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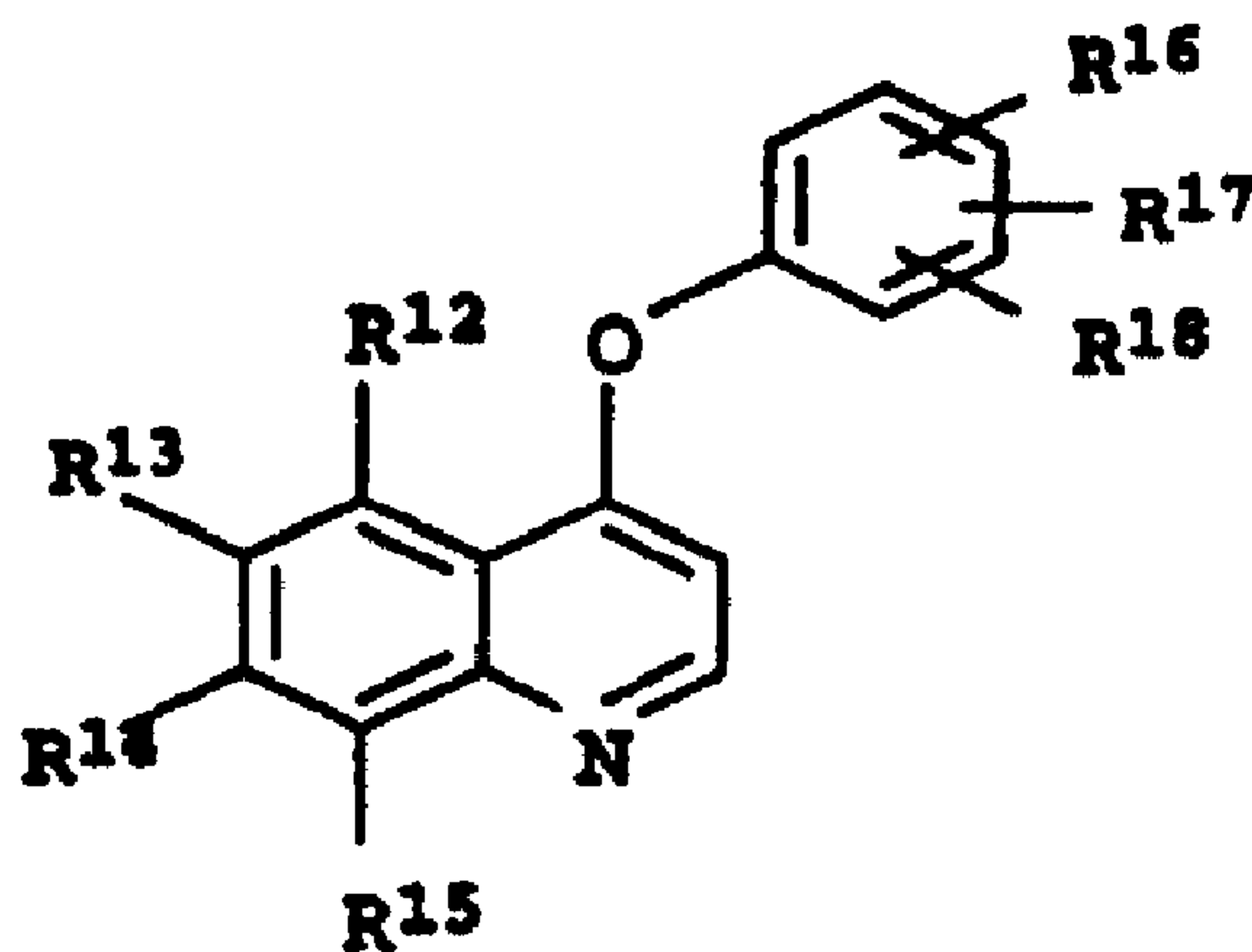
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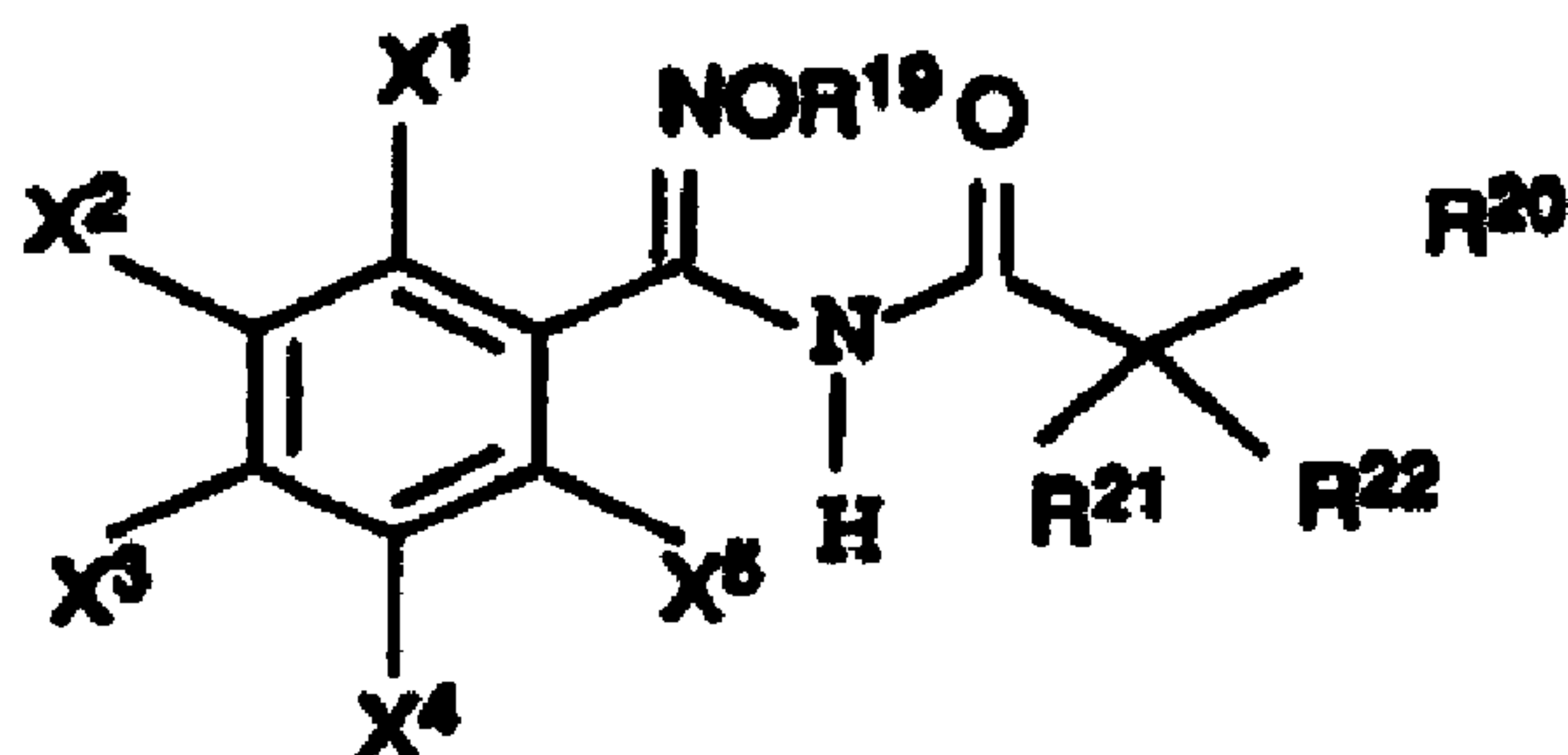
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(54) Titre : MELANGES FONGICIDES A BASE DE COMPOSES AMIDE ET DE DERIVES DE PYRIDINE
 (54) Title: FUNGICIDE MIXTURES BASED ON PYRIDINE CARBOXAMIDES



(II)



(III)

(57) Abrégé/Abstract:

The invention relates to fungicide mixtures containing, as active components, a) an amide compound of formula (I): A-CO-NR¹R² wherein A, R¹ and R² have the meanings given in the description, and b) compounds of formula (II), the N-oxide thereof or one of the salts thereof, whereby the substituents R¹² to R¹⁸ have the meanings given in the description; and/or c) compounds of formula (III), whereby the substituents X¹ to X⁵ and R¹⁹ to R²² have the meanings given in the description. The active components are provided in a synergistically effective quantity.



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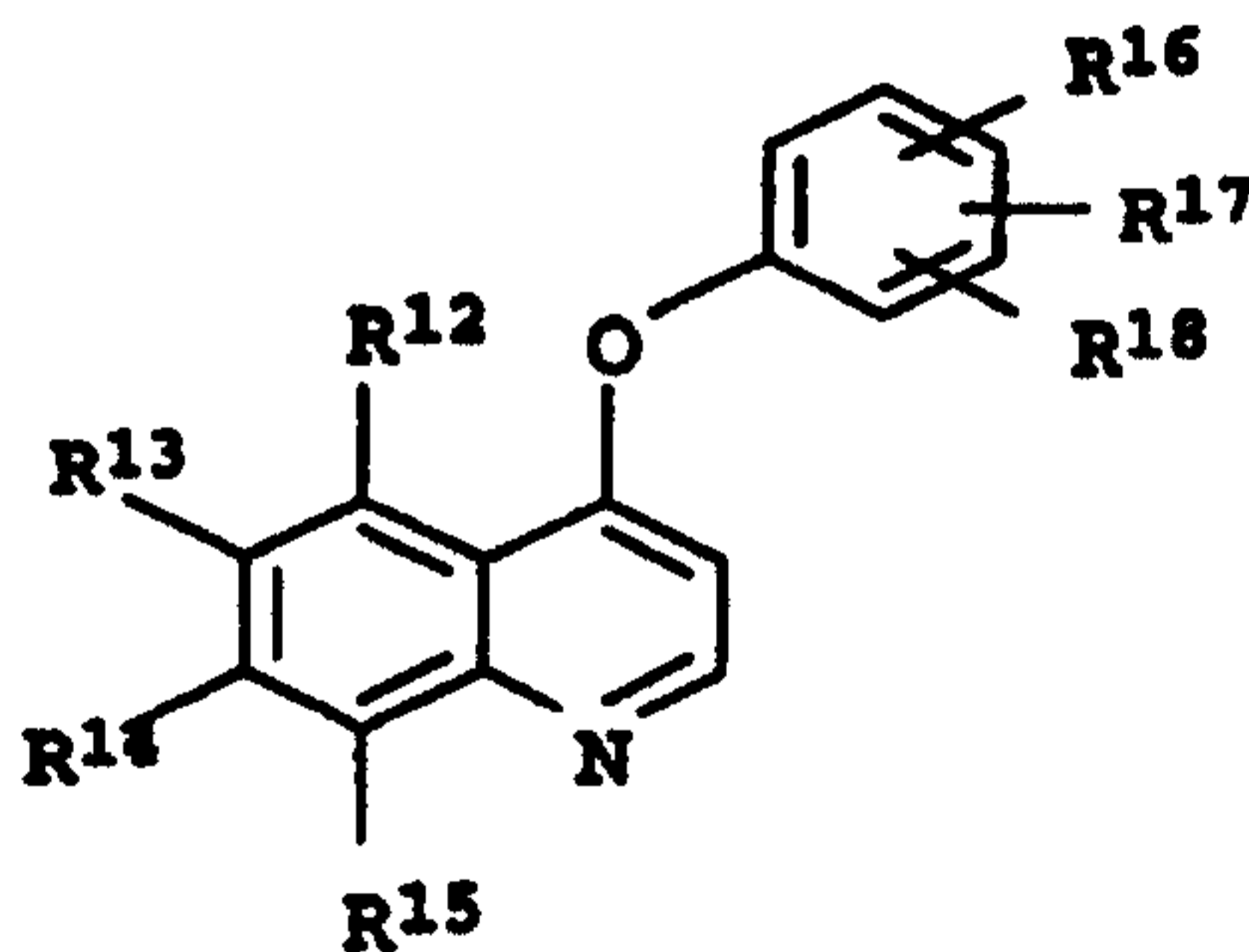
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(54) Title: **FUNGICIDE MIXTURES BASED ON AMIDE COMPOUNDS AND PYRIDINE DERIVATIVES**

(54) Bezeichnung: **FUNGIZIDE MISCHUNGEN AUF DER BASIS VON AMIDVERBINDUNGEN UND PYRIDINDERIVATEN**

(57) Abstract

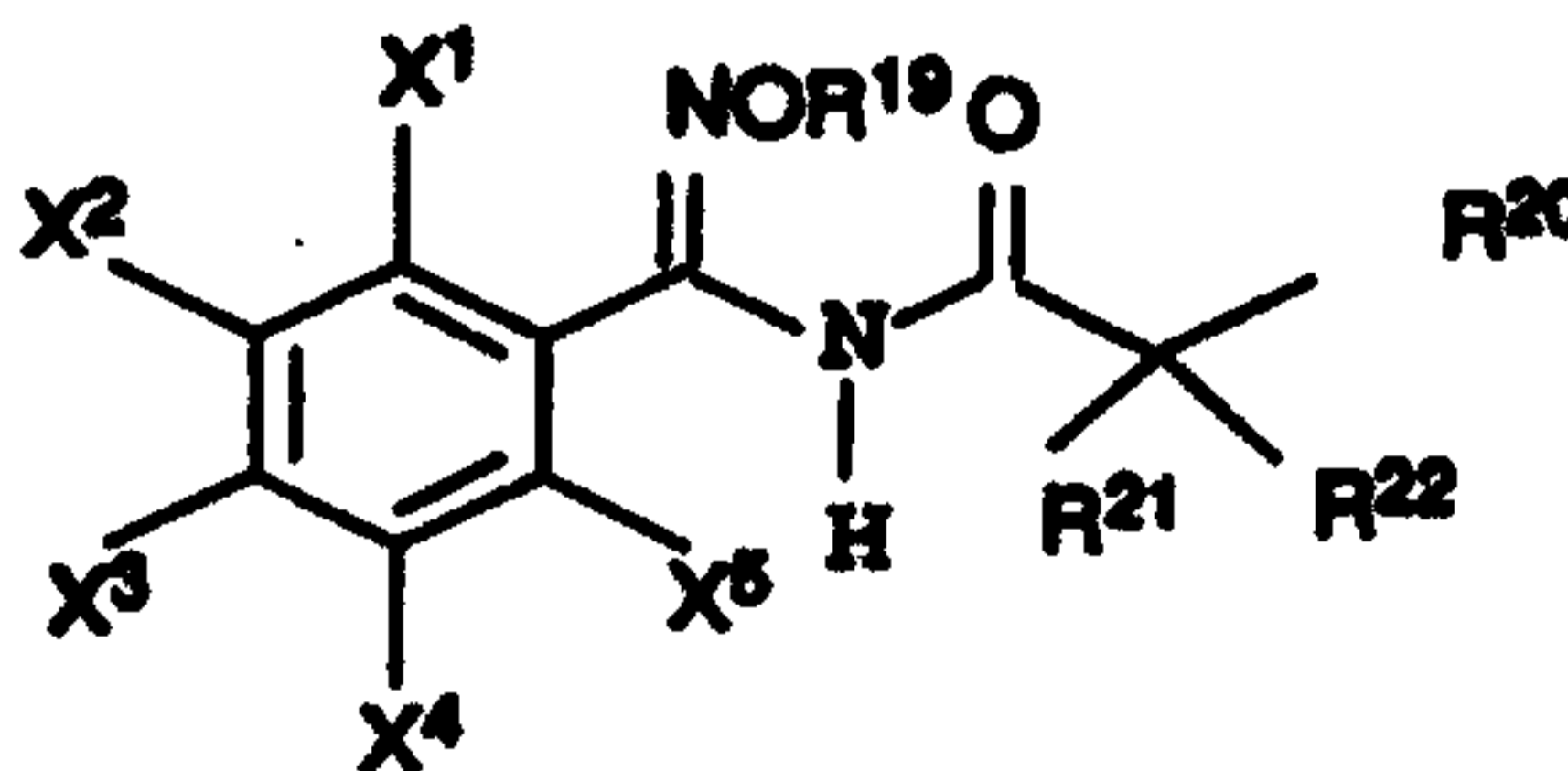
The invention relates to fungicide mixtures containing, as active components, a) an amide compound of formula (I): $A-CO-NR^1R^2$ wherein A, R¹ and R² have the meanings given in the description, and b) compounds of formula (II), the N-oxide thereof or one of the salts thereof, whereby the substituents R¹² to R¹⁸ have the meanings given in the description; and/or c) compounds of formula (III), whereby the substituents X¹ to X⁵ and R¹⁹ to R²² have the meanings given in the description. The active components are provided in a synergistically effective quantity.



(II)

(57) Zusammenfassung

Fungizide Mischungen, enthaltend als aktive Komponenten: a) eine Amidverbindung der Formel (I): $A-CO-NR^1R^2$, worin A, R¹ und R² die in der Beschreibung genannte Bedeutung haben, und b) Verbindungen der Formel (II), ihr N-Oxid oder eines ihrer Salze, wobei die Substituenten R¹² bis R¹⁸ die in der Beschreibung genannten Bedeutungen haben; und/oder c) Verbindungen der Formel (III), wobei die Substituenten X¹ bis X⁵ und R¹⁹ bis R²² die in der Beschreibung genannte Bedeutung haben, in einer synergistisch wirksamen Menge.



(III)

FUNGICIDE MIXTURES BASED ON PYRIDINE CARBOXAMIDES

The present invention as broadly disclosed hereinafter, relates to fungicidal mixtures for controlling harmful fungi, which mixtures comprise:

amide compounds of the formula I:



in which

10 A is an aryl group or an aromatic or non-aromatic, 5- or 6-membered heterocycle which has from 1 to 3 hetero atoms selected from O, N and S;

where the aryl group or the heterocycle may or may not have 1, 2 or 3 substituents which are selected, independently of one another, from alkyl, halogen, CHF₂, CF₃, alkoxy, haloalkoxy, alkylthio, alkylsulfynyl and alkylsulfonyl;

R¹ is a hydrogen atom;

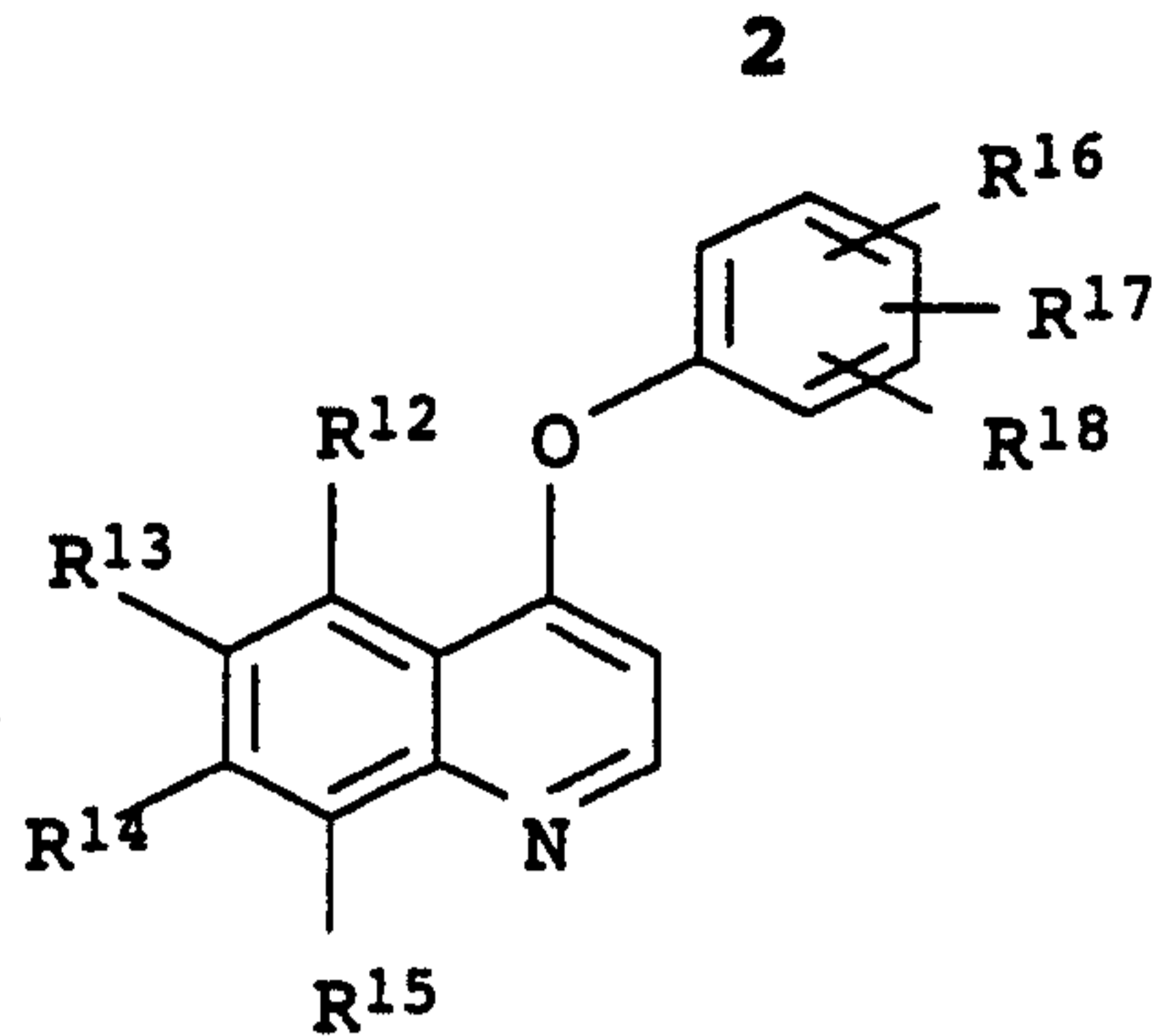
20 R² is a phenyl or cycloalkyl group which may or may not have 1, 2 or 3 substituents which are selected from alkyl, alkenyl, alkynyl, alkoxy, alkenyloxy, alkynyloxy, cycloalkyl, cycloalkenyl, cycloalkyloxy, cycloalkenyloxy, phenyl and halogen, where the aliphatic and cycloaliphatic radicals may be partially or fully halogenated and/or the cycloaliphatic radicals may be substituted by from 1 to 3 alkyl groups and where the phenyl group may have from 1 to 5 halogen atoms and/or from 1 to 3 substituents which are selected, independently of one another, from alkyl, haloalkyl, alkoxy, haloalkoxy, alkylthio and haloalkylthio, and where the amidic phenyl group may or may not be condensed with a saturated 5-membered ring which may or may not be substituted by one or more alkyl groups and/or may have a hetero atom selected from O and S,

and

compounds of the formula II, their N-oxide or one of their salts

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where the substituents are as defined below:

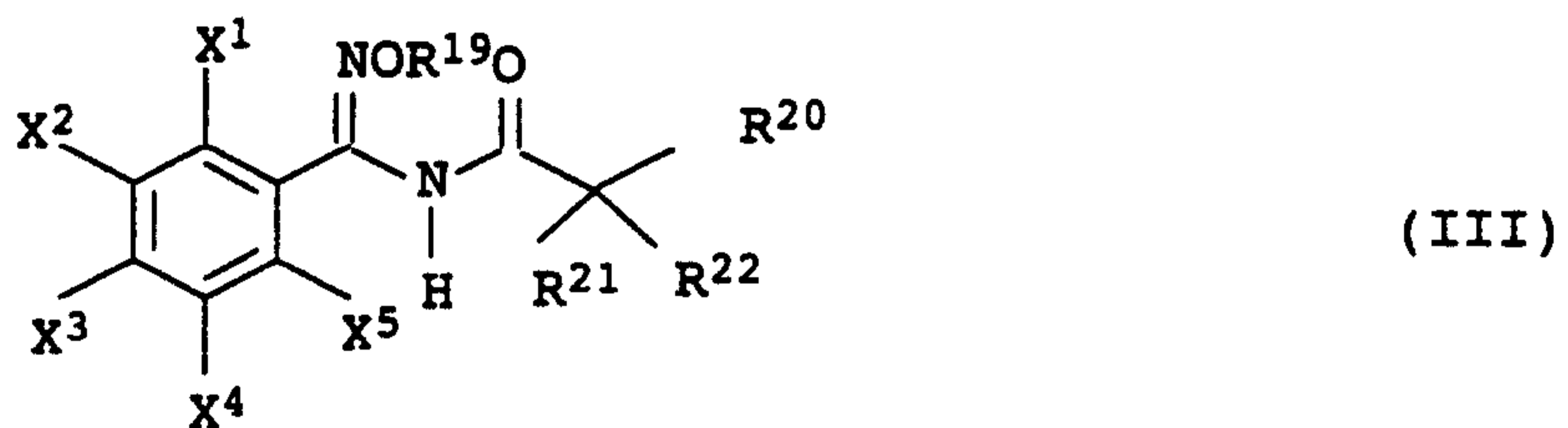
$R^{12}, R^{13}, R^{14}, R^{15}$ independently of one another are hydrogen, hydroxyl, nitro, halogen, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkoxy, C_1 - C_4 -alkylthio, C_1 - C_4 -haloalkylthio;

R^{16}, R^{17}, R^{18} independently of one another are hydrogen, hydroxyl, cyano, nitro, halogen, C_1 - C_7 -alkyl, C_1 - C_7 -haloalkyl, C_1 - C_7 -alkoxy, C_1 - C_7 -haloalkoxy, C_1 - C_7 -alkylthio, C_1 - C_7 -haloalkylthio, C_1 - C_7 -hydroxyalkyl, C_2 - C_4 -acyl, aryl, aryloxy, where the radicals containing an aryl group may for their part carry from one to three of the following groups: cyano, nitro, halogen, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkoxy, C_1 - C_4 -alkylthio and C_1 - C_4 -haloalkylthio

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and/or compounds of the formula III

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where the substituents X^1 to X^5 and R^{19} to R^{22} are as defined below:

45

x^1 to x^5 independently of one another are hydrogen, halogen, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkoxy, C_1 - C_4 -alkylthio, C_1 - C_4 -thioalkoxy, C_1 - C_4 -sulfonylalkyl, nitro, amino, N - C_1 - C_4 -carboxylamino, N - C_1 - C_4 -alkylamino;

R^{19} is C_1 - C_4 -alkyl, C_2 - C_4 -alkenyl, C_2 - C_4 -alkynyl, C_1 - C_4 -alkyl- C_3 - C_7 -cycloalkyl, where these radicals may carry substituents selected from halogen, cyano and C_1 - C_4 -alkoxy;

10 R^{20} is a phenyl radical or a 5- or 6-membered saturated or unsaturated heterocyclyl radical having at least one hetero atom selected from the group N, O and S, where the cyclic radicals may have from one to three substituents selected from the group consisting of halogen, C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkyl, C_1 - C_4 -haloalkoxy, C_1 - C_4 -alkoxy- C_2 - C_4 -alkenyl, C_1 - C_4 -alkoxy- C_2 - C_4 -alkynyl;

R^{21} and R^{22} independently of one another are hydrogen, C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -alkylthio, N - C_1 - C_4 -alkylamino, C_1 - C_4 -haloalkyl or C_1 - C_4 -haloalkoxy

20 in a synergistically effective amount.

The invention as claimed is however restricted to mixtures which comprise the compounds of the formulae I and II, those of formulae III being only optional.

The amide compounds of the formula I are known per se and are described in the literature (EP-A 545 099).

WO 97/08952 describes fungicidal mixtures which, in addition to compounds of the formula I, also comprise fenazaquin as further components. These are described as being very effective against Botrytis.

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The compounds of the formula II are known per se and are described, for example, in US-A 5,240,940. Fungicidal mixtures

which comprise the compounds of the formula II in addition to other fungicidally active compounds are also already known and are described in CA-A2,208,141.

The compounds of the formula III and processes for their preparation are described in WO-A 96/19442.

10 It is an object of the present inventions to provide mixtures which have an improved activity against harmful fungi combined with a reduced total amount of active ingredients applied (synergistic mixtures), with a view to reducing the application rates and to improving the activity spectrum of the known compounds.

We have found that this object is achieved by the mixtures defined at the outset. Moreover, we have found that better control of harmful fungi is possible by applying the compounds I and the compounds II to III simultaneously, that is either together or separately, or by applying the compounds I and the compounds II to III in succession than when the compounds I or II to III are applied on their own.

20 The mixtures according to the invention have synergistic action and are therefore particularly suitable for controlling harmful fungi and in particular powdery mildew fungi in vegetables, grapevines and cereals.

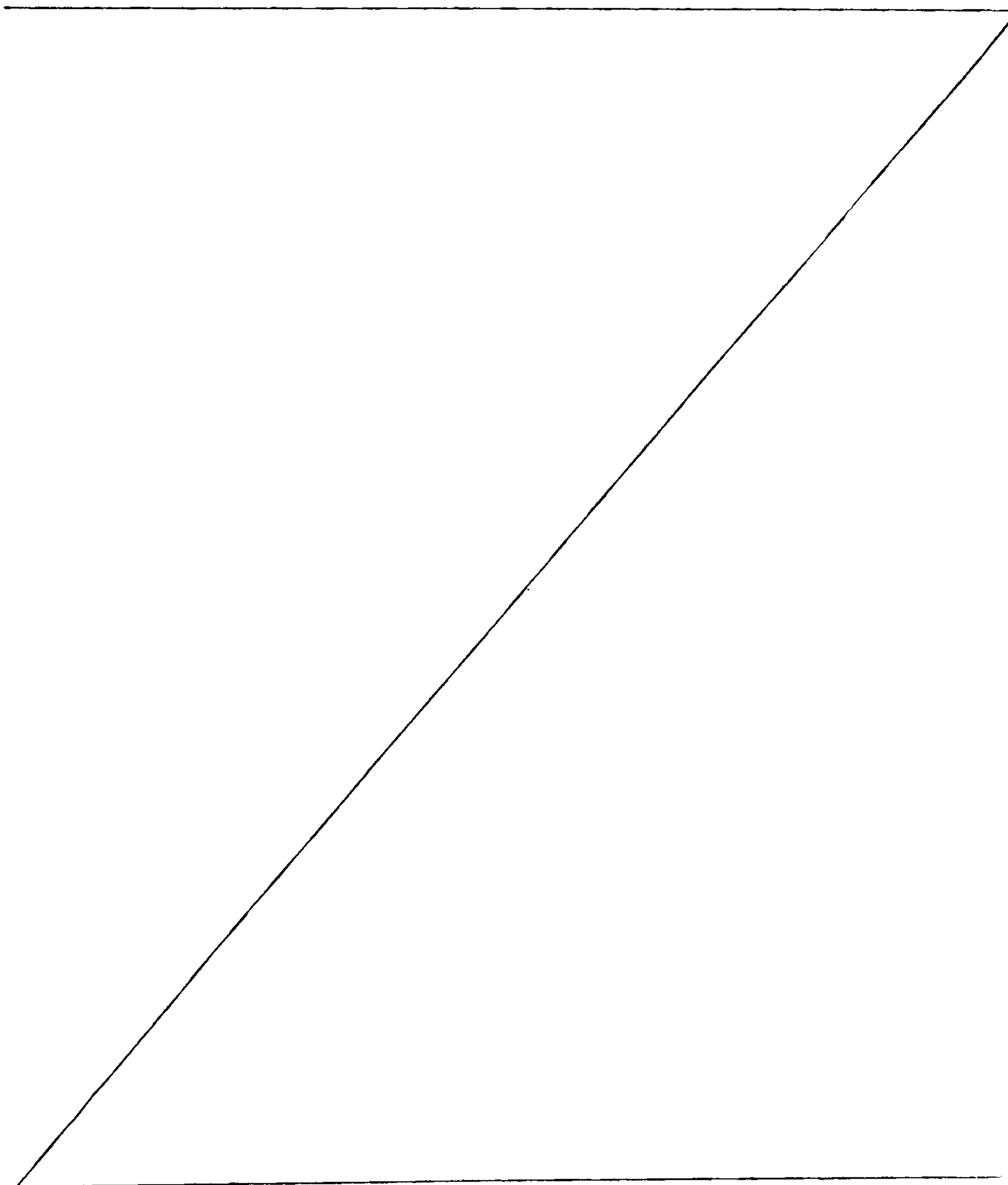
In the context of the present invention, halogen is fluorine, chlorine, bromine and iodine and is in particular fluorine, chlorine and bromine.

30 The term "alkyl" includes straight-chain and branched alkyl groups. These are preferably straight-chain or branched C₁-C₁₂-alkyl and in particular C₁-C₆-alkyl groups. Examples of alkyl groups are alkyl such as, in particular, methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, n-pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, 2,2-dimethylpropyl, 1-ethylpropyl, n-hexyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,3-dimethylbutyl, 1,1-dimethylbutyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethylbutyl,

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2-ethylbutyl, 1-ethyl-2-methylpropyl, n-heptyl, 1-methylhexyl, 1-ethylpentyl, 2-ethylpentyl, 1-propylbutyl, octyl, decyl, dodecyl.

Haloalkyl is an alkyl group as defined above which is partially or fully halogenated by one or more halogen atoms, in particular by fluorine and chlorine. Preferably, there are from 1 to 3 halogen atoms present, and the difluoromethane or the trifluoromethyl group is particularly preferred.



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The above statements for the alkyl group and the haloalkyl group apply in a corresponding manner to the alkyl and haloalkyl groups in alkoxy, haloalkoxy, alkylthio, haloalkylthio, alkylsulfynyl and alkylsulfonyl.

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The alkenyl group includes straight-chain and branched alkenyl groups. These are preferably straight-chain or branched C₃-C₁₂-alkenyl groups and in particular C₃-C₆-alkenyl groups.

Examples of alkenyl groups are 2-propenyl, 2-butenyl, 3-butenyl,
 10 1-methyl-2-propenyl, 2-methyl-2-propenyl, 2-pentenyl, 3-pentenyl,
 4-pentenyl, 1-methyl-2-butenyl, 2-methyl-2-butenyl,
 3-methyl-2-butenyl, 1-methyl-3-butenyl, 2-methyl-3-butenyl,
 3-methyl-3-butenyl, 1,1-dimethyl-2-propenyl,
 1,2-dimethyl-2-propenyl, 1-ethyl-2-propenyl, 2-hexenyl,
 15 3-hexenyl, 4-hexenyl, 5-hexenyl, 1-methyl-2-pentenyl,
 2-methyl-2-pentenyl, 3-methyl-2-pentenyl, 4-methyl-2-pentenyl,
 1-methyl-3-pentenyl, 2-methyl-3-pentenyl, 3-methyl-3-pentenyl,
 4-methyl-3-pentenyl, 1-methyl-4-pentenyl, 2-methyl-4-pentenyl,
 3-methyl-4-pentenyl, 4-methyl-4-pentenyl, 1,1-dimethyl-2-butenyl,
 20 1,1-dimethyl-3-butenyl, 1,1-dimethyl-3-butenyl [sic],
 1,2-dimethyl-2-butenyl, 1,2-dimethyl-3-butenyl,
 1,3-dimethyl-2-butenyl, 1,3-dimethyl-3-butenyl,
 2,2-dimethyl-3-butenyl, 2,3-dimethyl-2-butenyl,
 2,3-dimethyl-3-butenyl, 1-ethyl-2-butenyl, 1-ethyl-3-butenyl,
 25 2-ethyl-2-butenyl, 2-ethyl-3-butenyl, 1,1,2-trimethyl-2-propenyl,
 1-ethyl-1-methyl-2-propenyl and 1-ethyl-2-methyl-2-propenyl, in
 particular 2-propenyl, 2-butenyl, 3-methyl-2-butenyl and
 3-methyl-2-pentenyl.

30

The alkenyl group may be partially or fully halogenated by one or more halogen atoms, in particular by fluorine or chlorine. The alkenyl group preferably has from 1 to 3 halogen atoms.

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The alkynyl group includes straight-chain and branched alkynyl groups. These are preferably straight-chain and branched C₃-C₁₂-alkynyl groups and in particular C₃-C₆-alkynyl groups.

Examples of alkynyl groups are 2-propynyl, 2-butynyl, 3-butynyl,
 1-methyl-2-propynyl, 2-pentynyl, 3-pentynyl, 4-pentynyl,
 40 1-methyl-3-butynyl, 2-methyl-3-butynyl, 1-methyl-2-butynyl,
 1,1-dimethyl-2-propynyl, 1-ethyl-2-propynyl, 2-hexynyl,
 3-hexynyl, 4-alkynyl [sic], 5-hexynyl, 1-methyl-2-pentynyl,
 1-methyl-3-pentynyl, 1-methyl-4-pentynyl, 2-methyl-3-pentynyl,
 2-methyl-4-pentynyl, 3-methyl-4-pentynyl, 4-methyl-2-pentynyl,
 45 1,2-dimethyl-2-butynyl, 1,1-dimethyl-3-butynyl,
 1,2-dimethyl-3-butynyl, 2,2-dimethyl-3-butynyl,

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1-ethyl-2-butynyl, 1-ethyl-3-butynyl, 2-ethyl-3-butynyl and 1-ethyl-1-methyl-2-propynyl.

5 The above statements for the alkenyl group and its halogen substituents and for the alkynyl group apply in a corresponding manner to alkenyloxy and alkynyloxy.

10 The cycloalkyl group is preferably a C₃-C₆-cycloalkyl group, such as cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl. If the cycloalkyl group is substituted, it preferably has from 1 to 3 C₁-C₄-alkyl radicals as substituents.

15 Cycloalkenyl is preferably a C₄-C₆-cycloalkenyl group, such as cyclobutenyl, cyclopentenyl or cyclohexenyl. If the cycloalkenyl group is substituted, it preferably has from 1 to 3 C₁-C₄-alkyl radicals as substituents.

20 A cycloalkoxy group is preferably a C₅-C₆-cycloalkoxy group, such as cyclopentyloxy or cyclohexyloxy. If the cycloalkoxy group is substituted, it preferably has from 1 to 3 C₁-C₄-alkyl radicals as substituents.

25 The cycloalkenyloxy group is preferably a C₅-C₆-cycloalkenyloxy group, such as cyclopentyloxy or cyclohexyloxy. If the cycloalkenyloxy group is substituted, it preferably has from 1 to 3 C₁-C₄-alkyl radicals as substituents.

30 Aryl is preferably phenyl.

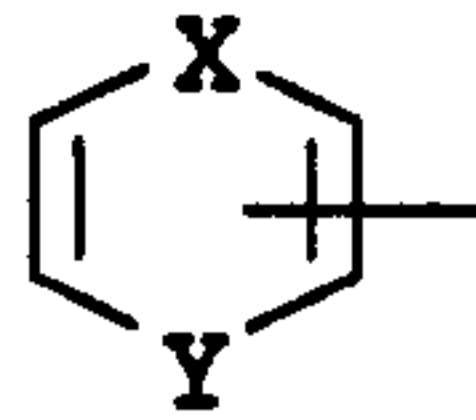
If A is a phenyl group, this may have one, two or three of the abovementioned substituents in any position. These substituents are preferably selected, independently of one another, from 35 alkyl, difluoromethyl, trifluoromethyl and halogen, in particular chlorine, bromine and iodine. Particularly preferably, the phenyl group has a substituent in the 2-position.

If A is a 5-membered heterocycle, it is in particular a furyl, 40 thiazolyl, pyrazolyl, imidazolyl, oxazolyl, thienyl, triazolyl or thiadiazolyl radical or the corresponding dihydro or tetrahydro derivatives thereof. Preference is given to a thiazolyl or pyrazolyl radical.

45 If A is a 6-membered heterocycle, it is in particular a pyridyl radical or a radical of the formula:

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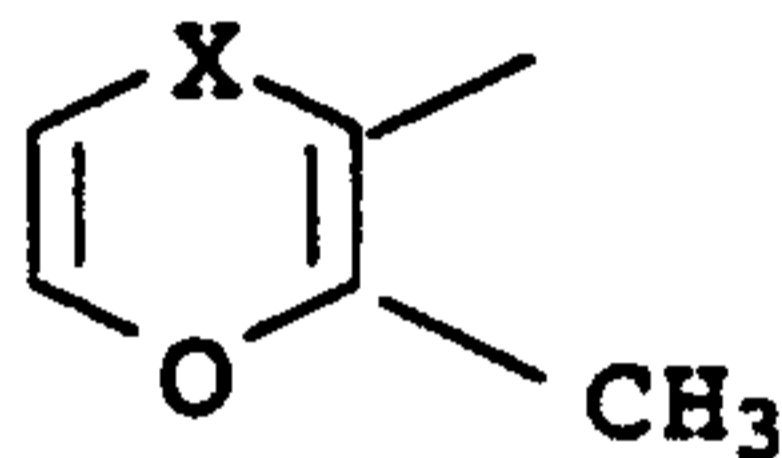
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in which one of the radicals X and Y is O, S or NR²³, where R²³ is H or alkyl, and the other of the radicals X and Y is CH₂, S, SO, SO₂ or NR²³. The dotted line means that a double bond may or may not be present.

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The 6-membered aromatic heterocycle is particularly preferably a pyridyl radical, in particular a 3-pyridyl radical, or a radical of the formula

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(A3)

in which X is CH₂, S, SO or SO₂.

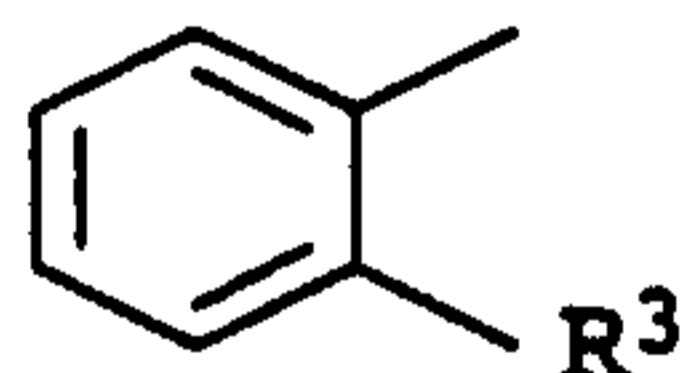
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The abovementioned heterocyclic radicals may or may not have 1, 2 or 3 of the abovementioned substituents, where these substituents are preferably selected, independently of one another, from alkyl, halogen, difluoromethyl or trifluoromethyl.

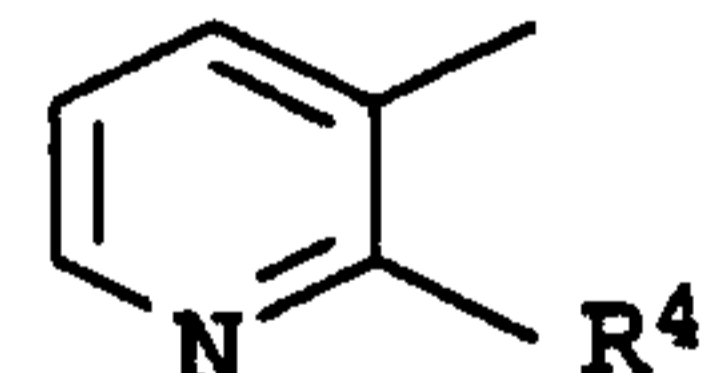
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A is particularly preferably a radical of the formulae:

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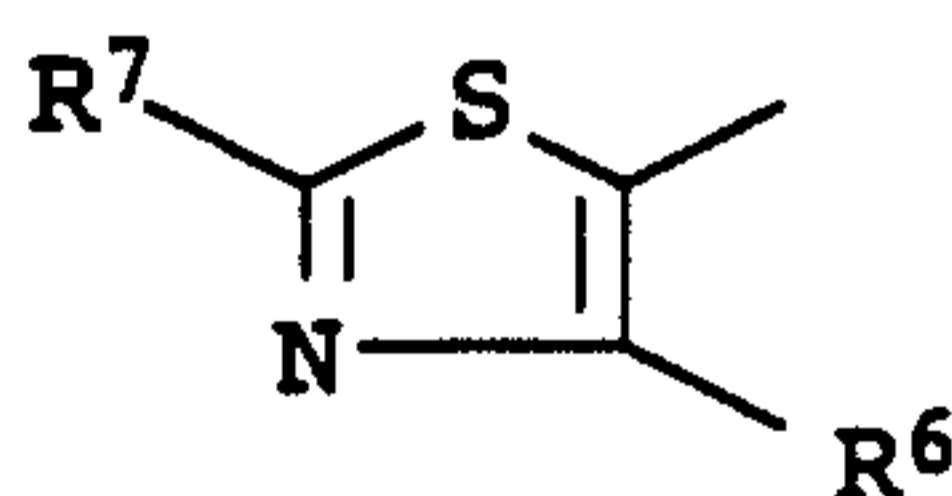


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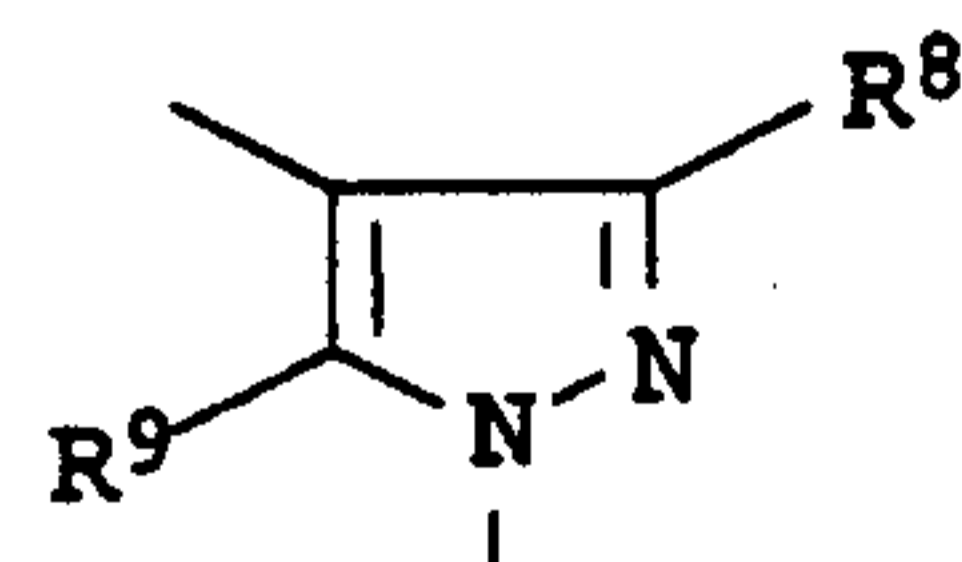


(A2)

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(A5)

(A7) CH₃

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in which R^3 , R^4 , R^6 , R^7 , R^8 and R^9 independently of one another are hydrogen, alkyl, in particular methyl, halogen, in particular chlorine, CHF_2 or CF_3 .

5 The radical R^1 in the formula I is preferably a hydrogen atom.

The radical R^2 in the formula I is preferably a phenyl radical. R^2 preferably has at least one substituent which is particularly preferably in the 2-position. The substituent (or the
10 substituents) is (are) preferably selected from the group consisting of alkyl, cycloalkyl, cycloalkenyl, halogen or phenyl.

The substituents of the radical R^2 may in turn be substituted
15 again. The aliphatic or cycloaliphatic substituents may be partially or fully halogenated, in particular fluorinated or chlorinated. They preferably have 1, 2 or 3 fluorine or chlorine atoms. If the substituent of the radical R^2 is a phenyl group, this phenyl group may preferably be substituted by from 1 to 3
20 halogen atoms, in particular chlorine atoms, and/or by a radical which is preferably selected from alkyl and alkoxy. Particularly preferably, the phenyl group is substituted with a halogen atom in the p-position, i.e. the particularly preferred substituent of the radical R^2 is a p-halogen-substituted phenyl radical. The
25 radical R^2 may also be condensed with a saturated 5-membered ring, where this ring for its part may have from 1 to 3 alkyl substituents.

R^2 is in this case, for example, indanyl, thiaindanyl and
30 oxaindanyl. Preference is given to indanyl and 2-oxaindanyl which are attached to the nitrogen atom in particular via the 4-position.

According to a preferred embodiment, the composition according to
35 the invention comprises as amide compound a compound of the formula I in which A is as defined below:

phenyl, pyridyl, dihydropyranyl, dihydrooxathiynyl,
40 dihydrooxathiynyloxide, dihydrooxathiynyldioxide, furyl, thiazolyl, pyrazolyl or oxazolyl, where these groups may have 1, 2 or 3 substituents which are selected, independently of one another, from alkyl, halogen, difluoromethyl and trifluoromethyl.

45 According to a further preferred embodiment, A is one of the following groups:

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pyridin-3-yl, which may or may not be substituted in the 2-position by halogen, methyl, difluoromethyl, trifluoromethyl, methoxy, methylthio, methylsulfynyl or methylsulfonyl;

5 phenyl, which may or may not be substituted in the 2-position by methyl, trifluoromethyl, chlorine, bromine or iodine;

2-methyl-5,6-dihydropyran-3-yl;

10 2-methyl-5,6-dihydro-1,4-oxathiyn-3-yl or the 4-oxide or 4,4-dioxide thereof;

2-methylfuran-3-yl, which may or may not be substituted in the 4-
15 and/or 5-position by methyl;

thiazol-5-yl, which may or may not be substituted in the 2- and/or 4-position by methyl, chlorine, difluoromethyl or trifluoromethyl;

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thiazol-4-yl, which may or may not be substituted in the 2- and/or 5-position by methyl, chlorine, difluoromethyl or trifluoromethyl;

25

1-methylpyrazol-4-yl, which may or may not be substituted in the 3- and/or 5-position by methyl, chlorine, difluoromethyl or trifluoromethyl; or

30 oxazol-5-yl, which may or may not be substituted in the 2- and/or 4-position by methyl or chlorine.

According to a further preferred embodiment, the compositions according to the invention comprise as amide compound a compound
35 of the formula I in which R² is a phenyl group which may or may not be substituted by 1, 2 or 3 of the abovementioned substituents.

40 According to a further preferred embodiment, the compositions according to the invention comprise as amide compound a compound of the formula I in which R² is a phenyl group which has one of the following substituents in the 2-position:

C₃-C₆-alkyl, C₅-C₆-cycloalkenyl, C₅-C₆-cycloalkyloxy,
45 cycloalkenyloxy, where these groups may be substituted by 1, 2 or 3 C₁-C₄-alkyl groups,

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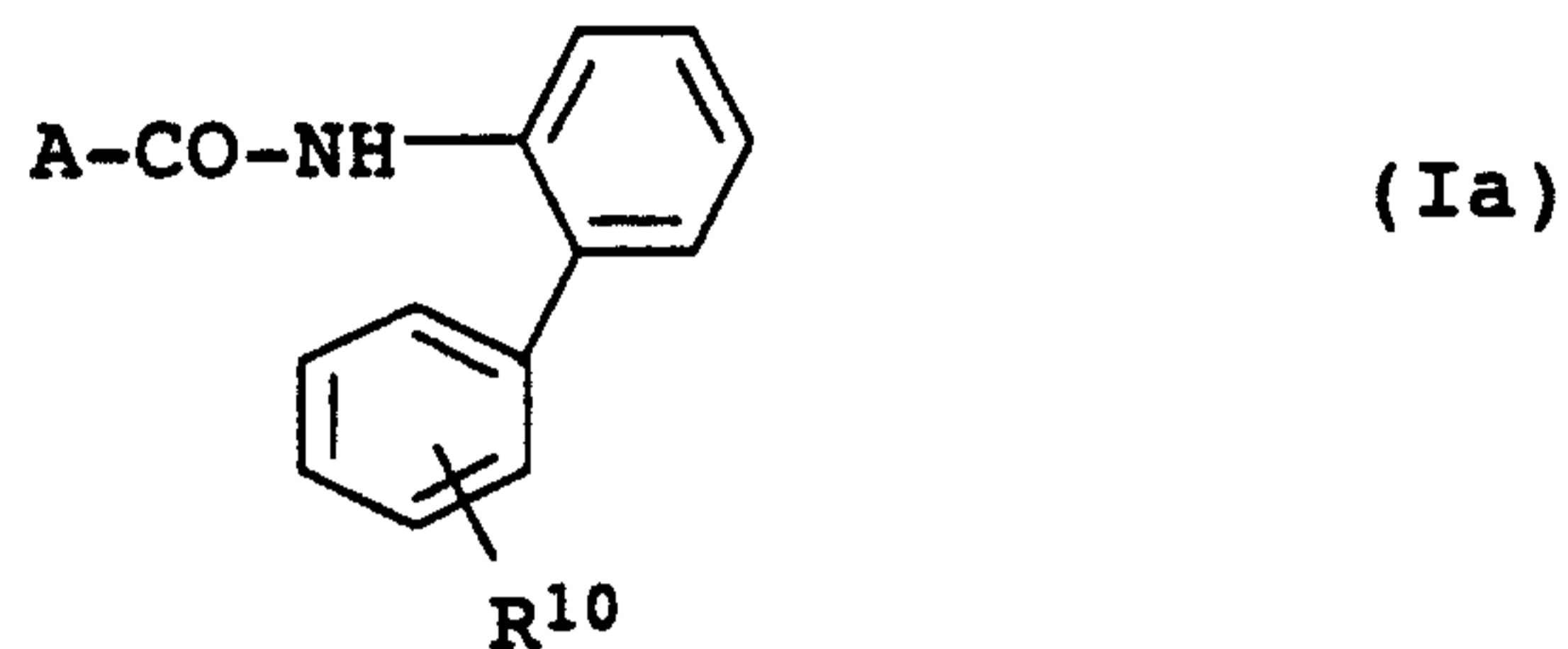
phenyl, which is substituted by from 1 to 5 halogen atoms and/or from 1 to 3 groups which are selected, independently of one another, from C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio and C₁-C₄-haloalkylthio,

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indanyl or oxaindanyl which may or may not be substituted by 1, 2 or 3 C₁-C₄-alkyl groups.

10 According to a further preferred embodiment, the compositions according to the invention comprise as amide compound a compound of the formula Ia,

15

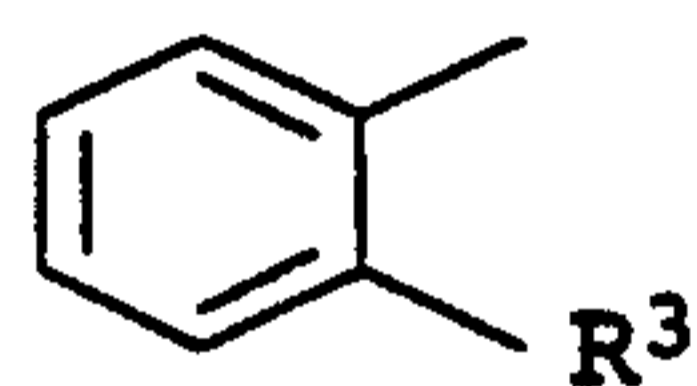


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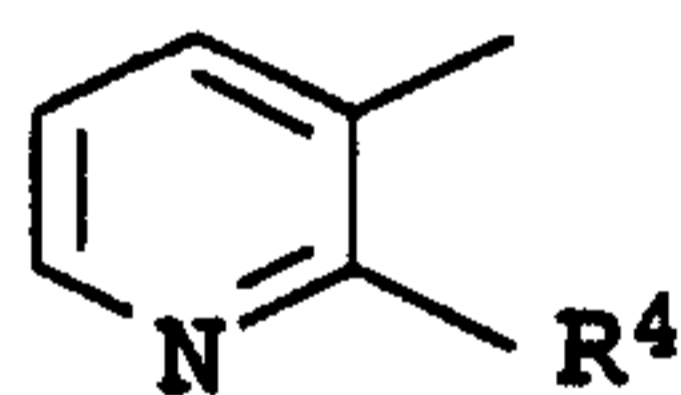
in which

A is

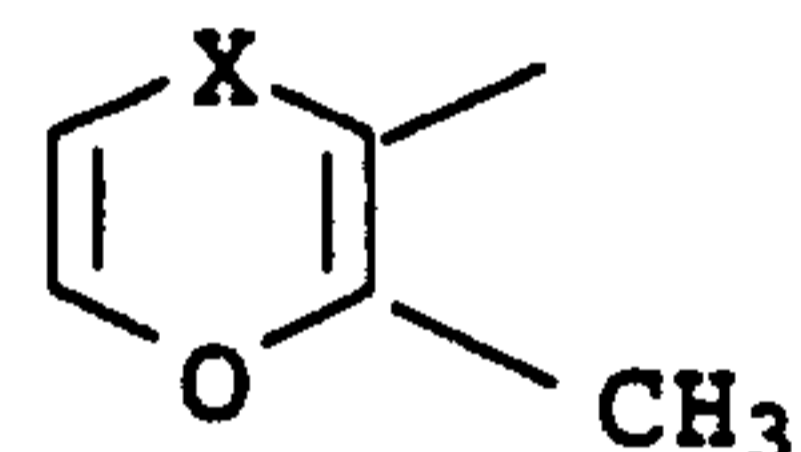
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(A1)

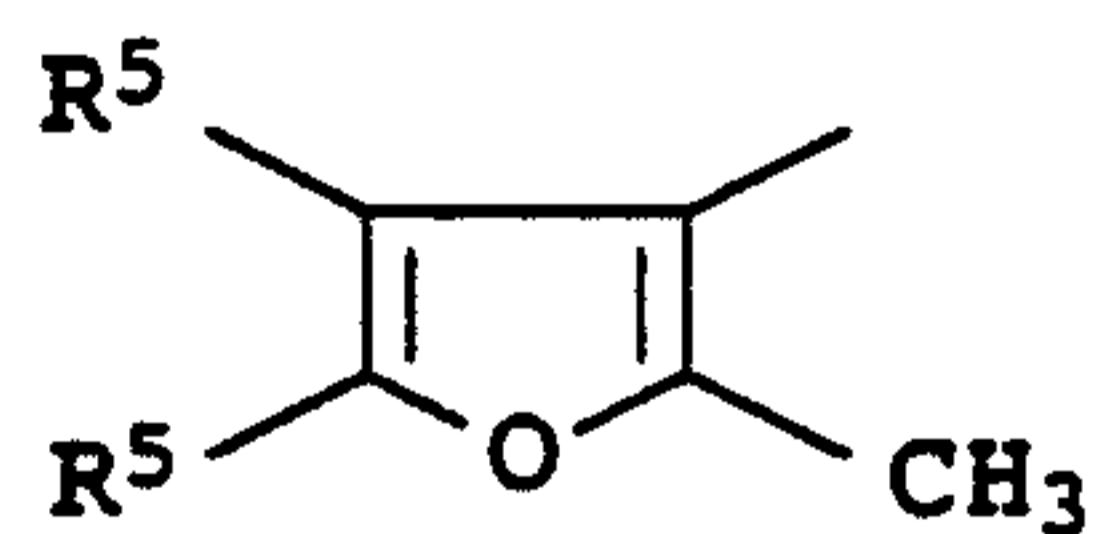


(A2)

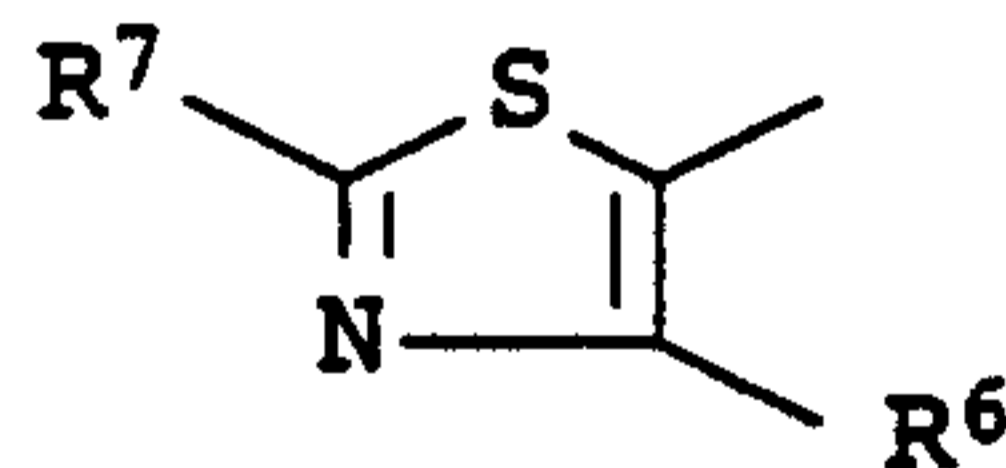


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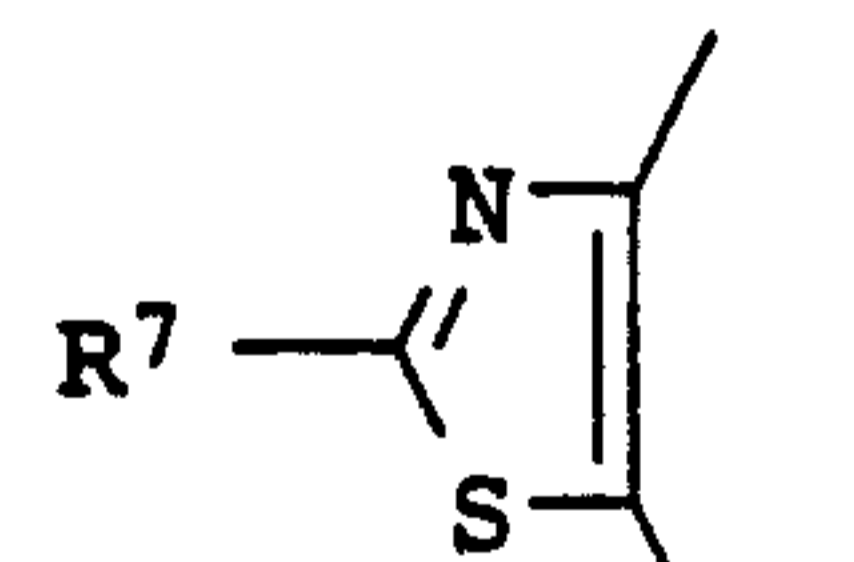
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(A4)



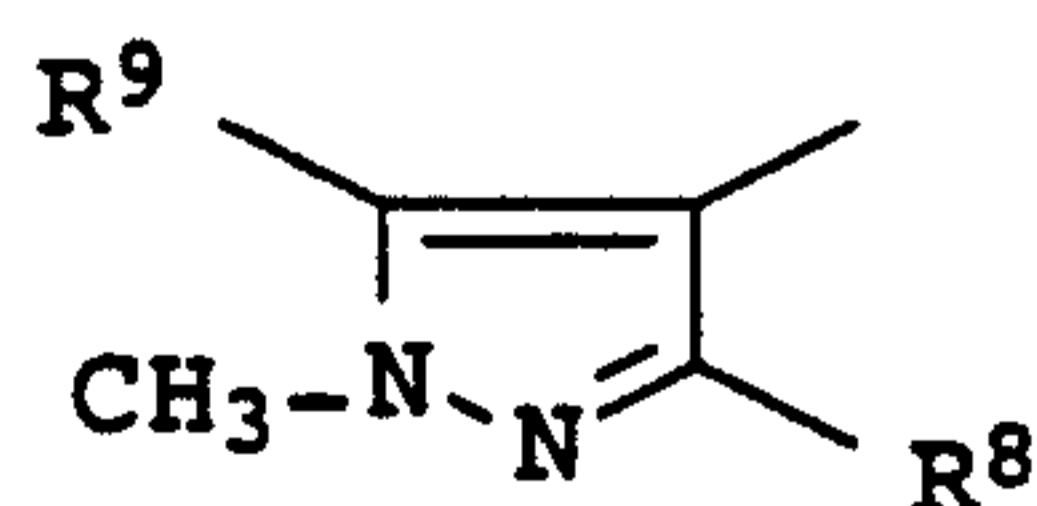
(A5)



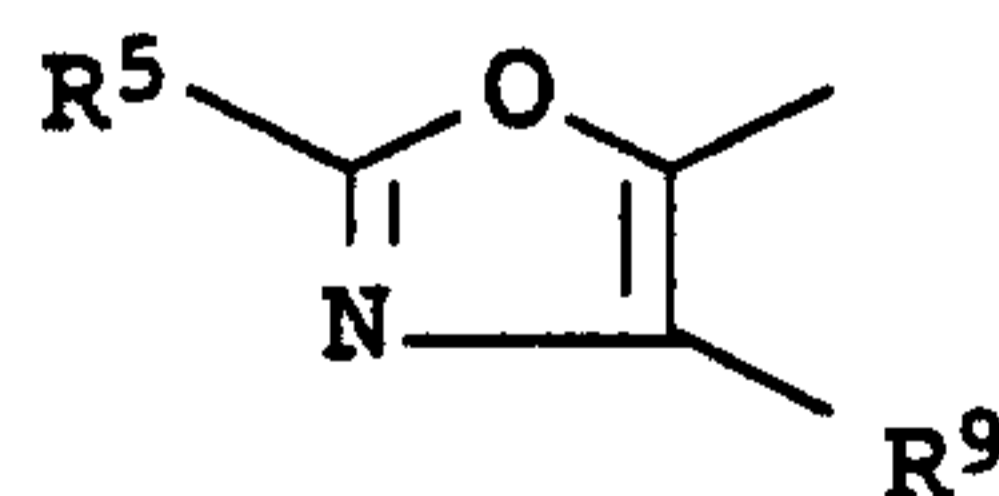
(A6)

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(A7)

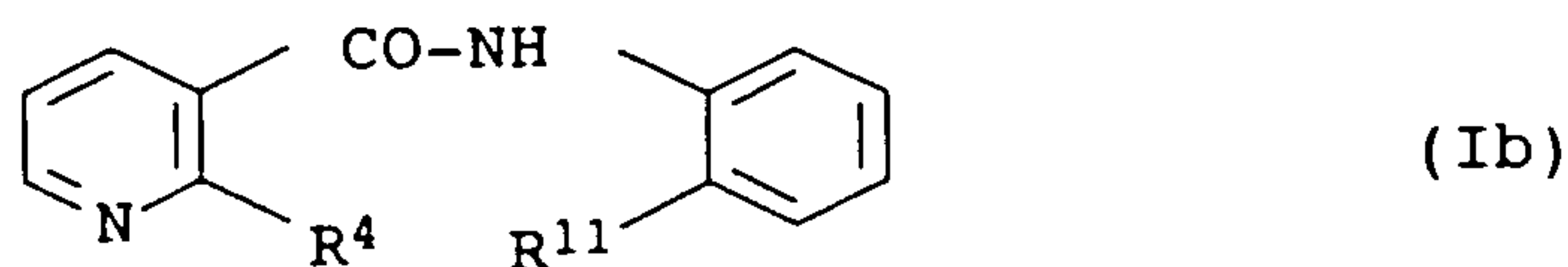


(A8)

45

- X is methylene, sulfur, sulfonyl or sulfonyl (SO₂),
 R³ is methyl, difluoromethyl, trifluoromethyl, chlorine, bromine or iodine,
 R⁴ is trifluoromethyl or chlorine,
 R⁵ is hydrogen or methyl,
 R⁶ is methyl, difluoromethyl, trifluoromethyl or chlorine,
 R⁷ is hydrogen, methyl or chlorine,
 R⁸ is methyl, difluoromethyl or trifluoromethyl,
 R⁹ is hydrogen, methyl, difluoromethyl, trifluoromethyl or chlorine,
 10 R¹⁰ is C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄-alkylthio or halogen.

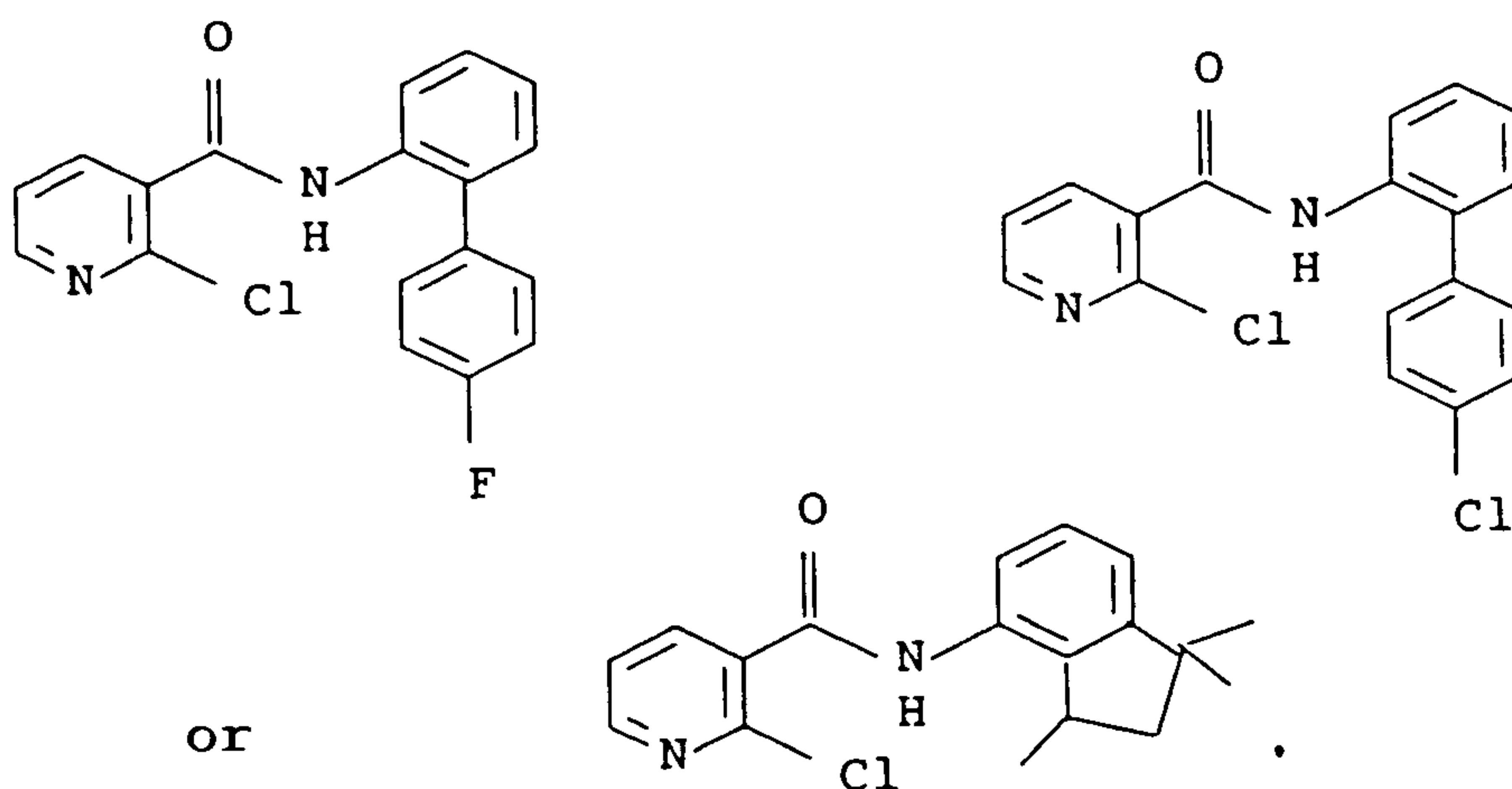
According to a particularly preferred embodiment, the compositions comprise as amide compound a compound of the formula Ib



in which

- 20 R⁴ is halogen and
 R¹¹ is phenyl which is substituted by halogen.

Preferably also, the amide compound can be of the formula :

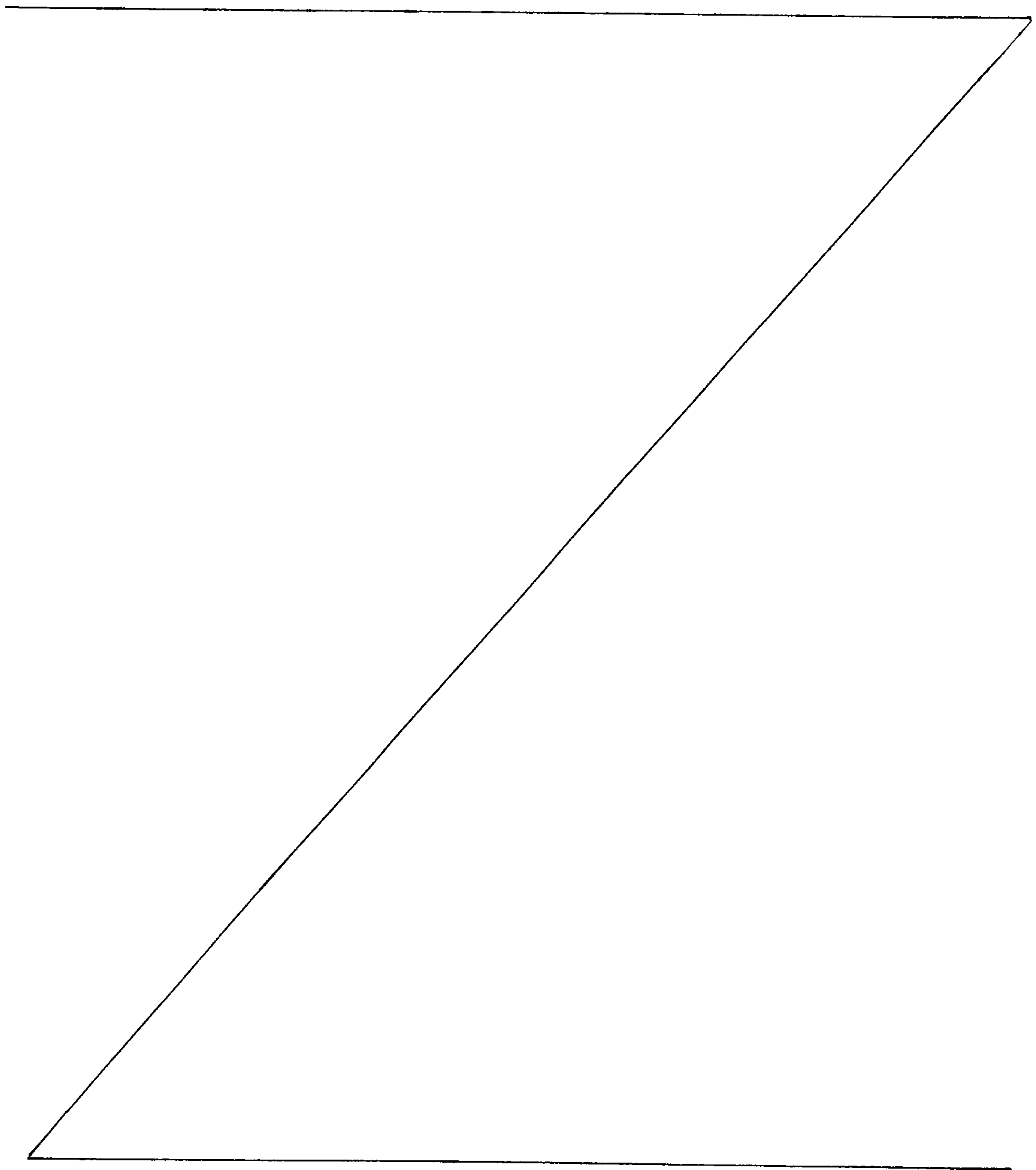


11a

Useful amide compounds of the formula I are mentioned in EP-A-545 099 and 589 301.

The preparation of the amide compounds of the formula I is known, for example, from EP-A-545 099 or 589 301 or can be carried out by similar processes.

Particularly preferred components b) are the compounds IIa of Table 1 below.

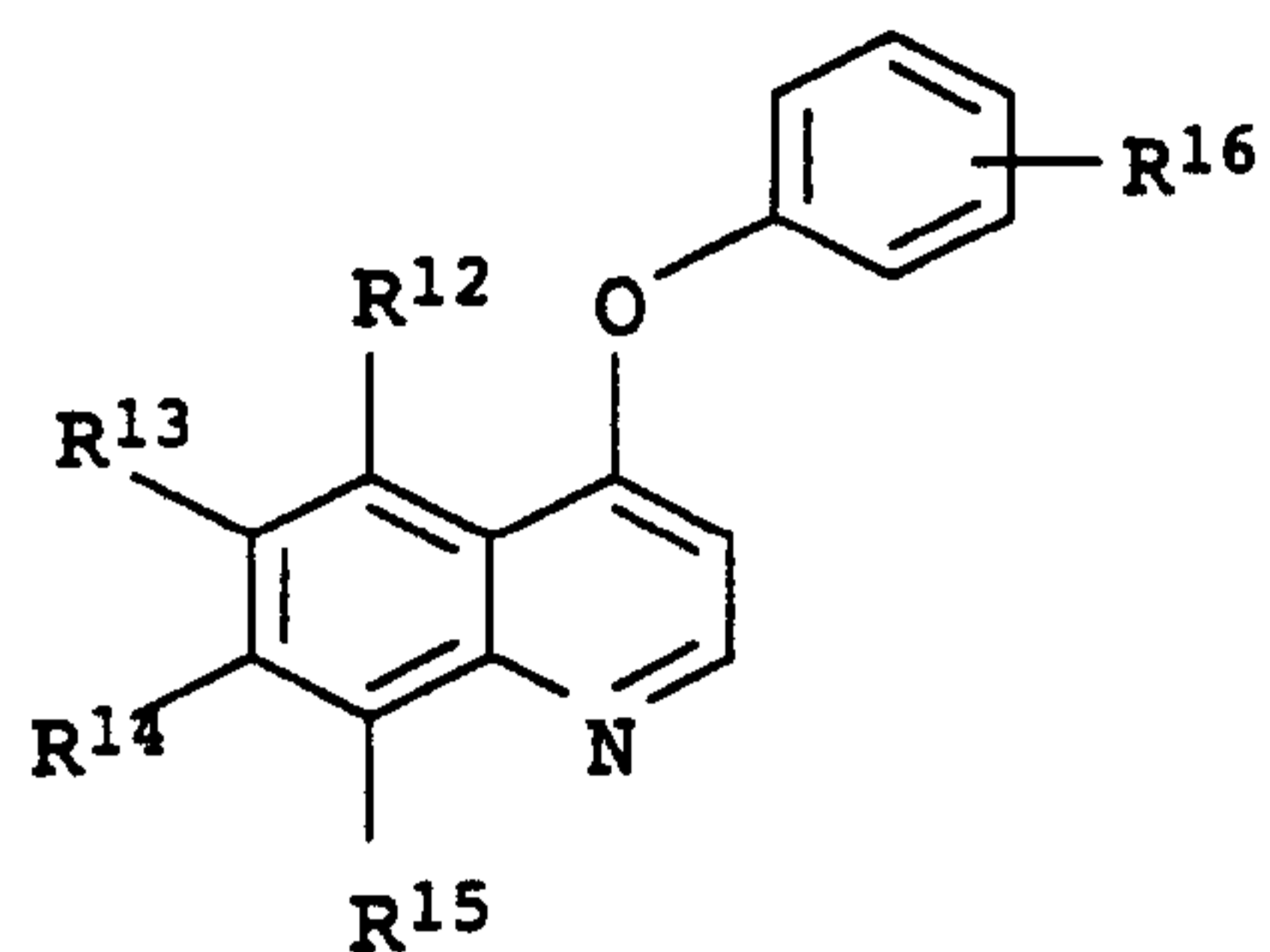


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Table 1

5



(IIa)

10

No.	R ¹²	R ¹³	R ¹⁴	R ¹⁵	R ¹⁶	
15	II.1	H	H	Cl	H	2-F
	II.2	H	H	Cl	H	2-C(CH ₃) ₃
	II.3	H	H	Cl	H	2-CH ₃
	II.4	H	H	Cl	H	2-OCH ₃
	II.5	H	H	Cl	H	3-F
20	II.6	H	H	Cl	H	3-Cl
	II.7	H	H	Cl	H	3-CF ₃
	II.8	H	H	Cl	H	3-CN
	II.9	H	H	Cl	H	3-OCH ₃
25	II.10	H	H	Cl	H	3-phenyl
	II.11	H	H	Cl	H	4-Cl
	II.12	H	H	Cl	H	4-Br
	II.13	H	H	Cl	H	4-CF ₃
	II.14	H	H	Cl	H	4-CH ₃
30	II.15	H	H	Cl	H	4-CH(CH ₃) ₂
	II.16	H	H	Cl	H	4-CN
	II.17	H	H	Cl	H	2-Cl-4-F
	II.18	H	H	Cl	H	2,4-di-Br
35	II.19	H	H	Cl	H	2,4-di-NO ₂
	II.20	H	H	Cl	H	2-CH ₃ -4-F
	II.21	H	H	Cl	H	2,6-di-F
	II.22	H	H	Cl	H	2,4,6-tri-CH ₃
40	II.23	F	H	H	H	4-F
	II.24	Cl	H	H	H	4-F
	II.25	NO ₂	H	H	H	4-F
	II.26	H	F	H	H	4-F
45	II.27	H	Cl	H	H	4-F
	II.28	H	CH ₃	H	H	4-F
	II.29	H	NO ₂	H	H	4-F

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No.	R12	R13	R14	R15	R16	
5	II.30	H	OC ₂ H ₅	H	H	4-F
	II.31	H	H	F	H	4-F
	II.32	H	H	Cl	H	4-F
	II.33	H	H	Br	H	4-F
	II.34	H	H	NO ₂	H	4-F
	II.35	H	H	OCF ₃	H	4-F
10	II.36	H	H	C ₂ H ₅	H	4-F
	II.37	H	H	SCF ₃	H	4-F
	II.38	H	H	O-C ₂ H ₅	H	4-F
	II.39	H	H	H	F	4-F
	II.40	H	H	H	Cl	4-F
15	II.41	H	H	H	CF ₃	4-F
	II.42	F	H	F	H	4-F
	II.43	O-CH ₃	H	O-CH ₃	H	4-F
	II.44	Cl	F	H	H	4-F
20	II.45	Cl	Cl	H	H	4-F
	II.46	Cl	CH ₃	H	H	4-F
	II.47	H	Br	H	Cl	4-F
	II.48	H	Cl	H	OH	4-F
25	II.49	H	O-CH ₃	H	NO ₂	4-F
	II.50	H	F	Cl	H	4-F
	II.51	H	CH ₃	Cl	H	4-F
	II.52	H	H	Cl	Cl	4-F
	II.53	Cl	H	H	Cl	4-F
30	II.54	Cl	F	Cl	H	4-F
	II.55	H	H	Cl	CN	4-F
	II.56	Cl	CH ₃	Cl	H	4-F
	II.57	Cl	Cl	Cl	H	4-F
35	II.58	Cl	Cl	Cl	Cl	4-F
	II.59	H	H	H	Cl	2-F-4-Br
	II.60	H	H	H	Cl	2,3-di-CH ₃
	II.61	H	H	H	Cl	2-F-4-Cl
40	II.62	H	H	H	Cl	2,4-di-Cl-6-F
	II.63	H	H	H	Cl	2,4-di-F
	II.64	H	H	H	Cl	2,4-di-CH ₃
	II.65	H	H	H	Cl	2-C ₂ H ₅
45	II.66	H	H	H	Cl	2-CH ₃ -4-F
	II.67	H	H	H	Cl	3-CH ₃ -4-Cl
	II.68	H	H	Cl	H	H

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No.	R ¹²	R ¹³	R ¹⁴	R ¹⁵	R ¹⁶
II.69	Cl	H	Cl	H	H
II.70	H	H	Cl	H	4-C(CH ₃) ₃

5

Very particular preference is given to the compounds IIa of Table 2 and to the hydrochloride and the N-oxide of the compound 2.78 mentioned therein.

10

Table 2

No.	R ¹²	R ¹³	R ¹⁴	R ¹⁵	R ¹⁶
15 II.71	H	H	Cl	H	2-Cl
II.72	H	H	Cl	H	2-Br
II.73	H	H	Cl	H	2-CN
20 II.74	H	H	Cl	H	2-CF ₃
II.75	H	H	Cl	H	2-NO ₂
II.76	H	H	Cl	H	4-F
II.77	H	H	Cl	H	2,4-di-F
25 II.78	Cl	H	Cl	H	4-F
II.79	H	H	H	Cl	2-Cl-4-F
II.80	CH ₃	H	CH ₃	H	4-F

30 The compounds of the formula IIa mentioned in or in connection with Tables 1 and 2 are known from US-A 5 240 940 and/or ACS Sympos. Ser. 443, page 538 to page 552 (1991).

35 Among the compounds of the formula III, preference is given to those in which X¹ is a C₁-C₄-haloalkyl, in particular a trifluoromethyl, group and X² and X³ are a hydrogen atom or a halogen group, in particular a hydrogen atom. X⁴ and X⁵ are preferably hydrogen, halogen (in particular Cl or F), C₁-C₄-alkoxy (in particular methoxy or ethoxy), C₁-C₄-alkylthio (in particular methylthio or ethylthio), C₁-C₄-haloalkyl (in particular trifluoromethyl) or C₁-C₄-haloalkoxy (in particular trifluoromethoxy).

45 Preferred substituents R¹⁹ are C₁-C₄-alkyl (methyl, ethyl, n- and i-propyl and t-butyl), C₁-C₄-alkylene-C₃-C₇-cycloalkyl, C₁-C₄-alkenyl (in particular ethenyl, propenyl and butenyl, which

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15

may be substituted in particular with halogen (preferably Cl)), propynyl, cyanomethyl and methoxymethyl. Among the C₁-C₄-alkylene-C₃-C₇-cycloalkyl substituents, particular preference is given to methylene-substituted compounds, in particular methylenecyclopropyl, methylenecyclopentyl, methylenecyclohexyl and methylenecyclohexenyl. The rings in these substituents may be substituted preferably with halogen.

Substituents R²⁰ that may be mentioned in addition to phenyl are in particular (substituted or unsubstituted) thienyl, pyrazolyl, pyrrolyl, imidazolyl, thiazolyl, furyl, pyridazinyl and pyrimidinyl. Preferred substituents on these ring systems are halogen (in particular F and Cl), C₁-C₄-alkoxy (in particular methoxy) and C₁-C₄-alkyl (in particular methyl, ethyl). The number of the ring substituents may be from 1 to 3, in particular from 1 to 2. Particular preference is given to phenyl or substituted phenyl.

Preferred substituents R²¹ and R²² are hydrogen, F, Cl, methyl, ethyl, methoxy, thiomethyl and N-methylamino. R³ and R⁴ together may also form a grouping =O.

Preferred compounds of the formula III are shown in the tables of WO 96/019442, which has already been mentioned. Among these, particular preference is given in particular to the compounds listed in Table 3 below (R²¹ and R²² are each hydrogen).

Table 3:

No.	X ¹	X ²	X ³	X ⁴	X ⁵	R ¹⁹	R ²⁰
III.1	CF ₃	H	H	H	H	ethyl	Ph-4-OMe
III.2	CF ₃	H	H	H	H	methyl	Ph-4-OMe
III.3	CF ₃	H	H	H	H	-CH ₂ -cPr	2-thienyl
III.4	CF ₃	H	H	H	H	-CH ₂ -cPr	3-thienyl
III.5	CF ₃	H	H	H	H	-CH ₂ -cPr	Ph-2,4-F ₂
III.6	CF ₃	H	H	H	H	-CH ₂ -cPr	Ph-2-F
III.7	CF ₃	H	H	H	H	-CH ₂ -cPr	Ph-2-F-4-OMe
III.8	CF ₃	H	H	H	H	-CH ₂ -cPr	Ph-3-Me
III.9	CF ₃	H	H	H	H	-CH ₂ -cPr	Ph-3-Me-4-OMe
III.10	CF ₃	H	H	H	H	-CH ₂ -cPr	Ph-4-F
III.11	CF ₃	H	H	H	H	-CH ₂ -cPr	Ph-4-Me
III.12	CF ₃	H	H	H	H	-CH ₂ -cPr	Ph-4-OMe
III.13	CF ₃	H	H	H	H	-CH ₂ -cPr	Ph
III.14	CF ₃	H	H	H	H	-CH ₂ -CH=CH ₂	Ph

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No.	X ¹	X ²	X ³	X ⁴	X ⁵	R ¹⁹	R ²⁰	
5	III.15	CF ₃	H	H	H	H	-CH ₂ -CH=CH ₂	Ph-4-OMe
	III.16	CF ₃	H	H	H	H	-CH ₂ -CH=CCl ₂	Ph-4-OMe
	III.17	CF ₃	H	H	H	F	-CH ₂ -CH ₃	Ph-4-OMe
	III.18	CF ₃	H	H	H	F	-CH ₂ CH ₃	Ph
	III.19	CF ₃	H	H	H	F	-CH ₃	Ph-4-OMe
10	III.20	CF ₃	H	H	H	F	-CH ₂ -cPr	Ph
	III.21	CF ₃	H	H	H	F	-CH ₂ -cPr	Ph-2-F
	III.22	CF ₃	H	H	H	F	-CH ₂ -cPr	Ph-2,4-F ₂
	III.23	CF ₃	H	H	H	F	-CH ₂ -cPr	Ph-2-F-3-Me
	III.24	CF ₃	H	H	H	F	-CH ₂ -cPr	Ph-2-F-4-OMe
15	III.25	CF ₃	H	H	H	F	-CH ₂ -cPr	Ph-3,5-Me ₂
	III.26	CF ₃	H	H	H	F	-CH ₂ -cPr	3-methylpyrazol-1-yl
	III.27	CF ₃	H	H	H	F	-CH ₂ -cPr	3-methyl-2-thienyl
	III.28	CF ₃	H	H	H	F	-CH ₂ -cPr	2-thienyl
	III.29	CF ₃	H	H	H	F	-CH ₂ -cPr	3-thienyl
20	III.30	CF ₃	H	H	H	F	-CH ₂ -CHF ₂	Ph-4-OMe
	III.31	CF ₃	H	H	H	F	-CH ₂ -OCH ₃	Ph-4-OMe
	III.32	CF ₃	H	H	H	F	-CH ₂ -OCH ₃	Ph
	III.33	CF ₃	H	H	H	F	-CH ₂ CN	Ph-4-Ome
	III.34	CF ₃	H	H	H	F	-CH ₂ CN	Ph
25	III.35	CF ₃	H	H	H	F	-CH ₂ -C≡CH	Ph
	III.36	CF ₃	H	H	H	F	-CH ₂ -C≡CH	Ph-4-OMe
	III.37	CF ₃	H	H	H	F	-CH ₂ -C≡CH	Ph-2-F
	III.38	CF ₃	H	H	H	F	-CH ₂ -C≡CH	Ph-4-Me
	III.39	CF ₃	H	H	H	F	-CH ₂ -C≡CH	2-thienyl
30	III.40	CF ₃	H	H	H	F	-CH ₂ -C≡CH	Ph-2-F-4-OMe
	III.41	CF ₃	H	H	H	F	i-propyl	Ph
	III.42	CF ₃	H	H	H	F	n-butyl	Ph
	III.43	CF ₃	H	H	H	F	n-propyl	Ph
	III.44	CF ₃	H	H	H	F	t-butyl	Ph
35	III.45	CF ₃	H	H	H	Cl	-CH ₃	
	III.46	CF ₃	H	H	H	Cl	-CH ₂ CN	Ph-4-OMe
	III.47	CF ₃	H	H	H	Cl	-CH ₂ -OMe	Ph-4-OMe
	III.48	CF ₃	H	H	H	Cl	-CH ₂ -cPr	Ph
	III.49	CF ₃	H	H	H	Cl	-CH ₂ -cPr	3-methylpyrazol-1-yl
40	III.50	CF ₃	H	H	H	Cl	-CH ₂ -cPr	2-thienyl
	III.51	CF ₃	H	H	H	Cl	-CH ₂ -cPr	Ph-2,4-F ₂

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No.	X ¹	X ²	X ³	X ⁴	X ⁵	R ¹⁹	R ²⁰	
5	III.52	CF ₃	H	H	H	Cl	-CH ₂ -C≡CH	Ph-4-OMe
	III.53	CF ₃	H	H	H	CF ₃	-CH ₃	Ph-4-OMe
	III.54	CF ₃	H	H	H	CF ₃	-CH ₂ CH ₂ Cl	Ph-4-OMe
	III.55	CF ₃	H	H	H	CF ₃	-CH ₂ -cPr	2-thienyl
	III.56	CF ₃	H	H	H	CF ₃	-CH ₂ -cPr	Ph-2-F-5-Me
	III.57	CF ₃	H	H	H	CF ₃	-CH ₂ -cPr	Ph-4-OMe
10	III.58	CF ₃	H	H	H	CF ₃	-CH ₂ -cPr	Ph
	III.59	CF ₃	H	H	H	OCH ₃	-CH ₂ CH ₃	Ph-4-OMe
	III.60	CF ₃	H	H	H	OCH ₃	-CH ₂ -cPr	Ph-4-OMe
	III.61	CF ₃	H	H	H	OCH ₃	-CH ₂ -cPr	Ph
	III.62	CF ₃	H	H	H	SCH ₃	-CH ₂ -cPr	Ph
15	III.63	CF ₃	H	H	H	SCH ₃	-CH ₂ -cPr	Ph-4-Ome
	III.64	CF ₃	H	H	Cl	F	-CH ₂ -CH ₂ Cl	Ph
	III.65	CF ₃	H	H	Cl	F	-CH ₂ -CH=CH ₂	Ph-4-OMe
	III.66	CF ₃	H	H	Cl	F	-CH ₂ -cPr	2-thienyl
20	III.67	CF ₃	H	H	Cl	F	-CH ₂ -cPr	Ph-2-F
	III.68	CF ₃	H	H	Cl	F	-CH ₂ -cPr	Ph
	III.69	CF ₃	H	H	Cl	F	-CH ₂ -cPr	Ph-2-F-5-Me
	III.70	CF ₃	H	H	Cl	Cl	-CH ₂ -CH=CH ₂	Ph-4-OMe
25	III.71	CF ₃	H	H	Cl	Cl	-CH ₂ CH ₂ Cl	Ph
	III.72	CF ₃	H	H	Cl	Cl	-CH ₂ CH ₃	Ph-2-F-5-Me
	III.73	CF ₃	H	H	Cl	Cl	-CH ₂ -cPr	Ph-3,5-Me ₂
	III.74	CF ₃	H	H	SCH ₃	F	-CH ₂ -cPr	Ph-4-OMe
30	III.75	CF ₃	H	H	OCH ₃	F	-CH ₂ -cPr	Ph-4-OMe
	III.76	CF ₃	H	F	H	H	-CH ₂ -cPr	Ph
	III.77	CF ₃	H	F	H	H	-CH ₂ -CH ₃	Ph-4-OMe
	III.78	CF ₃	H	H	F	F	-CH ₂ CH ₃	Ph
	III.79	CF ₃	H	H	F	F	-CH ₂ -CH ₂ Cl	Ph-2-F-5-Me
35	III.80	CF ₃	H	H	F	F	-CH ₂ -OCH ₃	Ph-4-OMe
	III.81	CF ₃	H	H	F	F	-CH ₂ -cPr	Ph
	III.82	CF ₃	H	H	F	F	-CH ₂ -cPr	3-methylpyrazol-1-yl
40	III.83	CF ₃	H	H	F	F	-CH ₂ -cPr	3-methyl-2-thienyl
	III.84	CF ₃	H	H	F	F	-CH ₂ -cPr	Ph-2-F-3-Me
	III.85	CF ₃	H	H	F	F	-CH ₂ -cPr	Ph-2-F-4-OMe
	III.86	CF ₃	H	H	F	F	-CH ₂ -cPr	Ph-2-F-5-Me
45	III.87	CF ₃	H	H	F	F	-CH ₂ -cPr	Ph-4-OMe
	III.88	CF ₃	H	H	F	F	-CH ₂ -cPr	Ph-4F
	III.89	CF ₃	H	H	F	F	i-propyl	Ph-4-OMe

No.	X ¹	X ²	X ³	X ⁴	X ⁵	R ¹⁹	R ²⁰
III.90	CF ₃	H	H	F	F	n-butyl	Ph-4-OMe
III.91	CF ₃	H	H	F	F	-CH ₂ -C≡CH	Ph-4-OMe
III.92	CF ₃	H	H	CF ₃	F	-CH ₃	Ph-4-OMe
III.93	CF ₃	H	H	CF ₃	F	-CH ₂ -CH=CH ₂	Ph
III.94	CF ₃	H	H	CF ₃	F	-CH ₂ -cPr	Ph
III.95	CF ₃	H	H	Cl	Cl	-CH ₂ -CH _x e-3	Ph
III.96	CF ₃	H	H	F	H	-CH ₂ -cPr	Ph-4-F
III.97	CF ₃	H	H	Cl	Cl	-CH ₂ -cHex	Ph
III.98	CF ₃	H	H	H	F	-CH ₂ -SCH ₃	Ph
III.99	CF ₃	H	H	H	F	-CH ₂ -SOCH ₃	Ph
III.100	CF ₃	H	H	H	F	-CH ₂ -SO ₂ CH ₃	Ph
III.101	CF ₃	H	H	H	F	-CH ₂ -NHMe	Ph
III.102	CF ₃	H	H	H	F	CH ₂ -CONH ₂	Ph
III.103	CF ₃	H	H	H	F	CH ₂ CON(CH ₃) ₂	Ph

10

In the above table, cPr is cyclopropyl, cH_xe-n is cyclohexenyl which is unsaturated in position n, c-Hex is cyclohexyl and Ph is phenyl.

20

Particular preference is given to compounds III in which R¹⁹ is a radical CH₂-cPr and R²⁰ is a phenyl radical with or without substitution. Among these, preference is given to the compounds in which X⁴ and X⁵ are halogen, preferably F.

The physical data of these compounds and processes for their preparation are given in WO 96/19442, which has already been mentioned.

30

To unfold the synergistic activity, even a small amount of the amide compound of the formula I is sufficient. Preference is given to employing amide compound and active ingredient of the formula II and/or III in a weight ratio in the range of from 50:1 to 1:50, in particular from 10:1 to 1:10. It is also possible here to employ ternary mixtures which, in addition to amide compounds I, comprise both compounds II and compounds III. In such mixtures, the mixing ratio of the compounds II and III with each other is usually in the range of from 50:1 to 1:50, preferably from 10:1 to 1:10.

Owing to the basic character of their nitrogen atoms, the compounds II are capable of forming salts or adducts with inorganic or organic acids or with metal ions.

Examples of inorganic acids are hydrohalic acids such as hydrofluoric acid, hydrochloric acid, hydrobromic acid and hydriodic acid, sulfuric acid, phosphoric acid and nitric acid.

10 Suitable organic acids are, for example, formic acid, carbonic acid and alkanolic acids, such as acetic acid, trifluoroacetic acid, trichloroacetic acid and propionic acid, and also glycolic acid, thiocyanic acid, lactic acid, succinic acid, citric acid, benzoic acid, cinnamic acid, oxalic acid, alkylsulfonic acids (sulfonic acids having straight-chain or branched alkyl radicals of 1 to 20 carbon atoms), arylsulfonic acids or aryldisulfonic acids (aromatic radicals, such as phenyl and naphthyl, which carry one or two sulfo groups), alkylphosphonic acids (phosphonic acids having straight-chain or branched alkyl radicals of 1 to 20 carbon atoms), arylphosphonic acids or aryldiphosphonic acids (aromatic radicals, such as phenyl and naphthyl, which carry one or two phosphoric acid radicals), it being possible for the alkyl or aryl radicals to carry further substituents, eg. p-toluenesulfonic acid, salicylic acid, p-aminosalicylic acid, 2-phenoxybenzoic acid, 2-acetoxybenzoic acid, etc.

20 Suitable metal ions are, in particular, the ions of the elements of the first to eighth sub-group, in particular chromium, manganese, iron, cobalt, nickel, copper, zinc and furthermore of the second main group, in particular calcium and magnesium, and of the third and fourth main group, in particular aluminum, tin and lead. The metals can exist in the various valencies which they can assume.

When preparing the mixtures, it is preferred to employ the pure active ingredients I and II [lacuna], to which further active ingredients against harmful fungi or other pests, such as insects, arachnids or nematodes, or else herbicidal or growth-regulating active ingredients or fertilizers can be admixed.

30

The mixtures of the compounds I and II and/or III, or the

compounds I and II and/or III used simultaneously, jointly or separately, exhibit outstanding activity against a wide range of phytopathogenic fungi, in particular from the classes of the Ascomycetes, Basidiomycetes, Phycomycetes and Deuteromycetes.

Some of them act systemically and can therefore be employed as foliar- and soil-acting fungicides.

10 They are especially important for controlling a large number of fungi in a variety of crop plants, such as cotton, vegetable species (eg. cucumbers, beans, tomatoes, potatoes and cucurbits), barley, grass, oats, bananas, coffee, maize, fruit species, rice, rye, soya, grapevine, wheat, ornamentals, sugar cane, and a variety of seeds.

20 They are particularly suitable for controlling the following phytopathogenic fungi: *Erysiphe graminis* (powdery mildew) in cereals, *Erysiphe cichoracearum* and *Sphaerotheca fuliginea* in cucurbits, *Podosphaera leucotricha* in apples, *Uncinula necator* in grapevines, *Puccinia* species in cereals, *Rhizoctonia* species in cotton, rice and lawns, *Ustilago* species in cereals and sugar cane, *Venturia inaequalis* (scab) in apples, *Helminthosporium* species in cereals, *Septoria nodorum* in wheat, *Botrytis cinera* (gray mold) in strawberries, vegetables, ornamentals and grapevines, *Cercospora arachidicola* in groundnuts, *Pseudocercospora herpotrichoides* in wheat and barley, *Pyricularia oryzae* in rice, *Phytophthora infestans* in potatoes and tomatoes, *Plasmopara viticola* in grapevines, *Pseudoperonospora* species in hops and cucumbers, *Alternaria* species in vegetables and fruit, *Mycosphaerella* species in bananas and *Fusarium* and *Verticillium* species.

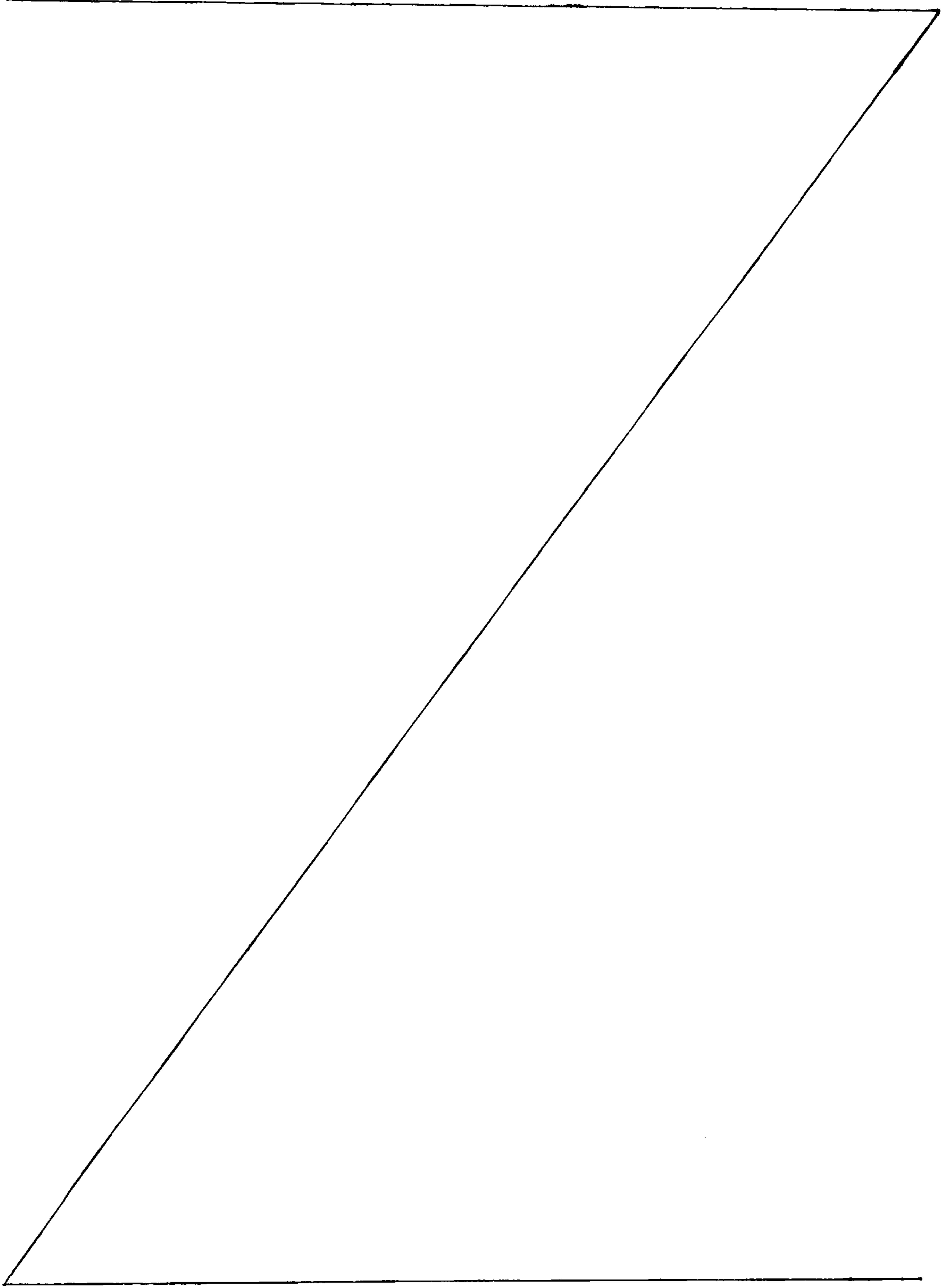
The mixtures according to the invention may particularly preferably be employed for controlling powdery mildew fungi in crops of grapevines and vegetables, and also in ornamentals and cereals.

30 The compounds I and II and/or III can be applied simultaneously, either together or separately, or in succession, the sequence, in the case of separate application, generally not having any effect on the result of the control measures.

Depending on the kind of effect desired, the application rates of

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the mixtures according to the invention are, in particular in agricultural crop areas, from 0.01 to 8 kg/ha, preferably 0.1 to 5 kg/ha, in particular 0.2 to 3.0 kg/ha.



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The application rates of the compounds I are from 0.01 to 2.5 kg/ha, preferably 0.05 to 2.5 kg/ha, in particular 0.1 to 1.0 kg/ha.

- 5 Correspondingly, in the case of the compounds II and/or III, the application rates are from 0.001 to 5 kg/ha, preferably 0.005 to 2 kg/ha, in particular 0.01 to 1.0 kg/ha.
- 10 For seed treatment, the application rates of the mixture are generally from 0.001 to 250 g/kg of seed, preferably 0.01 to 100 g/kg, in particular 0.01 to 50 g/kg.

15 If phytopathogenic harmful fungi are to be controlled, the separate or joint application of the compounds I and II and/or III or of the mixtures of the compounds I and II and/or III is effected by spraying or dusting the seeds, the plants or the soils before or after sowing of the plants, or before or after plant emergence.

20 The fungicidal synergistic mixtures according to the invention, or the compounds I and II and/or III, can be formulated for example in the form of ready-to-spray solutions, powders and suspensions or in the form of highly concentrated aqueous, oily
25 or other suspensions, dispersions, emulsions, oil dispersions, pastes, dusts, materials for broadcasting or granules, and applied by spraying, atomizing, dusting, broadcasting or watering. The use form depends on the intended purpose; in any case, it should ensure as fine and uniform as possible a
30 distribution of the mixture according to the invention.

The formulations are prepared in a known manner, eg. by extending the active ingredient with solvents and/or carriers, if desired using emulsifiers and dispersants, it being possible also to use
35 other organic solvents as auxiliary solvents if water is used as the diluent. Suitable auxiliaries for this purpose are essentially: solvents such as aromatics (eg. xylene), chlorinated aromatics (eg. chlorobenzenes), paraffins (eg. mineral oil fractions), alcohols (eg. methanol, butanol), ketones (eg.
40 cyclohexanone), amines (eg. ethanolamine, dimethylformamide) and water; carriers such as ground natural minerals (eg. kaolins, clays, talc, chalk) and ground synthetic minerals (eg. finely divided silica, silicates); emulsifiers such as nonionic and anionic emulsifiers (eg. polyoxyethylene fatty alcohol ethers,
45 alkylsulfonates and arylsulfonates) and dispersants such as lignosulfite waste liquors and methylcellulose.

Suitable surfactants are the alkali metal salts, alkaline earth metal salts and ammonium salts of aromatic sulfonic acids, eg. ligno-, phenol-, naphthalene- and dibutylnaphthalenesulfonic acid, and of fatty acids, alkyl- and alkylarylsulfonates, alkyl, lauryl ether and fatty alcohol sulfates, and salts of sulfated hexa-, hepta- and octadecanols, or of fatty alcohol glycol ethers, condensates of sulfonated naphthalene and its derivatives with formaldehyde, condensates of naphthalene or of the naphthalenesulfonic acids with phenol and formaldehyde, polyoxyethylene octylphenol ether, ethoxylated isoctyl-, octyl- or nonylphenol, alkylphenol polyglycol ethers, tributylphenyl polyglycol ethers, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers or polyoxypropylene, lauryl alcohol polyglycol ether acetate, sorbitol esters, lignosulfite waste liquors or methylcellulose.

Powders, materials for broadcasting and dusts can be prepared by mixing or jointly grinding the compounds I or II and/or III, or the mixture of the compounds I and II and/or III, with a solid carrier.

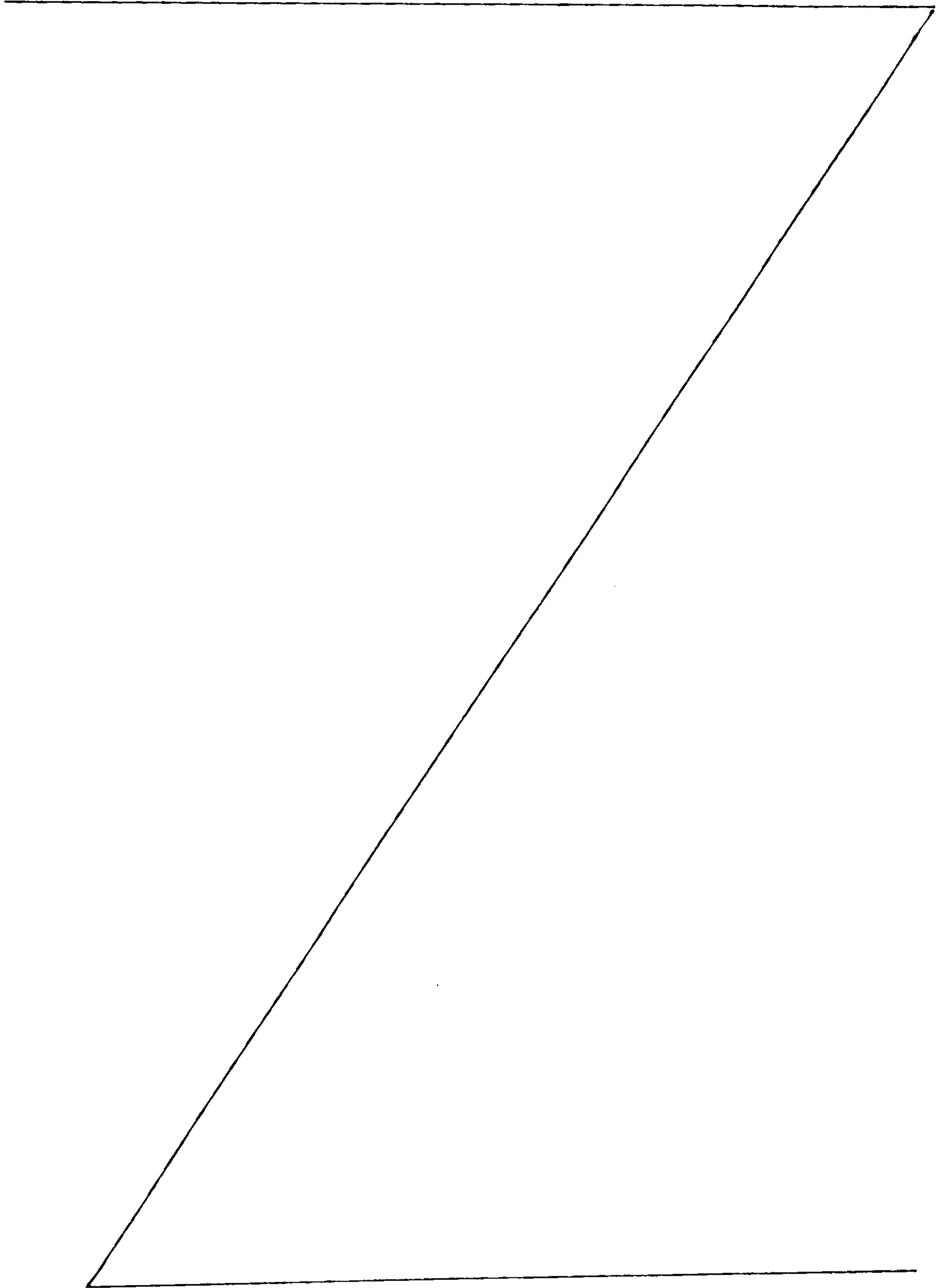
Granules (eg. coated granules, impregnated granules or homogeneous granules) are usually prepared by binding the active ingredient, or active ingredients, to a solid carrier.

Fillers or solid carriers are, for example, mineral earths, such as silica gel, silicas, silica gels, silicates, talc, kaolin, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials and fertilizers, such as ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders or other solid carriers.

The formulations generally comprise from 0.1 to 95% by weight, preferably 0.5 to 90% by weight, of one of the compounds I or II and/or III or of the mixture of the compounds I and II and/or III. The active ingredients are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR or HPLC) spectrum.

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The compounds I and II and/or III, the mixtures, or the corresponding formulations, are applied by treating the harmful fungi, their habitat, or the plants, seeds, soils, areas,



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materials or spaces to be kept free from them with a fungicidally effective amount of the mixture, or of the compounds I and II and/or III in the case of separate application.

- 5 Application can be effected before or after infection by the harmful fungi.

Examples of such preparations comprising the active ingredients
10 are:

- I. A solution of 90 parts by weight of the active ingredients and 10 parts by weight of N-methylpyrrolidone; this solution is suitable for use in the form of microdrops;
- 15 II. A mixture of 20 parts by weight of the active ingredients, 80 parts by weight of xylene, 10 parts by weight of the adduct of 8 to 10 mol of ethylene oxide to 1 mol of oleic acid N-monoethanolamide, 5 parts by weight of the calcium salt of dodecylbenzenesulfonate, 5 parts by weight of the
20 adduct of 40 mol of ethylene oxide and 1 mol of castor oil; a dispersion is obtained by finely distributing the solution in water;
- III. An aqueous dispersion of 20 parts by weight of the active
25 ingredients, 40 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 20 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil;
- IV. An aqueous dispersion of 20 parts by weight of the active
30 ingredients, 25 parts by weight of cyclohexanol, 65 parts by weight of a mineral oil fraction of boiling point 210 to 280°C, and 10 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil;
- V. A mixture, ground in a hammer mill, of 80 parts by weight
35 of the active ingredients, 3 parts by weight of the sodium salt of diisobutyl-naphthalene-1-sulfonate, 10 parts by weight of the sodium salt of a lignosulfonic acid from a sulfite waste liquor and 7 parts by weight of pulverulent silica gel; a spray mixture is obtained by finely
40 distributing the mixture in water;
- VI. An intimate mixture of 3 parts by weight of the active
45 ingredients and 97 parts by weight of finely divided kaolin; this dust comprises 3% by weight of active ingredient;
- VII. An intimate mixture of 30 parts by weight of the active ingredients, 92 parts by weight of pulverulent silica gel and 8 parts by weight of paraffin oil which had been

sprayed onto the surface of this silica gel; this formulation imparts good adhesion to the active ingredient;

- VIII. A stable aqueous dispersion of 40 parts by weight of the active ingredients, 10 parts by weight of the sodium salt of a phenolsulfonic acid/urea/formaldehyde condensate, 2 parts by weight of silica gel and 48 parts by weight of water; this dispersion may be diluted further;
- IX. A stable oily dispersion of 20 parts by weight of the active ingredients, 2 parts by weight of the calcium salt of dodecylbenzenesulfonate, 8 parts by weight of fatty alcohol polyglycol ether, 20 parts by weight of the sodium salt of a phenolsulfonic acid/urea/formaldehyde condensate and 88 parts by weight of a paraffinic mineral oil.

Use Example

The synergistic activity of the mixtures according to the invention can be demonstrated by the following experiments:

The active ingredients, separately or together, are formulated as a 10% emulsion in a mixture of 63% by weight of cyclohexanone and 27% by weight of emulsifier, and diluted with water to the desired concentration.

Evaluation is carried out by determining the infected leaf areas in percent. These percentages are converted into efficacies. The efficacy (W) is calculated as follows using Abbot's formula:

$$W = (1 - \alpha) \cdot 100 / \beta$$

α corresponds to the fungal infection of the treated plants in % and

β corresponds to the fungal infection of the untreated (control) plants in %

An efficacy of 0 means that the infection level of the treated plants corresponds to that of the untreated control plants; an efficacy of 100 means that the treated plants were not infected.

The expected efficacies of the mixtures of the active ingredients were determined using Colby's formula [R.S. Colby, Weeds 15, 20-22 (1967)] and compared with the observed efficacies.

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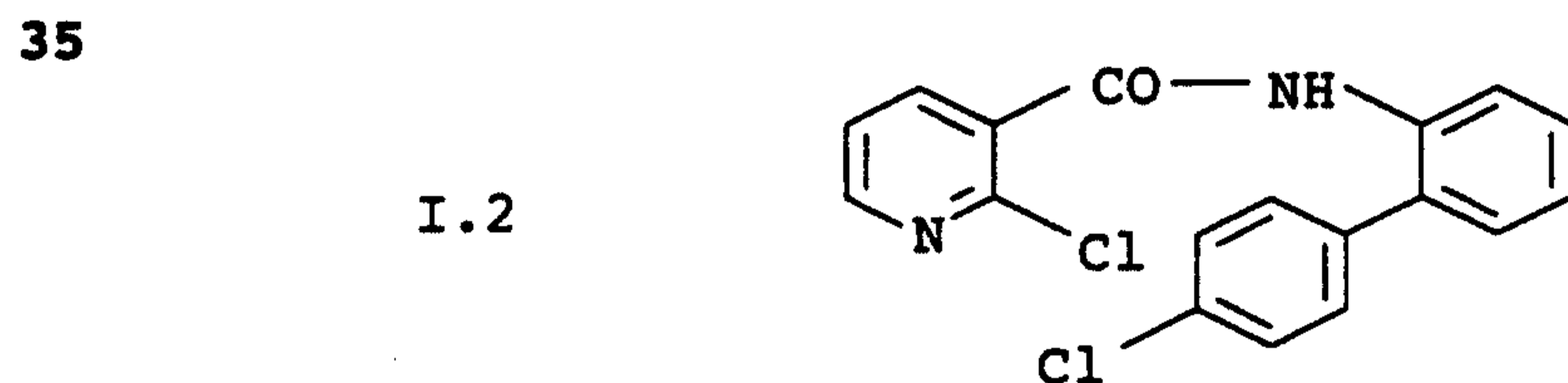
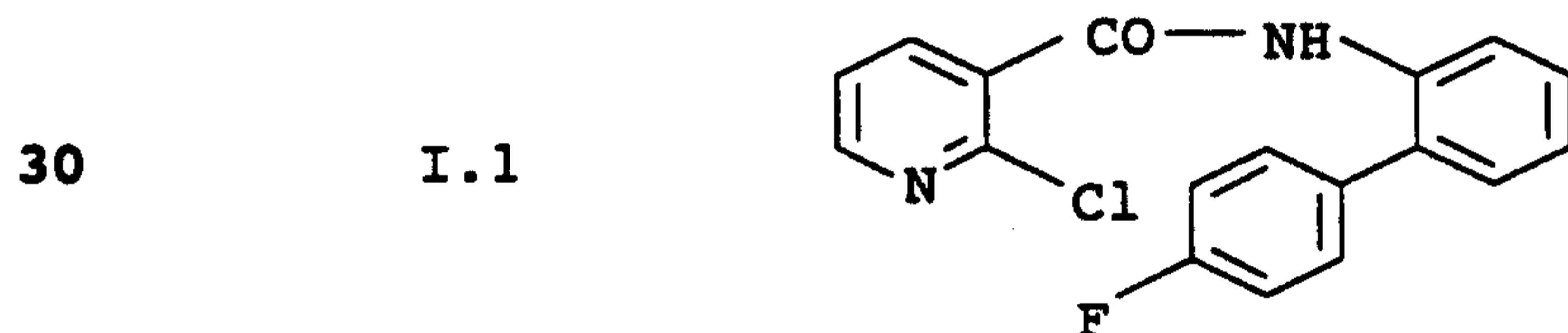
Colby formula: $E = x + y - x \cdot y / 100$

- 5 E expected efficacy, expressed in % of the untreated control, when using the mixture of the active ingredients A and B at the concentrations a and b
- x efficacy, expressed in % of the untreated control, when using active ingredient A at a concentration of a
- 10 y efficacy, expressed in % of the untreated control, when using active ingredient B at a concentration of b

Activity against powdery mildew of wheat

15 Leaves of potted weed seedlings of the variety "Frühgold" were sprayed to runoff point with an aqueous formulation of active ingredient prepared from a stock solution consisting of 10% of active ingredient, 63% of cyclohexanone and 27% of emulsifier. 24 hours after the spray coating had dried on, the leaves were dusted with spores of powdery mildew of wheat (*Erysiphe graminis* 20 *forma specialis tritici*). The test plants were subsequently kept in a greenhouse at 20-24°C and 60-90% relative atmospheric humidity. After 7 days, the extent of the mildew development was determined visually in % infection of the total leaf area.

25 The compounds of the formula I used were the following components:



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The results are shown in Tables 4 and 5 below.

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Table 4

Ex.	Active ingredient	Concentration of active ingredient in the spray liquor in ppm	Efficacy in % of the untreated control
5 1C	Control (untreated)	0 (98% infection)	0
2C	I.1	63 16	0 0
10 3C	I.2	63 16	0 0
4C	Compound II.78 from Table 2	1 0.25	0 0
15 5C	Compound III.17 from Table 3	0.25	85

Table 5

Ex.	Mixtures according to the invention (content in ppm)	Observed efficacy	Calculated efficacy*)
20 6	63 ppm I.1 + 1 ppm II.78	29	0
25 7	63 ppm I.2 + 1 ppm II.78	59	0
8	16 ppm I.2 + 0.25 ppm II.78	19	0
30 9	16 ppm I.1 + 0.25 ppm III.17	97	85
35 10	16 ppm I.2 + 0.25 ppm III.17	100	85

*) calculated using Colby's formula

The test results show that the observed efficacy is higher than
40 the efficacy which was calculated beforehand using Colby's
formula.

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WHAT IS CLAIMED IS:

1. A fungicidal mixture, comprising as active components

a) an amide compound of the formula I



in which

A is an aryl group or an aromatic or non-aromatic, 5- or 6-membered heterocycle which has from 1 to 3 hetero atoms selected from O, N and S;

where the aryl group or the heterocycle may or may not have 1, 2 or 3 substituents which are selected, independently of one another, from alkyl, halogen, CHF₂, CF₃, alkoxy, haloalkoxy, alkylthio, alkylsulfynyl and alkylsulfonyl;

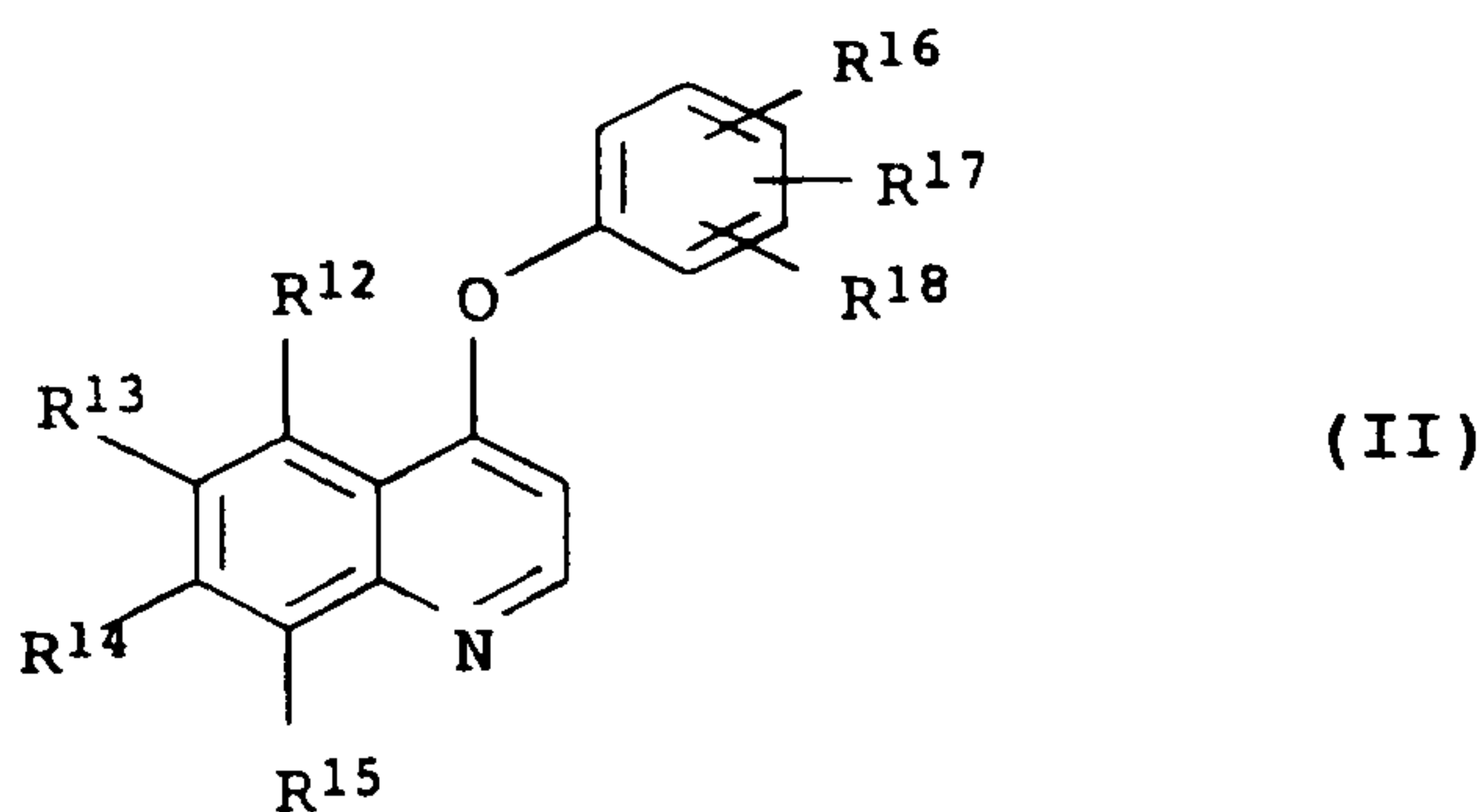
R¹ is a hydrogen atom;

R² is a phenyl or cycloalkyl group which may or may not have 1, 2 or 3 substituents which are selected, independently of one another, from alkyl, alkenyl, alkynyl, alkoxy, alkenyloxy, alkynyloxy, cycloalkyl, cycloalkenyl, cycloalkyloxy, cycloalkenyloxy, phenyl and halogen, where the aliphatic and cycloaliphatic radicals may be partially or fully halogenated and/or the cycloaliphatic radicals may be substituted by from 1 to 3 alkyl groups and where the phenyl group may have from 1 to 5 halogen atoms and/or from 1 to 3 substituents which are selected, independently of one another, from alkyl, haloalkyl, alkoxy, haloalkoxy, alkylthio and haloalkylthio, and where the amidic phenyl group may or may not be condensed with a saturated 5-membered ring which may or may not be substituted by one or more alkyl groups and/or may have a hetero atom selected from O and S, and

b) at least one compound of the formula II, its N-oxide or one of its

salts

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where the substituents are as defined below:

- 10 $R^{12}, R^{13}, R^{14}, R^{15}$ independently of one another are hydrogen, hydroxyl, nitro, halogen, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkoxy, C_1 - C_4 -alkylthio, C_1 - C_4 -haloalkylthio;

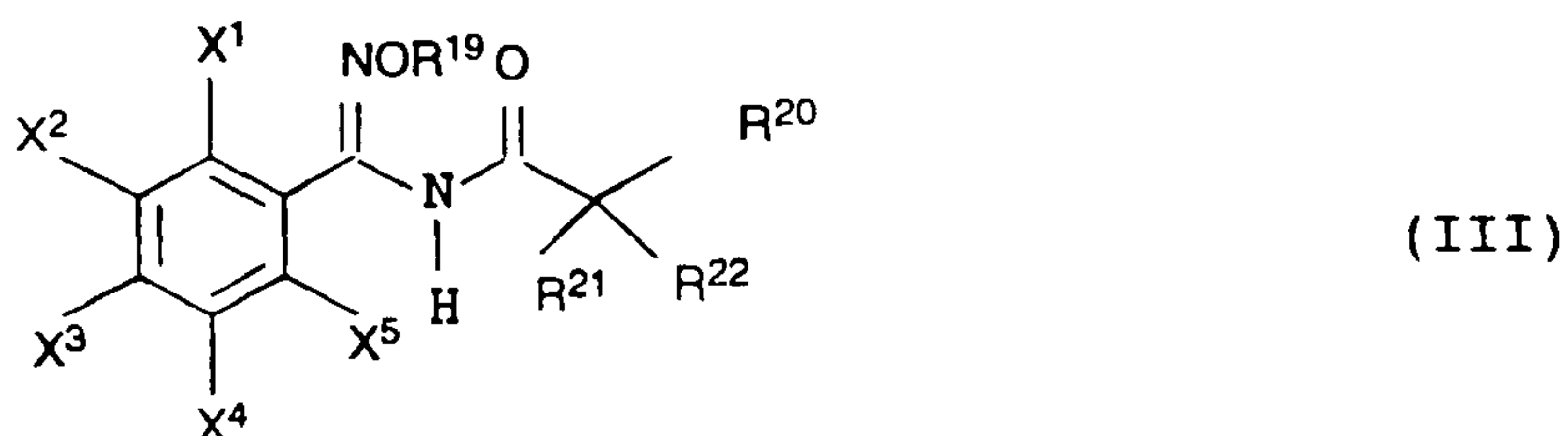
R^{16}, R^{17}, R^{18} independently of one another are hydrogen, hydroxyl, cyano, nitro, halogen, C_1 - C_7 -alkyl, C_1 - C_7 -haloalkyl, C_1 - C_7 -alkoxy, C_1 - C_7 -haloalkoxy, C_1 - C_7 -alkylthio, C_1 - C_7 -haloalkylthio, C_1 - C_7 -hydroxyalkyl, C_2 - C_4 -acyl, aryl, aryloxy, where the radicals containing an aryl group may for their part carry from one to three of the following groups: cyano, nitro, halogen, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkoxy, C_1 - C_4 -alkylthio and C_1 - C_4 -haloalkylthio

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in a synergistically effective amount.

2. A fungicidal mixture as claimed in claim 1, comprising as further active component:

- c) at least one compound of the formula III



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where the substituents X^1 to X^5 and R^{19} to R^{22} are as defined below:

- X^1 to X^5 independently of one another are hydrogen, halogen, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkoxy, C_1 - C_4 -alkylthio, C_1 - C_4 -thioalkoxy, C_1 - C_4 -sulfonylalkyl, nitro, amino, N - C_1 - C_4 -carboxylamino, N - C_1 - C_4 -alkylamino;
- 10 R^{19} is C_1 - C_4 -alkyl, C_2 - C_4 -alkenyl, C_2 - C_4 -alkynyl, C_1 - C_4 -alkyl- C_3 - C_7 -cycloalkyl, where these radicals may carry substituents selected from halogen, cyano and C_1 - C_4 -alkoxy;
- R^{20} is a phenyl radical or a 5- or 6-membered saturated or unsaturated heterocyclyl radical having at least one hetero atom selected from the group N, O and S, where the cyclic radicals may have from one to three substituents selected from the group consisting of halogen, C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkyl, C_1 - C_4 -haloalkoxy, C_1 - C_4 -alkoxy- C_2 - C_4 -alkenyl, C_1 - C_4 -alkoxy- C_2 - C_4 -alkynyl;
- 20 R^{21} and R^{22} independently of one another are hydrogen, C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -alkylthio, N - C_1 - C_4 -alkylamino, C_1 - C_4 -haloalkyl or C_1 - C_4 -haloalkoxy.

3. A fungicidal mixture as claimed in claim 1 or 2, wherein in the formula I the radical A is one of the following groups:
phenyl, pyridyl, dihydropyranyl, dihydrooxathiynyl, dihydrooxathiynyloxy, dihydrooxathiynyldioxide, furyl, thiazolyl, pyrazolyl or oxazolyl, where these groups may have 1, 2 or 3 substituents which are selected, independently of one another, from alkyl, halogen, difluoromethyl and trifluoromethyl.

4. A fungicidal mixture as claimed in claim 1 or 2, wherein in the formula I the radical A is one of the following groups:

pyridin-3-yl, which is optionally substituted in the 2-position by halogen, methyl, difluoromethyl, trifluoromethyl, methoxy, methylthio, methylsulfonyl or methylsulfonyl;

phenyl, which may or may not be substituted in the 2-position by methyl, trifluoromethyl, chlorine, bromine or iodine;

2-methyl-5,6-dihydropyran-3-yl;

10

2-methyl-5,6-dihydro-1,4-oxathien-3-yl or the 4-oxide or 4,4-dioxide thereof;

2-methylfuran-3-yl, which may or may not be substituted in the 4- and/or 5-position by methyl;

thiazol-5-yl, which may or may not be substituted in the 2- and/or 4-position by methyl, chlorine, difluoromethyl or trifluoromethyl;

thiazol-4-yl, which may or may not be substituted in the 2- and/or 5-position by methyl, chlorine, difluoromethyl or trifluoromethyl;

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1-methylpyrazol-4-yl, which may or may not be substituted in the 3- and/or 5-position by methyl, chlorine, difluoromethyl or trifluoromethyl; or

oxazol-5-yl, which may or may not be substituted in the 2- and/or 4-position by methyl or chlorine.

5. A fungicidal mixture as claimed in any one of claims 1 to 4, wherein the formula I, R² is a phenyl group which is optionally substituted by 1, 2 or 3 of the substituents mentioned in claim 1.

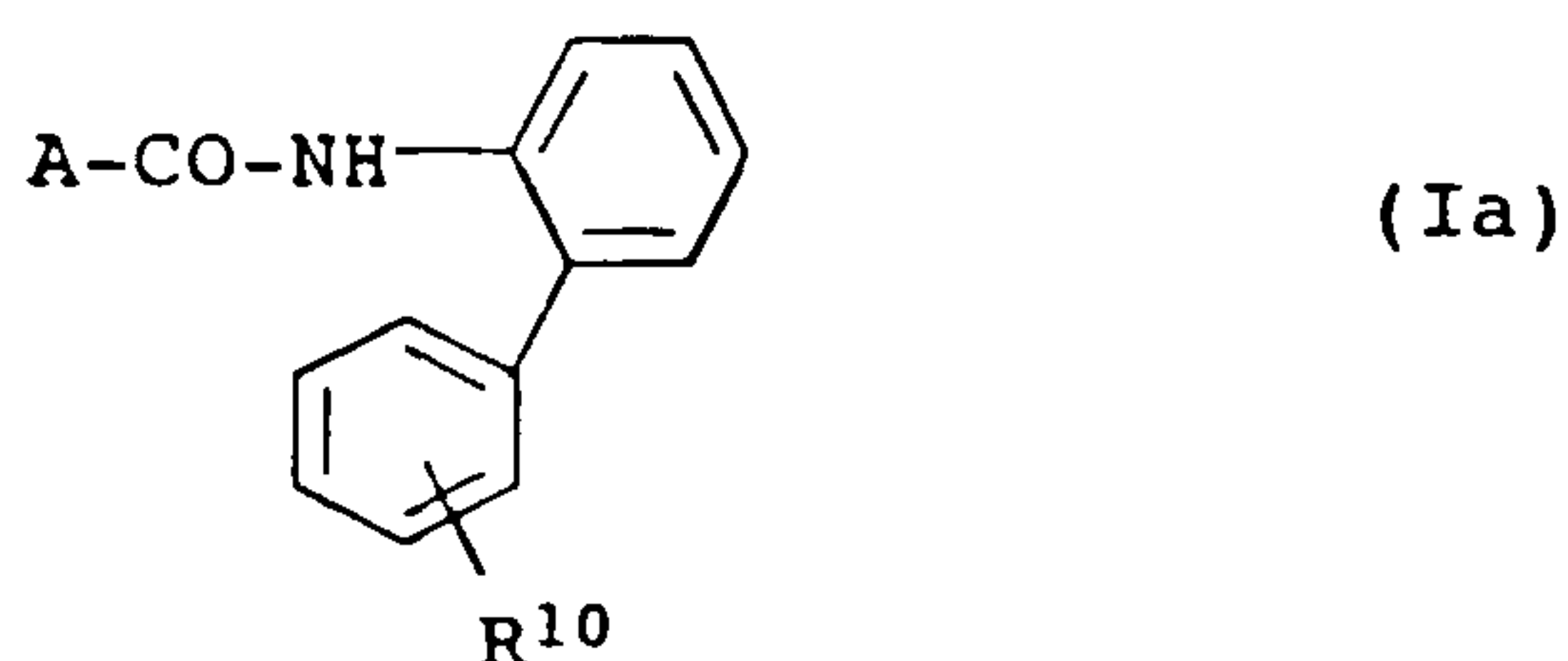
6. A fungicidal mixture as claimed in claim 5, where R^2 is a phenyl group which has one of the following substituents in the 2-position:

C_3 - C_6 -alkyl, C_5 - C_6 -cycloalkenyl, C_5 - C_6 -cycloalkyloxy, cycloalkenyloxy, where these groups may be substituted by 1, 2 or 3 C_1 - C_4 -alkyl groups,

phenyl which is substituted by from 1 to 5 halogen atoms and/or from 1 to 3 groups which are selected, independently of one another, from C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkoxy, C_1 - C_4 -alkylthio and C_1 - C_4 -haloalkylthio,

or where R^2 is indanyl or oxaindanyl which is optionally substituted by 1, 2 or 3 C_1 - C_4 -alkyl groups.

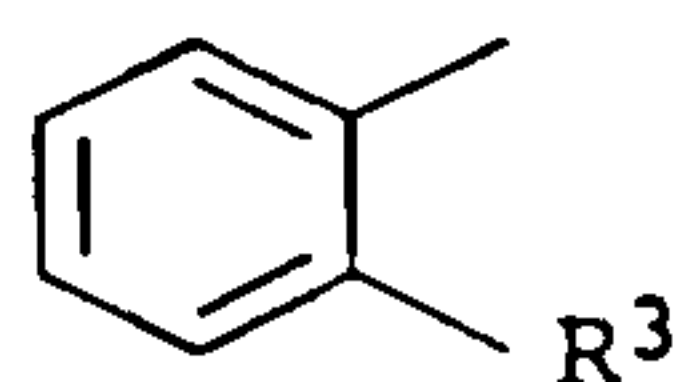
10 7. A fungicidal mixture as claimed in claim 1 or 2, wherein the amide compound is of the formula Ia below:



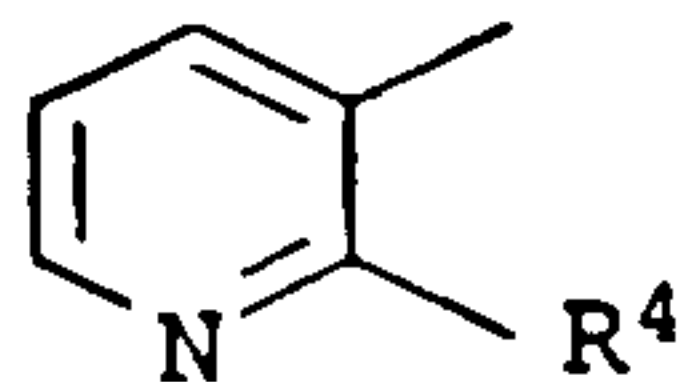
in which

A is

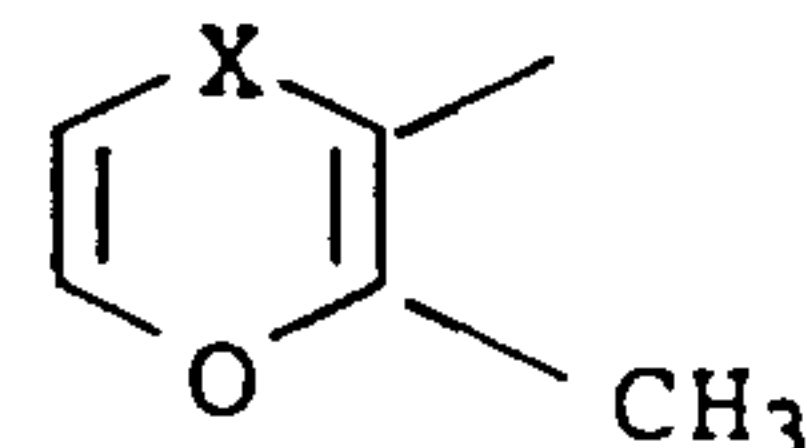
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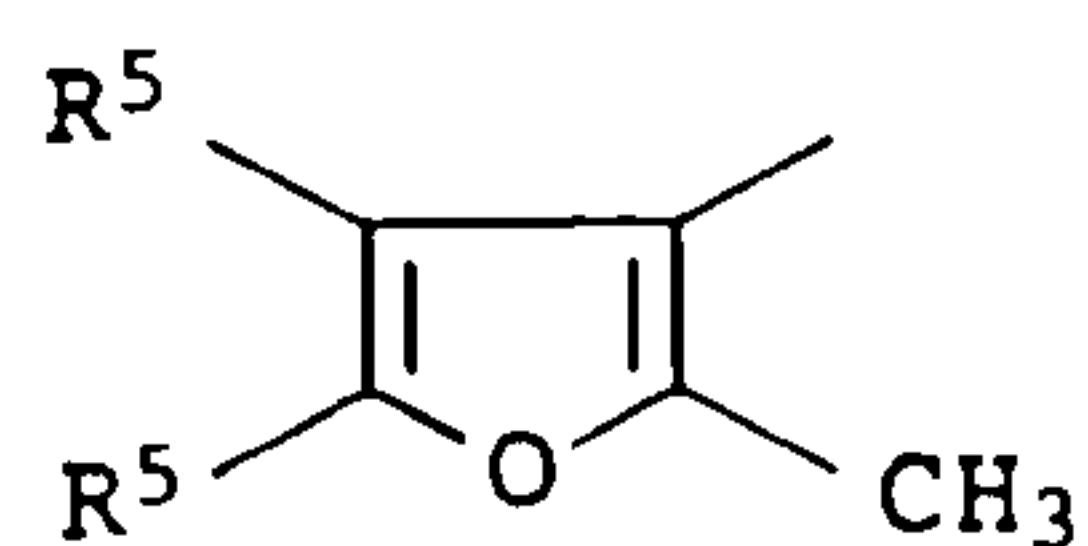
(A1)



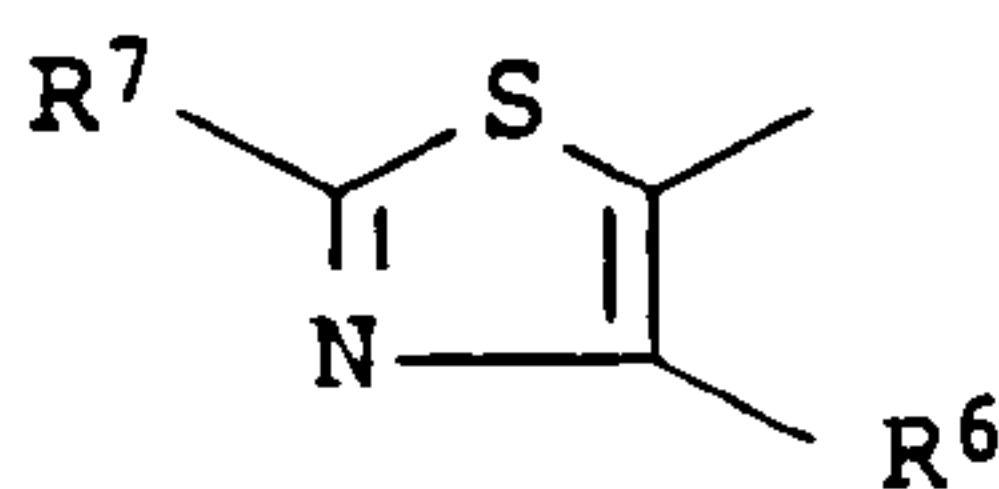
(A2)



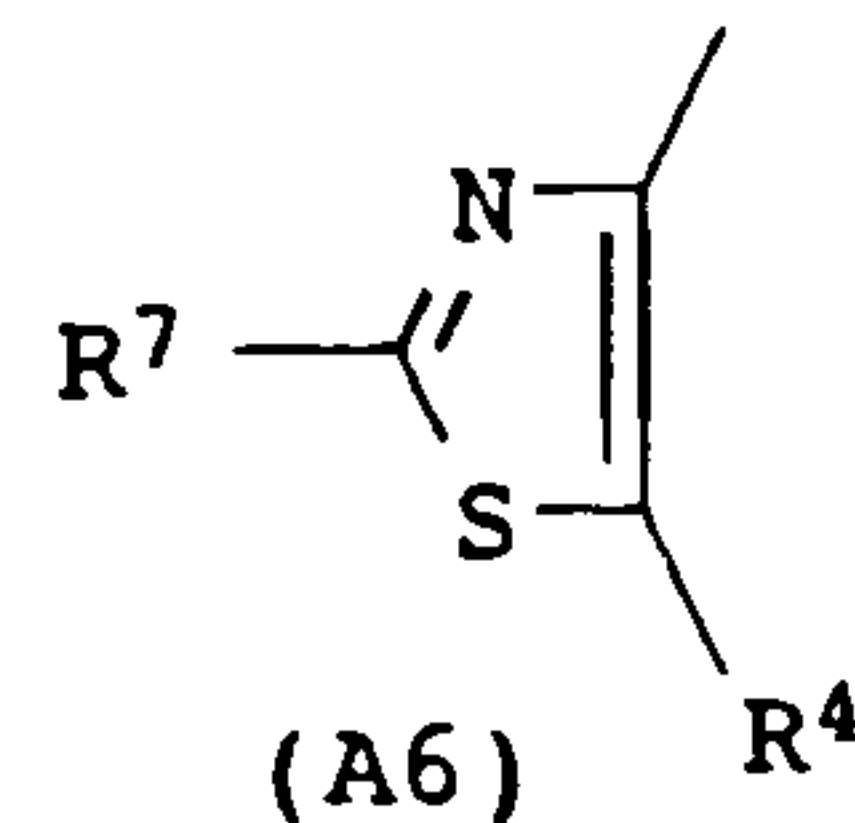
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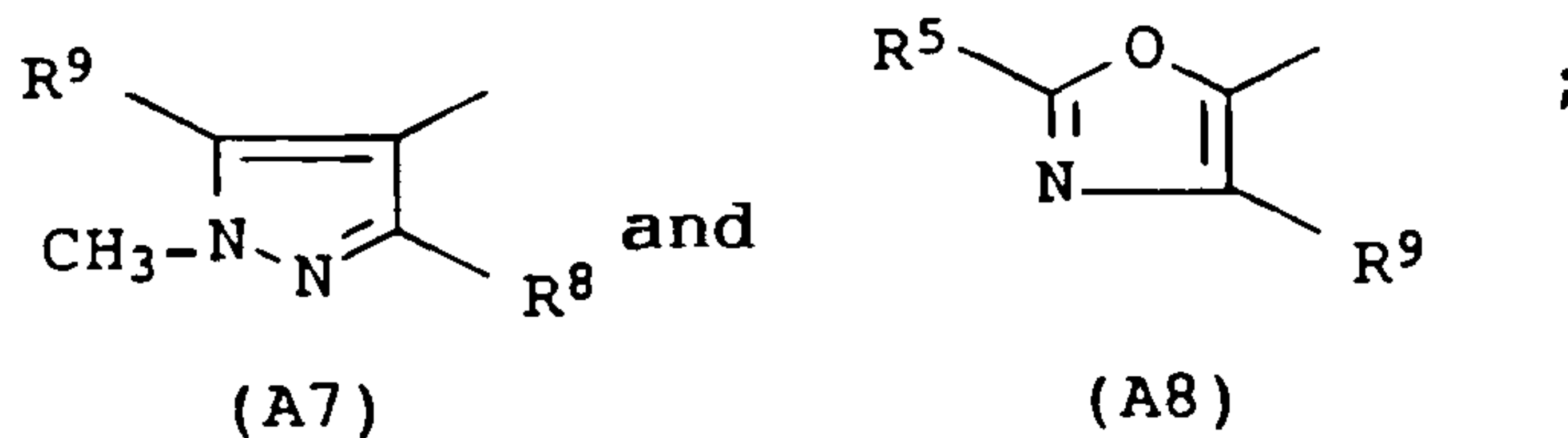
(A4)



(A5)



(A6)

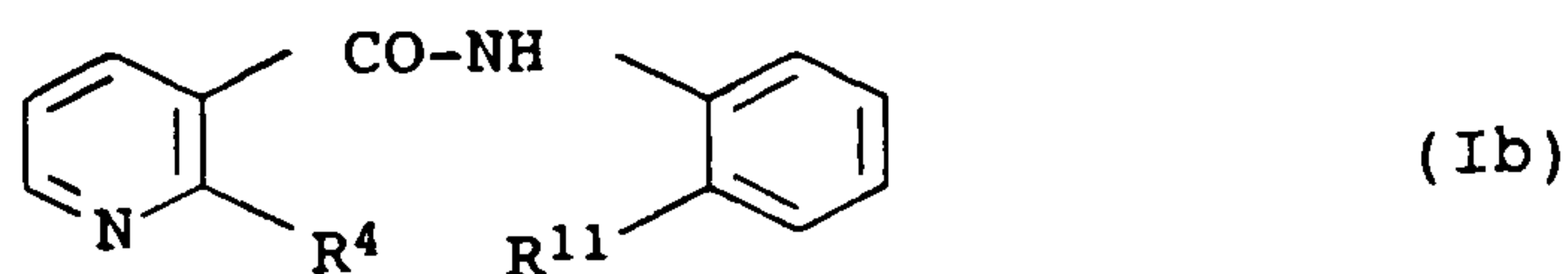


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- X is methylene, sulfur, sulfonyl or sulfonyl (SO₂),
 R³ is methyl, difluoromethyl, trifluoromethyl, chlorine, bromine or iodine,
 R⁴ is trifluoromethyl or chlorine,
 R⁵ is hydrogen or methyl,
 R⁶ is methyl, difluoromethyl, trifluoromethyl or chlorine,
 R⁷ is hydrogen, methyl or chlorine,
 R⁸ is methyl, difluoromethyl or trifluoromethyl,
 R⁹ is hydrogen, methyl, difluoromethyl, trifluoromethyl or chlorine,
 R¹⁰ is C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄-alkylthio or halogen.

8. A fungicidal mixture as claimed in claim 1 or 2, wherein the amide compound is of the formula Ib below:

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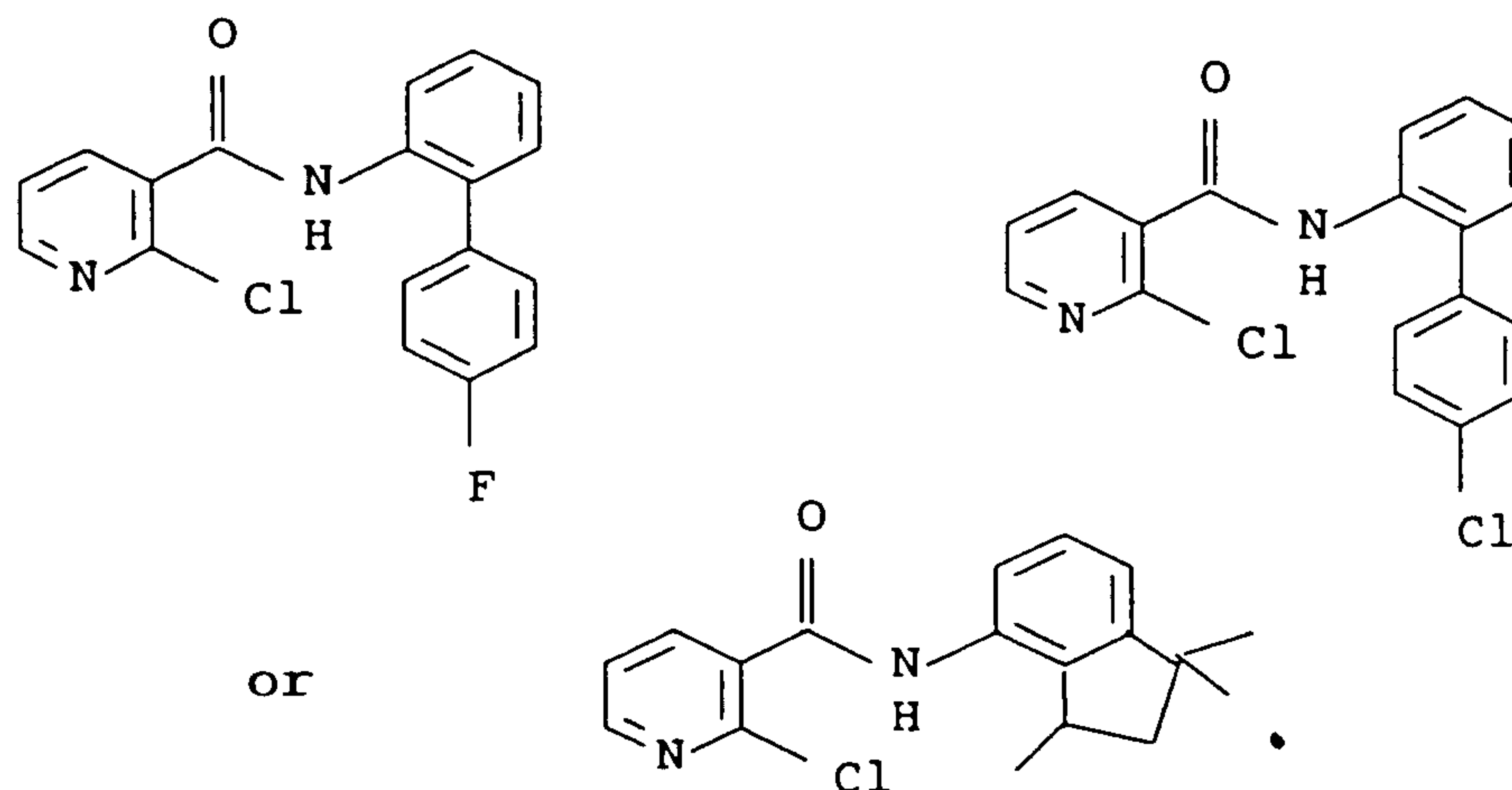


in which

R⁴ is halogen and

R¹¹ is phenyl which is substituted by halogen.

9. A fungicidal mixture as claimed in claim 1 or 2, wherein the amide compound is a compound of the formulae below:

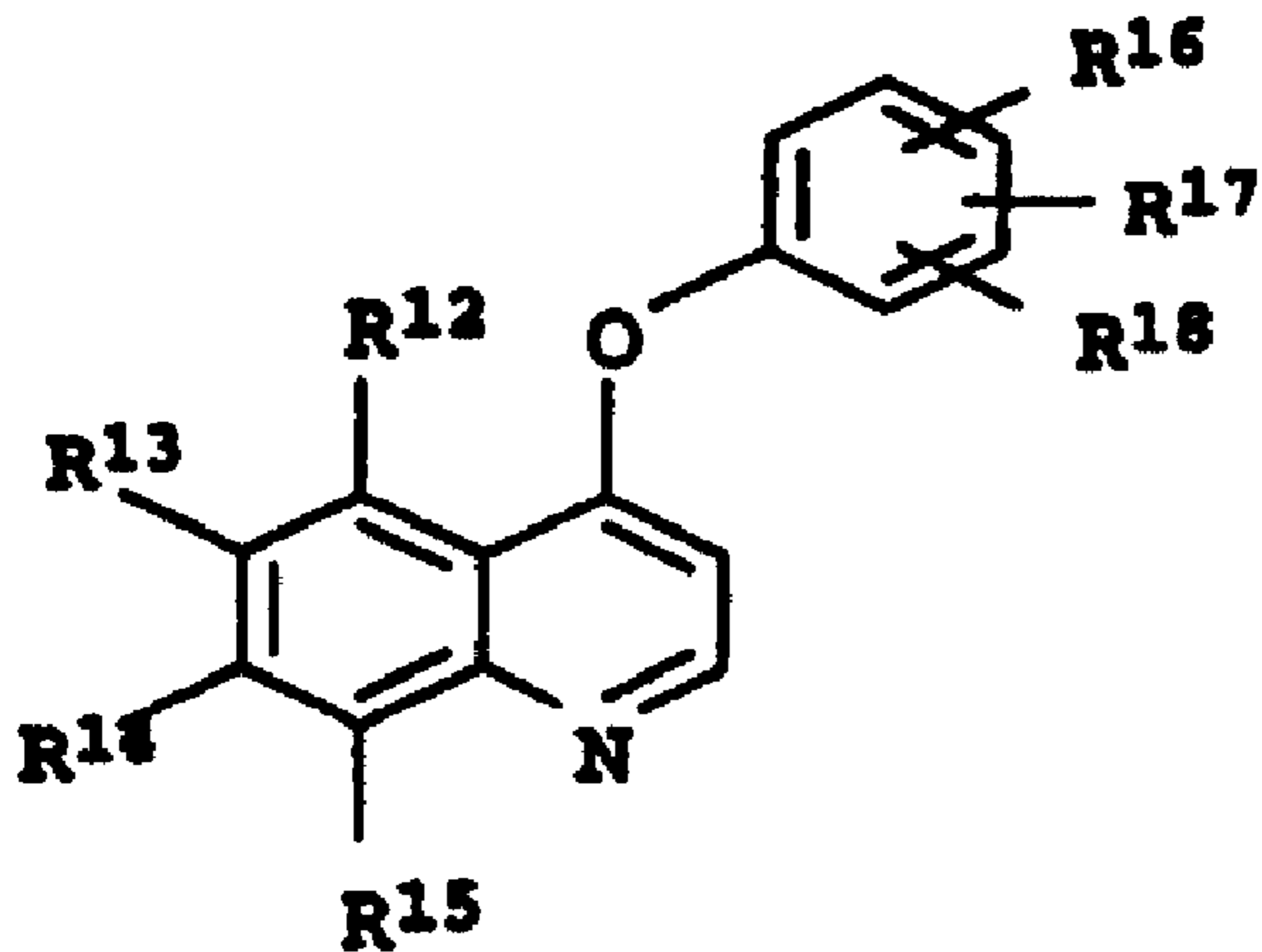


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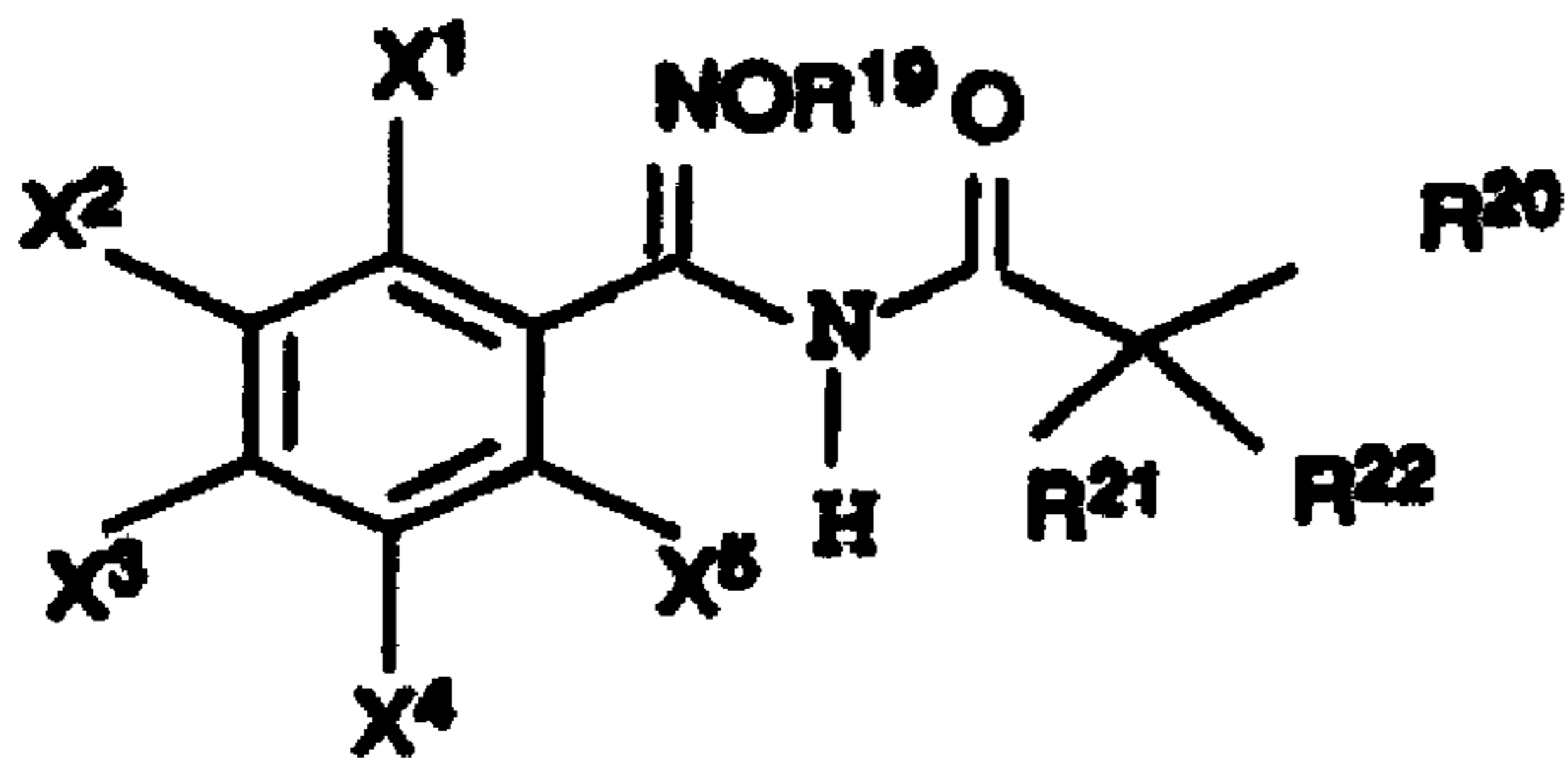
10. A fungicidal mixture as claimed in any one of the claims 1 to 9, which is conditioned in two parts, one part comprising the amide compound of the formula I in a solid or liquid carrier and the other part comprising the compound(s) of the formula II and the compound(s) of the formula III, if present, in a solid or liquid carrier.

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11. A method for controlling harmful fungi, which comprises treating the fungi, their habitat, or the materials, plants, seeds, soils, areas or spaces to be protected against fungal attack with a fungicidal mixture as claimed in any one of claims 1 to 10, where the application of the amide compound of the formula I and of the compound(s) of the formula II and the one of the formula III, if present, is carried out simultaneously or in succession.



(II)



(III)