,  
 5 Traps (Takitrapline y + b®) + TX, Zenox® + TX;

Bacillus mojavensis strain R3B (Accession No. NCAIM (P) B001389) (WO 2013/034938) from Certis USA LLC + TX, Bacillus pumilus, in particular strain BU F-33, having NRRL Accession No. 50185 (CARTISSA® from BASF, EPA Reg. No. 71840-19) + TX, Bacillus subtilis CX-9060 from Certis USA LLC + TX, Bacillus sp., in particular strain D747 (available as DOUBLE  
 10 NICKEL® from Kumiai Chemical Industry Co, Ltd.), having Accession No. FERM BP-8234, (U.S. Patent No. 7,094,592) + TX, Bacillus subtilis strain BU1814 (VELONDIS® PLUS, VELONDIS® FLEX and VELONDIS® EXTRA from BASF SE) + TX, Bacillus subtilis var. amyloliquefaciens strain FZB24 having Accession No. DSM 10271 (available from Novozymes as TAEGRO® or TAEGRO® ECO (EPA Registration No. 70127-5)) + TX, Bacillus subtilis, in particular strain  
 15 QST713/AQ713 (having NRRL Accession No. B-21661 and described in U.S. Patent No. 6,060,051, available as SERENADE® OPTI or SERENADE® ASO from Bayer CropScience LP, US) + TX, Paenibacillus polymyxa, in particular strain AC-1 (e.g. TOPSEED® from Green Biotech Company Ltd.) + TX, Paenibacillus sp. strain having Accession No. NRRL B-50972 or Accession No. NRRL B-67129 + TX, WO 2016/154297 + TX, Pantoea agglomerans, in particular  
 20 strain E325 (Accession No. NRRL B-21856) (available as BLOOMTIME BIOLOGICAL™ FD BIOPESTICIDE from Northwest Agri Products) + TX, Pseudomonas proradix (e.g. PRORADIX® from Sourcon Padena) + TX;

Aureobasidium pullulans, in particular blastospores of strain DSM14940 + TX, blastospores of strain DSM 14941 or mixtures of blastospores of strains DSM14940 and  
 25 DSM14941 (e.g., BOTECTOR® and BLOSSOM PROTECT® from bio-ferm, CH) + TX, Pseudozyma aphidis (as disclosed in WO2011/151819 by Yissum Research Development Company of the Hebrew University of Jerusalem) + TX, Saccharomyces cerevisiae, in particular strains from Lesaffre et Compagnie (e.g. CNCM No. 1-393, CNCM No. 1-3937, CNCM No. 1-3938 or CNCM No. 1-3939 (WO 2010/086790) + TX;

bacteria including Agrobacterium radiobacter strain K84 (e.g. GALLTROL-A® from AgBioChem, CA) + TX, Bacillus amyloliquefaciens isolate B246 (e.g. AVOGREEN™ from University of Pretoria) + TX, Bacillus amyloliquefaciens strain F727 (also known as strain MBI110) (NRRL Accession No. B-50768 + TX, WO 2014/028521) (STARGUS® from Marrone Bio Innovations) + TX, Bacillus amyloliquefaciens strain FZB42 + TX, Accession No. DSM 23117  
 35 (available as RHIZOVITAL® from ABiTEP, DE) + TX, Bacillus amyloliquefaciens, in particular strain D747 (available as Double Nickel™ from Kumiai Chemical Industry Co., Ltd., having accession number FERM BP-8234, US Patent No. 7,094,592) + TX, Bacillus licheniformis FMCH001 and Bacillus subtilis FMCH002 (QUARTZO® (WG) and PRESENCE® (WP) from FMC Corporation) + TX, Bacillus licheniformis, in particular strain SB3086, having Accession No.

ATCC 55406, WO 2003/000051 (available as ECOGUARD® Biofungicide and GREEN RELEAF™ from Novozymes) + TX, *Bacillus methylotrophicus* strain BAC-9912 (from Chinese Academy of Sciences' Institute of Applied Ecology) + TX, *Bacillus mycoides* + TX, isolate + TX, having Accession No. B-30890 (available as BMJ TGAI® or WG and LifeGard™ from Certis USA LLC) + TX, *Bacillus pumilus*, in particular strain GB34 (available as Yield Shield® from Bayer AG, DE) + TX, *Bacillus pumilus*, in particular strain QST2808 (available as SONATA® from Bayer CropScience LP, US, having Accession No. NRRL B-30087 and described in U.S. Patent No. 6,245,551) + TX, *Bacillus subtilis* CX-9060 from Certis USA LLC + TX, *Bacillus subtilis* IAB/BS03 (AVIV™ from STK Bio-Ag Technologies + TX, PORTENTO® from Idai Nature) + TX, *Bacillus subtilis* KTSB strain (FOLIACTIVE® from Donaghys) + TX, *Bacillus subtilis* strain BU1814 + TX, (available as VELONDIS® PLUS + TX, VELONDIS® FLEX and VELONDIS® EXTRA from BASF SE) + TX, *Bacillus subtilis* strain GB03 (available as Kodiak® from Bayer AG, DE) + TX, *Bacillus subtilis* strain MBI 600 (available as SUBTILEX from BASF SE) + TX, having Accession Number NRRL B-50595 + TX, U.S. Patent No. 5,061,495 + TX, *Bacillus subtilis* strain Y1336 (available as BIOBAC® WP from Bion-Tech + TX, Taiwan + TX, registered as a biological fungicide in Taiwan under Registration Nos. 4764 + TX, 5454 + TX, 5096 and 5277) + TX, *Bacillus subtilis* var. *amyloliquefaciens* strain FZB24 having Accession No. DSM 10271 (available from Novozymes as TAEGRO® or TAEGRO® ECO (EPA Registration No. 70127-5)) + TX, *Bacillus subtilis* Y1336 (available as BIOBAC® WP from Bion-Tech + TX, Taiwan + TX, registered as a biological fungicide in Taiwan under Registration Nos. 4764 + TX, 5454 + TX, 5096 and 5277) + TX, *Paenibacillus epiphyticus* (WO 2016/020371) from BASF SE + TX, *Paenibacillus polymyxa* ssp. *plantarum* (WO 2016/020371) from BASF SE + TX, *Paenibacillus* sp. strain having Accession No. NRRL B-50972 or Accession No. NRRL B-67129 + TX, WO 2016/154297 + TX, *Pseudomonas chlororaphis* strain AFS009 + TX, having Accession No. NRRL B-50897 + TX, WO 2017/019448 (e.g., HOWLER™ and ZIO® from AgBiome Innovations, US) + TX, *Pseudomonas chlororaphis*, in particular strain MA342 (e.g. CEDOMON®, CERALL®, and CEDRESS® by Bioagri and Koppert) + TX, *Pseudomonas fluorescens* strain A506 (e.g. BLIGHTBAN® A506 by NuFarm) + TX, *Pseudomonas proradix* (e.g. PRORADIX® from Sourcon Padena) + TX, *Streptomyces griseoviridis* strain K61 (also known as *Streptomyces galbus* strain K61) (Accession No. DSM 7206) (MYCOSTOP® from Verdera, PREFENCE® from BioWorks, cf. Crop Protection 2006, 25, 468-475) + TX, *Streptomyces lydicus* strain WYEC108 (also known as *Streptomyces lydicus* strain WYCD108US) (ACTINO-IRON® and ACTINOVATE® from Novozymes) + TX;

*Trichoderma atroviride* strain T11 (IMI352941/ CECT20498) + TX, *Ampelomyces quisqualis* strain AQ10, having Accession No. CNCM 1-807 (e.g. AQ 10® by IntrachemBio, Italia) + TX, *Ampelomyces quisqualis*, in particular strain AQ 10 (e.g. AQ 10® by IntrachemBio Italia) + TX, *Aspergillus flavus* strain NRRL 21882 (products known as AFLA-GUARD® from Syngenta/ChemChina) + TX, *Aureobasidium pullulans*, in particular blastospores of strain DSM 14941 + TX, *Aureobasidium pullulans*, in particular blastospores of strain DSM14940 + TX,



Aureobasidium pullulan, in particular mixtures of blastospores of strains DSM14940 and DSM 14941 (e.g. Botector® by bio-ferm, CH) + TX, Chaetomium cupreum (Accession No. CABI 353812) (e.g. BOKUPRUM™ by AgriLife) + TX, Chaetomium globosum (available as RIVADIOM® by Rivale) + TX, Cladosporium cladosporioides, strain H39, having Accession No. 5 CBS122244, US 2010/0291039 (by Stichting Dienst Landbouwkundig Onderzoek) + TX, Coniothyrium minitans, in particular strain CON/M/91-8 (Accession No. DSM9660, e.g. Contans® from Bayer CropScience Biologics GmbH) + TX, Cryptococcus flavescens, strain 3C (NRRL Y-50378) + TX, Dactylaria candida + TX, Dilocephora alopecuri (available as TWIST FUNGUS®) + TX, Fusarium oxysporum, strain Fo47 (available as FUSACLEAN® by Natural Plant Protection) 10 + TX, Gliocladium catenulatum (Synonym: Clonostachys rosea f. catenulate) strain J1446 (e.g. Prestop® by Lallemand) + TX, Gliocladium roseum (also known as Clonostachys rosea f rosea) strain IK726 (Jensen DF, et al. Development of a biocontrol agent for plant disease control with special emphasis on the near commercial fungal antagonist Clonostachys rosea strain 'IK726, Australasian Plant Pathol. 2007,36(2):95-101) + TX, Gliocladium roseum (also known as 15 Clonostachys rosea f rosea), in particular strain 321U from Adjuvants Plus, strain ACM941 as disclosed in Xue A.G. (Efficacy of Clonostachys rosea strain ACM941 and fungicide seed treatments for controlling the root rot complex of field pea, Can Jour Plant Sci 2003 + TX, 83(3): 519-524) + TX, Metschnikowia fructicola, in particular strain NRRL Y-30752 + TX, Microsphaeropsis ochracea + TX, Penicillium steckii (DSM 27859 + TX, WO 2015/067800) from 20 BASF SE + TX, mixtures of Trichoderma asperellum strain ICC 012 (also known as Trichoderma harzianum ICC012) + TX, having Accession No. CABI CC IMI 392716 and Trichoderma gamsii (formerly T. viride) strain ICC 080 + TX, having Accession No. IMI 392151 (e.g., BIO-TAM™ from Isagro USA, Inc. or BIODERMA® by Agrobiosol de Mexico, S.A. de C.V.) + TX, Penicillium vermiculatum + TX, Phlebiopsis gigantea strain VRA 1992 (ROTSTOP® C from Danstar 25 Ferment) + TX, Pseudozyma flocculosa, strain PF-A22 UL (available as SPORODEX® L by Plant Products Co., CA) + TX, Saccharomyces cerevisiae strain LAS117 cell walls (CEREVISANE® from Lesaffre, ROMEO® from BASF SE) + TX, Saccharomyces cerevisiae strain from Lesaffre et Compagnie, FR (e.g. CNCM No. 1-3936, CNCM No. 1-3937, CNCM No. 1-3938, or CNCM No. 1-3939 (WO 2010/086790)) + TX, Saccharomyces cerevisiae, in particular strain LASO2 (from 30 Agro-Levures et Dérivés) + TX, Simplicillium lanosoniveum strain T34 ((e.g. T34 Biocontrol by Biocontrol Technologies S.L., ES) or strain ICC 012 from Isagro, or strain WRL-076 (NRRL Y-30842), U.S. Patent No. 7,579,183) + TX, Talaromyces flavus, strain V117b + TX, Trichoderma asperelloides JM41R (Accession No. NRRL B-50759) (TRICHO PLUS® from BASF SE) + TX, Trichoderma asperellum, in particular strain SKT-1, having Accession No. FERM P-16510 (e.g. ECO-HOPE® from Kumiai Chemical Industry) + TX, Trichoderma asperellum, in particular strain 35 kd (e.g. T-Gro from Andermatt Biocontrol) + TX, Trichoderma atroviride strain 77B (T77 from Andermatt Biocontrol) + TX, Trichoderma atroviride strain ATCC 20476 (IMI 206040) + TX, Trichoderma atroviride strain LC52 (e.g. Tenet by Agrimm Technologies Limited) + TX, Trichoderma atroviride strain LU132 (e.g. Sentinel from Agrimm Technologies Limited) + TX,

Trichoderma atroviride strain NMI no. V08/002388 + TX, Trichoderma atroviride strain NMI no. V08/002389 + TX, Trichoderma atroviride strain NMI no. V08/002390 + TX, Trichoderma atroviride strain no. V08/002387 + TX, Trichoderma atroviride strain SKT-1 (FERM P-16510) + TX, JP Patent Publication (Kokai) 11-253151 A + TX, Trichoderma atroviride strain SKT-2 (FERM P-16511) + TX, JP Patent Publication (Kokai) 11-253151 A + TX, Trichoderma atroviride strain SKT-3 (FERM P-17021) + TX, JP Patent Publication (Kokai) 11-253151 A + TX, Trichoderma atroviride, in particular strain SC1 (Accession No. CBS 122089, WO 2009/116106 and U.S. Patent No. 8,431,120 (from Bi-PA)) + TX, Trichoderma atroviride, strain CNCM 1-1237 (e.g. Esquive® WP from Agrauxine + TX) + TX, Trichoderma fertile (e.g. product TrichoPlus from BASF) + TX, Trichoderma gamsii (formerly T. viride) + TX, Trichoderma gamsii (formerly T. viride) strain ICC 080 (IMI CC 392151 CABI) (available as BIODERMA® by AGROBIOSOL DE MEXICO, S.A. DE C.V.) + TX, + TX, Trichoderma gamsii strain ICC080 (IMI CC 392151 CABI + TX, e.g. BioDerma by AGROBIOSOL DE MEXICO, S.A. DE C.V.) + TX, + TX, Trichoderma harmatum + TX, Trichoderma harmatum + TX, having Accession No. ATCC 28012 + TX, Trichoderma harzianum + TX, Trichoderma harzianum rifai T39 (e.g. Trichodex® from Makhteshim, US) + TX, Trichoderma harzianum strain Cepa SimbT5 (from Simbiose Agro) + TX, + TX, Trichoderma harzianum strain DB 103 (available as T-GRO® 7456 by Dagutat Biolab) + TX, Trichoderma harzianum strain ITEM 908 (e.g. Trianum-P from Koppert) + TX, Trichoderma harzianum strain T-22 (e.g. Trianum-P from Andermatt Biocontrol or Koppert) + TX, Trichoderma harzianum strain TH35 (e.g. Root-Pro by Mycontrol) + TX, Trichoderma polysporum strain IMI 206039 (e.g. Binab TF WP by BINAB Bio-Innovation AB + TX, Sweden) + TX, Trichoderma stromaticum having Accession No. Ts3550 (e.g. Tricovab by CEPLAC, Brazil) + TX, Trichoderma virens (also known as Gliocladium virens) in particular strain GL-21 (e.g. SoilGard by Certis, US) + TX, Trichoderma virens strain G-41 + TX, formerly known as Gliocladium virens (Accession No. ATCC 20906) (e.g., ROOTSHIELD® PLUS WP and TURFSHIELD® PLUS WP from BioWorks, US) + TX, Trichoderma viride in particular strain B35 (Pietr et al. + TX, 1993 + TX, Zesz. Nauk. A R w Szczecinie 161: 125-137) + TX, Trichoderma viride strain TV1 (e.g. Trianum-P by Koppert) + TX, Ulocladium oudemansii strain U3, having Accession No. NM 99/06216 (e.g., BOTRY-ZEN® by Botry-Zen Ltd, New Zealand and BOTRYSTOP® from BioWorks, Inc.) + TX, Verticillium albo-atrum (formerly V. dahliae) strain WCS850 having Accession No. WCS850, deposited at the Central Bureau for Fungi Cultures (e.g., DUTCH TRIG® by Tree Care Innovations) + TX, Verticillium chlamydosporium + TX;

bacteria including a mixture of Azotobacter vinelandii and Clostridium pasteurianum (available as INVIGORATE® from Agrinos) + TX, a mixture of Bacillus licheniformis FMCH001 and Bacillus subtilis FMCH002 (available as QUARTZO® (WG), PRESENCE® (WP) from FMC Corporation), Azorhizobium caulinodans, in particular strain ZB-SK-5 + TX, Azospirillum brasilense (e.g., VIGOR® from KALO, Inc.) + TX, Azospirillum lipoferum (e.g., VERTEX-IF™ from TerraMax, Inc.) + TX, Azotobacter chroococcum, in particular strain H23 + TX, Azotobacter vinelandii, in particular strain ATCC 12837 + TX, Bacillus amyloliquefaciens BS27 (Accession

No. NRRL B-5015) + TX, *Bacillus amyloliquefaciens* in particular strain FZB42 (e.g. RHIZOVITAL® from ABITEP, DE) + TX, *Bacillus amyloliquefaciens* in particular strain IN937a + TX, *Bacillus amyloliquefaciens* pm414 (LOLI-PEPTA® from Biofilm Crop Protection) + TX, *Bacillus amyloliquefaciens* SB3281 (ATCC # PTA-7542 + TX, WO 2017/205258) + TX, *Bacillus amyloliquefaciens* TJ1000 (available as QUIKROOTS® from Novozymes) + TX, *Bacillus cereus* family member EE128 (NRRL No. B-50917) + TX, *Bacillus cereus* family member EE349 (NRRL No. B-50928) + TX, *Bacillus cereus* in particular strain BP01 (ATCC 55675 + TX, e.g. MEPICHLOR® from Arysta Lifescience, US) + TX, *Bacillus mycoides* BT155 (NRRL No. B-50921) + TX, *Bacillus mycoides* BT46-3 (NRRL No. B-50922) + TX, *Bacillus mycoides* EE118 (NRRL No. B-50918) + TX, *Bacillus mycoides* EE141 (NRRL No. B-50916) + TX, *Bacillus pumilus* in particular strain GB34 (e.g. YIELD SHIELD® from Bayer Crop Science, DE) + TX, *Bacillus pumilus* in particular strain QST2808 (Accession No. NRRL No. B-30087) + TX, *Bacillus siamensis* in particular strain KCTC 13613T + TX, *Bacillus subtilis* in particular strain AQ30002 (Accession No. NRRL No. B-50421 and described in U.S. Patent Application No. 13/330,576) + TX, *Bacillus subtilis* in particular strain AQ30004 (NRRL No. B-50455 and described in U.S. Patent Application No. 13/330,576) + TX, *Bacillus subtilis* in particular strain MBI 600 (e.g. SUBTILEX® from BASF SE) + TX, *Bacillus subtilis* rm303 (RHIZOMAX® from Biofilm Crop Protection) + TX, *Bacillus subtilis* strain BU1814 (available as TEQUALIS® from BASF SE) + TX, *Bacillus tequilensis* in particular strain NII-0943 + TX, *Bacillus thuringiensis* BT013A (NRRL No. B-50924) also known as *Bacillus thuringiensis* 4Q7 + TX, *Bradyrhizobium japonicum* (e.g. OPTIMIZE® from Novozymes) + TX, *Delftia acidovorans* in particular strain RAY209 (e.g. BIOBOOST® from Brett Young Seeds) + TX, *Lactobacillus* sp. (e.g. LACTOPLANT® from LactoPAFI) + TX, *Mesorhizobium cicer* (e.g., NODULATOR from BASF SE) + TX, *Paenibacillus polymyxa* in particular strain AC-1 (e.g. TOPSEED® from Green Biotech Company Ltd.) + TX, *Pseudomonas aeruginosa* in particular strain PN1 + TX, *Pseudomonas proradix* (e.g. PRORADIX® from Sourcon Padena) + TX, *Rhizobium leguminosarium* biovar *viciae* (e.g., NODULATOR from BASF SE) + TX, *Rhizobium leguminosarum* in particular bv. *viciae* strain Z25 (Accession No. CECT 4585) + TX, *Serratia marcescens* in particular strain SRM (Accession No. MTCC 8708) + TX, + TX, *Sinorhizobium meliloti* strain NRG-185-1 (NITRAGIN® GOLD from Bayer CropScience) + TX, *Thiobacillus* sp. (e.g. CROPAID® from Cropaid Ltd UK) + TX;

*Myrothecium verrucaria* strain AARC-0255 (e.g. DiTera™ from Valent Biosciences) + TX, *Penicillium bilaii* strain ATCC 22348 (e.g. JumpStart® from Acceleron BioAg) + TX, *Penicillium bilaii* strain ATCC ATCC20851 + TX, *Purpureocillium lilacinum* (previously known as *Paecilomyces lilacinus*) strain 251 (AGAL 89/030550 + TX, e.g. BioAct from Bayer CropScience Biologics GmbH) + TX, *Pythium oligandrum* strain DV74 + TX, *Pythium oligandrum* strain M1 (ATCC 38472 e.g. Polyversum from Bioprepaty, CZ) + TX, *Rhizopogon amylopogon* (Myco-Sol from Agri-Enterprise, LLC, formerly Helena Chemical Company) + TX, *Rhizopogon fulvigleba* (e.g. Myco-Sol from Agri-Enterprise, LLC, formerly Helena Chemical Company) + TX,

Talaromyces flavus strain V117b + TX, Trichoderma asperellum strain (Eco-T from Plant Health Products + TX, ZA) + TX;

mercuric oxide + TX, octhilonone + TX, thiophanate-methyl + TX;

MGK 264 + TX, 2-(2-butoxyethoxy)-ethyl piperonylate + TX, 2-isovalerylindan-1,3-dione +

- 5 TX, 4-(quinoxalin-2-ylamino)benzenesulfonamide + TX, 5-(1,3-benzodioxol-5-yl)-3-hexylcyclohex-2-enone + TX, acibenzolar + TX, acibenzolar-S-methyl + TX, alpha-bromadiolone + TX, alpha-chlorohydrin + TX, aluminium phosphide + TX, anthraquinone + TX, antu + TX, arsenous oxide + TX, barium carbonate + TX, benoxacor + TX, bisthiosemi + TX, brodifacoum + TX, bromadiolone + TX, bromethalin + TX, calcium cyanide + TX, chloralose + TX,
- 10 chlorophacinone + TX, cholecalciferol + TX, cloquintocet (including cloquintocet-mexyl) + TX, copper naphthenate + TX, copper oxychloride + TX, coumachlor + TX, coumafuryl + TX, coumatetralyl + TX, crimidine + TX, cyprosulfamide + TX, diazinon + TX, dichlormid + TX, dicyclopentadiene + TX, difenacoum + TX, difethialone + TX, diphacinone + TX, ergocalciferol + TX, farnesol + TX, farnesol with nerolidol + TX, fenchlorazole (including fenchlorazole-ethyl) +
- 15 TX, fenclorim + TX, flocoumafen + TX, fluoroacetamide + TX, flupropradine + TX, flupropradine hydrochloride + TX, fluxofenim + TX, furilazole + TX, gamma-HCH + TX, guazatine + TX, guazatine acetates + TX, HCH + TX, hydrogen cyanide + TX, imanin + TX, iodomethane + TX, isoxadifen (including isoxadifen-ethyl) + TX, lindane + TX, magnesium phosphide + TX, MB-599 + TX, mefenpyr (including mefenpyr-diethyl) + TX, metcamifen + TX, methiocarb + TX, methyl
- 20 bromide + TX, nerolidol + TX, norbormide + TX, petroleum oils + TX, phosacetim + TX, phosphine + TX, phosphorus + TX, pindone + TX, piperonyl butoxide + TX, piprotal + TX, potassium arsenite + TX, probenazole + TX, propyl isomer + TX, pyridin-4-amine + TX, pyrinuron + TX, Reynoutria sachalinensis extract + TX, ribavirin + TX, S421 + TX, scilliroside + TX, sesamex + TX, sesasmolin + TX, sodium arsenite + TX, sodium cyanide + TX, sodium
- 25 fluoro-acetate + TX, strychnine + TX, sulfoxide + TX, thallium sulfate + TX, thiram + TX, trimethacarb + TX, warfarin + TX, zinc naphthenate + TX, zinc phosphide + TX, ziram + 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; 30 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 35 Common Names, Copyright © 1995-2004]; for example, the compound "acetoprole" is described under the internet address <http://www.alanwood.net/pesticides/acetoprole.html>.

Most of the active ingredients described above are referred to hereinabove by a so-called "common name", the relevant "ISO common name" or another "common name" being used in individual cases. If the designation is not a "common name", the nature of the designation used instead is given

in round brackets for the particular compound; in that case, the IUPAC name, the IUPAC/Chemical Abstracts name, a "chemical name", a "traditional name", a "compound name" or a "development code" is used or, if neither one of those designations nor a "common name" is used, an "alternative name" is employed. "CAS Reg. No" means the Chemical Abstracts Registry Number.

5           The active ingredient mixture of the compounds of formula (I) selected from the compounds defined in the Tables A-1 to A-21, and Table P with active ingredients described above comprises a compound selected from one compound defined in the Tables A-1 to A-21, and Table P 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  
10 especially from 5:1 to 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 by weight.

15           The compounds and mixtures as described above can be used in a method for controlling pests, which comprises applying a composition comprising a compound or mixture respectively 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 practiced on the human or animal body.

          The mixtures comprising a compound of formula (I) selected from the compounds defined in the  
20 Tables A-1 to A-21, and Table P 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 compounds of formula  
25 (I) and the active ingredients as described above is not essential for working the present invention.

          The compositions according to the invention can also comprise further solid or liquid auxiliaries, such as stabilizers, for example unepoxidized or epoxidized vegetable oils (for example epoxidized coconut oil, rapeseed oil or soya oil), antifoams, for example silicone oil, preservatives, viscosity regulators, binders and/or tackifiers, fertilizers or other active ingredients for achieving specific effects,  
30 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  
35 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.

5 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  
10 be metered into the flooded paddy-field.

The compounds of formula (I) of the invention and compositions thereof 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 compound prior to planting, for example seed can be treated prior to sowing. Alternatively, the  
15 compound 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. Typical treatment rates would depend on the plant and pest/fungi  
20 to be controlled and are generally between 1 to 200 grams per 100 kg of seeds, preferably between 5 to 150 grams per 100 kg of seeds, such as between 10 to 100 grams per 100 kg of seeds.

The term seed embraces seeds and plant propagules of all kinds including but not limited to true seeds, seed pieces, suckers, corns, bulbs, fruit, tubers, grains, rhizomes, cuttings, cut shoots and the like and means in a preferred embodiment true seeds.

25 The present invention also comprises seeds coated or treated with or containing a compound of formula (I). The term "coated or treated with and/or containing" generally signifies that the active ingredient is for the most part on the surface of the seed at the time of application, although a greater or lesser part of the ingredient may penetrate into the seed material, depending on the method of application. When the said seed product is (re)planted, it may absorb the active ingredient. In an  
30 embodiment, the present invention makes available a plant propagation material adhered thereto with a compound of formula (I). Further, it is hereby made available, a composition comprising a plant propagation material treated with a compound of formula (I).

Seed treatment comprises all suitable seed treatment techniques known in the art, such as seed dressing, seed coating, seed dusting, seed soaking and seed pelleting. The seed treatment application  
35 of the compound formula (I) can be carried out by any known methods, such as spraying or by dusting the seeds before sowing or during the sowing/planting of the seeds.

The compounds of the invention can be distinguished from other similar compounds by virtue of greater efficacy at low application rates and/or different pest control, which can be verified by the person skilled in the art using the experimental procedures, using lower concentrations if necessary, for

example 10 ppm, 5 ppm, 2 ppm, 1 ppm or 0.2 ppm; or lower application rates, such as 300, 200 or 100, mg of AI per m<sup>2</sup>. The greater efficacy can be observed by an increased safety profile (against non-target organisms above and below ground (such as fish, birds and bees), improved physico-chemical properties, or increased biodegradability).

5 In each aspect and embodiment of the invention, “consisting essentially” and inflections thereof are a preferred embodiment of “comprising” and its inflections, and “consisting of” and inflections thereof are a preferred embodiment of “consisting essentially of” and its inflections.

The disclosure in the present application makes available each and every combination of embodiments disclosed herein.

10 It should be noted that the disclosure herein in respect of a compound of formula (I) applies equally in respect of a compound of each of formulae (I\*), (I'), (I-A) and Tables A-1 to A-21.

## EXAMPLES

### 15 Formulation examples

The following Examples further illustrate, but do not limit, the invention.

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

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

20

<u>Powders for dry seed treatment</u>	a)	b)	c)
active ingredients	25 %	50 %	75 %
light mineral oil	5 %	5 %	5 %
highly dispersed silicic acid	5 %	5 %	-
Kaolin	65 %	40 %	-
Talcum	-	-	20 %

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

Emulsifiable concentrate

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

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

<u>Dusts</u>	a)	b)	c)
Active ingredients	5 %	6 %	4 %
Talcum	95 %	-	-
Kaolin	-	94 %	-
mineral filler	-	-	96 %

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

5

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

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

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

10

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

<u>Suspension concentrate</u>	
active ingredients	40 %
propylene glycol	10 %
nonylphenol polyethylene glycol ether (15 mol of ethylene oxide)	6 %
Sodium lignosulfonate	10 %
carboxymethylcellulose	1 %



silicone oil (in the form of a 75 % emulsion in water)	1 %
Water	32 %

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

5

<u>Flowable concentrate for seed treatment</u>	
active ingredients	40 %
propylene glycol	5 %
copolymer butanol PO/EO	2 %
Tristyrenephenole with 10-20 moles EO	2 %
1,2-benzisothiazolin-3-one (in the form of a 20% solution in water)	0.5 %
monoazo-pigment calcium salt	5 %
Silicone oil (in the form of a 75 % emulsion in water)	0.2 %
Water	45.3 %

The finely ground combination is intimately mixed with the adjuvants, giving a 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.

10

#### Slow Release Capsule Suspension

28 parts of the combination are mixed with 2 parts of an aromatic solvent and 7 parts of toluene diisocyanate/polymethylene-polyphenylisocyanate-mixture (8:1). This mixture is emulsified in a mixture of 1.2 parts of polyvinylalcohol, 0.05 parts of a defoamer and 51.6 parts of water until the desired particle size is achieved. To this emulsion a mixture of 2.8 parts 1,6-diaminohexane in 5.3 parts of water is added. The mixture is agitated until the polymerization reaction is completed. The obtained capsule suspension is stabilized by adding 0.25 parts of a thickener and 3 parts of a dispersing agent. The capsule suspension formulation contains 28% of the active ingredients. The medium capsule diameter is 8-15 microns. The resulting formulation is applied to seeds as an aqueous suspension in an apparatus suitable for that purpose.

20

Formulation types include an emulsion concentrate (EC), a suspension concentrate (SC), a suspo-emulsion (SE), a capsule suspension (CS), a water dispersible granule (WG), an emulsifiable granule (EG), an emulsion, water in oil (EO), an emulsion, oil in water (EW), a micro-emulsion (ME), an oil dispersion (OD), an oil miscible flowable (OF), an oil miscible liquid (OL), a soluble concentrate (SL), an ultra-low volume suspension (SU), an ultra-low volume liquid (UL), a technical concentrate (TK), a dispersible concentrate (DC), a wettable powder (WP), a soluble granule (SG) or any technically feasible formulation in combination with agriculturally acceptable adjuvants.

25

**Preparation examples**

The following examples further illustrate, but do not limit, the invention. Those skilled in the art will promptly recognize appropriate variations from the procedures both as to reactants and as to reaction conditions and techniques. Throughout this description, temperatures are given in degrees Celsius (°C).  
5 "Mp" means melting point in °C. Unless indicated otherwise, <sup>1</sup>H NMR spectra are recorded at 400 MHz and <sup>19</sup>F NMR spectra are recorded at 377 MHz. Chemical shifts are recorded in ppm relevant to a TMS standard. The following abbreviations are used: s = singlet; br s = broad singlet; d = doublet; br d = broad doublet; dd = double doublet; dt = double triplet; t = triplet, tt = triple triplet, q = quartet, quin =  
10 quintuplet, sept = septet; m = multiplet. Either one of the LCMS methods below was used to characterize the compounds. The characteristic LCMS values obtained for each compound were the retention time ("Rt", recorded in minutes) and the measured molecular ion (M+H)<sup>+</sup> or (M-H)<sup>-</sup>.

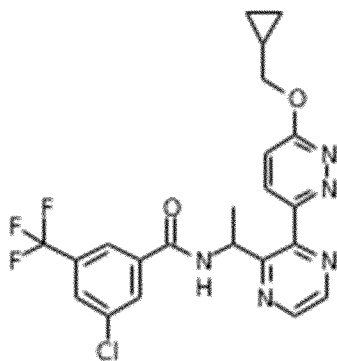
LCMS Methods:15 Method 1:

Spectra were recorded on a Mass Spectrometer from Waters (SQD, SQDII or QDA Single quadrupole mass spectrometer) equipped with an electrospray source (Polarity: positive and negative ions), Capillary: 0.8-3.00 kV, Cone: 5-30 V, Source Temperature: 120-150°C, Desolvation Temperature: 350-600°C, Cone Gas Flow: 50-150 l/h, Desolvation Gas Flow: 650-1000 l/h, Mass range: 50 to 900 Da and  
20 an Acquity UPLC from Waters Corporation: Binary pump, heated column compartment, diode-array detector and ELSD. Column: Waters UPLC HSS T3, 1.8 μm, 30 x 2.1 mm, Temp: 60°C, DAD Wavelength range (nm): 210 to 400, Runtime: 1.5 min; Solvents: A = water + 5% MeOH + 0.05 % HCOOH, B= Acetonitrile + 0.05 % HCOOH; Flow (ml/min) 0.85, Gradient: 10% B isocratic for 0.2 min, then 10-100% B in 1.0 min, 100% B isocratic for 0.2min, 100-10% B in 0.05min, 10% B isocratic for 0.05  
25 min.

Method 2:

Spectra were recorded on a ACQUITY Mass Spectrometer from Waters Corporations (SQD or SQDII Single quadrupole mass spectrometer) equipped with an electrospray source (Polarity: positive or negative ions, Capillary: 3.0 kV, Cone: 30V, Extractor: 3.00 V, Source Temperature: 150°C, Desolvation  
30 Temperature: 400°C, Cone Gas Flow: 60 L/hr, Desolvation Gas Flow: 700 L/hr, Mass range: 140 to 800 Da) and an ACQUITY UPLC from Waters Corporations with solvent degasser, binary pump, heated column compartment and diode-array detector. Column: Waters UPLC HSS T3, 1.8 μm, 30 x 2.1 mm, Temp: 60 °C, DAD Wavelength range (nm): 210 to 400, Solvent Gradient: A = Water/Methanol 9:1 + 0.1% formic acid, B= Acetonitrile + 0.1% formic acid, gradient: 0-100% B in 2.5 min; Flow (ml/min) 0.75.

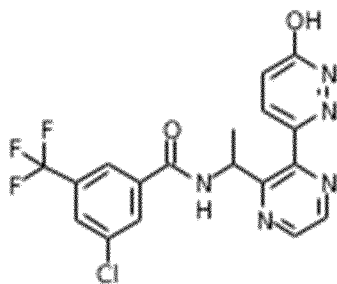
35 **Example 1:** Preparation of 3-chloro-N-[1-[3-[6-(cyclopropylmethoxy)pyridazin-3-yl]pyrazin-2-yl]ethyl]-5-(trifluoromethyl)benzamide (compound P2)



(P2)

To a solution of 1-[3-[6-(cyclopropylmethoxy)pyridazin-3-yl]pyrazin-2-yl]ethanamine (I-21, prepared from intermediates Int-B and I-4 below by following in analogy preparation Example PI-2, steps C, D, E, F) (49.3 mg, 0.182 mmol) and 3-chloro-5-(trifluoromethyl)benzoic acid (CAS 53985-49-2) (40.0 mg, 0.178 mmol) in ethyl acetate (0.71 mL) was added propanephosphonic acid anhydride (T3P<sup>®</sup>, 0.159 mL, 0.267 mmol) and diisopropylethylamine (0.122 mL, 0.713 mmol). The reaction mixture was stirred at room temperature for 1 hour, then diluted with water and ethyl acetate. The layers were separated, the aqueous phase extracted with ethyl acetate, the combined organic layers washed with water, dried over magnesium sulfate, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (ethyl acetate in cyclohexane) to afford the title compound which was further triturated with diethyl ether. The white precipitate was filtered, dried *in vacuo* and pure 3-chloro-N-[1-[3-[6-(cyclopropylmethoxy)pyridazin-3-yl]pyrazin-2-yl]ethyl]-5-(trifluoromethyl)benzamide (compound P2) was obtained. LCMS (method 1): retention time 1.18 min,  $m/z$  478/480 [M+H]<sup>+</sup>.  
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 8.64 (m, 2H), 8.19 (d, 1H), 7.94-8.03 (m, 3H), 7.74 (s, 1H), 7.21 (d, 1H), 6.15 (quin, 1H), 4.50 (d, 2H), 1.76 (d, 3H), 1.42 (m, 1H), 0.71 (m, 2H), 0.46 (m, 2H).

**Example 2:** Preparation of 3-chloro-N-[1-[3-(6-hydroxypyridazin-3-yl)pyrazin-2-yl]ethyl]-5-(trifluoromethyl)benzamide (compound P13)



(P13)

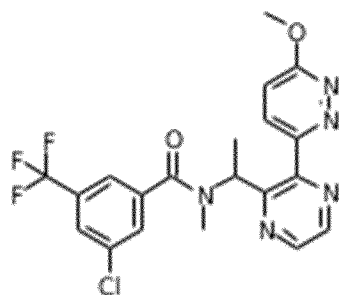
To a solution of 3-chloro-N-[1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethyl]-5-(trifluoromethyl)benzamide (compound P12, prepared from 3-chloro-5-(trifluoromethyl)benzoic acid and intermediate I-9 by following in analogy preparation Example 1 above) (31.0 mg, 0.071 mmol) in 1,4-dioxane (0.24 mL) was added hydrochloric acid (4.0M solution in 1,4-dioxane, 0.0195 mL, 0.078 mmol). The reaction mixture was stirred at 40°C for 4.5 hours, then concentrated under reduced pressure to afford 3-chloro-N-[1-[3-(6-hydroxypyridazin-3-yl)pyrazin-2-yl]ethyl]-5-

(trifluoromethyl)benzamide (compound P13) as light brown solid. LCMS (method 1): retention time 0.91 min,  $m/z$  424/426  $[M+H]^+$ .

$^1H$  NMR (400 MHz,  $d_6$ -DMSO)  $\delta$  ppm 13.42 (d, 1H), 9.34 (d, 1H), 8.70 (d, 1H), 8.66 (d, 1H), 8.19 (s, 1H), 8.14 (s, 1H), 8.05 (s, 1H), 7.99 (d, 1H), 7.07 (dd, 1H), 5.75 (quin, 1H), 1.61 (d, 3H).

5

**Example 3:** Preparation of 3-chloro-N-[1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethyl]-N-methyl-5-(trifluoromethyl)benzamide (compound P14)



(P14)

To a solution of 3-chloro-N-[1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethyl]-5-

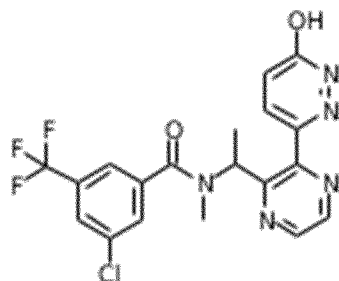
10 (trifluoromethyl)benzamide (compound P12, prepared from 3-chloro-5-(trifluoromethyl)benzoic acid and intermediate I-9 by following in analogy preparation Example 1 above) (54.0 mg, 0.123 mmol) and iodomethane (0.0386 mL, 0.617 mmol) in a mixture of acetonitrile (0.74 mL) and N,N-dimethylacetamide (0.74 mL) was added cesium carbonate (121 mg, 0.370 mmol) at room temperature. The reaction mixture was stirred for 20 hours at room temperature, then diluted with

15 water and the product extracted with ethylacetate and TBME. The combined organic layers were washed with an aqueous solution of lithium chloride, then with water, dried over magnesium sulfate, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (ethyl acetate in cyclohexane) to afford 3-chloro-N-[1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethyl]-N-methyl-5-(trifluoromethyl)benzamide (compound P14) as colorless oil. LCMS (method 1): retention

20 time 1.05 min,  $m/z$  452/454  $[M+H]^+$ .

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  ppm selected signals 6.18 (m, 1H,  $\underline{CH-CH_3}$ ), 1.88 (br d, 3H,  $CH-\underline{CH_3}$ ).

**Example 4:** Preparation of 3-chloro-N-[1-[3-(6-hydroxypyridazin-3-yl)pyrazin-2-yl]ethyl]-N-methyl-5-(trifluoromethyl)benzamide (compound P15)

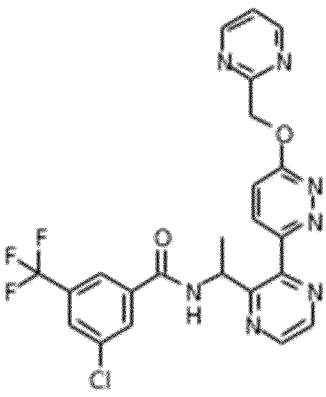
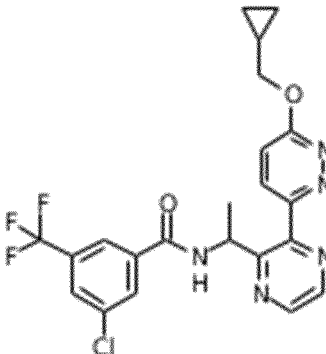
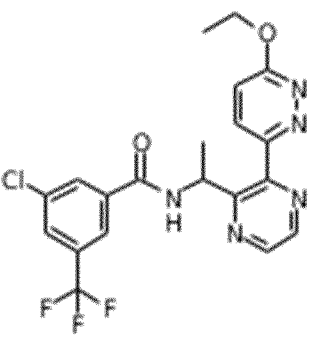


(P15)

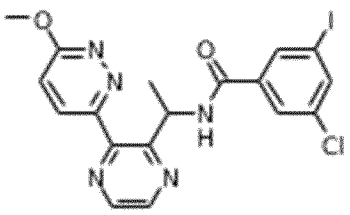
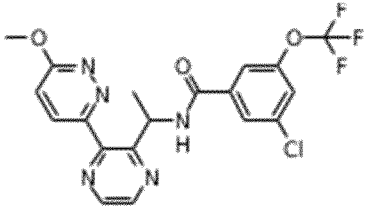
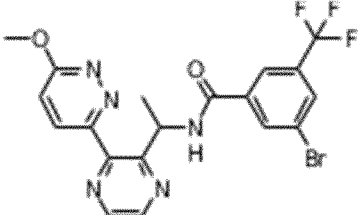
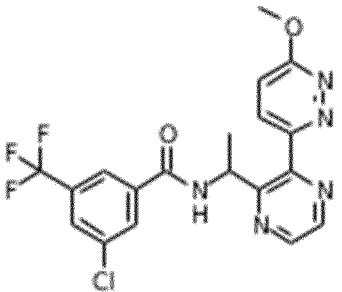
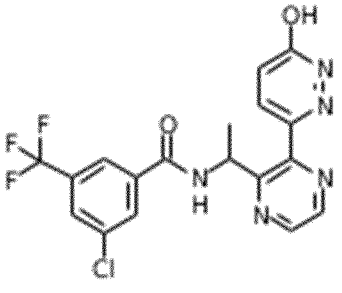
25

To a solution of 3-chloro-N-[1-[3-(6-methoxy)pyridazin-3-yl]pyrazin-2-yl]ethyl]-N-methyl-5-(trifluoromethyl)benzamide (compound P14, prepared as described above) (28 mg, 0.062 mmol) in 1,4-dioxane (0.207 mL) was added hydrochloric acid (4.0M solution in 1,4-dioxane, 0.017 mL, 0.068 mmol). The reaction mixture was stirred at 60°C for 4.5 hours, overnight at room temperature and additional 4 hours at 60°C. Concentration of the mixture under reduced pressure afforded 3-chloro-N-[1-[3-(6-hydroxypyridazin-3-yl)pyrazin-2-yl]ethyl]-N-methyl-5-(trifluoromethyl)benzamide (compound P15) as white foam. LCMS (method 1): retention time 0.87 min, m/z 438/440 [M+H]<sup>+</sup>.

Table P: Physical data of compounds of formula (I)

Entry	IUPAC name	Structure	RT (min)	[M+H] <sup>+</sup> (measured)	Method	mp (°C)
P1	3-chloro-N-[1-[3-(6-(pyrimidin-2-ylmethoxy)pyridazin-3-yl)pyrazin-2-yl]ethyl]-5-(trifluoromethyl)benzamide		0.99	516/618	1	-
P2	3-chloro-N-[1-[3-(6-(cyclopropylmethoxy)pyridazin-3-yl)pyrazin-2-yl]ethyl]-5-(trifluoromethyl)benzamide		1.18	478/480	1	-
P3	3-chloro-N-[1-[3-(6-ethoxy)pyridazin-3-yl)pyrazin-2-yl]ethyl]-5-(trifluoromethyl)benzamide		1.11	452/454	1	-

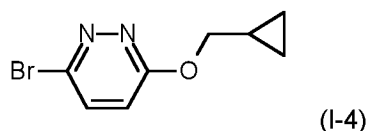
Entry	IUPAC name	Structure	RT (min)	[M+H] <sup>+</sup> (measured)	Method	mp (°C)
P4	3-chloro-N-[1-[3-[6-(2,2-difluoroethoxy)pyridazin-3-yl]pyrazin-2-yl]ethyl]-5-(trifluoromethyl)benzamide		1.10	488/490	1	-
P5	2-bromo-6-(1-cyanocyclopropyl)-N-[1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethyl]pyridine-4-carboxamide		0.98	480/482	1	193 - 195
P6	3-bromo-5-iodo-N-[1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethyl]benzamide		1.62	540.08	2	-
P7	3-(difluoromethoxy)-N-[1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethyl]-5-(trifluoromethyl)benzamide		1.54	470.26	2	-
P8	3,5-dibromo-N-[1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethyl]benzamide		1.58	492.10	2	-

Entry	IUPAC name	Structure	RT (min)	[M+H] <sup>+</sup> (measured)	Method	mp (°C)
P9	3-chloro-5-iodo-N-[1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethyl]benzamide		1.59	496.13	2	-
P10	3-chloro-N-[1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethyl]-5-(trifluoromethoxy)benzamide		1.63	454.20	2	-
P11	3-bromo-N-[1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethyl]-5-(trifluoromethyl)benzamide		1.61	482.18	2	-
P12	3-chloro-N-[1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethyl]-5-(trifluoromethyl)benzamide		1.05	438/440	1	190 - 192
P13	3-chloro-N-[1-[3-(6-hydroxypyridazin-3-yl)pyrazin-2-yl]ethyl]-5-(trifluoromethyl)benzamide		0.91	424/426	1	-

Entry	IUPAC name	Structure	RT (min)	[M+H] <sup>+</sup> (measured)	Method	mp (°C)
P14	3-chloro-N-[1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethyl]-N-methyl-5-(trifluoromethyl)benzamide		1.05	452/454	1	-
P15	3-chloro-N-[1-[3-(6-hydroxypyridazin-3-yl)pyrazin-2-yl]ethyl]-N-methyl-5-(trifluoromethyl)benzamide		0.87	438/440	1	-

## Preparation of intermediates

**Example PI-1:** Preparation of 3-bromo-6-(cyclopropylmethoxy)pyridazine (compound I-4)

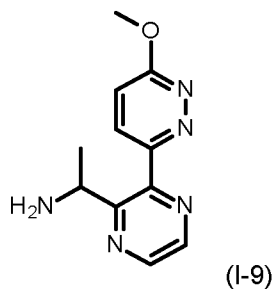


- 5 To a solution of cyclopropylmethanol (CAS 2516-33-8) (235.2 mg, 0.26 mL, 3.26 mmol) in 1,4-dioxane (13 mL) at 0-5°C was added sodium hydride (60 mass% in oil, 130.5 mg, 3.26 mmol) portionwise. The reaction mixture was stirred at 0-5°C for 5 minutes, then allowed to warm to room temperature, stirred at this temperature for 20 minutes before 3,6-dibromopyridazine (CAS 17973-86-3) (800 mg, 3.26 mmol) was added portionwise. The mixture was stirred at room temperature for 3 days, diluted with water and
- 10 the product extracted twice with EtOAc. The combined organic phases were washed with brine, dried over magnesium sulfate, filtered and concentrated under reduce pressure. The residue was purified by combiflash (gradient EtOAc in cyclohexane) to afford 3-bromo-6-(cyclopropylmethoxy)-pyridazine (I-4) as an off-white solid. LCMS (method 1): retention time 0.87 min, m/z 229/231 [M+H]<sup>+</sup>.  
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm 7.49 (d, 1H), 6.90 (d, 1H), 4.34 (d, 2H), 1.35 (m, 1H), 0.65 (m, 2H),
- 15 0.40 (m, 2H).

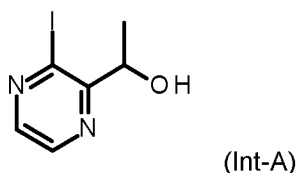
Similarly, intermediates I-1 (CAS 17321-29-8), I-2 (CAS 17321-30-1), I-3 and I-5 can be prepared from 3,6-dibromopyridazine by following in analogy above preparation Example PI-1.

- 20 **Example PI-2:** Preparation of 1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethanamine (compound I-9)



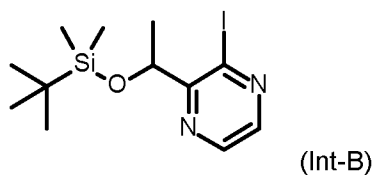


Step A: Preparation of 1-(3-iodopyrazin-2-yl)ethanol (Int-A)



- Under an argon atmosphere THF (35 mL) was cooled to 0°C. Then 2,2,6,6-tetramethylpiperidine (5.4 mL, 30.9 mmol, 1.34 equiv.) was added at 0°C followed by a dropwise addition of 2.5M n-BuLi (12 mL, 29.98 mmol, 1.3 equiv.). The reaction mixture was cooled to -78°C, then a solution of 2-iodopyrazine (5.0 g, 23.06 mmol, 1.0 equiv.) in THF (5 mL) was added dropwise. After stirring for 1 hour, acetaldehyde (12 mL, 210 mmol, 9.2 equiv.) was added dropwise at -78°C. After addition, the reaction mixture was allowed to warm up to room temperature before it was quenched with saturated aqueous ammonium chloride solution. The reaction mixture was diluted with water and a mixture of TBME and ethyl acetate. The aqueous layer was acidified with 1M HCl to pH 1-2. The phases were separated and the organic layer was washed with brine, dried over sodium sulfate, filtered and concentrated *in vacuo*. The crude extract was purified by flash chromatography (0-10% ethyl acetate in cyclohexane) to afford 1-(3-iodopyrazin-2-yl)ethanol.
- LCMS (method 1): retention time 0.54 min, m/z 251 [M+H]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm 8.47 (d, 1H), 8.31 (d, 1H), 5.10 (dd, 1H), 3.66-3.73 (m, 1H), 1.52 (d, 3H).

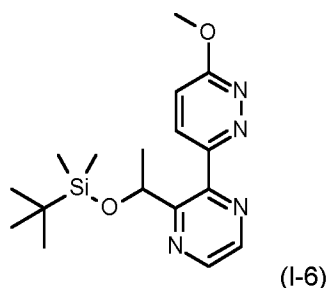
Step B: Preparation of tert-butyl-[1-(3-iodopyrazin-2-yl)ethoxy]-dimethyl-silane (Int-B)



- To a solution of 1-(3-iodopyrazin-2-yl)ethanol (Int-A) (1.20 g, 4.80 mmol, 1.0 equiv.) in THF (10 mL) was added imidazole (660 mg, 9.60 mmol, 2.0 equiv.) followed by tert-butyldimethylchlorosilane (1.1 mL, 5.76 mmol, 1.2 equiv.). The resulting reaction mixture was heated to 50°C and was stirred at this temperature for 2 hours before it was allowed to cool down to room temperature. The reaction mixture was filtered. The filtration cake was washed with TBME and the filtrate was concentrated *in vacuo*. The crude extract was purified by flash chromatography (0-3% ethyl acetate in cyclohexane) to afford tert-butyl-[1-(3-iodopyrazin-2-yl)ethoxy]-dimethyl-silane.

LCMS (method 1): retention time 1.30 min,  $m/z$  365  $[M+H]^+$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  ppm 8.52 (d, 1H), 8.24 (d, 1H), 5.31 (q, 1H), 1.51 (d, 3H), 0.88 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H).

Step C: Preparation of tert-butyl-[1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethoxy]-dimethyl-silane (compound I-6)

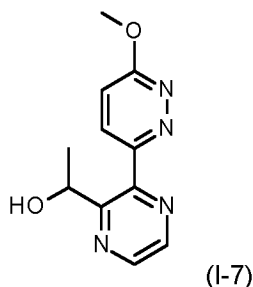


To a degassed solution of tert-butyl-[1-(3-iodopyrazin-2-yl)ethoxy]-dimethyl-silane (Int-B) (500 mg, 1.37 mmol) in THF (8.9 mL) under argon at 0°C was added isopropylmagnesium chloride (2.0M in THF, 0.89 mL, 1.78 mmol) dropwise. After aging for 30 minutes, zinc chloride (1.9M in 2-methyl-tetrahydrofuran, 0.72 mL, 1.37 mmol) was added dropwise at 0°C and the mixture stirred at 0°C for 40 minutes, then allowed to warm to room temperature. A degassed solution of 3-bromo-6-methoxy-pyridazine (I-1, CAS 17321-29-8) (311 mg, 1.65 mmol) in a mixture of THF (0.75 mL) and toluene (0.75 mL) was added at room temperature, followed by a degassed solution of (2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl) [2-(2'-amino-1,1'-biphenyl)]palladium(II) methanesulfonate (SPhos Pd G3, 52 mg, 0.065 mmol) in a mixture of THF (0.75 mL) and toluene (0.75 mL). The reaction mixture was stirred at 60°C overnight, cooled, quenched carefully with a saturated aqueous ammonium chloride solution, and diluted with water and EtOAc. The layers were separated and the aqueous phase extracted once with EtOAc, the combined organic layer washed with brine, dried over magnesium sulfate, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (gradient ethyl acetate in cyclohexane) to afford tert-butyl-[1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethoxy]-dimethyl-silane (I-6) as an oil.

LCMS (method 1): retention time 1.24 min,  $m/z$  347  $[M+H]^+$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  ppm 8.72 (d, 1H), 8.58 (d, 1H), 8.06 (d, 1H), 7.15 (d, 1H), 5.83 (q, 1H), 4.26 (s, 3H), 1.75 (d, 3H), 0.73 (s, 9H), -0.17 (s, 3H), -0.22 (s, 3H).

Similarly, intermediates I-10, I-14, I-18 and I-22 can be prepared from intermediate Int-B by following in analogy above preparation Example PI-2, step C.

Step D: Preparation of 1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethanol (compound I-7)



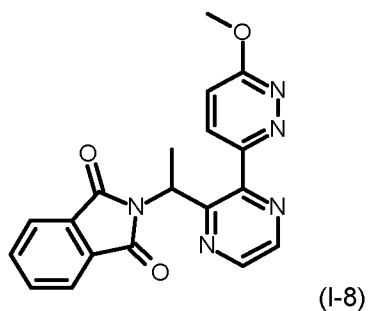
To a solution under argon of tert-butyl-[1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethoxy]-dimethylsilane (I-6) (548 mg, 1.58 mmol) in THF (15.8 mL) at 0°C was added tetrabutylammonium fluoride (1M solution in THF, 2.4 mL, 2.4 mmol). The reaction mixture was stirred at room temperature for 3 hours, then diluted with brine and ethyl acetate. The phases were separated and the aqueous layer basified with aqueous sodium hydrogen carbonate until pH 8 and extracted with ethyl acetate. The combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (ethyl acetate/ethanol in cyclohexane) to afford 1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethanol (I-7), as a white solid.

LCMS (method 1): retention time 0.60 min, m/z 233 [M+H]<sup>+</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm 8.66 (d, 1H), 8.62 (d, 1H), 8.28 (d, 1H), 7.20 (d, 1H), 5.42 (quin, 1H), 5.30 (d, 1H), 4.25 (s, 3H), 1.66 (d, 3H).

Similarly, intermediates I-11, I-15, I-19 and I-23 can be prepared in analogy by following above preparation Example PI-2, step D.

Step E: Preparation of 2-[1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethyl]isoindoline-1,3-dione (compound I-8)



To a solution under argon of 1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethanol (I-7) (330 mg, 1.42 mmol), phthalimide (232 mg, 1.56 mmol) and triphenylphosphine (452 mg, 1.71 mmol) in THF (4.3 mL) at 0°C was added diisopropyl azodicarboxylate (0.376 mL, 383 mg, 1.71 mmol). The reaction mixture was stirred at 0°C for 20 minutes, then at room temperature for 1.7 hours. The mixture was diluted with water and ethyl acetate, the layers were separated and the aqueous phase extracted once with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (gradient ethyl acetate in cyclohexane)

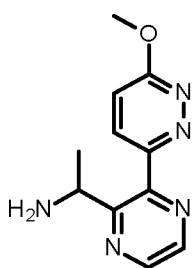
to afford 2-[1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethyl]isoindoline-1,3-dione (I-8), as a white solid. LCMS (method 1): retention time 0.86 min, m/z 362 [M+H]<sup>+</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm 8.60 (d, 1H), 8.57 (d, 1H), 8.09 (d, 1H), 7.79 (m, 2H), 7.69 (m, 2H), 7.08 (d, 1H), 6.60 (q, 1H), 4.24 (s, 3H), 2.07 (d, 3H).

5

Similarly, intermediates I-12, I-16, I-20 and I-24 can be prepared in analogy by following above preparation Example PI-2, step E.

Step F: Preparation of 1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethanamine (compound I-9)



(I-9)

10

To a suspension of 2-[1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethyl]isoindoline-1,3-dione (I-8) (420 mg, 1.16 mmol) in EtOH (11.6 mL) was added hydrazine monohydrate (0.068 mL, 1.40 mmol). The reaction mixture was heated at 80°C for 6 hours, then cooled to 20°C and diluted with EtOAc and water. The mixture was acidified with aqueous 2M HCl and the organic layer separated and discarded. The aqueous layer was basified with aqueous 4N NaOH and extracted once each with EtOAc, Me-THF and EtOAc/EtOH (4:1). The combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure to afford 1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethanamine (compound I-9) as light brown solid, which was used without further purification.

15

LCMS (method 1): retention time 0.27 min, m/z 232 [M+H]<sup>+</sup>.

20

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm 8.64 (d, 1H), 8.54 (d, 1H), 8.10 (d, 1H), 7.15 (d, 1H), 4.91 (br q, 1H), 4.24 (s, 3H), 2.22 (br s, 2H), 1.54 (d, 3H).

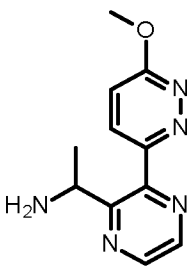
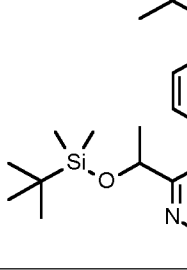
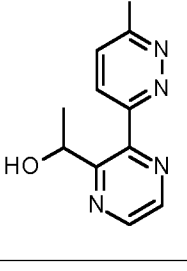
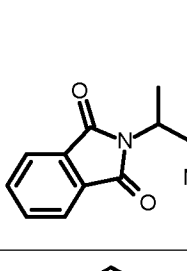
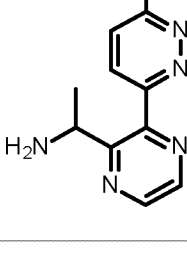
Similarly, intermediates I-13, I-17, I-21 and I-25 can be prepared in analogy by following above preparation Example PI-2, step F.

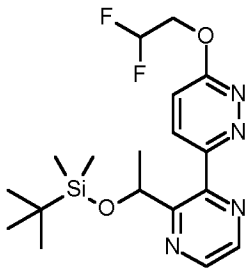
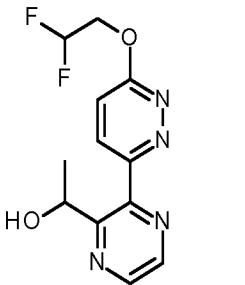
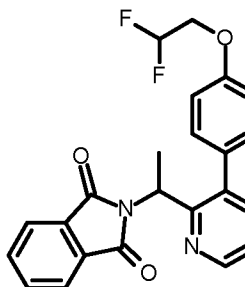
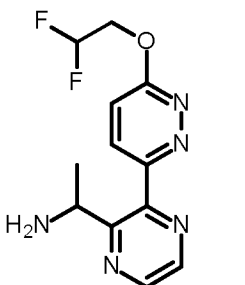
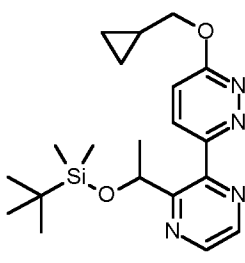
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Table PI: Examples of intermediates

Entry	IUPAC name	Structure	RT (min)	[M+H] <sup>+</sup> (measured)	Method	mp (°C)
I-1	3-bromo-6-methoxy-pyridazine		0.52	189/191	1	-

Entry	IUPAC name	Structure	RT (min)	[M+H] <sup>+</sup> (measured)	Method	mp (°C)
I-2	3-bromo-6-ethoxy-pyridazine		0.74	203/205	1	-
I-3	3-bromo-6-(2,2-difluoroethoxy)pyridazine		0.75	239/241	1	-
I-4	3-bromo-6-(cyclopropylmethoxy)pyridazine		0.87	229/231	1	-
I-5	3-bromo-6-(pyrimidin-2-ylmethoxy)pyridazine		0.58	267/269	1	-
I-6	tert-butyl-[1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethoxy]-dimethyl-silane		1.24	347	1	-
I-7	1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethanol		0.60	233	1	-
I-8	2-[1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethyl]isoindoline-1,3-dione		0.86	362	1	-

Entry	IUPAC name	Structure	RT (min)	[M+H] <sup>+</sup> (measured)	Method	mp (°C)
I-9	1-[3-(6-methoxypyridazin-3-yl)pyrazin-2-yl]ethanamine		0.27	232	1	-
I-10	tert-butyl-[1-[3-(6-ethoxypyridazin-3-yl)pyrazin-2-yl]ethoxy]-dimethyl-silane		1.24	361	1	-
I-11	1-[3-(6-ethoxypyridazin-3-yl)pyrazin-2-yl]ethanol		0.69	247	1	-
I-12	2-[1-[3-(6-ethoxypyridazin-3-yl)pyrazin-2-yl]ethyl]isoindoline-1,3-dione		0.94	376	1	-
I-13	1-[3-(6-ethoxypyridazin-3-yl)pyrazin-2-yl]ethanamine		0.53	246	1	-

Entry	IUPAC name	Structure	RT (min)	[M+H] <sup>+</sup> (measured)	Method	mp (°C)
I-14	tert-butyl-[1-[3-[6-(2,2-difluoroethoxy)pyridazin-3-yl]pyrazin-2-yl]ethoxy]-dimethyl-silane		1.20	397	1	-
I-15	1-[3-[6-(2,2-difluoroethoxy)pyridazin-3-yl]pyrazin-2-yl]ethanol		0.72	283	1	-
I-16	2-[1-[3-[6-(2,2-difluoroethoxy)pyridazin-3-yl]pyrazin-2-yl]ethyl]isoindoline-1,3-dione		0.94	412	1	-
I-17	1-[3-[6-(2,2-difluoroethoxy)pyridazin-3-yl]pyrazin-2-yl]ethanamine		0.52	282	1	-
I-18	tert-butyl-[1-[3-[6-(cyclopropylmethoxy)pyridazin-3-yl]pyrazin-2-yl]ethoxy]-dimethyl-silane		1.29	387	1	-

Entry	IUPAC name	Structure	RT (min)	[M+H] <sup>+</sup> (measured)	Method	mp (°C)
I-19	1-[3-[6-(cyclopropylmethoxy)pyridazin-3-yl]pyrazin-2-yl]ethanol		0.82	273	1	-
I-20	2-[1-[3-[6-(cyclopropylmethoxy)pyridazin-3-yl]pyrazin-2-yl]ethyl]isoindoline-1,3-dione		1.01	402	1	-
I-21	1-[3-[6-(cyclopropylmethoxy)pyridazin-3-yl]pyrazin-2-yl]ethanamine		0.58	272	1	-
I-22	tert-butyl-dimethyl-[1-[3-[6-(pyrimidin-2-ylmethoxy)pyridazin-3-yl]pyrazin-2-yl]ethoxy]silane		1.07	425	1	-
I-23	1-[3-[6-(pyrimidin-2-ylmethoxy)pyridazin-3-yl]pyrazin-2-yl]ethanol		0.59	311	1	-



Entry	IUPAC name	Structure	RT (min)	[M+H] <sup>+</sup> (measured)	Method	mp (°C)
I-24	2-[1-[3-[6-(pyrimidin-2-ylmethoxy)pyridazin-3-yl]pyrazin-2-yl]ethyl]isoindoline-1,3-dione		0.82	440	1	-
I-25	1-[3-[6-(pyrimidin-2-ylmethoxy)pyridazin-3-yl]pyrazin-2-yl]ethanamine		0.29	310	1	-

#### List of Abbreviations

	ACN	= acetonitrile
	Boc	= tert-butyloxycarbonyl
5	CPME	= cyclopentyl methyl ether (or methoxy cyclopentane)
	DCM	= dichloromethane
	DMF	= dimethylformamide
	DMSO	= dimethylsulfoxide
	DMSO- <i>d</i> <sub>6</sub>	= deuterated dimethylsulfoxide
10	EtOAc	= ethyl acetate
	EtOH	= ethanol
	HCl	= hydrochloric acid
	Me-THF	= 2-methyltetrahydrofuran
	MeOH	= methanol
15	n-BuLi	= n-butyllithium
	NaHCO <sub>3</sub>	= sodium hydrogen carbonate
	NaOH	= sodium hydroxide
	PdCl <sub>2</sub> dppf	= 1,1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloride
	TBME	= methyl tertiary-butyl ether
20	THF	= tetrahydrofuran
	XPhos	= 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl
	aq.	= aqueous

°C = degrees Celsius

equiv. = equivalent

h = hour(s)

LCMS = Liquid Chromatography Mass Spectrometry (description of the apparatus and the methods used for LCMS analysis are given above)

M = molar

MHz = megahertz

min = minutes

mp = melting point

ppm = parts per million

RT = room temperature

R<sub>t</sub> = retention time

RBF = round-bottom flask

## 15 **Biological examples**

The Examples which follow serve to illustrate the invention. Certain compounds of the invention can be distinguished from known compounds by virtue of greater efficacy at low application rates, which can be verified by the person skilled in the art using the experimental procedures outlined in the Examples, using lower application rates if necessary, for example 50 ppm, 24 ppm, 12.5 ppm, 6 ppm, 3 ppm, 1.5 ppm, 0.8 ppm or 0.2 ppm.

### Example B1: Activity against *Chilo suppressalis* (Striped rice stemborer)

24-well microtiter plates with artificial diet were treated with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions by pipetting. After drying, the plates were infested with L2 larvae (6-8 per well). The samples were assessed for mortality, anti-feeding effect, and growth inhibition in comparison to untreated samples 6 days after infestation. Control of *Chilo suppressalis* by a test sample is given when at least one of the categories mortality, anti-feedant effect, and growth inhibition is higher than the untreated sample.

The following compounds resulted in at least 80% control in at least one of the three categories (mortality, anti-feedant effect, or growth inhibition) at an application rate of 200 ppm: P1, P2, P3, P6, P7, P8, P9, P10, P11, P12, P13, P14, P15.

### Example B2: Activity against *Diabrotica balteata* (Corn root worm)

Maize sprouts placed onto an agar layer in 24-well microtiter plates were treated with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions by spraying. After drying, the plates were infested with L2 larvae (6 to 10 per well). The samples were assessed for mortality and growth inhibition in comparison to untreated samples 4 days after infestation.

The following compounds gave an effect of at least 80% control in at least one of the two categories (mortality or growth inhibition) at an application rate of 200 ppm: P1, P2, P3, P6, P7, P8, P9, P10, P11, P12, P13, P14, P15.

5 Example B3: Activity against *Frankliniella occidentalis* (Western flower thrips). Feeding/contact activity  
Sunflower leaf discs were placed on agar in 24-well microtiter plates and sprayed with aqueous test solutions prepared from 10'000 DMSO stock solutions. After drying the leaf discs were infested with a *Frankliniella* population of mixed ages. The samples were assessed for mortality 7 days after infestation. The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: P13.

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Example B4: Activity against *Myzus persicae* (Green peach aphid). Feeding/Contact activity  
Sunflower leaf discs were placed onto agar in a 24-well microtiter plate and sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying, the leaf discs were infested with an aphid population of mixed ages. The samples were assessed for mortality 6 days after

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infestation.  
The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: P6, P8, P9, P13, P14, P15.

Example B5: Activity against *Myzus persicae* (Green peach aphid). Intrinsic activity

20 Test compounds prepared from 10'000 ppm DMSO stock solutions were applied by pipette into 24-well microtiter plates and mixed with sucrose solution. The plates were closed with a stretched Parafilm. A plastic stencil with 24 holes was placed onto the plate and infested pea seedlings were placed directly on the Parafilm. The infested plate was closed with a gel blotting paper and another plastic stencil and then turned upside down. The samples were assessed for mortality 5 days after infestation.

25 The following compounds resulted in at least 80% mortality at a test rate of 12 ppm: P1, P6, P7, P8, P13, P14, P15.

Example B6: Activity against *Plutella xylostella* (Diamond back moth)

30 24-well microtiter plates with artificial diet were treated with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions by pipetting. After drying, *Plutella* eggs were pipetted through a plastic stencil onto a gel blotting paper and the plate was closed with it. The samples were assessed for mortality and growth inhibition in comparison to untreated samples 8 days after infestation.

The following compounds gave an effect of at least 80% control in at least one of the two categories (mortality or growth inhibition) at an application rate of 200 ppm: P1, P3, P4, P6, P7, P8, P9, P10, P11,

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P12, P13, P14, P15.

Example B7: Activity against *Spodoptera littoralis* (Egyptian cotton leaf worm)

Cotton leaf discs were placed onto agar in 24-well microtiter plates and sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying the leaf discs were infested

with five L1 larvae. The samples were assessed for mortality, anti-feeding effect, and growth inhibition in comparison to untreated samples 3 days after infestation. Control of *Spodoptera littoralis* by a test sample is given when at least one of the categories mortality, anti-feedant effect, and growth inhibition is higher than the untreated sample.

- 5 The following compounds resulted in at least 80% control in at least one of the three categories (mortality, anti-feedant effect, or growth inhibition) at an application rate of 200 ppm: P1, P2, P3, P6, P7, P8, P9, P10, P11, P12, P13, P14, P15.

Example B8: Activity against *Pseudoplusia includens* (Soybean looper). Larvicide, feeding/contact

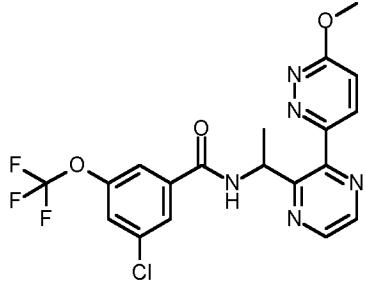
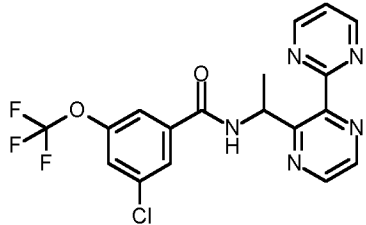
- 10 Soybean plants were treated in a spray chamber, cut off and placed into petri dishes containing wet filter paper. 1d after application leaves were infested with 5 L2 larvae and covered with a fabric filter and plastic lids. 5 days after infestation the samples were assessed for mortality and growth inhibition. The following compounds gave an effect of at least 80% in at least one of the two categories (mortality or growth inhibition) at an application rate of 50 ppm: P12.

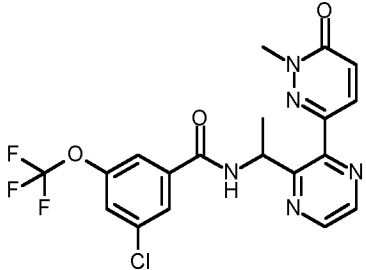
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Example B9: Comparison of the insecticidal activity of compound P10 with structurally comparable compounds from the state of the art

- Table B9 shows the activity of compound P10 (Table P) according to the preparatory examples, and of structurally similar compounds from WO2020/070049 and WO2023/072849, against *Spodoptera littoralis* (Example B7 above), *Plutella xylostella* (Example B6 above) and *Chilo suppressalis* (Example B1 above). The tests were performed as described in Examples B7, B6 and B1 above.

Table B9:

Compound	Concentration (ppm)	Insect	Mortality (%)
<u>Compound P10 (present application)</u>			
	3.12	<i>Spodoptera littoralis</i>	80
	12.5	<i>Plutella xylostella</i>	100
	3.12	<i>Chilo suppressalis</i>	80
<u>Compound P16 in WO20/070049</u>			
	3.12	<i>Spodoptera littoralis</i>	0
	12.5	<i>Plutella xylostella</i>	0
	3.12	<i>Chilo suppressalis</i>	0
<u>Comparative</u>			

Compound	Concentration (ppm)	Insect	Mortality (%)
Compound P11 in WO23/072849			
	3.12	<i>Spodoptera littoralis</i>	0
	12.5	<i>Plutella xylostella</i>	50
	3.12	<i>Chilo suppressalis</i>	0
Comparative			

This shows that compound P10 has a substantially better insecticidal action against *Spodoptera littoralis*, *Plutella xylostella* and *Chilo suppressalis*, than some compounds from the state of the art. This enhanced effect could not be expected in view of the structural similarity of these compounds.

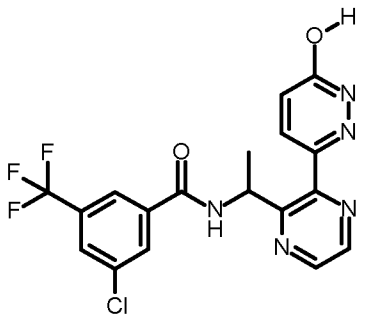
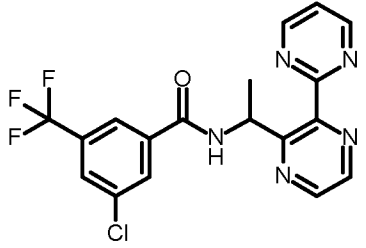
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Example B10: Comparison of the insecticidal activity of compound P13 according to the invention with structurally most closely comparable compounds from the state of the art:

Table B10 shows the activity of compound P13 (Table P) according to the preparatory examples, and of structurally similar compounds from WO2020/070049 and WO2023/072849, against *Spodoptera littoralis* (Example B7 above), *Plutella xylostella* (Example B6 above) and *Chilo suppressalis* (Example B1 above). The tests were performed as described in Examples B7, B6 and B1 above.

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Table B10:

Compound	Concentration (ppm)	Insect	Mortality (%)
Compound P13 (present application)			
	50	<i>Spodoptera littoralis</i>	100
	12.5	<i>Plutella xylostella</i>	80
	12.5	<i>Chilo suppressalis</i>	100
Compound P21 in WO20/070049			
	50	<i>Spodoptera littoralis</i>	80
	12.5	<i>Plutella xylostella</i>	0
	12.5	<i>Chilo suppressalis</i>	0
Comparative			

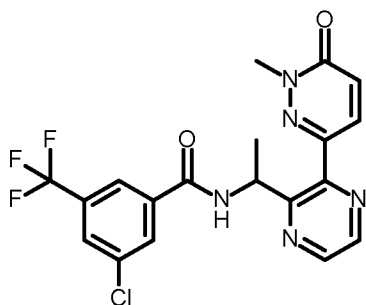
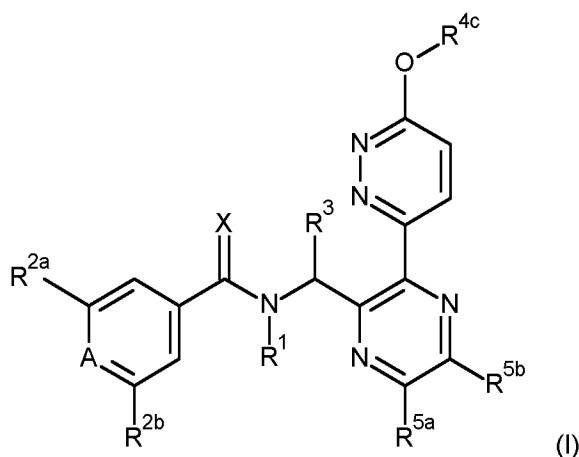
Compound	Concentration (ppm)	Insect	Mortality (%)
Compound P7 in WO23/072849			
	50	<i>Spodoptera littoralis</i>	100
	12.5	<i>Plutella xylostella</i>	0
	12.5	<i>Chilo suppressalis</i>	80
Comparative			

Table B10 shows that compound P13 has a moderately to substantially better insecticidal action against *Spodoptera littoralis*, *Plutella xylostella* and *Chilo suppressalis*, than some compounds from the state of the art. This enhanced effect could not to be expected in view of the structural similarity of these compounds.

## CLAIMS

1. A compound of the formula (I)



- 5 wherein:

A is N or CR<sup>Y</sup>;

- R<sup>1</sup> is hydrogen, C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>cyanoalkyl, aminocarbonylC<sub>1</sub>-C<sub>6</sub>alkyl, hydroxycarbonylC<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>nitroalkyl, trimethylsilaneC<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy-C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>haloalkyl, C<sub>2</sub>-C<sub>6</sub>alkenyl, C<sub>2</sub>-C<sub>6</sub>haloalkenyl, C<sub>2</sub>-C<sub>6</sub>alkynyl, C<sub>2</sub>-C<sub>6</sub>haloalkynyl, C<sub>3</sub>-C<sub>4</sub>cycloalkyl-C<sub>1</sub>-C<sub>2</sub>alkyl, C<sub>3</sub>-C<sub>4</sub>cycloalkyl-C<sub>1</sub>-C<sub>2</sub>alkyl wherein the C<sub>3</sub>-C<sub>4</sub>cycloalkyl group is substituted with 1 or 2 halogen atoms, oxetan-3-yl-CH<sub>2</sub>-, C<sub>1</sub>-C<sub>6</sub>alkylcarbonyl, C<sub>1</sub>-C<sub>6</sub>alkoxycarbonyl, phenyloxycarbonyl, benzyloxycarbonyl, benzyl, or benzyl substituted with 1 to 3 substituents independently selected from halogen, C<sub>1</sub>-C<sub>6</sub>alkoxy and C<sub>1</sub>-C<sub>6</sub>haloalkyl;

- R<sup>2a</sup> and R<sup>2b</sup> are independently selected from hydrogen, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>haloalkylsulfanyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, C<sub>1</sub>-C<sub>3</sub>haloalkoxy, halogen, NO<sub>2</sub>, SF<sub>5</sub>, CN, C(O)NH<sub>2</sub>, C(O)OH, C(S)NH<sub>2</sub>, C<sub>3</sub>-C<sub>6</sub>cycloalkyl, C<sub>3</sub>-C<sub>6</sub>cycloalkyl substituted with one to three substituents independently selected from R<sup>X</sup>; C<sub>3</sub>-C<sub>6</sub>cycloalkylcarbonyl, phenyl, phenyl substituted with one to three substituents independently selected from R<sup>X</sup>; heteroaryl, heteroaryl substituted with one to three substituents independently selected from R<sup>X</sup>; OR<sup>6</sup>, piperidin-2-one-1-yl, piperidin-2-one-1-yl substituted with one to two substituents independently selected from R<sup>X</sup>; pyridin-2-one-1-yl, pyridin-2-one-1-yl substituted with one to two substituents independently selected from R<sup>X</sup>; azetidin-1-yl, azetidin-1-yl substituted with one to two substituents independently selected from R<sup>X</sup>; pyrrolidin-1-yl, pyrrolidin-1-yl substituted with one to two substituents independently selected from R<sup>X</sup>; C<sub>3</sub>-C<sub>6</sub>cycloalkyl-C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>3</sub>-C<sub>6</sub>cycloalkyl-C<sub>1</sub>-C<sub>4</sub>alkyl substituted with one to two substituents independently selected from R<sup>Z</sup>; C<sub>3</sub>-C<sub>6</sub>cycloalkyl-C<sub>1</sub>-C<sub>3</sub>alkoxy, C<sub>3</sub>-C<sub>6</sub>cycloalkyl-C<sub>1</sub>-C<sub>3</sub>alkoxy substituted with one to two substituents independently selected from R<sup>X</sup>; C<sub>1</sub>-C<sub>5</sub>cyanoalkyl, C<sub>1</sub>-C<sub>5</sub>cyanoalkoxy, C<sub>1</sub>-C<sub>4</sub>alkylsulfanyl, C<sub>1</sub>-C<sub>4</sub>alkylsulfanyl substituted with one to three substituents independently selected from R<sup>X</sup>; C<sub>1</sub>-C<sub>4</sub>alkylsulfonyl, C<sub>1</sub>-C<sub>4</sub>alkylsulfonyl substituted with one to three substituents independently selected from R<sup>X</sup>; C<sub>1</sub>-C<sub>4</sub>alkylsulfinyl, and C<sub>1</sub>-C<sub>4</sub>alkylsulfinyl substituted with one to three substituents independently selected from R<sup>X</sup>;

- R<sup>3</sup> is C<sub>1</sub>-C<sub>3</sub>alkyl or C<sub>1</sub>-C<sub>3</sub>haloalkyl;

R<sup>4c</sup> is hydrogen, C<sub>1</sub>-C<sub>3</sub>alkyl optionally substituted with a single substituent selected from cyano, C<sub>1</sub>-C<sub>3</sub>alkylsulfanyl, C<sub>1</sub>-C<sub>3</sub>alkylsulfinyl, C<sub>1</sub>-C<sub>3</sub>alkylsulfonyl, and -C(O)NR<sup>4d</sup>R<sup>4e</sup>; C<sub>1</sub>-C<sub>3</sub>haloalkyl, allyl, propargyl, C<sub>3</sub>-C<sub>6</sub>cycloalkylC<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>2</sub>alkoxyC<sub>1</sub>-C<sub>3</sub>alkyl, -C(O)NR<sup>4d</sup>R<sup>4e</sup>, -N=CR<sup>4f</sup>R<sup>4g</sup>, or benzyl optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, and C<sub>3</sub>-C<sub>4</sub>cycloalkyl; or

R<sup>4c</sup> is heteroaryl-methyl, where said heteroaryl group is optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, and C<sub>3</sub>-C<sub>4</sub>cycloalkyl; or

R<sup>4c</sup> is -C(O)C<sub>1</sub>-C<sub>6</sub>alkyl, or -C(O)OC<sub>1</sub>-C<sub>6</sub>alkyl, each optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, and C<sub>1</sub>-C<sub>3</sub>alkoxy;

R<sup>4d</sup> and R<sup>4e</sup> are independently hydrogen, or C<sub>1</sub>-C<sub>5</sub>alkyl optionally substituted with 1 to 3 substituents independently selected from halogen, cyano, and C<sub>1</sub>-C<sub>3</sub>alkoxy;

R<sup>4f</sup> and R<sup>4g</sup> are independently C<sub>1</sub>-C<sub>3</sub>alkyl, or R<sup>4f</sup> and R<sup>4g</sup> form, together with the carbon atom they are attached to, a C<sub>4</sub>-C<sub>6</sub>cycloalkyl or a 4- to 6-membered saturated heterocycle containing one oxygen atom;

R<sup>5a</sup> and R<sup>5b</sup> are, independently of each other, selected from hydrogen, halogen, -CN, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>3</sub>-C<sub>4</sub>cycloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, and C<sub>1</sub>-C<sub>3</sub>haloalkoxy;

R<sup>6</sup> is phenyl, benzyl, heteroaryl, or C<sub>3</sub>-C<sub>6</sub>cycloalkyl; or

R<sup>6</sup> is phenyl, benzyl, heteroaryl, or C<sub>3</sub>-C<sub>6</sub>cycloalkyl, each of which, independently of each other, is substituted with one to three substituents independently selected from R<sup>X</sup>;

R<sup>X</sup> is independently selected from halogen, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, C<sub>1</sub>-C<sub>3</sub>haloalkoxy, NO<sub>2</sub>, SF<sub>5</sub>, CN, -C(O)NH<sub>2</sub>, -C(S)NH<sub>2</sub>, C<sub>1</sub>-C<sub>4</sub>haloalkylsulfanyl, C<sub>1</sub>-C<sub>4</sub>haloalkylsulfinyl, C<sub>1</sub>-C<sub>4</sub>haloalkylsulfonyl, C<sub>1</sub>-C<sub>4</sub>alkylsulfanyl, C<sub>1</sub>-C<sub>4</sub>alkylsulfinyl and C<sub>1</sub>-C<sub>4</sub>alkylsulfonyl;

R<sup>Y</sup> is selected from hydrogen, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, hydroxy, C<sub>1</sub>-C<sub>3</sub>alkoxy, C<sub>1</sub>-C<sub>3</sub>haloalkoxy, halogen, -CN and cyclopropyl;

R<sup>Z</sup> is selected from oxo, halogen, C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>1</sub>-C<sub>3</sub>haloalkyl, C<sub>1</sub>-C<sub>3</sub>alkoxy, C<sub>1</sub>-C<sub>3</sub>haloalkoxy and CN;

X is O or S;

or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer, or N-oxide of the compound of formula (I).

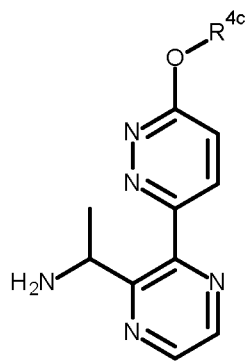
2. The compound according to claim 1, wherein X is oxygen.

3. The compound according to claim 1 or 2, wherein A is N or CH.

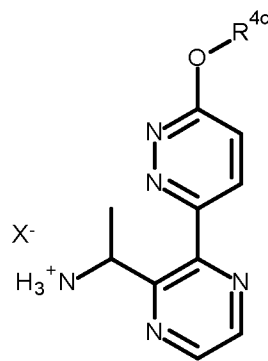
4. The compound according to any one of claims 1 to 3, wherein R<sup>1</sup> is hydrogen, methyl, propargyl or cyclopropyl-methyl.



5. The compound according to any one of claims 1 to 4, wherein R<sup>2a</sup> and R<sup>2b</sup> are independently selected from chlorine, bromine, iodine, trifluoromethyl, difluoromethoxy, trifluoromethoxy, and 1-cyanocyclopropyl
- 5 6. The compound according to any one of claims 1 to 5, wherein R<sup>3</sup> is methyl or trifluoromethyl.
7. The compound according to any one of claims 1 to 4, wherein R<sup>4c</sup> is hydrogen, methyl, ethyl, 2,2-difluoroethyl, cyclopropylmethyl, or pyrimidin-2-ylmethyl.
- 10 8. The compound according to any one of claims 1 to 4, wherein R<sup>5a</sup> and R<sup>5b</sup> are hydrogen.
9. A composition comprising a compound as defined in any one of claims 1 to 8, one or more auxiliaries and diluent, and optionally one or more other active ingredient.
- 15 10. A method of combating and controlling insects, acarines, nematodes or molluscs which comprises applying to a pest, to a locus of a pest, or to a plant susceptible to attack by a pest an insecticidally, acaricidally, nematocidally or molluscicidally effective amount of a compound as defined in any one of claims 1 to 8, or a composition as defined in claim 9.
- 20 11. A method for the protection of plant propagation material from the attack by insects, acarines, nematodes or molluscs, which comprises treating the propagation material or the site, where the propagation material is planted, with an effective amount of a compound as defined in any one of claims 1 to 8, or a composition as defined in claim 9.
- 25 12. A method of controlling parasites in or on an animal in need thereof comprising administering an effective amount of a compound as defined in any one of claims 1 to 8, or a composition as defined in claim 9.
13. A plant propagation material, such as a seed, comprising, or treated with or adhered thereto, a  
30 compound as defined in any one of claims 1 to 8, or a composition as defined in claim 9.
14. A compound of formula (III-1)(i), or (III-2)(i):



(III-1)(i)



(III-2)(i)

wherein R<sup>4c</sup> is as defined in claim 1 or 7; and X<sup>-</sup> is an anion.

# INTERNATIONAL SEARCH REPORT

International application No  
**PCT/EP2023/087084**

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> <b>INV. C07D403/04 C07D403/14 C07D401/14 A01N43/58 A01N43/60</b> <b>A01P7/02 A01P7/04</b> <b>ADD.</b> According to International Patent Classification (IPC) or to both national classification and IPC				
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) <b>C07D A01N A01P</b>  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) <b>EPO-Internal, CHEM ABS Data</b>				
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
<b>X</b>	<b>WO 2020/201079 A1 (SYNGENTA CROP PROTECTION AG [CH])</b> <b>8 October 2020 (2020-10-08)</b> <b>cited in the application</b>	<b>13</b>		
<b>A</b>	<b>page 119 to page 131, table P, examples P1 to P50</b> <b>page 168 to page 171, examples B1 to B13</b> <b>claims 1 and 13</b>  -----	<b>1-12,14</b>		
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <span style="margin-left: 200px;"><input checked="" type="checkbox"/> See patent family annex.</span>				
* Special categories of cited documents : <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;">           "A" document defining the general state of the art which is not considered to be of particular relevance            "E" earlier application or patent but published on or after the international filing date            "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)            "O" document referring to an oral disclosure, use, exhibition or other means            "P" document published prior to the international filing date but later than the priority date claimed         </td> <td style="width: 50%; border: none; vertical-align: top;">           "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            "&amp;" document member of the same patent family         </td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family			
Date of the actual completion of the international search	Date of mailing of the international search report			
<b>13 March 2024</b>	<b>27/03/2024</b>			
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  <b>Cortés Suárez, José</b>			

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2023/087084

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2020201079 A1	08-10-2020	AU 2020254918 A1	30-09-2021
		CA 3130640 A1	08-10-2020
		CL 2021002519 A1	29-04-2022
		CN 113631549 A	09-11-2021
		CO 2021012549 A2	30-09-2021
		EP 3947358 A1	09-02-2022
		IL 286422 A	31-10-2021
		JP 2022526795 A	26-05-2022
		KR 20210146968 A	06-12-2021
		MA 55492 A	09-02-2022
		PE 20212328 A1	14-12-2021
		TW 202102489 A	16-01-2021
		US 2022185789 A1	16-06-2022
		UY 38623 A	30-10-2020
		WO 2020201079 A1	08-10-2020

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