



(51) International Patent Classification:

C07D 471/04 (2006.01) A01N 43/90 (2006.01)

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(21) International Application Number:

PCT/EP2017/078988

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))

(22) International Filing Date:

13 November 2017 (13.11.2017)

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

16199356.3 17 November 2016 (17.11.2016) EP

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

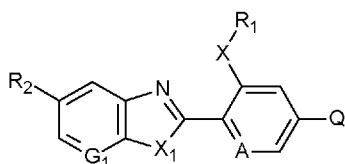
(72) Inventors: EDMUNDS, Andrew; Syngenta Crop Protection AG Schaffhauserstrasse, 4332 Stein (CH). MUEHLEBACH, Michel; Syngenta Crop Protection AG Schaffhauserstrasse, 4332 Stein (CH). JUNG, Pierre, Joseph, Marcel; Syngenta Crop Protection AG Schaffhauserstrasse, 4332 Stein (CH). JEANGUENAT, André; Syngenta Crop Protection AG Schaffhauserstrasse, 4332 Stein (CH). RENDLER, Sebastian; Syngenta Crop Protection AG Schaffhauserstrasse, 4332 Stein (CH).

(74) Agent: SYNGENTA INTERNATIONAL AG; Schwarzwaldallee 215 (WRO B8-Z1-30), 4058 Basel (CH).

(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, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, 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.

(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,

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



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



-1-

Pesticidally active heterocyclic derivatives with sulphur containing substituents

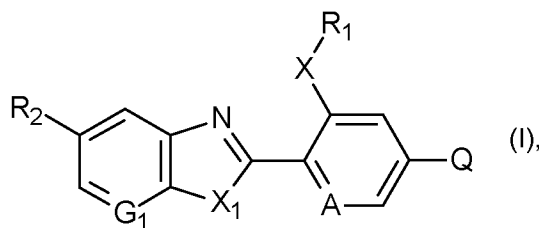
The present invention relates to pesticidally active, in particular insecticidally active heterocyclic derivatives containing sulphur substituents, to intermediates for the preparation of those compounds, to compositions comprising those compounds, and to their use for controlling animal pests (including 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 2012/086848, WO 2013/018928, WO 2014/142292, WO 2015/000715, WO 2015/133603 and WO 2015/198859.

- 10 There have now been found novel pesticidally active heterocyclic 6/5-bicyclic ring derivatives with sulphur containing phenyl and pyridyl substituents.

The present invention accordingly relates to compounds of formula I,



15

wherein

A represents CH or N;

Q is phenyl which is mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkylsulfanyl, C₁-C₄alkylsulfinyl, C₁-C₄alkylsulfonyl, C₁-C₄haloalkoxy, C₁-C₄alkoxy and C₁-C₄haloalkylsulfanyl; or

20

Q is pyrimidyl which is mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkoxy and C₁-C₄haloalkylsulfanyl; or

Q is pyrazolyl which is linked via a nitrogen atom to the ring which contains the substituent A, said pyrazolyl can be substituted by halogen, cyano or C₁-C₄haloalkyl; or

25

Q is triazolyl which is linked via a nitrogen atom to the ring which contains the substituent A, said triazolyl can be substituted by halogen, cyano or C₁-C₄haloalkyl;

X is S, SO or SO₂;

R₁ is C₁-C₄alkyl, C₁-C₄haloalkyl, C₂-C₆alkenyl, C₂-C₆haloalkenyl, C₂-C₆alkynyl or C₃-C₆cycloalkyl-C₁-C₄alkyl;

30

-2-

R₂ is halogen, C₁-C₆haloalkyl, C₁-C₄haloalkylsulfanyl, C₁-C₄haloalkylsulfanyl, C₁-C₄haloalkylsulfonyl or C₁-C₆haloalkoxy;

X₁ is O, S or NR₃, wherein R₃ is hydrogen, C₁-C₄alkyl, C₂-C₆alkenyl, C₂-C₆alkynyl, C₁-C₄alkoxy-C₁-C₄alkyl or C₃-C₆cycloalkyl; and

- 5 G₁ is N or CH; and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of the compounds of formula I.

Compounds of formula I which have at least one basic centre can form, for example, acid addition salts, for example with strong inorganic acids such as mineral acids, for example perchloric acid, sulfuric acid, nitric acid, a phosphorus acid or a hydrohalic acid, with strong organic carboxylic acids, such as C₁-C₄alkanecarboxylic acids which are unsubstituted or substituted, for example by halogen, for example acetic acid, such as saturated or unsaturated dicarboxylic acids, for example oxalic acid, malonic acid, succinic acid, maleic acid, fumaric acid or phthalic acid, such as hydroxycarboxylic acids, for example ascorbic acid, lactic acid, malic acid, tartaric acid or citric acid, or such as benzoic acid, or with organic sulfonic acids, such as C₁-C₄alkane- or arylsulfonic acids which are unsubstituted or substituted, for example by halogen, for example methane- or p-toluenesulfonic acid. Compounds of formula I which have at least one acidic group can form, for example, salts with bases, for example mineral salts such as alkali metal or alkaline earth metal salts, for example sodium, potassium or magnesium salts, or salts with ammonia or an organic amine, such as morpholine, piperidine, pyrrolidine, a mono-, di- or tri-lower-alkylamine, for example ethyl-, diethyl-, triethyl- or dimethylpropylamine, or a mono-, di- or trihydroxy-lower-alkylamine, for example mono-, di- or triethanolamine.

The alkyl groups occurring in the definitions of the substituents can be straight-chain or branched and are, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, pentyl, hexyl, and their branched isomers. Alkylsulfanyl, alkylsulfanyl, alkylsulfonyl, alkoxy, alkenyl and alkynyl radicals are derived from the alkyl radicals mentioned. The alkenyl and alkynyl groups can be mono- or polyunsaturated. C₁-di-alkylamino is dimethylamino.

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

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

-3-

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.

5 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.

10 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.

15 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 6 carbon atoms. Haloalkoxy is, for example, difluoromethoxy, trifluoromethoxy or 2,2,2-trifluoroethoxy.

20 According to the present invention, Q as a "triazolyl group which is linked via a nitrogen atom" may be selected from (1H-1,2,3-triazol-1-yl)-; (2H-1,2,3-triazol-2-yl)-; (4H-1,2,4-triazol-4-yl)- and (1H-1,2,4-triazol-1-yl)-. Preferred is a triazolyl group selected from (4H-1,2,4-triazol-4-yl)- and (1H-1,2,4-triazol-1-yl)-, even more preferred is (1H-1,2,4-triazol-1-yl)-.

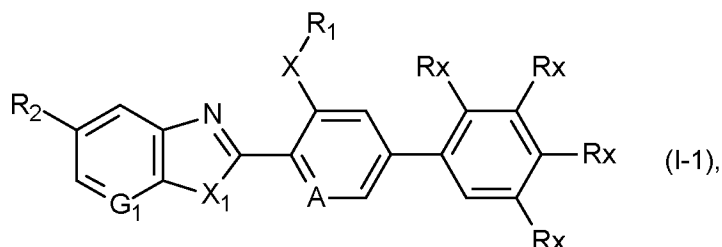
25 In the context of this invention "mono- to polysubstituted" in the definition of the substituents, means typically, depending on the chemical structure of the substituents, monosubstituted to four-times substituted, preferably monosubstituted to three-times substituted, more preferably mono-, or double-substituted.

30 Free radicals represent methyl groups.

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

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

-4-



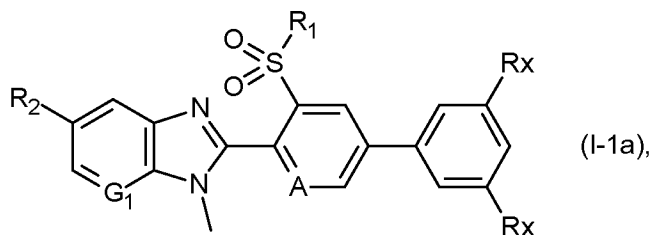
wherein G_1 , R_1 , R_2 , A and X_1 are as defined under formula I above;

X is S, SO or SO_2 ; and

R_x is independently selected from the group consisting of hydrogen, 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 alkylsulfanyl, C_1 - C_4 alkylsulfinyl, C_1 - C_4 alkylsulfonyl, and C_1 - C_4 haloalkylsulfanyl with the proviso that at least one R_x is different from hydrogen.

In this preferred group of compounds of formula I-1, R_1 is preferably ethyl, R_2 is preferably C_1 - C_6 haloalkyl or C_1 - C_4 haloalkylsulfanyl, X is preferably SO_2 , and X_1 is preferably $N(CH_3)$.

Preferred compounds of formula I-1 are represented by compounds of formula I-1a,

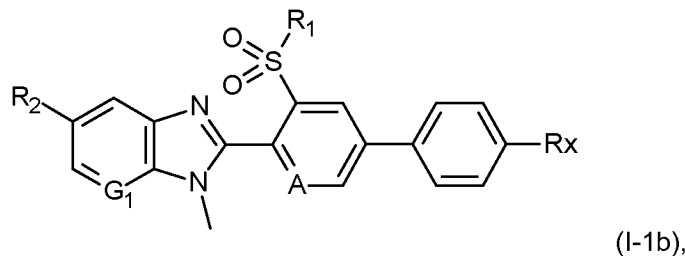


wherein G_1 , R_1 , R_2 and A are as defined under formula I above;

R_x is independently selected from the group consisting of hydrogen and halogen with the proviso that at least one R_x is different from hydrogen.

In this preferred group of compounds of formula I-1a, R_1 is preferably ethyl, R_2 is preferably C_1 - C_6 haloalkyl. Even more preferred compounds of formula I-1a are those in which R_2 is CF_3 , R_1 is ethyl, A is nitrogen, G_1 is nitrogen and R_x is independently hydrogen or halogen, preferably fluorine or chlorine, with the proviso that at least one R_x is different from hydrogen.

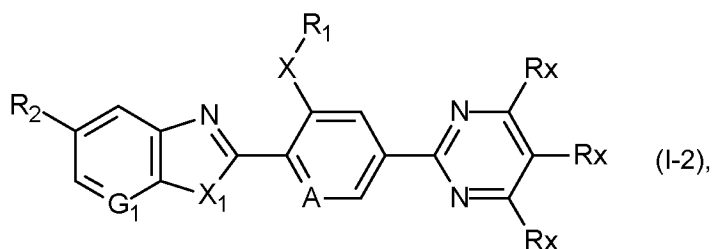
Further preferred compounds of formula I-1 are represented by compounds of formula I-1b



-5-

wherein G_1 , R_1 , R_2 , and A are as defined under formula I above; and wherein R_x is halogen or C_1 - C_4 haloalkyl. In this preferred group of compounds of formula I-1b, R_2 is preferably C_1 - C_6 haloalkyl and R_1 is preferably ethyl. Even more preferred compounds of formula I-1b are those in which R_2 is CF_3 , R_1 is ethyl, A is nitrogen, G_1 is nitrogen and R_x is CF_3 , fluorine or chlorine.

- 5 A further preferred group of compounds of formula I is represented by the compounds of formula I-2

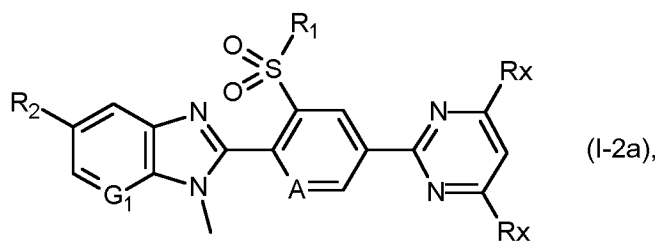


wherein G_1 , R_1 , R_2 , A and X_1 are as defined under formula I above;

X is S , SO or SO_2 ; and

- 10 R_x is independently selected from the group consisting of hydrogen, 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 alkylsulfanyl, C_1 - C_4 alkylsulfinyl, C_1 - C_4 alkylsulfonyl, and C_1 - C_4 haloalkylsulfanyl; with the proviso that at least one R_x is different from hydrogen. In this preferred group of compounds of formula I-2, R_1 is preferably ethyl, R_2 is preferably C_1 - C_6 halo-alkyl or C_1 - C_4 haloalkylsulfanyl, X is preferably SO_2 , and X_1 is preferably $N(CH_3)$.

- 15 Preferred compounds of formula I-2 are represented by compounds of formula I-2a

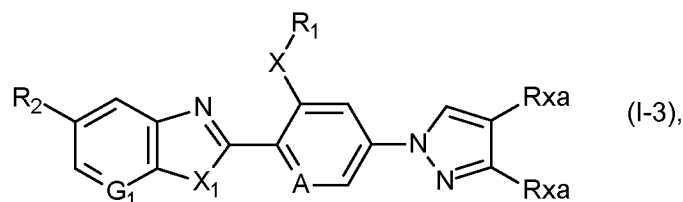


wherein G_1 , R_1 , R_2 , and A are as defined under formula I above; and R_x is hydrogen or halogen. In this preferred group of compounds of formula I-2a, R_2 is preferably C_1 - C_6 haloalkyl and R_1 is preferably ethyl. Even more preferred compounds of formula I-3a are those in which R_2 is CF_3 , R_1 is ethyl, A is nitrogen, G_1 is nitrogen and R_x is hydrogen or halogen, preferably fluorine or chlorine, with the proviso that at least one R_x is different from hydrogen. In a further preferred embodiment of the formula I-2a, both R_x are independently fluorine or chlorine.

20

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

-6-



wherein G_1 , R_1 , R_2 , A and X_1 are as defined under formula I above;

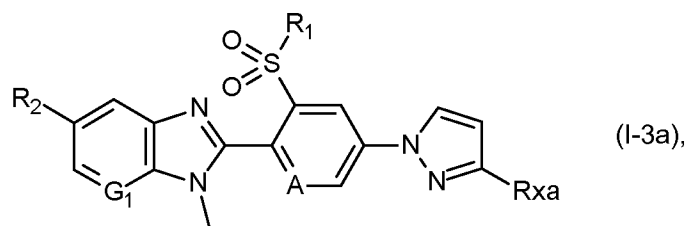
X is S, SO or SO_2 ; and

R_{xa} is independently selected from the group consisting of hydrogen, halogen, cyano or C_1 -

5 C_4 haloalkyl.

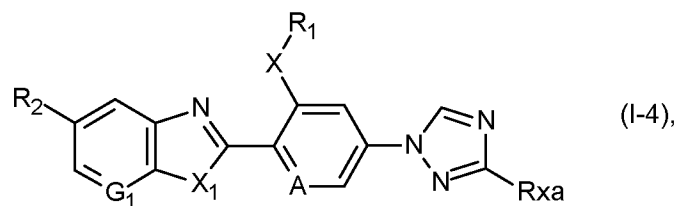
In this preferred group of compounds of formula I-3, R_1 is preferably ethyl, R_2 is preferably C_1 - C_6 haloalkyl or C_1 - C_4 haloalkylsulfanyl, X is preferably SO_2 , and X_1 is preferably $N(CH_3)$.

Preferred compounds of formula I-3 are represented by compounds of formula I-3a



10 wherein G_1 , R_1 , R_2 , and A are as defined under formula I above; and wherein R_{xa} is hydrogen, halogen, cyano or C_1 - C_4 haloalkyl. In this preferred group of compounds of formula I-3a, R_2 is preferably C_1 - C_6 haloalkyl and R_1 is preferably ethyl. Even more preferred compounds of formula I-3a are those in which R_2 is CF_3 , R_1 is ethyl, A is nitrogen, G_1 is nitrogen and R_{xa} is hydrogen, halogen, cyano or C_1 - C_4 haloalkyl, preferably hydrogen, fluorine, chlorine, cyano or CF_3 .

15 A preferred group of compounds of formula I is represented by the compounds of formula I-4



wherein G_1 , R_1 , R_2 , A and X_1 are as defined under formula I above;

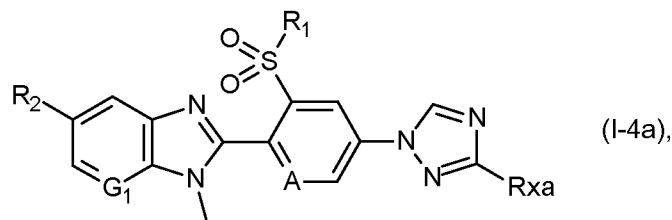
X is S, SO or SO_2 ; and

R_{xa} is hydrogen, halogen, cyano or C_1 - C_4 haloalkyl.

20 In this preferred group of compounds of formula I-4, R_1 is preferably ethyl, R_2 is preferably C_1 - C_6 haloalkyl or C_1 - C_4 haloalkylsulfanyl, X is preferably SO_2 , and X_1 is preferably $N(CH_3)$.

-7-

Preferred compounds of formula I-4 are represented by compounds of formula I-4a



wherein G_1 , R_1 , R_2 , and A are as defined under formula I above; and wherein R_{xa} is hydrogen, halogen, cyano or C_1 - C_4 haloalkyl. In this preferred group of compounds of formula I-4a, R_2 is preferably C_1 - C_6 haloalkyl and R_1 is preferably ethyl. Even more preferred compounds of formula I-4a are those in which R_2 is CF_3 , R_1 is ethyl, A is nitrogen, G_1 is nitrogen and R_{xa} is hydrogen, halogen, cyano or C_1 - C_4 haloalkyl, preferably hydrogen, fluorine, chlorine, cyano or CF_3 .

In an outstanding group of compounds of formula I,

R_1 is C_1 - C_4 alkyl;

R_2 is C_1 - C_4 haloalkyl;

G_1 is N;

X is S or SO_2 ;

X_1 is $N(CH_3)$;

A is N; and

Q is phenyl, which is mono- or disubstituted by substituents selected from the group consisting of halogen and C_1 - C_4 haloalkyl;

or Q is pyrazolyl, mono-substituted by C_1 - C_4 haloalkyl;

or Q is triazolyl, which is unsubstituted; and the N-oxides of said outstanding compounds of formula I.

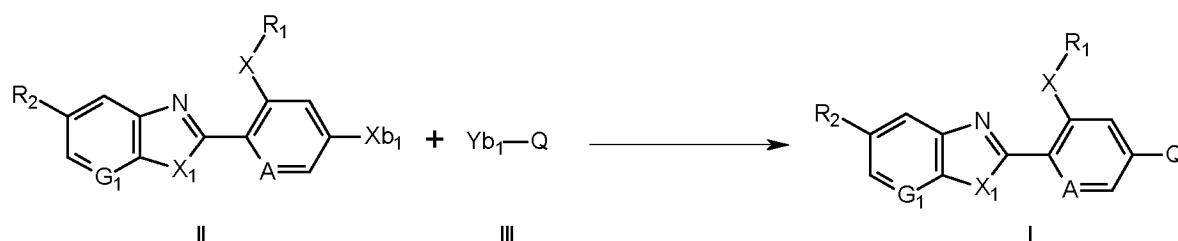
The process according to the invention for preparing compounds of formula I is carried out in principle by methods known to those skilled in the art. The following processes describe the preparation of compounds of formula I. Throughout the process discussion detailed below (schemes 1 to 19), the group G_1 is as described under formula I.

More specifically, compounds of formula I can be prepared (as depicted in scheme 1) by reacting compounds of formula II with compounds of formula III, wherein X_{b1} can be a halogen, preferentially chlorine, bromine or iodine, or a sulfonate, like for example a trifluoromethanesulfonate and Y_{b1} can be a boron-derived functional group, as for example $B(OH)_2$ or $B(OR_{b1})_2$ wherein R_{b1} can be a C_1 - C_6 alkyl group or the two groups OR_{b1} can form together with the boron atom a five- or six-membered ring, as for example a pinacol boronic ester (Suzuki cross-coupling, see for example Tetrahedron Letters, 43(39), 6987-6990; 2002). In formula II and III, A , X_1 , R_1 , R_2 , X and Q are as described in formula I. The reaction can be catalyzed by a palladium based catalyst, for example tetrakis(triphenylphosphine)

-8-

palladium(0), bis(triphenylphosphine)palladium(II) dichloride, chloro(2-dicyclohexylphosphino-2',4',6'-triisopropyl-1,1'-biphenyl)[2-(2'-amino-1,1'-biphenyl)]palladium(II) (XPhos palladacycle), (1,1'-bis(diphenylphosphino)-ferrocene)dichloropalladium-dichloromethane (1:1 complex) or palladium acetate plus phosphine ligands (such as, for example, triphenylphosphine or tricyclohexylphosphine) in presence of a base, like sodium carbonate, tripotassium phosphate or cesium fluoride, in a solvent (such as toluene, 1,2-dimethoxyethane DME, ethanol, iso-propyl alcohol, tetrahydrofuran or dioxane) or a solvent mixture, like, for example a mixture of 1,2-dimethoxyethane (or dioxane, toluene, or tetrahydrofuran) and water, preferably under inert atmosphere. The reaction temperature can preferably range from ambient temperature to the boiling point of the reaction mixture, or alternatively heating may be performed under microwave irradiation.

Scheme 1:



Compounds of formula II, wherein A, X₁, R₁, R₂ and X are as described in formula I, and wherein X_{b1} is a halogen, preferably chlorine, bromine or iodine, and in which G₁ is N or CH, may be prepared in analogy to descriptions found in the literature.

Alternatively, compounds of formula II, wherein X_{b1} can be a halogen, preferentially chlorine, bromine or iodine, or a sulfonate, like for example a trifluoromethanesulfonate, may be reacted with compounds of formula III, wherein Y_{b1} is a magnesium halide group, such as -MgBr (Kumada cross-coupling), optionally in the presence of additives, such as zind halides (Journal of Organic Chemistry, 75(19), 6677-6680; 2010). The reaction may be catalyzed by a palladium based catalyst, or may involve a nickel based catalyst, such as 1,3-is(diphenylphosphino)propanenickel dichloride (dppp)NiCl₂.

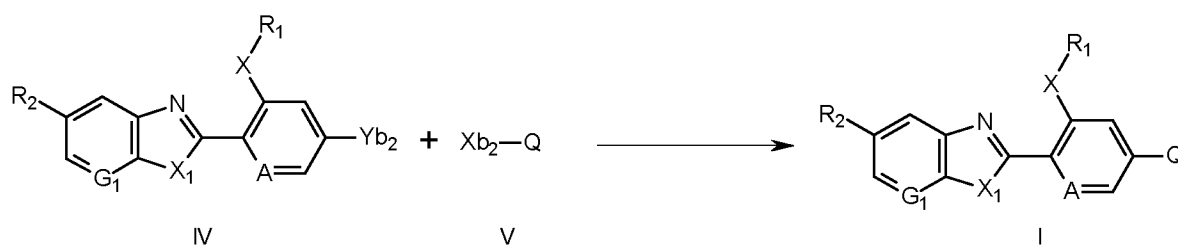
Also known are reactions between compounds of formula II, wherein X_{b1} can be a halogen, preferentially chlorine, bromine or iodine, or a sulfonate, like for example a trifluoromethanesulfonate, with compounds of formula III, wherein Y_{b1} is a zinc halide group, such as -ZnBr (Negishi cross-coupling), as illustrated for example in Synthetic Communications, 28(2), 225-232; 1998. The reaction may be catalyzed by a palladium based catalyst, such as for example, (1,1'-bis(diphenylphosphino)-ferrocene)dichloropalladium Pd(dppf)Cl₂ or bis(triphenylphosphine)palladium(II) dichloride, optionally in the presence of phosphine additives (such as, for example, 2-dicyclohexyl-phosphino-2',6'-dimethoxy-biphenyl S-PHOS), in a solvent, like, for example 1,2-dimethoxyethane, dioxane, toluene,

-9-

or tetrahydrofuran, preferably under inert atmosphere. The reaction temperature can preferentially range from ambient temperature to the boiling point of the reaction mixture.

Compounds of formula I can also be made (as depicted in scheme 2) by reacting compounds of formula IV with compounds of formula V, wherein X_{b2} can be a halogen, preferentially chlorine, bromine or iodine, or a sulfonate, like for example a trifluoromethanesulfonate and Y_{b2} can be a boron-derived functional group, as for example $B(OH)_2$ or $B(OR_{b2})_2$ wherein R_{b2} can be a C_1 - C_6 alkyl group or the two groups OR_{b2} can form together with the boron atom a five- or six-membered ring, as for example a pinacol boronic ester. In formulae IV and V, A, X_1 , R_1 , R_2 , X and Q are as described in formula I. The reaction can be catalyzed by a palladium based catalyst, for example tetrakis(triphenylphosphine)-palladium(0), bis(triphenyl-phosphine) palladium(II) dichloride or (1,1'-bis(diphenylphosphino)-ferrocene)dichloropalladium-dichloromethane (1:1 complex), in presence of a base, like sodium carbonate, tripotassium phosphate or cesium fluoride, in a solvent (such as toluene, 1,2-dimethoxyethane DME, ethanol, iso-propyl alcohol, tetrahydrofuran or dioxane) or a solvent mixture, like, for example a mixture of 1,2-dimethoxyethane and water, or of dioxane and water, preferably under inert atmosphere. The reaction temperature can preferentially range from ambient temperature to the boiling point of the reaction mixture, or alternatively heating may be performed under microwave irradiation.

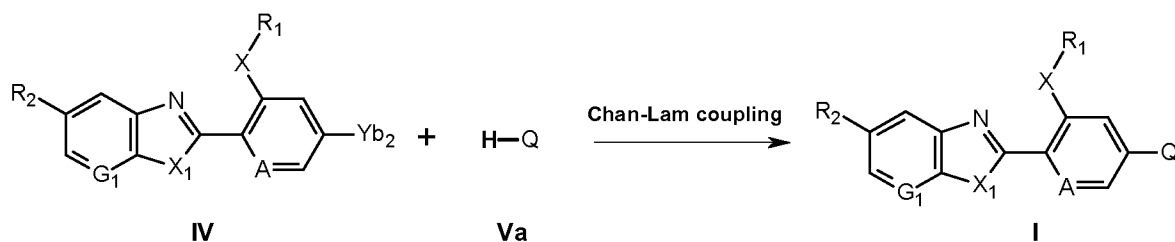
Scheme 2



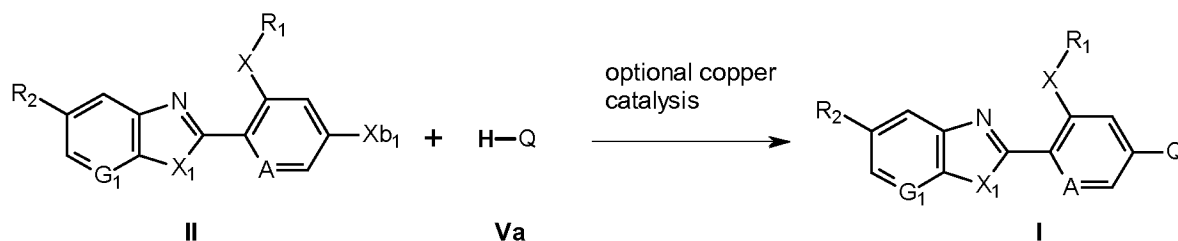
In the particular case where compounds of formula I have the group Q attached through a nitrogen atom (i.e. those situations where Q is a nitrogen containing heteroring system), these compounds can be advantageously accessed by reacting a compound of the formula IV with a compound of the formula Va, wherein Y_{b2} can be a boron-derived functional group, such as for example $B(OH)_2$ or $B(OR_{b2})_2$ wherein R_{b2} can be a C_1 - C_6 alkyl group or the two groups OR_{b2} can form together with the boron atom a five - or six-membered ring, as for example a pinacol boronic ester (scheme 2a). In formulae IV and Va, A, R_1 , R_2 , X and X_1 are as defined under formula I above and Q is as described in formula I, with the condition that the attachment point is a nitrogen atom. 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. 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

-10-

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 temperature.

5 Scheme 2a

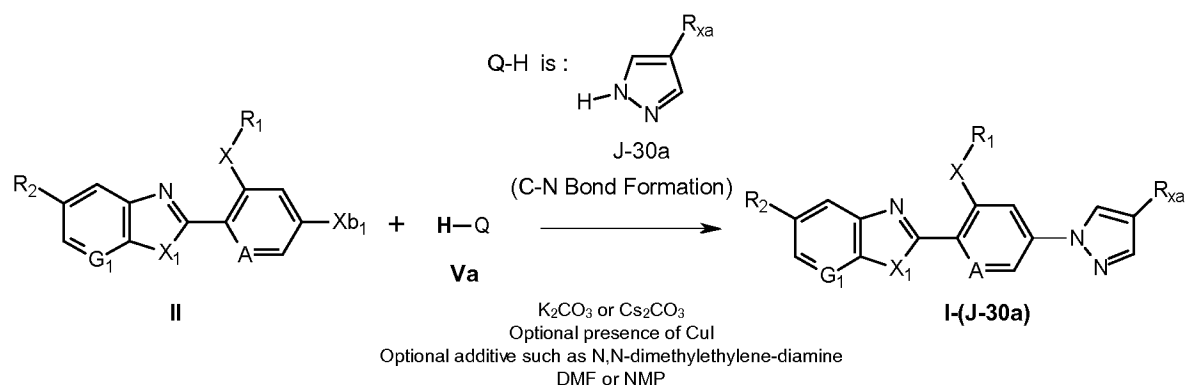
In the particular case where compounds of formula I have the group Q attached through a nitrogen atom (i.e. those situations where Q is a nitrogen containing heteroring system such as pyrazolyl or triazolyl), these compounds can be alternatively accessed by reacting a compound of the formula II with a compound of the formula Va, wherein X_{b1} can be a halogen, preferentially chlorine, bromine or iodine, or a sulfonate, like for example a trifluoromethanesulfonate (scheme 2b). In formulae II and Va, A, R_1 , R_2 , X and X_1 are as defined under formula I above and Q is pyrazolyl or triazolyl, with the condition that the attachment point is a nitrogen atom. Such a reaction with a heterocycle Q-H (which contains an appropriate NH functionality) of formula Va may be operated 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 N,N-dimethylformamide DMF at temperatures between 30-150°C, optionally under microwave irradiation.

Scheme 2b

Such a reaction (C-N Bond Formation) is illustrated below (scheme 2c) for the heterocycle Q-H J-30a, wherein R_{xa} is halogen, cyano or C_1 - C_4 haloalkyl, to give a compound of formula I-(J-30a), a particular sub-group of compounds of formula I, wherein R_{xa} , A, X, R_1 , X_1 and R_2 are as previously defined.

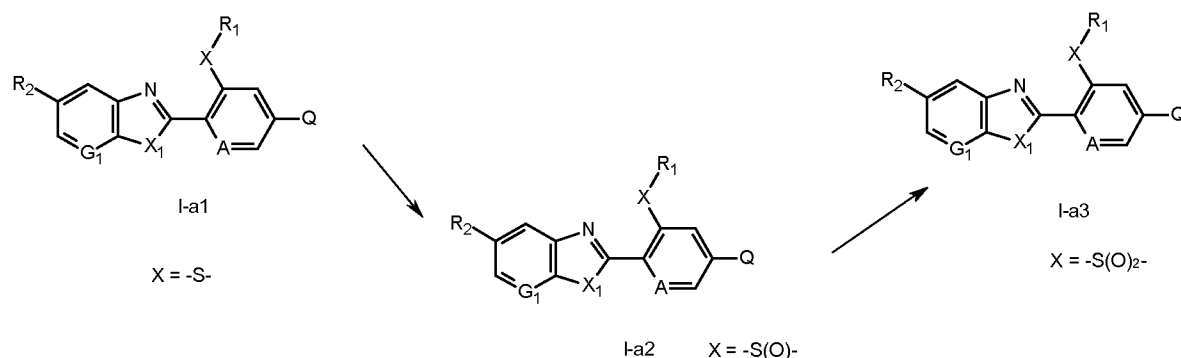
-11-

Scheme 2c



Compounds of formula I-a3, wherein A, R_1 , R_2 , X_1 and Q have the values defined in formula I, and X is $-SO_2-$, can be prepared by oxidation of compounds of formula I-a2, wherein A, R_1 , R_2 , X_1 and Q have the values defined in formula I, and X is $-SO-$. The reaction can be performed with reagents like, for example, a peracid such as peracetic acid or m-chloroperbenzoic acid, or a hydroperoxide, as for example, hydrogen peroxide or tert-butylhydroperoxide, or an inorganic oxidant, like a monoperoxo-disulfate salt or potassium permanganate. In a similar way, compounds of formula I-a2, wherein A, R_1 , R_2 , X_1 and Q have the values defined in formula I, and X is $-SO-$, can be prepared by oxidation of compounds of formula I-a1, wherein A, R_1 , R_2 , X_1 and Q have the values defined in formula I, and X is $-S-$, under analogous conditions described above. These reactions can be performed in various organic (dichloromethane for example) or aqueous solvents compatible to these conditions, by temperatures from below $0^\circ C$ up to the boiling point of the solvent system. The transformation of compounds of the formula I-a1 into compounds of the formula I-a2 and I-a3 is represented in scheme 3.

Scheme 3

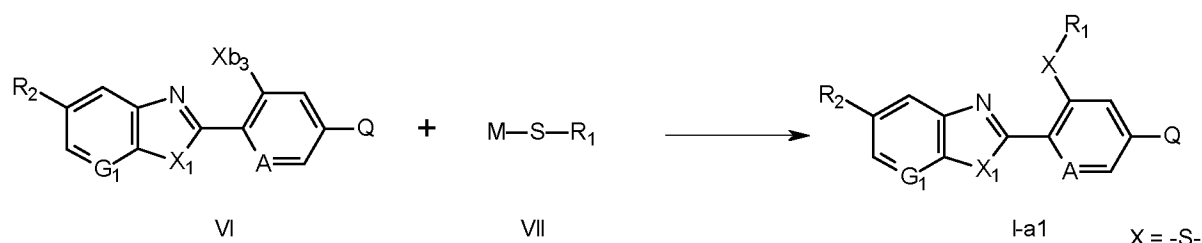


Compounds of formula I-a1 may also be prepared (scheme 4) by reacting a compound of the formula VI with a compound of the formula VII, wherein A, R_1 , R_2 , X_1 and Q have the values defined in formula I and X is sulphur and M is a metal or non-metal cation. In the scheme 4, the cation M is assumed to

-12-

be monovalent, but polyvalent cations associated with more than one S-R₁ group can also be considered. Preferred cations are, for example lithium, sodium, potassium or cesium. For this transformation to work, X_{b3} is a leaving group like, for example, fluorine, chlorine, bromine or iodine, or an aryl- or alkylsulfonate, but many other leaving groups could be considered. The reaction can be performed in a solvent, preferably aprotic (such as N,N-dimethylformamide or acetonitrile), at temperatures below 0°C or up to boiling temperature of the reaction mixture.

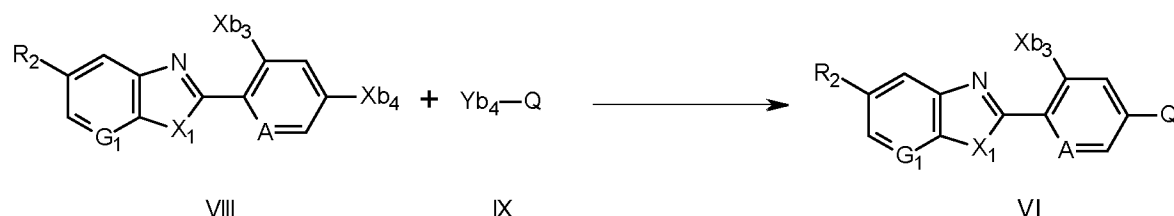
Scheme 4



- Compounds of formula VI, wherein X_{b3} is a leaving group like, for example, fluorine, chlorine, bromine or iodine, or an aryl- or alkylsulfonate such as trifluoromethanesulfonate, or any other similar leaving group, can be prepared (scheme 5) by reacting compounds of formula VIII with compounds of formula IX, wherein X_{b4} can be a halogen, preferentially chlorine, bromine or iodine, or a sulfonate, like for example a trifluoromethanesulfonate, most preferably bromine or iodine and Y_{b4} can be a boron-derived functional group, as for example B(OH)₂ or B(OR_{b4})₂ wherein R_{b4} can be a C₁-C₆alkyl group or the two groups OR_{b4} can form together with the boron atom a five- or six-membered ring, as for example a pinacol boronic ester. In formula VI, VIII and IX, A, X₁, R₂ and Q are as described in formula I. The reaction can be catalyzed by a palladium based catalyst, for example tetrakis(triphenylphosphine)palladium(0), bis(triphenylphosphine) palladium(II) dichloride or (1,1'-bis(diphenylphosphino)-ferrocene)dichloropalladium-dichloromethane (1:1 complex), in presence of a base, like sodium carbonate, tripotassium phosphate or cesium fluoride, in a solvent (such as toluene, 1,2-dimethoxy-ethane DME, ethanol, iso-propyl alcohol, tetrahydrofuran or dioxane) or a solvent mixture, like, for example a mixture of 1,2-dimethoxyethane and water, or of dioxane and water, preferably under inert atmosphere. The reaction temperature can preferentially range from ambient temperature to the boiling point of the reaction mixture, or alternatively heating may be performed under microwave irradiation.

Scheme 5

-13-



Alternatively, compounds of formula VIII, wherein X_{b4} can be a halogen, preferentially chlorine, bromine or iodine, or a sulfonate, like for example a trifluoromethanesulfonate, may be reacted with compounds of formula IX, wherein Y_{b4} is a magnesium halide group, such as $-\text{MgBr}$ (Kumada cross-coupling), optionally in the presence of additives, such as zinc halides (Journal of Organic Chemistry, 75(19), 6677-6680; 2010). The reaction may be catalyzed by a palladium based catalyst, or may involve a nickel based catalyst, such as 1,3-is(diphenylphosphino)propanenickel dichloride (dppp) NiCl_2 .

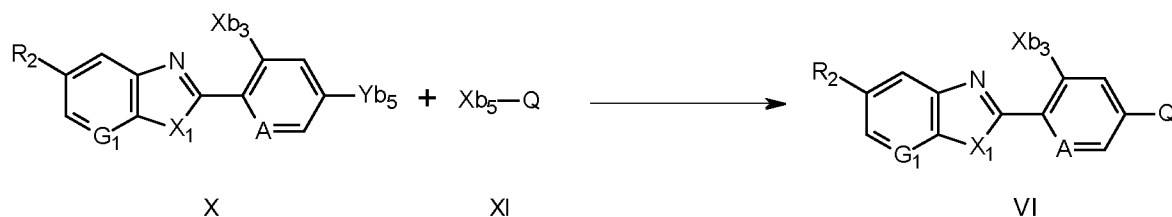
Also known are reactions between compounds of formula VIII, wherein X_{b4} can be a halogen, preferentially chlorine, bromine or iodine, or a sulfonate, like for example a trifluoromethanesulfonate, with compounds of formula IX, wherein Y_{b4} is a zinc halide group, such as $-\text{ZnBr}$ (Negishi cross-coupling), as illustrated for example in Synthetic Communications, 28(2), 225-232; 1998. The reaction may be catalyzed by a palladium based catalyst, such as for example, (1,1'-bis(diphenylphosphino)-ferrocene)dichloropalladium $\text{Pd}(\text{dppf})\text{Cl}_2$ or bis(triphenylphosphine)palladium(II) dichloride, optionally in the presence of phosphine additives (such as, for example, 2-dicyclohexyl-phosphino-2',6'-dimethoxy-biphenyl S-PHOS), in a solvent, like, for example 1,2-dimethoxyethane, dioxane, toluene, or tetrahydrofuran, preferably under inert atmosphere. The reaction temperature can preferentially range from ambient temperature to the boiling point of the reaction mixture.

In an alternative way depicted in scheme 6, compounds of formula VI can also be prepared by reacting compounds of formula X, wherein X_{b3} is a leaving group like, for example, fluorine, chlorine, bromine or iodine, or an aryl- or alkylsulfonate such as trifluoromethanesulfonate, or any other similar leaving group, with compounds of formula XI, wherein X_{b5} can be a halogen, preferentially chlorine, bromine or iodine, or a sulfonate, like for example a trifluoromethanesulfonate, most preferably bromine or iodine, and Y_{b5} can be a boron-derived functional group, as for example $\text{B}(\text{OH})_2$ or $\text{B}(\text{OR}_{b5})_2$ wherein R_{b5} can be a C_1 - C_6 alkyl group or the two groups OR_{b5} can form together with the boron atom a five- or six-membered ring, as for example a pinacol boronic ester. In formula VI, X and XI, A, X_1 , R_2 and Q are as described in formula I. The reaction can be catalyzed by a palladium based catalyst, for example tetrakis(triphenylphosphine)palladium(0), bis(triphenylphosphine) palladium(II) dichloride or (1,1'-bis(diphenylphosphino)-ferrocene)dichloropalladium-dichloromethane (1:1 complex), in presence of a base, like sodium carbonate, tripotassium phosphate or cesium fluoride, in a solvent (such as toluene, 1,2-dimethoxy-ethane DME, ethanol, iso-propyl alcohol, tetrahydrofuran or dioxane) or a solvent mixture, like, for example a mixture of 1,2-dimethoxyethane and water, or of dioxane and

-14-

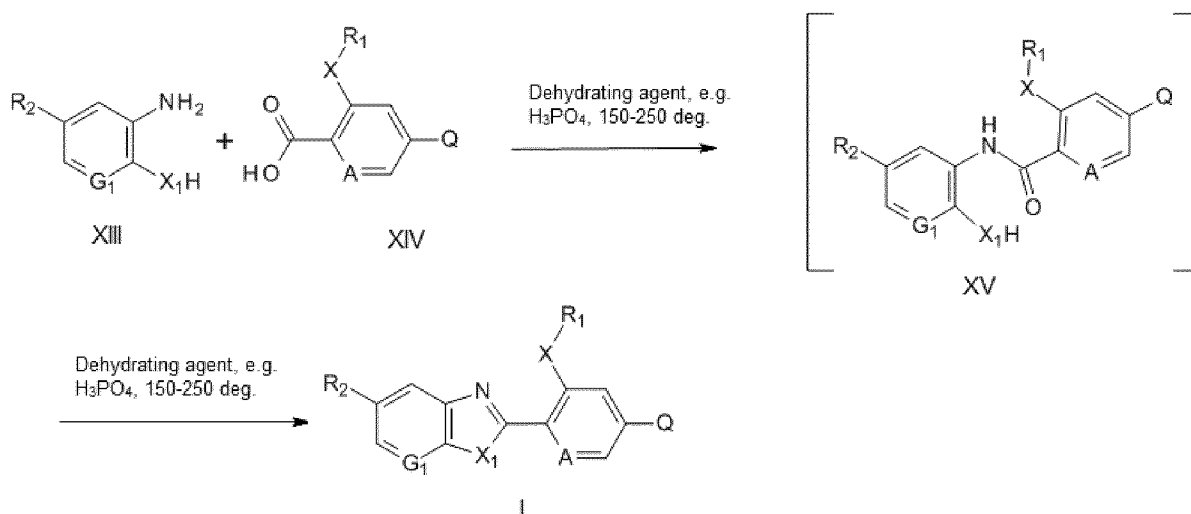
water, preferably under inert atmosphere. The reaction temperature can preferentially range from ambient temperature to the boiling point of the reaction mixture, or alternatively heating may be performed under microwave irradiation.

Scheme 6



Compounds of formula I can also be prepared (scheme 7) by reacting compounds of formula XIII and compounds of formula XIV under various formal dehydration conditions, wherein A, R₁, R₂, X, X₁ and Q have the values defined in formula I. These methods are known to those skilled in the art or described for example in WO 2009/131237, WO 2011/043404, WO 2011/040629, WO 2010/125985, WO 2012/086848, WO 2013/018928, WO 2013/191113, WO 2013/180193 and WO 2013/180194. Such processes are well known and have been described for example in WO 2011/040629 or WO 2009131237 (X₁ is oxygen), WO 2011088990 or *Inorg. Chimica Acta*, 358(9), 2701-2710; **2005** (X₁ is sulfur) and *J. Am. Chem. Soc.*, 132(5), 1545-1557, **2010** or WO 2008128968 (X₁ is NR₃). The preparation of compounds of formula XIII, wherein X₁ and R₂ are as defined above, is described in detail, for example, in WO 2012/086848.

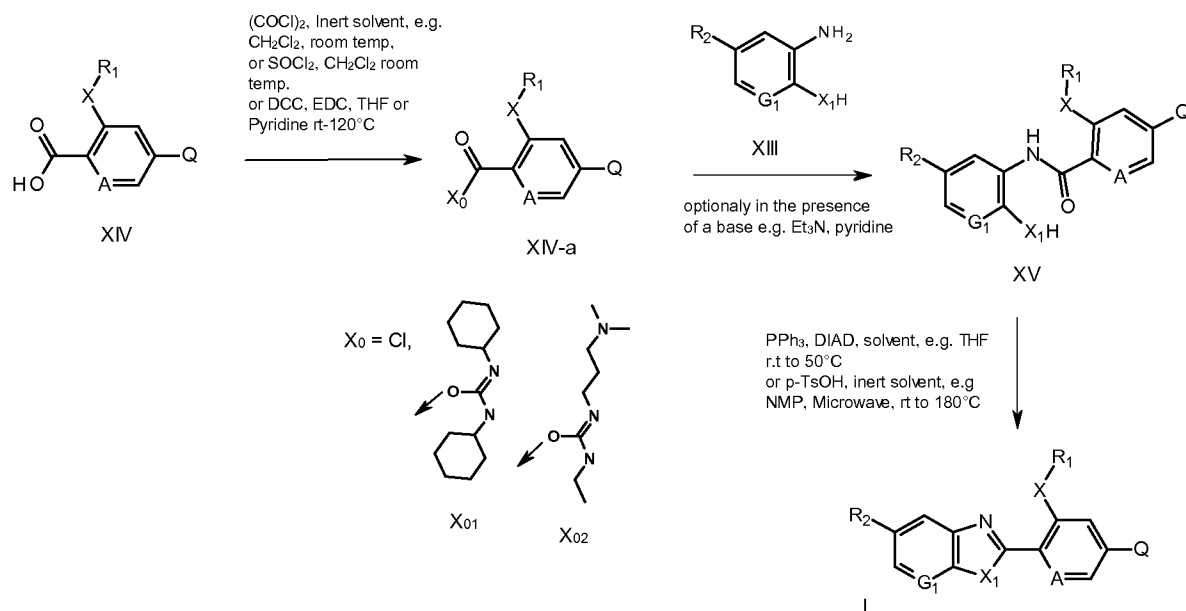
Scheme 7



The process describing the reaction between compounds of formula XIII and compounds of formula XIV towards compounds of formula I is summarized in more details in scheme 8:

Scheme 8

-15-



Compounds of formula XIV, wherein A, R₁, X and Q are as previously described, are activated (scheme 8) to compounds of formula XIV-a by methods known to those skilled in the art and described in for example *Tetrahedron*, 61 (46), 10827-10852, **2005**. For example compounds where

5 X₀ is chlorine are formed by treatment with for example, oxalyl chloride or thionyl chloride in the presence of catalytic quantities of DMF in inert solvents such as methylene chloride or THF at temperatures between 20 °C to 100 °C, preferably 25 °C. Treatment of XIV-a with compounds of formula XIII, wherein R₂ and X₁ are as described in formula I, optionally in the presence of a base, e.g. triethylamine or pyridine, leads to compounds of formula XV. Alternatively, compounds of formula

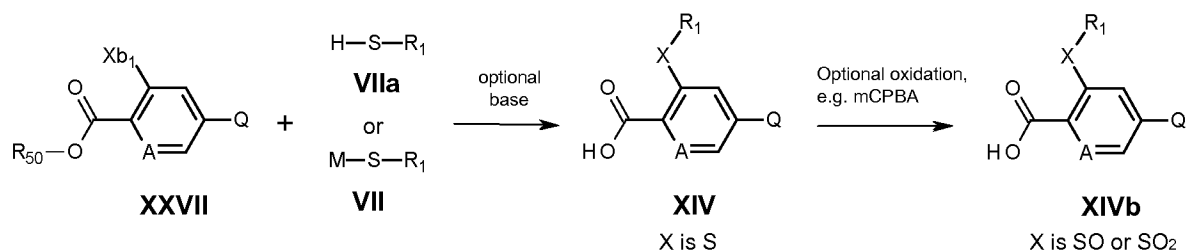
10 I can be prepared by treatment of compounds of formula XIV with dicyclohexyl carbodiimide (DCC) or 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) to give the activated species XIV-a, wherein X₀ is X₀₁ and X₀₂ respectively, in an inert solvent, e.g. pyridine, or tetrahydrofuran (THF) optionally in the presence of a base, e.g. triethylamine, at temperatures between 50-180 °C. Compounds of formula XV so obtained can then be converted to compounds of formula I by dehydration, eg. by heating the

15 compounds, optionally under microwave irradiation, in the presence of an acid catalyst, for example methanesulfonic acid, or *para*-toluenesulfonic acid p-TsOH, in an inert solvent such as N-methyl pyrrolidone or xylene, at temperatures between 25-180 °C, preferably 130-170 °C. Such processes have been described previously in WO 2010/125985. Alternatively, compounds of formula XV can be converted to compounds of formula I (wherein X₁ is O) using triphenylphosphine, di-isopropyl

20 azodicarboxylate in an inert solvent such as THF at temperatures between 25-50°C. Such Mitsunobu conditions have been previously described for such transformations (see WO 2009/131237).

Compounds of formula XIV, wherein X is S, and wherein A, R₁ and Q are as defined above,

-16-

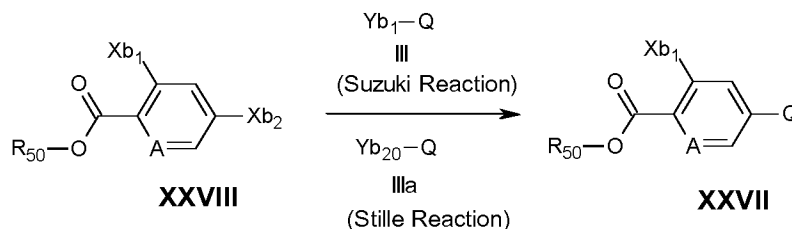


may be prepared by reacting a compound of formula XXVII, wherein A and Q are as defined above, and wherein R₅₀ is C₁-C₄alkyl and in which Xb₁ is a leaving group such as, for example, a halogen (preferably fluorine, chlorine or bromine) or nitro, with a compound of formula VIIa, or a salt thereof VII, 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, 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 VIIa include compounds of the formula VII



wherein R₁ is as defined above and wherein M is, for example, sodium or potassium. Oxidation of compounds of formula XIV, wherein X is S, and wherein A, R₁ and Q are as defined above, with a suitable oxidizing agent, into compounds of formula XIVb, wherein X is SO or SO₂ may be achieved under conditions already described above.

Compounds of formula XXVII, wherein A is as defined above, and in which Q is optionally substituted phenyl, pyridyl or pyrimidyl, and wherein R₅₀ is C₁-C₄alkyl and in which Xb₁ is a leaving group such as, for example, a halogen (preferably fluorine, chlorine or bromine) or nitro,



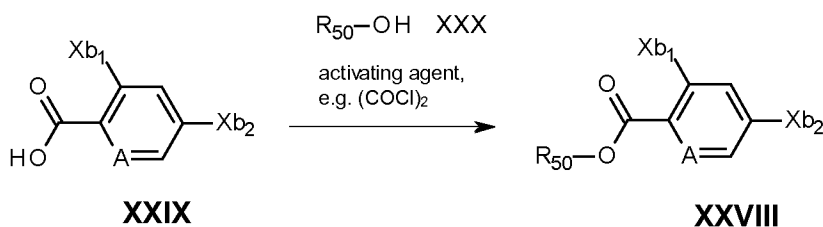
-17-

may be prepared by a Suzuki reaction, which involves for example, reacting compounds of formula XXVIII, wherein A, R₅₀ and Xb₁ are as defined above, and wherein Xb₂ is a leaving group like, for example, chlorine, bromine or iodine (preferably bromine), or an aryl- or alkylsulfonate such as trifluoromethane-sulfonate, with compounds of formula III, wherein Q is optionally substituted phenyl, pyridyl or pyrimidyl, 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 C₁-C₄alkyl 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 catalyzed by a palladium based catalyst, for example *tetrakis*(triphenylphosphine)-palladium(0), or bis(triphenylphosphine)palladium(II) dichloride or (1,1'-bis(diphenylphosphino)ferrocene)dichloro-palladium-dichloromethane (1:1 complex), in presence of a base, like sodium carbonate or cesium fluoride, in a solvent or a solvent mixture, like, for example a mixture of 1,2-dimethoxyethane and water or of dioxane and water, preferably under inert atmosphere. The reaction temperature can preferentially range from room temperature to the boiling point of the reaction mixture. Such Suzuki reactions are well known to those skilled in the art and have been reviewed, for example, in *J. Orgmet. Chem.* 576, **1999**, 147–168.

Alternatively compounds of formula XXVII, wherein A, Q, R₅₀ and Xb₁ are as defined above, may be prepared by a Stille reaction between compounds of formula IIIa, wherein Q is as defined above, and wherein Y_{b20} is a trialkyl tin derivative, preferably tri-*n*-butyl tin, and compounds of formula XXVIII, wherein A, R₅₀ and Xb₁ are as defined above, and wherein Xb₂ is a leaving group like, for example, chlorine, bromine or iodine (preferably bromine), or an aryl- or alkylsulfonate such as trifluoromethane-sulfonate. 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 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.

A large number of compounds of the formula III and IIIa are commercially available or can be prepared by those skilled in the art.

Ester compounds of formula XXVIII, wherein A, R₅₀, Xb₁ and Xb₂ are as defined above,

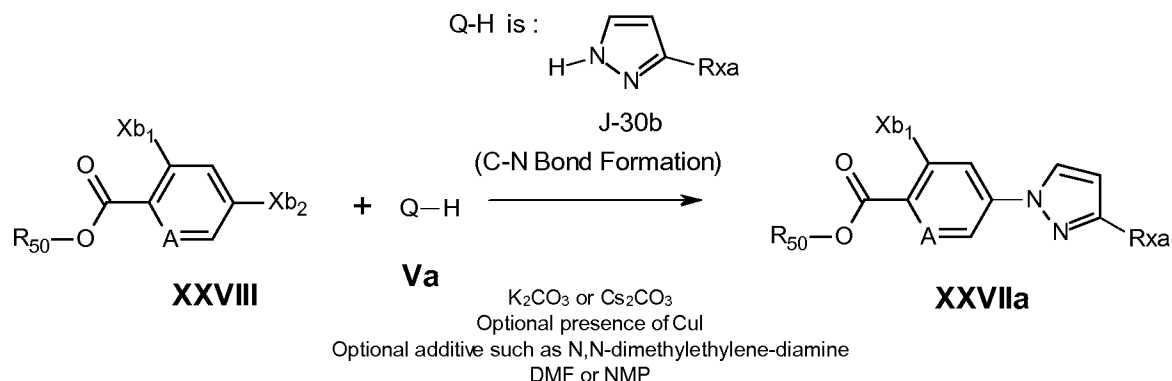


-18-

may be prepared from the corresponding carboxylic acid compounds of formula XXIX, wherein A, Xb₁ and Xb₂ are as defined above, by reaction with an alcohol of formula XXX, wherein R₅₀ is C₁-C₄alkyl, optionally in the presence of an acid (such as sulfuric acid), or alternatively optionally in presence of an activating agent, such as for example oxalyl chloride (COCl)₂. Such esterification methods are well known to a person skilled in the art.

When Q is optionally substituted pyrazolyl or triazolyl, then compounds of formula XXVII, wherein A, R₅₀ and Xb₁ are as defined above, may be prepared from compounds of formula XXVIII, wherein A, R₅₀ and Xb₁ are as defined above, and wherein Xb₂ 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) Va, wherein Q is optionally substituted pyrazolyl or triazolyl, in the presence of a base, such as potassium carbonate K₂CO₃ or cesium carbonate Cs₂CO₃, 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 dioxane, N-methylpyrrolidone NMP or N,N-dimethylformamide DMF at temperatures between 30-150°C.

Such a reaction (C-N Bond Formation) is illustrated below for the heterocycle Q-H J-30b, wherein R_xa is halogen, cyano or C₁-C₄haloalkyl,



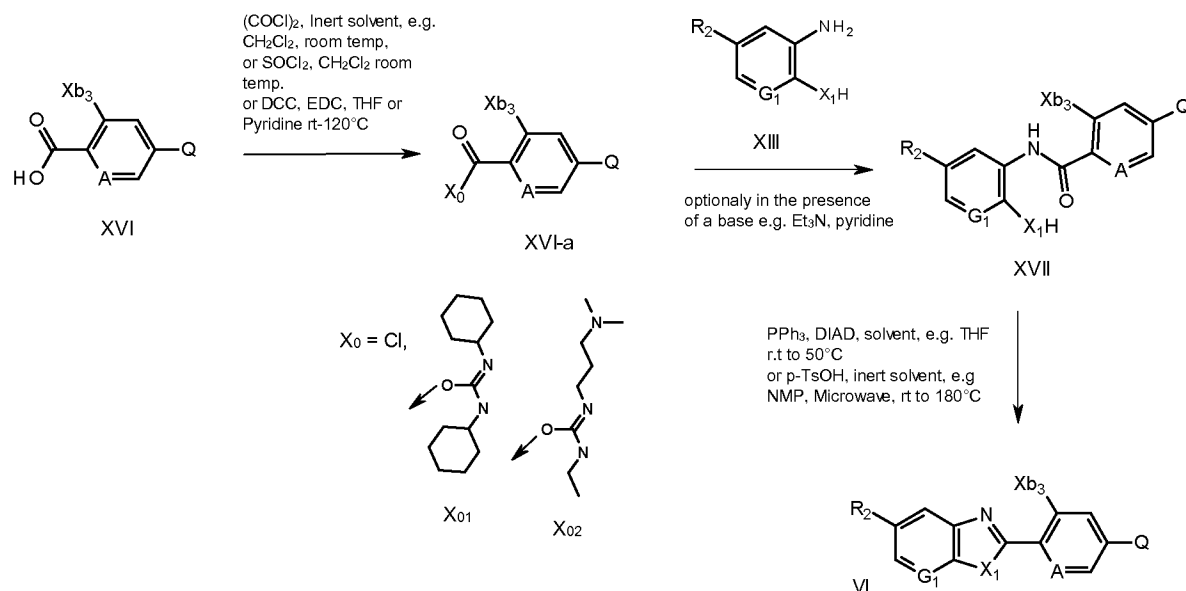
to give compounds of formula XXVIIa, a particular sub-group of compounds of formula XXVII, wherein R_xa, A, R₅₀ and Xb₁ are as previously defined.

In an analogous way (scheme 9), compounds of formula VI, wherein Xb₃ is a leaving group like, for example, fluorine, chlorine, bromine or iodine, or an aryl- or alkylsulfonate such as trifluoromethanesulfonate, or any other similar leaving group, can be prepared by reacting compounds of formula XVI, wherein A and Q have the values defined for formula I, with an activating agent, like, for example oxalyl chloride or thionyl chloride or a carbodiimid reagent to generate the activated species XVI-a, followed by reaction with compounds of formula XIII, wherein R₂ and X₁ are as described in formula I. The intermediate compounds of formula XVII may be isolated, but are preferentially converted into the

-19-

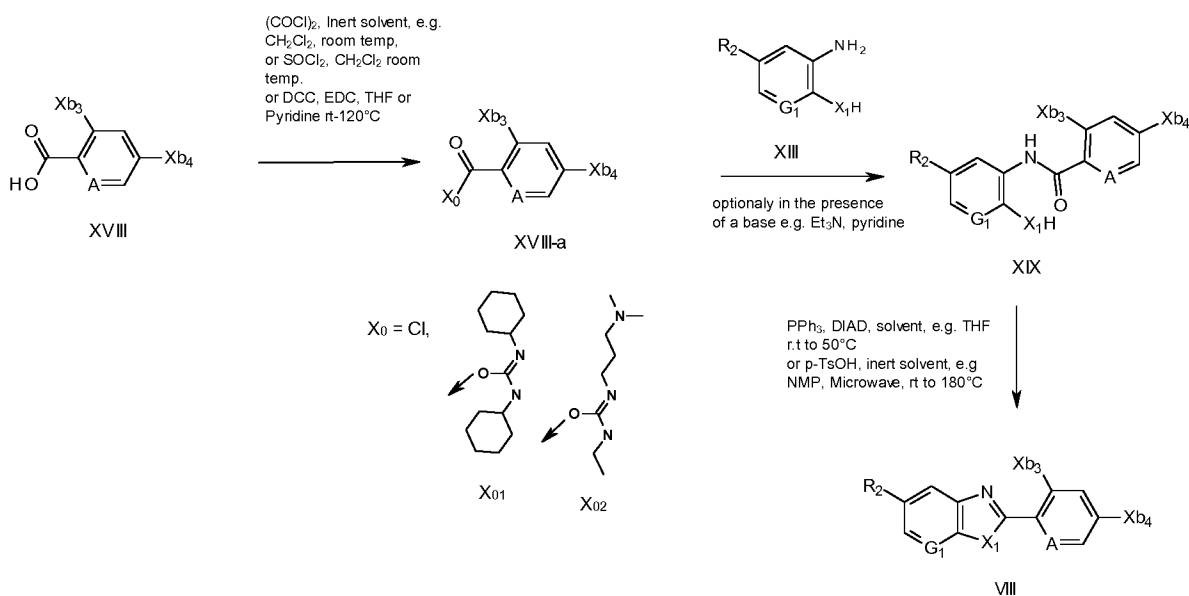
compounds of formula VI in a similar way as described above for the transformation of compounds XV into compounds of formula I.

Scheme 9



- 5 In a similar way as described above, compounds of formula VIII can be prepared as described in scheme 10,

Scheme 10



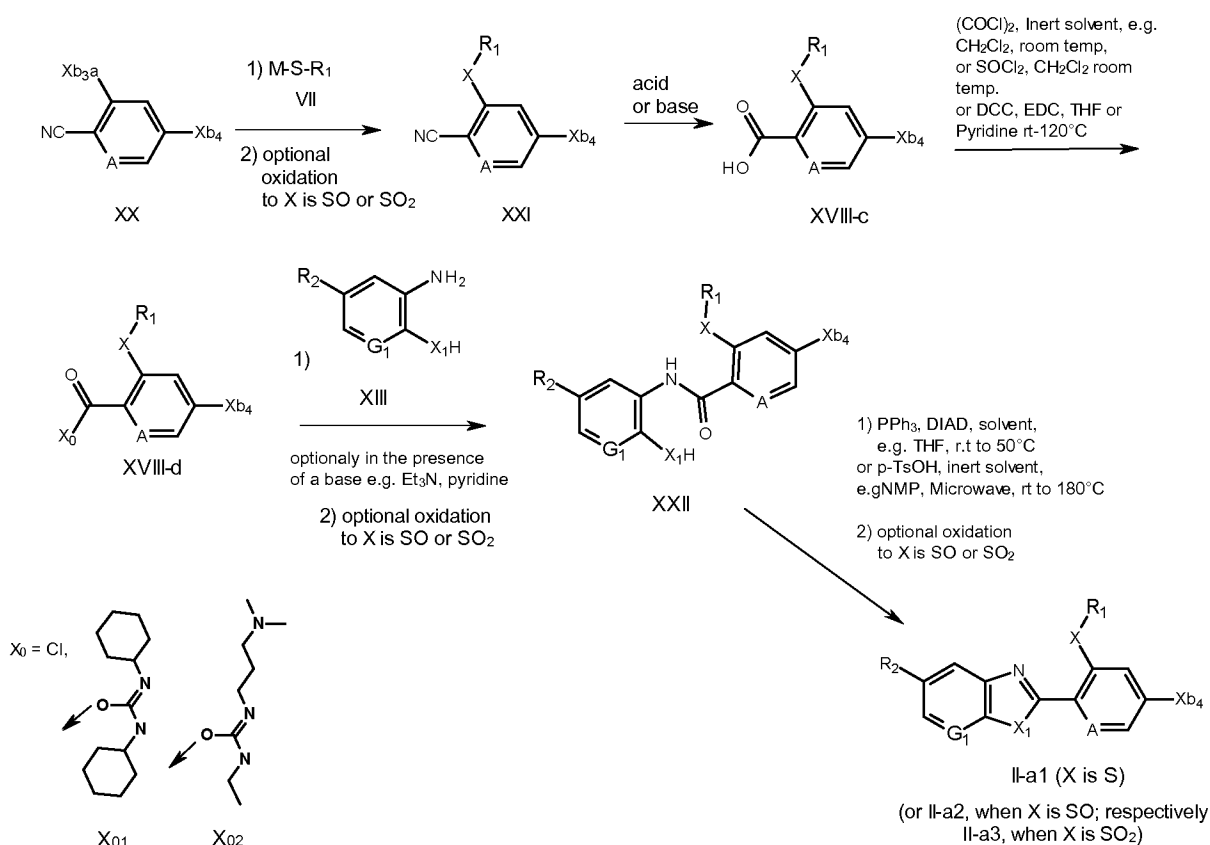
- 10 by reacting compounds of formula XVIII, respectively an activated form XVIII-a of compounds of formula XVIII, wherein A is carbon or nitrogen, and X_{b3} is a leaving group like, for example fluorine, chlorine, bromine or iodine, or an aryl- or alkylsulfonate such as trifluoromethane-sulfonate, and X_{b4}

-20-

can be a halogen, preferentially chlorine, bromine or iodine, or a sulfonate, like for example a trifluoromethanesulfonate, most preferably bromine or iodine, with compounds of the formula XIII, wherein X_1 and R_2 are as defined in formula I. The intermediate compounds of formula XIX may be isolated, but are preferentially converted into the compounds of formula VIII in a similar way as described above (transformation of compounds XV into compounds of formula I).

Compounds of formula XXI can be prepared as described in scheme 10a, by reacting compounds of formula XX, wherein A is CH or nitrogen, and X_{b3a} is a leaving group like, for example nitro, fluorine, chlorine, bromine or iodine, or an aryl- or alkylsulfonate such as trifluoromethane-sulfonate, and X_{b4} can be a halogen, preferentially chlorine, bromine or iodine, or a sulfonate, like for example a trifluoromethanesulfonate, most preferably bromine or iodine, with a compound of formula VII, wherein R_1 is as defined in formula I, and M is a metal or non-metal cation. In scheme 10a, the cation M is assumed to be monovalent, but polyvalent cations associated with more than one S- R_1 group can also be considered. Preferred cations are, for example lithium, sodium, potassium or cesium. The reaction can be performed in a solvent, preferably polar aprotic, such as THF, N,N-dimethylformamide or MeCN, at temperatures between -78°C and the boiling temperature of the reaction mixture.

Scheme 10a

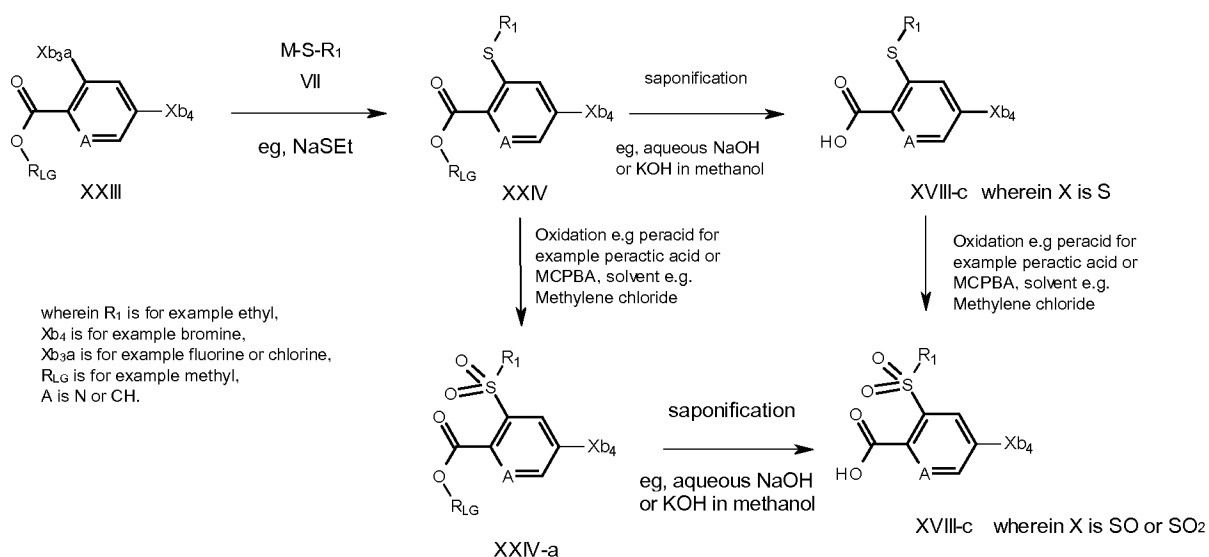


-21-

Compounds of formula XVIII-c can be prepared by hydrolysis of compounds of formula XXI under acidic (e.g. HCl or H₂SO₄) or basic conditions (e.g. NaOH or KOH) as described in scheme 10a, under conditions known to a person skilled in the art. Compounds of formula II-a2 can be prepared, as described in scheme 10a, by reacting compounds of formula XVIII-c respectively an activated form XVIII-d of compounds of formula XVIII-c with compounds of formula XIII, wherein X₁ and R₂ are as defined in formula I. The intermediate compounds of formula XXII may be isolated, but are preferentially converted into the compounds of formula II-a2 in a similar way as described above (transformation of compounds XV into compounds of formula I). In compounds of formula XXI, XVIII-c, XVIII-d, XXII and II-a2, X can be S, SO or SO₂. The appropriate oxidation forms of the sulfur atom in compounds of formula XXI, XVIII-c, XVIII-d, XXII and II-a2 wherein X is SO or SO₂, can be prepared by oxidation of compounds of formula XXI, XVIII-c, XVIII-d, XXII and II-a2 wherein X is S. The reaction can be performed with reagents like, for example a peracid as peracetic acid or m-chloroperbenzoic acid, or a hydroperoxide as for example hydrogen peroxide or tert-butylhydroperoxide, or an inorganic oxidant, like a mono-peroxodisulfate salt or potassium permanganate, preferentially meta-chloro-perbenzoic acid.

Compounds of formula XVIII-c, wherein X is S, SO or SO₂, can alternatively be prepared by analogous methods to those described in the literature (scheme 10b). For example, a compound of formula XVIII-c, wherein X is S, may be prepared by saponification of a compound of formula XXIV, wherein R_{LG} is C₁-C₄alkyl, under conditions known to a person skilled in the art (R₁ is as defined in formula I, A is N or CH, and X_{b4} can be a halogen, preferentially chlorine, bromine or iodine, or a sulfonate, like for example a trifluoromethanesulfonate, most preferably bromine or iodine).

Scheme 10b

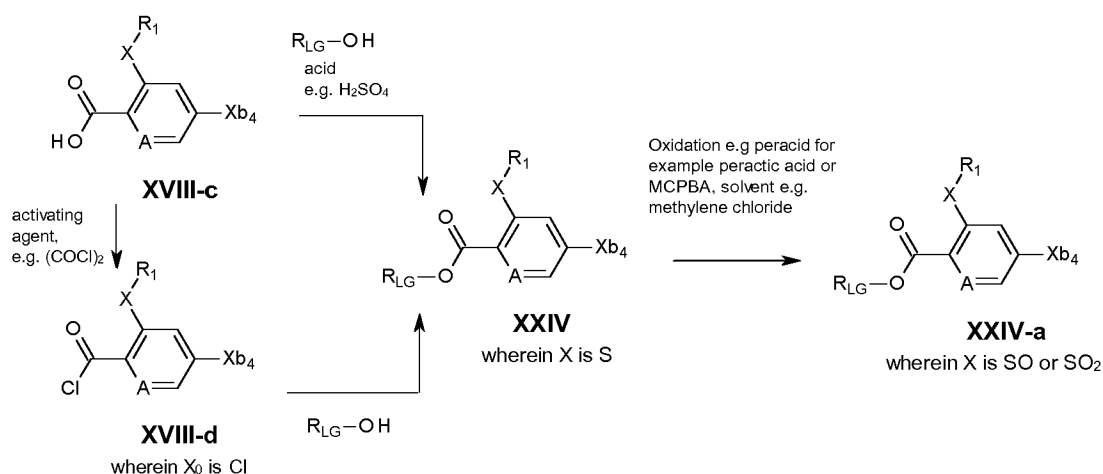


-22-

Compounds of formula XXIV, wherein R_{LG} is C_1 - C_4 alkyl, may be prepared by treatment of compounds of formula XXIII, wherein Xb_3a is a leaving group like, for example nitro, fluorine, chlorine, bromine or iodine, or an aryl- or alkylsulfonate such as trifluoromethanesulfonate, and wherein R_{LG} is C_1 - C_4 alkyl, with a reagent $M-S-R_1$ of formula VII, wherein R_1 is as defined in formula I and M is a metal or non-metal cation, under conditions described above. Such processes involving for example sodium methane- or ethanethiolate as reagents $M-S-R_1$ are well known and have been described previously in, for example, WO2014/152738. Compounds of formula XXIV can be oxidised to compounds of formula XXIV-a using methods known to those skilled in the art and described for example in Scheme 12, and then saponified to compounds of formula XVIII-c, wherein X is SO or SO_2 . Alternatively compounds of formula XXIV can be first saponified to compounds of formula XVIII-c, wherein X is S , and then oxidised to compounds of formula XVIII-c, wherein X is SO or SO_2 . Compounds of formula XXIII are either commercial or have been described in WO 2012/086848.

Changing order of reaction conditions that have been described above may also allow to convert compounds of the formula XVIII-c, or their activated form XVIII-d, into useful compounds of the formula XXIV, or their oxidized form XXIV-a. This is illustrated in scheme 10c.

Scheme 10c:

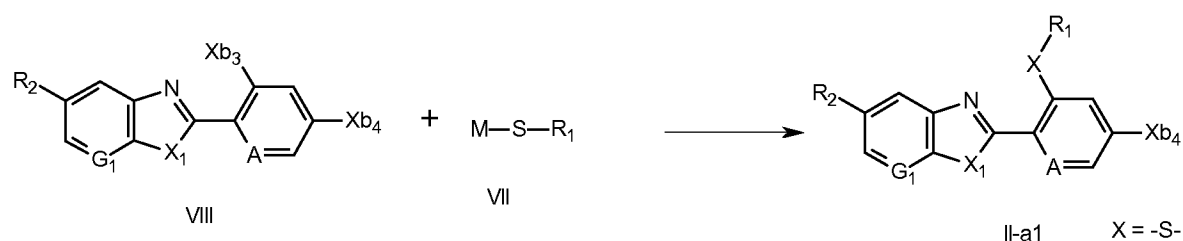


As described in scheme 10c, ester compounds of formula XXIV, wherein X is S and R_{LG} is C_1 - C_4 alkyl, may be prepared from the corresponding carboxylic acid compounds of formula XVIII-c, wherein X is S , by reaction with an alcohol of formula $R_{LG}OH$, wherein R_{LG} is C_1 - C_4 alkyl, optionally in the presence of an acid (such as sulfuric acid), or alternatively optionally in presence of an activating agent, such as for example oxalyl chloride $(COCl)_2$. Such esterification methods are well known to a person skilled in the art and described in the literature. Compounds of formula XXIV can be oxidised to compounds of formula XXIV-a as discussed in scheme 10b. The substituent definitions in compounds of formula XVIII-c, XVIII-d, XXIV and XXIV-a are as previously described.

-23-

Compounds of formula II-a1, wherein X is sulfur, can be prepared (scheme 11) by reacting a compound of the formula VIII, wherein A, R₂ and X₁ are as defined in formula I, and wherein X_{b3} is a leaving group like, for example, fluorine, chlorine, bromine or iodine, or an aryl- or alkylsulfonate such as trifluoromethanesulfonate, preferentially fluorine or chlorine, and wherein X_{b4} is a halogen, preferentially chlorine, bromine or iodine, or a sulfonate, like for example a trifluoromethanesulfonate, most preferably bromine or iodine, with a compound of the formula VII, wherein R₁ is as defined in formula I, and M is a metal or non-metal cation. In scheme 11, the cation M is assumed to be monovalent, but polyvalent cations associated with more than one S-R₁ group can also be considered. Preferred cations are, for example lithium, sodium, potassium or cesium. The reaction can be performed in a solvent, preferably polar aprotic, at temperatures below 0°C or up to boiling temperature of the reaction mixture.

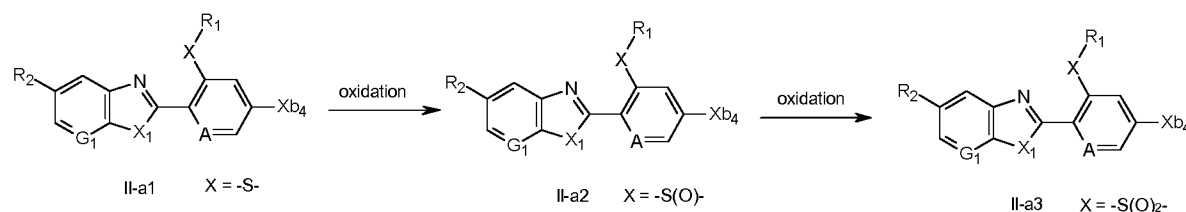
Scheme 11



Compounds of formula II-a3, wherein A, R₁, R₂ and X₁ have the values defined in formula I, and X is -SO₂-, and wherein X_{b4} is a halogen, preferentially chlorine, bromine or iodine, or a sulfonate, like for example a trifluoromethanesulfonate, can be prepared (scheme 12) by oxidation of compounds of formula II-a2, wherein A, R₁, R₂ and X₁ have the values defined in formula I, and X is -SO-, and wherein X_{b4} is a halogen, preferentially chlorine, bromine or iodine, or a sulfonate, like for example a trifluoromethanesulfonate. The reaction can be performed with reagents like, for example a peracid as peracetic acid or m-chloroperbenzoic acid, or a hydroperoxide as for example hydrogen peroxide or tert-butylhydroperoxide, or an inorganic oxidant, like a mono-peroxodisulfate salt or potassium permanganate, preferentially meta-chloroperbenzoic acid. In a similar way, compounds of formula II-a2, wherein A, R₁, R₂ and X₁ have the values defined in formula I, and X is -SO-, and wherein X_{b4} is a halogen, preferentially chlorine, bromine or iodine, or a sulfonate like for example a trifluoromethanesulfonate, can be prepared by oxidation of compounds of formula II-a1, wherein A, R₁, R₂ and X₁ have the values defined in formula I, and X is -S-, and wherein X_{b4} is a halogen, preferentially chlorine, bromine or iodine, or a sulfonate, like for example a trifluoromethanesulfonate. These reactions can be performed in various organic or aqueous solvents compatible to these conditions, by temperatures from below 0°C up to the boiling point of the solvent system.

Scheme 12

-24-



Many compounds of the formula V and XI, wherein Q has the values defined in formula I, and wherein X_{b2} and X_{b5} are as defined above, are commercially available or can be accessible to the person skilled in the art, by analogy to procedures described in the literature.

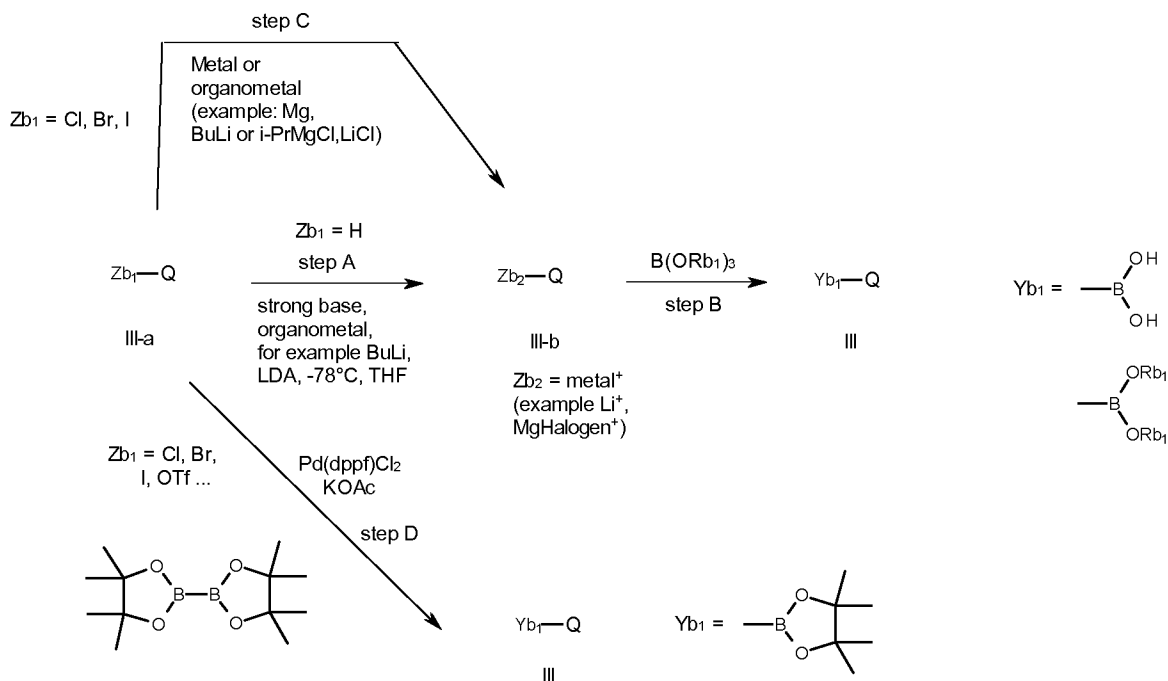
- 5 A large number of compounds of the formula III are commercially available or can be prepared by those skilled in the art. Many chemical transformations, well known by those skilled in the art, can be used to access boronic acid derivatives of formula III, starting from various and easily available starting materials, as for example, to cite only a few (scheme 13), hydrogen abstraction on a compound of the formula III-a wherein Zb_1 is hydrogen, with a strong base (step A), like butyllithium or
- 10 lithium diisopropylamide or (i-PrMgCl, LiCl), followed by reaction of the metallated intermediate of the formula III-b, wherein Zb_2 is a metal such as Li^+ or $MgCl^+$ for example, with, for example, a trialkylborate (step B). Another way to access an organometal intermediate of the formula III-b is from a compound of the formula III-a wherein Zb_1 is chlorine, bromine or iodine, via metal-halogen
- 15 exchange with an organometallic species (step C), like butyllithium or an organomagnesium compound, or direct metallation with a metal, like magnesium.

Introduction of a pinacolborate functional group via a palladium catalyzed reaction with bispinacol diborane on a compound of the formula III-a, wherein Zb_1 is chlorine, bromine, iodine or triflate, is another common strategy (scheme 13, step D). In the compounds of formula III-a, III-b and III within scheme 13, Q has the values defined for the formula I. A person skilled in the art will be able to select

20 an adequate preparation method to access compounds of formula III from III-a depending on the values of Q.

Scheme 13

-25-

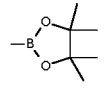


The very same preparation methods described in scheme 13 may be applied for the synthesis of intermediates of the formula IX.

Compounds of formula IV, wherein A, X, X₁, R₁ and R₂ are as described in formula I, can be prepared from compounds of formula II (scheme 14), wherein A, X, X₁, R₁ and R₂ are as described in formula I. Indeed, compounds of formula II, wherein Xb₁ is chlorine, bromine or iodine, can be treated with an organometallic species like, for example, butyllithium or an organomagnesium compound, to generate an intermediate compound of the formula II-a, wherein Zb₃ is as defined in the scheme, via metal-halogen exchange. This reaction is preferentially performed in an anhydrous aprotic solvent, such as THF, at low temperature (between -120°C and 0°C), preferentially between -110°C and -60°C). The intermediate organometal compound of formula II-a is preferably directly converted into compound of formula IV by reaction with a boronate compound B(OR_{b2})₃, wherein R_{b2} is a C₁-C₆alkyl group.

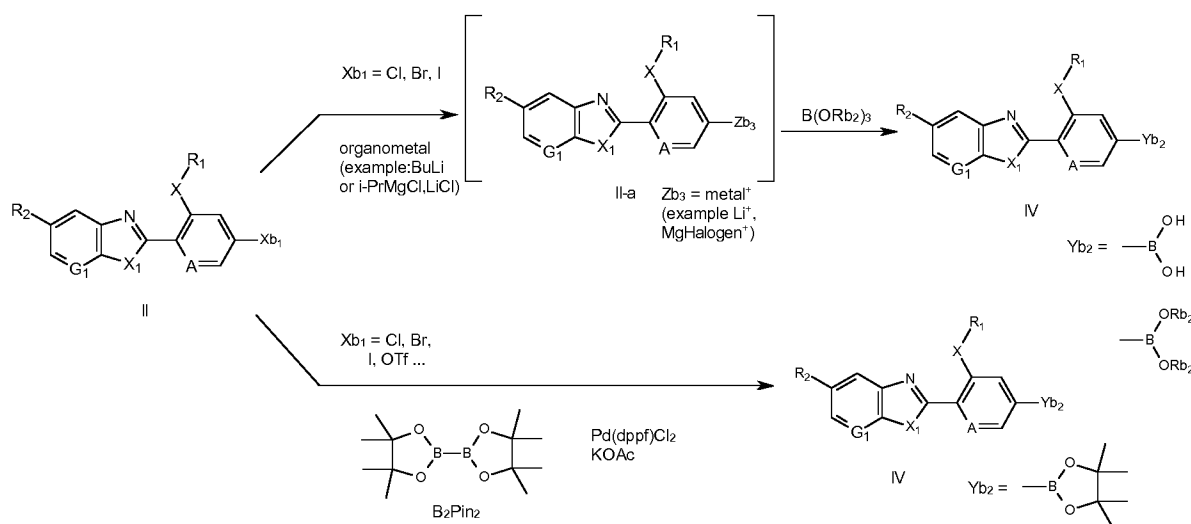
Depending on the nature of the boronate, the reaction treatment conditions and the workup conditions, the boronic acid IV, wherein Yb₂ is -B(OH)₂, or a dialkylboronate IV, wherein Yb₂ is -B(OR_{b2})₂, can be formed.

Introduction of a pinacolborate functional group via a palladium catalyzed reaction with bispinacol diborane B₂Pin₂ on a compound of the formula II, wherein A, X, X₁, R₁ and R₂ are as described in formula I, and wherein Xb₁ is chlorine, bromine, iodine or triflate, is another common strategy. This

reaction, generating a cyclic boronate IV, wherein Yb₂ is , can be performed in an aprotic solvent, in presence of a base, preferentially a weak base, such as potassium acetate KOAc.

-26-

[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 comprised between 0°C and the boiling point of the reaction mixture, or alternatively heating may be performed under microwave irradiation.

5 Scheme 14

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

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

-27-

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 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.
- 10

- 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.
- 15

- 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.
- 20

- 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.
- 25

- 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.
- 30

- 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
- 35

-28-

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 and/or chromatography.

10

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

15

20

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

25

N-oxides can be prepared by reacting a compound of the formula I with a suitable oxidizing agent, for example the H_2O_2 /urea adduct in the presence of an acid anhydride, e.g. trifluoroacetic anhydride.

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.

The compounds according to the following Tables 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 The tables below illustrate specific compounds of the invention.

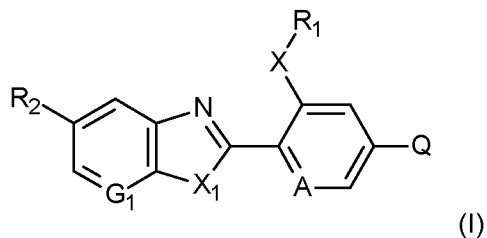
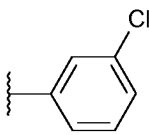
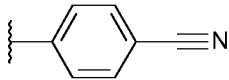
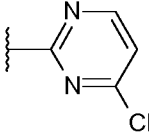
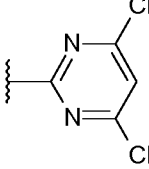
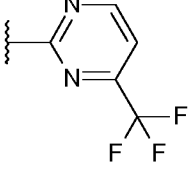
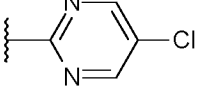
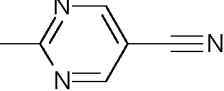
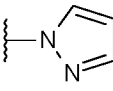
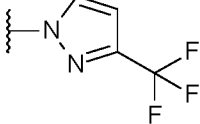


Table A-1 provides 22 compounds A-1.001 to A-1.022 of formula (I) wherein X is SO₂, R₁ is ethyl and A is N and wherein R₂, G₁, X₁ and Q are defined as in table X.

- 10 Table X: Substituent definitions of R₂, G₁, X₁ and A₁:

Entry	R ₂	G ₁	X ₁	Q
1	CF ₃	N	N(CH ₃)	
2	CF ₃	N	N(CH ₃)	
3	CF ₃	N	N(CH ₃)	
4	CF ₃	N	N(CH ₃)	
5	CF ₃	N	N(CH ₃)	

-30-

Entry	R ₂	G ₁	X ₁	Q
6	CF ₃	N	N(CH ₃)	
7	CF ₃	N	N(CH ₃)	
8	CF ₃	N	N(CH ₃)	
9	CF ₃	N	N(CH ₃)	
10	CF ₃	N	N(CH ₃)	
11	CF ₃	N	N(CH ₃)	
12	CF ₃	N	N(CH ₃)	
13	CF ₃	N	N(CH ₃)	
14	CF ₃	N	N(CH ₃)	

-31-

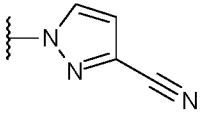
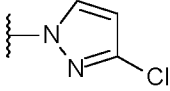
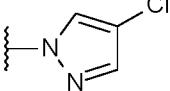
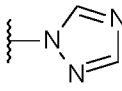
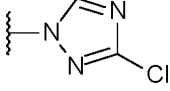
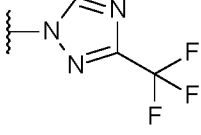
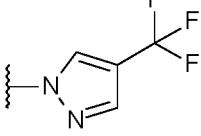
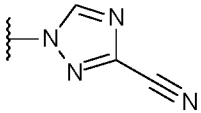
Entry	R ₂	G ₁	X ₁	Q
15	CF ₃	N	N(CH ₃)	
16	CF ₃	N	N(CH ₃)	
17	CF ₃	N	N(CH ₃)	
18	CF ₃	N	N(CH ₃)	
19	CF ₃	N	N(CH ₃)	
20	CF ₃	N	N(CH ₃)	
21	CF ₃	N	N(CH ₃)	
22	CF ₃	N	N(CH ₃)	

Table A-2 provides 22 compounds A-2.001 to A-2.022 of formula (I) wherein X is SO, R₁ is ethyl and A is N and wherein R₂, G₁, X₁ and Q are defined as in table X.

- 5 Table A-3 provides 22 compounds A-3.001 to A-3.022 of formula (I) wherein X is S, R₁ is ethyl and A is N and wherein R₂, G₁, X₁ and Q are defined as in table X. The compounds of formula I according to

-32-

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

- 10 Examples of the 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,
15 Hyalomma spp., Ixodes spp., Olygonychus spp, Ornithodoros spp., Polyphagotarsonus latus,
Panonychus spp., Phyllocoptura oleivora, Phytoneumus spp, Polyphagotarsonemus spp, Psoroptes
spp., Rhipicephalus spp., Rhizoglyphus spp., Sarcoptes spp., Steneotarsonemus spp, Tarsonemus
spp. and Tetranychus spp.;
- from the order *Anoplura*, for example,
- 20 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.,
25 Diloboderus abderus, Epilachna spp., Eremnus spp., Heteronychus arator, Hypothenemus hampei,
Lagria vilosa, Leptinotarsa decemlineata, Lissorhoptrus spp., Liogenys spp, Maecolaspis spp,
Maladera castanea, Megascelis spp, Meligethes aeneus, Melolontha spp., Myochrous armatus,
Orycaephilus spp., Otiorhynchus spp., Phyllophaga spp, Phlyctinus spp., Popillia spp., Psylliodes spp.,
Rhyssomatus aubtilis, Rhizopertha spp., Scarabeidae, Sitophilus spp., Sitotroga spp., Somaticus spp,
30 Sphenophorus spp, Sternechus subsignatus, Tenebrio spp., Tribolium spp. and Trogoderma spp.;
- from the order *Diptera*, for example,
- Aedes spp., Anopheles spp, Antherigona soccata, Bactrocea oleae, Bibio hortulanus, Bradysia spp,
Calliphora erythrocephala, Ceratitis spp., Chrysomyia spp., Culex spp., Cuterebra spp., Dacus spp.,
Delia spp, Drosophila melanogaster, Fannia spp., Gastrophilus spp., Geomyza tripunctata, Glossina
35 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.;

-33-

from the order *Hemiptera*, for example,

Acanthocoris scabrator, Acrosternum spp, Adelphocoris lineolatus, Amblypelta nitida, Bathycoelia thalassina, Blissus spp, Cimex spp., Clavigralla tomentosicollis, Creontiades spp, Distantiella theobroma, Dichelops furcatus, Dysdercus spp., Edessa spp, Euchistus spp., Eurydema pulchrum, Eurygaster spp., Halyomorpha halys, Horcias nobilellus, Leptocoris spp., Lygus spp, Margarodes spp, Murgantia histrionic, Neomegalotomus spp, Nesidiocoris tenuis, Nezara spp., Nysius simulans, Oebalus insularis, Piesma spp., Piezodorus spp, Rhodnius spp., Sahlbergella singularis, Scaptocoris castanea, Scotinophara spp., Thyanta spp, Triatoma spp., Vatica illudens;

Acyrtosium pisum, Adalges spp, Agalliana ensigera, Agonoscena targionii, Aleurodicus spp,

Aleurocanthus spp, Aleurolobus barodensis, Aleurothrixus floccosus, Aleyrodes brassicae, Amarasca biguttula, Amritodus atkinsoni, Aonidiella spp., Aphididae, Aphis spp., Aspidiotus spp., Aulacorthum solani, Bactericera cockerelli, Bemisia spp, Brachycaudus spp, Brevicoryne brassicae, Cacopsylla spp, Cavariella aegopodii Scop., Ceroplaster spp., Chrysomphalus aonidium, Chrysomphalus dictyospermi, Cicadella spp, Cofana spectra, Cryptomyzus spp, Cicadulina spp, Coccus hesperidum,

Dalbulus maidis, Dialeurodes spp, Diaphorina citri, Diuraphis noxia, Dysaphis spp, Empoasca spp., Eriosoma larigerum, Erythroneura spp., Gascardia spp., Glycaspis brimblecombei, Hyadaphis pseudobrassicae, Hyalopterus spp, Hyperomyzus pallidus, Idioscopus clypealis, Jacobiasca lybica, Laodelphax spp., Lecanium corni, Lepidosaphes spp., Lopaphis erysimi, Lyogenys maidis, Macrosiphum spp., Mahanarva spp, Metcalfa pruinosa, Metopolophium dirhodum, Myndus crudus,

Myzus spp., Neotoxoptera sp, Nephrotettix spp., Nilaparvata spp., Nippolachnus piri Mats, Odonaspis ruthae, Oregma lanigera Zehnter, Parabemisia myricae, Paratrioza cockerelli, Parlatoria spp., Pemphigus spp., Peregrinus maidis, Perkinsiella spp, Phorodon humuli, Phylloxera spp, Planococcus spp., Pseudaulacaspis spp., Pseudococcus spp., Pseudatomoscelis seriatus, Psylla spp., Pulvinaria 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 erytraeae, Unaspis citri, Zyginia flammigera, Zyginidia scutellaris, ;

from the order *Hymenoptera*, for example,

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

from the order *Isoptera*, for example,

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

from the order *Lepidoptera*, for example,

Acleris spp., Adoxophyes spp., Aegeria spp., Agrotis spp., Alabama argillaceae, Amylois spp., Anticarsia gemmatilis, Archips spp., Argyroresthia spp, Argyrotaenia spp., Autographa spp., Bucculatrix thurberiella, Busseola fusca, Cadra cautella, Carposina nipponensis, Chilo spp., Choristoneura spp.,

-34-

- Chrysoteuchia topiaria, Clysia ambiguella, Cnaphalocrocis spp., Cnephasia spp., Cochylis spp., Coleophora spp., Colias lesbia, Cosmophila flava, Crambus spp, Crocidolomia binotalis, Cryptophlebia leucotreta, Cydalima perspectalis, Cydia spp., Diaphania perspectalis, Diatraea spp., Diparopsis castanea, Earias spp., Eldana saccharina, Ephestia spp., Epinotia spp, Estigmene acrea, Etiella zinckinella, Eucosma spp., Eupoecilia ambiguella, Euproctis spp., Euxoa spp., Feltia jaculiferia, Grapholita spp., Hedya nubiferana, Heliothis spp., Hellula undalis, Herpetogramma spp, Hyphantria cunea, Keiferia lycopersicella, Lasmopalpus lignosellus, Leucoptera scitella, Lithocollethis spp., Lobesia botrana, Loxostege bifidalis, Lymantria spp., Lyonetia spp., Malacosoma spp., Mamestra brassicae, Manduca sexta, Mythimna spp, Noctua spp, Operophtera spp., Orniodes indica, Ostrinia nubilalis, Pammene spp., Pandemis spp., Panolis flammea, Papaipema nebris, Pectinophora gossypiella, Perileucoptera coffeella, Pseudaletia unipuncta, Phthorimaea operculella, Pieris rapae, Pieris spp., Plutella xylostella, Prays spp., Pseudoplusia spp, Rachiplusia nu, Richia albicosta, Scirpophaga spp., Sesamia spp., Sparganothis spp., Spodoptera spp., Sylepta derogate, Synanthedon spp., Thaumetopoea spp., Tortrix spp., Trichoplusia ni, Tuta absoluta, and Yponomeuta spp.;
- from the order *Mallophaga*, for example, Damalinae spp. and Trichodectes spp.;
- from the order *Orthoptera*, for example, Blatta spp., Blattella spp., Gryllotalpa spp., Leucophaea maderae, Locusta spp., Neocurtilla hexadactyla, Periplaneta spp., Scapteriscus spp, and Schistocerca spp.;
- from the order *Psocoptera*, for example, Liposcelis spp.;
- from the order *Siphonaptera*, for example, Ceratophyllus spp., Ctenocephalides spp. and Xenopsylla cheopis;
- from the order *Thysanoptera*, for example, Calliothrips phaseoli, Frankliniella spp., Heliothrips spp, Hercinothrips spp., Parthenothrips spp, Scirtothrips aurantii, Sericothrips variabilis, Taeniothrips spp., Thrips spp;
- from the order *Thysanura*, for example, Lepisma saccharina.
- The active ingredients according to the invention can be used for controlling, i. e. containing or destroying, pests of the abovementioned type which occur in particular on plants, especially on useful plants and ornamentals in agriculture, in horticulture and in forests, or on organs, such as fruits, flowers, foliage, stalks, tubers or roots, of such plants, and in some cases even plant organs which are formed at a later point in time remain protected against these pests.
- Suitable target crops are, in particular, cereals, such as wheat, barley, rye, oats, rice, maize or sorghum; beet, such as sugar or fodder beet; fruit, for example pomaceous fruit, stone fruit or soft fruit, such as apples, pears, plums, peaches, almonds, cherries or berries, for example strawberries,

-35-

raspberries or blackberries; leguminous crops, such as beans, lentils, peas or soya; oil crops, such as oilseed rape, mustard, poppies, olives, sunflowers, coconut, castor, cocoa or ground nuts; cucurbits, such as pumpkins, cucumbers or melons; fibre plants, such as cotton, flax, hemp or jute; citrus fruit, such as oranges, lemons, grapefruit or tangerines; vegetables, such as spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes or bell peppers; Lauraceae, such as avocado, Cinnamomum or camphor; and also tobacco, nuts, coffee, eggplants, sugarcane, tea, pepper, grapevines, hops, the plantain family and latex plants.

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

For example the invention may be used on any of the following ornamental species: *Ageratum* spp., *Alonsoa* spp., *Anemone* spp., *Anisodonteia capensis*, *Anthemis* spp., *Antirrhinum* spp., *Aster* spp., *Begonia* spp. (e.g. *B. elatior*, *B. semperflorens*, *B. tubéux*), *Bougainvillea* spp., *Brachycome* spp., *Brassica* spp. (ornamental), *Calceolaria* spp., *Capsicum annuum*, *Catharanthus roseus*, *Canna* spp., *Centaurea* spp., *Chrysanthemum* spp., *Cineraria* spp. (*C. maritime*), *Coreopsis* spp., *Crassula coccinea*, *Cuphea ignea*, *Dahlia* spp., *Delphinium* spp., *Dicentra spectabilis*, *Dorotheantus* spp., *Eustoma grandiflorum*, *Forsythia* spp., *Fuchsia* spp., *Geranium gnaphalium*, *Gerbera* spp., *Gomphrena globosa*, *Heliotropium* spp., *Helianthus* spp., *Hibiscus* spp., *Hortensia* spp., *Hydrangea* spp., *Hypoestes phyllostachya*, *Impatiens* spp. (*I. Walleriana*), *Iresines* spp., *Kalanchoe* spp., *Lantana camara*, *Lavatera trimestris*, *Leonotis leonurus*, *Lilium* spp., *Mesembryanthemum* spp., *Mimulus* spp., *Monarda* spp., *Nemesia* spp., *Tagetes* spp., *Dianthus* spp. (carnation), *Canna* spp., *Oxalis* spp., *Bellis* spp., *Pelargonium* spp. (*P. peltatum*, *P. Zonale*), *Viola* spp. (pansy), *Petunia* spp., *Phlox* spp., *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*), *Citrillus lanatus*, *Cucumis* spp. (*C. sativus*, *C. melo*), *Cucurbita* spp. (*C. pepo*, *C. maxima*), *Cyanara* spp. (*C. scolymus*, *C. cardunculus*), *Daucus carota*, *Foeniculum vulgare*, *Hypericum* spp., *Lactuca sativa*, *Lycopersicon* spp. (*L. esculentum*, *L. lycopersicum*), *Mentha* spp., *Ocimum basilicum*, *Petroselinum crispum*, *Phaseolus* spp. (*P. vulgaris*, *P. coccineus*), *Pisum sativum*, *Raphanus sativus*, *Rheum raphonticum*, *Rosemarinus* spp., *Salvia* spp., *Scorzonera hispanica*, *Solanum melongena*, *Spinacea oleracea*, *Valerianella* spp. (*V. locusta*, *V. eriocarpa*) and *Vicia faba*.

-36-

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

- 5 The active ingredients according to the invention are especially suitable for controlling *Aphis craccivora*, *Diabrotica balteata*, *Heliothis virescens*, *Myzus persicae*, *Plutella xylostella* and *Spodoptera littoralis* in cotton, vegetable, maize, rice and soya crops. The active ingredients according to the invention are further especially suitable for controlling *Mamestra* (preferably in vegetables), *Cydia pomonella* (preferably in apples), *Empoasca* (preferably in vegetables, vineyards), *Leptinotarsa*
10 (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 nematodes), especially plant parasitic nematodes such as root knot nematodes, *Meloidogyne hapla*,
15 *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*
20 *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, *Hemicyclophora* species and *Hemicriconemoides* species; *Hirshmanniella*
25 species; Lance nematodes, *Hoploaimus* species; false rootknot nematodes, *Nacobbus* species; Needle nematodes, *Longidorus elongatus* and other *Longidorus* species; Pin nematodes, *Pratylenchus* species; Lesion nematodes, *Pratylenchus neglectus*, *Pratylenchus penetrans*, *Pratylenchus curvatus*, *Pratylenchus goodeyi* and other *Pratylenchus* species; Burrowing nematodes, *Radopholus similis* and other *Radopholus* species; Reniform nematodes, *Rotylenchus robustus*,
30 *Rotylenchus reniformis* and other *Rotylenchus* species; *Scutellonema* species; Stubby root nematodes, *Trichodorus primitivus* and other *Trichodorus* species, *Paratrichodorus* species; Stunt nematodes, *Tylenchorhynchus claytoni*, *Tylenchorhynchus dubius* and other *Tylenchorhynchus* species; Citrus nematodes, *Tylenchulus* species; Dagger nematodes, *Xiphinema* species; and other plant parasitic nematode species, such as *Subanguina* spp., *Hypsoperine* spp., *Macroposthonia* spp.,
35 *Melinius* spp., *Punctodera* spp., and *Quinisulcius* spp..

-37-

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

The term "crops" is to be understood as including also crop plants which have been so transformed by the use of recombinant DNA techniques that they are capable of synthesising one or more selectively acting toxins, such as are known, for example, from toxin-producing bacteria, especially those of the genus *Bacillus*.

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

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

-38-

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

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

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

Further examples of such transgenic crops are:

1. **Bt11 Maize** from Syngenta Seeds SAS, Chemin de l'Hobit 27, F-31 790 St. Sauveur, France, registration number C/FR/96/05/10. Genetically modified *Zea mays* which has been rendered resistant to attack by the European corn borer (*Ostrinia nubilalis* and *Sesamia nonagrioides*) by transgenic expression of a truncated Cry1Ab toxin. Bt11 maize also transgenically expresses the enzyme PAT to achieve tolerance to the herbicide glufosinate ammonium.

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

3. **MIR604 Maize** from Syngenta Seeds SAS, Chemin de l'Hobit 27, F-31 790 St. Sauveur, France, registration number C/FR/96/05/10. Maize which has been rendered insect-resistant by transgenic expression of a modified Cry3A toxin. This toxin is Cry3A055 modified by insertion of a cathepsin-G-

-39-

protease recognition sequence. The preparation of such transgenic maize plants is described in WO 03/018810.

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

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

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

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

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

The term "crops" is to be understood as including also crop plants which have been so transformed by the use of recombinant DNA techniques that they are capable of synthesising antipathogenic substances having a selective action, such as, for example, the so-called "pathogenesis-related proteins" (PRPs, see e.g. EP-A-0 392 225). Examples of such antipathogenic substances and transgenic plants capable of synthesising such antipathogenic substances are known, for example, from EP-A-0 392 225, WO 95/33818 and EP-A-0 353 191. The methods of producing such transgenic plants are generally known to the person skilled in the art and are described, for example, in the publications mentioned above.

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

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

-40-

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

- 5 Antipathogenic substances which can be expressed by such transgenic plants include, for example, ion channel blockers, such as blockers for sodium and calcium channels, for example the viral KP1, KP4 or KP6 toxins; stilbene synthases; bibenzyl synthases; chitinases; glucanases; the so-called "pathogenesis-related proteins" (PRPs; see e.g. EP-A-0 392 225); antipathogenic substances produced by microorganisms, for example peptide antibiotics or heterocyclic antibiotics (see e.g.
- 10 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
- 15 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
- 20 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
- 25 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
- 30 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
- 35 which can be used in the manufacture of) netting, clothing, bedding, curtains and tents.

Substrates including non-woven, fabrics or netting to be treated may be made of natural fibres such as cotton, raffia, jute, flax, sisal, hessian, or wool, or synthetic fibres such as polyamide, polyester,

polypropylene, polyacrylonitrile or the like. The polyesters are particularly suitable. The methods of textile treatment are known, e.g. WO 2008/151984, WO 03/034823, US 5631072, WO 2005/64072, WO2006/128870, EP 1724392, WO 2005/113886 or WO 2007/090739.

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

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

- 10 Table A. Examples of exotic woodborers of economic importance.

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

Table B. Examples of native woodborers of economic importance.

Family	Species	Host or Crop Infested
Buprestidae	<i>Agrilus anxius</i>	Birch
	<i>Agrilus politus</i>	Willow, Maple
	<i>Agrilus sayi</i>	Bayberry, Sweetfern
	<i>Agrilus vittaticollis</i>	Apple, Pear, Cranberry, Serviceberry, Hawthorn
	<i>Chrysobothris femorata</i>	Apple, Apricot, Beech, Boxelder, Cherry, Chestnut, Currant, Elm, Hawthorn, Hackberry, Hickory, Horsechestnut, Linden, Maple, Mountain-ash, Oak, Pecan, Pear,

-42-

Family	Species	Host or Crop Infested
		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
	<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, Nettleleaf 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

-43-

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

-44-

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

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

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

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

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

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

- Of the order Blattellidae, for example Blatta orientalis, Periplaneta americana, Blattella germanica and
20 Supella spp..

- Of the subclass Acarina (Acarida) and the orders Meta- and Mesostigmata, for example Argas spp.,
Ornithodoros spp., Otobius spp., Ixodes spp., Amblyomma spp., Boophilus spp., Dermacentor spp.,
Haemaphysalis spp., Hyalomma spp., Rhipicephalus spp., Dermanyssus spp., Raillietia spp.,
25 Pneumonyssus spp., Sternostoma spp. and Varroa spp..

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

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

The compositions according to the invention can be used, for example, against the following pests:
beetles such as Hylotrupes bajulus, Chlorophorus pilosus, Anobium punctatum, Xestobium

-46-

rufovillosum, Ptilinuspecticornis, Dendrobium pertinex, Ernobius mollis, Priobium carpini, Lyctus brunneus, Lyctus africanus, Lyctus planicollis, Lyctus linearis, Lyctus pubescens, Trogoxylon aequale, Minthesrugicollis, Xyleborus spec., Tryptodendron spec., Apate monachus, Bostrychus capucins, Heterobostrychus brunneus, Sinoxylon spec. and Dinoderus minutus, and also hymenopterans such as Sirex juvencus, Urocerus gigas, Urocerus gigas taignus and Urocerus augur, and termites such as Kaloterms flavicollis, Cryptoterms brevis, Heteroterms indicola, Reticuliterms flavipes, Reticuliterms santonensis, Reticuliterms lucifugus, Mastoterms darwiniensis, Zootermopsis nevadensis and Coptoterms formosanus, and bristletails such as Lepisma saccharina.

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

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

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

-47-

The formulation adjuvants that are suitable for the preparation of the compositions according to the invention are known *per se*. As liquid carriers there may be used: water, toluene, xylene, petroleum ether, vegetable oils, acetone, methyl ethyl ketone, cyclohexanone, acid anhydrides, acetonitrile, acetophenone, amyl acetate, 2-butanone, butylene carbonate, chlorobenzene, cyclohexane, cyclohexanol, alkyl esters of acetic acid, diacetone alcohol, 1,2-dichloropropane, diethanolamine, p-diethylbenzene, diethylene glycol, diethylene glycol abietate, diethylene glycol butyl ether, diethylene glycol ethyl ether, diethylene glycol methyl ether, *N,N*-dimethylformamide, dimethyl sulfoxide, 1,4-dioxane, dipropylene glycol, dipropylene glycol methyl ether, dipropylene glycol dibenzoate, diproxitol, alkylpyrrolidone, ethyl acetate, 2-ethylhexanol, ethylene carbonate, 1,1,1-trichloroethane, 2-heptanone, alpha-pinene, d-limonene, ethyl lactate, ethylene glycol, ethylene glycol butyl ether, ethylene glycol methyl ether, gamma-butyrolactone, glycerol, glycerol acetate, glycerol diacetate, glycerol triacetate, hexadecane, hexylene glycol, isoamyl acetate, isobornyl acetate, isooctane, isophorone, isopropylbenzene, isopropyl myristate, lactic acid, laurylamine, mesityl oxide, methoxypropanol, methyl isoamyl ketone, methyl isobutyl ketone, methyl laurate, methyl octanoate, methyl oleate, methylene chloride, m-xylene, *n*-hexane, *n*-octylamine, octadecanoic acid, octylamine acetate, oleic acid, oleylamine, o-xylene, phenol, polyethylene glycol, propionic acid, propyl lactate, propylene carbonate, propylene glycol, propylene glycol methyl ether, p-xylene, toluene, triethyl phosphate, triethylene glycol, xylenesulfonic acid, paraffin, mineral oil, trichloroethylene, perchloroethylene, ethyl acetate, amyl acetate, butyl acetate, propylene glycol methyl ether, diethylene glycol methyl ether, methanol, ethanol, isopropanol, and alcohols of higher molecular weight, such as amyl alcohol, tetrahydrofurfuryl alcohol, hexanol, octanol, ethylene glycol, propylene glycol, glycerol, *N*-methyl-2-pyrrolidone and the like.

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

A large number of surface-active substances can advantageously be used in both solid and liquid formulations, especially in those formulations which can be diluted with a carrier prior to use. Surface-active substances may be anionic, cationic, non-ionic or polymeric and they can be used as emulsifiers, wetting agents or suspending agents or for other purposes. Typical surface-active substances include, for example, salts of alkyl sulfates, such as diethanolammonium lauryl sulfate; salts of alkylarylsulfonates, such as calcium dodecylbenzenesulfonate; alkylphenol/alkylene oxide addition products, such as nonylphenol ethoxylate; alcohol/alkylene oxide addition products, such as tridecylalcohol ethoxylate; soaps, such as sodium stearate; salts of alkyl naphthalenesulfonates, such as sodium dibutyl naphthalenesulfonate; dialkyl esters of sulfosuccinate salts, such as sodium di(2-ethylhexyl)sulfosuccinate; sorbitol esters, such as sorbitol oleate; quaternary amines, such as lauryltrimethylammonium chloride, polyethylene glycol esters of fatty acids, such as polyethylene glycol stearate; block copolymers of ethylene oxide and propylene oxide; and salts of mono- and di-

-48-

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

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

The compositions according to the invention can include an additive comprising an oil of vegetable or animal origin, a mineral oil, alkyl esters of such oils or mixtures of such oils and oil derivatives. The amount of oil additive in the composition according to the invention is generally from 0.01 to 10 %, based on the mixture to be applied. For example, the oil additive can be added to a spray tank in the desired concentration after a spray mixture has been prepared. Preferred oil additives comprise mineral oils or an oil of vegetable origin, for example rapeseed oil, olive oil or sunflower oil, emulsified vegetable oil, alkyl esters of oils of vegetable origin, for example the methyl derivatives, or an oil of animal origin, such as fish oil or beef tallow. Preferred oil additives comprise alkyl esters of C₈-C₂₂ fatty acids, especially the methyl derivatives of C₁₂-C₁₈ fatty acids, for example the methyl esters of lauric acid, palmitic acid and oleic acid (methyl laurate, methyl palmitate and methyl oleate, respectively). Many oil derivatives are known from the Compendium of Herbicide Adjuvants, 10th Edition, Southern Illinois University, 2010.

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

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

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

Emulsifiable concentrates:

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

-49-

Dusts:

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

5

Suspension concentrates:

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

10

Wettable powders:

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

15

Granules:

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

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

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

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

-50-

<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.

<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 %

- 5 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.

-51-

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

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

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

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.

5 Suspension concentrate

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

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

10 Flowable concentrate for seed treatment

-52-

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

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

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.
- 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:

-53-

"Mp" means melting point in °C. Free radicals represent methyl groups. ¹H NMR measurements were recorded on a Bruker 400MHz spectrometer, chemical shifts are given in ppm relevant to a TMS standard. Spectra measured in deuterated solvents as indicated. Either one of the LCMS methods below was used to characterize the compounds. The characteristic LCMS values obtained for each compound were the retention time ("Rt", recorded in minutes) and the measured molecular ion (M+H)⁺ or (M-H)⁻.

LCMS Methods:

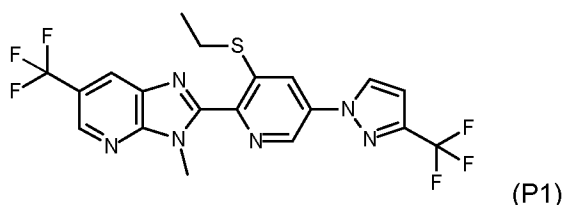
Method 1:

Spectra were recorded on a Mass Spectrometer from Waters (SQD or ZQ Single quadrupole mass spectrometer) equipped with an electrospray source (Polarity: positive or negative ions, Capillary: 3.00 kV, Cone range: 30-60 V, Extractor: 2.00 V, Source Temperature: 150°C, Desolvation Temperature: 350°C, Cone Gas Flow: 0 L/Hr, Desolvation Gas Flow: 650 L/Hr, Mass range: 100 to 900 Da) and an Acquity UPLC from Waters: Binary pump, heated column compartment and diode-array detector. Solvent degasser, binary pump, heated column compartment and diode-array detector. Column: Waters UPLC HSS T3, 1.8 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; 1.2-1.5 min 100% B; Flow (ml/min) 0.85.

Method 2:

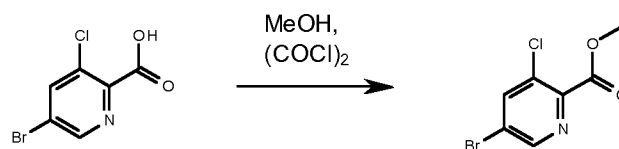
Spectra were recorded on a Mass Spectrometer from Waters (SQD or ZQ Single quadrupole mass spectrometer) equipped with an electrospray source (Polarity: positive or negative ions, Capillary: 3.00 kV, Cone range: 30-60 V, Extractor: 2.00 V, Source Temperature: 150°C, Desolvation Temperature: 350°C, Cone Gas Flow: 0 L/Hr, Desolvation Gas Flow: 650 L/Hr, Mass range: 100 to 900 Da) and an Acquity UPLC from Waters: Binary pump, heated column compartment and diode-array detector. Solvent degasser, binary pump, heated column compartment and diode-array detector. Column: Waters UPLC HSS T3, 1.8 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; 2.7-3.0 min 100% B; Flow (ml/min) 0.85.

EXAMPLE P1: Preparation of 2-[3-ethylsulfanyl-5-[3-(trifluoromethyl)pyrazol-1-yl]-2-pyridyl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound P1):



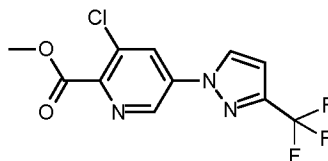
-54-

Step 1: Preparation of methyl 5-bromo-3-chloro-pyridine-2-carboxylate



To a slightly cloudy solution of 5-bromo-3-chloro-pyridine-2-carboxylic acid (60 g, 183.2 mmol) in dichloromethane (700 ml) was added dropwise N,N-dimethylformamide (1 ml) and oxalylchloride (24.9
 5 ml, 286.9 mmol). The cloudy solution was stirred for 3 hours at ambient temperature. The resulting yellow solution was cooled to 10°C and methanol (30.8 ml, 761.3 mmol) was added dropwise to the mixture, keeping the temperature between 15° and 20°C. The solution was stirred overnight at ambient temperature. After neutralisation with an aqueous saturated solution of sodium hydrogen carbonate, the organic layer was washed with brine, dried over sodium sulfate, filtrated and
 10 evaporated to give methyl 5-bromo-3-chloro-pyridine-2-carboxylate (55 g) as a yellow solid, which was used without further purification. LCMS (method 2): 250/252/254 (M+1)⁺, retention time 1.12 min.

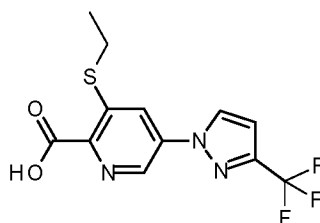
Step 2: Preparation of methyl 3-chloro-5-[3-(trifluoromethyl)pyrazol-1-yl]pyridine-2-carboxylate



To a solution of methyl 5-bromo-3-chloro-pyridine-2-carboxylate (preparation described before, 40.0 g,
 15 160 mmol) in dioxane (1000 ml) was added 3-trifluoromethyl-1H-pyrazole (32.6 g, 240 mmol), (1R,2R)-N1,N2-dimethylcyclohexane-1,2-diamine (4.78 g, 5.30 ml), potassium carbonate (48.4 g, 479 mmol) and copper(I) iodide (15.2 g, 79.8 mmol). The reaction mixture was stirred under reflux for 24 hours. The reaction mixture was filtered through a Hyflo pad, which was rinsed with MeOH, then the solvent was evaporated under vacuum. The solid was dissolved in AcOEt and washed with HCl 0.5N,
 20 the organic phase was dried on magnesium sulfate, filtered and concentrated under vacuum. The residue was subjected to column chromatography over silica gel, eluting with ethyl acetate / cyclohexane. The selected fractions were evaporated to yield the title compound as colorless solid (18g). LCMS (method 1): 305/307 (M+H)⁺, retention time 0.99 min.

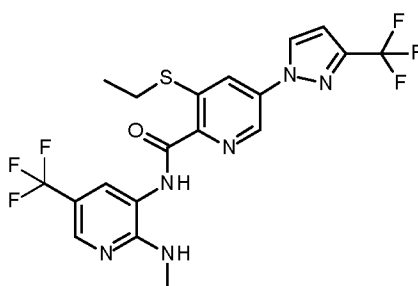
Step 3: Preparation of 3-ethylsulfanyl-5-[3-(trifluoromethyl)pyrazol-1-yl]pyridine-2-carboxylic acid

-55-



To a solution of methyl 3-chloro-5-[3-(trifluoromethyl)pyrazol-1-yl]pyridine-2-carboxylate (18.0 g, 58.9 mmol) in N,N-dimethylformamide (200 ml) was added sodium ethanethiolate (27.4 g, 290 mmol). The reaction mixture was stirred for one hour at ambient temperature. The solution was diluted with *tert*-butyl methyl ether and ice water, the aqueous phase was separated and neutralized with acetic acid. The precipitate formed was filtered off and washed with diethyl ether. The solid was suspended in 80ml of iPrOH and refluxed for 1.5 hours. It was filtered (hot) and the filtrate was allowed to cool down under stirring, then filtered to give the desired 3-ethylsulfanyl-5-[3-(trifluoromethyl)pyrazol-1-yl]pyridine-2-carboxylic acid (4.13 g). LCMS (method 1): 318 (M+H)⁺, 316 (M-H)⁻, retention time 0.92 min.

- 10 Step 4: Preparation of 3-ethylsulfanyl-N-[2-(methylamino)-5-(trifluoromethyl)-3-pyridyl]-5-[3-(trifluoromethyl)pyrazol-1-yl]pyridine-2-carboxamide



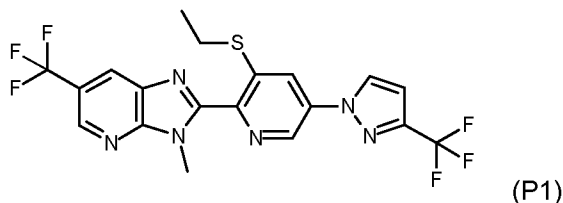
To a suspension of 3-ethylsulfanyl-5-[3-(trifluoromethyl)pyrazol-1-yl]pyridine-2-carboxylic acid (0.5478 g, 1.72 mmol) in dichloromethane (7.8 ml) was added one drop of N,N-dimethylformamide and oxalyl dichloride (0.5082 g, 0.3493 ml). The resulting dark yellow mixture was stirred for one hour at room temperature and concentrated *in vacuo* to afford 3-ethylsulfanyl-5-[3-(trifluoromethyl)pyrazol-1-yl]pyridine-2-carbonyl chloride.

To a solution of N2-methyl-5-(trifluoromethyl)pyridine-2,3-diamine (0.3 g, 1.569 mmol) and triethylamine (0.401 g, 0.55 ml, 3.924 mmol) in tetrahydrofuran (7.8 ml) at 0-5°C was added the above prepared 3-ethylsulfanyl-5-[3-(trifluoromethyl)pyrazol-1-yl]pyridine-2-carbonyl chloride dropwise, and the reaction mixture was stirred one hour at ambient temperature, then 5 hours at 65°C. Ethyl acetate and an aqueous solution of sodium hydrogen carbonate were added to the mixture, the layers separated, the organic phase dried over magnesium sulfate and concentrated under vacuum. The residue was purified by flash chromatography to afford 3-ethylsulfanyl-N-[2-(methylamino)-5-(trifluoromethyl)-3-pyridyl]-5-[3-(trifluoromethyl)pyrazol-1-yl]pyridine-2-carboxamide (699 mg). LCMS

-56-

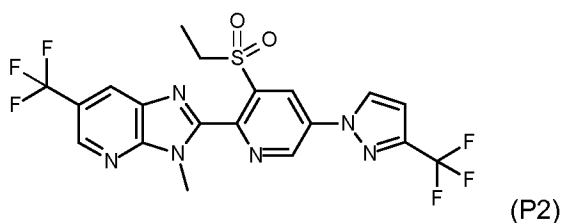
(method 1): 491 (M+H)⁺, 489 (M-H)⁻, retention time 1.16 min. ¹H NMR (400 MHz, CDCl₃) □ ppm: 1.49 (t, 3H), 3.05 (q, 2H), 3.09 (d, 3H), 5.04 (br s, 1H), 6.85 (d, 1H), 7.93 (d, 1H), 8.04 (m, 1H), 8.13 (d, 1H), 8.36 (d, 1H), 8.65 (d, 1H), 9.50 (s, 1H).

Step 5: Preparation of 2-[3-ethylsulfanyl-5-[3-(trifluoromethyl)pyrazol-1-yl]-2-pyridyl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound P1)



A solution of 3-ethylsulfanyl-N-[2-(methylamino)-5-(trifluoromethyl)-3-pyridyl]-5-[3-(trifluoromethyl)pyrazol-1-yl]pyridine-2-carboxamide (699 mg, 1.425 mmol) in acetic acid (7.13 ml) was heated at 150°C for one hour in the microwave. The reaction mixture was diluted with water and ethyl acetate, the layers separated, the organic phase dried over magnesium sulfate and concentrated under vacuum. The residue was purified by flash chromatography to afford 2-[3-ethylsulfanyl-5-[3-(trifluoromethyl)pyrazol-1-yl]-2-pyridyl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound P1) as a solid (673 mg). LCMS (method 1): 473 (M+H)⁺, retention time 1.21 min. ¹H NMR (400 MHz, CDCl₃) □ ppm: 1.43 (t, 3H), 3.09 (q, 2H), 4.10 (s, 3H), 6.85 (d, 1H), 8.12 (d, 1H), 8.20 (d, 1H), 8.43 (d, 1H), 8.76 (d, 1H), 8.83 (d, 1H).

EXAMPLE P2: Preparation of 2-[3-ethylsulfonyl-5-[3-(trifluoromethyl)pyrazol-1-yl]-2-pyridyl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound P2):

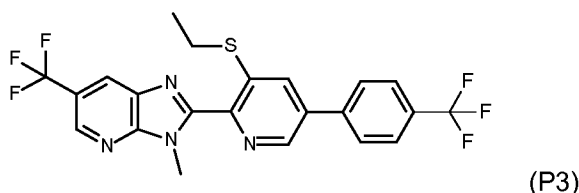


To a solution of 2-[3-ethylsulfanyl-5-[3-(trifluoromethyl)pyrazol-1-yl]-2-pyridyl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (670 mg, 1.14 mmol) in dichloromethane (10 ml) was added meta-chloroperbenzoic acid (3.62 mmol, 2.3 eq.) at room temperature. The yellow solution was stirred for one hour and poured into an aqueous saturated solution of sodium hydrogen carbonate. The product was extracted twice with dichloromethane, the combined organic phases were dried over magnesium sulfate and concentrated under vacuum. The residue was purified by flash chromatography to afford 2-[3-ethylsulfonyl-5-[3-(trifluoromethyl)pyrazol-1-yl]-2-pyridyl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-

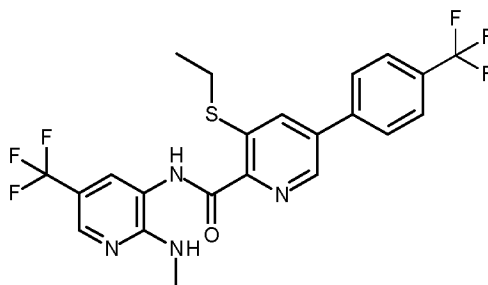
-57-

b]pyridine (compound P2) as a white solid (580 mg). LCMS (method 1): 505 (M+H)⁺, retention time 1.12 min. ¹H NMR (400 MHz, CDCl₃) δ ppm: 1.44 (t, 3H), 3.93 (s, 3H), 3.99 (q, 2H), 6.91 (d, 1H), 8.22 (d, 1H), 8.33 (d, 1H), 8.79 (d, 1H), 8.83 (d, 1H), 9.47 (d, 1H).

5 EXAMPLE P3: Preparation of 2-[3-ethylsulfanyl-5-[4-(trifluoromethyl)phenyl]-2-pyridyl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound P3):



Step 1: Preparation of 3-ethylsulfanyl-N-[2-(methyamino)-5-(trifluoromethyl)-3-pyridyl]-5-[4-(trifluoromethyl)phenyl]pyridine-2-carboxamide

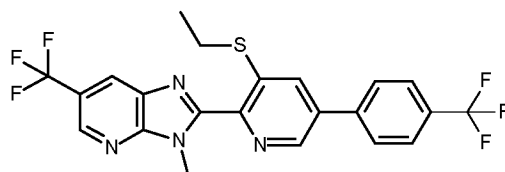


To a solution of N2-methyl-5-(trifluoromethyl)pyridine-2,3-diamine (545 mg, 2.85 mmol) and triethylamine (1.01 ml, 7.12 mmol) in tetrahydrofuran (15 ml) at 0-5°C was added 3-ethylsulfanyl-5-[4-(trifluoromethyl)phenyl]pyridine-2-carboxyl chloride (prepared from 3-ethylsulfanyl-5-[4-(trifluoromethyl)phenyl]pyridine-2-carboxylic acid in analogy to EXAMPLE 1, step 4) (1.084 g, 3.13 mmol) dissolved in tetrahydrofuran (5 ml) dropwise. The mixture was stirred for 3 hours at room temperature, then quenched with water and extracted with ethyl acetate. The combined organic phases were washed with brine, dried over magnesium sulfate and reduced under vacuum. The residue was purified by flash chromatography to afford 3-ethylsulfanyl-N-[2-(methyamino)-5-(trifluoromethyl)-3-pyridyl]-5-[4-(trifluoromethyl)phenyl]pyridine-2-carboxamide (708 mg) as a solid. LCMS (method 1): 501 (M+H)⁺, 499 (M-H)⁻, retention time 1.08 min. ¹H NMR (400 MHz, CDCl₃) δ ppm:

1.48 (t, 3H), 3.03 (q, 2H), 3.09 (d, 3H), 5.08 (br s, 1H), 7.73 (d, 2H), 7.82 (d, 2H), 7.85 (d, 1H), 7.96 (d, 1H), 8.35 (d, 1H), 8.53 (d, 1H), 9.66 (s, 1H).

Step 2: Preparation of 2-[3-ethylsulfanyl-5-[4-(trifluoromethyl)phenyl]-2-pyridyl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound P3)

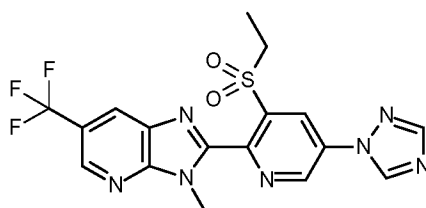
-58-



(P3)

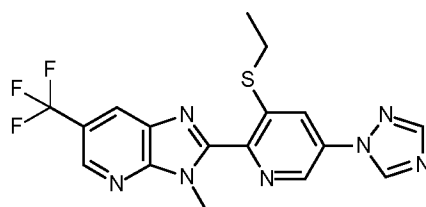
A solution of 3-ethylsulfanyl-N-[2-(methylamino)-5-(trifluoromethyl)-3-pyridyl]-5-[4-(trifluoromethyl)phenyl]pyridine-2-carboxamide (485 mg, 0.969 mmol) in acetic acid (20 ml) was stirred at 120°C for 3 hours. The solvent was removed *in vacuo* and the residue purified by flash chromatography to afford
 5 2-[3-ethylsulfanyl-5-[4-(trifluoromethyl)phenyl]-2-pyridyl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound P3) as a solid (426 mg), mp 137-138°C. LCMS (method 2): 483 (M+H)⁺, retention time 2.17 min. ¹H NMR (400 MHz, CDCl₃) □ ppm: 1.40 (t, 3H), 3.05 (q, 2H), 4.12 (s, 3H), 7.79 (m, 4H), 7.92 (d, 1H), 8.42 (d, 1H), 8.72-8.78 (m, 2H).

10 EXAMPLE P4: Preparation of 2-[3-ethylsulfonyl-5-(1,2,4-triazol-1-yl)-2-pyridyl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound P8):



(P8)

Step 1: Preparation of 2-[3-ethylsulfanyl-5-(1,2,4-triazol-1-yl)-2-pyridyl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound P7)



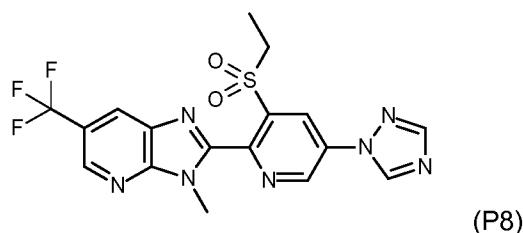
(P7)

To an ice cooled solution of 1H-1,2,4-triazole (42.3 mg, 0.606 mmol) in N,N-dimethylformamide (4 ml) was added sodium hydride (27 mg, 0.671 mmol; 60 weight% in paraffin oil), followed by 2-(5-chloro-3-ethylsulfanyl-2-pyridyl)-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (200 mg, 0.536 mmol) after 15 minutes. The mixture was heated 2 days at 120°C, then quenched with water and extracted with
 15 ethyl acetate. The combined organic phases were washed with brine, dried over magnesium sulfate and reduced under vacuum. The residue was purified by flash chromatography to afford 2-[3-ethylsulfanyl-5-(1,2,4-triazol-1-yl)-2-pyridyl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound
 20 P7) as a solid (59 mg). LCMS (method 1): 406 (M+H)⁺, retention time 0.97 min. ¹H NMR (400 MHz,

-59-

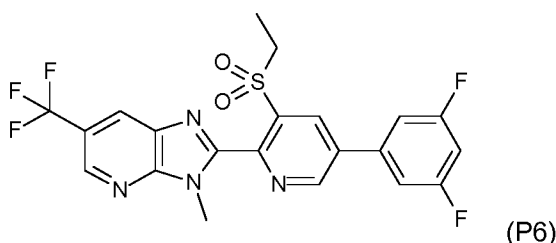
CDCl_3 δ ppm: 1.43 (t, 3H), 3.07 (q, 2H), 4.12 (s, 3H), 8.14 (d, 1H), 8.22 (s, 1H), 8.43 (d, 1H), 8.72 - 8.78 (m, 2H), 8.83 (d, 1H).

Step 2: Preparation of 2-[3-ethylsulfonyl-5-(1,2,4-triazol-1-yl)-2-pyridyl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound P8)



Obtained from 2-[3-ethylsulfonyl-5-(1,2,4-triazol-1-yl)-2-pyridyl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound P7) (54 mg, 0.133 mmol) and mCPBA (64.4 mg, 0.280 mmol) in dichloromethane (10 ml) according to procedure Example P2. The mixture was stirred at room temperature for 2 hours. Workup afforded 2-[3-ethylsulfonyl-5-(1,2,4-triazol-1-yl)-2-pyridyl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound P8) as a solid (57 mg). LCMS (method 1): 438 (M+H)⁺, retention time 0.90 min. ¹H NMR (400 MHz, CDCl_3) δ ppm: 1.44 (t, 3H), 3.91-4.04 (m, 5H), 8.27 (s, 1H), 8.34 (d, 1H), 8.79 (d, 1H), 8.83-8.89 (m, 2H), 9.44 (d, 1H).

EXAMPLE P5: Preparation of 2-[5-(3,5-difluorophenyl)-3-ethylsulfonyl-2-pyridyl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound P6):

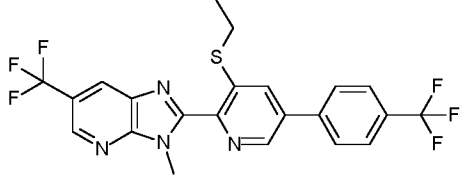
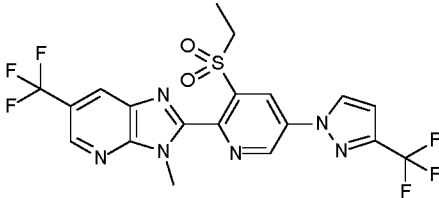
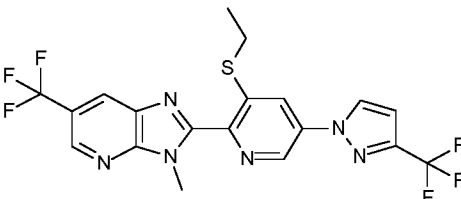
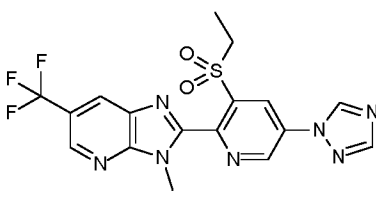
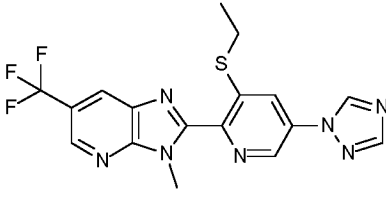
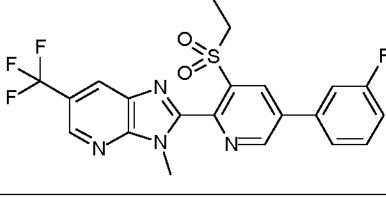


A solution of 2-(5-bromo-3-ethylsulfonyl-2-pyridyl)-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (600 mg, 1.336 mmol), (3,5-difluorophenyl)boronic acid (210.9 mg, 1.336 mmol) and an aqueous 1M sodium carbonate solution (2.671 ml, 2.671 mmol) in iso-propyl alcohol (26.7 ml) was flushed with argon. Tetrakis(triphenylphosphine)palladium(0) (47.3 mg, 0.0401 mmol) was added, and the mixture was stirred at 100°C for 4 hours. The reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic phases were washed with brine, dried over sodium sulfate and reduced under vacuum. The residue was purified by flash chromatography to afford 2-[5-(3,5-difluorophenyl)-3-ethylsulfonyl-2-pyridyl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound P6) as a solid (420 mg). LCMS (method 1): 483 (M+H)⁺, retention time 1.15 min. ¹H NMR (400 MHz, CDCl_3)

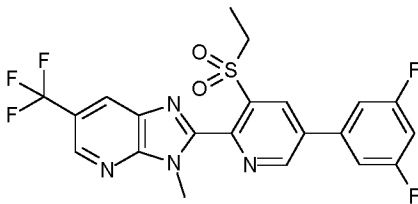
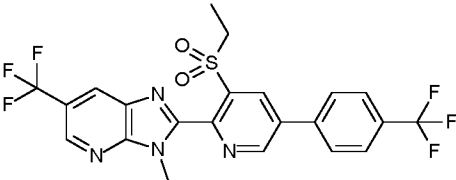
-60-

δ ppm: 1.44 (t, 3H), 3.92 (q, 2H), 3.94 (s, 3H), 7.00 (m, 1H), 7.26-7.30 (m, 2H), 8.33 (d, 1H), 8.66 (d, 1H), 8.78 (d, 1H), 9.17 (d, 1H).

5 Table P1: Compounds of formula (I)

Compound No.	Structures	LCMS			Mp (°C)
		R _t (min)	[M+H] ⁺ (measured)	Method	
P1		2.17	483	2	137 - 138
P2		1.12	505	1	
P3		1.21	473	1	
P4		0.90	438	1	
P5		0.97	406	1	
P6		1.12	465	1	

-61-

Compound No.	Structures	LCMS			Mp (°C)
		R _t (min)	[M+H] ⁺ (measured)	Method	
P7		1.15	483	1	
P8		1.93	515	2	98 - 99

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

The following mixtures of the compounds of formula I with active ingredients are preferred (the abbreviation "TX" means "one compound selected from the group consisting of the compounds described in Tables A-1, A-2, A-3 and P1 of the present invention"):

an adjuvant selected from the group of substances consisting of petroleum oils (628) + TX,
 an acaricide selected from the group of substances consisting of 1,1-bis(4-chlorophenyl)-2-ethoxyethanol (IUPAC name) (910) + TX, 2,4-dichlorophenyl benzenesulfonate (IUPAC/Chemical Abstracts name) (1059) + TX, 2-fluoro-*N*-methyl-*N*-1-naphthylacetamide (IUPAC name) (1295) + TX, 4-chlorophenyl phenyl sulfone (IUPAC name) (981) + TX, abamectin (1) + TX, acequinocyl (3) + TX, acetoprole [CCN] + TX, acrinathrin (9) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, alpha-cypermethrin (202) + TX, amidithion (870) + TX, amidoflume [CCN] + TX, amidothioate (872) + TX, amiton (875) + TX, amiton hydrogen oxalate (875) + TX, amitraz (24) + TX, aramite (881) +

-62-

TX, arsenous oxide (882) + TX, AVI 382 (compound code) + TX, AZ 60541 (compound code) + TX, azinphos-ethyl (44) + TX, azinphos-methyl (45) + TX, azobenzene (IUPAC name) (888) + TX, azocyclotin (46) + TX, azothoate (889) + TX, benomyl (62) + TX, benoxafos [CCN] + TX, benzoximate (71) + TX, benzyl benzoate (IUPAC name) [CCN] + TX, bifenazate (74) + TX, 5 bifenthrin (76) + TX, binapacryl (907) + TX, brofenvalerate + TX, bromocyclen (918) + TX, bromophos (920) + TX, bromophos-ethyl (921) + TX, bromopropylate (94) + TX, buprofezin (99) + 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) 10 (125) + TX, chinomethionat (126) + TX, chlorbenside (959) + TX, chlordimeform (964) + TX, chlordimeform hydrochloride (964) + TX, chlorfenapyr (130) + TX, chlorfenethol (968) + TX, chlorfenson (970) + TX, chlorfensulfide (971) + TX, chlorfenvinphos (131) + TX, chlorobenzilate (975) + TX, chloromebuform (977) + TX, chloromethiuron (978) + TX, chloropropylate (983) + TX, chlorpyrifos (145) + TX, chlorpyrifos-methyl (146) + TX, chlorthiophos (994) + TX, cinerin I (696) + 15 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, 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, 20 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, diafenthion (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 25 (1089) + TX, dinobuton (269) + TX, dinocap (270) + TX, dinocap-4 [CCN] + TX, dinocap-6 [CCN] + TX, dinocton (1090) + TX, dinopenton (1092) + TX, dinosulfon (1097) + TX, dinoterbon (1098) + TX, dioxathion (1102) + TX, diphenyl sulfone (IUPAC name) (1103) + TX, disulfiram [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, 30 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, fentrifanil (1161) + TX, fenvalerate (349) + TX, fipronil (354) + TX, fluacrypyrim (360) + TX, fluazuron (1166) + TX, flubenzimine (1167) + TX, flucycloxuron (366) + TX, flucythrinate (367) + 35 TX, fluenetil (1169) + TX, flufenoxuron (370) + TX, flumethrin (372) + TX, fluorbenside (1174) + TX, fluvalinate (1184) + TX, FMC 1137 (development code) (1185) + TX, formetanate (405) + TX, formetanate hydrochloride (405) + TX, formothion (1192) + TX, formparanate (1193) + TX, gamma-HCH (430) + TX, glyodin (1205) + TX, halfenprox (424) + TX, heptenophos (432) + TX,

-63-

- 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,
- 5 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,
- 10 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) +
- 15 TX, petroleum oils (628) + TX, phenkapton (1330) + TX, phenthoate (631) + TX, phorate (636) + TX, phosalone (637) + TX, phosfolan (1338) + TX, phosmet (638) + TX, phosphamidon (639) + TX, phoxim (642) + TX, pirimiphos-methyl (652) + TX, polychloroterpenes (traditional name) (1347) + TX, polynactins (653) + TX, proclonol (1350) + TX, profenofos (662) + TX, promacyl (1354) + TX, propargite (671) + TX, propetamphos (673) + TX, propoxur (678) + TX,
- 20 prothidathion (1360) + TX, prothoate (1362) + TX, pyrethrin I (696) + TX, pyrethrin II (696) + TX, pyrethrins (696) + TX, pyridaben (699) + TX, pyridaphenthion (701) + TX, pyrimidifen (706) + TX, pyrimitate (1370) + TX, quinalphos (711) + TX, quintiofos (1381) + TX, R-1492 (development code) (1382) + TX, RA-17 (development code) (1383) + TX, rotenone (722) + TX, schradan (1389) + TX, sebufos + TX, selamectin [CCN] + TX, SI-0009 (compound code) + TX, sophamide (1402)
- 25 + TX, spirodiclofen (738) + TX, spiromesifen (739) + TX, SSI-121 (development code) (1404) + TX, sulfiram [CCN] + TX, sulfluramid (750) + TX, sulfotep (753) + TX, sulfur (754) + TX, SZI-121 (development code) (757) + TX, tau-fluvalinate (398) + TX, tebufenpyrad (763) + TX, TEPP (1417) + TX, terbam + TX, tetrachlorvinphos (777) + TX, tetradifon (786) + TX, tetranactin (653) + TX, tetrasul (1425) + TX, thiafenox + TX, thiocarboxime (1431) + TX, thiofanox (800) + TX,
- 30 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
- 35 dioctanoate (IUPAC name) (170) + TX, copper sulfate (172) + TX, cybutryne [CCN] + TX, dichlone (1052) + TX, dichlorophen (232) + TX, endothal (295) + TX, fentin (347) + TX, hydrated lime [CCN] + TX, nabam (566) + TX, quinoclamine (714) + TX, quinonamid (1379) + TX, simazine

-64-

(730) + TX, triphenyltin acetate (IUPAC name) (347) and triphenyltin hydroxide (IUPAC name) (347) + TX,

an anthelmintic selected from the group of substances consisting of abamectin (1) + TX, crufomate (1011) + TX, doramectin [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,

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, oclothilone (590) + TX, oxolinic acid (606) + TX, oxytetracycline (611) + TX, potassium hydroxyquinoline sulfate (446) + TX, probenazole (658) + TX, streptomycin (744) + TX, streptomycin sesquisulfate (744) + TX, tecloftalam (766) + TX, and thiomersal [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, *Anagrapha 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, *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. (596) + TX, *Paecilomyces fumosoroseus* (613) + TX, *Phytoseiulus persimilis* (644) + TX, *Spodoptera exigua* multicapsid nuclear polyhedrosis virus (scientific name) (741) + TX, *Steinernema*

-65-

bibionis (742) + TX, *Steinernema carpocapsae* (742) + TX, *Steinernema feltiae* (742) + TX, *Steinernema glaseri* (742) + TX, *Steinernema riobrave* (742) + TX, *Steinernema riobravus* (742) + TX, *Steinernema scapterisci* (742) + TX, *Steinernema* spp. (742) + TX, *Trichogramma* spp. (826) + TX, *Typhlodromus occidentalis* (844) and *Verticillium lecanii* (848) + TX,

- 5 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, thiotepa [CCN] + TX, tretamine [CCN] and uredepa [CCN] + TX,
- 10 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-ol (IUPAC name) (782) + TX, (*Z*)-tetradec-9-en-1-ol (IUPAC name) (783) + TX, (*Z*)-tetradec-9-en-1-yl acetate (IUPAC name) (784) + TX, (*7E,9Z*)-dodeca-7,9-dien-1-yl acetate (IUPAC name) (283) + TX, (*9Z,11E*)-tetradeca-9,11-dien-1-yl acetate (IUPAC name) (780) + TX, (*9Z,12E*)-tetradeca-9,12-dien-1-yl acetate (IUPAC name) (781) + TX, 14-methyloctadec-1-ene (IUPAC name) (545) + TX, 4-methylnonan-5-ol with 4-methylnonan-5-one (IUPAC name) (544) + TX, alpha-multistriatin [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, frontalinal [CCN] + TX, gossypolure (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,
- 35 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

-66-

- 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, methylnodecanamide [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
- 10 (IUPAC name) (1451) + TX, 2,2-dichlorovinyl 2-ethylsulfinyethyl 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
- 15 (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-
- 20 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
- 25 phosphide (640) + TX, amidithion (870) + TX, amidothioate (872) + TX, aminocarb (873) + TX, amiton (875) + TX, amiton hydrogen oxalate (875) + TX, amitraz (24) + TX, anabasine (877) + TX, athidathion (883) + TX, AVI 382 (compound code) + TX, AZ 60541 (compound code) + TX, azadirachtin (41) + TX, azamethiphos (42) + TX, azinphos-ethyl (44) + TX, azinphos-methyl (45) + TX, azothoate (889) + TX, *Bacillus thuringiensis* delta endotoxins (52) + TX, barium
- 30 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) +
- 35 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,

-67-

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
 5 name) (946) + TX, carbophenothion (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,
 chlorethoxyfos (129) + TX, chlorfenapyr (130) + TX, chlorfenvinphos (131) + TX, chlorfluazuron
 (132) + TX, chlormephos (136) + TX, chloroform [CCN] + TX, chloropicrin (141) + TX,
 10 chlorphoxim (989) + TX, chlorprazophos (990) + TX, chlorpyrifos (145) + TX, chlorpyrifos-methyl
 (146) + TX, chlorthiophos (994) + TX, chromafenozide (150) + TX, cinerin I (696) + TX, cinerin II
 (696) + TX, cinerins (696) + TX, cis-resmethrin + TX, cismethrin (80) + TX, clocythrins + TX,
 cloethocarb (999) + TX, closantel [CCN] + TX, clothianidin (165) + TX, copper acetoarsenite
 [CCN] + TX, copper arsenate [CCN] + TX, copper oleate [CCN] + TX, coumaphos (174) + TX,
 15 coumithoate (1006) + TX, crotamiton [CCN] + TX, crotoxyphos (1010) + TX, cruformate (1011) +
 TX, cryolite (177) + TX, CS 708 (development code) (1012) + TX, cyanofenphos (1019) + TX,
 cyanophos (184) + TX, cyanthoate (1020) + TX, cyclothrin [CCN] + TX, cycloprothrin (188) + TX,
 cyfluthrin (193) + TX, cyhalothrin (196) + TX, cypermethrin (201) + TX, cyphenothrin (206) + TX,
 cyromazine (209) + TX, cythioate [CCN] + TX, *d*-limonene [CCN] + TX, *d*-tetramethrin (788) +
 20 TX, DAEP (1031) + TX, dazomet (216) + TX, DDT (219) + TX, decarbofuran (1034) + TX,
 deltamethrin (223) + TX, demephion (1037) + TX, demephion-O (1037) + TX, demephion-S (1037)
 + TX, demeton (1038) + TX, demeton-methyl (224) + TX, demeton-O (1038) + TX, demeton-O-
 methyl (224) + TX, demeton-S (1038) + TX, demeton-S-methyl (224) + TX, demeton-S-
 methylsulphon (1039) + TX, diafenthiuron (226) + TX, dialifos (1042) + TX, diamidafos (1044) +
 25 TX, diazinon (227) + TX, dicapthon (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)
 30 + TX, dinex (1089) + TX, dinex-diclexine (1089) + TX, dinoprop (1093) + TX, dinosam (1094) +
 TX, dinoseb (1095) + TX, dinotefuran (271) + TX, diofenolan (1099) + TX, dioxabenzofos (1100)
 + TX, dioxacarb (1101) + TX, dioxathion (1102) + TX, disulfoton (278) + TX, dithicrofos (1108) +
 TX, DNOC (282) + TX, doramectin [CCN] + TX, DSP (1115) + TX, ecdysterone [CCN] + TX, EI
 1642 (development code) (1118) + TX, emamectin (291) + TX, emamectin benzoate (291) + TX,
 35 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

-68-

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, fenoxycarb (340) + TX, fenpirithrin (1155) + TX, fenpropathrin (342) + TX, fenpyrad + TX, fensulfathion (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, isoprocab (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*-cumenyl methylcarbamate (IUPAC name) (1014) + TX, magnesium phosphide (IUPAC name) (640) + TX, malathion (492) + TX, malonoben (1254) + TX, mazidox (1255) + TX, mecarbam (502) + TX, mecarphon (1258) + TX, menazon (1260) + TX, mephosfolan (1261) + TX, mercurous chloride (513) + TX, mesulfenfos (1263) + TX, metaflumizone (CCN) + TX, metam (519) + TX, metam-potassium (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, 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 code) + TX, nor nicotine (traditional name) (1319) + TX, novaluron (585) + TX, noviflumuron (586) + TX, O-5-dichloro-4-iodophenyl O-ethyl ethylphosphonothioate (IUPAC name) (1057) + TX, O,O-diethyl O-4-methyl-2-oxo-2*H*-chromen-7-yl phosphorothioate (IUPAC name) (1074) + TX, O,O-diethyl O-6-methyl-2-propylpyrimidin-4-yl phosphorothioate (IUPAC name) (1075) + TX, O,O,O',O'-tetrapropyl dithiopyrophosphate (IUPAC name) (1424) + TX, oleic acid (IUPAC name) (593) + TX, omethoate (594) + TX, oxamyl (602) + TX, oxydemeton-methyl (609) + TX, oxydeprofos (1324) + TX, oxydisulfoton (1325) + TX, pp'-DDT (219) + TX, para-dichlorobenzene [CCN] + TX, parathion (615) + TX, parathion-methyl (616) + TX, penfluron [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, phenthoate (631) + TX, phorate (636) + TX, phosalone (637) + TX, phosfolan (1338) + TX, phosmet (638) + TX, phosnichlor (1339) + TX, phosphamidon (639) + TX, phosphine (IUPAC name) (640) + TX, phoxim (642) + TX, phoxim-methyl (1340) + TX, pirimethaphos (1344) + TX, pirimicarb (651) + TX, pirimiphos-ethyl (1345) + TX, pirimiphos-methyl (652) + TX, polychlorodicyclopentadiene isomers (IUPAC name) (1346) + TX, polychloroterpenes (traditional name) (1347) + TX, potassium arsenite [CCN] + TX, potassium thiocyanate [CCN] + TX, prallethrin (655) + TX, precocene I [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, 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, quintiofos (1381) + TX, R-1492 (development code) (1382) + TX, 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,

-70-

sodium fluoride (IUPAC/Chemical Abstracts name) (1399) + TX, sodium hexafluorosilicate (1400) + TX, sodium pentachlorophenoxide (623) + TX, sodium selenate (IUPAC name) (1401) + TX, sodium thiocyanate [CCN] + TX, sophamide (1402) + TX, spinosad (737) + TX, spiromesifen (739) + TX, spirotetmat (CCN) + TX, sulcofuron (746) + TX, sulcofuron-sodium (746) + TX, sulfluramid (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) + 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, thiafenox + TX, thiamethoxam (792) + TX, thicofos (1428) + TX, thiocarboxime (1431) + TX, thiocyclam (798) + TX, thiocyclam hydrogen oxalate (798) + TX, thiodicarb (799) + TX, thiofanox (800) + TX, thiometon (801) + TX, thionazin (1434) + TX, thiosultap (803) + TX, thiosultap-sodium (803) + TX, thuringiensin [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, triprene (1459) + TX, vamidothion (847) + 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 [187166-40-1 + 187166-15-0] + TX, spirotetramat [203313-25-1] + TX, sulfoxaflor [946578-00-3] + TX, flufiprole [704886-18-0] + TX, meperfluthrin [915288-13-0] + TX, tetramethylfluthrin [84937-88-2] + TX, triflumezopyrim (disclosed in WO 2012/092115) + TX, fluxametamide (WO 2007/026965) + TX, epsilon-metofluthrin [240494-71-7] + TX, epsilon-momfluorothrin [1065124-65-3] + TX, fluazaindolizine [1254304-22-7] + TX, chloroprallethrin [399572-87-3] + TX, fluxametamide [928783-29-3] + TX, cyhalodiamide [1262605-53-7] + TX, tioxazafen [330459-31-9] + TX, broflanilide [1207727-04-5] + TX, flufiprole [704886-18-0] + TX, cyclaniliprole [1031756-98-5] + TX, tetraniliprole [1229654-66-3] + TX, guadiopyr (described in WO2010/060231) + TX, cycloxaprid (described in WO2005/077934) + TX,

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

-71-

(1454) + TX, trimethacarb (840) + TX, triphenyltin acetate (IUPAC name) (347) and triphenyltin hydroxide (IUPAC name) (347) + TX, pyriprole [394730-71-3] + TX,
 a nematicide selected from the group of substances consisting of AKD-3088 (compound code) + TX,
 1,2-dibromo-3-chloropropane (IUPAC/Chemical Abstracts name) (1045) + TX, 1,2-dichloropropane
 5 (IUPAC/ Chemical Abstracts name) (1062) + TX, 1,2-dichloropropane with 1,3-dichloropropene
 (IUPAC name) (1063) + TX, 1,3-dichloropropene (233) + TX, 3,4-dichlorotetrahydrothiophene 1,1-
 dioxide (IUPAC/Chemical Abstracts name) (1065) + TX, 3-(4-chlorophenyl)-5-methylrhodanine
 (IUPAC name) (980) + TX, 5-methyl-6-thioxo-1,3,5-thiadiazinan-3-ylacetic acid (IUPAC name) (1286)
 + TX, 6-isopentenylaminopurine (210) + TX, abamectin (1) + TX, acetoprole [CCN] + TX,
 10 alanycarb (15) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, AZ 60541 (compound code) + TX,
 benclonthiaz [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,
 DBCP (1045) + TX, DCIP (218) + TX, diamidafos (1044) + TX, dichlofenthion (1051) + TX,
 15 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)
 (423) + TX, heterophos [CCN] + TX, iodomethane (IUPAC name) (542) + TX, isamidofos (1230) +
 20 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
 (602) + TX, phorate (636) + TX, phosphamidon (639) + TX, phosphocarb [CCN] + TX, sebufos +
 25 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, xyleneols [CCN] + TX, YI-5302 (compound
 code) and zeatin (210) + TX, fluensulfone [318290-98-1] + TX,
 a nitrification inhibitor selected from the group of substances consisting of potassium ethylxanthate
 30 [CCN] and nitrapyrin (580) + TX,
 a plant activator selected from the group of substances consisting of acibenzolar (6) + TX,
 acibenzolar-S-methyl (6) + TX, probenazole (658) and *Reynoutria sachalinensis* extract (720) + TX,
 a rodenticide selected from the group of substances consisting of 2-isovalerylindan-1,3-dione (IUPAC
 name) (1246) + TX, 4-(quinoxalin-2-ylamino)benzenesulfonamide (IUPAC name) (748) + TX, alpha-
 35 chlorohydrin [CCN] + TX, aluminium phosphide (640) + TX, antu (880) + TX, arsenous oxide (882)
 + TX, barium carbonate (891) + TX, bithiosemi (912) + TX, brodifacoum (89) + TX,
 bromadiolone (91) + TX, bromethalin (92) + TX, calcium cyanide (444) + TX, chloralose (127) +
 TX, chlorophacinone (140) + TX, cholecalciferol (850) + TX, coumachlor (1004) + TX,

-72-

- 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, epoxiconazole [106325-08-0] + TX, fenbuconazole [114369-43-6] + TX, fluquinconazole [136426-54-5] + TX, flusilazole [85509-19-9] + TX, flutriafol [76674-21-0] + TX, hexaconazole [79983-71-4] + TX, imazalil [35554-44-0] + TX, imibenconazole [86598-92-7] + TX, ipconazole [125225-28-7] + TX, metconazole [125116-23-6] + TX, myclobutanil [88671-89-0] + TX, pefurazoate [101903-30-4] + TX, penconazole [66246-88-6] + TX, prothioconazole [178928-70-6] + TX, pyrifenox [88283-41-4] + TX, prochloraz [67747-09-5] + TX, propiconazole [60207-90-1] + TX, simeconazole [149508-90-7] + TX, tebuconazole [107534-96-3] + TX, tetraconazole [112281-77-3] + TX, triadimefon [43121-43-3] + TX, triadimenol [55219-65-3] + TX, triflumizole [99387-89-0] + TX, triticonazole [131983-72-7] + TX, ancymidol [12771-68-5] + TX, fenarimol [60168-88-9] + TX, nuarimol [63284-71-9] + TX,

-73-

- 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, benalaxyl [71626-11-4] + TX, furalaxyl [57646-30-7] + TX, metalaxyl [57837-19-1] + TX, R-metalaxyl [70630-17-0] + TX, ofurace [58810-48-3] + TX, oxadixyl [77732-09-3] + TX, benomyl [17804-35-2] + TX, carbendazim [10605-21-7] + TX, debacarb [62732-91-6] + TX, fuberidazole [3878-19-1] + TX, thiabendazole [148-79-8] + TX, chlozolinate [84332-86-5] + TX, dichlozoline [24201-58-9] + TX, iprodione [36734-19-7] + TX, myclozoline
- 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, maneb [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-lar-S-methyl [135158-54-2] + TX, anilazine [101-05-3] + TX, benthiavalicarb [413615-35-7] + TX, blasticidin-S [2079-00-7] + TX, chinomethionat [2439-01-2] + TX, chloroneb [2675-77-6] + TX,
- 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, flusulfamid [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-

-74-

- 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, quinoxifen [124495-18-7] + TX, quintozone [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 (disclosed in WO 2007/048556) + TX, 3-difluoromethyl-1-methyl-1H-
- 10 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-
- 15 pyrazole-4-carboxamide [926914-55-8] + TX, lancotrione [1486617-21-3] + TX, florpiauxifen [943832-81-3] + TX, ipfentrifluconazole [1417782-08-1] + TX, mefentrifluconazole [1417782-03-6] + TX, quinfumelin [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, dipymetitron [16114-35-5] + TX, pyraziflumid [942515-63-1] + TX, kappa-tefluthrin [391634-71-2] + TX, fempicoxamid [517875-34-2] + TX; fluindapyr [1383809-87-7] + TX; alpha-bromadiolone [28772-56-7] + TX; flupyrimin [1689566-03-7] + TX; benzpyrimoxan [1449021-97-9] + TX; acynonapyr [1332838-17-1] + TX; inpyrfluxam [1352994-67-2] + TX,
- 25 isoflucypram [1255734-28-1] + TX; rescalure [64309-03-1] + TX; aminopyrifin [1531626-08-0] + TX; tyclopyrazoflor [1477919-27-9] + TX; and spiropidion [1229023-00-0] + TX; and
- microbials including: *Acinetobacter lwoffii* + TX, *Acremonium alternatum* + TX + TX, *Acremonium cephalosporium* + TX + TX, *Acremonium diospyri* + TX, *Acremonium obclavatum* + TX, *Adoxophyes orana granulovirus* (AdoxGV) (Capex®) + TX, *Agrobacterium radiobacter* strain K84 (Galltrol-A®) +
- 30 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,
- 35 *Bacillus cereus* + TX, *Bacillus chitosporus* strain CM-1 + TX, *Bacillus chitosporus* 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,

-75-

- Bacillus marismortui* + TX, *Bacillus megaterium* + TX, *Bacillus mycoides* strain AQ726 + TX, *Bacillus papillae* (Milky Spore Powder®) + TX, *Bacillus pumilus* spp. + TX, *Bacillus pumilus* strain GB34 (Yield Shield®) + TX, *Bacillus pumilus* strain AQ717 + TX, *Bacillus pumilus* strain QST 2808 (Sonata® + TX, Ballad Plus®) + TX, *Bacillus spahericus* (VectoLex®) + TX, *Bacillus* spp. + TX, *Bacillus* spp. strain AQ175 + TX, *Bacillus* spp. strain AQ177 + TX, *Bacillus* spp. strain AQ178 + TX, *Bacillus subtilis* strain QST 713 (CEASE® + TX, Serenade® + TX, Rhapsody®) + TX, *Bacillus subtilis* strain QST 714 (JAZZ®) + TX, *Bacillus subtilis* strain AQ153 + TX, *Bacillus subtilis* strain AQ743 + TX, *Bacillus subtilis* strain QST3002 + TX, *Bacillus subtilis* strain QST3004 + TX, *Bacillus subtilis* var. *amyloliquefaciens* strain FZB24 (Taegro® + TX, Rhizopro®) + TX, *Bacillus thuringiensis* Cry 2Ae + TX, *Bacillus thuringiensis* Cry1Ab + TX, *Bacillus thuringiensis aizawai* GC 91 (Agree®) + TX, *Bacillus thuringiensis israelensis* (BMP123® + TX, Aquabac® + TX, VectoBac®) + TX, *Bacillus thuringiensis kurstaki* (Javelin® + TX, Deliver® + TX, CryMax® + TX, Bonide® + TX, Scutella WP® + TX, Turilav WP® + TX, Astuto® + TX, Dipel WP® + TX, Biobit® + TX, Foray®) + TX, *Bacillus thuringiensis kurstaki* BMP 123 (Baritone®) + TX, *Bacillus thuringiensis kurstaki* HD-1 (Bioprotec-CAF / 3P®) + TX, *Bacillus thuringiensis* strain BD#32 + TX, *Bacillus thuringiensis* strain AQ52 + TX, *Bacillus thuringiensis* var. *aizawai* (XenTari® + TX, DiPel®) + TX, bacteria spp. (GROWMEND® + TX, GROWSWEET® + TX, Shootup®) + TX, bacteriophage of *Clavipacter michiganensis* (AgriPhage®) + TX, Bakflor® + TX, *Beauveria bassiana* (Beaugenic® + TX, Brocaril WP®) + TX, *Beauveria bassiana* GHA (Mycotrol ES® + TX, Mycotrol O® + TX, BotaniGuard®) + TX, *Beauveria brongniartii* (Engerlingspilz®) + TX, Schweizer *Beauveria*® + TX, Melocont®) + TX, *Beauveria* spp. + TX, *Botrytis cineria* + TX, *Bradyrhizobium japonicum* (TerraMax®) + TX, *Brevibacillus brevis* + TX, *Bacillus thuringiensis tenebrionis* (Novodor®) + TX, BtBooster + TX, *Burkholderia cepacia* (Deny® + TX, Intercept® + TX, Blue Circle®) + TX, *Burkholderia gladii* + TX, *Burkholderia gladioli* + TX, *Burkholderia* spp. + TX, Canadian thistle fungus (CBH Canadian Bioherbicide®) + TX, *Candida butyri* + TX, *Candida famata* + TX, *Candida fructus* + TX, *Candida glabrata* + TX, *Candida guilliermondii* + TX, *Candida melibiosica* + TX, *Candida oleophila* strain O + TX, *Candida parapsilosis* + TX, *Candida pelliculosa* + TX, *Candida pulcherrima* + TX, *Candida reukaufii* + TX, *Candida saitoana* (Bio-Coat® + TX, Biocure®) + TX, *Candida sake* + TX, *Candida* spp. + TX, *Candida tenuis* + TX, *Cedecea dravisae* + TX, *Cellulomonas flavigena* + TX, *Chaetomium cochliodes* (Nova-Cide®) + TX, *Chaetomium globosum* (Nova-Cide®) + TX, *Chromobacterium subtsugae* strain PRAA4-1T (Grandevo®) + TX, *Cladosporium cladosporioides* + TX, *Cladosporium oxysporum* + TX, *Cladosporium chlorocephalum* + TX, *Cladosporium* spp. + TX, *Cladosporium tenuissimum* + TX, *Clonostachys rosea* (EndoFine®) + TX, *Colletotrichum acutatum* + TX, *Coniothyrium minitans* (Cotans WG®) + TX, *Coniothyrium* spp. + TX, *Cryptococcus albidus* (YIELDPLUS®) + TX, *Cryptococcus humicola* + TX, *Cryptococcus infirmo-minutus* + 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* +

-76-

- 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 gigantea* (Rotstop®) + TX, phosphate solubilizing bacteria (Phosphomeal®) + TX, *Phytophthora cryptogea* + TX, *Phytophthora palmivora* (Devine®) + TX, *Pichia anomala* + TX, *Pichia guillemontii* + TX, *Pichia membranaefaciens* + TX, *Pichia onychis* + TX, *Pichia stipites* + TX, *Pseudomonas aeruginosa* + TX, *Pseudomonas aureofaciens* (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*

-77-

- graminis + TX, *Rhodotorula mucilagnosa* + TX, *Rhodotorula rubra* + TX, *Saccharomyces cerevisiae* + TX, *Salinococcus roseus* + TX, *Sclerotinia minor* + TX, *Sclerotinia minor* (SARRITOR®) + TX, *Scytalidium* spp. + TX, *Scytalidium uredinicola* + TX, *Spodoptera exigua nuclear polyhedrosis virus* (Spod-X® + TX, Spexit®) + TX, *Serratia marcescens* + TX, *Serratia plymuthica* + TX, *Serratia* spp. + TX, *Sordaria fimicola* + TX, *Spodoptera littoralis nucleopolyhedrovirus* (Littovir®) + TX, *Sporobolomyces roseus* + TX, *Stenotrophomonas maltophilia* + TX, *Streptomyces ahygroscopicus* + TX, *Streptomyces albaduncus* + TX, *Streptomyces exfoliates* + TX, *Streptomyces galbus* + TX, *Streptomyces griseoplanus* + TX, *Streptomyces griseoviridis* (Mycostop®) + TX, *Streptomyces lydicus* (Actinovate®) + TX, *Streptomyces lydicus* WYEC-108 (ActinoGrow®) + TX, *Streptomyces violaceus* + TX, *Tilletiopsis minor* + TX, *Tilletiopsis* spp. + TX, *Trichoderma asperellum* (T34 Biocontrol®) + TX, *Trichoderma gamsii* (Tenet®) + TX, *Trichoderma atroviride* (Plantmate®) + TX, *Trichoderma hamatum* TH 382 + TX, *Trichoderma harzianum rifai* (Mycostar®) + TX, *Trichoderma harzianum* T-22 (Trianum-P® + TX, PlantShield HC® + TX, RootShield® + TX, Trianum-G®) + TX, *Trichoderma harzianum* T-39 (Trichodex®) + TX, *Trichoderma inhamatum* + TX, *Trichoderma koningii* + TX, *Trichoderma* spp. LC 52 (Sentinel®) + TX, *Trichoderma lignorum* + TX, *Trichoderma longibrachiatum* + TX, *Trichoderma polysporum* (Binab T®) + TX, *Trichoderma taxi* + TX, *Trichoderma virens* + TX, *Trichoderma virens* (formerly *Gliocladium virens* GL-21) (SoilGuard®) + TX, *Trichoderma viride* + TX, *Trichoderma viride* strain ICC 080 (Remedier®) + TX, *Trichosporon pullulans* + TX, *Trichosporon* spp. + TX, *Trichothecium* spp. + TX, *Trichothecium roseum* + TX, *Typhula phacorrhiza* strain 94670 + TX, *Typhula phacorrhiza* strain 94671 + TX, *Ulocladium atrum* + TX, *Ulocladium oudemansii* (Botry-Zen®) + TX, *Ustilago maydis* + TX, various bacteria and supplementary micronutrients (Natural II®) + TX, various fungi (Millennium Microbes®) + TX, *Verticillium chlamydosporium* + TX, *Verticillium lecanii* (Mycotal® + TX, Vertalec®) + TX, Vip3Aa20 (VIPtera®) + TX, *Virgibacillus marismortui* + TX, *Xanthomonas campestris* pv. *Poae* (Camperico®) + TX, *Xenorhabdus bovienii* + TX, *Xenorhabdus nematophilus*; and
- Plant extracts including: pine oil (Retenol®) + TX, azadirachtin (Plasma Neem Oil® + TX, AzaGuard® + TX, MeemAzal® + TX, Molt-X® + TX, Botanical IGR (Neemazad® + TX, Neemix®) + TX, canola oil (Lilly Miller Vegol®) + TX, *Chenopodium ambrosioides near ambrosioides* (Requiem®) + TX, *Chrysanthemum* extract (Crisant®) + TX, extract of neem oil (Trilogy®) + TX, essentials oils of *Labiatae* (Botania®) + TX, extracts of clove rosemary peppermint and thyme oil (Garden insect killer®) + TX, Glycinebetaine (Greenstim®) + TX, garlic + TX, lemongrass oil (GreenMatch®) + TX, neem oil + TX, *Nepeta cataria* (Catnip oil) + TX, *Nepeta catarina* + TX, nicotine + TX, oregano oil (MossBuster®) + TX, *Pedaliaceae* oil (Nematon®) + TX, pyrethrum + TX, *Quillaja saponaria* (NemaQ®) + TX, *Reynoutria sachalinensis* (Regalia® + TX, Sakalia®) + TX, rotenone (Eco Roten®) + TX, *Rutaceae* plant extract (Soleo®) + TX, soybean oil (Ortho ecosense®) + TX, tea tree oil (Timorex Gold®) + TX, thymus oil + TX, AGNIQUE® MMF + TX, BugOil® + TX, mixture of rosemary sesame peppermint thyme and cinnamon extracts (EF 300®) + TX, mixture of clove rosemary and peppermint extract (EF

-78-

400®) + TX, mixture of clove pepermint garlic oil and mint (Soil Shot®) + TX, kaolin (Screen®) + TX, storage glucan 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,

- 5 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)-
10 3 + TX,8 + TX,11 Tetradecatrienyl acetate + TX, (Z + TX,Z + TX,E)-7 + TX,11 + TX,13-Hexadecatrienyl + 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,

- 15 *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,
20 TX, *Amblyseius womersleyi* (WomerMite®) + TX, *Amitus hesperidum* + TX, *Anagrus atomus* + TX, *Anagrus fusciventris* + TX, *Anagrus kamali* + TX, *Anagrus loecki* + TX, *Anagrus pseudococci* (Citripar®) + TX, *Anicetus benefices* + TX, *Anisopteromalus calandrae* + TX, *Anthocoris nemoralis* (Anthocoris-System®) + TX, *Aphelinus abdominalis* (Apheline® + TX, Aphiline®) + TX, *Aphelinus asychis* + TX, *Aphidius colemani* (Aphipar®) + TX, *Aphidius ervi* (Ervipar®) + TX, *Aphidius gifuensis* + TX,
25 TX, *Aphidius matricariae* (Aphipar-M®) + TX, *Aphidoletes aphidimyza* (Aphidend®) + TX, *Aphidoletes aphidimyza* (Aphidoline®) + TX, *Aphytis lingnanensis* + TX, *Aphytis melinus* + TX, *Aprostocetus hagenowii* + TX, *Atheta coriaria* (Staphyline®) + TX, *Bombus* spp. + TX, *Bombus terrestris* (Natupol Beehive®) + TX, *Bombus terrestris* (Beeline® + TX, Tripol®) + TX, *Cephalonomia stephanoderis* + TX, *Chilocorus nigritus* + TX, *Chrysoperla carnea* (Chrysoline®) + TX, *Chrysoperla carnea* (Chrysopa®) + TX, *Chrysoperla rufilabris* + TX, *Cirrospilus ingenuus* + TX, *Cirrospilus quadristriatus* + TX, *Citrostichus phyllocnistoides* + TX, *Closterocerus chamaeleon* + TX, *Closterocerus* spp. + TX, *Coccidoxenoides perminutus* (Planopar®) + TX, *Coccophagus cowperi* + TX, *Coccophagus lycimnia* + TX, *Cotesia flavipes* + TX, *Cotesia plutellae* + TX, *Cryptolaemus montrouzieri* (Cryptobug® + TX, Cryptoline®) + TX, *Cybocephalus nipponicus* + TX, *Dacnusa sibirica* + TX, *Dacnusa sibirica* (Minusa®) + TX, *Diglyphus isaea* (Diminex®) + TX, *Delphastus catalinae* (Delphastus®) + TX,
35 *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*

-79-

- spp. + TX, *Encarsia citrina* + TX, *Encarsia formosa* (Encarsia max® + TX, Encarline® + TX, En-Strip®) + TX, *Eretmoceris eremicus* (Enermix®) + TX, *Encarsia guadeloupae* + TX, *Encarsia haitiensis* + TX, *Episyrphus balteatus* (Syrphidend®) + TX, *Eretmoceris siphonini* + TX, *Eretmoceris californicus* + TX, *Eretmoceris eremicus* (Ercal® + TX, Eretline e®) + TX, *Eretmoceris eremicus* (Bemimix®) + TX, *Eretmoceris hayati* + TX, *Eretmoceris mundus* (Bemipar® + TX, Eretline m®) + TX, *Eretmoceris siphonini* + TX, *Exochomus quadripustulatus* + TX, *Feltiella acarisuga* (Spidend®) + TX, *Feltiella acarisuga* (Feltiline®) + TX, *Fopius arisanus* + TX, *Fopius ceratitivorus* + TX, Formononetin (Wirless Beehome®) + TX, *Franklinothrips vespiformis* (Vespop®) + TX, *Galendromus occidentalis* + TX, *Goniozus legneri* + TX, *Habrobracon hebetor* + TX, *Harmonia axyridis* (HarmoBeetle®) + TX, *Heterorhabditis* spp. (Lawn Patrol®) + TX, *Heterorhabditis bacteriophora* (NemaShield HB® + TX, Nemaseek® + TX, Terranem-Nam® + TX, Terranem® + TX, Larvanem® + TX, B-Green® + TX, NemAttack® + TX, Nematop®) + TX, *Heterorhabditis megidis* (Nemasys H® + TX, BioNem H® + TX, Exhibitline hm® + TX, Larvanem-M®) + TX, *Hippodamia convergens* + TX, *Hypoaspis aculeifer* (Aculeifer-System® + TX, Entomite-A®) + TX, *Hypoaspis miles* (Hypoline m® + TX, Entomite-M®) + TX, *Lbalia leucospoides* + TX, *Lecanoideus floccissimus* + TX, *Lemophagus errabundus* + TX, *Leptomastidea abnormis* + TX, *Leptomastix dactylopii* (Leptopar®) + TX, *Leptomastix epona* + TX, *Lindorus lophanthae* + TX, *Lipolexis oregmae* + TX, *Lucilia caesar* (NatuFly®) + TX, *Lysiphlebus testaceipes* + TX, *Macrolophus caliginosus* (Mirical-N® + TX, Macroline c® + TX, Mirical®) + TX, *Mesoseiulus longipes* + TX, *Metaphycus flavus* + TX, *Metaphycus lounsburyi* + TX, *Micromus angulatus* (Milacewing®) + TX, *Microterys flavus* + TX, *Muscidifurax raptorellus* and *Spalangia cameroni* (Biopar®) + TX, *Neodryinus typhlocybae* + TX, *Neoseiulus californicus* + TX, *Neoseiulus cucumeris* (THRYPEX®) + TX, *Neoseiulus fallacis* + TX, *Nesideocoris tenuis* (NesidioBug® + TX, Nesibug®) + TX, *Ophyra aenescens* (Biofly®) + TX, *Orius insidiosus* (Thripor-l® + TX, Oriline i®) + TX, *Orius laevigatus* (Thripor-L® + TX, Oriline l®) + TX, *Orius majusculus* (Oriline m®) + TX, *Orius strigicollis* (Thripor-S®) + TX, *Pauesia juniperorum* + TX, *Pediobius foveolatus* + TX, *Phasmarhabditis hermaphrodita* (Nemaslug®) + TX, *Phymastichus coffea* + TX, *Phytoseiulus macropilus* + TX, *Phytoseiulus persimilis* (Spidex® + TX, Phytoline p®) + TX, *Podisus maculiventris* (Podisus®) + TX, *Pseudacteon curvatus* + TX, *Pseudacteon obtusus* + TX, *Pseudacteon tricuspis* + TX, *Pseudaphycus maculipennis* + TX, *Pseudleptomastix mexicana* + TX, *Psyllaephagus pilosus* + TX, *Psytalia concolor* (complex) + TX, *Quadrastichus* spp. + TX, *Rhyzobius lophanthae* + TX, *Rodolia cardinalis* + TX, *Rumina decollate* + TX, *Semiellacher 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 radiata* + TX, *Tetrastichus setifer* + TX,

-80-

Thripobius semiluteus + TX, *Torymus sinensis* + TX, *Trichogramma brassicae* (Tricholine b®) + TX, *Trichogramma brassicae* (Tricho-Strip®) + TX, *Trichogramma evanescens* + TX, *Trichogramma minutum* + TX, *Trichogramma ostrinae* + TX, *Trichogramma platneri* + TX, *Trichogramma pretiosum* + TX, *Xanthopimpla stemmator*, and

- 5 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 (Takitrapiine y + b®) + TX.

The references in brackets behind the active ingredients, e.g. [3878-19-1] refer to the Chemical Abstracts Registry number. The above described mixing partners are known. Where the active ingredients are included in "The Pesticide Manual" [The Pesticide Manual - A World Compendium; Thirteenth Edition; Editor: C. D. S. Tomlin; The British Crop Protection Council], they are described therein under the entry number given in round brackets hereinabove for the particular compound; for example, the compound "abamectin" is described under entry number (1). Where "[CCN]" is added hereinabove to the particular compound, the compound in question is included in the "Compendium of Pesticide Common Names", which is accessible on the internet [A. Wood; Compendium of Pesticide Common Names, Copyright © 1995-2004]; for example, the compound "acetoprole" is described under the internet address <http://www.alanwood.net/pesticides/acetoprole.html>.

Most of the active ingredients described above are referred to hereinabove by a so-called "common name", the relevant "ISO common name" or another "common name" being used in individual cases. If the designation is not a "common name", the nature of the designation used instead is given in round brackets for the particular compound; in that case, the IUPAC name, the IUPAC/Chemical Abstracts name, a "chemical name", a "traditional name", a "compound name" or a "development code" is used. "CAS Reg. No" means the Chemical Abstracts Registry Number.

The active ingredient mixture of the compounds of formula I selected from Tables -1, A-2, A-3 and P1 with active ingredients described above comprises a compound selected from Tables -1, A-2, A-3 and P1 and an active ingredient as described above preferably in a mixing ratio of from 100:1 to 1:6000,

-81-

especially from 50:1 to 1:50, more especially in a ratio of from 20:1 to 1:20, even more especially from 10:1 to 1:10, very especially from 5:1 and 1:5, special preference being given to a ratio of from 2:1 to 1:2, and a ratio of from 4:1 to 2:1 being likewise preferred, above all in a ratio of 1:1, or 5:1, or 5:2, or 5:3, or 5:4, or 4:1, or 4:2, or 4:3, or 3:1, or 3:2, or 2:1, or 1:5, or 2:5, or 3:5, or 4:5, or 1:4, or 2:4, or 3:4, or 1:3, or 2:3, or 1:2, or 1:600, or 1:300, or 1:150, or 1:35, or 2:35, or 4:35, or 1:75, or 2:75, or 4:75, or 1:6000, or 1:3000, or 1:1500, or 1:350, or 2:350, or 4:350, or 1:750, or 2:750, or 4:750. Those mixing ratios are by weight.

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

The mixtures comprising a compound of formula I selected from Tables -1, A-2, A-3 and P1 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, A-2, A-3 and P1 and the active ingredients as described above is not essential for working the present invention.

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

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

The application methods for the compositions, that is the methods of controlling pests of the abovementioned type, such as spraying, atomizing, dusting, brushing on, dressing, scattering or pouring - which are to be selected to suit the intended aims of the prevailing circumstances - and the use of the compositions for controlling pests of the abovementioned type are other subjects of the

-82-

invention. Typical rates of concentration are between 0.1 and 1000 ppm, preferably between 0.1 and 500 ppm, of active ingredient. The rate of application per hectare is generally 1 to 2000 g of active ingredient per hectare, in particular 10 to 1000 g/ha, preferably 10 to 600 g/ha.

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

- The compounds of the invention and compositions thereof are also be suitable for the protection of plant propagation material, for example seeds, such as fruit, tubers or kernels, or nursery plants,
15 against pests of the abovementioned type. The propagation material can be treated with the compound prior to planting, for example seed can be treated prior to sowing. Alternatively, the compound can be applied to seed kernels (coating), either by soaking the kernels in a liquid composition or by applying a layer of a solid composition. It is also possible to apply the compositions when the propagation material is planted to the site of application, for example into the seed furrow
20 during drilling. These treatment methods for plant propagation material and the plant propagation material thus treated are further subjects of the invention. Typical treatment rates would depend on the plant and pest/fungi to be controlled and are generally between 1 to 200 grams per 100 kg of seeds, preferably between 5 to 150 grams per 100 kg of seeds, such as between 10 to 100 grams per
25 100 kg of seeds.

- The term seed embraces seeds and plant propagules of all kinds including but not limited to true seeds, seed pieces, suckers, corns, bulbs, fruit, tubers, grains, rhizomes, cuttings, cut shoots and the like and means in a preferred embodiment true seeds.
- 30 The present invention also comprises seeds coated or treated with or containing a compound of formula I. The term "coated or treated with and/or containing" generally signifies that the active ingredient is for the most part on the surface of the seed at the time of application, although a greater or lesser part of the ingredient may penetrate into the seed material, depending on the method of application. When the said seed product is (re)planted, it may absorb the active ingredient. In an
35 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).

-83-

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.

5

Biological Examples:Example B1: *Bemisia tabaci* (Cotton white fly)

Cotton leaf discs were placed on agar in 24-well microtiter plates and sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying the leaf discs were infested with adult white flies. The samples were checked for mortality 6 days after incubation. The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: P2, P4, and P7.

Example B2: *Diabrotica balteata* (Corn root worm)

Maize sprouts, placed on an agar layer in 24-well microtiter plates were treated with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions by spraying. After drying, the plates were infested with L2 larvae (6 to 10 per well). The samples were assessed for mortality and growth inhibition in comparison to untreated samples 4 days after infestation. The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: P1, P2, P3, P4, P6, P7, and P8.

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

Soybean leaves on agar in 24-well microtiter plates were sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying the 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. 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, P4, P6, P7 and P8.

Example B4: *Myzus persicae* (Green peach aphid)

Sunflower leaf discs were placed on agar in a 24-well microtiter plate and sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying, the leaf discs were infested with an aphid population of mixed ages. The samples were assessed for mortality 6 days after infestation. The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: P2, P4, P6, P7 and P8.

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

Roots of pea seedlings infested with an aphid population of mixed ages were placed directly in the aqueous test solutions prepared from 10'000 DMSO stock solutions. The samples were assessed for mortality 6 days after placing seedlings in test solutions. The following compounds resulted in at least 80% mortality at a test rate of 24 ppm: P4.

-84-

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

24-well microtiter plates with artificial diet were treated with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions by pipetting. After drying, the plates were infested with L2 larvae (10 to 15 per well). The samples were assessed for mortality and growth inhibition in comparison to untreated samples 5 days after infestation. The following compounds gave an effect of at least 80% in at least one of the two categories (mortality or growth inhibition) at an application rate of 200 ppm: P2, P3, P4, P6, P7 and P8.

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

Cotton leaf discs were placed on agar in 24-well microtiter plates and sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying the leaf discs were infested with five L1 larvae. The samples were assessed for mortality, anti-feedant effect, and growth inhibition in comparison to untreated samples 3 days after infestation. Control of *Spodoptera littoralis* by a test sample is when at least one of mortality, anti-feedant effect, and growth inhibition is higher than the untreated sample. The following compounds resulted in at least 80% control at an application rate of 200 ppm: P1, P2, P4, P6, P7 and P8.

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

Test compounds were applied by pipette from 10'000 ppm DMSO stock solutions into 24-well plates and mixed with agar. Lettuce seeds were placed on the agar and the multi well plate was closed by another plate which contains also agar. After 7 days the compound was absorbed by the roots and the lettuce grew into the lid plate. The lettuce leaves were now cut off into the lid plate. *Spodoptera* eggs were pipetted through a plastic stencil on a humid gel blotting paper and the plate closed with it. The samples were assessed for mortality, anti-feedant effect and growth inhibition in comparison to untreated samples 6 days after infestation. The following compounds gave an effect of at least 80% in at least one of the three categories (mortality, anti-feeding, or growth inhibition) at a test rate of 12.5 ppm: P2, P4, P6 and P8.

Example B9: *Frankliniella occidentalis* (Western flower thrips)

Sunflower leaf discs were placed on agar in 24-well microtiter plates and sprayed with aqueous test solutions prepared from 10'000 DMSO stock solutions. After drying the leaf discs were infested with a *Frankliniella* population of mixed ages. The samples were assessed for mortality 7 days after infestation. The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: P6 and P7.

Example B10: 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 knockdown was made one hour after introduction, and mortality was assessed at 24 and 48 hours

-85-

after introduction. The following compounds gave at least 80% control of *Aedes aegypti* after 48h: P1, P2, P3, P5, P6, P7 and P8002E

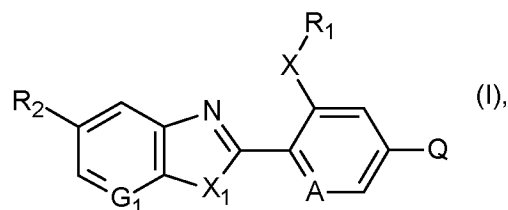
Example B11: Activity against *Anopheles stephensi* (Indian malaria mosquito)

5 Test solutions, at an application rate of 200 ppm 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. The following compounds gave at least 80% control of *Anopheles stephensi* after 48h and/or 24h: P2, P6, P7, and P8.

-86-

Claims:

1. A compound of formula I,



5 wherein

A represents CH or N;

Q is phenyl which is mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkylsulfanyl, C₁-C₄alkylsulfinyl, C₁-C₄alkylsulfonyl, C₁-C₄haloalkoxy, C₁-C₄alkoxy and C₁-C₄haloalkylsulfanyl; or

10 Q is pyrimidyl which is mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkoxy and C₁-C₄haloalkylsulfanyl; or

Q is pyrazolyl which is linked via a nitrogen atom to the ring which contains the substituent A, said pyrazolyl can be substituted by halogen, cyano or C₁-C₄haloalkyl; or

15 Q is triazolyl which is linked via a nitrogen atom to the ring which contains the substituent A, said triazolyl can be substituted by halogen, cyano or C₁-C₄haloalkyl;

X is S, SO or SO₂;

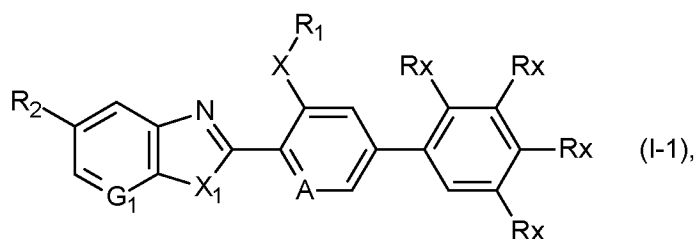
R₁ is C₁-C₄alkyl, C₁-C₄haloalkyl, C₂-C₆alkenyl, C₂-C₆haloalkenyl, C₂-C₆alkynyl or C₃-C₆cycloalkyl-C₁-C₄alkyl;

20 R₂ is halogen, C₁-C₆haloalkyl, C₁-C₄haloalkylsulfanyl, C₁-C₄haloalkylsulfinyl, C₁-C₄haloalkylsulfonyl or C₁-C₆haloalkoxy;

X₁ is O, S or NR₃, wherein R₃ is hydrogen, C₁-C₄alkyl, C₂-C₆alkenyl, C₂-C₆alkynyl, C₁-C₄alkoxy-C₁-C₄alkyl or C₃-C₆cycloalkyl; and

25 G₁ is N or CH; and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of the compounds of formula I.

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



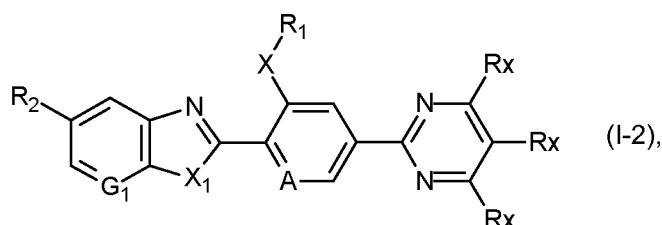
-87-

wherein G_1 , R_1 , R_2 , A and X_1 are as defined under formula I in claim 1;

X is S, SO or SO_2 ; and

R_x is independently selected from the group consisting of hydrogen, 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 alkylsulfanyl, C_1 - C_4 alkylsulfinyl, C_1 - C_4 alkylsulfonyl, and C_1 - C_4 haloalkylsulfanyl with the proviso that at least one R_x is different from hydrogen.

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

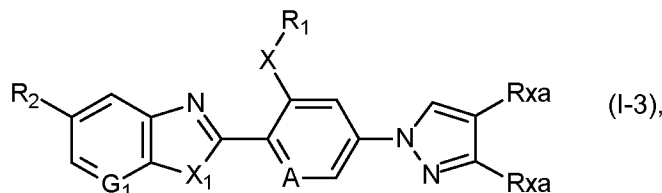


wherein G_1 , R_1 , R_2 , A and X_1 are as defined under formula I in claim 1;

X is S, SO or SO_2 ; and

R_x is independently selected from the group consisting of hydrogen, halogen, cyano, C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_1 - C_4 haloalkoxy, C_1 - C_4 alkoxy and C_1 - C_4 haloalkylsulfanyl; with the proviso that at least one R_x is different from hydrogen.

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

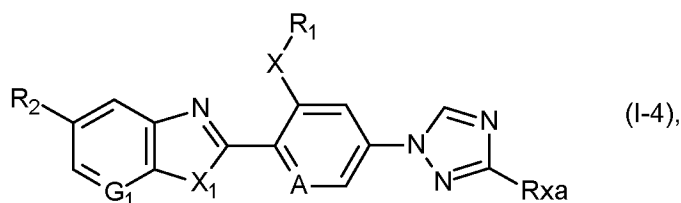


wherein G_1 , R_1 , R_2 , A and X_1 are as defined under formula I in claim 1;

X is S, SO or SO_2 ; and

R_x is independently selected from the group consisting of hydrogen, halogen, cyano or C_1 - C_4 haloalkyl.

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



wherein G_1 , R_1 , R_2 , A and X_1 are as defined under formula I in claim 1;

-88-

X is S, SO or SO₂; and

R_x is hydrogen, halogen, cyano or C₁-C₄haloalkyl.

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

5 R₁ is C₁-C₄alkyl;

R₂ is C₁-C₄haloalkyl;

G₁ is N;

X is S or SO₂;

X₁ is N(CH₃);

10 A is N; and

Q is phenyl, which is mono- or disubstituted by substituents selected from the group consisting of halogen and C₁-C₄haloalkyl;

or Q is pyrazolyl, mono-substituted by C₁-C₄haloalkyl;

or Q is triazolyl, which is unsubstituted.

15

7. 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.

20

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

25

9. 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 7.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/078988

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

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

B. FIELDS SEARCHED

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

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, BIOSIS, 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.
X	WO 2016/002594 A1 (SUMITOMO CHEMICAL CO [JP]) 7 January 2016 (2016-01-07)	1-3,6-9
Y	Entries 250, 333, 431, 559-562, 791 and 934 given in the tables of pages 21-49.; paragraph [0086]; claims	4,5
X	EP 2 739 624 A1 (SUMITOMO CHEMICAL CO [JP]) 11 June 2014 (2014-06-11)	1-3,6-9
Y	cited in the application paragraphs [0541] - [0543], [0563] - [0565], [0585] - [587etc.and752], [0766]; claims 1-20; tables 40, 49, 55; compounds 111-114, 343, 486	4,5
Y	WO 2016/030229 A1 (SYNGENTA PARTICIPATIONS AG [CH]) 3 March 2016 (2016-03-03) claims; compounds P2, P9-11, P14, P16, P17, P22, P61, P74, P84, etc.	1,3-9
	-/--	



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

6 March 2018

Date of mailing of the international search report

20/03/2018

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

Stroeter, Thomas

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/078988

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2016/046071 A1 (SYNGENTA PARTICIPATIONS AG [CH]) 31 March 2016 (2016-03-31) claims; table 1; compounds 1.009-1.028 -----	1,3-9
Y	WO 2016/059145 A1 (SYNGENTA PARTICIPATIONS AG [CH]) 21 April 2016 (2016-04-21) claims; examples P2, P10 -----	1,4-9
Y	WO 2015/133603 A1 (SUMITOMO CHEMICAL CO [JP]) 11 September 2015 (2015-09-11) cited in the application claims; examples -----	1,4-9
Y	WO 2015/198859 A1 (SUMITOMO CHEMICAL CO [JP]) 30 December 2015 (2015-12-30) cited in the application claims; examples -----	1,4-9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2017/078988

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 2(completely); 1, 6-9(partially)

Compounds of formula (I) wherein Q = phenyl (substituted) and subject-matter directed to the agrochemical use of such compounds

2. claims: 3(completely); 1, 7-9(partially)

Compounds of formula (I) wherein Q = pyrimidinyl (substituted) and subject-matter directed to the agrochemical use of such compounds

3. claims: 4, 5(completely); 1, 6-9(partially)

Compounds of formula (I) wherein Q = pyrazolyl or triazolyl (N-linked) and subject-matter directed to the agrochemical use of such compounds

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/078988

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2016002594 A1	07-01-2016	JP 2014208695 A WO 2016002594 A1	06-11-2014 07-01-2016
EP 2739624 A1	11-06-2014	AR 087467 A1 AU 2012290923 A1 BR 112014001175 A2 CA 2844241 A1 CN 103717598 A EP 2739624 A1 ES 2571488 T3 HU E028396 T2 IL 229835 A IL 243374 A JP 5990057 B2 JP 2014005263 A KR 20140068920 A RU 2014108038 A TW 201321363 A TW 201630897 A US 2014194290 A1 US 2015197532 A1 US 2016009715 A1 US 2016159743 A1 WO 2013018928 A1 ZA 201309160 B	26-03-2014 09-01-2014 10-01-2017 07-02-2013 09-04-2014 11-06-2014 25-05-2016 28-12-2016 31-08-2016 31-08-2016 07-09-2016 16-01-2014 09-06-2014 10-09-2015 01-06-2013 01-09-2016 10-07-2014 16-07-2015 14-01-2016 09-06-2016 07-02-2013 24-06-2015
WO 2016030229 A1	03-03-2016	CN 106604922 A EP 3186249 A1 JP 2017526678 A US 2017267672 A1 WO 2016030229 A1	26-04-2017 05-07-2017 14-09-2017 21-09-2017 03-03-2016
WO 2016046071 A1	31-03-2016	NONE	
WO 2016059145 A1	21-04-2016	CN 106795167 A EP 3207044 A1 JP 2017537882 A US 2017240554 A1 WO 2016059145 A1	31-05-2017 23-08-2017 21-12-2017 24-08-2017 21-04-2016
WO 2015133603 A1	11-09-2015	AR 099677 A1 AU 2015224876 A1 CA 2941452 A1 CN 106103433 A EP 3115363 A1 JP WO2015133603 A1 KR 20160120748 A TW 201623299 A US 2017135348 A1 WO 2015133603 A1	10-08-2016 18-08-2016 11-09-2015 09-11-2016 11-01-2017 06-04-2017 18-10-2016 01-07-2016 18-05-2017 11-09-2015
WO 2015198859 A1	30-12-2015	NONE	