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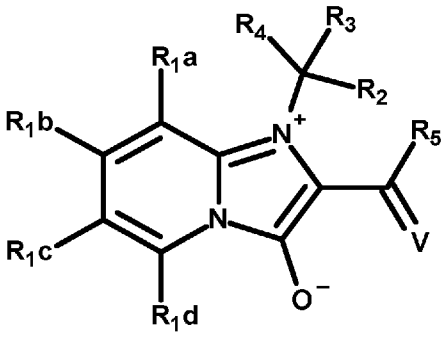
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(54) Title: PESTICIDALLY ACTIVE MESOIONICS HETEROCYCLIC COMPOUNDS



(I)

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

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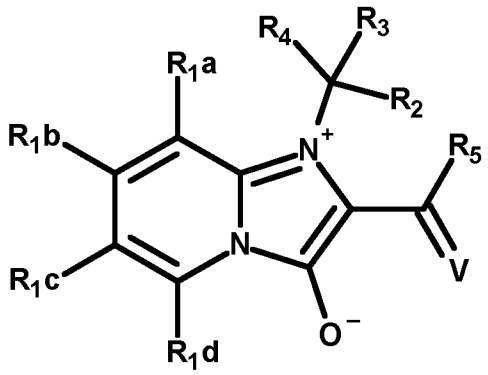
PESTICIDALLY ACTIVE MESOIONICS HETEROCYCLIC COMPOUNDS

The present invention relates to pesticidally active, in particular insecticidally active mesoionics heterocyclic compounds, to compositions comprising those compounds, and to their use for controlling animal pests (including arthropods and in particular insects or representatives of the order *lepidoptera and coleoptera*).

Mesoionics heterocyclic compounds with pesticidal action are known and described, for example, in WO09099929, WO11017334, WO11017347, WO11017342, WO12092115, WO12106495, WO12136724, WO14033244, WO14202582, WO14167084, WO16055431, WO16171053 and WO17093214.

There have now been found novel pesticidally active mesoionics heterocyclic compounds.

The present invention accordingly, in a first aspect, relates to compounds of formula I,



(I),

wherein

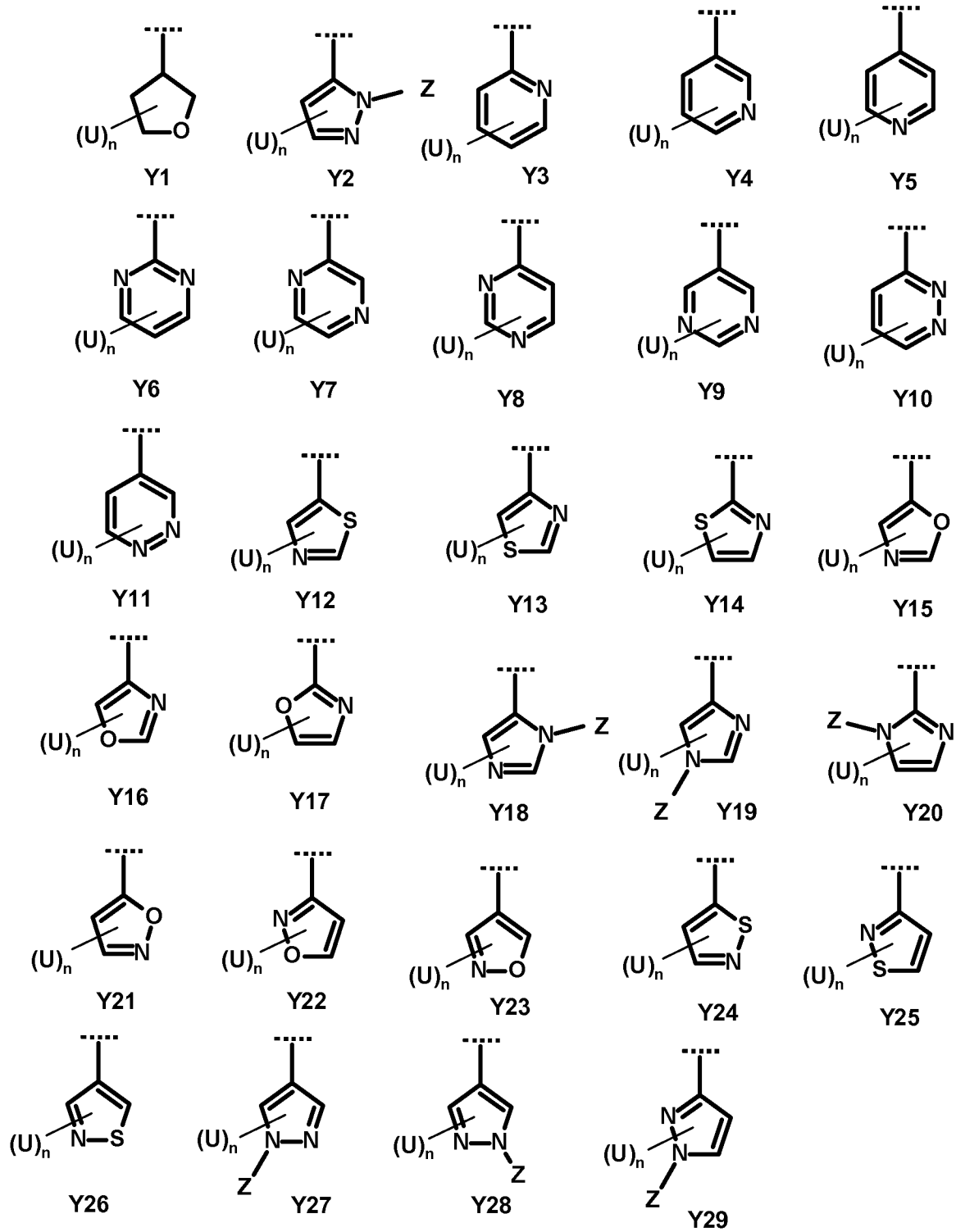
V is S or O;

R_{1a}, R_{1b}, R_{1c} and R_{1d} are independently selected from hydrogen, halogen, amino, hydroxyl, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_1-C_6 haloalkoxy, C_1-C_6 alkoxy, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl and cyano;

R_2 is hydrogen, halogen, hydroxyl, amino, cyano, C_1-C_6 alkyl, mono- or poly-substituted C_1-C_6 alkyl (where the substituents are independently selected from the group consisting of halogen, hydroxyl, amino, cyano, nitro, C_1-C_6 haloalkoxy, C_1-C_6 alkoxy, C_1-C_6 alkylsulfanyl, C_1-C_6 alkylsulfinyl, C_1-C_6 alkylsulfonyl, C_1-C_6 haloalkylsulfanyl, C_1-C_6 haloalkylsulfinyl and C_1-C_6 haloalkylsulfonyl), C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, triazole, pyrazole, imidazole, or tetrazole, wherein said triazole, pyrazole, imidazole and tetrazole can be mono- or polysubstituted by substituents independently selected from the group consisting of halogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl and cyano;

R_3 is hydrogen or C_1-C_6 alkyl;

R_4 is hydrogen or a 5 or 6 membered heteroaromatic ring Y, optionally independently substituted with a substituent from the group U, wherein Y is a ring selected from Y1 to Y29



wherein Z is hydrogen, cyano, nitro, hydroxyl, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkoxy, C_1-C_4 haloalkoxy-C_1-C_4 alkyl or C_1-C_4 alkoxy-C_1-C_4 alkyl;

n is 0, 1, 2, or 3;

U is independently selected from the group consisting of halogen, cyano, nitro, hydroxyl, amino, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkoxy, C_1-C_4 haloalkoxy-C_1-C_4 alkyl, C_1-C_4 alkoxy-C_1-C_4 alkyl, C_1-C_4 alkylsulfanyl, C_1-C_4 alkylsulfinyl, C_1-C_4 alkylsulfonyl, C_1-C_4 haloalkylsulfanyl, C_1-C_4

haloalkylsulfinyl, C_1-C_4 haloalkylsulfonyl, formyl, C_3-C_6cycloalkyl, C_3-C_6halocycloalkyl, C_1-C_6 alkylcarbonyl and C_3-C_6 cycloalkylcarbonyl; and

R_5 is hydrogen, -OR_6, -NR_8R_7, -$N(R_8)N(R_8R_7)$; or

R_5 is a 5 to 12 membered aromatic ring, which can be monocyclic or polycyclic, which ring system can be mono- or polysubstituted by substituents independently selected from the group U_2; or

R_5 is a 3 to 12 membered heteroaromatic ring, or a 3 to 12 membered saturated or partially saturated heterocyclic ring, each of which can be monocyclic or polycyclic, which ring system can contain 1 to 4 heteroatoms selected from the group consisting of nitrogen, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, wherein the nitrogen heteroatom can be substituted by Z and said 3 to 12-membered ring system can be mono- or polysubstituted by substituents independently selected from the group U_2; or

R_5 is C_3-C_6 cycloalkyl, which can be mono- or poly-substituted by substituents independently selected from the group U_3; or

R_5 is C_1-C_6 alkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3; or

R_5 is C_2-C_4 alkenyl which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3; or

R_5 is C_2-C_4 alkynyl which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3;

U_2 is selected from the group consisting of halogen, nitro, cyano, amino, hydroxyl, -SCN, -CO_2H, C_1-C_6 alkyl, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl, C_3-C_6 cycloalkyl-C_1-C_4 alkyl, C_3-C_6 halocycloalkyl-C_1-C_4 alkyl,C_1-C_6 haloalkyl, C_1-C_6 alkoxy, C_1-C_4 alkoxy-C_1-C_4 alkyl, C_1-C_4 alkoxy-C_1-C_4 alkoxy, cyano-C_1-C_4 alkyl, cyano-C_1-C_4 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_1-C_6 haloalkoxy, C_1-C_4 haloalkoxy-C_1-C_4 alkyl, C_1-C_6 alkylsulfanyl, C_1-C_6 alkylsulfinyl, C_1-C_6 alkylsulfonyl, C_1-C_6 haloalkylsulfanyl, C_1-C_6 haloalkylsulfinyl, C_1-C_6 haloalkylsulfonyl, C_1-C_6 alkylcarbonyl, C_1-C_6 alkoxycarbonyl, C_1-C_6 haloalkylcarbonyl, C_1-C_6 haloalkoxycarbonyl, (C_1-C_6 alkyl)NH, (C_1-C_6 alkyl)$_2$N, (C_3-C_6 cycloalkyl)NH, (C_3-C_6 cycloalkyl)$_2$N, C_1-C_6 alkylcarbonylamino, C_3-C_6 cycloalkylcarbonylamino, C_1-C_6 haloalkylcarbonylamino, C_3-C_6 halocycloalkylcarbonylamino, C_1-C_6 alkylaminocarbonyl, C_3-C_6 cycloalkylaminocarbonyl, C_1-C_6 haloalkylaminocarbonyl, C_3-C_6 halocycloalkylaminocarbonyl, C_3-C_6 cycloalkylcarbonyl, C_3-C_6 halocycloalkylcarbonyl, -SF_5 and -$C(O)NH_2$;

U_3 is selected from the group consisting of halogen, nitro, cyano, amino, hydroxyl, -SCN, -CO_2H, C_1-C_6 alkyl, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl, C_3-C_6 cycloalkyl-C_1-C_4 alkyl, C_3-C_6 halocycloalkyl-C_1-C_4 alkyl,C_1-C_6 haloalkyl, C_1-C_6 alkoxy, C_1-C_4 alkoxy-C_1-C_4 alkyl, C_1-C_4 alkoxy-C_1-C_4 alkoxy, cyano-C_1-C_4 alkyl, cyano-C_1-C_4 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_1-C_6 haloalkoxy, C_1-C_4 haloalkoxy-C_1-C_4 alkyl, C_1-C_6 alkylsulfanyl, C_1-C_6 alkylsulfinyl, C_1-C_6 alkylsulfonyl, C_1-C_6 haloalkylsulfanyl, C_1-C_6 haloalkylsulfinyl, C_1-C_6 haloalkylsulfonyl, C_1-C_6 alkylcarbonyl, C_1-C_6 alkoxycarbonyl, C_1-C_6 haloalkylcarbonyl, C_1-C_6 haloalkoxycarbonyl, (C_1-C_6 alkyl)NH, (C_1-C_6 alkyl)$_2$N, (C_3-C_6 cycloalkyl)NH, (C_3-C_6 cycloalkyl)$_2$N, C_1-C_6 alkylcarbonylamino, C_3-C_6

cycloalkylcarbonylamino, C_1-C_6 haloalkylcarbonylamino, C_3-C_6 halocycloalkylcarbonylamino, C_1-C_6 alkylaminocarbonyl, C_3-C_6 cycloalkylaminocarbonyl, C_1-C_6 haloalkylaminocarbonyl, C_3-C_6 halocycloalkylaminocarbonyl, C_3-C_6 cycloalkylcarbonyl, C_3-C_6 halocycloalkylcarbonyl, -SF_5 and -$C(O)NH_2$; or

U_3 is a 5 to 6 membered aromatic ring, 5 to 6 membered heteroaromatic ring, or 5 to 6 membered saturated or partially saturated carbocyclic or heterocyclic ring system, wherein heteroaromatic or heterocyclic ring can contain 1 to 4 hetero atoms selected from the group consisting of nitrogen substituted or not, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, said 5 to 6-membered ring system can be mono- or polysubstituted by substituents independently selected from the group U_2;

R_6 is selected from the group consisting of hydrogen, amino, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_1-C_6 haloalkoxy, C_1-C_4 haloalkoxy-C_1-C_4 alkyl, C_1-C_6 alkoxy-C_1-C_6 alkyl, C_1-C_6 alkoxy, C_1-C_4 alkylsulfanyl, C_1-C_4 alkylsulfinyl, C_1-C_4 alkylsulfonyl, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_3-C_6 cycloalkyl, cyano-C_1-C_4 alkyl, cyano-C_1-C_4 haloalkyl and C_3-C_6 halocycloalkyl;

R_8 is selected from the group consisting of hydrogen, hydroxyl, cyano, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_1-C_6 haloalkoxy, C_1-C_4 haloalkoxy-C_1-C_4 alkyl, C_1-C_6 alkoxy-C_1-C_6 alkyl, C_1-C_6 alkoxy, C_1-C_4 alkylsulfanyl, C_1-C_4 alkylsulfinyl, C_1-C_4 alkylsulfonyl, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, cyano-C_1-C_4 alkyl, cyano-C_1-C_4 haloalkyl, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl, phenyl, pyridyl and pyrimidyl, wherein said phenyl, pyridyl or pyrimidyl ring system can be mono- or polysubstituted by substituents independently selected from the group consisting of halogen, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 haloalkoxy, and C_1-C_4 alkoxy; and

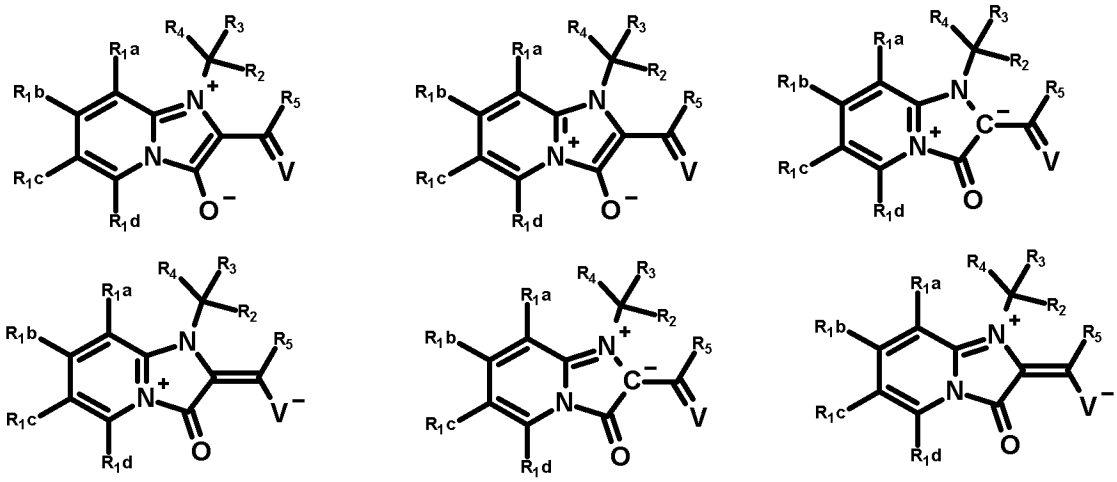
R_7 is selected from the group consisting of hydrogen, cyano, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_1-C_6 haloalkoxy, C_1-C_4 haloalkoxy-C_1-C_4 alkyl, C_1-C_6 alkoxy-C_1-C_6 alkyl, C_1-C_6 alkoxy, C_1-C_4 alkylsulfanyl, C_1-C_4 alkylsulfinyl, C_1-C_4 alkylsulfonyl, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, cyano-C_1-C_4 alkyl, cyano-C_1-C_4 haloalkyl, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl, phenyl, pyridyl and pyrimidyl, wherein said phenyl, pyridyl or pyrimidyl ring system can be mono- or polysubstituted by substituents independently selected from the group consisting of halogen, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 haloalkoxy, and C_1-C_4 alkoxy; and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of the compounds of formula I, wherein in the instance the moiety –$NCR_2R_3R_4$ is –NCH_2CH_3, R_5 is not phenyl, methyl or ethyl.

Compounds of formula I which have at least one basic centre can form, for example, acid addition salts, for example with strong inorganic acids such as mineral acids, for example perchloric acid, sulfuric acid, nitric acid, a phosphorus acid or a hydrohalic acid, with strong organic carboxylic acids, such as C_1-C_4alkanecarboxylic acids which are unsubstituted or substituted, for example by halogen, for example acetic acid, such as saturated or unsaturated dicarboxylic acids, for example oxalic acid, malonic acid, succinic acid, maleic acid, fumaric acid or phthalic acid, such as hydroxycarboxylic

acids, for example ascorbic acid, lactic acid, malic acid, tartaric acid or citric acid, or such as benzoic acid, or with organic sulfonic acids, such as C_1-C_4-alkane- or arylsulfonic acids which are unsubstituted or substituted, for example by halogen, for example methane- or p-toluenesulfonic acid.

Compounds of formula I which have at least one acidic group can form, for example, salts with bases, for example mineral salts such as alkali metal or alkaline earth metal salts, for example sodium, potassium or magnesium salts, or salts with ammonia or an organic amine, such as morpholine, piperidine, pyrrolidine, a mono-, di- or tri-lower-alkylamine, for example ethyl-, diethyl-, triethyl- or dimethylpropylamine, or a mono-, di- or trihydroxy-lower-alkylamine, for example mono-, di- or triethanolamine.

The compounds of formula I are mesoionic compounds (also known as inner salts or zwitterions), which are understood to be compounds that are neutral but carry a formal positive and a negative charge on different atoms within the compounds. There are literature papers that have described these types of compounds, such as, for example Tetrahedron (1985), 41(12), 2239-329 or Tetrahedron 69 (2013) 4146-4159. Examples of mesoionics of formula I could be described by the following structures:



Accordingly, compounds according to the present invention can be represented by any one of the charge distribution above.

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

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

A haloalkyl group is an alkyl group having one or more independently selected halogen atoms on the alkyl group. 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.

An alkoxy group is an alkyl group connected to an oxygen atom, wherein the alkoxy group is connected to the rest of the compound via the oxygen atom. 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.

A cycloalkyl group has at least three carbon atoms in a ring, for example cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl, preferably cyclopropyl.

A haloalkoxy group is an alkoxy group having one or more independently selected halogen atoms on the alkyl group of the alkoxy group. Haloalkoxy is, for example, difluoromethoxy, trifluoromethoxy or 2,2,2-trifluoroethoxy.

An alkoxyalkyl group has one or more alkoxy groups and an alkyl group, wherein the alkoxy groups are in a chain with one of the oxygen atoms of the alkoxy chain connected to the alkyl group, which alkoxyalkyl group is connected to the rest of the compound via a carbon atom of the alkyl group. Alkoxyalkyl is, for example, methoxymethyl, methoxyethyl, ethoxymethyl, ethoxyethyl, n-propoxymethyl, n-propoxyethyl, isopropoxymethyl, isopropoxyethyl or a dialkoxyalkyl group such as for example CH3OCH2CH2OCH2-.

A haloalkoxyalkyl group is an alkoxyalkyl group having one or more independently selected halogen atoms on the alkoxyalkyl group (for example the halogenation can be on the carbon atoms forming part of the alkyl and/or any one of the alkoxy group). Examples of haloalkoxyalkyl are, trifluoromethyloxymethyl, trifluoromethyloxyethyl, methoxyfluromethyl, trifluoroethyloxymethyl or a dihaloalkoxyalkyl group such as for example CF3OCH2CH2OCH2-, CH3OCH2CF2OCH2-, C(Cl)F2OCH2CH2OCH2-, and CH3OCH2C(Cl)2OCH2-.

An alkylcarbonyl group is an alkyl group connected to a carbonyl group, which alkylcarbonyl group is connected to the rest of the compound via the carbon atom of the carbonyl moiety. Examples are CH3C(O)-, and (CH3)2CHC(O)-.

A cycloalkylcarbonyl group is a cycloalkyl group connected to a carbonyl group, which cycloalkylcarbonyl group is connected to the rest of the compound via the carbon atom of the carbonyl moiety. Examples are cyclopropylC(O)-, and cyclobutylC(O)-.

A cycloalkylalkyl group is a cycloalkyl group connected to an alkyl group, which cycloalkylalkyl group is connected to the rest of the compound via a carbon atom of the alkyl group. Examples are -CyclopropylCH2-, and Cyclopropyl(CH3)CH-.

A haloalkylcarbonyl group is an alkylcarbonyl group, wherein the alkyl group has one or more halogen atoms, which haloalkylcarbonyl group is connected to the rest of the compound via the carbon atom of the carbonyl moiety. An example of such is CF3C(O)-.

An alkoxycarbonyl group is an alkoxy group connected to the carbon atom of a carbonyl group via the oxygen of the alkoxy group, which alkoxycarbonyl group is connected to the rest of the compound via the carbon atom of the carbonyl group. An example is CH3OC(O)-.

An haloalkoxycarbonyl group is an alkoxycarbonyl group wherein the alkoxy group is halogenated by one or more independently selected halogen atoms, for example, CF3OC(O)-.

An alkylcarbonylamino group is an alkylcarbonyl group connected to the nitogen atom of an amino group via the carbon atom of the carbonyl group, which alkylcarbonylamino group is connected to the rest of the compound via the nitrogen atom of the amino group, such as for example CH3C(O)NH-.

A cycloalkylcarbonylamino group is a cycloalkylcarbonyl group connected to the nitogen atom of an amino group via the carbon atom of the carbonyl group, which cycloalkylcarbonylamino is connected to the rest of the compound via the nitrogen atom of the amino group, such as for example, cyclopropylC(O)NH-.

An alkylaminocarbonyl group has an alkyl group, an amino group and a carbonyl group, wherein a carbon atom of the the alkyl group is connected to a nitrogen atom of the amino group and then a nitrogen atom of the amino group is connected to the carbon atom of the carbonyl group, which alkylaminocarbonyl is connected to the rest of the compound via the carbon atom of the carbonyl group, such as for example, CH3NHC(O) -.

A cycloalkylaminocarbonyl group has a cycloalkyl group, an amino group and a carbonyl group, wherein a carbon atom of the cycloalkyl group is connected to a nitrogen atom of the amino group and then a nitrogen atom of the amino group is connected to the carbon atom of the carbonyl group, which cycloalkylaminocarbonyl is connected to the rest of the compound via the carbon atom of the carbonyl group, such as for example, cyclopropylNHC(O) -.

A haloalkylcarbonylamino group is an alkylcarbonylamino group having one or more independently selected halogen atoms on the alkyl group, which haloalkylcarbonylamino group is connected to the rest of the compound via the nitrogen atom of the amino group, such as for example, CFH2C(O)NH-.

A halocycloalkylcarbonylamino group is an cycloalkylcarbonylamino group having one or more independently selected halogen atoms on the cycloalkyl group, which halocycloalkylcarbonylamino group is connected to the rest of the compound via the nitrogen atom of the amino group, such as for example, 2-fluoro-cyclopropylC(O)NH-.

A haloalkylaminocarbonyl group is an alkylaminocarbonyl group having one or more independently selected halogen atoms on the alkyl group, which haloalkylaminocarbonyl is connected to the rest of the compound via the carbon atom of the carbonyl group, such as for example, CFH2NHC(O) -.

A halocycloalkylaminocarbonyl group is a cycloalkylaminocarbonyl group having one or more independently selected halogen atoms on the cycloalkyl group, which halocycloalkylaminocarbonyl is connected to the rest of the compound via the carbon atom of the carbonyl group, such as for example 2-fluorocyclopropylNHC(O) -.

In the context of this invention “mono- to poly-substituted” in the definition of the substituents, means typically, depending on the chemical structure of the substituents, generally mono-substituted to seven-times substituted, preferably mono-substituted to five-times substituted, more preferably mono-, di- or tri-substituted.

As used herein, the term "C_2-C_6 alkynyl" refers to a straight or branched hydrocarbon chain radical group consisting solely of carbon and hydrogen atoms, containing at least one triple bond, having from two to six carbon atoms, and which is attached to the rest of the molecule by a single bond. The term

"C_2-C_4alkynyl" and "C_2-C_3alkynyl" are to be construed accordingly. Examples of C_2-C_6 alkynyl include, but are not limited to, ethynyl, prop-1-ynyl, but-1-ynyl and but-2-ynyl.

As used herein, the term "C_2-C_6 alkenyl" refers to a straight or branched hydrocarbon chain radical group consisting solely of carbon and hydrogen atoms, containing at least one double bond, having from two to six carbon atoms, and which is attached to the rest of the molecule by a single bond. The term "C_2-C_4alkenyl" and "C_2-C_3alkenyl" are to be defined accordingly. Examples of C_2-C_6 alkenyl include, but are not limited to prop-1-enyl, but-1-enyl and but-2-enyl.

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

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

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

Haloalkylsulfanyl is for example difluoromethylsulfanyl, trifluoromethylsulfanyl, 2,2,2-trifluoroethylsulfanyl or pentafluoroethylsulfanyl.

Haloalkylsulfinyl is for example difluoromethylsulfinyl, trifluoromethylsulfinyl, 2,2,2-trifluoroethylsulfinyl or pentafluoroethylsulfinyl.

Haloalkylsulfonyl is for example difluoromethylsulfonyl, trifluoromethylsulfonyl, 2,2,2-trifluoroethylsulfonyl or pentafluoroethylsulfonyl.

Examples of a 5 to 12 membered aromatic ring system, which can be monocyclic or polycyclic, include phenyl, naphthyl, anthracenyl and biphenyl; preferred are phenyl, naphthyl, and biphenyl.

Examples of a 3 to 12 membered heteroaromatic ring system, which can be monocyclic or polycyclic, include pyridyl, pyrimidyl, pyrrolyl, pyrazolyl, furyl, thienyl, imidazolyl, isoxazolyl, oxazolyl, thiazolyl, isothiazolyl, triazolyl, oxadiazolyl, thiadiazolyl, tetrazolyl, pyrazinyl, pyridazinyl, triazinyl, pyranyl, quinazolinyl, isoquinolinyl, indolizinyl, isobenzofuranylnaphthyridinyl, quinoxalinyl, isochinolinyl, cinnolinyl, phthalazinyl, benzothiazolyl, benzoxazolyl, benzotriazolyl, indazolyl, indolyl, tetrahydroquinolynyl, benzofuryl, benzisofuryl, benzothienyl, benzisothienyl, isoindolyl, naphthyridinyl, benzisothiazolyl, benzisoxazolyl, benzoxazolyl, benzotriazinyl, purinyl, chinazolinyl, chinoxalinyl, teridinyl, Indolizinyl, phenylpyridyl, and pyridylphenyl; preferred are pyridyl, pyrimidyl, phenylpyridyl, pyridylphenyl, and thienyl.

Examples of a 3 to 12 membered saturated or partially saturated heterocyclic ring system, which can be monocyclic or polycyclic, include dihydropyranyl, tetrahydrofuryl, tetrahydrofuranyl, tetrahydrothienyl, pyrrolidinyl, pyrrolidinyl, isoxazolidinyl, isothiazolidinyl, pyrazolidinyl, oxazolidinyl, thiazolidinyl, imidazolidinyl, oxadiazolidinyl,thiadiazolidinyl, dihydrofuryl, dihydrothienyl, pyrrolinyl, isoxazolinyl, dihydropyrazolyl, dihydrooxazolyl, piperidinyl, dioxanyl, tetrahydropyranyl, tetrahydrothienyl, hexahydropyridazinyl, hexahydropyrimidinyl, oxiranyl, and piperazinyl; preferred is tetrahydrofuryl.

Example of a 5 to 6 membered aromatic ring system includes phenyl.

Examples of a 5 to 6 membered heteroaromatic ring system include pyridyl, pyrimidyl, pyrrolyl, pyrazolyl, furyl, thienyl, imidazolyl, isoxazolyl, oxazolyl, thiazolyl, isothiazolyl, triazolyl, oxadiazolyl, thiadiazolyl, tetrazolyl, pyrazinyl, pyridazinyl, triazinyl, and pyranyl; preferred are pyridyl, pyrimidyl, and thienyl.

Examples of a 5 to 6 membered saturated or partially saturated carbocyclic or heterocyclic ring system include dihydropyranyl, tetrahydrofuryl, tetrahydrofuranyl, tetrahydrothienyl, pyrrolidinyl, pyrrolidinyl, isoxazolidinyl, isothiazolidinyl, pyrazolidinyl, oxazolidinyl, thiazolidinyl, imidazolidinyl, oxadiazolidinyl,thiadiazolidinyl, dihydrofuryl, dihydrothienyl, pyrrolinyl, isoxazolinyl, dihydropyrazolyl, dihydrooxazolyl, piperidinyl, dioxanyl, tetrahydropyranyl, tetrahydrothienyl, hexahydropyridazinyl, hexahydropyrimidinyl, piperazinyl; prefererd is tetrahydrofuryl.

Polycyclic as used herein refers to fused cyclic rings, and substituted cyclic rings, in which the substituent is another cyclic ring (such as an aryl or heteroaryl ring). An example of a fused ring is naphthyl or benzisoxazolyl or benzoxazolyl, whereas an example of a substituted ring is biphenyl or 2-phenylpyridyl or 2-pyridylphenyl.

A “ring system” as used herein refers in entirety to the ring substitutent whether monocyclic or polycyclic. For example, in the instance of “R_5 being a 3 to 12 membered heteroaromatic ring, which ring system can contain 1 to 4 heteroatoms selected from the group consisting of nitrogen, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, wherein the nitrogen heteroatom can be substituted by Z and said 3 to 12-membered ring system can be mono- or polysubstituted by substituents independently selected from the group U_2”, the ring sytem refers to the fact that only 1 to 4 heteroatoms can be present in total and not per ring.

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

In an embodiment, independent of the different aspects or embodiments, V is O.

In an embodiment, independent of the different aspects or embodiments, U is halogen, cyano, C_1-C_4 alkyl, C_1-C_4 haloalky, C_1-C_4 alkoxy, or C_1-C_4 haloalkoxy; preferably U is halogen; more preferably chloro, or fluoro.

In an embodiment, independent of the different aspects or embodiments, n is 0 or 1.

In an embodiment, independent of the different aspects or embodiments, U_2 is halogen, cyano, C_1-C_6 alkyl, C_1-C_6 alkoxy, or C_1-C_6 haloalkyl; preferably U_2 is halogen, cyano, C_1-C_4 alkyl, C_3-C_6 cycloalkyl, C_1-C_4 haloalkyl or C_1-C_4 alkoxy.. Especially U_2 is chloro, fluoro, cyano, methyl, cyclopropyl, trifluoromethyl or methoxy.

In an embodiment, independent of the different aspects or embodiments, U_3 is halogen, nitro, cyano, C_1-C_6 alkyl, C_3-C_6 cycloalkyl, C_1-C_6 haloalkyl, C_1-C_6 alkoxy,or a phenyl, optionally mono- or polysubstituted by substituents independently selected from the group U_2; more preferably U_3 is halogen or phenyl; especially U_3 is fluoro or phenyl

In an embodiment, independent of the different aspects or embodiments, Z is cyano, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, or C_1-C_4 haloalkoxy; preferably Z is C_1-C_4 alkyl; more preferably Z is methyl.

In an embodiment, independent of the different aspects or embodiments, R_{1a}, R_{1b}, R_{1c} and R_{1d} are independently selected from hydrogen, C_1-C_6alkyl, C_1-C_6 alkoxy, and C_1-C_6 haloalkyl. Preferably R_{1b}, R_{1c} and R_{1d} are each hydrogen and R_{1a} is hydrogen, C_1-C_6alkyl, C_1-C_6 alkoxy or C_1-C_6 haloalkyl; more preferably R_{1b}, R_{1c} and R_{1d} are each hydrogen and R_{1a} is hydrogen, C_1-C_4alkyl, C_1-C_4 alkoxy or C_1-C_4 haloalkyl; and especially R_{1b}, R_{1c} and R_{1d} are each hydrogen and R_{1a} is hydrogen, methyl, methoxy, or trifluoromethyl.

In an embodiment, independent of the different aspects or embodiments, R_2 is hydrogen, C_1-C_6 alkyl, or mono- or poly-substituted C_1-C_6 alkyl, where the substituents are independently selected from the group consisting of halogen, hydroxyl, amino, cyano, nitro, C_1-C_6 haloalkoxy, C_1-C_6 alkoxy, C_1-C_6 alkylsulfanyl, C_1-C_6 alkylsulfinyl, C_1-C_6 alkylsulfonyl, C_1-C_6 haloalkylsulfanyl, C_1-C_6 haloalkylsulfinyl and C_1-C_6 haloalkylsulfonyl; preferably R_2 is hydrogen, C_1-C_6 alkyl, or mono- or poly- substituted C_1-C_6 alkyl, where the substituents are independently selected from the group consisting of halogen, hydroxyl, amino, cyano, nitro, C_1-C_6 haloalkoxy, and C_1-C_6 alkoxy; more preferably R_2 is hydrogen, C_1-C_4 alkyl or mono-substituted is C_1-C_4 alkyl whee the substiuent is selected from the group consisting of halogen, hydroxyl, amino, and cyano; especially R_2 is hydrogen, methyl or cyanomethyl.

In an embodiment, independent of the different aspects or embodiments, R_3 is hydrogen or C_1-C_4 alkyl; preferably R_3 is hydrogen, methyl, ethyl, or propyl; more preferably R_3 is hydrogen, methyl, or ethyl; especially R_3 is hydrogen, or methyl.

In an embodiment, independent of the different aspects or embodiments, R_4 is a heteroaromatic ring Y selected from Y1 to Y29 independently substituted with a substituent from the group U, wherein n, Z and U are as defined in the first aspect; preferably R_4 is heteroaromatic ring Y selected from selected from Y1, Y4, Y9 and Y12 substituted with a substituent from the group U, wherein n and U are as defined herein; more preferably R_4 is heteroaromatic ring Y selected from selected from Y4, Y9 and Y12 substituted with a substituent from the group U, wherein n and U are as defined herein.

In an embodiment, independent of the different aspects or embodiments, R_5 is a 5 to 12 membered aromatic ring, which can be monocyclic or polycyclic, which ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2 as defined herein; preferably R_5 is 6 to 12, more preferably 6, 10 and 12 membered aromatic rings, which can be monocyclic or polycyclic, which ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2 as defined herein; more preferably R_5 is phenyl or napthyl, which can optionally be mono- or polysubstituted by substituents independently selected from the group U_2 as defined herein.

In an embodiment, independent of the different aspects or embodiments, R_5 is a 3 to 12 membered heteroaromatic ring system, which can be monocyclic or polycyclic, which ring system can contain 1 to 4 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, wherein the nitrogen heteroatom can be substituted by Z and said ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2 wherein Z and U_2 are as defined herein. Preferably R_5 is a 5 to 12, more preferably 5, 6, 10 or 12, membered heteroaromatic

ring, which can be monocyclic or polycyclic, which ring system can contain 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, wherein the nitrogen heteroatom can be substituted by Z and said ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2 wherein Z and U_2 are as defined herein. More preferably R_5 is a thiophenyl, pyridyl, or pyridylphenyl, and said ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2 wherein U_2 is as defined herein.

In an embodiment, independent of the different aspects or embodiments, R_5 is a 3 to 12 membered saturated or partially saturated heterocyclic ring system, which can be monocyclic or polycyclic, which ring system can contain 1 to 4 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, wherein the nitrogen heteroatom can be substituted by Z and said ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2 wherein Z and U_2 are as defined herein. Preferably R_5 is a 3 to 6, more preferably 3, 5 and 6, membered saturated or partially saturated heterocyclic ring system, which can be monocyclic or polycyclic, which ring system can contain 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, wherein the nitrogen heteroatom can be substituted by Z and said ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2 wherein Z and U_2 are as defined herein. More preferably R_5 is a tetrahydrofuryl.

In an embodiment, independent of the different aspects or embodiments, R_5 is C_3-C_6 cycloalkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3, wherein U_3 is defined herein. Preferably R_5 is C_3 cycloalkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3, wherein U_3 is as defined herein.

In an embodiment, independent of the different aspects or embodiments, R_5 is C_1-C_6 alkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3, wherein U_3 is as defined herein. Preferably R_5 is C_1-C_4 alkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3 wherein U_3 is as defined herein. More preferably R_5 is C_1-C_4 alkyl, C_1-C_4 haloalkyl or phenyl-C_1-C_4 alkyl. Especially R_5 is methyl, trifluoromethyl, heptafluoropropyl or benzyl.

Preferred compounds of formula I are where V is oxygen; R_{1a}, R_{1b}, R_{1c} and R_{1d} are independently selected from hydrogen, C_1-C_6alkyl, C_1-C_6 alkoxy, or C_1-C_6 haloalkyl; R_2 is hydrogen, C_1-C_6 alkyl, or mono- or poly-substituted C_1-C_6 alkyl, where the substiuents are independently selected from the group consisting of halogen, hydroxyl, amino, cyano, nitro, C_1-C_6 haloalkoxy, C_1-C_6 alkoxy, C_1-C_6 alkylsulfanyl, C_1-C_6 alkylsulfinyl, C_1-C_6 alkylsulfonyl, C_1-C_6 haloalkylsulfanyl, C_1-C_6 haloalkylsulfinyl and C_1-C_6 haloalkylsulfonyl; R_3 is hydrogen or C_1-C_4 alkyl; R_4 is a heteroaromatic ring Y selected from Y1 to Y29; and R_5 is a 5 to 12 membered aromatic ring, which can be monocyclic or polycyclic, which ring

system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is a 3 to 12 membered heteroaromatic ring system or 3 to 12 membered saturated or partially saturated heterocyclic ring system, each of which can be monocyclic or polycyclic, which ring system can contain 1 to 4 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, wherein the nitrogen heteroatom can be substituted by Z and said ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is C_3-C_6 cycloalkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3; or R_5 is C_1-C_6 alkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3, wherein n is 0 or 1; Z is cyano, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, or C_1-C_4 haloalkoxy; U is halogen, cyano, C_1-C_4 alkyl, C_1-C_4 haloalky, C_1-C_4 alkoxy, or C_1-C_4 haloalkoxy; U_2 is halogen, cyano, C_1-C_6 alkyl, C_1-C_6 alkoxy, or C_1-C_6 haloalkyl; and U_3 is halogen, nitro, cyano, C_1-C_6 alkyl, C_3-C_6 cycloalkyl, C_1-C_6 haloalkyl, C_1-C_6 alkoxy,or a phenyl, which phenyl is optionally mono- or polysubstituted by substituents independently selected from the group U_2.

Preferred compounds of formula I are where V is oxygen; R_{1b}, R_{1c} and R_{1d} are each hydrogen and R_{1a} is hydrogen, C_1-C_6alkyl, C_1-C_6 alkoxy or C_1-C_6 haloalkyl; R_2 is hydrogen, C_1-C_6 alkyl, or mono- or poly- substituted C_1-C_6 alkyl, where the substiuents are independently selected from the group consisting of halogen, hydroxyl, amino, cyano, nitro, C_1-C_6 haloalkoxy, and C_1-C_6 alkoxy; R_3 is hydrogen, methyl, ethyl, or propyl; R_4 is heteroaromatic ring Y selected from selected from Y1, Y4, Y9 and Y12; and R_5 is 6 to 12 membered aromatic ring, which can be monocyclic or polycyclic, which ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is a 5 to 12 membered heteroaromatic ring system, which can be monocyclic or polycyclic, which ring system can contain 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, wherein the nitrogen heteroatom can be substituted by Z and said ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is a 3 to 6 membered saturated or partially saturated heterocyclic ring system, which can be monocyclic or polycyclic, which ring system can contain 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, wherein the nitrogen heteroatom can be substituted by Z and said ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is C_3 cycloalkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3; or R_5 is C_1-C_4 alkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3; wherein n is 0 or 1; Z is cyano, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkoxy; U is halogen, cyano, C_1-C_4 alkyl, C_1-C_4 haloalky, C_1-C_4 alkoxy, or C_1-C_4 haloalkoxy; U_2 is halogen, cyano, C_1-C_6 alkyl, C_1-C_6 alkoxy, or C_1-C_6 haloalkyl; and U_3 is halogen, nitro, cyano, C_1-C_6 alkyl, C_3-C_6 cycloalkyl, C_1-C_6

haloalkyl, C_1-C_6 alkoxy,or a phenyl, which phenyl is optionally mono- or polysubstituted by substituents independently selected from the group U_2.

Preferred compounds of formula I are where V is oxygen; R_{1b}, R_{1c} and R_{1d} are each hydrogen and R_{1a} is hydrogen, C_1-C_4alkyl, C_1-C_4 alkoxy or C_1-C_4 haloalkyl; R_2 is hydrogen, C_1-C_4 alkyl or mono-substituted C_1-C_4 alkyl, where the substiuents are selected from the group consisting of halogen, hydroxyl, amino, and cyano; R_3 is hydrogen, or methyl, or ethyl; R_4 is heteroaromatic ring Y selected from selected from Y4, Y9 and Y12; and R_5 is 6 to 12 membered aromatic ring, which can be monocyclic or polycyclic, which ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is a 5 to 12 membered heteroaromatic ring system, which can be monocyclic or polycyclic, which ring system can contain 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, wherein the nitrogen heteroatom can be substituted by Z and said ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is a 3 to 6 membered saturated or partially saturated heterocyclic ring system, which can be monocyclic or polycyclic, which ring system can contain 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, wherein the nitrogen heteroatom can be substituted by Z and said ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is C_3 cycloalkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3; or R_5 is C_1-C_4 alkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3; wherein n is 0 or 1; Z is cyano, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, or C_1-C_4 haloalkoxy; U is halogen, cyano, C_1-C_4 alkyl, C_1-C_4 haloalky, C_1-C_4 alkoxy, or C_1-C_4 haloalkoxy; U_2 is halogen, cyano, C_1-C_6 alkyl, C_1-C_6 alkoxy, or C_1-C_6 haloalkyl; and U_3 is halogen, nitro, cyano, C_1-C_6 alkyl, C_3-C_6 cycloalkyl, C_1-C_6 haloalkyl, C_1-C_6 alkoxy,or a phenyl, which phenyl is optionally mono- or polysubstituted by substituents independently selected from the group U_2

Preferred compounds of formula I are where V is oxygen; R_{1b}, R_{1c} and R_{1d} are each hydrogen and R_{1a} is hydrogen, methyl, methoxy, or trifluoromethyl; R_2 is hydrogen, methyl or cyanomethyl; R_3 is hydrogen, or methyl; R_4 is heteroaromatic ring Y selected from selected from Y4, Y9 and Y12; and R_5 is 6 to 12 membered aromatic ring, which can be monocyclic or polycyclic, which ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is a 5 to 12 membered heteroaromatic ring system, or 5 to 12 membered saturated or partially saturated heterocyclic ring system, each of which can be monocyclic or polycyclic, which ring system can contain 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, wherein the nitrogen heteroatom can be substituted by Z and said ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is a 3 to 6 membered saturated or partially saturated heterocyclic ring system, which can be monocyclic or polycyclic, which ring system can contain 1 to 3 hetero atoms selected from the group consisting of

nitrogen, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, wherein the nitrogen heteroatom can be substituted by Z and said ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is C_3 cycloalkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3; or R_5 is C_1-C_4 alkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3; wherein n is 0 or 1; Z is cyano, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkoxy; U is halogen, cyano, C_1-C_4 alkyl, C_1-C_4 haloalky, C_1-C_4 alkoxy, or C_1-C_4 haloalkoxy; U_2 is halogen, cyano, C_1-C_6 alkyl, C_1-C_6 alkoxy, or C_1-C_6 haloalkyl; and U_3 is halogen, nitro, cyano, C_1-C_6 alkyl, C_3-C_6 cycloalkyl, C_1-C_6 haloalkyl, C_1-C_6 alkoxy,or a phenyl, which phenyl is optionally mono- or polysubstituted by substituents independently selected from the group U_2.

Preferred compounds of formula I are where V is oxygen; R_{1b}, R_{1c} and R_{1d} are each hydrogen and R_{1a} is hydrogen, methyl, methoxy, or trifluoromethyl; R_2 is hydrogen, methyl or cyanomethyl; R_3 is hydrogen, or methyl; R_4 is heteroaromatic ring Y selected from selected from Y4, Y9 and Y12; and R_5 is 6, 10 or 12 membered aromatic ring, which can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is a 5, 6, 10 or 12 membered heteroaromatic ring system, or 5, 6, 10 or 12 membered saturated or partially saturated heterocyclic ring system, each of which can be monocyclic or polycyclic, which ring system can contain 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, wherein the nitrogen heteroatom can be substituted by Z and said ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is a 3, 5, or 6 membered saturated or partially saturated heterocyclic ring system, which ring system can contain 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, wherein the nitrogen heteroatom can be substituted by Z and said ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is C_3 cycloalkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3; or R_5 is C_1-C_4 alkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3; wherein n is 0 or 1; Z is C_1-C_4 alkyl; U is halogen; U_2 is halogen, cyano, C_1-C_4 alkyl, C_3-C_6 cycloalkyl, C_1-C_4 haloalkyl or C_1-C_4 alkoxy; and U_3 is halogen or phenyl.

Preferred compounds of formula I are where V is oxygen; R_{1b}, R_{1c} and R_{1d} are each hydrogen and R_{1a} is hydrogen, methyl, methoxy, or trifluoromethyl; R_2 is hydrogen, methyl or cyanomethyl; R_3 is hydrogen, or methyl; R_4 is heteroaromatic ring Y selected from selected from Y4, Y9 and Y12; and R_5 is phenyl, biphenyl or napthyl, which can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is pyridyl, pyrimidyl, phenylpyridyl, pyridylphenyl, thienyl or tetrahydrofuryl, which can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is C_3 cycloalkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3; or R_5 is C_1-C_4 alkyl, which

can optionally be mono- or poly-substituted by substituents independently selected from the group U_3; wherein n is 0 or 1; Z is C_1-C_4 alkyl; U is halogen; U_2 is halogen, cyano, C_1-C_4 alkyl, C_3-C_6 cycloalkyl, C_1-C_4 haloalkyl or C_1-C_4 alkoxy; and U_3 is halogen or phenyl.

Preferred compounds of formula I are where V is each oxygen; R_{1b}, R_{1c} and R_{1d} are each hydrogen and R_{1a} is hydrogen, methyl, methoxy, or trifluoromethyl; R_2 is hydrogen, methyl or cyanomethyl; R_3 is hydrogen, or methyl; R_4 is heteroaromatic ring Y selected from selected from Y4, Y9 and Y12; and R_5 is phenyl, which can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is C_3 cycloalkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3; or R_5 is C_1-C_4 alkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3; wherein n is 0 or 1; U is halogen; U_2 is halogen, cyano, C_1-C_4 alkyl, C_3-C_6 cycloalkyl, C_1-C_4 haloalkyl or C_1-C_4 alkoxy; and U_3 is halogen or phenyl.

Preferred compounds of formula I are where V is oxygen; R_{1b}, R_{1c} and R_{1d} are each hydrogen and R_{1a} is methyl, methoxy, or trifluoromethyl; R_2 is hydrogen, methyl or cyanomethyl; R_3 is hydrogen, or methyl; R_4 is heteroaromatic ring Y selected from selected from Y4, Y9 and Y12; and R_5 is 6, 10 or 12 membered aromatic ring, which can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is a 5, 6, 10 or 12 membered heteroaromatic ring system, or 5, 6, 10 or 12 membered saturated or partially saturated heterocyclic ring system, each of which can be monocyclic or polycyclic, which ring system can contain 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, wherein the nitrogen heteroatom can be substituted by Z and said ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is a 3, 5, or 6 membered saturated or partially saturated heterocyclic ring system, which ring system can contain 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, wherein the nitrogen heteroatom can be substituted by Z and said ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is C_3 cycloalkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3; wherein n is 0 or 1; Z is C_1-C_4 alkyl; U is halogen; U_2 is halogen, cyano, C_1-C_4 alkyl, C_3-C_6 cycloalkyl, C_1-C_4 haloalkyl or C_1-C_4 alkoxy; and U_3 is halogen or phenyl.

Preferred compounds of formula I are where V is oxygen; R_{1b}, R_{1c} and R_{1d} are each hydrogen and R_{1a} is methyl, methoxy, or trifluoromethyl; R_2 is hydrogen, or methyl; R_3 is hydrogen, or methyl; R_4 is heteroaromatic ring Y selected from selected from Y4, Y9 and Y12; and R_5 is 6, 10 or 12 membered aromatic ring, which can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is a 5, 6, 10 or 12 membered heteroaromatic ring system, or 5, 6, 10 or 12 membered saturated or partially saturated heterocyclic ring system, each of which can be monocyclic or polycyclic, which ring system can contain 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms

or more than 2 sulfur atoms, wherein the nitrogen heteroatom can be substituted by Z and said ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is a 3, 5, or 6 membered saturated or partially saturated heterocyclic ring system, which ring system can contain 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, wherein the nitrogen heteroatom can be substituted by Z and said ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is C_3 cycloalkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3; wherein n is 0 or 1; Z is C_1-C_4 alkyl; U is halogen; U_2 is halogen, cyano, C_1-C_4 alkyl, C_3-C_6 cycloalkyl, C_1-C_4 haloalkyl or C_1-C_4 alkoxy; and U_3 is halogen or phenyl.

Preferred compounds of formula I are where V is oxygen; R_{1b}, R_{1c} and R_{1d} are each hydrogen and R_{1a} is methyl, methoxy, or trifluoromethyl; R_2 is hydrogen, or methyl; R_3 is hydrogen, or methyl; R_4 is heteroaromatic ring Y selected from selected from Y4, Y9 and Y12; and R_5 is phenyl, biphenyl or napthyl, which can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is pyridyl, pyrimidyl, phenylpyridyl, pyridylphenyl, thienyl or tetrahydrofuryl, which can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is C_3 cycloalkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3; wherein n is 0 or 1; U is halogen; U_2 is halogen, cyano, C_1-C_4 alkyl, C_3-C_6 cycloalkyl, C_1-C_4 haloalkyl or C_1-C_4 alkoxy; and U_3 is halogen or phenyl.

Preferred compounds of formula I are where V is each oxygen; R_{1b}, R_{1c} and R_{1d} are each hydrogen and R_{1a} is methyl, methoxy, or trifluoromethyl; R_2 is hydrogen, or methyl; R_3 is hydrogen, or methyl; R_4 is heteroaromatic ring Y selected from selected from Y4, Y9 and Y12; and R_5 is phenyl, which can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is C_3 cycloalkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3; wherein n is 0 or 1; U is halogen; U_2 is halogen, cyano, C_1-C_4 alkyl, C_3-C_6 cycloalkyl, C_1-C_4 haloalkyl or C_1-C_4 alkoxy; and U_3 is halogen or phenyl.

Preferred compounds of formula I are where V is oxygen; R_{1b}, R_{1c} and R_{1d} are each hydrogen and R_{1a} is hydrogen, methyl, methoxy, or trifluoromethyl; R_2 is hydrogen, methyl; R_3 is hydrogen, or methyl; R_4 is heteroaromatic ring Y selected from selected from Y4, Y9 and Y12; and R_5 is biphenyl or napthyl, which can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; or R_5 is pyrimidyl, phenylpyridyl, pyridylphenyl, or tetrahydrofuryl, which can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; wherein n is 0 or 1; U is halogen; and U_2 is halogen, cyano, C_1-C_4 alkyl, C_3-C_6 cycloalkyl, C_1-C_4 haloalkyl or C_1-C_4 alkoxy.

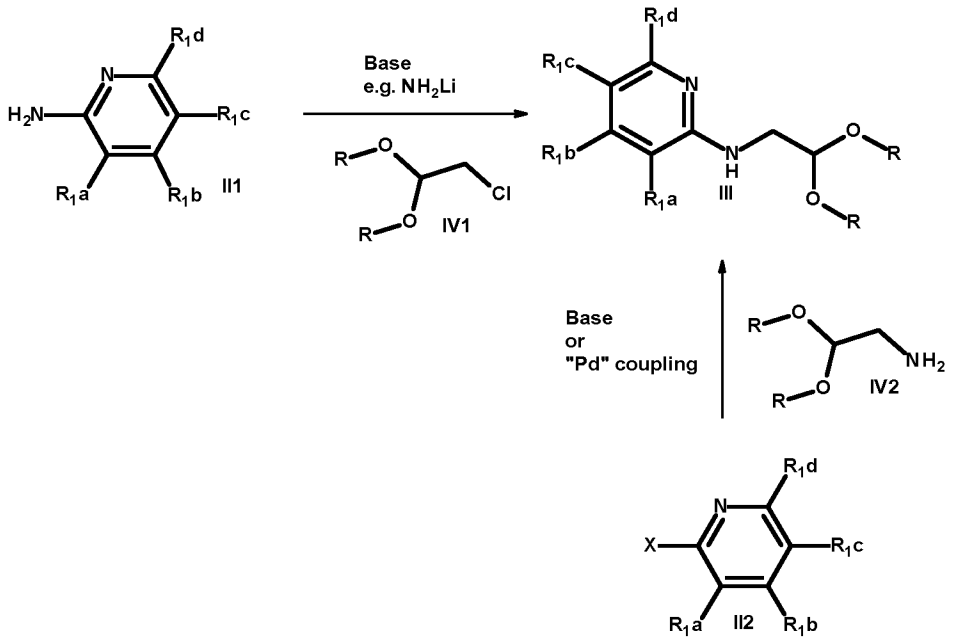
Preferred compounds of formula I are where V is oxygen; R_{1b}, R_{1c} and R_{1d} are each hydrogen and R_{1a} is hydrogen, methyl, methoxy, or trifluoromethyl; R_2 is hydrogen, or methyl; R_3 is hydrogen, or methyl; R_4 is heteroaromatic ring Y selected from selected from Y4, Y9 and Y12; and R_5 is selected from the groups (i) to (iii): (i) benzyl, 3-Cl-Phenyl, 3,5-diCl-Phenyl, 2-Cl-Phenyl, 2-F-Phenyl, 4-F-Phenyl, 3-I-Phenyl, 2-methyl-Phenyl, 3,5-diBr-Phenyl, ,3-Br-5-CF_3-Phenyl, 3-Br-5-OCF_3-Phenyl, 3-

OCF_3-Phenyl, 3-SCH_3-Phenyl, 4-methoxy-Phenyl, 3-methoxy-Phenyl, 3-Br-Phenyl, 4-F-Phenyl., 4-CF_3-Phenyl, 3-CHF_2-Phenyl, or 3,4,5-tri-fluroro-Phenyl; (ii) heptafluoropropyl, 2-CF_3--cyclopropyl-, $CH_3CF_2CH_2$-, or $(CF_3)_2CH$-; and (iii) biphenyl, napthyl, phenylpyridyl, pyridylphenyl, or tetrahydrofuryl, which can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; wherein U_2 is halogen, cyano, C_1-C_4 alkyl, C_3-C_6 cycloalkyl, C_1-C_4 haloalkyl or C_1-C_4 alkoxy.

Whenever a substiutent list (e.g. Z or U_2 or U_3) is used in more than one substiuent in the compound, the substituent list is independently selected for each substituent (e..g in the instance of Z, it can be used on the nitrogen atom of the ring Y29, and also on atom of the heteroatomic ring R_5; or in the instance of U_2, it can be a substituent on the 5 to 12 membered aromatic ring R_5 and also on a 5 or 6 membered aromatic ring R_5; or in the instance of U_3, it can be a substiuent on C_3-C_6 cycloalkyl R_5 or C_1-C_6 alkyl R_5, etc),

The compounds according to the invention can be prepared by methods known to those skilled in the art, in particular, for example, see Canadian Journal of Chemistry (1971), 49(4), 668-71 or Journal of the Chemical Society (1959), 2865-71.

Scheme 1



The compounds of formula III, wherein R_1a, R_1b, R_1c and R_1d as described under formula I above and wherein R is a C_1-C_4 alkyl, can be prepared from compounds of formula II1 wherein R_1a, R_1b, R_1c and R_1d are as described in formula I, via alkylation of compound II1 with compound of formula IV1 wherein R is a C_1-C_4 alkyl, in presence of a base, such as lithium amide, in a appropriate solvent such as for example toluene, to generate a compound of formula III at temperatures between -20 and 150°C, preferably between 20°C and 130°C. . These methods are known to those skilled in the art and described in, for example, in JACS (1951), 5467-5469.

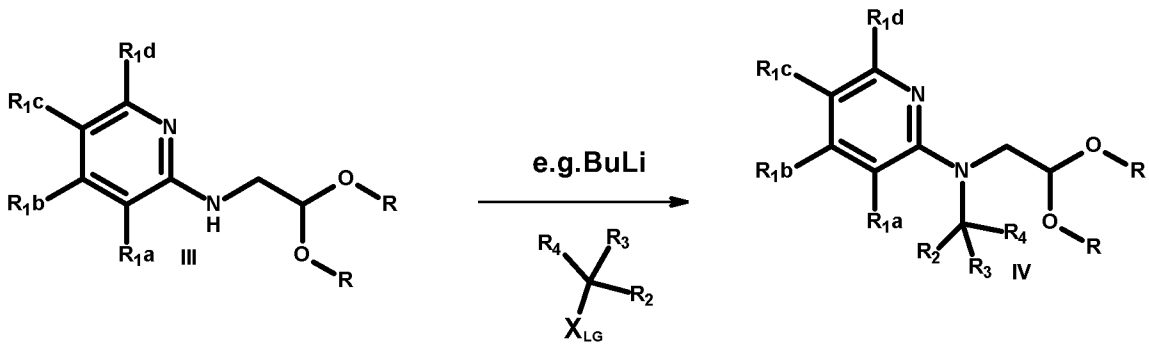
Alternatively, the compound of formula III, wherein R_1a, R_1b, R_1c, R_1d are as described under formula I above and wherein R is a C_1-C_4 alkyl, can be prepared from compounds of formula II2 via palladium coupling (Buchwald-Hartwig cross coupling), which involves for example, reacting

compounds of formula II2, wherein R_1a, R_1b, R_1c and R_1d are as described in formula I and wherein X is a leaving group, for example, chlorine, bromine or iodine with, for example, compounds of formula IV2 wherein R is a C_1-C_4 alkyl. The reaction can be catalyzed by a palladium based catalyst, for example palladium acetate, in presence of a base, like cesium carbonate or sodium tert-butoxide, in a solvent or a solvent mixture, like, for example toluene, preferably under inert atmosphere and in presence of chelating phosphine such as BINAP or Xamtphos. The reaction temperature can preferentially range from ambient temperature to the boiling point of the reaction mixture. Such Buchwald-Hartwig cross coupling are well known to those skilled in the art, many variation are described in literature and have been reviewed, for example in Strategic Applications of Named Reactions in Organic Synthesis (Kurti, Laszlo, Czako, Barbara, Editors. Ed. ELSEVIER) 2005, p70 and cited references, Modern Tools for the Synthesis of Complex Bioactive Molecules (Chapter 3: Metal-catalyzed C-heteroatom cross-coupling reactions) 2012, p.77-109. See for example European Journal of Medicinal Chemistry, 109, 294-304, 2016.

Alternatively, compounds of formula III, wherein R_1a, R_1b, R_1c and R_1d are as defined in formula I above, and R is a C_1-C_4 alkyl) can be prepared by nucleophile substitution which involves for example, reaction of compounds of formula II2, wherein X is a leaving group, for example, fluorine with compounds of formula IV2 wherein R is a C_1-C_4 alkyl, under basic condition or not, with or without solvent, via heating or under microwave irradiation (see for example WO2016029146 or Journal of the Chemical Society, Perkin T 1 Organic and Bio-Organic Chemistry 1980, p 132).

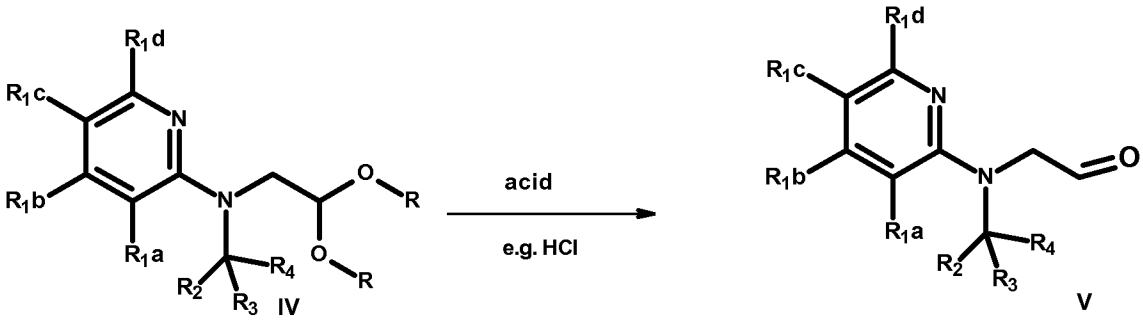
Other alternatives are possible and well known to those skilled in the art and described in, see for example Tetrahedron 64 (2008) 10798–1080.

Scheme 2



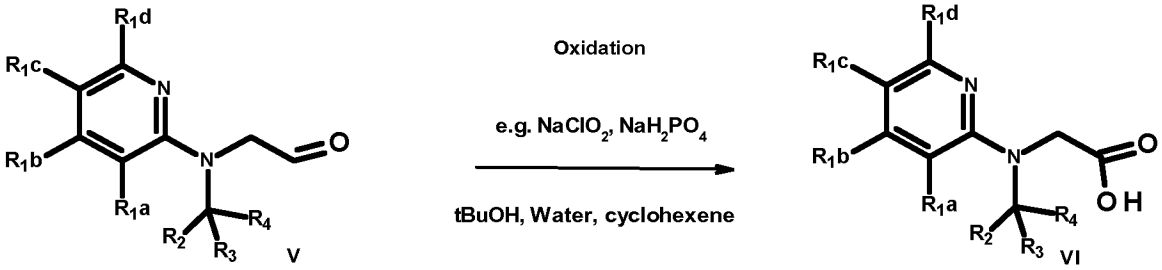
The preparation of compounds of formula IV, wherein R_1a, R_1b, R_1c, R_1d, R_2, R_3 and R_4 are as described under formula I above and R is C_1-C_4 alkyl from compounds of formula III wherein R_1a, R_1b, R_1c and R_1d are as described under formula I above and R is C_1-C_4 alkyl, may involve (scheme 2) alkylation of compound III with $R_2R_3R_4C$-X_{LG} wherein R_2, R_3 and R_4 are as described under formula I above and wherein X_{LG} is a leaving group, such as a halogen, preferably iodine, bromine or chlorine, in presence of a base, such as butyllithium or sodium hydride, in a appropriate solvent such as for example tetrahydrofuran, N,N-dimethylformamide, N,N-dimethylacetamide or acetonitrile, at temperatures between -78°C and 150°C, preferably between -78°C and 50°C.

Scheme 3



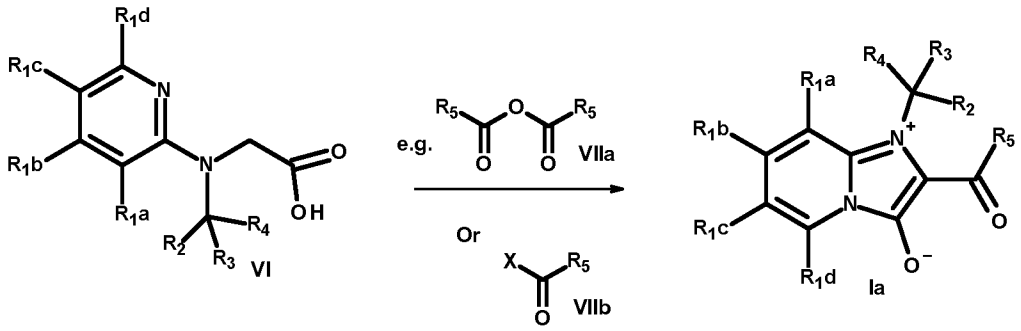
The preparation of compounds of formula V wherein R_1a, R_1b, R_1c, R_1d, R_2, R_3 and R_4 are as described under formula I above, from compounds of formula IV wherein R_1a, R_1b, R_1c and R_1d are as described under formula I above and R is C_1-C_4 alkyl, may involve (scheme 3) cleavage of the acetal group to aldehyde in presence of an acid, such as hydrochloric acid or trifluoroacetic acid in a appropriate solvent such as for example water or acetone, at temperatures between -20 and 100°C, preferably between 0°C and 80°C. Such transformations are known from the literature and will be recognize to those skilled in the art, for example the conditions described in Protective groups in organic synthesis (third edition, Theodora W. Greene, Peter G. M. Wuts 1999) p299.

Scheme 4



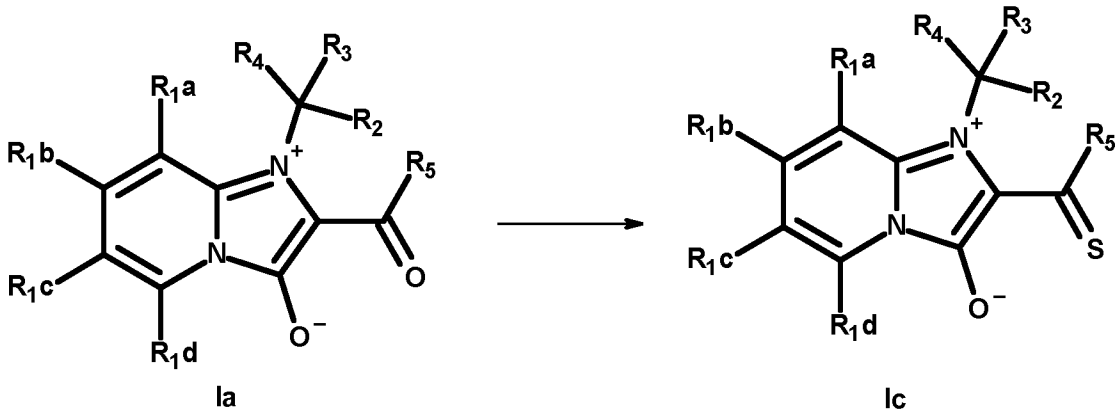
Compounds of the formula V, wherein R_1a, R_1b, R_1c, R_1d, R_2, R_3 and R_4 are as described under formula I above, can be oxidized to their corresponding acid VI under standard conditions (scheme 4). For example, with sodium chlorite in presence of sodium dihydrogenphosphate and cyclohexene in mixture of terbutanol, water at temperatures between 0°C and refluxing conditions, or alternatively by using a suitable oxidizing agent, such oxidations are known from the literature and will be recognize to those skilled in the art, for example the conditions described in Comprehensive Organic Transformations: A Guide to Functional Group Preparations. Edited by Richard C. Larock 1989 p 838, VCH publishers could be apply for this transformation.

Scheme 5



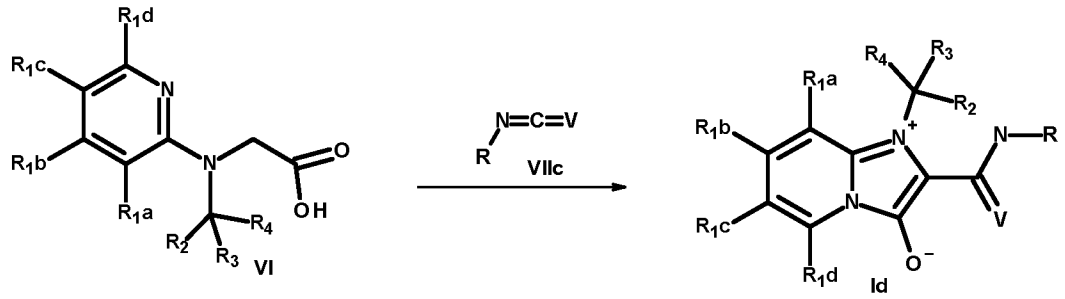
The preparation of compounds of formula Ia wherein R_1a, R_1b, R_1c, R_1d, R_2, R_3, R_4 and R_5 are as described under formula I above, from compounds of formula VI wherein R_1a, R_1b, R_1c, R_1d, R_2, R_3 and R_4 are as described under formula I above, may involve (scheme 5) cyclisation and acylation in presence of an anhydride VIIa or a acid halide VIIb wherein X is halogen such as fluoride and R_5 is as described under formula I above with or without solvent at temperatures between -20 and 140°C, preferably between 0°C and 80°C.

Scheme 6



Compounds of formula Ic, wherein V is S, can be prepared (scheme 6) by reacting compounds of formula Ia wherein V is O with a reagent that could transfer a sulphur atom such as, for example, the Lawesson's reagent in a solvent such as, for example dimethylformamide or toluene, usually at temperature between 50 to 150°C. This type of transformation is known to a person skilled in the art and are, for example, described in Heteroatom Chem. 2014, 25:548–555, Science of Synthesis 2004, 27, 215-243.

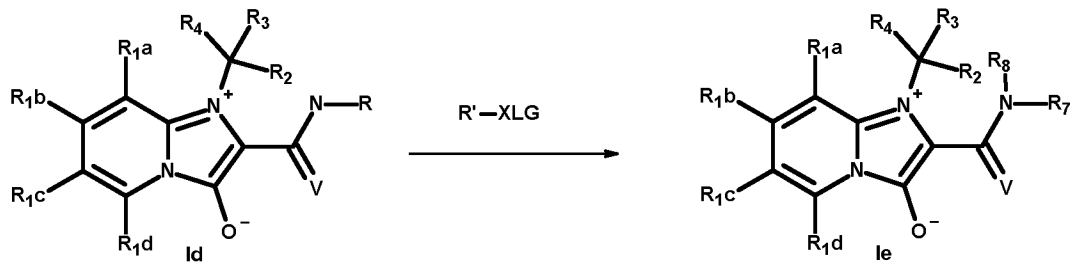
Scheme 7



Compounds of formula Id, wherein and R is R_7 or R_8, V is S or O, R_1a, R_1b, R_1c, R_1d, R_2, R_3 and R_4 are as described under formula I above, can be prepared (scheme 7) by reacting compounds of formula VI with a compound of formula VIIc wherein V is S or O and N-R is defined as NHR_7 or NHR_8 in formula I, in a solvent such as, for example acetonitrile, usually at temperature between -50 to 100°C, preferably between 20 to 100°C.

Compound of formula VIIc are known to the person skilled in the art and are commercialy available or could be made easely by the person skilled in the art, examples of theses type of preparation could be find in , for example, Chemical Reviews (Washington, DC, United States) (1948), 43, p 203-18, Chemical Reviews (Washington, DC, United States) (1957), 57, 47-76, Chem. Soc. Rev., 1974,3, 209-230 or Green Chemistry Letters and Reviews 2011, 4:1, 1-34.

Scheme 8



Compounds of formula Ie, wherein V is S or O, R_1a, R_1b, R_1c, R_1d, R_2, R_3, R_4, R_7 and R_8 are as described under formula I above, can be prepared (scheme 8) by reacting compounds of formula Id, wherein and R is R_7 or R_8, V is S or O, R_1a, R_1b, R_1c, R_1d, R_2, R_3 and R_4 are as described under formula I above, with a compound of formula R'-XLG, wherein R' is R_8 or R_7 as described under formula I above and XLG a leaving group, such as halogen, preferably iodine, bromine or chlorine, in presence of a base, such as sodium carbonate, potassium carbonate or cesium carbonate, or sodium hydride, in a appropriate solvent such as for example N,N-dimethylformamide, N,N-dimethylacetamide or acetonitrile, usually at temperature between -50 to 100°C, preferably between 20 to 100°C.

The reactants can be reacted in the presence of a base. Examples of suitable bases are alkali metal or alkaline earth metal hydroxides, alkali metal or alkaline earth metal hydrides, alkali metal or alkaline earth metal amides, alkali metal or alkaline earth metal alkoxides, alkali metal or alkaline earth metal acetates, alkali metal or alkaline earth metal carbonates, alkali metal or alkaline earth metal dialkylamides or alkali metal or alkaline earth metal alkylsilylamides, alkylamines, alkylenediamines, free or N-alkylated saturated or unsaturated cycloalkylamines, basic heterocycles, ammonium

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

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

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

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

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

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

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 tautomer's thereof, in each case in free form or in salt form, can be present in the form of one of the isomers which are possible or as a

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

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

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.

Compounds of formula I wherein V is S can be prepared by reacting a compound of the formula I wherein V is O with a suitable agent, for example the Lawesson reagent or diphosphorus pentasulfide in presence of a solvent or not such as dimethylformamide. Such reactions are known to the person skilled in the art and are described, for example, Tetrahedron, 63(48), 11862-11877, 2007, Inorganic Chemistry, 43(21), 6534-6536, 2004 or Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, Fourth Edition by Jerry March, **1992** (Publisher Wiley New York, N. Y.) pages 1184-1185.

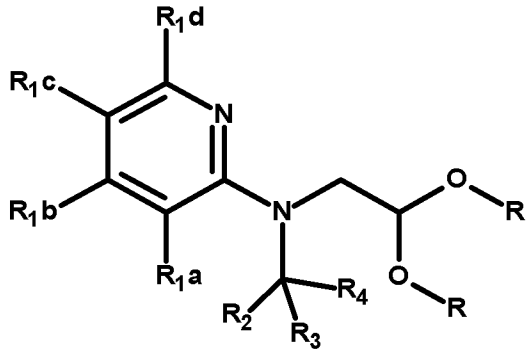
It is advantageous to isolate or synthesize in each case the biologically more effective isomer, for example enantiomer or diastereomer, or isomer mixture, for example enantiomer mixture or diastereomer mixture, if the individual components have a different biological activity.

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.

Certain intermediates used in the process are also novel.

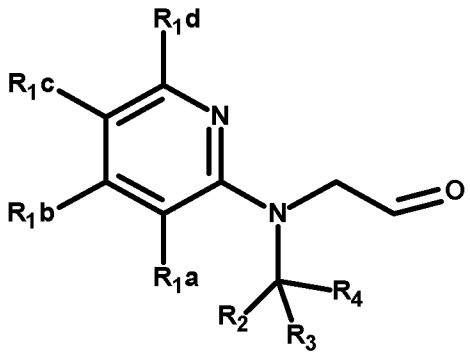
Accordingly in a further aspect, the present invention provides a compound of formula IV



(IV)

wherein R_{1a}, R_{1b}, R_{1c}, R_{1d}, R_2, and R_3 are as defined in formula I; and R_4 is a heteroaromatic ring Y selected from Y4, Y9 and Y12 substituted with a substituent from the group U, wherein n and U are as defined in formula I; and R is C_1-C_4 alkyl; and acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of the compounds of formula IV. Preferably R is methyl or ethyl.

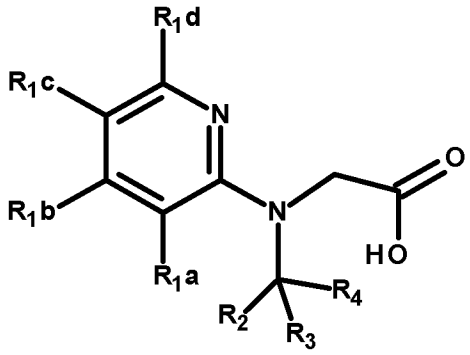
Accordingly in a further aspect, the present invention provides a compound of formula V



(V)

wherein R_{1a}, R_{1b}, R_{1c}, R_{1d}, R_2, and R_3 are as defined in formula I; and R_4 is a heteroaromatic ring Y selected from Y4, Y9 and Y12, substituted with a substituent from the group U, wherein n and U are as defined in formula I; and acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of the compounds of formula V.

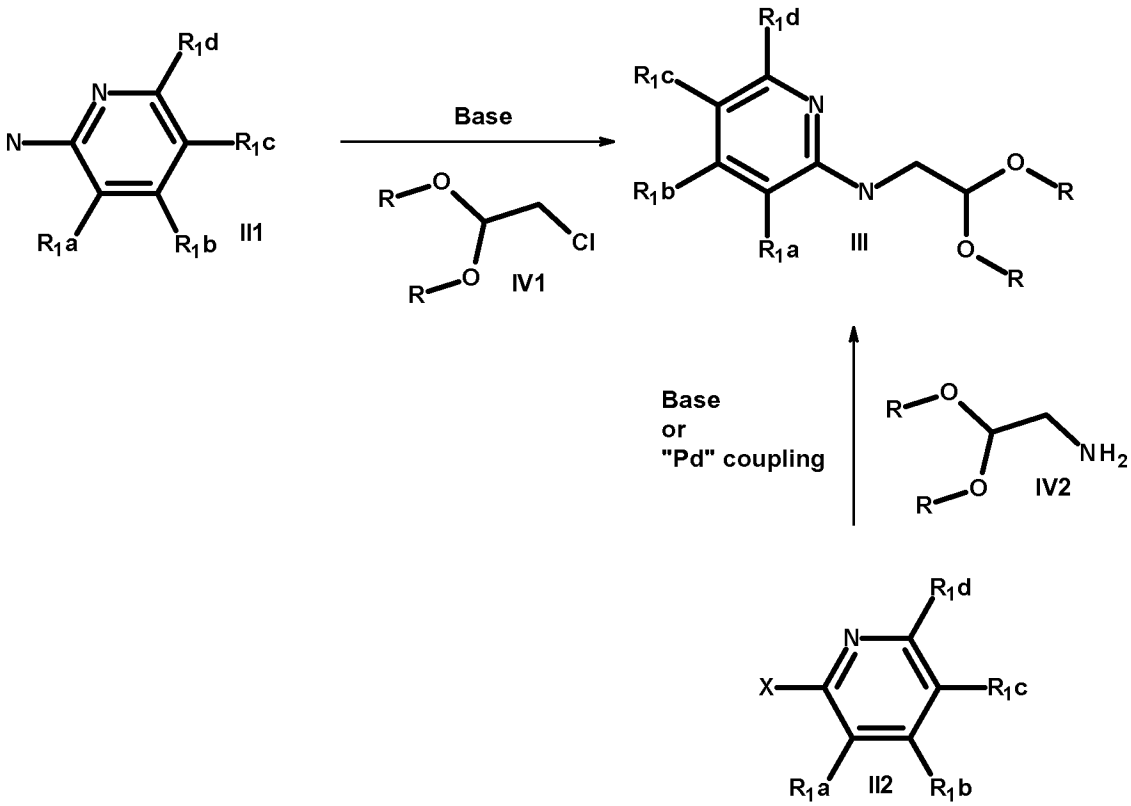
Accordingly in a further aspect, the present invention provides a compound of formula VI



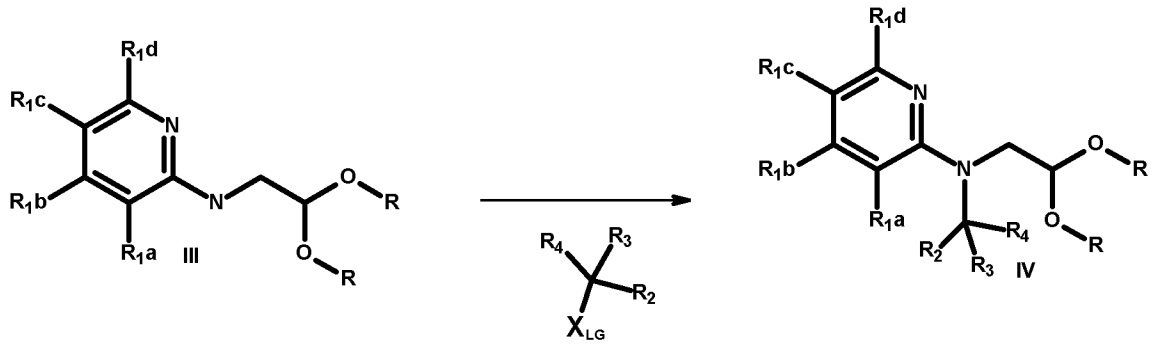
(VI)

wherein-R_{1a}, R_{1b}, R_{1c}, R_{1d}, R_2 and R_3 are as defined in formula I; and R_4 is a heteroaromatic ring Y selected from Y4, Y9 and Y12 substituted with a substituent from the group U, wherein n and U are as defined in formula I; and acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of the compounds of formula VI.

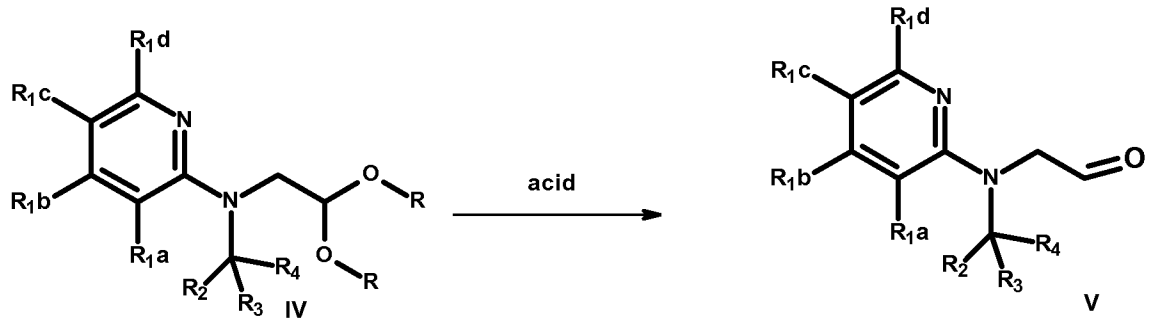
In a further aspect, the present invention makes available a process for preparing a compound of formula Ia, wherein (1) a compound of formula III is prepared from compound of formula II1 via alkylation with a compound of formula IV1, in presence of a base to generate a compound of formula III; or the compound of formula III is prepared from a compound of formula II2 via palladium coupling with a compound of formula IV2; or a compound of formula III is prepared by nucleophile substitution, in presence of a base, with a compound of formula IV2;



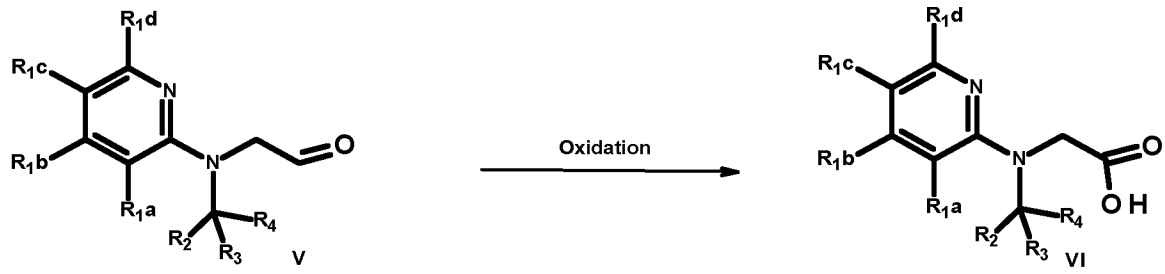
(2) a compound of formula IV is prepared from a compound of formula III by alkylation with $R_2R_3R_4C$-X_{LG};



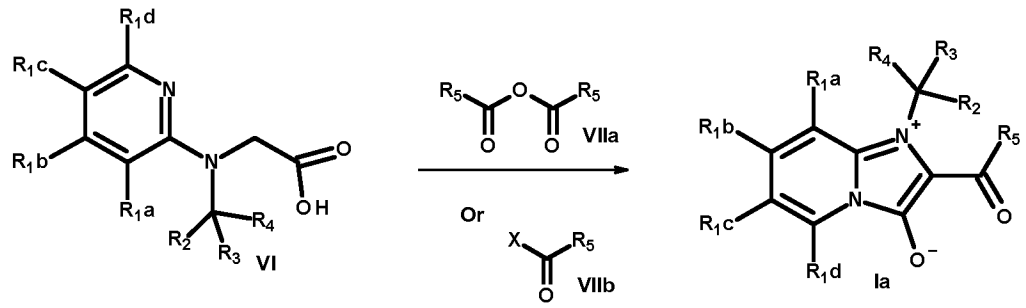
(3) a compound of formula V is prepared from a compound of formula IV by cleavage of the acetal group to aldehyde in presence of an acid;



(4) a compound of the formula V is oxidized to its corresponding acid of formula VI; and



(5) a compound of formula Ia is prepared from a compound of formula VI by cyclisation and acylation in presence of an anhydride of formula VIIa or acid halide of formula VIIb,



wherein R is C_1-C_4 alkyl; X_{LG} and X are independently of each other a leaving group; and R_{1a}, R_{1b}, R_{1c} and R_{1d}, R_2, R_3, R_4 and R_5 are as described for formula I herein.

The compounds according to the following Tables 1, 2, 3 and 4 below can be prepared according to the methods described herein. The compounds which follow are intended to illustrate the invention and show particularly preferred compounds of formula I, IVa, Va, and VIa. "Ph" represents the phenyl group.

Table 1: This table discloses 139 compounds of the formula I:

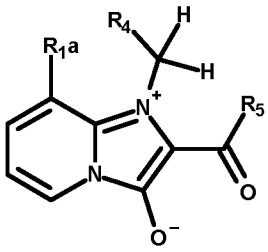
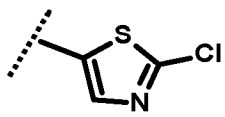
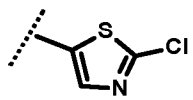
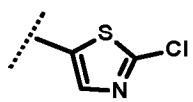
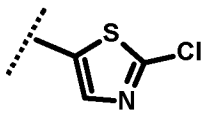
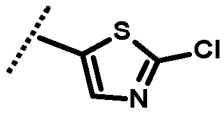
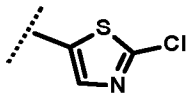
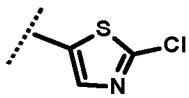
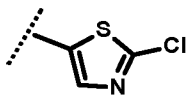
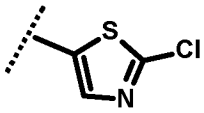
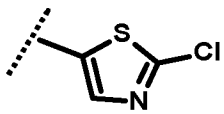
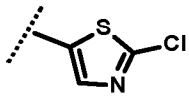
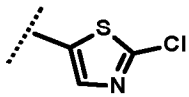
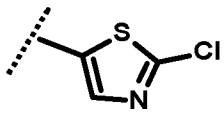
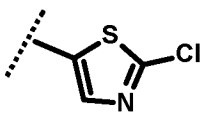
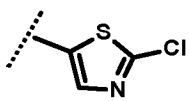
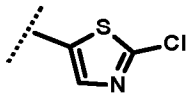
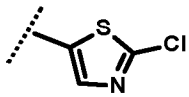
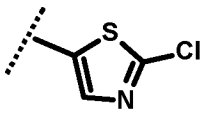
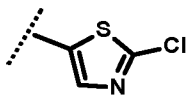
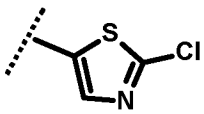
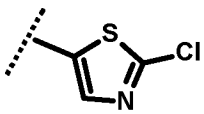
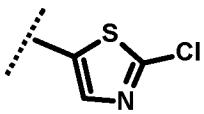
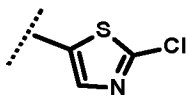
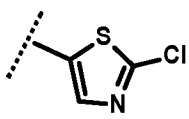
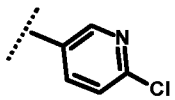
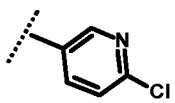
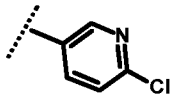
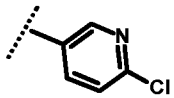
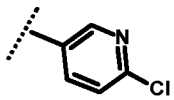
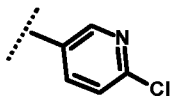
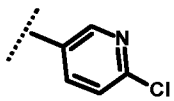
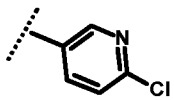
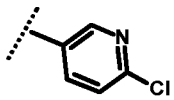
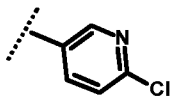
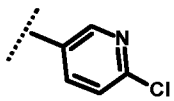
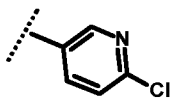
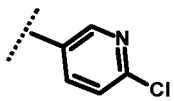
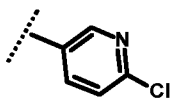

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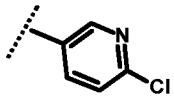
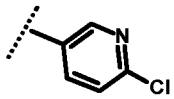
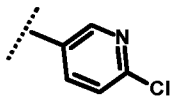
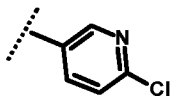
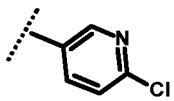
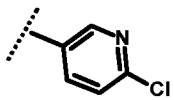
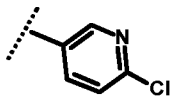
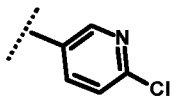
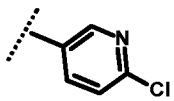
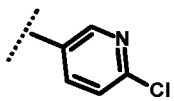
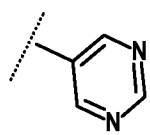
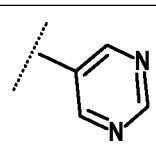
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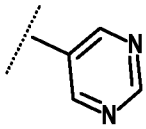
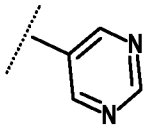
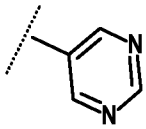
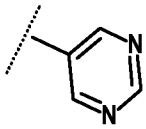
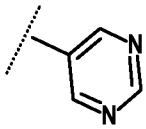
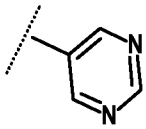
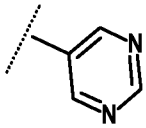
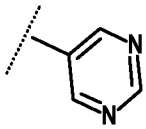
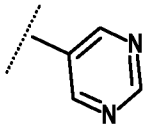
Comp. No.	R_{1a}	R_2	R_4	R_5
1.001	H	H		Phenyl
1.002	H	H		-CH_2Ph
1.003	H	H		3-Cl-Phenyl
1.004	H	H		3,5-diCl-Phenyl

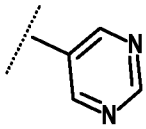
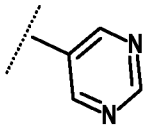
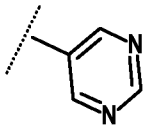
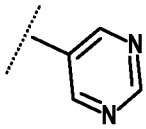
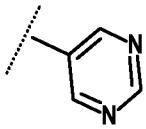
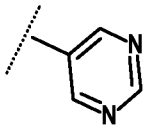
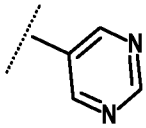
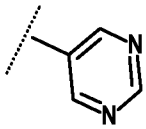
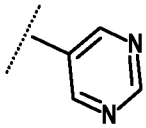
Comp. No.	R_{1a}	R_2	R_4	R_5
1.005	H	H		$-CF_3$
1.006	H	H		$-CF_2CF_3$
1.007	H	H		CH_3
1.008	H	H		3-Br-Phenyl
1.009	H	H		4-F-Phenyl
1.010	H	H		4-Cl-Phenyl
1.011	H	H		Thiophenyl-2
1.012	H	H		Thiophenyl-3
1.013	CH_3	H		Phenyl
1.014	CH_3	H		$-CH_2Ph$
1.015	CH_3	H		3-Cl-Phenyl

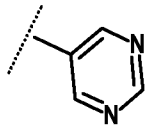
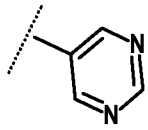
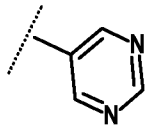
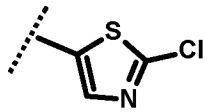
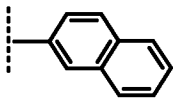
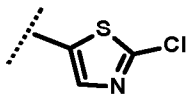
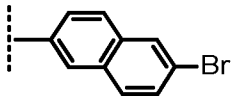
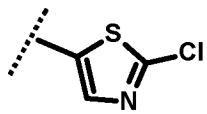
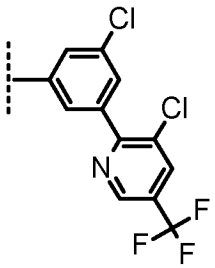
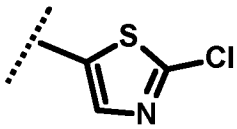
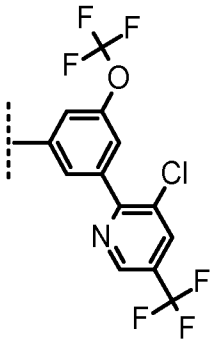
Comp. No.	R_{1a}	R_2	R_4	R_5
1.016	CH_3	H		3,5-diCl-Phenyl
1.017	CH_3	H		$-CF_3$
1.018	CH_3	H		$-CF_2CF_3$
1.019	CH_3	H		CH_3
1.020	CH_3	H		3-Br-Phenyl
1.021	CH_3	H		4-F-Phenyl
1.022	CH_3	H		4-Cl-Phenyl
1.023	CH_3	H		Thiophenyl-2
1.024	CH_3	H		Thiophenyl-3
1.025	H	H		Phenyl
1.026	H	H		$-CH_2Ph$

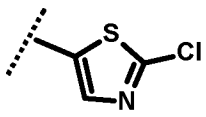
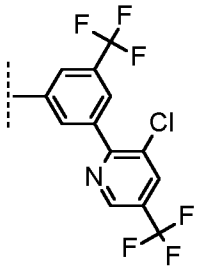
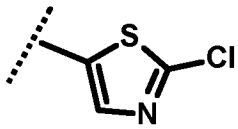
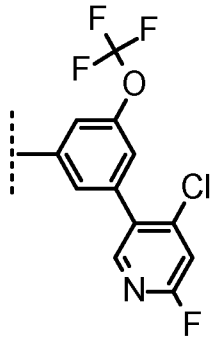
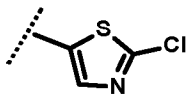
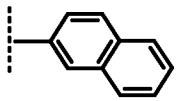
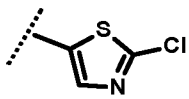
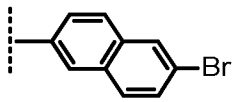
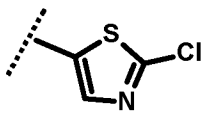
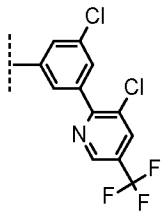
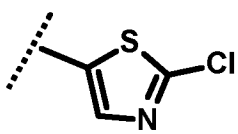
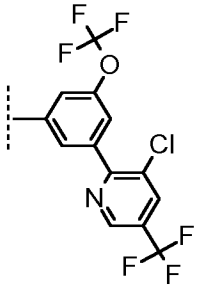
Comp. No.	R_{1a}	R_2	R_4	R_5
1.027	H	H		3-Cl-Phenyl
1.028	H	H		3,5-diCl-Phenyl
1.029	H	H		$-CF_3$
1.030	H	H		$-CF_2CF_3$
1.031	H	H		CH_3
1.032	H	H		3-Br-Phenyl
1.033	H	H		4-F-Phenyl
1.034	H	H		4-Cl-Phenyl
1.035	H	H		Thiophenyl-2
1.036	H	H		Thiophenyl-3
1.037	CH_3	H		Phenyl
1.038	CH_3	H		$-CH_2Ph$

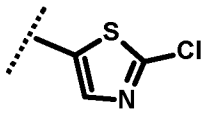
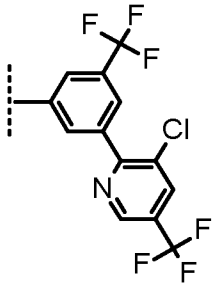
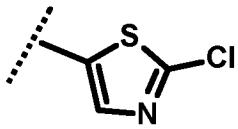
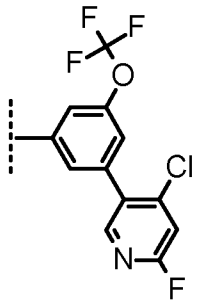
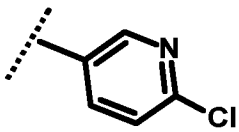
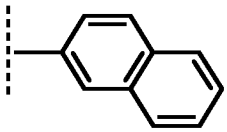
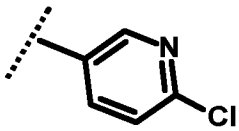
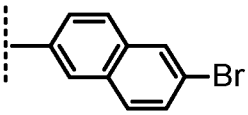
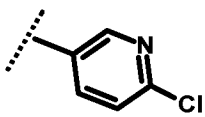
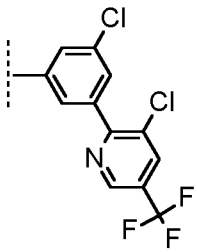
Comp. No.	R_{1a}	R_2	R_4	R_5
1.039	CH_3	H		3-Cl-Phenyl
1.040	CH_3	H		3,5-diCl-Phenyl
1.041	CH_3	H		$-CF_3$
1.042	CH_3	H		$-CF_2CF_3$
1.043	CH_3	H		CH_3
1.044	CH_3	H		3-Br-Phenyl
1.045	CH_3	H		4-F-Phenyl
1.046	CH_3	H		4-Cl-Phenyl
1.047	CH_3	H		Thiophenyl-2
1.048	CH_3	H		Thiophenyl-3
1.049	H	H		Phenyl
1.050	H	H		$-CH_2Ph$

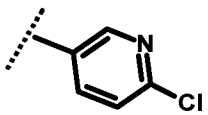
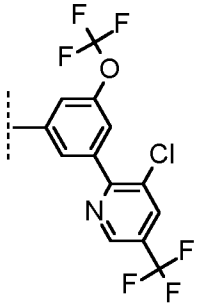
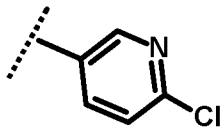
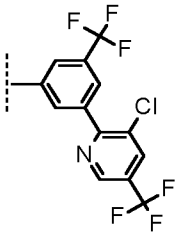
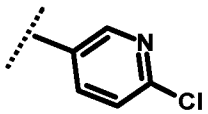
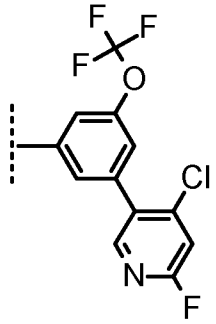
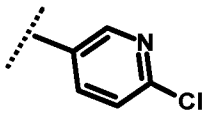
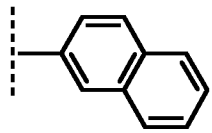
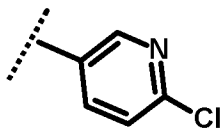
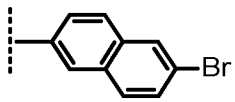
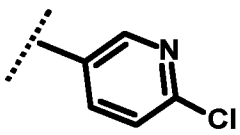
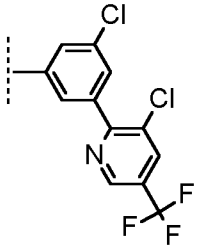
Comp. No.	R_{1a}	R_2	R_4	R_5
1.051	H	H		3-Cl-Phenyl
1.052	H	H		3,5-diCl-Phenyl
1.053	H	H		$-CF_3$
1.054	H	H		$-CF_2CF_3$
1.055	H	H		CH_3
1.056	H	H		3-Br-Phenyl
1.057	H	H		4-F-Phenyl
1.058	H	H		4-Cl-Phenyl
1.059	H	H		Thiophenyl-2

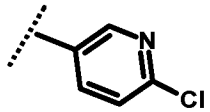
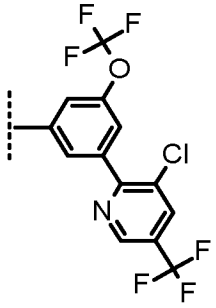
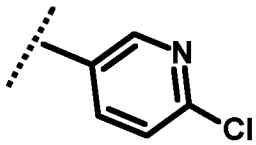
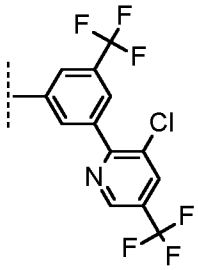
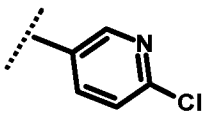
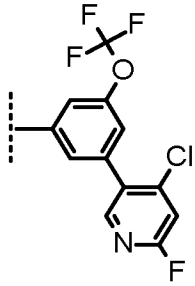
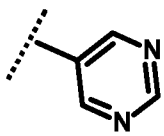
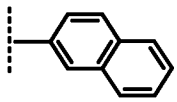
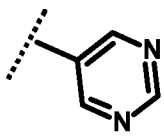
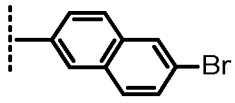
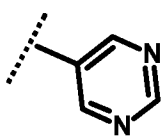
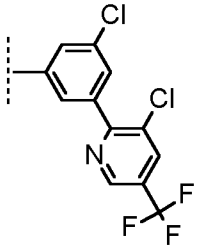
Comp. No.	R_{1a}	R_2	R_4	R_5
1.060	H	H		Thiophenyl-3
1.061	CH_3	H		Phenyl
1.062	CH_3	H		$-CH_2Ph$
1.063	CH_3	H		3-Cl-Phenyl
1.064	CH_3	H		3,5-diCl-Phenyl
1.065	CH_3	H		$-CF_3$
1.066	CH_3	H		$-CF_2CF_3$
1.067	CH_3	H		CH_3
1.068	CH_3	H		3-Br-Phenyl

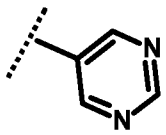
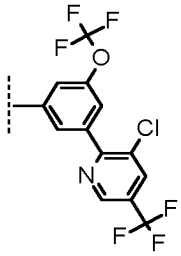
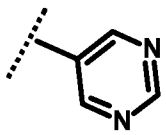
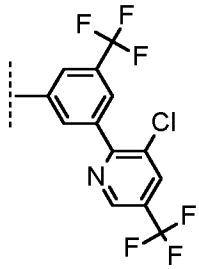
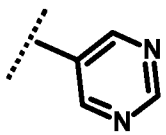
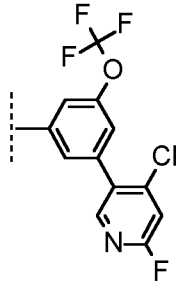
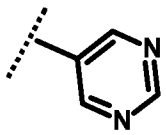
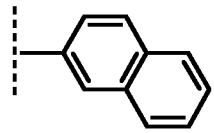
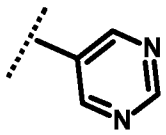
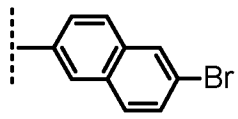
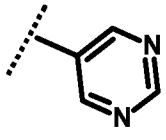
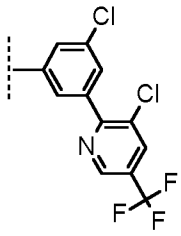
Comp. No.	R_{1a}	R_2	R_4	R_5
1.069	CH_3	H		4-F-Phenyl
1.070	CH_3	H		4-Cl-Phenyl
1.071	CH_3	H		Thiophenyl-2
1.072	H	H		
1.073	H	H		
1.074	H	H		
1.075	H	H		

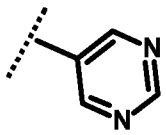
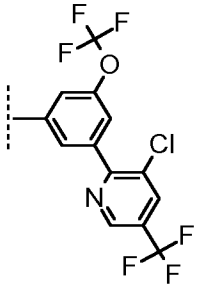
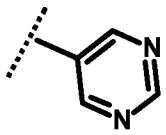
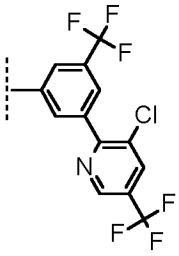
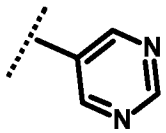
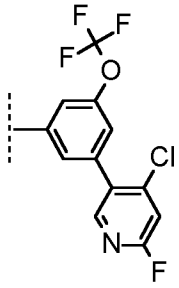
Comp. No.	R_{1a}	R_2	R_4	R_5
1.076	H	H		
1.077	H	H		
1.078	CH_3	H		
1.079	CH_3	H		
1.080	CH_3	H		
1.081	CH_3	H		

Comp. No.	R_{1a}	R_2	R_4	R_5
1.082	CH_3	H		
1.083	CH_3	H		
1.084	H	H		
1.085	H	H		
1.086	H	H		

Comp. No.	R_{1a}	R_2	R_4	R_5
1.087	H	H		
1.088	H	H		
1.089	H	H		
1.090	CH_3	H		
1.091	CH_3	H		
1.092	CH_3	H		

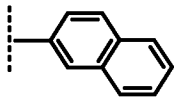
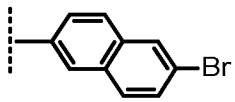
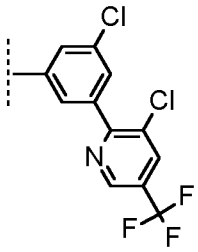
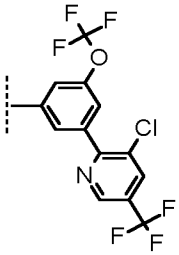
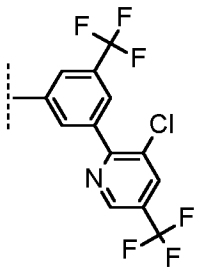
Comp. No.	R_{1a}	R_2	R_4	R_5
1.093	CH_3	H		
1.094	CH_3	H		
1.095	CH_3	H		
1.096	H	H		
1.097	H	H		
1.098	H	H		

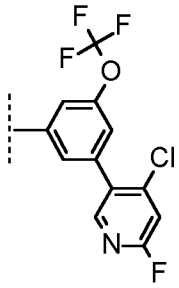
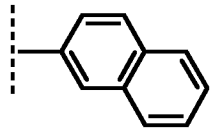
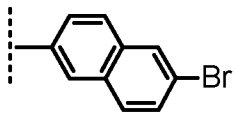
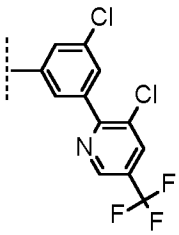
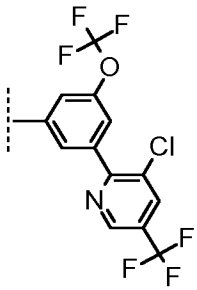
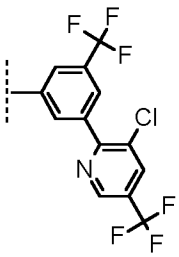
Comp. No.	R_{1a}	R_2	R_4	R_5
1.099	H	H		
1.100	H	H		
1.101	H	H		
1.102	CH_3	H		
1.103	CH_3	H		
1.104	CH_3	H		

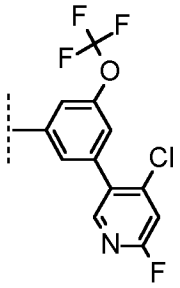
Comp. No.	R_{1a}	R_2	R_4	R_5
1.105	CH_3	H		
1.106	CH_3	H		
1.107	CH_3	H		
1.108	H		H	$-CF_3$
1.109	H		H	$-CF_2CF_3$
1.110	H		H	CH_3

Comp. No.	R_{1a}	R_2	R_4	R_5
1.111	H		H	3-Br-Phenyl
1.112	H		H	4-F-Phenyl
1.113	H		H	4-Cl-Phenyl
1.114	H		H	Thiophenyl-2
1.115	H		H	Thiophenyl-3
1.116	H		H	Phenyl
1.117	H		H	$-CH_2Ph$
1.118	H		H	3-Cl-Phenyl

Comp. No.	R_{1a}	R_2	R_4	R_5
1.119	H		H	3,5-diCl-Phenyl
1.120	CH_3		H	$-CF_3$
1.121	CH_3		H	$-CF_2CF_3$
1.122	CH_3		H	CH_3
1.123	CH_3		H	3-Br-Phenyl
1.124	CH_3		H	4-F-Phenyl
1.125	CH_3		H	4-Cl-Phenyl
1.126	CH_3		H	Thiophenyl-2

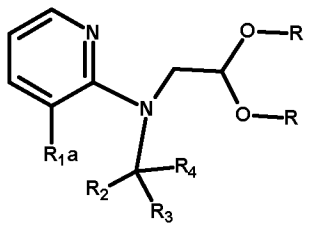
Comp. No.	R_{1a}	R_2	R_4	R_5
1.127	CH_3		H	Thiophenyl-3
1.128	H		H	
1.129	H		H	
1.130	H		H	
1.131	H		H	
1.132	H		H	

Comp. No.	R_{1a}	R_2	R_4	R_5
1.133	H		H	
1.134	CH_3		H	
1.135	CH_3		H	
1.136	CH_3		H	
1.137	CH_3		H	
1.138	CH_3		H	

Comp. No.	R_{1a}	R_2	R_4	R_5
1.139	CH_3		H	

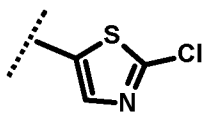
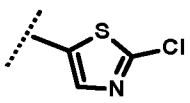
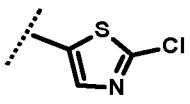
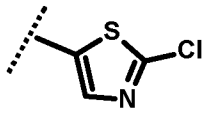
and the N-oxides of the compounds of Table 1.

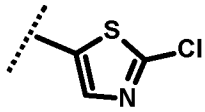
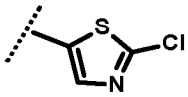
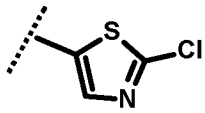
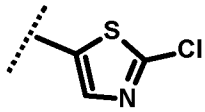
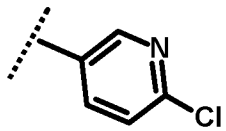
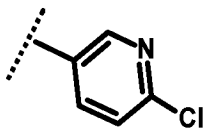
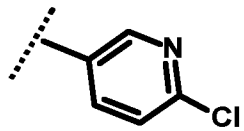
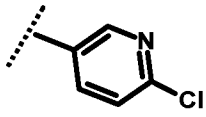
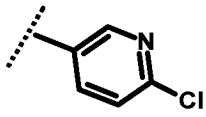
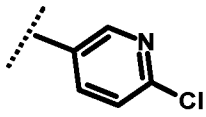
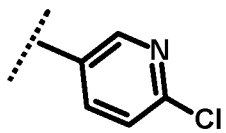
Table 2: This table discloses 32 compounds of intermediates of formula (IVa) :

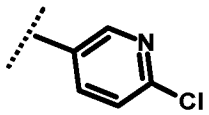
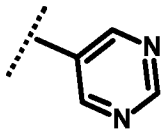
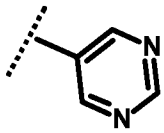
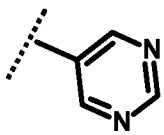
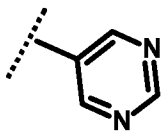
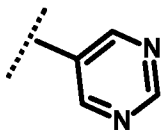
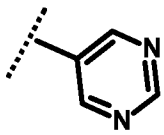
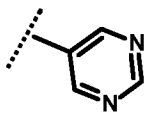
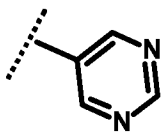


(IVa)

Table 2:

Comp. No.	R_{1a}	R_4	R_2	R_3	R
2.001	H		H	H	CH_3
2.002	CH_3		H	H	CH_3
2.003	H		H	H	CH_2CH_3
2.004	CH_3		H	H	CH_2CH_3

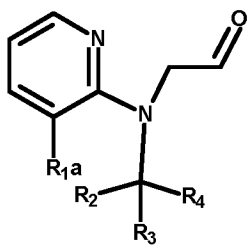
Comp. No.	R_{1a}	R_4	R_2	R_3	R
2.005	CF_3		H	H	CH_3
2.006	CF_3		H	H	CH_2CH_3
2.007	OCH_3		H	H	CH_3
2.008	OCH_3		H	H	CH_2CH_3
2.009	H		H	H	CH_3
2.010	CH_3		H	H	CH_3
2.011	H		H	H	CH_2CH_3
2.012	CH_3		H	H	CH_2CH_3
2.013	CF_3		H	H	CH_3
2.014	CF_3		H	H	CH_2CH_3
2.015	OCH_3		H	H	CH_3

Comp. No.	R_{1a}	R_4	R_2	R_3	R
2.016	OCH_3		H	H	CH_2CH_3
2.017	H		H	H	CH_3
2.018	CH_3		H	H	CH_3
2.019	H		H	H	CH_2CH_3
2.020	CH_3		H	H	CH_2CH_3
2.021	CF_3		H	H	CH_3
2.022	CF_3		H	H	CH_2CH_3
2.023	OCH_3		H	H	CH_3
2.024	OCH_3		H	H	CH_2CH_3
2.025	H	H		H	CH_3

Comp. No.	R_{1a}	R_4	R_2	R_3	R
2.026	CH_3	H		H	CH_3
2.027	H	H		H	CH_2CH_3
2.028	CH_3	H		H	CH_2CH_3
2.029	CF_3	H		H	CH_3
2.030	CF_3	H		H	CH_2CH_3
2.031	OCH_3	H		H	CH_3
2.032	OCH_3	H		H	CH_2CH_3

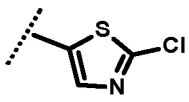
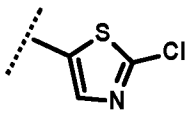
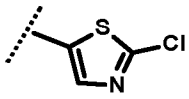
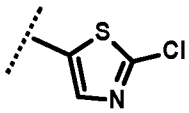
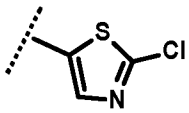
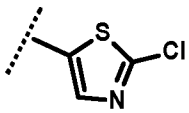
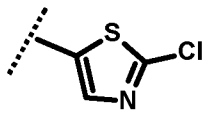
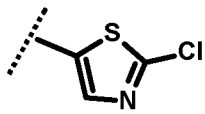
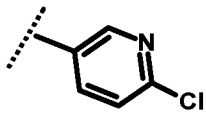
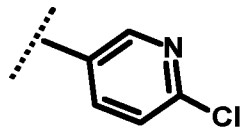
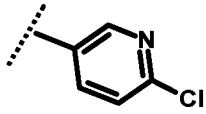
and the N-oxides of the compounds of Table 2.

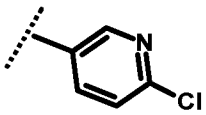
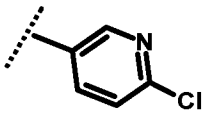
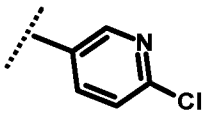
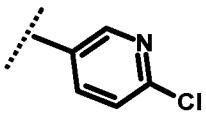
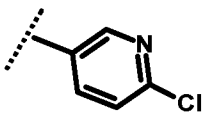
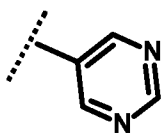
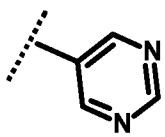
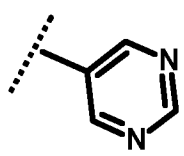
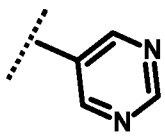
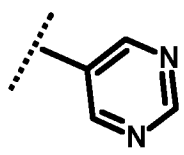
Table 3: This table discloses 32 compounds of intermediates of formula (Va):

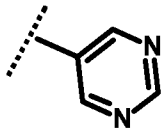
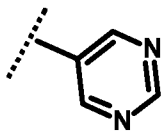
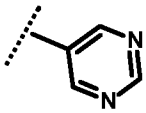


(Va)

Table 3:

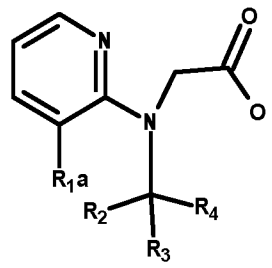
Comp. No.	R_{1a}	R_4	R_2	R_3
3.001	H		H	H
3.002	CH_3		H	H
3.003	H		H	H
3.004	CH_3		H	H
3.005	CF_3		H	H
3.006	CF_3		H	H
3.007	OCH_3		H	H
3.008	OCH_3		H	H
3.009	H		H	H
3.010	CH_3		H	H
3.011	H		H	H

Comp. No.	R_{1a}	R_4	R_2	R_3
3.012	CH_3		H	H
3.013	CF_3		H	H
3.014	CF_3		H	H
3.015	OCH_3		H	H
3.016	OCH_3		H	H
3.017	H		H	H
3.018	CH_3		H	H
3.019	H		H	H
3.020	CH_3		H	H
3.021	CF_3		H	H

Comp. No.	R_{1a}	R_4	R_2	R_3
3.022	CF_3		H	H
3.023	OCH_3		H	H
3.024	OCH_3		H	H
3.025	H	H		H
3.026	CH_3	H		H
3.027	H	H		H
3.028	CH_3	H		H
3.029	CF_3	H		H
3.030	CF_3	H		H
3.031	OCH_3	H		H
3.032	OCH_3	H		H

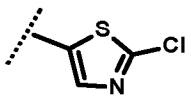
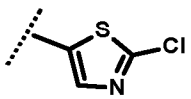
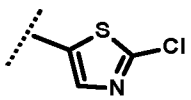
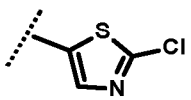
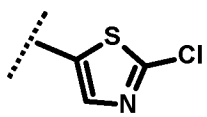
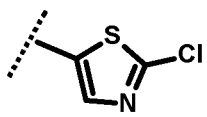
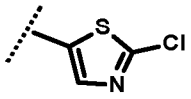
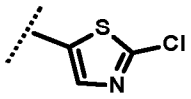
and the N-oxides of the compounds of Table 3.

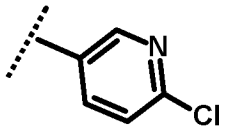
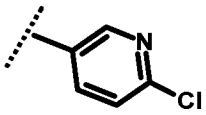
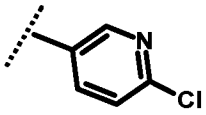
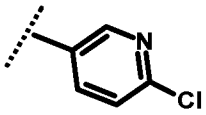
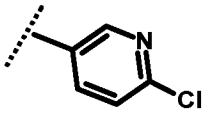
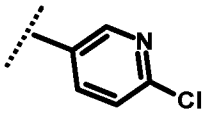
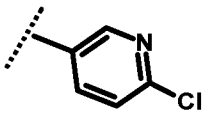
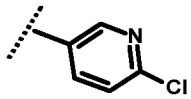
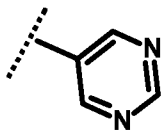
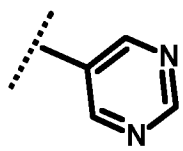
Table 4: This table discloses 32 compounds of intermediates of formula (VIa):

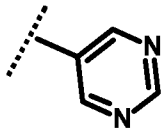
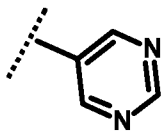
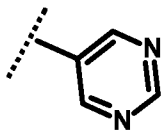
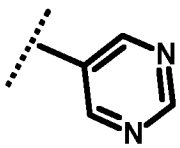
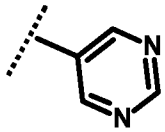
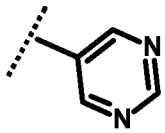


(VIa)

Table 4:

Comp. No.	R_{1a}	R_4	R_2	R_3
4.001	H		H	H
4.002	CH_3		H	H
4.003	H		H	H
4.004	CH_3		H	H
4.005	CF_3		H	H
4.006	CF_3		H	H
4.007	OCH_3		H	H
4.008	OCH_3		H	H

Comp. No.	R_{1a}	R_4	R_2	R_3
4.009	H		H	H
4.010	CH_3		H	H
4.011	H		H	H
4.012	CH_3		H	H
4.013	CF_3		H	H
4.014	CF_3		H	H
4.015	OCH_3		H	H
4.016	OCH_3		H	H
4.017	H		H	H
4.018	CH_3		H	H

Comp. No.	R_{1a}	R_4	R_2	R_3
4.019	H		H	H
4.020	CH_3		H	H
4.021	CF_3		H	H
4.022	CF_3		H	H
4.023	OCH_3		H	H
4.024	OCH_3		H	H
4.025	H	H		H
4.026	CH_3	H		H
4.027	H	H		H
4.028	CH_3	H		H

Comp. No.	R_{1a}	R_4	R_2	R_3
4.029	CF_3	H		H
4.030	CF_3	H		H
4.031	OCH_3	H		H
4.032	OCH_3	H		H

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

The compounds of formula I (including compounds of formula Ia and Ib) 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 compounds of formula I are safe towards non-target species, such as bees, and accordingly have a good toxicity profile. The active ingredients according to the invention act against all or individual developmental stages of normally sensitive, but also resistant, animal pests, such as insects or representatives of the order Acarina. The insecticidal or acaricidal activity of the active ingredients according to the invention can manifest itself directly, i. e. in destruction of the pests, which takes place either immediately or only after some time has elapsed, for example during ecdysis, or indirectly, for example in a reduced oviposition and/or hatching rate.

Examples of the abovementioned animal pests are:

from the order *Acarina*, for example,

Acalitus spp, Aculus spp, Acaricalus spp, Aceria spp, Acarus siro, Amblyomma spp., Argas spp., Boophilus spp., Brevipalpus spp., Bryobia spp, Calipitrimerus spp., Chorioptes spp., Dermanyssus gallinae, Dermatophagoides spp, Eotetranychus spp, Eriophyes spp., Hemitarsonemus spp, Hyalomma spp., Ixodes spp., Olygonychus spp, Ornithodoros spp., Polyphagotarsone latus, Panonychus spp., Phyllocoptruta oleivora, Phytonemus spp, Polyphagotarsonemus spp, Psoroptes spp., Rhipicephalus spp., Rhizoglyphus spp., Sarcoptes spp., Steneotarsonemus spp, Tarsonemus spp. and Tetranychus spp.,

from the order *Anoplura*, for example,

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

from the order *Coleoptera*, for example,

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

from the order *Diptera,* for example,

Aedes spp., Anopheles spp, Antherigona soccata,Bactrocea oleae, Bibio hortulanus, Bradysia spp, Calliphora erythrocephala, Ceratitis spp., Chrysomyia spp., Culex spp., Cuterebra spp., Dacus spp., Delia spp, Drosophila melanogaster, Fannia spp., Gastrophilus spp., Geomyza tripunctata, Glossina spp., Hypoderma spp., Hyppobosca spp., Liriomyza spp., Lucilia spp., Melanagromyza spp., Musca spp., Oestrus spp., Orseolia spp., Oscinella frit, Pegomyia hyoscyami, Phorbia spp., Rhagoletis spp, Rivelia quadrifasciata, Scatella spp, Sciara spp., Stomoxys spp., Tabanus spp., Tannia spp. and Tipula spp.,

from the order *Hemiptera,* for example,

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

Acyrthosium pisum, Adalges spp, Agalliana ensigera, Agonoscena targionii, Aleurodicus spp, Aleurocanthus spp, Aleurolobus barodensis, Aleurothrixus floccosus, Aleyrodes brassicae, Amarasca biguttula, Amritodus atkinsoni, Aonidiella spp., Aphididae, Aphis spp., Aspidiotus spp., Aulacorthum solani, Bactericera cockerelli, Bemisia spp, Brachycaudus spp, Brevicoryne brassicae, Cacopsylla spp, Cavariella aegopodii Scop., Ceroplaster spp., Chrysomphalus aonidium, Chrysomphalus dictyospermi, Cicadella spp, Cofana spectra, Cryptomyzus spp, Cicadulina spp, Coccus hesperidum, Dalbulus maidis, Dialeurodes spp, Diaphorina citri, Diuraphis noxia, Dysaphis spp, Empoasca spp., Eriosoma larigerum, Erythroneura spp., Gascardia spp., Glycaspis brimblecombei, Hyadaphis pseudobrassicae, Hyalopterus spp, Hyperomyzus pallidus, Idioscopus clypealis, Jacobiasca lybica, Laodelphax spp., Lecanium corni, Lepidosaphes spp., Lopaphis erysimi, Lyogenys maidis, Macrosiphum spp., Mahanarva spp, Metcalfa pruinosa, Metopolophium dirhodum, Myndus crudus, Myzus spp., Neotoxoptera sp, Nephotettix spp., Nilaparvata spp., Nippolachnus piri Mats, Odonaspis ruthae, Oregma lanigera Zehnter, Parabemisia myricae, Paratrioza cockerelli, Parlatoria spp.,

Pemphigus spp., Peregrinus maidis, Perkinsiella spp, Phorodon humuli, Phylloxera spp, Planococcus spp., Pseudaulacaspis spp., Pseudococcus spp., Pseudatomoscelis seriatus, Psylla spp., Pulvinaria aethiopica, Quadraspidiotus spp., Quesada gigas, Recilia dorsalis, Rhopalosiphum spp., Saissetia spp., Scaphoideus spp., Schizaphis spp., Sitobion spp., Sogatella furcifera, Spissistilus festinus, Tarophagus Proserpina, Toxoptera spp, Trialeurodes spp, Tridiscus sporoboli, Trionymus spp, Trioza erytreae , Unaspis citri, Zygina flammigera, Zyginidia scutellaris,

from the order *Hymenoptera*, for example,

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

from the order *Isoptera*, for example,

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

from the order *Lepidoptera*, for example,

Acleris spp., Adoxophyes spp., Aegeria spp., Agrotis spp., Alabama argillaceae, Amylois spp., Anticarsia gemmatalis, Archips spp., Argyresthia spp, Argyrotaenia spp., Autographa spp., Bucculatrix thurberiella, Busseola fusca, Cadra cautella, Carposina nipponensis, Chilo spp., Choristoneura spp., Chrysoteuchia topiaria, Clysia ambiguella, Cnaphalocrocis spp., Cnephasia spp., Cochylis spp., Coleophora spp., Colias lesbia, Cosmophila flava, Crambus spp, Crocidolomia binotalis, Cryptophlebia leucotreta, Cydalima perspectalis, Cydia spp., Diaphania perspectalis, Diatraea spp., Diparopsis castanea, Earias spp., Eldana saccharina, Ephestia spp., Epinotia spp, Estigmene acrea, Etiella zinckinella, Eucosma spp., Eupoecilia ambiguella, Euproctis spp., Euxoa spp., Feltia jaculiferia, Grapholita spp., Hedya nubiferana, Heliothis spp., Hellula undalis, Herpetogramma spp, Hyphantria cunea, Keiferia lycopersicella, Lasmopalpus lignosellus, Leucoptera scitella, Lithocollethis spp., Lobesia botrana, Loxostege bifidalis, Lymantria spp., Lyonetia spp., Malacosoma spp., Mamestra brassicae, Manduca sexta, Mythimna spp, Noctua spp, Operophtera spp., Orniodes indica, Ostrinia nubilalis, Pammene spp., Pandemis spp., Panolis flammea, Papaipema nebris, Pectinophora gossypiela, Perileucoptera coffeella, Pseudaletia unipuncta, Phthorimaea operculella, Pieris rapae, Pieris spp., Plutella xylostella, Prays spp., Pseudoplusia spp, Rachiplusia nu, Richia albicosta, Scirpophaga spp., Sesamia spp., Sparganothis spp., Spodoptera spp., Sylepta derogate, Synanthedon spp., Thaumetopoea spp., Tortrix spp., Trichoplusia ni, Tuta absoluta, and Yponomeuta spp.,

from the order *Mallophaga*, for example,

Damalinea spp. and Trichodectes spp.,

from the order *Orthoptera*, for example,

Blatta spp., Blattella spp., Gryllotalpa spp., Leucophaea maderae, Locusta spp., Neocurtilla hexadactyla, Periplaneta spp. , Scapteriscus spp, and Schistocerca spp.,

from the order *Psocoptera*, for example,

Liposcelis spp.,

from the order *Siphonaptera*, for example,

Ceratophyllus spp., Ctenocephalides spp. and Xenopsylla cheopis,

from the order *Thysanoptera*, for example,

Calliothrips phaseoli, Frankliniella spp., Heliothrips spp, Hercinothrips spp., Parthenothrips spp, Scirtothrips aurantii, Sericothrips variabilis, Taeniothrips spp., Thrips spp,

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

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

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

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

In a further aspect, the invention may also relate to a method of controlling damage to plant and parts thereof by plant parasitic nematodes (Endoparasitic-, Semiendoparasitic- and Ectoparasitic nematodes), especially plant parasitic nematodes such as root knot nematodes, Meloidogyne hapla, Meloidogyne incognita, Meloidogyne javanica, Meloidogyne arenaria and other Meloidogyne species, cyst-forming nematodes, Globodera rostochiensis and other Globodera species, Heterodera avenae, Heterodera glycines, Heterodera schachtii, Heterodera trifolii, and other Heterodera species, Seed gall nematodes, Anguina species, Stem and foliar nematodes, Aphelenchoides species, Sting nematodes, Belonolaimus longicaudatus and other Belonolaimus species, Pine nematodes, Bursaphelenchus xylophilus and other Bursaphelenchus species, Ring nematodes, Criconema species, Criconemella species, Criconemoides species, Mesocriconema species, Stem and bulb nematodes, Ditylenchus destructor, Ditylenchus dipsaci and other Ditylenchus species, Awl nematodes, Dolichodorus species, Spiral nematodes, Heliocotylenchus multicinctus and other Helicotylenchus species, Sheath and sheathoid nematodes, Hemicycliophora species and Hemicriconemoides species, Hirshmanniella

species, Lance nematodes, Hoploaimus species, false rootknot nematodes, Nacobbus species, Needle nematodes, Longidorus elongatus and other Longidorus species, Pin nematodes, Pratylenchus species, Lesion nematodes, Pratylenchus neglectus, Pratylenchus penetrans, Pratylenchus curvitatus, Pratylenchus goodeyi and other Pratylenchus species, Burrowing nematodes, Radopholus similis and other Radopholus species, Reniform nematodes, Rotylenchus robustus, Rotylenchus reniformis and other Rotylenchus species, Scutellonema species, Stubby root nematodes, Trichodorus primitivus and other Trichodorus species, Paratrichodorus species, Stunt nematodes, Tylenchorhynchus claytoni, Tylenchorhynchus dubius and other Tylenchorhynchus species, Citrus nematodes, Tylenchulus species, Dagger nematodes, Xiphinema species, and other plant parasitic nematode species, such as Subanguina spp., Hypsoperine spp., Macroposthonia spp., Melinius spp., Punctodera spp., and Quinisulcius spp..

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.

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

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

In the context of the present invention there are to be understood by δ-endotoxins, for example Cry1Ab, Cry1Ac, Cry1F, Cry1Fa2, Cry2Ab, Cry3A, Cry3Bb1 or Cry9C, or vegetative insecticidal

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

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

The processes for the preparation of such transgenic plants are generally known to the person skilled in the art and are described, for example, in the publications mentioned above. Cryl-type deoxyribonucleic acids and their preparation are known, for example, from WO 95/34656, EP-A-0 367 474, EP-A-0 401 979 and WO 90/13651.

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

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

Further examples of such transgenic crops are:

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

2. **Bt176 Maize** from Syngenta Seeds SAS, Chemin de l'Hobit 27, F-31 790 St. Sauveur, France, registration number C/FR/96/05/10. Genetically modified *Zea mays* which has been rendered resistant to attack by the European corn borer (*Ostrinia nubilalis* and *Sesamia nonagrioides*) by transgenic

expression of a Cry1Ab toxin. Bt176 maize also transgenically expresses the enzyme PAT to achieve tolerance to the herbicide glufosinate ammonium.

3. **MIR604 Maize** from Syngenta Seeds SAS, Chemin de l'Hobit 27, F-31 790 St. Sauveur, France, registration number C/FR/96/05/10. Maize which has been rendered insect-resistant by transgenic expression of a modified Cry3A toxin. This toxin is Cry3A055 modified by insertion of a cathepsin-G-protease recognition sequence. The preparation of such transgenic maize plants is described in WO 03/018810.

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

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

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

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

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

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

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

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

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.

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

Further areas of use of the compositions according to the invention are the protection of stored goods and store ambients 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 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. A further object of the invention is therefore a substrate selected from nonwoven and fabric material comprising a composition which contains a compound of formula I.

In one embodiment, the method for controlling such pests comprises applying a pesticidally effective amount of the compositions of the invention to the target pests, to their locus, or to a surface or substrate so as to provide effective residual pesticidal activity on the surface or substrate. Such application may be made by brushing, rolling, spraying, spreading or dipping the pesticidal composition of the invention. By way of example, an IRS application of a surface such as a wall, ceiling or floor surface is contemplated by the method of the invention so as to provide effective residual pesticidal activity on the surface. In another embodiment, it is contemplated to apply such compositions for residual control of pests on a substrate such as a fabric material in the form of (or which can be used in the manufacture of) netting, clothing, bedding, curtains and tents.

Substrates including non-woven, fabrics or netting to be treated may be made of natural fibres such as cotton, raffia, jute, flax, sisal, hessian, or wool, or synthetic fibres such as polyamide, polyester, polypropylene, polyacrylonitrile or the like. The polyesters are particularly suitable. The methods of textile treatment are known, e.g. WO 2008/151984, WO 03/034823, US 5631072, WO 2005/64072, WO 2006/128870, EP 1724392, WO 2005113886 or WO 2007/090739.

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

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

Table A. Examples of exotic woodborers of economic importance.

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

Table B. Examples of native woodborers of economic importance.

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

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

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

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

In particular, the present invention may be used to control insect pests that feed on the roots of turfgrass including white grubs (such as *Cyclocephala spp.* (e.g. masked chafer, *C. lurida*), *Rhizotrogus spp.* (e.g. European chafer, *R. majalis*), *Cotinus spp.* (e.g. Green June beetle, *C. nitida*), *Popillia spp.* (e.g. Japanese beetle, *P. japonica*), *Phyllophaga spp.* (e.g. May/June beetle), *Ataenius spp.* (e.g. Black turfgrass ataenius, *A. spretulus*), *Maladera spp.* (e.g. Asiatic garden beetle, *M. castanea*) and *Tomarus spp.*), ground pearls (*Margarodes* spp.), mole crickets (tawny, southern, and short-winged, *Scapteriscus* spp., *Gryllotalpa africana*) and leatherjackets (European crane fly, *Tipula spp.*).

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

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

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

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

Examples of such parasites are:

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

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

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

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

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

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

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

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

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

The compositions according to the invention can be used, for example, against the following pests: beetles such as Hylotrupes bajulus, Chlorophorus pilosis, Anobium punctatum, Xestobium rufovillosum, Ptilinuspecticornis, Dendrobium pertinex, Ernobius mollis, Priobium carpini, Lyctus brunneus, Lyctus africanus, Lyctus planicollis, Lyctus linearis, Lyctus pubescens, Trogoxylon aequale, Minthesrugicollis, Xyleborus spec.,Tryptodendron spec., Apate monachus, Bostrychus capucins, Heterobostrychus brunneus, Sinoxylon spec. and Dinoderus minutus, and also hymenopterans such

as Sirex juvencus, Urocerus gigas, Urocerus gigas taignus and Urocerus augur, and termites such as Kalotermes flavicollis, Cryptotermes brevis, Heterotermes indicola, Reticulitermes flavipes, Reticulitermes santonensis, Reticulitermes lucifugus, Mastotermes darwiniensis, Zootermopsis nevadensis and Coptotermes formosanus, and bristletails such as Lepisma saccharina.

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

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

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

The formulation adjuvants that are suitable for the preparation of the compositions according to the invention are known *per se*. As liquid carriers there may be used: water, toluene, xylene, petroleum ether, vegetable oils, acetone, methyl ethyl ketone, cyclohexanone, acid anhydrides, acetonitrile, acetophenone, amyl acetate, 2-butanone, butylene carbonate, chlorobenzene, cyclohexane, cyclohexanol, alkyl esters of acetic acid, diacetone alcohol, 1,2-dichloropropane, diethanolamine, p-diethylbenzene, diethylene glycol, diethylene glycol abietate, diethylene glycol butyl ether, diethylene

glycol ethyl ether, diethylene glycol methyl ether, *N,N*-dimethylformamide, dimethyl sulfoxide, 1,4-dioxane, dipropylene glycol, dipropylene glycol methyl ether, dipropylene glycol dibenzoate, diproxitol, alkylpyrrolidone, ethyl acetate, 2-ethylhexanol, ethylene carbonate, 1,1,1-trichloroethane, 2-heptanone, alpha-pinene, d-limonene, ethyl lactate, ethylene glycol, ethylene glycol butyl ether, ethylene glycol methyl ether, gamma-butyrolactone, glycerol, glycerol acetate, glycerol diacetate, glycerol triacetate, hexadecane, hexylene glycol, isoamyl acetate, isobornyl acetate, isooctane, isophorone, isopropylbenzene, isopropyl myristate, lactic acid, laurylamine, mesityl oxide, methoxy-propanol, methyl isoamyl ketone, methyl isobutyl ketone, methyl laurate, methyl octanoate, methyl oleate, methylene chloride, m-xylene, *n*-hexane, *n*-octylamine, octadecanoic acid, octylamine acetate, oleic acid, oleylamine, o-xylene, phenol, polyethylene glycol, propionic acid, propyl lactate, propylene carbonate, propylene glycol, propylene glycol methyl ether, p-xylene, toluene, triethyl phosphate, triethylene glycol, xylenesulfonic acid, paraffin, mineral oil, trichloroethylene, perchloroethylene, ethyl acetate, amyl acetate, butyl acetate, propylene glycol methyl ether, diethylene glycol methyl ether, methanol, ethanol, isopropanol, and alcohols of higher molecular weight, such as amyl alcohol, tetrahydrofurfuryl alcohol, hexanol, octanol, ethylene glycol, propylene glycol, glycerol, *N*-methyl-2-pyrrolidone and the like.

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

A large number of surface-active substances can advantageously be used in both solid and liquid formulations, especially in those formulations which can be diluted with a carrier prior to use. Surface-active substances may be anionic, cationic, non-ionic or polymeric and they can be used as emulsifiers, wetting agents or suspending agents or for other purposes. Typical surface-active substances include, for example, salts of alkyl sulfates, such as diethanolammonium lauryl sulfate, salts of alkylarylsulfonates, such as calcium dodecylbenzenesulfonate, alkylphenol/alkylene oxide addition products, such as nonylphenol ethoxylate, alcohol/alkylene oxide addition products, such as tridecylalcohol ethoxylate, soaps, such as sodium stearate, salts of alkylnaphthalenesulfonates, such as sodium dibutylnaphthalenesulfonate, dialkyl esters of sulfosuccinate salts, such as sodium di(2-ethylhexyl)sulfosuccinate, sorbitol esters, such as sorbitol oleate, quaternary amines, such as lauryltrimethylammonium chloride, polyethylene glycol esters of fatty acids, such as polyethylene glycol stearate, block copolymers of ethylene oxide and propylene oxide, and salts of mono- and di-alkylphosphate esters, and also further substances described e.g. in McCutcheon's Detergents and Emulsifiers Annual, MC Publishing Corp., Ridgewood New Jersey (1981).

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

The compositions according to the invention can include an additive comprising an oil of vegetable or animal origin, a mineral oil, alkyl esters of such oils or mixtures of such oils and oil derivatives. The amount of oil additive in the composition according to the invention is generally from 0.01 to 10 %, based on the mixture to be applied. For example, the oil additive can be added to a spray tank in the desired concentration after a spray mixture has been prepared. Preferred oil additives comprise mineral oils or an oil of vegetable origin, for example rapeseed oil, olive oil or sunflower oil, emulsified vegetable oil, alkyl esters of oils of vegetable origin, for example the methyl derivatives, or an oil of animal origin, such as fish oil or beef tallow. Preferred oil additives comprise alkyl esters of C_8-C_{22} fatty acids, especially the methyl derivatives of C_{12}-C_{18} fatty acids, for example the methyl esters of lauric acid, palmitic acid and oleic acid (methyl laurate, methyl palmitate and methyl oleate, respectively). Many oil derivatives are known from the Compendium of Herbicide Adjuvants, 10th Edition, Southern Illinois University, 2010.

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

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

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

Emulsifiable concentrates:

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

Dusts:

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

Suspension concentrates:

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

Wettable powders:

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

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

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

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

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

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

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

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

Emulsifiable concentrate	

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

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

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

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

Extruder granules	
Active ingredients	15 %
sodium lignosulfonate	2 %
carboxymethylcellulose	1 %
Kaolin	82 %

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

Coated granules	
Active ingredients	8 %

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

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

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

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

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

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

Slow Release Capsule Suspension

28 parts of the combination are mixed with 2 parts of an aromatic solvent and 7 parts of toluene diisocyanate/polymethylene-polyphenylisocyanate-mixture (8:1). This mixture is emulsified in a mixture of 1.2 parts of polyvinylalcohol, 0.05 parts of a defoamer and 51.6 parts of water until the desired particle size is achieved. To this emulsion a mixture of 2.8 parts 1,6-diaminohexane in 5.3 parts of water is added. The mixture is agitated until the polymerization reaction is completed. The obtained capsule suspension is stabilized by adding 0.25 parts of a thickener and 3 parts of a dispersing agent.

The capsule suspension formulation contains 28% of the active ingredients. The medium capsule diameter is 8-15 microns. The resulting formulation is applied to seeds as an aqueous suspension in an apparatus suitable for that purpose.

Formulation types include an emulsion concentrate (EC), a suspension concentrate (SC), a suspo-emulsion (SE), a capsule suspension (CS), a water dispersible granule (WG), an emulsifiable granule (EG), an emulsion, water in oil (EO), an emulsion, oil in water (EW), a micro-emulsion (ME), an oil dispersion (OD), an oil miscible flowable (OF), an oil miscible liquid (OL), a soluble concentrate (SL), an ultra-low volume suspension (SU), an ultra-low volume liquid (UL), a technical concentrate (TK), a dispersible concentrate (DC), a wettable powder (WP), a soluble granule (SG) or any technically feasible formulation in combination with agriculturally acceptable adjuvants.

In a further aspect, the present invention makes available a pesticidal composition comprising a compound of the first aspect, one or more formulation additives and a carrier.

The activity of the compositions according to the invention can be broadened considerably, and adapted to prevailing circumstances, by adding other insecticidally, acaricidally and/or fungicidally active ingredients. The mixtures of the compounds of formula I with other insecticidally, acaricidally and/or fungicidally active ingredients may also have further surprising advantages which can also be described, in a wider sense, as synergistic activity. For example, better tolerance by plants, reduced phytotoxicity, insects can be controlled in their different development stages or better behaviour during their production, for example during grinding or mixing, during their storage or during their use.

Suitable additions to active ingredients here are, for example, representatives of the following classes of active ingredients: organophosphorus compounds, nitrophenol derivatives, thioureas, juvenile hormones, formamidines, benzophenone derivatives, ureas, pyrrole derivatives, carbamates, pyrethroids, chlorinated hydrocarbons, acylureas, pyridylmethyleneamino derivatives, macrolides, neonicotinoids and Bacillus thuringiensis preparations.

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 and A of the present invention"):

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

an acaricide selected from the group of substances consisting of 1,1-bis(4-chlorophenyl)-2-ethoxyethanol (IUPAC name) (910) + TX, 2,4-dichlorophenyl benzenesulfonate (IUPAC/Chemical Abstracts name) (1059) + TX, 2-fluoro-*N*-methyl-*N*-1-naphthylacetamide (IUPAC name) (1295) + TX, 4-chlorophenyl phenyl sulfone (IUPAC name) (981) + TX, abamectin (1) + TX, acequinocyl (3) + TX, acetoprole [CCN] + TX, acrinathrin (9) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, alpha-cypermethrin (202) + TX, amidithion (870) + TX, 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 [CCN] + TX, benzoximate (71) + TX, benzyl benzoate (IUPAC name) [CCN] + TX, bifenazate (74) + TX,

bifenthrin (76) + TX, binapacryl (907) + TX, brofenvalerate + TX, bromocyclen (918) + TX, bromophos (920) + TX, bromophos-ethyl (921) + TX, bromopropylate (94) + TX, buprofezin (99) + TX, butocarboxim (103) + TX, butoxycarboxim (104) + TX, butylpyridaben + TX, calcium polysulfide (IUPAC name) (111) + TX, camphechlor (941) + TX, carbanolate (943) + TX, carbaryl (115) + TX, carbofuran (118) + TX, carbophenothion (947) + TX, CGA 50'439 (development code) (125) + TX, chinomethionat (126) + TX, chlorbenside (959) + TX, chlordimeform (964) + TX, chlordimeform hydrochloride (964) + TX, chlorfenapyr (130) + TX, chlorfenethol (968) + TX, chlorfenson (970) + TX, chlorfensulfide (971) + TX, chlorfenvinphos (131) + TX, chlorobenzilate (975) + TX, chloromebuform (977) + TX, chloromethiuron (978) + TX, chloropropylate (983) + TX, chlorpyrifos (145) + TX, chlorpyrifos-methyl (146) + TX, chlorthiophos (994) + TX, cinerin I (696) + TX, cinerin II (696) + TX, cinerins (696) + TX, clofentezine (158) + TX, closantel [CCN] + TX, coumaphos (174) + TX, crotamiton [CCN] + TX, crotoxyphos (1010) + TX, cufraneb (1013) + TX, cyanthoate (1020) + TX, cyflumetofen (CAS Reg. No.: 400882-07-7) + TX, cyhalothrin (196) + TX, cyhexatin (199) + TX, cypermethrin (201) + TX, DCPM (1032) + TX, DDT (219) + TX, demephion (1037) + TX, demephion-O (1037) + TX, demephion-S (1037) + TX, demeton (1038) + TX, demeton-methyl (224) + TX, demeton-O (1038) + TX, demeton-O-methyl (224) + TX, demeton-S (1038) + TX, demeton-S-methyl (224) + TX, demeton-S-methylsulfon (1039) + TX, diafenthiuron (226) + TX, dialifos (1042) + TX, diazinon (227) + TX, dichlofluanid (230) + TX, dichlorvos (236) + TX, dicliphos + TX, dicofol (242) + TX, dicrotophos (243) + TX, dienochlor (1071) + TX, dimefox (1081) + TX, dimethoate (262) + TX, dinactin (653) + TX, dinex (1089) + TX, dinex-diclexine (1089) + TX, dinobuton (269) + TX, dinocap (270) + TX, dinocap-4 [CCN] + TX, dinocap-6 [CCN] + TX, dinocton (1090) + TX, dinopenton (1092) + TX, dinosulfon (1097) + TX, dinoterbon (1098) + TX, dioxathion (1102) + TX, diphenyl sulfone (IUPAC name) (1103) + TX, disulfiram [CCN] + TX, disulfoton (278) + TX, DNOC (282) + TX, dofenapyn (1113) + TX, doramectin [CCN] + TX, endosulfan (294) + TX, endothion (1121) + TX, EPN (297) + TX, eprinomectin [CCN] + TX, ethion (309) + TX, ethoate-methyl (1134) + TX, etoxazole (320) + TX, etrimfos (1142) + TX, fenazaflor (1147) + TX, fenazaquin (328) + TX, fenbutatin oxide (330) + TX, fenothiocarb (337) + TX, fenpropathrin (342) + TX, fenpyrad + TX, fenpyroximate (345) + TX, fenson (1157) + TX, fentrifanil (1161) + TX, fenvalerate (349) + TX, fipronil (354) + TX, fluacrypyrim (360) + TX, fluazuron (1166) + TX, flubenzimine (1167) + TX, flucycloxuron (366) + TX, flucythrinate (367) + TX, fluenetil (1169) + TX, flufenoxuron (370) + TX, flumethrin (372) + TX, fluorbenside (1174) + TX, fluvalinate (1184) + TX, FMC 1137 (development code) (1185) + TX, formetanate (405) + TX, formetanate hydrochloride (405) + TX, formothion (1192) + TX, formparanate (1193) + TX, gamma-HCH (430) + TX, glyodin (1205) + TX, halfenprox (424) + TX, heptenophos (432) + TX, hexadecyl cyclopropanecarboxylate (IUPAC/Chemical Abstracts name) (1216) + TX, hexythiazox (441) + TX, iodomethane (IUPAC name) (542) + TX, isocarbophos (473) + TX, isopropyl *O*-(methoxyaminothiophosphoryl)salicylate (IUPAC name) (473) + TX, ivermectin [CCN] + TX, jasmolin I (696) + TX, jasmolin II (696) + TX, jodfenphos (1248) + TX, lindane (430) + TX, lufenuron (490) + TX, malathion (492) + TX, malonoben (1254) + TX,

mecarbam (502) + TX, mephosfolan (1261) + TX, mesulfen [CCN] + TX, methacrifos (1266) + TX, methamidophos (527) + TX, methidathion (529) + TX, methiocarb (530) + TX, methomyl (531) + TX, methyl bromide (537) + TX, metolcarb (550) + TX, mevinphos (556) + TX, mexacarbate (1290) + TX, milbemectin (557) + TX, milbemycin oxime [CCN] + TX, mipafox (1293) + TX, monocrotophos (561) + TX, morphothion (1300) + TX, moxidectin [CCN] + TX, naled (567) + TX, NC-184 (compound code) + TX, NC-512 (compound code) + TX, nifluridide (1309) + TX, nikkomycins [CCN] + TX, nitrilacarb (1313) + TX, nitrilacarb 1:1 zinc chloride complex (1313) + TX, NNI-0101 (compound code) + TX, NNI-0250 (compound code) + TX, omethoate (594) + TX, oxamyl (602) + TX, oxydeprofos (1324) + TX, oxydisulfoton (1325) + TX, pp'-DDT (219) + TX, parathion (615) + TX, permethrin (626) + TX, petroleum oils (628) + TX, phenkapton (1330) + TX, phenthoate (631) + TX, phorate (636) + TX, phosalone (637) + TX, phosfolan (1338) + TX, phosmet (638) + TX, phosphamidon (639) + TX, phoxim (642) + TX, pirimiphos-methyl (652) + TX, polychloroterpenes (traditional name) (1347) + TX, polynactins (653) + TX, proclonol (1350) + TX, profenofos (662) + TX, promacyl (1354) + TX, propargite (671) + TX, propetamphos (673) + TX, propoxur (678) + TX, prothidathion (1360) + TX, prothoate (1362) + TX, pyrethrin I (696) + TX, pyrethrin II (696) + TX, pyrethrins (696) + TX, pyridaben (699) + TX, pyridaphenthion (701) + TX, pyrimidifen (706) + TX, pyrimitate (1370) + TX, quinalphos (711) + TX, quintiofos (1381) + TX, R-1492 (development code) (1382) + TX, RA-17 (development code) (1383) + TX, rotenone (722) + TX, schradan (1389) + TX, sebufos + TX, selamectin [CCN] + TX, SI-0009 (compound code) + TX, sophamide (1402) + TX, spirodiclofen (738) + TX, spiromesifen (739) + TX, SSI-121 (development code) (1404) + TX, sulfiram [CCN] + TX, sulfluramid (750) + TX, sulfotep (753) + TX, sulfur (754) + TX, SZI-121 (development code) (757) + TX, tau-fluvalinate (398) + TX, tebufenpyrad (763) + TX, TEPP (1417) + TX, terbam + TX, tetrachlorvinphos (777) + TX, tetradifon (786) + TX, tetranactin (653) + TX, tetrasul (1425) + TX, thiafenox + TX, thiocarboxime (1431) + TX, thiofanox (800) + TX, thiometon (801) + TX, thioquinox (1436) + TX, thuringiensin [CCN] + TX, triamiphos (1441) + TX, triarathene (1443) + TX, triazophos (820) + TX, triazuron + TX, trichlorfon (824) + TX, trifenofos (1455) + TX, trinactin (653) + TX, vamidothion (847) + TX, vaniliprole [CCN] and YI-5302 (compound code) + TX,

an algicide selected from the group of substances consisting of bethoxazin [CCN] + TX, copper dioctanoate (IUPAC name) (170) + TX, copper sulfate (172) + TX, cybutryne [CCN] + TX, dichlone (1052) + TX, dichlorophen (232) + TX, endothal (295) + TX, fentin (347) + TX, hydrated lime [CCN] + TX, nabam (566) + TX, quinoclamine (714) + TX, quinonamid (1379) + TX, simazine (730) + TX, triphenyltin acetate (IUPAC name) (347) and triphenyltin hydroxide (IUPAC name) (347) + TX,

an anthelmintic selected from the group of substances consisting of abamectin (1) + TX, crufomate (1011) + TX, doramectin [CCN] + TX, emamectin (291) + TX, emamectin benzoate (291) + TX, eprinomectin [CCN] + TX, ivermectin [CCN] + TX, milbemycin oxime [CCN] + TX,

moxidectin [CCN] + TX, piperazine [CCN] + TX, selamectin [CCN] + TX, spinosad (737) and thiophanate (1435) + TX,

an avicide selected from the group of substances consisting of chloralose (127) + TX, endrin (1122) + TX, fenthion (346) + TX, pyridin-4-amine (IUPAC name) (23) and strychnine (745) + TX,

a bactericide selected from the group of substances consisting of 1-hydroxy-1*H*-pyridine-2-thione (IUPAC name) (1222) + TX, 4-(quinoxalin-2-ylamino)benzenesulfonamide (IUPAC name) (748) + TX, 8-hydroxyquinoline sulfate (446) + TX, bronopol (97) + TX, copper dioctanoate (IUPAC name) (170) + TX, copper hydroxide (IUPAC name) (169) + TX, cresol [CCN] + TX, dichlorophen (232) + TX, dipyrithione (1105) + TX, dodicin (1112) + TX, fenaminosulf (1144) + TX, formaldehyde (404) + TX, hydrargaphen [CCN] + TX, kasugamycin (483) + TX, kasugamycin hydrochloride hydrate (483) + TX, nickel bis(dimethyldithiocarbamate) (IUPAC name) (1308) + TX, nitrapyrin (580) + TX, 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 [CCN] + TX,

a biological agent selected from the group of substances consisting of *Adoxophyes orana* GV (12) + TX, *Agrobacterium radiobacter* (13) + TX, *Amblyseius* spp. (19) + TX, *Anagrapha falcifera* NPV (28) + TX, *Anagrus atomus* (29) + TX, *Aphelinus abdominalis* (33) + TX, *Aphidius colemani* (34) + TX, *Aphidoletes aphidimyza* (35) + TX, *Autographa californica* NPV (38) + TX, *Bacillus firmus* (48) + TX, *Bacillus sphaericus* Neide (scientific name) (49) + TX, *Bacillus thuringiensis* Berliner (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *aizawai* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *israelensis* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *japonensis* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *kurstaki* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *tenebrionis* (scientific name) (51) + TX, *Beauveria bassiana* (53) + TX, *Beauveria brongniartii* (54) + TX, *Chrysoperla carnea* (151) + TX, *Cryptolaemus montrouzieri* (178) + TX, *Cydia pomonella* GV (191) + TX, *Dacnusa sibirica* (212) + TX, *Diglyphus isaea* (254) + TX, *Encarsia formosa* (scientific name) (293) + TX, *Eretmocerus eremicus* (300) + TX, *Helicoverpa zea* NPV (431) + TX, *Heterorhabditis bacteriophora* and *H. megidis* (433) + TX, *Hippodamia convergens* (442) + TX, *Leptomastix dactylopii* (488) + TX, *Macrolophus caliginosus* (491) + TX, *Mamestra brassicae* NPV (494) + TX, *Metaphycus helvolus* (522) + TX, *Metarhizium anisopliae* var. *acridum* (scientific name) (523) + TX, *Metarhizium anisopliae* var. *anisopliae* (scientific name) (523) + TX, *Neodiprion sertifer* NPV and *N. lecontei* NPV (575) + TX, *Orius* spp. (596) + TX, *Paecilomyces fumosoroseus* (613) + TX, *Phytoseiulus persimilis* (644) + TX, *Spodoptera exigua* multicapsid nuclear polyhedrosis virus (scientific name) (741) + TX, *Steinernema bibionis* (742) + TX, *Steinernema carpocapsae* (742) + TX, *Steinernema feltiae* (742) + TX, *Steinernema glaseri* (742) + TX, *Steinernema riobrave* (742) + TX, *Steinernema riobravis* (742) + TX, *Steinernema scapterisci* (742) + TX, *Steinernema* spp. (742) + TX, *Trichogramma* spp. (826) + TX, *Typhlodromus occidentalis* (844) and *Verticillium lecanii* (848) + TX,

a soil sterilant selected from the group of substances consisting of iodomethane (IUPAC name) (542) and methyl bromide (537) + TX,

a chemosterilant selected from the group of substances consisting of apholate [CCN] + TX, bisazir [CCN] + TX, busulfan [CCN] + TX, diflubenzuron (250) + TX, dimatif [CCN] + TX, hemel [CCN] + TX, hempa [CCN] + TX, metepa [CCN] + TX, methiotepa [CCN] + TX, methyl apholate [CCN] + TX, morzid [CCN] + TX, penfluron [CCN] + TX, tepa [CCN] + TX, thiohempa [CCN] + TX, thiotepa [CCN] + TX, tretamine [CCN] and uredepa [CCN] + TX,

an insect pheromone selected from the group of substances consisting of (*E*)-dec-5-en-1-yl acetate with (*E*)-dec-5-en-1-ol (IUPAC name) (222) + TX, (*E*)-tridec-4-en-1-yl acetate (IUPAC name) (829) + TX, (*E*)-6-methylhept-2-en-4-ol (IUPAC name) (541) + TX, (*E,Z*)-tetradeca-4,10-dien-1-yl acetate (IUPAC name) (779) + TX, (*Z*)-dodec-7-en-1-yl acetate (IUPAC name) (285) + TX, (*Z*)-hexadec-11-enal (IUPAC name) (436) + TX, (*Z*)-hexadec-11-en-1-yl acetate (IUPAC name) (437) + TX, (*Z*)-hexadec-13-en-11-yn-1-yl acetate (IUPAC name) (438) + TX, (*Z*)-icos-13-en-10-one (IUPAC name) (448) + TX, (Z)-tetradec-7-en-1-al (IUPAC name) (782) + TX, (*Z*)-tetradec-9-en-1-ol (IUPAC name) (783) + TX, (Z)-tetradec-9-en-1-yl acetate (IUPAC name) (784) + TX, (7*E*,9*Z*)-dodeca-7,9-dien-1-yl acetate (IUPAC name) (283) + TX, (9*Z*,11*E*)-tetradeca-9,11-dien-1-yl acetate (IUPAC name) (780) + TX, (9*Z*,12*E*)-tetradeca-9,12-dien-1-yl acetate (IUPAC name) (781) + TX, 14-methyloctadec-1-ene (IUPAC name) (545) + TX, 4-methylnonan-5-ol with 4-methylnonan-5-one (IUPAC name) (544) + TX, alpha-multistriatin [CCN] + TX, brevicomin [CCN] + TX, codlelure [CCN] + TX, codlemone (167) + TX, cuelure (179) + TX, disparlure (277) + TX, dodec-8-en-1-yl acetate (IUPAC name) (286) + TX, dodec-9-en-1-yl acetate (IUPAC name) (287) + TX, dodeca-8 + TX, 10-dien-1-yl acetate (IUPAC name) (284) + TX, dominicalure [CCN] + TX, ethyl 4-methyloctanoate (IUPAC name) (317) + TX, eugenol [CCN] + TX, frontalin [CCN] + TX, gossyplure (420) + TX, grandlure (421) + TX, grandlure I (421) + TX, grandlure II (421) + TX, grandlure III (421) + TX, grandlure IV (421) + TX, hexalure [CCN] + TX, ipsdienol [CCN] + TX, ipsenol [CCN] + TX, japonilure (481) + TX, lineatin [CCN] + TX, litlure [CCN] + TX, looplure [CCN] + TX, medlure [CCN] + TX, megatomoic acid [CCN] + TX, methyl eugenol (540) + TX, muscalure (563) + TX, octadeca-2,13-dien-1-yl acetate (IUPAC name) (588) + TX, octadeca-3,13-dien-1-yl acetate (IUPAC name) (589) + TX, orfralure [CCN] + TX, oryctalure (317) + TX, ostramone [CCN] + TX, siglure [CCN] + TX, sordidin (736) + TX, sulcatol [CCN] + TX, tetradec-11-en-1-yl acetate (IUPAC name) (785) + TX, trimedlure (839) + TX, trimedlure A (839) + TX, trimedlure B_1 (839) + TX, trimedlure B_2 (839) + TX, trimedlure C (839) and trunc-call [CCN] + TX,

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

an insecticide selected from the group of substances consisting of 1-dichloro-1-nitroethane (IUPAC/Chemical Abstracts name) (1058) + TX, 1,1-dichloro-2,2-bis(4-ethylphenyl)ethane (IUPAC name) (1056), + TX, 1,2-dichloropropane (IUPAC/Chemical Abstracts name) (1062) + TX, 1,2-dichloropropane with 1,3-dichloropropene (IUPAC name) (1063) + TX, 1-bromo-2-chloroethane (IUPAC/Chemical Abstracts name) (916) + TX, 2,2,2-trichloro-1-(3,4-dichlorophenyl)ethyl acetate (IUPAC name) (1451) + TX, 2,2-dichlorovinyl 2-ethylsulfinylethyl methyl phosphate (IUPAC name) (1066) + TX, 2-(1,3-dithiolan-2-yl)phenyl dimethylcarbamate (IUPAC/ Chemical Abstracts name) (1109) + TX, 2-(2-butoxyethoxy)ethyl thiocyanate (IUPAC/Chemical Abstracts name) (935) + TX, 2-(4,5-dimethyl-1,3-dioxolan-2-yl)phenyl methylcarbamate (IUPAC/ Chemical Abstracts name) (1084) + TX, 2-(4-chloro-3,5-xylyloxy)ethanol (IUPAC name) (986) + TX, 2-chlorovinyl diethyl phosphate (IUPAC name) (984) + TX, 2-imidazolidone (IUPAC name) (1225) + TX, 2-isovalerylindan-1,3-dione (IUPAC name) (1246) + TX, 2-methyl(prop-2-ynyl)aminophenyl methylcarbamate (IUPAC name) (1284) + TX, 2-thiocyanatoethyl laurate (IUPAC name) (1433) + TX, 3-bromo-1-chloroprop-1-ene (IUPAC name) (917) + TX, 3-methyl-1-phenylpyrazol-5-yl dimethylcarbamate (IUPAC name) (1283) + TX, 4-methyl(prop-2-ynyl)amino-3,5-xylyl methylcarbamate (IUPAC name) (1285) + TX, 5,5-dimethyl-3-oxocyclohex-1-enyl dimethylcarbamate (IUPAC name) (1085) + TX, abamectin (1) + TX, acephate (2) + TX, acetamiprid (4) + TX, acethion [CCN] + TX, acetoprole [CCN] + TX, acrinathrin (9) + TX, acrylonitrile (IUPAC name) (861) + TX, alanycarb (15) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, aldrin (864) + TX, allethrin (17) + TX, allosamidin [CCN] + TX, allyxycarb (866) + TX, alpha-cypermethrin (202) + TX, alpha-ecdysone [CCN] + TX, aluminium phosphide (640) + TX, amidithion (870) + TX, amidothioate (872) + TX, aminocarb (873) + TX, amiton (875) + TX, amiton hydrogen oxalate (875) + TX, amitraz (24) + TX, anabasine (877) + TX, athidathion (883) + TX, AVI 382 (compound code) + TX, AZ 60541 (compound code) + TX, azadirachtin (41) + TX, azamethiphos (42) + TX, azinphos-ethyl (44) + TX, azinphos-methyl (45) + TX, azothoate (889) + TX, *Bacillus thuringiensis* delta endotoxins (52) + TX, barium hexafluorosilicate [CCN] + TX, barium polysulfide (IUPAC/Chemical Abstracts name) (892) + TX, barthrin [CCN] + TX, Bayer 22/190 (development code) (893) + TX, Bayer 22408 (development code) (894) + TX, bendiocarb (58) + TX, benfuracarb (60) + TX, bensultap (66) + TX, beta-cyfluthrin (194) + TX, beta-cypermethrin (203) + TX, bifenthrin (76) + TX, bioallethrin (78) + TX, bioallethrin *S*-cyclopentenyl isomer (79) + TX, bioethanomethrin [CCN] + TX, biopermethrin (908) + TX, bioresmethrin (80) + TX, bis(2-chloroethyl) ether (IUPAC name) (909) + TX, bistrifluron (83) + TX, borax (86) + TX, brofenvalerate + TX, bromfenvinfos (914) + TX, bromocyclen (918) + TX, bromo-DDT [CCN] + TX, bromophos (920) + TX, bromophos-ethyl (921) + TX, bufencarb (924) + TX, buprofezin (99) + TX, butacarb (926) + TX, butathiofos (927) + TX, butocarboxim (103) + TX, butonate (932) + TX, butoxycarboxim (104) + TX, butylpyridaben + TX, cadusafos (109) + TX, calcium arsenate [CCN] + TX, calcium cyanide (444) + TX, calcium polysulfide (IUPAC name) (111) + TX, camphechlor (941) + TX, carbanolate (943) + TX, carbaryl (115) + TX, carbofuran (118) + TX, carbon disulfide (IUPAC/Chemical Abstracts name) (945) + TX, carbon tetrachloride (IUPAC name) (946) + TX, carbophenothion (947) + TX, carbosulfan (119) + TX,

cartap (123) + TX, cartap hydrochloride (123) + TX, cevadine (725) + TX, chlorbicyclen (960) + TX, chlordane (128) + TX, chlordecone (963) + TX, chlordimeform (964) + TX, chlordimeform hydrochloride (964) + TX, chlorethoxyfos (129) + TX, chlorfenapyr (130) + TX, chlorfenvinphos (131) + TX, chlorfluazuron (132) + TX, chlormephos (136) + TX, chloroform [CCN] + TX, chloropicrin (141) + TX, chlorphoxim (989) + TX, chlorprazophos (990) + TX, chlorpyrifos (145) + TX, chlorpyrifos-methyl (146) + TX, chlorthiophos (994) + TX, chromafenozide (150) + TX, cinerin I (696) + TX, cinerin II (696) + TX, cinerins (696) + TX, cis-resmethrin + TX, cismethrin (80) + TX, clocythrin + TX, cloethocarb (999) + TX, closantel [CCN] + TX, clothianidin (165) + TX, copper acetoarsenite [CCN] + TX, copper arsenate [CCN] + TX, copper oleate [CCN] + TX, coumaphos (174) + TX, coumithoate (1006) + TX, crotamiton [CCN] + TX, crotoxyphos (1010) + TX, crufomate (1011) + TX, cryolite (177) + TX, CS 708 (development code) (1012) + TX, cyanofenphos (1019) + TX, cyanophos (184) + TX, cyanthoate (1020) + TX, cyclethrin [CCN] + TX, cycloprothrin (188) + TX, cyfluthrin (193) + TX, cyhalothrin (196) + TX, cypermethrin (201) + TX, cyphenothrin (206) + TX, cyromazine (209) + TX, cythioate [CCN] + TX, *d*-limonene [CCN] + TX, *d*-tetramethrin (788) + TX, DAEP (1031) + TX, dazomet (216) + TX, DDT (219) + TX, decarbofuran (1034) + TX, deltamethrin (223) + TX, demephion (1037) + TX, demephion-O (1037) + TX, demephion-S (1037) + TX, demeton (1038) + TX, demeton-methyl (224) + TX, demeton-O (1038) + TX, demeton-O-methyl (224) + TX, demeton-S (1038) + TX, demeton-S-methyl (224) + TX, demeton-S-methylsulphon (1039) + TX, diafenthiuron (226) + TX, dialifos (1042) + TX, diamidafos (1044) + TX, diazinon (227) + TX, dicapthon (1050) + TX, dichlofenthion (1051) + TX, dichlorvos (236) + TX, dicliphos + TX, dicresyl [CCN] + TX, dicrotophos (243) + TX, dicyclanil (244) + TX, dieldrin (1070) + TX, diethyl 5-methylpyrazol-3-yl phosphate (IUPAC name) (1076) + TX, diflubenzuron (250) + TX, dilor [CCN] + TX, dimefluthrin [CCN] + TX, dimefox (1081) + TX, dimetan (1085) + TX, dimethoate (262) + TX, dimethrin (1083) + TX, dimethylvinphos (265) + TX, dimetilan (1086) + TX, dinex (1089) + TX, dinex-diclexine (1089) + TX, dinoprop (1093) + TX, dinosam (1094) + TX, dinoseb (1095) + TX, dinotefuran (271) + TX, diofenolan (1099) + TX, dioxabenzofos (1100) + TX, dioxacarb (1101) + TX, dioxathion (1102) + TX, disulfoton (278) + TX, dithicrofos (1108) + TX, DNOC (282) + TX, doramectin [CCN] + TX, DSP (1115) + TX, ecdysterone [CCN] + TX, EI 1642 (development code) (1118) + TX, emamectin (291) + TX, emamectin benzoate (291) + TX, EMPC (1120) + TX, empenthrin (292) + TX, endosulfan (294) + TX, endothion (1121) + TX, endrin (1122) + TX, EPBP (1123) + TX, EPN (297) + TX, epofenonane (1124) + TX, eprinomectin [CCN] + TX, esfenvalerate (302) + TX, etaphos [CCN] + TX, ethiofencarb (308) + TX, ethion (309) + TX, ethiprole (310) + TX, ethoate-methyl (1134) + TX, ethoprophos (312) + TX, ethyl formate (IUPAC name) [CCN] + TX, ethyl-DDD (1056) + TX, ethylene dibromide (316) + TX, ethylene dichloride (chemical name) (1136) + TX, ethylene oxide [CCN] + TX, etofenprox (319) + TX, etrimfos (1142) + TX, EXD (1143) + TX, famphur (323) + TX, fenamiphos (326) + TX, fenazaflor (1147) + TX, fenchlorphos (1148) + TX, fenethacarb (1149) + TX, fenfluthrin (1150) + TX, fenitrothion (335) + TX, fenobucarb (336) + TX, fenoxacrim (1153) + TX, fenoxycarb (340) + TX, fenpirithrin (1155) + TX, fenpropathrin (342) + TX,

fenpyrad + TX, fensulfothion (1158) + TX, fenthion (346) + TX, fenthion-ethyl [CCN] + TX, fenvalerate (349) + TX, fipronil (354) + TX, flonicamid (358) + TX, flubendiamide (CAS. Reg. No.: 272451-65-7) + TX, flucofuron (1168) + TX, flucycloxuron (366) + TX, flucythrinate (367) + TX, fluenetil (1169) + TX, flufenerim [CCN] + TX, flufenoxuron (370) + TX, flufenprox (1171) + TX, flumethrin (372) + TX, fluvalinate (1184) + TX, FMC 1137 (development code) (1185) + TX, fonofos (1191) + TX, formetanate (405) + TX, formetanate hydrochloride (405) + TX, formothion (1192) + TX, formparanate (1193) + TX, fosmethilan (1194) + TX, fospirate (1195) + TX, fosthiazate (408) + TX, fosthietan (1196) + TX, furathiocarb (412) + TX, furethrin (1200) + TX, gamma-cyhalothrin (197) + TX, gamma-HCH (430) + TX, guazatine (422) + TX, guazatine acetates (422) + TX, GY-81 (development code) (423) + TX, halfenprox (424) + TX, halofenozide (425) + TX, HCH (430) + TX, HEOD (1070) + TX, heptachlor (1211) + TX, heptenophos (432) + TX, heterophos [CCN] + TX, hexaflumuron (439) + TX, HHDN (864) + TX, hydramethylnon (443) + TX, hydrogen cyanide (444) + TX, hydroprene (445) + TX, hyquincarb (1223) + TX, imidacloprid (458) + TX, imiprothrin (460) + TX, indoxacarb (465) + TX, iodomethane (IUPAC name) (542) + TX, IPSP (1229) + TX, isazofos (1231) + TX, isobenzan (1232) + TX, isocarbophos (473) + TX, isodrin (1235) + TX, isofenphos (1236) + TX, isolane (1237) + TX, isoprocarb (472) + TX, isopropyl *O*-(methoxyaminothiophosphoryl)salicylate (IUPAC name) (473) + TX, isoprothiolane (474) + TX, isothioate (1244) + TX, isoxathion (480) + TX, ivermectin [CCN] + TX, jasmolin I (696) + TX, jasmolin II (696) + TX, jodfenphos (1248) + TX, juvenile hormone I [CCN] + TX, juvenile hormone II [CCN] + TX, juvenile hormone III [CCN] + TX, kelevan (1249) + TX, kinoprene (484) + TX, lambda-cyhalothrin (198) + TX, lead arsenate [CCN] + TX, lepimectin (CCN) + TX, leptophos (1250) + TX, lindane (430) + TX, lirimfos (1251) + TX, lufenuron (490) + TX, lythidathion (1253) + TX, *m*-cumenyl methylcarbamate (IUPAC name) (1014) + TX, magnesium phosphide (IUPAC name) (640) + TX, malathion (492) + TX, malonoben (1254) + TX, mazidox (1255) + TX, mecarbam (502) + TX, mecarphon (1258) + TX, menazon (1260) + TX, mephosfolan (1261) + TX, mercurous chloride (513) + TX, mesulfenfos (1263) + TX, metaflumizone (CCN) + TX, metam (519) + TX, metam-potassium (519) + TX, metam-sodium (519) + TX, methacrifos (1266) + TX, methamidophos (527) + TX, methanesulfonyl fluoride (IUPAC/Chemical Abstracts name) (1268) + TX, methidathion (529) + TX, methiocarb (530) + TX, methocrotophos (1273) + TX, methomyl (531) + TX, methoprene (532) + TX, methoquin-butyl (1276) + TX, methothrin (533) + TX, methoxychlor (534) + TX, methoxyfenozide (535) + TX, methyl bromide (537) + TX, methyl isothiocyanate (543) + TX, methylchloroform [CCN] + TX, methylene chloride [CCN] + TX, metofluthrin [CCN] + TX, metolcarb (550) + TX, metoxadiazone (1288) + TX, mevinphos (556) + TX, mexacarbate (1290) + TX, milbemectin (557) + TX, milbemycin oxime [CCN] + TX, mipafox (1293) + TX, mirex (1294) + TX, monocrotophos (561) + TX, morphothion (1300) + TX, moxidectin [CCN] + TX, naftalofos [CCN] + TX, naled (567) + TX, naphthalene (IUPAC/Chemical Abstracts name) (1303) + TX, NC-170 (development code) (1306) + TX, NC-184 (compound code) + TX, nicotine (578) + TX, nicotine sulfate (578) + TX, nifluridide (1309) + TX, nitenpyram (579) + TX, nithiazine (1311) + TX, nitrilacarb (1313) + TX,

nitrilacarb 1:1 zinc chloride complex (1313) + TX, NNI-0101 (compound code) + TX, NNI-0250 (compound code) + TX, 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 [CCN] + TX, pentachlorophenol (623) + TX, pentachlorophenyl laurate (IUPAC name) (623) + TX, permethrin (626) + TX, petroleum oils (628) + TX, PH 60-38 (development code) (1328) + TX, phenkapton (1330) + TX, phenothrin (630) + TX, phenthoate (631) + TX, phorate (636) + TX, phosalone (637) + TX, phosfolan (1338) + TX, phosmet (638) + TX, phosnichlor (1339) + TX, phosphamidon (639) + TX, phosphine (IUPAC name) (640) + TX, phoxim (642) + TX, phoxim-methyl (1340) + TX, pirimetaphos (1344) + TX, pirimicarb (651) + TX, pirimiphos-ethyl (1345) + TX, pirimiphos-methyl (652) + TX, polychlorodicyclopentadiene isomers (IUPAC name) (1346) + TX, potassium arsenite [CCN] + TX, potassium thiocyanate [CCN] + TX, prallethrin (655) + TX, precocene I [CCN] + TX, precocene II [CCN] + TX, precocene III [CCN] + TX, primidophos (1349) + TX, profenofos (662) + TX, profluthrin [CCN] + TX, promacyl (1354) + TX, promecarb (1355) + TX, propaphos (1356) + TX, propetamphos (673) + TX, propoxur (678) + TX, prothidathion (1360) + TX, prothiofos (686) + TX, prothoate (1362) + TX, protrifenbute [CCN] + TX, pymetrozine (688) + TX, pyraclofos (689) + TX, pyrazophos (693) + TX, pyresmethrin (1367) + TX, pyrethrin I (696) + TX, pyrethrin II (696) + TX, pyrethrins (696) + TX, pyridaben (699) + TX, pyridalyl (700) + TX, pyridaphenthion (701) + TX, pyrimidifen (706) + TX, pyrimitate (1370) + TX, pyriproxyfen (708) + TX, quassia [CCN] + TX, quinalphos (711) + TX, quinalphos-methyl (1376) + TX, quinothion (1380) + TX, quintiofos (1381) + TX, R-1492 (development code) (1382) + TX, rafoxanide [CCN] + TX, resmethrin (719) + TX, rotenone (722) + TX, RU 15525 (development code) (723) + TX, RU 25475 (development code) (1386) + TX, ryania (1387) + TX, ryanodine (traditional name) (1387) + TX, sabadilla (725) + TX, schradan (1389) + TX, sebufos + TX, selamectin [CCN] + TX, SI-0009 (compound code) + TX, SI-0205 (compound code) + TX, SI-0404 (compound code) + TX, SI-0405 (compound code) + TX, silafluofen (728) + TX, SN 72129 (development code) (1397) + TX, sodium arsenite [CCN] + TX, sodium cyanide (444) + TX, sodium fluoride (IUPAC/Chemical Abstracts name) (1399) + TX, sodium hexafluorosilicate (1400) + TX, sodium pentachlorophenoxide (623) + TX, sodium selenate (IUPAC name) (1401) + TX, sodium thiocyanate [CCN] + TX, sophamide (1402) + TX, spinosad (737) + TX, spiromesifen (739) + TX, spiropidion (CCN) + TX, spirotetrmat (CCN) + TX, sulcofuron (746) + TX, sulcofuron-sodium (746) + TX, sulfluramid (750) + TX, sulfotep (753) + TX, sulfuryl fluoride (756) + TX, sulprofos (1408) + TX, tar oils (758) + TX, tau-fluvalinate (398) + TX, tazimcarb (1412) + TX, TDE (1414) + TX, tebufenozide (762) + TX, tebufenpyrad (763) + TX, tebupirimfos (764) + TX, teflubenzuron (768) +

TX, tefluthrin (769) + TX, temephos (770) + TX, TEPP (1417) + TX, terallethrin (1418) + TX, terbam + TX, terbufos (773) + TX, tetrachloroethane [CCN] + TX, tetrachlorvinphos (777) + TX, tetramethrin (787) + TX, theta-cypermethrin (204) + TX, thiacloprid (791) + TX, thiafenox + TX, thiamethoxam (792) + TX, thicrofos (1428) + TX, thiocarboxime (1431) + TX, thiocyclam (798) + TX, thiocyclam hydrogen oxalate (798) + TX, thiodicarb (799) + TX, thiofanox (800) + TX, thiometon (801) + TX, thionazin (1434) + TX, thiosultap (803) + TX, thiosultap-sodium (803) + TX, thuringiensin [CCN] + TX, tolfenpyrad (809) + TX, tralomethrin (812) + TX, transfluthrin (813) + TX, transpermethrin (1440) + TX, triamiphos (1441) + TX, triazamate (818) + TX, triazophos (820) + TX, triazuron + TX, trichlorfon (824) + TX, trichlormetaphos-3 [CCN] + TX, trichloronat (1452) + TX, trifenofos (1455) + TX, triflumuron (835) + TX, trimethacarb (840) + TX, triprene (1459) + TX, vamidothion (847) + TX, vaniliprole [CCN] + TX, veratridine (725) + TX, veratrine (725) + TX, XMC (853) + TX, xylylcarb (854) + TX, YI-5302 (compound code) + TX, zeta-cypermethrin (205) + TX, zetamethrin + TX, zinc phosphide (640) + TX, zolaprofos (1469) and ZXI 8901 (development code) (858) + TX, cyantraniliprole [736994-63-19 + TX, chlorantraniliprole [500008-45-7] + TX, cyenopyrafen [560121-52-0] + TX, cyflumetofen [400882-07-7] + TX, pyrifluquinazon [337458-27-2] + TX, spinetoram [187166-40-1 + 187166-15-0] + TX, spirotetramat [203313-25-1] + TX, sulfoxaflor [946578-00-3] + TX, flufiprole [704886-18-0] + TX, meperfluthrin [915288-13-0] + TX, tetramethylfluthrin [84937-88-2] + TX, triflumezopyrim (disclosed in WO 2012/092115) + TX,

a molluscicide selected from the group of substances consisting of bis(tributyltin) oxide (IUPAC name) (913) + TX, bromoacetamide [CCN] + TX, calcium arsenate [CCN] + TX, cloethocarb (999) + TX, copper acetoarsenite [CCN] + TX, copper sulfate (172) + TX, fentin (347) + TX, ferric phosphate (IUPAC name) (352) + TX, metaldehyde (518) + TX, methiocarb (530) + TX, niclosamide (576) + TX, niclosamide-olamine (576) + TX, pentachlorophenol (623) + TX, sodium pentachlorophenoxide (623) + TX, tazimcarb (1412) + TX, thiodicarb (799) + TX, tributyltin oxide (913) + TX, trifenmorph (1454) + TX, trimethacarb (840) + TX, triphenyltin acetate (IUPAC name) (347) and triphenyltin hydroxide (IUPAC name) (347) + TX, pyriprole [394730-71-3] + TX,

a nematicide selected from the group of substances consisting of AKD-3088 (compound code) + TX, 1,2-dibromo-3-chloropropane (IUPAC/Chemical Abstracts name) (1045) + TX, 1,2-dichloropropane (IUPAC/ Chemical Abstracts name) (1062) + TX, 1,2-dichloropropane with 1,3-dichloropropene (IUPAC name) (1063) + TX, 1,3-dichloropropene (233) + TX, 3,4-dichlorotetrahydrothiophene 1,1-dioxide (IUPAC/Chemical Abstracts name) (1065) + TX, 3-(4-chlorophenyl)-5-methylrhodanine (IUPAC name) (980) + TX, 5-methyl-6-thioxo-1,3,5-thiadiazinan-3-ylacetic acid (IUPAC name) (1286) + TX, 6-isopentenylaminopurine (210) + TX, abamectin (1) + TX, acetoprole [CCN] + TX, alanycarb (15) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, AZ 60541 (compound code) + TX, benclothiaz [CCN] + TX, benomyl (62) + TX, butylpyridaben + TX, cadusafos (109) + TX, carbofuran (118) + TX, carbon disulfide (945) + TX, carbosulfan (119) + TX, chloropicrin (141) + TX, chlorpyrifos (145) + TX, cloethocarb (999) + TX, cytokinins (210) + TX, dazomet (216) + TX, DBCP (1045) + TX, DCIP (218) + TX, diamidafos (1044) + TX,

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

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 (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 (850) + TX, coumachlor (1004) + TX, coumafuryl (1005) + TX, coumatetralyl (175) + TX, crimidine (1009) + TX, difenacoum (246) + TX, difethialone (249) + TX, diphacinone (273) + TX, ergocalciferol (301) + TX, flocoumafen (357) + TX, fluoroacetamide (379) + TX, flupropadine (1183) + TX, flupropadine hydrochloride (1183) + TX, gamma-HCH (430) + TX, HCH (430) + TX, hydrogen cyanide (444) + TX, iodomethane (IUPAC name) (542) + TX, lindane (430) + TX, magnesium phosphide (IUPAC name) (640) + TX, methyl bromide (537) + TX, norbormide (1318) + TX, phosacetim (1336) + TX, phosphine (IUPAC name) (640) + TX, phosphorus [CCN] + TX, pindone (1341) + TX, potassium arsenite [CCN] + TX, pyrinuron (1371) + TX, scilliroside (1390) + TX, sodium arsenite [CCN] + TX, sodium cyanide (444) + TX, sodium fluoroacetate (735) + TX, strychnine (745) + TX, thallium sulfate [CCN] + TX, warfarin (851) and zinc phosphide (640) + TX,

a synergist selected from the group of substances consisting of 2-(2-butoxyethoxy)ethyl piperonylate (IUPAC name) (934) + TX, 5-(1,3-benzodioxol-5-yl)-3-hexylcyclohex-2-enone (IUPAC name) (903) + TX, farnesol with nerolidol (324) + TX, MB-599 (development code) (498) + TX, MGK 264 (development code) (296) + TX, piperonyl butoxide (649) + TX, piprotal (1343) + TX,

propyl isomer (1358) + TX, S421 (development code) (724) + TX, sesamex (1393) + TX, sesasmolin (1394) and sulfoxide (1406) + TX,

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

a virucide selected from the group of substances consisting of imanin [CCN] and ribavirin [CCN] + TX,

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

and biologically active compounds selected from the group consisting of azaconazole (60207-31-0) + TX, bitertanol [70585-36-3] + TX, bromuconazole [116255-48-2] + TX, cyproconazole [94361-06-5] + TX, difenoconazole [119446-68-3] + TX, diniconazole [83657-24-3] + TX, epoxiconazole [106325-08-0] + TX, fenbuconazole [114369-43-6] + TX, fluquinconazole [136426-54-5] + TX, flusilazole [85509-19-9] + TX, flutriafol [76674-21-0] + TX, hexaconazole [79983-71-4] + TX, imazalil [35554-44-0] + TX, imibenconazole [86598-92-7] + TX, ipconazole [125225-28-7] + TX, metconazole [125116-23-6] + TX, myclobutanil [88671-89-0] + TX, pefurazoate [101903-30-4] + TX, penconazole [66246-88-6] + TX, prothioconazole [178928-70-6] + TX, pyrifenox [88283-41-4] + TX, prochloraz [67747-09-5] + TX, propiconazole [60207-90-1] + TX, simeconazole [149508-90-7] + TX, tebuconazole [107534-96-3] + TX, tetraconazole [112281-77-3] + TX, triadimefon [43121-43-3] + TX, triadimenol [55219-65-3] + TX, triflumizole [99387-89-0] + TX, triticonazole [131983-72-7] + TX, ancymidol [12771-68-5] + TX, fenarimol [60168-88-9] + TX, nuarimol [63284-71-9] + TX, bupirimate [41483-43-6] + TX, dimethirimol [5221-53-4] + TX, ethirimol [23947-60-6] + TX, dodemorph [1593-77-7] + TX, fenpropidine [67306-00-7] + TX, fenpropimorph [67564-91-4] + TX, spiroxamine [118134-30-8] + TX, tridemorph [81412-43-3] + TX, cyprodinil [121552-61-2] + TX, mepanipyrim [110235-47-7] + TX, pyrimethanil [53112-28-0] + TX, fenpiclonil [74738-17-3] + TX, fludioxonil [131341-86-1] + TX, benalaxyl [71626-11-4] + TX, furalaxyl [57646-30-7] + TX, metalaxyl [57837-19-1] + TX, R-metalaxyl [70630-17-0] + TX, ofurace [58810-48-3] + TX, oxadixyl [77732-09-3] + TX, benomyl [17804-35-2] + TX, carbendazim [10605-21-7] + TX, debacarb [62732-91-6] + TX, fuberidazole [3878-19-1] + TX, thiabendazole [148-79-8] + TX, chlozolinate [84332-86-5] + TX, dichlozoline [24201-58-9] + TX, iprodione [36734-19-7] + TX, myclozoline [54864-61-8] + TX, procymidone [32809-16-8] + TX, vinclozoline [50471-44-8] + TX, boscalid [188425-85-6] + TX, carboxin [5234-68-4] + TX, fenfuram [24691-80-3] + TX, flutolanil [66332-96-5] + TX, mepronil [55814-41-0] + TX, oxycarboxin [5259-88-1] + TX, penthiopyrad [183675-82-3] + TX, thifluzamide [130000-40-7] + TX, guazatine [108173-90-6] + TX, dodine [2439-10-3] [112-65-2] (free base) + TX, iminoctadine [13516-27-3] + TX, azoxystrobin [131860-33-8] + TX, dimoxystrobin [149961-52-4] + TX, enestroburin {Proc. BCPC, Int. Congr., Glasgow, 2003, **1**, 93} +

TX, fluoxastrobin [361377-29-9] + TX, kresoxim-methyl [143390-89-0] + TX, metominostrobin [133408-50-1] + TX, trifloxystrobin [141517-21-7] + TX, orysastrobin [248593-16-0] + TX, picoxystrobin [117428-22-5] + TX, pyraclostrobin [175013-18-0] + TX, ferbam [14484-64-1] + TX, mancozeb [8018-01-7] + TX, maneb [12427-38-2] + TX, metiram [9006-42-2] + TX, propineb [12071-83-9] + TX, thiram [137-26-8] + TX, zineb [12122-67-7] + TX, ziram [137-30-4] + TX, captafol [2425-06-1] + TX, captan [133-06-2] + TX, dichlofluanid [1085-98-9] + TX, fluoroimide [41205-21-4] + TX, folpet [133-07-3] + TX, tolylfluanid [731-27-1] + TX, bordeaux mixture [8011-63-0] + TX, copperhydroxid [20427-59-2] + TX, copperoxychlorid [1332-40-7] + TX, coppersulfat [7758-98-7] + TX, copperoxid [1317-39-1] + TX, mancopper [53988-93-5] + TX, oxine-copper [10380-28-6] + TX, dinocap [131-72-6] + TX, nitrothal-isopropyl [10552-74-6] + TX, edifenphos [17109-49-8] + TX, iprobenphos [26087-47-8] + TX, isoprothiolane [50512-35-1] + TX, phosdiphen [36519-00-3] + TX, pyrazophos [13457-18-6] + TX, tolclofos-methyl [57018-04-9] + TX, acibenzolar-S-methyl [135158-54-2] + TX, anilazine [101-05-3] + TX, benthiavalicarb [413615-35-7] + TX, blasticidin-S [2079-00-7] + TX, chinomethionat [2439-01-2] + TX, chloroneb [2675-77-6] + TX, chlorothalonil *[1897-45-6]* + TX, cyflufenamid *[180409-60-3]* + TX, cymoxanil *[57966-95-7]* + TX, dichlone *[117-80-6]* + TX, diclocymet [139920-32-4] + TX, diclomezine *[62865-36-5]* + TX, dicloran *[99-30-9]* + TX, diethofencarb *[87130-20-9]* + TX, dimethomorph *[110488-70-5]* + TX, SYP-LI90 (Flumorph) *[211867-47-9]* + TX, dithianon *[3347-22-6]* + TX, ethaboxam *[162650-77-3]* + TX, etridiazole *[2593-15-9]* + TX, famoxadone *[131807-57-3] + TX,* fenamidone *[161326-34-7]* + TX, fenoxanil *[115852-48-7]* + TX, fentin *[668-34-8]* + TX, ferimzone *[89269-64-7]* + TX, fluazinam *[79622-59-6]* + TX, fluopicolide [239110-15-7] + TX, flusulfamide [106917-52-6] + TX, fenhexamid [126833-17-8] + TX, fosetyl-aluminium [39148-24-8] + TX, hymexazol [10004-44-1] + TX, iprovalicarb [140923-17-7] + TX, IKF-916 (Cyazofamid) *[120116-88-3]* + TX, kasugamycin [6980-18-3] + TX, methasulfocarb *[66952-49-6]* + TX, metrafenone *[220899-03-6]* + TX, pencycuron *[66063-05-6]* + TX, phthalide [27355-22-2] + TX, polyoxins [11113-80-7] + TX, probenazole [27605-76-1] + TX, propamocarb [25606-41-1] + TX, proquinazid [189278-12-4] + TX, pyroquilon [57369-32-1] + TX, quinoxyfen [124495-18-7] + TX, quintozene [82-68-8] + TX, sulfur [7704-34-9] + TX, tiadinil [223580-51-6] + TX, triazoxide [72459-58-6] + TX, tricyclazole [41814-78-2] + TX, triforine [26644-46-2] + TX, validamycin [37248-47-8] + TX, zoxamide (RH7281) [156052-68-5] + TX, mandipropamid [374726-62-2] + TX, isopyrazam [881685-58-1] + TX, sedaxane [874967-67-6] + TX, 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (9-dichloromethylene-1,2,3,4-tetrahydro-1,4-methano-naphthalen-5-yl)-amide (dislosed in WO 2007/048556) + TX, 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (3',4',5'-trifluoro-biphenyl-2-yl)-amide (disclosed in WO 2006/087343) + TX, [(3*S*,4*R*,4a*R*,6*S*,6a*S*,12*R*,12a*S*,12b*S*)-3-[(cyclopropylcarbonyl)oxy]- 1,3,4,4a,5,6,6a,12,12a,12b-decahydro-6,12-dihydroxy-4,6a,12b-trimethyl-11-oxo-9-(3-pyridinyl)-2*H*,11*H*naphtho[2,1-*b*]pyrano[3,4-*e*]pyran-4-yl]methyl-cyclopropanecarboxylate [915972-17-7] + TX and 1,3,5-trimethyl-N-(2-methyl-1-oxopropyl)-N-[3-(2-methylpropyl)-4-[2,2,2-trifluoro-1-methoxy-1-(trifluoromethyl)ethyl]phenyl]-1H-pyrazole-4-carboxamide [926914-55-8] + TX, lancotrione [1486617-21-3] + TX, florpyrauxifen [943832-81-3]] + TX, ipfentrifluconazole[1417782-08-1] + TX, mefentrifluconazole [1417782-03-6] + TX,

quinofumelin [861647-84-9] + TX, chloroprallethrin [399572-87-3] + TX, cyhalodiamide [1262605-53-7]] + TX, fluazaindolizine [1254304-22-7] + TX, fluxametamide [928783-29-3] + TX, epsilon-metofluthrin [240494-71-7] + TX, epsilon-momfluorothrin [1065124-65-3] + TX, pydiflumetofen [1228284-64-7] + TX, kappa-bifenthrin [439680-76-9] + TX, broflanilide [1207727-04-5] + TX, dicloromezotiaz [1263629-39-5] + TX, dipymetitrone [16114-35-5] + TX, pyraziflumid [942515-63-1] + TX, kappa-tefluthrin [391634-71-2] + TX, fenpicoxamid [517875-34-2] + TX, fluindapyr [1383809-87-7] + TX, alpha-bromadiolone [28772-56-7] + TX, flupyrimin [1689566-03-7] + TX, benzpyrimoxan [1449021-97-9] + TX, acynonapyr [1332838-17-1] + TX, inpyrfluxam [1352994-67-2] + TX, isoflucypram [1255734-28-1] + TX, rescalure [64309-03-1] + TX, fluxametamide [928783-29-3] + TX, tetraniliprole [1229654-66-3] + TX, guadipyr (described in WO2010/060231) + TX, cycloxaprid (described in WO 2005/077934) + TX, Afidopyropen + TX, kappa-bifenthrin + TX, kappa-tefluthrin + TX, Tetrachloraniliprole + TX, aminopyrifen [1531626-08-0] + TX, tyclopyrazoflor [1477919-27-9] + TX, Dichloromezotiaz + TX, Momfluorothrin + TX, Fluopyram + TX, Terpenoid blend + TX, Fluhexafon + TX, Cyclaniliprole + TX, and spiropidion [1229023-00-0] + TX; and

microbials including: *Acinetobacter lwoffii* + TX, *Acremonium alternatum* + TX + TX, *Acremonium cephalosporium* + TX + TX, *Acremonium diospyri* + TX, *Acremonium obclavatum* + TX, *Adoxophyes orana granulovirus* (AdoxGV) (Capex®) + TX, *Agrobacterium radiobacter* strain K84 (Galltrol-A®) + TX, *Alternaria alternate* + TX, *Alternaria cassia* + TX, *Alternaria destruens* (Smolder®) + TX, *Ampelomyces quisqualis* (AQ10®) + TX, *Aspergillus flavus* AF36 (AF36®) + TX, *Aspergillus flavus* NRRL 21882 (Aflaguard®) + TX, *Aspergillus* spp. + TX, *Aureobasidium pullulans* + TX, *Azospirillum* + TX, (MicroAZ® + TX, TAZO B®) + TX, *Azotobacter* + TX, *Azotobacter chroococcum* (Azotomeal®) + TX, *Azotobacter* cysts (Bionatural Blooming Blossoms®) + TX, *Bacillus amyloliquefaciens* + TX, *Bacillus cereus* + TX, *Bacillus chitinosporus* strain CM-1 + TX, *Bacillus chitinosporus* strain AQ746 + TX, *Bacillus licheniformis* strain HB-2 (Biostart™ Rhizoboost®) + TX, *Bacillus licheniformis* strain 3086 (EcoGuard® + TX, Green Releaf®) + TX, *Bacillus circulans* + TX, *Bacillus firmus* (BioSafe®, BioNem-WP®, VOTiVO®) + TX, *Bacillus firmus* strain I-1582 + TX, *Bacillus macerans* + TX, *Bacillus marismortui* + TX, *Bacillus megaterium* + TX, *Bacillus mycoides* strain AQ726 + TX, *Bacillus papillae* (Milky Spore Powder®) + TX, *Bacillus pumilus* spp. + TX, *Bacillus pumilus* strain GB34 (Yield Shield®) + TX, *Bacillus pumilus* strain AQ717 + TX, *Bacillus pumilus* strain QST 2808 (Sonata® + TX, Ballad Plus®) + TX, *Bacillus spahericus* (VectoLex®) + TX, *Bacillus* spp. + TX, *Bacillus* spp. strain AQ175 + TX, *Bacillus* spp. strain AQ177 + TX, *Bacillus* spp. strain AQ178 + TX, *Bacillus subtilis* strain QST 713 (CEASE® + TX, Serenade® + TX, Rhapsody®) + TX, *Bacillus subtilis* strain QST 714 (JAZZ®) + TX, *Bacillus subtilis* strain AQ153 + TX, *Bacillus subtilis* strain AQ743 + TX, *Bacillus subtilis* strain QST3002 + TX, *Bacillus subtilis* strain QST3004 + TX, *Bacillus subtilis var. amyloliquefaciens* strain FZB24 (Taegro® + TX, Rhizopro®) + TX, *Bacillus thuringiensis* Cry 2Ae + TX, *Bacillus thuringiensis* Cry1Ab + TX, *Bacillus thuringiensis aizawai* GC 91 (Agree®) + TX, *Bacillus thuringiensis israelensis* (BMP123® + TX, Aquabac® + TX, VectoBac®) + TX, *Bacillus thuringiensis kurstaki* (Javelin® + TX, Deliver® + TX, CryMax® + TX, Bonide® + TX, Scutella WP® + TX, Turilav WP ® + TX, Astuto® + TX, Dipel WP® + TX, Biobit® + TX, Foray®) + TX, *Bacillus thuringiensis kurstaki* BMP 123 (Baritone®) +

TX, *Bacillus thuringiensis kurstaki* HD-1 (Bioprotec-CAF / 3P®) + TX, *Bacillus thuringiensis* strain BD#32 + TX, *Bacillus thuringiensis* strain AQ52 + TX, *Bacillus thuringiensis var. aizawai* (XenTari® + TX, DiPel®) + TX, bacteria spp. (GROWMEND® + TX, GROWSWEET® + TX, Shootup®) + TX, bacteriophage of *Clavipacter michiganensis* (AgriPhage®) + TX, Bakflor® + TX, *Beauveria bassiana* (Beaugenic® + TX, Brocaril WP®) + TX, *Beauveria bassiana* GHA (Mycotrol ES® + TX, Mycotrol O® + TX, BotaniGuard®) + TX, *Beauveria brongniartii* (Engerlingspilz® + TX, Schweizer Beauveria® + TX, Melocont®) + TX, *Beauveria* spp. + TX, *Botrytis cineria* + TX, *Bradyrhizobium japonicum* (TerraMax®) + TX, *Brevibacillus brevis* + TX, *Bacillus thuringiensis tenebrionis* (Novodor®) + TX, BtBooster + TX, *Burkholderia cepacia* (Deny® + TX, Intercept® + TX, Blue Circle®) + TX, *Burkholderia gladii* + TX, *Burkholderia gladioli* + TX, *Burkholderia* spp. + TX, Canadian thistle fungus (CBH Canadian Bioherbicide®) + TX, *Candida butyri* + TX, *Candida famata* + TX, *Candida fructus* + TX, *Candida glabrata* + TX, *Candida guilliermondii* + TX, *Candida melibiosica* + TX, *Candida oleophila* strain O + TX, *Candida parapsilosis* + TX, *Candida pelliculosa* + TX, *Candida pulcherrima* + TX, *Candida reukaufii* + TX, *Candida saitoana* (Bio-Coat® + TX, Biocure®) + TX, *Candida sake* + TX, *Candida* spp. + TX, *Candida tenius* + TX, *Cedecea dravisae* + TX, *Cellulomonas flavigena* + TX, *Chaetomium cochliodes* (Nova-Cide®) + TX, *Chaetomium globosum* (Nova-Cide®) + TX, *Chromobacterium subtsugae* strain PRAA4-1T (Grandevo®) + TX, *Cladosporium cladosporioides* + TX, *Cladosporium oxysporum* + TX, *Cladosporium chlorocephalum* + TX, *Cladosporium* spp. + TX, *Cladosporium tenuissimum* + TX, *Clonostachys rosea* (EndoFine®) + TX, *Colletotrichum acutatum* + TX, *Coniothyrium minitans* (Cotans WG®) + TX, *Coniothyrium* spp. + TX, *Cryptococcus albidus* (YIELDPLUS®) + TX, *Cryptococcus humicola* + TX, *Cryptococcus infirmo-miniatus* + TX, *Cryptococcus laurentii* + TX, *Cryptophlebia leucotreta granulovirus* (Cryptex®) + TX, *Cupriavidus campinensis* + TX, *Cydia pomonella granulovirus* (CYD-X®) + TX, *Cydia pomonella granulovirus* (Madex® + TX, Madex Plus® + TX, Madex Max/ Carpovirusine®) + TX, *Cylindrobasidium laeve* (Stumpout®) + TX, *Cylindrocladium* + TX, *Debaryomyces hansenii* + TX, *Drechslera hawaiinensis* + TX, *Enterobacter cloacae* + TX, *Enterobacteriaceae* + TX, *Entomophtora virulenta* (Vektor®) + TX, *Epicoccum nigrum* + TX, *Epicoccum purpurascens* + TX, *Epicoccum* spp. + TX, *Filobasidium floriforme* + TX, *Fusarium acuminatum* + TX, *Fusarium chlamydosporum* + TX, *Fusarium oxysporum* (Fusaclean® / Biofox C®) + TX, *Fusarium proliferatum* + TX, *Fusarium* spp. + TX, *Galactomyces geotrichum* + TX, *Gliocladium catenulatum* (Primastop® + TX, Prestop®) + TX, *Gliocladium roseum* + TX, *Gliocladium* spp. (SoilGard®) + TX, *Gliocladium virens* (Soilgard®) + TX, *Granulovirus* (Granupom®) + TX, *Halobacillus halophilus* + TX, *Halobacillus litoralis* + TX, *Halobacillus trueperi* + TX, *Halomonas* spp. + TX, *Halomonas subglaciescola* + TX, *Halovibrio variabilis* + TX, *Hanseniaspora uvarum* + TX, *Helicoverpa armigera nucleopolyhedrovirus* (Helicovex®) + TX, *Helicoverpa zea nuclear polyhedrosis virus* (Gemstar®) + TX, Isoflavone – formononetin (Myconate®) + TX, *Kloeckera apiculata* + TX, *Kloeckera* spp. + TX, *Lagenidium giganteum* (Laginex®) + TX, *Lecanicillium longisporum* (Vertiblast®) + TX, *Lecanicillium muscarium* (Vertikil®) + TX, *Lymantria Dispar nucleopolyhedrosis virus* (Disparvirus®) + TX, *Marinococcus halophilus* + TX, *Meira geulakonigii* + TX, *Metarhizium anisopliae* (Met52®) + TX, *Metarhizium anisopliae* (Destruxin WP®) + TX, *Metschnikowia*

fruticola (Shemer®) + TX, *Metschnikowia pulcherrima* + TX, *Microdochium dimerum* (Antibot®) + TX, *Micromonospora coerulea* + TX, *Microsphaeropsis ochracea* + TX, *Muscodor albus* 620 (Muscudor®) + TX, *Muscodor roseus* strain A3-5 + TX, *Mycorrhizae* spp. (AMykor® + TX, Root Maximizer®) + TX, *Myrothecium verrucaria* strain AARC-0255 (DiTera®) + TX, BROS PLUS® + TX, *Ophiostoma piliferum* strain D97 (Sylvanex®) + TX, *Paecilomyces farinosus* + TX, *Paecilomyces fumosoroseus* (PFR-97® + TX, PreFeRal®) + TX, *Paecilomyces linacinus* (Biostat WP®) + TX, *Paecilomyces lilacinus* strain 251 (MeloCon WG®) + TX, *Paenibacillus polymyxa* + TX, *Pantoea agglomerans* (BlightBan C9-1®) + TX, *Pantoea* spp. + TX, *Pasteuria* spp. (Econem®) + TX, *Pasteuria nishizawae* + TX, *Penicillium aurantiogriseum* + TX, *Penicillium billai* (Jumpstart® + TX, TagTeam®) + TX, *Penicillium brevicompactum* + TX, *Penicillium frequentans* + TX, *Penicillium griseofulvum* + TX, *Penicillium purpurogenum* + TX, *Penicillium* spp. + TX, *Penicillium viridicatum* + TX, *Phlebiopsis gigantean* (Rotstop®) + TX, phosphate solubilizing bacteria (Phosphomeal®) + TX, *Phytophthora cryptogea* + TX, *Phytophthora palmivora* (Devine®) + TX, *Pichia anomala* + TX, *Pichia guilermondii* + TX, *Pichia membranaefaciens* + TX, *Pichia onychis* + TX, *Pichia stipites* + TX, *Pseudomonas aeruginosa* + TX, *Pseudomonas aureofasciens* (Spot-Less Biofungicide®) + TX, *Pseudomonas cepacia* + TX, *Pseudomonas chlororaphis* (AtEze®) + TX, *Pseudomonas corrugate* + TX, *Pseudomonas fluorescens* strain A506 (BlightBan A506®) + TX, *Pseudomonas putida* + TX, *Pseudomonas reactans* + TX, *Pseudomonas* spp. + TX, *Pseudomonas syringae* (Bio-Save®) + TX, *Pseudomonas viridiflava* + TX, *Pseudomons fluorescens* (Zequanox®) + TX, *Pseudozyma flocculosa* strain PF-A22 UL (Sporodex L®) + TX, *Puccinia canaliculata* + TX, *Puccinia thlaspeos* (Wood Warrior®) + TX, *Pythium paroecandrum* + TX, *Pythium oligandrum* (Polygandron® + TX, Polyversum®) + TX, *Pythium periplocum* + TX, *Rhanella aquatilis* + TX, *Rhanella* spp. + TX, *Rhizobia* (Dormal® + TX, Vault®) + TX, *Rhizoctonia* + TX, *Rhodococcus globerulus* strain AQ719 + TX, *Rhodosporidium diobovatum* + TX, *Rhodosporidium toruloides* + TX, *Rhodotorula* spp. + TX, *Rhodotorula glutinis* + TX, *Rhodotorula graminis* + TX, *Rhodotorula mucilagnosa* + TX, *Rhodotorula rubra* + TX, *Saccharomyces cerevisiae* + TX, *Salinococcus roseus* + TX, *Sclerotinia minor* + TX, *Sclerotinia minor* (SARRITOR®) + TX, *Scytalidium* spp. + TX, *Scytalidium uredinicola* + TX, *Spodoptera exigua nuclear polyhedrosis virus* (Spod-X® + TX, Spexit®) + TX, *Serratia marcescens* + TX, *Serratia plymuthica* + TX, *Serratia* spp. + TX, *Sordaria fimicola* + TX, *Spodoptera littoralis nucleopolyhedrovirus* (Littovir®) + TX, *Sporobolomyces roseus* + TX, *Stenotrophomonas maltophilia* + TX, *Streptomyces ahygroscopicus* + TX, *Streptomyces albaduncus* + TX, *Streptomyces exfoliates* + TX, *Streptomyces galbus* + TX, *Streptomyces griseoplanus* + TX, *Streptomyces griseoviridis* (Mycostop®) + TX, *Streptomyces lydicus* (Actinovate®) + TX, *Streptomyces lydicus* WYEC-108 (ActinoGrow®) + TX, *Streptomyces violaceus* + TX, *Tilletiopsis minor* + TX, *Tilletiopsis* spp. + TX, *Trichoderma asperellum* (T34 Biocontrol®) + TX, *Trichoderma gamsii* (Tenet®) + TX, *Trichoderma atroviride* (Plantmate®) + TX, *Trichoderma hamatum* TH 382 + TX, *Trichoderma harzianum rifai* (Mycostar®) + TX, *Trichoderma harzianum* T-22 (Trianum-P® + TX, PlantShield HC® + TX, RootShield® + TX, Trianum-G®) + TX, *Trichoderma harzianum* T-39 (Trichodex®) + TX, *Trichoderma inhamatum* + TX, *Trichoderma koningii* + TX, *Trichoderma* spp. LC 52 (Sentinel®) + TX, *Trichoderma lignorum* + TX, *Trichoderma longibrachiatum* + TX, *Trichoderma*

polysporum (Binab T®) + TX, *Trichoderma taxi* + TX, *Trichoderma virens* + TX, *Trichoderma virens* (formerly Gliocladium virens GL-21) (SoilGuard®) + TX, *Trichoderma viride* + TX, *Trichoderma viride* strain ICC 080 (Remedier®) + TX, *Trichosporon pullulans* + TX, *Trichosporon* spp. + TX, *Trichothecium* spp. + TX, *Trichothecium roseum* + TX, *Typhula phacorrhiza* strain 94670 + TX, *Typhula phacorrhiza* strain 94671 + TX, *Ulocladium atrum* + TX, *Ulocladium oudemansii* (Botry-Zen®) + TX, *Ustilago maydis* + TX, various bacteria and supplementary micronutrients (Natural II®) + TX, various fungi (Millennium Microbes®) + TX, *Verticillium chlamydosporium* + TX, *Verticillium lecanii* (Mycotal® + TX, Vertalec®) + TX, Vip3Aa20 (VIPtera®) + TX, *Virgibaclillus marismortui* + TX, *Xanthomonas campestris pv. Poae* (Camperico®) + TX, *Xenorhabdus bovienii* + TX, *Xenorhabdus nematophilus*, and

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

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

Macrobials including: *Aphelinus abdominalis* + TX, *Aphidius ervi* (Aphelinus-System®) + TX, *Acerophagus papaya* + TX, *Adalia bipunctata* (Adalia-System®) + TX, *Adalia bipunctata* (Adaline®) + TX, *Adalia bipunctata* (Aphidalia®) + TX, *Ageniaspis citricola* + TX, *Ageniaspis fuscicollis* + TX, *Amblyseius andersoni* (Anderline® + TX, Andersoni-System®) + TX, *Amblyseius californicus* (Amblyline® + TX, Spical®) + TX, *Amblyseius cucumeris* (Thripex® + TX, Bugline cucumeris®) + TX,

Amblyseius fallacis (Fallacis®) + TX, *Amblyseius swirskii* (Bugline swirskii® + TX, Swirskii-Mite®) + TX, *Amblyseius womersleyi* (WomerMite®) + TX, *Amitus hesperidum* + TX, *Anagrus atomus* + TX, *Anagyrus fusciventris* + TX, *Anagyrus kamali* + TX, *Anagyrus loecki* + TX, *Anagyrus pseudococci* (Citripar®) + TX, *Anicetus benefices* + TX, *Anisopteromalus calandrae* + TX, *Anthocoris nemoralis* (Anthocoris-System®) + TX, *Aphelinus abdominalis* (Apheline® + TX, Aphiline®) + TX, *Aphelinus asychis* + TX, *Aphidius colemani* (Aphipar®) + TX, *Aphidius ervi* (Ervipar®) + TX, *Aphidius gifuensis* + TX, *Aphidius matricariae* (Aphipar-M®) + TX, *Aphidoletes aphidimyza* (Aphidend®) + TX, *Aphidoletes aphidimyza* (Aphidoline®) + TX, *Aphytis lingnanensis* + TX, *Aphytis melinus* + TX, *Aprostocetus hagenowii* + TX, *Atheta coriaria* (Staphyline®) + TX, *Bombus* spp. + TX, *Bombus terrestris* (Natupol Beehive®) + TX, *Bombus terrestris* (Beeline® + TX, Tripol®) + TX, *Cephalonomia stephanoderis* + TX, *Chilocorus nigritus* + TX, *Chrysoperla carnea* (Chrysoline®) + TX, *Chrysoperla carnea* (Chrysopa®) + TX, *Chrysoperla rufilabris* + TX, *Cirrospilus ingenuus* + TX, *Cirrospilus quadristriatus* + TX, *Citrostichus phyllocnistoides* + TX, *Closterocerus chamaeleon* + TX, *Closterocerus* spp. + TX, *Coccidoxenoides perminutus* (Planopar®) + TX, *Coccophagus cowperi* + TX, *Coccophagus lycimnia* + TX, *Cotesia flavipes* + TX, *Cotesia plutellae* + TX, *Cryptolaemus montrouzieri* (Cryptobug® + TX, Cryptoline®) + TX, *Cybocephalus nipponicus* + TX, *Dacnusa sibirica* + TX, *Dacnusa sibirica* (Minusa®) + TX, *Diglyphus isaea* (Diminex®) + TX, *Delphastus catalinae* (Delphastus®) + TX, *Delphastus pusillus* + TX, *Diachasmimorpha krausii* + TX, *Diachasmimorpha longicaudata* + TX, *Diaparsis jucunda* + TX, *Diaphorencyrtus aligarhensis* + TX, *Diglyphus isaea* + TX, *Diglyphus isaea* (Miglyphus® + TX, Digline®) + TX, *Dacnusa sibirica* (DacDigline® + TX, Minex®) + TX, *Diversinervus* spp. + TX, *Encarsia citrina* + TX, *Encarsia formosa* (Encarsia max® + TX, Encarline® + TX, En-Strip®) + TX, *Eretmocerus eremicus* (Enermix®) + TX, *Encarsia guadeloupae* + TX, *Encarsia haitiensis* + TX, *Episyrphus balteatus* (Syrphidend®) + TX, *Eretmoceris siphonini* + TX, *Eretmocerus californicus* + TX, *Eretmocerus eremicus* (Ercal® + TX, Eretline e®) + TX, *Eretmocerus eremicus* (Bemimix®) + TX, *Eretmocerus hayati* + TX, *Eretmocerus mundus* (Bemipar® + TX, Eretline m®) + TX, *Eretmocerus siphonini* + TX, *Exochomus quadripustulatus* + TX, *Feltiella acarisuga* (Spidend®) + TX, *Feltiella acarisuga* (Feltiline®) + TX, *Fopius arisanus* + TX, *Fopius ceratitivorus* + TX, Formononetin (Wirless Beehome®) + TX, *Franklinothrips vespiformis* (Vespop®) + TX, *Galendromus occidentalis* + TX, *Goniozus legneri* + TX, *Habrobracon hebetor* + TX, *Harmonia axyridis* (HarmoBeetle®) + TX, *Heterorhabditis* spp. (Lawn Patrol®) + TX, *Heterorhabditis bacteriophora* (NemaShield HB® + TX, Nemaseek® + TX, Terranem-Nam® + TX, Terranem® + TX, Larvanem® + TX, B-Green® + TX, NemAttack ® + TX, Nematop®) + TX, *Heterorhabditis megidis* (Nemasys H® + TX, BioNem H® + TX, Exhibitline hm® + TX, Larvanem-M®) + TX, *Hippodamia convergens* + TX, *Hypoaspis aculeifer* (Aculeifer-System® + TX, Entomite-A®) + TX, *Hypoaspis miles* (Hypoline m® + TX, Entomite-M®) + TX, *Lbalia leucospoides* + TX, *Lecanoideus floccissimus* + TX, *Lemophagus errabundus* + TX, *Leptomastidea abnormis* + TX, *Leptomastix dactylopii* (Leptopar®) + TX, *Leptomastix epona* + TX, *Lindorus lophanthae* + TX, *Lipolexis oregmae* + TX, *Lucilia caesar* (Natufly®) + TX, *Lysiphlebus testaceipes* + TX, *Macrolophus caliginosus* (Mirical-N® + TX, Macroline c® + TX, Mirical®) + TX, *Mesoseiulus longipes* + TX, *Metaphycus flavus* + TX, *Metaphycus lounsburyi*

+ TX, *Micromus angulatus* (Milacewing®) + TX, *Microterys flavus* + TX, *Muscidifurax raptorellus* and *Spalangia cameroni* (Biopar®) + TX, *Neodryinus typhlocybae* + TX, *Neoseiulus californicus* + TX, *Neoseiulus cucumeris* (THRYPEX®) + TX, *Neoseiulus fallacis* + TX, *Nesideocoris tenuis* (NesidioBug® + TX, Nesibug®) + TX, *Ophyra aenescens* (Biofly®) + TX, *Orius insidiosus* (Thripor-I® + TX, Oriline i®) + TX, *Orius laevigatus* (Thripor-L® + TX, Oriline l®) + TX, *Orius majusculus* (Oriline m®) + TX, *Orius strigicollis* (Thripor-S®) + TX, *Pauesia juniperorum* + TX, *Pediobius foveolatus* + TX, *Phasmarhabditis hermaphrodita* (Nemaslug®) + TX, *Phymastichus coffea* + TX, *Phytoseiulus macropilus* + TX, *Phytoseiulus persimilis* (Spidex® + TX, Phytoline p®) + TX, *Podisus maculiventris* (Podisus®) + TX, *Pseudacteon curvatus* + TX, *Pseudacteon obtusus* + TX, *Pseudacteon tricuspis* + TX, *Pseudaphycus maculipennis* + TX, *Pseudleptomastix mexicana* + TX, *Psyllaephagus pilosus* + TX, *Psyttalia concolor* (complex) + TX, *Quadrastichus* spp. + TX, *Rhyzobius lophanthae* + TX, *Rodolia cardinalis* + TX, *Rumina decollate* + TX, *Semielacher petiolatus* + TX, *Sitobion avenae* (Ervibank®) + TX, *Steinernema carpocapsae* (Nematac C® + TX, Millenium® + TX, BioNem C® + TX, NemAttack® + TX, Nemastar® + TX, Capsanem®) + TX, *Steinernema feltiae* (NemaShield® + TX, Nemasys F® + TX, BioNem F® + TX, Steinernema-System® + TX, NemAttack® + TX, Nemaplus® + TX, Exhibitline sf® + TX, Scia-rid® + TX, Entonem®) + TX, *Steinernema kraussei* (Nemasys L® + TX, BioNem L® + TX, Exhibitline srb®) + TX, *Steinernema riobrave* (BioVector® + TX, BioVektor®) + TX, *Steinernema scapterisci* (Nematac S®) + TX, *Steinernema* spp. + TX, *Steinernematid* spp. (Guardian Nematodes®) + TX, *Stethorus punctillum* (Stethorus®) + TX, *Tamarixia radiate* + TX, *Tetrastichus setifer* + TX, *Thripobius semiluteus* + TX, *Torymus sinensis* + TX, *Trichogramma brassicae* (Tricholine b®) + TX, *Trichogramma brassicae* (Tricho-Strip®) + TX, *Trichogramma evanescens* + TX, *Trichogramma minutum* + TX, *Trichogramma ostriniae* + TX, *Trichogramma platneri* + TX, *Trichogramma pretiosum* + TX, *Xanthopimpla stemmator*, and

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

The references in brackets behind the active ingredients, e.g. *[3878-19-1]* refer to the Chemical Abstracts Registry number. The above described mixing partners are known. Where the active ingredients are included in "The Pesticide Manual" [The Pesticide Manual - A World Compendium, Thirteenth Edition, Editor: C. D. S. TomLin, The British Crop Protection Council], they are described

therein under the entry number given in round brackets hereinabove for the particular compound, for example, the compound "abamectin" is described under entry number (1). Where "[CCN]" is added hereinabove to the particular compound, the compound in question is included in the "Compendium of Pesticide Common Names", which is accessible on the internet [A. Wood, Compendium of Pesticide Common Names, Copyright © 1995-2004], for example, the compound "acetoprole" is described under the internet address http://www.alanwood.net/pesticides/acetoprole.html.

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

The ratio (by weight) of active ingredient mixture of the compounds of formula I selected from Tables 1 and A with active ingredients described above is 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.

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

In a further aspect, the present invention provides a combination of active ingredients comprising a compound defined in the first aspect, and one or more further active ingredients (whether chemical or biological).

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

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

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

A preferred method of application in the field of crop protection is application to the foliage of the plants (foliar application), it being possible to select frequency and rate of application to match the danger of infestation with the pest in question. Alternatively, the active ingredient can reach the plants via the root system (systemic action), by drenching the locus of the plants with a liquid composition or by incorporating the active ingredient in solid form into the 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 compounds of the invention and compositions thereof are also be suitable for the protection of plant propagation material, for example seeds, such as fruit, tubers or kernels, or nursery plants, against pests of the abovementioned type. The propagation material can be treated with the compound prior to planting, for example seed can be treated prior to sowing. Alternatively, the compound can be applied to seed kernels (coating), either by soaking the kernels in a liquid composition or by applying a layer of a solid composition. It is also possible to apply the compositions when the propagation material is planted to the site of application, for example into the seed furrow during drilling. These treatment methods for plant propagation material and the plant propagation material thus treated are further subjects of the invention. Typical treatment rates would depend on the plant and pest/fungi to be controlled and are generally between 1 to 200 grams per 100 kg of seeds, preferably between 5 to 150 grams per 100 kg of seeds, such as between 10 to 100 grams per 100 kg of seeds.

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

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

application. When the said seed product is (re)planted, it may absorb the active ingredient. In an embodiment, the present invention makes available a plant propagation material adhered thereto with a compound of formula I . Further, it is hereby made available, a composition comprising a plant propagation material treated with a compound of formula I .

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

The compounds of the invention can be distinguished from other similar compounds by virtue of greater efficacy at low application rates, which can be verified by the person skilled in the art using the experimental procedures outlined in the Examples below, using lower concentrations if necessary, for example 10 ppm, 5 ppm, 2 ppm, 1 ppm or 0.2 ppm; or lower application rates, such as 300, 200 or 100, mg of AI per m^2.

An aspect of the present invention is a method of controlling insects, acarines, nematodes or molluscs which comprises applying an insecticidally, acaricidally, nematicidally or molluscicidally effective amount of a compound of formula I defined the first aspect, or a composition containing a compound of formula I defined the first aspect, to a pest, a locus of pest, preferably a plant, to a plant susceptible to attack by a pest or to plant propagation material thereof, such as a seed, provided if the the control were on a human or animal body, then it is non-therapeutical.

A further aspect is a plant propagation material comprising by way of treatment or coating one or more compounds of formula I defined the first aspect, optionally also comprising a colour pigment.

In each aspect and embodiment of the invention, "consisting essentially" and inflections thereof are a preferred embodiment of "comprising" and its inflections, and "consisting of" and inflections thereof are a preferred embodiment of "consisting essentially of" and its inflections.

The disclosure in the present application makes available each and every combination of embodiments disclosed herein.

The following Examples serve to illustrate the invention. They do not limit the invention. Temperatures are given in degrees Celsius; mixing ratios of solvents are given in parts by volume.

PREPARATORY EXAMPLES:

"Mp" means melting point in °C. Free radicals represent methyl groups. ^{1}H and ^{19}F NMR measurements were recorded on Brucker 400MHz or 300MHz spectrometers, chemical shifts are given in ppm relevant to a TMS standard. Spectra measured in deuterated solvents as indicated. Either one of the LCMS methods below was used to characterize the compounds. The characteristic LCMS values obtained for each compound were the retention time ("Rt", recorded in minutes) and the measured molecular ion $(M+H)^+$ and/or $(M-H)^-$.

LCMS Methods:

Method A - Standard: (SQD-ZDQ-ZCQ)

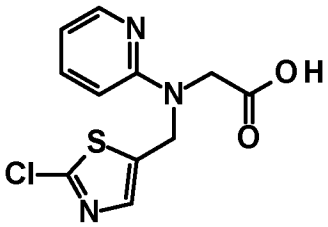
Spectra were recorded on a Mass Spectrometer from Waters (SQD or ZQ Single quadrupole mass spectrometer) equipped with an electrospray source (Polarity: positive or negative ions, Capillary: 3.00

kV, Cone range: 30-60 V, Extractor: 2.00 V, Source Temperature: 150°C, Desolvation Temperature: 350°C, Cone Gas Flow: 0 L/Hr, Desolvation Gas Flow: 650 L/Hr, Mass range: 100 to 900 Da) and an Acquity UPLC from Waters: Binary pump, heated column compartment and diode-array detector. Solvent degasser, binary pump, heated column compartment and diode-array detector. Column: Waters UPLC HSS T3, 1.8 μm, 30 x 2.1 mm, Temp: 60 °C, DAD Wavelength range (nm): 210 to 500, Solvent Gradient: A = water + 5% MeOH + 0.05 % HCOOH, B= Acetonitrile + 0.05 % HCOOH: gradient: gradient: 0 min 0% B, 100%A, 1.2-1.5min 100% B, Flow (ml/min) 0.85.

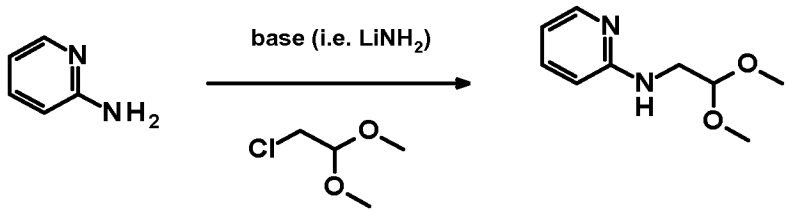
Method B - MobilePhase:A:water(0.1%HCOOH) B:ACN(0.08%HCOOH), Gradient :10%B increase to 95%B with 4min,95%B for 10min , Flow rate: 0.6ml/min. column :porpshell 120 C18 4.6*50mm,2.7um

a) Synthesis of intermediates:

Example I1: Preparation of 2-[(2-chlorothiazol-5-yl)methyl-(2-pyridyl)amino]acetic acid (compound B2 in table B)



Step I1-A: Synthesis of N-(2,2-dimethoxyethyl)pyridin-2-amine

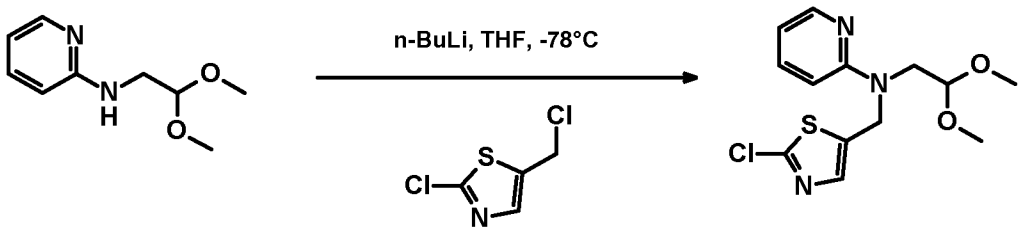


To a suspension of lithium amide ($LiNH_2$) (2.77 g) in anhydrous toluene (41 ml), under dry argon atmosphere, was added 2-aminopyridine (10.00 g), portion wise, while stirring. Once the evolution of ammonia has slowed down, the suspension is heated up to 110°C and stirred for 4 more hours. To the resulting purple-gray suspension was added 2-chloro-1,1-dimethoxyethane (13.24 g) within a few minutes, at the same temperature. The heating was continued for 14 hours, leading to a dark brown suspension.

After cooling down to 20°C the suspension was filtered through a pad of celite®. The residue was washed with diethyl ether and the filtrate was evaporated under reduced pressure to yield a dark brown oily residue. The crude product was submitted to flash chromatography over silica gel, eluting with a mixture of ethyl acetate-cyclohexane (60/40) to yield the title compound as a brown oil.

^{1}H-NMR ($CDCl_3$, 400 MHz, δ in ppm): 8.10 (m, 1H), 7.41 (m, 1H), 6.59 (m, 1H), 6.43 (d, 1H), 4.68 (br s, 1H), 4.56 (t, 1H), 3.49 (t, 2H), 3.43 (s, 6H).

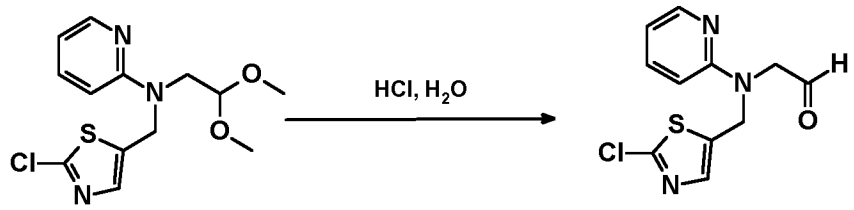
Step I1-B: Synthesis of N-[(2-chlorothiazol-5-yl)methyl]-N-(2,2-dimethoxyethyl)pyridin-2-amine (compound B5 in table B)



To a solution of N-(2,2-dimethoxyethyl)pyridin-2-amine (described above) (9.36 g) in anhydrous tetrahydrofuran (77 ml) stirred at 0°C, under inert atmosphere, was slowly added a solution of n-butyl lithium (1.6 M in hexanes) (32 ml), while keeping the temperature. After the addition, the mixture was further stirred at 0°C for 1 hour. At this point, 2-chloro-5-(chloromethyl)thiazole (preparation described in the literature) (8.63 g) was added. The reaction mixture was stirred at 0°C for 4 hours, then the cooling bath was removed and the reaction mixture was stirred at 20°C for 11 hours. Water (a few drops) was added carefully and the reaction mixture was evaporated. The residue was submitted to flash chromatography over silica gel, eluting with a mixture of ethyl acetate and cyclohexane. Evaporation of the selected fractions yielded the title compound as a light orange oil.

^{1}H-NMR ($CDCl_3$, 400 MHz, δ in ppm): 8.22 (d, 1H), 7.49 (m, 1H), 7.45 (s, 1H), 6.67 (m, 1H), 6.62 (d, 1H), 4.88 (s, 2H), 4.54 (t, 1H), 3.52 (d, 2H), 3.43 (s, 6H).

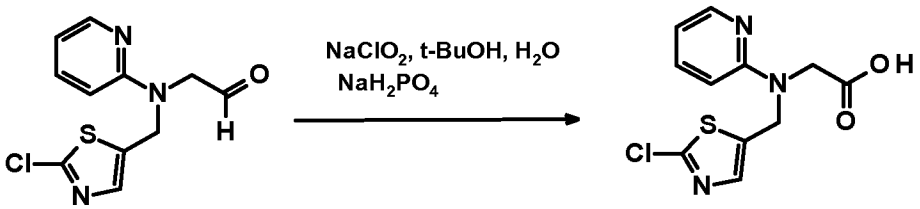
Step I1-C: Synthesis of 2-[(2-chlorothiazol-5-yl)methyl-(2-pyridyl)amino]acetaldehyde (compound B1 in table B)



N-[(2-chlorothiazol-5-yl)methyl]-N-(2,2-dimethoxyethyl)pyridin-2-amine (preparation described here above) (5.33 g) was treated with hydrochloric acid (2.0 M in water, 85 ml) under argon atmosphere. The mixture was stirred at 80°C for 20 minutes. The reaction mixture was then cooled to 0°C, diluted with dichloromethane (130 ml) and the pH was adjusted to pH = 9 by adding saturated aqueous sodium carbonate solution. The phases were separated and the aqueous phase was extracted twice with dichloromethane. The organic extracts were unified and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the aldehyde was used without purification in the following step. A sample of the crude 2-[(2-chlorothiazol-5-yl)methyl-(2-pyridyl)amino]acetaldehyde was characterized by ^{1}H-NMR.

^{1}H-NMR ($CDCl_3$, 400 MHz, δ in ppm): 9.58 (br s, 1H), 8.24 (d, 1H), 7.55 (m, 1H), 7.46 (s, 1H), 6.75 (dd, 1H), 6.55 (d, 1H), 4.87 (s, 2H), 4.20 (s, 2H).

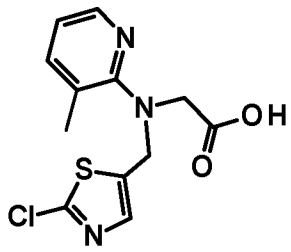
Step I1-D: Synthesis of 2-[(2-chlorothiazol-5-yl)methyl-(2-pyridyl)amino]acetic acid (compound B2 in table B)



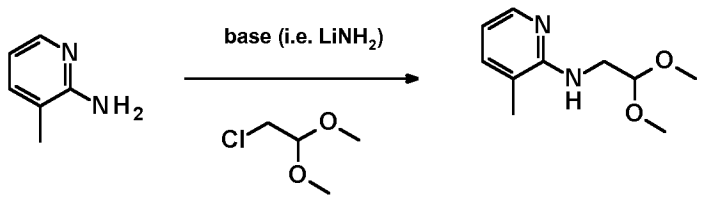
The crude product of the deprotection step (3.96 g) was dissolved in a mixture of tert-butyl alcohol (195 ml) and cyclohexene (37.5 ml) under argon atmosphere. To this solution was added at 20°C, under vigorous stirring, a freshly prepared solution of sodium chlorite (2.36 g) and sodium dihydrogen phosphate (2.40 g) in water (58 ml). After completion of the addition, it was stirred for 1.5 hour more, at which time the LC-MS analysis of a sample of the reaction mixture showed that the starting material was consumed. Diethyl ether was added and the phases were separated. The aqueous phase was extracted with ether and the combined organic phases were washed with brine and dried over sodium sulfate. Removal of the solvent under reduced pressure left a residue that was purified by chromatography over silica gel, eluting first with dichloromethane, then with a mixture of methanol and dichloromethane. The selected fraction were evaporated to leave the title compound characterized by ^{1}H-NMR.

^{1}H-NMR ($CDCl_3$, 400 MHz, δ in ppm): 8.21 (d, 1H), 7.58 (m, 1H), 7.47 (s, 1H), 6.78 (dd, 1H), 6.64 (d, 1H), 4.85 (s, 2H), 4.21 (s, 2H).

Example I2: Preparation of 2-[(2-chlorothiazol-5-yl)methyl-(3-methyl-2-pyridyl)amino]acetic acid (compound B4 in table B)



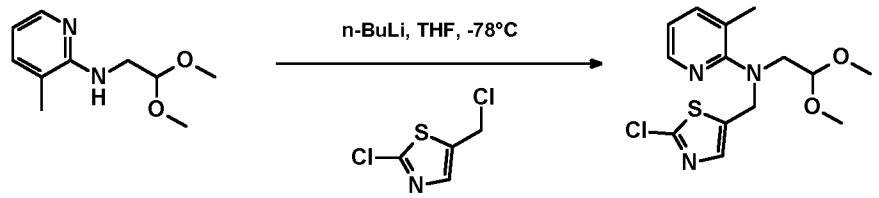
Step I2-A: Synthesis of N-(2,2-dimethoxyethyl)-3-methyl-pyridin-2-amine



In an analogous way as for N-(2,2-dimethoxyethyl)pyridin-2-amine described in step A of example I1, starting with 3-methylpyridine-2-amine instead of 2-aminopyridine, the title compound was obtained as an oil.

^{1}H-NMR ($CDCl_3$, 400 MHz, δ in ppm): 8.02 (d, 1H), 7.23 (d, 1H), 6.55 (dd, 1H), 4.58 (t, 1H), 4.39 (br s, 1H), 3.68 (t, 2H), 3.45 (s, 6H), 2.11 (s, 3H).

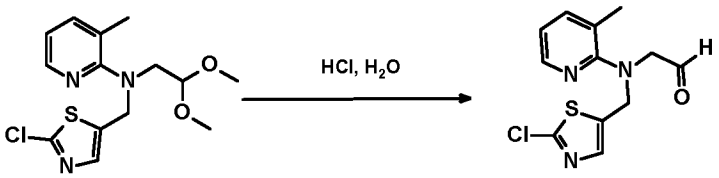
Step I2-B: Synthesis of N-[(2-chlorothiazol-5-yl)methyl]-N-(2,2-dimethoxyethyl)-3-methyl-pyridin-2-amine



In an analogous way as for N-[(2-chlorothiazol-5-yl)methyl]-N-(2,2-dimethoxyethyl)pyridin-2-amine described in step B of example I1, starting with N-(2,2-dimethoxyethyl)-3-methyl-pyridin-2-amine instead of N-(2,2-dimethoxyethyl)pyridin-2-amine, the title compound was obtained as an oil.

^{1}H-NMR ($CDCl_3$, 400 MHz, δ in ppm): 8.18 (d, 1H), 7.43 (d, 1H), 7.42 (s, 1H), 6.89 (dd, 1H), 4.68 (s, 2H), 4.52 (t, 1H), 3.35 (s, 6H), 3.28 (d, 2H), 2.32 (s, 3H).

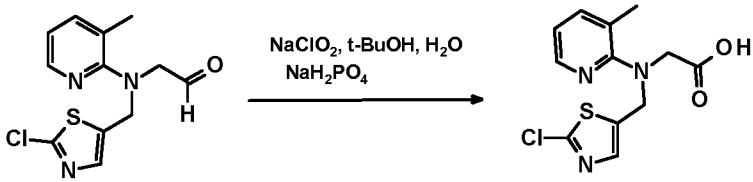
Step I2-C: Synthesis of 2-[(2-chlorothiazol-5-yl)methyl-(3-methyl-2-pyridyl)amino]acetaldehyde (compound B3 in table B)



The title compound was obtained in an similar way as for the preparation of 2-[(2-chlorothiazol-5-yl)methyl-(2-pyridyl)amino]acetic acid described in step C of example I1.

A sample of the crude 2-[(2-chlorothiazol-5-yl)methyl-(3-methyl-2-pyridyl)amino]acetaldehyde was characterized by ^{1}H-NMR: ^{1}H-NMR ($CDCl_3$, 400 MHz, δ in ppm): 9.50 (br s, 1H), 8.20 (d, 1H), 7.48 (d, 1H), 7.43 (s, 1H), 6.94 (dd, 1H), 4.64 (s, 2H), 3.93 (s, 2H), 2.34 (s, 3H).

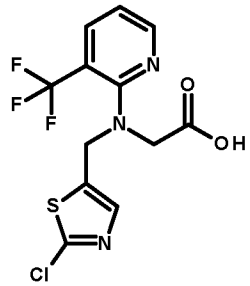
Step I2-D: Synthesis of 2-[(2-chlorothiazol-5-yl)methyl-(3-methyl-2-pyridyl)amino]acetic acid (compound B4 in table B)



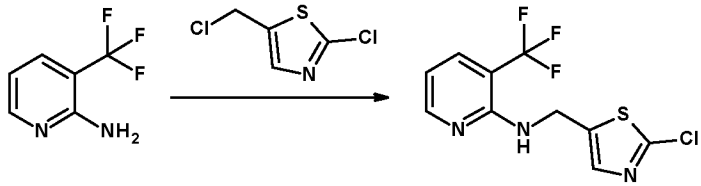
The crude product of the deprotection step was oxidized, as described in Step D of example I1, to the title compound, which was purified by chromatography over silica gel.

^{1}H-NMR ($CDCl_3$, 400 MHz, δ in ppm): 8.16 (d, 1H), 7.67 (d, 1H), 7.54 (s, 1H), 7.13 (dd, 1H), 4.46 (s, 2H), 4.00 (s, 2H), 2.42 (s, 3H).

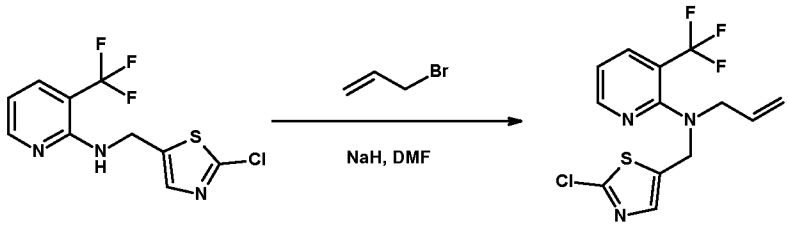
Example I3: Preparation of 2-[(2-chlorothiazol-5-yl)methyl-[3-(trifluoromethyl)-2-pyridyl]amino]acetic acid (compound B10 in table B)



Step I3-A: Synthesis of N-[(2-chlorothiazol-5-yl)methyl]-3-(trifluoromethyl)pyridin-2-amine

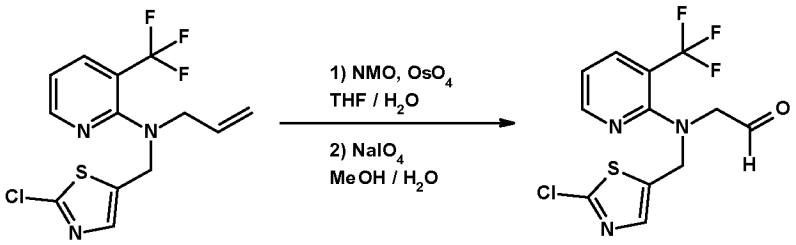


Step I3-B: Synthesis of N-allyl-N-[(2-chlorothiazol-5-yl)methyl]-3-(trifluoromethyl)pyridin-2-amine (compound B8 in table B)



Sodium hydride (313 mg, 7.83 mmol, 1.15 equiv.) was added to a solution of N-[(2-chlorothiazol-5-yl)methyl]-3-(trifluoromethyl)pyridin-2-amine (2.00 g, 6.81 mmol) in N,N-dimethylformamide (22 mL) was at 0°C. After stirring the mixture for 1 hour, 3-bromoprop-1-ene (0.68 mL, 7.83 mmol, 1.15 equiv.) was added dropwise, and the reaction was warmed up to room temperature and stirred overnight. The mixture was quenched by addition of water, the aqueous phase was extracted three times with ethyl acetate, the combined organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated. Purification by flash chromatography over silica gel (ethyl acetate in cyclohexane) afforded the desired compound as a yellowish oil. LCMS (method): 334 $(M+H)^+$, retention time: 1.21min. 1H NMR (400 MHz, $CDCl_3$) δ ppm 8.45 - 8.49 (m, 1 H) 7.90 - 7.94 (m, 1 H) 7.39 - 7.41 (m, 1 H) 7.01 - 7.07 (m, 1 H) 5.87 - 5.99 (m, 1 H) 5.24 - 5.31 (m, 2 H) 4.59 - 4.64 (m, 2 H) 3.79 - 3.83 (m, 2 H).

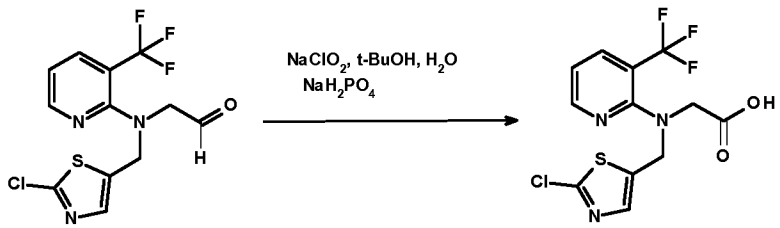
Step I3-C: Synthesis of 2-[(2-chlorothiazol-5-yl)methyl-[3-(trifluoromethyl)-2-pyridyl]amino]acetaldehyde (compound B9 in table B)



A 2.5% osmium tetroxide in tert-butanol (1.10 mL, 910 mg, 0.09 mmol, 0.03 equiv.) was added to a solution of N-allyl-N-[(2-chlorothiazol-5-yl)methyl]-3-(trifluoromethyl)pyridin-2-amine (compound B8 prepared as described above) (1.00 g, 3.00 mmol) in tetrahydrofuran (37.5 mL) and water (5.2 mL). After stirring overnight at room temperature, the reaction mixture was diluted with ethyl acetate, and the organic phase was wahed with a saturated ammonium chloride aqueous solution, brine, dried over sodium sulfate, filtered and concentrated. The crude 3-[(2-chlorothiazol-5-yl)methyl-[3-(trifluoromethyl)-2-pyridyl]amino]propane-1,2-diol was used directly without purification.

Sodium periodate (640 mg, 3.00 mmol, 1.00 equiv.) was added to a 0 °C cooled solution of crude 3-[(2-chlorothiazol-5-yl)methyl-[3-(trifluoromethyl)-2-pyridyl]amino]propane-1,2-diol (1.10 g, 3.00 mmol, 1.00 equiv.) in water (16 mL) and methanol (16 mL). After stirring at 0 °C for 30 min and at room temperature for 1 hour, more sodium periodate (640 mg, 3.00 mmol, 1.00 equiv.) was added the mixture again at 0°C. After stirring at 0 °C for 30 min and at room temperature for 1 hour, a third portion of sodium periodate (640 mg, 3.00 mmol, 1.00 equiv.) was added the mixture again at 0°C, and the reaction was stirred at room temperature for 3 hours. The reaction mixture was diluted with ethyl acetate, the organic layer was washed with a saturated ammonium chloride aqueous solution, brine, dried over sodium sulfate, filtered and concentrated. The crude must be kept in the freezer and can be used directly without purification. LC-MS (method A): 336 $(M+H)^+$, retention time: 0.57 min.

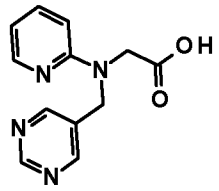
Step I3-D: Synthesis of 2-[(2-chlorothiazol-5-yl)methyl-[3-(trifluoromethyl)-2-pyridyl]amino]acetic acid (compound B10 in table B)



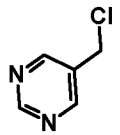
A freshly prepared colorless solution of sodium chlorite (189 mg, 1.50 equiv.) and sodium dihydrogen phosphate (193 mg, 1.25 equiv.) in water (4.70 mL) was added dropwise to a solution of crude freshly prepared 2-[(2-chlorothiazol-5-yl)methyl-[3-(trifluoromethyl)-2-pyridyl]amino]acetaldehyde (750 mg, 1.00 equiv.) in tert-butanol (15.6 mL) and cyclohexene (3.02 mL) under argon at room temperature. After stirring for 2 hours, an additional freshly prepared solution of sodium chlorite (189 mg, 1.50 equiv.) and sodium dihydrogen phosphate (193 mg, 1.25 equiv.) in water (4.70 mL) was added dropwise. After stirring for 1 hour more at room temperature, diethyl ether was added and the phases were separated. The organic layer was washed with brine, dried over sodium sulfate, filtered

and evaporated under vacuum. The crude material was purified by flash chromatography over silica gel (methanol in dichloromethane) to afford the desired compound (40mg, 10% yield) as a yellowish oil. . LC-MS (method A): 351 $(M+H)^+$, retention time: 0.93 min.

Example I4: Preparation of2-[2-pyridyl(pyrimidin-5-ylmethyl)amino]acetic acid

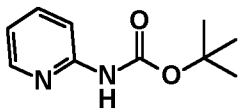


Step I3-A: Synthesis of 5-(chloromethyl)pyrimidine



To a stirred solution of pyrimidin-5-ylmethanol (5.00 g, 45.4 mmol) in dichloromethane (125 mL) was added thionyl chloride (9.88 mL, 136 mmol) drop wise at 0 °C, and allowed to stirred at room temperature for 2 h. The reaction mixture was analyzed by TLC (50% EtOAc/hexanes) and it showed no starting material. The reaction mixture was concentrated under reduced pressure to afford title compound (4.2 g, 69.3%) as a light brown solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.17 (s, 1H), 8.91 (s, 2H), 4.85 (s, 2H).

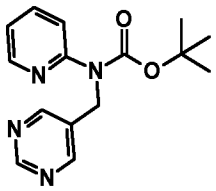
Step I3-B: Synthesis of tert-butyl N-(2-pyridyl)carbamate



To a stirred solution of 2-aminopyridine (6.00 g, 63.8 mmol) in THF (120.0 mL) was added NaHMDS (2.00 M, 63.8 mL, 128 mmol) drop wise at 0 °C and stirred at room temperature for 30 min. followed by addition of $(Boc)_2O$ (17.6 mL, 76.5 mmol) and stirred at room temperature for 30min. Reaction mixture was analyzed by TLC (50% EtOAc/hexanes) and it showed no starting material. Reaction mixture was diluted with H_2O (50 mL) and extracted with EtOAc (2 x 100 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford crude reaction mixture. The crude was purified by combiflash chromatography [eluent: EtOAc (50%) in hexanes] to afford title compound (8.3 g, 60.7%) as an off white solid.

^{1}H NMR (300 MHz, DMSO-d_6): δ 9.71 (s, 1H), 8.22 (d, 1H), 7.78 – 7.67 (m, 2 H), 6.99 (t, 1H), 1.45 (s, 9H).

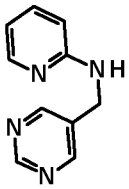
Step I3-C: Synthesis of tert-butyl N-(2-pyridyl)-N-(pyrimidin-5-ylmethyl)carbamate



To a stirred solution of tert-butyl N-(2-pyridyl)carbamate (3.60 g, 16.7 mmol) in DMF (150.0mL) was added sodium hydride (60.0 %, 2.00 g, 50.0 mmol), followed by 5-(chloromethyl)pyrimidine (2.80 g, 21.8 mmol) at 0 °C and stirred at room temperature for 3 h. Reaction mixture was analyzed by TLC (50% EtOAc/hexanes) and it showed no starting material.The reaction mixture was diluted with H_2O (50 mL) and extracted with EtOAc (2 x 100 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford crude reaction mixture. The crude was purified by combiflash chromatography [eluent: EtOAc (50%) in hexanes] to afford the title compound (4.5 g, 89.5%).

^{1}H NMR (300 MHz, DMSO-d_6): δ 9.08 (s, 1H), 8.75 (s, 2H), 8.40 (d, 1H), 7.82 (t, 1H), 7.68 (d, 1H), 7.19 – 7.15 (m, 1H), 5.08 (s, 2H), 1.38 (s, 9H).

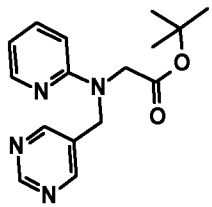
Step I3-D: Synthesis of N-(pyrimidin-5-ylmethyl)pyridin-2-amine



To a stirred solution of tert-butyl N-(2-pyridyl)-N-(pyrimidin-5-ylmethyl)carbamate (8.00 g, 20.6 mmol) in dichloromethane (100.0 mL) was added trifluoro acetic acid (15.7 mL, 206 mmol) at 0 °C and stirred at room temperature for 3 h. The reaction mixture was analyzed by TLC (50% EtOAc/hexanes) and it showed no starting material. The reaction mixture was diluted with saturated aqueous $NaHCO_3$(150 mL) and extracted with EtOAc (2 x 100 mL). The combined organic layers were washed with brine (150 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford the title compound (4.5 g, 82.3%).

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.12 (s, 1H), 8.76 (s, 2H), 8.10 (d, 1H), 7.45 – 7.40 (m, 1H), 6.66 – 6.63 (m, 1H), 6.42 (d, 1H), 4.87 (s, 1H), 4.61 (d, 2H).

Step I3-E: Synthesis of tert-butyl 2-[2-pyridyl(pyrimidin-5-ylmethyl)amino]acetate

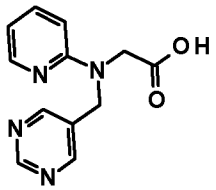


To a stirred solution of N-(pyrimidin-5-ylmethyl)pyridin-2-amine (2.50 g, 12.6 mmol) in THF (50.0 mL) was added NaHMDS (2.00 M, 18.9 mL, 37.9 mmol) at 0 °C and stirred for 1 h, followed by tert-butyl 2-bromoacetate (2.95 g, 15.1 mmol) was added at 0 °C, and allowed to stirred at room temperature for 4 h. Reaction mixture was analyzed by TLC (80% EtOAc/hexanes) and it showed no starting material. The reaction mixture was diluted with H_2O (100 mL) and extracted with EtOAc (2 x

100 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford crude reaction mixture. The crude was purified by combiflash chromatography [eluent: EtOAc (80%) in hexanes] to afford the title compound (1.5 g, 38.1%).

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.13 (s, 1H), 8.73 (s, 2H), 8.18 – 8.16 (m, 1H), 7.49 – 7.45 (m, 1H), 6.69 – 6.66 (m, 1H), 6.45 (d, 1H), 4.87 (s, 2H), 4.10 (s, 2H), 1.42 (s, 9 H).

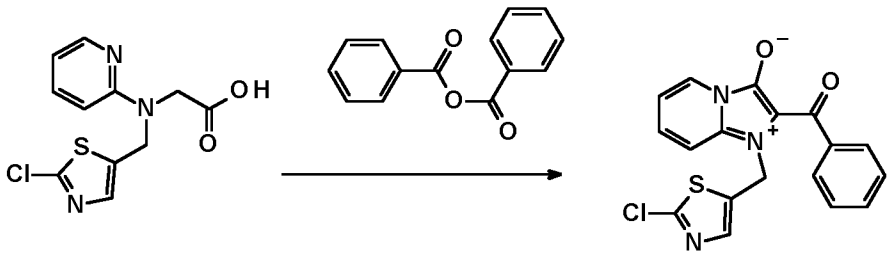
Step I3-F: Synthesis of 2-[2-pyridyl(pyrimidin-5-ylmethyl)amino]acetic acid



To a stirred solution of tert-butyl 2-[2-pyridyl(pyrimidin-5-ylmethyl)amino]acetate (1.20 g, 3.80 mmol) in dichloromethane (100.0 mL) was added trifluoro acetic acid (2.90 mL, 38.0 mmol) at 0 °C and stirred at room temperature for 3 h. The reaction mixture was analyzed by TLC (80% EtOAc/hexanes) and it showed no starting material. The reaction mixture was concentrated under reduced pressure to afford crude reaction mixture. The crude was purified by combiflash chromatography [eluent: EtOAc (90%) in hexanes] to afford the title compound (0.4 g, 45.6%).

^{1}H NMR (300 MHz, DMSO-d_6): δ 12.58 (s, 1H), 9.05 (s, 1H), 8.77 (s, 2H), 8.09 – 8.07 (m, 1H), 7.50 (d, 1H), 6.66 – 6.57 (m, 2H), 4.79 (s, 2H), 4.33 (s, 2H).

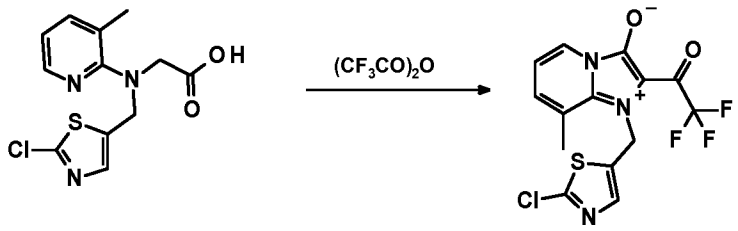
Example I: Preparation of 2-benzoyl-1-[(2-chlorothiazol-5-yl)methyl]imidazo[1,2-a]pyridin-1-ium-3-olate (example A1 in table A)



2-[(2-chlorothiazol-5-yl)methyl-(2-pyridyl)amino]acetic acid (preparation describe above) (0.056 g) and benzoic anhydride (0.55 g) were mixed in a vial under inert atmosphere and the mixture was heated to 60°C and stirred for 20 hours at that temperature. After cooling down, the mixture was submitted to flash chromatography over silica gel, eluting with a mixture of methanol in dichloromethane (5:95). The selected fractions yielded, after evaporation, the title compound showing the following NMR spectrum.

^{1}H-NMR ($CDCl_3$, 400 MHz, δ in ppm): 8.42 (d, 1H), 7.92 (d, 2H), 7.71 (dd, 1H), 7.66 (s, 1H), 7.58-7.40 (m, 4H), 7.02 (t, 1H), 5.92 (s, 2H).

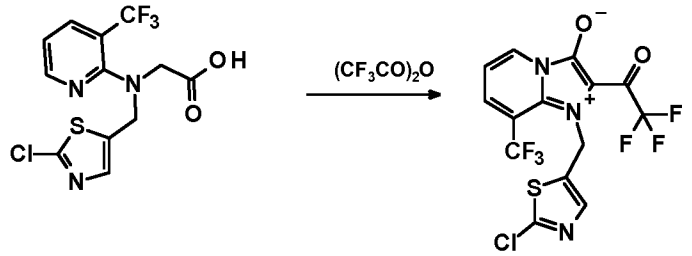
Example 2: 1-[(2-chlorothiazol-5-yl)methyl]-8-methyl-2-(2,2,2-trifluoroacetyl)imidazo[1,2-a]pyridin-1-ium-3-olate (example A2 in table A)



2-[(2-chlorothiazol-5-yl)methyl-(3-methyl-2-pyridyl)amino]acetic acid (preparation describe above) (0.100 g) was treated with trifluoroacetic anhydride (0.356 g) under argon atmosphere. The mixture was stirred at 40°C for 6 days. The reaction mixture was then evaporated under reduced pressure and the residue submitted to chromatography on reverse phase, eluting with mixtures of acetonitrile and water. Evaporation of the selected fractions yielded the title compound with the following NMR-data.

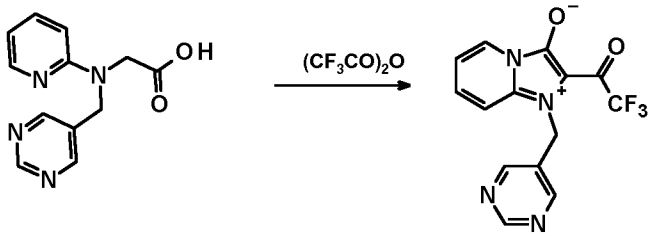
^{1}H-NMR ($CDCl_3$, 400 MHz, δ in ppm): 8.43 (d, 1H), 7.61 (d, 1H), 7.44 (s, 1H), 7.05 (t, 1H), 6.17 (br. s, 2H), 2.81 (s, 3H).

Example 3: 1-[(2-chlorothiazol-5-yl)methyl]-2-(2,2,2-trifluoroacetyl)-8-(trifluoromethyl)imidazo[1,2-a]pyridin-1-ium-3-olate (example A16 in table A)



A solution of 2-[(2-chlorothiazol-5-yl)methyl-[3-(trifluoromethyl)-2-pyridyl]amino]acetic acid (compound B10 prepared as described above) (25 mg, 0.071 mmol) and trifluoroacetic anhydride (19.8 μL, 0.142 mmol, 2.00 equiv.) in acetonitrile (0.852 mL.) was heated at 80°C for 1 hour. After cooling down to room temperature, the reaction mixture was evaporated and the crude residue directly purified by flash chromatography over silica gel (methanol in dichloromethane) to afford a yellow oil containing a mixture of desired compound contaminated by trifluoroacetic acid. The product was dissolved in dichloromethane, the organic layer was washed with a saturated sodium hydrogenocarbonate aqueous solution, dried over magnesium sulfate, filtered and concentrated to obtain the pure material as a yellow solid. (31 mg, quant.) with the following LC-MS and NMR-data. LC-MS (method A): 430 $(M+H)^+$, retention time: 0.94 min. 1H NMR (400 MHz, $CDCl_3$) δ ppm 8.75 - 8.79 (m, 1 H) 8.27 - 8.33 (m, 1 H) 7.45 - 7.49 (m, 1 H) 7.23 - 7.28 (m, 1 H) 5.98 - 6.33 (m, 2 H).

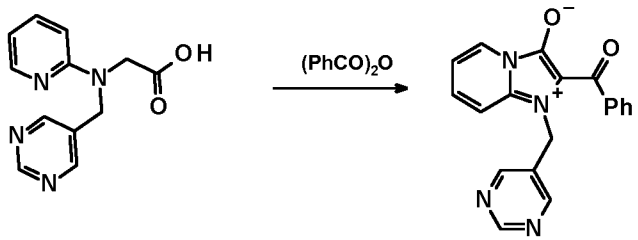
Example 4: 2-benzoyl-1-(pyrimidin-5-ylmethyl)imidazo[1,2-a]pyridin-1-ium-3-olate (example A18 in table A)



A 100 mL flask was charged with 2-[2-pyridyl(pyrimidin-5-ylmethyl)amino]acetic acid (0.40 g, 1.563 mmol), trifluoroacetic anhydride (1.03 g, 4.95 mmol) and stirred at 60 °C for 24 h. Reaction mixture was analyzed by TLC (100% EtOAc) and it showed no starting material. The reaction mixture was concentrated under reduced pressure to afford crude reaction mixture. The crude was purified by combiflash chromatography [eluent: EtOAc (100%)] to afford the title compound (0.05 g, 10.1%) as a light yellow solid.

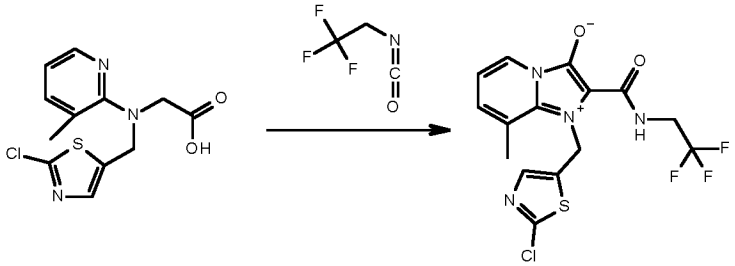
^{1}H NMR (300 MHz, DMSO-d_6): δ 9.10 (s, 1H), 8.71 (s, 2H), 8.43 (d, J = 5.7 Hz, 1H), 7.97 (s, 2H), 7.16 (s, 1H), 5.74 (s, 2H).

Example 5: 2-benzoyl-1-(pyrimidin-5-ylmethyl)imidazo[1,2-a]pyridin-1-ium-3-olate (example A17 in table A)



A 100 mL flask was charged with 2-[2-pyridyl(pyrimidin-5-ylmethyl)amino]acetic acid (0.20 g, 0.778 mmol), benzoic anhydride (2.11 g, 9.33 mmol) and stirred at 60°C for 24 h. The reaction mixture was analyzed by TLC (100% EtOAc) and it showed no starting material. The reaction mixture was concentrated under reduced pressure to afford crude reaction mixture. The crude was purified by combiflash chromatography [eluent: EtOAc (100%)] to afford the title compound (0.07 g, 26.2%).

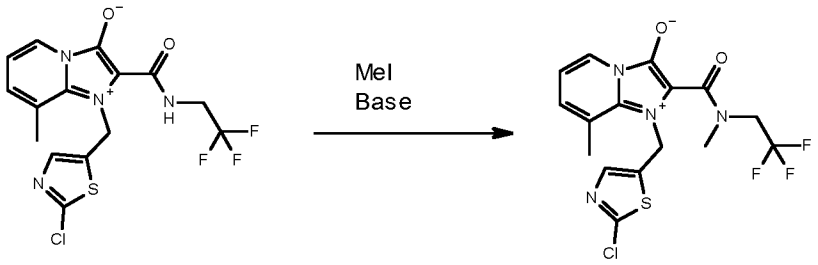
Example I6: Preparation of 1-[(2-chlorothiazol-5-yl)methyl]-8-methyl-2-(2,2,2-trifluoroethylcarbamoyl)imidazo[1,2-a]pyridin-1-ium-3-olate (example A92 in table A)



In a tube closed with a septum, under an argon atmosphere, 2-[(2-chlorothiazol-5-yl)methyl-(3-methyl-2-pyridyl)amino]acetic acid (preparation describe above) (0.050 g) was mixed in acetonitrile (0.13 g) at 20°C and 1,1,1-trifluoro-2-isocyanato-ethane (0.064 g) was added. The reaction mixture was stirred at 70°C. The conversion was checked by LC-MS analysis. After 3 hours, the reaction mixture was evaporated under reduced pressure and the residue was chromatographed on a silica gel column, eluting with a gradient of MeOH (0-5%) in dichloromethane. Evaporation of the selected fractions gave the title compound as a yellow solid.

^{1}H-NMR ($CDCl_3$, 400 MHz, δ in ppm): 9.04 (t, 1 H), 8.35 (d, 1 H), 7.44 (s, 1 H), 7.38 (d, 1 H), 6.99 (t, 1H), 4.10 (quint. 2 H), 2.79 (s, 3H).

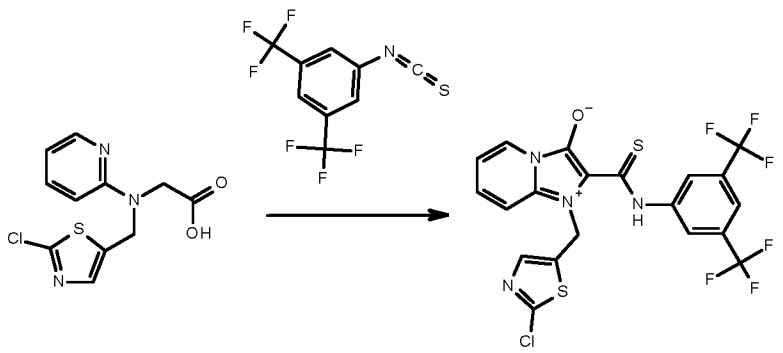
Example 7: 1-[(2-chlorothiazol-5-yl)methyl]-8-methyl-2-[methyl(2,2,2-trifluoroethyl)carbamoyl]-imidazo[1,2-a]pyridin-1-ium-3-olate (example A91 in table A)



1-[(2-chlorothiazol-5-yl)methyl]-8-methyl-2-(2,2,2-trifluoroethylcarbamoyl)imidazo[1,2-a]pyridin-1-ium-3-olate (preparation describe above) (0.042 g) dissolved in acetonitrile (1 ml) was treated with a suspension of sodium hydride (60% in oil) (3.0 equiv.) at 20°C under argon atmosphere and stirring. After the gas evolution stopped, iodomethane (0.020 ml) was added and the mixture was stirred for 2 hours.The starting material was fully converted (LC-MS analysis). A few drops of water were carefully added and the reaction mixture was concentrated under reduced pressure. The crude product was chromatographed on a silica gel column, eluting with a gradient of MeOH (0-10%) in dichloromethane. Evaporation of the selected fractions gave the title compound as a yellow solid.

^{1}H-NMR ($CDCl_3$, 400 MHz, δ in ppm): 8.38 (d, 1 H), 7.40-7.33 (m, 2 H), 6.99 (t, 1H), 6.03 (s, 2 H), 4.60-4.10 (broad signal, 2 H), 3.50-3.10 (broad signal, 3 H), 2.75 (s, 3H).

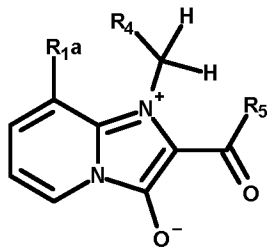
Example 8: Preparation of 2-[[3,5-bis(trifluoromethyl)phenyl]carbamothioyl]-1-[(2-chlorothiazol-5-yl)methyl]imidazo[1,2-a]pyridin-1-ium-3-olate (example A123 in table A3)



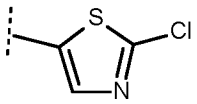
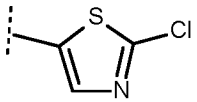
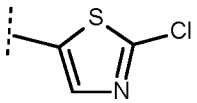
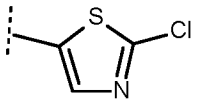
In a tube closed with a septum, under an argon atmosphere, 2-[(2-chlorothiazol-5-yl)methyl-(2-pyridyl)amino]acetic acid (preparation describe above) (0.050 g) was mixed with 1-isothiocyanato-3,5-bis(trifluoromethyl)benzene (0.244 g). The reaction mixture was stirred at 70°C for 24 hours. The conversion was checked by LC-MS analysis. After cooling to 20°C, the reaction mixture was submitted to chromatography on a silica gel, eluting with a mixture of 65% ethyl acetate in cyclohexane. Evaporation of the selected fractions gave the title compound as a brown solid.

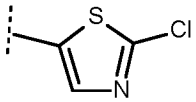
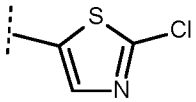
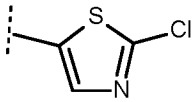
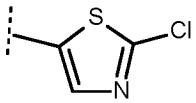
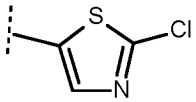
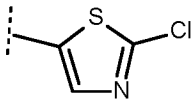
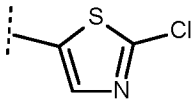
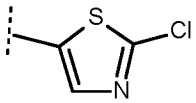
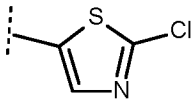
^{1}H-NMR ($CDCl_3$, 400 MHz, δ in ppm): 13.01 (s, 1 H), 8.44 (s, 2 H), 7.88 (dd, 1 H), 7.72 (s, 1 H), 7.69 (s, 1 H), 7.56 (d, 1 H), 7.38 (d, 1 H), 7.19 (t, 1H), 6.71 (s, 2 H).

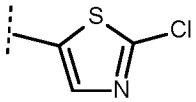
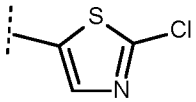
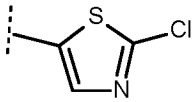
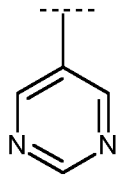
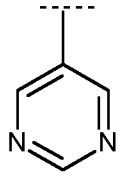
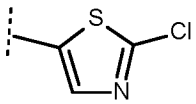
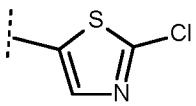
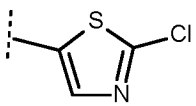
Table A: This table discloses compounds of the formula Ib :

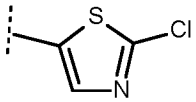
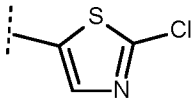
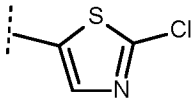
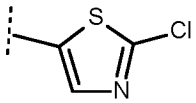
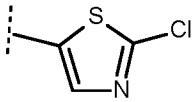
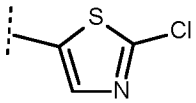
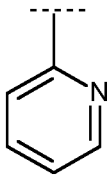
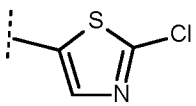
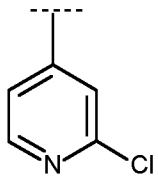
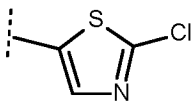
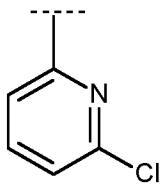


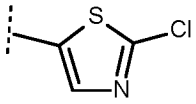
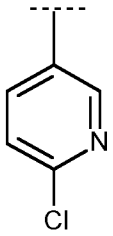
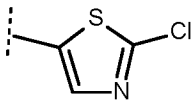
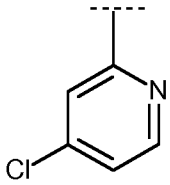
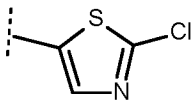
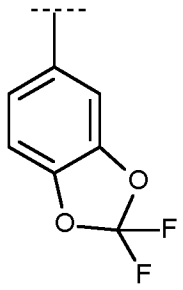
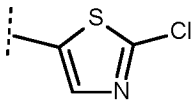
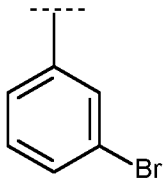
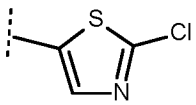
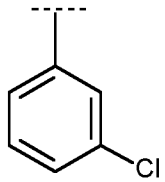
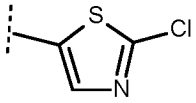
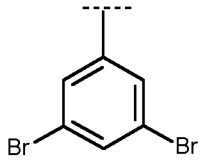
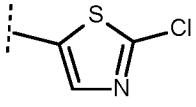
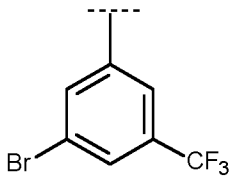
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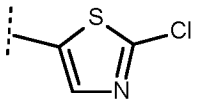
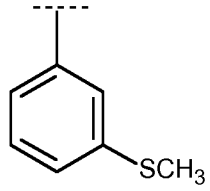
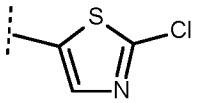
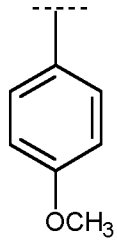
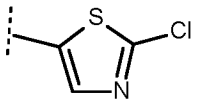
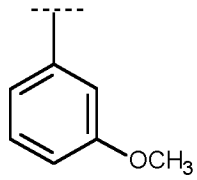
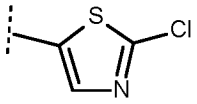
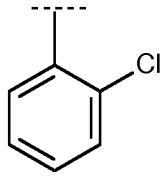
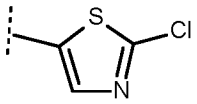
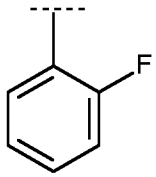
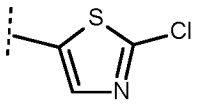
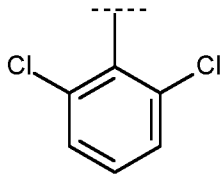
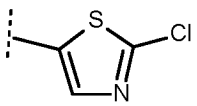
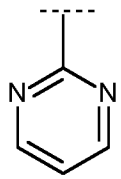
Comp. No.	R_{1a}	R_4	R_5	Analytical data
A1	H		Ph	See experimental part (Example 1)
A2	CH_3		CF_3	See experimental part (Example 2)
A3	CH_3		Ph	LC MS (method A) Rt 0.82(min): , $[M+H]^+$ (measured) 384
A4	H		OtBu	^{1}H-NMR ($CDCl_3$, 400 MHz, δ in ppm): 8.45 (d, 1H), 7.76 (m, 1H), 7.66 (s, 1H), 7.42 (d, 1H), 7.05 (t, 1H), 5.82 (s, 2H), 1.60 (s, 9H).

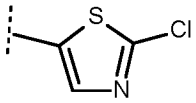
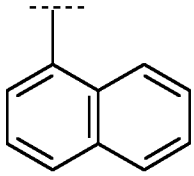
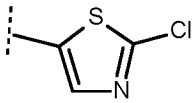
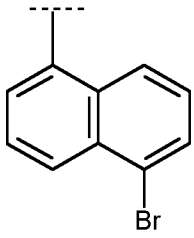
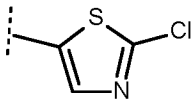
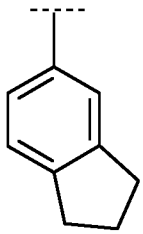
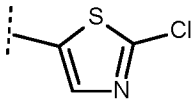
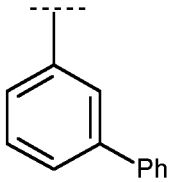
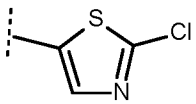
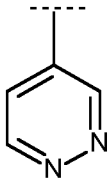
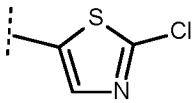
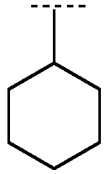
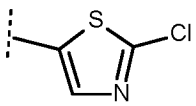
Comp. No.	R_{1a}	R_4	R_5	Analytical data
A5	CH_3		3,5-diClPh	LC MS (method A) Rt (min):1.03 , $[M+H]^+$ (measured) 454
A6	H		CH_2Ph	LC MS (method A) Rt (min): 0.89 , $[M+H]^+$ (measured) 384
A7	H		cyclopropyl	LC MS (method A) Rt (min): 0.77, $[M+H]^+$ (measured) 334
A8	H		CH_3	LC MS (method A) Rt (min): 0.65, $[M+H]^+$ (measured) 308
A9	H		CF_3	LC MS (method A) Rt (min): 0.83, $[M+H]^+$ (measured) 362
A10	H		3,5-diClPh	Mp°C 263-264°C
A11	H		$CF_2CF_2CF_3$	LC MS (method A) Rt (min): 1.00, $[M+H]^+$ (measured) 462
A12	H		3-CF_3Ph	LC MS (method A) Rt (min): 0.96, $[M+H]^+$ (measured) 438
A13	CH_3		$CF_2CF_2CF_3$	LC MS (method A) Rt (min): 1.03, $[M+H]^+$ (measured) 476

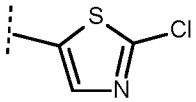
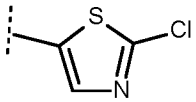
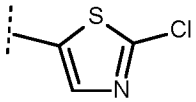
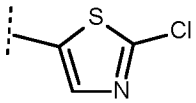
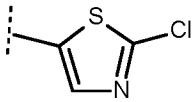
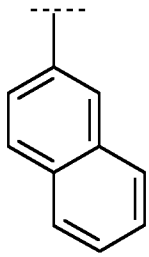
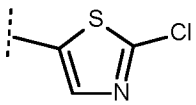
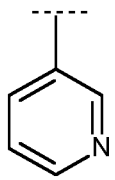
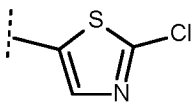
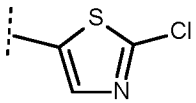
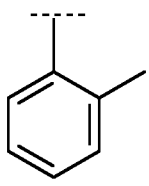
Comp. No.	R_{1a}	R_4	R_5	Analytical data
A14	CH_3		3-CF_3Ph	LC MS (method A) Rt (min): 0.98, $[M+H]^+$ (measured) 452
A15	H		CF_2Ph	LC MS (method A) Rt (min): 0.92, $[M+H]^+$ (measured) 420
A16	CF_3		CF_3	LC-MS (method A): 430 $(M+1)^+$, retention time 0.94 min
A17	H		Ph	See experimental Example 4~~5~~
A18	H		CF_3	See experimental Example ~~5~~ 4
A19	CF_3		3,5-diClPh	LC-MS (method A): 506 $(M+1)^+$, retention time 1.11 min
A20	CH_3O		CF_3	LC-MS (method A): 392 $(M+1)^+$, retention time 0.87 min
A21	CH_3O		3,5-diClPh	LC-MS (method A): 470 (M+1)+, retention time 1.07 min

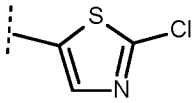
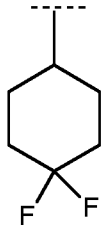
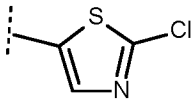
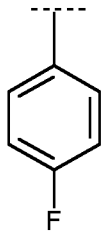
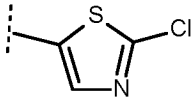
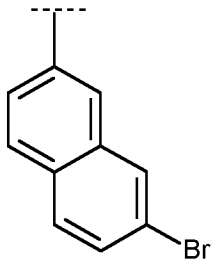
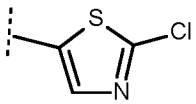
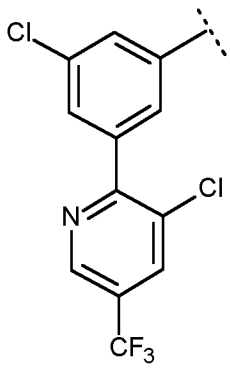
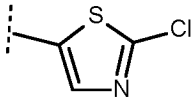
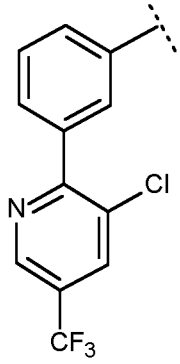
Comp. No.	R_{1a}	R_4	R_5	Analytical data
A22	CH_3O		Ph	LC-MS (method A): 400 (M+1)+, retention time 0.85 min
A23	CH_3 CH_2		CF_3	LC-MS (method A): 390 $(M+1)^+$, retention time 0.90 min
A24	CH_3 CH_2		3,5-diClPh	LC-MS (method A): 468 $(M+1)^+$, retention time 1.09 min
A25	$(CH_2)_2CH$		CF_3	LC-MS (method A): 402 $(M+1)^+$, retention time 0.92 min
A26	$(CH_2)_2CH$		3,5-diClPh	LC-MS (method A): 480 $(M+1)^+$, retention time 1.10 min
A27	CH_3			LC-MS (method A):385 (M+1)+, retention time 0.62 min
A28	CH_3			LC-MS (method A):419 (M+1)+, retention time 0.81 min
A29	CH_3			LC-MS (method A):419 (M+1)+, retention time 0.77 min

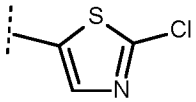
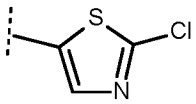
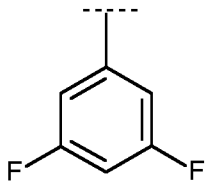
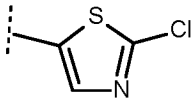
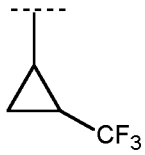
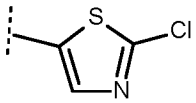
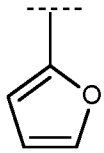
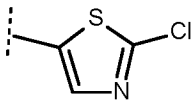
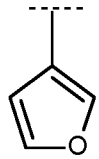
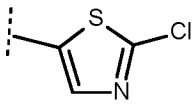
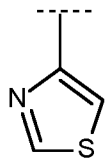
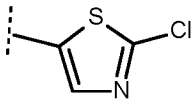
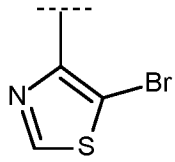
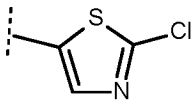
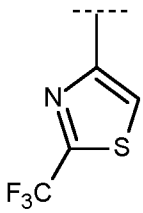
Comp. No.	R_{1a}	R_4	R_5	Analytical data
A30	CH_3			LC-MS (method A):419 (M+1)+, retention time 0.8 min
A31	CH_3			LC-MS (method A):419 (M+1)+, retention time 0.77 min
A32	CH_3			LC-MS (method A):464 (M+1)+, retention time 0.95 min
A33	CH_3			LC-MS (method A):462 (M+1)+, retention time 0.92 min
A34	CH_3			LC-MS (method A):418 (M+1)+, retention time 0.90 min
A35	CH_3			LC-MS (method A):No mass, retention time 1.05 min
A36	CH_3			LC-MS (method A):530 (M+1)+, retention time 1.06 min

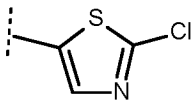
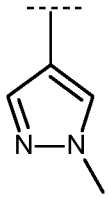
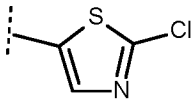
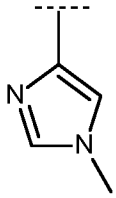
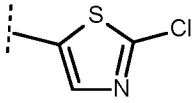
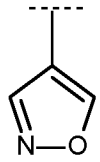
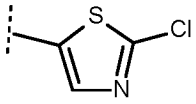
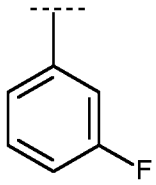
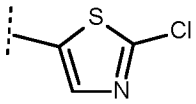
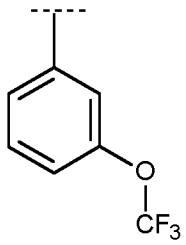
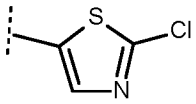
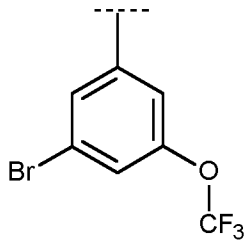
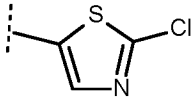
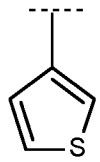
Comp. No.	R_{1a}	R_4	R_5	Analytical data
A37	CH_3			LC-MS (method A):430 (M+1)+, retention time 0.89 min
A38	CH_3			LC-MS (method A):414 (M+1)+, retention time 0.81 min
A39	CH_3			LC-MS (method A):414 (M+1)+, retention time 0.82 min
A40	CH_3			LC-MS (method A):418 (M+1)+, retention time 0.84 min
A41	CH_3			LC-MS (method A):402 (M+1)+, retention time 0.81 min
A42	CH_3			LC-MS (method A):452 (M+1)+, retention time 0.88 min
A43	CH_3			LC-MS (method A):386 (M+1)+, retention time 0.59 min

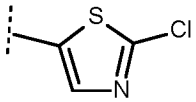
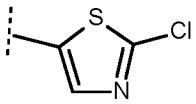
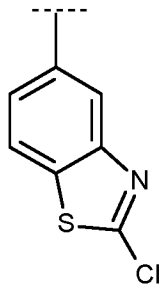
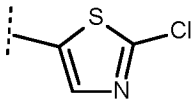
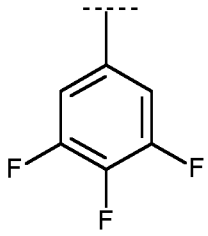
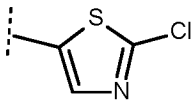
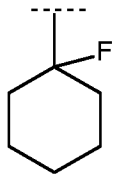
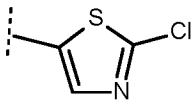
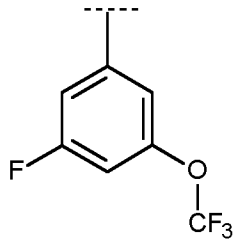
Comp. No.	R_{1a}	R_4	R_5	Analytical data
A44	CH_3			LC-MS (method A):434 (M+1)+, retention time 0.89 min
A45	CH_3			LC-MS (method A):No mass, retention time 1.00 min
A46	CH_3			LC-MS (method A):424 (M+1)+, retention time 0.92 min
A47	CH_3			LC-MS (method A):460 (M+1)+, retention time 0.99 min
A48	CH_3			LC-MS (method A):386 (M+1)+, retention time 0.64 min
A49	CH_3			LC-MS (method A):390 (M+1)+, retention time 0.94 min
A50	CH_3		CCl_3	LC-MS (method A):424 (M+1)+, retention time 0.92 min

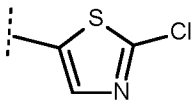
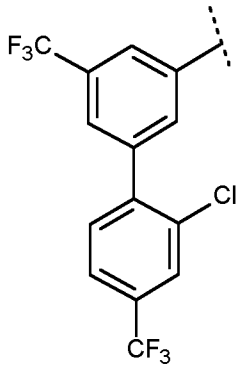
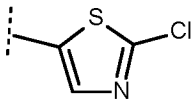
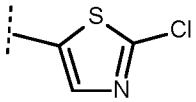
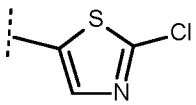
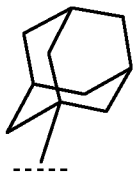
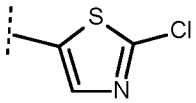
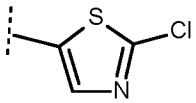
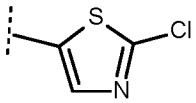
Comp. No.	R_{1a}	R_4	R_5	Analytical data
A51	CH_3		CF_2CF_2H	LC-MS (method A):408 (M+1)+, retention time 0.88 min
A52	CH_3		CF_2H	LC-MS (method A):358 (M+1)+, retention time 0.76 min
A53	CH_3		CF_2Cl	226 – 228°C
A54	CH_3		CH_2CF_3	LC-MS (method A):390 (M+1)+, retention time 0.84 min
A55	CH_3			LC-MS (method A): 434 (M+1)+, retention time 0.93min
A56	CH_3			LC-MS (method A): 385(M+1)+, retention time 0.60min
A57	CH_3		$(CH_2)_2CF_3$	LC-MS (method A): 426 (M+1)+, retention time 0.88min
A58	CH_3			LC-MS (method A): 398 (M+1)+, retention time 0.86min

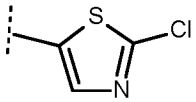
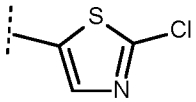
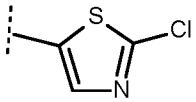
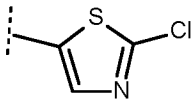
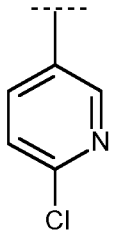
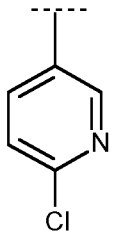
Comp. No.	R_{1a}	R_4	R_5	Analytical data
A59	CH_3			LC-MS (method A): 426 (M+1)+, retention time 0.91min
A60	CH_3			LC-MS (method A): 402 (M+1)+, retention time 0.86min
A61	CH_3			LC-MS (method A): No mass (M+1)+, retention time 1.02min
A62	CH_3			LC-MS (method A): 597 (M+1)+, retention time 1.13min
A63	CH_3			LC-MS (method A): 563 (M+1)+, retention time 1.03min

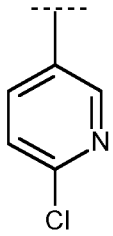
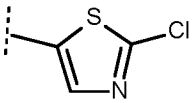
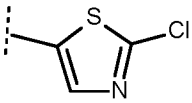
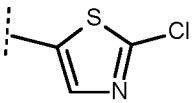
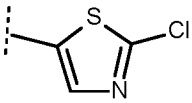
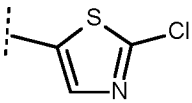
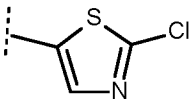
Comp. No.	R_{1a}	R_4	R_5	Analytical data
A64	CH_3		CF_2CH_3	LC-MS (method A): 372 (M+1)+, retention time 0.78min
A65	CH_3			LC-MS (method A): 420 (M+1)+, retention time 0.9 min
A66	CH_3			LC-MS (method A): 416 (M+1)+, retention time 0.93 min
A67	CH_3			LC-MS (method A): 374 (M+1)+, retention time 0.74 min
A68	CH_3			LC-MS (method A): 374 (M+1)+, retention time 0.78 min
A69	CH_3			LC-MS (method A): 391 (M+1)+, retention time 0.66 min
A70	CH_3			LC-MS (method A): 469 (M+1)+, retention time 0.79 min
A71	CH_3			LC-MS (method A): 459 (M+1)+, retention time 0.87 min

Comp. No.	R_{1a}	R_4	R_5	Analytical data
A72	CH_3			LC-MS (method A): 388 (M+1)+, retention time 0.68 min
A73	CH_3			LC-MS (method A): 388 (M+1)+, retention time 0.56 min
A74	CH_3			LC-MS (method A): 375 (M+1)+, retention time 0.69 min
A75	CH_3			LC-MS (method A): 402 (M+1)+, retention time 0.85 min
A76	CH_3			LC-MS (method A): 468 (M+1)+, retention time 0.97 min
A77	CH_3			LC-MS (method A): 546 (M+1)+, retention time 1.08 min
A78	CH_3			LC-MS (method A): 390 (M+1)+, retention time 0.80 min

Comp. No.	R_{1a}	R_4	R_5	Analytical data
A79	CH_3		$CH_2CF_2CH_3$	LC-MS (method A): 386 (M+1)+, retention time 0.82 min
A80	CH_3			LC-MS (method A): 519 (M+1)+, retention time 0.97 min
A81	CH_3			LC-MS (method A): 438 (M+1)+, retention time 0.94 min
A82	CH_3			LC-MS (method A): 408 (M+1)+, retention time 0.93 min
A83	CH_3			LC-MS (method A): 486 (M+1)+, retention time 1.01 min

Comp. No.	R_{1a}	R_4	R_5	Analytical data
A84	CH_3			LC-MS (method A): 630 (M+1)+, retention time 1.21 min
A85	CH_3		$CH(CF_3)_2$	LC-MS (method A): 458 (M+1)+, retention time 1.00 min
A86	CH_3		CH_2OCF_3	LC-MS (method A): 406 (M+1)+, retention time 0.86 min
A87	CH_3			LC-MS (method A): 442 (M+1)+, retention time 1.11 min
A88	CH_3O		CF_2CF_3	LC-MS (method A): 442 (M+1)+, retention time 1.01 min
A89	CH_3O		CF_2CF_2H	LC-MS (method A): 424 (M+1)+, retention time 0.95 min
A90	CH_3		$NHCH_2CH_2Cl$	LC MS (method A) Rt 0.78 min): $[M+H]^+$ 385

Comp. No.	R_{1a}	R_4	R_5	Analytical data
A91	CH_3		$N(CH_3)CH_2CF_3$	See experimental part (Example 7)
A92	CH_3		$N(H)CH_2CF_3$	See experimental part (Example 6)
A93	CH_3		N(H)2-BrPh	LC MS (method A) Rt 1.02 min): $[M+H]^+$ 479
A94	H		CH_2Cl	LC-MS (method A): 342 (M+1)+, retention time 0.73 min
A95	H		CF_3	LC-MS (method A): 356 (M+1)+, retention time 0.77 min
A96	H		Ph	LC-MS (method A): 364 (M+1)+, retention time 0.75 min
A97	H	CF_3	CF_3	LC-MS (method A): 313 (M+1)+, retention time 0.77 min
A98	H	CF_3	Ph	LC-MS (method A): 321 (M+1)+, retention time 0.76 min

Comp. No.	R_{1a}	R_4	R_5	Analytical data
A99	CH_3		Ph	LC-MS (method A): 378 (M+1)+, retention time 0.78 min
A100	H	CH_2CF_3	Ph	LC-MS (method A): 335 (M+1)+, retention time 0.79 min
A101	H	CH_2CF_3	CF_3	LC-MS (method A): 327 (M+1)+, retention time 0.80 min
A124	H		N(H)((3, 5-di CF_3)Ph)	LC-MS (method A): 521/523 (M+1)+, retention time 1.18 min
A125	H		N(CH_3)(4-ClPh)	LC-MS (method A): 433/435/437 (M+1)+, retention time 0.84 min
A126	H		N(H)(4-ClPh)	LC-MS (method A): 419/421/423 (M+1)+, retention time 1.02 min
A127	CH_3		m-I-Ph	LC-MS (method A): 510/512 (M+1)+, retention time 0.96 min
A128	CH_3		3-Cl, 5-Br-Ph	LC-MS (method A): 496/498/500 (M+1)+, retention time 1.04 min
A129	CH_3		4-pyridyl	LC-MS (method A): 384/386 (M+1)+, retention time 0.61 min

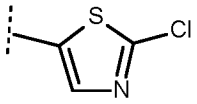
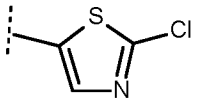
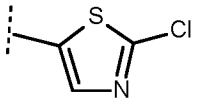
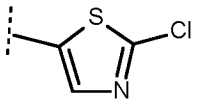
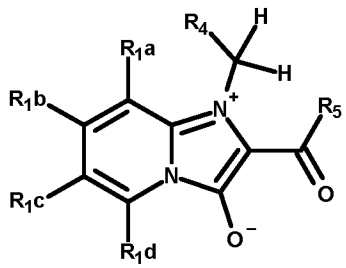
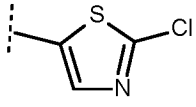
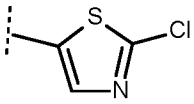
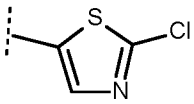
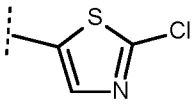
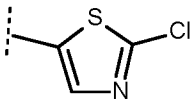
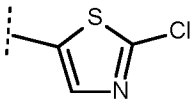
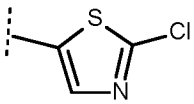
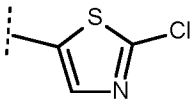
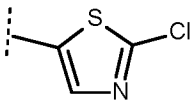
Comp. No.	R_{1a}	R_4	R_5	Analytical data
A130	CH_3		C_2F_5	LC-MS (method A): 426/428 (M+1)+, retention time 0.94 min
A131	CH_3		4-CF_3Ph	LC-MS (method A): 452/454 (M+1)+, retention time 0.97 min
A132	CH_3		2-CF_3Ph	LC-MS (method A): 452/454 (M+1)+, retention time 0.89 min
A133	H		-$CHCl_2$	LC-MS (method A): 376/378/380 (M+1)+, retention time 0.87 min

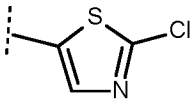
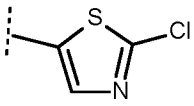
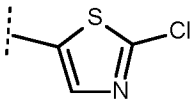
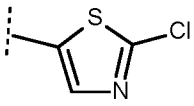
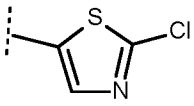
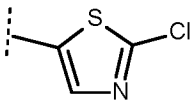
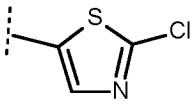
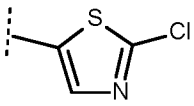
Table A2: This table discloses compounds of the formula Ia :



(Ia),

Comp. No.	R_{1a}	R_{1b}	R_{1c}	R_{1d}	R_4	R_5	Analytical data
A102	H	H	H	CH_3		Ph	LC-MS (method A): 384 (M+1)+, retention time 0.87 min

Comp. No.	R_{1a}	R_{1b}	R_{1c}	R_{1d}	R_4	R_5	Analytical data
A103	H	H	H	CF_3		CF_3	LC-MS (method A): 430 (M+1)+, retention time 0.92 min
A104	H	H	H	CH_3		CF_3	LC-MS (method A): 376 (M+1)+, retention time 0.88 min
A105	H	H	H	CF_3		Ph	LC-MS (method A): 438 (M+1)+, retention time 0.92 min
A106	CH_3	H	H	Cl		CF_3	LC-MS (method A): 410 (M+1)+, retention time 0.89 min
A107	CH_3	H	H	Cl		Ph	LC-MS (method A): 418 (M+1)+, retention time 0.87 min
A108	H	CH_3	H	H		3,5-diClPh	LC-MS (method A): 452 (M+1)+, retention time 1.05 min
A109	H	CH_3	H	H		CF3	LC-MS (method A): 376 (M+1)+, retention time 0.88 min
A110	H	H	CH_3	H		CF3	LC-MS (method A): 376 (M+1)+, retention time 0.88min

Comp. No.	R_{1a}	R_{1b}	R_{1c}	R_{1d}	R_4	R_5	Analytical data
A111	H	H	CH_3	H		3,5-diClPh	LC-MS (method A): 452 (M+1)+, retention time 1.06 min
A112	H	H	OCH_3	H		3,5-diClPh	LC-MS (method A): 392 (M+1)+, retention time 0.89 min
A113	H	H	OCH_3	H		CF3	LC-MS (method A): 468 (M+1)+, retention time 1.06 min
A114	H	H	F	H		CF3	LC-MS (method A): 380 (M+1)+, retention time 0.87 min
A115	H	H	F	H		3,5-diClPh	LC-MS (method A): 456 (M+1)+, retention time 1.05 min
A116	H	Cl	H	H		3,5-diClPh	LC-MS (method A): 474 (M+1)+, retention time 1.08 min
A117	H	Cl	H	H		CF3	LC-MS (method A): 396 (M+1)+, retention time 0.9 min
A118	H	OCH_3	H	H		CF_3	LC-MS (method A): 392 (M+1)+, retention time 0.87 min

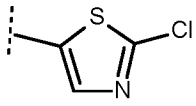
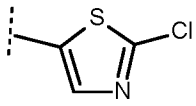
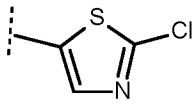
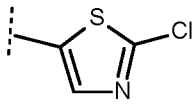
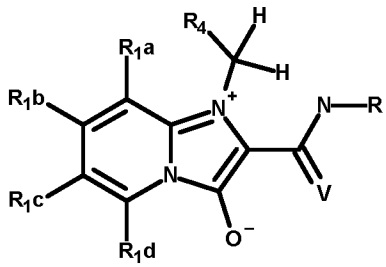
Comp. No.	R_{1a}	R_{1b}	R_{1c}	R_{1d}	R_4	R_5	Analytical data
A119	H	OCH_3	H	H		3,5-diClPh	LC-MS (method A): 468 (M+1)+, retention time 1.04 min
A120	H	F	H	H		CF_3	LC-MS (method A): 380 (M+1)+, retention time 0.86 min
A121	H	F	H	H		3,5-diClPh	LC-MS (method A): 456 (M+1)+, retention time 1.03 min
A122	H	H	Cl	H		3,5-diClPh	LC-MS (method A): 474 (M+1)+, retention time 1.09 min

Table A3: This table discloses compounds of the formula Id :



(Id),

Wherein R_{1a}, R_{1b}, R_{1c}, and R_{1d} are each Hydrogen, V is S and: .

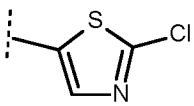
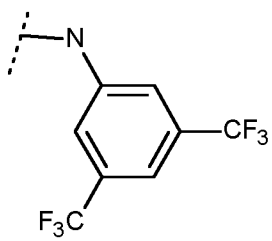
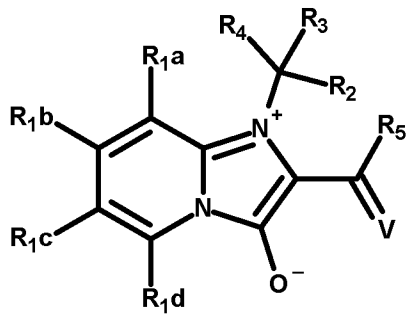
Comp. No.	R_4	N-R	Analytical data
A123			See experimental part (Example 8)

Table A4: This table discloses compounds of the formula I :

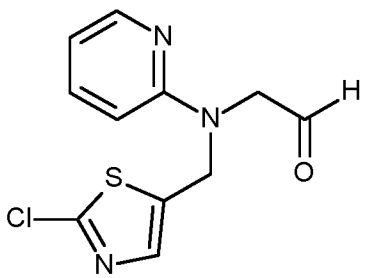
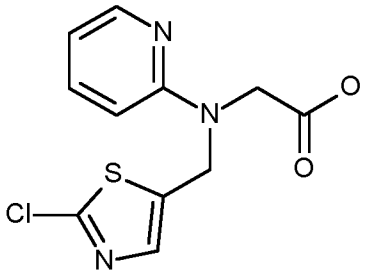


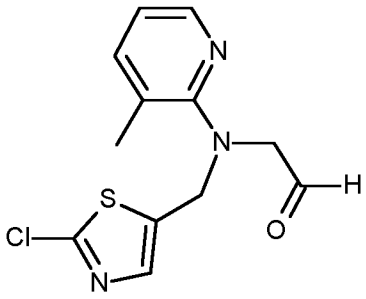
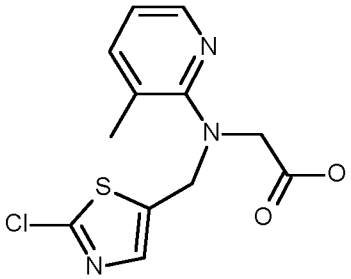
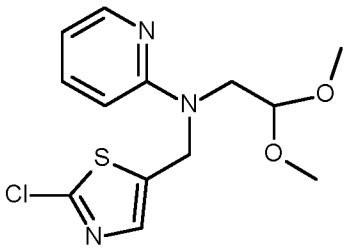
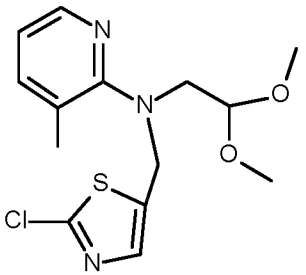
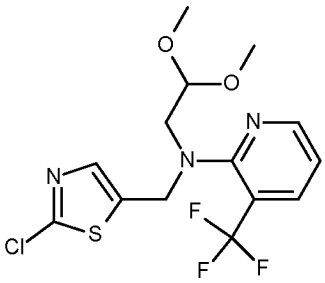
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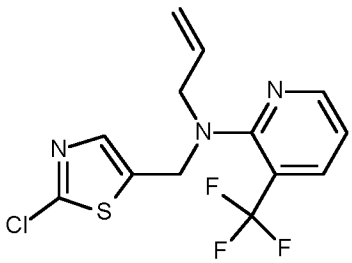
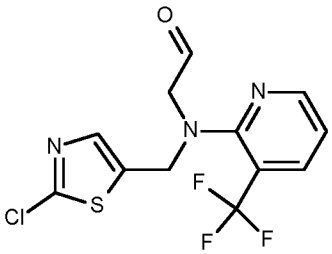
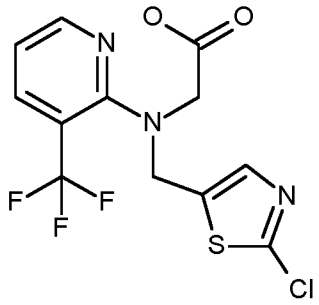
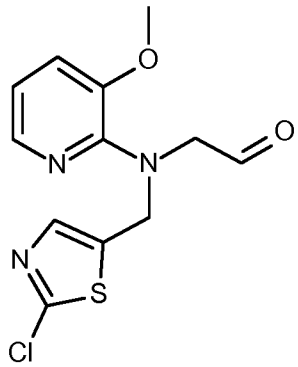
Wherein R_{1b}, R_{1c}, R_{1d}, R_3, R_4 are each Hydrogen, V is O, and:

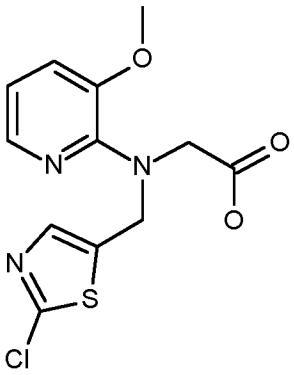
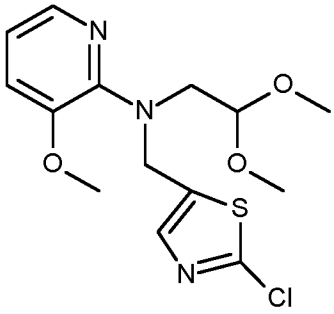
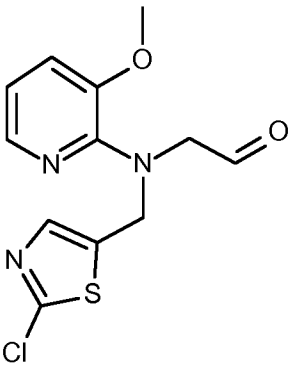
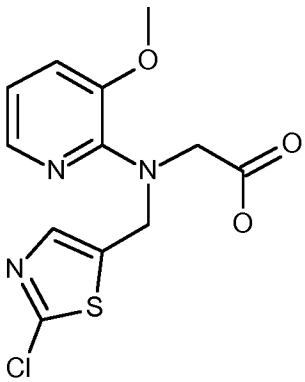
Comp. No.	R_{1a}	R_2	R_5	Analytical data
A134	CH_3	$-CH_2CN$	Ph	^{1}H-NMR (DMSO-d_6, 400 MHz, δ in ppm): 7.67 (d, 2 H), 7.48-7.42 (m, 2 H), 7.37 (t, 2 H), 6.67 (d, 1 H), 5.02 (t, 2H), 3.01 (t, 2 H), 2.83 (s, 3 H), 2.64 (s, 3 H).
A135	H	$-CH_2CN$	CF_3	LC-MS (method A): 284 (M+1)+, retention time 0.59 min

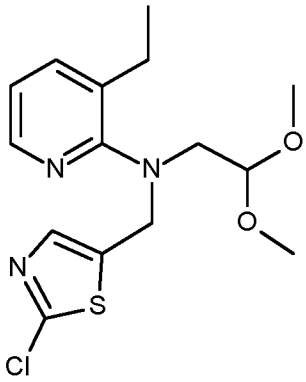
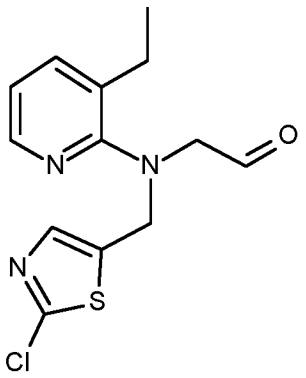
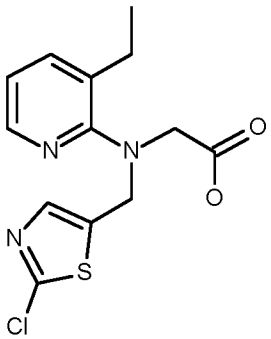
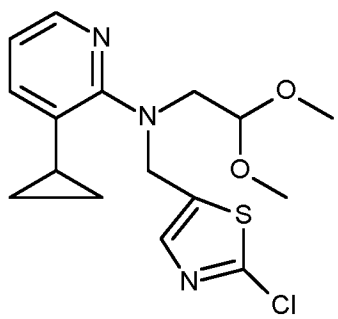
Table B: Examples of intermediates of formulae (IV), (V) and (VI)

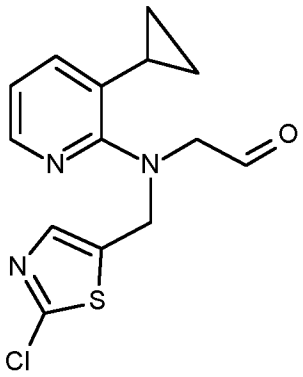
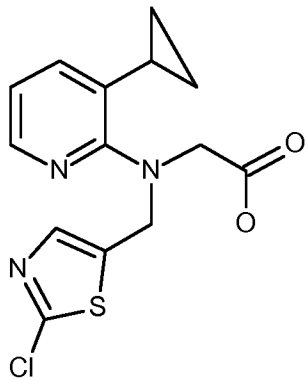
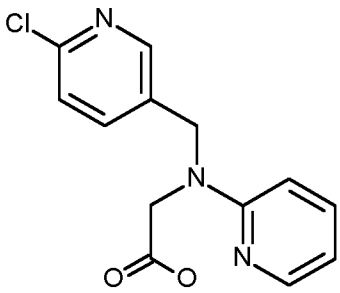
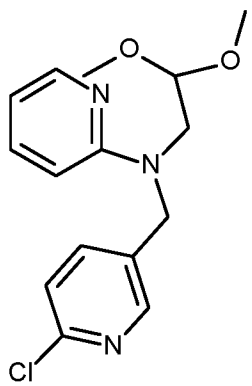
No.	IUPAC name	Structures	Analytical data
B1	2-[(2-chlorothiazol-5-yl)methyl-(2-pyridyl)amino]acetaldehyde		See experimental part step I1-C of example I1
B2	2-[(2-chlorothiazol-5-yl)methyl-(2-pyridyl)amino]acetic acid		See experimental part step I1-D of example I1

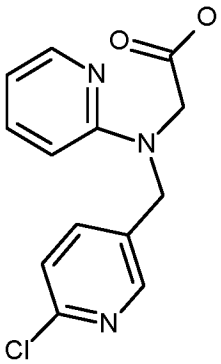
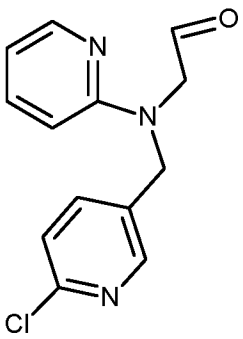
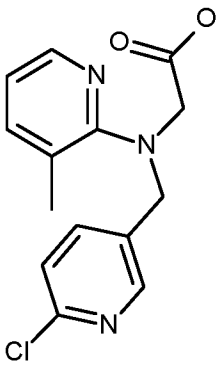
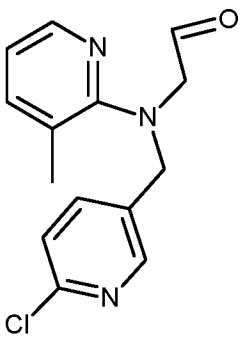
No.	IUPAC name	Structures	Analytical data
B3	2-[(2-chlorothiazol-5-yl)methyl-(3-methyl-2-pyridyl)amino]acetaldehyde		See experimental part step I2-C of example I2
B4	2-[(2-chlorothiazol-5-yl)methyl-(3-methyl-2-pyridyl)amino]acetic acid		See experimental part step I2-D of example I2
B5	N-[(2-chlorothiazol-5-yl)methyl]-N-(2,2-dimethoxyethyl)pyridin-2-amine		See experimental part step I1-B of example I1
B6	N-[(2-chlorothiazol-5-yl)methyl]-N-(2,2-dimethoxyethyl)-3-methyl-pyridin-2-amine		See experimental part step I2-B of example I2
B7	N-[(2-chlorothiazol-5-yl)methyl]-N-(2,2-dimethoxyethyl)-3-(trifluoromethyl)pyridin-2-amine		LC-MS (method A): 382 $(M+1)^+$, retention time 1.12 min

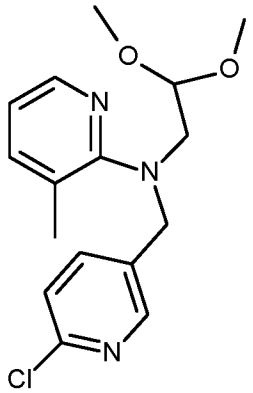
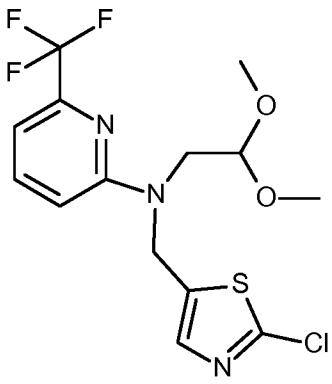
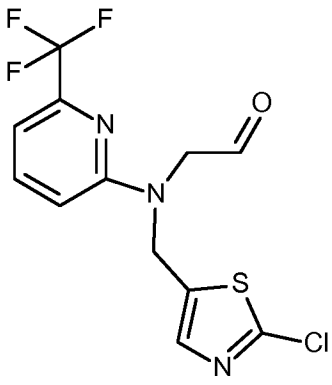
No.	IUPAC name	Structures	Analytical data
B8	N-allyl-N-[(2-chlorothiazol-5-yl)methyl]-3-(trifluoromethyl)pyridin-2-amine		LC-MS (method A): 334 $(M+1)^+$, retention time 1.21 min
B9	2-[(2-chlorothiazol-5-yl)methyl-[3-(trifluoromethyl)-2-pyridyl]amino]acetaldehyde		LC-MS (method A): 336 $(M+1)^+$, retention time 0.57 min
B10	2-[(2-chlorothiazol-5-yl)methyl-[3-(trifluoromethyl)-2-pyridyl]amino]acetic acid		LC-MS (method A): 351 $(M+1)^+$, retention time 0.93 min
B11	2-[(2-chlorothiazol-5-yl)methyl-(3-methoxy-2-pyridyl)amino]acetaldehyde		LC-MS (method A): 298 $(M+1)^+$, retention time 0.28 min

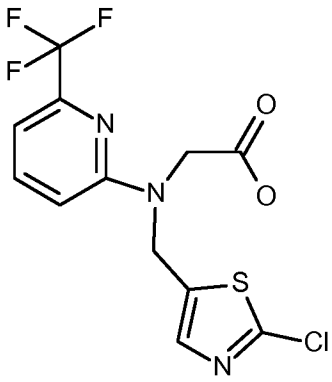
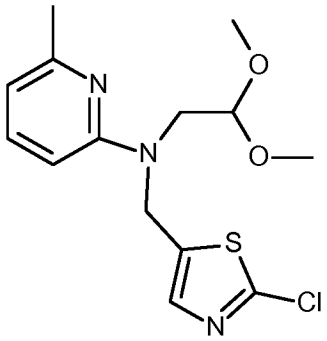
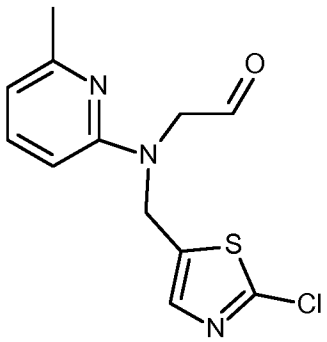
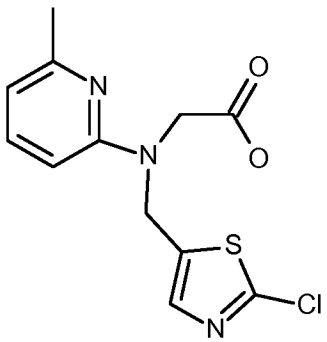
No.	IUPAC name	Structures	Analytical data
B12	2-[(2-chlorothiazol-5-yl)methyl-(3-methoxy-2-pyridyl)amino]acetic acid		LC-MS (method A): 314 $(M+1)^+$, retention time 0.81 min
B13	N-[(2-chlorothiazol-5-yl)methyl]-N-(2,2-dimethoxyethyl)-3-methoxy-pyridin-2-amine		LC-MS (method A): 444 $(M+1)^+$, retention time 1.01 min
B14	2-[(2-chlorothiazol-5-yl)methyl-(3-methoxy-2-pyridyl)amino]acetaldehyde		LC-MS (method A): 298 $(M+1)^+$, retention time 0.28 min
B15	2-[(2-chlorothiazol-5-yl)methyl-(3-methoxy-2-pyridyl)amino]acetic acid		LC-MS (method A): 314 $(M+1)^+$, retention time 0.81 min

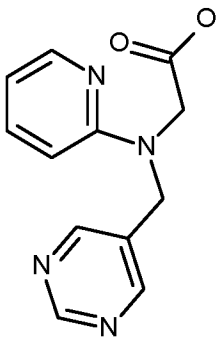
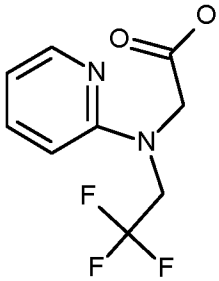
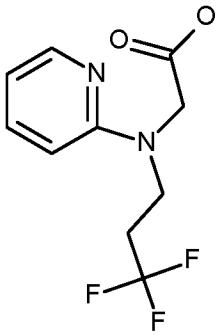
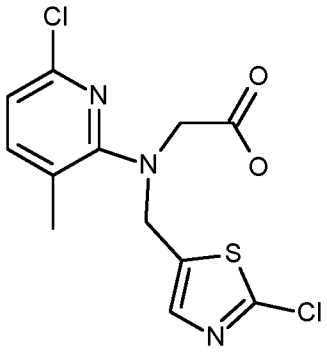
No.	IUPAC name	Structures	Analytical data
B16	N-[(2-chlorothiazol-5-yl)methyl]-N-(2,2-dimethoxyethyl)-3-ethyl-pyridin-2-amine		LC-MS (method A): 342 $(M+1)^+$, retention time 1.08 min
B17	2-[(2-chlorothiazol-5-yl)methyl-(3-ethyl-2-pyridyl)amino]acetaldehyde		LC-MS (method A): 296 $(M+1)^+$, retention time 0.5 min
B18	2-[(2-chlorothiazol-5-yl)methyl-(3-ethyl-2-pyridyl)amino]acetic acid		LC-MS (method A): 312 $(M+1)^+$, retention time 0.85 min
B19	N-[(2-chlorothiazol-5-yl)methyl]-3-cyclopropyl-N-(2,2-dimethoxyethyl)pyridin-2-amine		LC-MS (method A): 354 $(M+1)^+$, retention time 1.07 min

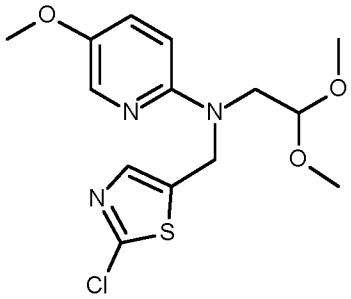
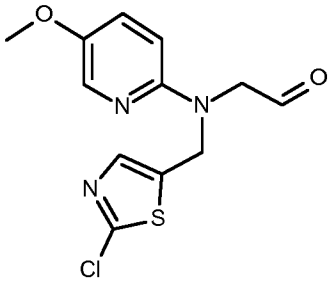
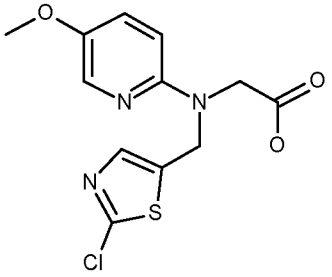
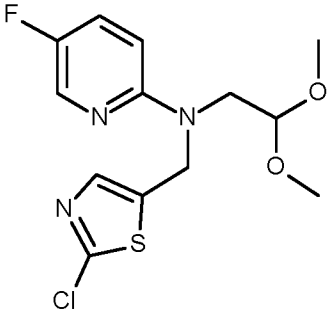
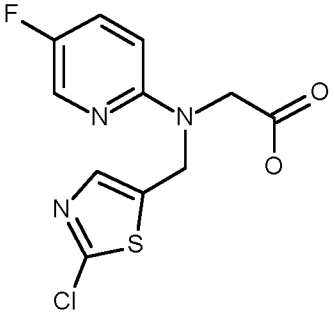
No.	IUPAC name	Structures	Analytical data
B20	2-[(2-chlorothiazol-5-yl)methyl-(3-cyclopropyl-2-pyridyl)amino]acetaldehyde		LC-MS (method A): 308 $(M+1)^+$, retention time 0.53 min
B21	2-[(2-chlorothiazol-5-yl)methyl-(3-cyclopropyl-2-pyridyl)amino]acetic acid		LC-MS (method A): 324 $(M+1)^+$, retention time 0.88 min
B22	2-[(6-chloro-3-pyridyl)methyl-(2-pyridyl)amino]acetic acid		LC-MS (method A): 278 (M+1)+, retention time 0.52 min
B23	N-[(6-chloro-3-pyridyl)methyl]-N-(2,2-dimethoxyethyl)pyridin-2-amine		^{1}H NMR (300 MHz, DMSO-d_6): δ 8.27 (s, 1H), 8.08 (d, 1H), 7.65 (d, 1H), 7.50 – 7.42 (m, 2H), 6.60 (d, 2H), 4.78 (s, 2H), 4.57 (t, 1H), 3.66 (d, 2H), 3.28 (s, 6H).

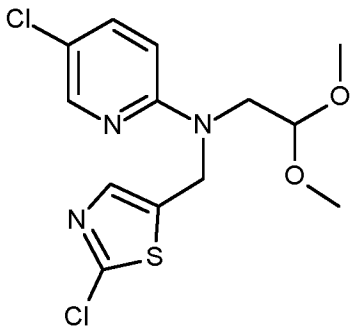
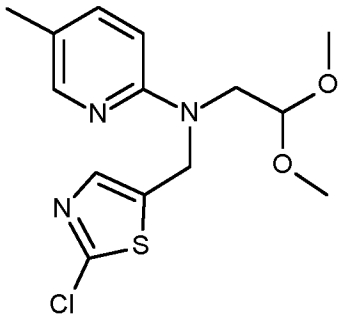
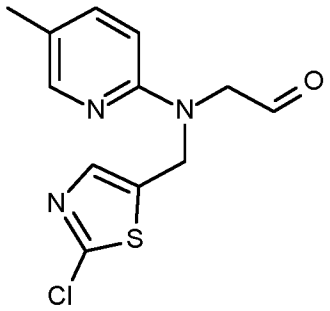
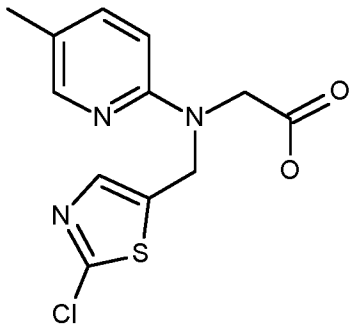
No.	IUPAC name	Structures	Analytical data
B24	2-[(6-chloro-3-pyridyl)methyl-(2-pyridyl)amino]acetic acid		^{1}H NMR (300 MHz, DMSO-d_6): δ 12.54 (s, 1H), 8.39 (s, 1H), 8.08 (s, 1H), 7.81 – 7.78 (m, 1H), 7.47 –7.44 (m, 2H), 6.65 – 6.53 (m, 2H), 4.77 (s, 2H), 4.29 (s, 2H).
B25	2-[(6-chloro-3-pyridyl)methyl-(2-pyridyl)amino]acetaldehyde		^{1}H NMR (400 MHz, $CDCl_3$): δ 9.67 (s, 1H), 8.32 (d, 1H), 8.16 – 8.14 (m, 1H), 7.62 (dd, 1H), 7.48 – 7.45 (m, 1H), 7.30 – 7.26 (m, 1H), 6.70 – 6.67 (m, 1H), 6.47 (d, 1H), 4.75 (s, 2H), 4.27 (s, 2H).
B26	2-[(6-chloro-3-pyridyl)methyl-(3-methyl-2-pyridyl)amino]acetic acid		^{1}H NMR (300 MHz, DMSO-d_6): δ 12.44 (s, 1H), 8.36 (s, 1H), 8.00 (s, 1H), 7.82 (d, 1H), 7.46 – 7.40 (m, 2H), 6.86 – 6.85 (m, 1H), 4.52 (s, 2H), 3.89 (s, 2H), 2.22 (s, 3H).
B27	2-[(6-chloro-3-pyridyl)methyl-(3-methyl-2-pyridyl)amino]acetaldehyde		^{1}H NMR (400 MHz, DMSO-d_6): δ 9.43 (brs, 1H), 8.36 (d, 1H), 8.00 (d, 1H), 7.82 (m, 1H), 7.54 (d, 1H), 7.48 (d, 1H), 6.91 – 6.88 (m, 1H), 4.55 (s, 2H), 3.95 (s, 2H), 2.25 (s, 3H).

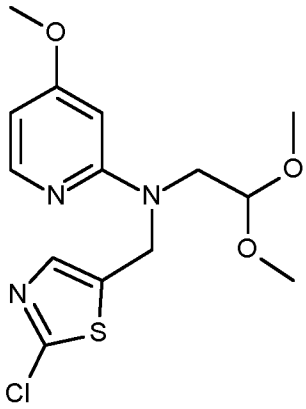
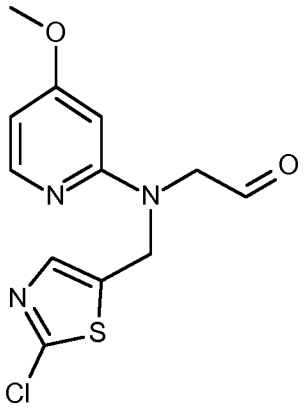
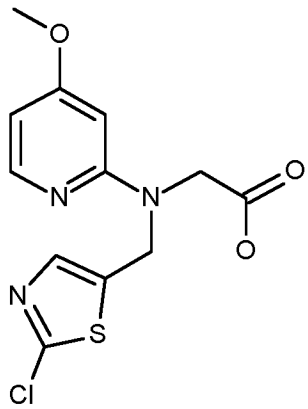
No.	IUPAC name	Structures	Analytical data
B28	N-[(6-chloro-3-pyridyl)methyl]-N-(2,2-dimethoxyethyl)-3-methyl-pyridin-2-amine		^{1}H NMR (300 MHz, DMSO-d_6): δ 8.29 (s, 1H), 8.06 (d, 1H), 7.72 (d, 1H), 7.51 (d, 1H), 7.42 (d, 1H), 6.91 (t, 1H), 4.47 – 4.45 (m, 2H), 3.28 – 3.24 (m, 3H), 3.19 (s, 6H), 2.27 (s, 3H).
B29	N-[(2-chlorothiazol-5-yl)methyl]-N-(2,2-dimethoxyethyl)-6-(trifluoromethyl)pyridin-2-amine		^{1}H NMR (300 MHz, DMSO-d_6): δ 7.78 (d, 1H), 7.74 (s, 1H), 7.12 – 7.05 (m, 2H), 4.86 (s, 2H), 4.55 (t, 1H), 3.58 (d, 2H), 3.31 (s, 6H).
B30	2-[(2-chlorothiazol-5-yl)methyl-[6-(trifluoromethyl)-2-pyridyl]amino]acetaldehyde		^{1}H NMR (300 MHz, DMSO-d_6): δ 9.55 (s, 1H), 7.79 – 7.74 (m, 2H), 7.13 (d, 1H), 6.98 (d, 1H), 4.87 (s, 2H), 4.52 (s, 2H).

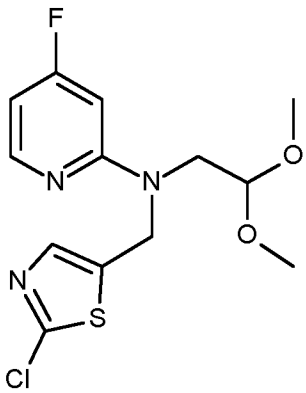
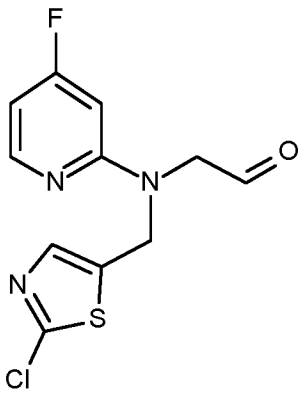
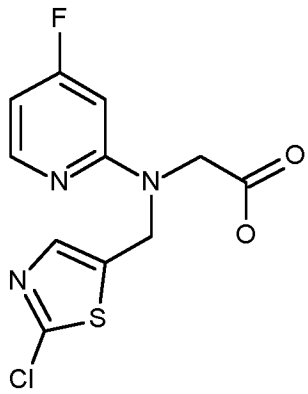
No.	IUPAC name	Structures	Analytical data
B31	2-[(2-chlorothiazol-5-yl)methyl-[6-(trifluoromethyl)-2-pyridyl]amino]acetic acid		^{1}H NMR (400 MHz, DMSO-d_6): δ 12.75 (s, 1H), 7.78 (t, 1H), 7.71 (s, 1H), 7.13 (d, 1H), 6.95 (d, 1H), 4.87 (s, 2H), 4.32 (s, 2H).
B32	N-[(2-chlorothiazol-5-yl)methyl]-N-(2,2-dimethoxyethyl)-6-methyl-pyridin-2-amine		^{1}H NMR (300 MHz, DMSO-d_6): δ 7.69 (s, 1H), 7.43 (t, 1H), 6.54 (d, 2H), 4.78 (s, 2H), 4.51 (t, 1H), 3.47 (d, 2H), 3.31 (s, 6H), 2.38 (s, 3H).
B33	2-[(2-chlorothiazol-5-yl)methyl-(6-methyl-2-pyridyl)amino]acetaldehyde		^{1}H NMR (300 MHz, DMSO-d_6): δ 9.25 (s, 1H), 7.66 (s, 1H), 7.41 (t, 1H), 6.53 – 6.49 (m, 2H), 4.86 (s, 2H), 3.23 (s, 2H), 2.38 (s, 3H).
B34	2-[(2-chlorothiazol-5-yl)methyl-(6-methyl-2-pyridyl)amino]acetic acid		^{1}H NMR (300 MHz, DMSO-d_6): δ 12.64 (s, 1H), 7.67 (s, 1H), 7.42 (t, 1H), 6.55 (d, 1H), 6.41 (d, *1*H), 4.80 (s, 2H), 4.20 (s, 2H), 2.38 (s, 3H).

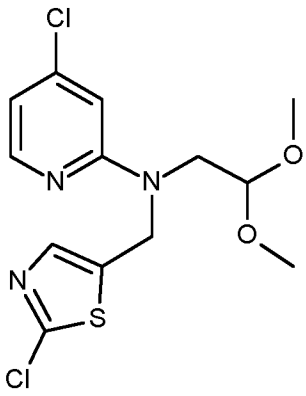
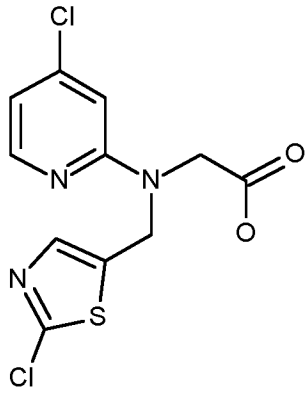
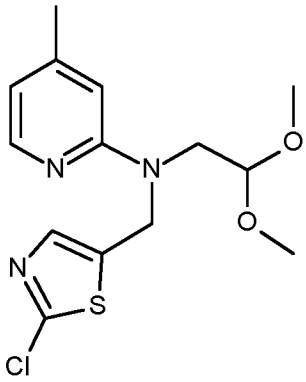
No.	IUPAC name	Structures	Analytical data
B35	2-[2-pyridyl(pyrimidin-5-ylmethyl)amino]acetic acid		^{1}H NMR (400 MHz, DMSO-d_6): δ 12.59 (s, 1H), 9.05 (s, 1H), 8.77 (s, 2H), 8.08 (d, 1H), 7.52 – 7.48 (m, 1H), 6.64 (t, 1H), 6.58 (d, 1H), 4.79 (s, 2H), 4.33 (s, 2H).
B36	2-[2-pyridyl(2,2,2-trifluoroethyl)amino]acetic acid		^{1}H NMR (300 MHz, DMSO-d_6): δ 8.11 (d, 1H), 7.64 – 7.58 (m, 1H), 6.84 (d, 1H), 6.77 – 6.73 (m, 1H), 4.49 – 4.40 (m, 2H), 4.26 (s, 2H).
B37	2-[2-pyridyl(3,3,3-trifluoropropyl)amino]acetic acid		^{1}H NMR (300 MHz, DMSO-d_6): δ 8.09 (d, 1H), 7.66 – 7.57 (m, 1H), 6.73 – 6.71 (m, 2H), 4.35 – 4.27 (m, 2H), 3.78 (t, 2H), 2.78 – 2.62 (m, 2H).
B38	2-[(6-chloro-3-methyl-2-pyridyl)-[(2-chlorothiazol-5-yl)methyl]amino]acetic acid		^{1}H NMR (400 MHz, DMSO-d_6): δ 12.68 (s, 1H), 7.67 (s, 1H), 7.50 (d, 1H), 6.91 (d, 1H), 4.63 (s, 2H), 3.98 (s, 2H), 2.19 (s, 3H).

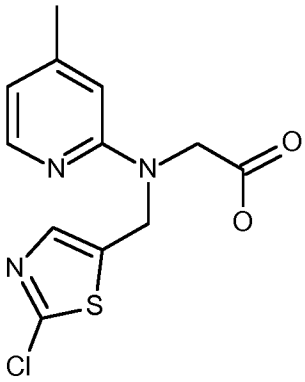
No.	IUPAC name	Structures	Analytical data
B39	N-[(2-chlorothiazol-5-yl)methyl]-N-(2,2-dimethoxyethyl)-5-methoxy-pyridin-2-amine		^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, 1H), 7.42 (s, 1H), 7.15 (d, 1H), 6.59 (d, 1H), 4.81 (s, 2H), 4.50 (t, 1H), 3.80 (s, 3H), 3.46 (d, 2H), 3.40 (s, 6H).
B40	2-[(2-chlorothiazol-5-yl)methyl-(5-methoxy-2-pyridyl)amino] acetaldehyde		^{1}H NMR (400 MHz, DMSO-d6) δ 9.43 (s, 1H), 7.85 (d, 1H), 7.57 (d, 1H), 7.27 (m, 1H), 6.68 (t, 1H), 4.79 (d, 2H), 4.25 (s, 2H), 3.71 (s, 3H).
B41	2-[(2-chlorothiazol-5-yl)methyl-(5-methoxy-2-pyridyl)amino]acetic acid		^{1}H-NMR (400 MHz, DMSO-d6) δ 12.48 (s, 1H), 7.88 (d, 1H), 7.62 (s, 1H), 7.25 (m, 1H), 6.59 (d, 1H), 4.77 (s, 2H), 4.14 (s, 2H), 3.70 (d, 3H).
B42	N-[(2-chlorothiazol-5-yl)methyl]-N-(2,2-dimethoxyethyl)-5-fluoro-pyridin-2-amine		^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.05 (d, 1H), 7.42 (s, 1H), 7.25 – 7.22 (m, 1H), 6.57 (dd, 1H), 4.80 (s, 2H), 4.49 (t, 1H), 3.45 (t, 2H), 3.40 (s, 6H).
B43	2-[(2-chlorothiazol-5-yl)methyl-(5-fluoro-2-pyridyl)amino]acetic acid		^{1}H-NMR (400 MHz, DMSO-d6) δ 12.61 (s, 1H), 8.11 (d, 1H), 7.64 (s, 1H), 7.50 (m, 1H), 6.65 (m, 1H), 4.80 (s, 2H), 4.20 (s, 2H).

No.	IUPAC name	Structures	Analytical data
B44	5-chloro-N-[(2-chlorothiazol-5-yl)methyl]-N-(2,2-dimethoxyethyl)pyridin-2-amine		^{1}H-NMR (400 MHz, DMSO-d6) δ 8.14 (d, 1H), 7.66 (s, 1H), 7.59 (dd, 1H), 6.78 (d, J1H), 4.80 (s, 2H), 4.54 – 4.46 (m, 1H), 3.50 (d, 2H), 3.27 (d, 6H).
B45	N-[(2-chlorothiazol-5-yl)methyl]-N-(2,2-dimethoxyethyl)-5-methyl-pyridin-2-amine		^{1}H-NMR (400 MHz, DMSO-d6) δ 7.96 (s, 1H), 7.63 (s, 1H), 7.35 (d, 1H), 6.65 (d, 1H), 4.77 (s, 2H), 4.49 (t, 1H), 3.44 (d, 2H), 3.27 (s, 6H), 2.13 (s, 3H).
B46	2-[(2-chlorothiazol-5-yl)methyl-(5-methyl-2-pyridyl)amino]acetaldehyde		LC-MS (method B): 282.1(M+H)+ Ret.Time: 1.18 min
B47	2-[(2-chlorothiazol-5-yl)methyl-(5-methyl-2-pyridyl)amino]acetic acid		^{1}H-NMR (400 MHz, DMSO-d6) δ 12.52 (s, 1H), 7.96 (s, 1H), 7.63 (s, 1H), 7.35 (d, 1H), 6.53 (d, 1H), 4.79 (s, 2H), 4.16 (s, 2H), 2.13 (s, 3H).

No.	IUPAC name	Structures	Analytical data
B48	N-[(2-chlorothiazol-5-yl)methyl]-N-(2,2-dimethoxyethyl)-4-methoxy-pyridin-2-amine		^{1}H-NMR (400 MHz, DMSO-d6) δ 7.96 (d, 1H), 7.65 (s, 1H), 6.31 (d, 1H), 6.17 (s, 1H), 4.79 (s, 2H), 4.51 (t, 1H), 3.46 (d, 2H), 3.28 (d, 6H).
B49	2-[(2-chlorothiazol-5-yl)methyl-(4-methoxy-2-pyridyl)amino]acetaldehyde		^{1}H-NMR (400 MHz, DMSO-d6) δ 9.42 (s, 1H), 7.93 (d, 1H), 7.62 (s, 1H), 6.34 (d, 1H), 6.18 (s, 1H), 4.84 (s, 2H), 4.30 (s, 2H), 3.74 (s, 3H).
B50	2-[(2-chlorothiazol-5-yl)methyl-(4-methoxy-2-pyridyl)amino]acetic acid		^{1}H-NMR (400 MHz, DMSO-d6) δ 12.82 (s, 1H), 7.95 (d, J = 5.7 Hz, 1H), 7.63 (s, 1H), 6.31 (d, 1H), 6.05 (s, 1H), 4.80 (s, 2H), 4.15 (s, 2H), 3.72 (s, 3H).

No.	IUPAC name	Structures	Analytical data
B51	N-[(2-chlorothiazol-5-yl)methyl]-N-(2,2-dimethoxyethyl)-4-fluoro-pyridin-2-amine		^{1}H-NMR (400 MHz, DMSO-d6) δ 8.15 (dd, 1H), 7.67 (s, 1H), 6.57 (d, 2H), 4.82 (s, 2H), 4.55 – 4.46 (m, 1H), 3.49 (d, 2H), 3.28 (t, 6H).
B52	2-[(2-chlorothiazol-5-yl)methyl-(4-fluoro-2-pyridyl)amino]acetaldehyde		^{1}H-NMR (400 MHz, DMSO-d6) δ 9.48 (s, 1H), 8.13 (m, 1H), 7.62 (s, 1H), 6.59 (t, 2H), 4.84 (s, 2H), 4.40 (s, 2H).
B53	2-[(2-chlorothiazol-5-yl)methyl-(4-fluoro-2-pyridyl)amino]acetic acid		^{1}H-NMR (400 MHz, DMSO-d6) δ 12.65 (s, 1H), 8.19 – 8.07 (m, 1H), 7.65 (s, 1H), 6.58 (t, 1H), 6.52 (d, 1H), 4.83 (s, 2H), 4.22 (s, 2H).

No.	IUPAC name	Structures	Analytical data
B54	4-chloro-N-[(2-chlorothiazol-5-yl)methyl]-N-(2,2-dimethoxyethyl)pyridin-2-amine		^{1}H-NMR (400 MHz, DMSO-d6) δ 8.10 (d, 1H), 7.67 (s, 1H), 6.82 (s, 1H), 6.74 (dd, 1H), 4.82 (s, 2H), 4.51 (t, 1H), 3.51 (d, 2H), 3.28 (s, 6H).
B55	2-[(4-chloro-2-pyridyl)-[(2-chlorothiazol-5-yl)methyl]amino]acetic acid		^{1}H-NMR (400 MHz, DMSO-d6) δ 12.66 – 12.48 (m, 1H), 8.10 (d, 1H), 7.65 (s, 1H), 6.79 – 6.70 (m, 2H), 4.84 (s, 2H), 4.24 (s, 2H).
B56	N-[(2-chlorothiazol-5-yl)methyl]-N-(2,2-dimethoxyethyl)-4-methyl-pyridin-2-amine		^{1}H-NMR (400 MHz, DMSO-d6) δ 7.99 (dd, 1H), 7.64 (d, 1H), 6.55 (s, 1H), 6.49 (d, 1H), 4.78 (s, 2H), 4.56 – 4.46 (m, 1H), 3.49 – 3.41 (m, 2H), 3.28 (d, 6H), 2.19 (d, 3H).

No.	IUPAC name	Structures	Analytical data
B57	2-[(2-chlorothiazol-5-yl)methyl-(4-methyl-2-pyridyl)amino]acetic acid		^{1}H-NMR (400 MHz, DMSO-d6) δ 12.56 (s, 1H), 7.98 (d, 1H), 7.64 (s, 1H), 6.51 (d, 1H), 6.43 (s, 1H), 4.80 (s, 2H), 4.17 (s, 2H), 2.18 (s, 3H).

BIOLOGICAL EXAMPLES:

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

The following compounds gave an effect of at least 80% in at least one of the two categories (i.e. mortality and growth inhibition) at an application rate of 200 ppm:

A1, A2, A3, A5, A6, A7, A9, A11, A12, A13, A14, A15, A20, A23, A24, A25, A28, A32, A33, A34, A35, A36, A41, A47, A51, A52, A53, A55, A60, A64, A65, A67, A68, A74, A75, A76, A77, A78, A83, A86, A88, A89, A92, A97, A110, A111, A114, A118, A122, A124, A127, A128, A130, A131

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

The following compounds gave an effect of at least 80% in at least one of the two categories (i.e mortality and growth inhibition) at an application rate of 200 ppm:

A2, A39, A53, A61, A64, A67, A70, A80, A101, A119, A135

Plutella xylostella (Diamond back moth)
24-well microtiter plates with artificial diet were treated with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions by pipetting. After drying, Plutella eggs were pipetted through a plastic stencil onto a gel blotting paper and the plate was closed with it. The samples were assessed for mortality and growth inhibition in comparison to untreated samples 8 days after infestation.

The following compounds gave an effect of at least 80% in at least one of the two categories (i.e mortality and growth inhibition) at an application rate of 200 ppm:

A16, A19, A23, A25, A26, A65, A66, A67, A68, A69, A70, A71, A72, A74, A75, A76, A77, A78, A79, A80, A81, A83, A84, A86, A89, A90, A114, A122

Myzus persicae (Green peach aphid):Feeding/Contact activity
Sunflower leaf discs were placed onto agar in a 24-well microtiter plate and sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying, the leaf discs were infested with an aphid population of mixed ages. The samples were assessed for mortality 6 days after infestation.

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

A3 , A5 , A9 , A17 , A127 , A128

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

The following compounds gave an effect of at least 80% in at least one of the two categories (i.e. mortality and growth inhibition) at an application rate of 200 ppm:

A1, A2, A5, A7, A8, A9, A10, A11, A12, A13, A14, A24, A32, A33, A34, A36, A41, A52, A62, A63, A64, A92, A127, A128

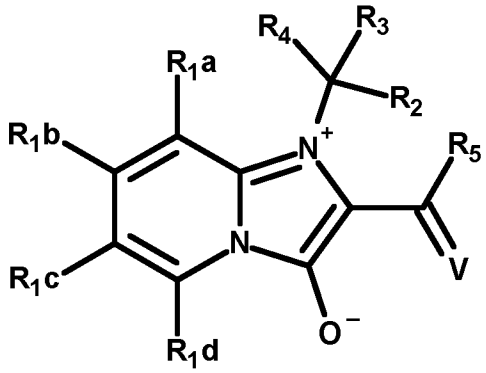
Spodoptera littoralis (Egyptian cotton leaf worm)
Cotton leaf discs were placed onto agar in 24-well microtiter plates and sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying the leaf discs were infested with five L1 larvae. The samples were assessed for mortality,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

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

A2, A3, A5, A9, A11, A12, A13, A14, A20, A21, A22, A23, A24, A25, A33, A34, A35, A36, A41, A51, A52, A53, A57, A62, A64, A67, A68, A71, A76, A77, A83, A86, A88, A89, A107, A127, A128, A130

CLAIMS:

1. A compound of formula I ,



(I),

wherein

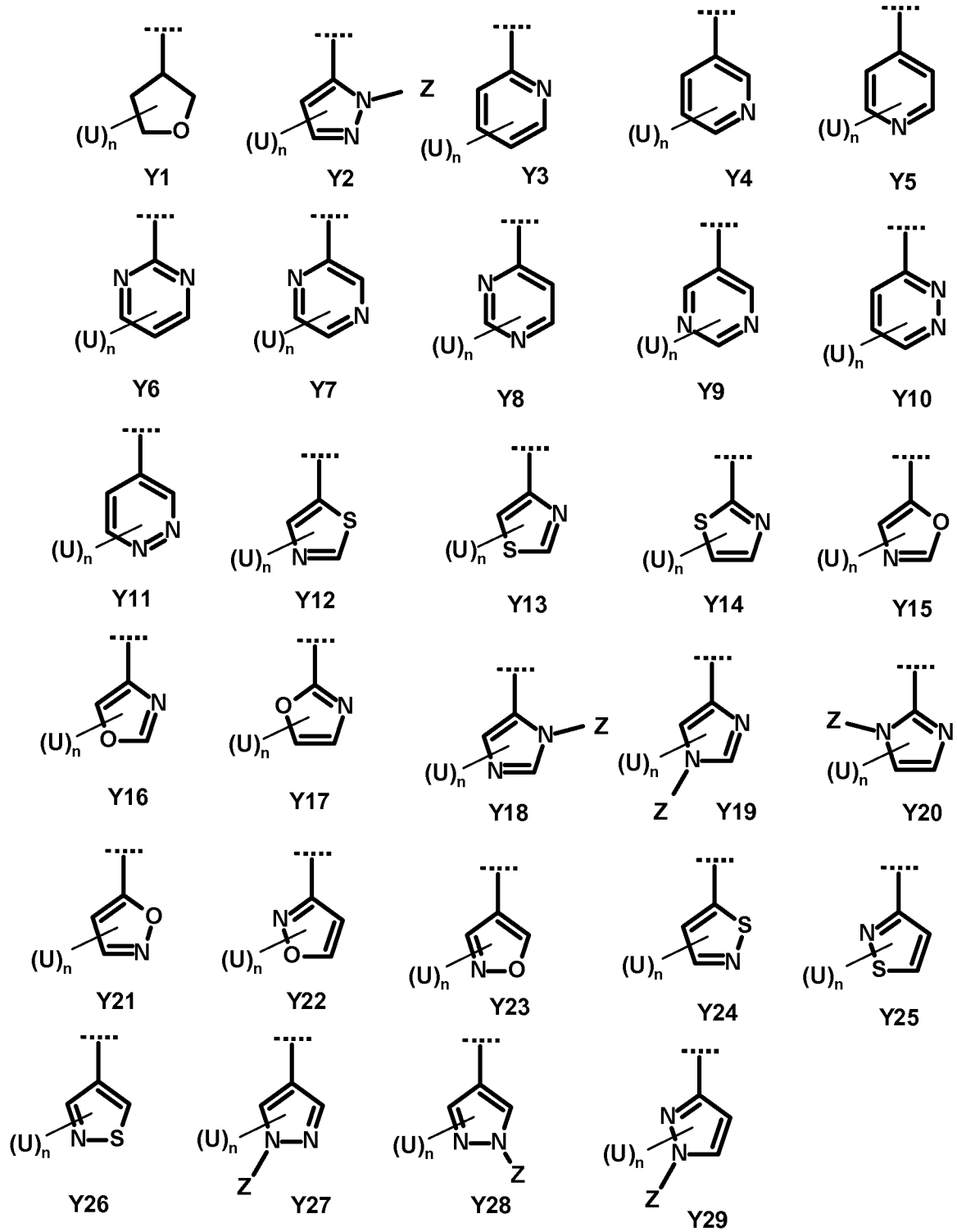
V is S or O;

R_{1a}, R_{1b}, R_{1c} and R_{1d} are independently selected from hydrogen, halogen, amino, hydroxyl, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_1-C_6 haloalkoxy, C_1-C_6 alkoxy, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl and cyano;

R_2 is hydrogen, halogen, hydroxyl, amino, cyano, C_1-C_6 alkyl, mono- or poly-substituted C_1-C_6 alkyl (where the substituents are independently selected from the group consisting of halogen, hydroxyl, amino, cyano, nitro, C_1-C_6 haloalkoxy, C_1-C_6 alkoxy, C_1-C_6 alkylsulfanyl, C_1-C_6 alkylsulfinyl, C_1-C_6 alkylsulfonyl, C_1-C_6 haloalkylsulfanyl, C_1-C_6 haloalkylsulfinyl and C_1-C_6 haloalkylsulfonyl), C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, triazole, pyrazole, imidazole, or tetrazole, wherein said triazole, pyrazole, imidazole and tetrazole can be mono- or polysubstituted by substituents independently selected from the group consisting of halogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl and cyano;

R_3 is hydrogen or C_1-C_6 alkyl;

R_4 is hydrogen or a 5 or 6 membered heteroaromatic ring Y, optionally independently substituted with a substituent from the group U, wherein Y is a ring selected from Y1 to Y29



wherein Z is hydrogen, cyano, nitro, hydroxyl, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkoxy, C_1-C_4 haloalkoxy-C_1-C_4 alkyl or C_1-C_4 alkoxy-C_1-C_4 alkyl;

n is 0, 1, 2, or 3;

U is independently selected from the group consisting of halogen, cyano, nitro, hydroxyl, amino, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkoxy, C_1-C_4 haloalkoxy-C_1-C_4 alkyl, C_1-C_4 alkoxy-C_1-C_4 alkyl, C_1-C_4 alkylsulfanyl, C_1-C_4 alkylsulfinyl, C_1-C_4 alkylsulfonyl, C_1-C_4 haloalkylsulfanyl, C_1-C_4

haloalkylsulfinyl, C_1-C_4 haloalkylsulfonyl, formyl, C_3-C_6cycloalkyl, C_3-C_6halocycloalkyl, C_1-C_6 alkylcarbonyl and C_3-C_6 cycloalkylcarbonyl; and

R_5 is hydrogen, -OR_6, -NR_8R_7, -$N(R_8)N(R_8R_7)$; or

R_5 is a 5 to 12 membered aromatic ring, which can be monocyclic or polycyclic, which ring system can be mono- or polysubstituted by substituents independently selected from the group U_2; or

R_5 is a 3 to 12 membered heteroaromatic ring, or a 3 to 12 membered saturated or partially saturated heterocyclic ring, each of which can be monocyclic or polycyclic, which ring system can contain 1 to 4 heteroatoms selected from the group consisting of nitrogen, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, wherein the nitrogen heteroatom can be substituted by Z and said 3 to 12-membered ring system can be mono- or polysubstituted by substituents independently selected from the group U_2; or

R_5 is C_3-C_6 cycloalkyl, which can be mono- or poly-substituted by substituents independently selected from the group U_3; or

R_5 is C_1-C_6 alkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3; or

R_5 is C_2-C_4 alkenyl which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3; or

R_5 is C_2-C_4 alkynyl which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3;

U_2 is selected from the group consisting of halogen, nitro, cyano, amino, hydroxyl, -SCN, -CO_2H, C_1-C_6 alkyl, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl, C_3-C_6 cycloalkyl-C_1-C_4 alkyl, C_3-C_6 halocycloalkyl-C_1-C_4 alkyl,C_1-C_6 haloalkyl, C_1-C_6 alkoxy, C_1-C_4 alkoxy-C_1-C_4 alkyl, C_1-C_4 alkoxy-C_1-C_4 alkoxy, cyano-C_1-C_4 alkyl, cyano-C_1-C_4 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_1-C_6 haloalkoxy, C_1-C_4 haloalkoxy-C_1-C_4 alkyl, C_1-C_6 alkylsulfanyl, C_1-C_6 alkylsulfinyl, C_1-C_6 alkylsulfonyl, C_1-C_6 haloalkylsulfanyl, C_1-C_6 haloalkylsulfinyl, C_1-C_6 haloalkylsulfonyl, C_1-C_6 alkylcarbonyl, C_1-C_6 alkoxycarbonyl, C_1-C_6 haloalkylcarbonyl, C_1-C_6 haloalkoxycarbonyl, (C_1-C_6 alkyl)NH, (C_1-C_6 alkyl)$_2$N, (C_3-C_6 cycloalkyl)NH, (C_3-C_6 cycloalkyl)$_2$N, C_1-C_6 alkylcarbonylamino, C_3-C_6 cycloalkylcarbonylamino, C_1-C_6 haloalkylcarbonylamino, C_3-C_6 halocycloalkylcarbonylamino, C_1-C_6 alkylaminocarbonyl, C_3-C_6 cycloalkylaminocarbonyl, C_1-C_6 haloalkylaminocarbonyl, C_3-C_6 halocycloalkylaminocarbonyl, C_3-C_6 cycloalkylcarbonyl, C_3-C_6 halocycloalkylcarbonyl, -SF_5 and -$C(O)NH_2$;

U_3 is selected from the group consisting of halogen, nitro, cyano, amino, hydroxyl, -SCN, -CO_2H, C_1-C_6 alkyl, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl, C_3-C_6 cycloalkyl-C_1-C_4 alkyl, C_3-C_6 halocycloalkyl-C_1-C_4 alkyl,C_1-C_6 haloalkyl, C_1-C_6 alkoxy, C_1-C_4 alkoxy-C_1-C_4 alkyl, C_1-C_4 alkoxy-C_1-C_4 alkoxy, cyano-C_1-C_4 alkyl, cyano-C_1-C_4 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_1-C_6 haloalkoxy, C_1-C_4 haloalkoxy-C_1-C_4 alkyl, C_1-C_6 alkylsulfanyl, C_1-C_6 alkylsulfinyl, C_1-C_6 alkylsulfonyl, C_1-C_6 haloalkylsulfanyl, C_1-C_6 haloalkylsulfinyl, C_1-C_6 haloalkylsulfonyl, C_1-C_6 alkylcarbonyl, C_1-C_6 alkoxycarbonyl, C_1-C_6 haloalkylcarbonyl, C_1-C_6 haloalkoxycarbonyl, (C_1-C_6 alkyl)NH, (C_1-C_6 alkyl)$_2$N, (C_3-C_6 cycloalkyl)NH, (C_3-C_6 cycloalkyl)$_2$N, C_1-C_6 alkylcarbonylamino, C_3-C_6 cycloalkylcarbonylamino, C_1-C_6 haloalkylcarbonylamino, C_3-C_6 halocycloalkylcarbonylamino, C_1-C_6 alkylaminocarbonyl, C_3-C_6

cycloalkylaminocarbonyl, C_1-C_6 haloalkylaminocarbonyl, C_3-C_6 halocycloalkylaminocarbonyl, C_3-C_6 cycloalkylcarbonyl, C_3-C_6 halocycloalkylcarbonyl, -SF_5 and -$C(O)NH_2$; or

U_3 is a 5 to 6 membered aromatic ring, 5 to 6 membered heteroaromatic ring, or 5 to 6 membered saturated or partially saturated carbocyclic or heterocyclic ring system, wherein heteroaromatic or heterocyclic ring can contain 1 to 4 hetero atoms selected from the group consisting of nitrogen substituted or not, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, said 5 to 6-membered ring system can be mono- or polysubstituted by substituents independently selected from the group U_2;

R_6 is selected from the group consisting of hydrogen, amino, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_1-C_6 haloalkoxy, C_1-C_4 haloalkoxy-C_1-C_4 alkyl, C_1-C_6 alkoxy-C_1-C_6 alkyl, C_1-C_6 alkoxy, C_1-C_4 alkylsulfanyl, C_1-C_4 alkylsulfinyl, C_1-C_4 alkylsulfonyl, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_3-C_6 cycloalkyl, cyano-C_1-C_4 alkyl, cyano-C_1-C_4 haloalkyl and C_3-C_6 halocycloalkyl;

R_8 is selected from the group consisting of hydrogen, hydroxyl, cyano, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_1-C_6 haloalkoxy, C_1-C_4 haloalkoxy-C_1-C_4 alkyl, C_1-C_6 alkoxy-C_1-C_6 alkyl, C_1-C_6 alkoxy, C_1-C_4 alkylsulfanyl, C_1-C_4 alkylsulfinyl, C_1-C_4 alkylsulfonyl, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, cyano-C_1-C_4 alkyl, cyano-C_1-C_4 haloalkyl, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl, phenyl, pyridyl and pyrimidyl, wherein said phenyl, pyridyl or pyrimidyl ring system can be mono- or polysubstituted by substituents independently selected from the group consisting of halogen, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 haloalkoxy, and C_1-C_4 alkoxy; and

R_7 is selected from the group consisting of hydrogen, cyano, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_1-C_6 haloalkoxy, C_1-C_4 haloalkoxy-C_1-C_4 alkyl, C_1-C_6 alkoxy-C_1-C_6 alkyl, C_1-C_6 alkoxy, C_1-C_4 alkylsulfanyl, C_1-C_4 alkylsulfinyl, C_1-C_4 alkylsulfonyl, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, cyano-C_1-C_4 alkyl, cyano-C_1-C_4 haloalkyl, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl, phenyl, pyridyl and pyrimidyl, wherein said phenyl, pyridyl or pyrimidyl ring system can be mono- or polysubstituted by substituents independently selected from the group consisting of halogen, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 haloalkoxy, and C_1-C_4 alkoxy; or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide of the compound of formula I, wherein in the instance the moiety $–NCR_2R_3R_4$ is $–NCH_2CH_3$, R_5 is not phenyl, methyl or ethyl.

2. The compound according to either claim 1, wherein R_{1a}, R_{1b}, R_{1c} and R_{1d} are independently selected from hydrogen, C_1-C_6alkyl, C_1-C_6 alkoxy, or C_1-C_6 haloalkyl.

3. The compound according to either claim 1 or claim 2, wherein n is 0 or 1.

4. The compound according to any one of claims 1 to 3, wherein R_2 is hydrogen, C_1-C_6 alkyl, or mono- or poly-substituted C_1-C_6 alkyl independently selected from the group consisting of halogen,

hydroxyl, amino, cyano, nitro, C_1-C_6 haloalkoxy, C_1-C_6 alkoxy, C_1-C_6 alkylsulfanyl, C_1-C_6 alkylsulfinyl, C_1-C_6 alkylsulfonyl, C_1-C_6 haloalkylsulfanyl, C_1-C_6 haloalkylsulfinyl and C_1-C_6 haloalkylsulfonyl.

5. The compound according to any one of claims 1 to 4, wherein R_3 is hydrogen or C_1-C_4 alkyl.

6. The compound according to any one of claims 1 to 5, wherein R_4 is heteroaromatic ring Y selected from Y1 to Y29 independently substituted with a substituent from the group U, wherein n, Z and U are as defined claim 1.

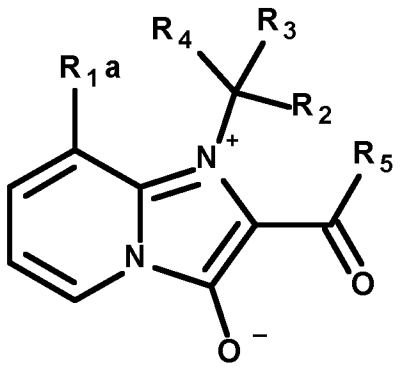
7. The compound according to any one of claims 1 to 6, wherein R_5 is 6 to 12 membered aromatic ring, which can be monocyclic or polycyclic, which ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2, wherein group U_2 is as defined in claim 1.

8. The compound according to any one of claims 1 to 6, wherein R_5 is 5 to 12 membered heteroaromatic ring system, which can be monocyclic or polycyclic, which ring system can contain 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, wherein the nitrogen heteroatom can be substituted by Z and said ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2, or R_5 is 3 to 6 membered saturated or partially saturated heterocyclic ring system, which can be monocyclic or polycyclic, which ring system can contain 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, with the proviso that each ring cannot contain more than 2 oxygen atoms or more than 2 sulfur atoms, wherein the nitrogen heteroatom can be substituted by Z and said ring system can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; wherein Z and U_2 are as defined in claim 1.

9. The compound according to any one of claims 1 to 6, wherein R_5 is a C_3-C_6 cycloalkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3, wherein U_3 is as defined in claim 1.

10. The compound according to any one of claims 1 to 6, wherein R_5 is a C_1-C_6 alkyl, which can optionally be mono- or poly-substituted by substituents independently selected from the group U_3, wheerein U_3 is as defined in claim 1.

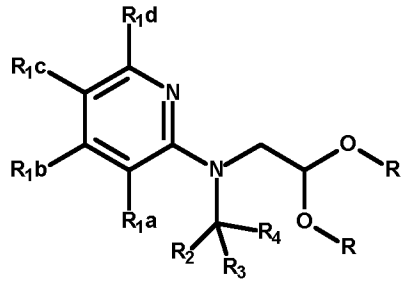
11. A compound of formula Ia



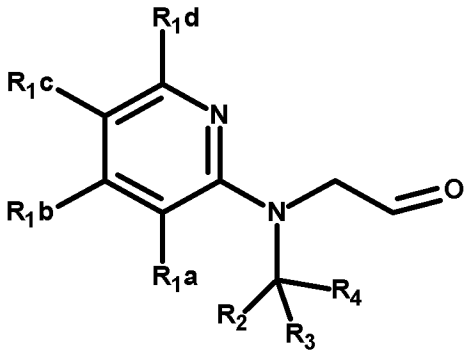
Ia

wherein R_{1a} is hydrogen, methyl, methoxy, or trifluoromethyl; R_2 is hydrogen, or methyl; R_3 is hydrogen, or methyl; R_4 is heteroaromatic ring Y selected from selected from Y4, Y9 and Y12 (as defined in claim 1); and R_5 is selected from the groups (i) to (iii): (i) benzyl, 3-Cl-Phenyl, 3,5-diCl-Phenyl, 2-Cl-Phenyl, 2-F-Phenyl, 4-F-Phenyl, 3-I-Phenyl, 2-methyl-Phenyl, 3,5-diBr-Phenyl, ,3-Br-5-CF_3-Phenyl, 3-Br-5-OCF_3-Phenyl, 3-OCF_3-Phenyl, 3-SCH_3-Phenyl, 4-methoxy-Phenyl, 3-methoxy-Phenyl, 3-Br-Phenyl, 4-F-Phenyl., 4-CF_3-Phenyl, 3-CHF_2-Phenyl, or 3,4,5-tri-fluroro-Phenyl; (ii) heptafluoropropyl, 2-CF_3--cyclopropyl-, $CH_3CF_2CH_2$-, or $(CF_3)_2CH$-; and (iii) biphenyl, napthyl, phenylpyridyl, pyridylphenyl, or tetrahydrofuryl, which can optionally be mono- or polysubstituted by substituents independently selected from the group U_2; wherein U_2 is halogen, cyano, C_1-C_4 alkyl, C_3-C_6 cycloalkyl, C_1-C_4 haloalkyl or C_1-C_4 alkoxy; or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide of the compound of formula Ia.

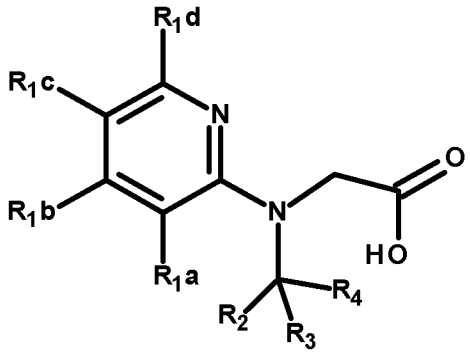
12. A compound of formulae IV, V, and VI



(IV)



(V)

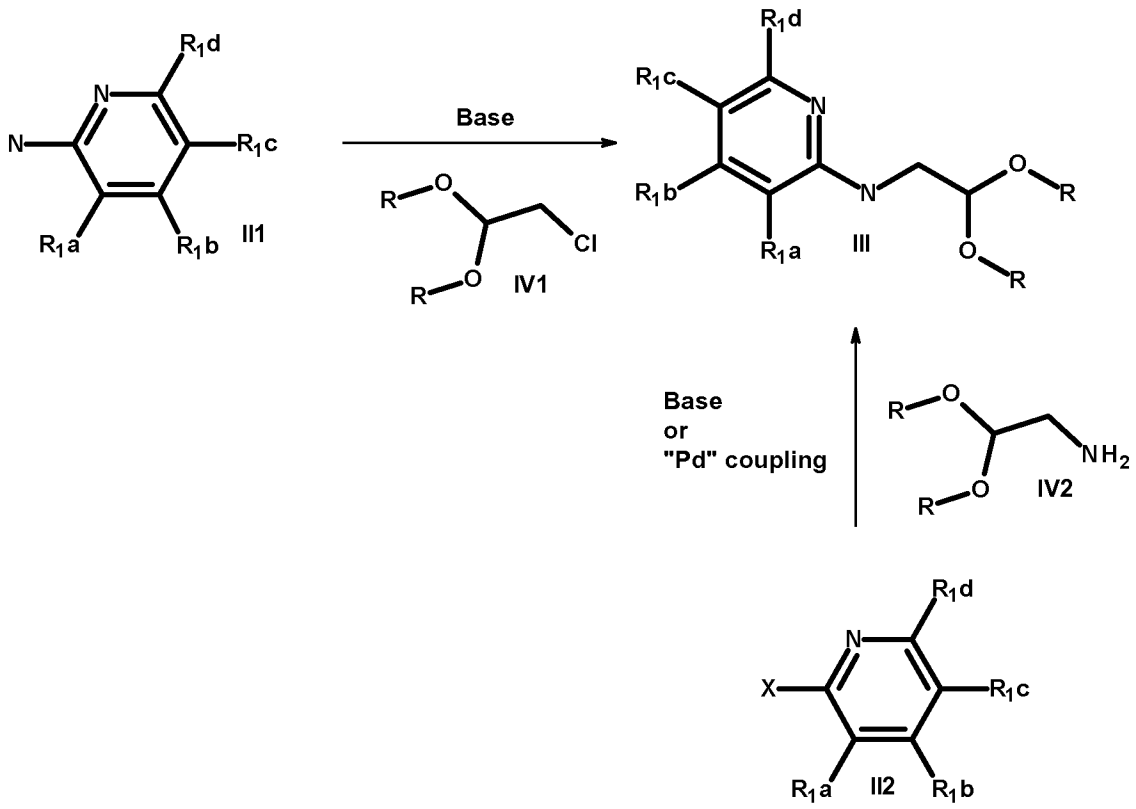


(VI)

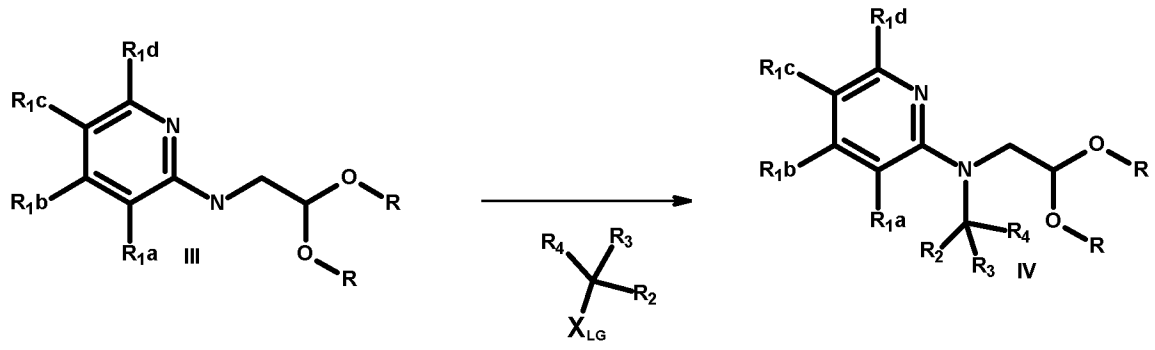
wherein R_{1a}, R_{1b}, R_{1c} and R_{1d}, R_2, R_3 are as defined in any one of claims 1, 2, 4, and 5; R_4 is a heteroaromatic ring Y selected from Y4, Y9 and Y12 substituted with a substituent from the group U, wherein n and U are as defined in claim 1; and R (for formila (IV)) is C_1-C_4 alkyl; and acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of the compounds of formulae IV, V and Vi respectively.

13. A process for preparing a compound of formula Ia, wherein

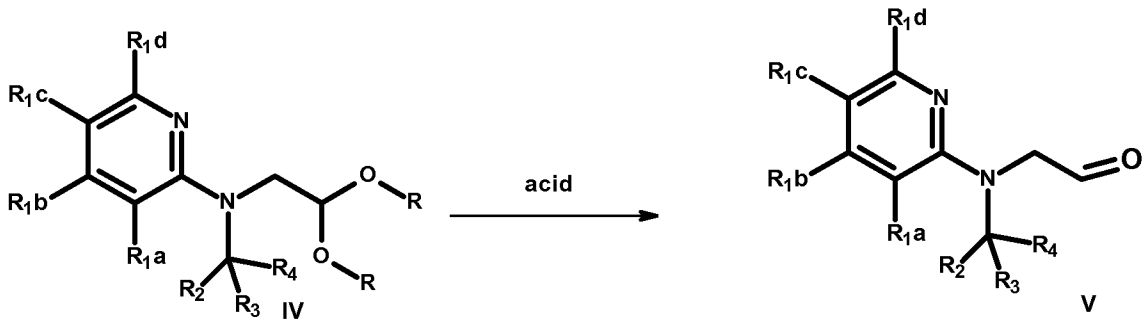
(1) a compound of formula III is prepared from compound of formula II1 via alkylation with a compound of formula IV1, in presence of a base to generate a compound of formula III; or the compound of formula III is prepared from a compound of formula II2 via palladium coupling with a compound of formula IV2; or a compound of formula III is prepared by nucleophile substitution, in presence of a base, with a compound of formula IV2;



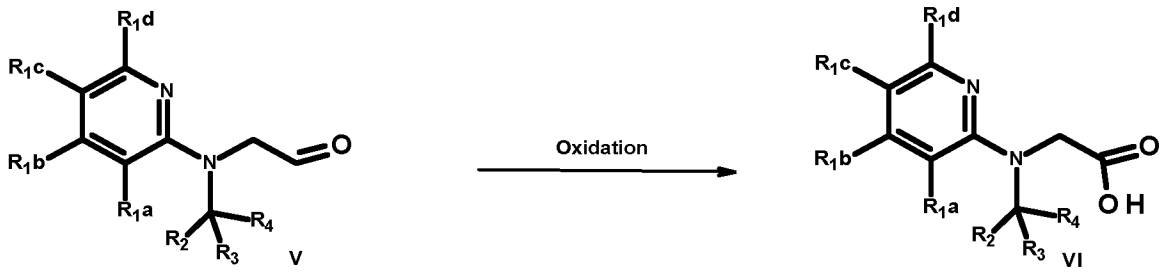
(2) a compound of formula IV is prepared from a compound of formula III by alkylation with $R_2R_3R_4C$-X_{LG};



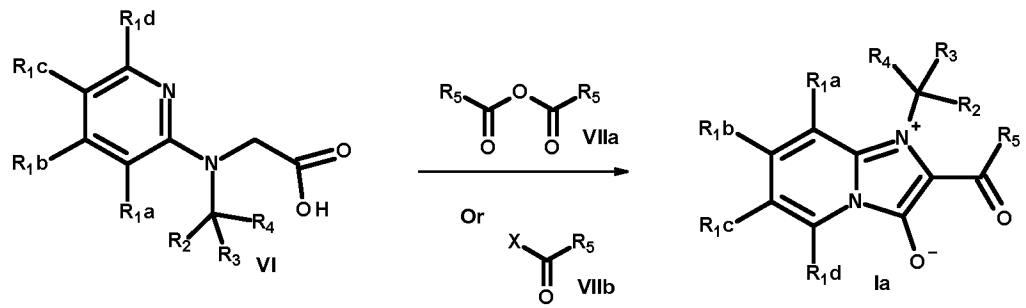
(3) a compound of formula V is prepared from a compound of formula IV by cleavage of the acetal group to aldehyde in presence of an acid;



(4) a compound of the formula V is oxidized to its corresponding acid of formula VI; and



(5) a compound of formula Ia is prepared from a compound of formula VI by cyclisation and acylation in presence of an anhydride of formula VIIa or acid halide of formula VIIb,



wherein R is C_1-C_4 alkyl; X_{LG} and X are independently of each other a leaving group; and R_{1a}, R_{1b}, R_{1c}, R_{1d}, R_2, R_3, R_4 and R_5 are as described for formula I in any one of claims 1 to 8.

14. A pesticidal composition comprising a compound of formula I as defined in any one of claims 1 to 11 and one or more formulation additives and a carrier.

15. A combination of active ingredients comprising a compound of formula I as defined in any one of claims 1 to 11, and one or more further active ingredients.

16. A method of controlling insects, acarines, nematodes or molluscs which comprises applying an insecticidally, acaricidally, nematicidally or molluscicidally effective amount of a compound of

formula I as defined in any one or claims 1 to 1, or a composition containing a compound of formula I as defined in any one or claims 1 to 11, to a pest, a locus of pest, preferably a plant, to a plant susceptible to attack by a pest or to plant propagation material thereof, such as a seed, provided if the control were on a human or animal body, then it is non-therapeutical.

17. A plant propagation material comprising by way of treatment or coating one or more compounds of formula I defined in any one of claims 1 to 11, optionally also comprising a colour pigment.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/079743

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D471/04 A01N43/50
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.
X	JOURNAL OF THE CHEMICAL SOCIETY, CHEMICAL SOCIETY, LETCHWORTH; GB, 1 January 1959 (1959-01-01), pages 2865-2871, XP009504229, ISSN: 0368-1769 compounds of type X; page 2866 page 2866, line 5 - line 6 Anhydro-(4-acetyl-3-ethyl-5-hydroxypyridin o(1',2'-1,2)imidazolium hydoxide (X; R = R' = H, R'' = R''' = Me); page 2869, line 6 - line 7 -----	1-5,10
X	WO 2017/093214 A1 (BAYER CROPSCIENCE AG [DE]) 8 June 2017 (2017-06-08) cited in the application	17
A	page 1, line 1 - line 3 claims 1-18 -----	1-16

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 December 2018	11/02/2019

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

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2018/079743

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2017093214 A1	08-06-2017	AU 2016363632 A1	07-06-2018
		CA 3007037 A1	08-06-2017
		CN 108602819 A	28-09-2018
		CO 2018005774 A2	10-07-2018
		EP 3383874 A1	10-10-2018
		KR 20180084138 A	24-07-2018
		TW 201731845 A	16-09-2017
		US 2018282323 A1	04-10-2018
		UY 37006 A	29-09-2017
		WO 2017093214 A1	08-06-2017