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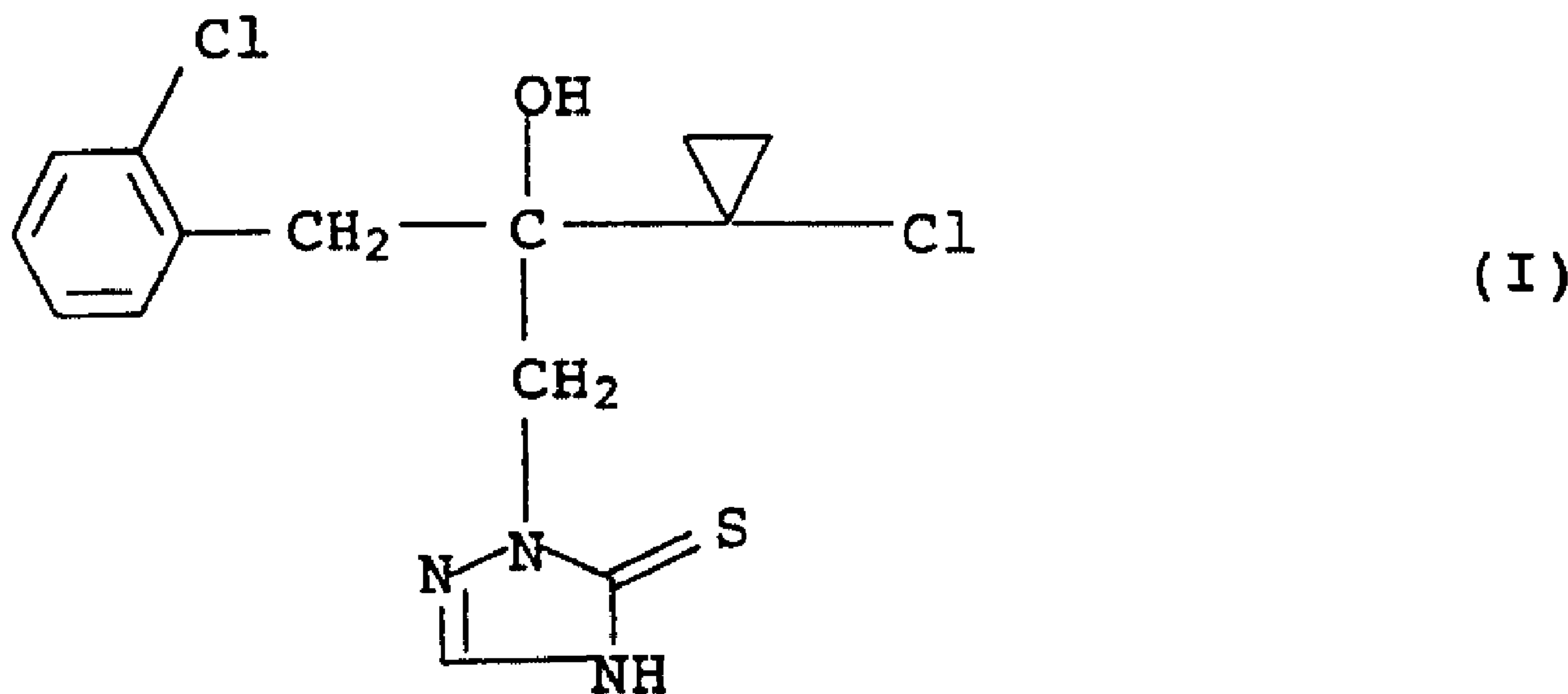
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(54) Titre : MELANGES FONGICIDES A BASE DE PROTHIOCONAZOL ET D'UN DERIVE DE STROBILURINE  
(54) Title: FUNGICIDAL MIXTURES BASED ON PROTHIOCONAZOLE AND A STROBILURIN DERIVATIVE



(57) Abrégé/Abstract:

Disclosed is a fungicidal mixture containing (1) 2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro-[1,2,4]-triazole-3-thion of formula (I) or the salts or adducts thereof, and at least one additional fungicidal compound or the salts or adducts thereof, selected among (2) trifloxystrobin of formula (II), (3) picoxystrobin of formula (III), (4) pyraclostrobin of formula (IV), (5) dimoxystrobin of formula (V), and (6) a strobilurin derivative of formula (VI), in a synergistically active quantity.

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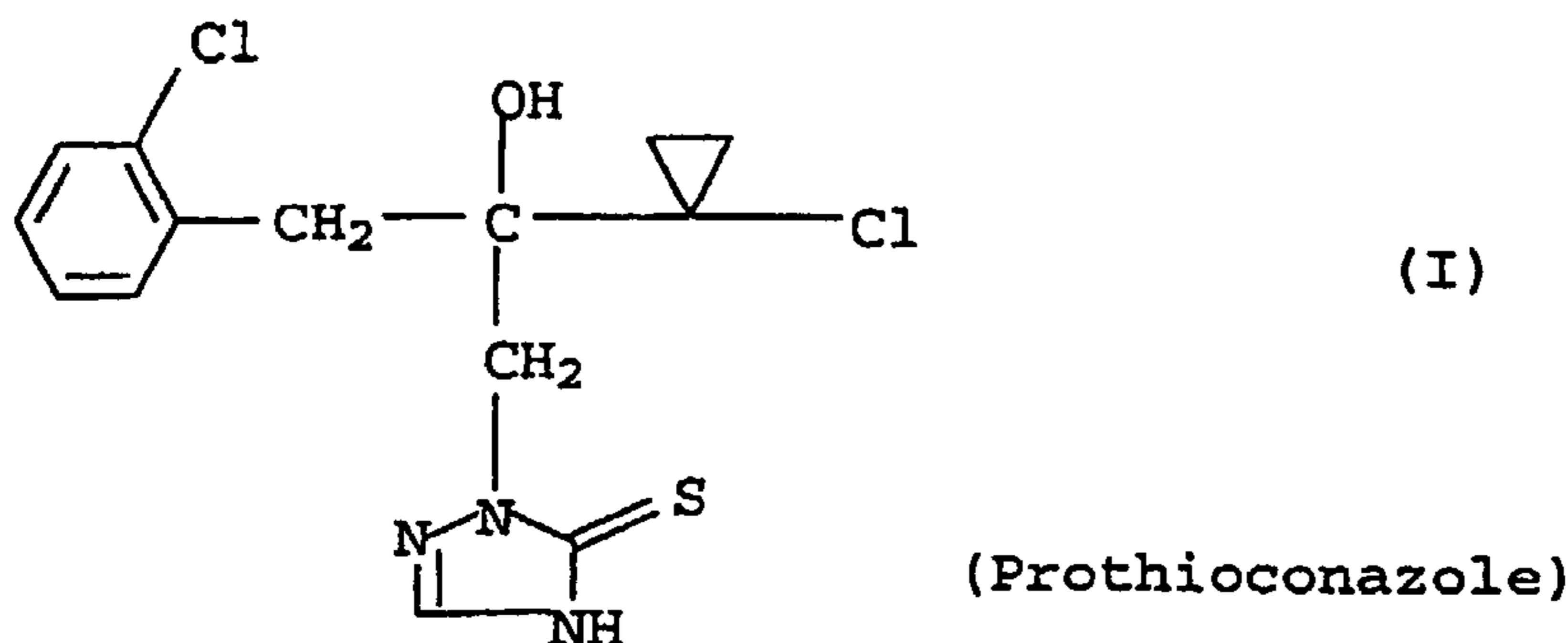
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(54) **Title:** FUNGICIDAL MIXTURES BASED ON PROTHIOCONAZOLE AND A STROBILURIN DERIVATIVE(54) **Bezeichnung:** FUNGIZIDE MISCHUNGEN AUF DER BASIS VON PROTHIOCONAZOL UND EINEM STROBILURIN-  
DERIVAT(57) **Abstract:** Disclosed is a fungicidal mixture containing (1) 2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro-[1,2,4]-triazole-3-thion of formula (I) or the salts or adducts thereof, and at least one additional fungicidal compound or the salts or adducts thereof, selected among (2) trifloxystrobin of formula (II), (3) picoxystrobin of formula (III), (4) pyraclostrobin of formula (IV), (5) dimoxystrobin of formula (V), and (6) a strobilurin derivative of

formula (VI), in a synergistically active quantity.

(57) **Zusammenfassung:** Fungizide Mischung, enthaltend (1) 2-[2-(1-Chlorcyclopropyl)-3-(2-chlorphenyl)-2-hydroxypropyl]-2,4-dihydro-[1,2,4]-triazol-3-thion der Formel (I) oder dessen Salze oder Addukte, und und mindestens einer weiteren fungiziden Verbindung oder deren Salze oder Addukte, ausgewählt aus, (2) einer Liste von 5 Strobilurin-Derivaten in einer synergistisch wirksamen Menge.

WO 2003/073852 A3

**WO 2003/073852 A3**



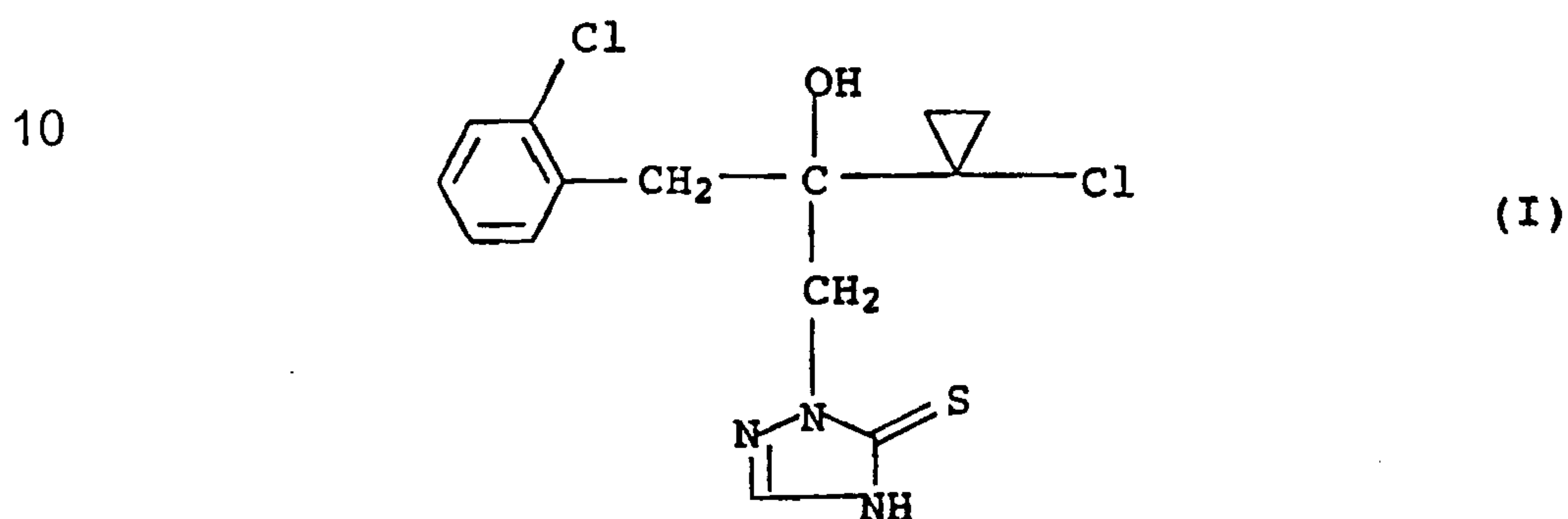
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*Zur Erklärung der Zweibuchstaben-Codes und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.*

**FUNGICIDAL MIXTURES BASED ON PROTHIOCONAZOLE AND A  
STROBILURIN DERIVATIVE**

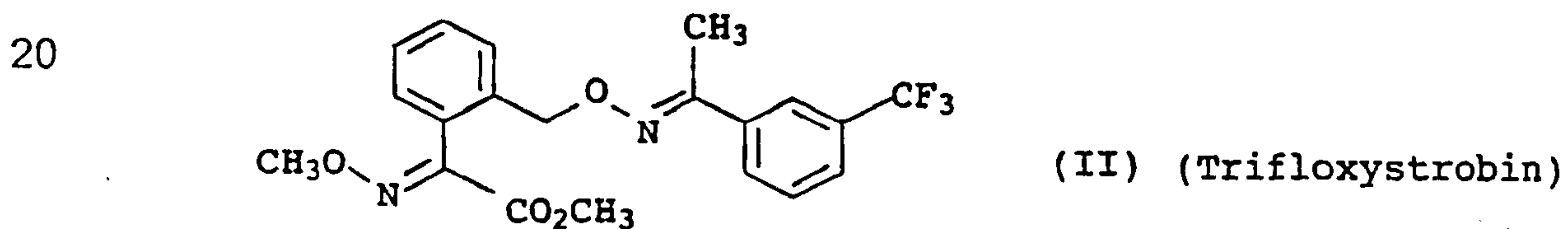
The present invention as broadly disclosed relates to a fungicidal mixture comprising:

- (1) 2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro-[1,2,4]-triazole-3-thione (prothioconazole) of the formula I or its salts or adducts



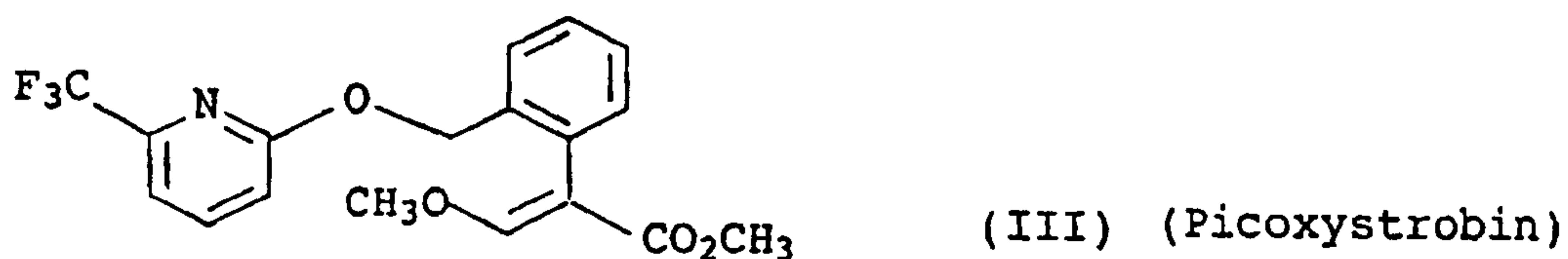
and at least one further fungicidal compound or its salts or adducts, selected from the group consisting of

- (2) trifloxystrobin of the formula II



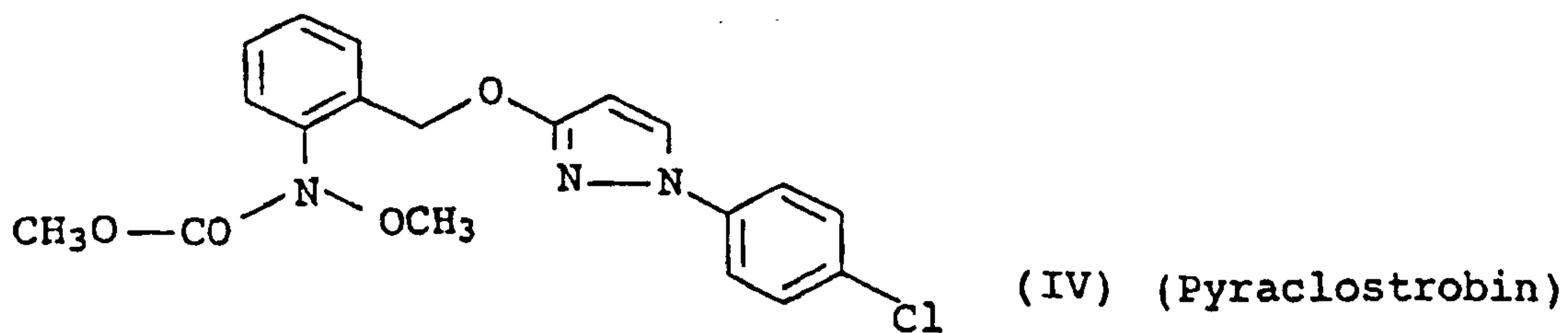
and

- (3) picoxystrobin of the formula III



and

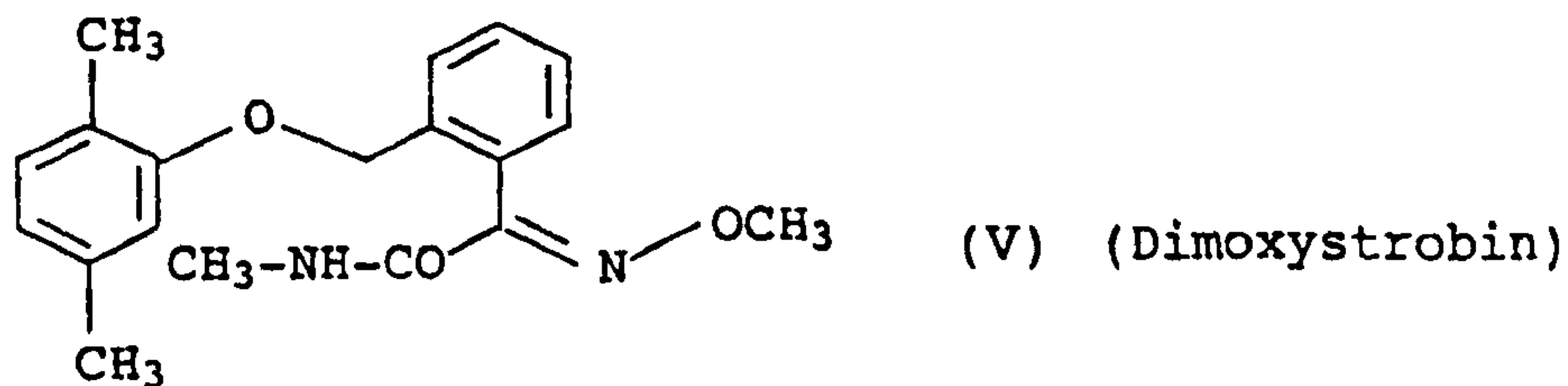
(4) pyraclostrobin of the formula IV



and

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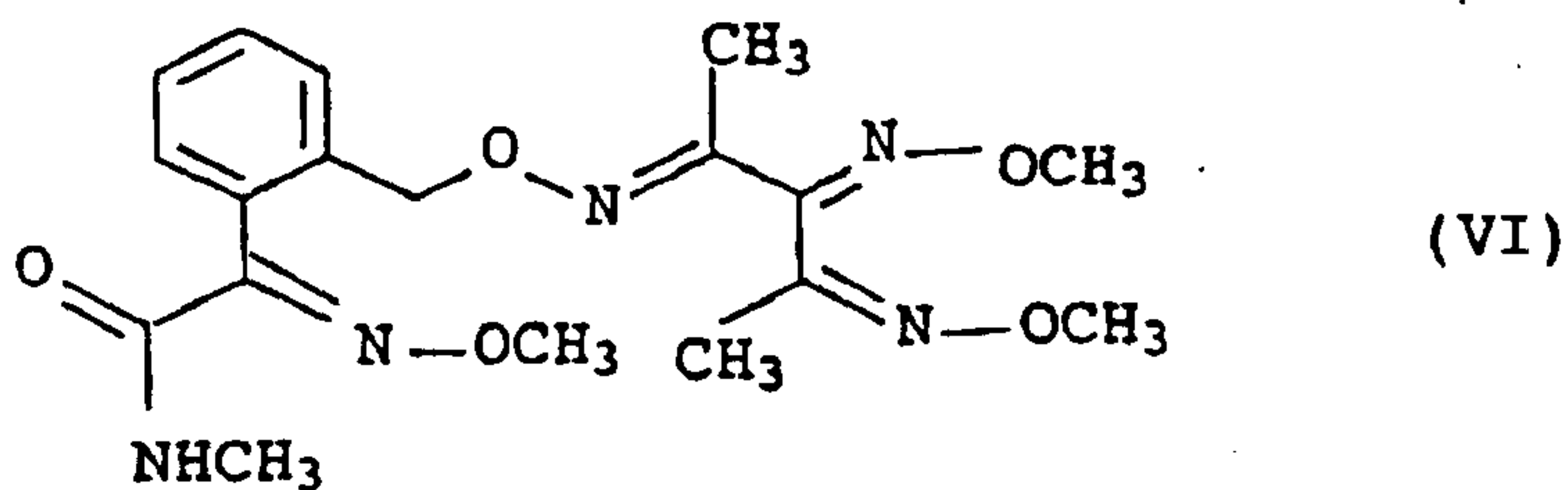
(5) dimoxystrobin of the formula V



and

(6) a strobilurin derivative of the formula VI

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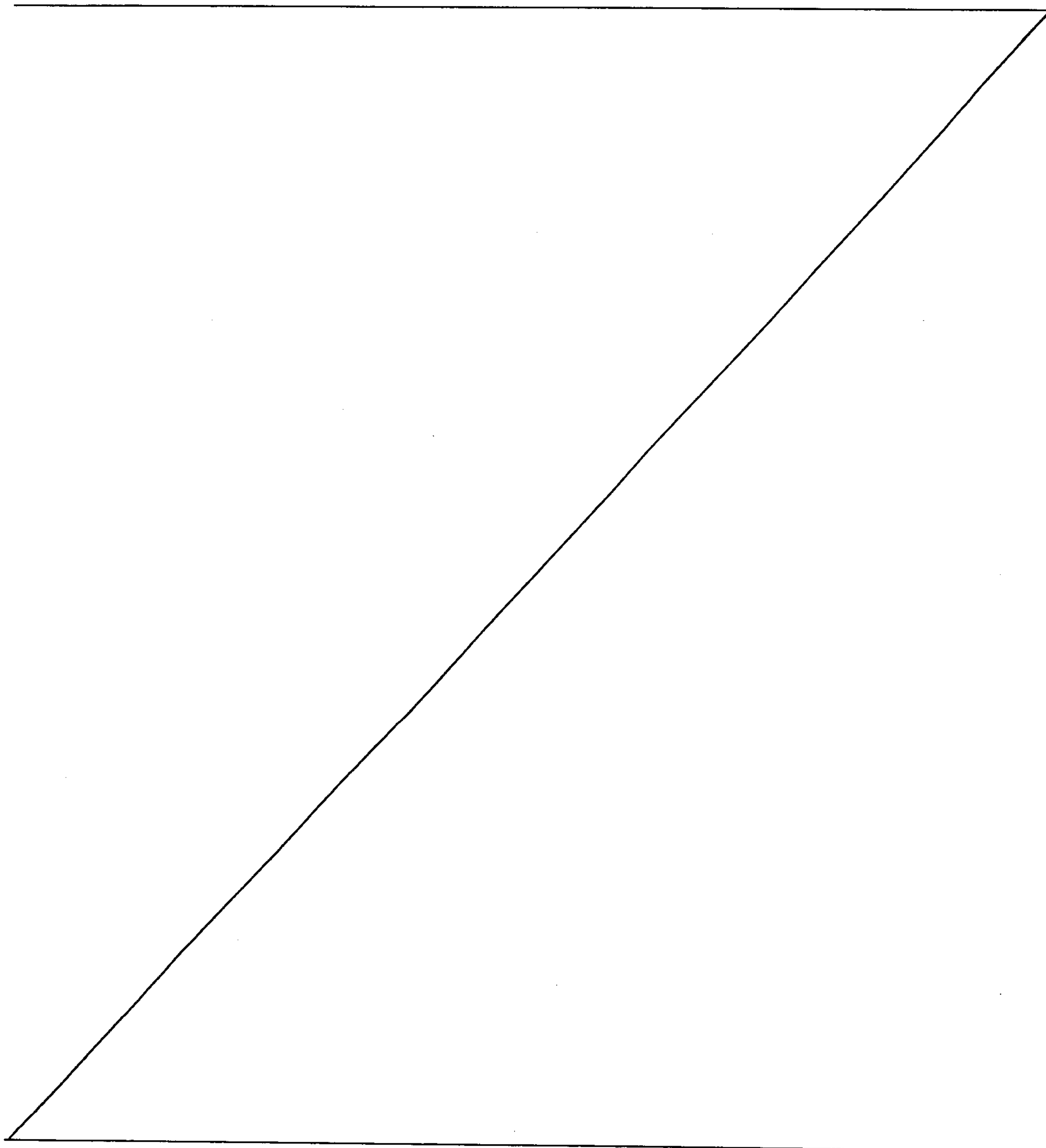
in a synergistically effective amount.

The invention as broadly disclosed also relates to a method for controlling harmful fungi using mixtures of the compound I with at least one of the compounds II, III, IV, V or VI, and to the use of the compounds I, II, III, IV, V and VI for preparing such mixtures, and to compositions comprising such mixtures.

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The invention as claimed is however restricted to a composition comprising the compound I and the compound II, and to its use.

The compound of the formula I, 2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro-[1,2,4]-triazole-3-thione (prothioconazole), has already been disclosed in WO 96/16048.



## 3

A number of active compound combinations of prothioconazole with a large number of other fungicidal compounds have been disclosed in WO 98/47367.

- 5 Trifloxystrobin of the formula II and its use as crop protection agent are described in EP-A-0 460 575.

Picoxystrobin has been disclosed in EP-A-0 326 330.

- 10 The strobilurin derivative of the formula IV is likewise already known and has been described in EP-A-0 804 421.

The strobilurin derivative of the formula V has been disclosed in EP-A-0 477 631.

15

Finally, the strobilurin derivative of the formula VI is likewise known and has been described in EP-A-0 876 332.

- It is an object of the present invention to provide mixtures  
20 which have further improved activity against harmful fungi combined with a reduced total amount of active compounds applied (synergistic mixtures), with a view to reducing the application rates and improving the activity spectrum of the known compounds I, II, III, IV, V and VI.

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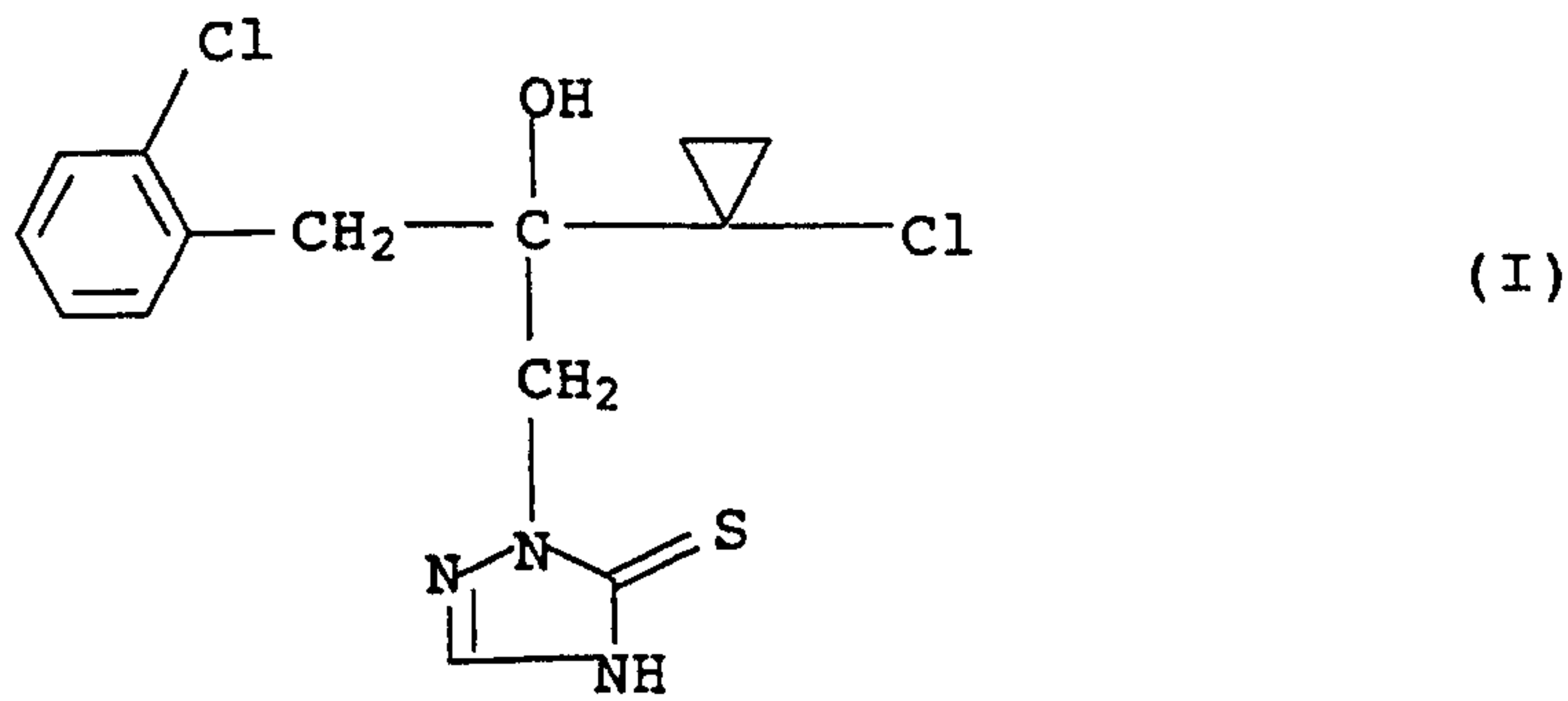
- We have found that this object is achieved by the mixture, defined at the outset, of prothioconazole with at least one strobilurin derivative. Moreover, we have found that applying the compound I and at least one of the compounds II, III, IV, V or VI  
30 simultaneously, i.e. together or separately, or applying the compound I and at least one of the compounds II, III, IV, V or VI in succession provides better control of harmful fungi than is possible with the individual compounds alone.

- 35 2-[2-(1-Chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro-[1,2,4]-triazole-3-thione of the formula I is known from WO 96-16 048. The compound can be present in the "thiono" form of the formula

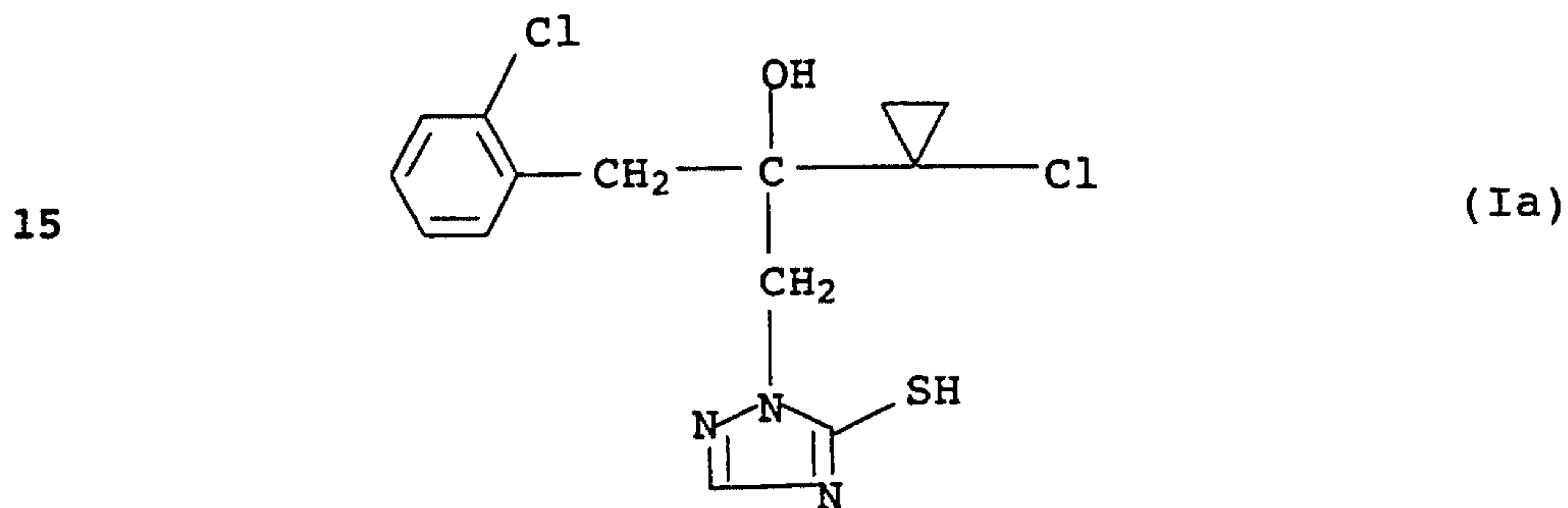
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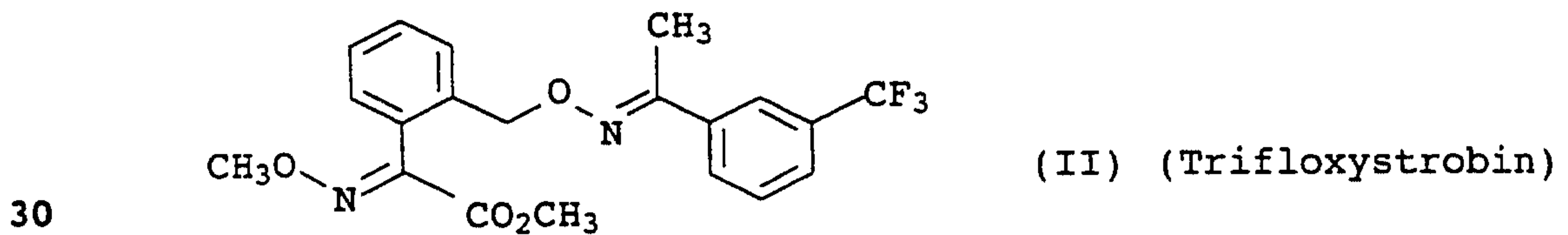
10 or in the tautomeric "mercapto" form of the formula



For the sake of simplicity, only the "thiono" form is shown in each case.

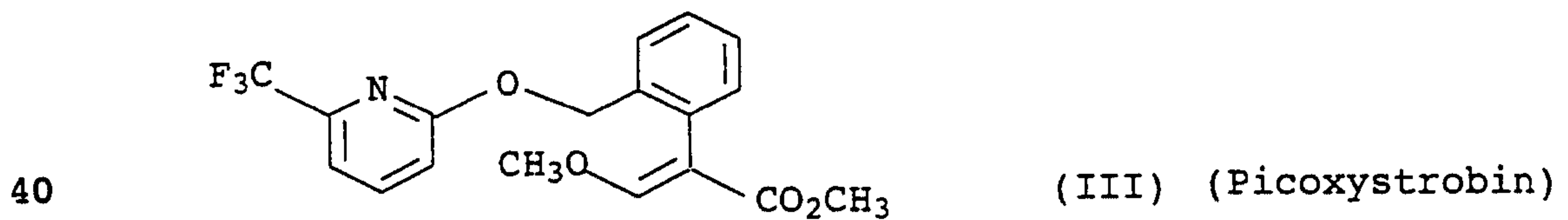
Trifloxystrobin of the formula II

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is known from EP-A 0 460 572.

35 Picoxystrobin of the formula III



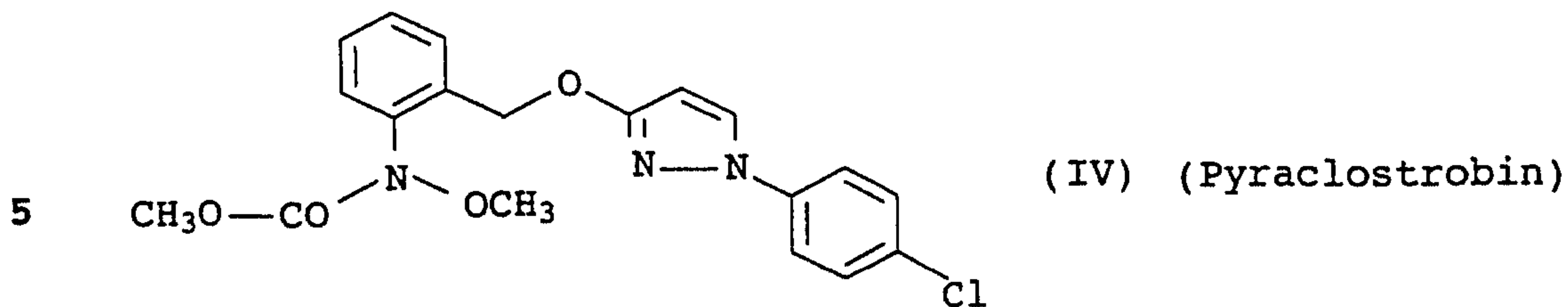
is known from EP-A-0 326 330.

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Pyraclostrobin of the formula IV



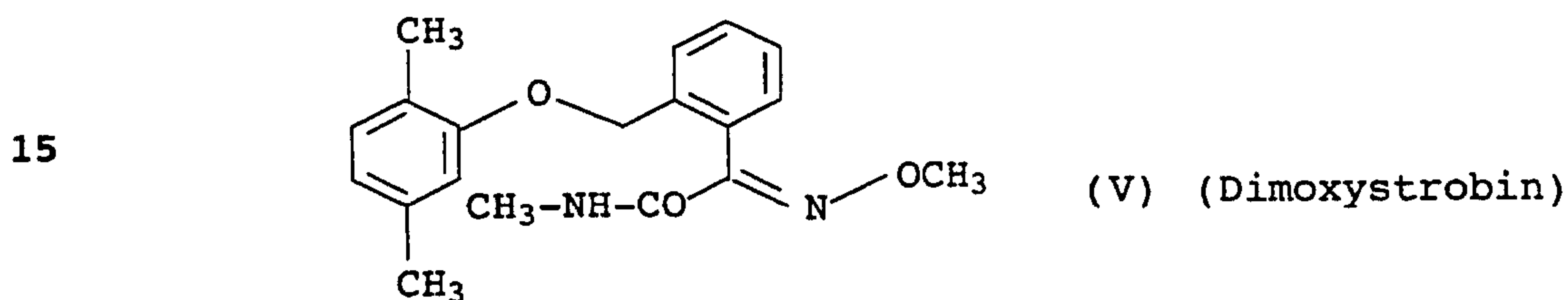
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is known from EP-A 0 804 421.

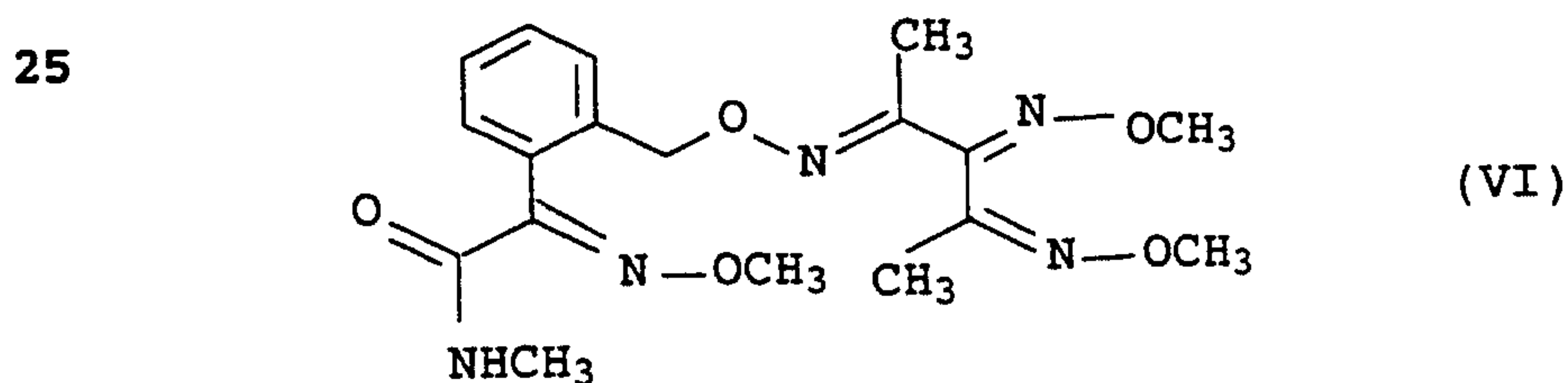
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Dimoxystrobin of the formula V



20 is known from EP-A 0 477 631.

The strobilurin derivative of the formula VI



is known from EP-A 0 876 332.

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

Examples of inorganic acids are hydrohalic acids, carbonic acid,  
such as hydrogen fluoride, hydrogen chloride, hydrogen bromide  
40 and hydrogen iodide, sulfuric acid, phosphoric acid and nitric  
acid.

Suitable organic acids are, for example, formic acid, carbonic  
acid and alkanolic acids, such as acetic acid, trifluoroacetic  
45 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

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(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 sulfonic acid groups), alkylphosphonic acids 5 (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 phosphonic acid radicals), it being possible for the alkyl or aryl radicals to carry further 10 substituents, for example p-toluenesulfonic acid, salicylic acid, p-aminosalicylic acid, 2-phenoxybenzoic acid, 2-acetoxybenzoic acid, etc.

Suitable metal ions are in particular the ions of the elements of 15 the second main group, in particular calcium and magnesium, of the third and fourth main group, in particular aluminum, tin and lead, and of the first to eighth transition group, in particular chromium, manganese, iron, cobalt, nickel, copper, zinc and others. Particular preference is given to the metal ions of the 20 elements of the transition groups of the fourth period. The metals can be present in the various valencies that they can assume.

Preference is given to mixtures of prothioconazole with 25 trifloxystrobin of the formula II.

Preference is also given to mixtures of prothioconazole with picoxystrobin of the formula III.

30 Preference is given to mixtures of prothioconazole with pyraclostrobin of the formula IV.

Preference is furthermore also given to mixtures of prothioconazole with dimoxystrobin of the formula V. 35

Preference is also given to mixtures of prothioconazole with the strobilurin derivative of the formula VI.

Preference is also given to three-component mixtures of 40 prothioconazole with two of the abovementioned strobilurin derivatives.

When preparing the mixtures, it is preferred to employ the pure active compounds I, II, III, IV, V and VI, to which may be added 45 further active compounds against harmful fungi or other pests,

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such as insects, arachnids or nematodes, or else herbicidal or growth-regulating active compounds or fertilizers.

The mixtures of the compound I with at least one of the compounds  
5 II, III, IV, V or VI or the compound I, used simultaneously,  
jointly or separately, with at least one of the compounds II,  
III, IV, V or VI exhibit outstanding activity against a wide  
range of phytopathogenic fungi, in particular from the classes of  
the Ascomycetes, Basidiomycetes, Phycomycetes and Deuteromycetes.  
10 Some of them act systemically and can therefore also be employed  
as folio- and soil-acting fungicides.

They are especially important for controlling a large number of  
fungi in a variety of crop plants, such as cotton, vegetable  
15 species (e.g. cucumbers, beans, tomatoes, potatoes and  
cucurbits), barley, grass, oats, bananas, coffee, corn, 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: *Blumeria 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  
25 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,  
30 *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  
35 bananas and *Fusarium* and *Verticillium* species.

They can furthermore be employed in the protection of materials  
(e.g. the protection of wood), for example against *Paecilomyces*  
*variotii*.

40

The compound I can be applied simultaneously, that is either  
together or separately, or successively with at least one of the  
compounds II, III, IV, V and VI, the sequence, in the case of  
separate application, generally not having any effect on the  
45 result of the control measures.

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The compounds I and II are usually applied in a weight ratio of from 20:1 to 1:20, in particular from 10:1 to 1:10, preferably from 5:1 to 1:5.

5 The compounds I and III are usually applied in a weight ratio of from 20:1 to 1:20, in particular from 10:1 to 1:10, preferably from 5:1 to 1:5.

The compounds I and IV are usually applied in a weight ratio of  
10 from 20:1 to 1:20, in particular from 10:1 to 1:10, preferably from 5:1 to 1:5.

The compounds I and V are usually applied in a weight ratio of  
15 from 20:1 to 1:20, in particular from 10:1 to 1:10, preferably from 5:1 to 1:5.

The compounds I and VI are usually applied in a weight ratio of from 20:1 to 1:20, in particular from 10:1 to 1:10, preferably from 5:1 to 1:5.

20

Depending on the kind of effect desired, the application rates of the mixtures according to the invention are, in particular in agricultural crop areas, from 0.01 to 8 kg/ha, preferably from 0.1 to 5 kg/ha, in particular from 0.1 to 3.0 kg/ha.

25

The application rates for the compound I are from 0.01 to 1 kg/ha, preferably from 0.05 to 0.5 kg/ha, in particular from 0.05 to 0.3 kg/ha.

30 Correspondingly, in the case of the compound II, the application rates are from 0.01 to 1 kg/ha, preferably from 0.02 to 0.5 kg/ha, in particular from 0.05 to 0.3 kg/ha.

Correspondingly, in the case of the compound III, the application  
35 rates are from 0.01 to 1 kg/ha, preferably from 0.02 to 0.5 kg/ha, in particular from 0.05 to 0.3 kg/ha.

Correspondingly, in the case of the compound IV, the application rates are from 0.01 to 1 kg/ha, preferably from 0.02 to  
40 0.5 kg/ha, in particular from 0.05 to 0.3 kg/ha.

Correspondingly, in the case of the compound V, the application rates are from 0.01 to 1 kg/ha, preferably from 0.02 to 0.5 kg/ha, in particular from 0.05 to 0.3 kg/ha.

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Correspondingly, in the case of the compound VI, the application rates are from 0.01 to 1 kg/ha, preferably from 0.02 to 0.5 kg/ha, in particular from 0.05 to 0.3 kg/ha.

5 For seed treatment, the application rates of the mixture are generally from 0.001 to 250 g/kg of seed, preferably from 0.01 to 100 g/kg of seed, in particular from 0.01 to 50 g/kg.

If phytopathogenic harmful fungi are to be controlled, the  
10 separate or joint application of the compound I with at least one of the compounds II, III, IV, V and VI or of the mixtures of the compound I with at least one of the compounds II, III, IV, V or VI is effected by spraying or dusting the seeds, the plants or the soils before or after sowing of the plants, or before or  
15 after plant emergence.

The fungicidal synergistic mixtures according to the invention or the compound I and at least one of the compounds II, III, IV, V and VI can be formulated, for example, in the form of  
20 ready-to-spray solutions, powders and suspensions or in the form of highly concentrated aqueous, oily 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  
25 intended purpose; in each case, it should ensure as fine and uniform as possible a distribution of the mixture according to the invention.

The formulations are prepared in a known manner, for example by  
30 adding solvents and/or carriers. Usually, inert additives, such as emulsifiers or dispersants, are added to the formulations.

Suitable surfactants are the alkali metal salts, alkaline earth metal salts and ammonium salts of aromatic sulfonic acids, for  
35 example ligno-, phenol-, naphthalene- and dibutyl-naphthalenesulfonic 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  
40 naphthalene and its derivatives with formaldehyde, condensates of naphthalene or of the naphthalenesulfonic acids with phenol and formaldehyde, polyoxyethylene octylphenyl ether, ethoxylated isooctyl-, octyl- or nonylphenol, alkylphenol or tributylphenyl polyglycol ethers, alkylaryl polyether alcohols, isotridecyl  
45 alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers or polyoxypropylene

## 10

alkyl ethers, lauryl alcohol polyglycol ether acetate, sorbitol esters, lignosulfite waste liquors or methylcellulose.

Powders, materials for broadcasting and dusts can be prepared by 5 mixing or jointly grinding the compound I and at least one of the compounds II, III, IV, V and VI or the mixture of the compound I with at least one compound II, III, IV, V or VI with a solid carrier.

10 Granules (for example coated granules, impregnated granules or homogeneous granules) are usually prepared by binding the active compound, or active compounds, to a solid carrier.

Fillers or solid carriers are, for example, mineral earths such 15 as silica gel, silicas, silicates, talc, kaolin, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, and also fertilizers, such as ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of 20 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 from 0.5 to 90% by weight, of the compound I and at 25 least one of the compounds II, III, IV, V or VI or of the mixture of the compound I with at least one compound II, III, IV, V or VI. The active compounds are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR spectrum or HPLC).

30 The compound I and at least one of the compounds II, III, IV, V and VI or the mixtures or the corresponding formulations are applied by treating the harmful fungi, their habitat, or the plants, seeds, soils, areas, materials or spaces to be kept free from them with a fungicidally effective amount of the mixture, or 35 of the compound I and at least one of the compounds II, III, IV, V or VI in the case of separate application.

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

40

Use example

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

45

The active compounds, separately or together, were formulated as a 10% emulsion in a mixture of 63% by weight of cyclohexanone and

## 11

27% by weight of emulsifier, and diluted with water to the desired concentration.

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

$$W = \left(1 - \frac{\alpha}{\beta}\right) \cdot 100$$

10

$\alpha$  corresponds to the fungal infection of the treated plants in % and

$\beta$  corresponds to the fungal infection of the untreated (control) plants in %

15

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.

20

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

25

$$\text{Colby's formula: } E = x + y - x \cdot y / 100$$

$E$  expected efficacy, expressed in % of the untreated control, when using the mixture of the active compounds A and B at the concentrations a and b

$x$  efficacy, expressed in % of the untreated control, when using the active compound A at the concentration a

$y$  efficacy, expressed in % of the untreated control, when using the active compound B at the concentration b

35 Use example 1: Activity against mildew of wheat caused by *Erysiphe* [syn. *Blumeria*] *graminis* forma *specialis. tritici*

Leaves of wheat seedlings of the cultivar "Kanzler" grown in pots were sprayed to runoff point with an aqueous preparation of active compound which had been prepared from a stock solution comprising 10% of active compound, 85% of cyclohexanone and 5% of emulsifier, and, 24 hours after the spray coating had dried on, the leaves were dusted with spores of mildew of wheat (*Erysiphe* [syn. *Blumeria*] *graminis* forma *specialis. tritici*). The test plants were then placed in a greenhouse at 20-24°C and 60-90% relative atmospheric humidity. After 7 days, the extent of the

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development of the mildew was determined visually in % infection of the entire leaf area.

The visually determined values for the percentage of diseased 5 leaf areas were converted into efficacies as % of the untreated control. An efficacy of 0 means the same disease level as in the untreated control, an efficacy of 100 means a disease level of 0%. The expected efficacies for the active compound combinations were determined using Colby's formula mentioned above and 10 compared with the observed efficacies.

Table 1

15	Active compound	Concentration of active compound in the spray liquor in ppm	Efficacy in % of the untreated control
	Control (untreated)	(90% infected)	0
20	Compound I = prothioconazole	4	22
		1	0
		0.25	0
		0.06	0
25		0.015	0
	Compound II = trifloxystrobin	4	83
		1	44
30		0.25	22
		0.06	0
35	Compound III = picoxystrobin	0.25	11
	Compound IV = pyraclostrobin	1	0
40		0.25	0



Table 2

	Combinations according to the invention	Observed efficacy	Calculated efficacy*)
5	Compound I = prothioconazole + Compound II = trifloxystrobin 0.015 + 0.25 ppm Mixture 1 : 16	33	22
10	Compound I = prothioconazole + Compound II = trifloxystrobin 1 : 4 ppm Mixture 1 : 4	94	83
	Compound I = prothioconazole + Compound II = trifloxystrobin 0.25 + 1 ppm Mixture 1 : 4	56	44
15	Compound I = prothioconazole + Compound II = trifloxystrobin 0.25 + 0.06 ppm Mixture 4 : 1	22	0
	Compound I = prothioconazole + Compound II = trifloxystrobin 4 + 0.25 ppm Mixture 16 : 1	55	40
20	Compound I = prothioconazole + Compound III = picoxystrobin 0.06 + 0.25 ppm Mixture 1 : 4	33	11
	Compound I = prothioconazole + Compound III = picoxystrobin 1 + 0.25 ppm Mixture 4 : 1	22	11
25	Compound I = prothioconazole + Compound IV = pyraclostrobin 0.06 + 1 ppm Mixture 1 : 16	33	0
	Compound I = prothioconazole + Compound IV = pyraclostrobin 0.015 + 0.25 ppm Mixture 1 : 16	33	0
30	Compound I = prothioconazole + Compound IV = pyraclostrobin 0.25 + 1 ppm Mixture 1 : 4	33	0
	Compound I = prothioconazole + Compound IV = pyraclostrobin 0.06 + 0.25 ppm Mixture 1 : 4	22	0
35	Compound I = prothioconazole + Compound IV = pyraclostrobin 4 + 1 ppm Mixture 4 : 1	33	22

\*) efficacy calculated using Colby's formula

40 The test results show that in all mixing ratios the observed efficacy is higher than the efficacy calculated beforehand using Colby's formula (from Synerg 171. XLS).

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Use example 2: Curative activity against brown rust of wheat caused by *Puccinia recondita*

Leaves of wheat seedlings of the cultivar "Kanzler" grown in pots 5 were dusted with spores of brown rust (*Puccinia recondita*). The pots were then placed in a chamber with high atmospheric humidity (90-95%), at 20-22°C, for 24 hours. During this time, the spores germinated and the germinal tubes penetrated into the leaf tissue. The next day, the infected plants were sprayed to runoff 10 point with an aqueous formulation of active compound prepared from a stock solution comprising 10% of active compound, 85% of cyclohexanone and 5% of emulsifier. After the spray coating had dried on, the test plants were cultivated in a greenhouse at 20-22°C and 65-70% relative atmospheric humidity for 7 days. 15 Thereafter, the extent of the rust fungus development on the leaves was determined.

The visually determined values for the percentage of diseased leaf areas were converted into efficacies as % of the untreated 20 control. An efficacy of 0 means the same disease level as in the untreated control, an efficacy of 100 means a disease level of 0%. The expected efficacies for the combinations of active compounds were determined using Colby's formula mentioned above and compared with the observed efficacies.

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Table 3

30	Active compound	Concentration of active compound in the spray liquor in ppm	Efficacy in % of the untreated control
	Control (untreated)	(90% infected)	0
35	Compound I = prothioconazole	1	0
		0.25	0
		0.015	0
		0.006	0
40	Compound II = trifloxystrobin	0.25	0
		0.06	0

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Active compound	Concentration of active compound in the spray liquor in ppm	Efficacy in % of the untreated control
5 Compound III = picoxystrobin	1	33
	0.25	0
	0.06	0
10 Compound IV = pyraclostrobin	0.25	0
	0.06	0

Table 4

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Combinations according to the invention	Observed efficacy	Calculated efficacy*)
20 Compound I = prothioconazole + Compound II = trifloxystrobin 0.015 + 0.25 ppm Mixture 1 : 16	22	0
Compound I = prothioconazole + Compound II = trifloxystrobin 0.06 : 0.25 ppm Mixture 1 : 4	22	0
25 Compound I = prothioconazole + Compound II = trifloxystrobin 1 + 0.25 ppm Mixture 4 : 1	67	0
Compound I = prothioconazole + Compound II = trifloxystrobin 0.25 + 0.06 ppm Mixture 4 : 1	67	0
30 Compound I = prothioconazole + Compound II = trifloxystrobin 1 + 0.06 ppm Mixture 16 : 1	11	0
Compound I = prothioconazole + Compound III = picoxystrobin 0.06 + 1 ppm Mixture 1 : 16	44	33
35 Compound I = prothioconazole + Compound III = picoxystrobin 0.06 + 0.25 ppm Mixture 1 : 4	11	0
Compound I = prothioconazole + Compound III = picoxystrobin 1 + 0.25 ppm Mixture 4 : 1	78	0
40 Compound I = prothioconazole + Compound III = picoxystrobin 0.25 + 0.06 ppm Mixture 4 : 1	78	0
Compound I = prothioconazole + Compound III = picoxystrobin 1 + 0.06 ppm Mixture 16 : 1	44	0
45 Compound I = prothioconazole + Compound IV = pyraclostrobin 0.015 + 0.25 ppm Mixture 1 : 16	94	0

16

	Combinations according to the invention	Observed efficacy	Calculated efficacy*)
5	Compound I = prothioconazole + Compound IV = pyraclostrobin 0.06 + 0.25 ppm Mixture 1 : 4	89	0
	Compound I = prothioconazole + Compound IV = pyraclostrobin 1 + 0.25 ppm Mixture 4 : 1	22	0
10	Compound I = prothioconazole + Compound IV = pyraclostrobin 0.25 + 0.06 ppm Mixture 4 : 1	22	0
	Compound I = prothioconazole + Compound IV = pyraclostrobin 1 + 0.06 ppm Mixture 16 : 1	89	0

\*) efficacy calculated using Colby's formula

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The test results show that in all mixing ratios the observed efficacy is higher than the efficacy calculated beforehand using Colby's formula (from Synerg 171. XLS).

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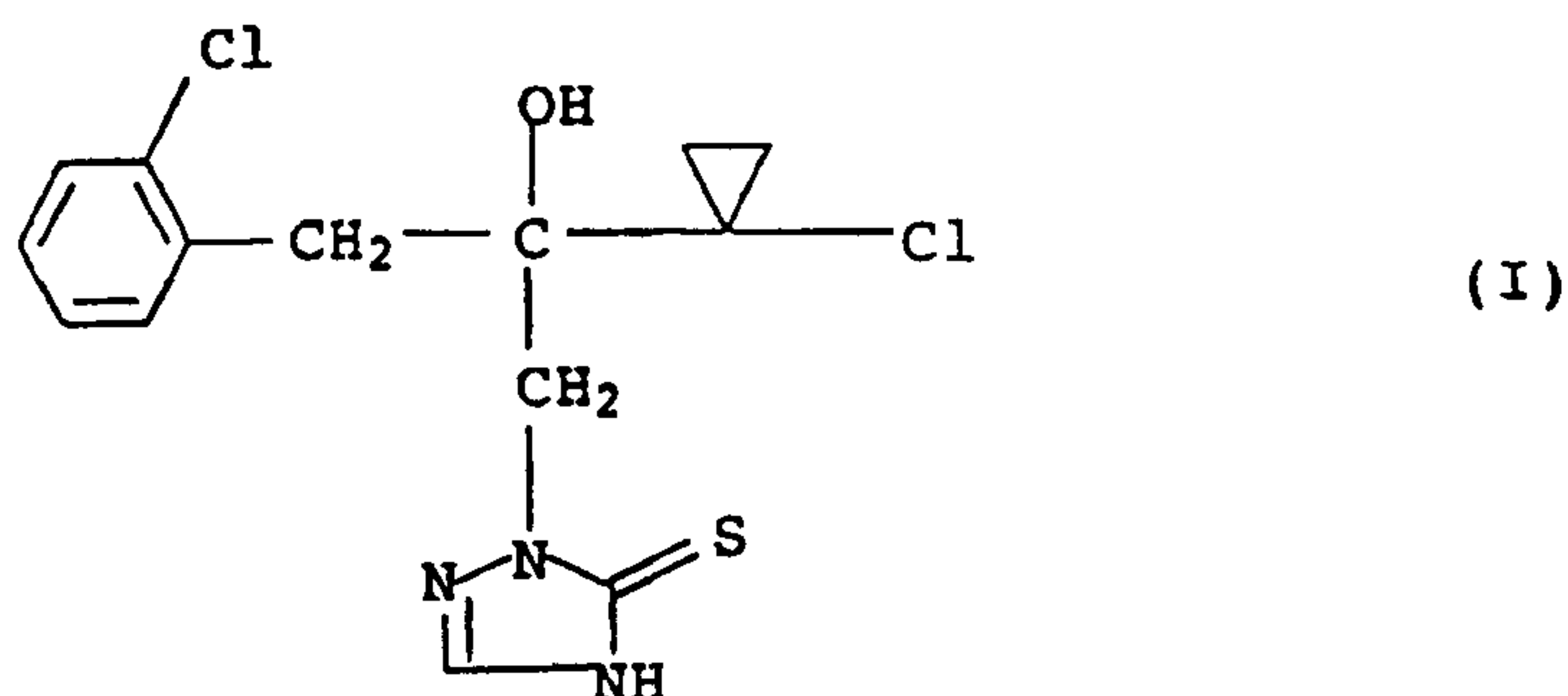
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**WHAT IS CLAIMED IS:**

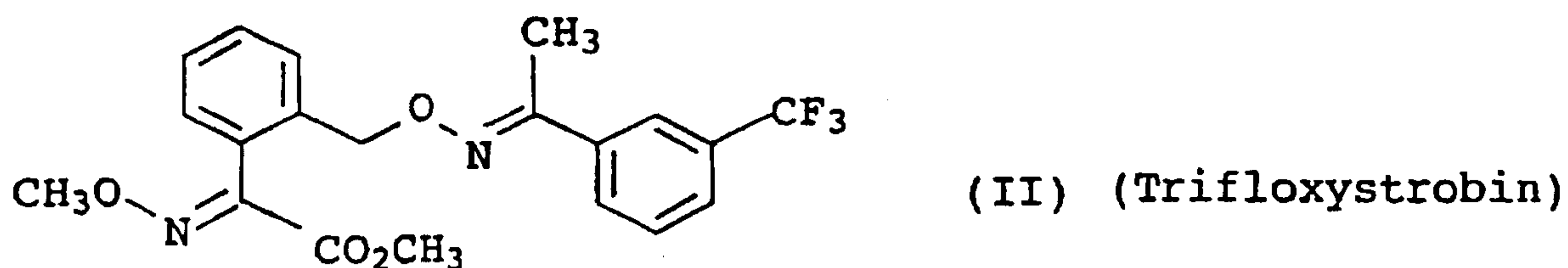
1. A fungicidal mixture, comprising:

- (1) 2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro-[1,2,4]-triazole-3-thione (prothioconazole) of the formula I or its salts or adducts



and

- (2) trifloxystrobin of the formula II:

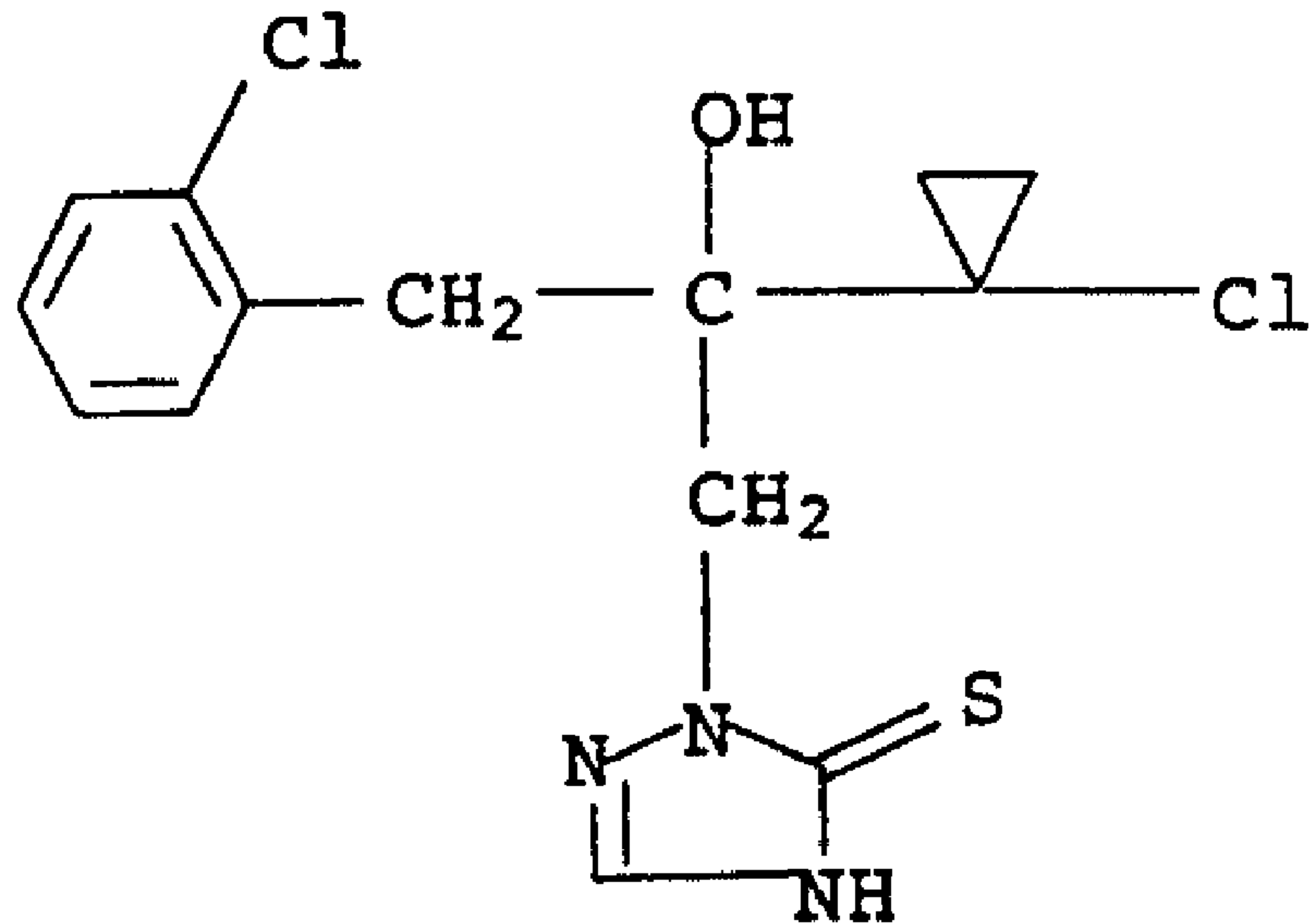


10 or the salts or adducts

in a synergistically effective amount.

2. A fungicidal mixture as claimed in claim 1, wherein the weight ratio of prothioconazole of the formula I to trifloxystrobin of the formula II is from 20:1 to 1:20.
3. A method for controlling harmful fungi, which comprises treating the harmful fungi, their habitat or the plants, seeds, soils, areas, materials or spaces to be kept free from them with the fungicidal mixture as claimed in claim 1 or 2.

4. A method as claimed in claim 3, wherein the compound of the formula I as set forth in claim 1 and the compound of the formula II as set forth in claim 1 are applied simultaneously, that is together or separately, or in succession.
5. A method as claimed in claim 3 or 4, wherein the fungicidal mixture or the compound of the formula I with the compound of the formula II as set forth in claim 1 is applied in an amount of from 0.01 to 8 kg/ha.
6. A fungicidal composition, comprising the fungicidal mixture as claimed in claim 1 or 2 and a solid or liquid carrier.



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