

TITLE

SUBSTITUTED TOLYL AS FUNGICIDES

FIELD OF THE INVENTION

This invention relates to certain tolyl fungicides, their *N*-oxides, salts and compositions,
 5 and methods of their use as fungicides.

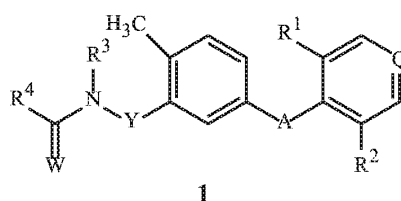
BACKGROUND OF THE INVENTION

The control of plant diseases caused by fungal plant pathogens is extremely important in achieving high crop efficiency. Plant disease damage to ornamental, vegetable, field, cereal, and fruit crops can cause significant reduction in productivity and thereby result in increased costs to the consumer. Many products are commercially available for these purposes, but the
 10 need continues for new compounds which are more effective, less costly, less toxic, environmentally safer or have different sites of action.

PCT Patent Publications WO 2015157005, WO 2014066120 WO 2011059619 and WO 2008124092 disclose tolyl fungicides and their use in agriculture.

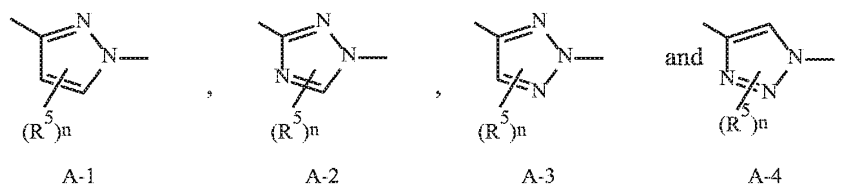
SUMMARY OF THE INVENTION

15 This invention is directed to compounds of Formula 1 (including all stereoisomers), *N*-oxides, and salts thereof, agricultural compositions containing them and their use as fungicides:



20 wherein

A is a radical selected from the group consisting of



wherein the bond extending to the right is attached to the ring containing Q and the
 bond extending to the left is attached to the phenyl ring bearing the
 Y-N(R³)C(=W)R⁴ substituent;

25 Q is CR⁶ or N;

Y is CR^{7a}R^{7b}, O or NR⁸;

W is O or S;

- R¹ and R² are each independently halogen, cyano, hydroxy, nitro, amino, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₂-C₆ cyanoalkyl, C₃-C₆ cycloalkyl, C₃-C₆ halocycloalkyl, C₄-C₈ cycloalkylalkyl, C₂-C₆ alkoxyalkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₂-C₆ alkenyloxy, C₂-C₆ haloalkenyloxy, C₂-C₆ alkynyloxy, C₂-C₆ haloalkynyloxy, C₂-C₆ cyanoalkoxy, C₃-C₆ cycloalkoxy, C₄-C₈ cycloalkylalkoxy, C₂-C₆ alkoxyalkoxy, C₁-C₆ alkylthio, C₁-C₆ haloalkylthio, C₁-C₆ alkylsulfinyl, C₁-C₆ haloalkylsulfinyl, C₁-C₆ alkylsulfonyl or C₁-C₆ haloalkylsulfonyl;
- R³ is H, C₁-C₃ alkyl, C₁-C₃ haloalkyl, cyclopropyl, C₂-C₄ alkylcarbonyl, C₂-C₄ haloalkylcarbonyl, C₂-C₄ alkoxy carbonyl or C₂-C₄ haloalkoxy carbonyl;
- R⁴ is C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₁-C₃ alkoxy, C₁-C₃ haloalkoxy, C₁-C₃ alkylamino or C₂-C₄ dialkylamino;
- each R⁵ is independently halogen, cyano, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₁-C₃ alkoxy or C₁-C₃ haloalkoxy;
- n is 0, 1 or 2;
- R⁶ is H, halogen, cyano, hydroxy, nitro, amino, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₂-C₆ cyanoalkyl, C₁-C₆ hydroxyalkyl, C₂-C₆ alkoxyalkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₂-C₆ alkenyloxy, C₂-C₆ haloalkenyloxy, C₂-C₆ alkynyloxy, C₂-C₆ haloalkynyloxy, C₂-C₆ cyanoalkoxy, C₂-C₆ alkoxyalkoxy, C₁-C₆ alkylamino, C₁-C₆ alkylthio, C₁-C₆ haloalkylthio, C₁-C₆ alkylsulfinyl, C₁-C₆ haloalkylsulfinyl, C₁-C₆ alkylsulfonyl, C₁-C₆ haloalkylsulfonyl, -ZC(=O)V, CR^{10a}=NOR^{10b}, ON=CR^{11a}R^{11b}, CR^{12a}=NNR^{12b}R^{12c} or -L-J;
- R^{7a} is H, hydroxy, halogen, cyano, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₂-C₃ alkoxyalkyl, C₁-C₃ alkoxy, C₁-C₃ haloalkoxy, C₁-C₃ alkylsulfinyl or C₁-C₃ alkylsulfonyl;
- R^{7b} is H, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₂-C₃ alkoxyalkyl, C₁-C₃ alkoxy or C₁-C₃ haloalkoxy;
- R⁸ is H, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₂-C₃ alkylcarbonyl or C₂-C₃ haloalkylcarbonyl;
- Z is a direct bond, O, S or NH; or CH₂ optionally substituted with up to 2 substituents independently selected from halogen, methyl or methoxy;
- V is R⁹ or OR⁹;
- R⁹, R^{10b}, R^{11a} and R^{12c} are each H, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₂-C₄ alkenyl, C₂-C₄ haloalkenyl, C₂-C₄ alkynyl, C₃-C₆ cycloalkyl, C₃-C₆ halocycloalkyl or C₄-C₈ cycloalkylalkyl;
- R^{10a}, R^{11b}, R^{12a} and R^{12b} are each independently H, C₁-C₃ alkyl or C₁-C₃ haloalkyl;
- L is a direct bond, CH₂, O, S, NR¹³, OCH₂, CH₂O, C(=O), S(=O) or S(=O)₂;

J is a 3- to 6-membered nonaromatic carbocyclic ring, wherein up to 3 carbon atom ring members are independently selected from C(=O) and C(=S), each ring optionally substituted with up to 4 substituents independently selected from R¹⁴; or

5 J is a 3- to 6-membered heterocyclic ring, each ring containing ring members selected from carbon atoms and 1 to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, wherein up to 3 carbon atom ring members are independently selected from C(=O) and C(=S), each ring optionally substituted with up to 4 substituents independently selected from R¹⁴;

10 R¹³ is H, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₂-C₃ alkylcarbonyl or C₂-C₃ haloalkylcarbonyl;

each R¹⁴ is independently halogen, hydroxy, cyano, nitro, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₂-C₄ alkenyl, C₂-C₄ haloalkenyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy or C(=O)OR¹⁵; and

15 each R¹⁵ is independently H, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₂-C₄ alkenyl, C₂-C₄ haloalkenyl, C₂-C₄ alkynyl, C₃-C₆ cycloalkyl or C₃-C₆ halocycloalkyl.

More particularly, this invention pertains to a compound of Formula 1 (including all stereoisomers), an *N*-oxide or a salt thereof.

20 This invention also relates to a fungicidal composition comprising (a) a compound of the invention (i.e. in a fungicidally effective amount); and (b) at least one additional component selected from the group consisting of surfactants, solid diluents and liquid diluents.

This invention also relates to a fungicidal composition comprising (a) a compound of the invention; and (b) at least one other fungicide (e.g., at least one other fungicide having a different site of action).

25 This invention further relates to a method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof, or to the plant seed, a fungicidally effective amount of a compound of the invention (e.g., as a composition described herein).

This invention also relates to a composition comprising a compound of Formula 1, an *N*-oxide, or a salt thereof, and at least one invertebrate pest control compound or agent.

30 DETAILS OF THE INVENTION

As used herein, the terms “comprises,” “comprising,” “includes,” “including,” “has,” “having,” “contains,” “containing,” “characterized by” or any other variation thereof, are intended to cover a non-exclusive inclusion, subject to any limitation explicitly indicated. For example, a composition, mixture, process, method, article, or apparatus that comprises a list of
35 elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such composition, mixture, process, method, article, or apparatus.

The transitional phrase “consisting of” excludes any element, step, or ingredient not specified. If in the claim, such would close the claim to the inclusion of materials other than those recited except for impurities ordinarily associated therewith. When the phrase “consisting of” appears in a clause of the body of a claim, rather than immediately following the preamble, it limits only the element set forth in that clause; other elements are not excluded from the claim as a whole.

The transitional phrase “consisting essentially of” is used to define a composition, method or apparatus that includes materials, steps, features, components, or elements, in addition to those literally disclosed, provided that these additional materials, steps, features, components, or elements do not materially affect the basic and novel characteristic(s) of the claimed invention. The term “consisting essentially of” occupies a middle ground between “comprising” and “consisting of”.

Where applicants have defined an invention or a portion thereof with an open-ended term such as “comprising,” it should be readily understood that (unless otherwise stated) the description should be interpreted to also describe such an invention using the terms “consisting essentially of” or “consisting of.”

Further, unless expressly stated to the contrary, “or” refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

Also, the indefinite articles “a” and “an” preceding an element or component of the invention are intended to be nonrestrictive regarding the number of instances (i.e. occurrences) of the element or component. Therefore “a” or “an” should be read to include one or at least one, and the singular word form of the element or component also includes the plural unless the number is obviously meant to be singular.

As referred to in the present disclosure and claims, “plant” includes members of Kingdom Plantae, particularly seed plants (Spermatopsida), at all life stages, including young plants (e.g., germinating seeds developing into seedlings) and mature, reproductive stages (e.g., plants producing flowers and seeds). Portions of plants include geotropic members typically growing beneath the surface of the growing medium (e.g., soil), such as roots, tubers, bulbs and corns, and also members growing above the growing medium, such as foliage (including stems and leaves), flowers, fruits and seeds.

As referred to herein, the term “seedling”, used either alone or in a combination of words means a young plant developing from the embryo of a seed.

As referred to herein, the term “broadleaf” used either alone or in words such as “broadleaf crop” means dicot or dicotyledon, a term used to describe a group of angiosperms characterized by embryos having two cotyledons.

As referred to in this disclosure, the terms “fungal pathogen” and “fungal plant pathogen” include pathogens in the Ascomycota, Basidiomycota and Zygomycota phyla classes, and the fungal-like Oomycota class that are the causal agents of a broad spectrum of plant diseases of economic importance, affecting ornamental, turf, vegetable, field, cereal and fruit crops. In the context of this disclosure, “protecting a plant from disease” or “control of a plant disease” includes preventative action (interruption of the fungal cycle of infection, colonization, symptom development and spore production) and/or curative action (inhibition of colonization of plant host tissues).

As used herein, the term “mode of action” (MOA) is as define by the Fungicide Resistance Action Committee (FRAC), and is used to distinguish fungicides according to their biochemical mode of action in the biosynthetic pathways of plant pathogens, and their resistance risk. FRAC-defined modes of actions include (A) nucleic acid synthesis, (B) mitosis and cell division, (C) respiration, (D) amino acid and protein synthesis, (E) signal transduction, (F) lipid synthesis and membrane integrity, (G) sterol biosynthesis in membranes, (H) cell wall biosynthesis, (I) melanin synthesis in cell wall, (P) host plant defense induction, (U) unknown mode of action, (NC) not classified, (M) multi-site contact activity and (BM) biologicals with multiple modes of action. Each mode of action (i.e. letters A through BM) contain one or more subgroups (e.g., A includes subgroups A1, A2, A3 and A4) based either on individual validated target sites of action, or in cases where the precise target site is unknown, based on cross resistance profiles within a group or in relation to other groups. Each of these subgroups (e.g., A1, A2, A3 and A4) is assigned a FRAC code (a number and/or letter). For example, the FRAC code for subgroup A1 is 4. Additional information on target sites and FRAC codes can be obtained from publicly available databases maintained, for example, by FRAC.

As used herein, the term “cross resistance” refers to the phenomenon that occurs when a pathogen develops resistance to one fungicide and simultaneously becomes resistant to one or more other fungicides. These other fungicides are typically, but not always, in the same chemical class or have the same target site of action, or can be detoxified by the same mechanism.

Generally, when a molecular fragment (i.e. radical) is denoted by a series of atom symbols (e.g., C, H, N, O and S) the implicit point or points of attachment will be easily recognized by those skilled in the art. In some instances herein, particularly when alternative points of attachment are possible, the point or points of attachment may be explicitly indicated by a hyphen (“-”). For example, “-NCS” indicates that the point of attachment is the nitrogen atom (i.e. isothiocyanato, not thiocyanato).

As used herein, the term “alkylating agent” refers to a chemical compound in which a carbon-containing radical is bound through a carbon atom to a leaving group such as halide or sulfonate, which is displaceable by bonding of a nucleophile to said carbon atom. Unless

otherwise indicated, the term “alkylating” does not limit the carbon-containing radical to alkyl; the carbon-containing radicals in alkylating agents include the variety of carbon-bound substituent radicals specified, for example, for R¹ and R².

In the above recitations, the term “alkyl”, used either alone or in compound words such as “alkylthio” or “haloalkyl” includes straight-chain or branched alkyl such as methyl, ethyl, *n*-propyl and *i*-propyl, or the different butyl, pentyl or hexyl isomers. “Alkenyl” includes straight-chain or branched alkenes such as ethenyl, 1-propenyl, 2-propenyl, and the different butenyl, pentenyl and hexenyl isomers. “Alkenyl” also includes polyenes such as 1,2-propadienyl and 2,4-hexadienyl. “Alkynyl” includes straight-chain or branched alkynes such as ethynyl, 1-propynyl, 2-propynyl and the different butynyl, pentynyl and hexynyl isomers. “Alkynyl” can also include moieties comprised of multiple triple bonds such as 2,5-hexadiynyl.

“Alkoxy” includes, for example, methoxy, ethoxy, *n*-propyloxy, *i*-propyloxy and the different butoxy, pentoxy and hexyloxy isomers. “Alkoxyalkyl” denotes alkoxy substitution on alkyl. Examples of “alkoxyalkyl” include CH₃OCH₂, CH₃OCH₂CH₂, CH₃CH₂OCH₂, CH₃CH₂CH₂CH₂OCH₂ and CH₃CH₂OCH₂CH₂. “Alkenyloxy” includes straight-chain or branched alkenyl attached to and linked through an oxygen atom. Examples of “alkenyloxy” include H₂C=CHCH₂O, (CH₃)₂C=CHCH₂O, CH₃CH=CHCH₂O, CH₃CH=C(CH₃)CH₂O and CH₂=CHCH₂CH₂O. “Alkynyloxy” includes straight-chain or branched alkynyl attached to and linked through an oxygen atom. Examples of “alkynyloxy” include HC≡CCH₂O, CH₃C≡CCH₂O and CH₃C≡CCH₂CH₂O. “Alkoxyalkoxy” denotes alkoxy substitution on another alkoxy moiety. Examples of “alkoxyalkoxy” include CH₃OCH₂O, CH₃OCH₂O and CH₃CH₂OCH₂O.

“Alkylthio” includes branched or straight-chain alkylthio moieties such as methylthio, ethylthio, and the different propyl, butyl, pentyl and hexylthio isomers. “Alkylsulfinyl” includes both enantiomers of an alkylsulfinyl group. Examples of “alkylsulfinyl” include CH₃S(=O), CH₃CH₂S(=O), CH₃CH₂CH₂S(=O), (CH₃)₂CHS(=O) and the different butylsulfinyl, pentylsulfinyl and hexylsulfinyl isomers. Examples of “alkylsulfonyl” include CH₃S(=O)₂, CH₃CH₂S(=O)₂, CH₃CH₂CH₂S(=O)₂, (CH₃)₂CHS(=O)₂ and the different butylsulfonyl, pentylsulfonyl and hexylsulfonyl isomers.

“Alkylamino” includes an NH radical substituted with straight-chain or branched alkyl. Examples of “alkylamino” include CH₃NH, CH₃CH₂NH, CH₃CH₂CH₂NH and (CH₃)₂CHNH. Examples of “dialkylamino” include (CH₃)₂N, (CH₃CH₂)₂N and CH₃CH₂(CH₃)N.

The term “cycloalkyl” denotes a saturated carbocyclic ring consisting of between 3 to 6 carbon atoms linked to one another by single bonds. Examples of “cycloalkyl” include cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl. The term “cycloalkylalkyl” denotes

cycloalkyl substitution on an alkyl group. Examples of “cycloalkylalkyl” include cyclopropylmethyl, cyclopentylethyl, and other cycloalkyl moieties bonded to straight-chain or branched alkyl groups. The term “cycloalkoxy” denotes cycloalkyl attached to and linked through an oxygen atom such as cyclopentyloxy and cyclohexyloxy. “Cycloalkylalkoxy”
5 denotes cycloalkyl substitution on an alkoxy group. Examples of “cycloalkylalkoxy” include cyclopropylmethoxy, cyclopentylethoxy, and other cycloalkyl moieties bonded to straight-chain or branched alkoxy groups.

“Alkylcarbonyl” denotes a straight-chain or branched alkyl group bonded to a C(=O) moiety. Examples of “alkylcarbonyl” include $\text{CH}_3\text{C}(=\text{O})$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})$ and $(\text{CH}_3)_2\text{CHC}(=\text{O})$. Examples of “alkoxycarbonyl” include $\text{CH}_3\text{OC}(=\text{O})$, $\text{CH}_3\text{CH}_2\text{OC}(=\text{O})$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OC}(=\text{O})$ and $(\text{CH}_3)_2\text{CHOC}(=\text{O})$.
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The term “halogen”, either alone or in compound words such as “haloalkyl”, or when used in descriptions such as “alkyl substituted with halogen” includes fluorine, chlorine, bromine or iodine. Further, when used in compound words such as “haloalkyl”, or when used
15 in descriptions such as “alkyl substituted with halogen” said alkyl may be partially or fully substituted with halogen atoms which may be the same or different. Examples of “haloalkyl” or “alkyl substituted with halogen” include F_3C , ClCH_2 , CF_3CH_2 and CF_3CCl_2 . The term “haloalkoxy”, and the like, are defined analogously to the term “haloalkyl”. Examples of “haloalkoxy” include CF_3O , $\text{CCl}_3\text{CH}_2\text{O}$, $\text{F}_2\text{CHCH}_2\text{CH}_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{O}$.

“Cyanoalkyl” denotes an alkyl group substituted with one cyano group. Examples of “cyanoalkyl” include NCCH_2 , NCCH_2CH_2 and $\text{CH}_3\text{CH}(\text{CN})\text{CH}_2$. The term “cyanoalkoxy” denotes an alkoxy group substituted with one cyano group. Examples of “cyanoalkoxy” include NCCH_2O , $\text{NCCH}_2\text{CH}_2\text{O}$ and $\text{CH}_3\text{CH}(\text{CN})\text{CH}_2\text{O}$. “Hydroxyalkyl” denotes an alkyl group substituted with one hydroxy group. Examples of “hydroxyalkyl” include HOCH_2CH_2 ,
20 $\text{CH}_3\text{CH}_2(\text{OH})\text{CH}$ and $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$.
25

The total number of carbon atoms in a substituent group is indicated by the “C_i-C_j” prefix where i and j are numbers from 1 to 6. For example, C₁-C₃ alkylsulfonyl designates methylsulfonyl through propylsulfonyl; C₂ alkoxyalkyl designates CH_3OCH_2 ; C₃ alkoxyalkyl designates, for example, $\text{CH}_3\text{OCH}_2\text{CH}_2$ or $\text{CH}_3\text{CH}_2\text{OCH}_2$; and C₄ alkoxyalkyl designates the various isomers of an alkyl group substituted with an alkoxy group containing a total of four carbon atoms, examples including $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_2$ and $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2$.
30

The term “unsubstituted” in connection with a group such as a ring means the group does not have any substituents other than its one or more attachments to the remainder of Formula 1. The term “optionally substituted” means that the number of substituents can be zero. Unless
35 otherwise indicated, optionally substituted groups may be substituted with as many optional substituents as can be accommodated by replacing a hydrogen atom with a non-hydrogen substituent on any available carbon or nitrogen atom. Commonly, the number of optional

substituents (when present) range from 1 to 3. As used herein, the term “optionally substituted” is used interchangeably with the phrase “substituted or unsubstituted” or with the term “(un)substituted.”

5 The number of optional substituents may be restricted by an expressed limitation. For example, the phrase “optionally substituted with up to 4 substituents independently selected from R¹⁴” means that 0, 1, 2, 3 or 4 substituents can be present.

10 When a compound is substituted with a substituent bearing a subscript that indicates the number of said substituents can vary (e.g., (R⁵)_n in Formula 1 wherein n is 0 to 2), then said substituents are independently selected from the group of defined substituents, unless otherwise indicated. When a variable group is shown to be optionally attached to a position, for example (R⁵)_n wherein n may be 0, then hydrogen may be at the position even if not recited in the definition of the variable group.

15 Naming of substituents in the present disclosure uses recognized terminology providing conciseness in precisely conveying to those skilled in the art the chemical structure. For sake of conciseness, locant descriptors may be omitted.

Unless otherwise indicated, a “ring” as a component of Formula 1 (e.g., J) is carbocyclic or heterocyclic. The term “ring member” refers to an atom (e.g., C, O, N or S) or other moiety (e.g., C(=O) and C(=S)) forming the backbone of a ring or ring system. The term “aromatic” indicates that each of the ring atoms is essentially in the same plane and has a *p*-orbital perpendicular to the ring plane, and that (4n + 2) π electrons, where n is a positive integer, are associated with the ring to comply with Hückel’s rule

20 The term “carbocyclic ring” denotes a ring wherein the atoms forming the ring backbone are selected only from carbon. Unless otherwise indicated, a carbocyclic ring can be a saturated, partially unsaturated, or fully unsaturated ring. When a fully unsaturated carbocyclic ring satisfies Hückel’s rule, then said ring is also called an “aromatic ring”. “Saturated carbocyclic” refers to a ring having a backbone consisting of carbon atoms linked to one another by single bonds; unless otherwise specified, the remaining carbon valences are occupied by hydrogen atoms.

30 As used herein, the term “partially unsaturated ring” or “partially unsaturated heterocycle” refers to a ring which contains unsaturated ring atoms and one or more double bonds but is not aromatic.

35 The terms “heterocyclic ring” or “heterocycle” denotes a ring wherein at least one of the atoms forming the ring backbone is other than carbon. Unless otherwise indicated, a heterocyclic ring can be a saturated, partially unsaturated, or fully unsaturated ring. When a fully unsaturated heterocyclic ring satisfies Hückel’s rule, then said ring is also called a “heteroaromatic ring” or aromatic heterocyclic ring. “Saturated heterocyclic ring” refers to a heterocyclic ring containing only single bonds between ring members.

Unless otherwise indicated, heterocyclic rings are attached to the remainder of Formula 1 through any available carbon or nitrogen atom by replacement of a hydrogen on said carbon or nitrogen atom.

Compounds of this invention can exist as one or more stereoisomers. Stereoisomers are isomers of identical constitution but differing in the arrangement of their atoms in space and include enantiomers, diastereomers, *cis*- and *trans*-isomers (also known as geometric isomers) and atropisomers. Atropisomers result from restricted rotation about single bonds where the rotational barrier is high enough to permit isolation of the isomeric species. One skilled in the art will appreciate that one stereoisomer may be more active and/or may exhibit beneficial effects when enriched relative to the other stereoisomer(s) or when separated from the other stereoisomer(s). Additionally, the skilled artisan knows how to separate, enrich, and/or to selectively prepare said stereoisomers. For a comprehensive discussion of all aspects of stereoisomerism, see Ernest L. Eliel and Samuel H. Wilen, *Stereochemistry of Organic Compounds*, John Wiley & Sons, 1994.

Compounds of this invention can exist as one or more conformational isomers due to restricted rotation about an amide bond (e.g., C(=O)-N) in Formula 1. This invention comprises mixtures of conformational isomers. In addition, this invention includes compounds that are enriched in one conformer relative to others.

This invention comprises all stereoisomers, conformational isomers and mixtures thereof in all proportions as well as isotopic forms such as deuterated compounds.

One skilled in the art will appreciate that not all nitrogen containing heterocycles can form *N*-oxides since the nitrogen requires an available lone pair for oxidation to the oxide; one skilled in the art will recognize those nitrogen-containing heterocycles which can form *N*-oxides. One skilled in the art will also recognize that tertiary amines can form *N*-oxides. Synthetic methods for the preparation of *N*-oxides of heterocycles and tertiary amines are very well known by one skilled in the art including the oxidation of heterocycles and tertiary amines with peroxy acids such as peracetic and *m*-chloroperbenzoic acid (MCPBA), hydrogen peroxide, alkyl hydroperoxides such as *t*-butyl hydroperoxide, sodium perborate, and dioxiranes such as dimethyldioxirane. These methods for the preparation of *N*-oxides have been extensively described and reviewed in the literature, see for example: T. L. Gilchrist in *Comprehensive Organic Synthesis*, vol. 7, pp 748-750, S. V. Ley, Ed., Pergamon Press; M. Tisler and B. Stanovnik in *Comprehensive Heterocyclic Chemistry*, vol. 3, pp 18-20, A. J. Boulton and A. McKillop, Eds., Pergamon Press; M. R. Grimmett and B. R. T. Keene in *Advances in Heterocyclic Chemistry*, vol. 43, pp 149-161, A. R. Katritzky, Ed., Academic Press; M. Tisler and B. Stanovnik in *Advances in Heterocyclic Chemistry*, vol. 9, pp 285-291, A. R. Katritzky and A. J. Boulton, Eds., Academic Press; and G. W. H. Cheeseman and E. S.

g. Werstiuk in *Advances in Heterocyclic Chemistry*, vol. 22, pp 390–392, A. R. Katritzky and A. J. Boulton, Eds., Academic Press.

One skilled in the art recognizes that because in the environment and under physiological conditions salts of chemical compounds are in equilibrium with their corresponding nonsalt forms, salts share the biological utility of the nonsalt forms. Thus, a wide variety of salts of the compounds of Formula 1 are useful for control of plant diseases caused by fungal plant pathogens (i.e. are agriculturally suitable). The salts of the compounds of Formula 1 include acid-addition salts with inorganic or organic acids such as hydrobromic, hydrochloric, nitric, phosphoric, sulfuric, acetic, butyric, fumaric, lactic, maleic, malonic, oxalic, propionic, salicylic, tartaric, 4-toluenesulfonic or valeric acids. When a compound of Formula 1 contains an acidic moiety such as a carboxylic acid, salts also include those formed with organic or inorganic bases such as pyridine, triethylamine or ammonia, or amides, hydrides, hydroxides or carbonates of sodium, potassium, lithium, calcium, magnesium or barium. Accordingly, the present invention comprises compounds selected from Formula 1, *N*-oxides and agriculturally suitable salts thereof.

Compounds selected from Formula 1, stereoisomers, *N*-oxides, and salts thereof, typically exist in more than one form, therefore Formula 1 includes all crystalline and non-crystalline forms of the compounds that Formula 1 represents. Non-crystalline forms include embodiments which are solids such as waxes and gums as well as embodiments which are liquids such as solutions and melts. Crystalline forms include embodiments which represent essentially a single crystal type and embodiments which represent a mixture of polymorphs (i.e. different crystalline types). The term “polymorph” refers to a particular crystalline form of a chemical compound that can crystallize in different crystalline forms, these forms having different arrangements and/or conformations of the molecules in the crystal lattice. Although polymorphs can have the same chemical composition, they can also differ in composition due to the presence or absence of co-crystallized water or other molecules, which can be weakly or strongly bound in the lattice. Polymorphs can differ in such chemical, physical and biological properties as crystal shape, density, hardness, color, chemical stability, melting point, hygroscopicity, suspensibility, dissolution rate and biological availability. One skilled in the art will appreciate that a polymorph of a compound represented by Formula 1 can exhibit beneficial effects (e.g., suitability for preparation of useful formulations, improved biological performance) relative to another polymorph or a mixture of polymorphs of the same compound represented by Formula 1. Preparation and isolation of a particular polymorph of a compound represented by Formula 1 can be achieved by methods known to those skilled in the art including, for example, crystallization using selected solvents and temperatures.

Embodiments of the present invention as described in the Summary of the Invention include those described below. In the following Embodiments, Formula 1 includes

stereoisomers, *N*-oxides and salts thereof, and reference to “a compound of Formula 1” includes the definitions of substituents specified in the Summary of the Invention unless further defined in the Embodiments.

- Embodiment 1. A compound of Formula 1 wherein A is A-1, A-3 or A-4.
- 5 Embodiment 1a. A compound of Embodiment 1 wherein A is A-1 or A-3.
- Embodiment 2. A compound of Embodiment 1 wherein A is A-1
- Embodiment 3. A compound of Embodiment 1 wherein A is A-3.
- Embodiment 4. A compound of Embodiment 1 wherein A is A-4.
- Embodiment 5. A compound of Formula 1 wherein A is A-2.
- 10 Embodiment 6. A compound of Formula 1 or any one of Embodiments 1 through 5 wherein Q is CR⁶.
- Embodiment 7. A compound of Formula 1 or any one of Embodiments 1 through 5 wherein Q is N.
- Embodiment 8. A compound of Formula 1 or any one of Embodiments 1 through 7 wherein Y is CR^{7a}R^{7b} or O.
- 15 Embodiment 9. A compound of Formula 1 or any one of Embodiments 1 through 7 wherein Y is CR^{7a}R^{7b} or NR⁸.
- Embodiment 10. A compound of Embodiments 8 or 9 wherein Y is CR^{7a}R^{7b}.
- Embodiment 11. A compound of Embodiment 8 wherein Y is O.
- 20 Embodiment 12. A compound of Embodiment 9 wherein Y is NR⁸.
- Embodiment 13. A compound of Formula 1 or any one of Embodiments 1 through 12 wherein W is O.
- Embodiment 14. A compound of Formula 1 or any one of Embodiments 1 through 12 wherein W is S.
- 25 Embodiment 15. A compound of Formula 1 or any one of Embodiments 1 through 14 wherein R¹ and R² are each independently halogen, cyano, hydroxy, nitro, amino, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₂-C₄ alkenyl, C₂-C₄ haloalkenyl, C₂-C₄ alkynyl, C₂-C₄ haloalkynyl, C₂-C₄ cyanoalkyl, C₃-C₆ cycloalkyl, C₃-C₆ halocycloalkyl, C₄-C₆ cycloalkylalkyl, C₂-C₄ alkoxyalkyl, C₁-C₃ alkoxy, C₁-C₃ haloalkoxy, C₂-C₄ alkenyloxy, C₂-C₄ haloalkenyloxy, C₂-C₄ alkynyloxy, C₂-C₄ haloalkynyloxy, C₂-C₄ cyanoalkoxy, C₃-C₆ cycloalkoxy, C₄-C₆ cycloalkylalkoxy, C₂-C₄ alkoxyalkoxy, C₁-C₃ alkylthio, C₁-C₃ haloalkylthio, C₁-C₃ alkylsulfinyl, C₁-C₃ haloalkylsulfinyl, C₁-C₃ alkylsulfonyl or C₁-C₃ haloalkylsulfonyl.
- 30 Embodiment 16. A compound of Embodiment 15 wherein R¹ and R² are each independently halogen, cyano, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₂-C₄ alkenyl, C₂-C₄ haloalkenyl, C₂-C₄ cyanoalkyl, C₂-C₄ alkoxyalkyl, C₁-C₃ alkoxy, C₁-C₃

haloalkoxy, C₂-C₄ alkenyloxy, C₂-C₄ haloalkenyloxy, C₂-C₄ cyanoalkoxy, C₂-C₄ alkoxyalkoxy, C₁-C₃ alkylthio, C₁-C₃ haloalkylthio, C₁-C₃ alkylsulfinyl, C₁-C₃ haloalkylsulfinyl, C₁-C₃ alkylsulfonyl or C₁-C₃ haloalkylsulfonyl.

5 Embodiment 17. A compound of Embodiment 16 wherein R¹ and R² are each independently halogen, cyano, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₂-C₄ alkoxyalkyl, C₁-C₃ alkoxy, C₁-C₃ haloalkoxy, C₂-C₄ alkenyloxy, C₂-C₄ haloalkenyloxy, C₂-C₄ alkoxyalkoxy or C₁-C₃ alkylthio.

10 Embodiment 18. A compound of Embodiment 17 wherein R¹ and R² are each independently halogen, cyano, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₁-C₃ alkoxy, C₁-C₃ haloalkoxy or C₁-C₃ alkylthio.

Embodiment 19. A compound of Embodiment 18 wherein R¹ and R² are each independently halogen, cyano, methyl, halomethyl, methoxy or halomethoxy.

Embodiment 20. A compound of Embodiment 19 wherein R¹ and R² are each independently Br, Cl, F, methyl, trifluoromethyl, methoxy or trifluoromethoxy.

15 Embodiment 21. A compound of Embodiment 20 wherein R¹ and R² are each independently Cl, F or methyl.

Embodiment 22. A compound of Embodiment 21 wherein R¹ and R² are each independently Cl or F.

Embodiment 23. A compound of Embodiment 22 wherein R¹ and R² are each F.

20 Embodiment 24. A compound of Formula 1 or any one of Embodiments 1 through 23 wherein R³ is H, C₁-C₃ alkyl, C₂-C₄ alkylcarbonyl or C₂-C₄ alkoxy carbonyl.

Embodiment 25. A compound of Embodiment 24 wherein R³ is H, methyl, methylcarbonyl or methoxycarbonyl.

Embodiment 26. A compound of Embodiment 25 wherein R³ is H or methyl.

25 Embodiment 27. A compound of Embodiment 26 wherein R³ is H.

Embodiment 28. A compound of Formula 1 or any one of Embodiments 1 through 27 wherein R⁴ is methyl, methoxy, ethoxy, methylamino or dimethylamino.

Embodiment 29. A compound of Embodiment 28 wherein R⁴ is methyl, methoxy or ethoxy.

30 Embodiment 30. A compound of Embodiment 29 wherein R⁴ is methoxy.

Embodiment 31. A compound of Formula 1 or any one of Embodiments 1 through 30 wherein each R⁵ is independently halogen, cyano, methyl or methoxy.

Embodiment 32. A compound of Embodiment 31 wherein each R⁵ is independently halogen or methyl.

35 Embodiment 33. A compound of Embodiment 32 wherein each R⁵ is methyl.

Embodiment 34. A compound of Formula 1 or any one of Embodiments 1 through 33 wherein n is 0 or 1.

Embodiment 35. A compound of Embodiment 34 wherein n is 0.

Embodiment 36. A compound of Formula 1 or any one of Embodiments 1 through 35

wherein R⁶ is H, halogen, nitro, amino, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₂-C₆ alkoxyalkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₂-C₆ alkenyloxy, C₂-C₆ haloalkenyloxy, C₂-C₆ alkynyloxy, C₂-C₆ haloalkynyloxy, C₂-C₆ alkoxyalkoxy, C₁-C₆ alkylthio, C₁-C₆ haloalkylthio, C₁-C₆ alkylsulfinyl, C₁-C₆ haloalkylsulfinyl, C₁-C₆ alkylsulfonyl, C₁-C₆ haloalkylsulfonyl, -ZC(=O)V, CR^{10a}=NOR^{10b}, ON=CR^{11a}R^{11b}, CR^{12a}=NNR^{12b}R^{12c} or -L-J.

Embodiment 37. A compound of Embodiment 36 wherein R⁶ is H, halogen, nitro, amino, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₂-C₆ alkoxyalkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₂-C₆ alkenyloxy, C₂-C₆ haloalkenyloxy, C₂-C₆ alkynyloxy, C₂-C₆ haloalkynyloxy, C₂-C₆ alkoxyalkoxy, C₁-C₆ alkylthio, C₁-C₆ haloalkylthio, -ZC(=O)V, CR^{10a}=NOR^{10b}, CR^{12a}=NNR^{12b}R^{12c} or -L-J.

Embodiment 38. A compound of Embodiment 37 wherein R⁶ is H, halogen, nitro, amino, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₂-C₆ alkenyloxy, C₂-C₆ haloalkenyloxy, C₂-C₆ alkynyloxy, C₂-C₆ haloalkynyloxy, C₁-C₆ alkylthio, C₁-C₆ haloalkylthio, CR^{10a}=NOR^{10b} or -L-J.

Embodiment 39. A compound of Embodiment 38 wherein R⁶ is H, halogen, amino, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₁-C₃ alkoxy, C₁-C₃ haloalkoxy, C₂-C₄ alkenyloxy, C₂-C₄ haloalkenyloxy, CR^{10a}=NOR^{10b} or -L-J.

Embodiment 40. A compound of Embodiment 39 wherein R⁶ is H, halogen, amino, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₁-C₃ alkoxy, C₁-C₃ haloalkoxy, CR^{10a}=NOR^{10b} or -L-J.

Embodiment 40a. A compound of Embodiment 40 wherein R⁶ is H, Br, Cl, I, amino, methyl, *i*-propyl, trifluoromethyl, CH₂F, CHF₂, methoxy, ethoxy, *i*-propyloxy, trifluoromethoxy, CH₂FO, CHF₂O, CH=NOCH₃, CH=NOCH₂CH₃,

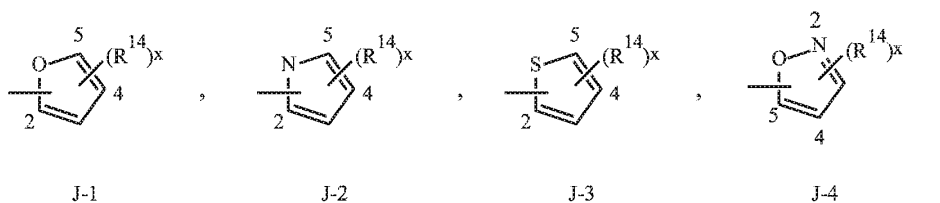
Embodiment 41. A compound of Embodiment 40a wherein R⁶ is H, Br, Cl, I, amino, methyl, *i*-propyl, trifluoromethyl, CHF₂, methoxy, ethoxy, *i*-propyloxy, trifluoromethoxy, CHF₂O, CH=NOCH₃, CH=NOCH₂CH₃, C(CH₃)=NOCH₃ or -L-J.

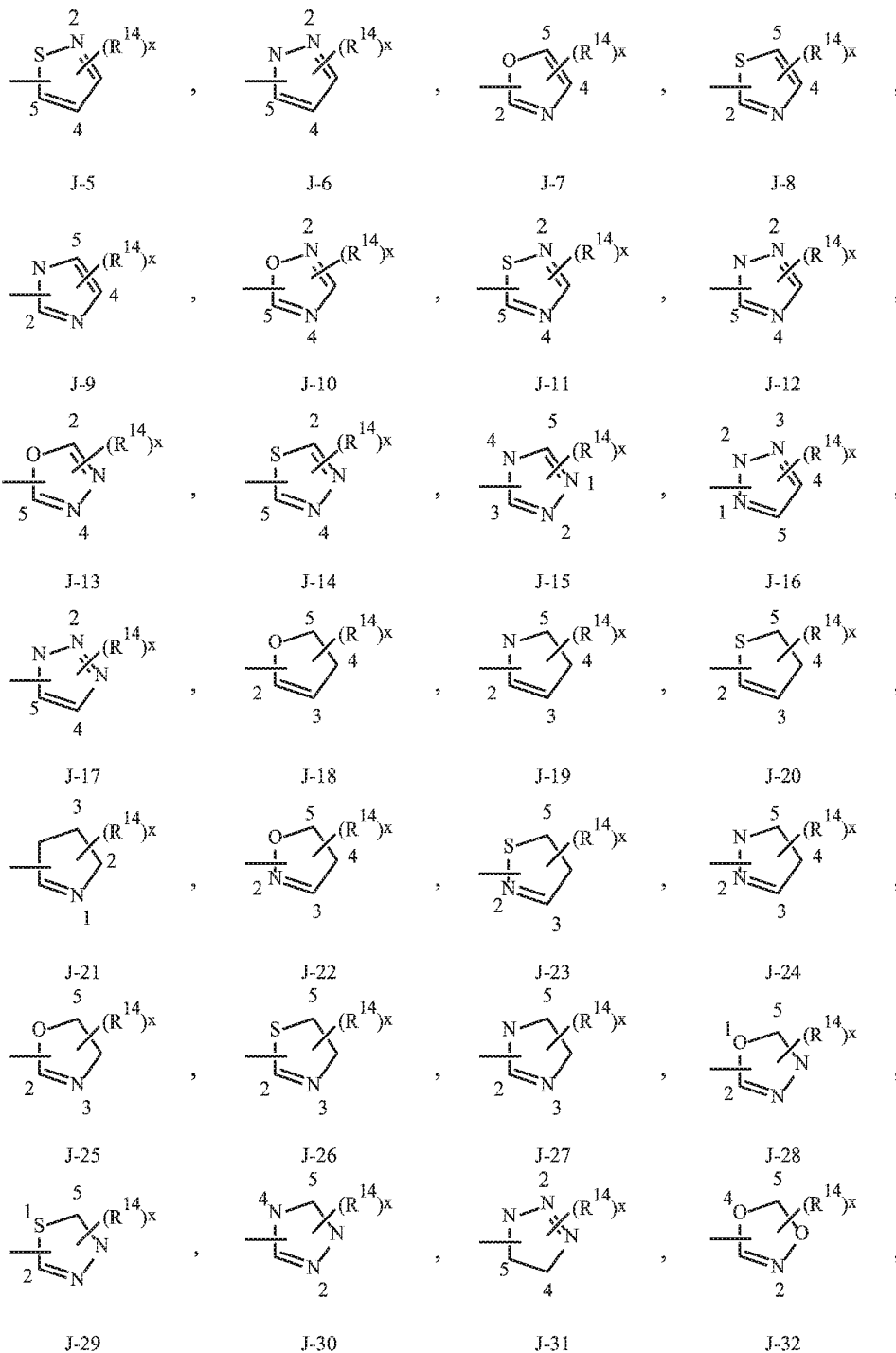
Embodiment 41a. A compound of Embodiment 41 wherein R⁶ is H, Br, Cl, I, amino, methoxy, ethoxy, *i*-propyloxy, trifluoromethoxy, CHF₂O, C(CH₃)=NOCH₃ or -L-J.

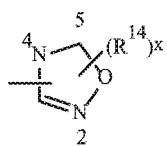
- Embodiment 42. A compound of Embodiment 41 wherein R⁶ is H, Br, Cl, I, amino, methoxy, ethoxy, *i*-propyloxy, trifluoromethoxy, C(CH₃)=NOCH₃ or -L-J.
- Embodiment 43. A compound of Embodiment 42 wherein R⁶ is H, Br, Cl, amino, methoxy, ethoxy or *i*-propyloxy.
- 5 Embodiment 44. A compound of Embodiment 43 wherein R⁶ is H, Br, Cl, amino or methoxy.
- Embodiment 45. A compound of Formula 1 or any one of Embodiments 1 through 44 wherein R^{7a} is H, hydroxy, halogen, cyano, methyl, halomethyl, methoxy or halomethoxy.
- 10 Embodiment 46. A compound of Embodiment 45 wherein R^{7a} is H, halogen, methyl or methoxy.
- Embodiment 47. A compound of Embodiment 46 wherein R^{7a} is H or methyl.
- Embodiment 48. A compound of Embodiment 47 wherein R^{7a} is H.
- Embodiment 49. A compound of Formula 1 or any one of Embodiments 1 through 48
15 wherein R^{7b} is H, methyl, halomethyl, methoxy or halomethoxy.
- Embodiment 50. A compound of Embodiment 49 wherein R^{7b} is H, methyl or methoxy.
- Embodiment 51. A compound of Embodiment 50 wherein R^{7b} is H or methyl.
- Embodiment 52. A compound of Embodiment 51 wherein R^{7b} is H.
- Embodiment 53. A compound of Formula 1 or any one of Embodiments 1 through 44
20 wherein R⁸ is H, methyl, halomethyl or methylcarbonyl.
- Embodiment 54. A compound of Embodiment 53 wherein R⁸ is H or methyl.
- Embodiment 55. A compound of Embodiment 54 wherein R⁸ is H.
- Embodiment 56. A compound of Formula 1 or any one of Embodiments 1 through 55 wherein Z is a direct bond, O, NH, CH₂ or CH(OCH₃).
- 25 Embodiment 57. A compound of Embodiment 56 wherein Z is a direct bond, O or CH₂.
- Embodiment 58. A compound of Embodiment 57 wherein Z is a direct bond.
- Embodiment 59. A compound of Embodiment 57 wherein Z is O.
- Embodiment 59a. A compound of Embodiment 57 wherein Z is CH₂.
- Embodiment 60. A compound of Formula 1 or any one of Embodiments 1 through 59a
30 wherein R⁹, R^{10b}, R^{11a} and R^{12c} are each H, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₂-C₄ alkenyl, C₂-C₄ haloalkenyl or C₂-C₄ alkynyl.
- Embodiment 61. A compound of Embodiment 60 wherein R⁹, R^{10b}, R^{11a} and R^{12c} are each H, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₂-C₄ alkenyl or C₂-C₄ haloalkenyl.
- Embodiment 62. A compound of Embodiment 61 wherein R⁹, R^{10b}, R^{11a} and R^{12c} are
35 each H, methyl, ethyl or C₂-C₄ alkenyl.
- Embodiment 63. A compound of Embodiment 62 wherein R⁹, R^{10b}, R^{11a} and R^{12c} are each H or methyl.

- Embodiment 64. A compound of Embodiment 63 wherein R^9 , R^{10b} , R^{11a} and R^{12c} are each H.
- Embodiment 65. A compound of Embodiment 63 wherein R^9 , R^{10b} , R^{11a} and R^{12c} are each methyl.
- 5 Embodiment 66. A compound of Formula 1 or any one of Embodiments 1 through 65 wherein R^{10a} , R^{11b} , R^{12a} and R^{12b} are each independently H, methyl or halomethyl.
- Embodiment 67. A compound of Embodiment 66 wherein R^{10a} , R^{11b} , R^{12a} and R^{12b} are each independently H or methyl.
- 10 Embodiment 68. A compound of Embodiment 67 wherein R^{10a} , R^{11b} , R^{12a} and R^{12b} are each H.
- Embodiment 69. A compound of Embodiment 68 wherein R^{10a} , R^{11b} , R^{12a} and R^{12b} are each methyl.
- Embodiment 70. A compound of Formula 1 or any one of Embodiments 1 through 69
15 wherein L is a direct bond, CH_2 , O, S, NR^{13} , OCH_2 , CH_2O or $C(=O)$.
- Embodiment 71. A compound of Embodiment 70 wherein L is a direct bond, CH_2 , O, OCH_2 , CH_2O or $C(=O)$.
- Embodiment 72. A compound of Embodiment 71 wherein L is a direct bond, CH_2 , O, OCH_2 or CH_2O .
- 20 Embodiment 73. A compound of Embodiment 72 wherein L is a direct bond, O or OCH_2 .
- Embodiment 74. A compound of Embodiment 72 wherein L is a direct bond.
- Embodiment 75. A compound of Embodiment 72 wherein L is CH_2 .
- Embodiment 76. A compound of Embodiment 72 wherein L is O.
- 25 Embodiment 77. A compound of Embodiment 72 wherein L is OCH_2 or CH_2O .
- Embodiment 78. A compound of Formula 1 or any one of Embodiments 1 through 797 wherein J is selected from J-1 through J-71 as depicted in Exhibit A

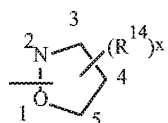
Exhibit A



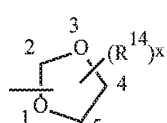




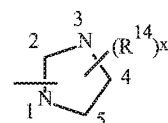
J-33



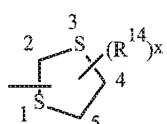
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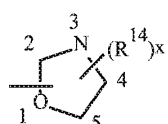
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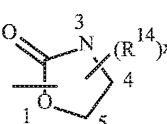
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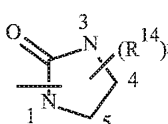
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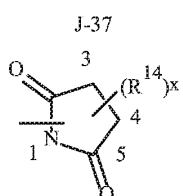
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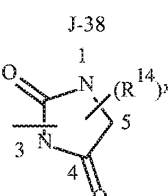
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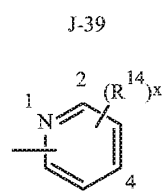
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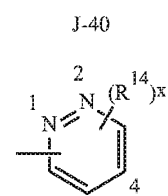
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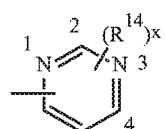
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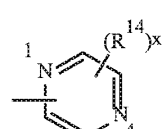
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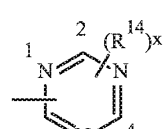
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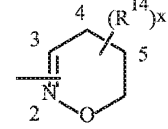
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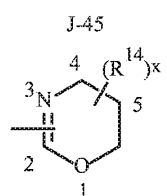
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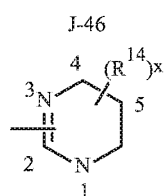
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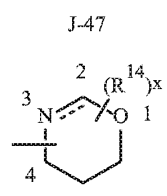
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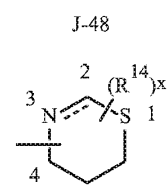
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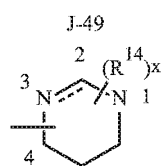
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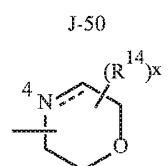
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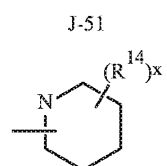
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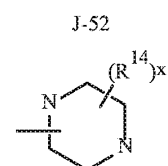
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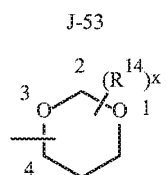
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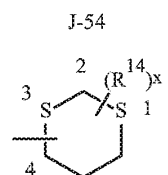
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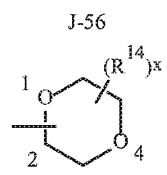
J-56



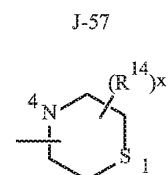
J-57



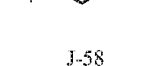
J-58



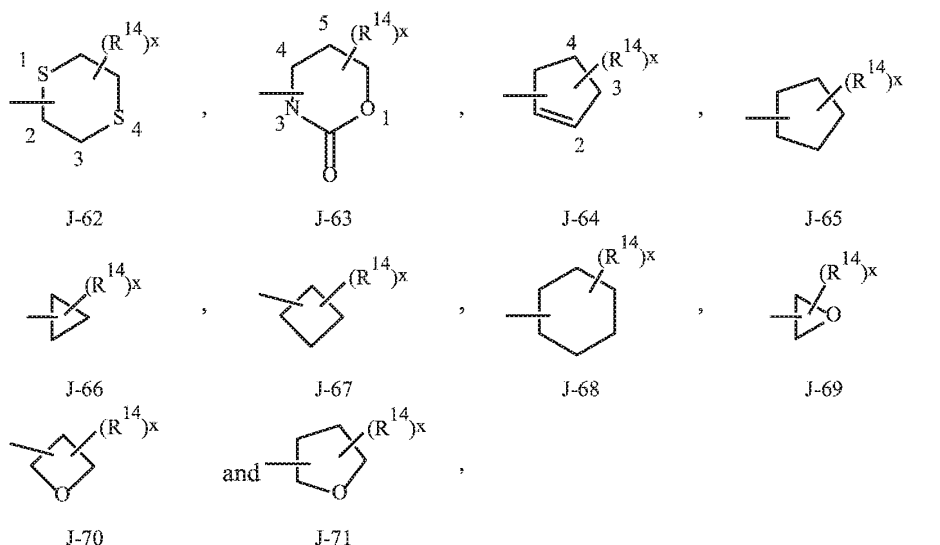
J-59



J-60



J-61



wherein the floating bond is connected to L through any available carbon or nitrogen atom of the depicted ring; and x is 0, 1, 2 or 3.

Embodiment 79. A compound of Embodiment 78 wherein J is J-4, J-5, J-6, J-7, J-8, J-9, J-18, J-19, J-20, J-21, J-22, J-23, J-24, J-25, J-26, J-27, J-34, J-35, J-36, J-37, J-38, J-56, J-57, J-58, J-59, J-60, J-61, J-63, J-64, J-65, J-66, J-67, J-69 or J-70.

Embodiment 80. A compound of Embodiment 79 wherein J is J-4, J-5, J-6, J-22, J-23, J-24, J-35, J-36, J-37, J-38, J-57, J-58, J-63, J-64, J-65, J-66, J-67, J-69 or J-70.

Embodiment 81. A compound of Embodiment 80 wherein J is J-6, J-22, J-35, J-37, J-58, J-64, J-65, J-66, J-67, J-69 or J-70.

Embodiment 82. A compound of Embodiment 81 wherein J is J-35.

Embodiment 83. A compound of Embodiment 81 wherein J is J-58.

Embodiment 84. A compound of Embodiment 81 wherein J is J-66.

Embodiment 85. A compound of Embodiment 81 wherein J is J-67.

Embodiment 86. A compound of Embodiment 81 wherein J is J-69.

Embodiment 87. A compound of Embodiment 81 wherein J is J-70.

Embodiment 88. A compound of Embodiment 81 wherein J is J-65, J-66 or J-67.

Embodiment 88a. A compound of Embodiment 88 wherein J is J-66 or J-67.

Embodiment 89. A compound of any one of Embodiments 78 through 88a wherein x is 0, 1 or 2.

Embodiment 89a. A compound of Embodiment 89 wherein x is 0 or 1.

Embodiment 90. A compound of any one of Embodiments 89 or 89a wherein x is 0.

Embodiment 91. A compound of Formula 1 or any one of Embodiments 1 through 89 wherein each R¹⁴ is independently halogen, cyano, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy or C(=O)OR¹⁵.

5 Embodiment 92. A compound of Embodiment 91 wherein each R¹⁴ is independently halogen, cyano, methyl, halomethyl, methoxy, halomethoxy or C(=O)OR¹⁵.

Embodiment 93. A compound of Embodiment 92 wherein each R¹⁴ is independently halogen, methyl, methoxy or C(=O)OR¹⁵.

Embodiment 94. A compound of Embodiment 93 wherein each R¹⁴ is independently halogen, methyl or C(=O)OR¹⁵.

10 Embodiment 95. A compound of Embodiment 94 wherein each R¹⁴ is independently halogen or methyl.

Embodiment 95a. A compound of Embodiment 95 wherein each R¹⁴ is independently Br, Cl, F or methyl.

15 Embodiment 96. A compound of Formula 1 or any one of Embodiments 1 through 94 wherein each R¹⁵ is independently C₁-C₃ alkyl, C₁-C₃ haloalkyl or cyclopropyl.

Embodiment 97. A compound of Embodiment 96 wherein each R¹⁵ is independently C₁-C₃ alkyl or C₁-C₃ haloalkyl.

Embodiment 98. A compound of Embodiment 97 wherein each R¹⁵ is independently methyl or ethyl.

20 Embodiment 99. A compound of Embodiment 98 wherein each R¹⁵ is methyl.

Embodiments of this invention, including Embodiments 1-99 above as well as any other embodiments described herein, can be combined in any manner, and the descriptions of variables in the embodiments pertain not only to the compounds of Formula 1 but also to the starting compounds and intermediate compounds useful for preparing the compounds of
25 Formula 1. In addition, embodiments of this invention, including Embodiments 1-99 above as well as any other embodiments described herein, and any combination thereof, pertain to the compositions and methods of the present invention.

Combinations of Embodiments 1-99 are illustrated by:

Embodiment A. A compound of Formula 1 wherein

30 A is A-1, A-3 or A-4;

Q is CR⁶;

Y is CR^{7a}CR^{7b};

W is O;

35 R¹ and R² are each independently halogen, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₂-C₄ alkoxyalkyl, C₁-C₃ alkoxy, C₁-C₃ haloalkoxy, C₂-C₄ alkenyloxy, C₂-C₄ haloalkenyloxy, C₂-C₄ alkoxyalkoxy or C₁-C₃ alkylthio;

R³ is H, methyl, methylcarbonyl or methoxycarbonyl;

R⁴ is methyl, methoxy, ethoxy, methylamino or dimethylamino;

each R⁵ is independently halogen or methyl;

R⁶ is H, halogen, nitro, amino, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₂-C₆ alkoxyalkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₂-C₆ alkenyloxy, C₂-C₆ haloalkenyloxy, C₂-C₆ alkynyloxy, C₂-C₆ haloalkynyloxy, C₂-C₆ alkoxyalkoxy, C₁-C₆ alkylthio, C₁-C₆ haloalkylthio, -ZC(=O)V, CR^{10a}=NOR^{10b}, CR^{12a}=NNR^{12b}R^{12c} or -L-J;

R^{7a} is H, halogen, methyl or methoxy;

R^{7b} is H or methyl;

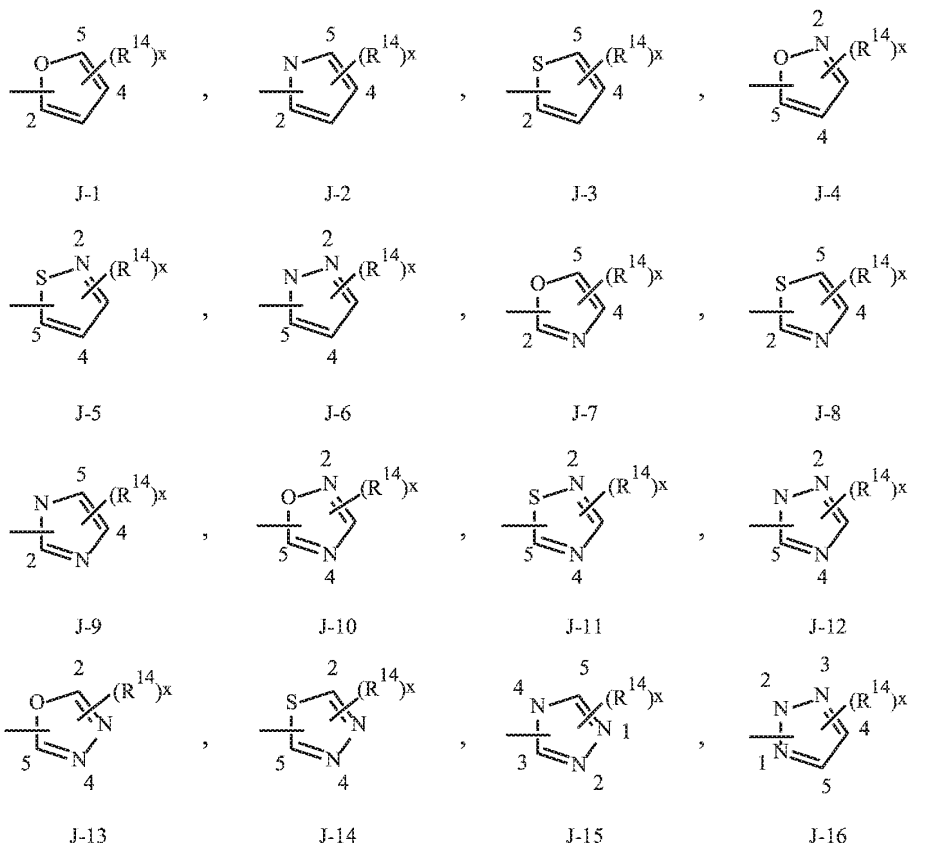
Z is a direct bond, O, NH, CH₂ or CH(OCH₃);

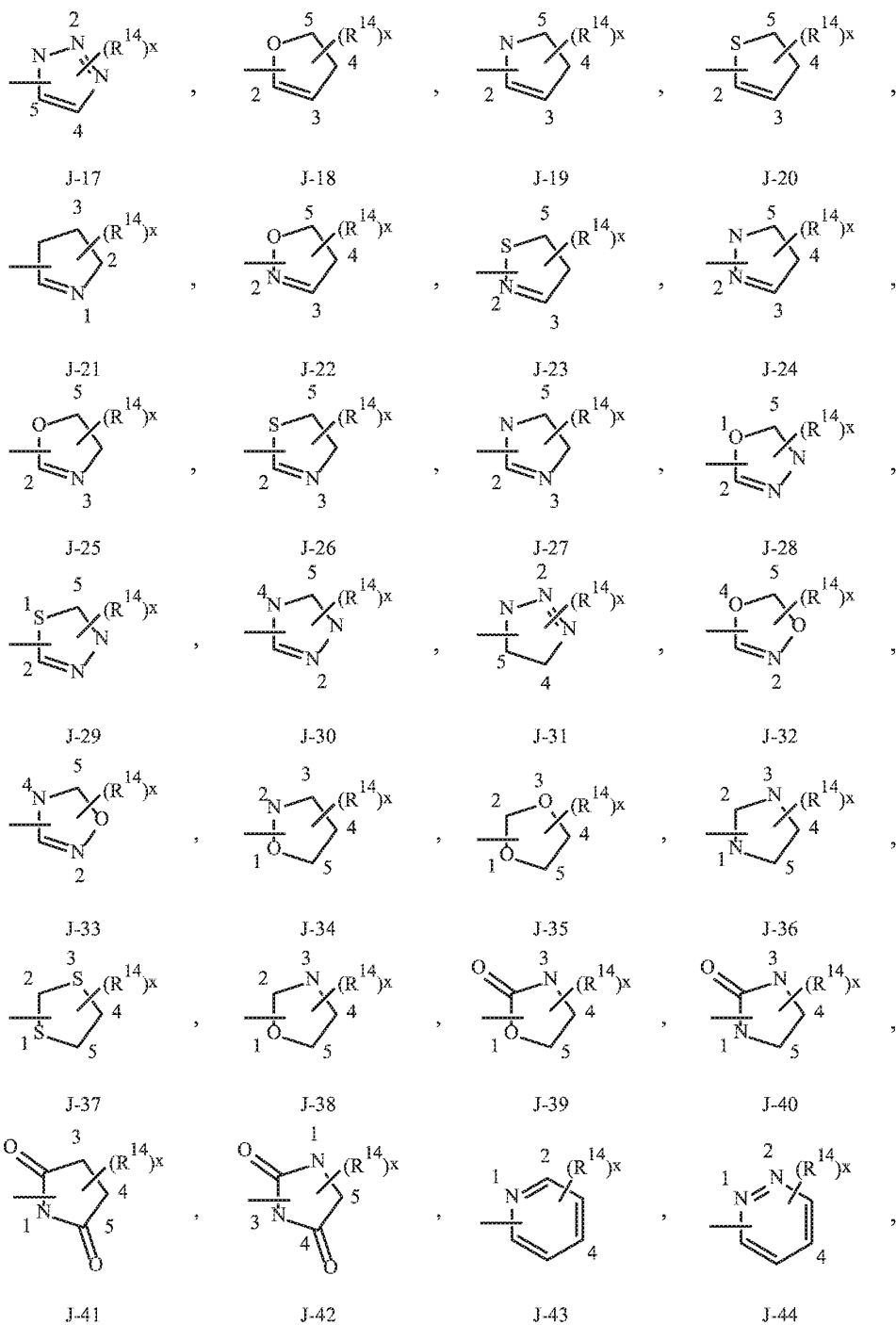
R⁹, R^{10b} and R^{12c} are each H, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₂-C₄ alkenyl or C₂-C₄ haloalkenyl;

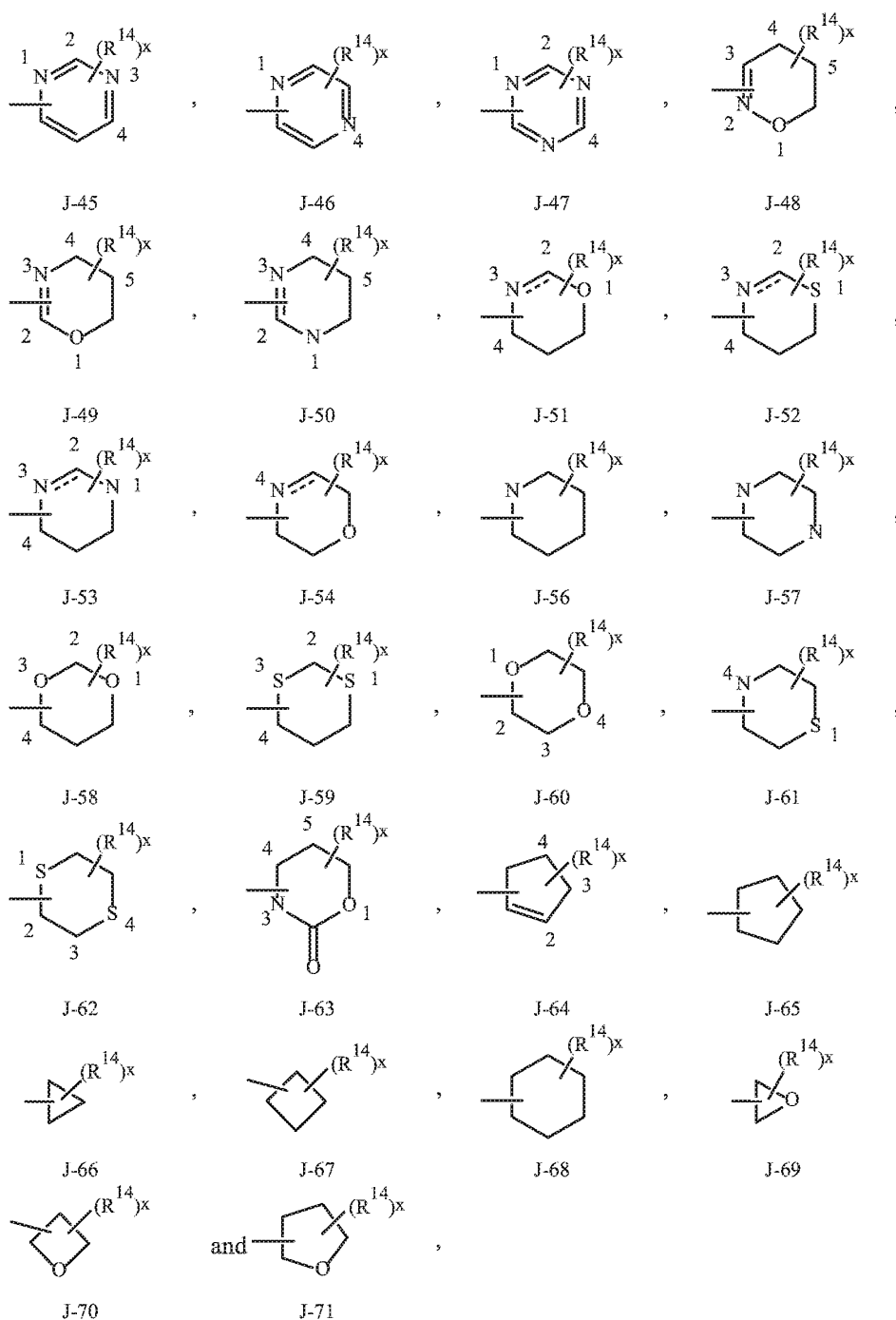
R^{10a}, R^{12a} and R^{12b} are each independently H, methyl or halomethyl;

L is a direct bond, CH₂, O, OCH₂ or CH₂O;

J is selected from J-1 through J-71







wherein the floating bond is connected to L through any available carbon or nitrogen atom of the depicted ring; and x is 0, 1, 2 or 3;

each R¹⁴ is independently independently halogen, methyl, methoxy or C(=O)OR¹⁵;
and

each R¹⁵ is independently C₁-C₃ alkyl, C₁-C₃ haloalkyl or cyclopropyl.

Embodiment B. A compound of Embodiment A wherein

- 5 A is A-1;
R¹ and R² are each independently Br, Cl, F, methyl, trifluoromethyl, methoxy or trifluoromethoxy;
R³ is H or methyl;
R⁴ is methyl, methoxy or ethoxy;
10 each R⁵ is methyl;
R⁶ is H, halogen, amino, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₁-C₃ alkoxy, C₁-C₃ haloalkoxy, C₂-C₄ alkenyloxy, C₂-C₄ haloalkenyloxy, CR^{10a}=NOR^{10b} or -L-J;
R^{7a} is H or methyl;
R^{7b} is H or methyl;
15 R^{10b} is H, methyl, C₂-C₄ alkenyl or C₂-C₄ haloalkenyl;
R^{10a} is H or methyl;
L is direct bond, O or OCH₂;
J is J-6, J-22, J-35, J-37, J-58, J-64, J-65, J-66, J-67, J-69 or J-70; and
each R¹⁴ is independently halogen or methyl.

20 Embodiment C. A compound of Embodiment B wherein

- R¹ and R² are each independently Cl, F or methyl;
R³ is H;
R⁴ is methoxy;
n is 0;
25 R⁶ is H, Br, Cl, I, amino, methyl, *i*-propyl, trifluoromethyl, CH₂F, CHF₂, methoxy, ethoxy, *i*-propyloxy, trifluoromethoxy, CH₂FO, CHF₂O, CH=NOCH₃, CH=NOCH₂CH₃, C(CH₃)=NOCH₃ or -L-J;
R^{7a} is H;
R^{7b} is H; and
30 J is J-65, J-66 or J-67.

Embodiment D. A compound of Embodiment C wherein

- R¹ and R² are each independently Cl or F;
R⁶ is H, Br, Cl, I, amino, methoxy, ethoxy, *i*-propyloxy, trifluoromethoxy, CHF₂O, C(CH₃)=NOCH₃ or -L-J;
35 J is J-66 or J-67;
x is 0, 1 or 2; and
R¹⁴ is Br, Cl, F or methyl.

Embodiment E. A compound of Embodiment D wherein

R¹ and R² are each F; and

R⁶ is H, Br, Cl, amino, methoxy, ethoxy or *i*-propyloxy.

Specific embodiments include compounds of Formula 1 selected from the group consisting of:

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- methyl *N*-[[5-[1-(2,6-difluoro-4-nitrophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 1);
- methyl *N*-[[5-[1-(2,6-difluoro-4-methoxyphenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 3);
- methyl *N*-[[5-[1-(2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 4);
- methyl *N*-[[5-[1-(4-amino-2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 5);
- methyl *N*-[[5-[1-(4-chloro-2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 6);
- methyl *N*-[[5-[1-(4-bromo-2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 7);
- methyl *N*-[[5-[1-(2,6-difluoro-4-iodophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 8);
- methyl *N*-[[5-[1-(2,6-difluoro-4-hydroxyphenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 10);
- methyl *N*-[[5-[1-(4-ethoxy-2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 11);
- methyl *N*-[[5-[1-[4-(cyclobutyloxy)-2,6-difluorophenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 13);
- methyl *N*-[[5-[1-[2,6-difluoro-4-(1-methylethoxy)phenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 14);
- methyl *N*-[[5-[1-[4-(difluoromethoxy)-2,6-difluorophenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 15);
- methyl *N*-[[5-[1-[2,6-difluoro-4-(2-propyn-1-yloxy)phenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 30);
- methyl *N*-[[5-[1-(2,6-difluoro-4-methoxyphenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 33);
- methyl *N*-[[5-[1-(4-cyclopropyl-2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 41);
- methyl *N*-[[5-[1-[4-[(1,1-dimethylethyl)thio]-2,6-difluorophenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 42);

methyl *N*-[[5-[1-[4-[(difluoromethyl)thio]-2,6-difluorophenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 43);

methyl *N*-[[5-[1-(4-ethynyl-2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 53);

methyl *N*-[[5-[1-[2,6-difluoro-4-(1-methylethyl)phenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 63);

methyl *N*-[[5-[1-[2,6-difluoro-4-(trifluoromethyl)phenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 64);

methyl *N*-[[5-[1-(2,6-dichloro-4-cyclopropylphenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 65);

methyl *N*-[[5-[1-[4-(cyclopropyloxy)-2,6-difluorophenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 66);

methyl *N*-[[5-[1-(2,6-difluoro-4-formylphenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 67);

methyl *N*-[[5-[1-(4-acetyl-2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 68);

methyl 3,5-difluoro-4-[3-[3-[(methoxycarbonyl)amino]methyl]-4-methylphenyl]-1*H*-pyrazol-1-yl]benzoate (Compound 70);

methyl *N*-[[5-[1-[2,6-difluoro-4-(hydroxymethyl)phenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 71);

methyl *N*-[[5-[1-[2,6-difluoro-4-(trifluoromethoxy)phenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 78);

methyl *N*-[[5-[1-[2,6-difluoro-4-[1-(methoxyimino)ethyl]phenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 83);

methyl *N*-[[5-[1-[4-(difluoromethyl)-2,6-difluorophenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 87);

methyl *N*-[[5-[2-[2,6-difluoro-4-(1-methylethyl)phenyl]-2*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate (Compound 108);

methyl *N*-[[5-[2-(4-amino-2,6-difluorophenyl)-2*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate (Compound 115);

methyl *N*-[[5-[2-(4-chloro-2,6-difluorophenyl)-2*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate (Compound 117);

methyl *N*-[[5-[2-(2,6-difluoro-4-nitrophenyl)-2*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate (Compound 118);

methyl *N*-[[5-[1-(4-chloro-2,6-difluorophenyl)-1*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate (Compound 121);

methyl *N*-[[5-[1-(4-amino-2,6-difluorophenyl)-1*H*-1,2,3-triazol-4-yl]-2-methyl-phenyl]methyl]carbamate (Compound 131); and
methyl *N*-[[5-[1-(2,6-difluoro-4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl]-2-methyl-phenyl]methyl]carbamate (Compound 132).

This invention provides a fungicidal composition comprising a compound of Formula 1 (including all stereoisomers, *N*-oxides, and salts thereof), and at least one other fungicide. Of note as embodiments of such compositions are compositions comprising a compound corresponding to any of the compound embodiments described above.

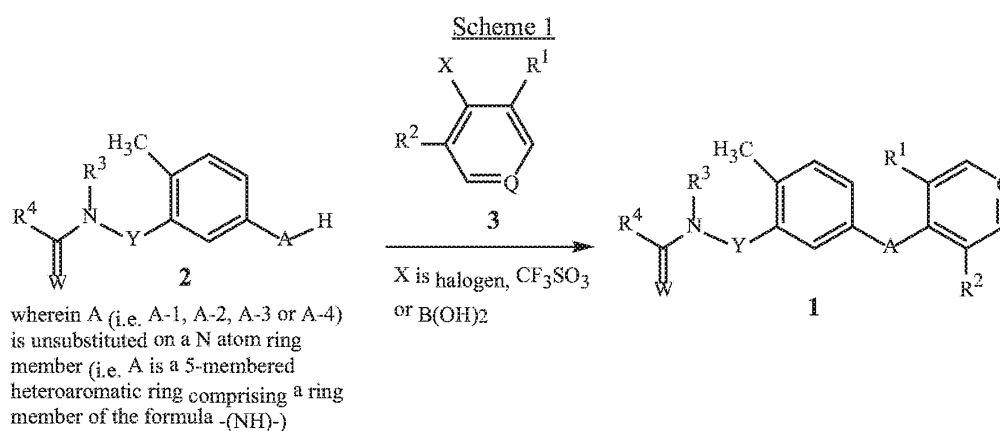
5 This invention provides a fungicidal composition comprising a compound of Formula 1 (including all stereoisomers, *N*-oxides, and salts thereof) (i.e. in a fungicidally effective amount), and at least one additional component selected from the group consisting of surfactants, solid diluents and liquid diluents. Of note as embodiments of such compositions are compositions comprising a compound corresponding to any of the compound embodiments
10 described above.

This invention provides a method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof, or to the plant seed, a fungicidally effective amount of a compound of Formula 1 (including all stereoisomers, *N*-oxides, and salts thereof). Of note as embodiments of such methods are methods comprising
15 applying a fungicidally effective amount of a compound corresponding to any of the compound embodiments describe above. Of particular note are embodiments where the compounds are applied as compositions of this invention.

One or more of the following methods and variations as described in Schemes 1-12 can be used to prepare the compounds of Formula 1. The definitions of A, Q, R¹, R², R³, R⁴, R⁵,
20 W, Y and n in the compounds of Formulae 1-16 below are as defined above in the Summary of the Invention unless otherwise noted. Compounds of Formulae 1a-1e are subsets of Formula 1, and all substituents for Formulae 1a-1e are as defined above for Formula 1 unless otherwise noted.

As shown in Scheme 1, compounds of Formula 1 can be prepared by reacting a
25 compound of Formula 2 with a compound of Formula 3 under copper or palladium catalyzed cross-coupling conditions. For compounds of Formula 3 wherein X is halogen or triflate, Ullmann or Buchwald-Hartwig conditions can be used. For relevant references, see for example, *Chemical Reviews* **2002**, 102(5), 1359-1470; *Angew. Chem. Int. Ed. Engl.* **2008**, 47(34), 6338-6361; and *Chem. Sci.* **2010**, 1(1), 13-31; and PCT patent application
30 WO 2014/066120. Also, present Example 1 illustrates the method of Scheme 1. These reactions typically require the presence of a base, such as a metal carbonate like potassium carbonate, and a suitable catalyst and ligand, such as copper(I) iodide and a ligand such as *trans*-1,2-diamino-*N,N'*-dimethylcyclohexane. The reaction is commonly run in an aprotic

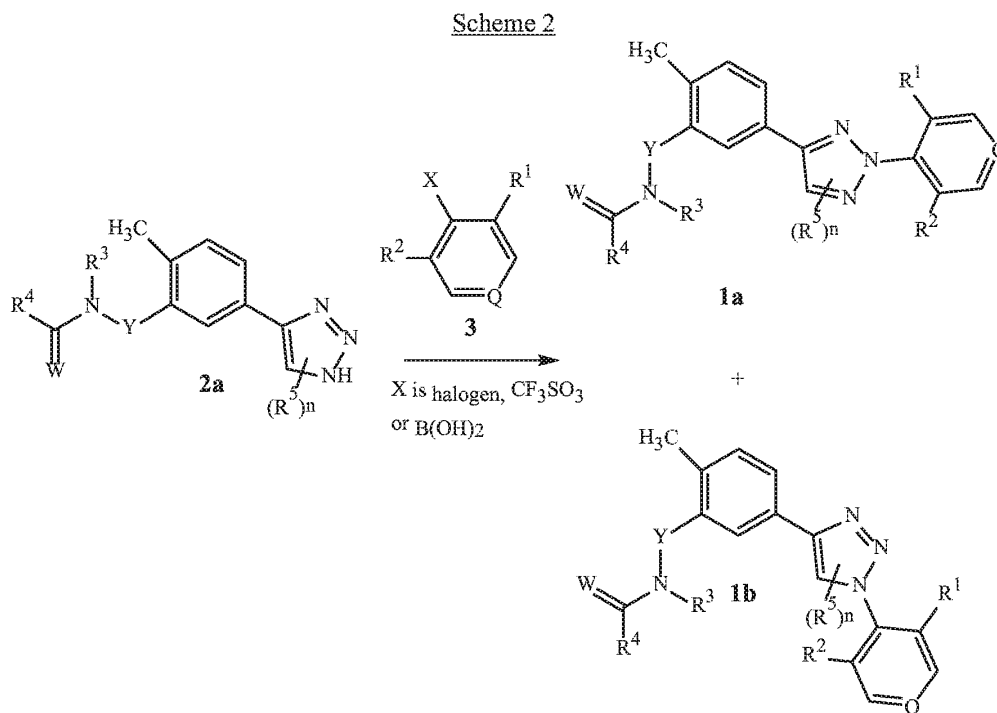
solvent such as dioxane or toluene at a temperature between ambient and the boiling point of the solvent. In cases where compounds of Formula 3 contain electron-withdrawing substituents (e.g., when R¹, R² and/or R⁶ are nitro, cyano or an ester) and X is halogen, direct nucleophilic displacement of X by compounds of Formula 2 can be achieved. These reactions are run in the presence of a base such as an alkali carbonate, hydride, alkoxide or trialkylamine at temperatures between about ambient to 130 °C in a solvent such as *N,N*-dimethylformamide, *N,N*-dimethylacetamide, dimethyl sulfoxide, dioxane, tetrahydrofuran or acetonitrile. For reactions conditions see, *Bioorganic & Medicinal Chemistry Letters* **2014**, 24(24), 5805-5813; *Bioorganic & Medicinal Chemistry Letters* **2010**, 20(15), 4521-4525; and *Journal of Materials Chemistry A: Materials for Energy and Sustainability* **2014**, 2(21), 7917-7926; and PCT patent application WO 2016/187667. Also, present Examples 2, 7, 11 and 17 (Step A) illustrate the preparation of a compound of Formula 1 by direct nucleophilic displacement. For compounds of Formula 3 wherein X is a boronic acid, Chan-Lam conditions can be used. These reactions are run in the presence of a suitable base such as pyridine or triethylamine and a catalyst such as copper(II) acetate. Typically the reaction is conducted in an aprotic solvent like dichloromethane or chloroform, at a temperature between about ambient and the boiling point of the solvent, and in the presence of oxygen. For leading references see for example, *Tetrahedron* **2018**, 74(5), 606-617; and *Tetrahedron Lett.* **1998**, 39(19), 2933-2936.



Compounds of Formula 3 are widely available from commercial sources and can easily be prepared using commercial precursors and known methods (see, for example, US 2013/0158004 and WO 2018/011094).

In some cases, the method of Scheme 1 results in two regioisomers. For example, as shown in Scheme 2, reaction of compounds of Formula 2a (i.e. Formula 2 wherein A is A-3) with a compound of Formula 3 typically provides an isomeric mixture of compounds of Formula 1a (i.e. Formula 1 wherein A is A-3) and Formula 1b (i.e. Formula 1 wherein A is

A-4). Purification of the regioisomers can be achieved using standard techniques such as column chromatography. For a relevant reference, see for example, PCT Patent Publication WO 2009/013211. Also, the method of Scheme 2 is illustrated in Example 18, Step F.

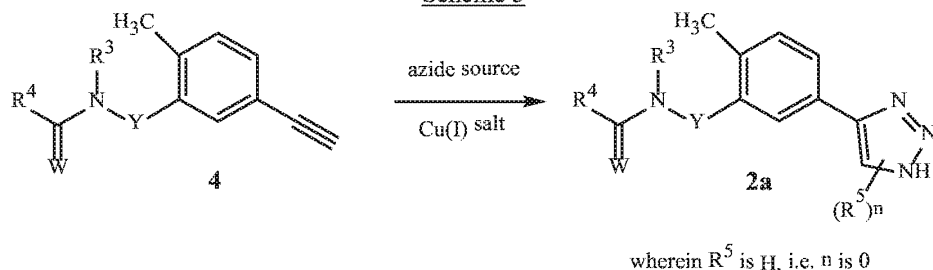


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As shown in Scheme 3, compounds of Formula **2a** can be prepared by reacting alkynes of Formula **4** with a suitable source of azide ions in the presence of a copper(I) salt. Suitable azide sources include, for example, trimethylsilyl azide and sodium azide. Suitable copper(I) salts include copper(I) iodide, copper(I) bromide and copper(I) chloride. Alternatively, a copper(II) salt can be used in combination with a mild reducing agent, for example copper(II) sulfate with sodium ascorbate. The reaction is typically run in a solvent such as *N,N*-dimethylformamide, tetrahydrofuran, methanol, *tert*-butanol, dimethyl sulfoxide (optionally comprising water), at temperatures from about 25 to 100 °C. The use of lower boiling solvents can in some cases necessitate the need for elevated pressure to facilitate running the reaction at temperatures higher than the normal boiling point of the solvent. For leading references, see for example, *Organic Letters* **2009**, 11(23), 5490-5493; *European J. Organic Chem.* **2004**, (18), 3789-3791; *Synlett* **2005**, (19), 2941-2947; and *Tetrahedron Letters* **2006**, 47(18), 3035-3038; and PCT Patent Publication WO 2004/072243. The method of Scheme 3 is also illustrated in present Example 18, Step E.

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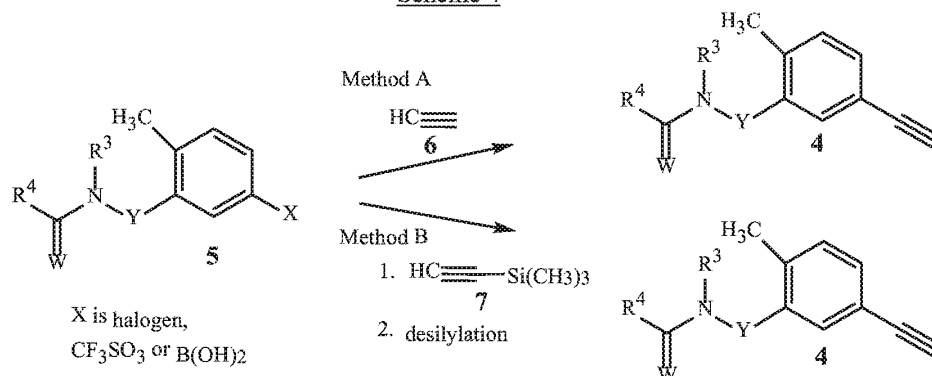
Scheme 3

wherein R⁵ is H, i.e. n is 0

- As shown below in Scheme 4, Method A, compounds of Formula **4** can be prepared from compounds of Formula **5** and alkynes of Formula **6** using Sonogashira reaction coupling conditions. Sonogashira couplings are well-known in the literature. See, for example, *Molecules* **2010**, *15*, 9157-9173; Sonogashira, K. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley-Interscience: New York, **2002**, pp 493-529; *Palladium in Heterocyclic Chemistry, A Guide for the Synthetic Chemist*, Li, J.; Gribble, G., Eds. in *Tetrahedron Organic Series*, Volume 20; Pergamon Press: New York, **2000**.
- As shown in Scheme 4, Method B, compounds of Formula **4** can be prepared by reacting a compound of Formula **5** with ethynyltrimethylsilane (Formula **7**) in the presence of a suitable palladium catalyst (such as tetrakis(triphenylphosphine)palladium or dichlorobis(triphenylphosphine)palladium(II)) and a suitable copper catalyst (such as copper(I) iodide). The reaction is preferably run in the presence of an amine base such as triethylamine, *N,N*-diisopropylethylamine, diethylamine or piperidine. The reaction is typically conducted in a solvent such as tetrahydrofuran, toluene or *N,N*-dimethylformamide; however, in some cases the reaction can be carried out without solvent other than the compound of Formula **5**, the ethynyltrimethylsilane and the amine base. Removal of the trimethylsilane group, to obtain a compound of Formula **4**, can be done using well-known conditions such as treatment with an alkali metal hydroxide or carbonate such as potassium hydroxide, sodium hydroxide or potassium carbonate in methanol or ethanol. The reaction is preferably conducted in a suitable organic solvent. Typically, the method is most satisfactorily conducted at a temperature ranging from about 0 °C to the reflux temperature of the solvent. For representative procedures, see *JACS* **2003**, *125*(38), 11545-11552 and *Bioorganic & Medicinal Chemistry* **2009**, *17*(24), 8149-8160; and present Example 18, Steps A and B.

30

Scheme 4

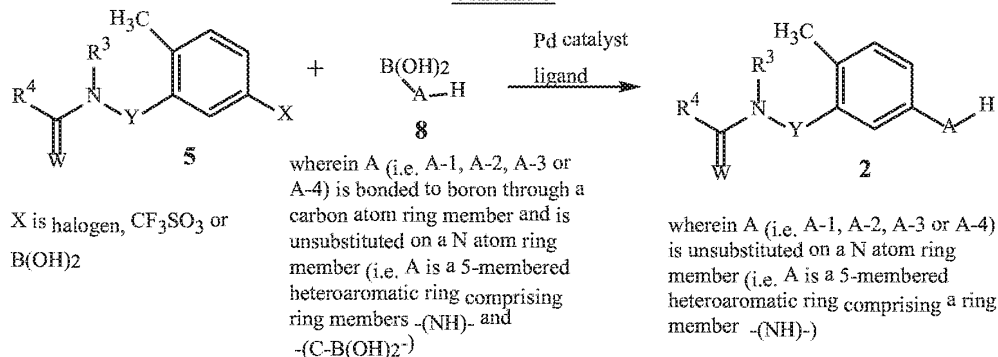


As shown in Scheme 5, Compounds of Formula 2 can be prepared by Suzuki coupling of compounds of Formula 5 with boron intermediates of Formula 8 wherein A (i.e. A-1, A-2, A-3 or A-4) is bonded to boron through a carbon atom ring member and is unsubstituted on a N atom ring member (i.e. A is a 5-membered heteroaromatic ring comprising ring members of -(NH)- and -(C-B(OH)₂)-). The reaction is run in the presence of Pd(0) or Pd(II) salts, a suitable ligand and a base. Suitable bases for this transformation are potassium carbonate or cesium carbonate, while Pd(II) salts such as Pd(OAc)₂ or PdCl₂ are used in conjunction with ligands such as triphenylphosphine or 1,1'-bis(diphenylphosphino)ferrocene (dppf). Conditions for Suzuki couplings are well documented in the literature; see, for example, *Angewandte Chemie International Edition* **2006**, 45(21), 3484-3488 and *Tetrahedron Letters* **2002**, 43(16), 2885-2888. Boron intermediates of Formula 8 are commercially available and can be prepared from corresponding halides or trifluoromethanesulfonates by methods known in the literature; see, for example, PCT Patent Publication WO 2007/043278; US Patent No. 8080566; *Organic Letters* **2011**, 13(6), 1366-1369; *European Journal of Medicinal Chemistry* **2014**, 87, 529-539 and *Organic Letters* **2012**, 14(2), 600-603.

Other coupling procedures offer a number of alternatives for introduction of the heterocyclic A ring onto Formula 5, including coupling methods published by Heck, Stille and Kumada. Also see, for example, Zifcsak *et al.*, *Tetrahedron* **2004**, 60, 8991-9016.

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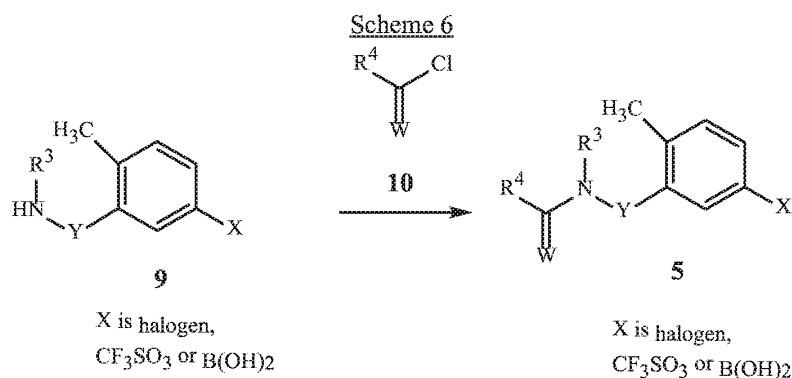
Scheme 5



As shown in Scheme 6, compounds of Formula 5 can be prepared by reacting an amine of Formula 9 with an acid chloride of Formula 10 in the presence of a base such as potassium carbonate, triethylamine or pyridine. The reaction can be carried out without solvent other than the compounds of Formulae 9, 10 and the base, or in a solvent such as acetonitrile, dichloromethane, chloroform, diethyl ether or tetrahydrofuran at temperatures ranging from about 0 to 50 °C. For reaction conditions see for example, PCT Patent Publication WO 2004/037770 and European patent EP 1586552. Also, the method of Scheme 6 is illustrated in present Example 18, Step D.

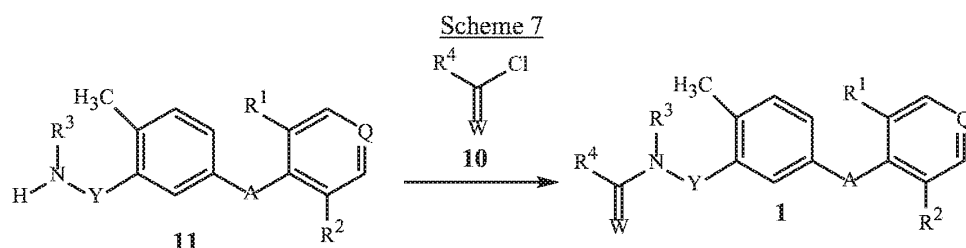
For synthesis of compounds of Formula 10, see *Advanced Organic Synthesis*, 4th Edition, Wiley & Sons 1992, 437, and references cited therein. Compounds of Formula 9 are commercially available and can be easily synthesized by general methods known to one skilled in the art.

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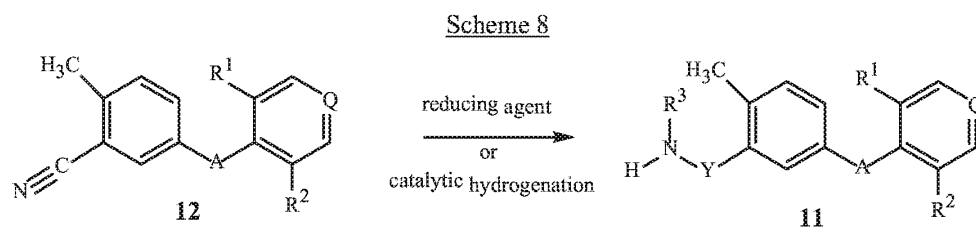
As shown in Scheme 7, compounds of Formula 1 can be prepared from compounds of Formula 11 by reaction with an acid chloride of Formula 10, analogous to the method of Scheme 6. The method of Scheme 7 is illustrated in present Example 17, Step F.

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As shown in Scheme 8, compounds of Formula **11** can be prepared from nitriles of Formula **12** using an appropriate reducing agent such as lithium aluminum hydride or a borane/tetrahydrofuran complex or tris(pentafluorophenyl)borane in an aprotic solvent such as tetrahydrofuran at a temperature between ambient and the boiling point of the solvent. For related examples, see the procedures and references contained within PCT patent applications WO 2011/079102 and WO 2011/073444. Also, the method of Scheme 8 is illustrated in present Example 17, Step E.

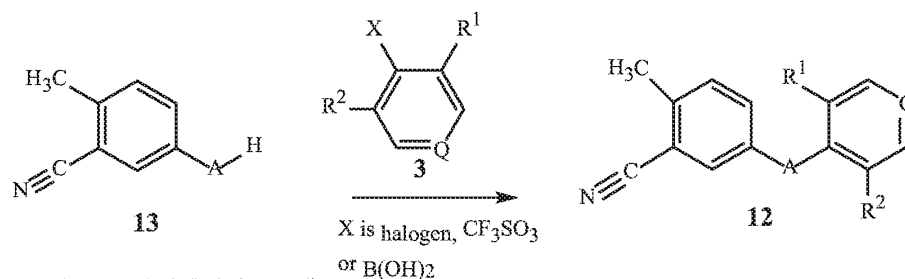
Nitriles of Formula **12** can also be converted to amines of Formula **11** by catalytic hydrogenation. These reactions are traditionally carried out in the presence of a transition metal catalyst such as palladium(0) on carbon, Raney nickel, or platinum oxide in a lower alcohol solvent such as methanol or ethanol at a temperature between ambient and 100 °C under an atmosphere of hydrogen gas at a pressure between 1 and 7500 kPa. For related examples, see the procedures and references contained within PCT patent applications WO 2009/152868 and WO 2010/023161.



As shown in Scheme 9, compounds of Formula **12** can be prepared by coupling compounds of Formula **13** wherein A (i.e. A-1, A-2, A-3 or A-4) is unsubstituted on a N atom ring member (i.e. A is a 5-membered heteroaromatic ring comprising a ring member -(NH)-) with compounds of Formula **3** using a method analogous to Scheme 1. Present Example 17, Step A, illustrates the method of Scheme 9.

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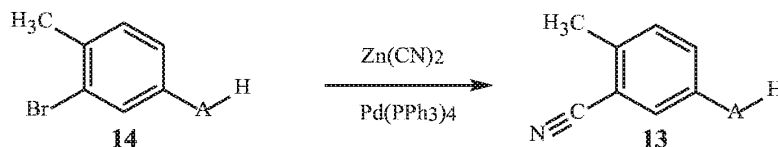
Scheme 9



wherein A (i.e. A-1, A-2, A-3 or A-4) is unsubstituted on a N atom ring member (i.e. A is a 5-membered heteroaromatic ring comprising a ring member $-(\text{NH})-$)

As shown in Scheme 10, compounds of Formula **13** can be prepared from compounds of Formula **14**. In a typical procedure, a compound of Formula **14** is contacted with a cyanide salt such as copper(I) cyanide or zinc(II) cyanide, in the presence of a suitable transition metal catalyst such as copper(I) iodide or tetrakis(triphenylphosphine) palladium(0), in a polar aprotic solvent such as *N,N*-dimethylformamide or dimethyl sulfoxide, at a temperature between about 50 to 150 °C. For related procedures see PCT patent applications WO 2012/032528 and WO 2011/133882 and references contained within.

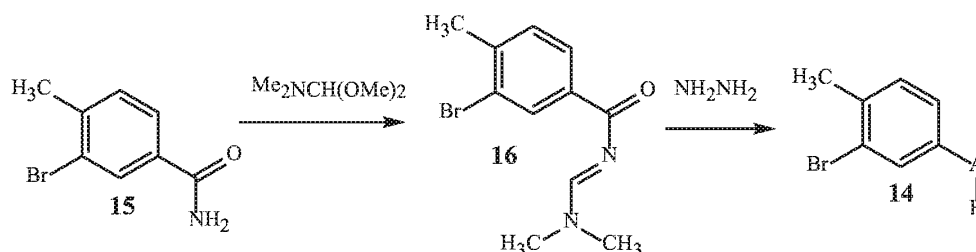
Scheme 10



As shown in Scheme 11, compounds of Formula **14** can be prepared by first reacting compounds of Formula **15** with *N,N*-dimethylformamide dimethyl acetal (DMF-DMA) at a temperature between about 40 to 100 °C in a solvent such as toluene or benzene, to provide an intermediate compound of Formula **16**. In a subsequent step, the compound of Formula **16** is reacted with hydrazine or a hydrazine salt in a lower alcohol solvent such as methanol or ethanol to provide a compound of Formula **14**.

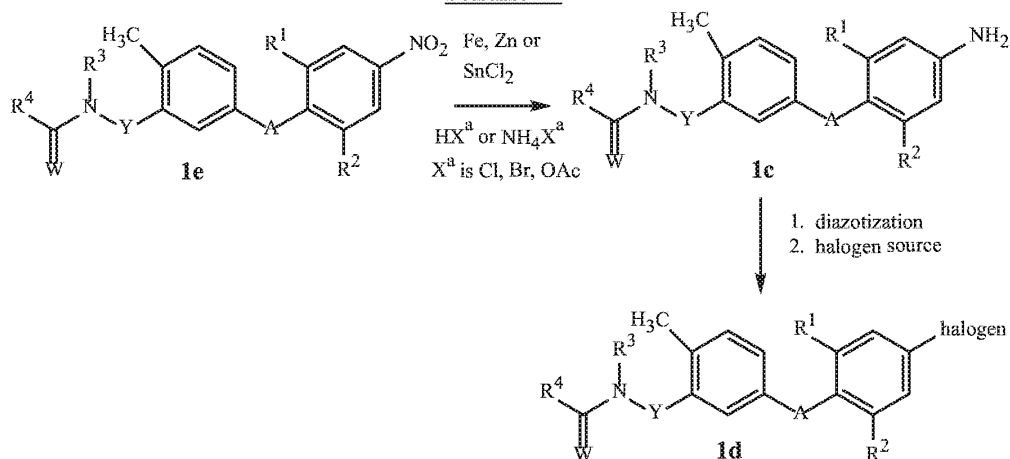
34

Scheme 11



Compounds of Formula 1 and their intermediates described herein can be subjected to various electrophilic, nucleophilic, organometallic, oxidation and reduction reactions to add substituents or modify existing substituents, and thus provide other functionalized compounds of Formula 1. For example, as shown in Scheme 12, compounds of Formula 1c (i.e. Formula 1 wherein Q is CR^6 and R^6 is NH_2) can be prepared by reduction of the corresponding nitro compounds of Formula 1e (i.e. Formula 1 wherein Q is CR^6 and R^6 is NO_2) using Fe, Zn or SnCl_2 in aqueous acidic solution at temperatures ranging from ambient to reflux. Alcohol co-solvents such as methanol, ethanol and *i*-propanol may also be employed. In a subsequent reaction, the amino compound of Formula 1c can be converted to a halogen under diazotization conditions in the presence of a halogen source to provide a Formula 1d (i.e. Formula 1 wherein Q is CR^6 and R^6 is halogen). A variety of halogen sources can be employed in the method of Scheme 12. The presence of a Lewis acid such as titanium(IV) isopropoxide can be advantageous. For example, addition of *tert*-butyl nitrite to a solution of an amino compound of Formula 1c in the presence of CuBr_2 in a solvent such as acetonitrile provides the corresponding bromide compound of Formula 1d. Likewise, amino compounds of Formula 1c can be converted to a diazonium salt and then to a corresponding compound of Formula 1d by treatment with sodium nitrite in solvents such as water, acetic acid or trifluoroacetic acid, in the presence of a mineral acid typically containing the same halide atom (such as aqueous HI solution for R^6 being I), followed by treatment with the corresponding copper(I) or copper(II) salt according to general procedures well-known to those skilled in the art. Many known reduction, diazotization and halogenation methods can be readily adapted to prepare compounds of Formulae 1c and 1d, for example, see the procedures and references contained within U.S. patent applications US 2017/0121300, US 2017/069105, and US 2017/038909, and PCT patent application WO 2017/036357. Also, the method of Scheme 12 is illustrated in present Examples 3 and 4.

Scheme 12



It is recognized that some reagents and reaction conditions described above for preparing compounds of Formula 1 may not be compatible with certain functionalities present in the intermediates. In these instances, the incorporation of protection/deprotection sequences or functional group interconversions into the synthesis will aid in obtaining the desired products. The use and choice of the protecting groups will be apparent to one skilled in chemical synthesis (see, for example, T. W. Greene and P. G. M. Wuts, *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley: New York, 1991). One skilled in the art will recognize that, in some cases, after the introduction of a given reagent as it is depicted in any individual scheme, it may be necessary to perform additional routine synthetic steps not described in detail to complete the synthesis of compounds of Formula 1. One skilled in the art will also recognize that it may be necessary to perform a combination of the steps illustrated in the above schemes in an order other than that implied by the particular sequence presented to prepare the compounds of Formula 1.

One skilled in the art will also recognize that compounds of Formula 1 and the intermediates described herein can be subjected to various electrophilic, nucleophilic, radical, organometallic, oxidation, and reduction reactions to add substituents or modify existing substituents.

Without further elaboration, it is believed that one skilled in the art using the preceding description can utilize the present invention to its fullest extent. The following examples are, therefore, to be construed as merely illustrative, and not limiting of the disclosure in any way whatsoever. Steps in the following examples illustrate a procedure for each step in an overall synthetic transformation, and the starting material for each step may not have necessarily been prepared by a particular preparative run whose procedure is described in other examples or steps. Percentages are by weight except for chromatographic solvent mixtures or where

otherwise indicated. Parts and percentages for chromatographic solvent mixtures are by volume unless otherwise indicated. ¹H NMR spectra are reported in ppm downfield from tetramethylsilane; “s” means singlet, “d” means doublet, “t” means triplet, “m” means multiplet, “br s” means broad singlet and “dd” means doublet of doublets. Mass spectra are reported as the molecular weight of the highest isotopic abundance parent ion (M+1) formed by addition of H⁺ (molecular weight of 1) to the molecule, observed by using liquid chromatography coupled to a mass spectrometer (LCMS) using either atmospheric pressure chemical ionization (AP⁺) or electrospray ionization (ESI⁺).

EXAMPLE 1

10 Preparation of methyl *N*-[[5-[1-(2,6-difluoro-4-methoxyphenyl)-1*H*-pyrazol-3-yl]-2-methyl-phenyl]methyl]carbamate (Compound 3)

To a mixture of methyl *N*-[[2-methyl-5-(1*H*-pyrazol-3-yl)phenyl]methyl]carbamate (1.12 g, 4.57 mmol) (see PCT Patent Publication WO 2008124092 for a method of preparation), copper(I) iodide (0.17 g, 0.914 mmol) and 2-bromo-1,3-difluoro-5-methoxy-
15 benzene (1.32 g, 5.94 mmol) was added potassium carbonate (11.4 mmol) followed by *N,N*-dimethylformamide (8 mL). Nitrogen gas was bubbled into the reaction mixture for 30 minutes, then *trans-N,N'*-dimethylcyclohexane-1,2-diamine (0.26 g, 1.83 mmol) was added. The reaction mixture was heated at 80 °C overnight, cooled to room temperature and diluted with ethyl acetate. The resulting mixture was washed with saturated aqueous sodium chloride
20 solution (4x), dried over magnesium sulfate, filtered and concentrated under reduced pressure. The resulting material was purified by silica gel column chromatography (eluting with a gradient of 20 to 80% ethyl acetate in hexanes) to provide the title compound, a compound of the present invention, as a colorless oil (0.43 g).

¹H NMR (CDCl₃): δ 7.74 (d, 1H), 7.67 (dd, 1H), 7.59 (d, 1H), 7.22 (d, 1H), 6.74 (d, 1H), 6.61
25 (d, 2H), 4.87 (br s, 1H), 4.41 (d, 2H), 3.84 (s, 3H), 3.69 (s, 3H), 2.36 (s, 3H).

LCMS: m/z: 388 [M+H]⁺

EXAMPLE 2

Preparation of methyl *N*-[[5-[1-(2,6-difluoro-4-nitrophenyl)-1*H*-pyrazol-3-yl]-2-methyl-phenyl]methyl]carbamate (Compound 1)

30 To a stirred solution of methyl *N*-[[2-methyl-5-(1*H*-pyrazol-3-yl)phenyl]methyl]carbamate (0.45 g, 1.84 mmol) (see PCT Patent Publication WO 2008124092 for a method of preparation) in dimethyl sulfoxide (5 mL) was added potassium carbonate (762 mg, 5.52 mmol) and 1,2,3-trifluoro-5-nitrobenzene (0.235 mL, 2.02 mmol). The reaction mixture was stirred at room temperature overnight and diluted with ethyl acetate. The resulting mixture
35 washed with saturated aqueous sodium chloride solution (4x), dried over magnesium sulfate, filtered and concentrated under reduced pressure. The resulting material was purified by

column chromatography (eluting with a gradient of 10 to 50% ethyl acetate in hexanes) to provide the title compound, a compound of the present invention, as a yellow solid (0.44 g).

¹H NMR (CDCl₃): δ 8.02 (d, 2H), 7.79 (dd, 1H), 7.75 (d, 1H), 7.69 (dd, 1H), 7.25 (d, 1H), 6.85 (d, 1H), 4.86 (br s, 1H), 4.44 (d, 2H), 3.71 (s, 3H), 2.38 (s, 3H).

5

EXAMPLE 3

Preparation of methyl *N*-[[5-[1-(4-amino-2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 5)

To a mixture of methyl *N*-[[5-[1-(2,6-difluoro-4-nitrophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (i.e. the product of Example 2) (0.4 g, 0.995 mmol) and ammonium chloride (32 mg, 0.597 mmol) in ethanol/water (9:1, 20 mL) was added iron powder (555 mg, 9.95 mmol) portionwise. The reaction mixture was heated at reflux for 1.5 h, and then cooled to room temperature and filtered through a pad of Celite® (diatomaceous filter aid), rinsing with ethyl acetate. The filtrate was washed with saturated aqueous sodium chloride solution (4x), dried over magnesium sulfate, filtered and concentrated under reduced pressure. The resulting material was purified by silica gel column chromatography (eluting with a gradient of 30 to 100% ethyl acetate in hexanes) to provide the title compound, a compound of the present invention, as a light-yellow solid (0.3 g).

¹H NMR (CDCl₃): δ 7.75 (d, 1H), 7.66 (dd, 1H), 7.56 (d, 1H), 7.21 (d, 1H), 6.72 (d, 1H), 6.31 (d, 2H), 4.82 (br s, 1H), 4.41 (d, 2H), 4.04 (br s, 2H), 3.69 (s, 3H), 2.36 (s, 3H).

20

EXAMPLE 4

Preparation of methyl *N*-[[5-[1-(4-bromo-2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 7)

To a mixture of methyl *N*-[[5-[1-(4-amino-2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (i.e. the product of Example 3) (90 mg, 0.242 mmol) in acetonitrile (2 mL) was added copper(II) bromide (65 mg, 0.290 mmol). The reaction mixture was cooled to about 0 °C and *n*-butyl nitrite (0.043 mL, 0.363 mmol) was added. The reaction mixture was stirred at room temperature overnight, and then quenched with hydrochloric acid (1 N aqueous solution). The resulting mixture was extracted with ethyl acetate (2x), and the combined extracts were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The resulting material was purified by silica gel column chromatography (eluting with a gradient of 10 to 40% ethyl acetate in hexanes). The resulting material was further purified by column chromatography (eluting with a gradient of 0 to 10% ethyl acetate in dichloromethane) to provide the title compound, a compound of the present invention, as a yellow oil (49 mg).

¹H NMR (CDCl₃): δ 7.74 (d, 1H), 7.67-7.65 (m, 2H), 7.29 (d, 2H), 7.23 (d, 1H), 6.78 (d, 1H), 4.83 (br s, 1H), 4.42 (d, 2H), 3.70 (s, 3H), 2.37 (s, 3H).

LCMS: m/z: 436 [M+H]⁺

EXAMPLE 5

Preparation of methyl *N*-[[5-[1-(2,6-difluoro-4-hydroxyphenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 10)

- 5 To a mixture of methyl *N*-[[5-[1-(2,6-difluoro-4-methoxyphenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (i.e. the product of Example 1) (1.20 g, 3.10 mmol) in dichloromethane (30 mL) at 0 °C was added boron tribromide (1 M solution in dichloromethane, 9.40 mL, 9.30 mmol) dropwise. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was slowly quenched with
10 water (35 mL), followed by a dropwise addition of methanol (35 mL), and then stirred at room temperature for 1 h. The layers were separated and the aqueous layer was extracted with dichloromethane (2x). The combined organic extracts were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The resulting material was purified by silica gel column chromatography (eluting with a gradient of 20 to 70% ethyl acetate in hexanes) to
15 provide the title compound, a compound of the present invention, as a white solid (0.87 g).
¹H NMR (CDCl₃): δ 7.74 (br s, 1H), 7.63 (dd, 1H), 7.60 (d, 1H), 7.24 (d, 1H), 6.75 (d, 1H), 6.46 (d, 2H), 4.95 (br s, 1H), 4.42 (d, 2H), 3.69 (s, 3H), 2.37 (s, 3H).

EXAMPLE 6

Preparation of methyl *N*-[[5-[1-[2,6-difluoro-4-(1-methylethoxy)phenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 14)

- 20 To a mixture of methyl *N*-[[5-[1-(2,6-difluoro-4-hydroxyphenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (i.e. the product of Example 5) (87 mg) in tetrahydrofuran (3 mL) was added triphenylphosphine (122 mg, 0.46 mmol), followed by 2-propanol (0.035 mL, 0.46 mmol) and diethyl azodicarboxylate (0.073 mL, 0.46 mmol). The reaction
25 mixture was stirred at room temperature for 48 h and concentrated under reduced pressure. The resulting material was purified by silica gel column chromatography (eluting with a gradient of 10 to 50% ethyl acetate in hexanes) to provide the title compound, a compound of the present invention, as a white solid (85 mg).
¹H NMR (CDCl₃): δ 7.75 (d, 1H), 7.67 (dd, 1H), 7.59 (d, 1H), 7.22 (d, 1H), 6.74 (d, 1H), 6.58
30 (d, 2H), 4.54 (m, 1H), 4.83 (br s, 1H), 4.42 (d, 2H), 3.70 (s, 3H), 2.36 (s, 3H), 1.37 (d, 6H).
LCMS: m/z: 416 [M+H]⁺

EXAMPLE 7

Preparation of methyl 3,5-difluoro-4-[3-[3-[(methoxycarbonyl)amino]methyl]-4-methylphenyl]-1*H*-pyrazol-1-yl]benzoate (Compound 70)

- 35 To a mixture of methyl *N*-[[2-methyl-5-(1*H*-pyrazol-3-yl)phenyl]methyl]carbamate (2.58 g, 10.5 mmol) (see PCT Patent Publication WO 2008124092 for a method of preparation)

and methyl 3,4,5-trifluorobenzoate (2.41 g, 12.6 mmol) in dimethyl sulfoxide (10 mL) was added potassium carbonate (4.35 g, 31.5 mmol). The reaction mixture was stirred at room temperature for 48 h and diluted with ethyl acetate. The resulting mixture was washed with saturated aqueous ammonium chloride solution (4x), dried over magnesium sulfate, filtered and concentrated under reduced pressure. The resulting material was purified by column chromatography (eluting with a gradient of 10 to 50% ethyl acetate in hexanes) to provide the title compound, a compound of the present invention, as a light pink solid (3.55 g).

¹H NMR (CDCl₃): δ 7.76 (d, 2H), 7.74 (m, 2H), 7.68 (d, 1H), 7.24 (d, 1H), 6.80 (d, 1H), 4.87 (br s, 1H), 4.42 (d, 2H), 3.97 (s, 3H), 3.70 (s, 3H), 2.37 (s, 3H).

EXAMPLE 8

Preparation of methyl *N*-[[5-[1-[2,6-difluoro-4-(hydroxymethyl)phenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 71)

To a mixture of methyl 3,5-difluoro-4-[3-[3-[[[(methoxycarbonyl)amino]methyl]-4-methylphenyl]-1*H*-pyrazol-1-yl]benzoate (i.e. the product Example 7) (3.55 g, 8.55 mmol) in methanol (45 mL) was added sodium borohydride (1.94 g, 51.3 mmol) portionwise. The reaction mixture was stirred at room temperature overnight, then quenched with hydrochloric acid (1 N aqueous solution) and filtered. The filtrate was extracted with ethyl acetate (3x) and the combined extracts were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The resulting material was purified by silica gel column chromatography (eluting with a gradient of 20 to 100% ethyl acetate in hexanes) to provide the title compound, a compound of the present invention, as a white solid (2.52 g).

¹H NMR (DMSO-*d*₆): δ 8.11 (d, 1H), 7.73 (d, 1H), 7.65 (t, 1H), 7.62 (dd, 1H), 7.29 (d, 1H), 7.22 (d, 1H), 6.94 (d, 1H), 5.59 (t, 1H), 4.60 (d, 2H), 4.21 (d, 2H), 3.55 (s, 3H), 2.30 (s, 3H).

EXAMPLE 9

Preparation of methyl *N*-[[5-[1-(2,6-difluoro-4-formylphenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 67)

To a mixture of methyl *N*-[[5-[1-[2,6-difluoro-4-(hydroxymethyl)phenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (i.e. the product of Example 8) (2.30 g, 5.94 mmol) in tetrahydrofuran (70 mL) was added Dess-Martin periodinane (2.52 g, 5.94 mmol) portionwise. The reaction mixture was stirred at room temperature overnight, then quenched with aqueous sodium carbonate solution and extracted with ethyl acetate (2x). The combined extracts were filtered, rinsed with ethyl acetate. The filtrate was washed with saturated aqueous sodium bicarbonate solution (3x), dried over magnesium sulfate, filtered and concentrated under reduced pressure. The resulting material was purified by silica gel column chromatography (eluting with a gradient of 20 to 60% ethyl acetate in hexanes) to provide the title compound, a compound of the present invention, as a white solid (1.78 g).

¹H NMR (CDCl₃): δ 9.98 (t, 1H), 7.76 (m, 2H), 7.69 (dd, 1H), 7.62 (d, 2H), 7.24 (d, 1H), 6.83 (d, 1H), 4.86 (br s, 1H), 4.43 (d, 2H), 3.71 (s, 3H), 2.38 (s, 3H).

EXAMPLE 10

Preparation of methyl *N*-[[5-[1-[4-(difluoromethyl)-2,6-difluorophenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 87)

To a mixture of methyl *N*-[[5-[1-(2,6-difluoro-4-formylphenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (i.e. the product of Example 9) (0.25 g, 0.65 mmol) in dichloromethane (10 mL) at about 0 °C was added Deoxo-Fluor® (0.36 mL, 1.95 mmol) dropwise, followed by ethanol (1 drop). The reaction mixture was stirred at room temperature overnight, and then slowly poured into a solution of saturated aqueous sodium carbonate (200 mL). After 30 minutes, the layers were separated, and the aqueous layer was extracted with dichloromethane (1x). The combined organics were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The resulting material was purified by silica gel column chromatography (eluting with a gradient of 10 to 50% ethyl acetate in hexanes) to provide the title compound, a compound of the present invention, as a colorless oil (0.23 g).
¹H NMR (CDCl₃): δ 7.75 (d, 1H), 7.71-7.68 (m, 2H), 7.27 (d, 2H), 7.23 (d, 1H), 6.80 (d, 1H), 6.78-6.55 (t, 1H), 4.85 (br s, 1H), 4.42 (d, 2H), 3.70 (s, 3H), 2.37 (s, 3H).
LCMS: m/z: 408 [M+H]⁺

EXAMPLE 11

Preparation of methyl *N*-[[5-[1-(4-acetyl-2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 68)

To a mixture of methyl *N*-[[2-methyl-5-(1*H*-pyrazol-3-yl)phenyl]methyl]carbamate (2.0 g, 8.16 mmol) (see PCT Patent Publication WO 2008124092 for a method of preparation) and 1-(3,4,5-trifluorophenyl)ethanone (2.0 g, 11.4 mmol) in dimethyl sulfoxide (9 mL) was added potassium carbonate (3.38 g, 24.5 mmol). The reaction mixture was stirred at room temperature overnight, and then diluted with ethyl acetate. The resulting mixture was washed with saturated aqueous ammonium chloride solution (4x), dried over magnesium sulfate, filtered and concentrated under reduced pressure. The resulting material was purified by silica gel column chromatography (eluting with a gradient of 10 to 70% ethyl acetate in hexanes) to provide the title compound, a compound of the present invention, as a pale-orange solid (2.10 g).
¹H NMR (CDCl₃): δ 7.75 (m, 2H), 7.69 (dd, 1H), 7.67 (d, 2H), 7.24 (d, 1H), 6.81 (d, 1H), 4.87 (br s, 1H), 4.43 (d, 2H), 3.70 (s, 3H), 2.64 (s, 3H), 2.37 (s, 3H).

EXAMPLE 12

Preparation of methyl *N*-[[5-[1-[2,6-difluoro-4-[1-(methoxyimino)ethyl]phenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 83)

A mixture of methyl *N*-[[5-[1-(4-acetyl-2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (i.e. the product of Example 11) (0.24 g, 0.602 mmol), *O*-methylhydroxylamine hydrochloride (60.3 mg, 0.722 mmol) and sodium acetate (59.2 mg, 0.722 mmol) in ethanol was heated at reflux overnight. The reaction mixture was cooled to room temperature and diluted with water. The resulting mixture was extracted with ethyl acetate (2x) and the combined extracts were dried over magnesium sulfate, filtered and concentrated under reduced pressure to provide the title compound, a compound of the present invention, as an amber-colored solid. (239 mg)

¹H NMR (CDCl₃): δ 7.75 (d, 1H), 7.68 (m, 2H), 7.41 (d, 2H), 7.23 (d, 1H), 6.78 (d, 1H), 4.85 (br s, 1H), 4.42 (d, 2H), 4.04 (s, 3H), 3.70 (s, 3H), 2.37 (s, 3H), 2.21 (s, 3H).

LCMS: m/z: 429 [M+H]⁺

EXAMPLE 13

Preparation of methyl *N*-[[5-[1-(2,6-difluoro-4-iodophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 8)

To a mixture of methyl *N*-[[5-[1-(4-amino-2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (i.e. the product of Example 3) (2.38 g, 6.40 mmol) in acetonitrile (50 mL) was added diiodomethane (2.1 mL, 25.6 mmol). The reaction mixture was cooled to about 0 °C, and then *tert*-butyl nitrite (0.84 mL, 7.04 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 5 h, and then more diiodomethane (12 mL, 150 mmol) was added. After stirring overnight, the reaction mixture was diluted with ethyl acetate and washed with saturated sodium metabisulfite solution (3x), saturated sodium chloride solution (2x) and hydrochloric acid (1 N aqueous solution). The mixture was dried over magnesium sulfate, filtered and concentrated under reduced pressure. The resulting material was purified by silica gel column chromatography (eluting with a gradient of 0 to 10% ethyl acetate in hexanes) to provide the title compound, a compound of the present invention, as an off-white solid (1.0 g).

¹H NMR (CDCl₃): δ 7.73 (d, 1H), 7.66-7.64 (m, 2H), 7.47 (d, 2H), 7.22 (d, 1H), 6.77 (d, 1H), 4.86 (br s, 1H), 4.42 (d, 2H), 3.70 (s, 3H), 2.36 (s, 3H).

EXAMPLE 14

Preparation of methyl *N*-[[5-[1-(4-ethynyl-2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 53)

Step A: Preparation of methyl *N*-[[5-[1-(2,6-difluorophenyl)-4-(2-(trimethylsilyl)ethynyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate

- To a mixture of methyl *N*-[[5-[1-(2,6-difluoro-4-iodophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (i.e. the product of Example 13) (0.2 g, 0.414 mmol), copper(I) iodide (8 mg, 0.041 mmol), *N,N*-dimethylformamide (4 mL), ethynyltrimethylsilane (0.088 mL, 0.621 mmol) and dichlorobis(triphenylphosphine)palladium (29 mg, 0.041 mmol) was added triethylamine (0.063 mL, 0.455 mmol). The reaction mixture was stirred at room temperature overnight, then diluted with ethyl acetate, washed with saturated sodium chloride solution (4x), dried over magnesium sulfate, filtered and concentrated under reduced pressure.
- The resulting material was purified by silica gel column chromatography (eluting with a gradient of 5 to 40% ethyl acetate in hexanes) to provide the title compound as a light brown oil (0.17 g).
- ¹H NMR (CDCl₃): δ 7.74 (d, 1H), 7.67 (m, 2H), 7.23 (d, 1H), 7.16 (d, 2H), 6.77 (d, 1H), 4.84 (br s, 1H), 4.42 (d, 2H), 3.70 (s, 3H), 2.37 (s, 3H), 0.27 (s, 9H).

Step B: Preparation of methyl *N*-[[5-[1-(4-ethynyl-2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 53)

- To a mixture of methyl *N*-[[5-[1-(2,6-difluorophenyl)-4-(2-(trimethylsilyl)ethynyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (i.e. the product of Step A) (0.12 g, 0.265 mmol) in methanol (6 mL) was added potassium carbonate (44 mg, 0.318 mmol). The reaction mixture was stirred at room temperature for 1.5 h, then diluted with ethyl acetate and water, and allowed to stand at room temperature overnight. The resulting mixture was washed with saturated sodium chloride solution (2x), dried over magnesium sulfate, filtered and concentrated under reduced pressure. The resulting material was purified by silica gel column chromatography (eluting with a gradient of 10 to 50% ethyl acetate in hexanes) to provide the title compound, a compound of the present invention, as an amber oil (0.109 g).
- ¹H NMR (CDCl₃): δ 7.75 (d, 1H), 7.68-7.66 (m, 2H), 7.23 (d, 1H), 7.20 (d, 2H), 6.78 (d, 1H), 4.84 (br s, 1H), 4.42 (d, 2H), 3.70 (s, 3H), 3.24 (s, 1H), 2.37 (s, 3H).
- LCMS *m/z*: 382 [M+H]⁺

EXAMPLE 15

Preparation of methyl *N*-[[5-[1-[4-[(1,1-dimethylethyl)thio]-2,6-difluorophenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 42)

- A mixture of methyl *N*-[[5-[1-(2,6-difluoro-4-iodophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (i.e. the product of Example 13) (0.217 g, 0.450 mmol) and *N,N*-dimethylformamide (2 mL) was purged with a stream of nitrogen gas for 10 to 15 minutes, and then tetrakis(triphenylphosphine)palladium (52 mg, 0.045 mmol) was added, followed by 2-methyl-2-propanethiol (0.100 mL, 0.900 mmol) and triethylamine (0.20 mL, 1.35 mmol). The reaction mixture was heated at 70 °C for 1 h, then cooled to room temperature, and diluted

with ethyl acetate. The resulting mixture was washed with saturated sodium chloride solution (3x), dried over magnesium sulfate, filtered and concentrated under reduced pressure. The resulting material was purified by silica gel column chromatography (eluting with a gradient of 10 to 50% ethyl acetate in hexanes) to provide the title compound, a compound of the present invention, as an orange oil (0.189 g).

¹H NMR (CDCl₃): δ 7.75 (d, 1H), 7.69-7.67 (m, 2H), 7.27 (d, 2H), 7.23 (d, 1H), 6.79 (d, 1H), 4.84 (br s, 1H), 4.42 (d, 2H), 3.70 (s, 3H), 2.37 (s, 3H), 1.37 (s, 9H).

EXAMPLE 16

Preparation of methyl *N*-[[5-[1-[4-[(difluoromethyl)thio]-2,6-difluorophenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 43)

Step A: Preparation of methyl *N*-[[5-[1-(2,6-difluoro-4-mercaptophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate

To a mixture of methyl *N*-[[5-[1-[4-[(1,1-dimethylethyl)thio]-2,6-difluorophenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (i.e. the product of Example 15) (0.16 g, 0.360 mmol) in dichloromethane (5 mL) at about 0 °C was added boron tribromide (1 M solution in dichloromethane, 1.10 mL, 1.08 mmol) dropwise. The reaction mixture was stirred at room temperature overnight and quenched with water (6 mL) and methanol (6 mL). After stirring for 2 h, the layers were separated and the aqueous layer was extracted with dichloromethane (2x). The combined organics were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The resulting material was purified by silica gel column chromatography (eluting with a gradient of 20 to 100% ethyl acetate in hexanes) to provide the title compound as a solid (77 mg).

¹H NMR (CDCl₃): δ 7.74 (d, 1H), 7.67 (dd, 1H), 7.62 (m, 1H), 7.22 (d, 1H), 6.98 (d, 2H), 6.75 (d, 1H), 4.83 (br s, 1H), 4.42 (d, 2H), 3.70 (s, 3H), 2.36 (s, 3H).

Step B: Preparation of methyl *N*-[[5-[1-[4-[(difluoromethyl)thio]-2,6-difluorophenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate

To a mixture of methyl *N*-[[5-[1-(2,6-difluoro-4-mercaptophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (i.e. the product of Step A) (77 mg, 0.198 mmol) in acetonitrile and water (1:1, 2 mL) was added potassium hydroxide (222 mg, 3.96 mmol), followed by diethyl (bromodifluoromethyl)phosphonate (0.070 mL, 0.396 mmol). The reaction mixture was stirred at room temperature for 1.5 h, and then diluted with ethyl acetate. The resulting mixture was washed with saturated sodium chloride solution (2x), dried over magnesium sulfate, filtered and concentrated under reduced pressure. The resulting material was purified by silica gel column chromatography (eluting with a gradient of 10 to 50% ethyl acetate in hexanes) to provide the title compound, a compound of the present invention, as an off-white solid (64 mg).

¹H NMR (CDCl₃): δ 7.75 (d, 1H), 7.70-7.68 (m, 2H), 7.34 (d, 2H), 7.24 (d, 1H), 7.02-6.80 (t, 1H), 6.80 (d, 1H), 4.84 (br s, 1H), 4.42 (d, 2H), 3.70 (s, 3H), 2.37 (s, 3H).
LCMS m/z: 440 [M+H]⁺

EXAMPLE 17

- 5 Preparation of methyl *N*-[[5-[1-(2,6-dichloro-4-cyclopropylphenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate (Compound 65)

Step A: Preparation of 5-[1-(2,6-dichloro-4-nitrophenyl)-1*H*-pyrazol-3-yl]-2-methylbenzonitrile

- 10 A mixture of 2-methyl-5-(1*H*-pyrazol-3-yl)benzonitrile (3.0 g, 16.4 mmol) (see PCT Patent Publication WO 2014066120 for a method of preparation), 1,3-dichloro-2-fluoro-5-nitrobenzene (4.12 g, 19.6 mmol) and potassium carbonate (2.72 g, 19.6 mmol) in *N,N*-dimethylformamide (51 mL) was heated at 80 °C for 4 h, and then stirred overnight at room temperature. The reaction mixture was diluted with water and the resulting precipitate was collected by filtration and rinsed with water. The solid precipitate was triturated in a mixture
15 of hexanes/1-chlorobutane, filtered and air-dried, to provide the title compound (3.59g).
¹H NMR (CDCl₃): δ 8.37 (s, 2H), 8.11 (s, 1H), 7.96 (d, 1H), 7.64 (s, 1H), 7.38 (d, 1H), 6.87 (s, 1H), 2.60 (s, 3H).

Step B: Preparation of 5-[1-(4-amino-2,6-dichlorophenyl)-1*H*-pyrazol-3-yl]-2-methylbenzonitrile

- 20 To a mixture of tin(II) chloride dihydrate (12.82 g, 56.82 mmol), acetic acid (51.78 mL) and concentrated hydrochloric acid (34.57 mL) was added 5-[1-(2,6-dichloro-4-nitrophenyl)-1*H*-pyrazol-3-yl]-2-methylbenzonitrile (i.e. the product of Step A) (6.07 g, 16.26 mmol) portionwise while maintaining the reaction temperature at about 25 °C. The reaction mixture was stirred overnight, and then slowly poured into a mixture of potassium hydroxide (200 g),
25 water (200 g) and ice (400 g). The resulting solid precipitate was collected by filtration and dried to provide the title product (6.8 g).
¹H NMR (CDCl₃): δ 8.22 (s, 1H), 7.98 (d, 1H), 7.55 (s, 1H), 7.35 (d, 1H), 6.76 (s, 1H), 6.71 (s, 2H), 4.06 (s, 2H), 2.57 (s, 3H).

- Step C: Preparation of 5-[1-(4-bromo-2,6-dichlorophenyl)-1*H*-pyrazol-3-yl]-2-methylbenzonitrile

- 30 A mixture of 5-[1-(4-amino-2,6-dichlorophenyl)-1*H*-pyrazol-3-yl]-2-methylbenzonitrile (i.e. the product of Step B) (6.75 g, 18.67 mmol) and *n*-butyl nitrite (27.38 mL, 233.7 mmol) was heated at reflux overnight, then cooled to room temperature and concentrated under reduced pressure. The resulting material was purified by silica gel column chromatography (eluting with 20% ethyl acetate in hexanes) to provide the title compound (4.3 g).

¹H NMR (CDCl₃): δ 8.22 (s, 1H), 7.96 (d, 1H), 7.66 (s, 2H), 7.58 (s, 1H), 7.36 (d, 1H), 6.80 (s, 1H), 2.57 (s, 3H).

Step D: Preparation of 5-[1-(2,6-dichloro-4-cyclopropylphenyl)-1*H*-pyrazol-3-yl]-2-methylbenzonitrile

5 A mixture of 5-[1-(4-bromo-2,6-dichlorophenyl)-1*H*-pyrazol-3-yl]-2-methylbenzonitrile (i.e. the product of Step C) (2.19 g, 5.37 mmol), cyclopropylboronic acid (0.53 g, 6.31 mmol), sodium carbonate (1.99 g, 18.75 mmol) and bis(triphenylphosphine)palladium(II) dichloride (0.46 g, 0.66 mmol) in 1,2-dimethoxyethane (43.7 mL) and water (10.03 mL) was heated at 85 °C overnight. The reaction mixture was cooled to room temperature and
10 partitioned between water and ethyl acetate. The organic layer was separated, dried over magnesium sulfate, filtered and concentrated under reduced pressure. The resulting material was purified by silica gel column chromatography (eluting with a gradient of 0 to 10% ethyl acetate in hexanes) to provide the title compound (0.90 g).

¹H NMR (CDCl₃): δ 8.13 (s, 1H), 7.97 (d, 1H), 7.55 (s, 1H), 7.34 (d, 1H), 7.15 (s, 2H), 6.78 (s, 1H), 2.57 (s, 3H), 1.98-1.90 (m, 1H), 1.14-1.08 (m, 2H), 0.81-0.75 (m, 2H).

Step E: Preparation of 5-[1-(2,6-dichloro-4-cyclopropylphenyl)-1*H*-pyrazol-3-yl]-2-methylbenzenemethanamine hydrochloride

To a mixture of 5-[1-(2,6-dichloro-4-cyclopropylphenyl)-1*H*-pyrazol-3-yl]-2-methylbenzonitrile (i.e. the product of Step D) (0.88 g, 2.39 mmol) in dichloromethane (5 mL) was added tris(2,3,4,5,6-pentafluorophenyl)borane (0.01 g, 0.07 mmol), followed by diethylsilane (0.53 g, 5.97 mmol). The reaction mixture was stirred at room temperature overnight, cooled to about 0-5 °C, and then hydrochloric acid (4 N solution in dioxane, 2.02 mL) was added dropwise. The resulting precipitate was collected by filtration and air-dried to provide the title compound as a solid (0.82 g).

25 ¹H NMR (CDCl₃): δ 8.30 (br s, 3H), 8.03 (s, 1H), 7.95 (s, 1H), 7.77 (d, 1H), 7.43 (s, 2H), 7.32 (d, 1H), 6.97 (s, 1H), 3.57 (s, 2H), 2.36 (s, 3H), 2.13-2.05 (m, 1H), 1.14-1.05 (m, 2H), 0.91-0.85 (m, 2H).

Step F: Preparation of methyl *N*-[[5-[1-(2,6-dichloro-4-cyclopropylphenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate

30 To a mixture of 5-[1-(2,6-dichloro-4-cyclopropylphenyl)-1*H*-pyrazol-3-yl]-2-methylbenzenemethanamine hydrochloride (i.e. the product of Step E) (0.82 g, 2.01 mmol) and potassium carbonate (0.83 g, 6.02 mmol) in acetonitrile (10 mL) at about 0-5 °C was added methyl chloroformate (0.21 g, 2.21 mmol). The reaction mixture was stirred overnight at room temperature and concentrated under reduced pressure. The resulting material was purified by
35 silica gel column chromatography (eluting with a gradient of 0% to 100% ethyl acetate in hexanes) to provide the title compound, a compound of the present invention, as a solid (0.87 g).

¹H NMR (CDCl₃): δ 7.78 (s, 1H), 7.70 (d, 1H), 7.63 (s, 1H), 7.22 (d, 1H), 7.15 (s, 2H), 6.76 (s, 1H), 4.82 (br s, 1H), 4.41 (br s, 2H), 3.70 (s, 3H), 2.37 (s, 3H), 1.95-1.88 (m, 1H), 1.12-1.08 (m, 2H), 0.80-0.72 (m, 2H).

LCMS: *m/z* 430 [M+H]⁺

5

EXAMPLE 18

Preparation of methyl *N*-[[5-[2-(2,6-difluoro-4-nitrophenyl)-2*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate (Compound 118), and methyl *N*-[[5-[1-(2,6-difluoro-4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate (Compound 132)

10 Step A: Preparation of 2-methyl-5-[2-(trimethylsilyl)ethynyl]benzonitrile

To a mixture of 2-amino-5-bromobenzonitrile (50 g, 255 mmol) and ethynyltrimethylsilane (181 mL, 1275 mmol) in tetrahydrofuran (600 mL) was added bis(triphenylphosphine)palladium(II) dichloride (26 g, 38 mmol), copper(I) iodide (14.5 g, 76.5 mmol), triphenylphosphine (20 g, 76.5 mmol) and triethylamine (600 mL). The reaction mixture was stirred at room temperature for 24 h, and concentrated under reduced pressure. The resulting material was purified by silica gel column chromatography (eluting with 5% ethyl acetate in petroleum ether) to provide the title compound as a solid (45 g).

¹H NMR (CDCl₃): δ 7.68 (d, *J*=1.6 Hz, 1H), 7.63 (dd, *J*=8.0, 1.6 Hz, 1H), 7.24 (s, 1H), 2.53 (s, 3H), 0.24 (s, 9H).

20 Step B: Preparation of 5-ethynyl-2-methylbenzonitrile

To a mixture of 2-methyl-5-[2-(trimethylsilyl)ethynyl]benzonitrile (i.e. the product of Step A) (40 g, 187.7 mmol) in methanol (800 mL) was added potassium hydroxide (67 mL, 1% in methanol). The reaction mixture was stirred at room temperature for 16 h, and then distilled to remove the methanol. The resulting mixture was diluted with water (200 mL) and extracted with ethyl acetate. The combined organic extracts were washed with saturated sodium chloride solution, dried over sodium sulfate, filtered and concentrated under reduced pressure. The resulting material was purified by silica gel column chromatography (eluting with 12% ethyl acetate in petroleum ether) to provide the title compound as a solid (15 g).

¹H NMR (CDCl₃): δ 7.70 (d, *J*=1.2 Hz, 1H), 7.57 (dd, *J*=8.4, 2.0 Hz, 1H), 7.28 (d, *J*=7.6 Hz, 1H), 3.12 (s, 1H), 2.55 (s, 3H).

30 Step C: Preparation of 5-ethynyl-2-methylbenzenemethanamine hydrochloride

To a mixture of diphenylsilane (81 mL, 443 mmol) in chloroform (250 mL) was added tris(2,3,4,5,6-pentafluorophenyl)borane, (2.7 g, 5.3 mmol), followed by a solution of 5-ethynyl-2-methylbenzonitrile (i.e. the product of Step B) (25 g, 177.3 mmol) in chloroform. The reaction mixture was stirred at room temperature for 16 h and concentrated under reduced pressure. Hydrochloric acid (2 N solution in diethyl ether) was added to the resulting material and the mixture

was stirring for 1 h. The resulting solid precipitate was collected by filtration and dried to provide the title compound as a solid (30 g).

¹H NMR (DMSO-*d*₆): δ 8.26 (br s, 3H), 7.53 (s, 1H), 7.37-7.39 (m, 1H), 7.27-7.25 (m, 1H), 4.19 (s, 1H), 4.01 (s, 2H), 2.35 (s, 3H).

5 Step D: Preparation of methyl [(5-ethynyl-2-methylphenyl)methyl]carbamate

To a mixture of 5-ethynyl-2-methylbenzenemethanamine hydrochloride (i.e. the product of Step C) (30 g, 165.7 mmol) and potassium carbonate (68.5 g, 497 mmol) in acetonitrile (330 mL) at 0 °C was added methyl chloroformate (23.3 g, 248.6 mmol) dropwise over 20 minutes. The reaction mixture was stirred at room temperature for 16 h, then diluted with water (200 mL) and extracted with ethyl acetate. The combined organic extracts were washed with saturated sodium chloride solution, dried over sodium sulfate, filtered and concentrated under reduced pressure. The resulting material was purified by column chromatography (eluting with 30% ethyl acetate in petroleum ether) to provide the title compound as a solid (25 g).

10 ¹H NMR (CDCl₃): δ 7.38 (br s, 1H), 7.33-7.31 (m, 1H), 7.13-7.11 (m, 1H), 4.83 (br s, 1H)
15 4.34 (d, *J*=5.6 Hz, 2H), 3.71 (s, 3H), 3.04 (s, 1H), 2.32 (s, 3H).

Step E: Preparation of methyl *N*-[[5-(1*H*-1,2,3-triazol-4-yl)-2-methylphenyl]methyl]-carbamate

To a mixture of methyl [(5-ethynyl-2-methylphenyl)methyl]carbamate (i.e. the product of Step D) (30 g, 165.7 mmol) in *N,N*-dimethylformamide (117 mL) was added methanol (12 mL), trimethylsilyl azide (11.7 mL, 88.6 mmol) and copper(I) iodide (0.56 g, 2.9 mmol). The reaction mixture was heated at 100 °C for 16 h, then diluted with saturated ammonium chloride solution and extracted with ethyl acetate. The combined organic extracts were washed with water and saturated sodium chloride solution, dried over sodium sulfate, filtered and concentrated under reduced pressure. The resulting material was purified by silica gel column chromatography (eluting with 20% ethyl acetate in petroleum ether) to provide the title compound as a solid (4 g).

25 ¹H NMR (CDCl₃): δ 11.8 (br s, 1H), 7.94 (s, 1H), 7.71 (s, 1H), 7.64-7.61 (m, 1H), 7.24 (s, 1H), 4.93 (br s, 1H), 4.43 (d, *J*=6.0 Hz, 2H), 3.71 (s, 3H), 2.37 (s, 3H).

Step F: Preparation of methyl *N*-[[5-[2-(2,6-difluoro-4-nitrophenyl)-2*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate (Compound 118) and methyl *N*-[[5-[1-(2,6-difluoro-4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate (Compound 132)

To a mixture of methyl *N*-[[5-(1*H*-1,2,3-triazol-4-yl)-2-methylphenyl]methyl]carbamate (i.e. the product of Step E) (4 g, 16.2 mmol) in dimethyl sulfoxide (40 mL) was added potassium carbonate (6.7 g, 48.6 mmol) followed by 1,2,3-trifluoro-5-nitrobenzene (3.1 g, 17.8 mmol). The reaction mixture was stirred at room temperature for 16 h, and then diluted with water (30 mL) and extracted with ethyl acetate. The combined organic extracts were washed with saturated sodium chloride solution, dried over sodium sulfate, filtered and concentrated under reduced pressure. The

resulting material was purified by silica gel chromatography (eluting with 20% ethyl acetate in petroleum ether) to provide methyl *N*-[[5-[2-(2,6-difluoro-4-nitrophenyl)-2*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate (Compound 118), a compound of the present invention, as a solid (2 g).

- 5 ¹H NMR (DMSO-*d*₆): δ 8.77 (s, 1H), 8.45 (dd, *J*=9.2, 2 Hz, 2H), 7.80 (s, 1H), 7.76-7.74 (m, 1H), 7.69-7.66 (m, 1H), 7.32 (d, *J*=8.0 Hz, 1H), 4.24 (d, *J*=5.6 Hz, 2H), 3.55 (s, 3H), 2.33 (s, 3H).

LCMS: *m/z*: 404 [M+H]⁺.

- Also obtained was a solid comprising a mixture of methyl *N*-[[5-[2-(2,6-difluoro-4-nitrophenyl)-2*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate (Compound 118) and methyl *N*-[[5-[1-(2,6-difluoro-4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate (Compound 132). Further purification of the solid by silica gel chromatography provided methyl *N*-[[5-[1-(2,6-difluoro-4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate (Compound 132), a compound of the present invention, as a solid (800 mg).

- 15 ¹H NMR (DMSO-*d*₆): δ 9.08 (s, 1H), 8.50 (d, *J*=7.6 Hz, 2H), 7.83-7.82 (m, 2H), 7.71-7.67 (m, 2H), 7.29 (d, 8.4 Hz, 1H), 4.24 (d, *J*=6.4 Hz, 2H), 3.57 (s, 3H), 2.32 (s, 3H).

LCMS: *m/z*: 404 [M+H]⁺.

EXAMPLE 19

Preparation of methyl *N*-[[5-[2-(4-amino-2,6-difluorophenyl)-2*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate (Compound 115)

- 20 To a mixture of methyl *N*-[[5-[2-(2,6-difluoro-4-nitrophenyl)-2*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate (i.e. the product of Example 18, Step F, Compound 118) (2 g, 4.9 mmol) in ethanol (18 mL) and water (2 mL) was added iron powder (2.7 g, 49.6 mmol) and ammonium chloride (0.16 g, 2.9 mmol). The reaction mixture was heated at reflux for 1.5 h, stirred at room temperature for 16 h, and then filtered through a pad of Celite® (diatomaceous filter aid), rinsing with ethyl acetate (30 mL). The filtrate was diluted with water and extracted with ethyl acetate. The combined organics were washed with saturated sodium chloride solution, dried over sodium sulfate, filtered and concentrated under reduce pressure. The resulting material was purified by silica gel chromatography (eluting with 30% ethyl acetate in petroleum ether) to provide the title compound, a compound of the present invention, as a solid (1.6 g).

30 ¹H NMR (CDCl₃): δ 8.08 (s, 1H), 7.74-7.73 (m, 1H), 7.67-7.65 (m, 1H), 7.24 (s, 1H), 6.33-6.30 (m, 2H), 4.89 (br s, 1H), 4.42 (d, *J*=5.2 Hz, 2H), 4.13 (s, 2H), 3.70 (s, 3H), 2.37 (s, 3H)

LCMS: *m/z*: 374 [M+H]⁺.

The following compound was prepared analogous to the method in Example 19:

- 35 methyl *N*-[[5-[1-(4-amino-2,6-difluorophenyl)-1*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate (Compound 131).

¹H NMR (CDCl₃): δ 7.91 (s, 1H), 7.81 (s, 1H), 7.70 (d, 1H), 7.25 (s, 1H), 6.35 (d, 2H), 4.93 (br s, 1H), 4.45 (s, 2H), 4.19 (br s, 2H), 3.71 (s, 3H), 2.39 (s, 3H).

EXAMPLE 20

Preparation of methyl *N*-[[5-[2-(4-chloro-2,6-difluorophenyl)-2*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate (Compound 117)

To a mixture of methyl *N*-[[5-[2-(4-amino-2,6-difluorophenyl)-2*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate (i.e. the product of Example 19) (1 g, 2.68 mmol) in carbon tetrachloride (125 mL) was added *n*-butyl nitrite (3.3 g, 32.17 mmol). The reaction mixture was heated at reflux for 16 h, and then filtered through a pad of Celite® (diatomaceous filter aid), rinsing with ethyl acetate (20 mL). The filtrate was diluted with water (60 mL) and extracted with ethyl acetate. The combined organics were washed with saturated sodium chloride solution, dried over sodium sulfate, filtered and concentrated under reduced pressure. The resulting material was purified by silica gel chromatography (eluting with 30% ethyl acetate in petroleum ether) to provide the title compound, a compound of the present invention, as a solid (0.12 g).

¹H NMR (CDCl₃): δ 8.13 (s, 1H), 7.74-7.73 (m, 1H), 7.66 (dd, *J*=8.0, 1.6 Hz, 1H), 7.28 (s, 1H), 7.19-7.15 (m, 2H), 4.90 (br s, 1H), 4.43 (d, *J*=5.6 Hz, 2H), 4.71 (s, 3H), 2.38 (s, 3H).

LCMS: *m/z*: 393 [M+H]⁺.

The following compound was prepared analogous to the method in Example 20:

methyl *N*-[[5-[1-(4-chloro-2,6-difluorophenyl)-1*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate (Compound 121).

¹H NMR (CDCl₃): δ 7.98 (s, 1H), 7.79 (br s, 1H), 7.70 (d, *J*=6.4 Hz, 1H), 7.27-7.20 (m, 3H), 4.91 (br s, 1H), 4.44-4.43 (m, 2H), 3.71 (s, 3H), 2.38 (s, 3H).

LCMS: *m/z*: 393 [M+H]⁺.

By the procedures described herein, together with methods known in the art, the following compounds of Tables 1A to 33D can be prepared. The following abbreviations are used in the Tables which follow: *n* means normal, *i* means iso, *c* means cyclo, Me means methyl, Et means ethyl, Pr means propyl, MeO means methoxy, EOt means ethoxy, MeS means methylthio, EtS means ethylthio, -CN means cyano and -NO₂ means nitro.

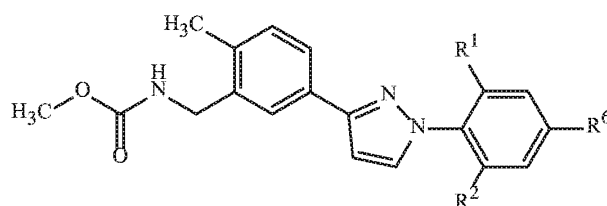


TABLE 1A

R ¹ and R ² are F			
R ⁶		R ⁶	R ⁶
H	CH=CHCH ₃	OCH ₂ (<i>c</i> -Pr)	CH ₂ OH
F	CH ₂ CH=CH ₂	CH ₂ (<i>c</i> -Pr)	CH ₂ OCH ₃

Cl	C=CH	OCH ₂ CH=CH ₂	CH ₂ CH ₂ OCH ₃
Br	C=CCH ₃	OCH ₂ CH=CH(CH ₃)	CH ₂ OCH ₂ CH ₃
I	CH ₂ C=CH	OCH ₂ C=CH	OCH ₂ CF ₃
CN	CF ₃	OCH ₂ C=CCH ₃	OCF ₂ CF ₂ H
NH ₂	CHF ₂	OCH ₂ CH=CHCl	CH=NOH
NO ₂	CH ₂ F	OCH ₂ CH=CCl ₂	C(Me)=NOH
Me	OMe	OCH ₂ C=CCF ₃	CH=NOMe
Et	OEt	OCH ₂ OCH ₃	C(Me)=NOMe
<i>n</i> -Pr	O(<i>n</i> -Pr)	OCH ₂ CH ₂ OCH ₃	CH=NOEt
<i>i</i> -Pr	OCF ₃	SMe	C(Me)=NOEt
<i>c</i> -Pr	OCHF ₂	SEt	CH=NOCH ₂ CH=CH ₂
CH=CH ₂	O(<i>c</i> -Pr)	CH ₂ CN	C(Me)=NOCH ₂ CH=CH ₂

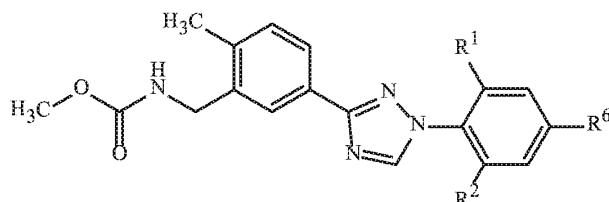
The present disclosure also includes Tables 2A through 33A, each of which is constructed the same as Table 1A above except that the row heading in Table 1A (i.e. “R¹ and R² are F”) is replaced with the respective row headings shown below. For example, in Table 2A the row heading is “R¹ and R² are Cl”, and R⁶ is as defined in Table 1A above.

Table	Table Headings	Table	Table Headings
2A	R ¹ and R ² are Cl	18A	R ¹ is I and R ² is MeO
3A	R ¹ and R ² are Br	19A	R ¹ is Cl and R ² is MeS
4A	R ¹ and R ² are I	20A	R ¹ is Br and R ² is MeS
5A	R ¹ and R ² are Me	21A	R ¹ is F and R ² is MeS
6A	R ¹ and R ² are MeO	22A	R ¹ is Br and R ² is NO ₂
7A	R ¹ and R ² are MeS	23A	R ¹ is CF ₃ and R ² is F
8A	R ¹ is Cl and R ² is Br	24A	R ¹ is CH ₂ F and R ² is F
9A	R ¹ is F and R ² is Br	25A	R ¹ is CHF ₂ and R ² is F
10A	R ¹ is I and R ² is Br	26A	R ¹ is Cl and R ² is EtO
11A	R ¹ is Me and R ² is Br	27A	R ¹ is F and R ² is EtO
12A	R ¹ is Br and R ² is F	28A	R ¹ is Cl and R ² is <i>n</i> -PrO
13A	R ¹ is Cl and R ² is F	29A	R ¹ is F and R ² is <i>n</i> -PrO
14A	R ¹ is I and R ² is F	30A	R ¹ is Cl and R ² is <i>c</i> -PrOCH ₂
15A	R ¹ is Me and R ² is F	31A	R ¹ is F and R ² is <i>c</i> -PrOCH ₂
16A	R ¹ is Cl and R ² is MeO	32A	R ¹ is Cl and R ² is CF ₃ O
17A	R ¹ is F and R ² is MeO	33A	R ¹ is F and R ² is CF ₃ O

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TABLE 1B

Table 1B is identical to Table 1A, except that the chemical structure in the Table 1A is replaced with the following structure:



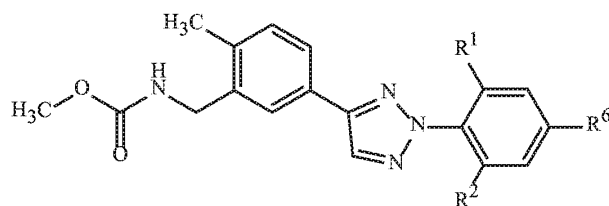
5

TABLES 2B-33B

Tables 2B through 33B are constructed in a similar manner as Tables 2A through 33A.

TABLE 1C

Table 1C is identical to Table 1A, except that the chemical structure in the Table 1A is replaced with the following structure:



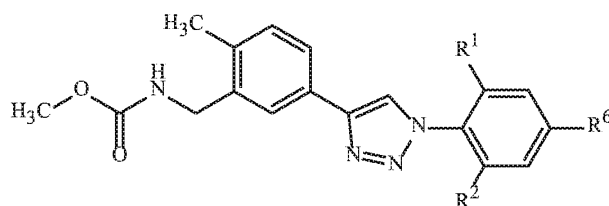
10

TABLES 2C-33C

Tables 2C through 33C are constructed in a similar manner as Tables 2A through 33A.

TABLE 1D

Table 1D is identical to Table 1A, except that the chemical structure in the Table 1A is replaced with the following structure:



15

TABLES 2D-33D

Tables 2D through 33D are constructed in a similar manner as Tables 2A through 33A.

Formulation/Utility

A compound of Formula 1 of this invention (including *N*-oxides, hydrates, and salts thereof) will generally be used as a fungicidal active ingredient in a composition, i.e. formulation, with at least one additional component selected from the group consisting of surfactants, solid diluents and liquid diluents, which serve as a carrier. The formulation or composition ingredients are selected to be consistent with the physical properties of the active ingredient, mode of application and environmental factors such as soil type, moisture and temperature.

Useful formulations include both liquid and solid compositions. Liquid compositions include solutions (including emulsifiable concentrates), suspensions, emulsions (including microemulsions and/or suspoemulsions) and the like, which optionally can be thickened into gels. The general types of aqueous liquid compositions are soluble concentrate, suspension concentrate, capsule suspension, concentrated emulsion, microemulsion and suspo-emulsion. The general types of nonaqueous liquid compositions are emulsifiable concentrate, microemulsifiable concentrate, dispersible concentrate and oil dispersion.

The general types of solid compositions are dusts, powders, granules, pellets, pills, pastilles, tablets, filled films (including seed coatings) and the like, which can be water-dispersible ("wetable") or water-soluble. Films and coatings formed from film-forming solutions or flowable suspensions are particularly useful for seed treatment. Active ingredient can be (micro)encapsulated and further formed into a suspension or solid formulation; alternatively the entire formulation of active ingredient can be encapsulated (or "overcoated"). Encapsulation can control or delay release of the active ingredient. An emulsifiable granule combines the advantages of both an emulsifiable concentrate formulation and a dry granular formulation. High-strength compositions are primarily used as intermediates for further formulation.

Sprayable formulations are typically extended in a suitable medium before spraying. Such liquid and solid formulations are formulated to be readily diluted in the spray medium, usually water, but occasionally another suitable medium like an aromatic or paraffinic hydrocarbon or vegetable oil. Spray volumes can range from about one to several thousand liters per hectare, but more typically are in the range from about ten to several hundred liters per hectare. Sprayable formulations can be tank mixed with water or another suitable medium for foliar treatment by aerial or ground application, or for application to the growing medium of the plant. Liquid and dry formulations can be metered directly into drip irrigation systems or metered into the furrow during planting. Liquid and solid formulations can be applied onto seeds of crops and other desirable vegetation as seed treatments before planting to protect developing roots and other subterranean plant parts and/or foliage through systemic uptake.

The formulations will typically contain effective amounts of active ingredient, diluent and surfactant within the following approximate ranges which add up to 100 percent by weight.

	Weight Percent		
	<u>Active Ingredient</u>	<u>Diluent</u>	<u>Surfactant</u>
Water-Dispersible and Water-soluble granules, Tablets and Powders.	0.001-90	0-99.999	0-15
Oil Dispersions, Suspensions, Emulsions, Solutions (including Emulsifiable Concentrates)	1-50	40-99	0-50
Dusts	1-25	70-99	0-5
Granules and Pellets	0.001-95	5-99.999	0-15
High Strength Compositions	90-99	0-10	0-2

Solid diluents include, for example, clays such as bentonite, montmorillonite, attapulgite and kaolin, gypsum, cellulose, titanium dioxide, zinc oxide, starch, dextrin, sugars (e.g., lactose, sucrose), silica, talc, mica, diatomaceous earth, urea, calcium carbonate, sodium carbonate and bicarbonate, and sodium sulfate. Typical solid diluents are described in Watkins et al., *Handbook of Insecticide Dust Diluents and Carriers*, 2nd Ed., Dorland Books, Caldwell, New Jersey.

Liquid diluents include, for example, water, *N,N*-dimethylalkanamides (e.g., *N,N*-dimethylformamide), limonene, dimethyl sulfoxide, *N*-alkylpyrrolidones (e.g., *N*-methylpyrrolidinone), alkyl phosphates (e.g., triethyl phosphate), ethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, polypropylene glycol, propylene carbonate, butylene carbonate, paraffins (e.g., white mineral oils, normal paraffins, isoparaffins), alkylbenzenes, alkylnaphthalenes, glycerine, glycerol triacetate, sorbitol, aromatic hydrocarbons, dearomatized aliphatics, alkylbenzenes, alkylnaphthalenes, ketones such as cyclohexanone, 2-heptanone, isophorone and 4-hydroxy-4-methyl-2-pentanone, acetates such as isoamyl acetate, hexyl acetate, heptyl acetate, octyl acetate, nonyl acetate, tridecyl acetate and isobornyl acetate, other esters such as alkylated lactate esters, dibasic esters, alkyl and aryl benzoates and γ -butyrolactone, and alcohols, which can be linear, branched, saturated or unsaturated, such as methanol, ethanol, *n*-propanol, isopropyl alcohol, *n*-butanol, isobutyl alcohol, *n*-hexanol, 2-ethylhexanol, *n*-octanol, decanol, isodecyl alcohol, isooctadecanol, cetyl alcohol, lauryl alcohol, tridecyl alcohol, oleyl alcohol, cyclohexanol, tetrahydrofurfuryl alcohol, diacetone alcohol, cresol and benzyl alcohol. Liquid diluents also include glycerol esters of saturated and unsaturated fatty acids (typically C_6 - C_{22}), such as plant seed and fruit oils (e.g., oils of olive, castor, linseed, sesame, corn (maize), peanut, sunflower, grapeseed, safflower, cottonseed, soybean, rapeseed, coconut and palm kernel), animal-sourced fats (e.g., beef tallow, pork tallow, lard, cod liver oil, fish oil),

and mixtures thereof. Liquid diluents also include alkylated fatty acids (e.g., methylated, ethylated, butylated) wherein the fatty acids may be obtained by hydrolysis of glycerol esters from plant and animal sources, and can be purified by distillation. Typical liquid diluents are described in Marsden, *Solvents guide*, 2nd Ed., Interscience, New York, 1950.

5 The solid and liquid compositions of the present invention often include one or more surfactants. When added to a liquid, surfactants (also known as "surface-active agents") generally modify, most often reduce, the surface tension of the liquid. Depending on the nature of the hydrophilic and lipophilic groups in a surfactant molecule, surfactants can be useful as wetting agents, dispersants, emulsifiers or defoaming agents.

10 Surfactants can be classified as nonionic, anionic or cationic. Nonionic surfactants useful for the present compositions include, but are not limited to: alcohol alkoxylates such as alcohol alkoxylates based on natural and synthetic alcohols (which may be branched or linear) and prepared from the alcohols and ethylene oxide, propylene oxide, butylene oxide or mixtures thereof; amine ethoxylates, alkanolamides and ethoxylated alkanolamides; alkoxylated
15 triglycerides such as ethoxylated soybean, castor and rapeseed oils; alkylphenol alkoxylates such as octylphenol ethoxylates, nonylphenol ethoxylates, dinonyl phenol ethoxylates and dodecyl phenol ethoxylates (prepared from the phenols and ethylene oxide, propylene oxide, butylene oxide or mixtures thereof); block polymers prepared from ethylene oxide or propylene oxide and reverse block polymers where the terminal blocks are prepared from propylene
20 oxide; ethoxylated fatty acids; ethoxylated fatty esters and oils; ethoxylated methyl esters; ethoxylated tristyrylphenol (including those prepared from ethylene oxide, propylene oxide, butylene oxide or mixtures thereof); fatty acid esters, glycerol esters, lanolin-based derivatives, polyethoxylate esters such as polyethoxylated sorbitan fatty acid esters, polyethoxylated sorbitol fatty acid esters and polyethoxylated glycerol fatty acid esters; other sorbitan
25 derivatives such as sorbitan esters; polymeric surfactants such as random copolymers, block copolymers, alkyl peg (polyethylene glycol) resins, graft or comb polymers and star polymers; polyethylene glycols (pegs); polyethylene glycol fatty acid esters; silicone-based surfactants; and sugar-derivatives such as sucrose esters, alkyl polyglycosides and alkyl polysaccharides.

Useful anionic surfactants include, but are not limited to: alkylaryl sulfonic acids and
30 their salts; carboxylated alcohol or alkylphenol ethoxylates; diphenyl sulfonate derivatives; lignin and lignin derivatives such as lignosulfonates; maleic or succinic acids or their anhydrides; olefin sulfonates; phosphate esters such as phosphate esters of alcohol alkoxylates, phosphate esters of alkylphenol alkoxylates and phosphate esters of styryl phenol ethoxylates; protein-based surfactants; sarcosine derivatives; styryl phenol ether sulfate; sulfates and
35 sulfonates of oils and fatty acids; sulfates and sulfonates of ethoxylated alkylphenols; sulfates of alcohols; sulfates of ethoxylated alcohols; sulfonates of amines and amides such as *N,N*-alkyltaurates; sulfonates of benzene, cumene, toluene, xylene, and dodecyl and

tridecylbenzenes; sulfonates of condensed naphthalenes; sulfonates of naphthalene and alkyl naphthalene; sulfonates of fractionated petroleum; sulfosuccinamates; and sulfosuccinates and their derivatives such as dialkyl sulfosuccinate salts.

Useful cationic surfactants include, but are not limited to: amides and ethoxylated
5 amides; amines such as *N*-alkyl propanediamines, tripropylenetriamines and dipropylenetetramines, and ethoxylated amines, ethoxylated diamines and propoxylated amines (prepared from the amines and ethylene oxide, propylene oxide, butylene oxide or mixtures thereof); amine salts such as amine acetates and diamine salts; quaternary ammonium salts such as quaternary salts, ethoxylated quaternary salts and diquaternary salts; and amine
10 oxides such as alkyldimethylamine oxides and bis-(2-hydroxyethyl)-alkylamine oxides.

Also useful for the present compositions are mixtures of nonionic and anionic surfactants or mixtures of nonionic and cationic surfactants. Nonionic, anionic and cationic surfactants and their recommended uses are disclosed in a variety of published references including
15 *McCutcheon's Emulsifiers and Detergents*, annual American and International Editions published by McCutcheon's Division, The Manufacturing Confectioner Publishing Co.; Sisely and Wood, *Encyclopedia of Surface Active Agents*, Chemical Publ. Co., Inc., New York, 1964; and A. S. Davidson and B. Milwidsky, *Synthetic Detergents*, Seventh Edition, John Wiley and Sons, New York, 1987.

Compositions of this invention may also contain formulation auxiliaries and additives,
20 known to those skilled in the art as formulation aids. Such formulation auxiliaries and additives may control: pH (buffers), foaming during processing (antifoams such polyorganosiloxanes (e.g., Rhodorsil® 416)), sedimentation of active ingredients (suspending agents), viscosity (thixotropic thickeners), in-container microbial growth (antimicrobials), product freezing (antifreezes), color (dyes/pigment dispersions (e.g., Pro-lzed® Colorant Red)), wash-off (film
25 formers or stickers), evaporation (evaporation retardants), and other formulation attributes. Film formers include, for example, polyvinyl acetates, polyvinyl acetate copolymers, polyvinylpyrrolidone-vinyl acetate copolymer, polyvinyl alcohols, polyvinyl alcohol copolymers and waxes. Examples of formulation auxiliaries and additives include those listed in *McCutcheon's Volume 2: Functional Materials*, annual International and North American
30 editions published by McCutcheon's Division, The Manufacturing Confectioner Publishing Co.; and PCT Publication WO 03/024222.

The compound of Formula 1 and any other active ingredients are typically incorporated into the present compositions by dissolving the active ingredient in a solvent or by grinding in a liquid or dry diluent. Solutions, including emulsifiable concentrates, can be prepared by
35 simply mixing the ingredients. If the solvent of a liquid composition intended for use as an emulsifiable concentrate is water-immiscible, an emulsifier is typically added to emulsify the active-containing solvent upon dilution with water. Active ingredient slurries, with particle

diameters of up to 2,000 μm can be wet milled using media mills to obtain particles with average diameters below 3 μm . Aqueous slurries can be made into finished suspension concentrates (see, for example, U.S. 3,060,084) or further processed by spray drying to form water-dispersible granules. Dry formulations usually require dry milling processes, which
5 produce average particle diameters in the 2 to 10 μm range. Dusts and powders can be prepared by blending and usually grinding (such as with a hammer mill or fluid-energy mill). granules and pellets can be prepared by spraying the active material upon preformed granular carriers or by agglomeration techniques. See Browning, "Agglomeration", *Chemical Engineering*, December 4, 1967, pp 147-48, *Perry's Chemical Engineer's Handbook*, 4th Ed., McGraw-Hill,
10 New York, 1963, pp 8-57 and following, and WO 91/13546. Pellets can be prepared as described in U.S. 4,172,714. Water-dispersible and water-soluble granules can be prepared as taught in U.S. 4,144,050, U.S. 3,920,442 and DE 3,246,493. Tablets can be prepared as taught in U.S. 5,180,587, U.S. 5,232,701 and U.S. 5,208,030. Films can be prepared as taught in gB 2,095,558 and U.S. 3,299,566.

15 One embodiment of the present invention relates to a method for controlling fungal pathogens, comprising diluting the fungicidal composition of the present invention (a compound of Formula 1 formulated with surfactants, solid diluents and liquid diluents or a formulated mixture of a compound of Formula 1 and at least one other fungicide) with water, and optionally adding an adjuvant to form a diluted composition, and contacting the fungal
20 pathogen or its environment with an effective amount of said diluted composition.

Although a spray composition formed by diluting with water a sufficient concentration of the present fungicidal composition can provide sufficient efficacy for controlling fungal pathogens, separately formulated adjuvant products can also be added to spray tank mixtures. These additional adjuvants are commonly known as "spray adjuvants" or "tank-mix
25 adjuvants", and include any substance mixed in a spray tank to improve the performance of a pesticide or alter the physical properties of the spray mixture. Adjuvants can be anionic or nonionic surfactants, emulsifying agents, petroleum-based crop oils, crop-derived seed oils, acidifiers, buffers, thickeners or defoaming agents. Adjuvants are used to enhancing efficacy (e.g., biological availability, adhesion, penetration, uniformity of coverage and durability of
30 protection), or minimizing or eliminating spray application problems associated with incompatibility, foaming, drift, evaporation, volatilization and degradation. To obtain optimal performance, adjuvants are selected with regard to the properties of the active ingredient, formulation and target (e.g., crops, insect pests).

The amount of adjuvants added to spray mixtures is generally in the range of about 2.5%
35 to 0.1 % by volume. The application rates of adjuvants added to spray mixtures are typically between about 1 to 5 L per hectare. Representative examples of spray adjuvants include: Adigor® (Syngenta) 47% methylated rapeseed oil in liquid hydrocarbons, Silwet® (Helena

Chemical Company) polyalkyleneoxide modified heptamethyltrisiloxane and Assist® (BASF) 17% surfactant blend in 83% paraffin based mineral oil.

One method of seed treatment is by spraying or dusting the seed with a compound of the invention (i.e. as a formulated composition) before sowing the seeds. Compositions formulated for seed treatment generally comprise a film former or adhesive agent. Therefore, typically a seed coating composition of the present invention comprises a biologically effective amount of a compound of Formula 1 and a film former or adhesive agent. Seeds can be coated by spraying a flowable suspension concentrate directly into a tumbling bed of seeds and then drying the seeds. Alternatively, other formulation types such as wetted powders, solutions, suspoemulsions, emulsifiable concentrates and emulsions in water can be sprayed on the seed. This process is particularly useful for applying film coatings on seeds. Various coating machines and processes are available to one skilled in the art. Suitable processes include those listed in P. Kusters et al., *Seed Treatment: Progress and Prospects*, 1994 BCPC Mongraph No. 57, and references listed therein.

For further information regarding the art of formulation, see T. S. Woods, "The Formulator's Toolbox - Product Forms for Modern Agriculture" in *Pesticide Chemistry and Bioscience, The Food-Environment Challenge*, T. Brooks and T. R. Roberts, Eds., Proceedings of the 9th International Congress on Pesticide Chemistry, The Royal Society of Chemistry, Cambridge, 1999, pp. 120-133. See also U.S. 3,235,361, Col. 6, line 16 through Col. 7, line 19 and Examples 10-41; U.S. 3,309,192, Col. 5, line 43 through Col. 7, line 62 and Examples 8, 12, 15, 39, 41, 52, 53, 58, 132, 138-140, 162-164, 166, 167 and 169-182; U.S. 2,891,855, Col. 3, line 66 through Col. 5, line 17 and Examples 1-4; Klingman, *Weed Control as a Science*, John Wiley and Sons, Inc., New York, 1961, pp 81-96; Hance et al., *Weed Control Handbook*, 8th Ed., Blackwell Scientific Publications, Oxford, 1989; and *Developments in formulation technology*, PJB Publications, Richmond, UK, 2000.

In the following Examples, all percentages are by weight and all formulations are prepared in conventional ways. Compound numbers refer to compounds in Index Tables A-G. Without further elaboration, it is believed that one skilled in the art using the preceding description can utilize the present invention to its fullest extent. The following Examples are, therefore, to be constructed as merely illustrative, and not limiting of the disclosure in any way whatsoever.

Example A

High Strength Concentrate

Compound 1	98.5%
silica aerogel	0.5%
synthetic amorphous fine silica	1.0%

Example B

Wettable Powder

Compound 3	65.0%
dodecylphenol polyethylene glycol ether	2.0%
sodium ligninsulfonate	4.0%
sodium silicoaluminate	6.0%
montmorillonite (calcined)	23.0%

Example CGranule

Compound 4	10.0%
attapulgit granules (low volatile matter, 0.71/0.30 mm; U.S.S. No. 25–50 sieves)	90.0%

Example DExtruded Pellet

Compound 5	25.0%
anhydrous sodium sulfate	10.0%
crude calcium ligninsulfonate	5.0%
sodium alkyl naphthalenesulfonate	1.0%
calcium/magnesium bentonite	59.0%

Example EEmulsifiable Concentrate

Compound 6	10.0%
polyoxyethylene sorbitol hexoleate	20.0%
C ₆ –C ₁₀ fatty acid methyl ester	70.0%

Example FMicroemulsion

Compound 7	5.0%
polyvinylpyrrolidone-vinyl acetate copolymer	30.0%
alkylpolyglycoside	30.0%
glyceryl monooleate	15.0%
water	20.0%

5

Example GSeed Treatment

Compound 8	20.00%
polyvinylpyrrolidone-vinyl acetate copolymer	5.00%
montan acid wax	5.00%
calcium ligninsulfonate	1.00%
polyoxyethylene/polyoxypropylene block copolymers	1.00%

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stearyl alcohol (POE 20)	2.00%
polyorganosilane	0.20%
colorant red dye	0.05%
water	65.75%

Example HFertilizer Stick

Compound 10	2.50%
pyrrolidone-styrene copolymer	4.80%
tristyrylphenyl 16-ethoxylate	2.30%
talc	0.80%
corn starch	5.00%
slow-release fertilizer	36.00%
kaolin	38.00%
water	10.60%

Example ISuspension Concentrate

Compound 33	35%
butyl polyoxyethylene/polypropylene block copolymer	4.0%
stearic acid/polyethylene glycol copolymer	1.0%
styrene acrylic polymer	1.0%
xanthan gum	0.1%
propylene glycol	5.0%
silicone based defoamer	0.1%
1,2-benzisothiazolin-3-one	0.1%
water	53.7%

Example JEmulsion in Water

Compound 41	10.0%
butyl polyoxyethylene/polypropylene block copolymer	4.0%
stearic acid/polyethylene glycol copolymer	1.0%
styrene acrylic polymer	1.0%
xanthan gum	0.1%
propylene glycol	5.0%
silicone based defoamer	0.1%
1,2-benzisothiazolin-3-one	0.1%
aromatic petroleum based hydrocarbon	20.0
water	58.7%

Example KOil Dispersion

Compound 68	25%
polyoxyethylene sorbitol hexaoleate	15%
organically modified bentonite clay	2.5%
fatty acid methyl ester	57.5%

Example LSuspoemulsion

Compound 115	10.0%
imidacloprid	5.0%
butyl polyoxyethylene/polypropylene block copolymer	4.0%
stearic acid/polyethylene glycol copolymer	1.0%
styrene acrylic polymer	1.0%
xanthan gum	0.1%
propylene glycol	5.0%
silicone based defoamer	0.1%
1,2-benzisothiazolin-3-one	0.1%
aromatic petroleum based hydrocarbon	20.0%
water	53.7%

Water-soluble and water-dispersible formulations are typically diluted with water to form aqueous compositions before application. Aqueous compositions for direct applications to the plant or portion thereof (e.g., spray tank compositions) typically contain at least about 1 ppm or more (e.g., from 1 ppm to 100 ppm) of the compound(s) of this invention.

Seed is normally treated at a rate of from about 0.001 g (more typically about 0.1 g) to about 10 g per kilogram of seed (i.e. from about 0.0001 to 1% by weight of the seed before treatment). A flowable suspension formulated for seed treatment typically comprises from about 0.5 to about 70% of the active ingredient, from about 0.5 to about 30% of a film-forming adhesive, from about 0.5 to about 20% of a dispersing agent, from 0 to about 5% of a thickener, from 0 to about 5% of a pigment and/or dye, from 0 to about 2% of an antifoaming agent, from 0 to about 1% of a preservative, and from 0 to about 75% of a volatile liquid diluent.

The compounds of this invention are useful as plant disease control agents. The present invention therefore further comprises a method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof to be protected, or to the plant seed to be protected, an effective amount of a compound of the invention or a fungicidal composition containing said compound. The compounds and/or compositions of this invention provide control of diseases caused by a broad spectrum of fungal plant pathogens in the Ascomycota, Basidiomycota, Zygomycota phyla, and the fungal-like Oomycata class. They

are effective in controlling a broad spectrum of plant diseases, particularly foliar pathogens of ornamental, turf, vegetable, field, cereal, and fruit crops. These pathogens include but are not limited to those listed in Table 1-1. For Ascomycetes and Basidiomycetes, names for both the sexual/teleomorph/perfect stage as well as names for the asexual/anamorph/imperfect stage (in parentheses) are listed where known. Synonymous names for pathogens are indicated by an equal sign. For example, the sexual/teleomorph/perfect stage name *Phaeosphaeria nodorum* is followed by the corresponding asexual/anamorph/imperfect stage name *Stagonospora nodorum* and the synonymous older name *Septoria nodorum*.

Table 1-1

Ascomycetes in the order Pleosporales including <i>Alternaria solani</i> , <i>A. alternata</i> and <i>A. brassicae</i> , <i>guignardia bidwellii</i> , <i>Venturia inaequalis</i> , <i>Pyrenophora tritici-repentis</i> (<i>Dreschlera tritici-repentis</i> = <i>Helminthosporium tritici-repentis</i>) and <i>Pyrenophora teres</i> (<i>Dreschlera teres</i> = <i>Helminthosporium teres</i>), <i>Corynespora cassiicola</i> , <i>Phaeosphaeria nodorum</i> (<i>Stagonospora nodorum</i> = <i>Septoria nodorum</i>), <i>Cochliobolus carbonum</i> and <i>C. heterostrophus</i> , <i>Leptosphaeria biglobosa</i> and <i>L. maculans</i> ;
Ascomycetes in the order Mycosphaerellales including <i>Mycosphaerella graminicola</i> (<i>Zymoseptoria tritici</i> = <i>Septoria tritici</i>), <i>M. berkeleyi</i> (<i>Cercosporidium personatum</i>), <i>M. arachidis</i> (<i>Cercospora arachidicola</i>), <i>Passalora sojae</i> (<i>Cercospora sojae</i>), <i>Cercospora zea-maydis</i> and <i>C. beticola</i> ;
Ascomycetes in the order Erysiphales (the powdery mildews) such as <i>Blumeria graminis</i> f.sp. <i>tritici</i> and <i>Blumeria graminis</i> f.sp. <i>hordei</i> , <i>Erysiphe polygoni</i> , <i>E. necator</i> (= <i>Uncinula necator</i>), <i>Podosphaera fuliginea</i> (= <i>Sphaerotheca fuliginea</i>), and <i>Podosphaera leucotricha</i> (= <i>Sphaerotheca fuliginea</i>);
Ascomycetes in the order Helotiales such as <i>Botryotinia fuckeliana</i> (<i>Botrytis cinerea</i>), <i>Oculimacula yallundae</i> (= <i>Tapesia yallundae</i> ; anamorph <i>Helgardia herpotrichoides</i> = <i>Pseudocercospora herpotrichoides</i>), <i>Monilinia fructicola</i> , <i>Sclerotinia sclerotiorum</i> , <i>Sclerotinia minor</i> , and <i>Sclerotinia homoeocarpa</i> ;
Ascomycetes in the order Hypocreales such as <i>Gibberella zeae</i> (<i>Fusarium graminearum</i>), <i>G. moniliformis</i> (<i>Fusarium moniliforme</i>), <i>Fusarium solani</i> and <i>Verticillium dahliae</i> ;
Ascomycetes in the order Eurotiales such as <i>Aspergillus flavus</i> and <i>A. parasiticus</i> ;
Ascomycetes in the order Diaporthales such as <i>Cryptosphaeria viticola</i> (= <i>Phomopsis viticola</i>), <i>Phomopsis longicolla</i> , and <i>Diaporthe phaseolorum</i> ;
Other Ascomycete pathogens including <i>Magnaporthe grisea</i> , <i>Gaeumannomyces graminis</i> , <i>Rhynchosporium secalis</i> , and anthracnose pathogens such as <i>Glomerella acutata</i> (<i>Colletotrichum acutatum</i>), <i>G. graminicola</i> (<i>C. graminicola</i>) and <i>G. lagenaria</i> (<i>C. orbiculare</i>);
Basidiomycetes in the order Uredinales (the rusts) including <i>Puccinia recondita</i> , <i>P. striiformis</i> , <i>Puccinia hordei</i> , <i>P. graminis</i> and <i>P. arachidis</i> , <i>Hemileia vastatrix</i> and <i>Phakopsora pachyrhizi</i> ;

Basidiomycetes in the order Ceratobasidiales such as <i>Thanatophorum cucumeris</i> (<i>Rhizoctonia solani</i>) and <i>Ceratobasidium oryzae-sativae</i> (<i>Rhizoctonia oryzae</i>);
Basidiomycetes in the order Polyporales such as <i>Athelia rolfsii</i> (<i>Sclerotium rolfsii</i>);
Basidiomycetes in the order Ustilaginales such as <i>Ustilago maydis</i> ;
Zygomycetes in the order Mucorales such as <i>Rhizopus stolonifer</i> ;
Oomycetes in the order Pythiales, including <i>Phytophthora infestans</i> , <i>P. megasperma</i> , <i>P. parasitica</i> , <i>P. sojae</i> , <i>P. cinnamomi</i> and <i>P. capsici</i> , and <i>Pythium</i> pathogens such as <i>Pythium aphanidermatum</i> , <i>P. graminicola</i> , <i>P. irregulare</i> , <i>P. ultimum</i> and <i>P. dissotocum</i> ;
Oomycetes in the order Peronosporales such as <i>Plasmopara viticola</i> , <i>P. halstedii</i> , <i>Peronospora hyoscyami</i> (= <i>Peronospora tabacina</i>), <i>P. manshurica</i> , <i>Hyaloperonospora parasitica</i> (= <i>Peronospora parasitica</i>), <i>Pseudoperonospora cubensis</i> and <i>Bremia lactucae</i> ;
and other genera and species closely related to all of the above pathogens.

In addition to their fungicidal activity, the compositions or combinations also have activity against bacteria such as *Erwinia amylovora*, *Xanthomonas campestris*, *Pseudomonas syringae*, and other related species. By controlling harmful microorganisms, the compounds of the invention are useful for improving (i.e. increasing) the ratio of beneficial to harmful microorganisms in contact with crop plants or their propagules (e.g., seeds, corns, bulbs, tubers, cuttings) or in the agronomic environment of the crop plants or their propagules.

Compounds of the invention are useful in treating all plants, plant parts and seeds. Plant and seed varieties and cultivars can be obtained by conventional propagation and breeding methods or by genetic engineering methods. genetically modified plants or seeds (transgenic plants or seeds) are those in which a heterologous gene (transgene) has been stably integrated into the plant's or seed's genome. A transgene that is defined by its particular location in the plant genome is called a transformation or transgenic event.

Genetically modified plant cultivars which can be treated according to the invention include those that are resistant against one or more biotic stresses (pests such as nematodes, insects, mites, fungi, etc.) or abiotic stresses (drought, cold temperature, soil salinity, etc.), or that contain other desirable characteristics. Plants can be genetically modified to exhibit traits of, for example, herbicide tolerance, insect-resistance, modified oil profiles or drought tolerance.

Treatment of genetically modified plants and seeds with compounds of the invention may result in super-additive or enhanced effects. For example, reduction in application rates, broadening of the activity spectrum, increased tolerance to biotic/abiotic stresses or enhanced storage stability may be greater than expected from just simple additive effects of the application of compounds of the invention on genetically modified plants and seeds.

Compounds of this invention are useful in seed treatments for protecting seeds from plant diseases. In the context of the present disclosure and claims, treating a seed means contacting

the seed with a biologically effective amount of a compound of this invention, which is typically formulated as a composition of the invention. This seed treatment protects the seed from soil-borne disease pathogens and generally can also protect roots and other plant parts in contact with the soil of the seedling developing from the germinating seed. The seed treatment
5 may also provide protection of foliage by translocation of the compound of this invention or a second active ingredient within the developing plant. Seed treatments can be applied to all types of seeds, including those from which plants genetically transformed to express specialized traits will germinate. Representative examples include those expressing proteins toxic to invertebrate pests, such as *Bacillus thuringiensis* toxin or those expressing herbicide
10 resistance such as glyphosate acetyltransferase, which provides resistance to glyphosate. Seed treatments with compounds of this invention can also increase vigor of plants growing from the seed.

Compounds of this invention and their compositions, both alone and in combination with other fungicides, nematicides and insecticides, are particularly useful in seed treatment for
15 crops including, but not limited to, maize or corn, soybeans, cotton, cereal (e.g., wheat, oats, barley, rye and rice), potatoes, vegetables and oilseed rape.

Furthermore, the compounds of this invention are useful in treating postharvest diseases of fruits and vegetables caused by fungi and bacteria. These infections can occur before, during and after harvest. For example, infections can occur before harvest and then remain dormant
20 until some point during ripening (e.g., host begins tissue changes in such a way that infection can progress); also infections can arise from surface wounds created by mechanical or insect injury. In this respect, the compounds of this invention can reduce losses (i.e. losses resulting from quantity and quality) due to postharvest diseases which may occur at any time from harvest to consumption. Treatment of postharvest diseases with compounds of the invention
25 can increase the period of time during which perishable edible plant parts (e.g., fruits, seeds, foliage, stems, bulbs, tubers) can be stored refrigerated or un-refrigerated after harvest, and remain edible and free from noticeable or harmful degradation or contamination by fungi or other microorganisms. Treatment of edible plant parts before or after harvest with compounds of the invention can also decrease the formation of toxic metabolites of fungi or other
30 microorganisms, for example, mycotoxins such as aflatoxins.

Plant disease control is ordinarily accomplished by applying an effective amount of a compound of this invention either pre- or post-infection, to the portion of the plant to be protected such as the roots, stems, foliage, fruits, seeds, tubers or bulbs, or to the media (soil or sand) in which the plants to be protected are growing. The compounds can also be applied
35 to seeds to protect the seeds and seedlings developing from the seeds. The compounds can also be applied through irrigation water to treat plants. Control of postharvest pathogens which infect the produce before harvest is typically accomplished by field application of a compound

of this invention, and in cases where infection occurs after harvest the compounds can be applied to the harvested crop as dips, sprays, fumigants, treated wraps and box liners.

Rates of application for these compounds (i.e. a fungicidally effective amount) can be influenced by factors such as the plant diseases to be controlled, the plant species to be protected, ambient moisture and temperature and should be determined under actual use conditions. One skilled in the art can easily determine through simple experimentation the fungicidally effective amount necessary for the desired level of plant disease control. Foliage can normally be protected when treated at a rate of from less than about 1 g/ha to about 5,000 g/ha of active ingredient. Seed and seedlings can normally be protected when seed is treated at a rate of from about 0.001 g (more typically about 0.1 g) to about 10 g per kilogram of seed.

Compounds of this invention can also be mixed with one or more other biologically active compounds or agents including fungicides, insecticides, nematocides, bactericides, acaricides, herbicides, herbicide safeners, growth regulators such as insect molting inhibitors and rooting stimulants, chemosterilants, semiochemicals, repellents, attractants, pheromones, feeding stimulants, plant nutrients, other biologically active compounds or entomopathogenic bacteria, virus or fungi to form a multi-component pesticide giving an even broader spectrum of agricultural protection. Thus the present invention also pertains to a composition comprising a compound of Formula 1 (in a fungicidally effective amount) and at least one additional biologically active compound or agent (in a biologically effective amount) and can further comprise at least one of a surfactant, a solid diluent or a liquid diluent. The other biologically active compounds or agents can be formulated in compositions comprising at least one of a surfactant, solid or liquid diluent. For mixtures of the present invention, one or more other biologically active compounds or agents can be formulated together with a compound of Formula 1, to form a premix, or one or more other biologically active compounds or agents can be formulated separately from the compound of Formula 1, and the formulations combined together before application (e.g., in a spray tank) or, alternatively, applied in succession.

As mentioned in the Summary of the Invention, one aspect of the present invention is a fungicidal composition comprising (i.e. a mixture or combination of) a compound of Formula 1, an *N*-oxide, or a salt thereof (i.e. component a), and at least one other fungicide (i.e. component b). Of note is such a combination where the other fungicidal active ingredient has different site of action from the compound of Formula 1. In certain instances, a combination with at least one other fungicidal active ingredient having a similar spectrum of control but a different site of action will be particularly advantageous for resistance management. Thus, a composition of the present invention can further comprise a fungicidally effective amount of at least one additional fungicidal active ingredient having a similar spectrum of control but a different site of action.

Of note is a composition which in addition to the Formula 1 compound of component (a), includes as component (b) at least one fungicidal compound selected from the group consisting of the FRAC-defined mode of action (MOA) classes (A) nucleic acid synthesis, (B) mitosis and cell division, (C) respiration, (D) amino acid and protein synthesis, (E) signal transduction, 5 (F) lipid synthesis and membrane integrity, (G) sterol biosynthesis in membranes, (H) cell wall biosynthesis in membranes, (I) melanin synthesis in cell wall, (P) host plant defense induction, multi-site contact activity and unknown mode of action.

FRAC-recognized or proposed target sites of action along with their FRAC target site codes belonging to the above MOA classes are (A1) RNA polymerase I, (A2) adenosine 10 deaminase, (A3) DNA/RNA synthesis (proposed), (A4) DNA topoisomerase, (B1-B3) β -tubulin assembly in mitosis, (B4) cell division (proposed), (B5) delocalization of spectrin-like proteins, (C1) complex I NADH oxidoreductase, (C2) complex II: succinate dehydrogenase, (C3) complex III: cytochrome *bc1* (ubiquinol oxidase) at Qo site, (C4) complex III: cytochrome *bc1* (ubiquinone reductase) at Qi site, (C5) uncouplers of oxidative phosphorylation, (C6) 15 inhibitors of oxidative phosphorylation, ATP synthase, (C7) ATP production (proposed), (C8) complex III: cytochrome *bc1* (ubiquinone reductase) at Qx (unknown) site, (D1) methionine biosynthesis (proposed), (D2-D5) protein synthesis, (E1) signal transduction (mechanism unknown), (E2-E3) MAP/histidine kinase in osmotic signal transduction, (F2) phospholipid biosynthesis, methyl transferase, (F3) lipid peroxidation (proposed), (F4) cell membrane 20 permeability, fatty acids (proposed), (F6) microbial disrupters of pathogen cell membranes, (F7) cell membrane disruption (proposed), (G1) C14- demethylase in sterol biosynthesis, (G2) $\Delta 14$ -reductase and $\Delta 8 \rightarrow \Delta 7$ -isomerase in sterol biosynthesis, (G3) 3-keto reductase, C4-demethylation, (G4) squalene epoxidase in sterol biosynthesis, (H3) trehalase and inositol biosynthesis, (H4) chitin synthase, (H5) cellulose synthase, (I1) reductase in melanin 25 biosynthesis and (I2) dehydratase in melanin biosynthesis.

Of particular note is a composition which in addition to the Formula 1 compound of component (a), includes as component (b) at least one fungicidal compound selected from the group consisting of the classes (b1) methyl benzimidazole carbamate (MBC) fungicides; (b2) dicarboximide fungicides; (b3) demethylation inhibitor (DMI) fungicides; (b4) phenylamide 30 fungicides; (b5) amine/morpholine fungicides; (b6) phospholipid biosynthesis inhibitor fungicides; (b7) succinate dehydrogenase inhibitor fungicides; (b8) hydroxy(2-amino-)pyrimidine fungicides; (b9) anilinopyrimidine fungicides; (b10) *N*-phenyl carbamate fungicides; (b11) quinone outside inhibitor (QoI) fungicides; (b12) phenylpyrrole fungicides; (b13) azanaphthalene fungicides; (b14) lipid peroxidation inhibitor fungicides; (b15) melanin 35 biosynthesis inhibitor-reductase (MBI-R) fungicides; (b16) melanin biosynthesis inhibitor-dehydratase (MBI-D) fungicides; (b17) sterol biosynthesis inhibitor (SBI); Class III fungicides; (b18) squalene-epoxidase inhibitor fungicides; (b19) polyoxin fungicides; (b20) phenylurea

fungicides; (b21) quinone inside inhibitor (Qil) fungicides; (b22) benzamide and thiazole carboxamide fungicides; (b23) enopyranuronic acid antibiotic fungicides; (b24) hexopyranosyl antibiotic fungicides; (b25) glucopyranosyl antibiotic: protein synthesis fungicides; (b26) glucopyranosyl antibiotic: trehalase and inositol biosynthesis fungicides; (b27) cyanoacetamideoxime fungicides; (b28) carbamate fungicides; (b29) oxidative phosphorylation uncoupling fungicides; (b30) organo tin fungicides; (b31) carboxylic acid fungicides; (b32) heteroaromatic fungicides; (b33) phosphonate fungicides; (b34) phthalamic acid fungicides; (b35) benzotriazine fungicides; (b36) benzene-sulfonamide fungicides; (b37) pyridazinone fungicides; (b38) thiophene-carboxamide fungicides; (b39) complex I NADH oxidoreductase inhibitor fungicides; (b40) carboxylic acid amide (CAA) fungicides; (b41) tetracycline antibiotic fungicides; (b42) thiocarbamate fungicides; (b43) benzamide fungicides; (b44) microbial fungicides; (b45) Q_xI fungicides; (b46) plant extract fungicides; (b47) host plant defense induction fungicides; (b48) multi-site contact activity fungicides; (b49) fungicides other than fungicides of classes (b1) through (b48); and salts of compounds of classes (b1) through (b48).

Further descriptions of these classes of fungicidal compounds are provided below.

(b1) "Methyl benzimidazole carbamate (MBC) fungicides" (FRAC code 1) inhibit mitosis by binding to β -tubulin during microtubule assembly. Inhibition of microtubule assembly can disrupt cell division, transport within the cell and cell structure. Methyl benzimidazole carbamate fungicides include benzimidazole and thiophanate fungicides. The benzimidazoles include benomyl, carbendazim, fuberidazole and thiabendazole. The thiophanates include thiophanate and thiophanate-methyl.

(b2) "Dicarboximide fungicides" (FRAC code 2) inhibit a MAP/histidine kinase in osmotic signal transduction. Examples include chlozolate, iprodione, procymidone and vinclozolin.

(b3) "Demethylation inhibitor (DMI) fungicides" (FRAC code 3) (Sterol Biosynthesis Inhibitors (SBI): Class I) inhibit C14-demethylase, which plays a role in sterol production. Sterols, such as ergosterol, are needed for membrane structure and function, making them essential for the development of functional cell walls. Therefore, exposure to these fungicides results in abnormal growth and eventually death of sensitive fungi. DMI fungicides are divided between several chemical classes: azoles (including triazoles and imidazoles), pyrimidines, piperazines, pyridines and triazolinthiones. The triazoles include azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole (including diniconazole-M), epoxiconazole, etaconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imibenconazole, ipconazole, mefentrifluconazole, metconazole, myclobutanil, penconazole, propiconazole, quinconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triticonazole, uniconazole, uniconazole-P, α -(1-chlorocyclopropyl)-

α -[2-(2,2-dichlorocyclopropyl)ethyl]-1*H*-1,2,4-triazole-1-ethanol, *rel*-1-[[*(2R,3S)*-3-(2-chlorophenyl)-2-(2,4-difluorophenyl)-2-oxiranyl]methyl]-1*H*-1,2,4-triazole, *rel*-2-[[*(2R,3S)*-3-(2-chlorophenyl)-2-(2,4-difluorophenyl)-2-oxiranyl]methyl]-1,2-dihydro-3*H*-1,2,4-triazole-3-thione, and *rel*-1-[[*(2R,3S)*-3-(2-chlorophenyl)-2-(2,4-difluorophenyl)-2-oxiranyl]methyl]-5-(2-propen-1-ylthio)-1*H*-1,2,4-triazole. The imidazoles include econazole, imazalil, oxpoconazole, prochloraz, pefurazoate and triflumizole. The pyrimidines include fenarimol, nuarimol and triarimol. The piperazines include triforine. The pyridines include buthiobate, pyrifenox, pyrisoxazole (3-[[*(3R)*-5-(4-chlorophenyl)-2,3-dimethyl-3-isoxazolidinyl]pyridine, mixture of *3R,5R*- and *3R,5S*-isomers) and (*αS*)-[3-(4-chloro-2-fluorophenyl)5-(2,4-difluorophenyl)-4-isoxazolyl]-3-pyridinemethanol. The triazolinthiones include prothioconazole and 2-[2-(1-chlorocyclopropyl)-4-(2,2-dichlorocyclopropyl)-2-hydroxybutyl]-1,2-dihydro-3*H*-1,2,4-triazole-3-thione. Biochemical investigations have shown that all of the above mentioned fungicides are DMI fungicides as described by K. H. Kuck et al. in *Modern Selective Fungicides - Properties, Applications and Mechanisms of Action*, H. Lyr (Ed.), Gustav Fischer Verlag, New York, 1995, 205-258.

(b4) "Phenylamide fungicides" (FRAC code 4) are specific inhibitors of RNA polymerase in Oomycete fungi. Sensitive fungi exposed to these fungicides show a reduced capacity to incorporate uridine into rRNA. growth and development in sensitive fungi is prevented by exposure to this class of fungicide. Phenylamide fungicides include acylalanine, oxazolidinone and butyrolactone fungicides. The acylalanines include benalaxyl, benalaxyl-M (also known as kiralaxyl), furalaxyl, metalaxyl and metalaxyl-M (also known as mefenoxam). The oxazolidinones include oxadixyl. The butyrolactones include ofurace.

(b5) "Amine/morpholine fungicides" (FRAC code 5) (SBI: Class II) inhibit two target sites within the sterol biosynthetic pathway, $\Delta^8 \rightarrow \Delta^7$ isomerase and Δ^{14} reductase. Sterols, such as ergosterol, are needed for membrane structure and function, making them essential for the development of functional cell walls. Therefore, exposure to these fungicides results in abnormal growth and eventually death of sensitive fungi. Amine/morpholine fungicides (also known as non-DMI sterol biosynthesis inhibitors) include morpholine, piperidine and spiroketal-amine fungicides. The morpholines include aldimorph, dodemorph, fenpropimorph, tridemorph and trimorphamide. The piperidines include fenpropidin and piperalin. The spiroketal-amines include spiroxamine.

(b6) "Phospholipid biosynthesis inhibitor fungicides" (FRAC code 6) inhibit growth of fungi by affecting phospholipid biosynthesis. Phospholipid biosynthesis fungicides include phosphorothiolate and dithiolane fungicides. The phosphorothiolates include edifenphos, iprobenfos and pyrazophos. The dithiolanes include isoprothiolane.

(b7) "Succinate dehydrogenase inhibitor (SDHI) fungicides" (FRAC code 7) inhibit Complex II fungal respiration by disrupting a key enzyme in the Krebs Cycle (TCA cycle)

named succinate dehydrogenase. Inhibiting respiration prevents the fungus from making ATP, and thus inhibits growth and reproduction. SDHI fungicides include phenylbenzamide, furan carboxamide, oxathiin carboxamide, thiazole carboxamide, pyrazole-4-carboxamide, pyridine carboxamide, phenyl oxoethyl thiophene amides and pyridinylethyl benzamides. The benzamides include benodanil, flutolanil and mepronil. The furan carboxamides include fenfuram. The oxathiin carboxamides include carboxin and oxycarboxin. The thiazole carboxamides include thifluzamide. The pyrazole-4-carboxamides include benzovindiflupyr (*N*-[9-(dichloromethylene)-1,2,3,4-tetrahydro-1,4-methanonaphthalen-5-yl]-3-(difluoromethyl)-1-methyl-1*H*-pyrazole-4-carboxamide), bixafen, fluindapyr, fluxapyroxad (3-(difluoromethyl)-1-methyl-*N*-(3',4',5'-trifluoro[1,1'-biphenyl]-2-yl)-1*H*-pyrazole-4-carboxamide), furametpyr, isoflucypram, isopyrazam (3-(difluoromethyl)-1-methyl-*N*-[1,2,3,4-tetrahydro-9-(1-methylethyl)-1,4-methanonaphthalen-5-yl]-1*H*-pyrazole-4-carboxamide), penflufen (*N*-[2-(1,3-dimethylbutyl)phenyl]-5-fluoro-1,3-dimethyl-1*H*-pyrazole-4-carboxamide), penthiopyrad, pydiflumetofen, sedaxane (*N*-[2-[1,1'-bicyclopropyl]-2-ylphenyl]-3-(difluoromethyl)-1-methyl-1*H*-pyrazole-4-carboxamide), *N*-[2-(1*S*,2*R*)-[1,1'-bicyclopropyl]-2-ylphenyl]-3-(difluoromethyl)-1-methyl-1*H*-pyrazole-4-carboxamide, 3-(difluoromethyl)-*N*-(2,3-dihydro-1,1,3-trimethyl-1*H*-inden-4-yl)-1-methyl-1*H*-pyrazole-4-carboxamide, *N*-[2-(2,4-dichlorophenyl)2-methoxy-1-methylethyl]-3-(difluoromethyl)-1-methyl-1*H*-pyrazole-4-carboxamide and *N*-cyclopropyl-3-(difluoromethyl)-5-fluoro-1-methyl-*N*-[[2-(1-methylethyl)phenyl]methyl]-1*H*-pyrazole-4-carboxamide. The pyridine carboxamides include boscalid. The phenyl oxoethyl thiophene amides include isofetamid (*N*-[1,1-dimethyl-2-[2-methyl-4-(1-methylethoxy)phenyl]-2-oxoethyl]-3-methyl-2-thiophenecarboxamide). The pyridinylethyl benzamides include fluopyram

(b8) "Hydroxy-(2-amino-)pyrimidine fungicides" (FRAC code 8) inhibit nucleic acid synthesis by interfering with adenosine deaminase. Examples include bupirimate, dimethirimol and ethirimol.

(b9) "Anilinopyrimidine fungicides" (FRAC code 9) are proposed to inhibit biosynthesis of the amino acid methionine and to disrupt the secretion of hydrolytic enzymes that lyse plant cells during infection. Examples include cyprodinil, mepanipyrim and pyrimethanil.

(b10) "*N*-Phenyl carbamate fungicides" (FRAC code 10) inhibit mitosis by binding to β -tubulin and disrupting microtubule assembly. Inhibition of microtubule assembly can disrupt cell division, transport within the cell and cell structure. Examples include diethofencarb.

(b11) "Quinone outside inhibitor (QoI) fungicides" (FRAC code 11) inhibit Complex III mitochondrial respiration in fungi by affecting ubiquinol oxidase. Oxidation of ubiquinol is blocked at the "quinone outside" (Q_o) site of the cytochrome bc_1 complex, which is located in the inner mitochondrial membrane of fungi. Inhibiting mitochondrial respiration prevents normal fungal growth and development. Quinone outside inhibitor fungicides include

methoxyacrylate, methoxycarbamate, oximinoacetate, oximinoacetamide and dihydrodioxazine fungicides (collectively also known as strobilurin fungicides), and oxazolidinedione, imidazolinone and benzylcarbamate fungicides. The methoxyacrylates include azoxystrobin, coumoxystrobin (methyl (αE)-2-[[[3-butyl-4-methyl-2-oxo-2*H*-1-benzopyran-7-yl]oxy]methyl]- α -(methoxymethylene)benzeneacetate), enoxastrobin (methyl (αE)-2-[[[(E)-[(2*E*)-3-(4-chlorophenyl)-1-methyl-2-propen-1-ylidene]amino]oxy]methyl]- α -(methoxymethylene)benzeneacetate) (also known as enestroburin), flufenoxystrobin (methyl (αE)-2-[[2-chloro-4-(trifluoromethyl)phenoxy]methyl]- α -(methoxymethylene)benzeneacetate), picoxystrobin, and pyraoxystrobin (methyl (αE)-2-[[[3-(4-chlorophenyl)-1-methyl-1*H*-pyrazol-5-yl]oxy]methyl]- α -(methoxymethylene)benzeneacetate). The methoxycarbamates include pyraclostrobin, pyrametostrobin (methyl *N*-[2-[[[1,4-dimethyl-3-phenyl-1*H*-pyrazol-5-yl]oxy]methyl]phenyl]-*N*-methoxycarbamate) and triclopyricarb (methyl *N*-methoxy-*N*-[2-[[[3,5,6-trichloro-2-pyridinyl]oxy]methyl]phenyl]carbamate). The oximinoacetates include kresoxim-methyl and trifloxystrobin. The oximinoacetamides include dimoxystrobin, fenaminstrobin ((αE)-2-[[[(E)-[(2*E*)-3-(2,6-dichlorophenyl)-1-methyl-2-propen-1-ylidene]amino]oxy]methyl]- α -(methoxyimino)-*N*-methylbenzeneacetamide), metominostrobin, orysastrobin and α -[methoxyimino]-*N*-methyl-2-[[[1-[3-(trifluoromethyl)phenyl]ethoxy]imino]methyl]benzeneacetamide. The dihydrodioxazines include fluoxastrobin. The oxazolidinediones include famoxadone. The imidazolinones include fenamidone. The benzylcarbamates include pyribencarb. Class (b11) also includes mandestrobin (2-[(2,5-dimethylphenoxy)methyl]- α -methoxy-*N*-benzeneacetamide).

(b12) "Phenylpyrrole fungicides" (FRAC code 12) inhibit a MAP/histidine kinase associated with osmotic signal transduction in fungi. Fenpiclonil and fludioxonil are examples of this fungicide class.

(b13) "Azanaphthalene fungicides" (FRAC code 13) are proposed to inhibit signal transduction by a mechanism which is as yet unknown. They have been shown to interfere with germination and/or appressorium formation in fungi that cause powdery mildew diseases. Azanaphthalene fungicides include aryloxyquinolines and quinazolinones. The aryloxyquinolines include quinoxifen. The quinazolinones include proquinazid.

(b14) "Lipid peroxidation inhibitor fungicides" (FRAC code 14) are proposed to inhibit lipid peroxidation which affects membrane synthesis in fungi. Members of this class, such as etridiazole, may also affect other biological processes such as respiration and melanin biosynthesis. Lipid peroxidation fungicides include aromatic hydrocarbon and 1,2,4-thiadiazole fungicides. The aromatic hydrocarbon fungicides include biphenyl, chloroneb, dicloran, quintozone, tecnazene and tolclofos-methyl. The 1,2,4-thiadiazoles include etridiazole.

(b15) "Melanin biosynthesis inhibitors-reductase (MBI-R) fungicides" (FRAC code 16.1) inhibit the naphthal reduction step in melanin biosynthesis. Melanin is required for host plant infection by some fungi. Melanin biosynthesis inhibitors-reductase fungicides include isobenzofuranone, pyrroloquinolinone and triazolobenzothiazole fungicides. The isobenzofuranones include fthalide. The pyrroloquinolinones include pyroquilon. The triazolobenzothiazoles include tricyclazole.

(b16) "Melanin biosynthesis inhibitors-dehydratase (MBI-D) fungicides" (FRAC code 16.2) inhibit scytalone dehydratase in melanin biosynthesis. Melanin is required for host plant infection by some fungi. Melanin biosynthesis inhibitors-dehydratase fungicides include cyclopropanecarboxamide, carboxamide and propionamide fungicides. The cyclopropanecarboxamides include carpropamid. The carboxamides include diclocymet. The propionamides include fenoxanil.

(b17) "Sterol Biosynthesis Inhibitor (SBI): Class III fungicides (FRAC code 17) inhibit 3-ketoreductase during C4-demethylation in sterol production. SBI: Class III inhibitors include hydroxylanilide fungicides and amino-pyrazolinone fungicides. Hydroxylanilides include fenhexamid. Amino-pyrazolinones include fenpyrazamine (*S*-2-propen-1-yl 5-amino-2,3-dihydro-2-(1-methylethyl)-4-(2-methylphenyl)-3-oxo-1*H*-pyrazole-1-carbothioate).

(b18) "Squalene-epoxidase inhibitor fungicides" (FRAC code 18) (SBI: Class IV) inhibit squalene-epoxidase in the sterol biosynthesis pathway. Sterols such as ergosterol are needed for membrane structure and function, making them essential for the development of functional cell walls. Therefore exposure to these fungicides results in abnormal growth and eventually death of sensitive fungi. Squalene-epoxidase inhibitor fungicides include thiocarbamate and allylamine fungicides. The thiocarbamates include pyributicarb. The allylamines include naftifine and terbinafine.

(b19) "Polyoxin fungicides" (FRAC code 19) inhibit chitin synthase. Examples include polyoxin.

(b20) "Phenylurea fungicides" (FRAC code 20) are proposed to affect cell division. Examples include penicucuron.

(b21) "Quinone inside inhibitor (QiI) fungicides" (FRAC code 21) inhibit Complex III mitochondrial respiration in fungi by affecting ubiquinone reductase. Reduction of ubiquinone is blocked at the "quinone inside" (Q_i) site of the cytochrome *bc*₁ complex, which is located in the inner mitochondrial membrane of fungi. Inhibiting mitochondrial respiration prevents normal fungal growth and development. Quinone inside inhibitor fungicides include cyanoimidazole and sulfamoyltriazole fungicides. The cyanoimidazoles include cyazofamid. The sulfamoyltriazoles include amisulbrom.

(b22) "Benzamide and thiazole carboxamide fungicides" (FRAC code 22) inhibit mitosis by binding to β -tubulin and disrupting microtubule assembly. Inhibition of microtubule

assembly can disrupt cell division, transport within the cell and cell structure. The benzamides include zoxamide. The thiazole carboxamides include ethaboxam.

(b23) "Enopyranuronic acid antibiotic fungicides" (FRAC code 23) inhibit growth of fungi by affecting protein biosynthesis. Examples include blasticidin-S.

5 (b24) "Hexopyranosyl antibiotic fungicides" (FRAC code 24) inhibit growth of fungi by affecting protein biosynthesis. Examples include kasugamycin.

(b25) "Glucopyranosyl antibiotic: protein synthesis fungicides" (FRAC code 25) inhibit growth of fungi by affecting protein biosynthesis. Examples include streptomycin.

10 (b26) "Glucopyranosyl antibiotic: trehalase and inositol biosynthesis fungicides" (FRAC code 26) inhibit trehalase and inositol biosynthesis. Examples include validamycin.

(b27) "Cyanoacetamideoxime fungicides (FRAC code 27) include cymoxanil.

15 (b28) "Carbamate fungicides" (FRAC code 28) are considered multi-site inhibitors of fungal growth. They are proposed to interfere with the synthesis of fatty acids in cell membranes, which then disrupts cell membrane permeability. Propamacarb, iodocarb, and prothiocarb are examples of this fungicide class.

(b29) "Oxidative phosphorylation uncoupling fungicides" (FRAC code 29) inhibit fungal respiration by uncoupling oxidative phosphorylation. Inhibiting respiration prevents normal fungal growth and development. This class includes 2,6-dinitroanilines such as fluazinam, and dinitrophenyl crotonates such as dinocap, meptyldinocap and binapacryl.

20 (b30) "Organo tin fungicides" (FRAC code 30) inhibit adenosine triphosphate (ATP) synthase in oxidative phosphorylation pathway. Examples include fentin acetate, fentin chloride and fentin hydroxide.

(b31) "Carboxylic acid fungicides" (FRAC code 31) inhibit growth of fungi by affecting deoxyribonucleic acid (DNA) topoisomerase type II (gyrase). Examples include oxolinic acid.

25 (b32) "Heteroaromatic fungicides" (Fungicide Resistance Action Committee (FRAC) code 32) are proposed to affect DNA/ribonucleic acid (RNA) synthesis. Heteroaromatic fungicides include isoxazoles and isothiazolones. The isoxazoles include hymexazole and the isothiazolones include oethilinone.

30 (b33) "Phosphonate fungicides" (FRAC code 33) include phosphorous acid and its various salts, including fosetyl-aluminum.

(b34) "Phthalamic acid fungicides" (FRAC code 34) include teclofthalam.

(b35) "Benzotriazine fungicides" (FRAC code 35) include triazoxide.

(b36) "Benzene-sulfonamide fungicides" (FRAC code 36) include flusulfamide.

(b37) "Pyridazinone fungicides" (FRAC code 37) include diclomezine.

35 (b38) "Thiophene-carboxamide fungicides" (FRAC code 38) are proposed to affect ATP production. Examples include silthiofam.

(b39) “Complex I NADH oxidoreductase inhibitor fungicides” (FRAC code 39) inhibit electron transport in mitochondria and include pyrimidinamines such as diflumetorim, and pyrazole-5-carboxamides such as tolfenpyrad.

(b40) “Carboxylic acid amide (CAA) fungicides” (FRAC code 40) inhibit cellulose synthase which prevents growth and leads to death of the target fungus. Carboxylic acid amide fungicides include cinnamic acid amide, valinamide and other carbamate, and mandelic acid amide fungicides. The cinnamic acid amides include dimethomorph, flumorph and pyrimorph (3-(2-chloro-4-pyridinyl)-3-[4-(1,1-dimethylethyl)phenyl]-1-(4-morpholinyl)-2-propene-1-one). The valinamide and other carbamates include bentiavalicarb, bentiavalicarb-isopropyl, iprovalicarb, tolprocarb (2,2,2-trifluoroethyl *N*-[(1*S*)-2-methyl-1-[(4-methylbenzoyl)amino]methyl]propyl]carbamate) and valifenalate (methyl *N*-[(1-methylethoxy)carbonyl]-L-valyl-3-(4-chlorophenyl)- β -alaninate) (also known as valiphenal). The mandelic acid amides include mandipropamid, *N*-[2-[4-[[3-(4-chlorophenyl)-2-propyn-1-yl]oxy]-3-methoxyphenyl]ethyl]-3-methyl-2-[(methylsulfonyl)amino]butanamide and *N*-[2-[4-[[3-(4-chlorophenyl)-2-propyn-1-yl]oxy]-3-methoxyphenyl]ethyl]-3-methyl-2-[(ethylsulfonyl)amino]butanamide.

(b41) “Tetracycline antibiotic fungicides” (FRAC code 41) inhibit growth of fungi by affecting protein synthesis. Examples include oxytetracycline.

(b42) “Thiocarbamate fungicides” (FRAC code 42) include methasulfocarb.

(b43) “Benzamide fungicides” (FRAC code 43) inhibit growth of fungi by delocalization of spectrin-like proteins. Examples include pyridinylmethyl benzamide fungicides such as fluopicolide (now FRAC code 7, pyridinylethyl benzamides).

(b44) “Microbial fungicides” (FRAC code 44) disrupt fungal pathogen cell membranes. Microbial fungicides include *Bacillus* species such as *Bacillus amyloliquefaciens* strains QST 713, FZB24, MB1600, D747 and the fungicidal lipopeptides which they produce.

(b45) “Q_xI fungicides” (FRAC code 45) inhibit Complex III mitochondrial respiration in fungi by affecting ubiquinone reductase at an unknown (Q_x) site of the cytochrome *bc*₁ complex. Inhibiting mitochondrial respiration prevents normal fungal growth and development. Q_xI fungicides include triazolopyrimidylamines such as ametocetradin (5-ethyl-6-octyl[1,2,4]triazolo[1,5-*a*]pyrimidin-7-amine).

(b46) “Plant extract fungicides” are proposed to act by cell membrane disruption. Plant extract fungicides include terpene hydrocarbons and terpene alcohols such as the extract from *Melaleuca alternifolia* (tea tree).

(b47) “Host plant defense induction fungicides” (FRAC code P) induce host plant defense mechanisms. Host plant defense induction fungicides include benzothiadiazoles, benzisothiazole and thiadiazole-carboxamide fungicides. The benzothiadiazoles include

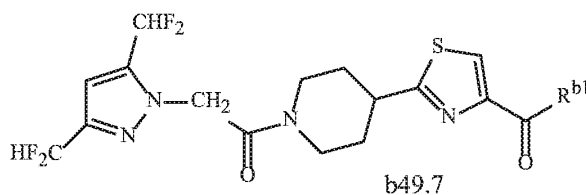
acibenzolar-S-methyl. The benzisothiazoles include probenazole. The thiadiazole-carboxamides include tiadinil and isotianil.

(b48) "Multi-site contact fungicides" inhibit fungal growth through multiple sites of action and have contact/preventive activity. This class of fungicides includes: (b48.1) "copper fungicides" (FRAC code M1)", (b48.2) "sulfur fungicides" (FRAC code M2), (b48.3) "dithiocarbamate fungicides" (FRAC code M3), (b48.4) "phthalimide fungicides" (FRAC code M4), (b48.5) "chloronitrile fungicides" (FRAC code M5), (b48.6) "sulfamide fungicides" (FRAC code M6), (b48.7) multi-site contact "guanidine fungicides" (FRAC code M7), (b48.8) "triazine fungicides" (FRAC code M8), (b48.9) "quinone fungicides" (FRAC code M9), (b48.10) "quinoxaline fungicides" (FRAC code M10) and (b48.11) "maleimide fungicides" (FRAC code M11). "Copper fungicides" are inorganic compounds containing copper, typically in the copper(II) oxidation state; examples include copper oxychloride, copper sulfate and copper hydroxide, including compositions such as Bordeaux mixture (tribasic copper sulfate). "Sulfur fungicides" are inorganic chemicals containing rings or chains of sulfur atoms; examples include elemental sulfur. "Dithiocarbamate fungicides" contain a dithiocarbamate molecular moiety; examples include mancozeb, metiram, propineb, ferbam, maneb, thiram, zineb and ziram. "Phthalimide fungicides" contain a phthalimide molecular moiety; examples include folpet, captan and captafol. "Chloronitrile fungicides" contain an aromatic ring substituted with chloro and cyano; examples include chlorothalonil. "Sulfamide fungicides" include dichlofluanid and tolyfluanid. Multi-site contact "guanidine fungicides" include, guazatine, iminoctadine albesilate and iminoctadine triacetate. "Triazine fungicides" include anilazine. "Quinone fungicides" include dithianon. "Quinoxaline fungicides" include quinomethionate (also known as chinomethionate). "Maleimide fungicides" include fluoroimide.

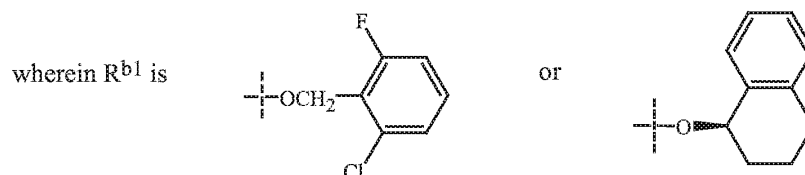
(b49) "Fungicides other than fungicides of classes (b1) through (b48)" include certain fungicides whose mode of action may be unknown. These include: (b49.1), "phenyl-acetamide fungicides" (FRAC code U6), (b49.2) "aryl-phenyl-ketone fungicides" (FRAC code U8), (b49.3) "guanidine fungicides" (FRAC code U12), (b49.4) "thiazolidine fungicides" (FRAC code U13), (b49.5) "pyrimidinone-hydrazone fungicides" (FRAC code U14) and (b49.6) compounds that bind to oxysterol-binding protein as described in PCT Patent Publication WO 2013/009971. The phenyl-acetamides include cyflufenamid and *N*-[[[(cyclopropylmethoxy)amino][6-(difluoromethoxy)-2,3-difluorophenyl]-methylene]-benzeneacetamide. The aryl-phenyl ketones include benzophenones such as metrafenone, and benzoylpyridines such as pyriofenone (5-chloro-2-methoxy-4-methyl-3-pyridinyl)(2,3,4-trimethoxy-6-methylphenyl)methanone). The guanidines include dodine. The thiazolidines include flutianil ((2*Z*)-2-[[2-fluoro-5-(trifluoromethyl)phenyl]thio]-2-[3-(2-methoxyphenyl)-2-thiazolidinylidene]acetonitrile). The pyrimidinonehydrazones include ferimzone. The

- (b49.6) class includes oxathiapiprolin (1-[4-[4-[5-(2,6-difluorophenyl)-4,5-dihydro-3-isoxazolyl]-2-thiazolyl]-1-piperidinyl]-2-[5-methyl-3-(trifluoromethyl)-1*H*-pyrazol-1-yl]ethanone) and its *R*-enantiomer which is 1-[4-[4-[5*R*-(2,6-difluorophenyl)-4,5-dihydro-3-isoxazolyl]-2-thiazolyl]-1-piperidinyl]-2-[5-methyl-3-(trifluoromethyl)-1*H*-pyrazol-1-yl]-ethanone (Registry Number 1003319-79-6). The (b49) class also includes bethoxazin, flometoquin (2-ethyl-3,7-dimethyl-6-[4-(trifluoromethoxy)phenoxy]-4-quinolinyl methyl carbonate), fluoroimide, neo-asozin (ferric methanearsonate), picarbutrazox (1,1-dimethylethyl *N*-[6-[[[(*Z*)-1-methyl-1*H*-tetrazol-5-yl]phenylmethylene]amino]oxy]methyl]-2-pyridinyl]carbamate), pyrrolnitrin, quinomethionate, tebufloquin (6-(1,1-dimethylethyl)-8-fluoro-2,3-dimethyl-4-quinolinyl acetate), tolnifanide (*N*-(4-chloro-2-nitrophenyl)-*N*-ethyl-4-methylbenzenesulfonamide), 2-butoxy-6-iodo-3-propyl-4*H*-1-benzopyran-4-one, 3-butyn-1-yl, *N*-[6-[[[(1-methyl-1*H*-tetrazol-5-yl)phenylmethylene]amino]oxy]methyl]-2-pyridinyl]-carbamate, (*N*-(4-chloro-2-nitrophenyl)-*N*-ethyl-4-methylbenzenesulfonamide), *N*'-[4-[4-chloro-3-(trifluoromethyl)phenoxy]-2,5-dimethylphenyl]-*N*-ethyl-*N*-methylmethanimid-
 15 amide, *N*-[[[(cyclopropylmethoxy)amino][6-(difluoromethoxy)-2,3-difluorophenyl]methylene]benzeneacetamide, 2,6-dimethyl-1*H*,5*H*-[1,4]dithiino[2,3-*c*:5,6-*c'*]dipyrrole-1,3,5,7(2*H*,6*H*)-tetrone, 5-fluoro-2-[(4-methylphenyl)methoxy]-4-pyrimidinamine, 5-fluoro-2-[(4-fluorophenyl)methoxy]-4-pyrimidinamine and 4-fluorophenyl *N*-[1-[[[1-(4-cyano-phenyl)ethyl]sulfonyl]methyl]propyl]carbamate, pentyl *N*-[6-[[[(1-methyl-1*H*-tetrazol-5-yl)-phenylmethylene]amino]oxy]methyl]-2-pyridinyl]carbamate, pentyl *N*-[4-[[[(1-methyl-1*H*-tetrazol-5-yl)phenylmethylene]amino]oxy]methyl]-2-thiazolyl]carbamate and pentyl *N*-[6-[[[(*Z*)-(1-methyl-1*H*-tetrazol-5-yl)phenylmethylene]amino]oxy]methyl]-2-pyridinyl]-
 20 carbamate. The (b46) class further includes mitosis- and cell division-inhibiting fungicides besides those of the particular classes described above (e.g., (b1), (b10) and (b22)).
 25 Additional "Fungicides other than fungicides of classes (1) through (46)" whose mode of action may be unknown, or may not yet be classified include a fungicidal compound selected from components (b49.7) through (b49.12), as shown below.

Component (b49.7) relates to a compound of Formula b49.7



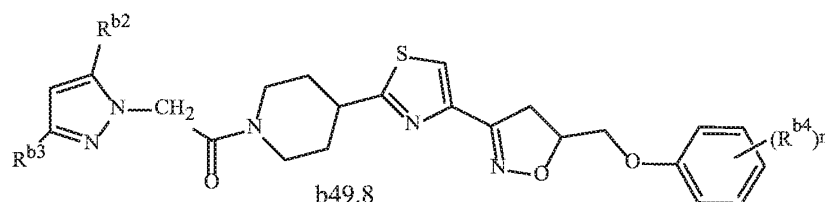
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Examples of a compound of Formula b49.7 include (b49.7a) (2-chloro-6-fluorophenyl)methyl 2-[1-[2-[3,5-bis(difluoromethyl)-1*H*-pyrazol-1-yl]acetyl]-4-piperidinyl]-4-thiazole-carboxylate (Registry Number 1299409-40-7) and (b49.7b) (1*R*)-1,2,3,4-tetrahydro-1-naphthalenyl 2-[1-[2-[3,5-bis(difluoromethyl)-1*H*-pyrazol-1-yl]acetyl]-4-piperidinyl]-4-thiazolecarboxylate (Registry Number 1299409-42-9). Methods for preparing compounds of

5 Formula b46.2 are described in PCT Patent Publications WO 2009/132785 and WO 2011/051243.

Component (b49.8) relates to a compound of Formula b49.8

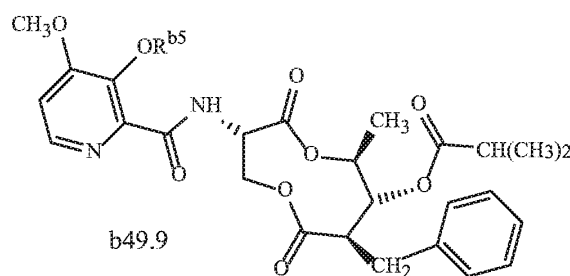


10 wherein R^{b2} is CH₃, CF₃ or CHF₂; R^{b3} is CH₃, CF₃ or CHF₂; R^{b4} is halogen or cyano; and n is 0, 1, 2 or 3.

Examples of a compound of Formula b49.8 include (b49.8a) 1-[4-[4-[5-[(2,6-difluorophenoxy)methyl]-4,5-dihydro-3-isoxazolyl]-2-thiazolyl]-1-piperidinyl]-2-[5-methyl-3-(trifluoromethyl)-1*H*-pyrazol-1-yl]ethanone. Methods for preparing compounds of

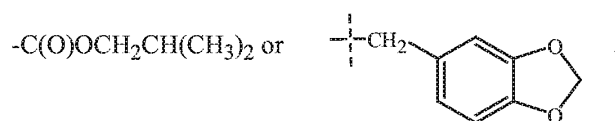
15 Formula b49.8 are described in PCT Patent Application PCT/US11/64324.

Component (b4799) relates to a compound of Formula b49.9



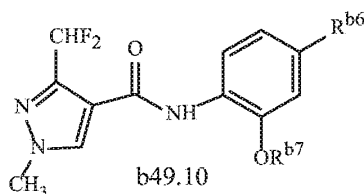
wherein R^{b5} is -CH₂OC(O)CH(CH₃)₂, -C(O)CH₃, -CH₂OC(O)CH₃,

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Examples of a compound of Formula b49.9 include (b49.9a) [[4-methoxy-2-[[[(3*S*,7*R*,8*R*,9*S*)-9-methyl-8-(2-methyl-1-oxopropoxy)-2,6-dioxo-7-(phenylmethyl)-1,5-dioxonan-3-yl]-amino]carbonyl]-3-pyridinyl]oxy]methyl 2-methylpropanoate (Registry Number 517875-34-2), (b49.9b) (3*S*,6*S*,7*R*,8*R*)-3-[[[3-(acetyloxy)-4-methoxy-2-pyridinyl]carbonyl]amino]-6-methyl-4,9-dioxo-8-(phenylmethyl)-1,5-dioxonan-7-yl 2-methylpropanoate (Registry Number 234112-93-7), (b49.9c) (3*S*,6*S*,7*R*,8*R*)-3-[[[3[(acetyloxy)methoxy]-4-methoxy-2-pyridinyl]carbonyl]amino]-6-methyl-4,9-dioxo-8-(phenylmethyl)-1,5-dioxonan-7-yl 2-methylpropanoate (Registry Number 517875-31-9), (b49.9d) (3*S*,6*S*,7*R*,8*R*)-3-[[[4-methoxy-3-[(2-methylpropoxy)carbonyl]oxy]-2-pyridinyl]carbonyl]amino]-6-methyl-4,9-dioxo-8-(phenylmethyl)-1,5-dioxonan-7-yl 2-methylpropanoate (Registry Number 328256-72-0), and (b49.9e) *N*-[[[3-(1,3-benzodioxol-5-ylmethoxy)-4-methoxy-2-pyridinyl]carbonyl]-*O*-(2,5-dideoxy-3-*O*-(2-methyl-1-oxopropyl)-2-(phenylmethyl)-*L*-arabinonoyl)]-*L*-serine, (1→4')-lactone (Registry Number 1285706-70-8). Methods for preparing compounds of Formula b49.9 are described in PCT Patent Publications WO 99/40081, WO 2001/014339, WO 2003/035617 and WO 2011044213.

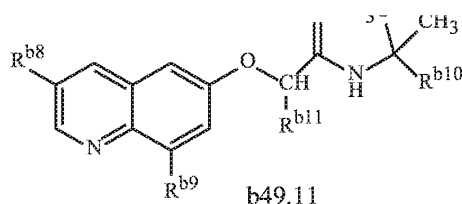
Component (b49.10) relates to a compound of Formula b49.10



wherein R^{b6} is H or F, and R^{b7} is $-\text{CF}_2\text{CHF}\text{CF}_3$ or $-\text{CF}_2\text{CF}_2\text{H}$. Examples of a compound of Formula b49.10 are (b49.10a) 3-(difluoromethyl)-*N*-[4-fluoro-2-(1,1,2,3,3,3-hexafluoropropoxy)phenyl]-1-methyl-1*H*-pyrazole-4-carboxamide (Registry Number 1172611-40-3) and (b49.10b) 3-(difluoromethyl)-1-methyl-*N*-[2-(1,1,2,2-tetrafluoroethoxy)phenyl]-1*H*-pyrazole-4-carboxamide (Registry Number 923953-98-4). Compounds of Formula 49.10 can be prepared by methods described in PCT Patent Publication WO 2007/017450.

Component b49.11 relates to a compound of Formula b49.11

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wherein

R^{b8} is halogen, C_1 - C_4 alkoxy or C_2 - C_4 alkynyl;

R^{b9} is H, halogen or C_1 - C_4 alkyl;

5 R^{b10} is C_1 - C_{12} alkyl, C_1 - C_{12} haloalkyl, C_1 - C_{12} alkoxy, C_2 - C_{12} alkoxyalkyl, C_2 - C_{12} alkenyl, C_2 - C_{12} alkynyl, C_4 - C_{12} alkoxyalkenyl, C_4 - C_{12} alkoxyalkynyl, C_1 - C_{12} alkylthio or C_2 - C_{12} alkylthioalkyl;

R^{b11} is methyl or $-Y^{b13}-R^{b12}$;

R^{b12} is C_1 - C_2 alkyl; and

10 Y^{b13} is CH_2 , O or S.

Examples of compounds of Formula b49.11 include (b49.11a) 2-[(3-bromo-6-quinolinyl)oxy]-*N*-(1,1-dimethyl-2-butyne-1-yl)-2-(methylthio)acetamide, (b49.11b) 2[(3-ethynyl-6-quinolinyl)oxy]-*N*-[1-(hydroxymethyl)-1-methyl-2-propyne-1-yl]-2-(methylthio)acetamide, (b49.11c) *N*-(1,1-dimethyl-2-butyne-1-yl)-2-[(3-ethynyl-6-quinolinyl)oxy]-2-(methylthio)-acetamide, (b49.11d) 2-[(3-bromo-8-methyl-6-quinolinyl)oxy]-*N*-(1,1-dimethyl-2-propyne-1-yl)-2-(methylthio)acetamide and (b49.11e) 2-[(3-bromo-6-quinolinyl)oxy]-*N*-(1,1-dimethylethyl)butanamide. Compounds of Formula b49.11, their use as fungicides and methods of preparation are generally known; see, for example, PCT Patent Publications WO 2004/047538, WO 2004/108663, WO 2006/058699, WO 2006/058700, 20 WO 2008/110355, WO 2009/030469, WO 2009/049716 and WO 2009/087098.

Component 49.12 relates to *N*'-[4-[[3-[(4-chlorophenyl)methyl]-1,2,4-thiadiazol-5-yl]oxy]-2,5-dimethylphenyl]-*N*-ethyl-*N*-methylmethanimidamide, which is believed to inhibit C24-methyl transferase involved in the biosynthesis of sterols.

Therefore of note is a mixture (i.e. composition) comprising a compound of Formula 1 and at least one fungicidal compound selected from the group consisting of the aforescribed classes (1) through (49). Also of note is a composition comprising said mixture (in fungicidally effective amount) and further comprising at least one additional component selected from the group consisting of surfactants, solid diluents and liquid diluents. Of particular note is a mixture (i.e. composition) comprising a compound of Formula 1 and at least one fungicidal 25 compound selected from the group of specific compounds listed above in connection with classes (1) through (49). Also of particular note is a composition comprising said mixture (in 30

fungicidally effective amount) and further comprising at least one additional surfactant selected from the group consisting of surfactants, solid diluents and liquid diluents.

Examples of component (b) fungicides include acibenzolar-S-methyl, aldimorph, ametoctradin, amisulbrom, anilazine, azaconazole, azoxystrobin, benalaxyl (including
 5 benalaxyl-M), benodanil, benomyl, benthiavalicarb (including benthiavalicarb-isopropyl), benzovindiflupyr, bethoxazin, binapacryl, biphenyl, bitertanol, bixafen, blastocidin-S, boscalid, bromuconazole, bupirimate, buthiobate, captafol, captan, carbendazim, carboxin, carpropamid, chloroneb, chlorothalonil, chlozolinate, clotrimazole, copper hydroxide, copper oxychloride, copper sulfate, coumoxystrobin, cyazofamid, cyflufenamid, cymoxanil, cyproconazole,
 10 cyprodinil, dichlofluanid, diclocymet, diclomezine, dicloran, diethofencarb, difenoconazole, diflumetorim, dimethirimol, dimethomorph, dimoxystrobin, diniconazole (including diniconazole-M), dinocap, dithianon, dithiolanes, dodemorph, dodine, econazole, edifenphos, enoxastrobin (also known as enestroburin), epoxiconazole, etaconazole, ethaboxam, ethirimol, etridiazole, famoxadone, fenamidone, fenarimol, fenaminstrobin, fenbuconazole, fenfuram,
 15 fenhexamid, fenoxanil, fenpiclonil, fenpropidin, fenpropimorph, fenpyrazamine, fentin acetate, fentin chloride, fentin hydroxide, ferbam, ferimzone, flometoquin, florylpicoxamid, fluazinam, fludioxonil, flufenoxystrobin, fluindapyr, flumorph, fluopicolide, fluopyram, flouroimide, fluoxastrobin, fluquinconazole, flusilazole, flusulfamide, flutianil, flutolanil, flutriafol, fluxapyroxad, folpet, fthalide, fuberidazole, furalaxyl, furametpyr, guazatine, hexaconazole,
 20 hymexazole, imazalil, imibenconazole, iminoctadine albesilate, iminoctadine triacetate, iodocarb, ipconazole, iprobenfos, iprodione, iprovalicarb, isoconazole, isofetamid, isoprothiolane, isoflucypram, isopyrazam, isotianil, kasugamycin, kresoxim-methyl, mancozeb, mandeppropamid, mandestrobin, maneb, mepanipyrim, mepronil, meptyldinocap, metalaxyl (including metalaxyl-M/mefenoxam), mefentrifluconazole, metconazole,
 25 methasulfocarb, metiram, metominostrobin, metrafenone, miconazole, myclobutanil, naftifine, neo-asozin, nuarimol, octhilinone, ofurace, orysastrobin, oxadixyl, oxathiapiprolin, oxolinic acid, oxpoconazole, oxycarboxin, oxytetracycline, pefurazoate, penconazole, pencycuron, penflufen, penthiopyrad, phosphorous acid (including salts thereof, e.g., fosetyl-aluminum), picarbutrazox, picoxystrobin, piperalin, polyoxin, probenazole, prochloraz, procymidone,
 30 propamacarb, propiconazole, propineb, proquinazid, prothiocarb, prothioconazole, pyraclostrobin, pyrametostrobin, pyraoxystrobin, pyrazophos, pyribencarb, pyributicarb, pyrifenoxy, pyrimethanil, pyriofenone, pyrisoxazole, pyroquilon, pyrrolnitrin, quinconazole, quinomethionate, quinoxifen, quintozone, sedaxane, silthiofam, simeconazole, spiroxamine, streptomycin, sulfur, tebuconazole, tebufloquin, teclofthalam, tecnazene, terbinafine,
 35 tetraconazole, thiabendazole, thifluzamide, thiophanate, thiophanate-methyl, thiram, tiadinil, tolclofos-methyl, tolnifanide, tolprocarb, tolyfluanid, triadimefon, triadimenol, triarimol, triticonazole, triazoxide, tribasic copper sulfate, tricyclazole, triclopyricarb, tridemorph,

trifloxystrobin, triflumizole, triforine, trimorphamide, uniconazole, uniconazole-P, validamycin, valifenalate (also known as valiphenal), vinclozolin, zineb, ziram, zoxamide, (3*S*,6*S*,7*R*,8*R*)-3-[[[3-[(acetyloxy)methoxy]-4-methoxy-2-pyridinyl]carbonyl]amino]-6-methyl-4,9-dioxo-8-(phenylmethyl)-1,5-dioxonan-7-yl 2-methylpropanoate, (3*S*,6*S*,7*R*,8*R*)-3-
5 [[3-(acetyloxy)-4-methoxy-2-pyridinyl]carbonyl]amino]-6-methyl-4,9-dioxo-8-(phenylmethyl)-1,5-dioxonan-7-yl 2-methylpropanoate, *N*-[[3-(1,3-benzodioxol-5-ylmethoxy)-4-methoxy-2-pyridinyl]carbonyl]-*O*-[2,5-dideoxy-3-*O*-(2-methyl-1-oxopropyl)-2-(phenylmethyl)-*L*-arabinonoyl]-*L*-serine, (1 $\rightarrow$ 4')-lactone, *N*-[2-(1*S*,2*R*)-[1,1'-bicyclopropyl]-2-ylphenyl]-3-(difluoromethyl)-1-methyl-1*H*-pyrazole-4-carboxamide, 2-[(3-bromo-6-quinolinyl)oxy]-*N*-(1,1-dimethyl-2-butyne-1-yl)-2-(methylthio)acetamide, 2-[(3-bromo-6-quinolinyl)oxy]-*N*-(1,1-dimethylethyl)butanamide, 2-[(3-bromo-8-methyl-6-quinolinyl)oxy]-*N*-(1,1-dimethyl-2-propyne-1-yl)-2-(methylthio)acetamide, 2-butoxy-6-iodo-3-propyl-4*H*-1-benzopyran-4-one, 3-butyne-1-yl *N*-[6-[[[(1-methyl-1*H*-tetrazol-5-yl)phenyl]methylene]-amino]oxy]methyl]-2-pyridinyl]carbamate, α -(1-chlorocyclopropyl)- α -[2-(2,2-dichlorocyclopropyl)ethyl]-1*H*-1,2,4-triazole-1-ethanol, 2-[2-(1-chlorocyclopropyl)-4-(2,2-dichlorocyclopropyl)-2-hydroxybutyl]-1,2-dihydro-3*H*-1,2,4-triazole-3-thione, (α *S*)-[3-(4-chloro-2-fluorophenyl)-5-(2,4-difluorophenyl)-4-isoxazolyl]-3-pyridinemethanol, *rel*-1-[[2*R*,3*S*]-3-(2-chlorophenyl)-2-(2,4-difluorophenyl)-2-oxiranyl]methyl]-1*H*-1,2,4-triazole, *rel*-2-[[2*R*,3*S*]-3-(2-chlorophenyl)-2-(2,4-difluorophenyl)-2-oxiranyl]methyl]-1,2-dihydro-3*H*-1,2,4-triazole-3-thione, *rel*-1-[[2*R*,3*S*]-3-(2-chlorophenyl)-2-(2,4-difluorophenyl)-2-oxiranyl]methyl]-5-(2-propen-1-ylthio)-1*H*-1,2,4-triazole, 3-[5-(4-chlorophenyl)-2,3-dimethyl-3-isoxazolidinyl]pyridine, (2-chloro-6-fluorophenyl)methyl 2-[1-[2-[3,5-bis(difluoromethyl)-1*H*-pyrazol-1-yl]acetyl]-4-piperidinyl]-4-thiazolecarboxylate, *N*'-[4-[[3-(4-chlorophenyl)-methyl]-1,2,4-thiadiazol-5-yl]oxy]-2,5-dimethylphenyl]-*N*-ethyl-*N*-methyl-methanimidamide, 25 *N*-[2-[4-[[3-(4-chlorophenyl)-2-propyne-1-yl]oxy]-3-methoxyphenyl]ethyl]-3-methyl-2-[(methylsulfonyl)amino]butanamide, *N*-[2-[4-[[3-(4-chlorophenyl)-2-propyne-1-yl]oxy]-3-methoxyphenyl]ethyl]-3-methyl-2-[(ethylsulfonyl)amino]butanamide, *N*'-[4-[4-chloro-3-(trifluoromethyl)phenoxy]-2,5-dimethylphenyl]-*N*-ethyl-*N*-methyl-methanimidamide, *N*-cyclopropyl-3-(difluoromethyl)-5-fluoro-1-methyl-*N*-[[2-(1-methylethyl)phenyl]methyl]-1*H*-pyrazole-4-carboxamide, *N*-[[cyclopropylmethoxy]amino][6-(difluoromethoxy)-2,3-difluorophenyl]methylene]benzeneacetamide, *N*-[2-(2,4-dichlorophenyl)-2-methoxy-1-methylethyl]-3-(difluoromethyl)-1-methyl-1*H*-pyrazole-4-carboxamide, *N*-(3',4'-difluoro[1,1'-biphenyl]-2-yl)-3-(trifluoromethyl)-2-pyrazinecarboxamide, 3-(difluoromethyl)-*N*-(2,3-dihydro-1,1,3-trimethyl-1*H*-inden-4-yl)-1-methyl-1*H*-pyrazole-4-carboxamide, 3-(difluoromethyl)-*N*-[4-fluoro-2-(1,1,2,3,3,3-hexafluoropropoxy)phenyl]-1-methyl-1*H*-pyrazole-4-carboxamide, 5,8-difluoro-*N*-[2-[3-methoxy-4-[[4-(trifluoromethyl)-2-pyridinyl]oxy]phenyl]-

ethyl]-4-quinazolinamine, 3-(difluoromethyl)-1-methyl-*N*-[2-(1,1,2,2-tetrafluoroethoxy) - phenyl]-1*H*-pyrazole-4-carboxamide, 1-[4-[4-[5*R*-[(2,6-difluorophenoxy)methyl]-4,5-dihydro-3-isoxazolyl]-2-thiazolyl]-1-piperdiny]-2-[5-methyl-3-(trifluoromethyl)-1*H*-pyrazol-1-yl]ethanone, *N*-(1,1-dimethyl-2-butyne-1-yl)-2-[(3-ethynyl-6-quinolinyl)oxy]-2-(methylthio)acetamide, 2,6-dimethyl-1*H*,5*H*-[1,4]dithiino[2,3-*c*:5,6-*c'*]dipyrrole-1,3,5,7(2*H*,6*H*)-tetrone, 2-[(3-ethynyl-6-quinolinyl)oxy]-*N*-[1-(hydroxymethyl)-1-methyl-2-propyne-1-yl]-2-(methylthio)acetamide, 4-fluorophenyl *N*-[1-[[[1-(4-cyanophenyl)ethyl]sulfonyl]methyl]-propyl]carbamate, 5-fluoro-2-[(4-fluorophenyl)methoxy]-4-pyrimidinamine, 5-fluoro-2-[(4-methylphenyl)methoxy]-4-pyrimidinamine, (3*S*,6*S*,7*R*,8*R*)-3-[[[4-methoxy-3-[(2-methylpropoxy)carbonyl]oxy]-2-pyridinyl]carbonyl]amino]-6-methyl-4,9-dioxo-8-(phenylmethyl)-1,5-dioxonan-7-yl-2-methylpropanoate, α -(methoxyimino)-*N*-methyl-2-[[[1-[3-(trifluoromethyl)phenyl]ethoxy]imino]methyl]benzeneacetamide, [[4-methoxy-2-[[[(3*S*,7*R*,8*R*,9*S*)-9-methyl-8-(2-methyl-1-oxopropoxy)-2,6-dioxo-7-(phenylmethyl)-1,5-dioxonan-3-yl]-amino]carbonyl]-3-pyridinyl]oxy]methyl 2-methylpropanoate, pentyl *N*-[6-[[[(1-methyl-1*H*-tetrazol-5-yl)phenylmethylene]amino]oxy]methyl]-2-pyridinyl]carbamate, pentyl *N*-[4-[[[(1-methyl-1*H*-tetrazol-5-yl)phenylmethylene]amino]oxy]methyl]-2-thiazolyl]carbamate, and pentyl *N*-[6-[[[(*Z*)-(1-methyl-1*H*-tetrazol-5-yl)phenylmethylene]amino]oxy]methyl]-2-pyridinyl]carbamate and (1*R*)-1,2,3,4-tetrahydro-1-naphthalenyl 2-[1-[2-[3,5-bis(difluoromethyl)-1*H*-pyrazol-1-yl]acetyl]-4-piperidinyl]-4-thiazolecarboxylate. Therefore of note is a fungicidal composition comprising as component (a) a compound of Formula 1 (or an *N*-oxide or salt thereof) and as component (b) at least one fungicide selected from the preceding list.

Of particular note are combinations of compounds of Formula 1 (or an *N*-oxide or salt thereof) (i.e. Component (a) in compositions) with azoxystrobin, benzovindiflupyr, bixafen, captan, carpropamid, chlorothalonil, copper hydroxide, copper oxychloride, copper sulfate, cymoxanil, cyproconazole, cyprodinil, diethofencarb, difenoconazole, dimethomorph, epoxiconazole, ethaboxam, fenarimol, fenhexamid, fluazinam, fludioxonil, fluindapyr, fluopyram, flusilazole, flutianil, flutriafol, fluxapyroxad, folpet, iprodione, isofetamid, isoflucypram, isopyrazam, kresoxim-methyl, mancozeb, mandestrobin, meptyldinocap, metalaxyl (including metalaxyl-M/mefenoxam), mefentrifluconazole, metconazole, metrafenone, myclobutanil, oxathiapiprolin, penflufen, penthiopyrad, phosphorous acid (including salts thereof, e.g., fosetyl-aluminum), picoxystrobin, propiconazole, proquinazid, prothioconazole, pyraclostrobin, pyrimethanil, sedaxane spiroxamine, sulfur, tebuconazole, thiophanate-methyl, trifloxystrobin, zoxamide, α -(1-chlorocyclopropyl)- α -[2-(2,2-dichlorocyclopropyl)ethyl]-1*H*-1,2,4-triazole-1-ethanol, 2-[2-(1-chlorocyclopropyl)-4-(2,2-dichlorocyclopropyl)-2-hydroxybutyl]-1,2-dihydro-3*H*-1,2,4-triazole-3-thione, *N*-[2-(2,4-dichlorophenyl)-2-methoxy-1-methylethyl]-3-(difluoromethyl)-1-methyl-1*H*-pyrazole-4-carboxamide, 3-(difluoromethyl)-*N*-(2,3-dihydro-1,1,3-trimethyl-1*H*-inden-4-yl)-1-methyl-

1*H*-pyrazole-4-carboxamide, 1-[4-[4-[5*R*-(2,6-difluorophenyl)-4,5-dihydro-3-isoxazolyl]-2-thiazolyl]-1-piperidinyl]-2-[5-methyl-3-(trifluoromethyl)-1*H*-pyrazol-1-yl]ethanone, 1,1-dimethylethyl *N*-[6-[[[(1-methyl-1*H*-tetrazol-5-yl)phenylmethylene]amino]oxy]methyl]-2-pyridinyl]carbamate, 2,6-dimethyl-1*H*,5*H*-[1,4]dithiino[2,3-*c*:5,6-*c'*]dipyrrole-1,3,5,7-
 5 (2*H*,6*H*)-tetrone, 5-fluoro-2-[(4-fluorophenyl)methoxy]-4-pyrimidinamine, 5-fluoro-2-[(4-methylphenyl)methoxy]-4-pyrimidinamine, (*αS*)-[3-(4-chloro-2-fluorophenyl)-5-(2,4-difluorophenyl)-4-isoxazolyl]-3-pyridinemethanol, *rel*-1-[[2*R*,3*S*]-3-(2-chlorophenyl)-2-(2,4-difluorophenyl)-2-oxiranyl]methyl]-1*H*-1,2,4-triazole, *rel*-2-[[2*R*,3*S*]-3-(2-chlorophenyl)-2-(2,4-difluorophenyl)-2-oxiranyl]methyl]-1,2-dihydro-3*H*-1,2,4-triazole-3-thione, and *rel*-1-
 10 [[2*R*,3*S*]-3-(2-chlorophenyl)-2-(2,4-difluorophenyl)-2-oxiranyl]methyl]-5-(2-propen-1-ylthio)-1*H*-1,2,4-triazole (i.e. as Component (b) in compositions).

Examples of other biologically active compounds or agents with which compounds of this invention can be formulated are: invertebrate pest control compounds or agents such as abamectin, acephate, acetamiprid, acrinathrin, afidopyropen
 15 ([3*S*,4*R*,4*aR*,6*S*,6*aS*,12*R*,12*aS*,12*bS*)-3-[(cyclopropylcarbonyl)oxy]-1,3,4,4*a*,5,6,6*a*,12,12*a*,12*b*-decahydro-6,12-dihydroxy-4,6*a*,12*b*-trimethyl-11-oxo-9-(3-pyridinyl)-2*H*,11*H*-naphtho[2,1-*b*]pyrano[3,4-*e*]pyran-4-yl]methyl cyclopropanecarboxylate), amidoflumet (S-1955), avermectin, azadirachtin, azinphos-methyl, bifenthrin, bifenazate, buprofezin, carbofuran, cartap, chlorantraniliprole, chlorfenapyr, chlorfluazuron, chlorpyrifos,
 20 chlorpyrifos-methyl, chromafenozide, clothianidin, cyantraniliprole (3-bromo-1-(3-chloro-2-pyridinyl)-*N*-[4-cyano-2-methyl-6-[(methylamino)carbonyl]phenyl]-1*H*-pyrazole-5-carboxamide), cyclaniliprole (3-bromo-*N*-[2-bromo-4-chloro-6-[(1-cyclopropylethyl)-amino]carbonyl]phenyl)-1-(3-chloro-2-pyridinyl)-1*H*-pyrazole-5-carboxamide), cycloxaprid ((5*S*,8*R*)-1-[(6-chloro-3-pyridinyl)methyl]-2,3,5,6,7,8-hexahydro-9-nitro-5,8-epoxy-1*H*-
 25 imidazo[1,2-*a*]azepine), cyflumetofen, cyfluthrin, beta-cyfluthrin, cyhalothrin, lambda-cyhalothrin, cypermethrin, cyromazine, deltamethrin, diafenthiuron, diazinon, dieldrin, diflubenzuron, dimefluthrin, dimethoate, dinotefuran, diofenolan, emamectin, endosulfan, esfenvalerate, ethiprole, fenothiocarb, fenoxycarb, fenpropathrin, fenvalerate, fipronil, flonicamid, flubendiamide, flucythrinate, flufenoxystrobin (methyl (*αE*)-2-[[2-chloro-4-(trifluoromethyl)phenoxy]methyl]-*α*-(methoxymethylene)benzeneacetate), fluensulfone (5-chloro-2-[(3,4,4-trifluoro-3-buten-1-yl)sulfonyl]thiazole), flupiprole (1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-[(2-methyl-2-propen-1-yl)amino]-4-[(trifluoromethyl)sulfinyl]-
 30 1*H*-pyrazole-3-carbonitrile), flupyradifurone (4-[[[(6-chloro-3-pyridinyl)methyl](2,2-difluoroethyl)amino]-2(5*H*)-furanone], tau-fluvalinate, flufenerim (UR-50701), flufenoxuron, fonophos, halofenozide, heptafluthrin ([2,3,5,6-tetrafluoro-4-(methoxymethyl)phenyl]methyl 2,2-dimethyl-3-[(1*Z*)-3,3,3-trifluoro-1-propen-1-yl]cyclopropanecarboxylate), hexaflumuron, hydramethylnon, imidacloprid, indoxacarb, isofenphos, lufenuron, malathion, meperfluthrin

([2,3,5,6-tetrafluoro-4-(methoxymethyl)phenyl]methyl (1*R*,3*S*)-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate), metaflumizone, metaldehyde, methamidophos, methidathion, methomyl, methoprene, methoxychlor, methoxyfenozide, metofluthrin, milbemycin oxime, momfluorothrin ([2,3,5,6-tetrafluoro-4-(methoxymethyl)phenyl]methyl-3-(2-cyano-1-propen-1-yl)-2,2-dimethylcyclopropanecarboxylate), monocrotophos, nicotine, nitenpyram, nithiazine, novaluron, noviflumuron (XDE-007), oxamyl, pyflubumide (1,3,5-trimethyl-*N*-(2-methyl-1-oxopropyl)-*N*-[3-(2-methylpropyl)-4-[2,2,2-trifluoro-1-methoxy-1-(trifluoromethyl)ethyl]phenyl]-1*H*-pyrazole-4-carboxamide), parathion, parathion-methyl, permethrin, phorate, phosalone, phosmet, phosphamidon, pirimicarb, profenofos, profluthrin, pymetrozine, pyrafluprole, pyrethrin, pyridalyl, pyrifluquinazon, pyriminostrobin (methyl (α *E*)-2-[[[2-[(2,4-dichlorophenyl)amino]-6-(trifluoromethyl)-4-pyrimidinyl]oxy]methyl]- α -(methoxymethylene)benzeneacetate), pyriprole, pyriproxyfen, rotenone, ryanodine, spinetoram, spinosad, spirotetramat, sulfoxaflo, sulprofos, tebufos, tetrachlorvinphos, tetramethylfluthrin, thiacloprid, thiamethoxam, thiodicarb, thiosultap-sodium, tolfenpyrad, tralomethrin, triazamate, trichlorfon and triflumuron; and biological agents including entomopathogenic bacteria, such as *Bacillus thuringiensis* subsp. *aizawai*, *Bacillus thuringiensis* subsp. *kurstaki*, and the encapsulated delta-endotoxins of *Bacillus thuringiensis* (e.g., Cellcap, MPV, MPVII); entomopathogenic fungi, such as green muscardine fungus; and entomopathogenic virus including baculovirus, nucleopolyhedro virus (NPV) such as HzNPV, AfNPV; and granulosis virus (GV) such as CpGV.

Compounds of this invention and compositions thereof can be applied to plants genetically transformed to express proteins toxic to invertebrate pests (such as *Bacillus thuringiensis* delta-endotoxins). The effect of the exogenously applied fungicidal compounds of this invention may provide an enhanced effect with the expressed toxin proteins.

General references for agricultural protectants (i.e. insecticides, fungicides, nematocides, acaricides, herbicides and biological agents) include *The Pesticide Manual, 13th Edition*, C. D. S. Tomlin, Ed., British Crop Protection Council, Farnham, Surrey, U.K., 2003 and *The BioPesticide Manual, 2nd Edition*, L. g. Copping, Ed., British Crop Protection Council, Farnham, Surrey, U.K., 2001.

For embodiments where one or more of these various mixing partners are used, the weight ratio of these various mixing partners (in total) to the compound of Formula 1 is typically between about 1:3000 and about 3000:1. Of note are weight ratios between about 1:300 and about 300:1 (for example ratios between about 1:30 and about 30:1). One skilled in the art can easily determine through simple experimentation the biologically effective amounts of active ingredients necessary for the desired spectrum of biological activity. It will be evident

that including these additional components may expand the spectrum of diseases controlled beyond the spectrum controlled by the compound of Formula 1 alone.

In certain instances, combinations of a compound of this invention with other biologically active (particularly fungicidal) compounds or agents (i.e. active ingredients) can result in a greater-than-additive (i.e. enhanced) effect. Reducing the quantity of active ingredients released in the environment while ensuring effective pest control is always desirable. When an enhanced effect of fungicidal active ingredients occurs at application rates giving agronomically satisfactory levels of fungal control, such combinations can be advantageous for reducing crop production cost and decreasing environmental load.

Also in certain instances, combinations of a compound of the invention with other biologically active compounds or agents can result in a less-than-additive (i.e. safening) effect on organisms beneficial to the agronomic environment. For example, a compound of the invention may safen a herbicide on crop plants or protect a beneficial insect species (e.g., insect predators, pollinators such as bees) from an insecticide.

Fungicides of note for formulation with compounds of Formula 1 to provide mixtures useful in seed treatment include but are not limited to amisulbrom, azoxystrobin, boscalid, carbendazim, carboxin, cymoxanil, cyproconazole, difenoconazole, dimethomorph, florypicoxamid, fluazinam, fludioxonil, flufenoxystrobin, fluquinconazole, fluopicolide, fluoxastrobin, flutriafol, fluxapyroxad, ipconazole, iprodione, metalaxyl, mefenoxam, mefentrifluconazole, metconazole, myclobutanil, paclobutrazole, penflufen, picoxystrobin, prothioconazole, pyraclostrobin, sedaxane, silthiofam, tebuconazole, thiabendazole, thiophanate-methyl, thiram, trifloxystrobin and triticonazole.

Invertebrate pest control compounds or agents with which compounds of Formula 1 can be formulated to provide mixtures useful in seed treatment include but are not limited to abamectin, acetamiprid, acrinathrin, afidopyropen, amitraz, avermectin, azadirachtin, bensultap, bifenthrin, buprofezin, cadusafos, carbaryl, carbofuran, cartap, chlorantraniliprole, chlorfenapyr, chlorpyrifos, clothianidin, cyantraniliprole, cyclaniliprole, cyfluthrin, beta-cyfluthrin, cyhalothrin, gamma-cyhalothrin, lambda-cyhalothrin, cypermethrin, alpha-cypermethrin, zeta-cypermethrin, cyromazine, deltamethrin, dieldrin, dinotefuran, diofenolan, emamectin, endosulfan, esfenvalerate, ethiprole, etofenprox, etoxazole, fenothiocarb, fenoxycarb, fenvalerate, fipronil, flonicamid, flubendiamide, fluensulfone, flufenoxuron, flufiprole, flupyradifurone, fluvalinate, formetanate, fosthiazate, heptafluthrin, hexaflumuron, hydramethylnon, imidacloprid, indoxacarb, lufenuron, meperfluthrin, metaflumizone, methiocarb, methomyl, methoprene, methoxyfenozide, momfluorothrin, nitenpyram, nithiazine, novaluron, oxamyl, pyflubumide, pymetrozine, pyrethrin, pyridaben, pyriminostrobin, pyridalyl, pyriproxyfen, ryanodine, spinetoram, spinosad, spirotetramat, spiromesifen, spirotetramat, sulfoxaflor, tebufenozide, tetramethrin, tetramethylfluthrin,

thiacloprid, thiamethoxam, thiodicarb, thiosultap-sodium, tralomethrin, triazamate, triflumuron, *Bacillus thuringiensis* delta-endotoxins, strains of *Bacillus thuringiensis* and strains of *Nucleo polyhydrosis* viruses.

Compositions comprising compounds of Formula 1 useful for seed treatment can further
5 comprise bacteria and fungi that have the ability to provide protection from the harmful effects of plant pathogenic fungi or bacteria and/or soil born animals such as nematodes. Bacteria exhibiting nematocidal properties may include but are not limited to *Bacillus firmus*, *Bacillus cereus*, *Bacillus subtilis* and *Pasteuria penetrans*. A suitable *Bacillus firmus* strain is strain CNCM I-1582 (GB-126) which is commercially available as BioNem™. A suitable *Bacillus*
10 *cereus* strain is strain NCMM I-1592. Both *Bacillus* strains are disclosed in US 6,406,690. Other suitable bacteria exhibiting nematocidal activity are *B. amyloliquefaciens* IN937a and *B. subtilis* strain gB03. Bacteria exhibiting fungicidal properties may include but are not limited to *B. pumilus* strain gB34. Fungal species exhibiting nematocidal properties may include but are not limited to *Myrothecium verrucaria*, *Paecilomyces lilacinus* and *Purpureocillium*
15 *lilacinum*.

Seed treatments can also include one or more nematocidal agents of natural origin such as the elicitor protein called harpin which is isolated from certain bacterial plant pathogens such as *Erwinia amylovora*. An example is the Harpin-N-Tek seed treatment technology available as N-Hibit™ gold CST.

Seed treatments can also include one or more species of legume-root nodulating bacteria such as the microsymbiotic nitrogen-fixing bacteria *Bradyrhizobium japonicum*. These inoculants can optionally include one or more lipo-chitooligosaccharides (LCOs), which are
20 nodulation (Nod) factors produced by rhizobia bacteria during the initiation of nodule formation on the roots of legumes. For example, the Optimize® brand seed treatment technology incorporates LCO Promoter Technology™ in combination with an inoculant.
25

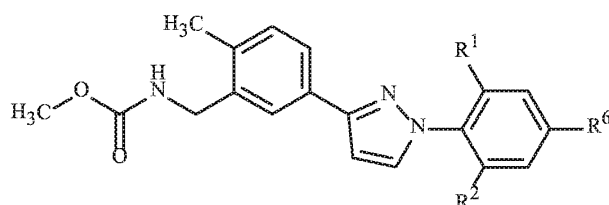
Seed treatments can also include one or more isoflavones which can increase the level of root colonization by mycorrhizal fungi. Mycorrhizal fungi improve plant growth by enhancing the root uptake of nutrients such as water, sulfates, nitrates, phosphates and metals. Examples of isoflavones include, but are not limited to, genistein, biochanin A, formononetin, daidzein,
30 glycitein, hesperetin, naringenin and pratensein. Formononetin is available as an active ingredient in mycorrhizal inoculant products such as PHC Colonize® AG.

Seed treatments can also include one or more plant activators that induce systemic acquired resistance in plants following contact by a pathogen. An example of a plant activator which induces such protective mechanisms is acibenzolar-*S*-methyl.

35 The following TESTS demonstrate the control efficacy of compounds of this invention on specific pathogens. The pathogen control protection afforded by the compounds is not limited, however, to these species. See Index Table A-E below for compound descriptions.

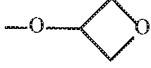
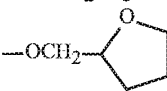
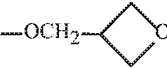
The following abbreviations are used in Index Table A-E: Me means methyl, *i*-Pr means isopropyl, *c*-Pr means cyclopropyl, *i*-Bu means isobutyl, *c*-Bu means cyclobutyl, *t*-Bu means *tert*-butyl and NO₂ means nitro. The abbreviation "Cmpd." stands for "Compound", and the abbreviation "Ex." stands for "Example" and is followed by a number indicating in which example the compound is prepared. The abbreviation "m.p." stands for melting point. The numerical value reported in the column "AP⁺ (M+1)", is the molecular weight of the observed molecular ion formed by addition of H⁺ (molecular weight of 1) to the molecule having the greatest isotopic abundance (i.e. M). The presence of molecular ions containing one or more higher atomic weight isotopes of lower abundance (e.g., ³⁷Cl, ⁸¹Br) is not reported. The reported MS peaks were observed by mass spectrometry using electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI).

INDEX TABLE A



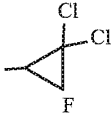
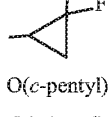
Cmpd. No.	R ¹	R ²	R ⁶	m.p. (°C)	AP ⁺ (M+1)
1 (Ex. 2)	F	F	NO ₂	131-134	
2	F	F	CN	171-174	
3 (Ex. 1)	F	F	OCH ₃	85-100	388
4	F	F	H	142-143	358
5 (Ex. 3)	F	F	NH ₂	168-171	374
6	F	F	Cl	148-149	392
7 (Ex. 4)	F	F	Br	138-139	436
8 (Ex. 13)	F	F	I		484
9	F	F	OCH ₂ (<i>c</i> -Pr)		428
10 (Ex. 5)	F	F	OH	178-180	374
11	F	F	OCH ₂ CH ₃	118-119	402
12	F	F	O(<i>i</i> -Bu)		430
13	F	F	O(<i>c</i> -Bu)	126-128	428
14 (Ex. 6)	F	F	O(<i>i</i> -Pr)	133-134	416
15	F	F	OCHF ₂	102-103	424
16	F	F	F		376
17	F	F	OC(=O)OCH ₃		432
18	F	F	OC(=O)CH ₃		416

86

Cmpd. No.	R ¹	R ²	R ⁶	m.p. (°C)	AP ⁺ (M+1)
19	F	SCH ₃	F		404
20	SCH ₃	SCH ₃	F		432
21	F	F			430
22	F	F	OCH ₂ CF ₃		456
23	F	F			458
24	F	F	NHC(=O)OCH ₃		431
25	F	F	NHC(=O)CH ₃		415
26	F	SCH ₃	I		512
27	F	F	SCH ₃		404
28	F	SCH ₃	SCH ₃		432
29	F	F	OCF ₂ CHF ₂		474
30	F	F	CH ₃	130-131	372
31	F	F	OCH ₂ (<i>c</i> -Bu)		442
32	F	F			444
33	F	F	OCH ₂ C≡CH	143-144	412
34	F	OCH ₃	OCH ₃		401
35	CH ₃	CH ₃	NO ₂		395
36	F	F	NHCH ₃		387
37	F	Cl	NO ₂		419
38	CH ₃	CH ₃	NH ₂		365
39	Cl	F	NH ₂		389
40	CH ₃	CH ₃	OCH ₃		380
41	F	F	<i>c</i> -Pr	89-91	398
42 (Ex. 15)	F	F	S(<i>t</i> -Bu)		446
43 (Ex. 16)	F	F	SCHF ₂		440
44	Cl	Cl	H		390
45	F	I	H		466
46	Br	F	H		420
47	Cl	F	H		374
48	CH ₃	CH ₃	Br		428
49	CH ₃	CH ₃	Cl		384
50	Cl	F	Br		452
51	Cl	F	Cl		408

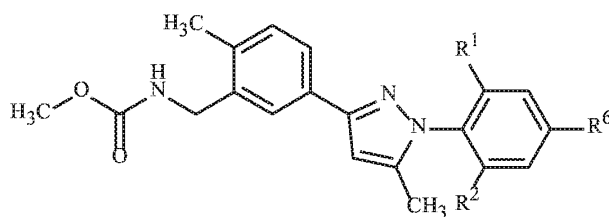
Cmpd. No.	R ¹	R ²	R ⁶	m.p. (°C)	AP ⁺ (M+1)
52	Br	I	H		526
53 (Ex. 14)	F	F	C≡CH		382
54	Cl	Cl	NO ₂		435
55	Cl	Cl	NH ₂		405
56	Cl	Cl	Br		468
57	Cl	Cl	Cl		424
58	Br	Br	H		480
59	Cl	I	H		482
60	Br	Cl	H		436
61	Br	CH ₃	H		416
62	F	F	C(=CH ₂)CH ₃		398
63	F	F	<i>i</i> -Pr	96-98	400
64	F	F	CF ₃	106-108	426
65 (Ex. 17)	Cl	Cl	<i>c</i> -Pr		430
66	F	F	O(<i>c</i> -Pr)	124-128	
67 (Ex. 9)	F	F	C(=O)H	156-160	386
68 (Ex. 11)	F	F	C(=O)CH ₃		400
69	F	F	C(Me)=NOH	160-161	415
70 (Ex. 7)	F	F	C(=O)OCH ₃	120-122	416
71 (Ex. 8)	F	F	CH ₂ OH	183-184	388
72	F	F	CH=NOH	134-139	401
73	F	F	OCH ₂ F		406
74	F	F			412
75	F	F	CH ₂ C(=O)CH ₃		414
76	F	F	CH(OMe)C(=O)CH ₃		444
77	F	F	CH ₂ F		390
78	F	F	OCF ₃		442
79	F	F	CH=NOCH ₃		415
80	F	F	CH=NOCH ₂ CH ₃		429
81	F	F	CH=NOCH ₂ CH=CH ₂		441
82	F	F	CH=NOCH(CH ₃) ₂		443
83 (Ex. 12)	F	F	C(Me)=NOCH ₃		429
84	F	F	C(Me)=NOCH ₂ CH ₃		443
85	F	F	C(Me)=NOCH ₂ CH=CH ₂		455
86	F	F	C(Me)=NOCH(CH ₃) ₂		457

88

Cmpd. No.	R ¹	R ²	R ⁶	m.p. (°C)	AP ⁺ (M+1)
87 (Ex. 10)	F	F	CHF ₂		408
88	F	F			466
89	F	F			434
90	F	F	O(<i>c</i> -pentyl)		442
91	F	F	O(<i>c</i> -hexyl)		456
92	F	F	OCH(Me)CH ₂ CH ₃		430
93	F	F	O(<i>t</i> -Bu)		430
94	F	F	OCH ₂ CH=CH ₂		414
95	F	F	C(Me) ₂ OH		416
96	F	F	CH(OH)CH ₃		402
97	F	F	CF(Me) ₂		418
98	F	F		134-136	464
99	F	F	C(Me)=NOCH ₃		429
133	F	F	1,3-dioxolan-2-yl		430
134	F	F	1,3-dioxan-2-yl		444
135	Cl	Cl	<i>i</i> -Pr		432
136	Br	Br	I	*	*
137	Br	Br	C(=CH ₂)CH ₃	*	*
138	Cl	Cl	CF(CF ₃) ₂		558

*See Index Table F for ¹H NMR data.

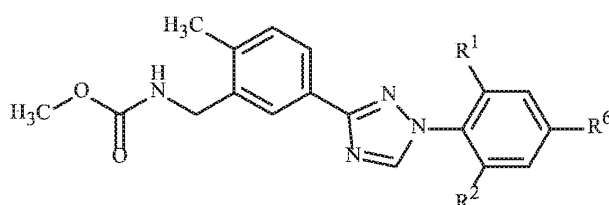
INDEX TABLE B



Cmpd. No.	R ¹	R ²	R ⁶	m.p. (°C)
100	F	F	H	125-129
101	Cl	Cl	H	146-150

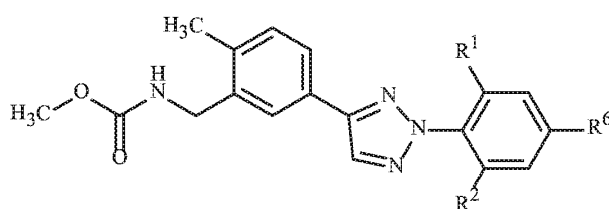
Cmpd. No.	R ¹	R ²	R ⁶	m.p. (°C)
102	F	F	OCH ₃	128-132

INDEX TABLE C



Cmpd. No.	R ¹	R ²	R ⁶	m.p. (°C)
103	F	F	CF ₃	168-172
104	F	F	Br	175-179
105	F	F	Cl	166-170
106	F	F	NH ₂	136-140
107	F	F	NO ₂	179-183

INDEX TABLE D



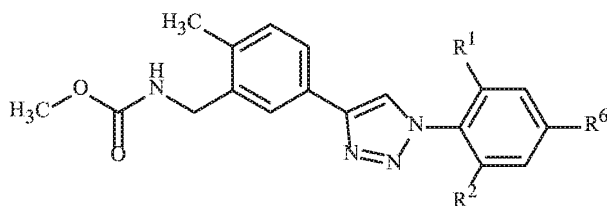
Cmpd. No.	R ¹	R ²	R ⁶	m.p. (°C)
108	F	F	<i>i</i> -Pr	102-106
109	F	F	<i>i</i> -Bu	*
110	F	F	C(=CH ₂)CH ₃	111-115
111	F	F	CH ₃	117-121
112	F	F	H	122-126
113	F	F	<i>c</i> -Pr	107-111
114	F	F	Br	136-140
115 (Ex. 19)	F	F	NH ₂	144-148
116	F	F	I	154-158
117 (Ex. 20)	F	F	Cl	108-112
118 (Ex. 18)	F	F	NO ₂	152-156
139	F	F	CH(Me)CH ₂ CH ₂	
140	F	F	C(=O)CH ₃	151-155
141	F	F	CF ₃	138-142

90

Cmpd. No.	R ¹	R ²	R ⁶	m.p. (°C)
142	F	F	C(Me)=NOCH ₂ CH ₃	104-108
143	F	F	C(Me)=NOCH(CH ₃) ₂	111-115

* See Index Table F for ¹H NMR data.

INDEX TABLE E



Cmpd. No.	R ¹	R ²	R ⁶	m.p. (°C)
119	F	F	CH ₃	143-147
120	Cl	OCH ₃	OCH ₃	145-148
121	F	F	Cl	159-163
122	F	Cl	F	125-129
123	Cl	Cl	OCH ₃	148-152
124	CH ₃	CH ₃	OCH ₃	110-114
125	F	F	I	166-170
126	F	F	Br	160-164
127	OCH ₃	OCH ₃	OCH ₃	*
128	Br	Br	OCH ₃	167-171
129	Br	NO ₂	OCH ₃	158-162
130	F	F	OCH ₃	146-150
131	F	F	NH ₂	194-198
132 (Ex. 18)	F	F	NO ₂	174-178

*See Index Table F for ¹H NMR data.

5

INDEX TABLE F

Compound No.	¹ H NMR Data (CDCl ₃ solution) ^a
109	δ 7.82 (m, 2H), 7.73 (d, 1H), 7.24 (d, 1H), 6.22 (s, 2H), 4.92 (br s, 1H), 4.44 (s, 2H), 3.89 (s, 3H), 3.76 (s, 6H), 3.72 (s, 3H), 2.38 (s, 3H).
127	δ 8.14 (s, 1H), 7.77 (s, 1H), 7.68 (d, 1H), 7.27 (s, 1H), 6.92 (d, 2H), 4.91 (br s, 1H), 4.44 (s, 2H), 3.72 (s, 3H), 2.55 (d, 2H), 2.39 (s, 3H), 1.92 (m, 1H), 0.96 (s, 3H), 0.95 (s, 3H).
136	δ 8.02 (s, 2H), 7.76 (s, 1H), 7.68 (d, 1H), 7.52 (m, 1H), 7.23 (d, 1H), 6.78 (m, 1H), 4.83 (br s, 1H), 4.42 (m, 2H), 3.71 (s, 3H), 2.37 (s, 3H).

137 δ 7.79 (m, 1H), 7.70 (m, 3H), 7.54 (d, 1H), 7.23 (d, 1H), 6.78, (d, 1H), 5.45 (s, 1H),
5.25 (s, 1H), 4.83 (br s, 1H), 4.42 (m, 2H), 3.70 (s, 3H), 2.37 (s, 3H), 2.15 (s, 3H).

^a ¹H NMR data are reported in ppm downfield from tetramethylsilane. Couplings are designated by (s)-singlet, (br s)-broad singlet, (d)-doublet, (m)-multiplet.

BIOLOGICAL EXAMPLES OF THE INVENTION

General protocol for preparing test suspensions for Tests A-F: the test compounds were
5 first dissolved in acetone in an amount equal to 3% of the final volume and then suspended at
the desired concentration (in ppm) in acetone and purified water (50/50 mix by volume)
containing 250 ppm of the surfactant PEG400 (polyhydric alcohol esters). The resulting test
suspensions were then used in Tests A-F.

TEST A

10 The test solution was sprayed to the point of run-off on wheat seedlings. The following
day the seedlings were inoculated with a spore suspension of *Zymoseptoria tritici* (the causal
agent of wheat leaf blotch) and incubated in a saturated atmosphere at 24 °C for 48 h, and then
moved to a growth chamber at 20 °C for 17 days, after which time disease ratings were made.

TEST B

15 The test solution was sprayed to the point of run-off on wheat seedlings. The following
day the seedlings were inoculated with a spore suspension of *Puccinia recondita* f. sp. *tritici*
(the causal agent of wheat leaf rust) and incubated in a saturated atmosphere at 20 °C for 24 h,
and then moved to a growth chamber at 20 °C for 7 days, after which time disease ratings were
made.

TEST C

20 The test suspension was sprayed to the point of run-off on wheat seedlings. The
following day the seedlings were inoculated with a spore dust of *Blumeria graminis*
f. sp. *tritici*, (also known as *Erysiphe graminis* f. sp. *tritici*, the causal agent of wheat powdery
mildew) and incubated in a growth chamber at 20 °C for 8 days, after which time visual disease
25 ratings were made.

TEST D

The test solution was sprayed to the point of run-off on soybean seedlings. The following
day the seedlings were inoculated with a spore suspension of *Phakopsora pachyrhizi* (the
causal agent of Asian soybean rust) and incubated in a saturated atmosphere at 22 °C for 24 h
30 and then moved to a growth chamber at 22 °C for 8 days, after which time visual disease ratings
were made.

TEST E

The test suspension was sprayed to the point of run-off on tomato seedlings. The
following day the seedlings were inoculated with a spore suspension of *Botrytis cinerea* (the

causal agent of tomato Botrytis) and incubated in a saturated atmosphere at 20 °C for 48 h, and then moved to a growth chamber at 24 °C for 3 days, after which time visual disease ratings were made.

TEST F

- 5 The test suspension was sprayed to the point of run-off on tomato seedlings. The following day the seedlings were inoculated with a spore suspension of *Alternaria solani* (the causal agent of tomato early blight) and incubated in a saturated atmosphere at 27 °C for 48 h, and then moved to a growth chamber at 20 °C for 3 days, after which time visual disease ratings were made.

- 10 Results for Tests A-F are given in Table A below. A rating of 100 indicates 100% disease control and a rating of 0 indicates no disease control (relative to the controls). A dash (–) indicates the compound was not tested.

TABLE A

Cmpd. No.	Rate in ppm	Test A	Test B	Test C	Test D	Test E	Test F
1	10	0	68	0	44	0	–
2	10	13	68	0	100	0	–
3	10	50	100	79	100	45	–
4	10	–	90	–	100	–	–
5	10	–	0	–	0	–	–
6	10	7	98	0	100	0	40
7	10	–	100	–	100	–	–
8	10	–	100	–	100	–	–
9	10	–	99	–	99	–	–
10	10	–	0	–	0	–	–
11	10	–	100	–	100	–	–
12	10	–	98	–	100	–	–
13	10	–	100	–	100	–	–
14	10	–	100	–	100	–	–
15	10	0	99	69	100	0	0
16	10	–	99	–	100	–	–
17	10	–	0	–	0	–	–
18	10	–	41	–	65	–	–
19	10	–	0	–	81	–	–
20	10	–	0	–	0	–	–
21	10	–	55	–	100	–	–
22	10	–	99	–	100	–	–

Cmpd. No.	Rate in ppm	Test A	Test B	Test C	Test D	Test E	Test F
23	10	--	68	--	25	--	--
24	10	--	0	--	75	--	--
25	10	--	8	--	81	--	--
26	10	--	73	--	87	--	--
27	10	--	99	--	100	--	--
28	10	--	0	--	100	--	--
29	10	--	100	--	100	--	--
30	10	--	98	--	100	--	--
31	10	--	91	--	0	--	--
32	10	--	0	--	77	--	--
33	10	--	99	--	100	--	--
34	10	--	28	--	96	--	--
35	10	--	0	--	0	--	--
36	10	--	68	--	100	--	--
37	10	--	26	--	0	--	--
38	10	--	0	--	0	--	--
39	10	--	0	--	0	--	--
40	10	--	0	--	99	--	--
41	10	--	100	--	100	--	--
42	10	--	100	--	73	--	--
43	10	--	100	--	100	--	--
44	10	--	68	--	100	--	--
45	10	--	0	--	100	--	--
46	10	--	68	--	100	--	--
47	10	--	74	--	100	--	--
48	10	--	68	--	99	--	--
49	10	--	68	--	99	--	--
50	10	--	100	--	100	--	--
51	10	--	100	--	100	--	--
52	10	--	0	--	99	--	--
53	10	--	100	--	100	--	--
54	10	--	0	--	0	--	--
55	10	--	0	--	0	--	--
56	10	--	80	--	100	--	--
57	10	--	74	--	100	--	--
58	10	--	68	--	100	--	--

Cmpd. No.	Rate in ppm	Test A	Test B	Test C	Test D	Test E	Test F
59	10	--	45	--	87	--	--
60	10	--	68	--	100	--	--
61	10	--	68	--	97	--	--
62	10	--	99	--	100	--	--
63	10	26	100	98	100	0	85
64	10	0	100	89	100	0	0
65	10	--	97	--	100	--	--
66	10	--	100	--	100	--	--
67	10	--	0	--	12	--	--
68	10	--	74	--	71	--	--
69	10	--	99	--	97	--	--
70	10	--	74	--	81	--	--
71	10	--	0	--	25	--	--
72	10	--	100	--	77	--	--
73	10	--	100	--	100	--	--
74	10	--	100	--	100	--	--
75	10	--	0	--	87	--	--
76	10	--	68	--	100	--	--
77	10	--	100	--	100	--	--
78	10	--	100	--	100	--	--
79	10	--	100	--	100	--	--
80	10	--	100	--	100	--	--
81	10	--	92	--	100	--	--
82	10	--	95	--	100	--	--
83	10	--	100	--	100	--	--
84	10	--	100	--	100	--	--
85	10	--	90	--	98	--	--
86	10	--	99	--	100	--	--
87	10	--	100	--	100	--	--
88	10	--	100	--	100	--	--
89	10	--	100	--	100	--	--
90	10	--	86	--	100	--	--
91	10	--	86	--	79	--	--
92	10	--	100	--	100	--	--
93	10	--	100	--	100	--	--
94	10	--	85	--	99	--	--

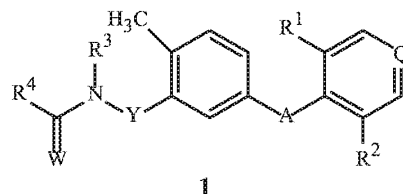
Cmpd. No.	Rate in ppm	Test A	Test B	Test C	Test D	Test E	Test F
95	10	--	0	--	53	--	--
96	10	--	68	--	79	--	--
97	10	--	100	--	100	--	--
98	10	--	99	--	100	--	--
99	10	--	100	--	100	--	--
100	10	--	0	--	0	--	--
101	10	--	0	--	0	--	--
102	10	--	0	--	0	--	--
103	10	--	100	--	86	--	--
104	10	--	100	--	90	--	--
105	10	--	100	--	92	--	--
106	-	--	--	--	--	--	--
107	250	28	80	43	0	0	0
108	2	--	100	--	100	--	--
109	10	--	91	--	100	--	--
110	10	--	95	--	100	--	--
111	10	--	99	--	100	--	--
112		--	--	--	--	--	--
113	10	--	100	--	100	--	--
114	10	--	100	--	100	--	--
115	-	--	--	--	--	--	--
116	10	--	100	--	100	--	--
117	10	--	100	--	100	--	--
118	250	1	0	0	0	0	0
119	10	--	100	--	0	--	--
120	10	--	0	--	0	--	--
121	10	--	68	--	0	--	--
122	250	71	99	0	100	0	0
123	10	--	0	--	0	--	--
124	10	--	0	--	0	--	--
125	10	--	68	--	0	--	--
126	10	--	57	--	0	--	--
127	10	--	0	--	0	--	--
128	10	--	0	--	0	--	--
129	10	--	0	--	0	--	--
130	10	--	68	--	0	--	--

Cmpd. No.	Rate in ppm	Test A	Test B	Test C	Test D	Test E	Test F
131	-	--	--	--	--	--	--
132	-	--	--	--	--	--	--
133	10	--	99	--	100	--	--
134	10	--	89	--	100	--	--
135	10	--	86	--	100	--	--
136	10	--	19	--	59	--	--
137	10	--	0	--	77	--	--
138	10	--	74	--	87	--	--
139	10	--	99	--	100	--	--
140	10	--	41	--	71	--	--
141	10	--	99	--	100	--	--
142	10	--	86	--	100	--	--
143	10	--	74	--	100	--	--

CLAIMS

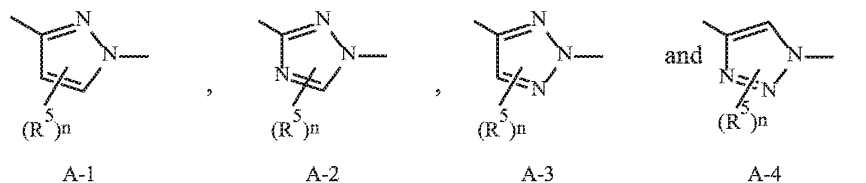
What is claimed is:

1. A compound selected from Formula 1, tautomers, *N*-oxides, and salts thereof,



5 wherein

A is a radical selected from the group consisting of



wherein the bond extending to the right is attached to the ring containing Q and the
bond extending to the left is attached to the phenyl ring bearing the
Y-N(R³)C(=W)R⁴ substituent;

10 Q is CR⁶ or N;

Y is CR^{7a}R^{7b}, O or NR⁸;

W is O or S;

R¹ and R² are each independently halogen, cyano, hydroxy, nitro, amino, C₁-C₆ alkyl,
C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆
15 haloalkynyl, C₂-C₆ cyanoalkyl, C₃-C₆ cycloalkyl, C₃-C₆ halocycloalkyl, C₄-C₈
cycloalkylalkyl, C₂-C₆ alkoxyalkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₂-C₆
alkenyloxy, C₂-C₆ haloalkenyloxy, C₂-C₆ alkynyloxy, C₂-C₆ haloalkynyloxy,
C₂-C₆ cyanoalkoxy, C₃-C₆ cycloalkoxy, C₄-C₈ cycloalkylalkoxy, C₂-C₆
alkoxyalkoxy, C₁-C₆ alkylthio, C₁-C₆ haloalkylthio, C₁-C₆ alkylsulfinyl, C₁-C₆
20 haloalkylsulfinyl, C₁-C₆ alkylsulfonyl or C₁-C₆ haloalkylsulfonyl;

R³ is H, C₁-C₃ alkyl, C₁-C₃ haloalkyl, cyclopropyl, C₂-C₄ alkylcarbonyl, C₂-C₄
haloalkylcarbonyl, C₂-C₄ alkoxy carbonyl or C₂-C₄ haloalkoxy carbonyl;

R⁴ is C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₁-C₃ alkoxy, C₁-C₃ haloalkoxy, C₁-C₃
alkylamino or C₂-C₄ dialkylamino;

25 each R⁵ is independently halogen, cyano, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₁-C₃ alkoxy
or C₁-C₃ haloalkoxy;

n is 0, 1 or 2;

- R^6 is H, halogen, cyano, hydroxy, nitro, amino, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_2 - C_6 alkenyl, C_2 - C_6 haloalkenyl, C_2 - C_6 alkynyl, C_2 - C_6 haloalkynyl, C_2 - C_6 cyanoalkyl, C_1 - C_6 hydroxyalkyl, C_2 - C_6 alkoxyalkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_2 - C_6 alkenyloxy, C_2 - C_6 haloalkenyloxy, C_2 - C_6 alkynyloxy, C_2 - C_6 haloalkynyloxy, C_2 - C_6 cyanoalkoxy, C_2 - C_6 alkoxyalkoxy, C_1 - C_6 alkylamino, C_1 - C_6 alkylthio, C_1 - C_6 haloalkylthio, C_1 - C_6 alkylsulfinyl, C_1 - C_6 haloalkylsulfinyl, C_1 - C_6 alkylsulfonyl, C_1 - C_6 haloalkylsulfonyl, $-ZC(=O)V$, $CR^{10a}=NOR^{10b}$, $ON=CR^{11a}R^{11b}$, $CR^{12a}=NNR^{12b}R^{12c}$ or $-L-J$;
- R^{7a} is H, hydroxy, halogen, cyano, C_1 - C_3 alkyl, C_1 - C_3 haloalkyl, C_2 - C_3 alkoxyalkyl, C_1 - C_3 alkoxy, C_1 - C_3 haloalkoxy, C_1 - C_3 alkylsulfinyl or C_1 - C_3 alkylsulfonyl;
- R^{7b} is H, C_1 - C_3 alkyl, C_1 - C_3 haloalkyl, C_2 - C_3 alkoxyalkyl, C_1 - C_3 alkoxy or C_1 - C_3 haloalkoxy;
- R^8 is H, C_1 - C_3 alkyl, C_1 - C_3 haloalkyl, C_2 - C_3 alkylcarbonyl or C_2 - C_3 haloalkylcarbonyl;
- Z is a direct bond, O, S or NH; or CH_2 optionally substituted with up to 2 substituents independently selected from halogen, methyl or methoxy;
- V is R^9 or OR^9 ;
- R^9 , R^{10b} , R^{11a} and R^{12c} are each H, C_1 - C_3 alkyl, C_1 - C_3 haloalkyl, C_2 - C_4 alkenyl, C_2 - C_4 haloalkenyl, C_2 - C_4 alkynyl, C_3 - C_6 cycloalkyl, C_3 - C_6 halocycloalkyl or C_4 - C_8 cycloalkylalkyl;
- R^{10a} , R^{11b} , R^{12a} and R^{12b} are each independently H, C_1 - C_3 alkyl or C_1 - C_3 haloalkyl;
- L is a direct bond, CH_2 , O, S, NR^{13} , OCH_2 , CH_2O , $C(=O)$, $S(=O)$ or $S(=O)_2$;
- J is a 3- to 6-membered nonaromatic carbocyclic ring, wherein up to 3 carbon atom ring members are independently selected from $C(=O)$ and $C(=S)$, each ring optionally substituted with up to 4 substituents independently selected from R^{14} ; or
- J is a 3- to 6-membered heterocyclic ring, each ring containing ring members selected from carbon atoms and 1 to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, wherein up to 3 carbon atom ring members are independently selected from $C(=O)$ and $C(=S)$, each ring optionally substituted with up to 4 substituents independently selected from R^{14} ;
- R^{13} is H, C_1 - C_3 alkyl, C_1 - C_3 haloalkyl, C_2 - C_3 alkylcarbonyl or C_2 - C_3 haloalkylcarbonyl;
- each R^{14} is independently halogen, hydroxy, cyano, nitro, C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_2 - C_4 alkenyl, C_2 - C_4 haloalkenyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy or $C(=O)OR^{15}$; and
- each R^{15} is independently H, C_1 - C_3 alkyl, C_1 - C_3 haloalkyl, C_2 - C_4 alkenyl, C_2 - C_4 haloalkenyl, C_2 - C_4 alkynyl, C_3 - C_6 cycloalkyl or C_3 - C_6 halocycloalkyl.

2. A compound of Claim 1 wherein:

A is A-1, A-3 or A-4;

Q is CR⁶;

Y is CR^{7a}CR^{7b};

5 W is O;

R¹ and R² are each independently halogen, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₂-C₄ alkoxyalkyl, C₁-C₃ alkoxy, C₁-C₃ haloalkoxy, C₂-C₄ alkenyloxy, C₂-C₄ haloalkenyloxy, C₂-C₄ alkoxyalkoxy or C₁-C₃ alkylthio;

R³ is H, methyl, methylcarbonyl or methoxycarbonyl;

10 R⁴ is methyl, methoxy, ethoxy, methylamino or dimethylamino;

each R⁵ is independently halogen or methyl;

R⁶ is H, halogen, nitro, amino, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₂-C₆ alkoxyalkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₂-C₆ alkenyloxy, C₂-C₆ haloalkenyloxy, C₂-C₆ alkynyloxy, C₂-C₆ haloalkynyloxy, C₂-C₆ alkoxyalkoxy, C₁-C₆ alkylthio, C₁-C₆ haloalkylthio, -ZC(=O)V, CR^{10a}=NOR^{10b}, CR^{12a}=NNR^{12b}R^{12c} or -L-J;

R^{7a} is H, halogen, methyl or methoxy;

R^{7b} is H or methyl;

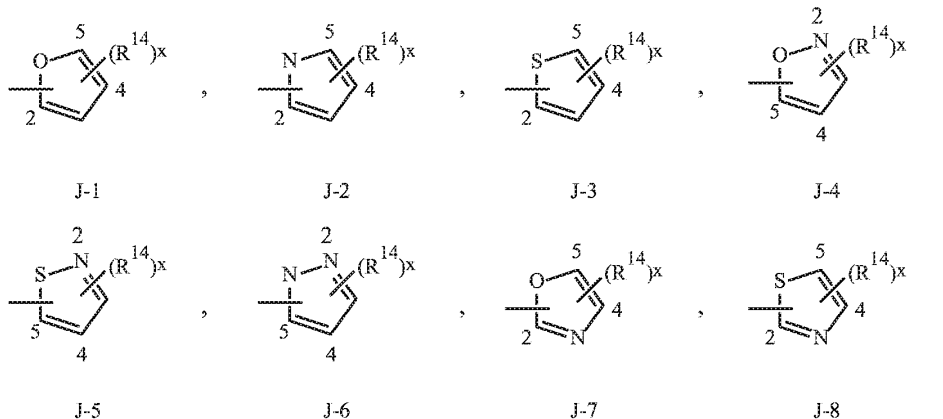
Z is a direct bond, O, NH, CH₂ or CH(OCH₃);

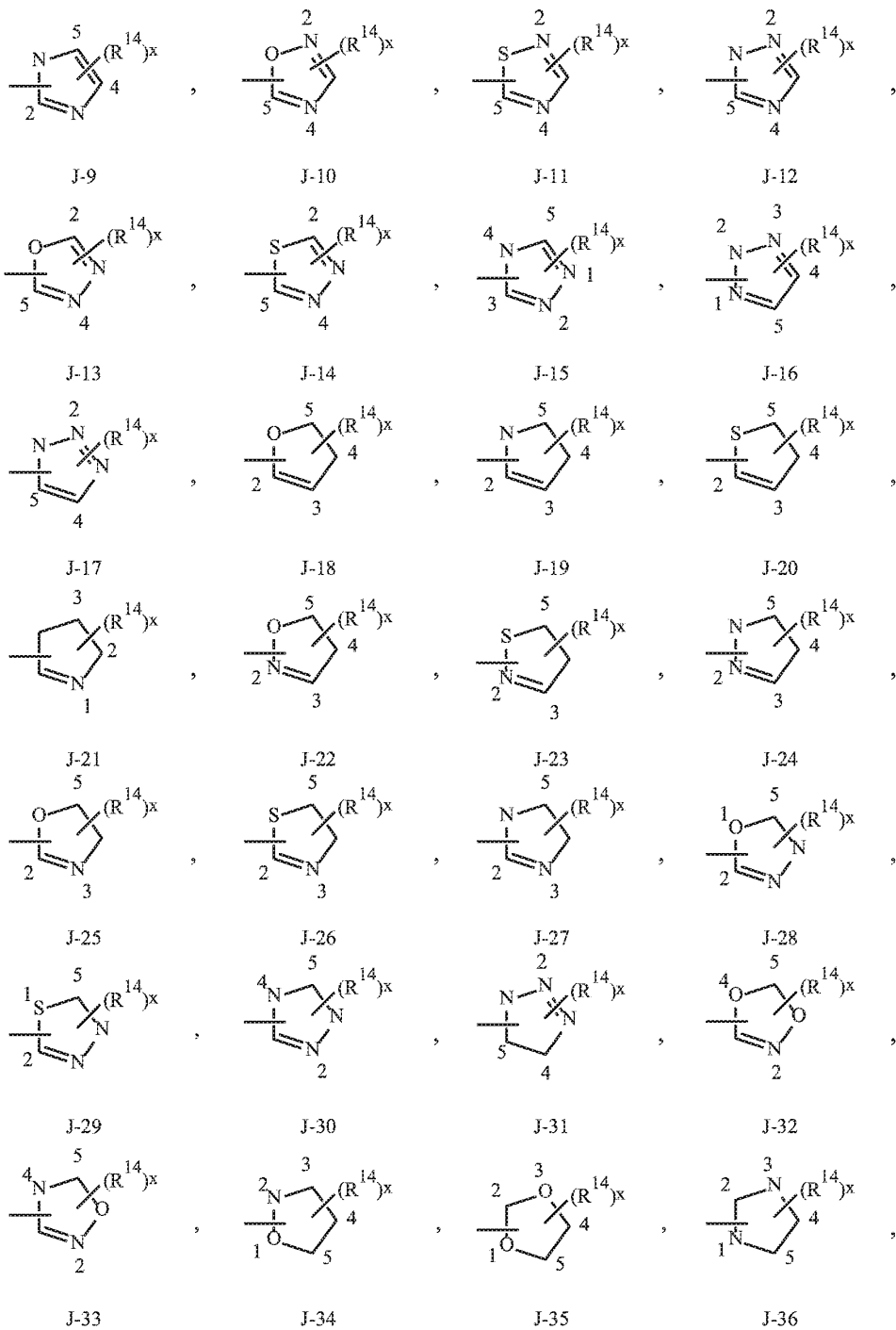
20 R⁹, R^{10b} and R^{12c} are each H, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₂-C₄ alkenyl or C₂-C₄ haloalkenyl;

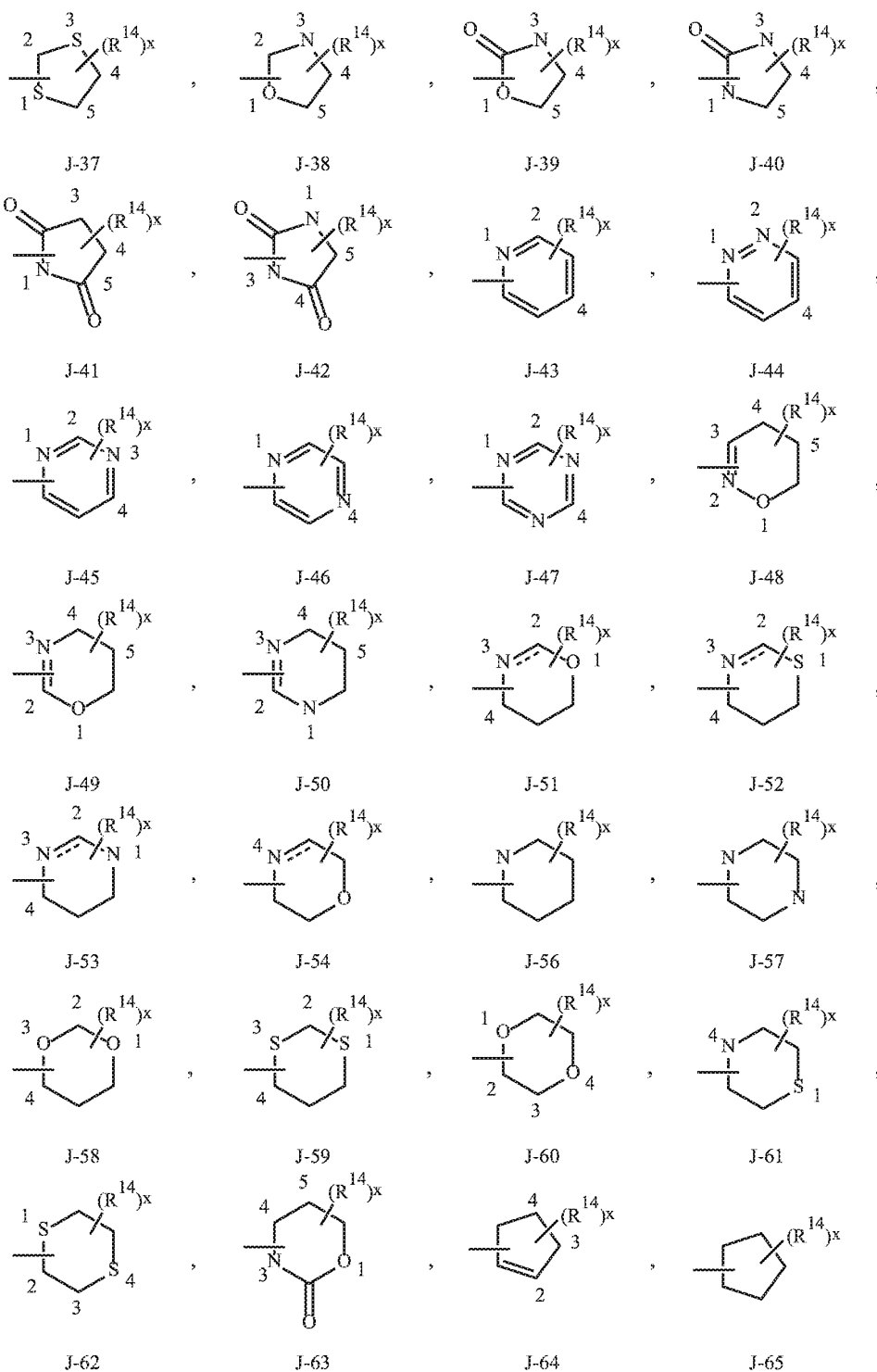
R^{10a}, R^{12a} and R^{12b} are each independently H, methyl or halomethyl;

L is a direct bond, CH₂, O, OCH₂ or CH₂O;

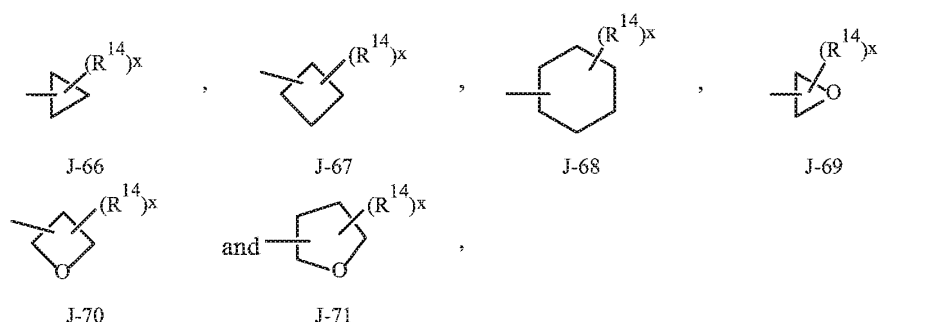
J is selected from J-1 through J-71







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wherein the floating bond is connected to L through any available carbon or nitrogen atom of the depicted ring; and x is 0, 1, 2 or 3;

each R^{14} is independently independently halogen, methyl, methoxy or $C(=O)OR^{15}$; and

5 each R^{15} is independently C_1 - C_3 alkyl, C_1 - C_3 haloalkyl or cyclopropyl.

3. A compound of Claim 2 wherein:

A is A-1;

R^1 and R^2 are each independently Br, Cl, F, methyl, trifluoromethyl, methoxy or trifluoromethoxy;

10 R^3 is H or methyl;

R^4 is methyl, methoxy or ethoxy;

each R^5 is methyl;

R^6 is H, halogen, amino, C_1 - C_3 alkyl, C_1 - C_3 haloalkyl, C_1 - C_3 alkoxy, C_1 - C_3 haloalkoxy, C_2 - C_4 alkenyloxy, C_2 - C_4 haloalkenyloxy, $CR^{10a}=NOR^{10b}$ or -L-J;

15 R^{7a} is H or methyl;

R^{7b} is H or methyl;

R^{10b} is H, methyl, C_2 - C_4 alkenyl or C_2 - C_4 haloalkenyl;

R^{10a} is H or methyl;

L is direct bond, O or OCH_2 ;

20 J is J-6, J-22, J-35, J-37, J-58, J-64, J-65, J-66, J-67, J-69 or J-70; and

each R^{14} is independently halogen or methyl.

4. A compound of Claim 3 wherein:

R^1 and R^2 are each independently Cl, F or methyl;

R^3 is H;

25 R^4 is methoxy;

n is 0;

R⁶ is H, Br, Cl, I, amino, methyl, *i*-propyl, trifluoromethyl, CH₂F, CHF₂, methoxy, ethoxy, *i*-propyloxy, trifluoromethoxy, CH₂FO, CHF₂O, CH=NOCH₃, CH=NOCH₂CH₃, C(CH₃)=NOCH₃ or -L-J;

R^{7a} is H;

5 R^{7b} is H; and

J is J-65, J-66 or J-67.

5. A compound of Claim 4 wherein:

R¹ and R² are each independently Cl or F;

10 R⁶ is H, Br, Cl, I, amino, methoxy, ethoxy, *i*-propyloxy, trifluoromethoxy, CHF₂O, C(CH₃)=NOCH₃ or -L-J;

J is J-66 or J-67;

x is 0, 1 or 2; and

R¹⁴ is Br, Cl, F or methyl.

6. A compound of Claim 5 wherein:

15 R¹ and R² are each F;

R⁶ is H, Br, Cl, amino, methoxy, ethoxy or *i*-propyloxy.

7. A compound of Claim 1 which is selected from the group:

methyl *N*-[[5-[1-(2,6-difluoro-4-nitrophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-(2,6-difluoro-4-methoxyphenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-(2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-(4-amino-2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-(4-chloro-2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-(4-bromo-2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-(2,6-difluoro-4-iodophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-(2,6-difluoro-4-hydroxyphenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-(4-ethoxy-2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-[4-(cyclobutyloxy)-2,6-difluorophenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-[2,6-difluoro-4-(1-methylethoxy)phenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-[4-(difluoromethoxy)-2,6-difluorophenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-[2,6-difluoro-4-(2-propyn-1-yloxy)phenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-(2,6-difluoro-4-methoxyphenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-(4-cyclopropyl-2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-[4-[(1,1-dimethylethyl)thio]-2,6-difluorophenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-[4-[(difluoromethyl)thio]-2,6-difluorophenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-(4-ethynyl-2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-[2,6-difluoro-4-(1-methylethyl)phenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-[2,6-difluoro-4-(trifluoromethyl)phenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-(2,6-dichloro-4-cyclopropylphenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-[4-(cyclopropyloxy)-2,6-difluorophenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-(2,6-difluoro-4-formylphenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-(4-acetyl-2,6-difluorophenyl)-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl 3,5-difluoro-4-[3-[3-[(methoxycarbonyl)amino]methyl]-4-methylphenyl]-1*H*-pyrazol-1-yl]benzoate;

methyl *N*-[[5-[1-[2,6-difluoro-4-(hydroxymethyl)phenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-[2,6-difluoro-4-(trifluoromethoxy)phenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;

methyl *N*-[[5-[1-[2,6-difluoro-4-[1-(methoxyimino)ethyl]phenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;
methyl *N*-[[5-[1-[4-(difluoromethyl)-2,6-difluorophenyl]-1*H*-pyrazol-3-yl]-2-methylphenyl]methyl]carbamate;
methyl *N*-[[5-[2-[2,6-difluoro-4-(1-methylethyl)phenyl]-2*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate;
methyl *N*-[[5-[2-(4-amino-2,6-difluorophenyl)-2*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate;
methyl *N*-[[5-[2-(4-chloro-2,6-difluorophenyl)-2*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate;
methyl *N*-[[5-[2-(2,6-difluoro-4-nitrophenyl)-2*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate;
methyl *N*-[[5-[1-(4-chloro-2,6-difluorophenyl)-1*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate;
methyl *N*-[[5-[1-(4-amino-2,6-difluorophenyl)-1*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate; and
methyl *N*-[[5-[1-(2,6-difluoro-4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl]-2-methylphenyl]methyl]carbamate.

8. A fungicidal composition comprising (a) a compound of Claim 1; and (b) at least one other fungicide.

9. A fungicidal composition comprising (a) a compound of Claim 1; and (b) at least one additional component selected from the group consisting of surfactants, solid diluents
5 and liquid diluents.

10. A method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof, or to the plant seed, a fungicidally effective amount of a compound of Claim 1.