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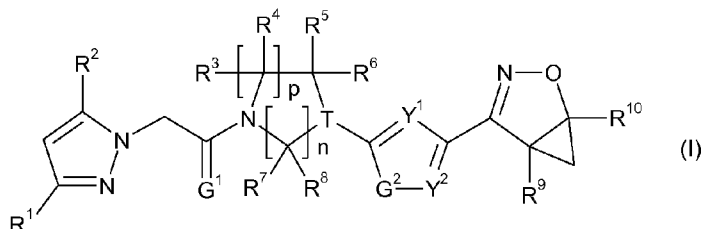
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(54) Title: MICROBIOCIDAL PYRAZOLE DERIVATIVES



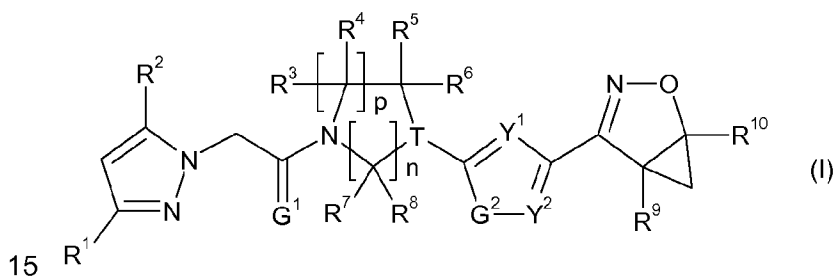
(57) Abstract: Compounds of the formula (I) wherein the substituents are as defined in claim 1, are useful as a pesticides.

Microbiocidal Pyrazole Derivatives

The present invention relates to microbiocidal pyrazole derivatives, e.g. as active ingredients, which have microbiocidal activity, in particular fungicidal activity. The invention also relates to preparation of these pyrazole derivatives, to pyrazole derivatives used as intermediates in the preparation of these pyrazole derivatives, to preparation of these intermediates, to agrochemical compositions which comprise at least one of the pyrazole derivatives, to preparation of these compositions and to use of the pyrazole derivatives or compositions in agriculture or horticulture for controlling or preventing infestation of plants, harvested food crops, seeds or non-living materials by phytopathogenic microorganisms, preferably fungi.

Certain compounds for use as fungicides are described in WO 2007/014290, WO 2008/013622, WO 2008/013925, WO 2008/091580, WO 2008/091594 and WO 2009/055514.

The present invention provides compounds of formula I:



wherein,

G¹ and G² are independently O or S;

T is CR¹¹ or N;

Y¹ and Y² are independently CR¹² or N;

n is 1 or 2;

p is 1 or 2, providing that when n is 2, p is 1;

R¹ and R² each independently are C₁-C₄alkyl, or C₁-C₄haloalkyl or C₃-C₅cycloalkyl;

R³, R⁴, R⁵, R⁶, R⁷ and R⁸ each independently are hydrogen, halogen, cyano, C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄haloalkyl, C₃-C₅cycloalkyl or C₁-C₄alkylthio;

R⁹ is hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄haloalkyl, C₃-C₅cycloalkyl, aryl or heteroaryl, wherein aryl or heteroaryl are optionally substituted by one or more R¹³;

R¹⁰ is C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₃-C₅cycloalkyl, C₂-C₄alkenyl, C₂-C₄haloalkenyl, C₂-C₄alkynyl, C₂-C₄haloalkynyl, C₁-C₄alkoxycarbonyl, C₁-C₄alkylaminocarbonyl, C₁-C₄alkylcarbonyl O-C₁-C₄alkyloxime, C₁-C₄alkylcarbonyl O-

aryloxime, aryl, heteroaryl, arylC₁-C₄alkyl or heteroarylC₁-C₄alkyl, wherein aryl and heteroaryl are optionally substituted by one or more R¹³;

R¹¹ is hydrogen, halogen or hydroxyl;

R¹² is hydrogen, halogen or cyano;

each R¹³ independently is halogen, cyano, C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₂-C₄alkenyloxy, C₂-C₄alkynyloxy, formyl, C₁-C₄alkylcarbonyl, C₁-C₄alkylcarbonyl oxime or C₁-C₄alkylcarbonyl O-C₁-C₄alkyloxime; or a salt or a N-oxide thereof.

- 5 Where substituents are indicated as being optionally substituted, this means that they may or may not carry one or more identical or different substituents, e.g. one to five substituents, e.g. one to three substituents. Normally not more than three such optional substituents are present at the same time. Where a group is indicated as being substituted, e.g. alkyl, unless stated otherwise this includes those groups that are part of other groups,
- 10 e.g. the alkyl in alkylthio.

The term "halogen" refers to fluorine, chlorine, bromine or iodine, preferably fluorine, chlorine or bromine.

- Alkyl substituents may be straight-chained or branched. Alkyl on its own or as part of another substituent is, depending upon the number of carbon atoms mentioned, for example,
- 15 methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl and the isomers thereof, for example, isopropyl, iso-butyl, sec-butyl, tert-butyl, iso-amyl or pivaloyl.

- Alkenyl substituents can be in the form of straight or branched chains, and the alkenyl moieties, where appropriate, can be of either the (E)- or (Z)-configuration. Examples are vinyl and allyl. The alkenyl groups are preferably C₂-C₆, more preferably C₂-C₄ and most preferably
- 20 C₂-C₃ alkenyl groups.

Alkynyl substituents can be in the form of straight or branched chains. Examples are ethynyl and propargyl. The alkynyl groups are preferably C₂-C₆, more preferably C₂-C₄ and most preferably C₂-C₃ alkynyl groups.

- Haloalkyl groups may contain one or more identical or different halogen atoms and, for
- 25 example, may stand for CH₂Cl, CHCl₂, CCl₃, CH₂F, CHF₂, CF₃, CF₃CH₂, CH₃CF₂, CF₃CF₂ or CCl₃CCl₂.

Haloalkenyl groups are alkenyl groups, respectively, which are substituted with one or more of the same or different halogen atoms and are, for example, 2,2-difluorovinyl or 1,2-dichloro-2-fluoro-vinyl.

- 30 Haloalkynyl groups are alkynyl groups, respectively, which are substituted with one or more of the same or different halogen atoms and are, for example, 1-chloro-prop-2-ynyl.

Alkoxy means a radical -OR, where R is alkyl, e.g. as defined above. Alkoxy groups include, but are not limited to, methoxy, ethoxy, 1-methylethoxy, propoxy, butoxy, 1-methylpropoxy and 2-methylpropoxy.

- 35 Cyano means a -CN group.

Amino means an NH₂ group.

Hydroxyl or hydroxy stands for a -OH group.

Aryl means a ring system which may be mono-, bi- or tricyclic. Examples of such rings include phenyl, naphthalenyl, anthracenyl, indenyl or phenanthrenyl. A preferred aryl group is phenyl.

Heteroaryl stands for aromatic ring systems comprising mono-, bi- or tricyclic systems wherein at least one oxygen, nitrogen or sulfur atom is present as a ring member. Monocyclic and bicyclic aromatic ring systems are preferred, monocyclic ring systems are more preferred. For example, monocyclic heteroaryl may be a 5- to 7-membered aromatic ring containing one to three heteroatoms selected from oxygen, nitrogen and sulfur, more preferably selected from nitrogen and sulfur. Bicyclic heteroaryl may be a 9- to 11-membered bicyclic ring containing one to five heteroatoms, preferably one to three heteroatoms, selected from oxygen, nitrogen and sulfur. Examples are furyl, thienyl, pyrrolyl, imidazolyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, oxadiazolyl, thiadiazolyl, triazolyl, tetrazolyl, pyridyl, pyridazinyl, pyrimidinyl, pyrazinyl, triazinyl, tetrazinyl, indolyl, benzothiophenyl, benzofuranyl, benzimidazolyl, indazolyl, benzotriazolyl, benzothiazolyl, benzoxazolyl, imiazothiazoyl, quinoliny, quinoxaliny, isoquinoliny, phthalazinyl, quinoxaliny, quinazolinyl, cinnoliny and naphthyridinyl, preferably pyridyl, pyrazinyl, pyridazinyl, pyrimidinyl, pyrrolyl, pyrazolyl, imidazolyl, triazolyl, furanyl, thienyl thiazolyl or thiadiazolyl. Heteroaryl rings do not contain adjacent oxygen ring atoms, adjacent sulfur ring atoms or adjacent oxygen and sulfur ring atoms. A link to a heteroaryl group can be via a carbon atom or via a nitrogen atom.

The presence of one or more possible asymmetric carbon atoms in a compound of formula I means that the compounds may occur in optically isomeric forms, i.e. enantiomeric or diastereomeric forms. Also atropisomers may occur as a result of restricted rotation about a single bond. Formula I is intended to include all those possible isomeric forms and mixtures thereof. The present invention includes all those possible isomeric forms and mixtures thereof for a compound of formula I. Likewise, formula I is intended to include all possible tautomers. The present invention includes all possible tautomeric forms for a compound of formula I.

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.

The following list provides definitions, including preferred definitions, for substituents R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , G^1 , G^2 , T, Y^1 , Y^2 , n and p with reference to compounds of formula I and other compounds of the invention carrying the same substituents. For any one of these substituents, any of the definitions given below may be

combined with any definition of any other substituent given below or elsewhere in this document.

G^1 and G^2 are independently O or S.

G^1 is preferably O.

5 G^2 is preferably S.

T is CR^{11} or N, preferably CH or N, more preferably CH.

Y^1 and Y^2 are independently CR^{12} or N.

Y^1 is preferably CH or N, more preferably N.

Y^2 is preferably CH or N; more preferably CH.

10 n is 1 or 2, preferably 2.

p is 1 or 2, providing that when n is 2, p is 1, preferably p is 1.

Preferably, p is 1 and n is 2.

R^1 and R^2 each independently are C_1 - C_4 alkyl, C_1 - C_4 haloalkyl or C_3 - C_5 cycloalkyl.

Preferably R^1 and R^2 are each independently methyl or halomethyl, more preferably methyl,
15 difluoromethyl or trifluoromethyl.

Preferably R^1 is difluoromethyl or trifluoromethyl. Preferably R^2 is methyl or difluoromethyl. In one group of compounds R^1 is trifluoromethyl and R^2 is methyl. In another group of compounds R^1 and R^2 are both difluoromethyl.

R^3 , R^4 , R^5 , R^6 , R^7 and R^8 each independently are hydrogen, halogen, cyano, C_1 -
20 C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkyl, C_3 - C_5 cycloalkyl or C_1 - C_4 alkylthio; preferably hydrogen, halogen, methyl, halomethyl or methylthio, more preferably hydrogen or methyl, most preferably hydrogen.

R^9 is hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkyl, C_3 - C_5 cycloalkyl, aryl or heteroaryl, wherein aryl or heteroaryl are optionally substituted by one or more R^{13} .

25 Preferably R^9 is hydrogen, C_1 - C_4 alkyl or C_3 - C_5 cycloalkyl, even more preferably hydrogen or methyl, most preferably hydrogen.

R^{10} is C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkyl, C_1 - C_4 haloalkoxy, C_3 - C_5 cycloalkyl, C_2 -
 C_4 alkenyl, C_2 - C_4 haloalkenyl, C_2 - C_4 alkynyl, C_2 - C_4 haloalkynyl, C_1 - C_4 alkoxycarbonyl, C_1 -
 C_4 alkylaminocarbonyl, C_1 - C_4 alkylcarbonyl O- C_1 - C_4 alkyloxime, C_1 - C_4 alkylcarbonyl O-
30 aryloxime, aryl, heteroaryl, aryl- C_1 - C_4 alkyl or heteroaryl- C_1 - C_4 alkyl, wherein aryl and heteroaryl are optionally substituted by one or more R^{13} ;

Preferably, R^{10} is C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_3 - C_5 cycloalkyl, aryl or heteroaryl, wherein aryl and heteroaryl are optionally substituted by one or more R^{13} ; more preferably C_1 - C_4 haloalkyl, aryl or heteroaryl, wherein aryl and heteroaryl are optionally substituted by
35 one or more R^{13} ; most preferably phenyl, thienyl and pyridyl, each of them optionally substituted by one or more R^{13} .

R^{11} is hydrogen, halogen or hydroxyl; preferably hydrogen or hydroxyl, more preferably hydrogen.

R¹² is hydrogen, halogen or cyano; preferably hydrogen or cyano, more preferably hydrogen.

- Each R¹³ independently is halogen, cyano, C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₂-C₄alkenyloxy, C₂-C₄alkynyloxy, formyl, C₁-C₄alkylcarbonyl, C₁-C₄alkylcarbonyl oxime or C₁-C₄alkylcarbonyl O-C₁-C₄alkyloxime; preferably halogen, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₂-C₄alkenyloxy or C₂-C₄alkynyloxy; more preferably halogen, C₁-C₄haloalkoxy or C₂-C₄alkynyloxy, most preferably fluoro or propargyloxy.

Preferably the compound of formula I is a compound wherein:

- G¹ is O
- 10 G² is S;
- T is CH or N;
- Y¹ and Y² are independently CH or N;
- n is 1 or 2;
- p is 1 or 2, providing that when n is 2, p is 1;
- 15 R¹ and R² each independently are methyl or halomethyl;
- R³, R⁴, R⁵, R⁶, R⁷ and R⁸ each independently are hydrogen, halogen, methyl, halomethyl or methylthio;
- R⁹ is hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄haloalkyl, C₃-C₅cycloalkyl, aryl or heteroaryl, wherein aryl or heteroaryl are optionally substituted by one or more R¹³;
- 20 R¹⁰ is C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₃-C₅cycloalkyl, C₂-C₄alkenyl, C₂-C₄haloalkenyl, C₂-C₄alkynyl, C₂-C₄haloalkynyl, C₁-C₄alkoxycarbonyl, C₁-C₄alkylaminocarbonyl, C₁-C₄alkylcarbonyl O-C₁-C₄alkyloxime, C₁-C₄alkylcarbonyl O-aryloxime, aryl, heteroaryl, arylC₁-C₄alkyl or heteroarylC₁-C₄alkyl, wherein aryl and heteroaryl are optionally substituted by one or more R¹³;
- 25 or a salt or a N-oxide thereof.

More preferably the compound of formula I is a compound wherein:

- G¹ is O
- G² is S;
- T is CH or N;
- 30 Y¹ and Y² are independently CH or N;
- n is 1 or 2;
- p is 1 or 2, providing that when n is 2, p is 1;
- R¹ and R² each independently are methyl or halomethyl;
- R³, R⁴, R⁵, R⁶, R⁷ and R⁸ each independently are hydrogen, halogen, methyl, halomethyl or
- 35 methylthio;
- R⁹ is hydrogen, C₁-C₄alkyl or C₃-C₅cycloalkyl;
- R¹⁰ is C₁-C₄alkyl, C₁-C₄haloalkyl, C₃-C₅cycloalkyl, aryl or heteroaryl, wherein aryl and heteroaryl are optionally substituted by one or more R¹³;

each R¹³ independently is halogen, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₂-C₄alkenyloxy, C₂-C₄alkynyloxy, formyl, C₁-C₄alkylcarbonyl, C₁-C₄alkylcarbonyl oxime or C₁-C₄alkylcarbonyl O-C₁-C₄alkyloxime;
or a salt or a N-oxide thereof.

5

Preferably the compound of formula I is a compound wherein:

G¹ is O

G² is S;

T is CH or N;

10 Y¹ and Y² are independently CH or N;

n is 1 or 2;

p is 1 or 2, providing that when n is 2, p is 1;

R¹ and R² each independently are methyl or halomethyl;

R³, R⁴, R⁵, R⁶, R⁷ and R⁸ each independently are hydrogen, halogen, methyl, methylthio or

15 halomethyl;

R⁹ is hydrogen or methyl.;

R¹⁰ is C₁-C₄haloalkyl, aryl or heteroaryl, wherein aryl and heteroaryl are optionally substituted by one or more R¹³.

Each R¹³ independently from each other, is halogen, C₁-C₄haloalkoxy or C₂-C₄alkynyloxy

20 or a salt or a N-oxide thereof.

Preferably the compound of formula I is a compound wherein:

G¹ is O

G² is S;

25 T is CH or N;

Y¹ and Y² are independently CH or N;

n is 1 or 2;

p is 1 or 2, providing that when n is 2, p is 1;

R¹ and R² each independently are methyl, difluoromethyl or trifluoromethyl;

30 R³, R⁴, R⁵, R⁶, R⁷ and R⁸ each independently are hydrogen, halogen, methyl, methylthio or halomethyl;

R⁹ is hydrogen;

R¹⁰ is phenyl, thienyl and pyridyl, each of them optionally substituted by one or more R¹³.

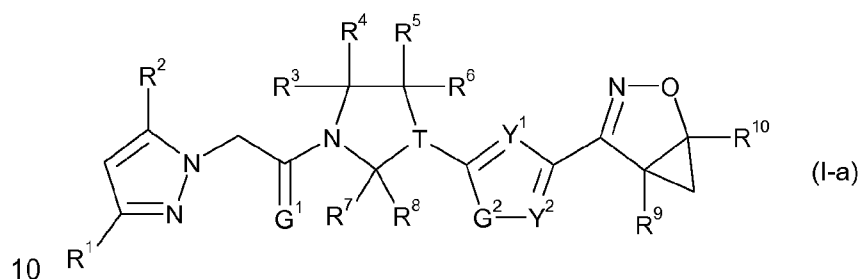
Each R¹³ independently from each other, is fluoro or propargyloxy.

35 or a salt or a N-oxide thereof.

Preferably the compound of formula I is a compound wherein G¹ is O, G² is S, T is CH, Y¹ is N, and Y² is CH.

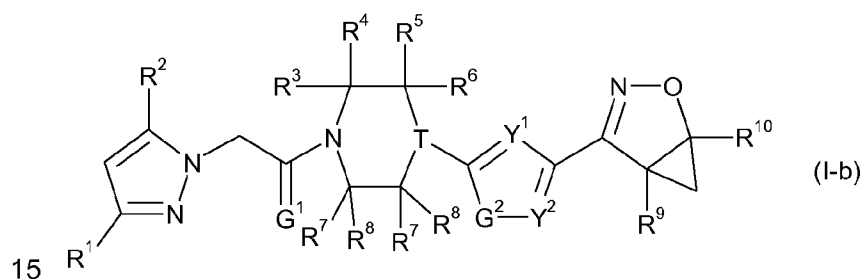
Preferably the compound of formula I is a compound wherein R^1 and R^2 each independently
 5 are methyl, difluoromethyl or trifluoromethyl and R^3 , R^4 , R^5 , R^6 , R^7 and R^8 each
 independently are hydrogen, or methyl, and preferably hydrogen.

For the avoidance of doubt, when n is 1 and p is 1 compounds of formula I have the
 formula according to formula I-a:



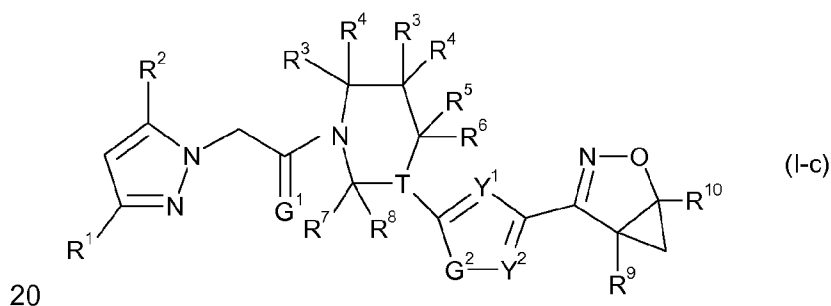
in which R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^1 , G^2 , T , Y^1 and Y^2 have the definitions as
 described for formula I.

When n is 2 and p is 1 compounds of formula I have the formula according to formula
 I-b:



in which R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^1 , G^2 , T , Y^1 and Y^2 have the definitions as
 described for formula I.

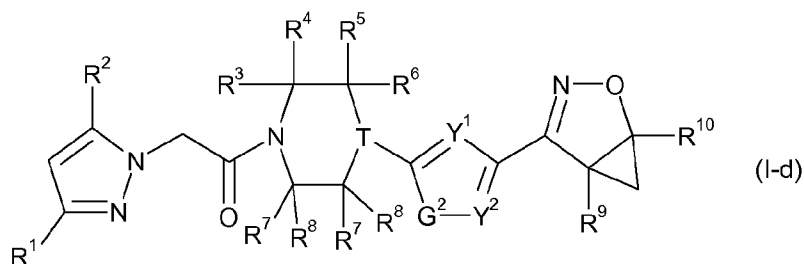
When n is 1 and p is 2, compounds of formula I have the formula according to formula
 I-c:



in which R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^1 , G^2 , T , Y^1 and Y^2 have the definitions as
 described for formula I.

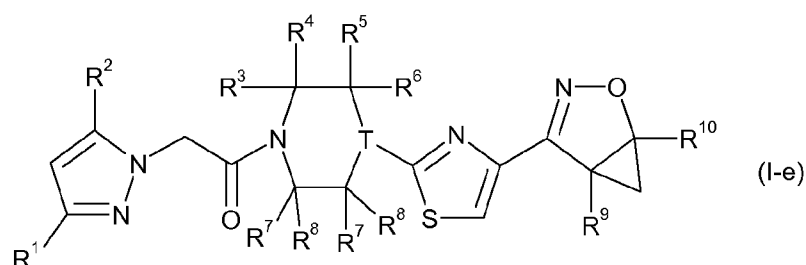
The invention also relates to compounds of formula I-a, formula I-b and formula I-c as shown above.

The invention also relates to compounds of formula I-d:



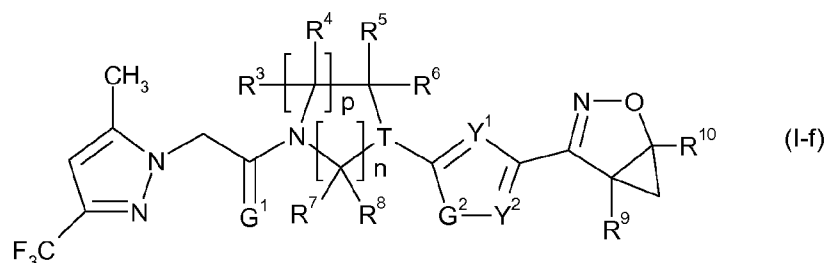
5 in which $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, G^2, T, Y^1$ and Y^2 have the definitions as described for formula I. Preferred definitions of $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, G^2, T, Y^1$ and Y^2 are as defined for formula I.

The invention also relates to compounds of formula I-e:



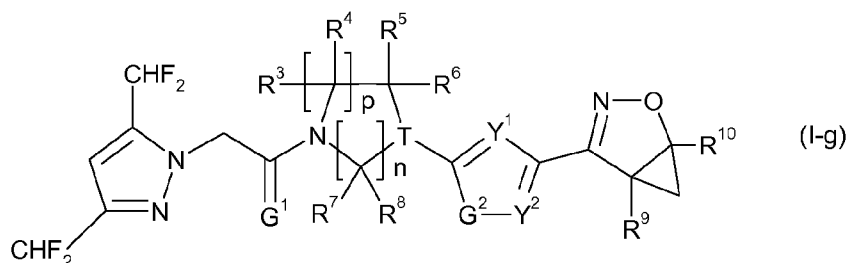
10 in which R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰ and T have the definitions as described for formula I. Preferred definitions of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰ and T are as defined for formula I.

The invention also relates to compounds of formula I-f:



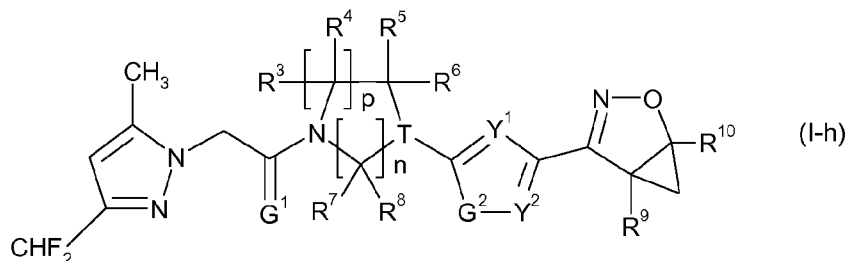
15 wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^1 , G^2 , T , Y^1 , Y^2 , n and p have the definition as described for formula I. Preferred definitions of R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^1 , G^2 , T , Y^1 , Y^2 , n and p are as defined for formula I.

The invention also relates to compounds of formula I-g:



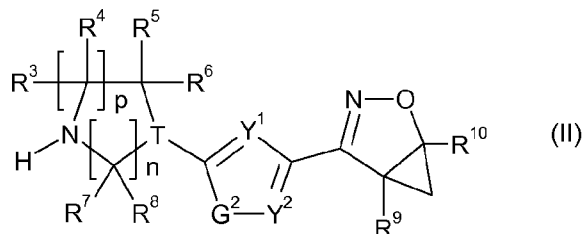
in which R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^1 , G^2 , T , Y^1 , Y^2 , n and p have the definitions as described for formula I. Preferred definitions of R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^1 , G^2 , T , Y^1 , Y^2 , n and p are as defined for formula I.

5 The invention also relates to compounds of formula I-h:



in which R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^1 , G^2 , T , Y^1 , Y^2 , n and p have the definitions as described for formula I. Preferred definitions of R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^1 , G^2 , T , Y^1 , Y^2 , n and p are as defined for formula I.

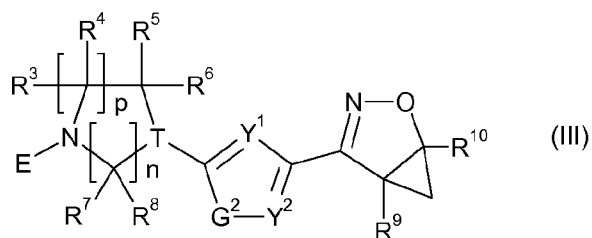
10 The invention includes compounds of formula II:



wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^2 , T , Y^1 , Y^2 , n and p are as defined for a compound of formula I. These compounds, including salts and N-oxides thereof, are useful as intermediates in the synthesis of compounds of formula I. Preferred definitions of R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^2 , T , Y^1 , Y^2 , n and p are as defined for formula I.

15

The invention includes compounds of formula III:



wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^2 , T , Y^1 , Y^2 , n and p are as defined for a compound of formula I and E is a protecting group, such as C_1 - C_4 alkylcarbonyl, benzyl or C_1 - C_4

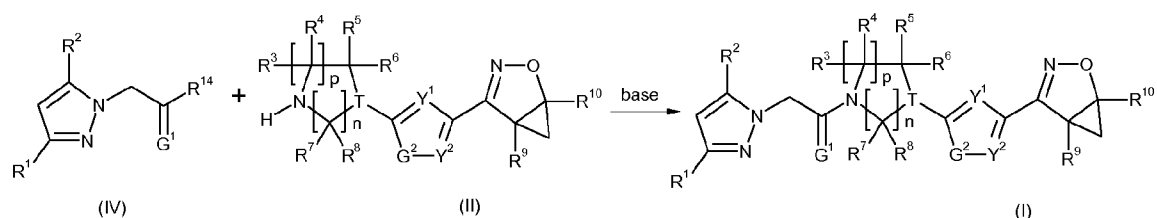
alkoxycarbonyl, in particular acetyl, benzyl or *tert*-butoxycarbonyl. These compounds, including salts and N-oxides thereof, are useful as intermediates in the synthesis of compounds of formula I. Preferred definitions of R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^2 , T, Y^1 , Y^2 , n and p are as defined for formula I.

- 5 Compounds of the present invention can be made as shown in the following schemes.

The compounds of formula I, wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^1 , G^2 , T, Y^1 , Y^2 , n and p are as defined for formula I can be obtained by transformation of a compound of formula IV, wherein R^1 , R^2 and G^1 are as defined for formula I and R^{14} is hydroxy,

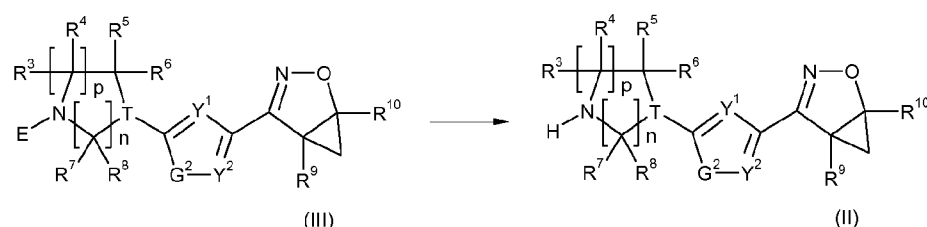
- 10 halogen, preferably fluoro, chloro or bromo, or alkoxy, such as methoxy or ethoxy, with a compound of formula II, wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^2 , T, Y^1 , Y^2 , n and p are as defined for formula I, and a base or an activating agent. This is shown in Scheme 1.

Scheme 1



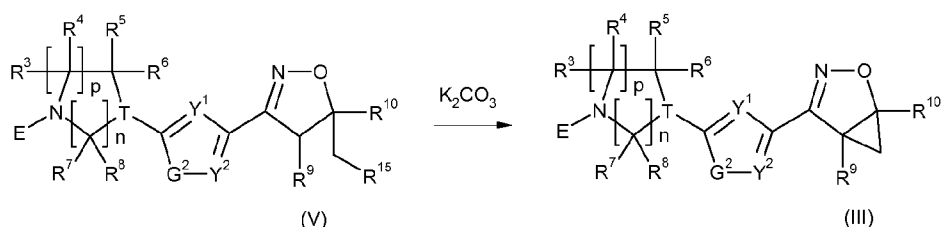
- 15 The compounds of formula II, wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^2 , T, Y^1 , Y^2 , n and p are as defined for formula I can be obtained by transformation of a compound of formula III, wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^2 , T, Y^1 , Y^2 , n and p are as defined for formula I and E is a protecting group such as acetyl, benzyl or *tert*-butoxycarbonyl, with a deprotecting agent such as a base, an acid or a hydrogenation system such as H_2/Pd . This
- 20 is shown in Scheme 2.

Scheme 2



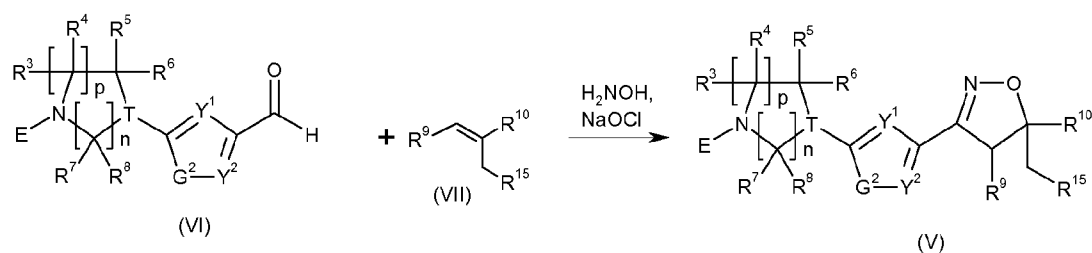
- The compounds of formula III, wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^2 , T, Y^1 , Y^2 , n and p are as defined for formula I and E is a protecting group such as acetyl, benzyl or *tert*-butoxycarbonyl, can be obtained by transformation of a compound of formula V, wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^2 , T, Y^1 , Y^2 , n and p are as defined for formula I, R^{15} is halogen, preferably chloro or bromo, or a sulfonate, such as mesylate, and E is a protecting group such as acetyl, benzyl or *tert*-butoxycarbonyl, with a base such as potassium carbonate. This
- 25 is shown in Scheme 3.

Scheme 3



The compounds of formula V, wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^2 , T, Y^1 , Y^2 , n and p are as defined for formula I, R^{15} is halogen, preferably chloro or bromo, or a sulfonate, such as mesylate, and E is a protecting group such as acetyl, benzyl or *tert*-butoxycarbonyl, can be obtained by transformation of a compound of formula VI, wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , G^2 , T, Y^1 , Y^2 , n and p are as defined for formula I and E is a protecting group such as acetyl, benzyl or *tert*-butoxycarbonyl, with a compound of formula VII, wherein R^9 and R^{10} are as defined for formula I and R^{15} is halogen, preferably chloro or bromo, or a sulfonate, such as mesylate, and hydroxylamine and sodium hypochlorite. This is shown in Scheme 4.

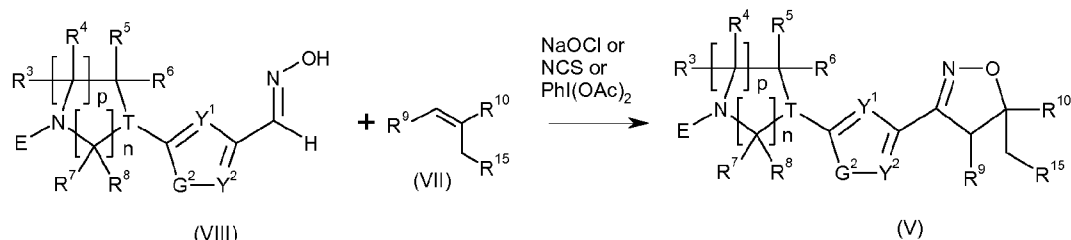
Scheme 4



15

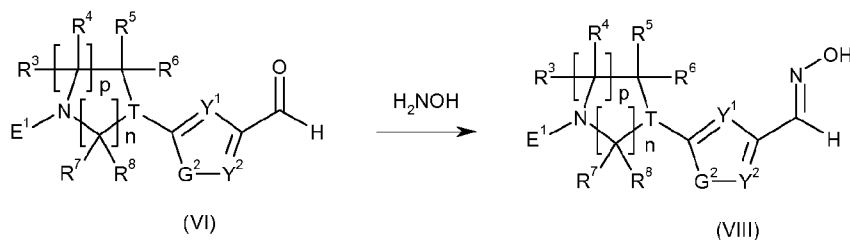
Alternatively, compounds of formula V, wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^2 , T, Y^1 , Y^2 , n and p are as defined for formula I, R^{15} is halogen, preferably chloro or bromo, or a sulfonate, such as mesylate, and E is a protecting group such as acetyl, benzyl or *tert*-butoxycarbonyl, can be obtained by transformation of a compound of formula VIII, wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , G^2 , T, Y^1 , Y^2 , n and p are as defined for formula I and E is a protecting group such as acetyl, benzyl or *tert*-butoxycarbonyl, with a compound of formula VII, wherein R^9 and R^{10} are as defined for formula I and R^{15} is halogen, preferably chloro or bromo, or a sulfonate, such as mesylate, and an oxidant such as sodium hypochlorite, *N*-chlorosuccinimide or diacetoxyiodobenzene. This is shown in Scheme 5.

Scheme 5



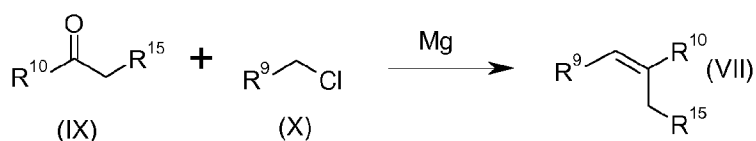
- 5 Compounds of formula VIII, wherein R³, R⁴, R⁵, R⁶, R⁷, R⁸, G², T, Y¹, Y², n and p are as defined for formula I and E is a protecting group such as acetyl, benzyl or *tert*-butoxycarbonyl, can be obtained by transformation of a compound of formula VI, wherein R³, R⁴, R⁵, R⁶, R⁷, R⁸, G², T, Y¹, Y², n and p are as defined for formula I and E is a protecting group such as acetyl, benzyl or *tert*-butoxycarbonyl, with hydroxylamine. This is shown in
- 10 Scheme 6.

Scheme 6



- The compound of formula VII, wherein R⁹ and R¹⁰ are as defined for formula I and R¹⁵ is
- 15 halogen, preferably chloro or bromo, or a sulfonate, such as mesylate, can be obtained by transformation of a compound of formula IX, wherein R¹⁰ are as defined for formula I and R¹⁵ is halogen, preferably chloro or bromo, or a sulfonate, such as mesylate, with a compound of formula X, wherein R⁹ is as defined for formula I, with magnesium. This route is shown in
- Scheme 7.

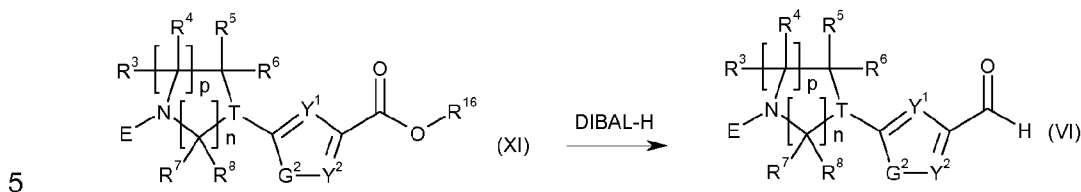
20 Scheme 7



- The compounds of formula VI, wherein R³, R⁴, R⁵, R⁶, R⁷, R⁸, G², T, Y¹, Y², n and p are as defined for formula I and E is a protecting group such as acetyl, benzyl or *tert*-butoxycarbonyl, can be obtained by transformation of a compound of formula XI, wherein R³,
- 25 R⁴, R⁵, R⁶, R⁷, R⁸, G², T, Y¹, Y², n and p are as defined for formula I, R¹⁶ is alkoxy, such as methoxy or ethoxy and E¹ is a protecting group such as acetyl, benzyl or *tert*-

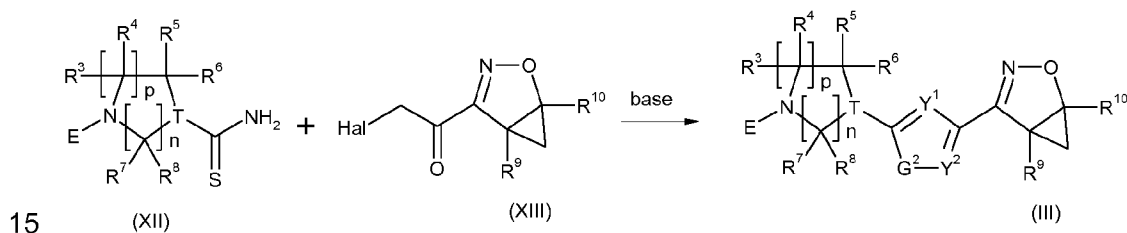
butoxycarbonyl, and a reducing agent, such as diisobutylaluminum hydride. This is shown in Scheme 8.

Scheme 8



Alternatively, the compounds of formula I, wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , T , Y^1 , Y^2 , n and p are as defined for formula I, G^2 is S and E is a protecting group such as acetyl, benzyl or *tert*-butoxycarbonyl, can be obtained by transformation of a compound of formula XII, wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , T , n and p are as defined for formula I and E is a protecting group such as acetyl, benzyl or *tert*-butoxycarbonyl, with a compound of formula XIII, wherein R^9 and R^{10} are as defined for formula I and Hal is halogen, preferably chloro or bromo, and a base. This is shown in Scheme 9.

Scheme 9



Surprisingly, it has now been found that the novel compounds of formula I have, for practical purposes, a very advantageous level of biological activity for protecting plants against diseases that are caused by fungi.

20 The compounds of formula I can be used in the agricultural sector and related fields of use e.g. as active ingredients for controlling plant pests or on non-living materials for control of spoilage microorganisms or organisms potentially harmful to man. The novel compounds are distinguished by excellent activity at low rates of application, by being well tolerated by plants and by being environmentally safe. They have very useful curative, preventive and systemic properties and may be used for protecting numerous cultivated plants. The compounds of formula I can be used to inhibit or destroy the pests that occur on plants or parts of plants (fruit, blossoms, leaves, stems, tubers, roots) of different crops of useful plants, while at the same time protecting also those parts of the plants that grow later e.g. from phytopathogenic microorganisms.

30 It is also possible to use compounds of formula I as dressing agents for the treatment of plant propagation material, e.g., seed, such as fruits, tubers or grains, or plant cuttings (for

example rice), for the protection against fungal infections as well as against phytopathogenic fungi occurring in the soil. The propagation material can be treated with a composition comprising a compound of formula I before planting: seed, for example, can be dressed before being sown. The active ingredients according to the invention can also be applied to 5 grains (coating), either by impregnating the seeds in a liquid formulation or by coating them with a solid formulation. The composition can also be applied to the planting site when the propagation material is being planted, for example, to the seed furrow during sowing. The invention relates also to such methods of treating plant propagation material and to the plant propagation material so treated.

10 Furthermore the compounds according to present invention can be used for controlling fungi in related areas, for example in the protection of technical materials, including wood and wood related technical products, in food storage, in hygiene management.

In addition, the invention could be used to protect non-living materials from fungal attack, e.g. lumber, wall boards and paint.

15 The compounds of formula I are, for example, effective against the phytopathogenic fungi of the following classes: Fungi imperfecti (e.g. *Alternaria* spp.), Basidiomycetes (e.g. *Corticium* spp., *Ceratobasidium* spp., *Waitea* spp., *Thanatephorus* spp., *Rhizoctonia* spp., *Hemileia* spp., *Puccinia* spp., *Phakopsora* spp., *Ustilago* spp., *Tilletia* spp.), Ascomycetes (e.g. *Venturia* spp., *Blumeria* spp., *Erysiphe* spp., *Podosphaera* spp., *Uncinula* spp., 20 *Monilinia* spp., *Sclerotinia* spp., *Colletotrichum* spp., *Glomerella* spp., *Fusarium* spp., *Gibberella* spp., *Monographella* spp., *Phaeosphaeria* spp., *Mycosphaerella* spp., *Cercospora* spp., *Pyrenophora* spp., *Rhynchosporium* spp., *Magnaporthe* spp., *Gaeumannomyces* spp., *Oculimacula* spp., *Ramularia* spp., *Botryotinia* spp.) and Oomycetes (e.g. *Phytophthora* spp., *Pythium* spp., *Plasmopara* spp., *Peronospora* spp., *Pseudoperonospora* spp. *Bremia* spp.). 25 Outstanding activity is observed against downy mildew (e.g. *Plasmopara viticola*) and late blight (e.g. *Phytophthora infestans*). Furthermore, the novel compounds of formula I are effective against phytopathogenic gram negative and gram positive bacteria (e.g. *Xanthomonas* spp, *Pseudomonas* spp, *Erwinia amylovora*, *Ralstonia* spp.) and viruses (e.g. tobacco mosaic virus).

30 Within the scope of present invention, target crops and/or useful plants to be protected typically comprise the following species of plants: cereal (wheat, barley, rye, oat, rice, maize, sorghum and related species); beet (sugar beet and fodder beet); pomes, drupes and soft fruit (apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries and blackberries); leguminous plants (beans, lentils, peas, soybeans); oil plants (rape, mustard, 35 poppy, olives, sunflowers, coconut, castor oil plants, cocoa beans, groundnuts); cucumber plants (pumpkins, cucumbers, melons); fibre plants (cotton, flax, hemp, jute); citrus fruit (oranges, lemons, grapefruit, mandarins); vegetables (spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, paprika); lauraceae (avocado, cinnamomum,

camphor) or plants such as tobacco, nuts, coffee, eggplants, sugar cane, tea, pepper, vines, hops, bananas and natural rubber plants, as well as turf and ornamentals.

The useful plants and / or target crops in accordance with the invention include conventional as well as genetically enhanced or engineered varieties such as, for example, insect resistant (e.g. Bt. and VIP varieties) as well as disease resistant, herbicide tolerant (e.g. glyphosate- and glufosinate-resistant maize varieties commercially available under the trade names RoundupReady® and LibertyLink®) and nematode tolerant varieties. By way of example, suitable genetically enhanced or engineered crop varieties include the Stoneville 5599BR cotton and Stoneville 4892BR cotton varieties.

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

The term "useful plants" and/or "target crops" is to be understood as including also useful 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*.

The term "useful plants" and/or "target crops" is to be understood as including also useful 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.

35 The term "locus" of a plant as used herein is intended to embrace the place on which the plants are growing, where the plant propagation materials of the plants are sown or where the plant propagation materials of the plants will be placed into the soil. An example for such a locus is a field, on which crop plants are growing.

The term "plant propagation material" is understood to denote generative parts of the plant, such as seeds, which can be used for the multiplication of the latter, and vegetative material, such as cuttings or tubers, for example potatoes. There may be mentioned for example seeds (in the strict sense), roots, fruits, tubers, bulbs, rhizomes and parts of plants.

5 Germinated plants and young plants which are to be transplanted after germination or after emergence from the soil, may also be mentioned. These young plants may be protected before transplantation by a total or partial treatment by immersion. Preferably "plant propagation material" is understood to denote seeds.

The compounds of formula I may be used in unmodified form or, preferably, together
10 with the adjuvants conventionally employed in the art of formulation. To this end they may be conveniently formulated in known manner to emulsifiable concentrates, coatable pastes, directly sprayable or dilutable solutions or suspensions, dilute emulsions, wettable powders, soluble powders, dusts, granulates, and also encapsulations e.g. in polymeric substances. As with the type of the compositions, the methods of application, such as spraying,
15 atomising, dusting, scattering, coating or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances. The compositions may also contain further adjuvants such as stabilizers, antifoams, viscosity regulators, binders or tackifiers as well as fertilizers, micronutrient donors or other formulations for obtaining special effects.

Suitable carriers and adjuvants, e.g. for agricultural use, can be solid or liquid and are
20 substances useful in formulation technology, e.g. natural or regenerated mineral substances, solvents, dispersants, wetting agents, tackifiers, thickeners, binders or fertilizers. Such carriers are for example described in WO 97/33890.

The compounds of formula I are normally used in the form of compositions and can be applied to the crop area or plant to be treated, simultaneously or in succession with further
25 compounds. These further compounds can be e.g. fertilizers or micronutrient donors or other preparations, which influence the growth of plants. They can also be selective herbicides or non-selective herbicides as well as insecticides, fungicides, bactericides, nematocides, molluscicides or mixtures of several of these preparations, if desired together with further carriers, surfactants or application promoting adjuvants customarily employed in the art of
30 formulation.

The compounds of formula I may be used in the form of (fungicidal) compositions for controlling or protecting against phytopathogenic microorganisms, comprising as active ingredient at least one compound of formula I or of at least one preferred individual compound as above-defined, in free form or in agrochemically usable salt form, and at least
35 one of the above-mentioned adjuvants.

The invention provides a composition, preferably a fungicidal composition, comprising at least one compound formula I an agriculturally acceptable carrier and optionally an adjuvant. An agricultural acceptable carrier is for example a carrier that is suitable for

agricultural use. Agricultural carriers are well known in the art. Preferably said composition may comprise at least one or more pesticidally active compounds, for example an additional fungicidal active ingredient in addition to the compound of formula I.

The compound of formula (I) may be the sole active ingredient of a composition or it
 5 may be admixed with one or more additional active ingredients such as a pesticide, fungicide, synergist, herbicide or plant growth regulator where appropriate. An additional active ingredient may, in some cases, result in unexpected synergistic activities. Examples of suitable additional active ingredients include the following: Azoxystrobin (131860-33-8), Dimoxystrobin (149961-52-4), Enestrobin (238410-11-2), Fluoxastrobin (193740-76-0),
 10 Kresoxim-methyl (143390-89-0), Metominostrobin (133408-50-1), Orysastrobin (248593-16-0), Picoxystrobin (117428-22-5), Pyraclostrobin (175013-18-0), trifloxystrobin (141517-21-7), Azaconazole (60207-31-0), Bromuconazole (116255-48-2), Cyproconazole (94361-06-5), Difenoconazole (119446-68-3), Diniconazole (83657-24-3), Diniconazole-M (83657-18-5), Epoxiconazole (13385-98-8), Fenbuconazole (114369-43-6), Fluquinconazole (136426-54-
 15 5), Flusilazole (85509-19-9), Flutriafol (76674-21-0), Hexaconazole (79983-71-4), Imazalil (58594-72-2), Imibenconazole (86598-92-7), Ipconazole (125225-28-7), Metconazole (125116-23-6), Myclobutanil (88671-89-0), Oxpoconazole (174212-12-5), Pefurazoate (58011-68-0), Penconazole (66246-88-6), Prochloraz (67747-09-5), Propiconazole (60207-90-1), Prothioconazole (178928-70-6), Simeconazole (149508-90-7), Tebuconazole
 20 (107534-96-3), Tetraconazole (112281-77-3), Triadimefon (43121-43-3), Triadimenol (55219-65-3), Triflumizole (99387-89-0), Triticonazole (131983-72-7), Diclobutrazol (76738-62-0), Etaconazole (60207-93-4), Fluconazole (86386-73-4), Fluconazole-cis (112839-32-4), Thiabendazole (148-79-8), Quinconazole (103970-75-8), Fenpiclonil (74738-17-3), Fludioxonil (131341-86-1), Cyprodinil (121552-61-2), Mepanipyrim (110235-47-7),
 25 Pyrimethanil (53112-28-0), Aldimorph (91315-15-0), Dodemorph (1593-77-7), Fenpropimorph (67564-91-4), Tridemorph (81412-43-3), Fenpropidin (67306-00-7), Spiroxamine (118134-30-8), Isopyrazam (881685-58-1), Sedaxane (874967-67-6), Bixafen (581809-46-3), Penthiopyrad (183675-82-3), Fluxapyroxad (907204-31-3), Boscalid (188425-85-6), Penflufen (494793-67-8), Fluopyram (658066-35-4), Mandipropamid (374726-62-2),
 30 Benthiavalicarb (413615-35-7), Dimethomorph (110488-70-5), Chlorothalonil (1897-45-6), Fluazinam (79622-59-6), Dithianon (3347-22-6), Metrafenone (220899-03-6), Tricyclazole (41814-78-2), Mefenoxam (70630-17-0), Metalaxyl (57837-19-1), Acibenzolar (126448-41-7) (Acibenzolar-S-methyl (126448-41-7)), Mancozeb (8018-01-7), Ametoctradine (865318-97-4) Cyflufenamid (180409-60-3), and Kresoxim-methyl (143390-89-0), Ipconazole (125225-28-
 35 7), Amisulbrom (348635-87-0), Cyflufenamid (180409-60-3), Ethaboxam (16650-77-3), Fluopicolide (239110-15-7), Fluthianil (304900-25-2), Isotianil (224049-04-1), Proquinazid (189278-12-4), Valiphenal (283159-90-0), 1-methyl-cyclopropene (3100-04-7), Trifloxystrobin (141517-21-7), Sulfur (7704-34-9), Copper ammoniumcarbonate (CAS 33113-08-5); Copper

oleate (CAS 1120-44-1); Folpet (133-07-3), Quinoxifen (124495-18-7), Captan (133-06-2), Fenhexamid (126833-17-8), Glufosinate and its salts (51276-47-2, 35597-44-5 (S-isomer)), Glyphosate (1071-83-6) and its salts (69254-40-6 (Diammonium), 34494-04-7 (Dimethylammonium), 38641-94-0 (Isopropylammonium), 40465-66-5 (Monoammonium), 5 70901-20-1 (Potassium), 70393-85-0 (Sesquisodium), 81591-81-3 (Trimesium)), 1-methyl-3-difluoromethyl-1H-pyrazole-4-carboxylic acid (2-dichloromethylene-3-ethyl-1-methyl-indan-4-yl)-amide (1072957-71-1), 1-methyl-3-difluoromethyl-1H-pyrazole-4-carboxylic acid (4'-methylsulfanyl-biphenyl-2-yl)-amide, 1-methyl-3-difluoromethyl-4H-pyrazole-4-carboxylic acid [2-(2,4-dichloro-phenyl)-2-methoxy-1-methyl-ethyl]-amide, (5-Chloro-2,4-dimethyl-pyridin-3-yl)-(2,3,4-trimethoxy-6-methyl-phenyl)-methanone, (5-Bromo-4-chloro-2-methoxy-pyridin-3-yl)-(2,3,4-trimethoxy-6-methyl-phenyl)-methanone, 2-{2-[(E)-3-(2,6-Dichloro-phenyl)-1-methyl-prop-2-en-(E)-ylideneaminoxymethyl]-phenyl}-2-[(Z)-methoxyimino]-N-methyl-acetamide, 3-[5-(4-Chloro-phenyl)-2,3-dimethyl-isoxazolidin-3-yl]-pyridine.

Another aspect of invention is related to the use of a compound of formula I or of a preferred individual compound as above-defined, of a composition comprising at least one 15 compound of formula I or at least one preferred individual compound as above-defined, or of a fungicidal mixture comprising at least one compound of formula I or at least one preferred individual compound as above-defined, in admixture with other fungicides, as described above, for controlling or preventing infestation of plants, e.g. useful plants such as crop 20 plants, propagation material thereof, e.g. seeds, harvested crops, e.g. harvested food crops, or non-living materials by phytopathogenic microorganisms, preferably fungal organisms.

A further aspect of invention is related to a method of controlling or preventing an infestation of plants, e.g. useful plants such as crop plants, propagation material thereof, e.g. seeds, harvested crops, e.g. harvested food crops, or of non-living materials by 25 phytopathogenic or spoilage microorganisms or organisms potentially harmful to man, especially fungal organisms, which comprises the application of a compound of formula I or of a preferred individual compound as above-defined as active ingredient to the plants, to parts of the plants or to the locus thereof, to the propagation material thereof, or to any part of the non-living materials.

30 Controlling or preventing means reducing infestation by phytopathogenic or spoilage microorganisms or organisms potentially harmful to man, especially fungal organisms, to such a level that an improvement is demonstrated.

A preferred method of controlling or preventing an infestation of crop plants by phytopathogenic microorganisms, especially fungal organisms, which comprises the 35 application of a compound of formula I, or an agrochemical composition which contains at least one of said compounds, is foliar application. The frequency of application and the rate of application will depend on the risk of infestation by the corresponding pathogen. However, the compounds of formula I can also penetrate the plant through the roots via the soil

(systemic action) by drenching the locus of the plant with a liquid formulation, or by applying the compounds in solid form to the soil, e.g. in granular form (soil application). In crops of water rice such granulates can be applied to the flooded rice field. The compounds of formula I may also be applied to seeds (coating) by impregnating the seeds or tubers either
5 with a liquid formulation of the fungicide or coating them with a solid formulation.

A formulation, e.g. a composition containing the compound of formula I, and, if desired, a solid or liquid adjuvant or monomers for encapsulating the compound of formula I, may be prepared in a known manner, typically by intimately mixing and/or grinding the compound with extenders, for example solvents, solid carriers and, optionally, surface active
10 compounds (surfactants).

The agrochemical formulations and/or compositions will usually contain from 0.1 to 99% by weight, preferably from 0.1 to 95% by weight, of the compound of formula I, 99.9 to 1% by weight, preferably 99.8 to 5% by weight, of a solid or liquid adjuvant, and from 0 to 25% by weight, preferably from 0.1 to 25% by weight, of a surfactant.

15 Advantageous rates of application are normally from 5g to 2kg of active ingredient (a.i.) per hectare (ha), preferably from 10g to 1kg a.i./ha, most preferably from 20g to 600g a.i./ha. When used as seed drenching agent, convenient dosages are from 10mg to 1g of active substance per kg of seeds.

Whereas it is preferred to formulate commercial products as concentrates, the end user
20 will normally use dilute formulations.

The following non-limiting examples illustrate the above-described invention in more detail.

25 Example 1: This example illustrates the preparation of 2-(5-methyl-3-trifluoromethyl-pyrazol-1-yl)-1-[4-[4-(1-phenyl-2-oxa-3-aza-bicyclo[3.1.0]hex-3-en-4-yl)-thiazol-2-yl]-piperidin-1-yl]ethanone (Compound No. I.j.01)

a) Preparation of 1-[4-[4-(5-bromomethyl-5-phenyl-4,5-dihydro-isoxazol-3-yl)-thiazol-2-yl]-piperidin-1-yl]-2-(5-methyl-3-trifluoromethyl-pyrazol-1-yl)-ethanone
30

To a solution of 1-(bromomethyl)vinylbenzene (108 mg, 0.548 mmol) in dioxane (2 mL) in a microwave vial was added a solution of (4Z)-N-hydroxy-2-[1-[2-[5-methyl-3-(trifluoromethyl)pyrazol-1-yl]acetyl]4-piperidyl]thiazole-4-carboximidoyl chloride (217 mg, 0.498 mmol) in dioxane (2 mL) followed by N,N-dimethylacetamide (1.5 mL) and potassium
35 hydrogen carbonate (254 mg, 2.49 mmol). The reaction mixture was stirred at room temperature for 1 h and then at 90 °C in the microwave for 45 minutes. The reaction mixture was cooled to room temperature and poured into a mixture of ethyl acetate and water. The organic phase was washed with water and brine, dried (MgSO₄), filtered and concentrated.

The residue was purified by column chromatography on silica gel using a mixture of dichloromethane/ethyl acetate (9:1 to 85:15) as eluent to give 122 mg of 1-{4-[4-(5-bromomethyl-5-phenyl-4,5-dihydro-isoxazol-3-yl)-thiazol-2-yl]-piperidin-1-yl}-2-(5-methyl-3-trifluoromethyl-pyrazol-1-yl)-ethanone as a white foam. ¹H-NMR (400 MHz, CDCl₃): δ = 1.7-1.9 (m, 2H), 2.1-2.25 (m, 2H), 2.32 (s, 3H), 2.88 (m, 1H), 3.3 (m, 2H), 3.7 (m, 1H), 3.8 (s, 2H), 4.05 (m, 2H), 4.58 (m, 1H), 4.98 (m, 2H), 6.33 (s, 1H), 7.35 (m, 1H), 7.41 (m, 2H), 7.52 (m, 2H), 7.66 (s, 1H).

b) Preparation of 2-(5-methyl-3-trifluoromethyl-pyrazol-1-yl)-1-{4-[4-(1-phenyl-2-oxa-3-aza-bicyclo[3.1.0]hex-3-en-4-yl)-thiazol-2-yl]-piperidin-1-yl}ethanone (Compound No. I.j.01)
To a solution of 1-{4-[4-(5-bromomethyl-5-phenyl-4,5-dihydro-isoxazol-3-yl)-thiazol-2-yl]-piperidin-1-yl}-2-(5-methyl-3-trifluoromethyl-pyrazol-1-yl)-ethanone (240 mg, 0.4 mmol) in ethanol (2 mL) was added potassium carbonate (80 mg, 0.57 mmol). The reaction mixture was stirred at room temperature for 1 h and then heated to 80°C and stirred at reflux for 48 h. Potassium carbonate (80 mg, 0.57 mmol) was added again and the reaction mixture was stirred at reflux for another 24 h. The reaction mixture was cooled to room temperature and poured into a mixture of ethyl acetate and water and the pH was adjusted with 1 N aqueous hydrochloric acid to pH 7. The organic phase was washed with water and brine, dried (MgSO₄), filtered and concentrated. The residue was purified by column chromatography on silica gel using a mixture of dichloromethane/ethyl acetate (8:2) as eluent to give 43 mg of 2-(5-methyl-3-trifluoromethyl-pyrazol-1-yl)-1-{4-[4-(1-phenyl-2-oxa-3-aza-bicyclo[3.1.0]hex-3-en-4-yl)-thiazol-2-yl]-piperidin-1-yl}ethanone (Compound No. I.j.01) as a yellow foam. ¹H-NMR (400 MHz, CDCl₃): δ = 0.93 (m, 1H), 1.8 (m, 2H), 1.85 (m, 1H), 2.15-2.3 (m, 2H), 2.32 (s, 3H), 2.88 (m, 1H), 3.13 (m, 1H), 3.32 (m, 2H), 4.05 (m, 1H), 4.6 (m, 1H), 5.0 (m, 2H), 6.32 (s, 1H), 7.32-7.47 (m, 5H), 7.69 (s, 1H).

Example 2: This example illustrates the preparation of 1-(4-{4-[1-(2,6-difluoro-phenyl)-2-oxa-3-aza-bicyclo[3.1.0]hex-3-en-4-yl]-thiazol-2-yl]-piperidin-1-yl}-2-(5-methyl-3-trifluoromethyl-pyrazol-1-yl)-ethanone (Compound No. I.ai.01)

30

a) Preparation of 1-(4-{4-[5-bromomethyl-5-(2,6-difluoro-phenyl)-4,5-dihydro-isoxazol-3-yl]-thiazol-2-yl]-piperidin-1-yl}-ethanone

To a solution of 0.3 g of 2-(1-bromomethyl-vinyl)-1,3-difluoro-benzene in 5 ml of methanol was added first 34 mg trifluoroacetic acid, followed by 0.43 g iodosobenzene diacetate. To this reaction mixture a solution of 0.3 g of 2-(1-acetyl-piperidin-4-yl)-thiazole-4-carbaldehyde oxime in 15 ml of methanol was added slowly within 45 mins. The resulting mixture was stirred for 20 h at room temperature and subsequently evaporated under reduced pressure. The remainder was purified by chromatography on silica gel, using dichloromethane / ethyl

acetate as eluents to deliver 1-(4-{4-[5-bromomethyl-5-(2,6-difluoro-phenyl)-4,5-dihydro-isoxazol-3-yl]-thiazol-2-yl}-piperidin-1-yl)-ethanone as a white foam. LC-MS: Rt = 1.46 min; MS: m/z 485 [M+1]⁺, 486 [M+2]⁺.

5 b) Preparation of 1-(4-{4-[1-(2,6-difluoro-phenyl)-2-oxa-3-aza-bicyclo[3.1.0]hex-3-en-4-yl]-thiazol-2-yl}-piperidin-1-yl)-ethanone

To a solution of 95 mg of 1-(4-{4-[5-bromomethyl-5-(2,6-difluoro-phenyl)-4,5-dihydro-isoxazol-3-yl]-thiazol-2-yl}-piperidin-1-yl)-ethanone in 1 ml of ethanol was added 55 mg of potassium carbonate. The reaction mixture was heated to 80 °C for 20 h, then cooled to
10 room temperature and diluted with water and ethyl acetate. The pH value was brought to pH 7 by addition of 1 N hydrochloric acid. The organic phase was separated, washed with water and brine, dried over magnesium sulphate and concentrated under reduced pressure to deliver directly 1-(4-{4-[1-(2,6-difluoro-phenyl)-2-oxa-3-aza-bicyclo[3.1.0]hex-3-en-4-yl]-thiazol-2-yl}-piperidin-1-yl)-ethanone as a white foam. LC-MS: Rt = 1.33 min; MS: m/z 404
15 [M+1]⁺.

c) Preparation of 1-(2,6-difluoro-phenyl)-4-(2-piperidin-4-yl-thiazol-4-yl)-2-oxa-3-aza-bicyclo[3.1.0]hex-3-ene

To a solution of 65 mg of 1-(4-{4-[1-(2,6-difluoro-phenyl)-2-oxa-3-aza-bicyclo[3.1.0]hex-3-en-4-yl]-thiazol-2-yl}-piperidin-1-yl)-ethanone in 1 ml of ethanol was added 0.4 ml of 5 N sodium hydroxide solution. The reaction mixture was stirred for 1 h at room temperature and then for
20 5 h at 80 °C. Subsequently the reaction mixture was cooled to room temperature and diluted with water and ethyl acetate. The pH value was brought to pH 7 by addition of 1 N hydrochloric acid. The organic phase was separated, washed with water and brine, dried
25 over magnesium sulphate and concentrated under reduced pressure to directly deliver 1-(2,6-difluoro-phenyl)-4-(2-piperidin-4-yl-thiazol-4-yl)-2-oxa-3-aza-bicyclo[3.1.0]hex-3-ene as a yellow foam. LC-MS: Rt = 0.88 min; MS: m/z 362 [M+1]⁺.

d) Preparation of 1-(4-{4-[1-(2,6-difluoro-phenyl)-2-oxa-3-aza-bicyclo[3.1.0]hex-3-en-4-yl]-thiazol-2-yl}-piperidin-1-yl)-2-(5-methyl-3-trifluoromethyl-pyrazol-1-yl)-ethanone
(Compound I.ai.01)

To a solution of 45 mg of 1-(2,6-difluoro-phenyl)-4-(2-piperidin-4-yl-thiazol-4-yl)-2-oxa-3-aza-bicyclo[3.1.0]hex-3-ene in 1 ml of dichloromethane was added 38 mg triethylamine. A solution of 31 mg of 2-[5-methyl-3-trifluoromethyl]pyrazol-1-yl]acetyl chloride in 0.5 ml of
35 dichloromethane was slowly added to this reaction mixture and stirring was continued for 20 h at room temperature.. Subsequently the reaction mixture was concentrated under reduced pressure and the remainder was taken up in water and ethyl acetate. The pH value was brought to pH 7 by addition of 1 N hydrochloric acid. The organic phase was separated,

washed with water and brine, dried over magnesium sulphate and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, using dichloromethane / ethyl acetate as eluents to deliver 1-(4-{4-[1-(2,6-difluoro-phenyl)-2-oxa-3-aza-bicyclo[3.1.0]hex-3-en-4-yl]-thiazol-2-yl}-piperidin-1-yl)-2-(5-methyl-3-trifluoromethyl-pyrazol-1-yl)-ethanone (Compound I.ai.01) as a white foam. ¹H-NMR (400 MHz, CDCl₃): δ = 1.08 (t, 1H), 1.60 (dd, 1H), (1.82 (m, 2H), 2.24 (m, 2H), 2.33 (s, 3H), 2.89 (dt, 1H), 3.24 (dd, 1H), 3.35 (m, 2H), 4.07 (dd, 1H), 4.61 (dd, 1H), 4.99 (q, 2H), 6.34 (s, 1H), 6.96 (t, 2H), 7.38 (m, 1H), 7.72 (s, 1H). LC-MS: Rt = 1.74 min; MS: m/z 552 [M+1]⁺, 553 [M+2]⁺,

- 10 Table 1 below illustrates examples of individual compounds of formula I according to the invention.

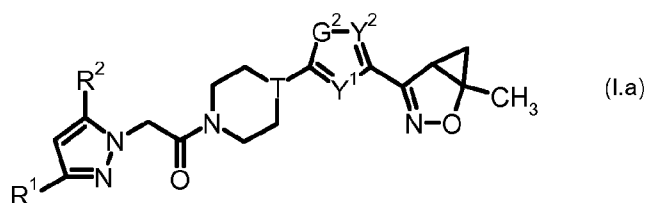
Table 1: individual compounds of formula I according to the invention

Comp. No.	R ¹	R ²	T	Y ¹	G ²	Y ²
01	F ₃ C	H ₃ C	CH	N	S	CH
02	F ₃ C	H ₃ C	CH	N	S	N
03	F ₃ C	H ₃ C	CH	N	O	CH
04	F ₃ C	H ₃ C	N	N	S	CH
05	F ₃ C	H ₃ C	N	N	S	N
06	F ₃ C	H ₃ C	N	N	O	CH
07	H ₃ C	H ₃ C	CH	N	S	CH
08	H ₃ C	H ₃ C	CH	N	S	N
09	H ₃ C	H ₃ C	CH	N	O	CH
10	H ₃ C	H ₃ C	N	N	S	CH
11	H ₃ C	H ₃ C	N	N	S	N
12	H ₃ C	H ₃ C	N	N	O	CH
13	F ₂ HC	H ₃ C	CH	N	S	CH
14	F ₂ HC	H ₃ C	CH	N	S	N
15	F ₂ HC	H ₃ C	CH	N	O	CH
16	F ₂ HC	H ₃ C	N	N	S	CH
17	F ₂ HC	H ₃ C	N	N	S	N
18	F ₂ HC	H ₃ C	N	N	O	CH
19	F ₂ HC	F ₂ HC	CH	N	S	CH
20	F ₂ HC	F ₂ HC	CH	N	S	N
21	F ₂ HC	F ₂ HC	CH	N	O	CH

22	F ₂ HC	F ₂ HC	N	N	S	CH
23	F ₂ HC	F ₂ HC	N	N	S	N
24	F ₂ HC	F ₂ HC	N	N	O	CH
25	F ₃ C	F ₃ C	CH	N	S	CH
26	F ₃ C	F ₃ C	CH	N	S	N
27	F ₃ C	F ₃ C	CH	N	O	CH
28	F ₃ C	F ₃ C	N	N	S	CH
29	F ₃ C	F ₃ C	N	N	S	N
30	F ₃ C	F ₃ C	N	N	O	CH

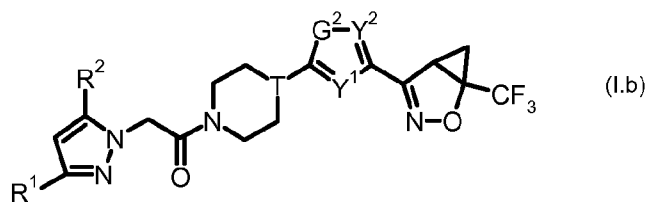
where

a) 30 compounds of formula (I.a):



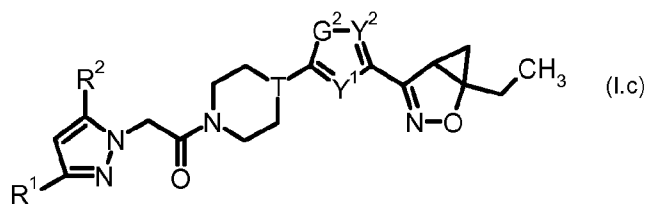
5 wherein R¹, R², G², T, Y¹ and Y² are as defined in Table 1.

b) 30 compounds of formula (I.b):



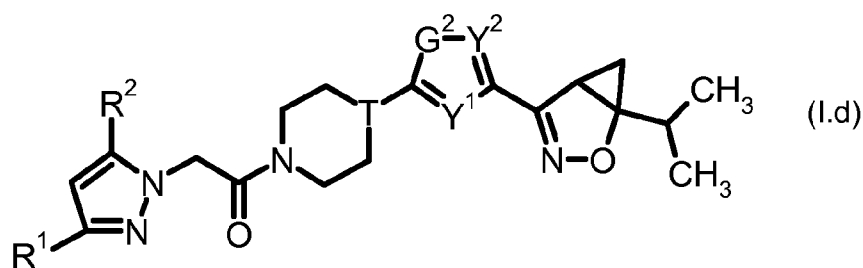
10 wherein R¹, R², G², T, Y¹ and Y² are as defined in Table 1.

c) 30 compounds of formula (I.c):



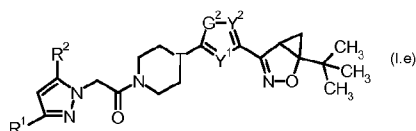
15 wherein R¹, R², G², T, Y¹ and Y² are as defined in Table 1.

d) 30 compounds of formula (I.d):



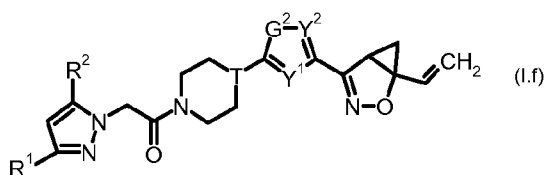
wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

5 e) 30 compounds of formula (I.e):



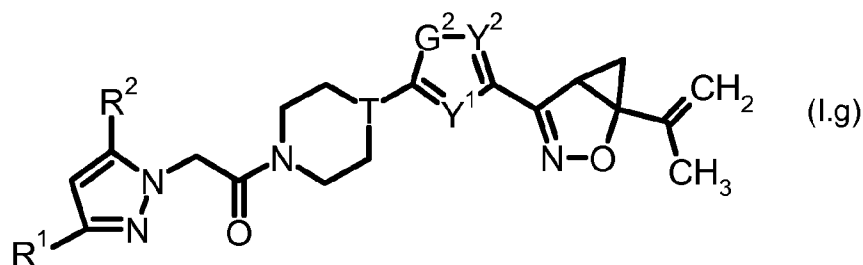
wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

10 f) 30 compounds of formula (I.f):



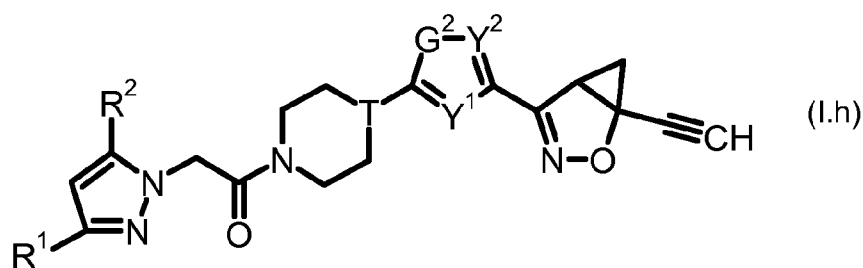
wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

15 g) 30 compounds of formula (I.g):



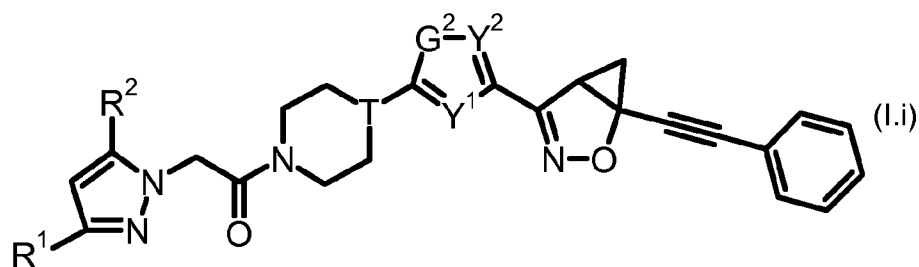
wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

20 h) 30 compounds of formula (I.h):



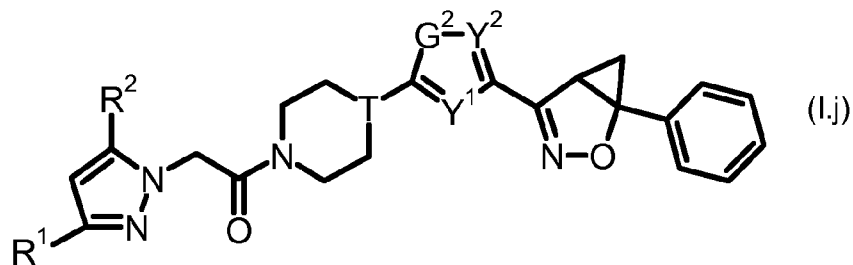
wherein R¹, R², G², T, Y¹ and Y² are as defined in Table 1.

5 i) 30 compounds of formula (I.i):



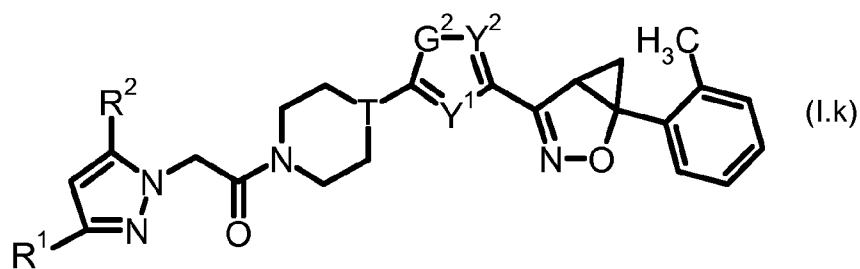
wherein R¹, R², G², T, Y¹ and Y² are as defined in Table 1.

10 j) 30 compounds of formula (I.j):



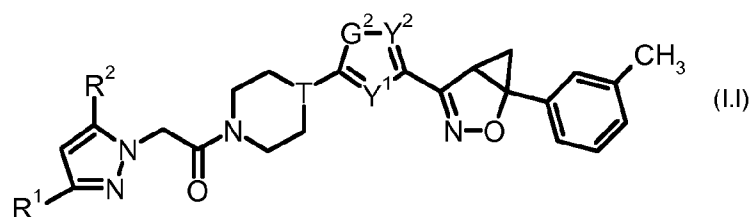
wherein R¹, R², G², T, Y¹ and Y² are as defined in Table 1.

15 k) 30 compounds of formula (I.k):



wherein R¹, R², G², T, Y¹ and Y² are as defined in Table 1.

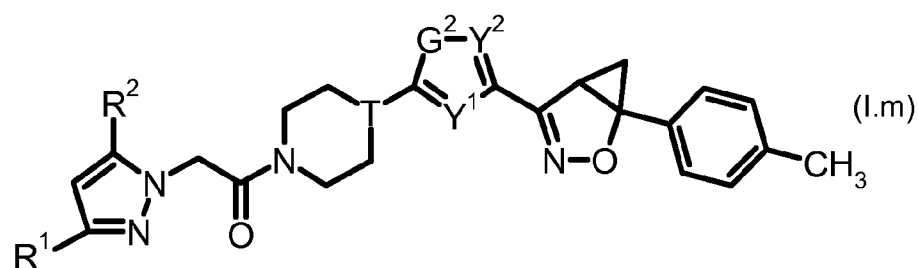
l) 30 compounds of formula (l.l):



wherein R¹, R², G², T, Y¹ and Y² are as defined in Table 1.

5

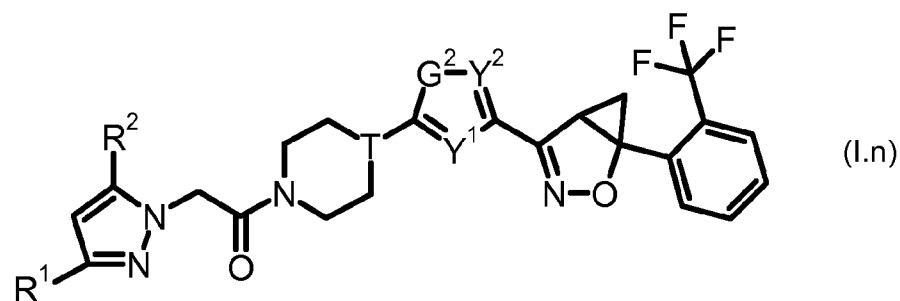
m) 30 compounds of formula (l.m):



wherein R¹, R², G², T, Y¹ and Y² are as defined in Table 1.

10

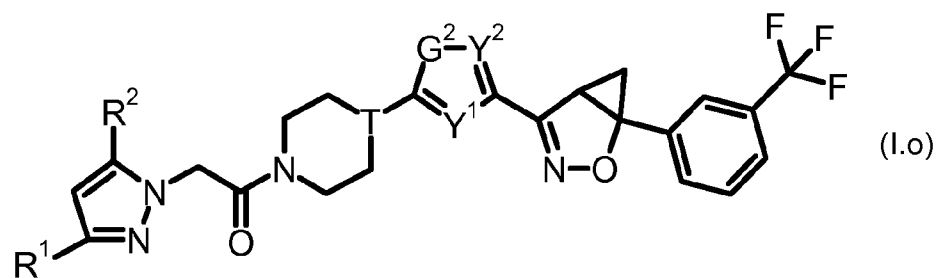
n) 30 compounds of formula (l.n):



wherein R¹, R², G², T, Y¹ and Y² are as defined in Table 1.

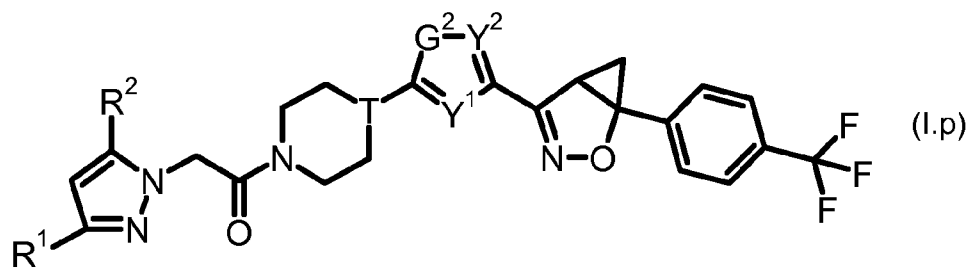
15

o) 30 compounds of formula (l.o):



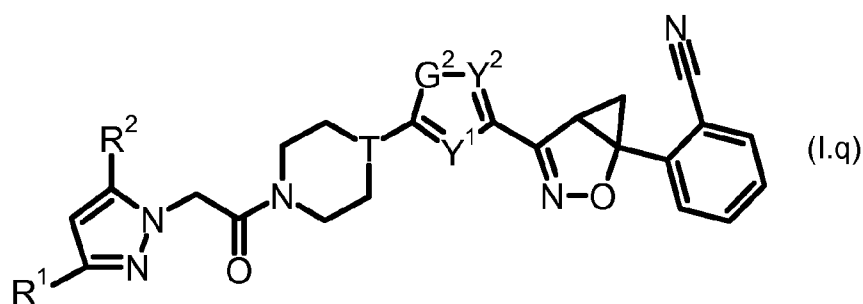
wherein R¹, R², G², T, Y¹ and Y² are as defined in Table 1.

p) 30 compounds of formula (l.p):



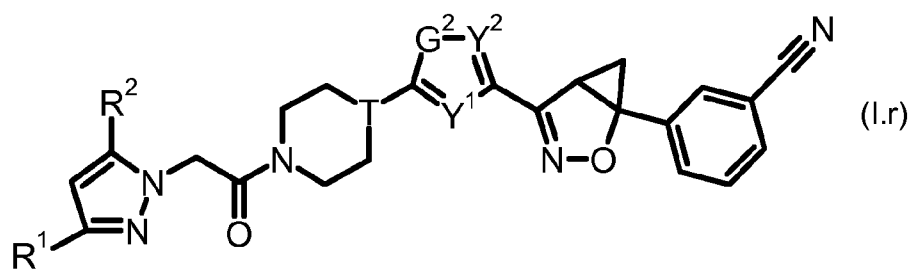
5 wherein R^1 , R^2 , G^2 , T, Y^1 and Y^2 are as defined in Table 1.

q) 30 compounds of formula (l.q):



10 wherein R^1 , R^2 , G^2 , T, Y^1 and Y^2 are as defined in Table 1.

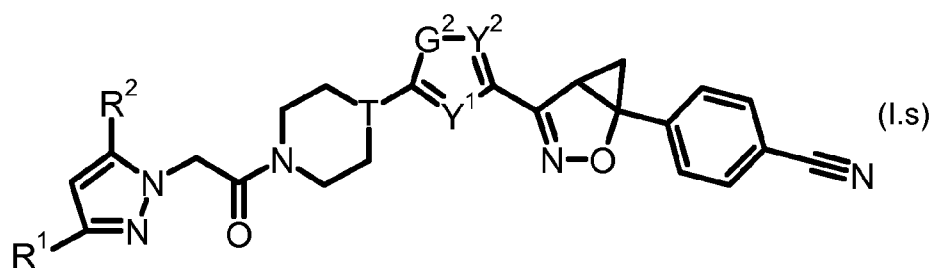
r) 30 compounds of formula (l.r):



15 wherein R^1 , R^2 , G^2 , T, Y^1 and Y^2 are as defined in Table 1.

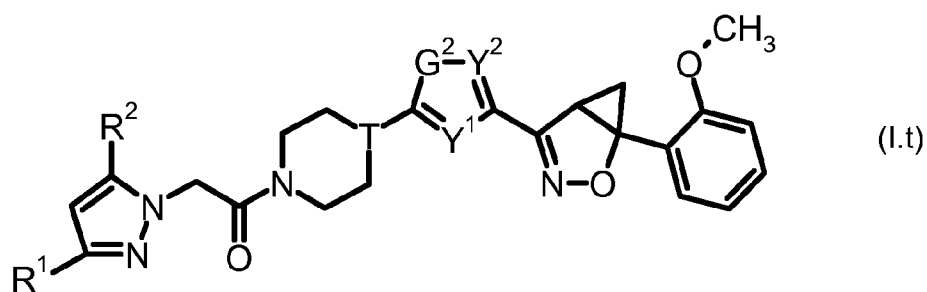
s) 30 compounds of formula (l.s):

28



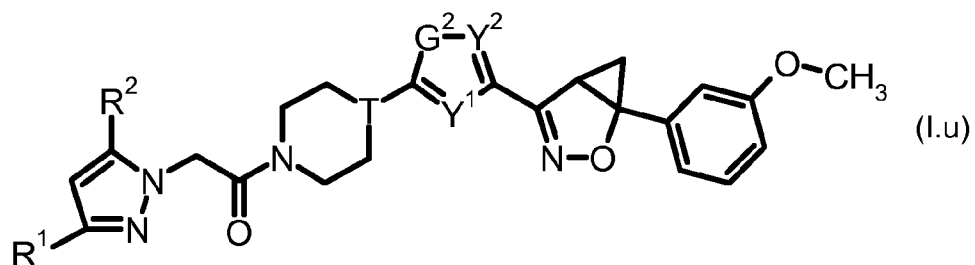
wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

5 t) 30 compounds of formula (I.t):



wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

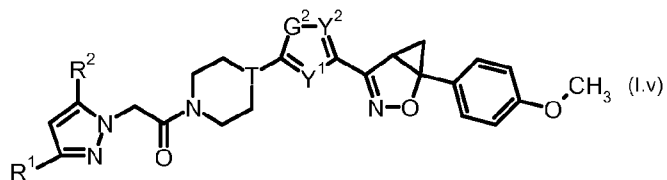
10 u) 30 compounds of formula (I.u):



wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

15

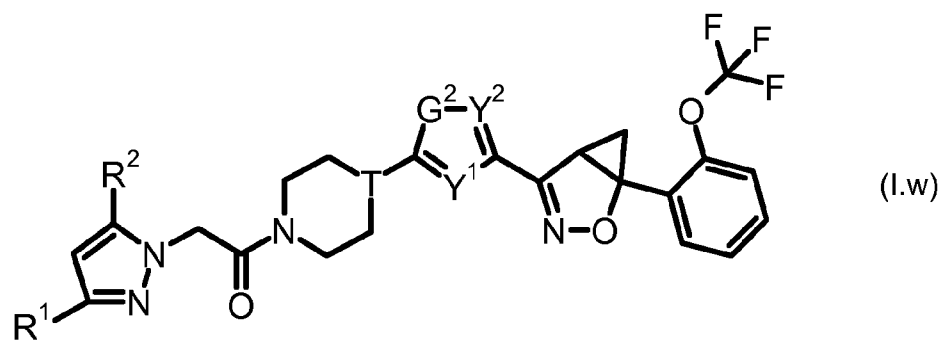
v) 30 compounds of formula (I.v):



wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

20

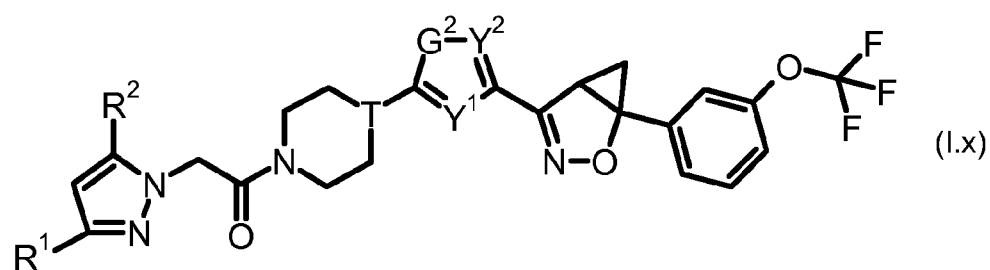
w) 30 compounds of formula (I.w):



wherein R¹, R², G², T, Y¹ and Y² are as defined in Table 1.

5

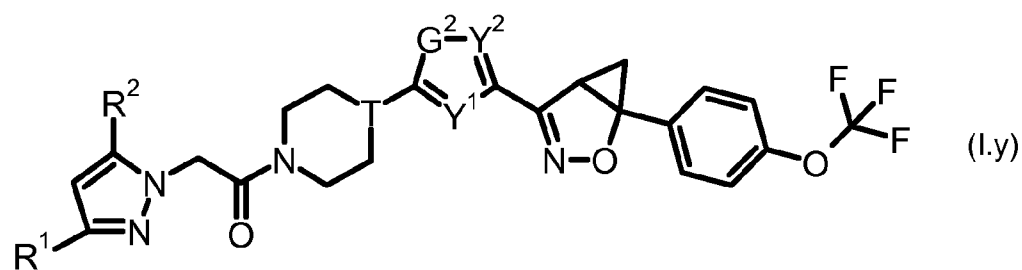
x) 30 compounds of formula (I.x):



wherein R¹, R², G², T, Y¹ and Y² are as defined in Table 1.

10

y) 30 compounds of formula (I.y):

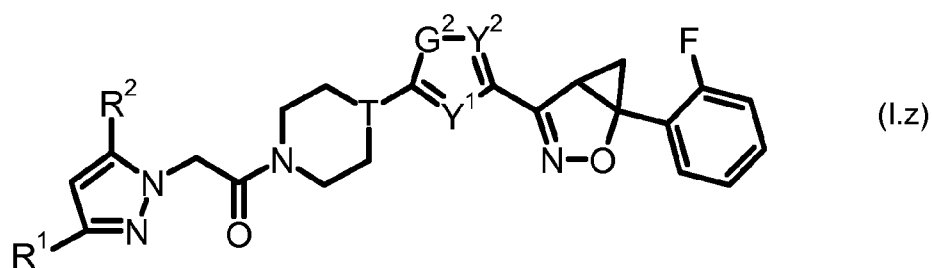


wherein R¹, R², G², T, Y¹ and Y² are as defined in Table 1.

15

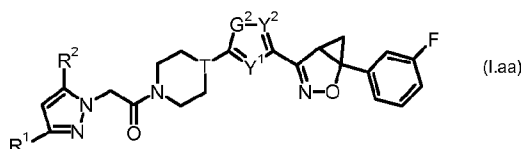
z) 30 compounds of formula (I.z):

30



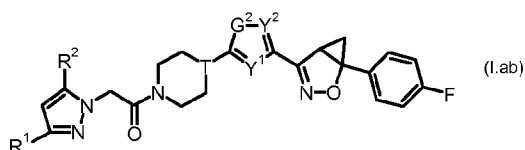
wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

5 aa) 30 compounds of formula (I.aa):



wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

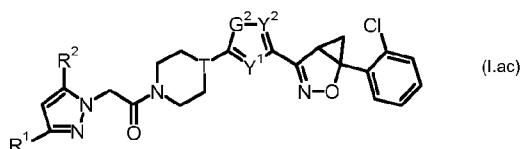
10 ab) 30 compounds of formula (I.ab):



wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

15

ac) 30 compounds of formula (I.ac):

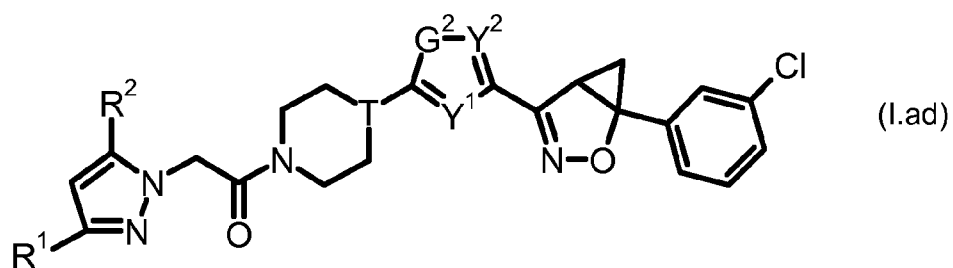


wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

20

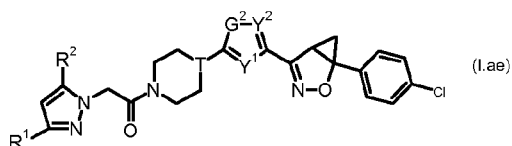
ad) 30 compounds of formula (I.ad):

31



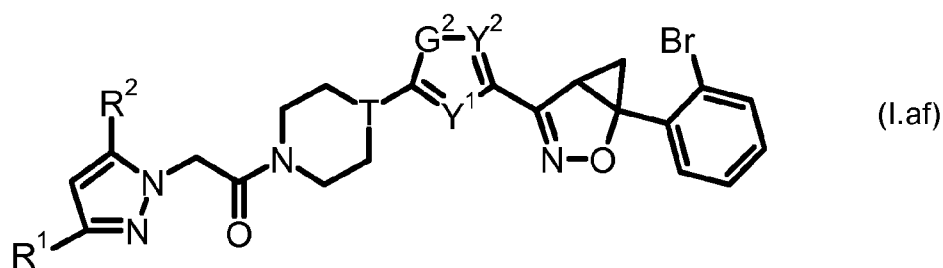
wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

5 ae) 30 compounds of formula (I.ae):



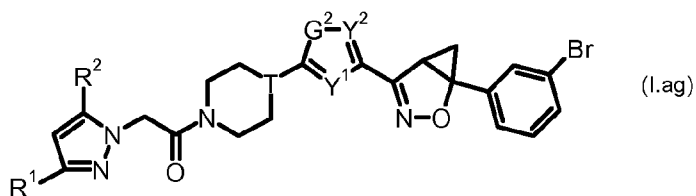
wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

10 af) 30 compounds of formula (I.af):



wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

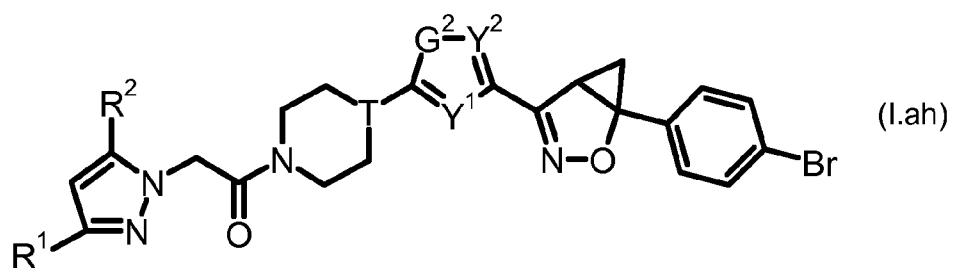
15 ag) 30 compounds of formula (I.ag):



wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

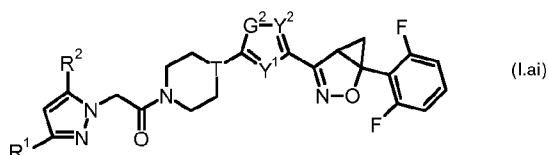
20 ah) 30 compounds of formula (I.ah):

32



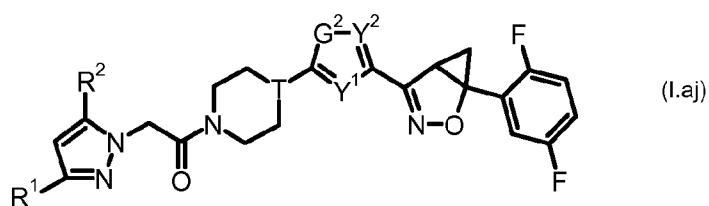
wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

5 ai) 30 compounds of formula (I.ai):



wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

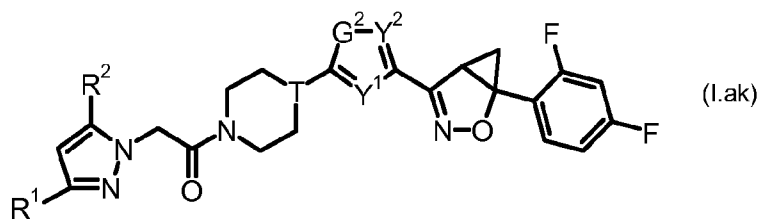
10 aj) 30 compounds of formula (I.aj):



wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

15

ak) 30 compounds of formula (I.ak):

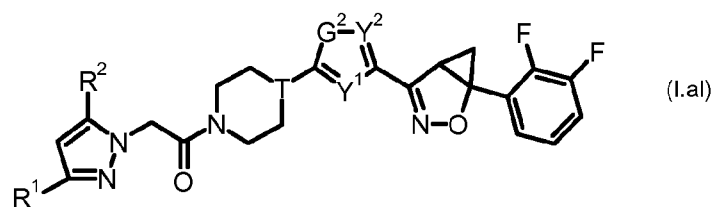


wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

20

al) 30 compounds of formula (I.al):

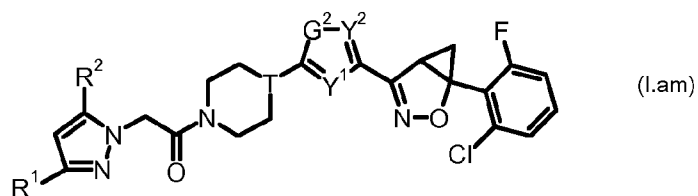
33



wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

5

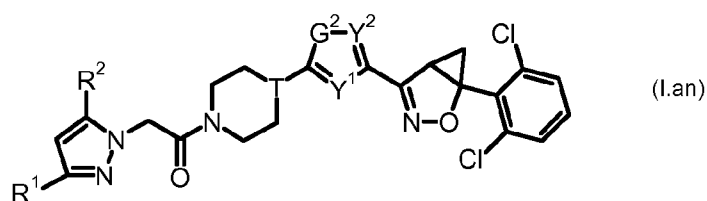
am) 30 compounds of formula (I.am):



wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

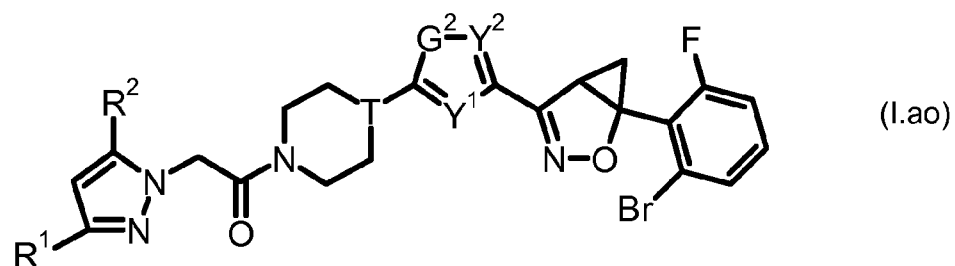
10

an) 30 compounds of formula (I.an):



15 wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

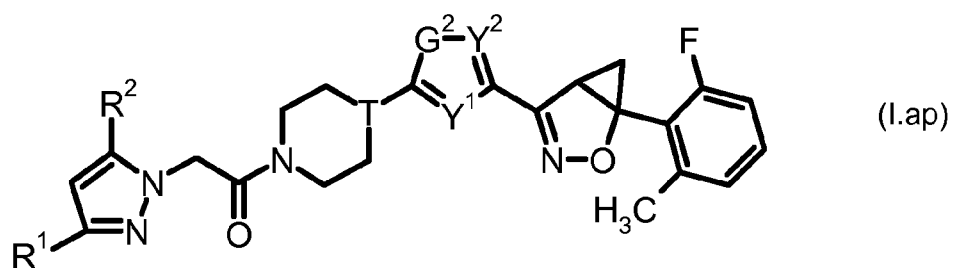
ao) 30 compounds of formula (I.ao):



20

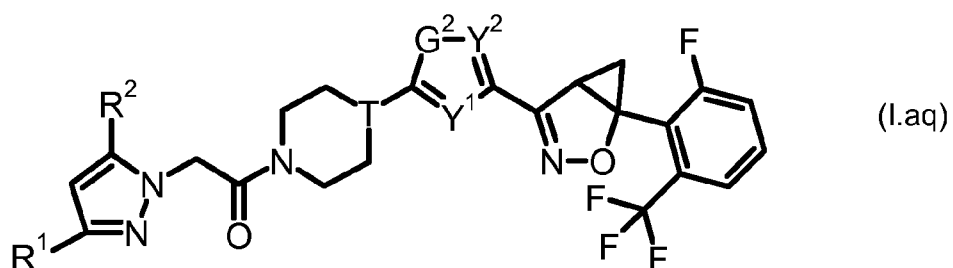
wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

ap) 30 compounds of formula (I.ap):



5 wherein R¹, R², G², T, Y¹ and Y² are as defined in Table 1.

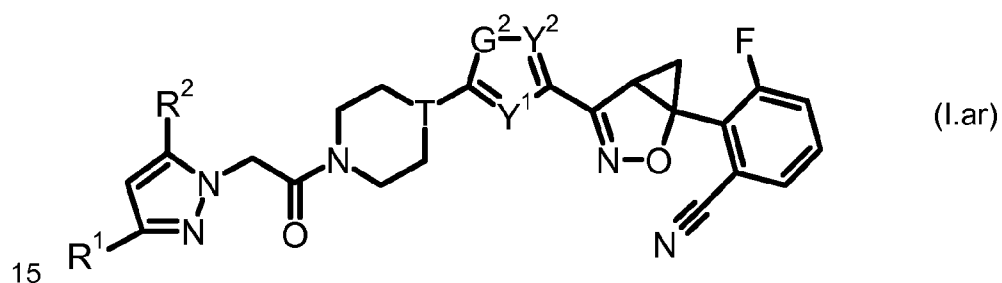
aq) 30 compounds of formula (I.aq):



10

wherein R¹, R², G², T, Y¹ and Y² are as defined in Table 1.

ar) 30 compounds of formula (I.ar):

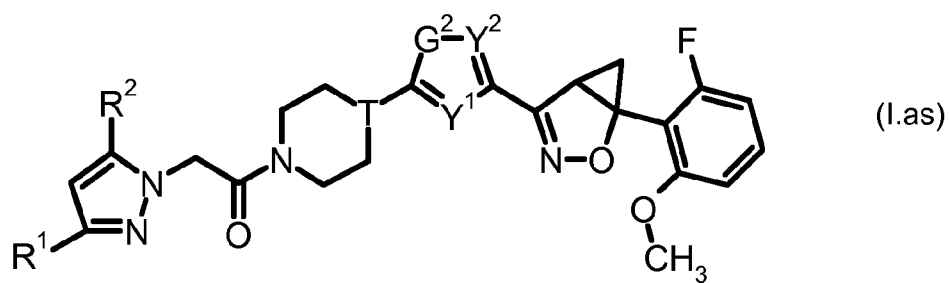


15

wherein R¹, R², G², T, Y¹ and Y² are as defined in Table 1.

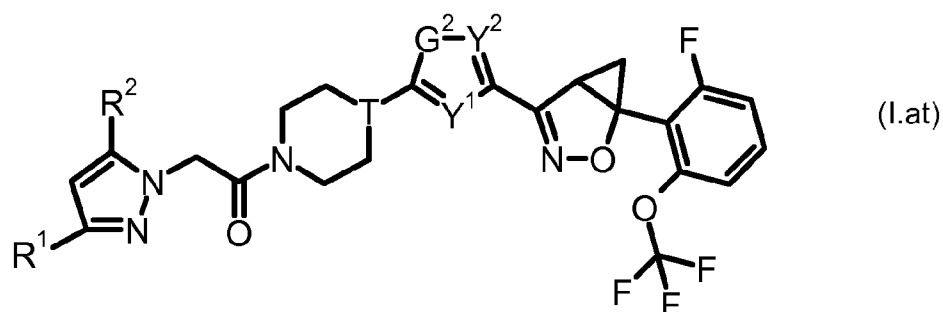
as) 30 compounds of formula (I.as):

35



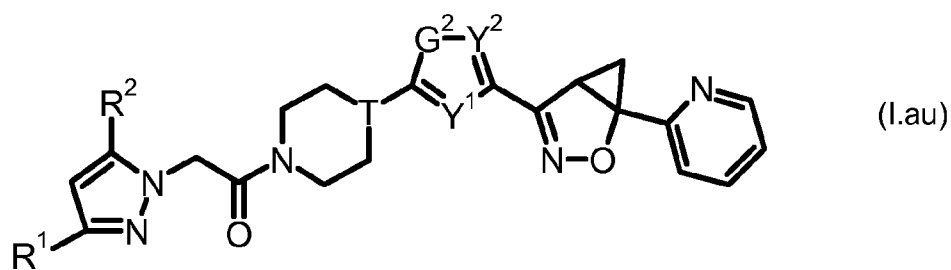
wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

5 at) 30 compounds of formula (I.at):



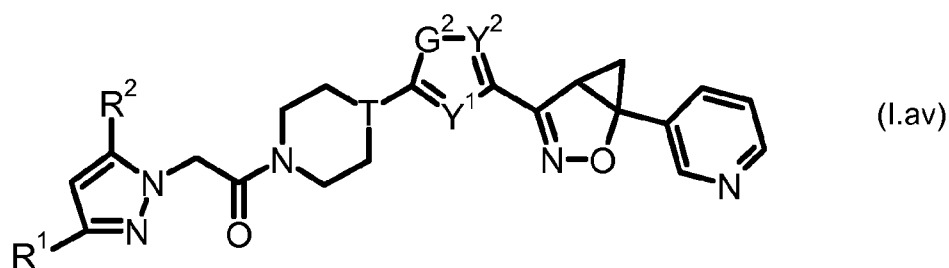
wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

10 au) 30 compounds of formula (I.au):



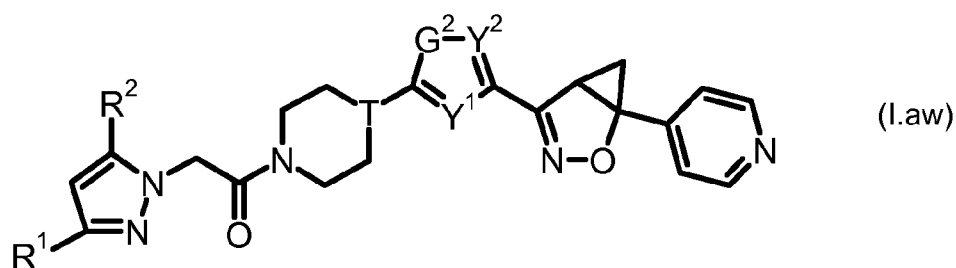
wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

av) 30 compounds of formula (I.av):



5 wherein R¹, R², G², T, Y¹ and Y² are as defined in Table 1.

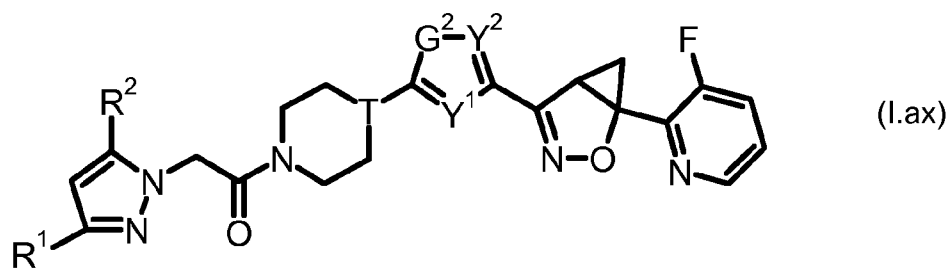
aw) 30 compounds of formula (I.aw):



10

wherein R¹, R², G², T, Y¹ and Y² are as defined in Table 1.

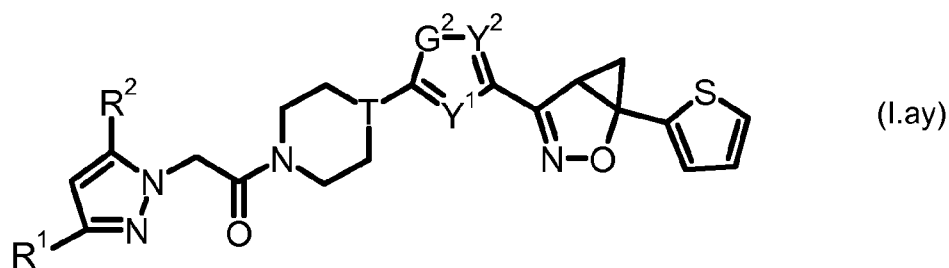
ax) 30 compounds of formula (I.ax):



15

wherein R¹, R², G², T, Y¹ and Y² are as defined in Table 1.

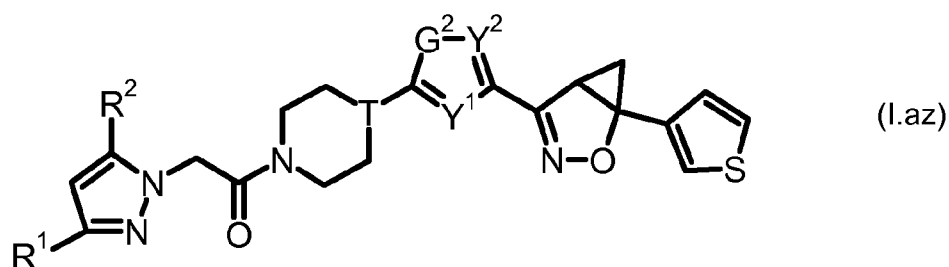
ay) 30 compounds of formula (I.ay):



wherein R^1 , R^2 , G^2 , T, Y^1 and Y^2 are as defined in Table 1.

5

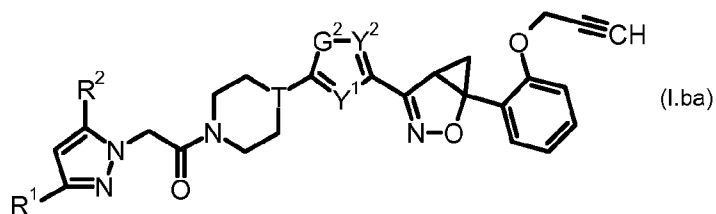
az) 30 compounds of formula (I.az):



wherein R^1 , R^2 , G^2 , T, Y^1 and Y^2 are as defined in Table 1.

10

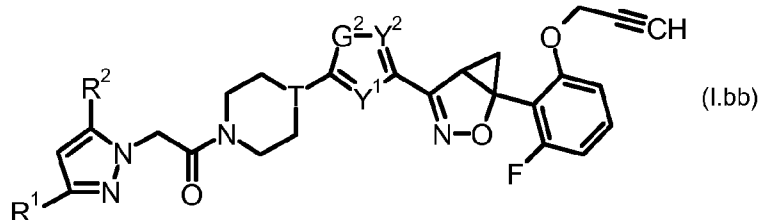
ba) 30 compounds of formula (I.ba):



wherein R^1 , R^2 , G^2 , T, Y^1 and Y^2 are as defined in Table 1.

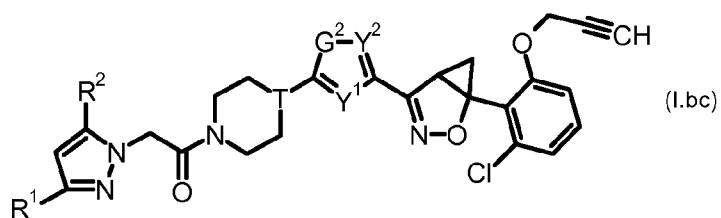
15

bb) 30 compounds of formula (I.bb):



20 wherein R^1 , R^2 , G^2 , T, Y^1 and Y^2 are as defined in Table 1.

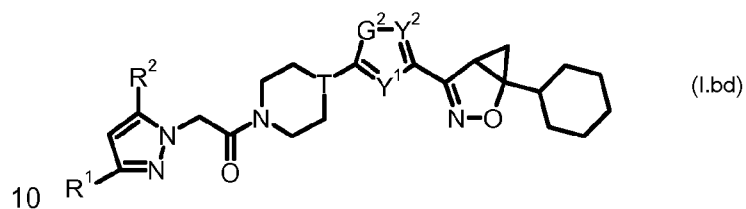
bc) 30 compounds of formula (I.bc):



5

wherein R^1 , R^2 , G^2 , T, Y^1 and Y^2 are as defined in Table 1.

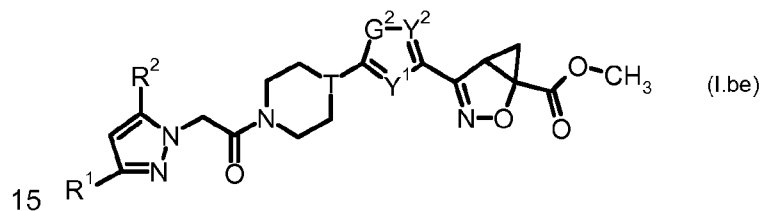
bd) 30 compounds of formula (I.bd):



10

wherein R^1 , R^2 , G^2 , T, Y^1 and Y^2 are as defined in Table 1.

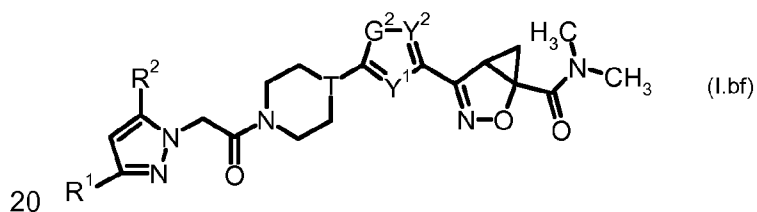
be) 30 compounds of formula (I.be):



15

wherein R^1 , R^2 , G^2 , T, Y^1 and Y^2 are as defined in Table 1.

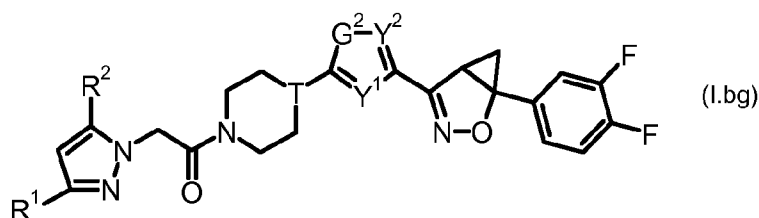
bf) 30 compounds of formula (I.bf):



20

wherein R^1 , R^2 , G^2 , T, Y^1 and Y^2 are as defined in Table 1.

bg) 30 compounds of formula (I.bg):



wherein R^1 , R^2 , G^2 , T , Y^1 and Y^2 are as defined in Table 1.

- 5 Throughout this description, temperatures are given in degrees Celsius and “m.p.” means melting point. LC/MS means Liquid Chromatography Mass Spectroscopy and the description of the apparatus and the method is:

Spectra were recorded on a Mass Spectrometer from Waters equipped with an electrospray source (Polarity: positive or negative ions, Capillary: 3.00 kV, Cone range: 30-
 10 60 V, Extractor: 2.00 V, Source Temperature: 150°C, Desolvation Temperature: 350°C, Cone Gas Flow: 0 L/Hr, Desolvation Gas Flow: 650 L/Hr, Mass range: 100 to 900 Da) and an Acquity UPLC from Waters: Binary pump, heated column compartment and diode-array detector. Solvent degasser, binary pump, heated column compartment and diode-array detector. Column: Waters UPLC HSS T3, 1.8 μ m, 30 x 2.1 mm, Temp: 60 °C, DAD
 15 Wavelength range (nm): 210 to 500, Solvent Gradient: A = water + 5% MeOH + 0.05 % HCOOH, B= Acetonitrile + 0.05 % HCOOH: gradient: gradient: 0 min 0% B, 100%A; 2.7-3.0 min 100% B; Flow (ml/min) 0.85

Table 2: Melting point and LC/MS data for compounds of Table 1

20

Compound No.	Melting point (°C)	LC/MS
I.b.01		Rt = 1.70 min; MS: m/z 508 [M+1] ⁺
I.j.01		Rt = 1.76 min; MS: m/z 516 [M+1] ⁺
I.j.19		Rt = 1.73 min; MS: m/z 534 [M+1] ⁺
I.ai.01		Rt = 1.75 min; MS: m/z 552 [M+1] ⁺
I.ai.19		Rt = 1.71 min; MS: m/z 570 [M+1] ⁺
I.u.01		Rt = 1.75 min; MS: m/z 546 [M+1] ⁺
I.t.01		Rt = 1.74 min; MS: m/z 546 [M+1] ⁺
I.t.19		Rt = 1.71 min; MS: m/z 564 [M+1] ⁺
I.z.01		Rt = 1.74 min; MS: m/z 534 [M+1] ⁺
I.z.19		Rt = 1.69 min; MS: m/z 552 [M+1] ⁺
I.ab.01		Rt = 1.77 min; MS: m/z 534 [M+1] ⁺
I.ac.01		Rt = 1.78 min; MS: m/z 550 [M+1] ⁺

I.af.01		Rt = 1.79 min; MS: m/z 594 [M+1] ⁺
I.ag.01		Rt = 1.90 min; MS: m/z 594 [M+1] ⁺
I.ba.01		Rt = 1.75 min; MS: m/z 570 [M+1] ⁺
I.bg.01		Rt = 1.82 min; MS: m/z 552 [M+1] ⁺
I.bg.19		Rt = 1.79 min; MS: m/z 570 [M+1] ⁺

The compounds according to the present invention can be prepared according to the above-mentioned reaction schemes, in which, unless otherwise stated, the definition of each variable is as defined above for a compound of formula (I).

5

Biological examples

Phytophthora infestans / tomato / leaf disc preventative (tomato late blight)

Tomato leaf disks are placed on water agar in multiwell plates (24-well format) and sprayed
 10 with the formulated test compound diluted in water. The leaf disks are inoculated with a spore suspension of the fungus 1 day after application. The inoculated leaf disks are incubated at 16°C and 75% rh under a light regime of 24 h darkness followed by 12 h light / 12 h darkness in a climate cabinet and the activity of a compound is assessed as percent disease control compared to untreated when an appropriate level of disease damage
 15 appears in untreated check leaf disks (5 – 7 days after application).

Compounds I.b.01, I.j.01, I.ai.01, I.ai.19, I.u.01, I.t.01, I.t.19, I.z.01, I.z.19, I.ab.01, I.ac.01, I.af.01, I.ag.01, I.ba.01, I.bg.01 and I.bg.19 at 200 ppm give at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development.

20

Phytophthora infestans / potato / preventative (potato late blight)

2-week old potato plants cv. Bintje are sprayed in a spray chamber with the formulated test compound diluted in water. The test plants are inoculated by spraying them with a sporangia suspension 2 days after application. The inoculated test plants are incubated at 18° C with 14
 25 h light/day and 100 % rh in a growth chamber and the percentage leaf area covered by disease is assessed when an appropriate level of disease appears on untreated check plants (5 – 7 days after application).

Compounds I.b.01, I.j.01, I.ai.01, I.ai.19, I.t.19, I.z.01, I.z.19, I.ab.01, I.ac.01, I.af.01, I.ba.01, and I.bg.19 at 200 ppm give at least 80% disease control in this test when compared
 30 to untreated control plants under the same conditions, which show extensive disease development.

Phytophthora infestans / potato / curative (potato late blight)

2-week old potato plants cv. Bintje are inoculated by spraying them with a sporangia suspension one day before application. The inoculated plants are sprayed in a spray chamber with the formulated test compound diluted in water. The inoculated test plants are incubated at 18° C with 14 h light/day and 100 % rh in a growth chamber and the percentage leaf area covered by disease is assessed when an appropriate level of disease appears on untreated check plants (3 – 4 days after application).

Compounds I.b.01, I.j.01, I.ai.01, I.ai.19, I.z.01, I.z.19, I.ab.01, I.ac.01, I.af.01, I.ba.01 and I.bg.19 at 200 ppm give at least 80% disease control in this test when compared to untreated control plants under the same conditions, which show extensive disease development.

Phytophthora infestans / potato / long lasting (potato late blight)

2-week old potato plants cv. Bintje are sprayed in a spray chamber with the formulated test compound diluted in water. The test plants are inoculated by spraying them with a sporangia suspension 6 days after application. The inoculated test plants are incubated at 18° C with 14 h light/day and 100 % rh in a growth chamber and the percentage leaf area covered by disease is assessed when an appropriate level of disease appears on untreated check plants (9 – 11 days after application).

Compounds I.b.01, I.j.01, I.ai.01, I.ai.19, I.t.19, I.z.01, I.z.19, I.ab.01, I.ac.01, I.af.01 and I.ba.01 at 200 ppm give at least 80% disease control in this test when compared to untreated control plants under the same conditions, which show extensive disease development.

Plasmopara viticola / grape / leaf disc preventative (grape downy mildew)

Grape vine leaf disks are placed on water agar in multiwell plates (24-well format) and sprayed with the formulated test compound diluted in water. The leaf disks are inoculated with a spore suspension of the fungus 1 day after application. The inoculated leaf disks are incubated at 19°C and 80% rh under a light regime of 12 h light / 12 h darkness in a climate cabinet and the activity of a compound is assessed as percent disease control compared to untreated when an appropriate level of disease damage appears in untreated check leaf disks (6 – 8 days after application).

Compounds I.b.01, I.j.01, I.ai.01, I.ai.19, I.u.01, I.t.01, I.t.19, I.z.01, I.z.19, I.ab.01, I.ac.01, I.af.01, I.ag.01, I.ba.01, I.bg.01 and I.bg.19 at 200 ppm give at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development.

Plasmopara viticola / grape / preventative (grape downy mildew)

5-week old grape seedlings cv. Gutedel are sprayed in a spray chamber with the formulated test compound diluted in water. The test plants are inoculated by spraying a sporangia suspension on their lower leaf surface one day after application. The inoculated test plants are incubated at 22° C and 100% rh in a greenhouse and the percentage leaf area covered by disease is assessed when an appropriate level of disease appears on untreated check plants (6 – 8 days after application).

Compounds I.b.01, I.j.01, I.ai.01, I.ai.19, I.u.01, I.z.19, I.ab.01, I.ac.01, I.af.01, I.ag.01, I.ba.01, and I.bg.19 at 200 ppm give at least 80% disease control in this test when compared to untreated control plants under the same conditions, which show extensive disease development.

Plasmopara viticola / grape / curative (grape downy mildew)

5-week-old grape seedlings cv. Gutedel are inoculated by spraying a sporangia suspension on their lower leaf surface one day before application. The inoculated grape plants are sprayed in a spray chamber with the formulated test compound diluted in water. The inoculated test plants are incubated at 22° C and 100% rh in a greenhouse and the percentage leaf area covered by disease is assessed when an appropriate level of disease appears on untreated check plants (4 – 6 days after application).

Compounds I.ai.01, I.ai.19, I.z.19, I.ac.01 and I.ag.01 at 200 ppm give at least 80% disease control in this test when compared to untreated control plants under the same conditions, which show extensive disease development.

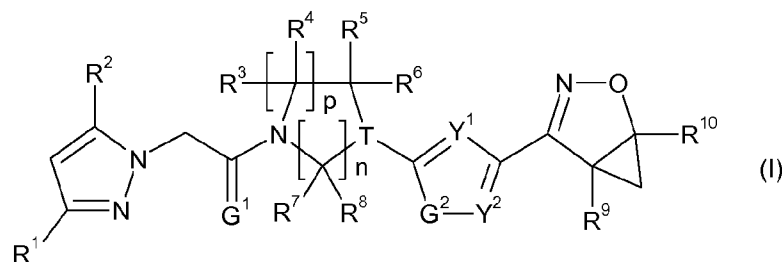
Plasmopara viticola / grape / long lasting (grape downy mildew)

5-week old grape seedlings cv. Gutedel are sprayed in a spray chamber with the formulated test compound diluted in water. The test plants are inoculated by spraying a sporangia suspension on their lower leaf surface 6 days after application. The inoculated test plants are incubated at 22° C and 100% rh in a greenhouse and the percentage leaf area covered by disease is assessed when an appropriate level of disease appears on untreated check plants (11 – 13 days after application).

Compounds I.b.01, I.j.01, I.ai.01, I.ai.19, I.t.01, I.z.01, I.z.19, I.ab.01, I.ac.01, I.ag.01 and I.ba.01 at 200 ppm give at least 80% disease control in this test when compared to untreated control plants under the same conditions, which show extensive disease development.

What is claimed is:

1. A compound of formula I:



5 wherein:

G^1 and G^2 are independently O or S;

T is CR^{11} or N;

Y^1 and Y^2 are independently CR^{12} or N;

n is 1 or 2;

10 p is 1 or 2, providing that when n is 2, p is 1;

R^1 and R^2 each independently are C_1 - C_4 alkyl, or C_1 - C_4 haloalkyl or C_3 - C_5 cycloalkyl;

R^3 , R^4 , R^5 , R^6 , R^7 and R^8 each independently are hydrogen, halogen, cyano, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkyl, C_3 - C_5 cycloalkyl or C_1 - C_4 alkylthio;

R^9 is hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkyl, C_3 - C_5 cycloalkyl, aryl or heteroaryl,

15 wherein aryl or heteroaryl are optionally substituted by one or more R^{13} ;

R^{10} is C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkyl, C_1 - C_4 haloalkoxy, C_3 - C_5 cycloalkyl, C_2 - C_4 alkenyl, C_2 - C_4 haloalkenyl, C_2 - C_4 alkynyl, C_2 - C_4 haloalkynyl, C_1 - C_4 alkoxycarbonyl, C_1 - C_4 alkylaminocarbonyl, C_1 - C_4 alkylcarbonyl O- C_1 - C_4 alkyloxime, C_1 - C_4 alkylcarbonyl O-aryloxime, aryl, heteroaryl, aryl- C_1 - C_4 alkyl or heteroaryl- C_1 - C_4 alkyl, wherein aryl and heteroaryl

20 are optionally substituted by one or more R^{13} ;

R^{11} is hydrogen, halogen or hydroxyl;

R^{12} is hydrogen, halogen or cyano;

each R^{13} independently is halogen, cyano, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkyl, C_1 - C_4 haloalkoxy, C_2 - C_4 alkenyloxy, C_2 - C_4 alkynyloxy, formyl, C_1 - C_4 alkylcarbonyl, C_1 -

25 C_4 alkylcarbonyl oxime or C_1 - C_4 alkylcarbonyl O- C_1 - C_4 alkyloxime;

or a salt or a N-oxide thereof.

2. A compound according to claim 1, wherein R^9 is hydrogen.

30 3. A compound according to claim 1, wherein R^{10} is C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_3 - C_5 cycloalkyl, aryl or heteroaryl, wherein aryl and heteroaryl are optionally substituted by one or more R^{13} .

4. A compound according to claim 1, wherein:
 G^1 is O
 G^2 is S;
T is CH or N;
- 5 Y^1 and Y^2 are independently CH or N;
n is 1 or 2;
p is 1 or 2, providing that when n is 2, p is 1;
 R^1 and R^2 each independently are methyl or halomethyl;
 R^3 , R^4 , R^5 , R^6 , R^7 and R^8 each independently are hydrogen, halogen, methyl, halomethyl or
10 methylthio;
 R^9 is hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄haloalkyl, C₃-C₅cycloalkyl, aryl or heteroaryl,
wherein aryl or heteroaryl are optionally substituted by one or more R^{13} ;
 R^{10} is C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₃-C₅cycloalkyl, C₂-
C₄alkenyl, C₂-C₄haloalkenyl, C₂-C₄alkynyl, C₂-C₄haloalkynyl, C₁-C₄alkoxycarbonyl, C₁-
15 C₄alkylaminocarbonyl, C₁-C₄alkylcarbonyl O-C₁-C₄alkyloxime, C₁-C₄alkylcarbonyl O-
aryloxime, aryl, heteroaryl, arylC₁-C₄alkyl or heteroarylC₁-C₄alkyl, wherein aryl and heteroaryl
are optionally substituted by one or more R^{13} ;
or a salt or a N-oxide thereof.
- 20 5. A compound according to claim 1, wherein:
 G^1 is O
 G^2 is S;
T is CH or N;
 Y^1 and Y^2 are independently CH or N;
25 n is 1 or 2;
p is 1 or 2, providing that when n is 2, p is 1;
 R^1 and R^2 each independently are methyl or halomethyl;
 R^3 , R^4 , R^5 , R^6 , R^7 and R^8 each independently are hydrogen, halogen, methyl, halomethyl or
methylthio;
30 R^9 is hydrogen, C₁-C₄alkyl or C₃-C₅cycloalkyl;
 R^{10} is C₁-C₄alkyl, C₁-C₄haloalkyl, C₃-C₅cycloalkyl, aryl or heteroaryl, wherein aryl and
heteroaryl are optionally substituted by one or more R^{13} ;
each R^{13} independently from each other, is halogen, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₂-
C₄alkenyloxy, C₂-C₄alkynyloxy, formyl, C₁-C₄alkylcarbonyl, C₁-C₄alkylcarbonyl oxime or C₁-
35 C₄alkylcarbonyl O-C₁-C₄alkyloxime,
or a salt or a N-oxide thereof.
6. A compound according to claim 1, wherein:

G¹ is O

G² is S;

T is CH or N;

Y¹ and Y² are independently CH or N;

5 n is 1 or 2;

p is 1 or 2, providing that when n is 2, p is 1;

R¹ and R² each independently are methyl or halomethyl;

R³, R⁴, R⁵, R⁶, R⁷ and R⁸ each independently are hydrogen, halogen, methyl, methylthio or halomethyl;

10 R⁹ is hydrogen or methyl;

R¹⁰ is C₁-C₄haloalkyl, aryl or heteroaryl, wherein aryl and heteroaryl are optionally substituted by one or more R¹³.

Each R¹³ independently from each other, is halogen, C₁-C₄haloalkoxy or C₂-C₄alkynyloxy or a salt or a N-oxide thereof.

15

7. A compound according to claim 1, wherein:

G¹ is O

G² is S;

T is CH or N;

20 Y¹ and Y² are independently CH or N;

n is 1 or 2;

p is 1 or 2, providing that when n is 2, p is 1;

R¹ and R² each independently are methyl, difluoromethyl or trifluoromethyl;

R³, R⁴, R⁵, R⁶, R⁷ and R⁸ each independently are hydrogen, halogen, methyl, methylthio or halomethyl;

25

R⁹ is hydrogen;

R¹⁰ is phenyl, thienyl and pyridyl, each of them optionally substituted by one or more R¹³.

Each R¹³ independently from each other, is fluoro or propargyloxy.

or a salt or a N-oxide thereof.

30

8. The compound according to any one of claims 1 to 7, wherein G¹, is O, G² is S, T is CH, Y¹ is N, and Y² is CH.

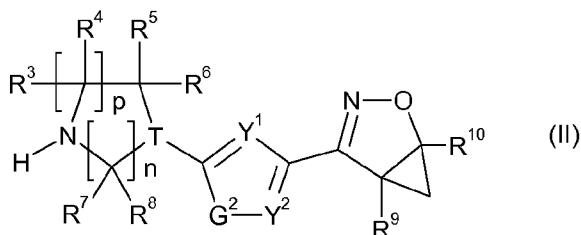
9. The compound according to any one of claims 1 to 8, wherein p is 1 and n is 2.

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10. The compound according to any one of the claims 1 to 9, wherein R¹ and R² each independently are methyl, difluoromethyl or trifluoromethyl and R³, R⁴, R⁵, R⁶, R⁷ and R⁸ each independently are hydrogen, or methyl, and preferably hydrogen.

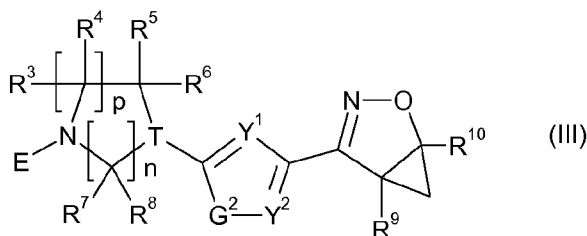
11. A compound according to anyone of claims 1 to 10, wherein R^3 , R^4 , R^5 , R^6 , R^7 and R^8 each independently are hydrogen.

5 12. A compound of formula II:



wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^2 , T , Y^1 , Y^2 , n and p are as defined in anyone of Claims 1-10 for a compound of formula I, and salts and N-oxides thereof,

Or a compound of formula III:



wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , G^2 , T , Y^1 , Y^2 , n and p are as defined for a compound of formula I and E is a protecting group and salts and N-oxides thereof.

13. A composition comprising at least one compound as defined in any one of claims 1 to 15 12 and an agriculturally acceptable carrier, optionally comprising an adjuvant, and optionally comprising one or more additional pesticidally active compounds.

14. A method of controlling or preventing an infestation of plants, propagation material thereof, harvested crops or of non-living materials by phytopathogenic or spoilage 20 microorganisms or organisms potentially harmful to man, which comprises the application of a compound as defined in any one of claims 1 to 11, to the plant, to parts of the plants or to the locus thereof, to propagation material thereof or to any part of the non-living materials.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/051571

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D417/14 A01N43/80 A01P3/00
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

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, CHEM ABS Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2008/013622 A2 (DU PONT [US]; PASTERIS ROBERT JAMES [US]; HANAGAN MARY ANN [US]; SHAPI) 31 January 2008 (2008-01-31) cited in the application the whole document -----	1-14
A	WO 2013/000941 A1 (SYNGENTA PARTICIPATIONS AG [CH]; SULZER-MOSSE SARAH [CH]; LAMBERTH CLE) 3 January 2013 (2013-01-03) the whole document -----	1-14
X,P	WO 2013/127808 A1 (SYNGENTA PARTICIPATIONS AG [CH]) 6 September 2013 (2013-09-06) page 61 - page 66; claims 1-3, 7-12 -----	1-9, 12-14



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2014/051571

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2008013622 A2	31-01-2008	AR 063213 A1	14-01-2009
		AU 2007277157 A1	31-01-2008
		CA 2653640 A1	31-01-2008
		CL 21852007 A1	13-06-2008
		CN 101888843 A	17-11-2010
		CN 102816148 A	12-12-2012
		CO 6150154 A2	20-04-2010
		EP 2049111 A2	22-04-2009
		GE P20125505 B	25-04-2012
		GT 200900017 A	06-09-2011
		JP 2010509190 A	25-03-2010
		KR 20090033496 A	03-04-2009
		ME 00586 A	20-12-2011
		PE 09522008 A1	10-09-2008
		PE 13862012 A1	25-10-2012
		RU 2009106871 A	10-09-2010
		TW 200822865 A	01-06-2008
		US 2009156592 A1	18-06-2009
		UY 30510 A1	29-02-2008
		WO 2008013622 A2	31-01-2008

WO 2013000941 A1	03-01-2013	TW 201313704 A	01-04-2013
		UY 34169 A	31-01-2013
		WO 2013000941 A1	03-01-2013

WO 2013127808 A1	06-09-2013	UY 34650 A	30-09-2013
		WO 2013127808 A1	06-09-2013
