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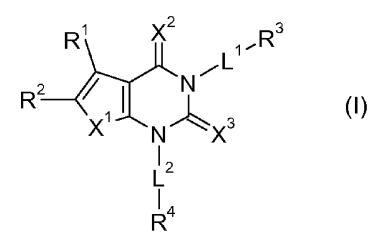
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(54) Title: MICROBIOCIDAL HETEROBICYCLIC DERIVATIVES



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





Microbiocidal Heterobicyclic Derivatives

The present invention relates to microbiocidal heterobicyclic derivatives, e.g. as active ingredients, which have microbiocidal activity, in particular fungicidal activity. The invention also relates to preparation of these heterobicyclic derivatives, to heterobicyclic derivatives

5 used as intermediates in the preparation of these heterobicyclic derivatives, to preparation of these intermediates, to agrochemical compositions which comprise at least one of the heterobicyclic derivatives, to preparation of these compositions and to use of the heterobicyclic derivatives or compositions in agriculture or horticulture for controlling or preventing infestation of plants, harvested food crops, seeds or non-living materials by

10 phytopathogenic microorganisms, preferably fungi.

Certain compounds for use as fungicides are described in WO 2013/071169. The present invention provides compounds of formula I:

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{X^{2}} X^{3} \qquad (I)$$

wherein,

15 X^1 , X^2 and X^3 are independently O, S or NR⁵;

 R^1 is halogen, cyano, C_1 - C_6 alkoxy, C_2 - C_6 alkenyloxy, C_2 - C_6 alkynyloxy, C_3 - C_6 cycloalkyloxy, C_1 - C_6 alkylthio, C_2 - C_6 alkenylthio, C_2 - C_6 alkynylthio or C_3 - C_6 cycloalkylthio, in which the alkoxy, alkenyl, alkynyl, cycloalkyl and alkyl groups are optionally substituted by one or more R^6 ; R^2 is -C(=O) R^6 or heterocyclyl, which can be optionally substituted by one or more R^6 ;

20 R^3 is $-C(=O)R^6$, $-S(=O)_2R^6$ or heterocyclyl, which can be optionally substituted by one or more R^6 ;

R⁴ is C₂-C₆alkynyl, C₃-C₆cycloalkyl, aryl or heterocyclyl, in which the alkynyl, cycloalkyl, aryl and heterocyclyl groups are optionally substituted by one or more R⁶;

 $R^5 \text{ is hydrogen, } C_1\text{-}C_6\text{alkyl, } C_1\text{-}C_6\text{alkoxy, } C_2\text{-}C_6\text{alkenyl, } C_2\text{-}C_6\text{alkenyloxy, } C_2\text{-}C_6\text{alkynyl, } C_2\text{-}C_6\text{alkenyloxy, } C_2\text{-}C_6\text{alkynyl, } C_2\text{-}C_6\text{alkenyloxy, } C_2\text{-}C_6\text{$

25 C₆alkynyloxy, C₃-C₆cycloalkyl, C₃-C₆cycloalkyloxy or aryl, in which the alkyl, alkoxy, alkenyl, alkynyl, cycloalkyl and aryl groups are optionally substituted by one or more R⁶;
R⁶ is hydrogen, halogen, cyano, hydroxyl, amino, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio, C₁-C₆haloalkylthio, C₂-C₆alkenyl, C₂-C₆haloalkenylthio, C₂-C₆alkenylthio, C₂-C₆alkenylthio, C₂-C₆alkynyl, C

30 C₆alkynyloxy, C₂-C₆alkynylthio, C₃-C₆cycloalkyl, C₃-C₆halocycloalkyl, C₃-C₆cycloalkyloxy, C₃-C₆cycloalkylthio, C₃-C₆halocycloalkyloxy, C₃-C₆halocycloalkylthio, -NH(C₁-C₆alkyl), -N(C₁-C₆alkyl)₂, -NH(C₁-C₆haloalkyl), -N(C₁-C₆haloalkyl)₂, -NH(C₂-C₆alkenyl), -N(C₂-C₆alkenyl)₂, -NH(C₂-C₆alkynyl), -N(C₂-C₆alkynyl)₂, -NH(C₃-C₆cycloalkyl), -N(C₃-C₆cycloalkyl)₂, -NH(C₃-C₆halocycloalkyl), -N(C₃-C₆halocycloalkyl)₂, -

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$$\begin{split} & \text{NHC}(=\text{O})(\text{C}_1-\text{C}_6\text{alkyl}), \ -\text{N}(\text{C}(=\text{O})(\text{C}_1-\text{C}_6\text{alkyl}))_2, \ -\text{NHC}(=\text{O})(\text{C}_1-\text{C}_6\text{haloalkyl}), \ \text{N}(\text{C}(=\text{O})(\text{C}_1-\text{C}_6\text{alkoxy}), \ -\text{N}(\text{C}(=\text{O})(\text{C}_1-\text{C}_6\text{alkoxy}))_2, \ -\text{NHC}(=\text{O})(\text{C}_1-\text{C}_6\text{alkoxy}))_2, \ -\text{NHC}(=\text{O})(\text{C}_2-\text{C}_6\text{alkenyl}), \ -\text{N}(\text{C}(=\text{O})(\text{C}_2-\text{C}_6\text{haloalkenyl}), \ -\text{N}(\text{C}(=\text{O})(\text{C}_2-\text{C}_6\text{haloalkenyl}))_2, \ -\text{NHC}(=\text{O})(\text{C}_2-\text{C}_6\text{haloalkenyl}), \ -\text{N}(\text{C}(=\text{O})(\text{C}_2-\text{C}_6\text{haloalkenyl}))_2, \ -\text{NHC}(=\text{O})(\text{C}_2-\text{C}_6\text{haloalkenyl})_2, \ -\text{NHC$$

- 5 C_6 alkenyloxy), $-N(C(=O)(C_2-C_6$ alkenyloxy))₂, $-NHC(=O)(C_2-C_6$ haloalkenyloxy), $-N(C(=O)(C_2-C_6$ alkynyl))₂, $-NHC(=O)(C_2-C_6$ alkynyl), $-N(C(=O)(C_2-C_6$ alkynyl))₂, $-NHC(=O)(C_2-C_6$ alkynyloxy), $-N(C(=O)(C_2-C_6$ alkynyloxy))₂, $-NHC(=O)(C_3-C_6$ cycloalkyl), $-N(C(=O)(C_3-C_6$ cycloalkyl))₂, $-NHC(=O)(C_3-C_6$ halocycloalkyl), $-N(C(=O)(C_3-C_6$ halocycloalkyl))₂, $-NHC(=O)(C_3-C_6$ cycloalkyloxy), $-N(C(=O)(C_3-C_6$ cycloalkyloxy))₂, $-NHC(=O)(C_3-C_6$
- 10 C_6 halocycloalkyloxy), -N(C(=O)(C_3 - C_6 halocycloalkyloxy))₂, -OC(=O)(C_1 - C_6 alkyl), -OC(=O)(C_1 - C_6 alkoxy), -OC(=O)(C_1 - C_6 haloalkoxy), -OC(=O)(C_2 - C_6 alkenyl), -OC(=O)(C_2 - C_6 haloalkenyl), -OC(=O)(C_2 - C_6 alkenyloxy), -OC(=O)(C_2 - C_6 haloalkenyloxy), -OC(=O)(C_3 - C_6 cycloalkyl), -OC(=O)(C_3 - C_6 cycloalkyl), -OC(=O)(C_3 - C_6 cycloalkyl), -OC(=O)(C_3 - C_6 cycloalkyloxy), -OC(=O)(C_3 - C_6 cycloalkyloxy)
- $\begin{aligned} &\text{15} \quad &\text{C(=O)(C$_1$-C_6alkyl), -C(=O)(C$_1$-C_6haloalkyl), -C(=O)(C$_1$-C_6alkoxy), -C(=O)(C$_1$-C_6haloalkoxy), -C(=O)(C$_2$-C_6alkenyl), -C(=O)(C$_2$-C_6alkenyloxy), -C(=O)(C$_2$-C_6alkynyl), -C(=O)(C$_2$-C_6alkynyloxy), -C(=O)(C$_3$-C_6cycloalkyl), -C(=O)(C$_3$-C_6cycloalkyloxy), -C(=O)(C$_3$-C_6halocycloalkyloxy), -C(=O)(C$_3$-C_6haloc$
- $\begin{array}{lll} 20 & -S(=O)_2(C_2-C_6alkenyl), \ -S(=O)_2(C_2-C_6haloalkenyl), \ -S(=O)_2(C_2-C_6alkenyloxy), \ -S(=O)_2(C_2-C_6alkynyl), \ -S(=O)_2(C_2-C_6alkynyloxy), \ -S(=O)_2(C_3-C_6haloalkyl), \ -S(=O)_2(C_3-C_6cycloalkyloxy), \ -S(=O)_2(C_3-C_6haloalkyl), \ -S(=O)_2(C_3-C_6cycloalkyloxy), \ -S(=O)_2(C_3-C_6haloalkyl), \ -S(=O)_2(C_3-C_6alkyl), \ -S(=O)_2(C_1-C_6alkyl), \ -S(=O)_2(C_1-C_6alkyl))_2, \ -NHS(=O)_2(C_1-C_6alkoxy), \ -NHS(=O)_2(C_1-C_6alkoxy), \ -N(S(=O)_2(C_1-C_6alkoxy))_2, \ -NHS(=O)_2(C_1-C_6alkoxy)_2, \ -NHS(=O)_2$
- $\begin{array}{lll} -NHS(=O)_2(C_1-C_6haloalkoxy), -N(S(=O)_2(C_1-C_6haloalkoxy))_2, -NHS(=O)_2(C_2-C_6alkenyl), -N(S(=O)_2(C_2-C_6alkenyl))_2, -NHS(=O)_2(C_2-C_6haloalkenyl), -N(S(=O)_2(C_2-C_6haloalkenyl))_2, -NHS(=O)_2(C_2-C_6alkenyloxy), -N(S(=O)_2(C_2-C_6alkenyloxy))_2, -NHS(=O)_2(C_2-C_6alkenyloxy))_2, -NHS(=O)_2(C_2-C_6alkynyl))_2, -NHS(=O)_2(C_2-C_6alkynyloxy), -N(S(=O)_2(C_2-C_6alkynyloxy), -N(S(=O)_2(C_2-C_6alkynyloxy))_2, -NHS(=O)_2(C_3-C_6cycloalkyl), -NHS(=O$
- 30 N(S(=O)₂(C₃-C₆cycloalkyl))₂, -NHS(=O)₂(C₃-C₆halocycloalkyl), -N(S(=O)₂(C₃-C₆cycloalkyl))₂, -NHS(=O)₂(C₃-C₆cycloalkyloxy), -N(S(=O)₂(C₃-C₆cycloalkyloxy))₂, -NHS(=O)₂(C₃-C₆halocycloalkyloxy), -N(S(=O)₂(C₃-C₆halocycloalkyloxy))₂, -CH(=NOC₁-C₆alkyl), -C(=NO(C₁-C₆alkyl))C₁-C₆alkyl))C₂-C₆alkenyl, -C(=NO(C₁-C₆alkyl))C₂-C₆alkynyl, -C(=NO(C₁-C₆alkyl))C₃-C₆cycloalkyl, -CH(=NN(C₁-C₆alkyl))₂, -
- 35 C(=NN(C₁-C₆alkyl)₂)C₁-C₆alkyl, -C(=NN(C₁-C₆alkyl)₂)C₂-C₆alkenyl, -C(=NN(C₁-C₆alkyl)₂)C₂-C₆alkynyl, -C(=NN(C₁-C₆alkyl)₂)C₃-C₆cycloalkyl, aryl or heterocyclyl; or two R⁶ linked to the same carbon atom can form a saturated 3- to 4-membered carbocyclic or heterocyclic ring;

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L¹ and L² are independently a direct bond, $-C(R^6)_2$ -z, $-C(R^6)_2$ -C(R⁶)₂-z, $-C(R^6)_2$ -C(R⁶)₂-C(R⁶)₂-z, $-C(R^6)_2$ -C(R⁶)₂-z, $-C(R^6)_2$ -C(R⁶)₂-C(R⁶)₂-z, $-C(R^6)_2$ -C(R⁶)₂-C, in each case z indicates the bond that is connected to R³ or R⁴;

5 or a salt or a N-oxide thereof.

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 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, this includes those groups that are part of other groups, 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, methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl and the isomers thereof, for example, isopropyl, iso-butyl, sec-butyl, tert-butyl or iso-amyl.

Alkenyl substituents can be in the form of straight or branched chains, and the alkenyl moieties, where appropriate, can be of either the (<u>E</u>)- or (<u>Z</u>)-configuration. Examples are vinyl and allyl. The alkenyl groups are preferably C₂-C₆, more preferably C₂-C₄ and most preferably 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 C_2 - C_6 , more preferably C_2 - C_4 and most preferably C_2 - C_3 alkynyl groups.

Haloalkyl groups may contain one or more identical or different halogen atoms and, for 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-diffuorovinyl or 1,2-dichloro-2-fluoro-vinyl.

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.

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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.

Heterocyclyl stands for saturated, partially unsaturated and aromatic heterocyclic ring 5 systems, which can be mono-, bi- or tricyclic and wherein at least one oxygen, nitrogen or sulfur atom is present as a ring member, which can be accompanied by other oxygen. nitrogen, sulphur, C(=O), C(=S), $C(=NR^5)$, $C(=NOR^5)$, $C(=NN(R^5)_2)$, S(=O) or $S(=O)_2$ as ring members. Monocyclic and bicyclic aromatic ring systems are preferred. For example, monocyclic heteocyclyl may be a 4- to 7-membered ring containing one to three heteroatoms 10 selected from oxygen, nitrogen and sulfur, more preferably selected from nitrogen and oxygen. Bicyclic heterocyclyl may be a 7- to 11-membered bicyclic ring containing one to five heteroatoms, preferably one to three heteroatoms, selected from oxygen, nitrogen and sulfur. The different rings of bi- and tricyclic heterocyclyl may be linked via one atom belonging to two different rings (spiro), via two adjacent ring atoms belonging to two different rings 15 (annelated) or via two different, not adjacent ring atoms belonging to two different rings (bridged). Examples for saturated heterocyclyl are azetidinyl, oxetanyl, thietanyl, pyrrolidinyl, tetrahydrofuranyl, tetrahydrothienyl, pyrazolidinyl, imidazolidinyl, oxazolidinyl, thiazolidinyl, isoxazolidinyl, isothiazolidinyl, oxadiazolidinyl, thiadiazolidinyl, dioxolanyl, dithiolanyl, piperidinyl, piperazinyl, tetrahydropyranyl, tetrahydrothiopyranyl, dithianyl and morpholinyl. 20 Examples for partially unsaturated heterocyclyl are pyrrolinyl, dihydrofuranyl, dihydrothienyl, pyrazolinyl, imidazolinyl, oxazolinyl, thiazolinyl, isoxazolinyl, isothiazinyl, oxadiazolinyl, thiadiazolinyl, dihydropyranyl, dihydrothiopyranyl, oxathiolyl and oxazinyl. Examples of aromatic heterocyclyl are furyl, thienyl, pyrrolyl, imidazolyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, oxadiazolyl, thiadiazolyl, triazolyl, tetrazolyl, pyridyl, pyridazinyl, 25 pyrimidinyl, pyrazinyl, triazinyl, tetrazinyl, indolyl, benzothiophenyl, benzofuranyl, benzimidazolyl, indazolyl, benzotriazolyl, benzothiazolyl, benzoxazolyl, quinolinyl, isoquinolinyl, phthalazinyl, quinoxalinyl, quinazolinyl, cinnolinyl and naphthyridinyl. Heterocyclyl rings do not contain adjacent oxygen ring atoms, adjacent sulfur ring atoms or adjacent oxygen and sulfur ring atoms. A link to a heterocyclyl group can be via a carbon 30 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.

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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 X^1 , X^2 , X^3 , R^1 , R^2 , R^3 , R^4 , L^1 and L^2 with reference to compounds of formula I. 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.

10 X^1 , X^2 and X^3 are independently O or S or NR⁵, preferably O or S.

X¹ is preferably S.

X² is preferably O.

X³ is preferably O.

R¹ is halogen, cyano, C₁-C₆alkoxy, C₂-C₆alkenyloxy, C₂-C₆alkynyloxy, C₃-

15 C₆cycloalkyloxy, C₁-C₆alkylthio, C₂-C₆alkenylthio, C₂-C₆alkynylthio or C₃-C₆cycloalkylthio, in which the alkoxy, alkenyl, alkynyl, cycloalkyl and alkyl groups are optionally substituted by one or more R⁶.

Preferably R¹ is halogen, cyano, C₁-C₆alkoxy, C₂-C₆alkynyloxy, C₃-C₆cycloalkyloxy or C₁-C₆alkylthio, in which the alkoxy, alkynyl, cycloalkyl and alkyl groups are optionally substituted by one or more R⁶, more preferably halogen, cyano or C₁-C₆alkoxy, even more preferably chloro, cyano or methoxy.

 R^2 is $-C(=O)R^6$ or heterocyclyl, which can be optionally substituted by one or more R^6 ; Preferably R^2 is $-C(=O)C_1-C_6$ alkoxy or a 5- to 6-membered aromatic heterocyclic ring system, more preferably $-C(=O)OCH_2CH_3$ or 2-oxazolyl.

25 R^3 is $-C(=O)R^6$, $-S(=O)_2R^6$ or heterocyclyl, which can be optionally substituted by one or more R^6 :

Preferably R^3 is $-C(=O)R^6$ or heterocyclyl, more preferably $-C(=O)NH(C_1-C_6alkyl)$, $-C(=O)N(C_1-C_6alkyl)_2$ or -C(=O)heterocyclyl, even more preferably $-C(=O)NH(C_1-C_6alkyl)$.

R⁴ is C₂-C₆alkynyl, C₃-C₆cycloalkyl, aryl or heterocyclyl, in which the alkynyl,

30 cycloalkyl, aryl and heterocyclyl groups are optionally substituted by one or more R⁶.

Preferably R⁴ is C₃-C₆cycloalkyl, aryl or heterocyclyl, in which cycloalkyl, aryl and heterocyclyl are optionally substituted by one or more R⁶, more preferably aryl or 5- to 6-membered aromatic heterocyclic ring system, even more preferably phenyl or thienyl.

R⁵ is hydrogen, C₁-C₆alkyl, C₁-C₆alkoxy, C₂-C₆alkenyl, C₂-C₆alkenyloxy, C₂-C₆alkynyl, 35 C₂-C₆alkynyloxy, C₃-C₆cycloalkyl, C₃-C₆cycloalkyloxy or aryl, in which the alkyl, alkoxy, alkenyl, alkynyl, cycloalkyl and aryl groups are optionally substituted by one or more R⁶;

Preferably R^5 is hydrogen, C_1 - C_6 alkyl, C_1 - C_6 alkoxy; more preferably hydrogen or C_1 - C_6 alkyl, even more preferably hydrogen or methyl.

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 $R^6 \text{ is hydrogen, halogen, cyano, nitro, hydroxyl, amino, C_1-C_6alkyl, C_1-C_6alkoxy, C_1-$C_6alkoxy, C_1-$C_6alkylthio, C_1-$C_6haloalkylthio, C_2-$C_6alkenyl, C_2-$C_6haloalkenyl, C_2-$C_6alkenyloxy, C_2-$C_6alkenylthio, C_2-$C_6haloalkenyloxy, C_2-$C_6alkynyloxy, C_2-$C_6alkynylthio, C_3-$C_6cycloalkyl, C_3-$C_6halocycloalkyl, C_3-$C_6alkynyloxy, C_2-$C_6alkynylthio, C_3-$C_6cycloalkyl, C_3-$C_6halocycloalkyl, C_3-$C_6halocycloalkyl,$

- 5 C₆cycloalkyloxy, C₃-C₆cycloalkylthio, C₃-C₆halocycloalkyloxy, C₃-C₆halocycloalkylthio, -NH(C₁-C₆alkyl), -N(C₁-C₆alkyl)₂, -NH(C₁-C₆haloalkyl), -N(C₁-C₆haloalkyl)₂, -NH(C₂-C₆alkenyl), -N(C₂-C₆alkenyl)₂, -NH(C₂-C₆haloalkenyl), -N(C₂-C₆haloalkenyl)₂, -NH(C₂-C₆alkynyl), -N(C₂-C₆alkynyl)₂, -NH(C₃-C₆cycloalkyl), -N(C₃-C₆cycloalkyl)₂, -NH(C₃-C₆halocycloalkyl), -N(C₃-C₆halocycloalkyl)₂, -NHC(=O)(C₁-C₆alkyl))₂, -NHC(=O)(C₁-C₆haloalkyl),
- $10 \quad N(C(=O)(C_1-C_6haloalkyl))_2, -NHC(=O)(C_1-C_6alkoxy), -N(C(=O)(C_1-C_6alkoxy))_2, -NHC(=O)(C_1-C_6haloalkoxy))_2, -NHC(=O)(C_2-C_6alkenyl), -N(C(=O)(C_2-C_6alkenyl))_2, -NHC(=O)(C_2-C_6haloalkenyl), -N(C(=O)(C_2-C_6haloalkenyl))_2, -NHC(=O)(C_2-C_6alkenyloxy), -N(C(=O)(C_2-C_6alkenyloxy))_2, -NHC(=O)(C_2-C_6alkenyloxy), -N(C(=O)(C_2-C_6alkenyloxy))_2, -NHC(=O)(C_2-C_6alkenyloxy))_2, -NHC(=O)(C_2-C_6alkenyloxy)_2, -NHC(=O)(C$
- 15 C_6 alkynyloxy), $-N(C(=O)(C_2-C_6$ alkynyloxy))₂, $-NHC(=O)(C_3-C_6$ cycloalkyl), $-N(C(=O)(C_3-C_6$ cycloalkyl))₂, $-NHC(=O)(C_3-C_6$ halocycloalkyl), $-N(C(=O)(C_3-C_6$ halocycloalkyl))₂, $-NHC(=O)(C_3-C_6$ cycloalkyloxy), $-N(C(=O)(C_3-C_6$ cycloalkyloxy))₂, $-NHC(=O)(C_3-C_6$ alkyloxy), $-N(C(=O)(C_3-C_6$ halocycloalkyloxy))₂, $-OC(=O)(C_1-C_6$ alkyl), $-OC(=O)(C_1-C_6$ alkoxy), $-OC(=O)(C_1-C_6$ alkoxy), $-OC(=O)(C_1-C_6$ alkoxy), $-OC(=O)(C_1-C_6$ alkoxy), $-OC(=O)(C_2-C_6$ alkenyl), $-OC(=O)(C_3-C_6$ alkoxy), $-OC(=O)(C_3-C_6$ alkenyl), $-OC(=O)(C_3-C_6$ alkoxy), $-OC(=O)(C_3-C_6$ alkoxy), $-OC(=O)(C_3-C_6$ alkoxy), $-OC(=O)(C_3-C_6$ alkenyl), $-OC(=O)(C_3-C_6$ alkoxy), $-OC(=O)(C_3-C_6)$ alkoxy), $-OC(=O)(C_3-C_6)$
- $\begin{array}{lll} 20 & OC(=O)(C_2-C_6haloalkenyl), -OC(=O)(C_2-C_6alkenyloxy), -OC(=O)(C_2-C_6haloalkenyloxy), -OC(=O)(C_2-C_6haloalkenyloxy), -OC(=O)(C_3-C_6cycloalkyl), -OC(=O)(C_3-C_6cycloalkyl), -OC(=O)(C_3-C_6cycloalkyloxy), -OC(=O)(C_3-C_6halocycloalkyloxy), -OC(=O)(C_3-C_6halocycloalkyloxy), -OC(=O)(C_1-C_6alkyl), -OC(=O)(C_1-C_6haloalkyl), -OC(=O)(C_1-C_6alkoxy), -OC(=O)(C_1-C_6haloalkoxy), -OC(=O)(C_2-C_6alkenyl), -O$
- 25 C_6 haloalkenyloxy), $-C(=O)(C_2-C_6$ alkynyl), $-C(=O)(C_2-C_6$ alkynyloxy), $-C(=O)(C_3-C_6$ cycloalkyl), $-C(=O)(C_3-C_6$ cycloalkyloxy), $-C(=O)(C_3-C_6$ halocycloalkyloxy), $-C(=O)(C_3-C_6$ halocycloalkyloxy), $-C(=O)(C_3-C_6$ halocycloalkyloxy), $-C(=O)(C_3-C_6$ halocycloalkyloxy), $-C(=O)(C_3-C_6$ halocycloalkyloxy), $-C(=O)(C_3-C_6$ haloalkyl), $-C(=O)(C_3-C_6$ haloalkoxy), $-C(=O)(C_3-C_6$ haloalkenyl), $-C(=O)(C_3-C_6$ alkenyloxy), $-C(=O)(C_3-C_6$ alkenyloxy), $-C(=O)(C_3-C_6$ alkynyl), $-C(=O)(C_3-C_6)$ alkynyl), $-C(=O)(C_3-C_6)$ alkynyl), $-C(=O)(C_3-C_6)$ alkynyl), $-C(=O)(C_3-C_6)$ alkynyl), $-C(=O)(C_3-C_6)$ alkynyl)
- 30 C_6 cycloalkyl), $-S(=O)_2(C_3-C_6$ halocycloalkyl), $-S(=O)_2(C_3-C_6$ cycloalkyloxy), $-S(=O)_2(C_3-C_6$ cycloalkyloxy), $-S(=O)_2(C_3-C_6$ cycloalkyloxy), $-S(=O)_2(C_3-C_6$ halocycloalkyloxy), $-S(=O)_2(C_1-C_6$ alkyl), $-S(=O)_2(C_1-C_6$ alkyl), $-S(=O)_2(C_1-C_6$ alkyl)), $-S(=O)_2(C_1-C_6$ alkoxy), $-S(=O)_2(C_1-C_6$ alkoxy), $-S(=O)_2(C_1-C_6$ alkoxy), $-S(=O)_2(C_1-C_6$ alkoxy)), $-S(=O)_2(C_1-C_6$ alkoxy), $-S(=O)_2(C_1-C_6$ alkoxy)), $-S(=O)_2(C_2-C_6$ alkenyl), $-S(=O)_2(C_2-C_6$ alkenyl)), $-S(=O)_2(C_2-C_6$ alkenyl)
- $\label{eq:substitute} 35 \quad NHS(=O)_2(C_2-C_6alkenyloxy), -N(S(=O)_2(C_2-C_6alkenyloxy))_2, -NHS(=O)_2(C_2-C_6haloalkenyloxy), -N(S(=O)_2(C_2-C_6alkynyl), -N(S(=O)_2(C_2-C_6alkynyl))_2, -NHS(=O)_2(C_2-C_6alkynyloxy), -N(S(=O)_2(C_2-C_6alkynyloxy))_2, -NHS(=O)_2(C_3-C_6cycloalkyl), -N(S(=O)_2(C_3-C_6cycloalkyl))_2, -NHS(=O)_2(C_3-C_6halocycloalkyl), -N(S(=O)_2(C_3-C_6cycloalkyl))_2, -NHS(=O)_2(C_3-C_6halocycloalkyl), -N(S(=O)_2(C_3-C_6cycloalkyl))_2, -NHS(=O)_2(C_3-C_6halocycloalkyl), -N(S(=O)_2(C_3-C_6halocycloalkyl))_2, -NHS(=O)_2(C_3-C_6halocycloalkyl)_2, -NHS(=O)_2(C_3-C_6halocycloalkyl)_2,$

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$$\begin{split} &C_6\text{halocycloalkyl}))_2,\ -\text{NHS}(=O)_2(C_3-C_6\text{cycloalkyloxy}),\ -\text{N}(S(=O)_2(C_3-C_6\text{cycloalkyloxy}))_2,\ -\text{NHS}(=O)_2(C_3-C_6\text{halocycloalkyloxy}),\ -\text{N}(S(=O)_2(C_3-C_6\text{halocycloalkyloxy}))_2,\ -\text{CH}(=\text{NOC}_1-C_6\text{alkyl}),\ -\text{C}(=\text{NO}(C_1-C_6\text{alkyl}))C_1-C_6\text{alkyl}),\ -\text{C}(=\text{NO}(C_1-C_6\text{alkyl}))C_2-C_6\text{alkynyl},\ -\text{C}(=\text{NO}(C_1-C_6\text{alkyl}))C_3-C_6\text{cycloalkyl},\ -\text{CH}(=\text{NN}(C_1-C_6\text{alkyl}))_2,\ -\text{CH}(=\text{NN}(C_1-C_6\text{alkyl}))_$$

5 C(=NN(C₁-C₆alkyl)₂)C₁-C₆alkyl, -C(=NN(C₁-C₆alkyl)₂)C₂-C₆alkenyl, -C(=NN(C₁-C₆alkyl)₂)C₂-C₆alkynyl, -C(=NN(C₁-C₆alkyl)₂)C₃-C₆cycloalkyl, aryl or heterocyclyl; or two R⁶ linked to the same carbon atom can form a saturated 3- to 4-membered carbocyclic or heterocyclic ring;

Preferably R^6 is halogen, cyano, nitro, hydroxyl, amino, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_1 - C_6 alkylthio, C_1 - C_6 haloalkylthio, C_2 - C_6 alkenyl, C_2 -

- 10 C₆haloalkenyl, C₂-C₆alkenyloxy, C₂-C₆haloalkenyloxy, C₂-C₆alkynyl, C₂-C₆alkynyloxy, C₃-C₆cycloalkyl, C₃-C₆cycloalkyl, C₃-C₆cycloalkyloxy, C₃-C₆halocycloalkyloxy, more preferably halogen, cyano, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₂-C₆alkenyl, C₂-C₆alkynyl, C₂-C₆alkynyloxy, C₃-C₆cycloalkyl, even more preferably halogen, cyano, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆haloalkoxy, C₂-C₆alkynyl or C₃-
- 15 C₆cycloalkyl, most preferably fluoro, chloro, cyano, methyl, trifluoromethyl, methoxy, ethynyl or cyclopropyl.

 $L^{1} \text{ and } L^{2} \text{ are independently a direct bond, } -C(R^{6})_{2}-z, -C(R^{6})_{2}-C(R^{6})_{2}-z, -C(R^{6})_{2}-$

 L^{1} is preferably $-C(R^{6})_{2}$ -z, $-C(R^{6})_{2}$ -C($R^{6})_{2}$ -z, $-C(R^{6})_{2}$ -NR⁵-z or $-C(R^{6})_{2}$ -O-z, more preferably $-C(R^{6})_{2}$ -z or $-C(R^{6})_{2}$ -z, even more preferably $-C(CH_{3})_{2}$ -z.

 $L^{2} \text{ is preferably -C}(R^{6})_{2}\text{-z, -C}(R^{6})_{2}\text{-z, -C}(R^{6})_{2}\text{-z, -C}(R^{6})_{2}\text{-c}(R^{6})_{2}\text{-z, -C}(R^{6})_{2}\text{-z, -C}(R$

Preferably the compound of formula I is a compound wherein:

X¹, X² and X³ are independently O, S or NR⁵;

R¹ is halogen, cyano, C₁-C₆alkoxy, C₂-C₆alkynyloxy, C₃-C₆cycloalkyloxy or C₁-C₆alkylthio, in which the alkoxy, alkynyl, cycloalkyl and alkyl groups are optionally substituted by one or more R⁶:

 R^2 is $-C(=O)C_1-C_6$ alkoxy or a 5- to 6-membered aromatic heterocyclic ring system; R^3 is $-C(=O)R^6$ or heterocyclyl;

R⁴ is C₃-C₆cycloalkyl, aryl or heterocyclyl, in which cycloalkyl, aryl and heterocyclyl are optionally substituted by one or more R⁶;

35 R⁵ is hydrogen, C_1 - C_6 alkyl or C_1 - C_6 alkoxy; R⁶ is halogen, cyano, nitro, hydroxyl, amino, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_1 - C_6 alkylthio, C_1 - C_6 haloalkylthio, C_2 - C_6 alkenyl, C_2 - C_6 haloalkenyl, C_2 - C₆alkenyloxy, C₂-C₆haloalkenyloxy, C₂-C₆alkynyl, C₂-C₆alkynyloxy, C₃-C₆cycloalkyl, C₃-

C₆halocycloalkyl, C₃-C₆cycloalkyloxy or C₃-C₆halocycloalkyloxy;

 L^{1} is $-C(R^{6})_{2}$ -z, $-C(R^{6})_{2}$ - $C(R^{6})_{2}$ -z, $-C(R^{6})_{2}$ -NR⁵-z or $-C(R^{6})_{2}$ -O-z;

$$L^2$$
 is $-C(R^6)_2-z$, $-C(R^6)_2-C(R^6)_2-z$, $-C(R^6)_2-C(R^6)_2-C(R^6)_2-z$, $-C(R^6)_2-RR^5-z$ or $-C(R^6)_2-C(R^6)_2-z$;

5 or a salt or a N-oxide thereof.

Preferably the compound of formula I is a compound wherein:

X¹, X² and X³ are independently O, S or NR⁵;

R¹ is halogen, cyano or C₁-C₆alkoxy;

R² is -C(=O)C₁-C₆alkoxy or a 5- to 6-membered aromatic heterocyclic ring system;

10 R^3 is $-C(=O)NH(C_1-C_6alkyl)$, $-C(=O)N(C_1-C_6alkyl)_2$ or -C(=O)heterocyclyl;

R⁴ is aryl or 5- to 6-membered aromatic heterocyclic ring system;

R⁵ is hydrogen or C₁-C₆alkyl;

 R^6 is halogen, cyano, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_2 - C_6 alkynyl, C_2 - C_6 alkynyloxy, C_3 - C_6 cycloalkyl;

15 L^1 is $-C(R^6)_2$ -z or $-C(R^6)_2$ - $C(R^6)_2$ -z;

$$L^2$$
 is $-C(R^6)_2-C(R^6)_2$ -z or $-C(R^6)_2$ -O-z;

or a salt or a N-oxide thereof.

Preferably the compound of formula I is a compound wherein:

X¹, X² and X³ are independently O, S or NR⁵;

20 R¹ is halogen, cyano or C₁-C₆alkoxy;

R² is -C(=O)C₁-C₆alkoxy or a 5- to 6-membered aromatic heterocyclic ring system;

 R^3 is $-C(=O)NH(C_1-C_6alkyl)$, $-C(=O)N(C_1-C_6alkyl)_2$ or -C(=O)heterocyclyl;

R⁴ is aryl or 5- to 6-membered aromatic heterocyclic ring system;

 R^5 is hydrogen or $\mathsf{C}_1\text{-}\mathsf{C}_6\mathsf{alkyl};$

25 R^6 is halogen, cyano, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_2 - C_6 alkynyl or C_3 - C_6 cycloalkyl;

 L^1 is $-C(R^6)_2$ -z or $-C(R^6)_2$ - $C(R^6)_2$ -z;

$$L^2$$
 is $-C(R^6)_2$ - $C(R^6)_2$ -z or $-C(R^6)_2$ -O-z;

or a salt or a N-oxide thereof.

30 Preferably the compound of formula I is a compound wherein:

X¹, X² and X³ are independently O, S or NR⁵;

R¹ is chloro, cyano or methoxy;

 R^2 is $-C(=O)OCH_2CH_3$ or 2-oxazolyl;

 R^3 is -C(=O)NH(C₁-C₆alkyl);

35 R⁴ is phenyl or thienyl;

R⁵ is hydrogen or methyl;

 $\ensuremath{\mathsf{R}}^6$ is fluoro, chloro, cyano, methyl, trifluoromethyl, methoxy, ethynyl or cyclopropyl.

$$L^1$$
 is $-C(R^6)_2$ -z or $-C(R^6)_2$ -C($R^6)_2$ -z;

 L^2 is $-C(R^6)_2-C(R^6)_2$ -z or $-C(R^6)_2$ -O-z;

or a salt or a N-oxide thereof.

Preferably the compound of formula I is a compound wherein:

X¹, X² and X³ are independently O, S or NR⁵;

5 R¹ is chloro, cyano or methoxy;

 R^2 is $-C(=O)OCH_2CH_3$ or 2-oxazolyl;

 R^3 is $-C(=O)NH(C_1-C_6alkyl)$;

R⁴ is phenyl or thienyl;

R⁵ is hydrogen or methyl;

10 L^1 is $-C(CH_3)_2-z$;

 L^2 is $CH_2CH(O(C_1-C_6alkyl))-z$;

or a salt or a N-oxide thereof.

Preferably the compound of formula I is a compound wherein:

X¹, X² and X³ are independently O or S;

15 R¹ is halogen, cyano, C₁-C₆alkoxy, C₂-C₆alkynyloxy, C₃-C₆cycloalkyloxy or C₁-C₆alkylthio, in which the alkoxy, alkynyl, cycloalkyl and alkyl groups are optionally substituted by one or more R⁶:

 R^2 is $-C(=O)C_1-C_6$ alkoxy or a 5- to 6-membered aromatic heterocyclic ring system; R^3 is $-C(=O)R^6$ or heterocyclyl;

20 R⁴ is C₃-C₆cycloalkyl, aryl or heterocyclyl, in which cycloalkyl, aryl and heterocyclyl are optionally substituted by one or more R⁶;

 R^6 is halogen, cyano, nitro, hydroxyl, amino, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_1 - C_6 alkylthio, C_1 - C_6 haloalkylthio, C_2 - C_6 alkenyl, C_2 - C_6 haloalkenyloxy, C_2 - C_6 alkynyloxy, C_2 - C_6 alkynyloxy, C_3 - C_6 cycloalkyl, C_3 -

25 C₆halocycloalkyl, C₃-C₆cycloalkyloxy or C₃-C₆halocycloalkyloxy;

L¹ is $-C(R^6)_2$ -z, $-C(R^6)_2$ -C(R⁶)₂-z, $-C(R^6)_2$ -NR⁵-z or $-C(R^6)_2$ -O-z;

 L^2 is $-C(R^6)_2$ -z, $-C(R^6)_2$ -C($R^6)_2$ -z, $-C(R^6)_2$ -C($R^6)_2$ -C($R^6)_2$ -z, $-C(R^6)_2$ -NR⁵-z or $-C(R^6)_2$ -O-z; or a salt or a N-oxide thereof.

Preferably the compound of formula I is a compound wherein:

30 X^1 , X^2 and X^3 are independently O or S;

R¹ is halogen, cyano or C₁-C₀alkoxy;

 R^2 is $-C(=O)C_1-C_6$ alkoxy or a 5- to 6-membered aromatic heterocyclic ring system;

 $R^3 \text{ is -C(=O)NH}(C_1\text{-}C_6\text{alkyI}), \text{-C(=O)N}(C_1\text{-}C_6\text{alkyI})_2 \text{ or -C(=O)heterocyclyI};$

R⁴ is aryl or 5- to 6-membered aromatic heterocyclic ring system;

35 R^6 is halogen, cyano, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_2 - C_6 alkynyl, C_2 - C_6 alkynyloxy, C_3 - C_6 cycloalkyl;

 L^1 is $-C(R^6)_2$ -z or $-C(R^6)_2$ - $C(R^6)_2$ -z;

 L^2 is $-C(R^6)_2$ - $C(R^6)_2$ -z or $-C(R^6)_2$ -O-z;

or a salt or a N-oxide thereof.

Preferably the compound of formula I is a compound wherein:

X¹, X² and X³ are independently O or S;

R¹ is chloro, cyano or methoxy;

5 R^2 is $-C(=O)OCH_2CH_3$ or 2-oxazolyl;

 R^3 is $-C(=O)NH(C_1-C_6alkyl)$;

R⁴ is phenyl or thienyl;

R⁶ is fluoro, chloro, cyano, methyl, trifluoromethyl, methoxy, ethynyl or cyclopropyl.

 L^1 is $-C(R^6)_2$ -z or $-C(R^6)_2$ - $C(R^6)_2$ -z;

10 L^2 is $-C(R^6)_2-C(R^6)_2$ -z or $-C(R^6)_2$ -O-z;

or a salt or a N-oxide thereof.

Preferably the compound of formula I is a compound wherein:

 X^1 is S, X^2 is O and X^3 is O.

The invention also relates to compounds of formula l-a:

in which X^1 , X^2 , X^3 , R^2 , R^3 , R^4 , L^1 and L^2 have the definitions as described for formula I.

Preferred definitions of X^1 , X^2 , X^3 , R^2 , R^3 , R^4 , L^1 and L^2 are as defined for formula I.

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

$$\begin{array}{c|c}
N & X^2 & R^3 \\
N & X^1 & N & X^3 \\
\downarrow & & & \downarrow \\
N & & & & \downarrow \\
N & & & & & \\
N & & & & \\
N & & & & & \\
N$$

20

wherein X^1 , X^2 , X^3 , R^1 , R^3 , R^4 , L^1 and L^2 have the definition as described for formula I.

Preferred definitions of X^1 , X^2 , X^3 , R^1 , R^3 , R^4 , L^1 and L^2 are as defined for formula I.

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

$$R^{1} \xrightarrow{X^{2}H_{3}C CH_{3}}$$

$$R^{2} \xrightarrow{N} X^{3}$$

$$\downarrow^{2}$$

$$\downarrow^{2}$$

$$\downarrow^{2}$$

$$\downarrow^{4}$$

$$\downarrow^{4}$$

$$\downarrow^{4}$$

$$\downarrow^{1}$$

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in which X^1 , X^2 , X^3 , R^1 , R^2 , R^3 , R^4 and L^2 have the definitions as described for formula I. Preferred definitions of X^1 , X^2 , X^3 , R^1 , R^2 , R^3 , R^4 and L^2 are as defined for formula I.

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

5 in which X¹, X², X³, R¹, R², R⁴, L¹ and L² have the definitions as described for formula I. Preferred definitions of X¹, X², X³, R¹, R², R⁴, L¹ and L² are as defined for formula I.

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

$$R^{2} \xrightarrow{X^{1}} X^{2} \xrightarrow{I_{1}} R^{3}$$

$$X^{3} \xrightarrow{CH_{3}} CH_{3}$$

$$R^{4} CH_{3}$$

$$(I-e)$$

in which X¹, X², X³, R¹, R², R³, R⁴ and L¹ have the definitions as described for formula I.

10 Preferred definitions of X¹, X², X³, R¹, R², R³, R⁴ and L¹ are as defined for formula I.

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

$$R^{1} \xrightarrow{X^{2}} L^{1} \xrightarrow{R^{3}}$$

$$R^{2} \xrightarrow{X^{1}} \underset{L^{2}}{N} X^{3}$$

$$H_{3}C^{-0} \xrightarrow{I}$$

$$(I-f)$$

15

in which X^1 , X^2 , X^3 , R^1 , R^2 , R^3 , L^1 and L^2 have the definitions as described for formula I. Preferred definitions of X^1 , X^2 , X^3 , R^1 , R^2 , R^3 , L^1 and L^2 are as defined for formula I.

Compounds of the present invention can be made as shown in the following schemes, in which, unless otherwise stated, the definition of each variable is as defined above for a compound of formula (I).

The compounds of formula I, wherein X¹, X², X³, R¹, R², R³, R⁴, L¹ and L² are as defined for formula I can be obtained by transformation of a compound of formula II, wherein X¹, X², X³, R¹, R², R³ and L¹ are as defined for formula I with a compound of formula III, wherein R⁴ and L² are as defined for formula I and R⁷ is hydroxyl, halogen, preferably chloro or bromo, or a sulfonate, preferably a mesylate or tosylate, under Mitsunobu reaction conditions or with a base. This is shown in Scheme 1.

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Scheme 1

$$R^{2} \xrightarrow{N} X^{3} \qquad (II) \qquad + \qquad R^{4} \xrightarrow{L^{2}} R^{7} \qquad (III) \qquad PPh_{3}, \\ DIAD \\ or base \\ R^{2} \xrightarrow{N} X^{3} \qquad (I)$$

The compounds of formula II, wherein X¹, X², X³, R¹, R², R³ and L¹ are as defined for formula I can be obtained by transformation of a compound of formula IV, wherein X¹, X², X³, 5 R¹, R², R³ and L¹ are as defined for formula I and R⁸ is C₁-C₆alkyl, with a base, suchg as sodium hydride or potassium tert-butoxide. This is shown in Scheme 2.

Scheme 2

The compounds of formula IV, wherein X¹, X², X³, R¹, R², R³ and L¹ are as defined for formula I and R⁸ is C₁-C₆alkyl can be obtained by transformation of a compound of formula V, wherein X¹, X², R¹ and R² are as defined for formula I and R⁸ is C₁-C₆alkyl, with a compound of formula VI, wherein R³ and L¹ are as defined for formula I, and a phosgene derivative, such as bis(trichloromethyl)carbonate (BTC) and a base. This is shown in Scheme 3.

Scheme 3

15

Alternatively, the compounds of formula IV, wherein X¹, X², X³, R¹, R², R³ and L¹ are as defined for formula I and R⁸ is C₁-C₆alkyl can be obtained by transformation of a compound of formula V, wherein X¹, X², R¹ and R² are as defined for formula I and R⁸ is C₁-C₆alkyl, with a compound of formula VII, wherein R³ and L¹ are as defined for formula I and Hal is halogen, preferably fluoro or chloro, and a base. This is shown in Scheme 4.

Scheme 4

Alternatively the compounds of formula II, wherein X¹, X², X³, R¹, R², R³ and L¹ are as defined for formula I can be obtained by transformation of a compound of formula VIII, wherein X¹, X², R¹, R², R³ and L¹ are as defined for formula I with a compound of formula 5 (IX), such as phosgene or a phosgene derivative, and a base. This is shown in Scheme 5.

Scheme 5

The compounds of formula VIII, wherein X¹, X², R¹, R², R³ and L¹ are as defined for formula I can be obtained by transformation of a compound of formula X, wherein X¹, X², R¹ and R²

10 are as defined for formula I and R⁹ is hydroxy, halogen or C₁-C₆alkoxy, with a compound of formula (VI), wherein R³ and L¹ are as defined for formula I, and a base. This is shown in Scheme 6.

Scheme 6

15

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.

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.

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It is also possible to use compounds of formula I as fungicide. The term "fungicide" as used herein means a compound that controls, modifies, or prevents the growth of fungi. The term "fungicidally effective amount" means the quantity of such a compound or combination of such compounds that is capable of producing an effect on the growth of fungi. Controlling or modifying effects include all deviation from natural development, such as killing, retardation and the like, and prevention includes barrier or other defensive formation in or on a plant to prevent fungal infection.

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 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.

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.

The compounds of formula I are for example, effective against Fungi and fungal vectors of disease as well as phytopathogenic bacteria and viruses. These Fungi and fungal vectors of disease as well as phytopathogenic bacteria and viruses are for example:

Absidia corymbifera, Alternaria spp, Aphanomyces spp, Ascochyta spp, Aspergillus spp. including A. flavus, A. fumigatus, A. nidulans, A. niger, A. terrus, Aureobasidium spp. including A. pullulans, Blastomyces dermatitidis, Blumeria graminis, Bremia lactucae,

Botryosphaeria spp. including B. dothidea, B. obtusa, Botrytis spp. inclusing B. cinerea, Candida spp. including C. albicans, C. glabrata, C. krusei, C. lusitaniae, C. parapsilosis, C. tropicalis, Cephaloascus fragrans, Ceratocystis spp, Cercospora spp. including C. arachidicola, Cercosporidium personatum, Cladosporium spp, Claviceps purpurea, Coccidioides immitis, Cochliobolus spp, Colletotrichum spp. including C. musae,

Cryptococcus neoformans, Diaporthe spp, Didymella spp, Drechslera spp, Elsinoe spp, Epidermophyton spp, Erwinia amylovora, Erysiphe spp. including E. cichoracearum, Eutypa lata, Fusarium spp. including F. culmorum, F. graminearum, F. langsethiae, F. moniliforme, F. oxysporum, F. proliferatum, F. subglutinans, F. solani, Gaeumannomyces

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graminis, Gibberella fujikuroi, Gloeodes pomigena, Gloeosporium musarum, Glomerella cingulate, Guignardia bidwellii, Gymnosporangium juniperi-virginianae, Helminthosporium spp, Hemileia spp, Histoplasma spp. including H. capsulatum, Laetisaria fuciformis, Leptographium lindbergi, Leveillula taurica, Lophodermium seditiosum, Microdochium nivale, 5 Microsporum spp, Monilinia spp, Mucor spp, Mycosphaerella spp, including M. graminicola, M. pomi, Oncobasidium theobromaeon, Ophiostoma piceae, Paracoccidioides spp, Penicillium spp. including P. digitatum, P. italicum, Petriellidium spp, Peronosclerospora spp. Including P. maydis, P. philippinensis and P. sorghi, Peronospora spp, Phaeosphaeria nodorum, Phakopsora pachyrhizi, Phellinus igniarus, Phialophora spp, Phoma spp, 10 Phomopsis viticola, Phytophthora spp. including P. infestans, Plasmopara spp. including P. halstedii, P. viticola, Pleospora spp., Podosphaera spp. including P. leucotricha, Polymyxa graminis, Polymyxa betae, Pseudocercosporella herpotrichoides, Pseudomonas spp, Pseudoperonospora spp. including P. cubensis, P. humuli, Pseudopeziza tracheiphila, Puccinia Spp. including P. hordei, P. recondita, P. striiformis, P. triticina, Pyrenopeziza spp, 15 Pyrenophora spp, Pyricularia spp. including P. oryzae, Pythium spp. including P. ultimum, Ramularia spp, Rhizoctonia spp, Rhizomucor pusillus, Rhizopus arrhizus, Rhynchosporium spp, Scedosporium spp. including S. apiospermum and S. prolificans, Schizothyrium pomi, Sclerotinia spp, Sclerotium spp, Septoria spp, including S. nodorum, S. tritici, Sphaerotheca macularis, Sphaerotheca fusca (Sphaerotheca fuliginea), Sporothorix spp, Stagonospora 20 nodorum, Stemphylium spp., Stereum hirsutum, Thanatephorus cucumeris, Thielaviopsis basicola, Tilletia spp, Trichoderma spp. including T. harzianum, T. pseudokoningii, T. viride, Trichophyton spp, Typhula spp, Uncinula necator, Urocystis spp, Ustilago spp, Venturia spp. including V. inaequalis, Verticillium spp, and Xanthomonas spp.

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

The compounds of the invention may be used for example on turf, ornamentals, such as flowers, shrubs, broad-leaved trees or evergreens, for example conifers, as well as for tree injection, pest management and the like.

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Examples of the abovementioned animal pests are:

from the order Acarina, for example,

- Acarus siro, Aceria sheldoni, Aculus schlechtendali, Amblyomma spp., Argas spp., Boophilus spp., Brevipalpus spp., Bryobia praetiosa, Calipitrimerus spp., Chorioptes spp., Derma-
- 5 nyssus gallinae, Eotetranychus carpini, Eriophyes spp., Hyalomma spp., Ixodes spp., Olygonychus pratensis, Ornithodoros spp., Panonychus spp., Phyllocoptruta oleivora, Polyphagotarsonemus latus, Psoroptes spp., Rhipicephalus spp., Rhizoglyphus spp., Sarcoptes spp., Tarsonemus spp. and Tetranychus spp.;
 - from the order Anoplura, for example,
- 10 Haematopinus spp., Linognathus spp., Pediculus spp., Pemphigus spp. and Phylloxera spp.; from the order *Coleoptera*, for example,
 - Agriotes spp., Anthonomus spp., Atomaria linearis, Chaetocnema tibialis, Cosmopolites spp., Curculio spp., Dermestes spp., Diabrotica spp., Epilachna spp., Eremnus spp., Leptinotarsa decemlineata, Lissorhoptrus spp., Melolontha spp., Orycaephilus spp., Otiorhynchus spp.,
- 15 Phlyctinus spp., Popillia spp., Psylliodes spp., Rhizopertha spp., Scarabeidae, Sitophilus spp., Sitotroga spp., Tenebrio spp., Tribolium spp. and Trogoderma spp.; from the order *Diptera*, for example,
 - Aedes spp., Antherigona soccata, Bibio hortulanus, Calliphora erythrocephala, Ceratitis spp., Chrysomyia spp., Culex spp., Cuterebra spp., Dacus spp., Drosophila melanogaster, Fannia
- 20 spp., Gastrophilus spp., 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 pomonella, Sciara spp., Stomoxys spp., Tabanus spp., Tannia spp. and Tipula spp.;
 - from the order *Heteroptera*, for example,
- 25 Cimex spp., Distantiella theobroma, Dysdercus spp., Euchistus spp., Eurygaster spp., Leptocorisa spp., Nezara spp., Piesma spp., Rhodnius spp., Sahlbergella singularis, Scotinophara spp. and Triatoma spp.;
 - from the order *Homoptera*, for example,
- Aleurothrixus floccosus, Aleyrodes brassicae, Aonidiella spp., Aphididae, Aphis spp., Aspi30 diotus spp., Bemisia tabaci, Ceroplaster spp., Chrysomphalus aonidium, Chrysomphalus
 dictyospermi, Coccus hesperidum, Empoasca spp., Eriosoma larigerum, Erythroneura spp.,
 Gascardia spp., Laodelphax spp., Lecanium corni, Lepidosaphes spp., Macrosiphus spp.,
 Myzus spp., Nephotettix spp., Nilaparvata spp., Parlatoria spp., Pemphigus spp., Planococcus spp., Pseudaulacaspis spp., Pseudococcus spp., Psylla spp., Pulvinaria aethiopica,
- 35 Quadraspidiotus spp., Rhopalosiphum spp., Saissetia spp., Scaphoideus spp., Schizaphis spp., Sitobion spp., Trialeurodes vaporariorum, Trioza erytreae and Unaspis citri; from the order *Hymenoptera*, for example,

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Acromyrmex, Atta spp., Cephus spp., Diprion spp., Diprionidae, Gilpinia polytoma, Hoplocampa spp., Lasius spp., Monomorium pharaonis, Neodiprion spp., Solenopsis spp. and Vespa spp.;

from the order *Isoptera*, for example,

5 Reticulitermes spp.;

from the order Lepidoptera, for example,

Acleris spp., Adoxophyes spp., Aegeria spp., Agrotis spp., Alabama argillaceae, Amylois spp., Anticarsia gemmatalis, Archips spp., Argyrotaenia spp., Autographa spp., Busseola fusca, Cadra cautella, Carposina nipponensis, Chilo spp., Choristoneura spp., Clysia ambi-

- guella, Cnaphalocrocis spp., Cnephasia spp., Cochylis spp., Coleophora spp., Crocidolomia binotalis, Cryptophlebia leucotreta, Cydia spp., Diatraea spp., Diparopsis castanea, Earias spp., Ephestia spp., Eucosma spp., Eupoecilia ambiguella, Euproctis spp., Euxoa spp., Grapholita spp., Hedya nubiferana, Heliothis spp., Hellula undalis, Hyphantria cunea, Keiferia lycopersicella, Leucoptera scitella, Lithocollethis spp., Lobesia botrana, Lymantria spp., Ly-
- onetia spp., Malacosoma spp., Mamestra brassicae, Manduca sexta, Operophtera spp., Ostrinia nubilalis, Pammene spp., Pandemis spp., Panolis flammea, Pectinophora gossypiela, Phthorimaea operculella, Pieris rapae, Pieris spp., Plutella xylostella, Prays spp., Scirpophaga spp., Sesamia spp., Sparganothis spp., Spodoptera spp., Synanthedon spp., Thaumetopoea spp., Tortrix spp., Trichoplusia ni and Yponomeuta spp.;
- 20 from the order *Mallophaga*, for example,

Damalinea spp. and Trichodectes spp.;

from the order Orthoptera, for example,

Blatta spp., Blattella spp., Gryllotalpa spp., Leucophaea maderae, Locusta spp., Periplaneta spp. and Schistocerca spp.;

25 from the order *Psocoptera*, for example,

Liposcelis spp.;

from the order Siphonaptera, for example,

Ceratophyllus spp., Ctenocephalides spp. and Xenopsylla cheopis;

from the order *Thysanoptera*, for example,

30 Frankliniella spp., Hercinothrips spp., Scirtothrips aurantii, Taeniothrips spp., Thrips palmi and Thrips tabaci;

from the order Thysanura, for example,

Lepisma saccharina;

nematodes, for example root knot nematodes, stem eelworms and foliar nematodes;

35 especially Heterodera spp., for example Heterodera schachtii, Heterodora avenae and Heterodora trifolii; Globodera spp., for example Globodera rostochiensis; Meloidogyne spp., for example Meloidogyne incoginita and Meloidogyne javanica; Radopholus spp., for example Radopholus similis; Pratylenchus, for example Pratylenchus neglectans and

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Pratylenchus penetrans; Tylenchulus, for example Tylenchulus semipenetrans; Longidorus, Trichodorus, Xiphinema, Ditylenchus, Aphelenchoides and Anguina; crucifer flea beetles (Phyllotreta spp.); root maggots (Delia spp.) and

The compounds of formula I can for example, be used for controlling, i. e. containing or destroying, animal pests of the abovementioned type which occur on useful plants in agriculture, in horticulture and in forests, or on organs of useful plants, such as fruits, flowers,

foliage, stalks, tubers or roots, and in some cases even on organs of useful plants which are

10 formed at a later point in time remain protected against these animal pests.

5 cabbage seedpod weevil (Ceutorhynchus spp.).

Within the scope of present invention, target crops and/or useful plants to be protected typically comprise perennial and annual crops, such as berry plants for example blackberries, blueberries, cranberries, raspberries and strawberries; cereals for example barley, maize (corn), millet, oats, rice, rye, sorghum triticale and wheat; fibre plants for example cotton, flax, 15 hemp, jute and sisal; field crops for example sugar and fodder beet, coffee, hops, mustard, oilseed rape (canola), poppy, sugar cane, sunflower, tea and tobacco; fruit trees for example apple, apricot, avocado, banana, cherry, citrus, nectarine, peach, pear and plum; grasses for example Bermuda grass, bluegrass, bentgrass, centipede grass, fescue, ryegrass, St. Augustine grass and Zoysia grass; herbs such as basil, borage, chives, coriander, lavender, 20 lovage, mint, oregano, parsley, rosemary, sage and thyme; legumes for example beans, lentils, peas and soya beans; nuts for example almond, cashew, ground nut, hazelnut, peanut, pecan, pistachio and walnut; palms for example oil palm; ornamentals for example flowers, shrubs and trees; other trees, for example cacao, coconut, olive and rubber; vegetables for example asparagus, aubergine, broccoli, cabbage, carrot, cucumber, garlic, 25 lettuce, marrow, melon, okra, onion, pepper, potato, pumpkin, rhubarb, spinach and tomato; and vines for example grapes.

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.

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)

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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 those which naturally are or have been rendered resistant to harmful insects. This includes plants

10 transformed by the use of recombinant DNA techniques, for example, to be capable of synthesising one or more selectively acting toxins, such as are known, for example, from toxin-producing bacteria. Examples of toxins which can be expressed include δ-endotoxins, vegetative insecticidal proteins (Vip), insecticidal proteins of bacteria colonising nematodes, and toxins produced by scorpions, arachnids, wasps and fungi. An example of a crop that

15 has been modified to express the *Bacillus thuringiensis* toxin is the Bt maize KnockOut® (Syngenta Seeds). An example of a crop comprising more than one gene that codes for insecticidal resistance and thus expresses more than one toxin is VipCot® (Syngenta Seeds). Crops or seed material thereof can also be resistant to multiple types of pests (so-called stacked transgenic events when created by genetic modification). For example, a plant can have the ability to express an insecticidal protein while at the same time being herbicide tolerant, for example Herculex I® (Dow AgroSciences, Pioneer Hi-Bred International).

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.

The term "locus" as used herein means fields in or on which plants are growing, or where seeds of cultivated plants are sown, or where seed will be placed into the soil. It includes soil, seeds, and seedlings, as well as established vegetation.

The term "plants" refers to all physical parts of a plant, including seeds, seedlings, 35 saplings, roots, tubers, stems, stalks, foliage, and fruits.

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

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example seeds (in the strict sense), roots, fruits, tubers, bulbs, rhizomes and parts of plants. 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 5 propagation material" is understood to denote seeds.

Pesticidal agents referred to herein using their common name are known, for example, from "The Pesticide Manual", 15th Ed., British Crop Protection Council 2009.

The compounds of formula I may be used in unmodified form or, preferably, together 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, 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 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 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, nematicides, 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 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 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

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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 may be admixed with one or more additional active ingredients such as a pesticide,

5 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 acycloamino acid fungicides, aliphatic nitrogen fungicides, amide fungicides, anilide fungicides, antibiotic fungicides, aromatic fungicides, arsenical fungicides, aryl phenyl ketone fungicides, 10 benzamide fungicides, benzanilide fungicides, benzimidazole fungicides, benzothiazole fungicides, botanical fungicides, bridged diphenyl fungicides, carbamate fungicides, carbanilate fungicides, conazole fungicides, copper fungicides, dicarboximide fungicides, dinitrophenol fungicides, dithiocarbamate fungicides, dithiolane fungicides, furamide fungicides, furanilide fungicides, hydrazide fungicides, imidazole fungicides, mercury 15 fungicides, morpholine fungicides, organophosphorous fungicides, organotin fungicides, oxathiin fungicides, oxazole fungicides, phenylsulfamide fungicides, polysulfide fungicides, pyrazole fungicides, pyridine fungicides, pyrimidine fungicides, pyrrole fungicides, quaternary ammonium fungicides, quinoline fungicides, quinone fungicides, quinoxaline fungicides, strobilurin fungicides, sulfonanilide fungicides, thiadiazole fungicides, thiazole fungicides, 20 thiazolidine fungicides, thiocarbamate fungicides, thiophene fungicides, triazine fungicides, triazole fungicides, triazolopyrimidine fungicides, urea fungicides, valinamide fungicides, and zinc fungicides.

Examples of suitable additional active ingredients also include the following: 3difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (9-dichloromethylene-1,2,3,4-25 tetrahydro-1,4-methano-naphthalen-5-yl)-amide, 3-difluoromethyl-1-methyl-1H-pyrazole-4carboxylic acid methoxy-[1-methyl-2-(2,4,6-trichlorophenyl)-ethyl]-amide, 1-methyl-3difluoromethyl-1H-pyrazole-4-carboxylic acid (2-dichloromethylene-3-ethyl-1-methyl-indan-4yl)-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 30 [2-(2,4-dichloro-phenyl)-2-methoxy-1-methyl-ethyl]-amide, (5-Chloro-2,4-dimethyl-pyridin-3yl)-(2,3,4-trimethoxy-6-methyl-phenyl)-methanone, (5-Bromo-4-chloro-2-methoxy-pyridin-3yl)-(2,3,4-trimethoxy-6-methyl-phenyl)-methanone, 2-{2-[(E)-3-(2,6-Dichloro-phenyl)-1methyl-prop-2-en-(E)-ylideneaminooxymethyl]-phenyl}-2-[(Z)-methoxyimino]-N-methylacetamide, 3-[5-(4-Chloro-phenyl)-2,3-dimethyl-isoxazolidin-3-yl]-pyridine, (E)-N-methyl-2-35 [2- (2, 5-dimethylphenoxymethyl) phenyl]-2-methoxy-iminoacetamide, 4-bromo-2-cyano-N, N-dimethyl-6-trifluoromethylbenzimidazole-1-sulphonamide, a- [N-(3-chloro-2, 6-xylyl)-2methoxyacetamido]-y-butyrolactone, 4-chloro-2-cyano-N, - dimethyl-5-p-tolylimidazole-1sulfonamide, N-allyl-4, 5,-dimethyl-2-trimethylsilylthiophene-3-carboxamide, N- (I-cyano-1, 2WO 2015/007451 22 PCT/EP2014/062844

dimethylpropyl)-2- (2, 4-dichlorophenoxy) propionamide, N- (2-methoxy-5-pyridyl)-cyclopropane carboxamide, (.+-.)-cis-1-(4-chlorophenyl)-2-(1H-1,2,4-triazol-1-yl)-cycloheptanol, 2-(1-tert-butyl)-1-(2-chlorophenyl)-3-(1,2,4-triazol-1-yl)-propan-2-ol, 2',6'-dibromo-2-methyl-4-trifluoromethoxy-4'-trifluoromethyl-1,3-thiazole- 5-carboxanilide, 1-

- 5 imidazolyl-1-(4'-chlorophenoxy)-3,3-dimethylbutan-2-one, methyl (E)-2-[2-[6-(2-cyanophenoxy)pyrimidin-4-yloxy]phenyl]3-methoxyacrylate, methyl (E)-2-[2-[6-(2-thioamidophenoxy)pyrimidin-4-yloxy]phenyl]-3-methoxyacrylate, methyl (E)-2-[2-[6-(2-fluorophenoxy)pyrimidin-4-yloxy]phenyl]-3-methoxyacrylate, methyl (E)-2-[2-[6-(2,6-difluorophenoxy)pyrimidin-4-yloxy]phenyl]-3-methoxyacrylate, methyl (E)-2-[2-[3-(pyrimidin-4-yloxy]phenyl]-3-methoxyacrylate, methyl (E)-2-[3-(pyrimidin-4-y
- 2-yloxy)phenoxy]phenyl]-3-methoxyacrylate, methyl (E)-2-[2-[3-(5-methylpyrimidin-2-yloxy)-phenoxy]phenyl]-3-methoxyacrylate, methyl (E)-2-[2-[3-(phenyl-sulphonyloxy)phenoxy]phenyl-3-methoxyacrylate, methyl (E)-2-[2-[3-(4-nitrophenoxy)phenoxy]phenyl]-3-methoxyacrylate, methyl (E)-2-[2-phenoxyphenyl]-3-methoxyacrylate, methyl (E)-2-[2-(3,5-dimethyl-benzoyl)pyrrol-1-yl]-3-methoxyacrylate,
- methyl (E)-2-[2-(3-methoxyphenoxy)phenyl]-3-methoxyacrylate, methyl (E)-2[2-(2-phenylethen-1-yl)-phenyl]-3-methoxyacrylate, methyl (E)-2-[2-(3,5-dichlorophenoxy)pyridin-3-yl]-3-methoxyacrylate, methyl (E)-2-(2-(3-(1,1,2,2-tetrafluoroethoxy)phenoxy)phenyl)-3-methoxyacrylate, methyl (E)-2-(2-[3-(alpha-hydroxybenzyl)phenoxy]phenyl)-3-methoxyacrylate, methyl (E)-2-(2-(4-phenoxypyridin-2-yloxy)phenyl)-3-methoxyacrylate,
- 20 methyl (E)-2-[2-(3-n-propyloxy-phenoxy)phenyl]3-methoxyacrylate, methyl (E)-2-[2-(3-isopropyloxyphenoxy)phenyl]-3-methoxyacrylate, methyl (E)-2-[2-[3-(2-fluorophenoxy)phenoxy]phenyl]-3-methoxyacrylate, methyl (E)-2-[2-(4-tert-butyl-pyridin-2-yloxy)phenyl]-3-methoxyacrylate, methyl (E)-2-[2-(3-cyanophenoxy)phenoxy]phenyl]-3-methoxyacrylate, methyl (E)-2-[2-[3-(3-cyanophenoxy)phenoxy]phenyl]-3-
- 25 methoxyacrylate, methyl (E)-2-[2-[(3-methyl-pyridin-2-yloxymethyl)phenyl]-3-methoxyacrylate, methyl (E)-2-[2-[6-(2-methyl-phenoxy)pyrimidin-4-yloxy]phenyl]-3-methoxyacrylate, methyl (E)-2-[2-(5-bromo-pyridin-2-yloxymethyl)phenyl]-3-methoxyacrylate, methyl (E)-2-[2-(3-iodopyridin-2-yloxy)phenoxy)phenyl]-3-methoxyacrylate, methyl (E)-2-[2-[6-(2-chloropyridin-3-yloxy)pyrimidin-4-yloxy]phenyl]-3-methoxyac rylate, methyl (E),(E)-2-
- 30 [2-(5,6-dimethylpyrazin-2-ylmethyloximinomethyl)phenyl]-3-methox yacrylate, methyl (E)-2-{2-[6-(6-methylpyridin-2-yloxy)pyrimidin-4-yloxy]phenyl}-3-methoxy-a crylate, methyl (E),(E)-2-{2-(3-methoxyphenyl)methyloximinomethyl]-phenyl}-3-methoxyacrylate, methyl (E)-2-{2-(6-(2-azidophenoxy)-pyrimidin-4-yloxy]phenyl}-3-methoxyacrylate, methyl (E),(E)-2-{2-[6-phenylpyrimidin-4-yl)-methyloximinomethyl]phenyl}-3-methox yacrylate, methyl (E),(E)-2-{2-
- 35 [(4-chlorophenyl)-methyloximinomethyl]-phenyl}-3-methoxyacryl ate, methyl (E)-2-{2-[6-(2-n-propylphenoxy)-1,3,5-triazin-4-yloxy]phenyl}-3-methoxyacrylate, methyl (E),(E)-2-{2-[(3-nitrophenyl)methyloximinomethyl]phenyl}-3-methoxyacrylate, 3-chloro-7-(2-aza-2,7,7-trimethyl-oct-3-en-5-ine), 2,6-dichloro-N-(4-trifluoromethylbenzyl)-benzamide, 3-iodo-2-

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propinyl alcohol, 4-chlorophenyl-3-iodopropargyl formal, 3-bromo-2,3-diiodo-2-propenyl ethylcarbamate, 2,3,3-triiodoallyl alcohol, 3-bromo-2,3-diiodo-2-propenyl alcohol, 3-iodo-2-propinyl n-butylcarbamate, 3-iodo-2-propinyl n-hexylcarbamate, 3-iodo-2-propinyl cyclohexylcarbamate, 3-iodo-2-propinyl phenylcarbamate; phenol derivatives, such as tribromophenol, tetrachlorophenol, 3-methyl-4-chlorophenol, 3,5-dimethyl-4-chlorophenol, phenoxyethanol,

- tetrachlorophenol, 3-methyl-4-chlorophenol, 3,5-dimethyl-4-chlorophenol, phenoxyethanol, dichlorophene, o-phenylphenol, m-phenylphenol, p-phenylphenol, 2-benzyl-4-chlorophenol, 5-hydroxy-2(5H)-furanone; 4,5-dichlorodithiazolinone, 4,5-benzodithiazolinone, 4,5-trimethylenedithiazolinone, 4,5-dichloro-(3H)-1,2-dithiol-3-one, 3,5-dimethyl-tetrahydro-1,3,5-thiadiazine-2-thione, N-(2-p-chlorobenzoylethyl)-hexaminium chloride, acibenzolar,
- 10 acypetacs, alanycarb, albendazole, aldimorph, allicin, allyl alcohol, ametoctradin, amisulbrom, amobam, ampropylfos, anilazine, asomate, aureofungin, azaconazole, azafendin, azithiram, azoxystrobin, barium polysulfide, benalaxyl, benalaxyl-M, benodanil, benomyl, benquinox, bentaluron, benthiavalicarb, benthiazole, benzalkonium chloride, benzamacril, benzamorf, benzohydroxamic acid, berberine, bethoxazin, biloxazol, binapacryl,
- biphenyl, bitertanol, bithionol, bixafen, blasticidin-S, boscalid, bromothalonil, bromuconazole, bupirimate, buthiobate, butylamine calcium polysulfide, captafol, captan, carbamorph, carbendazim, carbendazim chlorhydrate, carboxin, carpropamid, carvone, CGA41396, CGA41397, chinomethionate, chitosan, chlobenthiazone, chloraniformethan, chloranil, chlorfenazole, chloroneb, chloropicrin, chlorothalonil, chlorozolinate, chlozolinate, climbazole,
- 20 clotrimazole, clozylacon, copper containing compounds such as copper acetate, copper carbonate, copper hydroxide, copper naphthenate, copper oleate, copper oxychloride, copper oxyquinolate, copper silicate, copper sulphate, copper tallate, copper zinc chromate and Bordeaux mixture, cresol, cufraneb, cuprobam, cuprous oxide, cyazofamid, cyclafuramid, cycloheximide, cyflufenamid, cymoxanil, cypendazole, cyproconazole,
- 25 cyprodinil, dazomet, debacarb, decafentin, dehydroacetic acid, di-2-pyridyl disulphide 1, 1'dioxide, dichlofluanid, diclomezine, dichlone, dicloran, dichlorophen, dichlozoline,
 diclobutrazol, diclocymet, diethofencarb, difenoconazole, difenzoquat, diflumetorim, O, O-diiso-propyl-S-benzyl thiophosphate, dimefluazole, dimetachlone, dimetconazole,
 dimethomorph, dimethirimol, diniconazole, diniconazole-M, dinobuton, dinocap, dinocton,
- dinopenton, dinosulfon, dinoterbon, diphenylamine, dipyrithione, disulfiram, ditalimfos, dithianon, dithioether, dodecyl dimethyl ammonium chloride, dodemorph, dodicin, dodine, doguadine, drazoxolon, edifenphos, enestroburin, epoxiconazole, etaconazole, etem, ethaboxam, ethirimol, ethoxyquin, ethilicin, ethyl (Z)-N-benzyl-N ([methyl (methyl-thioethylideneamino-oxycarbonyl) amino] thio)-ß-alaninate, etridiazole, famoxadone,
- 35 fenamidone, fenaminosulf, fenapanil, fenarimol, fenbuconazole, fenfuram, fenhexamid, fenitropan, fenoxanil, fenpiclonil, fenpropidin, fenpropimorph, fenpyrazamine, fentin acetate, fentin hydroxide, ferbam, ferimzone, fluazinam, fludioxonil, flumetover, flumorph, flupicolide, fluopyram, fluoroimide, fluotrimazole, fluoxastrobin, fluquinconazole, flusilazole, flusulfamide,

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flutanil, flutolanil, flutriafol, fluxapyroxad, folpet, formaldehyde, fosetyl, fuberidazole, furalaxyl, furametpyr, furcarbanil, furconazole, furfural, furmecyclox, furophanate, glyodin, griseofulvin, guazatine, halacrinate, hexa chlorobenzene, hexachlorobutadiene, hexachlorophene, hexaconazole, hexylthiofos, hydrargaphen, hydroxyisoxazole, hymexazole, imazalil, imazalil 5 sulphate, imibenconazole, iminoctadine, iminoctadine triacetate, inezin, iodocarb, ipconazole, iprobenfos, iprodione, iprovalicarb, isopropanyl butyl carbamate, isoprothiolane, isopyrazam, isotianil, isovaledione, izopamfos, kasugamycin, kresoxim-methyl, LY186054, LY211795, LY248908, mancozeb, mandipropamid, maneb, mebenil, mecarbinzid, mefenoxam, mepanipyrim, mepronil, mercuric chloride, mercurous chloride, meptyldinocap, metalaxyl, 10 metalaxyl-M, metam, metazoxolon, metconazole, methasulfocarb, methfuroxam, methyl bromide, methyl iodide, methyl isothiocyanate, metiram, metiram-zinc, metominostrobin, metrafenone, metsulfovax, milneb, moroxydine, myclobutanil, myclozolin, nabam, natamycin, neoasozin, nickel dimethyldithiocarbamate, nitrostyrene, nitrothal-iso- propyl, nuarimol, octhilinone, ofurace, organomercury compounds, orysastrobin, osthol, oxadixyl, oxasulfuron, 15 oxine-copper, oxolinic acid, oxpoconazole, oxycarboxin, parinol, pefurazoate, penconazole, pencycuron, penflufen, pentachlorophenol, penthiopyrad, phenamacril, phenazin oxide, phosdiphen, phosetyl-Al, phosphorus acids, phthalide, picoxystrobin, piperalin, polycarbamate, polyoxin D, polyoxrim, polyram, probenazole, prochloraz, procymidone, propamidine, propamocarb, propiconazole, propineb, propionic acid, proquinazid, 20 prothiocarb, prothioconazole, pyracarbolid, pyraclostrobin, pyrametrostrobin, pyraoxystrobin, pyrazophos, pyribencarb, pyridinitril, pyrifenox, pyrimethanil, pyriofenone, pyroquilon, pyroxychlor, pyroxyfur, pyrrolnitrin, quaternary ammonium compounds, quinacetol, quinazamid, quinconazole, quinomethionate, quinoxyfen, quintozene, rabenzazole,

santonin, sedaxane, silthiofam, simeconazole, sipconazole, sodium

25 pentachlorophenate, solatenol, spiroxamine, streptomycin, sulphur, sultropen, tebuconazole, tebfloquin, tecloftalam, tecnazene, tecoram, tetraconazole, thiabendazole, thiadifluor, thicyofen, thifluzamide, 2- (thiocyanomethylthio) benzothiazole, thiophanate-methyl, thioquinox, thiram, tiadinil, timibenconazole, tioxymid, tolclofos-methyl, tolylfluanid, triadimefon, triadimenol, triamiphos, triarimol, triazbutil, triazoxide, tricyclazole, tridemorph, trifloxystrobin, triflumazole, triforine, triflumizole, triticonazole, uniconazole, urbacide, validamycin, valifenalate, vapam, vinclozolin, zarilamid, zineb, ziram, and zoxamide.

The compounds of the invention may also be used in combination with anthelmintic agents. Such anthelmintic agents include, compounds selected from the macrocyclic lactone class of compounds such as ivermectin, avermectin, abamectin, emamectin, eprinomectin, doramectin, selamectin, moxidectin, nemadectin and milbemycin derivatives as described in EP- 357460, EP-444964 and EP-594291. Additional anthelmintic agents include semisynthetic and biosynthetic avermectin/milbemycin derivatives such as those described in US-5015630, WO-9415944 and WO-9522552. Additional anthelmintic agents include the

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benzimidazoles such as albendazole, cambendazole, fenbendazole, flubendazole, mebendazole, oxfendazole, oxibendazole, parbendazole, and other members of the class. Additional anthelmintic agents include imidazothiazoles and tetrahydropyrimidines such as tetramisole, levamisole, pyrantel pamoate, oxantel or morantel. Additional anthelmintic agents include flukicides, such as triclabendazole and clorsulon and the cestocides, such as praziquantel and epsiprantel.

The compounds of the invention may be used in combination with derivatives and analogues of the paraherquamide/marcfortine class of anthelmintic agents, as well as the antiparasitic oxazolines such as those disclosed in US-5478855, US- 4639771 and DE- 19520936.

The compounds of the invention may be used in combination with derivatives and analogues of the general class of dioxomorpholine antiparasitic agents as described in WO-9615121 and also with anthelmintic active cyclic depsipeptides such as those described in WO-9611945, WO-9319053, WO-9325543, EP-626375, EP-382173, WO-9419334, EP-15 382173, and EP-503538.

The compounds of the invention may be used in combination with other ectoparasiticides; for example, fipronil; pyrethroids; organophosphates; insect growth regulators such as lufenuron; ecdysone agonists such as tebufenozide and the like; neonicotinoids such as imidacloprid and the like.

The compounds of the invention may be used in combination with terpene alkaloids, for example those described in International Patent Application Publication Numbers WO95/19363 or WO04/72086, particularly the compounds disclosed therein.

Other examples of such biologically active compounds that the compounds of the invention may be used in combination with include but are not restricted to the following:

Organophosphates: acephate, azamethiphos, azinphos-ethyl, azinphos- methyl, bromophos, bromophos-ethyl, cadusafos, chlorethoxyphos, chlorpyrifos, chlorfenvinphos, chlormephos, demeton, demeton-S-methyl, demeton-S-methyl sulphone, dialifos, diazinon, dichlorvos, dicrotophos, dimethoate, disulfoton, ethion, ethoprophos, etrimfos, famphur, fenamiphos, fenitrothion, fensulfothion, fenthion, flupyrazofos, fonofos, formothion,
fosthiazate, heptenophos, isazophos, isothioate, isoxathion, malathion, methacriphos, methamidophos, methidathion, methyl- parathion, mevinphos, monocrotophos, naled, omethoate, oxydemeton-methyl, paraoxon, parathion, parathion-methyl, phenthoate, phosalone, phosfolan, phosphocarb, phosmet, phosphamidon, phorate, phoxim, pirimiphos, pirimiphos- methyl, profenofos, propaphos, proetamphos, prothiofos, pyraclofos,
pyridapenthion, quinalphos, sulprophos, temephos, terbufos, tebupirimfos, tetrachlorvinphos, thimeton, triazophos, trichlorfon, vamidothion.

Carbamates: alanycarb, aldicarb, 2-sec-butylphenyl methylcarbamate, benfuracarb, carbaryl, carbofuran, carbosulfan, cloethocarb, ethiofencarb, fenoxycarb, fenthiocarb,

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furathiocarb, HCN-801, isoprocarb, indoxacarb, methiocarb, methomyl, 5-methyl-m-cumenylbutyryl(methyl)carbamate, oxamyl, pirimicarb, propoxur, thiodicarb, thiofanox, triazamate, UC-51717.

Pyrethroids: acrinathin, allethrin, alphametrin, 5-benzyl-3-furylmethyl (E) -

(1 R)-cis-2,2-dimethyl-3-(2-oxothiolan-3-ylidenemethyl)cyclopropanecarboxylate, bifenthrin, beta -cyfluthrin, cyfluthrin, a-cypermethrin, beta -cypermethrin, bioallethrin, cycloprothrin, cyhalothrin, cyphenothrin, deltamethrin, empenthrin, esfenvalerate, ethofenprox, fenfluthrin, fenpropathrin, fenvalerate, flucythrinate, flumethrin, fluvalinate (D isomer),
 imiprothrin, cyhalothrin, lambda-cyhalothrin, permethrin, phenothrin, prallethrin, pyrethrins (natural products), resmethrin, tetramethrin, transfluthrin, theta-cypermethrin, silafluofen, tfluvalinate, tefluthrin, tralomethrin, Zeta-cypermethrin.

Arthropod growth regulators: a) chitin synthesis inhibitors: benzoylureas: chlorfluazuron, diflubenzuron, fluazuron, flucycloxuron, flufenoxuron, hexaflumuron, lufenuron, novaluron, teflubenzuron, triflumuron, buprofezin, diofenolan, hexythiazox, etoxazole, chlorfentazine; b) ecdysone antagonists: halofenozide, methoxyfenozide, tebufenozide; c) juvenoids: pyriproxyfen, methoprene (including S-methoprene), fenoxycarb; d) lipid biosynthesis inhibitors: spirodiclofen.

Other antiparasitics: acequinocyl, amitraz, AKD-1022, ANS-118, azadirachtin,

Bacillus thuringiensis, bensultap, bifenazate, binapacryl, bromopropylate, BTG-504, BTG-505, camphechlor, cartap, chlorobenzilate, chlordimeform, chlorfenapyr, chromafenozide, clothianidine, cyromazine, diacloden, diafenthiuron, DBI-3204, dinactin, dihydroxymethyldihydroxypyrrolidine, dinobuton, dinocap, endosulfan, ethiprole, ethofenprox, fenazaquin, flumite, MTI- 800, fenpyroximate, fluacrypyrim, flubenzimine, flubrocythrinate,

flufenzine, flufenprox, fluproxyfen, halofenprox, hydramethylnon, IKI-220, kanemite, NC-196, neem guard, nidinorterfuran, nitenpyram, SD-35651, WL-108477, pirydaryl, propargite, protrifenbute, pymethrozine, pyridaben, pyrimidifen, NC-1111, R-195,RH-0345, RH-2485, RYI-210, S-1283, S-1833, SI-8601, silafluofen, silomadine, spinosad, tebufenpyrad, tetradifon, tetranactin, thiacloprid, thiocyclam, thiamethoxam, tolfenpyrad, triazamate, triethoxyspinosyn, trinactin, verbutin, vertalec, YI-5301.

Biological agents: Bacillus thuringiensis ssp aizawai, kurstaki, Bacillus thuringiensis delta endotoxin, baculovirus, entomopathogenic bacteria, virus and fungi.

Bactericides: chlortetracycline, oxytetracycline, streptomycin.

Other biological agents: enrofloxacin, febantel, penethamate, moloxicam, cefalexin, 35 kanamycin, pimobendan, clenbuterol, omeprazole, tiamulin, benazepril, pyriprole, cefquinome, florfenicol, buserelin, cefovecin, tulathromycin, ceftiour, carprofen, metaflumizone, praziquarantel, triclabendazole.

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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 compound of formula I or at least one preferred individual compound as above-defined, or of a fungicidal or insecticidal mixture comprising at least one compound of formula I or at least 5 one preferred individual compound as above-defined, in admixture with other fungicides or insecticides as described above, for controlling or preventing 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 non-living materials by insects or 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 insects or by phytopathogenic or spoilage microorganisms or organisms potentially harmful to man, especially fungal organisms, which comprises the application of a compound of formula I or 15 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.

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Controlling or preventing means reducing infestation by insects or by phytopathogenic or spoilage microorganisms or organisms potentially harmful to man, especially fungal 20 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, or insects which comprises the 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 25 rate of application will depend on the risk of infestation by the corresponding pathogen or insect. 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 30 of formula I may also be applied to seeds (coating) by impregnating the seeds or tubers either 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 35 with extenders, for example solvents, solid carriers and, optionally, surface active compounds (surfactants).

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.

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When used as seed drenching agent, convenient dosages are from 10mg to 1g of active substance per kg of seeds.

When the combinations of the present invention are used for treating seed, rates of 0.001 to 50 g of a compound of formula I per kg of seed, preferably from 0.01 to 10g per kg of seed are generally sufficient.

The compositions of the invention may be employed in any conventional form, for example in the form of a twin pack, a powder for dry seed treatment (DS), an emulsion for seed treatment (ES), a flowable concentrate for seed treatment (FS), a solution for seed treatment (LS), a water dispersible powder for seed treatment (WS), a capsule suspension for seed treatment (CF), a gel for seed treatment (GF), 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) or any technically feasible formulation in combination with agriculturally acceptable adjuvants.

Such compositions may be produced in conventional manner, e.g. by mixing the active ingredients with appropriate formulation inerts (diluents, solvents, fillers and optionally other formulating ingredients such as surfactants, biocides, anti-freeze, stickers, thickeners and compounds that provide adjuvancy effects). Also conventional slow release formulations may be employed where long lasting efficacy is intended. Particularly formulations to be applied in spraying forms, such as water dispersible concentrates (e.g. EC, SC, DC, OD, SE, EW, EO and the like), wettable powders and granules, may contain surfactants such as wetting and dispersing agents and other compounds that provide adjuvancy effects, e.g. the ondensation product of formaldehyde with naphthalene sulphonate, an alkylarylsulphonate, a lignin sulphonate, a fatty alkyl sulphate, and ethoxylated alkylphenol and an ethoxylated fatty alcohol.

A seed dressing formulation is applied in a manner known per se to the seeds
30 employing the combination of the invention and a diluent in suitable seed dressing
formulation form, e.g. as an aqueous suspension or in a dry powder form having good
adherence to the seeds. Such seed dressing formulations are known in the art. Seed
dressing formulations may contain the single active ingredients or the combination of active
ingredients in encapsulated form, e.g. as slow release capsules or microcapsules.

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In general, the formulations include from 0.01 to 90% by weight of active agent, from 0 to 20% agriculturally acceptable surfactant and 10 to 99.99% solid or liquid formulation inerts and adjuvant(s), the active agent consisting of at least the compound of formula I together

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with component (B) and (C), and optionally other active agents, particularly microbiocides or conservatives or the like. Concentrated forms of compositions generally contain in between about 2 and 80%, preferably between about 5 and 70% by weight of active agent. Application forms of formulation may for example contain from 0.01 to 20% by weight, preferably from 0.01 to 5% by weight of active agent. Whereas commercial products will preferably be formulated as concentrates, the end user will normally employ diluted formulations.

The Examples which follow serve to illustrate the invention

- 10 <u>Example 1</u>: This example illustrates the preparation of *tert*-butyl 2-[6-formyl-1-(2-isopropoxy-2-phenyl-ethyl)-5-methoxy-2,4-dioxo-thieno[2,3-d]pyrimidin-3-yl]-2-methyl-propanoate (Compound I.ad.501)
- a) Preparation of methyl 4-chloro-2-(9*H*-fluoren-9-ylmethoxycarbonylamino)-5-formyl-15 thiophene-3-carboxylate
- Methyl 2-(9*H*-fluoren-9-ylmethoxycarbonylamino)-4-oxo-thiophene-3-carboxylate (1.0 g, 2.53 mmol) in *N*, *N*-dimethylformamide (2.00 mL, 25.3 mmol) allowed to stir in ice bath. To this solution phosphorus (v) trichloride oxide (0.26 mL, 2.78 mmol) was added dropwise at <10°C over a period of 10 min. Reaction mixture was stirred at ambient temperature for 16hr. The reaction mixture was poured in 50 mL iced water and 20% Sodium hydroxide solution was added drop wise till pH=6. The product precipitated out as orange solid, which was filtered and washed with 10 mL water. Dried on vacuum to give methyl 4-chloro-2-(9*H*-fluoren-9-ylmethoxycarbonylamino)-5-formyl-thiophene-3-carboxylate. ¹H-NMR (400 MHz, CDCl₃): δ = 3.99 (s, 3H), 4.30 (m, 1H), 4.58 (d, 2H), 7.32 (t, 2H), 7.36 (t, 2H), 7.60 (d, 2H), 7.78 (d, 2H), 10.0 (s, 1H), 11.0 (s, 1H). MS: m/z = 442 (M+1)
 - b) Preparation of methyl 2-[(2-tert-butoxy-1,1-dimethyl-2-oxo-ethyl)carbamoylamino]-4-chloro-5-formyl-thiophene-3-carboxylate

30

Methyl 4-chloro-2-(9*H*-fluoren-9-ylmethoxycarbonylamino)-5-formyl-thiophene-3-carboxylate (0.2 g, 0.45 mmol) dissolved in *N*,*N*-dimethylformamide (2 mL). To this 1,8-diazabicyclo[5.4.0]undec-7-ene (0.1 mL, 0.67 mmol) added dropwise at 0°C and stirred for 1h. After completion of reaction, the mixture was cooled at 10°C, then *tert*-butyl 2-isocyanato-2-methyl-propanoate (0.15 g, 0.81 mmol) and sodium hydride (0.065 g, 1.36 mmol) was added portionwise at 10°C. Then, the reaction mixture was stirred at room temperature for another 1hr. It was then heated at 60°C and stirred at this temperature for 4 hours. Reaction mixture was cooled at room temperature and quenched with saturated

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ammonium chloride solution. Aqueous layer was extracted with ethyl acetate (2 × 25 mL) and washed with water (2 × 20mL), the organics were combined and concentrated to give a brown solid. Crude product was purified by flash column chromatography (10-50-% ethyl acetate/cyclohexane). 1 H-NMR (400 MHz, DMSO- d_{6}): δ = 1.3 (s, 9H), 1.40 (s, 6H), 3.90 (s, 5 3H), 8.64 (s, 1H), 9.92 (s, 1H), 10.6 (s, 1H). MS: m/z = 405 (M+1)

- c) Preparation of *tert*-butyl 2-(6-formyl-5-methoxy-2,4-dioxo-1*H*-thieno[2,3-*d*]pyrimidin-3-yl)-2-methyl-propanoate
- Methyl 2-[(2-tert-butoxy-1,1-dimethyl-2-oxo-ethyl)carbamoylamino]-4-chloro-5-formyl-thiophene-3-carboxylate (0.56 g, 1.38 mmol) was dissolved in dry tetrahydrofuran (10 mL) and to the yellow-green solution sodium hydride (0.26 g, 5.53 mmol) was added. As the effervescence subsided, the mixture was heated at 70 °C for 1 hr under nitrogen atmosphere. After 1 hr solution was diluted with ethyl acetates (10 mL), washed with saturated ammonium chloride solution (5 mL), dried over sodium sulphate, concentrated and purified by flash chromatography (ethyl acetate:Cyclohexane=20-40%) gave tert-butyl 2-(6-formyl-5-methoxy-2,4-dioxo-1*H*-thieno[2,3-d]pyrimidin-3-yl)-2-methyl-propanoate as yellow gummy mass. ¹H-NMR (400 MHz, CDCl₃): δ = 1.44 (s, 9H), 1.76 (s, 6H), 4.19 (s, 3H), 10.0 (s, 1H), 11.1 (brs, 1H). MS: m/z = 369 (M+1).

d) Preparation of *tert*-butyl 2-[6-formyl-1-(2-isopropoxy-2-phenyl-ethyl)-5-methoxy-2,4-dioxothieno[2,3-d]pyrimidin-3-yl]-2-methyl-propanoate (Compound I.ad.501)

20

tert-butyl 2-(6-formyl-5-methoxy-2,4-dioxo-1*H*-thieno[2,3-d]pyrimidin-3-yl)-2-methyl-propanoate (50.0 mg, 0.13 mmol) was suspended in *N*,*N*-dimethylformamide (0.7 mL) and potassium carbonate (0.056 g, 0.40 mmol) and (2-iodo-1-isopropoxy-ethyl)benzene (0.078 g, 0.27 mmol) were added. The reaction mixture was heated to 150°C for 4hrs. The reaction was cooled to room temperature and poured on 70 mL water. Aqueous was extracted with ethyl acetate (3 x 25 mL) and the organic layer was washed with brine, dried over sodium sulphate, filtered and concentrated under reduced pressure. Crude product was purified by flash chromatography (10-30 % ethyl acetate/cyclohexane) to give yellow gummy mass of *tert*-butyl 2-[6-formyl-1-(2-isopropoxy-2-phenyl-ethyl)-5-methoxy-2,4-dioxo-thieno[2,3-d]pyrimidin-3-yl]-2-methyl-propanoate (Compound I.ad.501). ¹H-NMR (400 MHz, CDCl₃): δ = 1.07 (d, 3H), 1.14 (d, 3H), 1.33 (s, 9H), 1.73 (s, 3H), 1.74 (s, 3H), 3.48 (s, 3H), 3.58 (m, 1H), 4.33 (m, 1H), 4.50 (m, 1H), 4.82 (m, 1H), 7.35 (m, 5H), 9.95 (s, 1H). MS: m/z = 531 (M+1)

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

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

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

Comp.	R ¹	R ²	X ¹	L ¹ -R ³
No.				4-MOR = 4-morpholinyl
001	F	-CO ₂ Me	S	-CH ₂ C(=O)NHCH ₃
002	F	-CO ₂ Et	S	-CH ₂ C(=O)NHCH ₃
003	F	2-oxazolyl	S	-CH ₂ C(=O)NHCH ₃
004	CI	-CO ₂ Me	S	-CH ₂ C(=O)NHCH ₃
005	CI	-CO ₂ Et	S	-CH ₂ C(=O)NHCH ₃
006	CI	2-oxazolyl	S	-CH ₂ C(=O)NHCH ₃
007	Br	-CO ₂ Me	S	-CH ₂ C(=O)NHCH ₃
008	Br	-CO ₂ Et	S	-CH ₂ C(=O)NHCH ₃
009	Br	2-oxazolyl	S	-CH ₂ C(=O)NHCH ₃
010	-CN	-CO ₂ Me	S	-CH ₂ C(=O)NHCH ₃
011	-CN	-CO ₂ Et	S	-CH ₂ C(=O)NHCH ₃
012	-CN	2-oxazolyl	S	-CH ₂ C(=O)NHCH ₃
013	-OCH ₃	-CO ₂ Me	S	-CH ₂ C(=O)NHCH ₃
014	-OCH ₃	-CO ₂ Et	S	-CH ₂ C(=O)NHCH ₃
015	-OCH ₃	2-oxazolyl	S	-CH ₂ C(=O)NHCH ₃
016	-OCH ₂ CH ₃	-CO ₂ Me	S	-CH ₂ C(=O)NHCH ₃
017	-OCH ₂ CH ₃	-CO ₂ Et	S	-CH ₂ C(=O)NHCH ₃
018	-OCH ₂ CH ₃	2-oxazolyl	S	-CH ₂ C(=O)NHCH ₃
019	-SCH₃	-CO ₂ Me	S	-CH ₂ C(=O)NHCH ₃
020	-SCH₃	-CO ₂ Et	S	-CH ₂ C(=O)NHCH ₃
021	-SCH₃	2-oxazolyl	S	-CH ₂ C(=O)NHCH ₃
022	-OCF ₃	-CO ₂ Me	S	-CH ₂ C(=O)NHCH ₃
023	-OCF ₃	-CO ₂ Et	S	-CH ₂ C(=O)NHCH ₃
024	-OCF ₃	2-oxazolyl	S	-CH ₂ C(=O)NHCH ₃
025	-OCHF ₂	-CO ₂ Me	S	-CH ₂ C(=O)NHCH ₃
026	-OCHF ₂	-CO ₂ Et	S	-CH ₂ C(=O)NHCH ₃
027	-OCHF ₂	2-oxazolyl	S	-CH ₂ C(=O)NHCH ₃
028	-SCF ₃	-CO ₂ Me	S	-CH ₂ C(=O)NHCH ₃
029	-SCF ₃	-CO ₂ Et	S	-CH ₂ C(=O)NHCH ₃

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030	-SCF ₃	2-oxazolyl	S	-CH ₂ C(=O)NHCH ₃
031	-OCH ₂ C≡CH	-CO ₂ Me	S	-CH ₂ C(=O)NHCH ₃
032	-OCH ₂ C≡CH	-CO ₂ Et	S	-CH ₂ C(=O)NHCH ₃
033	-OCH ₂ C≡CH	2-oxazolyl	S	-CH ₂ C(=O)NHCH ₃
034	CI	-CO ₂ Me	0	-CH ₂ C(=O)NHCH ₃
035	CI	-CO ₂ Et	0	-CH ₂ C(=O)NHCH ₃
036	CI	2-oxazolyl	0	-CH ₂ C(=O)NHCH ₃
037	-CN	-CO ₂ Me	0	-CH ₂ C(=O)NHCH ₃
038	-CN	-CO ₂ Et	0	-CH ₂ C(=O)NHCH ₃
039	-CN	2-oxazolyl	0	-CH ₂ C(=O)NHCH ₃
040	-OCH ₃	-CO ₂ Me	0	-CH ₂ C(=O)NHCH ₃
041	-OCH₃	-CO ₂ Et	0	-CH ₂ C(=O)NHCH ₃
042	-OCH₃	2-oxazolyl	0	-CH ₂ C(=O)NHCH ₃
043	CI	-CO ₂ Me	NH	-CH ₂ C(=O)NHCH ₃
044	CI	-CO ₂ Et	NH	-CH ₂ C(=O)NHCH ₃
045	CI	2-oxazolyl	NH	-CH ₂ C(=O)NHCH ₃
046	-CN	-CO ₂ Me	NH	-CH ₂ C(=O)NHCH ₃
047	-CN	-CO ₂ Et	NH	-CH ₂ C(=O)NHCH ₃
048	-CN	2-oxazolyl	NH	-CH ₂ C(=O)NHCH ₃
049	-OCH ₃	-CO ₂ Et	NH	-CH ₂ C(=O)NHCH ₃
050	-OCH ₃	2-oxazolyl	NH	-CH ₂ C(=O)NHCH ₃
051	F	-CO ₂ Me	S	-CH ₂ C(=O)NHCH ₂ CH ₃
052	F	-CO ₂ Et	S	-CH ₂ C(=O)NHCH ₂ CH ₃
053	F	2-oxazolyl	S	-CH ₂ C(=O)NHCH ₂ CH ₃
054	CI	-CO ₂ Me	S	-CH ₂ C(=O)NHCH ₂ CH ₃
055	CI	-CO ₂ Et	S	-CH ₂ C(=O)NHCH ₂ CH ₃
056	CI	2-oxazolyl	S	-CH ₂ C(=O)NHCH ₂ CH ₃
057	Br	-CO ₂ Me	S	-CH ₂ C(=O)NHCH ₂ CH ₃
058	Br	-CO ₂ Et	S	-CH ₂ C(=O)NHCH ₂ CH ₃
059	Br	2-oxazolyl	S	-CH ₂ C(=O)NHCH ₂ CH ₃
060	-CN	-CO ₂ Me	S	-CH ₂ C(=O)NHCH ₂ CH ₃
061	-CN	-CO ₂ Et	S	-CH ₂ C(=O)NHCH ₂ CH ₃
062	-CN	2-oxazolyl	S	-CH ₂ C(=O)NHCH ₂ CH ₃
063	-OCH ₃	-CO ₂ Me	S	-CH ₂ C(=O)NHCH ₂ CH ₃
064	-OCH ₃	-CO ₂ Et	S	-CH ₂ C(=O)NHCH ₂ CH ₃
065	-OCH ₃	2-oxazolyl	S	-CH ₂ C(=O)NHCH ₂ CH ₃
066	-OCH ₂ CH ₃	-CO ₂ Me	S	-CH ₂ C(=O)NHCH ₂ CH ₃

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067	-OCH ₂ CH ₃	-CO ₂ Et	S	-CH ₂ C(=O)NHCH ₂ CH ₃
068	-OCH ₂ CH ₃	2-oxazolyl	S	-CH ₂ C(=O)NHCH ₂ CH ₃
069	-SCH ₃	-CO ₂ Me	S	-CH ₂ C(=O)NHCH ₂ CH ₃
070	-SCH ₃	-CO ₂ Et	S	-CH ₂ C(=O)NHCH ₂ CH ₃
071	-SCH ₃	2-oxazolyl	S	-CH ₂ C(=O)NHCH ₂ CH ₃
072	-OCF ₃	-CO ₂ Me	S	-CH ₂ C(=O)NHCH ₂ CH ₃
073	-OCF ₃	-CO ₂ Et	S	-CH ₂ C(=O)NHCH ₂ CH ₃
074	-OCF ₃	2-oxazolyl	S	-CH ₂ C(=O)NHCH ₂ CH ₃
075	-OCHF ₂	-CO ₂ Me	S	-CH ₂ C(=O)NHCH ₂ CH ₃
076	-OCHF ₂	-CO ₂ Et	S	-CH ₂ C(=O)NHCH ₂ CH ₃
077	-OCHF ₂	2-oxazolyl	S	-CH ₂ C(=O)NHCH ₂ CH ₃
078	-SCF ₃	-CO ₂ Me	S	-CH ₂ C(=O)NHCH ₂ CH ₃
079	-SCF ₃	-CO ₂ Et	S	-CH ₂ C(=O)NHCH ₂ CH ₃
080	-SCF ₃	2-oxazolyl	S	-CH ₂ C(=O)NHCH ₂ CH ₃
081	-OCH ₂ C≡CH	-CO ₂ Me	S	-CH ₂ C(=O)NHCH ₂ CH ₃
082	-OCH ₂ C≡CH	-CO ₂ Et	S	-CH ₂ C(=O)NHCH ₂ CH ₃
083	-OCH ₂ C≡CH	2-oxazolyl	S	-CH ₂ C(=O)NHCH ₂ CH ₃
084	CI	-CO ₂ Me	0	-CH ₂ C(=O)NHCH ₂ CH ₃
085	CI	-CO ₂ Et	0	-CH ₂ C(=O)NHCH ₂ CH ₃
086	CI	2-oxazolyl	0	-CH ₂ C(=O)NHCH ₂ CH ₃
087	-CN	-CO ₂ Me	0	-CH ₂ C(=O)NHCH ₂ CH ₃
088	-CN	-CO ₂ Et	0	-CH ₂ C(=O)NHCH ₂ CH ₃
089	-CN	2-oxazolyl	0	-CH ₂ C(=O)NHCH ₂ CH ₃
090	-OCH ₃	-CO ₂ Me	0	-CH ₂ C(=O)NHCH ₂ CH ₃
091	-OCH ₃	-CO ₂ Et	0	-CH ₂ C(=O)NHCH ₂ CH ₃
092	-OCH ₃	2-oxazolyl	0	-CH ₂ C(=O)NHCH ₂ CH ₃
093	CI	-CO ₂ Me	NH	-CH ₂ C(=O)NHCH ₂ CH ₃
094	CI	-CO ₂ Et	NH	-CH ₂ C(=O)NHCH ₂ CH ₃
095	CI	2-oxazolyl	NH	-CH ₂ C(=O)NHCH ₂ CH ₃
096	-CN	-CO ₂ Me	NH	-CH ₂ C(=O)NHCH ₂ CH ₃
097	-CN	-CO ₂ Et	NH	-CH ₂ C(=O)NHCH ₂ CH ₃
098	-CN	2-oxazolyl	NH	-CH ₂ C(=O)NHCH ₂ CH ₃
099	-OCH ₃	-CO ₂ Et	NH	-CH ₂ C(=O)NHCH ₂ CH ₃
100	-OCH ₃	2-oxazolyl	NH	-CH ₂ C(=O)NHCH ₂ CH ₃
101	F	-CO ₂ Me	S	-CH(CH ₃)C(=O)NH ₂
102	F	-CO ₂ Et	S	-CH(CH ₃)C(=O)NH ₂
103	F	2-oxazolyl	S	-CH(CH ₃)C(=O)NH ₂

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104	CI	-CO ₂ Me	S	-CH(CH ₃)C(=O)NH ₂
105	Cl	-CO ₂ Et	S	-CH(CH ₃)C(=O)NH ₂
106	CI	2-oxazolyl	S	-CH(CH ₃)C(=O)NH ₂
107	Br	-CO ₂ Me	S	-CH(CH ₃)C(=O)NH ₂
108	Br	-CO ₂ Et	S	-CH(CH ₃)C(=O)NH ₂
109	Br	2-oxazolyl	S	-CH(CH ₃)C(=O)NH ₂
110	-CN	-CO ₂ Me	S	-CH(CH ₃)C(=O)NH ₂
111	-CN	-CO ₂ Et	S	-CH(CH ₃)C(=O)NH ₂
112	-CN	2-oxazolyl	S	-CH(CH ₃)C(=O)NH ₂
113	-OCH ₃	-CO ₂ Me	S	-CH(CH ₃)C(=O)NH ₂
114	-OCH ₃	-CO ₂ Et	S	-CH(CH ₃)C(=O)NH ₂
115	-OCH ₃	2-oxazolyl	S	-CH(CH ₃)C(=O)NH ₂
116	-OCH ₂ CH ₃	-CO ₂ Me	S	-CH(CH ₃)C(=O)NH ₂
117	-OCH ₂ CH ₃	-CO ₂ Et	S	-CH(CH ₃)C(=O)NH ₂
118	-OCH ₂ CH ₃	2-oxazolyl	S	-CH(CH ₃)C(=O)NH ₂
119	-SCH₃	-CO ₂ Me	S	-CH(CH ₃)C(=O)NH ₂
120	-SCH₃	-CO ₂ Et	S	-CH(CH ₃)C(=O)NH ₂
121	-SCH₃	2-oxazolyl	S	-CH(CH ₃)C(=O)NH ₂
122	-OCF ₃	-CO ₂ Me	S	-CH(CH ₃)C(=O)NH ₂
123	-OCF ₃	-CO ₂ Et	S	-CH(CH ₃)C(=O)NH ₂
124	-OCF ₃	2-oxazolyl	S	-CH(CH ₃)C(=O)NH ₂
125	-OCHF ₂	-CO ₂ Me	S	-CH(CH ₃)C(=O)NH ₂
126	-OCHF ₂	-CO ₂ Et	S	-CH(CH ₃)C(=O)NH ₂
127	-OCHF ₂	2-oxazolyl	S	-CH(CH ₃)C(=O)NH ₂
128	-SCF ₃	-CO ₂ Me	S	-CH(CH ₃)C(=O)NH ₂
129	-SCF ₃	-CO ₂ Et	S	-CH(CH ₃)C(=O)NH ₂
130	-SCF ₃	2-oxazolyl	S	-CH(CH ₃)C(=O)NH ₂
131	-OCH ₂ C≡CH	-CO ₂ Me	S	-CH(CH ₃)C(=O)NH ₂
132	-OCH ₂ C≡CH	-CO ₂ Et	S	-CH(CH ₃)C(=O)NH ₂
133	-OCH ₂ C≡CH	2-oxazolyl	S	-CH(CH ₃)C(=O)NH ₂
134	CI	-CO ₂ Me	0	-CH(CH ₃)C(=O)NH ₂
135	CI	-CO ₂ Et	0	-CH(CH ₃)C(=O)NH ₂
136	CI	2-oxazolyl	0	-CH(CH ₃)C(=O)NH ₂
137	-CN	-CO ₂ Me	0	-CH(CH ₃)C(=O)NH ₂
138	-CN	-CO ₂ Et	0	-CH(CH ₃)C(=O)NH ₂
139	-CN	2-oxazolyl	0	-CH(CH ₃)C(=O)NH ₂
140	-OCH ₃	-CO₂Me	0	-CH(CH ₃)C(=O)NH ₂

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141	-OCH ₃	-CO ₂ Et	0	-CH(CH ₃)C(=O)NH ₂
142	-OCH ₃	2-oxazolyl	0	-CH(CH ₃)C(=O)NH ₂
143	CI	-CO ₂ Me	NH	-CH(CH ₃)C(=O)NH ₂
144	CI	-CO ₂ Et	NH	-CH(CH ₃)C(=O)NH ₂
145	CI	2-oxazolyl	NH	-CH(CH ₃)C(=O)NH ₂
146	-CN	-CO ₂ Me	NH	-CH(CH ₃)C(=O)NH ₂
147	-CN	-CO ₂ Et	NH	-CH(CH ₃)C(=O)NH ₂
148	-CN	2-oxazolyl	NH	-CH(CH ₃)C(=O)NH ₂
149	-OCH ₃	-CO ₂ Et	NH	-CH(CH ₃)C(=O)NH ₂
150	-OCH ₃	2-oxazolyl	NH	-CH(CH ₃)C(=O)NH ₂
151	F	-CO ₂ Me	S	-CH(CH ₃)C(=O)NHCH ₃
152	F	-CO ₂ Et	S	-CH(CH ₃)C(=O)NHCH ₃
153	F	2-oxazolyl	S	-CH(CH ₃)C(=O)NHCH ₃
154	CI	-CO ₂ Me	S	-CH(CH ₃)C(=O)NHCH ₃
155	CI	-CO ₂ Et	S	-CH(CH ₃)C(=O)NHCH ₃
156	CI	2-oxazolyl	S	-CH(CH ₃)C(=O)NHCH ₃
157	Br	-CO ₂ Me	S	-CH(CH ₃)C(=O)NHCH ₃
158	Br	-CO ₂ Et	S	-CH(CH ₃)C(=O)NHCH ₃
159	Br	2-oxazolyl	S	-CH(CH ₃)C(=O)NHCH ₃
160	-CN	-CO ₂ Me	S	-CH(CH ₃)C(=O)NHCH ₃
161	-CN	-CO ₂ Et	S	-CH(CH ₃)C(=O)NHCH ₃
162	-CN	2-oxazolyl	S	-CH(CH ₃)C(=O)NHCH ₃
163	-OCH ₃	-CO ₂ Me	S	-CH(CH ₃)C(=O)NHCH ₃
164	-OCH ₃	-CO ₂ Et	S	-CH(CH ₃)C(=O)NHCH ₃
165	-OCH ₃	2-oxazolyl	S	-CH(CH ₃)C(=O)NHCH ₃
166	-OCH ₂ CH ₃	-CO ₂ Me	S	-CH(CH ₃)C(=O)NHCH ₃
167	-OCH ₂ CH ₃	-CO ₂ Et	S	-CH(CH ₃)C(=O)NHCH ₃
168	-OCH ₂ CH ₃	2-oxazolyl	S	-CH(CH ₃)C(=O)NHCH ₃
169	-SCH₃	-CO ₂ Me	S	-CH(CH ₃)C(=O)NHCH ₃
170	-SCH₃	-CO ₂ Et	S	-CH(CH ₃)C(=O)NHCH ₃
171	-SCH₃	2-oxazolyl	S	-CH(CH ₃)C(=O)NHCH ₃
172	-OCF ₃	-CO ₂ Me	S	-CH(CH ₃)C(=O)NHCH ₃
173	-OCF ₃	-CO ₂ Et	S	-CH(CH ₃)C(=O)NHCH ₃
174	-OCF ₃	2-oxazolyl	S	-CH(CH ₃)C(=O)NHCH ₃
175	-OCHF ₂	-CO ₂ Me	S	-CH(CH ₃)C(=O)NHCH ₃
176	-OCHF ₂	-CO ₂ Et	S	-CH(CH ₃)C(=O)NHCH ₃
177	-OCHF ₂	2-oxazolyl	S	-CH(CH ₃)C(=O)NHCH ₃

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178	-SCF ₃	-CO ₂ Me	S	-CH(CH ₃)C(=O)NHCH ₃
179	-SCF ₃	-CO ₂ Et	S	-CH(CH ₃)C(=O)NHCH ₃
180	-SCF ₃	2-oxazolyl	S	-CH(CH ₃)C(=O)NHCH ₃
181	-OCH ₂ C≡CH	-CO ₂ Me	S	-CH(CH ₃)C(=O)NHCH ₃
182	-OCH ₂ C≡CH	-CO ₂ Et	S	-CH(CH ₃)C(=O)NHCH ₃
183	-OCH ₂ C≡CH	2-oxazolyl	S	-CH(CH ₃)C(=O)NHCH ₃
184	CI	-CO ₂ Me	0	-CH(CH ₃)C(=O)NHCH ₃
185	CI	-CO ₂ Et	0	-CH(CH ₃)C(=O)NHCH ₃
186	CI	2-oxazolyl	0	-CH(CH ₃)C(=O)NHCH ₃
187	-CN	-CO ₂ Me	0	-CH(CH ₃)C(=O)NHCH ₃
188	-CN	-CO ₂ Et	0	-CH(CH ₃)C(=O)NHCH ₃
189	-CN	2-oxazolyl	0	-CH(CH ₃)C(=O)NHCH ₃
190	-OCH ₃	-CO ₂ Me	0	-CH(CH ₃)C(=O)NHCH ₃
191	-OCH ₃	-CO ₂ Et	0	-CH(CH ₃)C(=O)NHCH ₃
192	-OCH ₃	2-oxazolyl	0	-CH(CH ₃)C(=O)NHCH ₃
193	CI	-CO ₂ Me	NH	-CH(CH ₃)C(=O)NHCH ₃
194	CI	-CO ₂ Et	NH	-CH(CH ₃)C(=O)NHCH ₃
195	CI	2-oxazolyl	NH	-CH(CH ₃)C(=O)NHCH ₃
196	-CN	-CO ₂ Me	NH	-CH(CH ₃)C(=O)NHCH ₃
197	-CN	-CO ₂ Et	NH	-CH(CH ₃)C(=O)NHCH ₃
198	-CN	2-oxazolyl	NH	-CH(CH ₃)C(=O)NHCH ₃
199	-OCH ₃	-CO ₂ Et	NH	-CH(CH ₃)C(=O)NHCH ₃
200	-OCH ₃	2-oxazolyl	NH	-CH(CH ₃)C(=O)NHCH ₃
201	F	-CO ₂ Me	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
202	F	-CO ₂ Et	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
203	F	2-oxazolyl	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
204	CI	-CO ₂ Me	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
205	CI	-CO ₂ Et	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
206	CI	2-oxazolyl	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
207	Br	-CO ₂ Me	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
208	Br	-CO ₂ Et	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
209	Br	2-oxazolyl	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
210	-CN	-CO ₂ Me	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
211	-CN	-CO ₂ Et	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
212	-CN	2-oxazolyl	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
213	-OCH ₃	-CO ₂ Me	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
214	-OCH ₃	-CO ₂ Et	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃

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215	-OCH ₃	2-oxazolyl	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
216	-OCH ₂ CH ₃	-CO ₂ Me	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
217	-OCH ₂ CH ₃	-CO ₂ Et	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
218	-OCH ₂ CH ₃	2-oxazolyl	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
219	-SCH₃	-CO ₂ Me	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
220	-SCH₃	-CO ₂ Et	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
221	-SCH₃	2-oxazolyl	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
222	-OCF ₃	-CO ₂ Me	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
223	-OCF ₃	-CO ₂ Et	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
224	-OCF ₃	2-oxazolyl	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
225	-OCHF ₂	-CO ₂ Me	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
226	-OCHF ₂	-CO ₂ Et	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
227	-OCHF ₂	2-oxazolyl	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
228	-SCF ₃	-CO ₂ Me	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
229	-SCF ₃	-CO ₂ Et	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
230	-SCF ₃	2-oxazolyl	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
231	-OCH ₂ C≡CH	-CO ₂ Me	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
232	-OCH ₂ C≡CH	-CO ₂ Et	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
233	-OCH ₂ C≡CH	2-oxazolyl	S	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
234	CI	-CO ₂ Me	0	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
235	CI	-CO ₂ Et	0	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
236	CI	2-oxazolyl	0	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
237	-CN	-CO ₂ Me	0	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
238	-CN	-CO ₂ Et	0	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
239	-CN	2-oxazolyl	0	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
240	-OCH ₃	-CO ₂ Me	0	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
241	-OCH ₃	-CO ₂ Et	0	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
242	-OCH ₃	2-oxazolyl	0	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
243	CI	-CO ₂ Me	NH	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
244	CI	-CO ₂ Et	NH	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
245	Cl	2-oxazolyl	NH	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
246	-CN	-CO ₂ Me	NH	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
247	-CN	-CO ₂ Et	NH	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
248	-CN	2-oxazolyl	NH	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
249	-OCH ₃	-CO ₂ Et	NH	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
250	-OCH ₃	2-oxazolyl	NH	-CH(CH ₃)C(=O)NHCH ₂ CH ₃
251	F	-CO ₂ Me	S	-C(CH ₃) ₂ CO ₂ H

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252	F	-CO ₂ Et	S	-C(CH ₃) ₂ CO ₂ H
253	F	2-oxazolyl	S	-C(CH ₃) ₂ CO ₂ H
254	CI	-CO ₂ Me	S	-C(CH ₃) ₂ CO ₂ H
255	CI	-CO ₂ Et	S	-C(CH ₃) ₂ CO ₂ H
256	CI	2-oxazolyl	S	-C(CH ₃) ₂ CO ₂ H
257	Br	-CO ₂ Me	S	-C(CH ₃) ₂ CO ₂ H
258	Br	-CO ₂ Et	S	-C(CH ₃) ₂ CO ₂ H
259	Br	2-oxazolyl	S	-C(CH ₃) ₂ CO ₂ H
260	-CN	-CO ₂ Me	S	-C(CH ₃) ₂ CO ₂ H
261	-CN	-CO ₂ Et	S	-C(CH ₃) ₂ CO ₂ H
262	-CN	2-oxazolyl	S	-C(CH ₃) ₂ CO ₂ H
263	-OCH ₃	-CO ₂ Me	S	-C(CH ₃) ₂ CO ₂ H
264	-OCH ₃	-CO ₂ Et	S	-C(CH ₃) ₂ CO ₂ H
265	-OCH ₃	2-oxazolyl	S	-C(CH ₃) ₂ CO ₂ H
266	-OCH ₂ CH ₃	-CO ₂ Me	S	-C(CH ₃) ₂ CO ₂ H
267	-OCH ₂ CH ₃	-CO ₂ Et	S	-C(CH ₃) ₂ CO ₂ H
268	-OCH ₂ CH ₃	2-oxazolyl	S	-C(CH ₃) ₂ CO ₂ H
269	-SCH₃	-CO ₂ Me	S	-C(CH ₃) ₂ CO ₂ H
270	-SCH₃	-CO ₂ Et	S	-C(CH ₃) ₂ CO ₂ H
271	-SCH₃	2-oxazolyl	S	-C(CH ₃) ₂ CO ₂ H
272	-OCF ₃	-CO ₂ Me	S	-C(CH ₃) ₂ CO ₂ H
273	-OCF ₃	-CO ₂ Et	S	-C(CH ₃) ₂ CO ₂ H
274	-OCF ₃	2-oxazolyl	S	-C(CH ₃) ₂ CO ₂ H
275	-OCHF ₂	-CO ₂ Me	S	-C(CH ₃) ₂ CO ₂ H
276	-OCHF ₂	-CO ₂ Et	S	-C(CH ₃) ₂ CO ₂ H
277	-OCHF ₂	2-oxazolyl	S	-C(CH ₃) ₂ CO ₂ H
278	-SCF ₃	-CO ₂ Me	S	-C(CH ₃) ₂ CO ₂ H
279	-SCF ₃	-CO ₂ Et	S	-C(CH ₃) ₂ CO ₂ H
280	-SCF ₃	2-oxazolyl	S	-C(CH ₃) ₂ CO ₂ H
281	-OCH ₂ C≡CH	-CO ₂ Me	S	-C(CH ₃) ₂ CO ₂ H
282	-OCH ₂ C≡CH	-CO ₂ Et	S	-C(CH ₃) ₂ CO ₂ H
283	-OCH ₂ C≡CH	2-oxazolyl	S	-C(CH ₃) ₂ CO ₂ H
284	CI	-CO ₂ Me	0	-C(CH ₃) ₂ CO ₂ H
285	CI	-CO ₂ Et	0	-C(CH ₃) ₂ CO ₂ H
286	CI	2-oxazolyl	0	-C(CH ₃) ₂ CO ₂ H
287	-CN	-CO ₂ Me	0	-C(CH ₃) ₂ CO ₂ H
288	-CN	-CO ₂ Et	0	-C(CH ₃) ₂ CO ₂ H

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289	-CN	2-oxazolyl	0	-C(CH ₃) ₂ CO ₂ H
290	-OCH ₃	-CO ₂ Me	0	-C(CH ₃) ₂ CO ₂ H
291	-OCH ₃	-CO ₂ Et	0	-C(CH ₃) ₂ CO ₂ H
292	-OCH ₃	2-oxazolyl	0	-C(CH ₃) ₂ CO ₂ H
293	CI	-CO₂Me	NH	-C(CH ₃) ₂ CO ₂ H
294	CI	-CO ₂ Et	NH	-C(CH ₃) ₂ CO ₂ H
295	CI	2-oxazolyl	NH	-C(CH ₃) ₂ CO ₂ H
296	-CN	-CO ₂ Me	NH	-C(CH ₃) ₂ CO ₂ H
297	-CN	-CO ₂ Et	NH	-C(CH ₃) ₂ CO ₂ H
298	-CN	2-oxazolyl	NH	-C(CH ₃) ₂ CO ₂ H
299	-OCH ₃	-CO ₂ Et	NH	-C(CH ₃) ₂ CO ₂ H
300	-OCH ₃	2-oxazolyl	NH	-C(CH ₃) ₂ CO ₂ H
301	F	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NH ₂
302	F	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NH ₂
303	F	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NH ₂
304	CI	-CO₂Me	S	-C(CH ₃) ₂ C(=O)NH ₂
305	CI	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NH ₂
306	CI	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NH ₂
307	Br	-CO₂Me	S	-C(CH ₃) ₂ C(=O)NH ₂
308	Br	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NH ₂
309	Br	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NH ₂
310	-CN	-CO₂Me	S	-C(CH ₃) ₂ C(=O)NH ₂
311	-CN	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NH ₂
312	-CN	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NH ₂
313	-OCH ₃	-CO₂Me	S	-C(CH ₃) ₂ C(=O)NH ₂
314	-OCH ₃	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NH ₂
315	-OCH ₃	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NH ₂
316	-OCH ₂ CH ₃	-CO₂Me	S	-C(CH ₃) ₂ C(=O)NH ₂
317	-OCH ₂ CH ₃	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NH ₂
318	-OCH ₂ CH ₃	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NH ₂
319	-SCH ₃	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NH ₂
320	-SCH ₃	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NH ₂
321	-SCH ₃	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NH ₂
322	-OCF ₃	-CO₂Me	S	-C(CH ₃) ₂ C(=O)NH ₂
323	-OCF ₃	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NH ₂
324	-OCF ₃	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NH ₂
325	-OCHF ₂	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NH ₂

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326	-OCHF ₂	-CO ₂ Et	S	$-C(CH_3)_2C(=O)NH_2$
327	-OCHF ₂	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NH ₂
328	-SCF ₃	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NH ₂
329	-SCF ₃	-CO ₂ Et	S	$-C(CH_3)_2C(=O)NH_2$
330	-SCF ₃	2-oxazolyl	S	$-C(CH_3)_2C(=O)NH_2$
331	-OCH ₂ C≡CH	-CO ₂ Me	S	$-C(CH_3)_2C(=O)NH_2$
332	-OCH ₂ C≡CH	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NH ₂
333	-OCH₂C≡CH	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NH ₂
334	CI	-CO ₂ Me	0	-C(CH ₃) ₂ C(=O)NH ₂
335	CI	-CO ₂ Et	0	$-C(CH_3)_2C(=O)NH_2$
336	CI	2-oxazolyl	0	-C(CH3)2C(=O)NH2
337	-CN	-CO ₂ Me	0	-C(CH ₃) ₂ C(=O)NH ₂
338	-CN	-CO ₂ Et	0	-C(CH ₃) ₂ C(=O)NH ₂
339	-CN	2-oxazolyl	0	$-C(CH_3)_2C(=O)NH_2$
340	-OCH₃	-CO ₂ Me	0	-C(CH3)2C(=O)NH2
341	-OCH₃	-CO ₂ Et	0	-C(CH ₃) ₂ C(=O)NH ₂
342	-OCH₃	2-oxazolyl	0	-C(CH ₃) ₂ C(=O)NH ₂
343	CI	-CO ₂ Me	NH	$-C(CH_3)_2C(=O)NH_2$
344	CI	-CO ₂ Et	NH	-C(CH ₃) ₂ C(=O)NH ₂
345	CI	2-oxazolyl	NH	-C(CH3)2C(=O)NH2
346	-CN	-CO ₂ Me	NH	-C(CH3)2C(=O)NH2
347	-CN	-CO ₂ Et	NH	-C(CH ₃) ₂ C(=O)NH ₂
348	-CN	2-oxazolyl	NH	-C(CH ₃) ₂ C(=O)NH ₂
349	-OCH₃	-CO ₂ Et	NH	-C(CH ₃) ₂ C(=O)NH ₂
350	-OCH₃	2-oxazolyl	NH	-C(CH ₃) ₂ C(=O)NH ₂
351	F	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NHCH ₃
352	F	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NHCH ₃
353	F	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NHCH ₃
354	CI	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NHCH ₃
355	CI	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NHCH ₃
356	CI	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NHCH ₃
357	Br	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NHCH ₃
358	Br	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NHCH ₃
359	Br	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NHCH ₃
360	-CN	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NHCH ₃
361		00 5	C	C/CH / C/=O/NHCH
	-CN	-CO ₂ Et	S	$-C(CH_3)_2C(=O)NHCH_3$

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363	-OCH ₃	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NHCH ₃
364	-OCH ₃	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NHCH ₃
365	-OCH ₃	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NHCH ₃
366	-OCH ₂ CH ₃	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NHCH ₃
367	-OCH ₂ CH ₃	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NHCH ₃
368	-OCH ₂ CH ₃	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NHCH ₃
369	-SCH ₃	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NHCH ₃
370	-SCH₃	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NHCH ₃
371	-SCH₃	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NHCH ₃
372	-OCF ₃	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NHCH ₃
373	-OCF ₃	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NHCH ₃
374	-OCF ₃	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NHCH ₃
375	-OCHF ₂	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NHCH ₃
376	-OCHF ₂	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NHCH ₃
377	-OCHF ₂	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NHCH ₃
378	-SCF ₃	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NHCH ₃
379	-SCF ₃	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NHCH ₃
380	-SCF ₃	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NHCH ₃
381	-OCH ₂ C≡CH	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NHCH ₃
382	-OCH ₂ C≡CH	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NHCH ₃
383	-OCH ₂ C≡CH	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NHCH ₃
384	CI	-CO ₂ Me	0	-C(CH ₃) ₂ C(=O)NHCH ₃
385	CI	-CO ₂ Et	0	-C(CH ₃) ₂ C(=O)NHCH ₃
386	CI	2-oxazolyl	0	-C(CH ₃) ₂ C(=O)NHCH ₃
387	-CN	-CO ₂ Me	0	-C(CH ₃) ₂ C(=O)NHCH ₃
388	-CN	-CO ₂ Et	0	-C(CH ₃) ₂ C(=O)NHCH ₃
389	-CN	2-oxazolyl	0	-C(CH ₃) ₂ C(=O)NHCH ₃
390	-OCH ₃	-CO ₂ Me	0	-C(CH ₃) ₂ C(=O)NHCH ₃
391	-OCH ₃	-CO ₂ Et	0	-C(CH ₃) ₂ C(=O)NHCH ₃
392	-OCH ₃	2-oxazolyl	0	-C(CH ₃) ₂ C(=O)NHCH ₃
393	CI	-CO ₂ Me	NH	-C(CH ₃) ₂ C(=O)NHCH ₃
394	CI	-CO ₂ Et	NH	-C(CH ₃) ₂ C(=O)NHCH ₃
395	CI	2-oxazolyl	NH	-C(CH ₃) ₂ C(=O)NHCH ₃
396	-CN	-CO₂Me	NH	-C(CH ₃) ₂ C(=O)NHCH ₃
397	-CN	-CO ₂ Et	NH	-C(CH ₃) ₂ C(=O)NHCH ₃
398	-CN	2-oxazolyl	NH	-C(CH ₃) ₂ C(=O)NHCH ₃
399	-OCH ₃	-CO ₂ Et	NH	-C(CH ₃) ₂ C(=O)NHCH ₃

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400	-OCH ₃	2-oxazolyl	NH	-C(CH ₃) ₂ C(=O)NHCH ₃
401	F	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
402	F	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
403	F	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
404	CI	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
405	CI	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
406	CI	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
407	Br	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
408	Br	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
409	Br	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
410	-CN	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
411	-CN	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
412	-CN	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
413	-OCH ₃	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
414	-OCH ₃	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
415	-OCH ₃	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
416	-OCH ₂ CH ₃	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
417	-OCH ₂ CH ₃	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
418	-OCH ₂ CH ₃	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
419	-SCH₃	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
420	-SCH₃	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
421	-SCH₃	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
422	-OCF ₃	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
423	-OCF ₃	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
424	-OCF ₃	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
425	-OCHF ₂	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
426	-OCHF ₂	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
427	-OCHF ₂	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
428	-SCF ₃	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
429	-SCF ₃	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
430	-SCF ₃	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
431	-OCH ₂ C≡CH	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
432	-OCH ₂ C≡CH	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
433	-OCH ₂ C≡CH	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
434	CI	-CO ₂ Me	0	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
435	CI	-CO ₂ Et	0	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
436	CI	2-oxazolyl	0	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃

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437	-CN	-CO ₂ Me	0	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
438	-CN	-CO ₂ Et	0	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
439	-CN	2-oxazolyl	0	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
440	-OCH ₃	-CO ₂ Me	0	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
441	-OCH ₃	-CO ₂ Et	0	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
442	-OCH ₃	2-oxazolyl	0	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
443	Cl	-CO ₂ Me	NH	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
444	CI	-CO ₂ Et	NH	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
445	CI	2-oxazolyl	NH	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
446	-CN	-CO ₂ Me	NH	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
447	-CN	-CO ₂ Et	NH	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
448	-CN	2-oxazolyl	NH	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
449	-OCH ₃	-CO ₂ Et	NH	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
450	-OCH ₃	2-oxazolyl	NH	-C(CH ₃) ₂ C(=O)NHCH ₂ CH ₃
451	F	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)-4-MOR
452	F	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)-4-MOR
453	F	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)-4-MOR
454	CI	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)-4-MOR
455	CI	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)-4-MOR
456	CI	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)-4-MOR
457	Br	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)-4-MOR
458	Br	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)-4-MOR
459	Br	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)-4-MOR
460	-CN	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)-4-MOR
461	-CN	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)-4-MOR
462	-CN	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)-4-MOR
463	-OCH ₃	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)-4-MOR
464	-OCH ₃	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)-4-MOR
465	-OCH ₃	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)-4-MOR
466	-OCH ₂ CH ₃	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)-4-MOR
467	-OCH ₂ CH ₃	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)-4-MOR
468	-OCH ₂ CH ₃	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)-4-MOR
469	-SCH₃	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)-4-MOR
470	-SCH₃	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)-4-MOR
471	-SCH₃	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)-4-MOR
472	-OCF ₃	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)-4-MOR
473	-OCF ₃	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)-4-MOR

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474	-OCF ₃	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)-4-MOR
475	-OCHF ₂	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)-4-MOR
476	-OCHF ₂	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)-4-MOR
477	-OCHF ₂	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)-4-MOR
478	-SCF ₃	-CO₂Me	S	-C(CH ₃) ₂ C(=O)-4-MOR
479	-SCF ₃	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)-4-MOR
480	-SCF ₃	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)-4-MOR
481	-OCH ₂ C≡CH	-CO ₂ Me	S	-C(CH ₃) ₂ C(=O)-4-MOR
482	-OCH ₂ C≡CH	-CO ₂ Et	S	-C(CH ₃) ₂ C(=O)-4-MOR
483	-OCH ₂ C≡CH	2-oxazolyl	S	-C(CH ₃) ₂ C(=O)-4-MOR
484	CI	-CO ₂ Me	0	-C(CH ₃) ₂ C(=O)-4-MOR
485	CI	-CO ₂ Et	0	-C(CH ₃) ₂ C(=O)-4-MOR
486	CI	2-oxazolyl	0	-C(CH ₃) ₂ C(=O)-4-MOR
487	-CN	-CO ₂ Me	0	-C(CH ₃) ₂ C(=O)-4-MOR
488	-CN	-CO ₂ Et	0	-C(CH ₃) ₂ C(=O)-4-MOR
489	-CN	2-oxazolyl	0	-C(CH ₃) ₂ C(=O)-4-MOR
490	-OCH ₃	-CO ₂ Me	0	-C(CH ₃) ₂ C(=O)-4-MOR
491	-OCH ₃	-CO ₂ Et	0	-C(CH ₃) ₂ C(=O)-4-MOR
492	-OCH ₃	2-oxazolyl	0	-C(CH ₃) ₂ C(=O)-4-MOR
493	CI	-CO ₂ Me	NH	-C(CH ₃) ₂ C(=O)-4-MOR
494	CI	-CO ₂ Et	NH	-C(CH ₃) ₂ C(=O)-4-MOR
495	CI	2-oxazolyl	NH	-C(CH ₃) ₂ C(=O)-4-MOR
496	-CN	-CO ₂ Me	NH	-C(CH ₃) ₂ C(=O)-4-MOR
497	-CN	-CO ₂ Et	NH	-C(CH ₃) ₂ C(=O)-4-MOR
498	-CN	2-oxazolyl	NH	-C(CH ₃) ₂ C(=O)-4-MOR
499	-OCH ₃	-CO ₂ Et	NH	-C(CH ₃) ₂ C(=O)-4-MOR
500	-OCH ₃	2-oxazolyl	NH	-C(CH ₃) ₂ C(=O)-4-MOR
501	-OCH ₃	-CHO	S	-C(CH ₃) ₂ CO ₂ C(CH ₃) ₃
L	1	1		1

where

a) 501 compounds of formula (l.a):

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{N} O$$
 (I.a)

5 wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

b) 501 compounds of formula (l.b):

$$R^{2} \xrightarrow{N} O \qquad (I.b)$$

$$H_{3}C \xrightarrow{O}$$

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

5

c) 501 compounds of formula (l.c):

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{N} O$$

$$H_{3}C \xrightarrow{N} O$$

$$(I.c)$$

wherein R¹, R², R³, X¹ and L¹ are as defined in Table 1.

10 d) 501 compounds of formula (l.d):

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{N} O$$

$$H_{3}C$$

$$(I.d)$$

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

e) 501 compounds of formula (l.e):

$$R^{2} \xrightarrow{N} O \qquad (I.e)$$

15

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

f) 501 compounds of formula (I.f):

5

15

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{N} O$$

$$(I.f)$$

wherein R¹, R², R³, X¹ and L¹ are as defined in Table 1.

g) 501 compounds of formula (I.g):

wherein R¹, R², R³, X¹ and L¹ are as defined in Table 1.

h) 501 compounds of formula (l.h):

$$R^{2} \xrightarrow{N} O \qquad (I.h)$$

10 wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

i) 501 compounds of formula (l.i):

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{N} O$$

$$H_{3}C \xrightarrow{O}$$

$$(I.i)$$

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

j) 501 compounds of formula (l.j):

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{N} O$$

$$H_{3}C \xrightarrow{O} O$$

$$(I.j)$$

wherein R¹, R², R³, X¹ and L¹ are as defined in Table 1.

k) 501 compounds of formula (l.k):

$$R^{2} \xrightarrow{N} O \qquad (I.k)$$

$$H_{3}C \longrightarrow O$$

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

m) 501 compounds of formula (I.m):

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{N} O$$

$$H_{3}C \longrightarrow (I.m)$$

10 wherein R¹, R², R³, X¹ and L¹ are as defined in Table 1.

n) 501 compounds of formula (l.n):

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{O} O \qquad (I.n)$$

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

5

o) 501 compounds of formula (I.o):

$$R^{2} \xrightarrow{N \longrightarrow 0} R^{3}$$

$$CI$$

$$CI$$

$$CI$$

$$CI$$

$$CI$$

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

5 p) 501 compounds of formula (l.p):

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{O} CH_{3}$$
 (I.p)

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

q) 501 compounds of formula (I.q):

$$R^{1}$$
 O
 CH_{3}
 C
 O
 CH_{3}

10

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

r) 501 compounds of formula (l.r):

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{N} O CH_{3}$$

$$H_{3}C \xrightarrow{O} CH_{3}$$

$$(I.r)$$

15 wherein R¹, R², R³, X¹ and L¹ are as defined in Table 1.

s) 501 compounds of formula (l.s):

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

5 t) 501 compounds of formula (l.t):

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{O} CH_{3}$$

$$H_{3}C \xrightarrow{O} CH_{3}$$

$$(I.t)$$

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

u) 501 compounds of formula (l.u):

$$R^{1}$$
 O
 CH_{3}
 R^{1}
 O
 CH_{3}

10

wherein R¹, R², R³, X¹ and L¹ are as defined in Table 1.

v) 501 compounds of formula (l.v):

$$R^{2} \xrightarrow{N} CI \xrightarrow{N} CI \xrightarrow{N} CI$$

$$R^{3} \xrightarrow{N} CI \xrightarrow{N} CI$$

$$CI \xrightarrow{N} CI$$

$$CI \xrightarrow{N} CI$$

$$CI \xrightarrow{N} CI$$

$$CI \xrightarrow{N} CI$$

15 wherein R¹, R², R³, X¹ and L¹ are as defined in Table 1.

w) 501 compounds of formula (I.w):

$$R^{2} \xrightarrow{N \longrightarrow O} CH_{3}$$

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

5

x) 501 compounds of formula (l.x):

$$R^{2} \xrightarrow{X^{1}} \underset{N}{\overset{O}{\bigvee}} \underset{O}{\overset{L^{1}}{\bigvee}} R^{3}$$

$$R^{2} \xrightarrow{X^{1}} \underset{N}{\overset{N}{\bigvee}} \underset{O}{\overset{C}{\bigvee}} H_{3}$$

$$H_{3}C \xrightarrow{O} \xrightarrow{C} H_{3}$$

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

10 y) 501 compounds of formula (l.y):

$$R^{1} \xrightarrow{O} L^{1} \xrightarrow{R^{3}} (I.y)$$

$$R^{2} \xrightarrow{X^{1}} \xrightarrow{N} O CH_{3}$$

$$H_{3}C \xrightarrow{O} CH_{3}$$

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

z) 501 compounds of formula (l.z):

$$R^{2} \xrightarrow{N} C \xrightarrow{N} C CH_{3}$$

$$H_{3}C \xrightarrow{N} C CH_{3}$$

$$(I.z)$$

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wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

aa) 501 compounds of formula (l.aa):

$$R^{2}$$
 X^{1}
 X^{1

5 wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

ab) 501 compounds of formula (l.ab):

$$R^{2}$$
 X^{1}
 X^{1

10 wherein R¹, R², R³, X¹ and L¹ are as defined in Table 1.

ac) 501 compounds of formula (l.ac):

$$R^{2} \xrightarrow{N} O \xrightarrow{L^{1}} R^{3}$$

$$R^{2} \xrightarrow{N} O \xrightarrow{CH_{3}} CI$$

$$CI \xrightarrow{N} O \xrightarrow{CH_{3}}$$

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

ad) 501 compounds of formula (l.ad):

15

$$R^{2} \xrightarrow{N} O \xrightarrow{L^{1}} R^{3}$$

$$Q \xrightarrow{CH_{3}} CH_{3}$$

$$Q \xrightarrow{CH_{3}}$$

$$Q \xrightarrow{CH_{3}}$$

wherein R¹, R², R³, X¹ and L¹ are as defined in Table 1.

ae) 501 compounds of formula (l.ae):

$$R^{1}$$
 O
 CH_{3}
 CH_{3}
 CH_{3}

5 wherein R¹, R², R³, X¹ and L¹ are as defined in Table 1.

af) 501 compounds of formula (l.af):

$$R^{1}$$
 R^{2}
 X^{1}
 N
 O
 CH_{3}
 CH_{3}
 CH_{3}

10 wherein R¹, R², R³, X¹ and L¹ are as defined in Table 1.

ag) 501 compounds of formula (l.ag):

$$R^{2} \xrightarrow{X^{1}} \underset{N}{\overset{O}{\overset{}}} \underset{O}{\overset{}} \underset{CH_{3}}{\overset{}}$$

$$(I.ag)$$

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

ah) 501 compounds of formula (I.ah):

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{O} CH_{3}$$

$$H_{3}C \xrightarrow{CH_{3}} CH_{3}$$

$$(I.ah)$$

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

5 ai) 501 compounds of formula (I.ai):

$$R^{1}$$
 R^{2}
 R^{2}
 R^{3}
 CH_{3}
 CH_{3}
 R^{3}
 CH_{3}

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

aj) 501 compounds of formula (I.aj):

$$R^{2} \xrightarrow{N} O \xrightarrow{I_{1}} R^{3}$$

$$X^{1} \xrightarrow{N} O \xrightarrow{CH_{3}} CH_{3}$$

$$CI \xrightarrow{CH_{3}} CH_{3}$$

$$(I.aj)$$

10

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

ak) 501 compounds of formula (lak):

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{O} O \qquad (I.ak)$$

15 wherein R¹, R², R³, X¹ and L¹ are as defined in Table 1.

am) 501 compounds of formula (l.am):

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{N} O \qquad (I.am)$$

$$H_{3}C \xrightarrow{O} O$$

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

5

15

an) 501 compounds of formula (l.an):

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

10 ao) 501 compounds of formula (l.ao):

$$R^{2}$$
 X^{1}
 X^{1

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

ap) 501 compounds of formula (l.ap):

$$R^{2}$$
 X^{1}
 X^{1}
 X^{0}
 X^{0

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wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

aq) 501 compounds of formula (l.aq):

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{O} O \qquad (I.aq)$$

5 wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

ar) 501 compounds of formula (l.ar):

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{N} O \qquad (I.ar)$$

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

as) 501 compounds of formula (l.as):

10

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{N} O$$

$$CH_{3}$$

$$(I.as)$$

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

15 at) 501 compounds of formula (l.at):

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{N} O \qquad (I.at)$$

$$H_{3}C \xrightarrow{O}$$

wherein R¹, R², R³, X¹ and L¹ are as defined in Table 1.

au) 501 compounds of formula (l.au):

$$R^{1}$$
 Q
 CH_{3}
 CH_{3}
 CH_{3}
 CH_{3}

wherein R¹, R², R³, X¹ and L¹ are as defined in Table 1.

av) 501 compounds of formula (l.av):

$$R^{1}$$
 N
 CH_{3}
 $H_{3}C$
 CH_{3}
 CH_{3}
 CH_{3}

10 wherein R¹, R², R³, X¹ and L¹ are as defined in Table 1.

aw) 501 compounds of formula (l.aw):

$$R^{2}$$
 N
 CH_{3}
 $H_{3}C$
 $(I.aw)$

Wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

ax) 501 compounds of formula (I.ax):

$$R^{2} \xrightarrow{N} CH_{3}$$
(I.ax)

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

5 ay) 501 compounds of formula (l.ay):

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{N} O \qquad (I.ay)$$

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

az) 501 compounds of formula (l.az):

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{N} O$$
 (I.az)

10

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

ba) 501 compounds of formula (l.ba):

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{O} CH_{3}$$
 (I.ba)

15 wherein R¹, R², R³, X¹ and L¹ are as defined in Table 1.

bb) 501 compounds of formula (I.bb):

$$R^{2} \xrightarrow{N} O CH_{3}$$
 (I.bb)

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

5

bc) 501 compounds of formula (l.bc):

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{N} O \qquad (I.bc)$$

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

10 bd) 501 compounds of formula (l.bd):

$$R^{1}$$
 O
 CH_{3}
 CH_{3}

wherein R^1 , R^2 , R^3 , X^1 and L^1 are as defined in Table 1.

be) 501 compounds of formula (l.be):

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{O} O \qquad \qquad \text{(I.be)}$$

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wherein R¹, R², R³, X¹ and L¹ are as defined in Table 1.

bf) 501 compounds of formula (l.bf):

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{N} O \qquad (I.bf)$$

5 wherein R¹, R², R³, X¹ and L¹ are as defined in Table 1.

The Examples which follow serve to illustrate the invention, "active ingredient" denoting a mixture of compound I and compounds of component (B+C) in a specific mixing ratio.

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: (ACQUITY UPLC from Waters, Phenomenex Gemini C18, 3 μm particle size, 110 Angström, 30 x 3 mm column, 1.7mL/min., 60 °C, H₂O + 0.05% HCOOH (95%) / CH₃CN/MeOH 4:1 + 0.04% HCOOH (5%) – 2 min. – CH₃CN/MeOH 4:1 + 0.04% HCOOH (5%) – 0.8 min., ACQUITY SQD Mass Spectrometer from Waters, ionization method: electrospray (ESI), Polarity: positive ions, Capillary (kV) 3.00, Cone (V) 20.00, Extractor (V) 3.00, Source Temperature (°C) 150, Desolvation Temperature (°C) 400, Cone Gas Flow (L/Hr) 60, Desolvation Gas Flow (L/Hr) 700)).

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

Compound No.	Melting point (°C)	LC/MS
I.ad.501		Rt = 2.50 min; MS: m/z = 531 (M+1)

Formulation Examples

20

Wettable powders	a)	b)	c)
active ingredient [compound of formula (I)]	25 %	50 %	75 %
sodium lignosulfonate	5 %	5 %	-
sodium lauryl sulfate	3 %	-	5 %
sodium diisobutylnaphthalenesulfonate	-	6 %	10 %
phenol polyethylene glycol ether	-	2 %	-

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(7-8 mol of ethylene oxide)					
highly dispersed silicic acid		5 %	10 %	10 %	
Kaolin		62 %	27 %	_	

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

Powders for dry seed treatment	a)	b)	c)
active ingredient [compound of formula (I)]	25 %	50 %	75 %
light mineral oil	5 %	5 %	5 %
highly dispersed silicic acid	5 %	5 %	-
Kaolin	65 %	40 %	-
Talcum	_		20

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

Emulsifiable concentrate

active ingredient [compound of formula (I)]	10 %
octylphenol polyethylene glycol ether	3 %
(4-5 mol of ethylene oxide)	
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.

4	\sim
	.,

<u>Dusts</u>	a)	b)	c)
Active ingredient [compound of formula (I)]	5 %	6 %	4 %
talcum	95 %	-	-
Kaolin	-	94 %	-
mineral filler	_	_	96 %

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

Extruder granules

Active ingredient [compound of formula (I)]	15 %
sodium lignosulfonate	2 %

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carboxymethylcellulose	1 %	
Kaolin	82 %	

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

Coated granules

Active ingredient [compound of formula (I)]	8 %
polyethylene glycol (mol. wt. 200)	3 %
Kaolin	89 %

The finely ground active ingredient 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 ingredient [compound of formula (I)]	40 %
propylene glycol	10 %
nonylphenol polyethylene glycol ether (15 mol of ethylene oxide)	6 %
Sodium lignosulfonate	10 %
carboxymethylcellulose	1 %
silicone oil (in the form of a 75 % emulsion in water)	1 %
Water	32 %

The finely ground active ingredient 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 ingredient [compound of formula (I)]	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 active ingredient 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

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can be treated and protected against infestation by microorganisms, by spraying, pouring or immersion.

Slow Release Capsule Suspension

5 28 parts of a combination of the compound of formula I 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.

Biological examples

Alternaria solani / tomato / leaf disc (early blight)

20 Tomato leaf disks cv. Baby are placed on 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 2 days after application. The inoculated leaf disks are incubated at 23 °C / 21°C (day/night) and 80% rh under a light regime of 12/12 h (light/dark) 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 on untreated check disk leaf disks (5 – 7 days after application).

Blumeria graminis f. sp. tritici (Erysiphe graminis f. sp. tritici) / wheat / leaf disc preventative (Powdery mildew on wheat)

30 Wheat leaf segments cv. Kanzler are placed on agar in a multiwell plate (24-well format) and sprayed with the formulated test compound diluted in water. The leaf disks are inoculated by shaking powdery mildew infected plants above the test plates 1 day after application. The inoculated leaf disks are incubated at 20°C and 60% rh under a light regime of 24 h darkness followed by 12 h light / 12 h darkness in a climate chamber and the activity of a compound is assessed as percent disease control compared to untreated when an appropriate level of disease damage appears on untreated check leaf segments (6 – 8 days after application).

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Compound I.ad.501 at 200 ppm gives at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development.

5 Magnaporthe grisea (Pyricularia oryzae) / rice / leaf disc preventative (Rice Blast)

Rice leaf segments cv. Ballila are placed on agar in a multiwell plate (24-well format) and sprayed with the formulated test compound diluted in water. The leaf segments are inoculated with a spore suspension of the fungus 2 days after application. The inoculated leaf segments are incubated at 22°C and 80% 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 appears in untreated check leaf segments (5 – 7 days after application).

Monographella nivalis (Microdochium nivale) / liquid culture (foot rot cereals)

15 Conidia of the fungus from cryogenic storage are directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of test compound into a microtiter plate (96-well format), the nutrient broth containing the fungal spores is added. The test plates are incubated at 24°C and the inhibition of growth is determined photometrically 4-5 days after application.

20

Mycosphaerella arachidis (Cercospora arachidicola) / liquid culture (early leaf spot)

Conidia of the fungus from cryogenic storage are directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of test compound into a microtiter plate (96-well format), the nutrient broth containing the fungal spores is added. The test plates are incubated at 24°C and the inhibition of growth is determined photometrically 4-5 days after application.

Mycosphaerella graminicola (Septoria tritici) / liquid culture (Septoria blotch)

Conidia of the fungus from cryogenic storage are directly mixed into nutrient broth (PDB 30 potato dextrose broth). After placing a (DMSO) solution of test compound into a microtiter plate (96-well format), the nutrient broth containing the fungal spores is added. The test plates are incubated at 24°C and the inhibition of growth is determined photometrically 4-5 days after application.

35 <u>Phaeosphaeria nodorum (Septoria nodorum) / wheat / leaf disc preventative (Glume blotch)</u>
Wheat leaf segments cv. Kanzler are placed on agar in a multiwell plate (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 2 days after application. The inoculated test leaf disks

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are incubated at 20° C and 75% 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 (5 – 7 days after application).

5

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 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 appears in untreated check leaf disks (5 – 7 days after application).

15 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).

Compound I.ad.501 at 200 ppm gives at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development.

Puccinia recondita f. sp. tritici / wheat / leaf disc preventative (Brown rust)

Wheat leaf segments cv. Kanzler are placed on agar in multiwell plates (24-well format) and sprayed with the formulated test compound diluted in water. The leaf disks are inoculated 30 with a spore suspension of the fungus 1 day after application. The inoculated leaf segments are incubated at 19°C and 75% 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 segments (7 – 9 days after application).

35

Pyrenophora teres / barley / leaf disc preventative (Net blotch)

Barley leaf segments cv. Hasso are placed on agar in a multiwell plate (24-well format) and sprayed with the formulated test compound diluted in water. The leaf segmens are inoculated

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with a spore suspension of the fungus 2 days after application. The inoculated leaf segments are incubated at 20°C and 65% 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 disease control compared to untreated when an appropriate level of disease damage appears in untreated check leaf 5 segments (5 – 7 days after application).

What is claimed is:

1. A compound of formula I:

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{X^{2}} X^{3} \qquad (I)$$

$$R^{2} \xrightarrow{X^{1}} X^{3} \xrightarrow{X^{2}} X^{3}$$

Wherein:

5

X¹, X² and X³ are independently O, S or NR⁵;

 R^1 is halogen, cyano, C_1 - C_6 alkoxy, C_2 - C_6 alkenyloxy, C_2 - C_6 alkynyloxy, C_3 - C_6 cycloalkyloxy, C_1 - C_6 alkylthio, C_2 - C_6 alkenylthio, C_2 - C_6 alkynylthio or C_3 - C_6 cycloalkylthio, in which the alkoxy,

66

alkenyl, alkynyl, cycloalkyl and alkyl groups are optionally substituted by one or more R⁶; R² is -C(=O)R⁶ or heterocyclyl, which can be optionally substituted by one or more R⁶; R³ is -C(=O)R⁶, -S(=O)R⁶, -S(=O)₂R⁶ or heterocyclyl, which can be optionally substituted by one or more R⁶;

R⁴ is C₂-C₆alkynyl, C₃-C₆cycloalkyl, aryl or heterocyclyl, in which the alkynyl, cycloalkyl, aryl and heterocyclyl groups are optionally substituted by one or more R⁶;

R⁵ is hydrogen, C₁-C₆alkyl, C₁-C₆alkoxy, C₂-C₆alkenyl, C₂-C₆alkenyloxy, C₂-C₆alkynyl, C₂-C₆alkynyloxy, C₃-C₆cycloalkyl, C₃-C₆cycloalkyloxy or aryl, in which the alkyl, alkoxy, alkenyl, alkynyl, cycloalkyl and aryl groups are optionally substituted by one or more R⁶; R⁶ is hydrogen, halogen, cyano, hydroxyl, amino, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy,

- 20 C₁-C₆haloalkoxy, C₁-C₆alkylthio, C₁-C₆haloalkylthio, C₂-C₆alkenyl, C₂-C₆haloalkenyl, C₂-C₆haloalkenylthio, C₂-C₆haloalkenylthio, C₂-C₆haloalkenylthio, C₂-C₆alkynyl, C₂-C₆alkynyloxy, C₂-C₆alkynylthio, C₃-C₆cycloalkyl, C₃-C₆halocycloalkyl, C₃-C₆cycloalkyloxy, C₃-C₆cycloalkylthio, C₃-C₆halocycloalkylthio, -NH(C₁-C₆alkyl), -N(C₁-C₆alkyl)₂, -NH(C₁-C₆haloalkyl), -N(C₁-C₆haloalkyl)₂, -NH(C₂-C₆alkenyl), -N(C₂-C₆alkenyl)₂, -
- $25 \quad NH(C_2-C_6haloalkenyl), -N(C_2-C_6haloalkenyl)_2, -NH(C_2-C_6alkynyl), -N(C_2-C_6alkynyl)_2, -NH(C_3-C_6cycloalkyl), -N(C_3-C_6cycloalkyl)_2, -NH(C_3-C_6halocycloalkyl), -N(C_3-C_6halocycloalkyl)_2, -NHC(=O)(C_1-C_6alkyl), -N(C(=O)(C_1-C_6alkyl))_2, -NHC(=O)(C_1-C_6haloalkyl), N(C(=O)(C_1-C_6alkoxy), -N(C(=O)(C_1-C_6alkoxy))_2, -NHC(=O)(C_1-C_6alkoxy), -N(C(=O)(C_1-C_6alkoxy))_2, -NHC(=O)(C_2-C_6alkenyl), -N(C(=O)(C_2-C_6alkenyl), -N(C_2-C_6alkenyl), -N(C_2-C_6a$
- 30 C_6 alkenyl))₂, -NHC(=O)(C_2 - C_6 haloalkenyl), -N(C(=O)(C_2 - C_6 haloalkenyl))₂, -NHC(=O)(C_2 - C_6 alkenyloxy), -N(C(=O)(C_2 - C_6 alkenyloxy))₂, -NHC(=O)(C_2 - C_6 haloalkenyloxy))₂, -NHC(=O)(C_2 - C_6 alkynyl), -N(C(=O)(C_2 - C_6 alkynyl))₂, -NHC(=O)(C_2 - C_6 alkynyloxy), -N(C(=O)(C_3 - C_6 cycloalkyl), -N(C(=O)(C_3 - C_6 cycloalkyl))₂, -NHC(=O)(C_3 - C_6 cycloalkyl))₃, -NHC(=O)(C_3 - C_6 cycloalkyl)

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 $NHC(=O)(C_3-C_6 cycloalkyloxy), -N(C(=O)(C_3-C_6 cycloalkyloxy))_2, -NHC(=O)(C_3-C_6 halocycloalkyloxy), -N(C(=O)(C_3-C_6 halocycloalkyloxy))_2, -OC(=O)(C_1-C_6 alkyl), -OC(=O)(C_1-C_6 alkoxy), -OC(=O)(C_1-C_6 haloalkoxy), -OC(=O)(C_2-C_6 haloalkenyl), -OC(=O)(C_2-C_6 haloalkenyl), -OC(=O)(C_2-C_6 haloalkenyl), -OC(=O)(C_2-C_6 haloalkenyl), -OC(=O)(C_3-C_6 haloa$

- 5 $OC(=O)(C_2-C_6alkynyl)$, $-OC(=O)(C_2-C_6alkynyloxy)$, $-OC(=O)(C_3-C_6cycloalkyl)$, $-OC(=O)(C_3-C_6halocycloalkyl)$, $-OC(=O)(C_3-C_6halocycloalkyloxy)$, $-OC(=O)(C_3-C_6halocycloalkyloxy)$, $-OC(=O)(C_3-C_6halocycloalkyloxy)$, $-OC(=O)(C_1-C_6alkyl)$, $-OC(=O)(C_1-C_6haloalkyl)$, $-OC(=O)(C_1-C_6alkoxy)$, $-OC(=O)(C_1-C_6haloalkoxy)$, $-OC(=O)(C_2-C_6alkenyl)$, $-OC(=O)(C_2-C_6alkynyl)$, $-OC(=O)(C_2-C_6alkynyl)$, $-OC(=O)(C_3-C_6cycloalkyl)$, $-OC(=O)(C_3-C_6cycloalkyl)$
- 10 $C(=O)(C_3-C_6halocycloalkyl)$, $-C(=O)(C_3-C_6cycloalkyloxy)$, $-C(=O)(C_3-C_6halocycloalkyloxy)$, $-S(=O)_2(C_1-C_6alkyl)$, $-S(=O)_2(C_1-C_6alkoxy)$, $-S(=O)_2(C_1-C_6alkoxy)$, $-S(=O)_2(C_1-C_6alkoxy)$, $-S(=O)_2(C_2-C_6alkenyl)$, $-S(=O)_2(C_2-C_6alkenyl)$, $-S(=O)_2(C_2-C_6alkenyl)$, $-S(=O)_2(C_2-C_6alkynyl)$, $-S(=O)_2(C_2-C_6alkynyl)$, $-S(=O)_2(C_3-C_6alkynyl)$, $-S(=O)_2(C_3-C_6alkynyl)$
- $\begin{array}{ll} 15 & C_6 halocycloalkyloxy), \ -NHS(=O)_2(C_1-C_6alkyl), \ -N(S(=O)_2(C_1-C_6alkyl))_2, \ -NHS(=O)_2(C_1-C_6alkoxy), \ -N(S(=O)_2(C_1-C_6alkoxy))_2, \ -NHS(=O)_2(C_1-C_6haloalkoxy), \ -N(S(=O)_2(C_1-C_6haloalkoxy))_2, \ -NHS(=O)_2(C_2-C_6alkenyl), \ -N(S(=O)_2(C_2-C_6alkenyl))_2, \ -NHS(=O)_2(C_2-C_6alkenyl))_2, \ -NHS(=O)_2(C_2-C_6alkenyloxy), \ -N(S(=O)_2(C_2-C_6alkenyloxy), \ -N(S(=O)_2(C_2-C_6alkenyloxy))_2, \ -NHS(=O)_2(C_2-C_6haloalkenyloxy), \ -N(S(=O)_2(C_2-C_6alkenyloxy))_2, \ -NHS(=O)_2(C_2-C_6haloalkenyloxy), \ -N(S(=O)_2(C_2-C_6alkenyloxy))_2, \ -NHS(=O)_2(C_2-C_6alkenyloxy), \ -N(S(=O)_2(C_2-C_6alkenyloxy))_2, \ -NHS(=O)_2(C_2-C_6alkenyloxy)_2, \ -NHS(=O)_2$
- $\begin{array}{lll} 20 & -N(S(=O)_2(C_2-C_6haloalkenyloxy))_2, \ -NHS(=O)_2(C_2-C_6alkynyl), \ -N(S(=O)_2(C_2-C_6alkynyloxy))_2, \ -NHS(=O)_2(C_3-C_6alkynyloxy), \ -NHS(=O)_2(C_3-C_6cycloalkyl), \ -N(S(=O)_2(C_3-C_6cycloalkyl))_2, \ -NHS(=O)_2(C_3-C_6halocycloalkyl), \ -N(S(=O)_2(C_3-C_6cycloalkyloxy))_2, \ -NHS(=O)_2(C_3-C_6cycloalkyloxy), \ -N(S(=O)_2(C_3-C_6cycloalkyloxy))_2, \ -NHS(=O)_2(C_3-C_6halocycloalkyloxy), \ -N(S(=O)_2(C_3-C_6halocycloalkyloxy))_2, \ -CH(=NOC_1-C_6halocycloalkyloxy), \ -N(S(=O)_2(C_3-C_6halocycloalkyloxy))_2, \ -N(S(=O)_2$
- 25 C₆alkyl), -C(=NO(C₁-C₆alkyl))C₁-C₆alkyl, -C(=NO(C₁-C₆alkyl))C₂-C₆alkenyl, -C(=NO(C₁-C₆alkyl))C₂-C₆alkynyl, -C(=NO(C₁-C₆alkyl))C₃-C₆cycloalkyl, -CH(=NN(C₁-C₆alkyl)₂, -C(=NN(C₁-C₆alkyl)₂)C₁-C₆alkyl, -C(=NN(C₁-C₆alkyl)₂)C₂-C₆alkenyl, -C(=NN(C₁-C₆alkyl)₂)C₂-C₆alkynyl, -C(=NN(C₁-C₆alkyl)₂)C₃-C₆cycloalkyl, aryl or heterocyclyl; or two R⁶ linked to the same carbon atom can form a saturated 3- to 4-membered carbocyclic or heterocyclic ring;
 - L¹ and L² are independently a direct bond, $-C(R^6)_2$ -z, $-C(R^6)_2$ -C(R⁶)₂-z, $-C(R^6)_2$ -C(R⁶)₂-z, $-C(R^6)_2$ -C(R⁶)₂-z, $-C(R^6)_2$ -C(R⁶)₂-z, $-C(R^6)_2$ -C(R⁶)₂-z, $-C(R^6)_2$ -Z, $-C(R^6)_2$ -Z, $-C(R^6)_2$ -Z, $-C(R^6)_2$ -Z, $-C(R^6)_2$ -Z, $-C(R^6)_2$ -C(R⁶)₂-Z, $-C(R^6)_2$ -C(R⁶)₂-Z, $-C(R^6)_2$ -C(R⁶)₂-Z, $-C(R^6)_2$ -C(R⁶)₂-Z, $-C(R^6)_2$ -C(R⁶)₂-C, in each case z indicates the bond that is connected to R³ or R⁴;
- 35 or a salt or a N-oxide thereof.

- 2. A compound according to claim 1, wherein R^1 is halogen, cyano, C_1 - C_6 alkoxy, C_2 - C_6 alkynyloxy, C_3 - C_6 cycloalkyloxy or C_1 - C_6 alkylthio, in which the alkoxy, alkynyl, cycloalkyl and alkyl groups are optionally substituted by one or more R^6 ,
- 5 3. A compound according to claim 1, wherein R¹ is halogen, cyano or C₁-C₆alkoxy.
 - 4. A compound according to claim 1, wherein:

X¹, X² and X³ are independently O, S or NR⁵;

R¹ is halogen, cyano, C₁-C₆alkoxy, C₂-C₆alkynyloxy, C₃-C₆cycloalkyloxy or C₁-C₆alkylthio, in

10 which the alkoxy, alkynyl, cycloalkyl and alkyl groups are optionally substituted by one or more R⁶;

R² is -C(=O)C₁-C₆alkoxy or a 5- to 6-membered aromatic heterocyclic ring system;

 R^3 is $-C(=O)R^6$ or heterocyclyl;

R⁴ is C₃-C₆cycloalkyl, aryl or heterocyclyl, in which cycloalkyl, aryl and heterocyclyl are

15 optionally substituted by one or more R⁶;

R⁵ is hydrogen, C₁-C₆alkyl or C₁-C₆alkoxy;

 $R^6 \text{ is halogen, cyano, nitro, hydroxyl, amino, } C_1\text{-}C_6\text{alkyl, } C_1\text{-}C_6\text{haloalkyl, } C_1\text{-}C_6\text{alkoxy, } C_1\text{-}C_6\text{alkyl, } C_2\text{-}C_6\text{alkyl, } C_2\text{-}C_6\text{-}C_6\text{alkyl, } C_2\text{-}C_6\text{-}C_6\text{-}C_6\text{-}C_6\text{-}C_6\text{-}C_6\text{-$

C₆haloalkoxy, C₁-C₆alkylthio, C₁-C₆haloalkylthio, C₂-C₆alkenyl, C₂-C₆haloalkenyl, C₂-

 C_6 alkenyloxy, C_2 - C_6 haloalkenyloxy, C_2 - C_6 alkynyl, C_2 - C_6 alkynyloxy, C_3 - C_6 cycloalkyl, C_3 -

20 C₆halocycloalkyl, C₃-C₆cycloalkyloxy or C₃-C₆halocycloalkyloxy;

 L^{1} is $-C(R^{6})_{2}-z$, $-C(R^{6})_{2}-C(R^{6})_{2}-z$, $-C(R^{6})_{2}-NR^{5}-z$ or $-C(R^{6})_{2}-O-z$;

 $L^2 \text{ is } -C(R^6)_2 - z, \ -C(R^6)_2 - C(R^6)_2 - C$

or a salt or a N-oxide thereof.

25 5. A compound according to claim 1, wherein:

X¹, X² and X³ are independently O, S or NR⁵;

R¹ is halogen, cyano or C₁-C₆alkoxy;

R² is -C(=O)C₁-C₆alkoxy or a 5- to 6-membered aromatic heterocyclic ring system;

 R^3 is $-C(=O)NH(C_1-C_6alkyl)$, $-C(=O)N(C_1-C_6alkyl)_2$ or -C(=O)heterocyclyl;

30 R⁴ is aryl or 5- to 6-membered aromatic heterocyclic ring system;

R⁵ is hydrogen or C₁-C₆alkyl;

R⁶ is halogen, cyano, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₂-C₆alkenyl,

C₂-C₆alkynyl, C₂-C₆alkynyloxy, C₃-C₆cycloalkyl;

 L^1 is $-C(R^6)_2$ -z or $-C(R^6)_2$ - $C(R^6)_2$ -z;

35 L^2 is $-C(R^6)_2-C(R^6)_2$ -z or $-C(R^6)_2$ -O-z;

or a salt or a N-oxide thereof.

6. A compound according to claim 1, wherein:

X¹, X² and X³ are independently O, S or NR⁵;

R¹ is halogen, cyano or C₁-C₆alkoxy;

R² is -C(=O)C₁-C₆alkoxy or a 5- to 6-membered aromatic heterocyclic ring system;

 R^3 is $-C(=O)NH(C_1-C_6alkyl)$, $-C(=O)N(C_1-C_6alkyl)_2$ or -C(=O)heterocyclyl;

5 R⁴ is aryl or 5- to 6-membered aromatic heterocyclic ring system;

R⁵ is hydrogen or C₁-C₆alkyl;

 R^6 is halogen, cyano, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_2 - C_6 alkynyl or C_3 - C_6 cycloalkyl;

 L^1 is $-C(R^6)_2$ -z or $-C(R^6)_2$ - $C(R^6)_2$ -z;

10 L^2 is $-C(R^6)_2-C(R^6)_2$ -z or $-C(R^6)_2$ -O-z;

or a salt or a N-oxide thereof.

7. A compound according to claim 1, wherein:

X¹, X² and X³ are independently O, S or NR⁵;

15 R¹ is chloro, cyano or methoxy;

 R^2 is $-C(=O)OCH_2CH_3$ or 2-oxazolyl;

 R^3 is $-C(=O)NH(C_1-C_6alkyl)$;

R⁴ is phenyl or thienyl;

R⁵ is hydrogen or methyl;

20 R⁶ is fluoro, chloro, cyano, methyl, trifluoromethyl, methoxy, ethynyl or cyclopropyl.

 L^1 is $-C(R^6)_2$ -z or $-C(R^6)_2$ - $C(R^6)_2$ -z;

 L^2 is $-C(R^6)_2-C(R^6)_2$ -z or $-C(R^6)_2$ -O-z;

or a salt or a N-oxide thereof.

25 8. A compound according to claim 1, wherein:

X¹, X² and X³ are independently O, S or NR⁵;

R¹ is chloro, cyano or methoxy;

 R^2 is $-C(=O)OCH_2CH_3$ or 2-oxazolyl;

 R^3 is $-C(=O)NH(C_1-C_6alkyl)$;

30 R⁴ is phenyl or thienyl;

R⁵ is hydrogen or methyl;

 L^{1} is $-C(CH_{3})_{2}-z$;

 $L^2 \text{ is } CH_2CH(O(C_1\text{-}C_6alkyl))\text{-}z; \\$

or a salt or a N-oxide thereof.

35

9. A compound according to claim 1, wherein:

 X^1 , X^2 and X^3 are independently O or S;

 R^1 is halogen, cyano, C_1 - C_6 alkoxy, C_2 - C_6 alkynyloxy, C_3 - C_6 cycloalkyloxy or C_1 - C_6 alkylthio, in which the alkoxy, alkynyl, cycloalkyl and alkyl groups are optionally substituted by one or more R^6 ;

R² is -C(=O)C₁-C₆alkoxy or a 5- to 6-membered aromatic heterocyclic ring system;

5 R³ is -C(=O)R⁶ or heterocyclyl;

R⁴ is C₃-C₆cycloalkyl, aryl or heterocyclyl, in which cycloalkyl, aryl and heterocyclyl are optionally substituted by one or more R⁶;

 R^6 is halogen, cyano, nitro, hydroxyl, amino, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_1 - C_6 alkylthio, C_1 - C_6 haloalkylthio, C_2 - C_6 alkenyl, C_2 - C_6 haloalkenyl, C_2 -

10 C₆alkenyloxy, C₂-C₆haloalkenyloxy, C₂-C₆alkynyl, C₂-C₆alkynyloxy, C₃-C₆cycloalkyl, C₃-C₆halocycloalkyloxy;

$$L^1$$
 is $-C(R^6)_2$ -z, $-C(R^6)_2$ -C($R^6)_2$ -z, $-C(R^6)_2$ -NR⁵-z or $-C(R^6)_2$ -O-z;

 L^2 is $-C(R^6)_2$ -z, $-C(R^6)_2$ -c, $-C(R^6)_2$ -c, $-C(R^6)_2$ -C, $-C(R^6)_2$ -z, $-C(R^6)_2$ -z, $-C(R^6)_2$ -z, or a salt or a N-oxide thereof.

15

10. A compound according to claim 1, wherein:

X¹, X² and X³ are independently O or S:

R¹ is halogen, cyano or C₁-C₆alkoxy;

R² is -C(=O)C₁-C₆alkoxy or a 5- to 6-membered aromatic heterocyclic ring system;

20 R^3 is $-C(=O)NH(C_1-C_6alkyl)$, $-C(=O)N(C_1-C_6alkyl)_2$ or -C(=O)heterocyclyl;

R⁴ is aryl or 5- to 6-membered aromatic heterocyclic ring system;

 R^6 is halogen, cyano, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_2 - C_6 alkynyl, C_2 - C_6 alkynyloxy, C_3 - C_6 cycloalkyl;

$$L^1$$
 is $-C(R^6)_2$ -z or $-C(R^6)_2$ - $C(R^6)_2$ -z;

25 L^2 is $-C(R^6)_2-C(R^6)_2$ -z or $-C(R^6)_2$ -O-z;

or a salt or a N-oxide thereof.

11. A compound according to claim 1, wherein:

X¹, X² and X³ are independently O or S;

30 R¹ is chloro, cyano or methoxy;

 R^2 is $-C(=O)OCH_2CH_3$ or 2-oxazolyl;

 R^3 is $-C(=O)NH(C_1-C_6alkyl)$;

R⁴ is phenyl or thienyl;

R⁶ is fluoro, chloro, cyano, methyl, trifluoromethyl, methoxy, ethynyl or cyclopropyl.

35 L^1 is $-C(R^6)_2$ -z or $-C(R^6)_2$ - $C(R^6)_2$ -z;

 L^2 is $-C(R^6)_2$ - $C(R^6)_2$ -z or $-C(R^6)_2$ -O-z;

or a salt or a N-oxide thereof.

12. A compound according to claim 1, wherein X¹ is S, X² is O and X³ is O.

13. A compound of formula I-a:

$$R^{2} \xrightarrow{X^{1}} \xrightarrow{N} \xrightarrow{X^{2}} X^{3}$$

$$\downarrow^{2} \qquad \qquad \text{(I-a)}$$

$$\downarrow^{2} \qquad \qquad \downarrow^{2} \qquad \qquad \downarrow^{2}$$

$$\downarrow^{2} \qquad \qquad \downarrow^{4}$$

in which X^1 , X^2 , X^3 , R^2 , R^3 , R^4 , L^1 and L^2 have the definitions as described for formula I. Preferred definitions of X^1 , X^2 , X^3 , R^2 , R^3 , R^4 , L^1 and L^2 are as defined in anyone of claims 1 to 12 for a compound of formula I, and salts and N-oxides thereof, or a compound of formula I-b:

$$\begin{array}{c|c}
 & R^1 & X^2 \\
 & X^1 & X^3 \\
 & X^3 & X^3 \\
 & X^4 & X^4
\end{array}$$
(I-b)

10

5

wherein X^1 , X^2 , X^3 , R^1 , R^3 , R^4 , L^1 and L^2 are as defined in anyone of claims 1 to 12 for a compound of formula I, and salts and N-oxides thereof, or a compound of formula I-c:

15 in which X¹, X², X³, R¹, R², R³, R⁴ and L² are as defined in anyone of claims 1 to 12 for a compound of formula I, and salts and N-oxides thereof,

or a compound of formula I-d:

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{X^{2}} CH_{3}$$

$$\downarrow \qquad \qquad \downarrow \qquad \qquad$$

in which X^1 , X^2 , X^3 , R^1 , R^2 , R^4 , L^1 and L^2 are as defined in anyone of claims 1 to 12 for a compound of formula I, and salts and N-oxides thereof,

or a compound of formula I-e:

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{X^{2}} CH_{3}$$

$$R^{2} \xrightarrow{X^{1}} N \xrightarrow{X^{3}} CH_{3}$$

$$R^{4} CH_{3}$$

$$(I-e)$$

in which X^1 , X^2 , X^3 , R^1 , R^2 , R^3 , R^4 and L^1 are as defined in anyone of claims 1 to 12 for a compound of formula I, and salts and N-oxides thereof,

5 or a compound of formula I-f:

$$R^{2} \xrightarrow{X^{1}} X^{2} \xrightarrow{X^{3}} X^{3}$$

$$H_{3}C^{-0} \xrightarrow{L^{2}} X^{2}$$

$$(I-f)$$

in which X^1 , X^2 , X^3 , R^1 , R^2 , R^3 , L^1 and L^2 are as defined in anyone of claims 1 to 12 for a compound of formula I, and salts and N-oxides thereof.

- 10 14. A composition comprising at least one compound as defined in any one of claims 1 to 12 and an agriculturally acceptable carrier, optionally comprising an adjuvant, and optionally comprising one or more additional pesticidally active compounds.
- 15. A method of controlling or preventing an infestation of plants, propagation material thereof, harvested crops or of non-living materials by phytopathogenic or spoilage microorganisms or organisms potentially harmful to man, which comprises the application of a compound as defined in any one of claims 1 to 12, 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/EP2014/062844

A. CLASSI INV. ADD.	FICATION OF SUBJECT MATTER C07D487/04 C07D493/04 C07D495	/04 A01N43/90	
According to	o International Patent Classification (IPC) or to both national classifica	ation and IPC	
	SEARCHED		
Minimum do CO7D	ocumentation searched (classification system followed by classification	on symbols)	
	tion searched other than minimum documentation to the extent that s		
Electronic d	ata base consulted during the international search (name of data bas	se and, where practicable, search terms use	ed)
	ternal, CHEM ABS Data, WPI Data		
C. DOCUME	ENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the rele	evant passages	Relevant to claim No.
х	16 May 2013 (2013-05-16)		1-15
Y	cited in the application claim 1 paragraphs [0199] - [0120]		1-15
Y	WO 97/02262 A1 (DU PONT [US]; BE JAMES FRANCIS [US]; CHANG ZEN YU STERNBER) 23 January 1997 (1997-0 claims 1, 10	[US];	1-15
Furth	her documents are listed in the continuation of Box C.	X See patent family annex.	
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filling date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published after the international filling 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 "A" 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 "A" 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 "A" document member of the same patent family Date of the actual completion of the international search report		ation but cited to understand nvention laimed invention cannot be ered to involve an inventive e laimed invention cannot be p when the document is n documents, such combination e art	
1	5 July 2014	23/07/2014	
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 Gutke, Hans-Jürgen			en

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2014/062844

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2013071169 A1	16-05-2013	AU 2012335088 A1 TW 201350489 A US 2013123231 A1 WO 2013071169 A1	29-05-2014 16-12-2013 16-05-2013 16-05-2013
WO 9702262 A1	23-01-1997	AU 6478396 A BR 9609613 A CN 1195345 A DE 69618959 D1 DE 69618959 T2 EP 0836602 A1 ES 2167586 T3 JP 4010563 B2 JP H11508230 A PL 324486 A1 US 6066638 A US 6245770 B1 WO 9702262 A1	05-02-1997 25-05-1999 07-10-1998 14-03-2002 29-08-2002 22-04-1998 16-05-2002 21-11-2007 21-07-1999 25-05-1998 23-05-2000 12-06-2001 23-01-1997