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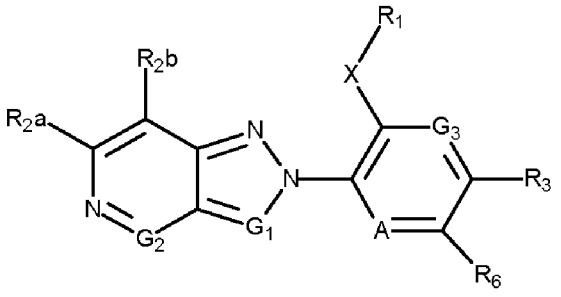
(54) **Title**: PESTICIDALLY ACTIVE HETEROCYCLIC DERIVATIVES WITH SULPHUR CONTAINING SUBSTITUENTS



(I),

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

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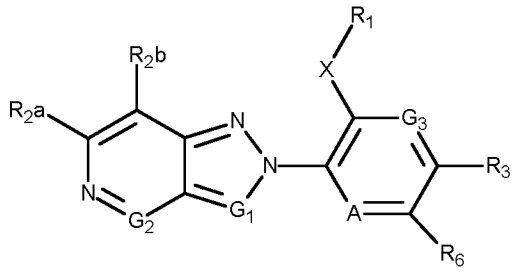
Pesticidally active heterocyclic derivatives with sulphur containing substituents

The present invention relates to pesticidally active, in particular insecticidally active heterocyclic derivatives containing sulphur substituents, 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 are known and described, for example, in WO 2012/086848, WO 2013/018928, WO 2013/191112 and WO 2013/191113.

There have now been found novel pesticidally active heterocyclic derivatives with sulphur containing phenyl and pyridyl substituents.

The present invention accordingly relates to compounds of formula I,



(I),

wherein

A is CH, N or CR_7; wherein R_7 is C_1-C_4alkyl, C_1-C_4haloalkyl, cyano, nitro or halogen;

X is S, SO or SO_2;

R_1 is C_1-C_4alkyl, C_1-C_4haloalkyl, C_3-C_6cycloalkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl, C_3-C_6cycloalkyl mono - or polysubstituted by substituents selected from the group consisting of halogen, cyano, C_1-C_4haloalkyl and C_1-C_4alkyl; or

R_1 is C_3-C_6cycloalkyl-C_1-C_4alkyl mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C_1-C_4haloalkyl and C_1-C_4alkyl; or

R_1 is C_2-C_6alkenyl, C_2-C_6haloalkenyl or C_2-C_6alkynyl;

R_{2a} and R_{2b} are, independently from each other, hydrogen, halogen, cyano, C_1-C_6haloalkyl or C_1-C_6haloalkyl substituted by one or two substituents selected from the group consisting of hydroxyl, methoxy and cyano; or

R_{2a} and R_{2b} are, independently from each other, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_1-C_4haloalkoxy, or –C(O)(C_1-C_4haloalkyl); or

R_{2a} and R_{2b} are, independently from each other, C_3-C_6cycloalkyl which can be mono - or polysubstituted by substituents selected from the group consisting of halogen, cyano, C_1-C_4haloalkyl and C_1-C_4alkyl;

R_3 is hydrogen, halogen, cyano, nitro, C_1-C_6alkyl, C_1-C_6alkoxy, C_1-C_4alkoxyC_1-C_4alkyl, C_1-C_6haloalkyl, C_3-C_6cycloalkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl, or

R_3 is C_3-C_6cycloalkyl which is mono- or di-substituted by substituents selected from the group consisting of halogen, C_1-C_4alkyl, C_1-C_4haloalkyl and cyano; or

R_3 is C_2-C_6alkenyl, C_2-C_6haloalkenyl, C_2-C_6alkynyl, C_2-C_6haloalkynyl; or

R_3 is phenyl which can be mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, nitro, C_2-C_6alkenyl, C_2-C_6haloalkenyl, C_2-C_6alkynyl, C_2-C_6haloalkynyl, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4haloalkoxy, C_1-C_4alkoxy, C_1-C_4alkoxy C_1-C_4alkyl, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_1-C_4alkylsulfanyl, C_1-C_4alkylsulfinyl, C_1-C_4alkylsulfonyl, and –C(O)C_1-C_4haloalkyl; or

R_3 is C_1-C_6haloalkylsulfanyl, C_1-C_6haloalkylsulfinyl, C_1-C_6haloalkylsulfonyl, C_1-C_6 haloalkoxy, –C(O)C_1-C_4haloalkyl, C_1-C_6alkylsulfanyl, C_1-C_6alkylsulfinyl, or C_1-C_6alkylsulfonyl; or

R_3 is pyrimidinyl which can be mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, nitro, C_2-C_6alkenyl, C_2-C_6haloalkenyl, C_2-C_6alkynyl, C_2-C_6haloalkynyl, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4haloalkoxy, C_1-C_4alkoxy, C_1-C_4alkoxy C_1-C_4alkyl, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_1-C_4alkylsulfanyl, C_1-C_4alkylsulfinyl, C_1-C_4alkylsulfonyl and –C(O)C_1-C_4haloalkyl; or

R_3 is pyridinyl which can be mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, nitro, C_2-C_6alkenyl, C_2-C_6haloalkenyl, C_2-C_6alkynyl, C_2-C_6haloalkynyl, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4haloalkoxy, C_1-C_4alkoxy, C_1-C_4alkoxy C_1-C_4alkyl, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_1-C_4alkylsulfanyl, C_1-C_4alkylsulfinyl, or C_1-C_4alkylsulfonyl and –C(O)C_1-C_4haloalkyl; or

R_3 is a five- to six-membered, aromatic, partially saturated or fully saturated ring system linked via a nitrogen atom to the ring which contains the substituent G_3, said ring system can be mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, nitro, C_2-C_6alkenyl, C_2-C_6haloalkenyl, C_2-C_6alkynyl, C_2-C_6haloalkynyl, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4haloalkoxy, C_1-C_4alkoxy, C_1-C_4alkoxy C_1-C_4alkyl, C_1-C_4alkylsulfanyl, C_1-C_4alkylsulfinyl, C_1-C_4alkylsulfonyl, –C(O)C_1-C_4alkyl, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl and –C(O)C_1-C_4haloalkyl; said ring system contains 1, 2 or 3 heteroatoms selected from the group consisting of nitrogen, oxygen and sulphur; where said ring system may not contain more than one oxygen atom and not more than one sulfur atom;

R_6 is hydrogen, C_1-C_4alkyl, C_1-C_4haloalkyl, halogen or cyano;

G_1 is CR_4, wherein R_4 is hydrogen, C_1-C_4alkyl, C_1-C_4haloalkyl, cyano or halogen;

G_2 is N or CR_5, wherein R_5 is hydrogen, C_1-C_4alkyl, C_1-C_4haloalkyl, cyano, nitro or halogen;

G_3 is N or CR_8, wherein R_8 is hydrogen, C_1-C_4alkyl, C_1-C_4haloalkyl, halogen or cyano; and

agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and 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, nitrose 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.

The alkyl groups occurring in the definitions of the substituents can be straight-chain or branched and are, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, pentyl, hexyl, nonyl, decyl and their branched isomers. Alkylsulfanyl, alkylsulfinyl, alkylsulfonyl, alkoxy, alkenyl and alkynyl radicals are derived from the alkyl radicals mentioned. The alkenyl and alkynyl groups can be mono- or polyunsaturated.

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

Haloalkyl groups preferably have a chain length of from 1 to 6 carbon atoms. Haloalkyl is, for example, fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, 2,2,2-trifluoroethyl, 2-fluoroethyl, 2-chloroethyl, pentafluoroethyl, 1,1-difluoro-2,2,2-trichloroethyl, 2,2,3,3-tetrafluoroethyl and 2,2,2-trichloroethyl.

Alkoxy is, for example, methoxy, ethoxy, propoxy, i-propoxy, n-butoxy, isobutoxy, sec-butoxy and tert-butoxy and also the isomeric pentyloxy and hexyloxy radicals.

Alkoxyalkyl groups preferably have a chain length of 1 to 6 carbon atoms.
Alkoxyalkyl is, for example, methoxymethyl, methoxyethyl, ethoxymethyl, ethoxyethyl, n-propoxymethyl, n-propoxyethyl, isopropoxymethyl or isopropoxyethyl.

Alkoxycarbonyl is for example methoxycarbonyl (which is C_1alkoxycarbonyl), ethoxycarbonyl, propoxycarbonyl, isopropoxycarbonyl, n-butoxycarbonyl, tert-butoxycarbonyl, n-pentoxycarbonyl or hexoxycarbonyl.

The cycloalkyl groups preferably have from 3 to 6 ring carbon atoms, for example cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl.

In the context of this invention, examples of a five- to six-membered, aromatic, partially saturated or fully saturated ring system are pyrazole, pyrrole, pyrrolidine, pyrrolidine-2-one, imidazole, triazole and pyridine-2-one.

In the context of this invention “mono- to polysubstituted” in the definition of the substituents, means typically, depending on the chemical structure of the substituents, monosubstituted to seven-times substituted, preferably monosubstituted to five-times substituted, more preferably mono-, double- or triple-substituted.

In the context of this invention pyrimidine or pyridine as R_3 may be both linked via any carbon atom to the ring which contains the substituent G_3.

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

Preferably R_1 is C_1-C_4alkyl, C_1-C_4haloalkyl, C_3-C_6cycloalkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl, C_3-C_6cycloalkyl mono - or polysubstituted by substituents selected from the group consisting of halogen, cyano and C_1-C_4alkyl; or R_1 is C_3-C_6cycloalkyl-C_1-C_4alkyl mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano and C_1-C_4alkyl;
or R_1 is C_2-C_6alkenyl, C_2-C_6haloalkenyl or C_2-C_6alkynyl;
R_3 is hydrogen, halogen, cyano, nitro, C_1-C_4alkyl, C_1-C_4haloalkyl, C_3-C_6cycloalkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl, or is C_3-C_6cycloalkyl which is mono- or di-substituted by substituents selected from the group consisting of halogen and cyano; or R_3 is C_2-C_6alkenyl, C_2-C_6haloalkenyl, C_2-C_6alkynyl, C_2-C_6haloalkynyl; or
R_3 is phenyl which can be mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, nitro, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4haloalkoxy, C_1-C_4alkoxy, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_1-C_4alkylsulfanyl, C_1-C_4alkylsulfinyl, C_1-C_4alkylsulfonyl, and –C(O)C_1-C_4haloalkyl;
or R_3 is C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_1-C_4haloalkoxy, –C(O)C_1-C_4haloalkyl, C_1-C_4alkylsulfanyl, C_1-C_4alkylsulfinyl, or C_1-C_4alkylsulfonyl; or

R_3 is pyrimidine which can be mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4haloalkoxy, C_1-C_4alkoxy, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl and –C(O)C_1-C_4haloalkyl; or

R_3 is pyridine which can be mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4haloalkoxy, C_1-C_4alkoxy, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl and –C(O)C_1-C_4haloalkyl; or

R_3 is a five- to six-membered, aromatic, partially saturated or fully saturated ring system linked via a nitrogen atom to the ring which contains the substituent G_3, said ring system can be mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4haloalkoxy, C_1-C_4alkoxy, C_1-C_4alkylsulfanyl, C_1-C_4alkylsulfinyl, C_1-C_4alkylsulfonyl and –C(O)C_1-C_4alkyl, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl and –C(O)C_1-C_4haloalkyl; and said ring system contains 1, 2 or 3 heteroatoms selected from the group consisting of nitrogen, oxygen and sulphur, where said ring system may not contain more than one oxygen atom and not more than one sulfur atom.

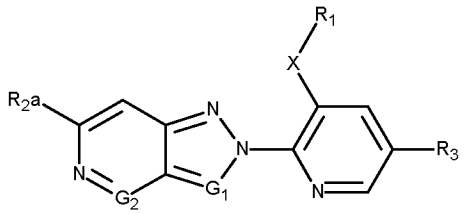
More preferably R_3 is hydrogen, halogen, cyano, nitro, C_1-C_4alkyl, C_1-C_4haloalkyl, C_3-C_6cycloalkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl, or is C_3-C_6cycloalkyl which is mono- or di-substituted by substituents selected from the group consisting of halogen and cyano; or R_3 is C_2-C_6alkenyl, C_2-C_6haloalkenyl, C_2-C_6alkynyl, C_2-C_6haloalkynyl; or

R_3 is phenyl which can be substituted by substituents selected from the group consisting of halogen, cyano, nitro, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4haloalkoxy, C_1-C_4alkoxy, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_1-C_4alkylsulfanyl, C_1-C_4alkylsulfinyl, C_1-C_4alkylsulfonyl, and –C(O)C_1-C_4haloalkyl;

or R_3 is C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_1-C_4haloalkoxy, –C(O)C_1-C_4haloalkyl, C_1-C_4alkylsulfanyl, C_1-C_4alkylsulfinyl, or C_1-C_4alkylsulfonyl; or

R_3 is pyrimidine or pyrimidine substituted by substituents selected from the group consisting of halogen, cyano, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4haloalkoxy, C_1-C_4alkoxy, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl and –C(O)C_1-C_4haloalkyl.

A preferred group of compounds of formula I is represented by the compounds of formula I-1



(I-1),

wherein G_1, G_2 R_1 and R_{2a} are as defined under formula I above, X is S, SO or SO_2; preferably S or SO_2; R_3 is hydrogen, halogen or C_1-C_4haloalkyl, in particular C_1-C_4haloalkyl; and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of those compounds.

Preferred are compounds of formula I-1, wherein G_1 is C-H; G_2 is C-H; and R_1, R_{2a} and R_3 are as defined under formula I-1 above.

Also preferred are compounds of formula I-1, wherein G_1 is C-H; G_2 is C-H; R_1 is C_1-C_4alkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl or C_3-C_6cycloalkyl; R_{2a} is halogen, C_1-C_4haloalkyl, cyano or C_3-C_6cycloalkyl which can be mono - or polysubstituted by substituents selected from the group consisting of halogen, cyano and C_1-C_4alkyl; and R_3 is hydrogen, halogen or C_1-C_4haloalkyl, preferably C_1-C_4haloalkyl.

Also preferred are compounds of formula I-1, wherein G_1 is C-H; G_2 is C-H; R_1 is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl; R_{2a} is halogen, trifluoromethyl, cyano or cyclopropyl which can be monosubstituted by cyano; and R_3 is hydrogen or trifluoromethyl.

In further preferred compounds of formula I-1, G_1 is C-H; G_2 is C-H; R_1 is ethyl, R_{2a} is trifluoromethyl and R_3 is hydrogen or trifluoromethyl.

Other preferred compounds of formula I-1 are those, wherein G_1 is C-H; G_2 is N; and R_1, R_{2a} and R_3 are as defined under formula I-1 above.

Also preferred are compounds of formula I-1, wherein G_1 is C-H; G_2 is N; R_1 is C_1-C_4 alkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl or C_3-C_6cycloalkyl; R_{2a} is halogen, C_1-C_4 haloalkyl, cyano or C_3-C_6cycloalkyl which can be mono - or polysubstituted by substituents selected from the group consisting of halogen, cyano and C_1-C_4alkyl; and R_3 is hydrogen, halogen or C_1-C_4haloalkyl.

Further preferred are compounds of formula I-1 are those, wherein G_1 is C-H; G_2 is N; R_1 is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl; R_{2a} is halogen, trifluoromethyl, cyano or is cyclopropyl which can be monosubstituted by cyano; and R_3 is hydrogen or trifluoromethyl.

Further preferred are compounds of formula I-1, wherein G_1 is C-H; G_2 is N; R_1 is ethyl; R_{2a} is trifluoromethyl; and R_3 is hydrogen or trifluoromethyl.

In other preferred compounds of formula I-1, G_1 is CR_4; wherein R_4 is as defined under formula I above; G_2 is C-H; and R_1, R_{2a} and R_3 are as defined under formula I-1 above.

Also preferred are compounds of formula I-1, wherein G_1 is CR_4; wherein R_4 is as defined under formula I above; G_2 is C-H; R_1 is C_1-C_4 alkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl or C_3-C_6cycloalkyl; R_{2a} is halogen, C_1-C_4haloalkyl, cyano or C_3-C_6cycloalkyl which can be mono - or polysubstituted by substituents selected from the group consisting of halogen, cyano and C_1-C_4alkyl; and R_3 is hydrogen, halogen or C_1-C_4haloalkyl.

In a further preferred group of compounds of formula I-1, G_1 is CR_4; wherein R_4 is as defined under formula I above; G_2 is C-H; R_1 is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl; R_{2a} is halogen, trifluoromethyl, cyano or is cyclopropyl which can be monosubstituted by cyano; and R_3 is hydrogen or trifluoromethyl.

Further preferred are compounds of formula I-1, wherein G_1 is CR_4; wherein R_4 is as defined under formula I above; G_2 is C-H; R_1 is ethyl; R_{2a} is trifluoromethyl and R_3 is hydrogen or trifluoromethyl.

Further preferred are compounds of formula I-1, wherein G_1 is CR_4, wherein R_4 is as defined under formula I above; G_2 is N; and R_1, R_{2a} and R_3 are as defined under formula I-1 above.

Also preferred are compounds of formula I-1, wherein G_1 is CR_4; wherein R_4 is as defined under formula I above; G_2 is N; R_1 is C_1-C_4alkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl or C_3-C_6cycloalkyl; R_{2a} is halogen, C_1-C_4haloalkyl, cyano or is C_3-C_6cycloalkyl which can be mono - or polysubstituted by substituents selected from the group consisting of halogen, cyano and C_1-C_4alkyl; and R_3 is hydrogen, halogen or C_1-C_4haloalkyl.

In another preferred group of compounds of formula I-1, G_1 is CR_4; wherein R_4 is as defined under formula I above; G_2 is N; R_1 is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl, R_{2a} is halogen, trifluoromethyl, cyano or is cyclopropyl which can be monosubstituted by cyano; and R_3 is hydrogen or trifluoromethyl.

Further preferred are compounds of formula I-1, wherein G_1 is CR_4; wherein R_4 is as defined under formula I above; G_2 is N; R_1 is ethyl; R_{2a} is trifluoromethyl; and R_3 is hydrogen or trifluoromethyl.

Also preferred are compounds of formula I-1, wherein G_1 is CR_4; wherein R_4 is hydrogen, methyl, cyano, chloro or bromo; G_2 is C-H; R_1 is C_1-C_4 alkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl or C_3-C_6cycloalkyl; R_{2a} is halogen, C_1-C_4haloalkyl, cyano, or is C_3-C_6cycloalkyl which can be mono - or polysubstituted by substituents selected from halogen, cyano and C_1-C_4alkyl; and R_3 is hydrogen, halogen or C_1-C_4haloalkyl.

In another preferred compounds of formula I-1, G_1 is CR_4; wherein R_4 is hydrogen, methyl, cyano, chloro or bromo; G_2 is C-H; R_1 is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl; R_{2a} is halogen, trifluoromethyl, cyano or is cyclopropyl which can be monosubstituted by cyano; and R_3 is hydrogen or trifluoromethyl.

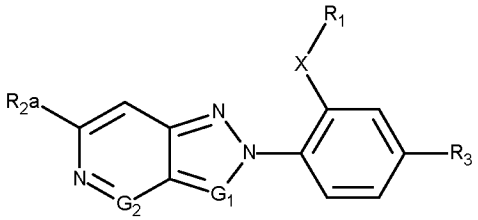
Further preferred compounds of formula I-1 are those, wherein G_1 is CR_4; wherein R_4 is hydrogen, methyl, cyano, chloro or bromo; G_2 is C-H; R_1 is ethyl, R_{2a} is trifluoromethyl and R_3 is hydrogen or trifluoromethyl.

Also preferred are compounds of formula I-1, wherein G_1 is CR_4; wherein R_4 is hydrogen, methyl, cyano, chloro or bromo; G_2 is N; R_1 is C_1-C_4 alkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl or C_3-C_6cycloalkyl; R_{2a} is halogen, C_1-C_4haloalkyl, cyano or C_3-C_6cycloalkyl which can be mono - or polysubstituted by substituents selected from the group consisting of halogen, cyano and C_1-C_4alkyl; and R_3 is hydrogen, halogen or C_1-C_4haloalkyl.

In another preferred group of compounds of formula I-1, G_1 is CR_4; wherein R_4 is hydrogen, methyl, cyano, chloro or bromo; G_2 is N; R_1 is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl; R_{2a} is halogen, trifluoromethyl, cyano or cyclopropyl which can be monosubstituted by cyano; and R_3 is hydrogen or trifluoromethyl.

In another preferred group of compounds of formula I-1; G_1 is CR_4; wherein R_4 is hydrogen, methyl, cyano, chloro or bromo, G_2 is N; R_1 is ethyl, R_{2a} is trifluoromethyl and R_3 is hydrogen or trifluoromethyl.

Another preferred group of compounds of formula I is represented by the compounds of formula I-2



(I-2),

wherein G_1, G_2 R_1 and R_{2a} are as defined under formula I above, X is S, SO or SO_2; preferably S or SO_2; R_3 is hydrogen, halogen or C_1-C_4haloalkyl, in particular C_1-C_4haloalkyl; and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of those compounds.

Preferred are compounds of formula I-2, wherein G_1 is C-H; G_2 is C-H; and R_1, R_{2a} and R_3 are as defined under formula I-2 above.

Also preferred are compounds of formula I-2, wherein G_1 is C-H; G_2 is C-H; R_1 is C_1-C_4alkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl or C_3-C_6cycloalkyl; R_{2a} is halogen, C_1-C_4haloalkyl, cyano or C_3-C_6cycloalkyl which can be mono - or polysubstituted by substituents selected from the group consisting of halogen, cyano and C_1-C_4alkyl; and R_3 is hydrogen, halogen or C_1-C_4haloalkyl, preferably C_1-C_4haloalkyl.

Also preferred are compounds of formula I-2, wherein G_1 is C-H; G_2 is C-H; R_1 is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl; R_{2a} is halogen, trifluoromethyl, cyano or cyclopropyl which can be monosubstituted by cyano; and R_3 is hydrogen or trifluoromethyl.

In further preferred compounds of formula I-2, G_1 is C-H; G_2 is C-H; R_1 is ethyl, R_{2a} is trifluoromethyl and R_3 is hydrogen or trifluoromethyl.

Other preferred compounds of formula I-2 are those, wherein G_1 is C-H; G_2 is N; and R_1, R_{2a} and R_3 are as defined under formula I-2 above.

Also preferred are compounds of formula I-2, wherein G_1 is C-H; G_2 is N; R_1 is C_1-C_4 alkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl or C_3-C_6cycloalkyl; R_{2a} is halogen, C_1-C_4 haloalkyl, cyano or C_3-C_6cycloalkyl which can be mono - or polysubstituted by substituents selected from the group consisting of halogen, cyano and C_1-C_4alkyl; and R_3 is hydrogen, halogen or C_1-C_4haloalkyl.

Further preferred are compounds of formula I-2 are those, wherein G_1 is C-H; G_2 is N; R_1 is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl; R_{2a} is halogen, trifluoromethyl, cyano or is cyclopropyl which can be monosubstituted by cyano; and R_3 is hydrogen or trifluoromethyl.

Further preferred are compounds of formula I-2, wherein G_1 is C-H; G_2 is N; R_1 is ethyl; R_{2a} is trifluoromethyl; and R_3 is hydrogen or trifluoromethyl.

In other preferred compounds of formula I-2, G_1 is CR_4; wherein R_4 is as defined under formula I above; G_2 is C-H; and R_1, R_{2a} and R_3 are as defined under formula I-2 above.

Also preferred are compounds of formula I-2, wherein G_1 is CR_4; wherein R_4 is as defined under formula I above; G_2 is C-H; R_1 is C_1-C_4 alkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl or C_3-C_6cycloalkyl; R_{2a} is halogen, C_1-C_4haloalkyl, cyano or C_3-C_6cycloalkyl which can be mono - or polysubstituted by substituents selected from the group consisting of halogen, cyano and C_1-C_4alkyl; and R_3 is hydrogen, halogen or C_1-C_4haloalkyl.

In a further preferred group of compounds of formula I-2, G_1 is CR_4; wherein R_4 is as defined under formula I above; G_2 is C-H; R_1 is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl; R_{2a} is halogen,

trifluoromethyl, cyano or is cyclopropyl which can be monosubstituted by cyano; and R_3 is hydrogen or trifluoromethyl.

Further preferred are compounds of formula I-2, wherein G_1 is CR_4; wherein R_4 is as defined under formula I above; G_2 is C-H; R_1 is ethyl; R_{2a} is trifluoromethyl and R_3 is hydrogen or trifluoromethyl.

Further preferred are compounds of formula I-2, wherein G_1 is CR_4, wherein R_4 is as defined under formula I above; G_2 is N; and R_1, R_{2a} and R_3 are as defined under formula I-2 above.

Also preferred are compounds of formula I-2, wherein G_1 is CR_4; wherein R_4 is as defined under formula I above; G_2 is N; R_1 is C_1-C_4alkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl or C_3-C_6cycloalkyl; R_{2a} is halogen, C_1-C_4haloalkyl, cyano or is C_3-C_6cycloalkyl which can be mono - or polysubstituted by substituents selected from the group consisting of halogen, cyano and C_1-C_4alkyl; and R_3 is hydrogen, halogen or C_1-C_4haloalkyl.

In another preferred group of compounds of formula I-2, G_1 is CR_4; wherein R_4 is as defined under formula I above; G_2 is N; R_1 is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl, R_{2a} is halogen, trifluoromethyl, cyano or is cyclopropyl which can be monosubstituted by cyano; and R_3 is hydrogen or trifluoromethyl.

Further preferred are compounds of formula I-2, wherein G_1 is CR_4; wherein R_4 is as defined under formula I above; G_2 is N; R_1 is ethyl; R_{2a} is trifluoromethyl; and R_3 is hydrogen or trifluoromethyl.

Also preferred are compounds of formula I-2, wherein G_1 is CR_4; wherein R_4 is hydrogen, methyl, cyano, chloro or bromo; G_2 is C-H; R_1 is C_1-C_4 alkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl or C_3-C_6cycloalkyl; R_{2a} is halogen, C_1-C_4haloalkyl, cyano, or is C_3-C_6cycloalkyl which can be mono - or polysubstituted by substituents selected from halogen, cyano and C_1-C_4alkyl; and R_3 is hydrogen, halogen or C_1-C_4haloalkyl.

In another preferred compounds of formula I-2, G_1 is CR_4; wherein R_4 is hydrogen, methyl, cyano, chloro or bromo; G_2 is C-H; R_1 is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl; R_{2a} is halogen, trifluoromethyl, cyano or is cyclopropyl which can be monosubstituted by cyano; and R_3 is hydrogen or trifluoromethyl.

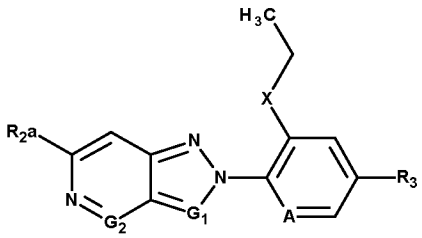
Further preferred compounds of formula I-2 are those, wherein G_1 is CR_4; wherein R_4 is hydrogen, methyl, cyano, chloro or bromo; G_2 is C-H; R_1 is ethyl, R_{2a} is trifluoromethyl and R_3 is hydrogen or trifluoromethyl.

Also preferred are compounds of formula I-2, wherein G_1 is CR_4; wherein R_4 is hydrogen, methyl, cyano, chloro or bromo; G_2 is N; R_1 is C_1-C_4 alkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl or C_3-C_6cycloalkyl; R_{2a} is halogen, C_1-C_4haloalkyl, cyano or C_3-C_6cycloalkyl which can be mono - or polysubstituted by substituents selected from the group consisting of halogen, cyano and C_1-C_4alkyl; and R_3 is hydrogen, halogen or C_1-C_4haloalkyl.

In another preferred group of compounds of formula I-2, G_1 is CR_4; wherein R_4 is hydrogen, methyl, cyano, chloro or bromo; G_2 is N; R_1 is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl; R_{2a} is halogen, trifluoromethyl, cyano or cyclopropyl which can be monosubstituted by cyano; and R_3 is hydrogen or trifluoromethyl.

In another preferred group of compounds of formula I-2, G_1 is CR_4; wherein R_4 is hydrogen, methyl, cyano, chloro or bromo; G_2 is N; R_1 is ethyl; R_{2a} is trifluoromethyl and R_3 is hydrogen or trifluoromethyl.

A further preferred group of compounds of formula I is represented by the compounds of formula I-3a



(I-3a),

wherein

X is S, SO or SO_2; preferably S or SO_2;

R_{2a} is C_1-C_4haloalkyl or halogen; in particular bromo or CF_3;

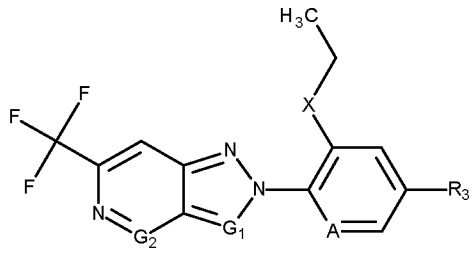
R_3 is hydrogen, C_1-C_4haloalkyl, C_3-C_6cycloalkyl, or is phenyl which can be monosubstituted by halogen or C_1-C_4haloalkyl;

G_1 is CR_4, wherein R_4 is hydrogen, C_1-C_4alkyl, cyano or halogen; in particular R_4 is hydrogen;

G_2 is CH or N; in particular CH; and

A is CH or N; and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of those compounds.

A further preferred group of compounds of formula I is represented by the compounds of formula I-3



(I-3),

wherein

X is S, SO or SO_2; preferably S or SO_2;

R_3 is hydrogen, C_1-C_4haloalkyl, C_3-C_6cycloalkyl or phenyl which can be monosubstituted by halogen or C_1-C_4haloalkyl;

G_1 is CR_4, wherein R_4 is hydrogen, C_1-C_4alkyl, cyano or halogen;

G_2 is CH; and

A is CH or N; and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of those compounds.

A further preferred group of compounds of formula I is represented by the compounds of formula I-3 wherein

X is S, SO or SO_2; preferably S or SO_2;

R_3 is hydrogen, CF_3 or phenyl which can be monosubstituted by halogen;

G_1 is CR_4, wherein R_4 is hydrogen, C_1-C_4alkyl, cyano or halogen;

G_2 is N; and

A is CH or N; and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of those compounds.

In especially preferred compounds of formula I,

R_1 is C_1-C_4alkyl;

R_2a is C_1-C_4haloalkyl or halogen, preferably C_1-C_4haloalkyl;

R_2b is hydrogen;

R_3 is hydrogen;

G_1 is CR_4;

R_4 is hydrogen;

G_2 is CR_5;

R_5 is hydrogen;

G_3 is CR_8;

R_8 is hydrogen;

X is S or SO_2; and

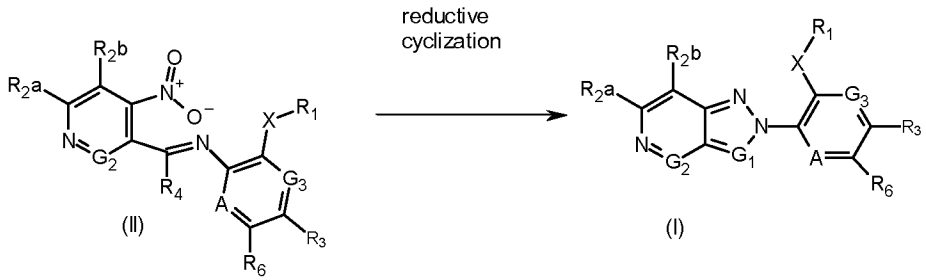
A is CH or N.

The process according to the invention for preparing compounds of formula (I) is carried out in principle by methods known to those skilled in the art, or in analogy to processes described in the literature, for example, in WO 2013/191113 using the appropriate starting materials.

More specifically, the subgroup of compounds of formula I, wherein X is SO (sulfoxide) and/or SO_2 (sulfone), may be obtained by means of an oxidation reaction of the corresponding sulfide compounds of formula I, wherein X is S, involving reagents such as, for example, m-chloroperoxybenzoic acid (mCPBA), hydrogen peroxide, oxone, sodium periodate, sodium hypochlorite or tert-butyl hypochlorite amongst other oxidants. The oxidation reaction is generally conducted in the presence of a solvent. Examples of the solvent to be used in the reaction include aliphatic halogenated hydrocarbons such as dichloromethane and chloroform; alcohols such as methanol and ethanol; acetic acid; water; and mixtures thereof. The amount of the oxidant to be used in the reaction is generally 1 to 3 moles, preferably 1 to 1.2 moles, relative to 1 mole of the sulfide compounds I to produce the sulfoxide compounds I, and preferably 2 to 2.2 moles of oxidant, relative to 1 mole of of the sulfide compounds I to produce the sulfone compounds I. Such oxidation reactions are disclosed, for example, in WO 2013/018928.

Indazoles, aza-indazoles and/or diaza-indazoles, may be made using processes that are well known and have been described for example in WO 2013/191113; Synlett (2013), 24(12), 1573-1577; Journal of the Chemical Society, Chemical Communications (1991), (20), 1466-7; Organic Letters (2014), 16(11), 3114-3117; or for a review on more general synthesis for this type of derivatives, see for example Science of Synthesis (2002), 12, 227-324 and European Journal of Organic Chemistry (2008), (24), 4073-4095. All of these process could be use to access indazoles derivatives. One possible process is summarized in scheme 1 for compounds of formula I:

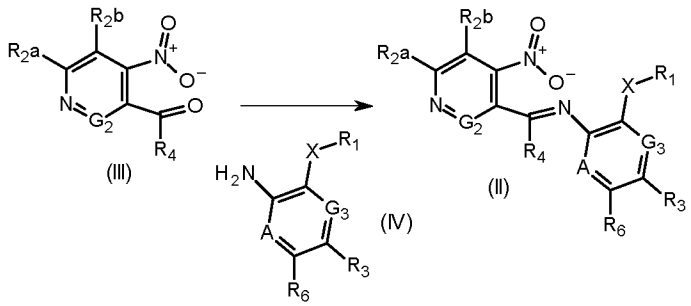
Scheme 1



Compounds of formula (I) may be prepared by reaction of a compound of formula (II) under reductive cyclisation conditions using a reducing agent, such as trialkyl phosphite (more specifically, for example triethyl phosphite), trialkylphosphine or triphenylphosphine. The principle of this reductive cyclisation is analogous to the known Cadogan reaction. Alternatively, this reaction may be conducted in presence

of a metal catalyst, for example a molybdenum(VI) catalyst such as $MoO_2Cl_2(dmf)_2$ [molybdenyl chloride-bis(dimethylformamide)], or more generally with transition metal complexes in combination with a reducing agent such as triethylphosphite, triphenylphosphine or CO. Suitable solvents may include use of excess of the reducing agent (such as triethyl phosphite), or for example toluene or xylene at temperatures between room temperature and 200°C, preferably between 50 and 160°C, optionally under microwave conditions.

Scheme 2

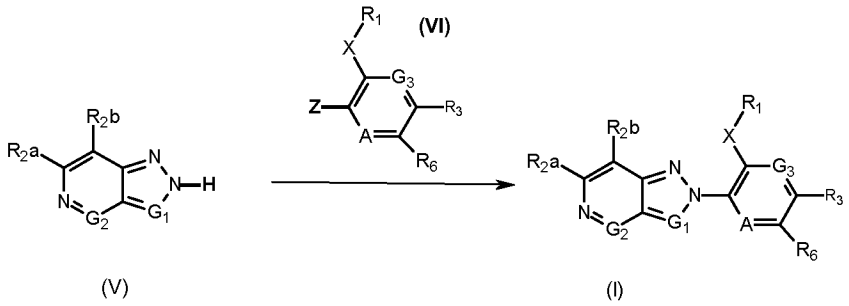


Compounds of formula (II) may be prepared (scheme 2) by reaction of aldehyde or ketone derivatives of formula (III) with amine derivatives of formula (IV), usually upon heating and optionally under microwave conditions. The formation of compounds of formula (II) may require water removal, either by azeotropical distillation, or with a drying agent such as for example $TiCl_4$ or molecular sieves. The formation of the Schiff bases of formula (II) is very well known to those skilled in the art, and methods are well described in the literature, see for example, Molbank (2006), M514 or March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, 5th Edition p 1185-1187 and cited documents therein. Suitable solvents may include for example toluene or xylene at temperatures between room temperature and 200°C, preferably between 50 and 160°C.

Compounds of formula (III) are either known, commercially available or may be made by methods known to a person skilled in the art.

Compounds of formula (IV) are either known, commercially available or may be made by methods known to a person skilled in the art.

Scheme 3

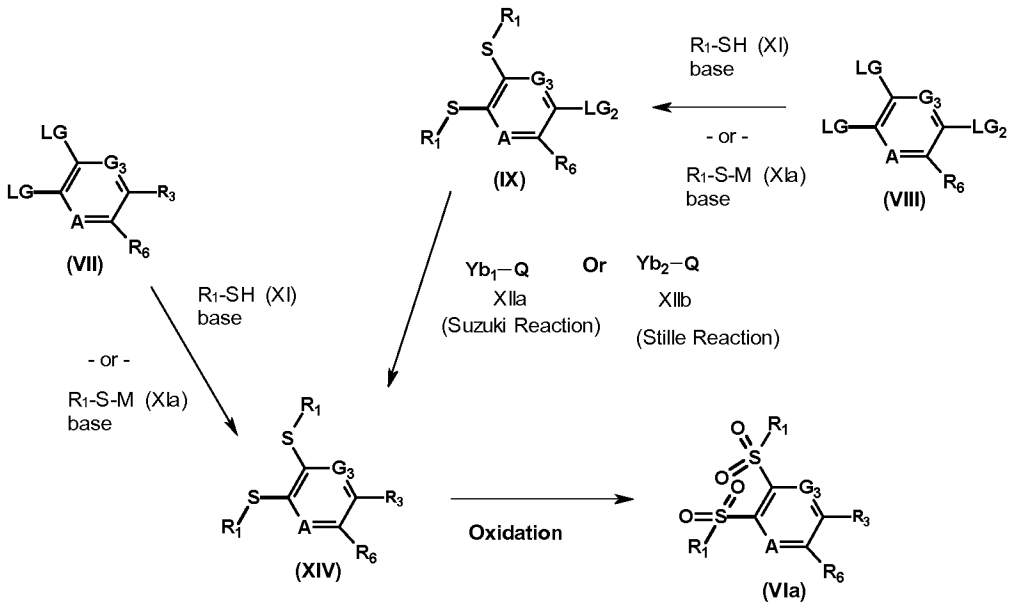


In an alternative method depicted in scheme 2, compounds of formula I can also be prepared by reacting compounds of formula V, wherein R_{2a}, R_{2b}, G_1, G_2 have the values defined in formula I with a compound of formula (VI) wherein Z is a leaving group like, for example, fluorine, chlorine, bromine or iodine, or an aryl- or alkylsulfonate, or any other similar leaving group. For example, this reaction, called S_NAr reaction (aromatic nucleophilic substitution reaction) can be done in a presence of base such as for example sodium, potassium or lithium carbonate, in a solvent such as dimethyl formamide, at temperatures between room temperature and 200°C, with or without microwave irradiation. An example of this type of reaction is described in WO 2007/113596 and Journal of Medicinal Chemistry, 52(22), 7170-7185, 2009. In an alternative method, a compound of formula (VI) wherein Z is chlorine, bromine or iodine, or any other appropriate leaving group, could be coupled with compounds of formula V by using copper catalyst coupling conditions, for example using copper(I) iodide as copper catalyst, with or without an additive such as L-proline or N,N'-dimethylethylenediamine, in presence of a base such as, for example potassium carbonate. Said alternative method is for example described in WO 2006/107771 and WO 2012/083105.

Compounds of formula (V) are either known, commercially available or may be made by methods known to a person skilled in the art.

Compounds of formula (VI) are either known, commercially available or may be made by methods known to a person skilled in the art. One particular example is described in scheme 4.

Scheme 4



Compounds of formula (VIa), wherein R_3, R_6, R_1, A and G_3 have the values defined in formula I may be prepared (scheme 4) by oxydation of compounds of formula (XIV). The reaction can be performed with reagents like, for example a peracid as peracetic acid or m-chloroperbenzoic acid, or a hydroperoxide as for example hydrogen peroxide or tert-butylhydroperoxide, or an inorganic oxidant, like a mono-peroxodisulfate salt or potassium permanganate, preferentially meta-chloroperbenzoic acid.

Compounds of formula (XIV) wherein R_3, R_6, R_1, A and G_3 have the values defined in formula I, may be prepared (scheme 4) by substitution of the two leaving groups (LG) of compounds of formula (VII), LG is, for example Cl or fluorine, by reaction with compounds of formula XI

$$R_1\text{-SH} \quad \text{(XI)},$$

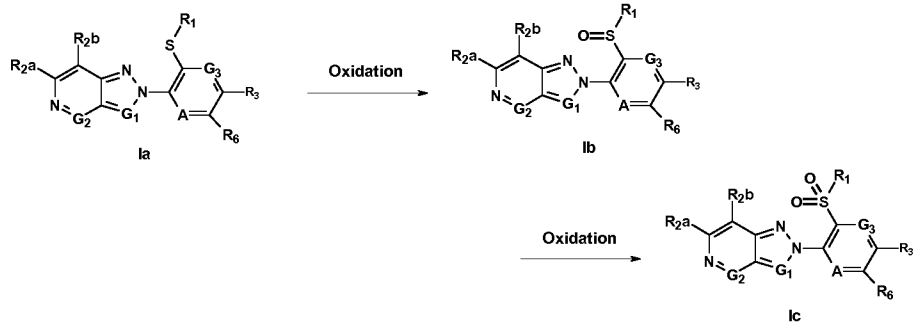
or a salt thereof, wherein R_1 is as defined in formula I, optionally in the presence of a suitable base, such as alkali metal carbonates, for example sodium carbonate and potassium carbonate, or alkali metal hydrides such as sodium hydride, or alkali metal hydroxides such as sodium hydroxide and potassium hydroxide, in an inert solvent at temperatures preferably between 25-120°C. Examples of solvent to be used include ethers such as THF, ethylene glycol dimethyl ether, tert-butylmethyl ether, and 1,4-dioxane, aromatic hydrocarbons such as toluene and xylene, nitriles such as acetonitrile or polar aprotic solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone or dimethyl sulfoxide. Examples of salts of the compound of formula X include compounds of the formula XIa

$$R_1\text{-S-M} \quad \text{(XIa)},$$

wherein R_1 is as defined above and wherein M is, for example, sodium or potassium.

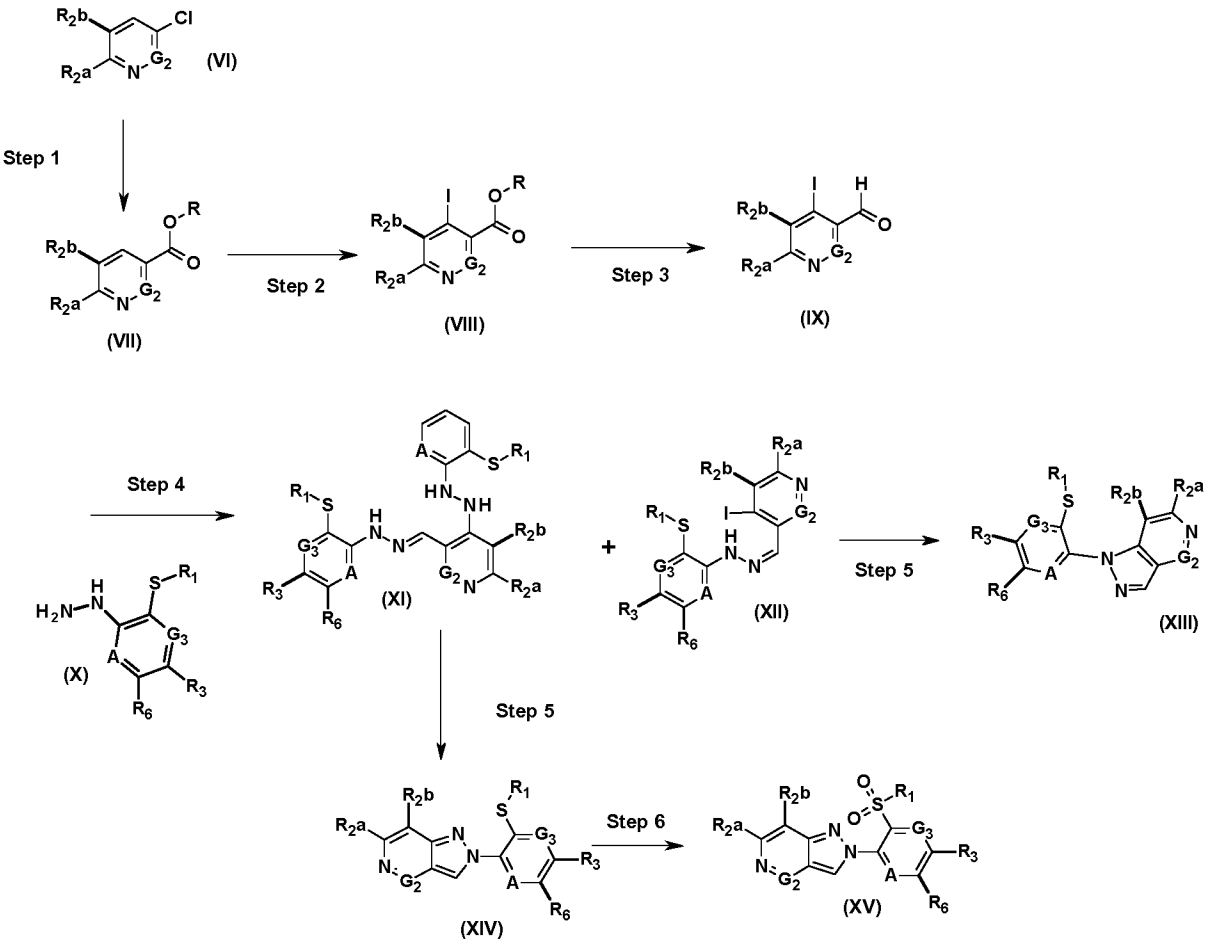
Under the similar condition, compounds of formula (IX) may be prepare from compounds of formula (VIII) wherein, LG is, for example Cl or fluorine and LG_2 is bromide or iodine. The transformation of compounds of formula (IX) to compounds of formula (XIV) via transformation of LG_2 to R_3 can be perform by methods well known to a person skilled in the art. For example, compounds of formula (XIV) wherein R_6, R_1, A and G_3 have the values defined in formula I and R_3 is, for example, cyclopropane, alkenyl, alkynyl, aral or heteroaryl can be prepared by a Stille reaction of compounds of formula XIIb wherein Y_{b2} is a trialkyl tin derivative, preferably tri-n-butyl tin, with compounds of formula XIV. Such Stille reactions are usually carried out in the presence of a palladium catalyst, for example *tetrakis*(triphenylphosphine)palladium(0), or (1,1'bis(diphenylphosphino)-ferrocene)dichloropalladium-dichloromethane (1:1 complex), in an inert solvent such as DMF, acetonitrile, or dioxane, optionally in the presence of an additive, such as cesium fluoride, or lithium chloride, and optionally in the presence of a further catalyst, for example copper(I)iodide. Such Stille couplings are also well known to those skilled in the art, and have been described in for example *J. Org. Chem.*, **2005**, *70*, 8601-8604, *J. Org. Chem.*, **2009**, *74*, 5599-5602, and *Angew. Chem. Int. Ed.,* **2004**, *43*, 1132-1136. Alternatively, compounds of formula (XIV) wherein R_6, R_1, A and G_3 have the values defined in formula I and R_3 is, for example, cyclopropane, alkenyl, alkynyl, aral or heteroaryl can be prepared by a Suzuki reaction, which involves reacting compounds of formula IX, wherein LG is a leaving group, for example, chlorine, bromine or iodine with compounds of formula XIIa, wherein Y_{b1} can be a boron-derived functional group, as for example $B(OH)_2$ or $B(OR_{b1})_2$ wherein R_{b1} can be a C_1-C_4alkyl group or the two groups OR_{b1} can form together with the boron atom a five membered ring, as for example a pinacol boronic ester. The reaction can be catalyzed by a palladium based catalyst, for example *tetrakis*(triphenylphosphine)-palladium or (1,1'bis(diphenylphosphino)-ferrocene)dichloropalladium-dichloromethane (1:1 complex), in presence of a base, like sodium carbonate or cesium fluoride, in a solvent or a solvent mixture, like, for example a mixture of 1,2-dimethoxyethane and water, or of dioxane and water, preferably under an inert atmosphere. The reaction temperature can preferentially range from room temperature to the boiling point of the reaction mixture. Such Suzuki reactions are well known to those skilled in the art and have been reviewed, for example *J.Orgmet. Chem.* 576, ***1999***, 147–168.

Scheme 5



Compounds of formula Ib, wherein A, R_1, R_{2a}, R_{2b}, R_3, R_6, G_1, G_2 and G_3 have the values defined in formula I, can be prepared (scheme 12) by oxidation of compounds of formula Ia, wherein A, R_1, R_{2a}, R_{2b}, R_3, R_6, G_1, G_2 and G_3 have the values defined in formula I. The reaction can be performed with reagents like, for example a peracid as peracetic acid or m-chloroperbenzoic acid, or a hydroperoxide as for example hydrogen peroxide or tert-butylhydroperoxide, or an inorganic oxidant, like a mono-peroxodisulfate salt or potassium permanganate, preferentially meta-chloroperbenzoic acid. In a similar way, compounds of formula Ic, wherein A, R_1, R_{2a}, R_{2b}, R_3, R_6, G_1, G_2 and G_3 have the values defined in formula I, can be prepared by oxidation of compounds of formula Ib. 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 and the number of equivalents of oxidant will determinate the degres of oxidation of the sulphur, e.g. with two or more equivalents of oxidant, the compound of formula Ic can be prepare directly from compound of formula Ia.

Scheme 6



Compounds of formula (XV) can be prepared, for example, as described in scheme 6: 1) by reacting compounds of formula (VI) with carbone monoxide in presence of metal catalyst a such as palladium catalyst (for example: palladium(II)acetate) in a alcohol such as methanol or ethanol and optionnaly in presence of ligan (for example: 1,1′-Ferrocenediyl-bis(diphenylphosphine) and, optionnaly, in presence of a base (for example: N,N-diethylethanamine). These reaction are well known in literature under the name of “carbonylative cross-coupling of Aryl Halides”. For examples of such reaction, see: Angewandte Chemie, International Edition (**2009**), 48(23), 4114-4133 or *Organometallics*. **2008**, *27*, 5402. 2) by halogenation of compounds of formula (VII) via, first, deprotonative metalation of compounds of formula (VII) to generate the organometallic derived from compounds of formula (VII) at low temperature in presence of an organometallic such as butyllithium, then followed by reaction with an halogen electrophile such as iodine or bromide. This transformation is well known by a person skilled in the art and many reagent could realize this transformation using different organometallic and conditions to generate the organometallic derived from compounds of formula (VII), see for some examples around these types of reaction: Journal of the American Chemical Society **1999**, 121(14),

3539-3540 or Angewandte Chemie, International Edition (2014), 53(30), 7928-7932). 3) reduction of the ester of the compound of formula (VIII) to aldehyde via reduction under standart condition: for example in presence of a reduction agent suvh as Diisobutylaluminium hydride in a solvent such as dichloromethane to give compound of formula (IX). Such reaction are well known by by a person skilled in the art (see for example of this transformation: Comprehensive Organic Transformations A Guide to Functional Group Preparations by Larock, R. C. 1989, p 619 (Publisher VCH Weinheim, Germany)) 4) the reaction of compounds of formula (IX) with compounds of formula (X) in a solvent such as methanol gave compounds of formula (XI) and optionnaly compounds of formula (XII). 5) heating of compounds of formula (XI) in a solvent such as dimethylformamide in microwaves or not gave compounds of formula (XIV). 6) oxidation of the sulphur group of compound of formula (XIV) in conditons similar as decribed in scheme 5 gave the desired compounds of formula (XV).

Compounds of formula (X) are either known, commercially available or may be made 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 reaction is 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.

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.

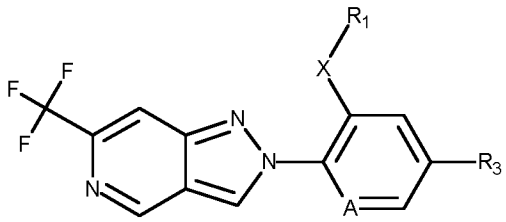
N-oxides can be prepared by reacting a compound of the formula I with a suitable oxidizing agent, for example the H_2O_2/urea adduct in the presence of an acid anhydride, e.g. trifluoroacetic anhydride. Such oxidations are known from the literature, for example from J. Med. Chem., 32 (12), 2561-73, 1989 or WO 00/15615.

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 1 to 3 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. “Ph” represents the phenyl group.

Table 1: This table discloses the 10 compounds of the formula I-1a:



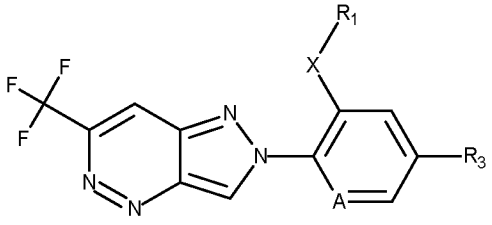
(I-1a),

Table 1:

Comp.No	X	R_1	R_3	A
1.001	S	$-CH_2CH_3$	CF_3	CH
1.002	$S(O)_2$	$-CH_2CH_3$	CF_3	CH
1.003	S	$-CH_2CH_3$	CF_3	N
1.004	$S(O)_2$	$-CH_2CH_3$	CF_3	N
1.005	S	$-CH_2CH_3$	H	CH
1.006	$S(O)_2$	$-CH_2CH_3$	H	CH
1.007	S	$-CH_2CH_3$	H	N
1.008	$S(O)_2$	$-CH_2CH_3$	H	N
1.009	S	$-CH_2CH_3$	4-Cl-Ph-	N
1.010	$S(O)_2$	$-CH_2CH_3$	4-Cl-Ph-	N

and the N-oxides of the compounds of Table 1.

Table 2: This table discloses 10 compounds of formula I-1b:



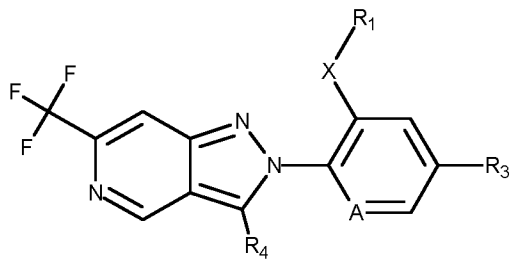
(I-1b),

Table 2:

Comp.No	X	R_1	R_3	A
2.001	S	$-CH_2CH_3$	CF_3	CH
2.002	$S(O)_2$	$-CH_2CH_3$	CF_3	CH
2.003	S	$-CH_2CH_3$	CF_3	N
2.004	$S(O)_2$	$-CH_2CH_3$	CF_3	N
2.005	S	$-CH_2CH_3$	H	CH
2.006	$S(O)_2$	$-CH_2CH_3$	H	CH
2.007	S	$-CH_2CH_3$	H	N
2.008	$S(O)_2$	$-CH_2CH_3$	H	N
2.009	S	$-CH_2CH_3$	4-Cl-Ph-	N
2.010	$S(O)_2$	$-CH_2CH_3$	4-Cl-Ph-	N

and the N-oxides of the compounds of Table 2.

Table 3: This table discloses 12 compounds of the formula I-1c:



(I-1c),

Table 3:

Comp.No	X	R_1	R_3	A	R_4
3.001	S	$-CH_2CH_3$	CF_3	N	Br
3.002	$S(O)_2$	$-CH_2CH_3$	CF_3	N	Br
3.003	S	$-CH_2CH_3$	CF_3	N	CN

Comp.No	X	R_1	R_3	A	R_4
3.004	$S(O)_2$	$-CH_2CH_3$	CF_3	N	CN
3.005	S	$-CH_2CH_3$	CF_3	N	CH_3
3.006	$S(O)_2$	$-CH_2CH_3$	CF_3	N	CH_3
3.007	S	$-CH_2CH_3$	H	N	Br
3.008	$S(O)_2$	$-CH_2CH_3$	H	N	Br
3.009	S	$-CH_2CH_3$	H	N	CN
3.010	$S(O)_2$	$-CH_2CH_3$	H	N	CN
3.011	S	$-CH_2CH_3$	H	N	CH_3
3.012	$S(O)_2$	$-CH_2CH_3$	H	N	CH_3

and the N-oxides of the compounds of Table 3.

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

Examples of the abovementioned 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, Euchistus 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 gossypiella, 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).

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..

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, WO 2006/128870, EP 1724392, WO 2005/113886 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
	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,

Family	Species	Host or Crop Infested
		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
	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

Family	Species	Host or Crop Infested
	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
	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 Brucker 400MHz or 300MHz spectrometers, chemical shifts are given in ppm relevant to a TMS standard. Spectra measured in deuterated solvents as indicated.

LCMS Methods:

Method A (HPLC purification):

Column : Gemini-NX C18 (75x30mm – 5mm , 110A)
Mobile phase : A (water) – B (Acetonitrile)
Flow: 50ml/min

Gradient:	Time (mins)	A(%)	B(%)
	0	60	40
	0.1	60	40
	6	40	60
	7.9	40	60
	8	0	100
	8.9	0	100
	9	60	40
	10	60	40

Analytic conditions:

Method B - Standard: (SQD-ZDQ-ZCQ)
Spectra were recorded on a Mass Spectrometer from Waters (SQD, SQDII or ZQ Single quadrupole mass spectrometer) equipped with an electrospray source (Polarity: positive or negative ions, Capillary: 3.00 kV, Cone range: 30-60 V, Extractor: 2.00 V, Source Temperature: 150°C, Desolvation Temperature: 350°C, Cone Gas Flow: 0 L/Hr, Desolvation Gas Flow: 650 L/Hr, Mass range: 100 to 900 Da) and an Acquity UPLC from Waters: Binary pump, heated column compartment and diode-array detector. Solvent degasser, binary pump, heated column compartment and diode-array detector. Column: Waters UPLC HSS T3 , 1.8 mm, 30 x 2.1 mm, Temp: 60 °C, DAD Wavelength range (nm): 210 to 500, Solvent Gradient: A = water + 5% MeOH + 0.05 % HCOOH, B= Acetonitrile + 0.05 % HCOOH, gradient: 10-100% B in 1.2 min; Flow (ml/min) 0.85

Method C- Standard long: (SQD-ZDQ-ZCQ)
Spectra were recorded on a Mass Spectrometer from Waters (SQD, SQDII or ZQ Single quadrupole mass spectrometer) equipped with an electrospray source (Polarity: positive or negative ions, Capillary: 3.00 kV, Cone range: 30-60 V, Extractor: 2.00 V, Source Temperature: 150°C, Desolvation Temperature: 350°C, Cone Gas Flow: 0 L/Hr, Desolvation Gas Flow: 650 L/Hr, Mass range: 100 to 900 Da) and an Acquity UPLC from Waters: Binary pump, heated column compartment and diode-array detector. Solvent degasser, binary pump, heated column compartment and diode-array detector. Column: Waters UPLC HSS T3, 1.8 mm, 30 x 2.1 mm, Temp: 60 °C, DAD Wavelength range (nm): 210 to 500, Solvent Gradient: A = water + 5% MeOH + 0.05 % HCOOH, B= Acetonitrile + 0.05 % HCOOH, gradient: 10-100% B in 2.7 min; Flow (ml/min) 0.85

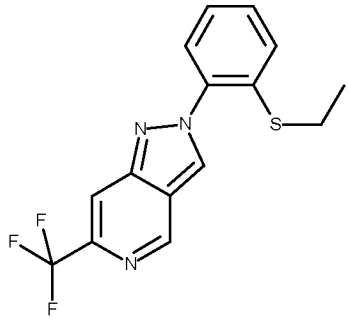
Method D - unpolar: (SQD-ZDQ-ZCQ)
Spectra were recorded on a Mass Spectrometer from Waters (SQD, SQDII or ZQ Single quadrupole mass spectrometer) equipped with an electrospray source (Polarity: positive or negative ions, Capillary: 3.00 kV, Cone range: 30-60 V, Extractor: 2.00 V, Source Temperature: 150°C, Desolvation Temperature: 350°C, Cone Gas Flow: 0 L/Hr, Desolvation Gas Flow: 650 L/Hr, Mass range: 100 to 900 Da) and an Acquity UPLC from Waters: Binary pump, heated column compartment and diode-array detector. Solvent degasser, binary pump, heated column compartment and diode-array detector. Column: Waters UPLC HSS T3, 1.8 mm, 30 x 2.1 mm, Temp: 60 °C, DAD Wavelength range (nm): 210 to 500, Solvent Gradient: A = water + 5% MeOH + 0.05 % HCOOH, B= Acetonitrile + 0.05 % HCOOH, gradient: 40-100% B in 1.2 min; Flow (ml/min) 0.85

Method E -GCMS Method: Standard CI/EI

GCMS was conducted on a Thermo, MS: DSQ and GC: TRACE GC ULTRA with a column from Zebron phenomenex: Phase ZB-5ms 15 m, diam: 0.25 mm, 0.25 µm, H_2 flow 1.7 ml/min, temp injector: 250°C, temp detector: 220°C, method: start at 70 °C, 25°C/min until 320°C, hold 2 min at 320°C, total time 12min.

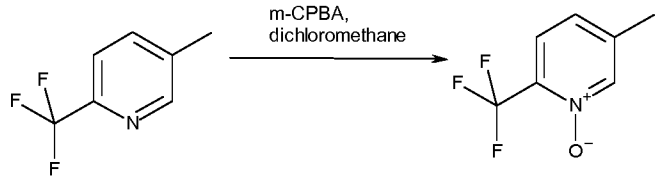
CI reagent gas: Methane, flow 1ml/min

Example P1: 2-(2-ethylsulfanylphenyl)-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine (compound 1.005)



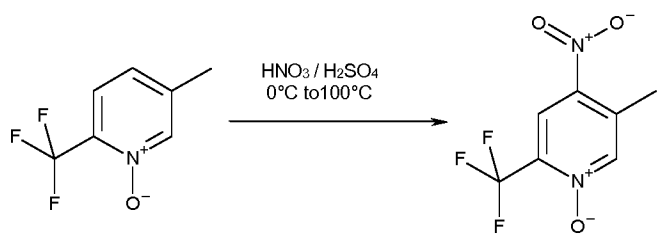
(1.005)

Step A: 5-methyl-2-(trifluoromethyl)pyridine 1-oxide



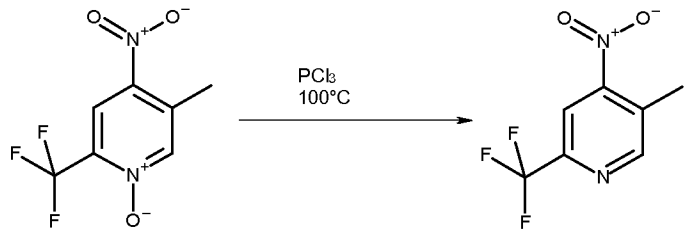
5-methyl-2-trifluoromethyl-pyridine (commercially available, 0.164g) was dissolved in dichloromethane (5 mL). Meta-chloroperoxybenzoic acid (m-CPBA, 0.486 g) was added, and the mixture was stirred 48 hours at ambient (rt) temperature. The solvent was remove under reduce pressure and the crude product was purified by chromatography (solvent: isohexane/diethyl ether 7/3 to diethylether) to give the title compound (120mg) as a white solid. ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) 8.17 (s, 1H), 7.57 (d, 1H), 7.16 (d, 1H), 2.38 (s, 3H) ppm.

Step B: 5-methyl-4-nitro-2-(trifluoromethyl)pyridine 1-oxide



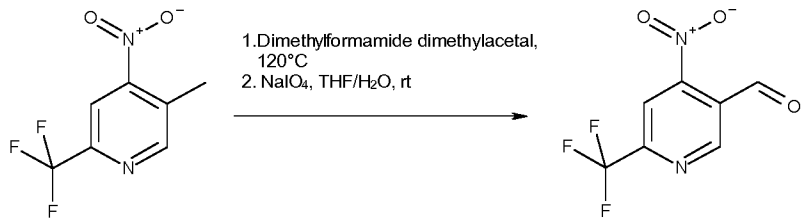
A solution of 5-methyl-2-(trifluoromethyl)pyridine 1-oxide (Step A, 0.787 g) in sulfuric acid H_2SO_4 (3 ml) was treated with a solution of nitric acid HNO_3 (4 ml) and sulfuric acid (2 mL) at 0° C. The reaction was stirred two hours at 100° C. Then, the reaction mixture was quentched with ice and the pH was adjusted to 7 by the addition of aqueous sodium hydroxide NaOH (4.0 M). The resulting solution was extracted three times with dichloromethane. The combined organic layers were washed with brine and dried on sodium sulfate and concentrated. The mixture was purified by flash chromatography eluting with hexanes and diethylether to give 5-methyl-4-nitro-2-(trifluoromethyl)pyridine 1-oxide (0.45 g). ^{1}H NMR (300MHz, CDCl3): δ (ppm) 8.42 (s, 1H), 8.22 (s, 1H), 2.68 (s, 3H) ppm.

Step C: 5-methyl-4-nitro-2-(trifluoromethyl)pyridine



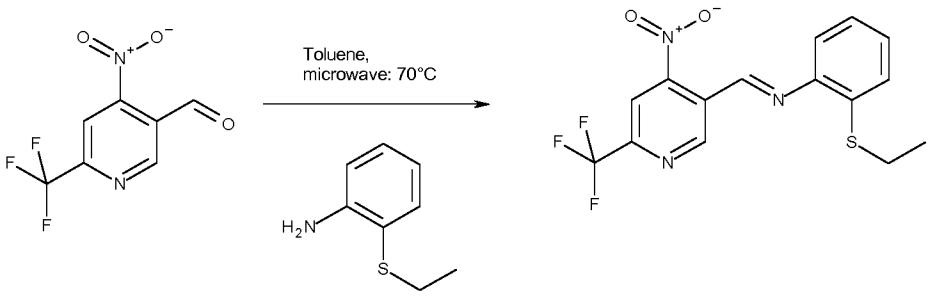
The 5-methyl-4-nitro-2-(trifluoromethyl)pyridine 1-oxide (Step B, 0.475g) was treated with phosphorus trichloride (1.13g). The mixture was heated at 100°C for 20 minutes. The residue was purified by chromatography (isohexane/diethyl ether 7/3) to give 5-methyl-4-nitro-2-(trifluoromethyl)pyridine (0.38g) . ^{1}H NMR (300MHz, CDCl3): δ (ppm) 8.85 (s, 1H), 8.16 (s, 1H), 2.70 (s, 3H) ppm.

Step D: 4-nitro-6-(trifluoromethyl)pyridine-3-carbaldehyde



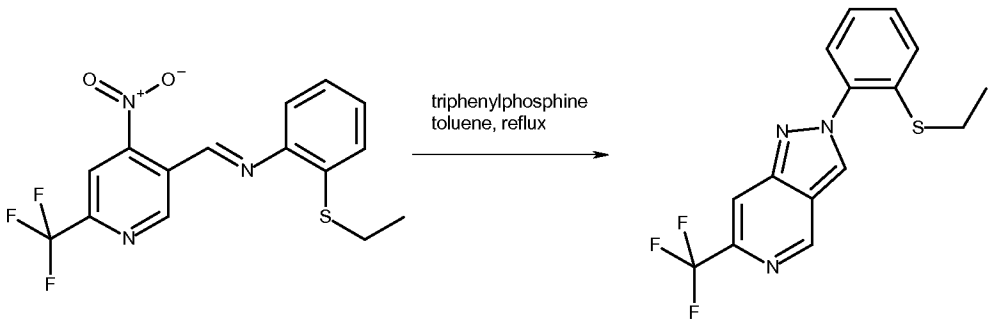
A mixture of 5-methyl-4-nitro-2-(trifluoromethyl)pyridine (Step C, 0.399 g) and N,N-dimethyl-formamide dimethyl acetal (0.361g) in dimethylformamide (2 ml) was stirred at 120°C for 2 hours. The solvent was evaporated under vacuum and the residue was poured into a mixture of sodium metaperiodate $NaIO_4$ (1.192g) dissolved in tetrahydrofuran (THF) and water (25ml:25ml). The mixture was stirred for 16 hours. The reaction mixture was filtered and the water layer was extracted, three times, with ethyl acetate. The combined organic layers were concentrated. The mixture was purified by flash chromatography (hexanes and diethyl ether) to give 4-nitro-6-(trifluoro-methyl)pyridine-3-carbaldehyde (0.405 g). ^{1}H NMR (300MHz, CDCl3): δ (ppm) 10.56 (s, 1H), 9.32 (s, 1H), 8.32 (s, 1H).

Step E: N-(2-ethylsulfanylphenyl)-1-[4-nitro-6-(trifluoromethyl)-3-pyridyl]methanimine



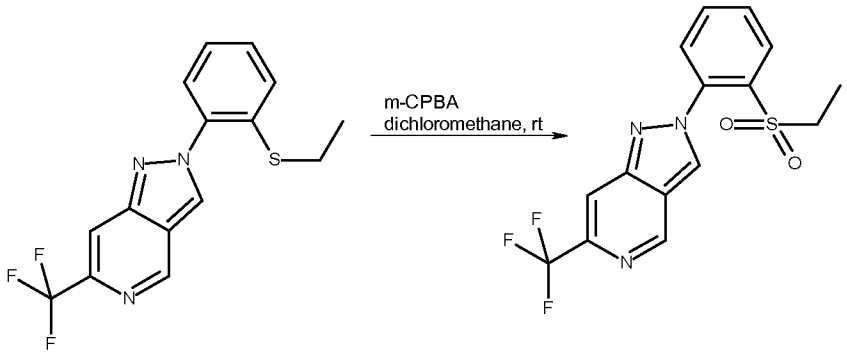
A mixture of 4-nitro-6-(trifluoromethyl)pyridine-3-carbaldehyde (Step D, 0.22g) and 2-(ethylthio)aniline (commercially available, 0.142g) in toluene was stirred at 70°C under microwave for 40 minutes. The reaction mixture was purified by flash chromatography (isohexane and diethylether) to give N-(2-ethylsulfanylphenyl)-1-[4-nitro-6-(trifluoromethyl)-3-pyridyl]methanimine (0.319 g). ^{1}H NMR (300MHz, CDCl3): δ (ppm) 9.82(s, 1H), 8.97 (s, 1H), 8.25(s, 1H), 7.23 (m, 3H), 7.11(m, 1H), 2.99 (q, 2H), 1.39 (t, 3H) ppm.

Step F: 2-(2-ethylsulfanylphenyl)-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine (compound 1.005)



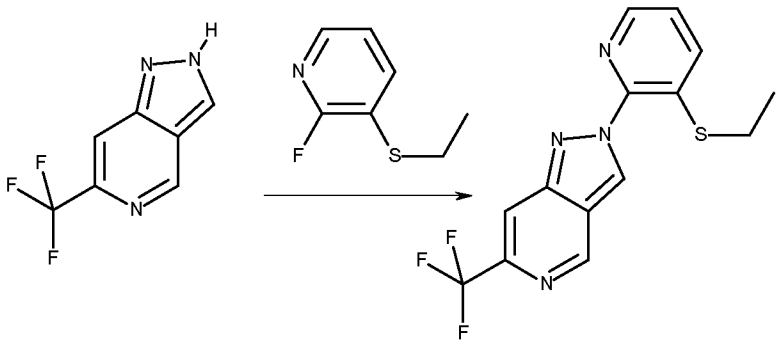
A mixture of N-(2-ethylsulfanylphenyl)-1-[4-nitro-6-(trifluoromethyl)-3-pyridyl]methanimine (Step E, 0.19g) and triphenylphosphine (0.54g) in toluene (10 mL) was stirred at reflux for 30 minutes. The solvent was evaporated in vacuo and the residue was purified by flash chromatography (isohexane and diethylether) to give 2-(2-ethylsulfanylphenyl)-6-(trifluoromethyl)pyrazolo [4,3-c]pyridine (title compound 1.005, 0.165 g). ^{1}H NMR (300MHz, CDCl3): δ (ppm) 9.36(s, 1H), 8.56 (s, 1H), 8.10 (s, 1H), 7.54 (m, 3H), 7.40(m, 1H), 2.82 (q, 2H), 1.21 (t, 3H) ppm.

Example P2: 2-(2-ethylsulfonylphenyl)-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine (compound 1.006)



To a solution of 2-(2-ethylsulfanylphenyl)-6-(trifluoromethyl)pyrazolo [4,3-c]pyridine (0.085 g) in dichloromethane (5 mL) was added meta-chloroperoxybenzoic acid m-CPBA (0.107 g). The resulting yellow solution was stirred overnight at room temperature. The reaction was stopped, and the solvent was evapored. The residue was purified by flash chromatography (diethyl ether) to give 2-(2-ethylsulfonylphenyl)-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine (title compound 1.006, 0.076g). ^{1}H NMR (400 MHz, $CDCl_3$): 9.38 (s, 1H), 8.61 (s, 1H), 8.26(d, 1H), 8.04(s, 1H), 7.85 (m, 2H), 7.59 (d, 1H), 3.23 (q, 2H), 1.24(t, 3H) ppm.

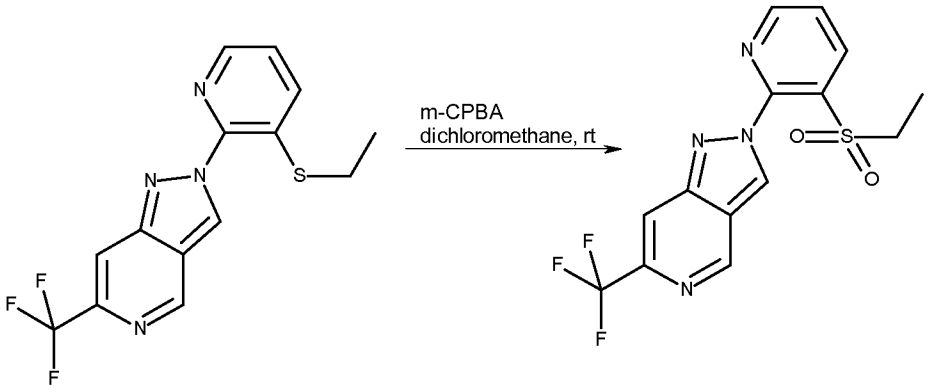
Example P3: 2-(3-ethylsulfanyl-2-pyridyl)-6-(bl)pyrazolo[4,3-c]pyridine (compound 1.007)



To a solution of 6-(trifluoromethyl)-2H-pyrazolo[4,3-c]pyridine (0.5 g) and 3-ethylsulfanyl-2-fluoro-pyridine (0.4 g, prepared as described in EP 341011) in dimethylformamide (5 mL) was added dilithium carbonic acid (0.2 g, 3 mmol). The resulting solution was stirred overnight at 100°C. The reaction was stopped by addition of water and the water layer was extracted, three times, with ethyl acetate. The combined organic layers was dried on magnesium sulfate and concentrated under vaccum. The residue was purified by flash chromatography (cyclohexane /ethyl acetate) to give 2-(3-ethylsulfanyl-2-pyridyl)-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine (compound 1.007, 0.053g). ^{1}H NMR (400 MHz, $CDCl_3$): 9.37 (d, 1H), 8.98 (d, 1H), 8.37(dd, 1H), 8.14(s, 1H), 7.86 (dd, 1H), 7.43 (dd, 1H), 2.96 (q, 2H), 1.32(t, 3H) ppm. The major product of the reaction is the isomer of position.

The compound **P5** (6-bromo-2-(3-ethylsulfanyl-2-pyridyl)pyrazolo[4,3-c]pyridine) was prepared using the same reaction with 6-(bromo)-2H-pyrazolo[4,3-c]pyridine as starting material. ^{1}H NMR (400 MHz, $CDCl_3$): 9.09 (s, 1H), 8.89 (s, 1H), 8.36(d, 1H), 7.93(s, 1H), 7.84 (dd, 1H), 7.42 (dd, 1H), 2.94 (q, 2H), 1.34(t, 3H) ppm.

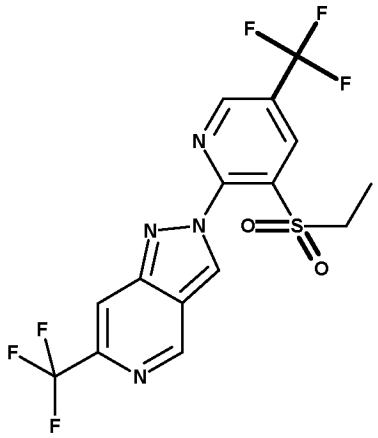
Example P4: 2-(3-ethylsulfonyl-2-pyridyl)-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine (compound 1.008)



To a solution of 2-(3-ethylsulfanyl-2-pyridyl)-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine (compound 1.007) (0.044 g) in dichloromethane (2.7 mL) was added meta-chloroperoxybenzoic acid (m-CPBA) (0.080 g). The resulting yellow solution was stirred 2 hours at ambient temperature. The reaction was stopped by addition of water and the water layer was extracted, three times, with dichloromethane. The combined organic layers was washed with a solution of NaOH 1M, dried on magnesium sulfate and concentrated under vaccum.The residue was purified by flash chromatography (cyclohexane / ethyl acetate) to give 2-(3-ethylsulfonyl-2-pyridyl)-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine (compound 1.008, 0.048g). ^{1}H NMR (400 MHz, $CDCl_3$): 9.39 (s, 1H), 8.92 (s, 1H), 8.84 (d, 1H), 8.65 (dd, 1H), 8.04(s, 1H), 7.76 (dd, 1H), 3.94 (q, 2H), 1.44(t, 3H) ppm.

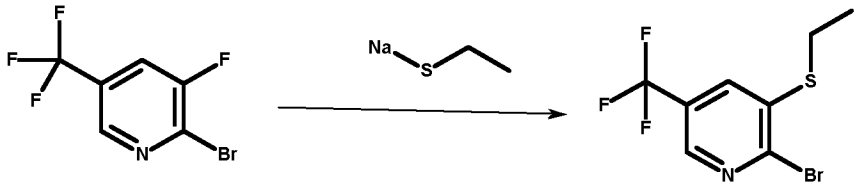
The compound **P6** (6-bromo-2-(3-ethylsulfonyl-2-pyridyl)pyrazolo[4,3-c]pyridine) was prepared using the same reaction with the 6-bromo-2-(3-ethylsulfanyl-2-pyridyl)pyrazolo[4,3-c]pyridine as starting material. ^{1}H NMR (400 MHz, $CDCl_3$): 9.10 (s, 1H), 8.82 (m, 2H), 8.64(dd, 1H), 7.83(s, 1H), 7.72 (dd, 1H), 3.91 (q, 2H), 1.41(t, 3H) ppm.

Example P7: 2-[3-ethylsulfonyl-5-(trifluoromethyl)-2-pyridyl]-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine



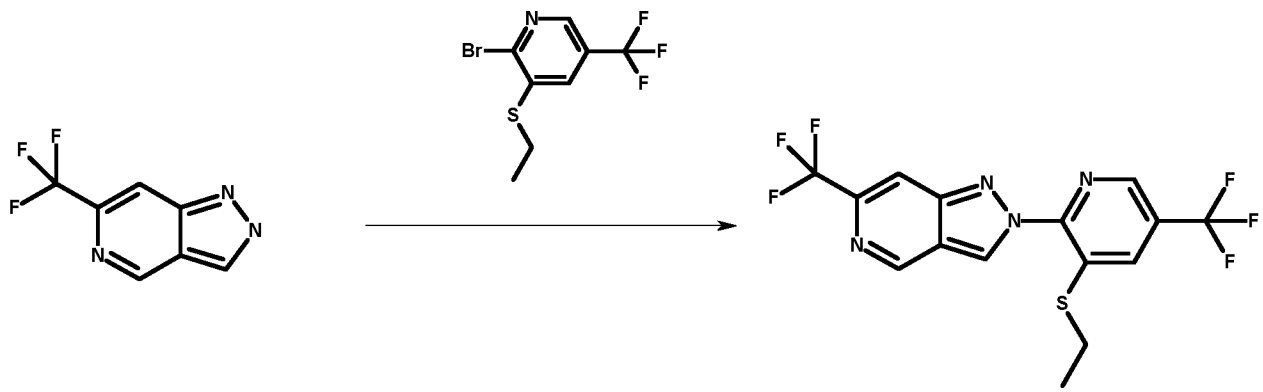
(1.004)

Step A: 2-bromo-3-ethylsulfanyl-5-(trifluoromethyl)pyridine



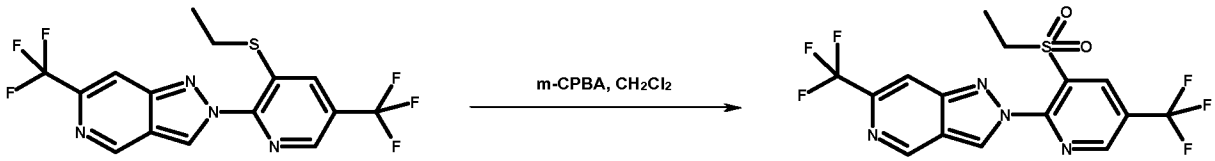
To a suspension of ethylsulfanylsodium (2.70g, 1.1 equiv.) in 30ml THF, tetrabutylammoniumbromide (0.35g, 0.05 equiv.) was added. A solution of 2-bromo-3-fluoro-5-(trifluoromethyl)pyridine (5g) in 20ml tetrahydrofuran was added dropwise within 20min. The temperature is risingfrom 20 to 35°C in this time. The mixture was filtred over celite and and concentrated under vaccum. The residue was purified by flash chromatography (cyclohexane / ethyl acetate), two times to give 2-bromo-3-ethylsulfanyl-5-(trifluoromethyl)pyridine (1.5g). ^{1}H NMR (400 MHz, $CDCl_3$): 8.38(s, 1H), 7.52 (s, 1H), 3.02 (q, 2H), 1.44 (m, 3H) ppm.

Step B: 2-[3-ethylsulfanyl-5-(trifluoromethyl)-2-pyridyl]-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine



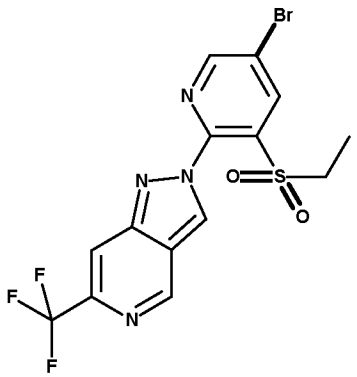
A mixture of 2-bromo-3-ethylsulfanyl-5-(trifluoromethyl)pyridine (0.2 g, 0.699 mmol) , 6-(trifluoromethyl)-2H-pyrazolo[4,3-c]pyridine (0.399 g, 2.13 mmol) , potassium phosphate (0.445 g, 2.097 mmol) , iodocopper (0.033 g, 0.175 mmol) , and trans-n,n'-dimethyl-1,2-cyclohexanediamine (0.0497 g, 0.055 mL, 0.35 mmol) in toluene (9.1 mL) was stirred and heated at 120°C for overnight. After cooling, 150 mg of 2-bromo-3-ethylsulfanyl-5-(trifluoromethyl)pyridine and the same quantities of CuI, trans-n,n'-dimethyl-1,2-cyclohexanediamine and potassium phosphate were added to the mixture. The reaction was stirred at 120°C for an extra night. The reaction was stopped by addition of a solution of water and ethyl acetate. The water layer was extracted, three times, with ethyl acetate. The combined organic layers was washed with brine then water, dried on magnesium sulfate and concentrated under vaccum. The residue was purified by flash chromatography (cyclohexane / ethyl acetate) to give 2-[3-ethylsulfanyl-5-(trifluoromethyl)-2-pyridyl]-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine (0.091g) and his isomer of position. ^{1}H NMR (400 MHz, $CDCl_3$): 9.39 (s, 1H), 9.13 (s, 1H), 8.58(s, 1H), 8.15(s, 1H), 8.00(s, 1H), 3.03 (q, 2H), 1.41(t, 3H) ppm.

Step C: 2-[3-ethylsulfonyl-5-(trifluoromethyl)-2-pyridyl]-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine



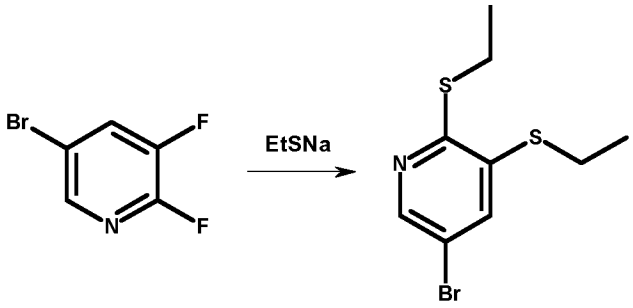
Using similar conditions described in Example P4, the title compound was prepared by reaction of the 2-[3-ethylsulfanyl-5-(trifluoromethyl)-2-pyridyl]-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine (prepared as described previewsly) with m-CPBA in dichloromethane. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.51 (t, 3 H), 4.10 (q, 2 H), 8.05(s, 1 H), 8.89 (d, 1 H), 9.04 (d, 1 H), 9.09 (s, 1 H), 9.42 (s, 1 H).

Example P8: 2-(5-bromo-3-ethylsulfonyl-2-pyridyl)-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine



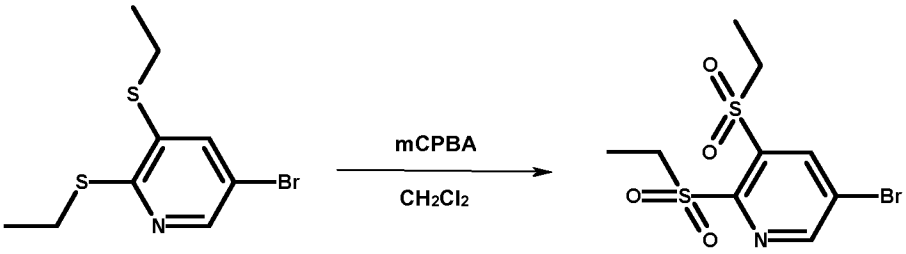
(P8)

Step A: 5-bromo-2,3-bis(ethylsulfanyl)pyridine



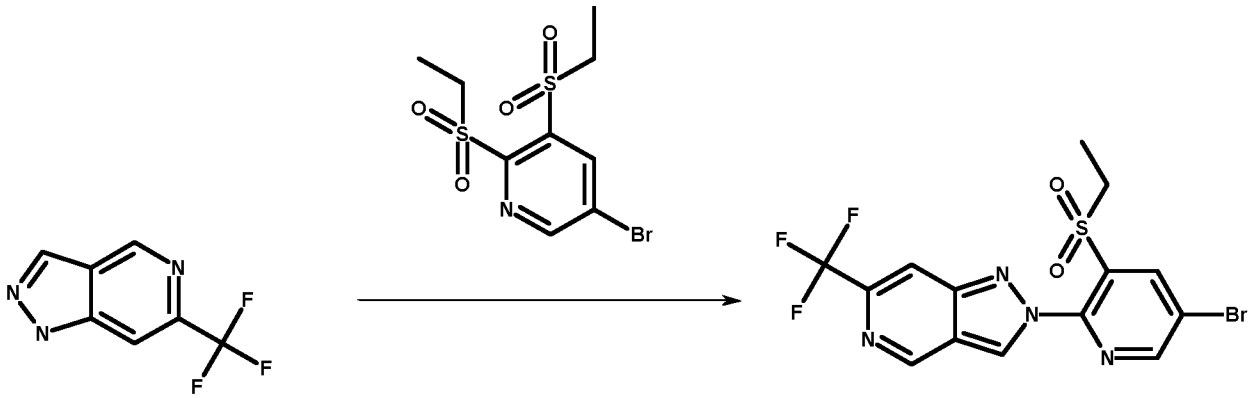
To a solution of 5-bromo-2,3-difluoro-pyridine (commercialy available, 13.61 g, 66.65 mmol) and N,N-dimethylformamide (94.4 g, 100 mL) was added sodium ethanethiol (18.44 g, 173.3 mmol) in three portions: the reaction was exothermic. The resulting solution was stirred for two hours at room temperature. The reaction was stopped by addition of a solution of water and ethyl acetate. The water layer was extracted, three times, with ethyl acetate. The combined organic layers was washed with brine then water, dried on magnesium sulfate and concentrated under vaccum.The residue was used without extra purification for the next step. ^{1}H NMR (400 MHz, $CDCl_3$): 8.32 (s, 1H), 7.56 (s, 1H), 3.18 (q, 2H), 2.95 (q, 2H), 1.40-1.32(m, 6H) ppm.

Step B: 5-bromo-2,3-bis(ethylsulfonyl)pyridine



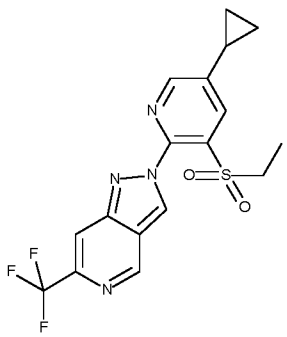
To a solution of 5-bromo-2,3-bis(ethylsulfanyl)pyridine (13.6 g, 48.9 mmol) in dichloromethane (250 mL) cooled with an ice bath, was added meta-chloroperoxybenzoic acid (45.6 g, 198 mmol). The resulting solution was stirred for an hour at room temperature. The reaction was stopped by addition of a solution of sodium thiosulfate and the water layer was extracted, three times, with dichloromethane. The combined organic layers was washed with a solution of NaOH 1M, dried on magnesium sulfate and concentrated under vaccum.The residue was purified by flash chromatography (cyclohexane / ethyl acetate) to give 5-bromo-2,3-bis(ethylsulfonyl)pyridine (6.54g). ^{1}H NMR (400 MHz, $CDCl_3$): 9.00 (s, 1H), 8.76 (s, 1H), 3.78 (q, 2H), 3.64 (q, 2H), 1.44-1.34(m, 6H) ppm.

Step C: 2-(5-bromo-3-ethylsulfonyl-2-pyridyl)-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine (P8)



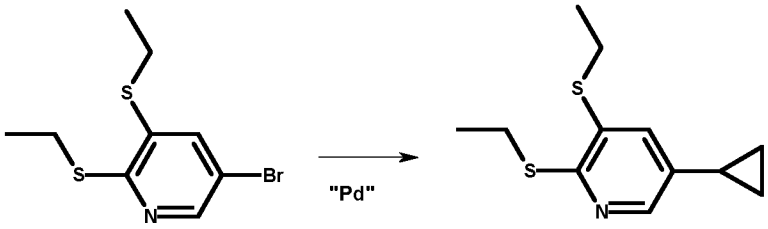
To a solution of 6-(trifluoromethyl)-2H-pyrazolo[4,3-c]pyridine (0.4679 g, 2.425 mmol) and 5-bromo-2,3-bis(ethylsulfonyl)pyridine (0.83 g, 2.425 mmol) in dimethylformamide (19 mL) was added dilithium carbonic acid (0.5523 g, 7.276 mmol). The resulting solution was stirred at 130°C for two hours then, overnight at 110°C. The reaction was stopped by addition of water and ethyl acetate.The water layer was extracted, three times, with ethyl acetate. The combined organic layers was dried on magnesium sulfate and concentrated under vaccum. The residue was purified by HPLC (see Method A) to give 2-(5-bromo-3-ethylsulfonyl-2-pyridyl)-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine (compound P8, 0.017g). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.47 (t, 3 H), 3.99 (q, 2 H) 8.03 (s, 1 H) 8.76 (d, 1 H) 8.88 (d, 1 H) 8.91 (d, 1 H) 9.40 (s, 1 H). The other product of the reaction is the isomer of position(1-(5-bromo-3-ethylsulfonyl-2-pyridyl)-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine) and the major product of the reaction is the substitution of the bromide (1-[5,6-bis(ethylsulfonyl)-3-pyridyl]-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine).

Example P9: 2-(5-cyclopropyl-3-ethylsulfonyl-2-pyridyl)-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine:



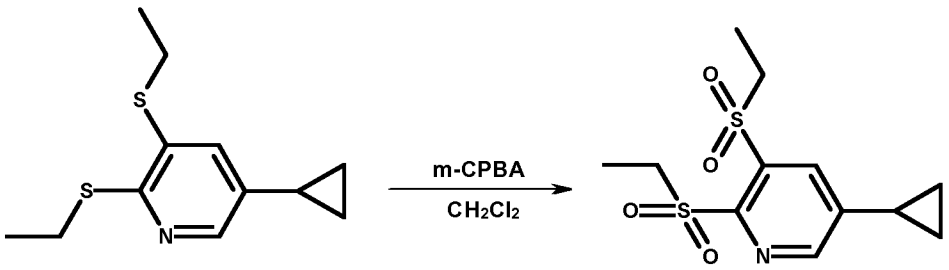
(P9).

Step A: 5-cyclopropyl-2,3-bis(ethylsulfanyl)pyridine:



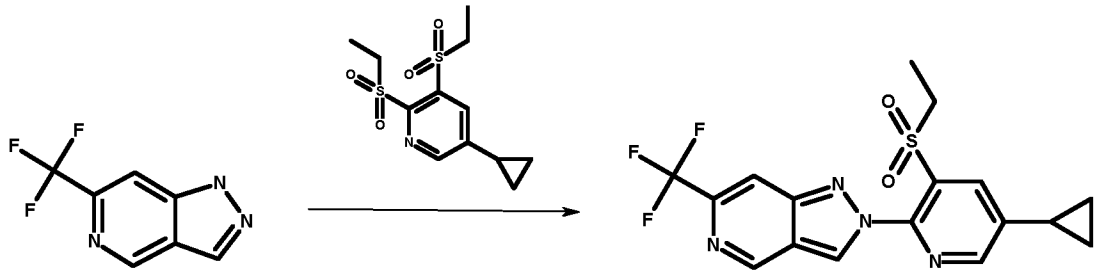
A 20mL sealed vial flushed with Argon was charged with 5-bromo-2,3-bis(ethylsulfanyl)pyridine (1.00 g, 3.59 mmol), then cyclopropylboronic acid (1.16 g, 12.9 mmol), tetrakis(triphenylphosphine) palladium(0) (0.416 g, 0.359 mmol), potassium phosphate tribasic (4.72 g, 1.84 mL, 21.6 mmol), toluene (4.33 g, 5 mL, 46.8 mmol) and water (5.000 g, 5 mL, 277.5 mmol).The mixture was then refluxed for 2 hours. The reaction was stopped by addition of a solution of water and ethyl acetate. The water layer was extracted, three times, with ethyl acetate. The combined organic layers were dried on magnesium sulfate and concentrated under vaccum. The residue was purified by flash chromatography (cyclohexane / ethyl acetate) to give the title compound (0.625 mg). ^{1}H NMR (400 MHz, $CDCl_3$): 8.12 (s, 1H), 7.18 (s, 1H), 3.18 (q, 2H), 2.92 (q, 2H), 1.82 (m, 1H), 1.39 (t, 3H), 1.30 (t, 3H), 0.98(m, 2H), 0.68 (m, 2H) ppm.

Step B: 5-cyclopropyl-2,3-bis(ethylsulfonyl)pyridine:



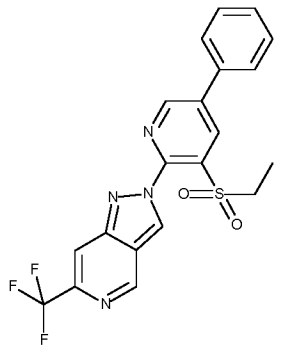
Using similar conditions described in Example P8 (Step B), the title compound was prepared by reaction of the 5-cyclopropyl-2,3-bis(ethylsulfanyl)pyridine (prepared as described previewsly) with m-CPBA in dichloromethane. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.94 (m, 2 H), 1.22-1.45 (m, 8 H) 2.10 (m, 1 H), 3.62 (q, 2 H), 3.75 (q, 2 H), 8.12 (s, 1 H), 8.67 (s, 1 H).

Step C: 2-(5-cyclopropyl-3-ethylsulfonyl-2-pyridyl)-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine:



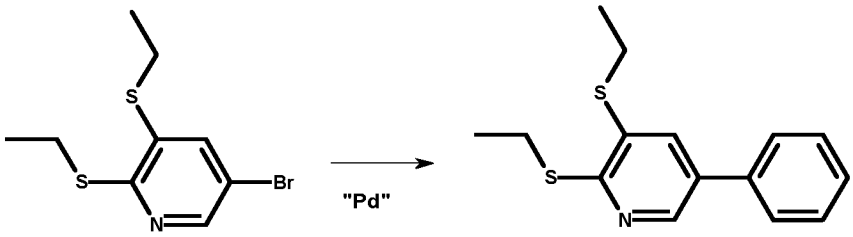
Using similar conditions described in Example P8 (Step C), the compound P9 was prepared by reaction of the 6-(trifluoromethyl)-2H-pyrazolo[4,3-c]pyridine and 5-cyclopropyl-2,3-bis(ethylsulfonyl)pyridine (prepared as described previously). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.95 (m, 2 H), 1.28 (m, 2 H), 1.40 (t, 3 H), 2.13 (m, 1 H), 3.85 (q, 2 H), 8.03 (s, 1 H), 8.17 (d, 1 H), 8.57 (d, 1 H), 8.84 (d, 1 H), 9.37 (s, 1 H).

Example P10: 2-(3-ethylsulfonyl-5-phenyl-2-pyridyl)-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine:



(P10).

Step A: 2,3-bis(ethylsulfanyl)-5-phenyl-pyridine:



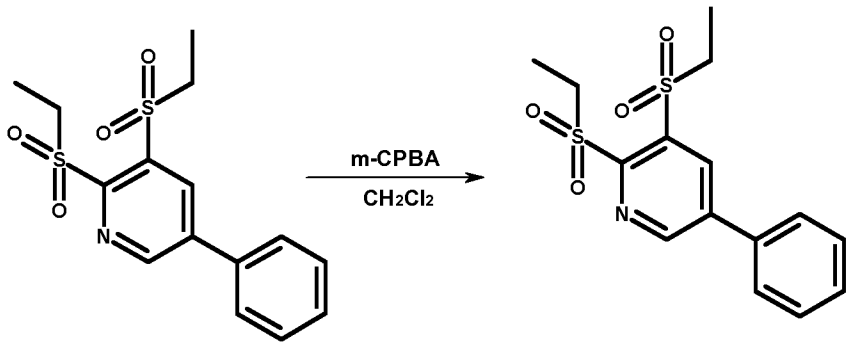
A 20mL sealed vial flushed with Argon was charged with 5-bromo-2,3-bis(ethylsulfanyl)pyridine (1.00 g, 3.59 mmol), then phenylboronic acid (1.63 g, 12.9 mmol), tetrakis(triphenylphosphine) palladium(0) (0.208 g, 0.180 mmol), potassium phosphate tribasic (4.72 g, 1.84 mL, 21.6 mmol), toluene (4.33 g, 5 mL, 46.8 mmol) and water (5.000 g, 5 mL, 277.5 mmol).The mixture was then refluxed for 2 hours. The reaction was stopped by addition of a solution of water and ethyl acetate. The water layer was

extracted, three times, with ethyl acetate. The combined organic layers were dried on magnesium sulfate and concentrated under vaccum. The residue was purified by flash chromatography (cyclohexane / ethyl acetate) to give the title compound (0.97 g). LC-MS(Method B) RT 1.29 (276, MH+).

Using similar conditions described, the 5-(4-chlorophenyl)-2,3-bis(ethylsulfanyl)pyridine was prepared. LC-MS(Method B) RT 1.36 (311, MH+)

Using similar conditions described, the 2,3-bis(ethylsulfanyl)-5-[3-(trifluoromethyl)phenyl]pyridine was prepared. LC-MS(Method B) RT 1.36 (344, MH+).

Step B: 2,3-bis(ethylsulfonyl)-5-phenyl-pyridine:

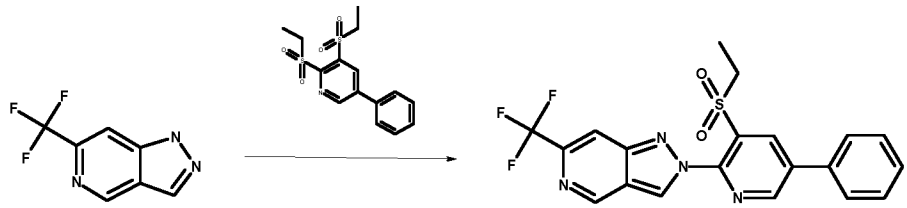


Using similar conditions described in Example P8 (Step B), the title compound (2,3-bis(ethylsulfonyl)-5-phenyl-pyridine) was prepared by reaction of the 2,3-bis(ethylsulfanyl)-5-phenyl-pyridine (prepared as described previously) with m-CPBA in dichloromethane. LC-MS(Method B) RT 0.92 (340, MH+)

Using similar conditions described in Example P8 (Step B), the 5-(4-chlorophenyl)-2,3-bis(ethylsulfonyl)pyridine was prepared by reaction of the 5-(4-chlorophenyl)-2,3-bis(ethylsulfanyl)pyridine (prepared as described previously) with m-CPBA in dichloromethane. LC-MS(Method B) RT 0.99 (374, MH+)

Using similar conditions described in Example P8 (Step B), the 2,3-bis(ethylsulfonyl)-5-[3-(trifluoromethyl)phenyl]pyridine was prepared by reaction of the 2,3-bis(ethylsulfanyl)-5-[3-(trifluoromethyl)phenyl]pyridine (prepared as described previously) with m-CPBA in dichloromethane. LC-MS(Method B) RT 1.02 (408, MH+).

Step C: 2-(3-ethylsulfonyl-5-phenyl-2-pyridyl)-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine:

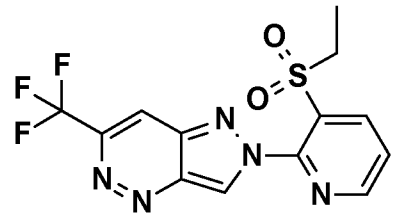


Using similar conditions described in Example P8 (Step C), the title compound P10 was prepared by reaction of the 6-(trifluoromethyl)-2H-pyrazolo[4,3-c]pyridine and 2,3-bis(ethylsulfonyl)-5-phenyl-pyridine (prepared as described previously). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.47 (t, 3 H), 3.96 (q, 2 H), 7.54 - 7.63 (m, 3 H), 7.68 - 7.76 (m, 2 H), 8.06 (s, 1 H), 8.80 (d, 1 H), 8.95 (s, 1 H), 9.02 (d, 1 H), 9.41 (s, 1 H).

Using similar conditions described in Example P8 (Step C), the compound P11 was prepared by reaction of the 6-(trifluoromethyl)-2H-pyrazolo[4,3-c]pyridine and 5-(4-chlorophenyl)-2,3-bis(ethylsulfonyl)pyridine (prepared as described previously). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.47 (t, 3 H), 3.98 (q, 2 H), 7.54 - 7.60 (m, 2 H), 7.62 - 7.69 (m, 2 H), 8.06 (s, 1 H), 8.77 (d, 1 H) 8.96 (s, 1 H), 8.99 (d, 1 H) 9.41 (s, 1 H).

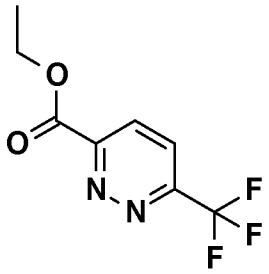
Using similar conditions described in Example P8 (Step C), the compound P12 was prepared by reaction of the 6-(trifluoromethyl)-2H-pyrazolo[4,3-c]pyridine and 2,3-bis(ethylsulfonyl)-5-[3-(trifluoromethyl)phenyl]pyridine (prepared as described previously). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.49 (t, 3 H), 4.02 (q, 2 H), 7.69 - 7.78 (m, 1 H), 7.79 - 7.86 (m, 1 H), 7.91 (d, 1 H), 7.94 (s, 1 H), 8.06 (s, 1 H), 8.81 (d, 1 H), 8.98 (d, 1 H), 9.04 (d, 1 H), 9.41 (s, 1 H).

Example P11: 2-(3-ethylsulfonyl-2-pyridyl)-6-(trifluoromethyl)pyrazolo[4,3-c]pyridazine **PP1:**



Example PP1

Step A: Ethyl-6-(trifluoromethyl)pyridazine-3-carboxylate:

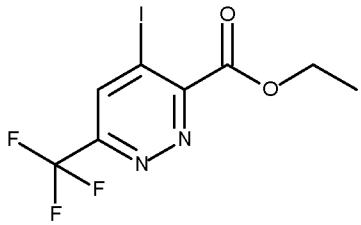


A solution of 3-chloro-6-(trifluoromethyl)pyridazine (4.5 g, 22 mmol, prepared as described in *Tetrahedron*, 65(21), 4212-4219, ***2009***), 1,1′-Ferrocenediyl-bis(diphenylphosphine) (0.74 g, 1.3 mmol), palladium(II)acetate (0.10 g, 0.44 mmol), N,N-diethylethanamine (2.7 g, 3.7 mL, 27 mmol), in ethanol (100 mL) was pressurised with CO (25 bar) in a hydrogenation vessel was pressurised with CO (25 bar) and stirred at 120°C for 5h. LCMS analysis showed reaction completion after this time. The reaction mixture was then cooled and filtered and the filtrate concentrated *in vacuo*. The crude product was purified by Comb flash chromatography with a column of 120 g and a gradient of cyclohexane + 0-70% ethyl acetate, to give the title compound as a beige solid.

LCMS (Standard method A); Ret. Time 0.73 min, 221(MH+).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm: 1.51 (t, *J*=7.15 Hz, 3 H); 4.60 (q, *J*=6.97 Hz, 2 H); 8.00 (d, *J*=8.80 Hz, 1 H); 8.39 (d, *J*=8.80 Hz, 1 H).

Step B: Ethyl-4-iodo-6-(trifluoromethyl)pyridazine-3-carboxylate:



A (2,2,6,6-tetramethyl-1-piperidyl)lithium (TMPLi) solution (0.63 M in THF) was prepared by slow addition of nBuLi (2.17 ml, 5.00 mmol, 2.3 M in hexane) to a solution of (2,2,6,6-tetramethyl-1-piperidyl) in THF (5 ml) at -40°C with stirring for 30min at -40°C.

Lithium chloride solution (0.7 Min THF) was prepared by drying lithium chloride (1.2 g) in a flask with septum under vacuum at 140°C for 5h. After cooling, dry THF (40 ml) was added and stirring was continued until all salts were dissolved.

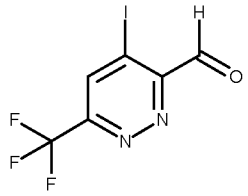
In a dry two necked flask (10 ml) under argon, Ethyl-6-(trifluoromethyl)pyridazine -3-carboxylate (0.150 g, 0.681 mmol) was dissolved in tetrahydrofurane (3 mL, 0.681 mmol). and treated with lithium chloride solution in THF (2 mL, 1.50 mmol, prepared as described above) and treated with zinc(II) chloride (1 mL, 0.749 mmol). The resulting mixture was cooled to -78°C and then TMPLi (1.6 mL, 1.02 mmol, prepared as described above) was added drop wise (10 min) at -78°C. Reaction mixture was stirred 1 hour at -78°C and then molecular iodine (0.173 g, 0.681 mmol)

dissolved in 1 ml of THF was added drop wise and the resulting mixture stirred for a further 20 min at -78°C. LC-MS and GC-MS after this time showed only the desired product. The reaction mixture was allowed to warm to room temperature and quenched with saturated aqueous ammonium chloride, the organic phase washed successively with sodium thiosulfate and brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude was purified by Combi flash chromatography with a column of 12 g and a gradient cyclohexane + 0-40% ethyl acetate, to give the title compound.

GCMS (chemical ionization, Method E): Ret. Time, 4.60 min, 347 (MH^+)

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 1.49 (t, *J*=7.15 Hz, 3 H) 4.58 (q, *J*=6.97 Hz, 2 H) 8.40 (s, 1 H).

Step C: 4-Iodo-6-(trifluoromethyl)pyridazine-3-carbaldehyde:

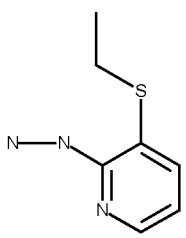


A solution of ethyl 4-iodo-6-(trifluoromethyl)pyridazine-3-carboxylate (0.3 g, 0.86695 mmol) in dichloromethane (4.5 mL) was cooled down at -78°C and treated with Diisobutylaluminium hydride (DIBAL, 1.7339 mL, 1.7339 mmol) was added drop wise at -70°C to -78°C. The reaction mixture was stirred 1h at -78°C, and then allowed to warm to RT and stirred one night. The reaction mixture was then cooled to 0°C, and quenched carefully with saturated NH_4Cl, and then the pH made acidic with 10% HCl. The mixture was extracted with EtOAc (3X), the combined organic layers washed with brine, dried over Na_2SO_4, filtrated and concentrated *in vacuo*. The crude product was purified by Combi flash chromatography with a column of 12 g and a gradient cyclohexane + 0- 60 % ethyl acetate to give pure title product.

LCMS (Standard method A); Ret. Time 0.81 min, 303 (MH+).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm: 8.52 (s, 1 H); 10.32 (s, 1 H).

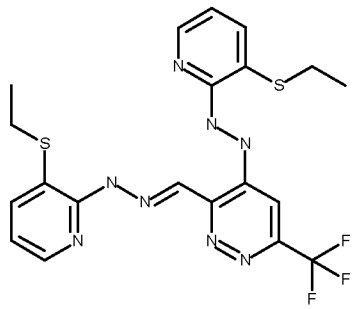
Step D: (3-ethylsulfanyl-2-pyridyl)hydrazine:



To a solution of 3-ethylsulfanyl-2-fluoro-pyridine (commercialy available or prepared as described in WO 8910694, 9.70 g, 61.7 mmol) in 1,4-dioxan (100 mL) was added hydrazine monohydrate (12.0 g,

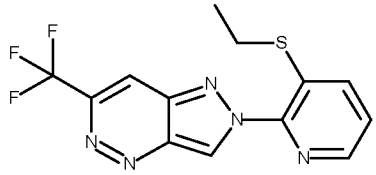
11.7 mL, 370 mmol). The resulting solution was refluxed overnight. The reaction was stopped by addition of water and ethyl acetate.The water layer was extracted, three times, with ethyl acetate. The combined organic layers was dried on magnesium sulfate and concentrated under vaccum to give (3-ethylsulfanyl-2-pyridyl)hydrazine (9.23 g, 88.4% Yield) as pure compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.12 (d, 1H), 7.55 (d, 1H), 6.72 (sb, 1H), 6.62 (m, 1H), 3.98 (sb, 2H), 2.75 (q, 2H), 1.22 (t, 3H).

Step E: 3-Ehylsulfanyl-N-[(E)-[4-[2-(3-ethylsulfanyl-2-pyridyl)hydrazino]-6-(trifluoromethyl) pyridazin-3-yl]methyleneamino]pyridin-2-amine:



In a flask under argon, 4-Iodo-6-(trifluoromethyl)pyridazine-3-carbaldehyde (0.077 g, 0.25498 mmol) and (3-ethylsulfanyl-2-pyridyl)hydrazine (prepared in step D, 0.053 g, 0.28 mmol) were stirred in methanol (3.03 g, 3.83 mL, 94.3 mmol) for 48h at room temperature. LCMS and TLC analysis showed consumption of the starting material to be complete. The reaction mixture was concentrated *in vacuo* and the crude product purified by Combi flash chromatography with a column of 12 g and a gradient cyclohexane + 0-100% ethyl acetate. This gave a mixture of the title compound and 3-ethylsulfanyl-N-[(Z)-[4-iodo-6- (trifluoromethyl) pyridazin -3-yl]methyleneamino]pyridin-2-amine in a ratio of 1:1. This mixture was used in the next step without further purification.
LCMS (Standard method A); Ret. Time 1.06 min, 494 (MH+) (Title compound) . The second compound in the mixture was 3-ethylsulfanyl-N-[(Z)-[4-iodo-6- (trifluoromethyl) pyridazin-3-yl]methyleneamino] pyridin-2-amine: LCMS (Standard method A); Ret. Time 0.99 min, 454 (MH+).

Step F: 2-(3-ethylsulfanyl-2-pyridyl)-6-(trifluoromethyl)pyrazolo[4,3-c]pyridazine:



In a microwave vial, the product obtained in step E was dissolved in DMF and the resulting mixture was stirred 10min at 160°C under microwave conditions.. DMF was removed by evaporation at 65°C

in vacuo, and the residue was dissolved in t-butly methyl ether and water, the organic layer separated and then washed successively with sodium thiosulfate sat aqueous sol, water and brine, dried over Na2SO4, filtered and concentrated *in vacuo*. The crude product was purified by Combi flash chromatography with a column of 4 g with a gradient cyclohexane + 0-50 % ethyl acetate.

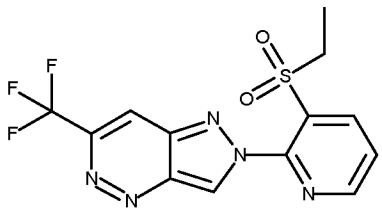
First eluting product is the by-product: 1-(3-ethylsulfanyl-2-pyridyl)-6-(trifluoromethyl)pyrazolo[4,3-c]pyridazine. LCMS (Standard method A); Ret. Time 0.95 min, 326 (MH+).

Second eluting product: 2: 2-(3-ethylsulfanyl-2-pyridyl)-6-(trifluoromethyl)pyrazolo[4,3-c] pyridazine.

LCMS (Standard method A); Ret. Time 0.93 min, 326 (MH+).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm: 1.36 (t, *J*=7.34 Hz, 3 H); 2.99 (q, *J*=7.46 Hz, 2 H); 7.50 (dd, *J*=8.07, 4.77 Hz, 1 H); 7.91 (dd, *J*=8.07, 1.47 Hz, 1 H); 8.32 (s, 1 H); 8.43 (dd, *J*=4.77, 1.47 Hz, 1 H); 9.60 (d, *J*=1.10 Hz, 1 H).

Step G: 2-(3-ethylsulfonyl-2-pyridyl)-6-(trifluoromethyl)pyrazolo[4,3-c]pyridazine **(PP1):**

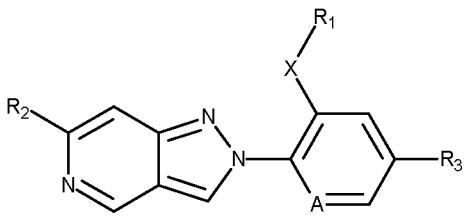


1-(3-ethylsulfanyl-2-pyridyl)-6-(trifluoromethyl)pyrazolo[4,3-c]pyridazine (15 mg, 0.046 mmol) was dissolved in dichloromethane (2 mL) and 3-chloroperbenzoic acid (21.7 mg, 0.097 mmol) was added slowly at 0°C. The resulting mixture was stirred 30min at 0°C and then over night at RT. After this time, a further 1 eq of m-CPBA was added and reaction mixture was stirred 30min at RT, by which time LCMS showed reaction completion. The reaction mixture was quenched with 2 ml of NaOH 1 N and 2 ml of sodium thiosulfate sat aqueous sol. The mixture was stirred 10 min, and then the aqueous layer was extracted 3 times with 10 ml of dichloromethane. The combined organic layers were washed with 10 ml of NaOH 1 N, dried over Na_2SO_4, filtered and concentrated *in vacuo* to give the title compound as a yellow oil.

LCMS (Standard method A); Ret. Time 0.82 min, 358 (MH+).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 1.46 (t, *J*=7.34 Hz, 3 H); 3.93 (q, *J*=7.70 Hz, 2 H); 7.84 (dd, *J*=8.07, 4.77 Hz, 1 H); 8.24 (s, 1 H); 8.69 (dd, *J*=7.89, 1.65 Hz, 1 H); 8.92 (dd, *J*=4.77, 1.83 Hz, 1 H); 9.53 (d, *J*=1.10 Hz, 1 H).

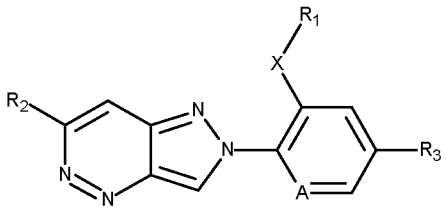
Table 4: Examples of compounds of formula (Ia) ("Ph" represents the phenyl group):



(Ia),

Comp. No.	R_1	R_2	R_3	X	A
P1 (1.005)	CH_2CH_3	CF_3	H	S	CH
P2 (1.006)	CH_2CH_3	CF_3	H	SO_2	CH
P3 (1.007)	CH_2CH_3	CF_3	H	S	N
P4 (1.008)	CH_2CH_3	CF_3	H	SO_2	N
P5	CH_2CH_3	Br	H	S	N
P6	CH_2CH_3	Br	H	SO_2	N
P7 (1.004)	CH_2CH_3	CF_3	CF_3	SO_2	N
P8	CH_2CH_3	CF_3	Br	SO_2	N
P9	CH_2CH_3	CF_3	cyclopropyl	SO_2	N
P10	CH_2CH_3	CF_3	Ph	SO_2	N
P11 (1.010)	CH_2CH_3	CF_3	4-ClPh	SO_2	N
P12	CH_2CH_3	CF_3	3-CF_3Ph	SO_2	N

Table 5: Examples of compounds of formula (Ia)



(Ia),

Comp. No.	R_1	R_2	R_3	X	A
PP1 (2.006)	CH_2CH_3	CF_3	H	SO_2	CH

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 1 to 5 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, cypermethrin (201) + TX, DCPM (1032) + TX, DDT (219) + TX, demephion (1037) + TX, demephion-O (1037) + TX, demephion-S (1037) + TX, demeton (1038) + TX, demeton-methyl (224) + TX, demeton-O (1038) + TX, demeton-O-methyl (224) + TX, demeton-S (1038) + TX, demeton-S-methyl (224) + TX, demeton-S-methylsulfon (1039) + TX, diafenthiuron (226) + TX, dialifos (1042) + TX, diazinon (227) + TX, dichlofluanid (230) + TX, dichlorvos (236) + TX, dicliphos (alternative name) + TX, dicofol (242) + TX, dicrotophos (243) + TX, dienochlor (1071) + TX, dimefox (1081) + TX, dimethoate (262) + TX, dinactin (alternative name) (653) + TX, dinex (1089) + TX, dinex-diclexine (1089) + TX, dinobuton (269) + TX, dinocap (270) + TX, dinocap-4 [CCN] + TX, dinocap-6 [CCN] + TX, dinocton (1090) + TX, dinopenton (1092) + TX, dinosulfon (1097) + TX, dinoterbon (1098) + TX, dioxathion (1102) + TX, diphenyl sulfone (IUPAC name) (1103) + TX, disulfiram (alternative name) [CCN] + TX, disulfoton (278) + TX, DNOC (282) + TX, dofenapyn (1113) + TX, doramectin (alternative name) [CCN] + TX, endosulfan (294) + TX, endothion (1121) + TX, EPN (297) + TX, eprinomectin (alternative name) [CCN] + TX, ethion (309) + TX, ethoate-methyl (1134) + TX, etoxazole (320) + TX, etrimfos (1142) + TX, fenazaflor (1147) + TX, fenazaquin (328) + TX, fenbutatin oxide (330) + TX, fenothiocarb (337) + TX, fenpropathrin (342) + TX, fenpyrad (alternative name) + TX, fenpyroximate (345) + TX, fenson (1157) + TX, fentrifanil (1161) + TX, fenvalerate (349) + TX, fipronil (354) + TX, fluacrypyrim (360) + TX, fluazuron (1166) + TX, flubenzimine (1167) + TX, flucycloxuron (366) + TX, flucythrinate (367) + TX, fluenetil (1169) + TX, flufenoxuron (370) + TX, flumethrin (372) + TX, fluorbenside (1174) + TX, fluvalinate (1184) + TX, FMC 1137 (development code) (1185) + TX, formetanate (405) + TX, formetanate hydrochloride (405) + TX, formothion (1192) + TX, formparanate (1193) + TX,

gamma-HCH (430) + TX, glyodin (1205) + TX, halfenprox (424) + TX, heptenophos (432) + TX, hexadecyl cyclopropanecarboxylate (IUPAC/Chemical Abstracts name) (1216) + TX, hexythiazox (441) + TX, iodomethane (IUPAC name) (542) + TX, isocarbophos (alternative name) (473) + TX, isopropyl *O*-(methoxyaminothiophosphoryl)salicylate (IUPAC name) (473) + TX, ivermectin (alternative name) [CCN] + TX, jasmolin I (696) + TX, jasmolin II (696) + TX, jodfenphos (1248) + TX, lindane (430) + TX, lufenuron (490) + TX, malathion (492) + TX, malonoben (1254) + TX, mecarbam (502) + TX, mephosfolan (1261) + TX, mesulfen (alternative name) [CCN] + TX, methacrifos (1266) + TX, methamidophos (527) + TX, methidathion (529) + TX, methiocarb (530) + TX, methomyl (531) + TX, methyl bromide (537) + TX, metolcarb (550) + TX, mevinphos (556) + TX, mexacarbate (1290) + TX, milbemectin (557) + TX, milbemycin oxime (alternative name) [CCN] + TX, mipafox (1293) + TX, monocrotophos (561) + TX, morphothion (1300) + TX, moxidectin (alternative name) [CCN] + TX, naled (567) + TX, NC-184 (compound code) + TX, NC-512 (compound code) + TX, nifluridide (1309) + TX, nikkomycins (alternative name) [CCN] + TX, nitrilacarb (1313) + TX, nitrilacarb 1:1 zinc chloride complex (1313) + TX, NNI-0101 (compound code) + TX, NNI-0250 (compound code) + TX, omethoate (594) + TX, oxamyl (602) + TX, oxydeprofos (1324) + TX, oxydisulfoton (1325) + TX, pp'-DDT (219) + TX, parathion (615) + TX, permethrin (626) + TX, petroleum oils (alternative name) (628) + TX, phenkapton (1330) + TX, phenthoate (631) + TX, phorate (636) + TX, phosalone (637) + TX, phosfolan (1338) + TX, phosmet (638) + TX, phosphamidon (639) + TX, phoxim (642) + TX, pirimiphos-methyl (652) + TX, polychloroterpenes (traditional name) (1347) + TX, polynactins (alternative name) (653) + TX, proclonol (1350) + TX, profenofos (662) + TX, promacyl (1354) + TX, propargite (671) + TX, propetamphos (673) + TX, propoxur (678) + TX, prothidathion (1360) + TX, prothoate (1362) + TX, pyrethrin I (696) + TX, pyrethrin II (696) + TX, pyrethrins (696) + TX, pyridaben (699) + TX, pyridaphenthion (701) + TX, pyrimidifen (706) + TX, pyrimitate (1370) + TX, quinalphos (711) + TX, quintiofos (1381) + TX, R-1492 (development code) (1382) + TX, RA-17 (development code) (1383) + TX, rotenone (722) + TX, schradan (1389) + TX, sebufos (alternative name) + TX, selamectin (alternative name) [CCN] + TX, SI-0009 (compound code) + TX, sophamide (1402) + TX, spirodiclofen (738) + TX, spiromesifen (739) + TX, SSI-121 (development code) (1404) + TX, sulfiram (alternative name) [CCN] + TX, sulfluramid (750) + TX, sulfotep (753) + TX, 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,

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,

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

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

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

phosphine (IUPAC name) (640) + TX, phosphorus [CCN] + TX, pindone (1341) + TX, potassium arsenite [CCN] + TX, pyrinuron (1371) + TX, scilliroside (1390) + TX, sodium arsenite [CCN] + TX, sodium cyanide (444) + TX, sodium fluoroacetate (735) + TX, strychnine (745) + TX, thallium sulfate [CCN] + TX, warfarin (851) and zinc phosphide (640) + TX,

a synergist selected from the group of substances consisting of 2-(2-butoxyethoxy)ethyl piperonylate (IUPAC name) (934) + TX, 5-(1,3-benzodioxol-5-yl)-3-hexylcyclohex-2-enone (IUPAC name) (903) + TX, farnesol with nerolidol (alternative name) (324) + TX, MB-599 (development code) (498) + TX, MGK 264 (development code) (296) + TX, piperonyl butoxide (649) + TX, piprotal (1343) + TX, propyl isomer (1358) + TX, S421 (development code) (724) + TX, sesamex (1393) + TX, sesasmolin (1394) and sulfoxide (1406) + TX,

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

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

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

and biologically active compounds selected from the group consisting of azaconazole (60207-31-0] + TX, bitertanol [70585-36-3] + TX, bromuconazole [116255-48-2] + TX, cyproconazole [94361-06-5] + TX, difenoconazole [119446-68-3] + TX, diniconazole [83657-24-3] + TX, epoxiconazole [106325-08-0] + TX, fenbuconazole [114369-43-6] + TX, fluquinconazole [136426-54-5] + TX, flusilazole [85509-19-9] + TX, flutriafol [76674-21-0] + TX, hexaconazole [79983-71-4] + TX, imazalil [35554-44-0] + TX, imibenconazole [86598-92-7] + TX, ipconazole [125225-28-7] + TX, metconazole [125116-23-6] + TX, myclobutanil [88671-89-0] + TX, pefurazoate [101903-30-4] + TX, penconazole [66246-88-6] + TX, prothioconazole [178928-70-6] + TX, 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 (dislosed 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 and 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 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®, BioNem-WP®, 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®, 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®) + TX; 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, Tetradecatrienyl acetate + 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.

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 1 to 5 with active ingredients described above comprises a compound selected from Tables 1 to 5 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 1 to 5 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 1 to 5 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:

Example B1: Activity against *Bemisia tabaci* (Cotton white fly):
Cotton leaf discs were placed on 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 adult white flies. The samples were checked for mortality 6 days after incubation.
The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: P1 and P2.

Example B2: Activity against *Diabrotica balteata* (Corn root worm)
Maize sprouts, placed on 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 4 days after infestation.

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

P1, P2, P3, P4, P6, P7, P8, P9, PP1, P10, P11 and P12.

Example B3: Activity against *Euschistus heros* (Neotropical Brown Stink Bug):

Soybean leaf 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 were infested with N-2 nymphs. The samples were assessed for 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, P3, P4, P7, P8, PP1, P10, P11 and P12.

Example B4: Activity against *Mysus persicae* (Green peach aphid):

Sunflower leaf discs were placed on 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, P6, P7, P8, PP1, P10 and P11.

Example B5: Activity against *Mysus persicae* (Green peach aphid):

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

The following compounds resulted in at least 80% mortality at a test rate of 24 ppm: P2 and P4.

Example B6: Activity against *Mysus persicae* (Green peach aphid):

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

The following compounds resulted in at least 80% mortality at a test rate of 12 ppm: P1 and P3.

Example B7: Activity against *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, P2, P3, P4, P7, P8, PP1, P10, P11 and P12.

Example B8: Activity against *Spodoptera littoralis* (Egyptian cotton leaf worm):

Cotton leaf discs were placed on 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-feedant effect, and growth inhibition in comparison to untreated samples 3 days after infestation. Control of Spodoptera littoralis by a test sample is when at least one of 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, P2, P3, P4, P7, P8, P9, PP1, P10, P11 and P12.

Example B9: Activity against *Spodoptera littoralis* (Egyptian cotton leaf worm):

Test compounds were applied by pipette from 10'000 ppm DMSO stock solutions into 24-well plates and mixed with agar. Lettuce seeds were placed on the agar and the multi well plate was closed by another plate which contains also agar. After 7 days the roots have absorbed the compound and the lettuce has grown into the lid plate. The lettuce leafs were now cut off into the lid plate. Spodoptera eggs were pipetted through a plastic stencil on a humid gel blotting paper and the plate closed with it. The samples were assessed for mortality, anti-feedant effect and growth inhibition in comparison to untreated samples 6 days after infestation.

The following compounds gave an effect of at least 80% in at least one of the three categories (mortality, anti-feedancy, or growth inhibition) at a test rate of 12.5 ppm:

P1, P3, P4 and P7.

Example B10: Activity against *Tetranychus urticae* (Two-spotted spider mite):Feeding/contact activity:

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 compound resulted in at least 80% mortality at an application rate of 200 ppm: P1.

Example B11: Activity against *Thrips tabaci* (Onion thrips) Feeding/Contact activity:

Sunflower leaf discs were placed on agar in 24-well microtiter plates and sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying the leaf discs were infested with a thrips population of mixed ages. The samples were assessed for mortality 6 days after infestation.

The following compound resulted in at least 80% mortality at an application rate of 200 ppm: P10.

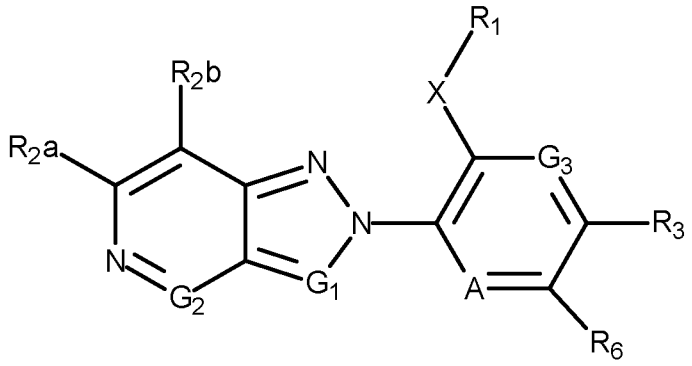
Example B11: Activity against *Aedes aegypti* (Yellow fever mosquito):

10 to 15 Aedes larvae (L2) together with a nutrition mixture were placed in 96-well microtiter plates. Test compounds were pipetted into the wells. After an incubation period of 2 days insects were assessed for mortality and growth inhibition.

The following compounds gave an effect of at least 80% in at least one of the two categories (mortality or growth inhibition) at a test rate of 5 ppm: P1 and P7.

Claims:

1. A compound of formula I,



(I),

wherein

A is CH, N or CR_7; wherein R_7 is C_1-C_4alkyl, C_1-C_4haloalkyl, cyano, nitro or halogen;

X is S, SO or SO_2;

R_1 is C_1-C_4alkyl, C_1-C_4haloalkyl, C_3-C_6cycloalkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl, C_3-C_6cycloalkyl mono - or polysubstituted by substituents selected from the group consisting of halogen, cyano, C_1-C_4haloalkyl and C_1-C_4alkyl; or

R_1 is C_3-C_6cycloalkyl-C_1-C_4alkyl mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C_1-C_4haloalkyl and C_1-C_4alkyl; or

R_1 is C_2-C_6alkenyl, C_2-C_6haloalkenyl or C_2-C_6alkynyl;

R_{2a} and R_{2b} are, independently from each other, hydrogen, halogen, cyano, C_1-C_6haloalkyl or C_1-C_6haloalkyl substituted by one or two substituents selected from the group consisting of hydroxyl, methoxy and cyano; or

R_{2a} and R_{2b} are, independently from each other, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_1-C_4haloalkoxy, or –C(O)(C_1-C_4haloalkyl); or

R_{2a} and R_{2b} are, independently from each other, C_3-C_6cycloalkyl which can be mono - or polysubstituted by substituents selected from the group consisting of halogen, cyano, C_1-C_4haloalkyl and C_1-C_4alkyl;

R_3 is hydrogen, halogen, cyano, nitro, C_1-C_6alkyl, C_1-C_6alkoxy, C_1-C_4alkoxyC_1-C_4alkyl, C_1-C_6haloalkyl, C_3-C_6cycloalkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl, or

R_3 is C_3-C_6cycloalkyl which is mono- or di-substituted by substituents selected from the group consisting of halogen, C_1-C_4alkyl, C_1-C_4haloalkyl and cyano; or

R_3 is C_2-C_6alkenyl, C_2-C_6haloalkenyl, C_2-C_6alkynyl, C_2-C_6haloalkynyl; or

R_3 is phenyl which can be mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, nitro, C_2-C_6alkenyl, C_2-C_6haloalkenyl, C_2-C_6alkynyl, C_2-C_6haloalkynyl, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4haloalkoxy, C_1-C_4alkoxy, C_1-C_4alkoxy C_1-C_4alkyl, C_1-C_4haloalkylsulfanyl, C_1-

C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_1-C_4alkylsulfanyl, C_1-C_4alkylsulfinyl, C_1-C_4alkylsulfonyl, and –C(O)C_1-C_4haloalkyl; or

R_3 is C_1-C_6haloalkylsulfanyl, C_1-C_6haloalkylsulfinyl, C_1-C_6haloalkylsulfonyl, C_1-C_6 haloalkoxy, –C(O)C_1-C_4haloalkyl, C_1-C_6alkylsulfanyl, C_1-C_6alkylsulfinyl, or C_1-C_6alkylsulfonyl; or

R_3 is pyrimidinyl which can be mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, nitro, C_2-C_6alkenyl, C_2-C_6haloalkenyl, C_2-C_6alkynyl, C_2-C_6haloalkynyl, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4haloalkoxy, C_1-C_4alkoxy, C_1-C_4alkoxy C_1-C_4alkyl, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_1-C_4alkylsulfanyl, C_1-C_4alkylsulfinyl, C_1-C_4alkylsulfonyl and –C(O)C_1-C_4haloalkyl; or

R_3 is pyridinyl which can be mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, nitro, C_2-C_6alkenyl, C_2-C_6haloalkenyl, C_2-C_6alkynyl, C_2-C_6haloalkynyl, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4haloalkoxy, C_1-C_4alkoxy, C_1-C_4alkoxy C_1-C_4alkyl, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_1-C_4alkylsulfanyl, C_1-C_4alkylsulfinyl, or C_1-C_4alkylsulfonyl and –C(O)C_1-C_4haloalkyl; or

R_3 is a five- to six-membered, aromatic, partially saturated or fully saturated ring system linked via a nitrogen atom to the ring which contains the substituent G_3, said ring system can be mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, nitro, C_2-C_6alkenyl, C_2-C_6haloalkenyl, C_2-C_6alkynyl, C_2-C_6haloalkynyl, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4haloalkoxy, C_1-C_4alkoxy, C_1-C_4alkoxy C_1-C_4alkyl, C_1-C_4alkylsulfanyl, C_1-C_4alkylsulfinyl, C_1-C_4alkylsulfonyl, –C(O)C_1-C_4alkyl, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl and –C(O)C_1-C_4haloalkyl; said ring system contains 1, 2 or 3 heteroatoms selected from the group consisting of nitrogen, oxygen and sulphur; where said ring system may not contain more than one oxygen atom and not more than one sulfur atom;

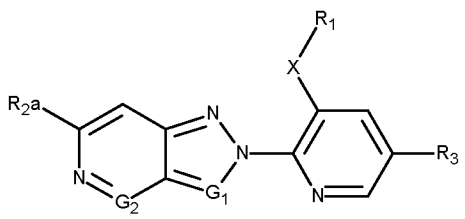
R_6 is hydrogen, C_1-C_4alkyl, C_1-C_4haloalkyl, halogen or cyano;

G_1 is CR_4, wherein R_4 is hydrogen, C_1-C_4alkyl, C_1-C_4haloalkyl, cyano or halogen;

G_2 is N or CR_5, wherein R_5 is hydrogen, C_1-C_4alkyl, C_1-C_4haloalkyl, cyano, nitro or halogen;

G_3 is N or CR_8, wherein R_8 is hydrogen, C_1-C_4alkyl, C_1-C_4haloalkyl, halogen or cyano; and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of the compounds of formula I.

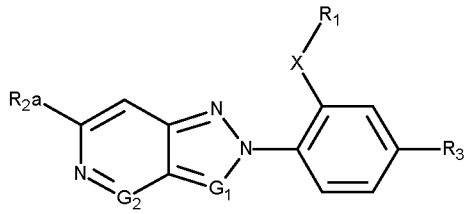
2. A compound of formula I according to claim 1 represented by the compounds of formula I-1



(I-1),

wherein X, G_1, G_2, R_1 and R_{2a} are as defined under formula I above; R_3 is hydrogen, halogen or C_1-C_4haloalkyl.

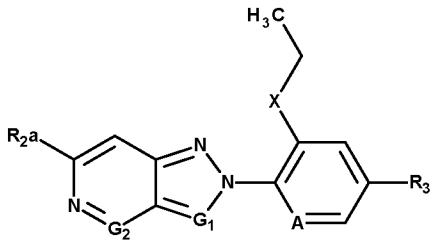
3. A compound of formula I according to claim 1 represented by the compounds of formula I-2



(I-2),

wherein X, G_1, G_2, R_1 and R_{2a} are as defined under formula I above; R_3 is hydrogen, halogen or C_1-C_4haloalkyl.

4. A compound of formula I is represented by the compounds of formula I-3a



(I-3a),

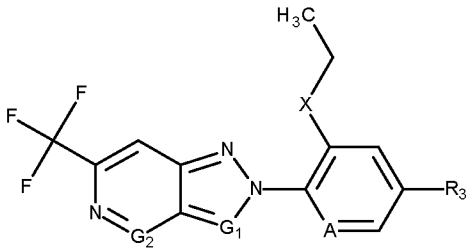
wherein

X is S, SO or SO_2; R_{2a} is C_1-C_4haloalkyl or halogen; R_3 is hydrogen, C_1-C_4haloalkyl, C_3-C_6cycloalkyl, or is phenyl which can be monosubstituted by halogen or C_1-C_4haloalkyl;

G_1 is CR_4, wherein R_4 is hydrogen, C_1-C_4alkyl, cyano or halogen; G_2 is CH or N; and

A is CH or N.

5. A compound of formula I according to claim 1 represented by the compounds of formula I-3



(I-3),

wherein

X is S, SO or SO_2;

R_3 is hydrogen, C_1-C_4haloalkyl, C_3-C_6cycloalkyl or phenyl which can be monosubstituted by halogen or C_1-C_4haloalkyl;

G_1 is CR_4, wherein R_4 is hydrogen, C_1-C_4alkyl, cyano or halogen;

G_2 is CH or N; and
A is CH or N.

6. A pesticidal composition, which comprises at least one compound of formula I according to claim 1 or, where appropriate, a tautomer thereof, in each case in free form or in agrochemically utilizable salt form, as active ingredient and at least one auxiliary.

7. A method for controlling pests, which comprises applying a composition according to claim 6 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.

8. A method for the protection of plant propagation material from the attack by pests, which comprises treating the propagation material or the site, where the propagation material is planted, with a composition according to claim 6.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/067677

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D471/04 A01N43/90 C07D487/04
ADD.

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

B. FIELDS SEARCHED

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

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2013/191113 A1 (SUMITOMO CHEMICAL CO [JP]) 27 December 2013 (2013-12-27) cited in the application abstract; tables 1-16,17	1-8
Y	WO 2013/018928 A1 (SUMITOMO CHEMICAL CO [JP]; TAKAHASHI MASAKI [JP]; TANABE TAKAMASA [JP]) 7 February 2013 (2013-02-07) cited in the application page 2, paragraph [0004]; claims 1,19,20; tables 1-35	1-8
Y	WO 2012/086848 A1 (SUMITOMO CHEMICAL CO [JP]; TAKYO HAYATO [JP]; TAKAHASHI MASAKI [JP]; T) 28 June 2012 (2012-06-28) cited in the application examples; page 2, paragraph 0005; claims 1,13,15	1-8

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 September 2015	09/09/2015

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2015/067677

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2013191113 A1	27-12-2013	CN 104379567 A	25-02-2015
		EP 2862853 A1	22-04-2015
		US 2015181880 A1	02-07-2015
		WO 2013191113 A1	27-12-2013
WO 2013018928 A1	07-02-2013	AR 087467 A1	26-03-2014
		AU 2012290923 A1	09-01-2014
		CA 2844241 A1	07-02-2013
		CN 103717598 A	09-04-2014
		EP 2739624 A1	11-06-2014
		JP 2014005263 A	16-01-2014
		KR 20140068920 A	09-06-2014
		TW 201321363 A	01-06-2013
		US 2014194290 A1	10-07-2014
		US 2015197532 A1	16-07-2015
		WO 2013018928 A1	07-02-2013
WO 2012086848 A1	28-06-2012	AR 084588 A1	29-05-2013
		CA 2822919 A1	28-06-2012
		CN 103261170 A	21-08-2013
		EP 2655337 A1	30-10-2013
		JP 2013136519 A	11-07-2013
		KR 20130140125 A	23-12-2013
		RU 2013134464 A	27-01-2015
		TW 201234965 A	01-09-2012
		US 2014018373 A1	16-01-2014
		US 2014364444 A1	11-12-2014
		WO 2012086848 A1	28-06-2012