

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization

International Bureau



(10) International Publication Number

WO 2017/016922 A1

(43) International Publication Date
2 February 2017 (02.02.2017)

WIPO | PCT

(51) International Patent Classification:

A01N 43/50 (2006.01) *A01P 7/04* (2006.01)
A01N 43/54 (2006.01) *C07D 233/64* (2006.01)
A01P 7/02 (2006.01) *C07D 239/64* (2006.01)

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(21) International Application Number:

PCT/EP2016/067113

(22) International Filing Date:

19 July 2016 (19.07.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

15178277.8 24 July 2015 (24.07.2015) EP

(71) Applicant: SYNGENTA PARTICIPATIONS AG [CH/CH]; Schwarzwaldallee 215, 4058 Basel (CH).

(72) Inventors: MUEHLEBACH, Michel; Syngenta Crop Protection AG, Schaffhauserstrasse, 4332 Stein (CH). TITULÄER, Ruud; Mercachem B.V. Kerkenbos 1013, 6546 BB Nijmegen (NL). EDMUNDIS, Andrew; Syngenta Crop Protection AG, Schaffhauserstrasse, 4332 Stein (CH). JUNG, Pierre, Joseph, Marcel; Syngenta Crop Protection AG, Schaffhauserstrasse, 4332 Stein (CH). EMERY, Daniel; Syngenta Crop Protection AG, Schaffhauserstrasse, 4332 Stein (CH). BUCHHOLZ, Anke; Syngenta Crop Protection AG, Schaffhauserstrasse, 4332 Stein (CH).

(74) Agent: SYNGENTA INTERNATIONAL AG; Schwarzwaldallee 215 (WRO B8-Z1-26), 4058 Basel (CH).

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

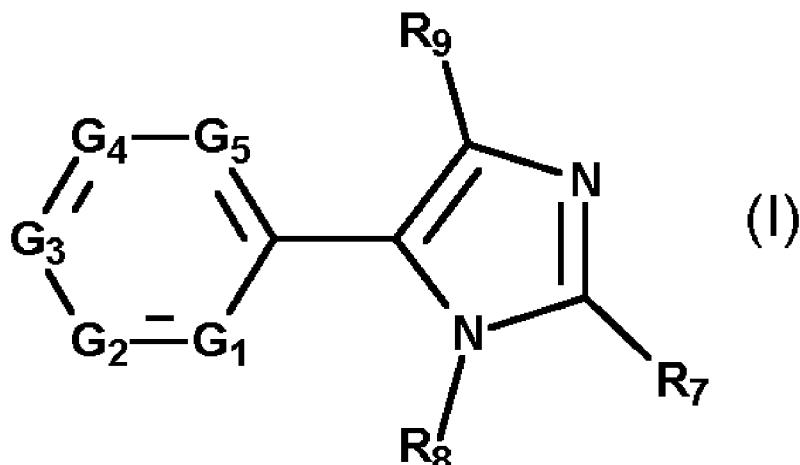
— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))

— of inventorship (Rule 4.17(iv))

Published:

— with international search report (Art. 21(3))

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



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

-1-

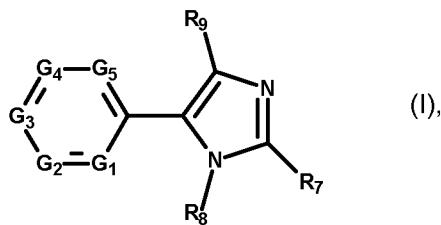
Pesticidally active heterocyclic derivatives with sulphur containing substituents

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

5

Heterocyclic compounds with pesticidal action are known and described, for example, in WO 2010/125985, WO 2013/018928, WO 2016/024587 and WO 2015/163478. There have now been found novel pesticidally active heterocyclic imidazole derivatives with sulphur containing phenyl and pyridyl substituents.

10 The present invention accordingly relates to compounds of formula I,



wherein

G₁ is nitrogen or CR₂;

G₂ is nitrogen or CR₃;

15 G₃ is nitrogen or CR₄;

G₄ is nitrogen or CR₅;

G₅ is nitrogen or CR₆, with the proviso that not more than 2 nitrogens as G may follow consecutively;

R₂, R₃, R₄, R₅ or R₆ are, independently from each other, hydrogen, halogen, C₁-C₄haloalkyl,

C₁-C₄haloalkyl substituted by one or two hydroxy, C₁-C₄haloalkyl substituted by one or two methoxy,

20 C₁-C₄haloalkyl substituted by one or two cyano; or

R₂, R₃, R₄, R₅ or R₆ are, independently from each other, C₁-C₄haloalkylsulfanyl, C₁-C₄haloalkylsulfinyl,

C₁-C₄haloalkylsulfonyl, C₁-C₄haloalkoxy, SF₅, phenylcarbonylthio, cyano, mercapto,

C₁-C₄alkoxycarbonyl, C₁-C₄alkylcarbonyl or -C(O)C₁-C₄haloalkyl; or

R₂, R₃, R₄, R₅ or R₆ are, independently from each other, C₃-C₆cycloalkyl which can be mono- or

25 polysizestituted by substituents selected from the group consisting of halogen, cyano and C₁-C₄alkyl;

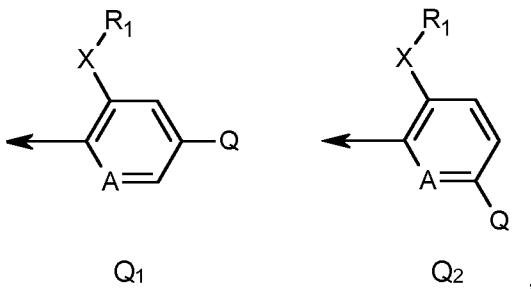
or two adjacent R_i, wherein R_i is selected from R₂, R₃, R₄, R₅ and R₆, taken together may form a fragment -OCH₂O- or -OCF₂O-;

R₈ is hydrogen, C₁-C₄alkyl or C₁-C₄haloalkyl;

R₉ is hydrogen, C₁-C₄alkyl, C₁-C₄haloalkyl, cyano or halogen;

30 R₇ is a radical selected from the group consisting of formula Q₁ and Q₂

-2-



wherein the arrow denotes the point of attachment to the imidazole ring;

and wherein A represents CH or N;

Q is phenyl which can be mono- or polysubstituted by substituents selected from the group consisting

5 of halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkoxy, C₁-C₄haloalkylsulfanyl, C₁-C₄haloalkylsulfinyl, C₁-C₄haloalkylsulfonyl and -C(O)C₁-C₄haloalkyl; or

Q is a five- to ten-membered monocyclic or fused bicyclic ring system linked via a carbon atom to the ring which contains the group A, said ring system can be aromatic, partially saturated or fully saturated and contains 1 to 4 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, it

10 not being possible for each ring system to contain more than 2 oxygen atoms and more than 2 sulfur atoms, said five- to ten-membered ring system can be mono- to polysubstituted by substituents independently selected from the group consisting of halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkoxy, C₁-C₄alkylsulfanyl, C₁-C₄alkylsulfinyl, C₁-C₄alkylsulfonyl, -C(O)C₁-C₄alkyl, C₁-C₄haloalkylsulfanyl, C₁-C₄haloalkylsulfinyl, C₁-C₄haloalkylsulfonyl and -C(O)C₁-C₄haloalkyl; or

15 Q is a five- to six-membered, aromatic, partially saturated or fully saturated ring system linked via a nitrogen atom to the ring which contains the group A, said ring system can be mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkoxy, C₁-C₄alkylsulfanyl, C₁-C₄alkylsulfinyl, C₁-C₄alkylsulfonyl, -C(O)C₁-C₄alkyl, C₁-C₄haloalkylsulfanyl, C₁-C₄haloalkylsulfinyl, C₁-C₄haloalkylsulfonyl and

20 -C(O)C₁-C₄haloalkyl; and said ring system contains 1, 2 or 3 heteroatoms selected from the group consisting of nitrogen, oxygen and sulfur, where said ring system may not contain more than one oxygen atom and not more than one sulfur atom; or

Q is C₃-C₆cycloalkyl, or C₃-C₆cycloalkyl mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₃-C₆cycloalkyl and phenyl, wherein

25 said phenyl can be mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkoxy, C₁-C₄haloalkylsulfanyl, C₁-C₄haloalkylsulfinyl, C₁-C₄haloalkylsulfonyl and -C(O)C₁-C₄haloalkyl; or

Q is C₂-C₆alkenyl, or C₂-C₆alkenyl mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₃-C₆cycloalkyl and phenyl, wherein said

30 phenyl can be mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkoxy, C₁-C₄haloalkylsulfanyl, C₁-C₄haloalkylsulfinyl, C₁-C₄haloalkylsulfonyl and -C(O)C₁-C₄haloalkyl; or

-3-

Q is C_2 - C_6 alkynyl, or C_2 - C_6 alkynyl mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_3 - C_6 cycloalkyl, tri(C_1 - C_4 alkyl)silyl and phenyl, wherein said phenyl can be mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_1 - C_4 haloalkoxy, C_1 - C_4 alkoxy, C_1 - C_4 halo-

5 alkylsulfanyl, C_1 - C_4 haloalkylsulfinyl, C_1 - C_4 haloalkylsulfonyl and $-C(O)C_1$ - C_4 haloalkyl; or

Q is C_1 - C_6 haloalkylsulfanyl, C_1 - C_6 haloalkylsulfinyl, C_1 - C_6 haloalkylsulfonyl, C_1 - C_6 haloalkoxy, $-C(O)C_1$ - C_4 haloalkyl, C_1 - C_6 alkylsulfanyl, C_1 - C_6 alkylsulfinyl, or C_1 - C_6 alkylsulfonyl;

X is S, SO or SO_2 ; and

R_1 is C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_3 - C_6 cycloalkyl, C_3 - C_6 cycloalkyl- C_1 - C_4 alkyl; or

10 R_1 is C_3 - C_6 cycloalkyl mono - or polysubstituted by substituents selected from the group consisting of halogen, cyano and C_1 - C_4 alkyl; or

R_1 is C_3 - C_6 cycloalkyl- C_1 - C_4 alkyl mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano and C_1 - C_4 alkyl; or

R_1 is C_2 - C_6 alkenyl, C_2 - C_6 haloalkenyl or C_2 - C_6 alkynyl;

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

Compounds of formula I which have at least one basic centre can form, for example, acid addition salts, for example with strong inorganic acids such as mineral acids, for example perchloric acid,

20 sulfuric acid, nitric acid, nitroso acid, a phosphorus acid or a hydrohalic acid, with strong organic carboxylic acids, such as C_1 - C_4 alkanecarboxylic acids which are unsubstituted or substituted, for example by halogen, for example acetic acid, such as saturated or unsaturated dicarboxylic acids, for example oxalic acid, malonic acid, succinic acid, maleic acid, fumaric acid or phthalic acid, such as hydroxycarboxylic acids, for example ascorbic acid, lactic acid, malic acid, tartaric acid or citric acid, or

25 such as benzoic acid, or with organic sulfonic acids, such as C_1 - C_4 alkane- or arylsulfonic acids which are unsubstituted or substituted, for example by halogen, for example methane- or p-toluenesulfonic acid. Compounds of formula I which have at least one acidic group can form, for example, salts with bases, for example mineral salts such as alkali metal or alkaline earth metal salts, for example sodium,

potassium or magnesium salts, or salts with ammonia or an organic amine, such as morpholine,

30 piperidine, pyrrolidine, a mono-, di- or tri-lower-alkylamine, for example ethyl-, diethyl-, triethyl- or dimethylpropylamine, or a mono-, di- or trihydroxy-lower-alkylamine, for example mono-, di- or triethanolamine.

The alkyl groups occurring in the definitions of the substituents can be straight-chain or branched and

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

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

5 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; preferably trichloromethyl, difluorochloromethyl, difluoromethyl, trifluoromethyl and dichlorofluoromethyl.

10 Alkoxy groups preferably have a preferred chain length of from 1 to 6 carbon atoms. 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; preferably methoxy and ethoxy.

15 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.

Alkylsulfanyl is for example methylsulfanyl, ethylsulfanyl, propylsulfanyl, isopropylsulfanyl, butylsulfanyl, pentylsulfanyl, and hexylsulfanyl.

20 Alkylsulfinyl is for example methylsulfinyl, ethylsulfinyl, propylsulfinyl, isopropylsulfinyl, a butylsulfinyl, pentylsulfinyl, and hexylsulfinyl.

Alkylsulfonyl is for example methylsulfonyl, ethylsulfonyl, propylsulfonyl, isopropylsulfonyl, butylsulfonyl, pentylsulfonyl, and hexylsulfonyl.

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

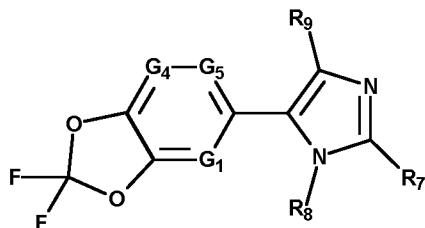
Haloalkoxy groups preferably have a chain length of from 1 to 4 carbon atoms. Haloalkoxy is, for example, difluoromethoxy, trifluoromethoxy or 2,2,2-trifluoroethoxy.

30 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 C₁-C₄haloalkylsulfinyl and C₁-C₄haloalkylsulfonyl, which may be, for example, trifluoromethylsulfinyl, trifluoromethylsulfonyl or 2,2,2-trifluoroethylsulfonyl.

-5-

According to the present invention, when two adjacent R_i , wherein R_i is selected from R_2 , R_3 , R_4 , R_5 and R_6 , taken together to form a fragment $-OCH_2O-$ or $-OCF_2O-$ then an additional five-membered dioxolane or difluoro-dioxolane ring is formed. For example, compounds of the formula I, wherein G_2 is CR_3 , G_3 is CR_4 , and in which R_3 and R_4 taken together form the fragment $-OCF_2O-$, has the following

5 structure:



In the context of this invention, examples of a five- to six-membered, aromatic, partially saturated or fully saturated ring system that are linked via a nitrogen atom to the ring which contains the group A, are selected from pyrazole, pyrrole, pyrrolidine, pyrrolidine-2-one, piperidine, morpholine, imidazole,

10 triazole and pyridine-2-one.

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

15 Free radicals represents methyl groups.

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

According to the present invention, Q as a five- to ten-membered monocyclic or fused bicyclic ring system that is linked via a carbon atom to the ring which contains the group A, said ring system can be

20 aromatic, partially saturated or fully saturated and contains 1 to 4 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, it not being possible for each ring system to contain more than 2 oxygen atoms and more than 2 sulfur atoms,

or Q as a three- to ten-membered, monocyclic or fused bicyclic ring system which may be aromatic, partially saturated or fully saturated,

25 is, depending of the number of ring members, preferably selected from the group consisting of the following heterocyclic groups:

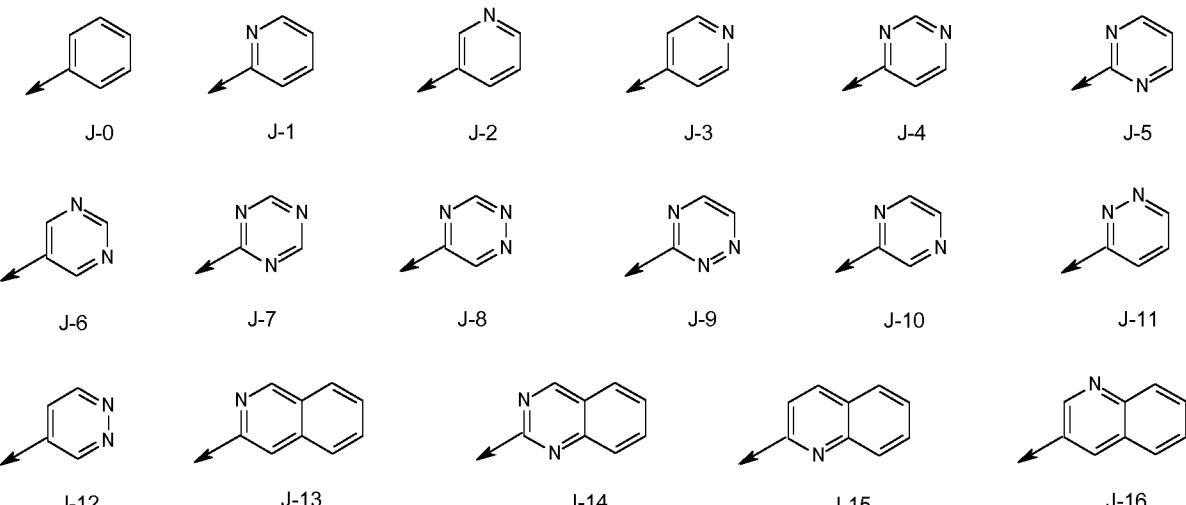
pyrrolyl; pyrazolyl; isoxazolyl; furanyl; thieryl; imidazolyl; oxazolyl; thiazolyl; isothiazolyl; triazolyl; oxadiazolyl; thiadiazolyl; tetrazolyl; furyl; pyridyl; pyrimidyl; pyrazinyl; pyridazinyl; triazinyl, pyranyl; quinazolinyl; isoquinolinyl; indolizinyl; isobenzofuranylaphthyridinyl; quinoxalinyl; cinnolinyl;

30 phthalazinyl; benzothiazolyl; benzoxazolyl; benzotriazolyl; indazolyl; indolyl; (1H-pyrrol-1-yl)-; (1H-pyrrol-2-yl)-; (1H-pyrrol-3-yl)-; (1H-pyrazol-1-yl)-; (1H-pyrazol-3-yl)-; (3H-pyrazol-3-yl)-; (1H-pyrazol-4-

-6-

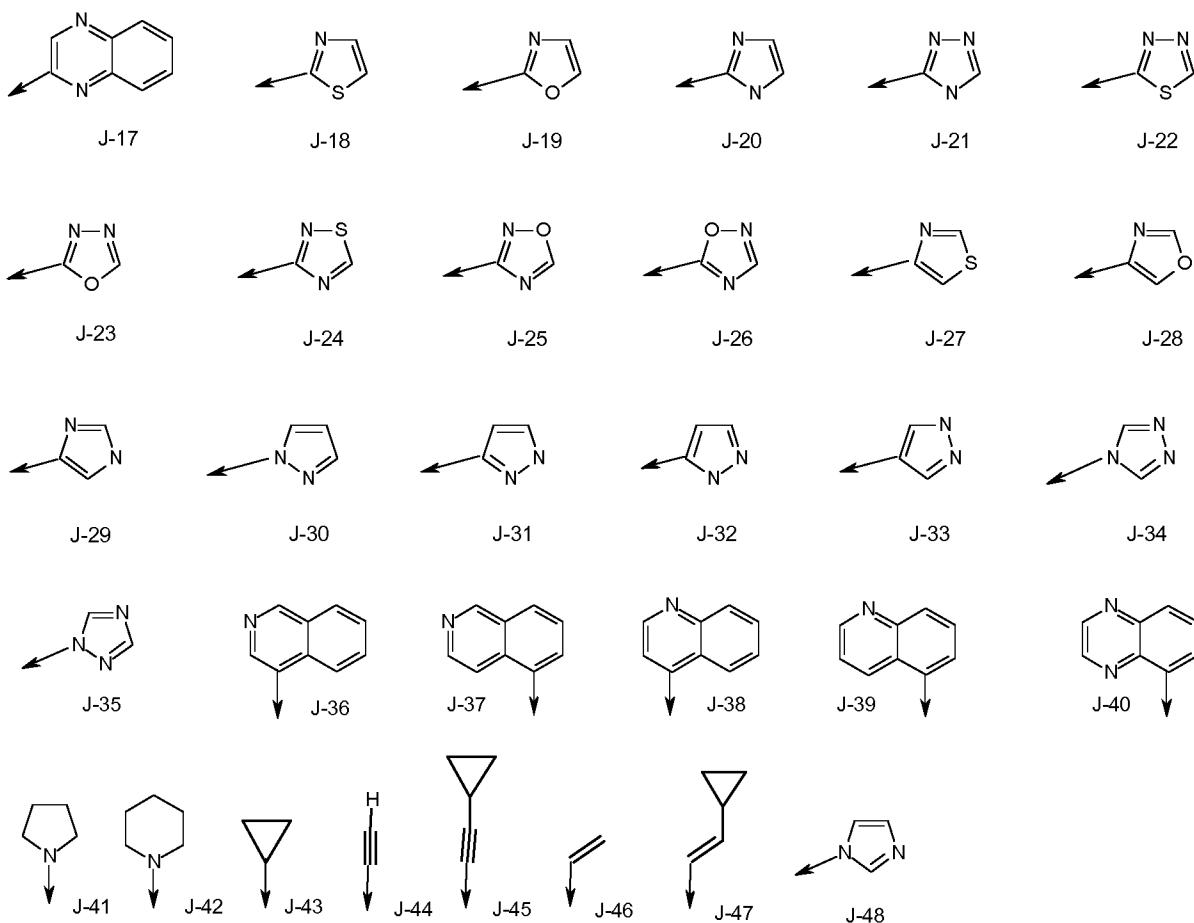
yl)-; (3-isoxazolyl)-; (5-isoxazolyl)-; (2-furanyl)-; (3-furanyl)-; (2-thienyl)-; (3-thienyl)-; (1H-imidazol-2-yl)-; (1H-imidazol-4-yl)-; (1H-imidazol-5-yl)-; (2-oxazol-2-yl)-; (oxazol-4-yl)-; (oxazol-5-yl)-; (thiazol-2-yl)-; (thiazol-4-yl)-; (thiazol-5-yl)-; (isothiazol-3-yl)-; (isothiazol-5-yl)-; (1H-1,2,3-triazol-1-yl)-; (1H-1,2,4-triazol-3-yl)-; (4H-1,2,4-triazol-4-yl)-; (1H-1,2,4-triazol-1-yl)-; (1,2,3-oxadiazol-2-yl)-; (1,2,4-oxadiazol-3-yl)-; (1,2,4-oxadiazol-4-yl)-; (1,2,4-oxadiazol-5-yl)-; (1,2,3-thiadiazol-2-yl)-; (1,2,4-thiadiazol-3-yl)-; (1,2,4-thiadiazol-4-yl)-; (1,3,4-thiadiazol-5-yl)-; (1H-tetrazol-1-yl)-; (1H-tetrazol-5-yl)-; (2H-tetrazol-5-yl)-; (2-pyridyl)-; (3-pyridyl)-; (4-pyridyl)-; (2-pyrimidinyl)-; (4-pyrimidinyl)-; (5-pyrimidinyl)-; (2-pyrazinyl)-; (3-pyridazinyl)-; (4-pyridazinyl)-; (1,3,5-triazin-2-yl)-; (1,2,4-triazin-5-yl)-; (1,2,4-triazin-6-yl)-; (1,2,4-triazin-3-yl)-; (furazan-3-yl)-; (2-quinolinyl)-; (3-quinolinyl)-; (4-quinolinyl)-; (5-quinolinyl)-; (6-quinolinyl)-; (3-isoquinolinyl)-; (4-isoquinolinyl)-; (2-quinoxolinyl)-; (2-quinoxalinyl)-; (5-quinoxalinyl)-; (pyrido[2,3-b]pyrazin-7-yl)-; (benzoxazol-5-yl)-; (benzothiazol-5-yl)-; (benzo[b]thien-2-yl)- and (benzo[1,2,5]oxadiazol-5-yl)-; indolinyl and tetrahydroquinolynyl.

In preferred compounds of formula I, Q is selected from the group consisting of J-0 to J-48 (where the arrow represents the point of attachment of the group J to the ring which contains the group A):



15

-7-

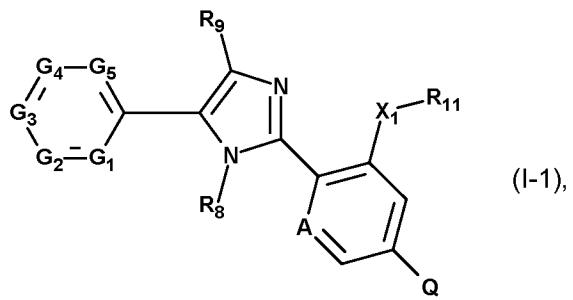


in particular selected from J-1 to J-47;

wherein each group J-0 to J-48 is mono-, di- or trisubstituted with Rx, wherein

5 each Rx is, independently selected from hydrogen, halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkoxy, C₁-C₄alkylsulfanyl, C₁-C₄alkylsulfinyl, C₁-C₄alkylsulfonyl, -C(O)C₁-C₄alkyl, C₁-C₄haloalkylsulfanyl, C₁-C₄haloalkylsulfinyl, C₁-C₄haloalkylsulfonyl and -C(O)C₁-C₄haloalkyl.

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



10

wherein A, Q, G₁, G₂, G₃, G₄, and G₅ are as defined under formula I above; and wherein X₁ is S, SO or SO₂; and R₁₁ is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl; R₈ is as defined above under formula I, preferably methyl, R₉ is as defined above under formula I, preferably hydrogen, and

-8-

agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of those compounds.

Also preferred are compounds of formula I-1 with G₃ defined as C(halogen), C(C₁-C₄haloalkyl),

5 C(C₁-C₄haloalkylsulfanyl) or C(C₁-C₄haloalkylsulfonyl), and G₁, G₂, G₄ and G₅ defined as CH.

Yet other preferred compounds of formula I-1 have G₂ defined as C(C₁-C₄haloalkylsulfanyl), and G₁, G₃, G₄ and G₅ defined as CH.

Further preferred compounds of formula I-1 have G₂ defined as N, G₃ defined as C(C₁-C₄haloalkyl), and G₁, G₄ and G₅ defined as CH.

10 Other preferred compounds of formula I-1 have G₂ defined as N, G₄ defined as C(C₁-C₄haloalkyl), and G₁, G₃ and G₅ defined as CH.

Yet further preferred compounds of formula I-1 have G₂ and G₄ defined as N, G₃ defined as C(C₁-C₄haloalkyl), and G₁ and G₅ defined as CH.

15

In an especially preferred group of compounds of formula I-1, G₃ is defined as C(F), C(CF₃), C(SCF₃) or C(SO₂CF₃), and G₁, G₂, G₄ and G₅ are defined as CH.

In an especially preferred group of compounds of formula I-1, G₂ is defined as C(SCF₃), and G₁, G₃, G₄ and G₅ are defined as CH.

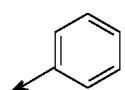
20 In an especially preferred group of compounds of formula I-1, G₂ is defined as N, G₃ is defined as C(CF₃), and G₁, G₄ and G₅ are defined as CH.

In an especially preferred group of compounds of formula I-1, G₂ is defined as N, G₄ is defined as C(CF₃), and G₁, G₃ and G₅ are defined as CH.

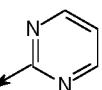
25 In an especially preferred group of compounds of formula I-1, G₂ and G₄ are defined as N, G₃ is defined as C(CF₃), and G₁ and G₅ are defined as CH.

In said especially preferred group of compounds of formula I-1, R₈ is preferably methyl and R₉ is preferably hydrogen. A further preferred embodiment of said especially preferred group of compounds of formula I-1 comprises compounds wherein A is preferably N, X₁ is preferably SO₂ and R₁₁ is preferably ethyl.

30 In compounds of formula I-1 and all of the preferred embodiments of compounds of formula I-1 mentioned above, Q is preferably selected from the group consisting of



and



J-0

J-5

,

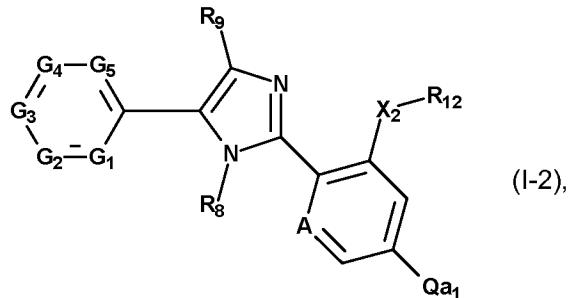
35 wherein each group J is mono-, di- or trisubstituted with Rx, wherein

-9-

each Rx is, independently selected from hydrogen, halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkoxy, C₁-C₄alkylsulfanyl, C₁-C₄alkylsulfinyl, C₁-C₄alkylsulfonyl, -C(O)C₁-C₄alkyl, C₁-C₄haloalkylsulfanyl, C₁-C₄haloalkylsulfinyl, C₁-C₄haloalkylsulfonyl and -C(O)C₁-C₄haloalkyl, in particular independently selected from hydrogen, halogen and C₁-C₄haloalkyl.

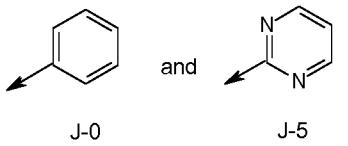
5

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



wherein A, G₁, G₂, G₃, G₄, and G₅ are as defined under formula I above; and wherein X₂ is S, SO or SO₂; and R₁₂ is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl; R₈ is as defined above under formula I, preferably methyl, R₉ is as defined above under formula I, preferably hydrogen, and wherein

10 Qa₁ is selected from the group consisting of



wherein each group J is mono-, di- or trisubstituted with Rx, wherein

each Rx is, independently selected from hydrogen, halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-

15 C₄haloalkoxy, C₁-C₄alkoxy, C₁-C₄alkylsulfanyl, C₁-C₄alkylsulfinyl, C₁-C₄alkylsulfonyl, -C(O)C₁-C₄alkyl, C₁-C₄haloalkylsulfanyl, C₁-C₄haloalkylsulfinyl, C₁-C₄haloalkylsulfonyl and -C(O)C₁-C₄haloalkyl, and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of those compounds.

Also preferred are compounds of formula I-2, wherein each Rx is, independently selected from

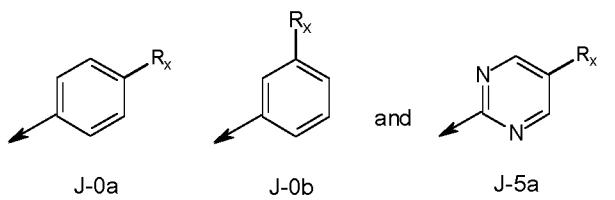
20 hydrogen, halogen and C₁-C₄haloalkyl.

More preferred compounds of formula I-2 are those, in which each Rx is, independently from each other, selected from hydrogen, fluorine, chlorine and trifluoromethyl.

In an especially preferred group of compounds of formula I-2, Qa₁ is selected from the group

25 consisting of

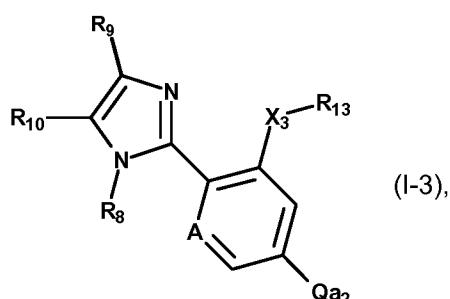
-10-



in particular selected from J-0a and J-5a;

wherein each Rx is, independently selected from hydrogen, halogen and C₁-C₄haloalkyl, preferably from hydrogen, fluorine, chlorine and trifluoromethyl.

- 5 In said especially preferred group of compounds of formula I-2, R₈ is preferably methyl and R₉ is preferably hydrogen. A further preferred embodiment of said especially preferred group of compounds of formula I-2 comprises compounds wherein A is preferably N, X₂ is preferably SO₂ and R₁₂ is preferably ethyl.
- 10 A further preferred embodiment of the invention comprises compounds of formula I represented by the compounds of formula I-3

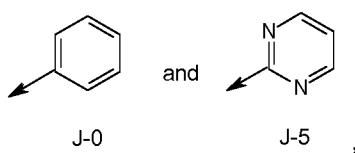


wherein

A is N or CH;

15 R_{10} is phenyl mono- or polysubstituted by substituents independently selected from the group consisting of halogen, C_1 - C_4 haloalkyl, C_1 - C_4 haloalkylsulfanyl and C_1 - C_4 haloalkylsulfonyl, in particular fluorine, trifluoromethyl, trifluoromethylsulfanyl and trifluoromethylsulfonyl; or
 R_{10} is pyridyl mono- or polysubstituted by substituents independently selected from the group consisting of halogen and C_1 - C_4 haloalkyl, in particular fluorine and trifluoromethyl; or

20 R_{10} is pyrimidyl mono- or polysubstituted by substituents independently selected from the group consisting of halogen and C_1 - C_4 haloalkyl, in particular fluorine and trifluoromethyl;
 X_3 is S, SO or SO_2 , in particular S or SO_2 , preferably SO_2 ;
 Qa_2 is selected from the group consisting of



-11-

wherein each group J is mono-, di- or trisubstituted with Rx, wherein each Rx is, independently selected from hydrogen, halogen and C₁-C₄haloalkyl;

R₁₃ is C₁-C₄alkyl, in particular methyl or ethyl;

R₈ is C₁-C₄alkyl, in particular methyl or ethyl;

5 R₉ is hydrogen;

and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of the compounds of formula I-3.

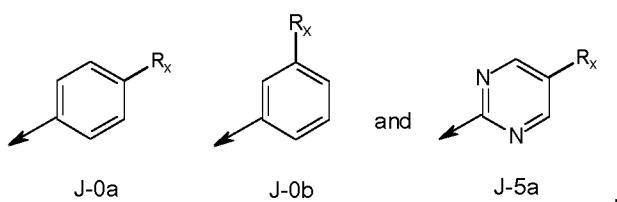
In said preferred embodiment comprising compounds of formula I-3, R₁₀ is preferably phenyl

10 monosubstituted by substituents independently selected from the group consisting of halogen, C₁-C₄haloalkyl, C₁-C₄haloalkylsulfanyl and C₁-C₄haloalkylsulfonyl, or R₁₀ is pyridyl monosubstituted by substituents independently selected from the group consisting of halogen and C₁-C₄haloalkyl, or R₁₀ is pyrimidyl monosubstituted by substituents independently selected from the group consisting of halogen and C₁-C₄haloalkyl; in particular, R₁₀ is preferably phenyl monosubstituted by substituents 15 independently selected from the group consisting of halogen, C₁-C₄haloalkyl, C₁-C₄haloalkylsulfanyl and C₁-C₄haloalkylsulfonyl, or R₁₀ is pyridyl monosubstituted by substituents independently selected from the group consisting of halogen and C₁-C₄haloalkyl.

Especially preferred substituents on the ring R₁₀ are selected from fluorine, trifluoromethyl,

20 trifluoromethylsulfanyl and trifluoromethylsulfonyl.

In said preferred embodiment comprising compounds of formula I-3, Qa₂ is preferably selected from the group consisting of



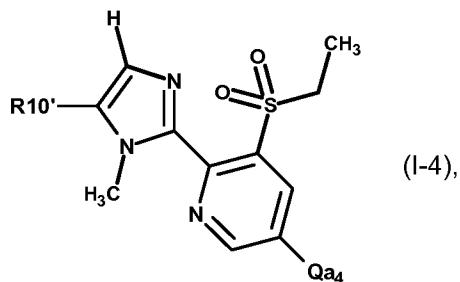
25 in particular selected from J-0a and J-5a;

wherein each Rx is, independently selected from hydrogen, halogen and C₁-C₄haloalkyl, preferably from hydrogen, fluorine, chlorine and trifluoromethyl.

An especially preferred embodiment of the invention comprises compounds of formula I represented

30 by the compounds of formula I-4

-12-

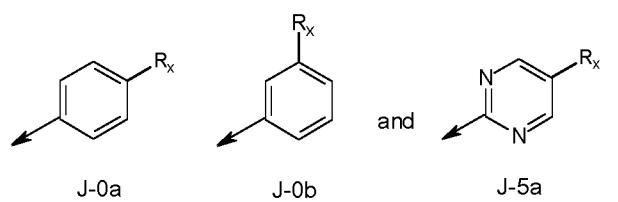


wherein

R_{10'} is phenyl monosubstituted by substituents independently selected from the group consisting of halogen, C₁-C₄haloalkyl, C₁-C₄haloalkylsulfanyl and C₁-C₄haloalkylsulfonyl, or R_{10'} is pyridyl

5 monosubstituted by substituents independently selected from the group consisting of halogen and C₁-C₄haloalkyl, or R_{10'} is pyrimidyl monosubstituted by substituents independently selected from the group consisting of halogen and C₁-C₄haloalkyl; and

Qa₄ is selected from the group consisting of



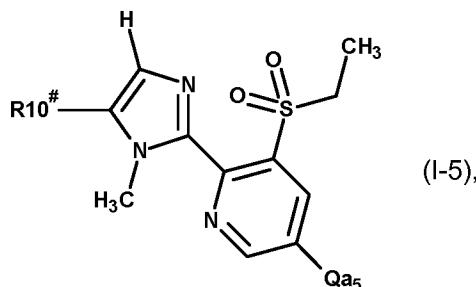
10 in particular selected from J-0a and J-5a;

wherein each Rx is, independently selected from hydrogen, halogen and C₁-C₄haloalkyl; and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of the compounds of formula I-4.

15 In said especially preferred embodiment comprising compounds of formula I-4, preferred substituents on the ring R_{10'} are selected from fluorine, trifluoromethyl, trifluoromethylsulfanyl and trifluoromethylsulfonyl; and

each Rx is, independently preferably selected from hydrogen, fluorine, chlorine and trifluoromethyl.

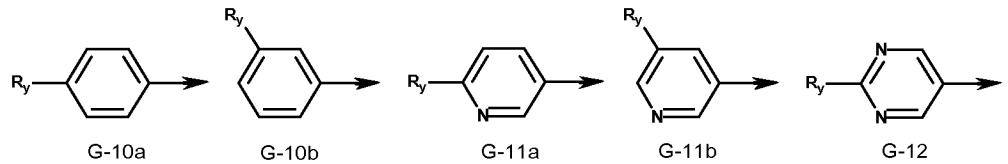
20 An even further especially preferred embodiment of the invention comprises compounds of formula I represented by the compounds of formula I-5



-13-

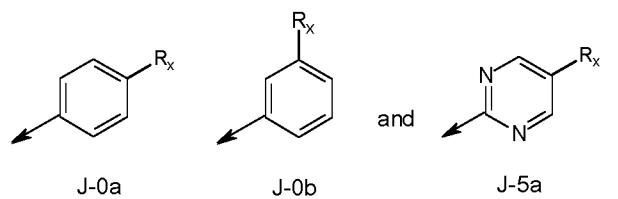
wherein

$R_{10}\#$ is a radical G-10 to G-12 independently selected from the group consisting of



wherein

5 the arrow denotes the point of attachment to the imidazole ring; and
 each R_y is, independently selected from halogen, C_1 - C_4 haloalkyl, C_1 - C_4 haloalkylsulfanyl and
 C_1 - C_4 haloalkylsulfonyl; and
 Qa_5 is selected from the group consisting of

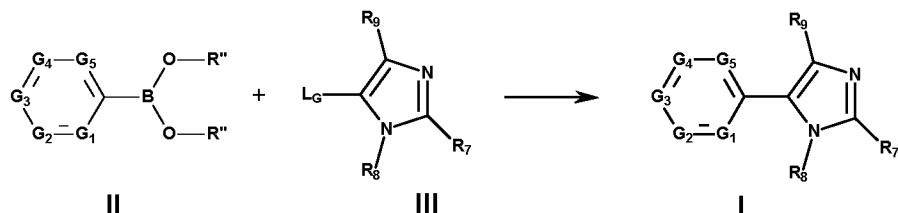


10 wherein each R_x is, independently selected from hydrogen, halogen and C_1 - C_4 haloalkyl;
 and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of the
 compounds of formula I-5.

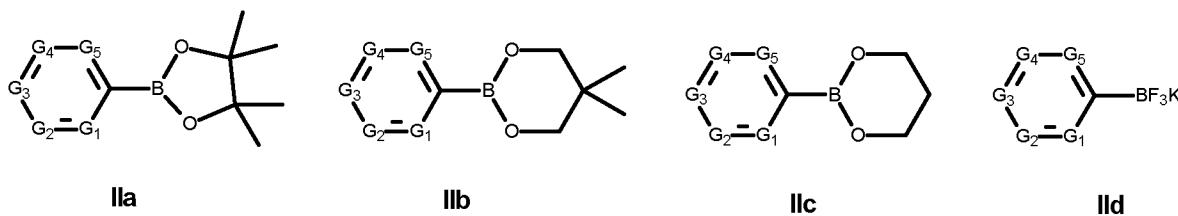
In said further especially preferred embodiment comprising compounds of formula I-5, each R_y is,
 15 independently preferably selected from fluorine, trifluoromethyl, trifluoromethylsulfanyl and
 trifluoromethylsulfonyl; and
 each R_x is, independently preferably selected from hydrogen, fluorine, chlorine and trifluoromethyl.

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

Compounds of formula I, wherein R_8 , R_9 , G_1 , G_2 , G_3 , G_4 , G_5 and R_7 are as defined above,

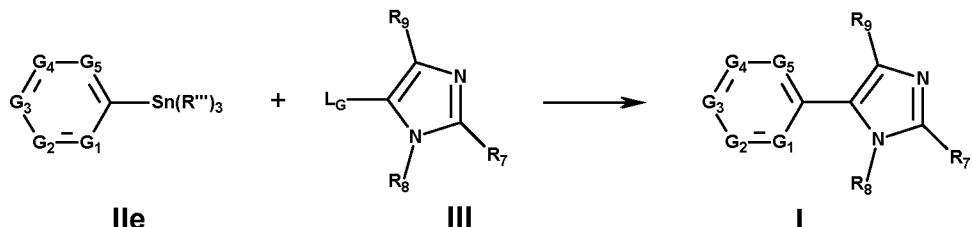


5 may be prepared by reacting a compound of formula II, wherein G₁, G₂, G₃, G₄ and G₅ are as defined above, and wherein R" is for example hydrogen (in that case the compound of the formula II is a boronic acid) or C₁-C₄alkyl (boronic ester), with a compound of formula III, wherein R₈, R₉ and R₇ are as defined above and wherein L_G is a halogen, preferably bromine or iodine, or a pseudohalogen such as C₁₋₄haloalkylsulfonate, especially triflate, by means of a transition metal-catalyzed reaction. Indeed, the boronic acid of the formula II, or a suitable salt or ester thereof, will react with a compound of the formula III under palladium- or nickel-catalyzed conditions, such as for example the Suzuki-Miyaura conditions. Such cross coupling reactions are carried out in the presence of a base, such as sodium, potassium or cesium carbonate, in an inert solvent, such as tetrahydrofuran, N,N-dimethylformamide, dioxane or 1,2-dimethoxyethane, or such as 1,2-dimethoxyethane-water mixtures, at temperatures between 25-200°C, preferably 50-150°C, optionally under microwave irradiation. A variety of metals, 10 catalysts and ligands may be used in this reaction type, such as for example [1,1-bis(diphenyl- 15 phosphino)ferrocene]dichloropalladium(II) (PdCl₂(dppf)), tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) or bis(triphenylphosphine)palladium(II) dichloride (PdCl₂(PPh₃)₂). Reaction conditions and catalytic systems for such a transformation have been described, for example, in WO08/071405. Alternative boron-based reagents of the formula type II may include boronic esters (also named 20 boronate esters) derived from 2,3-dimethyl-2,3-butanediol (IIa), 2,2-dimethyl-1,3-propanediol (IIb), and 1,3-propanediol (IIc), and salt analogues of II, such as organotrifluoroborates, for example potassium trifluoroborate salts (IId).



Alternatively, compounds of formula I, wherein R₈, R₉, G₁, G₂, G₃, G₄, G₅ and R₇ are as defined above,

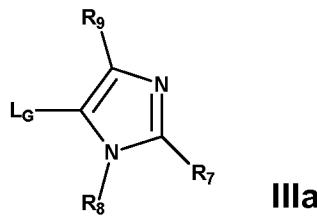
-15-



may be prepared by a Stille reaction between compound of formula III, wherein R₈, R₉ and R₇ are as defined above and wherein L_G is a halogen, preferably bromine or iodine, or a pseudohalogen such as C₁₋₄haloalkylsulfonate, especially triflate, and compounds of formula IIe, wherein G₁, G₂, G₃, G₄ and G₅

5 are as defined above, and wherein R''' is C_{1-C₄}alkyl. The trialkyl tin functionality –Sn(R''')₃ is preferably tri-n-butyl tin or tri-methyl-tin. Such Stille reactions are usually carried out in the presence of a palladium catalyst, for example tetrakis(triphenylphosphine)palladium(0), or bis(triphenylphosphine) palladium(II) dichloride, in an inert solvent such as N,N-dimethylformamide, acetonitrile, toluene or dioxane, optionally in the presence of an additive, such as cesium fluoride, or lithium chloride, and 10 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.

Compounds of formula IIIa

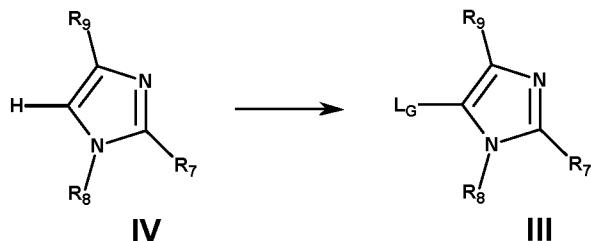


15

wherein R₈ and R₇ are as defined under formula I above, and wherein L_G is a halogen, preferably bromine or iodine, and wherein R₉ is preferably hydrogen, are novel and especially developed for the preparation of the compounds of formula I of this invention. The compounds of formula IIIa therefore constitute a further object of the invention. The preferred substituent definitions for the compounds of 20 formula I are also valid for the compounds of formula IIIa.

Compounds of formula III, wherein R₈, R₉ and R₇ are as defined above and wherein L_G is a halogen, preferably bromine or iodine,

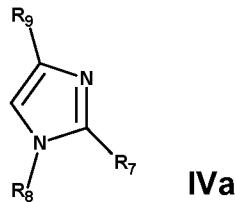
-16-



may be prepared by reacting a compound of formula IV, wherein R₈, R₉ and R₇ are as defined above, with a reagent such as N-chlorosuccinimide (NCS), N-bromosuccinimide (NBS) or N-iodosuccinimide (NIS), or alternatively chlorine, bromine or iodine. Such halogenation reactions are carried out in an

5 inert solvent, such as chloroform, carbon tetrachloride, 1,2-dichloroethane, acetic acid, ethers, acetonitrile or N,N-dimethylformamide, at temperatures between 25-200°C, preferably 25-100°C, as described, for example, in K.G. Holden et al., J. Org. Chem. 2002, 67, 5913-5918.

Compounds of formula IVa



10

wherein R₈ and R₇ are as defined under formula I above, and wherein R₉ is preferably hydrogen, are novel and especially developed for the preparation of the compounds of formula I of this invention.

The compounds of formula IVa therefore constitute a further object of the invention. The preferred substituent definitions for the compounds of formula I are also valid for the compounds of formula IVa.

15

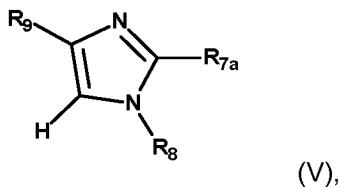
The subgroup of compounds of formula III and IV, wherein R₈, R₉, R₇ and L_G are as defined above and wherein X is SO (sulfoxide) and/or SO₂ (sulfone), may be obtained by means of an oxidation reaction

of the corresponding sulfide compounds of formula III or IV, wherein X is S (sulfide), involving reagents such as, for example, m-chloroperoxybenzoic acid (mCPBA), hydrogen peroxide, oxone, sodium

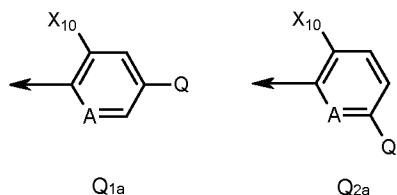
20 periodate, sodium hypochlorite or tert-butyl hypochlorite amongst other oxidants. The oxidation reaction is generally conducted in the presence of a solvent. Examples of the solvent to be used in the reaction include aliphatic halogenated hydrocarbons such as dichloromethane and chloroform; alcohols such as methanol and ethanol; acetic acid; water; and mixtures thereof. The amount of the oxidant to be used in the reaction is generally 1 to 3 moles, preferably 1 to 1.2 moles, relative to 1 mole of the sulfide compounds III or IV to produce the sulfoxide compounds III or IV, and preferably 2 to 2.2 moles of oxidant, relative to 1 mole of the sulfide compounds III or IV to produce the sulfone compounds III or IV. Such oxidation reactions are disclosed, for example, in WO 2013/018928.

-17-

Compounds of formula IV, wherein R₈, R₉ and R₇ are as defined above and wherein X is S (sulfide), can be prepared by reacting a compound of formula V



5 wherein R_8 and R_9 are as described in formula I and wherein R_{7a} is a radical selected from the group consisting of formula Q_{1a} to Q_{2a} :



wherein A and Q are as defined above, and wherein X_{10} is a halogen (preferably fluorine, chlorine or bromine), with a compound of formula VI

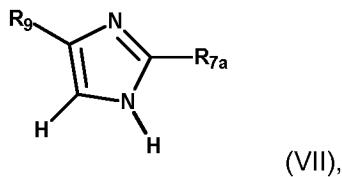


10 or a salt thereof, wherein R₁ is as defined in formula I, optionally in the presence of a suitable base, such as alkali metal carbonates, for example sodium carbonate and potassium carbonate, or alkali metal hydrides such as sodium hydride, or alkali metal hydroxides such as sodium hydroxide and potassium hydroxide, in an inert solvent at temperatures preferably between 25-120°C. Examples of solvent to be used include ethers such as THF, ethylene glycol dimethyl ether, tert-butylmethyl ether, 15 and 1,4-dioxane, aromatic hydrocarbons such as toluene and xylene, nitriles such as acetonitrile or polar aprotic solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone or dimethyl sulfoxide. Examples of salts of the compound of formula VI include compounds of the formula VIa



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

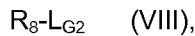
Compounds of formula V, wherein R_8 , R_9 and R_{7a} are as defined above, can be prepared by reacting a compound of formula VII



-18-

or a salt and/or a tautomer thereof, wherein R_9 and R_{7a} are as described above,

with an alkylating agent of the formula VIII



wherein R_8 is as defined above, and wherein L_{G2} is a halogen (especially bromine or iodine), or a

5 leaving group OSO_2R_{38} , wherein R_{38} is C_1-C_6 alkyl, C_1-C_6 haloalkyl, or phenyl optionally substituted by nitro or C_1-C_3 alkyl (especially a sulfonate such as mesylate, triflate or tosylate) or a sulfate (forming the alkylating agent VIII dimethylsulfate, in the particular situation where R_8 is methyl), preferably in the presence of a suitable base, such as sodium hydride or sodium, potassium or cesium carbonate, in an inert solvent such as tetrahydrofuran, dioxane, acetonitrile, N,N -dimethylformamide, N,N -dimethylacetamide, N -methyl-2-pyrrolidone or dimethyl sulfoxide, at temperatures between 20-150°C.

10

Compounds of formula VII, or a salt and/or a tautomer thereof, wherein R_9 and R_{7a} are as defined above, can be prepared by reacting a nitrile compound of formula IX



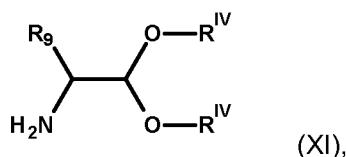
15 wherein R_{7a} is as described above,

sequentially with

i) a catalytic amount, preferably 0.01 to 0.5 equivalent, of a base such as an alkoxide, preferably sodium methoxide $NaOMe$ or sodium ethoxide $NaOEt$, in an alcoholic solvent, such as methanol or ethanol, at temperatures between 0-100°C, to generate an imidate intermediate of the formula INT_1 (or

20 a salt and/or a tautomer thereof); followed by

ii) acidification of the reaction mixture with, for example, acetic acid or the like, and treatment with an aminoacetal reagent of formula XI



or a salt thereof, wherein R^{IV} is C_1-C_6 alkyl and R_9 is as defined above, at temperatures between 0-

25 150°C, to generate an amidine-acetal intermediate of the formula INT_2 (or a salt and/or a tautomer thereof); followed by

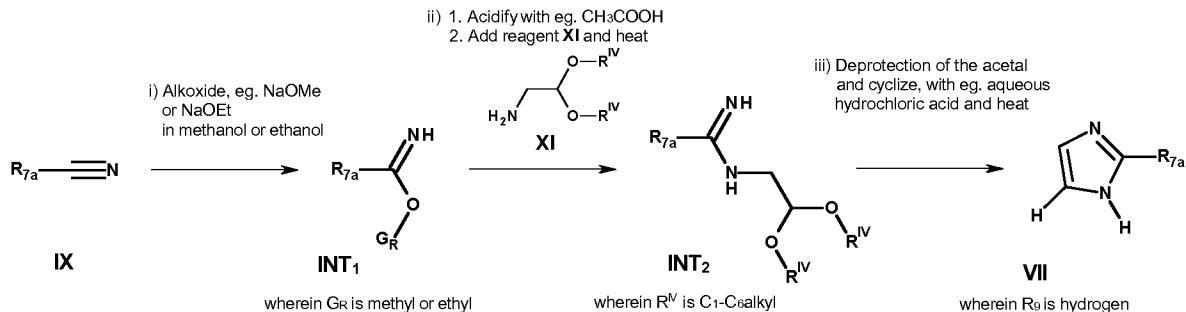
iii) deprotection of the acetal with, for example, aqueous hydrochloric acid or the like, and concomitant cyclization, at temperatures between 0-150°C, to form the compound of the formula VII, or a salt and/or a tautomer thereof. The described process to prepare compounds of the formula VII from

30 compounds of the formula IX may include isolation and purification of the intermediates INT_1 and INT_2 , (which may be isolated as free bases or as salts (e.g. a hydrohalide salt, more specifically a hydrochloride or hydrobromide salt, or any other equivalent salt)), however, this process is

-19-

advantageously conducted as a one-pot preparation as described, for example, in M.E. Voss et al., *Tetrahedron* 2008, 64, 645-651. The process is summarized in scheme 1 for the particular situation where R_9 is hydrogen:

Scheme 1



Compounds of the formula **INT₁** may alternatively be prepared under conditions and variants of the Pinner reaction known to a person skilled in the art, typically by treating a compound of the formula **IX** with a hydrohalide acid, preferably hydrochloric acid, in presence of alcoholic reagents such as methanol or ethanol, preferably in an inert solvent such as diethyl ether, tetrahydrofuran or dioxane, at temperatures between -40 and 50°C, preferably between -20 and 20°C.

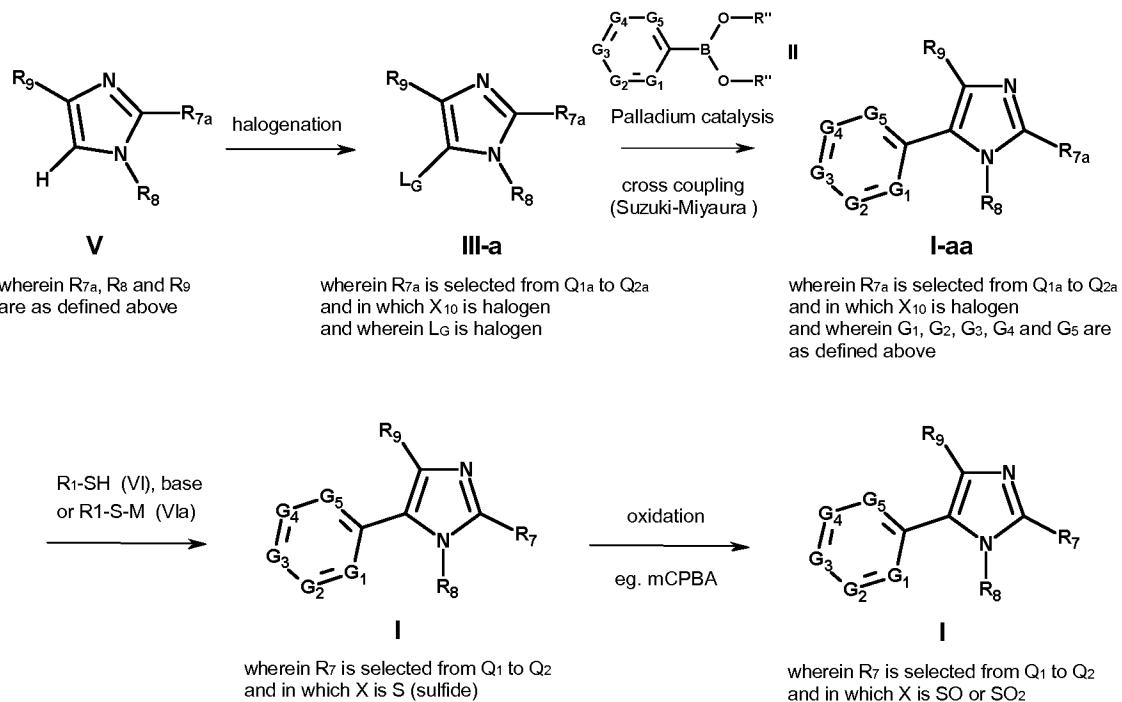
Compounds of formula **IX**, wherein R_{7a} is as described above and reagents of formula **XI**, wherein R_9 and R^{IV} are as described above, are known compounds or can be prepared by known methods, described in the literature.

15

Alternatively, compounds of formula **I** may be prepared from compounds of formula **V** involving the same chemistry as described above, but by changing the order of the steps. This alternative route is summarized in scheme 2.

Scheme 2

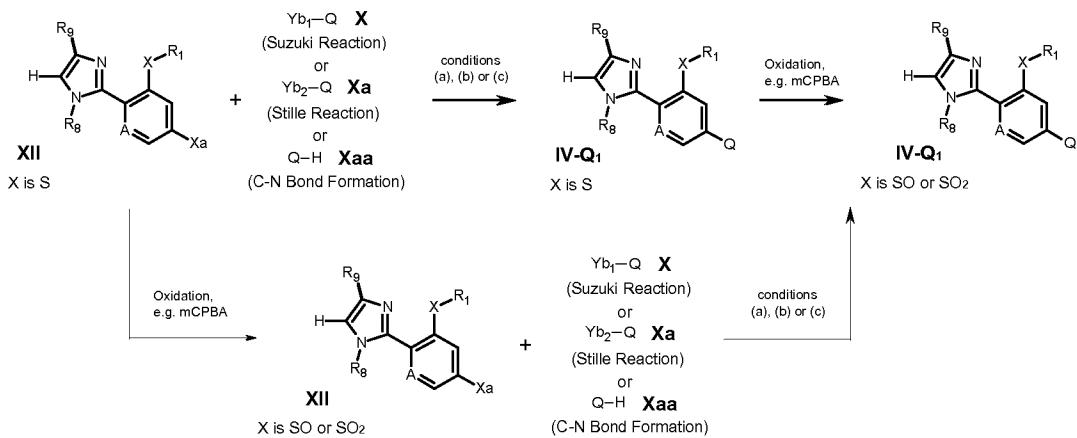
-20-



The subgroup of compounds of formula IV, wherein R_8 and R_9 are as defined above and wherein R_7 is defined as Q_1 , in which A , Q , X and R_1 are as defined above, may be defined as compounds of formula IV- Q_1 . Alternatively, compounds of formula IV- Q_1 , wherein X is SO or SO_2 ,

5

Scheme 3



(a) Suzuki reaction: Pd cat. (e.g. $Pd(PPh_3)_4$ or $Pd(dppf)Cl_2$), base (e.g. Na_2CO_3), solvent (e.g. 1,2-dimethoxyethane / water), 25-180°C.
 (b) Stille reaction: Pd cat. (e.g. $Pd(PPh_3)_4$ or $Pd(PPh_3)Cl_2$), solvent (e.g. toluene), 25-180°C.
 (c) C-N bond formation: Base (e.g. K_2CO_3 or Cs_2CO_3), optional presence of CuI , optional additive (such as N,N' -dimethylethylenediamine), solvent (e.g. N,N -dimethylformamide DMF or N -methylpyrrolidone NMP), 25-180°C.

10 may be prepared (scheme 3) by a Suzuki reaction, which involves for example, reacting compounds of formula XII, wherein A , R_1 , R_8 and R_9 are as defined above, and in which X is SO or SO_2 , and wherein Xa is a leaving group like, for example, chlorine, bromine or iodine (preferably bromine), or an aryl- or

-21-

alkylsulfonate such as trifluoromethanesulfonate, with compounds of formula X, wherein Q is as defined above, and wherein Y_{b1} can be a boron-derived functional group, such as for example $B(OH)_2$ or $B(OR_{b1})_2$ wherein R_{b1} can be a C_1 - C_4 alkyl 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 may be

5 catalyzed by a palladium based catalyst, for example tetrakis(triphenylphosphine)palladium(0), (1,1'bis(diphenylphosphino)ferrocene)dichloro-palladium-dichloromethane (1:1 complex) or chloro(2-dicyclohexylphosphino-2',4',6'-trisopropyl-1,1'-biphenyl)[2-(2'-amino-1,1'-biphenyl)]palladium(II) (XPhos palladacycle), in presence of a base, like sodium carbonate, tripotassium phosphate or cesium fluoride, in a solvent or a solvent mixture, like, for example dioxane, acetonitrile, N,N-dimethyl-
10 formamide, a mixture of 1,2-dimethoxyethane and water or of dioxane/water, or of toluene/water, preferably under inert atmosphere. The reaction temperature can preferentially range from room temperature to the boiling point of the reaction mixture, or the reaction may be performed under microwave irradiation. Such Suzuki reactions are well known to those skilled in the art and have been reviewed, for example, in *J. Orgmet. Chem.* 576, 1999, 147–168.

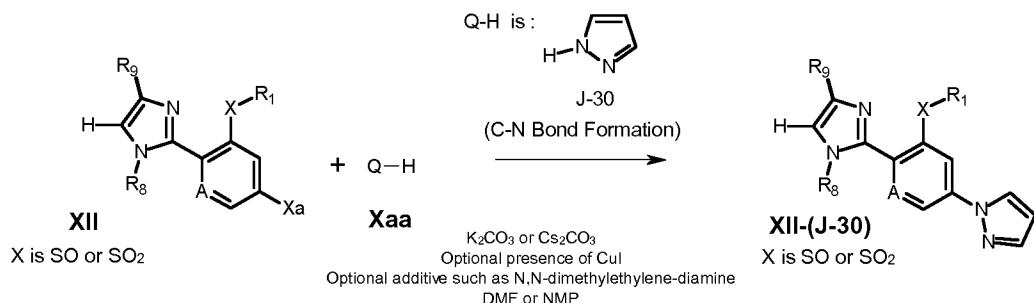
15 Alternatively compounds of formula IV-Q₁, wherein X is SO or SO_2 , may be prepared by a Stille reaction between compounds of formula Xa, wherein Q is as defined above, and wherein Y_{b2} is a trialkyl tin derivative, preferably tri-n-butyl tin or tri-methyl-tin, and compounds of formula XII, wherein A, R₁, R₈ and R₉ are as defined above, and in which X is SO or SO_2 , and wherein Xa is a leaving group like, for example, chlorine, bromine or iodine (preferably bromine), or an aryl- or alkylsulfonate
20 such as trifluoromethanesulfonate. Such Stille reactions are usually carried out in the presence of a palladium catalyst, for example tetrakis(triphenylphosphine)palladium(0), or bis(triphenylphosphine) palladium(II) dichloride, in an inert solvent such as N,N-dimethylformamide, acetonitrile, toluene 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
25 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.

When Q is a five- to six-membered, aromatic, partially saturated or fully saturated ring system linked via a nitrogen atom to the ring which contains the group A, then compounds of formula IV-Q₁, wherein

30 X is SO or SO_2 , may be prepared from compounds of formula XII, wherein A, R₁, R₈ and R₉ are as defined above, and in which X is SO or SO_2 , and wherein Xa is a leaving group like, for example, chlorine, bromine or iodine (preferably bromine), or an aryl- or alkylsulfonate such as trifluoromethanesulfonate, by reaction with a heterocycle Q-H (which contains an appropriate NH functionality) Xaa, wherein Q is as defined above, in the presence of a base, such as potassium carbonate K_2CO_3 or cesium carbonate Cs_2CO_3 , optionally in the presence of a copper catalyst, for example copper(I) iodide, with or without an additive such as L-proline, N,N'-dimethylcyclohexane-1,2-diamine or N,N'-dimethylethylene-diamine, in an inert solvent such as N-methylpyrrolidone NMP or

-22-

N,N-dimethylformamide DMF at temperatures between 30-150°C, optionally under microwave irradiation. Such a reaction (C-N Bond Formation) is illustrated below for the heterocycle Q-H J-30, wherein J30 is as defined above,



5 to give compounds of formula XII-(J-30), a particular sub-group of compounds of formula XII, wherein A, R₁, R₈ and R₉ are as previously defined.

Oxidation of compounds of formula XII, wherein A, R₁, R₈ and R₉ are as defined above, and in which X is S (sulfide), and wherein Xa is a leaving group like, for example, chlorine, bromine or iodine

10 (preferably bromine), or an aryl- or alkylsulfonate such as trifluoromethanesulfonate, with a suitable oxidizing agent, into compounds of formula XII, wherein X is SO or SO₂ may be achieved under conditions already described above.

A large number of compounds of the formula X, Xa and Xaa are commercially available or can be prepared by those skilled in the art.

Alternatively, compounds of formula IV-Q₁, wherein X is SO or SO₂, may be prepared from

15 compounds of formula XII, wherein X is S (sulfide) by involving the same chemistry as described above, but by changing the order of the steps (i.e. by running the sequence XII (X is S) to IV-Q₁ (X is S) via Suzuki, Stille or C-N bond formation, followed by an oxidation step to form IV-Q₁ (X is SO or SO₂).

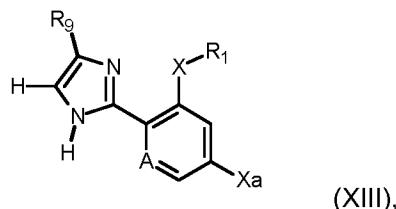
In the particular situation within scheme 3 when Q is an optionally substituted triazole linked via a

20 nitrogen atom to the ring which contains the group A, then compounds of formula IV-Q₁, wherein X is S, SO or SO₂, may be prepared from compounds of formula XII, wherein A, R₁, R₈ and R₉ are as defined above, and in which X is S, SO or SO₂, and wherein Xa is a leaving group like, for example, chlorine, bromine or iodine (preferably bromine), or an aryl- or alkylsulfonate such as trifluoromethanesulfonate, by reaction with an optionally substituted triazole Q-H (which contains an appropriate NH functionality) Xaa, wherein Q is N-linked triazolyl, in solvents such as alcohols (eg. methanol, ethanol, isopropanol, or higher boiling linear or branched alcohols), pyridine or acetic acid, optionally in the presence of an additional base, such as potassium carbonate K₂CO₃ or cesium carbonate Cs₂CO₃, optionally in the presence of a copper catalyst, for example copper(I) iodide, at temperatures between 30-180°C, optionally under microwave irradiation.

-23-

Compounds of formula XII, wherein A, R₁, R₈ and R₉ are as defined above, and in which X is S (sulfide), and wherein Xa is a leaving group like, for example, chlorine, bromine or iodine (preferably bromine), or an aryl- or alkylsulfonate such as trifluoromethanesulfonate, can be prepared by reacting

5 a compound of formula XIII

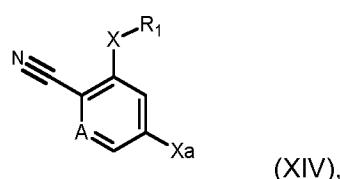


or a salt and/or a tautomer thereof, wherein Xa, A, R₁ and R₉ are as defined above, and in which X is S (sulfide), with an alkylating agent of the formula VIII



10 wherein R₈ is as defined above, and wherein L_{G2} is a halogen (especially bromine or iodine), or a leaving group OSO₂R₃₈, wherein R₃₈ is C₁-C₆alkyl, C₁-C₆haloalkyl, or phenyl optionally substituted by nitro or C₁-C₃alkyl (especially a sulfonate such as mesylate, triflate or tosylate) or a sulfate (forming the alkylating agent VIII dimethylsulfate, in the particular situation where R₈ is methyl), preferably in the presence of a suitable base, such as sodium hydride or sodium, potassium or cesium carbonate, 15 in an inert solvent such as tetrahydrofuran, dioxane, acetonitrile, N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone or dimethyl sulfoxide, at temperatures between 20-150°C.

Compounds of formula XIII, or a salt and/or a tautomer thereof, wherein Xa, A, R₁ and R₉ are as defined above, and in which X is S (sulfide), can be prepared by reacting a nitrile compound of 20 formula XIV

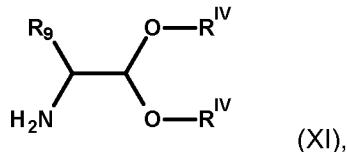


wherein Xa, A and R₁ are as defined above, and in which X is S (sulfide), sequentially with

i) a catalytic amount, preferably 0.01 to 0.5 equivalent, of a base such as an alkoxide, preferably 25 sodium methoxide NaOMe or sodium ethoxide NaOEt, in an alcoholic solvent, such as methanol or ethanol, at temperatures between 0-100°C, to generate an imidate intermediate of the formula INT₃ (or a salt and/or a tautomer thereof); followed by

-24-

ii) acidification of the reaction mixture with, for example, acetic acid or the like, and treatment with an aminoacetal reagent of formula XI



or a salt thereof, wherein R^{IV} is $\text{C}_1\text{-C}_6\text{alkyl}$ and R_9 is as defined above, at temperatures between 0-

5 150°C, to generate an amidine-acetal intermediate of the formula INT_4 (or a salt and/or a tautomer thereof); followed by

ii) deprotection of the acetal with, for example, aqueous hydrochloric acid or the like, and concomitant cyclization, at temperatures between 0-150°C, to form the compound of the formula XIII, or a salt and/or a tautomer thereof. The described process to prepare compounds of the formula XIII from

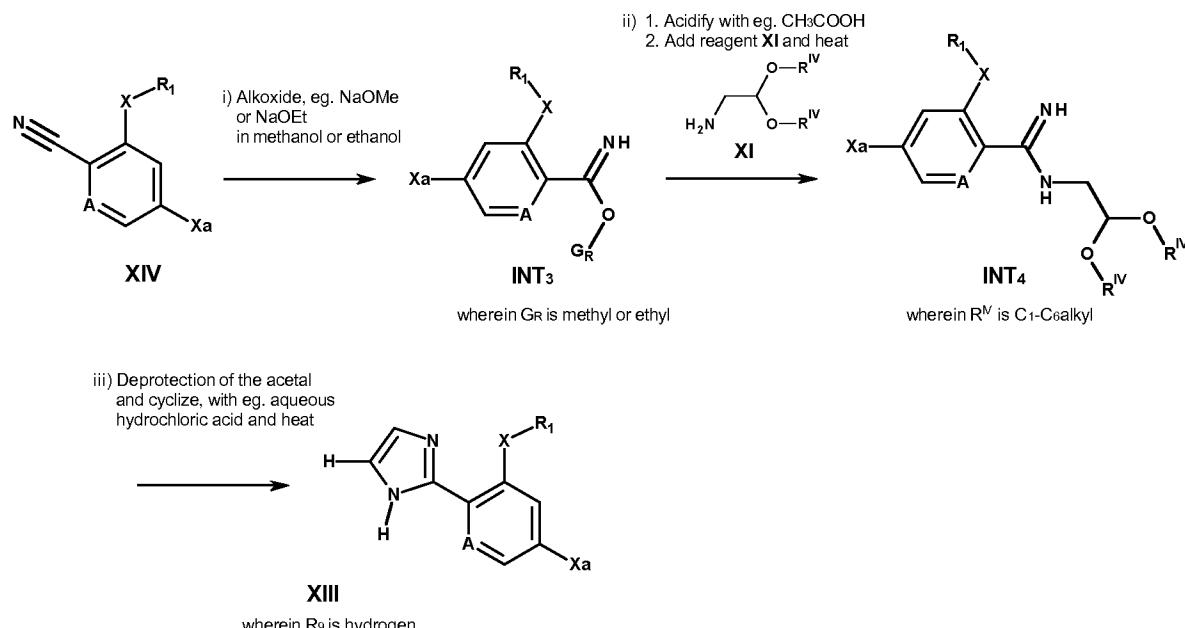
10 compounds of the formula XIV may include isolation and purification of the intermediates INT_3 and

INT_4 , (which may be isolated as free bases or as salts (e.g. a hydrohalide salt, more specifically a hydrochloride or hydrobromide salt, or any other equivalent salt)), however, this process is

advantageously conducted as a one-pot preparation as described, for example, in M.E. Voss et al., Tetrahedron 2008, 64, 645-651. The process is summarized in scheme 4 for the particular situation

15 where R_9 is hydrogen:

Scheme 4



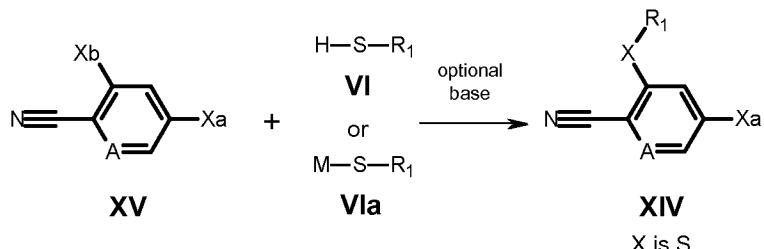
Compounds of the formula INT_3 may alternatively be prepared under conditions and variants of the Pinner reaction known to a person skilled in the art, typically by treating a compound of the formula

20 XIV with a hydrohalide acid, preferably hydrochloric acid, in presence of alcoholic reagents such as

-25-

methanol or ethanol, preferably in an inert solvent such as diethyl ether, tetrahydrofuran or dioxane, at temperatures between -40 and 50°C, preferably between -20 and 20°C.

Compounds of formula XIV, wherein X is S (sulfide), and wherein A, R₁ and Xa are as defined above,



5

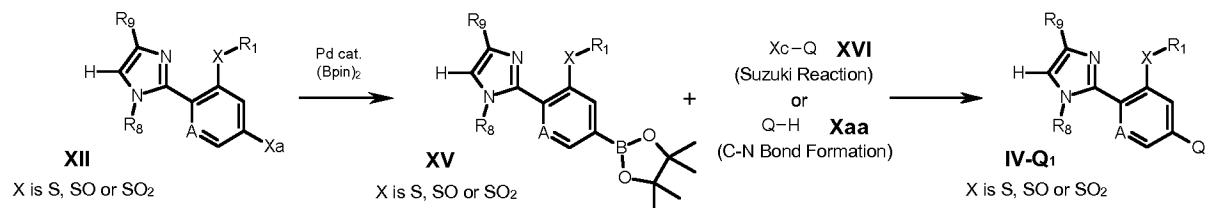
may be prepared by reacting compounds of formula XV, wherein A and Xa are as defined above, and in which Xb is a leaving group such as, for example, a halogen (preferably fluorine, chlorine or bromine) or nitro, with a compound of formula VI, or a salt thereof VIa, wherein R₁ is as defined in formula I, optionally in the presence of a suitable base, such as alkali metal carbonates, for example

10 sodium carbonate and potassium carbonate, or alkali metal hydrides such as sodium hydride, or alkali metal hydroxides such as sodium hydroxide and potassium hydroxide, optionally in the presence of a catalytic amount of an additive, such as an ammonium salt (for example tetrabutylammonium bromide TBAB), in an inert solvent at temperatures preferably between 25-120°C. Examples of solvent to be used include ethers such as THF, ethylene glycol dimethyl ether, tert-butylmethyl ether, and 1,4-dioxane, aromatic hydrocarbons such as toluene and xylene, nitriles such as acetonitrile, polar aprotic solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone or dimethyl sulfoxide, or water. Examples of salts of the compound of formula VI include compounds of the formula VIa

R₁-S-M (VIa),

20 wherein R₁ is as defined above and wherein M is, for example, sodium or potassium.

Compounds of formula IV-Q₁, wherein X is S, SO or SO₂, and in which A, Q, R₈, R₉ and R₁ are as defined above,



25 may alternatively be prepared by a Suzuki reaction, which involves for example, reacting compounds of formula XV (or analogous boronic acids and esters), wherein A, R₁, R₈ and R₉ are as defined above, and in which X is S, SO or SO₂, with compounds of formula XVI, wherein Q is as defined

-26-

above, and wherein Xc is a leaving group like, for example, chlorine, bromine or iodine (preferably bromine), or an aryl- or alkylsulfonate such as trifluoromethanesulfonate. The reaction may be catalyzed by a palladium based catalyst, for example tetrakis(triphenylphosphine)-palladium(0), (1,1'-bis(diphenylphosphino)ferrocene) dichloropalladium-dichloromethane (1:1 complex) or chloro(2-5 dicyclohexylphosphino-2',4',6'-triisopropyl-1,1'-biphenyl)[2-(2'-amino-1,1'-biphenyl)]palladium(II) (XPhos palladacycle), in presence of a base, like sodium carbonate, potassium carbonate, tripotassium phosphate or cesium fluoride, in a solvent or a solvent mixture, like, for example dioxane, acetonitrile, N,N-dimethylformamide, dimethyl sulfoxide, a mixture of 1,2-dimethoxy-ethane and water or of dioxane/water, or of toluene/water, or of dimethyl sulfoxide/ water, preferably under inert 10 atmosphere. The reaction temperature can preferentially range from room temperature to the boiling point of the reaction mixture, or the reaction may be performed under microwave irradiation. Such Suzuki reactions are well known to those skilled in the art and have been reviewed, for example, in *J.Orgmet. Chem.* 576, 1999, 147–168.

When Q is a five- to six-membered, aromatic, partially saturated or fully saturated ring system linked 15 via a nitrogen atom to the ring which contains the group A, then compounds of formula IV-Q₁, wherein X is S, SO or SO₂, may be prepared from compounds of formula XV, wherein A, R₁, R₈ and R₉ are as defined above, and in which X is S, SO or SO₂, by reaction with a heterocycle Q-H (which contains an appropriate NH functionality) Xaa, wherein Q is as defined above. The reaction, also known as Chan-Lam coupling (P. Y. S. Lam, C. G. Clark, S. Saubern, J. Adams, M. P. Winters, D. M. T. Chan, A. 20 Combs, *Tetrahedron Lett.* 1998, 39, 2941), is commonly performed with one to two equivalents of a base, like pyridine or triethylamine, in presence of one to two equivalents of a copper derivative, like for example copper (II) acetate and under an oxygen-containing atmosphere. The reaction can be run in an inert solvent, like dichloromethane, dioxane or dimethylformamide, usually at or around room 25 temperature.

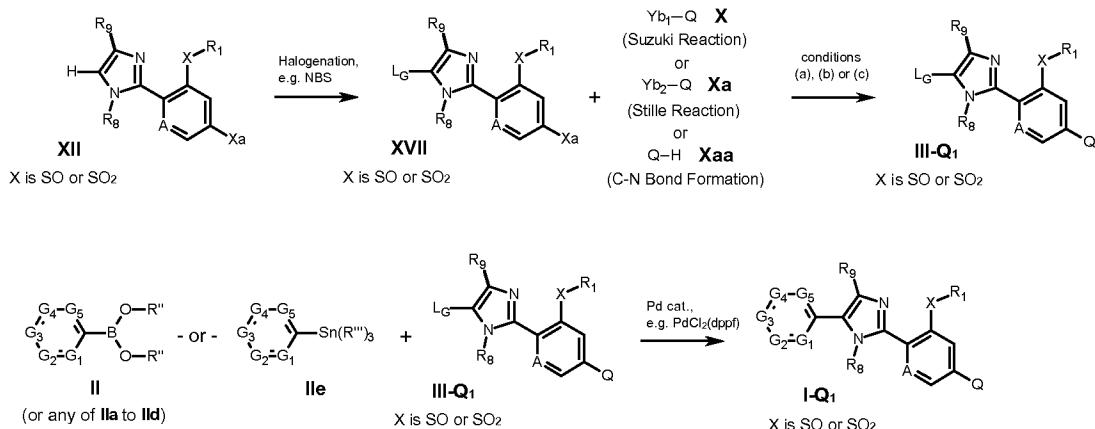
Compounds of formula XV, wherein A, R₁, R₈ and R₉ are as defined above, and in which X is S, SO or SO₂, may be prepared by reacting compounds of formula XII, wherein A, R₁, R₈ and R₉ are as defined above, and in which X is S, SO or SO₂, and wherein Xa is a leaving group like, for example, chlorine, bromine or iodine (preferably bromine), or an aryl- or alkylsulfonate such as trifluoromethanesulfonate, with bispinacol borane (Bpin)₂ under palladium catalysis. Such an introduction of a pinacolborate 30 functional group can be performed in an aprotic solvent, such as dioxane or dimethyl sulfoxide, in presence of a base, preferably a weak base, such as potassium acetate KOAc. [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II), also known as palladium dppf dichloride or Pd(dppf)Cl₂, is a common catalyst for this type of reaction. The temperature of the reaction is preferably performed between 0°C and the boiling point of the reaction mixture, or the reaction may be performed under 35 microwave irradiation.

-27-

The described 2-step process to prepare compounds of the formula IV-Q₁ from compounds of the formula XII may include isolation and optional purification of the intermediate of formula XV, however, this process is also advantageously conducted as a one-pot preparation (i.e. as a one-pot-two-steps procedure).

5 The subgroup of compounds of formula I, wherein R₈, R₉, G₁, G₂, G₃, G₄, and G₅ are as defined above and wherein R₇ is defined as Q₁, in which A, Q, X and R₁ are as defined above, may be defined as compounds of formula I-Q₁. Similarly, the subgroup of compounds of formula III, wherein R₈, R₉ and L_G are as defined above and wherein R₇ is defined as Q₁, in which A, Q, X and R₁ are as defined above, may be defined as compounds of formula III-Q₁. In yet another preparation method,

10 compounds of formula I-Q₁, wherein X is SO or SO₂,



(a) Suzuki reaction: Pd cat. (e.g. Pd(PPh₃)₄ or Pd(dppf)Cl₂), base (e.g. Na₂CO₃), solvent (e.g. 1,2-dimethoxyethane / water), 25-180°C.
 (b) Stille reaction: Pd cat. (e.g. Pd(PPh₃)₄ or Pd(PPh₃)Cl₂), solvent (e.g. toluene), 25-180°C.
 (c) C-N bond formation: Base (e.g. K₂CO₃ or Cs₂CO₃), optional presence of CuI, optional additive (such as N,N'-dimethylethylenediamine), solvent (e.g. N,N-dimethylformamide DMF or N-methylpyrrolidone NMP), 25-180°C.

may be prepared from compounds of formula XII, wherein A, R₁, R₈ and R₉ are as defined above, and in which X is SO or SO₂, and wherein Xa is a leaving group like, for example, chlorine, bromine or iodine (preferably bromine), or an aryl- or alkylsulfonate such as trifluoromethanesulfonate, through

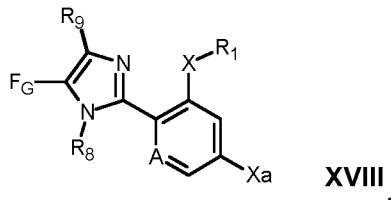
15 intermediate compounds XVII and compounds III-Q₁, involving the same chemistry and the same reagents as described above, but by changing the order of the steps. The substituent definitions for any of the compounds of formula XII, III-Q₁, II or IIe, X, Xa or Xaa, and I-Q₁ have been described above. Compounds of formula XVII, wherein X is SO or SO₂, have R₈, R₉ as well as A, Xa and R₁ defined identically as in compounds of formula XII, and L_G defined as halogen, preferably bromine or

20 iodine.

The described 2-step process to prepare compounds of the formula I-Q₁ from compounds of the formula XVII may include isolation and optional purification of the intermediate of formula III-Q₁, however, this process is also advantageously conducted as a one-pot preparation (i.e. as a one-pot-two-steps procedure).

-28-

Compounds of formula XVIII



wherein

R₈, A, X and R₁ are as defined under formula I above;

- 5 F_G is hydrogen or halogen; preferably hydrogen, bromine or iodine;
- R₉ is preferably hydrogen; and
- Xa is chlorine, bromine or iodine; preferably bromine or iodine,
- are novel and especially developed for the preparation of the compounds of formula I of this invention.
- The compounds of formula XVIII therefore constitute a further object of the invention. The preferred
- 10 substituent definitions for the compounds of formula I are also valid for the compounds of formula XVIII.

The reactants can be reacted in the presence of a base. Examples of suitable bases are alkali metal or alkaline earth metal hydroxides, alkali metal or alkaline earth metal hydrides, alkali metal or alkaline

- 15 earth metal amides, alkali metal or alkaline earth metal alkoxides, alkali metal or alkaline earth metal acetates, alkali metal or alkaline earth metal carbonates, alkali metal or alkaline earth metal dialkylamides or alkali metal or alkaline earth metal alkylsilylamides, alkylamines, alkylenediamines, free or N-alkylated saturated or unsaturated cycloalkylamines, basic heterocycles, ammonium hydroxides and carbocyclic amines. Examples which may be mentioned are sodium hydroxide,
- 20 sodium hydride, sodium amide, sodium methoxide, sodium acetate, sodium carbonate, potassium tert-butoxide, potassium hydroxide, potassium carbonate, potassium hydride, lithium diisopropylamide, potassium bis(trimethylsilyl)amide, calcium hydride, triethylamine, diisopropylethylamine, triethylenediamine, cyclohexylamine, N-cyclohexyl-N,N-dimethylamine, N,N-diethylaniline, pyridine, 4-(N,N-dimethylamino)pyridine, quinuclidine, N-methylmorpholine, benzyltrimethylammonium hydroxide
- 25 and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

The reactants can be reacted with each other as such, i.e. without adding a solvent or diluent. In most cases, however, it is advantageous to add an inert solvent or diluent or a mixture of these. If the

- reaction is carried out in the presence of a base, bases which are employed in excess, such as
- 30 triethylamine, pyridine, N-methylmorpholine or N,N-diethylaniline, may also act as solvents or diluents.

-29-

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.

5 A compound of formula I can be converted in a manner known per se into another compound of formula I by replacing one or more substituents of the starting compound of formula I in the customary manner by (an)other substituent(s) according to the invention.

Depending on the choice of the reaction conditions and starting materials which are suitable in each 10 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.

15 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.

20 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.

25 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.

30 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.

35 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

-30-

which occur in the molecule and/or depending on the configuration of non-aromatic double bonds which occur in the molecule; the invention relates to the pure isomers and also to all isomer mixtures which are possible and is to be understood in each case in this sense hereinabove and hereinbelow, even when stereochemical details are not mentioned specifically in each case.

5

Diastereomer mixtures or racemate mixtures of compounds of formula I, in free form or in salt form, which can be obtained depending on which starting materials and procedures have been chosen can be separated in a known manner into the pure diastereomers or racemates on the basis of the physicochemical differences of the components, for example by fractional crystallization, distillation 10 and/or chromatography.

Enantiomer mixtures, such as racemates, which can be obtained in a similar manner can be resolved into the optical antipodes by known methods, for example by recrystallization from an optically active solvent, by chromatography on chiral adsorbents, for example high-performance liquid

15 chromatography (HPLC) on acetyl cellulose, with the aid of suitable microorganisms, by cleavage with specific, immobilized enzymes, via the formation of inclusion compounds, for example using chiral crown ethers, where only one enantiomer is complexed, or by conversion into diastereomeric salts, for example by reacting a basic end-product racemate with an optically active acid, such as a carboxylic acid, for example camphor, tartaric or malic acid, or sulfonic acid, for example camphorsulfonic acid, 20 and separating the diastereomer mixture which can be obtained in this manner, for example by fractional crystallization based on their differing solubilities, to give the diastereomers, from which the desired enantiomer can be set free by the action of suitable agents, for example basic agents.

Pure diastereomers or enantiomers can be obtained according to the invention not only by separating 25 suitable isomer mixtures, but also by generally known methods of diastereoselective or enantioselective synthesis, for example by carrying out the process according to the invention with starting materials of a suitable stereochemistry.

N-oxides can be prepared by reacting a compound of the formula I with a suitable oxidizing agent, for example the H₂O₂/urea adduct in the presence of an acid anhydride, e.g. trifluoroacetic anhydride.

30 Such oxidations are known from the literature, for example from J. Med. Chem., 32 (12), 2561-73, 1989 or WO 00/15615.

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

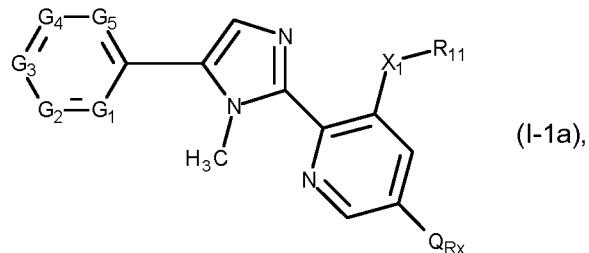
35 The compounds of formula I and, where appropriate, the tautomers thereof, in each case in free form or in salt form, can, if appropriate, also be obtained in the form of hydrates and/or include other solvents, for example those which may have been used for the crystallization of compounds which are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

-31-

The compounds according to the following Tables 1 to 6 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.

5

Table 1: This table discloses the 36 compounds 1.001 to 1.036 of the formula I-1a:



wherein X₁ is S, and Q_{Rx}, R₁₁, G₁, G₂, G₃, G₄ and G₅ are as defined below:

Table 1:

10

Comp. No	Q _{Rx}	R ₁₁	G ₁	G ₂	G ₃	G ₄	G ₅
1.001		-CH ₂ CH ₃	CH	CH	C(CF ₃)	CH	CH
1.002		-CH ₂ CH ₃	CH	CH	C(CF ₃)	CH	CH
1.003		-CH ₂ CH ₃	CH	CH	C(CF ₃)	CH	CH
1.004		-CH ₂ CH ₃	CH	CH	C(CF ₃)	CH	CH
1.005		-CH ₂ CH ₃	CH	CH	C(CF ₃)	CH	CH
1.006		-CH ₂ CH ₃	CH	CH	C(CF ₃)	CH	CH
1.007		-CH ₂ CH ₃	CH	CH	C(CF ₃)	CH	CH

-32-

Comp. No	Q _{Rx}	R ₁₁	G ₁	G ₂	G ₃	G ₄	G ₅
1.008		-CH ₂ CH ₃	CH	CH	C(CF ₃)	CH	CH
1.009		-CH ₂ CH ₃	CH	C(CF ₃)	CH	CH	CH
1.010		-CH ₂ CH ₃	CH	C(CF ₃)	CH	CH	CH
1.011		-CH ₂ CH ₃	CH	C(CF ₃)	CH	CH	CH
1.012		-CH ₂ CH ₃	CH	C(CF ₃)	CH	CH	CH
1.013		-CH ₂ CH ₃	CH	C(CF ₃)	CH	CH	CH
1.014		-CH ₂ CH ₃	CH	C(CF ₃)	CH	CH	CH
1.015		-CH ₂ CH ₃	CH	C(CF ₃)	CH	CH	CH
1.016		-CH ₂ CH ₃	CH	C(CF ₃)	CH	CH	CH
1.017		-CH ₂ CH ₃	CH	N	C(CF ₃)	CH	CH
1.018		-CH ₂ CH ₃	CH	N	C(CF ₃)	CH	CH
1.019		-CH ₂ CH ₃	CH	N	C(CF ₃)	CH	CH
1.020		-CH ₂ CH ₃	CH	N	C(CF ₃)	CH	CH
1.021		-CH ₂ CH ₃	CH	N	C(CF ₃)	CH	CH

-33-

Comp. No	Q _{Rx}	R ₁₁	G ₁	G ₂	G ₃	G ₄	G ₅
1.022		-CH ₂ CH ₃	CH	N	C(CF ₃)	CH	CH
1.023		-CH ₂ CH ₃	CH	N	C(CF ₃)	CH	CH
1.024		-CH ₂ CH ₃	CH	N	C(CF ₃)	CH	CH
1.025		-CH ₂ CH ₃	CH	N	CH	C(CF ₃)	CH
1.026		-CH ₂ CH ₃	CH	N	CH	C(CF ₃)	CH
1.027		-CH ₂ CH ₃	CH	N	CH	C(CF ₃)	CH
1.028		-CH ₂ CH ₃	CH	N	CH	C(CF ₃)	CH
1.029		-CH ₂ CH ₃	CH	N	CH	C(CF ₃)	CH
1.030		-CH ₂ CH ₃	CH	N	CH	C(CF ₃)	CH
1.031		-CH ₂ CH ₃	CH	N	CH	C(CF ₃)	CH
1.032		-CH ₂ CH ₃	CH	N	CH	C(CF ₃)	CH
1.033		-CH ₂ CH ₃	CH	CH	C(SCF ₃)	CH	CH
1.034		-CH ₂ CH ₃	CH	CH	C(SO ₂ CF ₃)	CH	CH
1.035		-CH ₂ CH ₃	CH	C(SCF ₃)	CH	CH	CH

-34-

Comp. No	Q _{Rx}	R ₁₁	G ₁	G ₂	G ₃	G ₄	G ₅
1.036		-CH ₂ CH ₃	CH	C(SO ₂ CF ₃)	CH	CH	CH

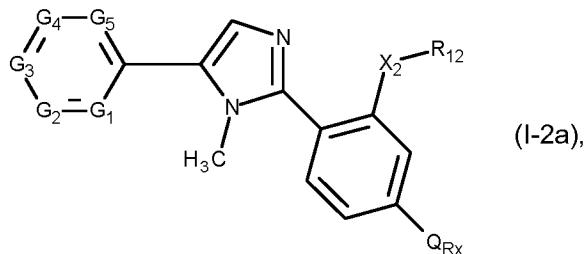
and the N-oxides of the compounds of Table 1.

Table 2: This table discloses the 36 compounds 2.001 to 2.036 of the formula I-1a, wherein X₁ is SO,

5 and Q_{Rx}, R₁₁, G₁, G₂, G₃, G₄ and G₅ are as defined in Table 1.

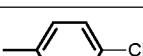
Table 3: This table discloses the 36 compounds 3.001 to 3.036 of the formula I-1a, wherein X₁ is SO₂,
and Q_{Rx}, R₁₁, G₁, G₂, G₃, G₄ and G₅ are as defined in Table 1.

Table 4: This table discloses the 4 compounds 4.001 to 4.004 of the formula I-2a:



10 wherein X₂ is S, and Q_{Rx}, R₁₂, G₁, G₂, G₃, G₄ and G₅ are as defined below:

Table 4:

Comp. No	Q _{Rx}	R ₁₂	G ₁	G ₂	G ₃	G ₄	G ₅
2.001		-CH ₂ CH ₃	CH	CH	C(CF ₃)	CH	CH
2.002		-CH ₂ CH ₃	CH	C(CF ₃)	CH	CH	CH
2.003		-CH ₂ CH ₃	CH	N	C(CF ₃)	CH	CH
2.004		-CH ₂ CH ₃	CH	N	CH	C(CF ₃)	CH

and the N-oxides of the compounds of Table 4.

-35-

Table 5: This table discloses the 4 compounds 5.001 to 5.004 of the formula I-2a, wherein X₁ is SO₂, and Q_{Rx}, R₁₂, G₁, G₂, G₃, G₄ and G₅ are as defined in Table 4.

Table 6: This table discloses the 4 compounds 6.001 to 6.004 of the formula I-2a, wherein X₁ is SO₂, and Q_{Rx}, R₁₂, G₁, G₂, G₃, G₄ and G₅ are as defined in Table 4.

5

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%.

15

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., Phyllocoptuta oleivora, Phytonomus spp, Polyphagotarsonemus spp, Psoroptes spp., Rhipicephalus spp., Rhizoglyphus spp., Sarcoptes spp., Steneotarsonemus spp, Tarsonemus spp. and Tetranychus spp.;

25

from the order *Anoplura*, for example,

Haematopinus spp., Linognathus spp., Pediculus spp., Pemphigus spp. and Phylloxera spp.;

from the order *Coleoptera*, for example,

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

35

from the order *Diptera*, for example,

-36-

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 scabrador, Acrosternum spp., Adelphocoris lineolatus, Amblypelta nitida, Bathycelia 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, Horcius nobilellus, Leptocoris spp., Lygus spp., Margarodes spp., Murgantia histrionica, Neomegalotomus spp., Nesidiocoris tenuis, Nezara spp., Nysius simulans, Oebalus insularis, Piesma spp., Piezodorus spp., Rhodnius spp., Sahlbergella singularis, Scaptocoris castanea, Scutinophara 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., Ceroplaste 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., Nephrotettix spp., Nilaparvata spp., Nippolachnus piri Mats., Odonaspis ruthae, Oregma lanigera Zehnter, Parabemisia myricae, Paratriozza 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, Zygina scutellaris, ;

from the order *Hymenoptera*, for example,

Acromyrmex, Arge spp., Atta spp., Cephus spp., Diprion spp., Diprionidae, Gilpinia polytoma, Hoplocampa spp., Lasius spp., Monomorium pharaonis, Neodiprion spp., Pogonomyrmex spp., Slenopsis invicta, Solenopsis spp. and Vespa spp.;

-37-

from the order *Isoptera*, for example,

Coptotermes spp., Cornitermes cumulans, Incisitermes spp., Macrotermes spp., Mastotermes spp., Microtermes spp., Reticulitermes spp.; Solenopsis geminata

from the order *Lepidoptera*, for example,

5 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 binotata, Cryptophlebia 10 leucotreta, Cydalima perspectalis, Cydia spp., Diaphania perspectalis, Diatraea spp., Diparopsis castanea, Earias spp., Eldana saccharina, Ephestia spp., Epinotia spp., Estigmene acrea, Etiella zinckenella, Eucosma spp., Eupoecilia ambiguella, Euproctis spp., Euxoa spp., Feltia jaculifera, Grapholita spp., Hedyia nubiferana, Heliothis spp., Hellula undalis, Herpetogramma spp., Hyphantria cunea, Keiferia lycopersicella, Lasmopalpus lignosellus, Leucoptera scitella, Lithoclethris spp., 15 Lobesia botrana, Loxostege bifidalis, Lymantria spp., Lyonetia spp., Malacosoma spp., Mamestra brassicae, Manduca sexta, Mythimna spp., Noctua spp., Operophtera spp., Orniodes indica, Ostrinia nubilalis, Pammene spp., Pandemis spp., Panolis flammea, Papaipema nebris, Pectinophora gossypiella, Perileucoptera coffeella, Pseudaletia unipuncta, Phthorimaea operculella, Pieris rapae, Pieris spp., Plutella xylostella, Prays spp., Pseudoplusia spp., Rachiplusia nu, Richia albicosta, Scirpophaga 20 spp., Sesamia spp., Sparganothis spp., Spodoptera spp., Sylepta derogata, Synanthedon spp., Thaumetopoea spp., Tortrix spp., Trichoplusia ni, Tuta absoluta, and Yponomeuta spp.;

from the order *Mallophaga*, for example,

Damalinea spp. and Trichodectes spp.;

from the order *Orthoptera*, for example,

25 Blatta spp., Blattella spp., Gryllotalpa spp., Leucophaea madera, Locusta spp., Neocurtilla hexadactyla, Periplaneta spp., Scapteriscus spp., and Schistocerca spp.;

from the order *Psocoptera*, for example,

Liposcelis spp.;

from the order *Siphonaptera*, for example,

30 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.;

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

The active ingredients according to the invention can be used for controlling, i. e. containing or destroying, pests of the abovementioned type which occur in particular on plants, especially on useful

-38-

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.

5 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, 10 such as pumpkins, cucumbers or melons; fibre plants, such as cotton, flax, hemp or jute; citrus fruit, such as oranges, lemons, grapefruit or tangerines; vegetables, such as spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes or bell peppers; Lauraceae, such as avocado, Cinnamomum or camphor; and also tobacco, nuts, coffee, eggplants, sugarcane, tea, pepper, grapevines, hops, the plantain family and latex plants.

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

For example the invention may be used on any of the following ornamental species: *Ageratum* spp., *Alonsoa* spp., *Anemone* spp., *Anisodontea capsenensis*, *Anthemis* spp., *Antirrhinum* spp., *Aster* spp.,

20 *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*, *Dorotheanthus* spp., *Eustoma grandiflorum*, *Forsythia* spp., *Fuchsia* spp., *Geranium gnaphalium*, *Gerbera* spp.,

25 *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.,

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

For example the invention may be used on any of the following vegetable species: *Allium* spp. (*A. sativum*, *A. cepa*, *A. oschaninii*, *A. Porrum*, *A. ascalonicum*, *A. fistulosum*), *Anthriscus cerefolium*, *Apium graveolus*, *Asparagus officinalis*, *Beta vulgaris*, *Brassica* spp. (*B. Oleracea*, *B. Pekinensis*, *B. rapa*), *Capsicum annuum*, *Cicer arietinum*, *Cichorium endivia*, *Cichorium* spp. (*C. intybus*, *C. endivia*),

-39-

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*,

5 *Rheum rhaboticum*, *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*,

10 *Hortensia*, rosemary, sage, St. Johnswort, mint, sweet pepper, tomato and cucumber.

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

15 *Cydia pomonella* (preferably in apples), *Emoiasca* (preferably in vegetables, vineyards), *Leptinotarsa* (preferably in potatoes) and *Chilo suppressalis* (preferably in rice).

In a further aspect, the invention may also relate to a method of controlling damage to plant and parts thereof by plant parasitic nematodes (Endoparasitic-, Semiendoparasitic- and Ectoparasitic

20 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, *Helicotylenchus multicinctus* and other *Helicotylenchus* species; Sheath and sheathoid nematodes, *Hemicycliophora* species and *Hemicriconemoides* species; *Hirshmanniella* species; Lance nematodes, *Hoploaimus* species; false rootknot nematodes, *Nacobbus* species; Needle nematodes, *Longidorus elongatus* and other *Longidorus* species; Pin nematodes, *Pratylenchus* species; Lesion nematodes, *Pratylenchus neglectus*, *Pratylenchus penetrans*, *Pratylenchus 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

-40-

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..

5

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. canaliculata*); *Vallonia* and *Zanitoides*.

10 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 15 acting toxins, such as are known, for example, from toxin-producing bacteria, especially those of the genus *Bacillus*.

20 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 25 *Xenorhabdus* spp., such as *Photorhabdus luminescens*, *Xenorhabdus nematophilus*; toxins produced by animals, such as scorpion toxins, arachnid toxins, wasp toxins and other insect-specific neurotoxins; toxins produced by fungi, such as *Streptomyces* toxins, plant lectins, such as pea lectins, barley lectins or snowdrop lectins; agglutinins; proteinase inhibitors, such as trypsin inhibitors, serine protease inhibitors, patatin, cystatin, papain inhibitors; ribosome-inactivating proteins (RIP), such as ricin, maize-RIP, abrin, luffin, saporin or bryodin; steroid metabolism enzymes, such as 30 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.

35 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

-41-

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).

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

The processes for the preparation of such transgenic plants are generally known to the person skilled in the art and are described, for example, in the publications mentioned above. Cry1-type

10 deoxyribonucleic acids and their preparation are known, for example, from WO 95/34656, EP-A-0 367 474, EP-A-0 401 979 and WO 90/13651.

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

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

Further examples of such transgenic crops are:

1. **Bt11 Maize** from Syngenta Seeds SAS, Chemin de l'Habit 27, F-31 790 St. Sauveur, France,

registration number C/FR/96/05/10. Genetically modified *Zea mays* which has been rendered resistant

30 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'Habit 27, F-31 790 St. Sauveur, France,

registration number C/FR/96/05/10. Genetically modified *Zea mays* which has been rendered resistant

35 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.

-42-

3. **MIR604 Maize** from Syngenta Seeds SAS, Chemin de l'Habit 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 5 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, 10 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.

15 7. **NK603 × MON 810 Maize** from Monsanto Europe S.A. 270-272 Avenue de Tervuren, B-1150 Brussels, Belgium, registration number C/GB/02/M3/03. Consists of conventionally bred hybrid maize varieties by crossing the genetically modified varieties NK603 and MON 810. NK603 × MON 810 Maize transgenically expresses the protein CP4 EPSPS, obtained from *Agrobacterium sp.* strain CP4, which imparts tolerance to the herbicide Roundup® (contains glyphosate), and also a Cry1Ab toxin 20 obtained from *Bacillus thuringiensis* subsp. *kurstaki* which brings about tolerance to certain Lepidoptera, include the European corn borer.

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

25 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, 30 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.

Antipathogenic substances which can be expressed by such transgenic plants include, for example, 35 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.

-43-

WO 95/33818) or protein or polypeptide factors involved in plant pathogen defence (so-called "plant disease resistance genes", as described in WO 03/000906).

Further areas of use of the compositions according to the invention are the protection of stored goods and store rooms and the protection of raw materials, such as wood, textiles, floor coverings or

5 buildings, and also in the hygiene sector, especially the protection of humans, domestic animals and productive livestock against pests of the mentioned type.

The present invention also provides a method for controlling pests (such as mosquitoes and other

disease vectors; see also http://www.who.int/malaria/vector_control/irs/en/). In one embodiment, the

10 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

15 can be used in the manufacture of) netting, clothing, bedding, curtains and tents.

In one embodiment, the method for controlling such pests comprises applying a pesticidally effective amount of the compositions of the invention to the target pests, to their locus, or to a surface or substrate so as to provide effective residual pesticidal activity on the surface or substrate. Such

20 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

25 which can be used in the manufacture of) netting, clothing, bedding, curtains and tents.

Substrates including non-woven, fabrics or netting to be treated may be made of natural fibres such as cotton, raffia, jute, flax, sisal, hessian, or wool, or synthetic fibres such as polyamide, polyester, polypropylene, polyacrylonitrile or the like. The polyesters are particularly suitable. The methods of

30 textile treatment are known, e.g. WO 2008/151984, WO 2003/034823, US 5631072, WO 2005/64072, WO2006/128870, EP 1724392, WO2005/113886 or WO 2007/090739.

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

35 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:

-44-

Table A. Examples of exotic woodborers of economic importance.

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

Table B. Examples of native woodborers of economic importance.

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

-45-

Family	Species	Host or Crop Infested
	<i>Goes tigrinus</i>	Oak
	<i>Neoclytus acuminatus</i>	Ash, Hickory, Oak, Walnut, Birch, Beech, Maple, Eastern hophornbeam, Dogwood, Persimmon, Redbud, Holly, Hackberry, Black locust, Honeylocust, Yellow-poplar, Chestnut, Osage-orange, Sassafras, Lilac, Mountain-mahogany, Pear, Cherry, Plum, Peach, Apple, Elm, Basswood, Sweetgum
	<i>Neoptychodes trilineatus</i>	Fig, Alder, Mulberry, Willow, Netleaf hackberry
	<i>Oberea ocellata</i>	Sumac, Apple, Peach, Plum, Pear, Currant, Blackberry
	<i>Oberea tripunctata</i>	Dogwood, Viburnum, Elm, Sourwood, Blueberry, Rhododendron, Azalea, Laurel, Poplar, Willow, Mulberry
	<i>Oncideres cingulata</i>	Hickory, Pecan, Persimmon, Elm, Sourwood, Basswood, Honeylocust, Dogwood, Eucalyptus, Oak, Hackberry, Maple, Fruit trees
	<i>Saperda calcarata</i>	Poplar
	<i>Strophiona nitens</i>	Chestnut, Oak, Hickory, Walnut, Beech, Maple
Scolytidae	<i>Corthylus columbianus</i>	Maple, Oak, Yellow-poplar, Beech, Boxelder, Sycamore, Birch, Basswood, Chestnut, Elm
	<i>Dendroctonus frontalis</i>	Pine

-46-

Family	Species	Host or Crop Infested
	<i>Dryocoetes betulae</i>	Birch, Sweetgum, Wild cherry, Beech, Pear
	<i>Monarthrum fasciatum</i>	Oak, Maple, Birch, Chestnut, Sweetgum, Blackgum, Poplar, Hickory, Mimosa, Apple, Peach, Pine
	<i>Phloeotribus liminaris</i>	Peach, Cherry, Plum, Black cherry, Elm, Mulberry, Mountain-ash
	<i>Pseudopityophthorus pruinosus</i>	Oak, American beech, Black cherry, Chickasaw plum, Chestnut, Maple, Hickory, Hornbeam, Hophornbeam
Sesiidae	<i>Paranthrene simulans</i>	Oak, American chestnut
	<i>Sannina uroceriformis</i>	Persimmon
	<i>Synanthedon exitiosa</i>	Peach, Plum, Nectarine, Cherry, Apricot, Almond, Black cherry
	<i>Synanthedon pictipes</i>	Peach, Plum, Cherry, Beach, Black Cherry
	<i>Synanthedon rubrofascia</i>	Tupelo
	<i>Synanthedon scitula</i>	Dogwood, Pecan, Hickory, Oak, Chestnut, Beech, Birch, Black cherry, Elm, Mountain-ash, Viburnum, Willow, Apple, Loquat, Ninebark, Bayberry
	<i>Vitacea polistiformis</i>	Grape

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

In particular, the present invention may be used to control insect pests that feed on the roots of turfgrass including white grubs (such as *Cyclocephala* spp. (e.g. masked chafer, *C. lurida*),

5

-47-

Rhizotrogus spp. (e.g. European chafer, *R. majalis*), *Cotinus spp.* (e.g. Green June beetle, *C. nitida*), *Popillia spp.* (e.g. Japanese beetle, *P. japonica*), *Phyllophaga spp.* (e.g. May/June beetle), *Ataenius spp.* (e.g. Black turfgrass ataenius, *A. spretulus*), *Maladera spp.* (e.g. Asiatic garden beetle, *M. castanea*) and *Tomarus spp.*), ground pearls (*Margarodes spp.*), mole crickets (tawny, southern, and short-winged; *Scapteriscus spp.*, *Gryllotalpa africana*) and leatherjackets (European crane fly, *Tipula spp.*).

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

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

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

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

Examples of such parasites are:

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

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

Of the order Diptera and the suborders Nematocerina and Brachycerina, for example *Aedes spp.*, *Anopheles spp.*, *Culex spp.*, *Simulium spp.*, *Eusimulium spp.*, *Phlebotomus spp.*, *Lutzomyia spp.*, *Culicoides spp.*, *Chrysops spp.*, *Hybomitra spp.*, *Atylotus spp.*, *Tabanus spp.*, *Haematopota spp.*, *Philipomyia spp.*, *Braula spp.*, *Musca spp.*, *Hydrotaea spp.*, *Stomoxyx spp.*, *Haematobia spp.*, *Morellia spp.*, *Fannia spp.*, *Glossina spp.*, *Calliphora spp.*, *Lucilia spp.*, *Chrysomyia spp.*, *Wohlfahrtia spp.*, *Sarcophaga spp.*, *Oestrus spp.*, *Hypoderma spp.*, *Gasterophilus spp.*, *Hippobosca spp.*, *Lipoptena spp.* and *Melophagus spp.*

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

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

5 Of the order Blattaria, for example *Blatta orientalis*, *Periplaneta americana*, *Blattelagermanica* and *Supella* spp..

Of the subclass Acaria (Acarida) and the orders Meta- and Meso-stigmata, for example *Argas* spp., *Ornithodoros* spp., *Otobius* spp., *Ixodes* spp., *Amblyomma* spp., *Boophilus* spp., *Dermacentor* spp.,

10 *Haemophysalis* spp., *Hyalomma* spp., *Rhipicephalus* spp., *Dermanyssus* spp., *Raillietia* spp., *Pneumonyssus* spp., *Sternostoma* spp. and *Varroa* spp..

Of the orders Actinedida (Prostigmata) and Acaridida (Astigmata), for example *Acarapis* spp.,

Cheyletiella spp., *Ornithocheyletia* spp., *Myobia* spp., *Psorergates* spp., *Demodex* spp., *Trombicula* spp.,

15 *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 *Laminoacoptes* spp..

The compositions according to the invention are also suitable for protecting against insect infestation

20 in the case of materials such as wood, textiles, plastics, adhesives, glues, paints, paper and card, leather, floor coverings and buildings.

The compositions according to the invention can be used, for example, against the following pests:

beetles such as *Hylotrupes bajulus*, *Chlorophorus pilosis*, *Anobium punctatum*, *Xestobium*

rufovillosum, *Ptilinuspecticornis*, *Dendrobium pertinax*, *Ernobius mollis*, *Priobium carpini*, *Lyctus*

25 *brunneus*, *Lyctus africanus*, *Lyctus planicollis*, *Lyctus linearis*, *Lyctus pubescens*, *Trogoxylon aequale*, *Minthesrubicollis*, *Xyleborus* spec., *Tryptodendron* spec., *Apate monachus*, *Bostrychus capucinus*, *Heterobostrychus brunneus*, *Sinoxylon* spec. and *Dinoderus minutus*, and also hymenopterans such as *Sirex juvencus*, *Urocerus gigas*, *Urocerus gigas tainus* and *Urocerus augur*, and termites such as *Kalotermes flavicollis*, *Cryptotermes brevis*, *Heterotermes indicola*, *Reticulitermes flavipes*, *30 Reticulitermes santonensis*, *Reticulitermes lucifugus*, *Mastotermes darwiniensis*, *Zootermopsis nevadensis* and *Coptotermes formosanus*, and bristletails such as *Lepisma saccharina*.

The compounds according to the invention can be used as pesticidal agents in unmodified form, but they are generally formulated into compositions in various ways using formulation adjuvants, such as

35 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

-49-

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.

5 The dilutions can be made, for example, with water, liquid fertilisers, micronutrients, biological organisms, oil or solvents.

The formulations can be prepared e.g. by mixing the active ingredient with the formulation adjuvants in order to obtain compositions in the form of finely divided solids, granules, solutions, dispersions or emulsions. The active ingredients can also be formulated with other adjuvants, such as finely divided

10 solids, mineral oils, oils of vegetable or animal origin, modified oils of vegetable or animal origin, organic solvents, water, surface-active substances or combinations thereof.

The active ingredients can also be contained in very fine microcapsules. Microcapsules contain the active ingredients in a porous carrier. This enables the active ingredients to be released into the environment in controlled amounts (e.g. slow-release). Microcapsules usually have a diameter of from

15 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
20 chemically modified polymers and starch xanthates or other polymers that are known to the person skilled in the art. Alternatively, very fine microcapsules can be formed in which the active ingredient is contained in the form of finely divided particles in a solid matrix of base substance, but the microcapsules are not themselves encapsulated.

The formulation adjuvants that are suitable for the preparation of the compositions according to the

25 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
30 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-

-50-

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,

5 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.

10 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.

15 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 20 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-25 alkylphosphate esters; and also further substances described e.g. in McCutcheon's Detergents and Emulsifiers Annual, MC Publishing Corp., Ridgewood New Jersey (1981).

30 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.

35 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

-51-

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 C₈-C₂₂ fatty acids, especially the methyl derivatives of C₁₂-C₁₈ fatty acids, for example the methyl esters of lauric

5 acid, palmitic acid and oleic acid (methyl laurate, methyl palmitate and methyl oleate, respectively).

Many oil derivatives are known from the Compendium of Herbicide Adjuvants, 10th Edition, Southern Illinois University, 2010.

The inventive compositions generally comprise from 0.1 to 99 % by weight, especially from 0.1 to 95 % by weight, of compounds of the present invention and from 1 to 99.9 % by weight of a formula-

10 tion adjuvant which preferably includes from 0 to 25 % by weight of a surface-active substance.

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

The rates of application vary within wide limits and depend on the nature of the soil, the method of application, the crop plant, the pest to be controlled, the prevailing climatic conditions, and other

15 factors governed by the method of application, the time of application and the target crop. As a general guideline compounds may be applied at a rate of from 1 to 2000 l/ha, especially from 10 to 1000 l/ha.

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

Emulsifiable concentrates:

20 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:

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

Suspension concentrates:

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

Wettable powders:

active ingredient: 0.5 to 90 %, preferably 1 to 80 %
35 surface-active agent: 0.5 to 20 %, preferably 1 to 15 %
solid carrier: 5 to 95 %, preferably 15 to 90 %

-52-

Granules:

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

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

5

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

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

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

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

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

-53-

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

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

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

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

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

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

<u>Coated granules</u>	
------------------------	--

-54-

Active ingredients	8 %
polyethylene glycol (mol. wt. 200)	3 %
Kaolin	89 %

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

Suspension concentrate

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

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

5 from which suspensions of any desired dilution can be obtained by dilution with water. Using such dilutions, living plants as well as plant propagation material can be treated and protected against infestation by microorganisms, by spraying, pouring or immersion.

Flowable concentrate for seed treatment

active ingredients	40 %
propylene glycol	5 %
copolymer butanol PO/EO	2 %
Tristyrenepheno 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 %

-55-

Water	45.3 %
-------	--------

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

5 Slow Release Capsule Suspension

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

10 15 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 20 dispersible concentrate (DC), a wettable powder (WP), a soluble granule (SG) or any technically feasible formulation in combination with agriculturally acceptable adjuvants.

Preparatory Examples:

25 "Mp" means melting point in °C. Free radicals represent methyl groups. ¹H NMR measurements were recorded on a Brucker 400MHz spectrometer, chemical shifts are given in ppm relevant to a TMS standard. Spectra measured in deuterated solvents as indicated. Common abbreviations: aq = aqueous, min = minute, h = hour, sat = saturated, R_t = retention time, mCPBA = meta-chloroperoxybenzoic acid, MeOH = methanol, NaHCO₃ = sodium hydrogen carbonate, Na₂CO₃ = sodium carbonate, HCl = hydrogen chloride, NBS = N-bromosuccinimide, PdCl₂(dppf) = [1,1-bis (30 (diphenylphosphino)ferrocene]dichloropalladium(II). Either one of the LCMS or GCMS methods below was used to characterize the compounds. The characteristic LCMS/GCMS values obtained for each compound were the retention time ("R_t", recorded in min) and the measured molecular ion (M)⁺ or (M+H)⁺.

-56-

LCMS or GCMS Methods:

Method 1:

SC BASE, Apparatus: Agilent 1100 Bin. Pump: G1312A, degasser; autosampler, ColCom, DAD: Agilent G1315B, 220-320 nm, MSD: Agilent LC/MSD G6130B ESI, pos/neg 100-800; ELSD PL-ELS2100 gas flow 1.1 ml/min, gas temp: 50°C ; column: Waters XSelect™ C18, 30x2.1mm, 3.5μ, Temp: 25 °C, Flow: 1 mL/min, Gradient: $t_0 = 2\% A$, $t_{1.6\text{min}} = 98\% A$, $t_{3\text{min}} = 98\% A$, Posttime: 1.3 min, Eluent A: 95% acetonitrile + 5% 10mM ammonium bicarbonate in water in acetonitrile, Eluent B: 10mM ammonium bicarbonate in water (pH=9.5).

Method 2:

AN BASE, Apparatus: Agilent 1100 Bin. Pump: G1312A, degasser; autosampler, ColCom, DAD: Agilent G1315B, 220-320 nm, MSD: Agilent LC/MSD G6130B ESI, pos/neg 100-800; ELSD PL-ELS2100 gas flow 1.1 ml/min, gas temp: 50°C; column: Waters XSelect™ C18, 50x2.1mm, 3.5μ, Temp: 25 °C, Flow: 0.8 mL/min, Gradient: $t_0 = 2\% A$, $t_{3.5\text{min}} = 98\% A$, $t_{6\text{min}} = 98\% A$, Posttime: 2 min, Eluent A: 95% acetonitrile + 5% 10mM ammonium bicarbonate in water in acetonitrile, Eluent B: 10mM ammonium bicarbonate in water (pH=9.5).

Method 3:

40S20, Instrument: GC: Agilent 6890N and MS: 5973 MSD, EI-positive, Det.temp.: 280°C Mass range: 50-550; Column: RXi-5MS 20m, ID 180μm, df 0.18μm; Average velocity: 50 cm/s; Injection vol: 1 μl; Injector temp: 250°C; Split ratio: 100/1; Carrier gas: He; Initial temp: 40°C; Initial time: 1.5 min; Solvent delay: 1.0 min; Rate 40°C/min; Final temp 250°C; Final time 2.0 min.

Method 4:

C20, Instrument: GC: Agilent 6890N and MS: 5973 MSD, EI-positive, Det.temp.: 280°C Mass range: 50-550; Column: RXi-5MS 20m, ID 180μm, df 0.18μm; Average velocity: 50 cm/s; Injection vol: 1 μl; Injector temp: 250°C; Split ratio: 100/1; Carrier gas: He; Initial temp: 100°C; Initial time: 1.0 min; Solvent delay: 1.0 min; Rate 75°C/min; Final temp 280°C; Final time 4.3 min.

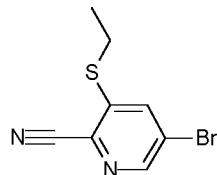
Method 5:

Spectra were recorded on a Mass Spectrometer from Waters (ZQ Single quadrupole mass spectrometer) equipped with an electrospray source (Polarity: positive or negative ions, Capillary: 3.00 kV, Cone range: 30-60 V, Extractor: 2.00 V, Source Temperature: 150°C, Desolvation Temperature: 350°C, Cone Gas Flow: 0 L/Hr, Desolvation Gas Flow: 650 L/Hr, Mass range: 100 to 900 Da) and an Acquity UPLC from Waters: Binary pump, heated column compartment and diode-array detector. Solvent degasser, binary pump, heated column compartment and diode-array detector. Column: Waters UPLC HSS T3 , 1.8 μm, 30 x 2.1 mm, Temp: 60 °C, DAD Wavelength range (nm): 210 to 500, Solvent Gradient: A = water + 5% MeOH + 0.05 % HCOOH, B= Acetonitrile + 0.05 % HCOOH: gradient: 0 min 0% B, 100%A; 1.2-1.5min 100% B; Flow (ml/min) 0.85.

-57-

EXAMPLE P1: Preparation of 3-ethylsulfonyl-2-[1-methyl-5-[6-(trifluoromethyl)-3-pyridyl]imidazol-2-yl]-5-[4-(trifluoromethyl)phenyl]pyridine (compound P1)

Step 1: Preparation of 5-bromo-3-ethylsulfanyl-pyridine-2-carbonitrile



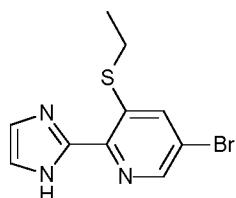
5

Under nitrogen atmosphere, a solution of 5-bromo-3-fluoro-pyridine-2-carbonitrile (1.005 g, 5.00 mmol) in dry N,N-dimethylformamide (15 ml) was cooled to -50°C and to this was added dropwise a freshly prepared solution of sodium ethanethiolate (0.429 g, 5.10 mmol) in dry N,N-dimethylformamide (5 ml). After stirring at -50°C for 30 min, the cooling bath was removed and the mixture was allowed to warm 10 to room temperature. Water and brine were added and the aqueous mixture was extracted with ethyl acetate. After separation, the organic layer was washed twice with brine, dried over sodium sulfate and concentrated. The crude product was purified over silica by flash column chromatography (0 to 40% gradient of ethyl acetate in heptane) to afford the title compound (0.93 g) as a solid. GCMS (method 3): 242/244 (M)⁺, retention time 6.33 min. ¹H-NMR (CDCl₃, ppm) 1.41 (3H), 3.06 (2H), 7.82 (1H), 8.49 (1H).

Alternative preparation method:

Under nitrogen atmosphere, a solution of 5-bromo-3-nitro-pyridine-2-carbonitrile (45.35 g, 199 mmol) in dry N,N-dimethylformamide (500 ml) was cooled to -50°C and to this was added dropwise a freshly 20 prepared solution of sodium ethanethiolate (17.4 g, 207 mmol) in dry N,N-dimethylformamide (200 ml) (not a completely clear solution). After complete addition, stirring was continued at -50°C for 30 min. Water and brine were added and the cooling bath was removed. The aqueous mixture was extracted with ethyl acetate. After separation, the water layer was extracted with ethyl acetate once more. The combined the organic layers were washed twice with brine, dried over sodium sulfate and 25 concentrated. The crude product was purified over silica by flash column chromatography (0 to 25% gradient of ethyl acetate in heptane) to afford the title compound (33.9 g) as a solid.

Step 2: Preparation of 5-bromo-3-ethylsulfanyl-2-(1H-imidazol-2-yl)pyridine



-58-

To a suspension of 5-bromo-3-ethylsulfanyl-pyridine-2-carbonitrile (10.0 g, 41.1 mmol) in methanol (80 ml) was added a solution of sodium methoxide in methanol (2.132 mmol, 0.40 ml, 30 wt%) and the mixture was stirred at ambient temperature overnight. A clear orange solution was obtained.

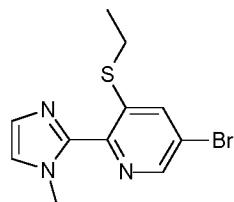
2,2-Diethoxy-ethanamine (5.95 g, 44.7 mmol, 6.5 ml) and acetic acid (5.25 g, 87 mmol, 5.0 ml) were

5 added and the reaction mixture was heated at reflux temperature for 45 min. 6N HCl (aq) (22 ml) was added and the mixture was heated at reflux temperature for 2.5 h. The reaction mixture was

concentrated. To the residue was added saturated aqueous sodium bicarbonate solution to make the water-layer slightly basic. The aqueous mixture was extracted twice with ethyl acetate. The combined organic layers were dried over sodium sulfate and concentrated. The crude product was purified over

10 silica by flash column chromatography (10 to 100% gradient of ethyl acetate in heptane) to afford the title compound (2.63 g) as a solid. LCMS (method 1): 284/286 (M+H)⁺, retention time 2.08 min. ¹H-NMR (DMSO-d6, ppm) 1.47 (3H), 3.00 (2H), 7.15 (1H), 7.38 (1H), 7.70 (1H), 8.31 (1H).

Step 3: Preparation of 5-bromo-3-ethylsulfanyl-2-(1-methylimidazol-2-yl)pyridine (compound P2.1)



15

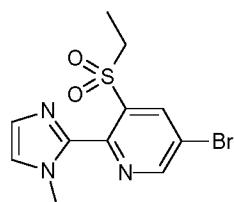
Under nitrogen, a solution of 5-bromo-3-ethylsulfanyl-2-(1H-imidazol-2-yl)pyridine (11.06 g, 38.9 mmol) in dry tetrahydrofuran (300 ml) was cooled in ice. To this was added sodium hydride (2.335 g, 58.4 mmol, 60 %) (vigorous gas evolution). When gas evolution had ceased, the cooling bath was

removed and stirring was continued at ambient temperature for 15 min. Iodomethane (10.44 g, 73.6 mmol, 4.6 ml) was added and the mixture was stirred at ambient temperature for 6 hours. An almost

20 clear brown solution was obtained. Water was carefully added, followed by brine and the aqueous mixture was extracted twice with ethyl acetate. The combined organic layers were dried over sodium sulfate and concentrated. The crude product was purified over silica by flash column chromatography (10 to 100% gradient of ethyl acetate in heptane) to afford the title compound (10.5 g) a solid. LCMS

25 (method 1): 298/300 (M+H)⁺, retention time 2.04 min. ¹H-NMR (CDCl₃, ppm) 1.37 (3H), 2.92 (2H), 3.85 (3H), 6.99 (1H), 7.22 (1H), 7.73 (1H), 8.41 (1H).

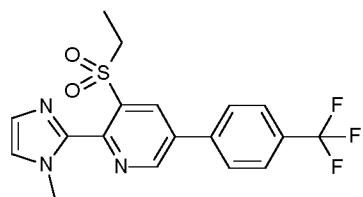
Step 4: Preparation of 5-bromo-3-ethylsulfonyl-2-(1-methylimidazol-2-yl)pyridine (compound P2.2)



-59-

A solution of 5-bromo-3-ethylsulfanyl-2-(1-methylimidazol-2-yl)pyridine (10.5 g, 35.2 mmol) in dichloromethane (300 ml) was cooled in ice and to this was added portionwise mCPBA (18.23 g, 73.9 mmol, 70 %). After complete addition, the mixture was stirred at 0°C for 15 min., followed by stirring at room temperature for 4 h. The reaction mixture was diluted with dichloromethane, washed three times 5 with saturated aqueous NaHCO₃ (first washing contained some sodium thiosulfate to destroy excess mCPBA), dried over sodium sulfate and concentrated. The crude product was purified over silica by flash column chromatography (10 to 100% gradient of ethyl acetate in heptane) to afford the title compound (10.1 g) as a solid, mp 135-136.5°C. LCMS (method 2): 330/332 (M+H)⁺, retention time 2.89 min. ¹H-NMR (CDCl₃, ppm) 1.35 (3H), 3.69 (3H), 3.94 (2H), 7.05 (1H), 7.14 (1H), 8.60 (1H), 8.93 10 (1H).

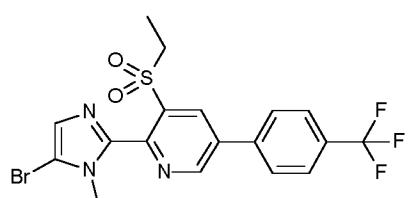
Step 5: Preparation of 3-ethylsulfonyl-2-(1-methylimidazol-2-yl)-5-[4-(trifluoromethyl)phenyl]pyridine (compound P2.3)



15 In a microwave vial, a mixture of 5-bromo-3-ethylsulfonyl-2-(1-methylimidazol-2-yl)pyridine (330 mg, 0.999 mmol), 4-(trifluoromethyl)phenylboronic acid (285 mg, 1.499 mmol) and potassium carbonate (414 mg, 3.00 mmol) in 1,2-dimethoxyethane (10 ml) and water (2.5 ml) was flushed with argon for 5 min. To this was added PdCl₂(dppf) (36.6 mg, 0.050 mmol), the vial was closed and the mixture was heated in the microwave at 120°C for 30 min. The crude reaction mixture was partitioned between 20 ethyl acetate and water/brine (1/3). After washing and separation, the organic layer was dried over sodium sulfate and concentrated. The crude product was purified over silica by flash column chromatography (0 to 4% gradient of methanol in dichloromethane) to afford the title compound (329 mg) as a solid, mp 167-169°C. LCMS (method 2): 396 (M+H)⁺, retention time 3.61 min. ¹H-NMR (CDCl₃, ppm) 1.37 (3H), 3.74 (3H), 3.96 (2H), 7.08 (1H), 7.17 (1H), 7.82 (4H), 8.67 (1H), 9.11 (1H).

25

Step 6: Preparation of 2-(5-bromo-1-methyl-imidazol-2-yl)-3-ethylsulfonyl-5-[4-(trifluoromethyl)phenyl]pyridine (compound P2.5)

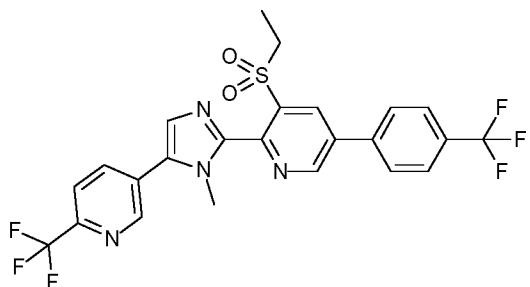


-60-

To a solution of 3-ethylsulfonyl-2-(1-methylimidazol-2-yl)-5-[4-(trifluoromethyl)phenyl]pyridine (568 mg, 1.437 mmol) in chloroform (15 ml) was added NBS (261 mg, 1.465 mmol) and the mixture was heated at 60°C (oil bath temp) for 1 h. The reaction mixture was concentrated and the crude product was purified over silica by flash column chromatography (10 to 100% gradient of ethyl acetate in heptane) to afford the title compound (527 mg) as a solid, mp 182-184°C. LCMS (method 2): 474/476 (M+H)⁺, retention time 4.08 min. ¹H-NMR (CDCl₃, ppm) 1.37 (3H), 3.68 (3H), 3.93 (2H), 7.17 (1H), 7.82 (4H), 8.67 (1H), 9.12 (1H).

Step 7: Preparation of 3-ethylsulfonyl-2-[1-methyl-5-[6-(trifluoromethyl)-3-pyridyl]imidazol-2-yl]-5-[4-

(trifluoromethyl)phenyl]pyridine (compound P1)

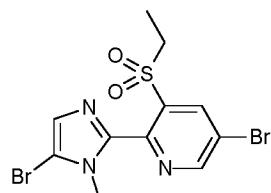


In a microwave vial, a mixture of 2-(5-bromo-1-methyl-imidazol-2-yl)-3-ethylsulfonyl-5-[4-(trifluoromethyl)phenyl]pyridine (450 mg, 0.949 mmol), (6-(trifluoromethyl)pyridin-3-yl)boronic acid (272 mg, 1.423 mmol) and potassium carbonate (393 mg, 2.85 mmol) in 1,2-dimethoxyethane (10 ml) and

water (2.5 ml) was flushed with argon for 5 min. To this was added PdCl₂(dppf) (34.7 mg, 0.047 mmol), the vial was closed and the mixture was heated in the microwave at 120°C for 1 h. The crude reaction mixture was diluted with ethyl acetate, washed with water/brine (1/3), dried over sodium sulfate and concentrated. The crude product was purified over silica by flash column chromatography (20 to 100% gradient of ethyl acetate in heptane) to afford the title compound P1 (319 mg) as a solid, mp 182-184°C. LCMS (method 2): 541 (M+H)⁺, retention time 4.09 min. ¹H-NMR (CDCl₃, ppm) 1.41 (3H), 3.71 (3H), 3.98 (2H), 7.38 (1H), 7.82 (1H), 8.01 (1H), 8.70 (1H), 8.91 (1H), 9.16 (1H).

EXAMPLE P2: Preparation of 3-ethylsulfonyl-2-[1-methyl-5-[4-(trifluoromethyl)phenyl]imidazol-2-yl]-5-[4-(trifluoromethyl)phenyl]pyridine (compound P2)

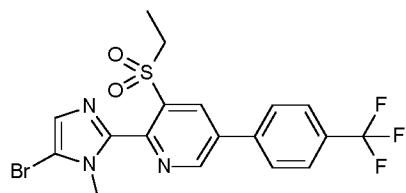
Step 1: Preparation of 5-bromo-2-(5-bromo-1-methyl-imidazol-2-yl)-3-ethylsulfonyl-pyridine (compound P2.4)



-61-

To a solution of 5-bromo-3-ethylsulfonyl-2-(1-methylimidazol-2-yl)pyridine (660 mg, 1.999 mmol) in chloroform (10 ml) was added NBS (363 mg, 2.039 mmol) and the mixture was heated at 60°C (oil bath temp) for 1 h. The reaction mixture was concentrated and the crude product was purified over silica by flash column chromatography (10 to 75% gradient of ethyl acetate in heptane) to afford the title compound (643 mg) as a solid, mp 115-118°C. GCMS (method 4): 407/409/411 (M)⁺, retention time 4.80 min. ¹H-NMR (CDCl₃, ppm) 1.35 (3H), 3.62 (3H), 3.89 (2H), 7.14 (1H), 8.60 (1H), 8.94 (1H).

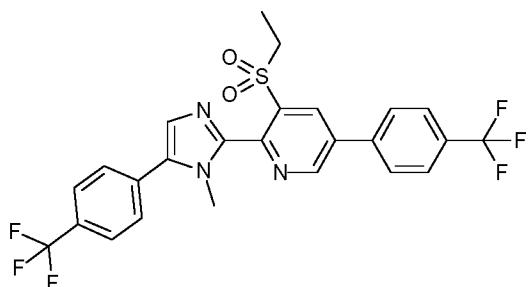
Step 2: Preparation of 2-(5-bromo-1-methyl-imidazol-2-yl)-3-ethylsulfonyl-5-[4-(trifluoromethyl)phenyl]pyridine (compound P2.5)



10

In a reaction vial, a mixture of 5-bromo-2-(5-bromo-1-methyl-imidazol-2-yl)-3-ethylsulfonyl-pyridine (205 mg, 0.501 mmol), (4-(trifluoromethyl)phenyl)boronic acid (105 mg, 0.551 mmol) and potassium carbonate (208 mg, 1.503 mmol) in 1,2-dimethoxyethane (4 ml) and water (1 ml) was flushed with argon for 5 min. To this was added PdCl₂(dppf) (14 mg, 0.019 mmol), the vial was closed and the mixture was heated at 60°C (oil bath temp) for 90 min. The crude reaction mixture was partitioned between ethyl acetate and water/brine (1/3). After washing and separation, the organic layer was dried over sodium sulfate and concentrated. The crude product was purified over silica by flash column chromatography (10 to 75% gradient of ethyl acetate in heptane) to afford the title compound (191 mg) as a solid, mp 182-184°C. LCMS (method 2): 474/476 (M+H)⁺, retention time 4.01 min. ¹H-NMR (CDCl₃, ppm) 1.37 (3H), 3.68 (3H), 3.93 (2H), 7.17 (1H), 7.82 (4H), 8.67 (1H), 9.12 (1H).

Step 3: Preparation of 3-ethylsulfonyl-2-[1-methyl-5-[4-(trifluoromethyl)phenyl]imidazol-2-yl]-5-[4-(trifluoromethyl)phenyl]pyridine (title compound P2)



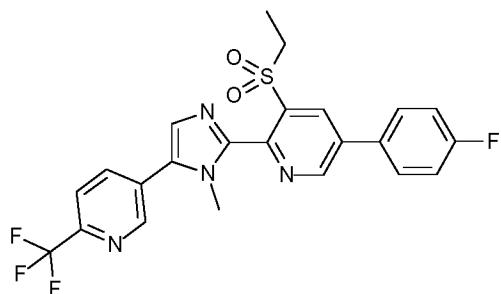
25 In a reaction vial, a mixture of 2-(5-bromo-1-methyl-imidazol-2-yl)-3-ethylsulfonyl-5-[4-(trifluoromethyl)phenyl]pyridine (182 mg, 0.384 mmol), (4-(trifluoromethyl)phenyl)boronic acid (100 mg, 0.527 mmol) and potassium carbonate (159 mg, 1.151 mmol) in 1,2-dimethoxyethane (3 ml) and water (0.75 ml)

-62-

was flushed with argon for 5 min. To this was added $\text{PdCl}_2(\text{dppf})$ (14 mg, 0.019 mmol), the vial was closed and the mixture was heated at 90°C (oil bath temp) for 90 min. The crude reaction mixture was partitioned between ethyl acetate and water/brine (1/3). After washing and separation, the organic layer was dried over sodium sulfate and concentrated. The crude product was purified over silica by 5 flash column chromatography (10 to 75% gradient of ethyl acetate in heptane) to afford the title compound P2 (115 mg) as a solid, mp 188-190°C. LCMS (method 2): 540 ($\text{M}+\text{H}$)⁺, retention time 4.25 min. ¹H-NMR (CDCl_3 , ppm) 1.40 (3H), 3.69 (3H), 3.99 (2H), 7.29 (1H), 7.63 (2H), 7.75 (2H), 7.84 (4H), 8.70 (1H), 9.15 (1H).

EXAMPLE P3: Preparation of 3-ethylsulfonyl-5-(4-fluorophenyl)-2-[1-methyl-5-[6-(trifluoromethyl)-3-

pyridyl]imidazol-2-yl]pyridine (compound P3)



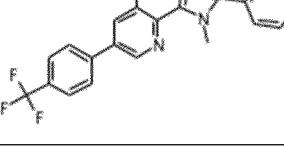
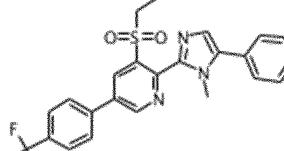
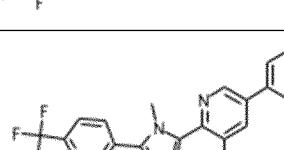
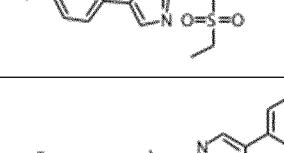
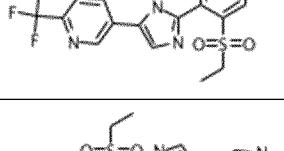
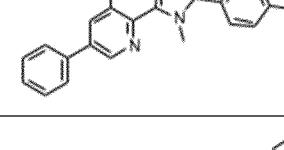
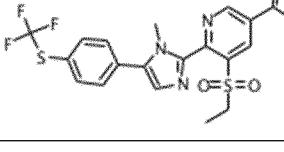
One-pot-two-steps procedure: in a reaction vial, a mixture of 5-bromo-2-(5-bromo-1-methyl-imidazol-2-yl)-3-ethylsulfonyl-pyridine (307 mg, 0.750 mmol), (4-fluorophenyl)boronic acid (116 mg, 0.825 mmol) and potassium carbonate (311 mg, 2.251 mmol) in 1,2-dimethoxyethane (6 ml) and water (1.5 ml) was 15 flushed with argon for 5 min. To this was added $\text{PdCl}_2(\text{dppf})$ (21.96 mg, 0.030 mmol), the vial was closed and the mixture was heated at 60°C (oil bath temperature, reaction was started at room temp) for 1 h. (6-(trifluoromethyl)pyridin-3-yl)boronic acid (201 mg, 1.051 mmol) was added, the vial was again closed and the mixture was heated at 90°C (oil bath temperature) for 1 h. The crude reaction mixture was partitioned between ethyl acetate and water/brine (1/3). After washing and separation, the 20 organic layer was dried and concentrated. The crude product was purified over silica by flash column chromatography (10 to 100% gradient of ethyl acetate in heptane). The fractions containing product were combined and concentrated. The product was again purified over silica by flash column chromatography (25 to 100% gradient of ethyl acetate in heptane, followed by 100% ethyl acetate) to afford the title compound P3 (130 mg) as a solid, mp 207-209°C. LCMS (method 2): 491 ($\text{M}+\text{H}$)⁺,

25 retention time 3.73 min. ¹H-NMR (CDCl_3 , ppm) 1.40 (3H), 3.69 (3H), 3.94 (2H), 7.27 (2H), 7.37 (1H), 7.70 (2H), 7.82 (1H), 8.01 (1H), 8.63 (1H), 8.90 (1H), 9.11 (1H).

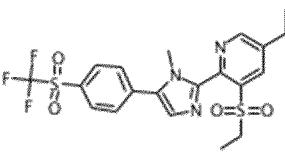
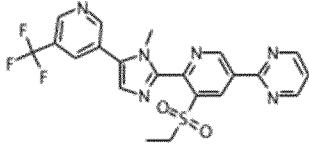
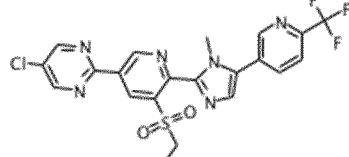
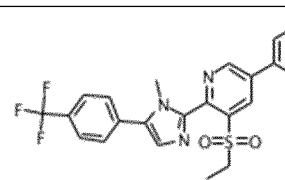
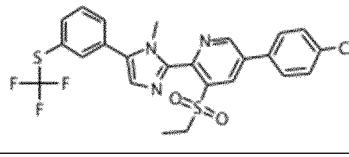
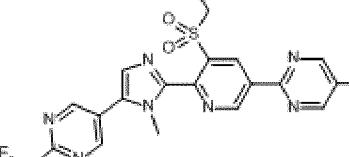
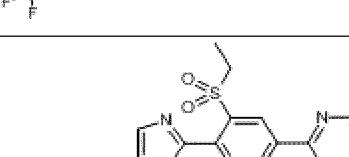
Table P: Examples of compounds of formula (I)

Compound No.	Structures	LCMS			Mp (°C)
		R_t (min)	[$\text{M}+\text{H}$] ⁺ (measured)	Method	

-63-

Compound No.	Structures	LCMS			Mp (°C)
		R _t (min)	[M+H] ⁺ (measured)	Method	
P1		4.09	541	2	182 - 184
P2		4.25	540	2	188 - 190
P3		3.73	491	2	207 - 209
P4		3.80	440	2	162 - 163.5
P5		3.93	507/509	2	206 - 207
P6		3.84	473	2	166 - 167.5
P7		4.31	538/540	2	179 - 180.5
P8		3.71	475	2	205 - 207

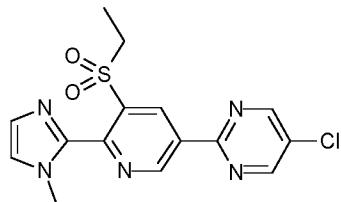
-64-

Compound No.	Structures	LCMS			Mp (°C)
		R _t (min)	[M+H] ⁺ (measured)	Method	
P9		4.17	570/572	2	217 - 218
P10		3.55	475	2	196 - 197
P11		3.91	509/511	2	199 - 200
P12		4.30	506/508	2	156.5 - 158
P13		4.34	538/540	2	193.5 - 195
P14		1.03	510/512	5	224 - 226
P15		0.93	476	5	231 - 233
P16		1.05	491	5	170 - 172

-65-

Compound No.	Structures	LCMS			Mp (°C)
		R _t (min)	[M+H] ⁺ (measured)	Method	
P17		1.04	492	5	193 - 195
P18		1.04	491	5	155 - 157

EXAMPLE P4: Preparation of intermediate compound 5-chloro-2-[5-ethylsulfonyl-6-(1-methylimidazol-2-yl)-3-pyridyl]pyrimidine (compound P2.7)



5

One-pot-two-steps procedure: a solution/suspension of 5-bromo-3-ethylsulfonyl-2-(1-methylimidazol-2-yl)pyridine (600 mg, 1.817 mmol), bis(pinacolato)diboron (508 mg, 1.999 mmol) and potassium acetate (535 mg, 5.45 mmol) in dimethyl sulfoxide (16 ml) was flushed with argon for 5 min. To this was added PdCl₂(dppf) (60 mg, 0.082 mmol) and the reaction mixture was heated at 80°C (oil bath

10 temp) under argon for 90 min. 2-Bromo-5-chloropyrimidine (527 mg, 2.73 mmol), water (4 ml) (flushed with argon before addition) and potassium carbonate (753 mg, 5.45 mmol) were added and the mixture was heated at 80°C under argon for 2 h. The reaction mixture was allowed to cool to room temperature and partitioned between ethyl acetate and water/brine (~1/3). After washing and separation, the organic layer was washed twice with brine, dried over sodium sulfate and

15 concentrated. The crude product was purified over silica by flash column chromatography (0 to 4% gradient of MeOH in CH₂Cl₂). The fractions containing product were combined and concentrated. The product was again purified over silica by flash column chromatography (20 to 100% gradient of ethyl acetate in heptane, followed by 100% ethyl acetate) to afford the title intermediate compound P2.7 (393 mg) as a solid, mp 228-229.5°C. LCMS (method 2): 364/366 (M+H)⁺, retention time 3.40 min. ¹H-

-66-

NMR (CDCl₃, ppm) 1.38 (3H), 3.75 (3H), 3.98 (2H), 7.08 (1H), 7.17 (1H), 8.84 (2H), 9.42 (1H), 9.83 (1H).

Table P2: Examples of intermediates of formula (IIIa), (IVa) and (XVIII)

Compound No.	Structures	LCMS			Mp (°C)
		R _t (min)	[M+H] ⁺ (measured)	Method	
P2.1		2.04	298/300	1	-
P2.2		2.89	330/332	2	135 - 136.5
P2.3		3.61	396	2	167 - 169
P2.4		4.80	407/409/411	4	115 - 118
P2.5		4.08	474/476	2	182 - 184
P2.6		2.88	330	2	194 - 196
P2.7		3.40	364/366	2	228 - 229.5

Compound No.	Structures	LCMS			Mp (°C)
		R _t (min)	[M+H] ⁺ (measured)	Method	
P2.8		3.68	362/364	2	198.5 - 200
P2.9		0.76	346	5	198 - 200
P2.10		1.01	424/426	5	179 - 181

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

5 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.

10 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, pyridylmethylenamino derivatives, macrolides, neonicotinoids and *Bacillus thuringiensis* preparations.

15

The following mixtures of the compounds of formula I with active ingredients are preferred (the abbreviation "TX" means "one compound selected from the group consisting of the compounds described in Tables 1 to 6 and P of the present invention"):

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

20 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) + 5 TX, azinphos-ethyl (44) + TX, azinphos-methyl (45) + TX, azobenzene (IUPAC name) (888) + TX, azocyclotin (46) + TX, azothoate (889) + TX, benomyl (62) + TX, benoxafos [CCN] + TX, benzoximate (71) + TX, benzyl benzoate (IUPAC name) [CCN] + TX, bifenazate (74) + TX, bifenthrin (76) + TX, binapacryl (907) + TX, brofenvalerate + TX, bromocyclen (918) + TX, bromophos (920) + TX, bromophos-ethyl (921) + TX, bromopropylate (94) + TX, buprofezin (99) + 10 TX, butocarboxim (103) + TX, butoxycarboxim (104) + TX, butylpyridaben + 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, 15 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 [CCN] + TX, coumaphos (174) + TX, crotamiton [CCN] + TX, crotoxyphos (1010) + TX, cufraneb (1013) + TX, 20 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 25 (226) + TX, dialifos (1042) + TX, diazinon (227) + TX, dichlofluanid (230) + TX, dichlorvos (236) + TX, dicliphos + TX, dicofol (242) + TX, dicrotophos (243) + TX, dienochlor (1071) + TX, dimefox (1081) + TX, dimethoate (262) + TX, dinactin (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) 30 + TX, dioxathion (1102) + TX, diphenyl sulfone (IUPAC name) (1103) + TX, disulfiram [CCN] + TX, disulfoton (278) + TX, DNOC (282) + TX, dofenapyn (1113) + TX, doramectin [CCN] + TX, endosulfan (294) + TX, endothion (1121) + TX, EPN (297) + TX, eprinomectin [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 + TX, fenpyroximate (345) + TX, fenson (1157) + TX, 35 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) +

-69-

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 (473) + TX, isopropyl O-(methoxyaminothiophosphoryl)salicylate (IUPAC name) (473) + TX, ivermectin [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 [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 [CCN] + TX, mipafox (1293) + TX, monocrotophos (561) + TX, morphothion (1300) + TX, moxidectin [CCN] + TX, naled (567) + TX, NC-184 (compound code) + TX, NC-512 (compound code) + TX, nifluridide (1309) + TX, nikkomycins [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 (628) + TX, phenkapton (1330) + TX, phentoate (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 (653) + TX, proclonol (1350) + TX, profenofos (662) + TX, promacyl (1354) + TX, propargite (671) + TX, propetamphos (673) + TX, propoxur (678) + TX, prothidathion (1360) + TX, prothoate (1362) + TX, pyrethrin I (696) + TX, pyrethrin II (696) + TX, pyrethrins (696) + TX, pyridaben (699) + TX, pyridaphenthion (701) + TX, pyrimidifen (706) + TX, 25 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 + TX, selamectin [CCN] + TX, SI-0009 (compound code) + TX, sophamide (1402) + TX, spirodiclofen (738) + TX, spiromesifen (739) + TX, SSI-121 (development code) (1404) + TX, sulfiram [CCN] + TX, sulfuramid (750) + TX, sulfotep (753) + TX, sulfur (754) + TX, S21-30 121 (development code) (757) + TX, tau-fluvalinate (398) + TX, tebufenpyrad (763) + TX, TEPP (1417) + TX, terbam + TX, tetrachlorvinphos (777) + TX, tetradifon (786) + TX, tetranactin (653) + TX, tetrasul (1425) + TX, thiafenox + TX, thiocarboxime (1431) + TX, thiofanox (800) + TX, thiometon (801) + TX, thioquinox (1436) + TX, thuringiensin [CCN] + TX, triamiphos (1441) + TX, triarathene (1443) + TX, triazophos (820) + TX, triazuron + TX, trichlorfon (824) + TX, trifenofos (1455) + TX, trinactin (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

-70-

(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,

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

10 an avicide selected from the group of substances consisting of chloralose (127) + TX, endrin (1122) + TX, fenthion (346) + TX, pyridin-4-amine (IUPAC name) (23) and strychnine (745) + TX, a bactericide selected from the group of substances consisting of 1-hydroxy-1*H*-pyridine-2-thione (IUPAC name) (1222) + TX, 4-(quinoxalin-2-ylamino)benzenesulfonamide (IUPAC name) (748) + TX, 8-hydroxyquinoline sulfate (446) + TX, bronopol (97) + TX, copper dioctanoate (IUPAC name) (170) + TX, copper hydroxide (IUPAC name) (169) + TX, cresol [CCN] + TX, dichlorophen (232) + TX, dipyrithione (1105) + TX, dodicin (1112) + TX, fenaminosulf (1144) + TX, formaldehyde (404) + TX, hydrargaphen [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

15 hydroxyquinoline sulfate (446) + TX, probenazole (658) + TX, streptomycin (744) + TX, streptomycin sesquisulfate (744) + TX, tecloftalam (766) + TX, and thiomersal [CCN] + TX, a biological agent selected from the group of substances consisting of *Adoxophyes orana* GV (12) + TX, *Agrobacterium radiobacter* (13) + TX, *Amblyseius* spp. (19) + TX, *Anagrypha falcifera* NPV (28) + TX, *Anagrus atomus* (29) + TX, *Aphelinus abdominalis* (33) + TX, *Aphidius colemani* (34) + TX, *Aphidoletes aphidimyza* (35) + TX, *Autographa californica* NPV (38) + TX, *Bacillus firmus* (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* (53) + TX, *Beauveria brongniartii* (54) + TX, *Chrysoperla carnea* (151) + TX, *Cryptolaemus montrouzieri* (178) + TX, *Cydia pomonella* GV (191) + TX, *Dacnusa sibirica* (212) + TX, *Diglyphus isaea* (254) + TX, *Encarsia formosa* (scientific name) (293) + TX, *Eretmocerus eremicus* (300) + TX, *Helicoverpa zea* NPV (431) + TX, *Heterorhabditis bacteriophora* and *H. megidis* (433) + TX,

20 30 *Hippodamia convergens* (442) + TX, *Leptomastix dactylopii* (488) + TX, *Macrolophus caliginosus* (491) + TX, *Mamestra brassicae* NPV (494) + TX, *Metaphycus helvolus* (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 (575) + TX, *Orius* spp.

35

(596) + TX, *Paecilomyces fumosoroseus* (613) + TX, *Phytoseiulus persimilis* (644) + TX, *Spodoptera exigua* multicapsid nuclear polyhedrosis virus (scientific name) (741) + TX, *Steinernema bibionis* (742) + TX, *Steinernema carpocapsae* (742) + TX, *Steinernema feltiae* (742) + TX, *Steinernema glaseri* (742) + TX, *Steinernema riobrave* (742) + TX, *Steinernema riobravis* (742) + TX, *Steinernema scapterisci* (742) + TX, *Steinernema* spp. (742) + TX, *Trichogramma* spp. (826) + TX, *Typhlodromus occidentalis* (844) and *Verticillium lecanii* (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 [CCN] + TX, busulfan [CCN] + TX, diflubenzuron (250) + TX, dimatif [CCN] + TX, hemel [CCN] + TX, hempa [CCN] + TX, metepa [CCN] + TX, methiotepa [CCN] + TX, methyl apholate [CCN] + TX, morzid [CCN] + TX, penfluron [CCN] + TX, tepa [CCN] + TX, thiohempa [CCN] + TX, thiotepea [CCN] + TX, tretamine [CCN] and uredepa [CCN] + TX, an insect pheromone selected from the group of substances consisting of (*E*)-dec-5-en-1-yl acetate with (*E*)-dec-5-en-1-ol (IUPAC name) (222) + TX, (*E*)-tridec-4-en-1-yl acetate (IUPAC name) (829) + TX, (*E*)-6-methylhept-2-en-4-ol (IUPAC name) (541) + TX, (*E,Z*)-tetradeca-4,10-dien-1-yl acetate (IUPAC name) (779) + TX, (*Z*)-dodec-7-en-1-yl acetate (IUPAC name) (285) + TX, (*Z*)-hexadec-11-enal (IUPAC name) (436) + TX, (*Z*)-hexadec-11-en-1-yl acetate (IUPAC name) (437) + TX, (*Z*)-hexadec-13-en-11-yn-1-yl acetate (IUPAC name) (438) + TX, (*Z*)-icos-13-en-10-one (IUPAC name) (448) + TX, (*Z*)-tetradec-7-en-1-al (IUPAC name) (782) + TX, (*Z*)-tetradec-9-en-1-ol (IUPAC name) (783) + TX, (*Z*)-tetradec-9-en-1-yl acetate (IUPAC name) (784) + TX, (7*E*,9*Z*)-dodeca-7,9-dien-1-yl acetate (IUPAC name) (283) + TX, (9*Z*,11*E*)-tetradeca-9,11-dien-1-yl acetate (IUPAC name) (780) + TX, (9*Z*,12*E*)-tetradeca-9,12-dien-1-yl acetate (IUPAC name) (781) + TX, 14-methyloctadec-1-ene (IUPAC name) (545) + TX, 4-methylnonan-5-ol with 4-methylnonan-5-one (IUPAC name) (544) + TX, alpha-multistriatin [CCN] + TX, brevicomin [CCN] + TX, codlelure [CCN] + TX, codlemone (167) + TX, cuelure (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 [CCN] + TX, ethyl 4-methyloctanoate (IUPAC name) (317) + TX, eugenol [CCN] + TX, frontalin [CCN] + TX, gossyplure (420) + TX, grandlure (421) + TX, grandlure I (421) + TX, grandlure II (421) + TX, grandlure III (421) + TX, grandlure IV (421) + TX, hexalure [CCN] + TX, ipsdienol [CCN] + TX, ipsenol [CCN] + TX, japonilure (481) + TX, lineatin [CCN] + TX, litlure [CCN] + TX, looplure [CCN] + TX, medlure [CCN] + TX, megatomoic acid [CCN] + TX, methyl eugenol (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 [CCN] + TX, oryctalure (317) + TX, ostramone [CCN] + TX, siglure [CCN] + TX, sordidin (736) + TX, sulcatol [CCN] + TX, tetradec-11-en-1-yl acetate (IUPAC name) (785) + TX, trimedlure (839) + TX, trimedlure A (839) + TX, trimedlure B₁ (839) + TX, trimedlure B₂ (839) + TX, trimedlure C (839) and trunc-call [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,
5 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 [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 [CCN] + TX, allyxycarb (866) + TX, alpha-cypermethrin (202) + TX, alpha-ecdysone [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, 30 azadirachtin (41) + TX, azamethiphos (42) + TX, azinphos-ethyl (44) + TX, azinphos-methyl (45) + TX, azothoate (889) + TX, *Bacillus thuringiensis* delta endotoxins (52) + TX, barium hexafluorosilicate [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 (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 + TX, bromfenvinfos (914) + TX, bromocyclen (918) + TX,

bromo-DDT [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 + 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, carbophenothon (947) + TX, carbosulfan (119) + TX, cartap (123) + TX, cartap hydrochloride (123) + TX, cevadine (725) + TX, chlorbicyclen (960) + TX, chlordane (128) + TX, chlordecone (963) + TX, chlordimeform (964) + TX, chlordimeform hydrochloride (964) + TX, 10 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, chromafenozone (150) + TX, cinerin I (696) + TX, cinerin II (696) + TX, cinerins (696) + TX, cis-resmethrin + TX, cismethrin (80) + TX, clopythrin + TX, 15 cloethocarb (999) + TX, closantel [CCN] + TX, clothianidin (165) + TX, copper acetoarsenite [CCN] + TX, copper arsenate [CCN] + TX, copper oleate [CCN] + TX, coumaphos (174) + TX, coumitoate (1006) + TX, crotamiton [CCN] + TX, crotoxyphos (1010) + TX, crufomate (1011) + TX, cryolite (177) + TX, CS 708 (development code) (1012) + TX, cyanofenphos (1019) + TX, cyanophos (184) + TX, cyanthoate (1020) + TX, cyclethrin [CCN] + TX, cycloprothrin (188) + TX, 20 cyfluthrin (193) + TX, cyhalothrin (196) + TX, cypermethrin (201) + TX, cyphenothon (206) + TX, cyromazine (209) + TX, cythioate [CCN] + TX, d-limonene [CCN] + TX, d-tetramethrin (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- 25 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, dicaphthon (1050) + TX, dichlofenthion (1051) + TX, dichlorvos (236) + TX, dicliphos + TX, dicresyl [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 [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, 30 DNOC (282) + TX, doramectin [CCN] + TX, DSP (1115) + TX, ecdysterone [CCN] + TX, EI 1642 (development code) (1118) + TX, emamectin (291) + TX, emamectin benzoate (291) + TX, EMPC (1120) + TX, empenthrin (292) + TX, endosulfan (294) + TX, endothion (1121) + TX, endrin (1122) + TX, EPBP (1123) + TX, EPN (297) + TX, epofenonane (1124) + TX, eprinomectin

[CCN] + TX, esfenvalerate (302) + TX, etaphos [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 (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, fenoxy carb (340) + TX, fenpirithrin (1155) + TX, fenpropothrin (342) + TX, fenpyrad + 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 (473) + TX, isodrin (1235) + TX, isofenphos (1236) + TX, isolane (1237) + TX, isoprocarb (472) + TX, isopropyl O-(methoxyaminothiophosphoryl)salicylate (IUPAC name) (473) + TX, isoprothiolane (474) + TX, isothioate (1244) + TX, isoxathion (480) + TX, ivermectin [CCN] + TX, jasmolin I (696) + TX, jasmolin II (696) + TX, jodfenphos (1248) + TX, juvenile hormone I [CCN] + TX, juvenile hormone II [CCN] + TX, juvenile hormone III [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-cumanyl 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 (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 (533) + TX, methoxychlor (534) + TX, methoxyfenozide (535) + TX,

methyl bromide (537) + TX, methyl isothiocyanate (543) + TX, methylchloroform [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 [CCN] + TX, mipafox (1293) + TX, mirex (1294) + TX, monocrotophos (561) + TX, 5 morphothion (1300) + TX, moxidectin [CCN] + TX, naftalofos [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 10 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'- 15 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 [CCN] + TX, pentachlorophenol (623) + TX, pentachlorophenyl laurate (IUPAC name) (623) + TX, permethrin (626) + TX, petroleum oils (628) + TX, PH 60-38 (development code) (1328) + TX, phenkapton (1330) + TX, phenothrin (630) + TX, 20 phentoate (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 25 name) (1347) + TX, potassium arsenite [CCN] + TX, potassium thiocyanate [CCN] + TX, prallethrin (655) + TX, precocene I [CCN] + TX, precocene II [CCN] + TX, precocene III [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, 30 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 [CCN] + TX, quinalphos (711) + TX, quinalphos-methyl (1376) + TX, quinothion (1380) + TX, quintofos (1381) + TX, R-1492 (development code) (1382) + TX, 35 rafoxanide [CCN] + TX, resmethrin (719) + TX, rotenone (722) + TX, RU 15525 (development code) (723) + TX, RU 25475 (development code) (1386) + TX, ryania (1387) + TX, ryanodine (traditional name) (1387) + TX, sabadilla (725) + TX, schradan (1389) + TX, sebufos + TX, selamectin [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, 5 sodium thiocyanate [CCN] + TX, sophamide (1402) + TX, spinosad (737) + TX, spiromesifen (739) + TX, spirotetramat (CCN) + TX, sulcofuron (746) + TX, sulcofuron-sodium (746) + TX, sulfuramid (750) + TX, sulfotep (753) + TX, sulfuryl fluoride (756) + TX, sulprofos (1408) + TX, tar oils (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) 10 + TX, temephos (770) + TX, TEPP (1417) + TX, terallethrin (1418) + TX, terbam + TX, terbufos (773) + TX, tetrachloroethane [CCN] + TX, tetrachlorvinphos (777) + TX, tetramethrin (787) + TX, theta-cypermethrin (204) + TX, thiacloprid (791) + TX, thiafenoxy + 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 15 (1434) + TX, thiosultap (803) + TX, thiosultap-sodium (803) + TX, thuringiensin [CCN] + TX, tolfenpyrad (809) + TX, tralomethrin (812) + TX, transfluthrin (813) + TX, transpermethrin (1440) + TX, triamiphos (1441) + TX, triazamate (818) + TX, triazophos (820) + TX, triazuron + TX, trichlorfon (824) + TX, trichlormetaphos-3 [CCN] + TX, trichloronat (1452) + TX, trifenofos (1455) + TX, triflumuron (835) + TX, trimethacarb (840) + TX, tripreno (1459) + TX, vamidothion (847) + 20 TX, vaniliprole [CCN] + TX, veratridine (725) + TX, veratrine (725) + TX, XMC (853) + TX, xylylcarb (854) + TX, YI-5302 (compound code) + TX, zeta-cypermethrin (205) + TX, zetamethrin + 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 25 [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 [928783-30 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, cycloxaapro (described in WO2005/077934) + TX, 35 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,

5 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)

10 + TX, 6-isopentenylaminopurine (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 + TX, cadusafos (109) + TX, carbofuran (118) + TX, carbon disulfide (945) + TX, carbosulfan (119) + TX, chloropicrin (141) + TX, chlorpyrifos (145) + TX, cloethocarb (999) + TX, cytokinins (210) + TX, dazomet (216) + TX,

15 DBCP (1045) + TX, DCIP (218) + TX, diamidafos (1044) + TX, dichlofenthion (1051) + TX, dicliphos + TX, dimethoate (262) + TX, doramectin [CCN] + TX, emamectin (291) + TX, emamectin benzoate (291) + TX, eprinomectin [CCN] + TX, ethoprophos (312) + TX, ethylene dibromide (316) + TX, fenamiphos (326) + TX, fenpyrad + TX, fensulfothion (1158) + TX, fosthiazate (408) + TX, fosthietan (1196) + TX, furfural [CCN] + TX, GY-81 (development code)

20 (423) + TX, heterophos [CCN] + TX, iodomethane (IUPAC name) (542) + TX, isamidofos (1230) + TX, isazofos (1231) + TX, ivermectin [CCN] + TX, kinetin (210) + TX, mecarphon (1258) + TX, metam (519) + TX, metam-potassium (519) + TX, metam-sodium (519) + TX, methyl bromide (537) + TX, methyl isothiocyanate (543) + TX, milbemycin oxime [CCN] + TX, moxidectin [CCN] + TX, *Myrothecium verrucaria* composition (565) + TX, NC-184 (compound code) + TX, oxamyl

25 (602) + TX, phorate (636) + TX, phosphamidon (639) + TX, phosphocarb [CCN] + TX, sebufos + TX, selamectin [CCN] + TX, spinosad (737) + TX, terbam + TX, terbufos (773) + TX, tetrachlorothiophene (IUPAC/ Chemical Abstracts name) (1422) + TX, thiafenox + TX, thionazin (1434) + TX, triazophos (820) + TX, triazuron + TX, xylenols [CCN] + TX, YI-5302 (compound code) and zeatin (210) + TX, fluensulfone [318290-98-1] + TX,

30 a nitrification inhibitor selected from the group of substances consisting of potassium ethylxanthate [CCN] and nitropyrin (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 (720) + TX, a rodenticide selected from the group of substances consisting of 2-isovalerylindan-1,3-dione (IUPAC

35 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) +

-78-

TX, chlorophacinone (140) + TX, cholecalciferol (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 (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 [CCN] and ribavirin [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, epiconazole [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, ancyimidol [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, 5 fludioxonil [131341-86-1] + TX, benalaxyll [71626-11-4] + TX, furalaxyll [57646-30-7] + TX, metalexyl [57837-19-1] + TX, R-metalexyl [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 10 [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, 15 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, manebe [12427-38-2] + TX, metiram [9006-42-2] + TX, propineb 20 [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 25 [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-ilar-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, 30 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, 35 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-

-80-

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 5 [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-dihydroxy-4,6a,12b-trimethyl-11-oxo-9-(3-pyridinyl)-2H,11Hnaphtho[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 20 [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; and kappa-tefluthrin [391634-71-2] + TX; and
microbials including: *Acinetobacter lwoffii* + TX, *Acremonium alternatum* + TX + TX, *Acremonium cephalosporium* + TX + TX, *Acremonium diospyri* + TX, *Acremonium obclavatum* + TX, *Adoxophyes 25 orana granulovirus* (AdoxGV) (Capex®) + TX, *Agrobacterium radiobacter* strain K84 (Galltrol-A®) + TX, *Alternaria alternate* + TX, *Alternaria cassia* + TX, *Alternaria destruens* (Smolder®) + TX, *Ampelomyces quisqualis* (AQ10®) + TX, *Aspergillus flavus* AF36 (AF36®) + TX, *Aspergillus flavus* NRRL 21882 (Aflaguard®) + TX, *Aspergillus* spp. + TX, *Aureobasidium pullulans* + TX, *Azospirillum* + TX, (MicroAZ® + TX, TAZO B®) + TX, *Azotobacter* + TX, *Azotobacter chroococcum* (Azotomeal®) + TX, *Azotobacter* cysts (Bionatural Blooming Blossoms®) + TX, *Bacillus amyloliquefaciens* + TX, *Bacillus cereus* + TX, *Bacillus chitinosporus* strain CM-1 + TX, *Bacillus chitinosporus* strain AQ746 + TX, *Bacillus licheniformis* strain HB-2 (Biostart™ Rhizoboost®) + TX, *Bacillus licheniformis* strain 3086 (EcoGuard® + TX, Green Releaf®) + TX, *Bacillus circulans* + TX, *Bacillus firmus* (BioSafe® + TX, BioNem-WP® + TX, VOTiVO®) + TX, *Bacillus firmus* strain I-1582 + TX, *Bacillus macerans* + TX, 30 *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 sphericus* (VectoLex®) + TX, *Bacillus* spp. + TX, *Bacillus* spp. strain 35

-81-

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* 5 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 10 123 (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 (Beaupenic® + TX, Brocaril WP®) + TX, Beauveria bassiana GHA (Mycotrol ES® 15 + TX, Mycotrol O® + TX, BotaniGuard®) + TX, Beauveria brongniartii (Engerlingspilz® + TX, Schweizer Beauveria® + TX, Melocont®) + TX, Beauveria spp. + TX, *Botrytis cinerea* + 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, 20 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 dravisa* + TX, *Cellulomonas* 25 *flavigena* + TX, *Chaetomium cochlioides* (Nova-Cide®) + TX, *Chaetomium globosum* (Nova-Cide®) + TX, *Chromobacterium subtsugae* strain PRAA4-1T (Grandevol®) + TX, *Cladosporium cladosporioides* + TX, *Cladosporium oxysporum* + TX, *Cladosporium chlороcephalum* + TX, *Cladosporium* spp. + TX, *Cladosporium tenuissimum* + TX, *Clonostachys rosea* (EndoFine®) + TX, *Colletotrichum acutatum* + TX, *Coniothyrium minitans* (Cotans WG®) + TX, *Coniothyrium* spp. + TX, *Cryptococcus albidus* 30 (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 hawaiiensis* + TX, *Enterobacter cloacae* + TX, *Enterobacteriaceae* + TX, *Entomophthora* virulenta (Vektor®) + TX, *Epicoccum nigrum* + TX, *Epicoccum purpurascens* + TX, *Epicoccum* spp. + TX, *Filobasidium floriforme* + TX, *Fusarium acuminatum* + TX, *Fusarium chlamydosporum* + TX, *Fusarium oxysporum* (Fusaclean® / 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 guillermondii* + 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, *Pseudomonas 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. +

-83-

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* 5 (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 10 (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, 15 *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, *Virgibacillus marismortui* + TX, 20 *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, 25 *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, 30 *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, 35 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)-5 3 + TX,8 + TX,11 Tetradeccatrienyl 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, 10 *Acerophagus papaya* + TX, *Adalia bipunctata* (Adalia-System®) + TX, *Adalia bipunctata* (Adaline®) + TX, *Adalia bipunctata* (Aphidalia®) + TX, *Ageniaspis citricola* + TX, *Ageniaspis fuscicollis* + TX, *Amblyseius andersoni* (Anderline® + TX, Andersoni-System®) + TX, *Amblyseius californicus* (Amblyline® + TX, Spical®) + TX, *Amblyseius cucumeris* (Thripex® + TX, Bugline cucumeris®) + TX, *Amblyseius fallacis* (Fallacis®) + TX, *Amblyseius swirskii* (Bugline swirskii® + TX, Swirskii-Mite®) + TX, *Amblyseius womersleyi* (WomerMite®) + TX, *Amitus hesperidum* + TX, *Anagrus atomus* + TX, 15 *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* (Ahipar®) + TX, *Aphidius ervi* (Ervipar®) + TX, *Aphidius gifuensis* + TX, *Aphidius matricariae* (Ahipar-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* 20 (Chrysopa®) + TX, *Chrysoperla rufilabris* + TX, *Cirrospilus ingenuus* + TX, *Cirrospilus quadristriatus* + TX, *Citrostichus phylloconistoides* + 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* 25 (Minusa®) + TX, *Diglyphus isaea* (Diminex®) + TX, *Delphastus catalinae* (Delphastus®) + TX, *Delphastus pusillus* + TX, *Diachasmimorpha krausii* + TX, *Diachasmimorpha longicaudata* + TX, *Diaparsis jucunda* + TX, *Diaphorencyrtus aligarhensis* + TX, *Diglyphus isaea* + TX, *Diglyphus isaea* (Miglyphus® + TX, Digline®) + TX, *Dacnusa sibirica* (DacDigline® + TX, Minex®) + TX, *Diversinervus* spp. + TX, *Encarsia citrina* + TX, *Encarsia formosa* (Encarsia max® + TX, Encarline® + TX, En- 30 Strip®) + TX, *Eretmocerus eremicus* (Enermix®) + TX, *Encarsia guadeloupae* + TX, *Encarsia haitiensis* + TX, *Episyphus 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

TX, *Eretmocerus siphonini* + TX, *Exochomus quadripustulatus* + TX, *Feltiella acarisuga* (Spidend®) + TX, *Feltiella acarisuga* (Feltiline®) + TX, *Fopius arisanus* + TX, *Fopius ceratitivorus* + TX, Formononetin (Wireless Beehome®) + TX, *Franklinothrips vespiformis* (Vespop®) + TX, *Galendromus occidentalis* + TX, *Goniozus legneri* + TX, *Habrobracon hebetor* + TX, *Harmonia axyridis*

5 (HarmoBeetle®) + TX, *Heterorhabdits* spp. (Lawn Patrol®) + TX, *Heterorhabdits bacteriophora* (NemaShield HB® + TX, Nemaseek® + TX, Terranem-Nam® + TX, Terranem® + TX, Larvanem® + TX, B-Green® + TX, NemAttack ® + TX, Nematop®) + TX, *Heterorhabdits 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 lophantheae* + 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*

10 + TX, *Micromus angulatus* (Milacewing®) + TX, *Microterys flavus* + TX, *Muscidifurax raptor* 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, *Phasmarhabdits 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, *Pseudoleptomastix mexicana* + TX, *Psyllaephagus pilosus* + TX, *Psyllalia concolor* (complex) + TX, *Quadra stichus* spp. + TX, *Rhyzobius lophantheae* + TX, *Rodolia cardinalis* + TX, *Rumina decollate* + TX, *Semielacher petiolatus* + TX, *Sitobion avenae* (Ervibank®) + TX, *Steinernema carpocapsae* (Nematac C® + TX, Millenium® + TX, BioNem C® + TX, NemAttack® + TX, Nemastar® + TX, Capsanem®) + TX, *Steinernema feltiae* (NemaShield® + TX, Nemasys F® + TX, BioNem F® + TX, Steinernema-System® + TX, NemAttack® + TX, Nemaplus® + TX, Exhibitline sf® + TX, Scia-rid® + TX, Entonem®) + TX, *Steinernema kraussei* (Nemasys L® + TX, BioNem L® + TX, Exhibitline srb®) + TX, *Steinernema riobrave* (BioVector® + TX, BioVektor®) + TX, *Steinernema scapterisci* (Nematac S®) + TX, *Steinernema* spp. + TX, *Steinernematid* spp. (Guardian Nematodes®) + TX, *Stethorus punctillum* (Stethorus®) + TX, *Tamarixia radiate* + TX, *Tetrastichus setifer* + TX, *Thripobius semiluteus* + TX, *Torymus sinensis* + TX, *Trichogramma brassicae* (Tricholine b®) + TX, *Trichogramma brassicae* (Tricho-Strip®) + TX, *Trichogramma evanescens* + TX, *Trichogramma minutum* + TX, *Trichogramma ostriniae* + TX, *Trichogramma platneri* + TX, *Trichogramma pretiosum* + TX, *Xanthopimpla stemmator*, and

-86-

other biologicals including: abscisic acid + TX, bioSea® + TX, *Chondrostereum purpureum* (Chontrol Paste®) + TX, *Colletotrichum gloeosporioides* (Collego®) + TX, Copper Octanoate (Cueva®) + TX, Delta traps (Trapline d®) + TX, *Erwinia amylovora* (Harpin) (ProAct® + TX, Ni-HIBIT Gold CST®) + TX, Ferri-phosphate (Ferramol®) + TX, Funnel traps (Trapline y®) + TX, Gallex® + TX, Grower's Secret® + TX, Homo-brassonolide + TX, Iron Phosphate (Lilly Miller Worry Free Ferramol Slug & Snail Bait®) + TX, MCP hail trap (Trapline f®) + TX, *Microctonus hyperodae* + TX, *Mycoleptodiscus terrestris* (Des-X®) + TX, BioGain® + TX, Aminomite® + TX, Zenox® + TX, Pheromone trap (Thripline ams®) + TX, potassium bicarbonate (MilStop®) + TX, potassium salts of fatty acids (Sanova®) + TX, potassium silicate solution (Sil-Matrix®) + TX, potassium iodide + potassiumthiocyanate (Enzicur®) + TX, SuffOil-X® + TX, Spider venom + TX, *Nosema locustae* (Semaspore Organic Grasshopper Control®) + TX, Sticky traps (Trapline YF® + TX, Rebell Amarillo®) + TX and Traps (Takitrapline y + b®) + TX.

The references in brackets behind the active ingredients, e.g. [3878-19-1] refer to the Chemical

15 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 20 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>.

25 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 30 or, if neither one of those designations nor a "common name" is used, an "alternative name" is employed. "CAS Reg. No" means the Chemical Abstracts Registry Number.

The active ingredient mixture of the compounds of formula I selected from Tables 1 to 6 and P with active ingredients described above comprises a compound selected from Tables 1 to 6 and P and an

35 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

-87-

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.

5

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.

10

The mixtures comprising a compound of formula I selected from Tables 1 to 6 and P and one or more active ingredients as described above can be applied, for example, in a single "ready-mix" form, in a combined spray mixture composed from separate formulations of the single active ingredient components, such as a "tank-mix", and in a combined use of the single active ingredients when applied in a sequential manner, i.e. one after the other with a reasonably short period, such as a few hours or days. The order of applying the compounds of formula I selected from Tables 1 to 6 and P and the active ingredients as described above is not essential for working the present invention.

20

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.

25

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.

30

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

A preferred method of application in the field of crop protection is application to the foliage of the plants (foliar application), it being possible to select frequency and rate of application to match the danger of infestation with the pest in question. Alternatively, the active ingredient can reach the plants 5 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.

10 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 15 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 20 seeds, preferably between 5 to 150 grams per 100 kg of seeds, such as between 10 to 100 grams per 100 kg of seeds.

The term seed embraces seeds and plant propagules of all kinds including but not limited to true seeds, seed pieces, suckers, corns, bulbs, fruit, tubers, grains, rhizomes, cuttings, cut shoots and the 25 like and means in a preferred embodiment true seeds.

The present invention also comprises seeds coated or treated with or containing a compound of formula I. The term "coated or treated with and/or containing" generally signifies that the active ingredient is for the most part on the surface of the seed at the time of application, although a greater or lesser part of the ingredient may penetrate into the seed material, depending on the method of 30 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).

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

Biological Examples:Example B1: Activity against *Spodoptera littoralis* (Egyptian cotton leaf worm)

5 Cotton leaf discs were placed on agar in 24-well microtiter plates and sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying the leaf discs were infested with five L1 larvae. The samples were assessed for mortality, anti-feedant effect, and growth inhibition in comparison to untreated samples 3 days after infestation. Control of *Spodoptera littoralis* by a test sample is when at least one of mortality, anti-feedant effect, and growth inhibition is higher than the 10 untreated sample.

The following compounds resulted in at least 80% control at an application rate of 200 ppm: P1, P2, P3, P4, P5, P6, P7, P8, P9, P10, P11, P12 and P13.

Example B2: Activity against *Spodoptera littoralis* (Egyptian cotton leaf worm)

15 Test compounds were applied by pipette from 10'000 ppm DMSO stock solutions into 24-well plates and mixed with agar. Lettuce seeds were placed on the agar and the multi well plate was closed by another plate which contains also agar. After 7 days the roots have absorbed the compound and the lettuce has grown into the lid plate. The lettuce leafs were now cut off into the lid plate. *Spodoptera* eggs were pipetted through a plastic stencil on a humid gel blotting paper and the plate closed with it. 20 The samples were assessed for mortality, anti-feedant effect and growth inhibition in comparison to untreated samples 6 days after infestation.

The following compounds gave an effect of at least 80% in at least one of the three categories (mortality, anti-feedancy, or growth inhibition) at a test rate of 12.5 ppm: P3, P4, P6, P8, P10 and P11.

25 Example B3: Activity against *Plutella xylostella* (Diamond back moth)

24-well microtiter plates with artificial diet were treated with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions by pipetting. After drying, the plates were infested with L2 larvae (10 to 15 per well). The samples were assessed for mortality and growth inhibition in comparison to untreated samples 5 days after infestation.

30 The following compounds gave an effect of at least 80% in at least one of the two categories (mortality or growth inhibition) at an application rate of 200 ppm: P1, P2, P3, P4, P5, P6, P7, P8, P9, P10, P11, P12 and P13.

Example B4: Activity against *Diabrotica balteata* (Corn root worm)

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

-90-

The following compounds gave an effect of at least 80% in at least one of the two categories (mortality or growth inhibition) at an application rate of 200 ppm: P1, P2, P3, P4, P5, P6, P7, P8, P9, P10, P11, P12 and P13.

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

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

10 The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: P3, P4, P5, P6, P8, P10 and P11.

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

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

The following compounds resulted in at least 80% mortality at a test rate of 24 ppm: P8 and P10.

Example B7: Activity against *Frankliniella occidentalis* (Western flower thrips)

20 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.

25 The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: P1, P2, P3, P5, P6, P8, P10 and P12.

25

Example B8: Activity against *Bemisia tabaci* (Cotton white fly)

Cotton leaf discs were placed on agar in 24-well microtiter plates and sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying the leaf discs were infested with adult white flies. The samples were checked for mortality 6 days after incubation.

30 The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: P4.

Example B9: Activity against *Euschistus heros* (Neotropical Brown Stink Bug)

35 Soybean leaf on agar in 24-well microtiter plates were sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying the leaf were infested with N-2 nymphs. The samples were assessed for mortality and growth inhibition in comparison to untreated samples 5 days after infestation.

-91-

The following compounds gave an effect of at least 80% in at least one of the two categories (mortality or growth inhibition) at an application rate of 200 ppm: P1, P5, P8, P10 and P11.

Example B10: Activity against *Tetranychus urticae* (Two-spotted spider mite)

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

The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: P3.

10

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

Test solutions, at an application rate of 200ppm in ethanol, were applied to 12-well tissue culture plates. Once the deposits were dry, five, two to five days old adult female *Aedes aegypti* were added to each well, and sustained with a 10% sucrose solution in a cotton wool plug. Assessment of 15 knockdown was made one hour after introduction, and mortality was assessed at 24 and 48 hours after introduction.

The following compounds gave at least 80% control of *Aedes aegypti* after 48h and/or 24h: P1, P2, P3, P5, P7, P9, P11 and P12.

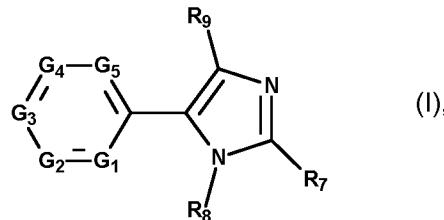
Example B12: Activity against *Anopheles stephensi* (Indian malaria mosquito)

20 Test solutions, at an application rate of 200ppm in ethanol, were applied to 12-well tissue culture plates. Once the deposits were dry, five, two to five day old adult female *Anopheles stephensi* were added to each well, and sustained with a 10% sucrose solution in a cotton wool plug. Assessment of knockdown was made one hour after introduction, and mortality was assessed at 24 and 48 hours after introduction.

25 The following compounds gave at least 80% control of *Anopheles stephensi* after 48h and/or 24h: P3, P5, P7, P9, P11 and P12.

Claims:

1. A compound of formula I



5 wherein

G₁ is nitrogen or CR₂;

G₂ is nitrogen or CR₃;

G₃ is nitrogen or CR₄;

G₄ is nitrogen or CR₅;

10 G₅ is nitrogen or CR₆, with the proviso that not more than 2 nitrogens as G may follow consecutively;

R₂, R₃, R₄, R₅ or R₆ are, independently from each other, hydrogen, halogen, C₁-C₄haloalkyl,

C₁-C₄haloalkyl substituted by one or two hydroxy, C₁-C₄haloalkyl substituted by one or two methoxy,

C₁-C₄haloalkyl substituted by one or two cyano; or

R₂, R₃, R₄, R₅ or R₆ are, independently from each other, C₁-C₄haloalkylsulfanyl, C₁-C₄haloalkylsulfinyl,

15 C₁-C₄haloalkylsulfonyl, C₁-C₄haloalkoxy, SF₅, phenylcarbonylthio, cyano, mercapto,

C₁-C₄alkoxycarbonyl, C₁-C₄alkylcarbonyl or -C(O)C₁-C₄haloalkyl; or

R₂, R₃, R₄, R₅ or R₆ are, independently from each other, C₃-C₆cycloalkyl which can be mono- or

polysubstituted by substituents selected from the group consisting of halogen, cyano and C₁-C₄alkyl;

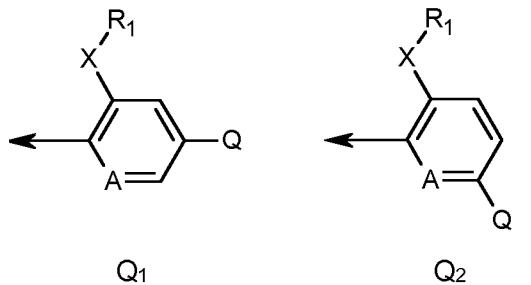
or two adjacent R_i, wherein R_i is selected from R₂, R₃, R₄, R₅ and R₆, taken together may form a

20 fragment -OCH₂O- or -OCF₂O-;

R₈ is hydrogen, C₁-C₄alkyl or C₁-C₄haloalkyl;

R₉ is hydrogen, C₁-C₄alkyl, C₁-C₄haloalkyl, cyano or halogen;

R₇ is a radical selected from the group consisting of formula Q₁ and Q₂



25 wherein the arrow denotes the point of attachment to the imidazole ring;
and wherein A represents CH or N;

-93-

Q is phenyl which can be mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkoxy, C₁-C₄haloalkylsulfanyl, C₁-C₄haloalkylsulfinyl, C₁-C₄haloalkylsulfonyl and -C(O)C₁-C₄haloalkyl; or

Q is a five- to ten-membered monocyclic or fused bicyclic ring system linked via a carbon atom to the

5 ring which contains the group A, said ring system can be aromatic, partially saturated or fully saturated and contains 1 to 4 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, it not being possible for each ring system to contain more than 2 oxygen atoms and more than 2 sulfur atoms, said five- to ten-membered ring system can be mono- to polysubstituted by substituents independently selected from the group consisting of halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-

10 C₄haloalkoxy, C₁-C₄alkoxy, C₁-C₄alkylsulfanyl, C₁-C₄alkylsulfinyl, C₁-C₄alkylsulfonyl, -C(O)C₁-C₄alkyl, C₁-C₄haloalkylsulfanyl, C₁-C₄haloalkylsulfinyl, C₁-C₄haloalkylsulfonyl and -C(O)C₁-C₄haloalkyl; or

Q is a five- to six-membered, aromatic, partially saturated or fully saturated ring system linked via a nitrogen atom to the ring which contains the group A, said ring system can be mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C₁-C₄alkyl, C₁-

15 C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkoxy, C₁-C₄alkylsulfanyl, C₁-C₄alkylsulfinyl, C₁-C₄alkylsulfonyl, -C(O)C₁-C₄alkyl, C₁-C₄haloalkylsulfanyl, C₁-C₄haloalkylsulfinyl, C₁-C₄haloalkylsulfonyl and

-C(O)C₁-C₄haloalkyl; and said ring system contains 1, 2 or 3 heteroatoms selected from the group consisting of nitrogen, oxygen and sulfur, where said ring system may not contain more than one oxygen atom and not more than one sulfur atom; or

20 Q is C₃-C₆cycloalkyl, or C₃-C₆cycloalkyl mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₃-C₆cycloalkyl and phenyl, wherein said phenyl can be mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkoxy, C₁-C₄haloalkylsulfanyl, C₁-C₄haloalkylsulfinyl, C₁-C₄haloalkylsulfonyl and -C(O)C₁-C₄haloalkyl; or

25 Q is C₂-C₆alkenyl, or C₂-C₆alkenyl mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₃-C₆cycloalkyl and phenyl, wherein said phenyl can be mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkoxy, C₁-C₄haloalkylsulfanyl, C₁-C₄haloalkylsulfinyl, C₁-C₄haloalkylsulfonyl and -C(O)C₁-C₄haloalkyl; or

30 Q is C₂-C₆alkynyl, or C₂-C₆alkynyl mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₃-C₆cycloalkyl, tri(C₁-C₄alkyl)silyl and phenyl, wherein said phenyl can be mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkoxy, C₁-C₄haloalkylsulfanyl, C₁-C₄haloalkylsulfinyl, C₁-C₄haloalkylsulfonyl and -C(O)C₁-C₄haloalkyl; or

35 Q is C₁-C₆haloalkylsulfanyl, C₁-C₆haloalkylsulfinyl, C₁-C₆haloalkylsulfonyl, C₁-C₆haloalkoxy, -C(O)C₁-C₄haloalkyl, C₁-C₆alkylsulfanyl, C₁-C₆alkylsulfinyl, or C₁-C₆alkylsulfonyl;

X is S, SO or SO₂; and

R₁ is C₁-C₄alkyl, C₁-C₄haloalkyl, C₃-C₆cycloalkyl, C₃-C₆cycloalkyl-C₁-C₄alkyl; or

-94-

R₁ is C₃-C₆cycloalkyl mono - or polysubstituted by substituents selected from the group consisting of halogen, cyano and C₁-C₄alkyl; or

R₁ is C₃-C₆cycloalkyl-C₁-C₄alkyl mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano and C₁-C₄alkyl; or

5 R₁ is C₂-C₆alkenyl, C₂-C₆haloalkenyl or C₂-C₆alkynyl;

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

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

10 Q is selected from the group consisting of the following heterocyclic groups:

pyrrolyl; pyrazolyl; isoxazolyl; furanyl; thienyl; imidazolyl; oxazolyl; thiazolyl; isothiazolyl; triazolyl; oxadiazolyl; thiadiazolyl; tetrazolyl; furyl; pyridyl; pyrimidyl; pyrazinyl; pyridazinyl; triazinyl, pyranyl; quinazolinyl; isoquinolinyl; indolizinyl; isobenzofuranyl naphthyridinyl; quinoxalinyl; cinnolinyl;

phthalazinyl; benzothiazolyl; benzoxazolyl; benzotriazolyl; indazolyl; indolyl; (1H-pyrrol-1-yl)-; (1H-

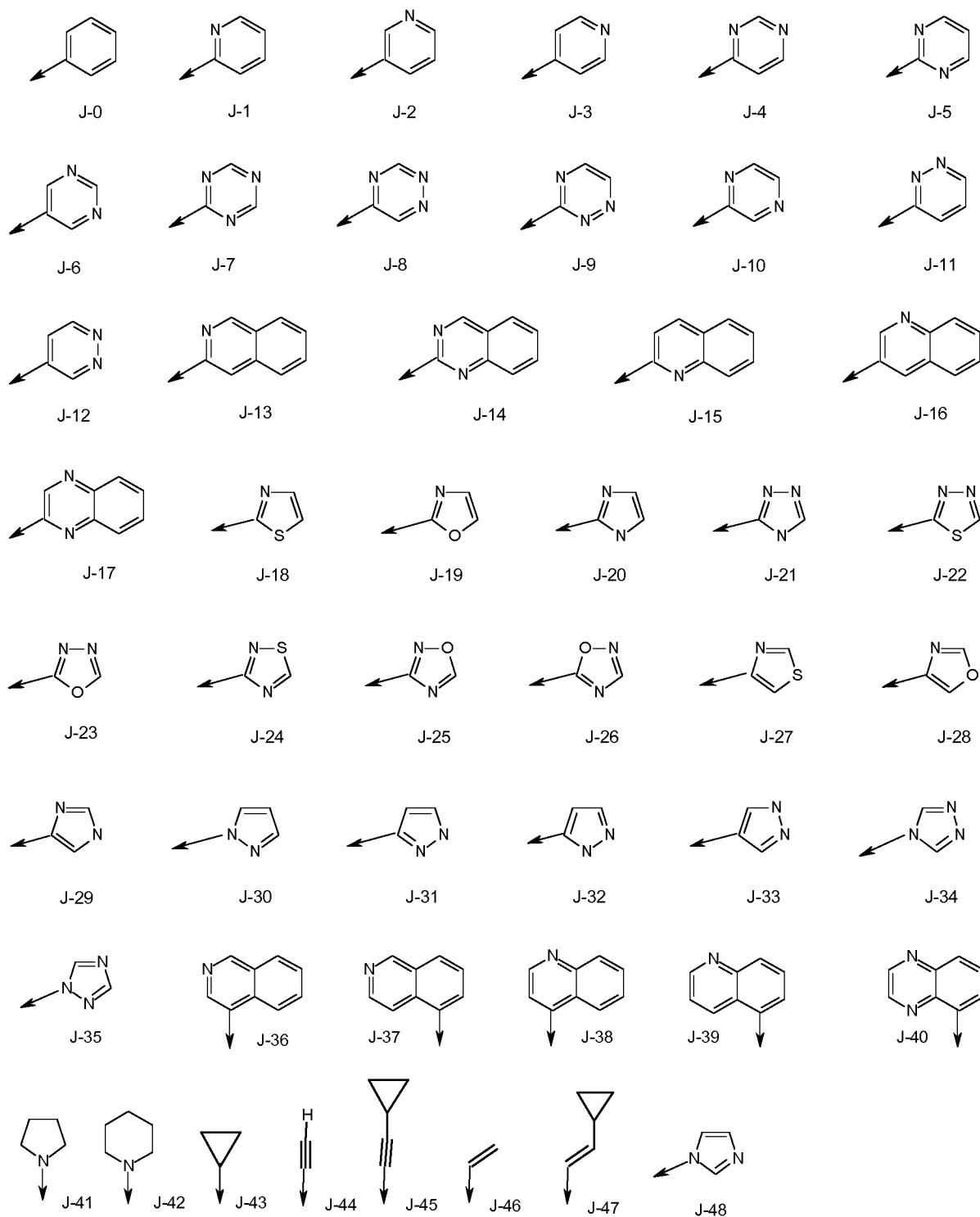
15 pyrrol-2-yl)-; (1H-pyrrol-3-yl)-; (1H-pyrazol-1-yl)-; (1H-pyrazol-3-yl)-; (3H-pyrazol-3-yl)-; (1H-pyrazol-4-yl)-; (3-isoxazolyl)-; (5-isoxazolyl)-; (2-furanyl)-; (3-furanyl)-; (2-thienyl)-; (3-thienyl)-; (1H-imidazol-2-yl)-; (1H-imidazol-4-yl)-; (1H-imidazol-5-yl)-; (2-oxazol-2-yl)-; (oxazol-4-yl)-; (oxazol-5-yl)-; (thiazol-2-yl)-; (thiazol-4-yl)-; (thiazol-5-yl)-; (isothiazol-3-yl)-; (isothiazol-5-yl)-; (1H-1,2,3-triazol-1-yl)-; (1H-1,2,4-triazol-3-yl)-; (4H-1,2,4-triazol-4-yl)-; (1H-1,2,4-triazol-1-yl)-; (1,2,3-oxadiazol-2-yl)-; (1,2,4-oxadiazol-3-yl)-; (1,2,4-oxadiazol-4-yl)-; (1,2,4-oxadiazol-5-yl)-; (1,2,3-thiadiazol-2-yl)-; (1,2,4-thiadiazol-3-yl)-;

20 (1,2,4-thiadiazol-4-yl)-; (1,3,4-thiadiazol-5-yl)-; (1H-tetrazol-1-yl)-; (1H-tetrazol-5-yl)-; (2H-tetrazol-5-yl)-; (2-pyridyl)-; (3-pyridyl)-; (4-pyridyl)-; (2-pyrimidinyl)-; (4-pyrimidinyl)-; (5-pyrimidinyl)-; (2-pyrazinyl)-; (3-pyridazinyl)-; (4-pyridazinyl)-; (1,3,5-triazin-2-yl)-; (1,2,4-triazin-5-yl)-; (1,2,4-triazin-6-yl)-; (1,2,4-triazin-3-yl)-; (furazan-3-yl)-; (2-quinolinyl)-; (3-quinolinyl)-; (4-quinolinyl)-; (5-quinolinyl)-; (6-quinolinyl)-; (3-isoquinolinyl)-; (4-isoquinolinyl)-; (2-quinoxolinyl)-; (2-quinoxalinyl)-; (5-quinoxalinyl)-; (pyrido[2,3-b]pyrazin-7-yl)-; (benzoxazol-5-yl)-; (benzothiazol-5-yl)-; (benzo[b]thien-2-yl)- and (benzo[1,2,5]oxadiazol-5-yl)-; indolinyl and tetrahydroquinolynyl.

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

Q is selected from the group consisting of J-0 to J-48:

-95-

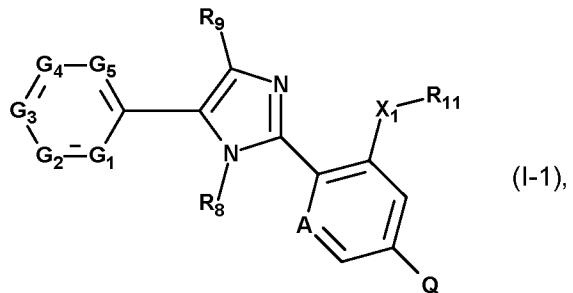


wherein each group J-0 to J-48 is mono-, di- or trisubstituted with Rx, wherein

5 each Rx is, independently selected from hydrogen, halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkoxy, C₁-C₄alkylsulfanyl, C₁-C₄alkylsulfinyl, C₁-C₄alkylsulfonyl, -C(O)C₁-C₄alkyl, C₁-C₄haloalkylsulfanyl, C₁-C₄haloalkylsulfinyl, C₁-C₄haloalkylsulfonyl and -C(O)C₁-C₄haloalkyl.

-96-

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

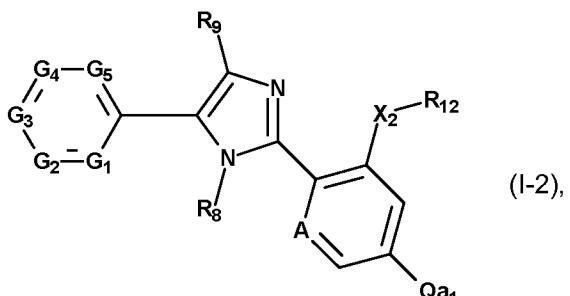


wherein

A, Q, G₁, G₂, G₃, G₄, and G₅ are as defined under formula I in claim 1;

5 X₁ is S, SO or SO₂;
 R₁₁ is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl;
 R₈ is as defined above under formula I in claim 1; and
 R₉ is as defined above under formula I in claim 1.

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

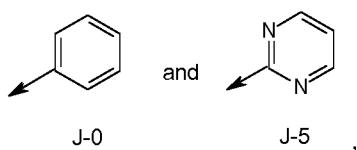


wherein

A, G₁, G₂, G₃, G₄, and G₅ are as defined under formula I in claim 1;

X₂ is S, SO or SO₂;

15 R₁₂ is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl;
 R₈ is as defined above under formula I in claim 1;
 R₉ is as defined above under formula I in claim 1; and
 Qa₁ is selected from the group consisting of

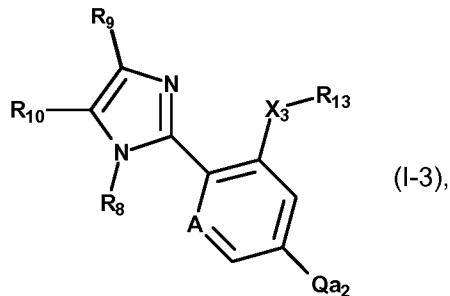


20 wherein each group J is mono-, di- or trisubstituted with Rx, wherein

-97-

each Rx is, independently selected from hydrogen, halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkoxy, C₁-C₄alkylsulfanyl, C₁-C₄alkylsulfinyl, C₁-C₄alkylsulfonyl, -C(O)C₁-C₄alkyl, C₁-C₄haloalkylsulfanyl, C₁-C₄haloalkylsulfinyl, C₁-C₄haloalkylsulfonyl and -C(O)C₁-C₄haloalkyl.

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



wherein

A is N or CH;

R₁₀ is phenyl mono- or polysubstituted by substituents independently selected from the group

10 consisting of halogen, C₁-C₄haloalkyl, C₁-C₄haloalkylsulfanyl and C₁-C₄haloalkylsulfonyl; or

R₁₀ is pyridyl mono- or polysubstituted by substituents independently selected from the group

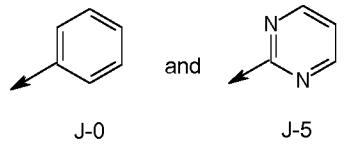
consisting of halogen and C₁-C₄haloalkyl; or

R₁₀ is pyrimidyl mono- or polysubstituted by substituents independently selected from the group

consisting of halogen and C₁-C₄haloalkyl, in particular fluorine and trifluoromethyl;

15 X₃ is S or SO₂;

Qa₂ is selected from the group consisting of



wherein each group J is mono-, di- or trisubstituted with Rx, wherein each Rx is, independently selected from hydrogen, halogen and C₁-C₄haloalkyl;

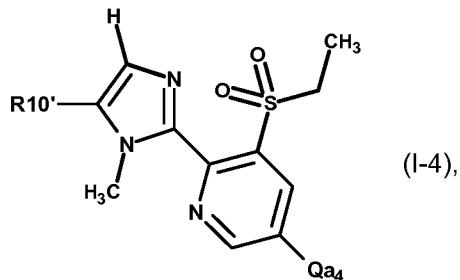
20 R₁₃ is C₁-C₄alkyl;

R₈ is C₁-C₄alkyl; and

R₉ is hydrogen.

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

-98-



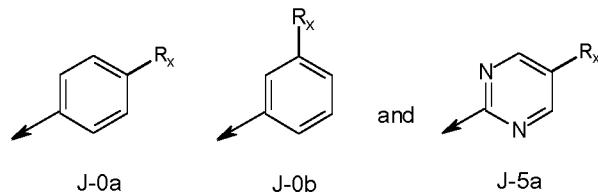
wherein

R_{10}' is phenyl monosubstituted by substituents independently selected from the group consisting of halogen, C_1 - C_4 haloalkyl, C_1 - C_4 haloalkylsulfanyl and C_1 - C_4 haloalkylsulfonyl; or

5 R_{10}' is pyridyl monosubstituted by substituents independently selected from the group consisting of halogen and C_1 - C_4 haloalkyl; or

R_{10}' is pyrimidyl monosubstituted by substituents independently selected from the group consisting of halogen and C_1 - C_4 haloalkyl; and

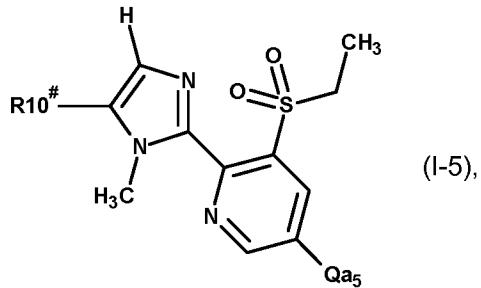
Qa_4 is selected from the group consisting of



10 ,

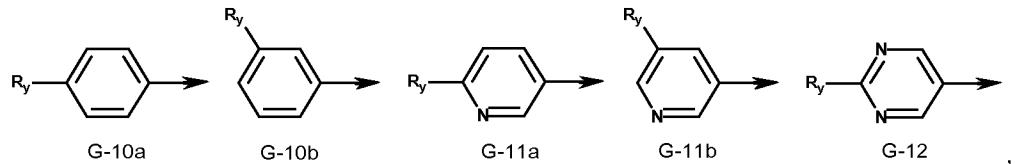
wherein each R_x is, independently selected from hydrogen, halogen and C_1 - C_4 haloalkyl.

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



15 wherein

$R_{10}^{\#}$ is a radical G-10 to G-12 independently selected from the group consisting of



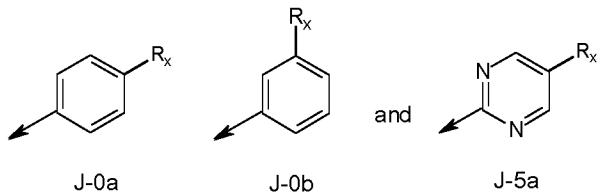
wherein

the arrow denotes the point of attachment to the imidazole ring; and

-99-

each Ry is, independently selected from halogen, C₁-C₄haloalkyl, C₁-C₄haloalkylsulfanyl and C₁-C₄haloalkylsulfonyl; and

Qa₅ is selected from the group consisting of



5 wherein each Rx is, independently selected from hydrogen, halogen and C₁-C₄haloalkyl.

9. 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.

10

10. A method for controlling pests, which comprises applying a composition according to claim 9 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.

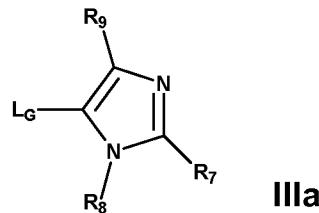
15

11. 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 9.

12. Plant propagation material treated in accordance with the method described in claim 11.

20

13. A compound of formula IIIa



wherein

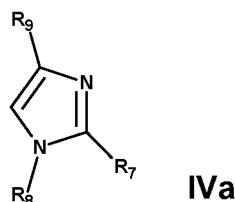
R₈ and R₇ are as defined under formula I in claim 1;

25 R₉ is hydrogen; and

L_G is iodine or bromine.

14. A compound of formula IVa

-100-



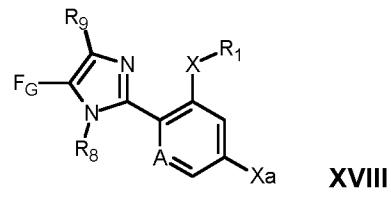
wherein

R₈ and R₇ are as defined under formula I in claim 1; and

R₉ is hydrogen.

5

15. A compound of formula XVIII



wherein

R₈, A, X and R₁ are as defined under formula I in claim 1;

10 F_G is hydrogen, bromine or iodine;

R₉ is hydrogen; and

Xa is chlorine, bromine or iodine.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/067113

A. CLASSIFICATION OF SUBJECT MATTER	INV.	A01N43/50	A01N43/54	A01P7/02	A01P7/04	C07D233/64
		C07D239/64				

ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A01N

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

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

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>GALLAGHER TIMOTHY F ET AL: "Regulation of stress-induced cytokine production by pyridinylimidazoles; inhibition of CSBP kinase", BIOORGANIC & MEDICINAL CHEMISTRY, vol. 5, no. 1, 1997, pages 49-64, XP028589860, ISSN: 0968-0896, DOI: 10.1016/S0968-0896(96)00212-X abstract page 55; table 5; compounds 41, 44, 46</p> <p>-----</p> <p>US 5 656 644 A (ADAMS JERRY LEROY [US] ET AL) 12 August 1997 (1997-08-12) column 1, lines 3-6 column 54; examples 84-86</p> <p>-----</p> <p style="text-align: center;">-/-</p>	1-15
A		1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 August 2016	24/08/2016

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

Authorized officer

Hateley, Martin

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/067113

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AKITO TANAKA ET AL: "A Novel and Useful Descriptor for Hydrophobicity, Partition Coefficient Micellar-Water, and Its Application to a QSAR Study of Antiplatelet Agents", JOURNAL OF MEDICINAL CHEMISTRY, vol. 37, no. 26, 1 December 1994 (1994-12-01), pages 4563-4566, XP055213110, ISSN: 0022-2623, DOI: 10.1021/jm00052a016 abstract page 4564; table 1; compound 9 -----	1-15
A	WO 2013/173218 A1 (DU PONT [US]) 21 November 2013 (2013-11-21) page 1, lines 1-4 page 1, line 16 - page 7, line 10; compounds 1, Q2a, Q2b pages 60-100; tables 7-12 pages 185-187; tables E-H page 185; table E; compound 89 -----	1-15
A	US 2012/178779 A1 (TAKAHASHI MASAKI [JP] ET AL) 12 July 2012 (2012-07-12) cited in the application abstract paragraphs [0002], [0005] - [0028] paragraph [0316]; tables 2-9, 12, 14, 16-29, 31, 33, 35, 37-48 -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/067113

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
US 5656644	A	12-08-1997	NONE		
WO 2013173218	A1	21-11-2013	AU 2013263071 A1		06-11-2014
			CN 104302637 A		21-01-2015
			EP 2850074 A1		25-03-2015
			JP 2015525205 A		03-09-2015
			KR 20150013751 A		05-02-2015
			US 2015126364 A1		07-05-2015
			WO 2013173218 A1		21-11-2013
US 2012178779	A1	12-07-2012	AR 076415 A1		08-06-2011
			CN 102414195 A		11-04-2012
			EP 2424856 A1		07-03-2012
			JP 5671835 B2		18-02-2015
			JP 2010275301 A		09-12-2010
			US 2012015975 A1		19-01-2012
			US 2012178779 A1		12-07-2012
			WO 2010125985 A1		04-11-2010