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(71) Applicant: **SYNGENTA CROP PROTECTION AG** [CH/CH]; Rosentalstrasse 67, 4058 Basel (CH).

(72) Inventors: **SIKERVAR, Vikas**; Syngenta Biosciences Private Ltd Santa Monica Works, Corlim, Ilhas, Goa 403 110 (IN). **SEN, Indira**; Syngenta Biosciences Private Ltd Santa Monica Works, Corlim, Ilhas, Goa 403110 (IN). **EDMUNDS, Andrew**; Syngenta Crop Protection AG, Schaffhauserstrasse, 4332 Stein (CH). **EMERY, Daniel**; Syngenta Crop Protection AG, Schaffhauserstrasse, 4332 Stein (CH). **RENDLER, Sebastian**; Syngenta Crop Protection AG, Rosentalstrasse 67, 4058 Basel (CH). **STOLLER, André**; Syngenta Crop Protection AG, Schaffhauserstrasse, 4332 Stein (CH). **MUEHLEBACH, Michel**; Syngenta Crop Protection AG, Schaffhauserstrasse, 4332 Stein (CH). **BUCHHOLZ, Anke**; Syngenta Crop Protection AG, Schaffhauserstrasse, 4332 Stein (CH).

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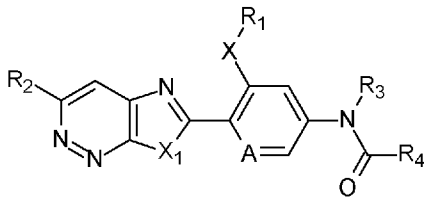
(54) Title: PESTICIDALLY ACTIVE HETEROCYCLIC DERIVATIVES WITH SULFUR CONTAINING SUBSTITUENTS



(I)

(57) Abstract: Compounds of the formula (I), wherein the subsitiuents are as defined in claim 1. Furthermore, the present invention relates to agrochemical compositions which comprise compounds of formula (I), to preparation of these compositions, and to the use of the compounds or compositions in agriculture or horticulture for combating, preventing or controlling animal pests, including arthropods and in particular insects, nematodes, molluscs or representatives of the order Acarina.

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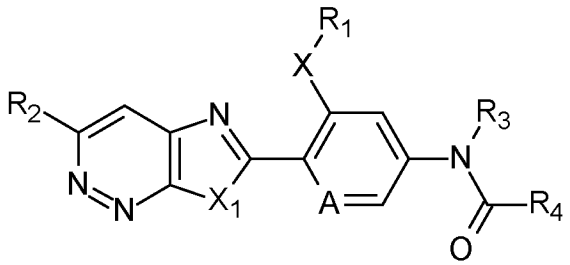
Pesticidally active heterocyclic derivatives with sulfur containing substituents

The present invention relates to pesticidally active, in particular insecticidally active heterocyclic derivatives containing sulfur substituents, to processes for their preparation, to compositions comprising those compounds, and to their use for controlling animal pests, including arthropods and in particular insects or representatives of the order *Acarina*.

Heterocyclic compounds with pesticidal action and with sulfur and cyclic or acyclic amide substitutents are known and described, for example, in WO2015121136, WO2016124557, WO2016104746, WO2014142292, WO2015002211, WO2014119672, WO2014119699, WO2014119494, WO2014119674, WO2014119679, WO2014119670, WO 2016030229, WO2016124563, WO2017055185, and WO2016039441.

It has now surprisingly been found that certain novel pesticidally active derivatives with sulfur and amide substitutents have favourable properties as pesticides.

The present invention therefore provides compounds of formula I,



(I),

wherein

A is CH or N;

X is S, SO or SO_2;

R_1 is C_1-C_4alkyl, C_1-C_4haloalkyl or C_3-C_6cycloalkyl-C_1-C_4alkyl;

R_2 is halogen, C_1-C_6haloalkyl, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl or C_1-C_6haloalkoxy;

R_3 is C_1-C_6alkyl, C_2-C_6alkenyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_1-C_6haloalkoxy, C_1-C_6cyanoalkyl, C_1-C_6hydroxyalkyl, C_1-C_6alkoxycarbonyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_4alkylthio-C_1-C_4alkyl, C_1-C_4alkylsulfinyl-C_1-C_4alkyl, C_1-C_4alkylsulfonyl-C_1-C_4alkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl, C_3-C_6halocycloalkyl-C_1-C_4alkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl substituted by a substituent selected from cyano, halogen, C_1-C_3haloalkyl, CO_2H, $CONH_2$, C_1-C_6alkylaminocarbonyl, C_1-C_6dialkylaminocarbonyl or C_1-C_4alkoxycarbonyl;

R_4 is C_1-C_6alkyl, C_2-C_6alkenyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_4alkylthio-C_1-C_4alkyl, C_1-C_4alkylsulfinyl-C_1-C_4alkyl, C_1-C_4alkylsulfonyl-C_1-C_4alkyl, C_3-C_6cycloalkyl-C_1-C_2alkyl, C_1-C_6cyanoalkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl which is mono- or poly-substituted by substituents independently selected from the group consisting of halogen, cyano, C_1-C_3haloalkyl, CO_2H, $CONH_2$, C_1-C_6alkylaminocarbonyl, C_1-C_6dialkylaminocarbonyl and C_1-C_4alkoxycarbonyl; or

R_4 is a four- to six-membered heterocyclic ring system which can be partially saturated or fully saturated, said ring system contains 1 to 2 ring heteroatoms selected from O, N, or S(O)n, wherein n is 0, 1 or 2, providing that the heterocyclic ring system does not contain adjacent ring oxygen atoms, adjacent ring sulphur atoms, or adjacent ring sulphur and ring oxygen atoms and that the ring nitrogen, when present, may be substituted by hydrogen or C_1-C_4 alkyl, and said ring system can be optionally mono- or di-substituted with substituents independently selected from the group consisting of halogen, cyano, C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4haloalkyl or oxo; or

R_3 and R_4 together with the -NC(O)- fragment to which they are attached form a 5- or 6-membered saturated heterocyclic ring system which may contain one or two additional ring heteroatoms selected from O, N, or S(O)n, wherein n is 0, 1 or 2, providing that the heterocyclic ring system does not contain adjacent ring oxygen atoms, adjacent ring sulphur atoms, or adjacent ring sulphur and ring oxygen atoms and that the additional ring nitrogen, when present, is substituted by hydrogen or C_1-C_4 alkyl, C_1-C_4alkoxy, or C_1-C_4haloalkoxy, and wherein the ring system can be optionally mono- or di-substituted with substituents independently selected from halogen, cyano, C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4haloalkyl or oxo;

X_1 is O, S or NR_5; wherein R_5 is hydrogen or C_1-C_4alkyl; or

agrochemically acceptable salts, stereoisomers, enantiomers, tautomers or N-oxides of the compounds of formula I.

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_1-C_4alkanecarboxylic 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_1-C_4alkane- 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.

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.

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

Where substituents are indicated as being itself further substituted, this means that they carry one or more identical or different substituents, e.g. one to four substituents. Normally not more than three such optional substituents are present at the same time. Preferably not more than two such substituents are present at the same time (i.e. the group is substituted by one or two of the substituents indicated). Where the additional substituent group is a larger group, such as cycloalkyl or phenyl, it is most preferred that only one such optional substituent is present. Where a group is indicated as being substituted, e.g. alkyl, this includes those groups that are part of other groups, e.g. the alkyl in alkylthio.

The term "C_1-$C_n$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 and is, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, pentyl, hexyl isohexyl and their branched isomers. For example, there also may be mentioned any one of the radicals 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2, 2-dimethylpropyl, 1-ethylpropyl, n-hexyl, n-pentyl, 1, 1-dimethylpropyl, 1, 2-dimethylpropyl, 1- methylpentyl, 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. Alkenyl radicals are derived from the alkyl radicals mentioned. The alkenyl groups can be mono- or polyunsaturated.

The term “C_2-Cn-alkenyl” as used herein refers to a straight-chain or branched unsaturated alkyl radical, for example, vinyl, allyl, homoallyl, but-1-eneyl, and but-2-eneyl. Where appropriate, the alkeneyl chains can be of either the (E)- or (Z)-configuration.

The term "C_1-$C_n$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. According a term "C_1-C_2-fluoroalkyl" would refer to a C_1-C_2-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 penta-fluoroethyl.

The term "C_1-$C_n$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 example, any one of methoxy, ethoxy, n-propoxy, 1-methylethoxy, n-butoxy, 1-methylpropoxy, 2-methylpropoxy or 1, 1-dimethylethoxy.

The term "C_1-$C_n$haloalkoxy" as used herein refers to a C_1-$C_n$alkoxy radical as mentioned above which is partially or fully substituted by fluorine, chlorine, bromine and/or iodine, i.e., for example, any one of chloromethoxy, dichloromethoxy, trichloromethoxy, fluoromethoxy, difluoromethoxy, trifluoromethoxy, chlorofluoromethoxy, dichlorofluoromethoxy, chlorodifluoromethoxy, 2-fluoroethoxy, 2-chloroethoxy, 2-bromoethoxy, 2-iodoethoxy, 2, 2-difluoroethoxy, 2,2, 2-trifluoroethoxy, 2-chloro-2-fluoroethoxy, 2-chloro-2, 2-difluoroethoxy, 2, 2-dichloro-2-fluoroethoxy, 2,2, 2-trichloroethoxy, pentafluoroeth- oxy, 2-fluoropropoxy, 3-fluoropropoxy, 2, 2-difluoropropoxy, 2, 3-difluoropropoxy, 2- chloropropoxy, 3-chloropropoxy, 2, 3-dichloropropoxy, 2-bromopropoxy, 3-bromopropoxy, 3,3, 3-trifluoropropoxy, 3,3, 3-trichloropropoxy, 2,2, 3,3, 3- pentafluoropropoxy, heptafluoropropoxy, 1- (fluoromethyl)-2-fluoroethoxy, 1- (chloromethyl)-2-chloroethoxy, 1-(bromomethyl)-2-bromoethoxy, 4-fluorobutoxy, 4- chlorobutoxy, or 4-bromobutoxy.

The term “C_1-C_n-alkylsulfanyl” or C_1-C_n-alkylthio 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 a sulfur atom, i.e., for example, any one of methylthio, ethylthio, n-propylthio, 1-methylethylthio, butylthio, 1-methylpropylthio, 2- methylpropylthio or 1, 1-dimethylethylthio.

The term "C_1-$C_n$alkylsulfinyl" 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* the sulfur atom of the sulfinyl group, i.e., for example, any one of methylsulfinyl, ethylsulfinyl, n-propylsulfinyl, 1-methylethyl-sulfinyl, n-butylsulfinyl, 1-methylpropylsulfinyl, 2-methylpropylsulfinyl, 1, 1-dimethyl-ethylsulfinyl, n-pentylsulfinyl, 1-methylbutylsulfinyl, 2-methylbutylsulfinyl, 3-methyl- butylsulfinyl, 1,

1-dimethylpropylsulfinyl, 1, 2-dimethylpropylsulfinyl, 2,2- dimethylpropylsulfinyl or 1-ethylpropylsulfinyl.

The term "C_1-$C_n$alkylsulfonyl" 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* the sulfur atom of the sulfonyl group, i.e., for example, any one of methylsulfonyl, ethylsulfonyl, n-propylsulfonyl, isopropylsulfonyl, n-butylsulfonyl, 1-methylpropylsulfonyl, 2-methylpropylsulfonyl or t-butylsulphonyl.

The term "C_1-$C_n$haloalkylsulfanyl" as used herein refers to a C_1-$C_n$alkylthio radical as mentioned above which is partially or fully substituted by fluorine, chlorine, bromine and/or iodine, i.e., for example, any one of fluoromethylthio, difluoromethylthio, trifluoromethylthio, chlorodifluoromethylthio, bromodifluoromethylthio, 2-fluoroethylthio, 2-chloroethylthio, 2-bromoethylthio, 2-iodoethylthio, 2, 2-difluoroethylthio, 2,2,2-trifluoroethylthio, 2,2, 2-trichloroethylthio, 2-chloro-2-fluoroethylthio, 2-chloro-2,2-difluoroethylthio, 2, 2-dichloro-2-fluoroethylthio, pentafluoroethylthio, 2-fluoropropylthio, 3-fluoropropylthio, 2-chloropropylthio, 3-chloropropylthio, 2-bromopropylthio, 3-bromopropylthio, 2,2-difluoropropylthio, 2,3-difluoropropylthio, 2, 3-dichloropropylthio, 3,3, 3- trifluoropropylthio, 3,3, 3-trichloropropylthio, 2,2, 3,3, 3-pentafluoropropylthio, heptafluoropropylthio, 1- (fluoromethyl)-2-fluoroethylthio, 1- (chloromethyl)-2-chloroethylthio, 1- (bromomethyl)-2-bromoethylthio, 4-fluorobutylthio, 4-chlorobutylthio, or 4- bromobutylthio.

The term "C_1-$C_n$haloalkylsulfinyl" and "C_1-$C_n$haloalkylsulfonyl" refers to the groups above but with the sulfur in oxidations state 1 or 2 respectively.

The term "C_1-$C_n$alkoxycarbonyl" as used herein refers to a straight chain or branched alkoxy radical having 1 to n carbon atoms (as mentioned above) which is attached via the carbon atom of the carbonyl group, i.e., for , any one of methoxycarbonyl, ethoxycarbonyl, n-propoxycarbonyl, 1-methylethoxycarbonyl, n-butoxycarbonyl, 1-methylpropoxycarbonyl, 2-methylpropoxycarbonyl or 1, 1-dimethylethoxycarbonyl.

The term "C_1-C_n-alkylaminocarbonyl" as used herein refers to a straight chain or branched saturated alkyl radical having 1 to n carbon atoms (as mentioned above) amino chain which is attached via a carbonyl group, for example, N-methylformamide, N-ethylformamaide, N-propylformamaide, N-butylformamide, and N-sec-butylformamide.

The term "C_1-C_n-dialkylaminocarbonyl" as used herein refers to two straight chain or branched saturated alkyl radicals having 1 to n carbon atoms (as mentioned above) amino chains which are attached via a carbonyl group, for example, N,N-dimethylformamide, N-ethyl-N-methyl-formamide,

N-isopropyl-N-methyl-formamide, N-ethyl-N-propyl-formamide, N-ethyl-N-isopropyl-formamide, and N-isobutyl-N-methyl-formamide

The term "C_1-$C_n$cyanoalkyl" as used herein refers to a straight chain or branched saturated alkyl radicals having 1 to n carbon atoms (as mentioned above) which is substituted by a cyano group, for example cyanomethylene, cyanoethylene, 1,1-dimethylcyanomethyl, cyanomethyl, cyanoethyl, and 1-dimethylcyanomethyl.

The term "C_3-C_6cycloalkyl" as used herein refers to 3-6 membered cycloylkyl groups such as cyclopropane, cyclobutane, cyclopropane, cyclopentane and cyclohexane.

The term "C_3-C_6halocycloalkyl" as used herein refers to 3-6 membered cycloalkyl group (as mentioned above) which is substituted by at least one halogen atom.

The prefix "-C_1-$C_n$alkyl" (as used, for example, in terms such as "C_1-$C_n$alkoxy-C_1-$C_n$alkyl"), 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) which is substituted by a C_1-$C_n$alkoxy, C_1-$C_n$alkylthio, C_1-$C_n$alkylsulfinyl, C_1-$C_n$alkylsulfonyl, C_3-C_6cycloalkyl, or C_3-C_6halocycloalkyl radical. Examples include methoxymethyl, methoxyethyl, 1-methylmethoxylmethyl CH_2SCH_3, $CH_2SO_2CH_3$, $CH_2CH_2SCH_3$, $CH_2CH_2SOCH_3$, $CH_2CH_2SO_2CH_3$, CH_2OCH_3, $CH_2CH_2OCH_3$, or $C(CH_3)_2OCH_3$.

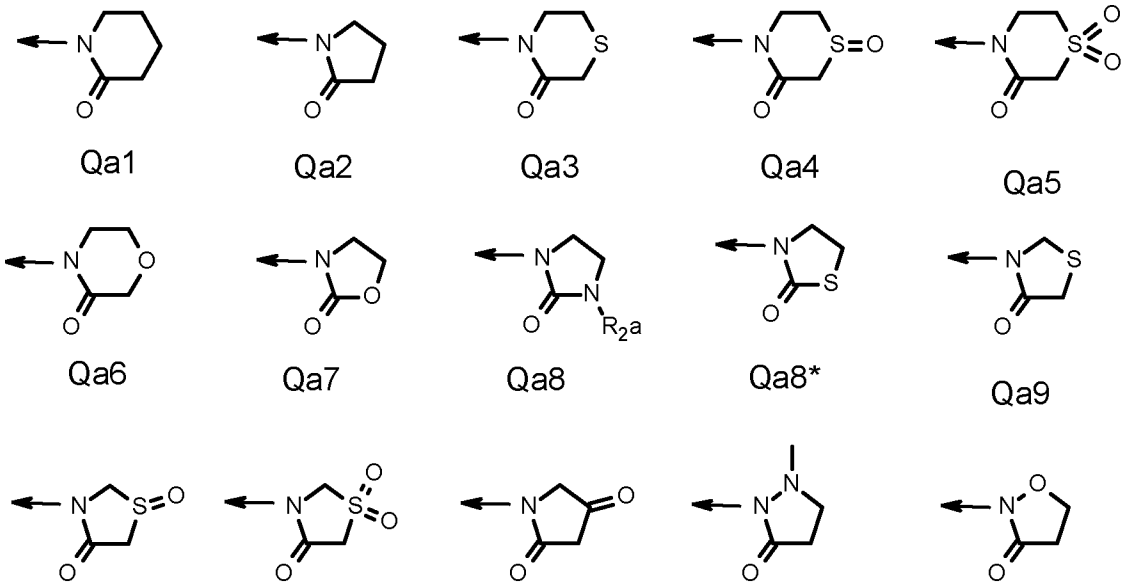
Halogen is generally fluorine, chlorine, bromine or iodine. This also applies, correspondingly, to halogen in combination with other meanings, such as haloalkyl.

The term "four- to six-membered heterocyclic ring system which can be partially saturated or fully saturated, said ring system contains 1 to 2 ring heteroatoms selected from O, N, or S(O)n, wherein n is 0, 1 or 2, providing that the heterocyclic ring system does not contain adjacent ring oxygen atoms, adjacent ring sulphur atoms, or adjacent ring sulphur and ring oxygen atoms and that the ring nitrogen, when present, may be substituted by hydrogen or C_1-C_4 alkyl, and said ring system can be optionally mono- or di-substituted with substituents independently selected from the group consisting of halogen, cyano, C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4haloalkyl or oxo" as used herein, are exemplified for example by azetidiyl, pyrrolidinyl, pyrazolinyl, imidazolinyl, pyrrolinyl, pyrazolinyl, imidazol inyl, tetrahydrofuranyl, dihydrofuranyl, 1,3-dioxolanyl, dioxolenyl, thiolanyl, dihydrothienyl, oxazolidinyl, isoxazol idinyl, oxazolinyl, isoxazolinyl, thiazol inyl, isothiazolinyl, thiazolidinyl, isothiazolidinyl, oxathiolanyl, piperidinyl, piperazinyl, pyranyl, dihydropyranyl, tetrahydropyranyl, dioxanyl, thiopyranyl, dihydrothiopyranyl, tetrahydrothiopyranyl, morpholinyl, thiazinyl and the like.

The term "R_3 and R_4 together with the -NC(O)- fragment to which they are attached form a 5- or 6-membered saturated heterocyclic ring system which may contain one or two additional ring

heteroatoms selected from O, N, or S(O)n, wherein n is 0, 1 or 2, providing that the heterocyclic ring system does not contain adjacent ring oxygen atoms, adjacent ring sulphur atoms, or adjacent ring sulphur and ring oxygen atoms and that the additional ring nitrogen, when present, is substituted by hydrogen or C_1-C_4 alkyl, C_1-C_4alkoxy, or C_1-C_4haloalkoxy, and wherein the ring system can be optionally mono- or di-substituted with substituents independently selected from halogen, cyano, C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4haloalkyl or oxo" as used herein, is best described by the phenyl or pyridyl group being substituted by a substituent Qa, wherein Qa is for example:

Qa is a radical of Qa1 to Qa15



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where the arrow shows the attachment point to the phenyl or pyridyl ring, and wherein each ring system can be mono- or poly-substituted by substituents independently selected from the group consisting of halogen, cyano, C_1-C_4alkyl, C_1-C_4alkoxy, and C_1-C_4haloalkyl; wherein R_{2a} is hydrogen, C_1-C_4alkyl, C_1-C_4alkoxy, and C_1-C_4haloalkoxy.

Preferred values of A, X, R_1, R_2, R_3, R_4, and X_1 are, in any combination thereof, as set out below:

Preferably A is N.

Preferably X is S or SO_2.

Most preferably X is SO_2.

Preferably R_1 is ethyl or cyclopropylmethyl.

Most preferably R_1 is ethyl.

Preferably R_2 is C_1-C_4haloalkyl, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl or C_1-C_4haloalkylsulfonyl.

More preferably R_2 is C_1-C_4haloalkyl.

Most preferably R_2 is trifluoromethyl.

Preferably R_3 is C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl mono-substituted by cyano.

More preferably R_3 is methyl, ethyl, isopropyl, 2,2,2-trifluoroethyl, methoxy, cyclopropyl or 1-cyanocyclopropyl.

Most preferably R_3 is methyl, ethyl, cyclopropyl or 1-cyanocyclopropyl.

Preferably R_4 is C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_4alkylthio-C_1-C_4alkyl, C_1-C_4alkylsulfinyl-C_1-C_4alkyl, C_1-C_4alkylsulfonyl-C_1-C_4alkyl, C_1-C_6cyanoalkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl mono-substituted by cyano.

More preferably R_4 is methyl, ethyl, isopropyl, t-butyl, trifluoromethyl, difluoromethyl, fluoromethyl, chloromethyl, 2,2,2-trifluoroethyl, 1-hydroxy-1-methyl-ethyl, methoxymethyl, methoxyethyl, methylsulfanylmethyl, methylsulfonylmethyl, 2-methylsulfanylethyl, 2-methylsulfonylethyl, 1-cyano-1-methyl-ethyl, cyclopropyl or 1-cyanocyclopropyl.

Most preferably R_4 is methyl, ethyl, 2,2,2-trifluoroethyl, methoxymethyl, 1-cyano-1-methyl-ethyl, cyclopropyl or 1-cyanocyclopropyl.

Preferably X_1 is NR_5; wherein R_5 is C_1-C_4alkyl.

Most preferably X_1 is N-CH_3.

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

Embodiment 1 provides compounds of formula I, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, as defined above.

Embodiment 2 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiment 1 wherein R_4 is C_1-C_6alkyl, C_2-C_6alkenyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_4alkylthio-C_1-C_4alkyl, C_1-C_4alkylsulfinyl-C_1-C_4alkyl, C_1-C_4alkylsulfonyl-C_1-C_4alkyl, C_3-C_6cycloalkyl-C_1-C_2alkyl, C_1-C_6cyanoalkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl which is mono- or poly-substituted by substituents independently selected from the group consisting of halogen, cyano, C_1-C_3haloalkyl, CO_2H, $CONH_2$, C_1-C_6alkylaminocarbonyl, C_1-C_6dialkylaminocarbonyl and C_1-C_4alkoxycarbonyl.

Embodiment 3 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to any one of embodiments 1 or 2 wherein R_1 is ethyl or cyclopropylmethyl.

Embodiment 4 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to any one of embodiments 1, 2 or 3 wherein R_2 is C_1-C_4haloalkyl, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl or C_1-C_4haloalkylsulfonyl.

Embodiment 5 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to any one of embodiments 1, 2, 3 or 4 wherein R_3 is C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl mono-substituted by cyano.

Embodiment 6 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to any one of embodiments 1, 2, 3, 4 or 5 wherein R_4 is C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_4alkylthio-C_1-C_4alkyl, C_1-C_4alkylsulfinyl-C_1-C_4alkyl, C_1-C_4alkylsulfonyl-C_1-C_4alkyl, C_1-C_6cyanoalkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl mono-substituted by cyano.

Embodiment 7 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to any one of embodiments 1, 2, 3, 4, 5 or 6 wherein X_1 is NR_5, wherein R_5 is C_1-C_4alkyl.

Embodiment 8 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to any one of embodiments 1, 2, 3, 4, 5, 6 or 7 wherein X is S or SO_2.

Embodiment 9 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to any one of embodiments 1, 2, 3, 4, 5, 6, 7 or 8 wherein R_1 is ethyl.

Embodiment 10 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to any one of embodiments 1, 2, 3, 4, 5, 6, 7, 8 or 9 wherein R_2 is C_1-C_4haloalkyl.

Embodiment 11 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to any one of embodiments 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10 wherein X_1 is N-CH_3.

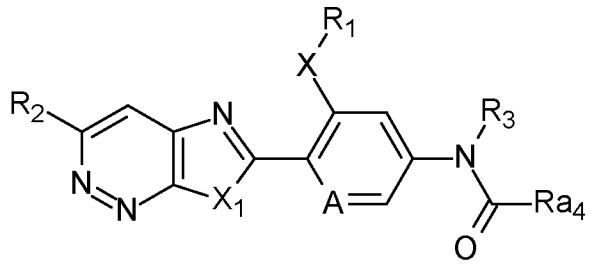
Embodiment 12 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to any one of embodiments 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or 11 wherein R_2 is trifluoromethyl.

Embodiment 13 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to any one of embodiments 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12 wherein X is SO_2.

Embodiment 14 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to any one of embodiments 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 or 13 wherein A is N.

Embodiment 15 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to any one of embodiments 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, or 13 wherein A is CH.

One group of compounds of formula I according to the invention are those of formula I-1



(I-1),

wherein A, X, R_1, R_2, R_3, and X_1 are as defined for compounds of formula I (above), or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, and wherein Ra_4 is C_1-C_6alkyl, C_2-C_6alkenyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_4alkylthio-C_1-C_4alkyl, C_1-C_4alkylsulfinyl-C_1-C_4alkyl, C_1-C_4alkylsulfonyl-C_1-C_4alkyl, C_3-C_6cycloalkyl-C_1-C_2alkyl, C_1-C_6cyanoalkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl which is mono- or poly-substituted by substituents independently selected from the group consisting of halogen, cyano, C_1-C_3haloalkyl, CO_2H, $CONH_2$, C_1-C_6alkylaminocarbonyl, C_1-C_6dialkylaminocarbonyl and C_1-C_4alkoxycarbonyl.

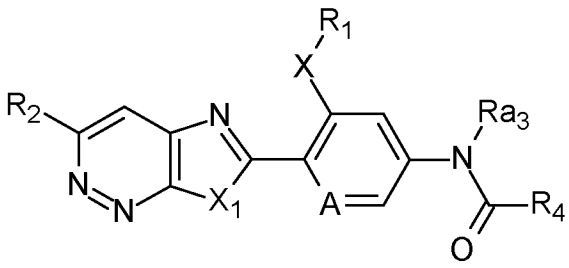
Preferred definitions of A, X, R_1, R_2, R_3, and X_1 are as defined for compounds of formula I (above), and preferably Ra_4 is C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_4alkylthio-C_1-C_4alkyl, C_1-C_4alkylsulfinyl-C_1-C_4alkyl, C_1-C_4alkylsulfonyl-C_1-C_4alkyl, C_1-C_6cyanoalkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl mono-substituted by cyano.

In one embodiment of formula I-1, preferably R_3 is C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl mono-substituted by cyano.

One group of compounds according to this embodiment are compounds of formula (I-1a) which are compounds of formula (I-1) wherein A is N.

Another group of compounds according to this embodiment are compounds of formula (I-1b) which are compounds of formula (I-1) wherein A is CH.

Another group of compounds of formula I according to the invention are those of formula I-2



(I-2),

wherein A, X, R_1, R_2, R_4, and X_1 are as defined for compounds of formula I (above), or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, and wherein Ra_3 is C_1-C_6alkyl, C_2-C_6alkenyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_1-C_6haloalkoxy, C_1-C_6cyanoalkyl, C_1-C_6hydroxyalkyl, C_1-C_6alkoxycarbonyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_4alkylthio-C_1-C_4alkyl, C_1-C_4alkylsulfinyl-C_1-C_4alkyl, C_1-C_4alkylsulfonyl-C_1-C_4alkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl, C_3-C_6halocycloalkyl-C_1-C_4alkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl substituted by a substituent selected from cyano, halogen, C_1-C_3haloalkyl, CO_2H, $CONH_2$, C_1-C_6alkylaminocarbonyl, C_1-C_6dialkylaminocarbonyl or C_1-C_4alkoxycarbonyl.

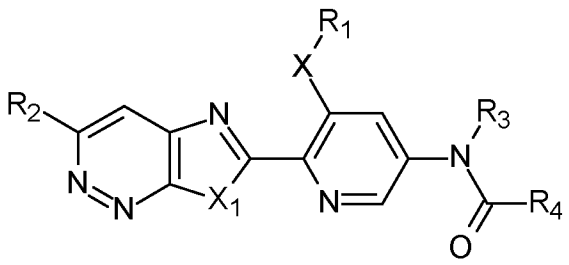
Preferred definitions of A, X, R_1, R_2, R_4, and X_1 are as defined for compounds of formula I (above), and preferably Ra_3 is C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl mono-substituted by cyano.

In one embodiment of formula I-2, R_4 is C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_4alkylthio-C_1-C_4alkyl, C_1-C_4alkylsulfinyl-C_1-C_4alkyl, C_1-C_4alkylsulfonyl-C_1-C_4alkyl, C_1-C_6cyanoalkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl mono-substituted by cyano.

One group of compounds according to this embodiment are compounds of formula (I-2a) which are compounds of formula (I-2) wherein A is N.

Another group of compounds according to this embodiment are compounds of formula (I-2b) which are compounds of formula (I-2) wherein A is CH.

Another group of compounds of formula I according to the invention are those of formula I-4



(I-4),

wherein X, R_1, R_2, R_3, R_4 and X_1 are as defined for compounds of formula I (above), or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof.

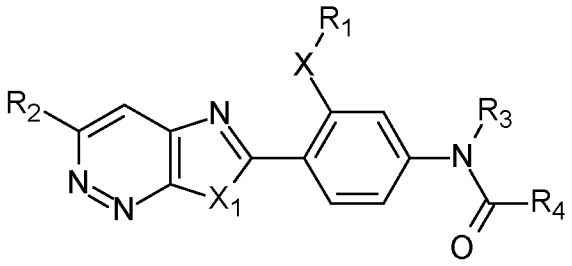
Preferred definitions of X, R_1, R_2, R_3, R_4 and X_1 are as defined for compounds of formula I (above).

In a preferred group of compounds of formula I-4, R_4 is C_1-C_6alkyl, C_2-C_6alkenyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_4alkylthio-C_1-C_4alkyl, C_1-C_4alkylsulfinyl-C_1-C_4alkyl, C_1-C_4alkylsulfonyl-C_1-C_4alkyl, C_3-C_6cycloalkyl-C_1-C_2alkyl, C_1-C_6cyanoalkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl which is mono- or poly-substituted by substituents independently selected from the group consisting of halogen, cyano, C_1-C_3haloalkyl, CO_2H, $CONH_2$, C_1-C_6alkylaminocarbonyl, C_1-C_6dialkylaminocarbonyl and C_1-C_4alkoxycarbonyl.

One group of compounds according to this embodiment are compounds of formula (I-4a) which are compounds of formula (I-4) wherein R_4 is C_1-C_6alkyl.
Another group of compounds according to this embodiment are compounds of formula (I-4b) which are compounds of formula (I-4) wherein R_4 is C_2-C_6alkenyl.
Another group of compounds according to this embodiment are compounds of formula (I-4c) which are compounds of formula (I-4) wherein R_4 is C_1-C_6haloalkyl.
Another group of compounds according to this embodiment are compounds of formula (I-4d) which are compounds of formula (I-4) wherein R_4 is C_1-C_6hydroxyalkyl.
Another group of compounds according to this embodiment are compounds of formula (I-4e) which are compounds of formula (I-4) wherein R_4 is C_1-C_4alkoxy-C_1-C_4alkyl.
Another group of compounds according to this embodiment are compounds of formula (I-4f) which are compounds of formula (I-4) wherein R_4 is C_1-C_4alkylthio-C_1-C_4alkyl.
Another group of compounds according to this embodiment are compounds of formula (I-4g) which are compounds of formula (I-4) wherein R_4 is C_1-C_4alkylsulfinyl-C_1-C_4alkyl.
Another group of compounds according to this embodiment are compounds of formula (I-4h) which are compounds of formula (I-4) wherein R_4 is C_1-C_4alkylsulfonyl-C_1-C_4alkyl.
Another group of compounds according to this embodiment are compounds of formula (I-4i) which are compounds of formula (I-4) wherein R_4 is C_3-C_6cycloalkyl-C_1-C_2alkyl.
Another group of compounds according to this embodiment are compounds of formula (I-4j) which are compounds of formula (I-4) wherein R_4 is C_1-C_6cyanoalkyl.
Another group of compounds according to this embodiment are compounds of formula (I-4k) which are compounds of formula (I-4) wherein R_4 is C_3-C_6cycloalkyl.
Another group of compounds according to this embodiment are compounds of formula (I-4l) which are compounds of formula (I-4) wherein R_4 is C_3-C_6cycloalkyl which is mono- or poly-substituted by substituents independently selected from the group consisting of halogen, cyano, C_1-C_3haloalkyl, CO_2H, $CONH_2$, C_1-C_6alkylaminocarbonyl, C_1-C_6dialkylaminocarbonyl and C_1-C_4alkoxycarbonyl.

In compounds of formula (I-4a) to (I-4l) the preferred definitions of X, R_1, R_2, R_3 and X_1 are as defined for compounds of formula I (above).

Another group of compounds of formula I according to the invention are those of formula I-5



(I-5),

wherein X, R_1, R_2, R_3, R_4 and X_1 are as defined for compounds of formula I (above), or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof.

Preferred definitions of X, R_1, R_2, R_3, R_4 and X_1 are as defined for compounds of formula I (above).

In a preferred group of compounds of formula I-5, R_4 is C_1-C_6alkyl, C_2-C_6alkenyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_4alkylthio-C_1-C_4alkyl, C_1-C_4alkylsulfinyl-C_1-C_4alkyl, C_1-C_4alkylsulfonyl-C_1-C_4alkyl, C_3-C_6cycloalkyl-C_1-C_2alkyl, C_1-C_6cyanoalkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl which is mono- or poly-substituted by substituents independently selected from the group consisting of halogen, cyano, C_1-C_3haloalkyl, CO_2H, $CONH_2$, C_1-C_6alkylaminocarbonyl, C_1-C_6dialkylaminocarbonyl and C_1-C_4alkoxycarbonyl.

One group of compounds according to this embodiment are compounds of formula (I-5a) which are compounds of formula (I-5) wherein R_4 is C_1-C_6alkyl.

Another group of compounds according to this embodiment are compounds of formula (I-5b) which are compounds of formula (I-5) wherein R_4 is C_2-C_6alkenyl.

Another group of compounds according to this embodiment are compounds of formula (I-5c) which are compounds of formula (I-5) wherein R_4 is C_1-C_6haloalkyl.

Another group of compounds according to this embodiment are compounds of formula (I-5d) which are compounds of formula (I-5) wherein R_4 is C_1-C_6hydroxyalkyl.

Another group of compounds according to this embodiment are compounds of formula (I-5e) which are compounds of formula (I-5) wherein R_4 is C_1-C_4alkoxy-C_1-C_4alkyl.

Another group of compounds according to this embodiment are compounds of formula (I-5f) which are compounds of formula (I-5) wherein R_4 is C_1-C_4alkylthio-C_1-C_4alkyl.

Another group of compounds according to this embodiment are compounds of formula (I-5g) which are compounds of formula (I-5) wherein R_4 is C_1-C_4alkylsulfinyl-C_1-C_4alkyl.

Another group of compounds according to this embodiment are compounds of formula (I-5h) which are compounds of formula (I-5) wherein R_4 is C_1-C_4alkylsulfonyl-C_1-C_4alkyl.

Another group of compounds according to this embodiment are compounds of formula (I-5i) which are compounds of formula (I-5) wherein R_4 is C_3-C_6cycloalkyl-C_1-C_2alkyl.

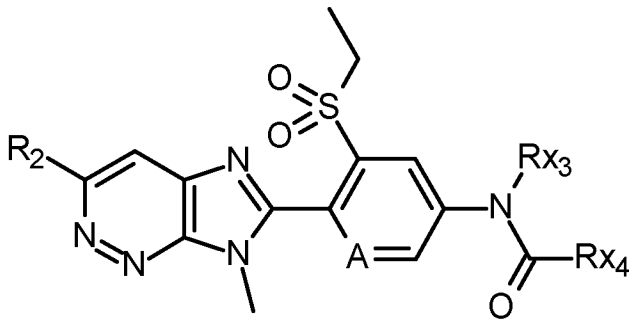
Another group of compounds according to this embodiment are compounds of formula (I-5j) which are compounds of formula (I-5) wherein R_4 is C_1-C_6cyanoalkyl.

Another group of compounds according to this embodiment are compounds of formula (I-5k) which are compounds of formula (I-5) wherein R_4 is C_3-C_6cycloalkyl.

Another group of compounds according to this embodiment are compounds of formula (I-5l) which are compounds of formula (I-5) wherein R_4 is C_3-C_6cycloalkyl which is mono- or poly-substituted by substituents independently selected from the group consisting of halogen, cyano, C_1-C_3haloalkyl, CO_2H, $CONH_2$, C_1-C_6alkylaminocarbonyl, C_1-C_6dialkylaminocarbonyl and C_1-C_4alkoxycarbonyl.

In compounds of formula (I-5a) to (I-5l) the preferred definitions of X, R_1, R_2, R_3 and X_1 are as defined for compounds of formula I (above).

A preferred group of compounds of formula I according to the invention are those of formula I-6



(I-6),

wherein

A is CH or N, preferably N;

R_2 is C_1-C_6haloalkyl, preferably trifluoromethyl;

Rx_3 is C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl mono-substituted by cyano; preferably Rx_3 is methyl, ethyl, isopropyl, 2,2,2-trifluoroethyl, methoxy, cyclopropyl or 1-cyanocyclopropyl; and

Rx_4 is C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_4alkylthio-C_1-C_4alkyl, C_1-C_4alkylsulfinyl-C_1-C_4alkyl, C_1-C_4alkylsulfonyl-C_1-C_4alkyl, C_1-C_6cyanoalkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl mono-substituted by cyano; preferably Rx_4 is methyl, ethyl, isopropyl, t-butyl, trifluoromethyl, difluoromethyl, fluoromethyl, chloromethyl, 2,2,2-trifluoroethyl, 1-hydroxy-1-methyl-ethyl, methoxymethyl, methoxyethyl, methylsulfanylmethyl, methylsulfonylmethyl, 2-methylsulfanylethyl, 2-methylsulfonylethyl, 1-cyano-1-methyl-ethyl, cyclopropyl or 1-cyanocyclopropyl; or

an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof.

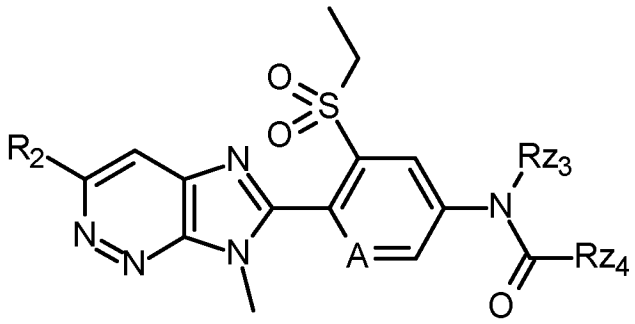
One further preferred group of compounds according to this embodiment are compounds of formula (I-6a) which are compounds of formula (I-6) wherein

Rx_3 is C_1-C_6alkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl mono-substituted by cyano, preferably methyl, ethyl, cyclopropyl or 1-cyanocyclopropyl.

One further preferred group of compounds according to this embodiment are compounds of formula (I-6b) which are compounds of formula (I-6) wherein

Rx_4 is C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_6cyanoalkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl mono-substituted by cyano, preferably methyl, ethyl, 2,2,2-trifluoroethyl, methoxymethyl, 1-cyano-1-methyl-ethyl, cyclopropyl or 1-cyanocyclopropyl.

An outstanding group of compounds of formula I according to the invention are those of formula I-8



(I-8),

wherein

A is CH or N, preferably N;

R_2 is C_1-C_6haloalkyl, preferably trifluoromethyl;

Rz_3 is C_1-C_6alkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl mono-substituted by cyano, preferably methyl, ethyl, cyclopropyl or 1-cyanocyclopropyl; and

Rz_4 is C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_6cyanoalkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl mono-substituted by cyano, preferably methyl, ethyl, 2,2,2-trifluoroethyl, methoxymethyl, 1-cyano-1-methyl-ethyl, cyclopropyl or 1-cyanocyclopropyl; or

an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof.

One further outstanding group of compounds according to this embodiment are compounds of formula (I-8a) which are compounds of formula (I-8) wherein

A is N.

One further outstanding group of compounds according to this embodiment are compounds of formula (I-8b) which are compounds of formula (I-8) wherein

A is CH.

One further outstanding group of compounds according to this embodiment are compounds of formula (I-8c) which are compounds of formula (I-8) wherein

A is N;

R_2 is C_1-C_6haloalkyl, preferably trifluoromethyl;
Rz_3 is C_1-C_6alkyl or C_3-C_6cycloalkyl, preferably methyl, ethyl or cyclopropyl; and
Rz_4 is C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_4alkoxy-C_1-C_4alkyl or C_3-C_6cycloalkyl, preferably methyl, ethyl, 2,2,2-trifluoroethyl, methoxymethyl or cyclopropyl.

One further outstanding group of compounds according to this embodiment are compounds of formula (I-8d) which are compounds of formula (I-8) wherein
A is N;
R_2 is C_1-C_6haloalkyl, preferably trifluoromethyl;
Rz_3 is C_3-C_6cycloalkyl mono-substituted by cyano, preferably 1-cyanocyclopropyl; and
Rz_4 is C_1-C_6alkyl, preferably methyl or ethyl.

One further outstanding group of compounds according to this embodiment are compounds of formula (I-8e) which are compounds of formula (I-8) wherein
A is N;
R_2 is C_1-C_6haloalkyl, preferably trifluoromethyl;
Rz_3 is is C_1-C_6alkyl, preferably methyl or ethyl; and
Rz_4 is C_1-C_6cyanoalkyl or C_3-C_6cycloalkyl mono-substituted by cyano, preferably 1-cyano-1-methyl-ethyl or 1-cyanocyclopropyl.

One further outstanding group of compounds according to this embodiment are compounds of formula (I-8f) which are compounds of formula (I-8) wherein
A is N;
R_2 is C_1-C_6haloalkyl, preferably trifluoromethyl;
Rz_3 is is C_1-C_6alkyl, preferably methyl or ethyl; and
Rz_4 is C_1-C_6alkyl, preferably methyl or ethyl.

In each case, the foregoing groups and embodiments of the compounds of formula I according to the invention are in free form, in oxidized form as an N-oxide or in salt form, e.g. an agronomically usable salt form. In addition, the present invention relates to stereoisomers, enantiomers, or tautomers of the compounds of formula I.

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, improved physico-chemical properties, or increased biodegradability or environmental profile). 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.

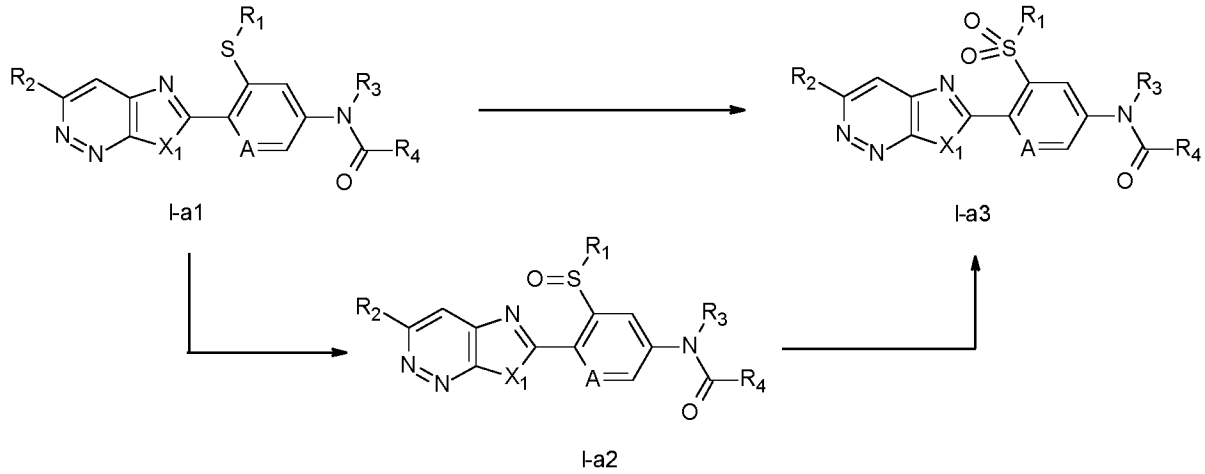
In another aspect the present invention provides a composition comprising an insecticidally, acaricidally, nematicidally or molluscicidally effective amount of a compound of formula (I), or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, as defined in any of embodiments 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 or 15 (above) or any of the embodiments under compounds of formula (I-1), (I-2), (I-4), (I-5), (I-6) and (I-8), and, optionally, an auxiliary or diluent.

In a further aspect the present invention provides 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, nematicidally or molluscicidally effective amount of a compound of formula (I), or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, as defined in any of embodiments 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 or 15 (above) or any of the embodiments under compounds of formula (I-1), (I-2), (I-4), (I-5), (I-6) and (I-8) (above) or a composition as defined above.

In a yet further aspect, the present invention provides 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 a composition as defined above.

The process according to the invention for preparing compounds of formula I is carried out by methods known to those skilled in the art. Compounds of formula I-a3, wherein X is SO_2 and A, X_1, R_1, R_2, R_3 and R_4 are defined as under formula I above, may be prepared by oxidation of compounds of formula I-a2, wherein X is SO and A, X_1, R_1, R_2, R_3 and R_4 are defined as under formula I above. The reaction can be performed with reagents such as a peracid, for example peracetic acid or m-chloroperbenzoic acid, or a hydroperoxide, as for example, hydrogen peroxide or tert-butylhydroperoxide, or an inorganic oxidant, such as a monoperoxo-disulfate salt or potassium permanganate. In a similar way, compounds of formula I-a2, wherein X is SO and A, X_1, R_1, R_2, R_3 and R_4 are defined as under formula I above, may be prepared by oxidation of compounds of formula I-a1, wherein X is S and A, X_1, R_1, R_2, R_3 and R_4 are defined as under formula I above, under analogous conditions as described above. These reactions can be performed in various organic or aqueous solvents compatible to these conditions, by temperatures from below 0°C up to the boiling point of the solvent system. Compounds of formula I-a1 can also be directly oxidized to compounds of formula I-a3 under similar conditions as described above. The transformation of compounds of the formula I-a1 into compounds of the formula I-a2 and I-a3 is represented in Scheme 1.

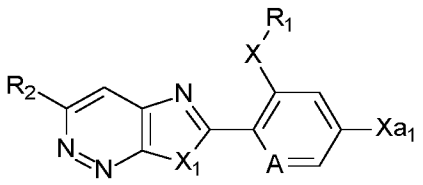
Scheme 1



I-a1 I-a3

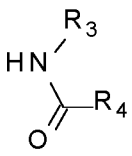
I-a2

Compounds of formula I can be prepared from compounds of formula II,



II,

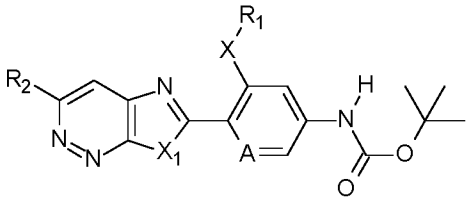
wherein R_2, X_1, X, R_1 and A are as described in compounds of formula I and Xa1 is halogen (or a pseudo-halogen leaving group, such as triflate), preferably iodine, bromine or chlorine, by treatment with compounds of formula III



III,

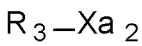
wherein R_3 and R_4 are as described in formula I, optionally in the presence of a base, such as potassium carbonate, cesium carbonate, sodium hydroxide, in an inert solvent, such as toluene, dimethylformamide DMF, N-methyl pyrrolidine, dimethyl sulfoxide DMSO, dioxane, tetrahydrofuran THF, and the like, optionally in the presence of a catalyst, for example palladium(II)acetate, bis(dibenzylideneacetone)palladium(0) ($Pd(dba)_2$) or tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$, optionally in form of a chloroform adduct), or a palladium pre-catalyst such as for example *tert*-BuBrettPhos Pd G3 [(2-Di-*tert*-butylphosphino-3,6-dimethoxy-2′,4′,6′-triisopropyl-1,1′-biphenyl)-2-(2′-amino-1,1′-biphenyl)]palladium(II) methanesulfonate or BrettPhos Pd G3 [(2-di-cyclohexylphosphino-3,6-dimethoxy-2′,4′,6′- triisopropyl-1,1′-biphenyl)-2-(2′-amino-1,1′ -biphenyl)]palladium(II) methanesulfonate, and optionally a ligand, for example SPhos, *t*-BuBrettPhos or Xantphos, at temperatures between 60-120°C, optionally under microwave irradiation. Such reactions are known in the literature and have been reported for example in *Tetrahedron*, **2009**, *65*, 6576, *Org. Lett.* **2013**, *15*, 2876.and *J. Am. Chem. Soc.* **2009**, *131*, 16720.

Alternatively (see summary in scheme 2), compounds of formula I can be obtained by treating compounds of formula II with tert-butyl carbamate $H_2NC(O)Ot\text{-}Bu$ under similar conditions to those described above. Similar reactions also have precedence in the literature, for example in *Green Chemistry*, 16(3), 1480-1488; **2014**. Compounds of formula IV thus obtained,



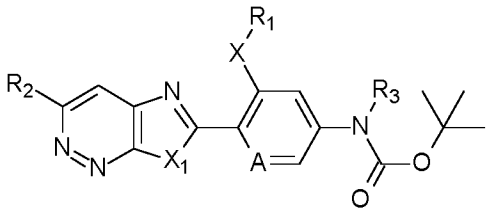
IV,

wherein R_2, X_1, X, R_1 and A are as described in compounds of formula I, can be alkylated with compounds of formula V



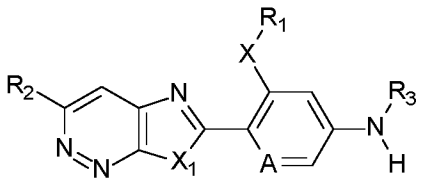
V,

wherein R_3 is as described under formula I, and in which Xa2 is a leaving group such as halogen, preferably iodine, bromine or chlorine (or a pseudo-halogen leaving group, such as a (halo)alkyl or phenyl sulfonate ester, e.g. triflate), in the presence of a base, such as sodium hydride or an alkaline earth metal hydride, carbonate (e.g. sodium carbonate, potassium carbonate or cesium carbonate) or hydroxide, in an inert solvent such as tetrahydrofuran, dioxane, dimethylformamide DMF, N,N-dimethylacetamide or acetonitrile and the like, at temperatures between 0 and 120°C, by procedures well known to those skilled in the art to give compounds of formula VI



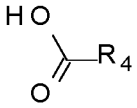
VI,

wherein R_2, X_1, X, R_1, R_3 and A are as described in compounds of formula I. Compounds of formula VI can be converted to compounds of formual VII



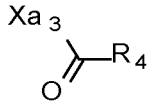
VII,

wherein R_2, X_1, X, R_1, R_3 and A are as described in compounds of formula I, by treatment with organic acids, for example trifluoroacetic acid, acetic acid and the like, or mineral acids such as hydrochloric acid, in inert solvents, such as dichloromethane or tetrahydrofuran THF, optionaly in the presence of water, at temperatures between 0 and 80°C, by methods well known to those skilled in the art. Compounds of formual VII thus obtained can be converted to compounds of formula I by treatment with compounds of formula VIII



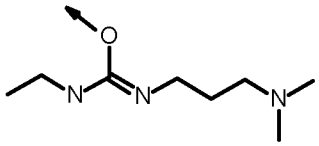
VIII,

wherein R_4 is as described as in formula I. To achieve such a reaction, compounds of formula VIII require activation to compounds of formula VIIIa

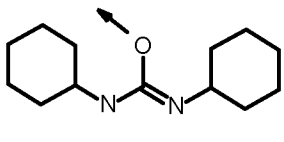


VIIIa,

wherein R_4 is as described in formula I, and wherein Xa3 is halogen, preferably chlorine, by methods known to those skilled in the art and described in for example *Tetrahedron*, *61* (46) , *10827-10852, **2005***. For example, compounds VIIIa where Xa_3 is halogen, preferably chlorine, are formed by treatment of VIII with, for example, oxalyl chloride $(COCl)_2$ or thionyl chloride $SOCl_2$, in the presence of catalytic quantities of N,N-dimethylformamide DMF in inert solvents such as methylene chloride or tetrahydrofuran THF at temperatures between 20 to 100°C, preferably 25°C. Alternatively, compounds of formula VIIIa can be prepared by treatment of compounds of formula VIII with 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) or dicyclohexyl carbodiimide (DCC) to give the activated species VIIIa, wherein Xa_3 is Xa_{31} or Xa_{32} respectively,



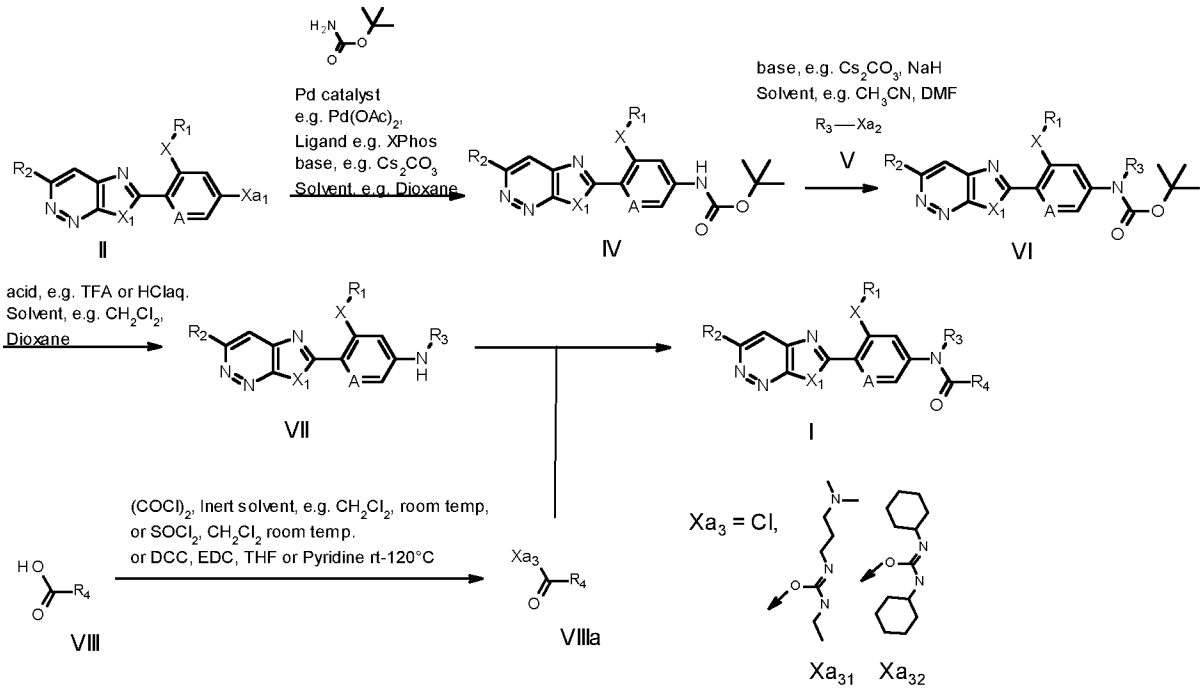
Xa_{31}



Xa_{32}

where the arrow represents the point of attachment to the radical COR_4, in an inert solvent, e.g. pyridine or tetrahydrofuran THF, optionally in the presence of a base, e.g. triethylamine, at temperatures between 50-180°C. Treatment of the activated species VIIIa, wherein R_4 is as defined in formula I, with compounds of the formula VII, wherein R_2, X_1, X, R_1, R_3 and A are as defined in formula I, in the presence of a base, such as triethylamine, N,N-diisopropyl-ethylamine or pyridine, optionally in the presence of a catalyst (such as 4-dimethylaminopyridine DMAP), in an inert solvents such as dichloromethane, tetrahydrofuran, dioxane, N,N-dimethylformamide, N,N-dimethylacetamide, acetonitrile, ethyl acetate or toluene, at temperatures between 0 and 50°C, will then form the compounds of formula I. Certain bases, such as pyridine and triethylamine, may be employed successfully as both base and solvent. This alternative synthesis of compounds of formula I is summarised in scheme 2.

Scheme 2

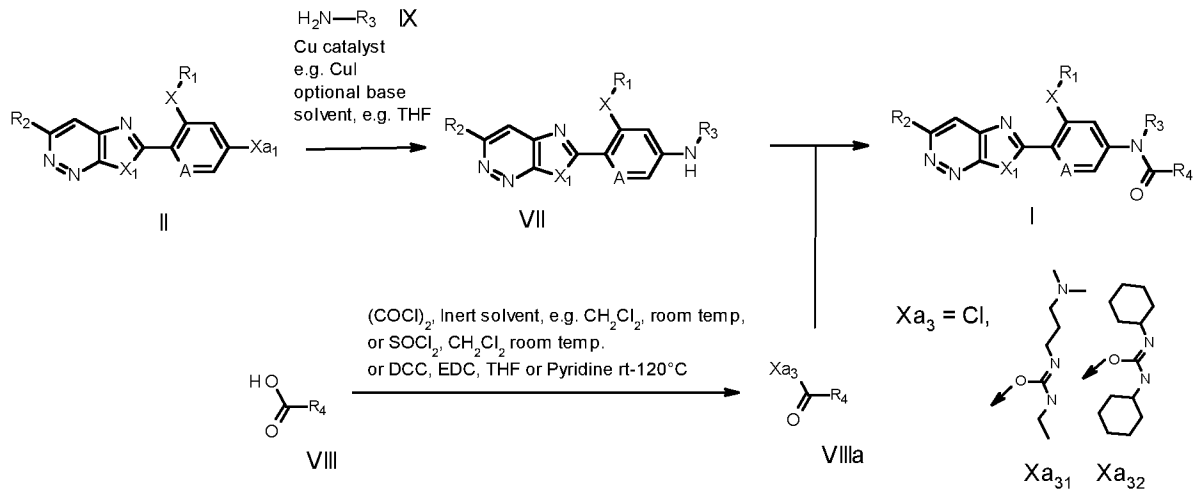


Alternatively, compounds of formula I can be prepared by reacting compounds of formula VII directly with compounds of formula VIII in the presence of, for example, phosphorus oxychloride, while involving bases, such as pyridine and triethylamine, that serve as both base and solvent/diluent, at temperatures between -30 and 60°C, preferably between -20°C and room temperature.

Also known to a person skilled in the art, anhydrides of the formula $R_4C(O)OC(O)R_4$, wherein R_4 is as defined in formula I, may be used as alternatives of the activated species VIIIa for the preparation of compounds of formula I.

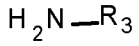
A further synthesis of compounds of formula I is illustrated in scheme 3.

Scheme 3



As shown in scheme 3, treatment of compounds of formula II, wherein R_2, X_1, X, R_1 and A are as

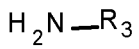
described in compounds of formula I and Xa1 is halogen (or a pseudo-halogen leaving group, such as triflate), preferably iodine, bromine or chlorine, with compounds of formula IX



IX,

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_3 is as defined under formula I, in the presence of a copper catalyst, such as copper powder, copper(I) iodide or copper sulfate (optionally in form of a hydrate), or mixtures thereof, in an inert solvent such as alcohols, amides, esters, ethers, nitriles and water, particularly preferred are methanol, ethanol, 2,2,2-trifluoroethanol, propanol, isopropanol, N,N-dimethylformamide, N,N-dimethylacetamide, dioxane, tetrahydrofuran, dimethoxyethane, acetonitrile, ethyl acetate, water or mixtures thereof, at temperatures between 0-150°C, preferably at temperatures ranging from room temperature to the boiling point of the reaction mixture, optionally under microwave irradiation or pressurized conditions using an autoclave, optionally in the presence of a base, leads to compounds of formula VII, wherein R_2, X_1, X, R_1, R_3 and A are as defined in formula I. This reaction is well known in the literature (known as an Ullmann reaction or variation around this type of reaction), see for example *Coord. Chem. Rev.* **2004,** 248, 2337-2364, *Tetrahedron*, 67(29), 5282-5288; **2011**, *Angew. Chem., Int. Ed.* **2003**, 42, 5400-5449; *Synlett* **2003**, 2428-2439; or *Ind. Eng. Chem. Res.* **2005**, 44, 789-798. The reaction is commonly performed with one or two equivalents of a base, such as potassium phosphate, in presence of a copper catalyst, for example copper (I) iodine, copper sulfate, or copper, and under an oxygen-containing atmosphere. The reaction can be run in an inert solvent, like dioxane, THF, or toluene, usually at temperature between 50 to 150°C and optionaly in presence an additional ligand, for example diamine ligands (e.g. *trans*-cyclohexyldiamine) or dibenzylideneacetone (dba), or 1,10-phenanthroline.

Alternatively, compounds of the formula VII, wherein R_2, X_1, X, R_1, R_3 and A are as described in compounds of formula I, can be prepared by reacting compounds of the formula II, wherein R_2, X_1, X, R_1 and A are as described in compounds of formula I and Xa1 is halogen (or a pseudo-halogen leaving group, such as triflate), preferably iodine, bromine or chlorine, with reagents of the formula IX



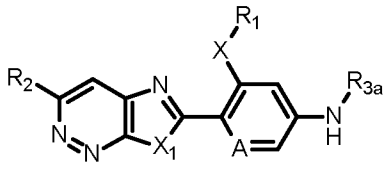
IX,

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_3 is as defined under formula I, in the presence of a palladium catalyst, for example palladium(II)acetate, bis(dibenzylideneacetone) palladium(0) ($Pd(dba)_2$) or tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$, optionally in form of a chloroform adduct), or a palladium pre-catalyst such as for example *tert*-BuBrettPhos Pd G3 [(2-Di-*tert*-butylphosphino-3,6-dimethoxy-2′,4′,6′-triisopropyl-1,1′-biphenyl)-2-(2′-amino-1,1′-biphenyl)]palladium(II) methanesulfonate or BrettPhos Pd G3 [(2-di-cyclohexylphosphino-3,6-dimethoxy-2′,4′,6′- triisopropyl-1,1′-biphenyl)-2-(2′-amino-1,1′ -biphenyl)]palladium(II) methanesulfonate, and optionally in the presence of a ligand, for example BINAP, SPhos, *t*-

BuBrettPhos or Xantphos, usually in the presence of a base, such as potassium carbonate, cesium carbonate, sodium or potassium tert-butylate, sodium hydroxide, in an inert solvent, such as toluene, dimethylformamide DMF, dimethylacetamide, N-methyl pyrrolidine, dimethyl sulfoxide DMSO, dioxane, tetrahydrofuran THF, and the like, at temperatures between 60-180°C, optionally under microwave irradiation. Such reactions, known to a person skilled in the art as the Buchwald–Hartwig amination, have been reported in the literature, for example in Org. Process Res. Dev. 2019, 23, 1478−1483.

Acylation of compounds of formula VII with compounds of formula VIIIa (alternatively direct reaction between compounds VII and compounds VIII) under the conditions described in scheme 2 leads to compounds of formual I.

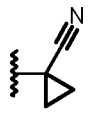
Compounds of formula VIIa



(VIIa),

wherein

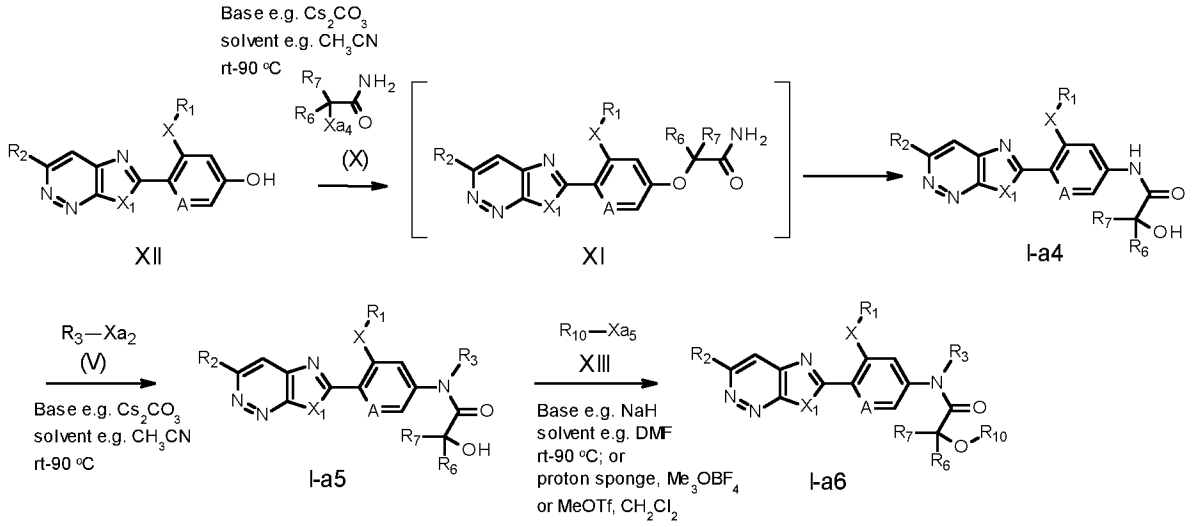
R_2, X_1, X, R_1 and A are as defined in formula I; and

R_{3a} is cyclopropyl or  ,

are novel, especially developed for the preparation of the compounds of formula I according to the invention and therefore represent a further object of the invention. The preferences and preferred embodiments of the substituents of the compounds of formula I are also valid for the compounds of formula VIIa. Preferably, R_2 is C_1-C_6haloalkyl; even more preferably R_2 is CF_3. Preferably, X_1 is N(C_1-C_4alkyl); even more preferably X_1 is NCH_3. Preferably, X is S or SO_2; even more preferably X is SO_2. Preferably, R_1 is C_1-C_4alkyl; even more preferably R_1 is ethyl. Preferably, A is N.

A further synthesis of compounds of formula I is illustrated in scheme 4 for the particular subgroup of compounds I-a4, I-a5 and I-a6, wherein A, X, X_1, R_1, R_2 and R_3 are defined as under formula I, and in which R_6 and R_7 are independently hydrogen or C_1-C_4alkyl, and wherein R_{10} is C_1-C_4alkyl.

Scheme 4



Compounds of formula XI (scheme 4), wherein A, X, X_1, R_1 and R_2 are as defined in formula I, and in which R_6 and R_7 are independently hydrogen or C_1-C_4alkyl, can be prepared by reaction of compounds of formula XII, wherein A, X, X_1, R_1 and R_2 are as defined in formula I, with compounds of formula (X), wherein R_6 and R_7 are independently hydrogen or C_1-C_4alkyl, and in which Xa4 is a leaving group such as a halogen, preferably iodine, bromine or chlorine, in presence of a base, for example sodium hydroxide, sodium hydride, sodium carbonate, potassium tert-butoxide, potassium hydroxide, potassium carbonate or cesium carbonate, in an inert solvent such as dimethylformamide DMF, acetonitrile, dimethylsulfoxide DMSO and the like, at temperatures between 20-180 °C, preferably room temperature to 90°C.

Compounds of formula XI can be isolated, or by extended reaction times, rearrange to compounds of formula I, respectively I-a4, wherein A, X, X_1, R_1 and R_2 are as defined in formula I, and in which R_6 and R_7 are independently hydrogen or C_1-C_4alkyl. This reaction is known as a Smiles rearrangement and is well precedented in the literature, for example *Organic Reactions. **18**: 99–215,* **2011** and references cited therein.

Compounds of formula I-a5, wherein A, X, X_1, R_1, R_2 and R_3 are as defined in formula I, and in which R_6 and R_7 are independently hydrogen or C_1-C_4alkyl, can be prepared by reaction of compounds of formula I-a4, wherein A, X, X_1, R_1 and R_2 are as defined in formula I, and in which R_6 and R_7 are independently hydrogen or C_1-C_4alkyl, with compounds of formula R_3-Xa2 (V), wherein R_3 is as defined in formula I, and in which Xa2 is a leaving group such as halogen, preferably iodine, bromine or chlorine (or a pseudo-halogen leaving group, such as a (halo)alkyl or phenyl sulfonate ester, e.g. triflate), in presence of a base, such as sodium carbonate, potassium carbonate or cesium carbonate, or sodium hydride, in an appropriate solvent such as for example tetrahydrofuran, dioxane, N,N-dimethylformamide, N,N-dimethylacetamide or acetonitrile, at temperatures between 0 and 150°C by methods known to those skilled in the art.

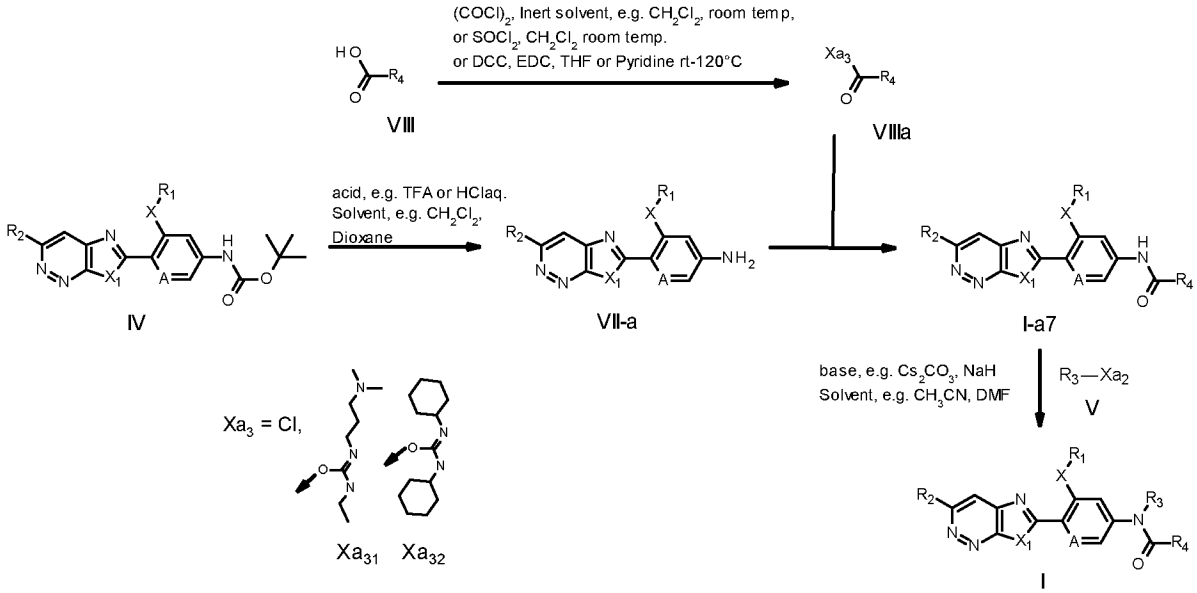
Compounds of formula I-a5, wherein A, X, X_1, R_1, R_2 and R_3 are as defined in formula I, and in which R_6 and R_7 are independently hydrogen or C_1-C_4alkyl, may in turn be further alkylated to compounds of formula I-a6, wherein A, X, X_1, R_1, R_2 and R_3 are as defined in formula I, and in which R_6 and R_7 are

independently hydrogen or C_1-C_4alkyl, and wherein R_{10} is C_1-C_4alkyl, by reaction with compounds of formula XIII, wherein R_{10} is C_1-C_4alkyl, and in which Xa5 is a leaving group such as halogen, preferably iodine, bromine or chlorine (or a pseudo-halogen leaving group, such as a (halo)alkyl or phenyl sulfonate ester, e.g. triflate), in presence of a base, such as sodium carbonate, potassium carbonate or cesium carbonate, or sodium hydride, in an appropriate solvent such as for example tetrahydrofuran, dioxane, N,N-dimethylformamide, N,N-dimethylacetamide or acetonitrile, at temperatures between 0 and 150°C by methods known to those skilled in the art.

Alternatively, and in the particular situation where R_{10} is methyl, it may be advantageous to alkylate the oxygen of compounds of formula I-a5 by using the method described by Evans, D.A.; Ratz, Andrew M.; Huff, Bret E.; Sheppard, George S. in Tet. Lett. (**1994**), *35*(39), 7171-2, which utilizes a proton sponge and an electrophilic methyl source such as methyl triflate (MeOTf) and trimethyloxonium fluoroborate (Me_3OBF_4), in an inert solvent such as dichloromethane.

Alternatively, compounds of formula I, wherein X, A, X_1, R_1, R_2, R_3 and R_4 are as defined above,

Scheme 5



can be prepared (scheme 5) by reacting compounds of the formula I wherein R_3 is hydrogen, defining compounds of the formula I-a7, wherein X, A, X_1, R_1, R_2 and R_4 are as defined in formula I, with compounds of formula R_3-Xa2 (V), wherein R_3 is as described in formula I, and in which Xa2 is a leaving group such as halogen, preferably iodine, bromine or chlorine (or a pseudo-halogen leaving group, such as a (halo)alkyl or phenyl sulfonate ester, e.g. triflate), in the presence of a base, such as sodium hydride or an alkaline earth metal hydride, carbonate (e.g. sodium carbonate, potassium carbonate or cesium carbonate) or hydroxide, in an inert solvent such as tetrahydrofuran, dioxane, N,N-dimethylformamide DMF, N,N-dimethylacetamide or acetonitrile and the like, at temperatures between 0 and 120°C, by procedures well known to those skilled in the art.

Compounds of the formula I-a7, wherein X, A, X_1, R_1, R_2 and R_4 are as defined in formula I, can be prepared by reacting compounds of the formula VII wherein R_3 is hydrogen, defining compounds of

the formula VII-a, wherein X, A, X_1, R_1 and R_2 are as defined in formula I, with compounds of formula VIIIa, wherein R_4 is as described in formula I, and wherein Xa3 is halogen, preferably chlorine, by methods known to those skilled in the art and already described above in scheme 2. Alternatively, compounds of formula I-a7 may be prepared by reacting compounds of formula VII-a directly with compounds of formula VIII under conditions already described above in scheme 2.
Compounds of the formula VII-a, wherein X, A, X_1, R_1 and R_2 are as defined in formula I, can be prepared by reacting compounds of the formula IV described above, wherein X, A, X_1, R_1 and R_2 are as defined in formula I, with organic acids, for example trifluoroacetic acid, acetic acid and the like, or mineral acids such as hydrochloric acid, under conditions already described above in scheme 2 (transformation of compounds VI into compounds VII).

Compounds of formula II, wherein R_2, X_1, X, R_1 and A are as described in formula I, and Xa1 is halogen, preferably iodine, bromine or chlorine, have been described in the literature, for example in WO18215304, WO18153778, WO17146221, WO17065183, WO16104746, WO16059145 and WO15000715.

Compounds of formula XII, wherein A, X, X_1, R_1 and R_2 are as defined in formula I, have been described in the literature, for example in WO18215304 and WO16039441.

Compounds of formula III, wherein R_3 and R_4 are as described in formula I; and
compounds of formula V, wherein R_3 is as described under formula I, and in which Xa2 is a leaving group such as halogen, preferably iodine, bromine or chlorine (or a pseudo-halogen leaving group, such as a (halo)alkyl or phenyl sulfonate ester, e.g. triflate); and
compounds of formula VIII, wherein R_4 is as described as in formula I; and
compounds of formula VIIIa, wherein R_4 is as described in formula I, and wherein Xa3 is halogen, preferably chlorine; and
compounds of formula IX, 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_3 is as defined under formula I; and
compounds of formula (X), wherein R_6 and R_7 are independently hydrogen or C_1-C_4alkyl, and in which Xa4 is a leaving group such as a halogen, preferably iodine, bromine or chlorine; and
compounds of formula XIII, wherein R_{10} is C_1-C_4alkyl, and in which Xa5 is a leaving group such as halogen, preferably iodine, bromine or chlorine;
are either known, commercially available or may be prepared by methods known to a person skilled in the art.

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.

A compound of formula I can be converted in a manner known per se into another compound of formula I by replacing one or more substituents of the starting compound of formula I in the customary manner by (an)other substituent(s) according to the invention, and by post modification of compounds of with reactions such as oxidation, alkylation, reduction, acylation and other methods known by those skilled in the art. 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 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 diasteromers 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 celulose, 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.

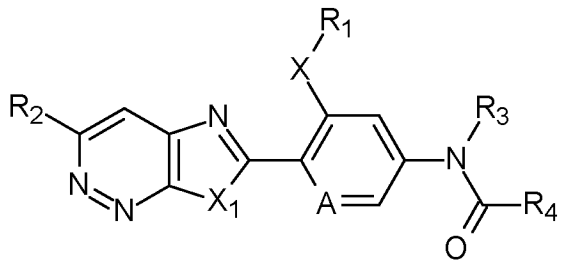
N-oxides can be prepared by reacting a compound of the formula I with a suitable oxidizing agent, for example the H_2O_2/urea adduct in the presence of an acid anhydride, e.g. trifluoroacetic anhydride. Such oxidations are known from the literature, for example from *J. Med. Chem.*, 32 (12), 2561-73, **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.

The compounds according to the following Tables A-1 to A-33 below 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.

The tables A-1 to A-33 below illustrate specific compounds of the invention.



Iaa

Table Y: Substituent definitions of R_4:

Index	R_4	Index	R_4
1	CH_3	**12**	$CH_2SO_2CH_3$
2	CH_2CH_3	**13**	$CH_2CH_2SCH_3$
3	$CH(CH_3)_2$	**14**	$CH_2CH_2SOCH_3$

Index	R_4	Index	R_4
4	Cyp	**15**	$CH_2CH_2SO_2CH_3$
5	CH_2Cl	**16**	CH_2OCH_3
6	CF_3	**17**	$CH_2CH_2OCH_3$
7	CHF_2	**18**	$C(CH_3)_2OH$
8	CH_2CF_3	**19**	$C(CH_3)_2OCH_3$
9	CH_2SCH_3	**20**	CH_2F
10	$C(CH_3)_3$	**21**	$C(CH_3)_2CN$
11	CH_2SOCH_3	**22**	

In the table Y and in tables A, “Cyp” represents cyclopropyl.

Table A-1 provides 22 compounds A-1.001 to A-1.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is CH_3, X is S, X_1 is NCH_3, A is N and R_4 is as defined in table Y.

Table A-2 provides 22 compounds A-2.001 to A-2.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is CH_3, X is SO, X_1 is NCH_3, A is N and R_4 is as defined in table Y.

Table A-3 provides 22 compounds A-3.001 to A-3.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is CH_3, X is SO_2, X_1 is NCH_3, A is N and R_4 is as defined in table Y.

Table A-4 provides 22 compounds A-4.001 to A-4.022 of formula aa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is Cyp, X is S, X_1 is NCH_3, A is N and R_4 is as defined in table Y.

Table A-5 provides 22 compounds A-5.001 to A-5.022 of formula aa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is Cyp, X is SO_2, X_1 is NCH_3, A is N and R_4 is as defined in table Y.

Table A-6 provides 22 compounds A-6.001 to A-6.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is OCH_3, X is SO_2, X_1 is NCH_3, A is N and R_4 is as defined in table Y.

Table A-7 provides 22 compounds A-7.001 to A-7.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is CH_3CH_2, X is SO_2, X_1 is NCH_3, A is N and R_4 is as defined in table Y.

Table A-8 provides 22 compounds A-8.001 to A-8.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is CH_2CF_3, X is SO_2, X_1 is NCH_3, A is N and R_4 is as defined in table Y.

Table A-9 provides 22 compounds A-9.001 to A-9.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is CH_3CH_2, X is S, X_1 is NCH_3, A is N and R_4 is as defined in table Y.

Table A-10 provides 22 compounds A-10.001 to A-10.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is CH_2CF_3, X is S, X_1 is NCH_3, A is N and R_4 is as defined in table Y.

Table A-11 provides 22 compounds A-11.001 to A-11.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is $CH(CH_3)_2$, X is S, X_1 is NCH_3, A is N and R_4 is as defined in table Y.

Table A-12 provides 22 compounds A-12.001 to A-12.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is $CH(CH_3)_2$, X is SO_2, X_1 is NCH_3, A is N and R_4 is as defined in table Y.

Table A-13 provides 22 compounds A-13.001 to A-13.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is $CH(CH_3)_2$, X is SO, X_1 is NCH_3, A is N and R_4 is as defined in table Y.

Table A-14 provides 22 compounds A-14.001 to A-14.022 of formula aa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is Cyp, X is SO, X_1 is NCH_3, A is N and R_4 is as defined in table Y.

Table A-15 provides 22 compounds A-15.001 to A-15.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is CH_3, X is SO, X_1 is NCH_3, A is CH and R_4 is as defined in table Y.

Table A-16 provides 22 compounds A-16.001 to A-16.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is CH_3, X is S, X_1 is NCH_3, A is CH and R_4 is as defined in table Y.

Table A-17 provides 22 compounds A-17.001 to A-17.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is CH_3, X is SO_2, X_1 is NCH_3, A is CH and R_4 is as defined in table Y.

Table A-18 provides 22 compounds A-18.001 to A-18.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is OCH_3, X is SO, X_1 is NCH_3, A is N and R_4 is as defined in table Y.

Table A-19 provides 22 compounds A-19.001 to A-19.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is 

, X is S, X_1 is NCH_3, A is CH and R_4 is as defined in table Y.

Table A-20 provides 22 compounds A-20.001 to A-20.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is 

, X is SO, X_1 is NCH_3, A is CH and R_4 is as defined in table Y.

Table A-21 provides 22 compounds A-21.001 to A-21.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is 

, X is SO_2, X_1 is NCH_3, A is CH and R_4 is as defined in table Y.

Table A-22 provides 22 compounds A-22.001 to A-22.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is CH_3CH_2, X is SO, X_1 is NCH_3, A is N and R_4 is as defined in table Y.

Table A-23 provides 22 compounds A-23.001 to A-23.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is OCH_3, X is S, X_1 is NCH_3, A is N and R_4 is as defined in table Y.

Table A-24 provides 22 compounds A-24.001 to A-24.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is CH_2CF_3, X is SO, X_1 is NCH_3, A is N and R_4 is as defined in table Y.

Table A-25 provides 22 compounds A-25.001 to A-25.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is 

, X is S, X_1 is NCH_3, A is N and R_4 is as defined in table Y.

Table A-26 provides 22 compounds A-26.001 to A-26.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is 

, X is SO, X_1 is NCH_3, A is N and R_4 is as defined in table Y.

Table A-27 provides 22 compounds A-27.001 to A-27.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is 

, X is SO_2, X_1 is NCH_3, A is N and R_4 is as defined in table Y.

Table A-28 provides 22 compounds A-28.001 to A-28.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is CH_2CH_3, X is S, X_1 is NCH_3, A is CH and R_4 is as defined in table Y.

Table A-29 provides 22 compounds A-29.001 to A-29.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is CH_2CH_3, X is SO, X_1 is NCH_3, A is CH and R_4 is as defined in table Y.

Table A-30 provides 22 compounds A-30.001 to A-30.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is CH_2CH_3, X is SO_2, X_1 is NCH_3, A is CH and R_4 is as defined in table Y.

Table A-31 provides 22 compounds A-31.001 to A-31.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is Cyp, X is S, X_1 is NCH_3, A is CH and R_4 is as defined in table Y.

Table A-32 provides 22 compounds A-32.001 to A-32.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is Cyp, X is SO, X_1 is NCH_3, A is CH and R_4 is as defined in table Y.

Table A-33 provides 22 compounds A-33.001 to A-33.022 of formula Iaa wherein R_1 is CH_2CH_3, R_2 is CF_3, R_3 is Cyp, X is SO_2, X_1 is NCH_3, A is CH and R_4 is as defined in table Y.

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, molluscs, nematodes or representatives of the order Acarina. The insecticidal, molluscicidal, nematicidal 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, a good activity corresponding to a destruction rate (mortality) of at least 50 to 60%.

In this regard, certain compounds of formula (I) 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 experimental procedures similar to or adapted from those outlined in the biological examples, using lower application rates if necessary, for example 50 ppm, 12.5 ppm, 6 ppm, 3 ppm, 1.5 ppm, 0.8 ppm or 0.2 ppm.

Further it has surprisingly found that that compounds of formula (I) show advantageous physico-chemical properties for application in crop protection, in particular reduced melting point, reduced lipophilicity and increased water solubility. Such properties have been found to be advantageous for plant uptake and systemic distribution, see for example A. Buchholz, S. Trapp, Pest Manag Sci 2016; 72: 929-939) in order to control certain pest species named below.

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, Calipitrimerus spp., Chorioptes spp., Dermanyssus gallinae, Dermatophagoides spp, Eotetranychus spp, Eriophyes spp., Hemitarsonemus spp, Hyalomma spp., Ixodes spp., Olygonychus spp, Ornithodoros spp., Polyphagotarsone latus, Panonychus spp., Phyllocoptruta 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.;
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 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.,

Rhyssomatus aubtilis, Rhizopertha spp., Scarabeidae, Sitophilus spp., Sitotroga spp., Somaticus spp, Sphenophorus spp, Sternechus subsignatus, Tenebrio spp., Tribolium spp. and Trogoderma spp.;
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 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, Amblypelta nitida, Bathycoelia thalassina, Blissus spp, Cimex spp., Clavigralla tomentosicollis, Creontiades spp, Distantiella theobroma, Dichelops furcatus, Dysdercus spp., Edessa spp, Euschistus spp., Eurydema pulchrum, Eurygaster spp., Halyomorpha halys, Horcias nobilellus, Leptocorisa 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 , Triatoma spp., Vatiga 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 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, Macrosiphum spp., Mahanarva spp, Metcalfa pruinosa, Metopolophium dirhodum, Myndus crudus, Myzus spp., Neotoxoptera sp, Nephotettix 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 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 erytreae , Unaspis citri, Zygina flammigera, Zyginidia scutellaris, ;
from the order *Hymenoptera*, for example,

Acromyrmex, Arge spp, Atta spp., Cephus spp., 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, Corniternes cumulans, Incisitermes spp, Macrotermes spp, Mastotermes spp, Microtermes spp, Reticulitermes spp.; Solenopsis geminate

from the order *Lepidoptera*, for example,

Acleris spp., Adoxophyes spp., Aegeria spp., Agrotis spp., Alabama argillaceae, Amylois spp., Anticarsia gemmatalis, Archips spp., Argyresthia 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 perspectalis, Diatraea spp., Diparopsis castanea, Earias spp., Eldana saccharina, Ephestia spp., Epinotia spp, Estigmene acrea, Etiella zinckinella, Eucosma spp., Eupoecilia ambiguella, Euproctis spp., Euxoa spp., Feltia jaculiferia, Grapholita spp., Hedya nubiferana, Heliothis spp., Hellula undalis, Herpetogramma spp, Hyphantria cunea, Keiferia lycopersicella, Lasmopalpus lignosellus, Leucoptera scitella, Lithocollethis 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 gossypiela, Perileucoptera coffeella, Pseudaletia unipuncta, Phthorimaea operculella, Pieris rapae, Pieris spp., Plutella xylostella, Prays spp., Pseudoplusia spp, 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,

Damalinea spp. and Trichodectes spp.;

from the order *Orthoptera*, for example,

Blatta spp., Blattella spp., Gryllotalpa spp., Leucophaea 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;

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.

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 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 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, Cinnamonium or camphor; and also tobacco, nuts, coffee, eggplants, sugarcane, tea, pepper, 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., *Anisodontea capsenisis*, *Anthemis* spp., *Antirrhinum* spp., *Aster* 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*, *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.
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 vulgarus, Brassica* spp. (*B. Oleracea, B. Pekinensis, B. rapa*), *Capsicum annuum, Cicer arietinum, Cichorium endivia, Cichorum* spp. (*C. intybus, C. endivia*),

Citrillus lanatus, *Cucumis* spp. (*C. sativus, C. melo*), *Cucurbita* spp. (*C. pepo, C. maxima*), *Cyanara* spp. (*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.*
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 potatos) and Chilo supressalis (preferably in rice).

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In a further aspect, the invention may also relate to a method of controlling damage to plant and 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 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; Spiral nematodes, Heliocotylenchus 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 curvitatus, 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, Paratrichodorus 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.. Particularly, the nematode species Meloidogyne spp.(*Melodoigyne incognita*), Heterodera spp. (*Heterodera schachtii*), Rotylenchus spp. and Pratylenchus spp. can be controlled by compounds of the invention.

The compounds of the invention may also have activity against the molluscs. Examples of which 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. gagates, M. marginatus, M. sowerbyi); Opeas; Pomacea (P. canaticulata); Vallonia and Zanitoides.

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

channels, juvenile hormone esterase, diuretic hormone receptors, stilbene synthase, bibenzyl synthase, chitinases and glucanases.

In the context of the present invention there are to be understood by δ-endotoxins, for example Cry1Ab, Cry1Ac, Cry1F, Cry1Fa2, Cry2Ab, Cry3A, Cry3Bb1 or Cry9C, or vegetative insecticidal proteins (Vip), for example Vip1, Vip2, Vip3 or Vip3A, expressly also hybrid toxins, truncated toxins and modified toxins. Hybrid toxins are produced recombinantly by a new combination of different domains of those proteins (see, for example, WO 02/15701). Truncated toxins, for example a truncated Cry1Ab, are known. In the case of modified toxins, one or more amino acids of the naturally occurring toxin are replaced. In such amino acid replacements, preferably non-naturally present protease recognition sequences are inserted into the toxin, such as, for example, in the case of Cry3A055, a cathepsin-G-recognition sequence is inserted into a Cry3A toxin (see WO 03/018810). Examples of such toxins or transgenic plants capable of synthesising such toxins are disclosed, for example, in EP-A-0 374 753, WO 93/07278, WO 95/34656, EP-A-0 427 529, EP-A-451 878 and WO 03/052073.

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

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

1. **Bt11 Maize** from Syngenta Seeds SAS, Chemin de l'Hobit 27, F-31 790 St. Sauveur, France, registration number C/FR/96/05/10. Genetically modified *Zea mays* which has been rendered resistant to attack by the European corn borer (*Ostrinia nubilalis* and *Sesamia nonagrioides*) by transgenic

expression of a truncated Cry1Ab toxin. Bt11 maize also transgenically expresses the enzyme PAT to achieve tolerance to the herbicide glufosinate ammonium.

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

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

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

5. **IPC 531 Cotton** from Monsanto Europe S.A. 270-272 Avenue de Tervuren, B-1150 Brussels, Belgium, registration number C/ES/96/02.

6. **1507 Maize** from Pioneer Overseas Corporation, Avenue Tedesco, 7 B-1160 Brussels, Belgium, registration number C/NL/00/10. Genetically modified maize for the expression of the protein Cry1F for achieving resistance to certain Lepidoptera insects and of the PAT protein for achieving tolerance to the herbicide glufosinate ammonium.

7. **NK603 × MON 810 Maize** from Monsanto Europe S.A. 270-272 Avenue de Tervuren, B-1150 Brussels, Belgium, registration number C/GB/02/M3/03. Consists of conventionally bred hybrid maize varieties by crossing the genetically modified varieties NK603 and MON 810. NK603 × MON 810 Maize transgenically expresses the protein CP4 EPSPS, obtained from *Agrobacterium sp.* strain CP4, which imparts tolerance to the herbicide Roundup® (contains glyphosate), and also a Cry1Ab toxin obtained from *Bacillus thuringiensis subsp. kurstaki* which brings about tolerance to certain Lepidoptera, include the European corn borer.

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 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/). 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.

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.

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:

Table A. Examples of exotic woodborers of economic importance.

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

Table B. Examples of native woodborers of economic importance.

Family	Species	Host or Crop Infested
Buprestidae	*Agrilus anxius*	Birch
	Agrilus politus	Willow, Maple
	Agrilus sayi	Bayberry, Sweetfern
	Agrilus vittaticolllis	Apple, Pear, Cranberry, Serviceberry, Hawthorn

Family	Species	Host or Crop Infested
	Chrysobothris femorata	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
	Texania campestris	Basswood, Beech, Maple, Oak, Sycamore, Willow, Yellow-poplar
Cerambycidae	*Goes pulverulentus*	Beech, Elm, Nuttall, Willow, Black oak, Cherrybark oak, Water oak, Sycamore
	Goes tigrinus	Oak
	Neoclytus acuminatus	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
	Neoptychodes trilineatus	Fig, Alder, Mulberry, Willow, Netleaf hackberry
	Oberea ocellata	Sumac, Apple, Peach, Plum, Pear, Currant, Blackberry
	Oberea tripunctata	Dogwood, Viburnum, Elm, Sourwood, Blueberry, Rhododendron, Azalea, Laurel, Poplar, Willow, Mulberry

Family	Species	Host or Crop Infested
	Oncideres cingulata	Hickory, Pecan, Persimmon, Elm, Sourwood, Basswood, Honeylocust, Dogwood, Eucalyptus, Oak, Hackberry, Maple, Fruit trees
	Saperda calcarata	Poplar
	Strophiona nitens	Chestnut, Oak, Hickory, Walnut, Beech, Maple
Scolytidae	*Corthylus columbianus*	Maple, Oak, Yellow-poplar, Beech, Boxelder, Sycamore, Birch, Basswood, Chestnut, Elm
	Dendroctonus frontalis	Pine
	Dryocoetes betulae	Birch, Sweetgum, Wild cherry, Beech, Pear
	Monarthrum fasciatum	Oak, Maple, Birch, Chestnut, Sweetgum, Blackgum, Poplar, Hickory, Mimosa, Apple, Peach, Pine
	Phloeotribus liminaris	Peach, Cherry, Plum, Black cherry, Elm, Mulberry, Mountain-ash
	Pseudopityophthorus pruinosus	Oak, American beech, Black cherry, Chickasaw plum, Chestnut, Maple, Hickory, Hornbeam, Hophornbeam
Sesiidae	*Paranthrene simulans*	Oak, American chestnut
	Sannina uroceriformis	Persimmon
	Synanthedon exitiosa	Peach, Plum, Nectarine, Cherry, Apricot, Almond, Black cherry
	Synanthedon pictipes	Peach, Plum, Cherry, Beach, Black Cherry
	Synanthedon rubrofascia	Tupelo

Family	Species	Host or Crop Infested
	Synanthedon scitula	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 cynodoniensis)*, rhodesgrass mealybug (*Antonina graminis),* two-lined spittlebug (*Propsapia 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 Nematocerina and Brachycerina, 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..

Of the order Siphonapterida, for example Pulex spp., Ctenocephalides spp., Xenopsylla spp., Ceratophyllus spp..

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

Of the order Blattarida, for example Blatta orientalis, Periplaneta americana, Blattelagermanica and Supella spp..

Of the subclass Acaria (Acarida) and the orders Meta- and Meso-stigmata, for example Argas spp., Ornithodorus 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..

Of the orders Actinedida (Prostigmata) and Acaridida (Astigmata), for example Acarapis spp., Cheyletiella spp., Ornithocheyletia spp., Myobia spp., Psorergatesspp., Demodex spp., Trombicula spp., Listrophorus 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..

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 pilosis, Anobium punctatum, Xestobium rufovillosum, Ptilinuspecticornis, Dendrobium pertinex, Ernobius mollis, Priobium carpini, Lyctus brunneus, Lyctus africanus, Lyctus planicollis, Lyctus linearis, Lyctus pubescens, Trogoxylon aequale, Minthesrugicollis, Xyleborus spec.,Tryptodendron spec., Apate monachus, Bostrychus capucins, 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 Kalotermes 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 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, microemulsifiable 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, hexadecane, hexylene glycol, isoamyl acetate, isobornyl acetate, isooctane, isophorone, isopropylbenzene, isopropyl myristate, lactic acid, laurylamine, mesityl oxide, methoxy-propanol, methyl isoamyl ketone, methyl isobutyl ketone, methyl laurate, methyl octanoate, methyl oleate, methylene chloride, m-xylene, *n*-hexane, *n*-octylamine, octadecanoic acid, octylamine acetate, oleic acid, oleylamine, o-xylene, phenol, polyethylene glycol, propionic acid, propyl lactate, propylene carbonate, 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.

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. 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 tridecylalcohol ethoxylate; soaps, such as sodium stearate; salts of alkylnaphthalenesulfonates, such as sodium dibutylnaphthalenesulfonate; dialkyl esters of sulfosuccinate salts, such as sodium di(2-ethylhexyl)sulfosuccinate; sorbitol esters, such as sorbitol oleate; quaternary amines, such as 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-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, 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 an oil of animal origin, such as fish oil or beef tallow. Preferred oil additives comprise alkyl esters of C_8-C_{22} fatty acids, especially the methyl derivatives of C_{12}-C_{18} 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, 10th Edition, Southern Illinois University, 2010.

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.
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.

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 %
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 %

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 %
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 %

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

Wettable powders	a)	b)	c)
active ingredients	25 %	50 %	75 %
sodium lignosulfonate	5 %	5 %	-
sodium lauryl sulfate	3 %	-	5 %
sodium diisobutylnaphthalenesulfonate	-	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.

Powders for dry seed treatment	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.

Dusts	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.

Extruder granules	
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.

Coated granules	
Active ingredients	8 %

polyethylene glycol (mol. wt. 200)	3 %
Kaolin	89 %

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

Suspension concentrate

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

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

Flowable concentrate for seed treatment

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

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

Slow Release Capsule Suspension

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

obtained capsule suspension is stabilized by adding 0.25 parts of a thickener and 3 parts of a dispersing agent. The capsule suspension formulation contains 28% of the active ingredients. The medium capsule diameter is 8-15 microns. The resulting formulation is applied to seeds as an aqueous suspension in an apparatus suitable for that purpose.

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

Preparatory Examples:

"Mp" means melting point in °C. Free radicals represent methyl groups. ^{1}H NMR measurements were recorded on a Brucker 400MHz spectrometer, chemical shifts are given in ppm relevant to a TMS standard. Spectra measured in deuterated solvents as indicated. 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 $(M+H)^+$.

LCMS Methods:

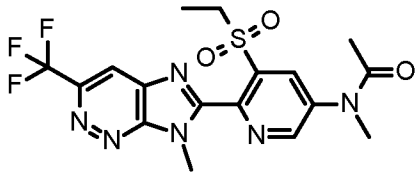
Method 1:

Spectra were recorded on a Mass Spectrometer from Agilent Technologies (6410 Triple Quadruple Mass Spectrometer) equipped with an electrospray source (Polarity: Positive and Negative Polarity Switch, Capillary: 4.00 kV, Fragmentor: 100.00 V, Gas Temperature: 350 °C, Gas Flow: 11 L/min, Nebulizer Gas: 45 psi, Mass range: 110-1000 Da, DAD Wavelength range: 210-400 nm). Column: KINETEX EVO C18, length 50 mm, diameter 4.6 mm, particle size 2.6 µm. Column oven temperature 40 °C. Solvent gradient: A= Water with 0.1% formic acid : Acetonitrile (95:5 v/v). B= Acetonitrile with 0.1% formic acid. Gradient= 0 min 90% A, 10% B; 0.9-1.8 min 0% A, 100% B, 2.2-2.5 min 90% A, 10% B. Flow rate 1.8 mL/min.

Method 2:

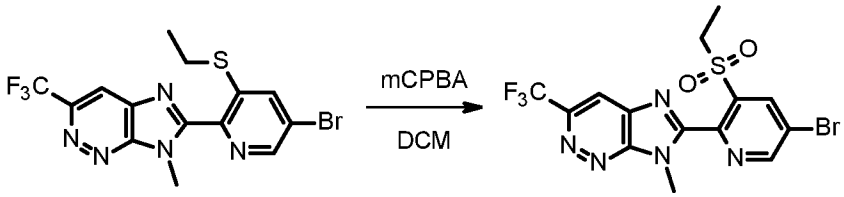
Spectra were recorded on a Mass Spectrometer from Waters (Acquity SDS Mass Spectrometer) equipped with an electrospray source (Polarity: Positive and Negative Polarity Switch, Capillary: 3.00 kV, Cone Voltage: 41.00 V, Source temperature: 150 °C, Desolvation Gas Flow: 1000 L/Hr, Desolvation temperature: 500 °C, Gas Flow @Cone: 50 L/hr, Mass range: 110-800 Da, PDA wavelength range: 210-400 nm.Column: Acquity UPLC HSS T3 C18, length 30 mm, diameter 2.1 mm, particle size 1.8 µm. Column oven temperature 40 °C. Solvent gradient: A= Water with 0.1% formic acid: Acetonitrile (95:5 v/v). B= Acetonitrile with 0.05% formic acid. Gradient= 0 min 90% A, 10% B; 0.2 min 50% A, 50% B; 0.7-1.3 min 0% A, 100% B; 1.4-1.6 min 90% A, 10% B. Flow rate 0.6 mL/min.

Example H1: Preparation of N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]-N-methyl-acetamide (compound P1)



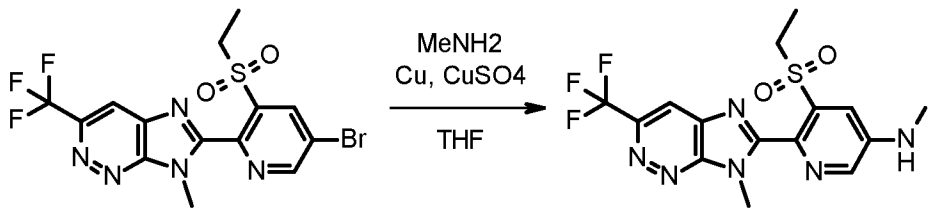
(P1)

Step A: Synthesis of 6-(5-bromo-3-ethylsulfonyl-2-pyridyl)-7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazine



To a solution of 6-(5-bromo-3-ethylsulfanyl-2-pyridyl)-7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazine (WO16/059145) (7.0 g, 16.74 mmol) in dichloromethane DCM (105 mL) was added m-chloroperoxybenzoic acid mCPBA (9.49 g, 38.50 mmol, 2.3 eq.) portionwise at 0-5°C. The reaction mixture was stirred at room temperature for 2 hours. Then a 2N aqueous NaOH solution was added and phases were separated. The organic layer was washed with water and brine, dried over anhydrous sodium sulfate, filtered and concentrate under reduce pressure. The crude was purified by chromatography over silica gel to afford 6-(5-bromo-3-ethylsulfonyl-2-pyridyl)-7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazine (7.1 g). LCMS (method 2): Rt: 1.05 min, 450/452 $(M+H)^+$. ^1H NMR (400 MHz, $CDCl_3$) δ ppm 1.42 (t, *J*=7.46 Hz, 3H), 3.84 (q, *J*=7.46 Hz, 2H), 4.10 (s, 3H), 8.21 (s, 1H), 8.71 (d, *J*=2.20 Hz, 1H), 9.11 (d, *J*=2.08 Hz, 1H).

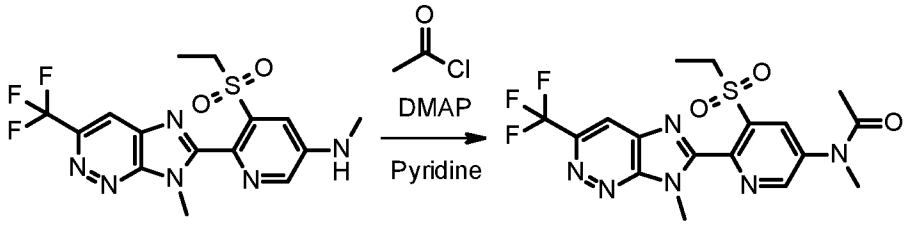
Step B: Synthesis of 5-ethylsulfonyl-N-methyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]pyridin-3-amine



A vessel was charged with a mixture of a 6-(5-bromo-3-ethylsulfonyl-2-pyridyl)-7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazine (3.0 g, 6.7 mmol), 40% aqueous methanamine $MeNH_2$ (7.2 mL, 80 mmol, 12 eq.), copper(II) sulfate (0.21 g, 1.3 mmol, 0.2 eq.) and copper (0.085 g, 1.3 mmol, 0.2 eq.) in tetrahydrofuran THF (3 mL). The vessel was closed and the mixture stirred at 100°C for 4 hours. The reaction mixture was cooled to room temperature, quenched with water and extracted with ethyl acetate (2x). The combined organic layers were washed with water and brine, dried with

anhydrous sodium sulfate and concentrated under reduced pressure. The crude was purified by flash chromatography over silica gel to afford 5-ethyl-sulfonyl-N-methyl-6-[7-methyl-3-(trifluoromethyl) imidazo[4,5-c]pyridazin-6-yl]pyridin-3-amine (1.86 g). LCMS (method 2): Rt: 1.02 min, 401 $(M+H)^+$.
^1H NMR (400 MHz, d_6-DMSO) δ ppm 1.21 (t, *J*=7.40 Hz, 3H), 2.89 (d, *J*=5.01 Hz, 3H), 3.79 (q, *J*=7.34 Hz, 2H), 3.92 (s, 3H), 7.28 (q, *J*=4.77 Hz, 1H), 7.48 (d, *J*=2.57 Hz, 1H), 8.36 (d, *J*=2.57 Hz, 1H), 8.67 (s, 1H).

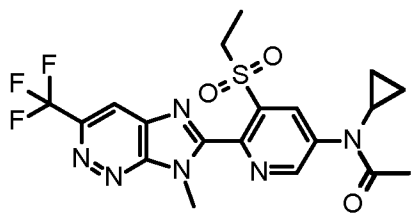
Step C: Synthesis of N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]-N-methyl-acetamide (title compound P1)



(P1)

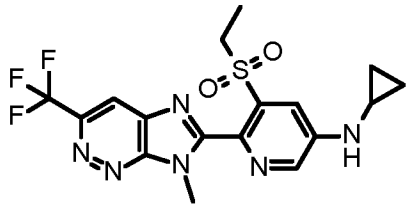
To a suspension of 5-ethylsulfonyl-N-methyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]pyridin-3-amine (1.86 g, 4.65 mmol) in pyridine (9.30 mL) was added N,N-dimethylpyridin-4-amine DMAP (0.115 g, 0.929 mmol, 0.2 eq.), followed by acetyl chloride (0.66 mL, 9.29 mmol, 2 eq.) dropwise at room temperature. The reaction mixture was stirred at room temperature for 2 hours, quenched with water (100 mL) and extracted with ethyl acetate (2x 100 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude was purified by flash chromatography over silica gel to afford N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]-N-methyl-acetamide (P1) (1.5 g).
LCMS (method 2): Rt: 0.90 min, 443 $(M+H)^+$.
^1H NMR (400 MHz, $CDCl_3$) δ ppm 1.41 (t, *J*=7.46 Hz, 3H), 2.31 (br s, 3H), 3.56 (s, 3H), 3.83 (q, *J*=7.46 Hz, 2H), 4.11 (s, 3H), 8.19 (s, 1H), 8.44 (d, *J*=2.20 Hz, 1H), 9.02 (br s, 1H).

Example H2: Preparation of N-cyclopropyl-N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]acetamide (compound P7)



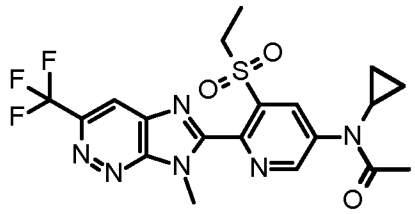
(P7)

Step A: Synthesis of N-cyclopropyl-5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]pyridin-3-amine



To a solution of 6-(5-bromo-3-ethylsulfonyl-2-pyridyl)-7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazine (prepared as described above) (1.0 g, 2.2 mmol) in anhydrous toluene (10 mL) was added cesium carbonate (1.1 g, 3.3 mmol) and the solution was degassed with nitrogen for 15 minutes. Tris(dibenzylideneacetone)dipalladium(0) (0.082 g, 0.089 mmol), 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP, 0.11 g, 0.18 mmol) and cyclopropanamine (0.19 g, 3.3 mmol, 0.23 mL) were added to the reaction mixture, which was heated at 110°C for 3 hours in the microwave. The mixture was diluted with water (20ml), the product extracted with ethyl acetate (3x 20ml), the combined organic layers dried over sodium sulfate, filtered and evaporated *in vacuo*. The crude was purified by combiflash (60% ethyl acetate in cyclohexane) to afford N-cyclopropyl-5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]pyridin-3-amine (300 mg). LCMS (method 2): Rt: 1.01 min, 427 $(M+H)^+$. ^1H NMR (400 MHz, MeOH-d_4) δ ppm 0.51 (m, 2H), 0.81 (m, 2H), 1.22 (t, 3H), 2.51 (m, 1H), 3.64 (q, 2H), 3.89 (s, 3H), 7.67 (d, 1H), 8.31 (s, 1H), 8.36 (d, 1H).

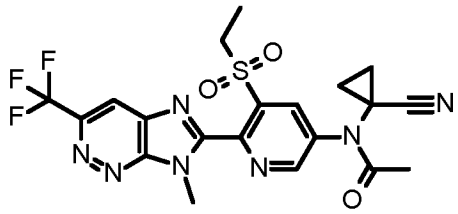
Step B: Synthesis of N-cyclopropyl-N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]acetamide (title compound P7)



(P7)

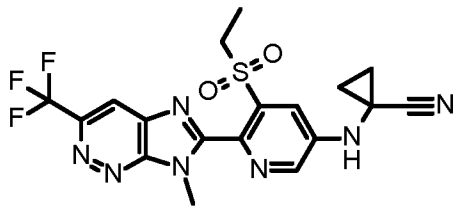
To a solution of N-cyclopropyl-5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]pyridin-3-amine (190 mg, 0.45 mmol) in pyridine (1.9 mL) was added N,N-dimethylpyridin-4-amine (11 mg, 0.089 mmol, 0.2 equiv), followed by acetyl chloride (0.070 g, 0.89 mmol) at room temperature. The reaction mixture was stirred at room temperature for 3 hours. The mixture was quenched with ice cold water, the product extracted with ethyl acetate (3x 50 mL), the combined organic layers dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The crude was purified by combiflash (70% ethyl acetate in cyclohexane) to afford N-cyclopropyl-N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]acetamide (compound P7) as a solid. LCMS (method 2): Rt: 0.98 min, 469 $(M+H)^+$. ^1H NMR (400 MHz, $CDCl_3$) δ ppm 0.79 (m, 2H), 1.27 (m, 2H), 1.41 (t, J=7.46 Hz, 3H), 2.53 (s, 3H), 3.26 (m, 1H), 3.81 (q, J=7.46 Hz, 2H), 4.11 (s, 3H), 8.18 (s, 1H), 8.47 (d, J=2.32 Hz, 1H), 9.06 (d, J=2.32 Hz, 1H).

Example H3: Preparation of N-(1-cyanocyclopropyl)-N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]acetamide (compound P8)



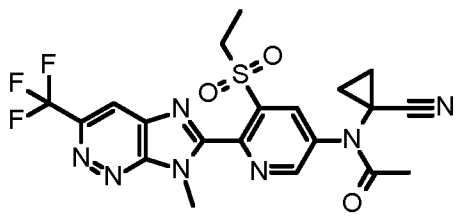
(P8)

Step A: Synthesis of 1-[[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]amino]cyclopropanecarbonitrile



To a solution of 6-(5-bromo-3-ethylsulfonyl-2-pyridyl)-7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazine (prepared as described above) (0.8 g, 1.78 mmol) in 1,4-dioxane (12 mL) were added cesium carbonate (2.32 g, 7.11 mmol), 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (XPHOS, 0.156 g, 0.32 mmol), and (1-cyanocyclopropyl)ammonium chloride (0.316 g, 2.66 mmol). The mixture was degassed with nitrogen for 20 minutes and palladium(II) acetate (0.024 g, 0.1066 mmol) was added. The reaction mixture was heated at 110°C for 1.5 hours in the microwave, then poured into water (30ml), and the product extracted with ethyl acetate (3x 20ml). The combined organic layers were washed with an aqueous saturated sodium chloride solution (30ml), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude was purified by combiflash (60-65% ethyl acetate in cyclohexane) to afford 1-[[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]amino]cyclopropanecarbonitrile (560 mg). LCMS (method 2): Rt: 0.96 min, 452 $(M+H)^+$. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 1.24 (t, 3H), 1.40 (m, 2H), 1.77 (m, 2H), 3.82 (q, 2H), 3.96 (s, 3H), 7.77 (d, 1H), 8.33 (s, 1H), 8.60 (d, 1H), 8.73 (s, 1H).

Step B: Synthesis of N-(1-cyanocyclopropyl)-N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]acetamide (title compound P8)

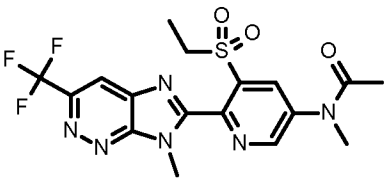
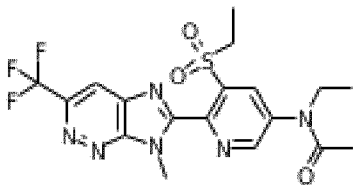
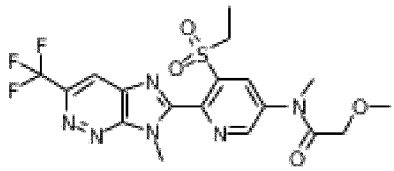
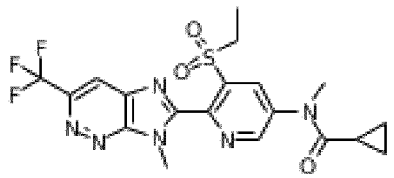
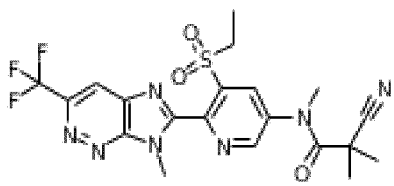
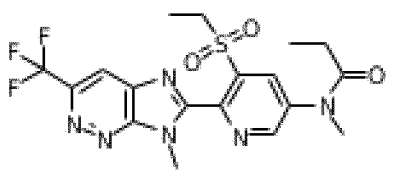


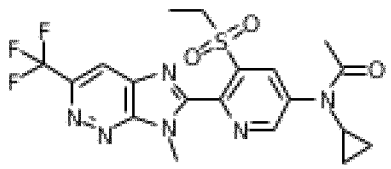
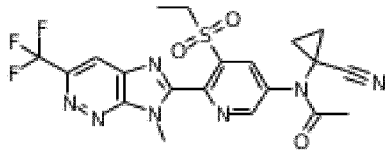
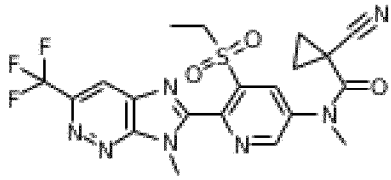
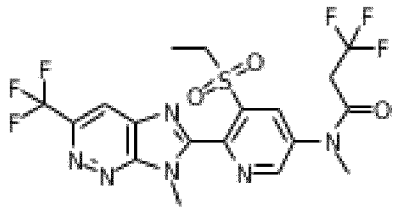
(P8)

To a solution of 1-[[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]amino]cyclopropanecarbonitrile (500 mg, 1.11 mmol) in N,N-dimethylformamide (10 mL) at 0°C was added sodium hydride (60 mass%, 37 mg, 2 eq.) and the mixture stirred for 20 minutes. Acetyl

acetate (0.467 g, 4.44 mmol, 0.433 mL) was added and the mixture stirred at room temperature for 6 hours. The reaction mixture was quenched with ice cold water (50ml) and the product extracted with ethyl acetate (3x 50ml). The combined organic layers were washed with water and brine, dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (50% ethyl acetate in cyclohexane) to afford N-(1-cyanocyclopropyl)-N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]acetamide (compound P8) as a white solid. LCMS (method 2): Rt: 0.98 min, 494 $(M+H)^+$. ^1H NMR (400 MHz, $CDCl_3$) δ ppm 1.44 (t, J=7.46 Hz, 3H), 1.51 (m, 2H), 1.99 (m, 2H), 2.55 (s, 3H), 3.87 (q, J=7.46 Hz, 2H), 4.16 (s, 3H), 8.22 (s, 1H), 8.49 (d, J=2.32 Hz, 1H), 9.07 (d, J=2.32 Hz, 1H).

Table P: Examples of compounds of formula (I)

Entry	IUPAC name	STRUCTURE	RT (min)	$[M+H]^+$	Method	mp °C
P1	N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl) imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]-N-methyl-acetamide		0.90	443	2	172 - 174
P2	N-ethyl-N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]acetamide		0.91	457	2	152 - 154
P3	N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]-2-methoxy-N-methyl-acetamide		0.91	473	2	103 - 105
P4	N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]-N-methyl-cyclopropanecarboxamide		0.93	469	2	154 - 156
P5	2-cyano-N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]-N,2-dimethyl-propanamide		1.01	496	2	106 - 108
P6	N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]-N-methyl-propanamide		0.96	457	2	166 - 168

Entry	IUPAC name	STRUCTURE	RT (min)	$[M+H]^+$	Method	mp °C
P7	N-cyclopropyl-N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]acetamide		0.98	469	2	167 - 169
P8	N-(1-cyanocyclopropyl)-N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]acetamide		0.98	494	2	179 - 180
P9	1-cyano-N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]-N-methyl-cyclopropanecarboxamide		0.98	494	2	233 - 235
P10	N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]-3,3,3-trifluoro-N-methyl-propanamide		1.02	511	2	160 - 161

The activity of the compositions according to the invention can be broadened considerably, and adapted to prevailing circumstances, by adding other insecticidally, acaricidally and/or fungicidally active ingredients. The mixtures of the compounds of formula I with other insecticidally, acaricidally and/or fungicidally active ingredients may also have further surprising advantages which can also be described, in a wider sense, as synergistic activity. For example, better tolerance by plants, reduced phytotoxicity, insects can be controlled in their different development stages or better behaviour during their production, for example during grinding or mixing, during their storage or during their use. Suitable additions to active ingredients here are, for example, representatives of the following classes of active ingredients: organophosphorus compounds, nitrophenol derivatives, thioureas, juvenile hormones, formamidines, benzophenone derivatives, ureas, pyrrole derivatives, carbamates, pyrethroids, chlorinated hydrocarbons, acylureas, pyridylmethyleneamino derivatives, macrolides, neonicotinoids and Bacillus thuringiensis preparations.

The following mixtures of the compounds of formula I with active ingredients are preferred (the abbreviation “TX” means “one compound selected from the group consisting of the compounds described in Tables A-1 to A-33 and Table P of the present invention”):
an adjuvant selected from the group of substances consisting of petroleum oils (alternative name) (628) + TX,
an acaricide selected from the group of substances consisting of 1,1-bis(4-chlorophenyl)-2-ethoxyethanol (IUPAC name) (910) + TX, 2,4-dichlorophenyl benzenesulfonate (IUPAC/Chemical

Abstracts name) (1059) + TX, 2-fluoro-*N*-methyl-*N*-1-naphthylacetamide (IUPAC name) (1295) + TX, 4-chlorophenyl phenyl sulfone (IUPAC name) (981) + TX, abamectin (1) + TX, acequinocyl (3) + TX, acetoprole [CCN] + TX, acrinathrin (9) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, alpha-cypermethrin (202) + TX, amidithion (870) + TX, amidoflumet [CCN] + TX, amidothioate (872) + TX, amiton (875) + TX, amiton hydrogen oxalate (875) + TX, amitraz (24) + TX, aramite (881) + TX, arsenous oxide (882) + TX, AVI 382 (compound code) + TX, AZ 60541 (compound code) + TX, azinphos-ethyl (44) + TX, azinphos-methyl (45) + TX, azobenzene (IUPAC name) (888) + TX, azocyclotin (46) + TX, azothoate (889) + TX, benomyl (62) + TX, benoxafos (alternative name) [CCN] + TX, benzoximate (71) + TX, benzyl benzoate (IUPAC name) [CCN] + TX, bifenazate (74) + TX, bifenthrin (76) + TX, binapacryl (907) + TX, brofenvalerate (alternative name) + TX, bromocyclen (918) + TX, bromophos (920) + TX, bromophos-ethyl (921) + TX, bromopropylate (94) + TX, buprofezin (99) + TX, butocarboxim (103) + TX, butoxycarboxim (104) + TX, butylpyridaben (alternative name) + TX, calcium polysulfide (IUPAC name) (111) + TX, camphechlor (941) + TX, carbanolate (943) + TX, carbaryl (115) + TX, carbofuran (118) + TX, carbophenothion (947) + TX, CGA 50'439 (development code) (125) + TX, chinomethionat (126) + TX, chlorbenside (959) + TX, chlordimeform (964) + TX, chlordimeform hydrochloride (964) + TX, chlorfenapyr (130) + TX, chlorfenethol (968) + TX, chlorfenson (970) + TX, chlorfensulfide (971) + TX, chlorfenvinphos (131) + TX, chlorobenzilate (975) + TX, chloromebuform (977) + TX, chloromethiuron (978) + TX, chloropropylate (983) + TX, chlorpyrifos (145) + TX, chlorpyrifos-methyl (146) + TX, chlorthiophos (994) + TX, cinerin I (696) + TX, cinerin II (696) + TX, cinerins (696) + TX, clofentezine (158) + TX, closantel (alternative name) [CCN] + TX, coumaphos (174) + TX, crotamiton (alternative name) [CCN] + TX, crotoxyphos (1010) + TX, cufraneb (1013) + TX, cyanthoate (1020) + TX, cyflumetofen (CAS Reg. No.: 400882-07-7) + TX, cyhalothrin (196) + TX, cyhexatin (199) + TX, cypermetrin (201) + TX, DCPM (1032) + TX, DDT (219) + TX, demephion (1037) + TX, demephion-O (1037) + TX, demephion-S (1037) + TX, demeton (1038) + TX, demeton-methyl (224) + TX, demeton-O (1038) + TX, demeton-O-methyl (224) + TX, demeton-S (1038) + TX, demeton-S-methyl (224) + TX, demeton-S-methylsulfon (1039) + TX, diafenthiuron (226) + TX, dimpropyridaz + TX, dialifos (1042) + TX, diazinon (227) + TX, dichlofluanid (230) + TX, dichlorvos (236) + TX, dicliphos (alternative name) + TX, dicofol (242) + TX, dicrotophos (243) + TX, dienochlor (1071) + TX, dimefox (1081) + TX, dimethoate (262) + TX, dinactin (alternative name) (653) + TX, dinex (1089) + TX, dinex-diclexine (1089) + TX, dinobuton (269) + TX, dinocap (270) + TX, dinocap-4 [CCN] + TX, dinocap-6 [CCN] + TX, dinocton (1090) + TX, dinopenton (1092) + TX, dinosulfon (1097) + TX, dinoterbon (1098) + TX, dioxathion (1102) + TX, diphenyl sulfone (IUPAC name) (1103) + TX, disulfiram (alternative name) [CCN] + TX, disulfoton (278) + TX, DNOC (282) + TX, dofenapyn (1113) + TX, doramectin (alternative name) [CCN] + TX, endosulfan (294) + TX, endothion (1121) + TX, EPN (297) + TX, eprinomectin (alternative name) [CCN] + TX, ethion (309) + TX, ethoate-methyl (1134) + TX, etoxazole (320) + TX, etrimfos (1142) + TX, fenazaflor (1147) + TX, fenazaquin (328) + TX, fenbutatin oxide (330) + TX, fenothiocarb (337) + TX, fenpropathrin (342) + TX, fenpyrad (alternative name) + TX, fenpyroximate (345) + TX,

fenson (1157) + TX, fentrifanil (1161) + TX, fenvalerate (349) + TX, fipronil (354) + TX, fluacrypyrim (360) + TX, fluazuron (1166) + TX, flubenzimine (1167) + TX, flucycloxuron (366) + TX, flucythrinate (367) + TX, fluenetil (1169) + TX, flufenoxuron (370) + TX, flumethrin (372) + TX, fluorbenside (1174) + TX, fluvalinate (1184) + TX, FMC 1137 (development code) (1185) + TX, formetanate (405) + TX, formetanate hydrochloride (405) + TX, formothion (1192) + TX, formparanate (1193) + TX, gamma-HCH (430) + TX, glyodin (1205) + TX, halfenprox (424) + TX, heptenophos (432) + TX, hexadecyl cyclopropanecarboxylate (IUPAC/Chemical Abstracts name) (1216) + TX, hexythiazox (441) + TX, iodomethane (IUPAC name) (542) + TX, isocarbophos (alternative name) (473) + TX, isopropyl *O*-(methoxyaminothiophosphoryl)salicylate (IUPAC name) (473) + TX, ivermectin (alternative name) [CCN] + TX, jasmolin I (696) + TX, jasmolin II (696) + TX, jodfenphos (1248) + TX, lindane (430) + TX, lufenuron (490) + TX, malathion (492) + TX, malonoben (1254) + TX, mecarbam (502) + TX, mephosfolan (1261) + TX, mesulfen (alternative name) [CCN] + TX, methacrifos (1266) + TX, methamidophos (527) + TX, methidathion (529) + TX, methiocarb (530) + TX, methomyl (531) + TX, methyl bromide (537) + TX, metolcarb (550) + TX, mevinphos (556) + TX, mexacarbate (1290) + TX, milbemectin (557) + TX, milbemycin oxime (alternative name) [CCN] + TX, mipafox (1293) + TX, monocrotophos (561) + TX, morphothion (1300) + TX, moxidectin (alternative name) [CCN] + TX, naled (567) + TX, NC-184 (compound code) + TX, NC-512 (compound code) + TX, nifluridide (1309) + TX, nikkomycins (alternative name) [CCN] + TX, nitrilacarb (1313) + TX, nitrilacarb 1:1 zinc chloride complex (1313) + TX, NNI-0101 (compound code) + TX, NNI-0250 (compound code) + TX, omethoate (594) + TX, oxamyl (602) + TX, oxydeprofos (1324) + TX, oxydisulfoton (1325) + TX, pp'-DDT (219) + TX, parathion (615) + TX, permethrin (626) + TX, petroleum oils (alternative name) (628) + TX, phenkapton (1330) + TX, phenthoate (631) + TX, phorate (636) + TX, phosalone (637) + TX, phosfolan (1338) + TX, phosmet (638) + TX, phosphamidon (639) + TX, phoxim (642) + TX, pirimiphos-methyl (652) + TX, polychloroterpenes (traditional name) (1347) + TX, polynactins (alternative name) (653) + TX, proclonol (1350) + TX, profenofos (662) + TX, promacyl (1354) + TX, propargite (671) + TX, propetamphos (673) + TX, propoxur (678) + TX, prothidathion (1360) + TX, prothoate (1362) + TX, pyrethrin I (696) + TX, pyrethrin II (696) + TX, pyrethrins (696) + TX, pyridaben (699) + TX, pyridaphenthion (701) + TX, pyrimidifen (706) + TX, pyrimitate (1370) + TX, quinalphos (711) + TX, quintiofos (1381) + TX, R-1492 (development code) (1382) + TX, RA-17 (development code) (1383) + TX, rotenone (722) + TX, schradan (1389) + TX, sebufos (alternative name) + TX, selamectin (alternative name) [CCN] + TX, SI-0009 (compound code) + TX, sophamide (1402) + TX, spirodiclofen (738) + TX, spiromesifen (739) + TX, SSI-121 (development code) (1404) + TX, sulfiram (alternative name) [CCN] + TX, sulfluramid (750) + TX, sulfotep (753) + TX, sulfur (754) + TX, SZI-121 (development code) (757) + TX, tau-fluvalinate (398) + TX, tebufenpyrad (763) + TX, TEPP (1417) + TX, terbam (alternative name) + TX, tetrachlorvinphos (777) + TX, tetradifon (786) + TX, tetranactin (alternative name) (653) + TX, tetrasul (1425) + TX, thiafenox (alternative name) + TX, thiocarboxime (1431) + TX, thiofanox (800) + TX, thiometon (801) + TX, thioquinox (1436) + TX, thuringiensin (alternative name) [CCN] + TX, triamiphos

(1441) + TX, triarathene (1443) + TX, triazophos (820) + TX, triazuron (alternative name) + TX, trichlorfon (824) + TX, trifenofos (1455) + TX, trinactin (alternative name) (653) + TX, vamidothion (847) + TX, vaniliprole [CCN] and YI-5302 (compound code) + TX,

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

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

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

a bactericide selected from the group of substances consisting of 1-hydroxy-1*H*-pyridine-2-thione (IUPAC name) (1222) + TX, 4-(quinoxalin-2-ylamino)benzenesulfonamide (IUPAC name) (748) + TX, 8-hydroxyquinoline sulfate (446) + TX, bronopol (97) + TX, copper dioctanoate (IUPAC name) (170) + TX, copper hydroxide (IUPAC name) (169) + TX, cresol [CCN] + TX, dichlorophen (232) + TX, dipyrithione (1105) + TX, dodicin (1112) + TX, fenaminosulf (1144) + TX, formaldehyde (404) + TX, hydrargaphen (alternative name) [CCN] + TX, kasugamycin (483) + TX, kasugamycin hydrochloride hydrate (483) + TX, nickel bis(dimethyldithiocarbamate) (IUPAC name) (1308) + TX, nitrapyrin (580) + TX, octhilinone (590) + TX, oxolinic acid (606) + TX, oxytetracycline (611) + TX, potassium hydroxyquinoline sulfate (446) + TX, probenazole (658) + TX, streptomycin (744) + TX, streptomycin sesquisulfate (744) + TX, tecloftalam (766) + TX, and thiomersal (alternative name) [CCN] + TX,

a biological agent selected from the group of substances consisting of *Adoxophyes orana* GV (alternative name) (12) + TX, *Agrobacterium radiobacter* (alternative name) (13) + TX, *Amblyseius* spp. (alternative name) (19) + TX, *Anagrapha falcifera* NPV (alternative name) (28) + TX, *Anagrus atomus* (alternative name) (29) + TX, *Aphelinus abdominalis* (alternative name) (33) + TX, *Aphidius colemani* (alternative name) (34) + TX, *Aphidoletes aphidimyza* (alternative name) (35) + TX, *Autographa californica* NPV (alternative name) (38) + TX, *Bacillus firmus* (alternative name) (48) + TX, *Bacillus sphaericus* Neide (scientific name) (49) + TX, *Bacillus thuringiensis* Berliner (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *aizawai* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *israelensis* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *japonensis* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *kurstaki* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *tenebrionis* (scientific name) (51) + TX, *Beauveria bassiana* (alternative

name) (53) + TX, *Beauveria brongniartii* (alternative name) (54) + TX, *Chrysoperla carnea* (alternative name) (151) + TX, *Cryptolaemus montrouzieri* (alternative name) (178) + TX, *Cydia pomonella* GV (alternative name) (191) + TX, *Dacnusa sibirica* (alternative name) (212) + TX, *Diglyphus isaea* (alternative name) (254) + TX, *Encarsia formosa* (scientific name) (293) + TX, *Eretmocerus eremicus* (alternative name) (300) + TX, *Helicoverpa zea* NPV (alternative name) (431) + TX, *Heterorhabditis bacteriophora* and *H. megidis* (alternative name) (433) + TX, *Hippodamia convergens* (alternative name) (442) + TX, *Leptomastix dactylopii* (alternative name) (488) + TX, *Macrolophus caliginosus* (alternative name) (491) + TX, *Mamestra brassicae* NPV (alternative name) (494) + TX, *Metaphycus helvolus* (alternative name) (522) + TX, *Metarhizium anisopliae* var. *acridum* (scientific name) (523) + TX, *Metarhizium anisopliae* var. *anisopliae* (scientific name) (523) + TX, *Neodiprion sertifer* NPV and *N. lecontei* NPV (alternative name) (575) + TX, *Orius* spp. (alternative name) (596) + TX, *Paecilomyces fumosoroseus* (alternative name) (613) + TX, *Phytoseiulus persimilis* (alternative name) (644) + TX, *Spodoptera exigua* multicapsid nuclear polyhedrosis virus (scientific name) (741) + TX, *Steinernema bibionis* (alternative name) (742) + TX, *Steinernema carpocapsae* (alternative name) (742) + TX, *Steinernema feltiae* (alternative name) (742) + TX, *Steinernema glaseri* (alternative name) (742) + TX, *Steinernema riobrave* (alternative name) (742) + TX, *Steinernema riobravis* (alternative name) (742) + TX, *Steinernema scapterisci* (alternative name) (742) + TX, *Steinernema* spp. (alternative name) (742) + TX, *Trichogramma* spp. (alternative name) (826) + TX, *Typhlodromus occidentalis* (alternative name) (844) and *Verticillium lecanii* (alternative name) (848) + TX,

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

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

an insect pheromone selected from the group of substances consisting of (*E*)-dec-5-en-1-yl acetate with (*E*)-dec-5-en-1-ol (IUPAC name) (222) + TX, (*E*)-tridec-4-en-1-yl acetate (IUPAC name) (829) + TX, (*E*)-6-methylhept-2-en-4-ol (IUPAC name) (541) + TX, (*E,Z*)-tetradeca-4,10-dien-1-yl acetate (IUPAC name) (779) + TX, (*Z*)-dodec-7-en-1-yl acetate (IUPAC name) (285) + TX, (*Z*)-hexadec-11-enal (IUPAC name) (436) + TX, (*Z*)-hexadec-11-en-1-yl acetate (IUPAC name) (437) + TX, (*Z*)-hexadec-13-en-11-yn-1-yl acetate (IUPAC name) (438) + TX, (*Z*)-icos-13-en-10-one (IUPAC name) (448) + TX, (*Z*)-tetradec-7-en-1-al (IUPAC name) (782) + TX, (*Z*)-tetradec-9-en-1-ol (IUPAC name) (783) + TX, (*Z*)-tetradec-9-en-1-yl acetate (IUPAC name) (784) + TX, (7*E*,9*Z*)-dodeca-7,9-dien-1-yl acetate (IUPAC name) (283) + TX, (9*Z*,11*E*)-tetradeca-9,11-dien-1-yl acetate (IUPAC name) (780) + TX, (9*Z*,12*E*)-tetradeca-9,12-dien-1-yl acetate (IUPAC name) (781) + TX, 14-methyloctadec-1-ene

(IUPAC name) (545) + TX, 4-methylnonan-5-ol with 4-methylnonan-5-one (IUPAC name) (544) + TX, alpha-multistriatin (alternative name) [CCN] + TX, brevicomin (alternative name) [CCN] + TX, codlelure (alternative name) [CCN] + TX, codlemone (alternative name) (167) + TX, cuelure (alternative name) (179) + TX, disparlure (277) + TX, dodec-8-en-1-yl acetate (IUPAC name) (286) + TX, dodec-9-en-1-yl acetate (IUPAC name) (287) + TX, dodeca-8 + TX, 10-dien-1-yl acetate (IUPAC name) (284) + TX, dominicalure (alternative name) [CCN] + TX, ethyl 4-methyloctanoate (IUPAC name) (317) + TX, eugenol (alternative name) [CCN] + TX, frontalin (alternative name) [CCN] + TX, gossyplure (alternative name) (420) + TX, grandlure (421) + TX, grandlure I (alternative name) (421) + TX, grandlure II (alternative name) (421) + TX, grandlure III (alternative name) (421) + TX, grandlure IV (alternative name) (421) + TX, hexalure [CCN] + TX, ipsdienol (alternative name) [CCN] + TX, ipsenol (alternative name) [CCN] + TX, japonilure (alternative name) (481) + TX, lineatin (alternative name) [CCN] + TX, litlure (alternative name) [CCN] + TX, looplure (alternative name) [CCN] + TX, medlure [CCN] + TX, megatomoic acid (alternative name) [CCN] + TX, methyl eugenol (alternative name) (540) + TX, muscalure (563) + TX, octadeca-2,13-dien-1-yl acetate (IUPAC name) (588) + TX, octadeca-3,13-dien-1-yl acetate (IUPAC name) (589) + TX, orfralure (alternative name) [CCN] + TX, oryctalure (alternative name) (317) + TX, ostramone (alternative name) [CCN] + TX, siglure [CCN] + TX, sordidin (alternative name) (736) + TX, sulcatol (alternative name) [CCN] + TX, tetradec-11-en-1-yl acetate (IUPAC name) (785) + TX, trimedlure (839) + TX, trimedlure A (alternative name) (839) + TX, trimedlure B_1 (alternative name) (839) + TX, trimedlure B_2 (alternative name) (839) + TX, trimedlure C (alternative name) (839) and trunc-call (alternative name) [CCN] + TX,

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

an insecticide selected from the group of substances consisting of 1-dichloro-1-nitroethane (IUPAC/Chemical Abstracts name) (1058) + TX, 1,1-dichloro-2,2-bis(4-ethylphenyl)ethane (IUPAC name) (1056), + TX, 1,2-dichloropropane (IUPAC/Chemical Abstracts name) (1062) + TX, 1,2-dichloropropane with 1,3-dichloropropene (IUPAC name) (1063) + TX, 1-bromo-2-chloroethane (IUPAC/Chemical Abstracts name) (916) + TX, 2,2,2-trichloro-1-(3,4-dichlorophenyl)ethyl acetate (IUPAC name) (1451) + TX, 2,2-dichlorovinyl 2-ethylsulfinylethyl methyl phosphate (IUPAC name) (1066) + TX, 2-(1,3-dithiolan-2-yl)phenyl dimethylcarbamate (IUPAC/ Chemical Abstracts name) (1109) + TX, 2-(2-butoxyethoxy)ethyl thiocyanate (IUPAC/Chemical Abstracts name) (935) + TX, 2-(4,5-dimethyl-1,3-dioxolan-2-yl)phenyl methylcarbamate (IUPAC/ Chemical Abstracts name) (1084) + TX, 2-(4-chloro-3,5-xylyloxy)ethanol (IUPAC name) (986) + TX, 2-chlorovinyl diethyl phosphate (IUPAC name) (984) + TX, 2-imidazolidone (IUPAC name) (1225) + TX, 2-isovalerylindan-1,3-dione (IUPAC name) (1246) + TX, 2-methyl(prop-2-ynyl)aminophenyl methylcarbamate (IUPAC name)

(1284) + TX, 2-thiocyanatoethyl laurate (IUPAC name) (1433) + TX, 3-bromo-1-chloroprop-1-ene (IUPAC name) (917) + TX, 3-methyl-1-phenylpyrazol-5-yl dimethylcarbamate (IUPAC name) (1283) + TX, 4-methyl(prop-2-ynyl)amino-3,5-xylyl methylcarbamate (IUPAC name) (1285) + TX, 5,5-dimethyl-3-oxocyclohex-1-enyl dimethylcarbamate (IUPAC name) (1085) + TX, abamectin (1) + TX, acephate (2) + TX, acetamiprid (4) + TX, acethion (alternative name) [CCN] + TX, acetoprole [CCN] + TX, acrinathrin (9) + TX, acrylonitrile (IUPAC name) (861) + TX, alanycarb (15) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, aldrin (864) + TX, allethrin (17) + TX, allosamidin (alternative name) [CCN] + TX, allyxycarb (866) + TX, alpha-cypermethrin (202) + TX, alpha-ecdysone (alternative name) [CCN] + TX, aluminium phosphide (640) + TX, amidithion (870) + TX, amidothioate (872) + TX, aminocarb (873) + TX, amiton (875) + TX, amiton hydrogen oxalate (875) + TX, amitraz (24) + TX, anabasine (877) + TX, athidathion (883) + TX, AVI 382 (compound code) + TX, AZ 60541 (compound code) + TX, azadirachtin (alternative name) (41) + TX, azamethiphos (42) + TX, azinphos-ethyl (44) + TX, azinphos-methyl (45) + TX, azothoate (889) + TX, *Bacillus thuringiensis* delta endotoxins (alternative name) (52) + TX, barium hexafluorosilicate (alternative name) [CCN] + TX, barium polysulfide (IUPAC/Chemical Abstracts name) (892) + TX, barthrin [CCN] + TX, Bayer 22/190 (development code) (893) + TX, Bayer 22408 (development code) (894) + TX, bendiocarb (58) + TX, benfuracarb (60) + TX, bensultap (66) + TX, beta-cyfluthrin (194) + TX, beta-cypermethrin (203) + TX, bifenthrin (76) + TX, bioallethrin (78) + TX, bioallethrin *S*-cyclopentenyl isomer (alternative name) (79) + TX, bioethanomethrin [CCN] + TX, biopermethrin (908) + TX, bioresmethrin (80) + TX, bis(2-chloroethyl) ether (IUPAC name) (909) + TX, bistrifluron (83) + TX, borax (86) + TX, brofenvalerate (alternative name) + TX, bromfenvinfos (914) + TX, bromocyclen (918) + TX, bromo-DDT (alternative name) [CCN] + TX, bromophos (920) + TX, bromophos-ethyl (921) + TX, bufencarb (924) + TX, buprofezin (99) + TX, butacarb (926) + TX, butathiofos (927) + TX, butocarboxim (103) + TX, butonate (932) + TX, butoxycarboxim (104) + TX, butylpyridaben (alternative name) + TX, cadusafos (109) + TX, calcium arsenate [CCN] + TX, calcium cyanide (444) + TX, calcium polysulfide (IUPAC name) (111) + TX, camphechlor (941) + TX, carbanolate (943) + TX, carbaryl (115) + TX, carbofuran (118) + TX, carbon disulfide (IUPAC/Chemical Abstracts name) (945) + TX, carbon tetrachloride (IUPAC name) (946) + TX, carbophenothion (947) + TX, carbosulfan (119) + TX, cartap (123) + TX, cartap hydrochloride (123) + TX, cevadine (alternative name) (725) + TX, chlorbicyclen (960) + TX, chlordane (128) + TX, chlordecone (963) + TX, chlordimeform (964) + TX, chlordimeform hydrochloride (964) + TX, chlorethoxyfos (129) + TX, chlorfenapyr (130) + TX, chlorfenvinphos (131) + TX, chlorfluazuron (132) + TX, chlormephos (136) + TX, chloroform [CCN] + TX, chloropicrin (141) + TX, chlorphoxim (989) + TX, chlorprazophos (990) + TX, chlorpyrifos (145) + TX, chlorpyrifos-methyl (146) + TX, chlorthiophos (994) + TX, chromafenozide (150) + TX, cinerin I (696) + TX, cinerin II (696) + TX, cinerins (696) + TX, cis-resmethrin (alternative name) + TX, cismethrin (80) + TX, clocythrin (alternative name) + TX, cloethocarb (999) + TX, closantel (alternative name) [CCN] + TX, clothianidin (165) + TX, copper acetoarsenite [CCN] + TX, copper arsenate [CCN] + TX, copper oleate [CCN] + TX, coumaphos (174) + TX, coumithoate (1006) +

TX, crotamiton (alternative name) [CCN] + TX, crotoxyphos (1010) + TX, crufomate (1011) + TX, cryolite (alternative name) (177) + TX, CS 708 (development code) (1012) + TX, cyanofenphos (1019) + TX, cyanophos (184) + TX, cyanthoate (1020) + TX, cyclethrin [CCN] + TX, cycloprothrin (188) + TX, cyfluthrin (193) + TX, cyhalothrin (196) + TX, cypermethrin (201) + TX, cyphenothrin (206) + TX, cyromazine (209) + TX, cythioate (alternative name) [CCN] + TX, *d*-limonene (alternative name) [CCN] + TX, *d*-tetramethrin (alternative name) (788) + TX, DAEP (1031) + TX, dazomet (216) + TX, DDT (219) + TX, decarbofuran (1034) + TX, deltamethrin (223) + TX, demephion (1037) + TX, demephion-O (1037) + TX, demephion-S (1037) + TX, demeton (1038) + TX, demeton-methyl (224) + TX, demeton-O (1038) + TX, demeton-O-methyl (224) + TX, demeton-S (1038) + TX, demeton-S-methyl (224) + TX, demeton-S-methylsulphon (1039) + TX, diafenthiuron (226) + TX, dialifos (1042) + TX, diamidafos (1044) + TX, diazinon (227) + TX, dicapthon (1050) + TX, dichlofenthion (1051) + TX, dichlorvos (236) + TX, dicliphos (alternative name) + TX, dicresyl (alternative name) [CCN] + TX, dicrotophos (243) + TX, dicyclanil (244) + TX, dieldrin (1070) + TX, diethyl 5-methylpyrazol-3-yl phosphate (IUPAC name) (1076) + TX, diflubenzuron (250) + TX, dilor (alternative name) [CCN] + TX, dimefluthrin [CCN] + TX, dimefox (1081) + TX, dimetan (1085) + TX, dimethoate (262) + TX, dimethrin (1083) + TX, dimethylvinphos (265) + TX, dimetilan (1086) + TX, dinex (1089) + TX, dinex-diclexine (1089) + TX, dinoprop (1093) + TX, dinosam (1094) + TX, dinoseb (1095) + TX, dinotefuran (271) + TX, diofenolan (1099) + TX, dioxabenzofos (1100) + TX, dioxacarb (1101) + TX, dioxathion (1102) + TX, disulfoton (278) + TX, dithicrofos (1108) + TX, DNOC (282) + TX, doramectin (alternative name) [CCN] + TX, DSP (1115) + TX, ecdysterone (alternative name) [CCN] + TX, EI 1642 (development code) (1118) + TX, emamectin (291) + TX, emamectin benzoate (291) + TX, EMPC (1120) + TX, empenthrin (292) + TX, endosulfan (294) + TX, endothion (1121) + TX, endrin (1122) + TX, EPBP (1123) + TX, EPN (297) + TX, epofenonane (1124) + TX, eprinomectin (alternative name) [CCN] + TX, esfenvalerate (302) + TX, etaphos (alternative name) [CCN] + TX, ethiofencarb (308) + TX, ethion (309) + TX, ethiprole (310) + TX, ethoate-methyl (1134) + TX, ethoprophos (312) + TX, ethyl formate (IUPAC name) [CCN] + TX, ethyl-DDD (alternative name) (1056) + TX, ethylene dibromide (316) + TX, ethylene dichloride (chemical name) (1136) + TX, ethylene oxide [CCN] + TX, etofenprox (319) + TX, etrimfos (1142) + TX, EXD (1143) + TX, famphur (323) + TX, fenamiphos (326) + TX, fenazaflor (1147) + TX, fenchlorphos (1148) + TX, fenethacarb (1149) + TX, fenfluthrin (1150) + TX, fenitrothion (335) + TX, fenobucarb (336) + TX, fenoxacrim (1153) + TX, fenoxycarb (340) + TX, fenpirithrin (1155) + TX, fenpropathrin (342) + TX, fenpyrad (alternative name) + TX, fensulfothion (1158) + TX, fenthion (346) + TX, fenthion-ethyl [CCN] + TX, fenvalerate (349) + TX, fipronil (354) + TX, flonicamid (358) + TX, flubendiamide (CAS. Reg. No.: 272451-65-7) + TX, flucofuron (1168) + TX, flucycloxuron (366) + TX, flucythrinate (367) + TX, fluenetil (1169) + TX, flufenerim [CCN] + TX, flufenoxuron (370) + TX, flufenprox (1171) + TX, flumethrin (372) + TX, fluvalinate (1184) + TX, FMC 1137 (development code) (1185) + TX, fonofos (1191) + TX, formetanate (405) + TX, formetanate hydrochloride (405) + TX, formothion (1192) + TX, formparanate (1193) + TX, fosmethilan (1194) + TX, fospirate

(1195) + TX, fosthiazate (408) + TX, fosthietan (1196) + TX, furathiocarb (412) + TX, furethrin (1200) + TX, gamma-cyhalothrin (197) + TX, gamma-HCH (430) + TX, guazatine (422) + TX, guazatine acetates (422) + TX, GY-81 (development code) (423) + TX, halfenprox (424) + TX, halofenozide (425) + TX, HCH (430) + TX, HEOD (1070) + TX, heptachlor (1211) + TX, heptenophos (432) + TX, heterophos [CCN] + TX, hexaflumuron (439) + TX, HHDN (864) + TX, hydramethylnon (443) + TX, hydrogen cyanide (444) + TX, hydroprene (445) + TX, hyquincarb (1223) + TX, imidacloprid (458) + TX, imiprothrin (460) + TX, indoxacarb (465) + TX, iodomethane (IUPAC name) (542) + TX, IPSP (1229) + TX, isazofos (1231) + TX, isobenzan (1232) + TX, isocarbophos (alternative name) (473) + TX, isodrin (1235) + TX, isofenphos (1236) + TX, isolane (1237) + TX, isoprocarb (472) + TX, isopropyl *O*-(methoxy-aminothiophosphoryl)salicylate (IUPAC name) (473) + TX, isoprothiolane (474) + TX, isothioate (1244) + TX, isoxathion (480) + TX, ivermectin (alternative name) [CCN] + TX, jasmolin I (696) + TX, jasmolin II (696) + TX, jodfenphos (1248) + TX, juvenile hormone I (alternative name) [CCN] + TX, juvenile hormone II (alternative name) [CCN] + TX, juvenile hormone III (alternative name) [CCN] + TX, kelevan (1249) + TX, kinoprene (484) + TX, lambda-cyhalothrin (198) + TX, lead arsenate [CCN] + TX, lepimectin (CCN) + TX, leptophos (1250) + TX, lindane (430) + TX, lirimfos (1251) + TX, lufenuron (490) + TX, lythidathion (1253) + TX, *m*-cumenyl methylcarbamate (IUPAC name) (1014) + TX, magnesium phosphide (IUPAC name) (640) + TX, malathion (492) + TX, malonoben (1254) + TX, mazidox (1255) + TX, mecarbam (502) + TX, mecarphon (1258) + TX, menazon (1260) + TX, mephosfolan (1261) + TX, mercurous chloride (513) + TX, mesulfenfos (1263) + TX, metaflumizone (CCN) + TX, metam (519) + TX, metam-potassium (alternative name) (519) + TX, metam-sodium (519) + TX, methacrifos (1266) + TX, methamidophos (527) + TX, methanesulfonyl fluoride (IUPAC/Chemical Abstracts name) (1268) + TX, methidathion (529) + TX, methiocarb (530) + TX, methocrotophos (1273) + TX, methomyl (531) + TX, methoprene (532) + TX, methoquin-butyl (1276) + TX, methothrin (alternative name) (533) + TX, methoxychlor (534) + TX, methoxyfenozide (535) + TX, methyl bromide (537) + TX, methyl isothiocyanate (543) + TX, methylchloroform (alternative name) [CCN] + TX, methylene chloride [CCN] + TX, metofluthrin [CCN] + TX, metolcarb (550) + TX, metoxadiazone (1288) + TX, mevinphos (556) + TX, mexacarbate (1290) + TX, milbemectin (557) + TX, milbemycin oxime (alternative name) [CCN] + TX, mipafox (1293) + TX, mirex (1294) + TX, monocrotophos (561) + TX, morphothion (1300) + TX, moxidectin (alternative name) [CCN] + TX, naftalofos (alternative name) [CCN] + TX, naled (567) + TX, naphthalene (IUPAC/Chemical Abstracts name) (1303) + TX, NC-170 (development code) (1306) + TX, NC-184 (compound code) + TX, nicotine (578) + TX, nicotine sulfate (578) + TX, nifluridide (1309) + TX, nitenpyram (579) + TX, nithiazine (1311) + TX, nitrilacarb (1313) + TX, nitrilacarb 1:1 zinc chloride complex (1313) + TX, NNI-0101 (compound code) + TX, NNI-0250 (compound code) + TX, nornicotine (traditional name) (1319) + TX, novaluron (585) + TX, noviflumuron (586) + TX, *O*-5-dichloro-4-iodophenyl *O*-ethyl ethylphosphonothioate (IUPAC name) (1057) + TX, *O,O*-diethyl *O*-4-methyl-2-oxo-2*H*-chromen-7-yl phosphorothioate (IUPAC name) (1074) + TX, *O,O*-diethyl *O*-6-methyl-2-propylpyrimidin-4-yl phosphorothioate (IUPAC name) (1075) + TX,

O,O,O',O'-tetrapropyl dithiopyrophosphate (IUPAC name) (1424) + TX, oleic acid (IUPAC name) (593) + TX, omethoate (594) + TX, oxamyl (602) + TX, oxydemeton-methyl (609) + TX, oxydeprofos (1324) + TX, oxydisulfoton (1325) + TX, pp'-DDT (219) + TX, para-dichlorobenzene [CCN] + TX, parathion (615) + TX, parathion-methyl (616) + TX, penfluron (alternative name) [CCN] + TX, pentachlorophenol (623) + TX, pentachlorophenyl laurate (IUPAC name) (623) + TX, permethrin (626) + TX, petroleum oils (alternative name) (628) + TX, PH 60-38 (development code) (1328) + TX, phenkapton (1330) + TX, phenothrin (630) + TX, phenthoate (631) + TX, phorate (636) + TX, phosalone (637) + TX, phosfolan (1338) + TX, phosmet (638) + TX, phosnichlor (1339) + TX, phosphamidon (639) + TX, phosphine (IUPAC name) (640) + TX, phoxim (642) + TX, phoxim-methyl (1340) + TX, pirimetaphos (1344) + TX, pirimicarb (651) + TX, pirimiphos-ethyl (1345) + TX, pirimiphos-methyl (652) + TX, polychlorodicyclopentadiene isomers (IUPAC name) (1346) + TX, polychloroterpenes (traditional name) (1347) + TX, potassium arsenite [CCN] + TX, potassium thiocyanate [CCN] + TX, prallethrin (655) + TX, precocene I (alternative name) [CCN] + TX, precocene II (alternative name) [CCN] + TX, precocene III (alternative name) [CCN] + TX, primidophos (1349) + TX, profenofos (662) + TX, profluthrin [CCN] + TX, promacyl (1354) + TX, promecarb (1355) + TX, propaphos (1356) + TX, propetamphos (673) + TX, propoxur (678) + TX, prothidathion (1360) + TX, prothiofos (686) + TX, prothoate (1362) + TX, protrifenbute [CCN] + TX, pymetrozine (688) + TX, pyraclofos (689) + TX, pyrazophos (693) + TX, pyresmethrin (1367) + TX, pyrethrin I (696) + TX, pyrethrin II (696) + TX, pyrethrins (696) + TX, pyridaben (699) + TX, pyridalyl (700) + TX, pyridaphenthion (701) + TX, pyrimidifen (706) + TX, pyrimitate (1370) + TX, pyriproxyfen (708) + TX, quassia (alternative name) [CCN] + TX, quinalphos (711) + TX, quinalphos-methyl (1376) + TX, quinothion (1380) + TX, quintiofos (1381) + TX, R-1492 (development code) (1382) + TX, rafoxanide (alternative name) [CCN] + TX, resmethrin (719) + TX, rotenone (722) + TX, RU 15525 (development code) (723) + TX, RU 25475 (development code) (1386) + TX, ryania (alternative name) (1387) + TX, ryanodine (traditional name) (1387) + TX, sabadilla (alternative name) (725) + TX, schradan (1389) + TX, sebufos (alternative name) + TX, selamectin (alternative name) [CCN] + TX, SI-0009 (compound code) + TX, SI-0205 (compound code) + TX, SI-0404 (compound code) + TX, SI-0405 (compound code) + TX, silafluofen (728) + TX, SN 72129 (development code) (1397) + TX, sodium arsenite [CCN] + TX, sodium cyanide (444) + TX, sodium fluoride (IUPAC/Chemical Abstracts name) (1399) + TX, sodium hexafluorosilicate (1400) + TX, sodium pentachlorophenoxide (623) + TX, sodium selenate (IUPAC name) (1401) + TX, sodium thiocyanate [CCN] + TX, sophamide (1402) + TX, spinosad (737) + TX, spiromesifen (739) + TX, spirotetrmat (CCN) + TX, sulcofuron (746) + TX, sulcofuron-sodium (746) + TX, sulfluramid (750) + TX, sulfotep (753) + TX, sulfuryl fluoride (756) + TX, sulprofos (1408) + TX, tar oils (alternative name) (758) + TX, tau-fluvalinate (398) + TX, tazimcarb (1412) + TX, TDE (1414) + TX, tebufenozide (762) + TX, tebufenpyrad (763) + TX, tebupirimfos (764) + TX, teflubenzuron (768) + TX, tefluthrin (769) + TX, temephos (770) + TX, TEPP (1417) + TX, terallethrin (1418) + TX, terbam (alternative name) + TX, terbufos (773) + TX, tetrachloroethane [CCN] + TX, tetrachlorvinphos (777) + TX, tetramethrin (787) + TX, theta-cypermethrin (204) + TX,

thiacloprid (791) + TX, thiafenox (alternative name) + TX, thiamethoxam (792) + TX, thicrofos (1428) + TX, thiocarboxime (1431) + TX, thiocyclam (798) + TX, thiocyclam hydrogen oxalate (798) + TX, thiodicarb (799) + TX, thiofanox (800) + TX, thiometon (801) + TX, thionazin (1434) + TX, thiosultap (803) + TX, thiosultap-sodium (803) + TX, thuringiensin (alternative name) [CCN] + TX, tolfenpyrad (809) + TX, tralomethrin (812) + TX, transfluthrin (813) + TX, transpermethrin (1440) + TX, triamiphos (1441) + TX, triazamate (818) + TX, triazophos (820) + TX, triazuron (alternative name) + TX, trichlorfon (824) + TX, trichlormetaphos-3 (alternative name) [CCN] + TX, trichloronat (1452) + TX, trifenofos (1455) + TX, triflumuron (835) + TX, trimethacarb (840) + TX, triprene (1459) + TX, vamidothion (847) + TX, vaniliprole [CCN] + TX, veratridine (alternative name) (725) + TX, veratrine (alternative name) (725) + TX, XMC (853) + TX, xylylcarb (854) + TX, YI-5302 (compound code) + TX, zeta-cypermethrin (205) + TX, zetamethrin (alternative name) + TX, zinc phosphide (640) + TX, zolaprofos (1469) and ZXI 8901 (development code) (858) + TX, cyantraniliprole [736994-63-19 + TX, chlorantraniliprole [500008-45-7] + TX, cyenopyrafen [560121-52-0] + TX, cyflumetofen [400882-07-7] + TX, pyrifluquinazon [337458-27-2] + TX, spinetoram [187166-40-1 + 187166-15-0] + TX, spirotetramat [203313-25-1] + TX, sulfoxaflor [946578-00-3] + TX, flufiprole [704886-18-0] + TX, meperfluthrin [915288-13-0] + TX, tetramethylfluthrin [84937-88-2] + TX, triflumezopyrim (disclosed in WO 2012/092115) + TX, fluxametamide (WO 2007/026965) + TX, epsilon-metofluthrin [240494-71-7] + TX, epsilon-momfluorothrin [1065124-65-3] + TX, fluazaindolizine [1254304-22-7] + TX, chloroprallethrin [399572-87-3] + TX, fluxametamide [928783-29-3] + TX, cyhalodiamide [1262605-53-7] + TX, tioxazafen [330459-31-9] + TX, broflanilide [1207727-04-5] + TX, flufiprole [704886-18-0] + TX, cyclaniliprole [1031756-98-5] + TX, tetraniliprole [1229654-66-3] + TX, guadipyr (described in WO2010/060231) + TX, cycloxaprid (described in WO 2005/077934) + TX, spiropidion + TX, Afidopyropen + TX, flupyrimin + TX, Momfluorothrin + TX, kappa-bifenthrin + TX, kappa-tefluthrin + TX, Dichloromezotiaz + TX, Tetrachloraniliprole + TX, benzpyrimoxan + TX;

a molluscicide selected from the group of substances consisting of bis(tributyltin) oxide (IUPAC name) (913) + TX, bromoacetamide [CCN] + TX, calcium arsenate [CCN] + TX, cloethocarb (999) + TX, copper acetoarsenite [CCN] + TX, copper sulfate (172) + TX, fentin (347) + TX, ferric phosphate (IUPAC name) (352) + TX, metaldehyde (518) + TX, methiocarb (530) + TX, niclosamide (576) + TX, niclosamide-olamine (576) + TX, pentachlorophenol (623) + TX, sodium pentachlorophenoxide (623) + TX, tazimcarb (1412) + TX, thiodicarb (799) + TX, tributyltin oxide (913) + TX, trifenmorph (1454) + TX, trimethacarb (840) + TX, triphenyltin acetate (IUPAC name) (347) and triphenyltin hydroxide (IUPAC name) (347) + TX, pyriprole [394730-71-3] + TX,

a nematicide selected from the group of substances consisting of AKD-3088 (compound code) + TX, 1,2-dibromo-3-chloropropane (IUPAC/Chemical Abstracts name) (1045) + TX, 1,2-dichloropropane (IUPAC/ Chemical Abstracts name) (1062) + TX, 1,2-dichloropropane with 1,3-dichloropropene (IUPAC name) (1063) + TX, 1,3-dichloropropene (233) + TX, 3,4-dichlorotetrahydrothiophene 1,1-dioxide (IUPAC/Chemical Abstracts name) (1065) + TX, 3-(4-chlorophenyl)-5-methylrhodanine (IUPAC name) (980) + TX, 5-methyl-6-thioxo-1,3,5-thiadiazinan-3-ylacetic acid (IUPAC name) (1286)

+ TX, 6-isopentenylaminopurine (alternative name) (210) + TX, abamectin (1) + TX, acetoprole [CCN] + TX, alanycarb (15) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, AZ 60541 (compound code) + TX, benclothiaz [CCN] + TX, benomyl (62) + TX, butylpyridaben (alternative name) + TX, cadusafos (109) + TX, carbofuran (118) + TX, carbon disulfide (945) + TX, carbosulfan (119) + TX, chloropicrin (141) + TX, chlorpyrifos (145) + TX, cloethocarb (999) + TX, cytokinins (alternative name) (210) + TX, dazomet (216) + TX, DBCP (1045) + TX, DCIP (218) + TX, diamidafos (1044) + TX, dichlofenthion (1051) + TX, dicliphos (alternative name) + TX, dimethoate (262) + TX, doramectin (alternative name) [CCN] + TX, emamectin (291) + TX, emamectin benzoate (291) + TX, eprinomectin (alternative name) [CCN] + TX, ethoprophos (312) + TX, ethylene dibromide (316) + TX, fenamiphos (326) + TX, fenpyrad (alternative name) + TX, fensulfothion (1158) + TX, fosthiazate (408) + TX, fosthietan (1196) + TX, furfural (alternative name) [CCN] + TX, GY-81 (development code) (423) + TX, heterophos [CCN] + TX, iodomethane (IUPAC name) (542) + TX, isamidofos (1230) + TX, isazofos (1231) + TX, ivermectin (alternative name) [CCN] + TX, kinetin (alternative name) (210) + TX, mecarphon (1258) + TX, metam (519) + TX, metam-potassium (alternative name) (519) + TX, metam-sodium (519) + TX, methyl bromide (537) + TX, methyl isothiocyanate (543) + TX, milbemycin oxime (alternative name) [CCN] + TX, moxidectin (alternative name) [CCN] + TX, *Myrothecium verrucaria* composition (alternative name) (565) + TX, NC-184 (compound code) + TX, oxamyl (602) + TX, phorate (636) + TX, phosphamidon (639) + TX, phosphocarb [CCN] + TX, sebufos (alternative name) + TX, selamectin (alternative name) [CCN] + TX, spinosad (737) + TX, terbam (alternative name) + TX, terbufos (773) + TX, tetrachlorothiophene (IUPAC/ Chemical Abstracts name) (1422) + TX, thiafenox (alternative name) + TX, thionazin (1434) + TX, triazophos (820) + TX, triazuron (alternative name) + TX, xylenols [CCN] + TX, YI-5302 (compound code) and zeatin (alternative name) (210) + TX, fluensulfone [318290-98-1] + TX, fluopyram + TX,

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

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

a rodenticide selected from the group of substances consisting of 2-isovalerylindan-1,3-dione (IUPAC name) (1246) + TX, 4-(quinoxalin-2-ylamino)benzenesulfonamide (IUPAC name) (748) + TX, alpha-chlorohydrin [CCN] + TX, aluminium phosphide (640) + TX, antu (880) + TX, arsenous oxide (882) + TX, barium carbonate (891) + TX, bisthiosemi (912) + TX, brodifacoum (89) + TX, bromadiolone (91) + TX, bromethalin (92) + TX, calcium cyanide (444) + TX, chloralose (127) + TX, chlorophacinone (140) + TX, cholecalciferol (alternative name) (850) + TX, coumachlor (1004) + TX, coumafuryl (1005) + TX, coumatetralyl (175) + TX, crimidine (1009) + TX, difenacoum (246) + TX, difethialone (249) + TX, diphacinone (273) + TX, ergocalciferol (301) + TX, flocoumafen (357) + TX, fluoroacetamide (379) + TX, flupropadine (1183) + TX, flupropadine hydrochloride (1183) + TX, gamma-HCH (430) + TX, HCH (430) + TX, hydrogen cyanide (444) +

TX, iodomethane (IUPAC name) (542) + TX, lindane (430) + TX, magnesium phosphide (IUPAC name) (640) + TX, methyl bromide (537) + TX, norbormide (1318) + TX, phosacetim (1336) + TX, phosphine (IUPAC name) (640) + TX, phosphorus [CCN] + TX, pindone (1341) + TX, potassium arsenite [CCN] + TX, pyrinuron (1371) + TX, scilliroside (1390) + TX, sodium arsenite [CCN] + TX, sodium cyanide (444) + TX, sodium fluoroacetate (735) + TX, strychnine (745) + TX, thallium sulfate [CCN] + TX, warfarin (851) and zinc phosphide (640) + TX,
a synergist selected from the group of substances consisting of 2-(2-butoxyethoxy)ethyl piperonylate (IUPAC name) (934) + TX, 5-(1,3-benzodioxol-5-yl)-3-hexylcyclohex-2-enone (IUPAC name) (903) + TX, farnesol with nerolidol (alternative name) (324) + TX, MB-599 (development code) (498) + TX, MGK 264 (development code) (296) + TX, piperonyl butoxide (649) + TX, piprotal (1343) + TX, propyl isomer (1358) + TX, S421 (development code) (724) + TX, sesamex (1393) + TX, sesasmolin (1394) and sulfoxide (1406) + TX,
an animal repellent selected from the group of substances consisting of anthraquinone (32) + TX, chloralose (127) + TX, copper naphthenate [CCN] + TX, copper oxychloride (171) + TX, diazinon (227) + TX, dicyclopentadiene (chemical name) (1069) + TX, guazatine (422) + TX, guazatine acetates (422) + TX, methiocarb (530) + TX, pyridin-4-amine (IUPAC name) (23) + TX, thiram (804) + TX, trimethacarb (840) + TX, zinc naphthenate [CCN] and ziram (856) + TX,
a virucide selected from the group of substances consisting of imanin (alternative name) [CCN] and ribavirin (alternative name) [CCN] + TX,
a wound protectant selected from the group of substances consisting of mercuric oxide (512) + TX, octhilinone (590) and thiophanate-methyl (802) + TX,

and biologically active compounds selected from the group of substances consisting of azaconazole (60207-31-0] + TX, bitertanol [70585-36-3] + TX, bromuconazole [116255-48-2] + TX, cyproconazole [94361-06-5] + TX, difenoconazole [119446-68-3] + TX, diniconazole [83657-24-3] + TX, epoxiconazole [106325-08-0] + TX, fenbuconazole [114369-43-6] + TX, fluquinconazole [136426-54-5] + TX, flusilazole [85509-19-9] + TX, flutriafol [76674-21-0] + TX, hexaconazole [79983-71-4] + TX, imazalil [35554-44-0] + TX, imibenconazole [86598-92-7] + TX, ipconazole [125225-28-7] + TX, metconazole [125116-23-6] + TX, myclobutanil [88671-89-0] + TX, pefurazoate [101903-30-4] + TX, penconazole [66246-88-6] + TX, prothioconazole [178928-70-6] + TX, pyrifenox [88283-41-4] + TX, prochloraz [67747-09-5] + TX, propiconazole [60207-90-1] + TX, simeconazole [149508-90-7] + TX, tebuconazole [107534-96-3] + TX, tetraconazole [112281-77-3] + TX, triadimefon [43121-43-3] + TX, triadimenol [55219-65-3] + TX, triflumizole [99387-89-0] + TX, triticonazole [131983-72-7] + TX, ancymidol [12771-68-5] + TX, fenarimol [60168-88-9] + TX, nuarimol [63284-71-9] + TX, bupirimate [41483-43-6] + TX, dimethirimol [5221-53-4] + TX, ethirimol [23947-60-6] + TX, dodemorph [1593-77-7] + TX, fenpropidine [67306-00-7] + TX, fenpropimorph [67564-91-4] + TX, spiroxamine [118134-30-8] + TX, tridemorph [81412-43-3] + TX, cyprodinil [121552-61-2] + TX, mepanipyrim [110235-47-7] + TX, pyrimethanil [53112-28-0] + TX, fenpiclonil [74738-17-3] + TX, fludioxonil [131341-86-1] + TX, benalaxyl [71626-11-4] + TX,

furalaxyl [57646-30-7] + TX, metalaxyl [57837-19-1] + TX, R-metalaxyl [70630-17-0] + TX, ofurace [58810-48-3] + TX, oxadixyl [77732-09-3] + TX, benomyl [17804-35-2] + TX, carbendazim [10605-21-7] + TX, debacarb [62732-91-6] + TX, fuberidazole [3878-19-1] + TX, thiabendazole [148-79-8] + TX, chlozolinate [84332-86-5] + TX, dichlozoline [24201-58-9] + TX, iprodione [36734-19-7] + TX, myclozoline [54864-61-8] + TX, procymidone [32809-16-8] + TX, vinclozoline [50471-44-8] + TX, boscalid [188425-85-6] + TX, carboxin [5234-68-4] + TX, fenfuram [24691-80-3] + TX, flutolanil [66332-96-5] + TX, mepronil [55814-41-0] + TX, oxycarboxin [5259-88-1] + TX, penthiopyrad [183675-82-3] + TX, thifluzamide [130000-40-7] + TX, guazatine [108173-90-6] + TX, dodine [2439-10-3] [112-65-2] (free base) + TX, iminoctadine [13516-27-3] + TX, azoxystrobin [131860-33-8] + TX, dimoxystrobin [149961-52-4] + TX, enestroburin {Proc. BCPC, Int. Congr., Glasgow, 2003, **1**, 93} + TX, fluoxastrobin [361377-29-9] + TX, kresoxim-methyl [143390-89-0] + TX, metominostrobin [133408-50-1] + TX, trifloxystrobin [141517-21-7] + TX, orysastrobin [248593-16-0] + TX, picoxystrobin [117428-22-5] + TX, pyraclostrobin [175013-18-0] + TX, ferbam [14484-64-1] + TX, mancozeb [8018-01-7] + TX, maneb [12427-38-2] + TX, metiram [9006-42-2] + TX, propineb [12071-83-9] + TX, thiram [137-26-8] + TX, zineb [12122-67-7] + TX, ziram [137-30-4] + TX, captafol [2425-06-1] + TX, captan [133-06-2] + TX, dichlofluanid [1085-98-9] + TX, fluoroimide [41205-21-4] + TX, folpet [133-07-3] + TX, tolylfluanid [731-27-1] + TX, bordeaux mixture [8011-63-0] + TX, copperhydroxid [20427-59-2] + TX, copperoxychlorid [1332-40-7] + TX, coppersulfat [7758-98-7] + TX, copperoxid [1317-39-1] + TX, mancopper [53988-93-5] + TX, oxine-copper [10380-28-6] + TX, dinocap [131-72-6] + TX, nitrothal-isopropyl [10552-74-6] + TX, edifenphos [17109-49-8] + TX, iprobenphos [26087-47-8] + TX, isoprothiolane [50512-35-1] + TX, phosdiphen [36519-00-3] + TX, pyrazophos [13457-18-6] + TX, tolclofos-methyl [57018-04-9] + TX, acibenzolar-S-methyl [135158-54-2] + TX, anilazine [101-05-3] + TX, benthiavalicarb [413615-35-7] + TX, blasticidin-S [2079-00-7] + TX, chinomethionat [2439-01-2] + TX, chloroneb [2675-77-6] + TX, chlorothalonil *[1897-45-6]* + TX, cyflufenamid *[180409-60-3]* + TX, cymoxanil *[57966-95-7]* + TX, dichlone *[117-80-6]* + TX, diclocymet [139920-32-4] + TX, diclomezine *[62865-36-5]* + TX, dicloran *[99-30-9]* + TX, diethofencarb *[87130-20-9]* + TX, dimethomorph *[110488-70-5]* + TX, SYP-LI90 (Flumorph) *[211867-47-9]* + TX, dithianon *[3347-22-6]* + TX, ethaboxam *[162650-77-3]* + TX, etridiazole *[2593-15-9]* + TX, famoxadone *[131807-57-3] + TX,* fenamidone *[161326-34-7]* + TX, fenoxanil *[115852-48-7]* + TX, fentin *[668-34-8]* + TX, ferimzone *[89269-64-7]* + TX, fluazinam *[79622-59-6]* + TX, fluopicolide [239110-15-7] + TX, flusulfamide [106917-52-6] + TX, fenhexamid [126833-17-8] + TX, fosetyl-aluminium [39148-24-8] + TX, hymexazol [10004-44-1] + TX, iprovalicarb [140923-17-7] + TX, IKF-916 (Cyazofamid) *[120116-88-3]* + TX, kasugamycin [6980-18-3] + TX, methasulfocarb *[66952-49-6]* + TX, metrafenone *[220899-03-6]* + TX, pencycuron *[66063-05-6]* + TX, phthalide [27355-22-2] + TX, polyoxins [11113-80-7] + TX, probenazole [27605-76-1] + TX, propamocarb [25606-41-1] + TX, proquinazid [189278-12-4] + TX, pyroquilon [57369-32-1] + TX, quinoxyfen [124495-18-7] + TX, quintozene [82-68-8] + TX, sulfur [7704-34-9] + TX, tiadinil [223580-51-6] + TX, triazoxide [72459-58-6] + TX, tricyclazole [41814-78-2] + TX, triforine [26644-46-2] + TX, validamycin [37248-47-8] + TX, zoxamide (RH7281) [156052-

68-5] + TX, mandipropamid [374726-62-2] + TX, isopyrazam [881685-58-1] + TX, sedaxane [874967-67-6] + TX, 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (9-dichloromethylene-1,2,3,4-tetrahydro-1,4-methano-naphthalen-5-yl)-amide (disclosed in WO 2007/048556) + TX, 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (3',4',5'-trifluoro-biphenyl-2-yl)-amide (disclosed in WO 2006/087343) + TX, [(3*S*,4*R*,4a*R*,6*S*,6a*S*,12*R*,12a*S*,12b*S*)-3-[(cyclopropylcarbonyl)oxy]-1,3,4,4a,5,6,6a,12,12a,12b-decahydro-6,12-dihydroxy-4,6a,12b-trimethyl-11-oxo-9-(3-pyridinyl)-2*H*,11*H*naphtho[2,1-*b*]pyrano[3,4-*e*]pyran-4-yl]methyl-cyclopropanecarboxylate [915972-17-7] + TX, 1,3,5-trimethyl-N-(2-methyl-1-oxopropyl)-N-[3-(2-methylpropyl)-4-[2,2,2-trifluoro-1-methoxy-1-(trifluoromethyl)ethyl]phenyl]-1H-pyrazole-4-carboxamide [926914-55-8] + TX, lancotrione [1486617-21-3] + TX, florpyrauxifen [943832-81-3] + TX, ipfentrifluconazole[1417782-08-1] + TX, mefentrifluconazole [1417782-03-6] + TX, quinofumelin [861647-84-9] + TX, chloroprallethrin [399572-87-3] + TX, cyhalodiamide [1262605-53-7] + TX, fluazaindolizine [1254304-22-7] + TX, fluxametamide [928783-29-3] + TX, epsilon-metofluthrin [240494-71-7] + TX, epsilon-momfluorothrin [1065124-65-3] + TX, pydiflumetofen [1228284-64-7] + TX, kappa-bifenthrin [439680-76-9] + TX, broflanilide [1207727-04-5] + TX, dicloromezotiaz [1263629-39-5] + TX, dipymetitrone [16114-35-5] + TX, pyraziflumid [942515-63-1] + TX, kappa-tefluthrin [391634-71-2] + TX, fenpicoxamid [517875-34-2] + TX; fluindapyr [1383809-87-7] + TX; flufenpyrrolidone + TX, alpha-bromadiolone [28772-56-7] + TX; flupyrimin [1689566-03-7] + TX; benzpyrimoxan [1449021-97-9] + TX; acynonapyr [1332838-17-1] + TX; inpyrfluxam [1352994-67-2] + TX, isoflucypram [1255734-28-1] + TX; isocycloseram + TX, rescalure [64309-03-1] + TX; aminopyrifen [1531626-08-0] + TX; tyclopyrazoflor [1477919-27-9] + TX; and spiropidion [1229023-00-0] + TX; and

microbials including: *Acinetobacter lwoffii* + TX, *Acremonium alternatum* + TX + TX, *Acremonium cephalosporium* + TX + 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* + TX, (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 CM-1 + TX, *Bacillus chitinosporus* strain AQ746 + TX, *Bacillus licheniformis* strain HB-2 (Biostart™ Rhizoboost®) + TX, *Bacillus licheniformis* strain 3086 (EcoGuard® + TX, Green Releaf®) + TX, *Bacillus circulans* + TX, *Bacillus firmus* (BioSafe® + TX, BioNem-WP® + TX, VOTiVO®) + TX, *Bacillus firmus* strain I-1582 + 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 GB34 (Yield Shield®) + TX, *Bacillus pumilus* strain AQ717 + TX, *Bacillus pumilus* strain QST 2808 (Sonata® + TX, Ballad Plus®) + TX, *Bacillus spahericus* (VectoLex®) + TX, *Bacillus* spp. + TX, *Bacillus* spp. strain AQ175 + TX, *Bacillus* spp. strain AQ177 + TX, *Bacillus* spp. strain AQ178 + TX, *Bacillus subtilis* strain QST 713 (CEASE® + TX, Serenade® + TX, Rhapsody®) + TX, *Bacillus subtilis* strain QST 714

(JAZZ®) + TX, *Bacillus subtilis* strain AQ153 + TX, *Bacillus subtilis* strain AQ743 + TX, *Bacillus subtilis* strain QST3002 + TX, *Bacillus subtilis* strain QST3004 + TX, *Bacillus subtilis var. amyloliquefaciens* strain FZB24 (Taegro® + TX, Rhizopro®) + TX, *Bacillus thuringiensis* Cry 2Ae + TX, *Bacillus thuringiensis* Cry1Ab + TX, *Bacillus thuringiensis aizawai* GC 91 (Agree®) + 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 BD#32 + TX, *Bacillus thuringiensis* strain AQ52 + 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, *Bacillus thuringiensis tenebrionis* (Novodor®) + TX, BtBooster + 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 tenius* + TX, *Cedecea dravisae* + TX, *Cellulomonas flavigena* + TX, *Chaetomium cochliodes* (Nova-Cide®) + TX, *Chaetomium globosum* (Nova-Cide®) + TX, *Chromobacterium subtsugae* strain PRAA4-1T (Grandevo®) + TX, *Cladosporium cladosporioides* + TX, *Cladosporium oxysporum* + TX, *Cladosporium chlorocephalum* + 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 infirmo-miniatus* + TX, *Cryptococcus laurentii* + TX, *Cryptophlebia leucotreta granulovirus* (Cryptex®) + TX, *Cupriavidus campinensis* + TX, *Cydia pomonella granulovirus* (CYD-X®) + TX, *Cydia pomonella granulovirus* (Madex® + TX, Madex Plus® + TX, Madex Max/ Carpovirusine®) + TX, *Cylindrobasidium laeve* (Stumpout®) + TX, *Cylindrocladium* + TX, *Debaryomyces hansenii* + TX, *Drechslera hawaiinensis* + TX, *Enterobacter cloacae* + TX, *Enterobacteriaceae* + TX, *Entomophtora virulenta* (Vektor®) + TX, *Epicoccum nigrum* + TX, *Epicoccum purpurascens* + TX, *Epicoccum* spp. + TX, *Filobasidium floriforme* + TX, *Fusarium acuminatum* + TX, *Fusarium chlamydosporum* + TX, *Fusarium oxysporum* (Fusaclean® / 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, Isoflavone – formononetin (Myconate®) + TX, *Kloeckera apiculata* + TX, *Kloeckera* spp. + TX, *Lagenidium giganteum* (Laginex®) + TX, *Lecanicillium longisporum* (Vertiblast®) + TX, *Lecanicillium muscarium* (Vertikil®) + TX, *Lymantria Dispar nucleopolyhedrosis virus* (Disparvirus®) + TX, *Marinococcus halophilus* + TX, *Meira geulakonigii* + TX, *Metarhizium anisopliae* (Met52®) + TX, *Metarhizium anisopliae* (Destruxin WP®) + TX, *Metschnikowia fruticola* (Shemer®) + TX, *Metschnikowia pulcherrima* + TX, *Microdochium dimerum* (Antibot®) + TX, *Micromonospora coerulea* + TX, *Microsphaeropsis ochracea* + TX, *Muscodor albus* 620 (Muscudor®) + TX, *Muscodor roseus* strain A3-5 + 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, *Paecilomyces fumosoroseus* (PFR-97® + TX, PreFeRal®) + TX, *Paecilomyces linacinus* (Biostat WP®) + TX, *Paecilomyces lilacinus* strain 251 (MeloCon WG®) + TX, *Paenibacillus polymyxa* + TX, *Pantoea agglomerans* (BlightBan C9-1®) + TX, *Pantoea* spp. + TX, *Pasteuria* spp. (Econem®) + TX, *Pasteuria nishizawae* + TX, *Penicillium aurantiogriseum* + TX, *Penicillium billai* (Jumpstart® + TX, TagTeam®) + TX, *Penicillium brevicompactum* + TX, *Penicillium frequentans* + TX, *Penicillium griseofulvum* + TX, *Penicillium purpurogenum* + TX, *Penicillium* spp. + TX, *Penicillium viridicatum* + TX, *Phlebiopsis gigantean* (Rotstop®) + TX, phosphate solubilizing bacteria (Phosphomeal®) + TX, *Phytophthora cryptogea* + TX, *Phytophthora palmivora* (Devine®) + TX, *Pichia anomala* + TX, *Pichia guilermondii* + TX, *Pichia membranaefaciens* + TX, *Pichia onychis* + TX, *Pichia stipites* + TX, *Pseudomonas aeruginosa* + TX, *Pseudomonas 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, *Pseudomons fluorescens* (Zequanox®) + TX, *Pseudozyma flocculosa* strain PF-A22 UL (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* spp. + TX, *Rhodotorula glutinis* + TX, *Rhodotorula graminis* + TX, *Rhodotorula mucilagnosa* + TX, *Rhodotorula rubra* + TX, *Saccharomyces cerevisiae* + TX, *Salinococcus roseus* + TX, *Sclerotinia minor* + TX, *Sclerotinia minor* (SARRITOR®) + TX, *Scytalidium* spp. + TX, *Scytalidium uredinicola* + TX, *Spodoptera exigua nuclear polyhedrosis virus* (Spod-X® + TX, Spexit®) + TX, *Serratia marcescens* + TX, *Serratia plymuthica* + TX, *Serratia* spp. + TX, *Sordaria fimicola* + TX, *Spodoptera littoralis nucleopolyhedrovirus* (Littovir®) + TX, *Sporobolomyces roseus* + TX, *Stenotrophomonas maltophilia* + TX, *Streptomyces ahygroscopicus* + 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 gamsii* (Tenet®) + TX, *Trichoderma atroviride* (Plantmate®) + 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* spp. LC 52 (Sentinel®) + TX, *Trichoderma lignorum* + TX, *Trichoderma longibrachiatum* + TX, *Trichoderma polysporum* (Binab T®) + 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* spp. + TX, *Trichothecium roseum* + TX, *Typhula phacorrhiza* strain 94670 + 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, *Verticillium lecanii* (Mycotal® + TX, Vertalec®) + TX, Vip3Aa20 (VIPtera®) + TX, *Virgibaclillus marismortui* + TX, *Xanthomonas campestris pv. Poae* (Camperico®) + TX, *Xenorhabdus bovienii* + TX, *Xenorhabdus nematophilus*; and

Plant extracts including: pine oil (Retenol®) + TX, azadirachtin (Plasma Neem Oil® + TX, AzaGuard® + TX, MeemAzal® + TX, Molt-X® + TX, Botanical IGR (Neemazad® + TX, Neemix®) + TX, canola oil (Lilly Miller Vegol®) + TX, *Chenopodium ambrosioides near ambrosioides* (Requiem®) + TX, *Chrysanthemum* extract (Crisant®) + TX, extract of neem oil (Trilogy®) + TX, essentials oils of *Labiatae* (Botania®) + TX, extracts of clove rosemary peppermint and thyme oil (Garden insect killer®) + TX, Glycinebetaine (Greenstim®) + TX, garlic + TX, lemongrass oil (GreenMatch®) + TX, neem oil + TX, *Nepeta cataria* (Catnip oil) + TX, *Nepeta catarina* + TX, nicotine + TX, oregano oil (MossBuster®) + TX, *Pedaliaceae* oil (Nematon®) + 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, tea tree oil (Timorex Gold®) + TX, thymus oil + TX, AGNIQUE® MMF + TX, BugOil® + TX, mixture of rosemary sesame pepermint thyme and cinnamon extracts (EF 300®) + TX, mixture of clove rosemary and peppermint extract (EF 400®) + TX, mixture of clove pepermint garlic oil and mint (Soil Shot®) + TX, kaolin (Screen®) + TX, storage glucam of brown algae (Laminarin®); and

pheromones including: blackheaded fireworm pheromone (3M Sprayable Blackheaded Fireworm Pheromone®) + TX, Codling Moth Pheromone (Paramount dispenser-(CM)/ Isomate C-Plus®) + TX, Grape Berry Moth Pheromone (3M MEC-GBM Sprayable Pheromone®) + TX, Leafroller pheromone (3M MEC – LR Sprayable Pheromone®) + TX, Muscamone (Snip7 Fly Bait® + TX, Starbar Premium Fly Bait®) + TX, Oriental Fruit Moth Pheromone (3M oriental fruit moth sprayable pheromone®) + TX, Peachtree Borer Pheromone (Isomate-P®) + TX, Tomato Pinworm Pheromone (3M Sprayable pheromone®) + TX, Entostat powder (extract from palm tree) (Exosex CM®) + TX, (E + TX,Z + TX,Z)-3 + TX,8 + TX,11 Tetradecatrienyl acetate + TX, (Z + TX,Z + TX,E)-7 + TX,11 + TX,13-

Hexadecatrienal + TX, (E + TX,Z)-7 + TX,9-Dodecadien-1-yl acetate + TX, 2-Methyl-1-butanol + TX, Calcium acetate + TX, Scenturion® + TX, Biolure® + TX, Check-Mate® + TX, Lavandulyl senecioate; and

Macrobials including: *Aphelinus abdominalis* + TX, *Aphidius ervi* (Aphelinus-System®) + 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® + TX, Andersoni-System®) + TX, *Amblyseius californicus* (Amblyline® + TX, Spical®) + TX, *Amblyseius cucumeris* (Thripex® + TX, Bugline cucumeris®) + TX, *Amblyseius fallacis* (Fallacis®) + TX, *Amblyseius swirskii* (Bugline swirskii® + TX, Swirskii-Mite®) + TX, *Amblyseius womersleyi* (WomerMite®) + TX, *Amitus hesperidum* + TX, *Anagrus atomus* + TX, *Anagyrus fusciventris* + TX, *Anagyrus kamali* + TX, *Anagyrus loecki* + TX, *Anagyrus pseudococci* (Citripar®) + TX, *Anicetus benefices* + TX, *Anisopteromalus calandrae* + TX, *Anthocoris nemoralis* (Anthocoris-System®) + TX, *Aphelinus abdominalis* (Apheline® + TX, Aphiline®) + TX, *Aphelinus asychis* + TX, *Aphidius colemani* (Aphipar®) + TX, *Aphidius ervi* (Ervipar®) + TX, *Aphidius gifuensis* + TX, *Aphidius matricariae* (Aphipar-M®) + TX, *Aphidoletes aphidimyza* (Aphidend®) + TX, *Aphidoletes aphidimyza* (Aphidoline®) + TX, *Aphytis lingnanensis* + TX, *Aphytis melinus* + TX, *Aprostocetus hagenowii* + TX, *Atheta coriaria* (Staphyline®) + TX, *Bombus* spp. + TX, *Bombus terrestris* (Natupol Beehive®) + TX, *Bombus terrestris* (Beeline® + TX, Tripol®) + TX, *Cephalonomia stephanoderis* + TX, *Chilocorus nigritus* + TX, *Chrysoperla carnea* (Chrysoline®) + TX, *Chrysoperla carnea* (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* + TX, *Dacnusa sibirica* (Minusa®) + TX, *Diglyphus isaea* (Diminex®) + TX, *Delphastus catalinae* (Delphastus®) + TX, *Delphastus pusillus* + TX, *Diachasmimorpha krausii* + TX, *Diachasmimorpha longicaudata* + TX, *Diaparsis jucunda* + TX, *Diaphorencyrtus aligarhensis* + TX, *Diglyphus isaea* + TX, *Diglyphus isaea* (Miglyphus® + TX, Digline®) + TX, *Dacnusa sibirica* (DacDigline® + TX, Minex®) + TX, *Diversinervus* spp. + TX, *Encarsia citrina* + TX, *Encarsia formosa* (Encarsia max® + TX, Encarline® + TX, En-Strip®) + TX, *Eretmocerus eremicus* (Enermix®) + TX, *Encarsia guadeloupae* + TX, *Encarsia haitiensis* + TX, *Episyrphus balteatus* (Syrphidend®) + TX, *Eretmoceris siphonini* + TX, *Eretmocerus californicus* + TX, *Eretmocerus eremicus* (Ercal® + TX, Eretline e®) + TX, *Eretmocerus eremicus* (Bemimix®) + TX, *Eretmocerus hayati* + TX, *Eretmocerus mundus* (Bemipar® + TX, Eretline m®) + TX, *Eretmocerus siphonini* + TX, *Exochomus quadripustulatus* + TX, *Feltiella acarisuga* (Spidend®) + TX, *Feltiella acarisuga* (Feltiline®) + TX, *Fopius arisanus* + 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* spp. (Lawn Patrol®) + 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, *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, *Psyttalia concolor* (complex) + TX, *Quadrastichus* spp. + TX, *Rhyzobius 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 ostriniae* + TX, *Trichogramma platneri* + TX, *Trichogramma pretiosum* + TX, *Xanthopimpla stemmator*; and

other biologicals including: abscisic acid + 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, 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, BioGain® + TX, Aminomite® + TX, Zenox® + TX, Pheromone trap (Thripline ams®) + TX, potassium bicarbonate (MilStop®) + TX, potassium salts of fatty acids (Sanova®) + TX,

potassium silicate solution (Sil-Matrix®) + TX, potassium iodide + potassiumthiocyanate (Enzicur®) + TX, SuffOil-X® + TX, Spider venom + TX, *Nosema locustae* (Semaspore Organic Grasshopper Control®) + TX, Sticky traps (Trapline YF® + TX, Rebell Amarillo®) + TX and Traps (Takitrapline y + b®) + TX; or a biologically active compound or agent selected from: Brofluthrinate + TX, Diflovidazine + TX, Flometoquin + TX, Fluhexafon + TX, Plutella xylostella Granulosis virus + TX, Cydia pomonella Granulosis virus + TX, Imicyafos + TX, Heliothis virescens Nucleopolyhedrovirus + TX, Heliothis punctigera Nucleopolyhedrovirus + TX, Helicoverpa zea Nucleopolyhedrovirus + TX, Spodoptera frugiperda Nucleopolyhedrovirus + TX, Plutella xylostella Nucleopolyhedrovirus + TX, p-cymene + TX, Pyflubumide + TX, Pyrafluprole + TX, QRD 420 + TX, QRD 452 + TX, QRD 460 + TX, Terpenoid blends + TX, Terpenoids + TX, Tetraniliprole + TX, and α-terpinene + TX;
or an active substance referenced by a code + TX, such as code AE 1887196 (BSC-BX60309) + TX, code NNI-0745 GR + TX, code IKI-3106 + TX, code JT-L001 + TX, code ZNQ-08056 + TX, code IPPA152201 + TX, code HNPC-A9908 (CAS: [660411-21-2]) + TX, code HNPC-A2005 (CAS: [860028-12-2]) + TX, code JS118 + TX, code ZJ0967 + TX, code ZJ2242 + TX, code JS7119 (CAS: [929545-74-4]) + TX, code SN-1172 + TX, code HNPC-A9835 + TX, code HNPC-A9955 + TX, code HNPC-A3061 + TX, code Chuanhua 89-1 + TX, code IPP-10 + TX, code ZJ3265 + TX, code JS9117 + TX, code ZJ3757 + TX, code ZJ4042 + TX, code ZJ4014 + TX, code ITM-121 + TX, code DPX-RAB55 (DKI-2301) + TX, code NA-89 + TX, code MIE-1209 + TX, code MCI-8007 + TX, code BCS-CL73507 + TX, code S-1871 + TX, code DPX-RDS63 + TX, code AKD-1193 + TX,
or other biologically active compounds or agents selected from: Quinofumelin + TX, mefentrifluconazol + TX, fenpicoxamid + TX, fluindapyr + TX, inpyrfluxam + TX or indiflumetpyr + TX, isoflucypram + TX, pyrapropoyne + TX, florylpicoxamid + TX, metyltetraprole + TX, ipflufenoquin + TX, pyridachlometyl + TX or chlopyridiflu + TX, tetrachlorantraniliprole + TX, tetrachloraniliprole + TX, Tetflupyrolimet + TX, Triflufenpyrrolidone + TX, Tyclopyrazoflor + TX, flupyrimin + TX or pyrifluramide + TX, benzpyrimoxan + TX, beflubutamid-M + TX, Benzosufyl + TX or oxazosulfyl + TX, etpyrafen + TX, acynonapyr + TX or pyrinonafen + TX, oxotrione + TX, bixlozone + TX or clofendizone + TX or dicloroxizone + TX, cyclopyranil + TX or pyrazocyclonil + TX or cyclopyrazonil + TX , alpha-bromadiolone + TX, Oxathiapiprolin + TX, Fluopyram + TX, Penflufen+ TX, Fluoxopyrosad+ TX, fluoxapiprolin + TX and Flupyradifurone + TX.

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

Common Names, Copyright © 1995-2004]; for example, the compound "acetoprole" is described under the internet address http://www.alanwood.net/pesticides/acetoprole.html.

Most of the active ingredients described above are referred to hereinabove by a so-called "common name", the relevant "ISO common name" or another "common name" being used in individual cases. If the designation is not a "common name", the nature of the designation used instead is given in round brackets for the particular compound; in that case, the IUPAC name, the IUPAC/Chemical Abstracts name, a "chemical name", a "traditional name", a "compound name" or a "develoment code" is used or, if neither one of those designations nor a "common name" is used, an "alternative name" is employed. “CAS Reg. No” means the Chemical Abstracts Registry Number.

The active ingredient mixture of the compounds of formula I selected from Tables A-1 to A-33 and Table P with active ingredients described above comprises a compound selected from Tables A-1 to A-33 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 especially from 5:1 and 1:5, special preference being given to a ratio of from 2:1 to 1:2, and a ratio of from 4:1 to 2:1 being likewise preferred, above all in a ratio of 1:1, or 5:1, or 5:2, or 5:3, or 5:4, or 4:1, or 4:2, or 4:3, or 3:1, or 3:2, or 2:1, or 1:5, or 2:5, or 3:5, or 4:5, or 1:4, or 2:4, or 3:4, or 1:3, or 2:3, or 1:2, or 1:600, or 1:300, or 1:150, or 1:35, or 2:35, or 4:35, or 1:75, or 2:75, or 4:75, or 1:6000, or 1:3000, or 1:1500, or 1:350, or 2:350, or 4:350, or 1:750, or 2:750, or 4:750. Those mixing ratios are by weight.

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

The mixtures comprising a compound of formula I selected from Tables A-1 to A-33 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 I selected from Tables A-1 to A-33 and Table P 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, for example bactericides, fungicides, nematocides, plant activators, molluscicides or herbicides.

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

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

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

The compounds of the invention and compositions thereof are also be 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 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 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.

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 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 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.

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, 12.5 ppm, 6 ppm, 3 ppm, 1.5 ppm, 0.8 ppm or 0.2 ppm.

Example B1: *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% in at least one of the two categories (mortality or growth inhibition) at an application rate of 200 ppm: P1, P2, P3, P4, P5, P6, P7, P9, P10.

Example B2: *Euschistus her*os (Neotropical Brown Stink Bug)

Soybean leaves on agar in 24-well microtiter plates were sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying the leaves were infested with N2 nymphs. The samples were assessed for mortality and growth inhibition in comparison to untreated samples 5 days after infestation.

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 200 ppm: P1, P2, P3, P4, P5, P6, P7, P8, P9, P10.

Example B3: *Frankliniella occidentalis* (Western flower thrips)

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: P1, P4.

Example B4: *Plutella xylostella* (Diamond back moth)

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% in at least one of the two categories (mortality or growth inhibition) at an application rate of 200 ppm: P1, P2, P3, P4, P5, P6, P7, P8, P9, P10.

Example B5: *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 infestation.

The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: P1, P2, P3, P4, P5, P6, P7, P8, P9, P10.

Example B6: *Myzus persicae* (Green peach aphid). Systemic activity

Roots of pea seedlings infested with an aphid population of mixed ages were placed directly into aqueous test solutions prepared from 10'000 DMSO stock solutions. The samples were assessed for mortality 6 days after placing seedlings into test solutions.

The following compounds resulted in at least 80% mortality at a test rate of 24 ppm: P1, P2, P3, P4, P5, P6, P7, P8, P9, P10.

Example B7: *Plutella xylostella* (Diamond back moth)

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 (10 to 15 per well). The samples were assessed for mortality and growth inhibition in comparison to untreated samples 5 days after infestation.

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 200 ppm: P1.

Example B8: *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.

The following compounds resulted in at least 80% control at an application rate of 200 ppm: P1, P3, P4, P5, P6, P7, P9, P10.

Example B9: *Nilaparvata lugens* (Brown plant hopper)

Rice plants were treated with the diluted test solutions in a spray chamber. After drying plants were infested with ~20 N3 nymphs. 7 days after the treatment samples were assessed for mortality and growth regulation.

The following compounds resulted in at least 80% mortality at an application rate of 50 ppm: P1.

Example B10: *Heterodera schachtii:* Juvenile mobility, in vitro profiling in 96 well plate

Test solutions are prepared from 10'000 ppm DMSO stock solutions with a TECAN robot to achieve 20 µL of 500, 100, 50, 25, 12.5 and 6.25 ppm. For each concentration three replicates are produced. Per well, 80 µL nematode solution is added containing 100 to 150 freshly harvested second stage juveniles of *Heterodera schachtii*. The plates are covered and stored at room temperature in the dark and incubated for 24 h. Mobility of the exposed juveniles in a treated well is measured using an imaging tool and compared to an average of 12 untreated replicates.

The following compounds achieved at least 80% control at 100 ppm after 48 h: P1.

Example B11: Comparison of the insecticidal activity of compound P1 according to the invention with compounds from the state of the art:

Activity of compound P1 according to the preparatory examples and of compound 4-9 from WO2016/104746 against *Spodoptera littoralis* (Example B8), *Diabrotica balteata* (Example B1) and *Myzus persicae* (systemic, Example B6) is summarized in Table B11:

Table B11:

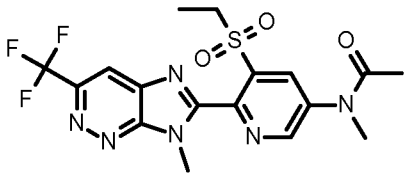
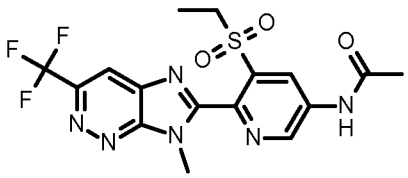
Compound	Concentration (ppm)	Insect	Mortality (%)
Compound P1  (present invention)	200 200 0.375	*Spodoptera littoralis* *Diabrotica balteata* *Myzus persicae* (systemic)	100 80 90
4-9, known from WO2016/104746  (state of the art)	200 200 0.375	*Spodoptera littoralis* *Diabrotica balteata* *Myzus persicae* (systemic)	0 0 0

Table B11 shows that compounds P1 according to the invention exerts a substantially better insecticidal action on *Spodoptera littoralis, Diabrotica balteata* and *Myzus persicae* than the compound from the state of the art. This enhanced effect was not to be expected on the basis of the structural similarity of these compounds.

Example B12: *Tetranychus urticae* (Two-spotted spider mite)

Bean leaf discs on agar in 24-well microtiter plates were sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying the leaf discs were infested with a mite population of mixed ages. The samples were assessed for mortality on mixed population (mobile stages) 8 days after infestation.

The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: P8.

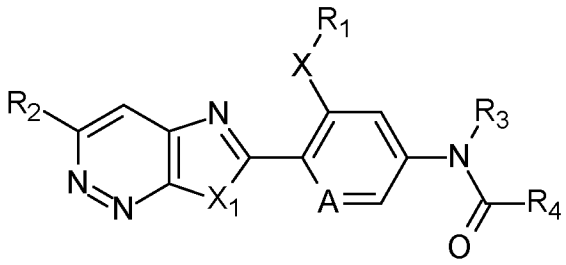
Example B13: *Chilo suppressalis* (Striped stem borer)

Rice plants were sprayed with diluted test solutions in an application chamber. Cut off plants were placed into petri dishes with wetted filter paper, infested with 5 L2 larvae and covered with a plastic lid. Samples were assessed 5 days after infestation for mortality, and growth regulation.

The following compounds resulted in at least 80% mortality at an application rate of 50 ppm: P1.

CLAIMS

1. A compound of formula (I)



(I),

wherein

A is CH or N;

X is S, SO or SO_2;

R_1 is C_1-C_4alkyl, C_1-C_4haloalkyl or C_3-C_6cycloalkyl-C_1-C_4alkyl;

R_2 is halogen, C_1-C_6haloalkyl, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl or C_1-C_6haloalkoxy;

R_3 is C_1-C_6alkyl, C_2-C_6alkenyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_1-C_6haloalkoxy, C_1-C_6cyanoalkyl, C_1-C_6hydroxyalkyl, C_1-C_6alkoxycarbonyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_4alkylthio-C_1-C_4alkyl, C_1-C_4alkylsulfinyl-C_1-C_4alkyl, C_1-C_4alkylsulfonyl-C_1-C_4alkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl, C_3-C_6halocycloalkyl-C_1-C_4alkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl substituted by a substituent selected from cyano, halogen, C_1-C_3haloalkyl, CO_2H, $CONH_2$, C_1-C_6alkylaminocarbonyl, C_1-C_6dialkylaminocarbonyl or C_1-C_4alkoxycarbonyl;

R_4 is C_1-C_6alkyl, C_2-C_6alkenyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_4alkylthio-C_1-C_4alkyl, C_1-C_4alkylsulfinyl-C_1-C_4alkyl, C_1-C_4alkylsulfonyl-C_1-C_4alkyl, C_3-C_6cycloalkyl-C_1-C_2alkyl, C_1-C_6cyanoalkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl which is mono- or poly-substituted by substituents independently selected from the group consisting of halogen, cyano, C_1-C_3haloalkyl, CO_2H, $CONH_2$, C_1-C_6alkylaminocarbonyl, C_1-C_6dialkylaminocarbonyl and C_1-C_4alkoxycarbonyl; or

R_4 is a four- to six-membered heterocyclic ring system which can be partially saturated or fully saturated, said ring system contains 1 to 2 ring heteroatoms selected from O, N, or S(O)n, wherein n is 0, 1 or 2 providing that the heterocyclic ring system does not contain adjacent ring oxygen atoms, adjacent ring sulphur atoms, or adjacent ring sulphur and ring oxygen atoms and that the ring nitrogen, when present, may be substituted by hydrogen or C_1-C_4 alkyl, and said ring system can be optionally mono- or di-substituted with substituents independently selected from the group consisting of halogen, cyano, C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4haloalkyl or oxo; or

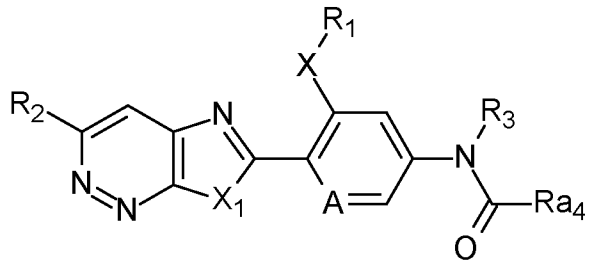
R_3 and R_4 together with the -NC(O)- fragment to which they are attached form a 5- or 6-membered saturated ring system which may contain one or two additional ring heteroatoms selected from O, N, or S(O)n, wherein n is 0, 1 or 2, providing that the heterocyclic ring system does not contain adjacent ring oxygen atoms, adjacent ring sulphur atoms, or adjacent ring

sulphur and ring oxygen atoms and that the additional ring nitrogen, when present, is substituted by hydrogen or C_1-C_4 alkyl, C_1-C_4alkoxy, or C_1-C_4haloalkoxy, and wherein the ring system can be optionally mono- or di-substituted with substituents independently selected from halogen, cyano, C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4haloalkyl or oxo; and

X_1 is O, S or NR_5; wherein R_5 is hydrogen or C_1-C_4alkyl;

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

2. A compound of formula I according to claim 1, represented by the compounds of formula I-1



(I-1),

wherein A, X, R_1, R_2, R_3, and X_1 are as defined are as defined under formula I in claim 1, and wherein

Ra_4 is C_1-C_6alkyl, C_2-C_6alkenyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_4alkylthio-C_1-C_4alkyl, C_1-C_4alkylsulfinyl-C_1-C_4alkyl, C_1-C_4alkylsulfonyl-C_1-C_4alkyl, C_3-C_6cycloalkyl-C_1-C_2alkyl, C_1-C_6cyanoalkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl which is mono- or poly-substituted by substituents independently selected from the group consisting of halogen, cyano, C_1-C_3haloalkyl, CO_2H, $CONH_2$, C_1-C_6alkylaminocarbonyl, C_1-C_6dialkylaminocarbonyl and C_1-C_4alkoxycarbonyl.

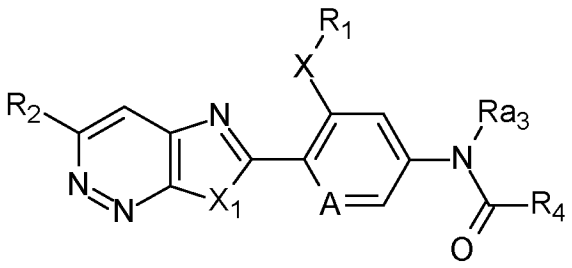
3. A compound of formula I-1 according to claim 2, wherein:

Ra_4 is C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_4alkylthio-C_1-C_4alkyl, C_1-C_4alkylsulfinyl-C_1-C_4alkyl, C_1-C_4alkylsulfonyl-C_1-C_4alkyl, C_1-C_6cyanoalkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl mono-substituted by cyano.

4. A compound of formula I-1 according to any one of claims 2 or 3, wherein:

R_3 is C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl mono-substituted by cyano.

5. A compound of formula I according to claim 1, represented by the compounds of formula I-2



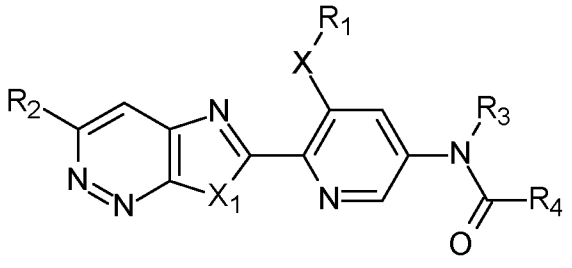
(I-2),

wherein A, X, R_1, R_2, R_4, and X_1 are as defined under formula I in claim 1, and wherein Ra_3 is C_1-C_6alkyl, C_2-C_6alkenyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_1-C_6haloalkoxy, C_1-C_6cyanoalkyl, C_1-C_6hydroxyalkyl, C_1-C_6alkoxycarbonyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_4alkylthio-C_1-C_4alkyl, C_1-C_4alkylsulfinyl-C_1-C_4alkyl, C_1-C_4alkylsulfonyl-C_1-C_4alkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl, C_3-C_6halocycloalkyl-C_1-C_4alkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl substituted by a substituent selected from cyano, halogen, C_1-C_3haloalkyl, CO_2H, $CONH_2$, C_1-C_6alkylaminocarbonyl, C_1-C_6dialkylaminocarbonyl or C_1-C_4alkoxycarbonyl.

6. A compound of formula I-2 according to claim 5, wherein:
Ra_3 is C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl mono-substituted by cyano.

7. A compound of formula I-2 according to any one of claims 5 or 6, wherein:
R_4 is C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_4alkylthio-C_1-C_4alkyl, C_1-C_4alkylsulfinyl-C_1-C_4alkyl, C_1-C_4alkylsulfonyl-C_1-C_4alkyl, C_1-C_6cyanoalkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl mono-substituted by cyano.

8. A compound of formula I according to claim 1, represented by the compounds of formula I-4

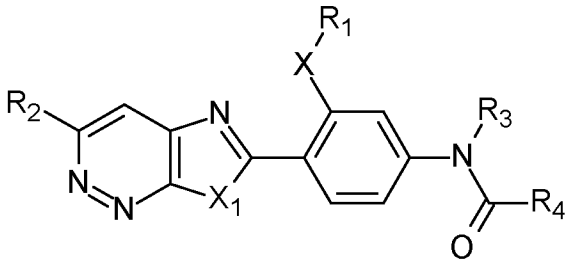


(I-4),

wherein X, R_1, R_2, R_3, R_4 and X_1 are as defined under formula I in claim 1.

9. A compound of formula I-4 according to claim 8, wherein:
R_4 is C_1-C_6alkyl, C_2-C_6alkenyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_4alkylthio-C_1-C_4alkyl, C_1-C_4alkylsulfinyl-C_1-C_4alkyl, C_1-C_4alkylsulfonyl-C_1-C_4alkyl, C_3-C_6cycloalkyl-C_1-C_2alkyl, C_1-C_6cyanoalkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl which is mono- or poly-substituted by substituents independently selected from the group consisting of halogen, cyano, C_1-C_3haloalkyl, CO_2H, $CONH_2$, C_1-C_6alkylaminocarbonyl, C_1-C_6dialkylaminocarbonyl and C_1-C_4alkoxycarbonyl.

10. A compound of formula I according to claim 1, represented by the compounds of formula I-5

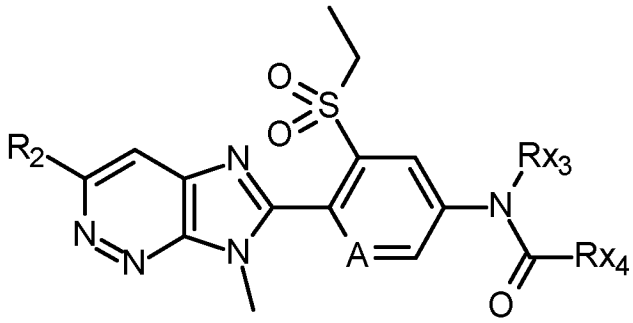


(I-5),

wherein X, R_1, R_2, R_3, R_4 and X_1 are as defined under formula I in claim 1.

11. A compound of formula I-5 according to claim 10, wherein:
R_4 is C_1-C_6alkyl, C_2-C_6alkenyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_4alkylthio-C_1-C_4alkyl, C_1-C_4alkylsulfinyl-C_1-C_4alkyl, C_1-C_4alkylsulfonyl-C_1-C_4alkyl, C_3-C_6cycloalkyl-C_1-C_2alkyl, C_1-C_6cyanoalkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl which is mono- or poly-substituted by substituents independently selected from the group consisting of halogen, cyano, C_1-C_3haloalkyl, CO_2H, $CONH_2$, C_1-C_6alkylaminocarbonyl, C_1-C_6dialkylaminocarbonyl and C_1-C_4alkoxycarbonyl.

12. A compound of formula I according to claim 1, represented by the compounds of formula I-6

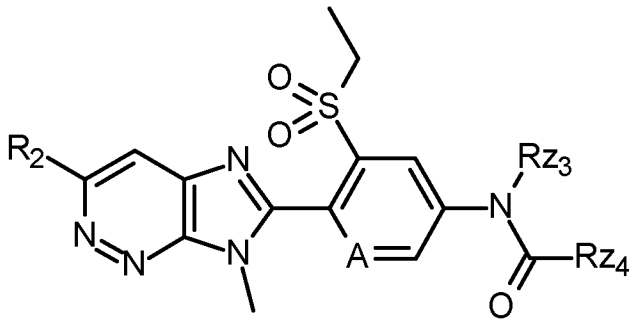


(I-6),

wherein
A is CH or N, preferably N;
R_2 is C_1-C_6haloalkyl, preferably trifluoromethyl;
Rx_3 is C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl mono-substituted by cyano; preferably Rx_3 is methyl, ethyl, isopropyl, 2,2,2-trifluoroethyl, methoxy, cyclopropyl or 1-cyanocyclopropyl; and
Rx_4 is C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_4alkylthio-C_1-C_4alkyl, C_1-C_4alkylsulfinyl-C_1-C_4alkyl, C_1-C_4alkylsulfonyl-C_1-C_4alkyl, C_1-C_6cyanoalkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl mono-substituted by cyano; preferably Rx_4 is methyl, ethyl, isopropyl, t-butyl, trifluoromethyl, difluoromethyl, fluoromethyl, chloromethyl, 2,2,2-trifluoroethyl, 1-hydroxy-1-methyl-ethyl, methoxymethyl, methoxyethyl, methylsulfanylmethyl,

methylsulfonylmethyl, 2-methylsulfanylethyl, 2-methylsulfonylethyl, 1-cyano-1-methyl-ethyl, cyclopropyl or 1-cyanocyclopropyl.

13. A compound of formula I according to claim 1, represented by the compounds of formula I-8



(I-8),

wherein

A is CH or N, preferably N;

R_2 is C_1-C_6haloalkyl, preferably trifluoromethyl;

Rz_3 is C_1-C_6alkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl mono-substituted by cyano, preferably methyl, ethyl, cyclopropyl or 1-cyanocyclopropyl; and

Rz_4 is C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_4alkoxy-C_1-C_4alkyl, C_1-C_6cyanoalkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl mono-substituted by cyano, preferably methyl, ethyl, 2,2,2-trifluoroethyl, methoxymethyl, 1-cyano-1-methyl-ethyl, cyclopropyl or 1-cyanocyclopropyl.

14. A compound of formula I according to claim 1, selected from N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl) imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]-N-methyl-acetamide (compound P1);
N-ethyl-N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]acetamide (compound P2);
N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]-2-methoxy-N-methyl-acetamide (compound P3);
N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]-N-methyl-cyclopropanecarboxamide (compound P4);
2-cyano-N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]-N,2-dimethyl-propanamide (compound P5);
N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]-N-methyl-propanamide (compound P6);
N-cyclopropyl-N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]acetamide (compound P7);
N-(1-cyanocyclopropyl)-N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]acetamide (compound P8);
1-cyano-N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]-N-methyl-cyclopropanecarboxamide (compound P9); and

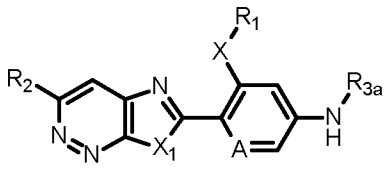
N-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]-3,3,3-trifluoro-N-methyl-propanamide (compound P10).

15. A composition comprising an insecticidally, acaricidally, nematicidally or molluscicidally effective amount of a compound of formula (I), or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, as defined in any of claims 1 – 14 and, optionally, an auxiliary or diluent.

16. 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, nematicidally or molluscicidally effective amount of a compound of formula (I), or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, as defined in any of claims 1 – 14 or a composition as defined claim 15.

17. 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 a composition according to claim 15.

18. A compound of formula VIIa



(VIIa),

wherein

R_2, X_1, X, R_1 and A are as defined under formula I in claim 1; and

R_{3a} is cyclopropyl or  .

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/070201

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D487/04 A01N43/90
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2016/104746 A1 (NIHON NOHYAKU CO LTD [JP]) 30 June 2016 (2016-06-30) cited in the application compounds 4-8 to 4-15 in table 6 on page 30; claims 1,4-6	1-18
Y	EP 3 018 130 A1 (SUMITOMO CHEMICAL CO [JP]) 11 May 2016 (2016-05-11) cited in the application claims 1,18,20,21; tables 22,23; compounds 9-12,17,18,22-24,28,29	1-18
A	WO 2016/059145 A1 (SYNGENTA PARTICIPATIONS AG [CH]) 21 April 2016 (2016-04-21) cited in the application claims 1,3,9-11; table P	1-18

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 August 2020	19/08/2020

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Guspanová, Jana

1

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/070201

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	WO 2019/138018 A1 (SYNGENTA PARTICIPATIONS AG [CH]) 18 July 2019 (2019-07-18) compounds of examples; claims 1,18-20; table B24 -----	1-18

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2020/070201

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2016104746 A1	30-06-2016	JP 2018052816 A	05-04-2018
		WO 2016104746 A1	30-06-2016
EP 3018130 A1	11-05-2016	BR 112015032689 A2	25-07-2017
		CN 105358555 A	24-02-2016
		EP 3018130 A1	11-05-2016
		JP 6350528 B2	04-07-2018
		JP 6547867 B2	24-07-2019
		JP 2018115176 A	26-07-2018
		JP WO2015002211 A1	23-02-2017
		US 2016368915 A1	22-12-2016
		WO 2015002211 A1	08-01-2015
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		CN 106795167 A	31-05-2017
		EP 3207044 A1	23-08-2017
		ES 2690131 T3	19-11-2018
		JP 6675390 B2	01-04-2020
		JP 2017537882 A	21-12-2017
		US 2017240554 A1	24-08-2017
		WO 2016059145 A1	21-04-2016
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		WO 2019138018 A1	18-07-2019