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(54) **PESTICIDALLY ACTIVE HETEROCYCLIC DERIVATIVES WITH SULFUR CONTAINING SUBSTITUENTS**

(71) Applicant: **SYNGENTA PARTICIPATIONS AG**, Basel (CH)

(72) Inventors: **Andrew EDMUNDS**, Stein (CH); **Sebastian RENDLER**, Stein (CH); **Michel MUEHLEBACH**, Stein (CH); **Daniel EMERY**, Stein (CH); **Anke BUCHHOLZ**, Stein (CH); **Vikas SIKERVAR**, Goa (IN); **Girish RAWAL**, Corlim, Ilhas Goa (IN)

(73) Assignee: **SYNGENTA PARTICIPATIONS AG**, Basel (CH)

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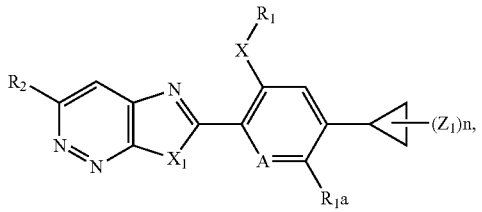
(57) **ABSTRACT**

Compounds of formula I, (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.

(I)



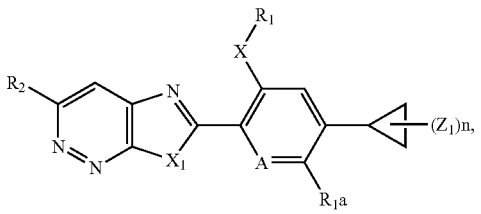
PESTICIDALLY ACTIVE HETEROCYCLIC DERIVATIVES WITH SULFUR CONTAINING SUBSTITUENTS

[0001] The present invention relates to pesticidally active, in particular insecticidally active tetracyclic 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).

[0002] Heterocyclic compounds with pesticidal action are known and described, for example, in WO 2012/086848, WO2016/104746 and WO 2014/142292.

[0003] There have now been found novel pesticidally active tetracyclic heterocyclic ring derivatives with sulphur substituents.

[0004] The present invention accordingly relates to compounds of formula I,



(I)

wherein

A is CH or N;

X is S, SO or SO_2;

[0005] R_1 is C_1-C_4alkyl, C_1-C_4haloalkyl, C_3-C_6cycloalkyl or C_3-C_6cycloalkyl-C_1-C_4alkyl; or

R_1 is 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_2 is 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_2 is C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, O(C_1-C_4haloalkyl), —C(O)C_1-C_4haloalkyl; or

R_2 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;

X_1 is O, S or NR_3, wherein R_3 is hydrogen, C_1-C_4alkyl, C_2-C_6alkenyl, C_2-C_6alkynyl, C_1-C_4alkoxy-C_1-C_4alkyl or C_3-C_6cycloalkyl;

Z_1 is cyano, formyl, hydroxyl, C_3-C_6cycloalkyl, hydroxycarbonyl, aminocarbonyl, C_1-C_4haloalkoxy, C_1-C_4alkoxy, C_1-C_4haloalkylsulfanyl, C_1-C_4halo-alkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_1-C_4alkoxycarbonyl, C_1-C_4haloalkoxycarbonyl, C_1-C_4alkylcarbonyl, C_1-C_4haloalkylcarbonyl, di-(C_1-C_4)alkylaminocarbonyl, C_1-C_4alkylaminocarbonyl, amino, C_1-C_4alkylcarbonylamino, di-(C_1-C_4)alkylcarbonylamino, C_1-C_4alkoxycarbonylamino or a group —$C(R_5)$=NOR_6, wherein R_5 and R_6 are independently hydrogen, C_1-C_4alkyl, C_1-C_4haloalkyl; or

Z_1 is phenyl, said phenyl 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

Z_1 is C_1-C_4alkyl which is mono- or polysubstituted by the group Z_2;

Z_2 is cyano, formyl, hydroxyl, C_3-C_6cycloalkyl, hydroxycarbonyl, aminocarbonyl, C_1-C_4haloalkoxy, C_1-C_4alkoxy, C_1-C_4haloalkylsulfanyl, C_1-C_4halo-alkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_1-C_4alkoxycarbonyl, C_1-C_4haloalkoxycarbonyl, C_1-C_4alkylcarbonyl, C_1-C_4haloalkylcarbonyl, di-(C_1-C_4)alkylaminocarbonyl, C_1-C_4alkylaminocarbonyl, amino, C_1-C_4alkylcarbonylamino, di-(C_1-C_4)alkylcarbonylamino, C_1-C_4alkoxycarbonylamino, a group —$C(R_5)$=NOR_6, wherein R_5 and R_6 are independently hydrogen, C_1-C_4alkyl or C_1-C_4haloalkyl;

R_{1a} is hydrogen, C_1-C_2alkyl, C_1-C_4alkoxy or halogen; and n is 1 or 2; and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of those compounds.

[0006] 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, 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.

[0007] 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. C_1-di-alkylamino is dimethylamino.

[0008] Halogen is generally fluorine, chlorine, bromine or iodine. This also applies, correspondingly, to halogen in combination with other meanings, such as haloalkyl or halophenyl.

[0009] 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.

[0010] Haloalkylsulfanyl groups preferably have a chain length of from 1 to 4 carbon atoms. Haloalkylsulfanyl is, for example, difluoromethylsulfanyl, trifluoromethylsulfanyl or 2,2,2-trifluoroethylsulfanyl. Similar considerations apply to the radicals C_1-C_4haloalkylsulfinyl and C_1-C_4haloalkylsulfonyl, which may be, for example, trifluoromethylsulfinyl, trifluoromethylsulfonyl or 2,2,2-trifluoroethylsulfonyl.

[0011] 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.

[0012] Haloalkoxy groups preferably have a chain length of from 1 to 4 carbon atoms. Haloalkoxy is, for example, difluoromethoxy, trifluoromethoxy or 2,2,2-trifluoroethoxy.

[0013] 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.

[0014] Alkoxycarbonyl is, for example, methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, isopropoxycarbonyl, n-butoxycarbonyl, isobutoxycarbonyl, sec-butoxycarbonyl or tert-butoxycarbonyl; preferably methoxycarbonyl or ethoxycarbonyl.

[0015] Alkylthio groups preferably have a chain length of from 1 to 6 carbon atoms. Alkylthio is, for example, methylthio, ethylthio, propylthio, isopropylthio, n-butylthio, isobutylthio, sec-butylthio or tert-butylthio, preferably methylthio and ethylthio. Alkylsulphinyl is, for example, methylsulphinyl, ethylsulphinyl, propylsulphinyl, isopropylsulphinyl, n-butylsulphinyl, isobutylsulphinyl, sec-butylsulphinyl, tert-butylsulphinyl; preferably methylsulphinyl and ethylsulphinyl.

[0016] Alkylsulphonyl is, for example, methylsulphonyl, ethylsulphonyl, propylsulphonyl, isopropylsulphonyl, n-butylsulphonyl, isobutylsulphonyl, sec-butylsulphonyl or tert-butylsulphonyl; preferably methylsulphonyl or ethylsulphonyl.

[0017] Alkylamino is, for example, methylamino, ethylamino, n-propylamino, isopropylamino or the isomeric butylamines. Dialkylamino is, for example, dimethylamino, methylethylamino, diethylamino, n-propylmethylamino, dibutylamino and diisopropylamino. Preference is given to alkylamino groups having a chain length of from 1 to 4 carbon atoms.

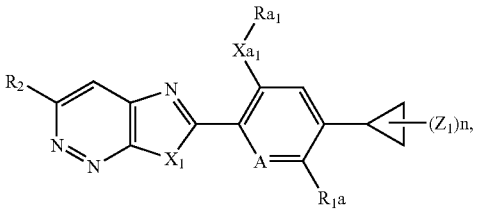
[0018] The cycloalkyl groups preferably have from 3 to 6 ring carbon atoms, for example cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl.

[0019] 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.

[0020] Free radicals represents methyl groups. In the designaition di-(C_1-C_4)alkylaminocarbonyl, the alkyl group of the di(C_1-C_4)alkylamino may be the same or may be different. The compounds of formula I according to the invention also include hydrates which may be formed during the salt formation.

[0021] A preferred group of compounds of formula I is represented by the compounds of formula I-1

(I-1)

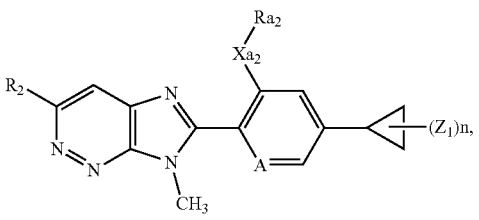


wherein X_1, A, R_2, R_{1a} and Z_1 are as defined under formula I above; and wherein Xa_1 is S, SO or SO_2; Ra_1 is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl. In said preferred group of compounds of formula I-1, R_2 is preferably C_1-C_4haloalkyl, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl or C_1-C_4haloalkylsulfonyl, Xa_1 is preferably SO_2 and Ra_1 is preferably ethyl. In said preferred group of compounds of formula I, Z_1 is cyano, formyl, hydroxycarbonyl, aminocarbonyl, C_1-C_4alkoxycarbonyl, C_1-C_4alkylcarbonyl, di-(C_1-C_4)alkylaminocarbonyl, C_1-C_4alkylaminocarbonyl, amino, (C_1-C_4)alkylcarbonylamino, di-(C_1-C_4)alkylcarbonylamino, (C_1-C_4)alkoxycarbonylamino or the group —C(R_5)═NOR_6, wherein R_5 and R_6 are independently hydrogen, C_1-C_4alkyl or C_1-C_4haloalkyl; or Z_1 is cyano-C_1-C_2-alkyl, hydroxyl-C_1-C_2-alkyl, formyl-C_1-C_2-alkyl, C_1-C_4alkoxy-C_1-C_2-alkyl, C_1-C_4haloalkoxy-C_1-C_2-alkyl C_1-C_4alkylsulfinyl-C_1-C_2-alkyl, C_1-C_4alkylsulfanyl-C_1-C_2-alkyl, C_1-C_4alkylsulfonyl-C_1-C_2-alkyl, C_1-C_4alkoxycarbonyloxy-C_1-C_2-alkyl, C_1-C_4alkoxycarbonyloxy-C_1-C_2-alkyl or C_1-C_4alkylaminocarbonyloxy-C_1-C_2-alkyl; and n is 1 or 2.

[0022] Especially preferred compounds of formula I-1 are those in which n is 1, and X_1 is NR_3, wherein R_3 is methyl or ethyl and R_{1a} is hydrogen.

[0023] A further preferred group of compounds of formula I is represented by the compounds of formula I-2

(I-2)



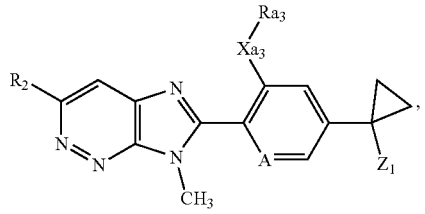
wherein A, R_2 and Z_1 are as defined under formula I above; Xa_2 is S, SO or SO_2; and Ra_2 is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl.

[0024] In said preferred group of compounds of formula I-2, R_2 is preferably C_1-C_4haloalkyl, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl or C_1-C_4haloalkylsulfonyl, Xa_2 is preferably SO_2 and Ra_2 is preferably ethyl. In said preferred group of compounds of formula I, Z_1 is cyano, formyl, hydroxycarbonyl, aminocarbonyl, C_1-C_4alkoxycarbonyl, di-(C_1-C_4)alkylaminocarbonyl, C_1-C_4alkylaminocarbonyl, amino, (C_1-C_4)alkylcarbonylamino, di-(C_1-C_4)alkylcarbonylamino, (C_1-C_4)alkoxycarbonylamino or a group —C(R_5)═NOR_6 wherein R_5 and R_6 are independently hydrogen, C_1-C_4alkyl or C_1-C_4haloalkyl; and n is 1 or 2.

[0025] Especially preferred compounds of formula I-2 are those, wherein n is 1, Ra_2 is ethyl and Xa_2 is SO_2.

[0026] Particularly preferred compounds of formula I are represented by the compounds of formula I-3

(I-3)



wherein

A is CH or N;

[0027] X_{a3} is S or SO_2;

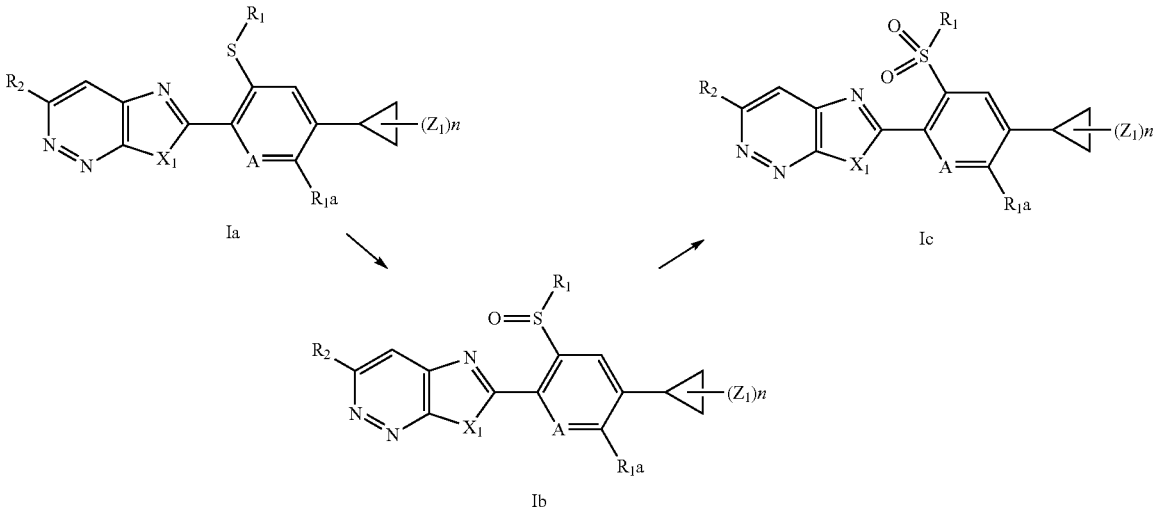
R_{a3} is ethyl;

R_2 is C_1-C_4haloalkyl, C_1-C_4haloalkylsulfanyl, C_1-C_2haloalkylsulfinyl, C_1-C_2haloalkylsulfonyl;

Z_1 is cyano, hydroxycarbonyl, aminocarbonyl, C_1-C_4alkoxycarbonyl, methylaminocarbonyl, dimethylaminocarbonyl, amino, methoxycarbonylamino, formyl, hydroxymethylene or methylhydroxymethylene. Especially preferred compounds of formula I-3 are those wherein R_2 is trifluoromethyl, pentafluoroethyl, trifluoromethylsulfanyl or trifluoromethysulfonyl.

[0028] The process according to the invention for preparing compounds of formula I is carried out by methods known to those skilled in the art. More specifically, compounds of formula I can be prepared (as depicted in scheme 1) from compounds of formula Ia, wherein A, R_1, R_{1a}, R_2, X_1, Z_1 and n 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 monoperoxo-disulfate salt or potassium permanganate. 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. The reactions can occur in a stepwise fashion through comounds of formula Ib. Those skilled in the art will appreciate that is therefore possible to control the reaction (depending on amount of oxidant added, the temperature, and time of reaction) to allow isolation of compounds of formula Ib.

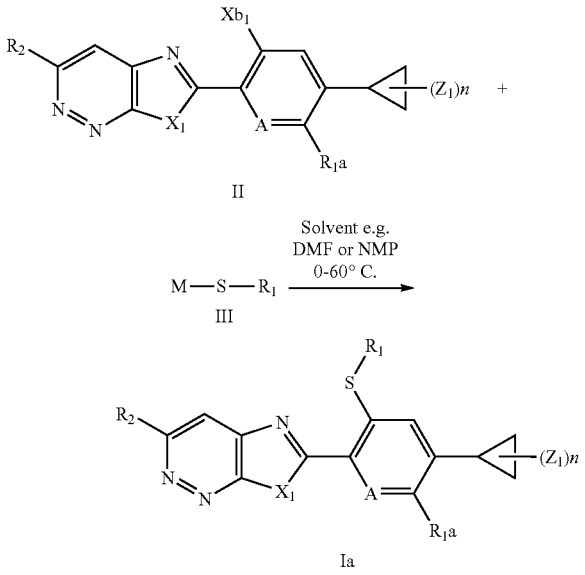
Scheme 1:



[0029] Compounds of formula Ia can be prepared (scheme 2) by reacting a compound of the formula II, wherein A, R_2, R_{1a} and X_1 are as defined in formula I, and wherein X_{b1} is a leaving group like, for example, fluorine, chlorine, bromine or iodine, or an aryl- or alkylsulfonate such as trifluoromethanesulfonate, preferentially fluorine or chlorine, with a compound of the formula III, wherein R_1 is as defined in formula I, and M is a metal or non-metal cation. In scheme

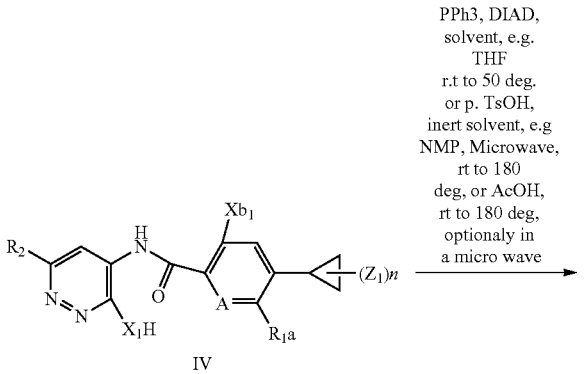
2, the cation M is assumed to be monovalent, but polyvalent cations associated with more than one S—R_1 group can also be considered. Preferred cations are, for example lithium, sodium, potassium or cesium. The reaction can be performed in a solvent, preferably polar aprotic, at temperatures below 0° C. or up to boiling temperature of the reaction mixture.

Scheme 2:



[0030] Compounds of formula II, wherein A, R_2, R_{1a}, X_1 and Z_1 and n have the values defined in formula I, and wherein X_{b1} is a halogen, preferentially chlorine, bromine or fluorine can be prepared from compounds of formula IV by dehydration, e.g. by heating the compounds in a microwave, in the presence of an acid catalyst, for example methane sulfonic acid, or para-toluene sulfonic acid, in an inert solvent such as N-methyl pyrollidine at temperatures between 25-180° C., preferably 130-170° C. (scheme 3).

Scheme 3:



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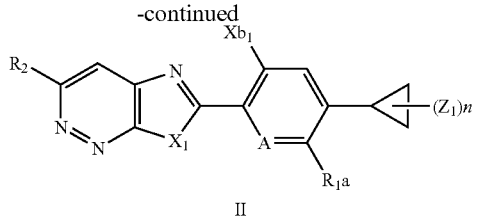
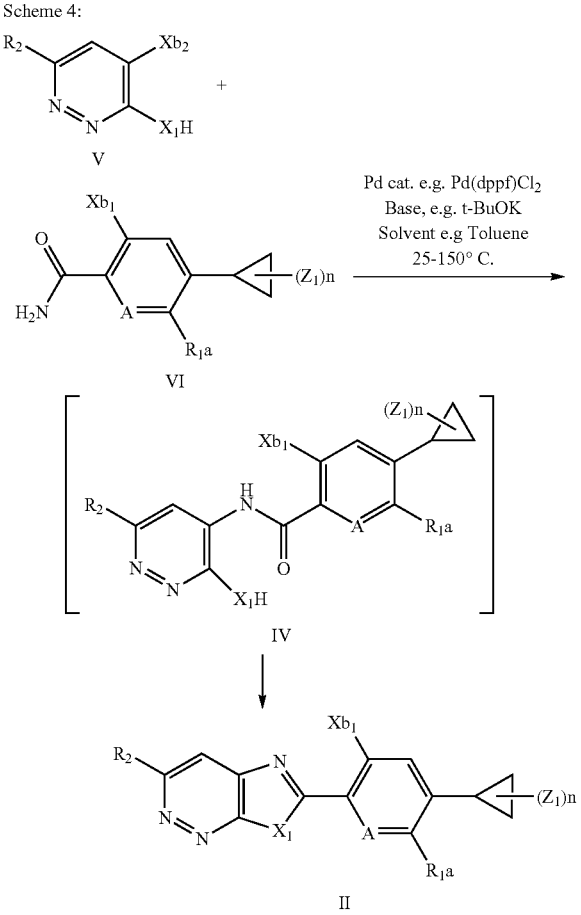


[0031] Such processes have been described previously in WO 2010/125985. Alternatively, compounds of formula II can be prepared from compounds of formulas IV by heating in a solvent, for example acetic acid, at temperatures between 80-120° C., optionally in a microwave. Compounds of formula IV can also be converted to compounds of formula Ia (wherein X_1 is O or S) using triphenyl phosphine, di-isopropyl azo dicarboxylate in an inert solvent such as THF at temperatures between 25-50° C. Such Mitsunobu conditions have been previously described for such transformations (see WO 2009/131237).

[0032] Compounds of formula IV are obtained by a subexample of the Buchwald-Hartwig amination reaction of compounds of formula V with compounds of formula VI (scheme 4):

Scheme 4:

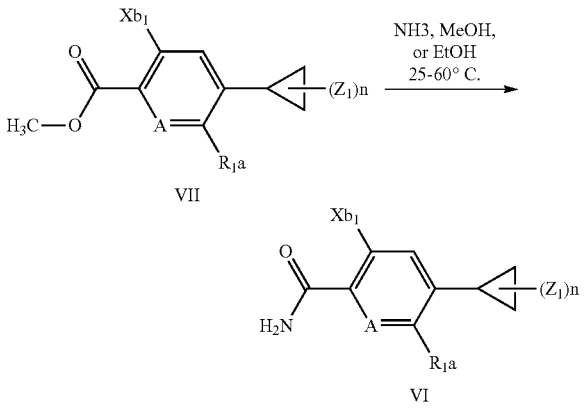


[0033] Such an amide nitrogen heteroarylation reaction, typically runs under transition metal-catalysed C—N bond formation conditions involving a catalytic system (such as for example [1,1'-bis(diphenylphosphino) ferrocene] dichloropalladium(II)), usually composed of a metal, such as a palladium source (for example palladium(0) precursors like Pd_2(dibenzylideneacetone)$_3$, or palladium(II) precursors like Pd(OAc)$_2$) and a ligand (for example phosphine-based or N-heterocyclic carbene-based), a base, such as alkoxides (for example sodium or potassium tert-butoxide), carbonates, phosphates or silyl amides (for example potassium or cesium carbonate, potassium phosphate, or lithium hexamethyl disilazane) or hydroxides (for example sodium or potassium hydroxide), and solvents such as toluene, tetrahydrofurane, dioxane, dimethoxyethane, N,N-dimethyl formamide, N-methyl pyrrolidone and dimethylsulfoxide, as well as their aqueous solutions. These methods are known to those skilled in the art and described, for example, in WO 2014/142292. Under those above described amide cross-coupling reaction conditions, the compounds of formula IV can be isolated (and converted to compounds of formula II as described above) but may also spontaneously ring-close into the compounds of formula II, especially in cases where X_1 is NR_3.

[0034] The preparation of pyridazine compounds of formula V, wherein R_2 and X_1 have the values defined in formula I, and wherein X_{b2} is a a halogen, preferentially chlorine, bromine or iodine, was detailed in WO 2014/142292, and WO 2016/116338.

[0035] Amides of the formula VI, wherein A, R_1, X and Q have the values defined in formula I, and X_b1 is a halogen, can be prepared from compounds of formula VII by reaction with an ammonia in an inert solvent such as methanol or ethanol, at temperatures between 25-60° C., preferably between 25-–40° C. (scheme 5).

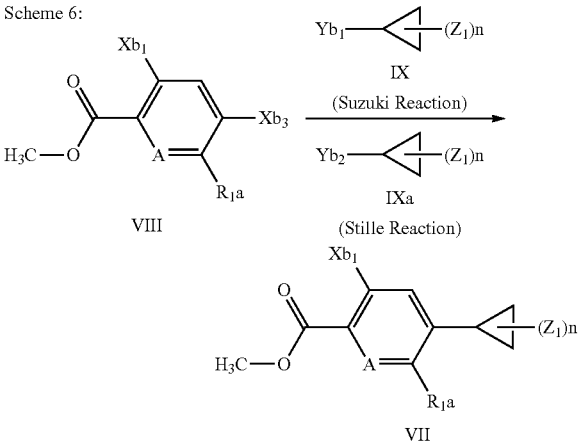
Scheme 5:



[0036] Compounds of formula VII can prepared (as shown in scheme 6) by a Suzuki reaction, which involves for example, reacting compounds of formula VIII, wherein Xb_3 is a leaving group like, for example, chlorine, bromine or iodine, or an aryl- or alkylsulfonate such as trifluoromethanesulfonate (especially preferred are those in which Xb1 is fluoro, chloro, or bromo) with compounds of formula IX, 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 inert atmosphere. The reaction temperature can preferentially range from ambient 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.

[0037] Alternatively compounds of formula VII can be prepared by a Stille reaction of compounds of formula IXa wherein Y_{b2} is a trialkyl tin derivative, preferably tri-n-butyl tin, with compounds of formula VIII and compounds of formula IXa. 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.

Scheme 6:



[0038] A large number of compounds of the formula IX and IXa are commercially available or can be prepared by those skilled in the art. Many chemical transformations, well known by those skilled in the art, can be used to access boronic acid derivatives of formula IX, starting from various and easily available starting materials, as for example, to cite only a few (scheme 7), hydrogen abstraction on a heteroaromatic compound of the formula IX_1 wherein Zb_1 is hydrogen, with a strong base (step A), like butyl lithium or lithium diisopropylamide or i-PrMgCl. LiCl, followed by reaction of the metallated intermediate of the formula IX_2, wherein Zb_2 is a metal such as Li^+ or $MgCl^+$ for example, with, for example, a trialkylborate (step B), or a tri-n-butyl tin chloride (step B). Another way to access an organometal inter-

mediate of the formula IX_2 is from a compound of the formula IX_1 wherein Zb_1 is chlorine, bromine or iodine, via metal-halogen exchange with an organometallic species (step C), like butyl lithium or an organ magnesium compound, or direct metallation with a metal, like magnesium. Introduction of a pinacolborate functional group via a palladium catalyzed reaction with bispinacol diborane, or hexa-n-butyldistannane, on a compound of the formula IX_1, wherein Zb_1 is chlorine, bromine, iodine or triflate, is another common strategy (scheme 7, step D). In the compounds of formula IX, and IX_1 within scheme 7, Z_1 and n has the values defined for the formula I. A person skilled in the art will be able to select an adequate preparation method to access compounds of formula IX and IX_1 depending on the values of Z_1 and n.

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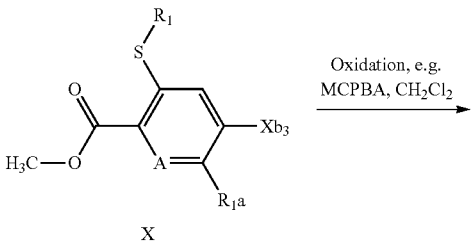
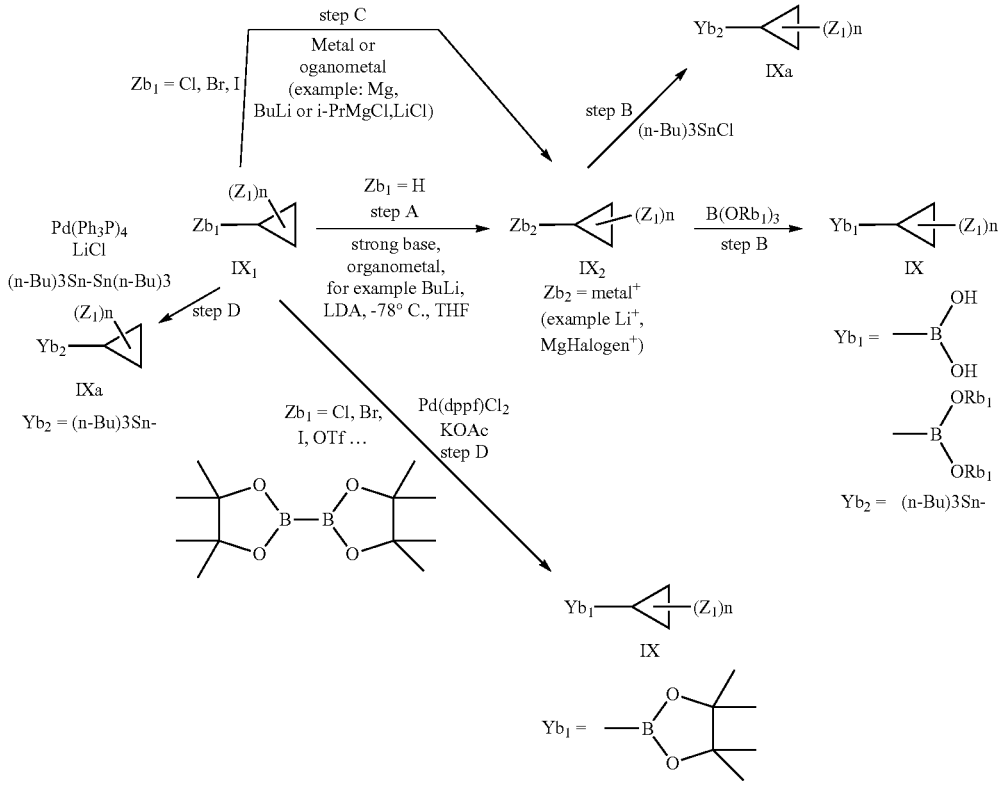


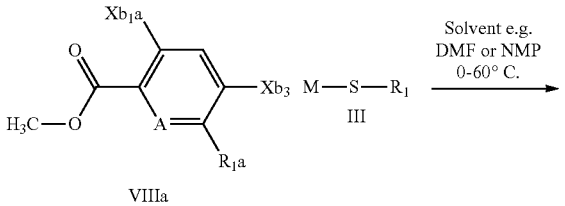
X

Scheme 7:



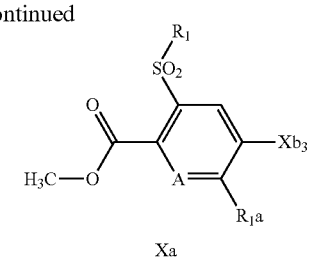
[0039] It will be apparent to those skilled in the art that the reactions may be carried out in a different order to obtain compounds of formula I. Thus, the substituent XR_1 can be introduced at an earlier stage in the synthesis, to give compounds of Formula X or Xa as shown in scheme 8.

Scheme 8:



VIIIa

-continued

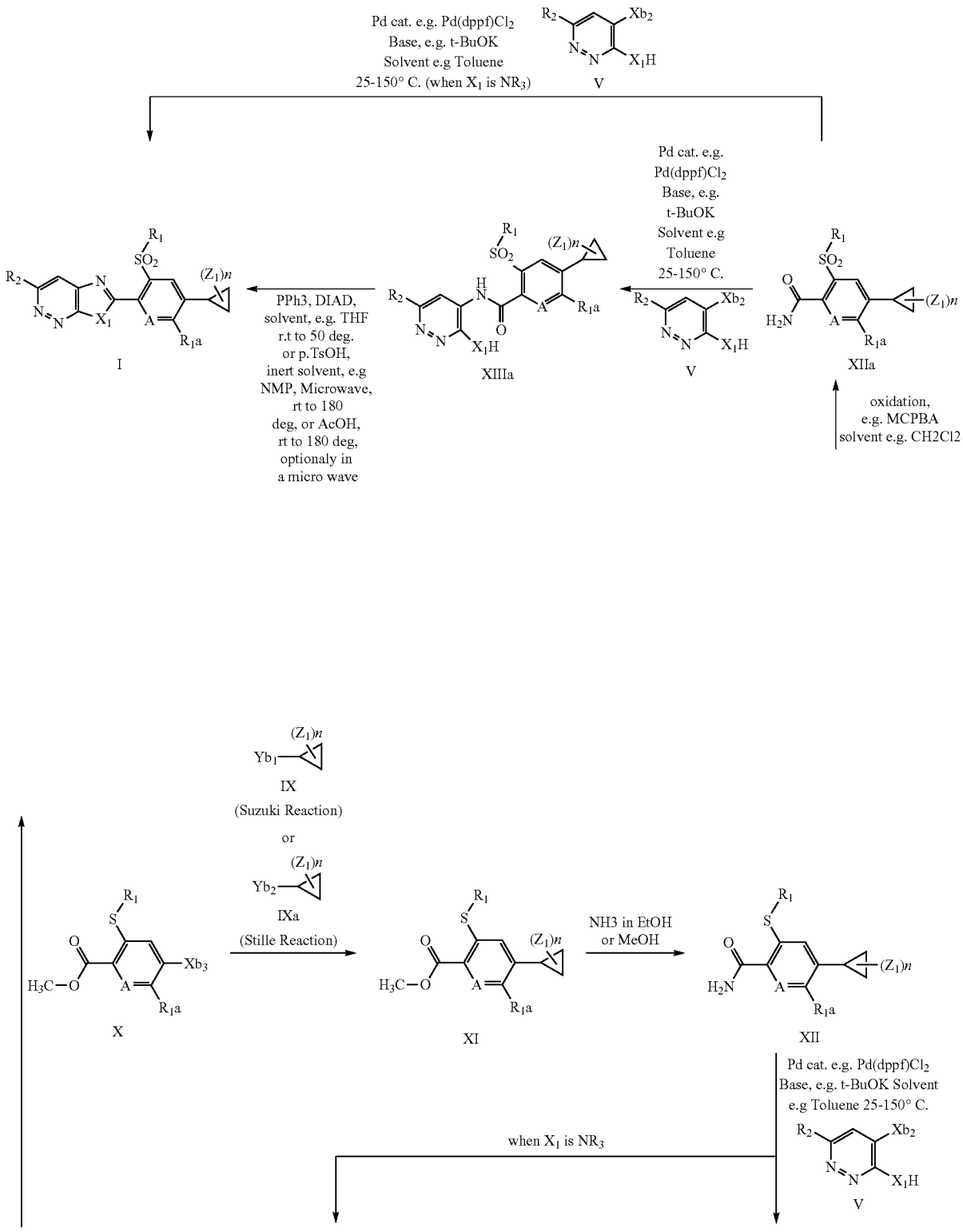


Xa

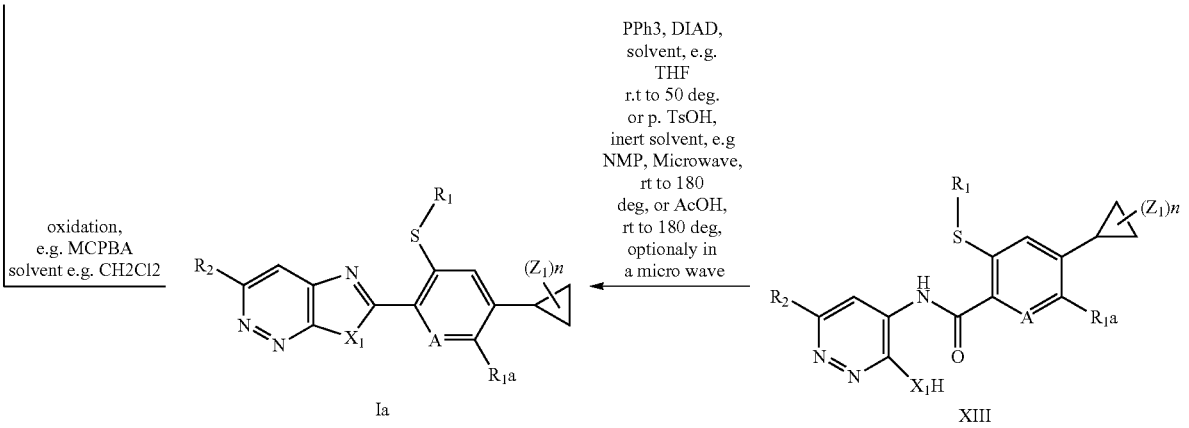
$Xb1_a$ = F, NO2, or Br
$Xb3_a$ = Br

[0040] Compounds of formula of X and Xa can then be converted to compounds of formula I as shown in schemes 9 and 10, using the reactions previously described and apparent to those skilled in the art.

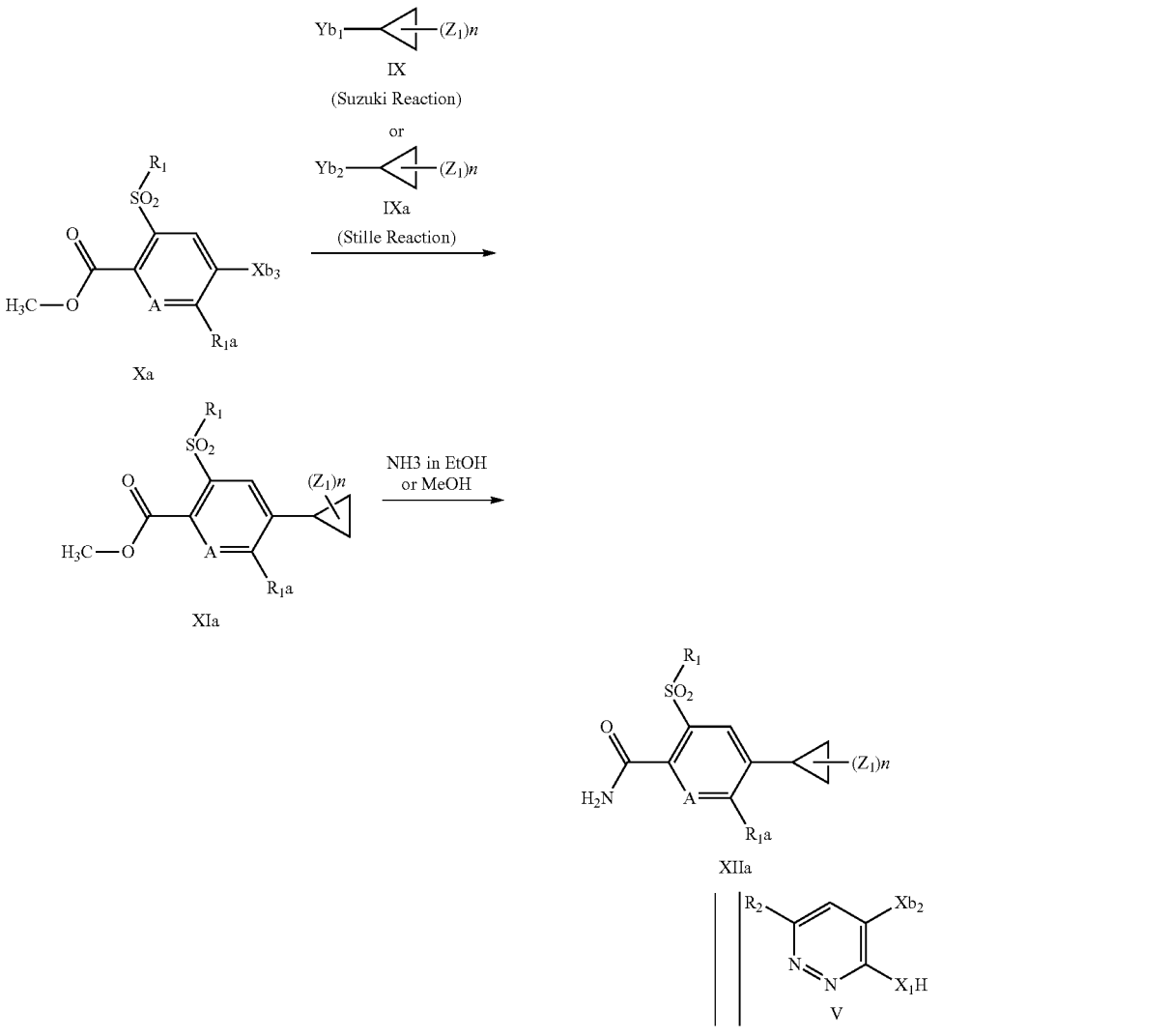
Scheme 9:


Pd cat. e.g. Pd(dppf)Cl2
Base, e.g. t-BuOK
Solvent e.g Toluene
25-150° C. (when X1 is NR3)
V
Pd cat. e.g. Pd(dppf)Cl2
Base, e.g. t-BuOK
Solvent e.g Toluene
25-150° C.
PPh3, DIAD,
solvent, e.g. THF
r.t to 50 deg.
or p.TsOH,
inert solvent, e.g
NMP, Microwave,
rt to 180
deg, or AcOH,
rt to 180 deg,
optionaly in
a micro wave
I
XIIIa
V
XIIa
oxidation,
e.g. MCPBA
solvent e.g. CH2Cl2
IX
(Suzuki Reaction)
or
IXa
(Stille Reaction)
X
XI
NH3 in EtOH
or MeOH
XII
Pd cat. e.g. Pd(dppf)Cl2
Base, e.g. t-BuOK Solvent
e.g Toluene 25-150° C.
when X1 is NR3
V

-continued



Scheme 10:



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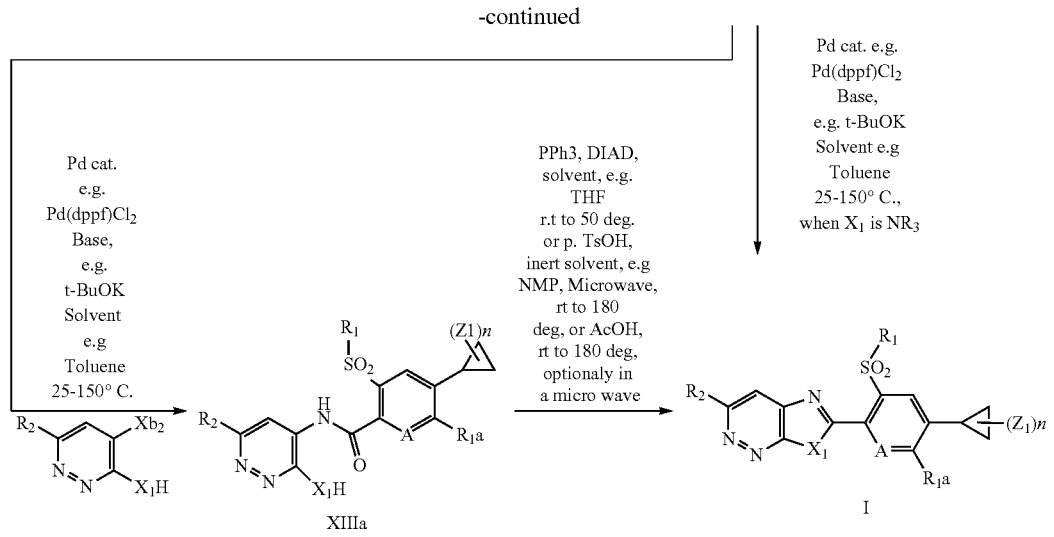
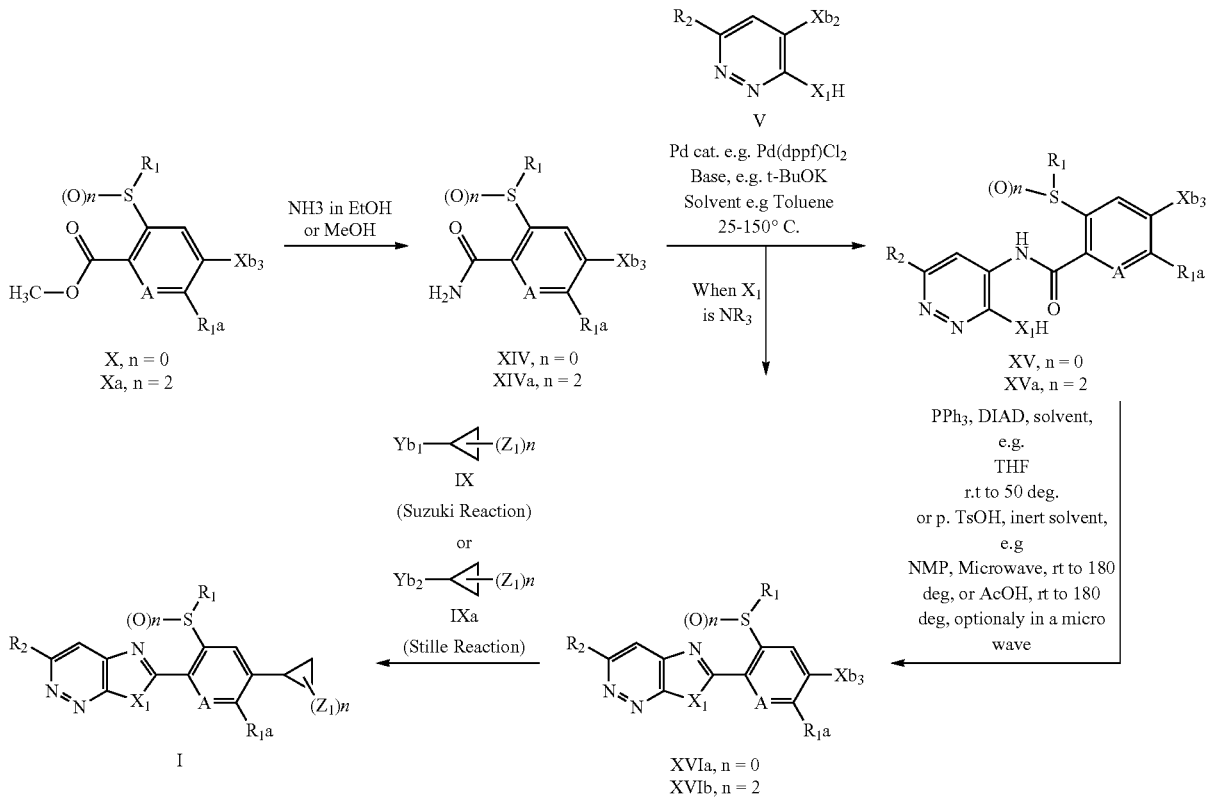


[0041] A further method to produce compounds of formula I again uses the same reactions previously described but changes their order to produce the final compounds. Thus, compounds of formula X and Xa are treated with ammonia as previously described to give compounds of formula XIV and XIVa. Palladium catalyzed reaction of XIV and XIVa with compounds of formula V lead to compounds of formula XV and XVa, which, when X_1 is NR_3 spontaneously cyclise to compounds of formula XVIa and XVIb. Alternatively compounds of formula XV and XVa can be cyclized in a separate step as previously discussed to XVIa and XVIb. Suzuki or Stille couplings with compounds of formula IX and IXa respectively yield the compounds of formula I. This is described in scheme 11.

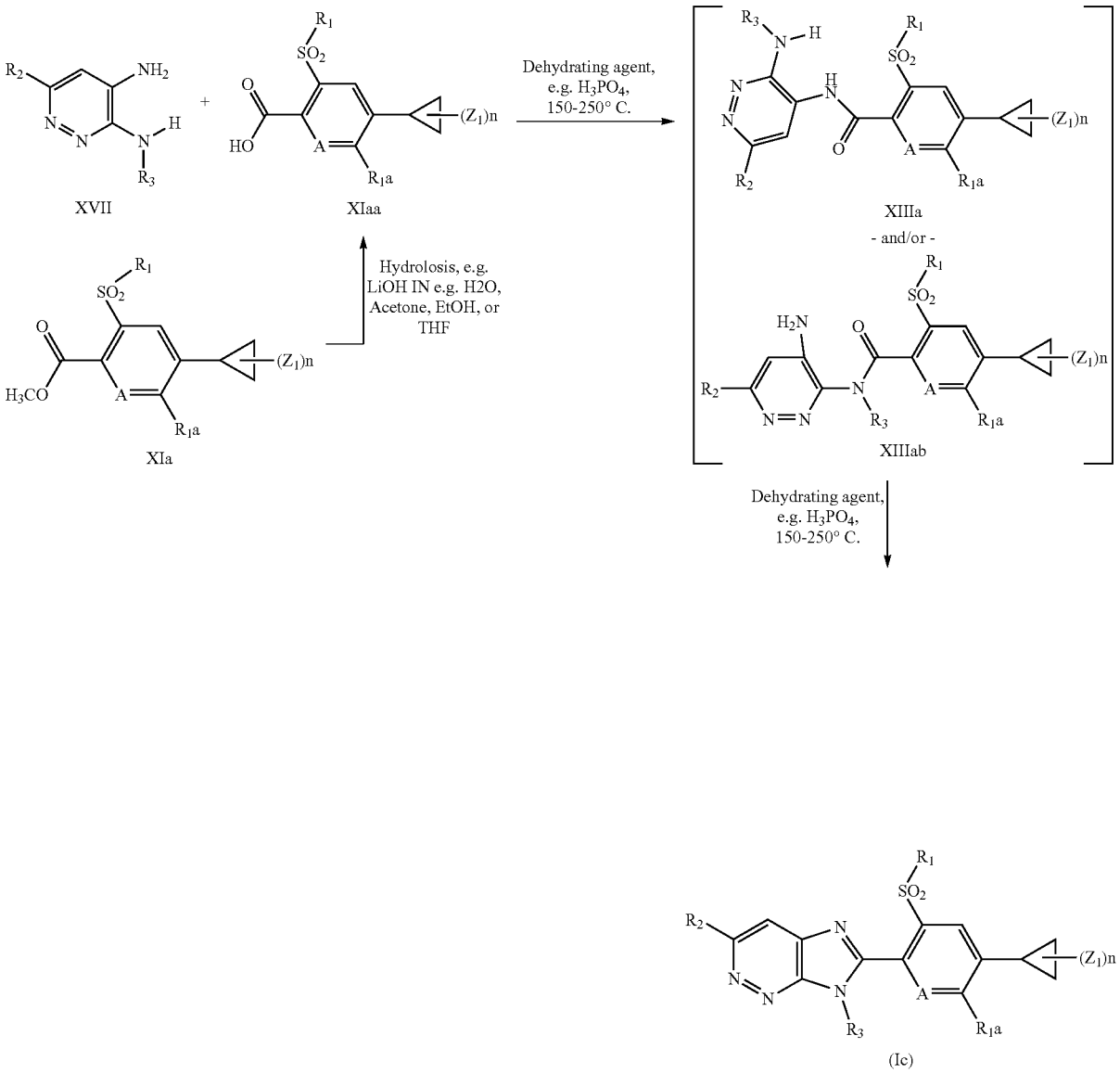
Scheme 11:



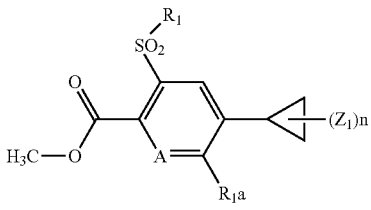
[0042] Compounds of formula I can also be prepared by reaction of a compound of formula XVII, wherein R_2 and R_3 are as described under formula I above, with a compound of formula XIaa in the presence of a de-hydrating agent, such as for example polyphosphoric acid at temperature between 150° C. to 250° C., to yield compounds of formula I, wherein the substituents are as described above and under formula I. Such processes are well known and have been described for example in WO 2008/128968, WO 2012/086848, WO 2013/018928, WO 2014/142292 and WO 2006/003440. The process is summarized in scheme 12 for compounds of formula Iaa:

[0043] As can be seen in scheme 12, the formation of compounds of formula Iaa occurs through the intermediacy of a compound of formula XIIIa (and/or its position isomer XIIIab). Intermediates XIIIa or intermediate XIIIab may form as a pure entity, or intermediates XIIIa and XIIIab may arise as a mixture of regioisomeric acylation products. It is in many cases advantageous to thus prepare compounds of formula (Ic) through such intermediates XIIIa/XIIIab, which may be isolated and optionally purified. This is illustrated for compounds of formula Ic in scheme 13:

Scheme 12:

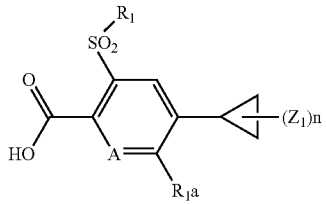


Scheme 13:



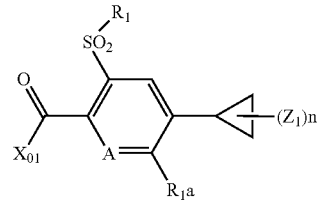
XIa

Hydrolysis, for example LiOH in for example H_2O, Acetone

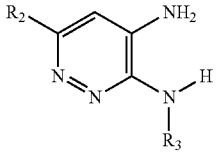


XIaa

$(COCl)_2$, insert solvent, e.g. CH_2Cl_2 room temp, or $SOCl_2$, CH_2Cl_2 room temp. or DCC, EDC, THF or pyridine, rt-120 deg.

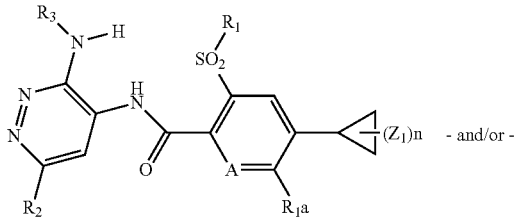


XIaab



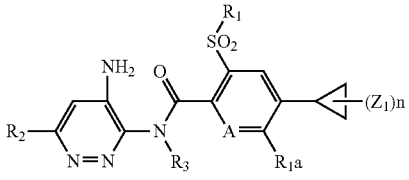
XVII

optionally in the presence of an additional base, such as triethylamine or pyridine



XIIIa

- and/or -



XIIIab

PPh3, DIAD, solvent, e.g. THF r.t to 50deg. or p. TsOH, inert solvent, e.g NMP, Microwave, rt to 180° C. or AcOH, 150° C.

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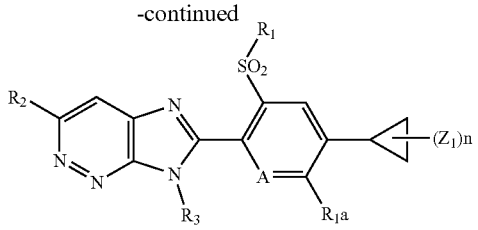
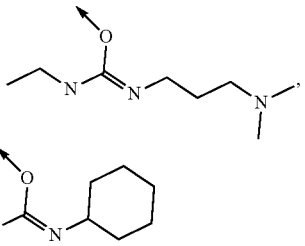


Ic

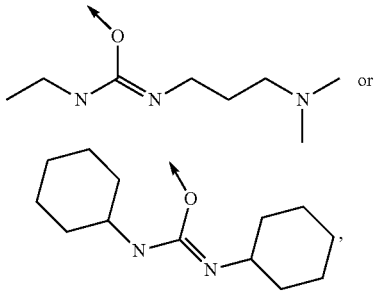
wherein:

X_{01} = Halogen,



[0044] Compounds of the formula XIIIa and/or XIIIab (or a mixture thereof), or a salt thereof, wherein R_1, R_2, R_3, R_{1a} and Z_1 and n are as described under formula I above, may be prepared by

i) activation of compound of formula XIaa, wherein Z_1 and n are as defined above, by methods known to those skilled in the art and described in, for example, *Tetrahedron,* 2005, 61 (46), 10827-10852, to form an activated species XIaab, wherein Z_1 and n are as defined above and wherein X_{01} is halogen, preferably chlorine. For example, compounds XIaab where X_{01} is halogen, preferably chlorine, are formed by treatment of XIaa, with, for example, oxalyl chloride $(COCl)_2$ or thionyl chloride $SOCl_2$ in the presence of catalytic quantities of N,N-dimethylformamide (DMF) in inert solvents such as methylene chloride or tetrahydrofurane at temperatures between 20 to 100° C., preferably 25° C. Alternatively, treatment of compounds of formula XIaa with, for example, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) or dicyclohexyl carbodiimide (DCC) will generate an activated species XIaab, wherein X_{01} is



or

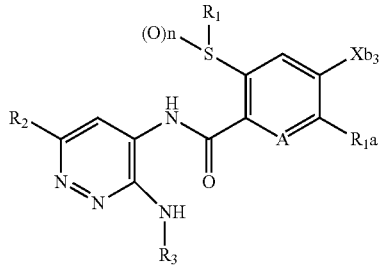
respectively, in an inert solvent, such as pyridine or tetrahydrofurane, optionally in the presence of a base, such as triethylamine, at temperatures between 25-180° C.; followed by

ii) treatment of the activated species XIaab with a compound of formula XVII (or a salt thereof), wherein wherein R_1 and R_2 are as described under formula I above, optionally in the presence of a base, such as triethylamine or pyridine, in an inert solvents such as dichloromethane, tetrahydrofurane,

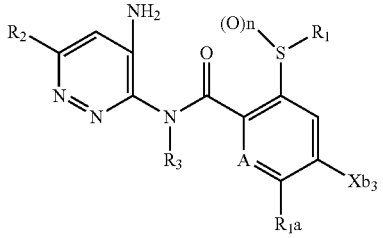
dioxane or toluene, at temperatures between 0 and 80° C., to form the compounds of formula XIIIa and/or XIIIab (or a mixture thereof), which may spontaneously cyclize to compounds of formula Ia.

[0045] Compounds of formula XIIIa and/or XIIIab (or a mixture thereof), can alternatively be isolated, and further be converted into compounds of formula Ia, as described previously. Compounds of formula XIaa are obtained by hydrolysis of compounds of formula XIa, by ester hydrolysis, using conditions known to those skilled in the art.

[0046] In the same way, compounds of formula XVIIIaa and XVIIIab may be prepared from compounds of formula X, Xa by the methods described in scheme 13. Intermediates obtained from such chemistry, namely, XVIIIaa, XVIIIab, XVIIIaaa and XVIIIaba,

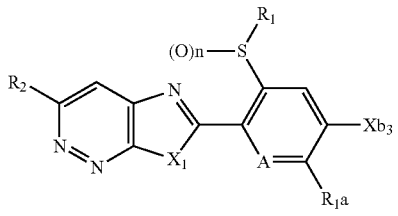


XVIIIaa, n = 0
XVIIIab, n = 2



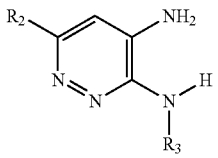
XVIIIaaa, n = 0
XVIIIaba, n = 2

are then converted to compounds of formula XVIa and XVIb wherein X_1 is NR_3 and R_2, R_1, R_{1a}, and Xb_3 are as previously described, as discussed in scheme 11.



XVIa, n = 0
XVIb, n = 2

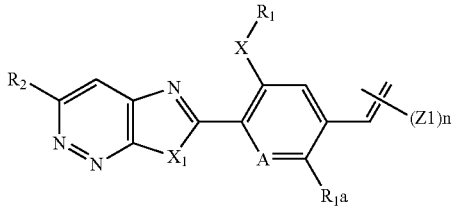
[0047] Compounds of formula XVII, wherein R_2 is halogen have been described in for example WO 2015/000715. Compounds of formula XVII wherein R_2 is C_1-C_2haloalkyl, or C_1haloalkylsulfanyl



XVII

have been prepared as described in WO 2016/059145 and WO 2016/039441.

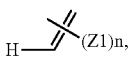
[0048] A further preparation of compounds of formula I utilises compounds of formula XIX



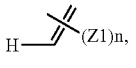
XIX

wherein Z_1 is C_3-C_6cycloalkyl, hydroxycarbonyl, amidocarbonyl, C_1-C_4haloalkoxy, C_1-C_4alkoxy, C_1-C_4haloalkylsulfanyl, C_1-C_4halo-alkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_1-C_6alkoxycarbonyl, —C(O)C_1-C_4haloalkyl and phenyl, whereby the phenyl group 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_4halo-alkylsulfinyl, C_1-C_4haloalkylsulfonyl and —C(O)C_1-C_4haloalkyl, and n is 1 or 2;

[0049] Compounds of the formula XIX can be prepared using Suzuki or Stille coupling reactions with compounds of formula XVIa or XVIb as described in Scheme 11, or for example, by reacting compounds of formula XVIa or XVIb with terminal alkenes of formula

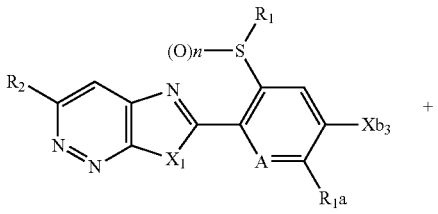


(scheme 14), wherein X_{b3} can be a halogen, preferentially chlorine, bromine or iodine, or a sulfonate, like for example a trifluoromethanesulfonate. In formula XVIa or XVIb, and

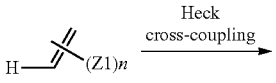


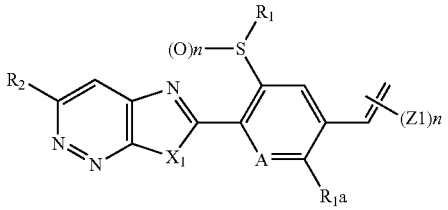
A, X_1, Z_1, n, R_1, R_{1a} and R_2 are as described previously. This type of reaction is well known to a person skilled in the art, and commonly described as the Heck cross-coupling reaction.

Scheme 14:



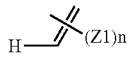
XVIa, n = 0
XVIb, n = 2





XIX

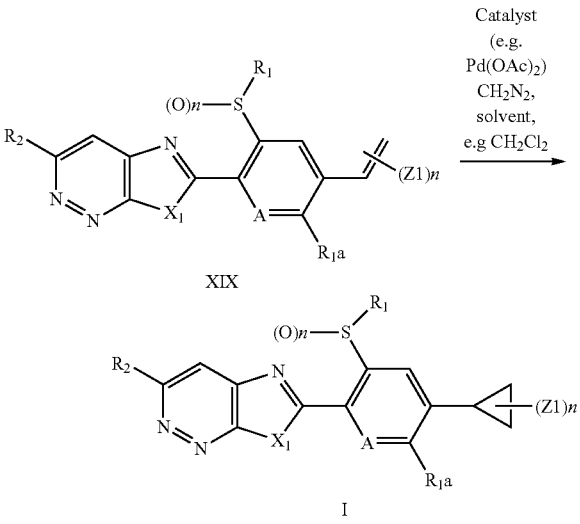
[0050] In this reaction, the substituted aromatic component of formula XVIa or XVIb is reacted with the terminal alkene of formula



in the presence of a palladium catalyst, optionally in the presence of a ligand, and a base in a solvent (for example dimethyl formamide) at elevated temperatures to give compounds of formula XIX. The catalyst can be for example tetrakis(triphenylphosphine)palladium(0), palladium chloride or palladium(II)acetate. The ligand can be for example triphenylphosphine, or BINAP, and the base for example triethylamine, potassium carbonate or sodium acetate. Such reactions are well known in the literature and have been described for example in Chem. Rev. 100 (8): 3009-3066. 2000. The compounds formed may have the trans-stereochemistry shown in scheme 17, but depending on the reaction conditions, one skilled in the art can also obtain compounds of formula I-d with a cis-double bond configuration.

[0051] Compounds of formula XIX can be further elaborated to compounds of formula I (Scheme 15) by Cyclopropanation, for example with diazomethane in the presence of a palladium catalyst (for example $Pd(OAc)_2$ (for example as described in *J. Org. Chem.*, 1980, 45, 695 and *Synthesis*, 1981, 714) or by Simmons-Smith zinc carbene chemistry (see *Org. React.* 1973, 20, page 1). Those skilled in the art will appreciate there are many other methods to cyclopropanate double bonds.

Scheme 15:

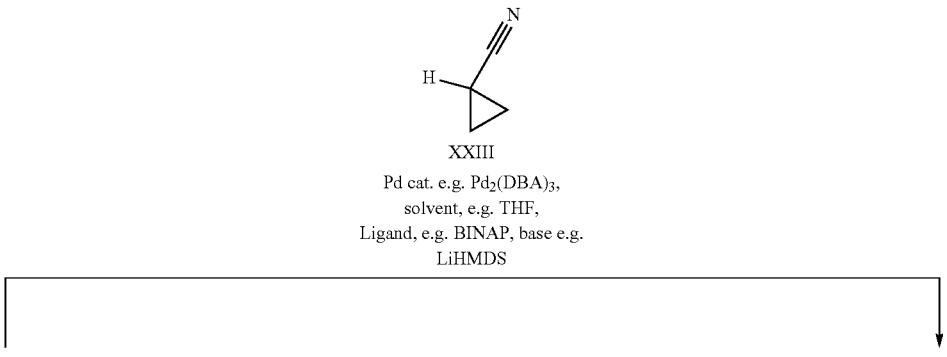


XIX

I

[0052] Further preparations of compounds of formula I are shown in scheme 16.

Scheme 16:



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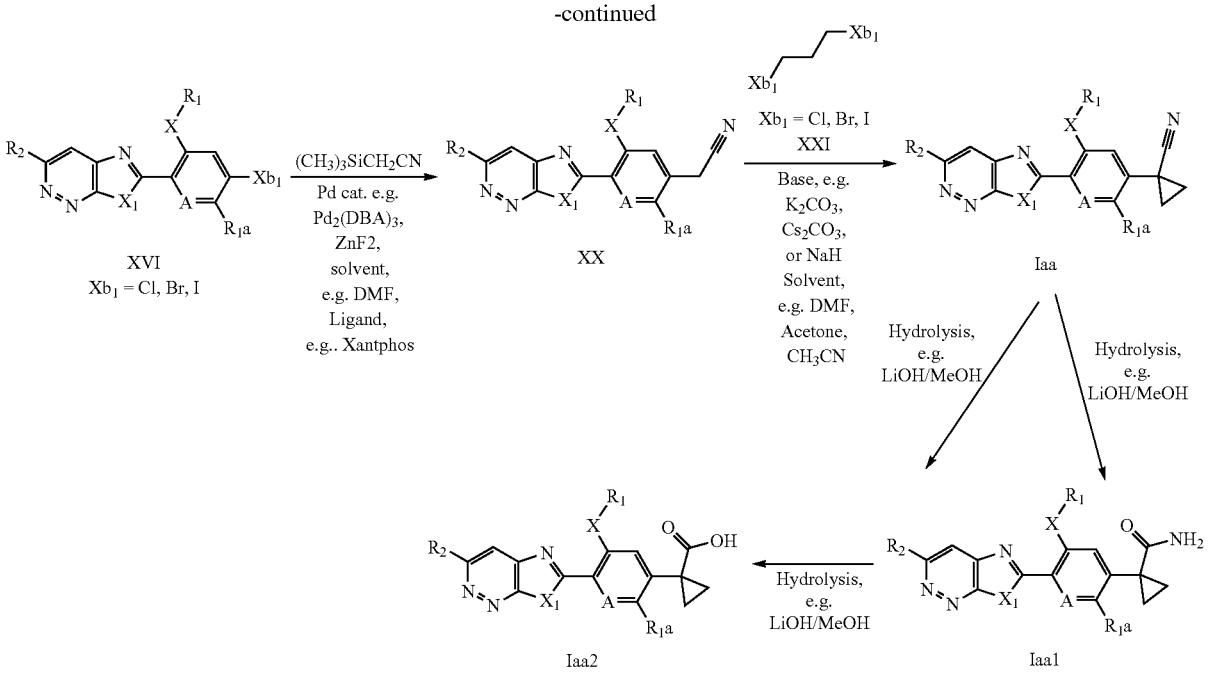
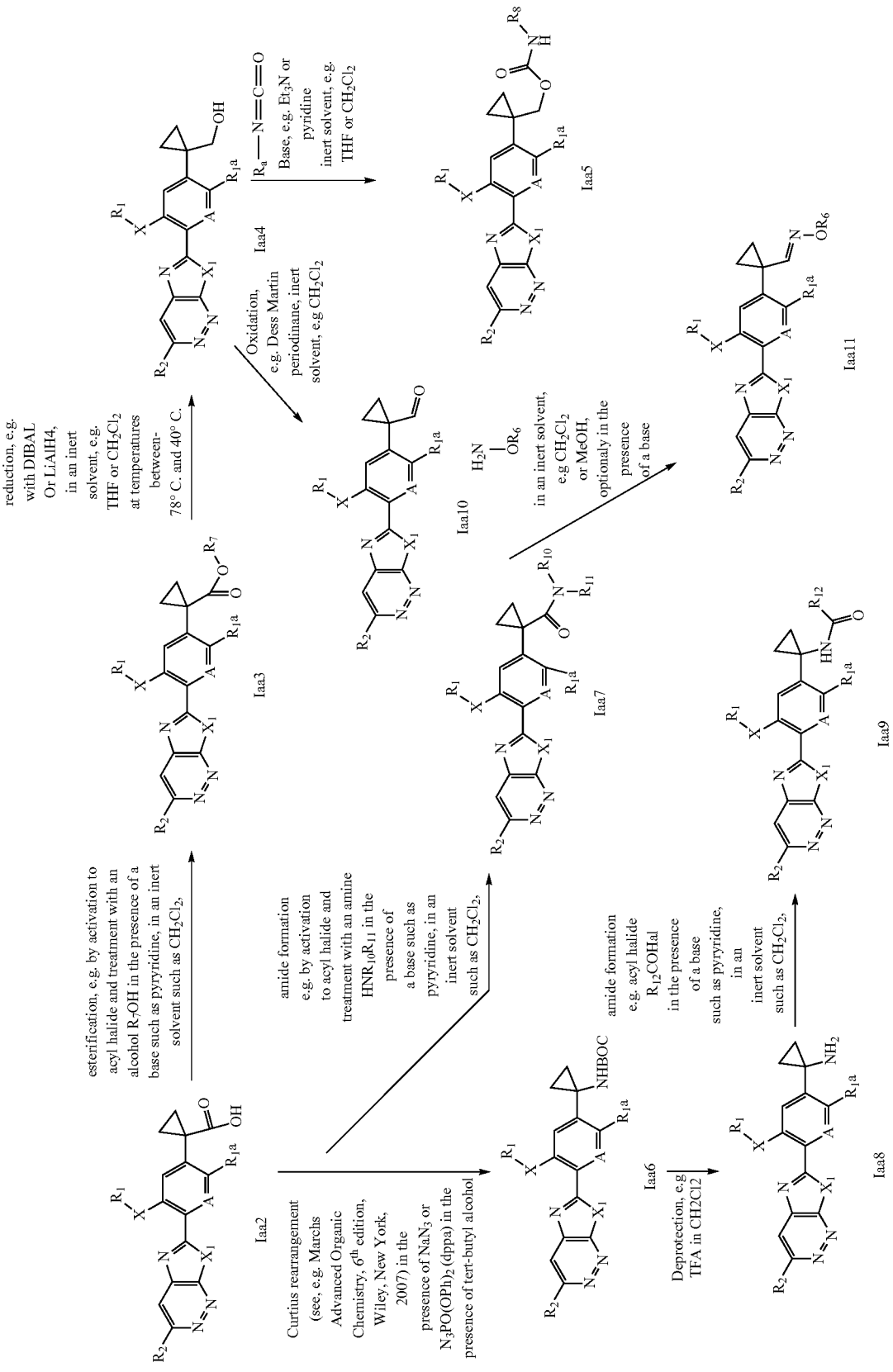


[0053] As shown in Scheme 16, treatment of compounds of formula XVI, where X is S, SO, SO_2, with trimethylsilylacetonitrile, in the presence of zinc(II)fluoride, and a palladium(0)catalyst such as Tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct ($Pd_2(dba)_3$), a ligand, for example Xantphos, in an inert solvent, such as DMF at temperatures between 100-160° C., optionally under microwave heating, leads to compounds of formula XX. Such chemistry has been described in the literature, e.g. in *Org. Lett.,* 16(24), 6314-6317; 2014. Compounds of formula XX can be treated with compounds of formula XXI, in the presence of a base such as sodium hydride, K_2CO_3, or Cs_2CO_3, in an inert solvent such as DMF, acetone, or acetonitrile, to give compounds of formula Iaa. Alternatively, compounds of formula Iaa can be prepared directly from compounds of formula XVI by treatment with compounds of formula XXIII, with $Pd_2(dba)_3$, a ligand, such as BINAP, a strong base such as LiHMDS, in an inert solvent such as THF at temperatures between 40-70° C. Such chemistry has been described in, for example, *J. Am. Chem. Soc.,* 127(45), 15824-15832; 2005. Compounds of formula Iaa can be converted to compounds of formula Iaa1 and Iaa2 by basic hydrolysis as known to those skilled in the art.

[0054] Compounds of formula I can also be prepared by a variety of reactions known to those skilled in the art, one the basic skeleton has been put together, for example using compound Iaa2 as starting material. Some typical reactions are shown in Scheme 17, all of which are known to those skilled in the art, and thus easily leading to compounds of formulae Iaa3-Iaa11.

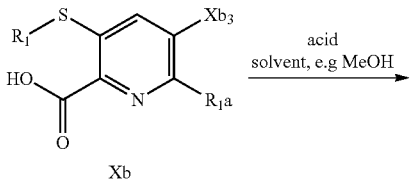
Scheme 17:


Iaa2
esterification, e.g. by activation to acyl halide and treatment with an alcohol R7OH in the presence of a base such as pyryridine, in an inert solvent such as CH_2Cl_2,
Iaa3
reduction, e.g. with DIBAL Or $LiAlH_4$, in an inert solvent, e.g. THF or CH_2Cl_2 at temperatures between- 78° C. and 40° C.
Iaa4
Oxidation, e.g. Dess Martin periodinane, inert solvent, e.g CH_2Cl_2
Iaa10
R_8—N=C=O
Base, e.g. Et_3N or pyridine
inert solvent, e.g. THF or CH_2Cl_2
Iaa5
Curtius rearrangement (see, e.g. Marchs Advanced Organic Chemistry, 6th edition, Wiley, New York, 2007) in the presence of NaN_3 or $N_3PO(OPh)_2$ (dppa) in the presence of tert-butyl alcohol
NHBOC
Iaa6
Deprotection, e.g TFA in CH2Cl2
NH_2
Iaa8
amide formation e.g. by activation to acyl halide and treatment with an amine $HNR_{10}R_{11}$ in the presence of a base such as pyryridine, in an inert solvent such as CH_2Cl_2,
Iaa7
H_2N—OR_6
in an inert solvent, e.g CH_2Cl_2 or MeOH, optionaly in the presence of a base
Iaa11
amide formation e.g. acyl halide $R_{12}COHal$ in the presence of a base such as pyryridine, in an inert solvent such as CH_2Cl_2,
Iaa9

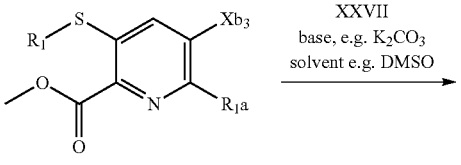
[0055] In Scheme 17, A, X, R_1, R_{1a}, R_2, X_1 and R_6 have the meanings described under formula I. In scheme 17, R_7, R_8, R_{10}, R_{11}, and R_{12} are independently hydrogen, C_1-C_4alkyl, C_1-C_4haloalkyl or phenyl whereby the phenyl group can be mono- or polysubstituted by substituents selected 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_4halo-alkylsulfinyl, C_1-C_4haloalkylsulfonyl and —C(O)C_1-C_4haloalkyl; or R_7, R_8, R_{10}, R_{11}, and R_{12} is C_1-C_4alkyl which is mono- or polysubstituted by the group Z_2; Z_2 is cyano, formyl, hydroxyl, C_3-C_6cycloalkyl, hydroxycarbonyl, aminocarbonyl, C_1-C_4haloalkoxy, C_1-C_4alkoxy, C_1-C_4haloalkylsulfanyl, C_1-C_4halo-alkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_1-C_4alkoxycarbonyl, C_1-C_4haloalkoxycarbonyl, C_1-C_4alkylcarbonyl, C_1-C_4haloalkylcarbonyl, di-(C_1-C_4)alkylaminocarbonyl (wherein the alkyl group of the di(C_1-C_4)alkylamino may be the same or may be different), C_1-C_4alkylaminocarbonyl, amino, C_1-C_4alkylcarbonylamino, di-(C_1-C_4)alkylcarbonylamino, C_1-C_4alkoxycarbonylamino, a group —C(R_5)=NOR_6, wherein R_5 and R_6 are independently hydrogen, C_1-C_4alkyl or C_1-C_4haloalkyl.

[0056] A further synthesis of compounds of formula I is shown in scheme 18:

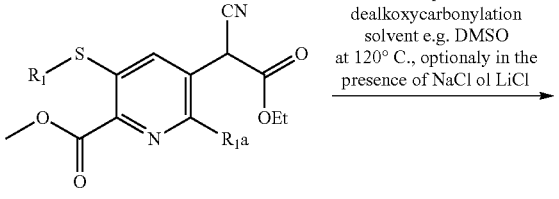
Scheme 18



Xb

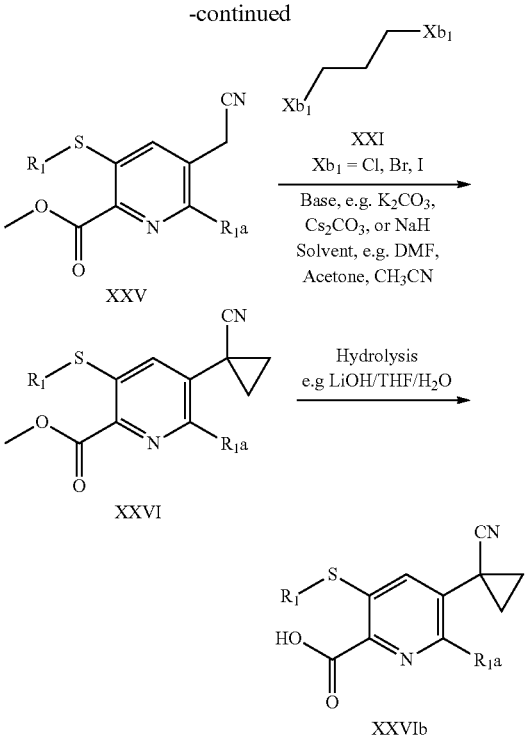


X



XXIV

-continued



[0057] In scheme 18, compounds of formula X can be prepared by esterification of compound Xb, for example, with strong acid as sulfuric acid in presence of methanol, or by other esterification methods known by those skilled in the art Compounds of formula X can be treated with compound of formula XXVII in presence of base for example K_2CO_3 and DMSO to give compound of formula XXIV by a mechanism known as SnAr substitution, well known by those skilled in the art, and exemplified for example in xxxxxx. Krapcho dealkoxycarbonylation of the resulting compound XXIV at temperatures between 70-180° C. gives the compound of formula XXV. Such Krapcho dealkoxycarbonylations are described for example in Krapcho, A. P.; Ciganek, E. *Org. React.* 2013, 81, 1. The resulting compound of formula XXV, can be treated with a compound XXI as described previously in scheme 16 to give compound of formula XXVI.

[0058] Compounds of formula XXVIb are obtained by ester hydrolysis of compounds of formula XXVI, by methods known to those skilled in the art. In compounds Xb, X, XXIV, XXV, XXI, XXVI, and XXVIb, the substituents R1, R1a, Xb3, and Xb1 are as previously defined.

[0059] For preparing all further compounds of the formula I functionalized according to the definitions of R_1, R_{1a}, R_2, Z_1, n and X_1, there are a large number of suitable known standard methods, for example alkylation, halogenation, acylation, amidation, oximation, oxidation and reduction, the choice of the preparation methods which are suitable depending on the properties (reactivity) of the substituents in the intermediates.

[0060] The reactions to give compounds of the formula I are advantageously carried out in aprotic inert organic solvents. Such solvents are hydrocarbons such as benzene, toluene, xylene or cyclohexane, chlorinated hydrocarbons such as dichloromethane, trichloromethane, tetrachlo-

romethane or chlorobenzene, ethers such as diethyl ether, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, tetrahydrofuran or dioxane, nitriles such as acetonitrile or propionitrile, amides such as N,N-dimethylformamide, diethylformamide or N-methylpyrrolidinone. The reaction temperatures are advantageously between −20° C. and +120° C. In general, the reactions are slightly exothermic and, as a rule, they can be carried out at ambient temperature. To shorten the reaction time, or else to start the reaction, the mixture may be heated briefly to the boiling point of the reaction mixture. The reaction times can also be shortened by adding a few drops of base as reaction catalyst. Suitable bases are, in particular, tertiary amines such as trimethylamine, triethylamine, quinuclidine, 1,4-diazabicyclo[2.2.2]octane, 1,5-diazabicyclo[4.3.0]non-5-ene or 1,5-diazabicyclo[5.4.0]undec-7-ene. However, inorganic bases such as hydrides, e.g. sodium hydride or calcium hydride, hydroxides, e.g. sodium hydroxide or potassium hydroxide, carbonates such as sodium carbonate and potassium carbonate, or hydrogen carbonates such as potassium hydrogen carbonate and sodium hydrogen carbonate may also be used as bases. The bases can be used as such or else with catalytic amounts of a phase-transfer catalyst, for example a crown ether, in particular 18-crown-6, or a tetraalkylammonium salt.

[0061] The compounds of the formula I can be isolated in the customary manner by concentrating and/or by evaporating the solvent and purified by recrystallization or trituration of the solid residue in solvents in which they are not readily soluble, such as ethers, aromatic hydrocarbons or chlorinated hydrocarbons.

[0062] 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.

[0063] 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.

[0064] 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.

[0065] 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.

[0066] 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.

[0067] 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.

[0068] 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.

[0069] 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 herein below, even when stereochemical details are not mentioned specifically in each case.

[0070] 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.

[0071] 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.

[0072] 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.

[0073] 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.

[0074] 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.

[0075] 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.

[0076] The compounds according to the following Tables A-1 and A-2 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.

[0077] Table A-1 provides 50 compounds A-1.001 to A-1.050 of formula Ia wherein R_{12a} is CH_2CH_3, A is N and R_{10a}, R_{13a}, X_2 are as defined in table B.

(1a)

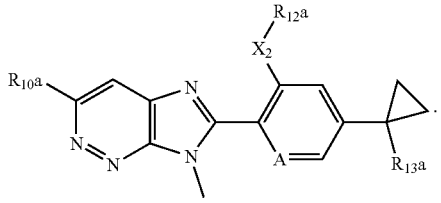


TABLE B

Substituent definitions of R_{10a}, R_{13a} and X_2:

Entry	R_{13a}	X_2	R_{10a}
1	CN	S	CF_3
2	CN	SO_2	CF_3
3	CO_2H	S	CF_3
4	CO_2H	SO_2	CF_3
5	CO_2CH_3	S	CF_3
6	CO_2CH_3	SO_2	CF_3
7	$CONHCH_3$	S	CF_3
8	$CONHCH_3$	SO_2	CF_3
9	$CONH_2$	S	CF_3
10	$CONH_2$	SO_2	CF_3
11	CN	S	CF_2CF_3
12	CN	SO_2	CF_2CF_3
13	CO_2H	S	CF_2CF_3
14	CO_2H	SO_2	CF_2CF_3
15	CO_2CH_3	S	CF_2CF_3
16	CO_2CH_3	SO_2	CF_2CF_3
17	$CONHCH_3$	S	CF_2CF_3
18	$CONHCH_3$	SO_2	CF_2CF_3
19	$CONH_2$	S	CF_2CF_3
20	$CONH_2$	SO_2	CF_2CF_3
21	CN	S	SCF_3
22	CN	SO_2	SCF_3
23	CO_2H	S	SCF_3
24	CO_2H	SO_2	SCF_3
25	CO_2CH_3	S	SCF_3
26	CO_2CH_3	SO_2	SCF_3
27	$CONHCH_3$	S	SCF_3
28	$CONHCH_3$	SO_2	SCF_3
29	$CONH_2$	S	SCF_3
30	$CONH_2$	SO_2	SCF_3
31	CN	S	$SOCF_3$
32	CN	SO_2	$SOCF_3$
33	CO_2H	S	$SOCF_3$

TABLE B-continued

Substituent definitions of R_{10a}, R_{13a} and X_2:

Entry	R_{13a}	X_2	R_{10a}
34	CO_2H	SO_2	$SOCF_3$
35	CO_2CH_3	S	$SOCF_3$
36	CO_2CH_3	SO_2	$SOCF_3$
37	$CONHCH_3$	S	$SOCF_3$
38	$CONHCH_3$	SO_2	$SOCF_3$
39	$CONH_2$	S	$SOCF_3$
40	$CONH_2$	SO_2	$SOCF_3$
41	CN	S	SO_2CF_3
42	CN	SO_2	SO_2CF_3
43	CO_2H	S	SO_2CF_3
44	CO_2H	SO_2	SO_2CF_3
45	CO_2CH_3	S	SO_2CF_3
46	CO_2CH_3	SO_2	SO_2CF_3
47	$CONHCH_3$	S	SO_2CF_3
48	$CONHCH_3$	SO_2	SO_2CF_3
49	$CONH_2$	S	SO_2CF_3
50	$CONH_2$	SO_2	SO_2CF_3

[0078] Table A-2 provides 50 compounds A-2.001 to A-2.050 of formula Ia wherein R_{12a} is CH_2CH_3, A is CH and R_{10a}, R_{13a}, X_2 are as defined in table B.

[0079] 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, a good activity corresponding to a destruction rate (mortality) of at least 50 to 60%.

[0080] 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.;

[0081] 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, Hoplo-campa* 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, Gra-pholita* 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 gossypi-ela, 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.;

[0082] 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.;

[0083] 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.*

[0084] 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.

[0085] 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.

[0086] 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.

[0087] 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.

[0088] 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.

[0089] 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).

[0090] 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.

[0091] 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*.

[0092] 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*.

[0093] 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.

[0094] 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.

[0095] 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. Cry1-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.

[0096] 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).

[0097] 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 Cry1 Fa2 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®.

[0098] 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. NK603xMON 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. NK603xMON 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.

[0099] 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).

[0100] 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.

[0101] 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.

[0102] Crops also include those that have enhanced resistance to nematodes, such as the soybean cyst nematode.

[0103] 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.

[0104] 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 defense (so-called "plant disease resistance genes", as described in WO 03/000906).

[0105] 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.

[0106] 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.

[0107] 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.

[0108] 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 03/034823, U.S. Pat. No. 5,631,072, WO 2005/64072, WO2006/128870, EP 1724392, WO 2005/113886 or WO 2007/090739.

[0109] 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.

[0110] 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 vittaticoillis	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, 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
	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

[0111] 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.

[0112] 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.).

[0113] 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*).

[0114] 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.

[0115] 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.

[0116] 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.

[0117] Examples of such parasites are:

[0118] Of the order Anoplurida: *Haematopinus* spp., *Linognathus* spp., *Pediculus* spp. and *Phtirus* spp., *Solenopotes* spp.

[0119] Of the order Mallophagida: *Trimenopon* spp., *Menopon* spp., *Trinoton* spp., *Bovicola* spp., *Werneckiella* spp., *Lepikentron* spp., *Damalina* spp., *Trichodectes* spp. and *Felicola* spp.

[0120] 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.

[0121] Of the order Siphonapterida, for example *Pulex* spp., *Ctenocephalides* spp., *Xenopsylla* spp., *Ceratophyllus* spp.

[0122] Of the order Heteropterida, for example *Cimex* spp., *Triatoma* spp., *Rhodnius* spp., *Panstrongylus* spp.

[0123] Of the order Blattarida, for example *Blatta orientalis, Periplaneta americana, Blattelagermanica* and *Supella* spp.

[0124] 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.

[0125] 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.

[0126] 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.

[0127] 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.*

[0128] 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.

[0129] 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.

[0130] 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.

[0131] 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.

[0132] 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.

[0133] 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 N.J. (1981).

[0134] 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.

[0135] 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, 10^{th} Edition, Southern Illinois University, 2010.

[0136] 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.

[0137] Whereas commercial products may preferably be formulated as concentrates, the end user will normally employ dilute formulations.

[0138] 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.

[0139] Preferred formulations can have the following compositions (weight %):

Emulsifiable Concentrates:

[0140] 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:

[0141] active ingredient: 0.1 to 10%, preferably 0.1 to 5%
solid carrier: 99.9 to 90%, preferably 99.9 to 99%

Suspension Concentrates:

[0142] 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:

[0143] 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:

[0144] active ingredient: 0.1 to 30%, preferably 0.1 to 15%
solid carrier: 99.5 to 70%, preferably 97 to 85%

[0145] 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%	—

[0146] 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%

[0147] 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%

[0148] 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%

[0149] 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%

[0150] 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%

[0151] 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

[0152]

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%

[0153] 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

[0154]

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%

[0155] 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

[0156] 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.

[0157] 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

[0158] "Mp" means melting point in ° C. Free radicals represent methyl groups. ^{1}H NMR and ^{19}F NMR Measurements: Measured on a Brucker 400 MHz or 300 MHz spectrometer, chemical shifts given in ppm relevant to a TMS standard. Spectra measured in solvents indicated.

LCMS Methods:

Method 1:

[0159] Spectra were recorded on a Mass Spectrometer from Waters (SQD, SQDII Single quadrupole mass spectrometer) equipped with an electrospray source (Polarity: positive and negative ions, Capillary: 3.00 kV, Cone range: 30 V, Extractor: 2.00 V, Source Temperature: 150° C., Desolvation Temperature: 350° C., Cone Gas Flow: 50 l/h, Desolvation Gas Flow: 650 l/h, Mass range: 100 to 900 Da) and an Acquity UPLC from Waters: Binary pump, heated column compartment, diode-array detector and ELSD detector. Column: Waters UPLC HSS T3, 1.8 μm, 30×2.1 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

Mass Spectroscopy Method MS

[0160] LC-20AD Mass Spectrometer from Shimadzu (Single quadrupole mass spectrometer)

Instrument Parameters:

[0161] Ionisation method: Electrospray

Polarity: positive and negative ions

Capillary (kV) 1.50

[0162] Cone (V) unknown

Extractor (V) 5.00

Source Temperature (° C.) 200

Desolvation Temperature (° C.) 250

Cone gas Flow (I/Hr) 90

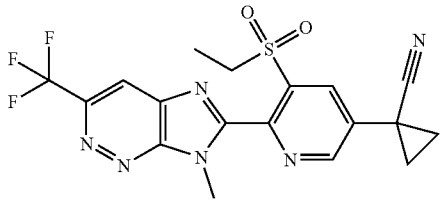
Desolvation gas Flow (I/Hr) 90

[0163] Mass range: 50 to 1000 Da

Example H1: Preparation of 1-[5-Ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]cyclopropanecarbonitrile

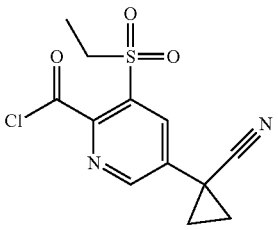
[0164]

(Example H1)



Step A: Preparation of 5-(1-cyanocyclopropyl)-3-ethylsulfonyl-pyridine-2-carbonyl chloride

[0165]

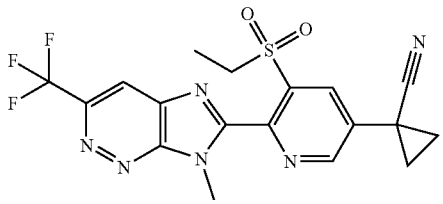


[0166] A sample of 5-(1-cyanocyclopropyl)-3-ethylsulfonyl-pyridine-2-carboxylic acid (0.21 g, 0.75 mmol, prepared as described in WO 2016/096584) dissolved in dichloromethane (5 mL) was treated with oxalyl chloride (0.38 g, 0.26 mL, 3.0 mmol) and 1-2 drops of DMF was added at ambient temperature. The resulting solution was stirred at rt. After this time the reaction mixture was evaporated to give the title compound as a yellow oil.

Step B: Preparation of 1-[5-Ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]cyclopropanecarbonitrile

[0167]

(Example H1)



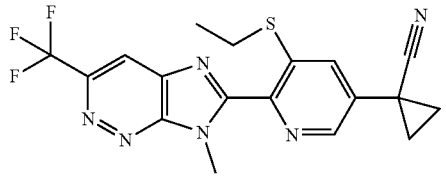
[0168] A mixture of 5-(1-cyanocyclopropyl)-3-ethylsulfonyl-pyridine-2-carbonyl chloride (0.22 g, 1.0 eq, 0.73 mmol) and N^3-methyl-6-(trifluoromethyl)pyridazine-3,4-diamine (0.14 g, 1.0 eq, 0.73 mmol, prepared as described in WO 2016/116338) in 1,4-dioxane (3 mL) were heated at reflux for 19 h. The reaction mixture was allowed to cool to ambient temperature, dissolved in dichloromethane and adsorbed onto TEFLON BULK SORBENTS. Purification over a silica gel cartridge (Rf200), eluting with Cyclohexane/EtOAc gave partially pure title product. Further purification could be achieved by purification over a silica GOLD cartridge (Rf200) eluting with dichloromethane: EtOAc. This gave the pure title compound as a white solid. LCMS (Method 1); RT 0.89 min., $[M+H]^+$ 437.

[0169] ^{1}H NMR (400 MHz, CHLOROFORM-d) 6 ppm; 1.39 (t, J=7.5 Hz, 4H); 1.66-1.77 (m, 2H); 2.05-2.12 (m, 2H); 3.82 (q, J=7.5 Hz, 2H); 4.08 (s, 3H); 8.20 (s, 1H); 8.28 (d, J=2.6 Hz, 1H); 9.08 (d, J=2.6 Hz, 1H).

Example H-2: Preparation of 1-[5-ethylsulfanyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]cyclopropanecarbonitrile

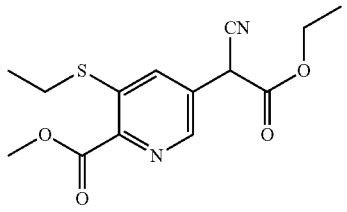
[0170]

Example H-2



Step A: Preparation of methyl 5-(1-cyano-2-ethoxy-2-oxo-ethyl)-3-ethylsulfanyl-pyridine-2-carboxylate

[0171]



[0172] Methyl-5-bromo-3-ethylsulfanyl-pyridine-2-carboxylate, prepared as described in patent WO 2017089190 (32 g, 115.88 mmol) was dissolved in dimethyl sulfoxide (350 mL). Then ethyl 2-cyanoacetate (18.5 mL, 173.82 mmol), potassium carbonate (40.442 g, 289.70 mmol) and tetrabutylammonium bromide (3.81 g, 11.588 mmol) were added successively at ambient temperature. The resulting suspension were stirred one night at 90° C. and then cooled to ambient temperature. Water and ethyl acetate were added, the resulting mixture was cooled down at 0° C. and hydrochloric acid (2M) was added slowly to acidify the reaction to pH 4-5. The aqueous layer was extracted with ethyl acetate three times. The combined organic layers were combined, dried over sodium sulfate, filtered and evaporated. The crude obtained was heated at 80° C. in ethanol (250 ml) for 1 hour. Then the solution obtained was cooled to 0° C., stirred 1 hour and filtered. The precipitate was

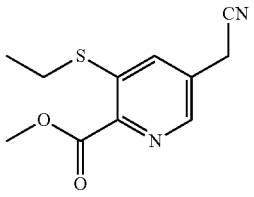
washed with cold ethanol to afford methyl 5-(1-cyano-2-ethoxy-2-oxo-ethyl)-3-ethylsulfanyl-pyridine-2-carboxylate.

[0173] LCMS (method 1): 309 (M+H)+; retention time: 0.85 min

[0174] 1H NMR (400 MHz, CHLOROFORM-d) δ ppm 1.33 (t, J=7.15 Hz, 3H) 1.45 (t, J=7.34 Hz, 3H) 2.98-3.05 (m, 2H) 4.04 (s, 3H) 4.28-4.35 (m, 2H) 4.84 (s, 1H) 7.83 (d, J=1.83 Hz, 1H) 8.49 (d, J=1.83 Hz, 1H)

Step B: Preparation of methyl 5-(cyanomethyl)-3-ethylsulfanyl-pyridine-2-carboxylate

[0175]



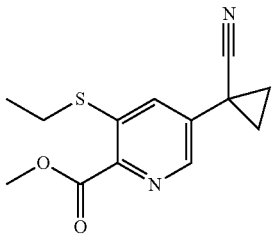
[0176] Methyl-5-(1-cyano-2-ethoxy-2-oxo-ethyl)-3-ethylsulfanyl-pyridine-2-(7.3 g, 24 mmol) was dissolved in dimethylsulfoxide (70 mL). To this was added NaCl (14 g, 240 mmol) and water (35 mL) successively at ambient temperature. The resulting suspension was stirred for 3 hours at 125° C. The reaction mixture was cooled to ambient temperature, diluted with 50 mL of water and 100 mL of ethyl acetate. The aqueous layer was extracted with ethyl acetate three times. The organic layers were combined, dried over sodium sulfate and concentrated. The crude product was purified over silica gel to afford methyl 5-(cyanomethyl)-3-ethylsulfanyl-pyridine-2-carboxylate.

[0177] LCMS (method 1): 237 (M+H)+; retention time: 0.72 min

[0178] 1H NMR (400 MHz, CHLOROFORM-d) δ ppm 1.45 (t, J=7.52 Hz, 3H) 3.01 (q, J=7.34 Hz, 2H) 3.87 (s, 2H) 4.04 (s, 3H) 7.72 (d, J=1.83 Hz, 1H) 8.35-8.41 (m, 1H)

Step C: Preparation of methyl 5-(1-cyanocyclopropyl)-3-ethylsulfanyl-pyridine-2-carboxylate

[0179]



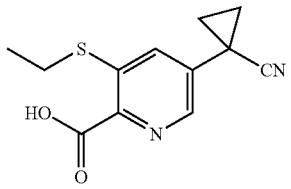
[0180] Methyl 5-(cyanomethyl)-3-ethylsulfanyl-pyridine-2-carboxylate (5 g, 21.16 mmol) was dissolved in acetonitrile (170 mL) and treated with cesium carbonate (20.7 g, 63.48 mmol) and 1,2-dibromoethane (2.19 mL, 25.39 mmol) at ambient temperature. The resulting mixture was stirred 3 h 30 hours at 80° C. and then at ambient temperature overnight. The reaction mixture was diluted with water and ethylacetate. The aqueous layer was extracted 3 times with ethylacetate. The combined organic layers were washed with brine, dried over sodium sulfate, filtered and evaporated to afford the crude product which was purified by chromatography to afford methyl 5-(1-cyanocyclopropyl)-3-ethylsulfanyl-pyridine-2-carboxylate.

[0181] LCMS (method 1): 263 (M+H)+; retention time: 0.85 min

[0182] 1H NMR (400 MHz, CHLOROFORM-d) δ ppm 1.45 (t, J=7.34 Hz, 3H) 1.54-1.62 (m, 2H) 1.89-1.96 (m, 2H) 3.01 (q, J=7.34 Hz, 2H) 4.02 (s, 3H) 7.74 (d, J=2.20 Hz, 1H) 8.17 (d, J=1.83 Hz, 1H)

Step D: Preparation of 5-(1-cyanocyclopropyl)-3-ethylsulfanyl-pyridine-2-carboxylic acid

[0183]



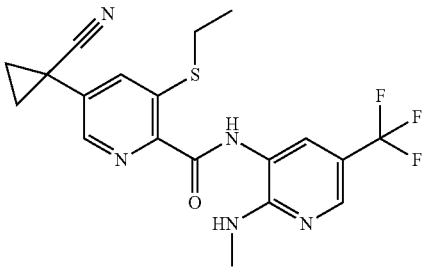
[0184] Methyl 5-(1-cyanocyclopropyl)-3-ethylsulfanyl-pyridine-2-carboxylate (2.63 g, 10.0 mmol) was dissolved in tetrahydrofuran (50 mL) and water (15 mL). Then lithium hydroxide (0.375 g, 15.0 mmol) was added and reaction was stirred one night at ambient temperature. After this time, a further portion of lithium hydroxide (0.160 g, 7.0 mmol) was added and the reaction was stirred for a further 2 hours at ambient temperature. The reaction mixture was evaporated and the residue was dissolved in dichloromethane. Aqueous HCl 1 M was added and the aqueous layer (pH 1) was extracted 3 times with dichloromethane. The combined organic layers were dried over sodium sulfate, filtered and evaporated to afford 5-(1-cyanocyclopropyl)-3-ethylsulfanyl-pyridine-2-carboxylic acid.

[0185] LCMS (method 1): 249 (M+H)+; retention time: 0.67 min

[0186] 1H NMR (400 MHz, DMSO-d) 6 ppm 1.26 (t, J=7.34 Hz, 3H) 1.70-1.78 (m, 2H) 1.83-1.92 (m, 2H) 3.03 (q, J=7.34 Hz, 2H) 7.63 (d, J=2.20 Hz, 1H) 8.37 (d, J=1.83 Hz, 1H) 13.16-13.40 (m, 1H)

Step E: Preparation of 5-(1-cyanocyclopropyl)-3-ethylsulfanyl-N-[2-(methylamino)-5-(trifluoromethyl)-3-pyridyl]pyridine-2-carboxamide

[0187]



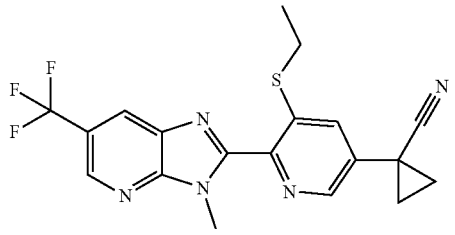
[0188] 5-(1-cyanocyclopropyl)-3-ethylsulfanyl-pyridine-2-carboxylic acid (2.4 g, 9.7 mmol) was dissolved in dichloromethane (100 mL). N,N-dimethylformamide (10.0 μL) was added follow by the addition of oxalyl dichloride (1 mL, 12 mmol) dropwise via syringe. The resulting yellowish suspension was stirred at ambient temperature for 1 hour then the solvent was evaporated. The resulting solid was dissolved in tetrahydrofuran (30 ml) and added to a solution of N-2-methyl-5-(trifluoromethyl)pyridine-2,3-diamine (1.8 g, 9.7 mmol) and N,N-diethylethanamine (3.3 mL, 23 mmol) in tetrahydrofuran (75 mL) at 0° C. The resulting mixture was stirred 30' at 0° C. then 2 hours at ambient temperature. The reaction mixture was treated with NH_4Cl sat sol and diluted with ethyl acetate. The aqueous layer was extracted 3 times with ethylacetate. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and evaporated to afford 5-(1-cyanocyclopropyl)-3-ethylsulfanyl-N-[2-(methylamino)-5-(trifluoromethyl)-3-pyridyl] pyridine-2-carboxamide which was used in the next step without further purification.

[0189] LCMS (method 1): 422 (M+H); retention time: 1.03 min

[0190] ^{1}H NMR (400 MHz, CHLOROFORM-d) δ ppm 1.48 (t, J=7.34 Hz, 3H) 1.58-1.63 (m, 2H) 1.93-1.99 (m, 2H) 3.01 (q, J=7.34 Hz, 2H) 3.09 (d, J=4.77 Hz, 3H) 5.02 (br d, J=4.03 Hz, 1H) 7.71 (d, J=2.20 Hz, 1H) 7.94 (d, J=2.20 Hz, 1H) 8.16 (d, J=2.20 Hz, 1H) 8.36 (d, J=0.73 Hz, 1H) 9.53-9.60 (m, 1H)

Step F: Preparation of 1-[5-ethylsulfanyl-6-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-3-pyridyl]cyclopropanecarbonitrile

[0191]



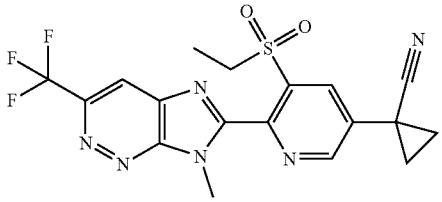
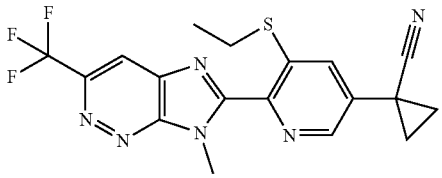
[0192] 5-(1-cyanocyclopropyl)-3-ethylsulfanyl-N-[2-(methylamino)-5-(trifluoromethyl)-3-pyridyl]pyridine-2-carboxamide (4.2 g, 10 mmol) was dissolved in acetic acid (100 mL) and the resulting solution was stirred 18 hours at 110° C. Acetic acid was removed by evaporation under vacuum and the crude was purified by chromatography over silica gel to afford 1-[5-ethylsulfanyl-6-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-3-pyridyl]cyclopropanecarbonitrile, Mp 142-144° C.

[0193] LCMS (method 1): 404 (M+H); retention time: 1.07 min

[0194] ^{1}H NMR (400 MHz, CHLOROFORM-d) δ ppm 1.40 (t, J=7.34 Hz, 3H) 1.59-1.64 (m, 2H) 1.90-1.97 (m, 2H) 3.03 (q, J=7.46 Hz, 2H) 4.07 (s, 3H) 7.77 (d, J=2.20 Hz, 1H) 8.35 (d, J=2.20 Hz, 1H) 8.42 (d, J=1.47 Hz, 1H) 8.73-8.78 (m, 1H).

[0195] The table H-1 shows the physical chemical and spectral data of compounds of formula I:

TABLE H-1

Example	IUPAC name	STRUCTURE	RT (min)	[M + H] (measured)	Method	Mp
H-1	1-[5-ethylsulfonyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]cyclopropanecarbonitrile		0.89	437	Standard	
H-2	1-[5-ethylsulfanyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-3-pyridyl]cyclopropanecarbonitrile		1.07	404	Standard	142-144

[0196] 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.

[0197] The following mixtures of the compounds of formula I with active ingredients are preferred (the abbreviation "TX" means "one compound selected from the group consisting of the compounds described in Tables A-1, A-2, H-1 and H-2 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 1 (696)+TX, pyrethrin 11 (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-1H-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, (7E,9Z)-dodeca-7,9-dien-1-yl acetate (IUPAC name) (283)+TX, (9Z,11E)-tetradeca-9,11-dien-1-yl acetate (IUPAC name) (780)+TX, (9Z,12E)-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 Bi (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, El 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, esprinomectin (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 1 (696)+TX, jasmolin 11 (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-2H-chromen-7-yl phosphorothioate (IUPAC name) (1074)+TX, O,O-diethyl O-6-methyl-2-propylpyrimidin-4-yl phosphorothioate (IUPAC name) (1075)+TX, O,O,O',O'-tetrapropyl dithiopyrophosphate (IUPAC name) (1424)+TX, oleic acid (IUPAC name) (593)+TX, omethoate (594)+TX, oxamyl (602)+TX, oxydemeton-methyl (609)+TX, oxydeprofos (1324)+TX, oxydisulfoton (1325)+TX, pp'-DDT (219)+TX, para-dichlorobenzene [CCN]+TX, parathion (615)+TX, parathion-methyl (616)+TX, penfluron (alternative name) [CCN]+TX, pentachlorophenol (623)+TX, pentachlorophenyl laurate (IUPAC name) (623)+TX, permethrin (626)+TX, petroleum oils (alternative name) (628)+TX, PH 60-38 (development code) (1328)+TX, phenkapton (1330)+TX, phenothrin (630)+TX, phenthoate (631)+TX, phorate (636)+TX, phosalone (637)+TX, phosfolan (1338)+TX, phosmet (638)+TX, phosnichlor (1339)+TX, phosphamidon (639)+TX, phosphine (IUPAC name) (640)+TX, phoxim (642)+TX, phoxim-methyl (1340)+TX, pirimetaphos (1344)+TX, pirimicarb (651)+TX, pirimiphos-ethyl (1345)+TX, pirimiphos-methyl (652)+TX, polychlorodicyclopentadiene isomers (IUPAC name) (1346)+TX, polychloroterpenes (traditional name) (1347)+TX, potassium arsenite [CCN]+TX, potassium thiocyanate [CCN]+TX, prallethrin (655)+TX, precocene I (alternative name) [CCN]+TX, precocene II (alternative name) [CCN]+TX, precocene III (alternative name) [CCN]+TX, primidophos (1349)+TX, profenofos (662)+TX, profluthrin [CCN]+TX, promacyl (1354)+TX, promecarb (1355)+TX, propaphos (1356)+TX, propetamphos (673)+TX, propoxur (678)+TX, prothidathion (1360)+TX, prothiofos (686)+TX, prothoate (1362)+TX, protrifenbute [CCN]+TX, pymetrozine (688)+TX, pyraclofos (689)+TX, pyrazophos (693)+TX, pyresmethrin (1367)+TX, pyrethrin I (696)+TX, pyrethrin II (696)+TX, pyrethrins (696)+TX, pyridaben (699)+TX, pyridalyl (700)+TX, pyridaphenthion (701)+TX, pyrimidifen (706)+TX, pyrimitate (1370)+TX, pyriproxyfen (708)+TX, quassia (alternative name) [CCN]+TX, quinalphos (711)+TX, quinalphos-methyl (1376)+TX, quinothion (1380)+TX, quintiofos (1381)+TX, R-1492 (development code) (1382)+TX, rafoxanide (alternative name) [CCN]+TX, resmethrin (719)+TX, rotenone (722)+TX, RU 15525 (development code) (723)+TX, RU 25475 (development code) (1386)+TX, ryania (alternative name) (1387)+TX, ryanodine (traditional name) (1387)+TX, sabadilla (alternative name) (725)+TX, schradan (1389)+TX, sebufos (alternative name)+TX, selamectin (alternative name) [CCN]+TX, SI-0009 (compound code)+TX, SI-0205 (compound code)+TX, SI-0404 (compound code)+TX, SI-0405 (compound code)+TX, silafluofen (728)+TX, SN 72129 (development code) (1397)+TX, sodium arsenite [CCN]+TX, sodium cyanide (444)+TX, sodium fluoride (IUPAC/Chemical Abstracts name) (1399)+TX, sodium hexafluorosilicate (1400)+TX, sodium pentachlorophenoxide (623)+TX, sodium selenate (IUPAC name) (1401)+TX, sodium thiocyanate [CCN]+TX, sophamide (1402)+TX, spinosad (737)+TX, spiromesifen (739)+TX, spirotetrmat (CCN)+TX, sulcofuron (746)+TX, sulcofuron-sodium (746)+TX, sulfluramid (750)+TX, sulfotep (753)+TX, sulfuryl fluoride (756)+TX, sulprofos (1408)+TX, tar oils (alternative name) (758)+TX, tau-fluvalinate (398)+TX, tazimcarb (1412)+TX, TDE (1414)+TX, tebufenozide (762)+TX, tebufenpyrad (763)+TX, tebupirimfos (764)+TX, teflubenzuron (768)+TX, tefluthrin (769)+TX, temephos (770)+TX, TEPP (1417)+TX, terallethrin (1418)+TX, terbam (alternative name)+TX, terbufos (773)+TX, tetrachloroethane [CCN]+TX, tetrachlorvinphos (777)+TX, tetramethrin (787)+TX, theta-cypermethrin (204)+TX, thiacloprid (791)+TX, thiafenox (alternative name)+TX, thiamethoxam (792)+TX, thicrofos (1428)+TX, thiocarboxime (1431)+TX, thiocyclam (798)+TX, thiocyclam hydrogen oxalate (798)+TX, thiodicarb (799)+TX, thiofanox (800)+TX, thiometon (801)+TX, thionazin (1434)+TX, thiosultap (803)+TX, thiosultap-sodium (803)+TX, thuringiensin (alternative name) [CCN]+TX, tolfenpyrad (809)+TX, tralomethrin (812)+TX, transfluthrin (813)+TX, transpermethrin (1440)+TX, triamiphos (1441)+TX, triazamate (818)+TX, triazophos (820)+TX, triazuron (alternative name)+TX, trichlorfon (824)+TX, trichlormetaphos-3 (alternative name) [CCN]+TX, trichloronat (1452)+TX, trifenofos (1455)+TX, triflumuron (835)+TX, trimethacarb (840)+TX, triprene (1459)+TX, vamidothion (847)+TX, vaniliprole [CCN]+TX, veratridine (alternative name) (725)+TX, veratrine (alternative name) (725)+TX, XMC (853)+TX, xylylcarb (854)+TX, YI-5302 (compound code)+TX, zeta-cypermethrin (205)+TX, zetamethrin (alternative name)+TX, zinc phosphide (640)+TX, zolaprofos (1469) and ZXI 8901 (development code) (858)+TX, cyantraniliprole [736994-63-19+TX, chlorantraniliprole [500008-45-7]+TX, cyenopyrafen [560121-52-0]+TX, cyflumetofen [400882-07-7]+TX, pyrifluquinazon [337458-27-2]+TX, spinetoram [187166-40-1+187166-15-0]+TX, spirotetramat [203313-25-1]+TX, sulfoxaflor [946578-00-3]+TX, flufiprole [704886-18-0]+TX, meperfluthrin [915288-13-0]+TX, tetramethylfluthrin [84937-88-2]+TX, triflumezopyrim (disclosed in WO 2012/092115)+TX, fluxametamide (WO 2007/026965)+TX, epsilon-metofluthrin [240494-71-7]+TX, epsilon-momfluorothrin [1065124-65-3]+TX, fluazaindolizine [1254304-22-7]+TX, chloroprallethrin [399572-87-3]+TX, fluxametamide [928783-29-3]+TX, cyhalodiamide [1262605-53-7]+TX, tioxazafen [330459-31-9]+TX, broflanilide [1207727-04-5]+TX, flufiprole [704886-18-0]+TX, cyclaniliprole [1031756-98-5]+TX, tetraniliprole [1229654-66-3]+TX, guadipyr (described in WO2010/060231)+TX, cycloxaprid (described in WO2005/077934)+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,

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, acibenzo-lar-S-methyl [135158-54-2]+TX, anilazine [101-05-3]+TX, benthiavalicarb [413615-35-7]+TX, blasticidin-S [2079-00-7]+TX, chinomethionat [2439-01-2]+TX, chloroneb [2675-77-6]+TX, chlorothalonil [1897-45-6]+TX, cyflufenamid [180409-60-3]+TX, cymoxanil [57966-95-7]+TX, dichlone [117-80-6]+TX, diclocymet [139920-32-4]+TX, diclomezine [62865-36-5]+TX, dicloran [99-30-9]+TX, diethofencarb [87130-20-9]+TX, dimethomorph [110488-70-5]+TX, SYP-LI90 (Flumorph) [211867-47-9]+TX, dithianon [3347-22-6]+TX, ethaboxam [162650-77-3]+TX, etridiazole [2593-15-9]+TX, famoxadone [131807-57-3]+TX, fenamidone [161326-34-7]+TX, fenoxanil [115852-48-7]+TX, fentin [668-34-8]+TX, ferimzone [89269-64-7]+TX, fluazinam [79622-59-6]+TX, fluopicolide [239110-15-7]+TX, flusulfamide [106917-52-6]+TX, fenhexamid [126833-17-8]+TX, fosetyl-aluminium [39148-24-8]+TX, hymexazol [10004-44-1]+TX, iprovalicarb [140923-17-7]+TX, IKF-916 (Cyazofamid) [120116-88-3]+TX, kasugamycin [6980-18-3]+TX, methasulfocarb [66952-49-6]+TX, metrafenone [220899-03-6]+TX, pencycuron [66063-05-6]+TX, phthalide [27355-22-2]+TX, polyoxins [11113-80-7]+TX, probenazole [27605-76-1]+TX, propamocarb [25606-41-1]+TX, proquinazid [189278-12-4]+TX, pyroquilon [57369-32-1]+TX, 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, [(3S,4R,4aR,6S,6aS,12R,12aS,12bS)-3-[(cyclopropylcarbonyl)oxy]-1,3,4,4a,5,6,6a,12,12a,12b-decahydro-6,12-dihyd roxy-4,6a, 12b-trimethyl-11-oxo-9-(3-pyridinyl)-2H,11 Hnaphtho[2,1-b]pyrano[3,4-e]pyran-4-yl]methyl-cyclopropanecarboxylate [915972-17-7]+TX, 1,3,5-trimethyl-N-(2-methyl-1-oxopropyl)-N-[3-(2-methylpropyl)-4-[2,2,2-trifluoro-1-methoxy-1-(trifluoromethyl) ethyl]phenyl]-1H-pyrazole-4-carboxamide [926914-55-8]+TX; lancotrione [1486617-21-3]+TX, florpyrauxifen [943832-81-3]]+TX, ipfentrifluconazole[1417782-08-1]+TX, mefentrifluconazole [1417782-03-6]+TX, quinofumelin [861647-84-9]+TX, chloroprallethrin [399572-87-3]+TX, cyhalodiamide [1262605-53-7]]+TX, fluazaindolizine [1254304-22-7]+TX, fluxametamide [928783-29-3]+TX, epsilon-metofluthrin [240494-71-7]+TX, epsilon-momfluorothrin [1065124-65-3]+TX, pydiflumetofen [1228284-64-7]+TX, kappa-bifenthrin [439680-76-9]+TX, broflanilide [1207727-04-5]+TX, dicloromezotiaz [1263629-39-5]+TX, dipymetitrone [16114-35-5]+TX, pyraziflumid [942515-63-1]+TX, kappa-tefluthrin [391634-71-2]+TX, fenpicoxamid [517875-34-2]+TX; fluindapyr [1383809-87-7]+TX; alpha-bromadiolone [28772-56-7]+TX; flupyrimin [1689566-03-7]+TX; benzpyrimoxan [1449021-97-9]+TX; acynonapyr [1332838-17-1]+TX; inpyrfluxam [1352994-67-2]+TX, isoflucypram [1255734-28-1]+TX; rescalure [64309-03-1]+TX; aminopyrifen [1531626-08-0]+TX; tyclopyrazoflor [1477919-27-9]+TX; and spiropidion [1229023-00-0]+TX; and

microbials including: *Acinetobacter lwoffii*+TX, *Acremonium alternatum*+TX+TX, *Acremonium cephalosporium*+TX+TX, *Acremonium diospyri*+TX, *Acremonium obclavatum*+TX, *Adoxophyes orana granulovirus* (AdoxGV) (Capex®)+TX, *Agrobacterium radiobacter* strain K84 (Galltrol-A®)+TX, *Alternaria alternate*+TX, *Alternaria cassia*+TX, *Alternaria destruens* (Smolder®)+TX, *Ampelomyces quisqualis* (AQ10®)+TX, *Aspergillus flavus* AF36 (AF36®)+TX, *Aspergillus flavus* NRRL 21882 (Aflaguard®)+TX, *Aspergillus* spp.+TX, *Aureobasidium pullulans*+TX, *Azospirillum*+TX, (MicroAZ®+TX, TAZO B®)+TX, *Azotobacter*+TX, *Azotobacter chroococcum*

(Azotomeal®)+TX, *Azotobacter* cysts (Bionatural Blooming Blossoms®)+TX, *Bacillus amyloliquefaciens*+TX, *Bacillus cereus*+TX, *Bacillus chitinosporus* strain CM-1+TX, *Bacillus chitinosporus* strain AQ746+TX, *Bacillus licheniformis* strain HB-2 (Biostart™ Rhizoboost®)+TX, *Bacillus licheniformis* strain 3086 (EcoGuard®+TX, Green Releaf®)+TX, *Bacillus circulans*+TX, *Bacillus firmus* (BioSafe®+TX, BioNem-WP®+TX, VOTiVO®)+TX, *Bacillus firmus* strain 1-1582+TX, *Bacillus macerans*+TX, *Bacillus marismortui*+TX, *Bacillus megaterium*+TX, *Bacillus mycoides* strain AQ726+TX, *Bacillus papillae* (Milky Spore Powder®)+TX, *Bacillus pumilus* spp.+TX, *Bacillus pumilus* strain GB34 (Yield Shield®)+TX, *Bacillus pumilus* strain AQ717+TX, *Bacillus pumilus* strain QST 2808 (Sonata®+TX, Ballad Plus®)+TX, *Bacillus spahericus* (VectoLex®)+TX, *Bacillus* spp.+TX, *Bacillus* spp. strain AQ175+TX, *Bacillus* spp. strain AQ177+TX, *Bacillus* spp. strain AQ178+TX, *Bacillus subtilis* strain QST 713 (CEASE®+TX, Serenade®+TX, Rhapsody®)+TX, *Bacillus subtilis* strain QST 714 (JAZZ®)+TX, *Bacillus subtilis* strain AQ153+TX, *Bacillus subtilis* strain AQ743+TX, *Bacillus subtilis* strain QST3002+TX, *Bacillus subtilis* strain QST3004+TX, *Bacillus subtilis* var. *amyloliquefaciens* strain FZB24 (Taegro®+TX, Rhizopro®)+TX, *Bacillus thuringiensis* Cry 2Ae+TX, *Bacillus thuringiensis* Cry1Ab+TX, *Bacillus thuringiensis aizawai* GC 91 (Agree®)+TX, *Bacillus thuringiensis israelensis* (BMP123®+TX, Aquabac®+TX, VectoBac®)+TX, *Bacillus thuringiensis kurstaki* (Javelin®+TX, Deliver®+TX, CryMax®+TX, Bonide®+TX, Scutella WP®+TX, Turilav WP®+TX, Astuto®+TX, Dipel WP®+TX, Biobit®+TX, Foray®)+TX, *Bacillus thuringiensis kurstaki* BMP 123 (Baritone®)+TX, *Bacillus thuringiensis kurstaki* HD-1 (Bioprotec-CAF/3P®)+TX, *Bacillus thuringiensis* strain BD#32+TX, *Bacillus thuringiensis* strain AQ52+TX, *Bacillus thuringiensis* var. *aizawai* (XenTari®+TX, DiPel®)+TX, bacteria spp. (GROWMEND®+TX, GROWSWEET®+TX, Shootup®)+TX, bacteriophage of *Clavipacter michiganensis* (AgriPhage®)+TX, Bakflor®+TX, *Beauveria bassiana* (Beaugenic®+TX, Brocaril WP®)+TX, *Beauveria bassiana* GHA (Mycotrol ES®+TX, Mycotrol O®+TX, BotaniGuard®)+TX, *Beauveria brongniartii* (Engerlingspilz®+TX, Schweizer Beauveria®+TX, Melocont®)+TX, *Beauveria* spp.+TX, *Botrytis cineria*+TX, *Bradyrhizobium japonicum* (TerraMax®)+TX, *Brevibacillus brevis*+TX, *Bacillus thuringiensis tenebrionis* (Novodor®)+TX, BtBooster+TX, *Burkholderia cepacia* (Deny®+TX, Intercept®+TX, Blue Circle®)+TX, *Burkholderia* gladii+TX, *Burkholderia gladioli*+TX, *Burkholderia* spp.+TX, Canadian thistle fungus (CBH Canadian Bioherbicide®)+TX, *Candida butyri*+TX, *Candida famata*+TX, *Candida fructus*+TX, *Candida glabrata*+TX, *Candida guilliermondii*+TX, *Candida melibiosica*+TX, *Candida oleophila* strain O+TX, *Candida parapsilosis*+TX, *Candida pelliculosa*+TX, *Candida pulcherrima*+TX, *Candida reukaufii*+TX, *Candida saitoana* (Bio-Coat®+TX, Biocure®)+TX, *Candida sake*+TX, *Candida* spp.+TX, *Candida tenius*+TX, *Cedecea dravisae*+TX, *Cellulomonas flavigena*+TX, *Chaetomium cochliodes* (Nova-Cide®)+TX, *Chaetomium globosum* (Nova-Cide®)+TX, *Chromobacterium subtsugae* strain PRAA4-1T (Grandevo®)+TX, *Cladosporium cladosporioides*+TX, *Cladosporium oxysporum*+TX, *Cladosporium chlorocephalum*+TX, *Cladosporium* spp.+TX, *Cladosporium tenuissimum*+TX, *Clonostachys rosea* (EndoFine®)+TX, *Colletotrichum acutatum*+TX, *Coniothyrium minitans* (Cotans WG®)+TX, *Coniothyrium* spp.+TX, *Cryptococcus albidus* (YIELDPLUS®)+TX, *Cryptococcus humicola*+TX, *Cryptococcus infirmo-miniatus*+TX, *Cryptococcus laurentii*+TX, *Cryptophlebia leucotreta* granulovirus (Cryptex®)+TX, *Cupriavidus campinensis*+TX, *Cydia pomonella* granulovirus (CYD-X®)+TX, *Cydia pomonella* granulovirus (Madex®+TX, Madex Plus®+TX, Madex Max/Carpovirusine®)+TX, *Cylindrobasidium laeve* (Stumpout®)+TX, Cylindrocladium+TX, *Debaryomyces hansenii*+TX, *Drechslera hawaiinensis*+TX, *Enterobacter cloacae*+TX, Enterobacteriaceae+TX, *Entomophtora virulenta* (Vektor®)+TX, *Epicoccum nigrum*+TX, *Epicoccum purpurascens*+TX, *Epicoccum* spp.+TX, *Filobasidium floriforme*+TX, *Fusarium acuminatum*+TX, *Fusarium chlamydosporum*+TX, *Fusarium oxysporum* (Fusaclean®/Biofox C®)+TX, *Fusarium proliferatum*+TX, *Fusarium* spp.+TX, *Galactomyces geotrichum*+TX, *Gliocladium catenulatum* (Primastop®+TX, Prestop®)+TX, *Gliocladium roseum*+TX, *Gliocladium* spp. (SoilGard®)+TX, *Gliocladium virens* (Soilgard®)+TX, Granulovirus (Granupom®)+TX, *Halobacillus halophilus*+TX, *Halobacillus litoralis*+TX, *Halobacillus trueperi*+TX, *Halomonas* spp.+TX, *Halomonas subglaciescola*+TX, *Halovibrio variabilis*+TX, *Hanseniaspora uvarum*+TX, *Helicoverpa armigera* nucleopolyhedrovirus (Helicovex®)+TX, *Helicoverpa zea* nuclear polyhedrosis virus (Gemstar®)+TX, Isoflavone-formononetin (Myconate®)+TX, *Kloeckera apiculata*+TX, *Kloeckera* spp.+TX, *Lagenidium giganteum* (Laginex®)+TX, *Lecanicillium longisporum* (Vertiblast®)+TX, *Lecanicillium muscarium* (Vertikil®)+TX, *Lymantria Dispar* nucleopolyhedrosis virus (Disparvirus®)+TX, *Marinococcus halophilus*+TX, *Meira geulakonigii*+TX, *Metarhizium anisopliae* (Met52®)+TX, *Metarhizium anisopliae* (Destruxin WP®)+TX, *Metschnikowia fruticola* (Shemer®)+TX, *Metschnikowia pulcherrima*+TX, *Microdochium dimerum* (Antibot®)+TX, *Micromonospora coerulea*+TX, *Microsphaeropsis ochracea*+TX, *Muscodor albus* 620 (Muscudor®)+TX, *Muscodor roseus* strain A3-5+TX, *Mycorrhizae* spp. (AMykor®+TX, Root Maximizer®)+TX, *Myrothecium verrucaria* strain AARC-0255 (DiTera®)+TX, BROS PLUS®+TX, *Ophiostoma piliferum* strain D97 (Sylvanex®)+TX, *Paecilomyces farinosus*+TX, *Paecilomyces fumosoroseus* (PFR-97®+TX, PreFeRal®)+TX, *Paecilomyces linacinus* (Biostat WP®)+TX, *Paecilomyces lilacinus* strain 251 (MeloCon WG®)+TX, *Paenibacillus polymyxa*+TX, *Pantoea agglomerans* (BlightBan C9-1®)+TX, *Pantoea* spp.+TX, *Pasteuria* spp. (Econem®)+TX, *Pasteuria nishizawae*+TX, *Penicillium aurantiogriseum*+TX, *Penicillium billai* (Jumpstart®+TX, TagTeam®)+TX, *Penicillium brevicompactum*+TX, *Penicillium frequentans*+TX, *Penicillium griseofulvum*+TX, *Penicillium purpurogenum*+TX, *Penicillium* spp.+TX, *Penicillium viridicatum*+TX, *Phlebiopsis gigantean* (Rotstop®)+TX, phosphate solubilizing bacteria (Phosphomeal®)+TX, *Phytophthora cryptogea*+TX, *Phytophthora palmivora* (Devine®)+TX, *Pichia anomala*+TX, *Pichia guilermondii*+TX, *Pichia membranaefaciens*+TX, *Pichia onychis*+TX, *Pichia stipites*+TX, *Pseudomonas aeruginosa*+TX, *Pseudomonas aureofasciens* (Spot-Less Biofungicide®)+TX, *Pseudomonas cepacia*+TX, *Pseudomonas chlororaphis* (AtEze®)+TX, *Pseudomonas corrugate*+TX, *Pseudomonas fluorescens* strain A506 (BlightBan A506®)+TX, *Pseudomonas putida*+TX, *Pseudomonas reactans*+TX, *Pseudomonas* spp.+TX, *Pseudomonas syringae* (Bio-Save®)+TX, *Pseudomonas*

viridiflava+TX, *Pseudomons fluorescens* (Zequanox®)+TX, *Pseudozyma flocculosa* strain PF-A22 UL (Sporodex L®)+TX, *Puccinia canaliculata*+TX, *Puccinia thlaspeos* (Wood Warrior®)+TX, *Pythium paroecandrum*+TX, *Pythium oligandrum* (Polygandron®+TX, Polyversum®)+TX, *Pythium periplocum*+TX, *Rhanella aquatilis*+TX, *Rhanella* spp.+TX, *Rhizobia* (Dormal®+TX, Vault®)+TX, *Rhizoctonia*+TX, *Rhodococcus globerulus* strain AQ719+TX, *Rhodosporidium diobovatum*+TX, *Rhodosporidium toruloides*+TX, *Rhodotorula* spp.+TX, *Rhodotorula glutinis*+TX, *Rhodotorula graminis*+TX, *Rhodotorula mucilagnosa*+TX, *Rhodotorula rubra*+TX, *Saccharomyces cerevisiae*+TX, *Salinococcus roseus*+TX, *Sclerotinia minor*+TX, *Sclerotinia minor* (SARRITOR®)+TX, *Scytalidium* spp.+TX, *Scytalidium uredinicola*+TX, *Spodoptera exigua* nuclear polyhedrosis virus (Spod-X®+TX, Spexit®)+TX, *Serratia marcescens*+TX, *Serratia plymuthica*+TX, *Serratia* spp.+TX, *Sordaria fimicola*+TX, *Spodoptera littoralis* nucleopolyhedrovirus (Littovir®)+TX, *Sporobolomyces roseus*+TX, *Stenotrophomonas maltophilia*+TX, *Streptomyces ahygroscopicus*+TX, *Streptomyces albaduncus*+TX, *Streptomyces exfoliates*+TX, *Streptomyces galbus*+TX, *Streptomyces griseoplanus*+TX, *Streptomyces griseoviridis* (Mycostop®)+TX, *Streptomyces lydicus* (Actinovate®)+TX, *Streptomyces lydicus* WYEC-108 (ActinoGrow®)+TX, *Streptomyces violaceus*+TX, *Tilletiopsis minor*+TX, *Tilletiopsis* spp.+TX, *Trichoderma asperellum* (T34 Biocontrol®)+TX, *Trichoderma gamsii* (Tenet®)+TX, *Trichoderma atroviride* (Plantmate®)+TX, *Trichoderma hamatum* TH 382+TX, *Trichoderma harzianum* rifai (Mycostar®)+TX, *Trichoderma harzianum* T-22 (Trianum-P®+TX, PlantShield HC®+TX, RootShield®+TX, Trianum-G®)+TX, *Trichoderma harzianum* T-39 (Trichodex®)+TX, *Trichoderma inhamatum*+TX, *Trichoderma koningii*+TX, *Trichoderma* spp. LC 52 (Sentinel®)+TX, *Trichoderma lignorum*+TX, *Trichoderma longibrachiatum*+TX, *Trichoderma polysporum* (Binab T®)+TX, *Trichoderma taxi*+TX, *Trichoderma virens*+TX, *Trichoderma virens* (formerly *Gliocladium virens* GL-21) (SoilGuard®)+TX, *Trichoderma viride*+TX, *Trichoderma viride* strain ICC 080 (Remedier®)+TX, *Trichosporon pullulans*+TX, *Trichosporon* spp.+TX, *Trichothecium* spp.+TX, *Trichothecium roseum*+TX, *Typhula phacorrhiza* strain 94670+TX, *Typhula phacorrhiza* strain 94671+TX, *Ulocladium atrum*+TX, *Ulocladium oudemansii* (Botry-Zen®)+TX, *Ustilago maydis*+TX, various bacteria and supplementary micronutrients (Natural II®)+TX, various fungi (Millennium Microbes®)+TX, *Verticillium chlamydosporium*+TX, *Verticillium lecanii* (Mycotal®+TX, Vertalec®)+TX, Vip3Aa20 (VIPtera®)+TX, *Virgibaclillus marismortui*+TX, *Xanthomonas campestris* pv. *Poae* (Camperico®)+TX, *Xenorhabdus bovienii*+TX, *Xenorhabdus nematophilus*; and

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

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

Macrobials including: *Aphelinus abdominalis*+TX, *Aphidius ervi* (*Aphelinus*-System®)+TX, *Acerophagus papaya*+TX, *Adalia bipunctata* (*Adalia*-System®)+TX, *Adalia bipunctata* (Adaline®)+TX, *Adalia bipunctata* (Aphidalia®)+TX, *Ageniaspis citricola*+TX, *Ageniaspis fuscicollis*+TX, *Amblyseius andersoni* (Anderline®+TX, *Andersoni*-System®)+TX, *Amblyseius californicus* (Amblyline®+TX, Spical®)+TX, *Amblyseius cucumeris* (Thripex®+TX, Bugline Cucumeris®)+TX, *Amblyseius fallacis* (Fallacis®)+TX, *Amblyseius swirskii* (Bugline Swirskii®+TX, *Swirskii*-Mite®)+TX, *Amblyseius womersleyi* (Womer-Mite®)+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* (Dac-Digline®+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* (Harmo-Beetle®)+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 I®)+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, Sciarid®+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+potassium-thiocyanate (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.

[0198] 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.

[0199] Most of the active ingredients described above are referred to hereinabove by a so-called "common name", the relevant "ISO common name" or another "common name" being used in individual cases. If the designation is not a "common name", the nature of the designation used instead is given in round brackets for the particular compound; in that case, the IUPAC name, the IUPAC/Chemical Abstracts name, a "chemical name", a "traditional name", a "compound name" or a "development code" is used or, if neither one of those designations nor a "common name" is used, an "alternative name" is employed. "CAS Reg. No" means the Chemical Abstracts Registry Number.

[0200] The active ingredient mixture of the compounds of formula I selected from Tables A-1, A-2, H-1 and H-2 with active ingredients described above comprises a compound selected from Tables A-1, A-2, H-1 and H-2 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.

[0201] 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.

[0202] The mixtures comprising a compound of formula I selected from Tables A-1, A-2, H-1 and H-2 and one or more active ingredients as described above can be applied, for example, in a single "ready-mix" form, in a combined spray mixture composed from separate formulations of the single active ingredient components, such as a "tank-mix", and in a combined use of the single active ingredients when applied in a sequential manner, i.e. one after the other with a reasonably short period, such as a few hours or days. The order of applying the compounds of formula I selected from Tables A-1, A-2, H-1 and H-2 and the active ingredients as described above is not essential for working the present invention.

[0203] 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.

[0204] 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.

[0205] 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.

[0206] 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.

[0207] 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.

[0208] 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.

[0209] 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).

[0210] 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: *Bemisia tabaci* (Cotton White Fly): Feeding/Contact Activity

[0211] 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.

[0212] The following compound resulted in at least 80% mortality at an application rate of 200 ppm: H-1.

Example B2: *Diabrotica Balteata* (Corn Root Worm)

[0213] Maize sprouts placed onto an agar layer in 24-well microtiter plates were treated with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions by spraying. After drying, the plates were infested with L2 larvae (6 to 10 per well). The samples were assessed for mortality and growth inhibition in comparison to untreated samples 4 days after infestation.

[0214] The following compound 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:

H-1 and H-2

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

[0215] Soybean leaves on agar in 24-well microtiter plates were sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying the leaves were infested with N2 nymphs. The samples were assessed for mortality and growth inhibition in comparison to untreated samples 5 days after infestation.

[0216] 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:

H-1 and H-2.

Example B4: *Frankliniella occidentalis* (Western Flower *Thrips*)

[0217] Feeding/contact activity Sunflower leaf discs were placed on agar in 24-well microtiter plates and sprayed with aqueous test solutions prepared from 10'000 DMSO stock solutions. After drying the leaf discs were infested with a *Frankliniella* population of mixed ages. The samples were assessed for mortality 7 days after infestation.

[0218] The following compounds resulted in at least 80% mortality at an application rate of 200 ppm:

H-1 and H-2.

Example B5: *Myzus persicae* (Green Peach Aphid):Feeding/Contact Activity

[0219] Sunflower leaf discs were placed onto agar in a 24-well microtiter plate and sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying, the leaf discs were infested with an aphid population of mixed ages. The samples were assessed for mortality 6 days after infestation.

[0220] The following compound resulted in at least 80% mortality at an application rate of 200 ppm:

H-1.

Example B6: *Myzus persicae* (Green Peach Aphid). Systemic Activity

[0221] Roots of pea seedlings infested with an aphid population of mixed ages were placed directly into aqueous test solutions prepared from 10'000 DMSO stock solutions. The samples were assessed for mortality 6 days after placing seedlings into test solutions.

[0222] The following compound resulted in at least 80% mortality at a test rate of 24 ppm:

H-1.

Example B7: *Myzus persicae* (Green Peach Aphid). Intrinsic Activity

[0223] Test compounds prepared from 10'000 ppm DMSO stock solutions were applied by pipette into 24-well microtiter plates and mixed with sucrose solution. The plates were closed with a stretched Parafilm. A plastic stencil with 24 holes was placed onto the plate and infested pea seedlings were placed directly on the Parafilm. The infested plate was closed with a gel blotting paper and another plastic stencil and then turned upside down. The samples were assessed for mortality 5 days after infestation.

Example B8: *Plutella xylostella* (Diamond Back Moth)

[0224] 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.

[0225] 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:

H-1 and H-2.

Example B9: *Spodoptera littoralis* (Egyptian Cotton Leaf Worm)

[0226] 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 onto the agar and the multi well plate was closed by another plate which contained also agar. After 7 days the compound was absorbed by the roots and the lettuce grew into the lid plate. The lettuce leaves were then cut off into the lid plate. *Spodoptera* eggs were pipetted through a plastic stencil onto a humid gel blotting paper and the lid plate was closed with it. The samples were assessed for mortality, anti-feedant effect and growth inhibition in comparison to untreated samples 6 days after infestation.

[0227] The following compound gave an effect of at least 80% in at least one of the three categories (mortality, anti-feeding, or growth inhibition) at a test rate of 12.5 ppm:

H-1.

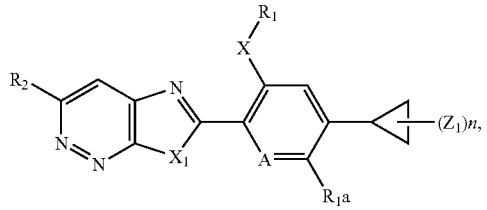
Example B10: *Tetranychus urticae* (Two-Spotted Spider Mite): Feeding/Contact Activity

[0228] 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.

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

[0229] 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.

1. A compound of formula I



(I)

wherein

A is CH or N;

X is S, SO or SO_2;

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

R_1 is 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_2 is 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_2 is C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, O(C_1-C_4haloalkyl), —C(O)C_1-C_4haloalkyl; or

R_2 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;

X_1 is O, S or NR_3, wherein R_3 is hydrogen, C_1-C_4alkyl, C_2-C_6alkenyl, C_2-C_6alkynyl, C_1-C_4alkoxy-C_1-C_4alkyl or C_3-C_6cycloalkyl;

Z_1 is cyano, formyl, hydroxyl, C_3-C_6cycloalkyl, hydroxycarbonyl, aminocarbonyl, C_1-C_4haloalkoxy, C_1-C_4alkoxy, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_1-C_4alkoxycarbonyl, C_1-C_4haloalkoxycarbonyl, C_1-C_4alkylcarbonyl, C_1-C_4haloalkylcarbonyl, di-(C_1-C_4)alkylaminocarbonyl, C_1-C_4alkylaminocarbonyl, amino, C_1-C_4alkylcarbonylamino, di-(C_1-C_4)alkylcarbonylamino, C_1-C_4alkoxycarbonylamino or a group —C(R_5)=NOR_6, wherein R_5 and R_6 are independently hydrogen, C_1-C_4alkyl, C_1-C_4haloalkyl; or

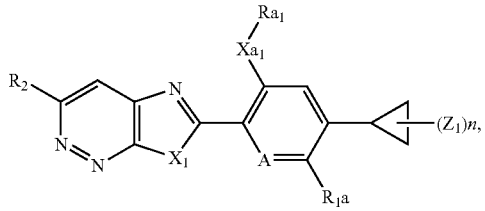
Z_1 is phenyl, said phenyl can be mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4haloalkoxy, C_1-C_4alkoxy, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl and —C(O)C_1-C_4haloalkyl; or

Z_1 is C_1-C_4alkyl which is mono- or polysubstituted by the group Z_2;

Z_2 is cyano, formyl, hydroxyl, C_3-C_6cycloalkyl, hydroxycarbonyl, aminocarbonyl, C_1-C_4haloalkoxy, C_1-C_4alkoxy, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_1-C_4alkoxycarbonyl, C_1-C_4haloalkoxycarbonyl, C_1-C_4alkylcarbonyl, C_1-C_4haloalkylcarbonyl, di-(C_1-C_4)alkylaminocarbonyl, C_1-C_4alkylaminocarbonyl, amino, C_1-C_4alkylcarbonylamino, di-(C_1-C_4)alkylcarbonylamino, C_1-C_4alkoxycarbonylamino, a group —C(R_5)=NOR_6, wherein R_5 and R_6 are independently hydrogen, C_1-C_4alkyl or C_1-C_4haloalkyl;

R_{1a} is hydrogen, C_1-C_2alkyl, C_1-C_4alkoxy or halogen; and n is 1 or 2; and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of those compounds.

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



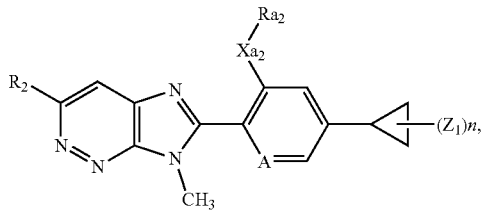
(I-1)

wherein X_1, A, R_2, R_{1a} and Z_1 are as defined under formula I in claim **1**;

Xa_1 is S, SO or SO_2; and

Ra_1 is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl.

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



(I-2)

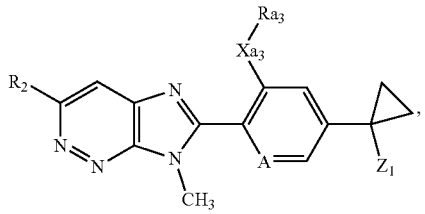
wherein A, R_2 and Z_1 are as defined under formula I in claim **1**;

Xa_2 is S, SO or SO_2; and

Ra_2 is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl.

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

(I-3)



wherein

A is CH or N;

X_{a3} is S or SO_2;

R_{a3} is ethyl;

R_2 is C_1-C_4haloalkyl, C_1-C_4haloalkylsulfanyl, C_1-C_2haloalkylsulfinyl, C_1-C_2haloalkylsulfonyl; and

Z_1 is cyano, hydroxycarbonyl, aminocarbonyl, C_1-C_4alkoxycarbonyl, methylaminocarbonyl, dimethylaminocarbonyl, amino, methoxycarbonylamino, formyl, hydroxymethylene or methylhydroxymethylene.

5. 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.

6. A method for controlling pests, which comprises applying a composition according to claim **5** 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.

7. 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 **5**.

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