

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

(19) World Intellectual Property
Organization
International Bureau



(10) International Publication Number
WO 2019/219689 A1

(43) International Publication Date
21 November 2019 (21.11.2019)

(51) International Patent Classification:

C07D 487/04 (2006.01) A01N 43/90 (2006.01)

(21) International Application Number:

PCT/EP2019/062355

(22) International Filing Date:

14 May 2019 (14.05.2019)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

201811018751 18 May 2018 (18.05.2018) IN
18191700.6 30 August 2018 (30.08.2018) EP

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,

SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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

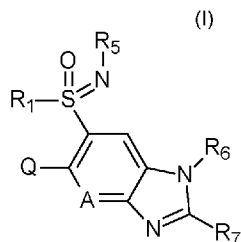
Declarations under Rule 4.17:

- 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 SULFOXIMINE CONTAINING SUBSTITUENTS



(57) Abstract: Compounds of the formula (I) wherein the substituents are as defined in claim 1. Furthermore, the present invention relates to agrochemical compositions which comprise compounds of formula (I), to preparation of these compositions, and to the use of the compounds or compositions in agriculture or horticulture for combating, preventing or controlling animal pests, including arthropods and in particular insects, nematodes, molluscs or representatives of the order *Acarina*.



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PESTICIDALLY ACTIVE HETEROCYCLIC DERIVATIVES WITH SULFOXIMINE CONTAINING
SUBSTITUENTS

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

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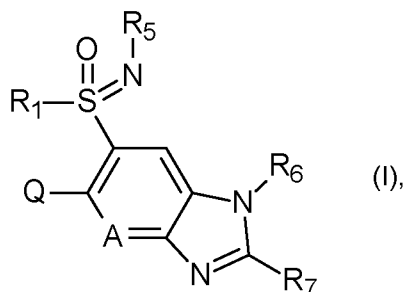
Pesticidally active hetero-bicyclic derivatives with sulfur-containing substituents are known and described in the literature, for example, in WO 2015/071180, WO 2016/091731, WO 2016/107742, WO 2016/142326, WO 2016/142327, WO 2017/001311, WO 2017/133994. Pesticidally active heterocyclic sulfoximine derivatives have previously been described in the literature, for example, in

10

It has now surprisingly been found that certain novel bicyclic sulfoximine-containing azabenzimidazole and, respectively, benzimidazole derivatives have favorable properties as pesticides.

15

The present invention therefore provides compounds of formula I,



A is CH or N;

20

R₁ is C₁-C₄alkyl;

R₅ is hydrogen, formyl, cyano, C₁-C₃alkyl, C₁-C₃alkylcarbonyl, C₁-C₃alkoxycarbonyl, C₁-C₃haloalkylcarbonyl;

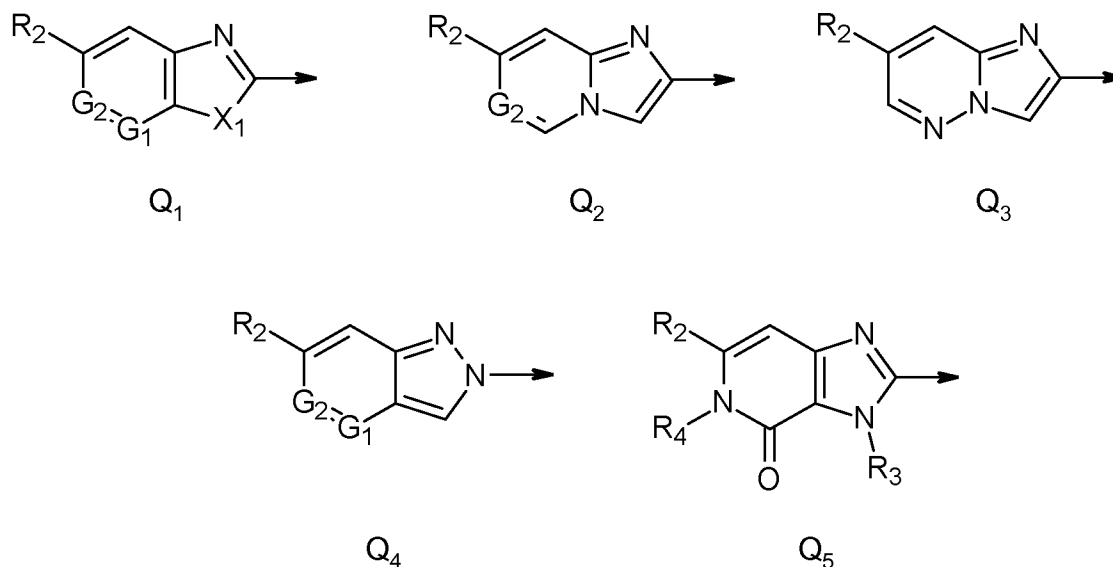
R₆ is hydrogen, C₁-C₄ alkyl, C₁-C₄haloalkyl, C₁-C₂alkoxy-C₁-C₂alkyl;

R₇ is hydrogen, halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄alkylthio, C₁-C₄haloalkoxy, C₁-

25

C₄haloalkylthio;

Q is a radical selected from the group consisting of formulae Q₁, Q₂, Q₃, Q₄ and Q₅



wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A ;

and wherein

- 5 R_2 is C_1 - C_6 haloalkyl, C_1 - C_4 haloalkylsulfanyl, C_1 - C_4 haloalkylsulfinyl, C_1 - C_4 haloalkylsulfonyl or C_1 - C_6 haloalkoxy;
- X_1 is O or NR_3 ;
- R_3 is C_1 - C_4 alkyl;
- R_4 is C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_1 - C_4 alkoxy, or C_3 - C_6 cycloalkyl;
- 10 G_1 and G_2 are, independently from each other, N or CH;
- or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide of a compound of formula I.

- 15 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, nitrous acid, a phosphorus acid or a hydrohalic acid, with strong organic carboxylic acids, such as C_1 - C_4 alkanecarboxylic 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
- 20 hydroxycarboxylic acids, for example ascorbic acid, lactic acid, malic acid, tartaric acid or citric acid, or such as benzoic acid, or with organic sulfonic acids, such as C_1 - C_4 alkane- or arylsulfonic acids which are unsubstituted or substituted, for example by halogen, for example methane- or p-toluenesulfonic acid. Compounds of formula I which have at least one acidic group can form, for example, salts with
- 25 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.

5 In each case, the compounds of formula (I) according to the invention are in free form, in oxidized form as a N-oxide or in salt form, e.g. an agronomically usable salt form.

N-oxides are oxidized forms of tertiary amines or oxidized forms of nitrogen containing heteroaromatic compounds. They are described for instance in the book "Heterocyclic N-oxides" by A. Albini and S. Pietra, CRC Press, Boca Raton 1991.

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

15 Where substituents are indicated as being itself further substituted, this means that they carry one or more identical or different substituents, e.g. one to four substituents. Normally not more than three such optional substituents are present at the same time. Preferably not more than two such substituents are present at the same time (i.e. the group is substituted by one or two of the substituents indicated). Where the additional substituent group is a larger group, such as cycloalkyl or phenyl, it is most preferred that only one such optional substituent is present. Where a group is
20 indicated as being substituted, e.g. alkyl, this includes those groups that are part of other groups, e.g. the alkyl in alkylthio.

The term "C₁-C_nalkyl" as used herein refers to a saturated straight-chain or branched hydrocarbon radical attached via any of the carbon atoms having 1 to n carbon atoms, for example, any one of
25 the radicals methyl, ethyl, n-propyl, isopropyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, neopentyl, n-hexyl, and isohexyl.

The term "C₁-C_nhaloalkyl" as used herein refers to a straight-chain or branched saturated alkyl radical attached via any of the carbon atoms having 1 to n carbon atoms (as mentioned above), where some
30 or all of the hydrogen atoms in these radicals may be replaced by fluorine, chlorine, bromine and/or iodine, i.e., for example, any one of chloromethyl, dichloromethyl, trichloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, chlorofluoromethyl, dichlorofluoromethyl, chlorodifluoromethyl, 2-fluoroethyl, 2-chloroethyl, 2-bromoethyl, 2-iodoethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2-chloro-2-fluoroethyl, 2-chloro-2,2-difluoroethyl, 2,2-dichloro-2-fluoroethyl, 2,2,2-trichloroethyl, pentafluoroethyl,
35 2-fluoropropyl, 3-fluoropropyl, 2,2-difluoropropyl, 2,3-difluoropropyl, 2-chloropropyl, 3-chloropropyl, 2,3-dichloropropyl, 2-bromopropyl, 3-bromopropyl, 3,3,3-trifluoropropyl, 3,3,3-trichloropropyl, 2,2,3,3,3-pentafluoropropyl, heptafluoropropyl, 1-(fluoromethyl)-2-fluoroethyl, 1-(chloromethyl)-2-chloroethyl, 1-(bromomethyl)-2-bromoethyl, 4-fluorobutyl, 4-chlorobutyl, 4-bromobutyl or nonafluorobutyl. According a term "C₁-C₂fluoroalkyl" would refer to a C₁-C₂alkyl radical which carries 1, 2, 3, 4, or 5 fluorine

atoms, for example, any one of difluoromethyl, trifluoromethyl, 1-fluoroethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 1,1,2,2-tetrafluoroethyl or pentafluoroethyl.

5 The term " C_1 - C_n alkoxy" as used herein refers to a straight-chain or branched saturated alkyl radical having 1 to n carbon atoms (as mentioned above) which is attached via an oxygen atom, i.e., for example, any one of methoxy, ethoxy, n-propoxy, 1-methylethoxy, n-butoxy, 1-methylpropoxy, 2-methylpropoxy or 1,1-dimethylethoxy.

10 The term " C_1 - C_n haloalkoxy" as used herein refers to a C_1 - C_n alkoxy radical as mentioned above which is partially or fully substituted by fluorine, chlorine, bromine and/or iodine, i.e., for example, any one of chloromethoxy, dichloromethoxy, trichloromethoxy, fluoromethoxy, difluoromethoxy, trifluoromethoxy, chlorofluoromethoxy, dichlorofluoromethoxy, chlorodifluoromethoxy, 2-fluoroethoxy, 2-chloroethoxy, 2-bromoethoxy, 2-iodoethoxy, 2,2-difluoroethoxy, 2,2,2-trifluoroethoxy, 2-chloro-2-fluoroethoxy, 2-chloro-2,2-difluoroethoxy, 2,2-dichloro-2-fluoroethoxy, 2,2,2-trichloroethoxy, pentafluoroethoxy, 2-
15 fluoropropoxy, 3-fluoropropoxy, 2,2-difluoropropoxy, 2,3-difluoropropoxy, 2-chloropropoxy, 3-chloropropoxy, 2,3-dichloropropoxy, 2-bromopropoxy, 3-bromopropoxy, 3,3,3-trifluoropropoxy, 3,3,3-trichloropropoxy, 2,2,3,3,3-pentafluoropropoxy, heptafluoropropoxy, 1-(fluoromethyl)-2-fluoroethoxy, 1-(chloromethyl)-2-chloroethoxy, 1-(bromomethyl)-2-bromoethoxy, 4-fluorobutoxy, 4-chlorobutoxy, or 4-bromobutoxy.

20 The term " C_1 - C_n alkylthio" as used herein refers to a straight chain or branched saturated alkyl radical having 1 to n carbon atoms (as mentioned above) which is attached via a sulfur atom, i.e., for example, any one of methylthio, ethylthio, n-propylthio, 1-methylethylthio, butylthio, 1-methylpropylthio, 2-methylpropylthio or 1,1-dimethylethylthio.

25 The term " C_1 - C_n haloalkylsulfanyl" as used herein refers to a C_1 - C_n alkylthio radical as mentioned above which is partially or fully substituted by fluorine, chlorine, bromine and/or iodine, i.e., for example, any one of fluoromethylthio, difluoromethylthio, trifluoromethylthio, chlorodifluoromethylthio, bromodifluoromethylthio, 2-fluoroethylthio, 2-chloroethylthio, 2-
30 bromoethylthio, 2-iodoethylthio, 2,2-difluoroethylthio, 2,2,2-trifluoroethylthio, 2,2,2-trichloroethylthio, 2-chloro-2-fluoroethylthio, 2-chloro-2,2-difluoroethylthio, 2,2-dichloro-2-fluoroethylthio, pentafluoroethylthio, 2-fluoropropylthio, 3-fluoropropylthio, 2-chloropropylthio, 3-chloropropylthio, 2-bromopropylthio, 3-bromopropylthio, 2,2-difluoropropylthio, 2,3-difluoropropylthio, 2,3-dichloropropylthio, 3,3,3-trifluoropropylthio, 3,3,3-trichloropropylthio, 2,2,3,3,3-
35 pentafluoropropylthio, heptafluoropropylthio, 1-(fluoromethyl)-2-fluoroethylthio, 1-(chloromethyl)-2-chloroethylthio, 1-(bromomethyl)-2-bromoethylthio, 4-fluorobutylthio, 4-chlorobutylthio, or 4-bromobutylthio.

The term "C₁-C_nhaloalkylsulfinyl" and "C₁-C_nhaloalkylsulfonyl" refers to the groups above but with the sulfur in a different oxidation state: sulfoxide –S(O)C₁-C_nhaloalkyl or sulfone –S(O)₂C₁-C_nhaloalkyl, respectively.

- 5 The term "C₃-C₆cycloalkyl" as used herein refers to 3-6 membered cycloalkyl groups such as cyclopropane, cyclobutane, cyclopropane, cyclopentane and cyclohexane.

- The prefix "-C₁-C_nalkyl" before terms such as "C₁-C_nalkoxy", wherein n is an integer from 1-4, as used herein refers to a straight chain or branched saturated alkyl radicals which is substituted by C₁-C_nalkoxy. Examples of C₁-C_nalkoxy-C₁-C_nalkyl are for example, methoxymethyl, methoxyethyl, and 1-methylmethoxymethyl.
- 10

- The term "C₁-C_nalkylcarbonyl" as used herein refers to a straight chain or branched alkyl radical having 1 to n carbon atoms (as mentioned above) which is attached via the carbon atom of the carbonyl group, i.e., for, any one of acetyl, n-propanoyl, 2-methylpropanoyl, 2,2-dimethylpropanoyl, n-butanoyl, and 3-methylbutanoyl.
- 15

- The term "C₁-C_nhaloalkylcarbonyl" as used herein refers to a straight chain or branched haloalkyl radical having 1 to n carbon atoms (as mentioned above) which is attached via the carbon atom of the carbonyl group.
- 20

- The term "C₁-C_nalkoxycarbonyl" as used herein refers to a straight chain or branched alkoxy radical having 1 to n carbon atoms (as mentioned above) which is attached via the carbon atom of the carbonyl group, i.e., for, any one of methoxycarbonyl, ethoxycarbonyl, n-propoxycarbonyl, 1-methylethoxycarbonyl, n-butoxycarbonyl, 1-methylpropoxycarbonyl, 2-methylpropoxycarbonyl or 1,1-dimethylethoxycarbonyl.
- 25

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

Embodiments according to the invention are provided as set out below.

- Embodiment 1 provides compounds of formula I, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, as defined above.
- 35

Embodiment 2 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiment 1 wherein:

A is CH or N;

R₁ is ethyl, propyl or isopropyl;

R₅ is hydrogen, cyano or C(O)R₂₅ wherein R₂₅ is C₁-C₂haloalkyl;

R₆ is C₁-C₄ alkyl or C₁-C₄haloalkyl; and

R₇ is C₁-C₄ alkyl, C₁-C₄haloalkyl or C₁-C₄alkoxy.

5 Embodiment 3 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiment 1 wherein:

A is CH or N;

R₁ is ethyl;

R₅ is hydrogen;

10 R₆ is methyl, ethyl or C₂haloalkyl; and

R₇ is C₁-C₂haloalkyl;

Embodiment 4 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiment 1 wherein:

15 A is CH or N;

R₁ is ethyl;

R₅ is hydrogen;

R₆ is methyl or ethyl; and

R₇ is trifluoromethyl;

20

Embodiment 5 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiment 1 wherein:

A is CH or N;

R₁ is ethyl;

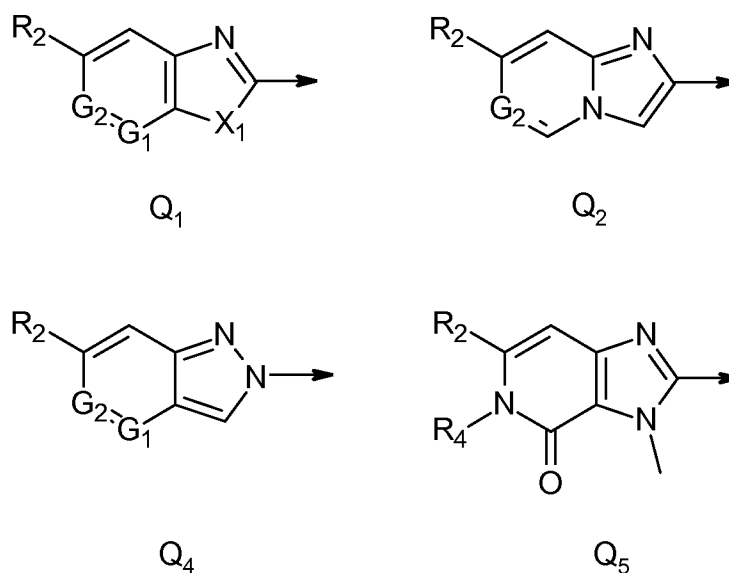
25 R₅ is hydrogen;

R₆ is methyl; and

R₇ is trifluoromethyl;

30 Embodiment 6 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiment 1 wherein:

Q is a radical selected from Q₁, Q₂, Q₄ and Q₅



wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring

5 incorporating the radical A;

and wherein

R₂ is C₁-C₂haloalkyl, C₁-C₂haloalkylsulfanyl, C₁-C₂haloalkylsulfinyl or C₁-C₂haloalkylsulfonyl;

X₁ is oxygen or NCH₃;

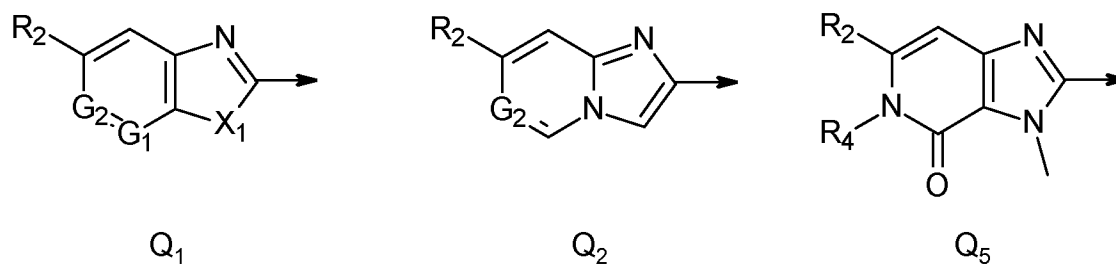
R₄ is C₁-C₂alkyl, C₁-C₂haloalkyl, C₁-C₂alkoxy or cyclopropyl;

10 G₁ and G₂ are, independently from each other, N or CH

Embodiment 7 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiment 1 wherein:

Q is a radical selected from Q₁, Q₂ and Q₅

15



wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A;

and wherein

20 R₂ is C₁-C₂fluoroalkyl, trifluoromethylsulfanyl, trifluoromethylsulfinyl, trifluoromethylsulfonyl, difluoromethylsulfanyl, difluoromethylsulfinyl, or difluoromethylsulfonyl;

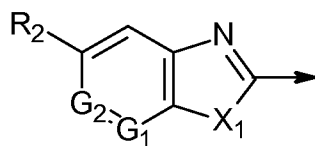
X₁ is NCH₃;

R₄ is methyl, ethyl, 2,2,2-trifluoroethyl, methoxy or cyclopropyl; and

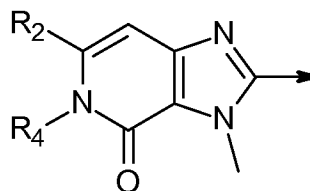
G₁ and G₂ are, independently from each other, N or CH.

- 5 Embodiment 8 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiment 1 wherein:

Q is a radical selected from Q₁ and Q₅



Q₁



Q₅

- 10 wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A;

and wherein

R₂ is trifluoromethyl, pentafluoroethyl, trifluoromethylsulfanyl, trifluoromethylsulfinyl or trifluoromethylsulfonyl;

- 15 X₁ is NCH₃;

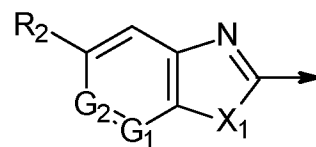
R₄ is ethyl, methoxy or cyclopropyl; and

G₁ is N and G₂ is CH or G₁ is CH and G₂ is N;

- Embodiment 9 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiment 1 wherein:

- 20 Q is radical Q₁

Q is radical Q₁



Q₁

- 25 wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A;

and wherein

R₂ is trifluoromethyl;

X₁ is NCH₃; and

G₁ is N and G₂ is CH or G₁ is CH and G₂ is N.

Embodiment 10 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiment 1 wherein:

A is CH or N;

5 R₁ is ethyl, propyl or isopropyl;

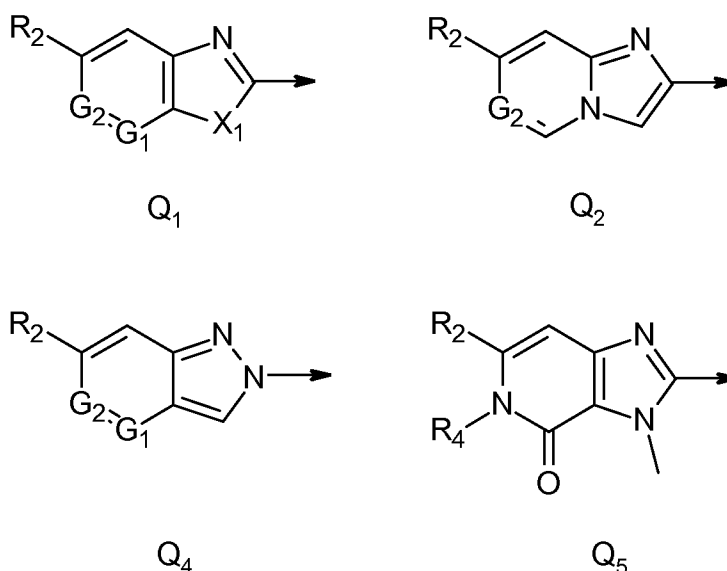
R₅ is hydrogen, cyano or C(O)R₂₅ wherein R₂₅ is C₁-C₂haloalkyl;

R₆ is C₁-C₄ alkyl or C₁-C₄haloalkyl;

R₇ is C₁-C₄ alkyl, C₁-C₄haloalkyl or C₁-C₄alkoxy;

Q is a radical selected from Q₁, Q₂, Q₄ and Q₅

10



wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A;

and wherein

15 R₂ is C₁-C₂haloalkyl, C₁-C₂haloalkylsulfanyl, C₁-C₂haloalkylsulfinyl or C₁-C₂haloalkylsulfonyl;

X₁ is oxygen or NCH₃;

R₄ is C₁-C₂alkyl, C₁-C₂haloalkyl, C₁-C₂alkoxy or cyclopropyl; and

G₁ and G₂ are, independently from each other, N or CH.

20 Embodiment 11 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiment 1 wherein:

A is CH or N;

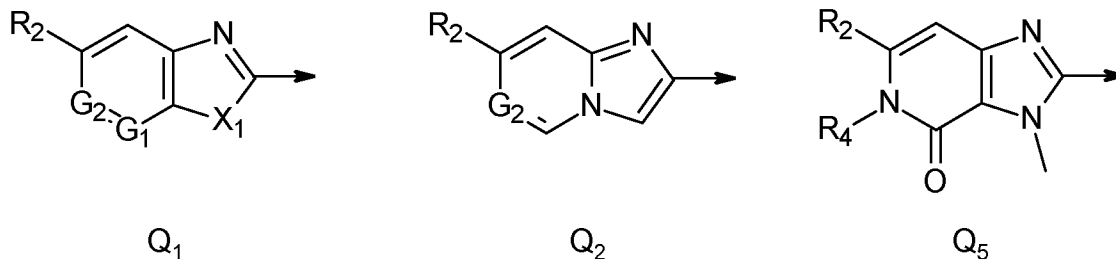
R₁ is ethyl;

R₅ is hydrogen;

25 R₆ is methyl, ethyl or C₂haloalkyl;

R₇ is C₁-C₂haloalkyl;

Q is a radical selected from Q₁, Q₂ and Q₅



wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A;

5 and wherein

R_2 is C_1 - C_2 fluoroalkyl, trifluoromethylsulfanyl, trifluoromethylsulfinyl, trifluoromethylsulfonyl, difluoromethylsulfanyl, difluoromethylsulfinyl, or difluoromethylsulfonyl;

X_1 is NCH_3 ;

R_4 is methyl, ethyl, 2,2,2-trifluoroethyl, methoxy or cyclopropyl; and

10 G_1 and G_2 are, independently from each other, N or CH.

Embodiment 12 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiment 1 wherein:

A is CH or N;

15 R_1 is ethyl;

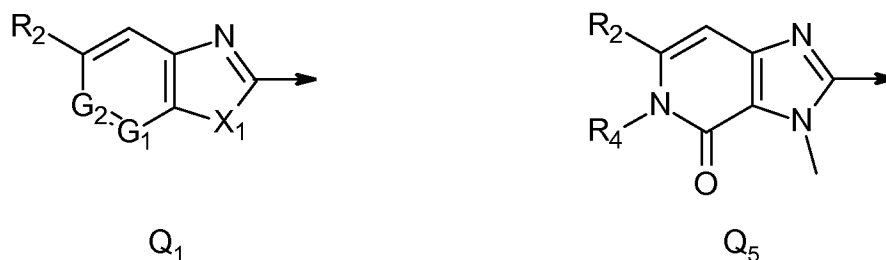
R_5 is hydrogen;

R_6 is methyl or ethyl;

R_7 is trifluoromethyl;

Q is a radical selected from Q_1 and Q_5

20



wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A;

and wherein

25 R_2 is trifluoromethyl, pentafluoroethyl, trifluoromethylsulfanyl, trifluoromethylsulfinyl or trifluoromethylsulfonyl;

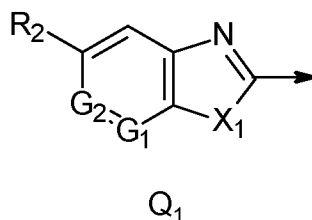
X_1 is NCH_3 ;

R_4 is ethyl, methoxy or cyclopropyl; and

G_1 is N and G_2 is CH or G_1 is CH and G_2 is N.

Embodiment 13 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiment 1 wherein:

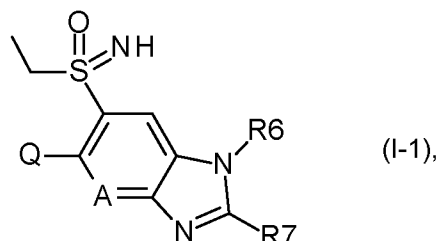
- 5 A is CH or N;
 R_1 is ethyl;
 R_5 is hydrogen;
 R_6 is methyl;
 R_7 is trifluoromethyl;
 10 Q is radical Q_1



wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A;

- 15 and wherein
 R_2 is trifluoromethyl;
 X_1 is NCH_3 ; and
 G_1 is N and G_2 is CH or G_1 is CH and G_2 is N.
- 20 Embodiment 14 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiment 1 wherein A, R_1 , R_2 , R_5 , R_6 and R_7 are, in any combination thereof, as set out below:
- A is CH or N;
 R_1 is ethyl, propyl or isopropyl; preferably ethyl;
- 25 R_2 is C_1 - C_2 haloalkyl, C_1 - C_2 haloalkylsulfanyl, C_1 - C_2 haloalkylsulfinyl or C_1 - C_2 haloalkylsulfonyl; preferably, R_2 is trifluoromethyl, pentafluoroethyl, trifluoromethylsulfanyl, trifluoromethylsulfinyl or trifluoromethylsulfonyl; and more preferably, R_2 is trifluoromethyl or trifluoromethylsulfonyl; most preferably R_2 is trifluoromethyl;
- R_5 is hydrogen, formyl, cyano, C_1 - C_3 alkylcarbonyl, C_1 - C_3 alkoxycarbonyl, C_1 - C_3 haloalkylcarbonyl;
- 30 preferably R_5 is hydrogen, formyl, cyano, $-C(O)OCH_3$, $-C(O)CH_3$, $-C(O)CH_2CH_3$, $-C(O)CF_3$; most preferably R_5 is hydrogen;
- R_6 is methyl, ethyl or C_2 haloalkyl; preferably R_6 is methyl or ethyl; most preferably R_6 is methyl;
- R_7 is C_1 - C_2 haloalkyl; preferably R_7 is $-CHF_2$ or $-CF_3$; most preferably R_7 is trifluoromethyl.

Embodiment 15 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to the invention represented by the compounds of formula (I-1)



5 wherein A, R₂, R₃, R₄, R₆, R₇, Q, X₁, G₁ and G₂ are as defined for compounds of formula I (above).

Embodiment 16 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiment 15 wherein A, R₂, R₆ and R₇ are, in any combination thereof, as set out below:

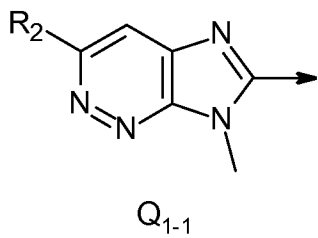
10 A is CH or N;

R₂ is C₁-C₂haloalkyl, C₁-C₂haloalkylsulfanyl, C₁-C₂haloalkylsulfinyl or C₁-C₂haloalkylsulfonyl; preferably, R₂ is trifluoromethyl, pentafluoroethyl, trifluoromethylsulfanyl, trifluoromethylsulfinyl or trifluoromethylsulfonyl; and more preferably, R₂ is trifluoromethyl or trifluoromethylsulfonyl; most preferably R₂ is trifluoromethyl;

15 R₆ is methyl, ethyl or C₂haloalkyl; preferably R₆ is methyl or ethyl; most preferably R₆ is methyl; R₇ is C₁-C₂haloalkyl; preferably R₇ is -CHF₂ or -CF₃; most preferably R₇ is trifluoromethyl.

Embodiment 17 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiments 1, 14, 15 or 16 wherein

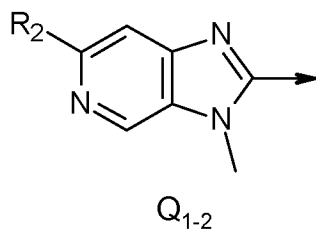
20 Q is radical Q₁₋₁



wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A.

25 Embodiment 18 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiments 1, 14, 15 or 16 wherein:

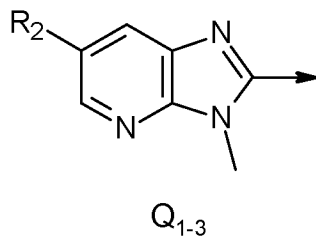
Q is radical Q₁₋₂



wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A.

- 5 Embodiment 19 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiments 1, 14, 15 or 16 wherein:

Q is radical Q₁₋₃

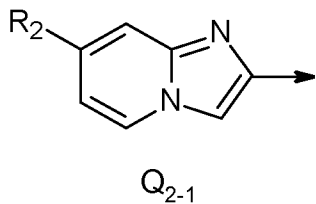


wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A.

10

Embodiment 20 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiments 1, 14, 15 or 16 wherein:

Q is radical Q₂₋₁



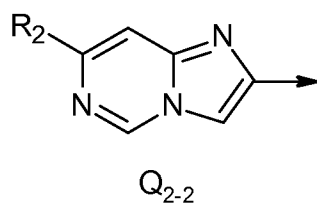
15

wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A.

- Embodiment 21 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiments 1, 14, 15 or 16 wherein:

20

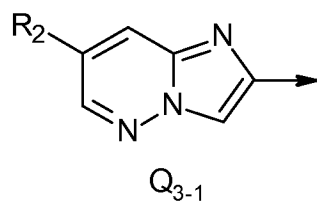
Q is radical Q₂₋₂



wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A.

- 5 Embodiment 22 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiments 1, 14, 15 or 16 wherein:

Q is radical Q_{3-1}

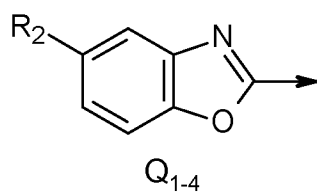


wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A.

10

Embodiment 23 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiments 1, 14, 15 or 16 wherein:

Q is radical Q_{1-4}



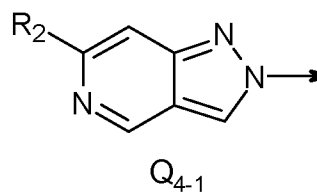
15

wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A.

Embodiment 24 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiments 1, 14, 15 or 16 wherein:

20

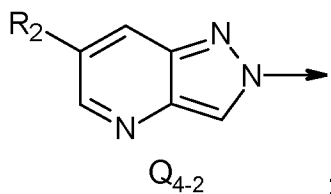
Q is radical Q_{4-1}



wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A.

Embodiment 25 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiments 1, 14, 15 or 16 wherein:

Q is radical Q₄₋₂

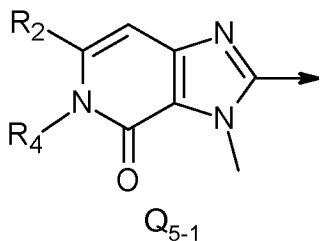


wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A.

10

Embodiment 26 provides compounds, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to embodiments 1, 14, 15 or 16 wherein:

Q is radical Q₅₋₁



15 wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A: and

R₄ is ethyl, methoxy or cyclopropyl.

In another aspect the present invention provides a composition comprising an insecticidally, acaricidally, nematocidally or molluscicidally effective amount of a compound of formula (I), or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, as defined in any of the foregoing embodiments 1 - 26 (above), and, optionally, an auxiliary or diluent.

In a further aspect the present invention provides a method of combating and controlling insects, acarines, nematodes or molluscs which comprises applying to a pest, to a locus of a pest, or to a plant susceptible to attack by a pest an insecticidally, acaricidally, nematocidally or molluscicidally effective amount of a compound of formula (I), or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, as defined in any of the foregoing embodiments 1 - 26 (above) or a composition as defined above.

30

In a yet further aspect the present invention provides a method for the protection of plant propagation material from the attack by insects, acarines, nematodes or molluscs, which comprises treating the propagation material or the site, where the propagation material is planted, with a composition as defined above.

5

The process according to the invention for preparing compounds of formula I is carried out by methods known to those skilled in the art.

10

Compounds of the formula I, wherein Q, R₁, R₅, R₆, R₇, and A are as defined above, may be prepared by methods described in Scheme 1. For example, compounds of formula I may be prepared by oxidation of compounds of the formula II, wherein Q, R₁, R₅, R₆, R₇, and A are as defined above.

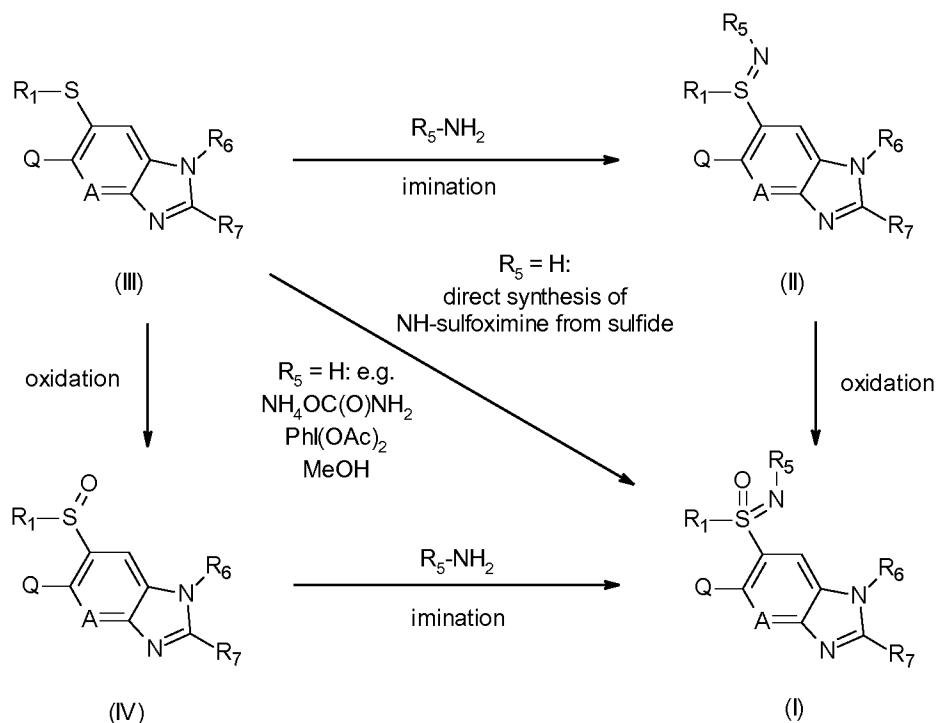
Compounds of the formula II, wherein Q, R₁, R₅, R₆, R₇, and A are as defined above, may be obtained by imination of compounds of the formula III, wherein Q, R₁, R₆, R₇, and A are as defined above.

15

Conversely, the order of the two steps may be reverted whereby the sulfoximine compounds of the formula I, wherein Q, R₁, R₅, R₆, R₇, and A are as defined above, may be prepared from sulfoxides of the formula IV, wherein Q, R₁, R₆, R₇, and A are as defined above, under appropriate imination reaction conditions. Compounds of the formula IV, wherein Q, R₁, R₆, R₇, and A are as defined above, may be obtained by oxidation of compounds of the formula III, wherein Q, R₁, R₆, R₇, and A are as defined above.

20

Scheme 1



Typical preparation methods and reaction conditions to access the compounds of the formula II from the sulfides III, or compounds of the formula I from the sulfoxides IV may be found, for example, in H. Okamura, C. Bolm, *Org. Lett.* 2004, 6, 1305-1307; H. Okamura, C. Bolm, *Chem. Lett.* 2004, 33, 482-487; D. Leca, K. Song, M. Amatore, L. Fensterbank, E. Lacôte, M. Malacria, *Chem. Eur. J.* 2004, 10, 906-916; or M. Reggelin, C. Zur, *Synthesis*, 2000, 1-64. Typical imination reagents/conditions may be defined as $\text{NaN}_3/\text{H}_2\text{SO}_4$, O-mesitylenesulfonyl-hydroxylamine (MSH), or metal-catalyzed methods [see O.G. Mancheno, C. Bolm, *Chem. Eur. J.* 2007, 13, 6674-6681] such as $\text{R}_5\text{-N}_3/\text{FeCl}_2$, $\text{R}_5\text{-NH}_2/\text{Fe}(\text{acac})_3/\text{PhI}=\text{O}$, $\text{PhI}=\text{N-R}_5/\text{Fe}(\text{OTf})_2$, $\text{PhI}=\text{N-R}_5/\text{CuOTf}$, $\text{PhI}=\text{N-R}_5/\text{Cu}(\text{OTf})_2$, $\text{PhI}=\text{N-R}_5/\text{CuPF}_6$, $\text{PhI}(\text{OAc})_2/\text{R}_5\text{-NH}_2/\text{MgO}/\text{Rh}_2(\text{OAc})_4$ or oxaziridines (e.g. 3-(4-cyano-phenyl)-oxaziridine-2-carboxylic acid tert-butyl ester).

Of particular interest are metal-free imination methods of sulfides of the formula III and/or sulfoxides of the formula IV to prepare sulfilimines of the formula II and/or sulfoximines of the formula I. Such imination reactions involve $\text{R}_5\text{-NH}_2$ and an oxidant, for example, $\text{PhI}(\text{OAc})_2/\text{R}_5\text{-NH}_2$ as described in G.Y. Cho, C. Bolm, *Tetrahedron Lett.* 2005, 46, 8007-8008; or N-bromosuccinimide (NBS)/ $\text{R}_5\text{-NH}_2$ and a base such as sodium or potassium tert-butoxide as described in C. Bolm et al., *Synthesis* 2010, No 17, 2922-2925. Oxidants such as N-iodosuccinimide (NIS) or iodine may be also used alternatively as described, for example, in O.G. Mancheno, C. Bolm, *Org. Lett.* 2007, 9, 3809-3811. An example of hypochlorite salts being used as oxidant, such as sodium hypochlorite NaOCl or calcium hypochlorite $\text{Ca}(\text{OCl})_2$, was described in WO2008/1060.

Alternatively, the compounds of the formula I wherein Q, R_1 , R_6 , R_7 , and A are as defined above, and R_5 is hydrogen, may be obtained from the corresponding sulfoxide of formula IV, wherein Q, R_1 , R_6 , R_7 , and A are as defined above, by treatment with $\text{PhI}(\text{OAc})_2/\text{NH}_2\text{COONH}_4$ as described in J. A. Bull, R. Luisi, et al, *Angew. Chem. Int. Ed.* 2016, 55, 7203 –7207.

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

Alternatively, compounds of the formula I wherein Q, R_1 , R_6 , R_7 , and A are as defined above, and R_5 is hydrogen, may be obtained directly from the corresponding sulfide of formula III, wherein Q, R_1 , R_6 , R_7 , and A are as defined above, by treatment with $\text{PhI}(\text{OAc})_2/\text{NH}_2\text{COONH}_4$ as described in J. A. Bull, R. Luisi, et al, *Chem. Comm.* 2017, 53, 348-351; 2017.

Alternatively, compounds of the formula I wherein Q, R_1 , R_6 , R_7 , and A are as defined above, and R_5 is hydrogen, may be obtained from compounds of the formula I wherein Q, R_1 , R_6 , R_7 , and A are as defined above, and R_5 is $\text{C}(\text{O})\text{CF}_3$, by treatment with a base such as sodium or potassium carbonate in a polar protic solvent such as methanol or ethanol as described, for example, in H. Okamura, C. Bolm, *Org. Lett.* 2004, 6, 1305-1307.

A compound of the formula I, wherein Q, R_1 , R_5 , R_6 , R_7 , and A are as defined above, and wherein R_5 is CN, may be transformed into a compound of the formula I, wherein Q, R_1 , R_5 , R_6 , R_7 , and A are as

defined above, and wherein R_5 is $C(O)CF_3$, by treatment with trifluoroacetic anhydride in a solvent such as dichloromethane as described, for example, in O.G. Mancheno, C. Bolm, Org. Lett. 2007, 9, 3809-3811.

5 A compound of the formula I, wherein wherein Q, R_1 , R_5 , R_6 , R_7 , and A are as defined above, and wherein R_5 is C_1 - C_3 alkyl, may be prepared from a compound of the formula I, wherein wherein Q, R_1 , R_5 , R_6 , R_7 , and A are as defined above, and wherein R_5 is hydrogen, by treatment with an alkylating agent of formula $LG-R_8$, wherein LG is a leaving group such as a halogen (especially bromine or iodine), a sulfonate OSO_2R_8 (especially mesylate or tosylate), wherein R_8 is C_1 - C_3 alkyl, C_1 - C_6 haloalkyl, or phenyl optionally substituted by nitro or C_1 - C_3 alkyl, or a sulfate (such as dimethylsulfate),
10 preferably in the presence of a suitable base, such as alkali metal carbonates, for example sodium carbonate or potassium carbonate, or alkali metal hydrides such as sodium hydride, or alkali metal hydroxides such as sodium hydroxide and potassium hydroxide, in an inert solvent at temperatures between -20 and 150 °C, preferably between 0 and 80 °C. Examples of solvent to be used include
15 ethers such as tetrahydrofuran, ethylene glycol dimethyl ether (1,2-dimethoxyethane), tert-butylmethyl ether, and 1,4-dioxane, aromatic hydrocarbons such as toluene and xylene, nitriles such as acetonitrile or polar aprotic solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone or dimethyl sulfoxide.

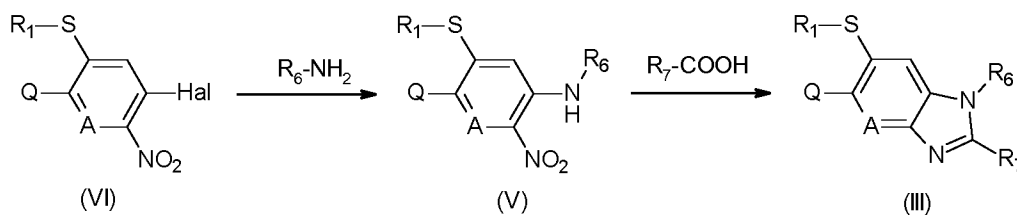
A compound of the formula I, wherein wherein Q, R_1 , R_5 , R_6 , R_7 , and A are as defined above, and
20 wherein R_5 is $C(O)R_9$ and R_9 is C_1 - C_3 alkyl or C_1 - C_3 haloalkyl, may be prepared from a compound of the formula I, wherein wherein Q, R_1 , R_5 , R_6 , R_7 , and A are as defined above, and wherein R_5 is hydrogen, by treatment with a reagent of formula $LG_1-C(O)R_9$ or an anhydride reagent of formula $R_9C(O)-O-C(O)R_9$, wherein R_9 is as defined above and LG_1 is a leaving group such as a halogen (especially chlorine), optionally in presence of an acylating catalyst, such as 4-dimethylaminopyridine (DMAP),
25 preferably in presence of a base, such as triethylamine, diisopropylethylamine or pyridine, in an inert solvent at temperatures between 0 and 50 °C. Examples of solvent to be used include ethers such as tetrahydrofuran, ethylene glycol dimethyl ether, tert-butylmethyl ether, and 1,4-dioxane, aromatic hydrocarbons such as toluene and xylene, halogenated hydrocarbons such as dichloromethane and chloroform, nitriles such as acetonitrile or polar aprotic solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone or dimethyl sulfoxide. The reaction may be carried out in
30 the presence of an excess of base, which then may also act as a solvent or diluent.

A compound of the formula I, wherein wherein Q, R_1 , R_5 , R_6 , R_7 , and A are as defined above, and wherein R_5 is $C(O)OR_{10}$ and R_{10} is C_1 - C_3 alkyl, may be prepared from a compound of the formula I,
35 wherein wherein Q, R_1 , R_5 , R_6 , R_7 , and A are as defined above, and wherein R_5 is hydrogen, by treatment with a reagent of formula $LG_2-C(O)OR_{10}$, wherein R_{10} is as defined above and LG_2 is a leaving group such as a halogen (especially chlorine), optionally in presence of an acylating catalyst, such as 4-dimethylaminopyridine (DMAP), preferably in presence of a base, such as triethylamine, diisopropylethylamine or pyridine, in an inert solvent at temperatures between 0 and 50 °C. Examples of solvent to be used include ethers such as tetrahydrofuran, ethylene glycol dimethyl ether, tert-

butylmethyl ether, and 1,4-dioxane, aromatic hydrocarbons such as toluene and xylene, halogenated hydrocarbons such as dichloromethane and chloroform, nitriles such as acetonitrile or polar aprotic solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone or dimethyl sulfoxide. The reaction may be carried out in the presence of an excess of base, which then may also act as a solvent or diluent.

Compounds of the formula III, wherein Q, R₁, R₆, R₇, and A are as defined above, can be prepared according to methods described in Scheme 2, for example, by cyclizing compounds of the formula V, wherein Q, R₁, R₆, and A are as defined above, with a compound of the formula R₇COOH, wherein R₇ is as defined above, under reductive cyclization conditions. Such reductive cyclization conditions can be achieved, for example, using zinc dust and compound R₇COOH (whereby R₇COOH can act both as reagent and solvent or diluent), at temperatures between 0 °C and 120 °C, preferably between 0 °C and reflux temperature.

15 Scheme 2:



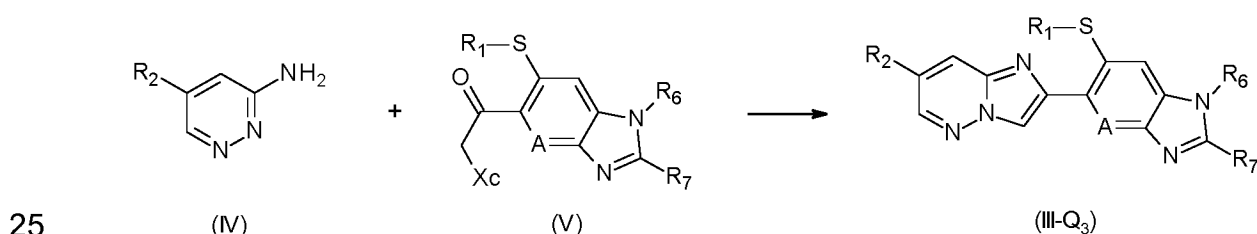
Compounds of the formula V, or a salt thereof (such as a hydrohalide salt, preferably a hydrochloride or a hydrobromide salt, or a trifluoroacetic acid salt, or any other equivalent salt), wherein Q, R₁, R₆, and A are as defined above, can be prepared by reacting compounds of the formula VI, wherein Q, R₁, and A are as defined above, and wherein Hal is a halogen such as, for example, fluorine, chlorine or bromine (preferably fluorine or chlorine), with a reagent R₆-NH₂, or a salt thereof (such as a hydrohalide salt, preferably a hydrochloride or a hydrobromide salt, or a trifluoroacetic acid salt, or any other equivalent salt), wherein R₆ is as defined in formula I, optionally in presence of an additional base. This transformation is preferably performed in suitable solvents (or diluents) such as alcohols, amides, esters, ethers, nitriles and water, particularly preferred are methanol, ethanol, 2,2,2-trifluoroethanol, propanol, iso-propanol, N,N-dimethylformamide, N,N-dimethylacetamide, dioxane, tetrahydrofuran, dimethoxy-ethane, acetonitrile, ethyl acetate, water or mixtures thereof, at temperatures between 0-150°C, preferably at temperatures ranging from room temperature to the boiling point of the reaction mixture, optionally under microwave irradiation or pressurized conditions using an autoclave.

Additional methods for the synthesis of compounds of formula III, wherein A, R₁, R₆ and R₇ are defined as under formula I above, and wherein Q = Q₁, are either known compounds, or may be prepared by known methods known to those skilled in the art (see for example WO2016/091731).

- 5 Similarly, methods for the preparation of compounds of formula III, wherein A, R₁, R₆ and R₇ are defined as under formula I above, and wherein Q = Q₂ are either known compounds, or may be prepared by known methods known to those skilled in the art (see for example WO 2016/107742).

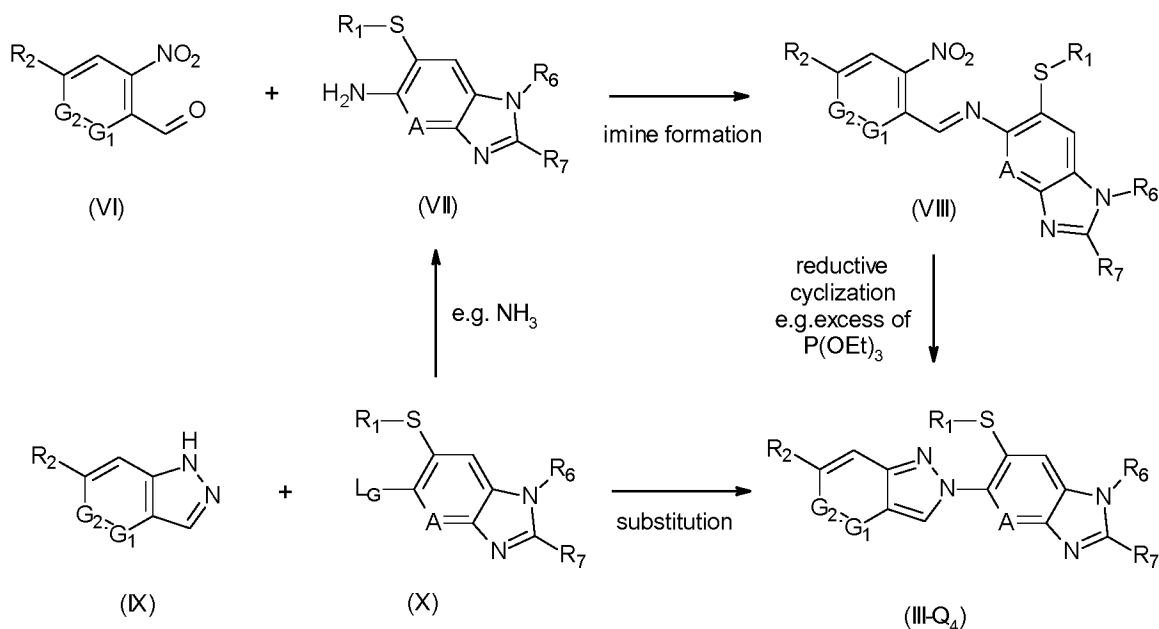
- 10 Compounds of formula III, wherein Q = Q₃ defining compounds of the formula III-Q₃, wherein R₁, R₂, R₆, R₇, and A are as defined in formula I, may be prepared as described in Scheme 3. Condensation of compounds of formula V, wherein R₁, R₆, R₇, and A are as defined in formula I, and in which X_c is a leaving group such as, for example, chlorine, bromine or iodine (preferably chlorine or bromine), with compounds of the formula IV, wherein R₂ is as defined in formula I, in an inert solvent, for example ethanol, toluene or acetonitrile, optionally in the presence of a suitable base, such as sodium,
15 potassium or cesium carbonate (or sodium or potassium hydrogen carbonate) at temperatures between 80 and 150°C, optionally under microwave heating conditions. Such processes have been described previously, for example, in WO 2011/074658. Compounds of formula IV, wherein R₂ is as defined in formula I, are either known compounds, commercially available or may be prepared by known methods known to those skilled in the art (see for example WO 2011/074658 and WO
20 2010/083145). Compounds of formula V are known compounds are either known compounds, commercially available or may be prepared by known methods known to those skilled in the art (see for example WO 2016/107742).

Scheme 3:



Compounds of formula III, wherein Q = Q₄ defining compounds of the formula III-Q₄, wherein R₁, R₂, R₆, R₇, A, G₁, and G₂ are as defined in formula I, may be as described in Scheme 4.

30 Scheme 4:



For example, compounds of formula II-Q₄ can be prepared by reductive cyclization of compounds of formula VIII, wherein R₁, R₂, R₆, R₇, A, G₁, and G₂ are as defined in formula I, in the presence of a reducing agent such as trialkyl phosphite (more specifically, for example, triethyl phosphite), trialkylphosphine or triphenylphosphine. The principle of this reductive cyclization is analogous to the known Cadogan reaction. Alternatively, this reaction may be conducted in presence of a metal catalyst, for example a molybdenum(VI) catalyst, such as MoO₂Cl₂(dmf)₂ [molybdenyl chloride-bis(dimethylformamide)], or more generally with transition metal complexes, in combination with a reducing agent such as triethylphosphite, triphenylphosphine or CO. Suitable solvents may include use of excess of the reducing agent (such as triethyl phosphite), or for example toluene or xylene, at temperatures between room temperature and 200°C, preferably between 50 and 160°C, optionally under microwave heating conditions. Such reductive cyclisation reaction conditions were described in, for example, WO 2017/134066.

Compounds of the formula VIII, wherein R₁, R₂, R₆, R₇, A, G₁, and G₂ are as defined in formula I, may be prepared by reaction between compounds of formula VII, wherein R₁, R₆, R₇, and A are as defined in formula I, and compounds of formula VI, wherein R₂, G₁, and G₂ are as defined in formula I, usually upon heating at temperatures between room temperature and 200°C, preferably between 40 and 160 °C, optionally under microwave heating conditions, in suitable solvents that may include, for example, toluene or xylene. The formation of compounds of formula VIII may require water removal, either by azeotropical distillation, or by means of a drying agent such as for example TiCl₄ or molecular sieves. Such formation of Schiff bases of formula VIII is known to those skilled in the art, and was described in, for example, WO 2017/134066.

25

Alternatively, compounds of the formula III-Q₄, wherein R₁, R₂, R₆, R₇, A, G₁, and G₂ are as defined in formula I, may be prepared by reacting compounds of formula X, wherein R₁, R₆, R₇, and A are defined as in formula I, and in which L_G is a leaving group such as, for example, chlorine, bromine or iodine (preferably chlorine or bromine), or an aryl-, alkyl- or haloalkylsulfonate such as trifluoromethanesulfonate, with compounds of formula IX, wherein G₁, G₂ and R₂ are as defined in formula I, in the presence of base such as for example cesium, sodium, potassium or lithium carbonate, or sodium hydride, optionally in the presence of a metal catalyst such as copper(I) iodide or a palladium catalyst, with or without additives such as L-proline, N,N'-dimethylethylenediamine or a phosphorus-based ligand, in an inert solvent such as acetonitrile, N,N-dimethylformamide, N-methyl-2-pyrrolidone or dimethyl sulfoxide at temperatures between room temperature and 200°C, optionally under microwave heating conditions. Such aromatic nucleophilic substitution reaction conditions were described in, for example, WO 2017/134066.

Compounds of formula VI and IX, wherein G₁, G₂ and R₂ are as defined in formula I, are either known compounds, commercially available or may be prepared by known methods known to those skilled in the art.

Compounds of formula VII, wherein R₁, R₂, R₆, R₇, A, G₁, and G₂ are as defined in formula I, may be obtained from compounds of formula X, by treatment with ammonia NH₃ (or a corresponding salt thereof, such as a hydrohalide salt, preferably a hydrochloride or a hydrobromide salt, or any other equivalent salt) or an ammonia equivalent such as for example ammonium hydroxide NH₄OH, ammonium chloride NH₄Cl, ammonium acetate NH₄OAc, ammonium carbonate (NH₄)₂CO₃, and other NH₃ surrogates. This transformation is preferably performed in suitable solvents (or diluents) such as alcohols, amides, esters, ethers, nitriles and water, particularly preferred are methanol, ethanol, 2,2,2-trifluoroethanol, propanol, isopropanol, N,N-dimethylformamide, N,N-dimethylacetamide, dioxane, tetrahydrofuran, dimethoxyethane, acetonitrile, ethyl acetate, water or mixtures thereof, optionally in presence of a base, at temperatures between 0-150 °C, preferably at temperatures ranging from room temperature to the boiling point of the reaction mixture, optionally under microwave irradiation.

Alternatively, compounds of formula III-Q₄ may be prepared by methods known to those skilled in the art following similar procedures to those reported in WO 2017/134066 or such compounds may be prepared by methods shown in Example P19.

Compounds of formula (III), wherein A, R₁, R₆ and R₇ are defined as under formula I above, and wherein Q = Q₅ are either known compounds, or may be prepared by known methods known to those skilled in the art (see for example WO2016/142326).

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 reactions are 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.

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.

5 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
10 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,
15 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 diastereomers or racemates on the basis of the
20 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
25 solvent, by chromatography on chiral adsorbents, for example high-performance liquid chromatography (HPLC) on acetyl cellulose, with the aid of suitable microorganisms, by cleavage with specific, immobilized enzymes, via the formation of inclusion compounds, for example using chiral crown ethers, where only one enantiomer is complexed, or by conversion into diastereomeric salts, for example by reacting a basic end-product racemate with an optically active acid, such as a carboxylic
30 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.

35 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 H₂O₂/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 2000/15615.

5

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.

10 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.

15

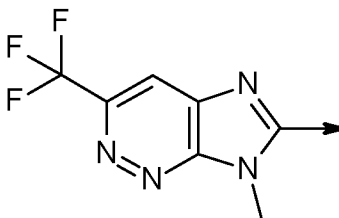
The compounds of formula I according to the following Tables X and A-1 to A-13 below can be prepared according to the methods described above. The examples which follow are intended to illustrate the invention and show preferred compounds of formula I.

5 Table X: Substituent definitions of R₅, R₆, R₇ and A of formula I:

Index	R ₆	R ₇	A	R ₅
1	Me	CF ₃	N	H
2	Me	CF ₃	CH	H
3	Me	CHF ₂	N	H
4	Me	CHF ₂	CH	H
5	Et	CF ₃	N	H
6	Et	CF ₃	CH	H
7	Et	CHF ₂	N	H
8	Et	CHF ₂	CH	H
9	Me	CF ₃	N	C(O)H
10	Me	CF ₃	CH	C(O)H
11	Me	CHF ₂	N	C(O)H
12	Me	CHF ₂	CH	C(O)H
13	Et	CF ₃	N	C(O)H
14	Et	CF ₃	CH	C(O)H
15	Et	CHF ₂	N	C(O)H
16	Et	CHF ₂	CH	C(O)H
17	Me	CF ₃	N	CN
18	Me	CF ₃	CH	CN
19	Me	CHF ₂	N	CN
20	Me	CHF ₂	CH	CN
21	Et	CF ₃	N	CN
22	Et	CF ₃	CH	CN
23	Et	CHF ₂	N	CN
24	Et	CHF ₂	CH	CN
25	Me	CF ₃	N	C(O)OMe
26	Me	CF ₃	CH	C(O)OMe
27	Me	CHF ₂	N	C(O)OMe
28	Me	CHF ₂	CH	C(O)OMe
29	Et	CF ₃	N	C(O)OMe
30	Et	CF ₃	CH	C(O)OMe
31	Et	CHF ₂	N	C(O)OMe
32	Et	CHF ₂	CH	C(O)OMe
33	Me	CF ₃	N	C(O)Me
34	Me	CF ₃	CH	C(O)Me
35	Me	CHF ₂	N	C(O)Me
36	Me	CHF ₂	CH	C(O)Me
37	Et	CF ₃	N	C(O)Me
38	Et	CF ₃	CH	C(O)Me

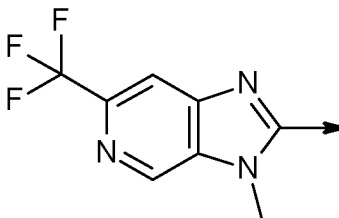
Index	R ₆	R ₇	A	R ₅
39	Et	CHF ₂	N	C(O)Me
40	Et	CHF ₂	CH	C(O)Me
41	Me	CF ₃	N	C(O)Et
42	Me	CF ₃	CH	C(O)Et
43	Me	CHF ₂	N	C(O)Et
44	Me	CHF ₂	CH	C(O)Et
45	Et	CF ₃	N	C(O)Et
46	Et	CF ₃	CH	C(O)Et
47	Et	CHF ₂	N	C(O)Et
48	Et	CHF ₂	CH	C(O)Et
49	Me	CF ₃	N	C(O)CF ₃
50	Me	CF ₃	CH	C(O)CF ₃
51	Me	CHF ₂	N	C(O)CF ₃
52	Me	CHF ₂	CH	C(O)CF ₃
53	Et	CF ₃	N	C(O)CF ₃
54	Et	CF ₃	CH	C(O)CF ₃
55	Et	CHF ₂	N	C(O)CF ₃
56	Et	CHF ₂	CH	C(O)CF ₃

Table A-1 provides 56 compounds A-1.001 to A-1.056 of formula I wherein R₁ is ethyl and R₅, R₆, R₇, A are as defined in table X and Q₁ is



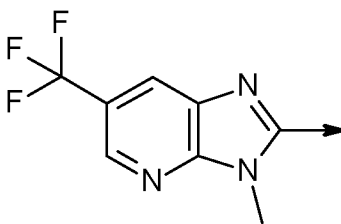
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Table A-2 provides 56 compounds A-2.001 to A-2.056 of formula I wherein R₁ is ethyl and R₅, R₆, R₇, A are as defined in table X and Q₁ is



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Table A-3 provides 56 compounds A-3.001 to A-3.056 of formula I wherein R₁ is ethyl and R₅, R₆, R₇, A are as defined in table X and Q₁ is



5 Table A-4 provides 56 compounds A-4.001 to A-4.056 of formula I wherein R₁ is ethyl and R₅, R₆, R₇, A are as defined in table X and Q₂ is

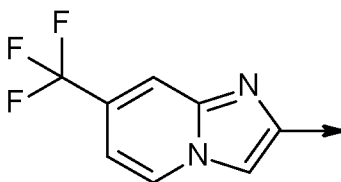
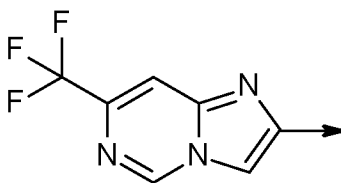


Table A-5 provides 56 compounds A-5.001 to A-5.056 of formula I wherein R₁ is ethyl and R₅, R₆, R₇, A are as defined in table X and Q₂ is



10 Table A-6 provides 56 compounds A-6.001 to A-6.056 of formula wherein R₁ is ethyl and R₅, R₆, R₇, A are as defined in table X and Q₃ is

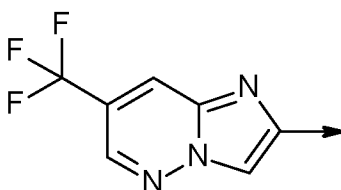


Table A-7 provides 56 compounds A-7.001 to A-7.056 of formula I wherein R₁ is ethyl and R₅, R₆, R₇, A are as defined in table X and Q₁ is

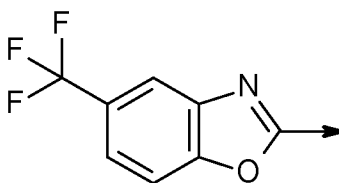
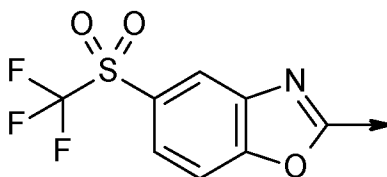


Table A-8 provides 56 compounds A-8.001 to A-8.056 of formula I wherein R₁ is ethyl and R₅, R₆, R₇, A are as defined in table X and Q₁ is



- 5 Table A-9 provides 56 compounds A-9.001 to A-9.056 of formula I wherein R₁ is ethyl and R₅, R₆, R₇, A are as defined in table X and Q₄ is

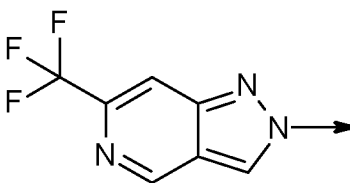
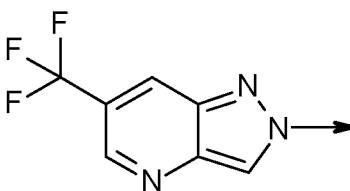


Table A-10 provides 56 compounds A-10.001 to A-10.056 of formula I wherein R₁ is ethyl and R₅, R₆, R₇, A are as defined in table X and Q₄ is



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Table A-11 provides 56 compounds A-11.001 to A-11.056 of formula I wherein R₁ is ethyl and R₅, R₆, R₇, A are as defined in table X and Q₅ is

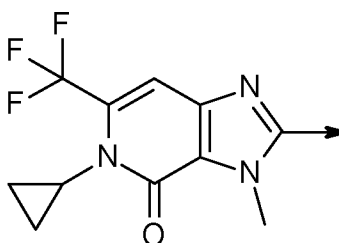
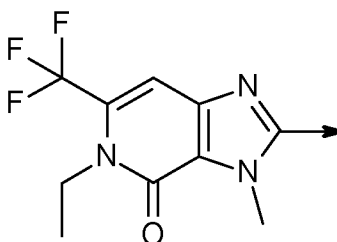
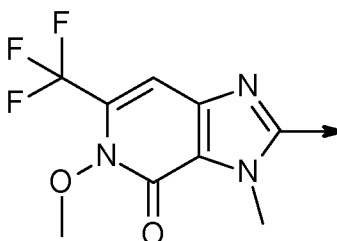


Table A-12 provides 56 compounds A-12.001 to A-12.056 of formula I wherein R₁ is ethyl and R₅, R₆, R₇, A are as defined in table X and Q₅ is



5 Table A-13 provides 56 compounds A-13.001 to A-13.056 of formula I wherein R₁ is ethyl and R₅, R₆, R₇, A are as defined in table X and Q₅ is



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
 10 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, molluscs, nematodes or representatives of the order Acarina. The insecticidal, molluscicidal, nematocidal or acaricidal activity of
 15 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.

Compounds of formula (I) according to the invention may possess any number of benefits including, inter alia, advantageous levels of biological activity for protecting plants against insects or superior
 20 properties for use as agrochemical active ingredients (for example, greater biological activity, an advantageous spectrum of activity, an increased safety profile, improved physico-chemical properties, or increased biodegradability or environmental profile). In particular, it has been surprisingly found that certain compounds of formula (I) show an advantageous safety profile with respect to non-target organisms, for example, non-target arthropods, in particular pollinators such as honey bees, solitary
 25 bees, and bumble bees. Most particularly, *Apis mellifera*.

In this regard, certain compounds of formula (I) of the invention can be distinguished from known compounds by virtue of greater efficacy at low application rates, which can be verified by the person

skilled in the art using experimental procedures similar to or adapted from those outlined in the biological examples, using lower application rates if necessary, for example 50 ppm, 12.5 ppm, 6 ppm, 3 ppm, 1.5 ppm, 0.8 ppm or 0.2 ppm.

- 5 Further it has surprisingly found that that compounds of formula (I) show advantageous physico-chemical properties for application in crop protection, in particular reduced melting point, reduced lipophilicity and increased water solubility. Such properties have been found to be advantageous for plant uptake and systemic distribution, see for example A. Buchholz, S. Trapp, *Pest Manag Sci* 2016; 72: 929-939) in order to control certain pest species named below.
- 10 Examples of the above mentioned 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
15 gallinae, Dermatophagoides spp, Eotetranychus spp, Eriophyes spp., Hemitarsonemus spp,
Hyalomma spp., Ixodes spp., Olygonychus spp, Ornithodoros spp., Polyphagotarsonne latus,
Panonychus spp., Phyllocoptruta oleivora, Phytoneumus spp, Polyphagotarsonemus spp, Psoroptes
spp., Rhipicephalus spp., Rhizoglyphus spp., Sarcoptes spp., Steneotarsonemus spp, Tarsonemus
spp. and Tetranychus spp.;
- 20 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,
25 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, Meligethes aeneus, Melolontha spp., Myochrous armatus,
Orycaephilus spp., Otorhynchus spp., Phyllophaga spp, Phlyctinus spp., Popillia spp., Psylliodes spp.,
30 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.,
35 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,
Rivellia 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, Euschistus spp., Eurydema pulchrum, 5 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., Vatica illudens; Acyrthosium pisum, Adalges spp, Agalliana ensigera, Agonosceana targionii, Aleurodicus spp, 10 Aleurocanthus spp, Aleurolobus barodensis, Aleurothrixus floccosus, Aleyrodes brassicae, Amarasca biguttula, Amritodus atkinsoni, Aonidiella spp., Aphididae, Aphis spp., Aspidiotus spp., Aulacorthum solani, Bactericera cockerelli, Bemisia spp, Brachycaudus spp, Brevicoryne brassicae, Cacopsylla spp, Cavariella aegopodii Scop., Ceroplaster spp., Chrysomphalus aonidium, Chrysomphalus dictyospermi, Cicadella spp, Cofana spectra, Cryptomyzus spp, Cicadulina spp, Coccus hesperidum, 15 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, 20 Myzus spp., Neotoxoptera sp, Nephrotettix spp., Nilaparvata spp., Nippolachnus piri Mats, Odonaspis ruthae, Oregma lanigera Zehnter, Parabemisia myricae, Paratrioza cockerelli, Parlatoria spp., Pemphigus spp., Peregrinus maidis, Perkinsiella spp, Phorodon humuli, Phylloxera spp, Planococcus spp., Pseudaulacaspis spp., Pseudococcus spp., Pseudatomoscelis seriatus, Psylla spp., Pulvinaria aethiopica, Quadraspidotus spp., Quesada gigas, Recilia dorsalis, Rhopalosiphum spp., Saissetia 25 spp., Scaphoideus spp., Schizaphis spp., Sitobion spp., Sogatella furcifera, Spissistilus festinus, Tarophagus Proserpina, Toxoptera spp, Trialeurodes spp, Tridiscus sporoboli, Trionymus spp, Trioza erythrae , Unaspis citri, Zyginia flammigera, Zyginidia scutellaris, ;

from the order *Hymenoptera*, for example,

Acromyrmex, Arge spp, Atta spp., Cephus spp., Diprion spp., Diprionidae, Gilpinia polytoma, Hoplo- 30 campa 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, 35 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,
- 5 Grapholita spp., Hedyia 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 gossypi-
- 10 ela, 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,
- 15 Damalinae spp. and Trichodectes spp.;
- from the order *Orthoptera*, for example,
- Blatta spp., Blattella spp., Gryllotalpa spp., Leucophaea maderae, Locusta spp., Neocurtilla hexadactyla, Periplaneta spp. , Scapteriscus spp, and Schistocerca spp.;
- from the order *Psocoptera*, for example,
- 20 Liposcelis spp.;
- from the order *Siphonaptera*, for example,
- Ceratophyllus spp., Ctenocephalides spp. and Xenopsylla cheopis;
- from the order *Thysanoptera*, for example,
- 25 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.

30 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.

35 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,
5 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.,
10 *Alonsoa* spp., *Anemone* spp., *Anisodonteia capsensis*, *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.,
15 *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*
20 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.*
25 *sativum*, *A. cepa*, *A. oschaninii*, *A. Porrum*, *A. ascalonicum*, *A. fistulosum*), *Anthriscus cerefolium*,
Apium graveolus, *Asparagus officinalis*, *Beta vulgaris*, *Brassica* spp. (*B. Oleracea*, *B. Pekinensis*, *B.*
rapa), *Capsicum annuum*, *Cicer arietinum*, *Cichorium endivia*, *Cichorium* spp. (*C. intybus*, *C. endivia*),
Citrillus lanatus, *Cucumis* spp. (*C. sativus*, *C. melo*), *Cucurbita* spp. (*C. pepo*, *C. maxima*), *Cyanara*
30 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*,
35 *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),
5 *Cydia pomonella* (preferably in apples), *Empoasca* (preferably in vegetables, vineyards), *Leptinotarsa* (preferably in potatoes) and *Chilo suppressalis* (preferably in rice).

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15 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*,
20 *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;
25 Spiral nematodes, *Helicotylenchus multicinctus* and other *Helicotylenchus* species; Sheath and sheathoid nematodes, *Hemicycliophora* species and *Hemicriconemoides* species; *Hirshmanniella* species; Lance nematodes, *Hoploaimus* species; false rootknot nematodes, *Nacobbus* species; Needle nematodes, *Longidorus elongatus* and other *Longidorus* species; Pin nematodes,
30 *Pratylenchus* species; Lesion nematodes, *Pratylenchus neglectus*, *Pratylenchus penetrans*, *Pratylenchus curvatus*, *Pratylenchus goodeyi* and other *Pratylenchus* species; Burrowing nematodes, *Radopholus similis* and other *Radopholus* species; Reniform nematodes, *Rotylenchus robustus*, *Rotylenchus reniformis* and other *Rotylenchus* species; *Scutellonema* species; Stubby root nematodes, *Trichodorus primitivus* and other *Trichodorus* species, *Paratrichodorus* species; Stunt
35 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*); Helicella (*H. itala*, *H. obvia*); Helicidae *Helicigona arbustorum*); Helicodiscus; Helix (*H. aperta*); Limax (*L. cinereoniger*, *L. flavus*, *L. marginatus*, *L. maximus*, *L. tenellus*); Lymnaea; Milax (*M. gagates*, *M. marginatus*, *M. sowerbyi*); Opeas; Pomacea (*P. canaticulata*); Vallonia and Zanioides.

10 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*.

15 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
20 by animals, such as scorpion toxins, arachnid toxins, wasp toxins and other insect-specific neurotoxins; toxins produced by fungi, such as *Streptomyces* toxins, plant lectins, such as pea lectins, barley lectins or snowdrop lectins; agglutinins; proteinase inhibitors, such as trypsin inhibitors, serine protease inhibitors, patatin, cystatin, papain inhibitors; ribosome-inactivating proteins (RIP), such as ricin, maize-RIP, abrin, luffin, saporin or bryodin; steroid metabolism enzymes, such as
25 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.

30 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
35 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.

- 5 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.
- 10 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
15 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
20 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
25 (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
30 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
35 to attack by the European corn borer (*Ostrinia nubilalis* and *Sesamia nonagrioides*) by transgenic expression of a Cry1Ab toxin. Bt176 maize also transgenically expresses the enzyme PAT to achieve tolerance to the herbicide glufosinate ammonium.

3. **MIR604 Maize** from Syngenta Seeds SAS, Chemin de l'Hobit 27, F-31 790 St. Sauveur, France, registration number C/FR/96/05/10. Maize which has been rendered insect-resistant by transgenic expression of a modified Cry3A toxin. This toxin is Cry3A055 modified by insertion of a cathepsin-G-protease recognition sequence. The preparation of such transgenic maize plants is described in WO 03/018810.
4. **MON 863 Maize** from Monsanto Europe S.A. 270-272 Avenue de Tervuren, B-1150 Brussels, Belgium, registration number C/DE/02/9. MON 863 expresses a Cry3Bb1 toxin and has resistance to certain Coleoptera insects.
5. **IPC 531 Cotton** from Monsanto Europe S.A. 270-272 Avenue de Tervuren, B-1150 Brussels, Belgium, registration number C/ES/96/02.
6. **1507 Maize** from Pioneer Overseas Corporation, Avenue Tedesco, 7 B-1160 Brussels, Belgium, registration number C/NL/00/10. Genetically modified maize for the expression of the protein Cry1F for achieving resistance to certain Lepidoptera insects and of the PAT protein for achieving tolerance to the herbicide glufosinate ammonium.
7. **NK603 × MON 810 Maize** from Monsanto Europe S.A. 270-272 Avenue de Tervuren, B-1150 Brussels, Belgium, registration number C/GB/02/M3/03. Consists of conventionally bred hybrid maize varieties by crossing the genetically modified varieties NK603 and MON 810. NK603 × MON 810 Maize transgenically expresses the protein CP4 EPSPS, obtained from *Agrobacterium sp.* strain CP4, which imparts tolerance to the herbicide Roundup® (contains glyphosate), and also a Cry1Ab toxin obtained from *Bacillus thuringiensis subsp. kurstaki* which brings about tolerance to certain Lepidoptera, include the European corn borer.
- Transgenic crops of insect-resistant plants are also described in BATS (Zentrum für Biosicherheit und Nachhaltigkeit, Zentrum BATS, Clarastrasse 13, 4058 Basel, Switzerland) Report 2003, (<http://bats.ch>).
- The term "crops" is to be understood as including also crop plants which have been so transformed by the use of recombinant DNA techniques that they are capable of synthesising antipathogenic substances having a selective action, such as, for example, the so-called "pathogenesis-related proteins" (PRPs, see e.g. EP-A-0 392 225). Examples of such antipathogenic substances and transgenic plants capable of synthesising such antipathogenic substances are known, for example, from EP-A-0 392 225, WO 95/33818 and EP-A-0 353 191. The methods of producing such transgenic plants are generally known to the person skilled in the art and are described, for example, in the publications mentioned above.
- Crops may also be modified for enhanced resistance to fungal (for example Fusarium, Anthracnose, or Phytophthora), bacterial (for example Pseudomonas) or viral (for example potato leafroll virus, tomato spotted wilt virus, cucumber mosaic virus) pathogens.

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

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

10 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).

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

20 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.

30 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.

35

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, 5 WO2006/128870, EP 1724392, WO 2005113886 or WO 2007/090739.

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

- 10 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	<i>Agrilus planipennis</i>	Ash
Cerambycidae	<i>Anoplura glabripennis</i>	Hardwoods
Scolytidae	<i>Xylosandrus crassiusculus</i>	Hardwoods
	<i>X. mutilatus</i>	Hardwoods
	<i>Tomicus piniperda</i>	Conifers

15

Table B. Examples of native woodborers of economic importance.

Family	Species	Host or Crop Infested
Buprestidae	<i>Agrilus anxius</i>	Birch
	<i>Agrilus politus</i>	Willow, Maple
	<i>Agrilus sayi</i>	Bayberry, Sweetfern
	<i>Agrilus vittaticollis</i>	Apple, Pear, Cranberry, Serviceberry, Hawthorn

Family	Species	Host or Crop Infested
	<i>Chrysobothris femorata</i>	Apple, Apricot, Beech, Boxelder, Cherry, Chestnut, Currant, Elm, Hawthorn, Hackberry, Hickory, Horsechestnut, Linden, Maple, Mountain-ash, Oak, Pecan, Pear, Peach, Persimmon, Plum, Poplar, Quince, Redbud, Serviceberry, Sycamore, Walnut, Willow
	<i>Texania campestris</i>	Basswood, Beech, Maple, Oak, Sycamore, Willow, Yellow-poplar
Cerambycidae	<i>Goes pulverulentus</i>	Beech, Elm, Nuttall, Willow, Black oak, Cherrybark oak, Water oak, Sycamore
	<i>Goes tigrinus</i>	Oak
	<i>Neoclytus acuminatus</i>	Ash, Hickory, Oak, Walnut, Birch, Beech, Maple, Eastern hophornbeam, Dogwood, Persimmon, Redbud, Holly, Hackberry, Black locust, Honeylocust, Yellow-poplar, Chestnut, Osage-orange, Sassafras, Lilac, Mountain-mahogany, Pear, Cherry, Plum, Peach, Apple, Elm, Basswood, Sweetgum
	<i>Neoptychodes trilineatus</i>	Fig, Alder, Mulberry, Willow, Netleaf hackberry
	<i>Oberea ocellata</i>	Sumac, Apple, Peach, Plum, Pear, Currant, Blackberry
	<i>Oberea tripunctata</i>	Dogwood, Viburnum, Elm, Sourwood, Blueberry, Rhododendron, Azalea, Laurel, Poplar, Willow, Mulberry

Family	Species	Host or Crop Infested
	<i>Oncideres cingulata</i>	Hickory, Pecan, Persimmon, Elm, Sourwood, Basswood, Honeylocust, Dogwood, Eucalyptus, Oak, Hackberry, Maple, Fruit trees
	<i>Saperda calcarata</i>	Poplar
	<i>Strophiona nitens</i>	Chestnut, Oak, Hickory, Walnut, Beech, Maple
Scolytidae	<i>Corthylus columbianus</i>	Maple, Oak, Yellow-poplar, Beech, Boxelder, Sycamore, Birch, Basswood, Chestnut, Elm
	<i>Dendroctonus frontalis</i>	Pine
	<i>Dryocoetes betulae</i>	Birch, Sweetgum, Wild cherry, Beech, Pear
	<i>Monarthrum fasciatum</i>	Oak, Maple, Birch, Chestnut, Sweetgum, Blackgum, Poplar, Hickory, Mimosa, Apple, Peach, Pine
	<i>Phloeotribus liminaris</i>	Peach, Cherry, Plum, Black cherry, Elm, Mulberry, Mountain-ash
	<i>Pseudopityophthorus pruinosis</i>	Oak, American beech, Black cherry, Chickasaw plum, Chestnut, Maple, Hickory, Hornbeam, Hophornbeam
Sesiidae	<i>Paranthrene simulans</i>	Oak, American chestnut
	<i>Sannina uroceriformis</i>	Persimmon
	<i>Synanthedon exitiosa</i>	Peach, Plum, Nectarine, Cherry, Apricot, Almond, Black cherry
	<i>Synanthedon pictipes</i>	Peach, Plum, Cherry, Beach, Black Cherry
	<i>Synanthedon rubrofascia</i>	Tupelo

Family	Species	Host or Crop Infested
	<i>Synanthedon scitula</i>	Dogwood, Pecan, Hickory, Oak, Chestnut, Beech, Birch, Black cherry, Elm, Mountain-ash, Viburnum, Willow, Apple, Loquat, Ninebark, Bayberry
	<i>Vitacea polistiformis</i>	Grape

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

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

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

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

5 Examples of such parasites are:

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

Of the order Mallophagida: *Trimenopon* spp., *Menopon* spp., *Trinoton* spp., *Bovicola* spp.,

10 *Werneckiella* spp., *Lepikentron* spp., *Damalina* spp., *Trichodectes* spp. and *Felicola* spp..

Of the order Diptera and the suborders Nematocera and Brachycera, for example *Aedes* spp., *Anopheles* spp., *Culex* spp., *Simulium* spp., *Eusimulium* spp., *Phlebotomus* spp., *Lutzomyia* spp., *Culicoides* spp., *Chrysops* spp., *Hybomitra* spp., *Atylotus* spp., *Tabanus* spp., *Haematopota* spp.,

15 *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..

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

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

25

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

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

30

Of the orders Actinotrichida (Prostigmata) and Actinotrichida (Astigmata), for example *Acarapis* spp.,

35 *Cheyletiella* spp., *Ornithocheyletia* spp., *Myobia* spp., *Psorergates* spp., *Demodex* spp., *Trombicula* spp., *Listrophorus* spp., *Acarus* spp., *Tyrophagus* spp., *Caloglyphus* spp., *Hypodectes* spp., *Pterolichus* spp., *Psoroptes* spp., *Chorioptes* spp., *Otodectes* spp., *Sarcoptes* spp., *Notoedres* spp., *Knemidocoptes* spp., *Cytodites* spp. and *Laminosioptes* spp..

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.

5 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*,
10 *Heterobostrychus brunneus*, *Sinoxylon spec.* and *Dinoderus minutus*, and also hymenopterans such as *Sirex juvencus*, *Urocerus gigas*, *Urocerus gigas taignus* and *Urocerus augur*, and termites such as *Kaloterme flavicollis*, *Cryptoterme brevis*, *Heteroterme indicola*, *Reticuliterme flavipes*, *Reticuliterme santonensis*, *Reticuliterme lucifugus*, *Mastoterme darwiniensis*, *Zootermopsis nevadensis* and *Coptoterme formosanus*, and bristletails such as *Lepisma saccharina*.

15 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-
20 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
25 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.

30 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.

35 The active ingredients can also be contained in very fine microcapsules. Microcapsules contain the active ingredients in a porous carrier. This enables the active ingredients to be released into the environment in controlled amounts (e.g. slow-release). Microcapsules usually have a diameter of from 0.1 to 500 microns. They contain active ingredients in an amount of about from 25 to 95 % by weight of the capsule weight. The active ingredients can be in the form of a monolithic solid, in the form of

fine particles in solid or liquid dispersion or in the form of a suitable solution. The encapsulating membranes can comprise, for example, natural or synthetic rubbers, cellulose, styrene/butadiene copolymers, polyacrylonitrile, polyacrylate, polyesters, polyamides, polyureas, polyurethane or chemically modified polymers and starch xanthates or other polymers that are known to the person skilled in the art. Alternatively, very fine microcapsules can be formed in which the active ingredient is contained in the form of finely divided particles in a solid matrix of base substance, but the microcapsules are not themselves encapsulated.

The formulation adjuvants that are suitable for the preparation of the compositions according to the invention are known *per se*. As liquid carriers there may be used: water, toluene, xylene, petroleum ether, vegetable oils, acetone, methyl ethyl ketone, cyclohexanone, acid anhydrides, acetonitrile, acetophenone, amyl acetate, 2-butanone, butylene carbonate, chlorobenzene, cyclohexane, cyclohexanol, alkyl esters of acetic acid, diacetone alcohol, 1,2-dichloropropane, diethanolamine, p-diethylbenzene, diethylene glycol, diethylene glycol abietate, diethylene glycol butyl ether, diethylene glycol ethyl ether, diethylene glycol methyl ether, *N,N*-dimethylformamide, dimethyl sulfoxide, 1,4-dioxane, dipropylene glycol, dipropylene glycol methyl ether, dipropylene glycol dibenzoate, diproxitol, alkylpyrrolidone, ethyl acetate, 2-ethylhexanol, ethylene carbonate, 1,1,1-trichloroethane, 2-heptanone, alpha-pinene, d-limonene, ethyl lactate, ethylene glycol, ethylene glycol butyl ether, ethylene glycol methyl ether, gamma-butyrolactone, glycerol, glycerol acetate, glycerol diacetate, glycerol triacetate, hexadecane, hexylene glycol, isoamyl acetate, isobornyl acetate, isooctane, isophorone, isopropylbenzene, isopropyl myristate, lactic acid, laurylamine, mesityl oxide, 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, attapulgitic 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).

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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.

15

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

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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.

30

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

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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 %):

5 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 %

10 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:

15 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:

20 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:

25 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.

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

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

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

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

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

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

10

<u>Dusts</u>	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.

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

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

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

5 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 %

10 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 %

15 The finely ground combination is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired dilution can be obtained by dilution with water. Using such 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. ¹H NMR measurements were recorded on a Bruker 400MHz spectrometer, chemical shifts are given in ppm relevant to a TMS standard. Spectra measured in deuterated solvents as indicated. Either one of the LCMS methods below was used to characterize the compounds. The characteristic LCMS values obtained for each compound were the retention time ("Rt", recorded in minutes) and the measured molecular ion (M+H)⁺.

LCMS and GCMS Methods:

Method 1:

LCMS Methods:

Method 1:

Spectra were recorded on a Mass Spectrometer from Waters (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: 50 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; 1.2-1.5min 100% B; Flow (mL/min) 0.85.

Method 2:

- 5 Spectra were recorded on a Mass Spectrometer from Waters (SQD or ZQ Single quadrupole mass spectrometer) equipped with an electrospray source (Polarity: positive or negative ions, Capillary: 3.00 kV, Cone range: 30-60 V, Extractor: 2.00 V, Source Temperature: 150°C, Desolvation Temperature: 350°C, Cone Gas Flow: 50 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.
- 10 Solvent degasser, binary pump, heated column compartment and diode-array detector. Column: Waters UPLC HSS T3 , 1.8 μm, 30 x 2.1 mm, Temp: 60 °C, DAD Wavelength range (nm): 210 to 500, Solvent Gradient: A = water + 5% MeOH + 0.05 % HCOOH, B= Acetonitrile + 0.05 % HCOOH; gradient: 0 min 0% B, 100% A; 2.7-3.0 min 100% B; Flow (mL/min) 0.85.

15 Method 3: :

- Spectra were recorded on a Mass Spectrometer from Agilent Technologies (6410 Triple Quadrupole mass spectrometer) equipped with an equipped with an electrospray source (Polarity: positive or negative ions, MS2 Scan, Capillary: 4.00 kV, Fragmentor: 100 V, Desolvation Temperature: 350°C, Gas Flow: 11 L/min, Nebulizer Gas: 45 psi, Mass range: 110 to 1000 Da) and a 1200 Series HPLC
- 20 from Agilent: quaternary pump, heated column compartment and diode-array detector. Column: KINETEX EVO C18, 2.6 μm, 50 x 4.6 mm, Temp: 40 °C, DAD Wavelength range (nm): 210 to 400, Solvent Gradient: A = water + 5% Acetonitrile + 0.1 % HCOOH, B= Acetonitrile + 0.1 % HCOOH: gradient: 0 min 0% B, 100%A; 0.9-1.8 min 100% B; Flow (mL/min) 1.8.

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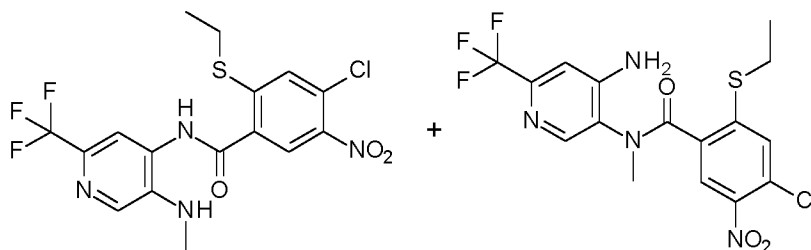
Method 4:

- Spectra were recorded on a Mass Spectrometer from Waters (SQD Single quadrupole mass spectrometer) equipped with an electrospray source (Polarity: positive or negative ions, Full Scan, Capillary: 3.00 kV, Cone range: 41 V, Source Temperature: 150°C, Desolvation Temperature: 500°C,
- 30 Cone Gas Flow: 50 L/Hr, Desolvation Gas Flow: 1000 L/Hr, Mass range: 110 to 800 Da) and a H-Class UPLC from Waters: Binary pump, heated column compartment and diode-array detector. Column: Waters UPLC HSS T3 C18, 1.8 μm, 30 x 2.1 mm, Temp: 40 °C, DAD Wavelength range (nm): 210 to 400, Solvent Gradient: A = water + 5% Acetonitrile + 0.1 % HCOOH, B= Acetonitrile + 0.1 % HCOOH: gradient: 0 min 10% B; 0.-0.2 min 10-50%B; 0.2-0.7 min 50-100% B; Flow (mL/min) 0.8.

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Example P1: Preparation of ethyl-[3-ethyl-6-[3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-2-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-imino-oxo-λ⁶-sulfane (Compound P1)

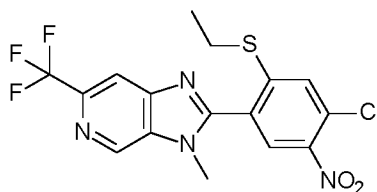
Step A: Preparation of the mixture of 4-chloro-2-ethylsulfanyl-N-[5-(methylamino)-2-(trifluoromethyl)-4-pyridyl]-5-nitro-benzamide and N-[4-amino-6-(trifluoromethyl)-3-pyridyl]-4-chloro-2-ethylsulfanyl-N-methyl-5-nitro-benzamide (Compound I1)



5 Oxalyl chloride (1.23 mL, 13.78 mmol, 1.80 eq.) was added dropwise to a solution of 4-chloro-2-ethylsulfanyl-5-nitro-benzoic acid (prepared according to WO 2016/091731) (2.00 g, 7.64 mmol) in dichloromethane (50 mL) with a catalytic amount of N,N-dimethylformamide (2 drops). Once the gas evolution had stopped the reaction mixture was stirred at room temperature for 1 hour and concentrated under vacuum to give 4-chloro-2-ethylsulfanyl-5-nitro-benzoyl chloride which was used
10 directly.

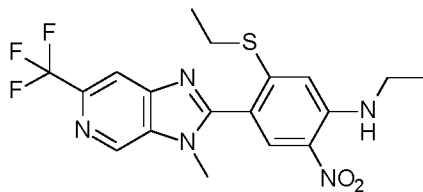
A solution of the crude acid chloride in tetrahydrofuran (20 mL) was added to a solution of N3-methyl-6-(trifluoromethyl)pyridine-3,4-diamine (prepared according to WO 2016/005263) (1.75 g, 9.17 mmol, 1.20 eq.) in ethyl acetate (50 mL) with Hunig's base (2.69 mL, 19.11 mmol, 2.50 eq.). The reaction
15 mixture was stirred at room temperature for 1 hour and concentrated under vacuum to give a crude mixture of 4-chloro-2-ethylsulfanyl-N-[5-(methylamino)-2-(trifluoromethyl)-4-pyridyl]-5-nitro-benzamide and N-[4-amino-6-(trifluoromethyl)-3-pyridyl]-4-chloro-2-ethylsulfanyl-N-methyl-5-nitro-benzamide, which was used without purification. LCMS (method 4): retention time 0.83 min, (M+H)⁺ 436.18.

20 Step B: Preparation of 2-(4-chloro-2-ethylsulfanyl-5-nitro-phenyl)-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridine (compound I2)



A mixture of 4-chloro-2-ethylsulfanyl-N-[5-(methylamino)-2-(trifluoromethyl)-4-pyridyl]-5-nitro-benzamide and N-[4-amino-6-(trifluoromethyl)-3-pyridyl]-4-chloro-2-ethylsulfanyl-N-methyl-5-nitro-benzamide (compound I1 prepared as described above, 18.0 g, 41.4 mmol) in acetic acid (225 mL)
25 was heated at reflux for 8 hours. After evaporation the residue was precipitated from cold water, the resulting solid was filtered off and washed with water then n-hexanes to afford the desired product as a yellow solid. LCMS (method 4): retention time 1.12 min, (M+H)⁺ 417.16.

Step C: Preparation of N-ethyl-5-ethylsulfanyl-4-[3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-2-yl]-2-nitro-aniline (compound I3)

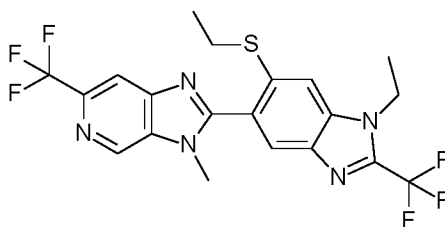


5

Ethylamine (55 mL, 110 mmol, 10.0 eq., 2.0 M in THF solution) was added dropwise to a solution of 2-(4-chloro-2-ethylsulfanyl-5-nitro-phenyl)-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridine (compound I2 prepared as described above, 4.50 g, 11.0 mmol) in tetrahydrofuran (30 mL) at room temperature. After completion of the reaction, the mixture was concentrated under reduced pressure and the residue was diluted with ethyl acetate. The organic phase was washed twice with water then brine, dried over sodium sulfate, filtered and concentrated to afford the crude material N-ethyl-5-ethylsulfanyl-4-[3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-2-yl]-2-nitro-aniline which was used without purification. LCMS (method 4): retention time 1.11 min, (M+H)⁺ 426.28.

10

15 Step D: Preparation of 2-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridine (compound I4)

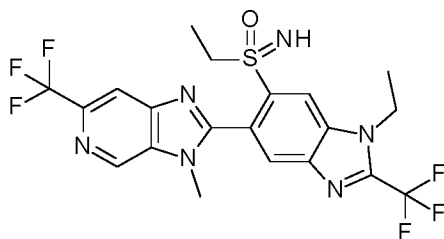


20

Zinc (3.08 g, 47.0 mmol, 4.0 eq.) was added to a solution of N-ethyl-5-ethylsulfanyl-4-[3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-2-yl]-2-nitro-aniline (compound I3 prepared as described above, 5.0 g, 11.8 mmol) in trifluoroacetic acid (100 mL). After refluxing for 6 hours, the reaction mixture was cooled down to room temperature and carefully poured over a saturated sodium hydrogenocarbonate solution. The aqueous phase was extracted twice with dichloromethane, the combined organic phases were filtered over Celite, and concentrated to afford the crude desired product which was used directly in the next step. LCMS (method 4): retention time 1.10 min, (M+H)⁺ 474.39.

25

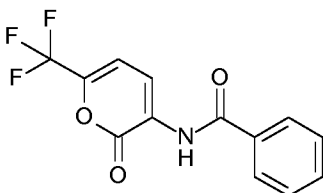
Step E: Preparation of ethyl-[3-ethyl-6-[3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-2-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-imino-oxo-λ⁶-sulfane (compound P1)



(Diacetoxyiodo)benzene (510 mg, 1.58 mmol, 2.5 eq.) and ammonium carbamate (99 mg, 1.27 mmol, 2.0 eq.) were added to a solution of 2-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridine (compound I4 prepared as described above, 300 mg, 0.64 mmol) in methanol (12.7 mL). After stirring for 1 hour at room temperature, the clear solution was poured over a sodium thiosulfate solution. The aqueous phase was extracted twice with dichloromethane, the combined organic layers were washed twice with water, then brine, dried over sodium sulfate, filtered and concentrated. The crude material was purified under reverse phase chromatography conditions (water/acetonitrile) to afford the desired compound as a white solid. LCMS (method 4): retention time 0.96 min, (M+H)⁺ 505.16.

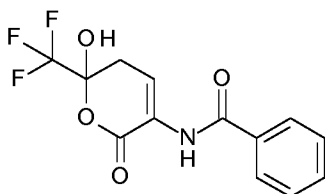
Example P2: Preparation of 2-[6-(ethylsulfonimidoyl)-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-5-methoxy-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (Compound P2)

Step A: Preparation of N-[2-oxo-6-(trifluoromethyl)pyran-3-yl]benzamide (compound I5)



A mixture of 2-benzamidoacetic acid (100 g, 553 mmol, 1.00) and 4-ethoxy-1,1,1-trifluoro-3-buten-2-one (97.8 g, 80.5 mL, 553 mmol, 1.00) in acetic anhydride (660 mL) was heated at 60°C for 20 hours. The red solution was concentrated under vacuum and the residue suspended in 400mL of a 3:1 mixture of cyclohexane and diethyl ether to afford a precipitate which was filtered and washed with cyclohexane. The residue was then suspended in toluene. Filtration afforded the desired compound as a yellow solid (79 g). Concentration of the mother liquor and trituration in toluene followed by filtration gave another portion of desired product. LCMS (method 1): retention time 0.98 min, (M+H)⁺ 284.0.

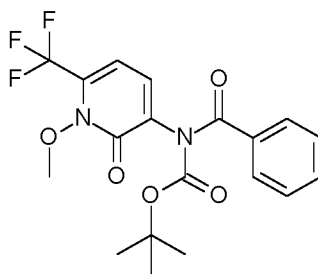
Step B: Preparation of N-[2-hydroxy-1-methoxy-6-oxo-2-(trifluoromethyl)-3H-pyridin-5-yl]benzamide (compound I6)



Sodium hydroxide (1.7 g, 42 mmol, 1.5 eq.) and 0.5 mL water were added to a solution of O-methylhydroxylamine hydrochloride (3.5 g, 42 mmol, 1.5 eq.) in tetrahydrofuran (20 mL). After stirring
5 at room temperature overnight, the clear solution was dried over sodium sulfate, filtered and used directly.

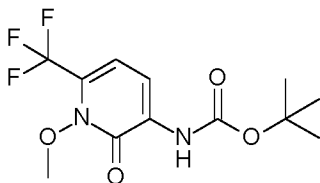
Acetic acid (3.2 mL, 56 mmol, 2.0 eq.) and the solution of O-methylhydroxylamine in tetrahydrofuran prepared above were added to a solution of N-[2-oxo-6-(trifluoromethyl)pyran-3-yl]benzamide (8.0 g, 28 mmol, compound 15 prepared as described above) in tetrahydrofuran (60 mL). After refluxing for
10 4.5 hours the reaction mixture was cooled down to room temperature and concentrated under vacuum. The residue was diluted with water (50 mL), the aqueous layer was extracted with ethyl acetate (3*100 mL), the combined organic layers were dried over sodium sulfate, filtered and concentrated under reduced pressure. Purification of the crude material by flash chromatography (silica gel, 30% ethyl acetate in cyclohexane) afforded the desired product. LCMS (method 3):
15 retention time 1.40 min, (M+H)⁺ 330.8.

Step C: Preparation of tert-butyl N-benzoyl-N-[1-methoxy-2-oxo-6-(trifluoromethyl)-3-pyridyl]carbamate (compound 17)



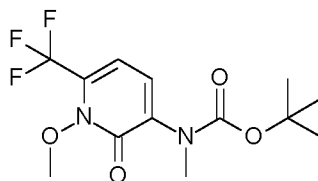
To a 0°C cooled solution of N-[2-hydroxy-1-methoxy-6-oxo-2-(trifluoromethyl)-3H-pyridin-5-yl]benzamide (prepared as described above, 2.0 g, 6.1 mmol, 1.0 eq.) in dichloromethane (20 mL) were added triethylamine (1.7 mL, 12 mmol, 2.0 eq.) and N,N-dimethylpyridin-4-amine (0.15 g, 1.8 mmol, 0.16 eq.). To this solution was added tert-butoxycarbonyl tert-butyl carbonate (3.3 g, 15 mmol, 2.5 eq.). The reaction was stirred for 18 hours at ambient temperature. The mixture was diluted with
25 water (20 mL) and extracted with dichloromethane (2x30 mL). The combined organic layers were dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (silica gel, 30% ethyl acetate-cyclohexane) to afford tert-butyl N-benzoyl-N-[1-methoxy-2-oxo-6-(trifluoromethyl)-3-pyridyl]carbamate. LCMS (method 3): retention time 1.18 min, (M+H)⁺ 412.6.

Step D: Preparation of tert-butyl-N-[1-methoxy-2-oxo-6-(trifluoromethyl)-3-pyridyl]carbamate (compound 18)



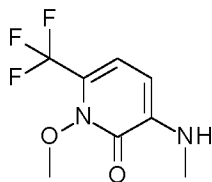
- 5 To a solution tert-butyl-N-benzoyl-N-[1-methoxy-2-oxo-6-(trifluoromethyl)-3-pyridyl]carbamate (compound 17 prepared as described above, 0.5 g, 1.2 mmol, 1.0 eq.) in tetrahydrofuran (5.0 mL) was added a solution of lithium hydroxide hydrate (0.08 g, 1.8 mmol, 1.5 eq.) in water (1.0 mL). After stirring at ambient temperature for 4 hours, the reaction was quenched with water (10 mL) and extracted with ethyl acetate (3x30 mL). The combined organic layers were dried over sodium sulfate,
- 10 filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (silica gel, 30% ethyl acetate-cyclohexane) to afford tert-butyl N-[1-methoxy-2-oxo-6-(trifluoromethyl)-3-pyridyl]carbamate. LCMS (method 3): retention time 1.63 min, [M(-Boc)]⁺ 208.8.

15 Step E: Preparation of tert-butyl N-[1-methoxy-2-oxo-6-(trifluoromethyl)-3-pyridyl]-N-methyl-carbamate (compound 19)



- To a 0°C cooled solution of tert-butyl-N-[1-methoxy-2-oxo-6-(trifluoromethyl)-3-pyridyl]carbamate (compound 18 prepared as described above, 1.9 g, 6.2 mmol, 1.0 eq.) in tetrahydrofuran (20 mL) was added sodium hydride (0.37 g, 9.2 mmol, 1.5 eq.). After stirring for 30 minutes at 0°C, iodomethane
- 20 (1.2 mL, 18 mmol, 3.0 eq.) was added, and the reaction was allowed to warm up to ambient temperature over 1-2 hours. Then, the reaction was diluted with water (15 mL), extracted with ethyl acetate (3x20 mL). The combined organic layers were dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (silica gel, 30% ethyl acetate-cyclohexane) to afford tert-butyl-N-[1-methoxy-2-oxo-6-(trifluoromethyl)-3-
- 25 pyridyl]-N-methyl-carbamate. LCMS (method 3): retention time 1.56 min, [M(-Boc)]⁺ 222.8.

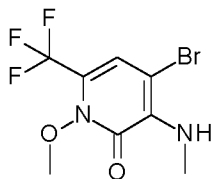
Step F: Preparation of 1-methoxy-3-(methylamino)-6-(trifluoromethyl)pyridin-2-one (compound 110)



To a solution of tert-butyl-N-[1-methoxy-2-oxo-6-(trifluoromethyl)-3-pyridyl]-N-methyl-carbamate (compound I 9 prepared as described above, 1.7 g, 5.3 mmol, 1.0 eq.) in dichloromethane (20 mL) was added 2,2,2-trifluoroacetic acid (2.0 mL, 26 mmol, 4.9 eq.). The reaction was stirred at ambient temperature for 18 hours. The reaction was diluted with water (15 mL), neutralised with sodium bicarbonate solution, extracted with dichloromethane (3x20 mL). The combined organic layers were dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (silica gel, 30% ethyl acetate-cyclohexane) to afford 1-methoxy-3-(methylamino)-6-(trifluoromethyl)pyridin-2-one. LCMS (method 3): retention time 1.38 min, (M+H)⁺ 222.8.

Step G: Preparation of 4-bromo-1-methoxy-3-(methylamino)-6-(trifluoromethyl)pyridin-2-one (compound I11)

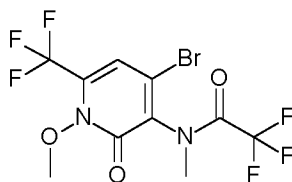
15



To a 0°C cooled solution of 1-methoxy-3-(methylamino)-6-(trifluoromethyl)pyridin-2-one (compound I10 prepared as described above, 1.1 g, 5.0 mmol, 1.0 eq.) in N,N-dimethylformamide (12 mL) was added N-bromosuccinimide (1.3 g, 7.4 mmol, 1.5 eq.). After stirring for 1 hour the reaction mixture was diluted with water (50 mL), and the aqueous phase was extracted with ethyl acetate (3x30 mL). The combined organic layers were dried over sodium sulfate, filtered and concentrated under reduced pressure. Purification of the crude material by flash chromatography (silica gel, 20% ethyl acetate-cyclohexane) afforded 4-bromo-1-methoxy-3-(methylamino)-6-(trifluoromethyl)pyridin-2-one. LCMS (method 4): retention time 1.48 min, (M+H)⁺ 300.7.

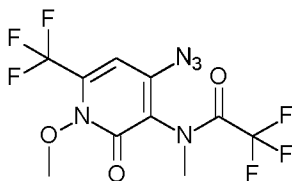
25

Step H: Preparation of N-[4-bromo-6-(difluoromethyl)-1-methoxy-2-oxo-3-pyridyl]-2,2,2-trifluoro-N-methyl-acetamide (compound I12)



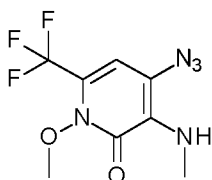
To a solution of 4-bromo-1-methoxy-3-(methylamino)-6-(trifluoromethyl)pyridin-2-one (compound I11 prepared as described above, 500 mg, 1.66 mmol, 1.0 eq.) in dichloromethane (5.0 mL) was added
 5 trifluoroacetic anhydride (0.709 mL, 5.00 mmol, 3.0 eq.) at room temperature. The reaction mixture was stirred for 30 minutes at room temperature and then evaporated to dryness under reduced pressure. Water (50 mL), and an aqueous saturated potassium carbonate solution (10 mL) were added and the aqueous layer was extracted with ethyl acetate (50 mL). The organic layer was washed with brine (15 mL), dried over sodium sulfate, filtered and concentrated. The crude product was
 10 purified over silica gel to afford pure N-[4-bromo-6-(difluoromethyl)-1-methoxy-2-oxo-3-pyridyl]-2,2,2-trifluoro-N-methyl-acetamide. LCMS (method 4): retention time 0.99 min, (M+H)⁺ 397/399.

Step I: Preparation of N-[4-azido-1-methoxy-2-oxo-6-(trifluoromethyl)-3-pyridyl]-2,2,2-trifluoro-N-methyl-acetamide (compound I13)



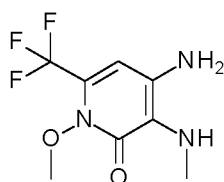
To a solution of N-[4-bromo-1-methoxy-2-oxo-6-(trifluoromethyl)-3-pyridyl]-2,2,2-trifluoro-N-methyl-acetamide (compound I12 prepared as described above, 11.8 g, 29.7 mmol) in N,N-dimethylformamide (110 mL) was added sodium azide (2.9 g, 44.6 mmol, 1.5 eq.) at room
 15 temperature. After stirring overnight at room temperature, the reaction mixture was diluted with cold water (500 mL) and extracted with ethyl acetate (3x150 mL). The combined organic layers were washed with water (100 mL) and brine, dried over sodium sulfate, filtered and concentrated under
 20 reduced pressure below 40°C to afford N-[4-azido-1-methoxy-2-oxo-6-(trifluoromethyl)-3-pyridyl]-2,2,2-trifluoro-N-methyl-acetamide. This material was used in the next step without further purification. LCMS (method 4): retention time 0.99 min, (M+H)⁺ 360.04.

25 Step J: Preparation of 4-azido-1-methoxy-3-(methylamino)-6-(trifluoromethyl)pyridin-2-one (compound I14)



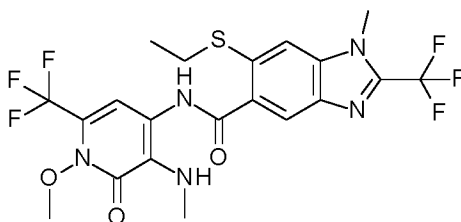
To a solution of N-[4-azido-1-methoxy-2-oxo-6-(trifluoromethyl)-3-pyridyl]-2,2,2-trifluoro-N-methylacetamide (compound I13, prepared as described above, 4.6 g, 13.0 mmol) in methanol (100 mL) was added potassium carbonate (4.7 g, 33.0 mmol, 2.5 eq.). After stirring at room temperature overnight, the reaction mixture was diluted with water (150 mL). The aqueous layer was extracted with ethyl acetate (2x75 mL), the combined organic layers were washed with brine (150 mL), dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified on silica gel (40% ethyl acetate in cyclohexane) to afford 4-azido-1-methoxy-3-(methylamino)-6-(trifluoromethyl)pyridin-2-one. LCMS (method 4): retention time 0.94 min, (M+H)⁺ 264.0.

10 Step K: Preparation of 4-amino-1-methoxy-3-(methylamino)-6-(trifluoromethyl)pyridin-2-one (compound I15)



To a solution of 4-azido-1-methoxy-3-(methylamino)-6-(trifluoromethyl)pyridin-2-one (compound I14, prepared as described above, 1.7 g, 6.5 mmol) in tetrahydrofuran (50 mL) and water (5 mL) at room temperature was added triphenylphosphine (5.1 g, 19 mmol, 3.0 eq.) and the resulting mixture stirred at room temperature for 2 hours. A 2M aqueous hydro-chloric acid solution (9 mL, 18 mmol, 2 mol/L) was added and stirring continued overnight at room temperature. The reaction mixture was concentrated and quenched using an aqueous saturated potassium carbonate solution (20 mL). The aqueous layer was extracted with ethyl acetate (2x75 mL), the combined organic layers washed with brine (100 mL), dried over sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified on silica gel (50-60% ethyl acetate in cyclohexane) to afford 4-amino-1-methoxy-3-(methylamino)-6-(trifluoromethyl)pyridin-2-one. LCMS (method 4): retention time 0.18 min, (M+H)⁺ 238.1.

25 Step L: Preparation of 6-ethylsulfanyl-N-[1-methoxy-3-(methylamino)-2-oxo-6-(trifluoromethyl)-4-pyridyl]-1-methyl-2-(trifluoromethyl)benzimidazole-5-carboxamide (compound I16)

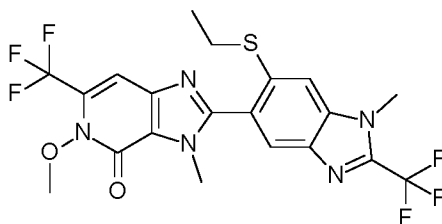


Oxalyl chloride (0.208 mL, 2.34 mmol, 1.2 eq.) was added dropwise to a solution of 6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazole-5-carboxylic acid (prepared according to WO 2016/091731) (600 mg, 1.97 mmol, 1.0 eq.) in dichloromethane (10 mL) with a catalytic amount of N,N-dimethylformamide (2 drops). Once the gas evolution had stopped the reaction mixture was stirred at

room temperature for 1 hour and concentrated under vacuum to give 6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazole-5-carboxyl chloride which was used directly.

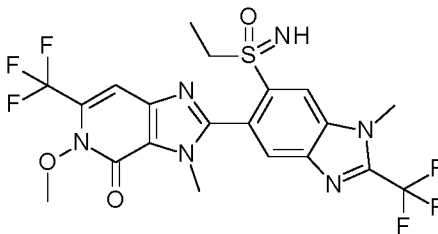
A solution of the crude acid chloride in tetrahydrofuran (20 mL) was added to a solution of 4-amino-1-methoxy-3-(methylamino)-6-(trifluoromethyl)pyridin-2-one (compound I15 prepared as described above, 684 mg, 2.88 mmol, 1.5 eq.) in tetrahydrofuran (20 mL) with Hunig's base (1.34 mL, 7.67 mmol, 4.0 eq.). After stirring for 3 hours at room temperature, the reaction mixture was poured over a potassium carbonate saturated solution (10 mL), diluted with water (50 mL), and the aqueous phase was extracted with ethyl acetate (2*50 mL). The combined organic layers were washed with brine (20 mL), dried over sodium sulfate and concentrated under vacuum to give the crude 6-ethylsulfanyl-N-[1-methoxy-3-(methylamino)-2-oxo-6-(trifluoromethyl)-4-pyridyl]-1-methyl-2-(trifluoromethyl)benzimidazole-5-carboxamide, which was used without purification. LCMS (method 4): retention time 0.88 min, (M+H)⁺ 524.2.

Step M: Preparation of 2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-5-methoxy-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (compound I17)



A solution of crude 6-ethylsulfanyl-N-[1-methoxy-3-(methylamino)-2-oxo-6-(trifluoromethyl)-4-pyridyl]-1-methyl-2-(trifluoromethyl)benzimidazole-5-carboxamide (compound I16, prepared as described above, 400 mg, 0.76 mmol) in acetic acid (10 mL) was heated at reflux for 3 days. After evaporation the residue was diluted in water (15 mL), neutralized carefully with a saturated potassium carbonate aqueous solution (15 mL), and the aqueous phase was extracted with ethyl acetate (2*30 mL). The combined organic layers were washed with brine (30 mL), dried over sodium sulfate, filtered and concentrated under vacuum. Purification of the crude material by flash chromatography (silica gel, 40% ethyl acetate in dichloromethane) afforded the desired compound. LCMS (method 4): retention time 1.02 min, (M+H)⁺ 506.4.

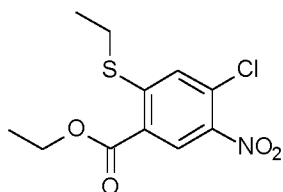
Step N: Preparation of 2-[6-(ethylsulfonimidoyl)-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-5-methoxy-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (Compound P2)



(Diacetoxyiodo)benzene (98 mg, 0.30 mmol, 2.5 eq.) and ammonium carbamate (19 mg, 0.24 mmol, 2.0 eq.) were added to a solution of 2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-5-methoxy-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (compound I17 prepared as described above, 60 mg, 0.12 mmol) in methanol (2.37 mL). After stirring for 2 hours at room temperature, the clear solution was quenched with water (10 mL), and the aqueous phase was extracted with dichloromethane (2*20 mL). The combined organic layers were washed twice with water, then brine, dried over sodium sulfate, filtered and concentrated. The crude material was purified by flash chromatography (silica gel, dichloromethane/MeOH 9:1) to afford the desired compound. LCMS (method 4): retention time 0.85 min, (M+H)⁺ 537.4.

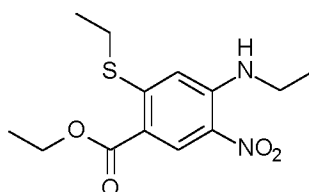
Example P3: Preparation of 2-[1-ethyl-6-(ethylsulfonimidoyl)-2-(trifluoromethyl)benzimidazol-5-yl]-5-methoxy-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (Compound P3)

Step A: Preparation of ethyl 4-chloro-2-ethylsulfanyl-5-nitro-benzoate (compound I18)



A solution of 4-chloro-2-ethylsulfanyl-5-nitro-benzoic acid (prepared as described in WO 2016/142326, 10g, 28.2 mmol) in methanol (100 mL) and concentrated sulfuric acid (10 mL) was heated at reflux and stirred overnight. After cooling down to room temperature, the solvent was removed under reduced pressure, and the residue was diluted with water and saturated sodium carbonate aqueous solution. The aqueous phase was extracted three times with ethyl acetate (100 mL), the combined organic phases were dried over sodium sulfate, filtered and concentrated. The crude material was used directly without further purification.

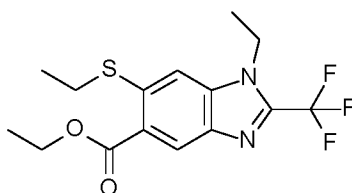
Step B: Preparation of ethyl 4-(ethylamino)-2-ethylsulfanyl-5-nitro-benzoate (compound I19)



Ethylamine (2.0 mol/L in tetrahydrofuran, 10 mL, 20.1 mmol, 6.0 eq.) was added dropwise to a solution of ethyl 4-chloro-2-ethylsulfanyl-5-nitro-benzoate (compound I18 prepared as described above, 1.0 g, 3.35 mmol, 1.0 eq.) in tetrahydrofuran (100 mL). After stirring for 3 hours at room temperature, the solvent was removed under reduced pressure, the residue was taken up in water and a saturated sodium bicarbonate solution, and the aqueous phase was extracted with ethyl acetate. The combined organic phases were washed with brine, dried over sodium sulfate, filtered and

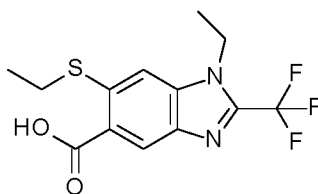
concentrated. Purification of the crude material by flash chromatography (silica gel, 10% ethyl acetate in cyclohexane) afforded the desired compound. LCMS (method 4): retention time 1.20 min, (M+H)⁺ 299.1.

5 Step C: Preparation of ethyl 1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazole-5-carboxylate (compound I20)



Zinc (0.5 g, 8.0 mmol, 4.0 eq.) was added to a 0°C cooled solution of ethyl 4-(ethylamino)-2-ethylsulfanyl-5-nitro-benzoate (compound I19 prepared as described above, 0.6 g, 2.0 mmol, 1.0 eq.) in trifluoroacetic acid (15 mL). The ice bath was removed and the reaction mixture refluxed overnight. After cooling down to room temperature the solvent was removed, the residue was diluted with water and carefully poured over a saturated sodium hydrogenocarbonate solution. The aqueous phase was extracted twice with ethyl acetate, the combined organic phases were washed with brine, filtered over Celite, and concentrated. Purification of the crude material by flash chromatography (silica gel, 30% ethyl acetate in cyclohexane) afforded the desired product. LCMS (method 4): retention time 1.18 min, (M+H)⁺ 347.5.

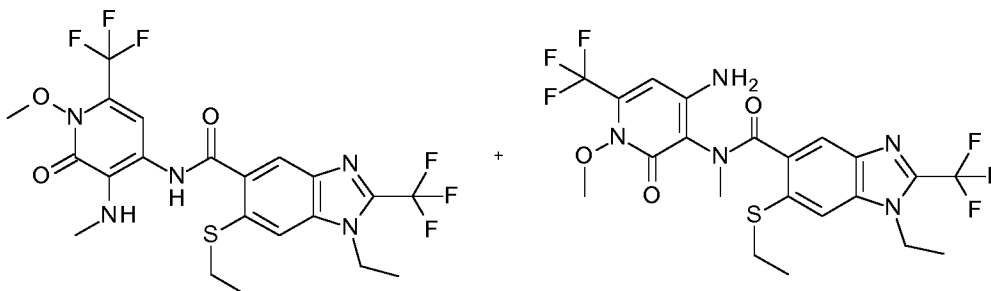
Step D: Preparation of 1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazole-5-carboxylic acid (compound I21)



Lithium hydroxide (156 mg, 3.72 mmol, 2.8 eq.) was added to a solution of ethyl 1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazole-5-carboxylate (compound I20 prepared as described above, 460mg, 1.33mmol, 1.0eq.) in methanol (20mL) and water (3.0mL). After heating at 50°C overnight the reaction mixture was cooled down and concentrated under reduced pressure to remove methanol. The crude was diluted with water, the pH was brought to 1 with addition of 2M hydrochloric acid, and the aqueous phase was extracted with ethyl acetate. The combined organic phases were dried over sodium sulfate, filtered and concentrated to afford 1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazole-5-carboxylic acid. The crude material was pure enough to be used without purification. LCMS (method 4): retention time 0.96 min, (M+H)⁺ 319.0.

30

Step E: Preparation of the mixture of 1-ethyl-6-ethylsulfanyl-N-[1-methoxy-3-(methylamino)-2-oxo-6-(trifluoromethyl)-4-pyridyl]-2-(trifluoromethyl)benzimidazole-5-carboxamide and N-[4-amino-1-methoxy-2-oxo-6-(trifluoromethyl)-3-pyridyl]-1-ethyl-6-ethylsulfanyl-N-methyl-2-(trifluoromethyl)benzimidazole-5-carboxamide (compound I22)



5

Oxalyl chloride (0.153 mL, 1.73 mmol, 1.2 eq.) was added dropwise to a solution 1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazole-5-carboxylic acid (compound I21 prepared as described above) (460 mg, 1.45 mmol, 1.0 eq.) in dichloromethane (50 mL) with a catalytic amount of N,N-dimethylformamide. Once the gas evolution had stopped the reaction mixture was stirred at room temperature for 1.5 hour and concentrated under vacuum to give 1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazole-5-carboxyl chloride which was used directly.

10

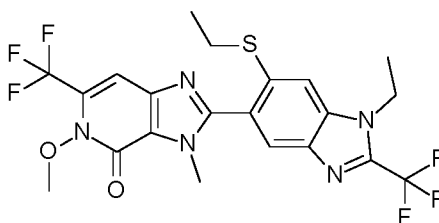
A solution of the crude acid chloride in tetrahydrofuran (100 mL) was added to a solution 4-amino-1-methoxy-3-(methylamino)-6-(trifluoromethyl)pyridin-2-one (compound I15 prepared as described above in example P2) (514 mg, 2.17 mmol, 1.5 eq.) in tetrahydrofuran (100 mL) with Hunig's base (1.01 mL, 5.78 mmol, 4.0 eq.) at 0°C. After stirring overnight at room temperature, the reaction mixture was poured over a potassium carbonate saturated solution (10 mL), diluted with water (100 mL), and the aqueous phase was extracted with ethyl acetate (2*100 mL). The combined organic layers were washed with brine (30 mL), dried over sodium sulfate and concentrated under vacuum to give the crude mixture of 1-ethyl-6-ethylsulfanyl-N-[1-methoxy-3-(methylamino)-2-oxo-6-(trifluoromethyl)-4-pyridyl]-2-(trifluoromethyl)benzimidazole-5-carboxamide and N-[4-amino-1-methoxy-2-oxo-6-(trifluoromethyl)-3-pyridyl]-1-ethyl-6-ethylsulfanyl-N-methyl-2-(trifluoromethyl)benzimidazole-5-carboxamide, which was used without purification. LCMS (method 3): retention time 0.96 min, (M+H)⁺ 538.3.

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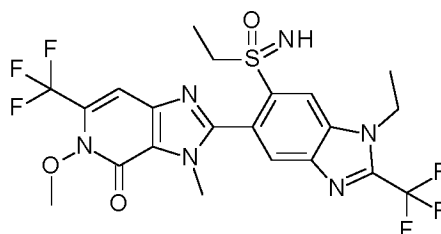
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Step F: Preparation of 2-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-5-methoxy-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (compound I23)



A solution of the crude mixture of 1-ethyl-6-ethylsulfanyl-N-[1-methoxy-3-(methylamino)-2-oxo-6-(trifluoromethyl)-4-pyridyl]-2-(trifluoromethyl)benzimidazole-5-carboxamide and N-[4-amino-1-methoxy-2-oxo-6-(trifluoromethyl)-3-pyridyl]-1-ethyl-6-ethylsulfanyl-N-methyl-2-(trifluoromethyl)benzimidazole-5-carboxamide (compound I22 prepared as described above, 500 mg, 0.93 mmol) in acetic acid (30 mL) was heated at reflux for 36 hours. After cooling down to room temperature the mixture was concentrated under vacuum, and the crude material was diluted with water. The aqueous phase was extracted with ethyl acetate, the combined organic phases were dried over sodium sulfate, filtered and concentrated to afford the crude desired product which was used directly without purification. LCMS (method 4): retention time 1.10 min, (M+H)⁺ 520.4.

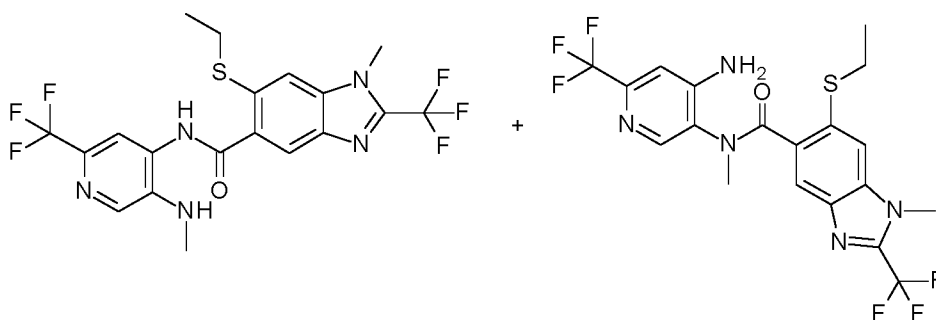
Step G: Preparation of 2-[1-ethyl-6-(ethylsulfonimidoyl)-2-(trifluoromethyl)benzimidazol-5-yl]-5-methoxy-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (Compound P3)



(Diacetoxyiodo)benzene (158 mg, 0.48 mmol, 2.5 eq.) and ammonium carbamate (30 mg, 0.39 mmol, 2.0 eq.) were added to a solution of 2-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-5-methoxy-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (compound I23 prepared as described above, 100 mg, 0.19 mmol) in methanol (10 mL). After stirring for 3 hours at room temperature, the clear solution was quenched with water (10 mL), and the aqueous phase was extracted with dichloromethane. The combined organic layers were washed with brine, dried over sodium sulfate, filtered and concentrated. The crude material was purified by flash chromatography (silica gel, ethyl acetate 60% in cyclohexane) to afford the desired compound. LCMS (method 4): retention time 0.95 min, (M+H)⁺ 551.44.

Example P4: Preparation of ethyl-imino-[3-methyl-6-[3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-2-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-oxo-λ⁶-sulfane (compound P4)

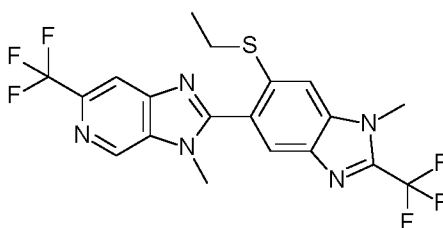
Step A: Preparation of the mixture of 6-ethylsulfanyl-1-methyl-N-[5-(methylamino)-2-(trifluoromethyl)-4-pyridyl]-2-(trifluoromethyl)benzimidazole-5-carboxamide and N-[4-amino-6-(trifluoromethyl)-3-pyridyl]-6-ethylsulfanyl-N,1-dimethyl-2-(trifluoromethyl)benzimidazole-5-carboxamide (compound I24)



Oxalyl chloride (0.071 mL, 0.80 mmol, 1.2 eq.) was added dropwise to a solution of 6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazole-5-carboxylic acid (prepared according to WO 2016/091731) (138 mg, 0.45 mmol, 1.02 eq.) in dichloromethane (5 mL) with a catalytic amount of N,N-dimethylformamide (2 drops). Once the gas evolution had stopped the reaction mixture was stirred at room temperature for 1 hour and concentrated under vacuum to give 6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazole-5-carboxyl chloride which was used directly.

A solution of the crude acid chloride in tetrahydrofuran (3.0 mL) was added to a solution of N3-methyl-6-(trifluoromethyl)pyridine-3,4-diamine (prepared according to WO 2016/005263) (85 mg, 0.44 mmol, 1.0 eq.) in ethyl acetate (5.0 mL) with triethylamine (0.157 mL, 1.11 mmol, 2.5 eq.). After stirring for 1 hour at room temperature, the reaction mixture was poured over a potassium carbonate saturated solution and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with 1M hydrochloric acid, then brine, dried over magnesium sulfate and concentrated under vacuum to give the crude mixture of 6-ethylsulfanyl-1-methyl-N-[5-(methylamino)-2-(trifluoromethyl)-4-pyridyl]-2-(trifluoromethyl)benzimidazole-5-carboxamide and N-[4-amino-6-(trifluoromethyl)-3-pyridyl]-6-ethylsulfanyl-N,1-dimethyl-2-(trifluoromethyl)benzimidazole-5-carboxamide, which was used without purification. LCMS (method 1): retention time 0.96 min, (M+H)⁺ 478.4.

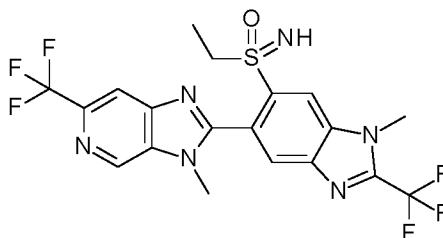
Step B: Preparation of 2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazole-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridine (compound I25)



A solution of crude mixture of 6-ethylsulfanyl-1-methyl-N-[5-(methylamino)-2-(trifluoromethyl)-4-pyridyl]-2-(trifluoromethyl)benzimidazole-5-carboxamide and N-[4-amino-6-(trifluoromethyl)-3-pyridyl]-6-ethylsulfanyl-N,1-dimethyl-2-(trifluoromethyl)benzimidazole-5-carboxamide (compound I24, prepared as described above, 160 mg, 0.34 mmol) in acetic acid (5 mL) was heated at 150°C for 1 hour under microwave irradiation. After cooling down to room temperature the residue was diluted in

water, the pH was brought to ca. 5 by careful addition of 1M sodium hydroxide aqueous solution, and the aqueous phase was extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered and concentrated under vacuum. Purification of the crude material by flash chromatography (silica gel, ethyl acetate in cyclohexane) afforded the desired compound as a slightly yellow solid. LCMS (method 1): retention time 1.04 min, (M+H)⁺ 460.5.

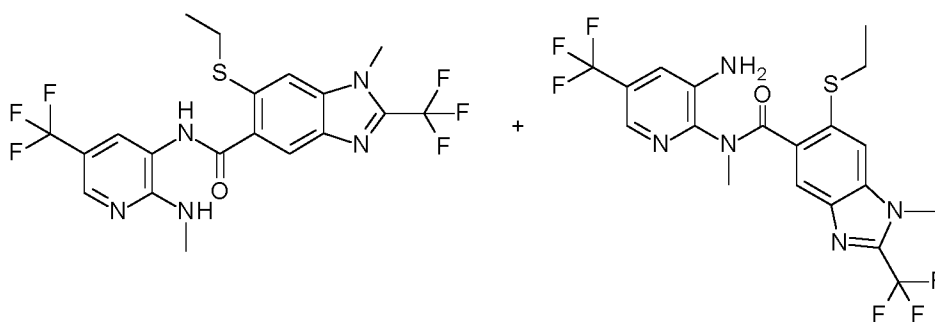
Step C: Preparation of ethyl-imino-[3-methyl-6-[3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-2-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-oxo-λ⁶-sulfane (Compound P4)



10 (Diacetoxyiodo)benzene (614 mg, 1.91 mmol, 2.5 eq.) and ammonium carbamate (119 mg, 1.52 mmol, 2.0 eq.) were added to a solution of 2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridine (compound I25 prepared as described above, 350 mg, 0.76 mmol) in methanol (1.52 mL). After stirring for 2 hours at room temperature, the clear solution was quenched with a saturated sodium thiosulfate aqueous solution, and the aqueous phase
15 was extracted with dichloromethane. The combined organic layers were washed twice with water, then brine, dried over sodium sulfate, filtered and concentrated. The crude material was purified by flash chromatography (silica gel, dichloromethane/MeOH 4:1) to afford the desired compound. LCMS (method 3): retention time 0.82 min, (M+H)⁺ 491.5.

20 **Example P5:** Preparation of ethyl-imino-[3-methyl-6-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-oxo-λ⁶-sulfane (compound P5, table P)

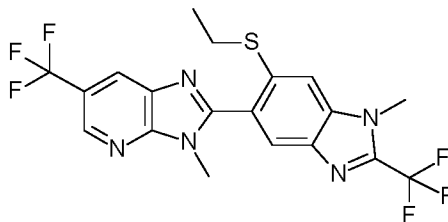
Step A: Preparation of the mixture of 6-ethylsulfanyl-1-methyl-N-[2-(methylamino)-5-(trifluoromethyl)-3-pyridyl]-2-(trifluoromethyl)benzimidazole-5-carboxamide and N-[3-amino-5-(trifluoromethyl)-2-pyridyl]-6-ethylsulfanyl-N,1-dimethyl-2-(trifluoromethyl)benzimidazole-5-carboxamide (compound I26)



Oxalyl chloride (0.084 mL, 0.94 mmol, 1.8 eq.) was added dropwise to a solution of 6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazole-5-carboxylic acid (prepared according to WO 2016/091731) (162mg, 0.53 mmol, 1.02 eq.) in dichloromethane (5 mL) with a catalytic amount of N,N-dimethylformamide (2 drops). Once the gas evolution had stopped the reaction mixture was stirred at room temperature for 1 hour and concentrated under vacuum to give 6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazole-5-carbonyl chloride which was used directly.

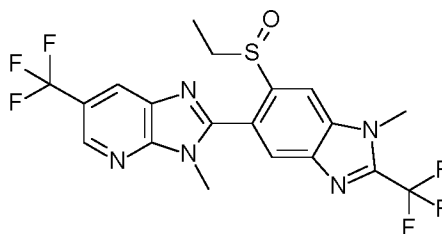
A solution of the crude acid chloride in tetrahydrofuran (3.0 mL) was added to a solution of N2-methyl-5-(trifluoromethyl)pyridine-2,3-diamine (prepared according to WO 2016/142327) (100 mg, 0.52 mmol, 1.0 eq.) in ethyl acetate (5.0 mL) with triethylamine (0.184 mL, 1.31 mmol, 2.5 eq.). After stirring for 1 hour at room temperature, the reaction mixture was poured over a potassium carbonate saturated solution and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with 1M hydrochloric acid, then brine, dried over magnesium sulfate and concentrated under vacuum to give the crude mixture of 6-ethylsulfanyl-1-methyl-N-[5-(methylamino)-2-(trifluoromethyl)-4-pyridyl]-2-(trifluoromethyl)benzimidazole-5-carboxamide and N-[4-amino-6-(trifluoromethyl)-3-pyridyl]-6-ethylsulfanyl-N,1-dimethyl-2-(trifluoromethyl)benzimidazole-5-carboxamide, which was used without purification. LCMS (method 1): retention time 1.02 min, (M+H)⁺ 478.6.

Step B: Preparation of 2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound I27)



A solution of crude mixture of 6-ethylsulfanyl-1-methyl-N-[5-(methylamino)-2-(trifluoromethyl)-4-pyridyl]-2-(trifluoromethyl)benzimidazole-5-carboxamide and N-[4-amino-6-(trifluoromethyl)-3-pyridyl]-6-ethylsulfanyl-N,1-dimethyl-2-(trifluoromethyl)benzimidazole-5-carboxamide (compound I26, prepared as described above, 250 mg, 0.52 mmol) in acetic acid (5 mL) was heated at 150°C for 1 hour under microwave irradiation. After cooling down to room temperature the residue was diluted in water, the pH was brought to ca. 5 by careful addition of 1M sodium hydroxide aqueous solution, and the aqueous phase was extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered and concentrated under vacuum. Purification of the crude material by flash chromatography (silica gel, ethyl acetate in cyclohexane) afforded the desired compound as a slightly yellow solid. LCMS (method 1): retention time 1.12 min, (M+H)⁺ 460.5.

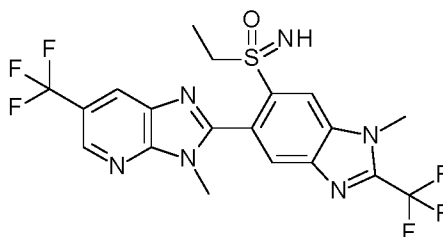
Step C: Preparation of 2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound I28)



3-Chlorobenzenecarboperoxoic acid (70% mass, 268 mg, 1.09 mmol, 1.0 eq.) was added to a solution of 2-[6-ethylsulfonyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound I27 prepared as described above, 500 mg, 1.09 mmol) in dichloromethane (15 mL). After stirring at room temperature for 1 hour, the reaction mixture was poured over iced water. The organic phase was washed carefully with a 50% aqueous sodium hydroxide solution, dried over sodium sulfate, filtered and concentrated. Purification of the crude material by flash chromatography (silica gel, 50% ethyl acetate in cyclohexane) afforded the desired product. LCMS (method 4): retention time 0.98 min, (M+H)⁺ 476.6.

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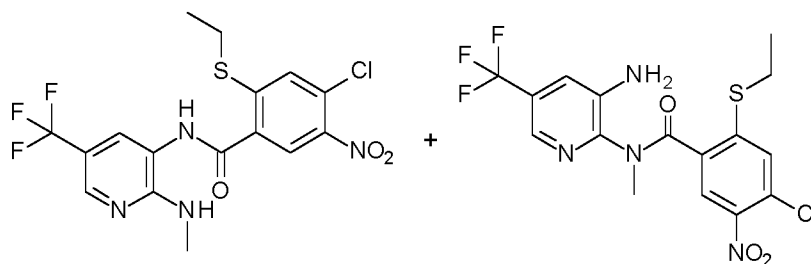
Step D: Preparation of ethyl-imino-[3-methyl-6-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-oxo-λ⁶-sulfane (Compound P5)



Sodium azide (34 mg, 0.52 mmol, 1.0 eq.) was added to a 0°C cooled solution of 2-[6-ethylsulfinyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound I28 prepared as described above, 250 mg, 0.52 mmol) in dichloromethane (15mL). After stirring at 0°C for 1 hour, concentrated sulfuric acid (92%, 1.0 mL) was added dropwise and the reaction mixture was cautiously warmed up to 45°C. After stirring for 5 hours, the reaction mixture was cooled down to room temperature and quenched with a 40% aqueous sodium hydroxide solution. Absence of sodium azide was controlled in the organic phase before drying over sodium sulfate, filtration and evaporation. The crude material was purified by flash chromatography (silica gel, pure ethyl acetate) to afford the desired compound. LCMS (method 4): retention time 0.89 min, (M+H)⁺ 491.5.

25 Example P6: Preparation of ethyl-[3-(2-fluoroethyl)-6-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-imino-oxo-λ⁶-sulfane (compound P6)

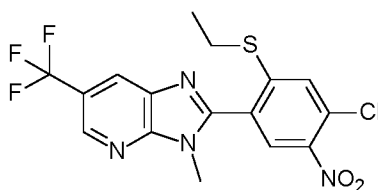
Step A: Preparation of the mixture of 4-chloro-2-ethylsulfanyl-N-[2-(methylamino)-5-(trifluoromethyl)-3-pyridyl]-5-nitro-benzamide and N-[3-amino-5-(trifluoromethyl)-2-pyridyl]-4-chloro-2-ethylsulfanyl-N-methyl-5-nitro-benzamide (Compound I29)



5 Oxalyl chloride (3.35 mL 37.7 mmol, 1.8 eq.) was added dropwise to a solution of 4-chloro-2-ethylsulfanyl-5-nitro-benzoic acid (prepared according to WO 2016/091731) (5.48 g, 20.9 mmol, 1.00 eq.) in dichloromethane (100 mL) with a catalytic amount of N,N-dimethylformamide (2 drops). Once the gas evolution had stopped the reaction mixture was stirred at room temperature for 1 hour and concentrated under vacuum to give 4-chloro-2-ethylsulfanyl-5-nitro-benzoyl chloride which was used
10 directly.

A solution of the crude acid chloride in tetrahydrofuran (20 mL) was added to a solution of N2-methyl-5-(trifluoromethyl)pyridine-2,3-diamine (prepared according to WO 2016/142327) (4.0 g, 20.9 mmol, 1.0 eq.) in ethyl acetate (50 mL) with triethylamine (7.37 mL, 52.3 mmol, 2.5 eq.). After stirring for 1 hour at room temperature, the reaction mixture was poured over a potassium carbonate saturated
15 solution and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with 1M hydrochloric acid, then brine, dried over magnesium sulfate and concentrated under vacuum. The crude material was purified by flash chromatography (silica gel, ethyl acetate in cyclohexane) to give the mixture of 4-chloro-2-ethylsulfanyl-N-[2-(methylamino)-5-(trifluoromethyl)-3-pyridyl]-5-nitro-benzamide and N-[3-amino-5-(trifluoromethyl)-2-pyridyl]-4-chloro-2-ethylsulfanyl-N-methyl-5-nitro-benzamide, which was used without purification. LCMS (method 1): retention time 1.06
20 min, (M+H)⁺ 435.3.

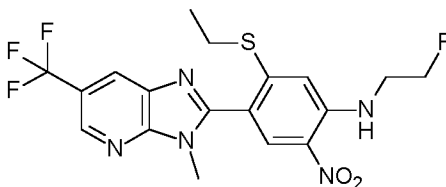
Step B: Preparation of 2-(4-chloro-2-ethylsulfanyl-5-nitro-phenyl)-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound I30)



25 A mixture of 4-chloro-2-ethylsulfanyl-N-[2-(methylamino)-5-(trifluoromethyl)-3-pyridyl]-5-nitro-benzamide and N-[3-amino-5-(trifluoromethyl)-2-pyridyl]-4-chloro-2-ethylsulfanyl-N-methyl-5-nitro-benzamide (compound I29 prepared as described above, 2.21 g, 5.08 mmol,) in acetic acid (17.7 mL) was heated at 150°C for 0.5 hour under microwave irradiation. After cooling down to room
30 temperature the residue was diluted in water, the pH was brought to ca. 5 by careful addition of 1M

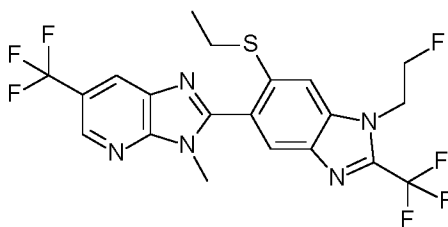
sodium hydroxide aqueous solution, and the aqueous phase was extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered and concentrated under vacuum. Purification of the crude material by flash chromatography (silica gel, ethyl acetate in cyclohexane) afforded the desired compound as a slightly yellow solid. LCMS (method 1): retention time 1.13 min, (M+H)⁺ 417.3.

Step C: Preparation of 5-ethylsulfanyl-N-(2-fluoroethyl)-4-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-2-nitro-aniline (compound I31)



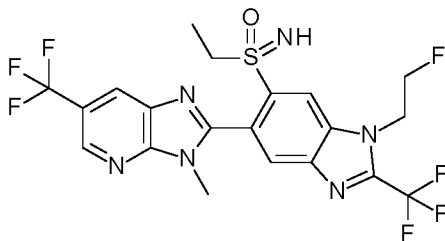
2-Fluoroethylamine hydrochloride (1.59 g, 14.4 mmol, 10.0 eq.) was added in three portions to a solution of 2-(4-chloro-2-ethylsulfanyl-5-nitro-phenyl)-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound I30 prepared as described above, 0.60 g, 1.44 mmol, 1.0 eq.) in tetrahydrofuran (6.0 mL) with triethylamine (0.63 mL, 4.46 mmol, 3.1 eq.) under reflux. After heating for 24 hours, the mixture was cooled down to room temperature and filtered, rinsing with ethyl acetate. The mother liquor was concentrated under vacuum. Precipitation of the crude material in methanol/water afforded the desired product as a yellow solid. LCMS (method 1): retention time 1.09 min, (M+H)⁺ 444.3.

Step D: Preparation of 2-[6-ethylsulfanyl-1-(2-fluoroethyl)-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound I32)



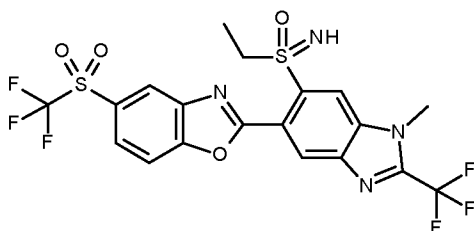
Zinc (146 mg, 2.23 mmol, 3.4 eq.) was added to a 0°C cooled solution of 5-ethylsulfanyl-N-(2-fluoroethyl)-4-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-2-nitro-aniline (compound I31 prepared as described above, 291 mg, 0.66 mmol) in trifluoroacetic acid (10 mL). After refluxing for 3 hours, the reaction mixture was cooled down to room temperature and poured over water. The aqueous phase was extracted with ethyl acetate, the combined organic phases were dried over sodium sulfate, filtered and concentrated. Purification of the crude material by flash chromatography (silica gel, ethyl acetate in cyclohexane) afforded the crude desired product. LCMS (method 1): retention time 1.09 min, (M+H)⁺ 492.7.

Step E: Preparation of ethyl-[3-(2-fluoroethyl)-6-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-imino-oxo- λ^6 -sulfane (compound P6)

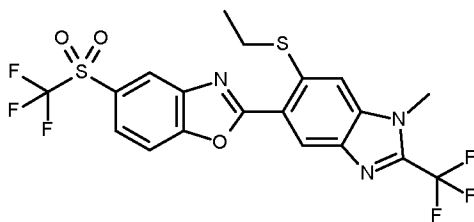


(Diacetoxyiodo)benzene (334 mg, 1.0 mmol, 2.5 eq.) and ammonium carbamate (64 mg, 0.82 mmol, 2.0 eq.) were added to a solution of 2-[6-ethylsulfanyl-1-(2-fluoroethyl)-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (200 mg, 0.41 mmol, compound I32 prepared as described above) in methanol (8.1 mL). After stirring for 2 hours at room temperature, the clear solution was poured over a sodium thiosulfate solution. The aqueous phase was extracted twice with dichloromethane, the combined organic layers were washed with brine, dried over sodium sulfate, filtered and concentrated. The crude material was purified by flash chromatography (silica gel, dichloromethane/methanol 4:1) to afford the desired compound. LCMS (method 4): retention time 0.97 min, (M+H)⁺ 523.4.

Example P7: Preparation of ethyl-imino-[3-methyl-2-(trifluoromethyl)-6-[5-(trifluoromethylsulfonyl)-1,3-benzoxazol-2-yl]benzimidazol-5-yl]-oxo- λ^6 -sulfane (compound P7)



Step A: Preparation of 2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-5-(trifluoromethylsulfonyl)-1,3-benzoxazole (compound I33).



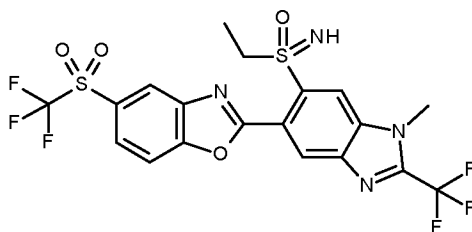
Phosphorus oxychloride (0.390 mL, 4.11 mmol, 2.50 eq.) was added at room temperature to a solution of 6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazole-5-carboxylic acid (prepared according to WO 2016/091731) (500 mg, 1.64 mmol, 1.00 eq.) in nitrobenzene (5.0 mL), followed by addition of 2-amino-4-(trifluoromethylsulfonyl)phenol (prepared according to WO 2017/014214) (369 mg, 1.64 mmol, 1.00 eq.). The reaction mixture was heated up to 120°C and stirred for 4 hours. After cooling

down to room temperature, the reaction mixture was carefully dropped over water, and the aqueous phase was extracted with ethyl acetate. The combined organic phases were washed with brine, dried over sodium sulfate, filtered and concentrated. Purification of the crude material by flash

5 chromatography over silica gel (ethyl acetate in cyclohexane) afforded the desired product. LCMS

(method 4): retention time 1.28 min, (M+H)⁺ 510.44. ¹H NMR (400 MHz, chloroform-d) δ ppm 1.43 - 1.55 (m, 3 H) 1.55 - 1.65 (m, 1 H) 3.14 (q, J = 7.30 Hz, 2 H) 4.01 (s, 3 H) 7.44 (s, 1 H) 7.90 (d, J = 8.56 Hz, 1 H) 8.10 (br d, J = 8.56 Hz, 1 H) 8.59 (s, 1 H) 8.69 (s, 1 H).

10 Step B: Preparation of ethyl-imino-[3-methyl-2-(trifluoromethyl)-6-[5-(trifluoromethylsulfonyl)-1,3-benzoxazol-2-yl]benzimidazol-5-yl]-oxo-λ⁶-sulfane (compound P7)

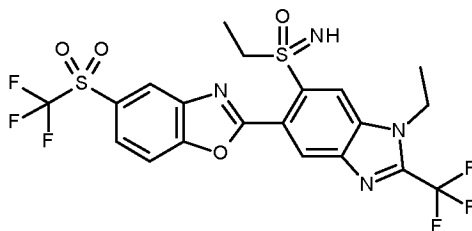


(Diacetoxyiodo)benzene (490 mg, 1.52 mmol, 2.50 eq.) and ammonium carbamate (95 mg, 1.22

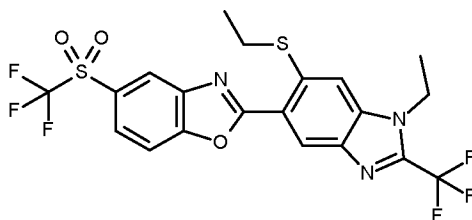
15 mmol, 2.00 eq.) were added to a solution of 2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-5-(trifluoromethylsulfonyl)-1,3-benzoxazole (compound I33 prepared as described above) (310 mg, 0.61 mmol) in methanol (12.2 mL). After stirring for 2 hours at room temperature, the clear solution was poured over a sodium thiosulfate solution. The aqueous phase was extracted twice with dichloromethane, the combined organic layers were washed with water, brine, dried over sodium sulfate, filtered and concentrated. The crude material was purified by

20 flash chromatography (silica gel, dichloromethane/methanol 9:1) to afford the desired compound. LCMS (method 4): retention time 1.09 min, (M+H)⁺ 541.42. ¹H NMR (400 MHz, dimethylsulfoxide-d₆) δ ppm 1.13 - 1.23 (m, 3 H) 4.00 - 4.17 (m, 5 H) 7.22 (d, J = 8.68 Hz, 1 H) 7.69 (dd, J₁ = 8.56, J₂ = 2.20 Hz, 1 H) 8.51 (d, J = 1.96 Hz, 1 H) 8.95 (m, 2 H) 10.38 (br s, 1 H)

25 Example P8: Preparation of ethyl-[3-ethyl-2-(trifluoromethyl)-6-[5-(trifluoromethylsulfonyl)-1,3-benzoxazol-2-yl]benzimidazol-5-yl]-imino-oxo-λ⁶-sulfane (compound P8)

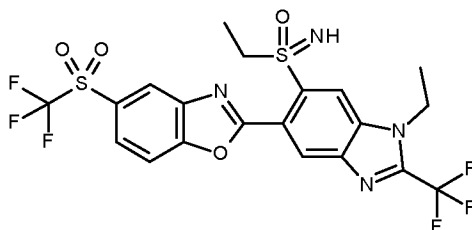


30 Step A: Preparation of 2-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-5-(trifluoromethylsulfonyl)-1,3-benzoxazole (compound I34)



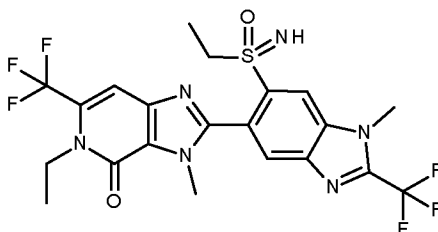
5 The product was prepared according to the same procedure described in step A of example P7 with 2-amino-4-(trifluoromethylsulfonyl)phenol (prepared according to WO 2017/014214) and 1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazole-5-carboxylic acid (compound I21 prepared as described in step D of example P3). LCMS (method 4): retention time 1.38 min, (M+H)⁺ 524.42. ¹H NMR (400 MHz, chloroform-d) δ ppm 1.49 (t, *J* = 7.34 Hz, 3 H) 1.57 (t, *J* = 7.27 Hz, 3 H) 3.13 (q, *J* = 7.34 Hz, 2 H) 4.44 (q, *J* = 7.21 Hz, 2 H) 7.44 (s, 1 H) 7.90 (d, *J* = 8.56 Hz, 1 H) 8.10 (dd, *J*₁ = 8.56, *J*₂ = 1.59 Hz, 1 H) 8.59 (d, *J* = 1.59 Hz, 1 H) 8.70 (s, 1 H)

10 Step B: Preparation of ethyl-[3-ethyl-2-(trifluoromethyl)-6-[5-(trifluoromethylsulfonyl)-1,3-benzoxazol-2-yl]benzimidazol-5-yl]-imino-oxo-λ⁶-sulfane (compound P8)

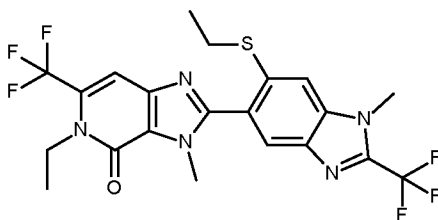


15 The desired product was obtained under the same conditions as described in step B of example P7 using 2-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-5-(trifluoromethylsulfonyl)-1,3-benzoxazole (compound I34 prepared as described above). LCMS (method 4): retention time 1.17 min, (M+H)⁺ 555.47. ¹H NMR (400 MHz, dimethylsulfoxide-d₆) δ ppm 1.19 (t, *J* = 7.21 Hz, 3 H) 1.49 (t, *J* = 7.21 Hz, 3 H) 4.07 (tt, *J*₁ = 14.90, *J*₂ = 7.29 Hz, 2 H) 4.51 - 4.66 (m, 2 H) 7.21 (d, *J* = 8.68 Hz, 1 H) 7.69 (dd, *J*₁ = 8.56, *J*₂ = 2.45 Hz, 1 H) 8.52 (d, *J* = 2.32 Hz, 1 H) 8.99 (d, *J* = 2.20 Hz, 2 H).

20 Example P9: Preparation of 5-ethyl-2-[6-(ethylsulfonimidoyl)-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (compound P9)



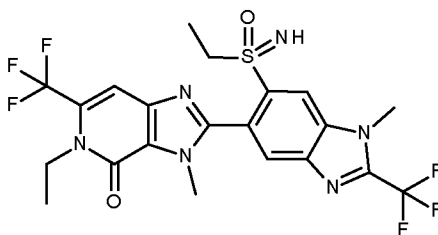
25 Step A: Preparation of 5-ethyl-2-[6-(ethylsulfanyl)-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (compound I35)



The product was prepared according to the same procedure described in step A of example P7 with 4-amino-1-ethyl-3-(methylamino)-6-(trifluoromethyl)pyridin-2-one (prepared according to WO 2016/142326) and 6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazole-5-carboxylic acid

- 5 (prepared according to WO 2016/091731). LCMS (method 4): retention time 1.14 min, (M+H)⁺ 504.45. ¹H NMR (400 MHz, chloroform-d) δ ppm 1.26 (t, *J* = 7.28 Hz, 3 H) 1.41 (t, *J* = 6.90 Hz, 3 H) 2.89 (q, *J* = 7.45 Hz, 2 H) 3.93 (s, 3 H) 4.02 (s, 3 H) 4.27 (q, *J* = 7.03 Hz, 2 H) 7.30 (s, 1 H) 7.54 (s, 1 H) 7.89 (s, 1 H).

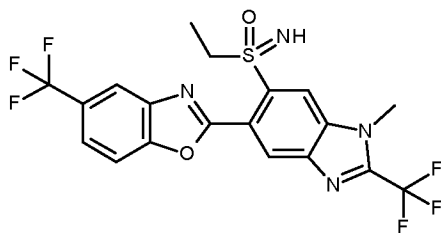
- 10 Step B: Preparation of 5-ethyl-2-[6-(ethylsulfonimidoyl)-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (compound P9)



The desired product was obtained under the same conditions as described in step B of example P7 using 5-ethyl-2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-

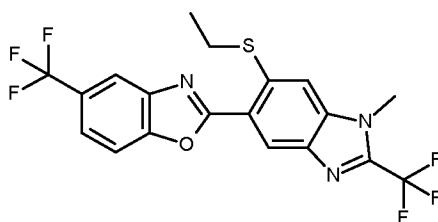
- 15 (trifluoromethyl)imidazo[4,5-c]pyridin-4-one (compound I35 prepared as described above). LCMS (method 4): retention time 0.92 min, (M+H)⁺ 491.39. ¹H NMR (400 MHz, dimethylsulfoxide-d₆) δ ppm 1.29 (t, *J* = 7.40 Hz, 3 H) 1.41 (t, *J* = 6.91 Hz, 3 H) 3.49-3.72 (m, 2 H) 3.89 (s, 3 H) 4.14 (s, 1 H) 4.13-4.15 (m, 1 H) 4.25 (q, *J* = 6.97 Hz, 2 H) 7.23 (s, 1 H) 7.94 (s, 1 H) 8.48 (s, 1 H).

- 20 Example P10: Preparation of ethyl-imino-[3-methyl-2-(trifluoromethyl)-6-[5-(trifluoromethyl)-1,3-benzoxazol-2-yl]benzimidazol-5-yl]-oxo-λ⁶-sulfane (compound P10)



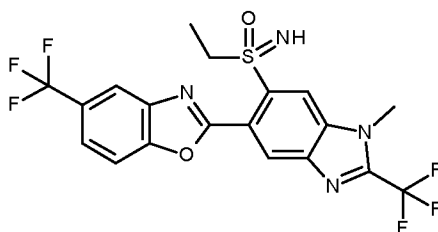
Step A: Preparation of 2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-5-(trifluoromethyl)-1,3-benzoxazole (compound I36).

- 25



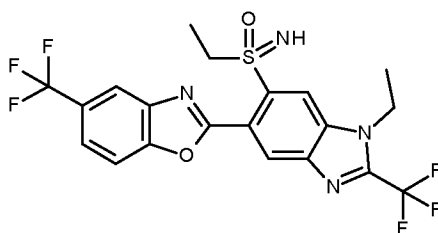
- 5 The product was prepared according to the same procedure described in step A of example P7 with 2-amino-4-(trifluoromethyl)-phenol (CAS 454-81-9) and 6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazole-5-carboxylic acid (prepared according to WO 2016/091731). LCMS (method 4): retention time 1.30 min, (M+H)⁺ 446.39.

Step B: Preparation of ethyl-imino-[3-methyl-2-(trifluoromethyl)-6-[5-(trifluoromethyl)-1,3-benzoxazol-2-yl]benzimidazol-5-yl]-oxo-λ⁶-sulfane (compound P10)

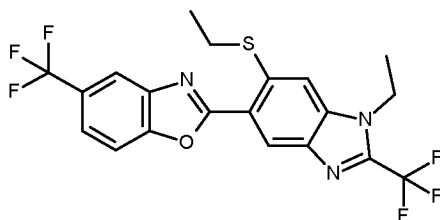


- 10 The desired product was obtained under the same conditions as described in step B of example P7 using 2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-5-(trifluoromethyl)-1,3-benzoxazole (compound I36 prepared as described above). LCMS (method 4): retention time 0.99 min, (M+H)⁺ 477.40. ¹H NMR (400 MHz, dimethylsulfoxide-d₆) δ ppm 1.08 - 1.20 (m, 3 H) 4.00 - 4.18 (m, 5 H) 7.01 (d, J = 8.31 Hz, 1 H) 7.29 (dd, J₁ = 8.44, J₂ = 1.71 Hz, 1 H) 8.20 (d, J = 2.08 Hz, 1 H)
- 15 8.95 (m, 2 H) 10.38 (br s, 1 H).

Example P11: Preparation of ethyl-[3-ethyl-2-(trifluoromethyl)-6-[5-(trifluoromethyl)-1,3-benzoxazol-2-yl]benzimidazol-5-yl]-imino-oxo-λ⁶-sulfane (compound P11)

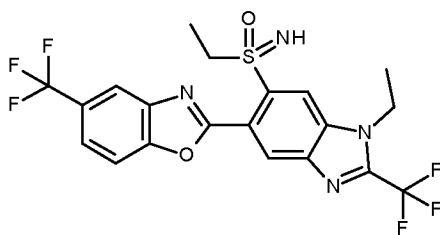


- 20 Step A: Preparation of 2-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-5-(trifluoromethyl)-1,3-benzoxazole (compound I37)



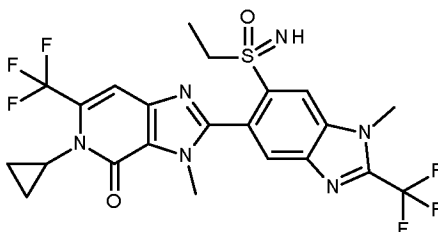
The product was prepared according to the same procedure described in step A of example P7 with 2-amino-4-(trifluoromethyl)-phenol (CAS 454-81-9) and 1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazole-5-carboxylic acid (compound I21 prepared as described in step D of example P3). LCMS (method 4): retention time 1.38 min, (M+H)⁺ 460.37. ¹H NMR (400 MHz, chloroform-d) δ ppm 1.47 (t, *J* = 7.40 Hz, 3 H) 1.57 (t, *J* = 7.28 Hz, 3 H) 3.11 (q, *J* = 7.28 Hz, 2 H) 4.43 (q, *J* = 7.28 Hz, 2 H) 7.43 (s, 1 H) 7.66 – 7.75 (m, 2 H) 8.18 (s, 1 H) 8.65 (s, 1 H).

Step B: Preparation of ethyl-[3-ethyl-2-(trifluoromethyl)-6-[5-(trifluoromethyl)-1,3-benzoxazol-2-yl]benzimidazol-5-yl]-imino-oxo-λ⁶-sulfane (compound P11)

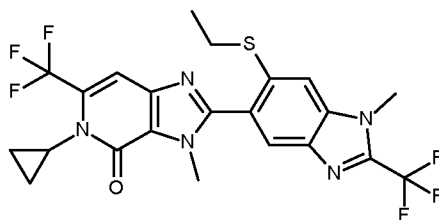


The desired product was obtained under the same conditions as described in step B of example P7 using 2-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-5-(trifluoromethylsulfonyl)-1,3-benzoxazole (compound I34 prepared as described above). LCMS (method 4): retention time 1.07 min, (M+H)⁺ 491.38. ¹H NMR (400 MHz, dimethylsulfoxide-d₆) δ ppm 1.14 (t, *J* = 7.15 Hz, 3 H) 1.49 (t, *J* = 7.28 Hz, 3 H) 3.99 – 4.18 (m, 2 H) 4.51 - 4.65 (m, 2 H) 7.01 (d, *J* = 8.53 Hz, 1 H) 7.29 (br d, *J* = 7.03 Hz, 1 H) 8.21 (s, 1 H) 8.97 (d, *J* = 6.53 Hz, 2 H) 9.32 (br s, 1 H).

Example P12: Preparation of 5-cyclopropyl-2-[6-(ethylsulfonimidoyl)-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (compound P12)



Step A: Preparation of 5-cyclopropyl-2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (compound I38)

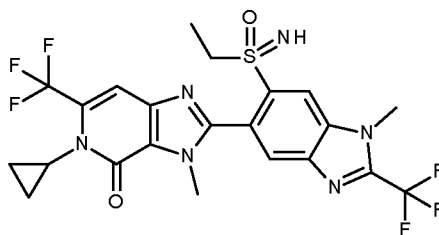


The product was prepared according to the same procedure described in step A of example P7 with 4-amino-1-cyclopropyl-3-(methylamino)-6-(trifluoromethyl)pyridin-2-one (prepared according to WO 2017/001311) and 6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazole-5-carboxylic acid

- 5 (prepared according to WO 2016/091731). LCMS (method 4): retention time 1.11 min, (M+H)⁺ 516.46. ¹H NMR (400 MHz, chloroform-d) δ ppm 1.07 (m, 2 H) 1.22 – 1.35 (m, 5H) 2.89 (q, 2 H) 3.07 – 3.15 (m, 1 H) 3.88 (s, 3 H) 4.01 (s, 3 H) 7.53 (s, 1 H) 7.87 (s, 1 H).

Step B: Preparation of 5-cyclopropyl-2-[6-(ethylsulfonimidoyl)-1-methyl-2-

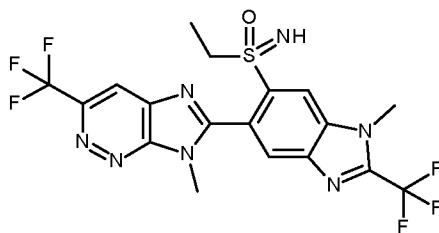
- 10 (trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (compound P12)



The desired product was obtained under the same conditions as described in step B of example P7 using 5-cyclopropyl-2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-

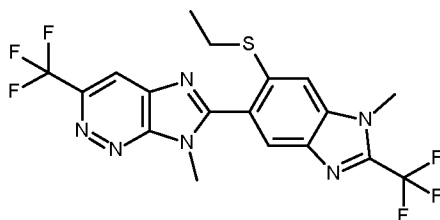
15 (trifluoromethyl)imidazo[4,5-c]pyridin-4-one (compound I38 prepared as described above). LCMS (method 4): retention time 0.94 min, (M+H)⁺ 547.52. ¹H NMR (400 MHz, chloroform-d) δ ppm 1.04 – 1.14 (m, 2 H) 1.25 – 1.31 (m, 5 H) 3.07 – 3.13 (m, 1 H) 3.48 – 3.72 (m, 2 H) 3.85 (s, 3 H) 4.13 (s, 3 H) 7.23 (s, 1 H) 7.94 (s, 1 H) 8.48 (s, 1 H)

- 20 **Example P13:** Preparation of ethyl-imino-[3-methyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-oxo-λ⁶-sulfane (compound P13)



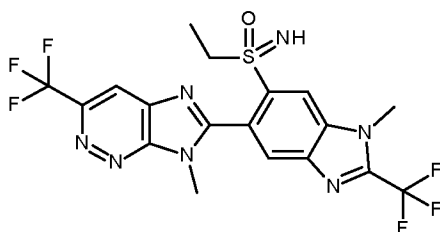
Step A: Preparation of 6-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-7-methyl-3-

25 (trifluoromethyl)imidazo[4,5-c]pyridazine (compound I39).



The product was prepared according to the same procedure described in step A of example P7 with N3-methyl-6-(trifluoromethyl)pyridazine-3,4-diamine (prepared according to WO 2016/059145) and 6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazole-5-carboxylic acid (prepared according to WO 2016/091731). LCMS (method 4): retention time 1.08 min, (M+H)⁺ 461.36. ¹H NMR (400 MHz, chloroform-d) δ ppm 1.23 (t, *J* = 7.28 Hz, 3 H) 2.89 (q, *J* = 7.28 Hz, 2 H) 3.93 (s, 3 H) 4.05 (s, 3 H) 7.65 (s, 1 H) 8.00 (s, 1 H) 8.21(s, 1 H).

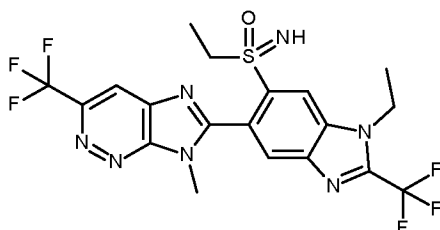
Step B: Preparation of ethyl-imino-[3-methyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-oxo-λ⁶-sulfane (compound P13)



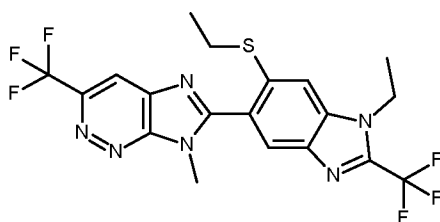
The desired product was obtained under the same conditions as described in step B of example P7 using 6-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazine (compound I39 prepared as described above). LCMS (method 3): retention time 1.32 min, (M+H)⁺ 492.10. ¹H NMR (400 MHz, chloroform-d) δ ppm 1.23 (t, *J* = 7.28 Hz, 3 H) 3.45 - 3.69 (m, 2 H) 3.89 (s, 3 H) 4.17 (s, 3 H) 8.03 (s, 1 H) 8.16 (s, 1 H) 8.53 (s, 1 H).

Example P14: Preparation of ethyl-[3-ethyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-imino-oxo-λ⁶-sulfane (compound P14)

20

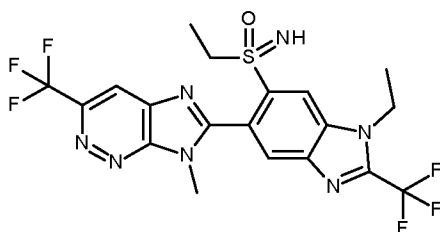


Step A: Preparation of 6-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazine (compound I40)



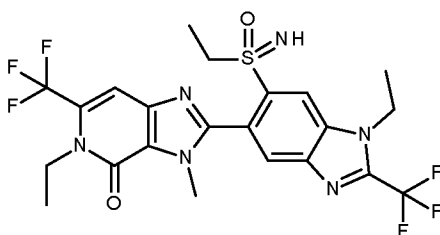
The product was prepared according to the same procedure described in step A of example P7 N3-methyl-6-(trifluoromethyl)pyridazine-3,4-diamine (prepared according to WO 2016/059145) and 1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazole-5-carboxylic acid (compound I21 prepared as described in step D of example P3). LCMS (method 4): retention time 1.15 min, (M+H)⁺ 475.42. ¹H NMR (400 MHz, chloroform-d) δ ppm 1.23 (t, *J* = 7.34 Hz, 3 H) 1.59 (t, *J* = 7.21 Hz, 3 H) 2.88 (q, *J* = 7.34 Hz, 2 H) 3.94 (s, 3 H) 4.48 (q, *J* = 7.21 Hz, 2 H) 7.65 (s, 1 H) 8.00 (s, 1 H) 8.21 (s, 1 H).

Step B: Preparation of ethyl-[3-ethyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-imino-oxo-λ⁶-sulfane (compound P14)

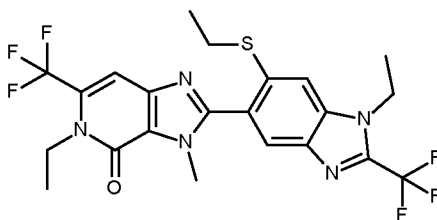


The desired product was obtained under the same conditions as described in step B of example P7 using 6-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazine (compound I40 prepared as described above). LCMS (method 4): retention time 1.07 min, (M+H)⁺ 491.38. ¹H NMR (400 MHz, chloroform-d) δ ppm 1.30 (t, *J* = 7.34 Hz, 3 H) 1.63 (t, *J* = 7.27 Hz, 3 H) 3.49 – 3.72 (m, 2 H) 3.90 (s, 3 H) 4.60 (q, *J* = 7.34 Hz, 2 H) 8.03 (s, 1 H) 8.51 (s, 1 H).

Example P15: Preparation of 5-ethyl-2-[1-ethyl-6-(ethylsulfonimidoyl)-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (compound P15)



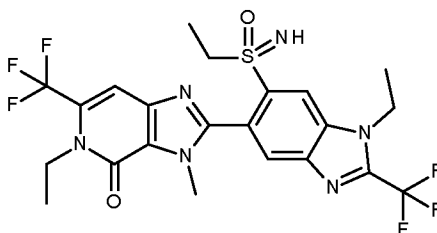
Step A: Preparation of 5-ethyl-2-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (compound I41)



The product was prepared according to the same procedure described in step A of example P7 with 4-amino-1-ethyl-3-(methylamino)-6-(trifluoromethyl)pyridin-2-one (prepared according to WO 2016/142326) and 1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazole-5-carboxylic acid

- 5 (compound I21 prepared as described in step D of example P3). LCMS (method 4): retention time 1.15 min, (M+H)⁺ 518.48. ¹H NMR (400 MHz, chloroform-d) δ ppm 1.25 (t, *J* = 7.28 Hz, 3 H) 1.41 (t, *J* = 6.90 Hz, 3 H) 1.57 (t, *J* = 7.15 Hz, 3 H) 2.88 (q, *J* = 7.36 Hz, 2 H) 3.94 (s, 3 H) 4.27 (q, *J* = 7.03 Hz, 2 H) 4.45 (q, *J* = 7.28 Hz, 2 H) 7.31 (s, 1 H) 7.55 (s, 1 H) 7.90 (s, 1 H).

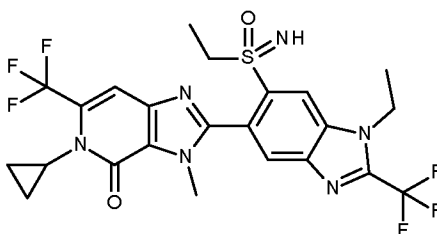
- 10 Step B: Preparation of 5-ethyl-2-[1-ethyl-6-(ethylsulfonimidoyl)-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (compound P15)



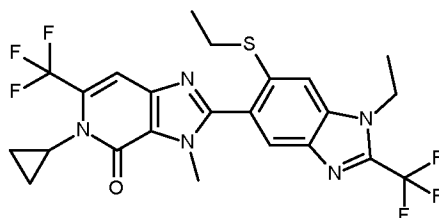
The desired product was obtained under the same conditions as described in step B of example P7 using 5-ethyl-2-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-

- 15 (trifluoromethyl)imidazo[4,5-c]pyridin-4-one (compound I41 prepared as described above). LCMS (method 4): retention time 1.04 min, (M+H)⁺ 549.57. ¹H NMR (400 MHz, chloroform-d) δ ppm 1.29 (t, *J* = 7.34 Hz, 3 H) 1.41 (t, *J* = 6.91 Hz, 3 H) 1.61 (t, *J* = 7.21 Hz, 3 H) 3.51-3.73 (m, 2 H) 3.90 (s, 3 H) 4.25 (q, *J* = 6.89 Hz, 2 H) 4.56 (q, *J* = 7.30 Hz, 2 H) 7.23 (s, 1 H) 7.94 (s, 1 H) 8.47 (s, 1 H).

- 20 Example P16: Preparation of 5-cyclopropyl-2-[1-ethyl-6-(ethylsulfonimidoyl)-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (compound P16)



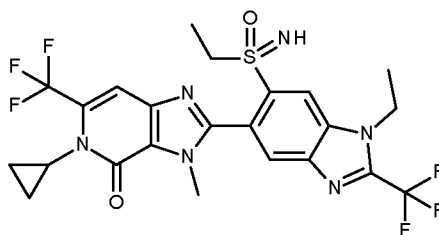
Step A: Preparation of 5-cyclopropyl-2-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (compound I42)



5 The product was prepared according to the same procedure described in step A of example P7 with 4-amino-1-cyclopropyl-3-(methylamino)-6-(trifluoromethyl)pyridin-2-one (prepared according to WO 2017/001311) and 1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazole-5-carboxylic acid (compound I21 prepared as described in step D of example P3). LCMS (method 4): retention time 1.18 min, (M+H)⁺ 530.50. ¹H NMR (400 MHz, dimethylsulfoxide-d₆) δ ppm 0.96 (m, 2 H) 1.16 – 1.22 (m, 5H) 1.43 (t, *J* = 7.15 Hz, 3 H) 3.05 – 3.10 (m, 3 H) 3.77 (s, 3 H) 4.54 (q, 2 H) 7.35 (s, 1 H) 7.94 d, *J* = 6.53 Hz, 2 H).

10

Step B: Preparation of 5-cyclopropyl-2-[1-ethyl-6-(ethylsulfonimidoyl)-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (compound P16)

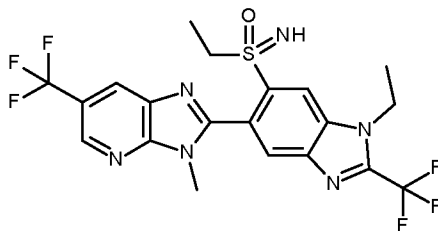


15 The desired product was obtained under the same conditions as described in step B of example P7 using 5-cyclopropyl-2-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (compound I42 prepared as described above). LCMS (method 4): retention time 1.03 min, (M+H)⁺ 561.56. ¹H NMR (400 MHz, chloroform-d) δ ppm 1.07 – 1.11 (m, 2 H) 1.21 – 1.30 (m, 5 H) 1.61 (t, *J* = 7.21 Hz, 3 H) 3.06 – 3.14 (m, 1 H) 3.51 – 3.72 (m, 2 H) 3.86 (s, 3 H) 4.56 (q, *J* = 7.05 Hz, 2 H) 7.20 (s, 1 H) 7.94 (s, 1 H) 8.47 (s, 1 H).

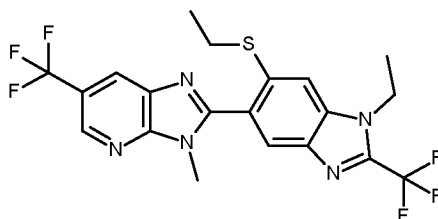
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Example P17: Preparation of ethyl-[3-ethyl-6-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-imino-oxo-λ⁶-sulfane (compound P17)

25

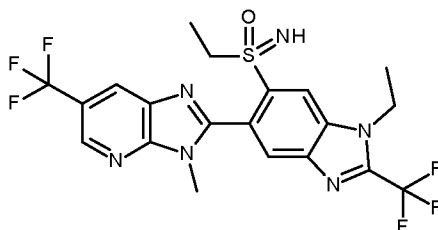


Step A: Preparation of 2-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound I43)



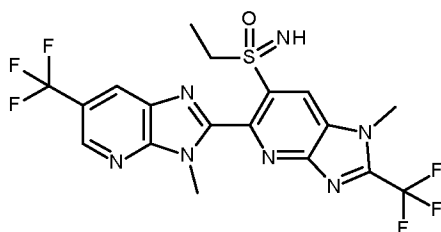
- 5 The product was prepared according to the same procedure described in step A of example P7 using N2-methyl-5-(trifluoromethyl)pyridine-2,3-diamine (prepared according to WO 2016/091731) and 1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazole-5-carboxylic acid (compound I21 prepared as described in step D of example P3). LCMS (method 4): retention time 1.15 min, (M+H)⁺ 475.42. ¹H NMR (400 MHz, chloroform-d) δ ppm 1.23 (t, J = 7.40 Hz, 3 H) 1.59 (t, J = 7.28 Hz, 3 H) 2.87 (q, J = 7.45 Hz, 2 H) 3.73 (s, 3 H) 4.47 (q, J = 7.28 Hz, 2 H) 7.60 (s, 1 H) 7.98 (s, 1 H) 8.36 (d, J = 1.76 Hz, 1 H) 8.74 (s, 1 H).

Step B: Preparation of ethyl-[3-ethyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-imino-oxo-λ⁶-sulfane (compound P17)



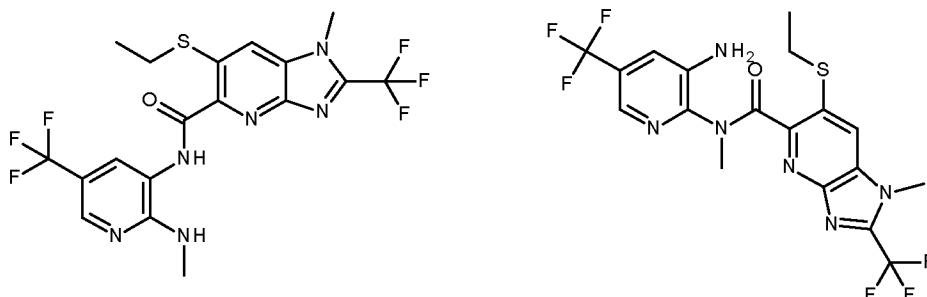
- 15 The desired product was obtained under the same conditions as described in step B of example P7 using 2-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound I43 prepared as described above). LCMS (method 4): retention time 1.01 min, (M+H)⁺ 505.45. ¹H NMR (400 MHz, chloroform-d) δ ppm 1.30 (t, J = 7.40 Hz, 3 H) 1.63 (t, J = 7.27 Hz, 3 H) 3.57 – 3.71 (m, 5 H) 4.58 (q, J = 7.25 Hz, 2 H) 8.01 (s, 1 H) 8.29 (d, J = 1.71 Hz, 1 H) 8.50 (s, 1 H) 8.75 (s, 1 H).

Example P18: Preparation of ethyl-imino-[1-methyl-5-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-2-(trifluoromethyl)imidazo[4,5-b]pyridin-6-yl]-oxo-λ⁶-sulfane (compound P18)



Step A: Preparation of the mixture of 6-ethylsulfanyl-1-methyl-N-[2-(methylamino)-5-(trifluoromethyl)-3-pyridyl]-2-(trifluoromethyl)imidazo[4,5-b]pyridine-5-carboxamide and N-[3-amino-5-(trifluoromethyl)-2-pyridyl]-6-ethylsulfanyl-N,1-dimethyl-2-(trifluoromethyl)imidazo[4,5-b]pyridine-5-carboxamide

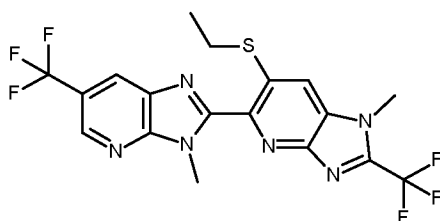
5 (compound I44)



The product was prepared according to the same procedure described in step A of example P4 using N2-methyl-5-(trifluoromethyl)pyridine-2,3-diamine (prepared according to WO 2016/091731) and 6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)imidazo[4,5-b]pyridine-5-carboxylic acid (prepared according to WO 2016/091731), and was used directly without any purification.

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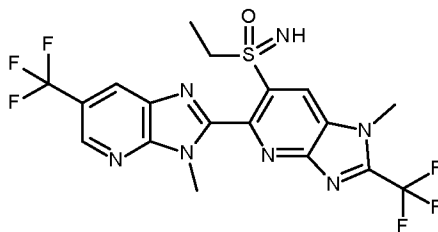
Step B: Preparation of 2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound I45).



15 The product was prepared according to the same procedure described in step B of example P4 using the mixture of 6-ethylsulfanyl-1-methyl-N-[2-(methylamino)-5-(trifluoromethyl)-3-pyridyl]-2-(trifluoromethyl)imidazo[4,5-b]pyridine-5-carboxamide and N-[3-amino-5-(trifluoromethyl)-2-pyridyl]-6-ethylsulfanyl-N,1-dimethyl-2-(trifluoromethyl)imidazo[4,5-b]pyridine-5-carboxamide (compound I44 prepared as described above). LCMS (method 4): retention time 1.04 min, (M+H)⁺ 461.45. ¹H NMR (400 MHz, chloroform-d) δ ppm 1.39 (t, J = 7.34 Hz, 3 H) 3.05 (q, J = 7.38 Hz, 2 H) 4.06 (s, 3 H) 4.11 (s, 3 H) 7.83 (s, 1 H) 8.41 (s, 1 H) 8.77 (s, 1 H).

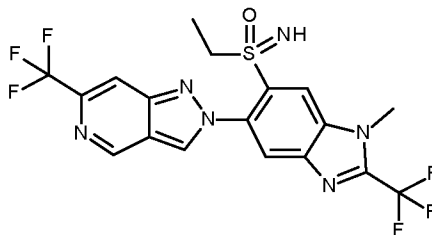
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Step C: Preparation of ethyl-imino-[1-methyl-5-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-2-(trifluoromethyl)imidazo[4,5-b]pyridin-6-yl]-oxo- λ^6 -sulfane (compound P18)

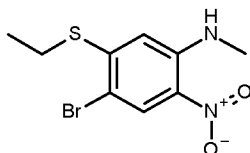


The desired product was obtained under the same conditions as described in step C of example P4 using 2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine (compound I45 prepared as described above). LCMS (method 3): retention time 1.32 min, (M+H)⁺ 492.10. ¹H NMR (400 MHz, dimethylsulfoxide-d₆) δ ppm 1.18 (t, *J* = 7.28 Hz, 3 H) 3.50 - 3.67 (m, 1 H) 3.67 - 3.75 (m, 4 H) 4.20 (s, 3 H) 8.31 (s, 1 H) 8.64 (s, 1 H) 8.87 (s, 1 H) 9.03 (s, 1 H).

Example P19: Preparation of ethyl-imino-[3-methyl-2-(trifluoromethyl)-6-[6-(trifluoromethyl)pyrazolo[4,3-c]pyridin-2-yl]benzimidazol-5-yl]-oxo- λ^6 -sulfane (compound P19)

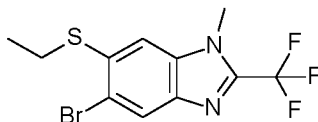


Step A: Preparation of 4-bromo-5-ethylsulfanyl-N-methyl-2-nitro-aniline (compound I46)



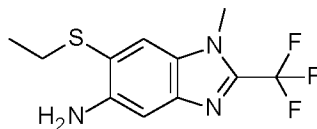
Sodium ethanethiolate (80% mass, 4.3 g, 41 mmol, 1.3 eq.) was added to a solution of 4-bromo-5-fluoro-N-methyl-2-nitro-aniline (prepared according to WO 2008/136378) (7.8 g, 31 mmol) in tetrahydrofuran (100 mL). After stirring for 3 hours at room temperature, the reaction mixture was concentrated. The crude material was poured over ice cold water, and the precipitate obtained was filtered off. The crude material thus obtained was purified by flash chromatography over silica gel (ethyl acetate in dichloromethane) to afford the desired compound. LCMS (method 4): retention time 1.20 min, (M+H)⁺ 291-293 (Br pattern). ¹H NMR (400 MHz, chloroform-d) δ ppm 1.48 (t, *J* = 7.40 Hz, 3 H) 2.98 - 3.07 (m, 5 H) 6.45 (s, 1 H) 8.15 (br s, 1 H) 8.34 (s, 1 H).

Step B: Preparation of 5-bromo-6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazole (compound I47)



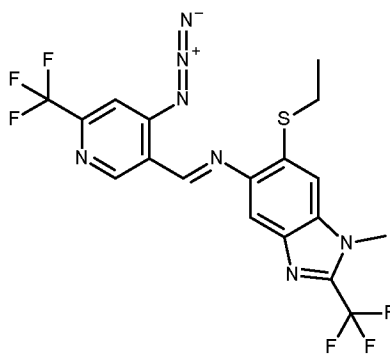
Zinc (7.19 g, 110 mmol, 4.00 eq.) was added to a 0°C cooled solution 4-bromo-5-ethylsulfanyl-N-methyl-2-nitro-aniline (compound 146 prepared as described above, 8.00 g, 27.5 mmol, 1.00 eq.) in trifluoroacetic acid (100 mL) and trifluoroacetic anhydride (30 mL). The ice bath was removed and the reaction mixture refluxed for 6 hours. After cooling down to room temperature the solvent was removed, the residue was diluted with water and carefully poured over a saturated sodium hydrogenocarbonate solution. The aqueous phase was extracted twice with ethyl acetate, the combined organic phases were washed with brine, filtered over Celite, and concentrated. Purification of the crude material by flash chromatography (silica gel, ethyl acetate in dichloromethane) afforded the desired product. LCMS (method 4): retention time 1.17 min, (M+H)⁺ 340.96. ¹H NMR (400 MHz, chloroform-d) δ ppm 1.42 (t, J = 7.40 Hz, 3 H) 3.00 - 3.07 (m, 2 H) 3.94 (s, 3 H) 7.31 (s, 1 H) 8.08 (s, 1 H).

Step C: Preparation of 6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-amine (compound 148)



To a solution of 5-bromo-6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazole (compound 147 prepared as described above) (1.00 g, 2.95 mmol) in tetrahydrofuran (5.00 mL) were added copper sulfate (94 mg, 0.59 mmol, 0.20 eq.), copper powder (38 mg, 0.59 mmol, 0.20 eq.) and ammonium hydroxide solution (30 mass % in water) (8.00 mL, 59.0 mmol, 20.0 eq.). The reaction mixture was heated at 140 °C in an autoclave for 24 hours. After cooling down to room temperature, the reaction mixture was poured over water, and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over sodium sulfate, filtered and concentrated. Purification of the crude material by flash chromatography over silica gel (methanol in dichloromethane) afforded the desired product. LCMS (method 4): retention time 0.95 min, (M+H)⁺ 276.11.

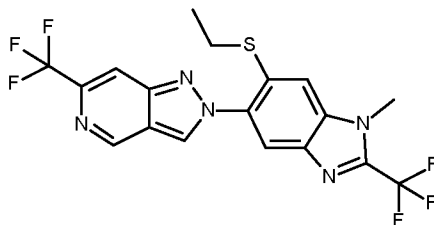
Step D: Preparation of (E)-1-[4-azido-6-(trifluoromethyl)-3-pyridyl]-N-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]methanimine (compound 149)



A 1 mol/L solution of titanium tetrachloride in dichloromethane (1.27 mL, 1.27 mmol, 1.10 eq.) was added dropwise to a 0 °C cooled mixture of 6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-amine (compound I48 prepared as described above) (319 mg, 1.16 mmol, 1.00 eq.),

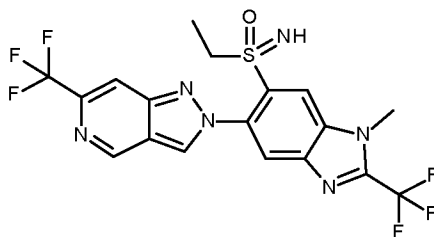
- 5 4-azido-6-(trifluoromethyl)pyridine-3-carbaldehyde (prepared according to WO 2018/052136) (250 mg, 1.16 mmol, 1.00 eq.) and triethylamine (0.53 mL, 3.82 mmol, 3.30 eq.) in dichloromethane (5.00 mL) under nitrogen. After stirring for 1 hour at 0 °C the reaction mixture was warmed up to room temperature and stirred for a further 2 hours. After evaporation under reduced pressure, the residue was suspended in toluene (10 mLX2) and filtered through a pad of Celite. The filtrate was concentrated to dryness under reduced pressure to afford the crude product which was used directly without
- 10 purification.

Step E: Preparation of 2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine (compound I50)



- 15 A mixture of (E)-1-[4-azido-6-(trifluoromethyl)-3-pyridyl]-N-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]methanimine (compound I49 prepared as described above) (380 mg, 0.80 mmol) in toluene (10 mL) was heated at reflux for 6 hours (apparatus equipped with sufficient gas outlet). After cooling down to room temperature, the reaction mixture was poured over ice cold
- 20 water, and the aqueous phase was extracted with ethyl acetate. The combined organic phases were dried over sodium sulfate, filtered and concentrated. The crude material was purified by flash chromatography over silica gel (ethyl acetate in cyclohexane) to afford the desired product. LCMS (method 4): retention time 1.13 min, (M+H)⁺ 446.49. ¹H NMR (400 MHz, chloroform-d) δ ppm 1.17 - 1.33 (m, 3 H) 2.81 (q, *J* = 7.13 Hz, 2 H) 4.05 (s, 3 H) 7.27 (s, 1 H) 7.59 (s, 1 H) 8.03 (s, 1 H) 8.12 (s,
- 25 1H) 8.57 (br s, 1 H) 9.39 (br s, 1 H).

Step F: Preparation of ethyl-imino-[3-methyl-2-(trifluoromethyl)-6-[6-(trifluoromethyl)pyrazolo[4,3-c]pyridin-2-yl]benzimidazol-5-yl]-oxo- λ^6 -sulfane (compound P19)



- The product was obtained by treating 2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine (compound I50 prepared as described above) under the same conditions described in step C of example P18. LCMS (method 4): retention time 0.89 min, (M+H)⁺ 477.57. ¹H NMR (400 MHz, dimethylsulfoxide-d₆) δ ppm 1.12 (t, *J* = 7.34 Hz, 3 H) 3.34 – 3.42 (m, 2 H) 4.17 (s, 3 H) 8.29 (s, 1 H) 8.35 (s, 1 H) 8.59 (s, 1 H) 9.17 (s, 1 H) 9.48 (s, 1 H).
- 10 Table P

Entry	IUPAC name	STRUCTURE	RT (min)	[M+H] ⁺	Method	MP °C
P1	ethyl-[3-ethyl-6-[3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-2-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-imino-oxo- λ^6 -sulfane		0.96	505.16	4	130 - 132
P2	2-[6-(ethylsulfonimidoyl)-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-5-methoxy-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one		0.85	537.42	4	145 - 147
P3	2-[1-ethyl-6-(ethylsulfonimidoyl)-2-(trifluoromethyl)benzimidazol-5-yl]-5-methoxy-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one		0.95	551.44	4	220 - 222
P4	ethyl-imino-[3-methyl-6-[3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-2-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-oxo- λ^6 -sulfane		0.82	491.51	3	166 - 168
P5	ethyl-imino-[3-methyl-6-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-oxo- λ^6 -sulfane		0.89	491.5	4	120 - 122
P6	ethyl-[3-(2-fluoroethyl)-6-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-imino-oxo- λ^6 -sulfane		0.97	523.4	4	130 - 132
P7	ethyl-imino-[3-methyl-2-(trifluoromethyl)-6-[5-(trifluoromethylsulfonyl)-1,3-benzoxazol-2-yl]benzimidazol-5-yl]-oxo- λ^6 -sulfane		1.09	541.42	4	279 - 281

P8	ethyl-[3-ethyl-2-(trifluoromethyl)-6-[5-(trifluoromethylsulfonyl)-1,3-benzoxazol-2-yl]benzimidazol-5-yl]-imino-oxo- λ^6 -sulfane		1.17	555.47	4	260 - 262
P9	5-ethyl-2-[6-(ethylsulfonimidoyl)-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one		0.92	491.39	4	254 - 256
P10	ethyl-imino-[3-methyl-2-(trifluoromethyl)-6-[5-(trifluoromethyl)-1,3-benzoxazol-2-yl]benzimidazol-5-yl]-oxo- λ^6 -sulfane		0.99	477.40	4	
P11	ethyl-[3-ethyl-2-(trifluoromethyl)-6-[5-(trifluoromethyl)-1,3-benzoxazol-2-yl]benzimidazol-5-yl]-imino-oxo- λ^6 -sulfane		1.07	491.38	4	280 - 999
P12	5-cyclopropyl-2-[6-(ethylsulfonimidoyl)-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one		0.94	547.52	4	
P13	ethyl-imino-[3-methyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-oxo- λ^6 -sulfane		1.32	492.10	3	
P14	ethyl-[3-ethyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-imino-oxo- λ^6 -sulfane		0.97	506.47	4	129 - 131

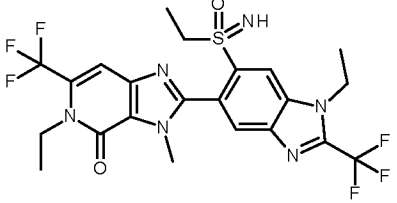
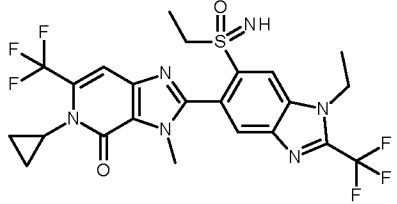
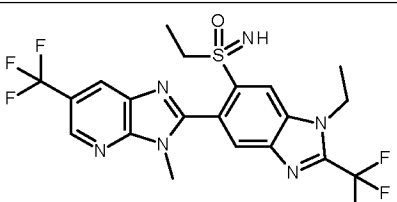
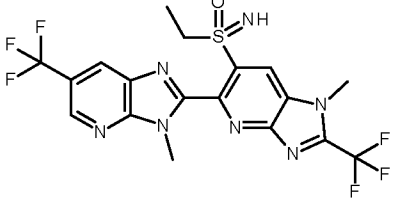
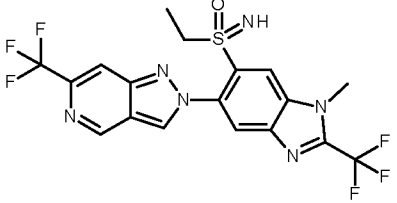
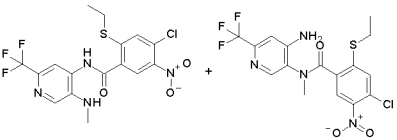
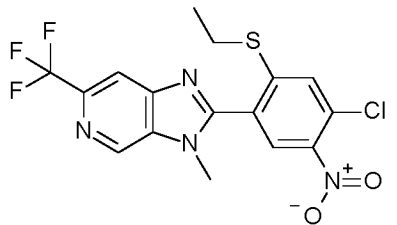
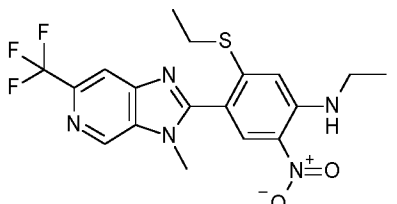
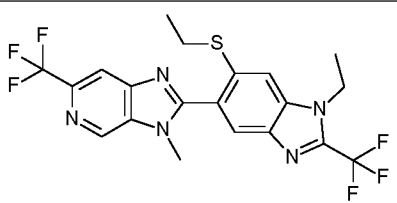
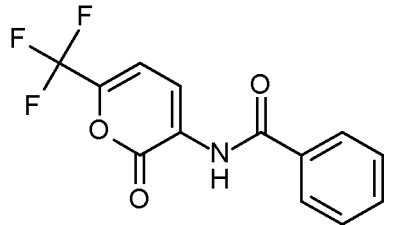
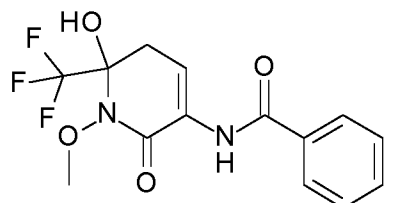
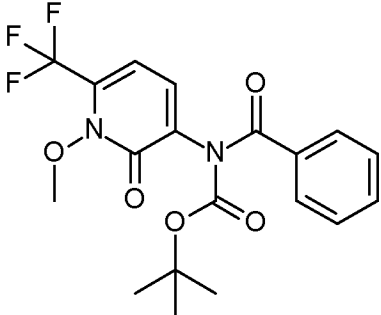
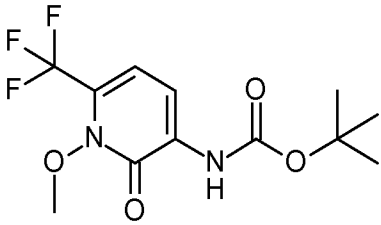
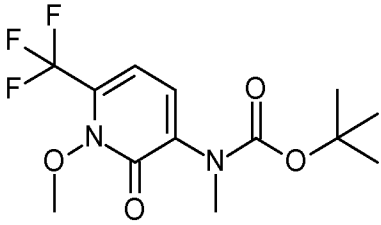
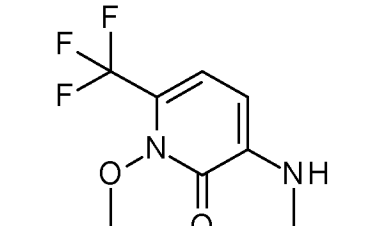
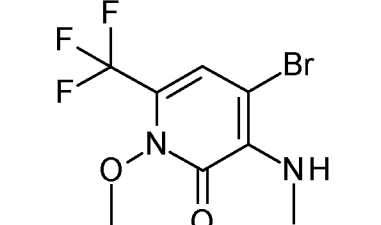
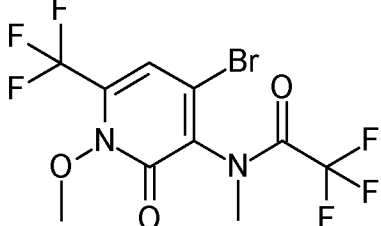
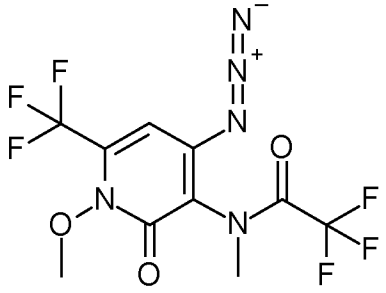
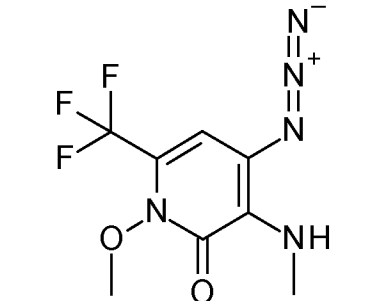
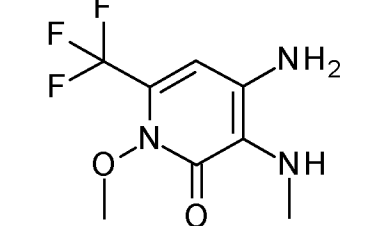
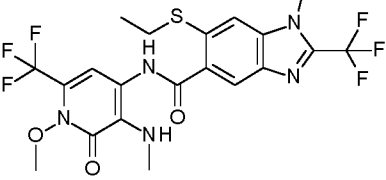
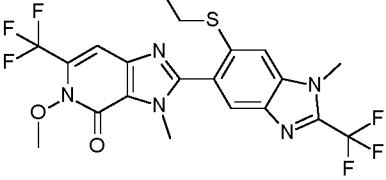
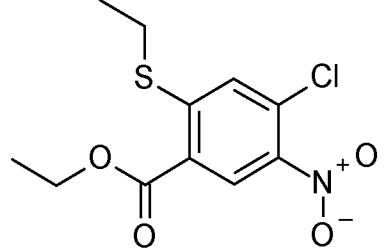
P15	5-ethyl-2-[1-ethyl-6-(ethylsulfonimidoyl)-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one		1.04	549.57	4	244 - 245
P16	5-cyclopropyl-2-[1-ethyl-6-(ethylsulfonimidoyl)-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one		1.03	561.56	4	128 - 130
P17	ethyl-[3-ethyl-6-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-imino-oxo-λ ⁶ -sulfane		1.01	505.45	4	107 - 109
P18	ethyl-imino-[1-methyl-5-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-2-(trifluoromethyl)imidazo[4,5-b]pyridin-6-yl]-oxo-λ ⁶ -sulfane		0.88	492.35	4	
P19	ethyl-imino-[3-methyl-2-(trifluoromethyl)-6-[6-(trifluoromethyl)pyrazolo[4,3-c]pyridin-2-yl]benzimidazol-5-yl]-oxo-λ ⁶ -sulfane		0.89	477.57	4	140 - 142

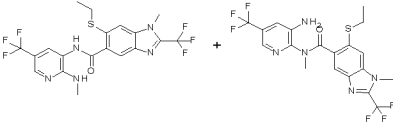
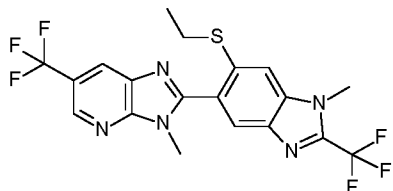
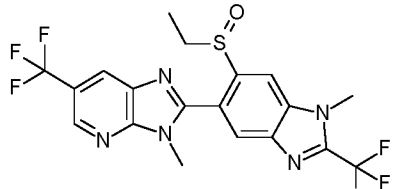
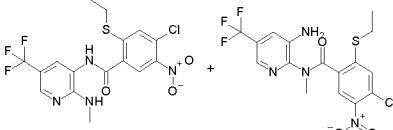
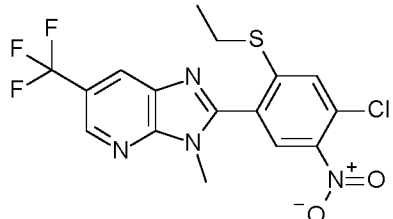
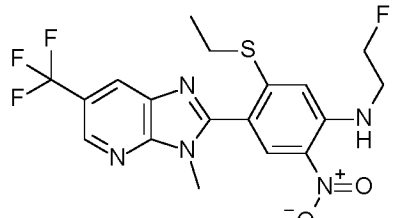
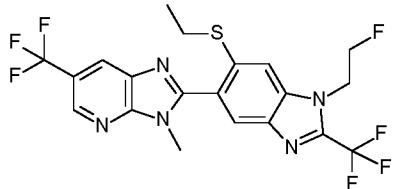
Table I

Entry	IUPAC name	STRUCTURE	RT (min)	[M+H] ⁺	Method	MP °C
I1	Mixture of 4-chloro-2-ethylsulfanyl-N-[5-(methylamino)-2-(trifluoromethyl)-4-pyridyl]-5-nitro-benzamide and N-[4-amino-6-(trifluoromethyl)-3-pyridyl]-4-chloro-2-ethylsulfanyl-N-methyl-5-nitro-benzamide		0.83	436.18	4	
I2	2-(4-chloro-2-ethylsulfanyl-5-nitro-phenyl)-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridine		1.12	417.16	4	
I3	N-ethyl-5-ethylsulfanyl-4-[3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-2-yl]-2-nitro-aniline		1.11	426.28	4	
I4	2-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridine		1.10	474.39	4	
I5	N-[2-oxo-6-(trifluoromethyl)pyran-3-yl]benzamide		0.98	284.00	1	
I6	N-[2-hydroxy-1-methoxy-6-oxo-2-(trifluoromethyl)-3H-pyridin-5-yl]benzamide		1.40	330.8	3	

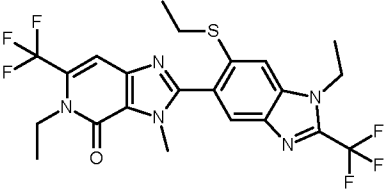
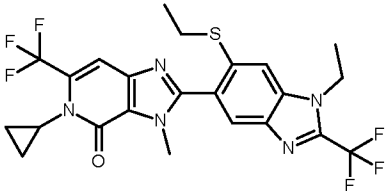
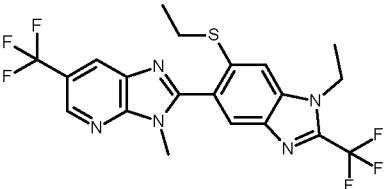
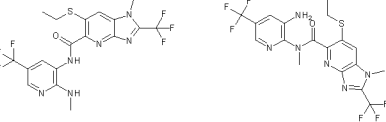
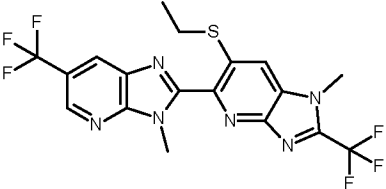
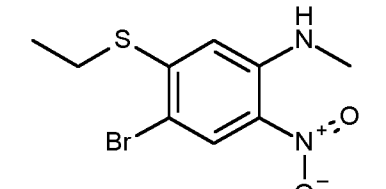
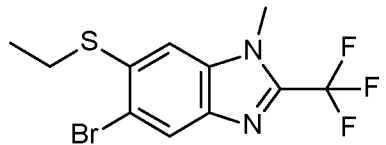
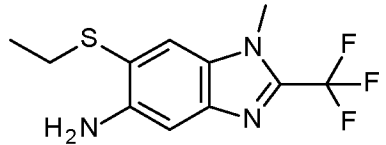
17	tert-butyl N-benzoyl-N-[1-methoxy-2-oxo-6-(trifluoromethyl)-3-pyridyl]carbamate		1.18	412.6	3	
18	tert-butyl-N-[1-methoxy-2-oxo-6-(trifluoromethyl)-3-pyridyl]carbamate		1.63	208.8 (-Boc)	3	
19	tert-butyl N-[1-methoxy-2-oxo-6-(trifluoromethyl)-3-pyridyl]-N-methylcarbamate		1.56	222.8 (-Boc)	3	
110	1-methoxy-3-(methylamino)-6-(trifluoromethyl)pyridin-2-one		1.38	222.8	3	
111	4-bromo-1-methoxy-3-(methylamino)-6-(trifluoromethyl)pyridin-2-one		1.48	300.7	4	
112	N-[4-bromo-6-(difluoromethyl)-1-methoxy-2-oxo-3-pyridyl]-2,2,2-trifluoro-N-methylacetamide		0.99	397/399	4	

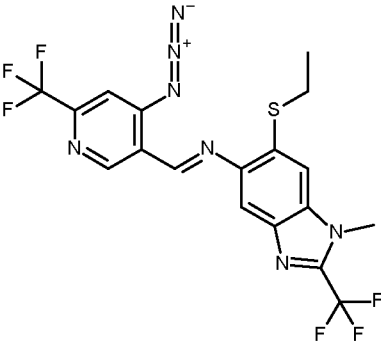
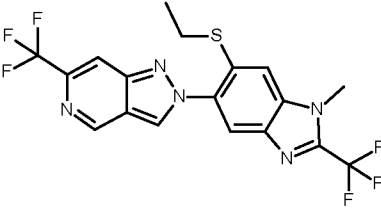
I13	N-[4-azido-1-methoxy-2-oxo-6-(trifluoromethyl)-3-pyridyl]-2,2,2-trifluoro-N-methyl-acetamide		0.99	360.04	4	
I14	4-azido-1-methoxy-3-(methylamino)-6-(trifluoromethyl)pyridin-2-one		0.94	264.04	4	
I15	4-amino-1-methoxy-3-(methylamino)-6-(trifluoromethyl)pyridin-2-one		0.18	238.09	4	
I16	6-ethylsulfanyl-N-[1-methoxy-3-(methylamino)-2-oxo-6-(trifluoromethyl)-4-pyridyl]-1-methyl-2-(trifluoromethyl)benzimidazole-5-carboxamide		0.88	524.19	4	
I17	2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-5-methoxy-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one		1.02	506.38	4	
I18	ethyl 4-chloro-2-ethylsulfanyl-5-nitrobenzoate					

I19	ethyl 4-(ethylamino)-2-ethylsulfanyl-5-nitrobenzoate		1.20	299.11	4	
I20	ethyl 1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazole-5-carboxylate		1.18	347.49	4	
I21	1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazole-5-carboxylic acid		0.96	319.09	4	
I22	mixture of 1-ethyl-6-ethylsulfanyl-N-[1-methoxy-3-(methylamino)-2-oxo-6-(trifluoromethyl)-4-pyridyl]-2-(trifluoromethyl)benzimidazole-5-carboxamide and N-[4-amino-1-methoxy-2-oxo-6-(trifluoromethyl)-3-pyridyl]-1-ethyl-6-ethylsulfanyl-N-methyl-2-(trifluoromethyl)benzimidazole-5-carboxamide		0,96	538.39	3	
I23	2-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-5-methoxy-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one		1.10	520.41	4	
I24	mixture of 6-ethylsulfanyl-1-methyl-N-[5-(methylamino)-2-(trifluoromethyl)-4-pyridyl]-2-(trifluoromethyl)benzimidazole-5-carboxamide and N-[4-amino-6-(trifluoromethyl)-3-pyridyl]-6-ethylsulfanyl-N,1-dimethyl-2-(trifluoromethyl)benzimidazole-5-carboxamide		0.96	478.4	1	
I25	2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridine		1.04	460.5	1	

I26	mixture of 6-ethylsulfanyl-1-methyl-N-[2-(methylamino)-5-(trifluoromethyl)-3-pyridyl]-2-(trifluoromethyl)benzimidazole-5-carboxamide and N-[3-amino-5-(trifluoromethyl)-2-pyridyl]-6-ethylsulfanyl-N,1-dimethyl-2-(trifluoromethyl)benzimidazole-5-carboxamide		1.02	478.6	1	
I27	2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine		1.12	460.5	1	
I28	2-[6-ethylsulfinyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine		0.98	476.6	4	
I29	mixture of 4-chloro-2-ethylsulfanyl-N-[2-(methylamino)-5-(trifluoromethyl)-3-pyridyl]-5-nitro-benzamide and N-[3-amino-5-(trifluoromethyl)-2-pyridyl]-4-chloro-2-ethylsulfanyl-N-methyl-5-nitro-benzamide		1.06	435.3	1	
I30	2-(4-chloro-2-ethylsulfanyl-5-nitro-phenyl)-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine		1.13	417.3	1	
I31	5-ethylsulfanyl-N-(2-fluoroethyl)-4-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-2-nitro-aniline		1.09	444.3	1	
I32	2-[6-ethylsulfanyl-1-(2-fluoroethyl)-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine		1.09	492.7	1	

I33	2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-5-(trifluoromethylsulfonyl)-1,3-benzoxazole		1.28	510.44	4	
I34	2-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-5-(trifluoromethylsulfonyl)-1,3-benzoxazole		1.38	524.42	4	
I35	5-ethyl-2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one		1.14	504.45	4	
I36	2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-5-(trifluoromethyl)-1,3-benzoxazole		1.30	446.39	4	
I37	2-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-5-(trifluoromethyl)-1,3-benzoxazole		1.38	460.37	4	
I38	5-cyclopropyl-2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one		1.11	516.46	4	
I39	6-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazine		1.08	461.36	4	
I40	6-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazine		1.15	475.42	4	

I41	5-ethyl-2-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one		1.21	518.48	4	
I42	5-cyclopropyl-2-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one		1.18	530.50	4	
I43	2-[1-ethyl-6-ethylsulfanyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridine		1.21	474.40	4	
I44	mixture of 6-ethylsulfanyl-1-methyl-N-[2-(methylamino)-5-(trifluoromethyl)-3-pyridyl]-2-(trifluoromethyl)imidazo[4,5-b]pyridine-5-carboxamide and N-[3-amino-5-(trifluoromethyl)-2-pyridyl]-6-ethylsulfanyl-N,1-dimethyl-2-(trifluoromethyl)imidazo[4,5-b]pyridine-5-carboxamide					
I45	6-ethylsulfanyl-1-methyl-5-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-2-(trifluoromethyl)imidazo[4,5-b]pyridine		1.04	461.45	4	
I46	4-bromo-5-ethylsulfanyl-N-methyl-2-nitro-aniline		1.20	291-293	4	
I47	5-bromo-6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazole		1.17	340.96	4	
I48	6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-amine		0.95	276.11	4	

I49	(E)-1-[4-azido-6-(trifluoromethyl)-3-pyridyl]-N-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]methanimine					
I50	2-[6-ethylsulfanyl-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-6-(trifluoromethyl)pyrazolo[4,3-c]pyridine		1.13	446.49	4	

- The activity of the compositions according to the invention can be broadened considerably, and adapted to prevailing circumstances, by adding other insecticidally, acaricidally and/or fungicidally active ingredients. The mixtures of the compounds of formula I with other insecticidally, acaricidally and/or fungicidally active ingredients may also have further surprising advantages which can also be described, in a wider sense, as synergistic activity. For example, better tolerance by plants, reduced phytotoxicity, insects can be controlled in their different development stages or better behaviour during their production, for example during grinding or mixing, during their storage or during their use.
- Suitable additions to active ingredients here are, for example, representatives of the following classes of active ingredients: organophosphorus compounds, nitrophenol derivatives, thioureas, juvenile hormones, formamidines, benzophenone derivatives, ureas, pyrrole derivatives, carbamates, pyrethroids, chlorinated hydrocarbons, acylureas, pyridylmethyleamino derivatives, macrolides, neonicotinoids and *Bacillus thuringiensis* preparations.
- The following mixtures of the compounds of formula I with active ingredients are preferred (the abbreviation "TX" means "one compound selected from the group consisting of the compounds described in Tables A-1, A-2, A-3, A-4, A-5, A-6, A-7, A-8, A-9, A-10, A-11, A-12, A-13 and P of the present invention"):
- an adjuvant selected from the group of substances consisting of petroleum oils (alternative name) (628) + TX,
- an acaricide selected from the group of substances consisting of 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, azotohoate (889) + TX, benomyl (62) + TX, benoxafos (alternative name) [CCN] + TX, benzoximate (71) + TX, benzyl benzoate (IUPAC name) [CCN] + TX, bifenazate (74) + TX, bifenthrin (76) + TX, binapacryl (907) + TX, brofenvalerate (alternative name) + TX, bromocyclen (918) + TX, bromophos (920) + TX, bromophos-ethyl (921) + TX, bromopropylate (94) + TX, buprofezin (99) + TX, butocarboxim (103) + TX, butoxycarboxim (104) + TX, butylpyridaben (alternative name) + TX, calcium polysulfide (IUPAC name) (111) + TX, camphechlor (941) + TX, carbanolate (943) + TX, carbaryl (115) + TX, carbofuran (118) + TX, carbophenothion (947) + TX, CGA 50'439 (development code) (125) + TX, chinomethionat (126) + TX, chlordbenside (959) + TX, chlordimeform (964) + TX, chlordimeform hydrochloride (964) + TX, chlorfenapyr (130) + TX, chlorfenethol (968) + TX, chlorfenson (970) + TX, chlorfensulfide (971) + TX, chlorfenvinphos (131) + TX, chlorobenzilate (975) + TX, chloromebuform (977) + TX, chloromethiuron (978) + TX, chloropropylate (983) + TX, chlorpyrifos (145) + TX, chlorpyrifos-methyl (146) + TX, chlorthiophos (994) + TX, cinerin I (696) + TX, cinerin II (696) + TX, cinerins (696) + TX, clofentezine (158) + TX, closantel (alternative name) [CCN] + TX, coumaphos (174) + TX, crotamiton (alternative name) [CCN] + TX, crotoxyphos (1010) + TX, cufraneb (1013) + TX, cyanthoate (1020) + TX, cyflumetofen (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, diafenthion (226) + TX, dimpropyridaz + TX, dialifos (1042) + TX, diazinon (227) + TX, dichlofluanid (230) + TX, dichlorvos (236) + TX, dicliphos (alternative name) + TX, dicofol (242) + TX, dicrotophos (243) + TX, dienochlor (1071) + TX, dimefox (1081) + TX, dimethoate (262) + TX, dinactin (alternative name) (653) + TX, dinex (1089) + TX, dinex-diclexine (1089) + TX, dinobuton (269) + TX, dinocap (270) + TX, dinocap-4 [CCN] + TX, dinocap-6 [CCN] + TX, dinocton (1090) + TX, dinopenton (1092) + TX, dinosulfon (1097) + TX, dinoterbon (1098) + TX, dioxathion (1102) + TX, diphenyl sulfone (IUPAC name) (1103) + TX, disulfiram (alternative name) [CCN] + TX, disulfoton (278) + TX, DNOC (282) + TX, dofenapyn (1113) + TX, doramectin (alternative name) [CCN] + TX, endosulfan (294) + TX, endothion (1121) + TX, EPN (297) + TX, eprinomectin (alternative name) [CCN] + TX, ethion (309) + TX, ethoate-methyl (1134) + TX, etoxazole (320) + TX, etrimfos (1142) + TX, fenazaflor (1147) + TX, fenazaquin (328) + TX, fenbutatin oxide (330) + TX, fenothiocarb (337) + TX, fenpropathrin (342) + TX, fenpyrad (alternative name) + TX, fenpyroximate (345) + TX, fenson (1157) + TX, fentrifanil (1161) + TX, fenvalerate (349) + TX, fipronil (354) + TX, fluacrypyrim (360) + TX, fluazuron (1166) + TX, flubenzimine (1167) + TX, flucycloxuron (366) + TX, flucythrinate (367) + TX, fluenetil (1169) + TX, flufenoxuron (370) + TX, flumethrin (372) + TX, fluorbenside (1174) + TX, fluvalinate (1184) + TX, FMC 1137 (development code) (1185) + TX,

formetanate (405) + TX, formetanate hydrochloride (405) + TX, formothion (1192) + TX, formparanate (1193) + TX, gamma-HCH (430) + TX, glyodin (1205) + TX, halfenprox (424) + TX, heptenophos (432) + TX, hexadecyl cyclopropanecarboxylate (IUPAC/Chemical Abstracts name) (1216) + TX, hexythiazox (441) + TX, iodomethane (IUPAC name) (542) + TX, isocarbophos (alternative name) (473) + TX, isopropyl O-(methoxyaminothiophosphoryl)salicylate (IUPAC name) (473) + TX, ivermectin (alternative name) [CCN] + TX, jasmolin I (696) + TX, jasmolin II (696) + TX, jodfenphos (1248) + TX, lindane (430) + TX, lufenuron (490) + TX, malathion (492) + TX, malonoben (1254) + TX, mecarbam (502) + TX, mephosfolan (1261) + TX, mesulfen (alternative name) [CCN] + TX, methacrifos (1266) + TX, methamidophos (527) + TX, methidathion (529) + TX, methiocarb (530) + TX, methomyl (531) + TX, methyl bromide (537) + TX, metolcarb (550) + TX, mevinphos (556) + TX, mexacarbate (1290) + TX, milbemectin (557) + TX, milbemycin oxime (alternative name) [CCN] + TX, mipafox (1293) + TX, monocrotophos (561) + TX, morphothion (1300) + TX, moxidectin (alternative name) [CCN] + TX, naled (567) + TX, NC-184 (compound code) + TX, NC-512 (compound code) + TX, nifluridide (1309) + TX, nikkomycins (alternative name) [CCN] + TX, nitrilacarb (1313) + TX, nitrilacarb 1:1 zinc chloride complex (1313) + TX, NNI-0101 (compound code) + TX, NNI-0250 (compound code) + TX, omethoate (594) + TX, oxamyl (602) + TX, oxydeprofos (1324) + TX, oxydisulfoton (1325) + TX, pp'-DDT (219) + TX, parathion (615) + TX, permethrin (626) + TX, petroleum oils (alternative name) (628) + TX, phenkapton (1330) + TX, phenthoate (631) + TX, phorate (636) + TX, phosalone (637) + TX, phosfolan (1338) + TX, phosmet (638) + TX, phosphamidon (639) + TX, phoxim (642) + TX, pirimiphos-methyl (652) + TX, polychloroterpenes (traditional name) (1347) + TX, polynactins (alternative name) (653) + TX, proclonol (1350) + TX, profenofos (662) + TX, promacyl (1354) + TX, propargite (671) + TX, propetamphos (673) + TX, propoxur (678) + TX, prothidathion (1360) + TX, prothoate (1362) + TX, pyrethrin I (696) + TX, pyrethrin II (696) + TX, pyrethrins (696) + TX, pyridaben (699) + TX, pyridaphenthion (701) + TX, pyrimidifen (706) + TX, pyrimitate (1370) + TX, quinalphos (711) + TX, quintiofos (1381) + TX, R-1492 (development code) (1382) + TX, RA-17 (development code) (1383) + TX, rotenone (722) + TX, schradan (1389) + TX, sebufos (alternative name) + TX, selamectin (alternative name) [CCN] + TX, SI-0009 (compound code) + TX, sophamide (1402) + TX, spirodiclofen (738) + TX, spiromesifen (739) + TX, SSI-121 (development code) (1404) + TX, sulfiram (alternative name) [CCN] + TX, sulfluramid (750) + TX, sulfotep (753) + TX, sulfur (754) + TX, SZI-121 (development code) (757) + TX, tau-fluvalinate (398) + TX, tebufenpyrad (763) + TX, TEPP (1417) + TX, terbam (alternative name) + TX, tetrachlorvinphos (777) + TX, tetradifon (786) + TX, tetranactin (alternative name) (653) + TX, tetrasul (1425) + TX, thiafenox (alternative name) + TX, thiocarboxime (1431) + TX, thiofanox (800) + TX, thiometon (801) + TX, thioquinox (1436) + TX, thuringiensin (alternative name) [CCN] + TX, triamiphos (1441) + TX, triarathene (1443) + TX, triazophos (820) + TX, triazuron (alternative name) + TX, trichlorfon (824) + TX, trifenofos (1455) + TX, trinactin (alternative name) (653) + TX, vamidothion (847) + TX, vaniliprole [CCN] and YI-5302 (compound code) + TX,

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 (alternative name) [CCN] + TX, emamectin (291) + TX, emamectin benzoate (291) + TX, eprinomectin (alternative name) [CCN] + TX, ivermectin (alternative name) [CCN] + TX, milbemycin oxime (alternative name) [CCN] + TX, moxidectin (alternative name) [CCN] + TX, piperazine [CCN] + TX, selamectin (alternative name) [CCN] + TX, spinosad (737) and thiophanate (1435) + TX,

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

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

a biological agent selected from the group of substances consisting of *Adoxophyes orana* GV (alternative name) (12) + TX, *Agrobacterium radiobacter* (alternative name) (13) + TX, *Amblyseius* spp. (alternative name) (19) + TX, *Anagrapha falcifera* NPV (alternative name) (28) + TX, *Anagrus atomus* (alternative name) (29) + TX, *Aphelinus abdominalis* (alternative name) (33) + TX, *Aphidius colemani* (alternative name) (34) + TX, *Aphidoletes aphidimyza* (alternative name) (35) + TX, *Autographa californica* NPV (alternative name) (38) + TX, *Bacillus firmus* (alternative name) (48) + TX, *Bacillus sphaericus* Neide (scientific name) (49) + TX, *Bacillus thuringiensis* Berliner (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *aizawai* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *israelensis* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *japonensis* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *kurstaki* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *tenebrionis* (scientific name) (51) + TX, *Beauveria bassiana* (alternative name) (53) + TX, *Beauveria brongniartii* (alternative name) (54) + TX, *Chrysoperla carnea* (alternative name) (151) + TX, *Cryptolaemus montrouzieri* (alternative name) (178) + TX, *Cydia pomonella* GV (alternative name) (191) + TX, *Dacnusa sibirica* (alternative name) (212) + TX,

- Diglyphus isaea* (alternative name) (254) + TX, *Encarsia formosa* (scientific name) (293) + TX, *Eretmocerus eremicus* (alternative name) (300) + TX, *Helicoverpa zea* NPV (alternative name) (431) + TX, *Heterorhabditis bacteriophora* and *H. megidis* (alternative name) (433) + TX, *Hippodamia convergens* (alternative name) (442) + TX, *Leptomastix dactylopii* (alternative name) (488) + TX,
- 5 *Macrolophus caliginosus* (alternative name) (491) + TX, *Mamestra brassicae* NPV (alternative name) (494) + TX, *Metaphycus helvolus* (alternative name) (522) + TX, *Metarhizium anisopliae* var. *acridum* (scientific name) (523) + TX, *Metarhizium anisopliae* var. *anisopliae* (scientific name) (523) + TX, *Neodiprion sertifer* NPV and *N. lecontei* NPV (alternative name) (575) + TX, *Orius* spp. (alternative name) (596) + TX, *Paecilomyces fumosoroseus* (alternative name) (613) + TX,
- 10 *Phytoseiulus persimilis* (alternative name) (644) + TX, *Spodoptera exigua* multicapsid nuclear polyhedrosis virus (scientific name) (741) + TX, *Steinernema bibionis* (alternative name) (742) + TX, *Steinernema carpocapsae* (alternative name) (742) + TX, *Steinernema feltiae* (alternative name) (742) + TX, *Steinernema glaseri* (alternative name) (742) + TX, *Steinernema riobrave* (alternative name) (742) + TX, *Steinernema riobravense* (alternative name) (742) + TX, *Steinernema scapterisci*
- 15 (alternative name) (742) + TX, *Steinernema* spp. (alternative name) (742) + TX, *Trichogramma* spp. (alternative name) (826) + TX, *Typhlodromus occidentalis* (alternative name) (844) and *Verticillium lecanii* (alternative name) (848) + TX,
- a soil sterilant selected from the group of substances consisting of iodomethane (IUPAC name) (542) and methyl bromide (537) + TX,
- 20 a chemosterilant selected from the group of substances consisting of apholate [CCN] + TX, bisazir (alternative name) [CCN] + TX, busulfan (alternative name) [CCN] + TX, diflubenzuron (250) + TX, dimatif (alternative name) [CCN] + TX, hemel [CCN] + TX, hempa [CCN] + TX, metepa [CCN] + TX, methiotepa [CCN] + TX, methyl apholate [CCN] + TX, morzid [CCN] + TX, penfluron (alternative name) [CCN] + TX, tepa [CCN] + TX, thiohempa (alternative name) [CCN] + TX,
- 25 thiotepa (alternative name) [CCN] + TX, tretamine (alternative name) [CCN] and uredepa (alternative name) [CCN] + TX,
- an insect pheromone selected from the group of substances consisting of (*E*)-dec-5-en-1-yl acetate with (*E*)-dec-5-en-1-ol (IUPAC name) (222) + TX, (*E*)-tridec-4-en-1-yl acetate (IUPAC name) (829) + TX, (*E*)-6-methylhept-2-en-4-ol (IUPAC name) (541) + TX, (*E,Z*)-tetradeca-4,10-dien-1-yl acetate
- 30 (IUPAC name) (779) + TX, (*Z*)-dodec-7-en-1-yl acetate (IUPAC name) (285) + TX, (*Z*)-hexadec-11-enal (IUPAC name) (436) + TX, (*Z*)-hexadec-11-en-1-yl acetate (IUPAC name) (437) + TX, (*Z*)-hexadec-13-en-11-yn-1-yl acetate (IUPAC name) (438) + TX, (*Z*)-icos-13-en-10-one (IUPAC name) (448) + TX, (*Z*)-tetradec-7-en-1-yl acetate (IUPAC name) (782) + TX, (*Z*)-tetradec-9-en-1-yl acetate (IUPAC name) (783) + TX, (*Z*)-tetradec-9-en-1-yl acetate (IUPAC name) (784) + TX, (*7E,9Z*)-dodeca-7,9-dien-1-yl acetate (IUPAC name) (283) + TX, (*9Z,11E*)-tetradeca-9,11-dien-1-yl acetate (IUPAC name) (780) + TX, (*9Z,12E*)-tetradeca-9,12-dien-1-yl acetate (IUPAC name) (781) + TX, 14-methyloctadec-1-ene (IUPAC name) (545) + TX, 4-methylnonan-5-ol with 4-methylnonan-5-one (IUPAC name) (544) + TX, alpha-multistriatin (alternative name) [CCN] + TX, brevicomin (alternative name) [CCN] + TX, codlelure (alternative name) [CCN] + TX, codlemone (alternative name) (167) + TX, cuelure
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(alternative name) (179) + TX, dispartlure (277) + TX, dodec-8-en-1-yl acetate (IUPAC name) (286) + TX, dodec-9-en-1-yl acetate (IUPAC name) (287) + TX, dodeca-8 + TX, 10-dien-1-yl acetate (IUPAC name) (284) + TX, dominicalure (alternative name) [CCN] + TX, ethyl 4-methyloctanoate (IUPAC name) (317) + TX, eugenol (alternative name) [CCN] + TX, frontalinal (alternative name) [CCN] + TX, gossyplure (alternative name) (420) + TX, grandlure (421) + TX, grandlure I (alternative name) (421) + TX, grandlure II (alternative name) (421) + TX, grandlure III (alternative name) (421) + TX, grandlure IV (alternative name) (421) + TX, hexalure [CCN] + TX, ipsdienol (alternative name) [CCN] + TX, ipsenol (alternative name) [CCN] + TX, japonilure (alternative name) (481) + TX, lineatin (alternative name) [CCN] + TX, littlure (alternative name) [CCN] + TX, looplure (alternative name) [CCN] + TX, medlure [CCN] + TX, megatomoic acid (alternative name) [CCN] + TX, methyl eugenol (alternative name) (540) + TX, muscalure (563) + TX, octadeca-2,13-dien-1-yl acetate (IUPAC name) (588) + TX, octadeca-3,13-dien-1-yl acetate (IUPAC name) (589) + TX, orfralure (alternative name) [CCN] + TX, oryctalure (alternative name) (317) + TX, ostramone (alternative name) [CCN] + TX, siglure [CCN] + TX, sordidin (alternative name) (736) + TX, sulcatol (alternative name) [CCN] + TX, tetradec-11-en-1-yl acetate (IUPAC name) (785) + TX, trimedlure (839) + TX, trimedlure A (alternative name) (839) + TX, trimedlure B₁ (alternative name) (839) + TX, trimedlure B₂ (alternative name) (839) + TX, trimedlure C (alternative name) (839) and trunc-call (alternative name) [CCN] + TX,

an insect repellent selected from the group of substances consisting of 2-(octylthio)ethanol (IUPAC name) (591) + TX, butopyronoxyl (933) + TX, butoxy(polypropylene glycol) (936) + TX, dibutyl adipate (IUPAC name) (1046) + TX, dibutyl phthalate (1047) + TX, dibutyl succinate (IUPAC name) (1048) + TX, diethyltoluamide [CCN] + TX, dimethyl carbate [CCN] + TX, dimethyl phthalate [CCN] + TX, ethyl hexanediol (1137) + TX, hexamide [CCN] + TX, methoquin-butyl (1276) + TX, methylnodecanamide [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-ethylsulfinyethyl methyl phosphate (IUPAC name) (1066) + TX, 2-(1,3-dithiolan-2-yl)phenyl dimethylcarbamate (IUPAC/ Chemical Abstracts name) (1109) + TX, 2-(2-butoxyethoxy)ethyl thiocyanate (IUPAC/Chemical Abstracts name) (935) + TX, 2-(4,5-dimethyl-1,3-dioxolan-2-yl)phenyl methylcarbamate (IUPAC/ Chemical Abstracts name) (1084) + TX, 2-(4-chloro-3,5-xylyloxy)ethanol (IUPAC name) (986) + TX, 2-chlorovinyl diethyl phosphate (IUPAC name) (984) + TX, 2-imidazolidone (IUPAC name) (1225) + TX, 2-isovalerylindan-1,3-dione (IUPAC name) (1246) + TX, 2-methyl(prop-2-ynyl)aminophenyl methylcarbamate (IUPAC name) (1284) + TX, 2-thiocyanatoethyl laurate (IUPAC name) (1433) + TX, 3-bromo-1-chloroprop-1-ene (IUPAC name) (917) + TX, 3-methyl-1-phenylpyrazol-5-yl dimethylcarbamate (IUPAC name) (1283) + TX, 4-methyl(prop-2-ynyl)amino-3,5-xylyl methylcarbamate (IUPAC name) (1285) + TX, 5,5-dimethyl-

3-oxocyclohex-1-enyl dimethylcarbamate (IUPAC name) (1085) + TX, abamectin (1) + TX, acephate (2) + TX, acetamiprid (4) + TX, acethion (alternative name) [CCN] + TX, acetoprole [CCN] + TX, acrinathrin (9) + TX, acrylonitrile (IUPAC name) (861) + TX, alanycarb (15) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, aldrin (864) + TX, allethrin (17) + TX, allosamidin (alternative name) [CCN] + TX, allyxycarb (866) + TX, alpha-cypermethrin (202) + TX, alpha-ecdysone (alternative name) [CCN] + TX, aluminium phosphide (640) + TX, amidithion (870) + TX, amidothioate (872) + TX, aminocarb (873) + TX, amiton (875) + TX, amiton hydrogen oxalate (875) + TX, amitraz (24) + TX, anabasine (877) + TX, athidathion (883) + TX, AVI 382 (compound code) + TX, AZ 60541 (compound code) + TX, azadirachtin (alternative name) (41) + TX, azamethiphos (42) + TX, azinphos-ethyl (44) + TX, azinphos-methyl (45) + TX, azothoate (889) + TX, *Bacillus thuringiensis* delta endotoxins (alternative name) (52) + TX, barium hexafluorosilicate (alternative name) [CCN] + TX, barium polysulfide (IUPAC/Chemical Abstracts name) (892) + TX, barthrin [CCN] + TX, Bayer 22/190 (development code) (893) + TX, Bayer 22408 (development code) (894) + TX, bendiocarb (58) + TX, benfuracarb (60) + TX, bensultap (66) + TX, beta-cyfluthrin (194) + TX, beta-cypermethrin (203) + TX, bifenthrin (76) + TX, bioallethrin (78) + TX, bioallethrin S-cyclopentenyl isomer (alternative name) (79) + TX, bioethanomethrin [CCN] + TX, biopermethrin (908) + TX, bioresmethrin (80) + TX, bis(2-chloroethyl) ether (IUPAC name) (909) + TX, bistrifluron (83) + TX, borax (86) + TX, brofenvalerate (alternative name) + TX, bromfenvinfos (914) + TX, bromocyclen (918) + TX, bromo-DDT (alternative name) [CCN] + TX, bromophos (920) + TX, bromophos-ethyl (921) + TX, bufencarb (924) + TX, buprofezin (99) + TX, butacarb (926) + TX, butathiofos (927) + TX, butocarboxim (103) + TX, butonate (932) + TX, butoxycarboxim (104) + TX, butylpyridaben (alternative name) + TX, cadusafos (109) + TX, calcium arsenate [CCN] + TX, calcium cyanide (444) + TX, calcium polysulfide (IUPAC name) (111) + TX, camphechlor (941) + TX, carbanolate (943) + TX, carbaryl (115) + TX, carbofuran (118) + TX, carbon disulfide (IUPAC/Chemical Abstracts name) (945) + TX, carbon tetrachloride (IUPAC name) (946) + TX, carbophenothion (947) + TX, carbosulfan (119) + TX, cartap (123) + TX, cartap hydrochloride (123) + TX, cevadine (alternative name) (725) + TX, chlorbicyclen (960) + TX, chlordane (128) + TX, chlordecone (963) + TX, chlordimeform (964) + TX, chlordimeform hydrochloride (964) + TX, chlorethoxyfos (129) + TX, chlorfenapyr (130) + TX, chlorfenvinphos (131) + TX, chlorfluazuron (132) + TX, chlormephos (136) + TX, chloroform [CCN] + TX, chloropicrin (141) + TX, chlorphoxim (989) + TX, chlorprazophos (990) + TX, chlorpyrifos (145) + TX, chlorpyrifos-methyl (146) + TX, chlorthiophos (994) + TX, chromafenozide (150) + TX, cinerin I (696) + TX, cinerin II (696) + TX, cinerins (696) + TX, cis-resmethrin (alternative name) + TX, cismethrin (80) + TX, clocythrin (alternative name) + TX, cloethocarb (999) + TX, closantel (alternative name) [CCN] + TX, clothianidin (165) + TX, copper acetoarsenite [CCN] + TX, copper arsenate [CCN] + TX, copper oleate [CCN] + TX, coumaphos (174) + TX, coumithoate (1006) + TX, crotamiton (alternative name) [CCN] + TX, crotoxyphos (1010) + TX, crufomate (1011) + TX, cryolite (alternative name) (177) + TX, CS 708 (development code) (1012) + TX, cyanofenphos (1019) + TX, cyanophos (184) + TX, cyanthoate (1020) + TX, cyclethrin [CCN] + TX,

cycloprothrin (188) + TX, cyfluthrin (193) + TX, cyhalothrin (196) + TX, cypermethrin (201) + TX, cyphenothrin (206) + TX, cyromazine (209) + TX, cythioate (alternative name) [CCN] + TX, *d*-limonene (alternative name) [CCN] + TX, *d*-tetramethrin (alternative name) (788) + TX, DAEP (1031) + TX, dazomet (216) + TX, DDT (219) + TX, decarbofuran (1034) + TX, deltamethrin (223) + TX, demephion (1037) + TX, demephion-O (1037) + TX, demephion-S (1037) + TX, demeton (1038) + TX, demeton-methyl (224) + TX, demeton-O (1038) + TX, demeton-O-methyl (224) + TX, demeton-S (1038) + TX, demeton-S-methyl (224) + TX, demeton-S-methylsulphon (1039) + TX, diafenthiuron (226) + TX, dialifos (1042) + TX, diamidafos (1044) + TX, diazinon (227) + TX, dicapthion (1050) + TX, dichlofenthion (1051) + TX, dichlorvos (236) + TX, dicliphos (alternative name) + TX, dicresyl (alternative name) [CCN] + TX, dicrotophos (243) + TX, dicyclanil (244) + TX, dieldrin (1070) + TX, diethyl 5-methylpyrazol-3-yl phosphate (IUPAC name) (1076) + TX, diflubenzuron (250) + TX, dilor (alternative name) [CCN] + TX, dimefluthrin [CCN] + TX, dimefox (1081) + TX, dimetan (1085) + TX, dimethoate (262) + TX, dimethrin (1083) + TX, dimethylvinphos (265) + TX, dimetilan (1086) + TX, dinex (1089) + TX, dinex-diclexine (1089) + TX, dinoprop (1093) + TX, dinosam (1094) + TX, dinoseb (1095) + TX, dinotefuran (271) + TX, diofenolan (1099) + TX, dioxabenzofos (1100) + TX, dioxacarb (1101) + TX, dioxathion (1102) + TX, disulfoton (278) + TX, dithicrofos (1108) + TX, DNOC (282) + TX, doramectin (alternative name) [CCN] + TX, DSP (1115) + TX, ecdysterone (alternative name) [CCN] + TX, EI 1642 (development code) (1118) + TX, emamectin (291) + TX, emamectin benzoate (291) + TX, EMPC (1120) + TX, empenthrin (292) + TX, endosulfan (294) + TX, endothion (1121) + TX, endrin (1122) + TX, EPBP (1123) + TX, EPN (297) + TX, epofenonane (1124) + TX, eprinomectin (alternative name) [CCN] + TX, esfenvalerate (302) + TX, etaphos (alternative name) [CCN] + TX, ethiofencarb (308) + TX, ethion (309) + TX, ethiprole (310) + TX, ethoate-methyl (1134) + TX, ethoprophos (312) + TX, ethyl formate (IUPAC name) [CCN] + TX, ethyl-DDD (alternative name) (1056) + TX, ethylene dibromide (316) + TX, ethylene dichloride (chemical name) (1136) + TX, ethylene oxide [CCN] + TX, etofenprox (319) + TX, etrimfos (1142) + TX, EXD (1143) + TX, famphur (323) + TX, fenamiphos (326) + TX, fenazaflor (1147) + TX, fenchlorphos (1148) + TX, fenethacarb (1149) + TX, fenfluthrin (1150) + TX, fenitrothion (335) + TX, fenobucarb (336) + TX, fenoxacrim (1153) + TX, fenoxycarb (340) + TX, fenspirithrin (1155) + TX, fenpropathrin (342) + TX, fenpyrad (alternative name) + TX, fensulfothion (1158) + TX, fenthion (346) + TX, fenthion-ethyl [CCN] + TX, fenvalerate (349) + TX, fipronil (354) + TX, flonicamid (358) + TX, flubendiamide (CAS. Reg. No.: 272451-65-7) + TX, flucofuron (1168) + TX, flucycloxuron (366) + TX, flucythrinate (367) + TX, fluenetil (1169) + TX, flufenerim [CCN] + TX, flufenoxuron (370) + TX, 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,
5 iodomethane (IUPAC name) (542) + TX, IPSP (1229) + TX, isazofos (1231) + TX, isobenzan
(1232) + TX, isocarbophos (alternative name) (473) + TX, isodrin (1235) + TX, isofenphos (1236)
+ TX, isolane (1237) + TX, isoprocarb (472) + TX, isopropyl *O*-(methoxy-
aminothiophosphoryl)salicylate (IUPAC name) (473) + TX, isoprothiolane (474) + TX, isothioate
(1244) + TX, isoxathion (480) + TX, ivermectin (alternative name) [CCN] + TX, jasmolin I (696) +
10 TX, jasmolin II (696) + TX, jodfenphos (1248) + TX, juvenile hormone I (alternative name) [CCN] +
TX, juvenile hormone II (alternative name) [CCN] + TX, juvenile hormone III (alternative name)
[CCN] + TX, kelevan (1249) + TX, kinoprene (484) + TX, lambda-cyhalothrin (198) + TX, lead
arsenate [CCN] + TX, lepimectin (CCN) + TX, leptophos (1250) + TX, lindane (430) + TX, lirimfos
(1251) + TX, lufenuron (490) + TX, lythidathion (1253) + TX, *m*-cumenyl methylcarbamate (IUPAC
15 name) (1014) + TX, magnesium phosphide (IUPAC name) (640) + TX, malathion (492) + TX,
malonoben (1254) + TX, mazidox (1255) + TX, mecarbam (502) + TX, mecarphon (1258) + TX,
menazon (1260) + TX, mephosfolan (1261) + TX, mercurous chloride (513) + TX, mesulfenfos
(1263) + TX, metaflumizone (CCN) + TX, metam (519) + TX, metam-potassium (alternative name)
(519) + TX, metam-sodium (519) + TX, methacrifos (1266) + TX, methamidophos (527) + TX,
20 methanesulfonyl fluoride (IUPAC/Chemical Abstracts name) (1268) + TX, methidathion (529) + TX,
methiocarb (530) + TX, methocrotophos (1273) + TX, methomyl (531) + TX, methoprene (532) +
TX, methoquin-butyl (1276) + TX, methothrin (alternative name) (533) + TX, methoxychlor (534) +
TX, methoxyfenozide (535) + TX, methyl bromide (537) + TX, methyl isothiocyanate (543) + TX,
methylchloroform (alternative name) [CCN] + TX, methylene chloride [CCN] + TX, metofluthrin
25 [CCN] + TX, metolcarb (550) + TX, metoxadiazone (1288) + TX, mevinphos (556) + TX,
mexacarbate (1290) + TX, milbemectin (557) + TX, milbemycin oxime (alternative name) [CCN] +
TX, mipafox (1293) + TX, mirex (1294) + TX, monocrotophos (561) + TX, morphothion (1300) +
TX, moxidectin (alternative name) [CCN] + TX, naftalofos (alternative name) [CCN] + TX, naled
(567) + TX, naphthalene (IUPAC/Chemical Abstracts name) (1303) + TX, NC-170 (development
30 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)
35 (1057) + TX, *O,O*-diethyl *O*-4-methyl-2-oxo-2*H*-chromen-7-yl phosphorothioate (IUPAC name) (1074)
+ TX, *O,O*-diethyl *O*-6-methyl-2-propylpyrimidin-4-yl phosphorothioate (IUPAC name) (1075) + TX,
O,O,O',O'-tetrapropyl dithiopyrophosphate (IUPAC name) (1424) + TX, oleic acid (IUPAC name)
(593) + TX, omethoate (594) + TX, oxamyl (602) + TX, oxydemeton-methyl (609) + TX,
oxydeprofos (1324) + TX, oxydisulfoton (1325) + TX, pp'-DDT (219) + TX, para-dichlorobenzene

[CCN] + TX, parathion (615) + TX, parathion-methyl (616) + TX, penfluron (alternative name) [CCN] + TX, pentachlorophenol (623) + TX, pentachlorophenyl laurate (IUPAC name) (623) + TX, permethrin (626) + TX, petroleum oils (alternative name) (628) + TX, PH 60-38 (development code) (1328) + TX, phenkapton (1330) + TX, phenothrin (630) + TX, phenthoate (631) + TX, phorate (636) + TX, phosalone (637) + TX, phosfolan (1338) + TX, phosmet (638) + TX, phosnichlor (1339) + TX, phosphamidon (639) + TX, phosphine (IUPAC name) (640) + TX, phoxim (642) + TX, phoxim-methyl (1340) + TX, pirimetaphos (1344) + TX, pirimicarb (651) + TX, pirimiphos-ethyl (1345) + TX, pirimiphos-methyl (652) + TX, polychlorodicyclopentadiene isomers (IUPAC name) (1346) + TX, polychloroterpenes (traditional name) (1347) + TX, potassium arsenite [CCN] + TX, potassium thiocyanate [CCN] + TX, prallethrin (655) + TX, precocene I (alternative name) [CCN] + TX, precocene II (alternative name) [CCN] + TX, precocene III (alternative name) [CCN] + TX, primidophos (1349) + TX, profenofos (662) + TX, profluthrin [CCN] + TX, promacyl (1354) + TX, promecarb (1355) + TX, propaphos (1356) + TX, propetamphos (673) + TX, propoxur (678) + TX, prothidathion (1360) + TX, prothiofos (686) + TX, prothoate (1362) + TX, protrifenbutate [CCN] + TX, pymetrozine (688) + TX, pyraclofos (689) + TX, pyrazophos (693) + TX, pyresmethrin (1367) + TX, pyrethrin I (696) + TX, pyrethrin II (696) + TX, pyrethrins (696) + TX, pyridaben (699) + TX, pyridalyl (700) + TX, pyridaphenthion (701) + TX, pyrimidifen (706) + TX, pyrimitate (1370) + TX, pyriproxyfen (708) + TX, quassia (alternative name) [CCN] + TX, quinalphos (711) + TX, quinalphos-methyl (1376) + TX, quinotion (1380) + TX, quintiofos (1381) + TX, R-1492 (development code) (1382) + TX, rafoxanide (alternative name) [CCN] + TX, resmethrin (719) + TX, rotenone (722) + TX, RU 15525 (development code) (723) + TX, RU 25475 (development code) (1386) + TX, ryania (alternative name) (1387) + TX, ryanodine (traditional name) (1387) + TX, sabadilla (alternative name) (725) + TX, schradan (1389) + TX, sebufos (alternative name) + TX, selamectin (alternative name) [CCN] + TX, SI-0009 (compound code) + TX, SI-0205 (compound code) + TX, SI-0404 (compound code) + TX, SI-0405 (compound code) + TX, silafluofen (728) + TX, SN 72129 (development code) (1397) + TX, sodium arsenite [CCN] + TX, sodium cyanide (444) + TX, sodium fluoride (IUPAC/Chemical Abstracts name) (1399) + TX, sodium hexafluorosilicate (1400) + TX, sodium pentachlorophenoxide (623) + TX, sodium selenate (IUPAC name) (1401) + TX, sodium thiocyanate [CCN] + TX, sophamide (1402) + TX, spinosad (737) + TX, spiromesifen (739) + TX, spirotetmat (CCN) + TX, sulcofuron (746) + TX, sulcofuron-sodium (746) + TX, sulfluramid (750) + TX, sulfotep (753) + TX, sulfuryl fluoride (756) + TX, sulprofos (1408) + TX, tar oils (alternative name) (758) + TX, tau-fluvalinate (398) + TX, tazimcarb (1412) + TX, TDE (1414) + TX, tebufenozide (762) + TX, tebufenpyrad (763) + TX, tebupirimfos (764) + TX, teflubenzuron (768) + TX, tefluthrin (769) + TX, temephos (770) + TX, TEPP (1417) + TX, terallethrin (1418) + TX, terbam (alternative name) + TX, terbufos (773) + TX, tetrachloroethane [CCN] + TX, tetrachlorvinphos (777) + TX, tetramethrin (787) + TX, theta-cypermethrin (204) + TX, thiacloprid (791) + TX, thiafenox (alternative name) + TX, thiamethoxam (792) + TX, thicrofos (1428) + TX, thiocarboxime (1431) + TX, thiocyclam (798) + TX, thiocyclam hydrogen oxalate (798) + TX, thiodicarb (799) + TX, thiofanox (800) + TX, thiometon (801) + TX, thionazin (1434) +

TX, thiosultap (803) + TX, thiosultap-sodium (803) + TX, thuringiensin (alternative name) [CCN] + TX, tolfenpyrad (809) + TX, tralomethrin (812) + TX, transluthrin (813) + TX, transpermethrin (1440) + TX, triamiphos (1441) + TX, triazamate (818) + TX, triazophos (820) + TX, triazuron (alternative name) + TX, trichlorfon (824) + TX, trichlormetaphos-3 (alternative name) [CCN] + TX, 5 trichloronat (1452) + TX, trifenofos (1455) + TX, triflumuron (835) + TX, trimethacarb (840) + TX, triprene (1459) + TX, vamidothion (847) + TX, vaniliprole [CCN] + TX, veratridine (alternative name) (725) + TX, veratrine (alternative name) (725) + TX, XMC (853) + TX, xylylcarb (854) + TX, YI-5302 (compound code) + TX, zeta-cypermethrin (205) + TX, zetamethrin (alternative name) + TX, zinc phosphide (640) + TX, zolaprofos (1469) and ZXI 8901 (development code) (858) + TX, 10 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, 15 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 WO 2005/077934) + TX, spiropidion + TX, Afidopyropen + TX, flupyrimin + TX, Momfluorothrin + TX, kappa-bifenthrin + TX, kappa-tefluthrin + TX, Dichloromezotiaz + TX, Tetrachloraniliprole + TX, benzpyrimoxan + 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, 25 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, 30 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 (alternative name) (210) + TX, abamectin (1) + TX, acetoprole [CCN] + TX, alanycarb (15) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, AZ 60541 (compound code) + TX, benclonthiaz [CCN] + TX, benomyl (62) + TX, butylpyridaben (alternative

name) + TX, cadusafos (109) + TX, carbofuran (118) + TX, carbon disulfide (945) + TX, carbosulfan (119) + TX, chloropicrin (141) + TX, chlorpyrifos (145) + TX, cloethocarb (999) + TX, cytokinins (alternative name) (210) + TX, dazomet (216) + TX, DBCP (1045) + TX, DCIP (218) + TX, diamidafos (1044) + TX, dichlofenthion (1051) + TX, dicliphos (alternative name) + TX, 5 dimethoate (262) + TX, doramectin (alternative name) [CCN] + TX, emamectin (291) + TX, emamectin benzoate (291) + TX, eprinomectin (alternative name) [CCN] + TX, ethoprophos (312) + TX, ethylene dibromide (316) + TX, fenamiphos (326) + TX, fenpyrad (alternative name) + TX, fensulfothion (1158) + TX, fosthiazate (408) + TX, fosthietan (1196) + TX, furfural (alternative name) [CCN] + TX, GY-81 (development code) (423) + TX, heterophos [CCN] + TX, iodomethane 10 (IUPAC name) (542) + TX, isamidofos (1230) + TX, isazofos (1231) + TX, ivermectin (alternative name) [CCN] + TX, kinetin (alternative name) (210) + TX, mecarphon (1258) + TX, metam (519) + TX, metam-potassium (alternative name) (519) + TX, metam-sodium (519) + TX, methyl bromide (537) + TX, methyl isothiocyanate (543) + TX, milbemycin oxime (alternative name) [CCN] + TX, moxidectin (alternative name) [CCN] + TX, *Myrothecium verrucaria* composition (alternative name) 15 (565) + TX, NC-184 (compound code) + TX, oxamyl (602) + TX, phorate (636) + TX, phosphamidon (639) + TX, phosphocarb [CCN] + TX, sebufos (alternative name) + TX, selamectin (alternative name) [CCN] + TX, spinosad (737) + TX, terbam (alternative name) + TX, terbufos (773) + TX, tetrachlorothiophene (IUPAC/ Chemical Abstracts name) (1422) + TX, thiafenox (alternative name) + TX, thionazin (1434) + TX, triazophos (820) + TX, triazuron (alternative name) 20 + TX, xylenols [CCN] + TX, YI-5302 (compound code) and zeatin (alternative name) (210) + TX, fluensulfone [318290-98-1] + TX, fluopyram + 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, 25 acibenzolar-S-methyl (6) + TX, probenazole (658) and *Reynoutria sachalinensis* extract (alternative name) (720) + TX, a rodenticide selected from the group of substances consisting of 2-isovalerylindan-1,3-dione (IUPAC name) (1246) + TX, 4-(quinoxalin-2-ylamino)benzenesulfonamide (IUPAC name) (748) + TX, alpha-chlorohydrin [CCN] + TX, aluminium phosphide (640) + TX, antu (880) + TX, arsenous oxide (882) 30 + TX, barium carbonate (891) + TX, bisthiosemi (912) + TX, brodifacoum (89) + TX, bromadiolone (91) + TX, bromethalin (92) + TX, calcium cyanide (444) + TX, chloralose (127) + TX, chlorophacinone (140) + TX, cholecalciferol (alternative name) (850) + TX, coumachlor (1004) + TX, coumafuryl (1005) + TX, coumatetralyl (175) + TX, crimidine (1009) + TX, difenacoum (246) + TX, difethialone (249) + TX, diphacinone (273) + TX, ergocalciferol (301) + TX, 35 flocoumafen (357) + TX, fluoroacetamide (379) + TX, flupropradine (1183) + TX, flupropradine hydrochloride (1183) + TX, gamma-HCH (430) + TX, HCH (430) + TX, hydrogen cyanide (444) + TX, iodomethane (IUPAC name) (542) + TX, lindane (430) + TX, magnesium phosphide (IUPAC name) (640) + TX, methyl bromide (537) + TX, norbormide (1318) + TX, phosacetim (1336) + TX, phosphine (IUPAC name) (640) + TX, phosphorus [CCN] + TX, pindone (1341) + TX, potassium

- arsenite [CCN] + TX, pyrinuron (1371) + TX, scilliroside (1390) + TX, sodium arsenite [CCN] + TX, sodium cyanide (444) + TX, sodium fluoroacetate (735) + TX, strychnine (745) + TX, thallium sulfate [CCN] + TX, warfarin (851) and zinc phosphide (640) + TX,
- 5 a synergist selected from the group of substances consisting of 2-(2-butoxyethoxy)ethyl piperonylate (IUPAC name) (934) + TX, 5-(1,3-benzodioxol-5-yl)-3-hexylcyclohex-2-enone (IUPAC name) (903) + TX, farnesol with nerolidol (alternative name) (324) + TX, MB-599 (development code) (498) + TX, MGK 264 (development code) (296) + TX, piperonyl butoxide (649) + TX, piprotal (1343) + TX, propyl isomer (1358) + TX, S421 (development code) (724) + TX, sesamex (1393) + TX, sesasmolin (1394) and sulfoxide (1406) + TX,
- 10 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,
- 15 a virucide selected from the group of substances consisting of imanin (alternative name) [CCN] and ribavirin (alternative name) [CCN] + TX,
- a wound protectant selected from the group of substances consisting of mercuric oxide (512) + TX, octhilinone (590) and thiophanate-methyl (802) + TX,
- 20 and biologically active compounds selected from the group of substances 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, pyrifenoxy [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,
- 25 cyprodinil [121552-61-2] + TX, mepanipyrim [110235-47-7] + TX, pyrimethanil [53112-28-0] + TX, fencpiclonil [74738-17-3] + TX, fludioxonil [131341-86-1] + TX, benalaxyl [71626-11-4] + TX, furalaxyl [57646-30-7] + TX, metalaxyl [57837-19-1] + TX, R-metalaxyl [70630-17-0] + TX, ofurace [58810-48-3] + TX, oxadixyl [77732-09-3] + TX, benomyl [17804-35-2] + TX, carbendazim [10605-21-7] + TX, debacarb [62732-91-6] + TX, fuberidazole [3878-19-1] + TX, thiabendazole [148-79-8]

+ TX, chlozolate [84332-86-5] + 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,
5 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, oryastrobin
10 [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
15 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,
20 acibenzolar-S-methyl [135158-54-2] + TX, anilazine [101-05-3] + TX, benthialalicarb [413615-35-7] + TX, blastidicid-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,
25 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,
30 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, quinoxifen [124495-18-7] + TX, quintozene [82-68-8] + TX, sulfur
35 [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 (disclosed 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, [(3S,4R,4aR,6S,6aS,12R,12aS,12bS)-3-[(cyclopropylcarbonyloxy)-
 1,3,4,4a,5,6,6a,12,12a,12b-decahydro-6,12-dihydroxy-4,6a,12b-trimethyl-11-oxo-9-(3-pyridinyl)-
 2H,11Hnaphtho[2,1-b]pyrano[3,4-e]pyran-4-yl]methyl-cyclopropanecarboxylate [915972-17-7] + TX
 5 and 1,3,5-trimethyl-N-(2-methyl-1-oxopropyl)-N-[3-(2-methylpropyl)-4-[2,2,2-trifluoro-1-methoxy-1-
 (trifluoromethyl)ethyl]phenyl]-1H-pyrazole-4-carboxamide [926914-55-8] + TX, lancotrione [1486617-
 21-3] + TX, florpyrauxifen [943832-81-3] + TX, ipfentrifluconazole[1417782-08-1] + TX,
 mefentrifluconazole [1417782-03-6] + TX, quinofumelin [861647-84-9] + TX, chlorprallethrin [399572-
 87-3] + TX, cyhalodiamide [1262605-53-7] + TX, fluazaindolizine [1254304-22-7] + TX, fluxametamide
 10 [928783-29-3] + TX, epsilon-metofluthrin [240494-71-7] + TX, epsilon-momfluorothrin [1065124-65-3]
 + TX, pydiflumetofen [1228284-64-7] + TX, kappa-bifenthrin [439680-76-9] + TX, broflanilide
 [1207727-04-5] + TX, dicloromezotiaz [1263629-39-5] + TX, dipymetitron [16114-35-5] + TX,
 pyraziflumid [942515-63-1] + TX, kappa-tefluthrin [391634-71-2] + TX, fencicoxamid [517875-34-2] +
 TX; flufenpyrrolidone + TX, benzpyrimoxan [1449021-97-9] + TX; isocycloseram + TX, rescalure
 15 [64309-03-1] + TX; aminopyrifen [1531626-08-0] + TX;and
 microbials including: *Acinetobacter lwoffii* + TX, *Acremonium alternatum* + TX + TX, *Acremonium*
cephalosporium + TX + TX, *Acremonium diospyri* + TX, *Acremonium obclavatum* + TX, *Adoxophyes*
orana granulovirus (AdoxGV) (Capex®) + TX, *Agrobacterium radiobacter* strain K84 (Galltrol-A®) +
 TX, *Alternaria alternate* + TX, *Alternaria cassia* + TX, *Alternaria destruens* (Smolder®) + TX,
 20 *Ampelomyces quisqualis* (AQ10®) + TX, *Aspergillus flavus* AF36 (AF36®) + TX, *Aspergillus flavus*
 NRRL 21882 (Aflaguard®) + TX, *Aspergillus* spp. + TX, *Aureobasidium pullulans* + TX, *Azospirillum* +
 TX, (MicroAZ® + TX, TAZO B®) + TX, *Azotobacter* + TX, *Azotobacter chroococcum* (Azotomeal®) +
 TX, *Azotobacter* cysts (Bionatural Blooming Blossoms®) + TX, *Bacillus amyloliquefaciens* + TX,
Bacillus cereus + TX, *Bacillus chitinosporus* strain CM-1 + TX, *Bacillus chitinosporus* strain AQ746 +
 25 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
 30 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*
 35 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, 5 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* (Engerlingspizl® + TX, Schweizer Beauveria® + TX, Melocont®) + TX, *Beauveria* spp. + TX, *Botrytis cineria* + TX, *Bradyrhizobium japonicum* (TerraMax®) + TX, *Brevibacillus brevis* + TX, *Bacillus thuringiensis* 10 *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* 15 *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, 20 *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* 25 (Madex® + TX, Madex Plus® + TX, Madex Max/ Carpovirusine®) + TX, *Cylindrobasidium laeve* (Stumpout®) + TX, *Cylindrocladium* + TX, *Debaryomyces hansenii* + TX, *Drechslera hawaiiensis* + TX, *Enterobacter cloacae* + TX, *Enterobacteriaceae* + TX, *Entomophthora virulenta* (Vektor®) + TX, *Epicoccum nigrum* + TX, *Epicoccum purpurascens* + TX, *Epicoccum* spp. + TX, *Filobasidium floriforme* + TX, *Fusarium acuminatum* + TX, *Fusarium chlamydosporum* + TX, *Fusarium oxysporum* 30 (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* 35 *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,

5 *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*

10 *aurantiogriseum* + TX, *Penicillium billai* (Jumpstart® + TX, TagTeam®) + TX, *Penicillium brevicompactum* + TX, *Penicillium frequentans* + TX, *Penicillium griseofulvum* + TX, *Penicillium purpurogenum* + TX, *Penicillium* spp. + TX, *Penicillium viridicatum* + TX, *Phlebiopsis gigantea* (Rotstop®) + TX, phosphate solubilizing bacteria (Phosphomeal®) + TX, *Phytophthora cryptogea* + TX, *Phytophthora palmivora* (Devine®) + TX, *Pichia anomala* + TX, *Pichia guillemontii* + TX, *Pichia membranaefaciens* + TX, *Pichia onychis* + TX, *Pichia stipites* + TX, *Pseudomonas aeruginosa* + TX,

15 *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,

20 *Pseudomonas fluorescens* (Zequanox®) + TX, *Pseudozyma flocculosa* strain PF-A22 UL (Sporodex L®) + TX, *Puccinia canaliculata* + TX, *Puccinia thlaspeos* (Wood Warrior®) + TX, *Pythium paroecandrum* + TX, *Pythium oligandrum* (Polygandron® + TX, Polyversum®) + TX, *Pythium periplocum* + TX, *Rhanelia aquatilis* + TX, *Rhanelia* spp. + TX, *Rhizobia* (Dormal® + TX, Vault®) + TX, *Rhizoctonia* + TX, *Rhodococcus globerulus* strain AQ719 + TX, *Rhodosporidium diobovatum* + TX,

25 *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. +

30 TX, *Sordaria fimicola* + TX, *Spodoptera littoralis nucleopolyhedrovirus* (Littovir®) + TX, *Sporobolomyces roseus* + TX, *Stenotrophomonas maltophilia* + TX, *Streptomyces ahngroscopicus* + 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* +

35 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,
- 5 *Trichothecium* spp. + TX, *Trichothecium roseum* + TX, *Typhula phacorrhiza* strain 94670 + TX, *Typhula phacorrhiza* strain 94671 + TX, *Ulocladium atrum* + TX, *Ulocladium oudemansii* (Botry-Zen®) + TX, *Ustilago maydis* + TX, various bacteria and supplementary micronutrients (Natural II®) + TX, various fungi (Millennium Microbes®) + TX, *Verticillium chlamydosporium* + TX, *Verticillium lecanii* (Mycotal® + TX, Vertalec®) + TX, Vip3Aa20 (VIPtera®) + TX, *Virgibacillus marismortui* + TX,
- 10 *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,
- 15 *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,
- 20 *Reynoutria sachalinensis* (Regalia® + TX, Sakalia®) + TX, rotenone (Eco Roten®) + TX, *Rutaceae* plant extract (Soleo®) + TX, soybean oil (Ortho ecosense®) + TX, tea tree oil (Timorex Gold®) + TX, thymus oil + TX, AGNIQUE® MMF + TX, BugOil® + TX, mixture of rosemary sesame peppermint thyme and cinnamon extracts (EF 300®) + TX, mixture of clove rosemary and peppermint extract (EF 400®) + TX, mixture of clove peppermint garlic oil and mint (Soil Shot®) + TX, kaolin (Screen®) + TX,
- 25 storage glucan of brown algae (Laminarin®); and
- pheromones including: blackheaded fireworm pheromone (3M Sprayable Blackheaded Fireworm Pheromone®) + TX, Codling Moth Pheromone (Paramount dispenser-(CM)/ Isomate C-Plus®) + TX, 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,
- 35 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,
 5 *Anagrus fusciventris* + TX, *Anagrus kamali* + TX, *Anagrus loecki* + TX, *Anagrus pseudococci*
 (Citripar®) + TX, *Anicetus benefices* + TX, *Anisopteromalus calandrae* + TX, *Anthocoris nemoralis*
 (Anthocoris-System®) + TX, *Aphelinus abdominalis* (Apheline® + TX, Aphiline®) + TX, *Aphelinus*
asychis + TX, *Aphidius colemani* (Ahipar®) + TX, *Aphidius ervi* (Ervipar®) + TX, *Aphidius gifuensis* +
 TX, *Aphidius matricariae* (Ahipar-M®) + TX, *Aphidoletes aphidimyza* (Aphidend®) + TX, *Aphidoletes*
 10 *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* +
 15 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,
 20 *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*
 25 *haitiensis* + TX, *Episyrphus balteatus* (Syrphidend®) + TX, *Eretmoceris siphonini* + TX, *Eretmoceris*
californicus + TX, *Eretmoceris eremicus* (Ercal® + TX, Eretline e®) + TX, *Eretmoceris eremicus*
 (Bemimix®) + TX, *Eretmoceris hayati* + TX, *Eretmoceris mundus* (Bemipar® + TX, Eretline m®) +
 TX, *Eretmoceris siphonini* + TX, *Exochomus quadripustulatus* + TX, *Feltiella acarisuga* (Spidend®) +
 TX, *Feltiella acarisuga* (Feltiline®) + TX, *Fopius arisanus* + TX, *Fopius ceratitivorius* + TX,
 30 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® +
 35 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, 5 *Neoseiulus cucumeris* (THRYPEX®) + TX, *Neoseiulus fallaxis* + TX, *Nesideocoris tenuis* (NesidioBug® + TX, Nesibug®) + TX, *Ophyra aenescens* (Biofly®) + TX, *Orius insidiosus* (Thripor-l® + TX, Oriline i®) + TX, *Orius laevigatus* (Thripor-L® + TX, Oriline l®) + TX, *Orius majusculus* (Oriline m®) + TX, *Orius strigicollis* (Thripor-S®) + TX, *Pauesia juniperorum* + TX, *Pediobius foveolatus* + TX, *Phasmarhabditis hermaphrodita* (Nemaslug®) + TX, *Phymastichus coffea* + TX, *Phytoseiulus* 10 *macropilus* + TX, *Phytoseiulus persimilis* (Spidex® + TX, Phytoline p®) + TX, *Podisus maculiventris* (Podisus®) + TX, *Pseudacteon curvatus* + TX, *Pseudacteon obtusus* + TX, *Pseudacteon tricuspis* + TX, *Pseudaphycus maculipennis* + TX, *Pseudleptomastix mexicana* + TX, *Psyllaephagus pilosus* + TX, *Psytalia concolor* (complex) + TX, *Quadrastichus* spp. + TX, *Rhyzobius lophanthae* + TX, *Rodolia cardinalis* + TX, *Rumina decollate* + TX, *Semielacher petiolatus* + TX, *Sitobion avenae* (Ervibank®) + 15 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* 20 *scapterisci* (Nematac S®) + TX, *Steinernema* spp. + TX, *Steinernematid* spp. (Guardian Nematodes®) + TX, *Stethorus punctillum* (Stethorus®) + TX, *Tamarixia radiata* + 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 ostrinae* + TX, *Trichogramma platneri* + TX, *Trichogramma pretiosum* + 25 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 30 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, *Mycocleptodiscus 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®) + 35 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; or a biologically active compound or agent selected from: Brofluthrinat + TX, Diflovidazine + TX, Flometoquin + TX, Fluhexafon + TX, *Plutella xylostella* Granulosis virus + TX, *Cydia pomonella*

Granulosis virus + TX, Imicyafos + TX, Heliiothis virescens Nucleopolyhedrovirus + TX, Heliiothis punctigera Nucleopolyhedrovirus + TX, Helicoverpa zea Nucleopolyhedrovirus + TX, Spodoptera frugiperda Nucleopolyhedrovirus + TX, Plutella xylostella Nucleopolyhedrovirus + TX, p-cymene + TX, Pyflubumide + TX, Pyrafluprole + TX, QRD 420 + TX, QRD 452 + TX, QRD 460 + TX, Terpenoid blends + TX, Terpenoids + TX, Tetranilprole + TX, and α -terpinene + TX;

5 or an active substance referenced by a code + TX, such as code AE 1887196 (BSC-BX60309) + TX, code NNI-0745 GR + TX, code IKI-3106 + TX, code JT-L001 + TX, code ZNQ-08056 + TX, code IPPA152201 + TX, code HNPC-A9908 (CAS: [660411-21-2]) + TX, code HNPC-A2005 (CAS: [860028-12-2]) + TX, code JS118 + TX, code ZJ0967 + TX, code ZJ2242 + TX, code JS7119 (CAS: [929545-74-4]) + TX, code SN-1172 + TX, code HNPC-A9835 + TX, code HNPC-A9955 + TX, code HNPC-A3061 + TX, code Chuanhua 89-1 + TX, code IPP-10 + TX, code ZJ3265 + TX, code JS9117 + TX, code ZJ3757 + TX, code ZJ4042 + TX, code ZJ4014 + TX, code ITM-121 + TX, code DPX-RAB55 (DKI-2301) + TX, code NA-89 + TX, code MIE-1209 + TX, code MCI-8007 + TX, code BCS-CL73507 + TX, code S-1871 + TX, code DPX-RDS63 + TX, code AKD-1193 + TX;

10 or other biologically active compounds or agents selected from: Quinofumelin + TX, mefentrifluconazol + TX, fempicoxamid + TX, fluidapyr + TX, inpyrfluxam + TX or indiflumetpyr + TX, isoflucypram + TX, pyrapropoyne + TX, florylpicoxamid + TX, metyltetraprole + TX, ipflufenquin + TX, pyridachlometyl + TX or chlopyridiflu + TX, tetrachlorantranilprole + TX, tetrachloranilprole + TX, Tetflupyrolimet + TX, Triflufenpyrrolidone + TX, Tyclopyrazoflor + TX, flupyrimin + TX or pyrfluramide + TX, benzpyrimoxan + TX, beflubutamid-M + TX, Benzosufyl + TX or oxazosufyl + TX, etpyrafen + TX, acynonapyr + TX

15 or pyrinonafen + TX, oxotrione + TX, bixlozone + TX or clofendizone + TX or dicloroxizone + TX, cyclopyranil + TX or pyrazocyclonil + TX or cyclopyrazonil + TX, alpha-bromadiolone + TX, Oxathiapiprolin + TX, Fluopyram + TX, Penflufen+ TX, Fluoxopyrosad+ TX, fluoxapiprolin + TX and Flupyradifurone + TX.

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25 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

30 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

35 under the internet address <http://www.alanwood.net/pesticides/acetoprole.html>.

Most of the active ingredients described above are referred to hereinabove by a so-called "common name", the relevant "ISO common name" or another "common name" being used in individual cases. If the designation is not a "common name", the nature of the designation used instead is given in

round brackets for the particular compound; in that case, the IUPAC name, the IUPAC/Chemical Abstracts name, a "chemical name", a "traditional name", a "compound name" or a "development code" is used 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.

5

The active ingredient mixture of the compounds of formula I selected from Tables 1, 2, 3 and Y with active ingredients described above comprises a compound selected from Tables 1, 2, 3 and Y 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.

10

15

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.

20

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

25

30

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.

35

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.

5 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
10 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
15 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.

20 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
25 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
30 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
35 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:

The biological examples which follow serve to illustrate the invention. Certain compounds of the invention can be distinguished from known compounds by virtue of greater efficacy at low application rates, which can be verified by the person skilled in the art using the experimental procedures outlined in the biological examples, using lower application rates if necessary, for example 50 ppm, 12.5 ppm, 6 ppm, 3 ppm, 1.5 ppm, 0.8 ppm or 0.2 ppm.

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

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

The following compounds resulted in at least 80% control in at least one of the three categories (mortality, anti-feedant effect, or growth inhibition) at an application rate of 200 ppm: P1, P2, P3, P4, P5, P9, P12, P15, P16, P17, P18, P19.

Example B2: *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 onto the agar and the multi well plate was closed by another plate which contained also agar. After 7 days the compound was absorbed by the roots and the lettuce grew into the lid plate. The lettuce leaves were then cut off into the lid plate. *Spodoptera* eggs were pipetted through a plastic stencil onto a humid gel blotting paper and the lid plate was closed with it. The samples were assessed for mortality, anti-feedant effect and growth inhibition in comparison to untreated samples 6 days after infestation.

Example B3: *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, P2, P3, P5, P6, P18.

Example B4: *Diabrotica balteata* (Corn root worm)

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

The following compounds gave an effect of at least 80% in at least one of the two categories (mortality or growth inhibition) at an application rate of 200 ppm: P1, P5, P6, P14, P16, P17, P18.

Example B5: *Myzus persicae* (Green peach aphid) : Feeding/Contact activity

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

The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: P1, P2, P3, P4, P5, P6, P9, P12, P13, P14, P15, P16, P17, P18, P19.

Example B6: *Myzus persicae* (Green peach aphid): Systemic activity

Roots of pea seedlings infested with an aphid population of mixed ages were placed directly into aqueous test solutions prepared from 10'000 DMSO stock solutions. The samples were assessed for mortality 6 days after placing seedlings into test solutions.

The following compounds resulted in at least 80% mortality at a test rate of 24 ppm: P1, P2, P3, P4, P5, P6, P9, P12, P13, P14, P15, P16, P17, P18, P19.

Example B7: *Plutella xylostella* (Diamond back moth)

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

The following compounds gave an effect of at least 80% in at least one of the two categories (mortality or growth inhibition) at an application rate of 200 ppm:
P7, P9, P12, P13, P14, P15, P16, P17, P19.

Example B8: *Bemisia tabaci* (Cotton white fly): Feeding/contact activity

Cotton leaf discs were placed on agar in 24-well microtiter plates and sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying the leaf discs were infested with adult white flies. The samples were checked for mortality 6 days after incubation.

The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: P1, P2, P3, P4, P5, P6, P9, P12, P13, P14, P15, P16, P17, P18, P19.

10 Example B9: *Euschistus heros* (Neotropical Brown Stink Bug)

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

15 The following compounds gave an effect of at least 80% in at least one of the two categories (mortality or growth inhibition) at an application rate of 200 ppm: P2, P3, P4, P6, P14, P15, P16, P17.

Example B10: *Myzus persicae* (Green Peach Aphid)

20 Test compounds prepared from 10'000 ppm DMSO stock solutions were applied by a liquid handling robot into 96-well microtiter plates and mixed with a sucrose solution. Parafilm was stretched over the 96-well microtiter plate and a plastic stencil with 96 holes was placed onto the plate. Aphids were sieved into the wells directly onto the Parafilm. The infested plates were closed with a gel blotting card and a second plastic stencil and then turned upside down. The samples were assessed for mortality 5 days after infestation.

25 The following compounds resulted in at least 80% mortality at an application rate of 50 ppm: P1, P2, P3, P4, P6, P18.

Example B11: *Aphis gossypii* (Cotton aphid)

30 Cotton leaf discs were placed onto agar in a 96-well microtiter plate and sprayed with aqueous test solutions prepared from 10'000 ppm DMSO stock solutions. After drying, the leaf discs were infested with an aphid population of mixed ages. The samples were assessed for mortality 6 days after infestation.

The following compounds resulted in at least 80% average mortality at an application rate of 1000 ppm:

35 P5.

Example B12: *Frankliniella occidentalis* (Western flower thrips): Feeding/contact activity

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

Frankliniella population of mixed ages. The samples were assessed for mortality 7 days after infestation.

The following compounds resulted in at least 80% mortality at an application rate of 200 ppm: P2, P12, P15, P16.

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Example B13: *Plutella xylostella* (Diamondback Moth)

96-well microtiter plates containing artificial diet were treated with aqueous test solutions, prepared from 10'000 ppm DMSO stock solutions, by a liquid handling robot. After drying, eggs (~30 per well) were infested onto a netted lid which was suspended above the diet. The eggs hatch and L1 larvae

10

move down to the diet. The samples were assessed for mortality 9 days after infestation.

The following compounds gave an effect of at least 80% average mortality at an application rate of 500 ppm:

P1, P2, P3, P4, P5, P6, P18.

15

Example B14: *Heterodera schachtii*: Juvenile mobility in vitro profiling in 96 well plate:

Test solutions are prepared from 10'000 ppm DMSO stock solutions with a TECAN robot to achieve 20 µL of 500, 100, 50, 25, 12.5 and 6.25 ppm. For each concentration three replicates are produced.
Per well, 80 µL nematode solution is added containing 100 to 150 freshly harvested second stage juveniles of *Heterodera schachtii*. The plates are covered and stored at room temperature in the dark and incubated for 24 h. Mobility of the exposed juveniles in a treated well is measured using an imaging tool and compared to an average of 12 untreated replicates.

20

The following compounds achieved at least 80% control at 100 ppm after 24 h.

P1, P3, P4, P5, P9, P12, P13, P14, P15, P16, P17, P19.

25

Example B15: *Heterodera schachtii*: Juvenile mobility in vitro profiling in 96 well plate

Test solutions are prepared from 10'000 ppm DMSO stock solutions with a TECAN robot to achieve 20 µL of 500, 100, 50, 25, 12.5 and 6.25 ppm. For each concentration three replicates are produced. Per well, 80 µL nematode solution is added containing 100 to 150 freshly harvested second stage juveniles of *Heterodera schachtii*. The plates are covered and stored at room temperature in the dark and incubated for 48 h. Mobility of the exposed juveniles in a treated well is measured using an imaging tool and compared to an average of 12 untreated replicates.

30

The following compounds achieved at least 60% control at 100 ppm after 48 h.

P1, P2, P3, P4, P5, P9, P12, P13, P14, P15, P16, P17, P19.

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Example B16: *Meloidogyne incognita* / wheat / leaf disc preventative

Test solutions are prepared from 10'000 ppm DMSO stock solutions with a TECAN robot to achieve 20 µL of 1000, 200, 100, 50, 25 and 12.5 ppm. For each concentration three replicates are produced. Per well, 80 µL nematode solution is added containing 100 to 150 freshly harvested second stage juveniles of *Meloidogyne incognita*. The plates are covered and stored at room temperature in the dark

and incubated for 24 h. Mobility of the exposed juveniles in a treated well is measured using an imaging tool and compared to an average of 12 untreated replicates.

The following compounds achieved at least 80% control at 200 ppm after 24 h.

P12, P16.

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Example B17: *Meloidogyne incognita*: Juvenile mobility in vitro profiling in 96 well plate

Test solutions are prepared from 10'000 ppm DMSO stock solutions with a TECAN robot to achieve 20 µL of 1000, 200, 100, 50, 25 and 12.5 ppm. For each concentration three replicates are produced.

Per well, 80 µL nematode solution is added containing 100 to 150 freshly harvested second stage

10 juveniles of *Meloidogyne incognita*. The plates are covered and stored at room temperature in the dark and incubated for 48 h. Mobility of the exposed juveniles in a treated well is measured using an imaging tool and compared to an average of 12 untreated replicates

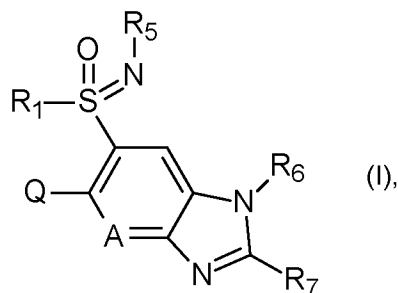
The following compounds achieved at least 60% control at 200 ppm after 48 h.

P2, P16.

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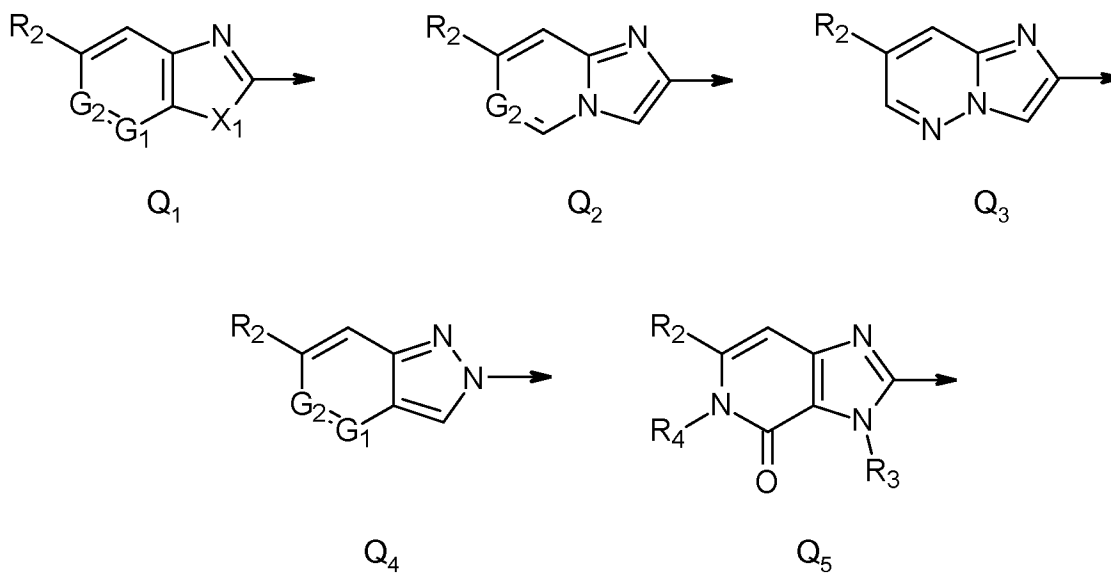
CLAIMS

1. A compound of formula (I)



wherein:

- 5 A is CH or N;
 R₁ is C₁-C₄alkyl;
 R₅ is hydrogen, formyl, cyano, C₁-C₃ alkyl, C₁-C₃alkylcarbonyl, C₁-C₃alkoxycarbonyl, C₁-C₃haloalkylcarbonyl;
 R₆ is hydrogen, C₁-C₄ alkyl, C₁-C₄haloalkyl, C₁-C₂alkoxy-C₁-C₂alkyl;
 10 R₇ is hydrogen, halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄alkylthio;
 Q is a radical selected from the group consisting of formulae Q₁, Q₂, Q₃, Q₄ and Q₅



- 15 wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A;
 and wherein
 R₂ is C₁-C₆haloalkyl, C₁-C₄haloalkylsulfanyl, C₁-C₄haloalkylsulfinyl, C₁-C₄haloalkylsulfonyl or C₁-C₆haloalkoxy;
 X₁ is O or NR₃;
 20 R₃ is C₁-C₄alkyl;

R₄ is C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, or C₃-C₆cycloalkyl;

G₁ and G₂ are, independently from each other, N or CH;

or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide of a compound of formula I.

5

2. A compound, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to claim 1, wherein:

A is CH or N;

R₁ is ethyl, propyl or isopropyl;

10 R₅ is hydrogen, cyano or C(O)R₂₅ wherein R₂₅ is C₁-C₂haloalkyl ;

R₆ is C₁-C₄ alkyl or C₁-C₄haloalkyl; and

R₇ is C₁-C₄ alkyl, C₁-C₄haloalkyl or C₁-C₄alkoxy.

15

3. A compound, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to claim 1, wherein:

A is CH or N;

R₁ is ethyl;

R₅ is hydrogen;

R₆ is methyl, ethyl or C₂haloalkyl; and

20 R₇ is C₁-C₂haloalkyl.

4. A compound, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to claim 1, wherein:

A is CH or N;

25 R₁ is ethyl;

R₅ is hydrogen;

R₆ is methyl or ethyl; and

R₇ is trifluoromethyl.

30 5. A compound, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to claim 1 wherein:

A is CH or N;

R₁ is ethyl;

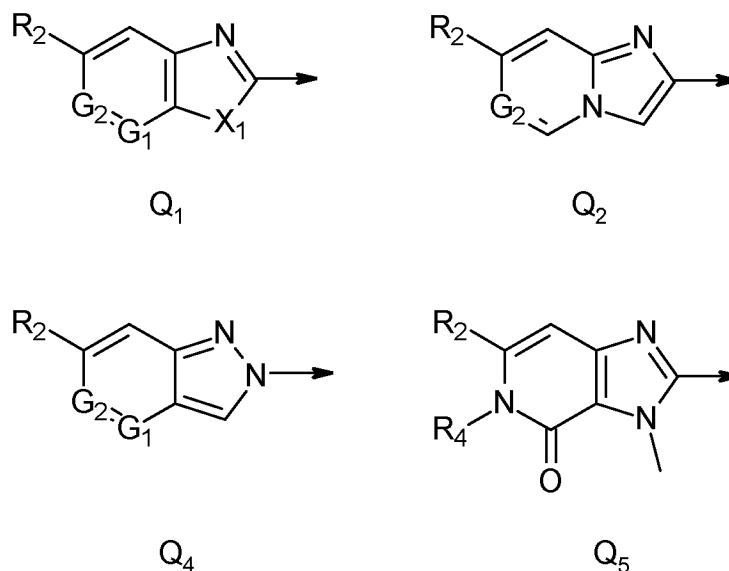
R₅ is hydrogen;

35 R₆ is methyl; and

R₇ is trifluoromethyl.

6. A compound, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to any one of claims 1 – 5 wherein:

Q is a radical selected from Q₁, Q₂, Q₄ and Q₅



wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A;

5

and wherein

R₂ is C₁-C₂haloalkyl, C₁-C₂haloalkylsulfanyl, C₁-C₂haloalkylsulfinyl or C₁-C₂haloalkylsulfonyl;

X₁ is oxygen or NCH₃;

R₄ is C₁-C₂alkyl, C₁-C₂haloalkyl, C₁-C₂alkoxy or cyclopropyl; and

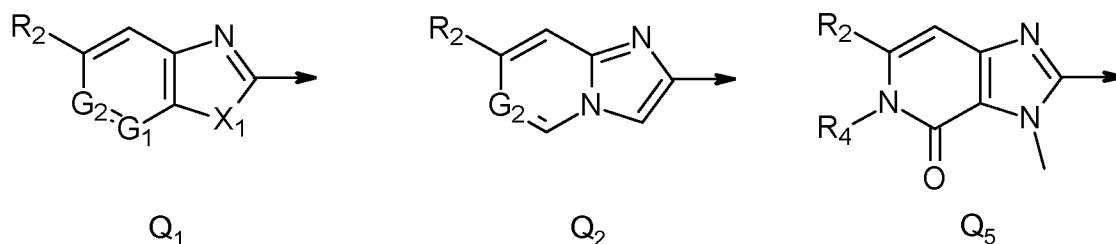
10

G₁ and G₂ are, independently from each other, N or CH.

7. A compound, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to any one of claims 1 – 5 wherein:

Q is a radical selected from Q₁, Q₂ and Q₅

15



wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A;

and wherein

20

R₂ is C₁-C₂fluoroalkyl, trifluoromethylsulfanyl, trifluoromethylsulfinyl, trifluoromethylsulfonyl, difluoromethylsulfanyl, difluoromethylsulfinyl, or difluoromethylsulfonyl;

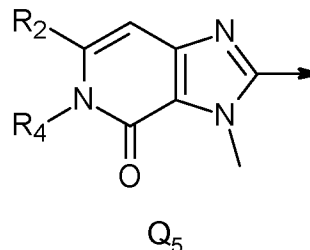
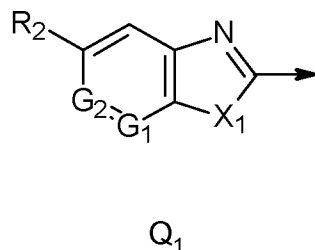
X₁ is NCH₃;

R₄ is methyl, ethyl, 2,2,2-trifluoroethyl, methoxy or cyclopropyl; and
G₁ and G₂ are, independently from each other, N or CH.

8. A compound, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to any one of claims 1 – 5 wherein:

5

Q is a radical selected from Q₁ and Q₅



wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring

10 incorporating the radical A;

and wherein

R₂ is trifluoromethyl, pentafluoroethyl, trifluoromethylsulfanyl, trifluoromethylsulfinyl or trifluoromethylsulfonyl;

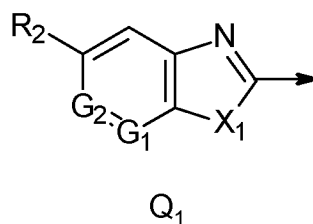
X₁ is NCH₃;

15 R₄ is ethyl, methoxy or cyclopropyl; and

G₁ is N and G₂ is CH or G₁ is CH and G₂ is N.

9. A compound, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to any one of claims 1 – 5 wherein:

20 Q is radical Q₁



wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A;

25 and wherein

R₂ is trifluoromethyl;

X₁ is NCH₃; and

G₁ is N and G₂ is CH or G₁ is CH and G₂ is N.

10. A compound, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to claim 1 wherein:

A is CH or N;

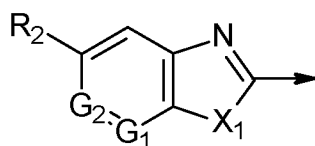
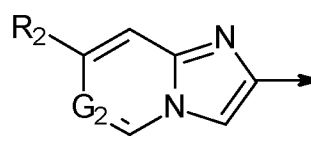
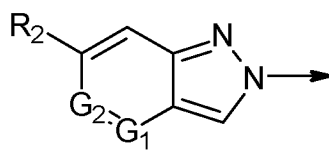
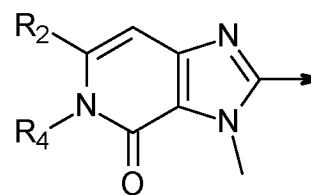
R₁ is ethyl, propyl or isopropyl;

5 R₅ is hydrogen, cyano or C(O)R₂₅ wherein R₂₅ is C₁-C₂haloalkyl ;

R₆ is C₁-C₄ alkyl or C₁-C₄haloalkyl;

R₇ is C₁-C₄ alkyl, C₁-C₄haloalkyl or C₁-C₄alkoxy;

Q is a radical selected from Q₁, Q₂, Q₄ and Q₅

Q₁Q₂Q₄Q₅

10

wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A;

and wherein

R₂ is C₁-C₂haloalkyl, C₁-C₂haloalkylsulfanyl, C₁-C₂haloalkylsulfinyl or C₁-C₂haloalkylsulfonyl;

15 X₁ is oxygen or NCH₃;

R₄ is C₁-C₂alkyl, C₁-C₂haloalkyl, C₁-C₂alkoxy or cyclopropyl;

G₁ and G₂ are, independently from each other, N or CH.

11. A compound, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to claim 1 wherein:

20 A is CH or N;

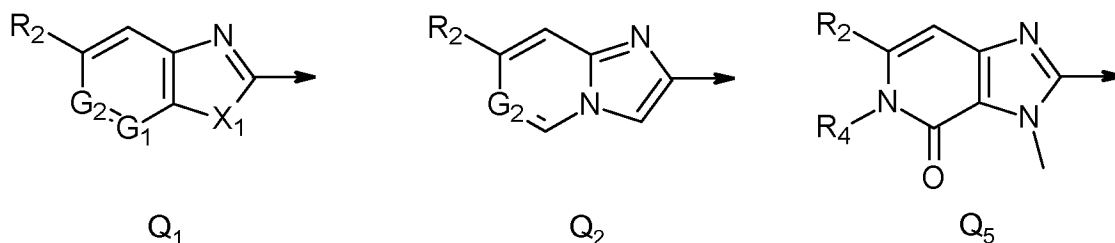
R₁ is ethyl;

R₅ is hydrogen;

R₆ is methyl, ethyl or C₂haloalkyl;

25 R₇ is C₁-C₂haloalkyl;

Q is a radical selected from Q₁, Q₂ and Q₅



wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A;

and wherein

- 5 R_2 is C_1 - C_2 fluoroalkyl, trifluoromethylsulfanyl, trifluoromethylsulfinyl, trifluoromethylsulfonyl, difluoromethylsulfanyl, difluoromethylsulfinyl, or difluoromethylsulfonyl;

X_1 is NCH_3 ;

R_4 is methyl, ethyl, 2,2,2-trifluoroethyl, methoxy or cyclopropyl;

G_1 and G_2 are, independently from each other, N or CH.

10

12. A compound, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to claim 1 wherein:

A is CH or N;

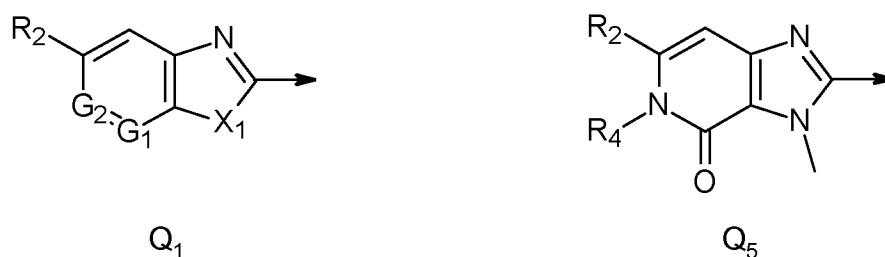
R_1 is ethyl;

- 15 R_5 is hydrogen;

R_6 is methyl or ethyl;

R_7 is trifluoromethyl;

Q is a radical selected from Q_1 and Q_5



20

wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A;

and wherein

- 25 R_2 is trifluoromethyl, pentafluoroethyl, trifluoromethylsulfanyl, trifluoromethylsulfinyl or trifluoromethylsulfonyl;

X_1 is NCH_3 ;

R_4 is ethyl, methoxy or cyclopropyl;

G_1 is N and G_2 is CH or G_1 is CH and G_2 is N.

13. A compound, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to claim 1 wherein:

A is CH or N;

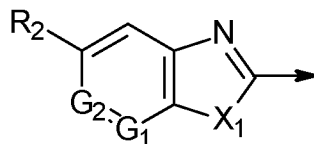
R₁ is ethyl;

5 R₅ is hydrogen;

R₆ is methyl;

R₇ is trifluoromethyl;

Q is radical Q₁



10

Q₁

wherein the arrow denotes the point of attachment to the bicyclic sulfoximine-containing ring incorporating the radical A;

and wherein

R₂ is trifluoromethyl;

15 X₁ is NCH₃;

G₁ is N and G₂ is CH or G₁ is CH and G₂ is N.

14. A compound, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to claim 1 wherein:

20 A is CH or N;

R₁ is ethyl, propyl or isopropyl; preferably ethyl;

R₂ is C₁-C₂haloalkyl, C₁-C₂haloalkylsulfanyl, C₁-C₂haloalkylsulfinyl or C₁-C₂haloalkylsulfonyl; preferably, R₂ is trifluoromethyl, pentafluoroethyl, trifluoromethylsulfanyl, trifluoromethylsulfinyl or trifluoromethylsulfonyl;

25 R₅ is hydrogen, formyl, cyano, C₁-C₃alkylcarbonyl, C₁-C₃alkoxycarbonyl, C₁-C₃haloalkylcarbonyl; preferably R₅ is hydrogen, formyl, cyano, -C(O)OCH₃, -C(O)CH₃, -C(O)CH₂CH₃, -C(O)CF₃;

R₆ is methyl, ethyl or C₂haloalkyl; preferably R₆ is methyl or ethyl; and

R₇ is C₁-C₂haloalkyl; preferably R₇ is -CHF₂ or -CF₃.

30 15. A compound, or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, according to claim 14 wherein:

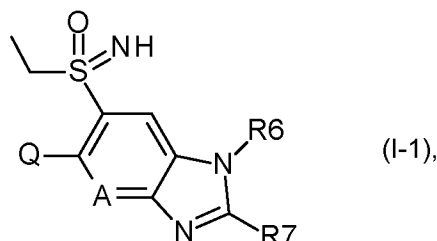
R₂ is trifluoromethyl or trifluoromethylsulfonyl; most preferably R₂ is trifluoromethyl;

R₅ is hydrogen;

R₆ is methyl; and

R₇ is trifluoromethyl.

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



5 wherein A, R₂, R₃, R₄, R₆, R₇, Q, X₁, G₁ and G₂ are as defined are as defined under formula I in claim 1.

17. A compound of formula I according to claim 1, selected from the group consisting of:

ethyl-[3-ethyl-6-[3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-2-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-imino-oxo-λ⁶-sulfane (Compound P1);

10 2-[6-(ethylsulfonimidoyl)-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-5-methoxy-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (Compound P2);

2-[1-ethyl-6-(ethylsulfonimidoyl)-2-(trifluoromethyl)benzimidazol-5-yl]-5-methoxy-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (Compound P3);

ethyl-imino-[3-methyl-6-[3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-2-yl]-2-

15 (trifluoromethyl)benzimidazol-5-yl]-oxo-λ⁶-sulfane (Compound P4);

ethyl-imino-[3-methyl-6-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-2-

(trifluoromethyl)benzimidazol-5-yl]-oxo-λ⁶-sulfane (Compound P5);

ethyl-[3-(2-fluoroethyl)-6-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-2-

(trifluoromethyl)benzimidazol-5-yl]-imino-oxo-λ⁶-sulfane (Compound P6);

20 ethyl-imino-[3-methyl-2-(trifluoromethyl)-6-[5-(trifluoromethylsulfonyl)-1,3-benzoxazol-2-yl]benzimidazol-5-yl]-oxo-λ⁶-sulfane (Compound P7);

ethyl-[3-ethyl-2-(trifluoromethyl)-6-[5-(trifluoromethylsulfonyl)-1,3-benzoxazol-2-yl]benzimidazol-5-yl]-imino-oxo-λ⁶-sulfane (Compound P8);

5-ethyl-2-[6-(ethylsulfonimidoyl)-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-

25 (trifluoromethyl)imidazo[4,5-c]pyridin-4-one (Compound P9);

ethyl-imino-[3-methyl-2-(trifluoromethyl)-6-[5-(trifluoromethyl)-1,3-benzoxazol-2-yl]benzimidazol-5-yl]-oxo-λ⁶-sulfane (Compound P10);

ethyl-[3-ethyl-2-(trifluoromethyl)-6-[5-(trifluoromethyl)-1,3-benzoxazol-2-yl]benzimidazol-5-yl]-imino-oxo-λ⁶-sulfane (Compound P11);

30 5-cyclopropyl-2-[6-(ethylsulfonimidoyl)-1-methyl-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (Compound P12);

ethyl-imino-[3-methyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-oxo-λ⁶-sulfane (Compound P13);

- ethyl-[3-ethyl-6-[7-methyl-3-(trifluoromethyl)imidazo[4,5-c]pyridazin-6-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-imino-oxo- λ^6 -sulfane (Compound P14);
- 5-ethyl-2-[1-ethyl-6-(ethylsulfonimidoyl)-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (Compound P15);
- 5 5-cyclopropyl-2-[1-ethyl-6-(ethylsulfonimidoyl)-2-(trifluoromethyl)benzimidazol-5-yl]-3-methyl-6-(trifluoromethyl)imidazo[4,5-c]pyridin-4-one (Compound P16);
- ethyl-[3-ethyl-6-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-2-(trifluoromethyl)benzimidazol-5-yl]-imino-oxo- λ^6 -sulfane (Compound P17);
- ethyl-imino-[1-methyl-5-[3-methyl-6-(trifluoromethyl)imidazo[4,5-b]pyridin-2-yl]-2-(trifluoromethyl)imidazo[4,5-b]pyridin-6-yl]-oxo- λ^6 -sulfane (Compound P18); and
- 10 ethyl-imino-[3-methyl-2-(trifluoromethyl)-6-[6-(trifluoromethyl)pyrazolo[4,3-c]pyridin-2-yl]benzimidazol-5-yl]-oxo- λ^6 -sulfane (Compound P19).
18. A composition comprising an insecticidally, acaricidally, nematocidally or molluscicidally effective amount of a compound of formula (I), or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, as defined in any of claims 1 – 17 and, optionally, an auxiliary or diluent.
- 15
19. A method of combating and controlling insects, acarines, nematodes or molluscs which comprises applying to a pest, to a locus of a pest, or to a plant susceptible to attack by a pest an insecticidally, acaricidally, nematocidally or molluscicidally effective amount of a compound of formula (I), or an agrochemically acceptable salt, stereoisomer, enantiomer, tautomer or N-oxide thereof, as defined in any of claims 1 – 17 or a composition as defined in claim 18.
- 20
20. A method for the protection of plant propagation material from the attack by insects, acarines, nematodes or molluscs, which comprises treating the propagation material or the site, where the propagation material is planted, with a composition according to claim 19.
- 25

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/062355

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D487/04 A01N43/90
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
C07D A01N
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2017/133994 A1 (SYNGENTA PARTICIPATIONS AG [CH]) 10 August 2017 (2017-08-10) cited in the application abstract; claims 3, 10-12; examples 1009-1032, 1041-1064; table 1 -----	1-20
Y	WO 2016/142326 A1 (SYNGENTA PARTICIPATIONS AG [CH]) 15 September 2016 (2016-09-15) cited in the application abstract; claims 10-12; examples 2097-2132; table 2 -----	1-20
Y	WO 2016/107742 A1 (SYNGENTA PARTICIPATIONS AG [CH]) 7 July 2016 (2016-07-07) cited in the application abstract; claims 12-14; examples 1093-1130, 2093-2130, 3093-3130; tables 1-3 -----	1-20
	-/--	

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"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</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search 3 June 2019	Date of mailing of the international search report 04/07/2019
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Goss, Ilaria
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/062355

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2015/071180 A1 (SYNGENTA PARTICIPATIONS AG [CH]) 21 May 2015 (2015-05-21) cited in the application abstract; claims 4-6; examples 001-010; tables 1, 4-19 -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/EP2019/062355

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2017133994	A1	10-08-2017	NONE
WO 2016142326	A1	15-09-2016	BR 112017019372 A2 03-07-2018
		CN 107428751 A	01-12-2017
		EP 3268365 A1	17-01-2018
		JP 2018509418 A	05-04-2018
		US 2018134697 A1	17-05-2018
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WO 2016107742	A1	07-07-2016	BR 112017014061 A2 17-07-2018
		CN 107108612 A	29-08-2017
		EP 3240788 A1	08-11-2017
		ES 2703172 T3	07-03-2019
		JP 2018502912 A	01-02-2018
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