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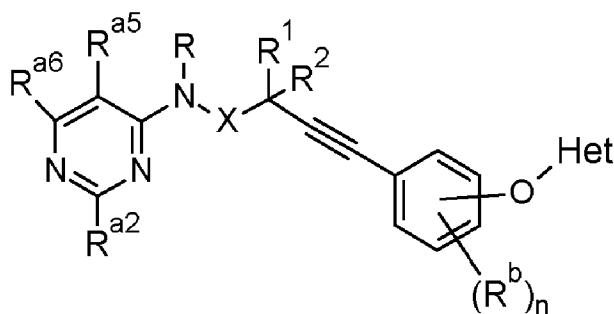
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(54) Title: FUNGICIDAL PYRIMIDINE COMPOUNDS

formula I



(57) Abstract: The present invention relates to fungicidal pyrimidine compounds, to their use and to methods for combating phytopathogenic fungi. The present invention also relates to seeds treated with at least one such compound. Furthermore the invention relates to processes for preparing compounds of formula I.

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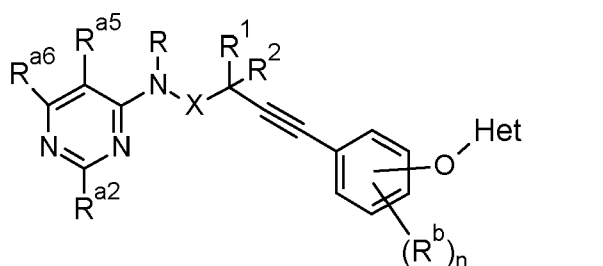
Fungicidal pyrimidine compounds

Description

- 5 The present invention relates to fungicidal pyrimidine compounds, to their use and to methods for combating phytopathogenic fungi. The present invention also relates to seeds treated with at least one such compound. Furthermore the invention relates to processes for preparing compounds of formula I.
- 10 WO 2011007839 A1 describes 4-(3-butynyl)aminopyrimidine derivatives, which are pest controlling agents for agricultural and horticultural use.
EP 264217 A2 discloses certain aralkylaminopyrimidine derivatives, which are useful as insecticides, acaricides and fungicides.
- 15 The compounds according to the present invention differ from those described in the abovementioned publication in that the central phenyl ring is always substituted by a heteroaryloxy substituent and that the linker between said phenyl ring and the aminopyrimidine moiety is a butynyl derived group as described herein.

20 In many cases, in particular at low application rates, the fungicidal activity of known fungicidal compounds is unsatisfactory. Based on this, it was an object of the present invention to provide compounds having improved activity and/or a broader activity spectrum against phytopathogenic fungi. This objective is achieved by the use of substituted pyrimidine compounds of formula I having good fungicidal activity against phytopathogenic harmful fungi.

- 25 Accordingly, the present invention relates to compounds of the formula I



wherein:

- 30 R^{a2} , R^{a5} , R^{a6} independently of each other are hydrogen, halogen, CN, NO₂, OH, SH, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-haloalkylthio, C₁-C₄-alkylsulfinyl, C₁-C₄-haloalkylsulfinyl, C₁-C₄-alkylsulfonyl, C₁-C₄-haloalkylsulfonyl, C₁-C₄-alkoxy-C₁-C₄-alkyl, C₁-C₄-alkoxy-C₁-C₄-alkoxy, C₂-C₄-alkenyl, C₂-C₄-alkynyl, C₂-C₄-haloalkenyl, C₂-C₄-haloalkynyl, C₃-C₈-cycloalkyl, C₃-C₈-cycloalkyloxy, C₃-C₈-cycloalkyl-C₁-C₄-alkyl, NR^AR^B, C(=O)R', C(=NOR'')R''' or -C(=NH)-O-R''';

- 35 R^A , R^B independently of one another are hydrogen, C₁-C₄-alkyl, C₂-C₄-alkenyl, C₂-C₄-alkynyl, phenyl, benzyl, C₃-C₈-cycloalkyl, C₃-C₈-cycloalkenyl or (C=O)-R';

R' is hydrogen, OH, NH₂, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₂-C₄-alkenyl, C₂-C₄-alkynyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylamino or di(C₁-C₄-alkyl)amino;

R'' is hydrogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₂-C₄-alkenyl, C₂-C₄-alkynyl or C₁-C₄-alkoxy-C₁-C₄-alkyl;

R''' is hydrogen or C₁-C₄-alkyl; or

R^{a5}, R^{a6} together with two ring member carbon atoms to which they are attached, form a fused 5-, 6- or 7-membered saturated, partially unsaturated or aromatic carbocycle or heterocycle, wherein the ring member atoms of the fused heterocycle include besides carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S, and wherein the fused carbocycle or heterocycle is unsubstituted or carries 1, 2, 3 or 4 identical or different radicals selected from the group consisting of halogen, CN, C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkyl and C₁-C₄-haloalkoxy;

R is hydrogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkoxy-C₁-C₄-alkyl, C₁-C₄-haloalkoxy-C₁-C₄-alkyl, C₂-C₄-alkenyl, C₂-C₄-haloalkenyl, C₂-C₄-alkynyl, C₂-C₄-haloalkynyl, CN, CH₂CN, NR^AR^B or CH₂-O-C(=O)R';

R¹, R² independently of each other are hydrogen, halogen, CN, OH, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkoxy-C₁-C₄-alkyl, C₁-C₄-haloalkoxy-C₁-C₄-alkyl, C₂-C₄-alkenyl, C₂-C₄-haloalkenyl, C₂-C₄-alkynyl, C₂-C₄-haloalkynyl, C₃-C₈-cycloalkyl, C₃-C₈-cycloalkyl-C₁-C₄-alkyl, C₃-C₈-cycloalkyloxy, NR^AR^B, C(=O)R', C(=NOR'')R''', C(=NH)-O-R''' or benzyl wherein the phenyl moiety of benzyl is unsubstituted or carries 1, 2, 3, 4, or 5 substituents selected from the group consisting of CN, halogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, (C₁-C₄-alkoxy)carbonyl and di(C₁-C₄-alkyl)aminocarbonyl;

or two radicals R¹ and R² that are bound to the same carbon atom form together with said carbon atom a saturated or partially unsaturated 3-, 4-, 5-, 6-, or 7-membered carbocycle or a saturated or partially unsaturated 3-, 4-, 5-, 6-, or 7-membered heterocycle, wherein the ring member atoms of the abovementioned heterocycle include beside carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S, and wherein the abovementioned cycle is unsubstituted or carries 1, 2, 3 or 4 substituents selected from halogen, CN, OH, SH, C₁-C₄-alkyl, C₁-C₄-alkoxy or C₁-C₄-alkylthio; and one or two CH₂ groups of the abovementioned cycles may be respectively be replaced by one or two C(=O) or C(=S) groups;

X is a divalent group selected from -CR³R⁴-, -C(=O)-, -C(=S)-, -C(=NR^D)- and -C(=NOR^D)-, wherein

R^D is hydrogen or C₁-C₄-alkyl, and wherein

R³ and R⁴ independently of each other are hydrogen, CN, C₁-C₄-hydroxyalkyl, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkoxy-C₁-C₄-alkyl, C₁-C₄-haloalkoxy-C₁-C₄-alkyl, C₂-C₄-alkenyl, C₂-C₄-haloalkenyl, C₂-C₄-alkynyl, C₂-C₄-haloalkynyl, C₃-C₈-cycloalkyl, C₃-C₈-cycloalkyl-C₁-C₄-alkyl, C₃-C₈-cycloalkyloxy, NR^AR^B, C(=O)R', C(=NOR'')R''', -C(=NH)-O-R''' or benzyl wherein the phenyl moiety of benzyl is unsubstituted or carries 1, 2, 3, 4, or 5 substituents selected from the group consisting of CN, halogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, (C₁-C₄-alkoxy)carbonyl and di(C₁-C₄-alkyl)aminocarbonyl, or

two radicals R³ and R⁴ that are bound to the same carbon atom form together with said carbon atom a saturated or partially unsaturated

3-, 4-, 5-, 6-, or 7-membered carbocycle or a saturated or partially unsaturated 3-, 4-, 5-, 6-, or 7-membered heterocycle, wherein the ring member atoms of the abovementioned heterocycle include beside carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S, and wherein the abovementioned cycle is unsubstituted or carries 1, 2, 3 or 4 substituents selected from halogen, CN, OH, SH, C₁-C₄-alkyl, C₁-C₄-alkoxy or C₁-C₄-alkylthio; and one or two CH₂ groups of the abovementioned cycles may be respectively replaced by one or two C(=O) or C(=S) groups;

n indicates the number of substituents R^b on the phenyl ring and n is 0, 1, 2, 3 or 4;

R^b is halogen, CN, NO₂, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₂-C₄-alkenyl, C₂-C₄-haloalkenyl, C₂-C₄-alkynyl, C₂-C₄-haloalkynyl, NR^AR^B, C(=O)R', C(=NOR'')R''' or -C(=NH)-O-R''',

it being possible for n = 2, 3 or 4 that R^b are identical or different;

Het is a 5- or 6-membered heteroaryl, wherein the ring member atoms of the heteroaryl include besides carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S and wherein the heteroaryl is unsubstituted or carries 1, 2, 3 or 4 identical or different groups R^c:

R^c is halogen, CN, NO₂, NH₂, C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy, C₁-C₆-alkylamino, di(C₁-C₆-alkyl)amino, C₁-C₆-alkylthio, C₁-C₆-haloalkylthio, C₁-C₆-alkylsulfinyl, C₁-C₆-haloalkylsulfinyl, C₁-C₆-alkylsulfonyl, C₁-C₆-haloalkylsulfonyl, C₁-C₆-alkoxy-C₁-C₄-alkyl, C₁-C₆-haloalkoxy-C₁-C₄-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl, C(=O)R', C(=NOR'')R''', C₃-C₈-cycloalkyl, C₃-C₈-cycloalkyl-C₁-C₄-alkyl, phenyl, phenoxy, phenoxy-C₁-C₄-alkyl or a 5- or 6-membered heteroaryl, wherein the ring member atoms of the heteroaryl include besides carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S, and wherein

the aforementioned cyclic radicals are unsubstituted or carry 1, 2, 3 or 4 identical or different substituents R^d :

R^d is halogen, CN, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy or C_1 - C_4 -haloalkoxy;

or two radicals R^c that are bound to adjacent ring member atoms of the Het group form together with said ring member atoms a fused

5-, 6- or 7-membered saturated, partially unsaturated or aromatic carbocycle or heterocycle, wherein the ring member atoms of the fused heterocycle include

besides carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S, and wherein the fused carbocycle or heterocycle is unsubstituted or carries 1, 2, 3 or 4 identical or different radicals groups R^e :

R^e is halogen, CN, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy or C_1 - C_4 -haloalkoxy;

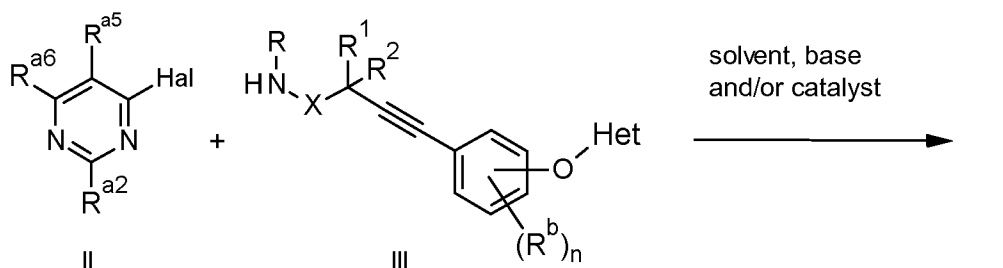
and the N-oxides and the agriculturally acceptable salts of the compounds of formula I.

The present invention furthermore relates to processes for preparing compounds of formula I.

The present invention furthermore relates to intermediates such as compounds of formulae III,

IIa and IIIa and to processes for preparing them. Accordingly a 4-halopyrimidine compound II, wherein Hal is halogen, preferably Cl or F, can be reacted with a suitable amine compound III, wherein X is $-CR^3R^4-$, to obtain a compound I according to the present invention, wherein X is $-CR^3R^4-$, as shown in scheme 1.

Scheme 1



Generally, this reaction is carried out at temperatures of from 0 to 200°C, preferably from 50 to 170°C, preferably in an inert organic solvent and preferably in presence of a base or a catalyst or a combination of a base and a catalyst.

Suitable catalysts are e.g. halides such as NaF, KF, LiF, NaBr, KBr, LiBr, NaI, KI, LiI; ionic liquids, such as imidazolium catalysts; transition metal catalysts like palladium, rhodium, ruthenium, iron, copper in the form of halides, pseudohalides, alkoxides, carboxylates (pre-ferred acetate), complexes with dibenzylidene acetone and ligands like phosphine, phosphites, phosphoramidate ligands. Preferred ligands are bidentate and sterically demanding phosphorous ligands, even more preferably the catalysts are selected from 2,2'-bis(diphenyl-phosphanyl)-1,1'-binaphthyl, 2,2'-Bis(diphenylphosphino)-1,1'-biphenyl, 2,4',6'-

diisopropyl-1,1'-biphenyl-2-ylidicyclohexylphosphine, 2-(dicyclohexylphosphino)-2',6' dimethoxy-1,1' bi-phenyl, 1,1-bis(diphenylphosphino)ferrocene, 9,9-dimethyl-4,5-bis(diphenylphosphino)-xanthene, 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-propanediylbis[diphenylphosphine], 1,4 butanediylbis[diphenylphosphine] and 1,1'-(1,2-ethanediyl)bis[1-(2-methoxyphenyl)-1 phenyl-diposphine].

Suitable solvents are aromatic hydrocarbons such as toluene, o-, m- and p-xylene; halogenated hydro-carbons chlorobenzene, dichlorobenzene; ethers such as dioxane, anisole and THF; nitriles such as acetonitrile and propionitrile; ketones such as acetone, methyl ethyl ketone, diethyl ketone and tert.-butyl methyl ketone; alcohols such as ethanol, n-propanol, isopropanol, n-butanol and tert.-butanol; and also DMSO, DMF, dimethyl acetamide, NMP, NEP and acetic acid ethyl ester, preferably THF, DMSO, DMF, dimethyl acetamide, NMP or NEP; even more preferably THF, DMF or NMP. It is also possible to use mixtures of the solvents mentioned.

Suitable bases are, in general, inorganic compounds, such as alkali metal and alkaline earth metal hydroxides such as lithium hydroxide, sodium hydroxide, potassium hydroxide and calcium hydroxide; alkali metal and alkaline earth metal oxides such as lithium oxide, sodium oxide, potassium oxide and calcium oxide; alkali metal and alkaline earth metal phosphates such as lithium phosphate, sodium phosphate, potassium phosphate and calcium phosphate; alkali metal amides such as lithium amide, sodium amide and potassium amide; alkali metal and alkaline earth metal hydrides lithium hydride, sodium hydride, potassium hydride and calcium hydride; alkali metal and alkaline earth metal carbonates such as lithium carbonate, potassium carbonate and calcium carbonate, caesium carbonate; moreover organic bases, for example tertiary amines such as trimethyl-amine (TMA), triethylamine (TEA), tributylamine (TBA), diisopropylethylamine (DIPEA) and N-methyl-2-pyrrolidone (NMP), pyridine, substituted pyridines such as collidine, lutidine and 4 dimethylaminopyridine (DMAP), and also bicyclic amines. Preference is given to sodium hydride, potassium hydride, lithium carbonate, potassium carbonate, caesium carbonate, TEA, TBA and DIPEA, in particular DIPEA. The bases are generally employed in equimolar amounts, in excess or, if appropriate, as solvent. The amount of base is typically 1.1 to 5.0 molar equivalents relative to 1 mole of compounds II.

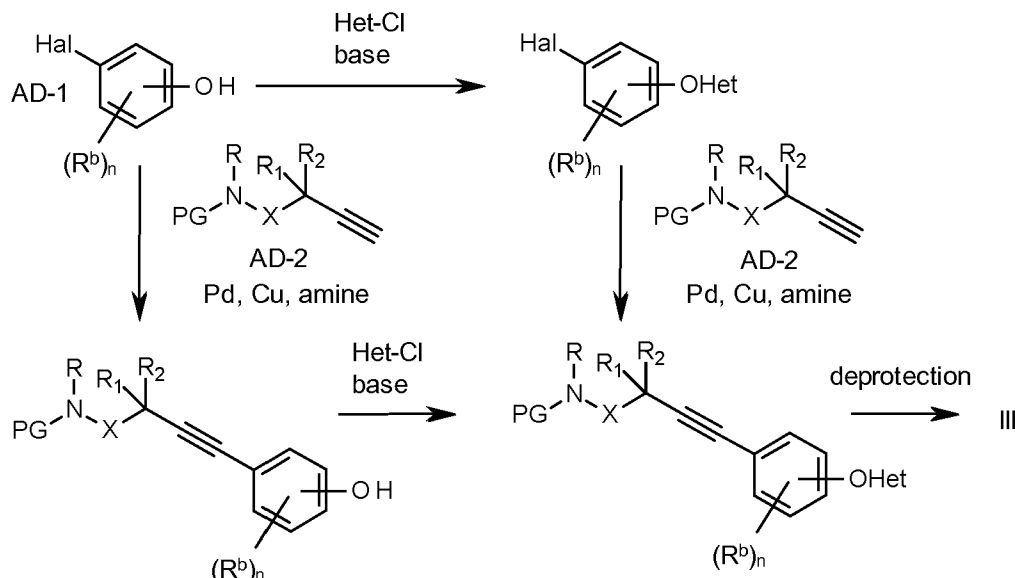
The starting materials are generally reacted with one another in equimolar amounts. In terms of yields, it may be advantageous to employ an excess of compounds III, based on 1.1 to 2.5 equivalents, preferred 1.1 to 1.5 equivalents of compounds II.

The compounds II are known from the literature or are commercially available or they can be prepared for example in analogy to methods described in: Heterocycles (2009) 78(7), 1627-1665; New J. Chem. (1994) 18(6), 701-8; WO 2005/095357; Science of Synthesis (2004) 16, 379-572; WO 2008/156726; WO 2006/072831; Organic Reactions (Hoboken, NJ, United States) (2000), 56; or Targets in Heterocyclic Systems (2008) 12, 59-84.

The alkyne amine compounds III are known from the literature or are commercially available or they can be prepared for example in analogy to methods described in WO 2011007839. The

compounds III can also be prepared for example in analogy to methods described in scheme 2, wherein PG in compound AD-2 stands for a suitable protection group for an amine, for example tert-butoxycarbonyl, benzyloxy carbonyl, benzyl, 4-methoxy benzyl, acetyl or trichloro acetyl.

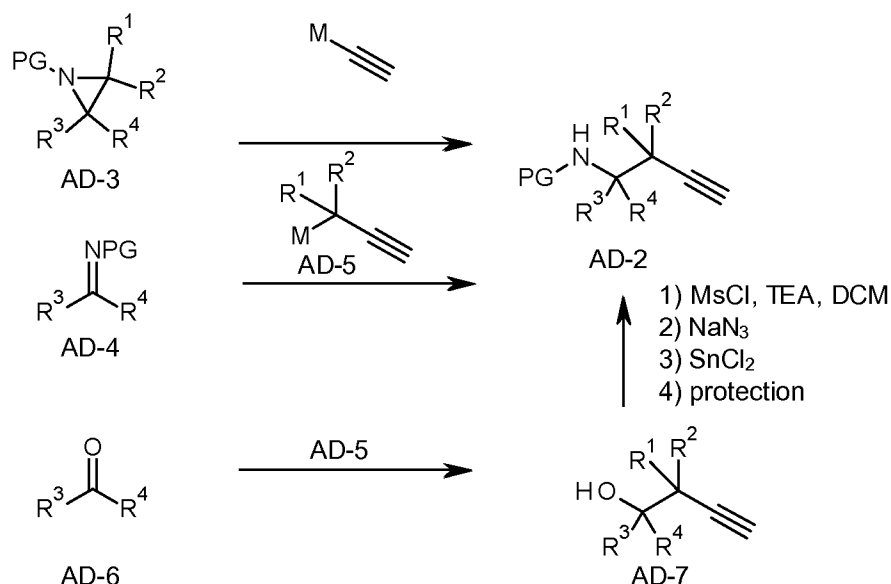
5 Scheme 2



According to scheme 2, butyne compounds can be synthesized via a palladium catalyzed crosscoupling of an aryl halide AD-1 with suitable alkynes AD-2 (US 20110105562 A1, Tetrahedron (1992), 48(15), 3239-50; WO 2004043458 A1); the heterocycle Het can be installed before or after the crosscoupling reaction.

Alkynes AD-2 are commercially available or they can be synthesized according to scheme 3.

Scheme 3



Ring opening of a substituted aziridine AD-3 with a metal acetylide, wherein M can be, for example, lithium, directly leads to the formation of AD-2 (Angewandte Chemie, International Edition (2011), 50(9), 2144-2147; Journal of the American Chemical Society (2010), 132(13), 4542-4543; Organic Letters (2007), 9(24), 5127-5130; WO 2006044412 A1). Nucleophilic

addition of a propargyl metal, wherein AD-5, wherein M can be, for example, lithium, to an imine AD-4 is another way to prepare the amine compound AD-2 (European Journal of Organic Chemistry (2010), (8), 1587-1592; Synlett (2008), (4), 578-582; Journal of Organic Chemistry (1999), 64(7), 2406-2410; Synthetic Communications (1997), 27(15), 2601-2614).

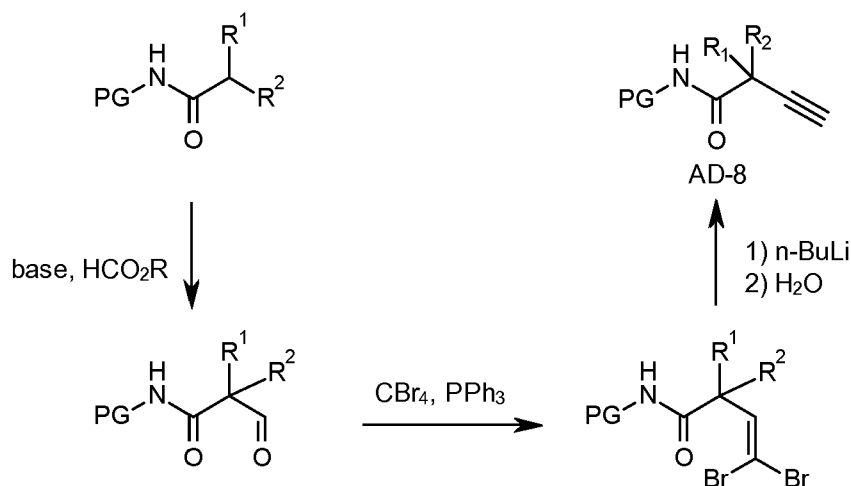
5

Alcohols AD-7 can be used to synthesize amines AD-2. Alcohols AD-7 are commercially available or methods for their preparation are described in the literature.

Conversion of AD-7 to an amine can be achieved in a three step reaction sequence comprising a) mesylation with methanesulfonic acid chloride (MsCl) in the presence of a base such as triethylamine, b) treatment of the intermediate methylsulfonate with sodium azide, and c), subsequent reduction of the alkylazide with a suitable reductant (e.g. SnCl₂; as described in Journal of Medicinal Chemistry (2011), 54(20), 7363-7374; WO 2011098603 A1, Bioorganic & Medicinal Chemistry (2011), 19(10), 3274-3279) followed by protection of the amino group. It is also possible to synthesize such compounds under Mitsunobu conditions as described in Journal of Organic Chemistry (2011), 76(14), 5661-5669 or Chemistry-A European Journal (2011), 17(6), 1764-1767 or by way of a Gabriel synthesis as described in European Journal of Medicinal Chemistry (2011), 46(8), 3227-3236, Chemistry-A European Journal (2010), 16(41), 12303-12306 or in WO 2010017047 A1.

Amide compounds AD-8 can be synthesized according to scheme 4. A suitably substituted acetamide can be formylated according to the synthesis described in Bulletin of the Chemical Society of Japan (1994), 67(9), 2514-21 or in Journal of Organic Chemistry (1983), 48(17), 2914-20.

25 Scheme 4

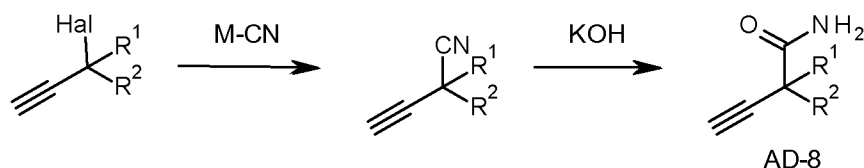


A subsequent Corey Fuchs cascade (formation of the dibromo alkene with tetrabromomethane and triphenylphosphine: US 4944795 A, rearrangement induced with n-butyllithium furnishing the alkyne: Organic Letters (2011), 13(9), 2204-2207, Journal of the Chemical Society, Perkin Transactions 1 (2002), (9), 1199-1212) produces the alkyne amide AD-2.

An alternative way to prepare compounds AD-8 wherein PG is hydrogen is described in scheme 5. A propargyl halide is reacted with a metal cyanid, wherein the metal M can be, for example

sodium or potassium, which is subsequently hydrolysed under basic aqueous conditions to give the alkyne.

Scheme 5



5 A 4-halopyrimidine compound II, wherein Hal is halogen, preferably Cl or F, can also be reacted with a suitable amide compound III, wherein X is -C(=O)- to obtain a compound I wherein X is -C(=O)- as shown in scheme 1.

Generally, this reaction is carried out at temperatures of from 0 to 200°C, preferably from 50 to 10 170°C, in an inert organic solvent preferably in the presence of a base or a catalyst or a combination of a base and a catalyst in a solvent.

Suitable catalysts are e.g. halides such as NaF, KF, LiF, NaBr, KBr, LiBr, NaI, KI, LiI; ionic liquids, such as imidazolium catalysts; transition metal catalysts like palladium, rhodium, 15 ruthenium, iron, copper in the form of halides, pseudohalides, alkoxides, carboxylates (preferred acetate), complexes with dibenzylidene acetone and ligands like phosphine, phosphites, phosphoramidate ligands. Preferred ligands are bidentate and sterically demanding phosphorous ligands, even more preferably the catalysts are selected from 2,2'-bis(diphenylphosphanyl)-1,1'-binaphthyl, 2,2'-bis(diphenylphosphino)-1,1'-biphenyl, 2,4',6'-diisopropyl-1,1'- 20 biphenyl-2-ylidicyclohexylphosphine, 2-(dicyclohexylphosphino)-2',6'-dimethoxy-1,1'-biphenyl, 1,1-bis(diphenylphosphino)ferrocene, 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene, 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-propanediylbis[diphenylphosphine], 1,4-butanediylbis[diphenylphosphine] and 1,1'-(1,2-ethanediyl)bis[1-(2-methoxyphenyl)-1-phenyl-diposphine.

25 Suitable solvents are aromatic hydrocarbons such as toluene, o-, m- and p-xylene; halogenated hydrocarbons such as chlorobenzene, dichlorobenzene; ethers such as dioxane, anisole and THF; nitriles such as acetonitrile and propionitrile; ketones such as acetone, methyl ethyl ketone, diethyl ketone and tert.-butyl methyl ketone; alcohols such as ethanol, n-propanol, 30 isopropanol, n-butanol and tert.-butanol; and also DMSO, DMF, dimethyl acetamide, NMP, NEP and acetic acid ethyl ester. Preferably THF, DMSO, DMF, dimethyl acetamide, NMP or NEP are used; even more preferably THF, DMF or NMP are used. It is also possible to use mixtures of the solvents mentioned.

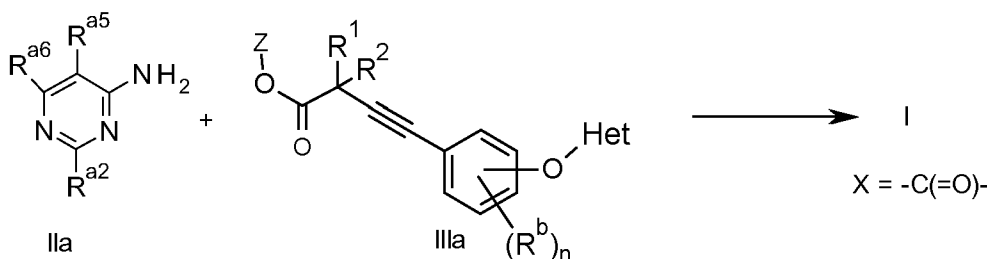
35 Suitable bases and their amounts are as described for the reaction with a phenethyl amine compound III, wherein X is -CR³R⁴-, as described above. The starting materials are generally reacted with one another in equimolar amounts. In terms of yields, it may be advantageous to

employ an excess of compounds III, based on 1.1 to 2.5 equivalents, preferred 1.1 to 1.5 equivalents of compounds II.

Alternatively, amide compounds I, wherein X is $-\text{C}(=\text{O})-$, can be synthesized by reacting

- 5 4-amino-pyrimidine compounds IIa [available by reaction of a chloropyrimidine II with excess of ammonia in analogy to methods described in WO 2011/147066, WO 2006/135719, US 2005/0245530 A1, J. Chem. Soc. (1951), 3439-44; Helv. Chim. Act. (1951), 34, 835-40] with compounds of the formula IIIa in which Z is hydrogen or C_1 - C_4 -alkyl, which are commercially available or which can be prepared as described above, preferably in the presence of $\text{Al}(\text{CH}_3)_3$ (1 to 3 equivalents) as stoichiometric reagent preferably in an inert organic solvent such as toluene (in analogy to US 2010/0063063 A1; WO 2005/011601; WO 2006/074884) as outlined in scheme 10.

Scheme 10



- 15 Compounds I, wherein X is $-\text{C}(=\text{S})-$, can be prepared for example in analogy to methods described in US 2010022538 A1, J. Med. Chem. (2011), 54(9), 3241-3250, J. Org. Chem. (2011), 76(6), 1546-1553, Org. Lett. (2010), 12(23), 5570-5572.

- 20 Compounds I, wherein X is $-\text{C}(=\text{NR}^{\text{D}})-$, can be prepared from compounds I, wherein X is $-\text{C}(=\text{O})-$, in analogy to Bioorg. Med. Chem. (2008) 16(8), 4600-4616, J. Med. Chem. (2004) 47(3), 663-672, Eur. J. Org. Chem. (2004) 5, 1025-1032, J. Med. Chem. (1987) 30(4), 720-1.

- 25 Compounds I, wherein X is $-\text{C}(=\text{NOR}^{\text{D}})-$, can be prepared from compounds I, wherein X is $-\text{C}(=\text{O})-$, in analogy to WO 2007/075598 or from compounds I, wherein X is $-\text{C}(=\text{S})-$, according to WO 2008/039520 and O'zbekiston Kimyo Jurnal (2004) 4, 3-6.

- Compounds I and intermediates, wherein R is hydrogen, can be converted by conventional processes such as alkylation. Examples of suitable alkylating agents include alkyl halides, such as alkyl chloride, alkyl bromide or alkyl iodide, examples being methyl chloride, methyl bromide or methyl iodide, or dialkyl sulfates such as dimethyl sulfate or diethyl sulfate. The reaction with the alkylating agent is carried out advantageously in the presence of a solvent. Solvents used for these reactions are - depending on temperature range - aliphatic, cycloaliphatic or aromatic hydrocarbons such as hexane, cyclohexane, toluene, xylene, chlorinated aliphatic and aromatic hydrocarbons such as DCM, chlorobenzene, open-chain dialkyl ethers such as diethyl ether, di-n-propyl ether, MTBE, cyclic ethers such as THF, 1,4-dioxane, glycol ethers such as dimethyl

glycol ether, and also DMSO, DMF, dimethyl acetamide, NMP, NEP and acetic acid ethyl ester, preferably DMF, DMSO, NMP or NEP, or mixtures of these solvents.

Compounds II, wherein R^{a5} and R^{a6} in each case constitute together with two ring member carbon atoms of the pyrimidine ring one of the following heterocyclic groups as defined in line 1 to line 26 in table A.2, wherein #5 and #6 indicate the point of attachment to the pyrimidine ring, each respectively corresponding to the positions of either substituent R^{a5} or R^{a6}, can be prepared according to commonly known procedures such as those given below or in analogy to those cited references or are commercially available.

Table A.2:

line	R ^{a5} /R ^{a6}
A.2-1	#5-CH=CH-CH=CH-#6
A.2-2	#5-CH ₂ -CH ₂ -CH ₂ -CH ₂ -#6
A.2-3	#5-CH=CH-CH=N-#6
A.2-4	#5-N=CH-CH=CH-#6
A.2-5	#5-CH=N-CH=N-#6
A.2-6	#5-N=CH-N=CH-#6
A.2-7	#5-CH ₂ -CH ₂ -CH ₂ -#6
A.2-8	#5-N=CH-CH=N-#6
A.2-9	#5-O-CH ₂ -O-#6
A.2-10	#5-NH-CH=N-#6
A.2-11	#5-S-CH=N-#6
A.2-12	#5-N=CH-S-#6
A.2-13	#5-O-CH=N-#6
A.2-14	#5-N=CH-O-#6
A.2-15	#5-O-CH=CH-#6
A.2-16	#5-S-CH=CH-#6
A.2-17	#5-O-N=CH-#6
A.2-18	#5-S-N=CH-#6
A.2-19	#5-CH=N-O-#6
A.2-20	#5-CH=N-S-#6
A.2-21	#5-N(CH ₃)-CH=CH-#6
A.2-22	#5-CH=CH-N(CH ₃)-#6
A.2-23	#5=CH-N(NH ₂)-N-#6
A.2-24	#5-CH=N-N(CH ₃)-#6
A.2-25	#5=N-N(CH ₃)-CH-#6
A.2-26	#5-N(CH ₃)-N=CH-#6

Compounds II wherein the meaning of R^{a5} and R^{a6} corresponds to line 1 of table A.2 can be prepared as described in EP 326329 A2, US 20050187231 A1, WO 2007071963 A2,

Tetrahedron (2004), 60(25), 5373-5382, Bioorganic & Medicinal Chemistry Letters (2009), 19(6), 1715-1717 or in WO 2010025451 A2.

Compounds II wherein the meaning of R^{a5} and R^{a6} corresponds to line 3 of table A.2 can be prepared as described in European Journal of Medicinal Chemistry (2011), 46(9), 3887-3899,
5 WO 2011104183 A1 or in Organic Process Research & Development (2011), 15(4), 918-924.

Compounds II wherein the meaning of R^{a5} and R^{a6} corresponds to line 4 of table A.2 can be prepared as described in WO 2011131741 A1, WO 2010101949 A1 or in Journal of Organic Chemistry (1979), 44(3), 435-40.

Compounds II wherein the meaning of R^{a5} and R^{a6} corresponds to line 5 or 20 of table A.2 can
10 be prepared as described in Organic Process Research & Development (2011), 15(4), 918-924; or in Tetrahedron (1998), 54(33), 9903-9910.

Compounds II wherein the meaning of R^{a5} and R^{a6} corresponds to line 6 of table A.2 can be prepared as described in WO 2010026262 A1 or in WO 2007092681 A2.

Compounds II wherein the meaning of R^{a5} and R^{a6} corresponds to line 8 of table A.2 can be
15 prepared as described in WO 2010038060 A1, Bioorganic & Medicinal Chemistry Letters (2010), 20(7), 2330-2334, CN 101544642 A or in Journal of the American Chemical Society (1956), 78, 225-8.

Compounds II wherein the meaning of R^{a5} and R^{a6} corresponds to line 11 of table A.2 can be prepared as described in US 20110028496 A1.

Compounds II wherein the meaning of R^{a5} and R^{a6} corresponds to line 12 of table A.2 can be
20 prepared as described in WO 2010014930, US 20110028496 A1 or in WO 2008057402 A2. Compounds II wherein the meaning of R^{a5} and R^{a6} corresponds to line 14 of table A.2 can be prepared as described in Australian Journal of Chemistry (1990), 43(1), 47-53 or in WO 2009013545 A2.

Compounds II wherein the meaning of R^{a5} and R^{a6} corresponds to line 24 of table A.2 can be
25 prepared as described in US 20090005359 A1 or in US 20070281949 A1.

Compounds II wherein the meaning of R^{a5} and R^{a6} corresponds to line 25 of table A.2 can be prepared as described in WO 2007013964 A1.

Compounds II wherein the meaning of R^{a5} and R^{a6} corresponds to line 26 of table A.2 can be
30 prepared as described in Journal of Medicinal Chemistry (1988), 31(2), 454-61 or in WO 2006046135 A2.

If individual compounds I cannot be obtained by the routes described above, they can be prepared by derivatization of other compounds I. The N-oxides may be prepared from the
35 compounds I according to conventional oxidation methods, e. g. by treating compounds I with an organic peracid such as metachloroperbenzoic acid (cf. WO 03/64572 or J. Med. Chem. (1995), 38(11), 1892-1903); or with inorganic oxidizing agents such as hydrogen peroxide (cf. J. Heterocyc. Chem. (1981), 18 (7), 1305-1308) or oxone (cf. J. Am. Chem. Soc. (2001), 123 (25), 5962-5973). The oxidation may lead to pure mono-N-oxides or to a mixture of different N-
40 oxides, which can be separated by conventional methods such as chromatography.

If the synthesis yields mixtures of isomers, a separation is generally not necessarily required since in some cases the individual isomers can be interconverted during work-up for use or during application (e. g. under the action of light, acids or bases). Such conversions may also take place after use, e. g. in the treatment of plants in the treated plant, or in the harmful fungus to be controlled.

The reaction mixtures are worked up in a customary manner, for example by mixing with water, separating the phases and, if appropriate, chromatic purification of the crude products. In some cases, the intermediates and end products are obtained in the form of colorless or slightly viscous oils which can be freed from volatile components or purified under reduced pressure and at moderately elevated temperatures. If the intermediates and end products are obtained as solids, purification can also be carried out by recrystallization or digestion.

The compounds of the present invention are useful for combating harmful fungi. Therefore the present invention furthermore relates to a method for combating harmful fungi, which process comprises treating the fungi or the materials, plants, the soil or seeds to be protected against fungal attack, with an effective amount of at least one compound of formula I or of an N-oxide or an agriculturally acceptable salt thereof.

Furthermore, the present invention also relates to seed comprising a compound of formula I, or an N-oxide or an agriculturally acceptable salt thereof, in an amount of from 0.1 g to 10 kg per 100 kg of seed.

Agriculturally useful salts of the compounds I encompass especially the salts of those cations or the acid addition salts of those acids whose cations and anions, respectively, have no adverse effect on the fungicidal action of the compounds I. Suitable cations are thus in particular the ions of the alkali metals, preferably sodium and potassium, of the alkaline earth metals, preferably calcium, magnesium and barium, of the transition metals, preferably manganese, copper, zinc and iron, and also the ammonium ion which, if desired, may carry one to four C₁-C₄-alkyl substituents and/or one phenyl or benzyl substituent, preferably diisopropylammonium, tetramethylammonium, tetrabutylammonium, trimethylbenzylammonium, furthermore phosphonium ions, sulfonium ions, preferably tri(C₁-C₄-alkyl)sulfonium, and sulfoxonium ions, preferably tri(C₁-C₄-alkyl)sulfoxonium.

Anions of useful acid addition salts are primarily chloride, bromide, fluoride, hydrogensulfate, sulfate, dihydrogenphosphate, hydrogenphosphate, phosphate, nitrate, bicarbonate, carbonate, hexafluorosilicate, hexafluorophosphate, benzoate, and the anions of C₁-C₄-alkanoic acids, preferably formate, acetate, propionate and butyrate. They can be formed by reacting a compound I with an acid of the corresponding anion, preferably of hydrochloric acid, hydrobromic acid, sulfuric acid, phosphoric acid or nitric acid.

Depending on the substitution pattern, the compounds of formula I and their N-oxides may have one or more centers of chirality, in which case they are present as pure enantiomers or pure

diastereomers or as enantiomer or diastereomer mixtures. Both, the pure enantiomers or diastereomers and their mixtures are subject matter of the present invention.

Compounds I can be present in different crystal modifications whose biological activity may differ. They also form part of the subject matter of the present invention. The compounds of formula I can be present in atropisomers arising from restricted rotation about a single bond of asymmetric groups. They also form part of the subject matter of the present invention.

In respect of the variables, the embodiments of the intermediates correspond to the embodiments of the compounds of formula I. The term "compounds I" refers to compounds of formula I. Likewise, the term "compounds IIa" refers to compounds of formula IIa.

The compounds of formula I can be present in atropisomers arising from restricted rotation about a single bond of asymmetric groups. They also form part of the subject matter of the present invention.

In the definitions of the variables given above, collective terms are used which are generally representative for the substituents in question. The term " C_n-C_m " indicates the number of carbon atoms possible in each case in the substituent or substituent moiety in question.

The term "halogen" refers to fluorine, chlorine, bromine and iodine.

The term " C_1-C_4 -alkyl" refers to a straight-chained or branched saturated hydrocarbon group having 1 to 4 carbon atoms, for example methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, and 1,1-dimethylethyl. Likewise, the term " C_1-C_6 -alkyl" refers to a straight-chained or branched saturated hydrocarbon group having 1 to 6 carbon atoms.

The term " C_1-C_4 -haloalkyl" refers to a straight-chained or branched alkyl group having 1 to 4 carbon atoms (as defined above), wherein some or all of the hydrogen atoms in these groups may be replaced by halogen atoms as mentioned above, for example chloromethyl, bromomethyl, dichloromethyl, trichloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, chlorofluoromethyl, dichlorofluoromethyl, chlorodifluoromethyl, 1-chloroethyl, 1-bromoethyl, 1-fluoroethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2-chloro-2-fluoroethyl, 2-chloro-2,2-difluoroethyl, 2,2-dichloro-2-fluoroethyl, 2,2,2-trichloroethyl and pentafluoroethyl, 2-fluoropropyl, 3-fluoropropyl, 2,2-difluoropropyl, 2,3-difluoropropyl, 2-chloropropyl, 3-chloropropyl, 2,3-dichloropropyl, 2-bromopropyl, 3-bromopropyl, 3,3,3-trifluoropropyl, 3,3,3-trichloropropyl, $CH_2-C_2F_5$, $CF_2-C_2F_5$, $CF(CF_3)_2$, 1-(fluoromethyl)-2-fluoroethyl, 1-(chloromethyl)-2-chloroethyl, 1-(bromomethyl)-2-bromoethyl, 4-fluorobutyl, 4-chlorobutyl, 4-bromobutyl or nonafluorobutyl. Likewise, the term " C_1-C_6 -haloalkyl" refers to a straight-chained or branched

alkyl group having 1 to 6 carbon atoms.

The term "C₁-C₄-alkoxy" refers to a straight-chain or branched alkyl group having 1 to 4 carbon atoms (as defined above) which is bonded via an oxygen, at any position in the alkyl group, for example methoxy, ethoxy, n-propoxy, 1-methylethoxy, butoxy, 1-methylpropoxy, 2-methylpropoxy or 1,1-dimethylethoxy. Likewise, the term "C₁-C₆-alkoxy" refers to a straight-chain or branched alkyl group having 1 to 6 carbon atoms.

The term "C₁-C₄-hydroxyalkyl" refers to a straight-chained or branched alkyl group having 2 to 4 carbon atoms (as defined above), wherein one hydrogen atom in these groups may be replaced by one hydroxy group, for example hydroxymethyl, 2-hydroxyethyl, 3-hydroxypropyl, 4-hydroxybutyl.

The term "C₁-C₄-haloalkoxy" refers to a C₁-C₄-alkoxy group as defined above, wherein some or all of the hydrogen atoms may be replaced by halogen atoms as mentioned above, for example, OCH₂F, OCHF₂, OCF₃, OCH₂Cl, OCHCl₂, OCCl₃, chlorofluoromethoxy, dichlorofluoromethoxy, chlorodifluoromethoxy, 2-fluoroethoxy, 2-chloroethoxy, 2-bromoethoxy, 2-iodoethoxy, 2,2-difluoroethoxy, 2,2,2-trifluoroethoxy, 2-chloro-2-fluoroethoxy, 2-chloro-2,2-difluoroethoxy, 2,2-dichloro-2-fluoroethoxy, 2,2,2-trichloroethoxy, OC₂F₅, 2-fluoropropoxy, 3-fluoropropoxy, 2,2-difluoropropoxy, 2,3-difluoropropoxy, 2-chloropropoxy, 3-chloropropoxy, 2,3-dichloropropoxy, 2-bromopropoxy, 3-bromopropoxy, 3,3,3-trifluoropropoxy, 3,3,3-trichloropropoxy, OCH₂-C₂F₅, OCF₂-C₂F₅, 1-(CH₂F)-2-fluoroethoxy, 1-(CH₂Cl)-2-chloroethoxy, 1-(CH₂Br)-2-bromoethoxy, 4-fluorobutoxy, 4-chlorobutoxy, 4-bromobutoxy or nonafluorobutoxy. Likewise, the term "C₁-C₆-haloalkoxy" refers to a C₁-C₆-alkoxy group as defined above, wherein some or all of the hydrogen atoms may be replaced by halogen atoms as mentioned above.

The term "C₁-C₄-alkoxy-C₁-C₄-alkyl" refers to alkyl having 1 to 4 carbon atoms (as defined above), wherein one hydrogen atom of the alkyl radical is replaced by a C₁-C₄-alkoxy group (as defined above). Likewise, the term "C₁-C₆-alkoxy-C₁-C₄-alkyl" refers to alkyl having 1 to 4 carbon atoms (as defined above), wherein one hydrogen atom of the alkyl radical is replaced by a C₁-C₆-alkoxy group (as defined above).

The term "C₁-C₄-haloalkoxy-C₁-C₄-alkyl" refers to alkyl having 1 to 4 carbon atoms (as defined above), wherein one hydrogen atom of the alkyl radical is replaced by a C₁-C₄-haloalkoxy group (as defined above). Likewise, the term "C₁-C₆-haloalkoxy-C₁-C₄-alkyl" refers to alkyl having 1 to 4 carbon atoms (as defined above), wherein one hydrogen atom of the alkyl radical is replaced by a C₁-C₆-alkoxy group (as defined above).

The term "C₁-C₄-alkylthio" as used herein refers to straight-chain or branched alkyl groups having 1 to 4 carbon atoms (as defined above) bonded via a sulfur atom, at any position in the alkyl group, for example methylthio, ethylthio, propylthio, isopropylthio, and n butylthio.

Likewise, the term "C₁-C₆-alkylthio" as used herein refers to straight-chain or branched alkyl

5 groups having 1 to 6 carbon atoms (as defined above) bonded via a sulfur atom. Accordingly, the terms "C₁-C₄-haloalkylthio" and "C₁-C₆-haloalkylthio" as used herein refer to straight-chain or branched haloalkyl groups having 1 to 4 or 1 to 6 carbon atoms (as defined above) bonded through a sulfur atom, at any position in the haloalkyl group.

10 The terms "C₁-C₄-alkylsulfinyl" or "C₁-C₆-alkylsulfinyl" refer to straight-chain or branched alkyl groups having 1 to 4 or 1 to 6 carbon atoms (as defined above) bonded through a -S(=O)- moiety, at any position in the alkyl group, for example methylsulfinyl and ethylsulfinyl, and the like. Accordingly, the terms "C₁-C₄-haloalkylsulfinyl" and "C₁-C₆-haloalkylsulfinyl", respectively, refer to straight-chain or branched haloalkyl groups having 1 to 4 and 1 to 6 carbon atoms (as
15 defined above), respectively, bonded through a -S(=O)- moiety, at any position in the haloalkyl group.

The terms "C₁-C₄-alkylsulfonyl" and "C₁-C₆-alkylsulfonyl", respectively, refer to straight-chain or branched alkyl groups having 1 to 4 and 1 to 6 carbon atoms (as defined above), respectively,
20 bonded through a -S(=O)₂- moiety, at any position in the alkyl group, for example methylsulfonyl. Accordingly, the terms "C₁-C₄-haloalkylsulfonyl" and "C₁-C₆-haloalkylsulfonyl", respectively, refer to straight-chain or branched haloalkyl groups having 1 to 4 and 1 to 6 carbon atoms (as defined above), respectively, bonded through a -S(=O)₂- moiety, at any position in the haloalkyl group.

25 The term "C₁-C₄-alkylamino" refers to an amino radical carrying one C₁-C₄-alkyl group (as defined above) as substituent, for example methylamino, ethylamino, propylamino, 1-methylethylamino, butylamino, 1-methylpropylamino, 2-methylpropylamino, 1,1-dimethylethylamino and the like. Likewise, the term "C₁-C₆-alkylamino" refers to an amino radical carrying one C₁-C₆-alkyl group (as defined above) as substituent.
30

The term "di(C₁-C₄-alkyl)amino" refers to an amino radical carrying two identical or different C₁-C₄-alkyl groups (as defined above) as substituents, for example dimethylamino, diethylamino, di-n-propylamino, diisopropylamino, N-ethyl-N-methylamino, N-(n-propyl)-N-methylamino, N-(isopropyl)-N-methylamino, N-(n-butyl)-N-methylamino, N-(n-pentyl)-N-methylamino, N-(2-butyl)-N-methylamino, N-(isobutyl)-N-methylamino, and the like. Likewise, the term "di(C₁-C₆-alkyl)amino" refers to an amino radical carrying two identical or different C₁-C₆-alkyl groups (as defined above) as substituents.
35

The term "(C₁-C₄-alkoxy)carbonyl" refers to a C₁-C₄-alkoxy radical (as defined above) which is attached via a carbonyl group.

The term "di(C₁-C₄-alkyl)aminocarbonyl" refers to a di(C₁-C₄)alkylamino radical as defined above which is attached via a carbonyl group.

The term "phenoxy" and refers to a phenyl radical which is attached via an oxygen atom. Likewise, the term "phenoxy-C₁-C₄-alkyl" and refers to a phenoxy radical which is attached via a C₁-C₄-alkyl group (as defined above).

The term "C₂-C₄-alkenyl" refers to a straight-chain or branched unsaturated hydrocarbon radical having 2 to 4 carbon atoms and a double bond in any position, such as ethenyl, 1-propenyl, 2-propenyl (allyl), 1-methylethenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl, 1-methyl-2-propenyl, 2-methyl-2-propenyl. Likewise, the term "C₂-C₆-alkenyl" refers to a straight-chain or branched unsaturated hydrocarbon radical having 2 to 6 carbon atoms and a double bond in any position.

The term "C₂-C₄-alkynyl" refers to a straight-chain or branched unsaturated hydrocarbon radical having 2 to 4 carbon atoms and containing at least one triple bond, such as ethynyl, 1-propynyl, 2-propynyl, 1-butyne, 2-butyne, 3-butyne, 1-methyl-2-propynyl. Likewise, the term "C₂-C₆-alkynyl" refers to a straight-chain or branched unsaturated hydrocarbon radical having 2 to 6 carbon atoms and at least one triple bond.

The term "C₃-C₈-cycloalkyl" refers to monocyclic saturated hydrocarbon radicals having 3 to 8 carbon ring members, such as cyclopropyl (C₃H₅), cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl or cyclooctyl.

The term "C₃-C₈-cycloalkyl-C₁-C₄-alkyl" refers to a cycloalkyl radical having 3 to 8 carbon atoms (as defined above), which is bonded via a C₁-C₄-alkyl group (as defined above).

The term "C₃-C₈-cycloalkyloxy" refers to a cycloalkyl radical having 3 to 8 carbon atoms (as defined above), which is bonded via an oxygen.

The term "saturated or partially unsaturated 3-, 4- 5-, 6- or 7-membered carbocycle" is to be understood as meaning both saturated or partially unsaturated carbocycles having 3, 4, 5, 6 or 7 ring members. Examples include cyclopropyl, cyclopentyl, cyclopentenyl, cyclopentadienyl, cyclohexyl, cyclohexenyl, cyclohexadienyl, cycloheptyl, cycloheptenyl, cycloheptadienyl, and the like.

The term "saturated or partially unsaturated 3-, 4-, 5-, 6-, or 7-membered heterocycle, wherein the ring member atoms of the heterocycle include besides carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S", is to be understood as meaning both saturated and partially unsaturated heterocycles, for example:

5

a 3- or 4-membered saturated heterocycle which contains 1 or 2 heteroatoms from the group consisting of N, O and S as ring members such as oxirane, aziridine, thiirane, oxetane, azetidine, thiethane, [1,2]dioxetane, [1,2]dithietane, [1,2]diazetidine; and

10

a 5- or 6-membered saturated or partially unsaturated heterocycle which contains 1, 2 or 3 heteroatoms from the group consisting of N, O and S as ring members such as 2-tetrahydrofuranyl, 3-tetrahydrofuranyl, 2-tetrahydrothienyl, 3-tetrahydrothienyl, 2-pyrrolidinyl, 3-pyrrolidinyl, 3-isoxazolidinyl, 4-isoxazolidinyl, 5-isoxazolidinyl, 3-isothiazolidinyl, 4-isothiazolidinyl, 5-isothiazolidinyl, 3-pyrazolidinyl, 4-pyrazolidinyl, 5-pyrazolidinyl, 2-oxazolidinyl, 4-oxazolidinyl, 5-oxazolidinyl, 2-thiazolidinyl, 4-thiazolidinyl, 5-thiazolidinyl, 2-imidazolidinyl, 4-imidazolidinyl, 1,2,4-oxadiazolidin-3-yl, 1,2,4-oxadiazolidin-5-yl, 1,2,4-thiadiazolidin-3-yl, 1,2,4-thiadiazolidin-5-yl, 1,2,4-triazolidin-3-yl, 1,3,4-oxadiazolidin-2-yl, 1,3,4-thiadiazolidin-2-yl, 1,3,4-triazolidin-2-yl, 2,3-dihydrofur-2-yl, 2,3-dihydrofur-3-yl, 2,4-dihydrofur-2-yl, 2,4-dihydrofur-3-yl, 2,3-dihydrothien-2-yl, 2,3-dihydrothien-3-yl, 2,4-dihydrothien-2-yl, 2,4-dihydrothien-3-yl, 2-pyrrolin-2-yl, 2-pyrrolin-3-yl, 3-pyrrolin-2-yl, 3-pyrrolin-3-yl, 2-isoxazolin-3-yl, 3-isoxazolin-3-yl, 4-isoxazolin-3-yl, 2-isoxazolin-4-yl, 3-isoxazolin-4-yl, 4-isoxazolin-4-yl, 2-isoxazolin-5-yl, 3-isoxazolin-5-yl, 4-isoxazolin-5-yl, 2-isothiazolin-3-yl, 3-isothiazolin-3-yl, 4-isothiazolin-3-yl, 2-isothiazolin-4-yl, 3-isothiazolin-4-yl, 4-isothiazolin-4-yl, 2-isothiazolin-5-yl, 3-isothiazolin-5-yl, 4-isothiazolin-5-yl, 2,3-dihydropyrazol-1-yl, 2,3-dihydropyrazol-2-yl, 2,3-dihydropyrazol-3-yl, 2,3-dihydropyrazol-4-yl, 2,3-dihydropyrazol-5-yl, 3,4-dihydropyrazol-1-yl, 3,4-dihydropyrazol-3-yl, 3,4-dihydropyrazol-4-yl, 3,4-dihydropyrazol-5-yl, 4,5-dihydropyrazol-1-yl, 4,5-dihydropyrazol-3-yl, 4,5-dihydropyrazol-4-yl, 4,5-dihydropyrazol-5-yl, 2,3-dihydrooxazol-2-yl, 2,3-dihydrooxazol-3-yl, 2,3-dihydrooxazol-4-yl, 2,3-dihydrooxazol-5-yl, 3,4-dihydrooxazol-2-yl, 3,4-dihydrooxazol-3-yl, 3,4-dihydrooxazol-4-yl, 3,4-dihydrooxazol-5-yl, 3,4-dihydrooxazol-2-yl, 3,4-dihydrooxazol-3-yl, 3,4-dihydrooxazol-4-yl, 2-piperidinyl, 3-piperidinyl, 4-piperidinyl, 1,3-dioxan-5-yl, 2-tetrahydropyranyl, 4-tetrahydropyranyl, 2-tetrahydrothienyl, 3-hexahydropyridazinyl, 4-hexahydropyridazinyl, 2-hexahydropyrimidinyl, 4-hexahydropyrimidinyl, 5-hexahydro-

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pyrimidinyl, 2-piperazinyl, 1,3,5-hexahydrotriazin-2-yl and 1,2,4-hexahydrotriazin-3-yl and also the corresponding -ylidene radicals; and

a 7-membered saturated or partially unsaturated heterocycle such as tetra- and
 5 hexahydroazepinyl, such as 2,3,4,5-tetrahydro[1H]azepin-1-, -2-, -3-, -4-, -5-, -6- or -7-yl,
 3,4,5,6-tetrahydro[2H]azepin-2-, -3-, -4-, -5-, -6- or -7-yl, 2,3,4,7-tetrahydro[1H]azepin-1-, -2-, -3-, -4-, -5-, -6- or -7-yl, 2,3,6,7-tetrahydro[1H]azepin-1-, -2-, -3-, -4-, -5-, -6- or -7-yl,
 hexahydroazepin-1-, -2-, -3- or -4-yl, tetra- and hexahydrooxepinyl such as 2,3,4,5-
 tetrahydro[1H]oxepin-2-, -3-, -4-, -5-, -6- or -7-yl, 2,3,4,7-tetrahydro[1H]oxepin-2-, -3-, -4-, -5-, -6- or -7-yl, 2,3,6,7-tetrahydro[1H]oxepin-2-, -3-, -4-, -5-, -6- or -7-yl, hexahydroazepin-1-, -2-, -3- or -4-yl, tetra- and hexahydro-1,3-diazepinyl, tetra- and hexahydro-1,4-diazepinyl, tetra- and hexahydro-1,3-oxazepinyl, tetra- and hexahydro-1,4-oxazepinyl, tetra- and hexahydro-1,3-dioxepinyl, tetra- and hexahydro-1,4-dioxepinyl and the corresponding -ylidene radicals; and

15 The term "5- or 6-membered heteroaryl, wherein the ring member atoms of the heteroaryl include besides carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S", refers to, for example,

20 a 5-membered heteroaryl such as pyrrol-1-yl, pyrrol-2-yl, pyrrol-3-yl, thien-2-yl, thien-3-yl, furan-2-yl, furan-3-yl, pyrazol-1-yl, pyrazol-3-yl, pyrazol-4-yl, pyrazol-5-yl, imidazol-1-yl, imidazol-2-yl, imidazol-4-yl, imidazol-5-yl, oxazol-2-yl, oxazol-4-yl, oxazol-5-yl, isoxazol-3-yl, isoxazol-4-yl, isoxazol-5-yl, thiazol-2-yl, thiazol-4-yl, thiazol-5-yl, isothiazol-3-yl, isothiazol-4-yl, isothiazol-5-yl, 1,2,4-triazolyl-1-yl, 1,2,4-triazol-3-yl, 1,2,4-triazol-5-yl, 1,2,4-oxadiazol-3-yl, 1,2,4-oxadiazol-5-yl and 1,2,4-thiadiazol-3-yl, 1,2,4-thiadiazol-5-yl; or

a 6-membered heteroaryl, such as pyridin-2-yl, pyridin-3-yl, pyridin-4-yl, pyridazin-3-yl, pyridazin-4-yl, pyrimidin-2-yl, pyrimidin-4-yl, pyrimidin-5-yl, pyrazin-2-yl and 1,3,5-triazin-2-yl and 1,2,4-triazin-3-yl.

30 The term "two radicals R^c that are bound to adjacent ring member atoms form together with said ring member atoms a fused cycle" refers to a condensed bicyclic ring system, wherein 5- or 6-membered heteroaryl carries a fused-on 5-, 6- or 7-membered carbocyclic or heterocyclic ring it being possible that these rings are saturated or partially saturated or aromatic.

35 The term "one or two CH₂ groups of the abovementioned cycles may be respectively replaced by one or two C(=O) or C(=S) groups" refers to an exchange of carbon atoms from a saturated or partially unsaturated 3-, 4-, 5-, 6- or 7-membered carbocycle or a saturated or partially

unsaturated 3-, 4-, 5-, 6- or 7-membered heterocycle, resulting in cycles such as cyclopropanone, cyclopentanone, cyclopropanethione, cyclopentanethione, 5-oxazolone, cyclohexane-1,4-dione, cyclohexane-1,4-dithione, cyclohex-2-ene-1,4-dione or cyclohex-2-ene-1,4-dithione.

5

As regards the fungicidal activity of the compounds I, preference is given to those compounds I wherein the substituents and variables (e.g. R^{a2} , R^{a5} , R^{a6} , R, X, R^1 , R^2 , R^3 , R^4 , R^b , R^c , R' , R'' , R''' , R^A , R^B , n and Het) have independently of each other or more preferably in combination the following meanings and the groups mentioned herein for a substituent or for a combination of substituents are furthermore, independently of the combination in which they are mentioned, a particularly preferred embodiment of the substituent or of the combination of substituents in question:

10

One embodiment of the present invention relates to compounds I wherein R^{a2} , R^{a5} and R^{a6} independently of each other are preferably selected from the group consisting of hydrogen, halogen, CN, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkoxy, C_1 - C_4 -alkylthio, C_1 - C_4 -haloalkylthio, C_1 - C_4 -alkoxy- C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy- C_1 - C_4 -alkoxy, C_2 - C_4 -alkenyl, C_2 - C_4 -alkynyl, C_3 - C_8 -cycloalkyl, C_3 - C_8 -cycloalkyloxy, (C_1 - C_4 -alkoxy)carbonyl.

15

A further embodiment relates to compounds I wherein R^{a2} , R^{a5} and R^{a6} independently of each other are preferably selected from the group consisting of hydrogen, halogen, CN, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkoxy, C_1 - C_4 -alkoxy- C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy- C_1 - C_4 -alkoxy and (C_1 - C_4 -alkoxy)carbonyl.

20

A further embodiment relates to compounds I wherein R^{a2} , R^{a5} and R^{a6} independently of each other are halogen, CN, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkoxy, C_1 - C_4 -alkoxy- C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy- C_1 - C_4 -alkoxy and (C_1 - C_4 -alkoxy)carbonyl, and it being possible that one or two of R^{a2} , R^{a5} or R^{a6} can in addition be hydrogen.

25

Further preferred embodiments relate to compounds I wherein R^{a2} , R^{a5} and R^{a6} independently of each other are preferably selected from the group consisting of hydrogen, Cl, F, CH_3 , CH_2CH_3 , OCH_3 , OCF_3 , CH_2OCH_3 , CN, OCH_2OCH_3 , CF_3 , $CHFCH_3$, $COOCH_3$ and $COOCH_2CH_3$.

30

Further preferred embodiments relate to compounds I wherein R^{a2} , R^{a5} and R^{a6} independently of each other are preferably selected from the group consisting of Cl, F, CH_3 , CH_2CH_3 , OCH_3 , OCF_3 , CH_2OCH_3 , CN, OCH_2OCH_3 , CF_3 , $CHFCH_3$, $COOCH_3$ and $COOCH_2CH_3$.

Further preferred embodiments relate to compounds I wherein R^{a2} , R^{a5} and R^{a6} independently of each other are hydrogen, Cl, CH_3 , OCH_3 , CN or $COOCH_3$.

35

Further preferred embodiments relate to compounds I wherein R^{a2} , R^{a5} and R^{a6} independently of each other are Cl, CH_3 , OCH_3 , CN or $COOCH_3$.

In another preferred embodiment of the invention R^{a2} is hydrogen, halogen, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy or C_1 - C_4 -haloalkoxy.

40

- In a further preferred embodiment R^{a5} and R^{a6} independently of each other are hydrogen, halogen, OH, CN, C₁-C₄-alkyl, C₂-C₄-alkenyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy or (C₁-C₄-alkoxy)carbonyl; or R^{a5} and R^{a6} together with two ring member carbon atoms to which they are attached, form a fused 5- or 6-membered saturated, partially unsaturated or aromatic carbocycle or heterocycle, wherein the ring member atoms of the fused heterocycle include besides carbon atoms 1, 2 or 3 heteroatoms selected from the group of N, O and S, and wherein the fused carbocycle or heterocycle is unsubstituted or carries 1, 2, 3 or 4 identical or different radicals selected from halogen, CN, C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkyl and C₁-C₄-haloalkoxy.
- In still another preferred embodiment R^{a5} and R^{a6} independently of each other are hydrogen, halogen, OH, CN, C₁-C₄-alkyl, C₂-C₄-alkenyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy or (C₁-C₄-alkoxy)carbonyl; or R^{a5} and R^{a6} together with two ring member carbon atoms to which they are attached, form a fused 5- or 6-membered aromatic carbocycle or heterocycle, wherein the ring member atoms of the fused heterocycle include besides carbon atoms 1, 2 or 3 heteroatoms selected from the group of N, O and S, and wherein the fused carbocycle or heterocycle is unsubstituted or carries 1, 2, 3 or 4 identical or different radicals selected from halogen, CN, C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkyl and C₁-C₄-haloalkoxy.

- A particularly preferred embodiment relates to compounds I wherein R^{a2} is Cl.
- A particularly preferred embodiment relates to compounds I wherein R^{a2} is F.
- A particularly preferred embodiment relates to compounds I wherein R^{a2} is CH₃.
- A particularly preferred embodiment relates to compounds I wherein R^{a2} is OCH₃.
- A particularly preferred embodiment relates to compounds I wherein R^{a2} is CO₂CH₃.
- A particularly preferred embodiment relates to compounds I wherein R^{a2} is CO₂CH₂CH₃.
- A particularly preferred embodiment relates to compounds I wherein R^{a5} is Cl.
- A particularly preferred embodiment relates to compounds I wherein R^{a5} is F.
- A particularly preferred embodiment relates to compounds I wherein R^{a5} is CH₃.
- A particularly preferred embodiment relates to compounds I wherein R^{a5} is OCH₃.
- A particularly preferred embodiment relates to compounds I wherein R^{a5} is CO₂CH₃.
- A particularly preferred embodiment relates to compounds I wherein R^{a5} is CO₂CH₂CH₃.
- A particularly preferred embodiment relates to compounds I wherein R^{a6} is Cl.
- A particularly preferred embodiment relates to compounds I wherein R^{a6} is F.
- A particularly preferred embodiment relates to compounds I wherein R^{a6} is CH₃.
- A particularly preferred embodiment relates to compounds I wherein R^{a6} is OCH₃.
- A particularly preferred embodiment relates to compounds I wherein R^{a6} is CO₂CH₃.
- A particularly preferred embodiment relates to compounds I wherein R^{a6} is CO₂CH₂CH₃.

Further preferred embodiments relate to compounds I wherein R^{a2} , R^{a5} and R^{a6} in each case are one of the following combinations in line A.1-1 to line A.1-1190 in table A.1, wherein Me stands for CH₃ and Et stands for CH₂CH₃.

Table A.1:

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-1	H	H	H
A.1-2	Me	H	H
A.1-3	Et	H	H
A.1-4	OMe	H	H
A.1-5	CH ₂ OMe	H	H
A.1-6	OCH ₂ OMe	H	H
A.1-7	CF ₃	H	H
A.1-8	CHFMe	H	H
A.1-9	CN	H	H
A.1-10	F	H	H
A.1-11	Cl	H	H
A.1-12	CO ₂ Me	H	H
A.1-13	CO ₂ Et	H	H
A.1-14	OCF ₃	H	H
A.1-15	H	Me	H
A.1-16	Me	Me	H
A.1-17	Et	Me	H
A.1-18	OMe	Me	H
A.1-19	CH ₂ OMe	Me	H
A.1-20	OCH ₂ OMe	Me	H
A.1-21	CF ₃	Me	H
A.1-22	CHFMe	Me	H
A.1-23	CN	Me	H
A.1-24	F	Me	H
A.1-25	Cl	Me	H
A.1-26	CO ₂ Me	Me	H
A.1-27	CO ₂ Et	Me	H
A.1-28	OCF ₃	Me	H
A.1-29	H	Et	H
A.1-30	Me	Et	H
A.1-31	Et	Et	H
A.1-32	OMe	Et	H
A.1-33	CH ₂ OMe	Et	H
A.1-34	OCH ₂ OMe	Et	H
A.1-35	CF ₃	Et	H
A.1-36	CHFMe	Et	H
A.1-37	CN	Et	H
A.1-38	F	Et	H
A.1-39	Cl	Et	H
A.1-40	CO ₂ Me	Et	H

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-41	CO ₂ Et	Et	H
A.1-42	OCF ₃	Et	H
A.1-43	H	OMe	H
A.1-44	Me	OMe	H
A.1-45	Et	OMe	H
A.1-46	OMe	OMe	H
A.1-47	CH ₂ OMe	OMe	H
A.1-48	OCH ₂ OMe	OMe	H
A.1-49	CF ₃	OMe	H
A.1-50	CHFMe	OMe	H
A.1-51	CN	OMe	H
A.1-52	F	OMe	H
A.1-53	Cl	OMe	H
A.1-54	CO ₂ Me	OMe	H
A.1-55	CO ₂ Et	OMe	H
A.1-56	OCF ₃	OMe	H
A.1-57	H	CH ₂ OMe	H
A.1-58	Me	CH ₂ OMe	H
A.1-59	Et	CH ₂ OMe	H
A.1-60	OMe	CH ₂ OMe	H
A.1-61	CH ₂ OMe	CH ₂ OMe	H
A.1-62	OCH ₂ OMe	CH ₂ OMe	H
A.1-63	CF ₃	CH ₂ OMe	H
A.1-64	CHFMe	CH ₂ OMe	H
A.1-65	CN	CH ₂ OMe	H
A.1-66	F	CH ₂ OMe	H
A.1-67	Cl	CH ₂ OMe	H
A.1-68	CO ₂ Me	CH ₂ OMe	H
A.1-69	CO ₂ Et	CH ₂ OMe	H
A.1-70	OCF ₃	CH ₂ OMe	H
A.1-71	H	OCH ₂ OMe	H
A.1-72	Me	OCH ₂ OMe	H
A.1-73	Et	OCH ₂ OMe	H
A.1-74	OMe	OCH ₂ OMe	H
A.1-75	CH ₂ OMe	OCH ₂ OMe	H
A.1-76	OCH ₂ OMe	OCH ₂ OMe	H
A.1-77	CF ₃	OCH ₂ OMe	H
A.1-78	CHFMe	OCH ₂ OMe	H
A.1-79	CN	OCH ₂ OMe	H
A.1-80	F	OCH ₂ OMe	H

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-81	Cl	OCH ₂ OMe	H
A.1-82	CO ₂ Me	OCH ₂ OMe	H
A.1-83	CO ₂ Et	OCH ₂ OMe	H
A.1-84	OCF ₃	OCH ₂ OMe	H
A.1-85	H	CF ₃	H
A.1-86	Me	CF ₃	H
A.1-87	Et	CF ₃	H
A.1-88	OMe	CF ₃	H
A.1-89	CH ₂ OMe	CF ₃	H
A.1-90	OCH ₂ OMe	CF ₃	H
A.1-91	CF ₃	CF ₃	H
A.1-92	CHFMe	CF ₃	H
A.1-93	CN	CF ₃	H
A.1-94	F	CF ₃	H
A.1-95	Cl	CF ₃	H
A.1-96	CO ₂ Me	CF ₃	H
A.1-97	CO ₂ Et	CF ₃	H
A.1-98	OCF ₃	CF ₃	H
A.1-99	H	CHFMe	H
A.1-100	Me	CHFMe	H
A.1-101	Et	CHFMe	H
A.1-102	OMe	CHFMe	H
A.1-103	CH ₂ OMe	CHFMe	H
A.1-104	OCH ₂ OMe	CHFMe	H
A.1-105	CF ₃	CHFMe	H
A.1-106	CHFMe	CHFMe	H
A.1-107	CN	CHFMe	H
A.1-108	F	CHFMe	H
A.1-109	Cl	CHFMe	H
A.1-110	CO ₂ Me	CHFMe	H
A.1-111	CO ₂ Et	CHFMe	H
A.1-112	OCF ₃	CHFMe	H
A.1-113	H	CN	H
A.1-114	Me	CN	H
A.1-115	Et	CN	H
A.1-116	OMe	CN	H
A.1-117	CH ₂ OMe	CN	H
A.1-118	OCH ₂ OMe	CN	H
A.1-119	CF ₃	CN	H
A.1-120	CHFMe	CN	H

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-121	CN	CN	H
A.1-122	F	CN	H
A.1-123	Cl	CN	H
A.1-124	CO ₂ Me	CN	H
A.1-125	CO ₂ Et	CN	H
A.1-126	OCF ₃	CN	H
A.1-127	H	F	H
A.1-128	Me	F	H
A.1-129	Et	F	H
A.1-130	OMe	F	H
A.1-131	CH ₂ OMe	F	H
A.1-132	OCH ₂ OMe	F	H
A.1-133	CF ₃	F	H
A.1-134	CHFMe	F	H
A.1-135	CN	F	H
A.1-136	F	F	H
A.1-137	Cl	F	H
A.1-138	CO ₂ Me	F	H
A.1-139	CO ₂ Et	F	H
A.1-140	OCF ₃	F	H
A.1-141	H	Cl	H
A.1-142	Me	Cl	H
A.1-143	Et	Cl	H
A.1-144	OMe	Cl	H
A.1-145	CH ₂ OMe	Cl	H
A.1-146	OCH ₂ OMe	Cl	H
A.1-147	CF ₃	Cl	H
A.1-148	CHFMe	Cl	H
A.1-149	CN	Cl	H
A.1-150	F	Cl	H
A.1-151	Cl	Cl	H
A.1-152	CO ₂ Me	Cl	H
A.1-153	CO ₂ Et	Cl	H
A.1-154	OCF ₃	Cl	H
A.1-155	H	CO ₂ Me	H
A.1-156	Me	CO ₂ Me	H
A.1-157	Et	CO ₂ Me	H
A.1-158	OMe	CO ₂ Me	H
A.1-159	CH ₂ OMe	CO ₂ Me	H
A.1-160	OCH ₂ OMe	CO ₂ Me	H

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-161	CF ₃	CO ₂ Me	H
A.1-162	CHFMe	CO ₂ Me	H
A.1-163	CN	CO ₂ Me	H
A.1-164	F	CO ₂ Me	H
A.1-165	Cl	CO ₂ Me	H
A.1-166	CO ₂ Me	CO ₂ Me	H
A.1-167	CO ₂ Et	CO ₂ Me	H
A.1-168	OCF ₃	CO ₂ Me	H
A.1-169	H	CO ₂ Et	H
A.1-170	Me	CO ₂ Et	H
A.1-171	Et	CO ₂ Et	H
A.1-172	OMe	CO ₂ Et	H
A.1-173	CH ₂ OMe	CO ₂ Et	H
A.1-174	OCH ₂ OMe	CO ₂ Et	H
A.1-175	CF ₃	CO ₂ Et	H
A.1-176	CHFMe	CO ₂ Et	H
A.1-177	CN	CO ₂ Et	H
A.1-178	F	CO ₂ Et	H
A.1-179	Cl	CO ₂ Et	H
A.1-180	CO ₂ Me	CO ₂ Et	H
A.1-181	CO ₂ Et	CO ₂ Et	H
A.1-182	OCF ₃	CO ₂ Et	H
A.1-183	H	OCF ₃	H
A.1-184	Me	OCF ₃	H
A.1-185	Et	OCF ₃	H
A.1-186	OMe	OCF ₃	H
A.1-187	CH ₂ OMe	OCF ₃	H
A.1-188	OCH ₂ OMe	OCF ₃	H
A.1-189	CF ₃	OCF ₃	H
A.1-190	CHFMe	OCF ₃	H
A.1-191	CN	OCF ₃	H
A.1-192	F	OCF ₃	H
A.1-193	Cl	OCF ₃	H
A.1-194	CO ₂ Me	OCF ₃	H
A.1-195	CO ₂ Et	OCF ₃	H
A.1-196	OCF ₃	OCF ₃	H
A.1-197	H	CH(Me) ₂	H
A.1-198	Me	CH(Me) ₂	H
A.1-199	Et	CH(Me) ₂	H
A.1-200	OMe	CH(Me) ₂	H

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-201	CH ₂ OMe	CH(Me) ₂	H
A.1-202	OCH ₂ OMe	CH(Me) ₂	H
A.1-203	CF ₃	CH(Me) ₂	H
A.1-204	CHFMe	CH(Me) ₂	H
A.1-205	CN	CH(Me) ₂	H
A.1-206	F	CH(Me) ₂	H
A.1-207	Cl	CH(Me) ₂	H
A.1-208	CO ₂ Me	CH(Me) ₂	H
A.1-209	CO ₂ Et	CH(Me) ₂	H
A.1-210	OCF ₃	CH(Me) ₂	H
A.1-211	H	CH=CH ₂	H
A.1-212	Me	CH=CH ₂	H
A.1-213	Et	CH=CH ₂	H
A.1-214	OMe	CH=CH ₂	H
A.1-215	CH ₂ OMe	CH=CH ₂	H
A.1-216	OCH ₂ OMe	CH=CH ₂	H
A.1-217	CF ₃	CH=CH ₂	H
A.1-218	CHFMe	CH=CH ₂	H
A.1-219	CN	CH=CH ₂	H
A.1-220	F	CH=CH ₂	H
A.1-221	Cl	CH=CH ₂	H
A.1-222	CO ₂ Me	CH=CH ₂	H
A.1-223	CO ₂ Et	CH=CH ₂	H
A.1-224	OCF ₃	CH=CH ₂	H
A.1-225	H	C≡CH	H
A.1-226	Me	C≡CH	H
A.1-227	Et	C≡CH	H
A.1-228	OMe	C≡CH	H
A.1-229	CH ₂ OMe	C≡CH	H
A.1-230	OCH ₂ OMe	C≡CH	H
A.1-231	CF ₃	C≡CH	H
A.1-232	CHFMe	C≡CH	H
A.1-233	CN	C≡CH	H
A.1-234	F	C≡CH	H
A.1-235	Cl	C≡CH	H
A.1-236	CO ₂ Me	C≡CH	H
A.1-237	CO ₂ Et	C≡CH	H
A.1-238	OCF ₃	C≡CH	H
A.1-239	H	H	F
A.1-240	Me	H	F

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-241	Et	H	F
A.1-242	OMe	H	F
A.1-243	CH ₂ OMe	H	F
A.1-244	OCH ₂ OMe	H	F
A.1-245	CF ₃	H	F
A.1-246	CHFMe	H	F
A.1-247	CN	H	F
A.1-248	F	H	F
A.1-249	Cl	H	F
A.1-250	CO ₂ Me	H	F
A.1-251	CO ₂ Et	H	F
A.1-252	OCF ₃	H	F
A.1-253	H	Me	F
A.1-254	Me	Me	F
A.1-255	Et	Me	F
A.1-256	OMe	Me	F
A.1-257	CH ₂ OMe	Me	F
A.1-258	OCH ₂ OMe	Me	F
A.1-259	CF ₃	Me	F
A.1-260	CHFMe	Me	F
A.1-261	CN	Me	F
A.1-262	F	Me	F
A.1-263	Cl	Me	F
A.1-264	CO ₂ Me	Me	F
A.1-265	CO ₂ Et	Me	F
A.1-266	OCF ₃	Me	F
A.1-267	H	Et	F
A.1-268	Me	Et	F
A.1-269	Et	Et	F
A.1-270	OMe	Et	F
A.1-271	CH ₂ OMe	Et	F
A.1-272	OCH ₂ OMe	Et	F
A.1-273	CF ₃	Et	F
A.1-274	CHFMe	Et	F
A.1-275	CN	Et	F
A.1-276	F	Et	F
A.1-277	Cl	Et	F
A.1-278	CO ₂ Me	Et	F
A.1-279	CO ₂ Et	Et	F
A.1-280	OCF ₃	Et	F

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-281	H	OMe	F
A.1-282	Me	OMe	F
A.1-283	Et	OMe	F
A.1-284	OMe	OMe	F
A.1-285	CH ₂ OMe	OMe	F
A.1-286	OCH ₂ OMe	OMe	F
A.1-287	CF ₃	OMe	F
A.1-288	CHFMe	OMe	F
A.1-289	CN	OMe	F
A.1-290	F	OMe	F
A.1-291	Cl	OMe	F
A.1-292	CO ₂ Me	OMe	F
A.1-293	CO ₂ Et	OMe	F
A.1-294	OCF ₃	OMe	F
A.1-295	H	CH ₂ OMe	F
A.1-296	Me	CH ₂ OMe	F
A.1-297	Et	CH ₂ OMe	F
A.1-298	OMe	CH ₂ OMe	F
A.1-299	CH ₂ OMe	CH ₂ OMe	F
A.1-300	OCH ₂ OMe	CH ₂ OMe	F
A.1-301	CF ₃	CH ₂ OMe	F
A.1-302	CHFMe	CH ₂ OMe	F
A.1-303	CN	CH ₂ OMe	F
A.1-304	F	CH ₂ OMe	F
A.1-305	Cl	CH ₂ OMe	F
A.1-306	CO ₂ Me	CH ₂ OMe	F
A.1-307	CO ₂ Et	CH ₂ OMe	F
A.1-308	OCF ₃	CH ₂ OMe	F
A.1-309	H	OCH ₂ OMe	F
A.1-310	Me	OCH ₂ OMe	F
A.1-311	Et	OCH ₂ OMe	F
A.1-312	OMe	OCH ₂ OMe	F
A.1-313	CH ₂ OMe	OCH ₂ OMe	F
A.1-314	OCH ₂ OMe	OCH ₂ OMe	F
A.1-315	CF ₃	OCH ₂ OMe	F
A.1-316	CHFMe	OCH ₂ OMe	F
A.1-317	CN	OCH ₂ OMe	F
A.1-318	F	OCH ₂ OMe	F
A.1-319	Cl	OCH ₂ OMe	F
A.1-320	CO ₂ Me	OCH ₂ OMe	F

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-321	CO ₂ Et	OCH ₂ OMe	F
A.1-322	OCF ₃	OCH ₂ OMe	F
A.1-323	H	CF ₃	F
A.1-324	Me	CF ₃	F
A.1-325	Et	CF ₃	F
A.1-326	OMe	CF ₃	F
A.1-327	CH ₂ OMe	CF ₃	F
A.1-328	OCH ₂ OMe	CF ₃	F
A.1-329	CF ₃	CF ₃	F
A.1-330	CHFMe	CF ₃	F
A.1-331	CN	CF ₃	F
A.1-332	F	CF ₃	F
A.1-333	Cl	CF ₃	F
A.1-334	CO ₂ Me	CF ₃	F
A.1-335	CO ₂ Et	CF ₃	F
A.1-336	OCF ₃	CF ₃	F
A.1-337	H	CHFMe	F
A.1-338	Me	CHFMe	F
A.1-339	Et	CHFMe	F
A.1-340	OMe	CHFMe	F
A.1-341	CH ₂ OMe	CHFMe	F
A.1-342	OCH ₂ OMe	CHFMe	F
A.1-343	CF ₃	CHFMe	F
A.1-344	CHFMe	CHFMe	F
A.1-345	CN	CHFMe	F
A.1-346	F	CHFMe	F
A.1-347	Cl	CHFMe	F
A.1-348	CO ₂ Me	CHFMe	F
A.1-349	CO ₂ Et	CHFMe	F
A.1-350	OCF ₃	CHFMe	F
A.1-351	H	CN	F
A.1-352	Me	CN	F
A.1-353	Et	CN	F
A.1-354	OMe	CN	F
A.1-355	CH ₂ OMe	CN	F
A.1-356	OCH ₂ OMe	CN	F
A.1-357	CF ₃	CN	F
A.1-358	CHFMe	CN	F
A.1-359	CN	CN	F
A.1-360	F	CN	F

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-361	Cl	CN	F
A.1-362	CO ₂ Me	CN	F
A.1-363	CO ₂ Et	CN	F
A.1-364	OCF ₃	CN	F
A.1-365	H	F	F
A.1-366	Me	F	F
A.1-367	Et	F	F
A.1-368	OMe	F	F
A.1-369	CH ₂ OMe	F	F
A.1-370	OCH ₂ OMe	F	F
A.1-371	CF ₃	F	F
A.1-372	CHFMe	F	F
A.1-373	CN	F	F
A.1-374	F	F	F
A.1-375	Cl	F	F
A.1-376	CO ₂ Me	F	F
A.1-377	CO ₂ Et	F	F
A.1-378	OCF ₃	F	F
A.1-379	H	Cl	F
A.1-380	Me	Cl	F
A.1-381	Et	Cl	F
A.1-382	OMe	Cl	F
A.1-383	CH ₂ OMe	Cl	F
A.1-384	OCH ₂ OMe	Cl	F
A.1-385	CF ₃	Cl	F
A.1-386	CHFMe	Cl	F
A.1-387	CN	Cl	F
A.1-388	F	Cl	F
A.1-389	Cl	Cl	F
A.1-390	CO ₂ Me	Cl	F
A.1-391	CO ₂ Et	Cl	F
A.1-392	OCF ₃	Cl	F
A.1-393	H	CO ₂ Me	F
A.1-394	Me	CO ₂ Me	F
A.1-395	Et	CO ₂ Me	F
A.1-396	OMe	CO ₂ Me	F
A.1-397	CH ₂ OMe	CO ₂ Me	F
A.1-398	OCH ₂ OMe	CO ₂ Me	F
A.1-399	CF ₃	CO ₂ Me	F
A.1-400	CHFMe	CO ₂ Me	F

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-401	CN	CO ₂ Me	F
A.1-402	F	CO ₂ Me	F
A.1-403	Cl	CO ₂ Me	F
A.1-404	CO ₂ Me	CO ₂ Me	F
A.1-405	CO ₂ Et	CO ₂ Me	F
A.1-406	OCF ₃	CO ₂ Me	F
A.1-407	H	CO ₂ Et	F
A.1-408	Me	CO ₂ Et	F
A.1-409	Et	CO ₂ Et	F
A.1-410	OMe	CO ₂ Et	F
A.1-411	CH ₂ OMe	CO ₂ Et	F
A.1-412	OCH ₂ OMe	CO ₂ Et	F
A.1-413	CF ₃	CO ₂ Et	F
A.1-414	CHFMe	CO ₂ Et	F
A.1-415	CN	CO ₂ Et	F
A.1-416	F	CO ₂ Et	F
A.1-417	Cl	CO ₂ Et	F
A.1-418	CO ₂ Me	CO ₂ Et	F
A.1-419	CO ₂ Et	CO ₂ Et	F
A.1-420	OCF ₃	CO ₂ Et	F
A.1-421	H	OCF ₃	F
A.1-422	Me	OCF ₃	F
A.1-423	Et	OCF ₃	F
A.1-424	OMe	OCF ₃	F
A.1-425	CH ₂ OMe	OCF ₃	F
A.1-426	OCH ₂ OMe	OCF ₃	F
A.1-427	CF ₃	OCF ₃	F
A.1-428	CHFMe	OCF ₃	F
A.1-429	CN	OCF ₃	F
A.1-430	F	OCF ₃	F
A.1-431	Cl	OCF ₃	F
A.1-432	CO ₂ Me	OCF ₃	F
A.1-433	CO ₂ Et	OCF ₃	F
A.1-434	OCF ₃	OCF ₃	F
A.1-435	H	CH(Me) ₂	F
A.1-436	Me	CH(Me) ₂	F
A.1-437	Et	CH(Me) ₂	F
A.1-438	OMe	CH(Me) ₂	F
A.1-439	CH ₂ OMe	CH(Me) ₂	F
A.1-440	OCH ₂ OMe	CH(Me) ₂	F

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-441	CF ₃	CH(Me) ₂	F
A.1-442	CHFMe	CH(Me) ₂	F
A.1-443	CN	CH(Me) ₂	F
A.1-444	F	CH(Me) ₂	F
A.1-445	Cl	CH(Me) ₂	F
A.1-446	CO ₂ Me	CH(Me) ₂	F
A.1-447	CO ₂ Et	CH(Me) ₂	F
A.1-448	OCF ₃	CH(Me) ₂	F
A.1-449	H	CH=CH ₂	F
A.1-450	Me	CH=CH ₂	F
A.1-451	Et	CH=CH ₂	F
A.1-452	OMe	CH=CH ₂	F
A.1-453	CH ₂ OMe	CH=CH ₂	F
A.1-454	OCH ₂ OMe	CH=CH ₂	F
A.1-455	CF ₃	CH=CH ₂	F
A.1-456	CHFMe	CH=CH ₂	F
A.1-457	CN	CH=CH ₂	F
A.1-458	F	CH=CH ₂	F
A.1-459	Cl	CH=CH ₂	F
A.1-460	CO ₂ Me	CH=CH ₂	F
A.1-461	CO ₂ Et	CH=CH ₂	F
A.1-462	OCF ₃	CH=CH ₂	F
A.1-463	H	C≡CH	F
A.1-464	Me	C≡CH	F
A.1-465	Et	C≡CH	F
A.1-466	OMe	C≡CH	F
A.1-467	CH ₂ OMe	C≡CH	F
A.1-468	OCH ₂ OMe	C≡CH	F
A.1-469	CF ₃	C≡CH	F
A.1-470	CHFMe	C≡CH	F
A.1-471	CN	C≡CH	F
A.1-472	F	C≡CH	F
A.1-473	Cl	C≡CH	F
A.1-474	CO ₂ Me	C≡CH	F
A.1-475	CO ₂ Et	C≡CH	F
A.1-476	OCF ₃	C≡CH	F
A.1-477	H	H	Cl
A.1-478	Me	H	Cl
A.1-479	Et	H	Cl
A.1-480	OMe	H	Cl

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-481	CH ₂ OMe	H	Cl
A.1-482	OCH ₂ OMe	H	Cl
A.1-483	CF ₃	H	Cl
A.1-484	CHFMe	H	Cl
A.1-485	CN	H	Cl
A.1-486	F	H	Cl
A.1-487	Cl	H	Cl
A.1-488	CO ₂ Me	H	Cl
A.1-489	CO ₂ Et	H	Cl
A.1-490	OCF ₃	H	Cl
A.1-491	H	Me	Cl
A.1-492	Me	Me	Cl
A.1-493	Et	Me	Cl
A.1-494	OMe	Me	Cl
A.1-495	CH ₂ OMe	Me	Cl
A.1-496	OCH ₂ OMe	Me	Cl
A.1-497	CF ₃	Me	Cl
A.1-498	CHFMe	Me	Cl
A.1-499	CN	Me	Cl
A.1-500	F	Me	Cl
A.1-501	Cl	Me	Cl
A.1-502	CO ₂ Me	Me	Cl
A.1-503	CO ₂ Et	Me	Cl
A.1-504	OCF ₃	Me	Cl
A.1-505	H	Et	Cl
A.1-506	Me	Et	Cl
A.1-507	Et	Et	Cl
A.1-508	OMe	Et	Cl
A.1-509	CH ₂ OMe	Et	Cl
A.1-510	OCH ₂ OMe	Et	Cl
A.1-511	CF ₃	Et	Cl
A.1-512	CHFMe	Et	Cl
A.1-513	CN	Et	Cl
A.1-514	F	Et	Cl
A.1-515	Cl	Et	Cl
A.1-516	CO ₂ Me	Et	Cl
A.1-517	CO ₂ Et	Et	Cl
A.1-518	OCF ₃	Et	Cl
A.1-519	H	OMe	Cl
A.1-520	Me	OMe	Cl

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-521	Et	OMe	Cl
A.1-522	OMe	OMe	Cl
A.1-523	CH ₂ OMe	OMe	Cl
A.1-524	OCH ₂ OMe	OMe	Cl
A.1-525	CF ₃	OMe	Cl
A.1-526	CHFMe	OMe	Cl
A.1-527	CN	OMe	Cl
A.1-528	F	OMe	Cl
A.1-529	Cl	OMe	Cl
A.1-530	CO ₂ Me	OMe	Cl
A.1-531	CO ₂ Et	OMe	Cl
A.1-532	OCF ₃	OMe	Cl
A.1-533	H	CH ₂ OMe	Cl
A.1-534	Me	CH ₂ OMe	Cl
A.1-535	Et	CH ₂ OMe	Cl
A.1-536	OMe	CH ₂ OMe	Cl
A.1-537	CH ₂ OMe	CH ₂ OMe	Cl
A.1-538	OCH ₂ OMe	CH ₂ OMe	Cl
A.1-539	CF ₃	CH ₂ OMe	Cl
A.1-540	CHFMe	CH ₂ OMe	Cl
A.1-541	CN	CH ₂ OMe	Cl
A.1-542	F	CH ₂ OMe	Cl
A.1-543	Cl	CH ₂ OMe	Cl
A.1-544	CO ₂ Me	CH ₂ OMe	Cl
A.1-545	CO ₂ Et	CH ₂ OMe	Cl
A.1-546	OCF ₃	CH ₂ OMe	Cl
A.1-547	H	OCH ₂ OMe	Cl
A.1-548	Me	OCH ₂ OMe	Cl
A.1-549	Et	OCH ₂ OMe	Cl
A.1-550	OMe	OCH ₂ OMe	Cl
A.1-551	CH ₂ OMe	OCH ₂ OMe	Cl
A.1-552	OCH ₂ OMe	OCH ₂ OMe	Cl
A.1-553	CF ₃	OCH ₂ OMe	Cl
A.1-554	CHFMe	OCH ₂ OMe	Cl
A.1-555	CN	OCH ₂ OMe	Cl
A.1-556	F	OCH ₂ OMe	Cl
A.1-557	Cl	OCH ₂ OMe	Cl
A.1-558	CO ₂ Me	OCH ₂ OMe	Cl
A.1-559	CO ₂ Et	OCH ₂ OMe	Cl
A.1-560	OCF ₃	OCH ₂ OMe	Cl

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-561	H	CF ₃	Cl
A.1-562	Me	CF ₃	Cl
A.1-563	Et	CF ₃	Cl
A.1-564	OMe	CF ₃	Cl
A.1-565	CH ₂ OMe	CF ₃	Cl
A.1-566	OCH ₂ OMe	CF ₃	Cl
A.1-567	CF ₃	CF ₃	Cl
A.1-568	CHFMe	CF ₃	Cl
A.1-569	CN	CF ₃	Cl
A.1-570	F	CF ₃	Cl
A.1-571	Cl	CF ₃	Cl
A.1-572	CO ₂ Me	CF ₃	Cl
A.1-573	CO ₂ Et	CF ₃	Cl
A.1-574	OCF ₃	CF ₃	Cl
A.1-575	H	CHFMe	Cl
A.1-576	Me	CHFMe	Cl
A.1-577	Et	CHFMe	Cl
A.1-578	OMe	CHFMe	Cl
A.1-579	CH ₂ OMe	CHFMe	Cl
A.1-580	OCH ₂ OMe	CHFMe	Cl
A.1-581	CF ₃	CHFMe	Cl
A.1-582	CHFMe	CHFMe	Cl
A.1-583	CN	CHFMe	Cl
A.1-584	F	CHFMe	Cl
A.1-585	Cl	CHFMe	Cl
A.1-586	CO ₂ Me	CHFMe	Cl
A.1-587	CO ₂ Et	CHFMe	Cl
A.1-588	OCF ₃	CHFMe	Cl
A.1-589	H	CN	Cl
A.1-590	Me	CN	Cl
A.1-591	Et	CN	Cl
A.1-592	OMe	CN	Cl
A.1-593	CH ₂ OMe	CN	Cl
A.1-594	OCH ₂ OMe	CN	Cl
A.1-595	CF ₃	CN	Cl
A.1-596	CHFMe	CN	Cl
A.1-597	CN	CN	Cl
A.1-598	F	CN	Cl
A.1-599	Cl	CN	Cl
A.1-600	CO ₂ Me	CN	Cl

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-601	CO ₂ Et	CN	Cl
A.1-602	OCF ₃	CN	Cl
A.1-603	H	F	Cl
A.1-604	Me	F	Cl
A.1-605	Et	F	Cl
A.1-606	OMe	F	Cl
A.1-607	CH ₂ OMe	F	Cl
A.1-608	OCH ₂ OMe	F	Cl
A.1-609	CF ₃	F	Cl
A.1-610	CHFMe	F	Cl
A.1-611	CN	F	Cl
A.1-612	F	F	Cl
A.1-613	Cl	F	Cl
A.1-614	CO ₂ Me	F	Cl
A.1-615	CO ₂ Et	F	Cl
A.1-616	OCF ₃	F	Cl
A.1-617	H	Cl	Cl
A.1-618	Me	Cl	Cl
A.1-619	Et	Cl	Cl
A.1-620	OMe	Cl	Cl
A.1-621	CH ₂ OMe	Cl	Cl
A.1-622	OCH ₂ OMe	Cl	Cl
A.1-623	CF ₃	Cl	Cl
A.1-624	CHFMe	Cl	Cl
A.1-625	CN	Cl	Cl
A.1-626	F	Cl	Cl
A.1-627	Cl	Cl	Cl
A.1-628	CO ₂ Me	Cl	Cl
A.1-629	CO ₂ Et	Cl	Cl
A.1-630	OCF ₃	Cl	Cl
A.1-631	H	CO ₂ Me	Cl
A.1-632	Me	CO ₂ Me	Cl
A.1-633	Et	CO ₂ Me	Cl
A.1-634	OMe	CO ₂ Me	Cl
A.1-635	CH ₂ OMe	CO ₂ Me	Cl
A.1-636	OCH ₂ OMe	CO ₂ Me	Cl
A.1-637	CF ₃	CO ₂ Me	Cl
A.1-638	CHFMe	CO ₂ Me	Cl
A.1-639	CN	CO ₂ Me	Cl
A.1-640	F	CO ₂ Me	Cl

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-641	Cl	CO ₂ Me	Cl
A.1-642	CO ₂ Me	CO ₂ Me	Cl
A.1-643	CO ₂ Et	CO ₂ Me	Cl
A.1-644	OCF ₃	CO ₂ Me	Cl
A.1-645	H	CO ₂ Et	Cl
A.1-646	Me	CO ₂ Et	Cl
A.1-647	Et	CO ₂ Et	Cl
A.1-648	OMe	CO ₂ Et	Cl
A.1-649	CH ₂ OMe	CO ₂ Et	Cl
A.1-650	OCH ₂ OMe	CO ₂ Et	Cl
A.1-651	CF ₃	CO ₂ Et	Cl
A.1-652	CHFMe	CO ₂ Et	Cl
A.1-653	CN	CO ₂ Et	Cl
A.1-654	F	CO ₂ Et	Cl
A.1-655	Cl	CO ₂ Et	Cl
A.1-656	CO ₂ Me	CO ₂ Et	Cl
A.1-657	CO ₂ Et	CO ₂ Et	Cl
A.1-658	OCF ₃	CO ₂ Et	Cl
A.1-659	H	OCF ₃	Cl
A.1-660	Me	OCF ₃	Cl
A.1-661	Et	OCF ₃	Cl
A.1-662	OMe	OCF ₃	Cl
A.1-663	CH ₂ OMe	OCF ₃	Cl
A.1-664	OCH ₂ OMe	OCF ₃	Cl
A.1-665	CF ₃	OCF ₃	Cl
A.1-666	CHFMe	OCF ₃	Cl
A.1-667	CN	OCF ₃	Cl
A.1-668	F	OCF ₃	Cl
A.1-669	Cl	OCF ₃	Cl
A.1-670	CO ₂ Me	OCF ₃	Cl
A.1-671	CO ₂ Et	OCF ₃	Cl
A.1-672	OCF ₃	OCF ₃	Cl
A.1-673	H	CH(Me) ₂	Cl
A.1-674	Me	CH(Me) ₂	Cl
A.1-675	Et	CH(Me) ₂	Cl
A.1-676	OMe	CH(Me) ₂	Cl
A.1-677	CH ₂ OMe	CH(Me) ₂	Cl
A.1-678	OCH ₂ OMe	CH(Me) ₂	Cl
A.1-679	CF ₃	CH(Me) ₂	Cl
A.1-680	CHFMe	CH(Me) ₂	Cl

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-681	CN	CH(Me) ₂	Cl
A.1-682	F	CH(Me) ₂	Cl
A.1-683	Cl	CH(Me) ₂	Cl
A.1-684	CO ₂ Me	CH(Me) ₂	Cl
A.1-685	CO ₂ Et	CH(Me) ₂	Cl
A.1-686	OCF ₃	CH(Me) ₂	Cl
A.1-687	H	CH=CH ₂	Cl
A.1-688	Me	CH=CH ₂	Cl
A.1-689	Et	CH=CH ₂	Cl
A.1-690	OMe	CH=CH ₂	Cl
A.1-691	CH ₂ OMe	CH=CH ₂	Cl
A.1-692	OCH ₂ OMe	CH=CH ₂	Cl
A.1-693	CF ₃	CH=CH ₂	Cl
A.1-694	CHFMe	CH=CH ₂	Cl
A.1-695	CN	CH=CH ₂	Cl
A.1-696	F	CH=CH ₂	Cl
A.1-697	Cl	CH=CH ₂	Cl
A.1-698	CO ₂ Me	CH=CH ₂	Cl
A.1-699	CO ₂ Et	CH=CH ₂	Cl
A.1-700	OCF ₃	CH=CH ₂	Cl
A.1-701	H	C≡CH	Cl
A.1-702	Me	C≡CH	Cl
A.1-703	Et	C≡CH	Cl
A.1-704	OMe	C≡CH	Cl
A.1-705	CH ₂ OMe	C≡CH	Cl
A.1-706	OCH ₂ OMe	C≡CH	Cl
A.1-707	CF ₃	C≡CH	Cl
A.1-708	CHFMe	C≡CH	Cl
A.1-709	CN	C≡CH	Cl
A.1-710	F	C≡CH	Cl
A.1-711	Cl	C≡CH	Cl
A.1-712	CO ₂ Me	C≡CH	Cl
A.1-713	CO ₂ Et	C≡CH	Cl
A.1-714	OCF ₃	C≡CH	Cl
A.1-715	H	H	CO ₂ Me
A.1-716	Me	H	CO ₂ Me
A.1-717	Et	H	CO ₂ Me
A.1-718	OMe	H	CO ₂ Me
A.1-719	CH ₂ OMe	H	CO ₂ Me
A.1-720	OCH ₂ OMe	H	CO ₂ Me

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-721	CF ₃	H	CO ₂ Me
A.1-722	CHFMe	H	CO ₂ Me
A.1-723	CN	H	CO ₂ Me
A.1-724	F	H	CO ₂ Me
A.1-725	Cl	H	CO ₂ Me
A.1-726	CO ₂ Me	H	CO ₂ Me
A.1-727	CO ₂ Et	H	CO ₂ Me
A.1-728	OCF ₃	H	CO ₂ Me
A.1-729	H	Me	CO ₂ Me
A.1-730	Me	Me	CO ₂ Me
A.1-731	Et	Me	CO ₂ Me
A.1-732	OMe	Me	CO ₂ Me
A.1-733	CH ₂ OMe	Me	CO ₂ Me
A.1-734	OCH ₂ OMe	Me	CO ₂ Me
A.1-735	CF ₃	Me	CO ₂ Me
A.1-736	CHFMe	Me	CO ₂ Me
A.1-737	CN	Me	CO ₂ Me
A.1-738	F	Me	CO ₂ Me
A.1-739	Cl	Me	CO ₂ Me
A.1-740	CO ₂ Me	Me	CO ₂ Me
A.1-741	CO ₂ Et	Me	CO ₂ Me
A.1-742	OCF ₃	Me	CO ₂ Me
A.1-743	H	Et	CO ₂ Me
A.1-744	Me	Et	CO ₂ Me
A.1-745	Et	Et	CO ₂ Me
A.1-746	OMe	Et	CO ₂ Me
A.1-747	CH ₂ OMe	Et	CO ₂ Me
A.1-748	OCH ₂ OMe	Et	CO ₂ Me
A.1-749	CF ₃	Et	CO ₂ Me
A.1-750	CHFMe	Et	CO ₂ Me
A.1-751	CN	Et	CO ₂ Me
A.1-752	F	Et	CO ₂ Me
A.1-753	Cl	Et	CO ₂ Me
A.1-754	CO ₂ Me	Et	CO ₂ Me
A.1-755	CO ₂ Et	Et	CO ₂ Me
A.1-756	OCF ₃	Et	CO ₂ Me
A.1-757	H	OMe	CO ₂ Me
A.1-758	Me	OMe	CO ₂ Me
A.1-759	Et	OMe	CO ₂ Me
A.1-760	OMe	OMe	CO ₂ Me

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-761	CH ₂ OMe	OMe	CO ₂ Me
A.1-762	OCH ₂ OMe	OMe	CO ₂ Me
A.1-763	CF ₃	OMe	CO ₂ Me
A.1-764	CHFMe	OMe	CO ₂ Me
A.1-765	CN	OMe	CO ₂ Me
A.1-766	F	OMe	CO ₂ Me
A.1-767	Cl	OMe	CO ₂ Me
A.1-768	CO ₂ Me	OMe	CO ₂ Me
A.1-769	CO ₂ Et	OMe	CO ₂ Me
A.1-770	OCF ₃	OMe	CO ₂ Me
A.1-771	H	CH ₂ OMe	CO ₂ Me
A.1-772	Me	CH ₂ OMe	CO ₂ Me
A.1-773	Et	CH ₂ OMe	CO ₂ Me
A.1-774	OMe	CH ₂ OMe	CO ₂ Me
A.1-775	CH ₂ OMe	CH ₂ OMe	CO ₂ Me
A.1-776	OCH ₂ OMe	CH ₂ OMe	CO ₂ Me
A.1-777	CF ₃	CH ₂ OMe	CO ₂ Me
A.1-778	CHFMe	CH ₂ OMe	CO ₂ Me
A.1-779	CN	CH ₂ OMe	CO ₂ Me
A.1-780	F	CH ₂ OMe	CO ₂ Me
A.1-781	Cl	CH ₂ OMe	CO ₂ Me
A.1-782	CO ₂ Me	CH ₂ OMe	CO ₂ Me
A.1-783	CO ₂ Et	CH ₂ OMe	CO ₂ Me
A.1-784	OCF ₃	CH ₂ OMe	CO ₂ Me
A.1-785	H	OCH ₂ OMe	CO ₂ Me
A.1-786	Me	OCH ₂ OMe	CO ₂ Me
A.1-787	Et	OCH ₂ OMe	CO ₂ Me
A.1-788	OMe	OCH ₂ OMe	CO ₂ Me
A.1-789	CH ₂ OMe	OCH ₂ OMe	CO ₂ Me
A.1-790	OCH ₂ OMe	OCH ₂ OMe	CO ₂ Me
A.1-791	CF ₃	OCH ₂ OMe	CO ₂ Me
A.1-792	CHFMe	OCH ₂ OMe	CO ₂ Me
A.1-793	CN	OCH ₂ OMe	CO ₂ Me
A.1-794	F	OCH ₂ OMe	CO ₂ Me
A.1-795	Cl	OCH ₂ OMe	CO ₂ Me
A.1-796	CO ₂ Me	OCH ₂ OMe	CO ₂ Me
A.1-797	CO ₂ Et	OCH ₂ OMe	CO ₂ Me
A.1-798	OCF ₃	OCH ₂ OMe	CO ₂ Me
A.1-799	H	CF ₃	CO ₂ Me
A.1-800	Me	CF ₃	CO ₂ Me

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-801	Et	CF ₃	CO ₂ Me
A.1-802	OMe	CF ₃	CO ₂ Me
A.1-803	CH ₂ OMe	CF ₃	CO ₂ Me
A.1-804	OCH ₂ OMe	CF ₃	CO ₂ Me
A.1-805	CF ₃	CF ₃	CO ₂ Me
A.1-806	CHFMe	CF ₃	CO ₂ Me
A.1-807	CN	CF ₃	CO ₂ Me
A.1-808	F	CF ₃	CO ₂ Me
A.1-809	Cl	CF ₃	CO ₂ Me
A.1-810	CO ₂ Me	CF ₃	CO ₂ Me
A.1-811	CO ₂ Et	CF ₃	CO ₂ Me
A.1-812	OCF ₃	CF ₃	CO ₂ Me
A.1-813	H	CHFMe	CO ₂ Me
A.1-814	Me	CHFMe	CO ₂ Me
A.1-815	Et	CHFMe	CO ₂ Me
A.1-816	OMe	CHFMe	CO ₂ Me
A.1-817	CH ₂ OMe	CHFMe	CO ₂ Me
A.1-818	OCH ₂ OMe	CHFMe	CO ₂ Me
A.1-819	CF ₃	CHFMe	CO ₂ Me
A.1-820	CHFMe	CHFMe	CO ₂ Me
A.1-821	CN	CHFMe	CO ₂ Me
A.1-822	F	CHFMe	CO ₂ Me
A.1-823	Cl	CHFMe	CO ₂ Me
A.1-824	CO ₂ Me	CHFMe	CO ₂ Me
A.1-825	CO ₂ Et	CHFMe	CO ₂ Me
A.1-826	OCF ₃	CHFMe	CO ₂ Me
A.1-827	H	CN	CO ₂ Me
A.1-828	Me	CN	CO ₂ Me
A.1-829	Et	CN	CO ₂ Me
A.1-830	OMe	CN	CO ₂ Me
A.1-831	CH ₂ OMe	CN	CO ₂ Me
A.1-832	OCH ₂ OMe	CN	CO ₂ Me
A.1-833	CF ₃	CN	CO ₂ Me
A.1-834	CHFMe	CN	CO ₂ Me
A.1-835	CN	CN	CO ₂ Me
A.1-836	F	CN	CO ₂ Me
A.1-837	Cl	CN	CO ₂ Me
A.1-838	CO ₂ Me	CN	CO ₂ Me
A.1-839	CO ₂ Et	CN	CO ₂ Me
A.1-840	OCF ₃	CN	CO ₂ Me

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-841	H	F	CO ₂ Me
A.1-842	Me	F	CO ₂ Me
A.1-843	Et	F	CO ₂ Me
A.1-844	OMe	F	CO ₂ Me
A.1-845	CH ₂ OMe	F	CO ₂ Me
A.1-846	OCH ₂ OMe	F	CO ₂ Me
A.1-847	CF ₃	F	CO ₂ Me
A.1-848	CHFMe	F	CO ₂ Me
A.1-849	CN	F	CO ₂ Me
A.1-850	F	F	CO ₂ Me
A.1-851	Cl	F	CO ₂ Me
A.1-852	CO ₂ Me	F	CO ₂ Me
A.1-853	CO ₂ Et	F	CO ₂ Me
A.1-854	OCF ₃	F	CO ₂ Me
A.1-855	H	Cl	CO ₂ Me
A.1-856	Me	Cl	CO ₂ Me
A.1-857	Et	Cl	CO ₂ Me
A.1-858	OMe	Cl	CO ₂ Me
A.1-859	CH ₂ OMe	Cl	CO ₂ Me
A.1-860	OCH ₂ OMe	Cl	CO ₂ Me
A.1-861	CF ₃	Cl	CO ₂ Me
A.1-862	CHFMe	Cl	CO ₂ Me
A.1-863	CN	Cl	CO ₂ Me
A.1-864	F	Cl	CO ₂ Me
A.1-865	Cl	Cl	CO ₂ Me
A.1-866	CO ₂ Me	Cl	CO ₂ Me
A.1-867	CO ₂ Et	Cl	CO ₂ Me
A.1-868	OCF ₃	Cl	CO ₂ Me
A.1-869	H	CO ₂ Me	CO ₂ Me
A.1-870	Me	CO ₂ Me	CO ₂ Me
A.1-871	Et	CO ₂ Me	CO ₂ Me
A.1-872	OMe	CO ₂ Me	CO ₂ Me
A.1-873	CH ₂ OMe	CO ₂ Me	CO ₂ Me
A.1-874	OCH ₂ OMe	CO ₂ Me	CO ₂ Me
A.1-875	CF ₃	CO ₂ Me	CO ₂ Me
A.1-876	CHFMe	CO ₂ Me	CO ₂ Me
A.1-877	CN	CO ₂ Me	CO ₂ Me
A.1-878	F	CO ₂ Me	CO ₂ Me
A.1-879	Cl	CO ₂ Me	CO ₂ Me
A.1-880	CO ₂ Me	CO ₂ Me	CO ₂ Me

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-881	CO ₂ Et	CO ₂ Me	CO ₂ Me
A.1-882	OCF ₃	CO ₂ Me	CO ₂ Me
A.1-883	H	CO ₂ Et	CO ₂ Me
A.1-884	Me	CO ₂ Et	CO ₂ Me
A.1-885	Et	CO ₂ Et	CO ₂ Me
A.1-886	OMe	CO ₂ Et	CO ₂ Me
A.1-887	CH ₂ OMe	CO ₂ Et	CO ₂ Me
A.1-888	OCH ₂ OMe	CO ₂ Et	CO ₂ Me
A.1-889	CF ₃	CO ₂ Et	CO ₂ Me
A.1-890	CHFMe	CO ₂ Et	CO ₂ Me
A.1-891	CN	CO ₂ Et	CO ₂ Me
A.1-892	F	CO ₂ Et	CO ₂ Me
A.1-893	Cl	CO ₂ Et	CO ₂ Me
A.1-894	CO ₂ Me	CO ₂ Et	CO ₂ Me
A.1-895	CO ₂ Et	CO ₂ Et	CO ₂ Me
A.1-896	OCF ₃	CO ₂ Et	CO ₂ Me
A.1-897	H	OCF ₃	CO ₂ Me
A.1-898	Me	OCF ₃	CO ₂ Me
A.1-899	Et	OCF ₃	CO ₂ Me
A.1-900	OMe	OCF ₃	CO ₂ Me
A.1-901	CH ₂ OMe	OCF ₃	CO ₂ Me
A.1-902	OCH ₂ OMe	OCF ₃	CO ₂ Me
A.1-903	CF ₃	OCF ₃	CO ₂ Me
A.1-904	CHFMe	OCF ₃	CO ₂ Me
A.1-905	CN	OCF ₃	CO ₂ Me
A.1-906	F	OCF ₃	CO ₂ Me
A.1-907	Cl	OCF ₃	CO ₂ Me
A.1-908	CO ₂ Me	OCF ₃	CO ₂ Me
A.1-909	CO ₂ Et	OCF ₃	CO ₂ Me
A.1-910	OCF ₃	OCF ₃	CO ₂ Me
A.1-911	H	CH(Me) ₂	CO ₂ Me
A.1-912	Me	CH(Me) ₂	CO ₂ Me
A.1-913	Et	CH(Me) ₂	CO ₂ Me
A.1-914	OMe	CH(Me) ₂	CO ₂ Me
A.1-915	CH ₂ OMe	CH(Me) ₂	CO ₂ Me
A.1-916	OCH ₂ OMe	CH(Me) ₂	CO ₂ Me
A.1-917	CF ₃	CH(Me) ₂	CO ₂ Me
A.1-918	CHFMe	CH(Me) ₂	CO ₂ Me
A.1-919	CN	CH(Me) ₂	CO ₂ Me
A.1-920	F	CH(Me) ₂	CO ₂ Me

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-921	Cl	CH(Me) ₂	CO ₂ Me
A.1-922	CO ₂ Me	CH(Me) ₂	CO ₂ Me
A.1-923	CO ₂ Et	CH(Me) ₂	CO ₂ Me
A.1-924	OCF ₃	CH(Me) ₂	CO ₂ Me
A.1-925	H	CH=CH ₂	CO ₂ Me
A.1-926	Me	CH=CH ₂	CO ₂ Me
A.1-927	Et	CH=CH ₂	CO ₂ Me
A.1-928	OMe	CH=CH ₂	CO ₂ Me
A.1-929	CH ₂ OMe	CH=CH ₂	CO ₂ Me
A.1-930	OCH ₂ OMe	CH=CH ₂	CO ₂ Me
A.1-931	CF ₃	CH=CH ₂	CO ₂ Me
A.1-932	CHFMe	CH=CH ₂	CO ₂ Me
A.1-933	CN	CH=CH ₂	CO ₂ Me
A.1-934	F	CH=CH ₂	CO ₂ Me
A.1-935	Cl	CH=CH ₂	CO ₂ Me
A.1-936	CO ₂ Me	CH=CH ₂	CO ₂ Me
A.1-937	CO ₂ Et	CH=CH ₂	CO ₂ Me
A.1-938	OCF ₃	CH=CH ₂	CO ₂ Me
A.1-939	H	C≡CH	CO ₂ Me
A.1-940	Me	C≡CH	CO ₂ Me
A.1-941	Et	C≡CH	CO ₂ Me
A.1-942	OMe	C≡CH	CO ₂ Me
A.1-943	CH ₂ OMe	C≡CH	CO ₂ Me
A.1-944	OCH ₂ OMe	C≡CH	CO ₂ Me
A.1-945	CF ₃	C≡CH	CO ₂ Me
A.1-946	CHFMe	C≡CH	CO ₂ Me
A.1-947	CN	C≡CH	CO ₂ Me
A.1-948	F	C≡CH	CO ₂ Me
A.1-949	Cl	C≡CH	CO ₂ Me
A.1-950	CO ₂ Me	C≡CH	CO ₂ Me
A.1-951	CO ₂ Et	C≡CH	CO ₂ Me
A.1-952	OCF ₃	C≡CH	CO ₂ Me
A.1-953	H	H	CO ₂ Et
A.1-954	Me	H	CO ₂ Et
A.1-955	Et	H	CO ₂ Et
A.1-956	OMe	H	CO ₂ Et
A.1-957	CH ₂ OMe	H	CO ₂ Et
A.1-958	OCH ₂ OMe	H	CO ₂ Et
A.1-959	CF ₃	H	CO ₂ Et
A.1-960	CHFMe	H	CO ₂ Et

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-961	CN	H	CO ₂ Et
A.1-962	F	H	CO ₂ Et
A.1-963	Cl	H	CO ₂ Et
A.1-964	CO ₂ Me	H	CO ₂ Et
A.1-965	CO ₂ Et	H	CO ₂ Et
A.1-966	OCF ₃	H	CO ₂ Et
A.1-967	H	Me	CO ₂ Et
A.1-968	Me	Me	CO ₂ Et
A.1-969	Et	Me	CO ₂ Et
A.1-970	OMe	Me	CO ₂ Et
A.1-971	CH ₂ OMe	Me	CO ₂ Et
A.1-972	OCH ₂ OMe	Me	CO ₂ Et
A.1-973	CF ₃	Me	CO ₂ Et
A.1-974	CHFMe	Me	CO ₂ Et
A.1-975	CN	Me	CO ₂ Et
A.1-976	F	Me	CO ₂ Et
A.1-977	Cl	Me	CO ₂ Et
A.1-978	CO ₂ Me	Me	CO ₂ Et
A.1-979	CO ₂ Et	Me	CO ₂ Et
A.1-980	OCF ₃	Me	CO ₂ Et
A.1-981	H	Et	CO ₂ Et
A.1-982	Me	Et	CO ₂ Et
A.1-983	Et	Et	CO ₂ Et
A.1-984	OMe	Et	CO ₂ Et
A.1-985	CH ₂ OMe	Et	CO ₂ Et
A.1-986	OCH ₂ OMe	Et	CO ₂ Et
A.1-987	CF ₃	Et	CO ₂ Et
A.1-988	CHFMe	Et	CO ₂ Et
A.1-989	CN	Et	CO ₂ Et
A.1-990	F	Et	CO ₂ Et
A.1-991	Cl	Et	CO ₂ Et
A.1-992	CO ₂ Me	Et	CO ₂ Et
A.1-993	CO ₂ Et	Et	CO ₂ Et
A.1-994	OCF ₃	Et	CO ₂ Et
A.1-995	H	OMe	CO ₂ Et
A.1-996	Me	OMe	CO ₂ Et
A.1-997	Et	OMe	CO ₂ Et
A.1-998	OMe	OMe	CO ₂ Et
A.1-999	CH ₂ OMe	OMe	CO ₂ Et
A.1-1000	OCH ₂ OMe	OMe	CO ₂ Et

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-1001	CF ₃	OMe	CO ₂ Et
A.1-1002	CHFMe	OMe	CO ₂ Et
A.1-1003	CN	OMe	CO ₂ Et
A.1-1004	F	OMe	CO ₂ Et
A.1-1005	Cl	OMe	CO ₂ Et
A.1-1006	CO ₂ Me	OMe	CO ₂ Et
A.1-1007	CO ₂ Et	OMe	CO ₂ Et
A.1-1008	OCF ₃	OMe	CO ₂ Et
A.1-1009	H	CH ₂ OMe	CO ₂ Et
A.1-1010	Me	CH ₂ OMe	CO ₂ Et
A.1-1011	Et	CH ₂ OMe	CO ₂ Et
A.1-1012	OMe	CH ₂ OMe	CO ₂ Et
A.1-1013	CH ₂ OMe	CH ₂ OMe	CO ₂ Et
A.1-1014	OCH ₂ OMe	CH ₂ OMe	CO ₂ Et
A.1-1015	CF ₃	CH ₂ OMe	CO ₂ Et
A.1-1016	CHFMe	CH ₂ OMe	CO ₂ Et
A.1-1017	CN	CH ₂ OMe	CO ₂ Et
A.1-1018	F	CH ₂ OMe	CO ₂ Et
A.1-1019	Cl	CH ₂ OMe	CO ₂ Et
A.1-1020	CO ₂ Me	CH ₂ OMe	CO ₂ Et
A.1-1021	CO ₂ Et	CH ₂ OMe	CO ₂ Et
A.1-1022	OCF ₃	CH ₂ OMe	CO ₂ Et
A.1-1023	H	OCH ₂ OMe	CO ₂ Et
A.1-1024	Me	OCH ₂ OMe	CO ₂ Et
A.1-1025	Et	OCH ₂ OMe	CO ₂ Et
A.1-1026	OMe	OCH ₂ OMe	CO ₂ Et
A.1-1027	CH ₂ OMe	OCH ₂ OMe	CO ₂ Et
A.1-1028	OCH ₂ OMe	OCH ₂ OMe	CO ₂ Et
A.1-1029	CF ₃	OCH ₂ OMe	CO ₂ Et
A.1-1030	CHFMe	OCH ₂ OMe	CO ₂ Et
A.1-1031	CN	OCH ₂ OMe	CO ₂ Et
A.1-1032	F	OCH ₂ OMe	CO ₂ Et
A.1-1033	Cl	OCH ₂ OMe	CO ₂ Et
A.1-1034	CO ₂ Me	OCH ₂ OMe	CO ₂ Et
A.1-1035	CO ₂ Et	OCH ₂ OMe	CO ₂ Et
A.1-1036	OCF ₃	OCH ₂ OMe	CO ₂ Et
A.1-1037	H	CF ₃	CO ₂ Et
A.1-1038	Me	CF ₃	CO ₂ Et
A.1-1039	Et	CF ₃	CO ₂ Et
A.1-1040	OMe	CF ₃	CO ₂ Et

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-1041	CH ₂ OMe	CF ₃	CO ₂ Et
A.1-1042	OCH ₂ OMe	CF ₃	CO ₂ Et
A.1-1043	CF ₃	CF ₃	CO ₂ Et
A.1-1044	CHFMe	CF ₃	CO ₂ Et
A.1-1045	CN	CF ₃	CO ₂ Et
A.1-1046	F	CF ₃	CO ₂ Et
A.1-1047	Cl	CF ₃	CO ₂ Et
A.1-1048	CO ₂ Me	CF ₃	CO ₂ Et
A.1-1049	CO ₂ Et	CF ₃	CO ₂ Et
A.1-1050	OCF ₃	CF ₃	CO ₂ Et
A.1-1051	H	CHFMe	CO ₂ Et
A.1-1052	Me	CHFMe	CO ₂ Et
A.1-1053	Et	CHFMe	CO ₂ Et
A.1-1054	OMe	CHFMe	CO ₂ Et
A.1-1055	CH ₂ OMe	CHFMe	CO ₂ Et
A.1-1056	OCH ₂ OMe	CHFMe	CO ₂ Et
A.1-1057	CF ₃	CHFMe	CO ₂ Et
A.1-1058	CHFMe	CHFMe	CO ₂ Et
A.1-1059	CN	CHFMe	CO ₂ Et
A.1-1060	F	CHFMe	CO ₂ Et
A.1-1061	Cl	CHFMe	CO ₂ Et
A.1-1062	CO ₂ Me	CHFMe	CO ₂ Et
A.1-1063	CO ₂ Et	CHFMe	CO ₂ Et
A.1-1064	OCF ₃	CHFMe	CO ₂ Et
A.1-1065	H	CN	CO ₂ Et
A.1-1066	Me	CN	CO ₂ Et
A.1-1067	Et	CN	CO ₂ Et
A.1-1068	OMe	CN	CO ₂ Et
A.1-1069	CH ₂ OMe	CN	CO ₂ Et
A.1-1070	OCH ₂ OMe	CN	CO ₂ Et
A.1-1071	CF ₃	CN	CO ₂ Et
A.1-1072	CHFMe	CN	CO ₂ Et
A.1-1073	CN	CN	CO ₂ Et
A.1-1074	F	CN	CO ₂ Et
A.1-1075	Cl	CN	CO ₂ Et
A.1-1076	CO ₂ Me	CN	CO ₂ Et
A.1-1077	CO ₂ Et	CN	CO ₂ Et
A.1-1078	OCF ₃	CN	CO ₂ Et
A.1-1079	H	F	CO ₂ Et
A.1-1080	Me	F	CO ₂ Et

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-1081	Et	F	CO ₂ Et
A.1-1082	OMe	F	CO ₂ Et
A.1-1083	CH ₂ OMe	F	CO ₂ Et
A.1-1084	OCH ₂ OMe	F	CO ₂ Et
A.1-1085	CF ₃	F	CO ₂ Et
A.1-1086	CHFMe	F	CO ₂ Et
A.1-1087	CN	F	CO ₂ Et
A.1-1088	F	F	CO ₂ Et
A.1-1089	Cl	F	CO ₂ Et
A.1-1090	CO ₂ Me	F	CO ₂ Et
A.1-1091	CO ₂ Et	F	CO ₂ Et
A.1-1092	OCF ₃	F	CO ₂ Et
A.1-1093	H	Cl	CO ₂ Et
A.1-1094	Me	Cl	CO ₂ Et
A.1-1095	Et	Cl	CO ₂ Et
A.1-1096	OMe	Cl	CO ₂ Et
A.1-1097	CH ₂ OMe	Cl	CO ₂ Et
A.1-1098	OCH ₂ OMe	Cl	CO ₂ Et
A.1-1099	CF ₃	Cl	CO ₂ Et
A.1-1100	CHFMe	Cl	CO ₂ Et
A.1-1101	CN	Cl	CO ₂ Et
A.1-1102	F	Cl	CO ₂ Et
A.1-1103	Cl	Cl	CO ₂ Et
A.1-1104	CO ₂ Me	Cl	CO ₂ Et
A.1-1105	CO ₂ Et	Cl	CO ₂ Et
A.1-1106	OCF ₃	Cl	CO ₂ Et
A.1-1107	H	CO ₂ Me	CO ₂ Et
A.1-1108	Me	CO ₂ Me	CO ₂ Et
A.1-1109	Et	CO ₂ Me	CO ₂ Et
A.1-1110	OMe	CO ₂ Me	CO ₂ Et
A.1-1111	CH ₂ OMe	CO ₂ Me	CO ₂ Et
A.1-1112	OCH ₂ OMe	CO ₂ Me	CO ₂ Et
A.1-1113	CF ₃	CO ₂ Me	CO ₂ Et
A.1-1114	CHFMe	CO ₂ Me	CO ₂ Et
A.1-1115	CN	CO ₂ Me	CO ₂ Et
A.1-1116	F	CO ₂ Me	CO ₂ Et
A.1-1117	Cl	CO ₂ Me	CO ₂ Et
A.1-1118	CO ₂ Me	CO ₂ Me	CO ₂ Et
A.1-1119	CO ₂ Et	CO ₂ Me	CO ₂ Et
A.1-1120	OCF ₃	CO ₂ Me	CO ₂ Et

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-1121	H	CO ₂ Et	CO ₂ Et
A.1-1122	Me	CO ₂ Et	CO ₂ Et
A.1-1123	Et	CO ₂ Et	CO ₂ Et
A.1-1124	OMe	CO ₂ Et	CO ₂ Et
A.1-1125	CH ₂ OMe	CO ₂ Et	CO ₂ Et
A.1-1126	OCH ₂ OMe	CO ₂ Et	CO ₂ Et
A.1-1127	CF ₃	CO ₂ Et	CO ₂ Et
A.1-1128	CHFMe	CO ₂ Et	CO ₂ Et
A.1-1129	CN	CO ₂ Et	CO ₂ Et
A.1-1130	F	CO ₂ Et	CO ₂ Et
A.1-1131	Cl	CO ₂ Et	CO ₂ Et
A.1-1132	CO ₂ Me	CO ₂ Et	CO ₂ Et
A.1-1133	CO ₂ Et	CO ₂ Et	CO ₂ Et
A.1-1134	OCF ₃	CO ₂ Et	CO ₂ Et
A.1-1135	H	OCF ₃	CO ₂ Et
A.1-1136	Me	OCF ₃	CO ₂ Et
A.1-1137	Et	OCF ₃	CO ₂ Et
A.1-1138	OMe	OCF ₃	CO ₂ Et
A.1-1139	CH ₂ OMe	OCF ₃	CO ₂ Et
A.1-1140	OCH ₂ OMe	OCF ₃	CO ₂ Et
A.1-1141	CF ₃	OCF ₃	CO ₂ Et
A.1-1142	CHFMe	OCF ₃	CO ₂ Et
A.1-1143	CN	OCF ₃	CO ₂ Et
A.1-1144	F	OCF ₃	CO ₂ Et
A.1-1145	Cl	OCF ₃	CO ₂ Et
A.1-1146	CO ₂ Me	OCF ₃	CO ₂ Et
A.1-1147	CO ₂ Et	OCF ₃	CO ₂ Et
A.1-1148	OCF ₃	OCF ₃	CO ₂ Et
A.1-1149	H	CH(Me) ₂	CO ₂ Et
A.1-1150	Me	CH(Me) ₂	CO ₂ Et
A.1-1151	Et	CH(Me) ₂	CO ₂ Et
A.1-1152	OMe	CH(Me) ₂	CO ₂ Et
A.1-1153	CH ₂ OMe	CH(Me) ₂	CO ₂ Et
A.1-1154	OCH ₂ OMe	CH(Me) ₂	CO ₂ Et
A.1-1155	CF ₃	CH(Me) ₂	CO ₂ Et
A.1-1156	CHFMe	CH(Me) ₂	CO ₂ Et
A.1-1157	CN	CH(Me) ₂	CO ₂ Et
A.1-1158	F	CH(Me) ₂	CO ₂ Et
A.1-1159	Cl	CH(Me) ₂	CO ₂ Et
A.1-1160	CO ₂ Me	CH(Me) ₂	CO ₂ Et

	R ^{a2}	R ^{a5}	R ^{a6}
A.1-1161	CO ₂ Et	CH(Me) ₂	CO ₂ Et
A.1-1162	OCF ₃	CH(Me) ₂	CO ₂ Et
A.1-1163	H	CH=CH ₂	CO ₂ Et
A.1-1164	Me	CH=CH ₂	CO ₂ Et
A.1-1165	Et	CH=CH ₂	CO ₂ Et
A.1-1166	OMe	CH=CH ₂	CO ₂ Et
A.1-1167	CH ₂ OMe	CH=CH ₂	CO ₂ Et
A.1-1168	OCH ₂ OMe	CH=CH ₂	CO ₂ Et
A.1-1169	CF ₃	CH=CH ₂	CO ₂ Et
A.1-1170	CHFMe	CH=CH ₂	CO ₂ Et
A.1-1171	CN	CH=CH ₂	CO ₂ Et
A.1-1172	F	CH=CH ₂	CO ₂ Et
A.1-1173	Cl	CH=CH ₂	CO ₂ Et
A.1-1174	CO ₂ Me	CH=CH ₂	CO ₂ Et
A.1-1175	CO ₂ Et	CH=CH ₂	CO ₂ Et
A.1-1176	OCF ₃	CH=CH ₂	CO ₂ Et
A.1-1177	H	C≡CH	CO ₂ Et
A.1-1178	Me	C≡CH	CO ₂ Et
A.1-1179	Et	C≡CH	CO ₂ Et
A.1-1180	OMe	C≡CH	CO ₂ Et
A.1-1181	CH ₂ OMe	C≡CH	CO ₂ Et
A.1-1182	OCH ₂ OMe	C≡CH	CO ₂ Et
A.1-1183	CF ₃	C≡CH	CO ₂ Et
A.1-1184	CHFMe	C≡CH	CO ₂ Et
A.1-1185	CN	C≡CH	CO ₂ Et
A.1-1186	F	C≡CH	CO ₂ Et
A.1-1187	Cl	C≡CH	CO ₂ Et
A.1-1188	CO ₂ Me	C≡CH	CO ₂ Et
A.1-1189	CO ₂ Et	C≡CH	CO ₂ Et
A.1-1190	OCF ₃	C≡CH	CO ₂ Et

Further preferred embodiments relate to compounds I wherein R^{a5} and R^{a6} in each case constitute together with two ring member carbon atoms of the pyrimidine ring one of the following heterocyclic groups as defined in line A.2-1 to line A.2-26 in table A, wherein #5 and #6 indicate the point of attachment to the pyrimidine ring, each respectively corresponding to the positions of either substituent R^{a5} or R^{a6}.

Table A.2:

line	R ^{a5} /R ^{a6}
A.2-1	#5-CH=CH-CH=CH-#6
A.2-2	#5-CH ₂ -CH ₂ -CH ₂ -CH ₂ -#6
A.2-3	#5-CH=CH-CH=N-#6
A.2-4	#5-N=CH-CH=CH-#6
A.2-5	#5-CH=N-CH=N-#6
A.2-6	#5-N=CH-N=CH-#6
A.2-7	#5-CH ₂ -CH ₂ -CH ₂ -#6
A.2-8	#5-N=CH-CH=N-#6
A.2-9	#5-O-CH ₂ -O-#6
A.2-10	#5-NH-CH=N-#6
A.2-11	#5-S-CH=N-#6
A.2-12	#5-N=CH-S-#6
A.2-13	#5-O-CH=N-#6
A.2-14	#5-N=CH-O-#6
A.2-15	#5-O-CH=CH-#6
A.2-16	#5-S-CH=CH-#6
A.2-17	#5-O-N=CH-#6
A.2-18	#5-S-N=CH-#6
A.2-19	#5-CH=N-O-#6
A.2-20	#5-CH=N-S-#6
A.2-21	#5-N(CH ₃)-CH=CH-#6
A.2-22	#5-CH=CH-N(CH ₃)-#6
A.2-23	#5=CH-N(NH ₂)-N-#6
A.2-24	#5-CH=N-N(CH ₃)-#6
A.2-25	#5=N-N(CH ₃)-CH-#6
A.2-26	#5-N(CH ₃)-N=CH-#6

In the compounds I according to the invention, R^A, R^B in radical R^{a2} preferably is hydrogen, C₁-C₄-alkyl.

- 5 In the compounds I according to the invention, R^A, R^B in radical R^{a5} preferably is hydrogen, C₁-C₄-alkyl.

In the compounds I according to the invention, R^A, R^B in radical R^{a6} preferably is hydrogen, C₁-C₄-alkyl.

- 10 In the compounds I according to the invention, R' in radical R^{a2} preferably is hydrogen, NH₂, C₁-C₄-alkyl, C₁-C₄-alkoxy.

In the compounds I according to the invention, R' in radical R^{a5} preferably is hydrogen, NH₂, C₁-C₄-alkyl, C₁-C₄-alkoxy.

In the compounds I according to the invention, R' in radical R^{a6} preferably is hydrogen, NH₂,

- 15 C₁-C₄-alkyl, C₁-C₄-alkoxy.

In the compounds I according to the invention, R'' in radical R^{a2} preferably is hydrogen, C₁-C₄-alkyl.

In the compounds I according to the invention, R'' in radical R^{a5} preferably is hydrogen, C₁-C₄-alkyl.

In the compounds I according to the invention, R'' in radical R^{a6} preferably is hydrogen, C₁-C₄-alkyl.

In the compounds I according to the invention, R''' in radical R^{a2} preferably is hydrogen.

In the compounds I according to the invention, R''' in radical R^{a5} preferably is hydrogen.

In the compounds I according to the invention, R''' in radical R^{a6} preferably is hydrogen.

In the compounds I according to the invention, R is preferably selected from the group consisting of hydrogen, C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄-alkoxy-C₁-C₄-alkyl, C₂-C₄-alkenyl, C₂-C₄-alkynyl, CN, CH₂CN or CH₂-O-C(=O)R', wherein R' is hydrogen, C₁-C₄-alkyl, C₁-C₄-alkoxy; more preferably R is selected from the group consisting of hydrogen, C₁-C₄-alkyl, C₁-C₄-alkoxy-C₁-C₄-alkyl, C₂-C₄-alkenyl and C₂-C₄-alkynyl; in another preferred embodiment R is hydrogen, C₁-C₄-alkyl, C₂-C₄-alkenyl or C₂-C₄-alkynyl; most preferably R is hydrogen or C₁-C₄-alkyl; more preferably R is hydrogen; a more preferred embodiment relates to compounds I wherein R is CH₃.

In the compounds I according to the invention, X is preferably a divalent group -CR³R⁴-, wherein R³ and R⁴ independently of each other are hydrogen, CN, C₁-C₄-hydroxyalkyl, C₁-C₄-alkyl, C₂-C₄-alkenyl, C₂-C₄-alkynyl or C₃-C₈-cycloalkyl; in another preferred embodiment X is -CH₂-, -CH(CH₃)-, -CH(CH₂CH₃)-, -C(CH₃)₂-, -CHCN-, -C(=O)-, -C(=S)-, -CH(C(=O)-C₁-C₄-alkoxy)-, -CH(C(=O)NH₂)-, -C(=O)N(C₁-C₄-alkyl)₂-, and -CH(C(=O)OH)-. Another preferred embodiment of the invention relates to compounds I, wherein X is -CH₂-, -C(=O)-, -CH(CH₃)-, -C(CH₃)₂-, -CHCN-, -CH(C(=O)-OCH₃) or -CH(C(=O)-OCH₂CH₃); more preferably X is -CH₂- or -CH(CH₃)-, in particular -CH₂-; more preferably X is -C(=O)-.

In the compounds I according to the invention, R¹ and R² independently of each other are preferably selected from the group consisting of hydrogen, CN, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy and C₃-C₈-cycloalkyl; more preferably R¹ and R² independently of each other are hydrogen, CN, CH₃, CH₂CH₃, F, Cl or OCH₃; another more preferred embodiment relates to compounds I wherein R¹ and R² independently of each other are hydrogen or C₁-C₄-alkyl; another more preferred embodiment relates to compounds I wherein R¹ and R² independently of each other are hydrogen or CH₃; more preferably R¹ and R² are hydrogen.

Further preferred embodiments relate to compounds I wherein R, X, R¹ and R² in each case are one of the following combinations B-1 to B-84 in table B:

Table B:

No.	R	R ¹	R ²	X
B-1	H	H	H	-CH ₂ -
B-2	H	CH ₃	H	-CH ₂ -
B-3	H	CN	H	-CH ₂ -
B-4	H	F	H	-CH ₂ -
B-5	H	Cl	H	-CH ₂ -
B-6	H	OCH ₃	H	-CH ₂ -
B-7	H	CH ₃	CH ₃	-CH ₂ -
B-8	H	H	H	-C(=O)-
B-9	H	CH ₃	H	-C(=O)-
B-10	H	CN	H	-C(=O)-
B-11	H	F	H	-C(=O)-
B-12	H	Cl	H	-C(=O)-
B-13	H	OCH ₃	H	-C(=O)-
B-14	H	CH ₃	CH ₃	-C(=O)-
B-15	H	H	H	-CH(CH ₃)-
B-16	H	CH ₃	H	-CH(CH ₃)-
B-17	H	CN	H	-CH(CH ₃)-
B-18	H	F	H	-CH(CH ₃)-
B-19	H	Cl	H	-CH(CH ₃)-
B-20	H	OCH ₃	H	-CH(CH ₃)-
B-21	H	CH ₃	CH ₃	-CH(CH ₃)-
B-22	H	H	H	-CH(CH ₃)-
B-23	H	CH ₃	H	-CH(CH ₃)-
B-24	H	CN	H	-CH(CH ₃)-
B-25	H	F	H	-CH(CH ₃)-
B-26	H	Cl	H	-CH(CH ₃)-
B-27	H	OCH ₃	H	-CH(CH ₃)-
B-28	H	CH ₃	CH ₃	-CH(CH ₃)-
B-29	H	H	H	-CH(C ₂ H ₅)-
B-30	H	CH ₃	H	-CH(C ₂ H ₅)-
B-31	H	CN	H	-CH(C ₂ H ₅)-
B-32	H	F	H	-CH(C ₂ H ₅)-
B-33	H	Cl	H	-CH(C ₂ H ₅)-
B-34	H	OCH ₃	H	-CH(C ₂ H ₅)-
B-35	H	CH ₃	CH ₃	-CH(C ₂ H ₅)-
B-36	H	H	H	-CHCN-
B-37	H	CH ₃	H	-CHCN-
B-38	H	CN	H	-CHCN-
B-39	H	F	H	-CHCN-

No.	R	R ¹	R ²	X
B-40	H	Cl	H	-CHCN-
B-41	H	OCH ₃	H	-CHCN-
B-42	H	CH ₃	CH ₃	-CHCN-
B-43	CH ₃	H	H	-CH ₂ -
B-44	CH ₃	CH ₃	H	-CH ₂ -
B-45	CH ₃	CN	H	-CH ₂ -
B-46	CH ₃	F	H	-CH ₂ -
B-47	CH ₃	Cl	H	-CH ₂ -
B-48	CH ₃	OCH ₃	H	-CH ₂ -
B-49	CH ₃	CH ₃	CH ₃	-CH ₂ -
B-50	CH ₃	H	H	-C(=O)-
B-51	CH ₃	CH ₃	H	-C(=O)-
B-52	CH ₃	CN	H	-C(=O)-
B-53	CH ₃	F	H	-C(=O)-
B-54	CH ₃	Cl	H	-C(=O)-
B-55	CH ₃	OCH ₃	H	-C(=O)-
B-56	CH ₃	CH ₃	CH ₃	-C(=O)-
B-57	CH ₃	H	H	-CH(CH ₃)-
B-58	CH ₃	CH ₃	H	-CH(CH ₃)-
B-59	CH ₃	CN	H	-CH(CH ₃)-
B-60	CH ₃	F	H	-CH(CH ₃)-
B-61	CH ₃	Cl	H	-CH(CH ₃)-
B-62	CH ₃	OCH ₃	H	-CH(CH ₃)-
B-63	CH ₃	CH ₃	CH ₃	-CH(CH ₃)-
B-64	CH ₃	H	H	-C(CH ₃) ₂ -
B-65	CH ₃	CH ₃	H	-C(CH ₃) ₂ -
B-66	CH ₃	CN	H	-C(CH ₃) ₂ -
B-67	CH ₃	F	H	-C(CH ₃) ₂ -
B-68	CH ₃	Cl	H	-C(CH ₃) ₂ -
B-69	CH ₃	OCH ₃	H	-C(CH ₃) ₂ -
B-70	CH ₃	CH ₃	CH ₃	-C(CH ₃) ₂ -
B-71	CH ₃	H	H	-CH(C ₂ H ₅)-
B-72	CH ₃	CH ₃	H	-CH(C ₂ H ₅)-
B-73	CH ₃	CN	H	-CH(C ₂ H ₅)-
B-74	CH ₃	F	H	-CH(C ₂ H ₅)-
B-75	CH ₃	Cl	H	-CH(C ₂ H ₅)-
B-76	CH ₃	OCH ₃	H	-CH(C ₂ H ₅)-
B-77	CH ₃	CH ₃	CH ₃	-CH(C ₂ H ₅)-
B-78	CH ₃	H	H	-CHCN-
B-79	CH ₃	CH ₃	H	-CHCN-

No.	R	R ¹	R ²	X
B-80	CH ₃	CN	H	-CHCN-
B-81	CH ₃	F	H	-CHCN-
B-82	CH ₃	Cl	H	-CHCN-
B-83	CH ₃	OCH ₃	H	-CHCN-
B-84	CH ₃	CH ₃	CH ₃	-CHCN-

In the compounds I according to the invention, R^b are independently selected from halogen, CN, NO₂, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkoxy-C₁-C₄-alkyl and (C₁-C₄-alkoxy)carbonyl; more preferably R^b are independently selected from halogen, CN, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy and (C₁-C₄-alkoxy)carbonyl; in another preferred embodiment R^b are independently selected from halogen and C₁-C₄-alkoxy; most preferably R^b are independently selected from halogen, CN, CH₃, CF₃ and OCH₃. A particularly preferred embodiment relates to compounds I wherein R^b is F. Another particularly preferred embodiment relates to compounds I wherein R^b is CH₃. A further particularly preferred embodiment relates to compounds I wherein R^b is CF₃. In yet another particularly preferred embodiment R^b is OCH₃. In still a further embodiment R^b is attached to the phenyl ring adjacent (in ortho-position) to the alkyne group. A further embodiment relates to compounds I wherein R^b is attached in meta-position to the alkyne group.

In the compounds I according to the invention, n is preferably 0.

A further embodiment relates to compounds I wherein n is preferably 1.

A further embodiment relates to compounds I wherein n is preferably 0 or 1.

A further embodiment relates to compounds I wherein n is preferably 2.

A further embodiment relates to compounds I wherein n is preferably 0, 1 or 2.

A further embodiment relates to compounds I wherein n is preferably 3.

A further embodiment relates to compounds I wherein n is preferably 0, 1, 2 or 3.

A further embodiment relates to compounds I wherein n is preferably 4. In the compounds I according to the invention, Het is preferably selected from the group consisting of pyrimidin-2-yl, pyrimidin-3-yl, pyrimidin-4-yl, pyridin-2-yl, pyridin-3-yl, pyridin-4-yl, thiazol-2-yl, thiazol-4-yl, thiazol-5-yl, isothiazol-3-yl, isothiazol-4-yl, isothiazol-5-yl, pyrazin-2-yl, pyridazin-3-yl, 1,3,5-triazin-2-yl, and 1,2,4-triazin-3-yl; more preferably Het is selected from pyrimidin-2-yl, pyrimidin-3-yl, pyrimidin-4-yl, pyridin-2-yl, pyridin-3-yl, pyridin-4-yl, thiazol-2-yl, pyrazin-2-yl, pyridazin-3-yl, 1,3,5-triazin-2-yl, and 1,2,4-triazin-3-yl; more preferably Het is selected from pyrimidin-2-yl, pyrimidin-3-yl, pyrimidin-4-yl, pyridin-2-yl, pyridin-3-yl, pyridin-4-yl; preferably Het is pyrimidin-2-yl, pyridin-2-yl, pyridin-3-yl, pyridin-4-yl, thiazol-2-yl.

In a further preferred embodiment Het is a pyridinyl or pyrimidinyl ring, wherein the moiety O-Het is bound in para- or meta-position to the phenyl ring; and wherein the pyridinyl or pyrimidinyl are unsubstituted or carry 1 or 2 groups R^c; wherein R^c is halogen, C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₁-C₄-alkoxy or (C₁-C₄-alkoxy)carbonyl.

According to one embodiment Het is unsubstituted; a further preferred embodiment relates to compounds I wherein Het is unsubstituted or substituted by 1 radical R^c; another preferred

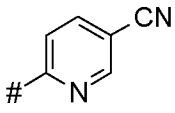
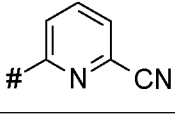
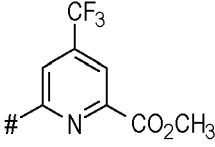
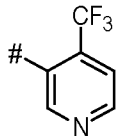
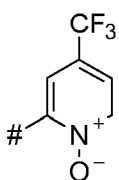
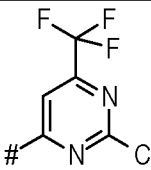
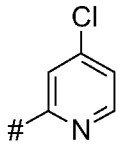
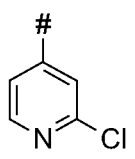
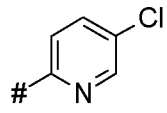
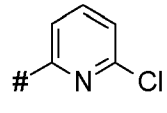
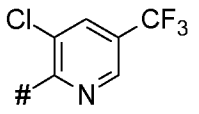
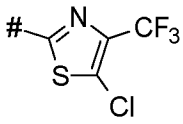
embodiment relates to compounds I wherein Het is unsubstituted or substituted by 1 or 2 independently selected radicals R^c ; yet another preferred embodiment relates to compounds I wherein Het is unsubstituted or substituted by 1, 2 or 3 independently selected radicals R^c ; another preferred embodiment relates to compounds I wherein Het is unsubstituted or substituted by 1, 2, 3, or 4 independently selected radicals R^c .

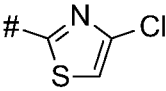
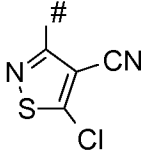
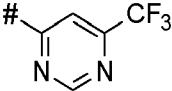
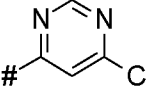
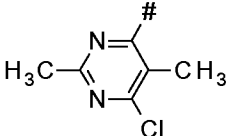
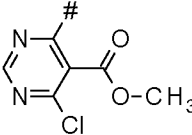
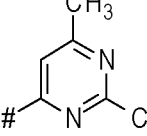
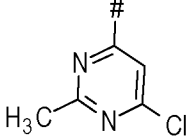
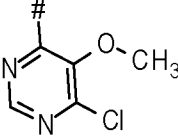
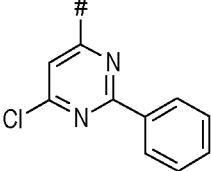
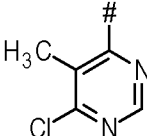
In the compounds I according to the invention, R^c are preferably independently selected from halogen, CN, C_1 - C_6 -alkyl, C_1 - C_6 -haloalkyl, C_1 - C_6 -alkoxy, C_1 - C_6 -haloalkoxy, C_2 - C_6 -alkenyl, C_2 - C_6 -alkynyl, $C(=O)R'$, $C(=NOR'')R'''$, C_3 - C_8 -cycloalkyl, phenyl and phenoxy. In another preferred embodiment R^c are independently selected from halogen, C_1 - C_6 -alkyl, C_1 - C_6 -haloalkyl, C_1 - C_4 -alkoxy and $(C_1$ - C_4 -alkoxy)carbonyl. A further preferred embodiment relates to compounds I wherein R^c are independently selected from F, Cl, CN, CH_3 , OCH_3 , CF_3 , OCF_3 and $COOCH_3$; most preferably R^c are independently selected from Cl, CN and CF_3 .

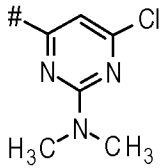
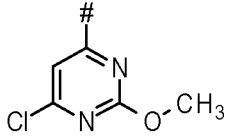
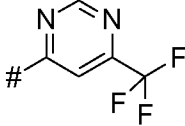
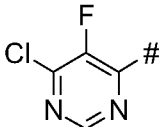
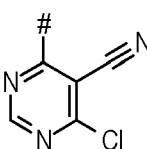
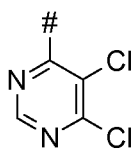
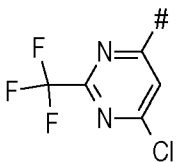
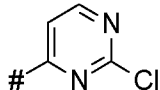
Preferred embodiments of the invention relate to compounds I, in which the group Het is one of the following radicals H-1 to H-38 in table H:

Table H:

No.	Het
H-1	
H-2	
H-3	
H-4	
H-5	
H-6	
H-7	

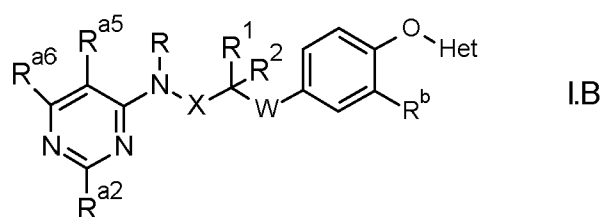
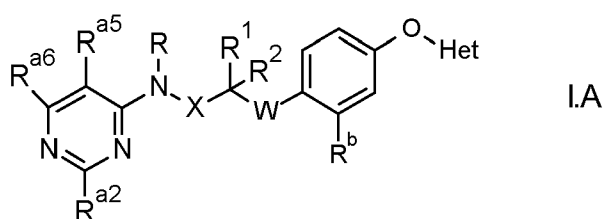
No.	Het
H-8	
H-9	
H-10	
H-11	
H-12	
H-13	
H-14	
H-15	
H-16	
H-17	
H-18	
H-19	

No.	Het
H-20	
H-21	
H-22	
H-23	
H-24	
H-25	
H-26	
H-27	
H-28	
H-29	
H-30	

No.	Het
H-31	
H-32	
H-33	
H-34	
H-35	
H-36	
H-37	
H-38	

in which # indicates the point of attachment.

With respect to their use, particular preference is given to the compounds I.A or I.B.



A skilled person will readily understand that the preferences given in connection with compounds of formula I also apply for formulae I.A or I.B as defined herein.

According to a further embodiment, the present invention relates to compounds of the formula I wherein:

R^{a2} is hydrogen, halogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy or C₁-C₄-haloalkoxy;

R^{a5} , R^{a6} independently of each other are hydrogen, halogen, OH, CN, C₁-C₄-alkyl, C₂-C₄-alkenyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy or (C₁-C₄-alkoxy)carbonyl; or

R^{a5} and R^{a6} together with two ring member carbon atoms to which they are attached, form a fused 5- or 6-membered saturated, partially unsaturated or aromatic carbocycle or heterocycle, wherein the ring member atoms of the fused heterocycle include besides carbon atoms 1, 2 or 3 heteroatoms selected from the group of N, O and S, and wherein the fused carbocycle or heterocycle is unsubstituted or carries 1, 2, 3 or 4 identical or different radicals selected from the group consisting of halogen, CN, C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkyl and C₁-C₄-haloalkoxy;

R is hydrogen, C₁-C₄-alkyl, C₂-C₄-alkenyl or C₂-C₄-alkynyl;

X is a divalent group -CR³R⁴-, wherein

R³ and R⁴ independently of each other are hydrogen, CN, C₁-C₄-hydroxyalkyl, C₁-C₄-alkyl, C₂-C₄-alkenyl, C₂-C₄-alkynyl, C₃-C₈-cycloalkyl;

R¹, R² are independently selected from hydrogen and C₁-C₄-alkyl;

n is 0 or 1;

R^b is halogen or C₁-C₄-alkoxy;

Het is a pyridinyl or pyrimidinyl ring; wherein the moiety O-Het is bound in para- or meta-position to the phenyl ring; and wherein the pyridinyl or pyrimidinyl are unsubstituted or carry 1 or 2 groups R^c; wherein

R^c are independently selected from halogen, C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₁-C₄-alkoxy and (C₁-C₄-alkoxy)carbonyl;

and the N-oxides and the agriculturally acceptable salts of the compounds of formula I.

The compounds I and the compositions according to the invention, respectively, are suitable as fungicides. They are distinguished by an outstanding effectiveness against a broad spectrum of phytopathogenic fungi, including soil-borne fungi, which derive especially from the classes of the Plasmodiophoromycetes, Peronosporomycetes (syn. Oomycetes), Chytridiomycetes, Zygomycetes, Ascomycetes, Basidiomycetes and Deuteromycetes (syn. Fungi imperfecti). Some are systemically effective and they can be used in crop protection as foliar fungicides, fungicides for seed dressing and soil fungicides. Moreover, they are suitable for controlling harmful fungi, which inter alia occur in wood or roots of plants.

The compounds I and the compositions according to the invention are particularly important in the control of a multitude of phytopathogenic fungi on various cultivated plants, such as cereals, e. g. wheat, rye, barley, triticale, oats or rice; beet, e. g. sugar beet or fodder beet; fruits, such as pomes, stone fruits or soft fruits, e. g. apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries, blackberries or gooseberries; leguminous plants, such as lentils,

peas, alfalfa or soybeans; oil plants, such as rape, mustard, olives, sunflowers, coconut, cocoa beans, castor oil plants, oil palms, ground nuts or soybeans; cucurbits, such as squashes, cucumber or melons; fiber plants, such as cotton, flax, hemp or jute; citrus fruit, such as oranges, lemons, grapefruits or mandarins; vegetables, such as spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, cucurbits or paprika; lauraceous plants, such as avocados, cinnamon or camphor; energy and raw material plants, such as corn, soybean, rape, sugar cane or oil palm; corn; tobacco; nuts; coffee; tea; bananas; vines (table grapes and grape juice grape vines); hop; turf; sweet leaf (also called Stevia); natural rubber plants or ornamental and forestry plants, such as flowers, shrubs, broad-leaved trees or evergreens, e. g. conifers; and on the plant propagation material, such as seeds, and the crop material of these plants. Preferably, compounds I and compositions thereof, respectively are used for controlling a multitude of fungi on field crops, such as potatoes sugar beets, tobacco, wheat, rye, barley, oats, rice, corn, cotton, soybeans, rape, legumes, sunflowers, coffee or sugar cane; fruits; vines; ornamentals; or vegetables, such as cucumbers, tomatoes, beans or squashes.

The term "plant propagation material" is to be understood to denote all the generative parts of the plant such as seeds and vegetative plant material such as cuttings and tubers (e. g. potatoes), which can be used for the multiplication of the plant. This includes seeds, roots, fruits, tubers, bulbs, rhizomes, shoots, sprouts and other parts of plants, including seedlings and young plants, which are to be transplanted after germination or after emergence from soil. These young plants may also be protected before transplantation by a total or partial treatment by immersion or pouring. Preferably, treatment of plant propagation materials with compounds I and compositions thereof, respectively, is used for controlling a multitude of fungi on cereals, such as wheat, rye, barley and oats; rice, corn, cotton and soybeans.

The term "cultivated plants" is to be understood as including plants which have been modified by breeding, mutagenesis or genetic engineering including but not limiting to agricultural biotech products on the market or in development (cf. <http://cera-gmc.org/>, see GM crop database therein). Genetically modified plants are plants, which genetic material has been so modified by the use of recombinant DNA techniques that under natural circumstances cannot readily be obtained by cross breeding, mutations or natural recombination. Typically, one or more genes have been integrated into the genetic material of a genetically modified plant in order to improve certain properties of the plant. Such genetic modifications also include but are not limited to targeted post-translational modification of protein(s), oligo- or polypeptides e. g. by glycosylation or polymer additions such as prenylated, acetylated or farnesylated moieties or PEG moieties.

Plants that have been modified by breeding, mutagenesis or genetic engineering, e. g. have been rendered tolerant to applications of specific classes of herbicides, such as auxin herbicides such as dicamba or 2,4-D; bleacher herbicides such as hydroxyphenylpyruvate dioxygenase (HPPD) inhibitors or phytoene desaturase (PDS) inhibitors; acetolactate synthase (ALS) inhibitors such as sulfonyl ureas or imidazolinones; enolpyruvylshikimate-3-phosphate synthase (EPSPS) inhibitors, such as glyphosate; glutamine synthetase (GS) inhibitors such as glufosinate; protoporphyrinogen-IX oxidase inhibitors; lipid biosynthesis inhibitors such as acetyl CoA carboxylase (ACCase) inhibitors; or oxynil (i. e. bromoxynil or ioxynil) herbicides as a result

of conventional methods of breeding or genetic engineering. Furthermore, plants have been made resistant to multiple classes of herbicides through multiple genetic modifications, such as resistance to both glyphosate and glufosinate or to both glyphosate and a herbicide from another class such as ALS inhibitors, HPPD inhibitors, auxin herbicides, or ACCase inhibitors.

5 These herbicide resistance technologies are e. g. described in Pest Managem. Sci. 61, 2005, 246; 61, 2005, 258; 61, 2005, 277; 61, 2005, 269; 61, 2005, 286; 64, 2008, 326; 64, 2008, 332; Weed Sci. 57, 2009, 108; Austral. J. Agricult. Res. 58, 2007, 708; Science 316, 2007, 1185; and references quoted therein. Several cultivated plants have been rendered tolerant to herbicides by conventional methods of breeding (mutagenesis), e. g. Clearfield® summer rape (Canola,
10 BASF SE, Germany) being tolerant to imidazolinones, e. g. imazamox, or ExpressSun® sunflowers (DuPont, USA) being tolerant to sulfonyl ureas, e. g. tribenuron. Genetic engineering methods have been used to render cultivated plants such as soybean, cotton, corn, beets and rape, tolerant to herbicides such as glyphosate and glufosinate, some of which are commercially available under the trade names RoundupReady® (glyphosate-tolerant, Monsanto,
15 U.S.A.), Cultivance® (imidazolinone tolerant, BASF SE, Germany) and LibertyLink® (glufosinate-tolerant, Bayer CropScience, Germany).

Furthermore, plants are also covered that are by the use of recombinant DNA techniques capable to synthesize one or more insecticidal proteins, especially those known from the bacterial genus *Bacillus*, particularly from *Bacillus thuringiensis*, such as δ -endotoxins, e. g.
20 CryIA(b), CryIA(c), CryIF, CryIF(a2), CryIIA(b), CryIIIA, CryIIIB(b1) or Cry9c; vegetative insecticidal proteins (VIP), e. g. VIP1, VIP2, VIP3 or VIP3A; insecticidal proteins of bacteria colonizing nematodes, e. g. *Photorhabdus* spp. or *Xenorhabdus* spp.; toxins produced by animals, such as scorpion toxins, arachnid toxins, wasp toxins, or other insect-specific neurotoxins; toxins produced by fungi, such Streptomyces toxins, plant lectins, such as pea or
25 barley lectins; agglutinins; proteinase inhibitors, such as trypsin inhibitors, serine protease inhibitors, patatin, cystatin or papain inhibitors; ribosome-inactivating proteins (RIP), such as ricin, maize-RIP, abrin, luffin, saporin or bryodin; steroid metabolism enzymes, such as 3-hydroxysteroid oxidase, ecdysteroid-IDP-glycosyl-transferase, cholesterol oxidases, ecdysone inhibitors or HMG-CoA-reductase; ion channel blockers, such as blockers of sodium or calcium
30 channels; juvenile hormone esterase; diuretic hormone receptors (helicokinin receptors); stilben synthase, bibenzyl synthase, chitinases or glucanases. In the context of the present invention these insecticidal proteins or toxins are to be understood expressly also as pre-toxins, hybrid proteins, truncated or otherwise modified proteins. Hybrid proteins are characterized by a new combination of protein domains, (see, e. g. WO 02/015701). Further examples of such toxins or
35 genetically modified plants capable of synthesizing such toxins are disclosed, e. g., in EP-A 374 753, WO 93/007278, WO 95/34656, EP-A 427 529, EP-A 451 878, WO 03/18810 und WO 03/52073. The methods for producing such genetically modified plants are generally known to the person skilled in the art and are described, e. g. in the publications mentioned above. These insecticidal proteins contained in the genetically modified plants impart to the plants
40 producing these proteins tolerance to harmful pests from all taxonomic groups of athropods, especially to beetles (Coeloptera), two-winged insects (Diptera), and moths (Lepidoptera) and to nematodes (Nematoda). Genetically modified plants capable to synthesize one or more

insecticidal proteins are, e. g., described in the publications mentioned above, and some of which are commercially available such as YieldGard® (corn cultivars producing the Cry1Ab toxin), YieldGard® Plus (corn cultivars producing Cry1Ab and Cry3Bb1 toxins), Starlink® (corn cultivars producing the Cry9c toxin), Herculex® RW (corn cultivars producing Cry34Ab1, Cry35Ab1 and the enzyme Phosphinothricin-N-Acetyltransferase [PAT]); NuCOTN® 33B (cotton cultivars producing the Cry1Ac toxin), Bollgard® I (cotton cultivars producing the Cry1Ac toxin), Bollgard® II (cotton cultivars producing Cry1Ac and Cry2Ab2 toxins); VIPCOT® (cotton cultivars producing a VIP-toxin); NewLeaf® (potato cultivars producing the Cry3A toxin); Bt-Xtra®, NatureGard®, KnockOut®, BiteGard®, Protecta®, Bt11 (e. g. Agrisure® CB) and Bt176 from Syngenta Seeds SAS, France, (corn cultivars producing the Cry1Ab toxin and PAT enzyme), MIR604 from Syngenta Seeds SAS, France (corn cultivars producing a modified version of the Cry3A toxin, c.f. WO 03/018810), MON 863 from Monsanto Europe S.A., Belgium (corn cultivars producing the Cry3Bb1 toxin), IPC 531 from Monsanto Europe S.A., Belgium (cotton cultivars producing a modified version of the Cry1Ac toxin) and 1507 from Pioneer Overseas Corporation, Belgium (corn cultivars producing the Cry1F toxin and PAT enzyme).

Furthermore, plants are also covered that are by the use of recombinant DNA techniques capable to synthesize one or more proteins to increase the resistance or tolerance of those plants to bacterial, viral or fungal pathogens. Examples of such proteins are the so-called "pathogenesis-related proteins" (PR proteins, see, e. g. EP-A 392 225), plant disease resistance genes (e. g. potato cultivars, which express resistance genes acting against *Phytophthora infestans* derived from the mexican wild potato *Solanum bulbocastanum*) or T4-lysozym (e. g. potato cultivars capable of synthesizing these proteins with increased resistance against bacteria such as *Erwinia amylovora*). The methods for producing such genetically modified plants are generally known to the person skilled in the art and are described, e. g. in the publications mentioned above.

Furthermore, plants are also covered that are by the use of recombinant DNA techniques capable to synthesize one or more proteins to increase the productivity (e. g. bio mass production, grain yield, starch content, oil content or protein content), tolerance to drought, salinity or other growth-limiting environmental factors or tolerance to pests and fungal, bacterial or viral pathogens of those plants.

Furthermore, plants are also covered that contain by the use of recombinant DNA techniques a modified amount of substances of content or new substances of content, specifically to improve human or animal nutrition, e. g. oil crops that produce health-promoting long-chain omega-3 fatty acids or unsaturated omega-9 fatty acids (e. g. Nexera® rape, DOW Agro Sciences, Canada).

Furthermore, plants are also covered that contain by the use of recombinant DNA techniques a modified amount of substances of content or new substances of content, specifically to improve raw material production, e. g. potatoes that produce increased amounts of amylopectin (e. g. Amflora® potato, BASF SE, Germany).

The compounds I and compositions thereof, respectively, are particularly suitable for controlling the following plant diseases:

Albugo spp. (white rust) on ornamentals, vegetables (e. g. *A. candida*) and sunflowers (e. g. *A. tragopogonis*); *Alternaria* spp. (*Alternaria* leaf spot) on vegetables, rape (*A. brassicola* or *brassicae*), sugar beets (*A. tenuis*), fruits, rice, soybeans, potatoes (e. g. *A. solani* or *A. alternata*), tomatoes (e. g. *A. solani* or *A. alternata*) and wheat; *Aphanomyces* spp. on sugar

5 beets and vegetables; *Ascochyta* spp. on cereals and vegetables, e. g. *A. tritici* (anthracnose) on wheat and *A. hordei* on barley; *Bipolaris* and *Drechslera* spp. (teleomorph: *Cochliobolus* spp.), e. g. Southern leaf blight (*D. maydis*) or Northern leaf blight (*B. zeicola*) on corn, e. g. spot blotch (*B. sorokiniana*) on cereals and e.g. *B. oryzae* on rice and turfs; *Blumeria* (formerly *Erysiphe*) *graminis* (powdery mildew) on cereals (e. g. on wheat or barley); *Botrytis cinerea*

10 (teleomorph: *Botryotinia fuckeliana*: grey mold) on fruits and berries (e. g. strawberries), vegetables (e. g. lettuce, carrots, celery and cabbages), rape, flowers, vines, forestry plants and wheat; *Bremia lactucae* (downy mildew) on lettuce; *Ceratocystis* (syn. *Ophiostoma*) spp. (rot or wilt) on broad-leaved trees and evergreens, e. g. *C. ulmi* (Dutch elm disease) on elms; *Cercospora* spp. (*Cercospora* leaf spots) on corn (e.g. Gray leaf spot: *C. zeae-maydis*), rice,

15 sugar beets (e. g. *C. beticola*), sugar cane, vegetables, coffee, soybeans (e. g. *C. sojae* or *C. kikuchii*) and rice; *Cladosporium* spp. on tomatoes (e. g. *C. fulvum*: leaf mold) and cereals, e. g. *C. herbarum* (black ear) on wheat; *Claviceps purpurea* (ergot) on cereals; *Cochliobolus* (anamorph: *Helminthosporium* of *Bipolaris*) spp. (leaf spots) on corn (*C. carbonum*), cereals (e. g. *C. sativus*, anamorph: *B. sorokiniana*) and rice (e. g. *C. miyabeanus*, anamorph: *H.*

20 *oryzae*); *Colletotrichum* (teleomorph: *Glomerella*) spp. (anthracnose) on cotton (e. g. *C. gossypii*), corn (e. g. *C. graminicola*: Anthracnose stalk rot), soft fruits, potatoes (e. g. *C. coccodes*: black dot), beans (e. g. *C. lindemuthianum*) and soybeans (e. g. *C. truncatum* or *C. gloeosporioides*); *Corticium* spp., e. g. *C. sasakii* (sheath blight) on rice; *Corynespora cassiicola* (leaf spots) on soybeans and ornamentals; *Cycloconium* spp., e. g. *C. oleaginum* on olive trees;

25 *Cylindrocarpon* spp. (e. g. fruit tree canker or young vine decline, teleomorph: *Nectria* or *Neonectria* spp.) on fruit trees, vines (e. g. *C. liriodendri*, teleomorph: *Neonectria liriodendri*: Black Foot Disease) and ornamentals; *Dematophora* (teleomorph: *Rosellinia*) necatrix (root and stem rot) on soybeans; *Diaporthe* spp., e. g. *D. phaseolorum* (damping off) on soybeans; *Drechslera* (syn. *Helminthosporium*, teleomorph: *Pyrenophora*) spp. on corn, cereals, such as

30 barley (e. g. *D. teres*, net blotch) and wheat (e. g. *D. tritici-repentis*: tan spot), rice and turf; Esca (dieback, apoplexy) on vines, caused by *Formitiporia* (syn. *Phellinus*) *punctata*, *F. mediterranea*, *Phaeomoniella chlamydospora* (earlier *Phaeoacremonium chlamydosporum*), *Phaeoacremonium aleophilum* and/or *Botryosphaeria obtusa*; *Elsinoe* spp. on pome fruits (*E. pyri*), soft fruits (*E. veneta*: anthracnose) and vines (*E. ampelina*: anthracnose); *Entyloma*

35 *oryzae* (leaf smut) on rice; *Epicoccum* spp. (black mold) on wheat; *Erysiphe* spp. (powdery mildew) on sugar beets (*E. betae*), vegetables (e. g. *E. pisi*), such as cucurbits (e. g. *E. cichoracearum*), cabbages, rape (e. g. *E. cruciferarum*); *Eutypa lata* (*Eutypa* canker or dieback, anamorph: *Cytosporina lata*, syn. *Libertella blepharis*) on fruit trees, vines and ornamental

40 woods; *Exserohilum* (syn. *Helminthosporium*) spp. on corn (e. g. *E. turcicum*); *Fusarium* (teleomorph: *Gibberella*) spp. (wilt, root or stem rot) on various plants, such as *F. graminearum* or *F. culmorum* (root rot, scab or head blight) on cereals (e. g. wheat or barley), *F. oxysporum* on tomatoes, *F. solani* on soybeans and *F. verticillioides* on corn; *Gaeumannomyces graminis*

(take-all) on cereals (e. g. wheat or barley) and corn; *Gibberella* spp. on cereals (e. g. *G. zeae*) and rice (e. g. *G. fujikuroi*: Bakanae disease); *Glomerella cingulata* on vines, pome fruits and other plants and *G. gossypii* on cotton; Grainstaining complex on rice; *Guignardia bidwellii* (black rot) on vines; *Gymnosporangium* spp. on rosaceous plants and junipers, e. g. *G. sabinae* (rust) on pears; *Helminthosporium* spp. (syn. *Drechslera*, teleomorph: *Cochliobolus*) on corn, cereals and rice; *Hemileia* spp., e. g. *H. vastatrix* (coffee leaf rust) on coffee; *Isariopsis clavispora* (syn. *Cladosporium vitis*) on vines; *Macrophomina phaseolina* (syn. *phaseoli*) (root and stem rot) on soybeans and cotton; *Microdochium* (syn. *Fusarium*) *nivale* (pink snow mold) on cereals (e. g. wheat or barley); *Microsphaera diffusa* (powdery mildew) on soybeans;

5 *Monilinia* spp., e. g. *M. laxa*, *M. fructicola* and *M. fructigena* (bloom and twig blight, brown rot) on stone fruits and other rosaceous plants; *Mycosphaerella* spp. on cereals, bananas, soft fruits and ground nuts, such as e. g. *M. graminicola* (anamorph: *Septoria tritici*, Septoria blotch) on wheat or *M. fijiensis* (black Sigatoka disease) on bananas; *Peronospora* spp. (downy mildew) on cabbage (e. g. *P. brassicae*), rape (e. g. *P. parasitica*), onions (e. g. *P. destructor*), tobacco

10 (*P. tabacina*) and soybeans (e. g. *P. manshurica*); *Phakopsora pachyrhizi* and *P. meibomia* (soybean rust) on soybeans; *Phialophora* spp. e. g. on vines (e. g. *P. tracheiphila* and *P. tetraspora*) and soybeans (e. g. *P. gregata*: stem rot); *Phoma lingam* (root and stem rot) on rape and cabbage and *P. betae* (root rot, leaf spot and damping-off) on sugar beets; *Phomopsis* spp. on sunflowers, vines (e. g. *P. viticola*: can and leaf spot) and soybeans (e. g. stem rot: *P.*

15 *phaseoli*, teleomorph: *Diaporthe phaseolorum*); *Physoderma maydis* (brown spots) on corn; *Phytophthora* spp. (wilt, root, leaf, fruit and stem rot) on various plants, such as paprika and cucurbits (e. g. *P. capsici*), soybeans (e. g. *P. megasperma*, syn. *P. sojae*), potatoes and tomatoes (e. g. *P. infestans*: late blight) and broad-leaved trees (e. g. *P. ramorum*: sudden oak death); *Plasmodiophora brassicae* (club root) on cabbage, rape, radish and other plants;

20 *Plasmopara* spp., e. g. *P. viticola* (grapevine downy mildew) on vines and *P. halstedii* on sunflowers; *Podosphaera* spp. (powdery mildew) on rosaceous plants, hop, pome and soft fruits, e. g. *P. leucotricha* on apples; *Polymyxa* spp., e. g. on cereals, such as barley and wheat (*P. graminis*) and sugar beets (*P. betae*) and thereby transmitted viral diseases;

25 *Pseudocercospora herpotrichoides* (eyespot, teleomorph: *Tapesia yallundae*) on cereals, e. g. wheat or barley; *Pseudoperonospora* (downy mildew) on various plants, e. g. *P. cubensis* on cucurbits or *P. humili* on hop; *Pseudopezizicola tracheiphila* (red fire disease or 'rotbrenner', anamorph: *Phialophora*) on vines; *Puccinia* spp. (rusts) on various plants, e. g. *P. triticina* (brown or leaf rust), *P. striiformis* (stripe or yellow rust), *P. hordei* (dwarf rust), *P. graminis* (stem or black rust) or *P. recondita* (brown or leaf rust) on cereals, such as e. g. wheat, barley or rye,

30 *P. kuehnii* (orange rust) on sugar cane and *P. asparagi* on asparagus; *Pyrenophora* (anamorph: *Drechslera*) *tritici-repentis* (tan spot) on wheat or *P. teres* (net blotch) on barley; *Pyricularia* spp., e. g. *P. oryzae* (teleomorph: *Magnaporthe grisea*, rice blast) on rice and *P. grisea* on turf and cereals; *Pythium* spp. (damping-off) on turf, rice, corn, wheat, cotton, rape, sunflowers, soybeans, sugar beets, vegetables and various other plants (e. g. *P. ultimum* or *P. aphani-*

35 *dermatum*); *Ramularia* spp., e. g. *R. collo-cygni* (Ramularia leaf spots, Physiological leaf spots) on barley and *R. beticola* on sugar beets; *Rhizoctonia* spp. on cotton, rice, potatoes, turf, corn, rape, potatoes, sugar beets, vegetables and various other plants, e. g. *R. solani* (root and stem

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rot) on soybeans, *R. solani* (sheath blight) on rice or *R. cerealis* (Rhizoctonia spring blight) on wheat or barley; *Rhizopus stolonifer* (black mold, soft rot) on strawberries, carrots, cabbage, vines and tomatoes; *Rhynchosporium secalis* (scald) on barley, rye and triticale; *Sarocladium oryzae* and *S. attenuatum* (sheath rot) on rice; *Sclerotinia* spp. (stem rot or white mold) on vegetables and field crops, such as rape, sunflowers (e. g. *S. sclerotiorum*) and soybeans (e. g. *S. rolfii* or *S. sclerotiorum*); *Septoria* spp. on various plants, e. g. *S. glycines* (brown spot) on soybeans, *S. tritici* (Septoria blotch) on wheat and *S.* (syn. *Stagonospora*) *nodorum* (Stagonospora blotch) on cereals; *Uncinula* (syn. *Erysiphe*) *necator* (powdery mildew, anamorph: *Oidium tuckeri*) on vines; *Setosphaeria* spp. (leaf blight) on corn (e. g. *S. turcicum*, syn. *Helminthosporium turcicum*) and turf; *Sphacelotheca* spp. (smut) on corn, (e. g. *S. reiliana*: head smut), sorghum und sugar cane; *Sphaerotheca fuliginea* (powdery mildew) on cucurbits; *Spongospora subterranea* (powdery scab) on potatoes and thereby transmitted viral diseases; *Stagonospora* spp. on cereals, e. g. *S. nodorum* (Stagonospora blotch, teleomorph: *Leptosphaeria* [syn. *Phaeosphaeria*] *nodorum*) on wheat; *Synchytrium endobioticum* on potatoes (potato wart disease); *Taphrina* spp., e. g. *T. deformans* (leaf curl disease) on peaches and *T. pruni* (plum pocket) on plums; *Thielaviopsis* spp. (black root rot) on tobacco, pome fruits, vegetables, soybeans and cotton, e. g. *T. basicola* (syn. *Chalara elegans*); *Tilletia* spp. (common bunt or stinking smut) on cereals, such as e. g. *T. tritici* (syn. *T. caries*, wheat bunt) and *T. controversa* (dwarf bunt) on wheat; *Typhula incarnata* (grey snow mold) on barley or wheat; *Urocystis* spp., e. g. *U. occulta* (stem smut) on rye; *Uromyces* spp. (rust) on vegetables, such as beans (e. g. *U. appendiculatus*, syn. *U. phaseoli*) and sugar beets (e. g. *U. betae*); *Ustilago* spp. (loose smut) on cereals (e. g. *U. nuda* and *U. avenae*), corn (e. g. *U. maydis*: corn smut) and sugar cane; *Venturia* spp. (scab) on apples (e. g. *V. inaequalis*) and pears; and *Verticillium* spp. (wilt) on various plants, such as fruits and ornamentals, vines, soft fruits, vegetables and field crops, e. g. *V. dahliae* on strawberries, rape, potatoes and tomatoes.

The compounds I and compositions thereof, respectively, are also suitable for controlling harmful fungi in the protection of stored products or harvest and in the protection of materials. The term "protection of materials" is to be understood to denote the protection of technical and non-living materials, such as adhesives, glues, wood, paper and paperboard, textiles, leather, paint dispersions, plastics, colling lubricants, fiber or fabrics, against the infestation and destruction by harmful microorganisms, such as fungi and bacteria. As to the protection of wood and other materials, the particular attention is paid to the following harmful fungi: Ascomycetes such as *Ophiostoma* spp., *Ceratocystis* spp., *Aureobasidium pullulans*, *Sclerophoma* spp., *Chaetomium* spp., *Humicola* spp., *Petriella* spp., *Trichurus* spp.; Basidiomycetes such as *Coniophora* spp., *Coriolus* spp., *Gloeophyllum* spp., *Lentinus* spp., *Pleurotus* spp., *Poria* spp., *Serpula* spp. and *Tyromyces* spp.; Deuteromycetes such as *Aspergillus* spp., *Cladosporium* spp., *Penicillium* spp., *Trichorma* spp., *Alternaria* spp., *Paecilomyces* spp. and Zygomycetes such as *Mucor* spp., and in addition in the protection of stored products and harvest the following yeast fungi are worthy of note: *Candida* spp. and *Saccharomyces cerevisiae*.

The compounds I and compositions thereof, respectively, may be used for improving the health of a plant. The invention also relates to a method for improving plant health by treating a

plant, its propagation material and/or the locus where the plant is growing or is to grow with an effective amount of compounds I and compositions thereof, respectively.

The term "plant health" is to be understood to denote a condition of the plant and/or its products which is determined by several indicators alone or in combination with each other such as yield (e. g. increased biomass and/or increased content of valuable ingredients), plant vigor (e. g. improved plant growth and/or greener leaves ("greening effect")), quality (e. g. improved content or composition of certain ingredients) and tolerance to abiotic and/or biotic stress. The above identified indicators for the health condition of a plant may be interdependent or may result from each other.

The compounds of formula I can be present in different crystal modifications whose biological activity may differ. They are likewise subject matter of the present invention.

The compounds I are employed as such or in form of compositions by treating the fungi or the plants, plant propagation materials, such as seeds, soil, surfaces, materials or rooms to be protected from fungal attack with a fungicidally effective amount of the active substances. The application can be carried out both before and after the infection of the plants, plant propagation materials, such as seeds, soil, surfaces, materials or rooms by the fungi.

Plant propagation materials may be treated with compounds I as such or a composition comprising at least one compound I prophylactically either at or before planting or transplanting. The invention also relates to agrochemical compositions comprising an auxiliary and at least one compound I according to the invention.

An agrochemical composition comprises a fungicidally effective amount of a compound I. The term "effective amount" denotes an amount of the composition or of the compounds I, which is sufficient for controlling harmful fungi on cultivated plants or in the protection of materials and which does not result in a substantial damage to the treated plants. Such an amount can vary in a broad range and is dependent on various factors, such as the fungal species to be controlled, the treated cultivated plant or material, the climatic conditions and the specific compound I used.

The compounds I, their N-oxides and salts can be converted into customary types of agrochemical compositions, e. g. solutions, emulsions, suspensions, dusts, powders, pastes, granules, pressings, capsules, and mixtures thereof. Examples for composition types are suspensions (e.g. SC, OD, FS), emulsifiable concentrates (e.g. EC), emulsions (e.g. EW, EO, ES, ME), capsules (e.g. CS, ZC), pastes, pastilles, wettable powders or dusts (e.g. WP, SP, WS, DP, DS), pressings (e.g. BR, TB, DT), granules (e.g. WG, SG, GR, FG, GG, MG), insecticidal articles (e.g. LN), as well as gel formulations for the treatment of plant propagation materials such as seeds (e.g. GF). These and further compositions types are defined in the "Catalogue of pesticide formulation types and international coding system", Technical Monograph No. 2, 6th Ed. May 2008, CropLife International.

The compositions are prepared in a known manner, such as described by Mollet and Grubemann, Formulation technology, Wiley VCH, Weinheim, 2001; or Knowles, New developments in crop protection product formulation, Agrow Reports DS243, T&F Informa, London, 2005.

Suitable auxiliaries are solvents, liquid carriers, solid carriers or fillers, surfactants, dispersants, emulsifiers, wetters, adjuvants, solubilizers, penetration enhancers, protective colloids, adhesion agents, thickeners, humectants, repellents, attractants, feeding stimulants, compatibilizers, bactericides, anti-freezing agents, anti-foaming agents, colorants, tackifiers and binders.

Suitable solvents and liquid carriers are water and organic solvents, such as mineral oil fractions of medium to high boiling point, e.g. kerosene, diesel oil; oils of vegetable or animal origin; aliphatic, cyclic and aromatic hydrocarbons, e. g. toluene, paraffin, tetrahydronaphthalene, alkylated naphthalenes; alcohols, e.g. ethanol, propanol, butanol, benzylalcohol, cyclohexanol; glycols; DMSO; ketones, e.g. cyclohexanone; esters, e.g. lactates, carbonates, fatty acid esters, gamma-butyrolactone; fatty acids; phosphonates; amines; amides, e.g. N-methylpyrrolidone, fatty acid dimethylamides; and mixtures thereof.

Suitable solid carriers or fillers are mineral earths, e.g. silicates, silica gels, talc, kaolins, limestone, lime, chalk, clays, dolomite, diatomaceous earth, bentonite, calcium sulfate, magnesium sulfate, magnesium oxide; polysaccharides, e.g. cellulose, starch; fertilizers, e.g. ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas; products of vegetable origin, e.g. cereal meal, tree bark meal, wood meal, nutshell meal, and mixtures thereof.

Suitable surfactants are surface-active compounds, such as anionic, cationic, nonionic and amphoteric surfactants, block polymers, polyelectrolytes, and mixtures thereof. Such surfactants can be used as emulsifier, dispersant, solubilizer, wetter, penetration enhancer, protective colloid, or adjuvant. Examples of surfactants are listed in McCutcheon's, Vol.1: Emulsifiers & Detergents, McCutcheon's Directories, Glen Rock, USA, 2008 (International Ed. or North American Ed.).

Suitable anionic surfactants are alkali, alkaline earth or ammonium salts of sulfonates, sulfates, phosphates, carboxylates, and mixtures thereof. Examples of sulfonates are alkylarylsulfonates, diphenylsulfonates, alpha-olefin sulfonates, lignine sulfonates, sulfonates of fatty acids and oils, sulfonates of ethoxylated alkylphenols, sulfonates of alkoxyated arylphenols, sulfonates of condensed naphthalenes, sulfonates of dodecyl- and tridecylbenzenes, sulfonates of naphthalenes and alkylnaphthalenes, sulfosuccinates or sulfosuccinamates. Examples of sulfates are sulfates of fatty acids and oils, of ethoxylated alkylphenols, of alcohols, of ethoxylated alcohols, or of fatty acid esters. Examples of phosphates are phosphate esters. Examples of carboxylates are alkyl carboxylates, and carboxylated alcohol or alkylphenol ethoxylates.

Suitable nonionic surfactants are alkoxyates, N-substituted fatty acid amides, amine oxides, esters, sugar-based surfactants, polymeric surfactants, and mixtures thereof. Examples of alkoxyates are compounds such as alcohols, alkylphenols, amines, amides, arylphenols, fatty acids or fatty acid esters which have been alkoxyated with 1 to 50 equivalents. Ethylene oxide and/or propylene oxide may be employed for the alkoxylation, preferably ethylene oxide.

Examples of N-substituted fatty acid amides are fatty acid glucamides or fatty acid alkanolamides. Examples of esters are fatty acid esters, glycerol esters or monoglycerides.

Examples of sugar-based surfactants are sorbitans, ethoxylated sorbitans, sucrose and glucose

esters or alkylpolyglucosides. Examples of polymeric surfactants are home- or copolymers of vinylpyrrolidone, vinylalcohols, or vinylacetate.

Suitable cationic surfactants are quaternary surfactants, for example quaternary ammonium compounds with one or two hydrophobic groups, or salts of long-chain primary amines. Suitable amphoteric surfactants are alkylbetains and imidazolines. Suitable block polymers are block polymers of the A-B or A-B-A type comprising blocks of polyethylene oxide and polypropylene oxide, or of the A-B-C type comprising alkanol, polyethylene oxide and polypropylene oxide. Suitable polyelectrolytes are polyacids or polybases. Examples of polyacids are alkali salts of polyacrylic acid or polyacid comb polymers. Examples of polybases are polyvinylamines or polyethyleneamines.

Suitable adjuvants are compounds, which have a neglectable or even no pesticidal activity themselves, and which improve the biological performance of the compound I on the target. Examples are surfactants, mineral or vegetable oils, and other auxiliaries. Further examples are listed by Knowles, Adjuvants and additives, Agrow Reports DS256, T&F Informa UK, 2006, chapter 5.

Suitable thickeners are polysaccharides (e.g. xanthan gum, carboxymethylcellulose), anorganic clays (organically modified or unmodified), polycarboxylates, and silicates.

Suitable bactericides are bronopol and isothiazolinone derivatives such as alkylisothiazolinones and benzisothiazolinones.

Suitable anti-freezing agents are ethylene glycol, propylene glycol, urea and glycerin.

Suitable anti-foaming agents are silicones, long chain alcohols, and salts of fatty acids.

Suitable colorants (e.g. in red, blue, or green) are pigments of low water solubility and water-soluble dyes. Examples are inorganic colorants (e.g. iron oxide, titan oxide, iron hexacyanoferrate) and organic colorants (e.g. alizarin-, azo- and phthalocyanine colorants).

Suitable tackifiers or binders are polyvinylpyrrolidons, polyvinylacetates, polyvinyl alcohols, polyacrylates, biological or synthetic waxes, and cellulose ethers.

Examples for composition types and their preparation are:

i) Water-soluble concentrates (SL, LS)

10-60 wt% of a compound I and 5-15 wt% wetting agent (e.g. alcohol alkoxyates) are dissolved in water and/or in a water-soluble solvent (e.g. alcohols) ad 100 wt%. The active substance dissolves upon dilution with water.

ii) Dispersible concentrates (DC)

5-25 wt% of a compound I and 1-10 wt% dispersant (e. g. polyvinylpyrrolidone) are dissolved in organic solvent (e.g. cyclohexanone) ad 100 wt%. Dilution with water gives a dispersion.

iii) Emulsifiable concentrates (EC)

15-70 wt% of a compound I and 5-10 wt% emulsifiers (e.g. calcium dodecylbenzenesulfonate and castor oil ethoxylate) are dissolved in water-insoluble organic solvent (e.g. aromatic hydrocarbon) ad 100 wt%. Dilution with water gives an emulsion.

iv) Emulsions (EW, EO, ES)

5-40 wt% of a compound I and 1-10 wt% emulsifiers (e.g. calcium dodecylbenzenesulfonate and castor oil ethoxylate) are dissolved in 20-40 wt% water-insoluble organic solvent (e.g.

aromatic hydrocarbon). This mixture is introduced into water ad 100 wt% by means of an emulsifying machine and made into a homogeneous emulsion. Dilution with water gives an emulsion.

v) Suspensions (SC, OD, FS)

- 5 In an agitated ball mill, 20-60 wt% of a compound I are comminuted with addition of 2-10 wt% dispersants and wetting agents (e.g. sodium lignosulfonate and alcohol ethoxylate), 0.1-2 wt% thickener (e.g. xanthan gum) and water ad 100 wt% to give a fine active substance suspension. Dilution with water gives a stable suspension of the active substance. For FS type composition up to 40 wt% binder (e.g. polyvinylalcohol) is added.

10 vi) Water-dispersible granules and water-soluble granules (WG, SG)

50-80 wt% of a compound I are ground finely with addition of dispersants and wetting agents (e.g. sodium lignosulfonate and alcohol ethoxylate) ad 100 wt% and prepared as water-dispersible or water-soluble granules by means of technical appliances (e. g. extrusion, spray tower, fluidized bed). Dilution with water gives a stable dispersion or solution of the active substance.

15 vii) Water-dispersible powders and water-soluble powders (WP, SP, WS)

50-80 wt% of a compound I are ground in a rotor-stator mill with addition of 1-5 wt% dispersants (e.g. sodium lignosulfonate), 1-3 wt% wetting agents (e.g. alcohol ethoxylate) and solid carrier (e.g. silica gel) ad 100 wt%. Dilution with water gives a stable dispersion or solution of the active substance.

20 viii) Gel (GW, GF)

In an agitated ball mill, 5-25 wt% of a compound I are comminuted with addition of 3-10 wt% dispersants (e.g. sodium lignosulfonate), 1-5 wt% thickener (e.g. carboxymethylcellulose) and water ad 100 wt% to give a fine suspension of the active substance. Dilution with water gives a stable suspension of the active substance.

25 ix) Microemulsion (ME)

5-20 wt% of a compound I are added to 5-30 wt% organic solvent blend (e.g. fatty acid dimethylamide and cyclohexanone), 10-25 wt% surfactant blend (e.g. alcohol ethoxylate and arylphenol ethoxylate), and water ad 100 %. This mixture is stirred for 1 h to produce spontaneously a thermodynamically stable microemulsion.

30 x) Microcapsules (CS)

An oil phase comprising 5-50 wt% of a compound I, 0-40 wt% water insoluble organic solvent (e.g. aromatic hydrocarbon), 2-15 wt% acrylic monomers (e.g. methylmethacrylate, methacrylic acid and a di- or triacrylate) are dispersed into an aqueous solution of a protective colloid (e.g. polyvinyl alcohol). Radical polymerization initiated by a radical initiator results in the formation of poly(meth)acrylate microcapsules. Alternatively, an oil phase comprising 5-50 wt% of a compound I according to the invention, 0-40 wt% water insoluble organic solvent (e.g. aromatic hydrocarbon), and an isocyanate monomer (e.g. diphenylmethene-4,4'-diisocyanatae) are dispersed into an aqueous solution of a protective colloid (e.g. polyvinyl alcohol). The addition of a polyamine (e.g. hexamethylenediamine) results in the formation of polyurea microcapsules. The monomers amount to 1-10 wt%. The wt% relate to the total CS composition.

40 xi) Dustable powders (DP, DS)

1-10 wt% of a compound I are ground finely and mixed intimately with solid carrier (e.g. finely divided kaolin) ad 100 wt%.

xii) Granules (GR, FG)

0.5-30 wt% of a compound I is ground finely and associated with solid carrier (e.g. silicate) ad 100 wt%. Granulation is achieved by extrusion, spray-drying or fluidized bed.

xiii) Ultra-low volume liquids (UL)

1-50 wt% of a compound I are dissolved in organic solvent (e.g. aromatic hydrocarbon) ad 100 wt%.

The compositions types i) to xiii) may optionally comprise further auxiliaries, such as 0.1-1 wt% bactericides, 5-15 wt% anti-freezing agents, 0.1-1 wt% anti-foaming agents, and 0.1-1 wt% colorants.

The agrochemical compositions generally comprise between 0.01 and 95%, preferably between 0.1 and 90%, and in particular between 0.5 and 75%, by weight of active substance. The active substances are employed in a purity of from 90% to 100%, preferably from 95% to 100% (according to NMR spectrum).

Solutions for seed treatment (LS), Suspoemulsions (SE), flowable concentrates (FS), powders for dry treatment (DS), water-dispersible powders for slurry treatment (WS), water-soluble powders (SS), emulsions (ES), emulsifiable concentrates (EC) and gels (GF) are usually employed for the purposes of treatment of plant propagation materials, particularly seeds. The compositions in question give, after two-to-tenfold dilution, active substance concentrations of from 0.01 to 60% by weight, preferably from 0.1 to 40%, in the ready-to-use preparations.

Application can be carried out before or during sowing. Methods for applying compound I and compositions thereof, respectively, on to plant propagation material, especially seeds include dressing, coating, pelleting, dusting, soaking and in-furrow application methods of the propagation material. Preferably, compound I or the compositions thereof, respectively, are applied on to the plant propagation material by a method such that germination is not induced, e. g. by seed dressing, pelleting, coating and dusting.

When employed in plant protection, the amounts of active substances applied are, depending on the kind of effect desired, from 0.001 to 2 kg per ha, preferably from 0.005 to 2 kg per ha, more preferably from 0.05 to 0.9 kg per ha, and in particular from 0.1 to 0.75 kg per ha.

In treatment of plant propagation materials such as seeds, e. g. by dusting, coating or drenching seed, amounts of active substance of from 0.1 to 1000 g, preferably from 1 to 1000 g, more preferably from 1 to 100 g and most preferably from 5 to 100 g, per 100 kilogram of plant propagation material (preferably seeds) are generally required.

When used in the protection of materials or stored products, the amount of active substance applied depends on the kind of application area and on the desired effect. Amounts customarily applied in the protection of materials are 0.001 g to 2 kg, preferably 0.005 g to 1 kg, of active substance per cubic meter of treated material.

Various types of oils, wetters, adjuvants, fertilizer, or micronutrients, and further pesticides (e.g. herbicides, insecticides, fungicides, growth regulators, safeners) may be added to the active

substances or the compositions comprising them as premix or, if appropriate not until immediately prior to use (tank mix). These agents can be admixed with the compositions according to the invention in a weight ratio of 1:100 to 100:1, preferably 1:10 to 10:1.

The user applies the composition according to the invention usually from a predosage device, a
 5 knapsack sprayer, a spray tank, a spray plane, or an irrigation system. Usually, the agrochemical composition is made up with water, buffer, and/or further auxiliaries to the desired application concentration and the ready-to-use spray liquor or the agrochemical composition according to the invention is thus obtained. Usually, 20 to 2000 liters, preferably 50 to 400 liters, of the ready-to-use spray liquor are applied per hectare of agricultural useful area.

10 According to one embodiment, individual components of the composition according to the invention such as parts of a kit or parts of a binary or ternary mixture may be mixed by the user himself in a spray tank and further auxiliaries may be added, if appropriate.

Mixing the compounds I or the compositions comprising them in the use form as fungicides with other fungicides results in many cases in an expansion of the fungicidal spectrum of activity
 15 being obtained or in a prevention of fungicide resistance development. Furthermore, in many cases, synergistic effects are obtained.

The following list of active substances, in conjunction with which the compounds I can be used, is intended to illustrate the possible combinations but does not limit them:

A) Respiration inhibitors

20 - Inhibitors of complex III at Q_o site (e.g. strobilurins): azoxystrobin, coumethoxystrobin, coumoxystrobin, dimoxystrobin, enestroburin, fenaminstrobin, fenoxystrobin/flufenoxystrobin, fluoxastrobin, kresoxim-methyl, metominostrobin, orysastrobin, picoxystrobin, pyraclostrobin, pyrametostrobin, pyraoxystrobin, trifloxystrobin, 2-[2-(2,5-dimethyl-phenoxy-methyl)-phenyl]-3-methoxy-acrylic acid methyl ester and 2-(2-(3-(2,6-dichlorophenyl)-1-methyl-allylideneamino-oxy-methyl)-phenyl)-2-methoxyimino-N-methyl-acetamide, pyribencarb, triclopyricarb/chlorodincarb, famoxadone, fenamidone;

- inhibitors of complex III at Q_i site: cyazofamid, amisulbrom, [(3S,6S,7R,8R)-8-benzyl-3-[(3-acetoxy-4-methoxy-pyridine-2-carbonyl)amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate, [(3S,6S,7R,8R)-8-benzyl-3-[[3-(acetoxymethoxy)-4-methoxy-pyridine-2-carbonyl]amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate, [(3S,6S,7R,8R)-8-benzyl-3-[(3-isobutoxycarbonyloxy-4-methoxy-pyridine-2-carbonyl)amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate, [(3S,6S,7R,8R)-8-benzyl-3-[[3-(1,3-benzodioxol-5-ylmethoxy)-4-methoxy-pyridine-2-carbonyl]amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate; (3S,6S,7R,8R)-3-[[3-(3-hydroxy-4-methoxy-2-pyridinyl)carbonyl]amino]-6-methyl-4,9-dioxo-8-(phenylmethyl)-1,5-dioxonan-7-yl 2-methylpropanoate
 35

- inhibitors of complex II (e. g. carboxamides): benodanil, benzovindiflupyr, bixafen, boscalid, carboxin, fenfuram, fluopyram, flutolanil, fluxapyroxad, furametpyr, isopyrazam, mepronil, oxycarboxin, penflufen, penthiopyrad, sedaxane, tecloftalam, thifluzamide, N-(4'-trifluoromethylthiobiphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-(2-(1,3,3-trimethyl-butyl)-phenyl)-1,3-dimethyl-5-fluoro-1H-pyrazole-4-carboxamide,
 40 3-(difluoromethyl)-1-methyl-N-(1,1,3-trimethylindan-4-yl)pyrazole-4-carboxamide, 3-(trifluoromethyl)-1-methyl-N-(1,1,3-trimethylindan-4-yl)pyrazole-4-carboxamide, 1,3-dimethyl-

N-(1,1,3-trimethylindan-4-yl)pyrazole-4-carboxamide, 3-(trifluoromethyl)-1,5-dimethyl-N-(1,1,3-trimethylindan-4-yl)pyrazole-4-carboxamide, 3-(difluoromethyl)-1,5-dimethyl-N-(1,1,3-trimethylindan-4-yl)pyrazole-4-carboxamide, 1,3,5-trimethyl-N-(1,1,3-trimethylindan-4-yl)pyrazole-4-carboxamide;

- 5 - other respiration inhibitors (e.g. complex I, uncouplers): diflumetorim, (5,8-difluoroquinazolin-4-yl)-{2-[2-fluoro-4-(4-trifluoromethylpyridin-2-yloxy)-phenyl]-ethyl}-amine; nitrophenyl derivatives: binapacryl, dinobuton, dinocap, fluazinam; ferimzone; organometal compounds: fentin salts, such as fentin-acetate, fentin chloride or fentin hydroxide; ametoctradin; and silthiofam;
- 10 B) Sterol biosynthesis inhibitors (SBI fungicides)
 - C14 demethylase inhibitors (DMI fungicides): triazoles: azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole, diniconazole-M, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imibenconazole, ipconazole, metconazole, myclobutanil, oxpoconazole, paclobutrazole, penconazole,
 - 15 propiconazole, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triticonazole, uniconazole,
1-[*rel*-(2*S*;3*R*)-3-(2-chlorophenyl)-2-(2,4-difluorophenyl)-oxiranylmethyl]-5-thiocyanato-1*H*-[1,2,4]triazole, 2-[*rel*-(2*S*;3*R*)-3-(2-chlorophenyl)-2-(2,4-difluorophenyl)-oxiranylmethyl]-2*H*-[1,2,4]triazole-3-thiol; imidazoles: imazalil, pefurazoate, prochloraz, triflumizol; pyrimidines,
 - 20 pyridines and piperazines: fenarimol, nuarimol, pyrifenoxy, triforine;
 - Delta14-reductase inhibitors: aldimorph, dodemorph, dodemorph-acetate, fenpropimorph, tridemorph, fenpropidin, piperalin, spiroxamine;
 - Inhibitors of 3-keto reductase: fenhexamid;
- C) Nucleic acid synthesis inhibitors
- 25 - phenylamides or acyl amino acid fungicides: benalaxyl, benalaxyl-M, kiralaxyl, metalaxyl, metalaxyl-M (mefenoxam), ofurace, oxadixyl;
 - others: hymexazole, oethilinone, oxolinic acid, bupirimate, 5-fluorocytosine, 5-fluoro-2-(*p*-tolylmethoxy)pyrimidin-4-amine, 5-fluoro-2-(4-fluorophenylmethoxy)pyrimidin-4-amine;
- D) Inhibitors of cell division and cytoskeleton
- 30 - tubulin inhibitors, such as benzimidazoles, thiophanates: benomyl, carbendazim, fuberidazole, thiabendazole, thiophanate-methyl; triazolopyrimidines: 5-chloro-7-(4-methylpiperidin-1-yl)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine
 - other cell division inhibitors: diethofencarb, ethaboxam, pencycuron, fluopicolide, zoxamide, metrafenone, pyriofenone;
- 35 E) Inhibitors of amino acid and protein synthesis
 - methionine synthesis inhibitors (anilino-pyrimidines): cyprodinil, mepanipyrim, pyrimethanil;
 - protein synthesis inhibitors: blasticidin-S, kasugamycin, kasugamycin hydrochloride-hydrate, mildiomyacin, streptomycin, oxytetracyclin, polyoxine, validamycin A;
- 40 F) Signal transduction inhibitors
 - MAP / histidine kinase inhibitors: fluoroimid, iprodione, procymidone, vinclozolin, fenpiclonil, fludioxonil;

- G protein inhibitors: quinoxifen;

G) Lipid and membrane synthesis inhibitors

- Phospholipid biosynthesis inhibitors: edifenphos, iprobenfos, pyrazophos, isoprothiolane;
- lipid peroxidation: dicloran, quintozone, tecnazene, tolclofos-methyl, biphenyl, chloroneb,
5 etridiazole;

- phospholipid biosynthesis and cell wall deposition: dimethomorph, flumorph,
mandipropamid, pyrimorph, benthiavalicarb, iprovalicarb, valifenalate and N-(1-(1-(4-cyano-
phenyl)ethanesulfonyl)-but-2-yl) carbamic acid-(4-fluorophenyl) ester;

- compounds affecting cell membrane permeability and fatty acids: propamocarb,
10 propamocarb-hydrochlorid

- fatty acid amide hydrolase inhibitors: oxathiapiprolin;

H) Inhibitors with Multi Site Action

- inorganic active substances: Bordeaux mixture, copper acetate, copper hydroxide, copper
oxychloride, basic copper sulfate, sulfur;

15 - thio- and dithiocarbamates: ferbam, mancozeb, maneb, metam, metiram, propineb,
thiram, zineb, ziram;

- organochlorine compounds (e.g. phthalimides, sulfamides, chloronitriles): anilazine,
chlorothalonil, captafol, captan, folpet, dichlofluanid, dichlorophen, hexachlorobenzene,
pentachlorophenol and its salts, phthalide, tolylfluanid, N-(4-chloro-2-nitro-phenyl)-N-ethyl-4-
20 methyl-benzenesulfonamide;

- guanidines and others: guanidine, dodine, dodine free base, guazatine, guazatine-
acetate, iminoctadine, iminoctadine-triacetate, iminoctadine-tris(albesilate), dithianon, 2,6-
dimethyl-1H,5H-[1,4]dithiino[2,3-c:5,6-c']dipyrrole-1,3,5,7(2H,6H)-tetraone;

I) Cell wall synthesis inhibitors

25 - inhibitors of glucan synthesis: validamycin, polyoxin B; melanin synthesis inhibitors:
pyroquilon, tricyclazole, carpropamid, dicyclomet, fenoxanil;

J) Plant defence inducers

- acibenzolar-S-methyl, probenazole, isotianil, tiadinil, prohexadione-calcium;
phosphonates: fosetyl, fosetyl-aluminum, phosphorous acid and its salts;

30 K) Unknown mode of action

- bronopol, chinomethionat, cyflufenamid, cymoxanil, dazomet, debacarb, diclomezine,
difenzoquat, difenzoquat-methylsulfate, diphenylamin, fenpyrazamine, flumetover, flusulfamide,
flutianil, methasulfocarb, nitrapyrin, nitrothal-isopropyl, oxathiapiprolin, 2-[3,5-
35 bis(difluoromethyl)-1H-pyrazol-1-yl]-1-[4-(4-{5-[2-(prop-2-yn-1-yloxy)phenyl]-4,5-dihydro-1,2-
oxazol-3-yl]-1,3-thiazol-2-yl)piperidin-1-yl]ethanone, 2-[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]-
1-[4-(4-{5-[2-fluoro-6-(prop-2-yn-1-yloxy)phenyl]-4,5-dihydro-1,2-oxazol-3-yl]-1,3-thiazol-2-
yl)piperidin-1-yl]ethanone, 2-[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]-1-[4-(4-{5-[2-chloro-6-
(prop-2-yn-1-yloxy)phenyl]-4,5-dihydro-1,2-oxazol-3-yl]-1,3-thiazol-2-yl)piperidin-1-yl]ethanone,
oxin-copper, proquinazid, tebufloquin, tecloftalam, triazoxide, 2-butoxy-6-iodo-3-propylchromen-
40 4-one, N-(cyclopropylmethoxyimino-(6-difluoro-methoxy-2,3-difluoro-phenyl)-methyl)-2-phenyl
acetamide, N'-(4-(4-chloro-3-trifluoromethyl-phenoxy)-2,5-dimethyl-phenyl)-N-ethyl-N-methyl
formamidine, N'-(4-(4-fluoro-3-trifluoromethyl-phenoxy)-2,5-dimethyl-phenyl)-N-ethyl-N-methyl

formamidine, N'-(2-methyl-5-trifluoromethyl-4-(3-trimethylsilanyl-propoxy)-phenyl)-N-ethyl-N-methyl formamidine, N'-(5-difluoromethyl-2-methyl-4-(3-trimethylsilanyl-propoxy)-phenyl)-N-ethyl-N-methyl formamidine, methoxy-acetic acid 6-tert-butyl-8-fluoro-2,3-dimethyl-quinolin-4-yl ester, 3-[5-(4-methylphenyl)-2,3-dimethyl-isoxazolidin-3-yl]-pyridine, 3-[5-(4-chloro-phenyl)-2,3-dimethyl-isoxazolidin-3-yl]-pyridine (pyrisoxazole),
 5 N-(6-methoxy-pyridin-3-yl) cyclopropanecarboxylic acid amide, 5-chloro-1-(4,6-dimethoxy-pyrimidin-2-yl)-2-methyl-1H-benzimidazole, 2-(4-chloro-phenyl)-
 N-[4-(3,4-dimethoxy-phenyl)-isoxazol-5-yl]-2-prop-2-ynyloxy-acetamide;

L) Antifungal biocontrol agents, plant bioactivators: *Ampelomyces quisqualis* (e.g. AQ 10®
 10 from Intrachem Bio GmbH & Co. KG, Germany), *Aspergillus flavus* (e.g. AFLAGUARD® from Syngenta, CH), *Aureobasidium pullulans* (e.g. BOTECTOR® from bio-ferm GmbH, Germany), *Bacillus pumilus* (e.g. NRRL Accession No. B-30087 in SONATA® and BALLAD® Plus from AgraQuest Inc., USA), *Bacillus subtilis* (e.g. isolate NRRL-Nr. B-21661 in RHAPSODY®, SERENADE® MAX and SERENADE® ASO from AgraQuest Inc., USA), *Bacillus subtilis* var.
 15 *amyloliquefaciens* FZB24 (e.g. TAEGR0® from Novozyme Biologicals, Inc., USA), *Candida oleophila* I-82 (e.g. ASPIRE® from Ecogen Inc., USA), *Candida saitoana* (e.g. BIOCURE® (in mixture with lysozyme) and BIOCOAT® from Micro Flo Company, USA (BASF SE) and Arysta), Chitosan (e.g. ARMOUR-ZEN from BotriZen Ltd., NZ), *Clonostachys rosea* f. *catenulata*, also named *Gliocladium catenulatum* (e.g. isolate J1446: PRESTOP® from Verdera, Finland),
 20 *Coniothyrium minitans* (e.g. CONTANS® from Prophyta, Germany), *Cryphonectria parasitica* (e.g. *Endothia parasitica* from CNICM, France), *Cryptococcus albidus* (e.g. YIELD PLUS® from Anchor Bio-Technologies, South Africa), *Fusarium oxysporum* (e.g. BIOFOX® from S.I.A.P.A., Italy, FUSACLEAN® from Natural Plant Protection, France), *Metschnikowia fructicola* (e.g. SHEMER® from Agrogreen, Israel), *Microdochium dimerum* (e.g. ANTIBOT® from Agrauxine,
 25 France), *Phlebiopsis gigantea* (e.g. ROTSOP® from Verdera, Finland), *Pseudozyma flocculosa* (e.g. SPORODEX® from Plant Products Co. Ltd., Canada), *Pythium oligandrum* DV74 (e.g. POLYVERSUM® from Remeslo SSRO, Biopreparaty, Czech Rep.), *Reynoutria sachlinensis* (e.g. REGALIA® from Marrone BioInnovations, USA), *Talaromyces flavus* V117b (e.g. PROTUS® from Prophyta, Germany), *Trichoderma asperellum* SKT-1 (e.g. ECO-HOPE® from
 30 Kumiai Chemical Industry Co., Ltd., Japan), *T. atroviride* LC52 (e.g. SENTINEL® from Agrimm Technologies Ltd, NZ), *T. harzianum* T-22 (e.g. PLANTSHIELD® der Firma BioWorks Inc., USA), *T. harzianum* TH 35 (e.g. ROOT PRO® from Mycontrol Ltd., Israel), *T. harzianum* T-39 (e.g. TRICHODEX® and TRICHODERMA 2000® from Mycontrol Ltd., Israel and Makhteshim
 35 Ltd., Israel), *T. harzianum* and *T. viride* (e.g. TRICHOPEL from Agrimm Technologies Ltd, NZ), *T. harzianum* ICC012 and *T. viride* ICC080 (e.g. REMEDIER® WP from Isagro Ricerca, Italy), *T. polysporum* and *T. harzianum* (e.g. BINAB® from BINAB Bio-Innovation AB, Sweden), *T. stromaticum* (e.g. TRICOVAB® from C.E.P.L.A.C., Brazil), *T. virens* GL-21 (e.g. SOILGARD® from Certis LLC, USA), *T. viride* (e.g. TRIECO® from Ecosense Labs. (India) Pvt. Ltd., Indien, BIO-CURE® F from T. Stanes & Co. Ltd., Indien), *T. viride* TV1 (e.g. T. viride TV1 from
 40 Agribiotec srl, Italy), *Ulocladium oudemansii* HRU3 (e.g. BOTRY-ZEN® from Botry-Zen Ltd, NZ);
 M) Growth regulators

abscisic acid, amidochlor, ancymidol, 6-benzylaminopurine, brassinolide, butralin, chlormequat (chlormequat chloride), choline chloride, cyclanilide, daminozide, dikegulac, dimethipin, 2,6-dimethylpuridine, ethephon, flumetralin, flurprimidol, fluthiacet, forchlorfenuron, gibberellic acid, inabenfide, indole-3-acetic acid, maleic hydrazide, mefluidide, mepiquat (mepiquat chloride),
 5 naphthaleneacetic acid, N-6-benzyladenine, paclobutrazol, prohexadione (prohexadione-calcium), prohydrojasmon, thidiazuron, triapenthenol, tributyl phosphorotrithioate, 2,3,5-tri-iodobenzoic acid, trinexapac-ethyl and uniconazole;

N) Herbicides

- acetamides: acetochlor, alachlor, butachlor, dimethachlor, dimethenamid, flufenacet,
 10 mefenacet, metolachlor, metazachlor, napropamide, naproanilide, pethoxamid, pretilachlor, propachlor, thenylchlor;
- amino acid derivatives: bilanafos, glyphosate, glufosinate, sulfosate;
- aryloxyphenoxypropionates: clodinafop, cyhalofop-butyl, fenoxaprop, fluazifop, haloxyfop, metamifop, propaquizafop, quizalofop, quizalofop-P-tefuryl;
- 15 - Bipyridyls: diquat, paraquat;
- (thio)carbamates: asulam, butylate, carbetamide, desmedipham, dimepiperate, eptam (EPTC), esprocarb, molinate, orbencarb, phenmedipham, prosulfocarb, pyributicarb, thiobencarb, triallate;
- cyclohexanediones: butoxydim, clethodim, cycloxydim, profoxydim, sethoxydim,
 20 tepraloxydim, tralkoxydim;
- dinitroanilines: benfluralin, ethalfluralin, oryzalin, pendimethalin, prodiamine, trifluralin;
- diphenyl ethers: acifluorfen, aclonifen, bifenox, diclofop, ethoxyfen, fomesafen, lactofen, oxyfluorfen;
- hydroxybenzonitriles: bomoxynil, dichlobenil, ioxynil;
- 25 - imidazolinones: imazamethabenz, imazamox, imazapic, imazapyr, imazaquin, imazethapyr;
- phenoxy acetic acids: clomeprop, 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4-DB, dichlorprop, MCPA, MCPA-thioethyl, MCPB, Mecoprop;
- pyrazines: chloridazon, flufenpyr-ethyl, fluthiacet, norflurazon, pyridate;
- 30 - pyridines: aminopyralid, clopyralid, diflufenican, dithiopyr, fluridone, fluroxypyr, picloram, picolinafen, thiazopyr;
- sulfonfyl ureas: amidosulfuron, azimsulfuron, bensulfuron, chlorimuron-ethyl, chlorsulfuron, cinosulfuron, cyclosulfamuron, ethoxysulfuron, flazasulfuron, flucetosulfuron, flupyrsulfuron, foramsulfuron, halosulfuron, imazosulfuron, iodosulfuron, mesosulfuron, metazosulfuron,
 35 metsulfuron-methyl, nicosulfuron, oxasulfuron, primisulfuron, prosulfuron, pyrazosulfuron, rimsulfuron, sulfometuron, sulfosulfuron, thifensulfuron, triasulfuron, tribenuron, trifloxysulfuron, triflusulfuron, tritosulfuron, 1-((2-chloro-6-propyl-imidazo[1,2-b]pyridazin-3-yl)sulfonyl)-3-(4,6-dimethoxy-pyrimidin-2-yl)urea;
- triazines: ametryn, atrazine, cyanazine, dimethametryn, ethiozin, hexazinone, metamitron,
 40 metribuzin, prometryn, simazine, terbutylazine, terbutryn, triaziflam;
- ureas: chlorotoluron, daimuron, diuron, fluometuron, isoproturon, linuron, metha-benzthiazuron, tebuthiuron;

- other acetolactate synthase inhibitors: bispyribac-sodium, cloransulam-methyl, diclosulam, florasulam, flucarbazone, flumetsulam, metosulam, ortho-sulfamuron, penoxsulam, propoxycarbazon, pyribambenz-propyl, pyribenzoxim, pyriftalid, pyriminobac-methyl, pyrimisulfan, pyriothiobac, pyroxasulfone, pyroxsulam;
- 5 - others: amicarbazone, aminotriazole, anilofos, beflubutamid, benazolin, bencarbazon, benfluresate, benzofenap, bentazon, benzobicyclon, bicyclopiron, bromacil, bromobutide, butafenacil, butamifos, cafenstrole, carfentrazone, cinidon-ethyl, chlorthal, cinmethylin, clomazone, cumyluron, cyprosulfamide, dicamba, difenzoquat, diflufenzopyr, *Drechslera monoceras*, endothal, ethofumesate, etobenzanid, fenoxasulfone, fentrazamide,
- 10 flumiclorac-pentyl, flumioxazin, flupoxam, flurochloridone, flurtamone, indanofan, isoxaben, isoxaflutole, lenacil, propanil, propyzamide, quinclorac, quinmerac, mesotrione, methyl arsonic acid, naptalam, oxadiargyl, oxadiazon, oxaziclomefone, pentoxazone, pinoxaden, pyraclonil, pyraflufen-ethyl, pyrasulfotole, pyrazoxyfen, pyrazolynate, quinclamine, saflufenacil, sulcotrione, sulfentrazone, terbacil, tefuryltrione, tembotrione, thiencarbazon, topramezone,
- 15 (3-[2-chloro-4-fluoro-5-(3-methyl-2,6-dioxo-4-trifluoromethyl-3,6-dihydro-2H-pyrimidin-1-yl)-phenoxy]-pyridin-2-yloxy)-acetic acid ethyl ester, 6-amino-5-chloro-2-cyclopropyl-pyrimidine-4-carboxylic acid methyl ester, 6-chloro-3-(2-cyclopropyl-6-methyl-phenoxy)-pyridazin-4-ol, 4-amino-3-chloro-6-(4-chloro-phenyl)-5-fluoro-pyridine-2-carboxylic acid, 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxy-phenyl)-pyridine-2-carboxylic acid methyl ester, and 4-amino-3-chloro-6-(4-chloro-3-dimethylamino-2-fluoro-phenyl)-pyridine-2-carboxylic acid methyl ester.
- 20 O) Insecticides
 - organo(thio)phosphates: acephate, azamethiphos, azinphos-methyl, chlorpyrifos, chlorpyrifos-methyl, chlorfenvinphos, diazinon, dichlorvos, dicrotophos, dimethoate, disulfoton, ethion, fenitrothion, fenthion, isoxathion, malathion, methamidophos, methidathion, methyl-
 - 25 parathion, mevinphos, monocrotophos, oxydemeton-methyl, paraoxon, parathion, phenthoate, phosalone, phosmet, phosphamidon, phorate, phoxim, pirimiphos-methyl, profenofos, prothiofos, sulprophos, tetrachlorvinphos, terbufos, triazophos, trichlorfon;
 - carbamates: alanycarb, aldicarb, bendiocarb, benfuracarb, carbaryl, carbofuran, carbosulfan, fenoxycarb, furathiocarb, methiocarb, methomyl, oxamyl, pirimicarb, propoxur,
 - 30 thiodicarb, triazamate;
 - pyrethroids: allethrin, bifenthrin, cyfluthrin, cyhalothrin, cyphenothrin, cypermethrin, alpha-cypermethrin, beta-cypermethrin, zeta-cypermethrin, deltamethrin, esfenvalerate, etofenprox, fenpropathrin, fenvalerate, imiprothrin, lambda-cyhalothrin, permethrin, prallethrin, pyrethrin I and II, resmethrin, silafluofen, tau-fluvalinate, tefluthrin, tetramethrin, tralomethrin, transfluthrin,
 - 35 profluthrin, dimefluthrin;
 - insect growth regulators: a) chitin synthesis inhibitors: benzoylureas: chlorfluazuron, cyramazin, diflubenzuron, flucyclohexuron, flufenoxuron, hexaflumuron, lufenuron, novaluron, teflubenzuron, triflumuron; buprofezin, diofenolan, hexythiazox, etoxazole, clofentazine; b) ecdysone antagonists: halofenozide, methoxyfenozide, tebufenozide, azadirachtin; c) juvenoids:
 - 40 pyriproxyfen, methoprene, fenoxycarb; d) lipid biosynthesis inhibitors: spirotetramat, spiromesifen, spirotetramat;

- nicotinic receptor agonists/antagonists compounds: clothianidin, dinotefuran, flupyradifurone, imidacloprid, thiamethoxam, nitenpyram, acetamiprid, thiacloprid, 1-2-chloro-thiazol-5-ylmethyl)-2-nitrimino-3,5-dimethyl-[1,3,5]triazinane;
- GABA antagonist compounds: endosulfan, ethiprole, fipronil, vaniliprole, pyrafluprole,
- 5 pyriprole, 5-amino-1-(2,6-dichloro-4-methyl-phenyl)-4-sulfinamoyl-1H-pyrazole-3-carbothioic acid amide;
- macrocyclic lactone insecticides: abamectin, emamectin, milbemectin, lepimectin, spinosad, spinetoram;
- mitochondrial electron transport inhibitor (METI) I acaricides: fenazaquin, pyridaben,
- 10 tebufenpyrad, tolfenpyrad, flufenimer;
- METI II and III compounds: acequinocyl, fluacyprim, hydramethylnon;
- Uncouplers: chlorfenapyr;
- oxidative phosphorylation inhibitors: cyhexatin, diafenthiuron, fenbutatin oxide, propargite;
- moulting disruptor compounds: cryomazine;
- 15 - mixed function oxidase inhibitors: piperonyl butoxide;
- sodium channel blockers: indoxacarb, metaflumizone;
- ryanodine receptor inhibitors: chlorantraniliprole, cyantraniliprole, flubendiamide, N-[4,6-dichloro-2-[(diethyl-lambda-4-sulfanylidene)carbamoyl]-phenyl]-2-(3-chloro-2-pyridyl)-5-(trifluoromethyl)pyrazole-3-carboxamide; N-[4-chloro-2-[(diethyl-lambda-4-
- 20 sulfanylidene)carbamoyl]-6-methyl-phenyl]-2-(3-chloro-2-pyridyl)-5-(trifluoromethyl)pyrazole-3-carboxamide; N-[4-chloro-2-[(di-2-propyl-lambda-4-sulfanylidene)carbamoyl]-6-methyl-phenyl]-2-(3-chloro-2-pyridyl)-5-(trifluoromethyl)pyrazole-3-carboxamide; N-[4,6-dichloro-2-[(di-2-propyl-lambda-4-sulfanylidene)carbamoyl]-phenyl]-2-(3-chloro-2-pyridyl)-5-(trifluoromethyl)pyrazole-3-carboxamide; N-[4,6-dichloro-2-[(diethyl-lambda-4-sulfanylidene)carbamoyl]-phenyl]-2-(3-chloro-
- 25 2-pyridyl)-5-(difluoromethyl)pyrazole-3-carboxamide; N-[4,6-dibromo-2-[(di-2-propyl-lambda-4-sulfanylidene)carbamoyl]-phenyl]-2-(3-chloro-2-pyridyl)-5-(trifluoromethyl)pyrazole-3-carboxamide; N-[4-chloro-2-[(di-2-propyl-lambda-4-sulfanylidene)carbamoyl]-6-cyano-phenyl]-2-(3-chloro-2-pyridyl)-5-(trifluoromethyl)pyrazole-3-carboxamide; N-[4,6-dibromo-2-[(diethyl-lambda-4-sulfanylidene)carbamoyl]-phenyl]-2-(3-chloro-2-pyridyl)-5-(trifluoromethyl)pyrazole-3-
- 30 carboxamide;
- others: benclothiaz, bifenazate, cartap, flonicamid, pyridalyl, pymetrozine, sulfur, thiocyclam, cyenopyrafen, flupyrzofos, cyflumetofen, amidoflumet, imicyafos, bistrifluron, pyrifluquinazon and 1,1'-[(3S,4R,4aR,6S,6aS,12R,12aS,12bS)-4-[[2-cyclopropylacetyl)oxy]methyl]-1,3,4,4a,5,6,6a,12,12a,12b-decahydro-12-hydroxy-4,6a,12b-
- 35 trimethyl-11-oxo-9-(3-pyridinyl)-2H,11H-naphtho[2,1-b]pyrano[3,4-e]pyran-3,6-diyl] cyclopropaneacetic acid ester.

The present invention furthermore relates to agrochemical compositions comprising a mixture of at least one compound I (component 1) and at least one further active substance useful for plant protection, e. g. selected from the groups A) to O) (component 2), in particular one further

40 fungicide, e. g. one or more fungicide from the groups A) to L), as described above, and if desired one suitable solvent or solid carrier. Those mixtures are of particular interest, since many of them at the same application rate show higher efficiencies against harmful fungi.

Furthermore, combating harmful fungi with a mixture of compounds I and at least one fungicide from groups A) to L), as described above, is more efficient than combating those fungi with individual compounds I or individual fungicides from groups A) to L). By applying compounds I together with at least one active substance from groups A) to O) a synergistic effect can be obtained, i.e. more than simple addition of the individual effects is obtained (synergistic mixtures).

This can be obtained by applying the compounds I and at least one further active substance simultaneously, either jointly (e. g. as tank-mix) or separately, or in succession, wherein the time interval between the individual applications is selected to ensure that the active substance applied first still occurs at the site of action in a sufficient amount at the time of application of the further active substance(s). The order of application is not essential for working of the present invention.

In binary mixtures, i.e. compositions according to the invention comprising one compound I (component 1) and one further active substance (component 2), e. g. one active substance from groups A) to O), the weight ratio of component 1 and component 2 generally depends from the properties of the active substances used, usually it is in the range of from 1:100 to 100:1, regularly in the range of from 1:50 to 50:1, preferably in the range of from 1:20 to 20:1, more preferably in the range of from 1:10 to 10:1 and in particular in the range of from 1:3 to 3:1.

In ternary mixtures, i.e. compositions according to the invention comprising one compound I (component 1) and a first further active substance (component 2) and a second further active substance (component 3), e. g. two active substances from groups A) to O), the weight ratio of component 1 and component 2 depends from the properties of the active substances used, preferably it is in the range of from 1:50 to 50:1 and particularly in the range of from 1:10 to 10:1, and the weight ratio of component 1 and component 3 preferably is in the range of from 1:50 to 50:1 and particularly in the range of from 1:10 to 10:1.

Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group A) (component 2) and particularly selected from azoxystrobin, dimoxystrobin, fluoxastrobin, kresoxim-methyl, orysastrobin, picoxystrobin, pyraclostrobin, trifloxystrobin; famoxadone, fenamidone; benzovindiflupyr, bixafen, boscalid, fluopyram, fluxapyroxad, isopyrazam, penflufen, penthiopyrad, sedaxane; ametoctradin, cyazofamid, fluazinam, fentin salts, such as fentin acetate.

Preference is given to mixtures comprising a compound of formula I (component 1) and at least one active substance selected from group B) (component 2) and particularly selected from cyproconazole, difenoconazole, epoxiconazole, fluquinconazole, flusilazole, flutriafol, metconazole, myclobutanil, penconazole, propiconazole, prothioconazole, triadimefon, triadimenol, tebuconazole, tetraconazole, triticonazole, prochloraz, fenarimol, triforine; dodemorph, fenpropimorph, tridemorph, fenpropidin, spiromamine; fenhexamid.

Preference is given to mixtures comprising a compound of formula I (component 1) and at least one active substance selected from group C) (component 2) and particularly selected from metalaxyl, (metalaxyl-M) mefenoxam, ofurace.

Preference is given to mixtures comprising a compound of formula I (component 1) and at least one active substance selected from group D) (component 2) and particularly selected from

benomyl, carbendazim, thiophanate-methyl, ethaboxam, fluopicolide, zoxamide, metrafenone, pyriofenone.

Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group E) (component 2) and particularly selected from

5 cyprodinil, mepanipyrim, pyrimethanil.

Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group F) (component 2) and particularly selected from iprodione, fludioxonil, vinclozolin, quinoxyfen.

10 Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group G) (component 2) and particularly selected from dimethomorph, flumorph, iprovalicarb, benthiavalicarb, mandipropamid, propamocarb.

Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group H) (component 2) and particularly selected from copper acetate, copper hydroxide, copper oxychloride, copper sulfate, sulfur, mancozeb, metiram,

15 propineb, thiram, captafol, folpet, chlorothalonil, dichlofluanid, dithianon.

Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group I) (component 2) and particularly selected from carpropamid and fenoxanil.

20 Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group J) (component 2) and particularly selected from acibenzolar-S-methyl, probenazole, tiadinil, fosetyl, fosetyl-aluminium, H₃PO₃ and salts thereof.

Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group K) (component 2) and particularly selected from cymoxanil, proquinazid and *N*-methyl-2-{1-[(5-methyl-3-trifluoromethyl-1H-pyrazol-1-yl)-acetyl]-

25 piperidin-4-yl}-*N*-[(1*R*)-1,2,3,4-tetrahydronaphthalen-1-yl]-4-thiazolecarboxamide.

Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group L) (component 2) and particularly selected from *Bacillus subtilis* strain NRRL No. B-21661, *Bacillus pumilus* strain NRRL No. B-30087 and *Ulocladium oudemansii*.

30 Accordingly, the present invention furthermore relates to compositions comprising one compound I (component 1) and one further active substance (component 2), which further active substance is selected from the column "Component 2" of the lines C-1 to C-381 of Table C.

A further embodiment relates to the compositions C-1 to C-381 listed in Table C, where a row of

35 Table C corresponds in each case to a fungicidal composition comprising one of the in the present specification individualized compounds of formula I (component 1) and the respective further active substance from groups A) to O) (component 2) stated in the row in question. Preferably, the compositions described comprise the active substances in synergistically effective amounts.

40

Table C: Composition comprising one individualized compound I and one further active substance from groups A) to O)

Mixture	Component 1	Component 2
C-1	one individualized compound I	Azoxystrobin
C-2	one individualized compound I	Coumethoxystrobin
C-3	one individualized compound I	Coumoxystrobin
C-4	one individualized compound I	Dimoxystrobin
C-5	one individualized compound I	Enestroburin
C-6	one individualized compound I	Fenaminstrobin
C-7	one individualized compound I	Fenoxystrobin/Flufenoxystrobin
C-8	one individualized compound I	Fluoxastrobin
C-9	one individualized compound I	Kresoxim-methyl
C-10	one individualized compound I	Metominostrobin
C-11	one individualized compound I	Orysastrobin
C-12	one individualized compound I	Picoxystrobin
C-13	one individualized compound I	Pyraclostrobin
C-14	one individualized compound I	Pyrametostrobin
C-15	one individualized compound I	Pyraoxystrobin
C-16	one individualized compound I	Pyribencarb
C-17	one individualized compound I	Trifloxystrobin
C-18	one individualized compound I	Triclopyricarb/Chlorodincarb
C-19	one individualized compound I	2-[2-(2,5-dimethyl-phenoxy-methyl)-phenyl]-3-methoxy-acrylic acid methyl ester
C-20	one individualized compound I	2-(2-(3-(2,6-dichlorophenyl)-1-methyl-allylideneamino-oxy-methyl)-phenyl)-2-methoxyimino-N-methyl-acetamide
C-21	one individualized compound I	Benalaxyl
C-22	one individualized compound I	Benalaxyl-M
C-23	one individualized compound I	Benodanil
C-24	one individualized compound I	Benzovindiflupyr
C-25	one individualized compound I	Bixafen
C-26	one individualized compound I	Boscalid
C-27	one individualized compound I	Carboxin
C-28	one individualized compound I	Fenfuram
C-29	one individualized compound I	Fenhexamid
C-30	one individualized compound I	Flutolanil
C-31	one individualized compound I	Fluxapyroxad
C-32	one individualized compound I	Furametpyr
C-33	one individualized compound I	Isopyrazam
C-34	one individualized compound I	Isotianil
C-35	one individualized compound I	Kiralaxyl
C-36	one individualized compound I	Mepronil

Mixture	Component 1	Component 2
C-37	one individualized compound I	Metalaxyl
C-38	one individualized compound I	Metalaxyl-M
C-39	one individualized compound I	Ofurace
C-40	one individualized compound I	Oxadixyl
C-41	one individualized compound I	Oxycarboxin
C-42	one individualized compound I	Penflufen
C-43	one individualized compound I	Penthiopyrad
C-44	one individualized compound I	Sedaxane
C-45	one individualized compound I	Tecloftalam
C-46	one individualized compound I	Thifluzamide
C-47	one individualized compound I	Tiadinil
C-48	one individualized compound I	2-Amino-4-methyl-thiazole-5-carboxylic acid anilide
C-49	one individualized compound I	N-(4'-trifluoromethylthiobiphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide
C-50	one individualized compound I	N-(2-(1,3,3-trimethyl-butyl)-phenyl)-1,3-dimethyl-5-fluoro-1H-pyrazole-4-carboxamide
C-51	one individualized compound I	3-(difluoromethyl)-1-methyl-N-(1,1,3-trimethylindan-4-yl)pyrazole-4-carboxamide
C-52	one individualized compound I	3-(trifluoromethyl)-1-methyl-N-(1,1,3-trimethylindan-4-yl)pyrazole-4-carboxamide
C-53	one individualized compound I	1,3-dimethyl-N-(1,1,3-trimethylindan-4-yl)pyrazole-4-carboxamide
C-54	one individualized compound I	3-(trifluoromethyl)-1,5-dimethyl-N-(1,1,3-trimethylindan-4-yl)pyrazole-4-carboxamide
C-55	one individualized compound I	3-(difluoromethyl)-1,5-dimethyl-N-(1,1,3-trimethylindan-4-yl)pyrazole-4-carboxamide
C-56	one individualized compound I	1,3,5-trimethyl-N-(1,1,3-trimethylindan-4-yl)pyrazole-4-carboxamide
C-57	one individualized compound I	Dimethomorph
C-58	one individualized compound I	Flumorph
C-59	one individualized compound I	Pyrimorph
C-60	one individualized compound I	Flumetover
C-61	one individualized compound I	Fluopicolide

Mixture	Component 1	Component 2
C-62	one individualized compound I	Fluopyram
C-63	one individualized compound I	Zoxamide
C-64	one individualized compound I	Carpropamid
C-65	one individualized compound I	Diclocymet
C-66	one individualized compound I	Mandipropamid
C-67	one individualized compound I	Oxytetracyclin
C-68	one individualized compound I	Silthiofam
C-69	one individualized compound I	N-(6-methoxy-pyridin-3-yl) cyclopropanecarboxylic acid amide
C-70	one individualized compound I	Azaconazole
C-71	one individualized compound I	Bitertanol
C-72	one individualized compound I	Bromuconazole
C-73	one individualized compound I	Cyproconazole
C-74	one individualized compound I	Difenoconazole
C-75	one individualized compound I	Diniconazole
C-76	one individualized compound I	Diniconazole-M
C-77	one individualized compound I	Epoxiconazole
C-78	one individualized compound I	Fenbuconazole
C-79	one individualized compound I	Fluquinconazole
C-80	one individualized compound I	Flusilazole
C-81	one individualized compound I	Flutriafol
C-82	one individualized compound I	Hexaconazol
C-83	one individualized compound I	Imibenconazole
C-84	one individualized compound I	Ipconazole
C-85	one individualized compound I	Metconazole
C-86	one individualized compound I	Myclobutanil
C-87	one individualized compound I	Oxpoconazol
C-88	one individualized compound I	Paclobutrazol
C-89	one individualized compound I	Penconazole
C-90	one individualized compound I	Propiconazole
C-91	one individualized compound I	Prothioconazole
C-92	one individualized compound I	Simeconazole
C-93	one individualized compound I	Tebuconazole
C-94	one individualized compound I	Tetraconazole
C-95	one individualized compound I	Triadimefon
C-96	one individualized compound I	Triadimenol
C-97	one individualized compound I	Triticonazole
C-98	one individualized compound I	Uniconazole

Mixture	Component 1	Component 2
C-99	one individualized compound I	1-[<i>rel</i> -(2 <i>S</i> ;3 <i>R</i>)-3-(2-chlorophenyl)-2-(2,4-difluorophenyl)-oxiranylmethyl]-5-thiocyanato-1H-[1,2,4]triazole,
C-100	one individualized compound I	2-[<i>rel</i> -(2 <i>S</i> ;3 <i>R</i>)-3-(2-chlorophenyl)-2-(2,4-difluorophenyl)-oxiranylmethyl]-2H-[1,2,4]triazole-3-thiol
C-101	one individualized compound I	Cyazofamid
C-102	one individualized compound I	Amisulbrom
C-103	one individualized compound I	Imazalil
C-104	one individualized compound I	Imazalil-sulfate
C-105	one individualized compound I	Pefurazoate
C-106	one individualized compound I	Prochloraz
C-107	one individualized compound I	Triflumizole
C-108	one individualized compound I	Benomyl
C-109	one individualized compound I	Carbendazim
C-110	one individualized compound I	Fuberidazole
C-111	one individualized compound I	Thiabendazole
C-112	one individualized compound I	Ethaboxam
C-113	one individualized compound I	Etridiazole
C-114	one individualized compound I	Hymexazole
C-115	one individualized compound I	2-(4-Chloro-phenyl)-N-[4-(3,4-dimethoxy-phenyl)-isoxazol-5-yl]-2-prop-2-yn-yloxy-acetamide
C-116	one individualized compound I	Fluazinam
C-117	one individualized compound I	Pyrifenoxy
C-118	one individualized compound I	3-[5-(4-Chloro-phenyl)-2,3-dimethyl-isoxazolidin-3-yl]-pyridine (Pyrisoxazole)
C-119	one individualized compound I	3-[5-(4-Methyl-phenyl)-2,3-dimethyl-isoxazolidin-3-yl]-pyridine
C-120	one individualized compound I	Bupirimate
C-121	one individualized compound I	Cyprodinil
C-122	one individualized compound I	5-Fluorocytosine
C-123	one individualized compound I	5-Fluoro-2-(p-tolylmethoxy)pyrimidin-4-amine
C-124	one individualized compound I	5-Fluoro-2-(4-fluorophenylmethoxy)-pyrimidin-4-amine
C-125	one individualized compound I	Diflumetorim
C-126	one individualized compound I	(5,8-Difluoroquinazolin-4-yl)-{2-[2-fluoro-4-(4-trifluoromethylpyridin-2-yloxy)-phenyl]-ethyl}-amine

Mixture	Component 1	Component 2
C-127	one individualized compound I	Fenarimol
C-128	one individualized compound I	Ferimzone
C-129	one individualized compound I	Mepanipyrim
C-130	one individualized compound I	Nitrapyrin
C-131	one individualized compound I	Nuarimol
C-132	one individualized compound I	Pyrimethanil
C-133	one individualized compound I	Triforine
C-134	one individualized compound I	Fenpiclonil
C-135	one individualized compound I	Fludioxonil
C-136	one individualized compound I	Aldimorph
C-137	one individualized compound I	Dodemorph
C-138	one individualized compound I	Dodemorph-acetate
C-139	one individualized compound I	Fenpropimorph
C-140	one individualized compound I	Tridemorph
C-141	one individualized compound I	Fenpropidin
C-142	one individualized compound I	Fluoroimid
C-143	one individualized compound I	Iprodione
C-144	one individualized compound I	Procymidone
C-145	one individualized compound I	Vinclozolin
C-146	one individualized compound I	Famoxadone
C-147	one individualized compound I	Fenamidone
C-148	one individualized compound I	Flutianil
C-149	one individualized compound I	Octhilinone
C-150	one individualized compound I	Probenazole
C-151	one individualized compound I	Fenpyrazamine
C-152	one individualized compound I	Acibenzolar-S-methyl
C-153	one individualized compound I	Ametoctradin
C-154	one individualized compound I	Amisulbrom
C-155	one individualized compound I	[(3S,6S,7R,8R)-8-benzyl-3-[(3-isobutyryloxymethoxy-4-methoxypyridine-2-carbonyl)amino]-6-methyl-4,9-dioxo-[1,5]dioxonan-7-yl] 2-methylpropanoate
C-156	one individualized compound I	[(3S,6S,7R,8R)-8-benzyl-3-[(3-acetoxy-4-methoxy-pyridine-2-carbonyl)amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate
C-157	one individualized compound I	[(3S,6S,7R,8R)-8-benzyl-3-[[3-(acetoxymethoxy)-4-methoxy-pyridine-2-carbonyl]amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate

Mixture	Component 1	Component 2
C-158	one individualized compound I	[(3S,6S,7R,8R)-8-benzyl-3-[(3-isobutoxycarbonyloxy-4-methoxy-pyridine-2-carbonyl)amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate
C-159	one individualized compound I	[(3S,6S,7R,8R)-8-benzyl-3-[[3-(1,3-benzodioxol-5-ylmethoxy)-4-methoxy-pyridine-2-carbonyl]amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate
C-160	one individualized compound I	(3S,6S,7R,8R)-3-[[3-(3-hydroxy-4-methoxy-2-pyridinyl)carbonyl]amino]-6-methyl-4,9-dioxo-8-(phenylmethyl)-1,5-dioxonan-7-yl 2-methylpropanoate
C-161	one individualized compound I	Anilazin
C-162	one individualized compound I	Blastidicin-S
C-163	one individualized compound I	Captafol
C-164	one individualized compound I	Captan
C-165	one individualized compound I	Chinomethionat
C-166	one individualized compound I	Dazomet
C-167	one individualized compound I	Debacarb
C-168	one individualized compound I	Diclomezine
C-169	one individualized compound I	Difenzoquat,
C-170	one individualized compound I	Difenzoquat-methylsulfate
C-171	one individualized compound I	Fenoxanil
C-172	one individualized compound I	Folpet
C-173	one individualized compound I	Oxolinsäure
C-174	one individualized compound I	Piperalin
C-175	one individualized compound I	Proquinazid
C-176	one individualized compound I	Pyroquilon
C-177	one individualized compound I	Quinoxifen
C-178	one individualized compound I	Triazoxid
C-179	one individualized compound I	Tricyclazole
C-180	one individualized compound I	2-Butoxy-6-iodo-3-propyl-chromen-4-one
C-181	one individualized compound I	5-Chloro-1-(4,6-dimethoxy-pyrimidin-2-yl)-2-methyl-1H-benzoimidazole
C-182	one individualized compound I	5-Chloro-7-(4-methyl-piperidin-1-yl)-6-(2,4,6-trifluoro-phenyl)-[1,2,4]triazolo[1,5-a]pyrimidine
C-183	one individualized compound I	Ferbam

Mixture	Component 1	Component 2
C-184	one individualized compound I	Mancozeb
C-185	one individualized compound I	Maneb
C-186	one individualized compound I	Metam
C-187	one individualized compound I	Methasulphocarb
C-188	one individualized compound I	Metiram
C-189	one individualized compound I	Propineb
C-190	one individualized compound I	Thiram
C-191	one individualized compound I	Zineb
C-192	one individualized compound I	Ziram
C-193	one individualized compound I	Diethofencarb
C-194	one individualized compound I	Benthiavalicarb
C-195	one individualized compound I	Iprovalicarb
C-196	one individualized compound I	Propamocarb
C-197	one individualized compound I	Propamocarb hydrochlorid
C-198	one individualized compound I	Valifenalate
C-199	one individualized compound I	N-(1-(1-(4-cyanophenyl)ethanesulfonyl)-but-2-yl) carbamic acid-(4-fluorophenyl) ester
C-200	one individualized compound I	Dodine
C-201	one individualized compound I	Dodine free base
C-202	one individualized compound I	Guazatine
C-203	one individualized compound I	Guazatine-acetate
C-204	one individualized compound I	Iminoctadine
C-205	one individualized compound I	Iminoctadine-triacetate
C-206	one individualized compound I	Iminoctadine-tris(albesilate)
C-207	one individualized compound I	Kasugamycin
C-208	one individualized compound I	Kasugamycin-hydrochloride-hydrate
C-209	one individualized compound I	Polyoxine
C-210	one individualized compound I	Streptomycin
C-211	one individualized compound I	Validamycin A
C-212	one individualized compound I	Binapacryl
C-213	one individualized compound I	Dicloran
C-214	one individualized compound I	Dinobuton
C-215	one individualized compound I	Dinocap
C-216	one individualized compound I	Nitrothal-isopropyl
C-217	one individualized compound I	Tecnazen
C-218	one individualized compound I	Fentin salts
C-219	one individualized compound I	Dithianon

Mixture	Component 1	Component 2
C-220	one individualized compound I	2,6-dimethyl-1H,5H-[1,4]dithiino [2,3-c:5,6-c']dipyrrole- 1,3,5,7(2H,6H)-tetraone
C-221	one individualized compound I	Isoprothiolane
C-222	one individualized compound I	Edifenphos
C-223	one individualized compound I	Fosetyl, Fosetyl-aluminium
C-224	one individualized compound I	Iprobenfos
C-225	one individualized compound I	Phosphorous acid (H ₃ PO ₃) and derivatives
C-226	one individualized compound I	Pyrazophos
C-227	one individualized compound I	Tolclofos-methyl
C-228	one individualized compound I	Chlorothalonil
C-229	one individualized compound I	Dichlofluanid
C-230	one individualized compound I	Dichlorophen
C-231	one individualized compound I	Flusulfamide
C-232	one individualized compound I	Hexachlorbenzene
C-233	one individualized compound I	Pencycuron
C-234	one individualized compound I	Pentachlorophenol and salts
C-235	one individualized compound I	Phthalide
C-236	one individualized compound I	Quintozene
C-237	one individualized compound I	Thiophanate Methyl
C-238	one individualized compound I	Tolyfluanid
C-239	one individualized compound I	N-(4-chloro-2-nitro- phenyl)-N-ethyl- 4-methyl- benzenesulfonamide
C-240	one individualized compound I	Bordeaux mixture
C-241	one individualized compound I	Copper acetate
C-242	one individualized compound I	Copper hydroxide
C-243	one individualized compound I	Copper oxychloride
C-244	one individualized compound I	basic Copper sulfate
C-245	one individualized compound I	Sulfur
C-246	one individualized compound I	Biphenyl
C-247	one individualized compound I	Bronopol
C-248	one individualized compound I	Cyflufenamid
C-249	one individualized compound I	Cymoxanil
C-250	one individualized compound I	Diphenylamin
C-251	one individualized compound I	Metrafenone
C-252	one individualized compound I	Pyriofenone
C-253	one individualized compound I	Mildiomycin

Mixture	Component 1	Component 2
C-254	one individualized compound I	Oxin-copper
C-255	one individualized compound I	Oxathiapiprolin
C-256	one individualized compound I	2-[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]-1-[4-(4-{5-[2-(prop-2-yn-1-yloxy)phenyl]-4,5-dihydro-1,2-oxazol-3-yl]-1,3-thiazol-2-yl)piperidin-1-yl]ethanone
C-257	one individualized compound I	2-[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]-1-[4-(4-{5-[2-fluoro-6-(prop-2-yn-1-yloxy)phenyl]-4,5-dihydro-1,2-oxazol-3-yl]-1,3-thiazol-2-yl)piperidin-1-yl]ethanone
C-258	one individualized compound I	2-[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]-1-[4-(4-{5-[2-chloro-6-(prop-2-yn-1-yloxy)phenyl]-4,5-dihydro-1,2-oxazol-3-yl]-1,3-thiazol-2-yl)piperidin-1-yl]ethanone
C-259	one individualized compound I	Prohexadione calcium
C-260	one individualized compound I	Spiroxamine
C-261	one individualized compound I	Tebufluoquin
C-262	one individualized compound I	Tolylfluanid
C-263	one individualized compound I	N-(Cyclopropylmethoxyimino-(6-difluoromethoxy-2,3-difluoro-phenyl)-methyl)-2-phenyl acetamide
C-264	one individualized compound I	N'-(4-(4-chloro-3-trifluoromethylphenoxy)-2,5-dimethyl-phenyl)-N-ethyl-N-methyl formamidine
C-265	one individualized compound I	N'-(4-(4-fluoro-3-trifluoromethylphenoxy)-2,5-dimethyl-phenyl)-N-ethyl-N-methyl formamidine
C-266	one individualized compound I	N'-(2-methyl-5-trifluoromethyl-4-(3-trimethylsilyl-propoxy)-phenyl)-N-ethyl-N-methyl formamidine
C-267	one individualized compound I	N'-(5-difluoromethyl-2-methyl-4-(3-trimethylsilyl-propoxy)-phenyl)-N-ethyl-N-methyl formamidine
C-268	one individualized compound I	Methoxy-acetic acid 6-tert-butyl-8-fluoro-2,3-dimethyl-quinolin-4-yl ester
C-269	one individualized compound I	<i>Bacillus subtilis</i> NRRL No. B-21661
C-270	one individualized compound I	<i>Bacillus pumilus</i> NRRL No. B-30087
C-271	one individualized compound I	<i>Ulocladium oudemansii</i>

Mixture	Component 1	Component 2
C-272	one individualized compound I	Carbaryl
C-273	one individualized compound I	Carbofuran
C-274	one individualized compound I	Carbosulfan
C-275	one individualized compound I	Methomylthiodicarb
C-276	one individualized compound I	Bifenthrin
C-277	one individualized compound I	Cyfluthrin
C-278	one individualized compound I	Cypermethrin
C-279	one individualized compound I	alpha-Cypermethrin
C-280	one individualized compound I	zeta-Cypermethrin
C-281	one individualized compound I	Deltamethrin
C-282	one individualized compound I	Esfenvalerate
C-283	one individualized compound I	Lambda-cyhalothrin
C-284	one individualized compound I	Permethrin
C-285	one individualized compound I	Tefluthrin
C-286	one individualized compound I	Diflubenzuron
C-287	one individualized compound I	Flufenoxuron
C-288	one individualized compound I	Lufenuron
C-289	one individualized compound I	Teflubenzuron
C-290	one individualized compound I	Spirotetramate
C-291	one individualized compound I	Clothianidin
C-292	one individualized compound I	Dinotefuran
C-293	one individualized compound I	Imidacloprid
C-294	one individualized compound I	Thiamethoxam
C-295	one individualized compound I	Flupyradifurone
C-296	one individualized compound I	Acetamiprid
C-297	one individualized compound I	Thiacloprid
C-298	one individualized compound I	Endosulfan
C-299	one individualized compound I	Fipronil
C-300	one individualized compound I	Abamectin
C-301	one individualized compound I	Emamectin
C-302	one individualized compound I	Spinosad
C-303	one individualized compound I	Spinetoram
C-304	one individualized compound I	Hydramethylnon
C-305	one individualized compound I	Chlorfenapyr
C-306	one individualized compound I	Fenbutatin oxide
C-307	one individualized compound I	Indoxacarb
C-308	one individualized compound I	Metaflumizone
C-309	one individualized compound I	Fonicamid
C-310	one individualized compound I	Flubendiamide
C-311	one individualized compound I	Chlorantraniliprole

Mixture	Component 1	Component 2
C-312	one individualized compound I	Cyantraniliprole
C-313	one individualized compound I	N-[4,6-dichloro-2-[(diethyl-lambda-4-sulfanylidene)carbamoyl]-phenyl]-2-(3-chloro-2-pyridyl)-5-(trifluoromethyl)pyrazole-3-carboxamide
C-314	one individualized compound I	N-[4-chloro-2-[(diethyl-lambda-4-sulfanylidene)carbamoyl]-6-methyl-phenyl]-2-(3-chloro-2-pyridyl)-5-(trifluoromethyl)pyrazole-3-carboxamide
C-315	one individualized compound I	N-[4-chloro-2-[(di-2-propyl-lambda-4-sulfanylidene)carbamoyl]-6-methyl-phenyl]-2-(3-chloro-2-pyridyl)-5-(trifluoromethyl)pyrazole-3-carboxamide
C-316	one individualized compound I	N-[4,6-dichloro-2-[(di-2-propyl-lambda-4-sulfanylidene)carbamoyl]-phenyl]-2-(3-chloro-2-pyridyl)-5-(trifluoromethyl)pyrazole-3-carboxamide
C-317	one individualized compound I	N-[4,6-dichloro-2-[(diethyl-lambda-4-sulfanylidene)carbamoyl]-phenyl]-2-(3-chloro-2-pyridyl)-5-(difluoromethyl)pyrazole-3-carboxamide
C-318	one individualized compound I	N-[4,6-dibromo-2-[(di-2-propyl-lambda-4-sulfanylidene)carbamoyl]-phenyl]-2-(3-chloro-2-pyridyl)-5-(trifluoromethyl)pyrazole-3-carboxamide
C-319	one individualized compound I	N-[4-chloro-2-[(di-2-propyl-lambda-4-sulfanylidene)carbamoyl]-6-cyano-phenyl]-2-(3-chloro-2-pyridyl)-5-(trifluoromethyl)pyrazole-3-carboxamide
C-320	one individualized compound I	N-[4,6-dibromo-2-[(diethyl-lambda-4-sulfanylidene)carbamoyl]-phenyl]-2-(3-chloro-2-pyridyl)-5-(trifluoromethyl)pyrazole-3-carboxamide
C-321	one individualized compound I	Cyflumetofen
C-322	one individualized compound I	Acetochlor
C-323	one individualized compound I	Dimethenamid
C-324	one individualized compound I	metolachlor
C-325	one individualized compound I	Metazachlor
C-326	one individualized compound I	Glyphosate
C-327	one individualized compound I	Glufosinate

Mixture	Component 1	Component 2
C-328	one individualized compound I	Sulfosate
C-329	one individualized compound I	Clodinafop
C-330	one individualized compound I	Fenoxaprop
C-331	one individualized compound I	Fluazifop
C-332	one individualized compound I	Haloxifop
C-333	one individualized compound I	Paraquat
C-334	one individualized compound I	Phenmedipham
C-335	one individualized compound I	Clethodim
C-336	one individualized compound I	Cycloxydim
C-337	one individualized compound I	Profoxydim
C-338	one individualized compound I	Sethoxydim
C-339	one individualized compound I	Tepraloxym
C-340	one individualized compound I	Pendimethalin
C-341	one individualized compound I	Prodiamine
C-342	one individualized compound I	Trifluralin
C-343	one individualized compound I	Acifluorfen
C-344	one individualized compound I	Bromoxynil
C-345	one individualized compound I	Imazamethabenz
C-346	one individualized compound I	Imazamox
C-347	one individualized compound I	Imazapic
C-348	one individualized compound I	Imazapyr
C-349	one individualized compound I	Imazaquin
C-350	one individualized compound I	Imazethapyr
C-351	one individualized compound I	2,4-Dichlorophenoxyacetic acid (2,4-D)
C-352	one individualized compound I	Chloridazon
C-353	one individualized compound I	Clopyralid
C-354	one individualized compound I	Fluroxypyr
C-355	one individualized compound I	Picloram
C-356	one individualized compound I	Picolinafen
C-357	one individualized compound I	Bensulfuron
C-358	one individualized compound I	Chlorimuron-ethyl
C-359	one individualized compound I	Cyclosulfamuron
C-360	one individualized compound I	Iodosulfuron
C-361	one individualized compound I	Mesosulfuron
C-362	one individualized compound I	Metsulfuron-methyl
C-363	one individualized compound I	Nicosulfuron
C-364	one individualized compound I	Rimsulfuron
C-365	one individualized compound I	Triflusulfuron
C-366	one individualized compound I	Atrazine
C-367	one individualized compound I	Hexazinone

Mixture	Component 1	Component 2
C-368	one individualized compound I	Diuron
C-369	one individualized compound I	Florasulam
C-370	one individualized compound I	Pyroxasulfone
C-371	one individualized compound I	Bentazone
C-372	one individualized compound I	Cinidon-ethyl
C-373	one individualized compound I	Cinmethylin
C-374	one individualized compound I	Dicamba
C-375	one individualized compound I	Diflufenzopyr
C-376	one individualized compound I	Quinclorac
C-377	one individualized compound I	Quinmerac
C-378	one individualized compound I	Mesotrione
C-379	one individualized compound I	Saflufenacil
C-380	one individualized compound I	Topramezone
C-381	one individualized compound I	1,1'-[(3S,4R,4aR,6S,6aS,12R,12aS,12bS)-4-[[[(2-cyclopropylacetyl)oxy]methyl]-1,3,4,4a,5,6,6a,12,12a,12b-decahydro-12-hydroxy-4,6a,12b-trimethyl-11-oxo-9-(3-pyridinyl)-2H,11H-naphtho[2,1-b]pyrano[3,4-e]pyran-3,6-diyl]cyclopropaneacetic acid ester

The active substances referred to as component 2, their preparation and their activity against harmful fungi is known (cf.: <http://www.alanwood.net/pesticides/>); these substances are commercially available. The compounds described by IUPAC nomenclature, their preparation

and their fungicidal activity are also known (cf. Can. J. Plant Sci. 48(6), 587-94, 1968; EP-A 141 317; EP-A 152 031; EP-A 226 917; EP-A 243 970; EP-A 256 503; EP-A 428 941; EP-A 532 022; EP-A 1 028 125; EP-A 1 035 122; EP-A 1 201 648; EP-A 1 122 244, JP 2002316902; DE 19650197; DE 10021412; DE 102005009458; US 3,296,272; US 3,325,503; WO 98/46608; WO 99/14187; WO 99/24413; WO 99/27783; WO 00/29404; WO 00/46148; WO 00/65913; WO 01/54501; WO 01/56358; WO 02/22583; WO 02/40431; WO 03/10149; WO 03/11853; WO 03/14103; WO 03/16286; WO 03/53145; WO 03/61388; WO 03/66609; WO 03/74491; WO 04/49804; WO 04/83193; WO 05/120234; WO 05/123689; WO 05/123690; WO 05/63721; WO 05/87772; WO 05/87773; WO 06/15866; WO 06/87325; WO 06/87343; WO 07/82098; WO 07/90624, WO 11/028657, WO2012/168188, WO 2007/006670, PCT/EP2012/065650 and PCT/EP2012/065651).

The mixtures of active substances can be prepared as compositions comprising besides the active ingredients at least one inert ingredient by usual means, e. g. by the means given for the compositions of compounds I.

Concerning usual ingredients of such compositions reference is made to the explanations given for the compositions containing compounds I.

The mixtures of active substances according to the present invention are suitable as fungicides, as are the compounds of formula I. They are distinguished by an outstanding effectiveness against a broad spectrum of phytopathogenic fungi, especially from the classes of the Ascomycetes, Basidiomycetes, Deuteromycetes and Peronosporomycetes (syn. Oomycetes). In addition, it is referred to the explanations regarding the fungicidal activity of the compounds and the compositions containing compounds I, respectively.

I. Synthesis examples

With appropriate modification of the starting materials, the procedures given in the synthesis examples below were used to obtain further compounds I. The compounds produced in this manner are listed in Table I below including corresponding physical data. 4-Chloro-6-ethyl-5-pyrimidinecarboxylic acid ethyl ester was synthesized according to a procedure given in US 5439911 A. 4-Chloro-6-methyl-5-pyrimidinecarboxylic acid methyl ester was prepared as described in EP 606011 A1.

Example 1: Preparation of 2-(4-iodophenoxy)-4-(trifluoromethyl)pyridine

To a solution of 4-iodophenol (200 g, 910 mmol) in *N,N*-dimethylformamide (1 L) was slowly added sodium hydride (47 g, 1.2 mol). The reaction was stirred for 30 min at room temperature, then 2-chloro-4-trifluoromethylpyridine (165 g, 910 mmol) was added and the solution was stirred at 110°C for 4 h and 12 h at room temperature. The reaction solution was poured into water and extracted with methyl *tert*-butylether (3x). The combined organic layers were washed successively with water, lithium chloride solution and 10% sodium hydroxide solution. The combined organic phases were then dried over sodium sulfate and the solvent was removed *in vacuo* to afford 91% (303 g, 830 mmol) yield of 2-(4-iodophenoxy)-4-(trifluoromethyl)pyridine.

Example 2: Preparation of 5-[4-[[4-(trifluoromethyl)-2-pyridyl]oxy]phenyl]pent-4-yn-2-amine

To a solution of 2-(4-iodophenoxy)-4-(trifluoromethyl)pyridine (102 g, 279 mmol) in tetrahydrofuran (500 mL) was added triethylamine (84 g, 838 mmol), copper(I) iodide (0.53 g, 3 mmol) and Pd(PPh₃)₂Cl₂ (2 g, 3 mmol), followed by pent-4-yn-2-ol (28 g, 335 mmol). The reaction was stirred at room temperature for 1 h and was then filtered over celite, followed by rinsing with methyl *tert*-butylether. Water and methyl *tert*-butylether were then added to the filtrate. The organic layer was separated and concentrated *in vacuo* to provide 93 g of crude 5-[4-[[4-(trifluoromethyl)-2-pyridyl]oxy]phenyl]pent-4-yn-2-ol. This material was redissolved in dichloromethane (1 L) and triethylamine (58 g, 576 mmol). The reaction solution was cooled to 5°C and methanesulfonyl chloride (42 g, 288 mmol) was added. The solution was allowed to warm to room temperature overnight. The reaction solution was poured into water and extracted with dichloromethane. The combined organic layers were dried over sodium sulfate and the solvent was then removed *in vacuo* to afford 121 g of the crude mesylate. The crude product was redissolved in *N,N*-dimethylformamide (600 mL) to which sodium azide was added (94 g, 1.4 mol). The reaction solution was heated to 80°C for 2 h then cooled to room temperature. Water and methyl *tert*-butylether were added, the organic layers were combined and

concentrated *in vacuo* to provide 91 g of the crude azide product. The azide was dissolved in methanol (700 mL) to which was added tin(II) chloride-H₂O (118 g, 523 mmol). The reaction was stirred at room temperature overnight and was then concentrated. To the residue was added 10% sodium hydroxide solution and the crude product was extracted with dichloromethane before it was dried over sodium sulfate and concentrated *in vacuo*. The residue was filtered over a silica gel plug to provide 96% of the desired product.

Example 3: Preparation of 6-chloro-5-methoxy-N-[1-methyl-4-[4-[[4-(trifluoromethyl)-2-pyridyl]oxy]phenyl]but-3-ynyl]pyrimidin-4-amine (I-27)

To a solution of 5-[4-[[4-(trifluoromethyl)-2-pyridyl]oxy]phenyl]pent-4-yn-2-amine (268 mg, 0.84 mmol) in *N,N*-dimethylformamide (5 mL) was added diisopropylethylamine (216 mg, 1.7 mmol). The solution was stirred for 5 min at room temperature at which time 4,6-dichloro-5-methoxypyrimidine (150 mg, 0.84 mmol) was added. The reaction mixture was stirred at 80°C overnight, then allowed to cool to room temperature. It was concentrated *in vacuo* and filtered over a plug of silica gel to provide 215 mg (0.47 mmol, 55%) of the brown oily product.

The compounds listed in Table I have been prepared in an analogous manner.

Table I: Compounds I-1 to I-82 of formula I as defined herein and wherein R, R¹ and R² in each case are hydrogen.

Ex. no	Ra2	Ra5	Ra6	Het	Pos. O-Het	X	(Rb) _n	HPLC R _t (min)	m.p. (°C)
I-1	H	Cl	Cl	H-1	para-	-CH ₂ -	n = 0	4.327	127
I-2	H	Cl	Me	H-1	para-	-CH ₂ -	n = 0	3.196	135
I-3	H	Cl	Et	H-1	para-	-CH ₂ -	n = 0	3.301	81
I-4	H	Cl	Me	H-1	para-	-CH(CH ₃)-	n = 0	1.126	92
I-5	H	Cl	Et	H-1	para-	-CH(CH ₃)-	n = 0	1.177	
I-6	H	Cl	Cl	H-1	para-	-CH(CH ₃)-	n = 0	1.504	
I-7	H	#5-CF=CCl-CH=CF-#6		H-1	para-	-CH ₂ -	n = 0	1.263	160
I-8	H	#5-CF=CH-CH=CF-#6		H-1	para-	-CH ₂ -	n = 0	1.122	157
I-9	H	#5-CF=CH-CH=CF-#6		H-1	para-	-CH(CH ₃)-	n = 0	1.181	147
I-10	H	#5-CF=CF-CH=CF-#6		H-1	para-	-CH(CH ₃)-	n = 0	1.318	144
I-11	H	Cl	CHFCH ₃	H-1	para-	-CH ₂ -	n = 0	1.28	79
I-12	H	Cl	CHFCH ₃	H-1	para-	-CH(CH ₃)-	n = 0	3.915	
I-13	H	#5-N(CH ₃)-N=CH-#6		H-1	para-	-CH(CH ₃)-	n = 0	1.07	205
I-14	H	#5-CH=CH-CH=CF-#6		H-1	para-	-CH(CH ₃)-	n = 0	1.084	126
I-15	H	#5-C(CH ₃)=CH-CH=CH-#6		H-1	para-	-CH(CH ₃)-	n = 0	1.107	
I-16	H	Me	Cl	H-1	para-	-CH(CH ₃)-	n = 0	1.381	
I-17	Me	Cl	Me	H-1	para-	-CH(CH ₃)-	n = 0	1.082	
I-18	H	#5-N=CH-S-#6		H-1	para-	-CH ₂ -	n = 0	1.239	155
I-19	H	#5-N=CH-S-#6		H-1	para-	-CH(CH ₃)-	n = 0	1.299	
I-20	H	OMe	H	H-1	para-	-CH(CH ₃)-	n = 0	1.034	
I-21	Me	Cl	Cl	H-1	para-	-CH(CH ₃)-	n = 0	1.519	
I-22	H	Cl	COOMe	H-1	para-	-CH(CH ₃)-	n = 0	1.36	109
I-23	H	Cl	CHFCH ₃	H-1	para-	-CH(CH ₃)-	o-F; n = 1	1.36	
I-24	H	Cl	Cl	H-1	para-	-CH(CH ₃)-	o-F; n = 1	1.48	
I-25	H	Cl	CHFCH ₃	H-1	para-	-CH ₂ -	o-F; n = 1	1.29	

97

Ex. no	Ra2	Ra5	Ra6	Het	Pos. O-Het	X	(Rb) _n	HPLC R _t (min)	m.p. (°C)
I-26	H	Cl	Cl	H-1	para-	-CH ₂ -	o-F; n = 1	1.41	
I-27	H	OMe	Cl	H-1	para-	-CH(CH ₃)-	n = 0	1.387	
I-28	H	#5-N=CH-S-#6		H-1	para-	-CH ₂ -	o-F; n = 1	1.25	119
I-29	H	#5-N(CH ₂ CH ₃)-N=CH-#6		H-1	para-	-CH ₂ -	n = 0	1.036	
I-30	H	F	Cl	5-trifluoromethyl-pyridin-3-yl	para-	-CH(CH ₃)-	n = 0	1.423	112
I-31	Cl	Cl	Cl	H-1	para-	-CH(CH ₃)-	n = 0	1.523	
I-32	H	COOEt	Et	H-1	para-	-CH(CH ₃)-	n = 0	1.193	91
I-33	H	#5-N=CH-CH=CH-#6		H-1	para-	-CH ₂ -	n = 0	1.025	124
I-34	H	#5-N=CH-CH=CH-#6		H-1	para-	-CH(CH ₃)-	n = 0	1.065	
I-35	H	OMe	COOMe	H-1	para-	-CH(CH ₃)-	n = 0	1.173	
I-36	H	COOMe	Me	H-1	para-	-CH(CH ₃)-	n = 0	1.135	
I-37	H	Br	Cl	H-1	para-	-CH(CH ₃)-	n = 0	1.503	
I-38	OMe	F	H	H-1	para-	-CH(CH ₃)-	n = 0	1.143	
I-39	H	Et	COOMe	H-1	para-	-CH(CH ₃)-	n = 0	1.127	
I-40	H	Br	F	H-1	para-	-CH(CH ₃)-	n = 0	1.473	
I-41	H	Br	OH	H-1	para-	-CH(CH ₃)-	n = 0	1.245	
I-42	H	#5-CF=CH-CH=CF-#6		H-4	para-	-CH(CH ₃)-	n = 0	1.193	
I-43	H	#5-CF=CH-CH=CF-#6		H-2	para-	-CH(CH ₃)-	n = 0	1.174	
I-44	H	#5-CF=CH-CH=CF-#6		H-3	para-	-CH(CH ₃)-	n = 0	1.186	97
I-45	Me	Me	Cl	H-1	para-	-CH(CH ₃)-	n = 0	1.307	113
I-46	H	F	F	H-1	para-	-CH(CH ₃)-	n = 0	1.393	
I-47	H	Cl	CHFCH ₃	H-2	para-	-CH(CH ₃)-	n = 0	1.297	
I-48	H	Cl	CHFCH ₃	H-3	para-	-CH(CH ₃)-	n = 0	1.329	
I-49	H	Cl	CHFCH ₃	H-4	para-	-CH(CH ₃)-	n = 0	1.314	
I-50	H	Cl	CHFCH ₃	3,5-dichloro-pyridin-2-yl	para-	-CH(CH ₃)-	n = 0	1.39	
I-51	H	Cl	Cl	H-2	para-	-CH(CH ₃)-	n = 0	1.419	
I-52	H	Cl	Cl	H-3	para-	-CH(CH ₃)-	n = 0	1.447	

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98

Ex. no	Ra2	Ra5	Ra6	Het	Pos. O-Het	X	(Rb) _n	HPLC R _t (min)	m.p. (°C)
I-53	H	Cl	Cl	H-4	para-	-CH(CH ₃)-	n = 0	1.434	
I-54	H	Cl	Cl	3,5-dichloro-pyridin-2-yl	para-	-CH(CH ₃)-	n = 0	1.519	
I-55	H	Me	Cl	H-2	para-	-CH(CH ₃)-	n = 0	1.321	
I-56	H	Me	Cl	H-3	para-	-CH(CH ₃)-	n = 0	1.35	
I-57	H	Me	Cl	H-4	para-	-CH(CH ₃)-	n = 0	1.344	
I-58	H	OMe	Cl	H-2	para-	-CH(CH ₃)-	n = 0	1.336	
I-59	H	OMe	Cl	H-3	para-	-CH(CH ₃)-	n = 0	1.361	
I-60	H	OMe	Cl	H-4	para-	-CH(CH ₃)-	n = 0	1.358	
I-61	H	OMe	Cl	3,5-dichloro-pyridin-2-yl	para-	-CH(CH ₃)-	n = 0	1.434	
I-62	Cl	Cl	Me	H-1	para-	-CH(CH ₃)-	n = 0	1.486	
I-63	OMe	Cl	Me	H-1	para-	-CH(CH ₃)-	n = 0	1.17	
I-64	H	CN	Cl	H-1	para-	-CH(CH ₃)-	n = 0	1.42	
I-65	H	Cl	CHFCH ₃	H-16	para-	-CH(CH ₃)-	n = 0	1.299	
I-66	H	Me	Cl	H-16	para-	-CH(CH ₃)-	n = 0	1.324	
I-67	H	OMe	Cl	H-16	para-	-CH(CH ₃)-	n = 0	1.338	
I-68	Me	H	Cl	H-1	para-	-CH(CH ₃)-	n = 0	1.302	
I-69	H	Et	Cl	H-1	para-	-CH(CH ₃)-	n = 0	1.43	
I-70	H	OMe	CH ₂ OCH ₃	H-1	para-	-CH(CH ₃)-	n = 0	1.07	
I-71	H	#5-CF=CH-CH=CF-#6	#5-CF=CH-CH=CF-#6	H-16	para-	-CH(CH ₃)-	n = 0	1.16	97
I-72	H	#5-N=N-S-#6		H-1	para-	-CH(CH ₃)-	n = 0	1.372	116
I-73	H	CN	Me	H-1	para-	-CH(CH ₃)-	n = 0	1.247	
I-74	H	#5-CF=CH-CH=CF-#6	#5-CF=CH-CH=CF-#6	3,5-dichloro-pyridin-2-yl	para-	-CH(CH ₃)-	n = 0	1.242	97
I-75	H	Cl	Cl	H-2	m-	-CH(CH ₃)-	n = 0	1.427	
I-76	OMe	H	Cl	H-1	para-	-CH(CH ₃)-	n = 0	1.372	
I-77	H	Cl	CHFCH ₃	H-2	para-	-CH(CH ₃)-	n = 0	1.270	
I-78	H	Cl	Cl	H-16	para-	-CH(CH ₃)-	n = 0	1.428	
I-79	H	CH=CH ₂	Cl	H-1	para-	-CH(CH ₃)-	n = 0	1.460	

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99

Ex. no	Ra2	Ra5	Ra6	Het	Pos. O-Het	X	(Rb) _n	HPLC R _t (min)	m.p. (°C)
I-80	H	Me	Cl	H-30	para-	-CH(CH ₃)-	n = 0	1,351	
I-81	H	OMe	Cl	H-28	para-	-CH(CH ₃)-	n = 0	1,308	
I-82	H	Me	COOMe	4-carboxymethyl-5-methyl- pyrimidin-6-yl	para-	-CH(CH ₃)-	n = 0	0,976	122

* The position of R^b or the group -O-Het on the phenyl ring is defined relative to the alkyne-moiety bound to the phenyl ring as being in ortho (o-), para- or meta (m-) position; n = 0 indicates that no substituent R^b is present on the phenyl ring. m.p. = melting point (°C); in cases where R^{a5} and R^{a6} together with two ring member carbon atoms of the pyrimidine ring constitute a fused ring system #5 and #6 indicate the point of attachment to the pyrimidine ring, each respectively corresponding to the positions of either substituent R^{a5} or R^{a6}.

- 5 HPLC: HPLC-column Kinetex XB C18 1,7μ (50 x 2,1 mm); eluent: acetonitrile / water + 0.1% TFA (gradient from 5:95 to 100 : 0 in 1.5 min at 60°C, flow gradient from 0.8 to 1.0 ml/min in 1.5 min). MS: Quadrupol Electrospray Ionisation, 80 V (positive mode)

II. Biological examples for fungicidal activity

The fungicidal action of the compounds I was demonstrated by the following experiments:

5 A. Glass house trials

The spray solutions were prepared in several steps: The stock solution were prepared: a mixture of acetone and/or dimethylsulfoxide and the wetting agent/emulsifier Wettol, which is based on ethoxylated alkylphenoles, in a relation (volume) solvent-emulsifier of 99 to 1 was added to 25 mg of the compound to give a total of 5 ml. Water was then added to total volume of 100 ml.

This stock solution was diluted with the described solvent-emulsifier-water mixture to the given concentration.

After the final cultivation period, the extent of fungal attack on the leaves was visually assessed as % diseased leaf area.

Use example 1: Control of late blight on tomatoes caused by *Phytophthora infestans*

Young seedlings of tomato plants were grown in pots. These plants were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient or their mixture mentioned in the table below. The next day, the treated plants were inoculated with an aqueous suspension of sporangia of *Phytophthora infestans*. After inoculation, the trial plants were immediately transferred to a humid chamber. After 6 days at 18 to 20°C and a relative humidity close to 100% the extent of fungal attack on the leaves was visually assessed as % diseased leaf area.

In this test, the plants which had been treated with 250 ppm of the active compound I-5, I-11, I-14, I-20, I-23, I-27, I-31, I-34, I-35, I-37, I-44, I-47, I-48, I-50, I-56, I-59, I-65, I-66, I-67, I-70, I-71, I-79, I-81 or I-82 showed a diseased leaf area of at most 20%, whereas the untreated plants showed 84% diseased leaf area.

Use example 2: Preventative control of leaf blotch on wheat caused by *Septoria tritici*

Leaves of pot-grown wheat seedling were sprayed to run-off with an aqueous suspension of the active compound or their mixture, prepared as described. The plants were allowed to air-dry. At the following day the plants were inoculated with an aqueous spore suspension of *Septoria tritici*. Then the trial plants were immediately transferred to a humid chamber at 18 to 22°C and a relative humidity close to 100%. After 4 days the plants were transferred to a chamber with 18 to 22°C and a relative humidity close to 70%. After 4 weeks the extent of fungal attack on the leaves was visually assessed as % diseased leaf area.

In this test, the plants which had been treated with 250 ppm of the active compound I-1, I-3, I-4, I-5, I-7, I-8, I-9, I-10, I-13, I-14, I-15, I-16, I-17, I-18, I-19, I-20, I-21, I-22, I-23, I-24, I-25, I-26, I-27, I-28, I-29, I-30, I-31, I-32, I-33, I-34, I-35, I-36, I-37, I-38, I-40, I-42, I-43, I-44, I-45, I-46, I-47, I-48, I-49, I-50, I-51, I-52, I-53, I-54, I-55, I-56, I-57, I-58, I-59, I-60, I-61, I-62, I-63, I-64, I-69, I-72, I-74, I-75 or I-76 showed a diseased leaf area of at most 20%, whereas the untreated plants showed 92% diseased leaf area.

Use example 3: Preventative control of brown rust on wheat caused by *Puccinia recondita*. The first two developed leaves of pot-grown wheat seedling were sprayed to run-off with an aqueous

suspension, containing the concentration of active ingredient or their mixture as described below. The next day the plants were inoculated with spores of *Puccinia recondita*. To ensure the success the artificial inoculation, the plants were transferred to a humid chamber without light and a relative humidity of 95 to 99% and 20 to 24°C for 24 h. Then the trial plants were cultivated for 6 days in a greenhouse chamber at 20 to 24°C and a relative humidity between 65 and 70%. The extent of fungal attack on the leaves was visually assessed as % diseased leaf area.

In this test, the plants which had been treated with 250 ppm of the active compound I-1, I-3, I-4, I-5, I-6, I-8, I-9, I-11, I-12, I-13, I-14, I-15, I-17, I-19, I-20, I-21, I-23, I-24, I-25, I-26, I-27, I-28, I-29, I-34, I-45, I-46, I-47, I-48, I-49, I-50, I-51, I-52, I-54, I-56, I-57, I-58, I-59, I-60, I-62, I-64, I-69 or I-73 showed a diseased leaf area of at most 20%, whereas the untreated plants showed 86% diseased leaf area.

Use example 4: Protective control of soy bean rust on soy beans caused by *Phakopsora pachyrhizi*. Leaves of pot-grown soy bean seedlings were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient or their mixture as described below. The plants were allowed to air-dry. The trial plants were cultivated for 1 day in a greenhouse chamber at 23 to 27°C and a relative humidity between 60 and 80%. Then the plants were inoculated with spores of *Phakopsora pachyrhizi*. To ensure the success the artificial inoculation, the plants were transferred to a humid chamber with a relative humidity of about 95% and 20 to 24°C for 24 h. The trial plants were cultivated for fourteen days in a greenhouse chamber at 23 to 27°C and a relative humidity between 60 and 80%. The extent of fungal attack on the leaves was visually assessed as % diseased leaf area.

In this test, the plants which had been treated with 250 ppm of the active compound I-2, I-4, I-9, I-10, I-18, I-20, I-22, I-27, I-29, I-30, I-31, I-31, I-33, I-36, I-37, I-39, I-42, I-43, I-46, I-48, I-49, I-50, I-51, I-52, I-55, I-56, I-58, I-59, I-62, I-64, I-65, I-66, I-67, I-68, I-69, I-71, I-73, I-77, I-80 or I-82 showed a diseased leaf area of at most 15%, whereas the untreated plants showed 94% diseased leaf area.

Use example 5: Preventative fungicidal control of *Botrytis cinerea* on leaves of green pepper. Young seedlings of green pepper were grown in pots to the 4 to 5 leaf stage. These plants were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient or their mixture mentioned in the table below. The next day the plants were inoculated with a aqueous biomalt solution containing the spore suspension of *Botrytis cinerea*. Then the plants were immediately transferred to a humid chamber and kept for 5 days at 22 to 24°C and a relative humidity close to 100 %.

In this test, the plants which had been treated with 250 ppm of the active compound I-2, I-18, I-22, I-27, I-29, I-33, I-35, I-36, I-39, I-41, I-42, I-43, I-60 or I-74 showed a diseased leaf area of at most 15%, whereas the untreated plants showed 95% diseased leaf area.

Use example 6: Control of late blight on tomatoes caused by *Phytophthora infestans*. Young seedlings of tomato plants were grown in pots. These plants were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient or their mixture mentioned in the table below. After seven days the treated plants were inoculated with an aqueous suspension of sporangia of *Phytophthora infestans*. After inoculation, the trial plants were immediately

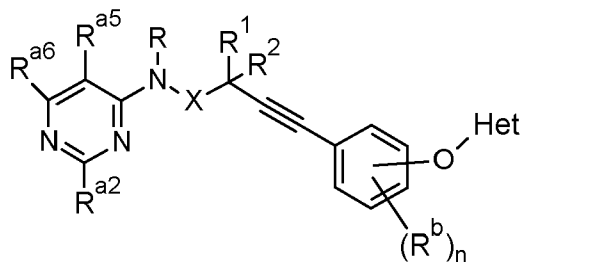
transferred to a humid chamber and kept for 6 days at 18 to 20°C and a relative humidity close to 100%.

In this test, the plants which had been treated with 250 ppm of the active compound I-27, I-29, I-35, I-37, I-44, I-45, I-47, I-48, I-49, I-50, I-56, I-59, I-65, I-66, I-67, I-70 or

- 5 I-78 showed a diseased leaf area of at most 20%, whereas the untreated plants showed 67% diseased leaf area.

We claim:

1. Compounds of formula I



5 wherein:

R^{a2} , R^{a5} , R^{a6} independently of each other are hydrogen, halogen, CN, NO_2 , OH, SH, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkoxy, C_1 - C_4 -alkylthio, C_1 - C_4 -haloalkylthio, C_1 - C_4 -alkylsulfinyl, C_1 - C_4 -haloalkylsulfinyl, C_1 - C_4 -alkylsulfonyl, C_1 - C_4 -haloalkylsulfonyl, C_1 - C_4 -alkoxy- C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy- C_1 - C_4 -alkoxy, C_2 - C_4 -alkenyl, C_2 - C_4 -alkynyl, C_2 - C_4 -haloalkenyl, C_2 - C_4 -haloalkynyl, C_3 - C_8 -cycloalkyl, C_3 - C_8 -cycloalkyloxy, C_3 - C_8 -cycloalkyl- C_1 - C_4 -alkyl, $\text{NR}^{\text{A}}\text{R}^{\text{B}}$, $\text{C}(=\text{O})\text{R}'$, $\text{C}(=\text{NOR}'')\text{R}'''$ or - $\text{C}(=\text{NH})\text{-O-R}'''$;

15 R^{A} , R^{B} independently of one another are hydrogen, C_1 - C_4 -alkyl, C_2 - C_4 -alkenyl, C_2 - C_4 -alkynyl, phenyl, benzyl, C_3 - C_8 -cycloalkyl, C_3 - C_8 -cycloalkenyl or $-(\text{C}=\text{O})\text{-R}'$;

20 R' is hydrogen, OH, NH_2 , C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_2 - C_4 -alkenyl, C_2 - C_4 -alkynyl, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkoxy, C_1 - C_4 -alkylamino or di(C_1 - C_4 -alkyl)amino;

R'' is hydrogen, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_2 - C_4 -alkenyl, C_2 - C_4 -alkynyl or C_1 - C_4 -alkoxy- C_1 - C_4 -alkyl;

25 R''' is hydrogen or C_1 - C_4 -alkyl; or

R^{a5} , R^{a6} together with two ring member carbon atoms to which they are attached, form a fused 5-, 6- or 7-membered saturated, partially unsaturated or aromatic carbocycle or heterocycle, wherein the ring member atoms of the fused heterocycle include besides carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S, and wherein the fused carbocycle or heterocycle is unsubstituted or carries 1, 2, 3 or 4 identical or different radicals selected from the group consisting of halogen, CN, C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkyl and C_1 - C_4 -haloalkoxy;

35

R is hydrogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkoxy-C₁-C₄-alkyl, C₁-C₄-haloalkoxy-C₁-C₄-alkyl, C₂-C₄-alkenyl, C₂-C₄-haloalkenyl, C₂-C₄-alkynyl, C₂-C₄-haloalkynyl, CN, CH₂CN, NR^AR^B or CH₂-O-C(=O)R';

R¹, R² independently of each other are hydrogen, halogen, CN, OH, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkoxy-C₁-C₄-alkyl, C₁-C₄-haloalkoxy-C₁-C₄-alkyl, C₂-C₄-alkenyl, C₂-C₄-haloalkenyl, C₂-C₄-alkynyl, C₂-C₄-haloalkynyl, C₃-C₈-cycloalkyl, C₃-C₈-cycloalkyl-C₁-C₄-alkyl, C₃-C₈-cycloalkyloxy, NR^AR^B, C(=O)R', C(=NOR'')R''', -C(=NH)-O-R''' or benzyl wherein the phenyl moiety of benzyl is unsubstituted or carries 1, 2, 3, 4, or 5 substituents selected from the group consisting of CN, halogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, (C₁-C₄-alkoxy)carbonyl and di(C₁-C₄-alkyl)aminocarbonyl;

or two radicals R¹ and R² that are bound to the same carbon atom form together with said carbon atom a saturated or partially unsaturated 3-, 4-, 5-, 6-, or 7-membered carbocycle or a saturated or partially unsaturated 3-, 4-, 5-, 6-, or 7-membered heterocycle, wherein the ring member atoms of the abovementioned heterocycle include beside carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S, and wherein the abovementioned cycle is unsubstituted or carries 1, 2, 3 or 4 substituents selected from halogen, CN, OH, SH, C₁-C₄-alkyl, C₁-C₄-alkoxy or C₁-C₄-alkylthio; and one or two CH₂ groups of the abovementioned cycles may respectively be replaced by one or two C(=O) or C(=S) groups;

X is a divalent group selected from -CR³R⁴-, -C(=O)-, -C(=S)-, -C(=NR^D)- and -C(=NOR^D)-, wherein

R^D is hydrogen or C₁-C₄-alkyl, and wherein

R³, R⁴ independently of each other are hydrogen, CN, C₁-C₄-hydroxyalkyl, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkoxy-C₁-C₄-alkyl, C₁-C₄-haloalkoxy-C₁-C₄-alkyl, C₂-C₄-alkenyl, C₂-C₄-haloalkenyl, C₂-C₄-alkynyl, C₂-C₄-haloalkynyl, C₃-C₈-cycloalkyl, C₃-C₈-cycloalkyl-C₁-C₄-alkyl, C₃-C₈-cycloalkyloxy, NR^AR^B, C(=O)R', C(=NOR'')R''', -C(=NH)-O-R''' or benzyl wherein the phenyl moiety of benzyl is unsubstituted or carries 1, 2, 3, 4, or 5 substituents selected from the group consisting of CN, halogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, (C₁-C₄-alkoxy)carbonyl and di(C₁-C₄-alkyl)aminocarbonyl, or

two radicals R³ and R⁴ that are bound to the same carbon atom form together with said carbon atom a saturated or partially unsaturated 3-, 4-, 5-, 6-, or 7-membered carbocycle or a saturated or partially unsaturated

3-, 4-, 5-, 6-, or 7-membered heterocycle, wherein the ring member atoms of the abovementioned heterocycle include beside carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S, and wherein the abovementioned cycle is unsubstituted or carries 1, 2, 3 or 4 substituents selected from halogen, CN, OH, SH, C₁-C₄-alkyl, C₁-C₄-alkoxy or C₁-C₄-alkylthio; and one or two CH₂ groups of the abovementioned cycles may be respectively replaced by one or two C(=O) or C(=S) groups;

n indicates the number of substituents R^b on the phenyl ring and n is 0, 1, 2, 3 or 4;

R^b is halogen, CN, NO₂, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₂-C₄-alkenyl, C₂-C₄-haloalkenyl, C₂-C₄-alkynyl, C₂-C₄-haloalkynyl, NR^AR^B, C(=O)R', C(=NOR'')R''' or -C(=NH)-O-R''',

it being possible for n = 2, 3 or 4 that R^b are identical or different;

Het is a 5- or 6-membered heteroaryl, wherein the ring member atoms of the heteroaryl include besides carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S and wherein the heteroaryl is unsubstituted or carries 1, 2, 3 or 4 identical or different groups R^c:

R^c is halogen, CN, NO₂, NH₂, C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy, C₁-C₆-alkylamino, di(C₁-C₆-alkyl)amino, C₁-C₆-alkylthio, C₁-C₆-haloalkylthio, C₁-C₆-alkylsulfinyl, C₁-C₆-haloalkylsulfinyl, C₁-C₆-alkylsulfonyl, C₁-C₆-haloalkylsulfonyl, C₁-C₆-alkoxy-C₁-C₄-alkyl, C₁-C₆-haloalkoxy-C₁-C₄-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl, C(=O)R', C(=NOR'')R''', C₃-C₈-cycloalkyl, C₃-C₈-cycloalkyl-C₁-C₄-alkyl, phenyl, phenoxy, phenoxy-C₁-C₄-alkyl or a 5- or 6-membered heteroaryl, wherein the ring member atoms of the heteroaryl include besides carbon atoms 1, 2, 3 or 4 heteroatoms selected from the group of N, O and S, and wherein the aforementioned cyclic radicals are unsubstituted or carry 1, 2, 3 or 4 identical or different substituents R^d:

R^d is halogen, CN, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy or C₁-C₄-haloalkoxy;

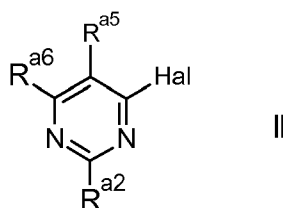
or two radicals R^c that are bound to adjacent ring member atoms of the Het group form together with said ring member atoms a fused 5-, 6- or 7-membered saturated, partially unsaturated or aromatic carbocycle or heterocycle, wherein the ring member atoms of the fused heterocycle include besides carbon atoms 1, 2, 3 or 4 heteroatoms selected from the

group of N, O and S, and wherein the fused carbocycle or heterocycle is unsubstituted or carries 1, 2, 3 or 4 identical or different radicals groups R^e:

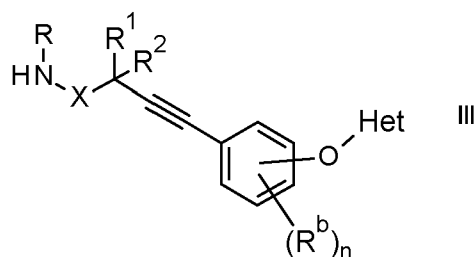
R^e is halogen, CN, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy or C₁-C₄-haloalkoxy;

and the N-oxides and the agriculturally acceptable salts of the compounds of formula I.

2. Compounds according to claim 1, wherein R^{a2}, R^{a5} and R^{a6} independently of each other are halogen, CN, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkoxy-C₁-C₄-alkyl, C₁-C₄-alkoxy-C₁-C₄-alkoxy or (C₁-C₄-alkoxy)carbonyl, and it being possible that one or two of R^{a2}, R^{a5} or R^{a6} can in addition be hydrogen.
3. Compounds according to claims 1 and 2, wherein X is -CH₂-, -C(=O)-, -CH(CH₃)-, -C(CH₃)₂-, -CHCN-, -CH(C(=O)-OCH₃)-, -CH(C(=O)-OCH₂CH₃)-.
4. Compounds according to any one of claims 1 to 3, wherein X is -CH₂-.
5. Compounds according to any one of the preceding claims, wherein X is -C(=O)-.
6. Compounds according to any one of the preceding claims, wherein Het is pyrimidin-2-yl, pyrimidin-3-yl, pyrimidin-4-yl, pyridin-2-yl, pyridin-3-yl, pyridin-4-yl, thiazol-2-yl, pyrazin-2-yl, pyridazin-3-yl, 1,3,5-triazin-2-yl, or 1,2,4-triazin-3-yl.
7. Compounds according to any one of the preceding claims, wherein Het carries 1 or 2 radicals R^c which are selected from F, Cl, Br, CN, C₁-C₂-alkylsulfonyl, C₁-C₂-alkoxycarbonyl, aminocarbonyl, C₁-C₂-alkylaminocarbonyl, di(C₁-C₂-alkyl)aminocarbonyl, C₁-C₂-alkoxy, CF₃, CHF₂, OCF₃ and OCHF₂.
8. A process for preparing compounds I according to claim 1, wherein X is -CR³R⁴- or -C(=O)-, which comprises reacting a compound of formula II



wherein R^{a2}, R^{a5} and R^{a6} are as defined in claim 1, Hal is fluorine, chlorine or bromine, with a compound of formula III



wherein R, R¹, R², R^b, n and Het are as defined in claim 1 and X is -CR³R⁴- or -C(=O)- as defined in claim 1 in the presence of a base or a catalyst or a combination of a base and a catalyst in a solvent.

9. An agrochemical composition which comprises an auxiliary and at least one compound of formula I or an N-oxide or an agriculturally acceptable salt thereof, according to any one of claims 1 to 7.
10. An agrochemical composition according to claim 9 comprising at least one further active substance.
11. A method for combating phytopathogenic harmful fungi, which process comprises treating the fungi or the materials, plants, the soil or seeds to be protected against fungal attack, with an effective amount of at least one compound of formula I or an N-oxide or an agriculturally acceptable salt thereof, according to any one of claims 1 to 7.
12. The use of compounds of formula I, their N-oxides or their agriculturally acceptable salts, according to any one of claims 1 to 7 for combating phytopathogenic harmful fungi.
13. Seed treated with a compound of formula I, or an N-oxide or an agriculturally acceptable salt thereof, as defined in any one of claims 1 to 7, in an amount of from 0.1 g to 10 kg per 100 kg of seed.