



(86) Date de dépôt PCT/PCT Filing Date: 1998/05/18  
 (87) Date publication PCT/PCT Publication Date: 1998/12/03  
 (45) Date de délivrance/Issue Date: 2007/04/10  
 (85) Entrée phase nationale/National Entry: 1999/11/15  
 (86) N° demande PCT/PCT Application No.: EP 1998/002914  
 (87) N° publication PCT/PCT Publication No.: 1998/053686  
 (30) Priorité/Priority: 1997/05/30 (DE19722656.6)

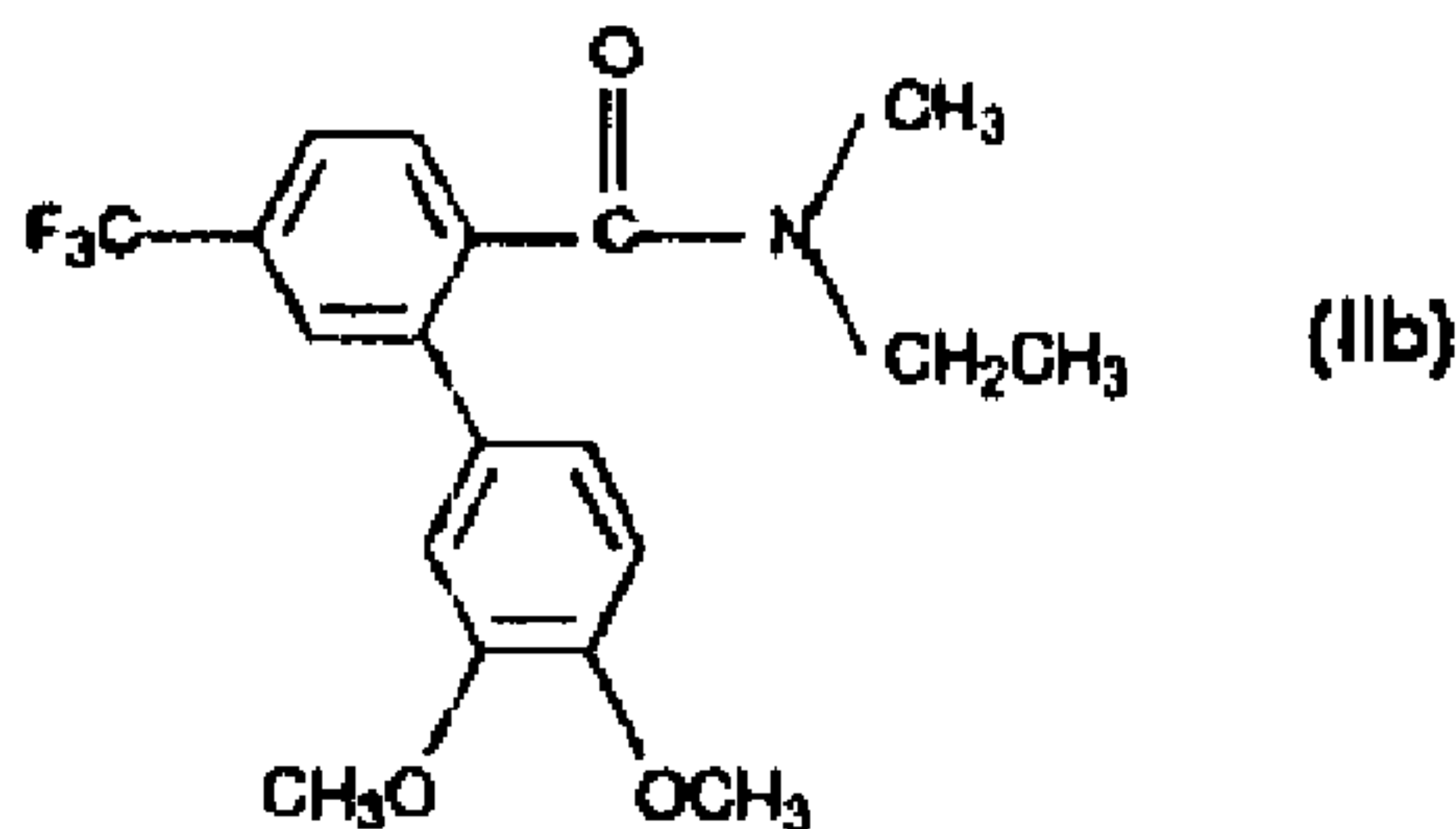
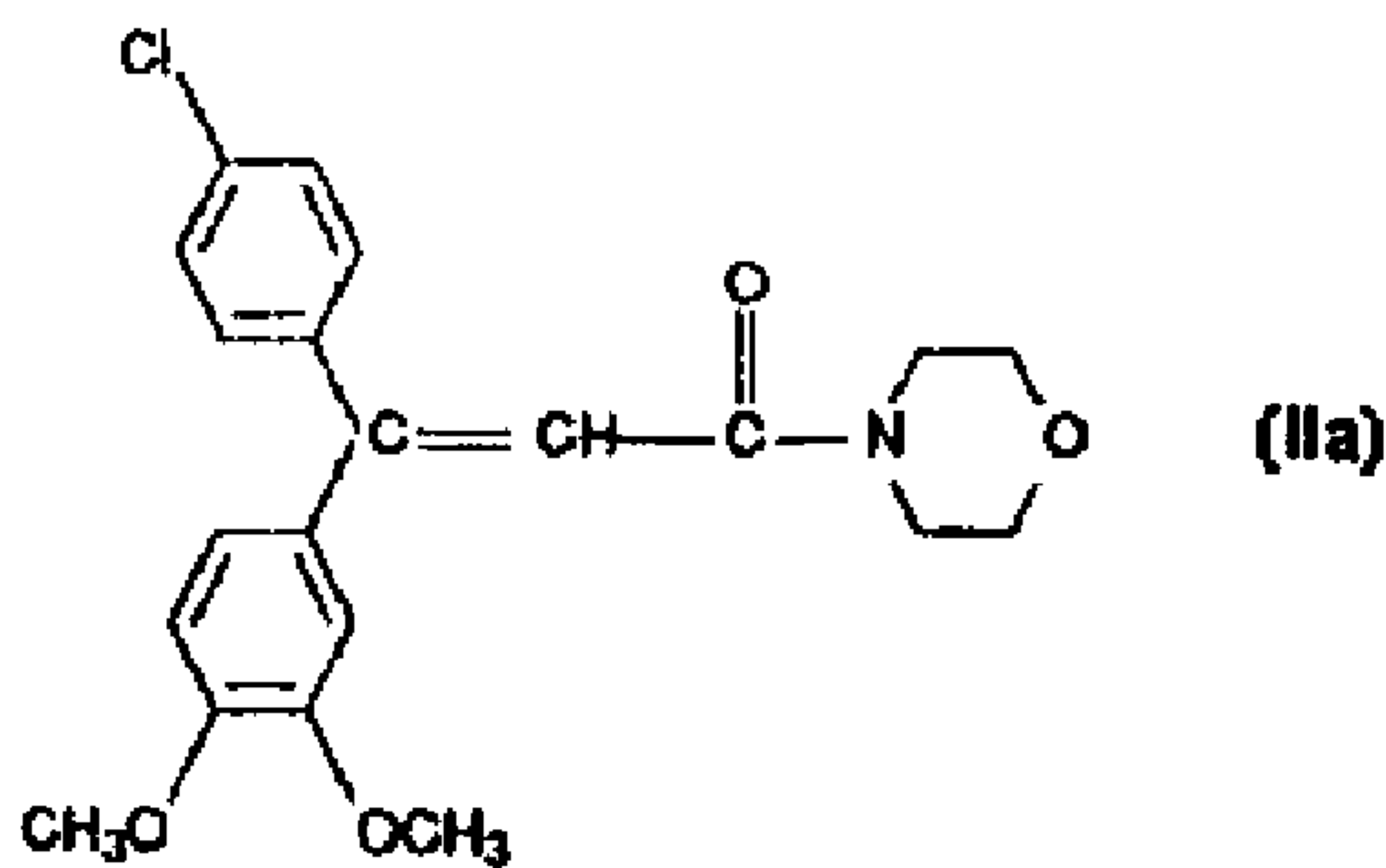
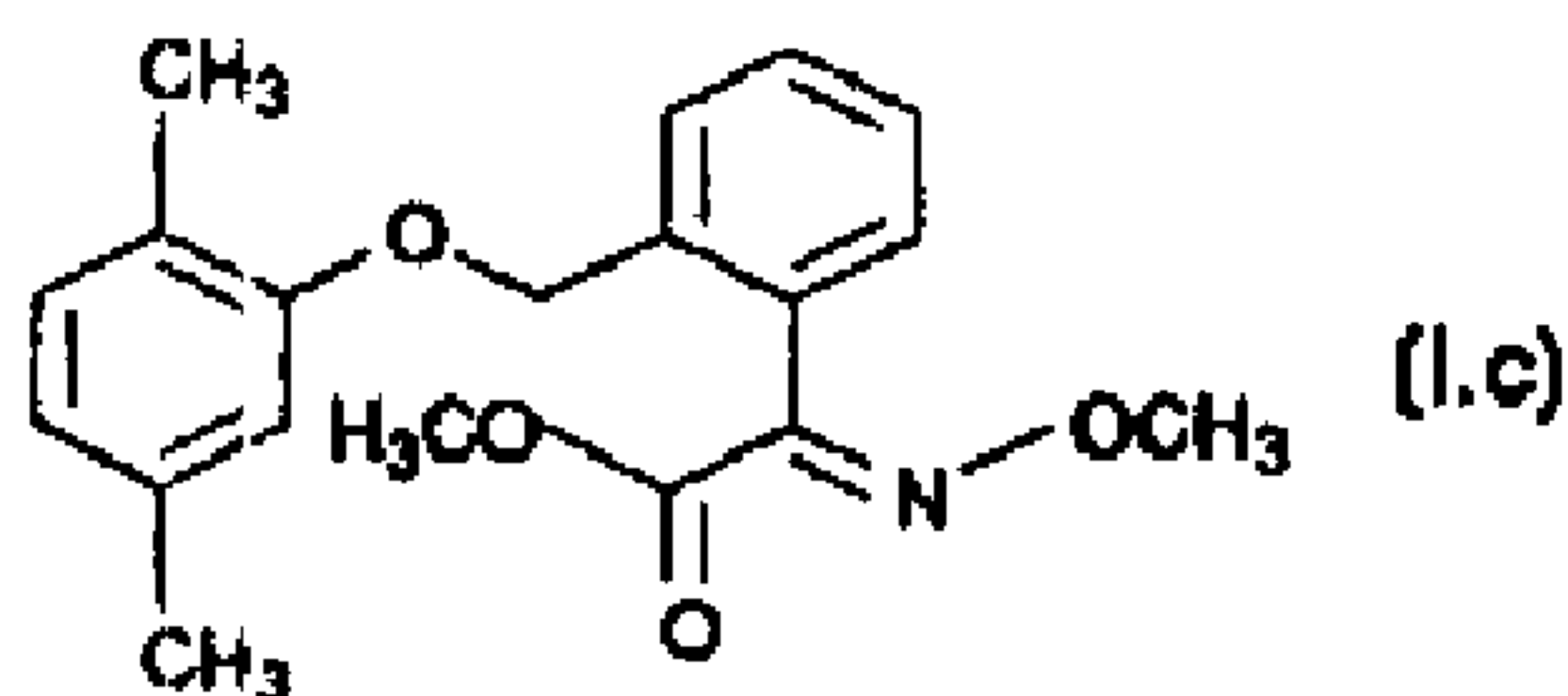
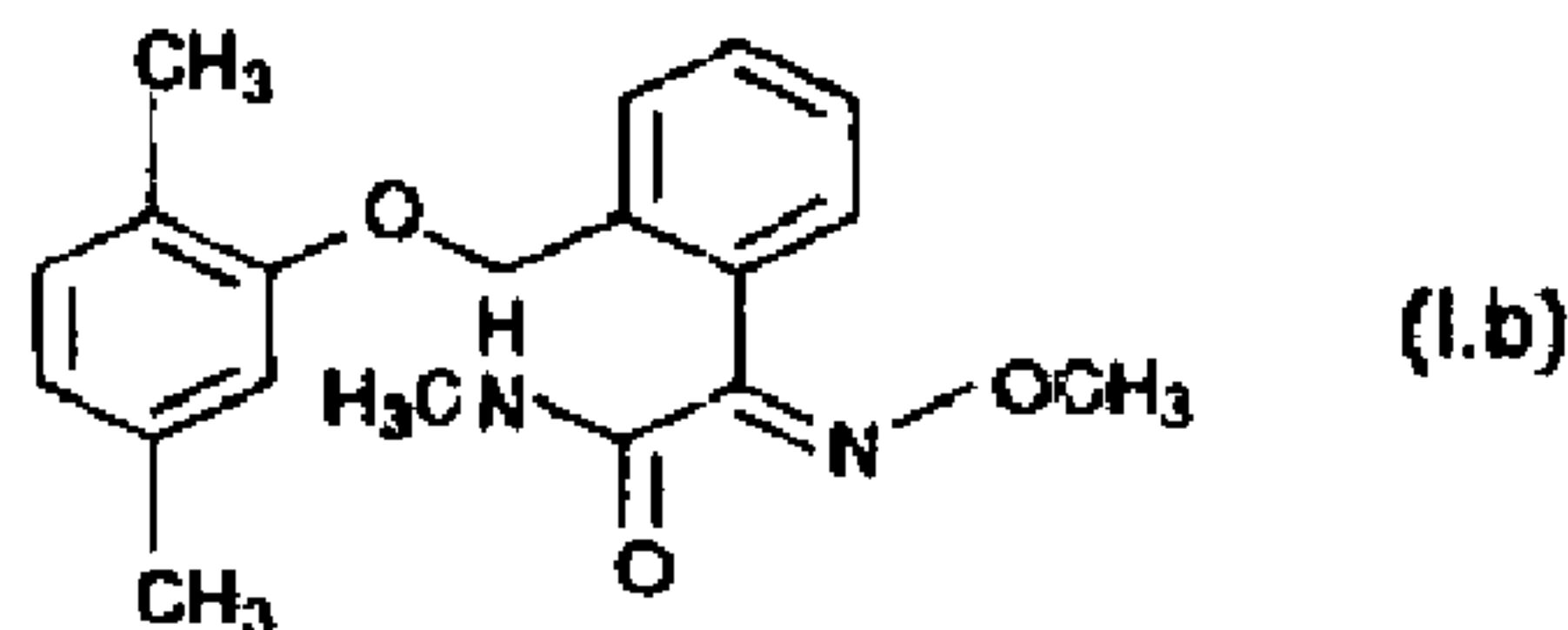
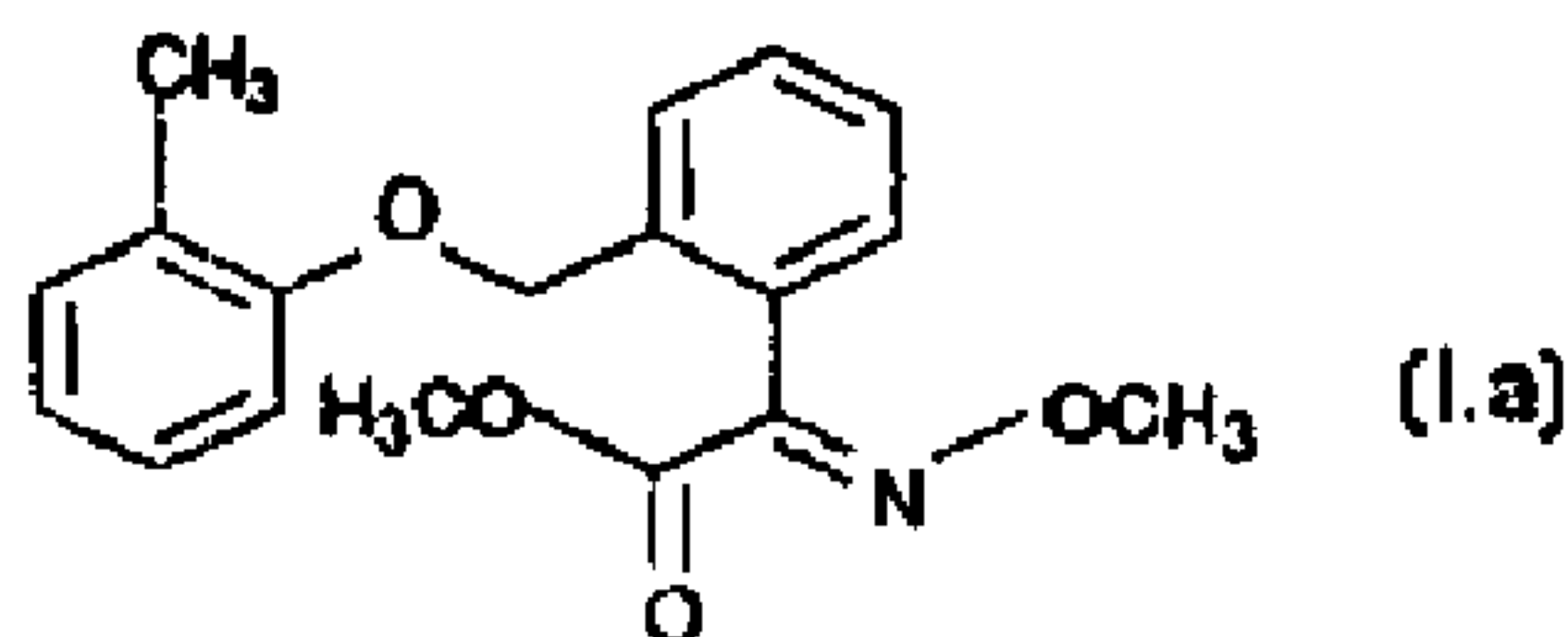
(51) Cl.Int./Int.Cl. *A01N 37/50* (2006.01),  
*A01N 43/84* (2006.01), *A01P 3/00* (2006.01)

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 (54) Title: FUNGICIDAL MIXTURE



(57) Abrégé/Abstract:

The invention relates to a fungicidal mixture, containing a synergistically effective amount of a) a phenyl-benzyl ether derivative of formula (I.a), (I.b) or (I.c) and b) a carboxylic acid amide (II) selected from the group of compounds (IIa) and (IIb).

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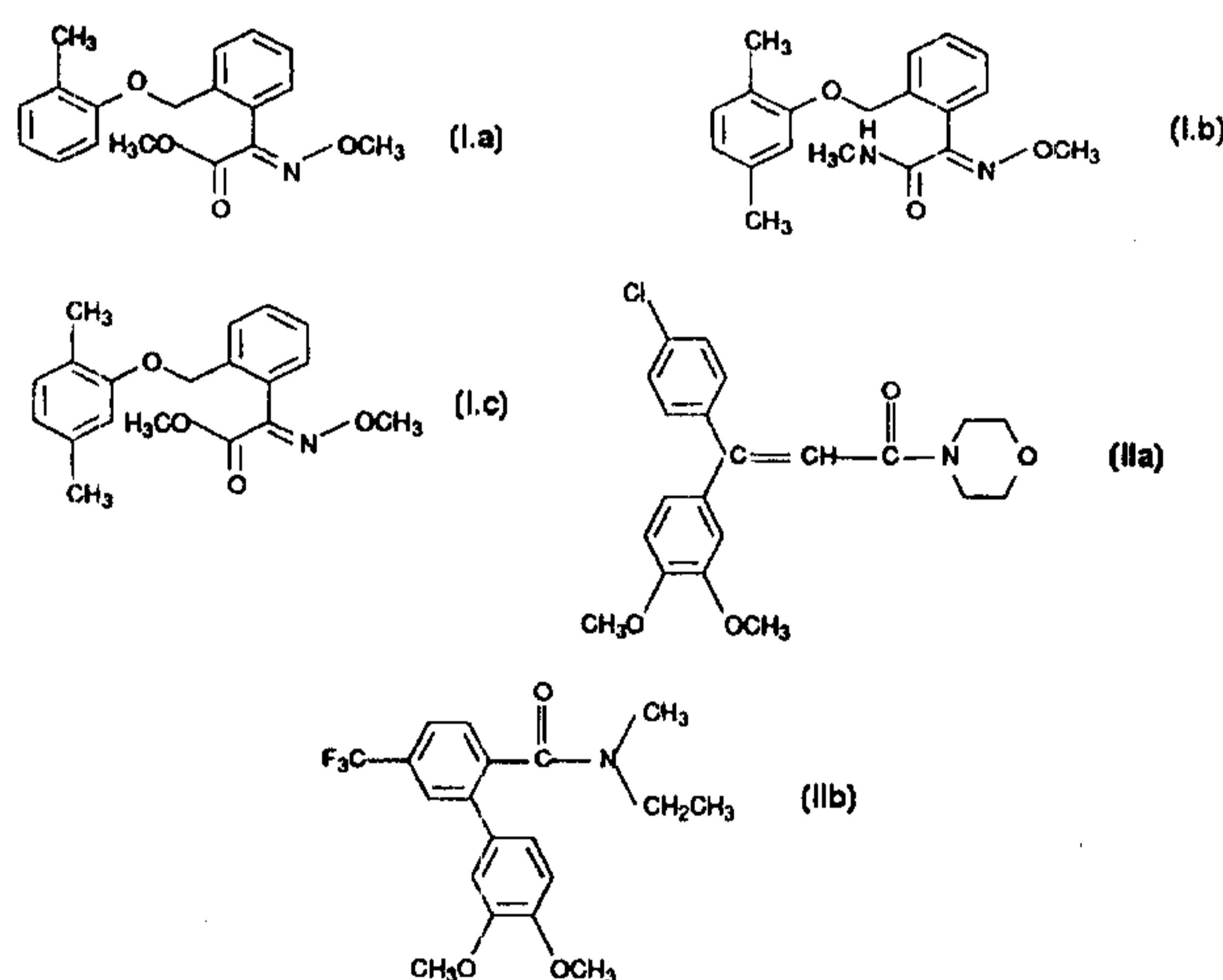


**PCT**  
WELTORGANISATION FÜR GEISTIGES EIGENTUM  
Internationales Büro  
INTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE  
INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

<p>(51) Internationale Patentklassifikation<sup>6</sup> : A01N 37/50 // (A01N 37/50, 37:38)</p>	<p>A1</p>	<p>(11) Internationale Veröffentlichungsnummer: <b>WO 98/53686</b> (43) Internationales Veröffentlichungsdatum: 3. Dezember 1998 (03.12.98)</p>
<p>(21) Internationales Aktenzeichen: PCT/EP98/02914 (22) Internationales Anmeldedatum: 18. Mai 1998 (18.05.98) (30) Prioritätsdaten: 197 22 656.6 30. Mai 1997 (30.05.97) DE (71) Anmelder (für alle Bestimmungsstaaten ausser US): BASF AKTIENGESELLSCHAFT [DE/DE]; D-67056 Ludwigshafen (DE). (72) Erfinder; und (75) Erfinder/Anmelder (nur für US): SCHELBERGER, Klaus [AT/DE]; Traminerweg 2, D-67161 Gönheim (DE). SCHERER, Maria [DE/DE]; Hermann-Jürgens-Strasse 30, D-76829 Landau (DE). SAUR, Reinhold [DE/DE]; Königsberger Strasse 9, D-67459 Böhl-Iggelheim (DE). SAUTER, Hubert [DE/DE]; Neckarpromenade 20, D-68167 Mannheim (DE). BIRNER, Erich [DE/DE]; Hauptstrasse 78, D-67317 Altleiningen (DE). LEYENDECKER, Joachim [DE/DE]; Stahlbühlring 79, D-68526 Ladenburg (DE). HAMPEL, Manfred [DE/DE]; Im Biengarten 15, D-67435 Neustadt (DE). AMMERMAN, Eberhard [DE/DE]; Von-Gagem-Strasse 2, D-64646 Heppenheim (DE). LORENZ, Gisela [DE/DE]; Erlenweg 13, D-67434</p>	<p>Neustadt (DE). STRATHMANN, Siegfried [DE/DE]; Donnersbergstrasse 9, D-67117 Limburgerhof (DE). (74) Gemeinsamer Vertreter: BASF AKTIENGESELLSCHAFT; D-67056 Ludwigshafen (DE). (81) Bestimmungsstaaten: AL, AU, BG, BR, BY, CA, CN, CZ, GE, HU, ID, IL, JP, KR, KZ, LT, LV, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TR, UA, US, eurasisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). <b>Veröffentlicht</b> <i>Mit internationalem Recherchenbericht. Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist; Veröffentlichung wird wiederholt falls Änderungen eintreffen.</i></p>	

(54) Title: FUNGICIDAL MIXTURE

(54) Bezeichnung: FUNGIZIDE MISCHUNG



(57) Abstract

The invention relates to a fungicidal mixture, containing a synergistically effective amount of a) a phenyl-benzyl ether derivative of formula (I.a), (I.b) or (I.c) and b) a carboxylic acid amide (II) selected from the group of compounds (IIa) and (IIb).

(57) Zusammenfassung

Fungizide Mischung, enthaltend a) ein Phenyl-benzyletherderivat der Formel (I.a), (I.b) oder (I.c), sowie b) ein Carbonsäureamid (II) ausgewählt aus der Gruppe der Verbindungen (IIa) und (IIb) in einer synergistisch wirksamen Menge.

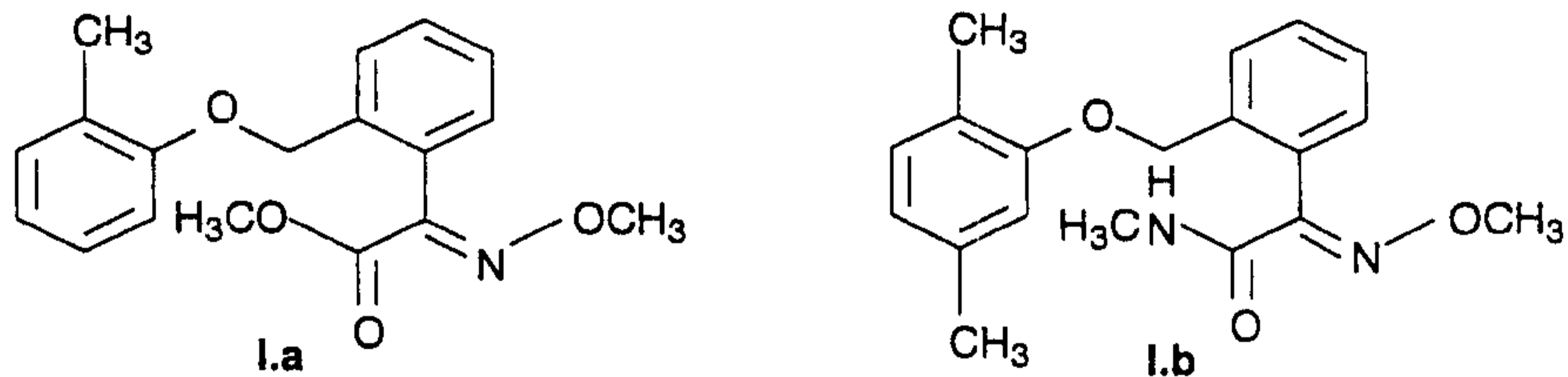
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## Fungicidal mixture

5 The present invention relates to a fungicidal mixture which comprises

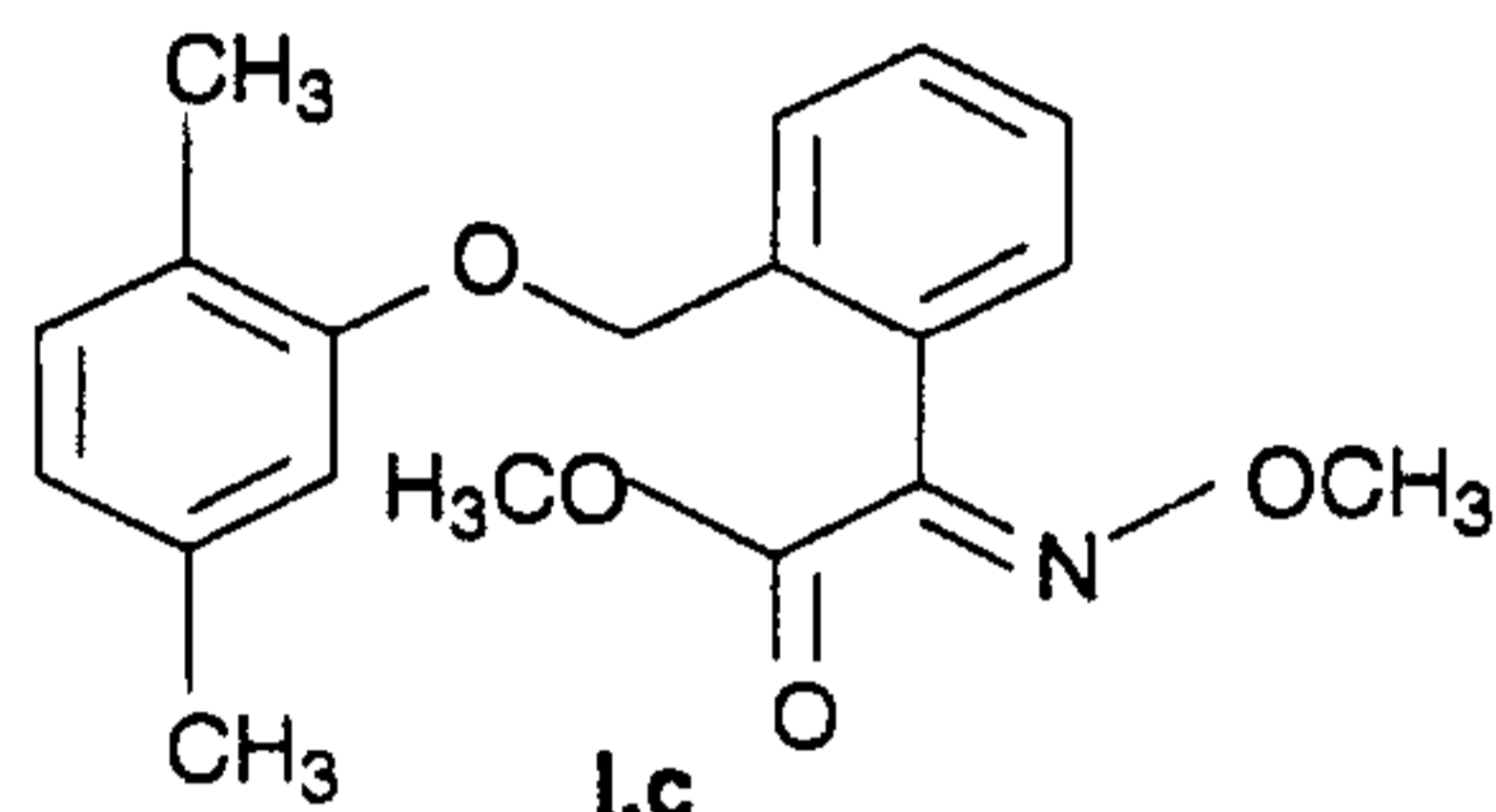
a) a phenyl benzyl ether derivative of the formula I.a, I.b or I.c,

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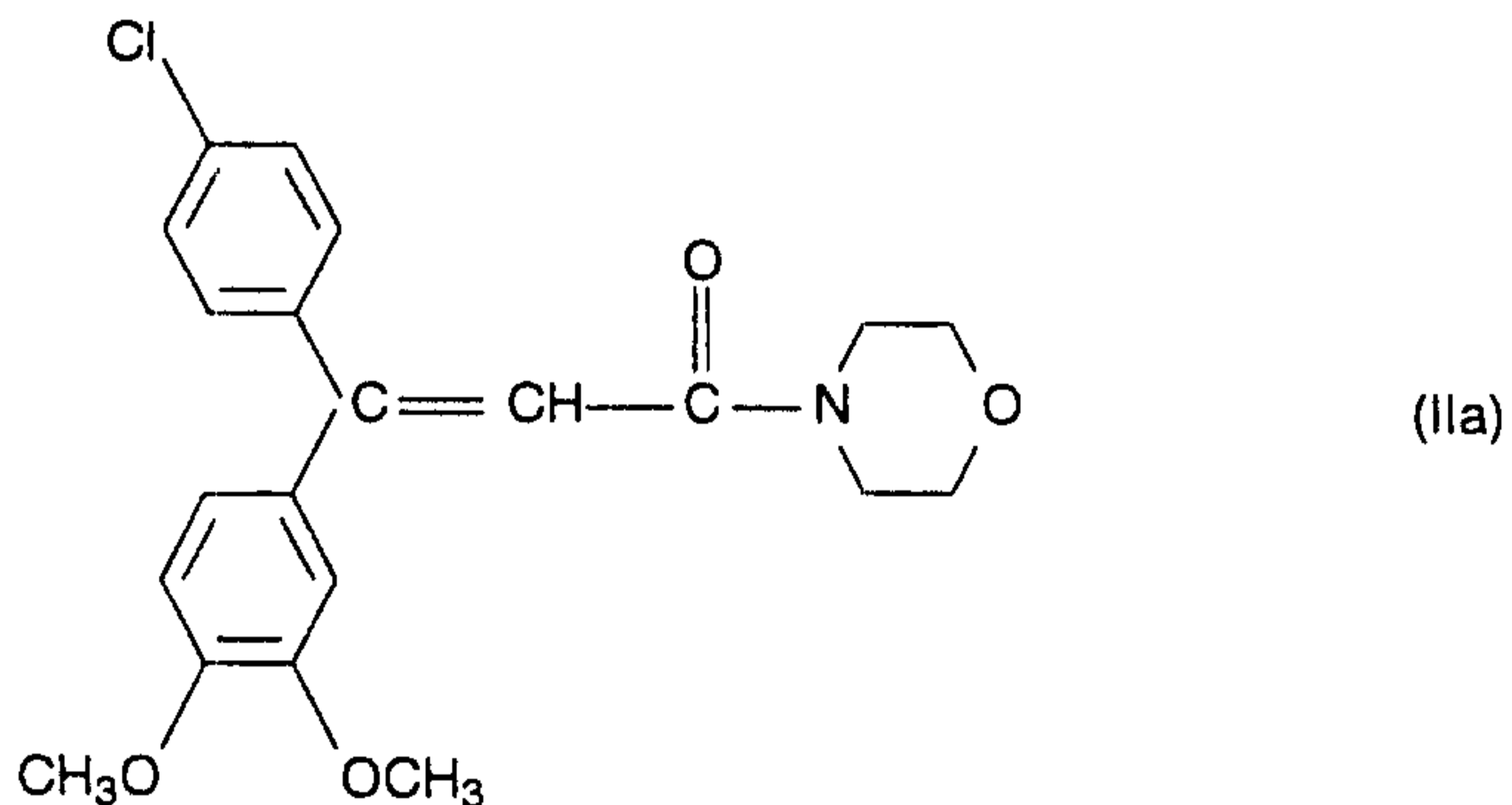
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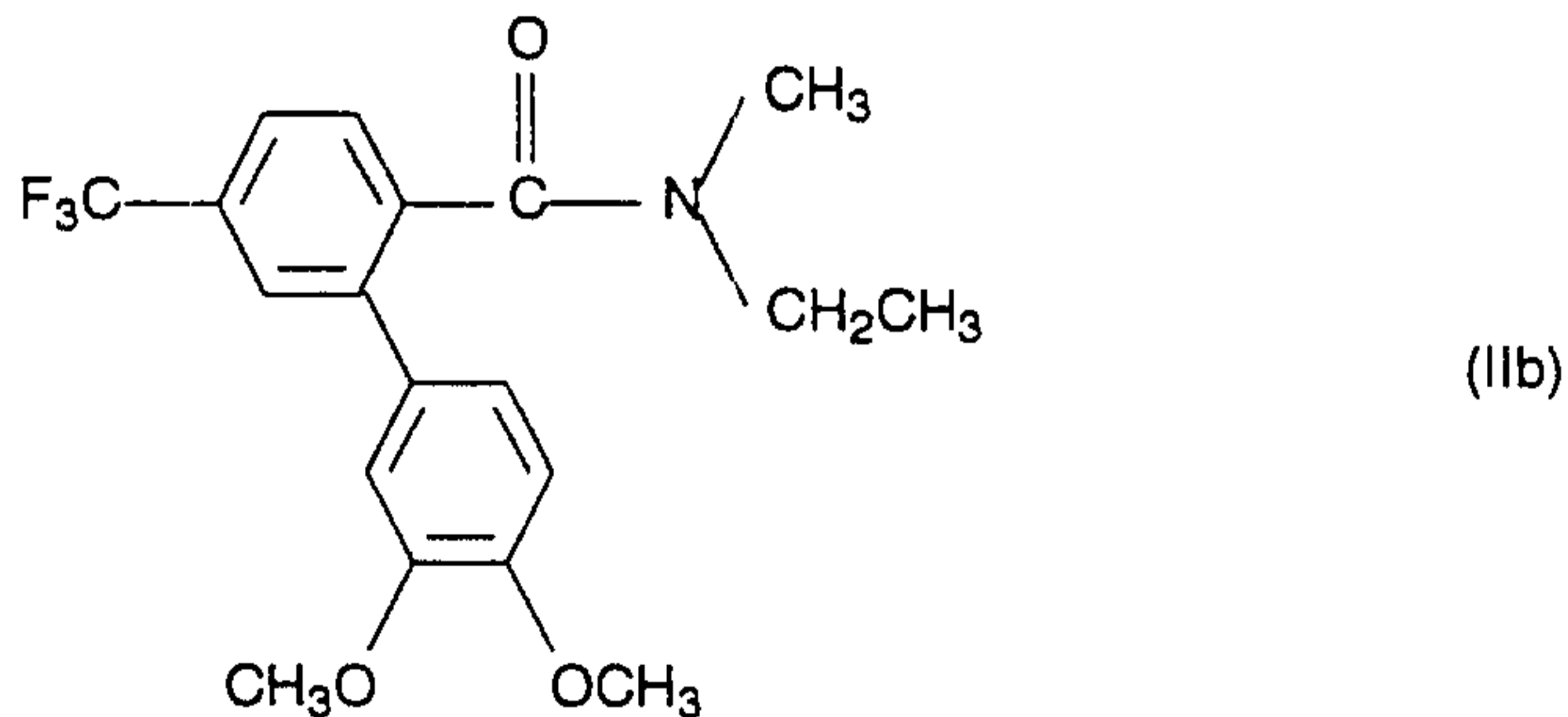
25 b) a carboxamide II selected from the group of the compounds IIa and IIb

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in a synergistically effective amount.

## 2

Moreover, the invention relates to methods for controlling harmful fungi using mixtures of the compounds I (I.a, I.b or I.c) and II (II.a or II.b) and to the use of the compound I and of the compound II for the preparation of such mixtures.

5

The compounds of the formula I, their preparation and their activity against harmful fungi are disclosed in the literature (EP-A 253 213; EP-A 254 426; EP-A 398 692).

10

Also disclosed are the carboxamides II [IIa: common name: Dimethomorph, EP-A 120 321; IIb: proposed common name: Flumetover, AGROW No. 243 (1995), 22], their preparation and their activity against harmful fungi.

15

It is an object of the present invention 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 compound I and the compound II simultaneously together or separately, or by applying the compounds I and the compounds II in succession than when the individual compounds are used.

Owing to the basic character, the compounds I and 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 hydroiodic acid, and furthermore 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 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

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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  
5 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.

10

Suitable metal ions are, in particular, the ions of the elements of 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 sub-group, in particular,  
15 chromium, manganese, iron, cobalt, nickel, copper, zinc and others. Particular preference is given to the metal ions of the elements of the sub-groups of the fourth period. The metals can exist in the various valencies which they can assume.

20

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

25

The mixtures of the compounds I and II, or the simultaneous joint or separate use of the compounds I and II, exhibit outstanding activity against a wide range of phytopathogenic  
30 fungi, in particular from the classes of the Ascomycetes, Basidiomycetes, Phycomycetes and Deuteromycetes. Some of them act systemically and can therefore be employed as folio- and soil-acting fungicides.

35 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,  
40 sugarcane, and a variety of seeds.

They are particularly suitable for controlling the following phytopathogenic fungi: *Erysiphe graminis* (powdery mildew) on cereals, *Erysiphe cichoracearum* and *Sphaerotheca fuliginea* in  
45 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

sugarcane, *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 ground  
5 nuts, *Pseudocercospora herpotrichoides* in wheat and barley, *Pyricularia oryzae* in rice, *Phytophthora infestans* in potatoes and tomatoes, *Plasmopara viticola* in grapevines, *Pseudocercospora* species in hops and cucumbers, *Alternaria* species in vegetables and fruit, *Mycosphaerella* species in  
10 bananas and *Fusarium* and *Verticillium* species.

Furthermore, they can be used in the protection of materials (eg. in the protection of wood), for example against *Paecilomyces variotii*.  
15

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

The compounds I and II are usually used in a weight ratio of 20:1 to 0.005:1, preferably 10:1 to 0.01:1, in particular 5:1 to 0.2:1.

25 Depending on the kind of effect desired, the application rates of the mixtures according to the invention are, in particular in agricultural crops, from 0.01 to 8 kg/ha, preferably 0.1 to 5 kg/ha, in particular 0.5 to 3.0 kg/ha.

30 Application rates of the compounds I are from 0.01 to 0.5 kg/ha, preferably 0.05 to 0.5 kg/ha, in particular 0.05 to 0.3 kg/ha.

35 Correspondingly, in the case of the compounds II, the application rates are from 0.005 to 1 kg/ha, preferably 0.1 bis 0.5 kg/ha, in particular 0.1 to 0.3 kg/ha.

40 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.

If phytopathogenic fungi are to be controlled, the separate or joined application of the compounds I and II or of the mixtures  
45 of the compounds I and II is affected by spraying or dusting the

seeds, the plants or the soils before the sowing of the plants, or before or after plant emergence.

The fungicidal synergistic mixtures according to the invention, or the compounds I and II, 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 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 guarantee as fine and as uniform as possible a distribution of the mixture according to the invention.

The formulations are prepared in a manner known per se, eg. by adding solvents and/or carriers. It is usual to admix inert additives, such as emulsifiers or dispersants, with the formulations.

Suitable surfactants are the alkali metal salts, alkaline earth metal salts and ammonium salts of aromatic sulfonic acids, eg. 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 naphthalene and its derivatives with formaldehyde, condensates of naphthalene or of the naphthalenesulfonic acids with phenol and formaldehyde, polyoxyethylene octylphenol ether, ethoxylated isooctyl-, octyl- or nonylphenol, alkylphenol polyglycol ethers or tributylphenyl polyglycol ethers, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ether 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 or the mixture of the compounds I and II 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.



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Fillers or solid carriers are, for example, mineral earths, such as silica gel, silicic acids, silicas, 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.

10

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 or of the mixture of the compounds I and II. The active ingredients are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR spectrum or HPLC).

The compounds I or II, 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 of the compounds I and II in the case of separate application.

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

Use example

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

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

Use example 1 - activity against *Phytophthora infestans* on tomatoes

Leaves of potted plants of the cultivar "Große Fleischtomate" were sprayed to runoff point with an aqueous suspension made from a stock solution of 10% of active compound, 63% of cyclohexanone and 27% of emulsifier. The next day, the leaves were infected with an aqueous zoospore suspension of *Phytophthora infestans*. The plants were subsequently placed in a water-vapor-saturated chamber at 16-18°C. After 6 days, the

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tomato blight on the untreated, but infected control plants had developed to such an extent that the infection could be determined visually in %.

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

$$10 \quad E = (1 - \alpha / \beta) \cdot 100$$

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

15  $\beta$  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 efficacy 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.

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

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

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

35 y efficacy, expressed in % of the untreated control, when using active ingredient B at a concentration of b

The test results are shown in Tables 2 and 3 below.

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Table 2

Ex.	Active ingredient	Concentration of active ingredient in the spray liquor in ppm	Efficacy in % of the untreated control
5	1 C	Control (untreated)	(100% infection) 0
10	2 C	Ia	1.25 0.31 0
	3 C	Ib	0.08 0
	4 C	IIa = dimethomorph	1.25 0.31 0.08 80 40 40
15	5 C	I Ib = flumetover	1.25 0.31 0.08 10 0 0

Table 3

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Mixtures according to the invention	Observed efficacy	Calculated efficacy*)
25	1.25 ppm Ia + 1,25 ppm IIa (mixture 1 : 1)	95 84
30	0.31 ppm Ia + 0.31 ppm IIa (mixture 1 : 1)	70 40
35	1.25 ppm Ia + 1.25 ppm IIb (mixture 1 : 1)	75 28
40	0.31 ppm Ia + 0.31 ppm IIb (Mischung 1 : 1)	40 0
45	0.08 ppm Ib + 0.08 ppm IIa) (mixture 1 : 1)	90 76
	0.08 ppm Ib + 0.08 ppm IIb (mixture 1 : 1)	95 60

\*) calculated using Colby's formula

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The test results show that the observed efficacy in all mixing ratios is higher than the efficacy which had been calculated beforehand using Colby's formula.

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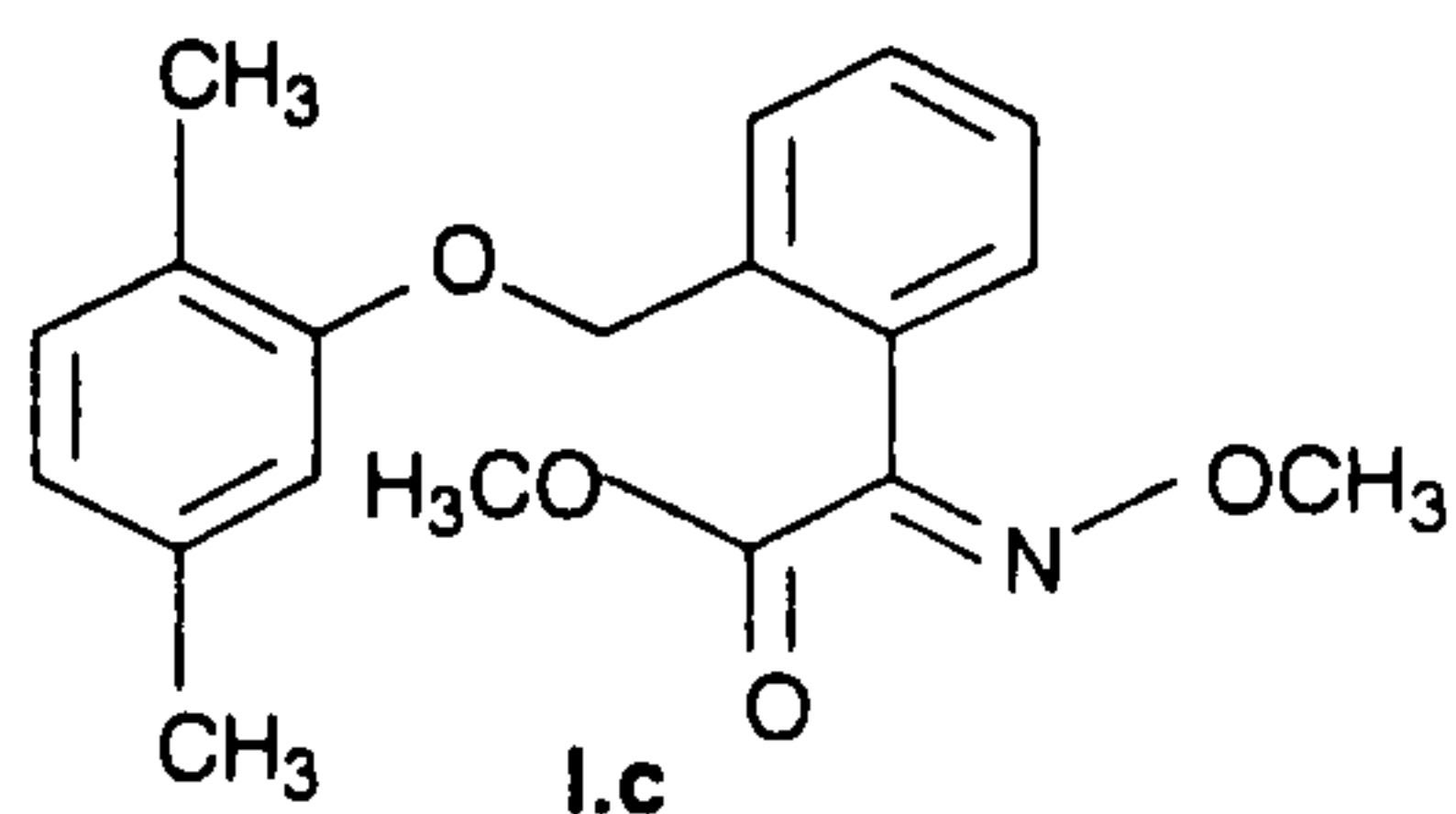
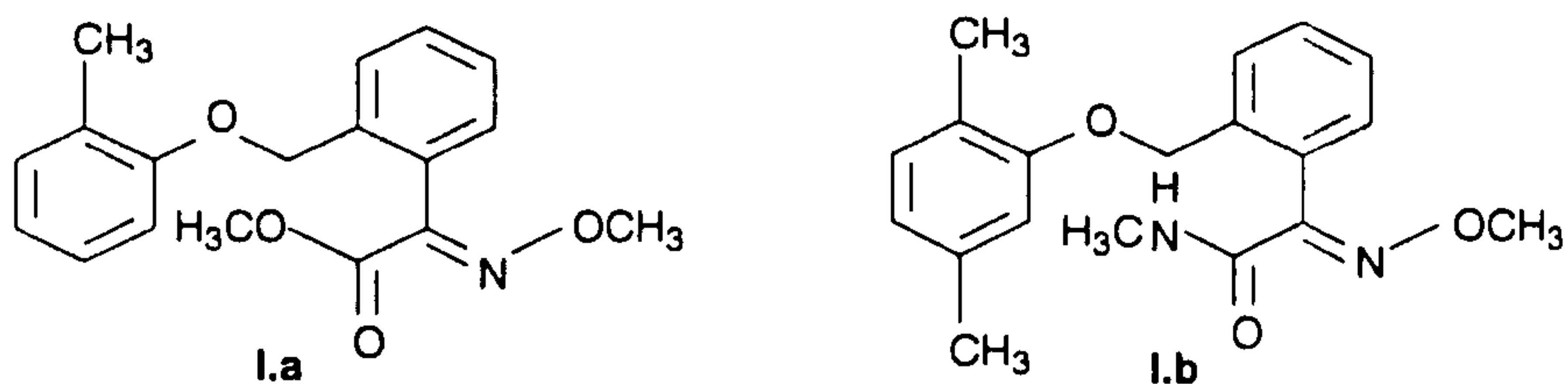
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We claim:

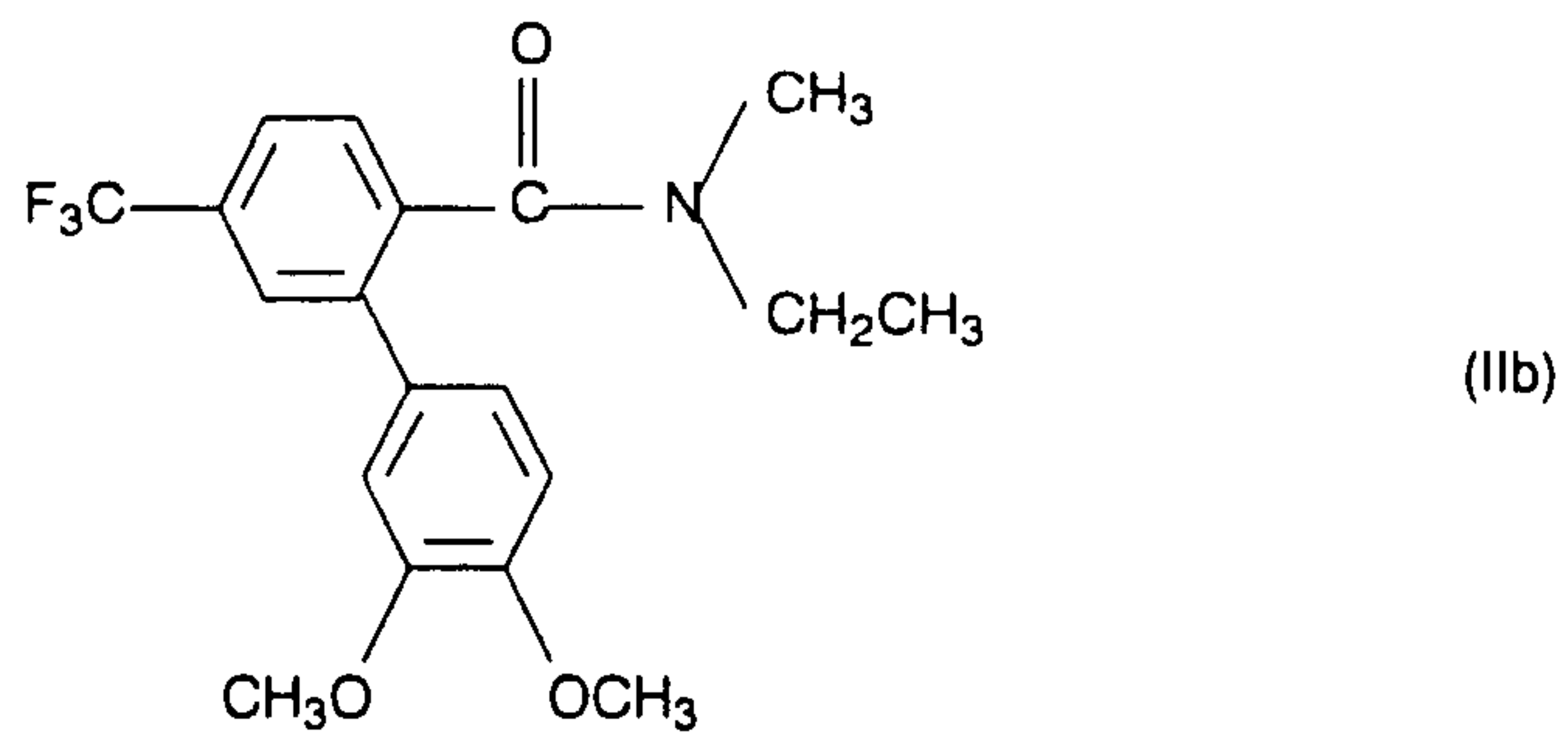
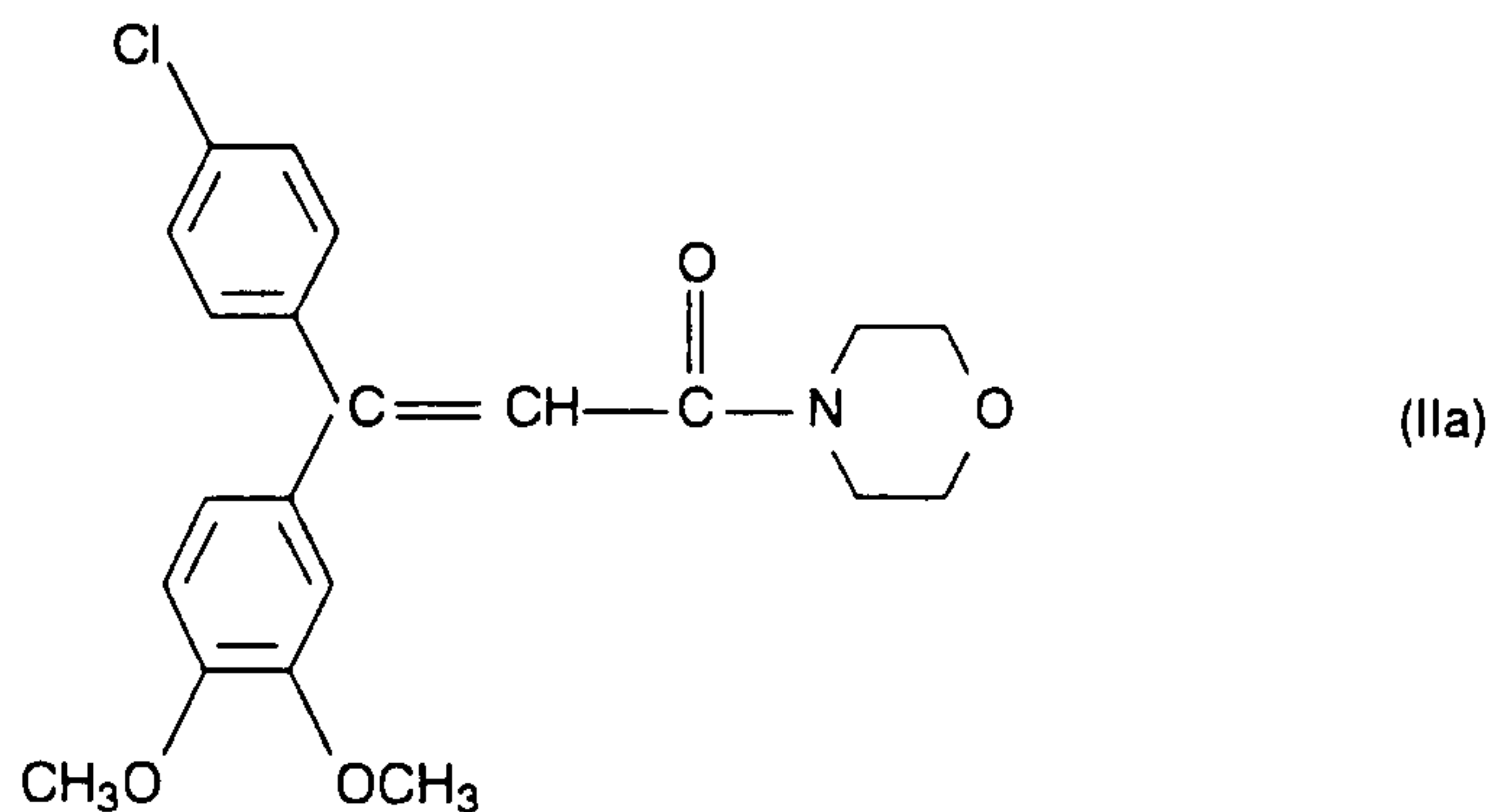
1. A fungicidal mixture, comprising

a) a phenyl benzyl ether I selected from the group of compounds of the formula I.a, I.b and I.c,



and

b) a carboxamide II selected from the group of compounds of the formula IIa and IIb



in a synergistically effective amount.

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2. A fungicidal mixture as claimed in claim 1, comprising the carboxamide IIa.
3. A fungicidal mixture as claimed in claim 1, comprising the carboxamide IIb.
4. A fungicidal mixture as claimed in any one of claims 1 to 3, wherein the weight ratio of the compound I to the compound II is 20:1 to 0.1:2.
5. 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 a compound of the formula I as set forth in claim 1 and the compound of the formula II as set forth in claim 1.
6. A method as claimed in claim 5, wherein the compound I as set forth in claim 1 and the compound II as set forth in claim 1 are applied simultaneously or in succession.
7. A method as claimed in claim 5, wherein the harmful fungi, their habitat, or the plants, seeds, soils, areas, materials or spaces to be kept free from them are treated with 0.01 to 0.5 kg/ha of a compound I as set forth in claim 1.
8. A method as claimed in claim 5, wherein the harmful fungi, their habitat, or the plants, seeds, soils, areas, materials or spaces to be kept free from them are treated with 0.05 to 1 kg/ha of a compound II as set forth in claim 1.
9. The use of a compound I as set forth in claim 1 for preparing a fungicidally effective synergic mixture as claimed in claim 1.
10. The use of the compounds II as set forth in claim 1 for preparing a fungicidally effective synergistic mixture as claimed in claim 1.
11. A fungicidal mixture as claimed in claim 1, which is conditioned in two parts, one part comprising a compound of the formula I as set forth in claim 1 in a solid or liquid carrier, and the other part comprising a compound of the formula II as set forth in claim 1 in a solid or liquid carrier.

