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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
23 April 2015 (23.04.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/055764 A1

(51) International Patent Classification:
C07D 213/74 (2006.01) *C07D 405/12* (2006.01)
C07D 213/75 (2006.01) *C07D 417/12* (2006.01)
C07D 401/12 (2006.01) *A01N 43/40* (2006.01)

(21) International Application Number:
PCT/EP2014/072212

(22) International Filing Date:
16 October 2014 (16.10.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
13189395.0 18 October 2013 (18.10.2013) EP

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

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

Declarations under Rule 4.17:

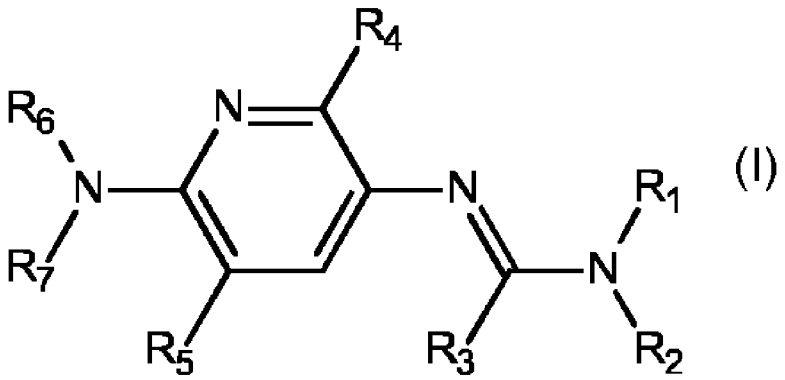
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *of inventorship (Rule 4.17(iv))*

Published:

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

(54) Title: 3-METHANIMIDAMID-PYRIDINE DERIVATIVES AS FUNGICIDES



(57) Abstract: The present invention provides a compound of formula (I) wherein R^1-R^7 as as defined in claim 1 useful as fungicides.

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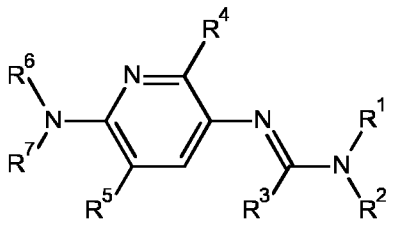
3-METHANIMIDAMID-PYRIDINE DERIVATIVES AS FUNGICIDES

The present invention relates to novel microbiocidally active, in particular fungicidally active, pyridylamidine compounds. It further relates to intermediates used in the preparation of these compounds, to compositions which comprise these compounds and to their use in agriculture or horticulture for controlling or preventing infestation of plants by phytopathogenic microorganisms, preferably fungi.

Certain pyridylamidines derivatives have been proposed in the literature as microbicidally active ingredients in pesticides. For example, WO 00/46184 and WO 03/093224 disclose pyridylamidines which are useful as fungicides. However, the biological properties of these known compounds are not entirely satisfactory for controlling or preventing infestation of plants by phytopathogenic microorganisms, which is why there is a need to provide other compounds which have microbicidal properties.

The present invention accordingly relates to compounds of formula I


(I),

wherein

R^1 and R^2 independently represent hydrogen or C_1-C_4 alkyl or C_3-C_6 cycloalkyl

R^3 represents hydrogen;

R^4 represents C_1-C_4 alkyl, C_1-C_4 haloalkyl or C_3-C_6 cycloalkyl;

R^5 represents hydrogen, halogen, cyano, hydroxy, formyl, carboxy, amino, C_1-C_4 alkyl, C_2-C_4 alkenyl, C_2-C_4 alkynl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, C_3-C_6 cycloalkyl, C_2-C_4 alkylcarbonyl, C_2-C_4 alkoxycarbonyl, C_1-C_4 alkylthio, C_1-C_4 alkylsulfinyl, C_1-C_4 alkylsulfonyl, $-N(R^8)(R^9)$, $-C(=O)N(R^8)(R^9)$ or $-S(=O)_2N(R^8)(R^9)$; or

R^5 represents a 5- or 6-member heterocycle containing 1-4 nitrogen atoms which may be optionally substituted by one or more groups selected from the group consisting of methyl, halogen and cyano;

R^6 represents hydrogen, C_1-C_4 alkyl, C_1-C_4 alkoxycarbonyl, C_1-C_4 alkylcarbonyl or formyl;

R^7 represents G^1, G^2-G^3-, G^4, G^5-G^3-, G^6, G^7-G^3-, G^8, G^9-G^3-, G^{10}, G^{11}, G^{12} or G^{13},

G^1 and G^2 represent an eight to ten-membered fused bicyclic ring system which can be aromatic, partially saturated or fully saturated and can contain 1 to 4 hetero atoms selected from the group consisting of N, $N(R^{10})$, O and S, it not being possible for each ring system to contain -O-O-, -S-S- and –O-S- fragments, and it being possible for the eight- to ten-membered ring system to be optionally substituted by one or more groups independently selected from the group consisting of hydrogen, halogen, cyano, nitro, hydroxy, mercapto, azido, formyl, carboxy, S(=O), $S(=O)_2$, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, C_2-C_4 alkylcarbonyl, C_1-C_4 haloalkoxy, $-N(R^8)(R^9)$, $-C(=O)$ $N(R^8)(R^9)$ and $-S(=O)_2N(R^8)(R^9)$;

G^3 represents methylene optionally substituted by one or two groups independently selected from halogen, C_1-C_4-alkyl, C_1-C_4-haloalkyl, CN, C_1-C_4-alkoxy and C_1-C_4-haloalkoxy;

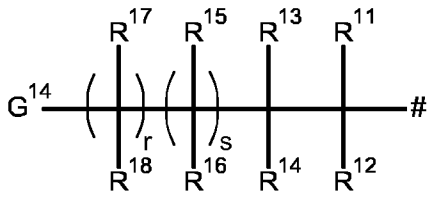
G^4 and G^5 represent a C_5-C_6 aromatic monocyclic system which contains 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, it not being possible for each ring system to contain -O-O-, -S-S- and -O-S- fragments, and is optionally substituted by one or more groups independently selected from hydrogen, halogen, CN, OH, CHO, COOH, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl, C_1-C_4 haloalkoxy, C_3-C_6 cycloalkyl, C_1-C_4 alkoxycarbonyl, $C(=O)N(R^8)(R^9)$ and $-S(=O)_2N(R^8)(R^9)$;

G^6 and G^7 represent phenyl optionally substituted by one or more groups independently selected from hydrogen, halogen, CN, NO_2, OH, SH, CHO, COOH, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl, C_2-C_4 alkenyl, C_2-C_4 haloalkenyl, C_1-C_4 haloalkoxy, C_1-C_4 alkylcarbonyl, $-C(=O)N(R^8)(R^9)$, $-C(=S)N(R^8)(R^9)$; and $-S(=O)_2N(R^8)(R^9)$;

G^8 and G^9 represent a five- or six-membered saturated monocyclic system which contains 1 or 2 members selected from the group consisting of N, $N(R^{10})$, O and S, it not being possible for each ring system to contain -O-O-, -S-S- and -O-S- fragments, and it being possible for the five- to six-membered ring system to be optionally substituted by one or more groups independently selected from the group consisting of hydrogen, halogen, CN, NO_2, OH, SH, CHO, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_3-C_6 cycloalkyl, C_2-C_6 alkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_1-C_4 alkoxy, C_1-C_4 haloalkoxy, C_3-C_6 alkynyloxy, =O, S(=O), $S(=O)_2$, and $-N(R^8)(R^9)$;

G^{10} represents a C_5-C_7 monocarbocyclic system optionally substituted by one or more groups independently selected from hydrogen, halogen, CN, OH, CHO, COOH, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl, C_1-C_4 haloalkoxy, C_3-C_6 cycloalkyl, C_1-C_4 alkylcarbonyl, $C(=O)N(R^8)(R^9)$, and $-S(=O)_2N(R^8)(R^9)$;

G^{11} represents



;

G^{12} represents C_4-C_7-alkylsulfonyl, C_4-C_7 alkenylsulfonyl, C_4-C_7 alkynylsulfonyl, C_4-C_7 cycloalkylsulfonyl, benzylsulfonyl or phenylsulfonyl, wherein the benzylsulfonyl and the phenylsulfonyl are optionally substituted by one or more groups independently selected from the group consisting of halogen, CN, OH, CHO, COOH, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy and C_1-C_4 haloalkoxy;

G^{13} represents C_4-C_7alkylcarbonyl, C_4-C_7 alkenylcarbonyl, C_4-C_7 alkynylcarbonyl, C_4-C_7 cycloalkylcarbonyl, benzylcarbonyl or phenylcarbonyl wherein the benzylcarbonyl and phenylcarbonyl can be optionally substituted by one or more substituents independently selected from the group consisting of halogen, CN, OH, SH, CHO, COOH, C_1-C_4 alkyl, and C_1-C_4haloalkyl;

G^{14} represents hydrogen, C_3-C_6 cycloalkyl, G^2, G^4, G^5, phenoxy or benzyloxy wherein the phenoxy or benzyloxy may be optionally substituted by one or more groups independently selected

from the group consisting of halogen, cyano, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy and C_1-C_4 haloalkyl;

R^8 and R^9, independently of each other represent hydrogen, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_3-C_6 cycloalkyl or C_3-C_6 halocycloalkyl, phenyl or benzyl; or

R^8 and R^9 together with their interconnecting nitrogen atom represent pyrazolino, pyrazolidino, pyrrolino, pyrrolidino, imidazolino, imidazolidino, morpholino or thiomorpholino;

R^{10} represents hydrogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 alkylcarbonyl, C_1-C_4 alkoxycarbonyl, -$C(=O)N(R^8)(R^9)$, -$S(=O)_2N(R^8)(R^9)$, benzyl or phenyl, wherein the benzyl and phenyl are optionally substituted by one or more groups independently selected from the group consisting of halogen, cyano, C_1-C_4 alkyl, C_1-C_4 haloalkyl, or C_1-C_4 alkoxy;

R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17} and R^{18} independently of each other represent hydrogen, halogen, cyano, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy or C_1-C_4 haloalkoxy;

r and s independently of each other represent 0 or 1;

or a salt or an N-oxide thereof.

Substituents at a nitrogen atom are always different from halogen. A hydroxy, mercapto or amino substituent is not to be placed on an α-carbon relative to a heteroatom of a core fragment.

Halogen, either as a lone substituent or in combination with another substituent (e.g. haloalkyl) is generally fluorine, chlorine, bromine or iodine, and usually fluorine, chlorine or bromine.

Each alkyl moiety (including the alkyl moiety of alkoxy, alkylthio, etc.) is a straight or branched chain and, depending on the number of carbon atoms it contains, is, for example, methyl, ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, *n*-hexyl, *iso*-propyl, *sec*-butyl, *iso*-butyl, *tert*-butyl, *neo*-pentyl, *n*-heptyl or 1,3-dimethylbutyl, and usually methyl or ethyl.

The alkenyl and alkynyl groups can be mono- or di-unsaturated and examples thereof are derived from the above mentioned alkyl groups.

The alkenyl group is an unsaturated straight or branched chain having a carbon-carbon double bond and, depending on the number of carbon atoms it contains, is, for example ethenyl, 1-propenyl, 2-propenyl, 1-methyl-ethenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl, 2-methyl-2-propenyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1-methyl-1-butenyl, 2-methyl-1-butenyl, 3-methyl-1-butenyl, 1-methyl-2-butenyl, 2-methyl-2-butenyl, 3-methyl-2-butenyl, 1-methyl-3-butenyl, 2-methyl-3-butenyl, 3-methyl-3-butenyl, 1,1-dimethyl-2-propenyl, 1,2-dimethyl-1-propenyl, 1,2-dimethyl-2-propenyl, 1-ethyl-2-propenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 4-hexenyl, 5-hexenyl, 1-methyl-1-pentenyl, 2-methyl-1-pentenyl, 3-methyl-1-pentenyl, 4-methyl-1-pentenyl, 1-methyl-2-pentenyl, 2-methyl-2-pentenyl, 3-methyl-2-pentenyl, 4-methyl-2-pentenyl, 1-methyl-3-pentenyl, 2-methyl-3-pentenyl, 3-methyl-3-pentenyl, 4-methyl-3-pentenyl, 1-methyl-4-pentenyl, 2-methyl-4-pentenyl, 3-methyl-4-pentenyl, 4-methyl-4-pentenyl, 1,1-dimethyl-2-butenyl, 1,1-dimethyl-3-butenyl, 1,2-dimethyl-1-butenyl, 1,2-dimethyl-2-butenyl, 1,2-dimethyl-3-butenyl, 1,3-dimethyl-1-butenyl, 1,3-dimethyl-2-butenyl, 1,3-dimethyl-3-butenyl, and usually 2-propenyl, 1-methyl-2-propenyl, 2-butenyl, 2-methyl-2-propenyl.

The alkynyl group is an unsaturated straight or branched chain having a carbon-carbon triple bond and, depending on the number of carbon atoms it contains, is, for example ethynyl, 1-propynyl, 2-propynyl, 1-butynyl, 2-butynyl, 3-butynyl, 1-methyl-2-propynyl, 1-pentynyl, 2-pentynyl, 3-pentynyl, 4-pentynyl, 3-methyl-1-butynyl, 1-methyl-2-butynyl, 1-methyl-3-butynyl, 2-methyl-3-butynyl, 1,1-dimethyl-

2-propynyl, 1-ethyl-2-propynyl, 1-hexynyl, 2-hexynyl, 3-hexynyl, 4-hexynyl, 5-hexynyl, 3-methyl-1-pentynyl, 4-methyl-1-pentynyl, 1-methyl-2-pentynyl, 4-methyl-2-pentynyl, 1-methyl-3-pentynyl, 2-methyl-3-pentynyl, 1-methyl-4-pentynyl, 2-methyl-4-pentynyl, 3-methyl-4-pentynyl, 3,3,-dimethyl-1-butynyl, 1-ethyl-2-butynyl, 1,1-dimethyl-2-butynyl, 1-ethyl-3-butynyl, 2-ethyl-3-butynyl, 1,1-dimethyl-3-butynyl, 2,2-dimethyl-3-butynyl, 1,2-dimethyl-3-butynyl.

Haloalkyl moieties are alkyl moieties which are substituted by one or more of the same or different halogen atoms and are, for example, monofluoromethyl, difluoromethyl, trifluoromethyl, monochloromethyl, dichloromethyl, trichloromethyl, 2,2,2-trifluoroethyl, 2,2-difluoroethyl, 2-fluoroethyl, 1,1-difluoroethyl, 1-fluoroethyl, 2-chloroethyl, pentafluoroethyl, 1,1-difluoro-2,2,2-trichloroethyl, 2,2,3,3-tetrafluoroethyl and 2,2,2-trichloroethyl, and typically trichloromethyl, difluorochloromethyl, difluoromethyl, trifluoromethyl and dichlorofluoromethyl.

Alkoxy is, for example, methoxy, ethoxy, propoxy, *iso*-propoxy, *n*-butoxy, *iso*-butoxy, *sec*-butoxy and *tert*-butoxy, and usually methoxy or ethoxy.

Haloalkoxy is, for example, fluoromethoxy, difluoromethoxy, trifluoromethoxy, 2,2,2-trifluoroethoxy, 1,1,2,2-tetrafluoroethoxy, 2-fluoroethoxy, 2-chloroethoxy, 2,2-difluoroethoxy and 2,2,2-trichloroethoxy, and usually difluoromethoxy, 2-chloroethoxy and trifluoromethoxy.

Alkylthio is, for example, methylthio, ethylthio, propylthio, *iso*-propylthio, *n*-butylthio, *iso*-butylthio, *sec*-butylthio or *tert*-butylthio, and usually methylthio or ethylthio.

Alkylsulphonyl is, for example, methylsulphonyl, ethylsulphonyl, propylsulphonyl, *iso*-propylsulphonyl, *n*-butylsulphonyl, *iso*-butylsulphonyl, *sec*-butylsulphonyl or *tert*-butylsulphonyl, and usually methylsulphonyl or ethylsulphonyl.

Alkylsulphinyl is, for example, methylsulphinyl, ethylsulphinyl, propylsulphinyl, *iso*-propylsulphinyl, *n*-butylsulphinyl, *iso*-butylsulphinyl, *sec*-butylsulphinyl or *tert*-butylsulphinyl, and usually methylsulphinyl or ethylsulphinyl.

Cycloalkyl may be saturated or partially unsaturated, preferably fully saturated, and is, for example, cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl.

Alkoxyalkyl is, for example, methoxymethyl, methoxyethyl, ethoxymethyl, ethoxyethyl, *n*-propoxymethyl, *n*-propoxyethyl, *iso*-propoxymethyl or *iso*-propoxyethyl.

Aryl includes phenyl, naphthyl, anthracyl, fluorenyl and indanyl, but is usually phenyl.

Carbocycle includes cycloalkyl groups and aryl groups.

Heterocycloalkyl is a non-aromatic ring that may be saturated or partially unsaturated, preferably fully saturated, containing carbon atoms as ring members and at least one heteroatom selected from O, S and N as ring members. Examples include oxiranyl, oxetanyl, tetrahydrofuranyl, tetrahydropyranyl, 1,3-dioxolanyl, 1,4-dioxanyl, aziridinyl, azetidinyl, pyrrolidinyl, piperidinyl, oxazinanyl, morpholinyl, thiomorpholinyl, imidazolidinyl, pyrazolidinyl and piperazinyl, preferably morpholinyl, pyrrolidinyl, piperdinyl and piperazinyl, more preferably morpholinyl and pyrollidinyl.

Heteroaryl is, for example, a monovalent monocyclic or bicyclic aromatic hydrocarbon radical. Examples of monocyclic groups include pyridyl, pyridazinyl, pyrimidinyl, pyrazinyl, pyrrolyl, pyrazolyl, imidazolyl, triazolyl, tetrazolyl, furanyl, thiophenyl, oxazolyl, isoxazolyl, oxadiazolyl, thiazolyl, isothiazolyl, and thiadiazolyl. Examples of bicyclic groups include quinolinyl, cinnolinyl, quinoxalinyl, benzimidazolyl,

benzothiophenyl, and benzothiadiazolyl. Monocyclic heteroaryl groups are preferred, preferably pyridyl, pyrrolyl, imidazolyl and triazolyl, e.g. 1,2,4 triazolyl, pyridyl and imidazolyl being most preferred.

The terms “heterocycle” and “heterocyclic ring” are used interchangeably and are defined to include heterocycloalkyl and heteroaryl groups. Any reference herein to a heterocycle or heterocyclic ring preferably refers to the specific examples given under the definition of heteroaryl and heterocycloalkyl above, and are preferably morpholinyl, pyrrolidinyl, piperdinyl, piperazinyl pyridyl, pyrrolyl, imidazolyl and triazolyl, e.g. 1,2,4 triazolyl, more preferably morpholinyl, pyrollidinyl, pyridyl and imidazolyl.

No heterocycle contains adjacent oxygen atoms, adjacent sulphur atoms, or adjacent oxygen and sulphur atoms.

Where a moiety is indicated as being (optionally) substituted, e.g. alkyl, this includes those moieties where they are part of a larger group, e.g. the alkyl in the alkylthio group. The same applies, e.g. to the phenyl moiety in phenylthio etc. Where a moiety is indicated as being optionally substituted by one or more other groups, preferably there are one to five optional substituents, more preferably one to three optional substituents. Where a moiety is substituted by a cyclic group, e.g. aryl, heteroaryl, cycloalkyl, preferably there are no more than two such substituents, more preferably no more than one such substituent.

The following list provides definitions, including preferred definitions, for substituents R^1, R^2, R^3, R^4, R^5, R^6 and R^7 with reference to compounds of formula I. For any one of these substituents, any of the definitions given below may be combined with any definition of any other substituent given below or elsewhere in this document.

R^1 and R^2 each independently represent hydrogen, C_1-C_4 alkyl or C_3-C_6 cycloalkyl.

Preferably, R^1 and R^2 each independently represent hydrogen, methyl, ethyl, isopropyl or cyclopropyl.

Most preferably, R^1 represents methyl and R^2 represents ethyl.

R^3 represents hydrogen.

R^4 represents C_1-C_4 alkyl, C_1-C_4 haloalkyl or C_3-C_6 cycloalkyl.

Preferably, R^4 represents methyl, ethyl, isopropyl, propyl or cyclopropyl.

Most preferably, R^4 represents methyl.

R^5 represents hydrogen, halogen, cyano, hydroxy, formyl, carboxy, amino, C_1-C_4 alkyl, C_2-C_4 alkenyl, C_2-C_4 alkynl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, C_3-C_6 cycloalkyl, C_2-C_4 alkylcarbonyl, C_2-C_4 alkoxycarbonyl, C_1-C_4 alkylthio, C_1-C_4 alkylsulfinyl, C_1-C_4 alkylsulfonyl, $-N(R^8)(R^9)$, $-C(=O)N(R^8)(R^9)$ or $-S(=O)_2N(R^8)(R^9)$; or

R^5 represents a 5- or 6-member heterocycle containing 1-4 nitrogen atoms, preferably selected from imidazoline, imidazole, triazole, tetrazole, oxazoline, oxazole, thiazoline, thiazole and pyridyl, which may be optionally substituted by one or more groups selected from the group consisting of methyl, halogen and cyano.

Preferably, R^5 represents hydrogen, halogen, cyano, hydroxy, formyl, carboxy, amino, C_1-C_4 alkyl, C_2-C_4 alkenyl, C_2-C_4 alkynl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, C_3-C_6 cycloalkyl, C_2-C_4 alkylcarbonyl, C_2-C_4 alkoxycarbonyl, C_1-C_4 alkylthio, C_1-C_4 alkylsulfinyl, C_1-C_4 alkylsulfonyl, $-N(R^8)(R^9)$, $-C(=O)N(R^8)(R^9)$ or $-S(=O)_2N(R^8)(R^9)$.

More preferably, R^5 represents hydrogen, halogen, CN, OH, methyl, ethyl, isopropyl, CHF_2, CF_3, methoxy, ethoxy, NMe_2, CHO, COOH, CO-Me, CO_2Me, CONHMe, $CONMe_2$ or $S(=O)_2NHMe$.

Most preferably, R_5 represents hydrogen, halogen, cyano, methyl, ethyl or CHF_2.

R^6 represents hydrogen, C_1-C_4 alkyl, C_1-C_4 alkoxycarbonyl, C_1-C_4 alkylcarbonyl or formyl.

Preferably, R^6 represents hydrogen, C_1-C_4 alkyl, C_1-C_2 alkoxycarbonyl, C_1-C_2 alkylcarbonyl or formyl.

More preferably, R^6 represents hydrogen, C_1-C_4 alkyl, C_1-C_2 alkoxycarbonyl or formyl.

Yet more preferably, R^6 represents hydrogen, methyl, ethyl, isopropyl, formyl or methoxycarbonyl.

Most preferably, R^6 represents hydrogen or methyl.

R^7 represents G^1, G^2-G^3-, G^4, G^5-G^3-, G^6, G^7-G^3-, G^8, G^9-G^3-, G^{10}, G^{11}, G^{12} or G^{13}.

Preferably, R^7 represents G^1, G^2-G^3-, G^4, G^6, G^7-G^3-, G^8, G^9-G^3-, G^{10}, G^{11}, G^{12} or G^{13}.

G^1 and G^2 represents a eight- to ten-membered fused bicyclic ring system which can be aromatic, partially saturated or fully saturated and can contain 1 to 4 hetero atoms selected from the group consisting of N, $N(R^{10})$, O and S, it not being possible for each ring system to contain -O-O-, -S-S- and –O-S- fragments, and it being possible for the eight- to ten-membered ring system to be optionally substituted by one or more groups independently selected from the group consisting of hydrogen, halogen, cyano, nitro, hydroxy, mercapto, azido, formyl, carboxy, S(=O), $S(=O)_2$, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, C_2-C_4 alkylcarbonyl, C_1-C_4 haloalkoxy, $-N(R^8)(R^9)$, $-C(=O)\ N(R^8)(R^9)$ and $-S(=O)_2N(R^8)(R^9)$.

Preferably, G^1 represents an eight- to ten-membered fused bicarbocyclic ring system optionally substituted by one or more groups independently selected from the group consisting of halogen, cyano, hydroxy, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkoxy.

Preferably, G^2 represents an eight- to ten-membered fused bicyclic ring system which can be aromatic, partially saturated or fully saturated and contains 1 to 2 oxygen atoms, it not being possible for each ring system to contain an -O-O- fragment, and it being possible for the eight- to ten-membered ring system to be itself substituted by one or more groups independently selected from the group consisting of halogen, cyano, hydroxy, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl and C_1-C_4 haloalkoxy.

G^3 represents methylene optionally substituted by one or two groups independently selected from halogen, C_1-C_4-alkyl, C_1-C_4-haloalkyl, CN, C_1-C_4-alkoxy and C_1-C_4-haloalkoxy.

Preferably, G^3 represents methylene optionally substituted by one or two groups independently selected from halogen, C_1-C_2-alkyl and C_1-C_2-haloalkyl.

G^4 and G^5 represent a C_5-C_6 aromatic monocyclic system which contains 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, it not being possible for each ring system to contain -O-O-, -S-S- and -O-S- fragments, and is optionally substituted by one or more groups independently selected from hydrogen, halogen, CN, OH, CHO, COOH, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl, C_1-C_4 haloalkoxy, C_3-C_6 cycloalkyl, C_1-C_4 alkoxycarbonyl, $C(=O)N(R^8)(R^9)$ and $-S(=O)_2N(R^8)(R^9)$.

Preferably, G^4 represents a C_5 aromatic monocyclic system which contains 1 or 2 nitrogen or sulfur atom(s), optionally substituted by one or more groups independently selected from halogen, CN, OH, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl, C_1-C_4 haloalkoxy and C_1-C_4 alkoxycarbonyl.

More preferably, G^4 represents a C_5 aromatic monocyclic system which contains 1 nitrogen atom or 1 sulfur atom optionally substituted by one or more groups independently selected from halogen, CN, OH, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl, C_1-C_4 haloalkoxy and C_1-C_4 alkoxycarbonyl.

Preferably, G^5 represents a C_5-C_6 aromatic monocyclic system which contains 1 to 3 hetero atoms selected from nitrogen and oxygen, it not being possible for each ring system to contain an -O-O- fragment, and it being possible for the C_5-C_6 aromatic monocyclic system to be optionally substituted by one or more groups independently selected from hydrogen, halogen, CN, OH, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl and C_1-C_4 haloalkoxy.

More preferably, G^5 represents a C_5-C_6 aromatic monocyclic system which contains 1 hetero atom selected from nitrogen and oxygen, optionally substituted by one or more groups independently selected from hydrogen, halogen, CN, OH, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl and C_1-C_4 haloalkoxy.

G^6 and G^7 represent phenyl optionally substituted by one or more groups independently selected from hydrogen, halogen, CN, NO_2, OH, SH, CHO, COOH, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl, C_2-C_4 alkenyl, C_2-C_4 haloalkenyl, C_1-C_4 haloalkoxy, C_1-C_4 alkylcarbonyl, -C(=O)N(R^8)(R^9), -C(=S)N(R^8)(R^9); and -S(=O)$_2$N(R^8)(R^9).

Preferably, G^6 and G^7 represent phenyl optionally substituted by one or more groups independently selected from halogen, CN, OH, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl and C_1-C_4 haloalkoxy.

G^8 and G^9 represent a five- or six-membered saturated monocyclic system which contains 1 or 2 members selected from the group consisting of N, N(R^{10}), O and S, it not being possible for each ring system to contain -O-O-, -S-S- and -O-S- fragments, and it being possible for the five- to six-membered ring system to be optionally substituted by one or more groups independently selected from the group consisting of hydrogen, halogen, CN, NO_2, OH, SH, CHO, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_3-C_6 cycloalkyl, C_2-C_6 alkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_1-C_4 alkoxy, C_1-C_4 haloalkoxy, C_3-C_6 alkynyloxy, =O, S(=O), S(=O)$_2$, and -N(R^8)(R^9).

Preferably, G^8 represents a five- or six-membered saturated monocyclic system which contains 1 or 2 members selected from the group consisting of N(R^{10}), optionally substituted by one or more groups independently selected from the group consisting of halogen, CN, OH, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy and C_1-C_4 haloalkoxy.

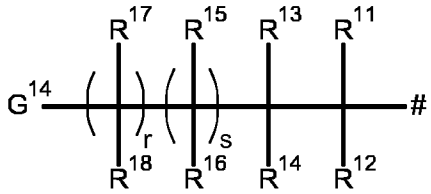
Preferably, G^9 represents a five-membered saturated monocyclic system which contains 1 or 2 oxygen atoms, it not being possible for each ring system to contain an -O-O- fragment, and it being possible for the five- to six-membered ring system to be itself substituted by one or more groups independently selected from the group consisting of halogen, CN, OH, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy and C_1-C_4 haloalkoxy.

G^{10} represents a C_5-C_7 monocarbocyclic system optionally substituted by one or more groups independently selected from hydrogen, halogen, CN, OH, CHO, COOH, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-

C_4 haloalkyl, C_1-C_4 haloalkoxy, C_3-C_6 cycloalkyl, C_1-C_4 alkylcarbonyl, $C(=O)N(R^8)(R^9)$, and -$S(=O)_2N(R^8)(R^9)$.

Preferably, G^{10} represents a C_5-C_7 monocarbocyclic system optionally substituted by one or more groups independently selected from hydrogen, halogen, CN, OH, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl and C_1-C_4 haloalkoxy.

G^{11} represents



G^{12} represents C_4-C_7 alkylsulfonyl, C_4-C_7 alkenylsulfonyl, C_4-C_7 alkynylsulfonyl, C_4-C_7 cycloalkylsulfonyl, benzylsulfonyl or phenylsulfonyl, wherein the benzylsulfonyl and the phenylsulfonyl are optionally substituted by one or more groups independently selected from the group consisting of halogen, CN, OH, CHO, COOH, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy and C_1-C_4 haloalkoxy.

Preferably, G^{12} represents benzylsulfonyl or phenylsulfonyl, each of which can be optionally substituted by one or more groups independently selected from the group consisting of halogen, CN, OH, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, and C_1-C_4 haloalkoxy.

G^{13} represents C_4-C_7alkylcarbonyl, C_4-C_7 alkenylcarbonyl, C_4-C_7 alkynylcarbonyl, C_4-C_7 cycloalkylcarbonyl, benzylcarbonyl or phenylcarbonyl wherein the benzylcarbonyl and phenylcarbonyl can be optionally substituted by one or more substituents independently selected from the group consisting of halogen, CN, OH, SH, CHO, COOH, C_1-C_4 alkyl, and C_1-C_4haloalkyl.

Preferably, G^{13} represents benzylcarbonyl or phenylcarbonyl, each of which are optionally substituted by substituents by one or more groups independently selected from the group consisting of halogen, CN, OH, C_1-C_4 alkyl and C_1-C_4haloalkyl;

G^{14} represents hydrogen, C_3-C_6 cycloalkyl, G^2, G^4, G^5, phenoxy or benzyloxy wherein the phenoxy or benzyloxy may be optionally substituted by one or more groups independently selected from the group consisting of halogen, cyano, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy and C_1-C_4 haloalkyl.

R^8 and R^9, independently of each other represent hydrogen, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_3-C_6 cycloalkyl or C_3-C_6 halocycloalkyl, benzyl or phenyl; or

R^8 and R^9 together with their interconnecting nitrogen atom represent pyrazolino, pyrazolidino, pyrrolino, pyrrolidino, imidazolino, imidazolidino, morpholino or thiomorpholino.

Preferably, R^8 and R^9 independently of each other represent hydrogen, C_1-C_4 alkyl, C_1-C_4 haloalkyl or phenyl.

R^{10} represents hydrogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 alkylcarbonyl, C_1-C_4 alkoxycarbonyl, -$C(=O)N(R^8)(R^9)$, -$S(=O)_2N(R^8)(R^9)$, benzyl or phenyl, wherein the benzyl and phenyl are optionally substituted by one or more groups independently selected from the group consisting of halogen, cyano, C_1-C_4 alkyl, C_1-C_4 haloalkyl, or C_1-C_4 alkoxy.

Preferably, R^{10} represents hydrogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 alkylcarbonyl, C_1-C_4 alkoxycarbonyl, $-S(=O)_2N(R^8)(R^9)$ or phenyl, wherein the phenyl is optionally substituted by one or more groups independently selected from the group consisting of halogen, cyano, C_1-C_4 alkyl, C_1-C_4 haloalkyl, or C_1-C_4 alkoxy.

R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17} and R^{18} independently of each other represent hydrogen, halogen, cyano, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy or C_1-C_4 haloalkyl.

Preferably, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17} and R^{18} independently of each other represent hydrogen, fluoro, cyano, C_1-C_4 alkyl optionally substituted by one or more fluorine atoms or C_1-C_4 alkoxy optionally substituted by one or more fluorine atoms.

More preferably, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17} and R^{18} independently of each other represent hydrogen, fluoro, cyano, C_1-C_4 alkyl or C_1-C_4 alkoxy.

Even more preferably, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17} and R^{18} independently of each other represent hydrogen or C_1-C_2 alkyl.

r and s independently of each other represent 0 or 1.

Preferably, r and s are both 0.

In one group of compounds of formula I,

R^7 represents

G^1, G^2-G^3-, G^4, G^6, G^7-G^3-, G^8, G^9-G^3-, G^{10}, G^{11}, G^{12} or G^{13};

G^1 represents an eight- to ten-membered fused bicarbocyclic ring system optionally substituted by one or more groups independently selected from the group consisting of halogen, cyano, hydroxy, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkoxy;

G^2 represents an eight- to ten-membered fused bicyclic ring system which can be aromatic, partially saturated or fully saturated and contains 1 to 2 oxygen atoms, it not being possible for each ring system to contain an -O-O- fragment, and it being possible for the eight- to ten-membered ring system to be itself substituted by one or more groups independently selected from the group consisting of halogen, cyano, hydroxy, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl and C_1-C_4 haloalkoxy;

G^3 represents methylene optionally one or two groups independently selected from halogen, C_1-C_4-alkyl, C_1-C_4-haloalkyl, CN, C_1-C_4-alkoxy and C_1-C_4-haloalkoxy;

G^4 represents a C_5 aromatic monocyclic system which contains 1 nitrogen atom or 1 sulfur atom optionally substituted by one or more groups independently selected from halogen, CN, OH, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl, C_1-C_4 haloalkoxy and C1-C4 alkoxycarbonyl;

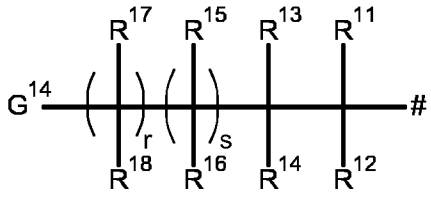
G^6 and G^7 represent phenyl optionally substituted by one or more groups independently selected from halogen, CN, OH, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl and C_1-C_4 haloalkoxy;

G^8 represents a five- or six-membered saturated monocyclic system which contains 1 or 2 members selected from the group consisting of $N(R^{10})$, optionally substituted by one or more groups independently selected from the group consisting of halogen, CN, OH, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy and C_1-C_4 haloalkoxy;

G^9 represents a five-membered saturated monocyclic system which contains 1 or 2 oxygen atoms, it being possible for the five- to six-membered ring system to be itself substituted by one or more groups independently selected from the group consisting of halogen, CN, OH, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy and C_1-C_4 haloalkoxy;

G^{10} represents a C_5-C_7 mono-carbocyclic system optionally substituted by one or more groups independently selected from hydrogen, halogen, CN, OH, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl and C_1-C_4 haloalkoxy;

G^{11} represents



;

G^{12} represents benzylsulfonyl or phenylsulfonyl, each of which can be optionally substituted by one or more groups independently selected from the group consisting of halogen, CN, OH, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, and C_1-C_4 haloalkoxy;

G^{13} represents benzylcarbonyl or phenylcarbonyl, each of which are optionally substituted by substituents by one or more groups independently selected from the group consisting of halogen, CN, OH, C_1-C_4 alkyl and C_1-C_4haloalkyl;

G^{14} represents hydrogen, C_3-C_6 cycloalkyl, G^2, G^4, G^5, phenoxy or benzyloxy wherein the phenoxy or benzyloxy may be optionally substituted by one or more groups independently selected from the group consisting of halogen, cyano, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy and C_1-C_4 haloalkoxy;

R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17} and R^{18} independently of each other represent hydrogen, fluoro, cyano, C_1-C_4 alkyl optionally substituted by one or more fluorine atoms or C_1-C_4 alkoxy;

r and s are both 0.

In another group of compounds of formula (I),

R^1 and R^2 independently represent hydrogen, methyl, ethyl, isopropyl or cyclopropyl;

R^4 represents methyl, ethyl, isopropyl, propyl or cyclopropyl;

R^5 represents hydrogen, halogen, CN, OH, methyl, ethyl, isopropyl, CHF_2, CF_3, methoxy, ethoxy, NMe_2, CHO, COOH, CO-Me, CO_2Me, CONHMe, $CONMe_2$ or $S(=O)_2NHMe$;

R_6 represents hydrogen, methyl, ethyl, isopropyl, formyl or C_1-C_2 alkoxycarbonyl.

In a further group of compounds of formula (I)

R_1 represents methyl;

R_2 represents ethyl;

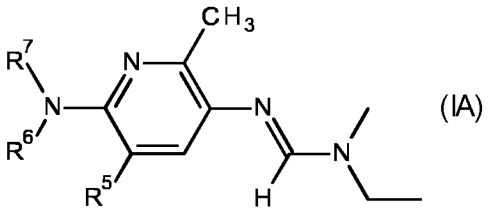
R_4 represents methyl;

R_5 represents hydrogen, halogen, cyano, methyl, ethyl or CHF_2;

R_6 represents hydrogen or methyl.

Tables 1 to 44: Compounds of formula (IA)

The invention is further illustrated by making available the following individual compounds of formula (IA) listed below in Tables 1 to 44.



(IA)

Each of Tables 1 to 44, which follow the Table P below, make available 96 compounds of the formula (IA) in which R^5 and R^6 are the substituents defined in Table P and R^7 is the substituent defined in the relevant Table 1 to 44. Thus Table 1 individualises 96 compounds of formula (IA) wherein for each row of Table P, R^7 is as defined in Table 1;

similarly, Table 2 individualises 96 compounds of formula (IA) wherein for each row of Table P, R^7 is as defined in Table 2; and so on for Tables 3 to 44.

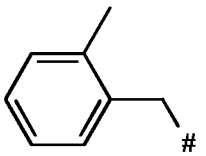
Table P

Compound No	R_5	R_6
P.001	H	H
P.002	Cl	H
P.003	Br	H
P.004	I	H
P.005	CN	H
P.006	Me	H
P.007	Et	H
P.008	CHO	H
P.009	NMe_2	H
P.010	OCH_3	H
P.011	$OCHF_2$	H
P.012	CO_2Me	H
P.013	COMe	H
P.014	CHF_2	H
P.015	CF_2	H
P.016	CH_2F	H
P.017	H	Me
P.018	Cl	Me
P.019	Br	Me
P.020	I	Me
P.021	CN	Me
P.022	Me	Me
P.023	Et	Me
P.024	CHO	Me
P.025	NMe_2	Me
P.026	OCH_3	Me
P.027	$OCHF_2$	Me
P.028	CO_2Me	Me
P.029	COMe	Me
P.030	CHF_2	Me

Compound No	R_5	R_6
P.031	CF_2	Me
P.032	CH_2F	Me
P.033	H	Et
P.034	Cl	Et
P.035	Br	Et
P.036	I	Et
P.037	CN	Et
P.038	Me	Et
P.039	Et	Et
P.040	CHO	Et
P.041	NMe_2	Et
P.042	OCH_3	Et
P.043	$OCHF_2$	Et
P.044	CO_2Me	Et
P.045	COMe	Et
P.046	CHF_2	Et
P.047	CF_2	Et
P.048	CH_2F	Et
P.049	H	i-Pr
P.050	Cl	i-Pr
P.051	Br	i-Pr
P.052	I	i-Pr
P.053	CN	i-Pr
P.054	Me	i-Pr
P.055	Et	i-Pr
P.056	CHO	i-Pr
P.057	NMe_2	i-Pr
P.058	OCH_3	i-Pr
P.059	$OCHF_2$	i-Pr
P.060	CO_2Me	i-Pr
P.061	COMe	i-Pr
P.062	CHF_2	i-Pr
P.063	CF_2	i-Pr
P.064	CH_2F	i-Pr
P.065	H	CHO
P.066	Cl	CHO
P.067	Br	CHO
P.068	I	CHO
P.069	CN	CHO
P.070	Me	CHO
P.071	Et	CHO
P.072	CHO	CHO
P.073	NMe_2	CHO
P.074	OCH_3	CHO

Compound No	R_5	R_6
P.075	$OCHF_2$	CHO
P.076	CO_2Me	CHO
P.077	COMe	CHO
P.078	CHF_2	CHO
P.079	CF_2	CHO
P.080	CH_2F	CHO
P.081	H	C(O)Me
P.082	Cl	C(O)Me
P.083	Br	C(O)Me
P.084	I	C(O)Me
P.085	CN	C(O)Me
P.086	Me	C(O)Me
P.087	Et	C(O)Me
P.088	CHO	C(O)Me
P.089	NMe_2	C(O)Me
P.090	OCH_3	C(O)Me
P.091	$OCHF_2$	C(O)Me
P.092	CO_2Me	C(O)Me
P.093	COMe	C(O)Me
P.094	CHF_2	C(O)Me
P.095	CF_2	C(O)Me
P.096	CH_2F	C(O)Me

Table 1: This table discloses 96 compounds 1.001 to 1.096 of the formula IA wherein R^7 is



(A1)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P. For example, compound 1.001 has the following structure:

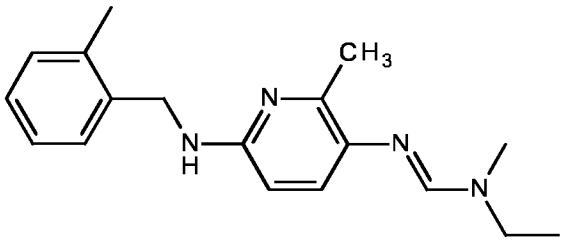
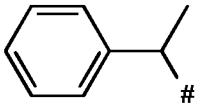


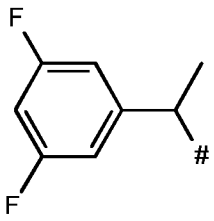
Table 2: This table discloses 96 compounds 2.001 to 2.096 of the formula IA wherein R^7 is



(A2)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

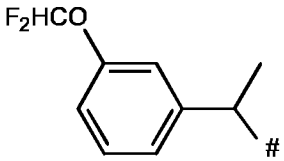
Table 3: This table discloses 96 compounds 3.001 to 3.096 of the formula IA wherein R^7 is



(A3)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

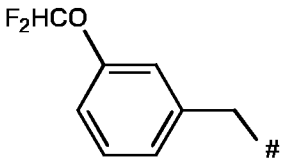
Table 4: This table discloses 96 compounds 4.001 to 4.096 of the formula IA wherein R^7 is



(A4)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

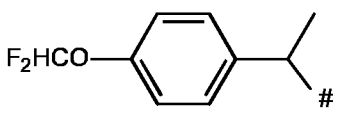
Table 5: This table discloses 96 compounds 5.001 to 5.096 of the formula IA wherein R^7 is



(A5)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

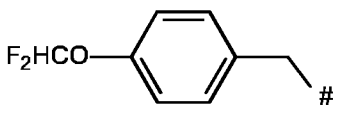
Table 6: This table discloses 96 compounds 6.001 to 6.096 of the formula IA wherein R^7 is



(A6)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

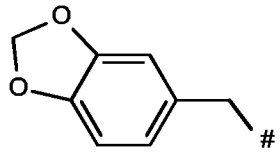
Table 7: This table discloses 96 compounds 7.001 to 7.096 of the formula IA wherein R^7 is



(A7)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

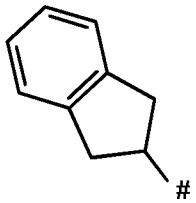
Table 8: This table discloses 96 compounds 8.001 to 8.096 of the formula IA wherein R^7 is



(A8)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

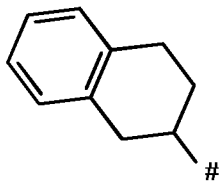
Table 9: This table discloses 96 compounds 9.001 to 9.096 of the formula IA wherein R^7 is



(A9)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

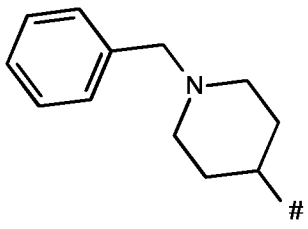
Table 10: This table discloses 96 compounds 10.001 to 11.096 of the formula IA wherein R^7 is



(A10)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

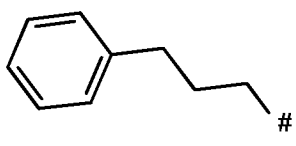
Table 11: This table discloses 96 compounds 11.001 to 11.096 of the formula IA wherein R^7 is



(A11)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

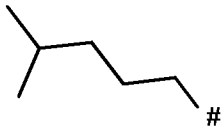
Table 12: This table discloses 96 compounds 12.001 to 12.096 of the formula IA wherein R^7 is



(A12)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

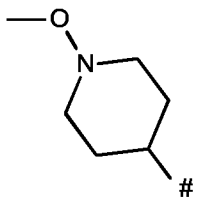
Table 13: This table discloses 96 compounds 13.001.001 to 13.001.096 of the formula IA wherein R^7 is



(A13)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

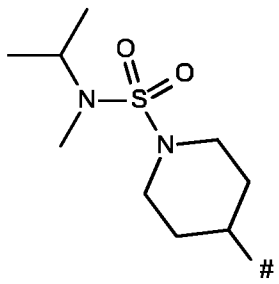
Table 14: This table discloses 96 compounds 14.001 to 14.096 of the formula IA wherein R^7 is



(A14)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

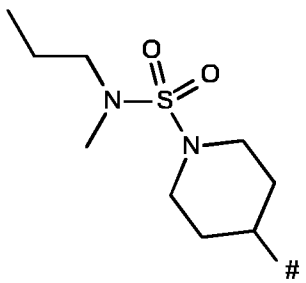
Table 15: This table discloses 96 compounds 15.001 to 15.096 of the formula IA wherein R^7 is



(A15)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

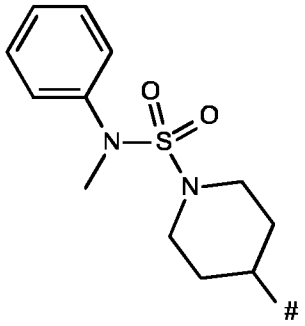
Table 16: This table discloses 96 compounds 16.001 to 16.096 of the formula IA wherein R^7 is



(A16)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

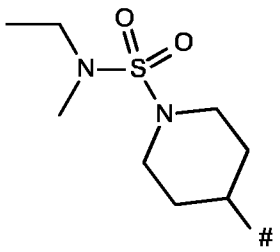
Table 17: This table discloses 96 compounds 17.001 to 17.096 of the formula IA wherein R^7 is



(A17)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

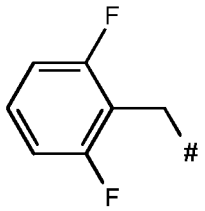
Table 18: This table discloses 96 compounds 18.001 to 18.096 of the formula IA wherein R^7 is



(A18)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

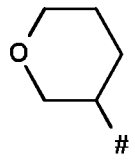
Table 19: This table discloses 96 compounds 19.001 to 19.096 of the formula IA wherein R^7 is



(A19)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

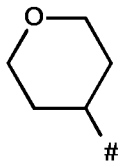
Table 20: This table discloses 96 compounds 20.001 to 20.096 of the formula IA wherein R^7 is



(A20)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

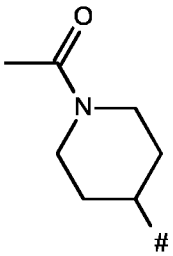
Table 21: This table discloses 96 compounds 21.001 to 21.096 of the formula IA wherein R^7 is



(A21)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

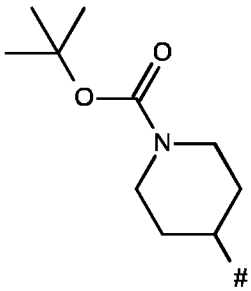
Table 22: This table discloses 96 compounds 22.001 to 22.096 of the formula IA wherein R^7 is



(A22)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

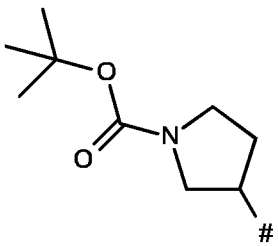
Table 23: This table discloses 96 compounds 23.001 to 23.096 of the formula IA wherein R^7 is



(A23)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

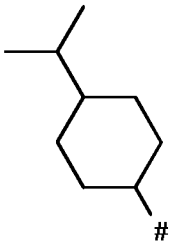
Table 24: This table discloses 96 compounds 24.001 to 24.096 of the formula IA wherein R^7 is



(A24)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

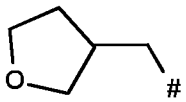
Table 25: This table discloses 96 compounds 25.001 to 25.096 of the formula IA wherein R^7 is



(A25)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

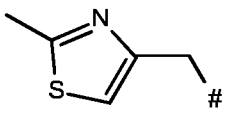
Table 26: This table discloses 96 compounds 26.001 to 26.096 of the formula IA wherein R^7 is



(A26)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

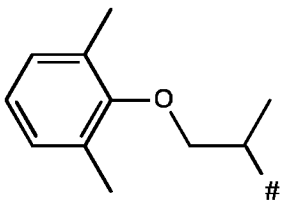
Table 27: This table discloses 96 compounds 27.001 to 27.096 of the formula IA wherein R^7 is



(A27)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

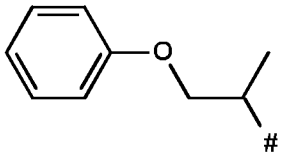
Table 28: This table discloses 96 compounds 28.001 to 28.096 of the formula IA wherein R^7 is



(A28)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

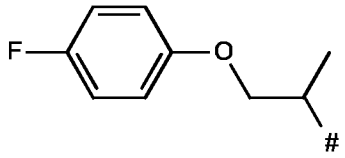
Table 29: This table discloses 96 compounds 29.001 to 29.096 of the formula IA wherein R^7 is



(A29)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

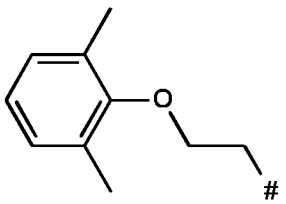
Table 30: This table discloses 96 compounds 30.001 to 30.096 of the formula IA wherein R^7 is



(A30)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

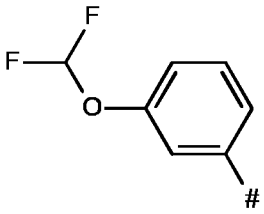
Table 31: This table discloses 96 compounds 31.001 to 31.096 of the formula IA wherein R^7 is



(A31)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

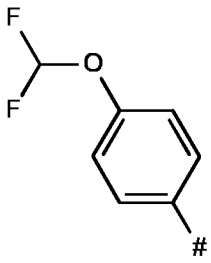
Table 32: This table discloses 96 compounds 32.001 to 32.096 of the formula IA wherein R^7 is



(A32)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

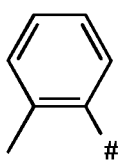
Table 33: This table discloses 96 compounds 33.001 to 33.096 of the formula IA wherein R^7 is



(A33)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

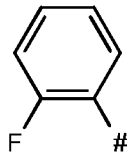
Table 34: This table discloses 96 compounds 34.001 to 34.096 of the formula IA wherein R^7 is



(A34)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

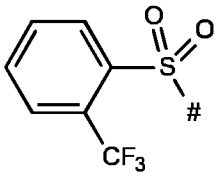
Table 35: This table discloses 96 compounds 35.001 to 35.096 of the formula IA wherein R^7 is



(A35)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

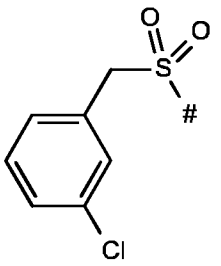
Table 36: This table discloses 96 compounds 36.001 to 36.096 of the formula IA wherein R^7 is



(A36)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

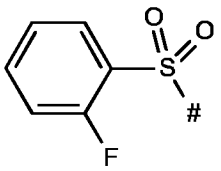
Table 37: This table discloses 96 compounds 37.001 to 37.096 of the formula IA wherein R^7 is



(A37)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

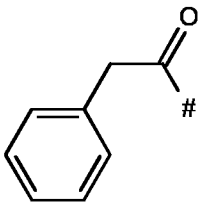
Table 38: This table discloses 96 compounds 38.001 to 38.096 of the formula IA wherein R^7 is



(A38)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

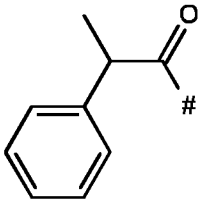
Table 39: This table discloses 96 compounds 39.001 to 39.096 of the formula IA wherein R^7 is



(A39)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

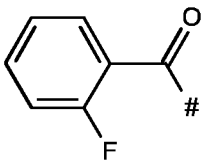
Table 40: This table discloses 96 compounds 40.001 to 40.096 of the formula IA wherein R^7 is



(A40)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

Table 41: This table discloses 96 compounds 41.001 to 41.096 of the formula IA wherein R^7 is

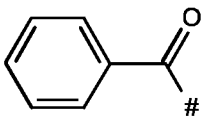


(A41)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

Table 42: This table discloses 96 compounds 42.001 to 42.096 of the formula IA wherein

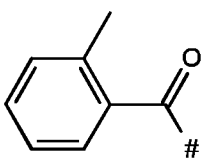
R^7 is



(A42)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

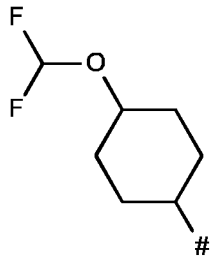
Table 43: This table discloses 96 compounds 43.001 to 43.096 of the formula IA wherein R^7 is



(A43)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

Table 44: This table discloses 96 compounds 44.001 to 44.096 of the formula IA wherein R^7 is



(A44)

Wherein the hash mark indicates the point of attachment of R^7 to the rest of the molecule, and in which the variables R^5 and R^6 has the specific meaning given in the corresponding line of Table P.

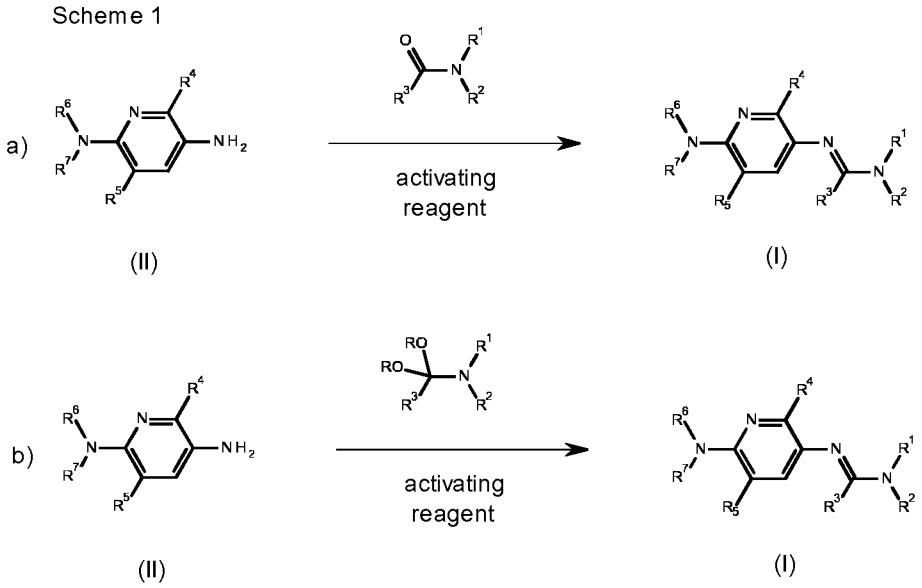
Compounds of formula I, as well as intermediates and reagents used, can be prepared by methods known to a skilled chemist in a variety of ways, or they are commercially available.

Compounds of formula I can be prepared by a number of known methods from amino compounds of formula II. Such methods include the following:

a) Scheme 1 below: An amide of formula $(R^3)C(=O)\text{-}N(R^1)(R^2)$ wherein R^1, R^2 and R^3 are as defined herein for a compound of formula I or a formamide of formula $HC(=O)\text{-}N(R^1)(R^2)$ wherein R^1 and R^2 are as defined herein for a compound of formula (I) is treated with an activating reagent such as $POCl_3$, PCl_3, $COCl_2$, $PhSO_2Cl$, Me_2NSO_2Cl, $(CF_3CO)_2O$, $(MeO)_2SO_2$ and then with an amino compound of formula II wherein R^4, R^5, R^6 and R^7 are as defined herein for a compound of formula (I).

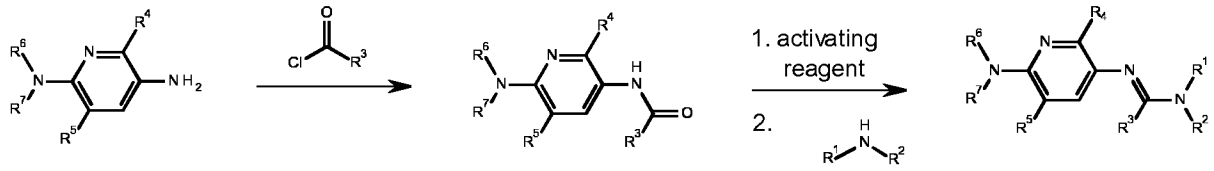
b) Scheme 1 below: Reacting the amino derivative of formula II with a compound of $(R^3)C(OR)_2\text{-}N(R^1)(R^2)$, wherein R_1, R_2, and R_3 are as defined herein for a compound of formula I and R is an alkyl or phenyl group or the two R together form an alkylidene fragment. R is preferably an alkyl group.

Scheme 1



c) Scheme 2 below: An amino derivative of formula II can be transformed into an amide or formamide intermediate, which can be converted into the final compound of formula I by a two-step sequence: activating reagent addition (eg. $POCl_3$ or $(MeO)_2SO_2$) followed by the introduction of an amine with the formula $HN(R^1)(R^2)$, wherein R^1 and R^2 are as defined herein for a compound of formula I.

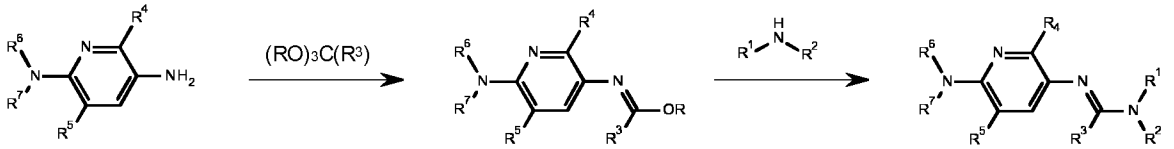
Scheme 2



(II) (I)

d) Scheme 3 below: An amino derivative of formula II can be transformed into an activated intermediate which can be converted into the final compound of formula I by a two-step sequence: Ortho ester or ortho amide addition in the presence of an acid reagent (eg. $POCl_3$ or $(MeO)_2SO_2$) then followed by the introduction of an amine with the formula $HN(R^1)(R^2)$, wherein R^1 and R^2 are as defined herein for a compound of formula I, in the presence of a base.

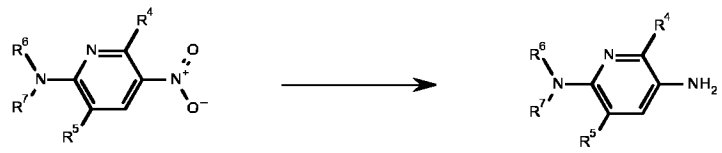
Scheme 3



(II) (I)

e) Scheme 4 below: Compounds of formula II can be prepared from reduction of a nitro group belonging to a compound formula III, wherein R^4, R^5, R^6 and R^7 are as defined herein for a compound of formula I, which takes place in the presence of a catalyst (eg. Pt, Pd, Ni-metal catalyst), molecular hydrogen, and a suitable solvent at ambient or elevated temperatures. The reaction may take place using a metal promoted reduction method (e.g. Fe, Sn, Zn metals) or $SnCl_2$ in acidic and/or protic medium.

Scheme 4

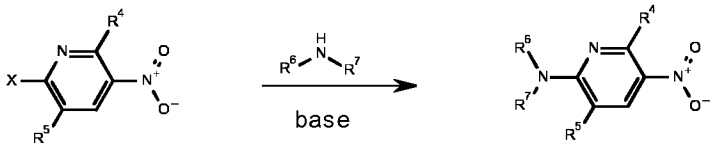


(III) (II)

f) Scheme 5 below: Compounds of formula III can be obtained from a compound of formula IV, wherein R^4 and R^5 are as defined herein for a compound of formula I and X is a halogen leaving group, preferentially F, through the introduction of an amine with the formula $HN(R^6)(R^7)$, wherein R^6 and R^7 are as defined herein for a compound of formula I above, in the presence of a base and elevated temperatures.

g) Scheme 5 Below: Compounds of formula III can also be obtained from reacting a compound of formula IV, wherein R^4 and R^5 are as defined herein for a compound of formula I and X is selected from Cl, Br, or I and an amine with the formula $HN(R^6)(R^7)$ wherein R^6 and R^7 are as defined herein for a compound of formula I above via a metal-catalyzed cross coupling reaction using Cu or Pd metal complexes in the presence of a base at elevated temperatures.

Scheme 5

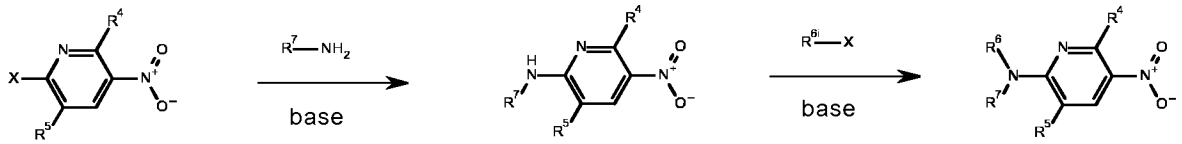


(IV) (III)

h) Scheme 6 below: Compounds of formula III can be obtained from a compound of formula V, wherein R^4, R^5 and R^7 are as defined herein for a compound of formula I, through a reaction with an electrophilic coupling partner (R^{6i})-X, wherein R^{6i} is is selected from formyl. alkyl, alkylcarbonyl and alkoxycarbonyl and X is a leaving group selected from I, Br, Cl, MeO_2SO-, or p-$CH_3C_6H_4O_2SO$-. The reaction is preferentially conducted in the presence of a suitable base at elevated temperatures.

Compounds of formula V can in turn be obtained from a compound of formula IV through the introduction of an amine of the formula (R^7)-NH_2, wherein R^7 is as defined herein for a compound of formula I, in the presence of a base and elevated temperatures.

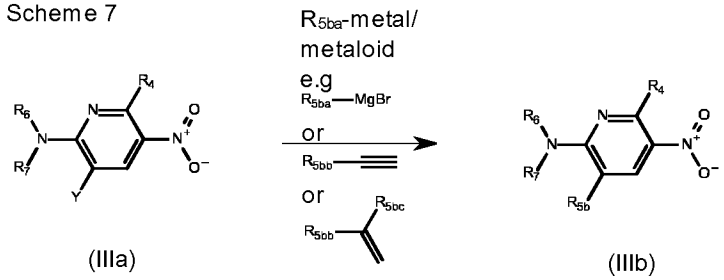
Scheme 6



(IV) (V) (III)

i) Scheme 7 below: Compounds of formula IIIb, wherein R^4, R^6 and R^7 are as defined herein for a compound of formula I and R^{5b} is selected from R^{5ba}, R^{5bb} and R^{5bc} wherein R^{5ba} is selected from alkyl, alkenyl, alkynyl, aryl and heteroaryl and R^{5bb} and R^{5bc} are selected from alkyl, can be prepared from a compound formula IIIa, wherein R^4, R^6 and R^7 are as defined herein for a compound of formula I above and Y is a halogen or pseudo-halogen (e.g. Cl, Br, I, or CF_3SO_2O-), through a metal catalyzed cross-coupling that can introduce R^{5b}, using any one of the numerous conditions described in the literature (i.e. Suzuki, Suzuki-Miyaura, Negishi, Stille, Hiyama, Sonagashira, or Heck reaction.

Scheme 7



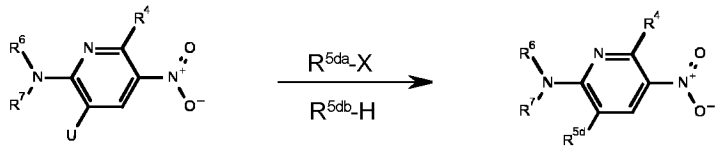
(IIIa) (IIIb)

R_{5ba}, R_{5bb}, R_{5bc} are such that the resulting R_{5b} is within the definition of R_5

j) Scheme 8 below: Compounds of formula IIId wherein R^4, R^6 and R^7 are as defined herein for a compound of formula I and R^{5d} is selected from R^{5da} and R^{5db} wherein R^{5da} is selected from alkenyl, alkynyl, aryl and heteroaryl and R^{5db} is selected from aryl and heteroaryl, can be prepared from a compound formula IIIc, wherein R_4, R_6 and R_7 are as defined herein for a compound of formula I and U

is a metal or metalloid group (e.g. tri-alkylstannane, boronic acid, or boronic ester). Compounds of formula IIId wherein R^{5d} is R^{5da} can be prepared from compounds of formula IIIa using well known methods that feature an electrophilic species (R^{5da})-X, where X is a halogen group such as Cl Br, I or pseudo halogen $-SO_2CF_3$). Compounds of formula IIId wherein R^5 is R^{5b} can be prepared from a compound formula IIIc using well known methods that feature a nucelophilic species (R^{5db})-H, wherein R^{5db} is selected from aryl and heteroaryl, which can be reacted with the core fragment under appropriate conditions.

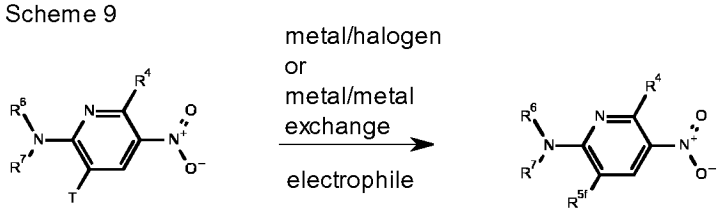
Scheme 8



(IIIc) (IIId)

k) Scheme 9 below: Compounds of formula IIIf wherein R^4, R^6 and R^7 are as defined herein for a compound of formula I and R^{5f} is selected from formyl, carboxy, alkyl, or alkylcarbonyl, can be prepared from a compound formula IIIe wherein R^4, R^6 and R^7 are as defined herein for a compound of formula I and T is a halogen, pseudo-halogen, or metal or metalloid group (e.g. Cl, Br, I, CF_3SO_2O-, tri-alkylstannane, boronic acid, or boronic ester) when treated with an organometallic reagent (e.g. Li, Mg, or Cu) so as to perform metal halogen exchange or trans-metalation followed by the introduction of an electrophile.

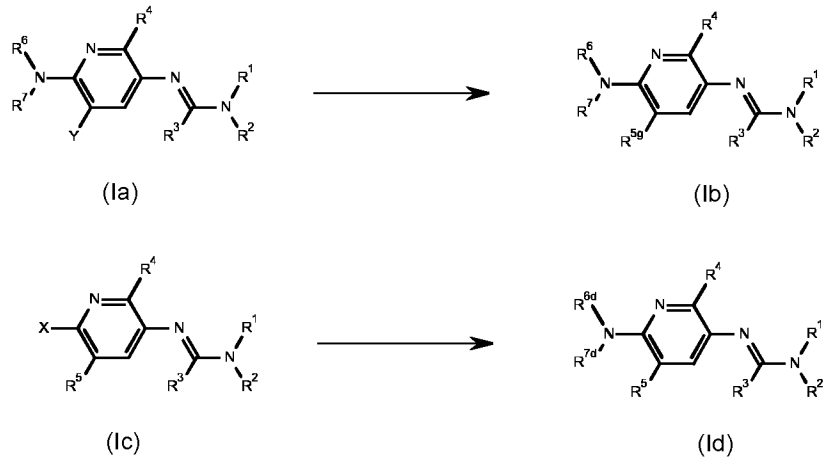
Scheme 9



(IIIe) (IIIf)

l) Scheme 10 below: There are certain cases were the chemistry described above in Schemes 5-9 is also valid in the presence of the amidine group or a related precursor, wherein R^1, R^2, and R^3 are as defined under formula I above, due to functional group compatibility and R^{5g}, R^{6d}, and R^{7d} are suitable subsets of R^5, R^6, and R^7, respectively.

Scheme 10



(Ia) (Ib)

(Ic) (Id)

It has now been found that the compounds of formula (I) according to the invention have, for practical purposes, a very advantageous spectrum of activities for protecting useful plants against diseases that are caused by phytopathogenic microorganisms, such as fungi, bacteria or viruses.

The invention therefore also relates to a method of controlling or preventing infestation of useful plants by phytopathogenic microorganisms, wherein a compound of formula (I) is applied as active ingredient to the plants, to parts thereof or the locus thereof. The compounds of formula (I) according to the invention are distinguished by excellent activity at low rates of application, by being well tolerated by plants and by being environmentally safe. They have very useful curative, preventive and systemic properties and are used for protecting numerous useful plants. The compounds of formula (I) can be used to inhibit or destroy the diseases that occur on plants or parts of plants (fruit, blossoms, leaves, stems, tubers, roots) of different crops of useful plants, while at the same time protecting also those parts of the plants that grow later e.g. from phytopathogenic micro-organisms.

It is also possible to use compounds of formula (I) as dressing agents for the treatment of plant propagation material, in particular of seeds (fruit, tubers, grains) and plant cuttings (e.g. rice), for the protection against fungal infections as well as against phytopathogenic fungi occurring in the soil.

Furthermore the compounds of formula (I) according to the invention may be used for controlling fungi in related areas, for example in the protection of technical materials, including wood and wood related technical products, in food storage or in hygiene management.

The compounds of formula (I) are, for example, effective against the phytopathogenic fungi of the following classes: Fungi imperfecti (e.g. Botrytis, Pyricularia, Helminthosporium, Fusarium, Septoria, Cercospora and Alternaria) and Basidiomycetes (e.g. Rhizoctonia, Hemileia, Puccinia). Additionally, they are also effective against the Ascomycetes classes (e.g. Venturia and Erysiphe, Podosphaera, Monilinia, Uncinula) and of the Oomycetes classes (e.g. Phytophthora, Pythium, Plasmopara). Within the scope of the invention, useful plants to be protected typically comprise the following species of plants: cereal (wheat, barley, rye, oat, rice, maize, sorghum and related species); beet (sugar beet and fodder beet); pomes, drupes and soft fruit (apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries and blackberries); leguminous plants (beans, lentils, peas, soybeans); oil plants (rape, mustard, poppy, olives, sunflowers, coconut, castor oil plants, cocoa beans, groundnuts); cucumber plants (pumpkins, cucumbers, melons); fibre plants (cotton, flax, hemp,

jute); citrus fruit (oranges, lemons, grapefruit, mandarins); vegetables (spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, paprika); lauraceae (avocado, cinnamomum, camphor) or plants such as tobacco, nuts, coffee, eggplants, sugar cane, tea, pepper, vines, hops, bananas and natural rubber plants, as well as ornamentals.

The term "useful plants" is to be understood as including also useful plants that have been rendered tolerant to herbicides like bromoxynil or classes of herbicides (such as, for example, HPPD inhibitors, ALS inhibitors, for example primisulfuron, prosulfuron and trifloxysulfuron, EPSPS (5-enol-pyrovyl-shikimate-3-phosphate-synthase) inhibitors, GS (glutamine synthetase) inhibitors or PPO (protoporphyrinogen-oxidase) inhibitors) as a result of conventional methods of breeding or genetic engineering. An example of a crop that has been rendered tolerant to imidazolinones, e.g. imazamox, by conventional methods of breeding (mutagenesis) is Clearfield® summer rape (Canola). Examples of crops that have been rendered tolerant to herbicides or classes of herbicides by genetic engineering methods include glyphosate- and glufosinate-resistant maize varieties commercially available under the trade names RoundupReady® , Herculex I® and LibertyLink®.

The term "useful plants" is to be understood as including also useful plants which have been so transformed by the use of recombinant DNA techniques that they are capable of synthesising one or more selectively acting toxins, such as are known, for example, from toxin-producing bacteria, especially those of the genus Bacillus.

Examples of such plants are: YieldGard® (maize variety that expresses a CryIA(b) toxin); YieldGard Rootworm® (maize variety that expresses a CryIIIB(b1) toxin); YieldGard Plus® (maize variety that expresses a CryIA(b) and a CryIIIB(b1) toxin); Starlink® (maize variety that expresses a Cry9(c) toxin); Herculex I® (maize variety that expresses a CryIF(a2) toxin and the enzyme phosphinothricine N-acetyltransferase (PAT) to achieve tolerance to the herbicide glufosinate ammonium); NuCOTN 33B® (cotton variety that expresses a CryIA(c) toxin); Bollgard I® (cotton variety that expresses a CryIA(c) toxin); Bollgard II® (cotton variety that expresses a CryIA(c) and a CryIIA(b) toxin); VIPCOT® (cotton variety that expresses a VIP toxin); NewLeaf® (potato variety that expresses a CryIIIA toxin); NatureGard® Agrisure® GT Advantage (GA21 glyphosate-tolerant trait), Agrisure® CB Advantage (Bt11 corn borer (CB) trait), Agrisure® RW (corn rootworm trait) and Protecta®.

The term "useful plants" is to be understood as including also useful plants which have been so transformed by the use of recombinant DNA techniques that they are capable of synthesising antipathogenic substances having a selective action, such as, for example, the so-called "pathogenesis-related proteins" (PRPs, see e.g. EP-A-0 392 225). Examples of such antipathogenic substances and transgenic plants capable of synthesising such antipathogenic substances are known, for example, from EP-A-0 392 225, WO 95/33818, and EP-A-0 353 191. The methods of producing such transgenic plants are generally known to the person skilled in the art and are described, for example, in the publications mentioned above.

The term “locus” of a useful plant as used herein is intended to embrace the place on which the useful plants are growing, where the plant propagation materials of the useful plants are sown or where the plant propagation materials of the useful plants will be placed into the soil. An example for such a locus is a field, on which crop plants are growing.

The term “plant propagation material” is understood to denote generative parts of the plant, such as seeds, which can be used for the multiplication of the latter, and vegetative material, such as cuttings or tubers, for example potatoes. There may be mentioned for example seeds (in the strict sense), roots, fruits, tubers, bulbs, rhizomes and parts of plants. Germinated plants and young plants which are to be transplanted after germination or after emergence from the soil, may also be mentioned. These young plants may be protected before transplantation by a total or partial treatment by immersion. Preferably “plant propagation material” is understood to denote seeds.

The compounds of formula (I) can be used in unmodified form or, preferably, together with carriers and adjuvants conventionally employed in the art of formulation.

Therefore the invention also relates to compositions for controlling and protecting against phytopathogenic microorganisms, comprising a compound of formula (I) and an inert carrier, and to a method of controlling or preventing infestation of useful plants by phytopathogenic microorganisms, wherein a composition, comprising a compound of formula (I) as active ingredient and an inert carrier, is applied to the plants, to parts thereof or the locus thereof.

To this end compounds of formula (I) and inert carriers are conveniently formulated in known manner to emulsifiable concentrates, coatable pastes, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granulates, and also encapsulations e.g. in polymeric substances. As with the type of the compositions, the methods of application, such as spraying, atomising, dusting, scattering, coating or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances. The compositions may also contain further adjuvants such as stabilizers, antifoams, viscosity regulators, binders or tackifiers as well as fertilizers, micronutrient donors or other formulations for obtaining special effects.

Suitable carriers and adjuvants (auxiliaries) can be solid or liquid and are substances useful in formulation technology, e.g. natural or regenerated mineral substances, solvents, dispersants, wetting agents, tackifiers, thickeners, binders or fertilizers. Such carriers are for example described in WO 97/33890.

The compounds of formula (I) or compositions, comprising a compound of formula (I) as active ingredient and an inert carrier, can be applied to the locus of the plant or plant to be treated, simultaneously or in succession with further compounds. These further compounds can be e.g. fertilizers or micronutrient donors or other preparations which influence the growth of plants. They can also be selective herbicides as well as insecticides, fungicides, bactericides, nematicides, molluscicides or mixtures of several of these preparations, if desired together with further carriers, surfactants or application promoting adjuvants customarily employed in the art of formulation.

A preferred method of applying a compound of formula (I), or a composition, comprising a compound of formula (I) as active ingredient and an inert carrier, is foliar application. The frequency of application and the rate of application will depend on the risk of infestation by the corresponding pathogen. However, the compounds of formula (I) may also penetrate the plant through the roots via the soil (systemic action) by drenching the locus of the plant with a liquid formulation, or by applying the compounds in solid form to the soil, e.g. in granular form (soil application). In crops of water rice such granulates can be applied to the flooded rice field. The compounds of formula (I) may also be applied

to seeds (coating) by impregnating the seeds or tubers either with a liquid formulation of the fungicide or coating them with a solid formulation.

A formulation, i.e. a composition comprising the compound of formula (I) and, if desired, a solid or liquid adjuvant, is prepared in a known manner, typically by intimately mixing and/or grinding the compound with extenders, for example solvents, solid carriers and, optionally, surface-active compounds (surfactants).

The agrochemical formulations will usually contain from 0.1 to 99% by weight, preferably from 0.1 to 95% by weight, of the compound of formula (I), 99.9 to 1% by weight, preferably 99.8 to 5% by weight, of a solid or liquid adjuvant, and from 0 to 25% by weight, preferably from 0.1 to 25% by weight, of a surfactant.

Whereas it is preferred to formulate commercial products as concentrates, the end user will normally use dilute formulations.

Advantageous rates of application are normally from 5g to 2kg of active ingredient (a.i.) per hectare (ha), preferably from 10g to 1kg a.i./ha, most preferably from 20g to 600g a.i./ha. When used as seed drenching agent, convenient rates of application are from 10mg to 1g of active substance per kg of seeds. The rate of application for the desired action can be determined by experiments. It depends for example on the type of action, the developmental stage of the useful plant, and on the application (location, timing, application method) and can, owing to these parameters, vary within wide limits.

The compounds of formula (I), or a pharmaceutical salt thereof, described above may also have an advantageous spectrum of activity for the treatment and/or prevention of microbial infection in an animal. “Animal” can be any animal, for example, insect, mammal, reptile, fish, amphibian, preferably mammal, most preferably human. “Treatment” means the use on an animal which has microbial infection in order to reduce or slow or stop the increase or spread of the infection, or to reduce the infection or to cure the infection. “Prevention” means the use on an animal which has no apparent signs of microbial infection in order to prevent any future infection, or to reduce or slow the increase or spread of any future infection.

According to the present invention there is provided the use of a compound of formula (I) in the manufacture of a medicament for use in the treatment and/or prevention of microbial infection in an animal. There is also provided the use of a compound of formula (I) as a pharmaceutical agent. There is also provided the use of a compound of formula (I) as an antimicrobial agent in the treatment of an animal. According to the present invention there is also provided a pharmaceutical composition comprising as an active ingredient a compound of formula (I), or a pharmaceutically acceptable salt thereof, and a pharmaceutically acceptable diluent or carrier. This composition can be used for the treatment and/or prevention of antimicrobial infection in an animal. This pharmaceutical composition can be in a form suitable for oral administration, such as tablet, lozenges, hard capsules, aqueous suspensions, oily suspensions, emulsions dispersible powders, dispersible granules, syrups and elixirs. Alternatively this pharmaceutical composition can be in a form suitable for topical application, such as a spray, a cream or lotion. Alternatively this pharmaceutical composition can be in a form suitable for parenteral administration, for example injection. Alternatively this pharmaceutical composition can be in inhalable form, such as an aerosol spray.

The compounds of formula (I) may be effective against various microbial species able to cause a microbial infection in an animal. Examples of such microbial species are those causing Aspergillosis such as *Aspergillus fumigatus, A. flavus, A. terrus, A. nidulans* and *A. niger*; those causing Blastomycosis such as *Blastomyces dermatitidis*; those causing Candidiasis such as *Candida albicans, C. glabrata, C. tropicalis, C. parapsilosis, C. krusei* and *C. lusitaniae*; those causing Coccidioidomycosis such as *Coccidioides immitis*; those causing Cryptococcosis such as *Cryptococcus neoformans*; those causing Histoplasmosis such as *Histoplasma capsulatum* and those causing Zygomycosis such as *Absidia corymbifera, Rhizomucor pusillus* and *Rhizopus arrhizus*. Further examples are Fusarium Spp such as *Fusarium oxysporum* and *Fusarium solani* and Scedosporium Spp such as *Scedosporium apiospermum* and *Scedosporium prolificans*. Still further examples are Microsporum Spp, Trichophyton Spp, Epidermophyton Spp, Mucor Spp, Sporothorix Spp, Phialophora Spp, Cladosporium Spp, Petriellidium spp, Paracoccidioides Spp and Histoplasma Spp.

The compositions of this invention may contain other compounds having biological activity, for example micronutrients or compounds having fungicidal activity or which possess plant growth regulating, herbicidal, insecticidal, nematicidal or acaricidal activity.

The present invention provides a fungicidal composition comprising a fungicidally effective amount of a compound of formula (I), optionally comprising at least one additional active ingredient.

The compound of formula I (herein after abbreviated by the term “TX” thus means a compound encompassed by the compounds of formula I, or preferably the term “TX” refers to a compound selected from the Tables 1-37, 39 and 41-42) may be the sole active ingredient of the composition or it may be admixed with one or more additional active ingredients such as a pesticide (insect, acarine, mollusc and nematode pesticide), fungicide, synergist, herbicide, safener or plant growth regulator where appropriate. The activity of the compositions according to the invention may thereby be broadened considerably and may have surprising advantages which can also be described, in a wider sense, as synergistic activity. An additional active ingredient may: provide a composition having a broader spectrum of activity or increased persistence at a locus; provide a composition demonstrating better plant/crop tolerance by reducing phytotoxicity; provide a composition controlling insects in their different development stages; synergise the activity or complement the activity (for example by increasing the speed of effect or overcoming repellency) of the TX; or help to overcome or prevent the development of resistance to individual components. The particular additional active ingredient will depend upon the intended utility of the composition. Examples of suitable pesticides include the following:

a) Pyrethroids, such as permethrin, cypermethrin, fenvalerate, esfenvalerate, deltamethrin, cyhalothrin (in particular lambda-cyhalothrin), bifenthrin, fenpropathrin, cyfluthrin, tefluthrin, fish safe pyrethroids (for example ethofenprox), natural pyrethrin, tetramethrin, s-bioallethrin, fenfluthrin, prallethrin or 5-benzyl-3-furylmethyl-(E)-(1R,3S)-2,2-dimethyl-3-(2-oxothiolan-3-ylidenemethyl)cyclopropane carboxylate;

b) Organophosphates, such as, profenofos, sulprofos, acephate, methyl parathion, azinphos-methyl, demeton-s-methyl, heptenophos, thiometon, fenamiphos, monocrotophos, profenofos, triazophos, methamidophos, dimethoate, phosphamidon, malathion, chlorpyrifos,

phosalone, terbufos, fensulfothion, fonofos, phorate, phoxim, pirimiphos-methyl, pirimiphos-ethyl, fenitrothion, fosthiazate or diazinon;

c) Carbamates (including aryl carbamates), such as pirimicarb, triazamate, cloethocarb, carbofuran, furathiocarb, ethiofencarb, aldicarb, thiofurox, carbosulfan, bendiocarb, fenobucarb, propoxur, methomyl or oxamyl;

d) Benzoyl ureas, such as diflubenzuron, triflumuron, hexaflumuron, flufenoxuron or chlorfluazuron;

e)Organic tin compounds, such as cyhexatin, fenbutatin oxide or azocyclotin;

f) Pyrazoles, such as tebufenpyrad and fenpyroximate;

g) Macrolides, such as avermectins or milbemycins, for example abamectin, emamectin benzoate, ivermectin, milbemycin, or spinosad, spinetoram or azadirachtin;

h) Hormones or pheromones;

i) Organochlorine compounds such as endosulfan, benzene hexachloride, DDT, chlordane or dieldrin;

j) Amidines, such as chlordimeform or amitraz;

k) Fumigant agents, such as chloropicrin, dichloropropane, methyl bromide or metam;

l) Neonicotinoid compounds such as imidacloprid, thiacloprid, acetamiprid, clothianidin, nitenpyram, dinotefuran or thiamethoxam;

m) Diacylhydrazines, such as tebufenozide, chromafenozide or methoxyfenozide;

n) Diphenyl ethers, such as diofenolan or pyriproxifen;

o) Indoxacarb;

p) Chlorfenapyr;

q) Pymetrozine or pyrifluquinazon;

r) Spirotetramat, spirodiclofen or spiromesifen;

s) Flubendiamide, chloranthraliniprole, or cyanthraniliprole;

t) Cyenopyrafen or cyflumetofen; or

u) Sulfoxaflor.

In addition to the major chemical classes of pesticide listed above, other pesticides having particular targets may be employed in the composition, if appropriate for the intended utility of the composition. For instance, selective insecticides for particular crops, for example stemborer specific insecticides (such as cartap) or hopper specific insecticides (such as buprofezin) for use in rice may be employed. Alternatively insecticides or acaricides specific for particular insect species/stages may also be included in the compositions (for example acaricidal ovo-larvicides, such as clofentezine, flubenzimine, hexythiazox or tetradifon; acaricidal motilicides, such as dicofol or propargite; acaricides, such as bromopropylate or chlorobenzilate; or growth regulators, such as hydramethylnon, cyromazine, methoprene, chlorfluazuron or diflubenzuron).

The following mixtures of the compounds of formula I with active ingredients are preferred, wherein, preferably, the term “TX” refers to a compound covered by the compounds of formula I or preferably the term “TX” refers to a compound selected from the Tables 1-45, more preferably a compound selected from I-001, I-002, I-003, I-004, I-005, I-006, I-007, I-008, I-010, I-011, I-013, I-014, I-016, I-019, I-020, I-021, I-022, I-023, I-024, I-025, I-026, I-027, I-028, I-029, I-030, I-031, I-032, I-033,

I-034, I-036, I-037, I-038, I-039, I-040, I-041, I-042, I-043, I-044, I-045, I-046, I-048, I-049, I-050, I-051, I-052, I-053, I-057, I-055, I-056, I-063, I-066, I-067, I-068, I-069, I-070, I-071, I-072 and the following List shows specific examples of mixtures comprising thecomponent TX and the component (B):

an adjuvant selected from the group of substances consisting of petroleum oils (alternative name) (628) + TX;

an acaricide selected from the group of substances consisting of 1,1-bis(4-chlorophenyl)-2-ethoxyethanol (IUPAC name) (910) + TX, 2,4-dichlorophenyl benzenesulfonate (IUPAC/Chemical Abstracts name) (1059) + TX, 2-fluoro-*N*-methyl-*N*-1-naphthylacetamide (IUPAC name) (1295) + TX, 4-chlorophenyl phenyl sulfone (IUPAC name) (981) + TX, abamectin (1) + TX, acequinocyl (3) + TX, acetoprole [CCN] + TX, acrinathrin (9) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, alpha-cypermethrin (202) + TX, amidithion (870) + TX, amidoflumet [CCN] + TX, amidothioate (872) + TX, amiton (875) + TX, amiton hydrogen oxalate (875) + TX, amitraz (24) + TX, aramite (881) + TX, arsenous oxide (882) + TX, AVI 382 (compound code) + TX, AZ 60541 (compound code) + TX, azinphos-ethyl (44) + TX, azinphos-methyl (45) + TX, azobenzene (IUPAC name) (888) + TX, azocyclotin (46) + TX, azothoate (889) + TX, benomyl (62) + TX, benoxafos (alternative name) [CCN] + TX, benzoximate (71) + TX, benzyl benzoate (IUPAC name) [CCN] + TX, bifenazate (74) + TX, bifenthrin (76) + TX, binapacryl (907) + TX, brofenvalerate (alternative name) + TX, bromocyclen (918) + TX, bromophos (920) + TX, bromophos-ethyl (921) + TX, bromopropylate (94) + TX, buprofezin (99) + TX, butocarboxim (103) + TX, butoxycarboxim (104) + TX, butylpyridaben (alternative name) + TX, calcium polysulfide (IUPAC name) (111) + TX, camphechlor (941) + TX, carbanolate (943) + TX, carbaryl (115) + TX, carbofuran (118) + TX, carbophenothion (947) + TX, CGA 50'439 (development code) (125) + TX, chinomethionat (126) + TX, chlorbenside (959) + TX, chlordimeform (964) + TX, chlordimeform hydrochloride (964) + TX, chlorfenapyr (130) + TX, chlorfenethol (968) + TX, chlorfenson (970) + TX, chlorfensulphide (971) + TX, chlorfenvinphos (131) + TX, chlorobenzilate (975) + TX, chloromebuform (977) + TX, chloromethiuron (978) + TX, chloropropylate (983) + TX, chlorpyrifos (145) + TX, chlorpyrifos-methyl (146) + TX, chlorthiophos (994) + TX, cinerin I (696) + TX, cinerin II (696) + TX, cinerins (696) + TX, clofentezine (158) + TX, closantel (alternative name) [CCN] + TX, coumaphos (174) + TX, crotamiton (alternative name) [CCN] + TX, crotoxyphos (1010) + TX, cufraneb (1013) + TX, cyanthoate (1020) + TX, cyflumetofen (CAS Reg. No.: 400882-07-7) + TX, cyhalothrin (196) + TX, cyhexatin (199) + TX, cypermethrin (201) + TX, DCPM (1032) + TX, DDT (219) + TX, demephion (1037) + TX, demephion-O (1037) + TX, demephion-S (1037) + TX, demeton (1038) + TX, demeton-methyl (224) + TX, demeton-O (1038) + TX, demeton-O-methyl (224) + TX, demeton-S (1038) + TX, demeton-S-methyl (224) + TX, demeton-S-methylsulphon (1039) + TX, diafenthiuron (226) + TX, dialifos (1042) + TX, diazinon (227) + TX, dichlofluanid (230) + TX, dichlorvos (236) + TX, dicliphos (alternative name) + TX, dicofol (242) + TX, dicrotophos (243) + TX, dienochlor (1071) + TX, dimefox (1081) + TX, dimethoate (262) + TX, dinactin (alternative name) (653) + TX, dinex (1089) + TX, dinex-diclexine (1089) + TX, dinobuton (269) + TX, dinocap (270) + TX, dinocap-4 [CCN] + TX, dinocap-6 [CCN] + TX, dinocton (1090) + TX, dinopenton (1092) + TX, dinosulfon (1097) + TX, dinoterbon (1098) + TX, dioxathion (1102) + TX, diphenyl sulfone (IUPAC name) (1103) + TX, disulfiram (alternative name) [CCN] + TX, disulfoton (278) + TX, DNOC (282) + TX, dofenapyn (1113) + TX, doramectin (alternative name) [CCN] + TX, endosulfan (294) + TX, endothion (1121) + TX, EPN

(297) + TX, eprinomectin (alternative name) [CCN] + TX, ethion (309) + TX, ethoate-methyl (1134) + TX, etoxazole (320) + TX, etrimfos (1142) + TX, fenazaflor (1147) + TX, fenazaquin (328) + TX, fenbutatin oxide (330) + TX, fenothiocarb (337) + TX, fenpropathrin (342) + TX, fenpyrad (alternative name) + TX, fenpyroximate (345) + TX, fenson (1157) + TX, fentrifanil (1161) + TX, fenvalerate (349) + TX, fipronil (354) + TX, fluacrypyrim (360) + TX, fluazuron (1166) + TX, flubenzimine (1167) + TX, flucycloxuron (366) + TX, flucythrinate (367) + TX, fluenetil (1169) + TX, flufenoxuron (370) + TX, flumethrin (372) + TX, fluorbenside (1174) + TX, fluvalinate (1184) + TX, FMC 1137 (development code) (1185) + TX, formetanate (405) + TX, formetanate hydrochloride (405) + TX, formothion (1192) + TX, formparanate (1193) + TX, gamma-HCH (430) + TX, glyodin (1205) + TX, halfenprox (424) + TX, heptenophos (432) + TX, hexadecyl cyclopropanecarboxylate (IUPAC/Chemical Abstracts name) (1216) + TX, hexythiazox (441) + TX, iodomethane (IUPAC name) (542) + TX, isocarbophos (alternative name) (473) + TX, isopropyl *O*-(methoxyaminothiophosphoryl)salicylate (IUPAC name) (473) + TX, ivermectin (alternative name) [CCN] + TX, jasmolin I (696) + TX, jasmolin II (696) + TX, jodfenphos (1248) + TX, lindane (430) + TX, lufenuron (490) + TX, malathion (492) + TX, malonoben (1254) + TX, mecarbam (502) + TX, mephosfolan (1261) + TX, mesulfen (alternative name) [CCN] + TX, methacrifos (1266) + TX, methamidophos (527) + TX, methidathion (529) + TX, methiocarb (530) + TX, methomyl (531) + TX, methyl bromide (537) + TX, metolcarb (550) + TX, mevinphos (556) + TX, mexacarbate (1290) + TX, milbemectin (557) + TX, milbemycin oxime (alternative name) [CCN] + TX, mipafox (1293) + TX, monocrotophos (561) + TX, morphothion (1300) + TX, moxidectin (alternative name) [CCN] + TX, naled (567) + TX, NC-184 (compound code) + TX, NC-512 (compound code) + TX, nifluridide (1309) + TX, nikkomycins (alternative name) [CCN] + TX, nitrilacarb (1313) + TX, nitrilacarb 1:1 zinc chloride complex (1313) + TX, NNI-0101 (compound code) + TX, NNI-0250 (compound code) + TX, omethoate (594) + TX, oxamyl (602) + TX, oxydeprofos (1324) + TX, oxydisulfoton (1325) + TX, pp'-DDT (219) + TX, parathion (615) + TX, permethrin (626) + TX, petroleum oils (alternative name) (628) + TX, phenkapton (1330) + TX, phenthoate (631) + TX, phorate (636) + TX, phosalone (637) + TX, phosfolan (1338) + TX, phosmet (638) + TX, phosphamidon (639) + TX, phoxim (642) + TX, pirimiphos-methyl (652) + TX, polychloroterpenes (traditional name) (1347) + TX, polynactins (alternative name) (653) + TX, proclonol (1350) + TX, profenofos (662) + TX, promacyl (1354) + TX, propargite (671) + TX, propetamphos (673) + TX, propoxur (678) + TX, prothidathion (1360) + TX, prothoate (1362) + TX, pyrethrin I (696) + TX, pyrethrin II (696) + TX, pyrethrins (696) + TX, pyridaben (699) + TX, pyridaphenthion (701) + TX, pyrimidifen (706) + TX, pyrimitate (1370) + TX, quinalphos (711) + TX, quintiofos (1381) + TX, R-1492 (development code) (1382) + TX, RA-17 (development code) (1383) + TX, rotenone (722) + TX, schradan (1389) + TX, sebufos (alternative name) + TX, selamectin (alternative name) [CCN] + TX, SI-0009 (compound code) + TX, sophamide (1402) + TX, spirodiclofen (738) + TX, spiromesifen (739) + TX, SSI-121 (development code) (1404) + TX, sulfiram (alternative name) [CCN] + TX, sulfluramid (750) + TX, sulfotep (753) + TX, sulphur (754) + TX, SZI-121 (development code) (757) + TX, tau-fluvalinate (398) + TX, tebufenpyrad (763) + TX, TEPP (1417) + TX, terbam (alternative name) + TX, tetrachlorvinphos (777) + TX, tetradifon (786) + TX, tetranactin (alternative name) (653) + TX, tetrasul (1425) + TX, thiafenox (alternative name) + TX, thiocarboxime (1431) + TX, thiofanox (800) + TX, thiometon (801) + TX, thioquinox (1436) + TX, thuringiensin (alternative name) [CCN] + TX, triamiphos (1441) + TX, triarathene (1443) + TX,

triazophos (820) + TX, triazuron (alternative name) + TX, trichlorfon (824) + TX, trifenofos (1455) + TX, trinactin (alternative name) (653) + TX, vamidothion (847) + TX, vaniliprole [CCN] and YI-5302 (compound code) + TX;

an algicide selected from the group of substances consisting of bethoxazin [CCN] + TX, copper dioctanoate (IUPAC name) (170) + TX, copper sulfate (172) + TX, cybutryne [CCN] + TX, dichlone (1052) + TX, dichlorophen (232) + TX, endothal (295) + TX, fentin (347) + TX, hydrated lime [CCN] + TX, nabam (566) + TX, quinoclamine (714) + TX, quinonamid (1379) + TX, simazine (730) + TX, triphenyltin acetate (IUPAC name) (347) and triphenyltin hydroxide (IUPAC name) (347) + TX;

an anthelmintic selected from the group of substances consisting of abamectin (1) + TX, crufomate (1011) + TX, doramectin (alternative name) [CCN] + TX, emamectin (291) + TX, emamectin benzoate (291) + TX, eprinomectin (alternative name) [CCN] + TX, ivermectin (alternative name) [CCN] + TX, milbemycin oxime (alternative name) [CCN] + TX, moxidectin (alternative name) [CCN] + TX, piperazine [CCN] + TX, selamectin (alternative name) [CCN] + TX, spinosad (737) and thiophanate (1435) + TX;

an avicide selected from the group of substances consisting of chloralose (127) + TX, endrin (1122) + TX, fenthion (346) + TX, pyridin-4-amine (IUPAC name) (23) and strychnine (745) + TX;

a bactericide selected from the group of substances consisting of 1-hydroxy-1*H*-pyridine-2-thione (IUPAC name) (1222) + TX, 4-(quinoxalin-2-ylamino)benzenesulfonamide (IUPAC name) (748) + TX, 8-hydroxyquinoline sulfate (446) + TX, bronopol (97) + TX, copper dioctanoate (IUPAC name) (170) + TX, copper hydroxide (IUPAC name) (169) + TX, cresol [CCN] + TX, dichlorophen (232) + TX, dipyrithione (1105) + TX, dodicin (1112) + TX, fenaminosulf (1144) + TX, formaldehyde (404) + TX, hydrargaphen (alternative name) [CCN] + TX, kasugamycin (483) + TX, kasugamycin hydrochloride hydrate (483) + TX, nickel bis(dimethyldithiocarbamate) (IUPAC name) (1308) + TX, nitrapyrin (580) + TX, octhilinone (590) + TX, oxolinic acid (606) + TX, oxytetracycline (611) + TX, potassium hydroxyquinoline sulfate (446) + TX, probenazole (658) + TX, streptomycin (744) + TX, streptomycin sesquisulfate (744) + TX, tecloftalam (766) + TX, and thiomersal (alternative name) [CCN] + TX;

a biological agent selected from the group of substances consisting of *Adoxophyes orana* GV (alternative name) (12) + TX, *Agrobacterium radiobacter* (alternative name) (13) + TX, *Amblyseius* spp. (alternative name) (19) + TX, *Anagrapha falcifera* NPV (alternative name) (28) + TX, *Anagrus atomus* (alternative name) (29) + TX, *Aphelinus abdominalis* (alternative name) (33) + TX, *Aphidius colemani* (alternative name) (34) + TX, *Aphidoletes aphidimyza* (alternative name) (35) + TX, *Autographa californica* NPV (alternative name) (38) + TX, *Bacillus firmus* (alternative name) (48) + TX, *Bacillus sphaericus* Neide (scientific name) (49) + TX, *Bacillus thuringiensis* Berliner (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *aizawai* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *israelensis* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *japonensis* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *kurstaki* (scientific name) (51) + TX, *Bacillus thuringiensis* subsp. *tenebrionis* (scientific name) (51) + TX, *Beauveria bassiana* (alternative name) (53) + TX, *Beauveria brongniartii* (alternative name) (54) + TX, *Chrysoperla carnea* (alternative name) (151) + TX, *Cryptolaemus montrouzieri* (alternative name) (178) + TX, *Cydia pomonella* GV (alternative name) (191) + TX, *Dacnusa sibirica* (alternative name) (212) + TX, *Diglyphus isaea* (alternative name) (254) + TX, *Encarsia formosa* (scientific name) (293) + TX, *Eretmocerus eremicus* (alternative name) (300) +

TX, *Helicoverpa zea* NPV (alternative name) (431) + TX, *Heterorhabditis bacteriophora* and *H. megidis* (alternative name) (433) + TX, *Hippodamia convergens* (alternative name) (442) + TX, *Leptomastix dactylopii* (alternative name) (488) + TX, *Macrolophus caliginosus* (alternative name) (491) + TX, *Mamestra brassicae* NPV (alternative name) (494) + TX, *Metaphycus helvolus* (alternative name) (522) + TX, *Metarhizium anisopliae* var. *acridum* (scientific name) (523) + TX, *Metarhizium anisopliae* var. *anisopliae* (scientific name) (523) + TX, *Neodiprion sertifer* NPV and *N. lecontei* NPV (alternative name) (575) + TX, *Orius* spp. (alternative name) (596) + TX, *Paecilomyces fumosoroseus* (alternative name) (613) + TX, *Phytoseiulus persimilis* (alternative name) (644) + TX, *Spodoptera exigua* multicapsid nuclear polyhedrosis virus (scientific name) (741) + TX, *Steinernema bibionis* (alternative name) (742) + TX, *Steinernema carpocapsae* (alternative name) (742) + TX, *Steinernema feltiae* (alternative name) (742) + TX, *Steinernema glaseri* (alternative name) (742) + TX, *Steinernema riobrave* (alternative name) (742) + TX, *Steinernema riobravis* (alternative name) (742) + TX, *Steinernema scapterisci* (alternative name) (742) + TX, *Steinernema* spp. (alternative name) (742) + TX, *Trichogramma* spp. (alternative name) (826) + TX, *Typhlodromus occidentalis* (alternative name) (844) and *Verticillium lecanii* (alternative name) (848) + TX;

a soil sterilant selected from the group of substances consisting of iodomethane (IUPAC name) (542) and methyl bromide (537) + TX;

a chemosterilant selected from the group of substances consisting of apholate [CCN] + TX, bisazir (alternative name) [CCN] + TX, busulfan (alternative name) [CCN] + TX, diflubenzuron (250) + TX, dimatif (alternative name) [CCN] + TX, hemel [CCN] + TX, hempa [CCN] + TX, metepa [CCN] + TX, methiotepa [CCN] + TX, methyl apholate [CCN] + TX, morzid [CCN] + TX, penfluron (alternative name) [CCN] + TX, tepa [CCN] + TX, thiohempa (alternative name) [CCN] + TX, thiotepa (alternative name) [CCN] + TX, tretamine (alternative name) [CCN] and uredepa (alternative name) [CCN] + TX;

an insect pheromone selected from the group of substances consisting of (*E*)-dec-5-en-1-yl acetate with (*E*)-dec-5-en-1-ol (IUPAC name) (222) + TX, (*E*)-tridec-4-en-1-yl acetate (IUPAC name) (829) + TX, (*E*)-6-methylhept-2-en-4-ol (IUPAC name) (541) + TX, (*E,Z*)-tetradeca-4,10-dien-1-yl acetate (IUPAC name) (779) + TX, (*Z*)-dodec-7-en-1-yl acetate (IUPAC name) (285) + TX, (*Z*)-hexadec-11-enal (IUPAC name) (436) + TX, (*Z*)-hexadec-11-en-1-yl acetate (IUPAC name) (437) + TX, (*Z*)-hexadec-13-en-11-yn-1-yl acetate (IUPAC name) (438) + TX, (*Z*)-icos-13-en-10-one (IUPAC name) (448) + TX, (Z)-tetradec-7-en-1-al (IUPAC name) (782) + TX, *(Z*)-tetradec-9-en-1-ol (IUPAC name) (783) + TX, (Z)-tetradec-9-en-1-yl acetate (IUPAC name) (784) + TX, (7*E*,9*Z*)-dodeca-7,9-dien-1-yl acetate (IUPAC name) (283) + TX, (9*Z*,11*E*)-tetradeca-9,11-dien-1-yl acetate (IUPAC name) (780) + TX, (9*Z,*12*E*)-tetradeca-9,12-dien-1-yl acetate (IUPAC name) (781) + TX, 14-methyloctadec-1-ene (IUPAC name) (545) + TX, 4-methylnonan-5-ol with 4-methylnonan-5-one (IUPAC name) (544) + TX, alpha-multistriatin (alternative name) [CCN] + TX, brevicomin (alternative name) [CCN] + TX, codlelure (alternative name) [CCN] + TX, codlemone (alternative name) (167) + TX, cuelure (alternative name) (179) + TX, disparlure (277) + TX, dodec-8-en-1-yl acetate (IUPAC name) (286) + TX, dodec-9-en-1-yl acetate (IUPAC name) (287) + TX, dodeca-8 + TX, 10-dien-1-yl acetate (IUPAC name) (284) + TX, dominicalure (alternative name) [CCN] + TX, ethyl 4-methyloctanoate (IUPAC name) (317) + TX, eugenol (alternative name) [CCN] + TX, frontalin (alternative name) [CCN] + TX, gossyplure

(alternative name) (420) + TX, grandlure (421) + TX, grandlure I (alternative name) (421) + TX, grandlure II (alternative name) (421) + TX, grandlure III (alternative name) (421) + TX, grandlure IV (alternative name) (421) + TX, hexalure [CCN] + TX, ipsdienol (alternative name) [CCN] + TX, ipsenol (alternative name) [CCN] + TX, japonilure (alternative name) (481) + TX, lineatin (alternative name) [CCN] + TX, litlure (alternative name) [CCN] + TX, looplure (alternative name) [CCN] + TX, medlure [CCN] + TX, megatomoic acid (alternative name) [CCN] + TX, methyl eugenol (alternative name) (540) + TX, muscalure (563) + TX, octadeca-2,13-dien-1-yl acetate (IUPAC name) (588) + TX, octadeca-3,13-dien-1-yl acetate (IUPAC name) (589) + TX, orfralure (alternative name) [CCN] + TX, oryctalure (alternative name) (317) + TX, ostramone (alternative name) [CCN] + TX, siglure [CCN] + TX, sordidin (alternative name) (736) + TX, sulcatol (alternative name) [CCN] + TX, tetradec-11-en-1-yl acetate (IUPAC name) (785) + TX, trimedlure (839) + TX, trimedlure A (alternative name) (839) + TX, trimedlure B_1 (alternative name) (839) + TX, trimedlure B_2 (alternative name) (839) + TX, trimedlure C (alternative name) (839) and trunc-call (alternative name) [CCN] + TX;

an insect repellent selected from the group of substances consisting of 2-(octylthio)ethanol (IUPAC name) (591) + TX, butopyronoxyl (933) + TX, butoxy(polypropylene glycol) (936) + TX, dibutyl adipate (IUPAC name) (1046) + TX, dibutyl phthalate (1047) + TX, dibutyl succinate (IUPAC name) (1048) + TX, diethyltoluamide [CCN] + TX, dimethyl carbate [CCN] + TX, dimethyl phthalate [CCN] + TX, ethyl hexanediol (1137) + TX, hexamide [CCN] + TX, methoquin-butyl (1276) + TX, methylneodecanamide [CCN] + TX, oxamate [CCN] and picaridin [CCN] + TX;

an insecticide selected from the group of substances consisting of 1-dichloro-1-nitroethane (IUPAC/Chemical Abstracts name) (1058) + TX, 1,1-dichloro-2,2-bis(4-ethylphenyl)ethane (IUPAC name) (1056), + TX, 1,2-dichloropropane (IUPAC/Chemical Abstracts name) (1062) + TX, 1,2-dichloropropane with 1,3-dichloropropene (IUPAC name) (1063) + TX, 1-bromo-2-chloroethane (IUPAC/Chemical Abstracts name) (916) + TX, 2,2,2-trichloro-1-(3,4-dichlorophenyl)ethyl acetate (IUPAC name) (1451) + TX, 2,2-dichlorovinyl 2-ethylsulphinylethyl methyl phosphate (IUPAC name) (1066) + TX, 2-(1,3-dithiolan-2-yl)phenyl dimethylcarbamate (IUPAC/ Chemical Abstracts name) (1109) + TX, 2-(2-butoxyethoxy)ethyl thiocyanate (IUPAC/Chemical Abstracts name) (935) + TX, 2-(4,5-dimethyl-1,3-dioxolan-2-yl)phenyl methylcarbamate (IUPAC/ Chemical Abstracts name) (1084) + TX, 2-(4-chloro-3,5-xylyloxy)ethanol (IUPAC name) (986) + TX, 2-chlorovinyl diethyl phosphate (IUPAC name) (984) + TX, 2-imidazolidone (IUPAC name) (1225) + TX, 2-isovalerylindan-1,3-dione (IUPAC name) (1246) + TX, 2-methyl(prop-2-ynyl)aminophenyl methylcarbamate (IUPAC name) (1284) + TX, 2-thiocyanatoethyl laurate (IUPAC name) (1433) + TX, 3-bromo-1-chloroprop-1-ene (IUPAC name) (917) + TX, 3-methyl-1-phenylpyrazol-5-yl dimethylcarbamate (IUPAC name) (1283) + TX, 4-methyl(prop-2-ynyl)amino-3,5-xylyl methylcarbamate (IUPAC name) (1285) + TX, 5,5-dimethyl-3-oxocyclohex-1-enyl dimethylcarbamate (IUPAC name) (1085) + TX, abamectin (1) + TX, acephate (2) + TX, acetamiprid (4) + TX, acethion (alternative name) [CCN] + TX, acetoprole [CCN] + TX, acrinathrin (9) + TX, acrylonitrile (IUPAC name) (861) + TX, alanycarb (15) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, aldrin (864) + TX, allethrin (17) + TX, allosamidin (alternative name) [CCN] + TX, allyxycarb (866) + TX, alpha-cypermethrin (202) + TX, alpha-ecdysone (alternative name) [CCN] + TX, aluminium phosphide (640) + TX, amidithion (870) + TX, amidothioate (872) + TX, aminocarb (873) + TX, amiton (875) + TX, amiton hydrogen oxalate (875) + TX, amitraz (24) + TX, anabasine

(877) + TX, athidathion (883) + TX, AVI 382 (compound code) + TX, AZ 60541 (compound code) + TX, azadirachtin (alternative name) (41) + TX, azamethiphos (42) + TX, azinphos-ethyl (44) + TX, azinphos-methyl (45) + TX, azothoate (889) + TX, *Bacillus thuringiensis* delta endotoxins (alternative name) (52) + TX, barium hexafluorosilicate (alternative name) [CCN] + TX, barium polysulfide (IUPAC/Chemical Abstracts name) (892) + TX, barthrin [CCN] + TX, Bayer 22/190 (development code) (893) + TX, Bayer 22408 (development code) (894) + TX, bendiocarb (58) + TX, benfuracarb (60) + TX, bensultap (66) + TX, beta-cyfluthrin (194) + TX, beta-cypermethrin (203) + TX, bifenthrin (76) + TX, bioallethrin (78) + TX, bioallethrin *S*-cyclopentenyl isomer (alternative name) (79) + TX, bioethanomethrin [CCN] + TX, biopermethrin (908) + TX, bioresmethrin (80) + TX, bis(2-chloroethyl) ether (IUPAC name) (909) + TX, bistrifluron (83) + TX, borax (86) + TX, brofenvalerate (alternative name) + TX, bromfenvinfos (914) + TX, bromocyclen (918) + TX, bromo-DDT (alternative name) [CCN] + TX, bromophos (920) + TX, bromophos-ethyl (921) + TX, bufencarb (924) + TX, buprofezin (99) + TX, butacarb (926) + TX, butathiofos (927) + TX, butocarboxim (103) + TX, butonate (932) + TX, butoxycarboxim (104) + TX, butylpyridaben (alternative name) + TX, cadusafos (109) + TX, calcium arsenate [CCN] + TX, calcium cyanide (444) + TX, calcium polysulfide (IUPAC name) (111) + TX, camphechlor (941) + TX, carbanolate (943) + TX, carbaryl (115) + TX, carbofuran (118) + TX, carbon disulfide (IUPAC/Chemical Abstracts name) (945) + TX, carbon tetrachloride (IUPAC name) (946) + TX, carbophenothion (947) + TX, carbosulfan (119) + TX, cartap (123) + TX, cartap hydrochloride (123) + TX, cevadine (alternative name) (725) + TX, chlorbicyclen (960) + TX, chlordane (128) + TX, chlordecone (963) + TX, chlordimeform (964) + TX, chlordimeform hydrochloride (964) + TX, chlorethoxyfos (129) + TX, chlorfenapyr (130) + TX, chlorfenvinphos (131) + TX, chlorfluazuron (132) + TX, chlormephos (136) + TX, chloroform [CCN] + TX, chloropicrin (141) + TX, chlorphoxim (989) + TX, chlorprazophos (990) + TX, chlorpyrifos (145) + TX, chlorpyrifos-methyl (146) + TX, chlorthiophos (994) + TX, chromafenozide (150) + TX, cinerin I (696) + TX, cinerin II (696) + TX, cinerins (696) + TX, cis-resmethrin (alternative name) + TX, cismethrin (80) + TX, clocythrin (alternative name) + TX, cloethocarb (999) + TX, closantel (alternative name) [CCN] + TX, clothianidin (165) + TX, copper acetoarsenite [CCN] + TX, copper arsenate [CCN] + TX, copper oleate [CCN] + TX, coumaphos (174) + TX, coumithoate (1006) + TX, crotamiton (alternative name) [CCN] + TX, crotoxyphos (1010) + TX, crufomate (1011) + TX, cryolite (alternative name) (177) + TX, CS 708 (development code) (1012) + TX, cyanofenphos (1019) + TX, cyanophos (184) + TX, cyanthoate (1020) + TX, cyclethrin [CCN] + TX, cycloprothrin (188) + TX, cyfluthrin (193) + TX, cyhalothrin (196) + TX, cypermethrin (201) + TX, cyphenothrin (206) + TX, cyromazine (209) + TX, cythioate (alternative name) [CCN] + TX, *d*-limonene (alternative name) [CCN] + TX, *d*-tetramethrin (alternative name) (788) + TX, DAEP (1031) + TX, dazomet (216) + TX, DDT (219) + TX, decarbofuran (1034) + TX, deltamethrin (223) + TX, demephion (1037) + TX, demephion-O (1037) + TX, demephion-S (1037) + TX, demeton (1038) + TX, demeton-methyl (224) + TX, demeton-O (1038) + TX, demeton-O-methyl (224) + TX, demeton-S (1038) + TX, demeton-S-methyl (224) + TX, demeton-S-methylsulphon (1039) + TX, diafenthiuron (226) + TX, dialifos (1042) + TX, diamidafos (1044) + TX, diazinon (227) + TX, dicapthon (1050) + TX, dichlofenthion (1051) + TX, dichlorvos (236) + TX, dicliphos (alternative name) + TX, dicresyl (alternative name) [CCN] + TX, dicrotophos (243) + TX, dicyclanil (244) + TX, dieldrin (1070) + TX, diethyl 5-methylpyrazol-3-yl phosphate (IUPAC name) (1076) + TX, diflubenzuron (250) +

TX, dilor (alternative name) [CCN] + TX, dimefluthrin [CCN] + TX, dimefox (1081) + TX, dimetan (1085) + TX, dimethoate (262) + TX, dimethrin (1083) + TX, dimethylvinphos (265) + TX, dimetilan (1086) + TX, dinex (1089) + TX, dinex-diclexine (1089) + TX, dinoprop (1093) + TX, dinosam (1094) + TX, dinoseb (1095) + TX, dinotefuran (271) + TX, diofenolan (1099) + TX, dioxabenzofos (1100) + TX, dioxacarb (1101) + TX, dioxathion (1102) + TX, disulfoton (278) + TX, dithicrofos (1108) + TX, DNOC (282) + TX, doramectin (alternative name) [CCN] + TX, DSP (1115) + TX, ecdysterone (alternative name) [CCN] + TX, EI 1642 (development code) (1118) + TX, emamectin (291) + TX, emamectin benzoate (291) + TX, EMPC (1120) + TX, empenthrin (292) + TX, endosulfan (294) + TX, endothion (1121) + TX, endrin (1122) + TX, EPBP (1123) + TX, EPN (297) + TX, epofenonane (1124) + TX, eprinomectin (alternative name) [CCN] + TX, esfenvalerate (302) + TX, etaphos (alternative name) [CCN] + TX, ethiofencarb (308) + TX, ethion (309) + TX, ethiprole (310) + TX, ethoate-methyl (1134) + TX, ethoprophos (312) + TX, ethyl formate (IUPAC name) [CCN] + TX, ethyl-DDD (alternative name) (1056) + TX, ethylene dibromide (316) + TX, ethylene dichloride (chemical name) (1136) + TX, ethylene oxide [CCN] + TX, etofenprox (319) + TX, etrimfos (1142) + TX, EXD (1143) + TX, famphur (323) + TX, fenamiphos (326) + TX, fenazaflor (1147) + TX, fenchlorphos (1148) + TX, fenethacarb (1149) + TX, fenfluthrin (1150) + TX, fenitrothion (335) + TX, fenobucarb (336) + TX, fenoxacrim (1153) + TX, fenoxycarb (340) + TX, fenpirithrin (1155) + TX, fenpropathrin (342) + TX, fenpyrad (alternative name) + TX, fensulfothion (1158) + TX, fenthion (346) + TX, fenthion-ethyl [CCN] + TX, fenvalerate (349) + TX, fipronil (354) + TX, flonicamid (358) + TX, flubendiamide (CAS. Reg. No.: 272451-65-7) + TX, flucofuron (1168) + TX, flucycloxuron (366) + TX, flucythrinate (367) + TX, fluenetil (1169) + TX, flufenerim [CCN] + TX, flufenoxuron (370) + TX, flufenprox (1171) + TX, flumethrin (372) + TX, fluvalinate (1184) + TX, FMC 1137 (development code) (1185) + TX, fonofos (1191) + TX, formetanate (405) + TX, formetanate hydrochloride (405) + TX, formothion (1192) + TX, formparanate (1193) + TX, fosmethilan (1194) + TX, fospirate (1195) + TX, fosthiazate (408) + TX, fosthietan (1196) + TX, furathiocarb (412) + TX, furethrin (1200) + TX, gamma-cyhalothrin (197) + TX, gamma-HCH (430) + TX, guazatine (422) + TX, guazatine acetates (422) + TX, GY-81 (development code) (423) + TX, halfenprox (424) + TX, halofenozide (425) + TX, HCH (430) + TX, HEOD (1070) + TX, heptachlor (1211) + TX, heptenophos (432) + TX, heterophos [CCN] + TX, hexaflumuron (439) + TX, HHDN (864) + TX, hydramethylnon (443) + TX, hydrogen cyanide (444) + TX, hydroprene (445) + TX, hyquincarb (1223) + TX, imidacloprid (458) + TX, imiprothrin (460) + TX, indoxacarb (465) + TX, iodomethane (IUPAC name) (542) + TX, IPSP (1229) + TX, isazofos (1231) + TX, isobenzan (1232) + TX, isocarbophos (alternative name) (473) + TX, isodrin (1235) + TX, isofenphos (1236) + TX, isolane (1237) + TX, isoprocarb (472) + TX, isopropyl *O*-(methoxyaminothiophosphoryl)salicylate (IUPAC name) (473) + TX, isoprothiolane (474) + TX, isothioate (1244) + TX, isoxathion (480) + TX, ivermectin (alternative name) [CCN] + TX, jasmolin I (696) + TX, jasmolin II (696) + TX, jodfenphos (1248) + TX, juvenile hormone I (alternative name) [CCN] + TX, juvenile hormone II (alternative name) [CCN] + TX, juvenile hormone III (alternative name) [CCN] + TX, kelevan (1249) + TX, kinoprene (484) + TX, lambda-cyhalothrin (198) + TX, lead arsenate [CCN] + TX, lepimectin (CCN) + TX, leptophos (1250) + TX, lindane (430) + TX, lirimfos (1251) + TX, lufenuron (490) + TX, lythidathion (1253) + TX, *m*-cumenyl methylcarbamate (IUPAC name) (1014) + TX, magnesium phosphide (IUPAC name) (640) + TX, malathion (492) + TX, malonoben (1254) + TX, mazidox (1255) + TX, mecarbam (502) + TX,

mecarphon (1258) + TX, menazon (1260) + TX, mephosfolan (1261) + TX, mercurous chloride (513) + TX, mesulfenfos (1263) + TX, metaflumizone (CCN) + TX, metam (519) + TX, metam-potassium (alternative name) (519) + TX, metam-sodium (519) + TX, methacrifos (1266) + TX, methamidophos (527) + TX, methanesulphonyl fluoride (IUPAC/Chemical Abstracts name) (1268) + TX, methidathion (529) + TX, methiocarb (530) + TX, methocrotophos (1273) + TX, methomyl (531) + TX, methoprene (532) + TX, methoquin-butyl (1276) + TX, methothrin (alternative name) (533) + TX, methoxychlor (534) + TX, methoxyfenozide (535) + TX, methyl bromide (537) + TX, methyl isothiocyanate (543) + TX, methylchloroform (alternative name) [CCN] + TX, methylene chloride [CCN] + TX, metofluthrin [CCN] + TX, metolcarb (550) + TX, metoxadiazone (1288) + TX, mevinphos (556) + TX, mexacarbate (1290) + TX, milbemectin (557) + TX, milbemycin oxime (alternative name) [CCN] + TX, mipafox (1293) + TX, mirex (1294) + TX, monocrotophos (561) + TX, morphothion (1300) + TX, moxidectin (alternative name) [CCN] + TX, naftalofos (alternative name) [CCN] + TX, naled (567) + TX, naphthalene (IUPAC/Chemical Abstracts name) (1303) + TX, NC-170 (development code) (1306) + TX, NC-184 (compound code) + TX, nicotine (578) + TX, nicotine sulfate (578) + TX, nifluridide (1309) + TX, nitenpyram (579) + TX, nithiazine (1311) + TX, nitrilacarb (1313) + TX, nitrilacarb 1:1 zinc chloride complex (1313) + TX, NNI-0101 (compound code) + TX, NNI-0250 (compound code) + TX, nornicotine (traditional name) (1319) + TX, novaluron (585) + TX, noviflumuron (586) + TX, *O*-5-dichloro-4-iodophenyl *O*-ethyl ethylphosphonothioate (IUPAC name) (1057) + TX, *O,O*-diethyl *O*-4-methyl-2-oxo-2*H*-chromen-7-yl phosphorothioate (IUPAC name) (1074) + TX, *O,O*-diethyl *O*-6-methyl-2-propylpyrimidin-4-yl phosphorothioate (IUPAC name) (1075) + TX, *O,O,O*',*O*'-tetrapropyl dithiopyrophosphate (IUPAC name) (1424) + TX, oleic acid (IUPAC name) (593) + TX, omethoate (594) + TX, oxamyl (602) + TX, oxydemeton-methyl (609) + TX, oxydeprofos (1324) + TX, oxydisulfoton (1325) + TX, pp'-DDT (219) + TX, para-dichlorobenzene [CCN] + TX, parathion (615) + TX, parathion-methyl (616) + TX, penfluron (alternative name) [CCN] + TX, pentachlorophenol (623) + TX, pentachlorophenyl laurate (IUPAC name) (623) + TX, permethrin (626) + TX, petroleum oils (alternative name) (628) + TX, PH 60-38 (development code) (1328) + TX, phenkapton (1330) + TX, phenothrin (630) + TX, phenthoate (631) + TX, phorate (636) + TX, phosalone (637) + TX, phosfolan (1338) + TX, phosmet (638) + TX, phosnichlor (1339) + TX, phosphamidon (639) + TX, phosphine (IUPAC name) (640) + TX, phoxim (642) + TX, phoxim-methyl (1340) + TX, pirimetaphos (1344) + TX, pirimicarb (651) + TX, pirimiphos-ethyl (1345) + TX, pirimiphos-methyl (652) + TX, polychlorodicyclopentadiene isomers (IUPAC name) (1346) + TX, polychloroterpenes (traditional name) (1347) + TX, potassium arsenite [CCN] + TX, potassium thiocyanate [CCN] + TX, prallethrin (655) + TX, precocene I (alternative name) [CCN] + TX, precocene II (alternative name) [CCN] + TX, precocene III (alternative name) [CCN] + TX, primidophos (1349) + TX, profenofos (662) + TX, profluthrin [CCN] + TX, promacyl (1354) + TX, promecarb (1355) + TX, propaphos (1356) + TX, propetamphos (673) + TX, propoxur (678) + TX, prothidathion (1360) + TX, prothiofos (686) + TX, prothoate (1362) + TX, protrifenbute [CCN] + TX, pymetrozine (688) + TX, pyraclofos (689) + TX, pyrazophos (693) + TX, pyresmethrin (1367) + TX, pyrethrin I (696) + TX, pyrethrin II (696) + TX, pyrethrins (696) + TX, pyridaben (699) + TX, pyridalyl (700) + TX, pyridaphenthion (701) + TX, pyrimidifen (706) + TX, pyrimitate (1370) + TX, pyriproxyfen (708) + TX, quassia (alternative name) [CCN] + TX, quinalphos (711) + TX, quinalphos-methyl (1376) + TX, quinothion (1380) + TX, quintiofos

(1381) + TX, R-1492 (development code) (1382) + TX, rafoxanide (alternative name) [CCN] + TX, resmethrin (719) + TX, rotenone (722) + TX, RU 15525 (development code) (723) + TX, RU 25475 (development code) (1386) + TX, ryania (alternative name) (1387) + TX, ryanodine (traditional name) (1387) + TX, sabadilla (alternative name) (725) + TX, schradan (1389) + TX, sebufos (alternative name) + TX, selamectin (alternative name) [CCN] + TX, SI-0009 (compound code) + TX, SI-0205 (compound code) + TX, SI-0404 (compound code) + TX, SI-0405 (compound code) + TX, silafluofen (728) + TX, SN 72129 (development code) (1397) + TX, sodium arsenite [CCN] + TX, sodium cyanide (444) + TX, sodium fluoride (IUPAC/Chemical Abstracts name) (1399) + TX, sodium hexafluorosilicate (1400) + TX, sodium pentachlorophenoxide (623) + TX, sodium selenate (IUPAC name) (1401) + TX, sodium thiocyanate [CCN] + TX, sophamide (1402) + TX, spinosad (737) + TX, spiromesifen (739) + TX, spirotetrmat (CCN) + TX, sulcofuron (746) + TX, sulcofuron-sodium (746) + TX, sulfluramid (750) + TX, sulfotep (753) + TX, sulphuryl fluoride (756) + TX, sulprofos (1408) + TX, tar oils (alternative name) (758) + TX, tau-fluvalinate (398) + TX, tazimcarb (1412) + TX, TDE (1414) + TX, tebufenozide (762) + TX, tebufenpyrad (763) + TX, tebupirimfos (764) + TX, teflubenzuron (768) + TX, tefluthrin (769) + TX, temephos (770) + TX, TEPP (1417) + TX, terallethrin (1418) + TX, terbam (alternative name) + TX, terbufos (773) + TX, tetrachloroethane [CCN] + TX, tetrachlorvinphos (777) + TX, tetramethrin (787) + TX, theta-cypermethrin (204) + TX, thiacloprid (791) + TX, thiafenox (alternative name) + TX, thiamethoxam (792) + TX, thicrofos (1428) + TX, thiocarboxime (1431) + TX, thiocyclam (798) + TX, thiocyclam hydrogen oxalate (798) + TX, thiodicarb (799) + TX, thiofanox (800) + TX, thiometon (801) + TX, thionazin (1434) + TX, thiosultap (803) + TX, thiosultap-sodium (803) + TX, thuringiensin (alternative name) [CCN] + TX, tolfenpyrad (809) + TX, tralomethrin (812) + TX, transfluthrin (813) + TX, transpermethrin (1440) + TX, triamiphos (1441) + TX, triazamate (818) + TX, triazophos (820) + TX, triazuron (alternative name) + TX, trichlorfon (824) + TX, trichlormetaphos-3 (alternative name) [CCN] + TX, trichloronat (1452) + TX, trifenofos (1455) + TX, triflumuron (835) + TX, trimethacarb (840) + TX, triprene (1459) + TX, vamidothion (847) + TX, vaniliprole [CCN] + TX, veratridine (alternative name) (725) + TX, veratrine (alternative name) (725) + TX, XMC (853) + TX, xylylcarb (854) + TX, YI-5302 (compound code) + TX, zeta-cypermethrin (205) + TX, zetamethrin (alternative name) + TX, zinc phosphide (640) + TX, zolaprofos (1469) and ZXI 8901 (development code) (858) + TX, cyantraniliprole [736994-63-19] + TX, chlorantraniliprole [500008-45-7] + TX, cyenopyrafen [560121-52-0] + TX, cyflumetofen [400882-07-7] + TX, pyrifluquinazon [337458-27-2] + TX, spinetoram [187166-40-1 + 187166-15-0] + TX, spirotetramat [203313-25-1] + TX, sulfoxaflor [946578-00-3] + TX, flufiprole [704886-18-0] + TX, meperfluthrin [915288-13-0] + TX, tetramethylfluthrin [84937-88-2] + TX;

a molluscicide selected from the group of substances consisting of bis(tributyltin) oxide (IUPAC name) (913) + TX, bromoacetamide [CCN] + TX, calcium arsenate [CCN] + TX, cloethocarb (999) + TX, copper acetoarsenite [CCN] + TX, copper sulfate (172) + TX, fentin (347) + TX, ferric phosphate (IUPAC name) (352) + TX, metaldehyde (518) + TX, methiocarb (530) + TX, niclosamide (576) + TX, niclosamide-olamine (576) + TX, pentachlorophenol (623) + TX, sodium pentachlorophenoxide (623) + TX, tazimcarb (1412) + TX, thiodicarb (799) + TX, tributyltin oxide (913) + TX, trifenmorph (1454) + TX, trimethacarb (840) + TX, triphenyltin acetate (IUPAC name) (347) and triphenyltin hydroxide (IUPAC name) (347) + TX, pyriprole [394730-71-3] + TX;

a nematicide selected from the group of substances consisting of AKD-3088 (compound code) + TX, 1,2-dibromo-3-chloropropane (IUPAC/Chemical Abstracts name) (1045) + TX, 1,2-dichloropropane (IUPAC/ Chemical Abstracts name) (1062) + TX, 1,2-dichloropropane with 1,3-dichloropropene (IUPAC name) (1063) + TX, 1,3-dichloropropene (233) + TX, 3,4-dichlorotetrahydrothiophene 1,1-dioxide (IUPAC/Chemical Abstracts name) (1065) + TX, 3-(4-chlorophenyl)-5-methylrhodanine (IUPAC name) (980) + TX, 5-methyl-6-thioxo-1,3,5-thiadiazinan-3-ylacetic acid (IUPAC name) (1286) + TX, 6-isopentenylaminopurine (alternative name) (210) + TX, abamectin (1) + TX, acetoprole [CCN] + TX, alanycarb (15) + TX, aldicarb (16) + TX, aldoxycarb (863) + TX, AZ 60541 (compound code) + TX, benclothiaz [CCN] + TX, benomyl (62) + TX, butylpyridaben (alternative name) + TX, cadusafos (109) + TX, carbofuran (118) + TX, carbon disulfide (945) + TX, carbosulfan (119) + TX, chloropicrin (141) + TX, chlorpyrifos (145) + TX, cloethocarb (999) + TX, cytokinins (alternative name) (210) + TX, dazomet (216) + TX, DBCP (1045) + TX, DCIP (218) + TX, diamidafos (1044) + TX, dichlofenthion (1051) + TX, dicliphos (alternative name) + TX, dimethoate (262) + TX, doramectin (alternative name) [CCN] + TX, emamectin (291) + TX, emamectin benzoate (291) + TX, eprinomectin (alternative name) [CCN] + TX, ethoprophos (312) + TX, ethylene dibromide (316) + TX, fenamiphos (326) + TX, fenpyrad (alternative name) + TX, fensulfothion (1158) + TX, fosthiazate (408) + TX, fosthietan (1196) + TX, furfural (alternative name) [CCN] + TX, GY-81 (development code) (423) + TX, heterophos [CCN] + TX, iodomethane (IUPAC name) (542) + TX, isamidofos (1230) + TX, isazofos (1231) + TX, ivermectin (alternative name) [CCN] + TX, kinetin (alternative name) (210) + TX, mecarphon (1258) + TX, metam (519) + TX, metam-potassium (alternative name) (519) + TX, metam-sodium (519) + TX, methyl bromide (537) + TX, methyl isothiocyanate (543) + TX, milbemycin oxime (alternative name) [CCN] + TX, moxidectin (alternative name) [CCN] + TX, *Myrothecium verrucaria* composition (alternative name) (565) + TX, NC-184 (compound code) + TX, oxamyl (602) + TX, phorate (636) + TX, phosphamidon (639) + TX, phosphocarb [CCN] + TX, sebufos (alternative name) + TX, selamectin (alternative name) [CCN] + TX, spinosad (737) + TX, terbam (alternative name) + TX, terbufos (773) + TX, tetrachlorothiophene (IUPAC/ Chemical Abstracts name) (1422) + TX, thiafenox (alternative name) + TX, thionazin (1434) + TX, triazophos (820) + TX, triazuron (alternative name) + TX, xylenols [CCN] + TX, YI-5302 (compound code) and zeatin (alternative name) (210) + TX, fluensulfone [318290-98-1] + TX;

a nitrification inhibitor selected from the group of substances consisting of potassium ethylxanthate [CCN] and nitrapyrin (580) + TX;

a plant activator selected from the group of substances consisting of acibenzolar (6) + TX, acibenzolar-*S*-methyl (6) + TX, probenazole (658) and *Reynoutria sachalinensis* extract (alternative name) (720) + TX;

a rodenticide selected from the group of substances consisting of 2-isovalerylindan-1,3-dione (IUPAC name) (1246) + TX, 4-(quinoxalin-2-ylamino)benzenesulfonamide (IUPAC name) (748) + TX, alpha-chlorohydrin [CCN] + TX, aluminium phosphide (640) + TX, antu (880) + TX, arsenous oxide (882) + TX, barium carbonate (891) + TX, bisthiosemi (912) + TX, brodifacoum (89) + TX, bromadiolone (91) + TX, bromethalin (92) + TX, calcium cyanide (444) + TX, chloralose (127) + TX, chlorophacinone (140) + TX, cholecalciferol (alternative name) (850) + TX, coumachlor (1004) + TX, coumafuryl (1005) + TX, coumatetralyl (175) + TX, crimidine (1009) + TX, difenacoum (246) + TX,

difethialone (249) + TX, diphacinone (273) + TX, ergocalciferol (301) + TX, flocoumafen (357) + TX, fluoroacetamide (379) + TX, flupropadine (1183) + TX, flupropadine hydrochloride (1183) + TX, gamma-HCH (430) + TX, HCH (430) + TX, hydrogen cyanide (444) + TX, iodomethane (IUPAC name) (542) + TX, lindane (430) + TX, magnesium phosphide (IUPAC name) (640) + TX, methyl bromide (537) + TX, norbormide (1318) + TX, phosacetim (1336) + TX, phosphine (IUPAC name) (640) + TX, phosphorus [CCN] + TX, pindone (1341) + TX, potassium arsenite [CCN] + TX, pyrinuron (1371) + TX, scilliroside (1390) + TX, sodium arsenite [CCN] + TX, sodium cyanide (444) + TX, sodium fluoroacetate (735) + TX, strychnine (745) + TX, thallium sulfate [CCN] + TX, warfarin (851) and zinc phosphide (640) + TX;

a synergist selected from the group of substances consisting of 2-(2-butoxyethoxy)ethyl piperonylate (IUPAC name) (934) + TX, 5-(1,3-benzodioxol-5-yl)-3-hexylcyclohex-2-enone (IUPAC name) (903) + TX, farnesol with nerolidol (alternative name) (324) + TX, MB-599 (development code) (498) + TX, MGK 264 (development code) (296) + TX, piperonyl butoxide (649) + TX, piprotal (1343) + TX, propyl isomer (1358) + TX, S421 (development code) (724) + TX, sesamex (1393) + TX, sesasmolin (1394) and sulfoxide (1406) + TX,

an animal repellent selected from the group of substances consisting of anthraquinone (32) + TX, chloralose (127) + TX, copper naphthenate [CCN] + TX, copper oxychloride (171) + TX, diazinon (227) + TX, dicyclopentadiene (chemical name) (1069) + TX, guazatine (422) + TX, guazatine acetates (422) + TX, methiocarb (530) + TX, pyridin-4-amine (IUPAC name) (23) + TX, thiram (804) + TX, trimethacarb (840) + TX, zinc naphthenate [CCN] and ziram (856) + TX;

a virucide selected from the group of substances consisting of imanin (alternative name) [CCN] and ribavirin (alternative name) [CCN] + TX;

a wound protectant selected from the group of substances consisting of mercuric oxide (512) + TX, octhilinone (590) and thiophanate-methyl (802) + TX;

and biologically active compounds selected from the group consisting of azaconazole (60207-31-0] + TX, bitertanol [70585-36-3] + TX, bromuconazole [116255-48-2] + TX, cyproconazole [94361-06-5] + TX, difenoconazole [119446-68-3] + TX, diniconazole [83657-24-3] + TX, epoxiconazole [106325-08-0] + TX, fenbuconazole [114369-43-6] + TX, fluquinconazole [136426-54-5] + TX, flusilazole [85509-19-9] + TX, flutriafol [76674-21-0] + TX, hexaconazole [79983-71-4] + TX, imazalil [35554-44-0] + TX, imibenconazole [86598-92-7] + TX, ipconazole [125225-28-7] + TX, metconazole [125116-23-6] + TX, myclobutanil [88671-89-0] + TX, pefurazoate [101903-30-4] + TX, penconazole [66246-88-6] + TX, prothioconazole [178928-70-6] + TX, pyrifenox [88283-41-4] + TX, prochloraz [67747-09-5] + TX, propiconazole [60207-90-1] + TX, simeconazole [149508-90-7] + TX, tebuconazole [107534-96-3] + TX, tetraconazole [112281-77-3] + TX, triadimefon [43121-43-3] + TX, triadimenol [55219-65-3] + TX, triflumizole [99387-89-0] + TX, triticonazole [131983-72-7] + TX, ancymidol [12771-68-5] + TX, fenarimol [60168-88-9] + TX, nuarimol [63284-71-9] + TX, bupirimate [41483-43-6] + TX, dimethirimol [5221-53-4] + TX, ethirimol [23947-60-6] + TX, dodemorph [1593-77-7] + TX, fenpropidine [67306-00-7] + TX, fenpropimorph [67564-91-4] + TX, spiroxamine [118134-30-8] + TX, tridemorph [81412-43-3] + TX, cyprodinil [121552-61-2] + TX, mepanipyrim [110235-47-7] + TX, pyrimethanil [53112-28-0] + TX, fenpiclonil [74738-17-3] + TX, fludioxonil [131341-86-1] + TX, benalaxyl [71626-11-4] + TX, furalaxyl [57646-30-7] + TX, metalaxyl [57837-19-1] + TX, R-metalaxyl [70630-17-0] + TX,

ofurace [58810-48-3] + TX, oxadixyl [77732-09-3] + TX, benomyl [17804-35-2] + TX, carbendazim [10605-21-7] + TX, debacarb [62732-91-6] + TX, fuberidazole [3878-19-1] + TX, thiabendazole [148-79-8] + TX, chlozolinate [84332-86-5] + TX, dichlozoline [24201-58-9] + TX, iprodione [36734-19-7] + TX, myclozoline [54864-61-8] + TX, procymidone [32809-16-8] + TX, vinclozoline [50471-44-8] + TX, boscalid [188425-85-6] + TX, carboxin [5234-68-4] + TX, fenfuram [24691-80-3] + TX, flutolanil [66332-96-5] + TX, mepronil [55814-41-0] + TX, oxycarboxin [5259-88-1] + TX, penthiopyrad [183675-82-3] + TX, thifluzamide [130000-40-7] + TX, guazatine [108173-90-6] + TX, dodine [2439-10-3] [112-65-2] (free base) + TX, iminoctadine [13516-27-3] + TX, azoxystrobin [131860-33-8] + TX, dimoxystrobin [149961-52-4] + TX, enestroburin {Proc. BCPC, Int. Congr., Glasgow, 2003, **1**, 93} + TX, fluoxastrobin [361377-29-9] + TX, kresoxim-methyl [143390-89-0] + TX, metominostrobin [133408-50-1] + TX, trifloxystrobin [141517-21-7] + TX, orysastrobin [248593-16-0] + TX, picoxystrobin [117428-22-5] + TX, pyraclostrobin [175013-18-0] + TX, ferbam [14484-64-1] + TX, mancozeb [8018-01-7] + TX, maneb [12427-38-2] + TX, metiram [9006-42-2] + TX, propineb [12071-83-9] + TX, thiram [137-26-8] + TX, zineb [12122-67-7] + TX, ziram [137-30-4] + TX, captafol [2425-06-1] + TX, captan [133-06-2] + TX, dichlofluanid [1085-98-9] + TX, fluoroimide [41205-21-4] + TX, folpet [133-07-3] + TX, tolylfluanid [731-27-1] + TX, bordeaux mixture [8011-63-0] + TX, copperhydroxid [20427-59-2] + TX, copperoxychlorid [1332-40-7] + TX, coppersulfat [7758-98-7] + TX, copperoxid [1317-39-1] + TX, mancopper [53988-93-5] + TX, oxine-copper [10380-28-6] + TX, dinocap [131-72-6] + TX, nitrothal-isopropyl [10552-74-6] + TX, edifenphos [17109-49-8] + TX, iprobenphos [26087-47-8] + TX, isoprothiolane [50512-35-1] + TX, phosdiphen [36519-00-3] + TX, pyrazophos [13457-18-6] + TX, tolclofos-methyl [57018-04-9] + TX, acibenzolar-S-methyl [135158-54-2] + TX, anilazine [101-05-3] + TX, benthiavalicarb [413615-35-7] + TX, blasticidin-S [2079-00-7] + TX, chinomethionat [2439-01-2] + TX, chloroneb [2675-77-6] + TX, chlorothalonil *[1897-45-6]* + TX, cyflufenamid *[180409-60-3]* + TX, cymoxanil *[57966-95-7]* + TX, dichlone *[117-80-6]* + TX, diclocymet [139920-32-4] + TX, diclomezine *[62865-36-5]* + TX, dicloran *[99-30-9]* + TX, diethofencarb *[87130-20-9]* + TX, dimethomorph *[110488-70-5]* + TX, SYP-LI90 (Flumorph) *[211867-47-9]* + TX, dithianon *[3347-22-6]* + TX, ethaboxam *[162650-77-3]* + TX, etridiazole *[2593-15-9]* + TX, famoxadone *[131807-57-3] + TX,* fenamidone *[161326-34-7]* + TX, fenoxanil *[115852-48-7]* + TX, fentin *[668-34-8]* + TX, ferimzone *[89269-64-7]* + TX, fluazinam *[79622-59-6]* + TX, fluopicolide [239110-15-7] + TX, flusulfamide [106917-52-6] + TX, fenhexamid [126833-17-8] + TX, fosetyl-aluminium [39148-24-8] + TX, hymexazol [10004-44-1] + TX, iprovalicarb [140923-17-7] + TX, IKF-916 (Cyazofamid) *[120116-88-3]* + TX, kasugamycin [6980-18-3] + TX, methasulfocarb *[66952-49-6]* + TX, metrafenone *[220899-03-6]* + TX, pencycuron *[66063-05-6]* + TX, phthalide [27355-22-2] + TX, polyoxins [11113-80-7] + TX, probenazole [27605-76-1] + TX, propamocarb [25606-41-1] + TX, proquinazid [189278-12-4] + TX, pyroquilon [57369-32-1] + TX, quinoxyfen [124495-18-7] + TX, quintozene [82-68-8] + TX, sulphur [7704-34-9] + TX, tiadinil [223580-51-6] + TX, triazoxide [72459-58-6] + TX, tricyclazole [41814-78-2] + TX, triforine [26644-46-2] + TX, validamycin [37248-47-8] + TX, zoxamide (RH7281) [156052-68-5] + TX, mandipropamid [374726-62-2] + TX, isopyrazam [881685-58-1] + TX, sedaxane [874967-67-6] + TX, 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (9-dichloromethylene-1,2,3,4-tetrahydro-1,4-methano-naphthalen-5-yl)-amide (dislosed in WO 2007/048556) + TX, 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid [2-(2,4-dichlorophenyl)-2-methoxy-1-methyl-ethyl]-amide (disclosed in WO 2008/148570) + TX, 1-[4-[4-[(5S)5-(2,6-

difluorophenyl)-4,5-dihydro-1,2-oxazol-3-yl]-1,3-thiazol-2-yl]piperidin-1-yl]-2-[5-methyl-3-(trifluoromethyl)-1H-pyrazol-1-yl]ethanone + TX, 1-[4-[4-[5-(2,6-difluorophenyl)-4,5-dihydro-1,2-oxazol-3-yl]-1,3-thiazol-2-yl]piperidin-1-yl]-2-[5-methyl-3-(trifluoromethyl)-1H-pyrazol-1-yl]ethanone [1003318-67-9], both disclosed in WO 2010/123791, WO 2008/013925, WO 2008/013622 and WO 2011/051243 page 20) +TX, *S*)-[3-(4-Chloro-2-fluoro-phenyl)-5 -(2,4-difluoro-phenyl)-isoxazol-4-y l]-pyridin-3-yl-methanol + TX, 3-(4-Chloro-2-fluoro-phenyl)-5 -(2,4-difluoro-phenyl)-isoxazol-4-y l]-pyridin-3-yl-methanol + TX, 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (3',4',5'-trifluoro-biphenyl-2-yl)-amide (disclosed in WO 2006/087343) + TX, 3-(difluoromethyl)-N-methoxy-1-methyl-N-[1-methyl-2-(2,4,6-trichlorophenyl)ethyl]-1H-Pyrazole-4-carboxamide + TX, 4-[(5*S*)-5-(3,5-dichlorophenyl)-5-(trifluoromethyl)-4H-isoxazol-3-yl]-2-methyl-N-(thietan-3-yl)benzamide (WO2011/104089) + TX, 4-[(5*R*)-5-(3,5-dichlorophenyl)-5-(trifluoromethyl)-4H-isoxazol-3-yl]-2-methyl-N-(thietan-3-yl)benzamide (WO2011/104089) + TX, 4-[(5*S*)-5-(3,5-dichlorophenyl)-5-(trifluoromethyl)-4H-isoxazol-3-yl]-2-methyl-N-(cis-1-oxo-thietan-3-yl)benzamide (WO2011/104089) + TX, 4-[(5*R*)-5-(3,5-dichlorophenyl)-5-(trifluoromethyl)-4H-isoxazol-3-yl]-2-methyl-N-(cis-1-oxo-thietan-3-yl)benzamide (WO2011/104089) + TX, 4-[(5*S*)-5-(3,5-dichlorophenyl)-5-(trifluoromethyl)-4H-isoxazol-3-yl]-2-methyl-N-(trans-1-oxo-thietan-3-yl)benzamide (WO2011/104089) + TX, 4-[(5*R*)-5-(3,5-dichlorophenyl)-5-(trifluoromethyl)-4H-isoxazol-3-yl]-2-methyl-N-(trans-1-oxo-thietan-3-yl)benzamide (WO2011/104089) + TX, 4-[(5*S*)-5-(3,5-dichlorophenyl)-5-(trifluoromethyl)-4H-isoxazol-3-yl]-N-(1,1-dioxothietan-3-yl)-2-methyl-benzamide (WO2011/104089) + TX, 4-[(5*R*)-5-(3,5-dichlorophenyl)-5-(trifluoromethyl)-4H-isoxazol-3-yl]-N-(1,1-dioxothietan-3-yl)-2-methyl-benzamide (WO2011/104089) + TX, 4-[(5*S*)-5-(3,5-dichlorophenyl)-5-(trifluoromethyl)-4H-isoxazol-3-yl]-2-methyl-N-[2-oxo-2-(2,2,2-trifluoroethylamino)ethyl]benzamide (WO2011/104089) + TX, 4-[(5*R*)-5-(3,5-dichlorophenyl)-5-(trifluoromethyl)-4H-isoxazol-3-yl]-2-methyl-N-[2-oxo-2-(2,2,2-trifluoroethylamino)ethyl]benzamide (WO2011/104089) + TX, Penflufen [494793-67-8] and TX, 5-[(5S)-5-(3,5-dichlorophenyl)-5-(trifluoromethyl)-4H-isoxazol-3-yl]-2-(1,2,4-triazol-1-yl)benzonitrile (WO2007/075459) + TX, 5-[(5R)-5-(3,5-dichlorophenyl)-5-(trifluoromethyl)-4H-isoxazol-3-yl]-2-(1,2,4-triazol-1-yl)benzonitrile (WO2007/075459) + TX.

The components (B) are known. The references in brackets behind the active ingredients, e.g. *[3878-19-1]* refer to the Chemical Abstracts Registry number. The above described mixing partners are known. Where the active ingredients are included in "The Pesticide Manual" [The Pesticide Manual - A World Compendium; Thirteenth Edition; Editor: C. D. S. TomLin; The British Crop Protection Council], they are described therein under the entry number given in round brackets hereinabove for the particular compound; for example, the compound "abamectin" is described under entry number (1). Where "[CCN]" is added hereinabove to the particular compound, the compound in question is included in the "Compendium of Pesticide Common Names", which is accessible on the internet under the internet address http://www.alanwood.net/pesticides/ [A. Wood; Compendium of Pesticide Common Names, Copyright © 1995-2012]; or preferably one of the further pesticides listed below.

In the above different lists of active ingredients to be mixed with a TX, the compound of the formula I is preferably a compound selected from the Tables 1-43; more preferably a compound selected from Table 44;

and even more preferably a compound selected from I-001, I-002, I-003, I-004, I-005, I-006, I-007, I-008, I-010, I-011, I-012, I-013, I-014, I-016, I-019, I-020, I-021, I-022, I-023, I-024, I-025, I-026, I-

027, I-028, I-029, I-030, I-031, I-032, I-033, I-034, I-036, I-037, I-038, I-039, I-040, I-041, I-042, I-043, I-044, I-045, I-046, I-048, I-049, I-050, I-051, I-052, I-053, I-055, I-056, I-057, I-063, I-066, I-067, I-068, I-069, I-070, I-071, I-072, I-073, I-074, I-075, I-076, I-076, I-078, I-079, I-080, I-081, I-082.

In the above-mentioned mixtures of compounds of formula I, in particular a compound selected from said Tables 1-44, with other insecticides, fungicides, herbicides, safeners, adjuvants and the like, the mixing ratios can vary over a large range and are, preferably 100:1 to 1:6000, especially 50:1 to 1:50, more especially 20:1 to 1:20, even more especially 10:1 to 1:10. Those mixing ratios are understood to include, on the one hand, ratios by weight and also, on other hand, molar ratios.

The mixtures can advantageously be used in the above-mentioned formulations (in which case "active ingredient" relates to the respective mixture of TX with the mixing partner).

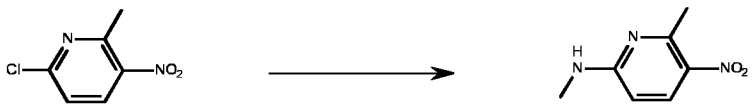
Some mixtures may comprise active ingredients which have significantly different physical, chemical or biological properties such that they do not easily lend themselves to the same conventional formulation type. In these circumstances other formulation types may be prepared. For example, where one active ingredient is a water insoluble solid and the other a water insoluble liquid, it may nevertheless be possible to disperse each active ingredient in the same continuous aqueous phase by dispersing the solid active ingredient as a suspension (using a preparation analogous to that of an SC) but dispersing the liquid active ingredient as an emulsion (using a preparation analogous to that of an EW). The resultant composition is a suspoemulsion (SE) formulation.

The mixtures comprising a TX selected from Tables 1-37, 39 and 41-42 and one or more active ingredients as described above can be applied, for example, in a single “ready-mix” form, in a combined spray mixture composed from separate formulations of the single active ingredient components, such as a “tank-mix”, and in a combined use of the single active ingredients when applied in a sequential manner, i.e. one after the other with a reasonably short period, such as a few hours or days. The order of applying the compounds of formula I selected from Tables 1-37, 39 and 41-42 and the active ingredients as described above is not essential for working the present invention.

The following non-limiting Examples illustrate the above-described invention in greater detail without limiting it. Those skilled in the art will promptly recognise appropriate variations from the procedures both as to reactants and as to reaction conditions and techniques. All references mentioned herein are incorporated by reference in their entirety.

Preparatory Examples

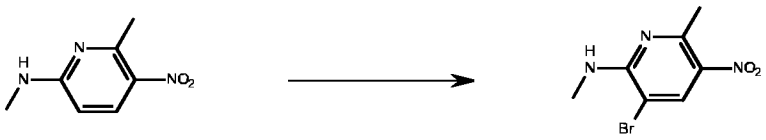
Preparation of N-6-Dimethyl-5-nitro-pyridin-2-amine



A solution of 6-chloro-2-methyl-3-nitro-pyridine (1.0 g) was treated with methylamine (11 mL, 33% in EtOH) and heated under reflux over-night. The mixture was concentrated under reduced pressure (1.44 g crude product), diluted with Ethyl acetate and brine, and then extracted with Ethyl acetate . The organic layer was washed with brine, dried over $MgSO_4$, filtered and evaporated obtaining the desired product as a yellow solid.

H^1 NMR (400 MHz, $CDCl_3$): δ 8.30 (m, 1H), 6.30 (m, 1H), 5.60 (brs, 1H), 3.05 (m, 3H), 2.80 (s, 3H).

Preparation of 3-Bromo-N-6-dimethyl-5-nitro-pyridin-2-amine

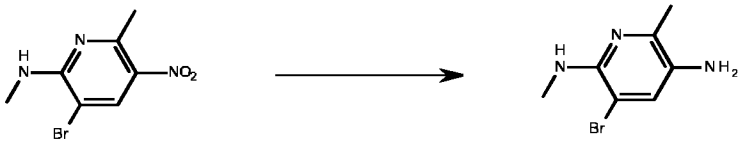


In a 25 mL flask, N-6-dimethyl-5-nitro-pyridin-2-amine (1.8 g) was dissolved in acetic acid (15 mL), then bromine (0.60 g) was added slowly so that the reaction temperature could be kept below 25°C. The yellow suspension was stirred at room temperature for 2 hr and monitored by LC-MS. Upon consumption of the starting material cold water (15 mL) was slowly added and the yellow precipitate was filtrated and washed with cold water. After drying at 40°C under vacuum the desired compound was isolated as a yellow solid.

mp = 160 - 164°C;

H^1 NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H), 5.60 (brs, 1H), 3.07 (m, 3H), 2.70 (s, 3H).

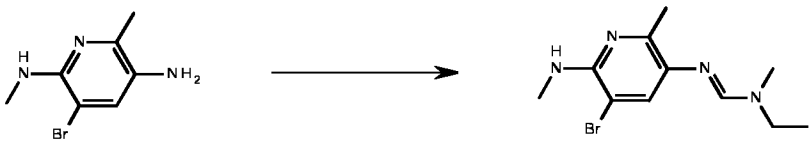
Preparation of 3-Bromo-N-2,6-dimethyl-pyridine-2,5-diamine



In a 4-neck-flask equipped with an mechanical stirrer 3-bromo-N-6-dimethyl-5-nitro-pyridin-2-amine (1.4 g) was dissolved in EtOH (30 mL) and water (6.0 mL), ammonium chloride (0.60 g), and Fe (1.3 g) were added sequentially. The reaction was left to stir overnight and upon completion the heterogeneous solution was filtered through a thin pad of celite, washed with ethyl acetate, and concentrated under reduced pressure. This crude residue was diluted with Ethyl acetate and washed sequentially with 1M NaOH aqueous solution (100 mL) and brine. The organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure to afford the desired compound as brown oil that was used directly without further purification.

H^1 NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H), 5.60 (brs, 1H), 3.07 (m, 3H), 2.70 (s, 3H).

Preparation of N'-[5-Bromo-2-methyl-6-(methylamino)-3-pyridyl]-N-ethyl-N-methyl-formamidine

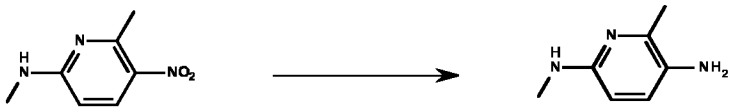


In a 25 mL one-neck flask N-ethyl-N-methyl-formamide (0.49 g, 5.6 mmol) was dissolved in CH_2Cl_2 (4 mL) and phosphorus oxychloride (0.90 g) was added with stirring for 90 min at rt. After the introduction of 3-bromo-N-2,6-dimethyl-pyridine-2,5-diamine (1.1 g) as a CH_2Cl_2 solution (8 mL), the reaction media was stirred for 1h at rt and then 3 h at 40 °C. The reaction was carefully quenched with water and basified with NaOH (1M), extracted with CH_2Cl_2 and then washed with brine. The combined organic phases were dried with sodium sulfate, filtred, and the solvent was removed under reduced

pressure. The crude residue was purified by column chromatography using a CH_2Cl_2/MeOH solvent gradient (0-10% MeOH) to afford the title compound as a light brown viscous oil.

H^1 NMR (400 MHz, $CDCl_3$): δ 7.35 (brs, 1H), 7.12 (s, 1H), 4.55 (brs, 1H), 3.35 (m, 3H), 3.04 (m, 3H), 2.95 (s, 3H), 2.38 (s, 3H), 1.18 (m, 3H).

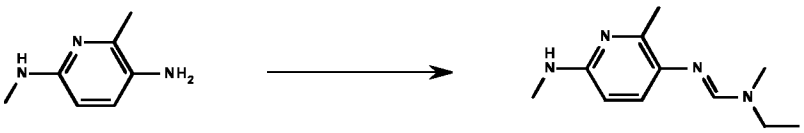
Preparation of N-2,6-Dimethylpyridine-2,5-diamine



In a 3-neck round bottom flask N,6-dimethyl-5-nitro-pyridin-2-amine (0.30 g) was dissolved in MeOH (40 mL) and ammonium formate (0.60 g) was added. The flask was then degassed and purged with argon and 5% Pd/C (0.060g) was introduced. The resultant heterogenous solution was allowed to stir at room temperature overnight. Upon completion, the reaction mixture was filtered over celite and washed repeatedly with MeOH. The solvent was removed under reduced pressure and the crude residue was purified via column chromatography using a CH_2Cl_2/MeOH solvent gradient (0-5% MeOH) to afford the desired compound as a brown oil.

H^1 NMR (400 MHz, $CDCl_3$): δ 8.62 (s, 1H), 7.22 (d, 1H), 6.39 (d, 1H), 2.78 (t, 3H), 2.70 (s, 3H), 2.40 (t, 3H).

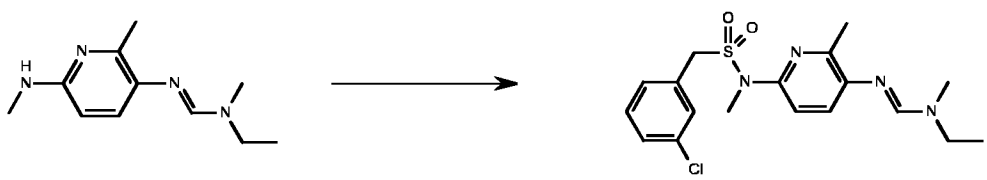
Preparation of N-Ethyl-N-methyl-N'-[2-methyl-6-(methylamino)-3-pyridyl]formamidine



In a 3-neck round bottom flask ethyl-(methoxymethylene)-methyl-ammonium; methyl sulfate (0.70 g) was dissolved in MeOH (2 mL) and the resultant solution was cooled using an ice bath. This was followed by the dropwise introduction of NaOMe (0.60 mL, 5.4 M in MeOH). After being warmed to rt for 0.5 h, a solution of N-2,6-dimethylpyridine-2,5-diamine (0.30 g) dissolved in MeOH (1 mL) was introduced dropwise and the reaction mixture was refluxed overnight. After cooling to room temperature, the MeOH was removed under reduced pressure the reaction was carefully quenched with water, basified with NaOH (1M), extracted with CH_2Cl_2, and washed with brine. The title compound was not additionally purified.

H^1 NMR (400 MHz, $CDCl_3$): δ 7.31 (brs, 1H), 6.90 (d, 1H), 6.20 (d, 1H), 4.25 (brs, 2H), 3.29 (m, 3H), 2.89 (s, 3H), 2.73 (s, 3H), 2.20 (s, 3H), 1.22 (m, 3H).

Preparation of N'-[6-[(3-Chlorophenyl)methylsulfonyl-methyl-amino]-2-methyl-3-pyridyl]-N-ethyl-N-methyl-formamidine

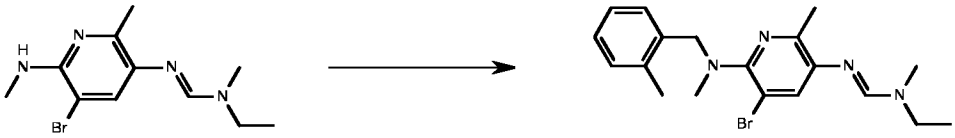


In a 3-neck round bottom flask N-ethyl-N-methyl-N'-[2-methyl-6-(methylamino)-3-pyridyl]formamidine (0.12 g) was dissolved in pyridine (2.0 mL) and (3-chlorophenyl)methanesulfonyl

chloride (0.16 g) was introduced dropwise. The contents were stirred vigorously and heated at 100 °C for 12h. Upon completion the reaction mixture was quenched with water and extracted with Ethyl acetate . The organic fractions were combined and washed with 1N HCl followed by brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified via column chromatography with a heptane/Ethyl acetate solvent gradient (10-50% Ethyl acetate) to afford the desired compound as a clear oil.

H^1 NMR (400 MHz, $CDCl_3$): δ 7.41 (m, 2H), 7.24 (m, 3H), 7.00 (m, 2H), 4.40 (s, 2H), 3.35 (brs, 1H), 3.26 (brs, 1H), 3.18 (s, 3H), 2.96 (brs, 3H), 2.42 (s, 3H), 1.29 (m, 3H).

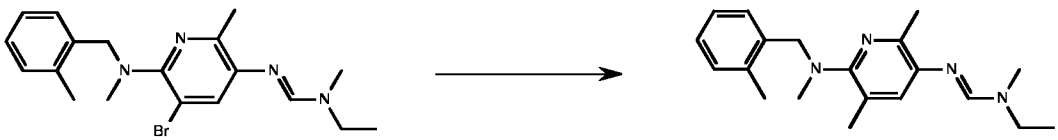
Preparation of N'-[5-Bromo-2-methyl-6-[methyl(o-tolylmethyl)amino]-3-pyridyl]-N-ethyl-N-methyl-formamidine



To a 3-neck round bottom flask containing N'-[5-bromo-2-methyl-6-(methylamino)-3-pyridyl]-N-ethyl-N-methyl-formamidine (0.10 g) dissolved in DMSO (2.0 mL) was added K_2CO_3 (0.10 g) followed by the dropwise introduction of 1-(bromomethyl)-2-methyl-benzene (0.10 g). The reaction mixture was then heated to 110 °C and stirred overnight. The next day, the contents were cooled to rt, diluted with water, and extracted with Ethyl acetate . The combined organic phases were dried over sodium sulfate and concentrated under reduced pressure. The crude residue was purified by preparative reverse phase chromatography to afford the desired compound.

H^1 NMR (400 MHz, $CDCl_3$): δ 7.55 (m, 1H), 7.42 (brs, 1H), 7.25 (s, 1H), 7.15 (m, 3H), 4.37 (s, 2H), 3.40 (brs, 2H), 3.00 (m, 3H), 2.80 (s, 3H), 2.42 (s, 3H), 2.32 (s, 3H), 1.22 (t, 3H).

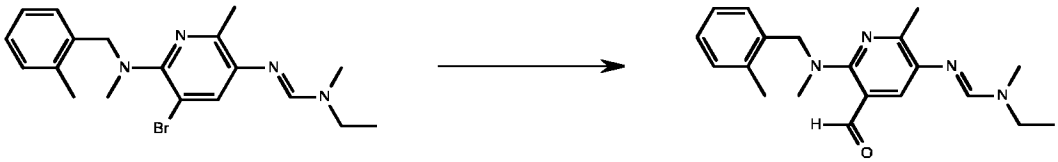
Preparation of N'-[2,5-Dimethyl-6-[methyl(o-tolylmethyl)amino]-3-pyridyl]-N-ethyl-N-methyl-formamidine



To a 10 mL pressure flask under argon and charged with MeMgBr (3.0 M in THF, 0.085 mL) in dry THF (1.0 mL) was added a solution of $ZnCl_2$ [(1.0M in Et_2O) 0.30 mL]. After stirring at rt for 2h, N'-[5-bromo-2-methyl-6-[methyl(o-tolylmethyl)amino]-3-pyridyl]-N-ethyl-N-methyl-formamidine (0.10 g) and [1,1′-bis(diphenylphosphino)-ferrocene] dichloropalladium(II) (8.0 mg) were introduced as a THF solution (2.0 mL) and the reaction media was stirred at 45°C for 18h. When the reaction was complete, it was cooled to room temperature and methanol (1.0 mL) followed by water were added. The reaction media was extracted with Ethyl acetate , washed with brine, and dried over sodium sulfate. The organic solvent was removed under reduced pressure and the crude residue was purified via column chromatography with a heptane/Ethyl acetate solvent gradient (10-50% Ethyl acetate) to afford the desired compound as a brown oil.

H^1 NMR (400 MHz, $CDCl_3$): δ 7.50 (m, 1H), 7.38 (brs, 1H), 7.25 (m, 3H), 6.80 (s, 1H), 4.45 (s, 2H), 3.35 (brs, 2H), 2.97 (m, 3H), 2.68 (s, 3H), 2.42 (s, 3H), 2.31 (s, 3H), 2.18 (s, 3H), 1.22 (t, 3H).

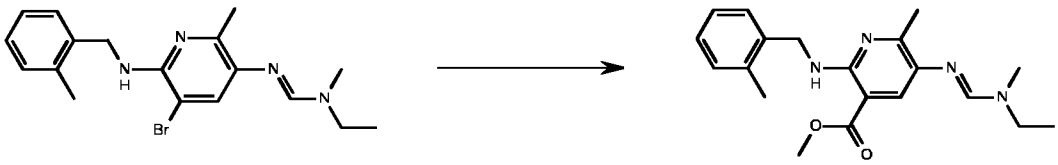
Preparation of N-Ethyl-N'-[5-formyl-2-methyl-6-[methyl(o-tolylmethyl)amino]-3-pyridyl]-N-methyl-formamidine



To a dry 10 mL flask under argon containing N'-[5-bromo-2-methyl-6-[methyl(*o*-tolylmethyl) amino]-3-pyridyl]-N-ethyl-N-methyl-formamidine (1.2 g) and dry THF (2.0 mL) cooled to −78°C was added *n*-BuLi [1.6 M in hexanes (0.21 mL)] dropwise and the orange solution was stirred for 1h after which EtO_2CH (0.030 mL) was introduced slowly. The reaction was stirred for an additional 2 h at -78°C and then the cold bath was removed. The mixture was quenched with saturated aqueous solution of NH_4Cl at 0 °C, extracted with Ethyl acetate and the combined organic fractions were washed with brine, dried with over sodium sulfate, and concentrated under reduced pressure. The crude material was purified via column chromatography with a heptane/Ethyl acetate solvent gradient (10-40% Ethyl acetate) to afford the desired compound as a yellow oil.

H^1 NMR (400 MHz, $CDCl_3$): δ 10.00 (s, 1H), 7.45 (brs, 1H), 7.33 (m, 1H), 7.15 (m, 3H), 4.60 (s, 2H), 3.30 (brs, 2H), 3.30 (m, 6H), 2.50 (s, 3H), 2.22 (s, 3H), 1.22 (t, 3H).

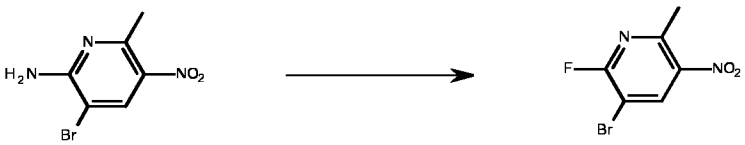
Preparation of Methyl 5-[(*E*)-[ethyl(methyl)amino]methyleneamino]-6-methyl-2-(*o*-tolylmethylamino)pyridine-3-carboxylate



An autoclave was charged with N'-[5-bromo-2-methyl-6-(o-tolylmethylamino)-3-pyridyl]-N-ethyl-N-methyl-formamidine (0.17 g), bis(benzonitrile) palladium chloride (0.0018 g) 1,1'-bis(diphenylphosphino)ferrocene (0.013 g), triethylamine (0.076 mL), and degassed methanol (9.0 mL). The vessel was then charged with CO gas (20 bar) and heated to 100°C with the contents left to react overnight. Upon completion, the reaction mixture was diluted with CH_2Cl_2, filtered over celite, and concentrated at reduced pressure. The crude material was purified via column chromatography with a heptane/Ethyl acetate solvent gradient (10-40% Ethyl acetate) to afford the desired compound as an orange oil.

H^1 NMR (400 MHz, $CDCl_3$): δ 9.72 (brs, 1H), 7.46 (s, 1H), 7.29 (m, 2H), 7.06 (m, 3H), 4.66 (d, 2H), 3.73 (s, 3H), 3.29 (brs, 2H), 2.93 (s, 3H), 2.37 (s, 3H), 2.32 (s, 3H), 1.15 (t, 3H).

Preparation of 3-Bromo-2-fluoro-6-methyl-5-nitro-pyridine



To a PFE container was added 3-bromo-6-methyl-5-nitro-pyridin-2-amine (5.0 g) followed by HF-pyridine [70% HF (21 g)]. The mixture was cooled to 0 °C and sodium nitrite (1.8 g) was added portion

wise over 5 min. After 30 min the ice bath was removed and the contents were allowed to reach rt overnight. Upon completion, the reaction was transferred into a separatory funnel containing a saturated aq. NH_4Cl and extracted with Ethyl acetate . The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. Precipitation using Et_2O afforded the desired compound as a pale amorphous solid.

H^1 NMR (400 MHz, $CDCl_3$): δ 8.57 (d, 1H), 2.73 (s, 3H);

F^{19} NMR (376.5MHz, $CDCl_3$): δ -56.0 (t).

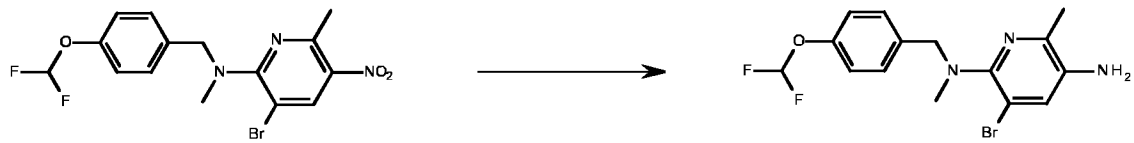
Preparation of 3-Bromo-N-[[4-(difluoromethoxy)phenyl]methyl]-N,6-dimethyl-5-nitro-pyridin-2-amine

A microwave vial was charged with 3-bromo-2-fluoro-6-methyl-5-nitro-pyridine (0.68 g), 1-[4-(difluoromethoxy) phenyl]-N-methyl-methanamine (0.54 g), triethylamine (0.58 g), and DMSO (4 mL). The contents were then irradiated at 150°C for 30 min. Upon completion, the reaction contents were transferred to a separatory funnel, diluted with water, and extracted with Ethyl acetate . The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude material was purified via column chromatography with a heptane/Ethyl acetate solvent gradient (0-30% Ethyl acetate) to afford the desired compound as an orange oil.

H^1 NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.25 (d, 2H), 7.03 (d, 2H), 6.44 (t, 1H), 4.78 (s, 2H), 3.08 (s, 3H), 2.67 (m, 3H);

F^{19} NMR (376.5 MHz, $CDCl_3$): δ -80.8 (s).

Preparation of 3-Bromo-N2-[[4-(difluoromethoxy)phenyl]methyl]-N2,6-dimethyl-pyridine-2,5-diamine

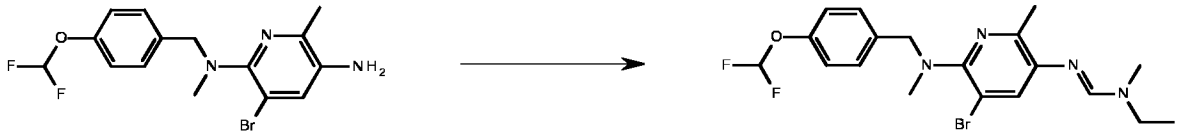


To a four-necked flask equipped with an mechanical stirrer and containing 3-bromo-N-[[4-(difluoromethoxy) phenyl]methyl]-N,6-dimethyl-5-nitro-pyridin-2-amine (0.97 g) was added EtOH (15 mL), water (4.0 mL), NH_4Cl (0.52 g), and Fe (1.1 g). The contents were then heated at 80°C for 18 hr. When the reaction was complete the heterogeneous solution was filtered over a thin pad of celite and concentrated under reduced pressure. This residue was dissolved in Ethyl acetate and washed sequentially with a 2M NaOH aqueous solution and brine, dried over sodium sulfate, and concentrated under reduced pressure. The crude material was purified via column chromatography with a heptane/Ethyl acetate solvent gradient (0-50% Ethyl acetate) to afford the desired compound as an orange oil.

H^1 NMR (400 MHz, $CDCl_3$): δ 7.37 (d, 2H), 7.10 (s, 1H), 6.99 (d, 2H), 6.42 (t, 1H), 4.16 (s, 2H), 3.32 (brs, 2H), 2.67 (s, 3H), 2.20 (s, 3H);

F^{19} NMR (376.5 MHz, $CDCl_3$): δ -80.4 (s).

Preparation of N'-[5-Bromo-6-[[4-(difluoromethoxy)phenyl]methyl-methyl-amino]-2-methyl-3-pyridyl]-N-ethyl-N-methyl-formamidine

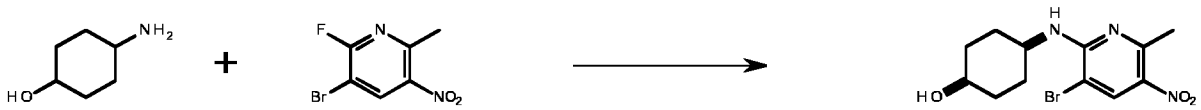


In a dry 25 mL one-neck flask under argon N-ethyl-N-methyl-formamide (1.8 g) was dissolved in CH_2Cl_2 (3 mL) and phosphorus oxychloride (0.32 g) was added dropwise. The mixture was stirred for 90 min at rt and then 3-bromo-N2-[[4-(difluoromethoxy)phenyl]methyl]-N-2,6-dimethyl-pyridine-2,5-diamine (0.71 g), taken up in CH_2Cl_2 (3.0 mL), was introduced dropwise. After stirring at rt for 1 h water (3.0 mL) was added and the solution was then basified with NaOH (2M) and extracted with CH_2Cl_2. The combined organic layers were dried over sodium sulfate and concentrated under reduced pressure. The crude material was purified via column chromatography with a heptane/Ethyl acetate + 0.1% triethylamine solvent gradient (0-40% Ethyl acetate) to furnish the title compound as an orange oil.

H^1 NMR (400 MHz, $CDCl_3$): δ 7.37 (d, 2H), 7.16 (s, 1H), 6.98 (d, 2H), 6.42 (t, 1H), 4.25 (s, 2H), 3.39 (s, 3H), 2.92 (s, 3H), 2.66 (s, 3H), 2.28 (s, 3H), 1.12 (t, 3H);

F^{19} NMR (376.5 MHz, $CDCl_3$): δ -80.4 (s).

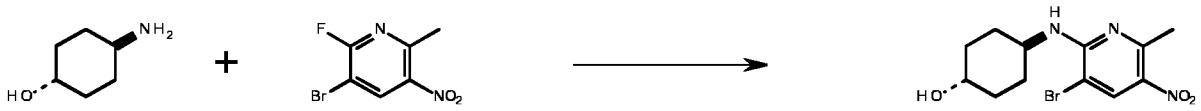
Preparation of cis-4-[(3-Bromo-6-methyl-5-nitro-2-pyridyl)amino]cyclohexanol



To a flask charged with 3-bromo-2-fluoro-6-methyl-5-nitro-pyridine (1.0 g) and DMSO (3 mL) was added triethylamine (2 equiv.) and 4-aminocyclohexanol (1.1 equiv., 50 mass %). The brown reaction mixture was stirred for 30 min. The reaction solution was poured into water (50 mL) and extracted with ethyl acetate (2 x 100 mL), the combined organic layers were washed with brine, dried over Na_2SO_4, filtrated, and concentrated to afford a brown residue. Purification by combiflash column chromatography over silica gel using a cyclohexane/ethyl acetate solvent gradient (0% − 100% ethyl acetate) afforded the title compound as an amorphous yellow solid.

H^1 NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 5.63 (m, 1H), 4.20 (m, 1H), 4.01 (m, 1H), 2.77 (s, 3H), 2.20 (m, 4H), 1.50 (m, 5H).

Preparation of trans-4-[(3-Bromo-6-methyl-5-nitro-2-pyridyl)amino]cyclohexanol

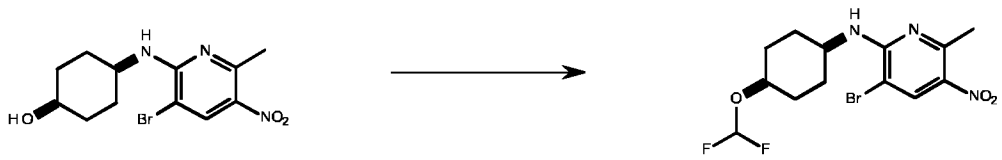


To a flask charged with 3-bromo-2-fluoro-6-methyl-5-nitro-pyridine (0.500 g) and DMSO (5 mL) was added triethylamine (3 equiv.) and trans-4-aminocyclohexanol hydrochloride (1.1 equiv.). The brown reaction mixture was stirred for 30 min. The reaction solution was poured into water (50 mL) and extracted with ethyl acetate (2 x 100 mL), the combined organic layers were washed with brine, dried over Na_2SO_4, filtrated, and concentrated to afford a brown residue. Purification by combiflash column

chromatography over silica gel using a cyclohexane/ethyl acetate solvent gradient (0% − 60% ethyl acetate) afforded the title compound as an amorphous yellow solid.

H^1 NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 5.42 (m, 1H), 4.09 (m, 1H), 3.70 (m, 1H), 2.77 (s, 3H), 2.17 (m, 2H), 2.05 (m, 2H), 1.47 (m, 3H), 1.33 (m, 2H).

Preparation of cis-3-Bromo-N-[4-(difluoromethoxy)cyclohexyl]-6-methyl-5-nitro-pyridin-2-amine

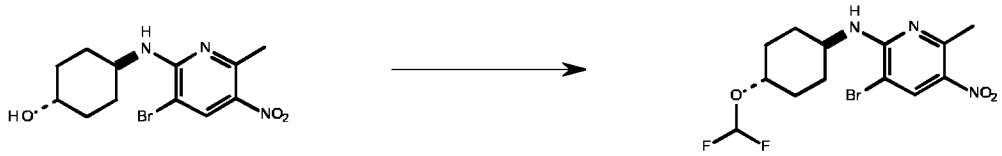


A 3-neck-flask equipped with a condenser under argon was charged with cis-4-[(3-bromo-6-methyl-5-nitro-2-pyridyl)amino]cyclohexanol (0.360 g, co-evaporated twice in dry acetonitrile), acetonitrile (2 mL), and CuI (0.2 equiv). The mixture was heated to 45 °C under argon for 5 min, and 2,2-difluoro-2-fluorosulfonyl-acetic acid (1.1 equiv.) in acetonitrile (2 mL) was added with a syringe pump over 60 min. The resulting mixture was stirred at 45 °C for 30 min. Upon completion, the reaction was quenched with water (10 mL) and extracted with ethyl acetate (2 x 10 mL). The organics were washed with brine (10 mL), dried and reduced under vacuum. Purification of the crude residue by combiflash column chromatography over silica gel using a cyclohexane/ethyl acetate solvent gradient (0% − 20% ethyl acetate) afforded the title compound as an amorphous yellow solid.

H^1 NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 1H), 6.27 (t, 1H), 5.55 (d, 1H), 4.42 (broad s, 1H), 4.17 (m, 1H), 2.76 (s, 3H), 1.97 (m, 4H), 1.70 (m, 2H), 1.45 (m, 2H).

F^{19} NMR (376.5 MHz, $CDCl_3$ δ ppm: −81.0 (s).

Preparation of trans-3-Bromo-N-[4-(difluoromethoxy)cyclohexyl]-6-methyl-5-nitro-pyridin-2-amine

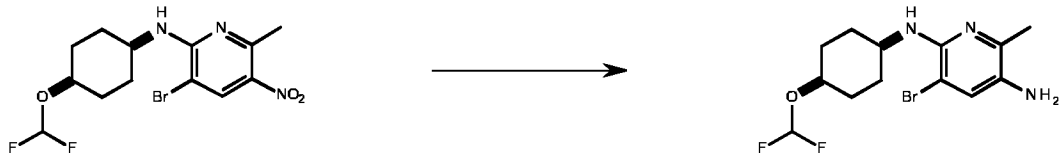


A 3-neck-flask equipped with a condenser under argon was charged with trans-4-[(3-bromo-6-methyl-5-nitro-2-pyridyl)amino]cyclohexanol (0.550 g, co-evaporated twice in dry acetonitrile), acetonitrile (4 mL), and CuI (0.2 equiv). The mixture was heated to 45 °C under argon for 5 min, and 2,2-difluoro-2-fluorosulfonyl-acetic acid (1.1 equiv.) in acetonitrile (2 mL) was added with a syringe pump over 60 min. The resulting mixture was stirred at 45 °C for 10 min. Upon completion, the reaction was quenched with water (30 mL) and extracted with ethyl acetate (2 x 50 mL). he organics were washed with brine (10 mL), dried and reduced under vacuum. Purification of the crude residue by combiflash column chromatography over silica gel using a cyclohexane/ethyl acetate solvent gradient (0% − 20% ethyl acetate) afforded the title compound as an amorphous yellow solid.

H^1 NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 6.26 (t, 1H), 5.44 (m, 1H), 4.14 (m, 2H), 2.77 (s, 3H), 2.16 (m, 2H), 2.08 (m, 2H), 1.66 (m, 2H), 1.42 (m, 2H).

F^{19} NMR (376.5 MHz, $CDCl_3$ δ ppm: −81.0 (s).

Preparation of cis-3-Bromo-N2-[4-(difluoromethoxy)cyclohexyl]-6-methyl-pyridine-2,5-diamine

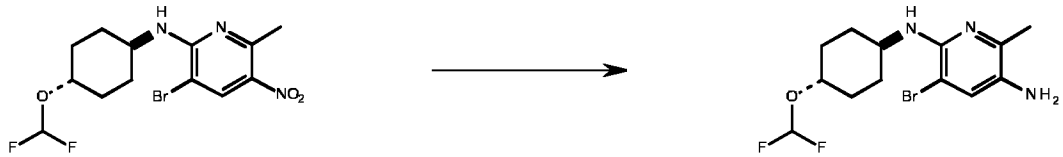


An autoclave was containing cis-3-bromo-N-[4-(difluoromethoxy)cyclohexyl]-N,6-dimethyl-5-nitro-pyridin-2-amine (0.131 g) and 5% Pt-sulfide/C (0.05 equiv. Johnson-Matthey type B109032-5) in THF (2 mL) was charged with hydrogen gas (5 bar) at rt and heated for 2 h at 40 °C. The reaction contents were filtered over celite and the solvent was evaporated under reduced pressure. The resultant crude residue was carried forward without further purification.

H^1 NMR (400 MHz, $CDCl_3$): δ 7.08 (s, 1H), 6.26 (t, 1H), 4.42 (m, 1H), 4.35 (m, 1H), 3.95 (m, 1H), 3.65 (m, 1H), 3.12 (broad s, 2H), 2.12 (m, 2H), 2.06 (m, 3H), 1.85 (m, 2H), 1.70 (m, 2H), 1.25 (m, 2H).

F^{19} NMR (376.5 MHz, $CDCl_3$ δ ppm: −80.6 (s).

Preparation of trans-3-Bromo-N2-[4-(difluoromethoxy)cyclohexyl]-6-methyl-pyridine-2,5-diamine

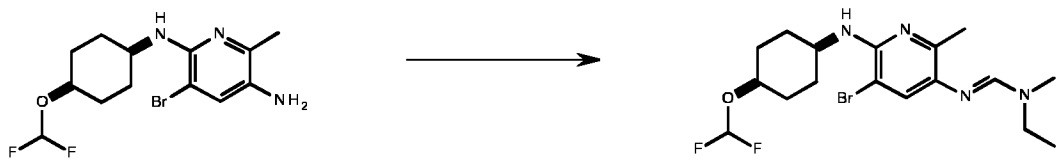


An autoclave containing trans-3-bromo-N-[4-(difluoromethoxy)cyclohexyl]-N,6-dimethyl-5-nitro-pyridin-2-amine (0.520 g) and 5% Pt-sulfide/C (0.05 equiv. Johnson-Matthey type B109032-5) in THF (5 mL) was charged with hydrogen gas (5 bar) at rt and heated for 2 h at 40 °C. The reaction contents were filtered over celite and the solvent was evaporated under reduced pressure. Purification of the crude residue by combiflash column chromatography over silica gel using a heptane/ethyl acetate solvent gradient (0% − 20% ethyl acetate) afforded the title compound as an amorphous solid.

H^1 NMR (400 MHz, $CDCl_3$): δ 7.15 (s, 1H), 6.25 (t, 1H), 4.04 (s, 1H), 3.38 (s, 2H), 3.26 (m, 1H), 2.67 (s, 3H), 2.29 (s, 3H), 2.05 (m, 2H), 1.86 (m, 2H), 1.53 (m, 4H).

F^{19} NMR (376.5 MHz, $CDCl_3$ δ ppm: −80.5 (s).

Preparation of cis-N'-[5-Bromo-6-[[4-(difluoromethoxy)cyclohexyl]amino]-2-methyl-3-pyridyl]-N-ethyl-N-methyl-formamidine



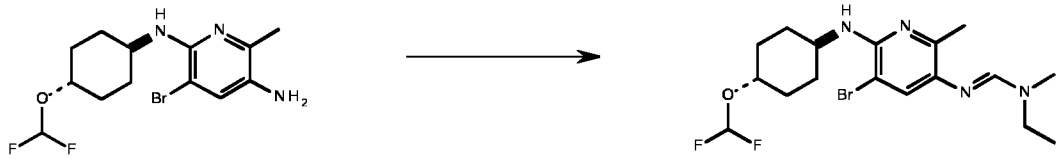
To a dry round bottom flask under argon containing N-ethyl-N-methyl-formamide (1.1 equiv.) dissolved in CH_2Cl_2 (2 mL) was introduced phosphorus oxychloride (1.1 equiv.) by dropwise addition. The mixture was stirred for 90 min at rt while becoming a slightly yellow solution. Then cis-3-bromo-N2-[4-(difluoromethoxy)cyclohexyl]-6-methyl-pyridine-2,5-diamine (0.132 g) dissolved in CH_2Cl_2 (1 mL) was added and the brown solution was stirred for 1 h at rt. Afterwards, the reaction media was basified with aqueous NaOH (2M), extracted with CH_2Cl_2 (2 x 30 mL) and the combined organic phases were

dried over Na_2SO_4, filtered, and then concentrated under reduced pressure. Purification of the crude orange residue by preparative reverse phase chromatography afforded the desired compound.

H^1 NMR (400 MHz, $CDCl_3$): δ 7.37 (broad s, 1H), 7.12 (s, 1H), 6.26 (t, 1H), 4.35 (m, 2H), 4.02 (m, 1H), 3.33 (broad s, 1H), 2.99 (s, 3H), 2.35 (s, 3H), 1.91 (m, 4H), 1.75 (m, 2H), 1.26 (m, 2H), 1.19 (t, 3H).

F^{19} NMR (376.5 MHz, $CDCl_3$ δ ppm: −80.5 (s).

Preparation of trans-N'-[5-Bromo-6-[[4-(difluoromethoxy)cyclohexyl]amino]-2-methyl-3-pyridyl]-N-ethyl-N-methyl-formamidine

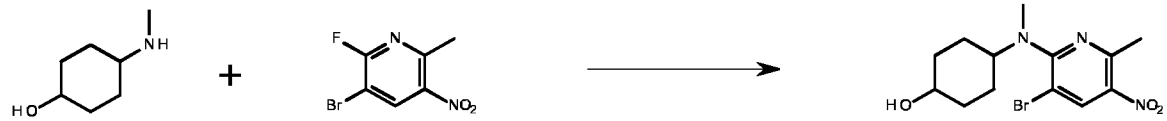


To a dry round bottom flask under argon containing N-ethyl-N-methyl-formamide (1.1 equiv.) dissolved in CH_2Cl_2 (2 mL) was introduced phosphorus oxychloride (1.1 equiv.) by dropwise addition. The mixture was stirred for 1h 30min at rt while becoming a slightly yellow solution. Then trans-3-bromo-N2-[4-(difluoromethoxy)cyclohexyl]-6-methyl-pyridine-2,5-diamine (0.376 g) dissolved in CH_2Cl_2 (3 mL) was introduced and the brown solution was stirred for 1h at rt. Afterwards, the reaction media was basified with aqueous NaOH (2M), extracted with CH_2Cl_2 (2 x 30 mL) and the combined organic phases were dried over Na_2SO_4, filtered, and then concentrated under reduced pressure. Purification of the crude orange residue by combiflash column chromatography over silica gel using a heptane/ethyl acetate solvent gradient (0% − 40% ethyl acetate) afforded the title compound as a yellow oil.

H^1 NMR (400 MHz, $CDCl_3$): δ 7.36 (broad s, 1H), 7.11 (s, 1H), 6.25 (t, 1H), 4.37 (d, 1H), 4.13 (m, 1H), 3.35 (broad s, 1H), 2.99 (s, 3H), 2.35 (s, 3H), 2.22 (m, 2H), 2.05 (m, 2H), 1.63 (m, 2H), 1.26 (m, 2H), 1.17 (t, 3H).

F^{19} NMR (376.5 MHz, $CDCl_3$ δ ppm: −80.6 (s).

Preparation 4-[(3-Bromo-6-methyl-5-nitro-2-pyridyl)-methyl-amino]cyclohexanol

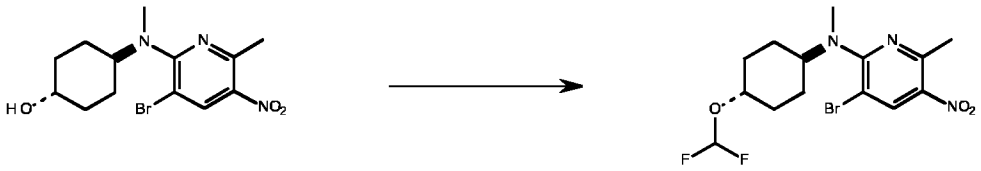


To a flask charged with 3-bromo-2-fluoro-6-methyl-5-nitro-pyridine (0.300 g) and DMSO (5 mL) was added triethylamine (2 equiv.) and 4-(methylamino)cyclohexanol (1.1 equiv.). The brown reaction mixture stirred for 30 min. The reaction solution was poured into 50 mL of water and extracted with ethyl acetate (2 x 100 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtrated, and concentrated to give a brown residue. Purification by combiflash column chromatography over silica gel using a cyclohexane/ethyl acetate solvent gradient (0% − 30% ethyl acetate) afforded the title compound as individual cis- and trans-diastereomers.

^1H NMR (400 MHz, $CDCl_3$, cis-diastereomer): δ 8.48 (s, 1H), 4.28 (m, 1H), 3.62 (m, 1H), 3.08 (s, 3H), 2.73 (s, 3H), 1.88 (m, 2H), 1.71 (m, 3H), 1.28 (m, 2H).

^{1}H NMR (400 MHz, $CDCl_3$, trans-diastereomer): δ 8.48 (s, 1H), 4.27 (m, 1H), 4.09 (m, 1H), 3.08 (s, 3H), 2.73 (s, 3H), 2.05 (m, 2H), 1.92 (m, 3H), 1.68 (t, 3H), 1.42 (t, 3H).

Preparation of trans-3-Bromo-N-[4-(difluoromethoxy)cyclohexyl]-N,6-dimethyl-5-nitro-pyridin-2-amine

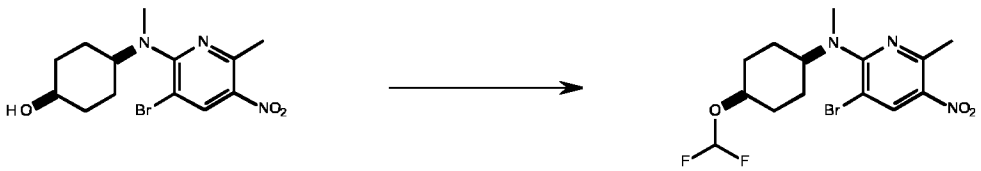


In a 3-neck-flask equipped with a condenser under argon trans-4-[(3-bromo-6-methyl-5-nitro-2-pyridyl)amino]cyclohexanol (0.357 g, co-evaporated twice in dry acetonitrile) and CuI (0.2 equiv) were suspended in acetonitrile (3 mL). The mixture was heated at 45 °C under argon for 5 min and 2,2-difluoro-2-fluorosulfonyl-acetic acid (1.1 equiv.) in acetonitrile (2 mL) was added with a syringe pump over 60 min. The resulting mixture was stirred at 45 °C for 10 min. Upon completion, the reaction was quenched with water (30 mL) and extracted with ethyl acetate (2 x 50 mL). The organics were washed with brine (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude residue by combiflash column chromatography over silica gel using a cyclohexane/ethyl acetate solvent gradient (0% − 20% ethyl acetate) afforded the title compound as a yellow oil.

H^1 NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 6.27 (t, 1H), 4.28 (s, 1H), 4.12 (m, 1H), 3.03 (s, 3H), 2.73 (s, 3H), 2.14 (m, 2H), 1.95 (m, 2H), 1.68 (m, 4H).

F^{19} NMR (376.5 MHz, $CDCl_3$ δ ppm: -80.9 (s).

Preparation of cis-3-Bromo-N-[4-(difluoromethoxy)cyclohexyl]-N,6-dimethyl-5-nitro-pyridin-2-amine

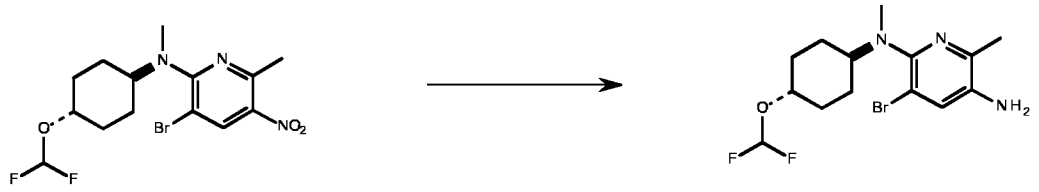


In a 3-neck-flask equipped with a condenser under argon cis-4-[(3-bromo-6-methyl-5-nitro-2-pyridyl)amino]cyclohexanol (0.445 g, co-evaporated twice in dry acetonitrile) and CuI (0.2 equiv) were suspended in acetonitrile (4 mL). The mixture was heated at 45 °C under argon for 5 min and 2,2-difluoro-2-fluorosulfonyl-acetic acid (1.1 equiv.) in acetonitrile (2 mL) was added with a syringe pump over 60 min. The resulting mixture was stirred at 45 °C for 10 min. Upon completion, the reaction was quenched with water (30 mL) and extracted with ethyl acetate (2 x 50 mL). The organics were washed with brine (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude residue by combiflash column chromatography over silica gel using a cyclohexane/ethyl acetate solvent gradient (0% − 20% ethyl acetate) afforded the title compound as a yellow oil.

H^1 NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 6.27 (t, 1H), 4.44 (s, 1H), 4.29 (m, 1H), 3.08 (s, 3H), 2.73 (s, 3H), 2.05 (m, 4H), 1.68 (m, 4H).

F^{19} NMR (376.5 MHz, $CDCl_3$ δ ppm: -80.9 (s).

Preparation of trans-3-Bromo-N2-[4-(difluoromethoxy)cyclohexyl]-N2,6-dimethyl-pyridine-2,5-diamine

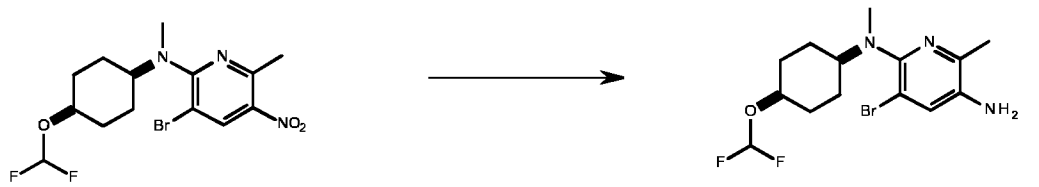


An autoclave charged with trans-3-bromo-N-[4-(difluoromethoxy)cyclohexyl]-N,6-dimethyl-5-nitro-pyridin-2-amine (0.380 g) and 5% Pt-sulfide/C (0.05 equiv., Johnson-Matthey type B109032-5) in THF (5 mL) was charged at rt with hydrogen gas (5 bar) and then heated for 2 h at 40 °C. The crude residue was filtered over celite and the solvent was removed under reduced pressure. Purification of the crude residue by combiflash column chromatography over silica gel using a heptane/ethyl acetate solvent gradient (0% − 20% ethyl acetate) afforded the title compound as an amorphous solid.

H^1 NMR (400 MHz, $CDCl_3$): δ 7.15 (s, 1H), 6.25 (t, 1H), 4.04 (s, 1H), 3.38 (s, 2H), 3.26 (m, 1H), 2.67 (s, 3H), 2.29 (s, 3H), 2.05 (m, 2H), 1.86 (m, 2H), 1.53 (m, 4H).

F^{19} NMR (376.5 MHz, $CDCl_3$ δ ppm: -80.5 (s).

Preparation of cis-3-Bromo-N2-[4-(difluoromethoxy)cyclohexyl]-N2,6-dimethyl-pyridine-2,5-diamine

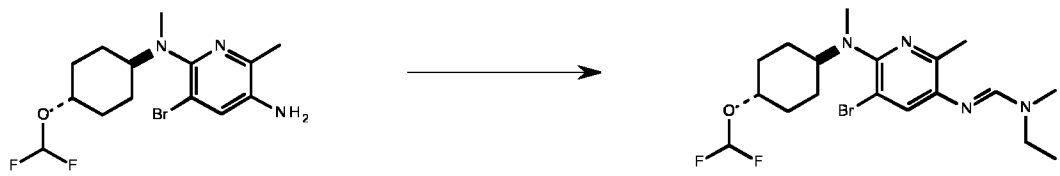


An autoclave containing trans-3-bromo-N-[4-(difluoromethoxy)cyclohexyl]-N,6-dimethyl-5-nitro-pyridin-2-amine (0.470 g) and 5% Pt-sulfide/C (0.05 equiv., Johnson-Matthey type B109032-5) in THF (5 mL) was charged at rt with hydrogen gas (5 bar) and then heated for 2 h at 40°C. The crude residue was filtered over celite and the solvent was removed under reduced pressure. Purification of the crude residue by combiflash column chromatography over silica gel using a heptane/ethyl acetate solvent gradient (0% − 20% ethyl acetate) afforded the title compound as an amorphous solid.

H^1 NMR (400 MHz, $CDCl_3$): δ 7.15 (s, 1H), 6.25 (t, 1H), 4.31 (s, 1H), 3.33 (m, 3H), 2.67 (s, 3H), 2.05 (s, 3H), 1.98 (m, 2H), 1.84 (m, 2H), 1.56 (m, 4H).

F^{19} NMR (376.5 MHz, $CDCl_3$ δ ppm: -80.5 (s).

Preparation of trans-N'-[5-Bromo-6-[[4-(difluoromethoxy)cyclohexyl]-methyl-amino]-2-methyl-3-pyridyl]-N-ethyl-N-methyl-formamidine



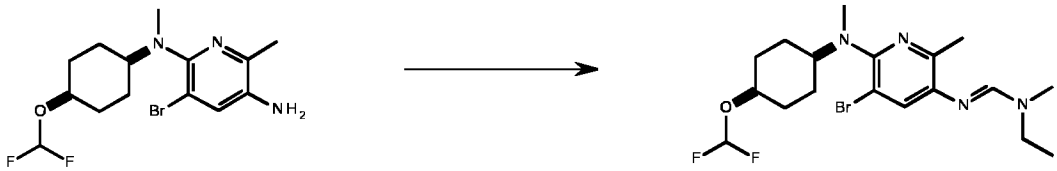
To a dry flask under argon containing N-ethyl-N-methyl-formamide (1.1 equiv.) dissolved in CH_2Cl_2 (3 mL) was introduced phosphorus oxychloride (1.1 equiv.) by dropwise addition. The mixture was stirred for 90 min at rt while becoming a slightly yellow solution. Then trans-3-bromo-N2-[4-(difluoromethoxy)cyclohexyl]-N2,6-dimethyl-pyridine-2,5-diamine (0.254 g) dissolved in CH_2Cl_2 (2 mL) was introduced and the brown solution was stirred for 1 h at rt. Afterwards, the reaction media was

basified with aqueous NaOH (2M), extracted with CH_2Cl_2 (2 x 30 mL) and the combined organic phases were dried over Na_2SO_4, filtered, and then concentrated under reduced pressure. Purification of the crude orange residue by combiflash column chromatography over silica gel using a heptane/ethyl acetate solvent gradient (0% − 40% ethyl acetate) afforded the title compound as a slightly yellow oil.

H^1 NMR (400 MHz, $CDCl_3$): δ 7.41 (broad s, 1H), 7.21 (s, 1H), 6.22 (t, 1H), 4.05 (m, 1H), 3.41 (m, 1H), 2.99 (s, 3H), 2.72 (s, 3H), 2.37 (s, 3H), 2.37 (s, 3H), 2.05 (m, 2H), 1.88 (m, 2H), 1.51 (m, 4H), 1.21 (t, 3H).

F^{19} NMR (376.5 MHz, $CDCl_3$ δ ppm: -80.5 (s).

Preparation of cis-N'-[5-Bromo-6-[[4-(difluoromethoxy)cyclohexyl]-methyl-amino]-2-methyl-3-pyridyl]-N-ethyl-N-methyl-formamidine

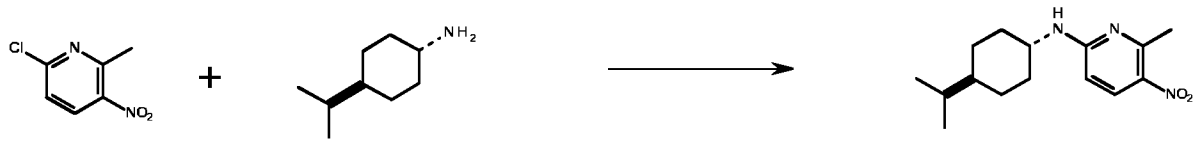


To a dry round bottom flask under argon containing N-ethyl-N-methyl-formamide (1.1 equiv.) dissolved in CH_2Cl_2 (3 mL) was introduced phosphorus oxychloride (1.1 equiv.) by dropwise addition. The mixture was stirred for 90 min at rt while becoming a slightly yellow solution. Then cis-3-bromo-N2-[4-(difluoromethoxy)cyclohexyl]-N2,6-dimethyl-pyridine-2,5-diamine (0.330 g) dissolved in CH_2Cl_2 (2 mL) was introduced and the brown solution was stirred for 1 h at rt. Afterwards, the reaction media was basified with aqueous NaOH (2M), extracted with CH_2Cl_2 (2 x 30mL) and the combined organic phases were dried over Na_2SO_4, filtered, and then concentrated under reduced pressure. Purification of the crude orange residue by combiflash column chromatography over silica gel using a heptane/ethyl acetate solvent gradient (0% − 40% ethyl acetate) afforded the title compound as a slightly yellow oil.

H^1 NMR (400 MHz, $CDCl_3$): δ 7.41 (broad s, 1H), 7.21 (s, 1H), 6.25 (t, 1H), 4.32 (m, 1H), 3.45 (m, 1H), 2.99 (s, 3H), 2.75 (s, 3H), 2.37 (s, 3H), 2.37 (s, 3H), 1.87 (m, 4H), 1.51 (m, 4H), 1.21 (t, 3H).

F^{19} NMR (376.5 MHz, $CDCl_3$ δ ppm: -80.6 (s).

Preparation of trans-N-(4-Isopropylcyclohexyl)-6-methyl-5-nitro-pyridin-2-amine

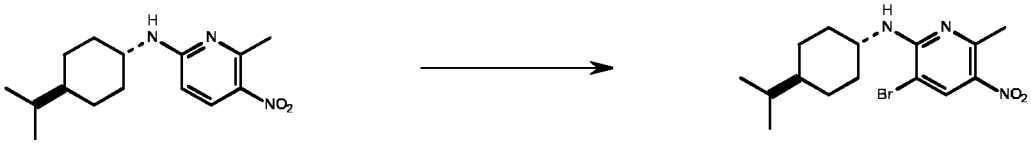


To a dry vial charged with CuI (0.1 equiv.), K_2CO_3 (1.6 equiv.), and trans-4-isopropylcyclohexanamine (1.1 equiv.) under an argon atmosphere was introduced dry DMF (4 mL) followed by cis-dimethylcyclohexane-1,2-diamine (0.25 equiv.) and then 6-chloro-2-methyl-3-nitro-pyridine (0.200 g) as a DMF solution (2 mL). The resultant dark-black-green solution was heated at 100 °C for 1 h after which the reaction solution was poured into an aqueous saturated NH_4Cl solution and extracted with CH_2Cl_2 (2 x 50 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude residue by

combiflash column chromatography over silica gel using a heptane/ethyl acetate solvent gradient (0% − 40% ethyl acetate) afforded the title compound as a viscous yellow oil.

H^1 NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 1H), 6.18 (d, 1H), 5.37 (broad s, 1H), 3.85 (broad s, 1H), 2.68 (s, 3H), 1.78 (m, 2H), 1.55 (m, 4H), 1.21 (m, 3H), 1.06 (m, 1H), 0.84 (d, 6H).

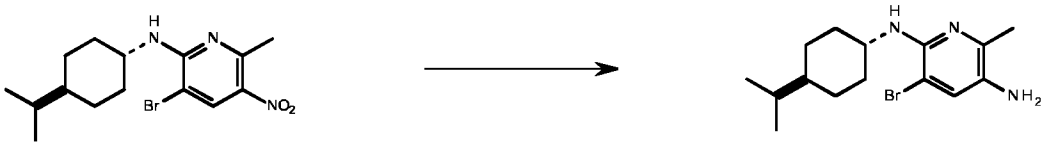
Preparation of trans-3-Bromo-N-(4-isopropylcyclohexyl)-6-methyl-5-nitro-pyridin-2-amine



In a round bottom flask, trans-N-(4-isopropylcyclohexyl)-6-methyl-5-nitro-pyridin-2-amine (0.455 g) was dissolved in acetic acid (10 mL) and then Br_2 (1.2 equiv.) was added slowly so that the reaction temperature could be kept below 25 °C. The orange suspension was stirred at rt for 2 h, becoming a clear solution before ultimately turning into a strong suspension. The reaction was slowly quenched with cold water (15 mL) and the resultant yellow precipitate was filtered, rinsed thoroughly with cold water, and dried at 40 °C under reduced pressure. The title compound was collected as a yellow solid (m.p. 68 – 72 °C) which was used without further purification.

^1H NMR (400 MHz, *d6*-DMSO): δ 8.43 (s, 1H), 6.63 (d, 1H), 4.23 (m, 1H), 2.67 (s, 3H), 1.82 (m, 2H), 1.65 (m, 2H), 1.55 (m, 2H), 1.46 (m, 3H), 1.22 (m, 1H), 0.84 (d, 6H).

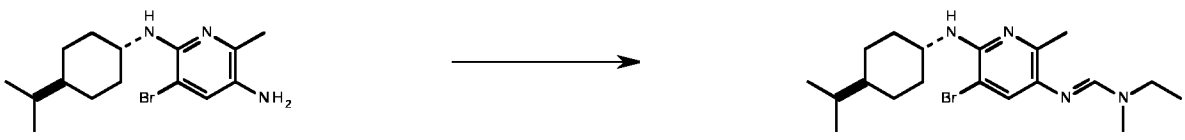
Preparation of 3-Bromo-N2-(4-isopropylcyclohexyl)-6-methyl-pyridine-2,5-diamine



In a flask equipped with an mechanical stirrer, trans-3-bromo-N-(4-isopropylcyclohexyl)-N,6-dimethyl-5-nitro-pyridin-2-amine (0.105 g) was dissolved in ethanol then water (2 mL), NH_4Cl (3 equiv.) and Fe (8 equiv.) were added. This heterogeneous reaction mixture was stirred overnight at 80 °C with vigorous stirring. The reaction solution was then filtered through a thin pad of celite which was washed with ethyl acetate and the filtrate solution was concentrated at reduced pressure. Purification of the crude residue by combiflash column chromatography over silica gel using a heptane/ethyl acetate solvent gradient (0% − 50% ethyl acetate) afforded the title compound as a brown oil.

^1H NMR (400 MHz, $CDCl_3$): δ 7.00 (s, 1H), 4.10 (broad s, 1H), 3.40 (m, 1H), 3.31 (broad s, 1H), 2.19 (s, 3H), 1.75 (m, 2H), 1.30 (m, 3H), 1.20 (m, 4H), 1.03 (m, 2H), 0.79 (d, 6H).

Preparation of trans-N'-[5-Bromo-6-[(4-isopropylcyclohexyl)amino]-2-methyl-3-pyridyl]-N-ethyl-N-methylformamidine

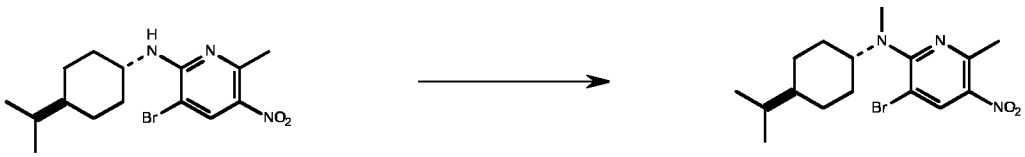


In a flask charged with N-ethyl-N-methyl-formamide (1.1 equiv.) dissolved in CH_2Cl_2 (2 mL) was added phosphorus oxychloride (1.1 equiv.) and the mixture was stirred for 90 min at rt while becoming a slightly yellow solution. Then trans-3-bromo-N2-(4-isopropylcyclohexyl)-6-methyl-pyridine-2,5-diamine

(0.085 g) was added as a solution in CH_2Cl_2 (2 mL) and the resultant brown solution was stirred for 2h at rt. The reaction solution was then quenched with water, basified to alkaline pH with aqueous NaOH (2M), and extracted with CH_2Cl_2 (2 x 50 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the crude brown residue by combiflash column chromatography over silica gel using a heptane/ethyl acetate solvent gradient (0% − 100% ethyl acetate) then a CH_2Cl_2/methanol solvent gradient (0% − 100% methanol) afforded the title compound as a red-brownish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (broad s, 1H), 7.04 (s, 1H), 4.74 (d, 1H), 4.17 (m, 1H), 3.35 (broad s, 2H), 3.27 (s, 3H), 2.27 (s, 3H), 1.67 (m, 2H), 1.60 (broad s, 1H), 1.51 (m, 2H), 1.42 (m, 2H), 1.21 (m, 2H), 1.11 (t, 3H), 1.05 (m, 1H), 0.71 (d, 6H).

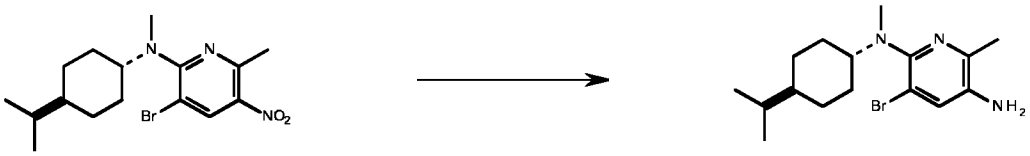
Preparation of 3-Bromo-N-(4-isopropylcyclohexyl)-N,6-dimethyl-5-nitro-pyridin-2-amine



In a round-bottom flask, sodium hydride (1.2 equiv., 60 mass %) was suspended in DMF (3 mL) and trans-3-bromo-N-(4-isopropylcyclohexyl)-6-methyl-5-nitro-pyridin-2-amine (0.432 g) was introduced portion wise over 10 min. The contents reacted for 1 h at rt and to the heterogenous solution iodomethane (2 equiv.) was added dropwise. After stirring for an additional 60 min the reaction solution was poured into brine and then extracted with CH_2Cl_2 (2 x 30 mL). The organic layers were combined and dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the crude residue by combiflash column chromatography over silica gel using a heptane/ethyl acetate solvent gradient (0% − 40% ethyl acetate) afforded the title compound as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (s, 1H), 4.34 (m, 1H), 2.99 (s, 3H), 2.63 (s, 3H), 1.82 (m, 2H), 1.70 (m, 3H), 1.55 (m, 3H), 1.36 (m, 2H), 0.89 (d, 6H).

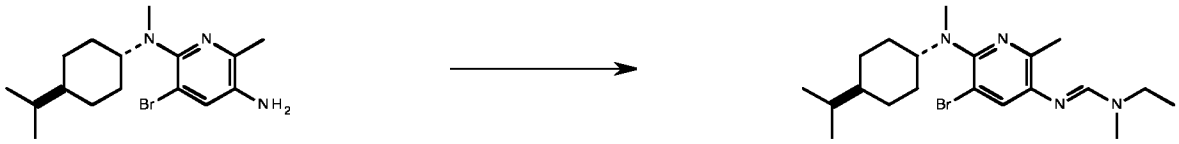
Preparation of trans-3-Bromo-N2-(4-isopropylcyclohexyl)-N2,6-dimethyl-pyridine-2,5-diamine



In a flask equipped with an mechanical stirrer, trans-3-bromo-N-(4-isopropylcyclohexyl)-N,6-dimethyl-5-nitro-pyridin-2-amine (0.419 g) was dissolved in ethanol and water (2 mL), NH_4Cl (3 equiv.) and Fe (8 equiv.) were added. This heterogeneous reaction mixture was stirred overnight at 80 °C with vigorous stirring. The reaction solution was then filtered through a thin pad of celite which was washed with ethyl acetate and the filtrate solution was concentrated at reduced pressure. Purification of the crude residue by combiflash column chromatography over silica gel using a heptane/ethyl acetate solvent gradient (0% − 50% ethyl acetate) afforded the title compound as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (s, 1H), 3.39 (m, 1H), 3.30 (broad s, 2H), 2.54 (s, 3H), 2.41 (s, 3H), 1.70 (m, 2H), 1.51 (m, 3H), 1.33 (m, 1H), 1.20 (m, 3H), 1.04 (m, 1H), 0.70 (d, 6H).

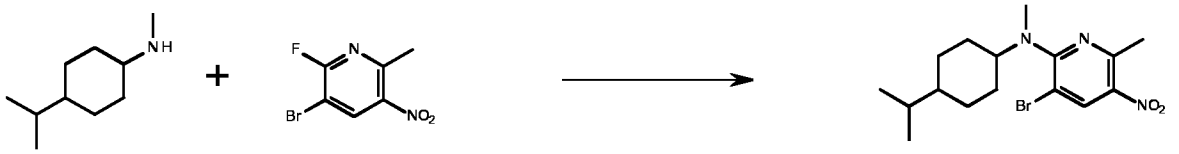
Preparation of trans-N'-[5-Bromo-6-[(4-isopropylcyclohexyl)-methyl-amino]-2-methyl-3-pyridyl]-N-ethyl-N-methyl-formamidine



To a flask charged with N-ethyl-N-methyl-formamide (1.1 equiv.) dissolved in CH_2Cl_2 (2 mL) was added phosphorus oxychloride (1.1 equiv.) and the mixture was stirred for 90 min at rt while becoming a slightly yellow solution. Then trans-3-bromo-N2-(4-isopropylcyclohexyl)-N2,6-dimethyl-pyridine-2,5-diamine (0.290 g) was added as a solution in CH_2Cl_2 (1 mL) and the resultant brown solution was stirred for 2 h at rt. The reaction solution was then quenched with water, basified to alkaline pH with 2 M aqueous NaOH, and extracted with CH_2Cl_2 (2 x 50 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the crude brown residue by combiflash column chromatography over silica gel using a heptane/ethyl acetate solvent gradient (0% − 100% ethyl acetate) then a CH_2Cl_2/methanol solvent gradient (0% − 100% methanol) afforded the title compound as a red-brownish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (broad s, 1H), 7.15 (s, 1H), 3.45 (m, 1H), 3.25 (broad s, 2H), 2.80 (s, 3H), 2.59 (s, 3H), 2.30 (s, 3H), 1.70 (m, 2H), 1.52 (m, 3H), 1.35 (m, 2H), 1.22 (m, 2H), 1.15 (t, 3H), 1.05 (m, 1H), 0.81 (d, 6H).

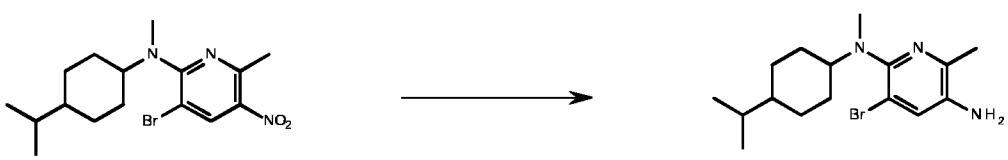
Preparation of 3-Bromo-N-(4-isopropylcyclohexyl)-N,6-dimethyl-5-nitro-pyridin-2-amine



To a flask charged with 3-bromo-2-fluoro-6-methyl-5-nitro-pyridine (1.9 g) and DMSO (5 mL) was added triethylamine (2 equiv.) and 4-isopropylcyclohexanol (1.1 equiv., 50 mass %) and the brown reaction mixture stirred for 30 min. The reaction solution was poured into water (50 mL) and extracted with ethyl acetate (2 x 100 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated to a brown residue. Purification by combiflash column chromatography over silica gel using a cyclohexane/ethyl acetate solvent gradient (0% − 100% ethyl acetate) afforded the title compound as an amorphous yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (s, 1H), 4.21 (m, 1H), 3.05 (s, 3H), 2.73 (s, 3H), 1.85 (m, 2H), 1.60 (m, 3H), 1.45 (m, 3H), 1.14 (m, 2H), 0.89 (m, 6H).

Preparation of 3-Bromo-N2-(4-isopropylcyclohexyl)-N2,6-dimethyl-pyridine-2,5-diamine

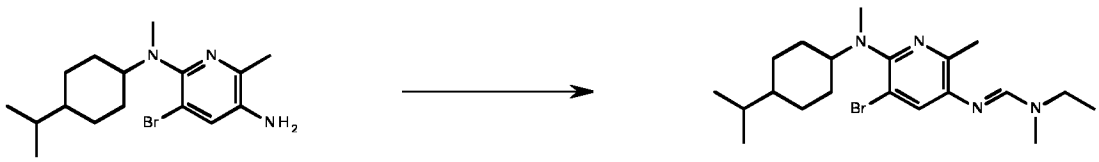


An autoclave containing 3-bromo-N-[4-(difluoromethoxy)cyclohexyl]-N,6-dimethyl-5-nitro-pyridin-2-amine (1.9 g) and 5% Pt-sulfide/C (0.05 equiv., Johnson-Matthey type B109032-5) in THF (26 mL)

was charged at rt with hydrogen gas (5 bar) and then heated for 2 h at 40 °C. The crude residue was filtered over celite and the solvent was removed under reduced pressure. Purification by combiflash column chromatography over silica gel using a heptane/ethyl acetate solvent gradient (0% − 40% ethyl acetate) afforded the title compound as a brownish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (s, 1H), 3.45 (m, 2H), 3.21 (m, 1H), 2.71 (s, 3H), 2.29 (s, 3H), 1.75 (m, 4H), 1.60 (m, 1H), 1.45 (m, 4H), 1.20 (m, 1H), 0.70 (d, 6H).

Preparation of N'-[5-Bromo-6-[(4-isopropylcyclohexyl)-methyl-amino]-2-methyl-3-pyridyl]-N-ethyl-N-methyl-formamidine



To a flask charged with N-ethyl-N-methyl-formamide (1.1 equiv.) dissolved in CH_2Cl_2 (2 mL) was added phosphorus oxychloride (1.1 equiv.) and the mixture was stirred for 90 min at rt while becoming a slightly yellow solution. Then 3-bromo-N2-(4-isopropylcyclohexyl)-N2,6-dimethyl-pyridine-2,5-diamine (1.38 g) was added as a solution in CH_2Cl_2 (3 mL) and the resultant brown solution was stirred for 2h at rt. The reaction solution was then quenched with water, basified to alkaline pH with 2M and extracted with CH_2Cl_2 (2 x 50 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the crude brown residue by combiflash column chromatography over silica gel using a heptane/ethyl acetate solvent gradient (0% − 40% ethyl acetate) afforded the title compound as a red-brownish oil. Separation of the individual diastereomers was perfomed by preparative reverse phase chromatography.

^{1}H NMR (400 MHz, $CDCl_3$, trans-diastereomer): δ 7.36 (broad s, 1H), 7.15 (s, 1H), 3.45 (m, 1H), 3.25 (broad s, 2H), 2.80 (s, 3H), 2.59 (s, 3H), 2.30 (s, 3H), 1.70 (m, 2H), 1.52 (m, 3H), 1.35 (m, 2H), 1.22 (m, 2H), 1.15 (t, 3H), 1.05 (m, 1H), 0.81 (d, 6H).

^{1}H NMR (400 MHz, $CDCl_3$, cis-diastereomer): δ 7.35 (broad s, 1H), 7.15 (s, 1H), 3.45 (m, 1H), 3.25 (broad s, 2H), 2.92 (s, 3H), 2.60 (s, 3H), 2.31 (s, 3H), 1.70 (m, 2H), 1.55 (m, 3H), 1.33 (m, 2H), 1.25 (m, 2H), 1.14 (t, 3H), 1.05 (m, 1H), 0.79 (d, 6H).

Table 45

The compounds of formula I in Table 45 were prepared using techniques analogous to those described above and additional techniques known to someone skilled in the art.

For each of compounds I-01 to I-72, R^1 is methyl and R^2 is ethyl. R^4-R^7 are as defined in Table 45.

Comp. No.	**R^4**	**R^5**	**R^6**	**R^7**	**Method**
I-001	CH_3	Br	CH_3	2-$CH_3C_6H_4CH_2$	R_t = 0.82 min.; MS : m/z = 389, 391 $(M+H)^+$

Comp. No.	R^4	R^5	R^6	R^7	Method
I-002	CH_3	H	CH_3	2-$CH_3C_6H_4CH_2$	R_t= 0.72 min.; MS : m/z = 311 $(M+H)^+$
I-003	CH_3	Cl	CH_3	2-$CH_3C_6H_4CH_2$	R_t = 0.89 min.; MS : m/z = 345 $(M+H)^+$
I-004	CH_3	Cl	H	2-$CH_3C_6H_4CH_2$	R_t = 0.75 min.; MS : m/z = 331 $(M+H)^+$
I-005	CH_3	CN	CH_3	2-$CH_3C_6H_4CH_2$	R_t = 0.82 min.; MS : m/z = 336 $(M+H)^+$
I-006	CH_3	CH_3	CH_3	2-$CH_3C_6H_4CH_2$	R_t = 0.84 min.; MS : m/z = 325 $(M+H)^+$
I-007	CH_3	CH_2CH_3	CH_3	2-$CH_3C_6H_4CH_2$	R_t = 0.80 min.; MS : m/z = 339 $(M+H)^+$
I-008	CH_3	CHO	CH_3	2-$CH_3C_6H_4CH_2$	R_t = 0.76 min.; MS : m/z = 339 $(M+H)^+$
I-009	CH_3	CO_2CH_3	H	2-$CH_3C_6H_4CH_2$	R_t = 0.79 min.; MS : m/z = 355 $(M+H)^+$
I-010	CH_3	Br	CH_3	2,5-F-$C_6H_4CH_2$	R_t = 0.88 min.; MS : m/z = 411, 413 $(M+H)^+$
I-011	CH_3	I	CH_3	2-$CH_3C_6H_4CH_2$	R_t = 0.88 min.; MS : m/z = 437 $(M+H)^+$
I-012	CH_3	Br	$CH(CH_3)_2$	2-$CH_3C_6H_4CH_2$	R_t = 1.00 min.; MS : m/z = 417, 419 $(M+H)^+$
I-013	CH_3	Br	CH_2CH_3	2-$CH_3C_6H_4CH_2$	R_t = 0.89 min.; MS : m/z = 403, 405 $(M+H)^+$
I-014	CH_3	Br	CHO	2-$CH_3C_6H_4CH_2$	R_t = 0.73 min.; MS : m/z = 401, 403 $(M+H)^+$
I-015	CH_3	Br	C(O)Me	2-$CH_3C_6H_4CH_2$	R_t = 0.75 min.; MS : m/z = 418, 420 $(M+H)^+$
I-016	CH_3	Br	CH_3	3,5-F-$C_6H_4CH(CH_3)$	R_t = 0.88 min.; MS : m/z = 426, 428 $(M+H)^+$
I-017	CH_3	H	CH_3	3,5-F-$C_6H_4CH(CH_3)$	R_t = 0.85 min.; MS : m/z = 347 $(M+H)^+$
I-018	CH_3	H	H	3,5-F-$C_6H_4CH(CH_3)$	R_t = 0.81 min.; MS : m/z = 333 $(M+H)^+$
I-019	CH_3	Br	CH_3	$PhCH(CH_3)$	R_t = 0.89 min.; MS : m/z = 390, 392 $(M+H)^+$
I-020	CH_3	Br	H	PhCH(Et)	R_t = 0.85 min.; MS : m/z = 325, 327 $(M+H)^+$
I-021	CH_3	Br	CH_3	4-$OCHF_2C_6H_4CH_2$	R_t = 0.77 min.; MS : m/z = 442, 444 $(M+H)^+$
I-022	CH_3	Br	CH_3	3-$OCHF_2C_6H_4CH_2$	R_t = 0.82 min.; MS : m/z = 442, 444 $(M+H)^+$
I-023	CH_3	Br	CH_3	4-$OCHF_2C_6H_4CH(CH_3)$	R_t = 0.83 min.; MS : m/z = 456, 458 $(M+H)^+$
I-024	CH_3	Br	CH_3	3-$OCHF_2C_6H_4CH_2(CH_3)$	H^1 NMR – see below

Comp. No.	R^4	R^5	R^6	R^7	Method
I-025	CH_3	Br	CH_3	(1,3-benzodiox-5-yl)CH_2	R_t = 0.74 min.; MS : m/z = 420, 422 $(M+H)^+$
I-026	CH_3	Br	CH_3	$(CH_3)_2CH(CH_2)_3CH_2$	R_t = 0.97 min.; MS : m/z = 384, 386 $(M+H)^+$
I-027	CH_3	Br	CH_3	$Ph(CH_2)_2CH_2$	R_t = 0.90 min.; MS : m/z = 403, 405 $(M+H)^+$
I-028	CH_3	Br	H	4-$(CH_3)_2$CH-cyclohexyl	R_t = 1.02 min.; MS : m/z = 394, 396 $(M+H)^+$
I-029	CH_3	Br	CH_3	4-$(CH_3)_2$CH-cyclohexyl	R_t = 1.01 min.; MS : m/z = 408, 410 $(M+H)^+$
I-030	CH_3	Br	CH_3	indan-2-yl	R_t = 0.92 min.; MS : m/z = 402, 404 $(M+H)^+$
I-031	CH_3	Br	CH_3	tetralin-2-yl	R_t = 0.93 min.; MS : m/z = 415, 417 $(M+H)^+$
I-032	CH_3	Br	CH_3	CH_3O-N-piperidin-4-yl	R_t = 0.67 min.; MS : m/z = 399, 401 $(M+H)^+$
I-033	CH_3	Br	CH_3	$CH_3C(O)$-N-piperidin-4-yl	R_t = 0.60 min.; MS : m/z = 411, 413 $(M+H)^+$
I-034	CH_3	Br	H	*t*-$BuCO_2$-N-piperidin-4-yl	R_t = 0.86 min.; MS : m/z = 455, 457 $(M+H)^+$
I-035	CH_3	Br	H	$PhCH_2$-N-piperidin-4-yl	R_t = 0.52 min.; MS : m/z = 445, 447 $(M+H)^+$
I-036	CH_3	Br	H	*i*-Pr(Me)N-SO_2-N-piperidin-4-yl	R_t = 0.75 min.; MS : m/z = 490, 492 $(M+H)^+$
I-037	CH_3	Br	H	*n*-Pr(Me)N-SO_2-N- piperidin-4-yl	R_t = 0.81 min.; MS : m/z = 490, 492 $(M+H)^+$
I-038	CH_3	Br	CH_3	*n*-Pr(Me)N-SO_2-N- piperidin-4-yl	R_t = 0.74 min.; MS : m/z = 475, 477 $(M+H)^+$
I-039	CH_3	Br	H	Et(Me)N-SO_2-N- piperidin-4-yl	R_t = 0.79 min.; MS : m/z = 524, 526 $(M+H)^+$
I-040	CH_3	Br	H	Ph(Me)N-SO_2-N- piperidin-4-yl	R_t = 0.83 min.; MS : m/z = 503, 505 $(M+H)^+$
I-041	CH_3	Br	CH_3	pyran-4-yl	R_t = 0.63 min.; MS : m/z = 370, 372 $(M+H)^+$
I-042	CH_3	Br	H	pyran-4-yl	R_t = 0.61 min.; MS : m/z = 356, 358 $(M+H)^+$
I-043	CH_3	Br	CH_3	pyran-3-yl	R_t = 0.83 min.; MS : m/z = 455, 457 $(M+H)^+$

Comp. No.	R^4	R^5	R^6	R^7	Method
I-044	CH_3	Br	H	pyran-3-yl	R_t = 0.64 min.; MS : m/z = 384, 386 $(M+H)^+$
I-045	CH_3	Br	CH_3CH_2	pyran-3-yl	R_t = 0.69 min.; MS : m/z = 384, 386 $(M+H)^+$
I-046	CH_3	Br	CH_3	$(CH_3)_3CO_2$-N-pyrolidin-2-yl	R_t = 0.83 min.; MS : m/z = 455, 457 $(M+H)^+$
I-047	CH_3	Br	H	$(CH_3)_3CO_2$-pyrolidin-2-yl	R_t = 0.85 min.; MS : m/z = 442, 444 $(M+H)^+$
I-048	CH_3	Br	CH_3	(tetrahydrofuran-3-yl)CH_2	R_t = 0.63 min.; MS : m/z = 370, 372 $(M+H)^+$
I-049	CH_3	Br	CH_3	(2-methylthiazol-4-yl)CH_2	R_t = 0.69 min.; MS : m/z = 397, 399 $(M+H)^+$
I-050	CH_3	Br	CH_3	4-$FC_6H_4OCH_2CH_2$	R_t = 0.82 min.; MS : m/z = 424, 426 $(M+H)^+$
I-051	CH_3	Br	CH_3	2,6-$CH_3C_6H_3OCH_2CH(CH_3)$	R_t = 0.98 min.; MS : m/z = 448, 448 $(M+H)^+$
I-052	CH_3	Br	CH_3	$C_6H_5OCH_2CH(CH_3)$	R_t = 0.86 min.; MS : m/z = 420, 422 $(M+H)^+$
I-053	CH_3	Br	CH_3CH_2	$C_6H_5OCH_2CH(CH_3)$	R_t = 1.01 min.; MS : m/z = 433, 435 $(M+H)^+$
I-054	CH_3	H	H	3-$ClC_6H_4CH_2S(O)_2$	H^1 NMR – see below
I-055	CH_3	H	CH_3	3-$ClC_6H_4CH_2S(O)_2$	R_t = 0.73 min.; MS : m/z = 395 $(M+H)^+$
I-056	CH_3	Br	CH_3	3-$ClC_6H_4CH_2S(O)_2$	R_t = 0.85 min.; MS : m/z = 473, 475 $(M+H)^+$
I-057	CH_3	H	CH_3	2-$CF_3C_6H_4S(O)_2$	R_t = 0.75 min.; MS : m/z = 415 $(M+H)^+$
I-058	CH_3	H	H	2-$CF_3C_6H_4S(O)_2$	R_t = 0.60 min.; MS : m/z = 351 $(M+H)^+$
I-059	CH_3	H	H	2-$CH_3C_6H_4C(O)$	R_t = 0.61 min.; MS : m/z = 311 $(M+H)^+$
I-060	CH_3	Br	H	2-$CH_3C_6H_4C(O)$	R_t = 0.63 min.; MS : m/z = 389, 391 $(M+H)^+$
I-061	CH_3	H	H	2-$FC_6H_4C(O)$	R_t = 0.58 min.; MS : m/z = 315 $(M+H)^+$
I-062	CH_3	Br	H	2-$FC_6H_4C(O)$	R_t = 0.60 min.; MS : m/z = 393, 395 $(M+H)^+$
I-063	CH_3	H	CH_3	$C_6H_5C(O)$	R_t = 0.39 min.; MS : m/z = 311 $(M+H)^+$
I-064	CH_3	Br	CH_3	$C_6H_5CH_2C(O)$	R_t = 0.69 min.; MS : m/z = 403, 405 $(M+H)^+$
I-065	CH_3	H	CH_3	$C_6H_5CH_2C(O)$	R_t = 0.52 min.; MS : m/z = 325 $(M+H)^+$

Comp. No.	R^4	R^5	R^6	R^7	Method
I-066	CH_3	H	H	$C_6H_5CH(CH_3)C(O)$	H^1 NMR – see below
I-067	CH_3	Br	H	2-FC_6H_4	R_t = 0.76 min.; MS : m/z = 367, 369 $(M+H)^+$
I-068	CH_3	Br	H	2-$CH_3C_6H_4$	Rt = 0.58 min. ; MS : m/z = 362, 364 $(M+H)^+$
I-069	CH_3	Br	H	4-$OCHF_2C_6H_4$	R_t = 0.75 min.; MS : m/z = 414, 416 $(M+H)^+$
I-070	CH_3	Br	H	3-$OCHF_2C_6H_4$	R_t = 0.76 min.; MS : m/z = 414, 416 $(M+H)^+$
I-071	CH_3	Br	H	3,5-$CH_3C_6H_3OCH_2CH_2$	R_t = 0.89 min.; MS : m/z = 433, 435 $(M+H)^+$
I-072	CH_3	Br	CH_3	3,5-$CH_3C_6H_3OCH_2CH(CH_3)$	R_t = 0.96 min.; MS : m/z = 448, 450 $(M+H)^+$
I-073	CH_3	Br	CH_3	4-$OCHF_2$-cyclohexyl	R_t = 0.88 min.; MS : m/z = 433, 435 $(M+H)^+$
I-074	CH_3	Br	CH_3	cis-4-$OCHF_2$-cyclohexyl	R_t = 0.87 min.; MS : m/z = 433, 435 $(M+H)^+$
I-075	CH_3	Br	CH_3	trans-4-$OCHF_2$-cyclohexyl	R_t = 0.88 min.; MS : m/z = 433, 435 $(M+H)^+$
I-076	CH_3	Br	H	4-$OCHF_2$-cyclohexyl	R_t = 0.91 min.; MS : m/z = 419, 421 $(M+H)^+$
I-077	CH_3	Br	H	cis-4-$OCHF_2$-cyclohexyl	R_t = 0.91 min.; MS : m/z = 419, 421 $(M+H)^+$
I-078	CH_3	Br	H	trans-4-$OCHF_2$-cyclohexyl	R_t = 0.81 min.; MS : m/z = 419, 421 $(M+H)^+$
I-079	CH_3	Br	H	cis-4-$(CH_3)_2CH$-cyclohexyl	R_t = 1.02 min.; MS : m/z = 394, 396 $(M+H)^+$
I-080	CH_3	Br	H	trans-4-$(CH_3)_2CH$-cyclohexyl	R_t = 1.02 min.; MS : m/z = 394, 396 $(M+H)^+$
I-081	CH_3	Br	CH_3	cis-4-$(CH_3)_2CH$-cyclohexyl	R_t = 1.01 min.; MS : m/z = 408, 410 $(M+H)^+$
I-082	CH_3	Br	CH_3	trans-4-$(CH_3)_2CH$-cyclohexyl	R_t = 1.01 min.; MS : m/z = 408, 410 $(M+H)^+$

Methods Used

Mass spectra were recorded on a Mass Spectrometer from Waters (SQD or ZQ Single quadrupole mass spectrometer) equipped with an electrospray source (Polarity: positive or negative ions, Capillary: 3.00 kV, Cone range: 30-60 V, Extractor: 2.00 V, Source Temperature: 150°C,

Desolvation Temperature: 350°C, Cone Gas Flow: 0 L/Hr, Desolvation Gas Flow: 650 L/Hr, Mass range: 100 to 900 Da) and an Acquity UPLC from Waters: Binary pump, heated column compartment and diode-array detector. Solvent degasser, binary pump, heated column compartment and diode-array detector. Column: Waters UPLC HSS T3 , 1.8 µm, 30 x 2.1 mm, Temp: 60 °C, DAD Wavelength range (nm): 210 to 500, Solvent Gradient: A = water + 5% MeOH + 0.05 % HCOOH, B= Acetonitrile + 0.05 % HCOOH: gradient: gradient: 0 min 0% B, 100%A; 1.2-1.5min 100% B; Flow (ml/min) 0.85

NMR data (H^1 NMR; 400 MHz, $CDCl_3$)

I-024: δ 7.36 (brs, 1H), 7.19 (m, 4H), 6.85 (m, 1H), 6.42 (t, 1H), 4.75 (t, 1H), 3.25 (m, 2H), 2.90 (s, 3H), 2.50 (s, 3H), 2.25 (s, 3H), 1.30 (d, 3H), 1.15 (t, 3H)

I-054: δ 7.45 (brs, 1H), 7.40 (s, 1H), 7.25 (m, 5H), 6.80 (d, 1H), 4.40 (s, 2H), 3.50 (s, 3H), 3.05 (s, 3H), 2.25 (m, 3H), 1.25 (m, 3H)

I-066: δ 7.45 (brs, 1H), 7.40 (s, 1H), 7.25 (m, 5H), 6.80 (d, 1H), 4.40 (s, 2H), 3.50 (s, 3H), 3.05 (s, 3H), 2.25 (m, 3H), 1.25 (m, 3H)

Biological examples

Blumeria graminis* f. sp. *tritici *(Erysiphe graminis* f. sp. *tritici)* / wheat / leaf disc preventative (Powdery mildew on wheat)

Wheat leaf segments cv. Kanzler were placed on agar in a multiwell plate (24-well format) and sprayed with the formulated test compound diluted in water. The leaf disks were inoculated by shaking powdery mildew infected plants above the test plates 1 day after application. The inoculated leaf disks were incubated at 20 °C and 60% rh under a light regime of 24 h darkness followed by 12 h light / 12 h darkness in a climate chamber and the activity of a compound was assessed as percent disease control compared to untreated when an appropriate level of disease damage appears on untreated check leaf segments (6 - 8 days after application).

The following compounds gave at 200 ppm give at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development:

I-001, I-002, I-003, I-004, I-005, I-006, I-007, I-008, I-010, I-011, I-013, I-014, I-016, I-019, I-020, I-021, I-022, I-023, I-024, I-025, I-026, I-027, I-028, I-029, I-030, I-031, I-032, I-036, I-037, I-038, I-039, I-040, I-041, I-042, I-043, I-044, I-045, I-046, I-048, I-049, I-050, I-051, I-052, I-053, I-055, I-056, I-063, I-066, I-071, I-072.

Puccinia recondita* f. sp. *tritici / wheat / leaf disc preventative (brown rust)

Wheat leaf segments cv. Kanzler were placed on agar in multiwell plates (24-well format) and sprayed with the formulated test compound diluted in water. The leaf disks were inoculated with a spore suspension of the fungus 1 day after application. The inoculated leaf segments were incubated at 19 °C and 75% rh under a light regime of 12 h light / 12 h darkness in a climate cabinet and the activity of a compound was assessed as percent disease control compared to untreated when an appropriate level of disease damage appears in untreated check leaf segments (7 – 9 days after application).

The following compounds gave at 200 ppm gave at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development:

I-001, II-003, I-004, I-005, I-006, I-007, I-008, I-010, I-011, I-013, I-014, I-016, I-019, I-021, I-022, I-023, I-024, I-025, I-027, I-028, I-029, I-030, I-031, I-032, I-045, I-046, I-049, I-050, I-052, I-055, I-066.

Puccinia recondita* f. sp. *tritici / wheat / leaf disc curative (Brown rust)

Wheat leaf segments cv. Kanzler are placed on agar in multiwell plates (24-well format). The leaf segments are inoculated with a spore suspension of the fungus. Plates were stored in darkness at 19°C and 75% rh. The formulated test compound diluted in water was applied 1 day after inoculation. The leaf segments were incubated at 19 °C and 75% rh under a light regime of 12 h light / 12 h darkness in a climate cabinet and the activity of a compound was assessed as percent disease control compared to untreated when an appropriate level of disease damage appears in untreated check leaf segments (6 – 8 days after application).

The following compounds gave at 200 ppm gaive at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development:

I-001, I-002, I-003, I-004, I-005, I-006, I-007, I-008, I-010, I-011, I-012, I-013, I-014, I-016, I I-019, I-021, I-022, I-023, I-024, I-025, I-026, I-027, I-028, I-029, I-030, I-031, I-032, I-033, I-034, I-038, I-039, I-040, I-041, I-042, I-043, I-044, I-045, I-046, I-048, I-049, I-050, I-052, I-053, I-055, I-057, I-067, I-068, I-069, I-070, I-072.

Phakopsora pachyrhizi / soybean / leaf disk preventative (soybean rust)

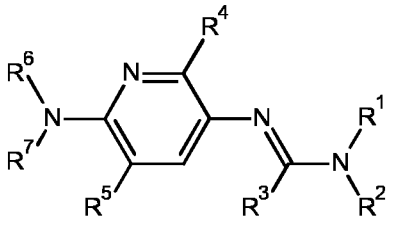
Four-week old soybean plants are sprayed in a spray chamber with the formulated test compound diluted in water. Leaf disks are cut from treated plants and placed on agar into 24-well plates one day after application. Leaf disks are inoculated by spraying them with a spore suspension on their lower leaf surface. After an incubation period in a climate cabinet of 24-36 hours in darkness at 20 °C and 75% rh, the leaf disks are then kept at 20 °C with 12 h light/day and 75% rh. The percentage leaf disk area covered by disease is assessed when an appropriate level of disease appears on untreated check plants (12 – 14 days after application).

The following compounds gave at 200 ppm gave at least 80% disease control in this test when compared to untreated control leaf disks under the same conditions, which show extensive disease development:

I-010, I-011, I-016, I-019, I-021, I-022, I-023, I-024, I-028, I-029, I-030, I-031, I-044, I-045, I-050, I-067, I-071.

WHAT IS CLAIMED IS:

1. A compound of formula I


(I),

wherein

R^1 and R^2 independently represent hydrogen or C_1-C_4 alkyl or C_3-C_6 cycloalkyl;

R^3 represents hydrogen;

R^4 represents C_1-C_4 alkyl, C_1-C_4 haloalkyl or C_3-C_6 cycloalkyl;

R^5 represents hydrogen, halogen, cyano, hydroxy, formyl, carboxy, amino, C_1-C_4 alkyl, C_2-C_4 alkenyl, C_2-C_4 alkynl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, C_3-C_6 cycloalkyl, C_2-C_4 alkylcarbonyl, C_2-C_4 alkoxycarbonyl, C_1-C_4 alkylthio, C_1-C_4 alkylsulfinyl, C_1-C_4 alkylsulfonyl, -$N(R^8)(R^9)$, -$C(=O)N(R^8)(R^9)$ or -$S(=O)_2N(R^8)(R^9)$; or

R^5 represents a 5- or 6-member heterocycle containing 1-4 nitrogen atoms which may be optionally substituted by one or more groups selected from the group consisting of methyl, halogen and cyano;

R^6 represents hydrogen, C_1-C_4 alkyl, C_1-C_4 alkoxycarbonyl, C_1-C_4 alkylcarbonyl or formyl;

R^7 represents G^1, G^2-G^3-, G^4, G^5-G^3-, G^6, G^7-G^3-, G^8, G^9-G^3-, G^{10}, G^{11}, G^{12} or G^{13};

G^1 and G^2 represent a eight- to ten-membered fused bicyclic ring system which can be aromatic, partially saturated or fully saturated and can contain 1 to 4 hetero atoms selected from the group consisting of N, $N(R^{10})$, O and S, it not being possible for each ring system to contain -O-O-, -S-S- and –O-S- fragments, and it being possible for the eight- to ten-membered ring system to be optionally substituted by one or more groups independently selected from the group consisting of hydrogen, halogen, cyano, nitro, hydroxy, mercapto, azido, formyl, carboxy, S(=O), $S(=O)_2$, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, C_2-C_4 alkylcarbonyl, C_1-C_4 haloalkoxy, -$N(R^8)(R^9)$, -$C(=O)$ $N(R^8)(R^9)$ and -$S(=O)_2N(R^8)(R^9)$;

G^3 represents methylene or methylene optionally substituted by one or two groups independently selected from halogen, C_1-C_4-alkyl, C_1-C_4-haloalkyl, CN, C_1-C_4-alkoxy and C_1-C_4-haloalkoxy;

G^4 and G^5 represent a C_5-C_6 aromatic monocyclic system which contains 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, it not being possible for each ring system to contain -O-O-, -S-S- and –O-S- fragments, and is optionally substituted by one or more groups independently selected from hydrogen, halogen, CN, OH, CHO, COOH, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl, C_1-C_4 haloalkoxy, C_3-C_6 cycloalkyl, C_1-C_4 alkoxycarbonyl, $C(=O)N(R^8)(R^9)$ and -$S(=O)_2N(R^8)(R^9)$;

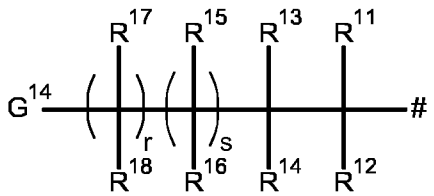
G^6 and G^7 represent phenyl optionally substituted by one or more groups independently selected from hydrogen, halogen, CN, NO_2, OH, SH, CHO, COOH, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl,

C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl, C_2-C_4 alkenyl, C_2-C_4 haloalkenyl, C_1-C_4 haloalkoxy, C_1-C_4 alkylcarbonyl, -C(=O)N(R^8)(R^9), -C(=S)N(R^8)(R^9); and -S(=O)$_2$N(R^8)(R^9);

G^8 and G^9 represents a five- or six-membered saturated monocyclic system which contains 1 or 2 members selected from the group consisting of N, N(R^{10}), O and S, it not being possible for each ring system to contain -O-O-, -S-S- and –O-S- fragments, and it being possible for the five- to six-membered ring system to be optionally substituted by one or more groups independently selected from the group consisting of hydrogen, halogen, CN, NO_2, OH, SH, CHO, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_3-C_6 cycloalkyl, C_2-C_6 alkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_1-C_4 alkoxy, C_1-C_4 haloalkoxy, C_3-C_6 alkynyloxy, =O, S(=O), S(=O)$_2$, and -N(R^8)(R^9);

G^{10} represents a C_5-C_7 monocarbocyclic system optionally substituted by one or more groups independently selected from hydrogen, halogen, CN, OH, CHO, COOH, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl, C_1-C_4 haloalkoxy, C_3-C_6 cycloalkyl, C_1-C_4 alkylcarbonyl, C(=O)N(R^8)(R^9), and -S(=O)$_2$N(R^8)(R^9);

G^{11} represents



;

G^{12} represents C_4-C_7-alkylsulfonyl, C_4-C_7 alkenylsulfonyl, C_4-C_7 alkynylsulfonyl, C_4-C_7 cycloalkylsulfonyl, benzylsulfonyl or phenylsulfonyl, wherein the benzylsulfonyl and the phenylsulfonyl are optionally substituted by one or more groups independently selected from the group consisting of halogen, CN, OH, CHO, COOH, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy and C_1-C_4 haloalkoxy;

G^{13} represents C_4-C_7alkylcarbonyl, C_4-C_7 alkenylcarbonyl, C_4-C_7 alkynylcarbonyl, C_4-C_7 cycloalkylcarbonyl, benzylcarbonyl or phenylcarbonyl wherein the benzylcarbonyl and phenylcarbonyl can be optionally substituted by one or more substituents independently selected from the group consisting of halogen, CN, OH, SH, CHO, COOH, C_1-C_4 alkyl, and C_1-C_4haloalkyl;

G^{14} represents hydrogen, C_3-C_6 cycloalkyl, G^2, G^4, G^5 phenoxy or benzyloxy wherein the phenoxy or benzyloxy may be optionally substituted by one or more groups independently selected from the group consisting of halogen, cyano, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy and C_1-C_4 haloalkyl;

R^8 and R^9, independently of each other represent hydrogen, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl, phenyl or benzyl; or

R^8 and R^9 together with their interconnecting nitrogen atom represent pyrazolino, pyrazolidino, pyrrolino, pyrrolidino, imidazolino, imidazolidino, morpholino or thiomorpholino;

R^{10} represents hydrogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 alkylcarbonyl, C_1-C_4 alkoxycarbonyl, -C(=O)N(R^8)(R^9), -S(=O)$_2$N(R^8)(R^9), benzyl or phenyl, wherein the benzyl and phenyl are optionally substituted by one or more groups independently selected from the group consisting of halogen, cyano, C_1-C_4 alkyl, C_1-C_4 haloalkyl, or C_1-C_4 alkoxy;

R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17} and R^{18} independently of each other represent hydrogen, halogen, cyano, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy or C_1-C_4 haloalkoxy;

r and s independently of each other represent 0 or 1;

or a salt or an N-oxide thereof.

2. A compound of formula (I) according to claim 1 wherein R^1 and R^2 each independently represent hydrogen, methyl, ethyl, isopropyl or cyclopropyl.

3. A compound of formula (I) according to either claim 1 or claim 2 wherein R^1 represents methyl and R^2 represents ethyl.

4. A compound of formula (I) according to any preceding claim wherein R^4 represents methyl, ethyl, isopropyl, propyl or cyclopropyl.

5. A compound of formula (I) according to any preceding claim wherein R^4 represents methyl.

6. A compound of formula (I) according to any preceding claim wherein R^5 represents hydrogen, halogen, cyano, hydroxy, formyl, carboxy, amino, C_1-C_4 alkyl, C_2-C_4 alkenyl, C_2-C_4 alkynl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, C_3-C_6 cycloalkyl, C_2-C_4 alkylcarbonyl, C_2-C_4 alkoxycarbonyl, C_1-C_4 alkylthio, C_1-C_4 alkylsulfinyl, C_1-C_4 alkylsulfonyl, $-N(R^8)(R^9)$, $-C(=O)N(R^8)(R^9)$ or $-S(=O)_2N(R^8)(R^9)$.

7. A compound of formula (I) according to any preceding claim wherein R^5 represents hydrogen, halogen, CN, OH, methyl, ethyl, isopropyl, CHF_2, CF_3, methoxy, ethoxy, NMe_2, CHO, COOH, CO-Me, CO_2Me, CONHMe, $CONMe_2$ or $S(=O)_2NHMe$.

8. A compound of formula (I) according to any preceding claim wherein R_5 represents hydrogen, halogen, cyano, methyl, ethyl or CHF_2.

9. A compound of formula (I) according to any preceding claim wherein R^6 represents hydrogen, C_1-C_4 alkyl, C_1-C_2 alkoxycarbonyl or formyl.

10. A compound of formula (I) according to any preceding claim wherein R^6 represents hydrogen, methyl, ethyl, isopropyl, formyl or methoxycarbonyl.

11. A compound of formula (I) according to any preceding claim wherein R^6 represents hydrogen or methyl.

12. A compound of formula (I) according to any preceding claim wherein R^7 represents G^1, G^2-G^3-, G^4, G^6, G^7-G^3-, G^8, G^9-G^3-, G^{10}, G^{11}, G^{12} or G^{13};

G^1 represents an eight to ten-membered fused bicarbocyclic ring system optionally substituted by one or more groups independently selected from the group consisting of halogen, cyano, hydroxy, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkoxy;

G^2 represents an eight to ten-membered fused bicyclic ring system which can be aromatic, partially saturated or fully saturated and contains 1 to 2 oxygen atoms, it not being possible for each ring system to contain an -O-O- fragment, and it being possible for the eight- to ten-membered ring system to be itself substituted by one or more groups independently selected from the group consisting of halogen, cyano, hydroxy, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl and C_1-C_4 haloalkoxy;

G^3 represents methylene optionally one or two groups independently selected from halogen, C_1-C_2-alkyl and C_1-C_2-haloalkyl;

G^4 represents a C_5 aromatic monocyclic system which contains 1 nitrogen atom or 1 sulfur atom optionally substituted by one or more groups independently selected from halogen, CN, OH, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl, C_1-C_4 haloalkoxy and C_1-C_4 alkoxycarbonyl;

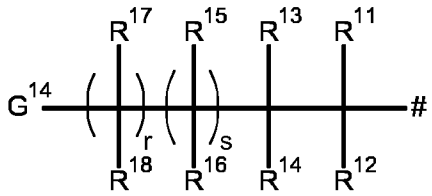
G^6 and G^7 represent phenyl optionally substituted by one or more groups independently selected from halogen, CN, OH, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl and C_1-C_4 haloalkoxy;

G^8 represents a five- or six-membered saturated monocyclic system which contains 1 or 2 members selected from the group consisting of $N(R^{10})$, optionally substituted by one or more groups independently selected from the group consisting of halogen, CN, OH, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy and C_1-C_4 haloalkoxy;

G^9 represents a five-membered saturated monocyclic system which contains 1 or 2 oxygen atoms, it not being possible for each ring system to contain an -O-O- fragment, and it being possible for the five- to six-membered ring system to be itself substituted by one or more groups independently selected from the group consisting of halogen, CN, OH, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy and C_1-C_4 haloalkoxy;

G^{10} represents a C_5-C_7 mono-carbocyclic system optionally substituted by one or more groups independently selected from hydrogen, halogen, CN, OH, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl and C_1-C_4 haloalkoxy;

G^{11} represents



;

G^{12} represents benzylsulfonyl or phenylsulfonyl, each of which can be optionally substituted by one or more groups independently selected from the group consisting of halogen, CN, OH, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, and C_1-C_4 haloalkoxy;

G^{13} represents benzylcarbonyl or phenylcarbonyl, each of which are optionally substituted by substituents by one or more groups independently selected from the group consisting of halogen, CN, OH, C_1-C_4 alkyl and C_1-C_4haloalkyl;

G^{14} represents hydrogen, C_3-C_6 cycloalkyl, G^2, G^4, G^5, phenoxy or benzyloxy wherein the phenoxy or benzyloxy may be optionally substituted by one or more groups independently selected from the group consisting of halogen, cyano, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy and C_1-C_4 haloalkyl;

R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17} and R^{18} independently of each other represent hydrogen, fluoro, cyano, C_1-C_4 alkyl optionally substituted by one or more fluorine atoms or C_1-C_4 alkoxy;

r and s are both 0.

13. A compound of formula (I) according to any preceding claim wherein R^8 and R^9 independently of each other represent hydrogen, C_1-C_4 alkyl, C_1-C_4 haloalkyl or phenyl.

14. A compound of formula (I) according to any preceding claim wherein R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17} and R^{18} independently of each other represent hydrogen or C_1-C_2 alkyl.

15. A compound of formula (I) according to any preceding claim wherein R^1 and R^2 independently represent hydrogen, methyl, ethyl, isopropyl or cyclopropyl;

R^4 represents methyl, ethyl, isopropyl, propyl or cyclopropyl;

R^5 represents hydrogen, halogen, CN, OH, methyl, ethyl, isopropyl, CHF_2, CF_3, methoxy, ethoxy, NMe_2, CHO, COOH, CO-Me, CO_2Me, CONHMe, $CONMe_2$ or $S(=O)_2NHMe$;

R_6 represents hydrogen, methyl, ethyl, isopropyl, formyl or C_1-C_2 alkoxycarbonyl.

16. A compound of formula (I) according to any preceding claim wherein

R_1 represents methyl;

R_2 represents ethyl;

R_4 represents methyl;

R_5 represents hydrogen, halogen, cyano, methyl, ethyl or CHF_2;

R_6 represents hydrogen or methyl.

17. A composition comprising a fungicidally effective amount of a compound of formula (I) as defined in any one of claims 1 to 16, optionally comprising at least one additional active ingredient.

18. A method of controlling or preventing phytopathogenic diseases on useful plants or on propagation material thereof, which comprises applying to the useful plants, the locus thereof or propagation material thereof a fungicidally effective amount of a compound of formula (I) as defined in any one of claims 1 to 16.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/072212

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D213/74 C07D213/75 C07D401/12 C07D405/12 C07D417/12
A01N43/40
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2008/101682 A2 (SYNGENTA PARTICIPATIONS AG [CH]; SYNGENTA LTD [GB]; WORTHINGTON PAUL A) 28 August 2008 (2008-08-28) claims; examples	1-18
Y	WO 03/093224 A1 (DU PONT [US]; TSENG CHI-PING [US]) 13 November 2003 (2003-11-13) cited in the application claims; examples; tables 3,5	1-18
Y	EP 2 264 010 A1 (BAYER CROPSCIENCE AG [DE]) 22 December 2010 (2010-12-22) claims; examples	1-18

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 November 2014	27/11/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Gavriliu, Daniela

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2014/072212

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