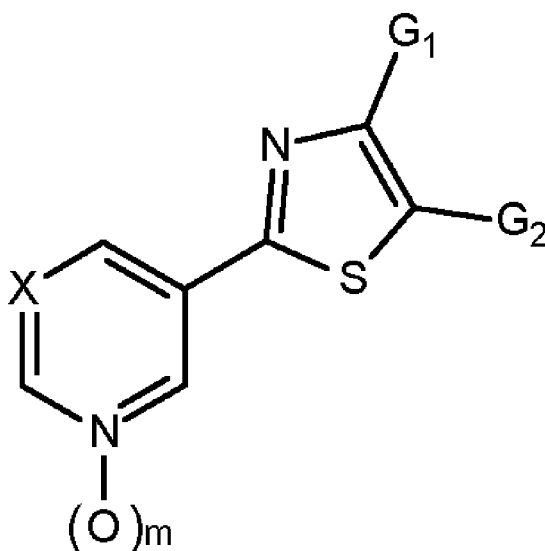




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[Continued on next page]

(54) **Title:** INSECTICIDALLY ACTIVE THIAZOLE DERIVATIVES

(I),

(57) **Abstract:** Compounds of formula (I), wherein the substituents are as defined in claim 1, and the agrochemically acceptable salts and all stereoisomers and tautomeric forms of the compounds of formula (I) can be used as agrochemical active ingredients and can be prepared in a manner known per se.



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

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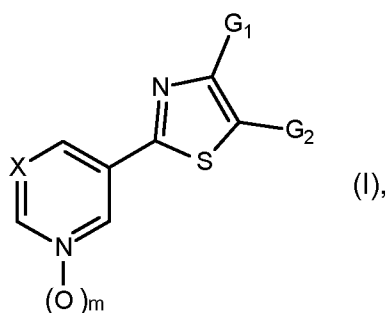
Insecticidally Active Thiazole Derivatives

The present invention relates to insecticidally active 2-(3-pyridyl)-thiazole derivatives, to processes for their preparation, to compositions comprising those compounds, and to their use for controlling insects or representatives of the order Acarina.

5

2-(3-Pyridyl)-thiazole derivatives with insecticidal action are known and described, for example, in US-4,080,457, US 4,260,765, WO 2009/149858, WO 2010/129497, WO 2010/006713, WO 2011/138285, WO 2012/000896 and WO2013/010946.

- 10 There have now been found novel 2-(3-pyridyl)-thiazole derivatives with pesticidal properties. The present invention accordingly relates to compounds of formula I



wherein

X is nitrogen or CR₇;

- 15 m is 0 or 1;

G₁ is a three- to four- membered ring which can be partially saturated or fully saturated and can contain one heteroatom selected from the group consisting of nitrogen, oxygen and sulphur; said three- to four- membered ring system can be mono- to polysubstituted by substituents independently selected from the group consisting of halogen, C₁-C₆alkyl, C₁-

- 20 C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆alkylthio, C₁-C₆alkylamino and C₁-C₆di-alkylamino; or

G₁ is C₂-C₆alkenyl which can be mono- to polysubstituted by substituents independently selected from the group consisting of halogen, C₁-C₆alkyl and C₁-C₆haloalkyl; with the proviso that if the double bond is not directly connected to the ring then the substituents on the carbon between the thiazole and the unsaturation are different from halogen; or

- 25 G₁ is C₂-C₆alkynyl which can be substituted by substituents independently selected from the group consisting of halogen, C₁-C₆alkyl and C₁-C₆haloalkyl; with the proviso that if the triple

-2-

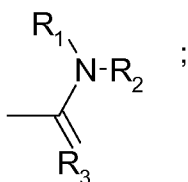
bond is not directly connected to the ring then the substituents on the carbon between the thiazole and the unsaturation are different from halogen;

G₂ is a five- to ten-membered monocyclic or fused bicyclic ring system which can be

aromatic, partially saturated or fully saturated and can contain 1 to 4 hetero atoms selected

- 5 from the group consisting of nitrogen, oxygen and sulfur, it not being possible for each ring system to contain more than 2 oxygen atoms and more than 2 sulfur atoms, said five- to ten-membered ring system can be mono- to polysubstituted by substituents independently selected from the group consisting of halogen, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆alkylthio, C₁-C₆alkoxycarbonyl, C₁-C₆alkylamino, C₁-C₆di-alkylamino, C₁-C₆alkoxycarbonylamino, pyrimidinyl, thiazolyl, pyridinyl, pyrazinyl, pyridazinyl, pyrazinyloxy, imidazolyl, dihydro-oxazolyl, oxazolyl, dioxolanyl, 1,3-dioxanyl and 5,6-dihydro-[1,4,2]dioxazinyl; wherein said pyrimidinyl, thiazolyl, pyridinyl, pyrazinyl, pyridazinyl, pyrazinyloxy, imidazolyl, dihydro-oxazolyl, oxazolyl, dioxolanyl, 1,3-dioxanyl and 5,6-dihydro-[1,4,2]dioxazinyl can be mono- to polysubstituted by substituents independently selected from the group consisting of halogen, C₁-C₆alkyl, di-C₁-C₄alkyl-phosphinoylmethyl-aminocarbonyl, C₁-C₆alkoxycarbonylamino, C₁-C₆alkoxy, C₁-C₆alkylthio, C₁-C₆alkylamino, C₁-C₆di-alkylamino, pyridinyl, pyrimidinyl, pyrazinyloxy and oxazolyl, wherein said pyridinyl, pyrimidinyl, pyrazinyloxy and oxazolyl can be substituted by substituents independently selected from the group consisting of halogen, C₁-C₆alkyl and C₁-C₆alkoxy; or

- 20 G₂ is



wherein

R₁ is hydrogen, C₁-C₆alkyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₃-C₆cycloalkyl, C₁-C₆alkylthio, C₁-C₆haloalkyl, C₁-

- 25 C₆alkylsulfinyl, C₁-C₆alkylsulfonyl, halogen, cyano, hydroxy, C₁-C₆alkoxy, C₂-C₆alkenyl, C₂-C₆alkynyl, C₁-C₆alkoxy-C₃-C₆alkynyl, oxolanyl, dioxolanyl, thienyl, thietanyl, thiethanyloxy, thiethanyldioxide, di-C₁-C₄alkyl-phosphinoylmethyl, 1-H-benzoimidazol-2-yl, benzo[1,3]dioxolyl, morpholinyl, piperidinyl, pyrimidinyl, pyrrolidinyl, benzylthio, 2,3-dihydro-benzo[1,4]dioxinyl, 1H-indolyl, furyl, -C=N-O-C₁-C₆alkyl, C₁-C₆alkylcarbonylamino, phenoxy and phenyl, said phenyl can be mono- to polysubstituted by substituents selected from the
- 30

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group consisting of hydroxy, halogen, C₁-C₆alkoxy, C₁-C₆haloalkoxy, pyrazolyl, piperidinyl, phenoxy and C₁-C₄alkylsulfonyl;

or R₁ is C₁-C₆alkyl, which is substituted by pyridyl, wherein said pyridyl can be mono- to polysubstituted by substituents selected from the group consisting of halogen and C₁-

5 C₄haloalkyl;

or R₁ is C₁-C₆alkyl, which is substituted by phenoxy, wherein said phenoxy can be mono- to polysubstituted by substituents selected from the group consisting of halogen and C₁-C₄alkyl;

or R₁ is C₁-C₆alkyl, which is substituted by phenylcarbonyl, wherein said phenylcarbonyl can be mono- to polysubstituted by substituents selected from the group consisting of halogen

10 and C₁-C₄haloalkoxy;

or R₁ is C₁-C₆alkyl, which is substituted by imidazolynyl, wherein said imidazolynyl can be mono- to polysubstituted by C₁-C₄alkyl;

or R₁ is C₁-C₆alkyl, which is substituted by isoxazolyl, wherein said isoxazolyl can be mono- to polysubstituted by halo-substituted phenyl;

15 or R₁ is pyridyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₄alkyl, C₁-C₄alkoxycarbonyl, phenyl and phenoxy;

or R₁ is pyrimidinyl, which can be mono- to polysubstituted by substituents selected from the group consisting of hydroxy, C₁-C₄alkoxy and C₁-C₄alkyl;

or R₁ is piperazinyl, which can be monosubstituted by benzyl;

20 or R₁ is piperidinyl, which can be mono- to polysubstituted by C₁-C₄alkyl;

or R₁ is pyrazolyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₄alkyl, cyano and phenyl;

or R₁ is thiethanyl, which can be substituted by C₁-C₄alkyl;

or R₁ is dihydro-thiophene-2-one-3-yl;

25 or R₁ is C₃-C₆cycloalkyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₃-C₆cycloalkyl, C₂-C₆alkynyl and =N-O-C₁-C₄haloalkyl;

or R₁ is azetidynyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₄haloalkyl and benzyl;

or R₁ is pyrrolidinyl which can be substituted by benzyl;

30 or R₁ is C₁-C₆alkoxycarbonylamino;

or R₁ is C₃-C₆cycloalkenyl which can be mono- to polysubstituted by C₁-C₆alkoxycarbonyl;

or R₁ is phenyl, which can be mono- to polysubstituted by substituents selected from the group consisting of halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkylthio, di(C₁-

C₄alkyl)aminosulfonyl, C₁-C₄alkoxy, phenyl, piperidyl, pyrrolyl, morpholynyl, indolyl,

35 phenylcarbonyl and C₁-C₄alkoxycarbonyl;

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or R₁ is quinolinyl, benzothiazolyl, oxolanyl or indazolyl;

or R₁ is benzothiophenyl, which can be monosubstituted by C₁-C₆alkoxycarbonyl;

or R₁ is thiazolyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₄alkyl, pyridyl, phenyl, pyrimidinyl and C₁-C₄alkylcarbonyl; wherein
 5 said phenyl can be mono- to polysubstituted by C₁-C₄alkyl and wherein said pyrimidinyl can be mono- to polysubstituted by C₁-C₄alkoxy;

or R₁ is benzothiazolyl which can be mono- to polysubstituted by C₁-C₄alkyl;

or R₁ is chromen-2-one which can be mono- to polysubstituted by C₁-C₄alkyl;

or R₁ is isoxazolyl, which can be mono- to polysubstituted by substituents selected from the
 10 group consisting of C₁-C₄alkyl and phenyl;

or R₁ is thiadiazolyl, which can be monosubstituted by substituents selected from the group consisting of C₁-C₄alkyl and halo-substituted phenyl;

or R₁ is furyl which can be mono- to polysubstituted by substituents selected from the group consisting of cyano and phenyl;

15 or R₁ is pyrazolopyridinyl which can be mono- to polysubstituted by C₁-C₄alkyl; or R₁ is thienyl which can be mono- to polysubstituted by C₁-C₄alkoxycarbonyl; or R₁ is thietanyloxide, thiethanyldioxide, bicyclo[2.2.1]heptyl or tetrahydrothienyl;

or R₁ is isoxazolidin-3-one, which can be monosubstituted by substituents selected from C₁-C₄alkyl and C₁-C₄haloalkyl;

20 or R₁ and R₂ form together with the nitrogen atom to which they are bonded a 3- to 6-membered saturated ring which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₄alkyl, C₁-C₄alkoxy and halogen; and further mono- to polysubstituted by substituents selected from the group consisting of phenylcarbonyl, phenoxy-C₁-C₄alkyl and phenoxy, wherein said phenylcarbonyl, phenoxy-C₁-
 25 C₄alkyl and phenoxy can be mono- to polysubstituted by halogen; and said saturated ring can be additionally substituted by an ethylene chain;

R₂ is hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl or C₃-C₆cycloalkyl;

R₃ is oxygen, sulfur, NR₈ or NOR₈;

R₈ is hydrogen, cyano, C₁-C₆alkyl, C₂-C₆alkenyl, C₃-C₁₀cycloalkyl, C₃-C₁₀cycloalkenyl, a
 30 three- to ten-membered, monocyclic or fused bicyclic ring system which may be aromatic, partially saturated or fully saturated, S(O)_nC₁-C₆alkyl or N(C₁-C₆alkyl)₂; or

R₈ is C₁-C₆alkyl, C₂-C₆alkenyl, C₃-C₁₀cycloalkyl, C₃-C₁₀cycloalkenyl or a three- to ten-membered, monocyclic or fused bicyclic ring system which can be aromatic, partially saturated or fully saturated; each mono- to polysubstituted by substituents independently
 35 selected from the group consisting of fluoro, chloro, bromo, iodo, cyano, nitro, C₁-C₆alkyl, C₂-

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C₆alkenyl, C₁-C₆haloalkyl, C₂-C₆haloalkenyl, C₁-C₆haloalkoxy, C₂-C₆haloalkenyloxy, C₃-C₁₀cycloalkyl, C₃-C₁₀cycloalkenyl, C₃-C₁₀halocycloalkyl, C₃-C₁₀halocycloalkenyl, OC₁-C₆alkyl, OC₁-C₆haloalkyl, S(O)_nC₁-C₆alkyl, S(O)_nOC₁-C₆alkyl and by a three- to ten-membered, monocyclic or fused bicyclic ring system which may be aromatic, partially saturated or fully saturated; and
n is 0, 1 or 2; and agrochemically acceptable salts, enantiomers, tautomers and N-oxides of those compounds.

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, sulphuric acid, nitric acid, nitroic 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, nonyl, decyl and their branched isomers. Alkoxy, alkenyl and alkynyl radicals are derived from the alkyl radicals mentioned. The alkenyl and alkynyl groups can be mono- or polyunsaturated.

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

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

Alkoxy groups preferably have a preferred chain length of from 1 to 6 carbon atoms. Alkoxy is, for example, methoxy, ethoxy, propoxy, i-propoxy, n-butoxy, isobutoxy, sec-butoxy and tert-butoxy and also the isomeric pentyloxy and hexyloxy radicals; preferably methoxy and
10 ethoxy.

Alkoxycarbonyl is, for example, methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, isopropoxycarbonyl, n-butoxycarbonyl, isobutoxycarbonyl, sec-butoxycarbonyl or tert-butoxycarbonyl; preferably methoxycarbonyl or ethoxycarbonyl. Haloalkoxy groups preferably have a chain length of from 1 to 6 carbon atoms. Haloalkoxy is, for example,
15 fluoromethoxy, difluoromethoxy, trifluoromethoxy, 2,2,2-trifluoroethoxy, 1,1,2,2-tetrafluoroethoxy, 2-fluoroethoxy, 2-chloroethoxy, 2,2-difluoroethoxy and 2,2,2-trichloroethoxy; preferably difluoromethoxy, 2-chloroethoxy and trifluoromethoxy.

Alkylthio groups preferably have a chain length of from 1 to 6 carbon atoms. Alkylthio is, for example, methylthio, ethylthio, propylthio, isopropylthio, n-butylthio, isobutylthio, sec-butylthio or tert-butylthio, preferably methylthio and ethylthio. Alkylsulphinyl is, for example, methylsulphinyl, ethylsulphinyl, propylsulphinyl, isopropylsulphinyl, n-butylsulphinyl, isobutylsulphinyl, sec-butylsulphinyl, tert-butylsulphinyl; preferably methylsulphinyl and ethylsulphinyl.
25

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

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

35 Alkoxyalkyl groups preferably have a chain length of 1 to 6 carbon atoms.

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Alkoxyalkyl is, for example, methoxymethyl, methoxyethyl, ethoxymethyl, ethoxyethyl, n-propoxymethyl, n-propoxyethyl, isopropoxymethyl or isopropoxyethyl.

The cycloalkyl groups preferably have from 3 to 6 ring carbon atoms, for example

5 cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl. Phenyl, also as part of a substituent such as phenoxy, benzyl, benzyloxy, benzoyl, phenylthio, phenylalkyl, phenoxyalkyl, may be substituted. In this case, the substituents can be in ortho, meta and/or para position. The preferred substituent positions are the ortho and para positions to the ring attachment point.

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

15 In the context of the present invention "halo-substituted phenyl" in the definition of the substituents, means for example a phenyl group which is mono- to polysubstituted by substituents selected from the group consisting of fluoro, chloro, bromo and iodo. Preferably "halo-substituted phenyl" is phenyl which is mono- di or tri-substituted by chloro, in particular mono-substituted by chloro.

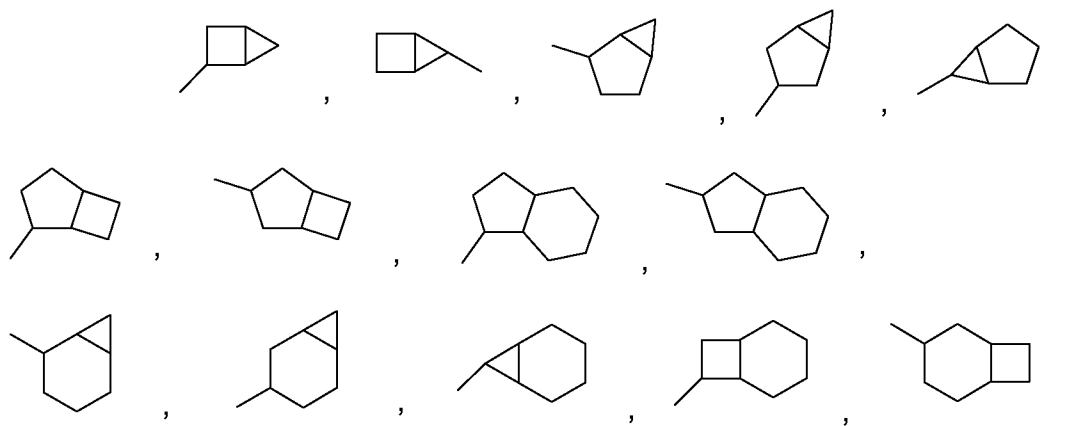
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In substituent definitions as for example $R_8C(=X_1)OR_9$, the free valence is located at the left side of the group, such as $-R_8C(=X_1)OR_9$.

According to the present invention, five- to ten-membered monocyclic or fused bicyclic ring

25 system which can be aromatic, partially saturated or fully saturated and can contain 1 to 4 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, it not being possible for each ring system to contain more than 2 oxygen atoms and more than 2 sulfur atoms or a three- to ten-membered, monocyclic or fused bicyclic ring system which may be aromatic, partially saturated or fully saturated; is, depending of the number of ring members,
30 for example, selected from the group consisting of cyclopropyl, cyclobutyl, oxetanyl, thietanyl,

-8-



cyclopentyl, cyclohexyl, where said cycloalkylgroups for their part may be preferably

unsubstituted or substituted by C₁-C₆alkyl or halogen, or is phenyl, benzyl, naphthyl or the

following heterocyclic groups: pyrrolyl; pyridyl; pyrazolyl; pyrimidyl; pyrazinyl; imidazolyl;

thiadiazolyl; quinazolinyl; furyl; oxadiazolyl; indolizinyl; pyranyl; isobenzofuranyl; thienyl;

naphthyridinyl; (1-methyl-1H-pyrazol-3-yl)-; (1-ethyl-1H-pyrazol-3-yl)-; (1-propyl-1H-pyrazol-3-

yl)-; (1H-pyrazol-3-yl)-; (1,5-dimethyl-1H-pyrazol-3-yl)-; (4-chloro-1-methyl-1H-pyrazol-3-yl)-;

(1H-pyrazol-1-yl)-; (3-methyl-1H-pyrazol-1-yl)-; (3,5-dimethyl-1H-pyrazol-1-yl)-; (3-isoxazolyl)-

; (5-methyl-3-isoxazolyl)-; (3-methyl-5-isoxazolyl)-; (5-isoxazolyl)-; (1H-pyrrol-2-yl)-; (1-

methyl-1H-pyrrol-2-yl)-; (1H-pyrrol-1-yl)-; (1-methyl-1H-pyrrol-3-yl)-; (2-furanyl)-; (5-methyl-2-

furanyl)-; (3-furanyl)-; (5-methyl-2-thienyl)-; (2-thienyl)-; (3-thienyl)-; (1-methyl-1H-imidazol-2-

yl)-; (1H-imidazol-2-yl)-; (1-methyl-1H-imidazol-4-yl)-; (1-methyl-1H-imidazol-5-yl)-; (4-

methyl-2-oxazolyl)-; (5-methyl-2-oxazolyl)-; (2-oxazolyl)-; (2-methyl-5-oxazolyl)-; (2-methyl-4-

oxazolyl)-; (4-methyl-2-thiazolyl)-; (5-methyl-2-thiazolyl)-; (2-thiazolyl)-; (2-methyl-5-

thiazolyl)-; (2-methyl-4-thiazolyl)-; (3-methyl-4-isothiazolyl)-; (3-methyl-5-isothiazolyl)-; (5-

methyl-3-isothiazolyl)-; (1-methyl-1H-1,2,3-triazol-4-yl)-; (2-methyl-2H-1,2,3-triazol-4-yl)-; (4-

methyl-2H-1,2,3-triazol-2-yl)-; (1-methyl-1H-1,2,4-triazol-3-yl)-; (1,5-dimethyl-1H-1,2,4-triazol-

3-yl)-; (3-methyl-1H-1,2,4-triazol-1-yl)-; (5-methyl-1H-1,2,4-triazol-1-yl)-; (4,5-dimethyl-4H-

1,2,4-triazol-3-yl)-; (4-methyl-4H-1,2,4-triazol-3-yl)-; (4H-1,2,4-triazol-4-yl)-; (5-methyl-1,2,3-

oxadiazol-4-yl)-; (1,2,3-oxadiazol-4-yl)-; (3-methyl-1,2,4-oxadiazol-5-yl)-; (5-methyl-1,2,4-

oxadiazol-3-yl)-; (4-methyl-3-furazanyl)-; (3-furazanyl)-; (5-methyl-1,2,4-oxadiazol-2-yl)-; (5-

methyl-1,2,3-thiadiazol-4-yl)-: (1,2,3-thiadiazol-4-yl)-: (3-methyl-1,2,4-thiadiazol-5-yl)-: (5-

methyl-1,2,4-thiadiazol-3-yl)-; (4-methyl-1,2,5-thiadiazol-3-yl)-; (5-methyl-1,3,4-thiadiazol-2-

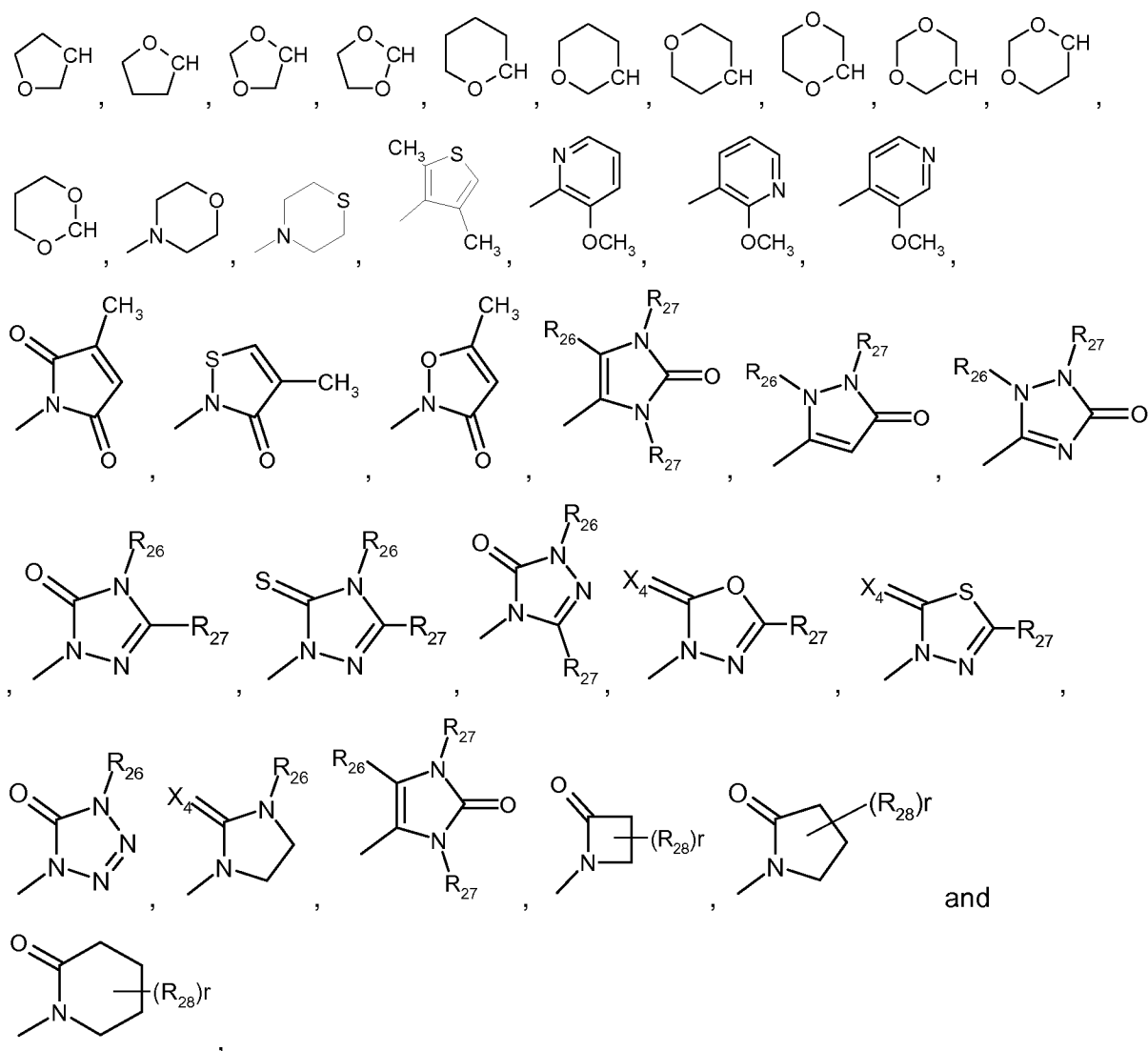
-yl); (1-methyl-1H-tetrazol-5-yl)-; (1H-tetrazol-5-yl); (5-methyl-1H-tetrazol-1-yl); (2-methyl-

2H-tetrazol-5-yl); (2-ethyl-2H-tetrazol-5-yl); (5-methyl-2H-tetrazol-2-yl); (2H-tetrazol-2-yl);

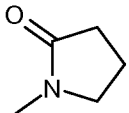
(2-pyridyl)-; (6-methyl-2-pyridyl)-; (4-pyridyl)-; (3-pyridyl)-; (6-methyl-3-pyridazinyl)-; (5-

-9-

methyl-3-pyridazinyl)-; (3-pyridazinyl)-; (4,6-dimethyl-2-pyrimidinyl)-; (4-methyl-2-pyrimidinyl)-; (2-pyrimidinyl)-; (2-methyl-4-pyrimidinyl)-; (2-chloro-4-pyrimidinyl)-; (2,6-dimethyl-4-pyrimidinyl)-; (4-pyrimidinyl)-; (2-methyl-5-pyrimidinyl)-; (6-methyl-2-pyrazinyl)-; (2-pyrazinyl)-; (4,6-dimethyl-1,3,5-triazin-2-yl)-; (4,6-dichloro-1,3,5-triazin-2-yl)-; (1,3,5-triazin-2-yl)-; (4-methyl-1,3,5-triazin-2-yl)-; (3-methyl-1,2,4-triazin-5-yl)-; (3-methyl-1,2,4-triazin-6-yl)-;



-10-

Where no free valency is indicated in those definitions, for example as in , the linkage site is located at the carbon atom labelled "CH" or in a case such as, for example, , at the bonding site indicated at the bottom left.

- 5 In preferred compounds of formula I,
 G_1 is a three- to four- membered ring which can be partially saturated or fully saturated and can contain one heteroatom selected from the group consisting of nitrogen, oxygen and sulphur; said three- to four- membered ring system can be mono- to polysubstituted by substituents independently selected from the group consisting of halogen, methyl and trifluoromethyl; or
- 10 G_1 is C_2 - C_6 alkenyl which can be mono- to polysubstituted by substituents independently selected from the group consisting of halogen, methyl and trifluoromethyl; or
 G_1 is C_2 - C_6 alkynyl which can be substituted by substituents selected from the group consisting of halogen, methyl and trifluoromethyl;
- 15 G_2 is selected from the group consisting of J-1 to J-24

-11-



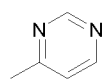
J-1



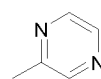
J-2



J-3



J-4



J-5



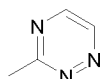
J-6



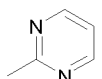
J-7



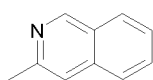
J-8



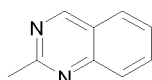
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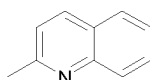
J-10



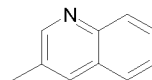
J-11



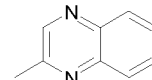
J-12



J-13



J-14



J-15



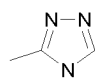
J-16



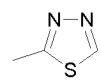
J-17



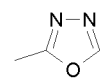
J-18



J-19



J-20



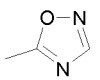
J-21



J-22



J-23



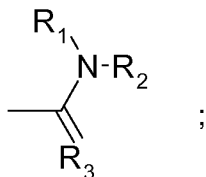
J-24

wherein each group J-1 to J-24 is mono- di- or trisubstituted with Rx, wherein

Rx is halogen, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆alkylthio, C₁-C₆alkoxycarbonyl, C₁-C₆alkylamino, C₁-C₆di-alkylamino, C₁-C₆alkoxycarbonylamino, pyrimidinyl, thiazolyl, pyridinyl, pyrazinyl, pyridazinyl, pyrazinyloxy, imidazolyl, dihydro-oxazolyl, oxazolyl, dioxolanyl, 1,3-dioxanyl and 5,6-dihydro-[1,4,2]dioxazinyl, wherein said pyrimidinyl, thiazolyl, pyridinyl, pyrazinyl, pyridazinyl, pyrazinyloxy, imidazolyl, dihydro-oxazolyl, oxazolyl, dioxolanyl, 1,3-dioxanyl and 5,6-dihydro-[1,4,2]dioxazinyl can be mono- to polysubstituted by substituents independently selected from the group consisting of halogen, C₁-C₆alkyl, di-C₁-C₄alkyl-phosphinoylmethyl-aminocarbonyl, C₁-C₆alkoxycarbonylamino, C₁-C₆alkoxy, C₁-C₆alkylthio, C₁-C₆alkylamino, C₁-C₆di-alkylamino, pyridinyl, pyrimidinyl, pyrazinyloxy and oxazolyl, wherein said pyridinyl, pyrimidinyl, pyrazinyloxy and oxazolyl can be mono- to polysubstituted by substituents independently selected from the group consisting of halogen, C₁-C₆alkyl and C₁-C₆alkoxy; or

G₂ is

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wherein

- R₁ is hydrogen, C₁-C₆alkyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₃-C₆cycloalkyl, C₁-C₆alkylthio, C₁-C₆haloalkyl, C₁-C₆alkylsulfinyl, C₁-C₆alkylsulfonyl, halogen, cyano, hydroxy, C₁-C₆alkoxy, C₂-C₆alkenyl, C₂-C₆alkynyl, C₁-C₆alkoxy-C₃-C₆alkynyl, oxolanyl, dioxolanyl, thienyl, thietanyl, thiethanyldioxide, 1-H-benzimidazol-2-yl, benzo[1,3]dioxolyl, morpholinyl, piperidinyl, pyrimidinyl, pyrrolidinyl, benzylthio, 2,3-dihydro-benzo[1,4]dioxinyl, 1H-indolyl, furyl, -C=N-O-C₁-C₆alkyl, C₁-C₆alkylcarbonylamino, phenoxy and phenyl, said phenyl can be mono- to polysubstituted by substituents selected from the group consisting of hydroxy, halogen, C₁-C₆alkoxy, C₁-C₆haloalkoxy, pyrazolyl, piperidinyl, phenoxy and C₁-C₄alkylsulfonyl;
- or R₁ is C₁-C₆alkyl, which is substituted by pyridyl, wherein said pyridyl can be mono- to polysubstituted by substituents selected from the group consisting of halogen and C₁-C₄haloalkyl;
- or R₁ is C₁-C₆alkyl, which is substituted by phenoxy, wherein said phenoxy can be mono- to polysubstituted by substituents selected from the group consisting of halogen and C₁-C₄alkyl;
- or R₁ is C₁-C₆alkyl, which is substituted by phenylcarbonyl, wherein said phenylcarbonyl can be mono- to polysubstituted by substituents selected from the group consisting of halogen and C₁-C₄haloalkoxy;
- or R₁ is C₁-C₆alkyl, which is substituted by imidazoliny, wherein said imidazoliny can be mono- to polysubstituted by C₁-C₄alkyl;
- or R₁ is C₁-C₆alkyl, which is substituted by isoxazolyl, wherein said isoxazolyl can be mono- to polysubstituted by halo-substituted phenyl;
- or R₁ is pyridyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₄alkyl, C₁-C₄alkoxycarbonyl, phenyl and phenoxy;
- or R₁ is pyrimidinyl which can be mono- to polysubstituted by substituents selected from the group consisting of hydroxy, C₁-C₄alkoxy and C₁-C₄alkyl;
- or R₁ is piperazinyl, which can be monosubstituted by benzyl;
- or R₁ is piperidinyl, which can be mono- to polysubstituted by C₁-C₄alkyl;
- or R₁ is pyrazolyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₄alkyl, cyano and phenyl;
- or R₁ is thiethanyl, which can be substituted by C₁-C₄alkyl;

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or R₁ is dihydro-thiophene-2-one-3-yl;

or R₁ is C₃-C₆cycloalkyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₃-C₆cycloalkyl, C₂-C₆alkynyl and =N-O-C₁-C₄haloalkyl;

or R₁ is azetidiny, which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₄haloalkyl and benzyl;

or R₁ is pyrrolidiny which can be substituted by benzyl;

or R₁ is C₁-C₆alkoxycarbonylamino;

or R₁ is C₃-C₆cycloalkenyl which can be mono- to polysubstituted by C₁-C₆alkoxycarbonyl;

or R₁ is phenyl, which can be mono- to polysubstituted by substituents selected from the

group consisting of halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkylthio, di(C₁-C₄alkyl)aminosulfonyl, C₁-C₄alkoxy, phenyl, piperidyl, pyrrolyl, morpholinyl, indolyl, phenylcarbonyl and C₁-C₄alkoxycarbonyl;

or R₁ is quinolinyl, benzothiazolyl, oxolanyl or indazolyl;

or R₁ is benzothiophenyl, which can be monosubstituted by C₁-C₆alkoxycarbonyl;

or R₁ is thiazolyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₄alkyl, pyridyl, phenyl, pyrimidinyl and C₁-C₄alkylcarbonyl; wherein said phenyl can be mono- to polysubstituted by C₁-C₄alkyl and wherein said pyrimidinyl can be mono- to polysubstituted by C₁-C₄alkoxy;

or R₁ is benzothiazolyl which can be mono- to polysubstituted by C₁-C₄alkyl;

or R₁ is chromen-2-one which can be mono- to polysubstituted by C₁-C₄alkyl;

or R₁ is isoxazolyl, which in can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₄alkyl and phenyl;

or R₁ is thiadiazolyl, which can be monosubstituted by substituents selected from the group consisting of C₁-C₄alkyl and halo-substituted phenyl;

or R₁ is furyl which can be mono- to polysubstituted by substituents selected from the group consisting of cyano and phenyl;

or R₁ is pyrazolopyridinyl which can be mono- to polysubstituted by C₁-C₄alkyl; or R₁ is thienyl which can be mono- to polysubstituted by C₁-C₄alkoxycarbonyl; or R₁ is thietanyloxide, thiethanyldioxide, bicyclo[2.2.1]heptyl or tetrahydrothienyl;

or R₁ is isoxazolidin-3-one, which can be monosubstituted by substituents selected from C₁-C₄alkyl and C₁-C₄haloalkyl;

or R₁ and R₂ form together with the nitrogen atom to which they are bonded a 3- to 6-membered saturated ring which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₄alkyl, C₁-C₄alkoxy and halogen; and further mono- to

polysubstituted by substituents selected from the group consisting of phenylcarbonyl,

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phenoxy-C₁-C₄alkyl and phenoxy, wherein said phenylcarbonyl, phenoxy-C₁-C₄alkyl and phenoxy can be mono- to polysubstituted by halogen; and said saturated ring can be additionally substituted by an ethylene chain;

R₂ is hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl or C₃-C₆cycloalkyl; and

5 R₃ is oxygen.

In said preferred compounds of formula I, preferably

m is 0;

G₁ is cyclopropyl, ethenyl or ethynyl;

10 R₇ is hydrogen, fluoro, chloro, bromo or iodo;

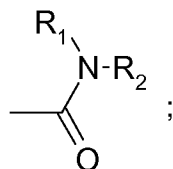
G₂ is J-1, J-4 or J-16;

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

Rx is halogen, C₁-C₆alkoxycarbonyl, pyrimidinyl, dihydro-oxazolyl, dioxolanyl, 1,3-dioxanyl and 5,6-dihydro-[1,4,2]dioxazinyl, wherein said pyrimidinyl, pyridinyl, dihydro-oxazolyl,

15 dioxolanyl, 1,3-dioxanyl and 5,6-dihydro-[1,4,2]dioxazinyl can be mono- to polysubstituted by C₁-C₆alkyl; or

G₂ is



wherein

20 R₁ is C₁-C₆alkyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₆alkylthio, C₁-C₆haloalkyl, C₁-C₆alkylsulfinyl, halogen, oxolanyl, thietanyl, thiethanyldioxide, pyrimidinyl and C₁-C₆alkylcarbonylamino;

or R₁ is C₁-C₆alkyl, which is substituted by pyridyl, wherein said pyridyl can be mono- to polysubstituted by substituents selected from the group consisting of halogen and C₁-

25 C₄haloalkyl;

or R₁ is thiethanyl, which can be substituted by C₁-C₄alkyl;

or is oxolanyl;

or R₁ is thietanyloxide, thiethanyldioxide or tetrahydrothienyl; and

R₂ is hydrogen or C₁-C₆alkyl; in particular

30 G₂ is J-1, J-4 or J-16;

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

-15-

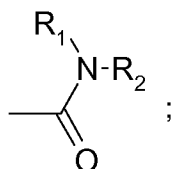
R_x is halogen, C₁-C₆alkoxycarbonyl, pyrimidinyl, dihydro-oxazolyl, dioxolanyl, 1,3-dioxanyl and 5,6-dihydro-[1,4,2]dioxazinyl, wherein said pyrimidinyl, pyridinyl, dihydro-oxazolyl, dioxolanyl, 1,3-dioxanyl and 5,6-dihydro-[1,4,2]dioxazinyl can be mono- to polysubstituted by C₁-C₆alkyl.

5

Further preferred are a group of compounds of formula I, wherein m is 0; and

R₇ is hydrogen, fluoro, chloro, bromo or iodo.

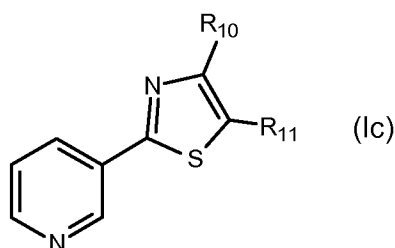
- 10 In said further preferred compounds of formula I,
G₂ is preferably



wherein

- 15 R₁ is C₁-C₆alkyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₆alkylthio, C₁-C₆haloalkyl, C₁-C₆alkylsulfinyl, halogen, oxolanyl, thietanyl, thiethanyldioxide, pyrimidinyl and C₁-C₆alkylcarbonylamino;
or R₁ is C₁-C₆alkyl, which is substituted by pyridyl, wherein said pyridyl can be mono- to polysubstituted by substituents selected from the group consisting of halogen and C₁-C₄haloalkyl;
20 or R₁ is thiethanyl, which can be substituted by C₁-C₄alkyl;
or R₁ is oxolanyl;
or R₁ is thietanyloxide, thiethanyldioxide or tetrahydrothienyl; and
R₂ is hydrogen or C₁-C₆alkyl.

- 25 An outstanding group of compounds of formula I is represented by the compounds of formula Ic



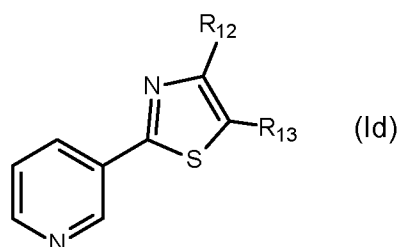
-16-

wherein

R₁₀ is C₃-C₄cycloalkyl which can be substituted by C₁-C₄haloalkyl, or is C₃-C₆cycloalkenyl which can be substituted by substituents selected from the group consisting of C₁-C₄haloalkyl and halogen, or is C₂-C₆alkenyl, C₂-C₆alkynyl, or C₂-C₆alkynyl substituted by C₁-C₄haloalkyl, or R₁₀ is a three- to four membered saturated ring which can contain one heteroatom selected from oxygen or nitro; and

R₁₁ is pyrimidinyl, pyridyl substituted by pyrimidinyl, or is C₁-C₄haloalkylaminocarbonyl.

Another outstanding group of compounds of formula I is represented by the compounds of formula Id

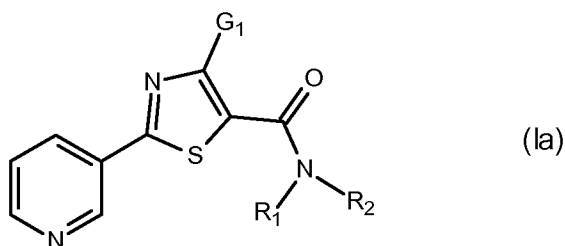


wherein

R₁₂ is C₃-C₄cycloalkyl which can contain a nitrogen atom, or is C₂-C₆alkynyl, C₂-C₆alkenyl, or C₂-C₆alkenyl substituted by halogen;

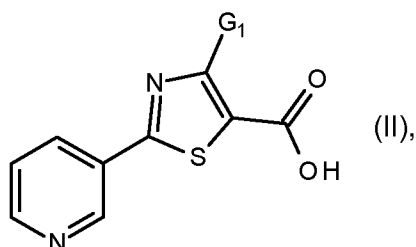
R₁₃ is pyrimidinyl which can be substituted by pyrimidinyl, or is pyridyl which can be substituted by substituents selected from the group consisting of pyrimidinyl, C₁-C₄alkoxyalkyl, dithianyl and dioxanyl, or is C₁-C₄haloalkylaminocarbonyl or C₁-C₄alkylsulfonylaminocarbonyl.

The method according to the invention for the preparation of compounds of formula Ia

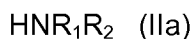


wherein G₁, R₁ and R₂ are as described under formula I above, comprises reacting a compound of formula II

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wherein G_1 is chlorine, with a compound of formula IIa



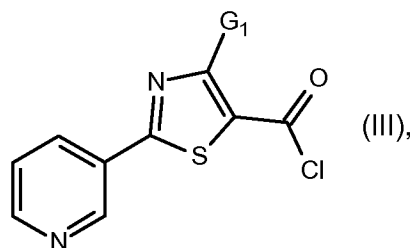
5

wherein R_1 and R_2 are as described under formula I above, in the presence of a coupling reagent as described e.g. by C. A. G. N. Montalbetti and V. Falque in Tetrahedron, 2005, 61, 10827 or in Aldrich ChemFiles, 2007, 7 (2), url:

http://www.sigmaaldrich.com/etc/medialib/docs/Aldrich/Brochure/al_chemfile_v7_n2.Par.000

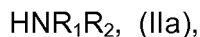
10 1.File.tmp/al_chemfile_v7_n2.pdf.

Alternatively, compounds of formula Ia can be prepared from compound of formula III



wherein G_1 is chlorine, and compound of formula IIa

15



wherein R_1 and R_2 are as described under formula I above, in the presence of a base and optionally in the presence of a catalyst such as dimethylaminopyridine.

20

Examples of a suitable base are 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) or 1,5-Diazabicyclo(4.3.0)non-5-ene (DBN).

25

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

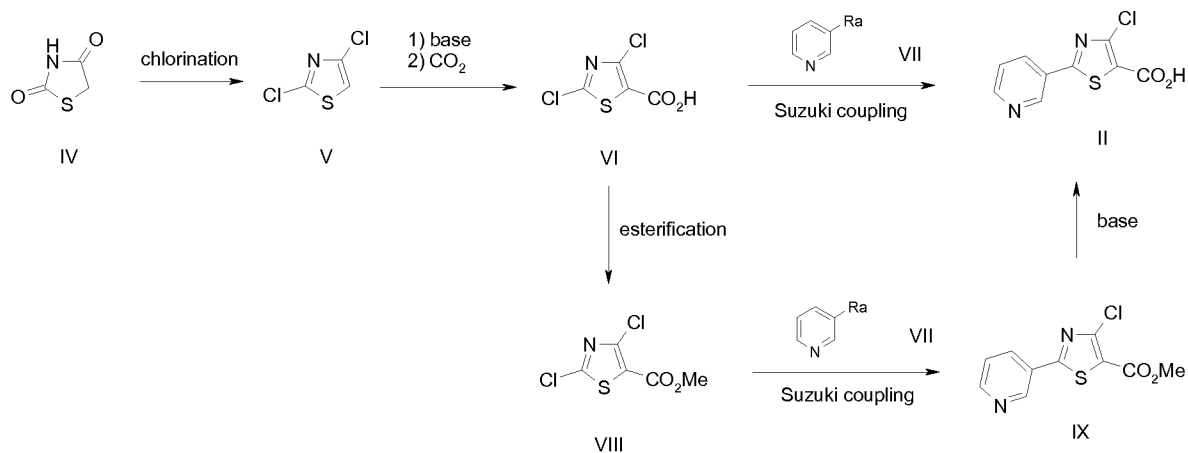
The reaction is advantageously carried out in a temperature range from approximately -80°C to approximately +140°C, preferably from approximately -30°C to approximately +100°C, in many cases in the range between ambient temperature and approximately +80°C.

The compound of formula III is prepared from the compound of formula II under routine reaction conditions as described in March's Advanced Organic Chemistry, 6th edition, Wiley, New York, 2007, p. 1440-1.

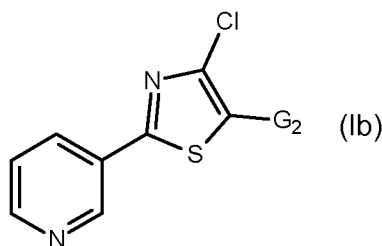
The compound of formula II is prepared according to reaction scheme 1. The known compound of formula IV is chlorinated to the compound of formula V, as described e.g. in WO 2008/083070 p. 63, which is deprotonated with a base such as LDA, LiHMDS, NaHMDS, KHMDS and reacted with CO₂ as described e.g. in J. Chem. Soc. Perkin Trans. I, 1992, 215. The compound of formula VI is coupled in a Suzuki reaction with a boronic derivative of formula VII wherein Ra is B(OH)₂, B(OMe)₂, B(OiPr)₂, BF₃K or B(-OCMe₂CMe₂O-) to compound of formula II. Alternatively compound of formula VI is esterified to compound of formula VIII which react with compound of formula VII to compound of formula IX, which is reacted in a Suzuki reaction with a compound of formula VII, with Ra as defined above, and then saponified to the compound of formula II. Methods of chlorination, esterification and saponification are described in March's Advanced Organic Chemistry, 6th edition, Wiley, New York, 2007. The Suzuki reaction is known from the literature e.g. J. P. Wolfe, J. S. Nakhla, The Suzuki Reaction in Name Reactions for Homologations, John Wiley & Sons, Inc., Hoboken, N. J, 2009, Pt. 1, 163.

Reaction Scheme 1:

-19-



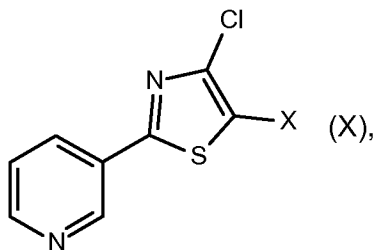
The method according to the invention for the preparation of compounds of formula Ib,



5

wherein G₂ is a 5- or 6-membered optionally substituted heterocycle; preferably G₂ is pyridyl or pyrimidyl, said pyridyl or pyrimidyl can be mono- to polysubstituted by substituents selected from the group consisting of pyrimidinyl, halogen and pyridyl, wherein said pyrimidinyl and pyridyl in turn can be mono- to polysubstituted by halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy; or is thiazolyl which can be substituted by substituents selected from the group consisting of halogen, di-C₁-C₄alkyl-phosphinoylmethyl-aminocarbonyl and C₁-C₆alkoxycarbonylamino; is [1,3,4]oxadiazole-2-yl, which can be substituted by pyridinyl which in turn can be substituted by C₁-C₄alkyl; or is [1,3,4]thiadiazole-2-yl, which can be substituted by pyridinyl which in turn can be substituted by C₁-C₄alkyl; comprises reacting a

15 compound of formula X,

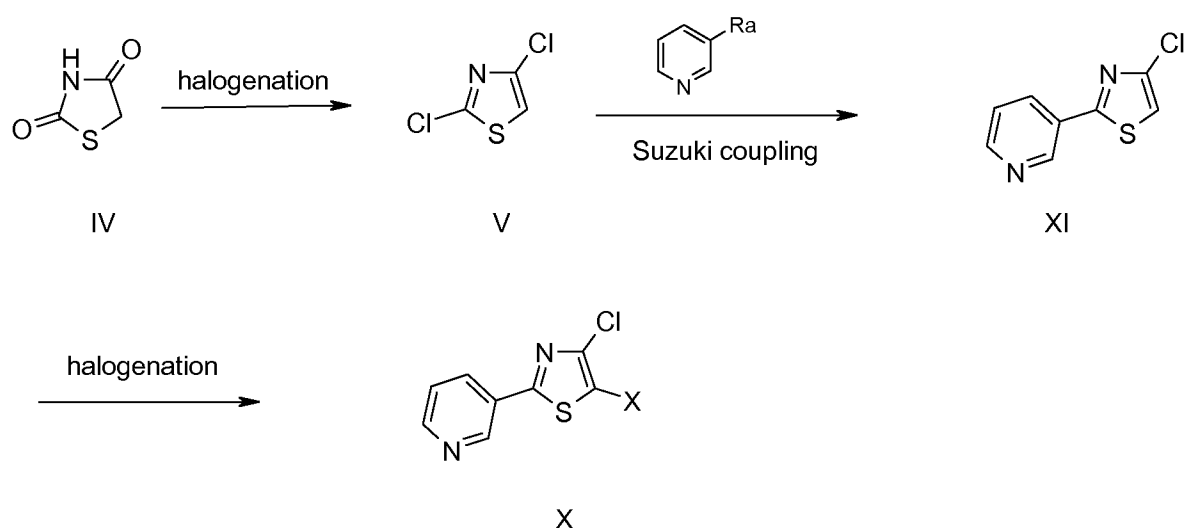


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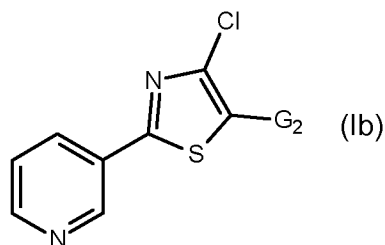
wherein X is chloro, bromo, iodo, OMesyl or trifluoromethanesulfonate (OTf), in a Suzuki reaction with a compound of formula G_2 -Ra, wherein G_2 is as described under formula Ib above and Ra is $B(OH)_2$, $B(OMe)_2$, $B(OiPr)_2$, BF_3K or $B(-OCMe_2CMe_2O-)$.

- 5 Compounds of formula X, wherein X is chloro, bromo or iodo, can be made from compounds of formula XI according to the reaction scheme 2. Halogenation reactions are known from literature, e.g. March's Advanced Organic Chemistry, 6th edition, Wiley, New York, 2007.

Reaction Scheme 2:



As depicted in the reaction scheme 3, the alternative method according to the invention for the preparation of compounds of formula Ib, wherein G_2 is as described above,

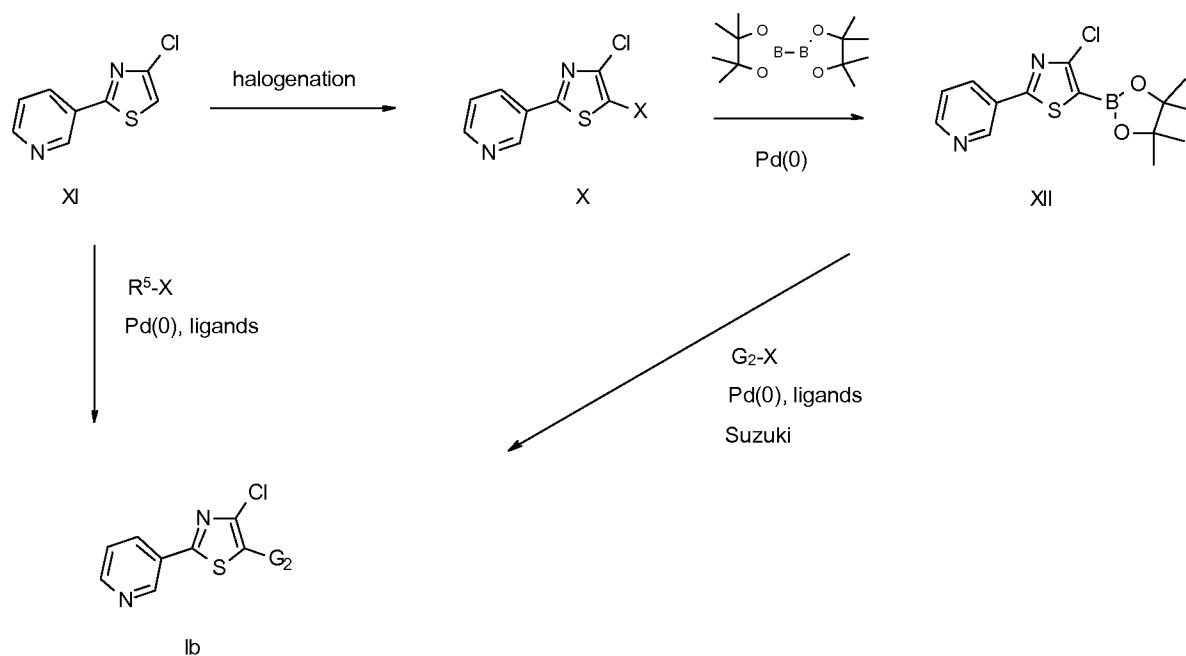


comprises reacting a compound of formula XI with a compound of formula G_2 -X, wherein X is chloro, bromo, iodo, OMesyl or trifluoromethanesulfonate (OTf), by a C-H functionalization method, as known from the literature (e.g. L. Ackermann et al. Angew. Chem. Int Ed. 2009, 48, 9792 or J. Q. Yu, Z. Shi Eds., Topics in Current Chemistry, 2010, vol. 292, Springer). Alternatively, the compound of formula X, wherein X is chloro, bromo, iodo OMesyl or trifluoromethanesulfonate, is borylated under known condition to a compound of formula XII,

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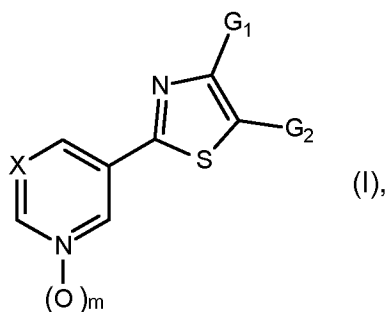
which react with a compound of formula G_2-X , wherein X is chloro, bromo, iodo, OMesyl or trifluoromethanesulfonate (OTf) in a Suzuki reaction to give a compound of formula Ib.

Reaction Scheme 3:



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As depicted in the reaction scheme 4, the method according to the invention for the preparation of compounds of formula I,



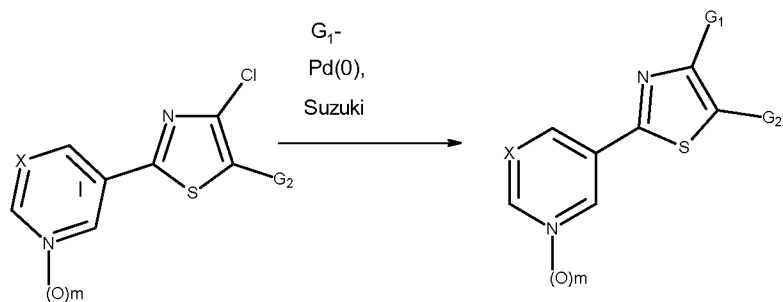
wherein m, X, G₁ and G₂ are as described above,

- 10 comprises reacting a compound of formula Ib, wherein G₂ is as described under formula I above, in a Suzuki reaction with a compound of formula G₁-Ra, wherein G₁ is as described under formula I above and Ra is B(OH)₂, B(OMe)₂, B(OiPr)₂, BF₃K or B(-OCMe₂CMe₂O-).

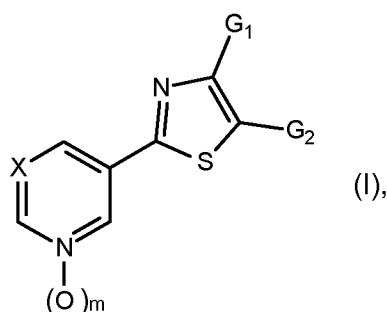
Reaction Scheme 4:

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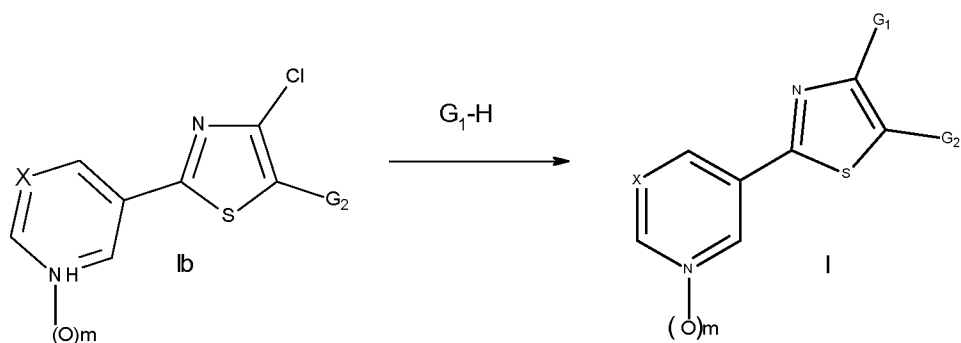


As shown in the reaction scheme 5, the method according to the invention for the preparation of compounds of formula I,



- 5 wherein m, X, G₁ and G₂ are as described above,
 comprises reacting a compound of formula Ib, wherein G₂ is as described under formula I above, in a nucleophilic aromatic substitution with a compound of formula G₁-H, wherein G₁ is as described under formula I above optionally in the presence of a base.

10 Reaction Scheme 5:



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,

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alkali metal or alkaline earth metal dialkylamides or alkali metal or alkaline earth metal alkylsilylamides, alkylamines, alkylenediamines, free or N-alkylated saturated or unsaturated cycloalkylamines, basic heterocycles, ammonium hydroxides and carbocyclic amines.

Examples which may be mentioned are sodium hydroxide, sodium hydride, sodium amide, sodium methoxide, sodium acetate, sodium carbonate, potassium tert-butoxide, potassium hydroxide, potassium carbonate, potassium hydride, lithium diisopropylamide, potassium bis(trimethylsilyl)amide, calcium hydride, triethylamine, diisopropylethylamine, triethylenediamine, cyclohexylamine, N-cyclohexyl-N,N-dimethylamine, N,N-diethylaniline, pyridine, 4-(N,N-dimethylamino)pyridine, quinuclidine, N-methylmorpholine, benzyltrimethylammonium hydroxide and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

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

The reaction is advantageously carried out in a temperature range from approximately -80°C to approximately +140°C, preferably from approximately -30°C to approximately +100°C, in many cases in the range between ambient temperature and approximately +80°C.

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

Depending on the choice of the reaction conditions and starting materials which are suitable in each case, it is possible, for example, in one reaction step only to replace one substituent by another substituent according to the invention, or a plurality of substituents can be replaced by other substituents according to the invention in the same reaction step.

Salts of compounds of formula I can be prepared in a manner known per se. Thus, for example, acid addition salts of compounds of formula I are obtained by treatment with a suitable acid or a suitable ion exchanger reagent and salts with bases are obtained by treatment with a suitable base or with a suitable ion exchanger reagent.

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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.

5

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.

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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.

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The compounds of formula I and, where appropriate, the tautomers thereof, in each case in free form or in salt form, can be present in the form of one of the isomers which are possible or as a mixture of these, for example in the form of pure isomers, such as antipodes and/or diastereomers, or as isomer mixtures, such as enantiomer mixtures, for example racemates, diastereomer mixtures or racemate mixtures, depending on the number, absolute and relative configuration of asymmetric carbon atoms which occur in the molecule and/or depending on the configuration of non-aromatic double bonds which occur in the molecule; the invention relates to the pure isomers and also to all isomer mixtures which are possible and is to be understood in each case in this sense hereinabove and hereinbelow, even when stereochemical details are not mentioned specifically in each case.

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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.

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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-

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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.

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

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

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

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

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

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during ecdysis, or indirectly, for example in a reduced oviposition and/or hatching rate, a good activity corresponding to a destruction rate (mortality) of at least 50 to 60%.

Examples of the abovementioned animal pests are:

- 5 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, Calipitimerus spp., Chorioptes spp., Dermanyssus gallinae, Dermatophagoides spp, Eotetranychus spp, Eriophyes spp., Hemitarsonemus spp, Hyalomma spp., Ixodes spp., Olygonychus spp, Ornithodoros spp.,
10 Polyphagotarsonus latus, Panonychus spp., Phyllocoptruta oleivora, Phytionemus spp, Polyphagotarsonemus spp, Psoroptes spp., Rhipicephalus spp., Rhizoglyphus spp., Sarcoptes spp., Steneotarsonemus spp, Tarsonemus spp. and Tetranychus spp.;
from the order *Anoplura*, for example,
Haematopinus spp., Linognathus spp., Pediculus spp., Pemphigus spp. and Phylloxera spp.;
15 from the order *Coleoptera*, for example,
Agriotes spp., Amphimallon majale, Anomala orientalis, Anthonomus spp., Aphodius spp, Astylus atomaculatus, Ataenius spp, Atomaria linearis, Chaetocnema tibialis, Cerotoma spp, Conoderus spp, Cosmopolites spp., Cotinis nitida, Curculio spp., Cyclocephala spp, Dermestes spp., Diabrotica spp., Diloboderus abderus, Epilachna spp., Eremnus spp.,
20 Heteronychus arator, Hypothenemus hampei, Lagria vilosa, Leptinotarsa decemlineata, Lissorhoptrus spp., Liogenys spp, Maecolaspis spp, Maladera castanea, Megascelis spp, Meligethes aeneus, Melolontha spp., Myochrous armatus, Oryzaephilus spp., Otiorhynchus spp., Phyllophaga spp, Phlyctinus spp., Popillia spp., Psylliodes spp., Rhyssomatus aubtilis, Rhizopertha spp., Scarabeidae, Sitophilus spp., Sitotroga spp., Somaticus spp,
25 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.,
30 Cuterebra spp., Dacus spp., Delia spp, Drosophila melanogaster, Fannia spp., Gastrophilus spp., Geomyza tripunctata, Glossina spp., Hypoderma spp., Hyppobosca spp., Liriomyza spp., Lucilia spp., Melanagromyza spp., Musca spp., Oestrus spp., Orseolia spp., Oscinella frit, Pegomyia hyoscyami, Phorbia spp., Rhagoletis spp, Rivelia quadrifasciata, Scatella spp, Sciara spp., Stomoxys spp., Tabanus spp., Tannia spp. and Tipula spp.;
35 from the order *Hemiptera*, for example,

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- 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, Lep-
 5 tocorisa 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;
 Acyrthosium pisum, Adalges spp, Agalliana ensigera, Agonoscaena targionii, Aleurodicus spp,
 10 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,
 15 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
 20 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.,
 25 Pseudatomoscelis seriatus, Psylla spp., Pulvinaria aethiopica, Quadraspidiotus spp., Quesada gigas, Recilia dorsalis, Rhopalosiphum spp., Saissetia spp., Scaphoideus spp., Schizaphis spp., Sitobion spp., Sogatella furcifera, Spissistilus festinus, Tarophagus Proserpina, Toxoptera spp, Trialeurodes spp, Tridiscus sporoboli, Trionymus spp, Trioza erytreae , Unaspis citri, Zyginia flammigera, Zyginidia scutellaris, ;
 30 from the order *Hymenoptera*, for example,
 Acromyrmex, Arge spp, Atta spp., Cephus spp., Diprion spp., Diprionidae, Gilpinia polytoma, Hoplocampa spp., Lasius spp., Monomorium pharaonis, Neodiprion spp., Pogonomyrmex spp, Slenopsis invicta, Solenopsis spp. and Vespa spp.;
- from the order *Isoptera*, for example,

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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

- 5 spp., Anticarsia gemmatilis, Archips spp., Argyresthia spp, Argyrotaenia spp., Autographa spp., Bucculatrix thurberiella, Busseola fusca, Cadra cautella, Carposina nipponensis, Chilo spp., Choristoneura spp., Chrysoteuchia topiaria, Clysia ambiguella, Cnaphalocrocis spp., Cnephasia spp., Cochylis spp., Coleophora spp., Colias lesbia, Cosmophila flava, Crambus spp, Crocidolomia binotalis, Cryptophlebia leucotreta, Cydalima perspectalis, Cydia spp.,
- 10 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
- 15 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,
- 20 Rachiplusia nu, Richia albicosta, Scirpophaga spp., Sesamia spp., Sparganothis spp., Spodoptera spp., Sylepta derogate, Synanthedon spp., Thaumetopoea spp., Tortrix spp., Trichoplusia ni, Tuta absoluta, and Yponomeuta spp.;

from the order *Mallophaga*, for example,

Damalinea spp. and Trichodectes spp.;

- 25 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.;

- 30 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

- 35 spp, Scirtothrips aurantii, Sericothrips variabilis, Taeniothrips spp., Thrips spp;

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

The active ingredients according to the invention can be used for controlling, i. e. containing or destroying, pests of the abovementioned type which occur in particular on plants, especially on useful plants and ornamentals in agriculture, in horticulture and in forests, or on organs, such as fruits, flowers, foliage, stalks, tubers or roots, of such plants, and in some cases even plant organs which are formed at a later point in time remain protected against these pests.

Suitable target crops are, in particular, cereals, such as wheat, barley, rye, oats, rice, maize or sorghum; beet, such as sugar or fodder beet; fruit, for example pomaceous fruit, stone fruit or soft fruit, such as apples, pears, plums, peaches, almonds, cherries or berries, for example strawberries, raspberries or blackberries; leguminous crops, such as beans, lentils, peas or soya; oil crops, such as oilseed rape, mustard, poppies, olives, sunflowers, coconut, castor, cocoa or ground nuts; cucurbits, such as pumpkins, cucumbers or melons; fibre plants, such as cotton, flax, hemp or jute; citrus fruit, such as oranges, lemons, grapefruit or tangerines; vegetables, such as spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes or bell peppers; Lauraceae, such as avocado, Cinnamomum or camphor; and also tobacco, nuts, coffee, eggplants, sugarcane, tea, pepper, grapevines, hops, the plantain family, latex plants and ornamentals.

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

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*,

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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).

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);

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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); Nature-Gard®, Agrisure® GT Advantage (GA21 glyphosate-tolerant trait), Agrisure® CB Advantage (Bt11 corn borer (CB) trait) and Protecta®.

Further examples of such transgenic crops are:

1. **Bt11 Maize** from Syngenta Seeds SAS, Chemin de l'Hobit 27, F-31 790 St. Sauveur, France, registration number C/FR/96/05/10. Genetically modified *Zea mays* which has been rendered resistant to attack by the European corn borer (*Ostrinia nubilalis* and *Sesamia nonagrioides*) by transgenic expression of a truncated Cry1Ab toxin. Bt11 maize also transgenically expresses the enzyme PAT to achieve tolerance to the herbicide glufosinate ammonium.
2. **Bt176 Maize** from Syngenta Seeds SAS, Chemin de l'Hobit 27, F-31 790 St. Sauveur, France, registration number C/FR/96/05/10. Genetically modified *Zea mays* which has been rendered resistant to attack by the European corn borer (*Ostrinia nubilalis* and *Sesamia nonagrioides*) by transgenic expression of a Cry1Ab toxin. Bt176 maize also transgenically expresses the enzyme PAT to achieve tolerance to the herbicide glufosinate ammonium.
3. **MIR604 Maize** from Syngenta Seeds SAS, Chemin de l'Hobit 27, F-31 790 St. Sauveur, France, registration number C/FR/96/05/10. Maize which has been rendered insect-resistant by transgenic expression of a modified Cry3A toxin. This toxin is Cry3A055 modified by insertion of a cathepsin-G-protease recognition sequence. The preparation of such transgenic maize plants is described in WO 03/018810.
4. **MON 863 Maize** from Monsanto Europe S.A. 270-272 Avenue de Tervuren, B-1150 Brussels, Belgium, registration number C/DE/02/9. MON 863 expresses a Cry3Bb1 toxin and has resistance to certain Coleoptera insects.
5. **IPC 531 Cotton** from Monsanto Europe S.A. 270-272 Avenue de Tervuren, B-1150 Brussels, Belgium, registration number C/ES/96/02.
6. **1507 Maize** from Pioneer Overseas Corporation, Avenue Tedesco, 7 B-1160 Brussels, Belgium, registration number C/NL/00/10. Genetically modified maize for the expression of

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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.

Antipathogenic substances which can be expressed by such transgenic plants include, for example, ion channel blockers, such as blockers for sodium and calcium channels, for example the viral KP1, KP4 or KP6 toxins; stilbene synthases; bibenzyl synthases; chitinases; glucanases; the so-called "pathogenesis-related proteins" (PRPs; see e.g. EP-A-0 392 225); antipathogenic substances produced by microorganisms, for example peptide antibiotics or heterocyclic antibiotics (see e.g. WO 95/33818) or protein or polypeptide factors involved in plant pathogen defence (so-called "plant disease resistance genes", as described in WO 03/000906).

Further areas of use of the compositions according to the invention are the protection of stored goods and storerooms and the protection of raw materials, such as wood, textiles, floor coverings or buildings, and also in the hygiene sector, especially the protection of humans, domestic animals and productive livestock against pests of the mentioned type.

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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:

- 5 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..

10

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

20

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

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

25

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

30

Of the subclass Acaria (Acarida) and the orders Meta- and Meso-stigmata, for example *Argas* spp., *Ornithodoros* spp., *Otobius* spp., *Ixodes* spp., *Amblyomma* spp., *Boophilus* spp.,
Dermacentor spp., *Haemophysalis* spp., *Hyalomma* spp., *Rhipicephalus* spp., *Dermanyssus* spp., *Raillietia* spp., *Pneumonyssus* spp., *Sternostoma* spp. and *Varroa* spp..

35

Of the orders Actinotrichida (Prostigmata) and Acaridida (Astigmata), for example *Acarapis* spp., *Cheyletiella* spp., *Ornithocheyletiella* spp., *Myobia* spp., *Psorergates* spp., *Demodex* spp.,
Trombicula spp., *Listrophorus* spp., *Acarus* spp., *Tyrophagus* spp., *Caloglyphus* spp.,

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Hypodectes spp., Pterolichus spp., Psoroptes spp., Chorioptes spp., Otodectes spp., Sarcoptes spp., Notoedres spp., Knemidocoptes spp., Cytodites spp. and Laminosioptes spp..

- 5 The compositions according to the invention are also suitable for protecting against insect infestation in the case of materials such as wood, textiles, plastics, adhesives, glues, paints, paper and card, leather, floor coverings and buildings.
- The compositions according to the invention can be used, for example, against the following pests: beetles such as *Hylotrupes bajulus*, *Chlorophorus pilosis*, *Anobium punctatum*,
10 *Xestobium rufovillosum*, *Ptilinuspecticornis*, *Dendrobium pertinex*, *Ernobius mollis*, *Priobium carpini*, *Lyctus brunneus*, *Lyctus africanus*, *Lyctus planicollis*, *Lyctus linearis*, *Lyctus pubescens*, *Trogoxylon aequale*, *Minthesrugicollis*, *Xyleborus spec.*, *Tryptodendron spec.*, *Apate monachus*, *Bostrychus capucins*, *Heterobostrychus brunneus*, *Sinoxylon spec.* and *Dinoderus minutus*, and also hymenopterans such as *Sirex juvencus*, *Urocerus gigas*,
15 *Urocerus gigas taignus* and *Urocerus augur*, and termites such as *Kaloterme flavicollis*, *Cryptotermes brevis*, *Heterotermes indicola*, *Reticulitermes flavipes*, *Reticulitermes santonensis*, *Reticulitermes lucifugus*, *Mastotermes darwiniensis*, *Zootermopsis nevadensis* and *Coptotermes formosanus*, and bristletails such as *Lepisma saccharina*.
- 20 The invention therefore also relates to pesticidal compositions such as emulsifiable concentrates, suspension concentrates, microemulsions, oil dispersibles, directly sprayable or dilutable solutions, spreadable pastes, dilute emulsions, soluble powders, dispersible powders, wettable powders, dusts, granules or encapsulations in polymeric substances, which comprise - at least - one of the active ingredients according to the invention and which
25 are to be selected to suit the intended aims and the prevailing circumstances.
- In these compositions, the active ingredient is employed in pure form, a solid active ingredient for example in a specific particle size, or, preferably, together with - at least - one of the auxiliaries conventionally used in the art of formulation, such as extenders, for example solvents or solid carriers, or such as surface-active compounds (surfactants).
- 30 Examples of suitable solvents are: unhydrogenated or partially hydrogenated aromatic hydrocarbons, preferably the fractions C₈ to C₁₂ of alkylbenzenes, such as xylene mixtures, alkylated naphthalenes or tetrahydronaphthalene, aliphatic or cycloaliphatic hydrocarbons, such as paraffins or cyclohexane, alcohols such as ethanol, propanol or butanol, glycols and their ethers and esters such as propylene glycol, dipropylene glycol ether, ethylene glycol or
35 ethylene glycol monomethyl ether or ethylene glycol monoethyl ether, ketones, such as

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cyclohexanone, isophorone or diacetone alcohol, strongly polar solvents, such as N-methylpyrrolid-2-one, dimethyl sulfoxide or N,N-dimethylformamide, water, unepoxidized or epoxidized vegetable oils, such as unexpodized or epoxidized rapeseed, castor, coconut or soya oil, and silicone oils.

- 5 Solid carriers which are used for example for dusts and dispersible powders are, as a rule, ground natural minerals such as calcite, talc, kaolin, montmorillonite or attapulgite. To improve the physical properties, it is also possible to add highly disperse silicas or highly disperse absorbtive polymers. Suitable adsorptive carriers for granules are porous types, such as pumice, brick grit, sepiolite or bentonite, and suitable non-sorptive carrier materials are
- 10 calcite or sand. In addition, a large number of granulated materials of inorganic or organic nature can be used, in particular dolomite or comminuted plant residues.

Suitable surface-active compounds are, depending on the type of the active ingredient to be formulated, non-ionic, cationic and/or anionic surfactants or surfactant mixtures which have

15 good emulsifying, dispersing and wetting properties. The surfactants mentioned below are only to be considered as examples; a large number of further surfactants which are conventionally used in the art of formulation and suitable according to the invention are described in the relevant literature.

Suitable non-ionic surfactants are, especially, polyglycol ether derivatives of aliphatic or cyc-

20 loaliphatic alcohols, of saturated or unsaturated fatty acids or of alkyl phenols which may contain approximately 3 to approximately 30 glycol ether groups and approximately 8 to approximately 20 carbon atoms in the (cyclo)aliphatic hydrocarbon radical or approximately 6 to approximately 18 carbon atoms in the alkyl moiety of the alkyl phenols. Also suitable are water-soluble polyethylene oxide adducts with polypropylene glycol, ethylenediaminopo-

25 lypropylene glycol or alkyl polypropylene glycol having 1 to approximately 10 carbon atoms in the alkyl chain and approximately 20 to approximately 250 ethylene glycol ether groups and approximately 10 to approximately 100 propylene glycol ether groups. Normally, the abovementioned compounds contain 1 to approximately 5 ethylene glycol units per propylene glycol unit. Examples which may be mentioned are nonylphenoxypolyethoxyethanol,

30 castor oil polyglycol ether, polypropylene glycol/polyethylene oxide adducts, tributylphenoxypolyethoxyethanol, polyethylene glycol or octylphenoxypolyethoxyethanol. Also suitable are fatty acid esters of polyoxyethylene sorbitan, such as polyoxyethylene sorbitan trioleate. The cationic surfactants are, especially, quarternary ammonium salts which generally have at

35 as further substituents (unhalogenated or halogenated) lower alkyl or hydroxyalkyl or benzyl

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radicals. The salts are preferably in the form of halides, methylsulfates or ethylsulfates. Examples are stearyltrimethylammonium chloride and benzylbis(2-chloroethyl)ethylammonium bromide.

Examples of suitable anionic surfactants are water-soluble soaps or water-soluble synthetic surface-active compounds. Examples of suitable soaps are the alkali, alkaline earth or (unsubstituted or substituted) ammonium salts of fatty acids having approximately 10 to approximately 22 C atoms, such as the sodium or potassium salts of oleic or stearic acid, or of natural fatty acid mixtures which are obtainable for example from coconut or tall oil; mention must also be made of the fatty acid methyl taurates. However, synthetic surfactants are used more frequently, in particular fatty sulfonates, fatty sulfates, sulfonated benzimidazole derivatives or alkylaryl sulfonates. As a rule, the fatty sulfonates and fatty sulfates are present as alkali, alkaline earth or (substituted or unsubstituted) ammonium salts and they generally have an alkyl radical of approximately 8 to approximately 22 C atoms, alkyl also to be understood as including the alkyl moiety of acyl radicals; examples which may be mentioned are the sodium or calcium salts of lignosulfonic acid, of the dodecylsulphuric ester or of a fatty alcohol sulfate mixture prepared from natural fatty acids. This group also includes the salts of the sulphuric esters and sulfonic acids of fatty alcohol/ethylene oxide adducts. The sulfonated benzimidazole derivatives preferably contain 2 sulphonyl groups and a fatty acid radical of approximately 8 to approximately 22 C atoms. Examples of alkylarylsulfonates are the sodium, calcium or triethanolammonium salts of decylbenzenesulfonic acid, of dibutyl-naphthalenesulfonic acid or of a naphthalenesulfonic acid/formaldehyde condensate. Also possible are, furthermore, suitable phosphates, such as salts of the phosphoric ester of a p-nonylphenol/(4-14)ethylene oxide adduct, or phospholipids.

As a rule, the compositions comprise 0.1 to 99%, especially 0.1 to 95%, of active ingredient and 1 to 99.9%, especially 5 to 99.9%, of at least one solid or liquid adjuvant, it being possible as a rule for 0 to 25%, especially 0.1 to 20%, of the composition to be surfactants(% in each case meaning percent by weight). Whereas concentrated compositions tend to be preferred for commercial goods, the end consumer as a rule uses dilute compositions which have substantially lower concentrations of active ingredient. Preferred compositions are composed in particular as follows (% = percent by weight):

Emulsifiable concentrates:

active ingredient:	1 to 95%, preferably 5 to 20%
surfactant:	1 to 30%, preferably 10 to 20 %
solvent:	5 to 98%, preferably 70 to 85%

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Dusts:

active ingredient: 0.1 to 10%, preferably 0.1 to 1%
solid carrier: 99.9 to 90%, preferably 99.9 to 99%

5 Suspension concentrates:

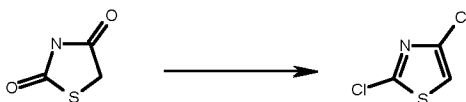
active ingredient: 5 to 75%, preferably 10 to 50%
water: 94 to 24%, preferably 88 to 30%
surfactant: 1 to 40%, preferably 2 to 30%

10 Wettable powders:

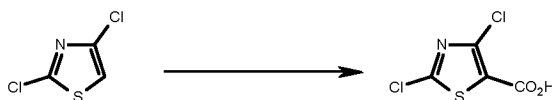
active ingredient: 0.5 to 90%, preferably 1 to 80%
surfactant: 0.5 to 20%, preferably 1 to 15%
solid carrier: 5 to 99%, preferably 15 to 98%

15 Granulates:

active ingredient: 0.5 to 30%, preferably 3 to 15%
solid carrier: 99.5 to 70%, preferably 97 to 85%

Preparatory Examples:20 Example P1: Preparation of 2,4-dichlorothiazole:

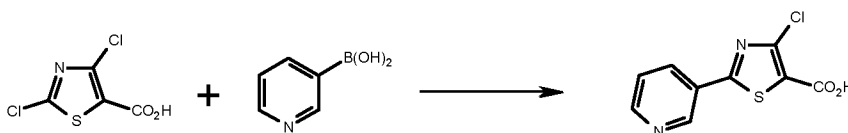
50 g (427 mmol) thiazolidine-2,4-dione was dissolved in 240 ml POCl₃ and 34 ml (422 mmol) pyridine were added at 5°C during 15 minutes. The reaction mixture was heated at 125°C for 4 hours and cooled down. Phosphoroxychloride was removed by evaporation and the residue was poured into a mixture of water and ice. 2,4-Dichlorothiazole crystallized and was filtered to give 34.8 g 2,4-dichlorothiazole in form of white crystals, Mp: 45-6°C.

Example P2: Preparation of 2,4-dichloro-thiazole-5-carboxylic acid:

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Diisopropylamine (42 ml, 297 mmol) was dissolved in 1000 ml THF and cooled to -70°C. 181.2 ml nBuLi (1.6M in hexane, 290 mmol) was added. The temperature was briefly raised to 0°C and the reaction mixture was again cooled down to -70°C. 2,4-Dichlorothiazole (40.8 g, 265 mmol) in 200 ml THF was slowly added at -70°C. Dry ice was put in a separate vessel connected to the reaction mixture with a teflon tube and the CO₂ formed bubbled in the reaction mixture at -78°C. The mixture was stirred for 18 hours in the cooling bath and the temperature reached 20°C. The mixture was quenched with 2N HCl. After saturating the water phase with NaCl, the mixture was extracted with ethyl acetate, dried with MgSO₄ and evaporated to give 48.0 g 2,4-dichloro-thiazole-5-carboxylic acid, Mp: 165 – 166°C.

10 Example P3: Preparation of 4-chloro-2-pyridin-3-yl-thiazole-5-carboxylic acid:



9.0 g (45 mmol) 2,4-dichloro-thiazole-5-carboxylic acid and 7.5 g (60 mmol) 3-pyridineboronic acid were dissolved in 180 ml dimethoxyethane. 12.0 g Na₂CO₃ in 60 ml water was added and the mixture was purged with argon for 5 min. Pd(PPh₃)₄ (1.5 g, 1.3 mmol) was added and the reaction was heated at 85°C for 18 hours. After cooling, 100 ml NaOH 1N and 150 ml ethyl acetate were added and the mixture was stirred 15 min. The water phase was separated and acidified with HCl 1N to pH 2-3. Crystals separated which were filtered and digested with diethyl ether/acetonitrile to give 9.4 g brown crystals of 4-chloro-2-pyridin-3-yl-thiazole-5-carboxylic acid. Mp.: 238-251°C.

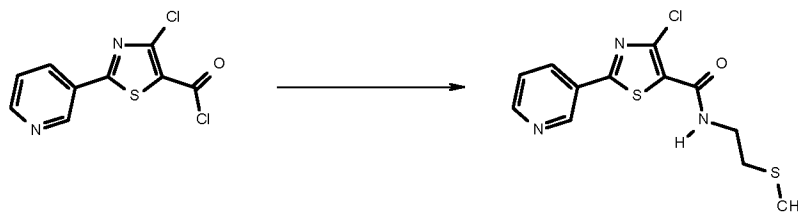
20 Example P4: Preparation of 4-chloro-2-pyridin-3-yl-thiazole-5-carbonyl chloride hydrochloride:



2.9 g (12.0 mmol) 4-chloro-2-pyridin-3-yl-thiazole-5-carboxylic acid was suspended in 50 ml CH₂Cl₂ and 15 ml oxalylchloride were added. After heating for 3 hours at 45°C, the mixture was evaporated to give 3.5 g 4-chloro-2-pyridin-3-yl-thiazole-5-carbonyl chloride hydrochloride which was directly used in the subsequent reaction.

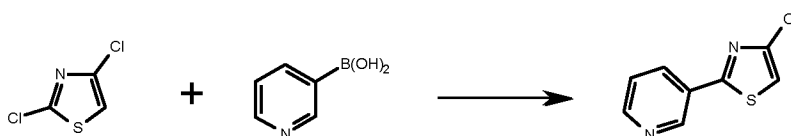
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Example P5: Preparation of 4-chloro-2-pyridin-3-yl-thiazole-5-carboxylic acid (2-methylsulfanyl-ethyl)-amide:



860 mg (2.9 mmol) 4-chloro-2-pyridin-3-yl-thiazole-5-carbonyl chloride hydrochloride was suspended in 20 ml THF. 2-Methylsulfanyl-ethylamine (264 mg, 2.9 mmol), triethylamine (1.2 ml, 8.7 mmol) and catalytic DMAP were added. The reaction was stirred overnight at RT. After filtration of the insoluble material, the residue was evaporated and directly submitted to flash-chromatography (ethyl acetate/ hexane 1:1 to ethyl acetate 100%) to give 430 mg of the desired compound. Mp: 97-98°C.

Example P6: Preparation of 3-(4-chloro-thiazol-2-yl)-pyridine:

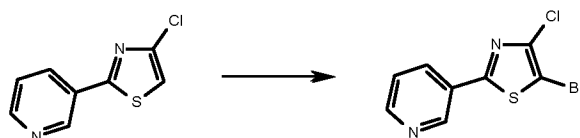


In a mixture of 600 ml toluene and 180 ml ethanol were suspended 26.0 g (169 mmol) 2,4-dichlorothiazole, 22.0 g (180 mmol) 3-pyridine boronic acid and a solution of 46 g K₂CO₃ in 350 ml water. The suspension was purged with argon for 5 min and 8.0 g (6.9 mmol)

Pd(PPh₃)₄ was added. The mixture was heated at 80°C for 18 hours. The mixture was cooled down, diluted with ethyl acetate and washed with water. The organic phase was concentrated and extracted with HCl 1N. The water phase was cooled with ice and neutralized with a 4M NaOH solution. Crystals separated which were filtered, solved in ethyl acetate. The organic phase was dried over MgSO₄ and evaporated. The residue was digested in petrol ether to give 16.1 g crystals of 3-(4-chloro-thiazol-2-yl)-pyridine. Mp: 87-90°C.

Example P7: Preparation of 3-(5-bromo-4-chloro-thiazol-2-yl)-pyridine:

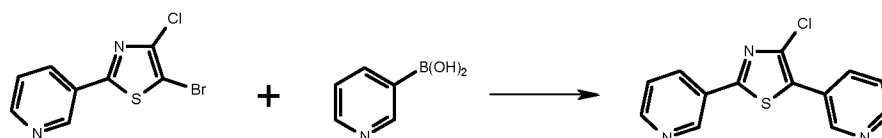
-40-



11.0 g (56 mmol) 3-(4-chloro-thiazol-2-yl)-pyridine was solved in 120 ml CH_2Cl_2 and cool to 0°C . 10 ml (mmol) bromine was slowly added at that temperature. The crystals formed were filtered. The crystals were suspended in 200 ml water and treated with sodium thiosulfate.

- 5 The solution was made basic with NaOH 1N (pH~12) and was extracted with ethyl acetate. After drying the organic phase (MgSO_4) and evaporating the solvent, the residue was crystallized in petrol ether / diisopropanol to give 12.9 g crystals of 2-[6-(4-chloro-2-pyridin-3-yl-thiazol-5-yl)-pyridin-2-yl]-pyrimidine. Mp: $114\text{--}115^\circ\text{C}$.

Example P8: Preparation of 3-(4-chloro-5-pyrid-3-yl-thiazol-2-yl)-pyridine:

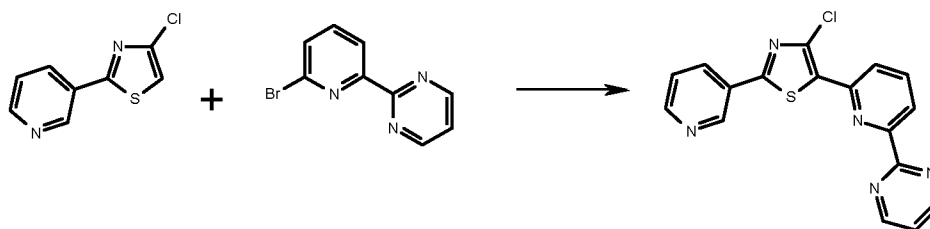


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In a solution of 50 ml toluene and 15 ml ethanol, 1 g (3.6 mmol) 3-(5-bromo-4-chloro-thiazol-2-yl)-pyridine, 0.5 g (4.0 mmol) pyridine-3-boronic acid and a solution of 1.1 g K_2CO_3 in 10 ml water were added. After purging with argon for 10 minutes, 0.5 g (0.43 mmol) $\text{Pd}(\text{PPh}_3)_4$ was added and the reaction was heated at reflux for 18 hours. After cooling, the mixture was

15 extracted with 1N HCl. The acidic phase was basified with NaOH 1M (pH~8-9) and crystals separated. After filtration and digestion of the crystals in acetonitrile, 0.31 of 3-(4-chloro-5-pyrid-3-yl-thiazol-2-yl)-pyridine was isolated. Mp: $145\text{--}147^\circ\text{C}$.

Example P9: Preparation of 4-chloro-2-(3-pyridyl)-5-(6-pyrimidin-2-yl-2-pyridyl)thiazole:



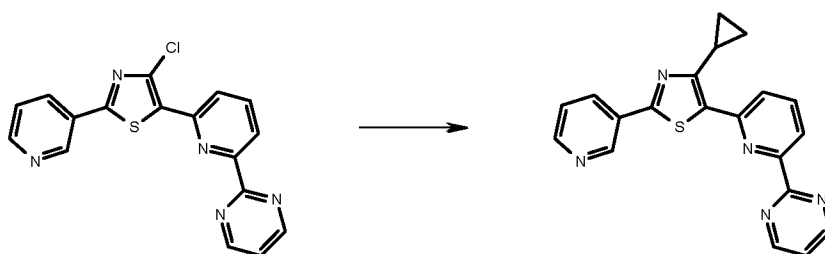
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In a solution of 30 ml dimethylformamide, 2 g (10.2 mmol) 3-(4-chloro-thiazol-2-yl)-pyridine, 2.18 g (9.23 mmol) 2-(6-bromo-2-pyridyl)pyrimidine, 3.19 g (13.9 mmol) benzyltriethylammonium chloride, 2.62 g (18.5 mmol) K_2CO_3 , 82.9 mg (0.369 mmol)

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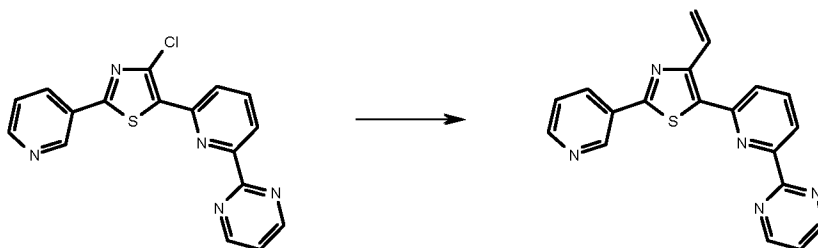
Pd(OAc)₂ and 3.7 mL (3.69 mmol) of a 1.0 M solution of tri-tert-butylphosphine in toluene were added under an argon atmosphere and the reaction was stirred at room temperature for 18 hours. The mixture was subsequently diluted with ethyl acetate, washed with water, the water phase was extracted twice with ethyl acetate, the combined organic phases were washed with brine, dried over sodium sulphate and evaporated. Chromatography on silica gel eluting with a gradient of cyclohexane and ethyl acetate afforded 1.29 g (3.67 mmol) of 4-chloro-2-(3-pyridyl)-5-(6-pyrimidin-2-yl-2-pyridyl)thiazole, Mp: 221-223°C.

Example P10: Preparation of 4-cyclopropyl-2-(3-pyridyl)-5-(6-pyrimidin-2-yl-2-pyridyl)thiazole:



100 mg (0.28 mmol) 4-chloro-2-(3-pyridyl)-5-(6-pyrimidin-2-yl-2-pyridyl)thiazole, 46 mg (0.31 mmol) potassium cyclopropyltrifluoroborate, 5.0 mg (0.008 mmol) XANTPHOS, 1.6 mg (0.007 mmol) palladium diacetate and 278 mg (0.85 mmol) cesium carbonate were solved in 1.5 ml Toluene/water (10:1) and heated in a microwave apparatus at 140°C for 20 min. The reaction mixture was diluted in water and ethyl acetate, the water phase was extracted twice with ethyl acetate, the organic phases were washed with brine, dried over MgSO₄ and evaporated. The residue was purified by column chromatography on silica gel with cyclohexane/ethyl acetate followed by CH₂Cl₂/MeOH to afford 31 mg (0.08 mmol) of 4-cyclopropyl-2-(3-pyridyl)-5-(6-pyrimidin-2-yl-2-pyridyl)thiazole as light yellow crystal. Mp: 128-130°C.

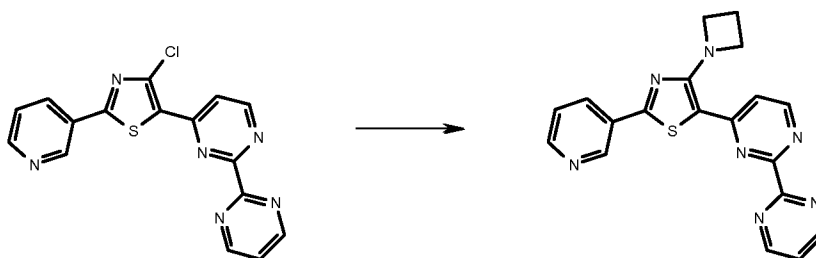
Example P11: Preparation of 2-(3-pyridyl)-5-(6-pyrimidin-2-yl-2-pyridyl)-4-vinyl-thiazole:



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250 mg (0.71 mmol) 4-chloro-2-(3-pyridyl)-5-(6-pyrimidin-2-yl-2-pyridyl)thiazole, 351 mg (2.49 mmol) potassium vinyltrifluoroborate, 18.5 mg (0.035 mmol), bis(tri-tert-butylphosphine)palladium were solved in 6.5 ml DME then 1.3 mL (2.49 mmol) sodium carbonate (1.2 M in water) were added and the mixture was heated in a microwave apparatus at 140°C for 20 min. The reaction mixture was diluted with water and ethyl acetate then filtered, the water phase was extracted twice with ethyl acetate, the organic phases were washed with brine, dried over MgSO₄ and evaporated. The residue was purified by column chromatography on silica gel with cyclohexane/ethyl acetate followed by CH₂Cl₂/MeOH to afford 126 mg (0.36 mmol) of 2-(3-pyridyl)-5-(6-pyrimidin-2-yl-2-pyridyl)-4-vinyl-thiazole as amorphous yellow crystal.

Example P12: Preparation of 4-(azetidin-1-yl)-2-(3-pyridyl)-5-(2-pyrimidin-2-ylpyrimidin-4-yl)thiazole:



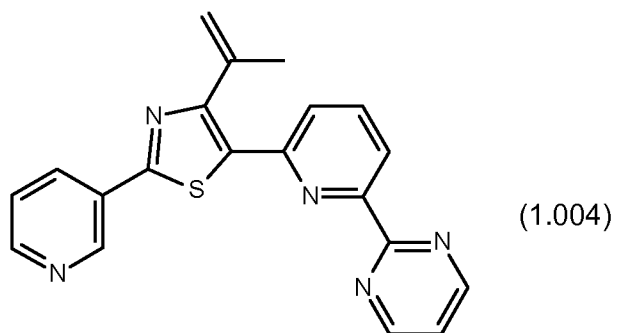
400 mg (1.13 mmol) 4-chloro-2-(3-pyridyl)-5-(6-pyrimidin-2-yl-2-pyridyl)thiazole and 324 mg (5.67 mmol) azetidine were solved in 10 ml DMF and the mixture was heated 18 hours at a temperature of 100°C. The reaction mixture was diluted with water and ethyl acetate, the water phase was extracted twice with ethyl acetate, the organic phases were washed with brine, dried over MgSO₄ and evaporated. The brown residue was taken in a minimum of DCM and upon addition of Et₂O precipitate was formed which afforded after filtration 94 mg (0.25 mmol) of 4-(azetidin-1-yl)-2-(3-pyridyl)-5-(2-pyrimidin-2-ylpyrimidin-4-yl)thiazole as brown solid. Mp: 157-159°C.

The compounds according to the following Table 1 can be prepared analogously. The examples which follow are intended to illustrate the invention and show preferred compounds of formula I.

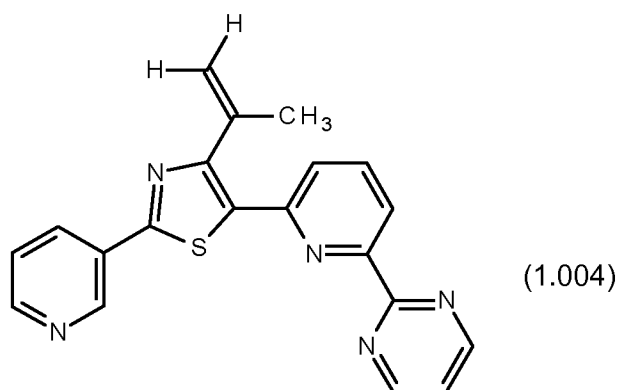
Table 1 Compounds of formula I:

In the drawings, free radicals signify a methyl group. Double bonds without substituents at the free radicals are substituted by hydrogen. For example, compound No. 1.004

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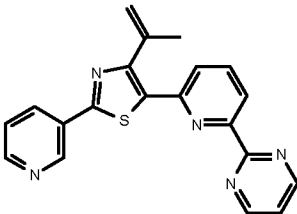
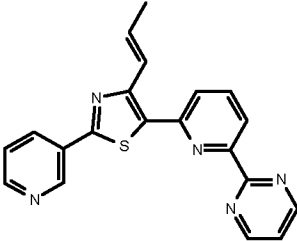
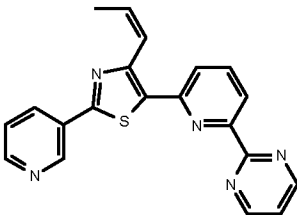
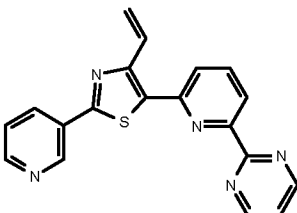
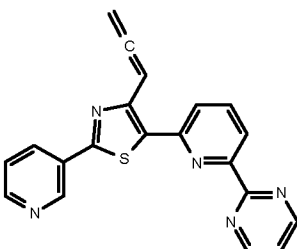


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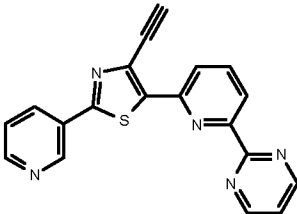
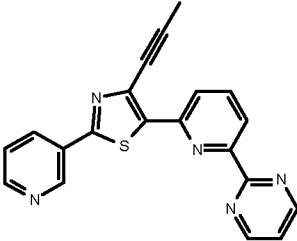
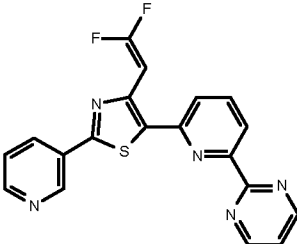
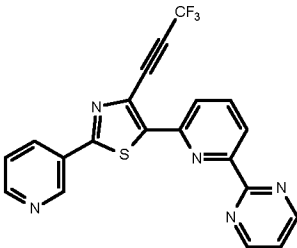
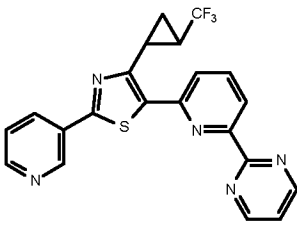


Compound No.	Structure	Phys. Data
1.001		Mp 140-142°C LCMS 0.85 min, 314 (M+H) ⁺ Method A
1.002		

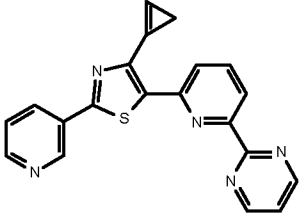
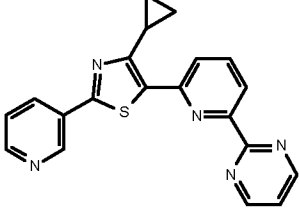
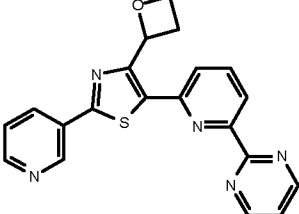
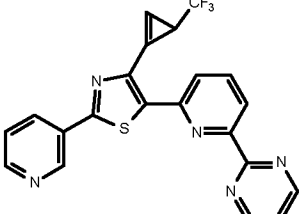
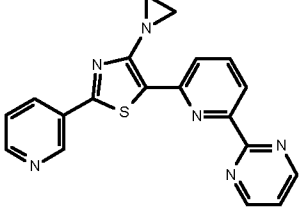
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Compound No.	Structure	Phys. Data
1.003		
1.004		LCMS 1.51 min, 358 (M+H) ⁺ Method B
1.005		LCMS 1.51 min, 358 (M+H) ⁺ Method B
1.006		LCMS 1.65 min, 344 (M+H) ⁺ Method C
1.007		

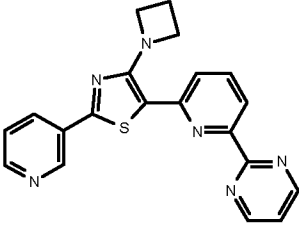
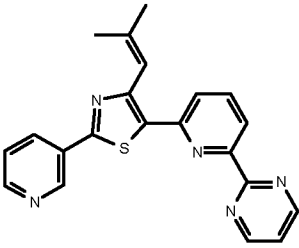
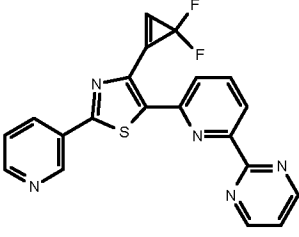
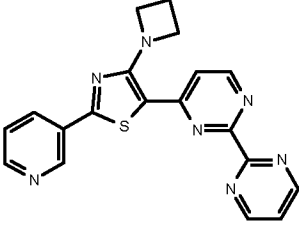
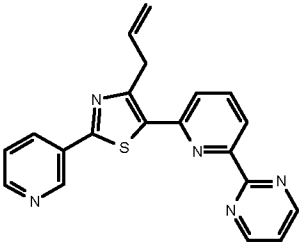
-45-

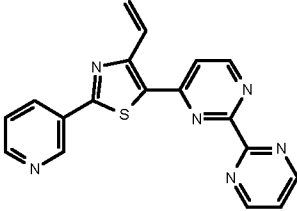
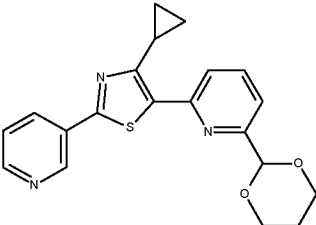
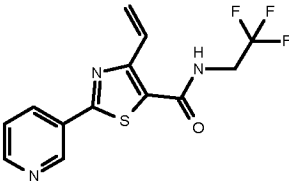
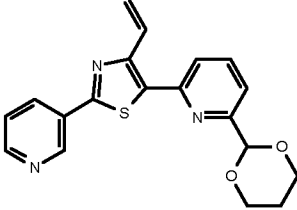
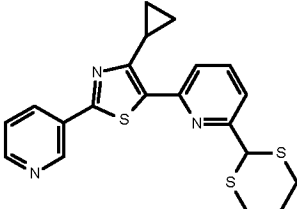
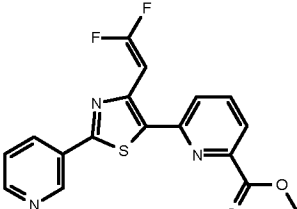
Compound No.	Structure	Phys. Data
1.008		LCMS 0.84 min, 342 (M+H) ⁺ Method A
1.009		LCMS 1.36 min, 356 (M+H) ⁺ Method B
1.010		
1.011		
1.012		

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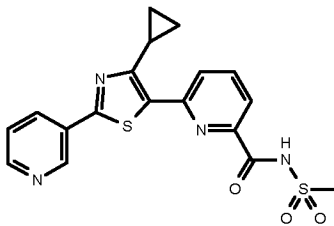
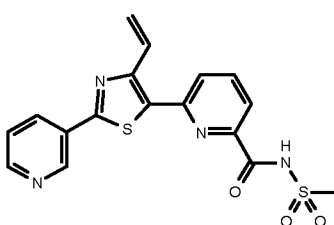
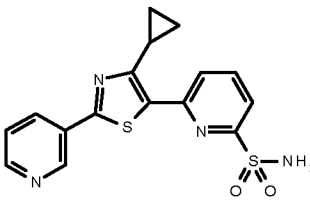
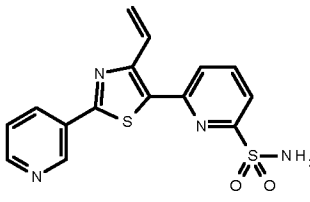
Compound No.	Structure	Phys. Data
1.013		
1.014		LCMS 0.94 min, 358 (M+H) ⁺ Method A
1.015		
1.016		
1.017		

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Compound No.	Structure	Phys. Data
1.018		
1.019		LCMS 1.57 min, 372 (M+H) ⁺ Method B
1.020		
1.021		Mp 157-159°C LCMS 0.75 min, 374 (M+H) ⁺ Method A
1.022		LCMS 1.34 min, 358 (M+H) ⁺ Method B

Compound No.	Structure	Phys. Data
1.023		LCMS 0.74 min, 345 (M+H) ⁺ Method A
1.024		LCMS 1.03 min, 366 (M+H) ⁺ Method A
1.025		Mp 141-143°C LCMS 0.85 min, 314 (M+H) ⁺ Method A
1.026		LCMS 0.98 min, 352 (M+H) ⁺ Method A
1.027		LCMS 1.15 min, 398 (M+H) ⁺ Method A
1.028		Mp 130-133°C LCMS 1.01 min, 360 (M+H) ⁺ Method A

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Compound No.	Structure	Phys. Data
1.029		
1.030		LCMS 0.89 min, 387 (M+H) ⁺ Method A
1.031		
1.032		

LCMS methods:method A:

5

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

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column compartment and diode-array detector. Column: Waters UPLC HSS T3 , 1.8 μ m, 30 x 2.1 mm, Temp: 60 °C, DAD Wavelength range (nm): 210 to 500, Solvent Gradient: A = water + 5% MeOH + 0.05 % HCOOH, B= Acetonitrile + 0.05 % HCOOH: gradient: 0 min 0% B, 100%A; 1.2-1.5min 100% B; Flow (ml/min) 0.85

5 method B:

Spectra were recorded on a Mass Spectrometer (ACQUITY SQD Single quadrupole mass spectrometer) equipped with an electrospray source (Polarity: positive, Capillary (kV) 3.00, Cone (V) 20.00, Extractor (V) 3.00, Source Temperature (°C) 150, Desolvation Temperature (°C) 400, Cone Gas Flow (L/Hr) 60, Desolvation Gas Flow (L/Hr) 700 Mass range: 100 to 800 Da) and an Acquity UPLC from Waters. Column: Waters UPLC HSS T3, Column length: 30 mm; Internal diameter of column: 2.1 mm; Particle Size: 1.8 micron; Temperature: 60°C, DAD Wavelength range (nm): 210 to 400, Solvent Gradient: (Solvent A: Water/Methanol 9:1,0.1% formic acid and Solvent B: Acetonitrile, 0.1% formic acid) gradient: 0 min 100% A; 0-2.5 min 0 to 100% B; 2.5-2.8 min 100%B; 2.8-3.0 min 100% to 0% B. Flow (ml/min) 1.7

15 method C:

Spectra were recorded on a ZQ Mass Spectrometer from Waters (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: 100°C, Desolvation Temperature: 250°C, Cone Gas Flow: 50 L/Hr, Desolvation Gas Flow: 400 L/Hr, Mass range: 100 to 900 Da) and an Agilent 1100 LC (Solvent degasser, binary pump, heated column compartment and diode-array detector. Column: Phenomenex Gemini C18, 3 μ m, 30 x 3 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; 2-2.8 min 100% B; 2.9-3 min 0%. Flow (ml/min) 1.7

Formulation examples (% = percent by weight)

<u>Example F1: Emulsion concentrates</u>	a)	b)	c)
Active ingredient	25 %	40 %	50 %
Calcium dodecylbenzenesulfonate	5 %	8 %	6 %
Castor oil polyethylene glycol ether (36 mol of EO)	5 %	-	-
Tributylphenoxypolyethylene glycol			

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ether (30 mol of EO)	-	12 %	4 %
Cyclohexanone	-	15 %	20 %
Xylene mixture	65 %	25 %	20 %

- 5 Emulsions of any desired concentration can be prepared from such concentrates by dilution with water.

Example F2: Solutions

	a)	b)	c)	d)
Active ingredient	80 %	10 %	5 %	95 %
10 Ethylene glycol monomethyl ether	20 %	-	-	-
Polyethylene glycol				
MW 400	-	70 %	-	-
N-Methylpyrrolid-2-one	-	20 %	-	-
15 Epoxidized coconut oil	-	-	1 %	5 %
Petroleum ether				
(boiling range: 160-190°)	-	-	94 %	-

The solutions are suitable for use in the form of microdrops.

20

Example F3: Granules

	a)	b)	c)	d)
Active ingredient	5 %	10 %	8 %	21 %
Kaolin	94 %	-	79 %	54 %
Highly disperse silica	1 %	-	13 %	7 %
25 Attapulgate	-	90 %	-	18 %

The active ingredient is dissolved in dichloromethane, the solution is sprayed onto the carrier(s), and the solvent is subsequently evaporated in vacuo.

Example F4: Dusts

	a)	b)
30 Active ingredient	2 %	5 %
Highly disperse silica	1 %	5 %
Talc	97 %	-
Kaolin	-	90 %

Ready-to-use dusts are obtained by intimately mixing the carriers and the active ingredient.

35

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Example F5: Wettable powders

	a)	b)	c)
Active ingredient	25 %	50 %	75 %
Sodium lignosulfonate	5 %	5 %	-
Sodium lauryl sulfate	3 %	-	5 %
5 Sodium diisobutyl-naphthalenesulfonate	-	6 %	10 %
Octylphenoxy polyethylene glycol ether (7-8 mol of EO)	-	2 %	-
Highly disperse silica	5 %	10 %	10 %
10 Kaolin	62 %	27 %	-

The active ingredient is mixed with the additives and the mixture is ground thoroughly in a suitable mill. This gives wettable powders, which can be diluted with water to give suspensions of any desired concentration.

15 Example F6: Extruder granules

Active ingredient	10 %
Sodium lignosulfonate	2 %
Carboxymethylcellulose	1 %
Kaolin	87 %

20 The active ingredient is mixed with the additives, and the mixture is ground, moistened with water, extruded, granulated and dried in a stream of air.

Example F7: Coated granules

Active ingredient	3 %
25 Polyethylene glycol (MW 200)	3 %
Kaolin	94 %

In a mixer, the finely ground active ingredient is applied uniformly to the kaolin, which has been moistened with the polyethylene glycol. This gives dust-free coated granules.

30 Example F8: Suspension concentrate

Active ingredient	40 %
Ethylene glycol	10 %
Nonylphenoxy polyethylene glycol ether (15 mol of EO)	6 %
Sodium lignosulfonate	10 %
35 Carboxymethylcellulose	1 %

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37 % aqueous formaldehyde solution	0.2 %
Silicone oil (75 % aqueous emulsion)	0.8 %
Water	32 %

The finely ground active ingredient is mixed intimately with the additives. Suspensions of any
 5 desired concentration can be prepared from the thus resulting suspension concentrate by dilution with water.

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
 10 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
 15 classes of active ingredients: organophosphorus compounds, nitrophenol derivatives, thioureas, juvenile hormones, formamidines, benzophenone derivatives, ureas, pyrrole derivatives, carbamates, pyrethroids, chlorinated hydrocarbons, acylureas, pyridyl-methyleneamino derivatives, macrolides, neonicotinoids and *Bacillus thuringiensis*
 20 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 No. 1.001 to No. 1.021 described in Table 1 of the present invention"):

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

an acaricide selected from the group of substances consisting of 1,1-bis(4-chlorophenyl)-2-ethoxyethanol (IUPAC name) (910) + TX, 2,4-dichlorophenyl benzenesulfonate

30 (IUPAC/Chemical Abstracts name) (1059) + TX, 2-fluoro-*N*-methyl-*N*-1-naphthylacetamide (IUPAC name) (1295) + TX, 4-chlorophenyl phenyl sulfone (IUPAC name) (981) + TX, abamectin (1) + TX, acequinocyl (3) + TX, acetoprole [CCN] + TX, acrinathrin (9) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, alpha-cypermethrin (202) + TX, amidithion (870) + TX, amidoflumet [CCN] + TX, amidothioate (872) + TX, amiton (875) + TX,

35 amiton hydrogen oxalate (875) + TX, amitraz (24) + TX, aramite (881) + TX, arsenous

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oxide (882) + TX, AVI 382 (compound code) + TX, AZ 60541 (compound code) + TX, azinphos-ethyl (44) + TX, azinphos-methyl (45) + TX, azobenzene (IUPAC name) (888) + TX, azocyclotin (46) + TX, azothoate (889) + TX, benomyl (62) + TX, benoxafos (alternative name) [CCN] + TX, benzoximate (71) + TX, benzyl benzoate (IUPAC name) [CCN] + TX, bifenazate (74) + TX, bifenthrin (76) + TX, binapacryl (907) + TX, brofenvalerate (alternative name) + TX, bromocyclen (918) + TX, bromophos (920) + TX, bromophos-ethyl (921) + TX, bromopropylate (94) + TX, buprofezin (99) + TX, butocarboxim (103) + TX, butoxycarboxim (104) + TX, butylpyridaben (alternative name) + TX, calcium polysulfide (IUPAC name) (111) + TX, camphechlor (941) + TX, carbanolate (943) + TX, carbaryl (115) + TX, carbofuran (118) + TX, carbophenothion (947) + TX, CGA 50'439 (development code) (125) + TX, chinomethionat (126) + TX, chlordbenside (959) + TX, chlordimeform (964) + TX, chlordimeform hydrochloride (964) + TX, chlorfenapyr (130) + TX, chlorfenethol (968) + TX, chlorfenson (970) + TX, chlorfensulphide (971) + TX, chlorfenvinphos (131) + TX, chlorobenzilate (975) + TX, chloromebuform (977) + TX, chloromethiuron (978) + TX, chloropropylate (983) + TX, chlorpyrifos (145) + TX, chlorpyrifos-methyl (146) + TX, chlorthiophos (994) + TX, cinerin I (696) + TX, cinerin II (696) + TX, cinerins (696) + TX, clofentezine (158) + TX, closantel (alternative name) [CCN] + TX, coumaphos (174) + TX, crotamiton (alternative name) [CCN] + TX, crotoxyphos (1010) + TX, cufraneb (1013) + TX, cyanthoate (1020) + TX, cyflumetofen (CAS Reg. No.: 400882-07-7) + TX, cyhalothrin (196) + TX, cyhexatin (199) + TX, cypermethrin (201) + TX, DCPM (1032) + TX, DDT (219) + TX, demephion (1037) + TX, demephion-O (1037) + TX, demephion-S (1037) + TX, demeton (1038) + TX, demeton-methyl (224) + TX, demeton-O (1038) + TX, demeton-O-methyl (224) + TX, demeton-S (1038) + TX, demeton-S-methyl (224) + TX, demeton-S-methylsulphon (1039) + TX, diafenthuron (226) + TX, dialifos (1042) + TX, diazinon (227) + TX, dichlofluanid (230) + TX, dichlorvos (236) + TX, dicliphos (alternative name) + TX, dicofol (242) + TX, dicrotophos (243) + TX, dienochlor (1071) + TX, dimefox (1081) + TX, dimethoate (262) + TX, dinactin (alternative name) (653) + TX, dinex (1089) + TX, dinex-diclexine (1089) + TX, dinobuton (269) + TX, dinocap (270) + TX, dinocap-4 [CCN] + TX, dinocap-6 [CCN] + TX, dinoocton (1090) + TX, dinopenton (1092) + TX, dinosulfon (1097) + TX, dinoterbon (1098) + TX, dioxathion (1102) + TX, diphenyl sulfone (IUPAC name) (1103) + TX, disulfiram (alternative name) [CCN] + TX, disulfoton (278) + TX, DNOC (282) + TX, dofenapyn (1113) + TX, doramectin (alternative name) [CCN] + TX, endosulfan (294) + TX, endothion (1121) + TX, EPN (297) + TX, eprinomectin (alternative name) [CCN] + TX, ethion (309) + TX, ethoate-methyl (1134) + TX, etoxazole (320) + TX, etrimfos

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(1142) + TX, fenazaflor (1147) + TX, fenazaquin (328) + TX, fenbutatin oxide (330) + TX, fenothiocarb (337) + TX, fenpropathrin (342) + TX, fenpyrad (alternative name) + TX, fenpyroximate (345) + TX, fenson (1157) + TX, fentrifanil (1161) + TX, fenvalerate (349) + TX, fipronil (354) + TX, fluacrypyrim (360) + TX, fluazuron (1166) + TX, flubenzimine (1167) + TX, flucycloxuron (366) + TX, flucythrinate (367) + TX, fluenetil (1169) + TX, flufenoxuron (370) + TX, flumethrin (372) + TX, fluorbenside (1174) + TX, fluvalinate (1184) + TX, FMC 1137 (development code) (1185) + TX, formetanate (405) + TX, formetanate hydrochloride (405) + TX, formothion (1192) + TX, formparanate (1193) + TX, gamma-HCH (430) + TX, glyodin (1205) + TX, halfenprox (424) + TX, heptenophos (432) + TX, hexadecyl cyclopropanecarboxylate (IUPAC/Chemical Abstracts name) (1216) + TX, hexythiazox (441) + TX, iodomethane (IUPAC name) (542) + TX, isocarbophos (alternative name) (473) + TX, isopropyl O-(methoxyaminothiophosphoryl)salicylate (IUPAC name) (473) + TX, ivermectin (alternative name) [CCN] + TX, jasmolin I (696) + TX, jasmolin II (696) + TX, jodfenphos (1248) + TX, lindane (430) + TX, lufenuron (490) + TX, malathion (492) + TX, malonoben (1254) + TX, mecarbam (502) + TX, mephosfolan (1261) + TX, mesulfen (alternative name) [CCN] + TX, methacrifos (1266) + TX, methamidophos (527) + TX, methidathion (529) + TX, methiocarb (530) + TX, methomyl (531) + TX, methyl bromide (537) + TX, metolcarb (550) + TX, mevinphos (556) + TX, mexacarbate (1290) + TX, milbemectin (557) + TX, milbemycin oxime (alternative name) [CCN] + TX, mipafox (1293) + TX, monocrotophos (561) + TX, morphothion (1300) + TX, moxidectin (alternative name) [CCN] + TX, naled (567) + TX, NC-184 (compound code) + TX, NC-512 (compound code) + TX, nifluridide (1309) + TX, nikkomycins (alternative name) [CCN] + TX, nitrilacarb (1313) + TX, nitrilacarb 1:1 zinc chloride complex (1313) + TX, NNI-0101 (compound code) + TX, NNI-0250 (compound code) + TX, omethoate (594) + TX, oxamyl (602) + TX, oxydeprofos (1324) + TX, oxydisulfoton (1325) + TX, pp'-DDT (219) + TX, parathion (615) + TX, permethrin (626) + TX, petroleum oils (alternative name) (628) + TX, phenkapton (1330) + TX, phenthoate (631) + TX, phorate (636) + TX, phosalone (637) + TX, phosfolan (1338) + TX, phosmet (638) + TX, phosphamidon (639) + TX, phoxim (642) + TX, pirimiphos-methyl (652) + TX, polychloroterpenes (traditional name) (1347) + TX, polynactins (alternative name) (653) + TX, proclonol (1350) + TX, profenofos (662) + TX, promacyl (1354) + TX, propargite (671) + TX, propetamphos (673) + TX, propoxur (678) + TX, prothidathion (1360) + TX, prothoate (1362) + TX, pyrethrin I (696) + TX, pyrethrin II (696) + TX, pyrethrins (696) + TX, pyridaben (699) + TX, pyridaphenthion (701) + TX, pyrimidifen (706) + TX, pyrimitate (1370) + TX, quinalphos (711) + TX, quintiofos (1381) + TX, R-1492

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- (development code) (1382) + TX, RA-17 (development code) (1383) + TX, rotenone (722) + TX, schradan (1389) + TX, sebufos (alternative name) + TX, selamectin (alternative name) [CCN] + TX, SI-0009 (compound code) + TX, sophamide (1402) + TX, spirodiclofen (738) + TX, spiromesifen (739) + TX, SSI-121 (development code) (1404) + TX, 5 TX, sulfiram (alternative name) [CCN] + TX, sulfluramid (750) + TX, sulfotep (753) + TX, sulphur (754) + TX, SZI-121 (development code) (757) + TX, tau-fluvalinate (398) + TX, tebufenpyrad (763) + TX, TEPP (1417) + TX, terbam (alternative name) + TX, tetrachlorvinphos (777) + TX, tetradifon (786) + TX, tetranactin (alternative name) (653) + TX, tetrasul (1425) + TX, thiafenox (alternative name) + TX, thiocarboxime (1431) + TX, 10 thiofanox (800) + TX, thiometon (801) + TX, thioquinox (1436) + TX, thuringiensin (alternative name) [CCN] + TX, triamiphos (1441) + TX, triarathene (1443) + TX, triazophos (820) + TX, triazuron (alternative name) + TX, trichlorfon (824) + TX, trifenofos (1455) + TX, trinactin (alternative name) (653) + TX, vamidothion (847) + TX, vaniliprole [CCN] and YI-5302 (compound code) + TX,
- 15 an algicide selected from the group of substances consisting of bethoxazin [CCN] + TX, copper dioctanoate (IUPAC name) (170) + TX, copper sulfate (172) + TX, cybutryne [CCN] + TX, dichlone (1052) + TX, dichlorophen (232) + TX, endothal (295) + TX, fentin (347) + TX, hydrated lime [CCN] + TX, nabam (566) + TX, quinoctamine (714) + TX, quinonamid (1379) + TX, simazine (730) + TX, triphenyltin acetate (IUPAC name) (347) and 20 triphenyltin hydroxide (IUPAC name) (347) + TX,
- an anthelmintic selected from the group of substances consisting of abamectin (1) + TX, crufomate (1011) + TX, doramectin (alternative name) [CCN] + TX, emamectin (291) + TX, emamectin benzoate (291) + TX, eprinomectin (alternative name) [CCN] + TX, ivermectin (alternative name) [CCN] + TX, milbemycin oxime (alternative name) [CCN] + TX,
- 25 moxidectin (alternative name) [CCN] + TX, piperazine [CCN] + TX, selamectin (alternative name) [CCN] + TX, spinosad (737) and thiophanate (1435) + TX,
- an avicide selected from the group of substances consisting of chloralose (127) + TX, endrin (1122) + TX, fenthion (346) + TX, pyridin-4-amine (IUPAC name) (23) and strychnine (745) + TX,
- 30 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, 35 TX, fenaminosulf (1144) + TX, formaldehyde (404) + TX, hydrargaphen (alternative

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name) [CCN] + TX, kasugamycin (483) + TX, kasugamycin hydrochloride hydrate (483) + TX, nickel bis(dimethyldithiocarbamate) (IUPAC name) (1308) + TX, nitrapyrin (580) + TX, othilinone (590) + TX, oxolinic acid (606) + TX, oxytetracycline (611) + TX, potassium hydroxyquinoline sulfate (446) + TX, probenazole (658) + TX, streptomycin (744) + TX, streptomycin sesquisulfate (744) + TX, tecloftalam (766) + TX, and thiomersal (alternative name) [CCN] + TX,

a biological agent selected from the group of substances consisting of *Adoxophyes orana* GV (alternative name) (12) + TX, *Agrobacterium radiobacter* (alternative name) (13) + TX, *Amblyseius* spp. (alternative name) (19) + TX, *Anagrapha falcifera* NPV (alternative name) (28) + TX, *Anagrus atomus* (alternative name) (29) + TX, *Aphelinus abdominalis* (alternative name) (33) + TX, *Aphidius colemani* (alternative name) (34) + TX, *Aphidoletes aphidimyza* (alternative name) (35) + TX, *Autographa californica* NPV (alternative name) (38) + TX, *Bacillus firmus* (alternative name) (48) + TX, *Bacillus sphaericus* Neide (scientific name) (49) + TX, *Bacillus thuringiensis* Berliner (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *aizawai* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *israelensis* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *japonensis* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *kurstaki* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *tenebrionis* (scientific name) (51) + TX, *Beauveria bassiana* (alternative name) (53) + TX, *Beauveria brongniartii* (alternative name) (54) + TX, *Chrysoperla carnea* (alternative name) (151) + TX, *Cryptolaemus montrouzieri* (alternative name) (178) + TX, *Cydia pomonella* GV (alternative name) (191) + TX, *Dacnusa sibirica* (alternative name) (212) + TX, *Diglyphus isaea* (alternative name) (254) + TX, *Encarsia formosa* (scientific name) (293) + TX, *Eretmocerus eremicus* (alternative name) (300) + TX, *Helicoverpa zea* NPV (alternative name) (431) + TX, *Heterorhabditis bacteriophora* and *H. megidis* (alternative name) (433) + TX, *Hippodamia convergens* (alternative name) (442) + TX, *Leptomastix dactylopii* (alternative name) (488) + TX, *Macrolophus caliginosus* (alternative name) (491) + TX, *Mamestra brassicae* NPV (alternative name) (494) + TX, *Metaphycus helvolus* (alternative name) (522) + TX, *Metarhizium anisopliae* var. *acridum* (scientific name) (523) + TX, *Metarhizium anisopliae* var. *anisopliae* (scientific name) (523) + TX, *Neodiprion sertifer* NPV and *N. lecontei* NPV (alternative name) (575) + TX, *Orius* spp. (alternative name) (596) + TX, *Paecilomyces fumosoroseus* (alternative name) (613) + TX, *Phytoseiulus persimilis* (alternative name) (644) + TX, *Spodoptera exigua* multicapsid nuclear polyhedrosis virus (scientific name) (741) + TX, *Steinernema bibionis* (alternative name) (742) + TX, *Steinernema carpocapsae* (alternative name) (742) + TX, *Steinernema feltiae* (alternative name) (742) + TX, *Steinernema glaseri* (alternative name) (742) + TX,

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- Steinernema riobrave* (alternative name) (742) + TX, *Steinernema riobravisi* (alternative name) (742) + TX, *Steinernema scapterisci* (alternative name) (742) + TX, *Steinernema* spp. (alternative name) (742) + TX, *Trichogramma* spp. (alternative name) (826) + TX, *Typhlodromus occidentalis* (alternative name) (844) and *Verticillium lecanii* (alternative name) (848) + TX,
- a soil sterilant selected from the group of substances consisting of iodomethane (IUPAC name) (542) and methyl bromide (537) + TX,
- a chemosterilant selected from the group of substances consisting of apholate [CCN] + TX, bisazir (alternative name) [CCN] + TX, busulfan (alternative name) [CCN] + TX,
- 10 diflubenzuron (250) + TX, dimatif (alternative name) [CCN] + TX, hemel [CCN] + TX, hempa [CCN] + TX, metepa [CCN] + TX, methiotepa [CCN] + TX, methyl apholate [CCN] + TX, morzid [CCN] + TX, penfluron (alternative name) [CCN] + TX, tepa [CCN] + TX, thiohempa (alternative name) [CCN] + TX, thiotepa (alternative name) [CCN] + TX, tretamine (alternative name) [CCN] and uredepa (alternative name) [CCN] + TX,
- 15 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-
- 20 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-yl acetate (IUPAC name) (782) + TX, (*Z*)-tetradec-9-en-1-yl acetate (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) +
- 25 TX, (*9Z,12E*)-tetradeca-9,12-dien-1-yl acetate (IUPAC name) (781) + TX, 14-methyloctadec-1-ene (IUPAC name) (545) + TX, 4-methylnonan-5-ol with 4-methylnonan-5-one (IUPAC name) (544) + TX, alpha-multistriatin (alternative name) [CCN] + TX, brevicomin (alternative name) [CCN] + TX, codlelure (alternative name) [CCN] + TX, codlemone (alternative name) (167) + TX, cuelure (alternative name) (179) + TX,
- 30 disparlure (277) + TX, dodec-8-en-1-yl acetate (IUPAC name) (286) + TX, dodec-9-en-1-yl acetate (IUPAC name) (287) + TX, dodeca-8 + TX, 10-dien-1-yl acetate (IUPAC name) (284) + TX, dominicalure (alternative name) [CCN] + TX, ethyl 4-methyloctanoate (IUPAC name) (317) + TX, eugenol (alternative name) [CCN] + TX, frontalinal (alternative name) [CCN] + TX, gossyplure (alternative name) (420) + TX, grandlure (421) + TX, grandlure I
- 35 (alternative name) (421) + TX, grandlure II (alternative name) (421) + TX, grandlure III

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(alternative name) (421) + TX, grandlure IV (alternative name) (421) + TX, hexalure [CCN] + TX, ipsdienol (alternative name) [CCN] + TX, ipsenol (alternative name) [CCN] + TX, japonilure (alternative name) (481) + TX, lineatin (alternative name) [CCN] + TX, litlure (alternative name) [CCN] + TX, looplure (alternative name) [CCN] + TX, medlure [CCN] + TX, megatomoic acid (alternative name) [CCN] + TX, methyl eugenol (alternative name) (540) + TX, muscalure (563) + TX, octadeca-2,13-dien-1-yl acetate (IUPAC name) (588) + TX, octadeca-3,13-dien-1-yl acetate (IUPAC name) (589) + TX, orfralure (alternative name) [CCN] + TX, oryctalure (alternative name) (317) + TX, ostramone (alternative name) [CCN] + TX, siglure [CCN] + TX, sordidin (alternative name) (736) + TX, sulcatol (alternative name) [CCN] + TX, tetradec-11-en-1-yl acetate (IUPAC name) (785) + TX, trimedlure (839) + TX, trimedlure A (alternative name) (839) + TX, trimedlure B₁ (alternative name) (839) + TX, trimedlure B₂ (alternative name) (839) + TX, trimedlure C (alternative name) (839) and trunc-call (alternative name) [CCN] + TX,

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

an insecticide selected from the group of substances consisting of 1-dichloro-1-nitroethane (IUPAC/Chemical Abstracts name) (1058) + TX, 1,1-dichloro-2,2-bis(4-ethylphenyl)ethane (IUPAC name) (1056), + TX, 1,2-dichloropropane (IUPAC/Chemical Abstracts name) (1062) + TX, 1,2-dichloropropane with 1,3-dichloropropene (IUPAC name) (1063) + TX, 1-bromo-2-chloroethane (IUPAC/Chemical Abstracts name) (916) + TX, 2,2,2-trichloro-1-(3,4-dichlorophenyl)ethyl acetate (IUPAC name) (1451) + TX, 2,2-dichlorovinyl 2-ethylsulphinyethyl methyl phosphate (IUPAC name) (1066) + TX, 2-(1,3-dithiolan-2-yl)phenyl dimethylcarbamate (IUPAC/ Chemical Abstracts name) (1109) + TX, 2-(2-butoxyethoxy)ethyl thiocyanate (IUPAC/Chemical Abstracts name) (935) + TX, 2-(4,5-dimethyl-1,3-dioxolan-2-yl)phenyl methylcarbamate (IUPAC/ Chemical Abstracts name) (1084) + TX, 2-(4-chloro-3,5-xylyloxy)ethanol (IUPAC name) (986) + TX, 2-chlorovinyl diethyl phosphate (IUPAC name) (984) + TX, 2-imidazolidone (IUPAC name) (1225) + TX, 2-isovalerylindan-1,3-dione (IUPAC name) (1246) + TX, 2-methyl(prop-2-ynyl)aminophenyl methylcarbamate (IUPAC name) (1284) + TX, 2-thiocyanatoethyl laurate (IUPAC name) (1433) + TX, 3-bromo-1-chloroprop-1-ene (IUPAC name) (917) + TX, 3-methyl-1-

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phenylpyrazol-5-yl dimethylcarbamate (IUPAC name) (1283) + TX, 4-methyl(prop-2-ynyl)amino-3,5-xylyl methylcarbamate (IUPAC name) (1285) + TX, 5,5-dimethyl-3-oxocyclohex-1-enyl dimethylcarbamate (IUPAC name) (1085) + TX, abamectin (1) + TX, acephate (2) + TX, acetamiprid (4) + TX, acethion (alternative name) [CCN] + TX,

5 acetoprole [CCN] + TX, acrinathrin (9) + TX, acrylonitrile (IUPAC name) (861) + TX, alanycarb (15) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, aldrin (864) + TX, allethrin (17) + TX, allosamidin (alternative name) [CCN] + TX, allyxycarb (866) + TX, alpha-cypermethrin (202) + TX, alpha-ecdysone (alternative name) [CCN] + TX, aluminium phosphide (640) + TX, amidithion (870) + TX, amidothioate (872) + TX, aminocarb (873)

10 + TX, amiton (875) + TX, amiton hydrogen oxalate (875) + TX, amitraz (24) + TX, anabasine (877) + TX, athidathion (883) + TX, AVI 382 (compound code) + TX, AZ 60541 (compound code) + TX, azadirachtin (alternative name) (41) + TX, azamethiphos (42) + TX, azinphos-ethyl (44) + TX, azinphos-methyl (45) + TX, azothoate (889) + TX, *Bacillus thuringiensis* delta endotoxins (alternative name) (52) + TX, barium

15 hexafluorosilicate (alternative name) [CCN] + TX, barium polysulfide (IUPAC/Chemical Abstracts name) (892) + TX, barthrin [CCN] + TX, Bayer 22/190 (development code) (893) + TX, Bayer 22408 (development code) (894) + TX, bendiocarb (58) + TX, benfuracarb (60) + TX, bensultap (66) + TX, beta-cyfluthrin (194) + TX, beta-cypermethrin (203) + TX, bifenthrin (76) + TX, bioallethrin (78) + TX, bioallethrin S-cyclopentenyl isomer (alternative

20 name) (79) + TX, bioethanomethrin [CCN] + TX, biopermethrin (908) + TX, bioresmethrin (80) + TX, bis(2-chloroethyl) ether (IUPAC name) (909) + TX, bistrifluron (83) + TX, borax (86) + TX, brofenvalerate (alternative name) + TX, bromfenvinfos (914) + TX, bromocyclen (918) + TX, bromo-DDT (alternative name) [CCN] + TX, bromophos (920) + TX, bromophos-ethyl (921) + TX, bufencarb (924) + TX, buprofezin (99) + TX, butacarb

25 (926) + TX, butathiofos (927) + TX, butocarboxim (103) + TX, butonate (932) + TX, butoxycarboxim (104) + TX, butylpyridaben (alternative name) + TX, cadusafos (109) + TX, calcium arsenate [CCN] + TX, calcium cyanide (444) + TX, calcium polysulfide (IUPAC name) (111) + TX, camphechlor (941) + TX, carbanolate (943) + TX, carbaryl (115) + TX, carbofuran (118) + TX, carbon disulfide (IUPAC/Chemical Abstracts name)

30 (945) + TX, carbon tetrachloride (IUPAC name) (946) + TX, carbophenothion (947) + TX, carbosulfan (119) + TX, cartap (123) + TX, cartap hydrochloride (123) + TX, cevadine (alternative name) (725) + TX, chlorbicyclen (960) + TX, chlordane (128) + TX, chlordecone (963) + TX, chlordimeform (964) + TX, chlordimeform hydrochloride (964) + TX, chlorethoxyfos (129) + TX, chlorfenapyr (130) + TX, chlorfenvinphos (131) + TX,

35 chlorfluazuron (132) + TX, chlormephos (136) + TX, chloroform [CCN] + TX, chloropicrin

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(141) + TX, chlorphoxim (989) + TX, chlorprazophos (990) + TX, chlorpyrifos (145) + TX, chlorpyrifos-methyl (146) + TX, chlorthiophos (994) + TX, chromafenozide (150) + TX, cinerin I (696) + TX, cinerin II (696) + TX, cinerins (696) + TX, cis-resmethrin (alternative name) + TX, cismethrin (80) + TX, clocythrin (alternative name) + TX, cloethocarb (999) + TX, closantel (alternative name) [CCN] + TX, clothianidin (165) + TX, copper acetoarsenite [CCN] + TX, copper arsenate [CCN] + TX, copper oleate [CCN] + TX, coumaphos (174) + TX, coumithoate (1006) + TX, crotamiton (alternative name) [CCN] + TX, crotoxyphos (1010) + TX, cruformate (1011) + TX, cryolite (alternative name) (177) + TX, CS 708 (development code) (1012) + TX, cyanofenphos (1019) + TX, cyanophos (184) + TX, cyanthoate (1020) + TX, cyclethrin [CCN] + TX, cycloprothrin (188) + TX, cyfluthrin (193) + TX, cyhalothrin (196) + TX, cypermethrin (201) + TX, cyphenothrin (206) + TX, cyromazine (209) + TX, cythioate (alternative name) [CCN] + TX, *d*-limonene (alternative name) [CCN] + TX, *d*-tetramethrin (alternative name) (788) + TX, DAEP (1031) + TX, dazomet (216) + TX, DDT (219) + TX, decarbofuran (1034) + TX, deltamethrin (223) + TX, demephion (1037) + TX, demephion-O (1037) + TX, demephion-S (1037) + TX, demeton (1038) + TX, demeton-methyl (224) + TX, demeton-O (1038) + TX, demeton-O-methyl (224) + TX, demeton-S (1038) + TX, demeton-S-methyl (224) + TX, demeton-S-methylsulphon (1039) + TX, diafenthion (226) + TX, dialifos (1042) + TX, diamidafos (1044) + TX, diazinon (227) + TX, dicapthon (1050) + TX, dichlofenthion (1051) + TX, dichlorvos (236) + TX, dicliphos (alternative name) + TX, dicresyl (alternative name) [CCN] + TX, dicrotophos (243) + TX, dicyclanil (244) + TX, dieldrin (1070) + TX, diethyl 5-methylpyrazol-3-yl phosphate (IUPAC name) (1076) + TX, diflubenzuron (250) + TX, dilor (alternative name) [CCN] + TX, dimefluthrin [CCN] + TX, dimefox (1081) + TX, dimetan (1085) + TX, dimethoate (262) + TX, dimethrin (1083) + TX, dimethylvinphos (265) + TX, dimetilan (1086) + TX, dinex (1089) + TX, dinex-diclexine (1089) + TX, dinoprop (1093) + TX, dinosam (1094) + TX, dinoseb (1095) + TX, dinotefuran (271) + TX, diofenolan (1099) + TX, dioxabenzofos (1100) + TX, dioxacarb (1101) + TX, dioxathion (1102) + TX, disulfoton (278) + TX, dithicrofos (1108) + TX, DNOC (282) + TX, doramectin (alternative name) [CCN] + TX, DSP (1115) + TX, ecdysterone (alternative name) [CCN] + TX, EI 1642 (development code) (1118) + TX, emamectin (291) + TX, emamectin benzoate (291) + TX, EMPC (1120) + TX, empenthrin (292) + TX, endosulfan (294) + TX, endothion (1121) + TX, endrin (1122) + TX, EPBP (1123) + TX, EPN (297) + TX, epofenonane (1124) + TX, eprinomectin (alternative name) [CCN] + TX, esfenvalerate (302) + TX, etaphos (alternative name) [CCN] + TX, ethiofencarb (308) + TX, ethion (309) + TX, ethiprole (310) + TX, ethoate-methyl (1134) +

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TX, ethoprophos (312) + TX, ethyl formate (IUPAC name) [CCN] + TX, ethyl-DDD (alternative name) (1056) + TX, ethylene dibromide (316) + TX, ethylene dichloride (chemical name) (1136) + TX, ethylene oxide [CCN] + TX, etofenprox (319) + TX, etrimfos (1142) + TX, EXD (1143) + TX, famphur (323) + TX, fenamiphos (326) + TX, 5 fenazaflor (1147) + TX, fenchlorphos (1148) + TX, fenethacarb (1149) + TX, fenfluthrin (1150) + TX, fenitrothion (335) + TX, fenobucarb (336) + TX, fenoxacrim (1153) + TX, fenoxycarb (340) + TX, fenpirithrin (1155) + TX, fenpropathrin (342) + TX, fenpyrad (alternative name) + TX, fensulfothion (1158) + TX, fenthion (346) + TX, fenthion-ethyl [CCN] + TX, fenvalerate (349) + TX, fipronil (354) + TX, flonicamid (358) + TX, 10 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 15 (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, 20 heptenophos (432) + TX, heterophos [CCN] + TX, hexaflumuron (439) + TX, HHDN (864) + TX, hydramethylnon (443) + TX, hydrogen cyanide (444) + TX, hydroprene (445) + TX, hyquincarb (1223) + TX, imidacloprid (458) + TX, imiprothrin (460) + TX, indoxacarb (465) + TX, iodomethane (IUPAC name) (542) + TX, IPSP (1229) + TX, isazofos (1231) + TX, isobenzan (1232) + TX, isocarbophos (alternative name) (473) + TX, isodrin (1235) + TX, isofenphos (1236) + TX, isolane (1237) + TX, isoprocab (472) + TX, isopropyl O- 25 (methoxyaminothiophosphoryl)salicylate (IUPAC name) (473) + TX, isoprothiolane (474) + TX, isothioate (1244) + TX, isoxathion (480) + TX, ivermectin (alternative name) [CCN] + TX, jasmolin I (696) + TX, jasmolin II (696) + TX, jodfenphos (1248) + TX, juvenile hormone I (alternative name) [CCN] + TX, juvenile hormone II (alternative name) [CCN] + 30 TX, juvenile hormone III (alternative name) [CCN] + TX, kelevan (1249) + TX, kinoprene (484) + TX, lambda-cyhalothrin (198) + TX, lead arsenate [CCN] + TX, lepimectin (CCN) + TX, leptophos (1250) + TX, lindane (430) + TX, lirimfos (1251) + TX, lufenuron (490) + TX, lythidathion (1253) + TX, *m*-cumenyl methylcarbamate (IUPAC name) (1014) + TX, magnesium phosphide (IUPAC name) (640) + TX, malathion (492) + TX, malonoben 35 (1254) + TX, mazidox (1255) + TX, mecarbam (502) + TX, mecarphon (1258) + TX,

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menazon (1260) + TX, mephosfolan (1261) + TX, mercurous chloride (513) + TX, mesulfenfos (1263) + TX, metaflumizone (CCN) + TX, metam (519) + TX, metam-potassium (alternative name) (519) + TX, metam-sodium (519) + TX, methacrifos (1266) + TX, methamidophos (527) + TX, methanesulphonyl fluoride (IUPAC/Chemical Abstracts name) (1268) + TX, methidathion (529) + TX, methiocarb (530) + TX, methocrotophos (1273) + TX, methomyl (531) + TX, methoprene (532) + TX, methoquin-butyl (1276) + TX, methothrin (alternative name) (533) + TX, methoxychlor (534) + TX, methoxyfenozide (535) + TX, methyl bromide (537) + TX, methyl isothiocyanate (543) + TX, methylchloroform (alternative name) [CCN] + TX, methylene chloride [CCN] + TX, metofluthrin [CCN] + TX, metolcarb (550) + TX, metoxadiazone (1288) + TX, mevinphos (556) + TX, mexacarbate (1290) + TX, milbemectin (557) + TX, milbemycin oxime (alternative name) [CCN] + TX, mipafox (1293) + TX, mirex (1294) + TX, monocrotophos (561) + TX, morphothion (1300) + TX, moxidectin (alternative name) [CCN] + TX, naftalofos (alternative name) [CCN] + TX, naled (567) + TX, naphthalene (IUPAC/Chemical Abstracts name) (1303) + TX, NC-170 (development code) (1306) + TX, NC-184 (compound code) + TX, nicotine (578) + TX, nicotine sulfate (578) + TX, nifluridide (1309) + TX, nitenpyram (579) + TX, nithiazine (1311) + TX, nitrilacarb (1313) + TX, nitrilacarb 1:1 zinc chloride complex (1313) + TX, NNI-0101 (compound code) + TX, NNI-0250 (compound code) + TX, 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-2H-chromen-7-yl phosphorothioate (IUPAC name) (1074) + TX, O,O-diethyl O-6-methyl-2-propylpyrimidin-4-yl phosphorothioate (IUPAC name) (1075) + TX, O,O,O',O'-tetrapropyl dithiopyrophosphate (IUPAC name) (1424) + TX, oleic acid (IUPAC name) (593) + TX, omethoate (594) + TX, oxamyl (602) + TX, oxydemeton-methyl (609) + TX, oxydeprofos (1324) + TX, oxydisulfoton (1325) + TX, pp'-DDT (219) + TX, para-dichlorobenzene [CCN] + TX, parathion (615) + TX, parathion-methyl (616) + TX, penfluron (alternative name) [CCN] + TX, pentachlorophenol (623) + TX, pentachlorophenyl laurate (IUPAC name) (623) + TX, permethrin (626) + TX, petroleum oils (alternative name) (628) + TX, PH 60-38 (development code) (1328) + TX, phenkapton (1330) + TX, phenothrin (630) + TX, phenthoate (631) + TX, phorate (636) + TX, phosalone (637) + TX, phosfolan (1338) + TX, phosmet (638) + TX, phosnichlor (1339) + TX, phosphamidon (639) + TX, phosphine (IUPAC name) (640) + TX, phoxim (642) + TX, phoxim-methyl (1340) + TX, pirimetaphos (1344) + TX, pirimicarb (651) + TX, pirimiphos-ethyl (1345) + TX, pirimiphos-methyl (652) + TX, polychlorodicyclopentadiene isomers (IUPAC name) (1346) +

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TX, polychloroterpenes (traditional name) (1347) + TX, potassium arsenite [CCN] + TX, potassium thiocyanate [CCN] + TX, prallethrin (655) + TX, precocene I (alternative name) [CCN] + TX, precocene II (alternative name) [CCN] + TX, precocene III (alternative name) [CCN] + TX, primidophos (1349) + TX, profenofos (662) + TX, profluthrin [CCN] + TX,

5 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,

10 pyridaphenthion (701) + TX, pyrimidifen (706) + TX, pyrimitate (1370) + TX, pyriproxyfen (708) + TX, quassia (alternative name) [CCN] + TX, quinalphos (711) + TX, quinalphos-methyl (1376) + TX, quinothion (1380) + TX, quintiofos (1381) + TX, R-1492 (development code) (1382) + TX, rafoxanide (alternative name) [CCN] + TX, resmethrin (719) + TX, rotenone (722) + TX, RU 15525 (development code) (723) + TX, RU 25475

15 (development code) (1386) + TX, ryania (alternative name) (1387) + TX, ryanodine (traditional name) (1387) + TX, sabadilla (alternative name) (725) + TX, schradan (1389) + TX, sebufos (alternative name) + TX, selamectin (alternative name) [CCN] + TX, SI-0009 (compound code) + TX, SI-0205 (compound code) + TX, SI-0404 (compound code) + TX, SI-0405 (compound code) + TX, silafluofen (728) + TX, SN 72129 (development code)

20 (1397) + TX, sodium arsenite [CCN] + TX, sodium cyanide (444) + TX, sodium fluoride (IUPAC/Chemical Abstracts name) (1399) + TX, sodium hexafluorosilicate (1400) + TX, sodium pentachlorophenoxide (623) + TX, sodium selenate (IUPAC name) (1401) + TX, sodium thiocyanate [CCN] + TX, sophamide (1402) + TX, spinosad (737) + TX, spiromesifen (739) + TX, spirotetmat (CCN) + TX, sulcofuron (746) + TX, sulcofuron-sodium (746) + TX, sulfluramid (750) + TX, sulfotep (753) + TX, sulphuryl fluoride (756) +

25 TX, sulprofos (1408) + TX, tar oils (alternative name) (758) + TX, tau-fluvalinate (398) + TX, tazimcarb (1412) + TX, TDE (1414) + TX, tebufenozide (762) + TX, tebufenpyrad (763) + TX, tebupirimfos (764) + TX, teflubenzuron (768) + TX, tefluthrin (769) + TX, temephos (770) + TX, TEPP (1417) + TX, terallethrin (1418) + TX, terbam (alternative

30 name) + TX, terbufos (773) + TX, tetrachloroethane [CCN] + TX, tetrachlorvinphos (777) + TX, tetramethrin (787) + TX, theta-cypermethrin (204) + TX, thiacloprid (791) + TX, thiafenox (alternative name) + TX, thiamethoxam (792) + TX, 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)

35 + TX, thiosultap (803) + TX, thiosultap-sodium (803) + TX, thuringiensin (alternative

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name) [CCN] + TX, tolfenpyrad (809) + TX, tralomethrin (812) + TX, transfluthrin (813) + TX, transpermethrin (1440) + TX, triamiphos (1441) + TX, triazamate (818) + TX, triazophos (820) + TX, triazuron (alternative name) + TX, trichlorfon (824) + TX, trichlormetaphos-3 (alternative name) [CCN] + TX, trichloronat (1452) + TX, trifenofos (1455) + TX, triflumuron (835) + TX, trimethacarb (840) + TX, triprene (1459) + TX, vamidothion (847) + TX, vaniliprole [CCN] + TX, veratridine (alternative name) (725) + TX, veratrine (alternative name) (725) + TX, XMC (853) + TX, xylylcarb (854) + TX, YI-5302 (compound code) + TX, zeta-cypermethrin (205) + TX, zetamethrin (alternative name) + TX, zinc phosphide (640) + TX, zolaprofos (1469) and ZXI 8901 (development code) (858) + TX, cyantraniliprole [736994-63-19 + TX, chlorantraniliprole [500008-45-7] + TX, cyenopyrafen [560121-52-0] + TX, cyflumetofen [400882-07-7] + TX, pyrifluquinazon [337458-27-2] + TX, spinetoram [187166-40-1 + 187166-15-0] + TX, spirotetramat [203313-25-1] + TX, sulfoxaflor [946578-00-3] + TX, flufiprole [704886-18-0] + TX, meperfluthrin [915288-13-0] + TX, tetramethylfluthrin [84937-88-2] + TX,

15 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,

20 pentachlorophenol (623) + TX, sodium pentachlorophenoxide (623) + TX, tazimcarb (1412) + TX, thiodicarb (799) + TX, tributyltin oxide (913) + TX, trifenmorph (1454) + TX, trimethacarb (840) + TX, triphenyltin acetate (IUPAC name) (347) and triphenyltin hydroxide (IUPAC name) (347) + TX, pyriprole [394730-71-3] + TX,

a nematicide selected from the group of substances consisting of AKD-3088 (compound code) + TX, 1,2-dibromo-3-chloropropane (IUPAC/Chemical Abstracts name) (1045) + TX,

25 1,2-dichloropropane (IUPAC/ Chemical Abstracts name) (1062) + TX, 1,2-dichloropropane with 1,3-dichloropropene (IUPAC name) (1063) + TX, 1,3-dichloropropene (233) + TX, 3,4-dichlorotetrahydrothiophene 1,1-dioxide (IUPAC/Chemical Abstracts name) (1065) + TX, 3-(4-chlorophenyl)-5-methylrhodanine (IUPAC name) (980) + TX, 5-methyl-6-thioxo-1,3,5-

30 thiadiazinan-3-ylacetic acid (IUPAC name) (1286) + TX, 6-isopentenylaminopurine (alternative name) (210) + TX, abamectin (1) + TX, acetoprole [CCN] + TX, alanycarb (15) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, AZ 60541 (compound code) + TX, benclothiaz [CCN] + TX, benomyl (62) + TX, butylpyridaben (alternative name) + TX, cadusafos (109) + TX, carbofuran (118) + TX, carbon disulfide (945) + TX, carbosulfan (119) + TX, chloropicrin (141) + TX, chlorpyrifos (145) + TX, cloethocarb (999) + TX,

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cytokinins (alternative name) (210) + TX, dazomet (216) + TX, DBCP (1045) + TX, DCIP (218) + TX, diamidafos (1044) + TX, dichlofenthion (1051) + TX, dicliphos (alternative name) + TX, dimethoate (262) + TX, doramectin (alternative name) [CCN] + TX, emamectin (291) + TX, emamectin benzoate (291) + TX, eprinomectin (alternative name) [CCN] + TX, ethoprophos (312) + TX, ethylene dibromide (316) + TX, fenamiphos (326) + TX, fenpyrad (alternative name) + TX, fensulfothion (1158) + TX, fosthiazate (408) + TX, fosthietan (1196) + TX, furfural (alternative name) [CCN] + TX, GY-81 (development code) (423) + TX, heterophos [CCN] + TX, iodomethane (IUPAC name) (542) + TX, isamidofos (1230) + TX, isazofos (1231) + TX, ivermectin (alternative name) [CCN] + TX, kinetin (alternative name) (210) + TX, mecarphon (1258) + TX, metam (519) + TX, metam-potassium (alternative name) (519) + TX, metam-sodium (519) + TX, methyl bromide (537) + TX, methyl isothiocyanate (543) + TX, milbemycin oxime (alternative name) [CCN] + TX, moxidectin (alternative name) [CCN] + TX, *Myrothecium verrucaria* composition (alternative name) (565) + TX, NC-184 (compound code) + TX, oxamyl (602) + TX, phorate (636) + TX, phosphamidon (639) + TX, phosphocarb [CCN] + TX, sebufos (alternative name) + TX, selamectin (alternative name) [CCN] + TX, spinosad (737) + TX, terbam (alternative name) + TX, terbufos (773) + TX, tetrachlorothiophene (IUPAC/ Chemical Abstracts name) (1422) + TX, thiafenox (alternative name) + TX, thionazin (1434) + TX, triazophos (820) + TX, triazuron (alternative name) + TX, xylenols [CCN] + TX, YI-5302 (compound code) and zeatin (alternative name) (210) + TX, fluensulfone [318290-98-1] + TX,

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

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

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

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- 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,
- 5 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,
- 10 a synergist selected from the group of substances consisting of 2-(2-butoxyethoxy)ethyl piperonylate (IUPAC name) (934) + TX, 5-(1,3-benzodioxol-5-yl)-3-hexylcyclohex-2-enone (IUPAC name) (903) + TX, farnesol with nerolidol (alternative name) (324) + TX, MB-599 (development code) (498) + TX, MGK 264 (development code) (296) + TX, piperonyl butoxide (649) + TX, piprotal (1343) + TX, propyl isomer (1358) + TX, S421
- 15 (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
- 20 (422) + TX, guazatine acetates (422) + TX, methiocarb (530) + TX, pyridin-4-amine (IUPAC name) (23) + TX, thiram (804) + TX, trimethacarb (840) + TX, zinc naphthenate [CCN] and ziram (856) + TX,
- a virucide selected from the group of substances consisting of imanin (alternative name) [CCN] and ribavirin (alternative name) [CCN] + TX,
- 25 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,
- 30 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,
- 35 myclobutanil [88671-89-0] + TX, pefurazoate [101903-30-4] + TX, penconazole [66246-88-

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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

5 [131983-72-7] + TX, ancymidol [12771-68-5] + TX, fenarimol [60168-88-9] + TX, nuarimol [63284-71-9] + TX, bupirimate [41483-43-6] + TX, dimethirimol [5221-53-4] + TX, ethirimol [23947-60-6] + TX, dodemorph [1593-77-7] + TX, fenpropidine [67306-00-7] + TX, fenpropimorph [67564-91-4] + TX, spiroxamine [118134-30-8] + TX, tridemorph [81412-43-3] + TX, cyprodinil [121552-61-2] + TX, mepanipyrim [110235-47-7] + TX,

10 pyrimethanil [53112-28-0] + TX, fencpiclonil [74738-17-3] + TX, fludioxonil [131341-86-1] + TX, benalaxyl [71626-11-4] + TX, furalaxyl [57646-30-7] + TX, metalaxyl [57837-19-1] + TX, R-metalaxyl [70630-17-0] + TX, ofurace [58810-48-3] + TX, oxadixyl [77732-09-3] + TX, benomyl [17804-35-2] + TX, carbendazim [10605-21-7] + TX, debacarb [62732-91-6] + TX, fuberidazole [3878-19-1] + TX, thiabendazole [148-79-8] + TX, chlozolate [84332-

15 86-5] + TX, dichlozoline [24201-58-9] + TX, iprodione [36734-19-7] + TX, myclozoline [54864-61-8] + TX, procymidone [32809-16-8] + TX, vinclozoline [50471-44-8] + TX, boscalid [188425-85-6] + TX, carboxin [5234-68-4] + TX, fenfuram [24691-80-3] + TX, flutolanil [66332-96-5] + TX, mepronil [55814-41-0] + TX, oxycarboxin [5259-88-1] + TX, penthiopyrad [183675-82-3] + TX, thifluzamide [130000-40-7] + TX, guazatine [108173-90-

20 6] + TX, dodine [2439-10-3] [112-65-2] (free base) + TX, iminoctadine [13516-27-3] + TX, azoxystrobin [131860-33-8] + TX, dimoxystrobin [149961-52-4] + TX, enestroburin {Proc. BCPC, Int. Congr., Glasgow, 2003, 1, 93} + TX, fluoxastrobin [361377-29-9] + TX, kresoxim-methyl [143390-89-0] + TX, metominostrobin [133408-50-1] + TX, trifloxystrobin [141517-21-7] + TX, orysastrobin [248593-16-0] + TX, picoxystrobin [117428-22-5] + TX,

25 pyraclostrobin [175013-18-0] + TX, ferbam [14484-64-1] + TX, mancozeb [8018-01-7] + TX, maneb [12427-38-2] + TX, metiram [9006-42-2] + TX, propineb [12071-83-9] + TX, thiram [137-26-8] + TX, zineb [12122-67-7] + TX, ziram [137-30-4] + TX, captafol [2425-06-1] + TX, captan [133-06-2] + TX, dichlofluanid [1085-98-9] + TX, fluoroimide [41205-21-4] + TX, folpet [133-07-3] + TX, tolylfluanid [731-27-1] + TX, bordeaux mixture [8011-

30 63-0] + TX, copperhydroxid [20427-59-2] + TX, copperoxychlorid [1332-40-7] + TX, coppersulfat [7758-98-7] + TX, copperoxid [1317-39-1] + TX, mancopper [53988-93-5] + TX, oxine-copper [10380-28-6] + TX, dinocap [131-72-6] + TX, nitrothal-isopropyl [10552-74-6] + TX, edifenphos [17109-49-8] + TX, iprobenphos [26087-47-8] + TX, isoprothiolane [50512-35-1] + TX, phosdiphen [36519-00-3] + TX, pyrazophos [13457-18-

35 6] + TX, tolclofos-methyl [57018-04-9] + TX, acibenzolar-S-methyl [135158-54-2] + TX,

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anilazine [101-05-3] + TX, benthiavalicarb [413615-35-7] + TX, blasticidin-S [2079-00-7] + TX, chinomethionat [2439-01-2] + TX, chloroneb [2675-77-6] + TX, chlorothalonil [1897-45-6] + TX, cyflufenamid [180409-60-3] + TX, cymoxanil [57966-95-7] + TX, dichlone [117-80-6] + TX, diclocymet [139920-32-4] + TX, diclomezine [62865-36-5] + TX, dicloran
 5 [99-30-9] + TX, diethofencarb [87130-20-9] + TX, dimethomorph [110488-70-5] + TX, SYP-LI90 (Flumorph) [211867-47-9] + TX, dithianon [3347-22-6] + TX, ethaboxam [162650-77-3] + TX, etridiazole [2593-15-9] + TX, famoxadone [131807-57-3] + TX, fenamidone [161326-34-7] + TX, fenoxanil [115852-48-7] + TX, fentin [668-34-8] + TX, ferimzone [89269-64-7] + TX, fluazinam [79622-59-6] + TX, fluopicolide [239110-15-7] +
 10 TX, flusulfamide [106917-52-6] + TX, fenhexamid [126833-17-8] + TX, fosetyl-aluminium [39148-24-8] + TX, hymexazol [10004-44-1] + TX, iprovalicarb [140923-17-7] + TX, IKF-916 (Cyazofamid) [120116-88-3] + TX, kasugamycin [6980-18-3] + TX, methasulfo-
 carb [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] +
 15 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, sulphur [7704-34-9] + TX, tiadinil [223580-51-6] + TX, triazoxide [72459-58-6] + TX, tricyclazole [41814-78-2] + TX, triforine [26644-46-2] + TX, validamycin [37248-47-8] + TX, zoxamide (RH7281) [156052-68-5] + TX, mandipropamid [374726-62-2] + TX, isopyrazam [881685-
 20 58-1] + TX, sedaxane [874967-67-6] + TX, 3-difluoromethyl-1-methyl-1H-pyrazole-4-
 carboxylic acid (9-dichloromethylene-1,2,3,4-tetrahydro-1,4-methano-naphthalen-5-yl)-amide (dislosed in WO 2007/048556) + TX, 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic
 acid (3',4',5'-trifluoro-biphenyl-2-yl)-amide (dislosed in WO 2006/087343) + TX,
 [(3S,4R,4aR,6S,6aS,12R,12aS,12bS)-3-[(cyclopropylcarbonyl)oxy]-
 25 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 and 1,3,5-trimethyl-N-(2-methyl-1-oxopropyl)-
 N-[3-(2-methylpropyl)-4-[2,2,2-trifluoro-1-methoxy-1-(trifluoromethyl)ethyl]phenyl]-1H-
 pyrazole-4-carboxamide [926914-55-8] + TX.

30

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
 35 Protection Council], they are described therein under the entry number given in round

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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
5 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
10 in individual cases. If the designation is not a "common name", the nature of the designation used instead is given in round brackets for the particular compound; in that case, the IUPAC name, the IUPAC/Chemical Abstracts name, a "chemical name", a "traditional name", a "compound name" or a "development code" is used or, if neither one of those designations nor a "common name" is used, an "alternative name" is employed. "CAS Reg. No" means the
15 Chemical Abstracts Registry Number.

The active ingredient mixture of the compounds of formula I selected from Table 1 with active ingredients described above comprises a compound selected from Table 1 and an active ingredient as described above preferably in a mixing ratio of from 100:1 to 1:6000, especially
20 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
25 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 understood to include, on the one hand, ratios by weight and also, on other hand, molar ratios.

The mixtures as described above can be used in a method for controlling pests, which
30 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 Table 1 and one or more
35 active ingredients as described above can be applied, for example, in a single "ready-mix"

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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 Table 1 and the active ingredients as described above is not essential for working the present invention.

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

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

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

A preferred method of application in the field of crop protection is application to the foliage of the plants (foliar application), it being possible to select frequency and rate of application to match the danger of infestation with the pest in question. Alternatively, the active ingredient can reach the plants via the root system (systemic action), by drenching the locus of the plants with a liquid composition or by incorporating the active ingredient in solid form into the

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locus of the plants, for example into the soil, for example in the form of granules (soil application). In the case of paddy rice crops, such granules can be metered into the flooded paddy-field.

- 5 The compositions according to the invention are also suitable for the protection of plant propagation material, for example seeds, such as fruit, tubers or kernels, or nursery plants, against pests of the abovementioned type. The propagation material can be treated with the compositions prior to planting, for example seed can be treated prior to sowing. Alternatively, the compositions can be applied to seed kernels (coating), either by soaking the kernels in a liquid composition or by applying a layer of a solid composition. It is also possible to apply the compositions when the propagation material is planted to the site of application, for example into the seed furrow during drilling. These treatment methods for plant propagation material and the plant propagation material thus treated are further subjects of the invention.

- 15 Biological Examples (% = per cent by weight, unless otherwise specified)

Example B1: Activity against *Myzus persicae* (green peach aphid)

(mixed population, feeding/residual contact activity, preventive)

- 20 Sunflower leaf discs were placed on agar in a 24-well microtiter plate and sprayed with test solutions. After drying, the leaf discs were infested with an aphid population of mixed ages. After an incubation period of 6 days, samples were checked for mortality and special effects (e.g. phytotoxicity). In this test, compounds No. 1.005, 1.009, 1.014, 1.019, 1.022, 1.023, 1.024 and 1.026 showed an activity of over 80% at a concentration of 200 ppm.

- 25 Example B2: Activity against *Bemisia tabaci* (cotton white fly):

(Adults, feeding/residual contact activity, preventive)

- 30 Cotton leaf discs are placed on agar in a 24-well microtiter plate and sprayed with test solutions. After drying, the leaf discs are infested with 12 to 18 adults. After an incubation period of 6 days after infestation, samples are checked for mortality and special effects (e.g. phytotoxicity). In this test, compounds 1.006, 1.024 and 1.028 showed an activity of over 80% at a concentration of 200 ppm.

Example B3: Activity against *Thrips tabaci* (Onion Thrips):

(feeding/residual contact activity, preventive)

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Sunflower leaf discs are placed on agar in a 24-well microtiter plate and sprayed with test solutions. After drying, the leaf discs are infested with a thrips population of mixed ages. After an incubation period of 7 days after infestation, samples are checked for mortality and special effects (e.g. phytotoxicity).

- 5 In this test, compound 1.019 showed an activity of over 80% at a concentration of 200 ppm.

Example B4: Activity against *Aphis craccivora* (Black bean aphid):

(mixed population, contact/feeding)

- 10 Pea seedlings, infested with an aphid population of mixed ages, are treated with diluted test solutions in a spray chamber. 6 days after treatment, samples are checked for mortality.

In this test, compounds No. 1.006, 1.014 and 1.024 showed an activity of over 80% at a concentration of 12.5 ppm.

Example B5: Activity against *Aonidiella aurantii* (Citrus red scale)

- 15 (larvicide, contact/feeding)

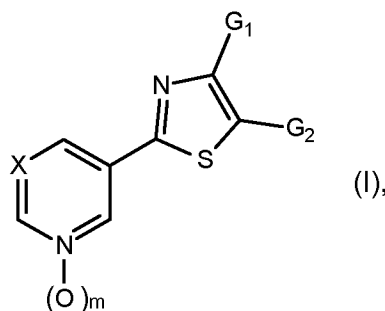
Potato tubers are infested with about 50 crawlers. After a 2 week settling period, the N₂ nymphs are treated through dipping the tubers in the test solution. 4-6 weeks after treatment, samples are checked for number of crawlers from the next generation.

- 20 In this test, compounds No. 1.006, 1.014 and 1.024 showed an activity of over 85% at a concentration of 50 ppm.

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What is claimed is:

1. A compound of formula I



5 wherein

X is nitrogen or CR₇;

m is 0 or 1;

G₁ is a three- to four- membered ring which can be partially saturated or fully saturated and can contain one heteroatom selected from the group consisting of nitrogen, oxygen and

10 sulphur; said three- to four- membered ring system can be mono- to polysubstituted by substituents independently selected from the group consisting of halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆alkylthio, C₁-C₆alkylamino and C₁-C₆di-alkylamino; or

G₁ is C₂-C₆alkenyl which can be mono- to polysubstituted by substituents independently selected from the group consisting of halogen, C₁-C₆alkyl and C₁-C₆haloalkyl; with the

15 proviso that if the double bond is not directly connected to the ring then the substituents on the carbon between the thiazole and the unsaturation are different from halogen; or

G₁ is C₂-C₆alkynyl which can be substituted by substituents independently selected from the group consisting of halogen, C₁-C₆alkyl and C₁-C₆haloalkyl; with the proviso that if the triple bond is not directly connected to the ring then the substituents on the carbon between the

20 thiazole and the unsaturation are different from halogen;

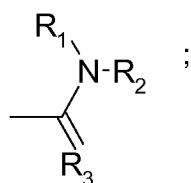
G₂ is a five- to ten-membered monocyclic or fused bicyclic ring system which can be aromatic, partially saturated or fully saturated and can contain 1 to 4 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, it not being possible for each ring system to contain more than 2 oxygen atoms and more than 2 sulfur atoms, said five- to ten-

25 membered ring system can be mono- to polysubstituted by substituents independently selected from the group consisting of halogen, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆alkylthio, C₁-C₆alkoxycarbonyl, C₁-C₆alkylamino, C₁-C₆di-alkylamino, C₁-C₆alkoxycarbonylamino, pyrimidinyl, thiazolyl, pyridinyl, pyrazinyl, pyridazinyl, pyrazinyloxy, imidazolyl, dihydro-

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oxazolyl, oxazolyl, dioxolanyl, 1,3-dioxanyl and 5,6-dihydro-[1,4,2]dioxazinyl; wherein said pyrimidinyl, thiazolyl, pyridinyl, pyrazinyl, pyridazinyl, pyrazinyloxy, imidazolyl, dihydro-oxazolyl, oxazolyl, dioxolanyl, 1,3-dioxanyl and 5,6-dihydro-[1,4,2]dioxazinyl can be mono- to polysubstituted by substituents independently selected from the group consisting of halogen, C₁-C₆alkyl, di-C₁-C₄alkyl-phosphinoylmethyl-aminocarbonyl, C₁-C₆alkoxycarbonylamino, C₁-C₆alkoxy, C₁-C₆alkylthio, C₁-C₆alkylamino, C₁-C₆di-alkylamino, pyridinyl, pyrimidinyl, pyrazinyloxy and oxazolyl, wherein said pyridinyl, pyrimidinyl, pyrazinyloxy and oxazolyl can be substituted by substituents independently selected from the group consisting of halogen, C₁-C₆alkyl and C₁-C₆alkoxy; or

G₂ is



wherein

R₁ is hydrogen, C₁-C₆alkyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₃-C₆cycloalkyl, C₁-C₆alkylthio, C₁-C₆haloalkyl, C₁-

C₆alkylsulfanyl, C₁-C₆alkylsulfonyl, halogen, cyano, hydroxy, C₁-C₆alkoxy, C₂-C₆alkenyl, C₂-C₆alkynyl, C₁-C₆alkoxy-C₃-C₆alkynyl, oxolanyl, dioxolanyl, thienyl, thietanyl, thiethanyloxy, thiethanyldioxide, di-C₁-C₄alkyl-phosphinoylmethyl, 1-H-benzimidazol-2-yl,

benzo[1,3]dioxolyl, morpholinyl, piperidinyl, pyrimidinyl, pyrrolidinyl, benzylthio, 2,3-dihydro-benzo[1,4]dioxinyl, 1H-indolyl, furyl, -C=N-O-C₁-C₆alkyl, C₁-C₆alkylcarbonylamino, phenoxy

and phenyl, said phenyl can be mono- to polysubstituted by substituents selected from the group consisting of hydroxy, halogen, C₁-C₆alkoxy, C₁-C₆haloalkoxy, pyrazolyl, piperidinyl, phenoxy and C₁-C₄alkylsulfonyl;

or R₁ is C₁-C₆alkyl, which is substituted by pyridyl, wherein said pyridyl can be mono- to polysubstituted by substituents selected from the group consisting of halogen and C₁-

C₄haloalkyl;

or R₁ is C₁-C₆alkyl, which is substituted by phenoxy, wherein said phenoxy can be mono- to polysubstituted by substituents selected from the group consisting of halogen and C₁-C₄alkyl;

or R₁ is C₁-C₆alkyl, which is substituted by phenylcarbonyl, wherein said phenylcarbonyl can be mono- to polysubstituted by substituents selected from the group consisting of halogen

and C₁-C₄haloalkoxy;

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or R₁ is C₁-C₆alkyl, which is substituted by imidazolynyl, wherein said imidazolynyl can be mono- to polysubstituted by C₁-C₄alkyl;

or R₁ is C₁-C₆alkyl, which is substituted by isoxazolyl, wherein said isoxazolyl can be mono- to polysubstituted by halo-substituted phenyl;

5 or R₁ is pyridyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₄alkyl, C₁-C₄alkoxycarbonyl, phenyl and phenoxy;

or R₁ is pyrimidinyl, which can be mono- to polysubstituted by substituents selected from the group consisting of hydroxy, C₁-C₄alkoxy and C₁-C₄alkyl;

or R₁ is piperazinyl, which can be monosubstituted by benzyl;

10 or R₁ is piperidinyl, which can be mono- to polysubstituted by C₁-C₄alkyl;

or R₁ is pyrazolyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₄alkyl, cyano and phenyl;

or R₁ is thiethanyl, which can be substituted by C₁-C₄alkyl;

or R₁ is dihydro-thiophene-2-one-3-yl;

15 or R₁ is C₃-C₆cycloalkyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₃-C₆cycloalkyl, C₂-C₆alkynyl and =N-O-C₁-C₄haloalkyl;

or R₁ is azetidynyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₄haloalkyl and benzyl;

or R₁ is pyrrolidinyl which can be substituted by benzyl;

20 or R₁ is C₁-C₆alkoxycarbonylamino;

or R₁ is C₃-C₆cycloalkenyl which can be mono- to polysubstituted by C₁-C₆alkoxycarbonyl;

or R₁ is phenyl, which can be mono- to polysubstituted by substituents selected from the group consisting of halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkylthio, di(C₁-C₄alkyl)aminosulfonyl, C₁-C₄alkoxy, phenyl, piperidyl, pyrrolyl, morpholynyl, indolyl,

25 phenylcarbonyl and C₁-C₄alkoxycarbonyl;

or R₁ is quinolynyl, benzothiazolyl, oxolanyl or indazolyl;

or R₁ is benzothiophenyl, which can be monosubstituted by C₁-C₆alkoxycarbonyl;

or R₁ is thiazolyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₄alkyl, pyridyl, phenyl, pyrimidinyl and C₁-C₄alkylcarbonyl; wherein

30 said phenyl can be mono- to polysubstituted by C₁-C₄alkyl and wherein said pyrimidinyl can be mono- to polysubstituted by C₁-C₄alkoxy;

or R₁ is benzothiazolyl which can be mono- to polysubstituted by C₁-C₄alkyl;

or R₁ is chromen-2-one which can be mono- to polysubstituted by C₁-C₄alkyl;

or R₁ is isoxazolyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₄alkyl and phenyl;

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or R₁ is thiadiazolyl, which can be monosubstituted by substituents selected from the group consisting of C₁-C₄alkyl and halo-substituted phenyl;

or R₁ is furyl which can be mono- to polysubstituted by substituents selected from the group consisting of cyano and phenyl;

- 5 or R₁ is pyrazolopyridinyl which can be mono- to polysubstituted by C₁-C₄alkyl; or R₁ is thienyl which can be mono- to polysubstituted by C₁-C₄alkoxycarbonyl; or R₁ is thietanyloxide, thiethanyldioxide, bicyclo[2.2.1]heptyl or tetrahydrothienyl;

or R₁ is isoxazolidin-3-one, which can be monosubstituted by substituents selected from C₁-C₄alkyl and C₁-C₄haloalkyl;

- 10 or R₁ and R₂ form together with the nitrogen atom to which they are bonded a 3- to 6-membered saturated ring which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₄alkyl, C₁-C₄alkoxy and halogen; and further mono- to polysubstituted by substituents selected from the group consisting of phenylcarbonyl, phenoxy-C₁-C₄alkyl and phenoxy, wherein said phenylcarbonyl, phenoxy-C₁-C₄alkyl and phenoxy can be mono- to polysubstituted by halogen; and said saturated ring
- 15 can be additionally substituted by an ethylene chain;

R₂ is hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl or C₃-C₆cycloalkyl;

R₃ is oxygen, sulfur, NR₈ or NOR₈;

- R₈ is hydrogen, cyano, C₁-C₆alkyl, C₂-C₆alkenyl, C₃-C₁₀cycloalkyl, C₃-C₁₀cycloalkenyl, a
- 20 three- to ten-membered, monocyclic or fused bicyclic ring system which may be aromatic, partially saturated or fully saturated, S(O)_nC₁-C₆alkyl or N(C₁-C₆alkyl)₂; or

R₈ is C₁-C₆alkyl, C₂-C₆alkenyl, C₃-C₁₀cycloalkyl, C₃-C₁₀cycloalkenyl or a three- to ten-membered, monocyclic or fused bicyclic ring system which can be aromatic, partially

- 25 saturated or fully saturated; each mono- to polysubstituted by substituents independently selected from the group consisting of fluoro, chloro, bromo, iodo, cyano, nitro, C₁-C₆alkyl, C₂-C₆alkenyl, C₁-C₆haloalkyl, C₂-C₆haloalkenyl, C₁-C₆haloalkoxy, C₂-C₆haloalkenyloxy, C₃-C₁₀cycloalkyl, C₃-C₁₀cycloalkenyl, C₃-C₁₀halocycloalkyl, C₃-C₁₀halocycloalkenyl, OC₁-C₆alkyl, OC₁-C₆haloalkyl, S(O)_nC₁-C₆alkyl, S(O)_nOC₁-C₆alkyl and by a three- to ten-membered, monocyclic or fused bicyclic ring system which may be aromatic, partially saturated or fully
- 30 saturated; and

n is 0, 1, or 2; and agrochemically acceptable salts, enantiomers, tautomers and N-oxides of those compounds.

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

-78-

G₁ is a three- to four- membered ring which can be partially saturated or fully saturated and can contain one heteroatom selected from the group consisting of nitrogen, oxygen and sulphur; said three- to four- membered ring system can be mono- to polysubstituted by substituents independently selected from the group consisting of halogen, methyl and

5 trifluoromethyl; or

G₁ is C₂-C₆alkenyl which can be mono- to polysubstituted by substituents independently selected from the group consisting of halogen, methyl and trifluoromethyl; or

G₁ is C₂-C₆alkynyl which can be substituted by substituents selected from the group consisting of halogen, methyl and trifluoromethyl;

10 G₂ is selected from the group consisting of J-1 to J-24



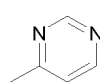
J-1



J-2



J-3



J-4



J-5



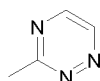
J-6



J-7



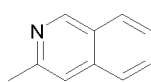
J-8



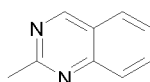
J-9



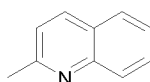
J-10



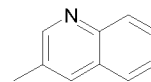
J-11



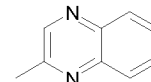
J-12



J-13



J-14



J-15



J-16



J-17



J-18



J-19



J-20



J-21



J-22



J-23



J-24

wherein each group J-1 to J-24 is mono- di- or trisubstituted with Rx, wherein

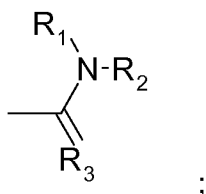
Rx is halogen, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆alkylthio, C₁-C₆alkoxycarbonyl, C₁-C₆alkylamino, C₁-C₆di-alkylamino, C₁-C₆alkoxycarbonylamino, pyrimidinyl, thiazolyl, pyridinyl, pyrazinyl, pyridazinyl, pyrazinyloxy, imidazolyl, dihydro-oxazolyl, oxazolyl, dioxolanyl, 1,3-dioxanyl and 5,6-dihydro-[1,4,2]dioxazinyl, wherein said pyrimidinyl, thiazolyl, pyridinyl, pyrazinyl, pyridazinyl, pyrazinyloxy, imidazolyl, dihydro-oxazolyl, oxazolyl, dioxolanyl, 1,3-dioxanyl and 5,6-dihydro-[1,4,2]dioxazinyl can be mono- to polysubstituted by substituents

15

-79-

independently selected from the group consisting of halogen, C₁-C₆alkyl, di-C₁-C₄alkyl-phosphinoylmethyl-aminocarbonyl, C₁-C₆alkoxycarbonylamino, C₁-C₆alkoxy, C₁-C₆alkylthio, C₁-C₆alkylamino, C₁-C₆di-alkylamino, pyridinyl, pyrimidinyl, pyrazinyloxy and oxazolyl, wherein said pyridinyl, pyrimidinyl, pyrazinyloxy and oxazolyl can be mono- to polysubstituted
 5 by substituents independently selected from the group consisting of halogen, C₁-C₆alkyl and C₁-C₆alkoxy; or

G₂ is



wherein

- 10 R₁ is hydrogen, C₁-C₆alkyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₃-C₆cycloalkyl, C₁-C₆alkylthio, C₁-C₆haloalkyl, C₁-C₆alkylsulfinyl, C₁-C₆alkylsulfonyl, halogen, cyano, hydroxy, C₁-C₆alkoxy, C₂-C₆alkenyl, C₂-C₆alkynyl, C₁-C₆alkoxy-C₃-C₆alkynyl, oxolanyl, dioxolanyl, thienyl, thietanyl, thiethanyldioxide, 1-H-benzoimidazol-2-yl, benzo[1,3]dioxolyl, morpholinyl, piperidinyl,
 15 pyrimidinyl, pyrrolidinyl, benzylthio, 2,3-dihydro-benzo[1,4]dioxinyl, 1H-indolyl, furyl, -C=N-O-C₁-C₆alkyl, C₁-C₆alkylcarbonylamino, phenoxy and phenyl, said phenyl can be mono- to polysubstituted by substituents selected from the group consisting of hydroxy, halogen, C₁-C₆alkoxy, C₁-C₆haloalkoxy, pyrazolyl, piperidinyl, phenoxy and C₁-C₄alkylsulfonyl;
 or R₁ is C₁-C₆alkyl, which is substituted by pyridyl, wherein said pyridyl can be mono- to
 20 polysubstituted by substituents selected from the group consisting of halogen and C₁-C₄haloalkyl;
 or R₁ is C₁-C₆alkyl, which is substituted by phenoxy, wherein said phenoxy can be mono- to polysubstituted by substituents selected from the group consisting of halogen and C₁-C₄alkyl;
 or R₁ is C₁-C₆alkyl, which is substituted by phenylcarbonyl, wherein said phenylcarbonyl can
 25 be mono- to polysubstituted by substituents selected from the group consisting of halogen and C₁-C₄haloalkoxy;
 or R₁ is C₁-C₆alkyl, which is substituted by imidazolyl, wherein said imidazolyl can be mono- to polysubstituted by C₁-C₄alkyl;
 or R₁ is C₁-C₆alkyl, which is substituted by isoxazolyl, wherein said isoxazolyl can be mono-
 30 to polysubstituted by halo-substituted phenyl;

-80-

or R₁ is pyridyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₄alkyl, C₁-C₄alkoxycarbonyl, phenyl and phenoxy;

or R₁ is pyrimidinyl which can be mono- to polysubstituted by substituents selected from the group consisting of hydroxy, C₁-C₄alkoxy and C₁-C₄alkyl;

5 or R₁ is piperazinyl, which can be monosubstituted by benzyl;

or R₁ is piperidinyl, which can be mono- to polysubstituted by C₁-C₄alkyl;

or R₁ is pyrazolyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₄alkyl, cyano and phenyl;

or R₁ is thiethanyl, which can be substituted by C₁-C₄alkyl;

10 or R₁ is dihydro-thiophene-2-one-3-yl;

or R₁ is C₃-C₆cycloalkyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₃-C₆cycloalkyl, C₂-C₆alkynyl and =N-O-C₁-C₄haloalkyl;

or R₁ is azetidyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₄haloalkyl and benzyl;

15 or R₁ is pyrrolidinyl which can be substituted by benzyl;

or R₁ is C₁-C₆alkoxycarbonylamino;

or R₁ is C₃-C₆cycloalkenyl which can be mono- to polysubstituted by C₁-C₆alkoxycarbonyl;

or R₁ is phenyl, which can be mono- to polysubstituted by substituents selected from the group consisting of halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkylthio, di(C₁-

20 C₄alkyl)aminosulfonyl, C₁-C₄alkoxy, phenyl, piperidyl, pyrrolyl, morpholyl, indolyl, phenylcarbonyl and C₁-C₄alkoxycarbonyl;

or R₁ is quinolyl, benzothiazolyl, oxolanyl or indazolyl;

or R₁ is benzothiophenyl, which can be monosubstituted by C₁-C₆alkoxycarbonyl;

or R₁ is thiazolyl, which can be mono- to polysubstituted by substituents selected from the

25 group consisting of C₁-C₄alkyl, pyridyl, phenyl, pyrimidinyl and C₁-C₄alkylcarbonyl; wherein said phenyl can be mono- to polysubstituted by C₁-C₄alkyl and wherein said pyrimidinyl can be mono- to polysubstituted by C₁-C₄alkoxy;

or R₁ is benzothiazolyl which can be mono- to polysubstituted by C₁-C₄alkyl;

or R₁ is chromen-2-one which can be mono- to polysubstituted by C₁-C₄alkyl;

30 or R₁ is isoxazolyl, which in can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₄alkyl and phenyl;

or R₁ is thiadiazolyl, which can be monosubstituted by substituents selected from the group consisting of C₁-C₄alkyl and halo-substituted phenyl;

35 or R₁ is furyl which can be mono- to polysubstituted by substituents selected from the group consisting of cyano and phenyl;

-81-

or R₁ is pyrazolopyridinyl which can be mono- to polysubstituted by C₁-C₄alkyl; or R₁ is thienyl which can be mono- to polysubstituted by C₁-C₄alkoxycarbonyl; or R₁ is thietanyloxide, thiethanyldioxide, bicyclo[2.2.1]heptyl or tetrahydrothienyl;

or R₁ is isoxazolidin-3-one, which can be monosubstituted by substituents selected from C₁-C₄alkyl and C₁-C₄haloalkyl;

or R₁ and R₂ form together with the nitrogen atom to which they are bonded a 3- to 6-membered saturated ring which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₄alkyl, C₁-C₄alkoxy and halogen; and further mono- to polysubstituted by substituents selected from the group consisting of phenylcarbonyl, phenoxy-C₁-C₄alkyl and phenoxy, wherein said phenylcarbonyl, phenoxy-C₁-C₄alkyl and phenoxy can be mono- to polysubstituted by halogen; and said saturated ring can be additionally substituted by an ethylene chain;

R₂ is hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl or C₃-C₆cycloalkyl; and R₃ is oxygen.

3. A compound of formula I according to claim 2, wherein m is 0;

G₁ is cyclopropyl, ethenyl or ethynyl;

R₇ is hydrogen, fluoro, chloro, bromo or iodo;

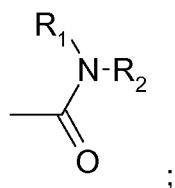
G₂ is J-1, J-4 or J-16;

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

Rx is halogen, C₁-C₆alkoxycarbonyl, pyrimidinyl, dihydro-oxazolyl, dioxolanyl, 1,3-dioxanyl and 5,6-dihydro-[1,4,2]dioxazinyl, wherein said pyrimidinyl, pyridinyl, dihydro-oxazolyl, dioxolanyl, 1,3-dioxanyl and 5,6-dihydro-[1,4,2]dioxazinyl can be mono- to polysubstituted by

C₁-C₆alkyl; or

G₂ is



wherein

R₁ is C₁-C₆alkyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₆alkylthio, C₁-C₆haloalkyl, C₁-C₆alkylsulfinyl, halogen, oxolanyl, thietanyl, thiethanyldioxide, pyrimidinyl and C₁-C₆alkylcarbonylamino;

-82-

or R₁ is C₁-C₆alkyl, which is substituted by pyridyl, wherein said pyridyl can be mono- to polysubstituted by substituents selected from the group consisting of halogen and C₁-C₄haloalkyl;

or R₁ is thiethanyl, which can be substituted by C₁-C₄alkyl;

5 or is oxolanyl;

or R₁ is thietanyloxide, thiethanyldioxide or tetrahydrothienyl; and

R₂ is hydrogen or C₁-C₆alkyl;

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

10 G₂ is J-1, J-4 or J-16;

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

Rx is halogen, C₁-C₆alkoxycarbonyl, pyrimidinyl, dihydro-oxazolyl, dioxolanyl, 1,3-dioxanyl and 5,6-dihydro-[1,4,2]dioxazinyl, wherein said pyrimidinyl, pyridinyl, dihydro-oxazolyl,

dioxolanyl, 1,3-dioxanyl and 5,6-dihydro-[1,4,2]dioxazinyl can be mono- to polysubstituted by

15 C₁-C₆alkyl.

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

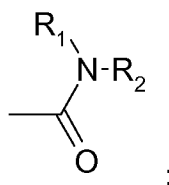
m is 0; and

R₇ is hydrogen, fluoro, chloro, bromo or iodo.

20

6. A compound of formula I according to claim 5, wherein

G₂ is



wherein

25 R₁ is C₁-C₆alkyl, which can be mono- to polysubstituted by substituents selected from the group consisting of C₁-C₆alkylthio, C₁-C₆haloalkyl, C₁-C₆alkylsulfinyl, halogen, oxolanyl, thietanyl, thiethanyldioxide, pyrimidinyl and C₁-C₆alkylcarbonylamino;

or R₁ is C₁-C₆alkyl, which is substituted by pyridyl, wherein said pyridyl can be mono- to polysubstituted by substituents selected from the group consisting of halogen and C₁-

30 C₄haloalkyl;

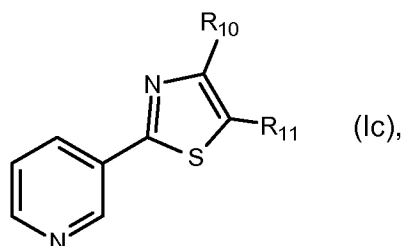
or R₁ is thiethanyl, which can be substituted by C₁-C₄alkyl;

or R₁ is oxolanyl;

-83-

or R₁ is thietanyloxide, thiethanyldioxide or tetrahydrothienyl; and
R₂ is hydrogen or C₁-C₆alkyl.

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



5

wherein

R₁₀ is C₃-C₄cycloalkyl which can be substituted by C₁-C₄haloalkyl, or is C₃-C₆cycloalkenyl which can be substituted by substituents selected from the group consisting of C₁-C₄haloalkyl and halogen, or is C₂-C₆alkenyl, C₂-C₆alkynyl, or C₂-C₆alkynyl substituted by C₁-C₄haloalkyl, or R₁₀ is a three- to four membered saturated ring which can contain one heteroatom selected from oxygen or nitro; and

10

R₁₁ is pyrimidinyl, pyridyl substituted by pyrimidinyl, or is C₁-C₄haloalkylaminocarbonyl.

8. 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.

15

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

20

10. 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 8.

25

11. Plant propagation material treated in accordance with the method described in claim 10.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/057784

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07D417/04 C07D417/14 A01N43/78
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07D A01N

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

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

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 260 765 A (HARRISON WILLIAM A ET AL) 7 April 1981 (1981-04-07) column 1, line 19 - column 2, line 22 & US 4 080 457 A (HARRISON WILLIAM A ET AL) 21 March 1978 (1978-03-21) -----	1,2,5, 8-11
A	WO 2010/006713 A2 (BAYER CROPSCIENCE AG [DE]; BRETSCHNEIDER THOMAS [DE]; FRANKEN EVA-MARI) 21 January 2010 (2010-01-21) cited in the application claims 1,8,9; tables 1,2 -----	1-5,7-11
A	WO 2009/149858 A1 (BAYER CROPSCIENCE AG [DE]; BRETSCHNEIDER THOMAS [DE]; FRANKEN EVA-MARI) 17 December 2009 (2009-12-17) cited in the application claims 1-4 ----- -/-	1-5,7-11



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 May 2013

Date of mailing of the international search report

25/07/2013

Name and mailing address of the ISA/

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Rufet, Jacques

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/057784

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2012/000896 A2 (BAYER CROPS SCIENCE AG [DE]; BRETSCHNEIDER THOMAS [DE]; FISCHER REINER []) 5 January 2012 (2012-01-05) cited in the application claims 1,2 -----	1-5,7-11
A	DATABASE REGISTRY [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; 11 April 2011 (2011-04-11), XP002684407, retrieved from STN Database accession no. 1052543-31-3 CAS Registry Number 1052543-31-3 -----	1,5
X	RONKIN S M ET AL: "Discovery of pyrazolthiazoles as novel and potent inhibitors of bacterial gyrase", BIOORGANIC & MEDICINAL CHEMISTRY LETTERS, PERGAMON, ELSEVIER SCIENCE, GB, vol. 20, no. 9, 1 May 2010 (2010-05-01), pages 2828-2831, XP027012843, ISSN: 0960-894X [retrieved on 2010-03-15] Compounds 2i, 2j, 15 -----	1,5

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/057784

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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			AU 4188172 A 08-11-1973
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			EP 2297130 A1 23-03-2011
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			KR 20110016955 A 18-02-2011
			TW 201010610 A 16-03-2010
			US 2011098287 A1 28-04-2011
			WO 2009149858 A1 17-12-2009
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			AU 2011273694 A1 07-02-2013
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			EP 2585451 A2 01-05-2013
			US 2012165345 A1 28-06-2012
			WO 2012000896 A2 05-01-2012

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2013/057784

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.:

7(completely); 1-5, 8-11(partially)

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: 7(completely); 1-5, 8-11(partially)

Compound of formula I wherein G1 is a 3 to 4 membered ring and G2 is a 5 to 10 membered ring system and their use for controlling insects

2. claims: 1-3, 5, 6, 8-11(all partially)

Compound of formula I wherein G1 is a 3 to 4 membered ring and G2 is -C(0)-NR1R2 and their use for controlling insects

3. claims: 1-5, 8-11(all partially)

Compound of formula I wherein G1 is a C2-C6 alkenyl and G2 is a 5 to 10 membered ring system and their use for controlling insects

4. claims: 1-3, 5, 6, 8-11(all partially)

Compound of formula I wherein G1 is a C2-C6 alkenyl and G2 is -C(0)-NR1R2 and their use for controlling insects

5. claims: 1-5, 8-11(all partially)

Compound of formula I wherein G1 is a C2-C6 alkynyl and G2 is a 5 to 10 membered ring system and their use for controlling insects

6. claims: 1-3, 5, 6, 8-11(all partially)

Compound of formula I wherein G1 is a C2-C6 alkynyl and G2 is -C(0)-NR1R2 and their use for controlling insects
