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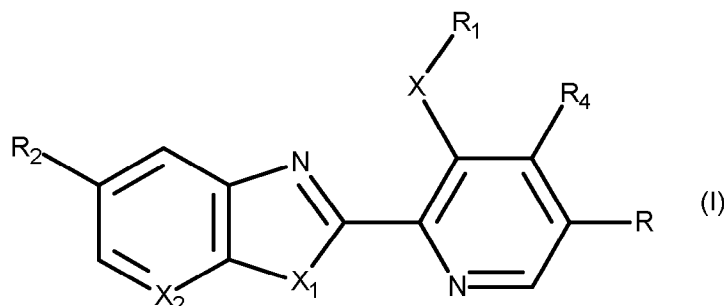
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(54) Title: PESTICIDALLY ACTIVE BICYCLIC HETEROCYCLES WITH SULPHUR CONTAINING SUBSTITUENTS



(57) Abstract: Compounds of the formula (I), and the agrochemically acceptable salts and N-oxides of those compounds, including all stereoisomers and tautomeric forms, and wherein the substituents are as defined in claim 1, are useful for controlling animal pests and can be prepared in a manner known per se.

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Pesticidally active bicyclic heterocycles with sulphur containing substituents

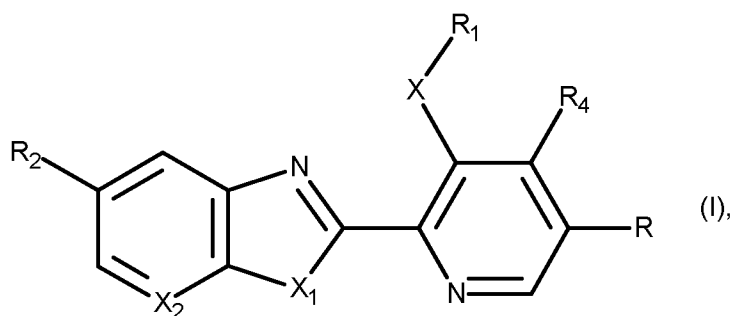
The present invention relates to insecticidally active heterocyclic sulphur containing derivatives, to processes for their preparation, to compositions comprising those compounds, and to their use for controlling animal pests (including arthropods and in particular insects or representatives of the order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

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Heterocyclic compounds with pesticidal action are known and described, for example, in WO 2009/131237, WO 2011/043404, WO 2011/040629, WO 2010/125985, WO 2012/086848, and WO 2013/018928.

10 There have now been found novel heterocyclic derivatives with pesticidal properties.

The present invention accordingly relates to compounds of formula I,



15

wherein X is S=N-R₁₀ or S(O)=N-R₁₀, wherein R₁₀ is hydrogen, nitro, cyano, C(O)R₂₆, C(O)OR₂₇, CONR₂₈R₂₉, SO₂R₃₀, CONH₂, C(S)NH₂; or R₁₀ is C₁-C₆alkyl, C₁-C₆haloalkyl, C₃-C₆cycloalkyl, C₃-C₆halocycloalkyl or C₁-C₆alkoxy-C₁-C₆alkyl;

R is hydrogen, halogen, C₁-C₄haloalkyl, OR₃₁ or S(O)_nR₃₂;

20 X₁ is O, S or N-R₃, wherein R₃ is C₁-C₄alkyl, C₁-C₄haloalkyl or C₁-C₆alkoxy-C₁-C₆alkyl, or X₁ is N-(4-methoxy-benzyl) or N-(propargyl);

X₂ is N, CH, C-halogen, C-CN, C-O-C₁-C₄alkyl, C-S-C₁-C₄alkyl, C-SO₂-C₁-C₄alkyl, C-S-phenyl, C-SO₂-phenyl or C-SO₂-C₁-C₄haloalkyl;

25 R₁ is C₁-C₆alkyl, C₁-C₆haloalkyl, C₃-C₆cycloalkyl, C₃-C₆halocycloalkyl, C₂-C₆alkenyl, C₂-C₆haloalkenyl or C₂-C₆alkynyl;

R₂ is halogen, C₁-C₄haloalkyl, OR₃₁, S(O)_nR₃₂, or SF₅;

R₄ is hydrogen or halogen;

R₂₆ is hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₃-C₆cycloalkyl, C₃-C₆halocycloalkyl or C₁-C₆alkoxy-C₁-C₆alkyl;

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R₂₇, R₂₈, R₂₉, R₃₀ independently of one another are C₁-C₆alkyl, C₁-C₆haloalkyl, C₃-C₆cycloalkyl, C₃-C₆halocycloalkyl or C₁-C₆alkoxy-C₁-C₆alkyl;

R₃₁ and R₃₂ independently of one another are C₁-C₄alkyl or C₁-C₄haloalkyl;

n is 0, 1 or 2; and

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

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 and
10 hexyl. 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.

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

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

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

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

35 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, 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,

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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.

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

Salts of compounds of formula I can be converted in the customary manner into the free compounds I, acid addition salts, for example, by treatment with a suitable basic compound or with a suitable ion exchanger reagent and salts with bases, for example, by treatment with a suitable acid or with a suitable ion exchanger reagent.

Salts of compounds of formula I can be converted in a manner known per se into other salts of compounds of formula I, acid addition salts, for example, into other acid addition salts, for example by treatment of a salt of inorganic acid such as hydrochloride with a suitable metal salt such as a sodium, barium or silver salt, of an acid, for example with silver acetate, in a suitable solvent in which an inorganic salt which forms, for example silver chloride, is insoluble and thus precipitates from the reaction mixture.

Depending on the procedure or the reaction conditions, the compounds of formula I, which have salt-forming properties can be obtained in free form or in the form of salts.

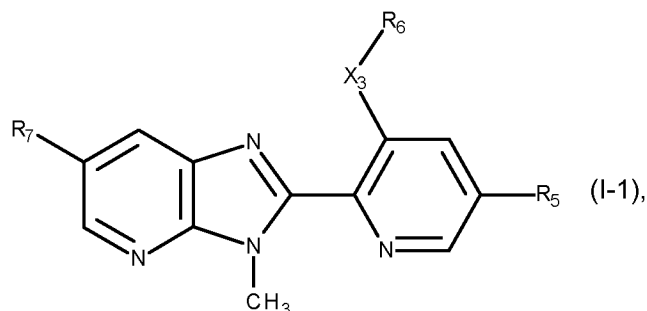
The compounds of formula I and, where appropriate, the tautomers thereof, in each case in free form or in salt form, can, if appropriate, also be obtained in the form of hydrates and/or include other solvents, for example those which may have been used for the crystallization of compounds which are present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

Compounds of formula I are preferred, wherein

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X is S=N-R₁₀ or S(O)=N-R₁₀, wherein R₁₀ is hydrogen, nitro, cyano, C(O)R₂₆, C(O)OR₂₇, CONR₂₈R₂₉, SO₂R₃₀; or R₁₀ is C₁-C₆alkyl, C₁-C₆haloalkyl, C₃-C₆cycloalkyl, C₃-C₆halocycloalkyl or C₁-C₆alkoxy-C₁-C₆alkyl; and agrochemically acceptable salts and N-oxides of those compounds.

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



wherein X₃ is S=N-R₁₀ or S(O)=N-R₁₀ and R₁₀ is preferably hydrogen, cyano or C(O)CF₃;
 R₅ is hydrogen, halogen or C₁-C₄haloalkyl; R₆ is methyl, ethyl, n-propyl or i-propyl; and R₇ is halogen
 10 or C₁-C₄haloalkyl; and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of those compounds.

In preferred compounds of formula I-1,

X₃ is as defined above and R₅ is hydrogen.

15 Further preferred compounds of formula I-1 are those, wherein

X₃ is as defined above and R₅ is trifluoromethyl.

In especially preferred compounds of formula I-1,

20 X₃ is S=NH, S=N-CN or S=N-C(O)CF₃, R₅ is hydrogen, R₆ is ethyl and R₇ is trifluoromethyl; or X₃ is S=NH, S=N-CN or S=N-C(O)CF₃, R₅ is trifluoromethyl, R₆ is ethyl and R₇ is trifluoromethyl.

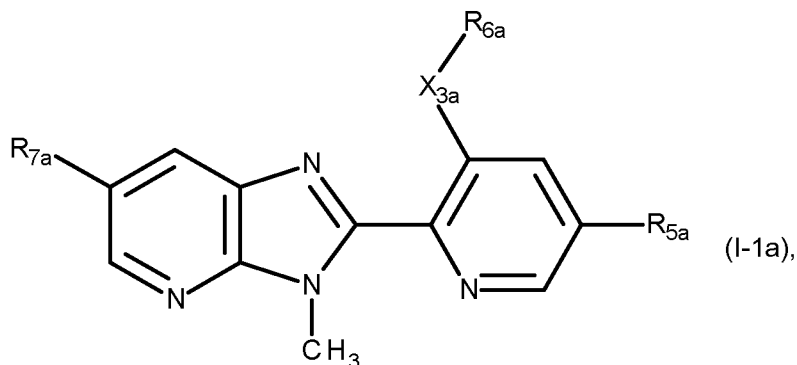
Another embodiment of the present invention groups compounds of formula I-1 wherein

X₃ is S(O)=NH, S(O)=N-CN or S(O)=N-C(O)CF₃, R₅ is hydrogen, R₆ is ethyl and R₇ is trifluoromethyl;
 or

25 X₃ is S(O)=NH, S(O)=N-CN or S(O)=N-C(O)CF₃, R₅ is trifluoromethyl, R₆ is ethyl and R₇ is trifluoromethyl.

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

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wherein X_{3a} is $S(O)=N-R_{10}$ and R_{10} is preferably C_1-C_6 alkyl, $C(O)R_{26}$, $C(O)OR_{27}$, $CONR_{28}R_{29}$, SO_2R_{30} , $CONH_2$ or $C(S)NH_2$ and in which R_{26} is preferably hydrogen, C_1-C_6 alkyl or C_1-C_6 haloalkyl, and R_{27} , R_{28} , R_{29} , R_{30} independently of one another are preferably C_1-C_6 alkyl; R_{5a} is hydrogen, halogen or C_1-C_4 haloalkyl; R_{6a} is methyl, ethyl, n-propyl or i-propyl; and R_{7a} is halogen or C_1-C_4 haloalkyl; and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of those compounds.

In preferred compounds of formula I-1a,

10 X_{3a} is as defined in formula I-1a above and R_{5a} is hydrogen.

Further preferred compounds of formula I-1a are those, wherein

X_{3a} is as defined in formula I-1a above and R_{5a} is trifluoromethyl.

15 In especially preferred compounds of formula I-1a,

X_{3a} is $S(O)=N-CH_3$, $S(O)=N-C(O)H$, $S(O)=N-C(O)CH_2CH_3$, $S(O)=N-C(O)OCH_3$, $S(O)=N-C(O)N(CH_3)_2$, $S(O)=N-C(O)NH_2$ or $S(O)=N-SO_2CH_3$; R_{5a} is hydrogen, R_{6a} is ethyl and R_{7a} is trifluoromethyl;

or X_{3a} is $S(O)=N-CH_3$, $S(O)=N-C(O)H$, $S(O)=N-C(O)CH_2CH_3$, $S(O)=N-C(O)OCH_3$,
 20 $S(O)=N-C(O)N(CH_3)_2$, $S(O)=N-C(O)NH_2$ or $S(O)=N-SO_2CH_3$; R_{5a} is trifluoromethyl, R_{6a} is ethyl and R_{7a} is trifluoromethyl.

In particular preferred compounds of formula I,

R is C_1-C_4 haloalkyl;

25 R_1 is C_1-C_6 alkyl;

R_2 is C_1-C_4 haloalkyl;

X_1 is $N-R_3$, wherein R_3 is C_1-C_4 alkyl;

X_2 is N;

R_4 is hydrogen; and

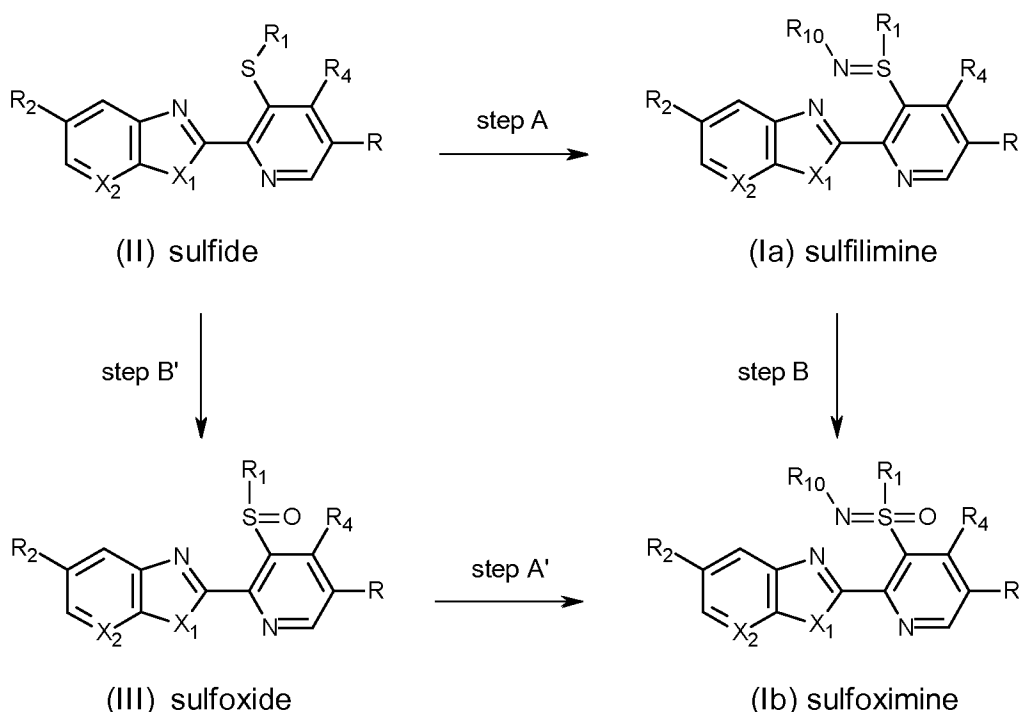
30 X is $S=N-R_{10}$ or $S(O)=N-R_{10}$, wherein R_{10} is hydrogen, cyano, C_1-C_6 haloalkylcarbonyl, aminocarbonyl, C_1-C_6 alkyl, C_1-C_6 alkylcarbonyl, C_1-C_6 alkoxycarbonyl, C_1-C_6 alkylsulfonyl,

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-C(O)H or di-(C₁-C₆alkyl)aminocarbonyl.

The process according to the invention for preparing compounds of formula (I) is carried out in principle by methods known to those skilled in the art. The subgroup of compounds of the formula I wherein X is S=N-R₁₀ defined as the sulfilimine Ia, wherein R, R₁, R₂, R₄, R₁₀, X₁ and X₂ are as defined above, may be prepared by reacting the corresponding sulfide of the formula II, wherein R, R₁, R₂, R₄, X₁ and X₂ are as defined above, under imination reaction conditions (step A, Scheme 1). The particular subgroup of compounds of the formula I wherein X is S(O)=N-R₁₀ defined as the sulfoximine Ib, wherein R, R₁, R₂, R₄, R₁₀, X₁ and X₂ are as defined above, may be obtained by oxidation of the sulfilimine compounds of the formula Ia, wherein R, R₁, R₂, R₄, R₁₀, X₁ and X₂ are as defined above (step B).

Scheme 1



Conversely, the order of the two steps may be reverted whereby the sulfoximine compounds of the formula Ib, wherein R, R₁, R₂, R₄, R₁₀, X₁ and X₂ are as defined above, may be prepared from sulfoxides of the formula III, wherein R, R₁, R₂, R₄, X₁ and X₂ are as defined above, under appropriate imination reaction conditions (step A').

Typical preparation methods and reaction conditions to access the compounds of the formula I, either towards the sulfilimines Ia (step A) or the sulfoximines Ib (step A'), may be found, for example, in H. Okamura, C. Bolm, *Org. Lett.* 2004, 6, 1305-1307; H. Okamura, C. Bolm, *Chem. Lett.* 2004, 33, 482-487; D. Leca, K. Song, M. Amatore, L. Fensterbank, E. Lacôte, M. Malacria, *Chem. Eur. J.* 2004, 10, 906-916; or M. Reggelin, C. Zur, *Synthesis*, 2000, 1-64. Typical imination reagents/conditions may be

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defined as $\text{NaN}_3/\text{H}_2\text{SO}_4$, O-mesitylenesulfonyl-hydroxylamine (MSH), or metal-catalyzed methods [see O.G. Mancheno, C. Bolm, Chem. Eur. J. 2007, 13, 6674-6681] such as $\text{R}_{10}\text{-N}_3/\text{FeCl}_2$, $\text{R}_{10}\text{-NH}_2/\text{Fe}(\text{acac})_3/\text{PhI}=\text{O}$, $\text{PhI}=\text{N-R}_{10}/\text{Fe}(\text{OTf})_2$, $\text{PhI}=\text{N-R}_{10}/\text{CuOTf}$, $\text{PhI}=\text{N-R}_{10}/\text{Cu}(\text{OTf})_2$, $\text{PhI}=\text{N-R}_{10}/\text{CuPF}_6$, $\text{PhI}(\text{OAc})_2/\text{R}_{10}\text{-NH}_2/\text{MgO}/\text{Rh}_2(\text{OAc})_4$ or oxaziridines (e.g. 3-(4-cyano-phenyl)-oxaziridine-2-carboxylic acid tert-butyl ester).

Of particular interest are metal-free imination methods of sulfides of the formula II and/or sulfoxides of the formula III to prepare sulfilimines of the formula Ia (step A) and/or sulfoximines of the formula Ib (step A'). Such imination reactions involve $\text{R}_{10}\text{-NH}_2$ and an oxidant, for example, $\text{PhI}(\text{OAc})_2/\text{R}_{10}\text{-NH}_2$ as described in G.Y. Cho, C. Bolm, Tetrahedron Lett. 2005, 46, 8007-8008; or N-bromosuccinimide (NBS)/ $\text{R}_{10}\text{-NH}_2$ and a base such as sodium or potassium ter-butoxide as described in C. Bolm et al., Synthesis 2010, No 17, 2922-2925. Oxidants such as N-iodosuccinimide (NIS) or iodine may be also used alternatively as described, for example, in O.G. Mancheno, C. Bolm, Org. Lett. 2007, 9, 3809-3811. An example of hypochlorite salts being used as oxidant, such as sodium hypochlorite NaOCl or calcium hypochlorite $\text{Ca}(\text{OCl})_2$, was described in WO2008/1060.

For the transformation of a sulfilimine Ia to a sulfoximine Ib (step B), classical oxidation reagents may involve, for example, KMnO_4 , NaMnO_4 , mCPBA, $\text{NaIO}_4/\text{RuO}_2$, $\text{NaIO}_4/\text{RuCl}_3$, H_2O_2 , oxone. In particular, the use of ruthenium salts in combination with alkali metal periodates and alternatively the use of alkali metal permanganates was described in WO2008/097235 and WO2008/106006.

Detailed preparation conditions useful for the synthesis of such sulfilimine and/or sulfoximine compounds of formula Ia respectively Ib are also given, for example, in WO2006/061200 or WO2007/080131.

The sulfide compounds of formula II and the sulfoxide compounds of formula III, wherein R, R_1 , R_2 , R_4 , X_1 and X_2 are as defined above, can be prepared according to the methods disclosed in WO2013/018928.

A compound of the formula I, wherein R, R_1 , R_2 , R_4 , X_1 and X_2 are as defined above and wherein R_{10} is CN, may be transformed into a compound of the formula I, wherein R, R_1 , R_2 , R_4 , X_1 and X_2 are as defined above and wherein R_{10} is $\text{C}(\text{O})\text{CF}_3$, by treatment with trifluoroacetic anhydride in a solvent such as dichloromethane as described, for example, in O.G. Mancheno, C. Bolm, Org. Lett. 2007, 9, 3809-3811.

A compound of the formula I, wherein R, R_1 , R_2 , R_4 , X_1 and X_2 are as defined above and wherein R_{10} is $\text{C}(\text{O})\text{CF}_3$, may be transformed into a compound of the formula I, wherein R, R_1 , R_2 , R_4 , X_1 and X_2 are as defined above and wherein R_{10} is hydrogen, by treatment with a base such as sodium or potassium carbonate in a polar protic solvent such as methanol or ethanol as described, for example, in H. Okamura, C. Bolm, Org. Lett. 2004, 6, 1305-1307.

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A compound of the formula I, wherein R, R₁, R₂, R₄, X₁ and X₂ are as defined above and wherein X is S(O)=N-R₁₀ in which R₁₀ is C(O)NH₂, may be prepared from a compound of the formula I, wherein R, R₁, R₂, R₄, X₁ and X₂ are as defined above and wherein X is S(O)=N-R₁₀ in which R₁₀ is CN, by treatment with a strong acid such as concentrated sulfuric acid in an organic solvent such as acetonitrile as described, for example, in WO09/111309.

A compound of the formula I, wherein R, R₁, R₂, R₄, X₁ and X₂ are as defined above and wherein X is S(O)=N-R₁₀ in which R₁₀ is C₁-C₆alkyl, may be prepared from a compound of the formula I, wherein R, R₁, R₂, R₄, X₁ and X₂ are as defined above and wherein X is S(O)=N-R₁₀ in which R₁₀ is hydrogen, by treatment with an alkylating agent of formula LG-R₁₀, wherein LG is a leaving group such as a halogen (especially bromine or iodine), a sulfonate OSO₂R₃₈ (especially mesylate or tosylate), wherein R₃₈ is C₁-C₆alkyl, C₁-C₆halo-alkyl, or phenyl optionally substituted by nitro or C₁-C₃alkyl, or a sulfate (such as dimethylsulfate), preferably in the presence of a suitable base, such as alkali metal carbonates, for example sodium carbonate or potassium carbonate, or alkali metal hydrides such as sodium hydride, or alkali metal hydroxides such as sodium hydroxide and potassium hydroxide, in an inert solvent at temperatures between -20 and 150°C, preferably between 0 and 80°C. Examples of solvent to be used include ethers such as tetrahydrofuran, ethylene glycol dimethyl ether (1,2-dimethoxyethane), tert-butylmethyl ether, and 1,4-dioxane, aromatic hydrocarbons such as toluene and xylene, nitriles such as acetonitrile or polar aprotic solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone or dimethyl sulfoxide.

A compound of the formula I, wherein R, R₁, R₂, R₄, X₁ and X₂ are as defined above and wherein X is S(O)=N-R₁₀ in which R₁₀ is C(O)R₂₆ and R₂₆ is C₁-C₆alkyl or C₁-C₆haloalkyl, may be prepared from a compound of the formula I, wherein R, R₁, R₂, R₄, X₁ and X₂ are as defined above and wherein X is S(O)=N-R₁₀ in which R₁₀ is hydrogen, by treatment with a reagent of formula LG₁-C(O)R₂₆ or an anhydride reagent of formula R₂₆C(O)-O-C(O)R₂₆, wherein R₂₆ is as defined above and LG₁ is a leaving group such as a halogen (especially chlorine), optionally in presence of an acylating catalyst, such as 4-dimethylaminopyridine (DMAP), preferably in presence of a base, such as triethylamine, diisopropylethylamine or pyridine, in an inert solvent at temperatures between 0 and 50°C. Examples of solvent to be used include ethers such as tetrahydrofuran, ethylene glycol dimethyl ether, tert-butylmethyl ether, and 1,4-dioxane, aromatic hydrocarbons such as toluene and xylene, halogenated hydrocarbons such as dichloromethane and chloroform, nitriles such as acetonitrile or polar aprotic solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone or dimethyl sulfoxide. The reaction may be carried out in the presence of an excess of base, which then may also act as a solvent or diluent.

A compound of the formula I, wherein R, R₁, R₂, R₄, X₁ and X₂ are as defined above and wherein X is S(O)=N-R₁₀ in which R₁₀ is C(O)OR₂₇ and R₂₇ is C₁-C₆alkyl, may be prepared from a compound of the formula I, wherein R, R₁, R₂, R₄, X₁ and X₂ are as defined above and wherein X is S(O)=N-R₁₀ in which R₁₀ is hydrogen, by treatment with a reagent of formula LG₂-C(O)OR₂₇, wherein R₂₇ is as defined

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above and LG_2 is a leaving group such as a halogen (especially chlorine), optionally in presence of an acylating catalyst, such as 4-dimethylaminopyridine (DMAP), preferably in presence of a base, such as triethylamine, diisopropylethylamine or pyridine, in an inert solvent at temperatures between 0 and 50°C. Examples of solvent to be used include ethers such as tetrahydrofuran, ethylene glycol dimethyl ether, tert-butylmethyl ether, and 1,4-dioxane, aromatic hydrocarbons such as toluene and xylene, halogenated hydrocarbons such as dichloromethane and chloroform, nitriles such as acetonitrile or polar aprotic solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone or dimethyl sulfoxide. The reaction may be carried out in the presence of an excess of base, which then may also act as a solvent or diluent.

10 A compound of the formula I, wherein R, R₁, R₂, R₄, X₁ and X₂ are as defined above and wherein X is S(O)=N-R₁₀ in which R₁₀ is CONR₂₈R₂₉ and R₂₈, R₂₉ independently of one another are C₁-C₆alkyl, may be prepared from a compound of the formula I, wherein R, R₁, R₂, R₄, X₁ and X₂ are as defined above and wherein X is S(O)=N-R₁₀ in which R₁₀ is hydrogen, by treatment with a reagent of formula LG₃-C(O)NR₂₈R₂₉, wherein R₂₈ and R₂₉ are as defined above and LG₃ is a leaving group such as a halogen (especially chlorine), optionally in presence of an acylating catalyst, such as 4-dimethylaminopyridine (DMAP), preferably in presence of a base, such as triethylamine, diisopropylethylamine or pyridine, in an inert solvent at temperatures between 0 and 50°C. Examples of solvent to be used include ethers such as tetrahydrofuran, ethylene glycol dimethyl ether, tert-butylmethyl ether, and 1,4-dioxane, aromatic hydrocarbons such as toluene and xylene, halogenated hydrocarbons such as dichloromethane and chloroform, nitriles such as acetonitrile or polar aprotic solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone or dimethyl sulfoxide. The reaction may be carried out in the presence of an excess of base, which then may also act as a solvent or diluent.

25 A compound of the formula I, wherein R, R₁, R₂, R₄, X₁ and X₂ are as defined above and wherein X is S(O)=N-R₁₀ in which R₁₀ is SO₂R₃₀ and R₃₀ is C₁-C₆alkyl, may be prepared from a compound of the formula I, wherein R, R₁, R₂, R₄, X₁ and X₂ are as defined above and wherein X is S(O)=N-R₁₀ in which R₁₀ is hydrogen, by treatment with a reagent of formula LG₄-SO₂R₃₀, wherein R₃₀ is as defined above and LG₄ is a leaving group such as a halogen (especially chlorine), optionally in presence of an acylating catalyst, such as 4-dimethylaminopyridine (DMAP), preferably in presence of a base, such as triethylamine, diisopropylethylamine or pyridine, in an inert solvent at temperatures between 0 and 50°C. Examples of solvent to be used include ethers such as tetrahydrofuran, ethylene glycol dimethyl ether, tert-butylmethyl ether, and 1,4-dioxane, aromatic hydrocarbons such as toluene and xylene, halogenated hydrocarbons such as dichloromethane and chloroform, nitriles such as acetonitrile or polar aprotic solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone or dimethyl sulfoxide. The reaction may be carried out in the presence of an excess of base, which then may also act as a solvent or diluent.

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A compound of the formula I, wherein R, R₁, R₂, R₄, X₁ and X₂ are as defined above and wherein X is S(O)=N-R₁₀ in which R₁₀ is C(O)R₂₆ and R₂₆ is hydrogen, may be prepared from a compound of the formula I, wherein R, R₁, R₂, R₄, X₁ and X₂ are as defined above and wherein X is S(O)=N-R₁₀ in which R₁₀ is hydrogen, by treatment with a trialkyl orthoformate, such as trimethyl orthoformate, optionally in the presence of an acid activator such as para-toluenesulfonic acid, optionally in the presence of an inert organic solvent, and at temperatures between 0 and 180°C. The reaction may be carried out in the presence of an excess of trialkyl orthoformate, which then may also act as a solvent or diluent. Such a process is illustrated, for example, in WO 2006/037945.

10 The reactants can be reacted in the presence of a base. Examples of suitable bases are alkali metal or alkaline earth metal hydroxides, alkali metal or alkaline earth metal hydrides, alkali metal or alkaline earth metal amides, alkali metal or alkaline earth metal alkoxides, alkali metal or alkaline earth metal acetates, alkali metal or alkaline earth metal carbonates, alkali metal or alkaline earth metal dialkylamides or alkali metal or alkaline earth metal alkylsilylamides, alkylamines, alkylenediamines, 15 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, 20 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.

30 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

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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.

5 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.

10 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.

15 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.

20 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.

25 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
30 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.

35 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-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.* **1989**, 32, 2561 or WO 2000/15615.

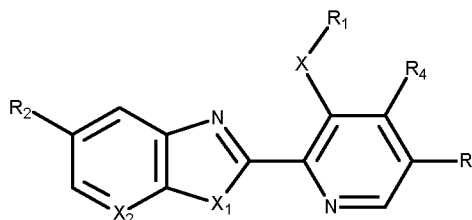
It is advantageous to isolate or synthesize in each case the biologically more effective isomer, for example enantiomer or diastereomer, or isomer mixture, for example enantiomer mixture or diastereomer mixture, if the individual components have a different biological activity.

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

The compounds according to the following Tables 1 to 19 below can be prepared according to the methods described above. The examples which follow are intended to illustrate the invention and show preferred compounds of formula I.

Table 1: This table discloses the 60 compounds 1.001 to 1.060 of the formula I:

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(I),

wherein X is S=N-CN and R, R₁, R₂, R₄, X₁ and X₂ are as defined below:

Table 1:

Comp.No	R	R ₁	R ₂	R ₄	X ₁	X ₂
1.001	H	-CH ₂ -CH ₃	CF ₃	H	N-CH ₃	N
1.002	CF ₃	-CH ₂ -CH ₃	CF ₃	H	N-CH ₃	N
1.003	H	-CH ₂ -CH ₃	-CF ₂ CF ₃	H	N-CH ₃	N
1.004	CF ₃	-CH ₂ -CH ₃	-CF ₂ CF ₃	H	N-CH ₃	N
1.005	H	-CH ₂ -CH ₃	OCF ₃	H	N-CH ₃	N
1.006	CF ₃	-CH ₂ -CH ₃	OCF ₃	H	N-CH ₃	N
1.007	H	-CH ₂ -CH ₃	SCF ₃	H	N-CH ₃	N
1.008	CF ₃	-CH ₂ -CH ₃	SCF ₃	H	N-CH ₃	N
1.009	H	-CH ₂ -CH ₃	S(O) ₂ CF ₃	H	N-CH ₃	N
1.010	CF ₃	-CH ₂ -CH ₃	S(O) ₂ CF ₃	H	N-CH ₃	N
1.011	H	-CH ₂ -CH ₃	CF ₃	H	S	N
1.012	CF ₃	-CH ₂ -CH ₃	CF ₃	H	S	N
1.013	H	-CH ₂ -CH ₃	-CF ₂ CF ₃	H	S	N
1.014	CF ₃	-CH ₂ -CH ₃	-CF ₂ CF ₃	H	S	N
1.015	H	-CH ₂ -CH ₃	OCF ₃	H	S	N
1.016	CF ₃	-CH ₂ -CH ₃	OCF ₃	H	S	N
1.017	H	-CH ₂ -CH ₃	SCF ₃	H	S	N
1.018	CF ₃	-CH ₂ -CH ₃	SCF ₃	H	S	N
1.019	H	-CH ₂ -CH ₃	S(O) ₂ CF ₃	H	S	N
1.020	CF ₃	-CH ₂ -CH ₃	S(O) ₂ CF ₃	H	S	N
1.021	H	-CH ₂ -CH ₃	CF ₃	H	O	N
1.022	CF ₃	-CH ₂ -CH ₃	CF ₃	H	O	N
1.023	H	-CH ₂ -CH ₃	-CF ₂ CF ₃	H	O	N
1.024	CF ₃	-CH ₂ -CH ₃	-CF ₂ CF ₃	H	O	N
1.025	H	-CH ₂ -CH ₃	OCF ₃	H	O	N
1.026	CF ₃	-CH ₂ -CH ₃	OCF ₃	H	O	N
1.027	H	-CH ₂ -CH ₃	SCF ₃	H	O	N

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Comp.No	R	R ₁	R ₂	R ₄	X ₁	X ₂
1.028	CF ₃	-CH ₂ -CH ₃	SCF ₃	H	O	N
1.029	H	-CH ₂ -CH ₃	S(O) ₂ CF ₃	H	O	N
1.030	CF ₃	-CH ₂ -CH ₃	S(O) ₂ CF ₃	H	O	N
1.031	H	-CH ₂ -CH ₃	CF ₃	H	N-CH ₃	CH
1.032	CF ₃	-CH ₂ -CH ₃	CF ₃	H	N-CH ₃	CH
1.033	H	-CH ₂ -CH ₃	-CF ₂ CF ₃	H	N-CH ₃	CH
1.034	CF ₃	-CH ₂ -CH ₃	-CF ₂ CF ₃	H	N-CH ₃	CH
1.035	H	-CH ₂ -CH ₃	OCF ₃	H	N-CH ₃	CH
1.036	CF ₃	-CH ₂ -CH ₃	OCF ₃	H	N-CH ₃	CH
1.037	H	-CH ₂ -CH ₃	SCF ₃	H	N-CH ₃	CH
1.038	CF ₃	-CH ₂ -CH ₃	SCF ₃	H	N-CH ₃	CH
1.039	H	-CH ₂ -CH ₃	S(O) ₂ CF ₃	H	N-CH ₃	CH
1.040	CF ₃	-CH ₂ -CH ₃	S(O) ₂ CF ₃	H	N-CH ₃	CH
1.041	H	-CH ₂ -CH ₃	CF ₃	H	S	CH
1.042	CF ₃	-CH ₂ -CH ₃	CF ₃	H	S	CH
1.043	H	-CH ₂ -CH ₃	-CF ₂ CF ₃	H	S	CH
1.044	CF ₃	-CH ₂ -CH ₃	-CF ₂ CF ₃	H	S	CH
1.045	H	-CH ₂ -CH ₃	OCF ₃	H	S	CH
1.046	CF ₃	-CH ₂ -CH ₃	OCF ₃	H	S	CH
1.047	H	-CH ₂ -CH ₃	SCF ₃	H	S	CH
1.048	CF ₃	-CH ₂ -CH ₃	SCF ₃	H	S	CH
1.049	H	-CH ₂ -CH ₃	S(O) ₂ CF ₃	H	S	CH
1.050	CF ₃	-CH ₂ -CH ₃	S(O) ₂ CF ₃	H	S	CH
1.051	H	-CH ₂ -CH ₃	CF ₃	H	O	CH
1.052	CF ₃	-CH ₂ -CH ₃	CF ₃	H	O	CH
1.053	H	-CH ₂ -CH ₃	-CF ₂ CF ₃	H	O	CH
1.054	CF ₃	-CH ₂ -CH ₃	-CF ₂ CF ₃	H	O	CH
1.055	H	-CH ₂ -CH ₃	OCF ₃	H	O	CH
1.056	CF ₃	-CH ₂ -CH ₃	OCF ₃	H	O	CH
1.057	H	-CH ₂ -CH ₃	SCF ₃	H	O	CH
1.058	CF ₃	-CH ₂ -CH ₃	SCF ₃	H	O	CH
1.059	H	-CH ₂ -CH ₃	S(O) ₂ CF ₃	H	O	CH
1.060	CF ₃	-CH ₂ -CH ₃	S(O) ₂ CF ₃	H	O	CH

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

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Table 2: This table discloses the 60 compounds 2.001 to 2.060 of the formula I, wherein X is S=N-C(O)CF₃ and R, R₁, R₂, R₄, X₁ and X₂ are as defined in Table 1.

Table 3: This table discloses the 60 compounds 3.001 to 3.060 of the formula I, wherein X is S=N-H and R, R₁, R₂, R₄, X₁ and X₂ are as defined in Table 1.

5 Table 4: This table discloses the 60 compounds 4.001 to 4.060 of the formula I, wherein X is S(O)=N-CN and R, R₁, R₂, R₄, X₁ and X₂ are as defined in Table 1.

Table 5: This table discloses the 60 compounds 5.001 to 5.060 of the formula I, wherein X is S(O)=N-C(O)CF₃ and R, R₁, R₂, R₄, X₁ and X₂ are as defined in Table 1.

10 Table 6: This table discloses the 60 compounds 6.001 to 6.060 of the formula I, wherein X is S(O)=N-H and R, R₁, R₂, R₄, X₁ and X₂ are as defined in Table 1.

Table 7: This table discloses the 60 compounds 7.001 to 7.060 of the formula I, wherein X is S(O)=N-C(O)NH₂ and R, R₁, R₂, R₄, X₁ and X₂ are as defined in Table 1.

Table 8: This table discloses the 60 compounds 8.001 to 8.060 of the formula I, wherein X is S(O)=N-C(O)NHCH₃ and R, R₁, R₂, R₄, X₁ and X₂ are as defined in Table 1.

15 Table 9: This table discloses the 60 compounds 9.001 to 9.060 of the formula I, wherein X is S(O)=N-C(O)N(CH₃)₂ and R, R₁, R₂, R₄, X₁ and X₂ are as defined in Table 1.

Table 10: This table discloses the 60 compounds 10.001 to 10.060 of the formula I, wherein X is S(O)=N-CH₃ and R, R₁, R₂, R₄, X₁ and X₂ are as defined in Table 1.

20 Table 11: This table discloses the 60 compounds 11.001 to 11.060 of the formula I, wherein X is S(O)=N-CH₂CH₃ and R, R₁, R₂, R₄, X₁ and X₂ are as defined in Table 1.

Table 12: This table discloses the 60 compounds 12.001 to 12.060 of the formula I, wherein X is S(O)=N-C(O)CH₃ and R, R₁, R₂, R₄, X₁ and X₂ are as defined in Table 1.

Table 13: This table discloses the 60 compounds 13.001 to 13.060 of the formula I, wherein X is S(O)=N-C(O)CH₂CH₃ and R, R₁, R₂, R₄, X₁ and X₂ are as defined in Table 1.

25 Table 14: This table discloses the 60 compounds 14.001 to 14.060 of the formula I, wherein X is S(O)=N-C(O)OCH₃ and R, R₁, R₂, R₄, X₁ and X₂ are as defined in Table 1.

Table 15: This table discloses the 60 compounds 15.001 to 15.060 of the formula I, wherein X is S(O)=N-C(O)OCH₂CH₃ and R, R₁, R₂, R₄, X₁ and X₂ are as defined in Table 1.

30 Table 16: This table discloses the 60 compounds 16.001 to 16.060 of the formula I, wherein X is S(O)=N-C(O)H and R, R₁, R₂, R₄, X₁ and X₂ are as defined in Table 1.

Table 17: This table discloses the 60 compounds 17.001 to 17.060 of the formula I, wherein X is S(O)=N-SO₂CH₃ and R, R₁, R₂, R₄, X₁ and X₂ are as defined in Table 1.

Table 18: This table discloses the 60 compounds 18.001 to 18.060 of the formula I, wherein X is S(O)=N-SO₂CH₂CH₃ and R, R₁, R₂, R₄, X₁ and X₂ are as defined in Table 1.

5 Table 19: This table discloses the 60 compounds 19.001 to 19.060 of the formula I, wherein X is S(O)=N-C(S)NH₂ and R, R₁, R₂, R₄, X₁ and X₂ are as defined in Table 1.

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
 10 ingredients according to the invention act against all or individual developmental stages of normally sensitive, but also resistant, animal pests, such as insects or representatives of the order Acarina. The insecticidal or acaricidal activity of the active ingredients according to the invention can manifest itself directly, i. e. in destruction of the pests, which takes place either immediately or only after some time has elapsed, for example during ecdysis, or indirectly, for example in a reduced oviposition and/or
 15 hatching rate, a good activity corresponding to a destruction rate (mortality) of at least 50%.

The compounds of formula I can be used to combat and control infestations of insect pests such as Lepidoptera, Diptera, Hemiptera, Thysanoptera, Orthoptera, Dictyoptera, Coleoptera, Siphonaptera, Hymenoptera and Isoptera and also other invertebrate pests, for
 20 example, acarine, nematode and mollusc pests. Insects, acarines, nematodes and molluscs are hereinafter collectively referred to as pests. The pests which may be combated and controlled by the use of the invention compounds include those pests associated with agriculture (which term includes the growing of crops for food and fibre products), horticulture and animal husbandry, companion animals, forestry and the storage of products of vegetable origin (such as fruit, grain and timber); those
 25 pests associated with the damage of man-made structures and the transmission of diseases of man and animals; and also nuisance pests (such as flies).

Examples of pest species which may be controlled by the compounds of formula I include: *Myzus persicae* (aphid), *Aphis gossypii* (aphid), *Aphis fabae* (aphid), *Lygus* spp. (capsids), *Dysdercus* spp. (capsids), *Nilaparvata lugens* (planthopper), *Nephotettix inciticeps* (leafhopper), *Nezara* spp. (stinkbugs), *Euschistus* spp. (stinkbugs), *Leptocorisa* spp. (stinkbugs), *Frankliniella occidentalis* (thrip),
 30 Thrips spp. (thrips), *Leptinotarsa decemlineata* (Colorado potato beetle), *Anthonomus grandis* (boll weevil), *Aonidiella* spp. (scale insects), *Trialeurodes* spp. (white flies), *Bemisia tabaci* (white fly), *Ostrinia nubilalis* (European corn borer), *Spodoptera littoralis* (cotton leafworm), *Heliothis virescens* (tobacco budworm), *Helicoverpa armigera* (cotton bollworm), *Helicoverpa zea* (cotton bollworm),
 35 *Sylepta derogata* (cotton leaf roller), *Pieris brassicae* (white butterfly), *Plutella xylostella* (diamond back moth), *Agrotis* spp. (cutworms), *Chilo suppressalis* (rice stem borer), *Locusta migratoria* (locust), *Chortiocetes terminifera* (locust), *Diabrotica* spp. (rootworms), *Panonychus ulmi* (European red mite),

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Panonychus citri (citrus red mite), *Tetranychus urticae* (two-spotted spider mite), *Tetranychus cinnabarinus* (carmine spider mite), *Phyllocoptruta oleivora* (citrus rust mite), *Polyphagotarsonemus latus* (broad mite), *Brevipalpus* spp. (flat mites), *Boophilus microplus* (cattle tick), *Dermacentor variabilis* (American dog tick), *Ctenocephalides felis* (cat flea), *Liriomyza* spp. (leafminer), *Musca domestica* (housefly), *Aedes aegypti* (mosquito), *Anopheles* spp. (mosquitoes), *Culex* spp. (mosquitoes), *Lucillia* spp. (blowflies), *Blattella germanica* (cockroach), *Periplaneta americana* (cockroach), *Blatta orientalis* (cockroach), termites of the Mastotermitidae (for example *Mastotermes* spp.), the Kalotermitidae (for example *Neotermes* spp.), the Rhinotermitidae (for example *Coptotermes formosanus*, *Reticulitermes flavipes*, *R. speratu*, *R. virginicus*, *R. hesperus*, and *R. santonensis*) and the Termitidae (for example *Globitermes sulphureus*), *Solenopsis geminata* (fire ant), *Monomorium pharaonis* (pharaoh's ant), *Damalinia* spp. and *Linognathus* spp. (biting and sucking lice), *Meloidogyne* spp. (root knot nematodes), *Globodera* spp. and *Heterodera* spp. (cyst nematodes), *Pratylenchus* spp. (lesion nematodes), *Rhodopholus* spp. (banana burrowing nematodes), *Tylenchulus* spp. (citrus nematodes), *Haemonchus contortus* (barber pole worm), *Caenorhabditis elegans* (vinegar eelworm), *Trichostrongylus* spp. (gastro intestinal nematodes) and *Deroceras reticulatum* (slug).

Further examples of the above mentioned pests are:

from the order *Acarina*, for example, *Acalitus* spp, *Aculus* spp, *Acaricalus* spp, *Aceria* spp, *Acarus siro*, *Amblyomma* spp., *Argas* spp., *Boophilus* spp., *Brevipalpus* spp., *Bryobia* spp, *Calipitimerus* spp., *Chorioptes* spp., *Dermanyssus gallinae*, *Dermatophagoides* spp, *Eotetranychus* spp, *Eriophyes* spp., *Hemitarsonemus* spp, *Hyalomma* spp., *Ixodes* spp., *Olygonychus* spp, *Ornithodoros* spp., *Polyphagotarsonemus latus*, *Panonychus* spp., *Phyllocoptruta oleivora*, *Phytonemus* spp, *Polyphagotarsonemus* spp, *Psoroptes* spp., *Rhipicephalus* spp., *Rhizoglyphus* spp., *Sarcoptes* spp., *Steneotarsonemus* spp, *Tarsonemus* spp. and *Tetranychus* spp.;

from the order *Anoplura*, for example, *Haematopinus* spp., *Linognathus* spp., *Pediculus* spp., *Pemphigus* spp. and *Phylloxera* spp.;

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

from the order *Diptera*, for example, *Aedes* spp., *Anopheles* spp, *Antherigona soccata*, *Bactrocea oleae*, *Bibio hortulanus*, *Bradysia* spp, *Calliphora erythrocephala*, *Ceratitis* spp., *Chrysomyia* spp., *Culex* spp., *Cuterebra* spp., *Dacus* spp., *Delia* spp, *Drosophila melanogaster*, *Fannia* spp.,

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- 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.;
- 5 from the order *Hemiptera*, for example, Acanthocoris scabrator, Acrosternum spp, Adelphocoris lineolatus, Amblypelta nitida, Bathycoelia thalassina, Blissus spp, Cimex spp., Clavigralla tomentosicollis, Creontiades spp, Distantiella theobroma, Dichelops furcatus, Dysdercus spp., Edessa spp, Euchistus spp., Eurydema pulchrum, Eurygaster spp., Halyomorpha halys, Horcias nobillellus, Leptocorisa spp., Lygus spp, Margarodes spp, Murgantia histrionic, Neomegalotomus spp,
- 10 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, Agonoscena targionii, Aleurodicus spp, Aleurocanthus spp, Aleurolobus barodensis, Aleurothrixus floccosus, Aleyrodes brassicae, Amarasca biguttula, Amritodus atkinsoni, Aonidiella spp., Aphididae, Aphis spp.,
- 15 Aspidiotus spp., Aulacorthum solani, Bactericera cockerelli, Bemisia spp, Brachycaudus spp, Brevicoryne brassicae, Cacopsylla spp, Cavariella aegopodii Scop., Ceroplaster spp., Chrysomphalus aonidium, Chrysomphalus dictyospermi, Cicadella spp, Cofana spectra, Cryptomyzus spp, Cicadulina spp, Coccus hesperidum, Dalbulus maidis, Dialeurodes spp, Diaphorina citri, Diuraphis noxia, Dysaphis spp, Empoasca spp., Eriosoma larigerum, Erythroneura spp., Gascardia spp., Glycaspis
- 20 brimblecombei, Hyadaphis pseudobrassicae, Hyalopterus spp, Hyperomyzus pallidus, Idioscopus clypealis, Jacobiasca lybica, Laodelphax spp., Lecanium corni, Lepidosaphes spp., Lopaphis erysimi, Lyogenys maidis, Macrosiphum spp., Mahanarva spp, Metcalfa pruinosa, Metopolophium dirhodum, Myndus crudus, Myzus spp., Neotoxoptera sp, Nephrotettix spp., Nilaparvata spp., Nippolachnus piri Mats, Odonaspis ruthae, Oregma lanigera Zehnter, Parabemisia myricae, Paratrioza cockerelli,
- 25 Parlatoria spp., Pemphigus spp., Peregrinus maidis, Perkinsiella spp, Phorodon humuli, Phylloxera spp, Planococcus spp., Pseudaulacaspis spp., Pseudococcus spp., Pseudatomoscelis seriatus, Psylla spp., Pulvinaria aethiopica, Quadraspidiotus spp., Quesada gigas, Recilia dorsalis, Rhopalosiphum spp., Saissetia spp., Scaphoideus spp., Schizaphis spp., Sitobion spp., Sogatella furcifera, Spissistilus festinus, Tarophagus Proserpina, Toxoptera spp, Trialeurodes spp, Tridiscus sporoboli, Trionymus
- 30 spp, Trioza erytrae , Unaspis citri, Zyginia flammigera, Zyginidia scutellaris;
- from the order *Heteroptera*, for example, Cimex spp., Distantiella theobroma, Dysdercus spp., Euchistus spp., Eurygaster spp., Leptocorisa spp., Nezara spp., Piesma spp., Rhodnius spp., Sahlbergella singularis, Scotinophara spp. and Triatoma spp.;
- from the order *Homoptera*, for example, Aleurothrixus floccosus, Aleyrodes brassicae, Aonidiella spp.,
- 35 Aphididae, Aphis spp., Aspidiotus spp., Bemisia tabaci, Ceroplaster spp., Chrysomphalus aonidium, Chrysomphalus dictyospermi, Coccus hesperidum, Empoasca spp., Eriosoma larigerum, Erythroneura spp., Gascardia spp., Laodelphax spp., Lecanium corni, Lepidosaphes spp., Macrosiphus spp., Myzus spp., Nephrotettix spp., Nilaparvata spp., Parlatoria spp., Pemphigus spp., Planococcus spp., Pseudaulacaspis spp., Pseudococcus spp., Psylla spp., Pulvinaria aethiopica, Quadraspidiotus spp.,

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- Rhopalosiphum spp., Saissetia spp., Scaphoideus spp., Schizaphis spp., Sitobion spp., Trialeurodes vaporariorum, Trioza erythrae and Unaspis citri;
 from the order *Hymenoptera*, for example, Acromyrmex, Arge spp, Atta spp., Cephus spp., Diprion spp., Diprionidae, Gilpinia polytoma, Hoplocampa spp., Lasius spp., Monomorium pharaonis,
 5 Neodiprion spp., Pogonomymex spp, Slenopsis invicta, Solenopsis spp. and Vespa spp.;
- from the order *Isoptera*, for example, Coptotermes spp, Cornitermes cumulans, Incisitermes spp, Macrotermes spp, Mastotermes spp, Microtermes spp, Reticulitermes spp.; Solenopsis geminate ;
 from the order *Lepidoptera*, for example, Acleris spp., Adoxophyes spp., Aegeria spp., Agrotis spp., Alabama argillaceae, Amylois spp., Anticarsia gemmatalis, Archips spp., Argyresthia spp,
 10 Argyrotaenia spp., Autographa spp., Bucculatrix thurberiella, Busseola fusca, Cadra cautella, Carposina nipponensis, Chilo spp., Choristoneura spp., Chrysoteuchia topiaria, Clysia ambiguella, Cnaphalocrocis spp., Cnephasia spp., Cochylis spp., Coleophora spp., Colias lesbia, Cosmophila flava, Crambus spp, Crocidolomia binotalis, Cryptophlebia leucotreta, Cydalima perspectalis, Cydia spp., Diaphania perspectalis, Diatraea spp., Diparopsis castanea, Earias spp., Eldana saccharina,
 15 Ephestia spp., Epinotia spp, Estigmene acrea, Etiella zinckinella, Eucosma spp., Eupoecilia ambiguella, Euproctis spp., Euxoa spp., Feltia jaculiferia, Grapholita spp., Hedya nubiferana, Heliiothis spp., Hellula undalis, Herpetogramma spp, Hyphantria cunea, Keiferia lycopersicella, Lasmopalpus lignosellus, Leucoptera scitella, Lithocollethis spp., Lobesia botrana, Loxostege bifidalis, Lymantria spp., Lyonetia spp., Malacosoma spp., Mamestra brassicae, Manduca sexta, Mythimna spp, Noctua
 20 spp, Operophtera spp., Orniodes indica, Ostrinia nubilalis, Pammene spp., Pandemis spp., Panolis flammea, Papaipema nebris, Pectinophora gossypiella, Perileucoptera coffeella, Pseudaletia unipuncta, Phthorimaea operculella, Pieris rapae, Pieris spp., Plutella xylostella, Prays spp., Pseudoplusia spp, Rachiplusia nu, Richia albicosta, Scirpophaga spp., Sesamia spp., Sparganothis spp., Spodoptera spp., Sylepta derogate, Synanthedon spp., Thaumetopoea spp., Tortrix spp.,
 25 Trichoplusia ni, Tuta absoluta, and Yponomeuta spp.;
- from the order *Mallophaga*, for example,
 Damalinae spp. and Trichodectes spp.;
- from the order *Orthoptera*, for example, Blatta spp., Blattella spp., Gryllotalpa spp., Leucophaea maderae, Locusta spp., Neocurtilla hexadactyla, Periplaneta spp. , Scapteriscus spp, and
 30 Schistocerca spp.;
- from the order *Psocoptera*, for example, Liposcelis spp.;
- from the order *Siphonaptera*, for example, Ceratophyllus spp., Ctenocephalides spp. and Xenopsylla cheopis;
- from the order *Thysanoptera*, for example,
 35 Calliothrips phaseoli, Frankliniella spp., Heliothrips spp, Hercinothrips spp., Parthenothrips spp, Scirtothrips aurantii, Sericothrips variabilis, Taeniothrips spp., Thrips spp; and
 from the order *Thysanura*, for example, Lepisma saccharina.

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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.

In a further aspect, the invention may also relate to a method of controlling damage to plant and parts thereof by plant parasitic nematodes (Endoparasitic-, Semiendoparasitic- and Ectoparasitic nematodes), especially plant parasitic nematodes such as root knot nematodes, *Meloidogyne hapla*, *Meloidogyne incognita*, *Meloidogyne javanica*, *Meloidogyne arenaria* and other *Meloidogyne* species; cyst-forming nematodes, *Globodera rostochiensis* and other *Globodera* species; *Heterodera avenae*, *Heterodera glycines*, *Heterodera schachtii*, *Heterodera trifolii*, and other *Heterodera* species; Seed gall nematodes, *Anguina* species; Stem and foliar nematodes, *Aphelenchoides* species; Sting nematodes, *Belonolaimus longicaudatus* and other *Belonolaimus* species; Pine nematodes, *Bursaphelenchus xylophilus* and other *Bursaphelenchus* species; Ring nematodes, *Criconema* species, *Criconemella* species, *Criconemoides* species, *Mesocriconema* species; Stem and bulb nematodes, *Ditylenchus destructor*, *Ditylenchus dipsaci* and other *Ditylenchus* species; Awl nematodes, *Dolichodorus* species; Spiral nematodes, *Helicotylenchus multicinctus* and other *Helicotylenchus* species; Sheath and sheathoid nematodes, *Hemicycliophora* species and *Hemicriconemoides* species; *Hirshmanniella* species; Lance nematodes, *Hoploaimus* species; false rootknot nematodes, *Nacobbus* species; Needle nematodes, *Longidorus elongatus* and other *Longidorus* species; Pin nematodes, *Pratylenchus* species; Lesion nematodes, *Pratylenchus neglectus*, *Pratylenchus penetrans*, *Pratylenchus curvatus*, *Pratylenchus goodeyi* and other *Pratylenchus* species; Burrowing nematodes, *Radopholus similis* and other *Radopholus* species; Reniform nematodes, *Rotylenchus robustus*, *Rotylenchus reniformis* and other *Rotylenchus* species; *Scutellonema* species; Stubby root nematodes, *Trichodorus primitivus* and other *Trichodorus* species, *Paratrichodorus* species; Stunt nematodes, *Tylenchorhynchus claytoni*, *Tylenchorhynchus dubius* and other *Tylenchorhynchus* species; Citrus nematodes, *Tylenchulus* species; Dagger nematodes, *Xiphinema* species; and other

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plant parasitic nematode species, such as *Subanguina* spp., *Hypsoperine* spp., *Macroposthonia* spp., *Melinius* spp., *Punctodera* spp., and *Quinisulcius* spp..

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

15 The term "crops" is to be understood as including also crops that have been rendered tolerant to herbicides like bromoxynil or classes of herbicides (such as, for example, HPPD inhibitors, ALS inhibitors, for example primisulfuron, prosulfuron and trifloxysulfuron, EPSPS (5-enol-pyrovyl-shikimate-3-phosphate-synthase) inhibitors, GS (glutamine synthetase) inhibitors) as a result of conventional methods of breeding or genetic engineering. An example of a crop that has been rendered tolerant to imidazolinones, e.g. imazamox, by conventional methods of breeding (mutagenesis) is Clearfield® summer rape (Canola). Examples of crops that have been rendered tolerant to herbicides or classes of herbicides by genetic engineering methods include glyphosate- and glufosinate-resistant maize varieties commercially available under the trade names RoundupReady® and LibertyLink®.

20 The term "crops" is also 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*.

25 Toxins that can be expressed by such transgenic plants include, for example, insecticidal proteins, for example insecticidal proteins from *Bacillus cereus* or *Bacillus popliae*; or insecticidal proteins from *Bacillus thuringiensis*, such as δ -endotoxins, e.g. CryIA(b), CryIA(c), CryIF, CryIF(a2), CryIIA(b), CryIIIA, CryIIIB(b1) or Cry9c, or vegetative insecticidal proteins (VIP), e.g. VIP1, VIP2, VIP3 or VIP3A; 30 or insecticidal proteins of bacteria colonising nematodes, for example *Photorhabdus* spp. or *Xenorhabdus* spp., such as *Photorhabdus luminescens*, *Xenorhabdus nematophilus*; toxins produced by animals, such as scorpion toxins, arachnid toxins, wasp toxins and other insect-specific neurotoxins; toxins produced by fungi, such as *Streptomyces* toxins, plant lectins, such as pea lectins, barley lectins or snowdrop lectins; agglutinins; proteinase inhibitors, such as trypsin inhibitors, 35 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

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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 CryIA(b), CryIA(c), CryIF, CryIF(a2), CryIIA(b), CryIIIA, CryIIIB(b1) 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 CryIA(b), 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 CryIIIA055, a cathepsin-D-recognition sequence is inserted into a CryIIIA 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 butterflies (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 CryIA(b) toxin); YieldGard Rootworm® (maize variety that expresses a CryIIIB(b1) toxin); YieldGard Plus® (maize variety that expresses a CryIA(b) and a CryIIIB(b1) toxin); Starlink® (maize variety that expresses a Cry9(c) toxin); Herculex I® (maize variety that expresses a CryIF(a2) toxin and the enzyme phosphinothricine N-acetyltransferase (PAT) to achieve tolerance to the herbicide glufosinate ammonium); NuCOTN 33B® (cotton variety that expresses a CryIA(c) toxin); Bollgard I® (cotton variety that expresses a CryIA(c) toxin); Bollgard II® (cotton variety that expresses a CryIA(c) and a CryIIA(b) toxin); VIPCOT® (cotton variety that expresses a VIP toxin); NewLeaf® (potato variety that expresses a CryIIIA toxin); NatureGard® Agrisure® GT Advantage (GA21 glyphosate-tolerant trait), Agrisure® CB Advantage (Bt11 corn borer (CB) trait) and Protecta®.

Further examples of such transgenic crops are:

1. Bt11 Maize from Syngenta Seeds SAS, Chemin de l'Hobit 27, F-31 790 St. Sauveur, France, registration number C/FR/96/05/10. Genetically modified *Zea mays* which has been rendered resistant

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to attack by the European corn borer (*Ostrinia nubilalis* and *Sesamia nonagrioides*) by transgenic expression of a truncated CryIA(b) toxin. Bt11 maize also transgenically expresses the enzyme PAT to achieve tolerance to the herbicide glufosinate ammonium.

5 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 CryIA(b) toxin. Bt176 maize also transgenically expresses the enzyme PAT to achieve tolerance to the herbicide glufosinate ammonium.

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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 CryIIIA toxin. This toxin is Cry3A055 modified by insertion of a cathepsin-D-protease recognition sequence. The preparation of such transgenic maize plants is described in WO
15 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 CryIIIB(b1) toxin and has resistance to certain Coleoptera insects.

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

6. 1507 Maize from Pioneer Overseas Corporation, Avenue Tedesco, 7 B-1160 Brussels, Belgium, registration number C/NL/00/10. Genetically modified maize for the expression of the protein Cry1F
25 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
30 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 CryIA(b) toxin obtained from *Bacillus thuringiensis subsp. kurstaki* which brings about tolerance to certain
Lepidoptera, include the European corn borer.

35 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.

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

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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).

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

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

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

Crops that exhibit enhanced yield or quality include those with improved flowering or fruit ripening properties (such as delayed ripening); modified oil, starch, amino acid, fatty acid, vitamin, phenolic or other content (such as Vistive™ soybean variety); enhanced nutrient utilisation (such as improved nitrogen assimilation); and enhanced quality plant product (such as higher quality cotton fibre).

Further areas of use of the compounds and 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.

The present invention also provides a method for controlling pests (such as mosquitoes and other disease vectors; see also http://www.who.int/malaria/vector_control/irs/en/). In one embodiment, the method for controlling pests comprises applying the compositions of the invention to the target pests, to their locus or to a surface or substrate by brushing, rolling, spraying, spreading or dipping. By way of example, an IRS (indoor residual spraying) application of a surface such as a wall, ceiling or floor

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surface is contemplated by the method of the invention. In another embodiment, it is contemplated to apply such compositions to a substrate such as non-woven or a fabric material in the form of (or which can be used in the manufacture of) netting, clothing, bedding, curtains and tents.

- 5 In one embodiment, the method for controlling such pests comprises applying a pesticidally effective amount of the compositions of the invention to the target pests, to their locus, or to a surface or substrate so as to provide effective residual pesticidal activity on the surface or substrate. Such application may be made by brushing, rolling, spraying, spreading or dipping the pesticidal composition of the invention. By way of example, an IRS application of a surface such as a wall,
 10 ceiling or floor surface is contemplated by the method of the invention so as to provide effective residual pesticidal activity on the surface. In another embodiment, it is contemplated to apply such compositions for residual control of pests on a substrate such as a fabric material in the form of (or which can be used in the manufacture of) netting, clothing, bedding, curtains and tents.
- 15 Substrates including non-woven, fabrics or netting to be treated may be made of natural fibres such as cotton, raffia, jute, flax, sisal, hessian, or wool, or synthetic fibres such as polyamide, polyester, polypropylene, polyacrylonitrile or the like. The polyesters are particularly suitable. The methods of textile treatment are known, e.g. WO 2008/151984, WO 2003/034823, US 5631072, WO 2005/64072, WO2006/128870, EP 1724392, WO2005113886 or WO 2007/090739.
- 20 Further areas of use of the compositions according to the invention are the field of tree injection/trunk treatment for all ornamental trees as well all sort of fruit and nut trees.

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

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Table A. Examples of exotic woodborers of economic importance.

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

Table B. Examples of native woodborers of economic importance.

Family	Species	Host or Crop Infested
Buprestidae	<i>Agrilus anxius</i>	Birch
	<i>Agrilus politus</i>	Willow, Maple
	<i>Agrilus sayi</i>	Bayberry, Sweetfern
	<i>Agrilus vittaticollis</i>	Apple, Pear, Cranberry, Serviceberry, Hawthorn
	<i>Chrysobothris femorata</i>	Apple, Apricot, Beech, Boxelder, Cherry, Chestnut, Currant, Elm, Hawthorn, Hackberry, Hickory, Horsechestnut, Linden, Maple, Mountain-ash, Oak, Pecan, Pear, Peach, Persimmon, Plum, Poplar, Quince, Redbud, Serviceberry, Sycamore, Walnut, Willow
	<i>Texania campestris</i>	Basswood, Beech, Maple, Oak, Sycamore, Willow, Yellow-poplar
Cerambycidae	<i>Goes pulverulentus</i>	Beech, Elm, Nuttall, Willow, Black oak, Cherrybark oak, Water oak, Sycamore
	<i>Goes tigrinus</i>	Oak
	<i>Neoclytus acuminatus</i>	Ash, Hickory, Oak, Walnut, Birch, Beech, Maple, Eastern hophornbeam, Dogwood, Persimmon, Redbud, Holly, Hackberry, Black locust, Honeylocust, Yellow-poplar, Chestnut, Osage-orange, Sassafras, Lilac, Mountain-mahogany, Pear, Cherry, Plum, Peach, Apple, Elm, Basswood, Sweetgum
	<i>Neoptychodes trilineatus</i>	Fig, Alder, Mulberry, Willow, Netleaf

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Family	Species	Host or Crop Infested
		hackberry
	<i>Oberea ocellata</i>	Sumac, Apple, Peach, Plum, Pear, Currant, Blackberry
	<i>Oberea tripunctata</i>	Dogwood, Viburnum, Elm, Sourwood, Blueberry, Rhododendron, Azalea, Laurel, Poplar, Willow, Mulberry
	<i>Oncideres cingulata</i>	Hickory, Pecan, Persimmon, Elm, Sourwood, Basswood, Honeylocust, Dogwood, Eucalyptus, Oak, Hackberry, Maple, Fruit trees
	<i>Saperda calcarata</i>	Poplar
	<i>Strophiona nitens</i>	Chestnut, Oak, Hickory, Walnut, Beech, Maple
Scolytidae	<i>Corthylus columbianus</i>	Maple, Oak, Yellow-poplar, Beech, Boxelder, Sycamore, Birch, Basswood, Chestnut, Elm
	<i>Dendroctonus frontalis</i>	Pine
	<i>Dryocoetes betulae</i>	Birch, Sweetgum, Wild cherry, Beech, Pear
	<i>Monarthrum fasciatum</i>	Oak, Maple, Birch, Chestnut, Sweetgum, Blackgum, Poplar, Hickory, Mimosa, Apple, Peach, Pine
	<i>Phloeotribus liminaris</i>	Peach, Cherry, Plum, Black cherry, Elm, Mulberry, Mountain-ash
	<i>Pseudopityophthorus pruinosis</i>	Oak, American beech, Black cherry, Chickasaw plum, Chestnut, Maple, Hickory, Hornbeam, Hophornbeam
Sesiidae	<i>Paranthrene simulans</i>	Oak, American chestnut

Family	Species	Host or Crop Infested
	<i>Sannina uroceriformis</i>	Persimmon
	<i>Synanthedon exitiosa</i>	Peach, Plum, Nectarine, Cherry, Apricot, Almond, Black cherry
	<i>Synanthedon pictipes</i>	Peach, Plum, Cherry, Beach, Black Cherry
	<i>Synanthedon rubrofascia</i>	Tupelo
	<i>Synanthedon scitula</i>	Dogwood, Pecan, Hickory, Oak, Chestnut, Beech, Birch, Black cherry, Elm, Mountain-ash, Viburnum, Willow, Apple, Loquat, Ninebark, Bayberry
	<i>Vitacea polistiformis</i>	Grape

In the hygiene sector, the compounds and 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.

5 Examples of such parasites are:

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

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

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

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

Of the order Heteroptera, for example *Cimex* spp., *Triatoma* spp., *Rhodnius* spp., *Panstrongylus* spp..
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Of the order Blattellidae, for example *Blattella germanica*, *Periplaneta americana*, *Blattella germanica* and *Supella* spp..

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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..

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

10

The compounds and 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.

15 The compositions according to the invention can be used, for example, against the following pests: beetles such as *Hylotrupes bajulus*, *Chlorophorus pilosis*, *Anobium punctatum*, *Xestobium rufovillosum*, *Ptilinuspecticornis*, *Dendrobium pertinex*, *Ernobius mollis*, *Priobium carpini*, *Lyctus brunneus*, *Lyctus africanus*, *Lyctus planicollis*, *Lyctus linearis*, *Lyctus pubescens*, *Trogoxylon aequale*, *Minthesrugicollis*, *Xyleborus* spec., *Tryptodendron* spec., *Apate monachus*, *Bostrychus capucins*,
20 *Heterobostrychus brunneus*, *Sinoxylon* spec. and *Dinoderus minutus*, and also hymenopterans such as *Sirex juvencus*, *Urocerus gigas*, *Urocerus gigas taignus* and *Urocerus augur*, and termites such as *Kaloterme flavicollis*, *Cryptotermes brevis*, *Heterotermes indicola*, *Reticulitermes flavipes*,
25 *Reticulitermes santonensis*, *Reticulitermes lucifugus*, *Mastotermes darwiniensis*, *Zootermopsis nevadensis* and *Coptotermes formosanus*, and bristletails such as *Lepisma saccharina*.

25

The present invention therefore provides an insecticidal, acaricidal, nematocidal or molluscicidal composition, preferably an insecticidal or acaricidal composition comprising an insecticidally, acaricidally, nematocidally or molluscicidally effective amount of a compound of formula I and a suitable carrier or diluent therefor.

30

In a further aspect the invention provides a method of combating and controlling pests which comprises applying an insecticidally, acaricidally, nematocidally or molluscicidally effective amount, preferably an insecticidally and acaricidally effective amount of a compound of formula I or a composition comprising a compound of formula I, to a pest, a locus of pest, or to a plant susceptible to
35 attack by a pest, 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 compounds of formula I are preferably used against insects or acarines.

The term "plant" as used herein includes seedlings, bushes and trees.

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The invention also relates to a pesticidal composition, which, in addition to comprising the compound of formula I, comprises formulation adjuvants.

5 The invention therefore also relates to pesticidal compositions such as emulsifiable concentrates, suspension concentrates, directly sprayable or dilutable solutions, spreadable pastes, dilute emulsions, soluble powders, dispersible powders, wetttable powders, dusts, granules or encapsulations in polymeric substances, which comprise - at least - one of the active ingredients according to the invention and which are to be selected to suit the intended aims and the prevailing circumstances.

10 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).

15 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 ethylene glycol monomethyl ether or ethylene glycol monoethyl ether, ketones, such as cyclohexanone, isophorone or diacetone alcohol, strongly polar
20 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.

25 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 absorbitive polymers. Suitable particulate adsorptive carriers for granules are porous types, such as pumice, brick grit, sepiolite or bentonite, and suitable non-sorptive carrier materials are 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.

30 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 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.

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

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(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, ethylenediaminopolypropylene 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, 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, quaternary ammonium salts which generally have at least one alkyl radical of approximately 8 to approximately 22 C atoms as substituents and as further substituents (unhalogenated or halogenated) lower alkyl or hydroxyalkyl or benzyl 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 dodecylsulfuric ester or of a fatty alcohol sulfate mixture prepared from natural fatty acids. This group also includes the salts of the sulfuric esters and sulfonic acids of fatty alcohol/ethylene oxide adducts. The sulfonated benzimidazole derivatives preferably contain 2 sulfonyl 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. Further suitable phosphates are tris-esters of phosphoric acid with aliphatic or aromatic alcohols and/or bis-esters of alkyl phosphonic acids with aliphatic or aromatic alcohols, which are a high performance oil-type adjuvant. These tris-esters have been described, for example, in WO 01/47356, WO 00/56146, EP-A-0579052 or EP-A-1018299 or are commercially available under their chemical name. Preferred tris-esters of phosphoric acid for use in the new compositions are tris-(2-ethylhexyl) phosphate, tris-n-

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octyl phosphate and tris-butoxyethyl phosphate, where tris-(2-ethylhexyl) phosphate is most preferred. Suitable bis-ester of alkyl phosphonic acids are bis-(2-ethylhexyl)-(2-ethylhexyl)-phosphonate, bis-(2-ethylhexyl)-(n-octyl)-phosphonate, dibutyl-butyl phosphonate and bis(2-ethylhexyl)-tripropylene-phosphonate, where bis-(2-ethylhexyl)-(n-octyl)-phosphonate is particularly preferred.

5 The compositions according to the invention can preferably additionally include an additive comprising an oil of vegetable or animal origin, a mineral oil, alkyl esters of such oils or mixtures of such oils and oil derivatives. The amount of oil additive used in the composition according to the invention is generally from 0.01 to 10 %, based on the spray mixture. For example, the oil additive can be added to the spray tank in the desired concentration after the spray mixture has been prepared. Preferred oil
10 additives comprise mineral oils or an oil of vegetable origin, for example rapeseed oil such as ADIGOR® and MERO®, olive oil or sunflower oil, emulsified vegetable oil, such as AMIGO® (Rhône-Poulenc Canada Inc.), alkyl esters of oils of vegetable origin, for example the methyl derivatives, or an oil of animal origin, such as fish oil or beef tallow. A preferred additive contains, for example, as active components essentially 80 % by weight alkyl esters of fish oils and 15 % by weight methylated
15 rapeseed oil, and also 5 % by weight of customary emulsifiers and pH modifiers. Especially preferred oil additives comprise alkyl esters of C₈-C₂₂ fatty acids, especially the methyl derivatives of C₁₂-C₁₈ fatty acids, for example the methyl esters of lauric acid, palmitic acid and oleic acid, being important. Those esters are known as methyl laurate (CAS-111-82-0), methyl palmitate (CAS-112-39-0) and methyl oleate (CAS-112-62-9). A preferred fatty acid methyl ester derivative is Emery® 2230 and 2231
20 (Cognis GmbH). Those and other oil derivatives are also known from the Compendium of Herbicide Adjuvants, 5th Edition, Southern Illinois University, 2000. Also, alkoxyated fatty acids can be used as additives in the inventive compositions as well as polymethylsiloxane based additives, which have been described in WO 2008/037373.

The application and action of the oil additives can be further improved by combining them with
25 surface-active substances, such as non-ionic, anionic or cationic surfactants. Examples of suitable anionic, non-ionic and cationic surfactants are listed on pages 7 and 8 of WO 97/34485. Preferred surface-active substances are anionic surfactants of the dodecylbenzylsulfonate type, especially the calcium salts thereof, and also non-ionic surfactants of the fatty alcohol ethoxylate type. Special preference is given to ethoxylated C₁₂-C₂₂ fatty alcohols having a degree of ethoxylation of from 5 to
30 40. Examples of commercially available surfactants are the Genapol types (Clariant AG). Also preferred are silicone surfactants, especially polyalkyl-oxide-modified heptamethyltrisiloxanes, which are commercially available e.g. as Silwet L-77®, and also perfluorinated surfactants. The concentration of surface-active substances in relation to the total additive is generally from 1 to 30 % by weight. Examples of oil additives that consist of mixtures of oils or mineral oils or derivatives thereof
35 with surfactants are Edenor ME SU®, Turbocharge® (Syngenta AG, CH) and Actipron® (BP Oil UK Limited, GB).

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The said surface-active substances may also be used in the formulations alone, that is to say without oil additives.

Furthermore, the addition of an organic solvent to the oil additive/surfactant mixture can contribute to a further enhancement of action. Suitable solvents are, for example, Solvesso® (ESSO) and Aromatic Solvent® (Exxon Corporation). The concentration of such solvents can be from 10 to 80 % by weight of the total weight. Such oil additives, which may be in admixture with solvents, are described, for example, in US-A-4 834 908. A commercially available oil additive disclosed therein is known by the name MERGE® (BASF Corporation). A further oil additive that is preferred according to the invention is SCORE® (Syngenta Crop Protection Canada.)

10 In addition to the oil additives listed above, in order to enhance the activity of the compositions according to the invention it is also possible for formulations of alkylpyrrolidones, (e.g. Agrimax®) to be added to the spray mixture. Formulations of synthetic latices, such as, for example, polyacrylamide, polyvinyl compounds or poly-1-p-menthene (e.g. Bond®, Courier® or Emerald®) can also be used. Solutions that contain propionic acid, for example Eurogkem Pen-e-trate®, can also be mixed into the
15 spray mixture as activity-enhancing agents.

The term "active ingredient" refers to one of the compounds of formula I, especially the compounds of formula I specifically disclosed in the tables. It also refers to mixtures of the compound of formula I, in particular a compound selected from said Table 1, with other insecticides, fungicides, herbicides, safeners, adjuvants and the like, which mixtures are specifically disclosed below.

20 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, in particular nitrogen containing fertilizers such as ammonium nitrates and urea as described in WO 2008/017388, which can enhance the efficacy of the inventive compounds; or other
25 active ingredients for achieving specific effects, for example ammonium or phosphonium salts, in particular halides, (hydrogen)sulphates, nitrates, (hydrogen)carbonates, citrates, tartrates, formiates and acetates, as described in WO 2007/068427 and WO 2007/068428, which also can enhance the efficacy of the inventive compounds and which can be used in combination with penetration enhancers such as alkoxalated fatty acids; bactericides, fungicides, nematocides, plant activators, molluscicides
30 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).

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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.

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

The 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 comprising a compound of formula (I) as defined above are further subjects of the invention.

Further methods of application of the compositions according to the invention comprise drip application onto the soil, dipping of parts of plants such as roots bulbs or tubers, drenching the soil, as well as soil injection. These methods are known in the art.

In order to apply a compound of formula I as an insecticide, acaricide, nematicide or molluscicide to a pest, a locus of pest, or to a plant susceptible to attack by a pest, a compound of formula I is usually formulated into a composition which includes, in addition to the compound of formula I, a suitable inert diluent or carrier and, optionally, a formulation adjuvant in form of a surface active agent (SFA) as described herein or, for example, in EP-B-1062217. SFAs are chemicals which are able to modify the properties of an interface (for example, liquid/solid, liquid/air or liquid/liquid interfaces) by lowering the interfacial tension and thereby leading to changes in other properties (for example dispersion, emulsification and wetting).

As a rule, the compositions comprise 0.1 to 99%, especially 0.1 to 95%, of active ingredient of the formula I 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.

5 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.

When used in a seed dressing, a compound of formula I is used at a rate of 0.0001g to 10g (for example 0.001 g or 0.05 g), preferably 0.005 g to 10 g, more preferably 0.005 g to 4 g, per kilogram of
10 seed.

Preferred seed treatment pre-mix formulations are aqueous suspension concentrates. The formulation can be applied to the seeds using conventional treating techniques and machines, such as fluidized bed techniques, the roller mill method, rotostatic seed treaters, and drum coaters. Other methods,
15 such as spouted beds may also be useful. The seeds may be presized before coating. After coating, the seeds are typically dried and then transferred to a sizing machine for sizing. Such procedures are known in the art.

The compositions can be chosen from a number of formulation types, including dustable powders (DP), soluble powders (SP), water soluble granules (SG), water dispersible granules (WG), wettable
20 powders (WP), granules (GR) (slow or fast release), soluble concentrates (SL), oil miscible liquids (OL), ultra low volume liquids (UL), emulsifiable concentrates (EC), dispersible concentrates (DC), emulsions (both oil in water (EW) and water in oil (EO)), micro-emulsions (ME), suspension concentrates (SC), oil-based suspension concentrate (OD), aerosols, fogging/smoke formulations,
25 capsule suspensions (CS) and seed treatment formulations. The formulation type chosen in any instance will depend upon the particular purpose envisaged and the physical, chemical and biological properties of the compound of formula I.

Dustable powders (DP) may be prepared by mixing a compound of formula I with one or more solid diluents (for example natural clays, kaolin, pyrophyllite, bentonite, alumina, montmorillonite,
30 kieselguhr, chalk, diatomaceous earths, calcium phosphates, calcium and magnesium carbonates, sulphur, lime, flours, talc and other organic and inorganic solid carriers) and mechanically grinding the mixture to a fine powder.

Soluble powders (SP) may be prepared by mixing a compound of formula I with one or more water-soluble inorganic salts (such as sodium bicarbonate, sodium carbonate or magnesium sulphate)
35 or one or more water-soluble organic solids (such as a polysaccharide) and, optionally, one or more wetting agents, one or more dispersing agents or a mixture of said agents to improve water dispersibility/solubility. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water soluble granules (SG).

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Wettable powders (WP) may be prepared by mixing a compound of formula I with one or more solid diluents or carriers, one or more wetting agents and, preferably, one or more dispersing agents and, optionally, one or more suspending agents to facilitate the dispersion in liquids. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water dispersible granules (WG).

Granules (GR) may be formed either by granulating a mixture of a compound of formula I and one or more powdered solid diluents or carriers, or from pre-formed blank granules by absorbing a compound of formula I (or a solution thereof, in a suitable agent) in a porous granular material (such as pumice, attapulgite clays, fuller's earth, kieselguhr, diatomaceous earths or ground corn cobs) or by adsorbing a compound of formula I (or a solution thereof, in a suitable agent) on to a hard core material (such as sands, silicates, mineral carbonates, sulphates or phosphates) and drying if necessary. Agents which are commonly used to aid absorption or adsorption include solvents (such as aliphatic and aromatic petroleum solvents, alcohols, ethers, ketones and esters) and sticking agents (such as polyvinyl acetates, polyvinyl alcohols, dextrans, sugars and vegetable oils). One or more other additives may also be included in granules (for example an emulsifying agent, wetting agent or dispersing agent).

Dispersible Concentrates (DC) may be prepared by dissolving a compound of formula I in water or an organic solvent, such as a ketone, alcohol or glycol ether. These solutions may contain a surface active agent (for example to improve water dilution or prevent crystallisation in a spray tank).

Emulsifiable concentrates (EC) or oil-in-water emulsions (EW) may be prepared by dissolving a compound of formula I in an organic solvent (optionally containing one or more wetting agents, one or more emulsifying agents or a mixture of said agents). Suitable organic solvents for use in ECs include aromatic hydrocarbons (such as alkylbenzenes or alkylnaphthalenes, exemplified by SOLVESSO 100, SOLVESSO 150 and SOLVESSO 200; SOLVESSO is a Registered Trade Mark), ketones (such as cyclohexanone or methylcyclohexanone) and alcohols (such as benzyl alcohol, furfuryl alcohol or butanol),

N-alkylpyrrolidones (such as N-methylpyrrolidone or N-octylpyrrolidone), dimethyl amides of fatty acids (such as C₈-C₁₀ fatty acid dimethylamide) and chlorinated hydrocarbons. An EC product may spontaneously emulsify on addition to water, to produce an emulsion with sufficient stability to allow spray application through appropriate equipment. Preparation of an EW involves obtaining a compound of formula I either as a liquid (if it is not a liquid at ambient temperature, it may be melted at a reasonable temperature, typically below 70°C) or in solution (by dissolving it in an appropriate solvent) and then emulsifying the resultant liquid or solution into water containing one or more SFAs, under high shear, to produce an emulsion. Suitable solvents for use in EWs include vegetable oils, chlorinated hydrocarbons (such as chlorobenzenes), aromatic solvents (such as alkylbenzenes or alkylnaphthalenes) and other appropriate organic solvents which have a low solubility in water.

Microemulsions (ME) may be prepared by mixing water with a blend of one or more solvents with one or more SFAs, to produce spontaneously a thermodynamically stable isotropic liquid formulation. A compound of formula I is present initially in either the water or the solvent/SFA blend. Suitable solvents for use in MEs include those hereinbefore described for use in ECs or in EWs. An ME may

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be either an oil-in-water or a water-in-oil system (which system is present may be determined by conductivity measurements) and may be suitable for mixing water-soluble and oil-soluble pesticides in the same formulation. An ME is suitable for dilution into water, either remaining as a microemulsion or forming a conventional oil-in-water emulsion.

5 Suspension concentrates (SC) may comprise aqueous or non-aqueous suspensions of finely divided insoluble solid particles of a compound of formula I. SCs may be prepared by ball or bead milling the solid compound of formula I in a suitable medium, optionally with one or more dispersing agents, to produce a fine particle suspension of the compound. One or more wetting agents may be included in the composition and a suspending agent may be included to reduce the rate at which the particles
10 settle. Alternatively, a compound of formula I may be dry milled and added to water, containing agents hereinbefore described, to produce the desired end product.

Oil-based suspension concentrate (OD) may be prepared similarly by suspending finely divided insoluble solid particles of a compound of formula I in an organic fluid (for example at least one mineral oil or vegetable oil). ODs may further comprise at least one penetration promoter (for example
15 an alcohol ethoxylate or a related compound), at least one non-ionic surfactants and/or at least one anionic surfactant, and optionally at least one additive from the group of emulsifiers, foam-inhibiting agents, preservatives, anti-oxidants, dyestuffs, and/or inert filler materials. An OD is intended and suitable for dilution with water before use to produce a spray solution with sufficient stability to allow spray application through appropriate equipment.

20 Aerosol formulations comprise a compound of formula I and a suitable propellant (for example *n*-butane). A compound of formula I may also be dissolved or dispersed in a suitable medium (for example water or a water miscible liquid, such as *n*-propanol) to provide compositions for use in non-pressurised, hand-actuated spray pumps.

A compound of formula I may be mixed in the dry state with a pyrotechnic mixture to form a
25 composition suitable for generating, in an enclosed space, a smoke containing said compound.

Capsule suspensions (CS) may be prepared in a manner similar to the preparation of EW formulations but with an additional polymerisation stage such that an aqueous dispersion of oil droplets is obtained, in which each oil droplet is encapsulated by a polymeric shell and contains a compound of formula I and, optionally, a carrier or diluent therefor. The polymeric shell may be produced by either an
30 interfacial polycondensation reaction or by a coacervation procedure. The compositions may provide for controlled release of the compound of formula I and they may be used for seed treatment. A compound of formula I may also be formulated in a biodegradable polymeric matrix to provide a slow, controlled release of the compound.

A compound of formula I may also be formulated for use as a seed treatment, for example as a
35 powder composition, including a powder for dry seed treatment (DS), a water soluble powder (SS) or a water dispersible powder for slurry treatment (WS), or as a liquid composition, including a flowable concentrate (FS), a solution (LS) or a capsule suspension (CS). The preparations of DS, SS, WS, FS and LS compositions are very similar to those of, respectively, DP, SP, WP, SC, OD and DC

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compositions described above. Compositions for treating seed may include an agent for assisting the adhesion of the composition to the seed (for example a mineral oil or a film-forming barrier).

A composition of the present invention may include one or more additives to improve the biological performance of the composition (for example by improving wetting, retention or distribution on

5 surfaces; resistance to rain on treated surfaces; or uptake or mobility of a compound of formula I).

Such additives include surface active agents (SFAs), spray additives based on oils, for example certain mineral oils, vegetable oils or natural plant oils (such as soy bean and rape seed oil), and blends of these with other bio-enhancing adjuvants (ingredients which may aid or modify the action of a compound of formula I). Increasing the effect of a compound of formula I may for example be

10 achieved by adding ammonium and/or phosphonium salts, and/or optionally at least one penetration promotor such as fatty alcohol alkoxyates (for example rape oil methyl ester) or vegetable oil esters.

Wetting agents, dispersing agents and emulsifying agents may be surface active agents (SFAs) of the cationic, anionic, amphoteric or non-ionic type.

Suitable SFAs of the cationic type include quaternary ammonium compounds (for example

15 cetyltrimethyl ammonium bromide), imidazolines and amine salts.

Suitable anionic SFAs include alkali metals salts of fatty acids, salts of aliphatic monoesters of sulphuric acid (for example sodium lauryl sulphate), salts of sulphonated aromatic compounds (for example sodium dodecylbenzenesulphonate, calcium dodecylbenzenesulphonate, butylnaphthalene

20 sulphates, alcohol ether sulphates (for example sodium laureth-3-sulphate), ether carboxylates (for example sodium laureth-3-carboxylate), phosphate esters (products from the reaction between one or more fatty alcohols and phosphoric acid (predominately mono-esters) or phosphorus pentoxide

(predominately di-esters), for example the reaction between lauryl alcohol and tetraphosphoric acid; additionally these products may be ethoxylated), sulphosuccinamates, paraffin or olefine sulphonates,

25 taurates and lignosulphonates.

Suitable SFAs of the amphoteric type include betaines, propionates and glycinates.

Suitable SFAs of the non-ionic type include condensation products of alkylene oxides, such as ethylene oxide, propylene oxide, butylene oxide or mixtures thereof, with fatty alcohols (such as oleyl alcohol or cetyl alcohol) or with alkylphenols (such as octylphenol, nonylphenol or octylcresol); partial

30 esters derived from long chain fatty acids or hexitol anhydrides; condensation products of said partial esters with ethylene oxide; block polymers (comprising ethylene oxide and propylene oxide); alkanolamides; simple esters (for example fatty acid polyethylene glycol esters); amine oxides (for example lauryl dimethyl amine oxide); and lecithins.

Suitable suspending agents include hydrophilic colloids (such as polysaccharides, polyvinylpyrrolidone or sodium carboxymethylcellulose) and swelling clays (such as bentonite or attapulgite).

35 A compound of formula I may be applied by any of the known means of applying pesticidal compounds. For example, it may be applied, formulated or unformulated, to the pests or to a locus of the pests (such as a habitat of the pests, or a growing plant liable to infestation by the pests) or to any part of the plant, including the foliage, stems, branches or roots, to the seed before it is planted or to

other media in which plants are growing or are to be planted (such as soil surrounding the roots, the soil generally, paddy water or hydroponic culture systems), directly or it may be sprayed on, dusted on, applied by dipping, applied as a cream or paste formulation, applied as a vapour or applied through distribution or incorporation of a composition (such as a granular composition or a composition packed

5 in a water-soluble bag) in soil or an aqueous environment.

A compound of formula I may also be injected into plants or sprayed onto vegetation using electrodynamic spraying techniques or other low volume methods, or applied by land or aerial irrigation systems.

Compositions for use as aqueous preparations (aqueous solutions or dispersions) are generally supplied in the form of a concentrate containing a high proportion of the active ingredient, the concentrate being added to water before use. These concentrates, which may include DCs, SCs, ODs, ECs, EWs, MEs SGs, SPs, WPs, WGs and CSs, are often required to withstand storage for prolonged periods and, after such storage, to be capable of addition to water to form aqueous preparations which remain homogeneous for a sufficient time to enable them to be applied by

15 conventional spray equipment. Such aqueous preparations may contain varying amounts of a compound of formula I (for example 0.0001 to 10%, by weight) depending upon the purpose for which they are to be used.

A compound of formula I may be used in mixtures with fertilisers (for example nitrogen-, potassium- or phosphorus-containing fertilisers, and more particularly ammonium nitrate and/or urea fertilizers).

20 Suitable formulation types include granules of fertiliser. The mixtures suitably contain up to 25% by weight of the compound of formula I.

Preferred compositions are composed in particular as follows (% = percent by weight):

Emulsifiable concentrates:

25 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%

Dusts:

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

Suspension concentrates:

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

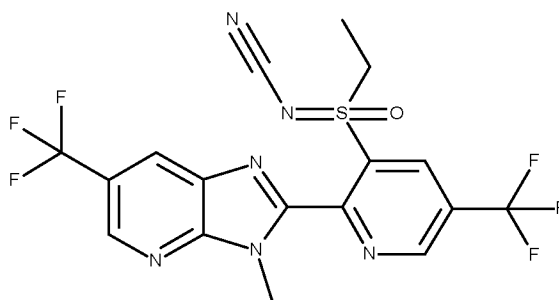
Wettable powders:

active ingredient: 0.5 to 90%, preferably 1 to 80%

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temperature for 18 hours. A total of 0.6 eq. of cyanamide and 0.6 eq. of iodobenzene diacetate were further added to the mixture in two portions and stirring continued at 40°C for 7 hours. The reaction mixture was diluted with dichloromethane, poured into water and the biphasic system treated with 10% aqueous NaHSO₃. After stirring for 30 minutes, the organic phase was separated, the water layer
 5 extracted with dichloromethane, the combined organic phases dried over magnesium sulfate, filtered and concentrated. The residue was purified by flash column chromatography (heptane / ethyl acetate) to afford the title product as a white solid (303 mg), mp: 187°C. ¹H-NMR (CDCl₃, 400 MHz): 1.71 (t, J=7.3 Hz, 3 H), 3.30 (dt, J=12.3, 7.3 Hz, 1 H), 3.88 (dt, J=12.3, 7.3 Hz, 1 H), 4.43 (s, 3 H), 8.39 (d, J=1.4 Hz, 1 H), 8.87 (d, J=1.4 Hz, 1 H), 9.06 (d, J=1.5 Hz, 1 H), 9.20 (d, J=1.5 Hz, 1 H). LCMS
 10 (method ZCQ13): 447 (MH⁺), retention time 1.72 min.

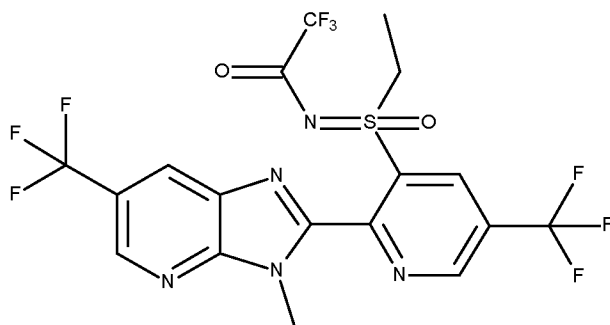
EXAMPLE 2: Preparation of [ethyl-[2-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-5-(trifluoromethyl)-3-pyridyl]-oxo-λ⁶-sulfanylidene]cyanamide (compound P1.2):



A solution of [ethyl-[2-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-5-(trifluoromethyl)-3-
 15 pyridyl]-λ⁴-sulfanylidene]cyanamide (280 mg, 0.627 mmol) dissolved in acetonitrile (1.5 ml) and dichloromethane (1.8 ml) was added to a solution of sodium periodate (271 mg, 1.254 mmol) in water (3.0 ml) at ambient temperature. Ruthenium(III) chloride hydrate (1.45mg, 0.007 mmol) was added and the mixture stirred at ambient temperature for 3.5 hours. After dilution with acetonitrile (6.0 ml), dichloromethane (2.0 ml) and water (3.0 ml), more sodium periodate (135 mg, 0.625 mmol) was added
 20 and stirring continued overnight. The organic phase was separated, the water layer extracted with dichloromethane, the combined organic phases washed with 10% aqueous NaHSO₃, dried over magnesium sulfate, filtered and concentrated to afford the title product as a white solid (253 mg), mp: 153°C. ¹H-NMR (CDCl₃, 400 MHz): 1.56 (t, J=7.3 Hz, 3 H), 4.12 (s, 3 H), 4.30 (dt, J=14.0, 7.3 Hz, 1 H), 4.64 (dt, J=14.0, 7.3 Hz, 1 H), 8.35 (d, J=1.5 Hz, 1 H), 8.82 (d, J=1.5 Hz, 1 H), 8.85 (d, J=1.2 Hz, 1 H), 9.34 (d, J=1.2 Hz, 1 H). LCMS (method ZCQ13): 463 (MH⁺), retention time 1.67 min.
 25

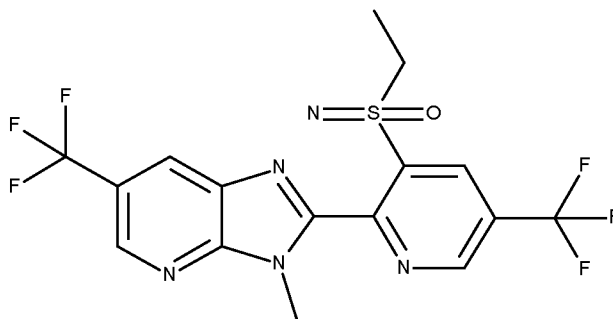
EXAMPLE 3: Preparation of N-[ethyl-[2-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-5-(trifluoromethyl)-3-pyridyl]-oxo-λ⁶-sulfanylidene]-2,2,2-trifluoro-acetamide (compound P1.3):

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To a solution of [ethyl-[2-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-5-(trifluoromethyl)-3-pyridyl]-oxo- λ^6 -sulfanylidene]cyanamide (218 mg, 0.472 mmol) in dichloromethane (21 ml) at 0°C was added trifluoroacetic acid anhydride (0.197 ml, 1.414 mmol). The mixture was stirred at ambient temperature for 18 hours. The reaction mixture was poured on water, the aqueous layer extracted with dichloromethane (3x 10 ml). The combined organic layers were dried over anhydrous magnesium sulfate, filtered and evaporated. The residue was purified by flash column chromatography (heptane / ethyl acetate) to give the title product as a white solid (178 mg), mp: 121°C. ¹H-NMR (CDCl₃, 400 MHz): 1.55 (t, *J*=7.3 Hz, 3 H), 3.92 (s, 3 H), 4.43 (dt, *J*=14.3, 7.3 Hz, 1 H), 4.73 (dt, *J*=14.3, 7.3 Hz, 1 H), 8.34 (d, *J*=1.2 Hz, 1 H), 8.82 (d, *J*=1.2 Hz, 1 H), 8.84 (d, *J*=1.2 Hz, 1 H), 9.30 (d, *J*=1.2 Hz, 1 H). LCMS (method ZCQ13): 534 (MH⁺), retention time 1.97 min.

EXAMPLE 4: Preparation of ethyl-imino-[2-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-5-(trifluoromethyl)-3-pyridyl]-oxo- λ^6 -sulfane (compound P1.4):

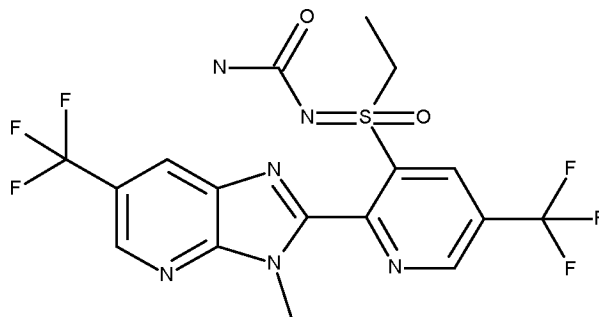


To a solution of N-[ethyl-[2-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-5-(trifluoromethyl)-3-pyridyl]-oxo- λ^6 -sulfanylidene]-2,2,2-trifluoro-acetamide (149 mg, 0.279 mmol) in methanol (25 ml) was added potassium carbonate (193 mg, 1.397 mmol) at ambient temperature, and the mixture was stirred for 15 minutes. After removal of the solvent under reduced pressure, the residue was diluted with ethyl acetate and filtered. The filtrate was concentrated and the residue purified by column chromatography (heptane / ethyl acetate) to afford the title product as a white solid (109 mg), mp: 102°C. ¹H-NMR (CDCl₃, 400 MHz): 1.40 (t, *J*=7.5 Hz, 3 H), 2.76 (s, 1 H), 3.83 (dt, *J*=14.2, 7.3 Hz, 1

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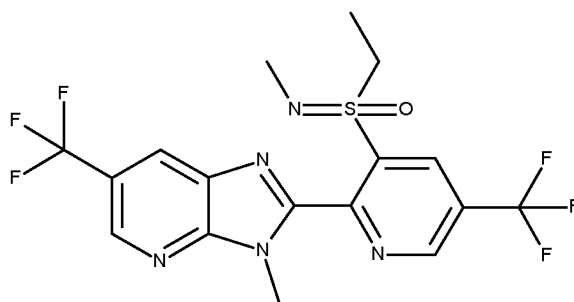
H), 3.90 (s, 3 H), 3.95 (dt, $J=14.2, 7.3$ Hz, 1 H), 8.33 (d, $J=1.5$ Hz, 1 H), 8.78 (d, $J=1.5$ Hz, 1 H), 8.83 (d, $J=1.5$ Hz, 1 H), 9.20 (d, $J=1.5$ Hz, 1 H). LCMS (method ZCQ13): 438 (MH^+), retention time 1.50 min.

5 EXAMPLE 5: Preparation of [ethyl-[2-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-5-(trifluoromethyl)-3-pyridyl]-oxo- λ^6 -sulfanylidene]urea (compound P1.5):



To a solution of [ethyl-[2-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-5-(trifluoromethyl)-3-pyridyl]-oxo- λ^6 -sulfanylidene]cyanamide (213 mg, 0.461 mmol) in acetonitrile (2 ml) was added concentrated sulfuric acid (33 μ l) and the reaction mixture was stirred at room temperature for one
 10 hour. The mixture was cooled to 5°C, neutralized by addition of aqueous 20% sodium hydroxide, diluted with ethyl acetate and the layers were separated. The organic layer was washed with saturated aqueous sodium chloride, dried over anhydrous sodium sulfate, filtered and evaporated. The residue was triturated with hexane/diethyl ether 4:1, filtered and the solid dried to afford the title product as a white solid (112 mg), mp: 206-208°C.

15 EXAMPLE 6: Preparation of ethyl-methylimino-[2-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-5-(trifluoromethyl)-3-pyridyl]-oxo- λ^6 -sulfane (compound P1.6):

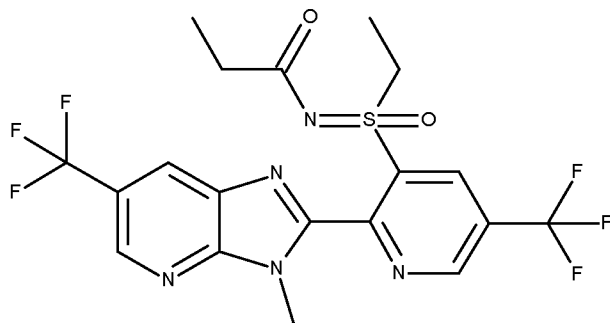


To a suspension of 60% sodium hydride (31.6 mg, 0.789 mmol) in 1,2-dimethoxyethane (4 ml) at room temperature was added ethyl-imino-[2-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-5-(trifluoromethyl)-3-pyridyl]-oxo- λ^6 -sulfane (150 mg, 0.343 mmol) and the mixture was stirred
 20 minutes until the gas evolution stopped. Methyl iodide (32.2 μ l, 0.514 mmol) was then added to the

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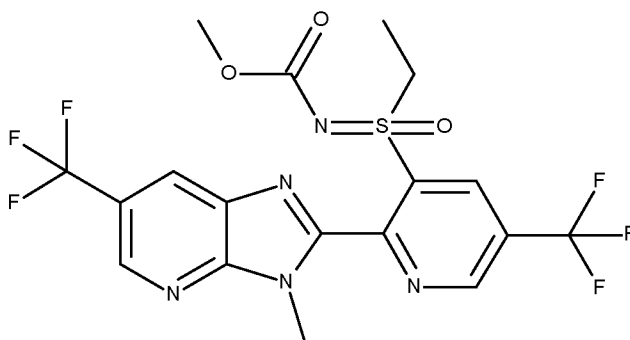
clear solution and the mixture stirred at room temperature for 1.5 hours. The mixture was concentrated under reduced pressure and the residue purified by column chromatography on silica (0-28% ethyl acetate gradient in heptane) to give the title product as a white solid (90 mg), mp: 172-173°C.

EXAMPLE 7: Preparation of N-[ethyl-[2-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-5-(trifluoromethyl)-3-pyridyl]-oxo- λ^6 -sulfanylidene]propanamide (compound P1.7):



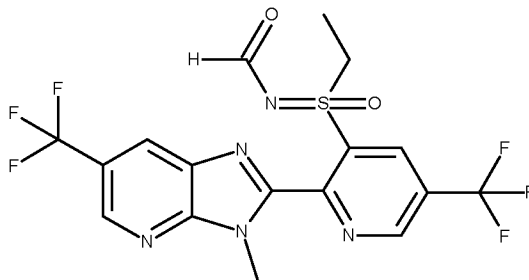
To a solution of ethyl-imino-[2-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-5-(trifluoromethyl)-3-pyridyl]-oxo- λ^6 -sulfane (150mg, 0.343 mmol) and triethylamine (61.8 μ l, 0.446 mmol) in dichloromethane (2 ml) at 0-5°C was added propanoyl chloride (30 μ l, 0.343 mmol) dropwise. The reaction mixture was stirred one hour at room temperature. After addition of further propanoyl chloride (3 μ l) to bring the reaction to completion, the mixture was poured on water and the layers separated. The organic layer was washed twice with water, dried over anhydrous sodium sulfate, filtered and evaporated. The residue purified by column chromatography on silica (0-30% ethyl acetate gradient in heptane) to give the title product as a solid (125 mg). LCMS (method 1): 494 (MH⁺), retention time 1.80 min.

EXAMPLE 8: Analogous preparation of methyl N-[ethyl-[2-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-5-(trifluoromethyl)-3-pyridyl]-oxo- λ^6 -sulfanylidene]carbamate (compound P1.8):



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EXAMPLE 11: Preparation of N-[ethyl-[2-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-5-(trifluoromethyl)-3-pyridyl]-oxo- λ^6 -sulfanylidene]formamide (compound P1.10):

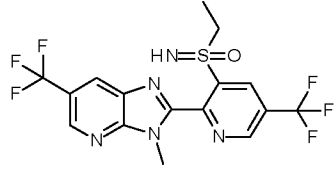
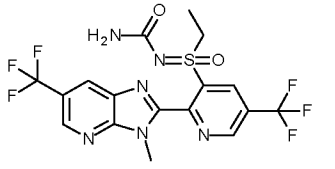
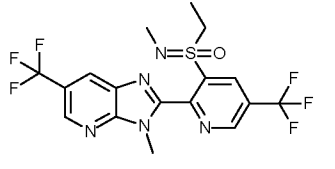
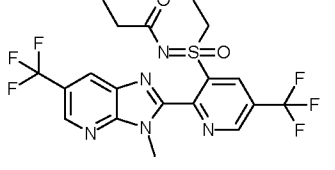
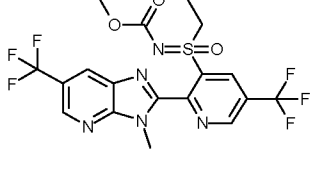
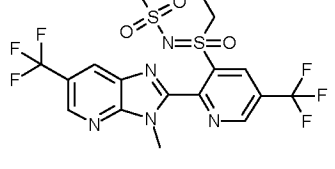
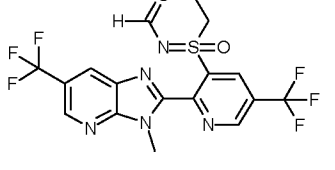
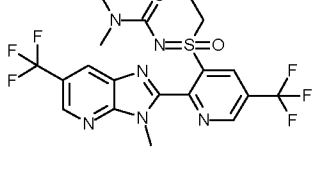


A solution of ethyl-imino-[2-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-5-(trifluoromethyl)-3-pyridyl]-oxo- λ^6 -sulfane (150mg, 0.343 mmol) in trimethyl orthoformate (1 ml) was heated at 90°C overnight. The reaction mixture was concentrated under reduced pressure and the residue purified by column chromatography on silica (0-20% ethyl acetate gradient in heptane). The fractions containing product were combined and concentrated. The product was again purified by C18 reversed-phase column chromatography (30-100% acetonitrile gradient in water) to afford the title compound (22 mg) as a solid, mp: 154-156°C.

Table P1: Examples of compounds of formula (I)

Compound No.	Structures	Melting Point	MS/NMR
P1.1		187°C	LCMS (method 1): 447 (M+H) ⁺ R _t = 1.72 min
P1.2		153°C	LCMS (method 1): 463 (M+H) ⁺ R _t = 1.67 min
P1.3		121°C	LCMS (method 1): 534 (M+H) ⁺ R _t = 1.97 min

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Compound No.	Structures	Melting Point	MS/NMR
P1.4		102°C	LCMS (method 1): 438 (M+H) ⁺ R _t = 1.50 min
P1.5		206-208°C	
P1.6		172-173°C	
P1.7		solid	LCMS (method 1): 494 (M+H) ⁺ R _t = 1.80 min
P1.8		gum	LCMS (method 1): 496 (M+H) ⁺ R _t = 1.68 min
P1.9		gum	LCMS (method 1): 516 (M+H) ⁺ R _t = 1.66 min
P1.10		154-156°C	
P1.11		195-197°C	

Further specific examples of compounds of the formula (I) are illustrated in the Tables 1 to 19 above.

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Formulation Examples (% = percent by weight)

<u>Example F1: Emulsion concentrates</u>		a)	b)	c)
5	Active ingredient	25 %	40 %	50 %
	Calcium dodecylbenzenesulfonate	5 %	8 %	6 %
	Castor oil polyethylene glycol ether (36 mol of EO)	5 %	-	-
10	Tributylphenoxy polyethylene glycol ether (30 mol of EO)	-	12 %	4 %
	Cyclohexanone	-	15 %	20 %
	Xylene mixture	65 %	25 %	20 %

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

<u>Example F2: Solutions</u>		a)	b)	c)	d)
	Active ingredient	80 %	10 %	5 %	95 %
20	Ethylene glycol monomethyl ether	20 %	-	-	-
	Polyethylene glycol MW 400	-	70 %	-	-
	N-Methylpyrrolid-2-one	20 %	-	-	
	Epoxidized coconut oil	-	1 %	5 %	
25	Petroleum ether (boiling range: 160-190°)	-	-	94 %	-

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

<u>Example F3: Granules</u>		a)	b)	c)	d)
30	Active ingredient	5 %	10 %	8 %	21 %
	Kaolin	94 %	-	79 %	54 %
	Highly disperse silica	1 %	-	13 %	7 %
	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.

<u>Example F4: Dusts</u>		a)	b)
	Active ingredient	2 %	5 %

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Highly disperse silica	1 %	5 %
Talc	97 %	-
Kaolin	-	90 %

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

5

Example F5: Wettable powders

	a)	b)	c)
Active ingredient	25 %	50 %	75 %
Sodium lignosulfonate		5 %	5 % -
Sodium lauryl sulfate	3 %	-	5 %
10 Sodium diisobutyl-naphthalenesulfonate	-	6 %	10 %
Octylphenoxypolyethylene glycol ether (7-8 mol of EO)	-	2 %	-
Highly disperse silica	5 %	10 %	10 %
15 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.

20 Example F6: Extruder granules

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

25 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 %
30 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.

35 Example F8: Suspension concentrate

Active ingredient	40 %
Ethylene glycol	10 %
Nonylphenoxypolyethylene glycol ether (15 mol of EO)	6 %
Sodium lignosulfonate	10 %

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Carboxymethylcellulose	1 %
37 % aqueous formaldehyde solution	0.2 %
Silicone oil (75 % aqueous emulsion)	0.8 %
Water	32 %

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

Example F9: Powders for dry seed treatment

	a)	b)	c)
active ingredient	25 %	50 %	75 %
light mineral oil	5 %	5 %	5 %
highly dispersed silicic acid	5 %	5 %	-
Kaolin	65 %	40 %	-
Talcum	-	-	20 %

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

10

Example F10: Emulsifiable concentrate

active ingredient	10 %
octylphenol polyethylene glycol ether (4-5 mol of ethylene oxide)	3 %
calcium dodecylbenzenesulfonate	3 %
castor oil polyglycol ether (35 mol of ethylene oxide)	4 %
Cyclohexanone	30 %
xylene mixture	50 %

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

Example F11: Flowable concentrate for seed treatment

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

15

The finely ground combination is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired dilution can be obtained by dilution with water. Using such

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dilutions, living plants as well as plant propagation material can be treated and protected against infestation by microorganisms, by spraying, pouring or immersion.

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

The following mixtures of the compounds of formula I with active ingredients are preferred (the abbreviation "TX" means "one compound selected from the group consisting of the compounds described in Tables 1 to 19 and P1 of the present invention"):

an adjuvant selected from the group of substances consisting of petroleum oils (alternative name) (628) + TX,
 an acaricide selected from the group of substances consisting of acequinocyl ([57960-19-7] [CCN]) + TX, fenpyroximate [134098-61-6][CCN] + TX, flucythrinate [70124-77-5][CCN] + TX, 1,1-bis(4-chlorophenyl)-2-ethoxyethanol (IUPAC name) (910) + TX, hexythiazox [78587-05-0][CCN] + TX, 2,4-dichlorophenyl benzenesulfonate (IUPAC/Chemical Abstracts name) (1059) + TX, 2-fluoro-*N*-methyl-*N*-1-naphthylacetamide (IUPAC name) (1295) + TX, 4-chlorophenyl phenyl sulfone (IUPAC name) (981) + TX, abamectin (1) + TX, acequinocyl (3) + TX, acetoprole [CCN] + TX, acrinathrin (9) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, alpha-cypermethrin (202) + TX, amidithion (870) + TX, amidoflumet [CCN] + TX, amidothioate (872) + TX, amiton (875) + TX, amiton hydrogen oxalate (875) + TX, amitraz (24) + TX, aramite (881) + TX, arsenous oxide (882) + TX, AVI 382 (compound code) + TX, AZ 60541 (compound code) + TX, azinphos-ethyl (44) + TX, azinphos-methyl (45) + TX, azobenzene (IUPAC name) (888) + TX, azocyclotin (46) + TX, azothoate (889) + TX, benomyl (62) + TX, benoxafos (alternative name) [CCN] + TX, benzoximate (71) + TX, benzyl benzoate (IUPAC name) [CCN] + TX, bifenazate (74) + TX, bifenthrin (76) + TX, binapacryl (907) + TX, brofenvalerate (alternative name) + TX, bromocyclen (918) + TX, bromophos (920) + TX, bromophos-ethyl (921) + TX, bromopropylate (94) + TX, buprofezin (99) + TX, butocarboxim (103) + TX, butoxycarboxim (104) + TX, butylpyridaben (alternative name) + TX, calcium polysulfide (IUPAC name) (111) + TX, camphechlor (941) + TX, carbanolate (943) + TX, carbaryl

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(115) + TX, carbofuran (118) + TX, carbophenothion (947) + TX, CGA 50'439 (development code) (125) + TX, chinomethionat (126) + TX, chlorbense (959) + TX, chlordimeform (964) + TX, chlordimeform hydrochloride (964) + TX, chlorfenapyr (130) + TX, chlorfenethol (968) + TX, chlorfenson (970) + TX, chlorfensulfide (971) + TX, chlorfenvinphos (131) + TX, chlorobenzilate (975) + TX, chloromebuform (977) + TX, chloromethiuron (978) + TX, chloropropylate (983) + TX, chlorpyrifos (145) + TX, chlorpyrifos-methyl (146) + TX, chlorthiophos (994) + TX, cinerin I (696) + TX, cinerin II (696) + TX, cinerins (696) + TX, clofentezine (158) + TX, closantel (alternative name) [CCN] + TX, coumaphos (174) + TX, crotamiton (alternative name) [CCN] + TX, crotoxyphos (1010) + TX, cufraneb (1013) + TX, cyanthoate (1020) + TX, cyflumetofen [400882-07-7] + TX, cyhalothrin (196) + TX, cyhexatin (199) + TX, cypermethrin (201) + TX, DCPM (1032) + TX, DDT (219) + TX, demephion (1037) + TX, demephion-O (1037) + TX, demephion-S (1037) + TX, demeton (1038) + TX, demeton-methyl (224) + TX, demeton-O (1038) + TX, demeton-O-methyl (224) + TX, demeton-S (1038) + TX, demeton-S-methyl (224) + TX, demeton-S-methylsulfon (1039) + TX, diafenthion (226) + TX, dialifos (1042) + TX, diazinon (227) + TX, dichlofluanid (230) + TX, dichlorvos (236) + TX, dicliphos (alternative name) + TX, dicofol (242) + TX, dicrotophos (243) + TX, dienochlor (1071) + TX, dimefox (1081) + TX, dimethoate (262) + TX, dinactin (alternative name) (653) + TX, dinex (1089) + TX, dinex-diclexine (1089) + TX, dinobuton (269) + TX, dinocap (270) + TX, dinocap-4 [CCN] + TX, dinocap-6 [CCN] + TX, dinocton (1090) + TX, dinopenton (1092) + TX, dinosulfon (1097) + TX, dinoterbon (1098) + TX, dioxathion (1102) + TX, diphenyl sulfone (IUPAC name) (1103) + TX, disulfiram (alternative name) [CCN] + TX, disulfoton (278) + TX, DNOC (282) + TX, dofenapyn (1113) + TX, doramectin (alternative name) [CCN] + TX, endosulfan (294) + TX, endothion (1121) + TX, EPN (297) + TX, eprinomectin (alternative name) [CCN] + TX, ethion (309) + TX, ethoate-methyl (1134) + TX, etoxazole (320) + TX, etrimfos (1142) + TX, fenazaflor (1147) + TX, fenazaquin (328) + TX, fenbutatin oxide (330) + TX, fenothiocarb (337) + TX, fenpropathrin (342) + TX, fenpyrad (alternative name) + TX, fenpyroximate (345) + TX, fenson (1157) + TX, fentrifanil (1161) + TX, fenvalerate (349) + TX, fipronil (354) + TX, fluacrypyrim (360) + TX, fluazuron (1166) + TX, flubenzimine (1167) + TX, flucycloxuron (366) + TX, flucythrinate (367) + TX, fluenetil (1169) + TX, flufenoxuron (370) + TX, flumethrin (372) + TX, fluorbense (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) +

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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, 5 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, 10 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, 15 pyrethrin II (696) + TX, pyrethrins (696) + TX, pyridaben (699) + TX, pyridaphenthion (701) + TX, pyrimidifen (706) + TX, pyrimitate (1370) + TX, quinalphos (711) + TX, quintiofos (1381) + TX, R-1492 (development code) (1382) + TX, RA-17 (development code) (1383) + TX, rotenone (722) + TX, schradan (1389) + TX, sebufos (alternative name) + TX, selamectin (alternative name) [CCN] + TX, SI-0009 (compound code) + TX, sophamide (1402) + TX, spirodiclofen (738) + TX, 20 spiromesifen (739) + TX, SSI-121 (development code) (1404) + TX, sulfiram (alternative name) [CCN] + TX, sulfluramid (750) + TX, sulfotep (753) + TX, sulfur (754) + TX, SZI-121 (development code) (757) + TX, tau-fluvalinate (398) + TX, tebufenpyrad (763) + TX, TEPP (1417) + TX, terbam (alternative name) + TX, tetrachlorvinphos (777) + TX, tetradifon (786) + TX, tetranactin (alternative name) (653) + TX, tetrasul (1425) + TX, thiafenox (alternative name) + TX, 25 thiocarboxime (1431) + TX, thiofanox (800) + TX, thiometon (801) + TX, thioquinox (1436) + TX, thuringiensin (alternative name) [CCN] + TX, triamiphos (1441) + TX, triarathene (1443) + TX, triazophos (820) + TX, triazuron (alternative name) + TX, trichlorfon (824) + TX, trifenofos (1455) + TX, trinactin (alternative name) (653) + TX, vamidothion (847) + TX, vaniliprole [CCN] and YI-5302 (compound code) + TX, 30 an algicide selected from the group of substances consisting of bethoxazin [CCN] + TX, copper dioctanoate (IUPAC name) (170) + TX, copper sulfate (172) + TX, cybutryne [CCN] + TX, dichlone (1052) + TX, dichlorophen (232) + TX, endothal (295) + TX, fentin (347) + TX, hydrated lime [CCN] + TX, nabam (566) + TX, quinoclamine (714) + TX, quinonamid (1379) + TX, simazine (730) + TX, triphenyltin acetate (IUPAC name) (347) and triphenyltin hydroxide (IUPAC name) (347) 35 + TX, an anthelmintic selected from the group of substances consisting of abamectin (1) + TX, crufomate (1011) + TX, doramectin (alternative name) [CCN] + TX, emamectin (291) + TX, emamectin benzoate (291) + TX, eprinomectin (alternative name) [CCN] + TX, ivermectin (alternative name) [CCN] + TX, milbemycin oxime (alternative name) [CCN] + TX, moxidectin (alternative name) [CCN]

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+ 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,
 5 a bactericide selected from the group of substances consisting of 1-hydroxy-1*H*-pyridine-2-thione (IUPAC name) (1222) + TX, 4-(quinoxalin-2-ylamino)benzenesulfonamide (IUPAC name) (748) + TX, 8-hydroxyquinoline sulfate (446) + TX, bronopol (97) + TX, copper dioctanoate (IUPAC name) (170) + TX, copper hydroxide (IUPAC name) (169) + TX, cresol [CCN] + TX, dichlorophen (232) + TX, dipyrithione (1105) + TX, dodicin (1112) + TX, fenaminosulf (1144) + TX, formaldehyde (404) + TX,
 10 TX, hydrargaphen (alternative name) [CCN] + TX, kasugamycin (483) + TX, kasugamycin hydrochloride hydrate (483) + TX, nickel bis(dimethyldithiocarbamate) (IUPAC name) (1308) + TX, nitrapyrin (580) + TX, octhilinone (590) + TX, oxolinic acid (606) + TX, oxytetracycline (611) + TX, potassium hydroxyquinoline sulfate (446) + TX, probenazole (658) + TX, streptomycin (744) + TX, streptomycin sesquisulfate (744) + TX, tecloftalam (766) + TX, and thiomersal (alternative name) [CCN] + TX,
 15 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,
 20 *Diglyphus isaea* (alternative name) (254) + TX, *Encarsia formosa* (scientific name) (293) + TX, *Eretmocerus eremicus* (alternative name) (300) + TX, *Helicoverpa zea* NPV (alternative name) (431) + TX, *Heterorhabditis bacteriophora* and *H. megidis* (alternative name) (433) + TX, *Hippodamia convergens* (alternative name) (442) + TX, *Leptomastix dactylopii* (alternative name) (488) + TX, *Macrolophus caliginosus* (alternative name) (491) + TX, *Mamestra brassicae* NPV (alternative name) (494) + TX, *Metaphycus helvolus* (alternative name) (522) + TX, *Metarhizium anisopliae* var. *acridum* (scientific name) (523) + TX, *Metarhizium anisopliae* var. *anisopliae* (scientific name) (523) + TX, *Neodiprion sertifer* NPV and *N. lecontei* NPV (alternative name) (575) + TX, *Orius* spp. (alternative name) (596) + TX, *Paecilomyces fumosoroseus* (alternative name) (613) + TX, *Phytoseiulus persimilis* (alternative name) (644) + TX, *Spodoptera exigua* multicapsid nuclear

- polyhedrosis virus (scientific name) (741) + TX, *Steinernema bibionis* (alternative name) (742) + TX, *Steinernema carpocapsae* (alternative name) (742) + TX, *Steinernema feltiae* (alternative name) (742) + TX, *Steinernema glaseri* (alternative name) (742) + TX, *Steinernema riobrave* (alternative name) (742) + TX, *Steinernema riobravus* (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,
- 10 a chemosterilant selected from the group of substances consisting of apholate [CCN] + TX, bisazir (alternative name) [CCN] + TX, busulfan (alternative name) [CCN] + TX, diflubenzuron (250) + TX, dimatif (alternative name) [CCN] + TX, hemel [CCN] + TX, hempa [CCN] + TX, metepa [CCN] + TX, methiotepa [CCN] + TX, methyl apholate [CCN] + TX, morzid [CCN] + TX, penfluron (alternative name) [CCN] + TX, tepa [CCN] + TX, thiohempa (alternative name) [CCN] + TX,
- 15 thiotepa (alternative name) [CCN] + TX, tretamine (alternative name) [CCN] and uredepa (alternative name) [CCN] + TX,
- an insect pheromone selected from the group of substances consisting of (*E*)-dec-5-en-1-yl acetate with (*E*)-dec-5-en-1-ol (IUPAC name) (222) + TX, (*E*)-tridec-4-en-1-yl acetate (IUPAC name) (829) + TX, (*E*)-6-methylhept-2-en-4-ol (IUPAC name) (541) + TX, (*E,Z*)-tetradeca-4,10-dien-1-yl acetate (IUPAC name) (779) + TX, (*Z*)-dodec-7-en-1-yl acetate (IUPAC name) (285) + TX, (*Z*)-hexadec-11-enal (IUPAC name) (436) + TX, (*Z*)-hexadec-11-en-1-yl acetate (IUPAC name) (437) + TX, (*Z*)-hexadec-13-en-11-yn-1-yl acetate (IUPAC name) (438) + TX, (*Z*)-icos-13-en-10-one (IUPAC name) (448) + TX, (*Z*)-tetradec-7-en-1-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) + 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, codlure (alternative name) [CCN] + TX, codlemone (alternative name) (167) + TX, cuelure (alternative name) (179) + TX, disarlure (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, gossypure (alternative name) (420) + TX, grandlure (421) + TX, grandlure I (alternative name) (421) + TX, grandlure II (alternative name) (421) + TX, grandlure III (alternative name) (421) + TX, grandlure IV (alternative name) (421) + TX, hexalure [CCN] + TX, ipsdienol (alternative name) [CCN] + TX, ipsenol (alternative name) [CCN] + TX, japonilure (alternative name) (481) + TX, lineatin (alternative name) [CCN] + TX, litlure (alternative name) [CCN] + TX, looplure (alternative name) [CCN] + TX, medlure [CCN] + TX, megatomoic acid (alternative name) [CCN] +

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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 momfluorothrin [609346-29-4] + TX, pyrafluprole [315208-17-4] + TX, flometoquin [875775-74-9] + TX, flupyradifuron [951659-40-8] + TX, 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-ethylsulfinyethyl methyl phosphate (IUPAC name) (1066) + TX, 2-(1,3-dithiolan-2-yl)phenyl dimethylcarbamate (IUPAC/Chemical Abstracts name) (1109) + TX, 2-(2-butoxyethoxy)ethyl thiocyanate (IUPAC/Chemical Abstracts name) (935) + TX, 2-(4,5-dimethyl-1,3-dioxolan-2-yl)phenyl methylcarbamate (IUPAC/Chemical Abstracts name) (1084) + TX, 2-(4-chloro-3,5-xylyloxy)ethanol (IUPAC name) (986) + TX, 2-chlorovinyl diethyl phosphate (IUPAC name) (984) + TX, 2-imidazolidone (IUPAC name) (1225) + TX, 2-isovalerylindan-1,3-dione (IUPAC name) (1246) + TX, 2-methyl(prop-2-ynyl)aminophenyl methylcarbamate (IUPAC name) (1284) + TX, 2-thiocyanatoethyl laurate (IUPAC name) (1433) + TX, 3-bromo-1-chloroprop-1-ene (IUPAC name) (917) + TX, 3-methyl-1-phenylpyrazol-5-yl dimethylcarbamate (IUPAC name) (1283) + TX, 4-methyl(prop-2-ynyl)amino-3,5-xylyl methylcarbamate (IUPAC name) (1285) + TX, 5,5-dimethyl-3-oxocyclohex-1-enyl dimethylcarbamate (IUPAC name) (1085) + TX, abamectin (1) + TX, acephate (2) + TX, acetamiprid (4) + TX, acethion (alternative name) [CCN] + TX, acetoprole [CCN] + TX, acrinathrin (9) + TX, acrylonitrile (IUPAC name) (861) + TX, alanycarb (15) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, aldrin (864) + TX, allethrin (17) + TX, allosamidin (alternative name) [CCN] + TX, allyxycarb (866) + TX, alpha-cypermethrin (202) + TX, alpha-ecdysone (alternative name) [CCN] + TX, aluminium phosphide (640) + TX, amidithion (870) + TX, amidothioate (872) + TX, aminocarb (873) + TX, amiton (875) + TX, amiton hydrogen oxalate (875) + TX, amitraz (24) + TX, anabasine (877) + TX, athidathion (883) + TX, AVI 382 (compound code) + TX, AZ 60541 (compound code) + TX, azadirachtin (alternative

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name) (41) + TX, azamethiphos (42) + TX, azinphos-ethyl (44) + TX, azinphos-methyl (45) + TX, azothoate (889) + TX, *Bacillus thuringiensis* delta endotoxins (alternative name) (52) + TX, barium hexafluorosilicate (alternative name) [CCN] + TX, barium polysulfide (IUPAC/Chemical Abstracts name) (892) + TX, barthrin [CCN] + TX, Bayer 22/190 (development code) (893) + TX, Bayer 22408 (development code) (894) + TX, bendiocarb (58) + TX, benfuracarb (60) + TX, bensultap (66) + TX, beta-cyfluthrin (194) + TX, beta-cypermethrin (203) + TX, bifenthrin (76) + TX, bioallethrin (78) + TX, bioallethrin S-cyclopentenyl isomer (alternative name) (79) + TX, bioethanomethrin [CCN] + TX, biopermethrin (908) + TX, bioresmethrin (80) + TX, bis(2-chloroethyl) ether (IUPAC name) (909) + TX, bistrifluron (83) + TX, borax (86) + TX, brofenvalerate (alternative name) + TX, bromfenvinfos (914) + TX, bromocyclen (918) + TX, bromo-DDT (alternative name) [CCN] + TX, bromophos (920) + TX, bromophos-ethyl (921) + TX, bufencarb (924) + TX, buprofezin (99) + TX, butacarb (926) + TX, butathiofos (927) + TX, butocarboxim (103) + TX, butonate (932) + TX, butoxycarboxim (104) + TX, butylpyridaben (alternative name) + TX, cadusafos (109) + TX, calcium arsenate [CCN] + TX, calcium cyanide (444) + TX, calcium polysulfide (IUPAC name) (111) + TX, camphechlor (941) + TX, carbanolate (943) + TX, carbaryl (115) + TX, carbofuran (118) + TX, carbon disulfide (IUPAC/Chemical Abstracts name) (945) + TX, carbon tetrachloride (IUPAC name) (946) + TX, carbophenothion (947) + TX, carbosulfan (119) + TX, cartap (123) + TX, cartap hydrochloride (123) + TX, cevadine (alternative name) (725) + TX, chlorbicyclen (960) + TX, chlordane (128) + TX, chlordecone (963) + TX, chlordimeform (964) + TX, chlordimeform hydrochloride (964) + TX, chlorethoxyfos (129) + TX, chlorfenapyr (130) + TX, chlorfenvinphos (131) + TX, chlorfluazuron (132) + TX, chlormephos (136) + TX, chloroform [CCN] + TX, chloropicrin (141) + TX, chlorphoxim (989) + TX, chlorprazophos (990) + TX, chlorpyrifos (145) + TX, chlorpyrifos-methyl (146) + TX, chlorthiophos (994) + TX, chromafenozide (150) + TX, cinerin I (696) + TX, cinerin II (696) + TX, cinerins (696) + TX, cis-resmethrin (alternative name) + TX, cismethrin (80) + TX, clocythrin (alternative name) + TX, cloethocarb (999) + TX, closantel (alternative name) [CCN] + TX, clothianidin (165) + TX, copper acetoarsenite [CCN] + TX, copper arsenate [CCN] + TX, copper oleate [CCN] + TX, coumaphos (174) + TX, coumithoate (1006) + TX, crotamiton (alternative name) [CCN] + TX, crotoxyphos (1010) + TX, crufomate (1011) + TX, cryolite (alternative name) (177) + TX, CS 708 (development code) (1012) + TX, cyanofenphos (1019) + TX, cyanophos (184) + TX, cyanthoate (1020) + TX, cyclethrin [CCN] + TX, cycloprothrin (188) + TX, cyfluthrin (193) + TX, cyhalothrin (196) + TX, cypermethrin (201) + TX, cyphenothrin (206) + TX, cyromazine (209) + TX, cythioate (alternative name) [CCN] + TX, *d*-limonene (alternative name) [CCN] + TX, *d*-tetramethrin (alternative name) (788) + TX, DAEP (1031) + TX, dazomet (216) + TX, DDT (219) + TX, decarbofuran (1034) + TX, deltamethrin (223) + TX, demephion (1037) + TX, demephion-O (1037) + TX, demephion-S (1037) + TX, demeton (1038) + TX, demeton-methyl (224) + TX, demeton-O (1038) + TX, demeton-O-methyl (224) + TX, demeton-S (1038) + TX, demeton-S-methyl (224) + TX, demeton-S-methylsulphon (1039) + TX, diafenthiuron (226) + TX, dialifos (1042) + TX, diamidafos (1044) + TX, diazinon (227) + TX, dicapthos (1050) + TX, dichlofenthion (1051) + TX, dichlorvos (236) + TX, dicliphos (alternative

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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, 5 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 10 (development code) (1118) + TX, emamectin (291) + TX, emamectin benzoate (291) + TX, EMPC (1120) + TX, empenithrin (292) + TX, endosulfan (294) + TX, endothion (1121) + TX, endrin (1122) + TX, EPBP (1123) + TX, EPN (297) + TX, epofenonane (1124) + TX, eprinomectin (alternative name) [CCN] + TX, esfenvalerate (302) + TX, etaphos (alternative name) [CCN] + TX, ethiofencarb (308) + TX, ethion (309) + TX, ethiprole (310) + TX, ethoate-methyl (1134) + TX, 15 ethoprophos (312) + TX, ethyl formate (IUPAC name) [CCN] + TX, ethyl-DDD (alternative name) (1056) + TX, ethylene dibromide (316) + TX, ethylene dichloride (chemical name) (1136) + TX, ethylene oxide [CCN] + TX, etofenprox (319) + TX, etrimfos (1142) + TX, EXD (1143) + TX, famphur (323) + TX, fenamiphos (326) + TX, fenazaflor (1147) + TX, fenchlorphos (1148) + TX, fenethacarb (1149) + TX, fenfluthrin (1150) + TX, fenitrothion (335) + TX, fenobucarb (336) + TX, 20 fenoxacrim (1153) + TX, fenoxycarb (340) + TX, fenpirithrin (1155) + TX, fenpropathrin (342) + TX, fenpyrad (alternative name) + TX, fensulfothion (1158) + TX, fenthion (346) + TX, fenthion-ethyl [CCN] + TX, fenvalerate (349) + TX, fipronil (354) + TX, flonicamid (358) + TX, flubendiamide (CAS. Reg. No.: 272451-65-7) + TX, flucofuron (1168) + TX, flucycloxuron (366) + TX, flucythrinate (367) + TX, fluenetil (1169) + TX, flufenerim [CCN] + TX, flufenoxuron (370) + TX, 25 flufenprox (1171) + TX, flumethrin (372) + TX, fluvalinate (1184) + TX, FMC 1137 (development code) (1185) + TX, fonofos (1191) + TX, formetanate (405) + TX, formetanate hydrochloride (405) + TX, formothion (1192) + TX, formparanate (1193) + TX, fosmethilan (1194) + TX, fospirate (1195) + TX, fosthiazate (408) + TX, fosthietan (1196) + TX, furathiocarb (412) + TX, furethrin (1200) + TX, gamma-cyhalothrin (197) + TX, gamma-HCH (430) + TX, guazatine (422) + TX, 30 guazatine acetates (422) + TX, GY-81 (development code) (423) + TX, halfenprox (424) + TX, halofenozide (425) + TX, HCH (430) + TX, HEOD (1070) + TX, heptachlor (1211) + TX, heptenophos (432) + TX, heterophos [CCN] + TX, hexaflumuron (439) + TX, HHDN (864) + TX, hydramethylnon (443) + TX, hydrogen cyanide (444) + TX, hydroprene (445) + TX, hyquincarb (1223) + TX, imidacloprid (458) + TX, improthrin (460) + TX, indoxacarb (465) + TX, 35 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-(methoxy-aminothiophosphoryl)salicylate (IUPAC name) (473) + TX, isoprothiolane (474) + TX, isothioate (1244) + TX, isoxathion (480) + TX, ivermectin (alternative name) [CCN] + TX, jasmolin I (696) +

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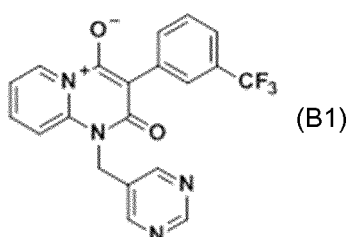
TX, jasmolin II (696) + TX, jodfenphos (1248) + TX, juvenile hormone I (alternative name) [CCN] + TX, juvenile hormone II (alternative name) [CCN] + TX, juvenile hormone III (alternative name) [CCN] + TX, kelevan (1249) + TX, kinoprene (484) + TX, lambda-cyhalothrin (198) + TX, lead arsenate [CCN] + TX, lepimectin (CCN) + TX, leptophos (1250) + TX, lindane (430) + TX, lirimfos (1251) + TX, lufenuron (490) + TX, lythidathion (1253) + TX, *m*-cumenyl methylcarbamate (IUPAC name) (1014) + TX, magnesium phosphide (IUPAC name) (640) + TX, malathion (492) + TX, malonoben (1254) + TX, mazidox (1255) + TX, mecarbam (502) + TX, mecarphon (1258) + TX, menazon (1260) + TX, mephosfolan (1261) + TX, mercurous chloride (513) + TX, mesulfenfos (1263) + TX, metaflumizone (CCN) + TX, metam (519) + TX, metam-potassium (alternative name) (519) + TX, metam-sodium (519) + TX, methacrifos (1266) + TX, methamidophos (527) + TX, methanesulfonyl fluoride (IUPAC/Chemical Abstracts name) (1268) + TX, methidathion (529) + TX, methiocarb (530) + TX, methocrotophos (1273) + TX, methomyl (531) + TX, methoprene (532) + TX, methoquin-butyl (1276) + TX, methothrin (alternative name) (533) + TX, methoxychlor (534) + TX, methoxyfenozide (535) + TX, methyl bromide (537) + TX, methyl isothiocyanate (543) + TX, methylchloroform (alternative name) [CCN] + TX, methylene chloride [CCN] + TX, metofluthrin [CCN] + TX, metolcarb (550) + TX, metoxadiazone (1288) + TX, mevinphos (556) + TX, mexacarbate (1290) + TX, milbemectin (557) + TX, milbemycin oxime (alternative name) [CCN] + TX, mipafox (1293) + TX, mirex (1294) + TX, monocrotophos (561) + TX, morphothion (1300) + TX, moxidectin (alternative name) [CCN] + TX, naftalofos (alternative name) [CCN] + TX, naled (567) + TX, naphthalene (IUPAC/Chemical Abstracts name) (1303) + TX, NC-170 (development code) (1306) + TX, NC-184 (compound code) + TX, nicotine (578) + TX, nicotine sulfate (578) + TX, nifluridide (1309) + TX, nitenpyram (579) + TX, nithiazine (1311) + TX, nitrilacarb (1313) + TX, nitrilacarb 1:1 zinc chloride complex (1313) + TX, NNI-0101 (compound code) + TX, NNI-0250 (compound code) + TX, nornicotine (traditional name) (1319) + TX, novaluron (585) + TX, noviflumuron (586) + TX, *O*-5-dichloro-4-iodophenyl *O*-ethyl ethylphosphonothioate (IUPAC name) (1057) + TX, *O,O*-diethyl *O*-4-methyl-2-oxo-2*H*-chromen-7-yl phosphorothioate (IUPAC name) (1074) + TX, *O,O*-diethyl *O*-6-methyl-2-propylpyrimidin-4-yl phosphorothioate (IUPAC name) (1075) + TX, *O,O,O',O'*-tetrapropyl dithiopyrophosphate (IUPAC name) (1424) + TX, oleic acid (IUPAC name) (593) + TX, omethoate (594) + TX, oxamyl (602) + TX, oxydemeton-methyl (609) + TX, oxydeprofos (1324) + TX, oxydisulfoton (1325) + TX, pp'-DDT (219) + TX, para-dichlorobenzene [CCN] + TX, parathion (615) + TX, parathion-methyl (616) + TX, penfluron (alternative name) [CCN] + TX, pentachlorophenol (623) + TX, pentachlorophenyl laurate (IUPAC name) (623) + TX, permethrin (626) + TX, petroleum oils (alternative name) (628) + TX, PH 60-38 (development code) (1328) + TX, phenkapton (1330) + TX, phenothrin (630) + TX, phenthoate (631) + TX, phorate (636) + TX, phosalone (637) + TX, phosfolan (1338) + TX, phosmet (638) + TX, phosnichlor (1339) + TX, phosphamidon (639) + TX, phosphine (IUPAC name) (640) + TX, phoxim (642) + TX, phoxim-methyl (1340) + TX, pirimetaphos (1344) + TX, pirimicarb (651) + TX, pirimiphos-ethyl (1345) + TX, pirimiphos-methyl (652) + TX, polychlorodicyclopentadiene isomers (IUPAC name) (1346) + TX, polychloroterpenes (traditional name) (1347) + TX, potassium arsenite [CCN] + TX,

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potassium thiocyanate [CCN] + TX, prallethrin (655) + TX, precocene I (alternative name) [CCN] + TX, precocene II (alternative name) [CCN] + TX, precocene III (alternative name) [CCN] + TX, primidophos (1349) + TX, profenofos (662) + TX, profluthrin [CCN] + TX, promacyl (1354) + TX, promecarb (1355) + TX, propaphos (1356) + TX, propetamphos (673) + TX, propoxur (678) + TX, 5 prothidathion (1360) + TX, prothiofos (686) + TX, prothoate (1362) + TX, protrifenbute [CCN] + TX, pymetrozine (688) + TX, pyraclofos (689) + TX, pyrazophos (693) + TX, pyresmethrin (1367) + TX, pyrethrin I (696) + TX, pyrethrin II (696) + TX, pyrethrins (696) + TX, pyridaben (699) + TX, pyridalyl (700) + TX, pyridaphenthion (701) + TX, pyrimidifen (706) + TX, pyrimitate (1370) + TX, pyriproxyfen (708) + TX, quassia (alternative name) [CCN] + TX, quinalphos (711) + TX, 10 quinalphos-methyl (1376) + TX, quinotion (1380) + TX, quintiofos (1381) + TX, R-1492 (development code) (1382) + TX, rafoxanide (alternative name) [CCN] + TX, resmethrin (719) + TX, rotenone (722) + TX, RU 15525 (development code) (723) + TX, RU 25475 (development code) (1386) + TX, ryania (alternative name) (1387) + TX, ryanodine (traditional name) (1387) + TX, sabadilla (alternative name) (725) + TX, schradan (1389) + TX, sebufos (alternative name) + TX, 15 selamectin (alternative name) [CCN] + TX, SI-0009 (compound code) + TX, SI-0205 (compound code) + TX, SI-0404 (compound code) + TX, SI-0405 (compound code) + TX, silafluofen (728) + TX, SN 72129 (development code) (1397) + TX, sodium arsenite [CCN] + TX, sodium cyanide (444) + TX, sodium fluoride (IUPAC/Chemical Abstracts name) (1399) + TX, sodium hexafluorosilicate (1400) + TX, sodium pentachlorophenoxide (623) + TX, sodium selenate (IUPAC 20 name) (1401) + TX, sodium thiocyanate [CCN] + TX, sophamide (1402) + TX, spinosad (737) + TX, spiromesifen (739) + TX, spirotetmat (CCN) + TX, sulcofuron (746) + TX, sulcofuron-sodium (746) + TX, sulfluramid (750) + TX, sulfotep (753) + TX, sulfuryl fluoride (756) + TX, sulprofos (1408) + TX, tar oils (alternative name) (758) + TX, tau-fluvalinate (398) + TX, tazimcarb (1412) + TX, TDE (1414) + TX, tebufenozide (762) + TX, tebufenpyrad (763) + TX, tebupirimfos (764) + 25 TX, teflubenzuron (768) + TX, tefluthrin (769) + TX, temephos (770) + TX, TEPP (1417) + TX, terallethrin (1418) + TX, terbam (alternative name) + TX, terbufos (773) + TX, tetrachloroethane [CCN] + TX, tetrachlorvinphos (777) + TX, tetramethrin (787) + TX, theta-cypermethrin (204) + TX, thiacloprid (791) + TX, thiafenox (alternative name) + TX, thiamethoxam (792) + TX, thicrofos (1428) + TX, thiocarboxime (1431) + TX, thiocyclam (798) + TX, thiocyclam hydrogen oxalate 30 (798) + TX, thiodicarb (799) + TX, thiofanox (800) + TX, thiometon (801) + TX, thionazin (1434) + TX, thiosultap (803) + TX, thiosultap-sodium (803) + TX, thuringiensin (alternative name) [CCN] + TX, tolfenpyrad (809) + TX, tralomethrin (812) + TX, transfluthrin (813) + TX, transpermethrin (1440) + TX, triamiphos (1441) + TX, triazamate (818) + TX, triazophos (820) + TX, triazuron (alternative name) + TX, trichlorfon (824) + TX, trichlormetaphos-3 (alternative name) [CCN] + TX, 35 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,

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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
 5 and a compound of the formula B1



with the common name triflumezopyrim (disclosed in WO 2012/092115) + TX;

a molluscicide selected from the group of substances consisting of bis(tributyltin) oxide (IUPAC name) (913) + TX, bromoacetamide [CCN] + TX, calcium arsenate [CCN] + TX, cloethocarb (999) + TX,
 10 copper acetoarsenite [CCN] + TX, copper sulfate (172) + TX, fentin (347) + TX, ferric phosphate (IUPAC name) (352) + TX, metaldehyde (518) + TX, methiocarb (530) + TX, niclosamide (576) + TX, niclosamide-olamine (576) + TX, pentachlorophenol (623) + TX, sodium pentachlorophenoxide (623) + TX, tazimcarb (1412) + TX, thiodicarb (799) + TX, tributyltin oxide (913) + TX, trifenmorph (1454) + TX, trimethacarb (840) + TX, triphenyltin acetate (IUPAC name) (347) and triphenyltin
 15 hydroxide (IUPAC name) (347) + TX, pyriprole [394730-71-3] + TX,
 a nematicide selected from the group of substances consisting of AKD-3088 (compound code) + TX, 1,2-dibromo-3-chloropropane (IUPAC/Chemical Abstracts name) (1045) + TX, 1,2-dichloropropane (IUPAC/ Chemical Abstracts name) (1062) + TX, 1,2-dichloropropane with 1,3-dichloropropene (IUPAC name) (1063) + TX, 1,3-dichloropropene (233) + TX, 3,4-dichlorotetrahydrothiophene 1,1-
 20 dioxide (IUPAC/Chemical Abstracts name) (1065) + TX, 3-(4-chlorophenyl)-5-methylrhodanine (IUPAC name) (980) + TX, 5-methyl-6-thioxo-1,3,5-thiadiazinan-3-ylacetic acid (IUPAC name) (1286) + TX, 6-isopentenylaminopurine (alternative name) (210) + TX, abamectin (1) + TX, acetoprole [CCN] + TX, alanycarb (15) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, AZ 60541 (compound code) + TX, benclotiaz [CCN] + TX, benomyl (62) + TX, butylpyridaben (alternative
 25 name) + TX, cadusafos (109) + TX, carbofuran (118) + TX, carbon disulfide (945) + TX, carbosulfan (119) + TX, chloropicrin (141) + TX, chlorpyrifos (145) + TX, cloethocarb (999) + TX, cytokinins (alternative name) (210) + TX, dazomet (216) + TX, DBCP (1045) + TX, DCIP (218) + TX, diamidafos (1044) + TX, dichlofenthion (1051) + TX, dicliphos (alternative name) + TX, dimethoate (262) + TX, doramectin (alternative name) [CCN] + TX, emamectin (291) + TX,
 30 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

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name) [CCN] + TX, kinetin (alternative name) (210) + TX, mecarphon (1258) + TX, metam (519) + TX, metam-potassium (alternative name) (519) + TX, metam-sodium (519) + TX, methyl bromide (537) + TX, methyl isothiocyanate (543) + TX, milbemycin oxime (alternative name) [CCN] + TX, moxidectin (alternative name) [CCN] + TX, *Myrothecium verrucaria* composition (alternative name) (565) + TX, NC-184 (compound code) + TX, oxamyl (602) + TX, phorate (636) + TX, phosphamidon (639) + TX, phosphocarb [CCN] + TX, sebufos (alternative name) + TX, selamectin (alternative name) [CCN] + TX, spinosad (737) + TX, terbam (alternative name) + TX, terbufos (773) + TX, tetrachlorothiophene (IUPAC/ Chemical Abstracts name) (1422) + TX, thiafenox (alternative name) + TX, thionazin (1434) + TX, triazophos (820) + TX, triazuron (alternative name) + TX, xylenols [CCN] + TX, YI-5302 (compound code) and zeatin (alternative name) (210) + TX, fluensulfone [318290-98-1] + TX,

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

a plant activator selected from the group of substances consisting of acibenzolar (6) + TX,

acibenzolar-S-methyl (6) + TX, probenazole (658) and *Reynoutria sachalinensis* extract (alternative name) (720) + TX,

a rodenticide selected from the group of substances consisting of 2-isovalerylindan-1,3-dione (IUPAC name) (1246) + TX, 4-(quinoxalin-2-ylamino)benzenesulfonamide (IUPAC name) (748) + TX, alpha-chlorohydrin [CCN] + TX, aluminium phosphide (640) + TX, antu (880) + TX, arsenous oxide (882) + TX, barium carbonate (891) + TX, bisthiosemi (912) + TX, brodifacoum (89) + TX, bromadiolone (91) + TX, bromethalin (92) + TX, calcium cyanide (444) + TX, chloralose (127) + TX, chlorophacinone (140) + TX, cholecalciferol (alternative name) (850) + TX, coumachlor (1004) + TX, coumafuryl (1005) + TX, coumatetralyl (175) + TX, crimidine (1009) + TX, difenacoum (246) + TX, difethialone (249) + TX, diphacinone (273) + TX, ergocalciferol (301) + TX, flocoumafen (357) + TX, fluoroacetamide (379) + TX, flupropradine (1183) + TX, flupropradine hydrochloride (1183) + TX, gamma-HCH (430) + TX, HCH (430) + TX, hydrogen cyanide (444) + TX, iodomethane (IUPAC name) (542) + TX, lindane (430) + TX, magnesium phosphide (IUPAC name) (640) + TX, methyl bromide (537) + TX, norbormide (1318) + TX, phosacetim (1336) + TX, phosphine (IUPAC name) (640) + TX, phosphorus [CCN] + TX, pindone (1341) + TX, potassium arsenite [CCN] + TX, pyrinuron (1371) + TX, scilliroside (1390) + TX, sodium arsenite [CCN] + TX, sodium cyanide (444) + TX, sodium fluoroacetate (735) + TX, strychnine (745) + TX, thallium sulfate [CCN] + TX, warfarin (851) and zinc phosphide (640) + TX,

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

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

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

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

10 and biologically active compounds selected from the group consisting of azaconazole (60207-31-0) + TX, bitertanol [70585-36-3] + TX, bromuconazole [116255-48-2] + TX, cyproconazole [94361-06-5] + TX, difenoconazole [119446-68-3] + TX, diniconazole [83657-24-3] + TX, epoxiconazole [106325-08-0] + TX, fenbuconazole [114369-43-6] + TX, fluquinconazole [136426-54-5] + TX,

15 flusilazole [85509-19-9] + TX, flutriafol [76674-21-0] + TX, hexaconazole [79983-71-4] + TX, imazalil [35554-44-0] + TX, imibenconazole [86598-92-7] + TX, ipconazole [125225-28-7] + TX, metconazole [125116-23-6] + TX, myclobutanil [88671-89-0] + TX, pefurazoate [101903-30-4] + TX, penconazole [66246-88-6] + TX, prothioconazole [178928-70-6] + TX, pyrifenoxy [88283-41-4] + TX, prochloraz [67747-09-5] + TX, propiconazole [60207-90-1] + TX, simeconazole [149508-90-7] + TX,

20 tebuconazole [107534-96-3] + TX, tetraconazole [112281-77-3] + TX, triadimefon [43121-43-3] + TX, triadimenol [55219-65-3] + TX, triflumizole [99387-89-0] + TX, triticonazole [131983-72-7] + TX, ancymidol [12771-68-5] + TX, fenarimol [60168-88-9] + TX, nuarimol [63284-71-9] + TX, bupirimate [41483-43-6] + TX, dimethirimol [5221-53-4] + TX, ethirimol [23947-60-6] + TX, dodemorph [1593-77-7] + TX, fenpropidine [67306-00-7] + TX, fenpropimorph [67564-91-4] + TX,

25 spiroxamine [118134-30-8] + TX, tridemorph [81412-43-3] + TX, cyprodinil [121552-61-2] + TX, mepanipyrim [110235-47-7] + TX, pyrimethanil [53112-28-0] + TX, fenpiclonil [74738-17-3] + TX, fludioxonil [131341-86-1] + TX, benalaxyl [71626-11-4] + TX, furalaxyl [57646-30-7] + TX, metalaxyl [57837-19-1] + TX, R-metalaxyl [70630-17-0] + TX, ofurace [58810-48-3] + TX, oxadixyl [77732-09-3] + TX, benomyl [17804-35-2] + TX, carbendazim [10605-21-7] + TX, debacarb [62732-91-6] + TX, fuberidazole [3878-19-1] + TX, thiabendazole [148-79-8] + TX, chlozolate [84332-86-5] + TX, dichlozoline [24201-58-9] + TX, iprodione [36734-19-7] + TX, myclozoline [54864-61-8] + TX, procymidone [32809-16-8] + TX, vinclozoline [50471-44-8] + TX, boscalid [188425-85-6] + TX, carboxin [5234-68-4] + TX, fenfuram [24691-80-3] + TX, flutolanil [66332-96-5] + TX, mepronil [55814-41-0] + TX, oxycarboxin [5259-88-1] + TX, penthiopyrad [183675-82-3] + TX,

35 TX, thifluzamide [130000-40-7] + TX, guazatine [108173-90-6] + TX, dodine [2439-10-3] [112-65-2] (free base) + TX, iminoctadine [13516-27-3] + TX, azoxystrobin [131860-33-8] + TX, mandestrobin [173662-97-0] + 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

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[248593-16-0] + TX, picoxystrobin [117428-22-5] + TX, pyraclostrobin [175013-18-0] + TX, ferbam [14484-64-1] + TX, 3-[5-(4-chlorophenyl)-2,3-dimethyl-3-isoxazolidinyl]pyridine (SYP-Z048), 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,

5 captafol [2425-06-1] + TX, captan [133-06-2] + TX, dichlofluanid [1085-98-9] + TX, fluoroimide [41205-21-4] + TX, folpet [133-07-3] + TX, tolylfluanid [731-27-1] + TX, bordeaux mixture [8011-63-0] + TX, copperhydroxid [20427-59-2] + TX, copperoxychlorid [1332-40-7] + TX, coppersulfat [7758-98-7] + TX, copperoxid [1317-39-1] + TX, mancopper [53988-93-5] + TX, oxine-copper [10380-28-6] + TX, dinocap [131-72-6] + TX, nitrothal-isopropyl [10552-74-6] + TX, edifenphos

10 [17109-49-8] + TX, iprobenphos [26087-47-8] + TX, isoprothiolane [50512-35-1] + TX, phosdiphen [36519-00-3] + TX, pyrazophos [13457-18-6] + TX, tolclofos-methyl [57018-04-9] + TX, acibenzo-lar-S-methyl [135158-54-2] + TX, anilazine [101-05-3] + TX, bentiavalicarb [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,

15 dichlone [117-80-6] + TX, diclocymet [139920-32-4] + TX, diclomezine [62865-36-5] + TX, dicloran [99-30-9] + TX, diethofencarb [87130-20-9] + TX, dimethomorph [110488-70-5] + TX, SYP-LI90 (Flumorph) [211867-47-9] + TX, dithianon [3347-22-6] + TX, ethaboxam [162650-77-3] + TX, etridiazole [2593-15-9] + TX, famoxadone [131807-57-3] + TX, fenamidone [161326-34-7] + TX, fenoxanil [115852-48-7] + TX, fentin [668-34-8] + TX, ferimzone [89269-64-7] + TX, fluazinam

20 [79622-59-6] + TX, fluopicolide [239110-15-7] + TX, flusulfamide [106917-52-6] + TX, fenhexamid [126833-17-8] + TX, fosetyl-aluminium [39148-24-8] + TX, hymexazol [10004-44-1] + TX, iprovalicarb [140923-17-7] + TX, IKF-916 (Cyazofamid) [120116-88-3] + TX, kasugamycin [6980-18-3] + TX, methasulfocarb [66952-49-6] + TX, metrafenone [220899-03-6] + TX, pencycuron [66063-05-6] + TX, phthalide [27355-22-2] + TX, polyoxins [11113-80-7] + TX, probenazole [27605-76-1] +

25 TX, propamocarb [25606-41-1] + TX, proquinazid [189278-12-4] + TX, pyroquilon [57369-32-1] + TX, quinoxifen [124495-18-7] + TX, quintozene [82-68-8] + TX, sulfur [7704-34-9] + TX, tiadinil [223580-51-6] + TX, triazoxide [72459-58-6] + TX, tricyclazole [41814-78-2] + TX, triforine [26644-46-2] + TX, validamycin [37248-47-8] + TX, zoxamide (RH7281) [156052-68-5] + TX,

mandipropamid [374726-62-2] + TX,

30 and SDHI inhibitors selected from the group consisting of penflufen ([494793-67-8], US 7538073 (*N*-[2-(1,3-dimethylbutyl)phenyl]-5-fluoro-1,3-dimethyl-1*H*-pyrazole-4-carboxamide) + TX, furametpyr ([123572-88-3] (5-chloro-*N*-(1,3-dihydro-1,1,3-trimethyl-4-isobenzofuranyl)-1,3-dimethyl-1*H*-pyrazole-4-carboxamide) + TX, penthiopyrad (US 5747518, [183675-82-3], (*N*-[2-(1,3-dimethylbutyl)-3-thienyl]-1-methyl-3-(trifluoromethyl)-1*H*-pyrazole-4-

35 carboxamide) + TX, bixafen (US 7329633, [581809-46-3], (*N*-(3',4'-dichloro-5-fluoro[1,1'-biphenyl]-2-yl)-3-(difluoromethyl)-1-methyl-1*H*-pyrazole-4-carboxamide) + TX, isopyrazam (US 7598395, [881685-58-1] (mixture of 2 *syn*-isomers 3-(difluoromethyl)-1-methyl-*N*-[(1*RS*,4*SR*,9*RS*)-1,2,3,4-tetrahydro-9-isopropyl-1,4-methanonaphthalen-5-yl]pyrazole-4-carboxamide and 2 *anti*-isomers 3-(difluoromethyl)-1-methyl-*N*-[(1*RS*,4*SR*,9*SR*)-1,2,3,4-tetrahydro-9-isopropyl-1,4-methanonaphthalen-5-yl]pyrazole-4-

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carboxamide) + TX, sedaxane (EP 1480955B1, [874967-67-6] (mixture of 2 *cis*-isomers 2'-
[(1*RS*,2*RS*)-1,1'-bicycloprop-2-yl]-3-(difluoromethyl)-1-methylpyrazole-4-carboxanilide and 2 *trans*-
isomers 2'-[(1*RS*,2*SR*)-1,1'-bicycloprop-2-yl]-3-(difluoromethyl)-1-methylpyrazole-4-carboxanilide) +
TX, fluxapyroxad (US 8008232, [907204-31-3] (3-(difluoromethyl)-1-methyl-*N*-(3',4',5'-trifluoro[1,1'-
5 biphenyl]-2-yl)-1*H*-pyrazole-4-carboxamide) + TX, solatenol (WO 2007/048556 (3-difluoromethyl-1-
methyl-1*H*-pyrazole-4-carboxylic acid (9-dichloromethylene-1,2,3,4-tetrahydro-1,4-methano-
naphthalen-5-yl)-amide,) + TX, the compound 3-(difluoromethyl)-*N*-methoxy-1-methyl-*N*-[1-methyl-2-
(2,4,6-trichlorophenyl)ethyl]pyrazole-4-carboxamide (described in WO 2010/063700) + TX,
thifluzamide (US 5045554, [130000-40-7] (*N*-[2,6-dibromo-4-(trifluoromethoxy)phenyl]-2-methyl-4-
10 (trifluoromethyl)-5-thiazolecarboxamide) + TX, boscalid (US 5589493, [188425-85-6 (2-chloro-*N*-(4'-
chloro[1,1'-biphenyl]-2-yl)-3-pyridinecarboxamide) + TX, oxycarboxin ([5259-88-1] (5,6-dihydro-2-
methyl-*N*-phenyl-1,4-oxathiin-3-carboxamide 4,4-dioxide,) + TX, carboxin ([5234-68-4] (5,6-dihydro-2-
methyl-*N*-phenyl-1,4-oxathiin-3-carboxamide) + TX, fluopyram (US 7572818, [658066-35-4], (*N*-[2-[3-
chloro-5-(trifluoromethyl)-2-pyridinyl]ethyl]-2-(trifluoromethyl)benzamide) + TX, flutolanil ([24691-80-3],
15 (2-methyl-*N*-phenyl-3-furancarboxamide, fenfuram), US 4093743, CA Reg. No. 66332-96-5 (*N*-[3-(1-
methylethoxy)phenyl]-2-(trifluoromethyl)benzamide) + TX, mepronil ([55814-41-0], (2-methyl-*N*-[3-(1-
methylethoxy)phenyl]benzamide) + TX and benodanil ([15310-01-7], (2-iodo-*N*-phenylbenzamide) +
TX;
and the compounds [(3*S*,4*R*,4*aR*,6*S*,6*aS*,12*R*,12*aS*,12*bS*)-3-[(cyclopropylcarbonyl)oxy]-
20 1,3,4,4*a*,5,6,6*a*,12,12*a*,12*b*-decahydro-6,12-dihydroxy-4,6*a*,12*b*-trimethyl-11-oxo-9-(3-pyridinyl)-
2*H*,11*H*naphtho[2,1-*b*]pyrano[3,4-*e*]pyran-4-yl]methyl-
cyclopropanecarboxylate [915972-17-7] + TX, 1,3,5-trimethyl-*N*-(2-methyl-1-oxopropyl)-*N*-[3-(2-
methylpropyl)-4-[2,2,2-trifluoro-1-methoxy-1-(trifluoromethyl)ethyl]phenyl]-1*H*-pyrazole-4-carboxamide
[926914-55-8] + TX, 4-oxo-4-[(2-phenylethyl)amino]-butyric acid (disclosed in WO 2010137677) + TX,
25 flufiprole [704886-18-0] + TX, cyclaniliprole [1031756-98-5] + TX, tetraniliprole [1229654-66-3]+ TX,
guadipyr (described in WO 2010/060231) + TX and cycloxaprid (described in WO 2005/077934) + TX.

The references in brackets behind the active ingredients, e.g. [3878-19-1] refer to the Chemical
Abstracts Registry number. The above described mixing partners are known. Where the active
30 ingredients are included in "The Pesticide Manual" [The Pesticide Manual - A World Compendium;
Thirteenth Edition; Editor: C. D. S. TomLin; The British Crop Protection Council], they are described
therein under the entry number given in round brackets hereinabove for the particular compound; for
example, the compound "abamectin" is described under entry number (1). Where "[CCN]" is added
hereinabove to the particular compound, the compound in question is included in the "Compendium of
35 Pesticide Common Names", which is accessible on the internet [A. Wood; Compendium of Pesticide
Common Names, Copyright © 1995-2013]; for example, the compound "acetoprole" is described
under the internet address <http://www.alanwood.net/pesticides/acetoprole.html>.

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Most of the active ingredients described above are referred to hereinabove by a so-called "common name", the relevant "ISO common name" or another "common name" being used in individual cases. If the designation is not a "common name", the nature of the designation used instead is given in round brackets for the particular compound; in that case, the IUPAC name, the IUPAC/Chemical Abstracts name, a "chemical name", a "traditional name", a "compound name" or a "development code" is used or, if neither one of those designations nor a "common name" is used, an "alternative name" is employed.

The active ingredient mixture of the compounds of formula I selected from Tables 1 to 19 and P1 with active ingredients described above comprises a compound selected from Tables 1 to 19 and P1 and an active ingredient as described above preferably in a mixing ratio of from 100:1 to 1:6000, especially from 50:1 to 1:50, more especially in a ratio of from 20:1 to 1:20, even more especially from 10:1 to 1:10, very especially from 5:1 and 1:5, special preference being given to a ratio of from 2:1 to 1:2, and a ratio of from 4:1 to 2:1 being likewise preferred, above all in a ratio of 1:1, or 5:1, or 5:2, or 5:3, or 5:4, or 4:1, or 4:2, or 4:3, or 3:1, or 3:2, or 2:1, or 1:5, or 2:5, or 3:5, or 4:5, or 1:4, or 2:4, or 3:4, or 1:3, or 2:3, or 1:2, or 1:600, or 1:300, or 1:150, or 1:35, or 2:35, or 4:35, or 1:75, or 2:75, or 4:75, or 1:6000, or 1:3000, or 1:1500, or 1:350, or 2:350, or 4:350, or 1:750, or 2:750, or 4:750. Those mixing ratios are 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 comprises applying a composition comprising a mixture as described above to the pests or their environment, with the exception of a method for treatment of the human or animal body by surgery or therapy and diagnostic methods practised on the human or animal body.

The mixtures comprising a compound of formula I selected from Tables 1 to 19 and P1 and one or more active ingredients as described above can be applied, for example, in a single "ready-mix" form, in a combined spray mixture composed from separate formulations of the single active ingredient components, such as a "tank-mix", and in a combined use of the single active ingredients when applied in a sequential manner, i.e. one after the other with a reasonably short period, such as a few hours or days. The order of applying the compounds of formula I selected from Tables 1 to 19 and P1 and the active ingredients as described above is not essential for working the present invention.

Biological Examples:

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

(larvicide, feeding/residual contact activity, preventive)

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 5 L1 larvae. The samples are checked for mortality, repellent effect, feeding behaviour, and growth regulation 3 days after treatment (DAT).

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In this test, compounds P1.2, P1.3, P1.4, P1.6, P1.7, P1.8 and P1.10 showed an activity of over 80% at a concentration of 400ppm.

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

5 (larvicide, feeding/residual contact activity, preventive)

Maize sprouts, placed on an agar layer in 24-well micro titer plates (MTP) are treated with test solutions by spraying. After drying, the MTPs are infested with larvae (L2, 6-10 per well). After an incubation period of 5 days, samples are checked for larval mortality, and growth regulation.

10 In this test, compounds P1.1, P1.2, P1.3, P1.5 and P1.6 showed an activity of over 80% at a concentration of 400ppm.

Example B3: Activity against *Spodoptera littoralis* (Egyptian cotton leaf worm)

(systemic activity):

15 Test compounds were applied by pipette into 24 well plates and mixed with agar. Lettuce seeds were placed on the agar and the multi well plate is closed by another plate which contains also agar. After 7 days the roots have absorbed the compound and the lettuce has grown into the lid plate. The lettuce leaves were now cut off into the lid plate. *Spodoptera* eggs were pipetted through a plastic stencil on a humid gel blotting paper and the plate closed with it. The samples are checked for mortality, repellent effect, feeding behavior, and growth regulation 5 days after infestation.

20 In this test, compound P1.3, P1.4, P1.6, P1.7, P1.8 and P1.10 showed an activity of at least 80% at a concentration of 12.5ppm.

Example B4: Activity against *Plutella xylostella* (Diamond back moth):

(larvicide, feeding/residual contact activity, preventive)

25 24-well microtiter plate (MTP) with artificial diet was treated with test solutions by pipetting. After drying, the MTPs were infested with L2 larvae (10-15 per well). After an incubation period of 5 days, samples were checked for larval mortality, antifeedant and growth regulation.

In this test, compounds P1.3, P1.4, P1.6, P1.7, P1.8 and P1.10 showed an activity of over 80% at a concentration of 400ppm.

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

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

30 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 DAT, samples were checked for mortality and special effects (e.g. phytotoxicity).

In this test, compounds P1.3, P1.4, P1.6, P1.7, P1.8 and P1.10 showed an activity of over 80% at a concentration of 400ppm.

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

(systemic/feeding activity, curative), mixed population

5 Roots of pea seedlings, infested with an aphid population of mixed ages, were placed directly in the test solutions. 6 days after introduction, samples were checked for mortality and special effects on the plant.

In this test, compounds P1.3, P1.4, P1.6, P1.8 and P1.10 showed an activity of at least 80% at a concentration of 24ppm.

Example B7: Activity against *Bemisia tabaci* (Cotton white fly):

(adulticide contact activity, preventative), adult

10 Cotton 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 adult white flies. After an incubation period of 7 DAT, samples were checked for mortality and special effects (e.g. phytotoxicity).

In this test, compounds P1.4, P1.6, P1.7, P1.8 and P1.10 showed an activity of over 80% at a concentration of 400ppm.

15 Example B8: Seed treatment activity against *Rhopalosiphum padi* (Bird Cherry Oat Aphid) (seed treatment systemic/feeding activity on barley, preventive, initial and residual activity (infestation 2 and 4 weeks after sowing)), mixed population

A treated barley seed is sown in a 350 ml pot filled with soil. Two weeks after sowing phytotoxicity is estimated and expressed in percentage compared to the control. Furthermore the barley seedling is
20 infested with an aphid population of mixed stages. After an incubation period of seven days the grade of efficacy compared to the control is estimated and expressed in percentage. Treatments with all replicates having a level of efficacy over 90% are re-infested with aphids 28 days after sowing for determination of residual activity. Assessment procedures remain the same as described above.

25 In this test, for example compound P1.4 gave at least 80% control of *Rhopalosiphum padi* after 28 days at an initial loading of 0.3mg a.i. per seed.

Example B9: Activity against *Aedes aegypti* (Yellow fever mosquito):

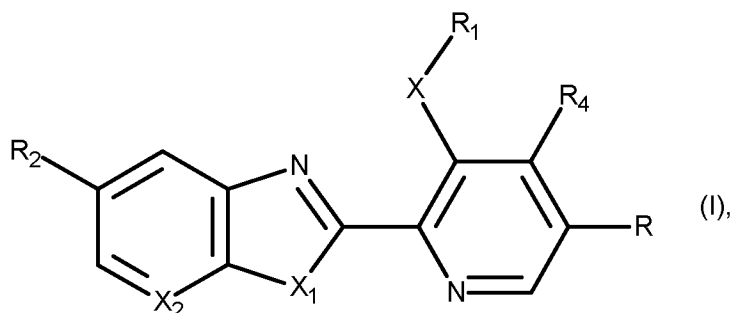
Test solutions, at an application rate of 200ppm in ethanol, were applied to 12-well tissue culture plates. Once the deposits were dry, five, two to five days old adult female *Aedes aegypti* were added to each well, and sustained with a 10% sucrose solution in a cotton wool plug. Assessment of
30 knockdown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

The following compounds gave at least 80% control of *Aedes aegypti* after 48h: P1.3, P1.5, P1.6, P1.7 and P1.8.

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Claims:

1. A compound of the formula I



5

wherein

X is S=N-R₁₀ or S(O)=N-R₁₀, wherein R₁₀ is hydrogen, nitro, cyano, C(O)R₂₆, C(O)OR₂₇, CONR₂₈R₂₉, SO₂R₃₀, CONH₂, C(S)NH₂; or R₁₀ is C₁-C₆alkyl, C₁-C₆haloalkyl, C₃-C₆cycloalkyl, C₃-C₆halocycloalkyl or C₁-C₆alkoxy-C₁-C₆alkyl;

10

R is hydrogen, halogen, C₁-C₄haloalkyl, OR₃₁ or S(O)_nR₃₂;

X₁ is O, S or N-R₃, wherein R₃ is C₁-C₄alkyl, C₁-C₄haloalkyl or C₁-C₆alkoxy-C₁-C₆alkyl, or X₁ is N-(4-methoxy-benzyl) or N-(propargyl);

15

X₂ is N, CH, C-halogen, C-CN, C-O-C₁-C₄alkyl, C-S-C₁-C₄alkyl, C-SO₂-C₁-C₄alkyl, C-S-phenyl, C-SO₂-phenyl or C-SO₂-C₁-C₄haloalkyl;

R₁ is C₁-C₆alkyl, C₁-C₆haloalkyl, C₃-C₆cycloalkyl, C₃-C₆halocycloalkyl, C₂-C₆alkenyl, C₂-C₆haloalkenyl or C₂-C₆alkynyl;

R₂ is halogen, C₁-C₄haloalkyl, OR₃₁, S(O)_nR₃₂, or SF₅;

R₄ is hydrogen or halogen;

20

R₂₆ is hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₃-C₆cycloalkyl, C₃-C₆halocycloalkyl or C₁-C₆alkoxy-C₁-C₆alkyl;

R₂₇, R₂₈, R₂₉, R₃₀ independently of one another are C₁-C₆alkyl, C₁-C₆haloalkyl, C₃-C₆cycloalkyl, C₃-C₆halocycloalkyl or C₁-C₆alkoxy-C₁-C₆alkyl;

R₃₁ and R₃₂ independently of one another are C₁-C₄alkyl or C₁-C₄haloalkyl;

25

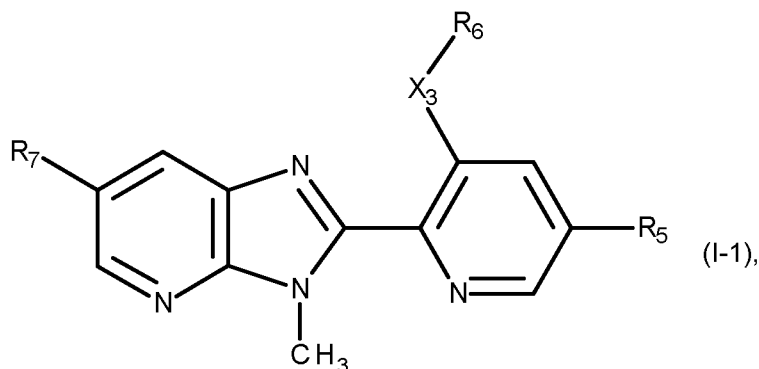
n is 0, 1 or 2; and

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

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

30

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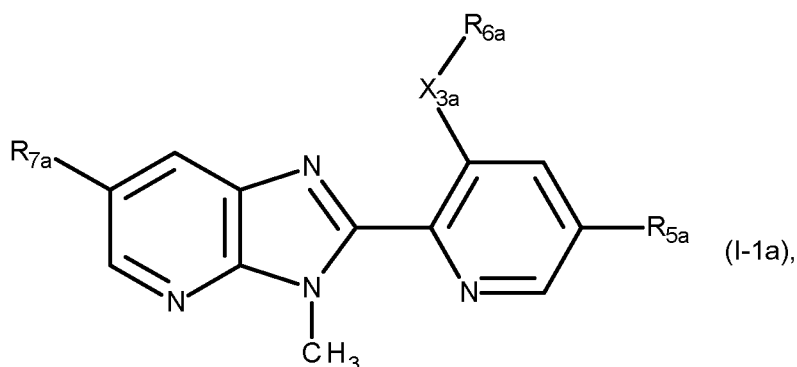


wherein

X_3 is $S=N-R_{10}$ or $S(O)=N-R_{10}$ and R_{10} is hydrogen, cyano or $C(O)CF_3$;

- 5 R_5 is hydrogen, halogen or C_1 - C_4 haloalkyl; R_6 is methyl, ethyl, n-propyl or i-propyl; and R_7 is halogen or C_1 - C_4 haloalkyl; and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of those compounds.

3. A compound of formula I according to claim 1, wherein the compound of formula I is represented by the compounds of formula I-1a



10

wherein

X_{3a} is $S(O)=N-R_{10}$ and R_{10} is C_1 - C_6 alkyl, $C(O)R_{26}$, $C(O)OR_{27}$, $CONR_{28}R_{29}$, SO_2R_{30} , $CONH_2$ or $C(S)NH_2$; in which R_{26} is hydrogen, C_1 - C_6 alkyl or C_1 - C_6 haloalkyl, and R_{27} , R_{28} , R_{29} , R_{30} independently of one another are C_1 - C_6 alkyl;

- 15 R_{5a} is hydrogen, halogen or C_1 - C_4 haloalkyl; R_{6a} is methyl, ethyl, n-propyl or i-propyl; and R_{7a} is halogen or C_1 - C_4 haloalkyl; and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of those compounds.

4. An insecticidal, acaricidal, nematocidal or molluscicidal composition, comprising an insecticidally, acaricidally, nematocidally or molluscicidally effective amount of a compound of formula I according to claim 1 and a suitable carrier or diluent therefor.
- 20

5. A method of combating and controlling pests which comprises applying a pesticidally effective

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amount of a compound of formula I according to claim 1, or of a composition comprising such a compound, to a pest, to a locus of a pest, or to a plant susceptible to attack by a pest.

- 5 6. A method of combating and controlling pests which comprises applying to a pest, to a locus of a pest, or to a plant susceptible to attack by a pest a pesticidal composition according to claim 4.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/073996

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D471/04 A01N43/90
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
C07D 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	EP 2 274 983 A1 (SUMITOMO CHEMICAL CO [JP]) 19 January 2011 (2011-01-19) cited in the application page 2, line 1; claims; examples -----	1-6
A	WO 2011/043404 A1 (SUMITOMO CHEMICAL CO [JP]; IWAKOSHI MITSUHIKO [JP]) 14 April 2011 (2011-04-14) cited in the application page 1, line 7 - page 1, line 9; claims; examples -----	1-6
A	WO 2010/125985 A1 (SUMITOMO CHEMICAL CO [JP]; TAKAHASHI MASAKI [JP]; IWAKOSHI MITSUHIKO []) 4 November 2010 (2010-11-04) cited in the application page 1, line 6 - page 1, line 8; claims; examples -----	1-6

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	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 26 November 2014	Date of mailing of the international search report 09/12/2014
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Schmid, Arnold
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/EP2014/073996

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