



(86) Date de dépôt PCT/PCT Filing Date: 2013/06/13
(87) Date publication PCT/PCT Publication Date: 2013/12/19
(45) Date de délivrance/Issue Date: 2021/11/30
(85) Entrée phase nationale/National Entry: 2014/12/04
(86) N° demande PCT/PCT Application No.: EP 2013/062306
(87) N° publication PCT/PCT Publication No.: 2013/186325
(30) Priorité/Priority: 2012/06/15 (ITMI2012A 001045)

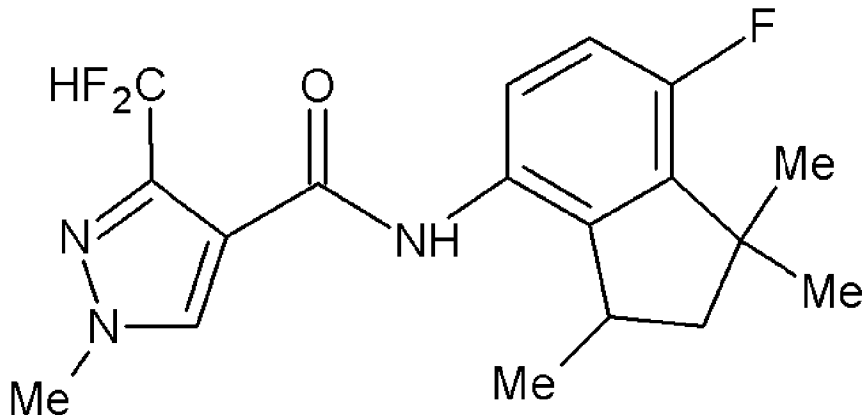
(51) Cl.Int./Int.Cl. *A01N 35/04* (2006.01),
A01N 37/34 (2006.01), *A01N 37/36* (2006.01),
A01N 37/38 (2006.01), *A01N 37/46* (2006.01),
A01N 37/50 (2006.01), *A01N 43/30* (2006.01),
A01N 43/36 (2006.01), *A01N 43/40* (2006.01),
A01N 43/50 (2006.01), *A01N 43/54* (2006.01),
A01N 43/56 (2006.01), ...

(72) Inventeurs/Inventors:
PELLACINI, FRANCO, IT;
VAZZOLA, MATTEO SANTINO, IT;
GUSMEROLI, MARILENA, IT;
SINANI, ENTELA, IT;
RISERVATO, MANUELA, IT

(73) Propriétaire/Owner:

(54) Titre : COMPOSITIONS SYNERGETIQUES POUR LA PROTECTION DE RECOLTES AGRICOLES ET LEUR UTILISATION

(54) Title: SYNERGISTIC COMPOSITIONS FOR THE PROTECTION OF AGRARIAN CROPS AND THE USE THEREOF



(I)

(57) Abrégé/Abstract:

Synergistic compositions comprising: one component (A), consisting of the compound having formula (I) 3-difluoromethyl-N- (7-fluoro-1, 1, 3-trimethyl-4-indanyl) -1 -methyl-4-pyrazolecarboxamide (I), one or more components (B) having fungicidal insecticidal activity, and their use the control of harmful insects in agrarian crops.

(51) Cl.Int./Int.Cl. (suite/continued) *A01N 43/653* (2006.01), *A01N 43/84* (2006.01), *A01N 43/88* (2006.01),
A01N 47/02 (2006.01), *A01N 47/12* (2006.01), *A01N 47/18* (2006.01)

(73) Propriétaires(suite)/Owners(continued):STICHTING I-F PRODUCT COLLABORATION, NL

(74) Agent: ROBIC

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(10) International Publication Number
WO 2013/186325 A1

(43) International Publication Date
19 December 2013 (19.12.2013)

(51) International Patent Classification:

A01N 35/04 (2006.01) *A01N 43/50* (2006.01)
A01N 37/34 (2006.01) *A01N 43/54* (2006.01)
A01N 37/36 (2006.01) *A01N 43/56* (2006.01)
A01N 37/38 (2006.01) *A01N 43/653* (2006.01)
A01N 37/46 (2006.01) *A01N 43/84* (2006.01)
A01N 37/50 (2006.01) *A01N 43/88* (2006.01)
A01N 43/30 (2006.01) *A01N 47/02* (2006.01)
A01N 43/36 (2006.01) *A01N 47/12* (2006.01)
A01N 43/40 (2006.01) *A01N 47/18* (2006.01)

(21) International Application Number:

PCT/EP2013/062306

(22) International Filing Date:

13 June 2013 (13.06.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

MI2012A 001045 15 June 2012 (15.06.2012) IT

(71) Applicant: **STICHTING I-F PRODUCT COLLABORATION** [NL/NL]; Prins Bernahardpein 200, NL-1097 JB Amsterdam (NL).

(72) Inventors: **PELLACINI, Franco**; Via Giacomo Balla, 14, I-20151 Milano (IT). **VAZZOLA, Matteo Santino**; Via P. Mascagni, 11, I-20815 Cogliate (mb) (IT). **GUSMEROLI, Marilena**; Viale Libertà 114/B, I-20900 Monza (mb) (IT). **SINANI, Entela**; Via Monte San Michele, 4, I-28100 No-

vara (IT). **RISERVATO, Manuela**; Via Maestra T.Q., 130, I-28100 Novara (IT).

(74) Agent: **BOTTERO, Carlo**; c/o Barzanò & Zanardo Milano S.p.A., Via Borgonuovo 10, I-20121 Milano (IT).

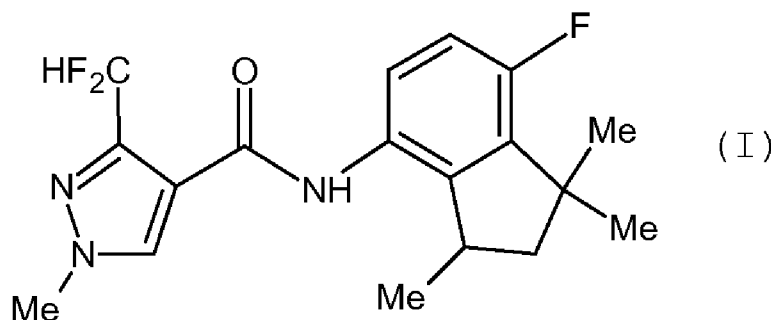
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: SYNERGISTIC COMPOSITIONS FOR THE PROTECTION OF AGRARIAN CROPS AND THE USE THEREOF



(57) Abstract: Synergistic compositions comprising: one component (A), consisting of the compound having formula (I) 3-difluoro-methyl-N- (7-fluoro-1, 1, 3-trimethyl-4-indanyl) -1 -methyl-4-pyrazolecarboxamide (I), one or more components (B) having fungicidal insecticidal activity, and their use the control of harmful insects in agrarian crops.

SYNERGISTIC COMPOSITIONS FOR THE PROTECTION OF AGRARIAN
CROPS AND THE USE THEREOF

The present invention relates to synergistic
5 compositions for the protection of agricultural crops
and use thereof.

In particular, object of the present invention are
compositions comprising one compound belonging to the
N-indanyl-pyrazolecarboxamides chemical class and one
10 or more fungicidal or insecticidal compounds.

In the application of antiparasitic products for
agricultural use, it is widely known to combine two or
more products having a different mechanism of action
and/or a different biological target, in order to
15 broaden the action range of the mixtures with respect
to the product used individually and to prevent the
occurrence of resistance phenomena from the harmful
organisms, phenomena which with time tend to reduce the
effectiveness of the antiparasitic products used.

20 Compositions of fungicidal N-indanyl-1-methyl-3-
(halo)alkyl-4-pyrazolecarboxamides with fungicidal or
insecticidal compounds such as azoles, strobilurins,
acylalanines, phenylpyrroles, chlorothalonil, dithio-
carbamates, abamectin, insecticidal diamides,
25 neonicotinoids, sulfoxaflor, pyrethroids, carbamates,
phenylpyrazoles, are describen in the patent
applications WO 2011/135833, WO 2011/135835, WO
2011/135836, WO 2011/135837, WO 2011/135838, WO
2011/135839, WO 2011/135827, WO 2011/135828, WO
30 2011/135830, WO 2011/135831, WO 2011/135832, WO
2011/135834, WO 2011/135840.

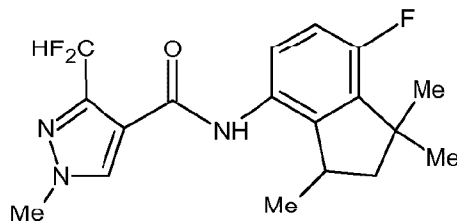
The applicant has now surprisingly found that

combining one specific fungicidal compound belonging to the class of N-indanyl-pyrazolecarboxamides with one or more compounds selected from a series of compounds having fungicidal or insecticidal activity,
 5 compositions are obtained having biological activities which are:

- 1) improved with respect to those expected on the basis of the activities of the products used alone;
- 2) superior to those achievable with the compositions
 10 disclosed in said prior art documents.

A first object of the present invention therefore relates to synergistic compositions for the protection of agricultural crops comprising:

- at least a component [A] consisting of the compound
 15 of formula (I) 3-difluoromethyl-N-(7-fluoro-1,1,3-trimethyl-4-indanyl)-1-methyl-4-pyrazolecarboxamide



(I)

wherein Me represents a methyl group CH₃-,

- 20 - at least a component [B] selected from fungicidal or insecticidal compounds belonging to one or more of the following groups of fungicidal and insecticidal compounds:

fungicidal compounds:

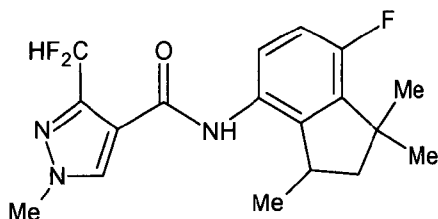
- 25 i) azoles;
- ii) amino-derivatives;
- iii) strobilurins;
- iv) specific anti-oidium compounds;

- v) aniline-pyrimidines;
- vi) benzimidazoles and analogues;
- vii) dicarboximides;
- viii) polyhalogenated fungicides;
- 5 ix) systemic acquired resistance (SAR) inductors;
- x) phenylpyrroles;
- xi) acylalanines;
- xii) anti-peronosporic compounds;
- xiii) dithiocarbamates;
- 10 xiv) arylamidines;
- xv) phosphorous acid and its derivatives;
- xvi) fungicidal copper compounds;
- xvii) fungicidal amides;
- xviii) nitrogen heterocycles;
- 15 insecticidal compounds:
- xix) neonicotinoids;
- xx) phenylpyrazoles;
- xxi) pyrethroids;
- xxii) carbamates;
- 20 xxiii) macrolides of microbial origin;
- xxiv) insecticidal diamides;
- xxv) trifluoromethylpyridyl derivatives.

In particular, an object of the present invention is a composition for the protection of agrarian crops comprising:

- at least one component (A), consisting of the compound having formula (I) 3-difluoromethyl-N-(7-fluoro-1,1,3-trimethyl-4-indanyl)-1-methyl-4-pyrazolecarboxamide

30



(I)

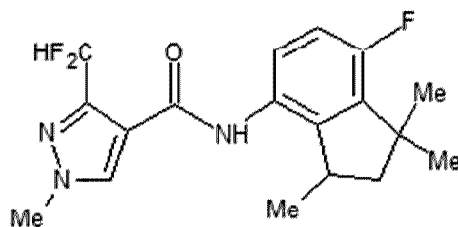
wherein Me represents a CH₃- methyl group, and

- 5 - at least one component [B] selected from compounds having a fungicidal or insecticidal activity belonging to one or more of the following groups of fungicidal and insecticidal compounds:
- fungicidal compounds:
- 10 i) azoles;
 ii) amino derivatives;
 iii) strobilurins;
 iv) specific anti-oidium compounds;
 v) anilinopyrimidines;
 15 vi) benzimidazoles and their analogues;
 vii) dicarboxyimides;
 viii) polyhalogenated fungicides;
 ix) inducers of acquired systemic resistance (SAR);
 x) phenylpyrroles;
 20 xi) acylalanines;
 xii) antiperonosporic compounds;
 xiii) dithiocarbamates;
 xiv) arylamidines;
 xv) phosphorous acid and its derivatives;
 25 xvi) copper-based cupric fungicides;
 xvii) fungicidal amides;
 xviii) nitrogenated heterocycles;
- insecticidal compounds:

- xix) neonicotinoids;
xx) phenylpyrazoles;
xxi) pyrethroids;
xxii) carbamates;
5 xxiii) macrolides of a microbial origin;
xxiv) insecticidal diamides; and
xxv) trifluoromethylpyridyl derivatives.

In particular, an object of the present invention is
10 a composition for the protection of agrarian crops
comprising:

- at least one component (A), consisting of the
compound having formula (I) 3-difluoromethyl-N-(7-
fluoro-1,1,3-trimethyl-4-indanyl)-1-methyl-4-
15 pyrazolecarboxamide



(I)

- 20 wherein Me represents a CH₃- methyl group, and
- at least one component [B] selected from compounds
having a fungicidal or insecticidal activity belonging
to one or more of the following groups of a) fungicidal
and b) insecticidal compounds:

25 a) fungicidal compounds:

- i) azoles;
ii) amino derivatives selected from the group consisting
of aldimorph, dodine, dodemorph, fenpropimorph,

fenpropidin, guazatine, iminoctadine, spiroxamine and tridemorph;

iii) strobilurins;

iv) specific anti-oidium compounds selected from the group consisting of cyflufenamid, flutianil, metrafenone, proquinazid, pyriofenone and quinoxifen;

v) anilinopyrimidines;

vi) benzimidazoles and their analogues selected from the group consisting of benomyl, carbendazim, fuberidazole, thiabendazole and thiophanate-methyl

vii) dicarboxyimides;

viii) polyhalogenated fungicides;

ix) inducers of acquired systemic resistance (SAR) selected from the group consisting of acibenzolar, probenazole, isotianil and tiadinil;

x) phenylpyrroles;

xi) acylalanines;

xii) antiperonosporic compounds selected from the group consisting of ametoctradin, amisulbrom, benthiavalicarb, cyazofamid, cymoxanil, dimethomorph, ethaboxam, famoxadone, fenamidone, flumetover, flumorph, fluopicolide, iprovalicarb and mandipropamid, valifenalate;

xiii) dithiocarbamates;

xiv) arylamidines;

xv) phosphorous acid and its derivatives selected from the group consisting of fosetyl-aluminium potassium phosphite, sodium phosphite and choline phosphite;

xvi) copper-based cupric fungicides;

xvii) fungicidal amides;

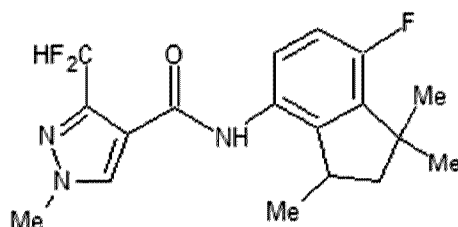
xviii) nitrogenated heterocycles;

b) insecticidal compounds:

- xix) neonicotinoids;
xx) phenylpyrazoles;
xxi) pyrethroids;
xxii) carbamates;
5 xxiii) macrolides of a microbial origin;
xxiv) insecticidal diamides; and
xxv) trifluoromethylpyridyl derivatives selected from the group consisting of flonicamid and sulfoxaflor.

10 Another object of the present invention is a synergistic composition for the protection of agrarian crops comprising:

- at least one component (A), consisting of the compound having formula (I) 3-difluoromethyl-N-(7-fluoro-1,1,3-trimethyl-4-indanyl)-1-methyl-4-pyrazolecarboxamide
- 15



20 (I)

wherein Me represents a CH₃- methyl group, and

- at least one component [B] selected from compounds having a fungicidal or insecticidal activity belonging to one or more of the following groups of a) fungicidal and b) insecticidal compounds:
- 25

a) fungicidal compounds:

- i) azoles;
ii) amino derivatives selected from the group consisting

- of aldimorph, dodine, dodemorph, fenpropimorph, fenpropidin, guazatine, iminoctadine, spiroxamine and tridemorph;
- iii) strobilurins;
- 5 iv) specific anti-oidium compounds selected from the group consisting of cyflufenamid, flutianil, metrafenone, proquinazid, pyriofenone and quinoxifen;
- v) anilinopyrimidines;
- vi) benzimidazoles and their analogues selected from the
- 10 group consisting of benomyl, carbendazim, fuberidazole, thiabendazole and thiophanate-methyl
- vii) dicarboxyimides;
- viii) polyhalogenated fungicides;
- ix) inducers of acquired systemic resistance (SAR)
- 15 selected from the group consisting of acibenzolar, probenazole, isotianil and tiadinil;
- x) phenylpyrroles;
- xi) acylalanines;
- xii) antiperonosporic compounds selected from the group
- 20 consisting of ametoctradin, amisulbrom, benthiavalicarb, cyazofamid, cymoxanil, dimethomorph, ethaboxam, famoxadone, fenamidone, flumetover, flumorph, fluopicolide, iprovalicarb and mandipropamid, valifenalate;
- xiii) dithiocarbamates;
- 25 xiv) arylamidines;
- xv) phosphorous acid and its derivatives selected from the group consisting of fosetyl-aluminium potassium phosphite, sodium phosphite and choline phosphite;
- 30 xvi) copper-based cupric fungicides;
- xvii) fungicidal amides;
- xviii) nitrogenated heterocycles;

b) insecticidal compounds:

- xix) neonicotinoids;
- xx) phenylpyrazoles;
- xxi) pyrethroids;
- 5 xxii) carbamates;
- xxiii) macrolides of a microbial origin;
- xxiv) insecticidal diamides; and
- xxv) trifluoromethylpyridyl derivatives selected from the group consisting of flonicamid and sulfoxaflor.

10

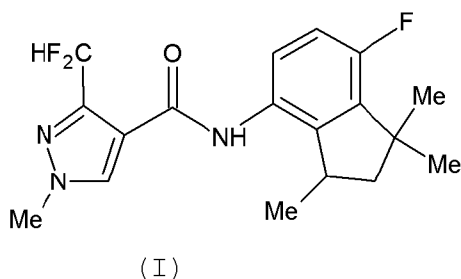
The invention provides a use of the composition as defined herein for the control of phytopathogenic fungi in agricultural crops.

15

The invention also provides a use of a composition comprising:

- at least one component (A), consisting of the compound having formula (I) 3-difluoromethyl-N-(7-fluoro-1,1,3-trimethyl-4-indanyl)-1-methyl-4-pyrazolecarboxamide

20



wherein Me represents a CH₃- methyl group, and

25

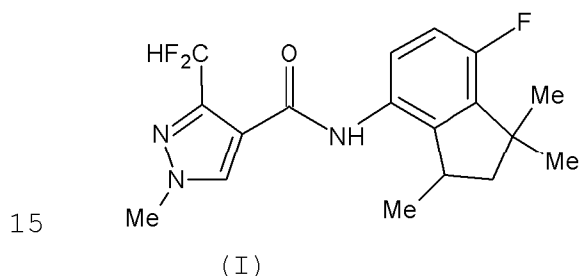
- at least one component [B] selected from compounds belonging to one or more of the following groups of fungicidal and insecticidal compounds:

- xix) neonicotinoids;

- xx) phenylpyrazoles;
xxi) pyretroids;
xxii) carbamates;
xxiii) macrolides of a microbial origin;
5 xxiv) insecticidal diamides; and
xxv) trifluoromethylpyridyl derivates,
for the control of harmful insects in agrarian crops.

The invention also provides a use of a composition
10 comprising:

- at least one component (A), consisting of the compound
having formula (I) 3-difluoromethyl-N-(7-fluoro-1,1,3-
trimethyl-4-indanyl)-1-methyl-4-pyrazolecarboxamide



wherein Me represents a CH₃- methyl group, and
- at least one component [B] selected from compounds
20 belonging to one or more of the following groups of
fungicidal and insecticidal compounds:

- xix) neonicotinoids;
xx) phenylpyrazoles;
xxi) pyretroids;
25 xxii) carbamates;
xxiii) macrolides of a microbial origin;
xxiv) insecticidal diamides; and
xxv) trifluoromethylpyridyl derivates selected from the

group consisting of flonicamid and sulfoxaflor,
for the control of harmful insects in agrarian crops.

5 The invention also provides a method for controlling
phytopathogenic fungi in agrarian crops, which comprises
applying an effective dose of at least one synergistic
composition as defined herein, on one or more parts of
the plants to be protected and/or on the seeds of said
plants before sowing and/or on the ground in which said
10 plants grow.

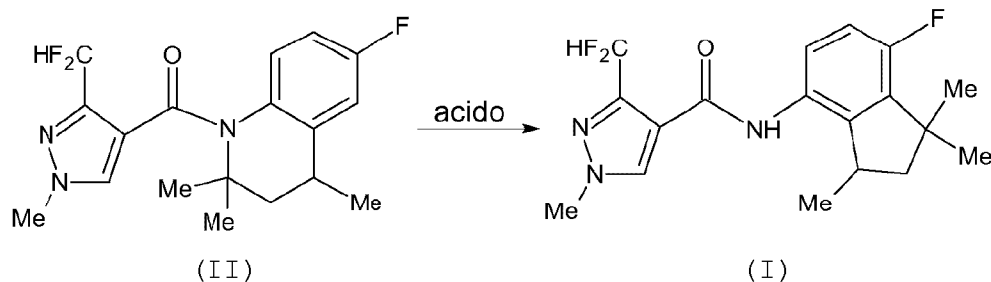
The invention also provides a method for controlling
harmful insects in agrarian crops, which comprises
applying an effective dose of at least one composition
15 as defined herein, on one or more parts of the plants to
be protected and/or on the seeds of said plants before
sowing and/or on the ground in which said plants grow

The compound of formula (I) can be prepared:

20 1) by acid isomerization of N-(3-difluoromethyl-1-methyl-
1H-4-pyrazolecarbonyl)-6-fluoro-2,2,4-trimethyl-
1,2,3,4-tetrahydro-quinoline (II), according to reaction
scheme 1, and as described in Example 1:

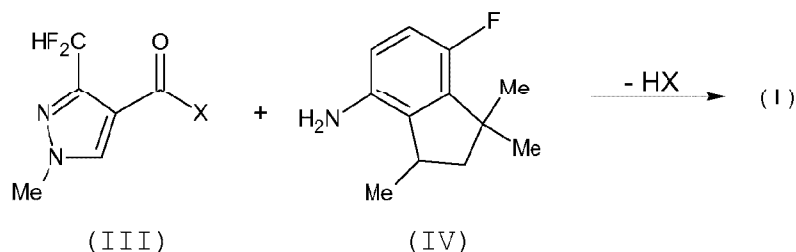
scheme 1

25



2) by condensation of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid or its derivative, of
 5 general formula (III), with 7-fluoro-1,1,3-trimethyl-4-aminoindane (IV), utilizing methods well known in organic chemistry, according to scheme 2:

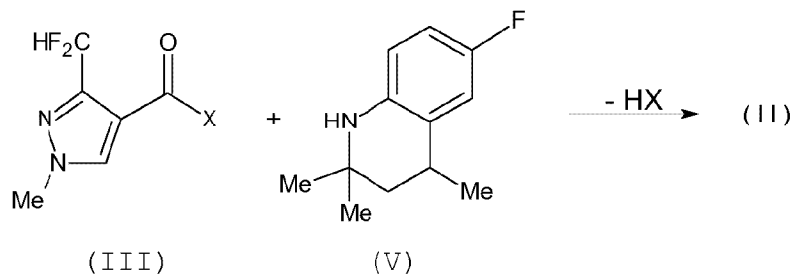
scheme 2



wherein X represents a group selected from OH, alkoxy C₁-C₆ or a halogen atom (preferably chlorine).

The intermediate of formula (II) is in turn obtained by condensation of a compound of general
 15 formula (III) with 6-fluoro-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline (V), according to scheme 3:

scheme 3

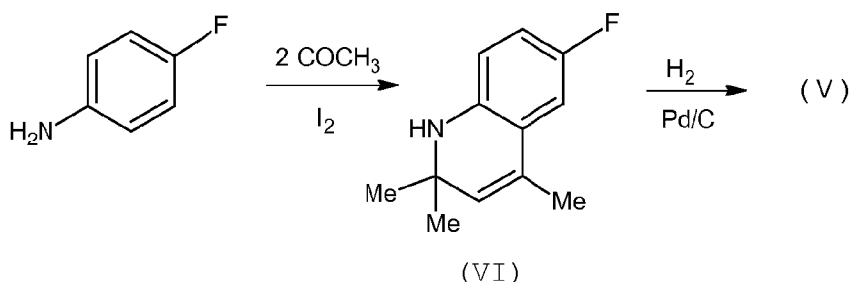


20 wherein X represents a group selected from OH, alkoxy C₁-C₆ or a halogen atom (preferably chlorine).

The 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid and its derivatives of general formula (III) are known products, described for example in the patent N. US 5,093,347.

5 The intermediate of formula (V) can be prepared, according to reaction scheme 4, by hydrogenation of 6-fluoro-2,2,4-trimethyl-1,2-dihydroquinoline (VI), in turn obtained according to a method described in Organic Synthesis, Coll. Vol. III, pag. 329, starting
10 from acetone and 4-fluoroaniline:

scheme 4



in the aforesaid formulas (I)-(VI) Me represents a
15 methyl group CH₃-.

The aminoindane of formula (IV) can be prepared, analogously to what described in the patent N. EP 0654464, by condensation of 6-fluoro-2,2,4-trimethyl-1,2-dihydroquinoline (VI) with a carboxylic acid or
20 its derivative, hydrogenation on Pd/C, isomerization with sulfuric acid and hydrolysis of the amide bond with water in acetic acid.

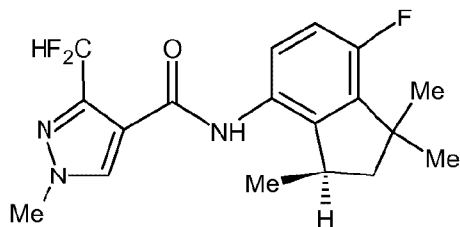
The compound of formula (I) contains an asymmetric carbon atom in position 3 of the indanyl group and it
25 is usually obtained as racemic mixture of the two enantiomers having configurations R and S (molar ratio R:S equal to 1:1). However, it is possible to prepare mixtures of the two enantiomers of the compound of

formula (I) wherein the ratio R:S is different from 1:1 (enriched mixtures).

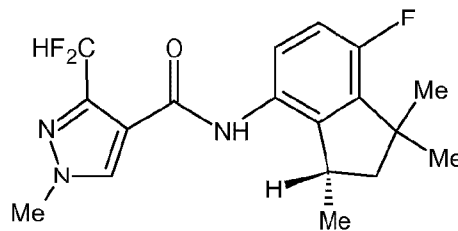
Moreover, it is possible to prepare the single enantiomers R and S of the compound of formula (I) in substantially pure form (> 99,99% by weight).

The aforesaid enantiomeric enriched mixtures and the substantially pure single enantiomers can be prepared, for example, by condensing the compounds of general formula (III) with enriched or enantiomerically pure forms (substantially pure single enantiomers) of the aminoindane of formula (IV), according to the reaction scheme 2; enriched or enantiomerically pure forms of the aminoindane of formula (IV) can be in turn obtained through enantioselective reactions and/or chemical and/or chromatographic separation of the enantiomers, according to methods described in literature for analogous products, for example as disclosed in the aforesaid EP 0654464.

In the synergistic compositions of the present invention the compound of formula (I) can be a racemic mixture, (I)-RS, or an enriched mixture of one of the two enantiomers, or even a substantially pure specific enantiomer (I)-R or (I)-S.



(I)-R



(I)-S

In the case of enriched mixtures of the compound of formula (I), those enriched in the enantiomer R are preferred, preferably with an R:S ratio of the two

enantiomers ranging from 51:49 to 99.99:0.01 by weight.

Among the two enantiomeric forms of the compound of formula (I), the substantially pure isomer R is preferred.

5 The compounds among which to select the component [B] of the synergistic compositions are here indicated with their common international ISO name; their chemical structures and CAS and IUPAC chemical names are reported on the Alan Wood's Website
10 (www.alanwood.net), Compendium of Pesticide Common Names; for most compounds, these features are also reported, together with chemical-physical data and biological features, in the "Pesticide Manual", C.D.S. Tomlin, 15th Edition, 2009, British Crop Production
15 Council Editor.

Examples of fungicidal arylamidines of group xiv are reported in the international patent applications WO 2000/46184, WO 2007/031508, WO 2009/156098.

Components [B] preferred of the compositions
20 object of the present invention are:

- i) azoles: azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, epoxyconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazalil, ipconazole,
25 metconazole, myclobutanil, penconazole, propiconazole, prochloraz, prothioconazole, simeconazole, tebuconazole, tetra-conazole, triadimefon, triadimenol, triflumizole, triticonazole;
- ii) amino-derivatives: aldimorph, dodine, dodemorph,
30 fen-propimorph, fenpropidin, guazatine, iminoctadine, spiroxamine, tridemorph;
- iii) strobilurins: azoxystrobin, dimoxystrobin, fluoxa-

- strobilin, kresoxim-methyl, metominostrobin, orysastrobin, picoxystrobin, pyraclostrobin, pyrametostrobin, pyraoxostrobin, trifloxystrobin;
- iv) specific anti-oidium compounds: cyflufenamid, 5 flutianil, metrafenone, proquinazid, pyriofenone, quinoxifen;
- v) aniline-pyrimidines: pyrimethanil, mepanipyrim, cyprodinil;
- vi) benzimidazoles and analogues: benomyl, carbendazim, 10 fuberidazole, thiabendazole, thiophanate-methyl;
- vii) dicarboximides: iprodione, procymidone;
- viii) polyhalogenated fungicides: chlorothalonil, captan, captafol, folpet, dichlofluanid, tolylfluanid;
- ix) SAR inductors: acibenzolar, probenazole, isotianil, 15 tiadinil;
- x) phenylpyrroles: fenpiclonil, fludioxonil;
- xi) acylalanines: benalaxyl, benalaxyl-M, furalaxyl, metalaxyl, metalaxyl-M;
- xii) anti-peronosporic compounds: ametoctradin, 20 amisulbrom, benthiavalicarb, cyazofamid, cymoxanil, dimethomorph, ethaboxam, famoxadone, fenamidone, flumetover, flumorph, fluopicolide, iprovalicarb, mandipropamid, valifenalate;
- xiii) dithiocarbamates: maneb, mancozeb, propineb, 25 zineb;
- xiv) arylamidines: N-ethyl-N-methyl-N'-{4-[3-(4-chlorobenzyl)-1,2,4-thiadiazolyl-5-oxy]-2,5-xylyl}-formamidine;
- xv) phosphorous acid and derivatives: fosetyl- 30 aluminium, potassium phosphite, sodium phosphite, choline phosphite;
- xvi) copper fungicides: copper (II) hydroxide, copper

- oxychloride, copper (II) sulfate, Bordeaux mixture, copper salicylate $C_7H_4O_3 \cdot Cu$, cuprous oxide Cu_2O ;
- xvii) fungicidal amides: carpropamid, fenhexamid, silthiofam, zoxamid, bixafen, boscalid, carboxin,
- 5 fluopicolide, fluopyram, flutolanil, fluxapyroxad, furametpyr, isopyrazam, oxycarboxin, penflufen, penthiopyrad, sedaxane, thifluzamide;
- xviii) nitrogen heterocycles: fenpyrazamine, fluazinam, pyribencarb, tebufloquin;
- 10 xix) neonicotinoids: acetamiprid, clothianidin, dinotefuran, flupyradifurone, imidacloprid, nitenpyram, thiacloprid, thiametoxam;
- xx) phenylpyrazoles: ethiprole, fipronil, flufiprole, pyrafluprole, pyriprole;
- 15 xxi) pyrethroids: bifenthrin, beta-cyfluthrin, lambda-cyhalothrin, cypermethrin, deltamethrin, tefluthrin;
- xxii) carbamates: oxamyl, thiodicarb, carbosulfan, methiocarb, carbofuran;
- xxiii) macrolides of microbial origin: abamectin,
- 20 emamectin benzoate, spinetoram, spinosad;
- xxiv) insecticidal diamides: chlorantraniliprole, cyantraniliprole, flubendiamide;
- xxv) trifluoromethylpyridyl derivatives: flonicamid, sulfoxaflor.
- 25 Among the aforesaid, components [B] particularly preferred are:
- i) cyproconazole, difenoconazole, epoxyconazole, flutriafol, penconazole, prochloraz, prothioconazole, tebuconazole, tetraconazole;
- 30 ii) fenpropimorph, spiroxamine;
- iii) azoxystrobin, fluoxastrobin, kresoxim-methyl, picoxystrobin, pyraclostrobin, trifloxystrobin;

- iv) metrafenone, proquinazid;
- v) mepanipyrim, cyprodinil;
- vi) iprodione, procymidone;
- vii) carbendazim, thiophanate-methyl;
- 5 viii) chlorothalonil;
- x) fludioxonil;
- xi) benalaxyl, benalaxyl-M, metalaxyl-M;
- xii) benthiavalicarb, cyazofamid, cymoxanil, dimetomorph, mandipropamid, valifenalate;
- 10 xvi) copper (II) hydroxide, copper oxychloride, copper (II) sulfate, copper salicylate $C_7H_4O_3 \cdot Cu$, cuprous oxide Cu_2O ;
- xix) clothianidir, imidacloprid, thiachloprid, thiametoxam;
- 15 xx) ethiprole, fipronil;
- xxi) lambda-cyhalothrin, deltamethrin, tefluthrin;
- xxiv) chlorantraniliprole, flubendiamide.

The weight ratios of components [A] and [B] in the compositions object of the present invention can vary within a wide range, even depending on the parasites to be controlled and on the single component [B] used (or the plurality of components [B] used), and are usually comprised between 1:20 and 20:1.

Preferred compositions are those comprising at least the following combinations of compounds:

- C1: (I)-RS + tetraconazole;
- C2: (I)-RS + tebuconazole;
- C3: (I)-RS + cyproconazole;
- C4: (I)-RS + difenoconazole;
- 30 C5: (I)-RS + epoxyconazole;
- C6: (I)-RS + flutriafol;
- C7: (I)-RS + penconazole;

- C8: (I)-RS + prothioconazole;
- C9: (I)-RS + prochloraz;
- C10: (I)-RS + fenpropimorph;
- C11: (I)-RS + spiroxamine;
- 5 C12: (I)-RS + azoxystrobin;
- C13: (I)-RS + fluoxastrobin;
- C14: (I)-RS + kresoxim-methyl;
- C15: (I)-RS + picoxystrobin;
- C16: (I)-RS + pyraclostrobin;
- 10 C17: (I)-RS + trifloxystrobin;
- C18: (I)-RS + metrafenone;
- C19: (I)-RS + proquinazid;
- C20: (I)-RS + mepanipyrim;
- C21: (I)-RS + cyprodinil;
- 15 C22: (I)-RS + iprodione;
- C23: (I)-RS + procymidone;
- C24: (I)-RS + carbendazim;
- C25: (I)-RS + thiophanate-methyl;
- C26: (I)-RS + chlorothalonil;
- 20 C27: (I)-RS + fludioxonil;
- C28: (I)-RS + benalaxyl-M;
- C29: (I)-RS + metalaxyl-M;
- C30: (I)-RS + benthiavalicarb;
- C31: (I)-RS + cyazofamid;
- 25 C32: (I)-RS + cymoxanil;
- C33: (I)-RS + dimethomorph;
- C34: (I)-RS + mandipropamid;
- C35: (I)-RS + valifenalate;
- C36: (I)-RS + copper salycilate $C_7H_4O_3 \cdot Cu$;
- 30 C37: (I)-RS + cuprous oxide Cu_2O ;
- C38: (I)-RS + clothianidin;
- C39: (I)-RS + imidacloprid;

- C40: (I)-RS + thiacloprid;
- C41: (I)-RS + thiamethoxam;
- C42: (I)-RS + ethiprole;
- C43: (I)-RS + fipronil;
- 5 C44: (I)-RS + lambda-cyhalothrin;
- C45: (I)-RS + deltamethrin;
- C46: (I)-RS + tefluthrin;
- C47: (I)-RS + chlorantraniliprole;
- C48: (I)-RS + flubendiamide;
- 10 C49: (I)-RS + tetraconazole + azoxystrobin;
- C50: (I)-RS + tebuconazole + azoxystrobin;
- C51: (I)-RS + epoxyconazole + azoxystrobin;
- C52: (I)-RS + cyproconazole + azoxystrobin;
- C53: (I)-RS + propiconazole + azoxystrobin;
- 15 C54: (I)-RS + prothioconazole + azoxystrobin;
- C55: (I)-RS + tetraconazole + picoxystrobin;
- C56: (I)-RS + tebuconazole + picoxystrobin;
- C57: (I)-RS + epoxyconazole + picoxystrobin;
- C58: (I)-RS + cyproconazole + picoxystrobin;
- 20 C59: (I)-RS + propiconazole + picoxystrobin;
- C60: (I)-RS + prothioconazole + picoxystrobin;
- C61: (I)-RS + tetraconazole + kresoxim methyl;
- C62: (I)-RS + tebuconazole + kresoxim methyl;
- C63: (I)-RS + epoxyconazole + kresoxim methyl;
- 25 C64: (I)-RS + cyproconazole + kresoxim methyl;
- C65: (I)-RS + propiconazole + kresoxim methyl;
- C66: (I)-RS + prothioconazole + kresoxim methyl;
- C67: (I)-RS + chlorothalonil + azoxystrobin;
- C68: (I)-RS + chlorothalonil + picoxystrobin;
- 30 C69: (I)-RS + chlorothalonil + pyraclostrobin;
- C70: (I)-RS + chlorothalonil + kresoxim methyl;
- C71: (I)-RS + copper (II) hydroxide + copper oxy-

chloride;

C72: (I)-RS + copper (II) hydroxide + copper oxy-chloride + copper salicylate $C_7H_4O_3 \cdot Cu$;

C73: (I)- R_8S_2 + tetraconazole;

5 C74: (I)- R_8S_2 + azoxystrobin;

C75: (I)- R_8S_2 + benalaxyl;

C76: (I)- R_9S_1 + tetraconazole;

C77: (I)- R_9S_1 + azoxystrobin;

C78: (I)-R + tetraconazole;

10 wherein:

- (I)-RS represents the compound of formula (I) in form of racemic mixture,

- (I)- R_8S_2 represents the compound having the enantiomers R and S in molar ratio R:S = 8:2,

15 - (I)- R_9S_1 represents the compound having the enantiomers R and S in molar ratio R:S = 9:1,

- (I)-R represents the enantiomer R in substantially pure form (>99,99 weight %).

Preferably, in said compositions C1-C25, C27-C35, 20 C-38-C48 e C73-C77 the weight ratio of components [A] e [B] ranges from 1:20 to 20:1.

Preferably, in said compositions C26, C36, C37 the weight ratio of components [A] e [B] ranges from 1:20 to a 20:10.

25 Preferably, in said compositions C49-C69 the weight ratio of component [A] with respect to the two components [B] ($[A]:[B_1]:[B_2]$) ranges from 1:20:20 to 20:1:1.

Preferably, in said composition C70 the weight 30 ratio of component [A] with respect to the two components [B] ($[A]:[B_1]:[B_2]$) ranges from 1:20:20 to 20:10:1, whereas in C71 the ratio $[A]:[B_1]:[B_2]$ ranges

from 1:20:20 to 20:10:10.

Preferably, in said composition C72, the weight ratio of component [A] with respect to the three components [B] ([A]:[B₁]:[B₂]:[B₃]) ranges from 1:20:20:20 to 20:10:10:10.

As said, the compositions object of the present invention exhibit a strong synergistic effect, which can be evaluated by applying the Colby's formula ("Weeds", 1967, 15, pag. 20-22):

$$E_t = E_A + E_B - (E_A \times E_B / 100)$$

wherein E_t is the expected efficacy percentage for the composition containing the compounds A and B at the dosages $d_A + d_B$, E_A is the efficacy percentage observed for the component A at the dosage d_A , E_B is the efficacy percentage observed for the component B at the dosage d_B .

When the efficacy observed for the composition A+B (E_{A+B}) is higher than the efficacy expected according to the Colby's formula ($E_{A+B}/E_t > 1$), there is the presence of a synergistic effect.

In case of ternary combinations, the Colby's formula becomes:

$$E_t = E_A + E_{B1} + E_{B2} - (E_A \cdot E_{B1} + E_A \cdot E_{B2} + E_{B1} \cdot E_{B2} / 100) + (E_A \cdot E_{B1} \cdot E_{B2} / 10000)$$

wherein E_t is the expected efficacy percentage for the composition containing the compounds A, B1 e B2 at the dosages $d_A + d_{B1} + d_{B2}$, E_A is the efficacy percentage observed for the component A at the dosage d_A , E_{B1} is the efficacy percentage observed for the component B1 at the dosage d_{B1} , E_{B2} is the efficacy percentage observed for the component B2 at the dosage d_{B2} . When the efficacy observed for the composition A+B1+B2 ($E_{A+B1+B2}$) is higher than the efficacy expected according to the

Colby's formula ($E_{A+B1+B2}/E_t > 1$), there is the presence of a synergistic effect.

Due to the high synergistic effects, the amplitude of the action range, the considerable reduction in resistance phenomena from the target microorganisms, the compositions object of the present invention are endowed with a very high fungicidal activity, which is exerted with respect to numerous phytopathogenic fungi attacking important agricultural crops.

Said compositions exert a fungicidal activity which can be curative, preventive or eradicant, and generally have a very low or null phytotoxicity on the treated crops.

It is therefore a further object of the present invention the use of the synergistic fungicidal compositions described above for the control of phytopathogenic fungi in agricultural crops.

Examples of phytopathogenic fungi that can be effectively treated and fought with the compositions of the present invention, are those belonging to the groups of Basidiomycetes, Ascomycetes, Deuteromycetes or imperfect fungi, Oomycetes: *Puccinia* spp., *Ustilago* spp., *Tilletia* spp., *Uromyces* spp., *Phakopsora* spp., *Rhizoctonia* spp., *Erysiphe* spp., *Sphaerotheca* spp., *Podosphaera* spp., *Uncinula* spp., *Helminthosporium* spp., *Rhynchosporium* spp., *Pyrenophora* spp., *Monilinia* spp., *Sclerotinia* spp., *Septoria* spp. (*Mycosphaerella* spp.), *Venturia* spp., *Botrytis* spp., *Alternaria* spp., *Fusarium* spp., *Cercospora* spp., *Cercospora* spp., *herpotrichoides*, *Colletotrichum* spp., *Pyricularia oryzae*, *Sclerotium* spp., *Phytophthora* spp., *Pythium* spp., *Plasmopara viticola*, *Peronospora* spp.,

Pseudoperonospora cubensis, *Bremia lactucae*.

The main crops that can be protected with the compositions according to the present invention comprise cereals (wheat, barley, rye, oats, rice, 5 maize, sorghum, etc.), fruit trees (apples, pears, plums, peaches, almonds, cherries, bananas, grapes, strawberries, raspberries, blackberries, etc.), citrus trees (oranges, lemons, mandarins, grapefruit, etc.), legumes (beans, peas, lentils, soybean, etc.), 10 vegetables (spinach, lettuce, asparagus, cabbage, carrots, onions, tomatoes, potatoes, eggplants, peppers, etc.), cucurbitaceae (pumpkins, zucchini, cucumbers, melons, watermelons, etc.), oleaginous plants (sunflower, rape, peanut, castor, coconut, 15 etc.), tobacco, coffee, tea, cocoa, sugar beet, sugar cane, cotton.

In particular, the compositions of the present invention have proved to be particularly effective in the control of *Plasmopara viticola* on vines, 20 *Phytophthora infestans* and *Botrytis Cinerea* on tomatoes, *Puccinia recondita*, *Erysiphe graminis*, *Helminthosporium teres*, *Septoria nodorum* and *Fusarium* spp. on cereals, in the control of *Phakopsora pachyrhizi* on soybean, in the control of *Uromyces* 25 *Appendiculatus* on beans, in the control of *Venturia inaequalis* on apple-trees, in the control of *Sphaerotheca fuliginea* on cucumbers.

In addition, the compositions of the present invention are also effective in the control of 30 phytopathogenic bacteria and viruses, such as, for example, *Xanthomonas* spp., *Pseudomonas* spp., *Erwinia amylovora*, the tobacco mosaic virus.

The compositions comprising at least a compound of formula (I) and, as component [B], at least an insecticidal compound selected from one or more of the aforesaid groups of compounds xix-xxv, besides to have
 5 an excellent fungicidal activity, also have an excellent insecticidal activity against numerous species of insects harmful to agricultural crops.

It is therefore a further object of the present invention the use of said compositions, comprising at
 10 least a compound of formula (I) and at least an insecticidal compound selected from one or more of the aforesaid groups of compounds xix-xxv, for the control of harmful insects in agricultural crops.

Examples of insects which can be controlled with
 15 the above said compositions, are those belonging to the order of Hemiptera, Lepidoptera, Tysanoptera, Diptera, Coleoptera, Orthoptera, Hymenoptera: *Aphis gossypii*, *Myzus persicae*, *Macrosiphum euphorbiae*, *Brevicoryne brassicae*, *Toxoptera citricidus*,
 20 *Trialeurodes vaporariorum*, *Bemisia tabaci*, *Aonidiella aurantii*, *Comstockaspis perniciosus*, *Unaspis citri*, *Psylla piri*, *Laodelphax striatellus*, *Nilaparvata lugens*, *Nephotettix cincticeps*, *Nephotettix virescens*, *Chilo suppressalis*, *Ostrinia* spp., *Spodoptera* spp.,
 25 *Mamestra brassicae*, *Agrotis* spp., *Thricoplusia* spp., *Heliothis* spp., *Helicoverpa* spp., *Pieris* spp., *Adoxophyes* spp., *Grapholita molesta*, *Cydia* spp., *Phyllonorycter blancardella*, *Lymantria* spp., *Plutella xylostella*, *Pectinophora gossypiella*, *Hyphantria cunea*,
 30 *Thrips* spp., *Frankliniella* spp., *Dacus* spp., *Ceratitis capitata*, *Liriomyza trifolii*, *Anthonomus grandis*, *Callosobruchus chinensis*, *Diabrotica* spp., *Agriotes*

spp., *Tribolium spp.*, *Locusta migratoria*, *Oxya spp.*, *Solenopsis spp.*, *Blattella germanica*, *Periplaneta spp.*

Even if the components [A] and [B] can be mixed and applied as such on the crops to be protected, for the practical use in agriculture, it is usually preferable to use the fungicidal compositions, according to the present invention, in the form of suitable phytosanitary formulations.

The component [A] and the components [B] can be formulated separately and mixed in the preselected diluent (for example water) at the moment of the treatment of the agricultural crops to be protected, or combined together in single formulation ready to use before treatment.

Both in the case of components formulated separately, and in the case of components [A] and [B] combined together in formulations ready to use, the formulations can be in the form of dry powders, wettable powders, emulsifiable concentrates, emulsions, micro-emulsions, pastes, granules, water-dispersible granules, solutions, suspensions, etc.: the selection of the type of formulation depends both on the characteristics of components A and B, and on the specific use.

The compositions are prepared with known methods, for example by diluting the active ingredients with a solid or liquid diluent, possibly in the presence of surfactants, dispersers, suspending agents, stabilizers, adjuvants, etc..

The following can be used, for example, as solid diluent or carriers: silica, kaolin, bentonite, talc, diatomaceous earth, dolomite, calcium carbonate,

magnesia, gypsum, clays, synthetic silicates, attapulgite, sepiolites.

The following can be used, for example, as solvents or liquid diluents, in addition to water, aromatic organic solvents (xyloles or alkylbenzole mixtures, chlorobenzene, etc.), paraffins (oil cuts), alcohols (methanol, propanol, butanol, octanol, glycerol, etc.), esters (ethyl acetate, isobutyl acetate, alkyl carbonates, alkyl esters of adipic acid, alkyl esters of glutaric acid, alkyl esters of succinic acid, alkyl esters of lactic acid, etc.), vegetable oils (rapeseed oil, sunflower oil, soybean oil, castor oil, corn oil, peanut oil, and their alkyl esters), ketones (cyclohexanone, acetone, acetophenone, isophorone, ethyl amyl ketone, etc.), amides (N, N-dimethylformamide, N-methylpyrrolidone, etc.), sulfoxides and sulfones (dimethylsulfoxide, dimethylsulfone, etc.) and mixtures thereof.

Surfactants that can be used are sodium salts, calcium salts, potassium salts, triethylamine or triethanolamine of alkylnaphthalensulfonates, polynaphthalenesulfonates, alkylsulfonates, arylsulfonates, alkylarylsulfonates, polycarboxylates, sulfosuccinates, alkylsulfosuccinates, lignin sulfonates, alkyl sulfates; and again polyethoxylated fatty alcohols, polyethoxylated alkyl phenols, polyethoxylated esters of sorbitol, polyethoxylated polypropoxy (block copolymers), can be used.

The compositions can also contain special additives for particular purposes, for example antifreeze agents such as propylene glycol, or adhesives such as Arabic gum, polyvinyl alcohol,

polyvinylpyrrolidone, etc..

If desired, other active ingredients compatible with [A] and [B] can be added to the compositions, such as, for example, further fungicidal or insecticidal compounds different from components [B] described above, phytohormones, antibiotics, herbicides, fertilizers and/or mixtures thereof.

Examples of fungicides, other than components [B], that can be included in the synergistic compositions object of the present invention are listed hereunder with their international ISO name: ampropylfos, anilazine, benodanil, blastocidin-S, bupirimate, buthiobate, chinomethionat, chloroneb, chlozolate, debacarb, dichlorone, diclobutrazol, diclomezine, dicloran, diclocymet, diethofencarb, diflumetorim, dimethirimol, dinocap, dipyrithione, ditalimfos, dithianon, edifenphos, ethirimol, ethoxyquin, etridiazole, fenaminosulf, fenapanil, fenarimol, fenfuram, fenoxanil, fentin, ferbam, ferimzone, fluoroimide, fluotrimazole, flusulfamide, hymexazol, hydroxy-quinoline sulfate, iprobenfos, isoprothiolane, kasugamycin, mancozeb, mebenil, mepronil, meptyldinocap, methfuroxam, metiram, metsulfos-methyl, nalbamycin, nitrothal-isopropyl, nuarimol, ofurace, oxadixyl, pefurazoate, pencycuron, pentachlorophenol and its salts, phthalide, piperidin, polyoxins, propamocarb, prothiocarb, pyracarbolid, pyrazophos, pyribencarb, pyrifenoxy, pyroquilon, pyroxyfur, quinacetol, quinazamid, quintozone, streptomycin, thiadiflur, thicyofen, thiram, tioxydim, tolclofos-methyl, triarimol, triazbutyl, triazoxide, tricyclazole, triforine, validamycin, vinclozolin,

ziram, sulfur.

The total concentration of components [A] and [B] in said compositions can vary within a wide range; it generally ranges from 1% to 99% by weight with respect
5 to the total weight of the composition, preferably from 5% to 90% by weight with respect to the total weight of the composition.

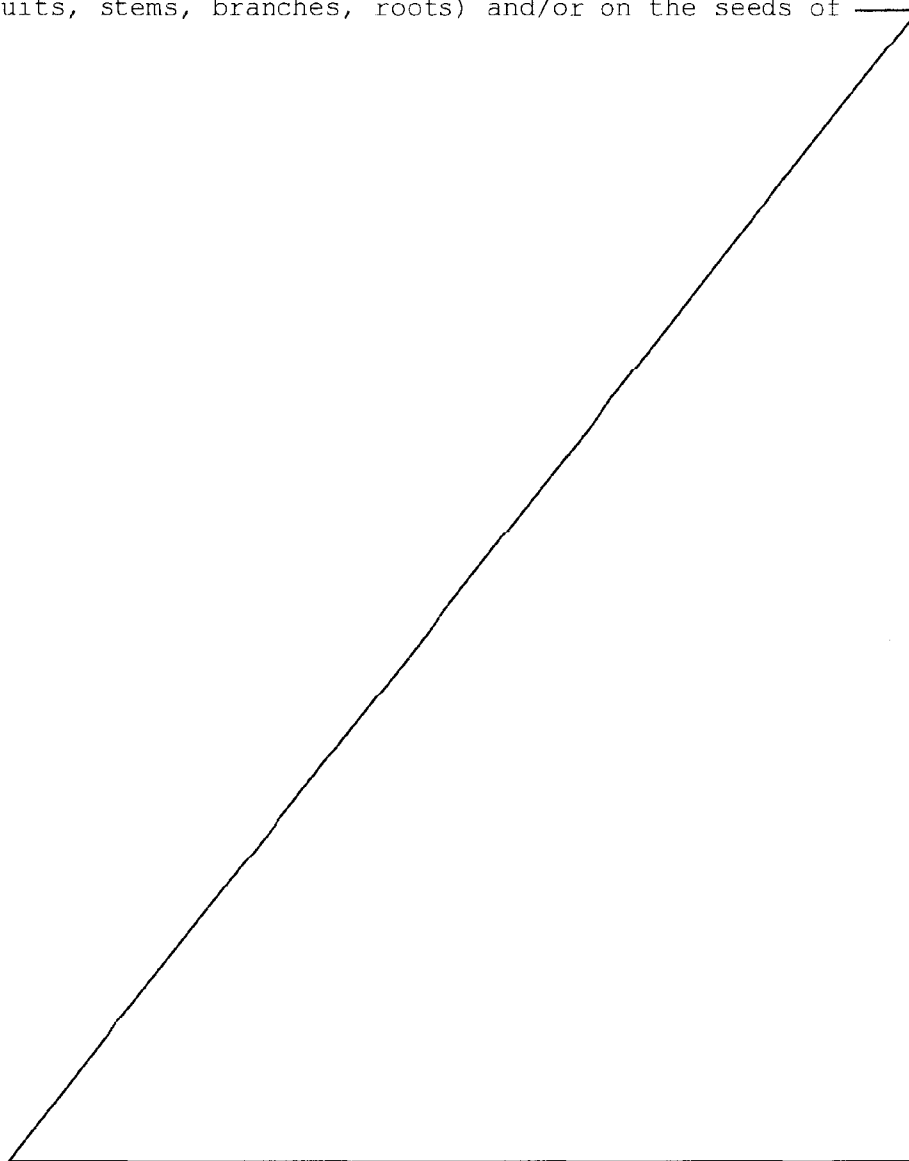
In order to protect the agricultural crops, the compositions object of the present invention can be
10 applied to any part of the plant, or on the seeds before sowing, or on the ground in which the plant grows.

A further object of the present invention therefore relates to a method for the control of
15 phytopathogenic fungi in agricultural crops, which comprises applying an effective dose of at least one synergistic fungicidal composition of the type described above on one or more parts of the plant to be protected (for example, on seedlings, leaves, fruits,
20 stems, branches, roots) and/or on the seeds of said plants before sowing, and/or on the ground in which the plant grows.

The invention provides a method for controlling harmful insects in agrarian crops, which comprises
25 applying an effective dose of at least one composition as defined herein, on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

30 A further aspect of the present invention is a method for the control of harmful insects in agricultural crops which comprises applying an

effective dose of at least one synergistic fungicidal composition comprising at least a compound of formula (I) and at least an insecticidal compound selected from one or more of the groups of compounds xix-xxv
5 described above, on one or more parts of the plant to be protected (for example, on seedlings, leaves, fruits, stems, branches, roots) and/or on the seeds of



said plants before sowing, and/or on the ground in which the plant grows.

Preferred way of application for the compositions comprising the compound (I) and at least an
5 insecticidal compound selected from one or more groups of compounds xix-xxv is the seed-dressing.

The total amount of components [A] and [B] to be applied in order to obtain the desired effect can vary according to different factors such as, for example,
10 the compounds used, the crop to be preserved, the type of pathogen or insect, the degree of infection, the climatic conditions, the application method, the formulation used.

Overall doses of components [A] and [B] ranging
15 from 10 g to 5 kg per hectare of agricultural crop generally provide a sufficient control.

The following examples are provided for a better understanding of the invention, which should be considered as being illustrative and non-limiting of
20 the same.

EXAMPLE 1

Preparation of the 3-difluoromethyl-N-(7-fluoro-1,1,3-trimethyl-4-indanyl)-1-methyl-4-pyrazolecarboxamide (I)

25 A solution of 40 g of 3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carbonyl chloride [compound of formula (III); MW 194,5] in 40 ml of dichloroethane, is dropped at room temperature in a solution of 34 g of 6-fluoro-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline [compound
30 of formula (V); MW 193] and 30 ml of triethylamine in 200 ml of dichloroethane.

After stirring for 3 hours at reflux, the reaction

mixture is poured in water (1,2 l) and extracted with dichloroethane. The organic layer is washed with 10% aqueous hydrochloric acid, anhydrified with sodium sulfate, concentrated under vacuum to afford 58 g of a
 5 crude solid product corresponding to N-(3-difluoromethyl-1-methyl-1H-4-pyrazolecarbonyl)-6-fluoro-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline [compound of formula (II); GC-mass: $M^+ = 351$].

To this crude product, 165 ml of 85% aqueous
 10 sulfuric acid are added and the mixture is then heated under stirring at 60°C for 30 minutes. After cooling the mixture is poured into water and ice, and extracted with dichloromethane. The organic layer is then washed with water, with a saturated solution of sodium
 15 bicarbonate in water, and with a saturated solution of sodium chloride in water. The organic layer is anhydrified with sodium sulfate and concentrated under vacuum: the residue is purified by chromatography on silica gel (eluent heptane/EtOAc 6:4) to give 48 g of a
 20 white solid with melting point 147°C, corresponding to the desired product in racemic form, (I)-RS. GC-mass: $M^+ = 351$.

^1H NMR (200 Mhz, CDCl_3) δ at: 1,43 (3H,d), 1,38 (3H,s),
 1,44 (3H,s), 1,66 (1H,dd), 2,21 (1H,dd), 3,38 (1H m),
 25 3,98 (3H,s), 6,81 (1H, bs), 6,95 (1H,t), 6,70. (1H, m),
 7,81 (1H,bs), 8,03 (1H,bs)

EXAMPLE 2

Preparation of separated enantiomers of compound (I).

30 36.8 g (1 eq) of racemic 7-fluoro-1,1,3-trimethyl-4-aminoindane [compound (IV)] and 14.3 g (0.5 eq) of D-(2S,3S)-(-)-tartaric acid in methanol (30 ml) were

mixed and heated at 70 °C for 1 hour.

The mixture was left to cool to room temperature; a precipitate was formed and the mixture kept for one night at 4 °C. The formed solid was filtered off, washed with a small amount of methanol and re-crystallized from methanol for six times to afford 14.8 g of an off white solid, corresponding to the 7-fluoro-1,1,3-trimethyl-4-aminoindane D-tartrate.

To the salt, a 5 % sodium hydroxide aqueous solution was added until pH $\geq$ 10, and the mixture extracted three times with diethyl ether. The reunited organic layers were washed with water and brine. Then, dried over Na₂SO₄ and concentrated under reduced pressure to obtain 6.38 g of (-)-4-amino-7-fluoro-1,1,3-trimethylindane as a white powder (yield 17%); e.e. > 99% (HPLC).

To a solution of 600 mg of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid [compound (III)] and a catalytic amount of N,N-dimethylformamide in dichloromethane (7 mL), 450 mg of thionyl chloride were added dropwise. The mixture was refluxed for 2h. The reaction was monitored by GC/MS. The solvent was evaporated in vacuo. The crude acid chloride obtained was used in the following step.

A solution of the crude 3-difluoromethyl-1-methyl-1H-pyrazole-4-carbonyl chloride in dichloroethane (6 mL) was added dropwise over a period of 10 minutes, under nitrogen atmosphere, to a solution of 660 mg of (-)-4-amino-7-fluoro-1,1,3-trimethylindane, a catalytic amount of 4-dimethylaminopyridine and 420 mg of triethylamine in dichloroethane (5 mL).

The mixture was stirred at room temperature

overnight. At completion of the reaction (monitored through GC-MS) the mixture was diluted with dichloromethane (20 mL) and cooled at 0°C; a solution (20 mL) of 5% HCl was added.

5 The layers were separated and the organic phase washed with 5% HCl solution (2 x 20 mL), water (2 x 20 mL) and brine, then dried over Na₂SO₄. The solvent was evaporated under reduced pressure to give 1.3 g of a pale yellow solid.

10 The crude product was purified by column chromatography (eluent: heptane/EtOAc 6:4) to give 1.1 g (yield 92%) of 99.5 % pure enantiomer (-) (e.e. > 99% determined by HPLC with chiral column) as a white solid with m.p. = 129-130°C.

15 GC-MS: M⁺ = 351; [α]_D²⁰ = - 59.5° (CHCl₃, 1g/100 ml).

 In analogous manner, starting from racemic 7-fluoro-1,1,3-trimethyl-4-aminoindane [compound (IV)] and L-(2R,3R)-(+)-tartaric acid, the 99.3 %pure enantiomer (+) was prepared (e.e. > 99% determined by
20 HPLC with chiral column): white solid with m.p. = 131-132°C.

 GC-MS: M⁺ = 351; [α]_D²⁰ = + 60.1° (CHCl₃, 1g/100 ml).

EXAMPLE 3

25 **Determination of "in vitro" activities of racemic (I) and enantiomers against phytopathogenic microorganisms.**

 Under sterile conditions, the technical racemic (I), the (-) and (+) enantiomers (prepared in Example 2) under testing, were dissolved in dimethylsulfoxide
30 and serially diluted 3-fold to obtain a growth

inhibition curve. Aqueous treatment solutions were prepared by adding DMSO stocks to water and mixing by pipet resulting in 2x final treatment concentration and 2x final DMSO concentration of 1.6%.

5 Sporulating plates of phytopathogenic micro-organisms were harvested under sterile conditions in 1/2 strength Potato Dextrose Broth. Spores were filtered with cheesecloth and diluted to about 40000 spores per ml. Spores were aliquotted into 96 well microtiter
10 plates at 150 microliters of spore suspension per well. Pathogenic spore suspensions were then treated with the 2x aqueous treatment solution or 1.6% DMSO for controls to give 1x final concentration or 0.8% DMSO. Plates were then held for 43 hours at room temperature.

15 After 43 hours at room temperature, plates were visually assessed microscopically for spore germination and growth inhibition. Plates were also quantitatively measured for growth inhibition by measuring optical density on a spectrophotometric plate reader at 405
20 nanometer wavelength. Optical density was corrected for absorbance of the media and active ingredient by subtracting the 405 nm readings for the 2x aqueous treatment solution or DMSO solution diluted with 1/2 strength POTATO DEXTROSE BROTH and no spores.

25 The % growth inhibition of the pathogen obtained for the technical racemic (I), (-) and (+) enantiomers was calculated according to the formula:
Percent Inhibition = ((1 - (OD trt - OD trt blank) / (OD untreated - OD untreated blank)) x 100)

wherein OD trt is the optical density at 405 nm for the spore suspension plus aqueous treatment solution and OD trt blank is the optical density at 405 nm for the 2x aqueous treatment solution plus ½ strength POTATO DEXTROSE BROTH and no spores and OD untreated is the optical density at 405 nm for the spores plus 1.6% DMSO and OD untreated blank is the optical density at 405nm for the 1.6% DMSO plus ½ strength POTATO DEXTROSE BROTH and no spores. Values are the average of three replicates. Concentrations of the racemic, (-) and (+) enantiomers giving 50% growth inhibition (pI50) were calculated using GraphPad Prism software Percent inhibition values were calculated using GraphPad Prism software Version 4.

Microorganisms tested were *Botrytis cinerea* (BC), *Stagonospora nodorum* (SN) and *Magnaporthe griseae* (MG).

The results are reported in Table 1.

Table 1.

Compound	BC pI50 (ppm)	SN pI50 (ppm)	MG pI50 (ppm)
Racemic (I)	0.32	1.1	0.72
(-) - (I)	0.17	0.42	0.46
(+) - (I)	n.i.	72	4.6

n.i. = no inhibition

EXAMPLE 4

Determination of the fungicidal activity in preventive application (5 days) against *Puccinia recondita* on wheat.

Leaves of wheat plants of the Salgemma variety, grown in pots in a conditioned environment kept at 20°C and 70% of relative humidity (R.H.), were treated by spraying both sides of the leaves with the compounds and the compositions under testing, dispersed in hydroacetic solutions at 20% by volume of acetone.

After remaining 5 days in a conditioned environment, the plants were sprayed on both sides of the leaves with an aqueous suspension of conidia of *Puccinia recondita* (2 mg of inoculum per 1 ml of solution for infection).

After being sprayed, the plants were kept in a humidity-saturated environment at a temperature ranging from 18 to 24°C for the incubation period of the fungus (1 day).

After this period, the plants were put in a greenhouse with R.H. of 70% and at a temperature of 18-24 °C for 14 days.

At the end of this period the external symptoms of the pathogen appeared and it was therefore possible to proceed with the visual assessment of the intensity of the infection. The fungicidal activity was expressed as percentage of reduction of affected leaves areas with respect to those of untreated plants used as control: the scale comprised, as extremes, the value 100 (full activity; healthy plant) and the value 0 (no activity; completely infected plant).

At the same time, the phytotoxicity (percentage of leaf necrosis) induced on the wheat plants by the

application of the products and compositions was evaluated: in this case, the scale ranged from 0 (no phytotoxicity) to 100 (completely necrotized plant).

In Table 2, the activities of racemic (I) and pure enantiomers of compound (I), prepared in Example 2, are reported.

Table 2.

Compound	Rate (ppm)	% Activity	% Phytotoxicity
Racemic (I)	125	98	0
	62.5	96	0
(-) - (I)	125	100	0
	62.5	96	0
(+) - (I)	125	45	0
	62.5	20	0

The synergism of the compositions (A+B) under testing was evaluated according to the Colby's formula:

$$E_t = E_A + E_B - (E_A \times E_B / 100)$$

wherein E_t is the expected efficacy percentage for the composition containing the compounds A and B at the dosages $d_A + d_B$, E_A is the efficacy percentage observed for the component A at the dosage d_A , E_B is the efficacy percentage observed for the component B at the dosage d_B .

When the efficacy observed for the composition A+B (E_{A+B}) is higher than the efficacy expected according to the Colby's formula ($E_{A+B}/E_t > 1$), a synergistic effect is confirmed.

EXAMPLE 5**Determination of synergistic effects "in vitro" against phytopathogenic microorganisms.**

Under sterile conditions, the products and the
5 compositions under testing were dissolved in
dimethylsulfoxide, diluted with water and added under
vigorous stirring to POTATO DEXTROSE AGAR, kept in a
thermostatic bath at 55°C. The AGAR preparations,
containing the compounds and the compositions under
10 testing at the desired rates, were poured into 60 mm
diameter Petri dishes (three for each product and
composition) and left to cool to ambient temperature.

After solidification of the agarized medium, AGAR
disks having 6 mm of diameter and supporting the
15 micelyum of the microorganism, were placed in the
centre of the Petri dishes; Petri dishes containing
untreated POTATO DEXTROSE AGAR were also inoculated
with the microorganism and used as control.

After incubation at 28°C, when control colonies
20 had grown over 30 mm in diameter, but without reaching
the edge of the dishes, the diameters of the developed
colonies in treated and untreated dishes were measured;
the percentage growth inhibition of the microorganism
obtained with products and compositions was calculated
25 according to the formula:

$$I = (1 - z_1/z_0) \times 100$$

wherein z_1 is the diameter (average of three replicates)
of the colonies treated with compounds and mixtures and
 z_0 is the diameter (average of three replicates) of

untreated colonies.

Microorganisms tested were *Botrytis cinerea*,
Fusarium culmorum, *Helminthosporium teres*, *Pyricularia*
oryzae, *Septoria nodorum*, *Venturia inaequalis*.

5 The synergism of a binary mixture (A + B) at the
dose ($d_A + d_B$) was evaluated according to the Colby's
formula:

$$I_t = I_A + I_B - (I_A \times I_B / 100)$$

wherein:

10 I_t is the % growth inhibition expected for the mixture;
 I_A is the % growth inhibition observed for compound A at
the dose d_A ; I_B is the % growth inhibition observed for
compound B at the dose d_B .

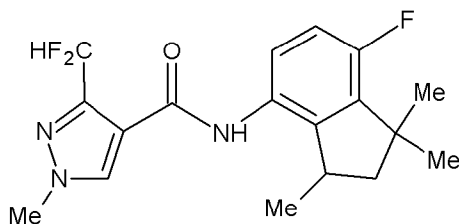
15 When the % growth inhibition observed for the
composition (A+B) is higher than that calculated by the
Colby's formula ($I_{A+B} > I_t$; $I_{A+B}/I_t > 1$) , a synergistic
effect is confirmed.

20 In some aspects, embodiments of the present
invention as described herein include the following
items:

1. A synergistic composition for the protection of
25 agrarian crops comprising:

- at least one component (A), consisting of the
compound having formula (I) 3-difluoromethyl-N-(7-
fluoro-1,1,3-trimethyl-4-indanyl)-1-methyl-4-
pyrazolecarboxamide

30



(I)

wherein Me represents a CH₃- methyl group, and

5 - at least one component [B] having a fungicidal or insecticidal activity and belonging to one or more of the following groups of a) fungicidal and b) insecticidal compounds:

a) fungicidal compounds:

- 10 i) azoles: difenoconazole, flutriafol, prothioconazole, tetraconazole;
- ii) amino derivatives: spiroxamine;
- iii) strobilurins: azoxystrobin, fluoxa-strobin, kresoxim-methyl, pyraclostrobin;
- 15 vii) dicarboxyimides: iprodione;
- viii) polyhalogenated fungicides: chlorothalonil;
- ix) inducers of acquired systemic resistance (SAR): acibenzolar;
- xi) acylalanines: benalaxyl;
- 20 xii) antiperonosporic compounds: valifenalate;
- xiii) dithiocarbamates: mancozeb;
- xvi) copper-based cupric fungicides: copper oxychloride; or
- xvii) fungicidal amides: boscalid, fluopyram,
- 25 fluxapyroxad, isopyrazam, penthiopyrad; or

b) insecticidal compounds:

- xix) neonicotinoids: imidacloprid; or

xxi) pyrethroids: bifenthrin.

2. The synergistic composition according to item 1,
wherein said compound having formula (I) is a racemic
5 mixture ((I)-RS).

3. The synergistic composition according to item 1 or
2, wherein said compound having formula (I) is:
- a mixture enriched in one of the enantiomers, or
10 - one of the two enantiomers R ((I)-R) or S ((I)-S)
having a purity form of >99.99% by weight.

4. The synergistic composition according to item 3,
wherein the mixture enriched in one of the enantiomers
15 is enriched in the enantiomer R.

5. The synergistic composition according to item 3 or
4, wherein the enantiomer R ((I)-R) having a purity
form of >99.99% by weight.

20

6. The synergistic composition according to any one
of items 1 to 5, wherein the weight ratio between said
at least one component [A] and said at least one
component [B] ranges from 1:20 to 20:1.

25

7. The synergistic composition according to any one
of items 1 to 6, wherein said composition is:

C1: (I)-RS + tetraconazole;

C4: (I)-RS + difenoconazole;

30 C6: (I)-RS + flutriafol;

C8: (I)-RS + prothioconazole;

C11: (I)-RS + spiroxamine;

C12: (I)-RS + azoxystrobin;
 C13: (I)-RS + fluoxastrobin;
 C14: (I)-RS + kresoxim-methyl;
 C16: (I)-RS + pyraclostrobin;
 5 C22: (I)-RS + iprodione;
 C26: (I)-RS + chlorothalonil;
 C35: (I)-RS + valifenalate;
 C39: (I)-RS + imidacloprid;
 C49: (I)-RS + tetraconazole + azoxystrobin;
 10 C50: (I)-RS + tebuconazole + azoxystrobin;
 C51: (I)-RS + epoxyconazole + azoxystrobin;
 C52: (I)-RS + cyproconazole + azoxystrobin;
 C53: (I)-RS + propiconazole + azoxystrobin;
 C54: (I)-RS + prothioconazole + azoxystrobin;
 15 C55: (I)-RS + tetraconazole + picoxystrobin;
 C60: (I)-RS + prothioconazole + picoxystrobin;
 C61: (I)-RS + tetraconazole + kresoxim methyl;
 C62: (I)-RS + tebuconazole + kresoxim methyl;
 C64: (I)-RS + cyproconazole + kresoxim methyl;
 20 C65: (I)-RS + propiconazole + kresoxim methyl;
 C66: (I)-RS + prothioconazole + kresoxim methyl;
 C67: (I)-RS + chlorothalonil + azoxystrobin;
 C68: (I)-RS + chlorothalonil + picoxystrobin;
 C69: (I)-RS + chlorothalonil + pyraclostrobin;
 25 C70: (I)-RS + chlorothalonil + kresoxim methyl;
 C71: (I)-RS + copper (II) hydroxide + copper
 oxychloride;
 C72: (I)-RS + copper (II) hydroxide + copper
 oxychloride + copper salicylate $C_7H_4O_3 \cdot Cu$;
 30 C73: (I)-R₃S₂ + tetraconazole;
 C74: (I)-R₃S₂ + azoxystrobin;
 C75: (I)-R₃S₂ + benalaxyl;

C76: (I)-R₉S₁ + tetraconazole;
C77: (I)-R₉S₁ + azoxystrobin; or
C78: (I)-R + tetraconazole;

wherein:

- 5 - (I)-RS indicates the compound having formula (I) in
the form of a racemic mixture,
- (I)-R₈S₂ indicates the compound containing the
enantiomers R and S in a molar ratio R:S = 8:2,
- (I)-R₉S₁ indicates the compound containing the
10 enantiomers R and S in a molar ratio R:S = 9:1,
- (I)-R indicates the enantiomer R in substantially
pure form, >99.99% by weight.

8. The synergistic composition according to any one
15 of items 1 to 7, wherein said at least one component
[A] and said at least one component [B], together or
separately, are diluted with one or more solid diluents
and/or one or more liquid diluents.

20 9. The synergistic composition according to item 8,
wherein said at least one component [A] and said at
least one component [B], together or separately, are
diluted with one or more solid diluents and/or one or
more liquid diluents, with the addition of one or more
25 surfactants, dispersing agents, suspending agents,
stabilizers, adjuvants, anti-freeze agents, and/or
adhesion agents.

10. The synergistic composition according to any one
30 of items 1 to 9, comprising at least a further active
principle, compatible with said components [A] and [B],
selected from fungicidal compounds or insecticidal

compounds different from said compounds [B],
phytoregulators, antibiotics, herbicides, fertilizers
and mixtures thereof.

5 11. Use of the synergistic composition as defined in
any one of items 1 to 10 for the control of
phytopathogenic fungi in agricultural crops.

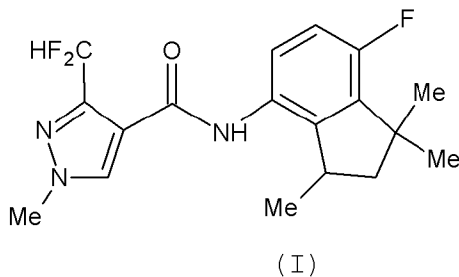
12. The use of the synergistic composition according
10 to item 11, for the control of phytopathogenic fungi
which are: Basidiomycetes, Ascomycetes, Deuteromycetes
or imperfect fungi, Oomycetes: *Puccinia* spp., *Ustilago*
spp., *Tilletia* spp., *Uromyces* spp., *Phakopsora* spp.,
Rhizoctonia spp., *Erysiphe* spp., *Sphaerotheca* spp.,
15 *Podosphaera* spp., *Uncinula* spp., *Helminthosporium*
spp., *Rhynchosporium* spp., *Pyrenophora* spp., *Monilinia*
spp., *Sclerotinia* spp., *Septoria* spp. (*Mycosphaerella*
spp.), *Venturia* spp., *Botrytis* spp., *Alternaria* spp.,
Fusarium spp., *Cercospora* spp., *Cercospora*
20 *herpotrichoides*, *Colletotrichum* spp., *Pyricularia*
oryzae, *Sclerotium* spp., *Phytophthora* spp., *Pythium*
spp., *Plasmopara viticola*, *Peronospora* spp.,
Pseudoperonospora cubensis, or *Bremia lactucae*.

25 13. The use of the synergistic composition according
to item 11 or 12, wherein the agrarian crops are
cereals, fruit trees, citrus fruits, legumes,
horticultural crops, cucurbits, oleaginous plants,
tobacco, coffee, tea, cocoa, sugar beet, sugar cane, or
30 cotton.

14. Use of a composition comprising:

- at least one component (A), consisting of the compound having formula (I) 3-difluoromethyl-N-(7-fluoro-1,1,3-trimethyl-4-indanyl)-1-methyl-4-pyrazolecarboxamide

5



wherein Me represents a CH₃- methyl group, and

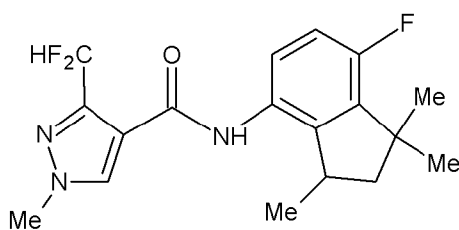
10 - at least one component [B] belonging to one or more of the following groups of fungicidal and insecticidal compounds:

- xix) neonicotinoids;
- xx) phenylpyrazoles;
- 15 xxi) pyretroids;
- xxii) carbamates;
- xxiii) macrolides of a microbial origin;
- xxiv) insecticidal diamides; or
- xxv) trifluoromethylpyridyl derivates : flonicamid
- 20 or sulfoxaflor,
- for the control of harmful insects in agrarian crops.

15. The use of the composition according to item 14,
25 wherein the agrarian crops are cereals, fruit trees, citrus fruits, legumes, horticultural crops, cucurbits, oleaginous plants, tobacco, coffee, tea, cocoa, sugar beet, sugar cane, or cotton.

16. A composition for the protecting of agrarian crops comprising:

- at least one component [A], consisting of the compound having formula (I), 3-difluoromethyl-N-(7-fluoro-1,1,3-trimethyl-4-indanyl)-1-methyl-4-pyrazo- lecarboxamide



wherein Me is a methyl group, and

- at least one component [B] which is an azole: azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, epoxyconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazail, ipconazole, metconazole, myclobutanil, penconazole, propiconazole, prochloraz, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triflumizole, or triticonazole.

20

17. The composition according to item 16, wherein said one or more components [B] are cyproconazole, difenoconazole, epoxyconazole, flutriafol, penconazole, prochloraz, prothioconazole, tebuconazole, or tetraconazole.

25

18. The composition according to item 16, wherein the azole is prochloraz, prothioconazole or tetraconazole.

19. The composition according to any one of items 16 to 18, wherein said compound having formula (I) is a racemic mixture (I RS).
- 5
20. The composition according to any one of items 16 to 19, wherein said compound having formula (I) is:
- (a) a mixture having one of the enantiomers-in a weight ratio of 51:49 to 99.99:0.01, by weight or
 - 10 - (b) one of the two enantiomers R ((I)-R) or S (I)-S) in a substantially pure form.
21. The composition according to item 20, wherein said compound having formula (I) is a mixture enriched in
- 15 the enantiomer R, wherein the enantiomer R has a purity of >99.99% by weight.
22. The composition according to any one of items 16 to 21, wherein the weight ratio between said at least one
- 20 component [A] and said at least one component [B] ranges from 1:20 to 20:1.
23. The composition according to any one of items 16 to 22, which comprises a composition of
- 25 - RS tetraconazole;
 - RS tebuconazole;
 - RS cyproconazole;
 - RS difenoconazole;
 - RS epoxyconazole;
 - 30 - RS flutriafol;
 - RS penconazole;

- RS prothioconazole;
 - RS prochloraz;
 - --R₈S₂ tetraconazole;
 - --R₉S₁ tetraconazole; or
- 5 - R tetraconazole;

wherein:

- RS indicates a compound of component [A] in the form of a racemic mixture,
- R₈S₂ indicates a compound of component [A]
- 10 containing the enantiomers R and S in a molar ratio R:S=8:2,
- R₉S₁ indicates a compound of component [A] containing the enantiomers R and S in a molar ratio R:S=9:1, and
- R indicates an enantiomer R of a compound of
- 15 component [A] in substantially pure form.

24. The composition according to any one of items 16 to 23, wherein said at least one component [A] and said at least one component [B], together or separately, are

20 diluted with one or more solid or liquid diluents, with the addition of one or more surfactants, dispersing agents, suspending agents, stabilizers, adjuvants, anti-freeze agents or adhesion agents.

25 25. The composition according to any one of items 16 to 24, comprising at least a further active principle, compatible with said components [A] and [B], selected from the group consisting of phyto regulators, antibiotics, herbicides, fertilizers and mixtures

30 thereof.

26. The composition according to any one of items 16 to 25, wherein said at least one component [A] and said at least one component [B], together or separately, are diluted with one or more solid or liquid diluents, dispersing agents, suspending agents, stabilizers, adjuvants, anti-freeze agents or adhesion agents.

27. A method for the control of phytopathogenic fungi in agricultural crops which comprises applying an effective amount of the synergistic composition as defined in any one of items 1 to 10 or the composition as defined in any one of items 16 to 26 to an agricultural crop.

28. The method for the control of phytopathogenic fungi according to item 27 where said phytopathogenic fungi are Basidiomycetes, Ascomycetes, Deuteromycetes or imperfect fungi, Oomycetes: *Puccinia* spp., *Ustilago* spp., *Tilletia* spp., *Uromyces* spp., *Phakopsora* spp., *Rhizoctonia* spp., *Erysiphe* spp., *Sphaerotheca* spp., *Podosphaera* spp., *Uncinula* spp., *Helminthosporium* spp., *Rhynchosporium* spp., *Pyrenophora* spp., *Monilinia* spp., *Sclerotinia* spp., *Septoria* spp. (*Mycosphaerella* spp.), *Venturia* spp., *Botrytis* spp., *Alternaria* spp., *Fusarium* spp., *Cercospora* spp., *Cercospora* spp., *herpotrichoides*, *Colletotrichum* spp., *Pyricularia oryzae*, *Sclerotium* spp., *Phytophthora* spp., *Pythium* spp., *Plasmopara viticola*, *Peronospora* spp., *Pseudoperonospora cubensis*, or *Bremia lactucae*.

29. The method for the control of phytopathogenic fungi according to item 27 or 28 wherein the agrarian crops

are cereals, fruit trees, citrus fruits, legumes, horticultural crops, cucurbits, oleaginous plants, tobacco, coffee, tea, cocoa, sugar beet, sugar cane, or cotton.

5

30. A method for controlling phytopathogenic fungi in agrarian crops, which comprises applying an effective dose of the synergistic composition as defined in any one of items 1 to 10 or the composition as defined in
10 any one of items 16 to 26, on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

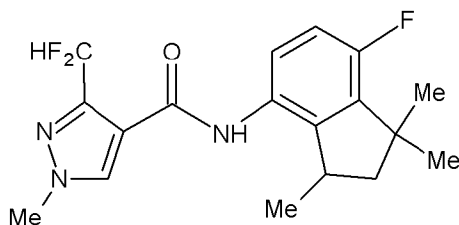
15 31. The method of item 30, wherein said phytopathogenic fungi are consisting of Basidiomycetes, Ascomycetes, Deuteromycetes or imperfect fungi, Oomycetes: *Puccinia* spp., *Ustilago* spp., *Tilletia* spp., *Uromyces* spp., *Phakopsora* spp., *Rhizoctonia* spp., *Erysiphe* spp.,
20 *Sphaerotheca* spp., *Podosphaera* spp., *Uncinula* spp., *Helminthosporium* spp., *Rhynchosporium* spp., *Pyrenophora* spp., *Monilinia* spp., *Sclerotinia* spp., *Septoria* spp. (*Mycosphaerella* spp.), *Venturia* spp., *Botrytis* spp., *Alternaria* spp., *Fusarium* spp., *Cercospora* spp.,
25 *Cercospora* spp., *herpotrichoides*, *Colletotrichum* spp., *Pyricularia oryzae*, *Sclerotium* spp., *Phytophthora* spp., *Pythium* spp., *Plasmopara viticola*, *Peronospora* spp., *Pseudoperonospora cubensis*, or *Bremia lactucae*.

30 32. A method for controlling harmful insects in agrarian crops, which comprises applying an effective dose of the synergistic composition as defined in any

one of items 1 to 10 or the composition as defined in
any one of items 16 to 26, on one or more parts of the
plants to be protected and/or on the seeds of said
plants before sowing and/or on the ground in which said
5 plants grow.

33. The method of any one of items 30 to 32, wherein
the agrarian crops are cereals, fruit trees, citrus
fruits, legumes, horticultural crops, cucurbits,
10 oleaginous plants, tobacco, coffee, tea, cocoa, sugar
beet, sugar cane, or cotton.

34. A synergistic combination for the protection of
agrarian crops comprising:
15 - at least one component (A), consisting of the
compound having formula (I) 3-difluoromethyl-N-(7-
fluoro-1,1,3-trimethyl-4-indanyl)-1-methyl-4-
pyrazolecarboxamide



20

(I)

wherein Me represents a CH₃- methyl group, and
- at least one component [B] having a fungicidal or
25 insecticidal activity and belonging to one or more of
the following groups of a) fungicidal and b)
insecticidal compounds:

- a) fungicidal compounds:
- i) azoles: difenoconazole, flutriafol, prothioconazole, tetraconazole;
 - ii) amino derivatives: spiroxamine;
 - 5 iii) strobilurins: azoxystrobin, fluoxa-strobin, kresoxim-methyl, pyraclostrobin;
 - vii) dicarboxyimides: iprodione;
 - viii) polyhalogenated fungicides: chlorothalonil;
 - ix) inducers of acquired systemic resistance (SAR): acibenzolar;
 - 10 xi) acylalanines: benalaxyl;
 - xii) antiperonosporic compounds: valifenalate;
 - xiii) dithiocarbamates: mancozeb;
 - xvi) copper-based cupric fungicides: copper oxychloride; or
 - 15 xvii) fungicidal amides: boscalid, fluopyram, fluxapyroxad, isopyrazam, penthiopyrad; or
- b) insecticidal compounds:
- 20 xix) neonicotinoids: imidacloprid; or
 - xxi) pyrethroids: bifenthrin.

35. The synergistic combination according to item 34, wherein said compound having formula (I) is a racemic mixture ((I)-RS).

25

36. The synergistic combination according to item 34 or 35, wherein said compound having formula (I) is:

- a mixture enriched in one of the enantiomers, or
- 30 - one of the two enantiomers R ((I)-R) or S ((I)-S) having a purity form of >99.99% by weight.

37. The synergistic combination according to item 36, wherein the mixture enriched in one of the enantiomers is enriched in the enantiomer R.
- 5 38. The synergistic combination according to item 36 or 37, wherein the enantiomer R ((I)-R) having a purity form of >99.99% by weight.
- 10 39. The synergistic combination according to any one of items 34 to 38, wherein the weight ratio between said at least one component [A] and said at least one component [B] ranges from 1:20 to 20:1.
- 15 40. The synergistic combination according to any one of items 34 to 39, wherein said combination is:
- C1: (I)-RS + tetraconazole;
C4: (I)-RS + difenoconazole;
C6: (I)-RS + flutriafol;
C8: (I)-RS + prothioconazole;
20 C11: (I)-RS + spiroxamine;
C12: (I)-RS + azoxystrobin;
C13: (I)-RS + fluoxastrobin;
C14: (I)-RS + kresoxim-methyl;
C16: (I)-RS + pyraclostrobin;
25 C22: (I)-RS + iprodione;
C26: (I)-RS + chlorothalonil;
C35: (I)-RS + valifenalate;
C39: (I)-RS + imidacloprid;
C49: (I)-RS + tetraconazole + azoxystrobin;
30 C50: (I)-RS + tebuconazole + azoxystrobin;
C51: (I)-RS + epoxyconazole + azoxystrobin;
C52: (I)-RS + cyproconazole + azoxystrobin;

- C53: (I)-RS + propiconazole + azoxystrobin;
 C54: (I)-RS + prothioconazole + azoxystrobin;
 C55: (I)-RS + tetraconazole + picoxystrobin;
 C60: (I)-RS + prothioconazole + picoxystrobin;
 5 C61: (I)-RS + tetraconazole + kresoxim methyl;
 C62: (I)-RS + tebuconazole + kresoxim methyl;
 C64: (I)-RS + cyproconazole + kresoxim methyl;
 C65: (I)-RS + propiconazole + kresoxim methyl;
 C66: (I)-RS + prothioconazole + kresoxim methyl;
 10 C67: (I)-RS + chlorothalonil + azoxystrobin;
 C68: (I)-RS + chlorothalonil + picoxystrobin;
 C69: (I)-RS + chlorothalonil + pyraclostrobin;
 C70: (I)-RS + chlorothalonil + kresoxim methyl;
 C71: (I)-RS + copper (II) hydroxide + copper
 15 oxychloride;
 C72: (I)-RS + copper (II) hydroxide + copper
 oxychloride + copper salicylate $C_7H_4O_3 \cdot Cu$;
 C73: (I)-R₃S₂ + tetraconazole;
 C74: (I)-R₃S₂ + azoxystrobin;
 20 C75: (I)-R₃S₂ + benalaxyl;
 C76: (I)-R₉S₁ + tetraconazole;
 C77: (I)-R₉S₁ + azoxystrobin; or
 C78: (I)-R + tetraconazole;
 wherein:
 25 - (I)-RS indicates the compound having formula (I) in
 the form of a racemic mixture,
 - (I)-R₃S₂ indicates the compound containing the
 enantiomers R and S in a molar ratio R:S = 8:2,
 - (I)-R₉S₁ indicates the compound containing the
 30 enantiomers R and S in a molar ratio R:S = 9:1,
 - (I)-R indicates the enantiomer R in substantially
 pure form, >99.99% by weight.

41. The synergistic combination according to any one of items 34 to 40, wherein said at least one component [A] and said at least one component [B], together or
5 separately, are diluted with one or more solid diluents and/or one or more liquid diluents.

42. The synergistic combination according to item 41, wherein said at least one component [A] and said at
10 least one component [B], together or separately, are diluted with one or more solid diluents and/or one or more liquid diluents, with the addition of one or more surfactants, dispersing agents, suspending agents, stabilizers, adjuvants, anti-freeze agents, and/or
15 adhesion agents.

43. The synergistic combination according to any one of items 34 to 42, comprising at least a further active principle, compatible with said components [A] and [B],
20 selected from fungicidal compounds or insecticidal compounds different from said compounds [B], phyto regulators, antibiotics, herbicides, fertilizers and mixtures thereof.

25 44. Use of the synergistic combination as defined in any one of items 34 to 43 for the control of phytopathogenic fungi in agricultural crops.

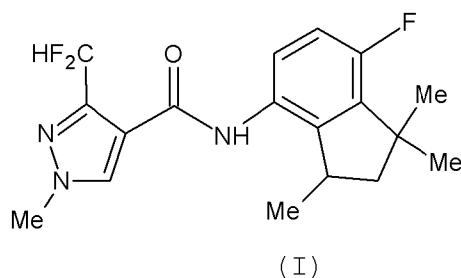
45. The use of the synergistic combination according
30 to item 44, for the control of phytopathogenic fungi which are: Basidiomycetes, Ascomycetes, Deuteromycetes or imperfect fungi, Oomycetes: *Puccinia* spp., *Ustilago*

spp., *Tilletia* spp., *Uromyces* spp., *Phakopsora* spp.,
Rhizoctonia spp., *Erysiphe* spp., *Sphaerotheca* spp.,
Podosphaera spp., *Uncinula* spp., *Helminthosporium*
 spp., *Rhynchosporium* spp., *Pyrenophora* spp., *Monilinia*
 5 spp., *Sclerotinia* spp., *Septoria* spp. (*Mycosphaerella*
 spp.), *Venturia* spp., *Botrytis* spp., *Alternaria* spp.,
Fusarium spp., *Cercospora* spp., *Cercospora*
herpotrichoides, *Colletotrichum* spp., *Pyricularia*
oryzae, *Sclerotium* spp., *Phytophthora* spp., *Pythium*
 10 spp., *Plasmopara viticola*, *Peronospora* spp.,
Pseudoperonospora cubensis, or *Bremia lactucae*.

46. The use of the synergistic combination according
 to item 44 or 45, wherein the agrarian crops are
 15 cereals, fruit trees, citrus fruits, legumes,
 horticultural crops, cucurbits, oleaginous plants,
 tobacco, coffee, tea, cocoa, sugar beet, sugar cane,
 and cotton.

20 47. Use of a combination comprising:
 - at least one component (A), consisting of the
 compound having formula (I) 3-difluoromethyl-N-(7-
 fluoro-1,1,3-trimethyl-4-indanyl)-1-methyl-4-
 pyrazolecarboxamide

25



wherein Me represents a CH₃- methyl group, and
- at least one component [B] belonging to one or more
of the following groups of fungicidal and insecticidal
compounds:

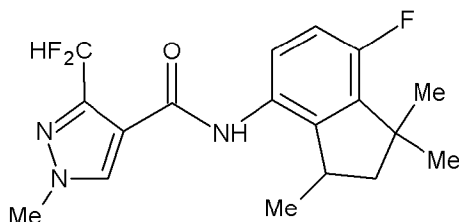
- 5 xix) neonicotinoids;
 xx) phenylpyrazoles;
 xxi) pyretroids;
 xxii) carbamates;
 xxiii) macrolides of a microbial origin;
10 xxiv) insecticidal diamides; or
 xxv) trifluoromethylpyridyl derivatives : flonicamid
 or sulfoxaflor,
 for the control of harmful insects in agrarian
 crops.

15

48. The use of the combination according to item 47,
wherein the agrarian crops are cereals, fruit trees,
citrus fruits, legumes, horticultural crops, cucurbits,
oleaginous plants, tobacco, coffee, tea, cocoa, sugar
20 beet, sugar cane, or cotton.

49. A combination for the protecting of agrarian crops
comprising:

- 25 - at least one component [A], consisting of the
 compound having formula (I), 3-difluoromethyl-N-
 (7-fluoro-1,1,3-trimethyl-4-indanyl)-1-methyl-4-
 pyrazo- lecarboxamide



wherein Me is a methyl group, and

- at least one component [B] which is an azole:
 azaconazole, bitertanol, bromuconazole, cyproconazole,
 5 difenoconazole, epoxyconazole, fenbuconazole,
 fluquinconazole, flusilazole, flutriafol, hexaconazole,
 imazail, ipconazole, metconazole, myclobutanil,
 penconazole, propiconazole, prochloraz,
 prothioconazole, simeconazole, tebuconazole,
 10 tetraconazole, triadimefon, triadimenol, triflumizole,
 or triticonazole.

50. The combination according to item 49, wherein said
 one or more components [B] are cyproconazole,
 15 difenoconazole, epoxyconazole, flutriafol, penconazole,
 prochloraz, prothioconazole, tebuconazole, or
 tetraconazole.

51. The combination according to item 49, wherein the
 20 azole is prochloraz, prothioconazole or tetraconazole.

52. The combination according to any one of items 49 to
 51, wherein said compound having formula (I) is a
 racemic mixture (I RS).

25

53. The combination according to any one of items 49 to
 52, wherein said compound having formula (I) is:

- (a) a mixture having one of the enantiomers-in a weight ratio of 51:49 to 99.99:0.01, by weight or
- (b) one of the two enantiomers R ((I)-R) or S ((I)-S) in a substantially pure form.

5

54. The combination according to item 53, wherein said compound having formula (I) is a mixture enriched in the enantiomer R, wherein the enantiomer R has a purity of >99.99% by weight.

10

55. The combination according to any one of items 49 to 54, wherein the weight ratio between said at least one component [A] and said at least one component [B] ranges from 1:20 to 20:1.

15

56. The combination according to any one of items 49 to 55, which comprises a combination of

- RS tetraconazole;
- RS tebuconazole;
- RS cyproconazole;
- RS difenoconazole;
- RS epoxyconazole;
- RS flutriafol;
- RS penconazole;
- RS prothioconazole;
- RS prochloraz;
- --R₈S₂ tetraconazole;
- --R₉S₁ tetraconazole; or
- R tetraconazole;

30 wherein:

--RS indicates a compound of component [A] in the form of a racemic mixture,

-- R₈S₂ indicates a compound of component [A] containing the enantiomers R and S in a molar ratio R:S=8:2,

-- R₉S₁ indicates a compound of component [A] containing the enantiomers R and S in a molar ratio R:S=9:1, and

--R indicates an enantiomer R of a compound of component [A] in substantially pure form.

10

57. The combination according to any one of items 49 to 56, wherein said at least one component [A] and said at least one component [B], together or separately, are diluted with one or more solid or liquid diluents, with the addition of one or more surfactants, dispersing agents, suspending agents, stabilizers, adjuvants, anti-freeze agents or adhesion agents.

58. The combination according to any one of items 49 to 57, comprising at least a further active principle, compatible with said components [A] and [B], selected from the group consisting of phyto regulators, antibiotics, herbicides, fertilizers and mixtures thereof.

25

59. The combination according to any one of items 49 to 58, wherein said at least one component [A] and said at least one component [B], together or separately, are diluted with one or more solid or liquid diluents, dispersing agents, suspending agents, stabilizers, adjuvants, anti-freeze agents or adhesion agents.

60. A method for the control of phytopathogenic fungi in agricultural crops which comprises applying an effective amount of the synergistic combination as defined in any one of items 34 to 43 or the combination as defined in any one of items 49 to 59 to an agricultural crop.

61. The method for the control of phytopathogenic fungi according to item 60 where said phytopathogenic fungi are Basidiomycetes, Ascomycetes, Deuteromycetes or imperfect fungi, Oomycetes: *Puccinia* spp., *Ustilago* spp., *Tilletia* spp., *Uromyces* spp., *Phakopsora* spp., *Rhizoctonia* spp., *Erysiphe* spp., *Sphaerotheca* spp., *Podosphaera* spp., *Uncinula* spp., *Helminthosporium* spp., *Rhynchosporium* spp., *Pyrenophora* spp., *Monilinia* spp., *Sclerotinia* spp., *Septoria* spp. (*Mycosphaerella* spp.), *Venturia* spp., *Botrytis* spp., *Alternaria* spp., *Fusarium* spp., *Cercospora* spp., *Cercospora* spp., *herpotrichoides*, *Colletotrichum* spp., *Pyricularia oryzae*, *Sclerotium* spp., *Phytophthora* spp., *Pythium* spp., *Plasmopara viticola*, *Peronospora* spp., *Pseudoperonospora cubensis*, or *Bremia lactucae*.

62. The method for the control of phytopathogenic fungi according to item 60 or 61 wherein the agrarian crops are cereals, fruit trees, citrus fruits, legumes, horticultural crops, cucurbits, oleaginous plants, tobacco, coffee, tea, cocoa, sugar beet, sugar cane, or cotton.

30

63. A method for controlling phytopathogenic fungi in agrarian crops, which comprises applying an effective

dose of the synergistic combination as defined in any one of items 34 to 43 or the combination as defined in any one of items 49 to 59, on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

64. The method of item 63, wherein said phytopathogenic fungi are consisting of Basidiomycetes, Ascomycetes, Deuteromycetes or imperfect fungi, Oomycetes: *Puccinia* spp., *Ustilago* spp., *Tilletia* spp., *Uromyces* spp., *Phakopsora* spp., *Rhizoctonia* spp., *Erysiphe* spp., *Sphaerotheca* spp., *Podosphaera* spp., *Uncinula* spp., *Helminthosporium* spp., *Rhynchosporium* spp., *Pyrenophora* spp., *Monilinia* spp., *Sclerotinia* spp., *Septoria* spp. (*Mycosphaerella* spp.), *Venturia* spp., *Botrytis* spp., *Alternaria* spp., *Fusarium* spp., *Cercospora* spp., *Cercospora* *herpotrichoides*, *Colletotrichum* spp., *Pyricularia oryzae*, *Sclerotium* spp., *Phytophthora* spp., *Pythium* spp., *Plasmopara viticola*, *Peronospora* spp., *Pseudoperonospora cubensis*, or *Bremia lactucae*.

65. A method for controlling harmful insects in agrarian crops, which comprises applying an effective dose of the synergistic combination as defined in any one of items 34 to 43 or the combination as defined in any one of items 49 to 59, on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

66. The method of any one of items 63 to 65, wherein

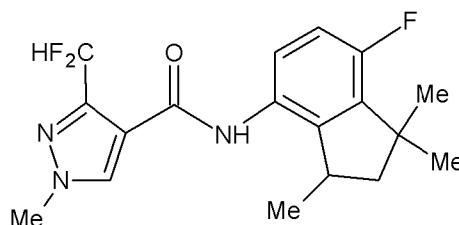
the agrarian crops are cereals, fruit trees, citrus fruits, legumes, horticultural crops, cucurbits, oleaginous plants, tobacco, coffee, tea, cocoa, sugar beet, sugar cane, or cotton.

5

CLAIMS

1. A synergistic composition for the protection of agrarian crops comprising:

- 5 - at least one component (A), consisting of the compound having formula (I) 3-difluoromethyl-N-(7-fluoro-1,1,3-trimethyl-4-indanyl)-1-methyl-4-pyrazolecarboxamide



10

(I)

wherein Me represents a CH₃- methyl group, and

- at least one component [B] having a fungicidal or
15 insecticidal activity and belonging to one or more of the following groups of a) fungicidal and b) insecticidal compounds:

a) fungicidal compounds:

- 20 i) azoles: difenoconazole, flutriafol, prothioconazole, tetraconazole;
ii) amino derivatives: spiroxamine;
iii) strobilurins: azoxystrobin, fluoxa-strobin, kresoxim-methyl, pyraclostrobin;
25 vii) dicarboxyimides: iprodione;
viii) polyhalogenated fungicides: chlorothalonil;
ix) inducers of acquired systemic resistance (SAR): acibenzolar;

- xi) acylalanines: benalaxyl;
- xii) antiperonosporic compounds: valifenalate;
- xiii) dithiocarbamates: mancozeb;
- xvi) copper-based cupric fungicides: copper
5 oxychloride; or
- xvii) fungicidal amides: boscalid, fluopyram,
fluxapyroxad, isopyrazam, penthiopyrad; or
- b) insecticidal compounds:
- 10 xix) neonicotinoids: imidacloprid; or
- xxi) pyrethroids: bifenthrin.

2. The synergistic composition according to claim 1,
wherein said compound having formula (I) is a racemic
15 mixture ((I)-RS).

3. The synergistic composition according to claim 1
or 2, wherein said compound having formula (I) is:
- a mixture enriched in one of the enantiomers, or
20 - one of the two enantiomers R ((I)-R) or S ((I)-S)
having a purity form of >99.99% by weight.

4. The synergistic composition according to claim 3,
wherein the mixture enriched in one of the enantiomers
25 is enriched in the enantiomer R.

5. The synergistic composition according to claim 3 or
4, wherein the enantiomer R ((I)-R) having a purity
form of >99.99% by weight.

30

6. The synergistic composition according to any one
of claims 1 to 5, wherein the weight ratio between said

at least one component [A] and said at least one component [B] ranges from 1:20 to 20:1.

7. The synergistic composition according to any one of claims 1 to 6, wherein said composition is:

- C1: (I)-RS + tetraconazole;
- C4: (I)-RS + difenoconazole;
- C6: (I)-RS + flutriafol;
- C8: (I)-RS + prothioconazole;
- 10 C11: (I)-RS + spiroxamine;
- C12: (I)-RS + azoxystrobin;
- C13: (I)-RS + fluoxastrobin;
- C14: (I)-RS + kresoxim-methyl;
- C16: (I)-RS + pyraclostrobin;
- 15 C22: (I)-RS + iprodione;
- C26: (I)-RS + chlorothalonil;
- C35: (I)-RS + valifenalate;
- C39: (I)-RS + imidacloprid;
- C49: (I)-RS + tetraconazole + azoxystrobin;
- 20 C50: (I)-RS + tebuconazole + azoxystrobin;
- C51: (I)-RS + epoxyconazole + azoxystrobin;
- C52: (I)-RS + cyproconazole + azoxystrobin;
- C53: (I)-RS + propiconazole + azoxystrobin;
- C54: (I)-RS + prothioconazole + azoxystrobin;
- 25 C55: (I)-RS + tetraconazole + picoxystrobin;
- C60: (I)-RS + prothioconazole + picoxystrobin;
- C61: (I)-RS + tetraconazole + kresoxim methyl;
- C62: (I)-RS + tebuconazole + kresoxim methyl;
- C64: (I)-RS + cyproconazole + kresoxim methyl;
- 30 C65: (I)-RS + propiconazole + kresoxim methyl;
- C66: (I)-RS + prothioconazole + kresoxim methyl;
- C67: (I)-RS + chlorothalonil + azoxystrobin;

C68: (I)-RS + chlorothalonil + picoxystrobin;
C69: (I)-RS + chlorothalonil + pyraclostrobin;
C70: (I)-RS + chlorothalonil + kresoxim methyl;
C71: (I)-RS + copper (II) hydroxide + copper
5 oxychloride;
C72: (I)-RS + copper (II) hydroxide + copper
oxychloride + copper salicylate $C_7H_4O_3 \cdot Cu$;
C73: (I)-R₃S₂ + tetraconazole;
C74: (I)-R₃S₂ + azoxystrobin;
10 C75: (I)-R₃S₂ + benalaxyl;
C76: (I)-R₉S₁ + tetraconazole;
C77: (I)-R₉S₁ + azoxystrobin; or
C78: (I)-R + tetraconazole;

wherein:

- 15 - (I)-RS indicates the compound having formula (I) in
the form of a racemic mixture,
- (I)-R₃S₂ indicates the compound containing the
enantiomers R and S in a molar ratio R:S = 8:2,
- (I)-R₉S₁ indicates the compound containing the
20 enantiomers R and S in a molar ratio R:S = 9:1,
- (I)-R indicates the enantiomer R in substantially
pure form, >99.99% by weight.

8. The synergistic composition according to any one
25 of claims 1 to 7, wherein said at least one component
[A] and said at least one component [B], together or
separately, are diluted with one or more solid diluents
and/or one or more liquid diluents.

30 9. The synergistic composition according to claim 8,
wherein said at least one component [A] and said at
least one component [B], together or separately, are

diluted with one or more solid diluents and/or one or more liquid diluents, with the addition of one or more surfactants, dispersing agents, suspending agents, stabilizers, adjuvants, anti-freeze agents, and/or
5 adhesion agents.

10. The synergistic composition according to any one of claims 1 to 9, comprising at least a further active principle, compatible with said components [A] and [B],
10 selected from fungicidal compounds or insecticidal compounds different from said compounds [B], phyto regulators, antibiotics, herbicides, fertilizers and mixtures thereof.

15 11. Use of the synergistic composition as defined in any one of claims 1 to 10 for the control of phytopathogenic fungi in agricultural crops.

12. The use of the synergistic composition according
20 to claim 11, for the control of phytopathogenic fungi which are: Basidiomycetes, Ascomycetes, Deuteromycetes or imperfect fungi, Oomycetes: *Puccinia* spp., *Ustilago* spp., *Tilletia* spp., *Uromyces* spp., *Phakopsora* spp., *Rhizoctonia* spp., *Erysiphe* spp., *Sphaerotheca* spp.,
25 *Podosphaera* spp., *Uncinula* spp., *Helminthosporium* spp., *Rhynchosporium* spp., *Pyrenophora* spp., *Monilinia* spp., *Sclerotinia* spp., *Septoria* spp. (*Mycosphaerella* spp.), *Venturia* spp., *Botrytis* spp., *Alternaria* spp., *Fusarium* spp., *Cercospora* spp., *Cercospora* spp.,
30 *herpotrichoides*, *Colletotrichum* spp., *Pyricularia oryzae*, *Sclerotium* spp., *Phytophthora* spp., *Pythium* spp., *Plasmopara viticola*, *Peronospora* spp.,

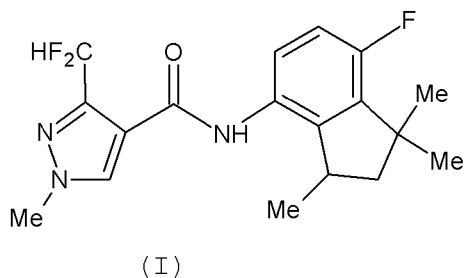
Pseudoperonospora cubensis, or *Bremia lactucae*.

13. The use of the synergistic composition according to claim 11 or 12, wherein the agrarian crops are
5 cereals, fruit trees, citrus fruits, legumes, horticultural crops, cucurbits, oleaginous plants, tobacco, coffee, tea, cocoa, sugar beet, sugar cane, or cotton.

10 14. Use of a composition comprising:

- at least one component (A), consisting of the compound having formula (I) 3-difluoromethyl-N-(7-fluoro-1,1,3-trimethyl-4-indanyl)-1-methyl-4-pyrazolecarboxamide

15



wherein Me represents a CH₃- methyl group, and

20 - at least one component [B] belonging to one or more of the following groups of fungicidal and insecticidal compounds:

xix) neonicotinoids;

xx) phenylpyrazoles;

25 xxi) pyretroids;

xxii) carbamates;

xxiii) macrolides of a microbial origin;

xxiv) insecticidal diamides; or

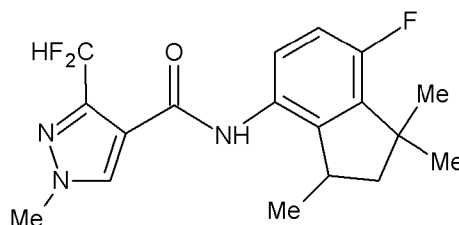
xxv) trifluoromethylpyridyl derivates : flonicamid or sulfoxaflor,
for the control of harmful insects in agrarian crops.

5 15. The use of the composition according to claim 14, wherein the agrarian crops are cereals, fruit trees, citrus fruits, legumes, horticultural crops, cucurbits, oleaginous plants, tobacco, coffee, tea, cocoa, sugar beet, sugar cane, or cotton.

10

16. A composition for the protecting of agrarian crops comprising:

- at least one component [A], consisting of the compound having formula (I), 3-difluoromethyl-N-(7-fluoro-1,1,3-trimethyl-4-indanyl)-1-methyl-4-pyrazo-
15 lecarboxamide



wherein Me is a methyl group, and

- at least one component [B] which is an azole:
20 azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, epoxyconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazail, ipconazole, metconazole, myclobutanil, penconazole, propiconazole, prochloraz,
25 prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triflumizole, or triticonazole.

17. The composition according to claim 16, wherein said one or more components [B] are cyproconazole, difenoconazole, epoxyconazole, flutriafol, penconazole, prochloraz, prothioconazole, tebuconazole, or
5 tetraconazole.

18. The composition according to claim 16, wherein theazole is prochloraz, prothioconazole or tetraconazole.

10 19. The composition according to any one of claims 16 to 18, wherein said compound having formula (I) is a racemic mixture (I RS).

20. The composition according to any one of claims 16
15 to 19, wherein said compound having formula (I) is:

- (a) a mixture having one of the enantiomers-in a weight ratio of 51:49 to 99.99:0.01, by weight or
- (b) one of the two enantiomers R ((I)-R) or S ((I)-S) in a substantially pure form.

20

21. The composition according to claim 20, wherein said compound having formula (I) is a mixture enriched in the enantiomer R, wherein the enantiomer R has a purity of >99.99% by weight.

25

22. The composition according to any one of claims 16 to 21, wherein the weight ratio between said at least one component [A] and said at least one component [B] ranges from 1:20 to 20:1.

30

23. The composition according to any one of claims 16 to 22, which comprises a composition of

- RS tetraconazole;
- RS tebuconazole;
- RS cyproconazole;
- RS difenoconazole;
- 5- RS epoxyconazole;
- RS flutriafol;
- RS penconazole;
- RS prothioconazole;
- RS prochloraz;
- 10- --R₈S₂ tetraconazole;
- --R₉S₁ tetraconazole; or
- R tetraconazole;

wherein:

- RS indicates a compound of component [A] in the form
- 15 of a racemic mixture,
- R₈S₂ indicates a compound of component [A] containing the enantiomers R and S in a molar ratio R:S=8:2,
- R₉S₁ indicates a compound of component [A] containing
- 20 the enantiomers R and S in a molar ratio R:S=9:1, and
- R indicates an enantiomer R of a compound of component [A] in substantially pure form.

24. The composition according to any one of claims 16
- 25 to 23, wherein said at least one component [A] and said at least one component [B], together or separately, are diluted with one or more solid or liquid diluents, with the addition of one or more surfactants, dispersing agents, suspending agents, stabilizers, adjuvants,
- 30 anti-freeze agents or adhesion agents.

25. The composition according to any one of claims 16 to 24, comprising at least a further active principle, compatible with said components [A] and [B], selected from the group consisting of phytohormones, antibiotics, herbicides, fertilizers and mixtures thereof.

26. The composition according to any one of claims 16 to 25, wherein said at least one component [A] and said at least one component [B], together or separately, are diluted with one or more solid or liquid diluents, dispersing agents, suspending agents, stabilizers, adjuvants, anti-freeze agents or adhesion agents.

27. A method for the control of phytopathogenic fungi in agricultural crops which comprises applying an effective amount of the synergistic composition as defined in any one of claims 1 to 10 or the composition as defined in any one of claims 16 to 26 to an agricultural crop.

28. The method for the control of phytopathogenic fungi according to claim 27 where said phytopathogenic fungi are Basidiomycetes, Ascomycetes, Deuteromycetes or imperfect fungi, Oomycetes: *Puccinia* spp., *Ustilago* spp., *Tilletia* spp., *Uromyces* spp., *Phakopsora* spp., *Rhizoctonia* spp., *Erysiphe* spp., *Sphaerotheca* spp., *Podosphaera* spp., *Uncinula* spp., *Helminthosporium* spp., *Rhynchosporium* spp., *Pyrenophora* spp., *Monilinia* spp., *Sclerotinia* spp., *Septoria* spp. (*Mycosphaerella* spp.), *Venturia* spp., *Botrytis* spp., *Alternaria* spp.,

Fusarium spp., *Cercospora* spp., *Cercosporella*
herpotrichoides, *Colletotrichum* spp., *Pyricularia*
oryzae, *Sclerotium* spp., *Phytophthora* spp., *Pythium*
spp., *Plasmopara viticola*, *Peronospora* spp.,
5 *Pseudoperonospora cubensis*, or *Bremia lactucae*.

29. The method for the control of phytopathogenic fungi
according to claim 27 or 28 wherein the agrarian crops
are cereals, fruit trees, citrus fruits, legumes,
10 horticultural crops, cucurbits, oleaginous plants,
tobacco, coffee, tea, cocoa, sugar beet, sugar cane, or
cotton.

30. A method for controlling phytopathogenic fungi in
15 agrarian crops, which comprises applying an effective
dose of the synergistic composition as defined in any
one of claims 1 to 10 or the composition as defined in
any one of claims 16 to 26, on one or more parts of the
plants to be protected and/or on the seeds of said
20 plants before sowing and/or on the ground in which said
plants grow.

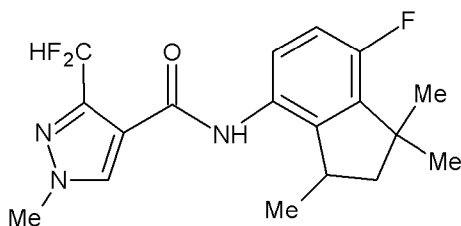
31. The method of claim 30, wherein said
phytopathogenic fungi are consisting of Basidiomycetes,
25 Ascomycetes, Deuteromycetes or imperfect fungi,
Oomycetes: *Puccinia* spp., *Ustilago* spp., *Tilletia* spp.,
Uromyces spp., *Phakopsora* spp., *Rhizoctonia* spp.,
Erysiphe spp., *Sphaerotheca* spp., *Podosphaera* spp.,
Uncinula spp., *Helminthosporium* spp., *Rhynchosporium*
30 spp., *Pyrenophora* spp., *Monilinia* spp., *Sclerotinia*
spp., *Septoria* spp. (*Mycosphaerella* spp.), *Venturia*
spp., *Botrytis* spp., *Alternaria* spp., *Fusarium* spp.,

Cercospora spp., *Cercospora* *herpotrichoides*,
Colletotrichum spp., *Pyricularia* *oryzae*, *Sclerotium*
spp., *Phytophthora* spp., *Pythium* spp., *Plasmopara*
viticola, *Peronospora* spp., *Pseudoperonospora* *cubensis*,
5 or *Bremia* *lactucae*.

32. A method for controlling harmful insects in
agrarian crops, which comprises applying an effective
dose of the synergistic composition as defined in any
10 one of claims 1 to 10 or the composition as defined in
any one of claims 16 to 26, on one or more parts of the
plants to be protected and/or on the seeds of said
plants before sowing and/or on the ground in which said
plants grow.

15 33. The method of any one of claims 30 to 32, wherein
the agrarian crops are cereals, fruit trees, citrus
fruits, legumes, horticultural crops, cucurbits,
oleaginous plants, tobacco, coffee, tea, cocoa, sugar
20 beet, sugar cane, or cotton.

34. A synergistic combination for the protection of
agrarian crops comprising:
- at least one component (A), consisting of the
25 compound having formula (I) 3-difluoromethyl-N-(7-
fluoro-1,1,3-trimethyl-4-indanyl)-1-methyl-4-
pyrazolecarboxamide



(I)

wherein Me represents a CH₃- methyl group, and

- 5 - at least one component [B] having a fungicidal or insecticidal activity and belonging to one or more of the following groups of a) fungicidal and b) insecticidal compounds:
- 10 a) fungicidal compounds:
 - i) azoles: difenoconazole, flutriafol, prothioconazole, tetraconazole;
 - ii) amino derivatives: spiroxamine;
 - iii) strobilurins: azoxystrobin, fluoxa-strobin,
 - 15 kresoxim-methyl, pyraclostrobin;
 - vii) dicarboxyimides: iprodione;
 - viii) polyhalogenated fungicides: chlorothalonil;
 - ix) inducers of acquired systemic resistance (SAR): acibenzolar;
 - 20 xi) acylalanines: benalaxyl;
 - xii) antiperonosporic compounds: valifenalate;
 - xiii) dithiocarbamates: mancozeb;
 - xvi) copper-based cupric fungicides: copper oxychloride; or
 - 25 xvii) fungicidal amides: boscalid, fluopyram, fluxapyroxad, isopyrazam, penthiopyrad; or
- b) insecticidal compounds:

xix) neonicotinoids: imidacloprid; or

xxi) pyrethroids: bifenthrin.

35. The synergistic combination according to claim 34,
5 wherein said compound having formula (I) is a racemic
mixture ((I)-RS).

36. The synergistic combination according to claim 34
or 35, wherein said compound having formula (I) is:
10 - a mixture enriched in one of the enantiomers, or
- one of the two enantiomers R ((I)-R) or S ((I)-S)
having a purity form of >99.99% by weight.

37. The synergistic combination according to claim 36,
15 wherein the mixture enriched in one of the enantiomers
is enriched in the enantiomer R.

38. The synergistic combination according to claim 36
or 37, wherein the enantiomer R ((I)-R) having a purity
20 form of >99.99% by weight.

39. The synergistic combination according to any one
of claims 34 to 38, wherein the weight ratio between
said at least one component [A] and said at least one
25 component [B] ranges from 1:20 to 20:1.

40. The synergistic combination according to any one
of claims 34 to 39, wherein said combination is:
C1: (I)-RS + tetraconazole;
30 C4: (I)-RS + difenoconazole;
C6: (I)-RS + flutriafol;
C8: (I)-RS + prothioconazole;

C11: (I)-RS + spiroxamine;
 C12: (I)-RS + azoxystrobin;
 C13: (I)-RS + fluoxastrobin;
 C14: (I)-RS + kresoxim-methyl;
 5 C16: (I)-RS + pyraclostrobin;
 C22: (I)-RS + iprodione;
 C26: (I)-RS + chlorothalonil;
 C35: (I)-RS + valifenalate;
 C39: (I)-RS + imidacloprid;
 10 C49: (I)-RS + tetraconazole + azoxystrobin;
 C50: (I)-RS + tebuconazole + azoxystrobin;
 C51: (I)-RS + epoxyconazole + azoxystrobin;
 C52: (I)-RS + cyproconazole + azoxystrobin;
 C53: (I)-RS + propiconazole + azoxystrobin;
 15 C54: (I)-RS + prothioconazole + azoxystrobin;
 C55: (I)-RS + tetraconazole + picoxystrobin;
 C60: (I)-RS + prothioconazole + picoxystrobin;
 C61: (I)-RS + tetraconazole + kresoxim methyl;
 C62: (I)-RS + tebuconazole + kresoxim methyl;
 20 C64: (I)-RS + cyproconazole + kresoxim methyl;
 C65: (I)-RS + propiconazole + kresoxim methyl;
 C66: (I)-RS + prothioconazole + kresoxim methyl;
 C67: (I)-RS + chlorothalonil + azoxystrobin;
 C68: (I)-RS + chlorothalonil + picoxystrobin;
 25 C69: (I)-RS + chlorothalonil + pyraclostrobin;
 C70: (I)-RS + chlorothalonil + kresoxim methyl;
 C71: (I)-RS + copper (II) hydroxide + copper
 oxychloride;
 C72: (I)-RS + copper (II) hydroxide + copper
 30 oxychloride + copper salicylate $C_7H_4O_3 \cdot Cu$;
 C73: (I)-R₃S₂ + tetraconazole;
 C74: (I)-R₃S₂ + azoxystrobin;

C75: (I)-R₃S₂ + benalaxyl;
C76: (I)-R₉S₁ + tetraconazole;
C77: (I)-R₉S₁ + azoxystrobin; or
C78: (I)-R + tetraconazole;

5 wherein:

- (I)-RS indicates the compound having formula (I) in the form of a racemic mixture,
- (I)-R₃S₂ indicates the compound containing the enantiomers R and S in a molar ratio R:S = 8:2,
- 10 - (I)-R₉S₁ indicates the compound containing the enantiomers R and S in a molar ratio R:S = 9:1,
- (I)-R indicates the enantiomer R in substantially pure form, >99.99% by weight.

15 41. The synergistic combination according to any one of claims 34 to 40, wherein said at least one component [A] and said at least one component [B], together or separately, are diluted with one or more solid diluents and/or one or more liquid diluents.

20

42. The synergistic combination according to claim 41, wherein said at least one component [A] and said at least one component [B], together or separately, are diluted with one or more solid diluents and/or one or
25 more liquid diluents, with the addition of one or more surfactants, dispersing agents, suspending agents, stabilizers, adjuvants, anti-freeze agents, and/or adhesion agents.

30 43. The synergistic combination according to any one of claims 34 to 42, comprising at least a further active principle, compatible with said components [A]

and [B], selected from fungicidal compounds or insecticidal compounds different from said compounds [B], phyto regulators, antibiotics, herbicides, fertilizers and mixtures thereof.

5

44. Use of the synergistic combination as defined in any one of claims 34 to 43 for the control of phytopathogenic fungi in agricultural crops.

10 45. The use of the synergistic combination according to claim 44, for the control of phytopathogenic fungi which are: Basidiomycetes, Ascomycetes, Deuteromycetes or imperfect fungi, Oomycetes: *Puccinia* spp., *Ustilago* spp., *Tilletia* spp., *Uromyces* spp., *Phakopsora* spp.,
15 *Rhizoctonia* spp., *Erysiphe* spp., *Sphaerotheca* spp., *Podosphaera* spp., *Uncinula* spp., *Helminthosporium* spp., *Rhynchosporium* spp., *Pyrenophora* spp., *Monilinia* spp., *Sclerotinia* spp., *Septoria* spp. (*Mycosphaerella* spp.), *Venturia* spp., *Botrytis* spp., *Alternaria* spp.,
20 *Fusarium* spp., *Cercospora* spp., *Cercosporiella* *herpotrichoides*, *Colletotrichum* spp., *Pyricularia* *oryzae*, *Sclerotium* spp., *Phytophthora* spp., *Pythium* spp., *Plasmopara* *viticola*, *Peronospora* spp., *Pseudoperonospora cubensis*, or *Bremia lactucae*.

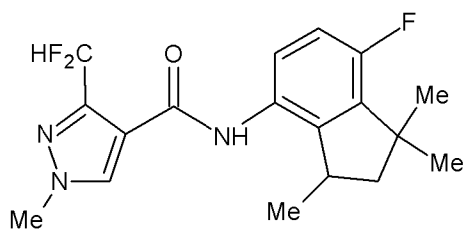
25

46. The use of the synergistic combination according to claim 44 or 45, wherein the agrarian crops are cereals, fruit trees, citrus fruits, legumes, horticultural crops, cucurbits, oleaginous plants,
30 tobacco, coffee, tea, cocoa, sugar beet, sugar cane, and cotton.

47. Use of a combination comprising:

- at least one component (A), consisting of the compound having formula (I) 3-difluoromethyl-N-(7-fluoro-1,1,3-trimethyl-4-indanyl)-1-methyl-4-

5 pyrazolecarboxamide



(I)

10 wherein Me represents a CH₃- methyl group, and

- at least one component [B] belonging to one or more of the following groups of fungicidal and insecticidal compounds:

xix) neonicotinoids;

15 xx) phenylpyrazoles;

xxi) pyretroids;

xxii) carbamates;

xxiii) macrolides of a microbial origin;

xxiv) insecticidal diamides; or

20 xxv) trifluoromethylpyridyl derivatives : flonicamid or sulfoxaflor,

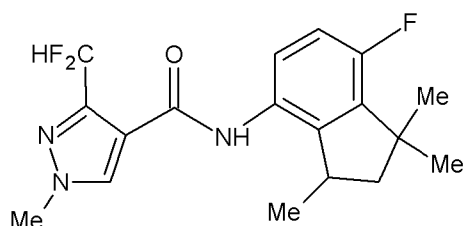
for the control of harmful insects in agrarian crops.

48. The use of the combination according to claim 47,

25 wherein the agrarian crops are cereals, fruit trees, citrus fruits, legumes, horticultural crops, cucurbits, oleaginous plants, tobacco, coffee, tea, cocoa, sugar beet, sugar cane, or cotton.

49. A combination for the protecting of agrarian crops comprising:

- at least one component [A], consisting of the compound having formula (I), 3-difluoromethyl-N-(7-fluoro-1,1,3-trimethyl-4-indanyl)-1-methyl-4-pyrazo- lecarboxamide



wherein Me is a methyl group, and

- at least one component [B] which is an azole:
azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, epoxyconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazail, ipconazole, metconazole, myclobutanil, penconazole, propiconazole, prochloraz, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triflumizole, or triticonazole.

- 50. The combination according to claim 49, wherein said one or more components [B] are cyproconazole, difenoconazole, epoxyconazole, flutriafol, penconazole, prochloraz, prothioconazole, tebuconazole, or tetraconazole.

25

- 51. The combination according to claim 49, wherein the azole is prochloraz, prothioconazole or tetraconazole.

52. The combination according to any one of claims 49 to 51, wherein said compound having formula (I) is a racemic mixture (I RS).

5 53. The combination according to any one of claims 49 to 52, wherein said compound having formula (I) is:

- (a) a mixture having one of the enantiomers-in a weight ratio of 51:49 to 99.99:0.01, by weight or
 - (b) one of the two enantiomers R ((I)-R) or S ((I)-S)
- 10 in a substantially pure form.

54. The combination according to claim 53, wherein said compound having formula (I) is a mixture enriched in the enantiomer R, wherein the enantiomer R has a purity

15 of >99.99% by weight.

55. The combination according to any one of claims 49 to 54, wherein the weight ratio between said at least one component [A] and said at least one component [B]

20 ranges from 1:20 to 20:1.

56. The combination according to any one of claims 49 to 55, which comprises a combination of

- RS tetraconazole;
- 25- RS tebuconazole;
- RS cyproconazole;
- RS difenoconazole;
- RS epoxyconazole;
- RS flutriafol;
- 30- RS penconazole;
- RS prothioconazole;

- RS prochloraz;
- --R₈S₂ tetraconazole;
- --R₉S₁ tetraconazole; or
- R tetraconazole;

5 wherein:

--RS indicates a compound of component [A] in the form of a racemic mixture,

-- R₈S₂ indicates a compound of component [A] containing the enantiomers R and S in a molar ratio

10 R:S=8:2,

-- R₉S₁ indicates a compound of component [A] containing the enantiomers R and S in a molar ratio R:S=9:1, and

--R indicates an enantiomer R of a compound of component [A] in substantially pure form.

15

57. The combination according to any one of claims 49 to 56, wherein said at least one component [A] and said at least one component [B], together or separately, are diluted with one or more solid or liquid diluents, with
20 the addition of one or more surfactants, dispersing agents, suspending agents, stabilizers, adjuvants, anti-freeze agents or adhesion agents.

58. The combination according to any one of claims 49
25 to 57, comprising at least a further active principle, compatible with said components [A] and [B], selected from the group consisting of phyto regulators, antibiotics, herbicides, fertilizers and mixtures thereof.

30

59. The combination according to any one of claims 49

to 58, wherein said at least one component [A] and said
at least one component [B], together or separately, are
diluted with one or more solid or liquid diluents,
dispersing agents, suspending agents, stabilizers,
5 adjuvants, anti-freeze agents or adhesion agents.

60. A method for the control of phytopathogenic fungi
in agricultural crops which comprises applying an
effective amount of the synergistic combination as
10 defined in any one of claims 34 to 43 or the
combination as defined in any one of claims 49 to 59 to
an agricultural crop.

61. The method for the control of phytopathogenic fungi
15 according to claim 60 where said phytopathogenic fungi
are Basidiomycetes, Ascomycetes, Deuteromycetes or
imperfect fungi, Oomycetes: *Puccinia* spp., *Ustilago*
spp., *Tilletia* spp., *Uromyces* spp., *Phakopsora* spp.,
Rhizoctonia spp., *Erysiphe* spp., *Sphaerotheca* spp.,
20 *Podosphaera* spp., *Uncinula* spp., *Helminthosporium*
spp., *Rhynchosporium* spp., *Pyrenophora* spp., *Monilinia*
spp., *Sclerotinia* spp., *Septoria* spp. (*Mycosphaerella*
spp.), *Venturia* spp., *Botrytis* spp., *Alternaria* spp.,
Fusarium spp., *Cercospora* spp., *Cercospora* spp.,
25 *herpotrichoides*, *Colletotrichum* spp., *Pyricularia*
oryzae, *Sclerotium* spp., *Phytophthora* spp., *Pythium*
spp., *Plasmopara viticola*, *Peronospora* spp.,
Pseudoperonospora cubensis, or *Bremia lactucae*.

30 62. The method for the control of phytopathogenic fungi
according to claim 60 or 61 wherein the agrarian crops
are cereals, fruit trees, citrus fruits, legumes,

horticultural crops, cucurbits, oleaginous plants, tobacco, coffee, tea, cocoa, sugar beet, sugar cane, or cotton.

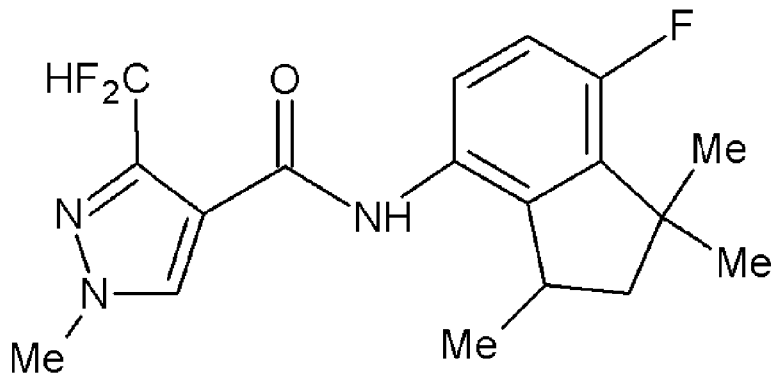
5 63. A method for controlling phytopathogenic fungi in agrarian crops, which comprises applying an effective dose of the synergistic combination as defined in any one of claims 34 to 43 or the combination as defined in any one of claims 49 to 59, on one or more parts of the
10 plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

64. The method of claim 63, wherein said
15 phytopathogenic fungi are consisting of Basidiomycetes, Ascomycetes, Deuteromycetes or imperfect fungi, Oomycetes: *Puccinia* spp., *Ustilago* spp., *Tilletia* spp., *Uromyces* spp., *Phakopsora* spp., *Rhizoctonia* spp., *Erysiphe* spp., *Sphaerotheca* spp., *Podosphaera* spp.,
20 *Uncinula* spp., *Helminthosporium* spp., *Rhynchosporium* spp., *Pyrenophora* spp., *Monilinia* spp., *Sclerotinia* spp., *Septoria* spp. (*Mycosphaerella* spp.), *Venturia* spp., *Botrytis* spp., *Alternaria* spp., *Fusarium* spp., *Cercospora* spp., *Cercospora* *herpotrichoides*,
25 *Colletotrichum* spp., *Pyricularia* *oryzae*, *Sclerotium* spp., *Phytophthora* spp., *Pythium* spp., *Plasmopara* *viticola*, *Peronospora* spp., *Pseudoperonospora cubensis*, or *Bremia lactucae*.

30 65. A method for controlling harmful insects in agrarian crops, which comprises applying an effective dose of the synergistic combination as defined in any

one of claims 34 to 43 or the combination as defined in
any one of claims 49 to 59, on one or more parts of the
plants to be protected and/or on the seeds of said
plants before sowing and/or on the ground in which said
5 plants grow.

66. The method of any one of claims 63 to 65, wherein
the agrarian crops are cereals, fruit trees, citrus
fruits, legumes, horticultural crops, cucurbits,
10 oleaginous plants, tobacco, coffee, tea, cocoa, sugar
beet, sugar cane, or cotton.



(I)