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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
21 July 2016 (21.07.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/113155 A1

(51) International Patent Classification:
C07D 231/12 (2006.01) *A01N 43/58* (2006.01)
C07D 401/04 (2006.01)

(21) International Application Number:
PCT/EP2016/050105

(22) International Filing Date:
6 January 2016 (06.01.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
15150990.8 13 January 2015 (13.01.2015) EP

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

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

(74) Agent: **SYNGENTA INTERNATIONAL AG**; Intellectual Property, WRO 1008-Z1-26, Schwarzwaldallee 215, 4058 Basel (CH).

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

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

Declarations under Rule 4.17:

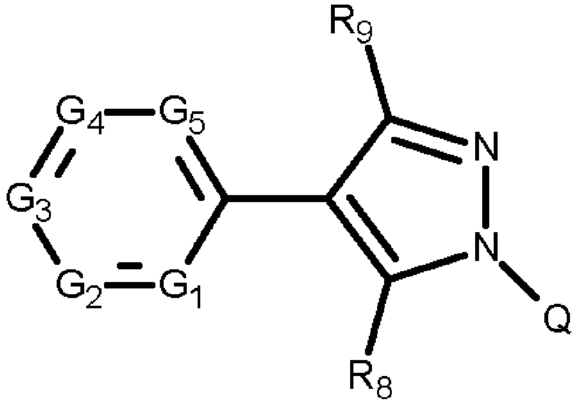
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *of inventorship (Rule 4.17(iv))*

Published:

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

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



(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 said compounds, can be used as insecticides and can be prepared in a manner known per se.

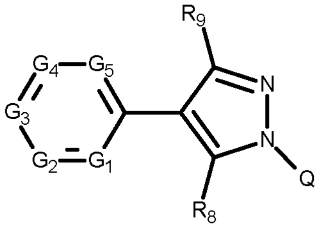
WO 2016/113155 A1

Pesticidally active heterocyclic derivatives with sulphur containing substituents

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

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

The present invention accordingly relates to compounds of formula I,



(I),

wherein

R_8 is hydrogen, C_1-C_4alkyl, C_1-C_4haloalkyl, halogen or cyano;

G_1 is nitrogen or CR_2;

G_2 is nitrogen or CR_3;

G_3 is nitrogen or CR_4;

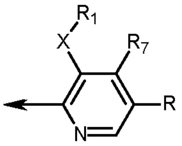
G_4 is nitrogen or CR_5;

G_5 is nitrogen or CR_6, with the proviso that not more than 2 nitrogens as G may follow consecutively;

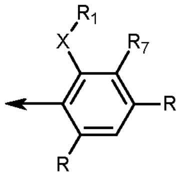
R_2, R_3, R_4, R_5 or R_6 are, independently from each other, hydrogen, halogen, cyano, C_1-C_6haloalkyl, or are C_1-C_6haloalkyl substituted by one or two substituents selected from the group consisting of hydroxyl, methoxy and cyano; or

R_2, R_3, R_4, R_5 or R_6 are, independently from each other, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, O(C_1-C_4haloalkyl), SF_5, phenylcarbonylthio, mercapto, C_1-C_4alkoxycarbonyl, or –C(O)C_1-C_4haloalkyl;

Q is a radical selected from the group consisting of formula Q_1 and Q_2,



Q1



Q2 ,

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

and wherein X is S, SO or SO_2;

each R is, independently from each other, hydrogen, halogen or C_1-C_4haloalkyl;

each R_1 is, independently from each other, C_1-C_4alkyl, C_1-C_4haloalkyl, C_3-C_6cycloalkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl; or

each R_1 is, independently from each other, C_3-C_6cycloalkyl mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano and C_1-C_4alkyl; or

each R_1 is, independently from each other, C_3-C_6cycloalkyl-C_1-C_4alkyl mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano and C_1-C_4alkyl; or

each R_1 is, independently from each other, C_2-C_6alkenyl, C_2-C_6haloalkenyl or C_2-C_6alkynyl;

each R_7 is, independently from each other, hydrogen or halogen; and

R_9 is hydrogen, C_1-C_4alkyl, C_1-C_4haloalkyl or halogen; with the exception of the compound 4-(4-fluorophenyl)-1-(2-methylsulfonylphenyl)pyrazole; and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of the compounds of formula I.

Compounds of formula I which have at least one basic centre can form, for example, acid addition salts, for example with strong inorganic acids such as mineral acids, for example perchloric acid, sulfuric acid, nitric acid, nitrose 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_4alkane- or arylsulfonic acids which are unsubstituted or substituted, for example by halogen, for example methane- or p-toluenesulfonic acid. Compounds of formula I which have at least one acidic group can form, for example, salts with bases, for example mineral salts such as alkali metal or alkaline earth metal salts, for example sodium, potassium or magnesium salts, or salts with ammonia or an organic amine, such as morpholine, piperidine, pyrrolidine, a mono-, di- or tri-lower-alkylamine, for example ethyl-, diethyl-, triethyl- or dimethylpropylamine, or a mono-, di- or trihydroxy-lower-alkylamine, for example mono-, di- or triethanolamine.

The alkyl groups occurring in the definitions of the substituents can be straight-chain or branched and are, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, pentyl, hexyl, nonyl, decyl and their branched isomers. 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.

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

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

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

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

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

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

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

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

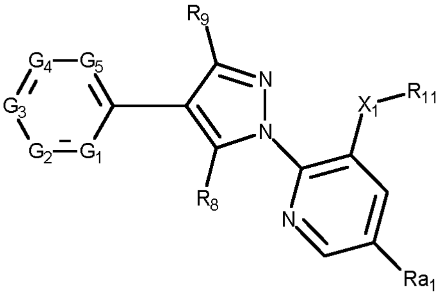
Haloalkylsulfanyl groups preferably have a chain length of from 1 to 4 carbon atoms. Haloalkylsulfanyl is, for example, difluoromethylsulfanyl, trifluoromethylsulfanyl or 2,2,2-trifluoroethylsulfanyl. Similar considerations apply to the radicals C_1-C_4haloalkylsulfinyl and C_1-C_4haloalkylsulfonyl, which may be, for example, trifluoromethylsulfinyl, trifluoromethylsulfonyl or 2,2,2-trifluoroethylsulfonyl.

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

Free radicals represents methyl groups.

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

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



(I-1),

wherein G_1, G_2, G_3, G_4 and G_5 are as defined under formula I above; X_1 is S, SO or SO_2; Ra_1 is hydrogen, halogen or C_1-C_4haloalkyl, in particular C_1-C_4haloalkyl or hydrogen; R_{11} is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl; R_8 is as defined above under formula I, preferably hydrogen or methyl; R_9 is as defined above under formula I, preferably hydrogen, and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of the compounds of formula I-1.

In said preferred group of compounds of formula I-1, one of the substituents selected from G_1, G_2, G_3, G_4, and G_5 is $C(CF_3)$, one of the remaining substituents selected from G_1, G_2, G_3, G_4, and G_5 is N or CH, and the remaining substituents G are CH.

Also preferred are compounds of formula I-1 wherein G_1 is N, G_2 is $C(CF_3)$, and G_3, G_4 and G_5 are CH.
In other preferred compounds of formula I-1, G_1 is N, G_3 is $C(CF_3)$ and G_2, G_4 and G_5 are CH.
In further preferred compounds of formula I-1, G_1 is N, G_4 is $C(CF_3)$ and G_2, G_3 and G_5 are CH.
In other preferred compounds of formula I-1, G_1, G_4 and G_5 are CH, G_2 is N and G_3 is $C(CF_3)$.
Also preferred are compounds of formula I-1. wherein G_1, G_3 and G_5 are CH, G_2 is N and G_4 is $C(CF_3)$.
In further preferred compounds of formula I-1, G_1, G_4 and G_5 are CH, G_3 is N and G_2 is $C(CF_3)$.
In another group of preferred compounds of formula I-1, G_1 and G_3 are N, G_4 and G_5 are CH, and G_2 is $C(CF_3)$.
In other preferred compounds of formula I-1, G_1 and G_4 are N, G_2 and G_5 are CH, and G_3 is $C(CF_3)$.

Also preferred are compounds of formula I-1, wherein G_1 and G_4 are N, G_3 and G_5 are CH, and G_2 is $C(CF_3)$.

In other preferred compounds of formula I-1, G_1 and G_5 are N, G_2 and G_4 are CH, and G_3 is $C(CF_3)$.

In further preferred compounds of formula I-1, G_1 and G_5 are N, G_3 and G_4 are CH, and G_2 is $C(CF_3)$.

In other preferred compounds of formula I-1, G_2 and G_4 are N, G_1 and G_5 are CH, and G_3 is $C(CF_3)$.

Also preferred are compounds of formula I-1, wherein G_1 and G_2 are N, G_4 and G_5 are CH, and G_3 is $C(CF_3)$.

In other preferred compounds of formula I-1, G_1 and G_2 are N, G_3 and G_5 are CH, and G_4 is $C(CF_3)$.

In further preferred compounds of formula I-1, G_1 and G_3 are N, G_2 and G_5 are CH, and G_4 is $C(CF_3)$.

In an especially preferred group of compounds of formula I-1, G_1 is CH, G_2 is CH, G_3 is $C(CF_3)$, G_4 is CH and G_5 is CH.

In another especially preferred group of compounds of formula I-1, G_1 is CH, G_2 is $C(CF_3)$, G_3 is CH, G_4 is CH and G_5 is CH.

In another especially preferred group of compounds of formula I-1, G_1 is CH, G_2 is N, G_3 is $C(CF_3)$, G_4 is CH and G_5 is CH.

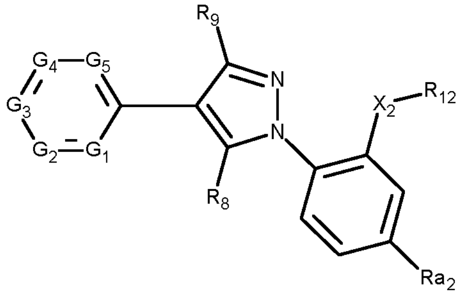
In an especially preferred group of compounds of formula I-1, G_1 is N, G_2 is CH, G_3 is $C(CF_3)$, G_4 is CH and G_5 is CH.

In another especially preferred group of compounds of formula I-1, G_1 is N, G_2 is CH, G_3 is CH, G_4 is $C(CF_3)$, and G_5 is CH.

In another especially preferred group of compounds of formula I-1, G_1 is CH, G_2 is N, G_3 is CH, G_4 is $C(CF_3)$, and G_5 is CH.

In all of said especially preferred groups of compounds of formula I-1 mentioned above, R_8 is preferably hydrogen or methyl, and R_9 is hydrogen.

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



(I-2),

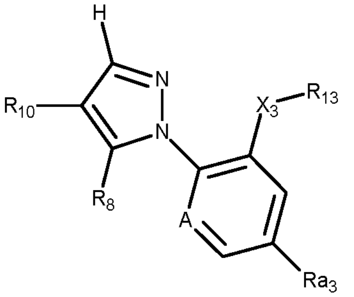
wherein G_1, G_2, G_3, G_4, and G_5 are as defined under formula I above; X_2 is S, SO or SO_2; Ra_2 is hydrogen, halogen or C_1-C_4haloalkyl, in particular C_1-C_4haloalkyl or hydrogen; R_{12} is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl; R_8 is as defined above under formula I, preferably hydrogen or methyl; R_9 is as defined above under formula I, preferably hydrogen, and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of the compounds of formula I-2.

In said preferred group of compounds of formula I-2, one of the substituents selected from G_1, G_2, G_3, G_4, and G_5 is $C(CF_3)$, one of the remaining substituents selected from G_1, G_2, G_3, G_4, and G_5 is N or CH, and the remaining substituents G are CH.

Also preferred are compounds of formula I-2 wherein G_1 is N, G_2 is $C(CF_3)$, and G_3, G_4 and G_5 are CH.
In other preferred compounds of formula I-2, G_1 is N, G_3 is $C(CF_3)$ and G_2, G_4 and G_5 are CH.
In further preferred compounds of formula I-2, G_1 is N, G_4 is $C(CF_3)$ and G_2, G_3 and G_5 are CH.
In other preferred compounds of formula I-2, G_1, G_4 and G_5 are CH, G_2 is N and G_3 is $C(CF_3)$.
Also preferred are compounds of formula I-2. wherein G_1, G_3 and G_5 are CH, G_2 is N and G_4 is $C(CF_3)$.
In further preferred compounds of formula I-2, G_1, G_4 and G_5 are CH, G_3 is N and G_2 is $C(CF_3)$.
In another group of preferred compounds of formula I-2, G_1 and G_3 are N, G_4 and G_5 are CH, and G_2 is $C(CF_3)$.
In other preferred compounds of formula I-2, G_1 and G_4 are N, G_2 and G_5 are CH, and G_3 is $C(CF_3)$.
Also preferred are compounds of formula I-2, wherein G_1 and G_4 are N, G_3 and G_5 are CH, and G_2 is $C(CF_3)$.
In other preferred compounds of formula I-2, G_1 and G_5 are N, G_2 and G_4 are CH, and G_3 is $C(CF_3)$.
In further preferred compounds of formula I-2, G_1 and G_5 are N, G_3 and G_4 are CH, and G_2 is $C(CF_3)$.
In other preferred compounds of formula I-2, G_2 and G_4 are N, G_1 and G_5 are CH, and G_3 is $C(CF_3)$.
Also preferred are compounds of formula I-2, wherein G_1 and G_2 are N, G_4 and G_5 are CH, and G_3 is $C(CF_3)$.
In other preferred compounds of formula I-2, G_1 and G_2 are N, G_3 and G_5 are CH, and G_4 is $C(CF_3)$.
In further preferred compounds of formula I-2, G_1 and G_3 are N, G_2 and G_5 are CH, and G_4 is $C(CF_3)$.

In an especially preferred group of compounds of formula I-2, G_1 is CH, G_2 is CH, G_3 is $C(CF_3)$, G_4 is CH and G_5 is CH.
In another especially preferred group of compounds of formula I-2, G_1 is CH, G_2 is $C(CF_3)$, G_3 is CH, G_4 is CH and G_5 is CH.
In another especially preferred group of compounds of formula I-2, G_1 is CH, G_2 is N, G_3 is $C(CF_3)$, G_4 is CH and G_5 is CH.
In an especially preferred group of compounds of formula I-2, G_1 is N, G_2 is CH, G_3 is $C(CF_3)$, G_4 is CH and G_5 is CH.
In another especially preferred group of compounds of formula I-2, G_1 is N, G_2 is CH, G_3 is CH, G_4 is $C(CF_3)$, and G_5 is CH.
In another especially preferred group of compounds of formula I-2, G_1 is CH, G_2 is N, G_3 is CH, G_4 is $C(CF_3)$, and G_5 is CH.
In all of said especially preferred groups of compounds of formula I-2 mentioned above, R_8 is preferably hydrogen or methyl, and R_9 is hydrogen.

A further preferred embodiment of the invention comprises compounds of formula I represented by the compounds of formula I-3

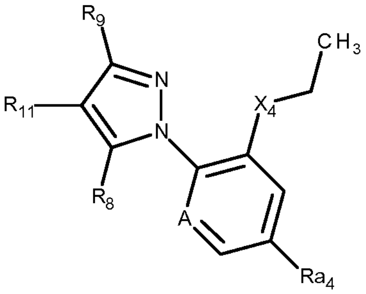


(I-3),

wherein
A is N or CH;
R_{10} is phenyl substituted by C_1-C_4haloalkyl or is pyridyl substituted by C_1-C_4haloalkyl; or
R_{10} is phenyl substituted by C_1-C_4haloalkylsulfanyl;
X_3 is S, SO or SO_2, in particular S or SO_2; Ra_3 is hydrogen, halogen or C_1-C_4haloalkyl, in particular C_1-C_4haloalkyl or hydrogen; and R_{13} is C_1-C_4alkyl, in particular ethyl; R_8 is hydrogen or C_1-C_4alkyl, in particular hydrogen or methyl, and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of the compounds of formula I-3.

In said preferred embodiment comprising compounds of formula I-3, R_{10} is preferably phenyl monosubstituted by C_1-C_4haloalkyl or C_1-C_4haloalkylsulfanyl; especially preferred is a substituent independently selected from trifluoromethyl and trifluoromethylsulfanyl. Or, R_{10} is preferably pyridyl monosubstituted by C_1-C_4haloalkyl, in particular by trifluoromethyl.

An outstandingly preferred embodiment of the invention comprises compounds of formula I represented by the compounds of formula I-4

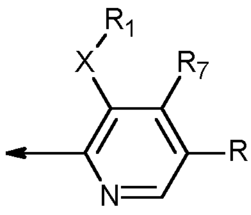


(I-4),

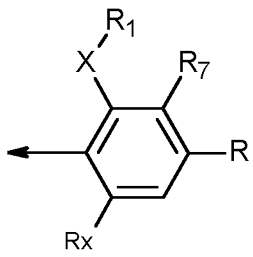
wherein
A is N or CH;
X_4 is S or SO_2;
Ra_4 is hydrogen or C_1-C_4haloalkyl;

R_8 is hydrogen or C_1-C_4alkyl;
R_9 is hydrogen; and
R_{11} is phenyl monosubstituted by C_1-C_4haloalkyl or C_1-C_4haloalkylsulfanyl; or
R_{11} is pyridyl monosubstituted by C_1-C_4haloalkyl; and the N-oxides of said outstanding compounds of formula I-4.

Further preferred compounds of formula I are those, wherein
G_1 is nitrogen or CR_2; R_2 is hydrogen;
G_2 is nitrogen or CR_3; R_3 is hydrogen;
G_3 is CR_4; R_4 is hydrogen, C_1-C_4haloalkyl or C_1-$_4$haloalkylsulfanyl;
G_4 is CR_5; R_5 is hydrogen, C_1-C_4haloalkyl or C_1-$_4$haloalkylsulfanyl;
G_5 is CR_6; R_6 is hydrogen;
Q is a radical selected from the group consisting of formula Q_1 and Q_{2x},



Q_1

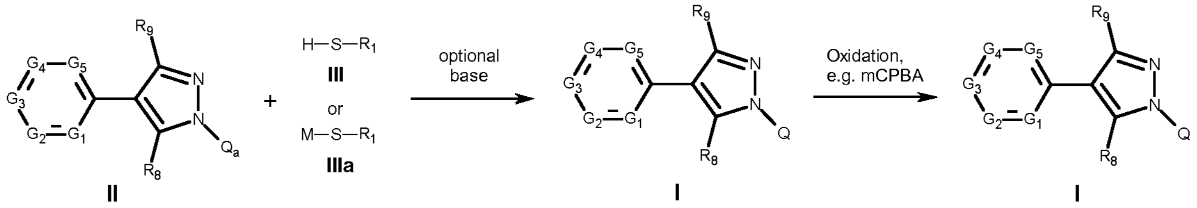


Q_{2x}

,

wherein the arrow denotes the point of attachment to the pyrazole ring;
X is S or SO_2;
R_1 is C_1-C_4alkyl, preferably ethyl;
R_7 is hydrogen;
R_8 is hydrogen or C_1-C_4alkyl;
R_9 is hydrogen;
Rx is hydrogen; and
R is hydrogen or C_1-C_4haloalkyl.

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

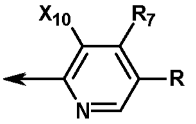


Q_a is selected from Q_{1a} and Q_{2a}

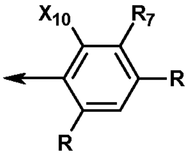
Q is selected from Q_1 and Q_2
X is S (sulfide)

Q is selected from Q_1 and Q_2
X is SO or SO_2

Compounds of formula I, wherein Q, R_8, R_9, G_1, G_2, G_3, G_4, and G_5 are as defined in formula I and wherein X is S (sulfide), can be prepared by reacting a compound of formula II, wherein R_8, R_9, G_1, G_2, G_3, G_4, and G_5 are as described in formula I and wherein Q_a is a radical selected from the group consisting of formula Q_{1a} to Q_{2a}:



Q_{1a}



Q_{2a}

wherein R and R_7 are as defined in formula I, and wherein X_{10} is a halogen, with a compound of formula III

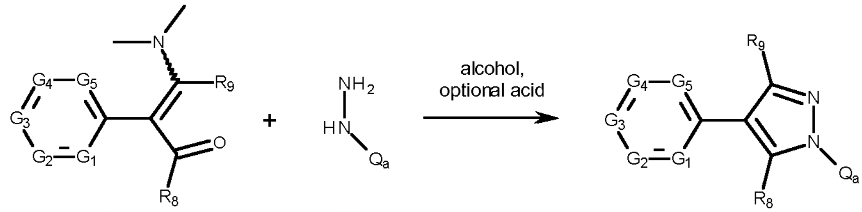
$$R_1\text{-SH} \quad \text{(III)},$$

or a salt thereof, wherein R_1 is as defined in formula I, optionally in the presence of a suitable base, such as alkali metal carbonates, for example sodium carbonate and potassium carbonate, or alkali metal hydrides such as sodium hydride, or alkali metal hydroxides such as sodium hydroxide and potassium hydroxide, in an inert solvent at temperatures preferably between 25-120°C. Examples of solvent to be used include ethers such as THF, ethylene glycol dimethyl ether, tert-butylmethyl ether, and 1,4-dioxane, aromatic hydrocarbons such as toluene and xylene, nitriles such as acetonitrile or polar aprotic solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone or dimethyl sulfoxide. Examples of salts of the compound of formula III include compounds of the formula IIIa

$$R_1\text{-S-M} \quad \text{(IIIa)},$$

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

The subgroup of compounds of formula II, wherein R_9 is hydrogen or C_1-C_4alkyl, and wherein R_8, G_1, G_2, G_3, G_4, and G_5 are as defined above and wherein Q_a is a radical selected from the group consisting of formula Q_{1a} to Q_{2a},



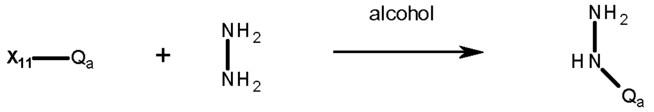
V **IV** **II**

Q_a is selected from Q_{1a} and Q_{2a}

Q_a is selected from Q_{1a} and Q_{2a}
R_9 is hydrogen or C_1-C_4alkyl

can be prepared by reacting a compound of formula IV, or a salt thereof (such as a hydrohalide salt, preferably a hydrochloride or a hydrobromide salt, or any other equivalent salt), wherein Q_a is a radical selected from the group consisting of formula Q_{1a} to Q_{2a}, with a compound of formula V, wherein R_9 is hydrogen or C_1-C_4alkyl, and wherein R_8, G_1, G_2, G_3, G_4, and G_5 are as defined above, in an alcohol solvent alone such as methanol, ethanol, or 2-methoxyethanol (if a hydrohalide salt of IV is used), or in an alcohol solvent in the presence of an acid (such as acetic acid) if the free bases of compounds IV are used. This reaction may also proceed in pure acidic media, such as acetic acid, irrespective of the nature (hydrohalide salt or free base) of the compounds of formula IV. Reaction temperatures preferably are between 25 and 200°C, preferably between 50 and 150°C, optionally under microwave irradiation. Such a process may be carried out in analogy to, for example, descriptions found in WO2014/089364.

Compounds of formula IV, or a salt thereof (such as a hydrohalide salt, preferably a hydrochloride or a hydrobromide salt, or any other equivalent salt), wherein Q_a is a radical selected from the group consisting of formula Q_{1a} to Q_{2a},



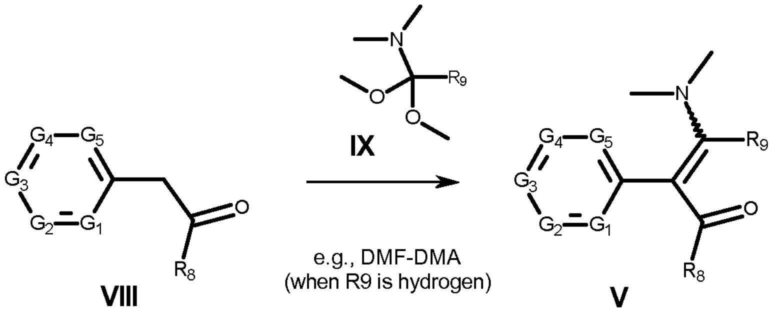
VI **VII** **IV**

Q_a is selected from Q_{1a} and Q_{2a}

Q_a is selected from Q_{1a} and Q_{2a}

may be prepared by reacting a compound of formula VI, wherein X_{11} is is a halogen (preferably fluorine, chlorine or bromine), and wherein Q_a is a radical selected from the group consisting of formula Q_{1a} to Q_{2a}, with a hydrazine compound of formula VII, possibly in form of a hydrate (such as for example hydrazine hydrate $NH_2NH_2{\bullet}H_2O$), or a salt thereof (such as a hydrohalide salt, preferably a hydrochloride or a hydrobromide salt, or any other equivalent salt), typically in an alcohol solvent such as methanol, ethanol, or butanol, or in an ether solvent such as tetrahydrofuran or dioxane, at temperatures between 25 and 200°C, preferably between 50 and 150°C, optionally under microwave irradiation. Such a process may be carried out in analogy to, for example, descriptions found in US 5'321'002.

Compounds of formula V, wherein R_9 is hydrogen or C_1-C_4alkyl, and wherein R_8, G_1, G_2, G_3, G_4, and G_5 are as defined above,

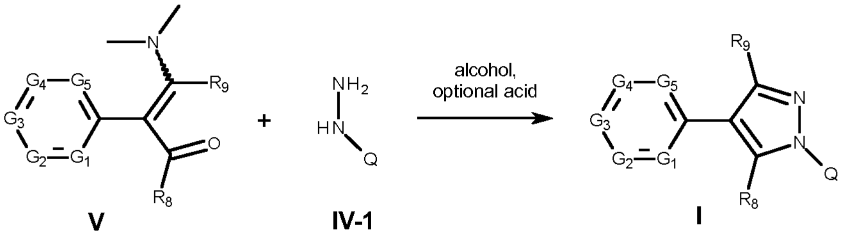


may be prepared by reacting a compound of formula VIII, wherein R_8, G_1, G_2, G_3, G_4, and G_5 are as defined above, with a compound of formula IX, wherein R_9 is hydrogen or C_1-C_4alkyl, under heating conditions, at temperatures between 25 and 180°C, preferably between 50 and 150°C. Such a process may be carried out in analogy to, for example, descriptions found in WO2014/089364.

Typically, a compound of formula IX is for example N,N-dimethylformamide dimethyl acetal DMF-DMA (R_9 is H) or 1,1-dimethoxy-N,N-dimethyl-ethanamine (R_9 is methyl), which are commercial or may be prepared according to known procedures.

Compounds of formula VIII, wherein R_8, G_1, G_2, G_3, G_4, and G_5 are as defined above, and compounds of formula VI, wherein X_{11} is is a halogen (preferably fluorine, chlorine or bromine), and wherein Q_a is a radical selected from the group consisting of formula Q_{1a} to Q_{2a} and is as defined above, are known compounds or can be prepared by known methods, described in the literature.

In analogy to the above and alternatively, the subgroup of compounds of formula I, wherein R_9 is hydrogen or C_1-C_4alkyl, and wherein R_8, G_1, G_2, G_3, G_4, and G_5 are as defined above and wherein Q is a radical selected from the group consisting of formula Q_1 to Q_2,

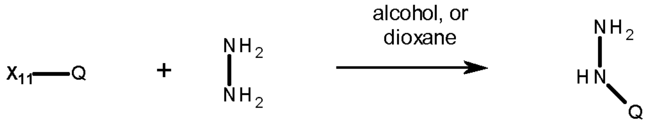


Q is selected from Q_1 and Q_2
X is S, SO or SO_2

Q is selected from Q_1 and Q_2
X is S, SO or SO_2
R_9 is hydrogen or C_1-C_4alkyl

can be prepared by reacting a compound of formula IV-1, or a salt thereof (such as a hydrohalide salt, preferably a hydrochloride or a hydrobromide salt, or any other equivalent salt), wherein Q is a radical selected from the group consisting of formula Q_1 to Q_2, with a compound of formula V, wherein R_9 is hydrogen or C_1-C_4alkyl, and wherein R_8, G_1, G_2, G_3, G_4, and G_5 are as defined above, in an alcohol solvent alone such as methanol, ethanol, or 2-methoxyethanol (if a hydrohalide salt of IV-1 is used), or in an alcohol solvent in the presence of an acid (such as acetic acid) if the free bases of compounds IV-1 are used. This reaction may also proceed in pure acidic media, such as acetic acid, irrespective of the nature (hydrohalide salt or free base) of the compounds of formula IV-1. Reaction temperatures preferably are between 25 and 200°C, preferably between 50 and 150°C, optionally under microwave irradiation.

Compounds of formula IV-1, or a salt thereof (such as a hydrohalide salt, preferably a hydrochloride or a hydrobromide salt, or any other equivalent salt), wherein Q is a radical selected from the group consisting of formula Q_1 to Q_2,



VI-1 **VII** **IV-1**

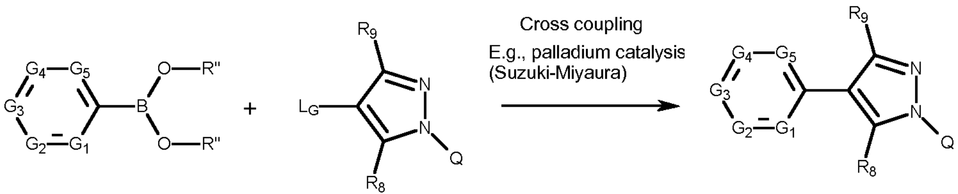
Q is selected from Q_1 and Q_2
X is SO or SO_2

Q is selected from Q_1 and Q_2
X is SO or SO_2

may be prepared by reacting a compound of formula VI-1, wherein X_{11} is is a halogen (preferably fluorine, chlorine or bromine), and wherein Q is a radical selected from the group consisting of formula Q_1 to Q_2, with a hydrazine compound of formula VII, possibly in form of a hydrate (such as for example hydrazine hydrate $NH_2NH_2{\bullet}H_2O$), or a salt thereof (such as a hydrohalide salt, preferably a hydrochloride or a hydrobromide salt, or any other equivalent salt), typically in an alcohol solvent such as methanol, ethanol, or butanol, or in an ether solvent such as tetrahydrofuran or dioxane, at temperatures between 25 and 200°C, preferably between 50 and 150°C, optionally under microwave irradiation.

Compounds of formula VI-1, wherein X_{11} is is a halogen (preferably fluorine, chlorine or bromine), and wherein Q is a radical selected from the group consisting of fomula Q_1 to Q_2 and is as defined above, are known compounds or can be prepared by known methods, described in the literature.

Alternatively, compounds of formula I, wherein Q, R_8, R_9, G_1, G_2, G_3, G_4, and G_5 are as defined in formula I and wherein X is S (sulfide), SO (sulfoxide) or SO_2 (sulfone),

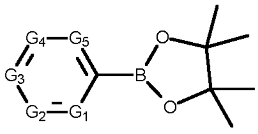


XI **X** **I**

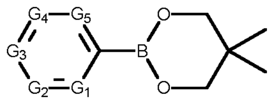
Q is selected from Q_1 and Q_2
X is S, SO or SO_2

Q is selected from Q_1 and Q_2
X is S, SO or SO_2

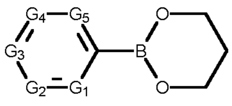
can be prepared by reacting a compound of formula (X), wherein Q, R_8 and R_9 are as defined above, and wherein L_G is a halogen, preferably bromine or iodine, or a pseudohalogen such as $C_{1\text{-}4}$haloalkylsulfonate, especially triflate, and wherein X is S (sulfide), SO (sulfoxide) or SO_2 (sulfone), with a compound of formula XI, wherein G_1, G_2, G_3, G_4 and G_5 are as defined above, and wherein R" is for example hydrogen (in that case the compound of the formula XI is a boronic acid) or C_1-C_4alkyl, by means of a transition metal-catalyzed reaction. Indeed, the boronic acid of the formula XI, or a suitable salt or ester thereof, will react with a compound of the formula (X) under palladium- or nickel-catalyzed conditions, such as for example the Suzuki-Miyaura conditions. Such cross coupling reactions are carried out in the presence of a base, such as sodium, potassium or cesium carbonate, tripotassium phosphate or cesium fluoride, in an inert solvent, such as tetrahydrofuran, N,N-dimethylformamide, dioxane, toluene or 1,2-dimethoxyethane, or such as 1,2-dimethoxyethane-water mixtures, at temperatures between 25-200°C, preferably 50-150°C, optionally under microwave irradiation. A variety of metals, catalysts and ligands may be used in this reaction type, such as for example [1,1-bis(diphenylphosphino)ferrocene] dichloropalladium(II) ($PdCl_2(dppf)$), tetrakis(triphenylphosphine)palladium(0) or bis(triphenylphosphine) palladium(II) dichloride. Reaction conditions and catalytic systems for such a transformation have been described, for example, in WO08/071405. Alternative boron-based reagents of the formula type XI may include boronic esters (also named boronate esters) derived from 2,3-dimethyl-2,3-butanediol (XIa), 2,2-dimethyl-1,3-propanediol (XIb), and 1,3-propanediol (XIc), and salt analogues of XI, such as organotrifluoroborates, for example potassium trifluoroborate salts (XId).



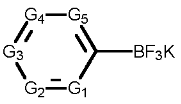
XIa



XIb

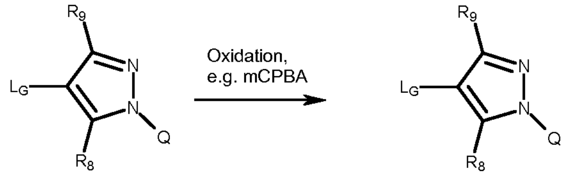


XIc



XId

The subgroup of compounds of formula (X), wherein X is SO_2 (sulfone),



XII

Q is selected from Q_1 and Q_2
X is S (sulfide)

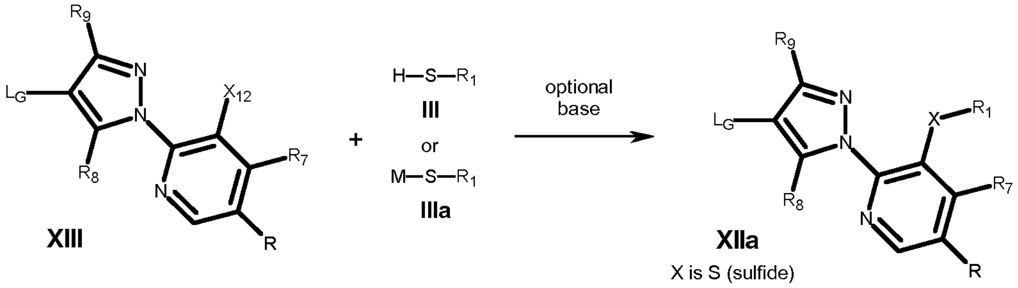
X

Q is selected from Q_1 and Q_2
X is SO_2

may be obtained by means of an oxidation reaction of the corresponding sulfide compounds of formula XII, wherein X is S, involving reagents such as, for example, m-chloroperoxybenzoic acid (mCPBA), hydrogen peroxide, oxone, sodium periodate, sodium hypochlorite or tert-butyl hypochlorite amongst other oxidants. The oxidation reaction is generally conducted in the presence of a solvent. Examples of the solvent to be used in the reaction include aliphatic halogenated hydrocarbons such as dichloromethane and chloroform; alcohols such as methanol and ethanol; acetic acid; water; and mixtures thereof. The amount of the oxidant to be used in the reaction is generally 1 to 3 moles, preferably 2 to 2.2

moles of oxidant, relative to 1 mole of of the sulfide compounds XII to produce the sulfone compounds (X). Such oxidation reactions have already been described above.

The subgroup of compounds of formula XII, wherein Q is Q_1 and X is S, and wherein L_G, R_8, R_9, R_1, R_7 and R are as defined above, defining compounds of formula XIIa,



may be prepared by reacting a compound of formula XIII, wherein L_G, R_8, R_9, R_7 and R are as defined above, and wherein X_{12} is is a halogen (preferably fluorine or chlorine), with a compound of formula III

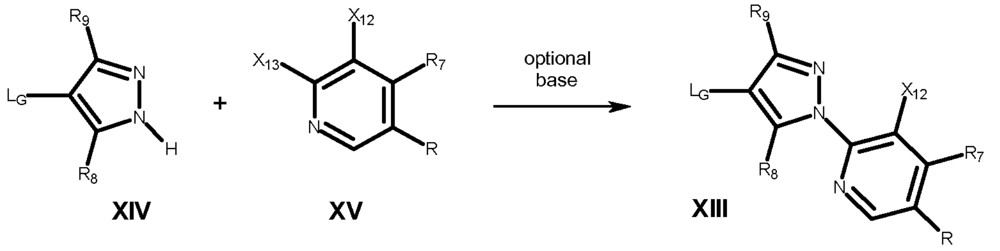
R_1-SH (III),

or a salt thereof, wherein R_1 is as defined in formula I, optionally in the presence of a suitable base, such as alkali metal carbonates, for example sodium carbonate and potassium carbonate, or alkali metal hydrides such as sodium hydride, or alkali metal hydroxides such as sodium hydroxide and potassium hydroxide, in an inert solvent at temperatures preferably between 25-120°C. Examples of solvent to be used include ethers such as THF, ethylene glycol dimethyl ether, tert-butylmethyl ether, and 1,4-dioxane, aromatic hydrocarbons such as toluene and xylene, nitriles such as acetonitrile or polar aprotic solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone or dimethyl sulfoxide. Examples of salts of the compound of formula III include compounds of the formula IIIa

R_1-S-M (IIIa),

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

The compounds of formula XIII, wherein L_G, R_8, R_9, R_7 and R are as defined above, and wherein X_{12} is is a halogen (preferably fluorine or chlorine),

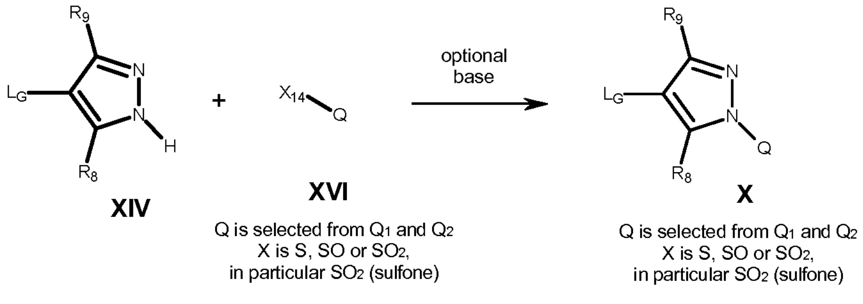


may be prepared by reacting a compound of formula XIV, or a salt thereof, wherein L_G, R_8 and R_9 are as defined above, with a compound of formula XV, wherein X_{12}, R_7 and R are as defined above, and wherein X_{13} is a leaving group such as, for example, fluorine, chlorine, bromine or iodine, or an aryl-, $C_{1\text{-}4}$alkyl- or

C_{1-4}haloalkylsulfonate (or any other similar leaving group), optionally in the presence of a suitable base, such as alkali metal carbonates, for example sodium, potassium, lithium or cesium carbonate, or alkali metal hydrides such as sodium hydride, or alkali metal hydroxides such as sodium hydroxide and potassium hydroxide, or sodium or potassium tert-butoxide, in an inert solvent at temperatures preferably between 25-180°C, optionally under microwave irradiation. Examples of solvent to be used include ethers such as THF, ethylene glycol dimethyl ether, tert-butylmethyl ether, and 1,4-dioxane, aromatic hydrocarbons such as toluene and xylene, nitriles such as acetonitrile or polar aprotic solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone or dimethyl sulfoxide. Such a process may be carried out in analogy to, for example, descriptions found in WO 2007/043677. This base mediated N-hetarylation reaction may optionally be transition metal mediated, or preferably catalyzed by transition metals, such as, for example, metalic copper or copper(I) salts, especially copper(I) halides like copper(I) chloride, copper(I) bromide, copper(I) iodide or copper(I) oxide (especially preferred is copper(I) iodide), or copper(II) salts, like for example copper(II) acetate. Optional additives such as diamine ligands (preferably 1,10-phenanthroline, 1,2-ethanediamine, *N,N'*-dimethyl-1,2-ethanediamine, *N,N*-dimethyl-1,2-ethanediamine, 1,2-cyclohexanediamine or *N,N'*-dimethyl-cyclohexane-1,2-diamine) or 8-quinolinol, glycine, dimethylglycine or proline may be used, as well as further additives such as sodium, potassium or lithium iodide.

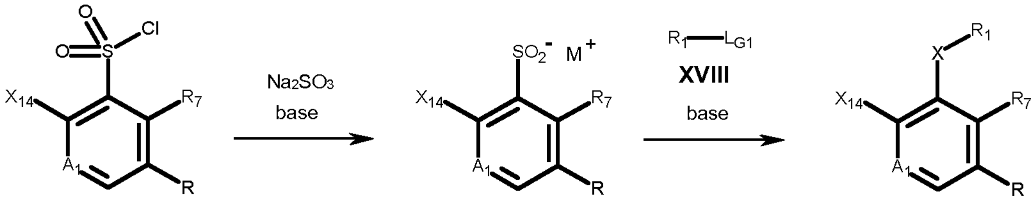
Compounds of formula XI, wherein R", G_1, G_2, G_3, G_4 and G_5 are as defined above (or alternatively analogue compounds of the formula XIa to XId), and compounds of formula XIV, wherein L_G, R_8 and R_9 are as defined above, and compounds of formula XV, wherein X_{12}, X_{13}, R_7 and R are as defined above, are known compounds or can be prepared by known methods, described in the literature.

Alternatively, compounds of formula (X), wherein L_G, Q, R_8 and R_9 are as defined above and wherein X is S (sulfide), SO (sulfoxide) or SO_2 (sulfone), preferably X is SO_2 (sulfone),



may be prepared by reacting a compound of formula XIV, or a salt thereof, wherein L_G, R_8 and R_9 are as defined above, with a compound of formula XVI, wherein Q is as defined in formula I, X is S, SO, SO_2 (preferably SO_2) and wherein X_{14} is is a leaving group such as, for example, fluorine, chlorine, bromine or iodine, or an aryl-, C_{1-4}alkyl- or C_{1-4}haloalkylsulfonate (or any other similar leaving group), optionally in the presence of a suitable base, such as alkali metal carbonates, for example sodium, potassium, lithium or cesium carbonate, or alkali metal hydrides such as sodium hydride, or alkali metal hydroxides such as sodium hydroxide and potassium hydroxide, or sodium or potassium tert-butoxide, in an inert solvent at temperatures preferably between 25-180°C, optionally under microwave irradiation. Examples of solvent to be used include ethers such as THF, ethylene glycol dimethyl ether, tert-butylmethyl ether, and 1,4-dioxane, aromatic hydrocarbons such as toluene and xylene, nitriles such as acetonitrile or polar aprotic solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone or dimethyl sulfoxide. Such a process may be carried out in analogy to, for example, descriptions found in WO 2003/072557 and US 5'824'802. This base mediated N-arylation or N-hetarylation reaction may optionally be transition metal mediated, or preferably catalyzed by transition metals, such as, for example, metalic copper or copper(I) salts, especially copper(I) halides like copper(I) chloride, copper(I) bromide, copper(I) iodide or copper(I) oxide (especially preferred is copper(I) iodide), or copper(II) salts, like for example copper(II) acetate. Optional additives such as diamine ligands (preferably 1,10-phenanthroline, 1,2-ethanediamine, *N,N'*-dimethyl-1,2-ethanediamine, *N,N*-dimethyl-1,2-ethanediamine, 1,2-cyclohexane-diamine or *N,N'*-dimethyl-cyclohexane-1,2-diamine) or 8-quinolinol, glycine, dimethylglycine or proline may be used, as well as further additives such as sodium, potassium or lithium iodide.

The subgroup of compounds of formula XVI, wherein Q is as defined above, X is SO_2 and wherein X_{14} is a leaving group such as, for example, fluorine, chlorine, bromine or iodine (preferably fluorine, chlorine or bromine), or an aryl-, C_{1-4}alkyl- or C_{1-4}haloalkylsulfonate (or any other similar leaving group), defining compounds of formula XVIa, wherein X is SO_2 and A_1 is N or CR (preferably CH), and wherein X_{14}, R_1, R_7 and R are as defined above,



X is SO2 (sulfone)

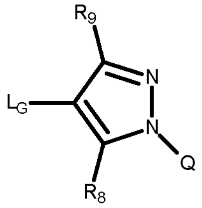
may be prepared by reacting a sulfinic acid salt of formula XVII, wherein M is, for example, sodium or potassium (preferably sodium), and wherein A_1 is N or CR (preferably CH) and X_{14}, R_7 and R are as defined above, with an alkylating reagent of formula XVIII, wherein R_1 is as defined above, and wherein L_{G1} is a leaving group such as, for example, fluorine, chlorine, bromine or iodine (preferably iodine or bromine), or an aryl-, C_{1-4}alkyl- or C_{1-4}haloalkylsulfonate (or any other similar leaving group), in the presence of a suitable base, such as alkali metal carbonates, for example sodium or potassium hydrogen carbonate, or sodium, potassium, lithium or cesium carbonate, or sodium or potassium phosphates, or alkali metal hydroxides such as sodium hydroxide and potassium hydroxide, in a solvent such as water, N,N-dimethylformamide, N,N-dimethylacetamide or N-methyl-2-pyrrolidone, or mixtures thereof, at temperatures preferably between 25-180°C, optionally under microwave irradiation. Such a process may be carried out in analogy to, for example, descriptions found in WO 2013/097601, WO 2010/055004 and WO 2008/113965.

Sulfinic acid salt compounds of formula XVII, wherein M is, for example, sodium or potassium (preferably sodium), and wherein A_1 is N or CR (preferably CH) and X_{14}, R_7 and R are as defined above, may be prepared by reacting a sulfonyl chloride compound of formula XIX, wherein A_1 is N or CR (preferably CH) and X_{14}, R_7 and R are as defined above, with a reagent such as typically sodium sulfite Na_2SO_3, in the presence of a suitable base, such as alkali metal carbonates, for example sodium or potassium hydrogen carbonate, or sodium, potassium, lithium or cesium carbonate, or sodium or potassium phosphates, or alkali metal hydroxides such as sodium hydroxide and potassium hydroxide, in a solvent such as water, or water in mixtures with dioxane or tetrahydrofuran for example, at temperatures preferably between 25-180°C, optionally under microwave irradiation. Such a process may be carried out in analogy to, for example, descriptions found in WO 2013/097601, WO 2010/055004 and WO 2008/113965.

The two steps (XIX→XVII) and (XVII→XVIa) may be advantageously conducted as a one-pot two-steps reaction, without formal isolation of the sulfinic acid salt of formula XVII. Conditions for each step are as described above. Such a process, optionally under microwave irradiation, may be carried out in analogy to, for example, descriptions found in European Journal of Medicinal Chemistry 2011, 46, 2984-2991 or European Journal of Medicinal Chemistry 2007, 42, 880-884.

Compounds of formula XIX, wherein wherein A_1 is N or CR (preferably CH) and X_{14}, R_7 and R are as defined above, are known compounds or can be prepared by known methods, described in the literature.

Compounds of formula (X)

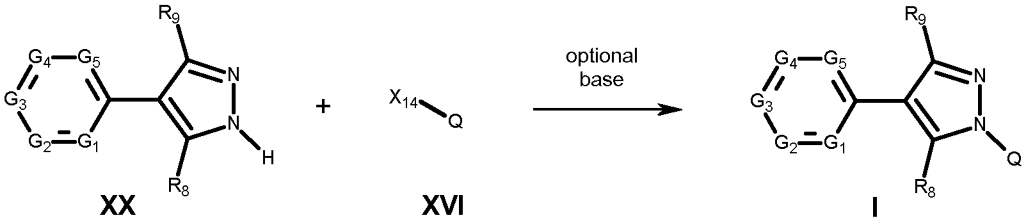


(X)

,

wherein Q, R_8 and R_9 are as defined under formula I above, and wherein L_G is a halogen, preferably iodine or bromine, are novel and especially developed for the preparation of the compounds of formula I of this invention. The compounds of formula (X) therefore constitute a further object of the invention. The preferred substituent definitions for the compounds of formula I are also valid for the compounds of formula (X).

Alternatively, compounds of formula I, wherein R_8, R_9, G_1, G_2, G_3, G_4, and G_5 are as defined above and wherein Q is a radical selected from the group consisting of formula Q_1 to Q_2, and in which X is S (sulfide), SO (sulfoxide) or SO_2 (sulfone), preferably X is SO_2 (sulfone),

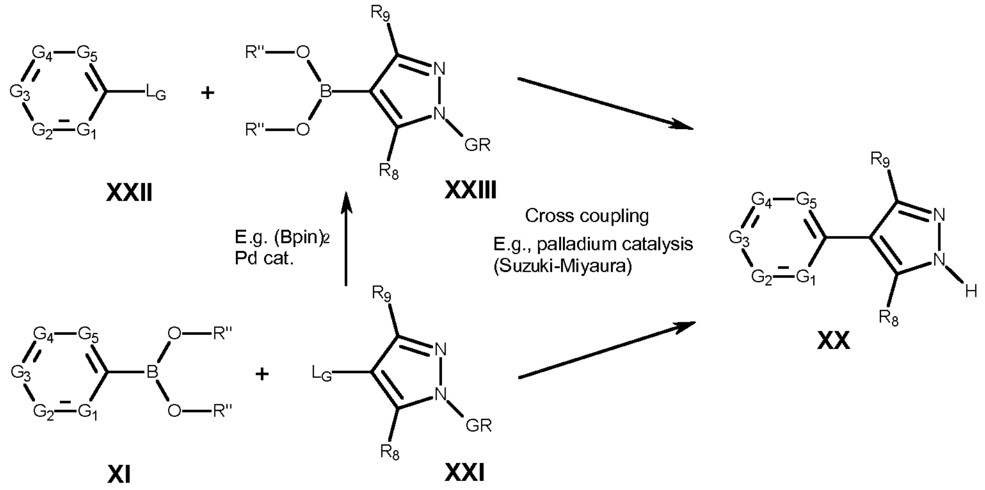


Q is selected from Q_1 and Q_2
X is S, SO or SO_2,
in particular SO_2 (sulfone)

Q is selected from Q_1 and Q_2
X is S, SO or SO_2,
in particular SO_2 (sulfone)

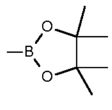
may be prepared by reacting a compound of formula XX, or a salt thereof, wherein R_8, R_9, G_1, G_2, G_3, G_4, and G_5 are as defined above, with a compound of formula XVI, wherein Q is as defined in formula I, X is S, SO, SO_2 (preferably SO_2) and wherein X_{14} is is a leaving group such as, for example, fluorine, chlorine, bromine or iodine, or an aryl-, C_{1-4}alkyl- or C_{1-4}haloalkylsulfonate (or any other similar leaving group), optionally in the presence of a suitable base, such as alkali metal carbonates, for example sodium, potassium, lithium or cesium carbonate, or alkali metal hydrides such as sodium hydride, or alkali metal hydroxides such as sodium hydroxide and potassium hydroxide, or sodium or potassium tert-butoxide, in an inert solvent at temperatures preferably between 25-180°C, optionally under microwave irradiation. Examples of solvent to be used include ethers such as THF, ethylene glycol dimethyl ether, tert-butylmethyl ether, and 1,4-dioxane, aromatic hydrocarbons such as toluene and xylene, nitriles such as acetonitrile or polar aprotic solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone or dimethyl sulfoxide. This base mediated N-arylation or N-hetarylation reaction may optionally be transition metal mediated, or preferably catalyzed by transition metals, such as, for example, metalic copper or copper(I) salts, especially copper(I) halides like copper(I) chloride, copper(I) bromide, copper(I) iodide or copper(I) oxide (especially preferred is copper(I) iodide), or copper(II) salts, like for example copper(II) acetate. Optional additives such as diamine ligands (preferably 1,10-phenanthroline, 1,2-ethanediamine, *N,N'*-dimethyl-1,2-ethanediamine, *N,N*-dimethyl-1,2-ethanediamine, 1,2-cyclohexane-diamine or *N,N'*-dimethyl-cyclohexane-1,2-diamine) or 8-quinolinol, glycine, dimethylglycine or proline may be used, as well as further additives such as sodium, potassium or lithium iodide.

Compounds of formula XX, or a salt thereof, wherein R_8, R_9, G_1, G_2, G_3, G_4, and G_5 are as defined above,



may be prepared by reacting a compound of formula XXI, or a salt thereof, wherein L_G, R_8 and R_9 are as defined above, and in which GR is hydrogen or a group $-COOR_{50}$, wherein R_{50} is C_1-C_4alkyl, with a compound of formula XI (including analogues XIa to XId), wherein G_1, G_2, G_3, G_4 and G_5 are as defined above, and wherein R" is for example hydrogen (in that case the compound of the formula XI is a boronic acid) or C_1-C_4alkyl, by means of a transition metal-catalyzed reaction already detailed beforehand (see transformation XI + X → I). Alternatively, the polarity at the two reacting centers may be inverted whereby compounds of formula XX, or a salt thereof, may be prepared by reacting a compound of formula XXIII, or a salt thereof, with a compound of formula XXII, wherein the substituent definitions for XXII and XXIII is as defined for compounds XI and XXI, and under the same reactions conditions described above.

Compounds of formula XXI, XXII and XXIII, wherein the substituent definitions are as described above, are known compounds or can be prepared by known methods, described in the literature. Compounds of formula XXIII in particular, may also be prepared by reacting a compound of formula XXI with bispinacol diborane $(Bpin)_2$ under palladium catalysis, as described, for example, in WO2014193647. Such an introduction of a pinacolborate functional group can be performed in an aprotic solvent, such as dioxane, in presence of a base, preferably a weak base, such as potassium acetate KOAc. [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II), also known as palladium dppf dichloride or $Pd(dppf)Cl_2$, is a common catalyst for this type of reaction. The temperature of the reaction is preferably performed between 0°C and the boiling point of the reaction mixture, or the reaction may be performed under microwave irradiation. Those particular reaction conditions are generating a cyclic boronate XXIII,

wherein the group $-B(OR")_2$ is represented by the functionality  .

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

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

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

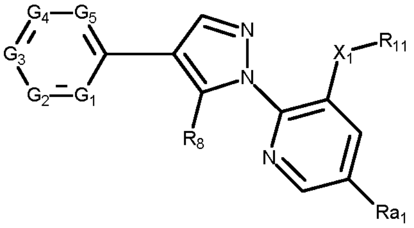
N-oxides can be prepared by reacting a compound of the formula I with a suitable oxidizing agent, for example the H_2O_2/urea adduct in the presence of an acid anhydride, e.g. trifluoroacetic anhydride. Such oxidations are known from the literature, for example from J. Med. Chem., 32 (12), 2561-73, 1989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

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

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

The compounds according to the following Tables 1 to 12 below can be prepared according to the methods described above. The examples which follow are intended to illustrate the invention and show preferred compounds of formula I.

Table X: This table discloses the 16 substituent definitions X.001 to X.016 of the formula I-1a:



(I-1a),

wherein Ra_1, R_{11}, G_1, G_2, G_3, G_4 and G_5 are as defined below:

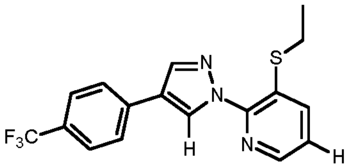
Table X:

Comp.No	Ra_1	R_{11}	G_1	G_2	G_3	G_4	G_5
X.001	H	$-CH_2CH_3$	CH	CH	$C(CF_3)$	CH	CH
X.002	CF_3	$-CH_2CH_3$	CH	CH	$C(CF_3)$	CH	CH
X.003	H	$-CH_2CH_3$	CH	$C(CF_3)$	CH	CH	CH
X.004	CF_3	$-CH_2CH_3$	CH	$C(CF_3)$	CH	CH	CH
X.005	H	$-CH_2CH_3$	N	$C(CF_3)$	CH	CH	CH
X.006	CF_3	$-CH_2CH_3$	N	$C(CF_3)$	CH	CH	CH
X.007	H	$-CH_2CH_3$	N	CH	$C(CF_3)$	CH	CH

Comp.No	Ra_1	R_{11}	G_1	G_2	G_3	G_4	G_5
X.008	CF_3	$-CH_2CH_3$	N	CH	$C(CF_3)$	CH	CH
X.009	H	$-CH_2CH_3$	N	CH	CH	$C(CF_3)$	CH
X.010	CF_3	$-CH_2CH_3$	N	CH	CH	$C(CF_3)$	CH
X.011	H	$-CH_2CH_3$	CH	N	$C(CF_3)$	CH	CH
X.012	CF_3	$-CH_2CH_3$	CH	N	$C(CF_3)$	CH	CH
X.013	H	$-CH_2CH_3$	CH	N	CH	$C(CF_3)$	CH
X.014	CF_3	$-CH_2CH_3$	CH	N	CH	$C(CF_3)$	CH
X.015	H	$-CH_2CH_3$	CH	$C(CF_3)$	N	CH	CH
X.016	CF_3	$-CH_2CH_3$	CH	$C(CF_3)$	N	CH	CH

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

Table 1: This table discloses the 16 compounds 1.001 to 1.016 of the formula I-1a, wherein X_1 is S, R_8 is H, and Ra_1, R_{11}, G_1, G_2, G_3, G_4 and G_5 are as defined in Table X. For example, compound No. 1.001 has the following structure:



(1.001)

Table 2: This table discloses the 16 compounds 2.001 to 2.016 of the formula I-1a, wherein X_1 is SO, R_8 is H, and Ra_1, R_{11}, G_1, G_2, G_3, G_4 and G_5 are as defined in Table X.

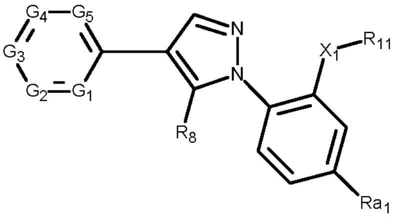
Table 3: This table discloses the 16 compounds 3.001 to 3.016 of the formula I-1a, wherein X_1 is SO_2, R_8 is H, and Ra_1, R_{11}, G_1, G_2, G_3, G_4 and G_5 are as defined in Table X.

Table 4: This table discloses the 16 compounds 4.001 to 4.016 of the formula I-1a, wherein X_1 is S, R_8 is CH_3, and Ra_1, R_{11}, G_1, G_2, G_3, G_4 and G_5 are as defined in Table X.

Table 5: This table discloses the 16 compounds 5.001 to 5.016 of the formula I-1a, wherein X_1 is SO, R_8 is CH_3, and Ra_1, R_{11}, G_1, G_2, G_3, G_4 and G_5 are as defined in Table X.

Table 6: This table discloses the 16 compounds 6.001 to 6.016 of the formula I-1a, wherein X_1 is SO_2, R_8 is CH_3, and Ra_1, R_{11}, G_1, G_2, G_3, G_4 and G_5 are as defined in Table X.

Table Y: This table discloses the 16 substituent definitions Y.001 to Y.016 of the formula I-1b:



(1-1b),

wherein Ra_1, R_{11}, G_1, G_2, G_3, G_4 and G_5 are as defined below:

Table Y:

Comp.No	Ra_1	R_{11}	G_1	G_2	G_3	G_4	G_5
Y.001	H	$-CH_2CH_3$	CH	CH	$C(CF_3)$	CH	CH
Y.002	CF_3	$-CH_2CH_3$	CH	CH	$C(CF_3)$	CH	CH
Y.003	H	$-CH_2CH_3$	CH	$C(CF_3)$	CH	CH	CH
Y.004	CF_3	$-CH_2CH_3$	CH	$C(CF_3)$	CH	CH	CH
Y.005	H	$-CH_2CH_3$	N	$C(CF_3)$	CH	CH	CH
Y.006	CF_3	$-CH_2CH_3$	N	$C(CF_3)$	CH	CH	CH
Y.007	H	$-CH_2CH_3$	N	CH	$C(CF_3)$	CH	CH
Y.008	CF_3	$-CH_2CH_3$	N	CH	$C(CF_3)$	CH	CH
Y.009	H	$-CH_2CH_3$	N	CH	CH	$C(CF_3)$	CH
Y.010	CF_3	$-CH_2CH_3$	N	CH	CH	$C(CF_3)$	CH
Y.011	H	$-CH_2CH_3$	CH	N	$C(CF_3)$	CH	CH
Y.012	CF_3	$-CH_2CH_3$	CH	N	$C(CF_3)$	CH	CH
Y.013	H	$-CH_2CH_3$	CH	N	CH	$C(CF_3)$	CH
Y.014	CF_3	$-CH_2CH_3$	CH	N	CH	$C(CF_3)$	CH
Y.015	H	$-CH_2CH_3$	CH	$C(CF_3)$	N	CH	CH
Y.016	CF_3	$-CH_2CH_3$	CH	$C(CF_3)$	N	CH	CH

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

Table 7: This table discloses the 16 compounds 7.001 to 7.016 of the formula I-1b, wherein X_1 is S, R_8 is H, and Ra_1, R_{11}, G_1, G_2, G_3, G_4 and G_5 are as defined in Table Y.

Table 8: This table discloses the 16 compounds 8.001 to 8.016 of the formula I-1b, wherein X_1 is SO, R_8 is H, and Ra_1, R_{11}, G_1, G_2, G_3, G_4 and G_5 are as defined in Table Y.

Table 9: This table discloses the 16 compounds 9.001 to 9.016 of the formula I-1b, wherein X_1 is SO_2, R_8 is H, and Ra_1, R_{11}, G_1, G_2, G_3, G_4 and G_5 are as defined in Table Y.

Table 10: This table discloses the 16 compounds 10.001 to 10.016 of the formula I-1b, wherein X_1 is S, R_8 is CH_3, and Ra_1, R_{11}, G_1, G_2, G_3, G_4 and G_5 are as defined in Table Y.

Table 11: This table discloses the 16 compounds 11.001 to 11.016 of the formula I-1b, wherein X_1 is SO, R_8 is CH_3, and Ra_1, R_{11}, G_1, G_2, G_3, G_4 and G_5 are as defined in Table Y.

Table 12: This table discloses the 16 compounds 12.001 to 12.016 of the formula I-1b, wherein X_1 is SO_2, R_8 is CH_3, and Ra_1, R_{11}, G_1, G_2, G_3, G_4 and G_5 are as defined in Table Y.

The compounds of formula I according to the invention are preventively and/or curatively valuable active ingredients in the field of pest control, even at low rates of application, which have a very favorable biocidal spectrum and are well tolerated by warm-blooded species, fish and plants. The active ingredients according to the invention act against all or individual developmental stages of normally sensitive, but also resistant, animal pests, such as insects or representatives of the order Acarina. The insecticidal or acaricidal activity of the active ingredients according to the invention can manifest itself directly, i. e. in destruction of the pests, which takes place either immediately or only after some time has elapsed, for example during ecdysis, or indirectly, for example in a reduced oviposition and/or hatching rate, a good activity corresponding to a destruction rate (mortality) of at least 50 to 60%.

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

from the order *Lepidoptera*, for example,

Acleris spp., Adoxophyes spp., Aegeria spp., Agrotis spp., Alabama argillaceae, Amylois spp., Anticarsia gemmatalis, Archips spp., Argyresthia spp, 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 and latex plants.

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

For example the invention may be used on any of the following ornamental species: *Ageratum* spp., *Alonsoa* spp., *Anemone* spp., *Anisodontea capsenisis*, *Anthemis* spp., *Antirrhinum* spp., *Aster* spp., *Begonia* spp. (e.g. *B. elatior*, *B. semperflorens*, *B. tubéreux*), *Bougainvillea* spp., *Brachycome* spp., *Brassica* spp. (ornamental), *Calceolaria* spp., *Capsicum annuum*, *Catharanthus roseus*, *Canna* spp., *Centaurea* spp., *Chrysanthemum* spp., *Cineraria* spp. (*C. maritime*), *Coreopsis* spp., *Crassula coccinea*, *Cuphea ignea*, *Dahlia* spp., *Delphinium* spp., *Dicentra spectabilis*, *Dorotheantus* spp., *Eustoma grandiflorum*, *Forsythia* spp., *Fuchsia* spp., *Geranium gnaphalium*, *Gerbera* spp., *Gomphrena globosa*, *Heliotropium* spp., *Helianthus* spp., *Hibiscus* spp., *Hortensia* spp., *Hydrangea* spp., *Hypoestes phyllostachya*, *Impatiens* spp. (*I. Walleriana*), *Iresines* spp., *Kalanchoe* spp., *Lantana camara*, *Lavatera trimestris*, *Leonotis leonurus*, *Lilium* spp., *Mesembryanthemum* spp., *Mimulus* spp., *Monarda* spp., *Nemesia* spp., *Tagetes* spp., *Dianthus* spp. (carnation), *Canna* spp., *Oxalis* spp., *Bellis* spp., *Pelargonium* spp. *(P. peltatum*, *P. Zonale*), *Viola* spp. (pansy), *Petunia* spp., *Phlox* spp., *Plecthranthus* spp., *Poinsettia* spp., *Parthenocissus* spp. *(P. quinquefolia*, *P. tricuspidata)*, *Primula* spp., *Ranunculus* spp., *Rhododendron* spp., *Rosa* spp. (rose), *Rudbeckia* spp., *Saintpaulia* spp., *Salvia* spp., *Scaevola aemola*, *Schizanthus wisetonensis*, *Sedum* spp., *Solanum* spp., *Surfinia* spp., *Tagetes* spp., *Nicotinia* spp., *Verbena* spp., *Zinnia* spp. and other bedding plants.

For example the invention may be used on any of the following vegetable species: *Allium* spp. (*A. sativum, A.. cepa, A. oschaninii, A. Porrum, A. ascalonicum, A. fistulosum*), *Anthriscus cerefolium, Apium graveolus, Asparagus officinalis, Beta vulgarus, Brassica* spp. (*B. Oleracea, B. Pekinensis, B. rapa*), *Capsicum annuum, Cicer arietinum, Cichorium endivia, Cichorum* spp. (*C. intybus, C. endivia*)*, Citrillus lanatus*, *Cucumis* spp. (*C. sativus, C. melo*)*, Cucurbita* spp. (*C. pepo, C. maxima*)*, Cyanara* spp. (*C. scolymus, C. cardunculus*)*, Daucus carota, Foeniculum vulgare, Hypericum* spp.*, Lactuca sativa, Lycopersicon* spp. (*L. esculentum, L. lycopersicum*)*, Mentha* spp.*, Ocimum basilicum, Petroselinum*

crispum, Phaseolus spp. (*P. vulgaris, P. coccineus*), *Pisum sativum, Raphanus sativus, Rheum rhaponticum, Rosemarinus* spp., *Salvia* spp., *Scorzonera hispanica, Solanum melongena, Spinacea oleracea, Valerianella* spp. (*V. locusta, V. eriocarpa*) and *Vicia faba.*
Preferred ornamental species include African violet, *Begonia*, *Dahlia*, *Gerbera*, *Hydrangea*, *Verbena*, *Rosa*, *Kalanchoe*, *Poinsettia*, *Aster*, *Centaurea*, *Coreopsis*, *Delphinium*, *Monarda*, *Phlox*, *Rudbeckia*, *Sedum, Petunia, Viola, Impatiens, Geranium, Chrysanthemum, Ranunculus, Fuchsia, Salvia, Hortensia*, rosemary, sage, St. Johnswort, mint, sweet pepper, tomato and cucumber.

The active ingredients according to the invention are especially suitable for controlling Aphis craccivora, Diabrotica balteata, Heliothis virescens, Myzus persicae, Plutella xylostella and Spodoptera littoralis in cotton, vegetable, maize, rice and soya crops. The active ingredients according to the invention are further especially suitable for controlling Mamestra (preferably in vegetables), 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. CryI-type deoxyribonucleic acids and their preparation are known, for example, from WO 95/34656, EP-A-0 367 474, EP-A-0 401 979 and WO 90/13651.

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

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

Further examples of such transgenic crops are:

1. **Bt11 Maize** from Syngenta Seeds SAS, Chemin de l'Hobit 27, F-31 790 St. Sauveur, France, registration number C/FR/96/05/10. Genetically modified *Zea mays* which has been rendered resistant to attack by the European corn borer (*Ostrinia nubilalis* and *Sesamia nonagrioides*) by transgenic expression of a truncated Cry1Ab toxin. Bt11 maize also transgenically expresses the enzyme PAT to achieve tolerance to the herbicide glufosinate ammonium.
2. **Bt176 Maize** from Syngenta Seeds SAS, Chemin de l'Hobit 27, F-31 790 St. Sauveur, France, registration number C/FR/96/05/10. Genetically modified *Zea mays* which has been rendered resistant to attack by the European corn borer (*Ostrinia nubilalis* and *Sesamia nonagrioides*) by transgenic expression of a Cry1Ab toxin. Bt176 maize also transgenically expresses the enzyme PAT to achieve tolerance to the herbicide glufosinate ammonium.
3. **MIR604 Maize** from Syngenta Seeds SAS, Chemin de l'Hobit 27, F-31 790 St. Sauveur, France, registration number C/FR/96/05/10. Maize which has been rendered insect-resistant by transgenic expression of a modified Cry3A toxin. This toxin is Cry3A055 modified by insertion of a cathepsin-G-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.

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.

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 2003/034823, US 5631072, WO 2005/64072, WO2006/128870, EP 1724392, WO2005113886 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, 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

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

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

A large number of surface-active substances can advantageously be used in both solid and liquid formulations, especially in those formulations which can be diluted with a carrier prior to use. Surface-active substances may be anionic, cationic, non-ionic or polymeric and they can be used as emulsifiers, wetting agents or suspending agents or for other purposes. Typical surface-active substances include, for example, salts of alkyl sulfates, such as diethanolammonium lauryl sulfate; salts of alkylarylsulfonates, such as calcium dodecylbenzenesulfonate; alkylphenol/alkylene oxide addition products, such as nonylphenol ethoxylate; alcohol/alkylene oxide addition products, such as tridecylalcohol ethoxylate; soaps, such as sodium stearate; salts of 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.

Preparatory Examples:

"Mp" means melting point in °C. Free radicals represent methyl groups. ^{1}H NMR measurements were recorded on a Brucker 400MHz spectrometer, chemical shifts are given in ppm relevant to a TMS standard. Spectra measured in deuterated solvents as indicated. Common abbreviations: aq = aqueous, min = minute, h = hour, sat = saturated, R_t = retention time, mCPBA = meta-chloroperoxybenzoic acid, MeOH = methanol, EtOH = ethanol, THF = tetrahydrofuran, EtOAc = ethyl acetate, $NaHCO_3$ = sodium hydrogen carbonate, Na_2CO_3 = sodium carbonate, HCl = hydrogen chloride, CH_2Cl_2 = dichloromethane, Et_3N = triethylamine, DMF = N,N-dimethylformamide, brine = saturated aqueous sodium chloride, $PdCl_2$(dppf) = [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloride. Either one of the LCMS or GCMS 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 $(M+H)^+$.

LCMS Methods:

Method 1:

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

Method 2:

AN_BASE, Apparatus: Agilent 1100 Bin. Pump: G1312A, degasser; autosampler, ColCom, DAD: Agilent G1315B, 220-320 nm, MSD: Agilent LC/MSD G6130B ESI, pos/neg 100-800; ELSD PL-ELS2100 gas flow 1.1 ml/min, gas temp: 50°C; column: Waters XSelect™ C18, 50x2.1mm, 3.5μ, Temp: 25 °C, Flow: 0.8 mL/min, Gradient: t_0 = 2% A, $t_{3.5min}$ = 98% A, t_{6min} = 98% A, Posttime: 2 min, Eluent A: 95% acetonitrile

+ 5% 10mM ammonium bicarbonate in water in acetonitrile, Eluent B: 10mM ammonium bicarbonate in water (pH=9.5).

GCMS Method:

Method 3:

S20, Instrument: GC: Agilent 6890N and MS: 5973 MSD, EI-positive, Det.temp.: 280°C Mass range: 50-550; Column: RXi-5MS 20m, ID 180µm, df 0.18µm; Average velocity: 50 cm/s; Injection vol: 1 µl; Injector temp: 250°C; Split ratio: 100/1; Carrier gas: He; Initial temp: 60°C; Initial time: 1.0 min; Solvent delay: 1.0 min; Rate 50°C/min; Final temp 250°C; Final time 3.5 min.

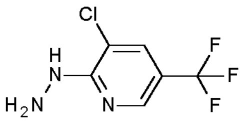
LCMS Method:

Method 4:

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

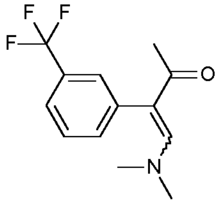
EXAMPLE P1: Preparation of 3-ethylsulfanyl-2-[5-methyl-4-[3-(trifluoromethyl)phenyl]pyrazol-1-yl]-5-(trifluoromethyl)pyridine (compound P1.1):

Step 1: Preparation of [3-chloro-5-(trifluoromethyl)-2-pyridyl]hydrazine:



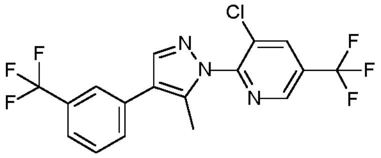
To a solution of hydrazine monohydrate (6.19 g, 124 mmol) in ethanol (40 ml) was added dropwise 2,3-dichloro-5-(trifluoromethyl)pyridine (8.1 g, 37.5 mmol). After complete addition the mixture was heated at 90°C overnight. The reaction mixture was concentrated and the solid residue was recrystallised from ethanol/water (2/1) to afford the title compound (4.9 g) as a solid. LCMS (method 1): 212/214 $(M+H)^+$, retention time 1.95 min. ^{1}H-NMR ($CDCl_3$, ppm) 4.50 (1H), 7.94 (1H), 8.38 (1H), 8.57 (1H).

Step 2: Preparation of 4-(dimethylamino)-3-[3-(trifluoromethyl)phenyl]but-3-en-2-one:



A mixture of 1-[3-(trifluoromethyl)phenyl]propan-2-one (5.0 g, 24.73 mmol) and N,N-dimethylformamide dimethyl acetal (3.3 g, 27.7 mmol, 3.71 ml) was heated at 95°C for 1.5 h. The crude solid reaction mixture was purified over silica by flash column chromatography (50 to 100% gradient of EtOAc in heptane, followed by 100% EtOAc) to afford the title compound (5.8 g) as a solid. LCMS (method 1): 258 $(M+H)^+$, retention time 2.05 min. ^{1}H-NMR ($CDCl_3$, ppm) 1.98 (3H), 2.70 (6H), 7.40 (2H), 7.43-7.47 (2H), 7.53 (1H), 7.61 (1H).

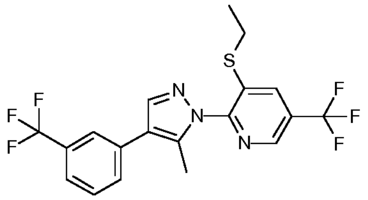
Step 3: Preparation of 3-chloro-2-[5-methyl-4-[3-(trifluoromethyl)phenyl]pyrazol-1-yl]-5-(trifluoromethyl)pyridine (compound P3.1):



(P3.1)

In a microwave vial, a mixture of [3-chloro-5-(trifluoromethyl)-2-pyridyl]hydrazine (1.058 g, 5.00 mmol) and 4-(dimethylamino)-3-[3-(trifluoromethyl)phenyl]but-3-en-2-one (1.415 g, 5.50 mmol) in ethanol/acetic acid (15 ml/3 ml) was heated in the microwave at 140°C for 1 h. The solid was filtered off, washed twice with a little ethanol and dried to afford the title compound P3.1 (0.80 g) as a solid, mp 129-130°C. LCMS (method 2): 406/408 $(M+H)^+$, retention time 4.21 min. ^{1}H-NMR ($CDCl_3$, ppm) 2.44 (3H), 7.55-7.65 (3H), 7.70 (1H), 7.92 (1H), 8.24 (1H), 8.79 (1H).

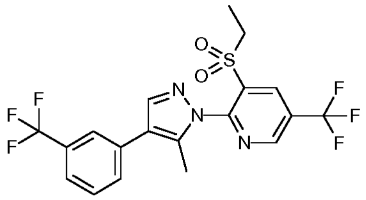
Step 4: Preparation of 3-ethylsulfanyl-2-[5-methyl-4-[3-(trifluoromethyl)phenyl]pyrazol-1-yl]-5-(trifluoromethyl)pyridine (title compound P1.1):



(P1.1)

Under nitrogen, a solution of 3-chloro-2-[5-methyl-4-[3-(trifluoromethyl)phenyl]pyrazol-1-yl]-5-(trifluoromethyl)pyridine (750 mg, 1.849 mmol) in dry N,N-dimethylformamide (5 ml) was cooled in ice and sodium ethanethiolate (163 mg, 1.941 mmol) was added. The cooling bath was removed and the mixture was stirred at room temperature for 1.5 h. The reaction mixture was diluted with water, brine was added and the product was extracted with EtOAc. The organic layer was washed twice with brine, dried over sodium sulfate and concentrated. The crude product was purified over silica by flash column chromatography (0 to 25% gradient of EtOAc in heptane) to afford the title compound P1.1 (505 mg) as a solid. LCMS (method 2): 432 $(M+H)^+$, retention time 4.35 min. ^{1}H-NMR ($CDCl_3$, ppm) 1.38 (3H), 2.47 (3H), 2.98 (2H), 7.54-7.58 (2H), 7.62-7.65 (1H), 7.71 (1H), 7.90 (1H), 7.92 (1H), 8.57 (1H).

EXAMPLE P2: Preparation of 3-ethylsulfonyl-2-[5-methyl-4-[3-(trifluoromethyl)phenyl]pyrazol-1-yl]-5-(trifluoromethyl)pyridine (compound P1.2):

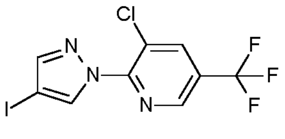


(P1.2)

To a solution of 3-ethylsulfanyl-2-[5-methyl-4-[3-(trifluoromethyl)phenyl]pyrazol-1-yl]-5-(trifluoromethyl)pyridine (435 mg, 1.008 mmol) in dichloromethane (10 ml) was added mCPBA (70 wt% in water) (547 mg, 2.218 mmol) in one portion and the mixture was stirred at room temperature overnight. The reaction mixture was diluted with CH_2Cl_2, washed three times with sat. $NaHCO_3$ (aq), dried over sodium sulfate and concentrated. The crude product was purified over silica by flash column chromatography (0 to 25% gradient of EtOAc in heptane). The fractions containing product were combined and partly concentrated, leaving a suspension in heptane. The solid was filtered off, washed with heptane and dried to afford the title compound P1.2 (382 mg) as a solid, mp 144-145°C. LCMS (method 2): 464 $(M+H)^+$, retention time 4.16 min. ^{1}H-NMR ($CDCl_3$, ppm) 1.42 (3H), 2.50 (3H), 3.89 (2H), 7.55-7.65 (3H), 7.71 (1H), 7.89 (1H), 8.79 (1H), 9.04 (1H).

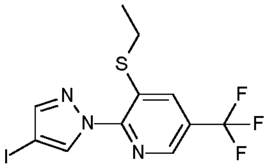
EXAMPLE P3: Preparation of 3-ethylsulfonyl-2-(4-iodopyrazol-1-yl)-5-(trifluoromethyl)pyridine (intermediate compound P3.2):

Step 1: Preparation of 3-chloro-2-(4-iodopyrazol-1-yl)-5-(trifluoromethyl)pyridine



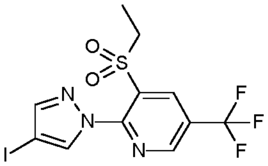
A mixture of 2,3-dichloro-5-(trifluoromethyl)pyridine (1.620 g, 7.5 mmol), 4-iodo-1H-pyrazole (1.164 g, 6.0 mmol) and potassium carbonate (1.658 g, 12.00 mmol) in dry N,N-dimethylformamide (17.5 ml) was heated in the microwave at 120°C for 1 h. The reaction mixture was partitioned between EtOAc and brine/water (1/1). After washing and separation, the organic layer was washed with brine, dried over sodium sulfate and concentrated. The crude product was purified over silica by flash column chromatography (0 to 25% gradient of EtOAc in heptane). The fractions containing product were combined and partly concentrated, leaving a suspension in heptane. The heptane was removed with a pipette, the solid was washed with heptane and dried in vacuo to afford the title compound (1.83 g) as a solid. LCMS (method 1): 374/376 $(M+H)^+$, retention time 2.34 min. ^1H-NMR ($CDCl_3$, ppm) 7.84 (1H), 8.16 (1H), 8.37 (1H), 8.67 (1H).

Step 2: Preparation of 3-ethylsulfanyl-2-(4-iodopyrazol-1-yl)-5-(trifluoromethyl)pyridine:



Under nitrogen, a solution of 3-chloro-2-(4-iodopyrazol-1-yl)-5-(trifluoromethyl)pyridine (2.08 g, 5.57 mmol) in dry N,N-dimethylformamide (15 ml) was cooled in ice and to this was added sodium ethanethiolate (0.50 g, 5.94 mmol) in one portion. After complete addition, the mixture was stirred at 0°C for 15 min, then at room temperature for 1 h. The reaction mixture was poured into water/brine (1/1) and extracted with EtOAc. The organic layer was washed twice with brine, dried over sodium sulfate and concentrated. The crude product was purified over silica by flash column chromatography (0 to 25% gradient of EtOAc in heptane) to afford a 4/1 mixture of the title compound (616 mg) and starting material as a solid, which was used as such for the next step. LCMS (method 1): 400 $(M+H)^+$, retention time 2.47 min. ^1H-NMR ($CDCl_3$, ppm) 1.39 (3H), 2.97 (2H), 7.82 (1H), 7.86 (1H), 8.43 (1H), 8.47 (1H).

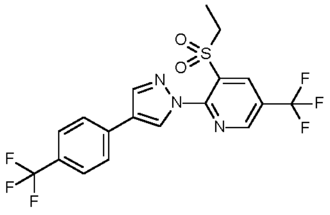
Step 3: Preparation of 3-ethylsulfonyl-2-(4-iodopyrazol-1-yl)-5-(trifluoromethyl)pyridine (title compound P3.2):



(P3.2)

To a solution of 3-ethylsulfanyl-2-(4-iodopyrazol-1-yl)-5-(trifluoromethyl)pyridine (604 mg, 1.210 mmol, 80 % pure) in dichloromethane (10 ml) was added mCPBA (70 wt% in water) (657 mg, 2.67 mmol) and the mixture was stirred at room temperature for 5 hours. The reaction mixture was diluted with CH_2Cl_2, washed three times with sat. $NaHCO_3$ (aq), dried over sodium sulfate and concentrated. The crude product was purified over silica by flash column chromatography (0 to 25% gradient of EtOAc in heptane) to afford the title compound P3.2 (295 mg) as a solid, mp. 149-151°C. LCMS (method 2): 432 $(M+H)^+$, retention time 3.92 min. ^{1}H-NMR ($CDCl_3$, ppm) 1.43 (3H), 4.03 (2H), 7.82 (1H), 8.46 (1H), 8.80 (1H), 8.89 (1H).

EXAMPLE P4: Preparation of 3-ethylsulfonyl-5-(trifluoromethyl)-2-[4-[4-(trifluoromethyl)phenyl] pyrazol-1-yl]pyridine (compound P1.3):

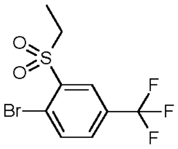


(P1.3)

In a microwave vial, 3-(ethylsulfonyl)-2-(4-iodo-1H-pyrazol-1-yl)-5-(trifluoromethyl)pyridine (250 mg, 0.580 mmol), [4-(trifluoromethyl)phenyl]boronic acid (220 mg, 1.160 mmol) and cesium carbonate (567 mg, 1.739 mmol) were dissolved in dimethoxyethane/water (4 ml/1ml) and flushed with argon for 5 min. To this was added $PdCl_2$(dppf) (21.21 mg, 0.029 mmol), the vial was closed and the mixture was heated in the microwave at 120°C for 30 min. The crude reaction mixture was partitioned between EtOAc and brine/water (1/1). After washing and separation, the organic layer was dried over sodium sulfate and concentrated. The crude product was purified over silica by flash column chromatography (0 to 25% gradient of EtOAc in heptane). The fractions containing product were combined and partly concentrated, leaving a suspension in heptane. The heptane was removed with a pipette, the product was washed with heptane and dried in vacuo to afford the title compound P1.3 (126 mg) as a solid, mp 172.5-173.5°C. LCMS (method 2): 450 $(M+H)^+$, retention time 4.13 min. ^{1}H-NMR ($CDCl_3$, ppm) 1.46 (3H), 4.11 (2H), 7.69 (4H), 8.16 (1H), 8.72 (1H), 8.83 (1H) , 8.93 (1H).

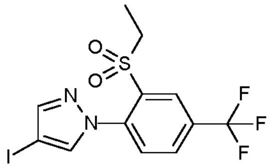
EXAMPLE P5: Preparation of 1-[2-ethylsulfonyl-4-(trifluoromethyl)phenyl]-4-iodo-pyrazole (intermediate compound P3.4):

Step 1: Preparation of 1-bromo-2-ethylsulfonyl-4-(trifluoromethyl)benzene



In a microwave vial , 2-bromo-5-(trifluoromethyl)benzenesulfonyl chloride (1.294 g, 4.00 mmol), sodium sulfite (1.008 g, 8.00 mmol) and sodium bicarbonate (1.008 g, 12.00 mmol) were dissolved in water (15 ml), the vial was capped and the mixture was heated in the microwave at 120°C for 1 h. The mixture was allowed to cool to room temperature, the pressure was released and the cap was removed. A solution of ethyl iodide (3.09 g, 19.80 mmol, 1.6 ml) in ethanol (2.4 ml) was added, the vial was capped and the mixture was again heated in the microwave at 100°C for 1 hour. The reaction mixture was partitioned between EtOAc and brine. After washing and separation, the water layer was extracted with EtOAc once more. The combined organic layers were dried over sodium sulfate and concentrated. The crude product was purified over silica by flash column chromatography (0 to 50% gradient of EtOAc in heptane) to afford the title compound (766 mg) as a solid, mp 78-79°C. GCMS (method 3): 316/318 $(M)^+$, retention time 4.42 min. ^{1}H-NMR ($CDCl_3$, ppm) 1.32 (3H), 3.50 (2H), 7.73 (1H), 7.93 (1H), 8.42 (1H).

Step 2: Preparation of 1-[2-ethylsulfonyl-4-(trifluoromethyl)phenyl]-4-iodo-pyrazole (title compound P3.4):

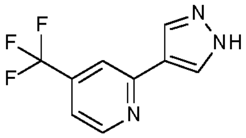


(P3.4)

In a microwave vial , 1-bromo-2-ethylsulfonyl-4-(trifluoromethyl)benzene (951 mg, 3 mmol) and 4-iodo-1H-pyrazole (698 mg, 3.60 mmol) were dissvoled in dry N,N-dimethylformamide (10 ml) and potassium carbonate (1.244 g, 9.00 mmol) was added. The vial was capped and the mixture was heated in the microwave at 160°C for 1 h. The reaction mixture was partitioned between EtOAc and brine/water (1/1). After washing and separation, the organic layer was washed twice with brine, dried over sodium sulfate and concentrated. The crude product was purified over silica by flash column chromatography (5 to 50% gradient of EtOAc in heptane) to afford the title compound (985 mg) as a solid, mp 126-127°C. LCMS (method 1): 431 $(M+H)^+$, retention time 2.31 min. ^{1}H-NMR ($CDCl_3$, ppm) 1.26 (3H), 3.28 (2H), 7.61 (1H), 7.79 (1H), 7.94 (1H), 8.01 (1H), 8.48 (1H).

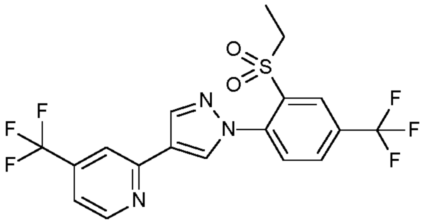
EXAMPLE P6: Preparation of 2-[1-[2-ethylsulfonyl-4-(trifluoromethyl)phenyl]pyrazol-4-yl]-4-(trifluoromethyl)pyridine (compound P1.10)

Step 1: Preparation of 2-(1H-pyrazol-4-yl)-4-(trifluoromethyl)pyridine



In a microwave vial, tert-butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrazole-1-carboxylate (0.93 g, 3.16 mmol), 2-bromo-4-(trifluoromethyl)pyridine (0.857 g, 3.79 mmol) and potassium carbonate (1.311 g, 9.48 mmol) were dissolved in 1,2-dimethoxyethane/water (12 ml / 3 ml) and flushed with argon for 5 minutes. To this was added $Pd(PPh_3)_4$ (0.183 g, 0.158 mmol), the vial was closed and the mixture was heated in the microwave at 120°C for 30 minutes. The reaction mixture was partitioned between EtOAc and brine. After washing and separation, the water layer was extracted with EtOAc once more. The combined organic layers were dried over sodium sulfate and concentrated. The crude product was purified over silica by flash column chromatography (10 to 100% gradient of EtOAc in heptane) to afford the title compound (253 mg) as a solid. LCMS (method 1): 214 $(M+H)^+$, retention time 1.89 min. ^{1}H-NMR ($CDCl_3$, ppm) 7.34 (1H), 7.68 (1H), 8.20 (2H), 8.75 (1H), 11.02 (1H).

Step 2: Preparation of 2-[1-[2-ethylsulfonyl-4-(trifluoromethyl)phenyl]pyrazol-4-yl]-4-(trifluoromethyl)pyridine (compound P1.10)

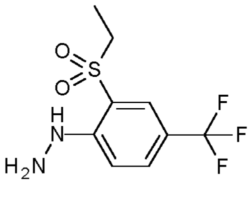


(P1.10)

In a microwave vial, 1-bromo-2-ethylsulfonyl-4-(trifluoromethyl)benzene (185 mg, 0.583 mmol) and 2-(1H-pyrazol-4-yl)-4-(trifluoromethyl)pyridine (149 mg, 0.700 mmol) were dissolved in dry N,N-dimethylformamide (2 ml) and potassium carbonate (242 mg, 1.750 mmol) was added. The vial was closed and the mixture was heated in the microwave at 160°C for 1 h. The reaction mixture was partitioned between EtOAc and brine/water (1/1). After washing and separation, the organic layer was washed twice with brine, dried over sodium sulfate and concentrated. The crude product was purified over silica by flash column chromatography (5 to 75% gradient of EtOAc in heptane). The fractions containing product were combined and partly concentrated leaving a suspension in heptane. The heptane was removed by pipetting and the residual heptane removed *in vacuo*. The product was recrystallized from acetonitrile to afford the title compound P1.10 (122 mg) as a solid, mp 176.5-177.5°C. LCMS (method 2): 450 $(M+H)^+$, retention time 3.92 min. ^{1}H-NMR ($CDCl_3$, ppm) 1.29 (3H), 3.40 (2H), 7.39 (1H), 7.72 (2H), 8.05 (1H), 8.32 (1H), 8.45 (1H), 8.50 (1H), 8.78 (1H).

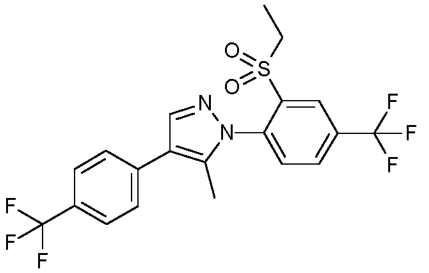
EXAMPLE P7: Preparation of 1-[2-ethylsulfonyl-4-(trifluoromethyl)phenyl]-5-methyl-4-[4-(trifluoromethyl)phenyl]pyrazole (compound P1.15)

Step 1: Preparation of [2-ethylsulfonyl-4-(trifluoromethyl)phenyl]hydrazine



In a microwave vial, 1-bromo-2-ethylsulfonyl-4-(trifluoromethyl)benzene (317 mg, 1.0 mmol) and hydrazine monohydrate (516 mg, 10.30 mmol, 0.50 ml) were dissolved in 1,4-dioxane (3 ml). The vial was closed and the mixture was heated in the microwave at 120°C for 1 h. The reaction mixture was concentrated and the residue was partitioned between CH_2Cl_2 and water. After washing and separation, the water layer was extracted with CH_2Cl_2 once more. The combined organic layers were dried over sodium sulfate and concentrated. The crude product was purified over silica by flash column chromatography (0 to 2.5% gradient of MeOH in CH_2Cl_2) to afford the title compound (243 mg) as a solid. LCMS (method 1): 269 $(M+H)^+$, retention time 2.14 min. ^1H-NMR ($CDCl_3$, ppm) 1.28 (3H), 3.15 (2H), 3.68 (2H), 7.61 (1H), 7.71 (2H), 7.94 (1H).

Step 2: Preparation of 1-[2-ethylsulfonyl-4-(trifluoromethyl)phenyl]-5-methyl-4-[4-(trifluoromethyl) phenyl]pyrazole (compound P1.15)

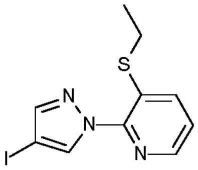


(P1.15)

In a microwave vial, [2-ethylsulfonyl-4-(trifluoromethyl)phenyl]hydrazine (201 mg, 0.75 mmol) and 4-(dimethylamino)-3-[4-(trifluoromethyl)phenyl]but-3-en-2-one (prepared in analogy to EXAMPLE P1, step 2) (212 mg, 0.825 mmol) were dissolved in ethanol (2.5 ml) and acetic acid (0.5 ml). The vial was closed and the mixture was heated in the microwave at 140°C for 1 h. The reaction mixture was concentrated and the residue was partitioned between EtOAc and sat. $NaHCO_3$ (aq). After washing and separation, the organic layer was washed with brine, dried over sodium sulfate and concentrated. The crude product was purified over silica by flash column chromatography (0 to 40% gradient of EtOAc in heptane) to afford the title compound P1.15 (171 mg) as a solid, mp 182-183°C. LCMS (method 2): 463 $(M+H)^+$, retention time 4.19 min. ^1H-NMR ($CDCl_3$, ppm) 1.28 (3H), 2.30 (3H), 3.40 (2H), 7.56-7.62 (3H), 7.69 (2H), 7.86 (1H), 8.07 (1H), 8.50 (1H).

EXAMPLE P8: Preparation of 3-ethylsulfanyl-2-[4-[6-(trifluoromethyl)-3-pyridyl]pyrazol-1-yl]pyridine (compound P1.19)

Step 1: Preparation of 3-ethylsulfanyl-2-(4-iodopyrazol-1-yl)pyridine (compound P3.5)

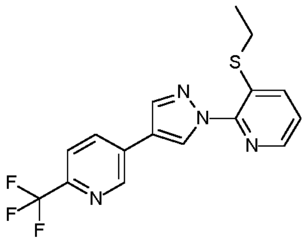


(P3.5)

To a solution of 3-ethylsulfanyl-2-fluoro-pyridine (1.2 g, 7.3 mmol) and 4-iodo-1H-pyrazole (1.5 g, 7.7 mmol) in N,N-dimethylformamide (10 ml) was added potassium carbonate (1.2 g, 8.5 mmol) and the mixture was flushed with argon for 10 minutes. The resulting suspension was heated in the microwave at

130°C for 50 minutes. After cooling, the reaction mixture was quenched with water and extracted with ethyl acetate (3x). The combined organic layers were washed with water and brine, dried over sodium sulfate, filtered and concentrated *in vacuo*. The residue was purified over silica by flash column chromatography (cyclohexane/ethyl acetate 3:1) to afford 3-ethylsulfanyl-2-(4-iodopyrazol-1-yl)pyridine (compound P3.5) as an gum (1.44 g). LCMS (method 4): 332 $(M+H)^+$, retention time 1.02 min. ^{1}H-NMR ($CDCl_3$, ppm) 1.34 (3H), 2.92 (2H), 7.25 (1H), 7.74 (1H), 7.78 (1H), 8.23 (1H), 8.32 (1H).

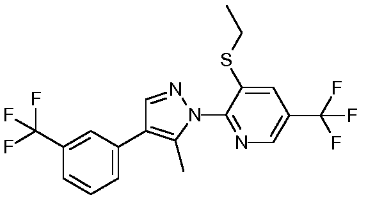
Step 2: Preparation of 3-ethylsulfanyl-2-[4-[6-(trifluoromethyl)-3-pyridyl]pyrazol-1-yl]pyridine (compound P1.19)

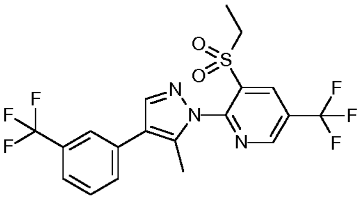
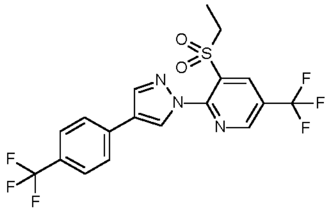
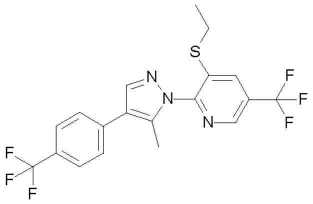
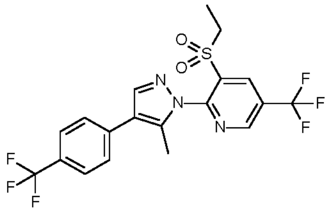
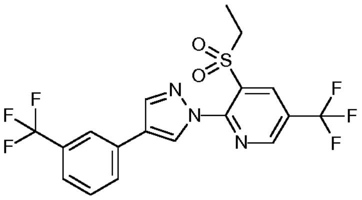
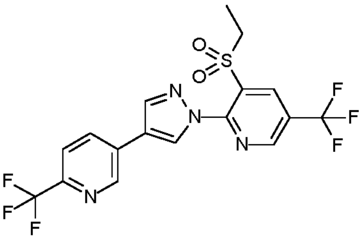


(P1.19)

Obtained from 3-ethylsulfanyl-2-(4-iodopyrazol-1-yl)pyridine (400 mg, 1.208 mmol), [6-(trifluoromethyl)-3-pyridyl]boronic acid (345.9 mg, 1.812 mmol), aqueous 2M sodium carbonate (1.81 ml, 3.62 mmol) and bis(triphenylphosphine) palladium(II)dichloride (8.5 mg, 0.012 mmol) in dimethoxyethane/water (2 ml) under argon according to procedure Example P4. The mixture was heated in the microwave at 110°C for 30 minutes. The crude product obtained after extractive workup was purified over silica by flash column chromatography (cyclohexane/ethyl acetate 4:1) to afford 3-ethylsulfanyl-2-[4-[6-(trifluoromethyl)-3-pyridyl]pyrazol-1-yl]pyridine (compound P1.19) as a solid (184 mg), mp 121-123°C. LCMS (method 4): 351 (M+H)+, retention time: 1.04 min. ^{1}H-NMR ($CDCl_3$, ppm) 1.37 (3H), 2.96 (2H), 7.30 (1H), 7.71 (1H), 7.78 (1H), 8.02 (1H), 8.14 (1H), 8.28 (1H), 8.66 (1H), 8.96 (1H).

Table P1: Examples of compounds of formula (I)

Compound No.	Structures	Melting Point	MS/NMR
P1.1		-	LCMS (method 2): 432 $(M+H)^+$ R_t = 4.35 min

Compound No.	Structures	Melting Point	MS/NMR
P1.2		144-145°C	LCMS (method 2): 464 $(M+H)^+$ R_t = 4.16 min
P1.3		172.5-173.5°C	LCMS (method 2): 450 $(M+H)^+$ R_t = 4.13 min
P1.4		113-114°C	LCMS (method 2): 432 $(M+H)^+$ R_t = 4.34 min
P1.5		152-154°C	LCMS (method 2): 464 $(M+H)^+$ R_t = 4.17 min
P1.6		150-152°C	LCMS (method 2): 450 $(M+H)^+$ R_t = 4.14 min
P1.7		226-228°C	LCMS (method 2): 451 $(M+H)^+$ R_t = 3.91 min

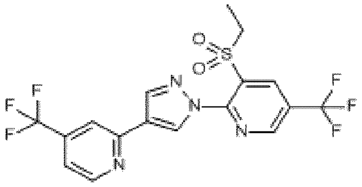
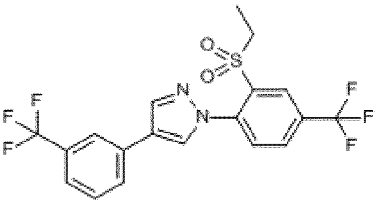
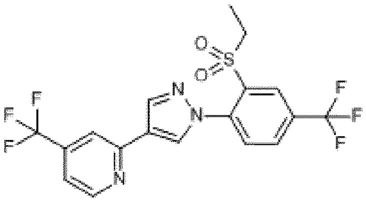
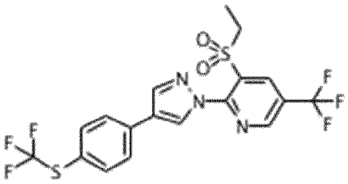
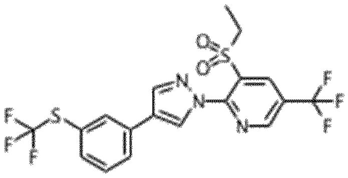
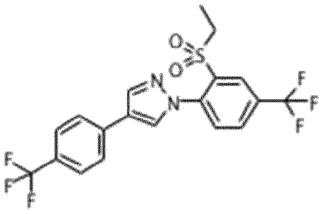
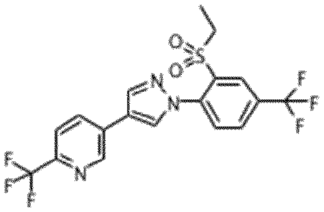
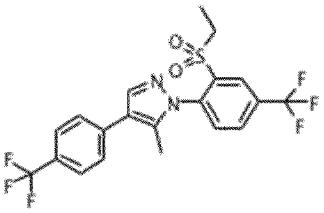
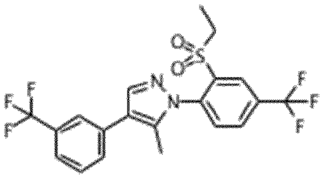
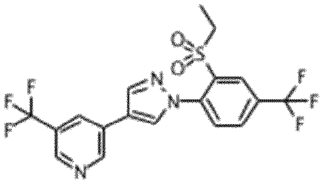
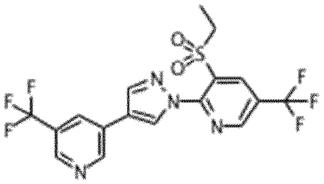
Compound No.	Structures	Melting Point	MS/NMR
P1.8		153-154°C	LCMS (method 2): 451 $(M+H)^+$ R_t = 3.97 min
P1.9		145-146°C	LCMS (method 2): 449 $(M+H)^+$ R_t = 4.14 min
P1.10		176.5-177.5°C	LCMS (method 2): 450 $(M+H)^+$ R_t = 3.92 min

Table P1 (continued): Examples of compounds of formula (I)

Compound No.	Structures	LCMS			Mp (°C)
		R_t (min)	$[M+H]^+$ (measured)	Method	
P1.11		4.35	482	2	181 - 182
P1.12		4.34	482	2	120 - 121

Compound No.	Structures	LCMS			Mp (°C)
		R_t (min)	$[M+H]^+$ (measured)	Method	
P1.13		4.14	449	2	156 - 157
P1.14		3.91	450	2	148 - 149
P1.15		4.19	463	2	182 - 183
P1.16		4.19	463	2	111 - 112
P1.17		3.86	450	2	155 - 156
P1.18		3.83	451	2	149 - 150

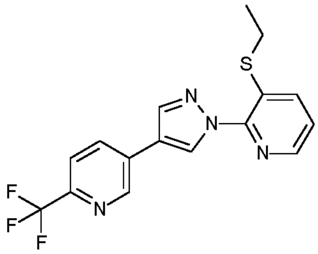
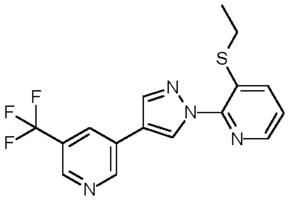
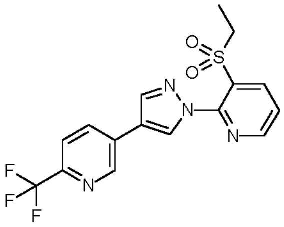
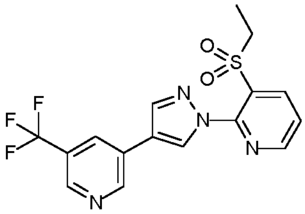
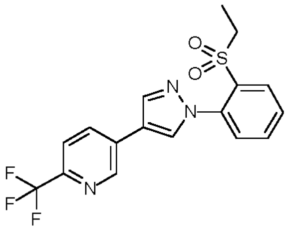
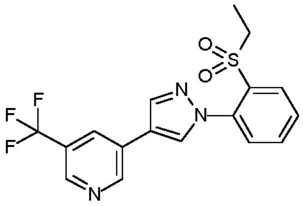
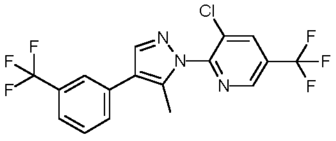
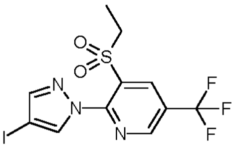
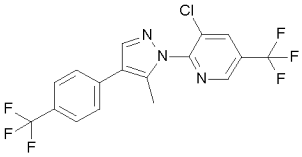
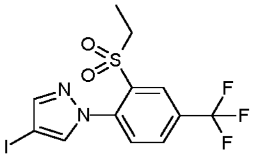
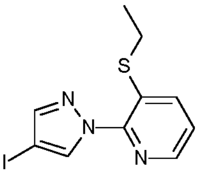
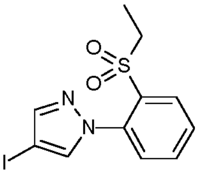
Compound No.	Structures	LCMS			Mp (°C)
		R_t (min)	$[M+H]^+$ (measured)	Method	
P1.19		1.04	351	4	121 - 123
P1.20		1.02	351	4	
P1.21		0.94	383	4	
P1.22		0.93	383	4	
P1.23		0.97	382	4	
P1.24		0.95	382	4	

Table P3: Examples of intermediates of formula (II) and (X)

Compound No.	Structures	Melting Point	MS/NMR
P3.1		129-130°C	LCMS (method 2): 406/408 $(M+H)^+$ R_t = 4.21 min
P3.2		149-151°C	LCMS (method 2): 432 $(M+H)^+$ R_t = 3.92 min
P3.3		127-128°C	LCMS (method 2): 406 $(M+H)^+$ R_t = 3.21 min
P3.4		126-127°C	LCMS (method 1): 431 $(M+H)^+$ R_t = 2.31 min
P3.5		gum	LCMS (method 4): 332 $(M+H)^+$ R_t = 1.02 min
P3.6		110-111°C	LCMS (method 4): 363 $(M+H)^+$ R_t = 0.91 min

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 to 12 and P1 of the present invention”):

an adjuvant selected from the group of substances consisting of petroleum oils (628) + TX,
an acaricide selected from the group of substances consisting of 1,1-bis(4-chlorophenyl)-2-ethoxyethanol (IUPAC name) (910) + TX, 2,4-dichlorophenyl benzenesulfonate (IUPAC/Chemical Abstracts name) (1059) + TX, 2-fluoro-*N*-methyl-*N*-1-naphthylacetamide (IUPAC name) (1295) + TX, 4-chlorophenyl phenyl sulfone (IUPAC name) (981) + TX, abamectin (1) + TX, acequinocyl (3) + TX, acetoprole [CCN] + TX, acrinathrin (9) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, alpha-cypermethrin (202) + TX, amidithion (870) + TX, 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*-(methoxy-aminothiophosphoryl)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, polychloroterpenes (traditional name) (1347) + TX, potassium arsenite [CCN] + TX, potassium thiocyanate [CCN] + TX, prallethrin (655) + TX, precocene I [CCN] + TX, precocene II [CCN] + TX, precocene III [CCN] + TX, primidophos (1349) + TX, profenofos (662) + TX, profluthrin [CCN] + TX, promacyl (1354) + TX, promecarb (1355) + TX, propaphos (1356) + TX, propetamphos (673) + TX, propoxur (678) + TX, prothidathion (1360) + TX, prothiofos (686) + TX, prothoate (1362) + TX, protrifenbute [CCN] + TX, pymetrozine (688) + TX, pyraclofos (689) + TX, pyrazophos (693) + TX, pyresmethrin (1367) + TX, pyrethrin I (696) + TX, pyrethrin II (696) + TX, pyrethrins (696) + TX, pyridaben (699) + TX, pyridalyl (700) + TX, pyridaphenthion (701) + TX, pyrimidifen (706) + TX, pyrimitate (1370) + TX, pyriproxyfen (708) + TX, quassia [CCN] + TX, quinalphos (711) + TX, quinalphos-methyl (1376) + TX, quinothion (1380) + TX, quintiofos (1381) +

TX, R-1492 (development code) (1382) + TX, rafoxanide [CCN] + TX, resmethrin (719) + TX, rotenone (722) + TX, RU 15525 (development code) (723) + TX, RU 25475 (development code) (1386) + TX, ryania (1387) + TX, ryanodine (traditional name) (1387) + TX, sabadilla (725) + TX, schradan (1389) + TX, sebufos + TX, selamectin [CCN] + TX, SI-0009 (compound code) + TX, SI-0205 (compound code) + TX, SI-0404 (compound code) + TX, SI-0405 (compound code) + TX, silafluofen (728) + TX, SN 72129 (development code) (1397) + TX, sodium arsenite [CCN] + TX, sodium cyanide (444) + TX, 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, 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, fluxametamide (WO 2007/026965) + TX, epsilon-metofluthrin [240494-71-7] + TX, epsilon-momfluorothrin [1065124-65-3] + TX, fluazaindolizine [1254304-22-7] + TX, chloroprallethrin [399572-87-3] + TX, fluxametamide [928783-29-3] + TX, cyhalodiamide [1262605-53-7] + TX, tioxazafen [330459-31-9] + TX, broflanilide [1207727-04-5] + TX, flufiprole [704886-18-0] + TX, cyclaniliprole [1031756-98-5] + TX, tetraniliprole [1229654-66-3] + TX, guadipyr (described in WO2010/060231) + TX, cycloxaprid (described in WO2005/077934) + TX,

a molluscicide selected from the group of substances consisting of bis(tributyltin) oxide (IUPAC name) (913) + TX, bromoacetamide [CCN] + TX, calcium arsenate [CCN] + TX, cloethocarb (999) + TX, copper acetoarsenite [CCN] + TX, copper sulfate (172) + TX, fentin (347) + TX, ferric phosphate (IUPAC name) (352) + TX, metaldehyde (518) + TX, methiocarb (530) + TX, niclosamide (576) + TX, niclosamide-olamine (576) + TX, pentachlorophenol (623) + TX, sodium pentachlorophenoxide (623) + TX, tazimcarb (1412) + TX, thiodicarb (799) + TX, tributyltin oxide (913) + TX, trifenmorph (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; 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 chroocuccum* (Azotomeal®) + TX, *Azotobacter* cysts (Bionatural Blooming Blossoms®) + TX, *Bacillus amyloliquefaciens* + TX, *Bacillus cereus* + TX, *Bacillus chitinosporus* strain CM-1 + TX, *Bacillus chitinosporus* strain AQ746 + TX, *Bacillus licheniformis* strain HB-2 (Biostart™ Rhizoboost®) + TX, *Bacillus licheniformis* strain 3086 (EcoGuard® + TX, Green Releaf®) + TX, *Bacillus circulans* + TX, *Bacillus firmus* (BioSafe® + TX, BioNem-WP® + TX, VOTiVO®) + TX, *Bacillus firmus* strain I-1582 + TX, *Bacillus macerans* + TX, *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® + TX, Neemix®) + TX, canola oil (Lilly Miller Vegol®) + TX, *Chenopodium ambrosioides near ambrosioides* (Requiem®) + TX, *Chrysanthemum* extract (Crisant®) + TX, extract of neem oil (Trilogy®) + TX, essentials oils of *Labiatae* (Botania®) + TX, extracts of clove rosemary peppermint and thyme oil (Garden insect killer®) + TX, Glycinebetaine (Greenstim®) + TX, garlic + TX, lemongrass oil (GreenMatch®) + TX, neem oil + TX, *Nepeta cataria* (Catnip oil) + TX, *Nepeta catarina* + TX, nicotine + TX, oregano oil (MossBuster®) + TX, *Pedaliaceae* oil (Nematon®) + TX, pyrethrum + TX, *Quillaja saponaria* (NemaQ®) + TX, *Reynoutria sachalinensis* (Regalia® + TX, Sakalia®) + TX, rotenone (Eco Roten®) + TX, *Rutaceae* plant extract (Soleo®) + TX, soybean oil (Ortho ecosense®) + TX, tea tree oil (Timorex Gold®) + TX, thymus oil + TX, AGNIQUE® MMF + TX, BugOil® + TX, mixture of rosemary sesame 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®); and

pheromones including: blackheaded fireworm pheromone (3M Sprayable Blackheaded Fireworm Pheromone®) + TX, Codling Moth Pheromone (Paramount dispenser-(CM)/ Isomate C-Plus®) + TX, Grape Berry Moth Pheromone (3M MEC-GBM Sprayable Pheromone®) + TX, Leafroller pheromone (3M MEC – LR Sprayable Pheromone®) + TX, Muscamone (Snip7 Fly Bait® + TX, Starbar Premium Fly Bait®) + TX, Oriental Fruit Moth Pheromone (3M oriental fruit moth sprayable pheromone®) + TX, Peachtree Borer Pheromone (Isomate-P®) + TX, Tomato Pinworm Pheromone (3M Sprayable pheromone®) + TX, Entostat powder (extract from palm tree) (Exosex CM®) + TX, (E + TX,Z + TX,Z)-3 + TX,8 + TX,11 Tetradecatrienyl acetate + TX, (Z + TX,Z + TX,E)-7 + TX,11 + TX,13-Hexadecatrienal + TX, (E + TX,Z)-7 + TX,9-Dodecadien-1-yl acetate + TX, 2-Methyl-1-butanol + TX, Calcium acetate + TX, Scenturion® + TX, Biolure® + TX, Check-Mate® + TX, Lavandulyl senecioate; and

Macrobials including: *Aphelinus abdominalis* + TX, *Aphidius ervi* (Aphelinus-System®) + TX, *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 "develoment code" is used or, if neither one of those designations nor a "common name" is used, an "alternative name" is employed. “CAS Reg. No” means the Chemical Abstracts Registry Number.

The active ingredient mixture of the compounds of formula I selected from Tables 1 to 12 and P1 with active ingredients described above comprises a compound selected from Tables 1 to 12 and P1 and an active ingredient as described above preferably in a mixing ratio of from 100:1 to 1:6000, especially from 50:1 to 1:50, more especially in a ratio of from 20:1 to 1:20, even more especially from 10:1 to 1:10, very especially from 5:1 and 1:5, special preference being given to a ratio of from 2:1 to 1:2, and a ratio of from 4:1 to 2:1 being likewise preferred, above all in a ratio of 1:1, or 5:1, or 5:2, or 5:3, or 5:4, or 4:1, or 4:2, or 4:3, or 3:1, or 3:2, or 2:1, or 1:5, or 2:5, or 3:5, or 4:5, or 1:4, or 2:4, or 3:4, or 1:3, or 2:3, or 1:2, or 1:600, or 1:300, or 1:150, or 1:35, or 2:35, or 4:35, or 1:75, or 2:75, or 4:75, or 1:6000, or 1:3000, or 1:1500, or 1:350, or 2:350, or 4:350, or 1:750, or 2:750, or 4:750. Those mixing ratios are by weight.

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

The mixtures comprising a compound of formula I selected from Tables 1 to 12 and P1 and one or more active ingredients as described above can be applied, for example, in a single “ready-mix” form, in a combined spray mixture composed from separate formulations of the single active ingredient components, such as a “tank-mix”, and in a combined use of the single active ingredients when applied in a sequential manner, i.e. one after the other with a reasonably short period, such as a few hours or days. The order of applying the compounds of formula I selected from Tables 1 to 12 and P1 and the active ingredients as described above is not essential for working the present invention.

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

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

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

Biological Examples:

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

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

The following compounds gave an effect of at least 80% control in at least one of the three categories (mortality, anti-feedancy or growth inhibition) at an application rate of 200 ppm: P1.2, P1.3, P1.6, P1.7, P1.8, P1.9, P1.10, P1.12, P1.13, P1.14, P1.15, P1.16, P1.17 and P1.18.

Example B2: Activity against *Plutella xylostella* (Diamond back moth)

24-well microtiter plates with artificial diet were treated with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions by pipetting. After drying, the plates were infested with L2 larvae (10 to 15 per well). The samples were assessed for mortality and growth inhibition in comparison to untreated samples 5 days after infestation. The following compounds gave an effect of at least 80% in at least one of the two categories (mortality or growth inhibition) at an application rate of 200 ppm: P1.3, P1.6, P1.7, P1.8, P1.9, P1.13, P1.14, P1.15, P1.16, P1.17 and P1.18.

Example B3: Activity against *Diabrotica balteata* (Corn root worm)

Maize sprouts, placed on an agar layer in 24-well microtiter plates were treated with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions by spraying. After drying, the plates were infested with L2 larvae (6 to 10 per well). The samples were assessed for mortality and growth inhibition in comparison to untreated samples 4 days after infestation. The following compounds gave an effect of at least 80% in at least one of the two categories (mortality or growth inhibition) at an application rate of 200 ppm: P1.1, P1.2, P1.6, P1.7, P1.8, P1.9, P1.10, P1.13, P1.14, P1.15, P1.16, P1.17 and P1.18.

Example B4: Activity against *Spodoptera littoralis* (Egyptian cotton leaf worm)

Test compounds were applied by pipette from 10'000 ppm DMSO stock solutions into 24-well plates and mixed with agar. Lettuce seeds were placed on the agar and the multi well plate was closed by another plate which contains also agar. After 7 days the roots have absorbed the compound and the lettuce has grown into the lid plate. The lettuce leafs were now cut off into the lid plate. Spodoptera eggs were pipetted through a plastic stencil on a humid gel blotting paper and the plate closed with it. The samples were assessed for mortality, anti-feedant effect and growth inhibition in comparison to untreated samples 6 days after infestation. The following compound gave an effect of at least 80% control in at least one of the three categories (mortality, anti-feedancy or growth inhibition) at an application rate of 12.5 ppm: P1.17 and P1.18.

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

Sunflower leaf discs were placed on agar in a 24-well microtiter plate and sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying, the leaf discs were infested with an aphid population of mixed ages. The samples were assessed for mortality 6 days after infestation. The following compound resulted in at least 80% mortality at an application rate of 200 ppm: P1.10, P1.14, P1.15, P1.16, P1.17 and P1.18.

Example B6: Activity against *Bemisia tabaci* (Cotton white fly)

Cotton leaf discs were placed on agar in 24-well microtiter plates and sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying the leaf discs were infested with adult white flies. The samples were checked for mortality 6 days after incubation. The following compound resulted in at least 80% mortality at an application rate of 200 ppm: P1.15, P1.16 and P1.17.

Example B7: Activity against *Euschistus heros* (Neotropical Brown Stink Bug)

Soybean leaf on agar in 24-well microtiter plates were sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying the leaf were infested with N-2 nymphs. The samples were assessed for mortality 5 days after infestation. The following compound resulted in at least 80% mortality at an application rate of 200 ppm: P1.13, P1.14, P1.16 and P1.17.

Example B8: Activity against *Tetranychus urticae* (Two-spotted spider mite)

Bean leaf discs on agar in 24-well microtiter plates were sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying the leaf discs were infested with a mite population of mixed ages. The samples were assessed for mortality on mixed population (mobile stages) 8 days after infestation.The following compound resulted in at least 80% mortality at an application rate of 200 ppm: P1.1.

Example B9: Activity against *Thrips tabaci* (Onion thrips)

Sunflower leaf discs were placed on agar in 24-well microtiter plates and sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying the leaf discs were infested with a thrips 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: P1.15.

Example B10: Activity against *Aedes aegypti* (Yellow fever mosquito)

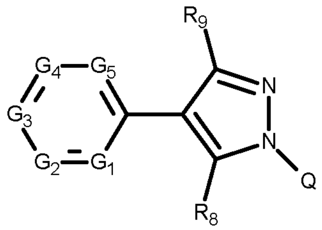
Test solutions, at an application rate of 200ppm in ethanol, were applied to 12 well tissue culture plates. Once the deposits were dry, five, two to five day old adult female Aedes aegypti were added to each well, and sustained with a 10% sucrose solution in a cotton wool plug. Assessment of knockdown was made one hour after introduction, and mortality was assessed at 24 and 48 hours after introduction. The following compounds gave at least 80% control of Aedes aegypti after 48h and/or 24h: P1.9, P1.14, P1.15 and P1.16.

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

Test solutions, at an application rate of 200 ppm in ethanol, were applied to 12 well tissue culture plates. Once the deposits were dry, five, two to five day old adult female Anopheles stephensi were added to each well, and sustained with a 10% sucrose solution in a cotton wool plug. Assessment of knockdown was made one hour after introduction, and mortality was assessed at 24 and 48 hours after introduction. The following compounds gave at least 80% control of Anopheles stephensi after 48h and/or 24h: P1.14.

Claims:

1. A compound of formula I,



(I),

wherein

R_8 is hydrogen, C_1-C_4alkyl, C_1-C_4haloalkyl, halogen or cyano;

G_1 is nitrogen or CR_2;

G_2 is nitrogen or CR_3;

G_3 is nitrogen or CR_4;

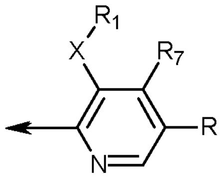
G_4 is nitrogen or CR_5;

G_5 is nitrogen or CR_6, with the proviso that not more than 2 nitrogens as G may follow consecutively;

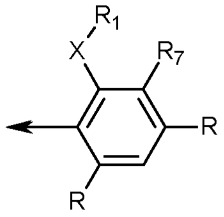
R_2, R_3, R_4, R_5 or R_6 are, independently from each other, hydrogen, halogen, cyano, C_1-C_6haloalkyl, or are C_1-C_6haloalkyl substituted by one or two substituents selected from the group consisting of hydroxyl, methoxy and cyano; or

R_2, R_3, R_4, R_5 or R_6 are, independently from each other, C_1-C_4haloalkylsulfanyl, C_1-C_4haloalkylsulfinyl, C_1-C_4haloalkylsulfonyl, $O(C_1$-C_4haloalkyl), SF_5, phenylcarbonylthio, mercapto, C_1-C_4alkoxycarbonyl, or $–C(O)C_1$-C_4haloalkyl;

Q is a radical selected from the group consisting of formula Q_1 and Q_2,



Q1



Q2 ,

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

and wherein X is S, SO or SO_2;

each R is, independently from each other, hydrogen, halogen or C_1-C_4haloalkyl;

each R_1 is, independently from each other, C_1-C_4alkyl, C_1-C_4haloalkyl, C_3-C_6cycloalkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl; or

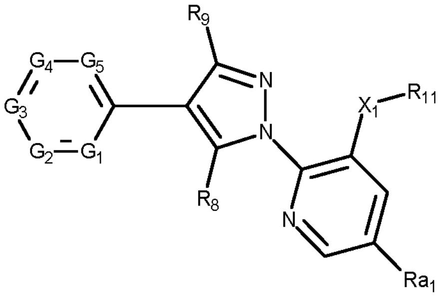
each R_1 is, independently from each other, C_3-C_6cycloalkyl mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano and C_1-C_4alkyl; or each R_1 is, independently from each other, C_3-C_6cycloalkyl-C_1-C_4alkyl mono- or polysubstituted by substituents selected from the group consisting of halogen, cyano and C_1-C_4alkyl; or

each R_1 is, independently from each other, C_2-C_6alkenyl, C_2-C_6haloalkenyl or C_2-C_6alkynyl;

each R_7 is, independently from each other, hydrogen or halogen; and

R_9 is hydrogen, C_1-C_4alkyl, C_1-C_4haloalkyl or halogen; with the exception of the compound 4-(4-fluorophenyl)-1-(2-methylsulfonylphenyl)pyrazole; and agrochemically acceptable salts, stereoisomers, enantiomers, tautomers and N-oxides of the compounds of formula I.

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



(I-1),

wherein

G_1, G_2, G_3, G_4, and G_5 are as defined under formula I in claim 1;

X_1 is S, SO or SO_2;

Ra_1 is hydrogen, halogen or C_1-C_4haloalkyl;

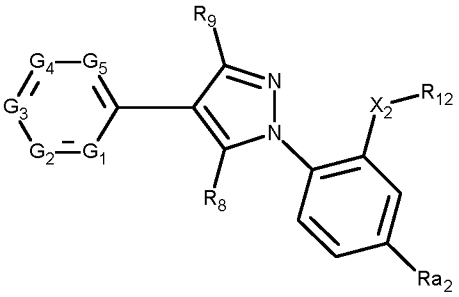
R_{11} is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl;

R_8 is as defined under formula I in claim 1;

R_9 is as defined under formula I in claim 1.

3. A compound of formula I-1 according to claim 2, wherein one of the substituents selected from G_1, G_2, G_3, G_4, and G_5 is $C(CF_3)$, one of the remaining substituents selected from G_1, G_2, G_3, G_4, and G_5 is N or CH, and the remaining substituents G are CH.

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



(I-2),

wherein

G_1, G_2, G_3, G_4, and G_5 are as defined under formula I in claim 1;

X_2 is S, SO or SO_2;

Ra_2 is hydrogen, halogen or C_1-C_4haloalkyl;

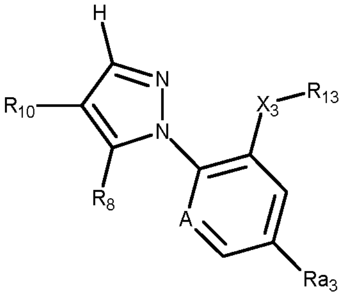
R_{12} is methyl, ethyl, n-propyl, i-propyl or cyclopropylmethyl;

R_8 is as defined under formula I in claim 1; and

R_9 is as defined under formula I in claim 1.

5. A compound of formula I-2 according to claim 4, wherein one of the substituents selected from G_1, G_2, G_3, G_4, and G_5 is $C(CF_3)$, one of the remaining substituents selected from G_1, G_2, G_3, G_4, and G_5 is N or CH, and the remaining substituents G are CH.

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



(I-3),

wherein

A is N or CH;

R_{10} is phenyl substituted by C_1-C_4haloalkyl or is pyridyl substituted by C_1-C_4haloalkyl; or

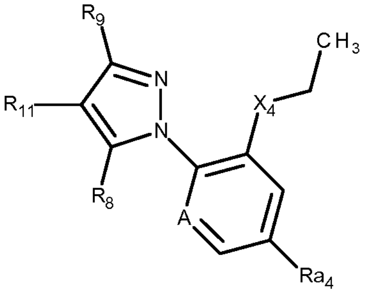
R_{10} is phenyl substituted by C_1-C_4haloalkylsulfanyl;

X_3 is S, SO or SO_2;

Ra_3 is hydrogen, halogen or C_1-C_4haloalkyl; and

R_{13} is C_1-C_4alkyl; R_8 is hydrogen or C_1-C_4alkyl.

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



(I-4),

wherein

A is N or CH;

X_4 is S or SO_2;

Ra_4 is hydrogen or C_1-C_4haloalkyl;

R_8 is hydrogen or C_1-C_4alkyl;

R_9 is hydrogen; and

R_{11} is phenyl monosubstituted by C_1-C_4haloalkyl or C_1-C_4haloalkylsulfanyl; or

R_{11} is pyridyl monosubstituted by C_1-C_4haloalkyl.

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

G_1 is nitrogen or CR_2; R_2 is hydrogen;

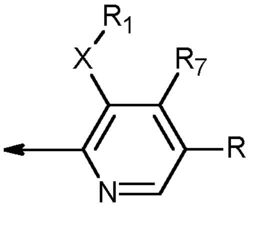
G_2 is nitrogen or CR_3; R_3 is hydrogen;

G_3 is CR_4; R_4 is hydrogen, C_1-C_4haloalkyl or C_{1}-$_4$haloalkylsulfanyl;

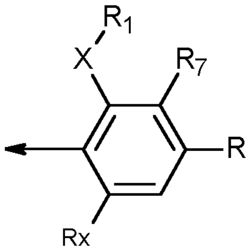
G_4 is CR_5; R_5 is hydrogen, C_1-C_4haloalkyl or C_{1}-$_4$haloalkylsulfanyl;

G_5 is CR_6; R_6 is hydrogen;

Q is a radical selected from the group consisting of formula Q_1 and Q_{2x},



Q_1



Q_{2x}

,

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

X is S or SO_2;

R_1 is C_1-C_4alkyl, preferably ethyl;

R_7 is hydrogen;

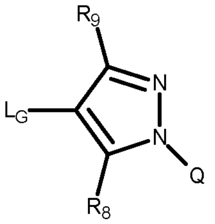
R_8 is hydrogen or C_1-C_4alkyl;
R_9 is hydrogen;
Rx is hydrogen; and
R is hydrogen or C_1-C_4haloalkyl.

9. A pesticidal composition, which comprises at least one compound of formula I according to claim 1 or, where appropriate, a tautomer thereof, in each case in free form or in agrochemically utilizable salt form, as active ingredient and at least one auxiliary.

10. A method for controlling pests, which comprises applying a composition according to claim 9 to the pests or their environment with the exception of a method for treatment of the human or animal body by surgery or therapy and diagnostic methods practised on the human or animal body.

11. A method for the protection of plant propagation material from the attack by pests, which comprises treating the propagation material or the site, where the propagation material is planted, with a composition according to claim 9.

12. A compound of formula (X)



(X),

wherein
Q, R_8 and R_9 are as defined under formula I in claim 1; and
L_G is iodine or bromine.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/050105

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D231/12 C07D401/04 A01N43/58
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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 846 686 A1 (PFIZER LTD [GB]; PFIZER [US]) 10 June 1998 (1998-06-10) "Acarina"; page 10, line 19 claims 1, 18-23 -----	1-12
X	WO 2010/017902 A1 (BAYER CROPSCIENCE AG [DE]; WERNER STEFAN [DE]; MUELLER KLAUS-HELMUT [D) 18 February 2010 (2010-02-18) "Acarina"; page 90, line 27 "Acarina"; page 92, line 28 claims 1, 5-10 ----- -/--	1-12

☒ 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 8 February 2016	Date of mailing of the international search report 17/02/2016
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Sarakinos, Georgios

1

International application No
PCT/EP2016/050105

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE PUBCHEM [Online] NIH; 30 November 2012 (2012-11-30), XP002737532,accession no. AGN-PC-0HK848 Database accession no. CID 67683727 4-(4-FLUOROPHENYL)-1-(2-METHYLSULFONYLPHENYL)PYRAZOLE -----	1-12
A	WO 01/07413 A1 (DIMENSIONAL PHARM INC [US]; HESKA CORP [US]) 1 February 2001 (2001-02-01) the whole document -----	1-12
A	EP 2 174 547 A1 (KUMIAI CHEMICAL INDUSTRY CO [JP]; IHARA CHEMICAL IND CO [JP]) 14 April 2010 (2010-04-14) the whole document -----	1-12

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/050105

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0846686 A1	10-06-1998	AT 211735 T	15-01-2002
		CA 2223237 A1	30-05-1998
		DE 69709532 D1	14-02-2002
		DE 69709532 T2	31-10-2002
		DK 0846686 T3	25-03-2002
		EP 0846686 A1	10-06-1998
		ES 2166954 T3	01-05-2002
		JP 3083278 B2	04-09-2000
		JP H10182614 A	07-07-1998
		PT 846686 E	31-05-2002
WO 2010017902 A1	18-02-2010	AU 2009281457 A1	18-02-2010
		BR PI0918430 A2	24-11-2015
		CA 2733958 A1	18-02-2010
		CN 102186809 A	14-09-2011
		CO 6341618 A2	21-11-2011
		CR 20110080 A	27-05-2011
		EC SP11010822 A	31-03-2011
		EP 2321262 A1	18-05-2011
		EP 2374791 A1	12-10-2011
		JP 2011530548 A	22-12-2011
		KR 20110044900 A	02-05-2011
		PE 06722011 A1	25-09-2011
		RU 2011109066 A	20-03-2013
		SV 2011003838 A	20-05-2011
		US 2011190365 A1	04-08-2011
		WO 2010017902 A1	18-02-2010
WO 0107413 A1	01-02-2001	AU 6116800 A	13-02-2001
		US 6518266 B1	11-02-2003
		WO 0107413 A1	01-02-2001
EP 2174547 A1	14-04-2010	EP 2174547 A1	14-04-2010
		JP 5436211 B2	05-03-2014
		US 2011067612 A1	24-03-2011
		WO 2009022548 A1	19-02-2009