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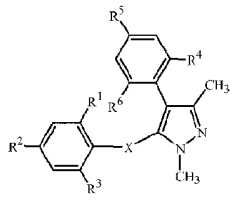

(1)

(57) Abstract: Disclosed is a fungicidal composition comprising (a) at least one compound selected from the compounds of Formula (1), *N*-oxides, and salts thereof, wherein R^1, R^2, R^3, R^4, R^5 and R^6 are as defined in the disclosure; and (b) at least one additional fungicidal compound. Also disclosed is 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), an *N*-oxide, or salt thereof (e.g., as a component in the aforesaid composition). Also disclosed is a composition comprising: (a) at least one compound selected from the compounds of Formula (1) described above, *N*-oxides, and salts thereof; and at least one invertebrate pest control compound or agent.

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TITLE

FUNGICIDAL PYRAZOLES AND THEIR MIXTURES

FIELD OF THE INVENTION

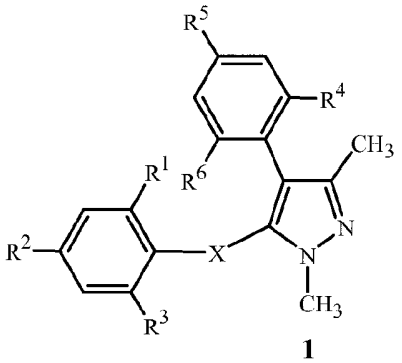
This invention relates to certain pyrazole derivatives, their *N*-oxides and salts, and to mixtures and compositions comprising such pyrazole derivatives and methods for using such pyrazole derivatives and their mixtures and compositions as fungicides.

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. In addition to often being highly destructive, plant diseases can be difficult to control and may develop resistance to commercial fungicides. Many products are commercially available for these purposes, but the need continues for new fungicidal compounds which are more effective, less costly, less toxic, environmentally safer or have different sites of action. Besides introduction of new fungicides, combinations of fungicides are often used to facilitate disease control, to broaden spectrum of control and to retard resistance development. Furthermore, certain rare combinations of fungicides demonstrate a greater-than-additive (i.e. synergistic) effect to provide commercially important levels of plant disease control. The advantages of particular fungicide combinations are recognized in the art to vary, depending on such factors as the particular plant species and plant disease to be treated, and whether the plants are treated before or after infection with the fungal plant pathogen. Accordingly new advantageous combinations are needed to provide a variety of options to best satisfy particular plant disease control needs. Such combinations have now been discovered. JP08208620 discloses *N*-phenyl-pyrazolylamine derivatives as insecticides, herbicides and fungicides; however the fungicidal pyrazoles of the present invention and their mixtures are not disclosed in this publication.

SUMMARY OF THE INVENTION

This invention relates to a fungicidal composition (i.e. combination) comprising (a) at least one compound selected from the compounds of Formula 1 (including all stereoisomers), *N*-oxides, and salts thereof:



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wherein

X is CHOH, O or NH;

R^1 is halogen or methyl;

R^2 is H, cyano, halogen or C_1–C_2 alkoxy;

R^3 is H, halogen or methyl;

R^4 is halogen;

R^5 is H, cyano, halogen or C_1–C_2 alkoxy; and

R^6 is H or halogen; and

(b) at least one additional fungicidal compound.

This invention also relates to a composition comprising: (a) at least one compound selected from the compounds of Formula **1** described above, *N*-oxides, and salts thereof; and at least one invertebrate pest control compound or agent.

This invention also relates to a composition comprising one of the aforesaid compositions comprising component (a) and at least one additional component selected from the group consisting of surfactants, solid diluents and liquid diluents.

This invention also 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 one of the aforesaid compositions.

The aforedescribed method can also be described as a method for protecting a plant or plant seed from diseases caused by fungal pathogens comprising applying a fungicidally effective amount of one of the aforesaid compositions to the plant (or portion thereof) or plant seed (directly or through the environment (e.g., growing medium) of the plant or plant seed).

This invention also relates to a compound of Formula **1** described above, or an *N*-oxide or salt thereof. This invention further relates to a fungicidal composition comprising a

compound of Formula **1**, or an *N*-oxide or salt thereof, and at least one additional component selected from the group consisting of surfactants, solid diluents and liquid diluents. This invention also further relates to a method for protecting a plant or plant seed from diseases caused by fungal pathogens comprising a fungicidally effective amount of a compound of Formula **1**, or an *N*-oxide or salt thereof, to the plant or plant seed.

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 or method that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such composition, mixture, process or method.

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 or method 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 corms, 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.

In the above recitations, the term "alkoxy" includes, for example, methoxy and ethoxy. The term "halogen" includes fluorine, chlorine, bromine or iodine.

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 2.

Compounds relevant to the compositions and methods of this invention can exist as one or more stereoisomers. The various stereoisomers include enantiomers, diastereomers, atropisomers and geometric isomers. 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. The compounds in the compositions of this invention may be present as a mixture of stereoisomers, individual stereoisomers or as an optically active form.

Synthetic methods for the preparation of *N*-oxides of heterocycles such as pyrazoles are very well known by one skilled in the art including the oxidation of heterocycles 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** alone and in mixtures 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. Accordingly, the present invention relates to mixtures of compounds selected from Formula **1**, *N*-oxides and agriculturally suitable salts thereof.

Compounds selected from Formula **1**, stereoisomers, tautomers, *N*-oxides, and salts thereof, typically exist in more than one form, and Formula **1** thus 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 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.

As described in the Summary of the Invention, an aspect of the present invention is directed at a composition comprising (a) at least one compound selected from Formula **1**, *N*-oxides, and salts thereof, with (b) at least one additional fungicidal compound. More particularly, Component (b) is selected from the group consisting of

(b1) methyl benzimidazole carbamate (MBC) fungicides;

(b2) dicarboximide fungicides;

(b3) demethylation inhibitor (DMI) fungicides;

(b4) phenylamide fungicides;

(b5) amine/morpholine fungicides;

(b6) phospholipid biosynthesis inhibitor fungicides;

(b7) carboxamide 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) quinoline fungicides;
(b14) lipid peroxidation inhibitor fungicides;
(b15) melanin biosynthesis inhibitors-reductase (MBI-R) fungicides;
(b16) melanin biosynthesis inhibitors-dehydratase (MBI-D) fungicides;
(b17) hydroxyanilide fungicides;
(b18) squalene-epoxidase inhibitor fungicides;
(b19) polyoxin fungicides;
(b20) phenylurea fungicides;
(b21) quinone inside inhibitor (QiI) fungicides;
(b22) benzamide 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) pyrimidinamide fungicides;
(b40) carboxylic acid amide (CAA) fungicides;
(b41) tetracycline antibiotic fungicides;
(b42) thiocarbamate fungicides;
(b43) benzamide fungicides;
(b44) host plant defense induction fungicides;

(b45) multi-site contact activity fungicides;

(b46) fungicides other than fungicides of component (a) and components (b1) through (b45); and

salts of compounds of (b1) through (b46).

Of note are embodiments wherein component (b) comprises at least one fungicidal compound from each of two different groups selected from (b1) through (b46).

"Methyl benzimidazole carbamate (MBC) fungicides (b1)" (FRAC (Fungicide Resistance Action Committee) 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.

"Dicarboximide fungicides (b2)" (FRAC code 2) are proposed to inhibit a lipid peroxidation in fungi through interference with NADH cytochrome c reductase. Examples include chlozolinate, iprodione, procymidone and vinclozolin.

"Demethylation inhibitor (DMI) fungicides (b3)" (FRAC code 3) 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 result in abnormal growth and eventually death of sensitive fungi. DMI fungicides are divided between several chemical classes: azoles (including triazoles and imidazoles), pyrimidines, piperazines and pyridines. The triazoles include azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole (including diniconazole-M), epoxiconazole, etaconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imibenconazole, ipconazole, metconazole, myclobutanil, penconazole, propiconazole, prothioconazole, quinconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triticonazole and uniconazole. The imidazoles include clotrimazole, econazole, imazalil, isoconazole, miconazole, oxpoconazole, prochloraz, pefurazoate and triflumizole. The pyrimidines include fenarimol, nuarimol and triarimol. The piperazines include triforine. The pyridines include buthiobate and pyrifenox. 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.

"Phenylamide fungicides (b4)" (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, furalaxyl, metalaxyl, metalaxyl-M (also known as mefenoxam). The oxazolidinones include oxadixyl. The butyrolactones include ofurace.

"Amine/morpholine fungicides (b5)" (FRAC code 5) 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.

"Phospholipid biosynthesis inhibitor fungicides (b6)" (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.

"Carboxamide fungicides (b7)" (FRAC code 7) inhibit Complex II (succinate dehydrogenase) 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. Carboxamide fungicides include benzamide, furan carboxamide, oxathiin carboxamide, thiazole carboxamide, pyrazole carboxamide and pyridine carboxamide. 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 carboxamides include bixafen, furametpyr, isopyrazam, fluxapyroxad, penthiopyrad, sedaxane (*N*-[2-(1*S*,2*R*)-[1,1'-bicyclopropyl]-2-ylphenyl]-3-(difluoromethyl)-1-methyl-1*H*-pyrazole-4-carboxamide) and penflufen (*N*-[2-(1,3-dimethylbutyl)phenyl]-5-fluoro-1,3-dimethyl-1*H*-pyrazole-4-carboxamide) (PCT Patent Publication WO 2003/010149). The pyridine carboxamides include boscalid.

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

"Anilinopyrimidine fungicides (b9)" (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.

"*N*-Phenyl carbamate fungicides (b10)" (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.

"Quinone outside inhibitor (QoI) fungicides (b11)" (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, enestroburin (SYP-Z071) and picoxystrobin. The methoxycarbamates include pyraclostrobin and pyrametostrobin. The oximinoacetates include kresoxim-methyl, pyraoxystrobin and trifloxystrobin. The oximinoacetamides include dimoxystrobin, 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.

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

"Quinoline fungicides (b13)" (FRAC code 13) are proposed to inhibit signal transduction by affecting G-proteins in early cell signaling. They have been shown to interfere with germination and/or appressorium formation in fungi that cause powdery mildew diseases. Quinoxyfen is an example of this class of fungicide.

"Lipid peroxidation inhibitor fungicides (b14)" (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 carbon and 1,2,4-thiadiazole fungicides. The aromatic carbons include biphenyl, chloroneb, dicloran, quintozene, tecnazene and tolclofos-methyl. The 1,2,4-thiadiazoles include etridiazole.

"Melanin biosynthesis inhibitors-reductase (MBI-R) fungicides (b15)" (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.

"Melanin biosynthesis inhibitors-dehydratase (MBI-D) fungicides (b16)" (FRAC code 16.2) inhibit scytalone dehydratase in melanin biosynthesis. Melanin in 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.

"Hydroxyanilide fungicides (b17)" (FRAC code 17) inhibit C4-demethylase which plays a role in sterol production. Examples include fenhexamid.

"Squalene-epoxidase inhibitor fungicides (b18)" (FRAC code 18) inhibit squalene-epoxidase in ergosterol 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 result 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.

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

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

"Quinone inside inhibitor (QiI) fungicides (b21)" (FRAC code 21) inhibit Complex III mitochondrial respiration in fungi by affecting ubiquinol reductase. Reduction of ubiquinol 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.

"Benzamide fungicides (b22)" (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. Examples include zoxamide.

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

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

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

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

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

"Carbamate fungicides (b28)" (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.

"Oxidative phosphorylation uncoupling fungicides (b29)" (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, pyrimidonehydrazones such as ferimzone and dinitrophenyl crotonates such as dinocap, meptyldinocap and binapacryl.

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

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

"Heteroaromatic fungicides (b32)" (FRAC code 32) are proposed to affect DNA/ribonucleic acid (RNA) synthesis. Heteroaromatic fungicides include isoxazole and isothiazolone fungicides. The isoxazoles include hymexazole and the isothiazolones include octhilinone.

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

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

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

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

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

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

"Pyrimidinamide fungicides (b39)" (FRAC code 39) inhibit growth of fungi by affecting phospholipid biosynthesis and include diflumetorim.

"Carboxylic acid amide (CAA) fungicides (b40)" (FRAC code 40) are proposed to inhibit phospholipid biosynthesis and cell wall deposition. Inhibition of these processes prevents growth and leads to death of the target fungus. Carboxylic acid amide fungicides include cinnamic acid amide, valinamide carbamate and mandelic acid amide fungicides. The cinnamic acid amides include dimethomorph and flumorph. The valinamide carbamates include benthiavalicarb, benthiavalicarb-isopropyl, iprovalicarb and valifenalate (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.

"Tetracycline antibiotic fungicides (b41)" (FRAC code 41) inhibit growth of fungi by affecting complex 1 nicotinamide adenine dinucleotide (NADH) oxidoreductase. Examples include oxytetracycline.

"Thiocarbamate fungicides (b42)" (FRAC code 42) include methasulfocarb.

"Benzamide fungicides (b43)" (FRAC code 43) inhibit growth of fungi by delocalization of spectrin-like proteins. Examples include acylpicolide fungicides such as fluopicolide and fluopyram.

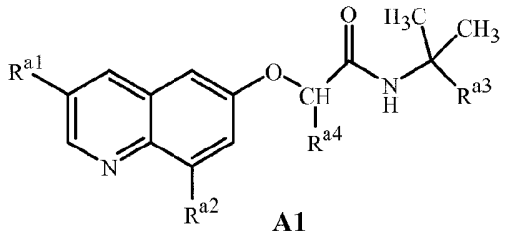
"Host plant defense induction fungicides (b44)" (FRAC code P) induce host plant defense mechanisms. Host plant defense induction fungicides include benzo-thiadiazole, benzisothiazole and thiadiazole-carboxamide fungicides. The benzo-thiadiazoles include acibenzolar-*S*-methyl. The benzisothiazoles include probenazole. The thiadiazole-carboxamides include tiadinil and isotianil.

"Multi-site contact fungicides (b45)" inhibit fungal growth through multiple sites of action and have contact/preventive activity. This class of fungicides includes: "copper fungicides (b45.1) (FRAC code M1)", "sulfur fungicides (b45.2) (FRAC code M2)", "dithiocarbamate fungicides (b45.3) (FRAC code M3)", "phthalimide fungicides (b45.4) (FRAC code M4)", "chloronitrile fungicides (b45.5) (FRAC code M5)", "sulfamide fungicides (b45.6) (FRAC code M6)", "guanidine fungicides (b45.7) (FRAC code M7)" "triazine fungicides (b45.8) (FRAC code M8)" and "quinone fungicides (b45.9) (FRAC code M9)". "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 tolylfluanid. "Guanidine fungicides" include dodine, guazatine and iminoctadine. "Triazine fungicides" include anilazine. "Quinone fungicides" include dithianon.

"Fungicides other than fungicides of component (a) and components (b1) through (b45); (b46)" include certain fungicides whose mode of action may be unknown. These include: (b46.1) "thiazole carboxamide fungicides" (FRAC code U5), (b46.2) "phenyl-acetamide fungicides" (FRAC code U6), (b46.3) "quinazolinone fungicides" (FRAC code U7), (b46.4) "benzophenone fungicides" (FRAC code U8) and (b46.5)

"triazolopyrimidylamine fungicides" (FRAC code 45). The thiazole carboxamides include ethaboxam. The phenyl-acetamides include cyflufenamid and *N*-[[(cyclopropyl-methoxy)amino][6-(difluoromethoxy)-2,3-difluorophenyl]-methylene]benzeneacetamide. The quinazolinones include proquinazid and 2-butoxy-6-iodo-3-propyl-4*H*-1-benzopyran-4-one. The benzophenones include metrafenone and pyriofenone. The triazolopyrimidylamines include ametoctradin and are believed to inhibit Complex III mitochondrial respiration by binding to an unelucidated site on ubiquinone-cytochrome bc1 reductase. The (b46) class also includes bethoxazin, neo-asozin (ferric methanearsonate), fenpyrazamine, pyrrolnitrin, quinomethionate, tebufloquin, 2-[[2-fluoro-5-(trifluoromethyl)phenyl]thio]-2-[3-(2-methoxyphenyl)-2-thiazolidinylidene]acetonitrile, 3-[5-(4-chlorophenyl)-2,3-dimethyl-3-isoxazolidinyl]pyridine, 4-fluorophenyl *N*-[1-[[[1-(4-cyanophenyl)ethyl]sulfonyl]methyl]propyl]carbamate, 5-chloro-6-(2,4,6-trifluorophenyl)-7-(4-methylpiperidin-1-yl)[1,2,4]triazolo[1,5-*a*]pyrimidine, *N*-(4-chloro-2-nitrophenyl)-*N*-ethyl-4-methylbenzenesulfonamide, *N'*-[4-[4-chloro-3-(trifluoromethyl)phenoxy]-2,5-dimethylphenyl]-*N*-ethyl-*N*-methylmethanimidamide and 1-[(2-propenylthio)carbonyl]-2-(1-methylethyl)-4-(2-methylphenyl)-5-amino-1*H*-pyrazol-3-one.

"Fungicides other than fungicides of component (a) and components (b1) through (b45); (b46)" also include (b46.5) 6-quinolinyloxyacetamide compounds of Formula **A1** and salts thereof



A1

wherein

R^{a1} is halogen, C_1–C_4 alkoxy or C_1–C_4 alkynyl;

R^{a2} is H, halogen or C_1–C_4 alkyl;

R^{a3} 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^{a4} is methyl or Y^{a1}-R^{a5};

R^{a5} is C_1–C_2 alkyl; and

Y^{a1} is CH_2, O or S.

Compounds of Formula **A1**, 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, WO 2008/110355, WO 2009/030469, WO 2009/049716 and WO 2009/087098. Examples of compounds of Formula **A1** include:

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2-[(3-bromo-6-quinolinyl)oxy]-*N*-(1,1-dimethyl-2-butyn-1-yl)-2-(methylthio)acetamide, *N*-(1,1-dimethyl-2-butyn-1-yl)-2-[(3-ethynyl-6-quinolinyl)oxy]-2-(methylthio)acetamide, 2-[(3-bromo-8-methyl-6-quinolinyl)oxy]-*N*-(1,1-dimethyl-2-propyn-1-yl)-2-(methylthio)acetamide and 2-[(3-bromo-6-quinolinyl)oxy]-*N*-(1,1-dimethylethyl)-butanamide.

"Fungicides other than fungicides of component (a) and components (b1) through (b45); (b46)" also include (b46.6) *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 biosynthesis of sterols.

In the embodiments of the present invention, including those described below, reference to Formula **1** includes *N*-oxides and salts thereof unless otherwise indicated, 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. The composition comprising components (a) and (b) described in the Summary of the Invention wherein in Formula **1**, X is CHOH or NH.

Embodiment 2. The composition of Embodiment 1 wherein X is CHOH.

Embodiment 3. The composition of Embodiment 1 wherein X is NH.

Embodiment 4. The composition comprising components (a) and (b) described in the Summary of the Invention or any one of Embodiments 1 through 3 wherein in Formula **1**, R^1 is halogen.

Embodiment 5. The composition of Embodiment 4 wherein R^1 is F, Cl or Br.

Embodiment 6. The composition of Embodiment 5 wherein R^1 is Cl or Br.

Embodiment 7. The composition comprising components (a) and (b) described in the Summary of the Invention or any one of Embodiments 1 through 6 wherein in Formula **1**, R^2 is H, cyano, F, Cl, Br or C_1–C_2 alkoxy.

Embodiment 8. The composition of Embodiment 7 wherein R^2 is H, cyano, F, Cl, Br or methoxy.

Embodiment 9. The composition of Embodiment 8 wherein R^2 is cyano, F, Cl or methoxy.

Embodiment 10. The composition of Embodiment 9 wherein R^2 is F or Cl.

Embodiment 11. The composition of Embodiment 8 wherein R^2 is H.

Embodiment 12. The composition comprising components (a) and (b) described in the Summary of the Invention or any one of Embodiments 1 through 11 wherein in Formula **1**, R^3 is H or halogen.

Embodiment 13. The composition of Embodiment 12 wherein R^3 is H, F, Cl or Br.

Embodiment 14. The composition of Embodiment 13 wherein R^3 is H, F or Cl.

Embodiment 15. The composition of Embodiment 14 wherein R^3 is H or F.

Embodiment 16. The composition comprising components (a) and (b) described in the Summary of the Invention or any one of Embodiments 1 through 11 wherein in Formula **1**, R^3 is halogen or methyl.

Embodiment 17. The composition of Embodiment 16 wherein R^3 is halogen.

Embodiment 18. The composition of Embodiment 17 wherein R^3 is F, Cl or Br.

Embodiment 19. The composition of Embodiment 14 or 18 wherein R^3 is F or Cl.

Embodiment 20. The composition of Embodiment 15 or 19 wherein R^3 is F.

Embodiment 21. The composition comprising components (a) and (b) described in the Summary of the Invention or any one of Embodiments 1 through 20 wherein in Formula **1**, R^4 is F, Cl or Br.

Embodiment 22. The composition of Embodiment 21 wherein R^4 is Cl or Br.

Embodiment 23. The composition comprising components (a) and (b) described in the Summary of the Invention or any one of Embodiments 1 through 22 wherein in Formula **1**, R^5 is H, cyano, F, Cl, Br or C_1–C_2 alkoxy.

Embodiment 24. The composition of Embodiment 23 wherein R^5 is H, cyano, F, Cl or methoxy.

Embodiment 25. The composition of Embodiment 24 wherein R^5 is cyano, F, Cl or methoxy.

Embodiment 26. The composition of Embodiment 25 wherein R^5 is cyano or F.

Embodiment 27. The composition of Embodiment 26 wherein R^5 is cyano.

Embodiment 28. The composition of Embodiment 26 wherein R^5 is F.

Embodiment 29. The composition comprising components (a) and (b) described in the Summary of the Invention or any one of Embodiments 1 through 28 wherein in Formula **1**, R^6 is H, F, Cl or Br.

Embodiment 30. The composition of Embodiment 29 wherein R^6 is H or F.

Embodiment 31. The composition of Embodiment 30 wherein R^6 is H.

Embodiment 32. The composition comprising components (a) and (b) described in the Summary of the Invention or any one of Embodiments 1 through 31 wherein in Formula **1**, at most, only one of R^2 and R^3 is H (i.e. only one of R^2 and R^3 is H, or neither R^2 nor R^3 is H).

Embodiment 33. The composition of Embodiment 32 wherein R^3 is H (and R^2 is other than H).

Embodiment 34. The composition of Embodiment 32 wherein R^2 is H (and R^3 is other than H).

Embodiment 35. The composition of Embodiment 32 wherein both R^2 and R^3 are other than H.

Embodiment 36. The composition comprising components (a) and (b) described in the Summary of the Invention or any one of Embodiments 1 through 35 wherein in

Formula **1**, at most, only one of R^5 and R^6 is H (i.e. only one of R^5 and R^6 is H, or neither R^5 nor R^6 is H).

Embodiment 37. The composition of Embodiment 36 wherein R^6 is H (and R^5 is other than H).

Embodiment 38. The composition of Embodiment 36 wherein R^5 is H (and R^6 is other than H).

Embodiment 39. The composition of Embodiment 36 wherein both R^5 and R^6 are other than H.

Embodiment 40. The composition comprising components (a) and (b) described in the Summary of the Invention or any one of Embodiments 1 through 39 wherein in Formula **1**, at most, only two of R^2, R^3, R^4 and R^6 are H.

Embodiment 41. The composition of Embodiment 40 wherein two of R^2, R^3, R^4 and R^6 are H.

Embodiment 42. The composition of Embodiment 40 wherein, at most, only one of R^2, R^3, R^4 and R^6 is H.

Embodiment 43. The composition of Embodiment 42 wherein one of R^2, R^3, R^4 and R^6 is H.

Embodiment 44. The composition comprising components (a) and (b) described in the Summary of the Invention or any one of Embodiments 1 through 43 wherein component (a) does not comprise an *N*-oxide of a compound of Formula **1**.

Embodiment 45. The composition comprising components (a) and (b) described in the Summary of the Invention or any one of Embodiments 1 through 44 wherein component (a) comprises a compound selected from the group consisting of
N,4-bis(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 47),
N-(2-bromo-4,6-difluorophenyl)-4-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 143),
N-(2-bromo-4,6-difluorophenyl)-4-(2-bromo-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 195),
N-(2-bromo-4,6-difluorophenyl)-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 144),
N-(4-chloro-2,6-difluorophenyl)-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazole-5-amine (Compound 81),
4-[5-[(4-chloro-2-fluorophenyl)amino]-1,3-dimethyl-1*H*-pyrazol-4-yl]-3,5-difluorobenzonitrile (Compound 40),
N-(2-chloro-4,6-difluorophenyl)-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 82),

4-[5-[(2-chloro-4,6-difluorophenyl)amino]-1,3-dimethyl-1*H*-pyrazol-4-yl]-3-fluorobenzonitrile (Compound 238),
4-[[4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-yl]oxy]-3,5-difluorobenzonitrile (Compound 13),
4-(2-chloro-4-fluorophenyl)-*N*-(2,4-dichloro-6-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 136),
4-(2-chloro-4-fluorophenyl)-*N*-(2,6-difluoro-4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 3),
4-(2-chloro-4-fluorophenyl)-α-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazole-5-methanol (Compound 122),
N-(2,4-dichloro-6-fluorophenyl)-4-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 161),
4-(2,4-dichlorophenyl)-*N*-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 17),
4-(2,6-difluoro-4-methoxyphenyl)-1,3-dimethyl-*N*-(2,4,6-trifluorophenyl)-1*H*-pyrazol-5-amine (Compound 7),
4-[[1,3-dimethyl-4-(2,4,6-trifluorophenyl)-1*H*-pyrazol-5-yl]oxy]-3,5-difluorobenzonitrile (Compound 8),
4-(2-chloro-4-fluorophenyl)-*N*-(2-chloro-6-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 239),
4-(2-bromo-4-fluorophenyl)-*N*-(2-chloro-6-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5 amine (Compound 240),
N-(2-bromo-6-fluorophenyl)-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 241),
4-(2-bromo-4-fluorophenyl)-*N*-(2-bromo-6-fluorophenyl)-1,3-dimethyl-*1H*-pyrazol-5-amine (Compound 244),
N-(2-bromo-6-fluorophenyl)-4-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 245),
N-(2-bromo-6-fluorophenyl)-4-(2,6-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 247),
4-(2-chloro-4-fluorophenyl)-*N*-(2-fluoro-6-methylphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 252),
4-(2-chloro-4-fluorophenyl)-*N*-(2-chloro-6-methylphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 253),
N-(2-bromo-6-methylphenyl)-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 254),
N-(2-chloro-6-methylphenyl)-4-(2-fluoro-4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 257),

N-(2-bromo-6-methylphenyl)-4-(2-fluoro-4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 258),
4-(2-fluoro-4-methoxyphenyl)-*N*-(2-fluoro-6-methylphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 259),
N-(2-chloro-6-fluorophenyl)-4-(2-fluoro-4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 260),
N-(2-bromo-6-fluorophenyl)-4-(2-fluoro-4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 261),
4-(2-chloro-4-methoxyphenyl)-*N*-(2-chloro-6-methylphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 262),
N-(2-bromo-6-methylphenyl)-4-(2-chloro-4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 263),
N-(2-bromo-6-methylphenyl)-4-(2-chloro-4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 264),
N-(2-bromo-6-methylphenyl)-4-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 265),
4-(2-bromo-4-fluoropheny)-*N*-(2-bromo-6-methylphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 266),
4-(2-bromo-4-fluorophenyl)-*N*-(2-fluoro-6-methylphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 267),
4-(2,4-difluorophenyl)-*N*-(2-fluoro-6-methylphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 268),
N-(2-chloro-6-methylphenyl)-4-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 269),
4-(2,4-difluorophenyl)-*N*-(2,6-dimethylphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 270),
4-(2-chloro-4-fluorophenyl)-*N*-(2,6-dimethylphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 271),
N-(2-bromo-6-fluorophenyl)-4-(2-chloro-4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 273),
N-(2-chloro-6-fluorophenyl)-4-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 275), and
4-(2-bromo-4-fluorophenyl)-*N*-(2-chloro-6-methylphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 276).

(to the extent that the compounds of the group are within the scope of the parent Embodiment).

Embodiment 46. The composition of Embodiment 45 wherein component (a) comprises a compound selected from the group consisting of Compounds 3, 7, 8, 13, 17, 40, 47, 81, 82, 122, 136, 143, 144, 161, 195, 238, 239, 240 and 241.

Embodiment 47. The composition of Embodiment 46 wherein component (a) comprises a compound selected from the group consisting of Compounds 3, 7, 8, 13, 17, 40, 47, 81, 82, 122, 136, 143, 144, 161, 195 and 238.

Embodiment 48. The composition of Embodiment 45 wherein component (a) comprises a compound selected from the group consisting of Compounds 239, 240, 241, 244, 245, 247, 252, 253, 254, 257, 258, 259, 260, 261, 262, 263, 264, 265, 266, 267, 268, 269, 270, 271, 273, 275 and 276.

Embodiment 49. The composition of Embodiment 48 wherein component (a) comprises a compound selected from the group consisting of Compounds 239, 240 and 241.

Embodiment 50. The composition of Embodiment 45 wherein component (a) comprises a compound selected from the group consisting of Compound 195 and Compound 238.

Embodiment 51. The composition comprising components (a) and (b) described in the Summary of the Invention or any one of Embodiments 1 through 50, provided that when component (a) consists of a compound selected from the group consisting of

4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-*N*-(2,4,6-trifluorophenyl)-1*H*-pyrazol-5-amine (Compound 4),

4-(2,6-difluoro-4-methoxyphenyl)-*N*-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 6),

4-(2,6-difluoro-4-methoxyphenyl)-1,3-dimethyl-*N*-(2,4,6-trifluorophenyl)-1*H*-pyrazol-5-amine (Compound 7),

4-(2,4-difluorophenyl)-1,3-dimethyl-*N*-(2,4,6-trifluorophenyl)-1*H*-pyrazol-5-amine (Compound 11),

4-[[4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-yl]oxy]-3,5-difluorobenzonitrile (Compound 13),

4-[[4-(2,6-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-yl]oxy]-3-fluorobenzonitrile (Compound 130),

4-(2-chloro-4-fluorophenyl)-*N*-(2,6-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 46),

4-[[4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-yl]oxy]-3-fluorobenzonitrile (Compound 33),

3-chloro-4-[[4-(2,6-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-yl]oxy]benzonitrile (Compound 127),

4-(2-chloro-4-fluorophenyl)-α-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazole-5-methanol (Compound 122),
N,4-bis(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 47),
N-(2-chloro-4-fluorophenyl)-4-(2-chloro-6-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 58),
N-(2-chloro-4,6-difluorophenyl)-4-(2,6-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 86),
N-(2-chloro-4,6-difluorophenyl)-4-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 117),
N-(4-chloro-2,6-difluorophenyl)-4-(2,6-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 121),
N-(4-chloro-2,6-difluorophenyl)-4-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 126),
3-chloro-4-[[4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-yl]oxy]benzonitrile (Compound 37),
4-[[4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-yl]amino]-3,5-difluorobenzonitrile (Compound 25),
N-(2-chloro-4-fluorophenyl)-4-(2,6-difluoro-4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 23),
α,4-bis(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazole-5-methanol (Compound 123),
N-(4-chloro-2,6-difluorophenyl)-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazole-5-amine (Compound 81),
N-(2-chloro-4,6-difluorophenyl)-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 82),
N-(2,6-dichloro-4-fluorophenyl)-4-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 137),
3-chloro-4-[5-[(2-chloro-4,6-difluorophenyl)amino]-1,3-dimethyl-1*H*-pyrazol-4-yl]benzonitrile (Compound 108),
3-chloro-4-[5-[(4-chloro-2,6-difluorophenyl)amino]-1,3-dimethyl-1*H*-pyrazol-4-yl]benzonitrile (Compound 111),
N-(2-bromo-4-fluorophenyl)-4-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 118),
4-(2-chloro-4-fluorophenyl)-*N*-(2,4-dichloro-6-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 136),
4-(2-chloro-4-fluorophenyl)-*N*-(2,6-dichloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 138),

4-[[4-(2-bromo-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-yl]oxy]-3-fluorobenzonitrile (Compound 79),
N-(2-bromo-4-fluorophenyl)-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 73),
4-(2-bromo-4-fluorophenyl)-1,3-dimethyl-*N*-(2,4,6-trifluorophenyl)-1*H*-pyrazol-5-amine (Compound 74),
N-(4-bromo-2,6-difluorophenyl)-4-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 133),
4-[[4-(2-bromo-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-yl]oxy]-3,5-difluorobenzonitrile (Compound 65),
4-(2-bromo-4-fluorophenyl)-*N*-(2-chloro-4,6-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 84),
4-(2-bromo-4-fluorophenyl)-*N*-(4-chloro-2,6-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 129),
N-(4-bromo-2,6-difluorophenyl)-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 134),
3-bromo-4-[[4-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-yl]oxy]benzonitrile (Compound 139),
3-chloro-4-[[4-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-yl]oxy]benzonitrile (Compound 140),
N-(2,4-dichloro-6-fluorophenyl)-4-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 141),
N-(2,6-dichloro-4-fluorophenyl)-4-(2,6-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 142),
N-(2-bromo-4,6-difluorophenyl)-4-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 143),
N-(2-bromo-4,6-difluorophenyl)-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 144),
N-(4-bromo-2,6-difluorophenyl)-4-(2,6-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 145),
N-(2-bromo-4,6-difluorophenyl)-4-(2,6-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 146),
N-(2-bromo-4,6-difluorophenyl)-4-(2-chloro-6-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 147),
α-(4-chloro-2,6-difluorophenyl)-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazole-5-methanol (Compound 148),
4-[5-[(2-chloro-4,6-difluorophenyl)amino]-1,3-dimethyl-1*H*-pyrazol-4-yl]-3-fluorobenzonitrile (Compound 238),

4-[5-[(4-chloro-2,6-difluorophenyl)amino]-1,3-dimethyl-1*H*-pyrazol-4-yl]-3-fluorobenzonitrile (Compound 150),
α-(2-chloro-4,6-difluorophenyl)-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazole-5-methanol (Compound 151),
α-(2-bromo-4-fluorophenyl)-4-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazole-5-methanol (Compound 152), and
α-(2-bromo-4-fluorophenyl)-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazole-5-methanol (Compound 153),
then component (b) comprises at least two fungicidal compounds, and

(1) when component (b) consists of a binary combination of two fungicidal compounds, wherein one of the fungicidal compounds is cyproconazole, difenconazole, epoxiconazole, metconazole, myclobutanil, prothioconazole or tebuconazole then the other fungicidal compound is other than azoxystrobin, bixafen, boscalid, cyflufenamid, fluopyram, isopyrazam, kresoxim-methyl, metrafenone, penthiopyrad, picoxystrobin, proquinazid, pyraclostrobin, quinoxyfen, sedaxane or trifloxystrobin, and

(2) when component (b) consists as a ternary combination of three fungicidal compounds, wherein one of the fungicidal compounds is cyproconazole, difenconazole, epoxiconazole, metconazole, myclobutanil, prothioconazole or tebuconazole, and another of the fungicidal compounds is picoxystrobin or trifloxystrobin, then the third fungicidal compound is other than proquinazid.

Embodiments of this invention, including Embodiments 1–51 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 compositions comprising compounds of Formula **1** with at least one other fungicidal compound but also to compositions comprising compounds of Formula **1** with at least one invertebrate pest control compound or agent, and also to the compounds of Formula **1** and their compositions, and also to the starting compounds and intermediate compounds useful for preparing the compounds of Formula **1**. In addition, embodiments of this invention, including Embodiments 1–51 above as well as any other embodiments described herein, and any combination thereof, pertain to the methods of the present invention. Therefore of note as a further embodiment is the composition disclosed above comprising (a) at least one compound selected from the compounds of Formula 1 described above, *N*-oxides, and salts thereof; and at least one invertebrate pest control compound or agent, provided that when component (a) is consists of a compound selected from the group listed in Embodiment 51, then the composition comprises at least two invertebrate pest control compounds or agents, or at least one

additional fungicidal compound (i.e. fungicidal compound in addition to the Formula **1** compound).

Combinations of Embodiments 1–51 are illustrated by:

Embodiment A1. The composition comprising components (a) and (b) described in the Summary of the Invention wherein component (a) comprises a compound of Formula **1** or salt thereof, wherein in Formula **1**,

at most, only one of R^2 and R^3 is H; and

at most, only one of R^5 and R^6 is H.

Embodiment A2. The composition of Embodiment A1 wherein in Formula **1**,

R^1 is F, Cl or Br;

R^2 is H, cyano, F, Cl, Br or methoxy;

R^3 is H, F or Cl;

R^4 is F, Cl or Br;

R^5 is H, cyano, F, Cl or methoxy; and

R^6 is H or F.

Embodiment A3. The composition of Embodiment A2 wherein in Formula **1**,

R^3 is H or F; and

R^5 is cyano, F, Cl or methoxy.

Embodiment A4. The composition of Embodiment A3 wherein component (a) comprises a compound selected from the group consisting of: Compound 3, Compound 7, Compound 8, Compound 13, Compound 17, Compound 40, Compound 47, Compound 81, Compound 82, Compound 122, Compound 136, Compound 143, Compound 144, Compound 161, Compound 195, Compound 238, Compound 239, Compound 240 and Compound 241.

Embodiment A5. The composition of Embodiment A4 wherein component (a) comprises a compound selected from the group consisting of: Compound 3, Compound 7, Compound 8, Compound 13, Compound 17, Compound 40, Compound 47, Compound 81, Compound 82, Compound 122, Compound 136, Compound 143, Compound 144, Compound 161, Compound 195 and Compound 238.

Embodiment A6. The composition comprising components (a) and (b) described in the Summary of the Invention wherein component (a) comprises a compound of Formula **1** or salt thereof, wherein in Formula **1**,

X is NH;

R^1 is halogen or methyl;

R^2 is H;

R^3 is halogen or methyl;

R^4 is halogen;

R^5 is H, cyano, halogen or C_1–C_2 alkoxy; and

R^6 is H or halogen;

provided that when R^1 is F, then R^3 is Cl, and when R^1 is Cl, then R^3 is F.

Embodiment A7. The composition of Embodiment A6 wherein in Formula **1**,

R^3 is F or Cl.

Embodiment A8. The composition of Embodiment A7 wherein in Formula **1**,

R^1 is Cl or Br; and

R^3 is F.

Embodiment A9. The composition of any one of Embodiments A6 through A8 wherein in Formula **1**, at most, only one of R^5 and R^6 is H.

Embodiment A10. The composition of Embodiment A9 wherein in Formula **1**,

R^4 is F, Cl or Br;

R^5 is H, cyano, F, Cl or methoxy; and

R^6 is H or F.

Embodiment A11. The composition of Embodiment A10 wherein in Formula **1**,

R^5 is cyano, F, Cl or methoxy.

Embodiment A12. The composition of Embodiment A6 wherein component (a) comprises a compound selected from the group consisting of: Compound 239, Compound 240, and Compound 241.

Embodiment B1. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b1) methyl benzimidazole carbamate fungicides such as benomyl, carbendazim and thiophanate-methyl.

Embodiment B2. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b2) dicarboximide fungicides such as procymidone, iprodione and vinclozolin.

Embodiment B3. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b3) demethylation inhibitor fungicides such as epoxiconazole, fluquinconazole, triadimenol, simeconazole, ipconazole, triforine, cyproconazole, difenconazole, flusilazole, flutriafol, metconazole, myclobutanil, prochloraz, propiconazole, prothioconazole, tebuconazole and tetraconazole.

Embodiment B4. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b4) phenylamide fungicides such as metalaxyl, metalaxyl-M, benalaxyl, benalaxyl-M, furalaxyl, ofurace and oxadixyl.

Embodiment B5. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b5) amine/morpholine fungicides such as aldimorph, dodemorph, fenpropimorph, tridemorph, trimorphamide, fenpropidin, piperalin and spiroxamine.

Embodiment B6. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b6) phospholipid biosynthesis inhibitor fungicides such as edifenphos and isoprothiolane.

Embodiment B7. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b7) carboxamide fungicides such as bixafen, boscalid, carboxin, isopyrazam, oxycarboxin, penflufen and penthiopyrad.

Embodiment B8. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b8) hydroxy(2-amino-)pyrimidine fungicides such as ethirimol.

Embodiment B9. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b9) anilinopyrimidine fungicides such as cyprodinil.

Embodiment B10. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b10) *N*-phenyl carbamate fungicides such as diethofencarb.

Embodiment B11. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one

compound selected from (b11) quinone outside inhibitor fungicides such as azoxystrobin, pyraclostrobin, pyrametostrobin, kresoxim-methyl, trifloxystrobin, picoxystrobin, pyraoxystrobin, pyribencarb, famoxadone, fenamidone, discostrobin, enestrobin, dimoxystrobin, metominostrobin, orysastrobin and fluoxastrobin.

Embodiment B12. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b12) phenylpyrrole fungicides compound such as fenpiclonil and fludioxonil.

Embodiment B13. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b13) quinoline fungicides such as quinoxyfen.

Embodiment B14. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b14) lipid peroxidation inhibitor fungicides such as chloroneb.

Embodiment B15. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b15) melanin biosynthesis inhibitors-reductase fungicides such as pyroquilon and tricyclazole.

Embodiment B16. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b16) melanin biosynthesis inhibitors-dehydratase fungicides such as carpropamid.

Embodiment B17. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b17) hydroxyanilide fungicides such as fenhexamid.

Embodiment B18. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b18) squalene-epoxidase inhibitor fungicides such as pyributicarb.

Embodiment B19. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b19) polyoxin fungicides such as polyoxin.

Embodiment B20. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b20) phenylurea fungicides such as pencycuron.

Embodiment B21. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b21) quinone inside inhibitor fungicides such as cyazofamid and amisulbrom.

Embodiment B22. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b22) benzamide fungicides such as zoxamide.

Embodiment B23. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b23) enopyranuronic acid antibiotic fungicides such as blasticidin-S.

Embodiment B24. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b24) hexopyranosyl antibiotic fungicides such as kasugamycin.

Embodiment B25. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b25) glucopyranosyl antibiotic: protein synthesis fungicides such as streptomycin.

Embodiment B26. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b26) glucopyranosyl antibiotic: trehalase and inositol biosynthesis fungicides such as validamycin.

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Embodiment B27. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b27) cyanoacetylamideoxime fungicides such as cymoxanil.

Embodiment B28. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b28) carbamate fungicides such as propamacarb, prothiocarb and iodocarb.

Embodiment B29. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b29) oxidative phosphorylation uncoupling fungicides such as fluazinam, binapacryl, ferimzone, meptyldinocap and dinocap.

Embodiment B30. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b30) organo tin fungicides such as fentin acetate.

Embodiment B31. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b31) carboxylic acid fungicides such as oxolinic acid.

Embodiment B32. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b32) heteroaromatic fungicides such as hymexazole.

Embodiment B33. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b33) phosphonate fungicides such as phosphorous acid and its various salts, including fosetyl-aluminum.

Embodiment B34. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b34) phthalamic acid fungicides such as teclofthalam.

Embodiment B35. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1

through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b35) benzotriazine fungicides such as triazoxide.

Embodiment B36. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b36) benzene-sulfonamide fungicides such as flusulfamide.

Embodiment B37. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b37) pyridazinone fungicides such as diclomezine.

Embodiment B38. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b38) thiophene-carboxamide fungicides such as silthiofam.

Embodiment B39. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b39) pyrimidinamide fungicides such as diflumetorim.

Embodiment B40. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b40) carboxylic acid amide fungicides such as dimethomorph, benthiavalicarb, benthiavalicarb-isopropyl, iprovalicarb, valifenalate, mandipropamid and flumorph.

Embodiment B41. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b41) tetracycline antibiotic fungicides such as oxytetracycline.

Embodiment B42. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b42) thiocarbamate fungicides such as methasulfocarb.

Embodiment B43. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one

compound selected from (b43) benzamide fungicides such as fluopicolide and fluopyram.

Embodiment B44. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b44) host plant defense induction fungicides such as acibenzolar-*S*-methyl.

Embodiment B45. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b45) multi-site contact fungicides such as copper oxychloride, copper sulfate, copper hydroxide, Bordeaux composition (tribasic copper sulfide), elemental sulfur, mancozeb, metiram, propineb, ferbam, maneb, thiram, zineb, ziram, folpet, captan, captafol and chlorothalonil.

Embodiment B46. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one compound selected from (b46) fungicides other than fungicides of component (a) and components (b1) through (b45), such as ethaboxam, cyflufenamid, proquinazid, metrafenone, pyriofenone, ametoctradin, bethoxazin, neo-asozin, fenpyrazamine, pyrrolnitrin, quinomethionate, tebufloquin, 5-chloro-6-(2,4,6-trifluorophenyl)-7-(4-methylpiperidin-1-yl)[1,2,4]triazolo[1,5-*a*]pyrimidine (BAS600), 2-butoxy-6-iodo-3-propyl-4*H*-1-benzopyran-4-one, 3-[5-(4-chlorophenyl)-2,3-dimethyl-3-isoxazolidinyl]pyridine (SYP-Z048), 4-fluorophenyl *N*-[1-[[[1-(4-cyanophenyl)ethyl]sulfonyl]methyl]propyl]carbamate (XR-539), *N*-[[(cyclopropylmethoxy)amino][6-(difluoromethoxy)-2,3-difluorophenyl]methylene]benzeneacetamide, *N'*-[4-[4-chloro-3-(trifluoromethyl)phenoxy]-2,5-dimethylphenyl]-*N*-ethyl-*N*-methylmethanimidamide, 2-[[2-fluoro-5-(trifluoromethyl)phenyl]thio]-2-[3-(2-methoxyphenyl)-2-thiazolidinylidene]acetonitrile (OK-5203), *N*-(4-chloro-2-nitrophenyl)-*N*-ethyl-4-methylbenzenesulfonamide (TF-991) and 1-[(2-propenylthio)carbonyl]-2-(1-methylethyl)-4-(2-methylphenyl)-5-amino-1*H*-pyrazol-3-one.

Embodiment B47. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one fungicidal compound (fungicide) selected from the group consisting of azoxystrobin, kresoxim-methyl, trifloxystrobin, pyraclostrobin, pyraoxystrobin,

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pyrametostrobin, picoxystrobin, dimoxystrobin, metominostrobin-/fenominostrobin, carbendazim, chlorothalonil, quinoxyfen, metrafenone, pyriofenone, cyflufenamid, fenpropidin, fenpropimorph, bromuconazole, cyproconazole, difenoconazole, epoxiconazole, fenbuconazole, flusilazole, hexaconazole, ipconazole, metconazole, myclobutanil, penconazole, propiconazole, proquinazid, prothioconazole, tebuconazole, triticonazole, famoxadone, prochloraz, penthiopyrad and boscalid (nicobifen).

Embodiment B48. The composition of Embodiment B47 wherein component (b) includes at least one compound selected from the group consisting of azoxystrobin, kresoxim-methyl, trifloxystrobin, pyraclostrobin, pyrametostrobin, pyraoxystrobin, picoxystrobin, dimoxystrobin, metominostrobin-/fenominostrobin, quinoxyfen, metrafenone, pyriofenone, cyflufenamid, fenpropidin, fenpropimorph, cyproconazole, difenoconazole, epoxiconazole, flusilazole, metconazole, myclobutanil, propiconazole, proquinazid, prothioconazole, tebuconazole, triticonazole, famoxadone and penthiopyrad.

Embodiment B49. The composition described in the Summary of the Invention (including but not limited to the composition of any one of Embodiments 1 through 51 and A1 through A12) wherein component (b) includes at least one fungicidal compound selected from compounds of Formula **A1** and salts thereof, wherein Formula **A1** and substituents thereon are as disclosed herein for the (b46.5) class of 6-quinolinyloxyacetamide compounds.

Embodiment B50. The composition of Embodiment B49 wherein component (b) includes at least one fungicidal compound selected from the group consisting of 2-[(3-bromo-6-quinolinyl)oxy]-*N*-(1,1-dimethyl-2-butyn-1-yl)-2-(methylthio)-acetamide, *N*-(1,1-dimethyl-2-butyn-1-yl)-2-[(3-ethynyl-6-quinolinyl)oxy]-2-(methylthio)acetamide, 2-[(3-bromo-8-methyl-6-quinolinyl)oxy]-*N*-(1,1-dimethyl-2-propyn-1-yl)-2-(methylthio)acetamide and 2-[(3-bromo-6-quinolinyl)oxy]-*N*-(1,1-dimethylethyl)butanamide.

Of note is the composition of any one of the embodiments described herein, including Embodiments 1 through 51, A1 through A12, and B1 through B50, wherein reference to Formula **1** includes salts thereof but not *N*-oxides thereof; therefore the phrase "a compound of Formula **1**" can be replaced by the phrase "a compound of Formula **1** or a salt thereof". In this composition of note, component (a) comprises a compound of Formula **1** or a salt thereof.

Also noteworthy as embodiments are fungicidal compositions of the present invention comprising a fungicidally effective amount of a composition of Embodiments 1 to 51, A1 to

A12, and B1 to B50 and at least one additional component selected from the group consisting of surfactants, solid diluents and liquid diluents.

Embodiments of the invention further include methods for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof, or to the plant seed or seedling, a fungicidally effective amount of a composition any one of Embodiments 1 to 51, A1 to A12, and B1 to B50 (e.g., as a composition including formulation ingredients as described herein). Embodiments of the invention also include methods for protecting a plant or plant seed from diseases caused by fungal pathogens comprising applying a fungicidally effective amount of a composition of any one of Embodiments 1 to 51, A1 to A12, and B1 to B50 to the plant or plant seed.

Some embodiments of the invention involve control of a plant disease or protection from a plant disease that primarily afflicts plant foliage and/or applying the composition of the invention to plant foliage (i.e. plants instead of seeds). The preferred methods of use include those involving the above preferred compositions; and the diseases controlled with particular effectiveness include plant diseases caused by fungal plant pathogens. Combinations of fungicides used in accordance with this invention can facilitate disease control and retard resistance development.

Method embodiments further include:

Embodiment C1. A method for protecting a plant from a disease selected from powdery mildew, rust and *Septoria* diseases comprising applying to the plant a fungicidally effective amount of the composition comprising components (a) and (b) described in the Summary of the Invention or any one of Embodiments 1 through 51.

Embodiment C2. The method of Embodiment C1 wherein the disease is a powdery mildew disease and component (b) of the composition includes at least one fungicidal compound selected from (b4) demethylation inhibitor (DMI) fungicides, (b11) quinine outside inhibitor (QoI) fungicides, and (b46.4) proquinazid.

Embodiment C3. The method of Embodiment C2 wherein the disease is wheat powdery mildew.

Embodiment C4. The method of Embodiment C2 or C3 wherein component (b) includes at least one fungicidal compound selected from (b4) DMI fungicides.

Embodiment C5. The method of Embodiment C4 wherein component (b) includes at least one fungicidal compound selected from the group consisting of cyproconazole, difenoconazole, epoxiconazole, myclobutanil, prothioconazole and tetraconazole.

Embodiment C6. The method of Embodiment C5 wherein component (b) includes at least one fungicidal compound selected from the group consisting of cyproconazole, difenoconazole and prothioconazole.

Embodiment C7. The method of Embodiment C2 or C3 wherein component (b) includes at least one fungicidal compound selected from (b11) QoI fungicides.

Embodiment C8. The method of Embodiment C7 wherein component (b) includes at least one fungicidal compound selected from the group consisting of azoxystrobin, picoxystrobin and pyraclostrobin.

Embodiment C9. The method of Embodiment C2 or C3 wherein component (b) includes (b46.4) proquinazid.

Embodiment C10. The method of Embodiment C1 wherein the disease is a rust disease and component (b) of the composition includes fenpropimorph.

Embodiment C11. The method of Embodiment C10 wherein the disease is wheat leaf rust.

Embodiment C12. The method of Embodiment C1 wherein the disease is a *Septoria* disease and component (b) of the composition includes at least one fungicidal compound selected from the group consisting of epoxiconazole, metalaxyl (including metalaxyl-M), iprovalicarb and fenpropimorph.

Embodiment C13. The method of Embodiment C12 wherein the disease is wheat leaf blotch.

Embodiment C14. A method for protecting a plant from a *Septoria* disease comprising applying to the plant a fungicidally effective amount of the composition of Embodiment B49 or B50.

Embodiment C15. The method of Embodiment C14 wherein the disease is caused by *Septoria tritici*.

Embodiment C16. The method of Embodiment C14 or C15 wherein the disease is wheat leaf blotch.

Embodiment C17. The method of any one of Embodiments C1 through C16 wherein components (a) and (b) are applied in synergistically effective amounts (and in a synergistic ratio relative to each other).

Of note are embodiments that are counterparts of Embodiments C1 through C17 relating to a method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof, a fungicidally effective amount of a fungicidal composition of the invention.

As noted in the Summary of the Invention, this invention also relates to a compound of Formula **1**, or an *N*-oxide or salt thereof. Also already noted is that the embodiments of this invention, including Embodiments 1–51, relate also to compounds of Formula **1**. Accordingly, combinations of Embodiments 1–51 are further illustrated by:

Embodiment D1. A compound of Formula **1**, or an *N*-oxide or salt thereof, wherein
X is NH;
R^1 is halogen or methyl;
R^2 is H;
R^3 is halogen or methyl;
R^4 is halogen;
R^5 is H, cyano, halogen or C_1–C_2 alkoxy; and
R^6 is H or halogen;
provided that when R^1 is F, then R^3 is Cl, and when R^1 is Cl, then R^3 is F.

Embodiment D2. A compound of Embodiment D1 wherein
R^3 is F or Cl.

Embodiment D3. A compound of Embodiment D2 wherein
R^1 is Cl or Br; and
R^3 is F.

Embodiment D4. A compound of any one of Embodiments D1 through D4 wherein, at most, only one of R^5 and R^6 is H.

Embodiment D5. A compound of Embodiment D4 wherein
R^4 is F, Cl or Br;
R^5 is H, cyano, F, Cl or methoxy; and
R^6 is H or F.

Embodiment D6. A compound of Embodiment D5 wherein
R^5 is cyano, F, Cl or methoxy.

Embodiment D7. A compound of any one of Embodiments D1 through D6 wherein the compound is other than in the form of an *N*-oxide (i.e. is in the form of Formula **1** or a salt thereof).

Embodiment D8. A compound of Embodiment D1 selected from the group consisting of:
4-(2-chloro-4-fluorophenyl)-*N*-(2-chloro-6-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 239),
4-(2-bromo-4-fluorophenyl)-*N*-(2-chloro-6-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5 amine (Compound 240), and
N-(2-bromo-6-fluorophenyl)-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 241).

Additional embodiments include a fungicidal composition comprising: (1) a compound of any one of Embodiments D1 through D8; and (2) at least one additional component selected from the group consisting of surfactants, solid diluents and liquid diluents. Additional embodiments also include a method for protecting a plant or plant seed from diseases caused by fungal pathogens comprising applying a fungicidally effective

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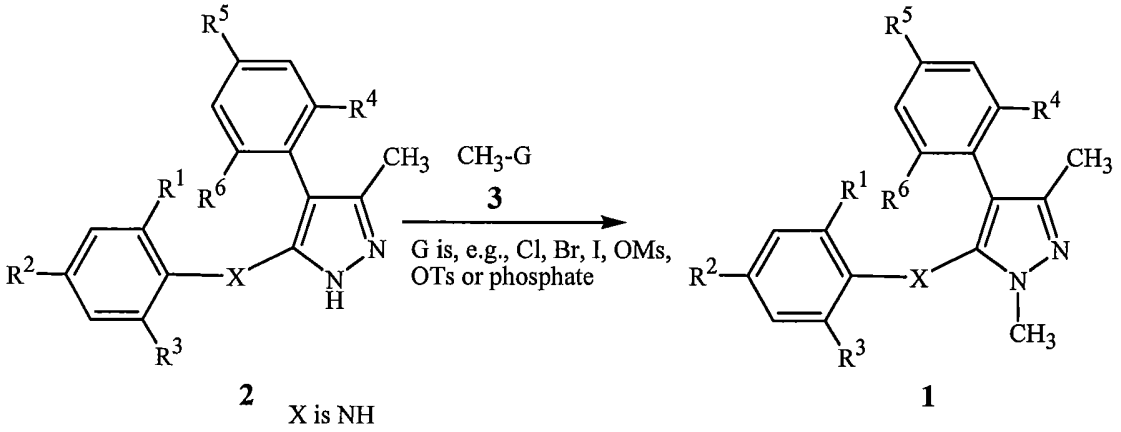
amount of the compound of any one of Embodiments D1 through D8 to the plant (or portion thereof) or plant seed (directly or through the environment (e.g., growing medium) of the plant or plant seed). Of note are embodiments relating to a method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof, a fungicidally effective amount of a compound of any one of Embodiments D1 through D8.

One or more of the following methods and variations as described in Schemes 1–17 can be used to prepare the compounds of Formula **1**. The definitions of R^1, R^2, R^3, R^4, R^5 and R^6 in the compounds of Formulae **1–26** below are as defined above in the Summary of the Invention unless otherwise noted. Formulae **1a** and **1b** are various subsets of Formula **1**; Formulae **4a** and **4b** are various subsets of Formula **4**; Formulae **6a** and **6b** are various subsets of Formula **6**; Formula **11a** is a subset of Formula **11**; and Formula **23a** is a subset of Formula **23**. Substituents for each subset formula are as defined for its parent formula unless otherwise noted.

As shown in Scheme 1, compounds of Formula **1** in which X is NH can be prepared by the reaction of 1*H*-pyrazole compounds of Formula **2** with various methylating agents (e.g., Formula **3**), such as iodomethane, methyl sulfonates (e.g., methyl mesylate (OMs) or tosylate (OTs)) or trimethyl phosphate, preferably in the presence of an organic or inorganic base such as 1,8-diazabicyclo[5.4.0]undec-7-ene, potassium carbonate or potassium hydroxide, and in a solvent such as *N*,*N*-dimethylformamide (DMF), tetrahydrofuran (THF), toluene or water.

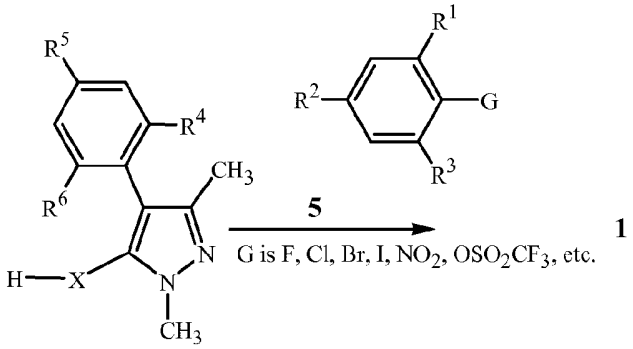
Scheme 1



As is shown in Scheme 2, compounds of Formula **1** can be prepared by the reaction of compounds of Formula **4** (i.e. 5-aminopyrazoles for X being NH, or 5-hydroxypyrazoles (5-pyrazolones) for X being O, with aromatic compounds of Formula **5** containing a leaving group G (i.e. halogen or (halo)alkylsulfonate), optionally in the presence of a metal catalyst,

and generally in the presence of a base and a polar aprotic solvent such as *N,N*-dimethylformamide or dimethyl sulfoxide. For example, compounds of Formula **5** wherein the benzene ring contains electron-withdrawing substituents react by direct displacement of the leaving group G from the ring to provide compounds of Formula **1**. The method of Scheme 2 is illustrated by Step D of Synthesis Example 6. Compounds of Formula **5** are commercially available or their preparation is known in the art.

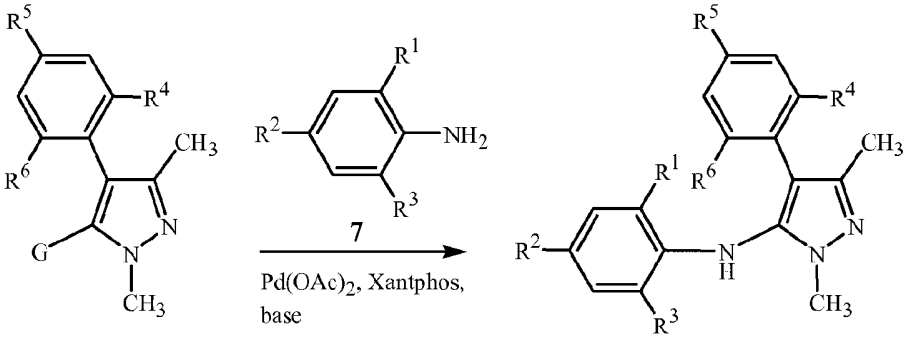
Scheme 2



4 X is NH or O

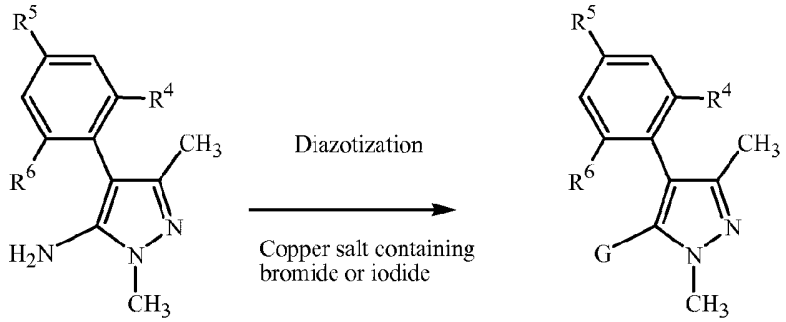
For reactions according to the method of Scheme 2 of a compound of Formula **4** wherein X is O or NH with a compound of Formula **5** wherein the aromatic ring lacks sufficiently electron-withdrawing substituents, or to improve reaction rate, yield or product purity, the use of a metal catalyst (e.g., metal or metal salt) in amounts ranging from catalytic up to superstoichiometric can facilitate the desired reaction. Typically for these conditions, G is Br or I or a sulfonate such as $OS(O)_2CF_3$ or $OS(O)_2(CF_2)_3CF_3$. For example, copper salt complexes (e.g., CuI with *N,N'*-dimethylethylenediamine, proline or bipyridyl), palladium complexes (e.g., tris(dibenzylideneacetone)dipalladium(0)) or palladium salts (e.g., palladium acetate) with ligands such as 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (i.e. "Xantphos"), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (i.e. "Xphos") or 2,2'-bis(diphenylphosphino)-1,1'-binaphthalene (i.e. "BINAP"), in the presence of a base such as potassium carbonate, cesium carbonate, sodium phenoxide or sodium *tert*-butoxide, in a solvent such as *N,N*-dimethylformamide, 1,2-dimethoxyethane, dimethyl sulfoxide, 1,4-dioxane or toluene, optionally mixed with alcohols such as ethanol, can be used. Alternatively as illustrated in Scheme 3, compounds of Formula **1a** (i.e. Formula **1** in which X is NH) can be prepared by reaction of compounds of Formula **6** (i.e. 5-bromopyrazoles or other pyrazoles substituted at the 5-position with a leaving group) with compounds of Formula **7** under metal-catalyzed conditions similar to those described above for Scheme 2. The method of Scheme 3 is illustrated by Step C of Synthesis Example 1 and Step E of Synthesis Example 2. Compounds of Formula **7** are commercially available or their preparation is known in the art.

Scheme 3



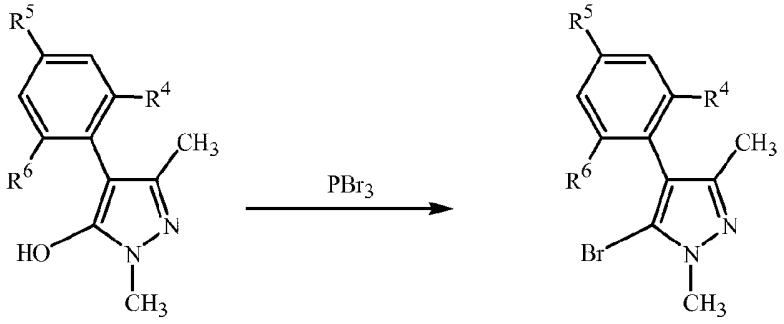
As shown in Scheme 4, compounds of Formula **6** wherein G is Br or I can be prepared by reaction of 5-aminopyrazoles of Formula **4a** (i.e. Formula **4** wherein X is NH) under diazotization conditions either in the presence of, or followed by combination with, copper salts containing bromide or iodide. For example, addition of *tert*-butyl nitrite to a solution of a 5-aminopyrazole of Formula **4a** in the presence of $CuBr_2$ in a solvent such as acetonitrile provides the corresponding 5-bromopyrazole of Formula **6**. Likewise, a 5-aminopyrazole of Formula **4a** can be converted to a diazonium salt and then to a corresponding 5-halopyrazole of Formula **6** 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 G 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. The method of Scheme 4 is illustrated by Step B of Synthesis Example 1 and Step D of Synthesis Example 2.

Scheme 4



As shown in Scheme 5, 5-bromopyrazoles of Formula **6a** (i.e. Formula **6** wherein G is Br) can be prepared by reacting 5-hydroxypyrazoles of Formula **4b** (i.e. Formula **4** wherein X is O) with phosphorus tribromide as described in *Tetrahedron Lett.* **2000**, *41*(24), 4713.

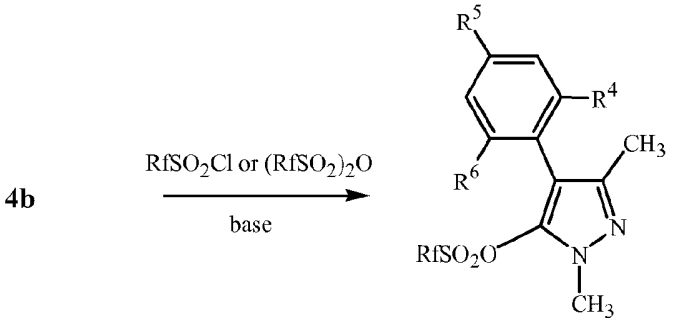
Scheme 5



4b **6a**

As shown in Scheme 6, 5-hydroxypyrazoles of Formula **4b** can also be used to prepare 5-fluoroalkylsulfonyl (e.g., 5-trifluoromethanesulfonyl, 5-nonafluorobutylsulfonyl) pyrazoles of Formula **6b** (i.e. Formula **6** wherein G is fluoroalkylsulfonyl) as described in *Synlett* **2004**, *5*, 795.

Scheme 6

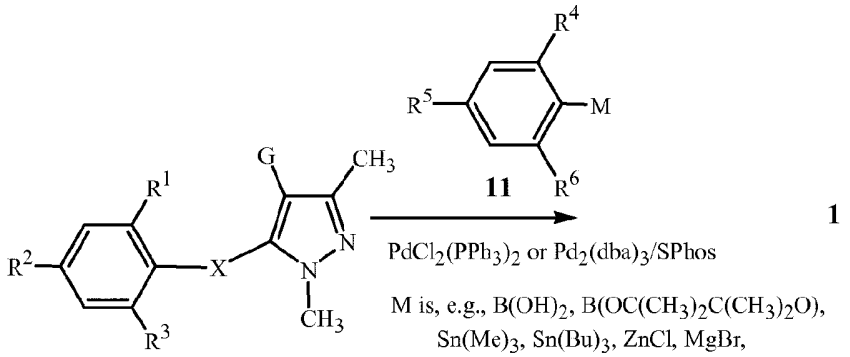


wherein Rf is fluoroalkyl such as CF_3 or $(CF_2)_2CF_3$ **6b**

As shown in Scheme 7, compounds of Formula **1** can be prepared by reaction of 4-bromo or iodo pyrazoles of Formula **10** wherein X is O or NH with organometallic compounds of Formula **11** under transition-metal-catalyzed cross-coupling reaction conditions. Reaction of a 4-bromo or iodo pyrazole of Formula **10** with a boronic acid, trialkyltin, zinc or organomagnesium reagent of Formula **11** in the presence of a palladium or nickel catalyst having appropriate ligands (e.g., triphenylphosphine (PPh_3), dibenzylideneacetone (dba), dicyclohexyl(2',6'-dimethoxy[1,1'-biphenyl]-2-yl)phosphine (SPhos)) and a base, if needed, affords the corresponding compound of Formula **1**. For example, a substituted aryl boronic acid or derivative e.g., Formula **11** wherein M is $B(OH)_2$, $B(OC(CH_3)_2C(CH_3)_2O)$) or $B(O\text{-}i\text{-}Pr)_3^{\ominus}$ $Li^{\oplus}$, reacts with a 4-bromo- or 4-iodopyrazole of Formula **10** in the presence of dichlorobis(triphenylphosphine) palladium(II) and aqueous base such as sodium carbonate or potassium hydroxide, in solvents such as 1,4-dioxane, 1,2-dimethoxyethane, toluene or ethyl alcohol, or under

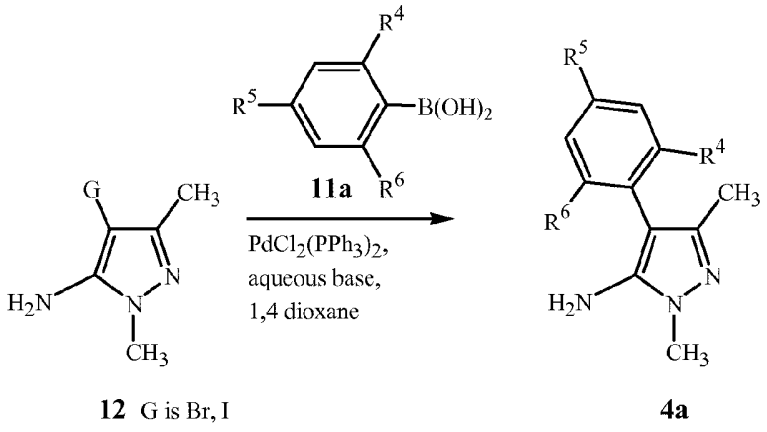
anhydrous conditions with a ligand such as phosphine oxide or phosphite ligand (e.g., diphenylphosphine oxide) and potassium fluoride in a solvent such as 1,4-dioxane (see *Angewandte Chemie, International Edition* **2008**, *47*(25), 4695–4698) to provide the corresponding compound of Formula **1**. The method of Scheme 7 is illustrated by Step C of present Synthesis Example 3.

Scheme 7



As illustrated in Scheme 8, compounds of Formula **4a** (i.e. Formula **4** wherein X is NH) can be prepared by reacting compounds of Formula **12** with compounds of Formula **11a** (e.g., compounds of Formula **11** wherein M is $B(OH)_2$) using transition-metal-catalyzed cross-coupling reaction conditions as described for the method of Scheme 7.

Scheme 8



As illustrated in Scheme 9, pyrazoles of Formula **10** wherein X is O or NH and G is Br or I are readily prepared by the reaction of pyrazoles unsubstituted at the 4-position (Formula **13**) with halogenating reagents such as bromine, sodium bromite, *N*-bromosuccinimide (NBS) or *N*-iodosuccinimide (NIS), in solvents such as acetic acid, acetonitrile, *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide or 1,4-dioxane, or a mixture of water with

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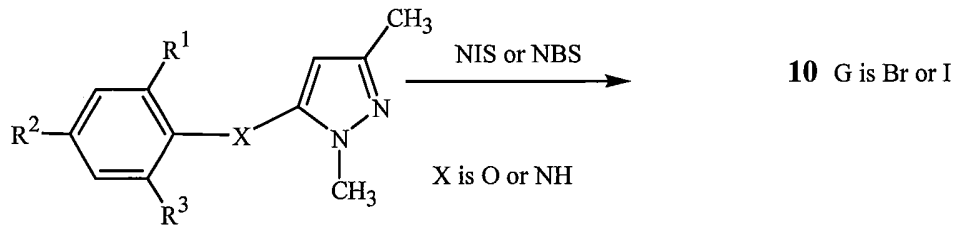
the aforementioned solvents, at temperatures ranging from ambient to the boiling point of the solvent. The method of Scheme 9 is illustrated by Step B of Synthesis Example 3.

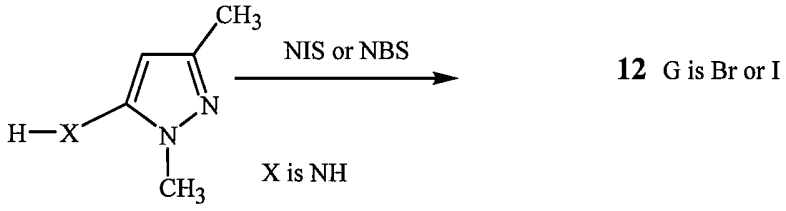
Scheme 9



13

As illustrated in Scheme 10, using reaction conditions similar to those for the method of Scheme 9, the pyrazole of Formula **14** wherein X is NH can be converted into intermediates **12** which are useful for preparing compounds of Formula **4a** as depicted in Scheme 8. The compound of Formula **14** wherein X is NH can be prepared by methods known in the art. Furthermore, the compound of Formula **14** wherein X is NH is commercially available.

Scheme 10



14

As shown in Scheme 11, compounds of Formula **13** wherein X is O or NH can be prepared from corresponding compounds of Formula **14** by procedures analogous to those used for the method of Scheme 2. The method of Scheme 11 is illustrated by Step A of Synthesis Example 3. Compounds of Formula **14** are commercially available or can be prepared by methods known in the art.

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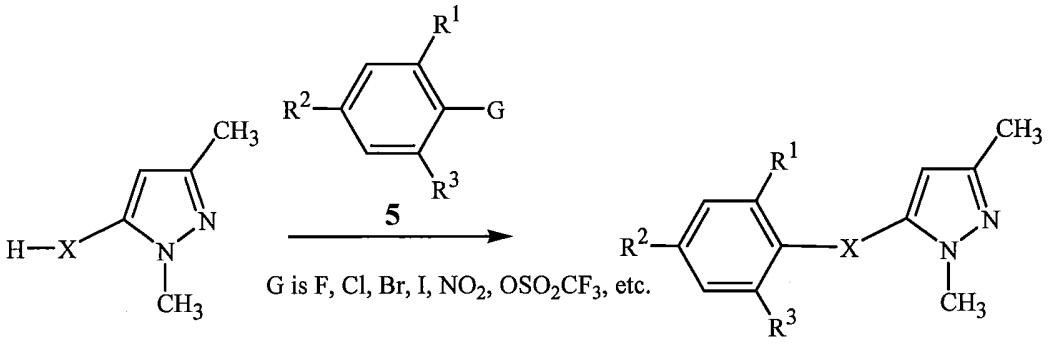
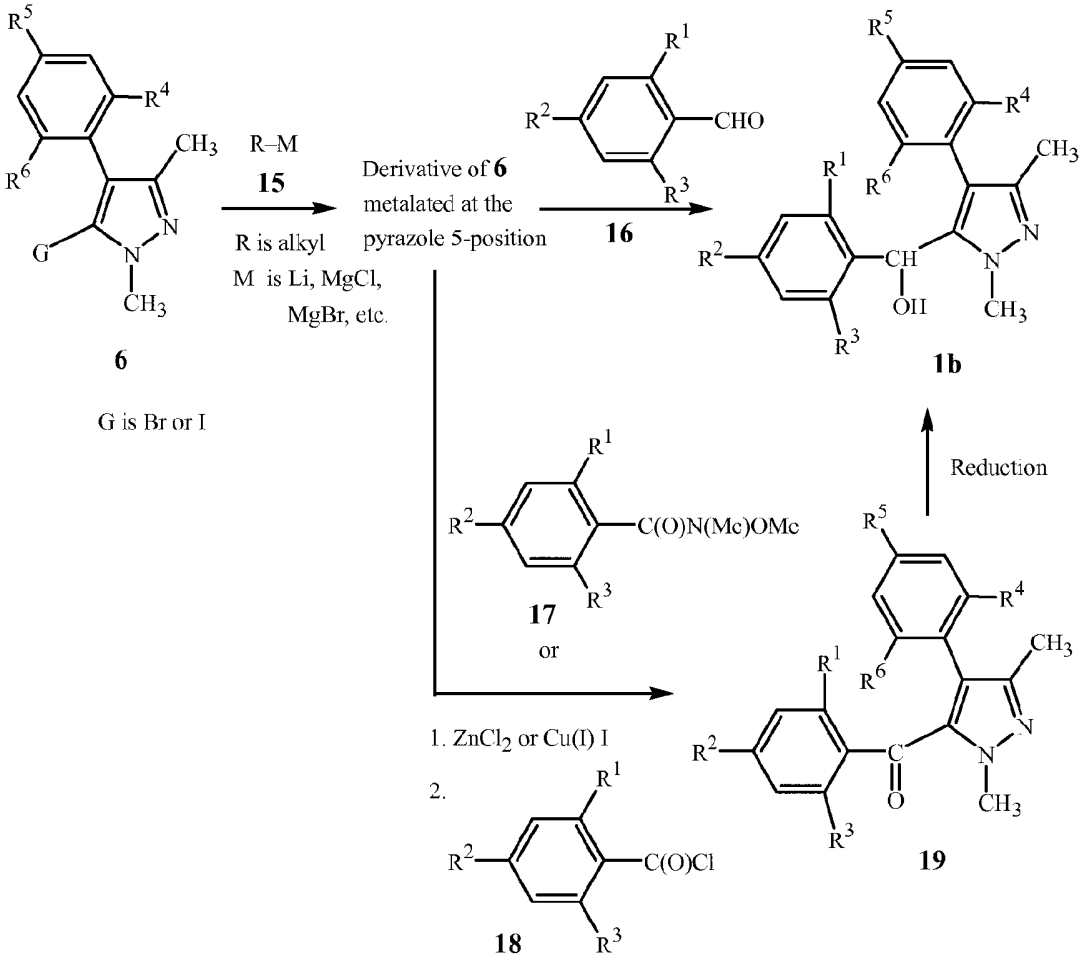
Scheme 11



14 X is NH or O **13**

As shown in Scheme 12, compounds of Formula **1b** (i.e. Formula **1** wherein X is CHOH), can be prepared by treatment of compounds of Formula **6** with an organometallic reagent (i.e. Formula **15**) such as an alkyllithium, preferably *n*-butyllithium, or an alkylmagnesium reagent, preferably isopropylmagnesium chloride (optionally complexed with lithium chloride), followed by the addition of a substituted benzaldehyde of Formula **16**. This method of Scheme 12 is illustrated by Synthesis Example 5. Alternatively, compounds of Formula **1b** can be prepared by reduction of ketones of Formula **19** using standard methods well known in the art (e.g., sodium borohydride in methanol or methanol). Ketones of Formula **19** can be prepared by reaction of the same metalated pyrazole derivative of the compound of Formula **6** with carbon electrophiles of Formula **17** or **18**. Reaction temperatures can range from –90 °C to the boiling point of the reaction solvent; temperatures of –78 °C to ambient temperature are generally preferred, with temperatures of –78 to –10 °C preferred when an alkyllithium reagent is used, and –20 °C to ambient temperature preferred with use of alkylmagnesium reagents. A variety of solvents are useful, such as toluene, ethyl ether, tetrahydrofuran or dimethoxymethane; anhydrous tetrahydrofuran is preferred. A second metallic component, such as zinc chloride, zinc bromide or a monovalent copper salt, such as copper(I) iodide or copper(I) cyanide, can advantageously be added before the electrophile in cases in which the electrophile is a compound of Formula **18**. The carbonyl intermediates of Formula **16, 17** and **18** are commercially available or can be prepared by methods known in the art.

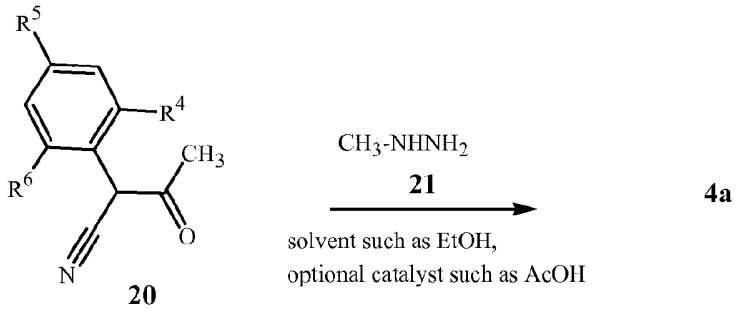
Scheme 12



It will be recognized by one skilled in the art that reactions analogous to those shown in Scheme 12 can also be utilized with pyrazoles lacking a substituent in the 4 position, thus affording certain compounds of Formula **13** that are useful in the method outlined in Scheme 9.

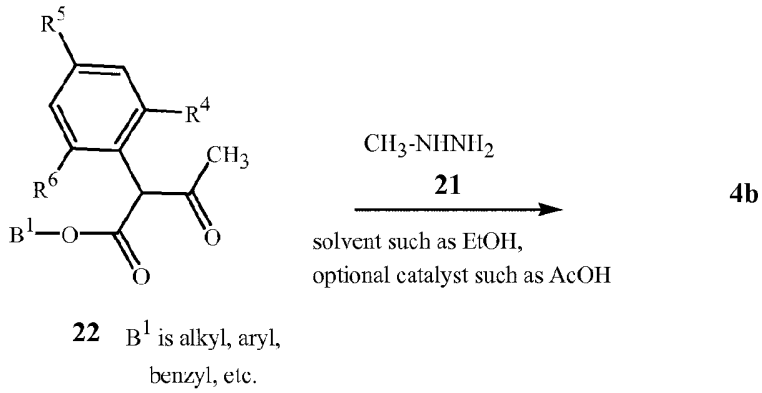
General methods useful for preparing 5-aminopyrazoles of Formula **4a** are well known in the art; see, for example, *Journal für Praktische Chemie (Leipzig)* **1911**, *83*, 171 and *J. Am. Chem. Soc.* **1954**, *76*, 501. Such a method is illustrated in Scheme 13. The method of Scheme 13 is illustrated by Step A of present Synthesis Example 1 and Step C of present Synthesis Example 2.

Scheme 13



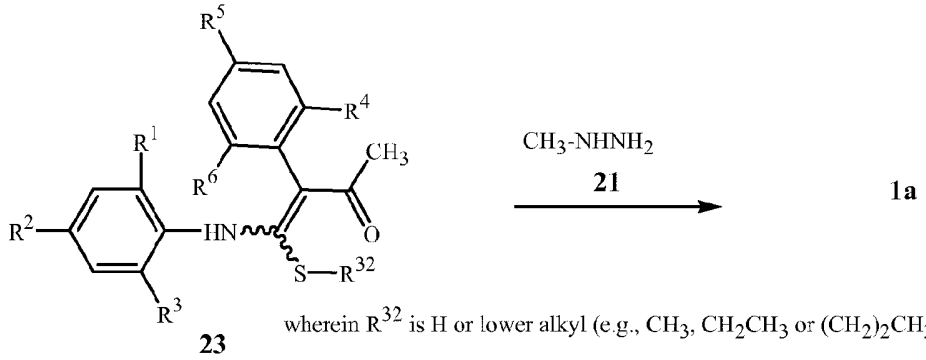
Similarly, general methods useful for preparing 5-hydroxypyrazoles of Formula **4b** are well known in the art; see, for example, *Annalen der Chemie* **1924**, *436*, 88. Such a method is illustrated in Scheme 14. The method of Scheme 14 is illustrated by Step C of present Synthesis Example 6.

Scheme 14



As shown in Scheme 15, compounds of Formula **1a** (i.e. Formula **1** wherein X is NH) can be prepared by condensing compounds of Formula **23** with methylhydrazine (Formula **21**) in a solvent such as ethanol or methanol and optionally in the presence of an acid or base catalyst such as acetic acid, piperidine or sodium methoxide, according to general procedures known in the art. The method of Scheme 15 is illustrated by Step B of Synthesis Example 4, and Step C of Synthesis Example 7.

Scheme 15

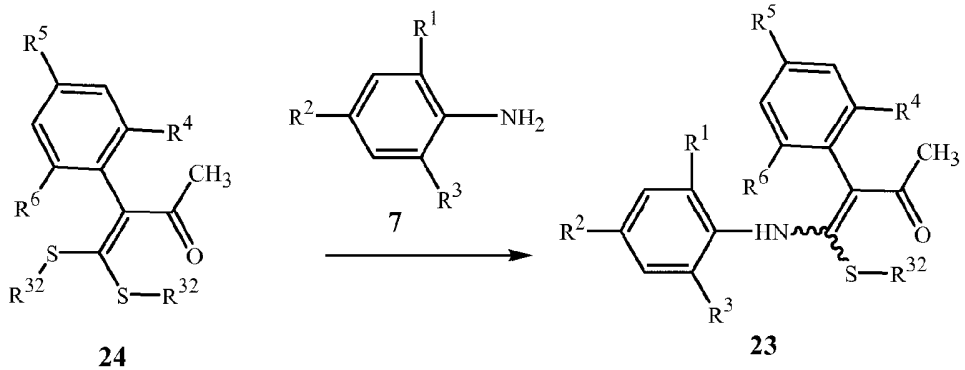


wherein R^{32} is H or lower alkyl (e.g., CH_3, CH_2CH_3 or $(CH_2)_2CH_3$)

In a manner analogous to the method of Scheme 15, compounds of Formula **2** wherein X is NH can be similarly prepared by condensing compounds of Formula **23** with hydrazine. This method is described in *Chemistry of Heterocyclic Compounds* **2005**, *41*(1), 105–110.

As shown in Scheme 16, compounds of Formula **23** (wherein, R^{32} is H or lower alkyl such as CH_3, CH_2CH_3 or $(CH_2)_2CH_3$) can be prepared by reaction of corresponding ketene dithioacetal compounds of Formula **24** with compounds of Formula 7 optionally in the presence of a base, such as sodium hydride or ethylmagnesium chloride, in solvents such as toluene, tetrahydrofuran or dimethoxymethane, at temperatures ranging from –10 °C to the boiling point of the solvent. See, for example, *J. Heterocycl. Chem.* **1975**, *12*(1), 139. Methods useful for preparing compounds of Formula **24** are known in the art.

Scheme 16

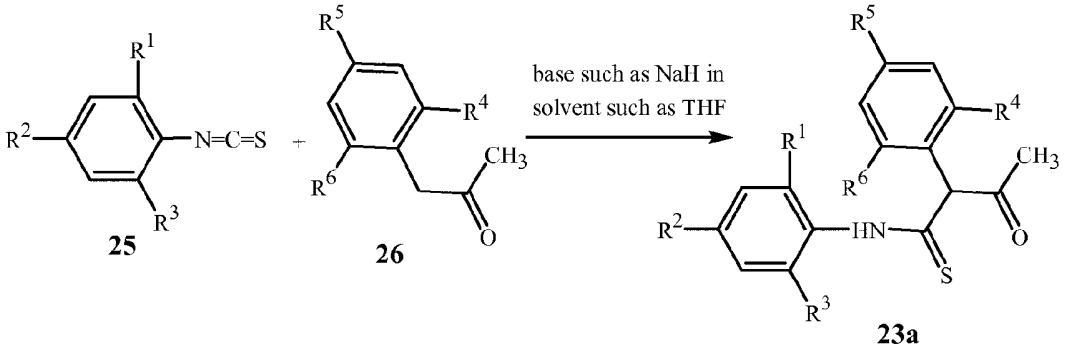


wherein R^{32} is H or lower alkyl (e.g., CH_3, CH_2CH_3 or $(CH_2)_2CH_3$)

As shown in Scheme 17, compounds of Formula **23a** (i.e. tautomer of Formula **23** wherein R^{32} is H) can be prepared by reaction of corresponding isothiocyanate compounds of Formula **25** with arylacetone compounds of Formula **26**; see, for example, *Zhurnal Organicheskoi Khimii* **1982**, *18*(12), 2501. Bases useful for this reaction include sodium hydride, alkoxide bases (e.g., potassium *tert*-butoxide or sodium ethoxide), potassium hydroxide, sodium hydroxide, potassium carbonate, or amine bases (e.g., triethylamine or

N,*N*-diisopropylethylamine). A variety of solvents are useful, such as tetrahydrofuran, ether, toluene, *N*,*N*-dimethylformamide, alcohols (e.g., ethanol), esters (e.g., ethyl acetate or isopropyl acetate), or mixtures thereof. Solvents are chosen for compatibility with the base selected, as is well-known in the art. Reaction temperatures can range from −78 °C to the boiling point of the solvent. One useful mixture of base and solvent is potassium *tert*-butoxide in tetrahydrofuran, to which at −70 to 0 °C is added a solution of an isothiocyanate of Formula **25** and a carbonyl compound of Formula **26**, which are either combined into one solution, or added separately, preferably by addition of the carbonyl compound followed by addition of the isothiocyanate. The method of Scheme 17 is illustrated by Step A of Synthesis Example 4, and Step C of Synthesis Example 7.

Scheme 17



Ketothioamides of Formula **23a** can be also be prepared by allowing the corresponding ketoamides to react with sulfurizing agents such as Lawesson's reagent or P_2S_5; see, for example, *Helv. Chim. Act.* **1998**, *81*(7), 1207.

It is recognized by one skilled in the art that various functional groups can be converted into others to provide different compounds of Formula **1**. For example, intermediates for the preparation of compounds of Formula **1** may contain aromatic nitro groups, which can be reduced to amino groups, and then be converted via reactions well known in the art such as the Sandmeyer reaction, to various halides, providing compounds of Formula **1**. By similar known reactions, aromatic amines (anilines) can be converted via diazonium salts to phenols, which can then be alkylated to prepare compounds of Formula **1** with alkoxy substituents. Likewise, aromatic halides such as bromides or iodides prepared via the Sandmeyer reaction can react with alcohols under copper-catalyzed conditions, such as the Ullmann reaction or known modifications thereof, to provide compounds of Formula **1** that contain alkoxy substituents. Additionally, some halogen groups, such as fluorine or chlorine, can be displaced with alcohols under basic conditions to provide compounds of Formula **1** containing the corresponding alkoxy substituents.

The above reactions can also in many cases be performed in alternate sequence, such as the preparation of 1*H* pyrazoles for use in the reaction in Scheme 2 by reactions illustrated later for the general preparation of substituted pyrazoles.

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, Greene, T. W.; Wuts, P. G. M. *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 Synthesis Examples are, therefore, to be construed as merely illustrative, and not limiting of the disclosure in any way whatsoever. Steps in the following Synthesis 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. ^{1}H NMR spectra are reported in ppm downfield from tetramethylsilane in $CDCl_3$ unless otherwise noted; "s" means singlet, "m" means multiplet, "br s" means broad singlet. Mass spectra (MS) 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 mass spectrometry using atmospheric pressure chemical ionization (AP^+) where "amu" stands for atomic mass units. The presence of molecular ions containing one or more higher atomic weight isotopes of lower abundance (e.g., ^{37}Cl, ^{81}Br) is not reported. "LC/MS" refers the combination of physical separation of chemical compounds by liquid chromatography and mass analysis of the separated compounds by mass spectrometry.

SYNTHESIS EXAMPLE 1

Preparation of 4-(2-Chloro-4-fluorophenyl)-*N*-(2,6-difluoro-4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 3)

Step A: Preparation of 4-[2-chloro-4-fluorophenyl]-1,3-dimethyl-1*H*-pyrazol-5-amine

A suspension of dry, solid sodium ethoxide (Aldrich, 10.2 g, 150 mmol) in a mixture of xylenes (60 mL) and anhydrous ethanol (25 mL) was stirred at 70 °C, and a solution of 2-chloro-4-fluorobenzeneacetonitrile (16.96 g, 100 mmol) in a mixture of ethyl acetate (30 mL) and ethanol (5 mL) was added dropwise to the hot reaction mixture over 20 minutes. The reaction mixture was heated at 75–78 °C for 3 h and then allowed to cool. Water (50 mL) was added to dissolve solids. The mixture was extracted once with ethyl acetate, and the extract was discarded. The aqueous phase was acidified to pH 2 by addition of 1 N aqueous hydrochloric acid, and then extracted with ethyl acetate (50 mL). The ethyl acetate phase was dried ($MgSO_4$) and evaporated to provide the intermediate product α-acetyl-2-chloro-4-fluorobenzeneacetonitrile as a solid (14.8 g).

A portion of the product obtained above (4.61 g, 21.8 mmol) was stirred in ethanol (15 mL), and glacial acetic acid (3 mL) and methylhydrazine (1.17 mL, 21.8 mol) were added. This reaction mixture was stirred and heated at overnight at reflux. The reaction mixture was then concentrated under reduced pressure, and the resultant residue was triturated with ethyl acetate. The resultant solids were collected on a glass frit and dried in air to afford the title compound as a white solid (2.42 g).

^{1}H NMR δ 7.2–7.3 (m, 2H), 7.0 (m, 1H), 3.7 (s, 3H), 3.4 (br s, 2H), 2.1 (s, 3H). MS: 240 amu (AP^+).

Step B: Preparation of 5-Bromo-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazole

Copper(II) bromide (3.94 g, 17.7 mmol) was added to a solution of 4-[2-chloro-4-fluorophenyl]-1,3-dimethyl-1*H*-pyrazol-5-amine (i.e. the product of Step A) (2.4 g, 10 mmol) in acetonitrile (50 mL), and the mixture was stirred and cooled in an ice-water bath while *tert*-butyl nitrite (90% technical grade, 2.33 mL, 17.7 mmol) was added dropwise over 5 min. The reaction mixture was allowed to warm slowly to ambient temperature. Aqueous HCl solution (20 mL) was added, and then ethyl acetate was added (20 mL). This mixture was filtered through a 2-cm pad of Celite® diatomaceous filter aid. The filter pad was washed with ethyl acetate (20 mL), and the phases were separated. The organic phase was washed with 1.0 N aqueous hydrochloric acid solution and brine, dried over $MgSO_4$, and concentrated to leave the title compound as an orange-brown semisolid (2.8 g).

^{1}H NMR δ 7.18–7.25 (m, 2H), 7.04 (m, 1H), 3.89 (s, 3H), 2.14 (s, 3H).

Step C: Preparation of 4-(2-Chloro-4-fluorophenyl)-*N*-(2,6-difluoro-4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine

5-Bromo-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazole (i.e. the product of Step B) (0.20 g, 0.66 mmol), palladium(II) acetate (15 mg, 0.066 mmol), 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (76 mg, 0.13 mmol) and powdered potassium carbonate (1.8 g, 13 mmol) were combined in anhydrous 1,4-dioxane (3 mL), and the mixture was sparged with a subsurface stream of N_2 gas for 10 min. 2,6-Difluoro-4-methoxyaniline (0.22 g, 1.3 mmol) was added in one portion, and the reaction mixture was heated at reflux for 22 h. The reaction mixture was filtered through Celite® diatomaceous filter aid, and the filter pad was washed with ethyl acetate (20 mL). The filtrate was washed with water (10 mL) and brine (10 mL), dried over $MgSO_4$, and concentrated to leave a semisolid residue. This residue was purified by column chromatography through 5 g of silica gel eluted with a gradient of hexanes/ethyl acetate (20:1 to 1:3) to give the title compound as a light-brown solid (48 mg).

^{1}H NMR δ 7.0–7.1 (m, 2H), 6.85 (m, 1H), 6.26 (m, 2H), 4.84 (br s, 1H), 3.78 (s, 3H), 3.66 (s, 3H), 2.08 (s, 3H). MS: 382 amu (AP^+).

SYNTHESIS EXAMPLE 2

Preparation of 4-(2,6-Difluoro-4-methoxyphenyl)-1,3-dimethyl-*N*-(2,4,6-trifluorophenyl)-1*H*-pyrazol-5-amine (Compound 7)

Step A: Preparation of 2,6-Difluoro-4-methoxybenzeneacetonitrile

A solution of KCN (0.88 g, 13 mmol) dissolved in water (2 mL) was added dropwise to a water-bath-cooled solution of 2,6-difluoro-4-methoxybenzyl bromide (2.50 g, 10.5 mmol) in *N*,*N*-dimethylformamide (10 mL). The reaction mixture was stirred for 20 min. Water was added (20 mL) and then the reaction mixture was poured into saturated aqueous $NaHCO_3$ solution (20 mL) and extracted with ether (50 mL). The organic phase was washed with water (5 × 25 mL), dried over $MgSO_4$, and concentrated to give an oil, which crystallized on standing to provide the title compound as a white solid (1.9 g).

^{1}H NMR δ 6.50 (m, 2H), 3.80 (s, 3H), 3.65 (s, 2H).

Step B: Preparation of α-Acetyl-2,6-difluoro-4-methoxybenzeneacetonitrile

Solid sodium ethoxide (4.7 g, 66 mmol) was stirred in a mixture of xylene (20 mL) and ethanol (10 mL) and heated to 50 °C. A solution of 2,6-difluoro-4-methoxybenzeneacetonitrile (i.e. the product of Step A) (8.0 g, 44 mmol) in ethyl acetate (10.4 mL) was added dropwise. The reaction mixture was heated at 50 °C for 4 h and then allowed to cool to ambient temperature. The reaction mixture was poured into water (100 mL) and extracted with ethyl acetate (25 mL). The aqueous phase was acidified with 3 N aqueous HCl to pH 4 and extracted with ethyl acetate (100 mL). This organic phase was washed with water

(50 mL), brine (50 mL), then dried over $MgSO_4$, and concentrated to leave the title compound as a tan semisolid (8.0 g).

^{1}H NMR δ 6.56 (m, 2H), 4.86 (s, 1H), 3.83 (s, 3H), 2.40 (s, 3H).

Step C: Preparation of 4-(2,6-Difluoro-4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrazole-5-amine

α-Acetyl-2,6-difluoro-4-methoxybenzeneacetonitrile (i.e. the product of Step B) (8.03 g, 35.7 mmol) and acetic acid (5 mL) were stirred in ethanol (35 mL), and methylhydrazine (1.91 mL, 35.7 mmol) was added. The reaction mixture was heated at reflux for 16 h, cooled, and then poured into water (100 mL). The resulting mixture was extracted with ethyl acetate (100 mL). The organic phase was washed with 1 N aqueous NaOH (50 mL) and then brine (50 mL), dried over $MgSO_4$, and concentrated to leave a solid. The solid was dissolved in methanol, and the resulting solution was warmed to 45 °C. Water (25 mL) was added dropwise, and the mixture was allowed to cool. The precipitate was collected on a glass frit to give the title compound as a white solid (3.88 g).

^{1}H NMR δ 6.55 (m, 2H), 3.81 (s, 3H), 3.67 (s, 3H), 3.43 (br s, 2H), 2.09 (s, 3H).

Step D: Preparation of 5-Bromo-4-(2,6-difluoro-4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrazole

Copper(II) bromide (3.81 g, 16.9 mmol) was added to a solution of 4-(2,6-difluoro-4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrazole-5-amine (i.e. the product of Step C) (3.88 g, 15.4 mmol) in acetonitrile (50 mL), and the mixture was stirred and cooled in an ice-water bath while *tert*-butyl nitrite (90% technical grade, 3.54 mL, 26.9 mmol) was added dropwise over 5 min. The reaction mixture was allowed to warm slowly to ambient temperature. Aqueous hydrochloric acid solution (25 mL) was added, then ethyl acetate (25 mL) was added, and the resulting mixture was filtered through a 2-cm pad of Celite® diatomaceous filter aid. The filter pad was washed with ethyl acetate (50 mL), and the phases were separated. The organic phase was washed with 1 N aqueous HCl solution (25 mL) and brine (25 mL), dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography through 24 g of silica gel eluted with a gradient of hexanes/ethyl acetate (9:1 to 1:1) to give the title compound as a white solid (3.25 g).

^{1}H NMR δ 6.54 (m, 2H), 3.88 (s, 3H), 3.83 (s, 3H), 2.16 (s, 3H).

Step E: Preparation of 4-(2,6-Difluoro-4-methoxyphenyl)-1,3-dimethyl-*N*-(2,4,6-trifluorophenyl)-1*H*-pyrazol-5-amine

5-Bromo-4-(2,6-difluoro-4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrazole (i.e. the product of Step D) (0.30 g, 0.94 mmol), palladium(II) acetate (20 mg, 0.090 mmol), 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (0.11 g, 0.19 mmol) and powdered potassium carbonate (2.6 g, 19 mmol) were combined in anhydrous 1,4-dioxane (4 mL), and the resulting mixture was sparged with a subsurface stream of N_2 gas for 10 min. 2,4,6-Trifluoroaniline (0.28 g, 1.9 mmol) was added in one portion, and the reaction mixture

was heated at reflux under nitrogen for 22 h. The reaction mixture was cooled, then filtered through Celite® diatomaceous filter aid. The filter pad was washed with ethyl acetate (20 mL), and the filtrate was washed with water (10 mL) and brine (10 mL), dried over $MgSO_4$, and concentrated to leave a semisolid residue. The residue was purified by column chromatography through 12 g of silica gel eluted with a gradient of hexanes/ethyl acetate (20:1 to 1:3) to give the title compound as a semisolid (73 mg).

^{1}H NMR (acetone-d_6) δ 6.84 (br s, 1H), 6.68 (m, 2H), 6.43 (m, 2H), 3.77 (s, 3H), 3.75 (s, 3H), 1.99 (s, 3H). MS: 384 amu (AP^+).

SYNTHESIS EXAMPLE 3

Preparation of 4-[[4-(2-Chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-yl]oxy]-3,5-difluorobenzonitrile (Compound 13)

Step A: Preparation of 4-[(1,3-Dimethyl-1*H*-pyrazol-5-yl)oxy]-3,5-difluorobenzonitrile

Potassium carbonate (1.38 g, 10 mmol) was added to a solution of 2,4-dihydro-2,5-dimethyl-3*H*-pyrazol-3-one (0.70 g, 6.3 mmol) in *N*,*N*-dimethylformamide (15 mL). 3,4,5-Trifluorobenzonitrile (0.94 g, 6.0 mmol) was added, and the reaction mixture was heated at 75 °C under a nitrogen atmosphere for 16 h, then allowed to cool. The reaction mixture was partitioned between water (60 mL) and ethyl acetate (30 mL). The organic phase was washed with water (2 × 30 mL) and brine (30 mL), dried over $MgSO_4$, and concentrated to give the title compound as a yellow oil (1.38 g).

^{1}H NMR δ 7.36 (m, 2H), 5.24 (s, 1H), 3.78 (s, 3H), 2.16 (s, 3H).

Step B: Preparation of 3,5-Difluoro-4-[(4-iodo-1,3-dimethyl-1*H*-pyrazol-5-yl)oxy]benzonitrile

A solution of 4-[(1,3-dimethyl-1*H*-pyrazol-5-yl)oxy]-3,5-difluorobenzonitrile (i.e. the product of Step A) (1.38 g, 5.5 mmol) in acetonitrile (20 mL) was stirred at ambient temperature, and *N*-iodosuccinimide (1.35 g, 6.0 mmol) was added in one portion. The reaction mixture was heated at reflux for 2 h, cooled, and then poured into water (40 mL). The resulting mixture was extracted with ethyl acetate (40 mL). The organic phase was washed with water (20 mL) and saturated aqueous $NaHCO_3$ solution (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure to give the title compound as a tan solid (2.1 g).

^{1}H NMR (acetone-d_6) δ 7.80 (m, 2H), 3.82 (s, 3H), 2.09 (s, 3H). MS: 376 amu (AP^+).

Step C: Preparation of 4-[[4-(2-Chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-yl]oxy]-3,5-difluorobenzonitrile

To a solution of 3,5-difluoro-4-[(4-iodo-1,3-dimethyl-1*H*-pyrazol-5-yl)oxy]-benzonitrile (i.e. the product of Step B) (1.0 g, 2.67 mmol) in 1,4-dioxane (6 mL) was added 2-chloro-4-fluorobenzeneboronic acid (alternatively named *B*-(2-chloro-4-fluorophenyl)-

boronic acid) (0.93 g, 5.33 mmol), dichloro (bis)triphenylphosphine palladium(II) (alternatively named bis(triphenylphosphine)palladium(II) dichloride) (93 mg, 0.13 mmol), potassium carbonate (0.74 g, 5.33 mmol), and water (4 mL). The resulting mixture was heated at reflux for 5 h, allowed to cool, and partitioned between water (20 mL) and ethyl acetate (20 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel with a gradient of hexanes / ethyl acetate to obtain the title compound as an off-white solid (110 mg).

^{1}H NMR δ 7.00–7.09 (m, 3H), 6.97 (m, 1H), 6.86 (m, 1H), 3.85 (s, 3H), 2.02 (s, 3H).

SYNTHESIS EXAMPLE 4

Preparation of 4-(2,4-Dichlorophenyl)-*N*-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 17)

Step A: Preparation of α-Acetyl-2,4-dichloro-*N*-(2,4-difluorophenyl)benzene-ethanethioamide

2,4-Difluorophenyl isothiocyanate (0.27 mL, 2.0 mmol) was added to a stirred suspension of sodium hydride (60% in mineral oil) (112 mg, 2.8 mmol) in anhydrous tetrahydrofuran (4 mL) cooled in an ice-water bath under a nitrogen atmosphere. A solution of 1-(2,4-dichlorophenyl)-2-propanone (570 mg, 2.8 mmol) in tetrahydrofuran (4 mL) was added dropwise over 5 min. The resultant yellow solution was stirred at 5–10 °C for 1 h. Water (10 mL) was carefully added, and the reaction mixture was extracted with ethyl acetate (10 mL). The aqueous phase was acidified to pH 3 with 1 N aqueous HCl, then extracted with ethyl acetate (20 mL). The organic extract was washed with water (10 mL) and brine (10 mL), dried over $MgSO_4$, and concentrated to leave a solid. The solid was triturated with hexanes / ethyl acetate (2:1), collected on a glass frit, and air-dried to give the title compound as a white solid (240 mg). MS: 373 amu (AP^+).

Step B: Preparation of 4-(2,4-Dichlorophenyl)-*N*-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine

Acetic acid (50 μL) and methylhydrazine (41 μL) were added to a stirred suspension of α-acetyl-2,4-dichloro-*N*-(2,4-difluorophenyl)benzeneethanethioamide (238 mg, 0.64 mmol) in ethanol (4 mL). The reaction mixture was heated at reflux for 2 h and allowed to cool. Then the reaction mixture was diluted with ethyl acetate (10 mL) and washed with 1 N aqueous NaOH (10 mL), water (10 mL) and brine (10 mL), dried over $MgSO_4$, and concentrated to leave a solid residue. The residue was purified by column chromatography on 5 g of silica gel with a gradient of hexanes/ethyl acetate (2:1 to 1:1) to give the title compound as a solid (170 mg).

^{1}H NMR δ 7.43 (s, 1H), 7.19 (m, 1H), 7.07 (m, 1H), 6.78 (m, 1H), 6.62 (m, 1H), 6.37 (m, 1H), 5.22 (br s, 1H), 3.70 (s, 3H), 2.18 (s, 3H). MS: 368 amu (AP^+).

SYNTHESIS EXAMPLE 5

Preparation of 4-(2-Chloro-4-fluorophenyl)-α-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazole-5-methanol (Compound 122)

5-Bromo-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazole (i.e. the product of Synthesis Example 1, Step B) (0.25 g, 0.82 mmol) was dissolved in anhydrous tetrahydrofuran (12 mL), and the mixture was cooled in a dry ice/acetone bath under a nitrogen atmosphere. A hexane solution of *n*-butyllithium (2.0 M, 0.49 mL, 0.98 mmol) was added dropwise over 5 minutes. After 15 minutes, a solution of 2,4-difluorobenzaldehyde (0.09 mL, 0.82 mmol) in anhydrous tetrahydrofuran (3 mL) was added slowly dropwise, causing the dark red-colored solution to lighten to a yellow color. After 45 minutes, the reaction mixture was quenched by the addition of saturated aqueous NH_4Cl solution (~20 mL) and allowed to warm to ambient temperature. This mixture was extracted with ethyl acetate, and the organic phase was washed with saturated aqueous NH_4Cl solution (25 mL) and with brine, dried over Na_2SO_4, and concentrated to leave a viscous residue. This residue was purified by column chromatography through silica gel eluted with a gradient of ethyl acetate in hexane (7% to 10%) to give the title compound as a white semi-solid (109 mg).

^{1}H NMR δ 7.5 (m, 1H), 7.1 (m, 2H), 7.0 (m, 1H), 6.85 (m, 2H), 6.0 (br s, 1H), 5.9 (s, 1H), 3.8 (s, 3H), 2.1 (s, 3H). MS: 367 amu (AP^+).

SYNTHESIS EXAMPLE 6

Preparation of 4-[[1,3-Dimethyl-4-(2,4,6-trifluorophenyl)-1*H*-pyrazol-5-yl]oxy]-3,5-difluorobenzonitrile (Compound 8)

Step A: Preparation of Methyl 2,4,6-trifluorobenzeneacetate

A solution of 2,4,6-trifluorobenzeneacetic acid (5.00 g, 26.3 mmol) in methanol (25 mL) was stirred at ambient temperature, and thionyl chloride (6 mL, ~3 eq.) was added dropwise, causing the temperature of the reaction mixture to reach 60 °C. The reaction mixture was allowed to cool to ambient temperature and was stirred for 3 h. Water (25 mL) was added with ice cooling. The mixture was extracted with ethyl acetate (2 × 100 mL). The combined organic phases were sequentially washed with water (2×), saturated aqueous sodium bicarbonate solution and brine, and then dried ($MgSO_4$). Concentration provided the title compound as a clear oil (5.38 g).

^{1}H NMR δ 6.68 (m, 2H), 3.72 (s, 3H), 3.66 (s, 2H).

Step B: Preparation of Methyl α-acetyl-2,4,6-trifluorobenzeneacetate

To a commercially obtained tetrahydrofuran solution of lithium bis(trimethylsilyl)amide (1.0 M, 21.0 mL) stirred under a nitrogen atmosphere and cooled to an internal temperature of –65 °C, was added dropwise over 30 minutes a solution of methyl 2,4,6-trifluorobenzeneacetate (i.e. the product of Step A) (2.04 g, 10.0 mmol) dissolved in dry tetrahydrofuran (10 mL). The reaction mixture was stirred for an additional 30 minutes,

and then while maintaining the –65 °C temperature, a solution of freshly distilled acetyl chloride (0.80 mL, 11 mmol) in dry tetrahydrofuran (3 mL) was added dropwise. The reaction mixture was allowed to warm slowly to ambient temperature, and then water (30 mL) was added. The resultant mixture was extracted with ethyl acetate (60 mL). The aqueous phase was acidified with 1 N hydrochloric acid and extracted with ethyl acetate (60 mL). Only the first ethyl acetate extract was retained, because thin layer chromatographic analysis showed the second extract to contain apparent polar impurities besides additional desired product. The first ethyl acetate extract was further sequentially washed with 1 N hydrochloric acid, water and brine, dried ($MgSO_4$), and concentrated to provide the title compound as a clear oil (1.86 g).

^{1}H NMR δ 6.69 (m, 2H), 3.7 (m, 1H and s, 3H), 1.87 (s, 3 H); minor resonances at 13.2 ppm and 4.9 ppm indicated presence of enolic tautomer.

Step C: Preparation of 1,3-Dimethyl-4-(2,4,6-trifluorophenyl)-1*H*-pyrazol-5-ol

To a solution of methyl α-acetyl-2,4,6-trifluorobenzeneacetate (i.e. the product of Step B) (2.46 g, 10.0 mmol) in methanol (15 mL) was added methylhydrazine (0.665 mL, 12.5 mmol), and the mixture was stirred at ambient temperature over 3 days. Aqueous citric acid solution (1 M, 10 mL) was added, and then water (50 mL) was added. The mixture was extracted with ethyl acetate (2 × 50 mL). The combined ethyl acetate extracts were sequentially washed with water and brine, dried ($MgSO_4$), and concentrated to leave a yellow solid. This solid was suspended in a small volume of ethyl acetate (~5 mL), an equal volume of hexanes was gradually added, and the suspension was stirred for 30 minutes. The solid component was collected on a glass frit, washed with small portions of ethyl acetate/ hexanes (1:1 and 1:2 v:v), and allowed to dry in air to provide a white solid (1.02 g). Evaporation of the mother liquor and treatment of the resultant residue with small volumes of ethyl acetate and hexanes as already described provided an additional 0.13 g of solid containing the title compound (1.15 g total). Analysis of the combined solids by LC/MS showed a primary component of mass 242 (AP^+) and a minor component, eluting later by reverse-phase LC, also having a mass of 242 (AP^+), thus being a regioisomer of the title compound. The apparent ratio of components was 94:6.

^{1}H NMR (acetone-d_6) δ 6.95 (m, 2H), 3.52 (s, 3H), 1.98 (s, 3H); 5-hydroxy resonance was not observed in this solvent.

Step D: Preparation of 4-[[1,3-Dimethyl-4-(2,4,6-trifluorophenyl)-1*H*-pyrazol-5-yl]oxy]-3,5-difluorobenzonitrile

A solution of 1,3-dimethyl-4-(2,4,6-trifluorophenyl)-1*H*-pyrazol-5-ol (i.e. the product of Step C) (104 mg, 0.43 mmol) in anhydrous *N*,*N*-dimethylformamide (2.5 mL) was cooled in an ice-water bath under a nitrogen atmosphere, and sodium hydride (60% suspension in mineral oil, 20 mg, 0.46 mmol) was added in one portion. After 15 minutes, 3,4,5-trifluorobenzonitrile (101 mg, 0.64 mmol) was added in one portion. The reaction mixture

was allowed to reach ambient temperature, and then it was heated at 40 °C for 2.5 h. Water (~10 mL) was added, and the mixture was extracted with ethyl acetate (2 × ~10 mL). The combined ethyl acetate extracts were sequentially washed with water (3 × 10 mL) and brine, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography on silica gel (5 g), eluting with a 2:1 mixture of hexanes–ethyl acetate, afforded a product (51 mg) containing the title compound in a 92:8 mixture with its regioisomer.

^{1}H NMR δ 7.1 (m, 2H), 6.5–6.6 (m, 2H), 3.85 (s, 3H), 2.05 (s, 3H). MS: 380 amu (AP+).

SYNTHESIS EXAMPLE 7

Preparation of 4-(2-Bromo-4-fluorophenyl)-*N*-(2-chloro-6-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine (Compound 240)

Step A: Preparation of 1-(2-Bromo-4-fluorophenyl)-2-propanone

A solution of sodium methoxide in methanol (25%, 34 mL, 157 mmol) was combined with toluene (200 mL). The methanol was then distilled off at 90 °C using a Dean-Stark trap. After the solution was cooled to 70 °C, 2-bromo-4-fluorobenzeneacetonitrile (21.4 g, 100 mmol) dissolved in ethyl acetate (40 mL) was added from a dropping funnel over 20 min with mechanical stirring. At this point additional toluene (150 mL) was added to facilitate stirring of a voluminous light pink precipitate. The reaction mixture was poured into water, and the organic phase was separated. The aqueous phase was acidified and extracted with ethyl acetate. The ethyl acetate phase was dried and concentrated under reduced pressure to provide the intermediate compound α-acetyl-2-bromo-4-fluorobenzeneacetonitrile as a crude oil.

The crude oil was dissolved in sulfuric acid (60%, 170 mL) and refluxed for 6.5 h. The reaction mixture was then extracted with hexanes (2 × 100 mL), and the combined hexane extracts were washed with water and brine, dried ($MgSO_4$) and concentrated under reduced pressure to yield the title compound as a yellow oil (14.7 g), which was used without further purification in Step C.

^{1}H NMR δ 7.33 (m, 1H), 7.18 (m, 1H), 7.01 (m, 1H), 3.85 (s, 2H), 2.23 (s, 3H).

Step B: Preparation of 1-Chloro-3-fluoro-2-isothiocyanatobenzene

To a solution of 2-chloro-6-fluorobenzenamine (5.0 g, 34 mmol) in chlorobenzene (52 mL) was added carbonothioic dichloride (thiophosgene) (5.1 g, 45 mmol) and DMF (0.27 mL). The reaction mixture was refluxed for 2 h and then concentrated to leave the title compound as a brown oil (6.15 g), which was used in Step C without further purification.

^{1}H NMR δ 7.18 (m, 2H), 7.07 (m, 1H).

Step C: Preparation of 4-(2-Bromo-4-fluorophenyl)-*N*-(2-chloro-6-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine

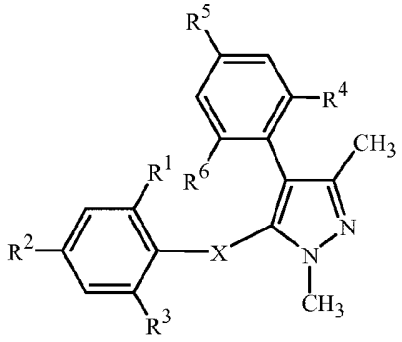
To a solution of potassium *tert*-butoxide (0.41 g, 3.3 mmol) in THF (20 mL) at 0 °C was added a solution of 1-(2-bromo-4-fluorophenyl)-2-propanone (i.e. the product of Step

A) (0.70 g, 3.0 mmol) in THF (10 mL) over 5 minutes. Stirring was continued for 1 h and then the temperature was reduced to −10 °C. A solution of 1-chloro-3-fluoro-2-isothiocyanatobenzene (i.e. the product of Step B) (0.57 g, 3.0 mmol) in THF (10 mL) was added over 6 minutes, and stirring was continued for 15 minutes. Iodomethane (0.54 g, 3.8 mmol) was added, and the cooling bath was removed to provide a reaction mixture containing the intermediate compound α-acetyl-2-bromo-*N*-(2-chloro-6-fluorophenyl)-4-fluorobenzeneethanethioamide. After 5 min, water (0.2 mL, 11 mmol), glacial acetic acid (0.53 mL, 9.1 mmol) and methylhydrazine (0.81 mL, 15 mmol) were added in rapid succession, and the reaction mixture was heated to reflux for 6 h. The crude reaction mixture was then concentrated under reduced pressure and purified by MPLC (0 to 100% ethyl acetate in hexanes as eluent) to provide the title product, a compound of the present invention, as an off-white solid (0.55 g).

^{1}H NMR δ 7.24 (m, 1H), 7.04 (m, 1H), 6.95 (m, 1H), 6.87 (m, 1H), 6.78 (m, 1H), 6.68 (m, 1H), 5.45 (d, 1H), 3.80 (s, 3H), 2.10 (s, 3H).

By the procedures described herein together with methods known in the art, the compounds disclosed in the Tables that follow can be prepared. The following abbreviations are used in the Tables which follow: Me means methyl, MeO means methoxy, EtO means ethoxy, and CN means cyano. Because of symmetry, R^1 can be interchanged with R^3, and R^4 can be interchanged with R^6, if allowed by the definitions of R^1, R^3, R^4 and R^6.

TABLE 1



R^4 is F, R^5 is H, R^6 is H, and X is NH.

R^1	R^2	R^3	R^1	R^2	R^3
F	H	H	F	H	F
F	F	H	F	F	F
F	CN	F	F	MeO	F
F	EtO	F	F	Cl	H
F	Cl	Cl	F	H	Cl
F	Br	H	F	H	Br
F	Cl	F	F	Br	F

R^1	R^2	R^3	R^1	R^2	R^3
F	I	H	F	F	I
F	I	F	F	CN	H
F	MeO	H	F	EtO	H
Cl	H	H	Cl	H	Cl
Cl	Cl	H	Cl	Cl	Cl
Cl	CN	Cl	Cl	MeO	Cl
Cl	EtO	Cl	Cl	F	H
Cl	F	F	Cl	F	Cl
Cl	Br	H	Cl	H	Br
Cl	Br	Br	Cl	Br	Cl
Cl	I	H	Cl	CN	H
Cl	MeO	H	Cl	EtO	H
Br	H	H	Br	F	H
Br	Cl	H	Br	Br	H
Br	F	F	Br	Br	F
Br	Cl	F	Br	F	Cl
Br	Cl	Cl	Br	F	Br
Br	CN	Br	Br	MeO	Br
Br	EtO	Br	Br	CN	H
Br	MeO	H	Br	EtO	H
Br	I	H	I	H	H
I	F	H	I	F	F
I	Cl	F	I	Cl	Cl
Br	H	Cl	Br	H	Br
I	H	F	I	H	Cl
Me	H	H	Me	H	F
Me	F	H	Me	F	F
Me	CN	F	Me	MeO	F
Me	EtO	F	Me	Cl	H
Me	Cl	Cl	Me	H	Cl
Me	Br	H	Me	H	Br
Me	Cl	F	Me	Br	F
Me	I	H	Me	F	I
Me	I	F	Me	CN	H
Me	MeO	H	Me	EtO	H
Me	H	Me	Me	Cl	Me

The present disclosure also includes Tables 2 through 180, each of which is constructed the same as Table 1 above, except that the row heading in Table 1 (i.e. "R^4 is F, R^5 is H, R^6 is H, and X is NH.") is replaced with the respective row heading shown below. For Example, in Table 2 the row heading is "R^4 is F, R^5 is H, R^6 is F, and X is NH.", and R^4, R^5, and R^6 are as defined in Table 1 above. Thus, the first entry in Table 2 specifically discloses 4-(2,6-difluorophenyl)-*N*-(2-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine).

Table	Row Heading	Table	Row Heading
2	R^4 is F, R^5 is H, R^6 is F, and X is NH.	92	R^4 is Cl, R^5 is F, R^6 is H, and X is O.
3	R^4 is F, R^5 is H, R^6 is Cl, and X is NH.	93	R^4 is Cl, R^5 is F, R^6 is Cl, and X is O.
4	R^4 is F, R^5 is H, R^6 is Br, and X is NH.	94	R^4 is Cl, R^5 is I, R^6 is H, and X is O.
5	R^4 is F, R^5 is Br, R^6 is H, and X is NH.	95	R^4 is Cl, R^5 is EtO, R^6 is Cl, and X is O.
6	R^4 is F, R^5 is Br, R^6 is F, and X is NH.	96	R^4 is Cl, R^5 is EtO, R^6 is H, and X is O.
7	R^4 is F, R^5 is Cl, R^6 is Cl, and X is NH.	97	R^4 is Cl, R^5 is MeO, R^6 is Cl, and X is O.
8	R^4 is F, R^5 is Cl, R^6 is F, and X is NH.	98	R^4 is Cl, R^5 is MeO, R^6 is H, and X is O.
9	R^4 is F, R^5 is Cl, R^6 is H, and X is NH.	99	R^4 is Br, R^5 is H, R^6 is H, and X is O.
10	R^4 is F, R^5 is -CN, R^6 is F, and X is NH.	100	R^4 is Br, R^5 is Br, R^6 is H, and X is O.
11	R^4 is F, R^5 is -CN, R^6 is H, and X is NH.	101	R^4 is Br, R^5 is Br, R^6 is F, and X is O.
12	R^4 is F, R^5 is F, R^6 is H, and X is NH.	102	R^4 is Br, R^5 is Cl, R^6 is H, and X is O.
13	R^4 is F, R^5 is F, R^6 is F, and X is NH.	103	R^4 is Br, R^5 is Cl, R^6 is F, and X is O.
14	R^4 is F, R^5 is F, R^6 is I, and X is NH.	104	R^4 is Br, R^5 is Cl, R^6 is Cl, and X is O.
15	R^4 is F, R^5 is I, R^6 is H, and X is NH.	105	R^4 is Br, R^5 is CN, R^6 is Br, and X is O.
16	R^4 is F, R^5 is I, R^6 is F, and X is NH.	106	R^4 is Br, R^5 is CN, R^6 is H, and X is O.
17	R^4 is F, R^5 is EtO, R^6 is F, and X is NH.	107	R^4 is Br, R^5 is F, R^6 is F, and X is O.
18	R^4 is F, R^5 is EtO, R^6 is H, and X is NH.	108	R^4 is Br, R^5 is F, R^6 is H, and X is O.
19	R^4 is F, R^5 is MeO, R^6 is F, and X is NH.	109	R^4 is Br, R^5 is F, R^6 is Cl, and X is O.
20	R^4 is F, R^5 is MeO, R^6 is H, and X is NH.	110	R^4 is Br, R^5 is F, R^6 is Br, and X is O.
21	R^4 is Cl, R^5 is H, R^6 is H, and X is NH.	111	R^4 is Br, R^5 is I, R^6 is H, and X is O.
22	R^4 is Cl, R^5 is H, R^6 is Cl, and X is NH.	112	R^4 is Br, R^5 is EtO, R^6 is Br, and X is O.
23	R^4 is Cl, R^5 is H, R^6 is Br, and X is NH.	113	R^4 is Br, R^5 is EtO, R^6 is H, and X is O.
24	R^4 is Cl, R^5 is Br, R^6 is H, and X is NH.	114	R^4 is Br, R^5 is MeO, R^6 is Br, and X is O.
25	R^4 is Cl, R^5 is Br, R^6 is Br, and X is NH.	115	R^4 is Br, R^5 is MeO, R^6 is H, and X is O.
26	R^4 is Cl, R^5 is Br, R^6 is Cl, and X is NH.	116	R^4 is I, R^5 is H, R^6 is H, and X is O.
27	R^4 is Cl, R^5 is Cl, R^6 is H, and X is NH.	117	R^4 is I, R^5 is Cl, R^6 is F, and X is O.
28	R^4 is Cl, R^5 is Cl, R^6 is Cl, and X is NH.	118	R^4 is I, R^5 is Cl, R^6 is Cl, and X is O.
29	R^4 is Cl, R^5 is -CN, R^6 is Cl, and X is NH.	119	R^4 is I, R^5 is F, R^6 is H, and X is O.
30	R^4 is Cl, R^5 is -CN, R^6 is H, and X is NH.	120	R^4 is I, R^5 is F, R^6 is F, and X is O.
31	R^4 is Cl, R^5 is F, R^6 is F, and X is NH.	121	R^4 is F, R^5 is H, R^6 is H, and X is CHOH.
32	R^4 is Cl, R^5 is F, R^6 is H, and X is NH.	122	R^4 is F, R^5 is H, R^6 is F, and X is CHOH.

Table	Row Heading
33	R^4 is Cl, R^5 is F, R^6 is Cl, and X is NH.
34	R^4 is Cl, R^5 is I, R^6 is H, and X is NH.
35	R^4 is Cl, R^5 is EtO, R^6 is Cl, and X is NH.
36	R^4 is Cl, R^5 is EtO, R^6 is H, and X is NH.
37	R^4 is Cl, R^5 is MeO, R^6 is Cl, and X is NH.
38	R^4 is Cl, R^5 is MeO, R^6 is H, and X is NH.
39	R^4 is Br, R^5 is H, R^6 is H, and X is NH.
40	R^4 is Br, R^5 is Br, R^6 is H, and X is NH.
41	R^4 is Br, R^5 is Br, R^6 is F, and X is NH.
42	R^4 is Br, R^5 is Cl, R^6 is H, and X is NH.
43	R^4 is Br, R^5 is Cl, R^6 is F, and X is NH.
44	R^4 is Br, R^5 is Cl, R^6 is Cl, and X is NH.
45	R^4 is Br, R^5 is -CN, R^6 is Br, and X is NH.
46	R^4 is Br, R^5 is -CN, R^6 is H, and X is NH.
47	R^4 is Br, R^5 is F, R^6 is F, and X is NH.
48	R^4 is Br, R^5 is F, R^6 is H, and X is NH.
49	R^4 is Br, R^5 is F, R^6 is Cl, and X is NH.
50	R^4 is Br, R^5 is F, R^6 is Br, and X is NH.
51	R^4 is Br, R^5 is I, R^6 is H, and X is NH.
52	R^4 is Br, R^5 is EtO, R^6 is Br, and X is NH.
53	R^4 is Br, R^5 is EtO, R^6 is H, and X is NH.
54	R^4 is Br, R^5 is MeO, R^6 is Br, and X is NH.
55	R^4 is Br, R^5 is MeO, R^6 is H, and X is NH.
56	R^4 is I, R^5 is H, R^6 is H, and X is NH.
57	R^4 is I, R^5 is Cl, R^6 is F, and X is NH.
58	R^4 is I, R^5 is Cl, R^6 is Cl, and X is NH.
59	R^4 is I, R^5 is F, R^6 is H, and X is NH.
60	R^4 is I, R^5 is F, R^6 is F, and X is NH.
61	R^4 is F, R^5 is H, R^6 is H, and X is O.
62	R^4 is F, R^5 is H, R^6 is F, and X is O.
63	R^4 is F, R^5 is H, R^6 is Cl, and X is O.
64	R^4 is F, R^5 is H, R^6 is Br, and X is O.
123	R^4 is F, R^5 is H, R^6 is Cl, and X is CHOH.
124	R^4 is F, R^5 is H, R^6 is Br, and X is CHOH.
125	R^4 is F, R^5 is Br, R^6 is H, and X is CHOH.
126	R^4 is F, R^5 is Br, R^6 is F, and X is CHOH.
127	R^4 is F, R^5 is Cl, R^6 is Cl, and X is CHOH.
128	R^4 is F, R^5 is Cl, R^6 is F, and X is CHOH.
129	R^4 is F, R^5 is Cl, R^6 is H, and X is CHOH.
130	R^4 is F, R^5 is CN, R^6 is F, and X is CHOH.
131	R^4 is F, R^5 is CN, R^6 is H, and X is CHOH.
132	R^4 is F, R^5 is F, R^6 is H, and X is CHOH.
133	R^4 is F, R^5 is F, R^6 is F, and X is CHOH.
134	R^4 is F, R^5 is F, R^6 is I, and X is CHOH.
135	R^4 is F, R^5 is I, R^6 is H, and X is CHOH.
136	R^4 is F, R^5 is I, R^6 is F, and X is CHOH.
137	R^4 is F, R^5 is EtO, R^6 is F, and X is CHOH.
138	R^4 is F, R^5 is EtO, R^6 is H, and X is CHOH.
139	R^4 is F, R^5 is MeO, R^6 is F, and X is CHOH.
140	R^4 is F, R^5 is MeO, R^6 is H, and X is CHOH.
141	R^4 is Cl, R^5 is H, R^6 is H, and X is CHOH.
142	R^4 is Cl, R^5 is H, R^6 is Cl, and X is CHOH.
143	R^4 is Cl, R^5 is H, R^6 is Br, and X is CHOH.
144	R^4 is Cl, R^5 is Br, R^6 is H, and X is CHOH.
145	R^4 is Cl, R^5 is Br, R^6 is Br, and X is CHOH.
146	R^4 is Cl, R^5 is Br, R^6 is Cl, and X is CHOH.
147	R^4 is Cl, R^5 is Cl, R^6 is H, and X is CHOH.
148	R^4 is Cl, R^5 is Cl, R^6 is Cl, and X is CHOH.
149	R^4 is Cl, R^5 is CN, R^6 is Cl, and X is CHOH.
150	R^4 is Cl, R^5 is CN, R^6 is H, and X is CHOH.
151	R^4 is Cl, R^5 is F, R^6 is F, and X is CHOH.
152	R^4 is Cl, R^5 is F, R^6 is H, and X is CHOH.
153	R^4 is Cl, R^5 is F, R^6 is Cl, and X is CHOH.
154	R^4 is Cl, R^5 is I, R^6 is H, and X is CHOH.

Table	Row Heading
65	R^4 is F, R^5 is Br, R^6 is H, and X is O.
66	R^4 is F, R^5 is Br, R^6 is F, and X is O.
67	R^4 is F, R^5 is Cl, R^6 is Cl, and X is O.
68	R^4 is F, R^5 is Cl, R^6 is F, and X is O.
69	R^4 is F, R^5 is Cl, R^6 is H, and X is O.
70	R^4 is F, R^5 is CN, R^6 is F, and X is O.
71	R^4 is F, R^5 is CN, R^6 is H, and X is O.
72	R^4 is F, R^5 is F, R^6 is H, and X is O.
73	R^4 is F, R^5 is F, R^6 is F, and X is O.
74	R^4 is F, R^5 is F, R^6 is I, and X is O.
75	R^4 is F, R^5 is I, R^6 is H, and X is O.
76	R^4 is F, R^5 is I, R^6 is F, and X is O.
77	R^4 is F, R^5 is EtO, R^6 is F, and X is O.
78	R^4 is F, R^5 is EtO, R^6 is H, and X is O.
79	R^4 is F, R^5 is MeO, R^6 is F, and X is O.
80	R^4 is F, R^5 is MeO, R^6 is H, and X is O.
81	R^4 is Cl, R^5 is H, R^6 is H, and X is O.
82	R^4 is Cl, R^5 is H, R^6 is Cl, and X is O.
83	R^4 is Cl, R^5 is H, R^6 is Br, and X is O.
84	R^4 is Cl, R^5 is Br, R^6 is H, and X is O.
85	R^4 is Cl, R^5 is Br, R^6 is Br, and X is O.
86	R^4 is Cl, R^5 is Br, R^6 is Cl, and X is O.
87	R^4 is Cl, R^5 is Cl, R^6 is H, and X is O.
88	R^4 is Cl, R^5 is Cl, R^6 is Cl, and X is O.
89	R^4 is Cl, R^5 is CN, R^6 is Cl, and X is O.
90	R^4 is Cl, R^5 is CN, R^6 is H, and X is O.
91	R^4 is Cl, R^5 is F, R^6 is F, and X is O.
155	R^4 is Cl, R^5 is EtO, R^6 is Cl, and X is CHOH.
156	R^4 is Cl, R^5 is EtO, R^6 is H, and X is CHOH.
157	R^4 is Cl, R^5 is MeO, R^6 is Cl, and X is CHOH.
158	R^4 is Cl, R^5 is MeO, R^6 is H, and X is CHOH.
159	R^4 is Br, R^5 is H, R^6 is H, and X is CHOH.
160	R^4 is Br, R^5 is Br, R^6 is H, and X is CHOH.
161	R^4 is Br, R^5 is Br, R^6 is F, and X is CHOH.
162	R^4 is Br, R^5 is Cl, R^6 is H, and X is CHOH.
163	R^4 is Br, R^5 is Cl, R^6 is F, and X is CHOH.
164	R^4 is Br, R^5 is Cl, R^6 is Cl, and X is CHOH.
165	R^4 is Br, R^5 is CN, R^6 is Br, and X is CHOH.
166	R^4 is Br, R^5 is CN, R^6 is H, and X is CHOH.
167	R^4 is Br, R^5 is F, R^6 is F, and X is CHOH.
168	R^4 is Br, R^5 is F, R^6 is H, and X is CHOH.
169	R^4 is Br, R^5 is F, R^6 is Cl, and X is CHOH.
170	R^4 is Br, R^5 is F, R^6 is Br, and X is CHOH.
171	R^4 is Br, R^5 is I, R^6 is H, and X is CHOH.
172	R^4 is Br, R^5 is EtO, R^6 is Br, and X is CHOH.
173	R^4 is Br, R^5 is EtO, R^6 is H, and X is CHOH.
174	R^4 is Br, R^5 is MeO, R^6 is Br, and X is CHOH.
175	R^4 is Br, R^5 is MeO, R^6 is H, and X is CHOH.
176	R^4 is I, R^5 is H, R^6 is H, and X is CHOH.
177	R^4 is I, R^5 is Cl, R^6 is F, and X is CHOH.
178	R^4 is I, R^5 is Cl, R^6 is Cl, and X is CHOH.
179	R^4 is I, R^5 is F, R^6 is H, and X is CHOH.
180	R^4 is I, R^5 is F, R^6 is F, and X is CHOH.

Formulation/Utility

A compound selected from compounds of Formula **1**, *N*-oxides, and salts thereof, or a mixture (i.e. composition) comprising the compound with at least one additional fungicidal compound as described in the Summary of the Invention, will generally be used to provide fungicidal active ingredients in further compositions, i.e. formulations, with at least one additional component selected from the group consisting of surfactants, solid diluents and

liquid diluents, which serves as a carrier. The formulation or composition ingredients are selected to be consistent with the physical properties of the active ingredients, mode of application and environmental factors such as soil type, moisture and temperature.

The mixtures of component (a) (i.e. at least one compound of Formula **1**, *N*-oxides, or salts thereof) with component (b) (e.g., selected from (b1) to (b46) and salts thereof as described above) and/or one or more other biologically active compound or agent (i.e. insecticides, other fungicides, nematocides, acaricides, herbicides and other biological agents) can be formulated in a number of ways, including:

(i) component (a), component (b) and/or one or more other biologically active compounds or agents can be formulated separately and applied separately or applied simultaneously in an appropriate weight ratio, e.g., as a tank mix; or

(ii) component (a), component (b) and/or one or more other biologically active compounds or agents can be formulated together in the proper weight ratio.

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, prills, pastilles, tablets, filled films (including seed coatings) and the like, which can be water-dispersible ("wettable") 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.

Of note is a composition embodiment wherein granules of a solid composition comprising a compound of Formula **1** (or an *N*-oxide or salt thereof) is mixed with granules of a solid composition comprising component (b). These mixtures can be further mixed with granules comprising additional agricultural protectants. Alternatively, two or more agricultural protectants (e.g., a component (a) (Formula 1) compound, a component (b) compound, an agricultural protectant other than component (a) or (b)) can be combined in the solid composition of one set of granules, which is then mixed with one or more sets of granules of solid compositions comprising one or more additional agricultural protectants.

These granule mixtures can be in accordance with the general granule mixture disclosure of PCT Patent Publication WO 94/24861 or more preferably the homogeneous granule mixture teaching of U.S. Patent 6,022,552.

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. Spray volumes can range from about 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		
	Active Ingredient	Diluent	Surfactant
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	0.001–99	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), 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, triacetin, 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 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 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.

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.

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 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 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 derivatives such as sorbitan esters; polymeric surfactants such as random copolymers, block copolymers, alkyd 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 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 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 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 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 *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, known to those skilled in the art as formulation aids (some of which may be considered to

also function as solid diluents, liquid diluents or surfactants). Such formulation auxiliaries and additives may control: pH (buffers), foaming during processing (antifoams such polyorganosiloxanes), sedimentation of active ingredients (suspending agents), viscosity (thixotropic thickeners), in-container microbial growth (antimicrobials), product freezing (antifreezes), color (dyes/pigment dispersions), wash-off (film 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 editions published by McCutcheon's Division, The Manufacturing Confectioner Publishing Co.; and PCT Publication WO 03/024222.

The compounds 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 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 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, New York, 1963, pages 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.

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 Table A. 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. Percentages are by weight except where otherwise indicated.

Example A

High Strength Concentrate

Compound 47	49.3%
penthiopyrad	49.2%
silica aerogel	0.5%
synthetic amorphous fine silica	1.0%

Example B

Wettable Powder

Compound 81	43.0%
quinoxyfen	22.0%
dodecylphenol polyethylene glycol ether	2.0%
sodium ligninsulfonate	4.0%
sodium silicoaluminate	6.0%
montmorillonite (calcined)	23.0%

Example C

Granule

Compound 136	7.5%
epoxiconazole	2.5%
attapulgite granules (low volatile matter, 0.71/0.30 mm; U.S.S. No. 25–50 sieves)	90.0%

Example D

Extruded Pellet

Compound 144	8.0%
spiroxamine	17.0%
anhydrous sodium sulfate	10.0%
crude calcium ligninsulfonate	5.0%
sodium alkylnaphthalenesulfonate	1.0%
calcium/magnesium bentonite	59.0%

Example E

Emulsifiable Concentrate

Compound 161	5.0%
azoxystrobin	5.0%
polyoxyethylene sorbitol hexoleate	20.0%
C_6–C_{10} fatty acid methyl ester	70.0%

Example F

Microemulsion

Compound 195	3.3%
picoxystrobin	1.7%
polyvinylpyrrolidone-vinyl acetate copolymer	30.0%
alkylpolyglycoside	30.0%
glyceryl monooleate	15.0%
water	20.0%

Example G

Seed Treatment

Compound 238	4.00%
iprodione	16.00%
polyvinylpyrrolidone-vinyl acetate copolymer	5.00%
montan acid wax	5.00%
calcium ligninsulfonate	1.00%
polyoxyethylene/polyoxypropylene block copolymers	1.00%
stearyl alcohol (POE 20)	2.00%
polyorganosilane	0.20%
colorant red dye	0.05%
water	65.75%

Example H

Emulsifiable Concentrate

Compound 239	10.0%
polyoxyethylene sorbitol hexoleate	20.0%
C_6–C_{10} fatty acid methyl ester	70.0%

Formulations such as those in the Formulation Table 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 comprise at least about 1 ppm or more (e.g., from 1 ppm to 100 ppm) of fungicidally active compounds according to the present invention.

Examples of component (b) fungicidal compounds include acibenzolar-*S*-methyl, aldimorph, ametoctradin, amisulbrom, anilazine, azaconazole, azoxystrobin, benalaxyl, benalaxyl-M, benodanil, benomyl, benthiavalicarb, benthiavalicarb-isopropyl, bethoxazin, binapacryl, biphenyl, bitertanol, bixafen, blasticidin-S, boscalid, bromuconazole, bupirimate, buthiobate, carboxin, carpropamid, captafol, captan, carbendazim, chloroneb, chlorothalonil, chlozolinate, clotrimazole, copper salts such as Bordeaux mixture (tribasic copper sulfate), copper hydroxide and copper oxychloride, cyazofamid, cyflufenamid, cymoxanil, cyproconazole, cyprodinil, dichlofluanid, diclocymet, diclomezine, dicloran, diethofencarb, difenoconazole, diflumetorim, dimethirimol, dimethomorph, dimoxystrobin, diniconazole, diniconazole-M, dinocap, dithianon, dodemorph, dodine, edifenphos, enestroburin, epoxiconazole, etaconazole, ethaboxam, ethirimol, etridiazole, famoxadone, fenamidone, fenarimol, fenbuconazole, fenfuram, fenhexamid, fenoxanil, fenpiclonil, fenpropidin, fenpropimorph, fenpyrazamine, fentin acetate, fentin chloride, fentin hydroxide, ferbam, ferimzone, fluazinam, fludioxonil, flumetover, flumorph, fluopicolide (also known as picobenzamid), fluopyram, fluoroimide, fluoxastrobin, fluquinconazole, flusilazole, flusulfamide, flutianil (2-[[2-fluoro-5-(trifluoromethyl)phenyl]thio]-2-[3-(2-methoxy-phenyl)-2-thiazolidinylidene]acetonitrile), flutolanil, flutriafol, fluxapyroxad, folpet, fosetyl-aluminum, fuberidazole, furalaxyl, furametpyr, hexaconazole, hymexazol, guazatine, imazalil, imibenconazole, iminoctadine, iodocarb, ipconazole, iprobenfos, iprodione, iprovalicarb, isoprothiolane, isopyrazam, isotianil, kasugamycin, kresoxim-methyl, mancozeb, mandipropamid, maneb, mepronil, meptyldinocap, metalaxyl, metalaxyl-M, metconazole, methasulfocarb, metiram, metominostrobin, mepanipyrim, metrafenone, myclobutanil, naftifine, neo-asozin (ferric methanearsonate), nuarimol, octhilinone, ofurace, orysastrobin, oxadixyl, oxolinic acid, oxpoconazole, oxycarboxin, oxytetracycline, penconazole, pencycuron, penflufen, penthiopyrad, pefurazoate, phosphorous acid and salts thereof, phthalide, picoxystrobin, piperalin, polyoxin, probenazole, prochloraz, procymidone, propamocarb, propamocarb-hydrochloride, propiconazole, propineb, proquinazid, prothioconazole, pyraclostrobin, pyrametostrobin, pyraoxystrobin, pyrazophos,

pyribencarb, pyributicarb, pyrifenox, pyrimethanil, pyriofenone, pyroquilon, pyrrolnitrin, quinconazole, quinomethionate, quinoxyfen, quintozene, sedaxane, silthiofam, simeconazole, spiroxamine, streptomycin, sulfur, tebuconazole, tebufloquin, tecloftalam, tecnazene, terbinafine, tetraconazole, thiabendazole, thifluzamide, thiophanate, thiophanate-methyl, thiram, tiadinil, tolclofos-methyl, tolylfluanid, triadimefon, triadimenol, triarimol, triazoxide, tricyclazole, tridemorph, triflumizole, tricyclazole, trifloxystrobin, triforine, trimorphamide, triticonazole, uniconazole, validamycin, valifenalate (valiphenal), vinclozolin, zineb, ziram, zoxamide, *N*'-[4-[4-chloro-3-(trifluoromethyl)phenoxy]-2,5-dimethylphenyl]-*N*-ethyl-*N*-methylmethanimidamide, 5-chloro-6-(2,4,6-trifluorophenyl)-7-(4-methylpiperidin-1-yl)[1,2,4]triazolo[1,5-*a*]pyrimidine (BAS600), *N*-[2-[4-[[3-(4-chlorophenyl)-2-propyn-1-yl]oxy]-3-methoxyphenyl]ethyl]-3-methyl-2-[(methylsulfonyl)-amino]butanamide, *N*-[2-[4-[[3-(4-chlorophenyl)-2-propyn-1-yl]oxy]-3-methoxyphenyl]-ethyl]-3-methyl-2-[(ethylsulfonyl)amino]butanamide, 2-butoxy-6-iodo-3-propyl-4*H*-1-benzopyran-4-one, 3-[5-(4-chlorophenyl)-2,3-dimethyl-3-isoxazolidinyl]pyridine, 4-fluorophenyl *N*-[1-[[[1-(4-cyanophenyl)ethyl]sulfonyl]methyl]propyl]carbamate, *N*-[[(cyclopropylmethoxy)amino][6-(difluoromethoxy)-2,3-difluorophenyl]methylene]-benzeneacetamide, α-(methoxyimino)-*N*-methyl-2-[[[1-[3-(trifluoromethyl)phenyl]ethoxy]-imino]methyl]benzeneacetamide, *N*'-[4-[4-chloro-3-(trifluoromethyl)phenoxy]-2,5-dimethyl-phenyl]-*N*-ethyl-*N*-methylmethanimidamide, *N*-(4-chloro-2-nitrophenyl)-*N*-ethyl-4-methyl-benzenesulfonamide, 2-[[[[3-(2,6-dichlorophenyl)-1-methyl-2-propen-1-ylidene]amino]-oxy]methyl]-α-(methoxyimino)-*N*-methylbenzeneacetamide, 1-[(2-propenylthio)carbonyl]-2-(1-methylethyl)-4-(2-methylphenyl)-5-amino-1*H*-pyrazol-3-one, ethyl-6-octyl-[1,2,4]-triazolo[1,5-a]pyrimidin-7-ylamine, pentyl *N*-[4-[[[[(1-methyl-1*H*-tetrazol-5-yl)phenyl-methylene]amino]oxy]methyl]-2-thiazolyl]carbamate, pentyl *N*-[6-[[[[(1-methyl-1*H*-tetrazol-5-yl)phenylmethylene]amino]oxy]methyl]-2-pyridinyl]carbamate, 2-[(3-bromo-6-quinolinyl)oxy]-*N*-(1,1-dimethyl-2-butyn-1-yl)-2-(methylthio)acetamide, 2-[(3-ethynyl-6-quinolinyl)oxy]-*N*-[1-(hydroxymethyl)-1-methyl-2-propyn-1-yl]-2-(methylthio)acetamide, *N*-(1,1-dimethyl-2-butyn-1-yl)-2-[(3-ethynyl-6-quinolinyl)oxy]-2-(methylthio)acetamide and *N*'-[4-[[3-[(4-chlorophenyl)methyl]-1,2,4-thiadiazol-5-yl]oxy]-2,5-dimethylphenyl]-*N*-ethyl-*N*-methylmethanimidamide. Of note is the preceding list also excluding *N*'-[4-[[3-[(4-chlorophenyl)methyl]-1,2,4-thiadiazol-5-yl]oxy]-2,5-dimethylphenyl]-*N*-ethyl-*N*-methylmethanimidamide. Of further note is the preceding list also excluding buthiobate, etaconazole, quinconazole, triarimol, 2-[(3-bromo-6-quinolinyl)oxy]-*N*-(1,1-dimethyl-2-butyn-1-yl)-2-(methylthio)acetamide, 2-[(3-ethynyl-6-quinolinyl)oxy]-*N*-[1-(hydroxy-methyl)-1-methyl-2-propyn-1-yl]-2-(methylthio)acetamide and *N*-(1,1-dimethyl-2-butyn-1-yl)-2-[(3-ethynyl-6-quinolinyl)oxy]-2-(methylthio)acetamide.

Of note as fungicidal compounds in component (b) of the present composition are azoxystrobin, kresoxim-methyl, trifloxystrobin, pyraclostrobin, pyrametostrobin,

pyraoxystrobin, picoxystrobin, dimoxystrobin, metominostrobin/fenominostrobin, carbendazim, chlorothalonil, quinoxyfen, metrafenone, pyriofenone, cyflufenamid, fenpropidin, fenpropimorph, bromuconazole, cyproconazole, difenoconazole, epoxiconazole, etaconazole, fenbuconazole, flusilazole, fluxapyroxad, hexaconazole, ipconazole, metconazole, myclobutanil, penconazole, propiconazole, proquinazid, prothioconazole, tebuconazole, triticonazole, famoxadone, prochloraz, penthiopyrad and boscalid (nicobifen).

Generally preferred for better control of plant diseases caused by fungal plant pathogens (e.g., lower use rate or broader spectrum of plant pathogens controlled) or resistance management are mixtures of a compound of Formula **1**, an *N*-oxide, or salt thereof, with a fungicidal compound selected from the group: azoxystrobin, kresoxim-methyl, trifloxystrobin, pyraclostrobin, pyrametostrobin, pyraoxystrobin, picoxystrobin, dimoxystrobin, metominostrobin/fenominostrobin, quinoxyfen, metrafenone, cyflufenamid, fenpropidin, fenpropimorph, cyproconazole, difenoconazole, epoxiconazole, etaconazole, flusilazole, metconazole, myclobutanil, propiconazole, proquinazid, prothioconazole, pyriofenone, tebuconazole, triticonazole, famoxadone and penthiopyrad.

In the fungicidal compositions of the present invention, component (a) (i.e. at least one compound selected from compounds of Formula **1**, *N*-oxides, and salts thereof) and component (b) are present in fungicidally effective amounts. The weight ratio of component (b) (i.e. one or more additional fungicidal compounds) to component (a) is generally between about 1:3000 to about 3000:1, and more typically between about 1:500 and about 500:1. Table B1 lists typical, more typical and most typical ranges of ratios involving particular fungicidal compounds of component (b). Tables A1 through A43 and C1 through C43 exemplify weight ratios for particular combinations of fungicidal compounds. Of note are compositions where in the weight ratio of component (a) to component (b) is from about 125:1 to about 1:125. With many fungicidal compounds of component (b), these compositions are particularly effective for controlling plant diseases caused by fungal plant pathogens. Of particular note are compositions wherein the weight ratio of component (a) to component (b) is from about 25:1 to about 1:25, or from about 5:1 to about 1:5. One skilled in the art can easily determine through simple experimentation the weight ratios and application rates of fungicidal compounds necessary for the desired spectrum of fungicidal protection and control. It will be evident that including additional fungicidal compounds in component (b) may expand the spectrum of plant diseases controlled beyond the spectrum controlled by component (a) alone.

Specific mixtures (compound numbers refer to compounds in Index Table A) are listed in Tables A1 through A43. In Table A1, each line below the column headings "Component (a)" and "Component (b)" specifically discloses a mixture of Component (a), which is Compound 3, with a Component (b) fungicidal compound. The entries under the heading "Illustrative Ratios" disclose three specific weight ratios of Component (b) to Component (a)

for the disclosed mixture. For example, the first line of Table A1 discloses a mixture of Compound 3 with acibenzolar-*S*-methyl and lists weight ratios of acibenzolar-*S*-methyl to Compound 3 of 1:1, 1:4 or 1:18.

Table A1

Component (a)	Component (b)	Illustrative Ratios(*)		
Compound 3	acibenzolar-*S*-methyl	1:1	1:4	1:18
Compound 3	aldimorph	7:1	3:1	1:1
Compound 3	ametoctradin	3:1	1:1	1:3
Compound 3	amisulbrom	1:1	1:2	1:6
Compound 3	anilazine	22:1	8:1	4:1
Compound 3	azaconazole	2:1	1:2	1:4
Compound 3	azoxystrobin	3:1	1:1	1:3
Compound 3	benalaxyl	1:1	1:2	1:6
Compound 3	benalaxyl-M	1:1	1:3	1:8
Compound 3	benodanil	4:1	2:1	1:2
Compound 3	benomyl	11:1	4:1	1:1
Compound 3	benthiavalicarb	1:1	1:4	1:12
Compound 3	benthiavalicarb-isopropyl	1:1	1:4	1:12
Compound 3	bethoxazin	15:1	5:1	2:1
Compound 3	binapacryl	15:1	5:1	2:1
Compound 3	biphenyl	15:1	5:1	2:1
Compound 3	bitertanol	3:1	1:1	1:2
Compound 3	bixafen	2:1	1:1	1:3
Compound 3	blasticidin-S	1:4	1:12	1:30
Compound 3	Bordeaux mixture (tribasic copper sulfate)	45:1	15:1	5:1
Compound 3	boscalid	4:1	2:1	1:2
Compound 3	bromuconazole	3:1	1:1	1:3
Compound 3	bupirimate	1:3	1:10	1:30
Compound 3	captafol	15:1	5:1	2:1
Compound 3	captan	15:1	5:1	2:1
Compound 3	carbendazim	11:1	4:1	2:1
Compound 3	carboxin	4:1	2:1	1:2
Compound 3	carpropamid	3:1	1:1	1:3
Compound 3	chloroneb	100:1	35:1	14:1
Compound 3	chlorothalonil	15:1	5:1	2:1
Compound 3	chlozolinate	11:1	4:1	2:1
Compound 3	clotrimazole	3:1	1:1	1:3
Compound 3	copper hydroxide	45:1	15:1	5:1

Component (a)	Component (b)	Illustrative Ratios(*)		
Compound 3	copper oxychloride	45:1	15:1	5:1
Compound 3	cyazofamid	1:1	1:2	1:6
Compound 3	cyflufenamid	1:2	1:6	1:24
Compound 3	cymoxanil	1:1	1:2	1:5
Compound 3	cyproconazole	1:1	1:2	1:6
Compound 3	cyprodinil	4:1	2:1	1:2
Compound 3	dichlofluanid	15:1	5:1	2:1
Compound 3	diclocymet	15:1	5:1	2:1
Compound 3	diclomezine	3:1	1:1	1:3
Compound 3	dicloran	15:1	5:1	2:1
Compound 3	diethofencarb	7:1	2:1	1:2
Compound 3	difenoconazole	1:1	1:3	1:12
Compound 3	diflumetorim	15:1	5:1	2:1
Compound 3	dimethirimol	1:3	1:8	1:30
Compound 3	dimethomorph	3:1	1:1	1:2
Compound 3	dimoxystrobin	2:1	1:1	1:4
Compound 3	diniconazole	1:1	1:3	1:8
Compound 3	diniconazole-M	1:1	1:3	1:12
Compound 3	dinocap	2:1	1:1	1:3
Compound 3	dithianon	5:1	2:1	1:2
Compound 3	dodemorph	7:1	3:1	1:1
Compound 3	dodine	10:1	4:1	2:1
Compound 3	edifenphos	3:1	1:1	1:3
Compound 3	enestroburin	2:1	1:1	1:4
Compound 3	epoxiconazole	1:1	1:3	1:7
Compound 3	etaconazole	1:1	1:3	1:7
Compound 3	ethaboxam	2:1	1:1	1:3
Compound 3	ethirimol	7:1	3:1	1:1
Compound 3	etridiazole	7:1	2:1	1:2
Compound 3	famoxadone	2:1	1:1	1:4
Compound 3	fenamidone	2:1	1:1	1:4
Compound 3	fenarimol	1:2	1:7	1:24
Compound 3	fenbuconazole	1:1	1:3	1:10
Compound 3	fenfuram	4:1	1:1	1:2
Compound 3	fenhexamid	10:1	4:1	2:1
Compound 3	fenoxanil	15:1	4:1	1:1
Compound 3	fenpiclonil	15:1	5:1	2:1

Component (a)	Component (b)	Illustrative Ratios(*)		
Compound 3	fenpropidin	7:1	2:1	1:1
Compound 3	fenpropimorph	7:1	2:1	1:1
Compound 3	fenpyrazamine	3:1	1:1	1:3
Compound 3	fentin salt such as fentin acetate, fentin chloride or fentin hydroxide	3:1	1:1	1:3
Compound 3	ferbam	30:1	10:1	4:1
Compound 3	ferimzone	7:1	2:1	1:2
Compound 3	fluazinam	3:1	1:1	1:2
Compound 3	fludioxonil	2:1	1:1	1:4
Compound 3	flumetover	3:1	1:1	1:2
Compound 3	flumorph	3:1	1:1	1:3
Compound 3	fluopicolide	1:1	1:2	1:6
Compound 3	fluopyram	3:1	1:1	1:3
Compound 3	fluoroimide	37:1	14:1	5:1
Compound 3	fluoxastrobin	1:1	1:2	1:6
Compound 3	fluquinconazole	1:1	1:2	1:4
Compound 3	flusilazole	3:1	1:1	1:3
Compound 3	flusulfamide	15:1	5:1	2:1
Compound 3	flutianil	1:1	1:2	1:6
Compound 3	flutolanil	4:1	1:1	1:2
Compound 3	flutriafol	1:1	1:2	1:4
Compound 3	fluxapyroxad	2:1	1:1	1:3
Compound 3	folpet	15:1	5:1	2:1
Compound 3	fosetyl-aluminum	30:1	12:1	5:1
Compound 3	fuberidazole	11:1	4:1	2:1
Compound 3	furalaxyl	1:1	1:2	1:6
Compound 3	furametpyr	15:1	5:1	2:1
Compound 3	guazatine	15:1	5:1	2:1
Compound 3	hexaconazole	1:1	1:2	1:5
Compound 3	hymexazol	75:1	25:1	9:1
Compound 3	imazalil	1:1	1:2	1:5
Compound 3	imibenconazole	1:1	1:2	1:5
Compound 3	iminoctadine	15:1	4:1	1:1
Compound 3	iodocarb	15:1	5:1	2:1
Compound 3	ipconazole	1:1	1:2	1:5
Compound 3	iprobenfos	15:1	5:1	2:1
Compound 3	iprodione	15:1	5:1	2:1

Component (a)	Component (b)	Illustrative Ratios(*)		
Compound 3	iprovalicarb	2:1	1:1	1:3
Compound 3	isoprothiolane	45:1	15:1	5:1
Compound 3	isopyrazam	2:1	1:1	1:3
Compound 3	isotianil	2:1	1:1	1:3
Compound 3	kasugamycin	1:2	1:7	1:24
Compound 3	kresoxim-methyl	2:1	1:1	1:4
Compound 3	mancozeb	22:1	7:1	3:1
Compound 3	mandipropamid	2:1	1:1	1:4
Compound 3	maneb	22:1	7:1	3:1
Compound 3	mepanipyrim	6:1	2:1	1:1
Compound 3	mepronil	1:1	1:2	1:6
Compound 3	meptyldinocap	2:1	1:1	1:3
Compound 3	metalaxyl	1:1	1:2	1:6
Compound 3	metalaxyl-M	1:1	1:4	1:12
Compound 3	metconazole	1:1	1:2	1:6
Compound 3	methasulfocarb	15:1	5:1	2:1
Compound 3	metiram	15:1	5:1	2:1
Compound 3	metominostrobin	3:1	1:1	1:3
Compound 3	metrafenone	2:1	1:1	1:4
Compound 3	myclobutanil	1:1	1:3	1:8
Compound 3	naftifine	15:1	5:1	2:1
Compound 3	neo-asozin (ferric methanearsonate)	15:1	5:1	2:1
Compound 3	nuarimol	3:1	1:1	1:3
Compound 3	octhilinone	15:1	4:1	1:1
Compound 3	ofurace	1:1	1:2	1:6
Compound 3	orysastrobin	3:1	1:1	1:3
Compound 3	oxadixyl	1:1	1:2	1:6
Compound 3	oxolinic acid	7:1	2:1	1:2
Compound 3	oxpoconazole	1:1	1:2	1:5
Compound 3	oxycarboxin	4:1	1:1	1:2
Compound 3	oxytetracycline	3:1	1:1	1:3
Compound 3	pefurazoate	15:1	5:1	2:1
Compound 3	penconazole	1:2	1:6	1:15
Compound 3	pencycuron	11:1	4:1	2:1
Compound 3	penflufen	2:1	1:1	1:3
Compound 3	penthiopyrad	2:1	1:1	1:3
Compound 3	phosphorous acid or a salt thereof	15:1	6:1	2:1

Component (a)	Component (b)	Illustrative Ratios(*)		
Compound 3	phthalide	15:1	6:1	2:1
Compound 3	picoxystrobin	1:1	1:2	1:5
Compound 3	piperalin	3:1	1:1	1:3
Compound 3	polyoxin	3:1	1:1	1:3
Compound 3	probenazole	3:1	1:1	1:3
Compound 3	prochloraz	7:1	2:1	1:2
Compound 3	procymidone	11:1	4:1	2:1
Compound 3	propamocarb or propamocarb-hydrochloride	10:1	4:1	2:1
Compound 3	propiconazole	1:1	1:2	1:5
Compound 3	propineb	11:1	4:1	2:1
Compound 3	proquinazid	1:1	1:3	1:12
Compound 3	prothiocarb	3:1	1:1	1:3
Compound 3	prothioconazole	1:1	1:2	1:5
Compound 3	pyraclostrobin	2:1	1:1	1:4
Compound 3	pyrametostrobin	2:1	1:1	1:4
Compound 3	pyraoxystrobin	2:1	1:1	1:4
Compound 3	pyrazophos	15:1	4:1	1:1
Compound 3	pyribencarb	4:1	1:1	1:2
Compound 3	pyributicarb	15:1	4:1	1:1
Compound 3	pyrifenox	3:1	1:1	1:3
Compound 3	pyrimethanil	3:1	1:1	1:2
Compound 3	pyriofenone	2:1	1:1	1:4
Compound 3	pyroquilon	3:1	1:1	1:3
Compound 3	pyrrolnitrin	15:1	5:1	2:1
Compound 3	quinconazole	1:1	1:2	1:4
Compound 3	quinomethionate	15:1	5:1	2:1
Compound 3	quinoxyfen	1:1	1:2	1:6
Compound 3	quintozene	15:1	5:1	2:1
Compound 3	silthiofam	2:1	1:1	1:4
Compound 3	simeconazole	1:1	1:2	1:5
Compound 3	spiroxamine	5:1	2:1	1:2
Compound 3	streptomycin	3:1	1:1	1:3
Compound 3	sulfur	75:1	25:1	9:1
Compound 3	tebuconazole	1:1	1:2	1:5
Compound 3	tebufloquin	3:1	1:1	1:3
Compound 3	tecloftalam	15:1	5:1	2:1
Compound 3	tecnazene	15:1	5:1	2:1

Component (a)	Component (b)	Illustrative Ratios(*)		
Compound 3	terbinafine	15:1	5:1	2:1
Compound 3	tetraconazole	1:1	1:2	1:5
Compound 3	thiabendazole	11:1	4:1	2:1
Compound 3	thifluzamide	3:1	1:1	1:3
Compound 3	thiophanate	11:1	4:1	2:1
Compound 3	thiophanate-methyl	11:1	4:1	2:1
Compound 3	thiram	37:1	14:1	5:1
Compound 3	tiadinil	2:1	1:1	1:3
Compound 3	tolclofos-methyl	37:1	14:1	5:1
Compound 3	tolylfluanid	15:1	5:1	2:1
Compound 3	triadimefon	1:1	1:2	1:5
Compound 3	triadimenol	1:1	1:2	1:5
Compound 3	triarimol	1:2	1:7	1:24
Compound 3	triazoxide	15:1	5:1	2:1
Compound 3	tricyclazole	3:1	1:1	1:3
Compound 3	tridemorph	7:1	2:1	1:1
Compound 3	trifloxystrobin	2:1	1:1	1:4
Compound 3	triflumizole	3:1	1:1	1:3
Compound 3	triforine	3:1	1:1	1:3
Compound 3	trimorphamide	7:1	2:1	1:2
Compound 3	triticonazole	1:1	1:2	1:5
Compound 3	uniconazole	1:1	1:2	1:5
Compound 3	validamycin	3:1	1:1	1:3
Compound 3	valifenalate	2:1	1:1	1:4
Compound 3	vinclozolin	15:1	6:1	2:1
Compound 3	zineb	37:1	14:1	5:1
Compound 3	ziram	37:1	14:1	5:1
Compound 3	zoxamide	2:1	1:1	1:4
Compound 3	5-chloro-6-(2,4,6-trifluorophenyl)-7-(4-methylpiperidin-1-yl)[1,2,4]triazolo[1,5-a]pyrimidine	1:1	1:2	1:6
Compound 3	*N*-[2-[4-[[3-(4-chlorophenyl)-2-propyn-1-yl]oxy]-3-methoxy-phenyl]ethyl]-3-methyl-2-[(methylsulfonyl)amino]-butanamide	2:1	1:1	1:4
Compound 3	*N*-[2-[4-[[3-(4-chlorophenyl)-2-propyn-1-yl]oxy]-3-methoxy-phenyl]ethyl]-3-methyl-2-[(ethylsulfonyl)amino]butanamide	2:1	1:1	1:4
Compound 3	2-butoxy-6-iodo-3-propyl-4*H*-1-benzopyran-4-one	1:1	1:3	1:12
Compound 3	3-[5-(4-chlorophenyl)-2,3-dimethyl-3-isoxazolidinyl]-	3:1	1:1	1:3

Component (a)	Component (b)	Illustrative Ratios(*)		
	pyridine			
Compound 3	*N'*-[4-[[3-[(4-chlorophenyl)methyl]-1,2,4-thiadiazol-5-yl]oxy]-2,5-dimethylphenyl]-*N*-ethyl-*N*-methylmethanimidamide	3:1	1:1	1:3
Compound 3	4-fluorophenyl *N*-[1-[[[1-(4-cyanophenyl)ethyl]sulfonyl]-methyl]propyl]carbamate	2:1	1:1	1:4
Compound 3	*N*-[[(cyclopropylmethoxy)amino][6-(difluoromethoxy)-2,3-difluorophenyl]methylene]benzeneacetamide	1:2	1:7	1:24
Compound 3	α-[methoxyimino]-*N*-methyl-2-[[[1-[3-(trifluoromethyl)-phenyl]ethoxy]imino]methyl]benzeneacetamide	3:1	1:1	1:3
Compound 3	*N'*-[4-[4-chloro-3-(trifluoromethyl)phenoxy]-2,5-dimethyl-phenyl]-*N*-ethyl-*N*-methylmethanimidamide	3:1	1:1	1:3
Compound 3	*N*-(4-chloro-2-nitrophenyl)-*N*-ethyl-4-methylbenzene-sulfonamide	3:1	1:1	1:3
Compound 3	2-[[[3-(2,6-dichlorophenyl)-1-methyl-2-propen-1-ylidene]-amino]oxy]methyl]-α-(methoxyimino)-*N*-methylbenzene-acetamide	3:1	1:1	1:3
Compound 3	pentyl *N*-[4-[[[[(1-methyl-1*H*-tetrazol-5-yl)phenyl-methylene]amino]oxy]methyl]-2-thiazolyl]carbamate	3:1	1:1	1:3
Compound 3	pentyl *N*-[6-[[[[(1-methyl-1*H*-tetrazol-5-yl)phenyl-methylene]amino]oxy]methyl]-2-pyridinyl]carbamate	3:1	1:1	1:3
Compound 3	2-[(3-bromo-6-quinolinyl)oxy]-*N*-(1,1-dimethyl-2-butyn-1-yl)-2-(methylthio)acetamide	2:1	1:1	1:4
Compound 3	2-[(3-ethynyl-6-quinolinyl)oxy]-*N*-[1-(hydroxymethyl)-1-methyl-2-propyn-1-yl]-2-(methylthio)acetamide	2:1	1:1	1:4
Compound 3	*N*-(1,1-dimethyl-2-butyn-1-yl)-2-[(3-ethynyl-6-quinolinyl)oxy]-2-(methylthio)acetamide	2:1	1:1	1:4

(*) Ratios of Component (b) relative to Component (a) by weight.

Tables A2 through A43 are each constructed the same as Table A1 above except that entries below the "Component (a)" column heading are replaced with the respective Component (a) Column Entry shown below. Thus, for example, in Table A2 the entries below the "Component (a)" column heading all recite "Compound 7", and the first line below the column headings in Table A2 specifically discloses a mixture of Compound 7 with acibenzolar-*S*-methyl. Tables A3 through A43 are constructed similarly.

Table Number	Component (a) Column Entry	Table Number	Component (a) Column Entry
A2	Compound 7	A23	Compound 252
A3	Compound 8	A24	Compound 253

Table Number	Component (a) Column Entry	Table Number	Component (a) Column Entry
A4	Compound 13	A25	Compound 254
A5	Compound 17	A26	Compound 257
A6	Compound 40	A27	Compound 258
A7	Compound 47	A28	Compound 259
A8	Compound 81	A29	Compound 260
A9	Compound 82	A30	Compound 261
A10	Compound 122	A31	Compound 262
A11	Compound 136	A32	Compound 263
A12	Compound 143	A33	Compound 264
A13	Compound 144	A34	Compound 265
A14	Compound 161	A35	Compound 266
A15	Compound 195	A36	Compound 267
A16	Compound 238	A37	Compound 268
A17	Compound 239	A38	Compound 269
A18	Compound 240	A39	Compound 270
A19	Compound 241	A40	Compound 271
A20	Compound 244	A41	Compound 273
A21	Compound 245	A42	Compound 275
A22	Compound 247	A43	Compound 276

Table B1 lists specific combinations of a Component (b) compound with Component (a) illustrative of the mixtures, compositions and methods of the present invention. The first column of Table B1 lists the specific Component (b) compound (e.g., "acibenzolar-*S*-methyl" in the first line). The second, third and fourth columns of Table B1 lists ranges of weight ratios for rates at which the Component (b) compound is typically applied to a field-grown crop relative to Component (a) (e.g., "2:1 to 1:180" of acibenzolar-*S*-methyl relative to Component (a) by weight). Thus, for example, the first line of Table B1 specifically discloses the combination of acibenzolar-*S*-methyl with Component (a) is typically applied in a weight ratio between 2:1 to 1:180. The remaining lines of Table B1 are to be construed similarly. Of particular note is a composition comprising a mixture of any one of the compounds listed in Embodiment 45 as Component (a) with a compound listed in the Component (b) column of Table B1 according to the weight ratios disclosed in Table B1. Table B1 thus supplements the specific ratios disclosed in Tables A1 through A43 with ranges of ratios for these combinations.

Table B1

Component (b)	Typical Weight Ratio	More Typical Weight Ratio	Most Typical Weight Ratio
acibenzolar-*S*-methyl	2:1 to 1:180	1:1 to 1:60	1:1 to 1:18
aldimorph	30:1 to 1:3	10:1 to 1:1	7:1 to 1:1
ametoctradin	9:1 to 1:18	3:1 to 1:6	3:1 to 1:3
amisulbrom	6:1 to 1:18	2:1 to 1:6	1:1 to 1:6
anilazine	90:1 to 2:1	30:1 to 4:1	22:1 to 4:1
azaconazole	7:1 to 1:18	2:1 to 1:6	2:1 to 1:4
azoxystrobin	9:1 to 1:12	3:1 to 1:4	3:1 to 1:3
benalaxyl	4:1 to 1:18	1:1 to 1:6	1:1 to 1:6
benalaxyl-M	4:1 to 1:36	1:1 to 1:12	1:1 to 1:8
benodanil	18:1 to 1:6	6:1 to 1:2	4:1 to 1:2
benomyl	45:1 to 1:4	15:1 to 1:1	11:1 to 1:1
benthiavalicarb or benthiavalicarb-isopropyl	2:1 to 1:36	1:1 to 1:12	1:1 to 1:12
bethoxazin	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
binapacryl	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
biphenyl	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
bitertanol	15:1 to 1:5	5:1 to 1:2	3:1 to 1:2
bixafen	12:1 to 1:9	4:1 to 1:3	2:1 to 1:3
blasticidin-S	3:1 to 1:90	1:1 to 1:30	1:4 to 1:30
boscalid	18:1 to 1:6	6:1 to 1:2	4:1 to 1:2
bromuconazole	15:1 to 1:9	5:1 to 1:3	3:1 to 1:3
bupirimate	3:1 to 1:90	1:1 to 1:30	1:3 to 1:30
captafol	90:1 to 1:4	30:1 to 1:2	15:1 to 2:1
captan	90:1 to 1:4	30:1 to 1:2	15:1 to 2:1
carbendazim	45:1 to 1:4	15:1 to 1:2	11:1 to 2:1
carboxin	18:1 to 1:6	6:1 to 1:2	4:1 to 1:2
carpropamid	15:1 to 1:9	5:1 to 1:3	3:1 to 1:3
chloroneb	300:1 to 2:1	100:1 to 4:1	100:1 to 14:1
chlorothalonil	90:1 to 1:4	30:1 to 1:2	15:1 to 2:1
chlozolinate	45:1 to 1:2	15:1 to 2:1	11:1 to 2:1
clotrimazole	15:1 to 1:9	5:1 to 1:3	3:1 to 1:3
copper salts such as Bordeaux mixture (tribasic copper sulfate), copper oxychloride, copper sulfate and copper hydroxide	450:1 to 1:1	150:1 to 4:1	45:1 to 5:1

Component (b)	Typical Weight Ratio	More Typical Weight Ratio	Most Typical Weight Ratio
cyazofamid	4:1 to 1:18	1:1 to 1:6	1:1 to 1:6
cyflufenamid	1:1 to 1:90	1:2 to 1:30	1:2 to 1:24
cymoxanil	6:1 to 1:18	2:1 to 1:6	1:1 to 1:5
cyproconazole	4:1 to 1:18	1:1 to 1:6	1:1 to 1:6
cyprodinil	22:1 to 1:9	7:1 to 1:3	4:1 to 1:2
dichlofluanid	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
diclocymet	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
diclomezine	15:1 to 1:9	5:1 to 1:3	3:1 to 1:3
dicloran	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
diethofencarb	22:1 to 1:9	7:1 to 1:3	7:1 to 1:2
difenoconazole	4:1 to 1:36	1:1 to 1:12	1:1 to 1:12
diflumetorim	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
dimethirimol	3:1 to 1:90	1:1 to 1:30	1:3 to 1:30
dimethomorph	9:1 to 1:6	3:1 to 1:2	3:1 to 1:2
dimoxystrobin	9:1 to 1:18	3:1 to 1:6	2:1 to 1:4
diniconazole	3:1 to 1:36	1:1 to 1:12	1:1 to 1:8
diniconazole M	3:1 to 1:90	1:1 to 1:30	1:1 to 1:12
dinocap	7:1 to 1:9	2:1 to 1:3	2:1 to 1:3
dithianon	15:1 to 1:4	5:1 to 1:2	5:1 to 1:2
dodemorph	30:1 to 1:3	10:1 to 1:1	7:1 to 1:1
dodine	30:1 to 1:2	10:1 to 2:1	10:1 to 2:1
edifenphos	30:1 to 1:9	10:1 to 1:3	3:1 to 1:3
enestroburin	9:1 to 1:18	3:1 to 1:6	2:1 to 1:4
epoxiconazole	3:1 to 1:36	1:1 to 1:12	1:1 to 1:7
etaconazole	3:1 to 1:36	1:1 to 1:12	1:1 to 1:7
ethaboxam	7:1 to 1:9	2:1 to 1:3	2:1 to 1:3
ethirimol	30:1 to 1:3	10:1 to 1:1	7:1 to 1:1
etridiazole	30:1 to 1:9	10:1 to 1:3	7:1 to 1:2
famoxadone	9:1 to 1:18	3:1 to 1:6	2:1 to 1:4
fenamidone	6:1 to 1:18	2:1 to 1:6	2:1 to 1:4
fenarimol	3:1 to 1:90	1:1 to 1:30	1:2 to 1:24
fenbuconazole	3:1 to 1:30	1:1 to 1:10	1:1 to 1:10
fenfuram	18:1 to 1:6	6:1 to 1:2	4:1 to 1:2
fenhexamid	30:1 to 1:2	10:1 to 2:1	10:1 to 2:1
fenoxanil	150:1 to 1:36	50:1 to 1:12	15:1 to 1:1

Component (b)	Typical Weight Ratio	More Typical Weight Ratio	Most Typical Weight Ratio
fenpiclonil	75:1 to 1:9	25:1 to 1:3	15:1 to 2:1
fenpropidin	30:1 to 1:3	10:1 to 1:1	7:1 to 1:1
fenpropimorph	30:1 to 1:3	10:1 to 1:1	7:1 to 1:1
fenpyrazamine	100:1 to 1:100	10:1 to 1:10	3:1 to 1:3
fentin salt such as the acetate, chloride or hydroxide	15:1 to 1:9	5:1 to 1:3	3:1 to 1:3
ferbam	300:1 to 1:2	100:1 to 2:1	30:1 to 4:1
ferimzone	30:1 to 1:5	10:1 to 1:2	7:1 to 1:2
fluazinam	22:1 to 1:5	7:1 to 1:2	3:1 to 1:2
fludioxonil	7:1 to 1:12	2:1 to 1:4	2:1 to 1:4
flumetover	9:1 to 1:6	3:1 to 1:2	3:1 to 1:2
flumorph	9:1 to 1:18	3:1 to 1:6	3:1 to 1:3
fluopicolide	3:1 to 1:18	1:1 to 1:6	1:1 to 1:6
fluopyram	15:1 to 1:90	5:1 to 1:30	3:1 to 1:3
fluoromide	150:1 to 2:1	50:1 to 4:1	37:1 to 5:1
fluoxastrobin	4:1 to 1:18	1:1 to 1:6	1:1 to 1:6
fluquinconazole	4:1 to 1:12	1:1 to 1:4	1:1 to 1:4
flusilazole	15:1 to 1:9	5:1 to 1:3	3:1 to 1:3
flusulfamide	90:1 to 1:2	30:1 to 2:1	15:1 to 2:1
flutianil	7:1 to 1:36	2:1 to 1:12	1:1 to 1:6
flutolanil	18:1 to 1:6	6:1 to 1:2	4:1 to 1:2
flutriafol	4:1 to 1:12	1:1 to 1:4	1:1 to 1:4
fluxapyroxad	12:1 to 1:9	4:1 to 1:3	2:1 to 1:3
folpet	90:1 to 1:4	30:1 to 1:2	15:1 to 2:1
fosetyl-aluminum	225:1 to 2:1	75:1 to 5:1	30:1 to 5:1
fuberidazole	45:1 to 1:4	15:1 to 1:2	11:1 to 2:1
furalaxyl	15:1 to 1:45	5:1 to 1:15	1:1 to 1:6
furametpyr	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
guazatine or iminoctadine	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
hexaconazole	15:1 to 1:36	5:1 to 1:12	1:1 to 1:5
hymexazol	225:1 to 2:1	75:1 to 4:1	75:1 to 9:1
imazalil	7:1 to 1:18	2:1 to 1:6	1:1 to 1:5
imibenconazole	15:1 to 1:36	5:1 to 1:12	1:1 to 1:5
iodocarb	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
ipconazole	15:1 to 1:36	5:1 to 1:12	1:1 to 1:5

Component (b)	Typical Weight Ratio	More Typical Weight Ratio	Most Typical Weight Ratio
iprobenfos	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
iprodione	120:1 to 1:2	40:1 to 2:1	15:1 to 2:1
iprovalicarb	9:1 to 1:9	3:1 to 1:3	2:1 to 1:3
isoprothiolane	150:1 to 2:1	50:1 to 4:1	45:1 to 5:1
isopyrazam	12:1 to 1:9	4:1 to 1:3	2:1 to 1:3
isotianil	12:1 to 1:9	4:1 to 1:3	2:1 to 1:3
kasugamycin	7:1 to 1:90	2:1 to 1:30	1:2 to 1:24
kresoxim-methyl	7:1 to 1:18	2:1 to 1:6	2:1 to 1:4
mancozeb	180:1 to 1:3	60:1 to 2:1	22:1 to 3:1
mandipropamid	6:1 to 1:18	2:1 to 1:6	2:1 to 1:4
maneb	180:1 to 1:3	60:1 to 2:1	22:1 to 3:1
mepanipyrim	18:1 to 1:3	6:1 to 1:1	6:1 to 1:1
mepronil	7:1 to 1:36	2:1 to 1:12	1:1 to 1:6
meptyldinocap	7:1 to 1:9	2:1 to 1:3	2:1 to 1:3
metalaxyl	15:1 to 1:45	5:1 to 1:15	1:1 to 1:6
metalaxyl-M	7:1 to 1:90	2:1 to 1:30	1:1 to 1:12
metconazole	3:1 to 1:18	1:1 to 1:6	1:1 to 1:6
methasulfocarb	150:1 to 1:36	50:1 to 1:12	15:1 to 1:1
metiram	150:1 to 1:36	50:1 to 1:12	15:1 to 1:1
metominostrobin	9:1 to 1:12	3:1 to 1:4	3:1 to 1:3
metrafenone	6:1 to 1:12	2:1 to 1:4	2:1 to 1:4
myclobutanil	5:1 to 1:26	1:1 to 1:9	1:1 to 1:8
naftifine	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
neo-asozin (ferric methanearsonate)	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
nuarimol	15:1 to 1:9	5:1 to 1:3	3:1 to 1:3
octhilinone	150:1 to 1:36	50:1 to 1:12	15:1 to 1:1
ofurace	15:1 to 1:45	5:1 to 1:15	1:1 to 1:6
orysastrobin	9:1 to 1:12	3:1 to 1:4	3:1 to 1:3
oxadixyl	15:1 to 1:45	5:1 to 1:15	1:1 to 1:6
oxolinic acid	30:1 to 1:9	10:1 to 1:3	7:1 to 1:2
oxpoconazole	15:1 to 1:36	5:1 to 1:12	1:1 to 1:5
oxycarboxin	18:1 to 1:6	6:1 to 1:2	4:1 to 1:2
oxytetracycline	15:1 to 1:9	5:1 to 1:3	3:1 to 1:3
pefurazoate	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
penconazole	1:1 to 1:45	1:2 to 1:15	1:2 to 1:15

Component (b)	Typical Weight Ratio	More Typical Weight Ratio	Most Typical Weight Ratio
pencycuron	150:1 to 1:2	50:1 to 2:1	11:1 to 2:1
penflufen	12:1 to 1:9	4:1 to 1:3	2:1 to 1:3
penthiopyrad	12:1 to 1:9	4:1 to 1:3	2:1 to 1:3
phosphorous acid and salts thereof	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
phthalide	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
picoxystrobin	7:1 to 1:18	2:1 to 1:6	1:1 to 1:5
piperalin	15:1 to 1:9	5:1 to 1:3	3:1 to 1:3
polyoxin	15:1 to 1:9	5:1 to 1:3	3:1 to 1:3
probenazole	15:1 to 1:9	5:1 to 1:3	3:1 to 1:3
prochloraz	22:1 to 1:4	7:1 to 1:1	7:1 to 1:2
procymidone	45:1 to 1:3	15:1 to 1:1	11:1 to 2:1
propamocarb or propamocarb-hydrochloride	30:1 to 1:2	10:1 to 2:1	10:1 to 2:1
propiconazole	4:1 to 1:18	1:1 to 1:6	1:1 to 1:5
propineb	45:1 to 1:2	15:1 to 2:1	11:1 to 2:1
proquinazid	3:1 to 1:36	1:1 to 1:12	1:1 to 1:12
prothiocarb	9:1 to 1:18	3:1 to 1:6	3:1 to 1:3
prothioconazole	6:1 to 1:18	2:1 to 1:6	1:1 to 1:5
pyraclostrobin	9:1 to 1:18	3:1 to 1:6	2:1 to 1:4
pyrametostrobin	9:1 to 1:18	3:1 to 1:6	2:1 to 1:4
pyraoxystrobin	9:1 to 1:18	3:1 to 1:6	2:1 to 1:4
pyrazophos	150:1 to 1:36	50:1 to 1:12	15:1 to 1:1
pyribencarb	15:1 to 1:6	5:1 to 1:2	4:1 to 1:2
pyrifenox	15:1 to 1:9	5:1 to 1:3	3:1 to 1:3
pyrimethanil	30:1 to 1:6	10:1 to 1:2	3:1 to 1:2
pyriofenone	6:1 to 1:12	2:1 to 1:4	2:1 to 1:4
pyroquilon	15:1 to 1:9	5:1 to 1:3	3:1 to 1:3
pyrrolnitrin	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
quinconazole	4:1 to 1:12	1:1 to 1:4	1:1 to 1:4
quinmethionate	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
quinoxyfen	4:1 to 1:18	1:1 to 1:6	1:1 to 1:6
quintozene	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
silthiofam	7:1 to 1:18	2:1 to 1:6	2:1 to 1:4
simeconazole	15:1 to 1:36	5:1 to 1:12	1:1 to 1:5
spiroxamine	22:1 to 1:4	7:1 to 1:2	5:1 to 1:2

Component (b)	Typical Weight Ratio	More Typical Weight Ratio	Most Typical Weight Ratio
streptomycin	15:1 to 1:9	5:1 to 1:3	3:1 to 1:3
sulfur	300:1 to 3:1	100:1 to 9:1	75:1 to 9:1
tebuconazole	7:1 to 1:18	2:1 to 1:6	1:1 to 1:5
tebufloquin	100:1 to 1:100	10:1 to 1:10	3:1 to 1:3
tecloftalam	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
tecnazene	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
terbinafine	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
tetraconazole	15:1 to 1:36	5:1 to 1:12	1:1 to 1:5
thiabendazole	45:1 to 1:4	15:1 to 1:2	11:1 to 2:1
thifluzamide	15:1 to 1:9	5:1 to 1:3	3:1 to 1:3
thiophanate	45:1 to 1:3	15:1 to 2:1	11:1 to 2:1
thiophanate-methyl	45:1 to 1:3	15:1 to 2:1	11:1 to 2:1
thiram	150:1 to 1:2	50:1 to 2:1	37:1 to 5:1
tiadinil	12:1 to 1:9	4:1 to 1:3	2:1 to 1:3
tolclofos-methyl	150:1 to 1:2	50:1 to 2:1	37:1 to 5:1
tolylfluanid	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
triadimefon	15:1 to 1:36	5:1 to 1:12	1:1 to 1:5
triadimenol	15:1 to 1:36	5:1 to 1:12	1:1 to 1:5
triarimol	3:1 to 1:90	1:1 to 1:30	1:2 to 1:24
triazoxide	150:1 to 1:36	50:1 to 1:12	15:1 to 2:1
tricyclazole	15:1 to 1:9	5:1 to 1:3	3:1 to 1:3
tridemorph	30:1 to 1:3	10:1 to 1:1	7:1 to 1:1
trifloxystrobin	6:1 to 1:18	2:1 to 1:6	2:1 to 1:4
triflumizole	15:1 to 1:9	5:1 to 1:3	3:1 to 1:3
triforine	15:1 to 1:9	5:1 to 1:3	3:1 to 1:3
trimorphamide	45:1 to 1:9	15:1 to 1:3	7:1 to 1:2
triticonazole	15:1 to 1:36	5:1 to 1:12	1:1 to 1:5
uniconazole	15:1 to 1:36	5:1 to 1:12	1:1 to 1:5
validamycin	150:1 to 1:36	50:1 to 1:12	3:1 to 1:3
valifenalate	6:1 to 1:18	2:1 to 1:6	2:1 to 1:4
vinclozolin	120:1 to 1:2	40:1 to 2:1	15:1 to 2:1
zineb	150:1 to 1:2	50:1 to 2:1	37:1 to 5:1
ziram	150:1 to 1:2	50:1 to 2:1	37:1 to 5:1
zoxamide	6:1 to 1:18	2:1 to 1:6	2:1 to 1:4

Component (b)	Typical Weight Ratio	More Typical Weight Ratio	Most Typical Weight Ratio
5-chloro-6-(2,4,6-trifluorophenyl)-7-(4-methylpiperidin-1-yl)[1,2,4]triazolo-[1,5-a]pyrimidine	15:1 to 1:36	5:1 to 1:12	1:1 to 1:6
N-[2-[4-[[3-(4-chlorophenyl)-2-propyn-1-yl]oxy]-3-methoxyphenyl]ethyl]-3-methyl-2-[(methylsulfonyl)amino]-butanamide	6:1 to 1:18	2:1 to 1:6	2:1 to 1:4
N-[2-[4-[[3-(4-chlorophenyl)-2-propyn-1-yl]oxy]-3-methoxyphenyl]ethyl]-3-methyl-2-[(ethylsulfonyl)amino]butanamide	6:1 to 1:18	2:1 to 1:6	2:1 to 1:4
2-butoxy-6-iodo-3-propyl-4*H*-1-benzopyran-4-one	3:1 to 1:36	1:1 to 1:12	1:1 to 1:12
3-[5-(4-chlorophenyl)-2,3-dimethyl-3-isoxazolidinyl]pyridine	15:1 to 1:9	5:1 to 1:3	3:1 to 1:3
N'-[4-[[3-[(4-chlorophenyl)methyl]-1,2,4-thiadiazol-5-yl]oxy]-2,5-dimethylphenyl]-*N*-ethyl-*N*-methylmethanimidamide	20:1 to 1:20	8:1 to 1:8	3:1 to 1:3
4-fluorophenyl *N*-[1-[[[1-(4-cyanophenyl)-ethyl]sulfonyl]methyl]propyl]carbamate	6:1 to 1:18	2:1 to 1:6	2:1 to 1:4
N-[[(cyclopropylmethoxy)amino][6-(difluoromethoxy)-2,3-difluorophenyl]-methylene]benzeneacetamide	1:1 to 1:90	1:2 to 1:30	1:2 to 1:24
α-[methoxyimino]-*N*-methyl-2-[[[1-[3-(trifluoromethyl)phenyl]ethoxy]imino]-methyl]benzeneacetamide	9:1 to 1:18	3:1 to 1:6	3:1 to 1:3
N'-[4-[4-chloro-3-(trifluoromethyl)-phenoxy]-2,5-dimethylphenyl]-*N*-ethyl-*N*-methylmethanimidamide	15:1 to 1:18	5:1 to 1:6	3:1 to 1:3
N-(4-chloro-2-nitrophenyl)-*N*-ethyl-4-methylbenzenesulfonamide	15:1 to 1:18	5:1 to 1:6	3:1 to 1:3
2-[[[3-(2,6-dichlorophenyl)-1-methyl-2-propen-1-ylidene]amino]oxy]methyl]-α-(methoxyimino)-*N*-methylbenzeneacetamide	9:1 to 1:18	3:1 to 1:6	3:1 to 1:3

Component (b)	Typical Weight Ratio	More Typical Weight Ratio	Most Typical Weight Ratio
pentyl *N*-[4-[[[[(1-methyl-1*H*-tetrazol-5-yl)phenylmethylene]amino]oxy]methyl]-2-thiazolyl]carbamate	9:1 to 1:18	3:1 to 1:6	3:1 to 1:3
pentyl *N*-[6-[[[[(1-methyl-1*H*-tetrazol-5-yl)phenylmethylene]amino]oxy]methyl]-2-pyridinyl]carbamate	9:1 to 1:18	3:1 to 1:6	3:1 to 1:3
2-[(3-bromo-6-quinolinyl)oxy]-*N*-(1,1-dimethyl-2-butyn-1-yl)-2-(methylthio)acetamide	5:1 to 1:22	2:1 to 1:8	2:1 to 1:4
2-[(3-ethynyl-6-quinolinyl)oxy]-*N*-[1-(hydroxymethyl)-1-methyl-2-propyn-1-yl]-2-(methylthio)acetamide	5:1 to 1:22	2:1 to 1:8	2:1 to 1:4
N-(1,1-dimethyl-2-butyn-1-yl)-2-[(3-ethynyl-6-quinolinyl)oxy]-2-(methylthio)acetamide	5:1 to 1:22	2:1 to 1:8	2:1 to 1:4

As already noted, the present invention includes embodiments wherein in the composition comprising components (a) and (b), component (b) comprises at least one fungicidal compound from each of two groups selected from (b1) through (b46). Tables C1 through C43 list specific mixtures (compound numbers refer to compounds in Index Table A) to illustrate embodiments wherein component (b) includes at least one fungicidal compound from each of two groups selected from (b1) through (b46). In Table C1, each line below the column headings "Component (a)" and "Component (b)" specifically discloses a mixture of Component (a), which is Compound 3, with at least two Component (b) fungicidal compounds. The entries under the heading "Illustrative Ratios" disclose three specific weight ratios of Component (a) to each Component (b) fungicidal compound in sequence for the disclosed mixture. For example, the first line discloses a mixture of Compound 3 with cyproconazole and azoxystrobin and lists weight ratios of Compound 3 to cyproconazole to azoxystrobin of 1:1:1 , 2:1:1 or 3:1:1.

Table C1

Component (a)	Component (b)		Illustrative Ratios(*)		
Compound 3	cyproconazole	azoxystrobin	1:1:1	2:1:1	3:1:1
Compound 3	cyproconazole	kresoxim-methyl	1:1:1	2:1:1	3:1:1
Compound 3	cyproconazole	picoxystrobin	1:1:1	2:1:1	3:1:1
Compound 3	cyproconazole	pyraclostrobin	1:1:1	2:1:1	3:1:1
Compound 3	cyproconazole	pyrametrostrobin	1:1:1	2:1:1	3:1:1
Compound 3	cyproconazole	pyraoxystrobin	1:1:1	2:1:1	3:1:1

Component (a)	Component (b)			Illustrative Ratios(*)		
Compound 3	cyproconazole	trifloxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	cyproconazole	bixafen		1:1:2	2:1:2	3:1:2
Compound 3	cyproconazole	boscalid		1:1:2	2:1:2	3:1:2
Compound 3	cyproconazole	cyflufenamid		1:2:1	2:2:1	3:2:1
Compound 3	cyproconazole	fluopyram		1:1:2	2:1:2	3:1:2
Compound 3	cyproconazole	isopyrazam		1:1:2	2:1:2	3:1:2
Compound 3	cyproconazole	metrafenone		1:1:2	2:1:2	3:1:2
Compound 3	cyproconazole	penthiopyrad		1:1:2	2:1:2	3:1:2
Compound 3	cyproconazole	proquinazid		1:1:1	2:1:1	3:1:1
Compound 3	cyproconazole	pyriofenone		1:1:2	2:1:2	3:1:2
Compound 3	cyproconazole	quinoxyfen		1:1:1	2:1:1	3:1:1
Compound 3	cyproconazole	sedaxane		1:1:2	2:1:2	3:1:2
Compound 3	cyproconazole	picoxystrobin	proquinazid	1:1:1:1	2:1:1:1	3:1:1:1
Compound 3	cyproconazole	trifloxystrobin	proquinazid	1:1:1:1	2:1:1:1	3:1:1:1
Compound 3	difenconazole	azoxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	difenconazole	kresoxim-methyl		1:1:1	2:1:1	3:1:1
Compound 3	difenconazole	picoxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	difenconazole	pyraclostrobin		1:1:1	2:1:1	3:1:1
Compound 3	difenconazole	pyrametostrobin		1:1:1	2:1:1	3:1:1
Compound 3	difenoconazole	pyraoxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	difenconazole	trifloxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	difenconazole	bixafen		1:1:2	2:1:2	3:1:2
Compound 3	difenconazole	boscalid		1:1:2	2:1:2	3:1:2
Compound 3	difenconazole	cyflufenamid		1:2:1	2:2:1	3:2:1
Compound 3	difenconazole	fluopyram		1:1:2	2:1:2	3:1:2
Compound 3	difenconazole	isopyrazam		1:1:2	2:1:2	3:1:2
Compound 3	difenconazole	metrafenone		1:1:2	2:1:2	3:1:2
Compound 3	difenconazole	penthiopyrad		1:1:2	2:1:2	3:1:2
Compound 3	difenconazole	proquinazid		1:1:1	2:1:1	3:1:1
Compound 3	difenconazole	pyriofenone		1:1:2	2:1:2	3:1:2
Compound 3	difenconazole	quinoxyfen		1:1:1	2:1:1	3:1:1
Compound 3	difenconazole	sedaxane		1:1:2	2:1:2	3:1:2
Compound 3	difenconazole	picoxystrobin	proquinazid	1:1:1:1	2:1:1:1	3:1:1:1
Compound 3	difenconazole	trifloxystrobin	proquinazid	1:1:1:1	2:1:1:1	3:1:1:1
Compound 3	epoxiconazole	azoxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	epoxiconazole	kresoxim-methyl		1:1:1	2:1:1	3:1:1

Component (a)	Component (b)			Illustrative Ratios(*)		
Compound 3	epoxiconazole	picoxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	epoxiconazole	pyraclostrobin		1:1:1	2:1:1	3:1:1
Compound 3	epoxiconazole	pyrametostrobin		1:1:1	2:1:1	3:1:1
Compound 3	epoxiconazole	pyraoxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	epoxiconazole	trifloxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	epoxiconazole	bixafen		1:1:2	2:1:2	3:1:2
Compound 3	epoxiconazole	boscalid		1:1:2	2:1:2	3:1:2
Compound 3	epoxiconazole	cyflufenamid		1:2:1	2:2:1	3:2:1
Compound 3	epoxiconazole	fluopyram		1:1:2	2:1:2	3:1:2
Compound 3	epoxiconazole	isopyrazam		1:1:2	2:1:2	3:1:2
Compound 3	epoxiconazole	metrafenone		1:1:2	2:1:2	3:1:2
Compound 3	epoxiconazole	penthiopyrad		1:1:2	2:1:2	3:1:2
Compound 3	epoxiconazole	proquinazid		1:1:1	2:1:1	3:1:1
Compound 3	epoxiconazole	pyriofenone		1:1:2	2:1:2	3:1:2
Compound 3	epoxiconazole	quinoxyfen		1:1:1	2:1:1	3:1:1
Compound 3	epoxiconazole	sedaxane		1:1:2	2:1:2	3:1:2
Compound 3	epoxiconazole	picoxystrobin	proquinazid	1:1:1:1	2:1:1:1	3:1:1:1
Compound 3	epoxiconazole	trifloxystrobin	proquinazid	1:1:1:1	2:1:1:1	3:1:1:1
Compound 3	metconazole	azoxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	metconazole	kresoxim-methyl		1:1:1	2:1:1	3:1:1
Compound 3	metconazole	picoxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	metconazole	pyraclostrobin		1:1:1	2:1:1	3:1:1
Compound 3	metconazole	pyrametostrobin		1:1:1	2:1:1	3:1:1
Compound 3	metconazole	pyraoxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	metconazole	trifloxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	metconazole	bixafen		1:1:2	2:1:2	3:1:2
Compound 3	metconazole	boscalid		1:1:2	2:1:2	3:1:2
Compound 3	metconazole	cyflufenamid		1:2:1	2:2:1	3:2:1
Compound 3	metconazole	fluopyram		1:1:2	2:1:2	3:1:2
Compound 3	metconazole	isopyrazam		1:1:2	2:1:2	3:1:2
Compound 3	metconazole	metrafenone		1:1:2	2:1:2	3:1:2
Compound 3	metconazole	penthiopyrad		1:1:2	2:1:2	3:1:2
Compound 3	metconazole	proquinazid		1:1:1	2:1:1	3:1:1
Compound 3	metconazole	pyriofenone		1:1:2	2:1:2	3:1:2
Compound 3	metconazole	quinoxyfen		1:1:1	2:1:1	3:1:1
Compound 3	metconazole	sedaxane		1:1:2	2:1:2	3:1:2

Component (a)	Component (b)			Illustrative Ratios(*)		
Compound 3	metconazole	picoxystrobin	proquinazid	1:1:1:1	2:1:1:1	3:1:1:1
Compound 3	metconazole	trifloxystrobin	proquinazid	1:1:1:1	2:1:1:1	3:1:1:1
Compound 3	myclobutanil	azoxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	myclobutanil	kresoxim-methyl		1:1:1	2:1:1	3:1:1
Compound 3	myclobutanil	picoxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	myclobutanil	pyraclostrobin		1:1:1	2:1:1	3:1:1
Compound 3	myclobutanil	pyrametostrobin		1:1:1	2:1:1	3:1:1
Compound 3	myclobutanil	pyraoxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	myclobutanil	trifloxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	myclobutanil	bixafen		1:1:2	2:1:2	3:1:2
Compound 3	myclobutanil	boscalid		1:1:2	2:1:2	3:1:2
Compound 3	myclobutanil	cyflufenamid		1:2:1	2:2:1	3:2:1
Compound 3	myclobutanil	fluopyram		1:1:2	2:1:2	3:1:2
Compound 3	myclobutanil	isopyrazam		1:1:2	2:1:2	3:1:2
Compound 3	myclobutanil	metrafenone		1:1:2	2:1:2	3:1:2
Compound 3	myclobutanil	penthiopyrad		1:1:2	2:1:2	3:1:2
Compound 3	myclobutanil	proquinazid		1:1:1	2:1:1	3:1:1
Compound 3	myclobutanil	pyriofenone		1:1:2	2:1:2	3:1:2
Compound 3	myclobutanil	quinoxyfen		1:1:1	2:1:1	3:1:1
Compound 3	myclobutanil	sedaxane		1:1:2	2:1:2	3:1:2
Compound 3	myclobutanil	picoxystrobin	proquinazid	1:1:1:1	2:1:1:1	3:1:1:1
Compound 3	myclobutanil	trifloxystrobin	proquinazid	1:1:1:1	2:1:1:1	3:1:1:1
Compound 3	prothioconazole	azoxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	prothioconazole	kresoxim-methyl		1:1:1	2:1:1	3:1:1
Compound 3	prothioconazole	picoxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	prothioconazole	pyraclostrobin		1:1:1	2:1:1	3:1:1
Compound 3	prothioconazole	pyrametostrobin		1:1:1	2:1:1	3:1:1
Compound 3	prothioconazole	pyraoxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	prothioconazole	trifloxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	prothioconazole	bixafen		1:1:2	2:1:2	3:1:2
Compound 3	prothioconazole	boscalid		1:1:2	2:1:2	3:1:2
Compound 3	prothioconazole	cyflufenamid		1:2:1	2:2:1	3:2:1
Compound 3	prothioconazole	fluopyram		1:1:2	2:1:2	3:1:2
Compound 3	prothioconazole	isopyrazam		1:1:2	2:1:2	3:1:2
Compound 3	prothioconazole	metrafenone		1:1:2	2:1:2	3:1:2
Compound 3	prothioconazole	penthiopyrad		1:1:2	2:1:2	3:1:2

Component (a)	Component (b)			Illustrative Ratios(*)		
Compound 3	prothioconazole	proquinazid		1:1:1	2:1:1	3:1:1
Compound 3	prothioconazole	pyriofenone		1:1:2	2:1:2	3:1:2
Compound 3	prothioconazole	quinoxyfen		1:1:1	2:1:1	3:1:1
Compound 3	prothioconazole	sedaxane		1:1:2	2:1:2	3:1:2
Compound 3	prothioconazole	picoxystrobin	proquinazid	1:1:1:1	2:1:1:1	3:1:1:1
Compound 3	prothioconazole	trifloxystrobin	proquinazid	1:1:1:1	2:1:1:1	3:1:1:1
Compound 3	tebuconazole	azoxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	tebuconazole	kresoxim-methyl		1:1:1	2:1:1	3:1:1
Compound 3	tebuconazole	picoxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	tebuconazole	pyraclostrobin		1:1:1	2:1:1	3:1:1
Compound 3	tebuconazole	pyrametostrobin		1:1:1	2:1:1	3:1:1
Compound 3	tebuconazole	pyraoxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	tebuconazole	trifloxystrobin		1:1:1	2:1:1	3:1:1
Compound 3	tebuconazole	bixafen		1:1:2	2:1:2	3:1:2
Compound 3	tebuconazole	boscalid		1:1:2	2:1:2	3:1:2
Compound 3	tebuconazole	cyflufenamid		1:2:1	2:2:1	3:2:1
Compound 3	tebuconazole	fluopyram		1:1:2	2:1:2	3:1:2
Compound 3	tebuconazole	isopyrazam		1:1:2	2:1:2	3:1:2
Compound 3	tebuconazole	metrafenone		1:1:2	2:1:2	3:1:2
Compound 3	tebuconazole	penthiopyrad		1:1:2	2:1:2	3:1:2
Compound 3	tebuconazole	proquinazid		1:1:1	2:1:1	3:1:1
Compound 3	tebuconazole	pyriofenone		1:1:2	2:1:2	3:1:2
Compound 3	tebuconazole	quinoxyfen		1:1:1	2:1:1	3:1:1
Compound 3	tebuconazole	sedaxane		1:1:2	2:1:2	3:1:2
Compound 3	tebuconazole	picoxystrobin	proquinazid	1:1:1:1	2:1:1:1	3:1:1:1
Compound 3	tebuconazole	trifloxystrobin	proquinazid	1:1:1:1	2:1:1:1	3:1:1:1

(*) Ratios of Component (a) relative to Component (b) in sequence, by weight.

Tables C2 through C43 are each constructed the same as Table C1 above except that entries below the "Component (a)" column heading are replaced with the respective Component (a) Column Entry shown below. Thus, for example, in Table C2 the entries below the "Component (a)" column heading all recite "Compound 7", and the first line in below the column headings in Table C2 specifically discloses a mixture of Compound 7 with cyproconazole and azoxystrobin, and the illustrative weight ratios of 1:1:1, 2:1:1 and 3:1:1 of Compound 7:cyproconazole:azoxystrobin. Tables C3 through C43 are constructed similarly.

Table Number	Component (a) Column Entry	Table Number	Component (a) Column Entry
C2	Compound 7	C23	Compound 252
C3	Compound 8	C24	Compound 253
C4	Compound 13	C25	Compound 254
C5	Compound 17	C26	Compound 257
C6	Compound 40	C27	Compound 258
C7	Compound 47	C28	Compound 259
C8	Compound 81	C29	Compound 260
C9	Compound 82	C30	Compound 261
C10	Compound 122	C31	Compound 262
C11	Compound 136	C32	Compound 263
C12	Compound 143	C33	Compound 264
C13	Compound 144	C34	Compound 265
C14	Compound 161	C35	Compound 266
C15	Compound 195	C36	Compound 267
C16	Compound 238	C37	Compound 268
C17	Compound 239	C38	Compound 269
C18	Compound 240	C39	Compound 270
C19	Compound 241	C40	Compound 271
C20	Compound 244	C41	Compound 273
C21	Compound 245	C42	Compound 275
C22	Compound 247	C43	Compound 276

Of note is a composition of the present invention comprising a compound of Formula **1** (or an *N*-oxide or salt thereof) with at least one other fungicidal compound that has a different site of action from the compound of Formula **1**. In certain instances, a combination with at least one other fungicidal compound 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 advantageously comprise at least one fungicidal active compound selected from the group consisting of (b1) through (b46) as described above, having a similar spectrum of control but a different site of action.

Compositions of component (a), or component (a) with component (b), can be further mixed with one or more other biologically active compounds or agents including 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 fungicidally effective amount of component (a), or a mixture of component (a) with component (b), and a biologically effective amount of at least one additional biologically active compound or agent 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 also be separately formulated in compositions comprising at least one of a surfactant, solid or liquid diluent. For compositions of the present invention, one or more other biologically active compounds or agents can be formulated together with one or both of components (a) and (b) to form a premix, or one or more other biologically active compounds or agents can be formulated separately from components (a) and (b) and the formulations combined together before application (e.g., in a spray tank) or, alternatively, applied in succession.

Examples of such biologically active compounds or agents with which compositions of component (a), or component (a) with component (b), can be formulated are: insecticides such as abamectin, acephate, acetamiprid, acetoprole, acrinathrin, aldicarb, amidoflumet, amitraz, avermectin, azadirachtin, azinphos-methyl, bifenthrin, bifenazate, bistrifluron, buprofezin, carbofuran, cartap, chinomethionat, chlorfenapyr, chlorfluazuron, chlorantraniliprole, chlorpyrifos, chlorpyrifos-methyl, chlorobenzilate, chromafenozide, clothianidin, cyantraniliprole, cyflumetofen, cyfluthrin, beta-cyfluthrin, cyhalothrin, gamma-cyhalothrin, lambda-cyhalothrin, cyhexatin, cypermethrin, cyromazine, deltamethrin, diafenthiuron, diazinon, dicofol, dieldrin, dienochlor, diflubenzuron, dimefluthrin, dimethoate, dinotefuran, diofenolan, emamectin, endosulfan, esfenvalerate, ethiprole, etoxazole, fenamiphos, fenazaquin, fenbutatin oxide, fenothiocarb, fenoxycarb, fenpropathrin, fenpyroximate, fenvalerate, fipronil, flonicamid, flubendiamide, flucythrinate, tau-fluvalinate, flufenerim, flufenoxuron, fonophos, halofenozide, hexaflumuron, hexythiazox, hydramethylnon, imicyafos, imidacloprid, indoxacarb, isofenphos, lufenuron, malathion, meperfluthrin, metaflumizone, metaldehyde, methamidophos, methidathion, methomyl, methoprene, methoxychlor, methoxyfenozide, metofluthrin, milbemycin oxime, monocrotophos, nicotine, nitenpyram, nithiazine, novaluron, noviflumuron, oxamyl, parathion, parathion-methyl, permethrin, phorate, phosalone, phosmet, phosphamidon, pirimicarb, profenofos, profluthrin, propargite, prothiocarb, protrifenbute, pymetrozine, pyrafluprole, pyrethrin, pyridaben, pyridalyl, pyrifluquinazon, pyriprole, pyriproxyfen, rotenone, ryanodine, spinetoram, spinosad, spiridiclofen, spiromesifen, spirotetramat, sulfoxaflor, sulprofos, tebufenozide, tebufenpyrad, teflubenzuron, tefluthrin, terbufos, tetrachlorvinphos, tetramethylfluthrin, thiacloprid, thiamethoxam, thiodicarb, thiosultap-sodium, tolfenpyrad, tralomethrin, triazamate, trichlorfon, triflumuron; nematocides such as aldicarb, imicyafos, oxamyl and fenamiphos; bactericides such as streptomycin; acaricides such as amitraz, chinomethionat, chlorobenzilate, cyenopyrafen, cyhexatin, dicofol, dienochlor, etoxazole, fenazaquin, fenbutatin oxide, fenpropathrin, fenpyroximate,

hexythiazox, propargite, pyridaben and tebufenpyrad; 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.

General references for these 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 component (a), or a mixture of component (a) with component (b), is generally between about 1:3000 and about 3000:1. Of note are weight ratios between about 1:100 and about 3000:1, or between about 1:30 and about 300:1 (for example ratios between about 1:1 and about 30:1). It will be evident that including these additional components may expand the spectrum of diseases controlled beyond the spectrum controlled by component (a), or a mixture of component (a) with component (b).

Component (a) compounds and/or combinations thereof with component (b) compounds and/or one or more other biologically active compounds or agents 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 present component (a) alone or in combination with component (b) may be synergistic with the expressed toxin proteins.

Of note is the combination or the composition comprising component (a), or components (a) and (b), as described in the Summary of the Invention further comprising at least one invertebrate pest control compound or agent (e.g., insecticide, acaricide). Of particular note is a composition comprising component (a) and at least one (i.e. one or more) invertebrate pest control compound or agent, which then can be subsequently combined with component (b) to provide a composition comprising components (a) and (b) and the one or more invertebrate pest control compounds or agents. Alternatively without first mixing with component (b), a biologically effective amount of the composition comprising component (a) with at least one invertebrate pest control agent can be applied to a plant or plant seed (directly or through the environment of the plant or plant seed) to protect the plant or plant seed from diseases caused by fungal pathogens and injury caused by invertebrate pests.

For embodiments where one or more of invertebrate pest control compounds are used, the weight ratio of these compounds (in total) to the component (a) compounds 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.

Of note is a composition of the present invention which comprises in addition to a component (a) compound, alone or in combination with component (b), at least one invertebrate pest control compound or agent selected from the group consisting of abamectin, acephate, acetamiprid, acetoprole, acrinathrin, aldicarb, amidoflumet, amitraz, avermectin, azadirachtin, azinphos-methyl, bifenthrin, bifenazate, bistrifluron, buprofezin, carbofuran, cartap, chinomethionat, chlorfenapyr, chlorfluazuron, chlorantraniliprole, chlorpyrifos, chlorpyrifos-methyl, chlorobenzilate, chromafenozide, clothianidin, cyantraniliprole, cyflumetofen, cyfluthrin, beta-cyfluthrin, cyhalothrin, gamma-cyhalothrin, lambda-cyhalothrin, cyhexatin, cypermethrin, cyromazine, deltamethrin, diafenthiuron, diazinon, dicofol, dieldrin, dienochlor, diflubenzuron, dimefluthrin, dimethoate, dinotefuran, diofenolan, emamectin, endosulfan, esfenvalerate, ethiprole, etoxazole, fenamiphos, fenazaquin, fenbutatin oxide, fenothiocarb, fenoxycarb, fenpropathrin, fenpyroximate, fenvalerate, fipronil, flonicamid, flubendiamide, flucythrinate, tau-fluvalinate, flufenerim, flufenoxuron, fonophos, halofenozide, hexaflumuron, hexythiazox, hydramethylnon, imicyafos, imidacloprid, indoxacarb, isofenphos, lufenuron, malathion, meperfluthrin, metaflumizone, metaldehyde, methamidophos, methidathion, methomyl, methoprene, methoxychlor, methoxyfenozide, metofluthrin, milbemycin oxime, monocrotophos, nicotine, nitenpyram, nithiazine, novaluron, noviflumuron, oxamyl, parathion, parathion-methyl, permethrin, phorate, phosalone, phosmet, phosphamidon, pirimicarb, profenofos, profluthrin, propargite, protrifenbute, pymetrozine, pyrafluprole, pyrethrin, pyridaben, pyridalyl, pyrifluquinazon, pyriprole, pyriproxyfen, rotenone, ryanodine, spinetoram, spinosad, spiridiclofen, spiromesifen, spirotetramat, sulfoxaflor, sulprofos, tebufenozide, tebufenpyrad, teflubenzuron, tefluthrin, terbufos, tetrachlorvinphos, tetramethylfluthrin, thiacloprid, thiamethoxam, thiodicarb, thiosultap-sodium, tolfenpyrad, tralomethrin, triazamate, trichlorfon, triflumuron, *Bacillus thuringiensis* subsp. *aizawai*, *Bacillus thuringiensis* subsp. *kurstaki*, nucleopolyhedro viruses, encapsulated delta-endotoxins of *Bacillus thuringiensis*, baculoviruses, entomopathogenic bacteria, entomopathogenic viruses and entomopathogenic fungi. Of note is the aforedescribed list excluding meperflutrin, sulfoxaflor and tetramethylfluthrin.

In certain instances, combinations of a component (a) compound, alone or in mixture with component (b), with other biologically active (particularly invertebrate pest control) compounds or agents (i.e. active ingredients) can result in a greater-than-additive (i.e. synergistic) effect. Reducing the quantity of active ingredients released in the environment while ensuring effective pest control is always desirable. When synergism of invertebrate

pest control active ingredients occurs at application rates giving agronomically satisfactory levels of invertebrate pest control, such combinations can be advantageous for reducing crop production cost and decreasing environmental load.

Table D1 lists specific combinations of invertebrate pest control agents with Compound 3 (identified in Index Table A) as a component (a) compound illustrative of mixtures and compositions comprising these active ingredients and methods using them according to the present invention. The second column of Table D1 lists the specific invertebrate pest control agents (e.g., "Abamectin" in the first line). The third column of Table D1 lists the mode of action (if known) or chemical class of the invertebrate pest control agents. The fourth column of Table D1 lists embodiment(s) of ranges of weight ratios for rates at which the invertebrate pest control agent is typically applied relative to Compound 3 alone or in combination with component (b) (e.g., "50:1 to 1:50" of abamectin relative to a Compound 3 by weight). Thus, for example, the first line of Table D1 specifically discloses the combination of Compound 3 with abamectin is typically applied in a weight ratio between 50:1 to 1:50. The remaining lines of Table D1 are to be construed similarly.

Table D1

Component (a)	Invertebrate Pest Control Agent	Mode of Action or Chemical Class	Typical Weight Ratio
Compound 3	Abamectin	macrocyclic lactones	50:1 to 1:50
Compound 3	Acetamiprid	neonicotinoids	150:1 to 1:200
Compound 3	Amitraz	octopamine receptor ligands	200:1 to 1:100
Compound 3	Avermectin	macrocyclic lactones	50:1 to 1:50
Compound 3	Azadirachtin	ecdysone agonists	100:1 to 1:120
Compound 3	Beta-cyfluthrin	sodium channel modulators	150:1 to 1:200
Compound 3	Bifenthrin	sodium channel modulators	100:1 to 1:10
Compound 3	Buprofezin	chitin synthesis inhibitors	500:1 to 1:50
Compound 3	Cartap	nereistoxin analogs	100:1 to 1:200
Compound 3	Chlorantraniliprole	ryanodine receptor ligands	100:1 to 1:120
Compound 3	Chlorfenapyr	mitochondrial electron transport inhibitors	300:1 to 1:200
Compound 3	Chlorpyrifos	cholinesterase inhibitors	500:1 to 1:200
Compound 3	Clothianidin	neonicotinoids	100:1 to 1:400
Compound 3	Cyantraniliprole	ryanodine receptor ligands	100:1 to 1:120
Compound 3	Cyfluthrin	sodium channel modulators	150:1 to 1:200
Compound 3	Cyhalothrin	sodium channel modulators	150:1 to 1:200
Compound 3	Cypermethrin	sodium channel modulators	150:1 to 1:200
Compound 3	Cyromazine	chitin synthesis inhibitors	400:1 to 1:50

Component (a)	Invertebrate Pest Control Agent	Mode of Action or Chemical Class	Typical Weight Ratio
Compound 3	Deltamethrin	sodium channel modulators	50:1 to 1:400
Compound 3	Dieldrin	cyclodiene insecticides	200:1 to 1:100
Compound 3	Dinotefuran	neonicotinoids	150:1 to 1:200
Compound 3	Diofenolan	molting inhibitor	150:1 to 1:200
Compound 3	Emamectin	macrocyclic lactones	50:1 to 1:10
Compound 3	Endosulfan	cyclodiene insecticides	200:1 to 1:100
Compound 3	Esfenvalerate	sodium channel modulators	100:1 to 1:400
Compound 3	Ethiprole	GABA-regulated chloride channel blockers	200:1 to 1:100
Compound 3	Fenothiocarb		150:1 to 1:200
Compound 3	Fenoxycarb	juvenile hormone mimics	500:1 to 1:100
Compound 3	Fenvalerate	sodium channel modulators	150:1 to 1:200
Compound 3	Fipronil	GABA-regulated chloride channel blockers	150:1 to 1:100
Compound 3	Flonicamid		200:1 to 1:100
Compound 3	Flubendiamide	ryanodine receptor ligands	100:1 to 1:120
Compound 3	Flufenoxuron	chitin synthesis inhibitors	200:1 to 1:100
Compound 3	Hexaflumuron	chitin synthesis inhibitors	300:1 to 1:50
Compound 3	Hydramethylnon	mitochondrial electron transport inhibitors	150:1 to 1:250
Compound 3	Imidacloprid	neonicotinoids	1000:1 to 1:1000
Compound 3	Indoxacarb	sodium channel modulators	200:1 to 1:50
Compound 3	Lambda-cyhalothrin	sodium channel modulators	50:1 to 1:250
Compound 3	Lufenuron	chitin synthesis inhibitors	500:1 to 1:250
Compound 3	Meperfluthrin	sodium channel modulators	100:1 to 1:400
Compound 3	Metaflumizone		200:1 to 1:200
Compound 3	Methomyl	cholinesterase inhibitors	500:1 to 1:100
Compound 3	Methoprene	juvenile hormone mimics	500:1 to 1:100
Compound 3	Methoxyfenozide	ecdysone agonists	50:1 to 1:50
Compound 3	Nitenpyram	neonicotinoids	150:1 to 1:200
Compound 3	Nithiazine	neonicotinoids	150:1 to 1:200
Compound 3	Novaluron	chitin synthesis inhibitors	500:1 to 1:150
Compound 3	Oxamyl	cholinesterase inhibitors	200:1 to 1:200
Compound 3	Pymetrozine		200:1 to 1:100
Compound 3	Pyrethrin	sodium channel modulators	100:1 to 1:10

Component (a)	Invertebrate Pest Control Agent	Mode of Action or Chemical Class	Typical Weight Ratio
Compound 3	Pyridaben	mitochondrial electron transport inhibitors	200:1 to 1:100
Compound 3	Pyridalyl		200:1 to 1:100
Compound 3	Pyriproxyfen	juvenile hormone mimics	500:1 to 1:100
Compound 3	Ryanodine	ryanodine receptor ligands	100:1 to 1:120
Compound 3	Spinetoram	macrocyclic lactones	150:1 to 1:100
Compound 3	Spinosad	macrocyclic lactones	500:1 to 1:10
Compound 3	Spirodiclofen	lipid biosynthesis inhibitors	200:1 to 1:200
Compound 3	Spiromesifen	lipid biosynthesis inhibitors	200:1 to 1:200
Compound 3	Sulfoxaflor		200:1 to 1:200
Compound 3	Tebufenozide	ecdysone agonists	500:1 to 1:250
Compound 3	Tetramethylfluthrin	sodium channel modulators	100:1 to 1:40
Compound 3	Thiacloprid	neonicotinoids	100:1 to 1:200
Compound 3	Thiamethoxam	neonicotinoids	1250:1 to 1:1000
Compound 3	Thiodicarb	cholinesterase inhibitors	500:1 to 1:400
Compound 3	Thiosultap-sodium		150:1 to 1:100
Compound 3	Tralomethrin	sodium channel modulators	150:1 to 1:200
Compound 3	Triazamate	cholinesterase inhibitors	250:1 to 1:100
Compound 3	Triflumuron	chitin synthesis inhibitors	200:1 to 1:100
Compound 3	*Bacillus thuringiensis*	biological agents	50:1 to 1:10
Compound 3	*Bacillus thuringiensis* delta-endotoxin	biological agents	50:1 to 1:10
Compound 3	NPV (e.g., Gemstar)	biological agents	50:1 to 1:10

Tables D2 through D43 are each constructed the same as Table D1 above except that entries below the "Component (a)" column heading are replaced with the respective Component (a) Column Entry shown below. Thus, for example, in Table D2 the entries below the "Component (a)" column heading all recite "Compound 7", and the first line in below the column headings in Table D2 specifically discloses a mixture of Compound 7 with abamectin. Tables D3 through D43 are constructed similarly.

Table Number	Component (a) Column Entries	Table Number	Component (a) Column Entries
D2	Compound 7	D23	Compound 252
D3	Compound 8	D24	Compound 253
D4	Compound 13	D25	Compound 254
D5	Compound 17	D26	Compound 257
D6	Compound 40	D27	Compound 258

Table Number	Component (a) Column Entries	Table Number	Component (a) Column Entries
D7	Compound 47	D28	Compound 259
D8	Compound 81	D29	Compound 260
D9	Compound 82	D30	Compound 261
D10	Compound 122	D31	Compound 262
D11	Compound 136	D32	Compound 263
D12	Compound 143	D33	Compound 264
D13	Compound 144	D34	Compound 265
D14	Compound 161	D35	Compound 266
D15	Compound 195	D36	Compound 267
D16	Compound 238	D37	Compound 268
D17	Compound 239	D38	Compound 269
D18	Compound 240	D39	Compound 270
D19	Compound 241	D40	Compound 271
D20	Compound 244	D41	Compound 273
D21	Compound 245	D42	Compound 275
D22	Compound 247	D43	Compound 276

One embodiment of invertebrate pest control agents (e.g., insecticides and acaricides) for mixing with compounds of component (a) include sodium channel modulators such as bifenthrin, cypermethrin, cyhalothrin, lambda-cyhalothrin, cyfluthrin, beta-cyfluthrin, deltamethrin, dimefluthrin, esfenvalerate, fenvalerate, indoxacarb, meperfluthrin, metofluthrin, profluthrin, pyrethrin, tetramethylfluthrin and tralomethrin; cholinesterase inhibitors such as chlorpyrifos, methomyl, oxamyl, thiodicarb and triazamate; neonicotinoids such as acetamiprid, clothianidin, dinotefuran, imidacloprid, nitenpyram, nithiazine, thiacloprid and thiamethoxam; insecticidal macrocyclic lactones such as spinetoram, spinosad, abamectin, avermectin and emamectin; GABA (γ-aminobutyric acid)-regulated chloride channel blockers such as endosulfan, ethiprole and fipronil; chitin synthesis inhibitors such as buprofezin, cyromazine, flufenoxuron, hexaflumuron, lufenuron, novaluron, noviflumuron and triflumuron; juvenile hormone mimics such as diofenolan, fenoxycarb, methoprene and pyriproxyfen; octopamine receptor ligands such as amitraz; ecdysone agonists such as azadirachtin, methoxyfenozide and tebufenozide; ryanodine receptor ligands such as ryanodine, anthranilic diamides such as chlorantraniliprole, cyantraniliprole and flubendiamide; nereistoxin analogs such as cartap; mitochondrial electron transport inhibitors such as chlorfenapyr, hydramethylnon and pyridaben; lipid biosynthesis inhibitors such as spirodiclofen and spiromesifen; cyclodiene insecticides such as dieldrin; cyflumetofen; fenothiocarb; flonicamid; metaflumizone; pyrafluprole; pyridalyl; pyriprole; pymetrozine; spirotetramat; and thiosultap-sodium. One embodiment of

biological agents for mixing with compounds of component (a) include nucleopolyhedro virus such as HzNPV and AfNPV; *Bacillus thuringiensis* and encapsulated delta-endotoxins of *Bacillus thuringiensis* such as Cellcap, MPV and MPVII; as well as naturally occurring and genetically modified viral insecticides including members of the family Baculoviridae as well as entomophagous fungi. Of note is a composition comprising component (a) and at least one additional biologically active compound or agent selected from the Invertebrate Pest Control Agents listed in Table D1 above.

The compositions 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 or vegetative propagation unit to be protected, an effective amount of a composition of the invention (e.g., a composition comprising component (a), or components (a) and (b)). This aspect of the present invention can also be described as a method for protecting a plant or plant seed from diseases caused by fungal pathogens comprising applying a fungicidally effective amount of a composition of the invention to the plant (or portion thereof) or plant seed (directly or through the environment (e.g., growing medium) of the plant or plant seed).

Plant disease control is ordinarily accomplished by applying an effective amount of a composition of the invention (e.g., comprising component (a), or a mixture of components (a) and (b)), typically as a formulated composition, either pre- or post-infection, to the portion of the plant to be protected such as the roots, stems, foliage, fruit, seeds, tubers or bulbs, or to the media (soil or sand) in which the plants to be protected are growing. Component (a) or mixtures thereof can also be applied to seeds to protect the seeds and seedlings developing from the seeds. The mixtures can also be applied through irrigation water to treat plants.

Suitable rates of application (e.g., fungicidally effective amounts) of component (a) (i.e. at least one compound selected from compounds of Formula **1**, *N*-oxides and salts thereof) as well as suitable rates of applicaton (e.g., biologically effective amounts, fungicidally effective amounts or insecticidally effective amounts) for the mixtures and compositions comprising component (a) according to this invention can be influenced by many factors of the environment and should be determined under actual use conditions. 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 ingredients. Seed and seedlings can normally be protected when seed is treated at a rate of from about 0.1 to about 10 g per kilogram of seed; and vegetative propagation units (e.g., cuttings and tubers) can normally be protected when propagation unit is treated at a rate of from about 0.1 to about 10 g per kilogram of propagation unit. One skilled in the art can easily determine through simple experimentation the application rates of component (a), and mixtures and compositions thereof, containing particular

combinations of active ingredients according to this invention needed to provide the desired spectrum of plant protection and control of plant diseases and optionally other plant pests.

The compounds of Formula **1**, *N*-oxides, and salts thereof, are particularly efficacious for controlling plant diseases caused by fungal pathogens, particularly in the Basidomycete and Ascomycete classes. Combining these compounds with other fungicidal compounds can provide control of diseases caused by a broad spectrum of fungal plant pathogens in the Basidiomycete, Ascomycete, Oomycete and Deuteromycete classes. Accordingly, mixtures and compositions described herein can control a broad spectrum of plant diseases, foliar pathogens of crops including: cereal grain crops such as wheat, barley, oats, rye, triticale, rice, maize, sorghum and millet; vine crops such as table and wine grapes; field crops such as oilseed rape (canola), sunflower; sugar beets, sugar cane, soybean, peanuts (groundnut), tobacco, alfafa, clover, lespedeza, trefoil and vetch; pome fruits such as apple, pear, crabapple, loquat, mayhaw and quince; stone fruits such as peaches, cherries, plums, apricots, nectarines and almonds; citrus fruits such as lemons, limes, oranges, grapefruit, mandarin (tangerines) and kumquat; root and tuber vegetables and field crops (and their foliage) such as artichoke, garden and sugar beet, carrot, cassava, ginger, ginseng, horseradish, parsnip, potato, radish, rutabaga, sweet potato, turnip and yam; bulb vegetables such as garlic, leek, onion and shallot; leafy vegetables such as arugula (roquette), celery, celery, cress, endive (escarole), fennel, head and leaf lettuce, parsley, radicchio (red chicory), rhubarb, spinach and Swiss chard; brassica (cole) leafy vegetables such as broccoli, broccoli raab (rapini), Brussels sprouts, cabbage, bok choy, cauliflower, collards, kale, kohlrabi, mustard and greens; legume vegetables (succulent or dried) such as lupin, bean (*Phaseolus* spp.) (including field bean, kidney bean, lima bean, navy bean, pinto bean, runner bean, snap bean, tepary bean and wax bean), bean (*Vigna* spp.) (including adzuki bean, asparagus bean, blackeyed pea, catjang, Chinese longbean, cowpea, crowder pea, moth bean, mung bean, rice bean, southern pea, urd bean and yardlong bean), broad bean (fava), chickpea (garbanzo), guar, jackbean, lablab bean, lentil and pea (*Pisum* spp.) (including dwarf pea, edible-podded pea, English pea, field pea, garden pea, green pea, snowpea, sugar snap pea, pigeon pea and soybean); fruiting vegetables such as eggplant, groundcherry (*Physalis* spp.), pepino and pepper (including bell pepper, chili pepper, cooking pepper, pimento, sweet pepper; tomatillo and tomato); cucurbit vegetables such as Chayote (fruit), Chinese waxgourd (Chinese preserving melon), citron melon, cucumber, gherkin, edible gourd (including hyotan, cucuzza, hechima, and Chinese okra), *Momordica* spp. (including balsam apple, balsam pear, bittermelon and Chinese cucumber), muskmelon (including cantaloupe and pumpkin), summer and winter squash (including butternut squash, calabaza, hubbard squash, acorn squash, spaghetti squash) and watermelon; berries such as blackberry (including bingleberry, boysenberry, dewberry, lowberry, marionberry, olallieberry and youngberry), blueberry, cranberry, currant, elderberry, gooseberry, huckleberry, loganberry,

raspberry and strawberry; tree nuts such as almond, beech nut, Brazil nut, butternut, cashew, chestnut, chinquapin, filbert (hazelnut), hickory nut, macadamia nut, pecan and walnut; tropical fruits and other crops such as bananas, plantains, mangos, coconuts, papaya, guava, avocado, lichee, agave, coffee, cacao, sugar cane, oil palm, sesame, rubber and spices; fiber crops such as cotton, flax and hemp; turfgrasses (including warm- and cool-season turfgrasses) such as bentgrass, Kentucky bluegrass, St. Augustine grass, tall fescue and Bermuda grass.

These pathogens include: Oomycetes, including *Phytophthora* pathogens such as *Phytophthora infestans*, *Phytophthora megasperma*, *Phytophthora parasitica*, *Phytophthora cinnamomi* and *Phytophthora capsici*, *Pythium* pathogens such as *Pythium aphanidermatum*, and pathogens in the Peronosporaceae family such as *Plasmopara viticola*, *Peronospora* spp. (including *Peronospora tabacina* and *Peronospora parasitica*), *Pseudoperonospora* spp. (including *Pseudoperonospora cubensis)* and *Bremia lactucae*; Ascomycetes, including *Alternaria* pathogens such as *Alternaria solani* and *Alternaria brassicae*, *Guignardia* pathogens such as *Guignardia bidwelli*, *Venturia* pathogens such as *Venturia inaequalis*, *Septoria* pathogens such as *Septoria nodorum* and *Septoria tritici*, powdery mildew disease pathogens such as *Blumeria* spp. (including *Blumeria graminis*) and *Erysiphe* spp. (including *Erysiphe polygoni*), *Uncinula necatur*, *Sphaerotheca fuligena* and *Podosphaera leucotricha*, *Pseudocercosporella herpotrichoides*, *Botrytis* pathogens such as *Botrytis cinerea*, *Monilinia fructicola*, *Sclerotinia* pathogens such as *Sclerotinia sclerotiorum*, *Magnaporthe grisea*, *Phomopsis viticola*, *Helminthosporium* pathogens such as *Helminthosporium tritici repentis*, *Pyrenophora teres*, anthracnose disease pathogens such as *Glomerella* or *Colletotrichum* spp. (such as *Colletotrichum graminicola* and *Colletotrichum orbiculare*), and *Gaeumannomyces graminis*; Basidiomycetes, including rust diseases caused by *Puccinia* spp. (such as *Puccinia recondita*, *Puccinia striiformis*, *Puccinia hordei*, *Puccinia graminis* and *Puccinia arachidis)*, *Hemileia vastatrix* and *Phakopsora pachyrhizi*; other pathogens including *Rhizoctonia* spp. (such as *Rhizoctonia solani and Rhizoctonia oryzae)*; *Fusarium* pathogens such as *Fusarium roseum*, *Fusarium graminearum* and *Fusarium oxysporum*; *Verticillium dahliae*; *Sclerotium rolfsii*; *Rynchosporium secalis*; *Cercosporidium personatum*, *Cercospora arachidicola* and *Cercospora beticola; Rutstroemia floccosum* (also known as *Sclerontina homoeocarpa*); and other genera and species closely related to these pathogens. Commonly, pathogens are referred to as diseases, and thus in the preceding sentence the word "pathogen" also refers to the plant disease caused by the pathogen. More precisely, plant diseases are caused by pathogens. Therefore, for example, powdery mildew diseases are plant diseases caused by powdery mildew pathogens, *Septoria* diseases are plant diseases caused by *Septoria* pathogens, and rust diseases are plant diseases caused by rust disease pathogens. Certain fungicidal compounds are also bactericidal, and therefore in addition to their fungicidal activity, the compositions or combinations can also have activity

against bacteria such as *Erwinia amylovora*, *Xanthomonas campestris*, *Pseudomonas syringae*, and other related species.

Remarkably, 2,6-substituted aniline-pyrazole compounds of Formula **1** (i.e. Formula **1** wherein X is NH, and R^1 and R^3 are other than H) wherein R^2 is H have now been discovered to have significantly improved pharmacokinetic properties compared to corresponding compounds wherein R^2 is other than H. In particular in vertebrate animals, compounds wherein R^2 is H instead of other than H have been found to have a significantly diminished distribution into fat, thereby reducing the possibility of bioaccumulation. Illustrative of 2,6-substituted aniline-pyrazole compounds of Formula **1** wherein R^2 is H are Compounds 239, 240, 241, 244, 245, 247, 252, 253, 254, 257, 258, 259, 260, 261, 262, 263, 264, 265, 266, 267, 268, 269, 270, 271, 273, 275 and 276 identified in Index Table A. Furthermore, in addition to having more favorable pharmacokinetic properties in vertebrate animals, 2,6-substituted anilino-pyrazole compounds of Formula **1** wherein R^1 is halogen, or more particularly Cl or Br, and R^3 is F or Cl, or more particularly F, have been discovered to retain remarkably high activity when R^2 is H against plant fungal diseases, such as caused by *Septoria tritici*.

The pharmacokinetic properties of compounds of Formula **1** can be measured using a wide variety of assay protocols known in the science of pharmacology. In one illustrative method involving a single oral dose, three male and three female rats receive a single dose of a test substance via oral gavage. Approximately 0.25 mL of blood is collected via tail vein immediately prior to dosing, and then at 0.25, 0.5, 1, 2, 4, 8, 12, 24 h and every 24 h thereafter until sacrifice. At sacrifice, fat is also collected to determine the fat:plasma ratio at sacrifice. Blood is collected into tubes that contain ethylenediaminetetracetic acid (EDTA) and centrifuged at 2500 x g in order to separate plasma from blood cells. The plasma is then extracted by protein precipitation using, for example, acetonitrile and a protein precipitation plate (e.g., Strata Impact Protein Precipitation Plate, part number CEO-7565 of Phenomenex, Torrance, CA, U.S.A.) following directions provided for the plate. Alternatively, the plasma is extracted just with acetonitrile, vortexed (i.e. mixed using a vortex mixer), and centrifuged to pellet the proteins. After removal of the proteins, the plasma is analyzed for parent compound and/or metabolites by liquid chromatography-mass spectrometry (LC/MS). The fat is homogenized and extracted by an organic solvent such as acetonitrile. The extract is then analyzed for parent compound and/or metabolites by LC/MS. The plasma pharmacokinetic data is then analyzed using nonlinear modeling software (e.g., WinNonlin™ from Pharsight, Cary, NC, U.S.A.) to determine half-life of the administered compound in plasma, the time after administration when the maximum plasma concentration is reached (T_{max}), the maximum plasma concentration (C_{max}) and the area under the plasma concentration curve (AUC). As analysis of fat requires rat sacrifice, fat data is obtained at single time points (i.e.the time of rat sacrifice). However, by using

multiple rats sacrificed after different intervals from time of dosing, such parameters as C_{max} for fat are determined. Using the above described method, Compounds 239, 240 and 241 identified in Index Table A are found to have a significantly diminished distribution into fat compared to corresponding compounds wherein R^2 is other than H.

In the present fungicidal compositions, the Formula **1** compounds of component (a) can work synergically with the additional fungicidal compounds of component (b) to provide such beneficial results as broadening the spectrum of plant diseases controlled, extending duration of preventative and curative protection, and suppressing proliferation of resistant fungal pathogens. In particular embodiments, compositions are provided in accordance with this invention that comprise proportions of component (a) and component (b) that are especially useful for controlling particular fungal diseases (such as *Alternaria solani*, *Blumeria graminis* f. sp. *tritici*, *Botrytis cinerea*, *Puccinia recondita* f. sp. *tritici*, *Rhizoctonia solani*, *Septoria nodorum*, *Septoria tritici*).

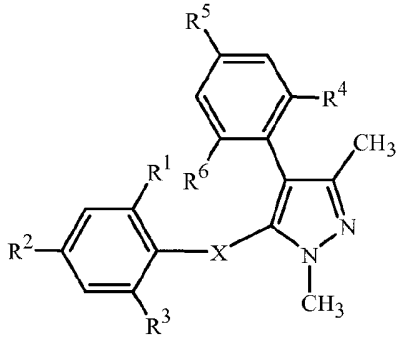
Mixtures of fungicides may also provide significantly better disease control than could be predicted based on the activity of the individual components. This synergism has been described as "the cooperative action of two components of a mixture, such that the total effect is greater or more prolonged than the sum of the effects of the two (or more) taken independently" (see P. M. L. Tames, *Neth. J. Plant Pathology* **1964**, *70*, 73–80). In methods providing plant disease control in which synergy is exhibited from a combination of active ingredients (e.g., fungicidal compounds) applied to the plant or seed, the active ingredients are applied in a synergistic weight ratio and synergistic (i.e. synergistically effective) amounts. Measures of disease control, inhibition and prevention cannot exceed 100%. Therefore expression of substantial synergism typically requires use of application rates of active ingredients wherein the active ingredients separately provide much less than 100% effect, so that their additive effect is substantially less than 100% to allow the possibility of increase in effect as result of synergism. On the other hand, application rates of active ingredients that are too low may show not show much activity in mixtures even with the benefit of synergism. One skilled in the art can easily identify and optimize through simple experimentation the weight ratios and application rates (i.e. amounts) of fungicidal compounds providing synergy.

The following Tests include tests demonstrating the efficacy of the present compounds for controlling specific pathogens; this efficacy is thus provided to fungicidal mixtures comprising the present compounds. The following Tests also include tests demonstrating the control efficacy of the mixtures of this invention on specific pathogens. The disease control afforded by the present compounds alone or in mixtures is not limited, however, to the pathogenic fungi species exemplified.

See Index Table A for compound descriptions. See Index Table B for melting point data. See Index Table C for ^{1}H NMR data. The following abbreviations are used in the

Index Tables which follow: Me is methyl, MeO is methoxy, EtO is ethoxy, and -CN is cyano. Because of symmetry, R^1 can be interchanged with R^3, and R^4 can be interchanged with R^6, if allowed by the definitions of R^1, R^3, R^4 and R^6. The abbreviation "Cmpd." stands for "Compound", and the abbreviation "Ex." stands for "Example" and is followed by a number indicating in which Synthesis Example the compound is prepared. Mass spectra (M.S.) 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 mass spectrometry using atmospheric pressure chemical ionization (AP^+). The presence of molecular ions containing one or more higher atomic weight isotopes of lower abundance (e.g., ^{37}Cl, ^{81}Br) is not reported.

INDEX TABLE A



Cmpd No.	R^1	R^2	R^3	R^4	R^5	R^6	X	M.S.
1	F	H	H	Cl	F	H	NH	334
2	F	F	H	Cl	F	H	NH	352
3 (Ex. 1)	F	MeO	F	Cl	F	H	NH	**
4	F	F	F	Cl	F	H	NH	370
5	F	MeO	H	Cl	F	H	O	365
6	F	F	H	F	MeO	F	NH	366
7 (Ex. 2)	F	F	F	F	MeO	F	NH	**
8 (Ex. 6)	F	-CN	F	F	F	F	O	**
9	Cl	Cl	H	F	F	F	O	387
10	Cl	Cl	H	F	MeO	F	O	399
11	F	F	F	F	F	H	NH	354
12	F	MeO	F	F	F	H	NH	366
13 (Ex. 3)	F	-CN	F	Cl	F	H	O	**
14	F	-CN	F	F	MeO	H	O	374
15	F	Cl	F	F	MeO	F	O	***

Cmpd No.	R^1	R^2	R^3	R^4	R^5	R^6	X	M.S.
16	F	MeO	F	Cl	Cl	H	NH	398
17 (Ex. 4)	F	F	H	Cl	Cl	H	NH	**
18	F	F	F	Cl	Cl	H	NH	386
19	F	MeO	F	F	F	F	NH	384
20	F	-CN	F	F	MeO	F	NH	391
21	F	MeO	F	F	MeO	F	NH	396
22	F	H	F	F	MeO	F	O	367
23	Cl	F	H	F	MeO	F	NH	382
24	F	Br	F	F	MeO	F	O	447
25	F	-CN	F	Cl	F	H	NH	377
26	F	-CN	F	F	F	F	NH	379
27	F	-CN	H	F	F	F	O	362
28	Cl	-CN	H	F	F	F	O	378
29	F	F	F	Cl	MeO	H	NH	382
30	F	F	H	F	-CN	F	NH	361
31	Cl	F	H	F	-CN	F	NH	*
32	Cl	-CN	H	F	MeO	F	NH	389
33	F	-CN	H	Cl	F	H	O	360
34	F	-CN	H	F	F	F	NH	361
35	F	F	F	F	-CN	F	NH	*
36	F	MeO	F	F	-CN	F	NH	*
37	Cl	-CN	H	Cl	F	H	O	376
38	F	-CN	F	F	MeO	F	O	392
39	F	F	H	F	EtO	F	NH	380
40	F	Cl	H	F	-CN	F	NH	*
41	F	-CN	F	Cl	MeO	H	O	390
42	F	F	H	Cl	MeO	H	NH	364
43	F	H	F	Cl	MeO	H	NH	364
44	Cl	-CN	H	Cl	F	H	NH	375
45	F	-CN	F	F	F	H	O	362
46	F	H	F	Cl	F	H	NH	352
47	Cl	F	H	Cl	F	H	NH	368

Cmpd No.	R^1	R^2	R^3	R^4	R^5	R^6	X	M.S.
48	F	F	H	Cl	H	F	NH	352
49	F	F	H	F	H	F	NH	*
50	Cl	Cl	H	F	H	F	NH	*
51	F	MeO	H	F	H	F	NH	*
52	F	F	H	F	H	H	NH	318
53	F	F	F	F	H	H	NH	336
54	F	MeO	F	F	H	H	NH	348
55	F	MeO	F	Cl	H	F	NH	382
56	F	F	F	Cl	H	F	NH	369
57	F	-CN	F	Cl	H	F	NH	377
58	Cl	F	H	Cl	H	F	NH	368
59	F	-CN	H	F	H	F	NH	343
60	Cl	MeO	H	F	H	F	NH	*
61	Cl	F	H	F	F	H	NH	*
62	F	F	H	F	MeO	F	CHOH	381
63	F	MeO	H	F	F	H	NH	*
64	F	F	H	F	F	H	NH	336
65	F	-CN	F	Br	F	H	O	423
66	Cl	MeO	H	F	F	H	NH	*
67	Cl	Cl	H	F	F	H	NH	*
68	F	-CN	H	F	F	H	NH	*
69	F	H	F	F	H	F	NH	*
70	F	F	F	Br	H	H	NH	398
71	F	H	F	F	F	H	NH	*
72	F	MeO	F	F	H	F	NH	*
73	Br	F	H	Cl	F	H	NH	413
74	F	F	F	Br	F	H	NH	415
75	F	-CN	F	Cl	H	H	O	*
76	F	-CN	F	Br	H	H	O	*
77	Cl	Cl	H	Cl	MeO	H	NH	397
78	Cl	Cl	H	Cl	H	F	NH	386
79	F	-CN	H	Br	F	H	O	406

Cmpd No.	R^1	R^2	R^3	R^4	R^5	R^6	X	M.S.
80	Cl	-CN	H	Br	F	H	O	422
81	F	Cl	F	Cl	F	H	NH	386
82	Cl	F	F	Cl	F	H	NH	386
83	F	-CN	F	F	F	H	NH	*
84	Cl	F	F	Br	F	H	NH	431
85	Cl	MeO	Cl	Cl	F	H	NH	413
86	Cl	F	F	F	H	F	NH	370
87	Cl	F	F	Cl	H	F	NH	386
88	Cl	Cl	H	Cl	F	H	NH	383
89	F	F	F	F	H	F	NH	*
90	F	-CN	F	F	H	F	NH	*
91	F	-CN	F	F	H	H	O	*
92	F	-CN	H	Cl	MeO	H	O	372
93	Cl	-CN	H	Cl	MeO	H	O	388
94	F	F	H	Br	F	H	NH	398
95	Br	F	H	Br	F	H	NH	458
96	Cl	F	H	Br	F	H	NH	414
97	F	F	H	Cl	H	H	NH	334
98	Cl	F	Cl	Br	F	H	NH	448
99	Cl	-CN	H	Br	MeO	H	O	433
100	F	-CN	H	Br	MeO	H	O	418
101	Cl	MeO	H	Cl	F	H	NH	380
102	Cl	MeO	Cl	Br	F	H	NH	459
103	Cl	MeO	H	Br	F	H	NH	425
104	Cl	EtO	H	Cl	F	H	NH	394
105	Cl	Cl	H	Cl	H	Cl	NH	*
106	F	-CN	F	Cl	F	F	NH	395
107	F	F	H	Cl	-CN	H	NH	359
108	Cl	F	F	Cl	-CN	H	NH	393
109	Cl	F	H	Cl	H	Cl	NH	*
110	F	H	F	Cl	-CN	H	NH	359
111	F	Cl	F	Cl	-CN	H	NH	393

Cmpd No.	R^1	R^2	R^3	R^4	R^5	R^6	X	M.S.
112	Cl	F	H	Cl	-CN	H	NH	375
113	F	F	H	Cl	H	Cl	NH	*
114	Br	F	H	Cl	H	Cl	NH	*
115	Cl	F	Cl	Cl	H	Cl	NH	*
116	F	-CN	H	Cl	H	F	O	360
117	Cl	F	F	F	F	H	NH	369
118	Br	F	H	F	F	H	NH	398
119	F	-CN	H	F	Cl	H	O	360
120	Br	F	Cl	F	F	H	NH	432
121	F	Cl	F	F	H	F	NH	370
122 (Ex. 5)	F	F	H	Cl	F	H	CHOH	**
123	Cl	F	H	Cl	F	H	CHOH	383
124	F	H	F	Cl	Cl	H	NH	*
125	Cl	F	H	Cl	Cl	H	NH	*
126	F	Cl	F	F	F	H	NH	370
127	Cl	-CN	H	F	H	F	O	360
128	F	-CN	H	F	F	H	O	376
129	F	Cl	F	Br	F	H	NH	432
130	F	-CN	H	F	H	F	O	344
131	Cl	-CN	H	Cl	Cl	H	O	394
132	Cl	F	Cl	Cl	Cl	H	NH	*
133	F	Br	F	F	F	H	NH	416
134	F	Br	F	Cl	F	H	NH	432
135	F	Br	H	Cl	F	H	NH	414
136	Cl	Cl	F	Cl	F	H	NH	402
137	Cl	F	Cl	F	F	H	NH	386
138	Cl	F	Cl	Cl	F	H	NH	404
139	Br	-CN	H	F	F	H	O	406
140	Cl	-CN	H	F	F	H	O	360
141	Cl	Cl	F	F	F	H	NH	386
142	Cl	F	Cl	F	H	F	NH	386
143	Br	F	F	F	F	H	NH	416

Cmpd No.	R^1	R^2	R^3	R^4	R^5	R^6	X	M.S.
144	Br	F	F	Cl	F	H	NH	432
145	F	Br	F	F	H	F	NH	416
146	Br	F	F	F	H	F	NH	416
147	Br	F	F	Cl	H	F	NH	
148	F	Cl	F	Cl	F	H	CHOH	401 ‡
150	F	Cl	F	F	-CN	H	NH	377
151	Cl	F	F	Cl	F	H	CHOH	
152	Br	F	H	F	F	H	CHOH	
153	Br	F	H	Cl	F	H	CHOH	427 †
154	F	Br	H	F	F	H	NH	396
155	Cl	Br	Cl	F	F	H	NH	448
156	Cl	F	F	Cl	Cl	H	NH	*
157	F	Cl	F	Cl	Cl	H	NH	*
158	F	Cl	H	Cl	F	H	O	369
159	F	-CN	H	F	F	H	O	344
160	F	Cl	H	F	F	H	NH	352
161	Cl	Cl	F	F	F	H	NH	386
162	F	Cl	H	F	H	F	NH	352
163	F	Br	F	Br	F	H	NH	474
164	Cl	Br	Cl	Cl	F	H	NH	464
165	Cl	Cl	Cl	F	F	H	NH	404
167	Cl	Br	H	F	F	H	NH	414
168	Cl	Br	Cl	Br	F	H	NH	508
169	F	Br	H	Br	F	H	NH	458
170	Cl	Cl	Cl	Cl	F	H	NH	420
172	Cl	Br	H	Cl	F	H	NH	430
173	Cl	Br	H	Br	F	H	NH	474
174	Cl	Cl	Cl	Br	F	H	NH	464
175	I	F	H	F	F	H	NH	444
177	F	Cl	H	Cl	F	H	CHOH	384
178	F	F	F	Cl	F	H	CHOH	385
179	F	-CN	H	Cl	F	H	CHOH	374

Cmpd No.	R^1	R^2	R^3	R^4	R^5	R^6	X	M.S.
180	F	Cl	I	F	F	H	NH	478
181	I	F	H	Cl	F	H	NH	460
182	F	Cl	I	Cl	F	H	NH	494
183	Br	Br	H	Cl	F	H	NH	474
184	Br	Br	H	F	F	H	NH	458
185	F	Cl	F	F	MeO	H	NH	382
186	F	Cl	Br	Cl	F	H	NH	448
187	F	F	Cl	F	MeO	H	NH	396
188	F	F	Cl	F	EtO	H	NH	396
189	F	Cl	F	F	EtO	H	NH	396
190	F	Cl	Cl	F	EtO	H	NH	412
191	F	Cl	Cl	F	MeO	H	NH	398
192	Cl	F	Cl	F	EtO	H	NH	412
193	F	F	H	F	EtO	H	NH	***
194	Cl	F	Cl	F	MeO	H	NH	398
195	Br	F	F	Br	F	H	NH	476
196	F	F	Cl	F	EtO	F	NH	414
197	Cl	Cl	I	Cl	F	H	NH	512
198	Cl	Cl	F	F	EtO	F	NH	430
199	F	Cl	F	F	EtO	F	NH	414
200	Cl	F	Cl	F	EtO	F	NH	430
201	F	Cl	Cl	Cl	MeO	H	NH	416
202	F	Cl	Cl	Cl	EtO	H	NH	430
203	F	F	Cl	Cl	MeO	H	NH	398
204	F	Cl	F	Cl	MeO	H	NH	398
205	Cl	F	Cl	Cl	MeO	H	NH	416
206	F	F	Cl	Cl	EtO	H	NH	412
207	F	Cl	F	Cl	EtO	H	NH	412
208	Cl	F	Cl	Cl	EtO	H	NH	430
209	F	F	H	Cl	EtO	H	NH	378
210	Cl	Cl	I	F	F	H	NH	494
211	Br	Br	F	F	F	H	NH	476

Cmpd No.	R^1	R^2	R^3	R^4	R^5	R^6	X	M.S.
212	Br	Br	F	Cl	F	H	NH	492
213	F	F	I	Cl	F	H	NH	478
214	F	F	I	F	F	H	NH	462
215	F	F	I	Br	F	H	NH	524
216	F	I	F	F	F	H	NH	462
217	F	I	F	Cl	F	H	NH	478
218	F	I	F	Br	F	H	NH	524
219	I	F	F	Cl	MeO	H	NH	490
220	F	I	F	Cl	MeO	H	NH	490
221	F	F	Br	Cl	MeO	H	NH	444
222	Cl	Cl	F	I	F	H	NH	494
223	Br	Br	F	I	F	H	NH	584
224	F	Cl	F	Cl	MeO	H	CHOH	413
225	F	Cl	F	I	F	H	NH	478
226	Br	F	F	I	F	H	NH	524
227	Cl	F	Cl	F	Cl	H	NH	*
228	Cl	F	F	F	Cl	H	NH	*
229	Br	F	F	F	Cl	H	NH	*
230	F	Cl	F	F	Cl	H	NH	*
231	F	Cl	Cl	F	Cl	H	NH	*
232	Cl	F	H	F	Br	H	NH	*
233	Cl	F	Cl	F	Br	H	NH	*
234	Cl	F	F	F	Br	H	NH	*
235	Br	F	F	F	Br	H	NH	*
236	F	Cl	F	F	Br	H	NH	*
237	F	Cl	Cl	F	Br	H	NH	*
238	Cl	F	F	F	-CN	H	NH	*
239	Cl	H	F	Cl	F	H	NH	*
240 (Ex. 7)	Cl	H	F	Br	F	H	NH	414
241	Br	H	F	Cl	F	H	NH	414
242	Br	H	H	Br	F	H	NH	440
243	I	H	H	Br	F	H	NH	488

Cmpd No.	R^1	R^2	R^3	R^4	R^5	R^6	X	M.S.
244	Br	H	F	Br	F	H	NH	*
245	Br	H	F	F	F	H	NH	*
246	I	H	H	F	F	H	NH	426
247	Br	H	F	F	H	F	NH	*
248	Cl	F	H	F	-CN	H	NH	***
249	Cl	F	Cl	F	-CN	H	NH	*
250	-CN	F	F	F	-CN	H	NH	*
251	Cl	H	Cl	F	F	H	NH	367
252	Me	H	F	Cl	F	H	NH	348
253	Me	H	Cl	Cl	F	H	NH	364
254	Me	H	Br	Cl	F	H	NH	410
255	Cl	H	Cl	Cl	F	H	NH	*
256	Cl	H	Cl	Br	F	H	NH	*
257	Me	H	Cl	F	MeO	H	NH	360
258	Me	H	Br	F	MeO	H	NH	406
259	Me	H	F	F	MeO	H	NH	344
260	Cl	H	F	F	MeO	H	NH	364
261	Br	H	F	F	MeO	H	NH	410
262	Me	H	Cl	Cl	MeO	H	NH	376
263	Me	H	Br	Cl	MeO	H	NH	422
264	Cl	H	F	Cl	MeO	H	NH	380
265	Me	H	Br	F	F	H	NH	394
266	Me	H	Br	Br	F	H	NH	454
267	Me	H	F	Br	F	H	NH	394
268	Me	H	F	F	F	H	NH	332
269	Me	H	Cl	F	F	H	NH	348
270	Me	H	Me	F	F	H	NH	328
271	Me	H	Me	Cl	F	H	NH	344
272	Cl	H	H	Br	F	H	NH	396
273	Br	H	F	Cl	MeO	H	NH	426
274	Br	H	H	Cl	F	H	NH	396
275	Cl	H	F	F	F	H	NH	352

Cmpd No.	R^1	R^2	R^3	R^4	R^5	R^6	X	M.S.
276	Me	H	Cl	Br	F	H	NH	410

* Melting Point (MP) data are listed in Index Table B.

** AP^+ data or ^1H NMR data are listed in the Synthesis Examples.

*** ^1H NMR data are listed in Index Table C.

† Parent ion (M), not M+1, peak was observed.

‡ 402 (M+2) peak was also observed.

INDEX TABLE B

Cmpd No.	Melting Point [a]	Cmpd No.	Melting Point	Cmpd No.	Melting Point
31	80–82	72	172–174	156	181–183
35	160–162	75	132–135	157	155–157
36	228–230	76	132–134	227	183–184
40	93–95	83	181–183	228	180–182
49	110–112	89	178–180	229	154–155
50	105–107	90	168–170	230	190–191
51	130–132	91	101–105	231	154–155
60	109–111	114	137–139	238	177–179
61	57–59	115	151–153	239	166–168
63	133–135	124	169–171	244	154–156
66	91–93	125	111–113	245	149–151
67	82–84	132	229–231	247	127–129
68	182–184	232	88–89	249	200–202
69	156–158	233	186–187	250	200–202
71	171–173	234	182–183	255	183–185
105	118–120	235	167–169	256	199–201
109	117–119	236	199–201		
113	135–136	237	160–162		

[a] Melting point data are °C.

INDEX TABLE C

Cmpd No.	^1H NMR Data ($CDCl_3$ solution unless indicated otherwise)[a]
15	δ 6.74 (m, 2H), 6.30 (m, 2H), 3.83 (s, 3H), 3.75 (s, 3H), 2.03 (s, 3H).
193	δ 7.01 (m, 1 H) 6.79 (ddd, 1H) 6.63 (m, 3 H) 6.34 (td, 1H) 5.34 (br s, 1H) 3.99 (m, 2H) 3.68 (s, 3H) 2.23 (s, 3H) 1.39 (m, 3H).
248	δ 7.30 (m, 2H), 7.25–7.30 (m, 1H), 7.08 (m, 1H), 6.76 (m, 1H), 6.28 (m, 1H), 5.67 (br s, 1H), 3.69 (s, 3H), 2.27 (s, 3H).

[a] ^{1}H NMR data are in ppm downfield from tetramethylsilane. Couplings are designated by (s)-singlet, (br s)-broad singlet, (ddd)-doublet of doublets of doublets, (td)-triplet of doublets and (m)-multiplet.

BIOLOGICAL EXAMPLES OF THE INVENTION

General protocol for preparing test suspensions for Tests A–I: the test compounds were 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 Trem® 014 (polyhydric alcohol esters). The resulting test suspensions were then used in Tests A–I. Each test was conducted in triplicate, and the results were averaged. Spraying a 200 ppm test suspension to the point of run-off on the test plants was the equivalent of a rate of about 800 g/ha. Unless otherwise indicated, the rating values indicate a 200 ppm test suspension was used. (An asterisk "*" next to the rating value indicates a 40 ppm test suspension was used.)

TEST A

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 saturated atmosphere at 20 °C for 48 h, and then moved to a growth chamber at 24 °C for 3 additional days, after which time visual disease ratings were made.

TEST B

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 5 days, after which time visual disease ratings were made.

TEST C

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 *Phytophthora infestans* (the causal agent of tomato late blight) and incubated in a saturated atmosphere at 20 °C for 24 h, and then moved to a growth chamber at 20 °C for 5 days, after which time visual disease ratings were made.

TEST D

The test suspension was sprayed to the point of run-off on creeping bent grass (*Agrostis* sp.) seedlings. The following day the seedlings were inoculated with a bran and mycelial slurry of *Rhizoctonia solani* (the causal agent of turf brown patch) and incubated in a saturated atmosphere at 27 °C for 48 h, and then moved to a growth chamber at 27 °C for 3 days, after which time disease ratings were made.

TEST E

The test suspension was sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore suspension of *Septoria nodorum* (the causal agent of *Septoria* glume blotch) and incubated in a saturated atmosphere at 24 °C for 48 h, and then moved to a growth chamber at 20 °C for 9 days, after which time visual disease ratings were made.

TEST F

The test suspension was sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore suspension of *Septoria tritici* (the causal agent of wheat leaf blotch) and incubated in saturated atmosphere at 24 °C for 48 h. and then the seedlings were moved to a growth chamber at 20 °C for 19 additional days, after which time visual disease ratings were made.

TEST G

Wheat 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 2 days. At the end of this time the test suspension was sprayed to the point of run-off, and then the seedlings were moved to a growth chamber at 20 °C for 4 days after which time visual disease ratings were made.

TEST H

The test suspension 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 6 days, after which time visual disease ratings were made.

TEST I

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 ratings were made.

Results for Tests A–I are given in Table A. In the Table, a rating of 100 indicates 100% disease control and a rating of 0 indicates no disease control (relative to the controls). A hyphen (-) indicates no test results.

TABLE A

Cmpd No.	Test A	Test B	Test C	Test D	Test E	Test F	Test G	Test H	Test I
1	99	93	0	99	0	100	-	99	100

Cmpd No.	Test A	Test B	Test C	Test D	Test E	Test F	Test G	Test H	Test I
2	99	100	0	98	64	100	-	100	99
3	100	100	-	-	93	97	96	100	100
4	99	100	-	-	99	95	99	100	100
5	98	100	-	-	97	97*	-	100	99
6	98	100	-	-	99	93	92	100	100
7	98	100	-	-	0	94	9	97	100
8	99*	98*	-	-	0*	47*	15*	79*	60*
9	99	9	-	-	0	97	0	99	99
10	99	0	-	-	0	94	92	99	99
11	100	99	-	-	90	94	0	100	99
12	100	0	-	-	0	93	0	94	82
13	100	100	-	-	100	100	7	100	100
14	99	100	-	-	99	100	37	100	99
15	98	100	-	-	89	98	82	100	100
16	99	98	-	-	84	98	98	99	99
17	100	73	-	-	60	99	91	99	100
18	100	98	-	-	98	99	95	99	97
19	99	82	-	-	0	98	0	89	91
20	100	100	-	-	40	99	0	68	13
21	100	100	-	-	89	99	99	96	94
22	100	100	-	-	78	100	98	100	99
23	100	100	-	-	95	98	85	99	100
24	99	95	-	-	84	100	0	98	100
25	100	99	-	-	95	99	0	100	100
26	100	100	-	-	99	100	41	99	100
27	99	99	-	-	99	100	9	99	100
28	100	17	-	-	69	100	26	99	99
29	100	99	-	-	97	99	99	99	100
30	100	99	-	-	90	100	82	99	100
31	100	98	-	-	99	99	53	100	100
32	99	97	-	-	82	100	11	98	97
33	100	100	-	-	98	100	99	100	99
34	100	99	9	-	94	100	0	99	99
35	100	100	-	-	60	99	0	100	94
36	99	0	-	-	0	99	0	41	0
37	100	86	-	-	100	100	69	99	100
38	99	94	-	-	87	99	0	96	97

Cmpd No.	Test A	Test B	Test C	Test D	Test E	Test F	Test G	Test H	Test I
39	99	99	-	-	98	100	0	99	100
40	99	99	-	-	100	100	63	100	100
41	100	99	-	-	100	100	92	100	99
42	98	99	-	-	0	99	8	100	100
43	98	100	-	-	0	100	95	100	98
44	99	0	-	-	0	99	8	98	94
45	100	99	0	-	99	98	0	100	99
46	100	100	-	-	87	100	0	99	100
47	100	99	0	-	82	96	93	99	100
48	100	100	-	-	73	98	0	83	100
49	100	100	-	-	80	98	0	83	100
50	100	99	-	-	73	95	0	93	100
51	100	99	-	-	0	98	0	68	100
52	94	44	-	-	0	100	0	60	98
53	97	99	-	-	87	100	0	95	99
54	97	100	-	-	67	99	27	94	99
55	99	99	-	-	80	100	94	100	99
56	98	100	-	-	0	100	0	97	99
57	97	100	-	-	73	100	0	99	99
58	99	100	-	-	0	100	32	99	100
59	99	94	0	-	73	100	9	98	98
60	99	97	-	-	20	100	18	97	99
61	100	93	-	-	64	100	0	99	100
62	100	100	-	-	99	100	0	99	99
63	99	99	-	-	0	99	0	80	99
64	99	99	-	-	0	100	0	97	100
65	100	99	-	-	99	100	0	100	100
66	99	37	-	-	0	100	0	91	100
67	100	64	-	-	0	100	0	97	100
68	99	51	-	-	0	100	0	80	100
69	100	99	-	-	60	100	0	99	100
70	99	26	-	-	73	100	0	99	100
71	99	99	-	-	96	100	0	99	100
72	100	99	-	-	0	100	0	97	98
73	100	99	-	-	78	100	90	100	100
74	100	100	-	-	98	100	0	100	100
75	100	99	-	-	99	100	0	99	98

Cmpd No.	Test A	Test B	Test C	Test D	Test E	Test F	Test G	Test H	Test I
76	100	97	-	-	99	99	0	99	99
77	99	98	-	-	0	99*	0	99	100
78	99	65	-	-	0	99*	9	99	100
79	99	99	-	-	100	100*	28	100	100
80	98	0	-	-	60	100*	9	99	99
81	100	99	0	-	90	100	99	100	100
82	99	100	0	-	100	100	97	100	100
83	100	99	-	-	87	100	0	100	100
84	100	99	-	-	96	100	92	100	100
85	99	0	-	-	0	100	0	99	99*
86	100	99	-	-	90	100	0	100	100
87	100	93	-	-	87	100	0	100	100
88	100	95	-	-	51	100*	41	100	100
89	100	99	-	-	82	100	9	99	100
90	99	87	-	-	87	100	0	98	99
91	99	99	-	-	94	100	0	99	99
92	100	99	-	-	99	100	0	99	96
93	100	0	-	-	60	100	0	99	91
95	100	97	-	-	51	100	91	100	100
96	100	95	-	-	0	100	94	100	100
97	99	99	-	-	0	100	0	96	100
98	99	0	-	-	0	99	9	99	96
99	99	0	-	-	0	100	0	97	89
100	92	88	-	-	100	100	0	99	95
101	100	93	-	-	0	100	99	100	100
102	98	0	-	-	0	98	0	94	95*
103	99	83	-	-	0	100	63	99	99
104	100	0	-	-	0	100	0	97	99
105	99	0	-	-	0	100	0	96	99
107	100	80	-	-	73	100	8	100	97
109	100	0	-	-	0	100	0	97	100
111	100	97	-	-	95	100	94	100	99
112	100	37	-	-	40	100	8	100	99
113	100	0	-	-	0	100	0	98	100
114	99	0	-	-	0	100	0	91	100
115	99	0	-	-	0	99	0	99	93
116	100	33	-	-	99	100	0	100	100

Cmpd No.	Test A	Test B	Test C	Test D	Test E	Test F	Test G	Test H	Test I
117	100	100	-	-	97	100	91	100	100
118	100	93	-	-	69	100	75	97	100
119	99	94	-	-	94	100	0	91	99
120	100	80	-	-	94	100	19	100	100
122	100	99	-	-	92	100	96	100	99
123	100	86	-	-	60	100	6	100	95
124	97	17	-	-	0	99	3	99	99
125	99	0	-	-	0	100	82	98	100
126	100	86	-	-	87	100	0	99	100
127	99	0	-	-	0	100	0	97	97
128	100	99	-	-	97	100	0	100	99
129	100	97	-	-	95	100	79	100	100
130	100	90	-	-	0	100	0	100	100
131	100	0	-	-	0	100	0	96	96
132	93 (Note 1)	0	-	-	0	99	0	96	43
133	99	97	-	-	88	100	0	99	100
134	100	99	-	-	64	100	74	100	100
135	100	58	-	-	0	100	9	99	100
136	100	100	0	-	100	100	100	100	100
137	100	95	-	-	87	100	87	99	100
138	100	66	0	-	0	100	17	100	99
139	82	0	-	-	0	100	9	89	0
140	67	0	-	-	0	100	9	97	97
141	99	99	-	-	99	100	97	100	100
142	100	96	0	-	92	100	0	100	100
143	100	100	0	-	100	100	100	100	100
144	100	99	-	-	100	100	100	100	100
145	99	0	0	-	0	100	0	28	90
146	-	100	0	-	100	100	74	98	100
148	100	0	-	-	60	100	0	100	64
150	100	-	-	-	-	100	-	100	100
153	-	0	-	-	0	100	0	96	0
154	100	9	-	-	0	100	68	98	99
155	100	0	-	-	0	100	94	97	99
156	100	99	-	-	73	100	31	99	99
157	100	97	0	-	87	100	27	100	99

Cmpd No.	Test A	Test B	Test C	Test D	Test E	Test F	Test G	Test H	Test I
158	100*	80*	-	-	0*	99*	37*	98*	96*
159	100*	97*	-	-	86*	100*	0*	98*	96*
160	100	99	-	-	0	100	0	99	100
161	100	99	0	-	100	99	100	100	100
162	100	88	0	-	0	100	9	100	100
163	100*	77*	-	-	60*	100*	91*	100*	100*
164	99	0	-	-	0	100	99	100	99
165	100	0	0	-	0	100	67	99	99
167	100	0	-	-	0	100	6	92	98
168	0	0	-	-	0	100	97	91	48
169	100	0	-	-	60	100	23	96	99
170	65	0	-	-	0	100	79	98	79
172	100	73	-	-	60	100	0	100	100
173	100	0	-	-	40	100	0	99	99
174	95	0	-	-	0	100	0	99	99*
175	100	97	-	-	73	100	41	100	100
177	99	0	-	-	0	-	0	0	48
178	100	33	-	-	0	-	98	100	74
179	96	16	-	-	0	-	9	99	0
180	100	100	9	-	99	100	98	100	100
181	100	99	-	-	99	100	99	99	100
182	100	100	-	-	100	100	100	100	100
183	100	0	-	-	0	100	54	96	98
184	100	58	-	-	60	100	0	98	100
185	100	99	0	-	60	100	0	99	100
186	100	100	0	-	100	100	100	100	100
187	100	100	0	-	89	-	32	100	100
188	100	99	0	-	92	-	0	98	98
189	100	88	0	-	90	-	0	98	98
190	100	82	0	-	0	-	9	96	95
191	100	99	0	-	92	-	46	99	99
192	33	66	0	-	0	100	0	65	35
193	-	58	-	-	0	100	0	27	92
194	-	93	-	-	87	100	0	95	63
195	99	100	0	-	99	100	89	100	100
196	100	100	0	-	95	100	0	94	100
197	100	77	-	-	0	100	9	97	94

Cmpd No.	Test A	Test B	Test C	Test D	Test E	Test F	Test G	Test H	Test I
198	100	100	-	-	60	100	9	80	96
199	100	100	68	-	69	100	0	83	99
200	98	97	31	-	0	100	0	86	79
201	100	100	-	-	99	100	98	100	97
202	99	77	-	-	0	100	35	92	95
203	95	100	-	-	73	100	79	100	98
204	99	99	-	-	99	100	99	100	100
205	59	31	-	-	0	100	0	99	21
206	99	100	-	-	99	100	0	99	100
207	94	99	-	-	86	100	0	94	99
208	18	0	-	-	0	99	0	85	27
209	98	95	-	-	0	100	0	92	100
210	3	0	-	-	0	100	0	97	0
211	98	99	-	-	99	100	82	100	100
212	98	100	-	-	100	100	97	100	100
213	100	100	-	-	100	100	100	100	100
214	100	100	-	-	99	100	99	99	100
215	100	100	-	-	99	100	100	100	100
216	100	0	-	-	60	100	18	95	99
217	100	58	-	-	86	100	41	99	99
218	100	68	-	-	86	100	0	99	99
219	100	100	-	-	100	100	99	100	99
220	100	69	-	-	73	100	0	97	96
221	100	100	-	-	97	100	73	99	100
222	98	77	-	-	0	100	0	90	96
223	98	88	-	-	0	100	0	97	99
224	-	100	-	-	89	100	54	100	94
225	99	68	-	-	0	100	0	99	100
226	97	97	-	-	60	100	0	99	100
227	0	0	-	-	0	100	0	95	96
228	68	40	-	-	0	100	0	96	81
229	99	99	-	-	64	100	9	97	98
230	40	0	-	-	0	100	0	94	95
231	33	58	-	-	0	100	9	94	99
232	79	-	-	-	-	100	-	90	99
233	36	-	-	-	-	100	-	91	89
234	97	-	-	-	-	100	-	91	79

Cmpd No.	Test A	Test B	Test C	Test D	Test E	Test F	Test G	Test H	Test I
235	99	-	-	-	-	100	-	96	90
236	47	-	-	-	-	100	-	28	0
237	99	-	-	-	-	100	-	92	95
238	100	-	-	-	-	100	-	100	100
239	100	100	0	-	99	100	100	100	99
240	100	-	-	-	-	100	-	100	100
241	100	-	-	-	-	100	-	100	100
242	99*	-	-	-	-	100*	-	96*	99*
243	100	-	-	-	-	100	-	99	100
244	100	-	-	-	-	100	-	100	100
245	100	-	-	-	-	100	-	100	100
246	100	-	-	-	-	100	-	98	99
247	100	-	-	-	-	100	-	100	100
248	99	-	-	-	-	100	-	99	99
249	100	-	-	-	-	100	-	98	92
250	0	-	-	-	-	100	-	100	89
251	100	-	-	-	-	100	-	100	100
252	100	-	-	-	-	100	-	100	100
253	100	-	-	-	-	100	-	100	100
254	100	-	-	-	-	100	-	100	100
255	100*	-	-	-	-	100*	-	99*	81*
256	99*	-	-	-	-	100*	-	95*	64*
257	100*	-	-	-	31*	100*	-	63*	27*
258	100*	-	-	-	0*	100*	-	9*	0*
259	100*	-	-	-	0*	100*	-	82*	90*
260	100*	-	-	-	0*	100*	-	85*	90*
261	-	-	-	-	0*	100*	-	97*	95*
262	97*	-	-	-	0*	100*	-	85*	79*
263	99*	-	-	-	0*	100*	-	79*	13*
264	100*	-	-	-	0*	100*	-	97*	81*
265	100	-	-	-	-	100	-	99	100
266	99	-	-	-	-	100	-	99	99
267	100	-	-	-	-	100	-	100	100
268	100	-	-	-	-	100	-	99	100
269	100	-	-	-	-	100	-	99	100
270	98*	-	-	-	-	100*	-	41*	91*
271	99*	-	-	-	-	100*	-	97*	98*

Cmpd No.	Test A	Test B	Test C	Test D	Test E	Test F	Test G	Test H	Test I
272	100	-	-	-	-	100	-	99	100
275	100	99	0	-	60	100	9	95	100
276	100*	-	-	-	-	100*	-	99*	92*

"Cmpd No." means compound number.

Note 1: Rating was "65" in earlier test.

TESTS K, L and M

The general protocol for preparing test compositions for Tests K, L and M was as follows. Compound 81, bixafen, 5-chloro-6-(2,4,6-trifluorophenyl)-7-(4-methylpiperidin-1-yl)[1,2,4]triazolo[1,5-a]pyrimidine (BAS600), cyproconazole, isopyrazam, penthiopyrad, probenazole, quinoxyfen and spiroxamine were obtained as unformulated, technical-grade materials. Azoxystrobin, boscalid, chlorothalonil, copper hydroxide, cymoxanil, difenoconazole, dimethomorph, epoxiconazole, fenpropimorph, fluazinam, fludioxonil, folpet, iprodione, iprovalicarb, mancozeb, mefenoxam (also known as metalaxyl-M), myclobutanil, picoxystrobin, proquinazid, prothioconazole, pyraclostrobin, tetraconazole and tricyclozole were obtained as formulated products marketed under the trademarks AMISTAR, ENDURA, BRAVO, KOCIDE, CURZATE, SCORE, ACROBAT, OPUS, CORBEL, OMEGA, MAXIM, PHALTAN, ROVRAL, MELODY, MANZATE, RIDOMIL GOLD, NOVA, ACANTO, TALIUS, PROLINE, HEADLINE, DOMARK and BEAM, respectively. Unformulated materials were first dissolved in acetone 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 Trem® 014 (polyhydric alcohol esters). Formulated materials were dispersed in sufficient water to give the desired concentration, and neither organic solvent nor surfactant was added to the suspension. The resulting test mixtures were then used in Tests K, L and M. Spraying a 200 ppm test suspension to the point of run-off on the test plants was the equivalent of a rate of about 800 g/ha. The tests were replicated three times and the results reported as the mean average of the three replicates.

The presence of a synergistic effect between two active ingredients was established with the aid of the Colby equation (see Colby, S. R. "Calculating Synergistic and Antagonistic Responses of Herbicide Combinations", *Weeds*, (1967), 15, 20-22):

$$p = A + B - \left[\frac{A \times B}{100}\right]$$

Using the method of Colby, the presence of a synergistic interaction between two active ingredients is established by first calculating the predicted activity, p, of the mixture based on activities of the two components applied alone. If p is lower than the experimentally established effect, synergism has occurred. In the equation above, A is the

fungicidal activity in percentage control of one component applied alone at rate x. The B term is the fungicidal activity in percentage control of the second component applied at rate y. The equation estimates p, the expected fungicidal activity of the mixture of A at rate x with B at rate y if their effects are strictly additive and no interaction has occurred.

TEST K (i.e. Tests K1, K2, K3, K4, K5)

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 7 days, after which time visual disease ratings were made.

TEST L (i.e. Tests L1, L2, L3, L4, L5)

The test suspension 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 6 days, after which time visual disease ratings were made.

TEST M (i.e. Tests M1, M2, M3, M4, M5)

The test suspension was sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore suspension of *Septoria tritici* (the causal agent of wheat leaf blotch) and incubated in saturated atmosphere at 24 °C for 48 h. and then the seedlings moved to a growth chamber at 20 °C for 19 additional days, after which time visual disease ratings were made.

Results for Tests K–M are presented in the following Tables B through K. A rating of 100 indicates 100% disease control and a rating of 0 indicates no disease control (relative to the controls). A dash (–) indicates no test results. Columns labeled "Obsd" indicate the average of results observed from three replications. Columns labeled "Exp" indicate the expected effect for each treatment mixture calculated using the Colby Equation.

TABLE B

Observed and Expected Effects of Compound 81 Alone and Mixtures with Quinoxyfen, Probenazole, Mancozeb, Iprodione, Boscalid, Copper Hydroxide, Cymoxanil or Proquinazid for Control of Wheat Powder Mildew or Leaf Rust

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test K1		Test L1	
			Obsd	Exp	Obsd	Exp
0	None	0	0		0	
1	None	0	0		88	

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test K1		Test L1	
			Obsd	Exp	Obsd	Exp
2	None	0	87		68	
5	None	0	99		91	
10	None	0	100		98	
0	quinoxyfen	10			0	
0	quinoxyfen	40			0	
0	quinoxyfen	200			0	
2	quinoxyfen	10			18	68
2	quinoxyfen	40			23	68
2	quinoxyfen	200			38	68
5	quinoxyfen	10			60	91
5	quinoxyfen	40			41	91
5	quinoxyfen	200			47	91
0	probenazole	10	68		9	
0	probenazole	40	21		18	
0	probenazole	200	71		18	
2	probenazole	10	97	96	54	71
2	probenazole	40	99	90	85	74
2	probenazole	200	98	96	74	74
5	probenazole	10	100	100	92	92
5	probenazole	40	100	99	96	93
5	probenazole	200	100	100	94	93
0	mancozeb	10	0		54	
0	mancozeb	40	0		88	
0	mancozeb	200	0		98	
2	mancozeb	10	79	87	80	85
2	mancozeb	40	87	87	91	96
2	mancozeb	200	84	87	99	99
5	mancozeb	10	96	99	85	96
5	mancozeb	40	99	99	98	99
5	mancozeb	200	99	99	99	100
0	iprodione	10	0		0	
0	iprodione	40	0		0	
0	iprodione	200	21		0	
2	iprodione	10	96	87	27	68

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test K1		Test L1	
			Obsd	Exp	Obsd	Exp
2	iprodione	40	92	87	27	68
2	iprodione	200	94	90	41	68
5	iprodione	10	99	99	68	91
5	iprodione	40	99	99	80	91
5	iprodione	200	99	99	85	91
0	boscalid	10	0		0	
0	boscalid	40	0		54	
0	boscalid	200	0		92	
2	boscalid	10	0	87	76	68
2	boscalid	40	0	87	86	85
2	boscalid	200	64	87	99	97
5	boscalid	10	86	99	89	91
5	boscalid	40	94	99	98	96
5	boscalid	200	97	99	98	99
0	copper hydroxide	10	0		0	
0	copper hydroxide	40	0		0	
0	copper hydroxide	200	0		0	
2	copper hydroxide	10	71	87	9	68
2	copper hydroxide	40	0	87	0	68
2	copper hydroxide	200	0	87	0	68
5	copper hydroxide	10	97	99	41	91
5	copper hydroxide	40	94	99	18	91
5	copper hydroxide	200	93	99	41	91
0	cymoxanil	10	0		0	
0	cymoxanil	40	0		0	
0	cymoxanil	200	50		18	
2	cymoxanil	10	73	87	9	68
2	cymoxanil	40	89	87	9	68
2	cymoxanil	200	91	93	54	74
5	cymoxanil	10	96	99	18	91
5	cymoxanil	40	98	99	54	91
5	cymoxanil	200	97	100	74	93
0	proquinazid	10			0	
0	proquinazid	40			0	

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test K1		Test L1	
			Obsd	Exp	Obsd	Exp
0	proquinazid	200			0	
2	proquinazid	10			0	68
2	proquinazid	40			18	68
2	proquinazid	200			27	68
5	proquinazid	10			18	91
5	proquinazid	40			27	91
5	proquinazid	200			68	91

TABLE C

Observed and Expected Effects of Compound 81 Alone and Mixtures with Chlorothalonil, Tricyclazole, Fluazinam, Dimethomorph, Fludioxonil, Iprovalicarb, Metalaxyl-M or Folpet for Control of Wheat Powder Mildew or Leaf Rust

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test K2		Test L2	
			Obsd	Exp	Obsd	Exp
0	None	0	63		0	
1	None	0	91		9	
2	None	0	91		27	
5	None	0	91		74	
10	None	0	100		91	
0	chlorothalonil	10	58		0	
0	chlorothalonil	40	68		41	
0	chlorothalonil	200	79		91	
2	chlorothalonil	10	92	96	18	27
2	chlorothalonil	40	100	97	85	57
2	chlorothalonil	200	97	98	96	93
5	chlorothalonil	10	100	96	66	74
5	chlorothalonil	40	100	97	88	85
5	chlorothalonil	200	100	98	96	98
0	tricyclazole	10	0		0	
0	tricyclazole	40	29		0	
0	tricyclazole	200	79		0	
2	tricyclazole	10	99	91	27	27
2	tricyclazole	40	99	94	27	27

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test K2		Test L2	
			Obsd	Exp	Obsd	Exp
2	tricyclazole	200	98	98	27	27
5	tricyclazole	10	100	91	55	74
5	tricyclazole	40	100	94	68	74
5	tricyclazole	200	100	98	80	74
0	fluazinam	10	85		18	
0	fluazinam	40	96		41	
0	fluazinam	200	100		74	
2	fluazinam	10	84	99	41	41
2	fluazinam	40	99	100	68	57
2	fluazinam	200	99	100	91	81
5	fluazinam	10	100	99	80	79
5	fluazinam	40	100	100	80	85
5	fluazinam	200	100	100	91	93
0	dimethomorph	10	82		9	
0	dimethomorph	40	71		9	
0	dimethomorph	200	82		0	
2	dimethomorph	10	99	98	18	34
2	dimethomorph	40	100	98	18	34
2	dimethomorph	200	99	98	27	27
5	dimethomorph	10	100	98	60	76
5	dimethomorph	40	100	98	68	76
5	dimethomorph	200	100	98	68	74
0	fludioxonil	10	82		0	
0	fludioxonil	40	92		0	
0	fludioxonil	200	96		9	
2	fludioxonil	10	100	98	27	27
2	fludioxonil	40	99	99	27	27
2	fludioxonil	200	100	100	27	34
5	fludioxonil	10	100	98	41	74
5	fludioxonil	40	100	99	55	74
5	fludioxonil	200	100	100	74	76
0	iprovalicarb	10	71		0	
0	iprovalicarb	40	74		0	
0	iprovalicarb	200	56		9	

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test K2		Test L2	
			Obsd	Exp	Obsd	Exp
2	iprovalicarb	10	100	98	27	27
2	iprovalicarb	40	100	98	27	27
2	iprovalicarb	200	99	96	27	34
5	iprovalicarb	10	100	98	74	74
5	iprovalicarb	40	100	98	74	74
5	iprovalicarb	200	100	96	85	76
0	metalaxyl-M	10	56		0	
0	metalaxyl-M	40	64		0	
0	metalaxyl-M	200	21		0	
2	metalaxyl-M	10	96	96	27	27
2	metalaxyl-M	40	99	97	27	27
2	metalaxyl-M	200	99	93	27	27
5	metalaxyl-M	10	100	96	55	74
5	metalaxyl-M	40	100	97	55	74
5	metalaxyl-M	200	100	93	68	74
0	folpet	10	0		0	
0	folpet	40	0		27	
0	folpet	200	21		55	
2	folpet	10	93	91	0	27
2	folpet	40	96	91	27	47
2	folpet	200	66	93	80	67
5	folpet	10	100	91	74	74
5	folpet	40	100	91	88	81
5	folpet	200	100	93	93	88

TABLE D

Observed and Expected Effects of Compound 81 Alone and Mixtures with Isopyrazam, BAS600, Bixafen, Penthiopyrad, Spiroxamine, Myclobutanil or Fenpropimorph for Control of Wheat Powdery Mildew or Leaf Rust

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test K3		Test L3	
			Obsd	Exp	Obsd	Exp
0	None	0	0		0	
1	None	0	0		9	

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test K3		Test L3	
			Obsd	Exp	Obsd	Exp
2	None	0	0		9	
5	None	0	90		41	
10	None	0	99		88	
0	isopyrazam	0.08	0			
0	isopyrazam	0.4	50			
0	isopyrazam	2	99			
0	isopyrazam	10	99			
2	isopyrazam	0.08	0	0		
2	isopyrazam	0.4	64	50		
2	isopyrazam	2	94	99		
2	isopyrazam	10	100	99		
5	isopyrazam	0.08	99	90		
5	isopyrazam	0.4	100	95		
5	isopyrazam	2	100	100		
5	isopyrazam	10	100	100		
0	BAS600	0.08	0		74	
0	BAS600	0.4	0		88	
0	BAS600	2	96		99	
0	BAS600	10	100		100	
2	BAS600	0.08	0	0	74	76
2	BAS600	0.4	0	0	94	89
2	BAS600	2	93	96	100	99
2	BAS600	10	99	100	100	100
5	BAS600	0.08	100	90	92	84
5	BAS600	0.4	99	90	99	93
5	BAS600	2	100	100	100	99
5	BAS600	10	100	100	100	100
0	bixafen	0.08	0		9	
0	bixafen	0.4	0		88	
0	bixafen	2	64		99	
0	bixafen	10	99		100	
2	bixafen	0.08	0	0	18	17
2	bixafen	0.4	0	0	80	89
2	bixafen	2	90	64	99	99

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test K3		Test L3	
			Obsd	Exp	Obsd	Exp
2	bixafen	10	99	99	100	100
5	bixafen	0.08	99	90	68	46
5	bixafen	0.4	100	90	94	93
5	bixafen	2	100	96	100	99
5	bixafen	10	100	100	100	100
0	penthiopyrad	0.08	0			
0	penthiopyrad	0.4	0			
0	penthiopyrad	2	99			
0	penthiopyrad	10	100			
2	penthiopyrad	0.08	0	0		
2	penthiopyrad	0.4	42	0		
2	penthiopyrad	2	99	99		
2	penthiopyrad	10	100	100		
5	penthiopyrad	0.08	99	90		
5	penthiopyrad	0.4	100	90		
5	penthiopyrad	2	100	100		
5	penthiopyrad	10	100	100		
0	spiroxamine	0.4	0		0	
0	spiroxamine	2	0		0	
0	spiroxamine	10	0		0	
0	spiroxamine	40	99		91	
2	spiroxamine	0.4	0	0	18	9
2	spiroxamine	2	0	0	9	9
2	spiroxamine	10	0	0	9	9
2	spiroxamine	40	100	99	60	92
5	spiroxamine	0.4	97	90	45	41
5	spiroxamine	2	96	90	41	41
5	spiroxamine	10	98	90	80	41
5	spiroxamine	40	100	100	95	95
0	myclobutanil	0.4	0		0	
0	myclobutanil	2	86		0	
0	myclobutanil	10	99		41	
0	myclobutanil	40	100		99	
2	myclobutanil	0.4	42	0	0	9

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test K3		Test L3	
			Obsd	Exp	Obsd	Exp
2	myclobutanil	2	93	86	0	9
2	myclobutanil	10	100	99	41	46
2	myclobutanil	40	100	100	100	99
5	myclobutanil	0.4	98	90	27	41
5	myclobutanil	2	99	99	68	41
5	myclobutanil	10	100	100	93	65
5	myclobutanil	40	100	100	100	99
0	fenpropimorph	0.4	50		0	
0	fenpropimorph	2	96		0	
0	fenpropimorph	10	100		88	
0	fenpropimorph	40	100		100	
2	fenpropimorph	0.4	85	50	0	9
2	fenpropimorph	2	97	96	41	9
2	fenpropimorph	10	100	100	97	89
2	fenpropimorph	40	100	100	100	100
5	fenpropimorph	0.4	96	95	54	41
5	fenpropimorph	2	100	100	83	41
5	fenpropimorph	10	100	100	99	93
5	fenpropimorph	40	100	100	100	100

TABLE E

Observed and Expected Effects of Compound 81 Alone and Mixtures with Difenoconazole, Azoxystrobin, Tetraconazole, Pyraclostrobin, Prothioconazole, Picoxystrobin or Epoxiconazole for Control of Wheat Powdery Mildew or Leaf Rust

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test K4		Test L4	
			Obsd	Exp	Obsd	Exp
0	None	0	0		0	
1	None	0	0		0	
2	None	0	0		27	
5	None	0	0		68	
10	None	0	–		88	
0	difenoconazole	0.08	0			
0	difenoconazole	0.4	0			

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test K4		Test L4	
			Obsd	Exp	Obsd	Exp
0	difenoconazole	2	81			
0	difenoconazole	10	99			
2	difenoconazole	0.08	0	0		
2	difenoconazole	0.4	21	0		
2	difenoconazole	2	90	81		
2	difenoconazole	10	100	99		
5	difenoconazole	0.08	98	0		
5	difenoconazole	0.4	97	0		
5	difenoconazole	2	98	81		
5	difenoconazole	10	100	99		
0	azoxystrobin	0.08	0			
0	azoxystrobin	0.4	0			
0	azoxystrobin	2	0			
0	azoxystrobin	10	96			
2	azoxystrobin	0.08	0	0		
2	azoxystrobin	0.4	0	0		
2	azoxystrobin	2	0	0		
2	azoxystrobin	10	97	96		
5	azoxystrobin	0.08	97	0		
5	azoxystrobin	0.4	96	0		
5	azoxystrobin	2	98	0		
5	azoxystrobin	10	100	96		
0	tetraconazole	0.08	0		0	
0	tetraconazole	0.4	21		0	
0	tetraconazole	2	93		27	
0	tetraconazole	10	97		99	
2	tetraconazole	0.08	0	0	0	27
2	tetraconazole	0.4	0	21	9	27
2	tetraconazole	2	55	93	60	47
2	tetraconazole	10	99	97	100	99
5	tetraconazole	0.08	94	0	74	68
5	tetraconazole	0.4	94	21	74	68
5	tetraconazole	2	97	93	98	77
5	tetraconazole	10	100	97	100	100

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test K4		Test L4	
			Obsd	Exp	Obsd	Exp
0	pyraclostrobin	0.08	0		9	
0	pyraclostrobin	0.4	0		80	
0	pyraclostrobin	2	0		98	
0	pyraclostrobin	10	93		100	
2	pyraclostrobin	0.08	0	0	27	34
2	pyraclostrobin	0.4	0	0	85	85
2	pyraclostrobin	2	58	0	97	99
2	pyraclostrobin	10	94	93	100	100
5	pyraclostrobin	0.08	97	0	74	71
5	pyraclostrobin	0.4	96	0	94	94
5	pyraclostrobin	2	98	0	100	99
5	pyraclostrobin	10	99	93	100	100
0	prothioconazole	0.08	0		0	
0	prothioconazole	0.4	0		0	
0	prothioconazole	2	0		9	
0	prothioconazole	10	93		9	
2	prothioconazole	0.08	0	0	0	27
2	prothioconazole	0.4	0	0	0	27
2	prothioconazole	2	47	0	0	34
2	prothioconazole	10	98	93	27	34
5	prothioconazole	0.08	96	0	80	68
5	prothioconazole	0.4	96	0	74	68
5	prothioconazole	2	97	0	55	71
5	prothioconazole	10	98	93	74	71
0	picoxystrobin	0.08	0		0	
0	picoxystrobin	0.4	0		9	
0	picoxystrobin	2	0		82	
0	picoxystrobin	10	99		100	
2	picoxystrobin	0.08	0	0	0	27
2	picoxystrobin	0.4	0	0	27	34
2	picoxystrobin	2	42	0	85	87
2	picoxystrobin	10	100	99	100	100
5	picoxystrobin	0.08	93	0	60	68
5	picoxystrobin	0.4	95	0	80	71

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test K4		Test L4	
			Obsd	Exp	Obsd	Exp
5	picoxystrobin	2	96	0	90	94
5	picoxystrobin	10	100	99	100	100
0	epoxiconazole	0.08	0		0	
0	epoxiconazole	0.4	90		93	
0	epoxiconazole	2	98		99	
0	epoxiconazole	10	100		100	
2	epoxiconazole	0.08	0	0	55	27
2	epoxiconazole	0.4	29	90	97	95
2	epoxiconazole	2	99	98	99	99
2	epoxiconazole	10	100	100	100	100
5	epoxiconazole	0.08	93	0	91	68
5	epoxiconazole	0.4	98	90	100	98
5	epoxiconazole	2	100	98	100	100
5	epoxiconazole	10	100	100	100	100

TABLE F

Observed and Expected Effects of Compound 81 Alone and Mixtures with Quinoxyfen, Cyproconazole, Penthiopyrad, Isopyrazam, Difenoconazole, Azoxystrobin or Proquinazid for Control of Wheat Powdery Mildew or Leaf Rust

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test K5		Test L5	
			Obsd	Exp	Obsd	Exp
0	None	0	0		0	
1	None	0	0		18	
2	None	0	0		27	
5	None	0	0		55	
10	None	0	100		82	
0	quinoxyfen	0.016	21		–	
0	quinoxyfen	0.08	29			
0	quinoxyfen	0.4	64			
0	quinoxyfen	2	93		–	
2	quinoxyfen	0.016	90	21	–	
2	quinoxyfen	0.08	87	29	–	
2	quinoxyfen	0.4	90	64	–	

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test K5		Test L5	
			Obsd	Exp	Obsd	Exp
2	quinoxyfen	2	99	93	–	
5	quinoxyfen	0.016	99	21	–	
5	quinoxyfen	0.08	100	29	–	
5	quinoxyfen	0.4	100	64	–	
5	quinoxyfen	2	100	93	–	
0	cyproconazole	0.016	64		27	
0	cyproconazole	0.08	64		80	
0	cyproconazole	0.4	79		92	
0	cyproconazole	2	96		100	
2	cyproconazole	0.016	42	64	55	47
2	cyproconazole	0.08	64	64	74	85
2	cyproconazole	0.4	96	79	93	94
2	cyproconazole	2	100	96	100	100
5	cyproconazole	0.016	100	64	68	67
5	cyproconazole	0.08	99	64	97	91
5	cyproconazole	0.4	100	79	98	96
5	cyproconazole	2	100	96	100	100
0	penthiopyrad	0.016	–		9	
0	penthiopyrad	0.08	–		55	
0	penthiopyrad	0.4	–		68	
0	penthiopyrad	2	–		99	
2	penthiopyrad	0.016	–		55	34
2	penthiopyrad	0.08	–		68	67
2	penthiopyrad	0.4	–		68	77
2	penthiopyrad	2	–		99	99
5	penthiopyrad	0.016	–		74	59
5	penthiopyrad	0.08	–		80	79
5	penthiopyrad	0.4	–		88	85
5	penthiopyrad	2	–		100	100
0	isopyrazam	0.016	–		68	
0	isopyrazam	0.08	–		89	
0	isopyrazam	0.4	–		100	
0	isopyrazam	2	–		100	
2	isopyrazam	0.016	–		74	77

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test K5		Test L5	
			Obsd	Exp	Obsd	Exp
2	isopyrazam	0.08	–		88	92
2	isopyrazam	0.4	–		100	100
2	isopyrazam	2	–		100	100
5	isopyrazam	0.016	–		88	85
5	isopyrazam	0.08	–		99	95
5	isopyrazam	0.4	–		100	100
5	isopyrazam	2	–		100	100
0	difenoconazole	0.016	–		68	
0	difenoconazole	0.08	–		68	
0	difenoconazole	0.4	–		92	
0	difenoconazole	2	–		100	
2	difenoconazole	0.016	–		27	77
2	difenoconazole	0.08	–		41	77
2	difenoconazole	0.4	–		99	94
2	difenoconazole	2	–		100	100
5	difenoconazole	0.016	–		74	85
5	difenoconazole	0.08	–		80	85
5	difenoconazole	0.4	–		100	96
5	difenoconazole	2	–		100	100
0	azoxystrobin	0.016	–		0	
0	azoxystrobin	0.08	–		68	
0	azoxystrobin	0.4	–		100	
0	azoxystrobin	2	–		100	
2	azoxystrobin	0.016	–		27	27
2	azoxystrobin	0.08	–		74	77
2	azoxystrobin	0.4	–		100	100
2	azoxystrobin	2	–		100	100
5	azoxystrobin	0.016	–		74	55
5	azoxystrobin	0.08	–		97	85
5	azoxystrobin	0.4	–		100	100
5	azoxystrobin	2	–		100	100
0	proquinazid	0.016	0		–	
0	proquinazid	0.08	0		–	
0	proquinazid	0.4	0		–	

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test K5		Test L5	
			Obsd	Exp	Obsd	Exp
0	proquinazid	2	71		–	
2	proquinazid	0.016	0	0	–	
2	proquinazid	0.08	0	0	–	
2	proquinazid	0.4	0	0	–	
2	proquinazid	2	87	71	–	
5	proquinazid	0.016	87	0	–	
5	proquinazid	0.08	89	0	–	
5	proquinazid	0.4	93	0	–	
5	proquinazid	2	98	71	–	

TABLE G

Observed and Expected Effects of Compound 81 Alone and Mixtures with Probenazole, Mancozeb, Iprodione, Boscalid, Copper hydroxide, Cymoxanil or Chlorothalonil for Control of Wheat Leaf Blotch

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test M1	
			Obsd	Exp
0	None	0	0	
0.01	None	0	0	
0.1	None	0	0	
1	None	0	86	
10	None	0	100	
0	probenazole	10	0	
0	probenazole	40	0	
0	probenazole	200	0	
0.1	probenazole	10	0	0
0.1	probenazole	40	0	0
0.1	probenazole	200	25	0
1	probenazole	10	87	86
1	probenazole	40	94	86
1	probenazole	200	87	86
0	mancozeb	10	0	
0	mancozeb	40	55	
0	mancozeb	200	91	
0.1	mancozeb	10	0	0

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test M1	
			Obsd	Exp
0.1	mancozeb	40	63	55
0.1	mancozeb	200	96	91
1	mancozeb	10	81	86
1	mancozeb	40	98	94
1	mancozeb	200	100	99
0	iprodione	10	0	
0	iprodione	40	0	
0	iprodione	200	0	
0.1	iprodione	10	0	0
0.1	iprodione	40	0	0
0.1	iprodione	200	22	0
1	iprodione	10	88	86
1	iprodione	40	91	86
1	iprodione	200	98	86
0	boscalid	10	77	
0	boscalid	40	90	
0	boscalid	200	99	
0.1	boscalid	10	72	77
0.1	boscalid	40	98	90
0.1	boscalid	200	98	99
1	boscalid	10	99	97
1	boscalid	40	100	99
1	boscalid	200	100	100
0	copper hydroxide	10	0	
0	copper hydroxide	40	45	
0	copper hydroxide	200	77	
0.1	copper hydroxide	10	0	0
0.1	copper hydroxide	40	25	45
0.1	copper hydroxide	200	87	77
1	copper hydroxide	10	72	86
1	copper hydroxide	40	93	92
1	copper hydroxide	200	99	97
0	cymoxanil	10	0	
0	cymoxanil	40	0	
0	cymoxanil	200	0	

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test M1	
			Obsd	Exp
0.1	cymoxanil	10	0	0
0.1	cymoxanil	40	0	0
0.1	cymoxanil	200	0	0
1	cymoxanil	10	96	86
1	cymoxanil	40	85	86
1	cymoxanil	200	96	86
0	chlorothalonil	10	0	
0	chlorothalonil	40	42	
0	chlorothalonil	200	99	
0.1	chlorothalonil	10	0	0
0.1	chlorothalonil	40	75	42
0.1	chlorothalonil	200	98	99
1	chlorothalonil	10	72	86
1	chlorothalonil	40	80	92
1	chlorothalonil	200	99	100

TABLE H

Observed and Expected Effects of Compound 81 Alone and Mixtures with BAS600, Isopyrazam, Penthiopyrad, Bixafen or Cyproconazole for Control of Wheat Leaf Blotch

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test M2	
			Obsd	Exp
0	None	0	0	
0.01	None	0	0	
0.1	None	0	0	
1	None	0	95	
10	None	0	100	
0	BAS600	0.016	0	
0	BAS600	0.08	0	
0	BAS600	0.4	93	
0	BAS600	2	100	
0.1	BAS600	0.02	0	0
0.1	BAS600	0.08	38	0
0.1	BAS600	0.40	96	93
0.1	BAS600	2	100	100

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test M2	
			Obsd	Exp
1	BAS600	0.02	65	95
1	BAS600	0.08	85	95
1	BAS600	0.40	97	100
1	BAS600	2	99	100
0	isopyrazam	0.08	0	
0	isopyrazam	0.40	77	
0	isopyrazam	2	93	
0	isopyrazam	10	100	
0.1	isopyrazam	0.08	0	0
0.1	isopyrazam	0.40	72	77
0.1	isopyrazam	2	–	
0.1	isopyrazam	10	–	
1	isopyrazam	0.08	–	
1	isopyrazam	0.40	80	99
1	isopyrazam	2	–	
1	isopyrazam	10	100	100
0	penthiopyrad	0.08	0	
0	penthiopyrad	0.40	0	
0	penthiopyrad	2	–	
0	penthiopyrad	10	–	
0.1	penthiopyrad	0.08	0	0
0.1	penthiopyrad	0.40	17	0
0.1	penthiopyrad	2	–	
0.1	penthiopyrad	10	99	
1	penthiopyrad	0.08	83	95
1	penthiopyrad	0.40	73	95
1	penthiopyrad	2	–	
1	penthiopyrad	10	99	
0	bixafen	0.08	0	
0	bixafen	0.40	33	
0	bixafen	2	89	
0	bixafen	10	–	
0.1	bixafen	0.08	0	0
0.1	bixafen	0.40	33	33

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test M2	
			Obsd	Exp
0.1	bixafen	2	83	89
0.1	bixafen	10	100	
1	bixafen	0.08	–	
1	bixafen	0.4	85	97
1	bixafen	2	–	
1	bixafen	10	–	
0	cyproconazole	0.4	0	
0	cyproconazole	2	0	
0	cyproconazole	10	0	
0	cyproconazole	40	98	
0.1	cyproconazole	0.4	0	0
0.1	cyproconazole	2	0	0
0.1	cyproconazole	10	0	0
0.1	cyproconazole	40	98	98
1	cyproconazole	0.4	73	95
1	cyproconazole	2	63	95
1	cyproconazole	10	97	95
1	cyproconazole	40	100	100

TABLE I

Observed and Expected Effects of Compound 81 Alone and Mixtures with Fludioxonil, Epoxiconazole, Prothioconazole, Difenoconazole or Fenpropimorph for Control of Wheat Leaf Blotch

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test M3	
			Obsd	Exp
0	None	0	0	
0.01	None	0	0	
0.1	None	0	0	
1	None	0	52	
10	None	0	100	
0	fludioxonil	0.08	0	
0	fludioxonil	0.4	0	
0	fludioxonil	2	37	

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test M3	
			Obsd	Exp
0	fludioxonil	10	67	
0.1	fludioxonil	0.08	0	0
0.1	fludioxonil	0.4	0	0
0.1	fludioxonil	2	30	37
0.1	fludioxonil	10	57	67
1	fludioxonil	0.08	83	52
1	fludioxonil	0.4	45	52
1	fludioxonil	2	68	69
1	fludioxonil	10	78	84
0	epoxiconazole	0.4	0	
0	epoxiconazole	2	0	
0	epoxiconazole	10	76	
0	epoxiconazole	40	100	
0.1	epoxiconazole	0.4	0	0
0.1	epoxiconazole	2	0	0
0.1	epoxiconazole	10	75	76
0.1	epoxiconazole	40	98	100
1	epoxiconazole	0.4	78	52
1	epoxiconazole	2	78	52
1	epoxiconazole	10	97	89
1	epoxiconazole	40	100	100
0	prothioconazole	0.4	0	
0	prothioconazole	2	0	
0	prothioconazole	10	18	
0	prothioconazole	40	85	
0.1	prothioconazole	0.4	0	0
0.1	prothioconazole	2	0	0
0.1	prothioconazole	10	25	18
0.1	prothioconazole	40	–	
1	prothioconazole	0.4	48	52
1	prothioconazole	2	25	52
1	prothioconazole	10	73	61
1	prothioconazole	40	88	93
0	difenoconazole	0.4	0	

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test M3	
			Obsd	Exp
0	difenoconazole	2	0	
0	difenoconazole	10	52	
0	difenoconazole	40	95	
0.1	difenoconazole	0.4	0	0
0.1	difenoconazole	2	0	0
0.1	difenoconazole	10	57	52
0.1	difenoconazole	40	98	95
1	difenoconazole	0.4	78	52
1	difenoconazole	2	50	52
1	difenoconazole	10	88	77
1	difenoconazole	40	100	97
0	fenpropimorph	2	0	
0	fenpropimorph	10	0	
0	fenpropimorph	40	0	
0	fenpropimorph	200	0	
0.1	fenpropimorph	2	0	0
0.1	fenpropimorph	10	0	0
0.1	fenpropimorph	40	0	0
0.1	fenpropimorph	200	0	0
1	fenpropimorph	2	85	52
1	fenpropimorph	10	75	52
1	fenpropimorph	40	86	52
1	fenpropimorph	200	98	52

TABLE J

Observed and Expected Effects of Compound 81 Alone and Mixtures with Pyraclostrobin, Tricyclazole, Fluazinam, Dimethomorph, Iprovalicarb, Metalaxyl-M, Folpet or Myclobutanil for Control of Wheat Leaf Blotch

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test M4	
			Obsd	Exp
0	None	0	0	
0.01	None	0	0	
0.1	None	0	23	

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test M4	
			Obsd	Exp
1	None	0	66	
10	None	0	100	
0	pyraclostrobin	10	0	
0	pyraclostrobin	40	26	
0	pyraclostrobin	200	93	
0.1	pyraclostrobin	10	0	23
0.1	pyraclostrobin	40	32	43
0.1	pyraclostrobin	200	91	94
1	pyraclostrobin	10	79	66
1	pyraclostrobin	40	90	75
1	pyraclostrobin	200	97	98
0	tricyclazole	10	0	
0	tricyclazole	40	0	
0	tricyclazole	200	0	
0.1	tricyclazole	10	0	23
0.1	tricyclazole	40	0	23
0.1	tricyclazole	200	0	23
1	tricyclazole	10	74	66
1	tricyclazole	40	93	66
1	tricyclazole	200	74	66
0	fluazinam	10	0	
0	fluazinam	40	0	
0	fluazinam	200	93	
0.1	fluazinam	10	13	23
0.1	fluazinam	40	60	23
0.1	fluazinam	200	85	95
1	fluazinam	10	76	66
1	fluazinam	40	97	66
1	fluazinam	200	100	98
0	dimethomorph	10	0	
0	dimethomorph	40	0	
0	dimethomorph	200	0	
0.1	dimethomorph	10	0	23
0.1	dimethomorph	40	0	23

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test M4	
			Obsd	Exp
0.1	dimethomorph	200	16	23
1	dimethomorph	10	93	66
1	dimethomorph	40	91	66
1	dimethomorph	200	0	66
0	iprovalicarb	10	0	
0	iprovalicarb	40	0	
0	iprovalicarb	200	0	
0.1	iprovalicarb	10	0	23
0.1	iprovalicarb	40	23	23
0.1	iprovalicarb	200	53	23
1	iprovalicarb	10	81	66
1	iprovalicarb	40	96	66
1	iprovalicarb	200	96	66
0	metalaxyl-M	10	0	
0	metalaxyl-M	40	0	
0	metalaxyl-M	200	0	
0.1	metalaxyl-M	10	0	23
0.1	metalaxyl-M	40	0	23
0.1	metalaxyl-M	200	32	23
1	metalaxyl-M	10	86	66
1	metalaxyl-M	40	96	66
1	metalaxyl-M	200	96	66
0	folpet	10	0	
0	folpet	40	73	
0	folpet	200	91	
0.1	folpet	10	32	23
0.1	folpet	40	86	79
0.1	folpet	200	93	93
1	folpet	10	91	66
1	folpet	40	91	91
1	folpet	200	98	97
0	myclobutanil	10	0	
0	myclobutanil	40	44	
0	myclobutanil	200	74	

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test M4	
			Obsd	Exp
0.1	myclobutanil	10	13	23
0.1	myclobutanil	40	0	57
0.1	myclobutanil	200	61	80
1	myclobutanil	10	16	66
1	myclobutanil	40	91	81
1	myclobutanil	200	74	91

TABLE K

Observed and Expected Effects of Compound 81 Alone and Mixtures with Quinoxyfen, Azoxystrobin, Picoxystrobin, Tetraconazole, Spiroxamine or Proquinazid for Control of Wheat Leaf Blotch

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test M5	
			Obsd	Exp
0	None	0	0	
0.01	None	0	0	
0.1	None	0	3	
1	None	0	90	
10	None	0	100	
0	quinoxyfen	10	0	
0	quinoxyfen	40	0	
0	quinoxyfen	200	8	
0.1	quinoxyfen	10	0	3
0.1	quinoxyfen	40	0	3
0.1	quinoxyfen	200	0	11
1	quinoxyfen	10	95	90
1	quinoxyfen	40	99	90
1	quinoxyfen	200	99	91
0	azoxystrobin	10	0	
0	azoxystrobin	40	20	
0	azoxystrobin	200	50	
0.1	azoxystrobin	10	0	3
0.1	azoxystrobin	40	3	23
0.1	azoxystrobin	200	61	52

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test M5	
			Obsd	Exp
1	azoxystrobin	10	90	90
1	azoxystrobin	40	94	92
1	azoxystrobin	200	93	95
0	picoxystrobin	10	0	
0	picoxystrobin	40	0	
0	picoxystrobin	200	0	
0.1	picoxystrobin	10	0	3
0.1	picoxystrobin	40	0	3
0.1	picoxystrobin	200	0	3
1	picoxystrobin	10	79	90
1	picoxystrobin	40	70	90
1	picoxystrobin	200	85	90
0	tetraconazole	10	0	
0	tetraconazole	40	7	
0	tetraconazole	200	99	
0.1	tetraconazole	10	13	3
0.1	tetraconazole	40	60	10
0.1	tetraconazole	200	99	99
1	tetraconazole	10	87	90
1	tetraconazole	40	99	91
1	tetraconazole	200	100	100
0	spiroxamine	10	0	
0	spiroxamine	40	3	
0	spiroxamine	200	0	
0.1	spiroxamine	10	0	3
0.1	spiroxamine	40	0	7
0.1	spiroxamine	200	7	3
1	spiroxamine	10	88	90
1	spiroxamine	40	85	90
1	spiroxamine	200	100	90
0	proquinazid	10	0	
0	proquinazid	40	0	
0	proquinazid	200	0	
0.1	proquinazid	10	0	3

Application Rate (ppm) of Compound 81	Component (b)	Application Rate (ppm) of Component (b)	Test M5	
			Obsd	Exp
0.1	proquinazid	40	0	3
0.1	proquinazid	200	0	3
1	proquinazid	10	22	90
1	proquinazid	40	55	90
1	proquinazid	200	25	90

Tables B through K show compositions of the present invention comprising mixtures of a representative Formula **1** compound with a variety of component (b) compounds demonstrating, in some instances, synergistic control of wheat powdery mildew, leaf rust, and leaf blotch. As control cannot exceed 100%, increased activity above expected fungicidal activity was not always observed in mixtures but more likely observed when the separate active ingredient components alone were at application rates providing considerably less than 100% control. Synergy may not be evident at low application rates where the individual active ingredient components alone have little activity. However, in some instances greater activity was observed for combinations wherein individual active ingredients alone at the same application rates had little or no activity. As demonstrated above, this invention provides a method for controlling powdery mildew (*Blumeria graminis* f. sp. *tritici*), leaf rust (*Puccinia recondita* f. sp. *tritici*), and wheat leaf blotch (*Septoria tritici*).

TESTS N1 and N2

Tests N1 and N2 involved evaluation of mixtures of Compound 81 with 2-[(3-bromo-8-methyl-6-quinolinyl)oxy]-*N*-(1,1-dimethyl-2-propyn-1-yl)-2-(methylthio)acetamide (Compound A1) and 2-[(3-bromo-6-quinolinyl)oxy]-*N*-(1,1-dimethylethyl)butanamide (Compound A2), respectively, for inhibiting the growth of *Septoria tritici* (the causal agent of wheat leaf blotch). The general protocol for preparing test compositions was as follows. Compound 81 (Tests N1 and N2), Compound A1 (Test N1) and Compound A2 (Test N2) were obtained as unformulated, technical-grade materials. Unformulated test compounds were first dissolved in DMSO at the appropriate concentration to provide the desired concentration (in μM) after mixing with the fungal growth medium in the wells of 96-well plates containing 200 μL fungal growth medium per well. The ranges of compound concentrations were chosen to span a range of inhibitory activity from 0 to near 100% to identify any synergistic action when *Septoria tritici* was treated with compounds added in combination. The DMSO solutions of the test compounds were added to the wells prior to addition of the fungal growth medium.

The fungal growth solid medium was prepared by forming an aqueous mixture containing dipotassium hydrogen phosphate (3.0 g/L), potassium dihydrogen phosphate (4.0 g/L), sodium chloride (0.5 g/L), ammonium chloride (1.0 g/L), magnesium sulfate heptahydrate (0.2 g) and calcium chloride dihydrate (0.01 g/L), also containing 1 mL/L of a trace element solution (manganese sulfate hydrate (0.1 mg/mL), zinc sulfate heptahydrate (0.2 mg/mL), copper(II) sulfate pentahydrate (0.2 mg/mL), iron(II) sulfate heptahydrate (0.2 mg/mL), sodium molybdate dihydrate (0.1 mg/mL), cobalt(II) sulfate heptahydrate (0.06 mg/mL), boric acid (0.08 mg/mL)), and supplemented with 50 μL/L of a biotin stock solution (0.1 mg/mL). The pH was adjusted to 6.8 with aqueous 1 M sodium carbonate solution. The mixture was further supplemented with 1 g/L of yeast extract, and GELRITE gellan gum (Kelco) (4 g/L) was added. Sufficient water was added to bring the volume to 90% of final volume (e.g., 900 mL volume for preparation of 1 L of fungal growth medium). The mixture was autoclaved. On cooling to 60 °C, 100 mL/L of aqueous dextrose solution (10 g/L), 500 μL/L of aqueous ampicillin solution (100 mg/mL) and 500 μL/L of rifampicin solution (10 mg/mL in DMSO) were added to provide the final volume of fungal growth medium, which was then dispensed while still warm using a microliter pipette to the wells of the 96-well plates. The dispensed fungal growth medium in each well was agitated using the tip of the dispensing pipette to mix it with the DMSO solution containing the test compounds.

After the fungal growth medium in the wells had cooled to room temperature and solidified, the top surface of the growth medium in each well was inoculated with 20 μL of a suspension of fungus containing 8×10^4 cells. Following a 2 h period of drying in a sterile hood, plates were placed in a dark incubator at 25 °C for 5 d.

Fungal growth was assessed on a plate reader set to measure absorbance of 600 nm light. The percent growth inhibition observed (Obsd.) in Tests N1 and N2, as well as the percent growth inhibition expected (Exp.) from calculation using the Colby equation, are listed in Tables L and M, respectively.

TABLE L

Observed and Expected Effects of Compound 81 Alone and in Mixtures with Compound A1 as Component (b) for Control of *Septoria tritici*

Application Rate of Compound 81 (μM)	Application Rate of Compound A1 (μM)	% inhibition	
		Obsd.	Exp.
0.2	0	98.0	
0.04	0	93.5	
0.008	0	10.0	
0.0016	0	5.0	

Application Rate of Compound 81 (μM)	Application Rate of Compound A1 (μM)	% inhibition	
		Obsd.	Exp.
0.00032	0	9.0	
0	0	0	
0	0.2	98.0	
0	0.04	97	
0	0.008	14.5	
0	0.0016	5	
0	0.00032	3	
0	0	0	0
0.2	0.2	98	98
0.2	0.04	98	98
0.2	0.008	98	98
0.2	0.0016	98	98
0.2	0.00032	98	98
0.04	0.2	98	99.0
0.04	0.04	98	99.0
0.04	0.008	98	96.0
0.04	0.0016	94.2	94.0
0.04	0.00032	92	96.0
0.008	0.2	98.0	99.0
0.008	0.04	97.0	99.0
0.008	0.008	62.0	22.0
0.008	0.0016	6.0	14.0
0.008	0.00032	5.0	13.0
0.016	0.2	98.0	98.0
0.016	0.04	97.0	96.0
0.016	0.008	32.0	18.0
0.016	0.0016	5.0	10.0
0.016	0.00032	9.0	8.0
0.0032	0.2	98.0	97.0
0.0032	0.04	94.0	96.0
0.0032	0.008	8.0	22.0
0.0032	0.0016	8.0	14.0
0.0032	0.00032	6.0	12.0

TABLE M

Observed and Expected Effects of Compound 81 Alone and in Mixtures with Compound A2 as Component (b) for Control of *Septoria tritici*

Application Rate of Compound 81 (μM)	Application Rate of Compound A2 (μM)	% inhibition	
		Obsd.	Exp.
0.2	0	96.0	
0.04	0	93.5	
0.008	0	29.0	
0.0016	0	0.0	
0.00032	0	0.0	
0	0	0	
0	20	96.0	
0	4	95.0	
0	0.8	11.5	
0	0.16	6.5	
0	0.032	0.0	
0	0	0	
0.2	20	96	100
0.2	4	96	100
0.2	0.8	96	96
0.2	0.16	96	96
0.2	0.032	96	96
0.04	20	96.0	100
0.04	4	96.0	100
0.04	0.8	96.0	94.2
0.04	0.16	95.5	93.9
0.04	0.032	95.0	93.5
0.008	20	96.0	97.2
0.008	4	96.0	96.5
0.008	0.8	68.0	37.2
0.008	0.16	0.0	33.6
0.008	0.032	0.0	29.0
0.016	20	96.0	96.0
0.016	4	96.0	95.0
0.016	0.8	46.5	11.5
0.016	0.16	6.5	6.5

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Application Rate of Compound 81 (μM)	Application Rate of Compound A2 (μM)	% inhibition	
		Obsd.	Exp.
0.016	0.032	0.0	0.0
0.0032	20	96.0	96.0
0.0032	4	95.0	95.0
0.0032	0.8	13.0	11.5
0.0032	0.16	24.5	6.5
0.0032	0.032	1.5	0.0

The observed and expected results from mixtures of Compound 81 with Compound A1 in Test N1 presented in Table L show greater than expected activity (i.e. synergy) at application rates wherein Compound 81 and Compound A1 separately provide much less than 100% inhibition (to allow expression of synergistic increase in inhibition) but also wherein the application rates are not greatly reduced from the application rates providing high inhibition by Compounds 81 and Compound A1 separately (e.g., application rates of 0.008 or 0.016 μM of Compound 81 and an application rate of 0.008 μM of Compound A1). Similarly, the observed and expected results from mixtures of Compound 81 with Compound A2 in Test N2 presented in Table M show greater than expected activity at application rates wherein Compound 81 and Compound A2 separately provide much less than 100% inhibition but also wherein the application rates are not greatly reduced from the application rates providing high inhibition by Compounds 81 and Compound A2 separately (e.g., application rates of 0.008 or 0.016 μM of Compound 81 and an application rate of 0.8 μM of Compound A2).

Where the terms "comprise", "comprises", "comprised" or "comprising" are used in this specification, they are to be interpreted as specifying the presence of the stated features, integers, steps or components referred to, but not to preclude the presence or addition of one or more other feature, integer, step, component or group thereof.

Further, any prior art reference or statement provided in the specification is not to be taken as an admission that such art constitutes, or is to be understood as constituting, part of the common general knowledge in Australia.

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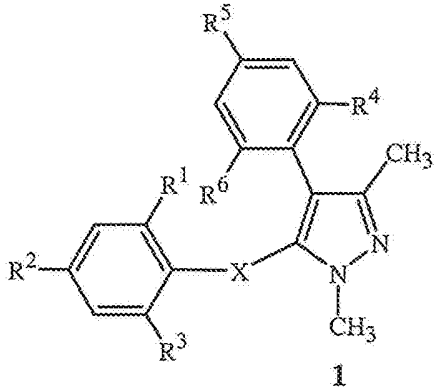
The Claims defining the invention are as follows:

1. A fungicidal composition comprising:

(a) at least one compound selected from the compounds of Formula **1**, *N*-oxides, and salts thereof:



1

wherein

X is NH;

R^1 is halogen;

R^2 is H;

R^3 is halogen;

R^4 is halogen;

R^5 is H, cyano, halogen or C_1–C_2 alkoxy; and

R^6 is H or halogen; and

(b) at least one additional fungicidal compound;

provided that when R^1 is F, then R^3 is Cl, and when R^1 is Cl, then R^3 is F.

2. The composition of Claim 1, wherein component (a) comprises a compound of Formula **1** or salt thereof, wherein in Formula **1**,

at most, only one of R^5 and R^6 is H.

3. The composition of Claim 2, wherein in Formula **1**,

R^1 is F, Cl or Br;

R^2 is H;

R^3 is F or Cl;

R^4 is F, Cl or Br;

R^5 is H, cyano, F, Cl or methoxy; and

R^6 is H or F.

4. The composition of Claim 3, wherein in Formula **1**,

R^3 is F; and

R^5 is cyano, F, Cl or methoxy.

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5. The composition of Claim 1, wherein component (a) comprises a compound selected from the group consisting of

4-(2-chloro-4-fluorophenyl)-*N*-(2-chloro-6-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine,

4-(2-bromo-4-fluorophenyl)-*N*-(2-chloro-6-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine,

N-(2-bromo-6-fluorophenyl)-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine,

4-(2-bromo-4-fluorophenyl)-*N*-(2-bromo-6-fluorophenyl)-1,3-dimethyl-*1H*-pyrazol-5-amine,

N-(2-bromo-6-fluorophenyl)-4-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine,

N-(2-bromo-6-fluorophenyl)-4-(2,6-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine,

N-(2-chloro-6-fluorophenyl)-4-(2-fluoro-4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine,

N-(2-bromo-6-fluorophenyl)-4-(2-fluoro-4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine,

N-(2-bromo-6-fluorophenyl)-4-(2-chloro-4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine, and

N-(2-chloro-6-fluorophenyl)-4-(2,4-difluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine.

6. The composition of Claim 1, wherein component (a) is 4-(2-bromo-4-fluorophenyl)-*N*-(2-chloro-6-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine.

7. The composition of any one of Claims 1 to 6, wherein component (b) comprises at least one fungicidal compound from each of two different groups selected from the group consisting of:

(b1) methyl benzimidazole carbamate fungicides;

(b2) dicarboximide fungicides;

(b3) demethylation inhibitor fungicides;

(b4) phenylamide fungicides;

(b5) amine/morpholine fungicides;

(b6) phospholipid biosynthesis inhibitor fungicides;

(b7) carboxamide fungicides;

(b8) hydroxy(2-amino-)pyrimidine fungicides;

(b9) anilinopyrimidine fungicides;

(b10) *N*-phenyl carbamate fungicides;

(b11) quinone outside inhibitor fungicides;

(b12) phenylpyrrole fungicides;

(b13) quinoline fungicides;

(b14) lipid peroxidation inhibitor fungicides;

(b15) melanin biosynthesis inhibitors-reductase fungicides;

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(b16) melanin biosynthesis inhibitors-dehydratase fungicides;
(b17) hydroxyanilide fungicides;
(b18) squalene-epoxidase inhibitor fungicides;
(b19) polyoxin fungicides;
(b20) phenylurea fungicides;
(b21) quinone inside inhibitor fungicides;
(b22) benzamide 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) pyrimidinamide fungicides;
(b40) carboxylic acid amide fungicides;
(b41) tetracycline antibiotic fungicides;
(b42) thiocarbamate fungicides;
(b43) benzamide fungicides;
(b44) host plant defense induction fungicides;
(b45) multi-site contact activity fungicides;
(b46) fungicidal compounds other than fungicidal compounds of component (a) and components (b1) through (b45); and salts of compounds of (b1) through (b46).

8. The composition of any one of Claims 1 to 6, wherein component (b) includes at least one compound selected from acibenzolar-*S*-methyl, aldimorph, ametoctradin, amisulbrom, anilazine, azaconazole, azoxystrobin, benalaxyl, benalaxyl-M, benodanil, benomyl, benthiavalicarb, benthiavalicarb-isopropyl, bethoxazin, binapacryl, biphenyl, bitertanol, bixafen, blasticidin-S, boscalid, bromuconazole, bupirimate, carboxin, carpropamid, captafol, captan, carbendazim, chloroneb, chlorothalonil, chlozolinate, clotrimazole, copper salts, cyazofamid, cyflufenamid, cymoxanil, cyproconazole, cyprodinil,

dichlofluanid, diclocymet, diclomezine, dicloran, diethofencarb, difenoconazole, diflumetorim, dimethirimol, dimethomorph, dimoxystrobin, diniconazole, diniconazole-M, dinocap, dithianon, dodemorph, dodine, edifenphos, enestroburin, epoxiconazole, ethaboxam, ethirimol, etridiazole, famoxadone, fenamidone, fenarimol, fenbuconazole, fenfuram, fenhexamid, fenoxanil, fenpiclonil, fenpropidin, fenpropimorph, fenpyrazamine, fentin acetate, fentin chloride, fentin hydroxide, ferbam, ferimzone, fluazinam, fludioxonil, flumetover, flumorph, fluopicolide, fluopyram, fluoroimide, fluoxastrobin, fluquinconazole, flusilazole, flusulfamide, flutianil, flutolanil, flutriafol, fluxapyroxad, folpet, fosetyl-aluminum, fuberidazole, furalaxyl, furametpyr, hexaconazole, hymexazol, guazatine, imazalil, imibenconazole, iminoctadine, iodocarb, ipconazole, iprobenfos, iprodione, iprovalicarb, isoprothiolane, isopyrazam, isotianil, kasugamycin, kresoxim-methyl, mancozeb, mandipropamid, maneb, mepronil, meptyldinocap, metalaxyl, metalaxyl-M, metconazole, methasulfocarb, metiram, metominostrobin, mepanipyrim, metrafenone, myclobutanil, naftifine, neo-asozin (ferric methanearsonate), nuarimol, octhilinone, ofurace, orysastrobin, oxadixyl, oxolinic acid, oxpoconazole, oxycarboxin, oxytetracycline, penconazole, pencycuron, penflufen, penthiopyrad, pefurazoate, phosphorous acid and salts thereof, phthalide, picoxystrobin, piperalin, polyoxin, probenazole, prochloraz, procymidone, propamocarb, propamocarb-hydrochloride, propiconazole, propineb, proquinazid, prothiocarb, prothioconazole, pyraclostrobin, pyrametostrobin, pyraoxystrobin, pyrazophos, pyribencarb, pyributicarb, pyrifenox, pyrimethanil, pyriofenone, pyroquilon, pyrrolnitrin, quinomethionate, quinoxyfen, quintozene, sedaxane, silthiofam, simeconazole, spiroxamine, streptomycin, sulfur, tebuconazole, tebufloquin, tecloftalam, tecnazene, terbinafine, tetraconazole, thiabendazole, thifluzamide, thiophanate, thiophanate-methyl, thiram, tiadinil, tolclofos-methyl, tolylfluanid, triadimefon, triadimenol, triazoxide, tricyclazole, tridemorph, triflumizole, tricyclazole, trifloxystrobin, triforine, trimorphamide, triticonazole, uniconazole, validamycin, valifenalate, vinclozolin, zineb, ziram, zoxamide, *N*'-[4-[4-chloro-3-(trifluoro-methyl)phenoxy]-2,5-dimethylphenyl]-*N*-ethyl-*N*-methylmethanimidamide, 5-chloro-6-(2,4,6-trifluorophenyl)-7-(4-methylpiperidin-1-yl)[1,2,4]triazolo[1,5-*a*]pyrimidine, *N*-[2-[4-[[3-(4-chlorophenyl)-2-propyn-1-yl]oxy]-3-methoxyphenyl]ethyl]-3-methyl-2-[(methylsulfonyl)amino]butanamide, *N*-[2-[4-[[3-(4-chlorophenyl)-2-propyn-1-yl]oxy]-3-methoxyphenyl]ethyl]-3-methyl-2-[(ethylsulfonyl)amino]butanamide, 2-butoxy-6-iodo-3-propyl-4*H*-1-benzopyran-4-one, 3-[5-(4-chlorophenyl)-2,3-dimethyl-3-isoxazolidinyl]-pyridine, 4-fluorophenyl *N*-[1-[[[1-(4-cyanophenyl)ethyl]sulfonyl]methyl]propyl]carbamate, *N*-[[(cyclopropylmethoxy)amino][6-(difluoromethoxy)-2,3-difluoro-phenyl]methylene]benzeneacetamide, α-(methoxyimino)-*N*-methyl-2-[[[1-[3-(trifluoro-methyl)phenyl]ethoxy]imino]methyl]benzeneacetamide, *N*'-[4-[4-chloro-3-(trifluoro-methyl)phenoxy]-2,5-dimethylphenyl]-*N*-ethyl-*N*-methylmethanimidamide, *N*-(4-chloro-2-nitrophenyl)-*N*-ethyl-4-methylbenzenesulfonamide, 2-[[[[3-(2,6-dichlorophenyl)-1-methyl-2-propen-1-ylidene]amino]oxy]methyl]-α-(methoxyimino)-*N*--methylbenzeneacetamide, 1-[(2-propenylthio)carbonyl]-2-(1-methylethyl)-4-(2-methylphenyl)-5-amino-1*H*-pyrazol-3-one, 5-

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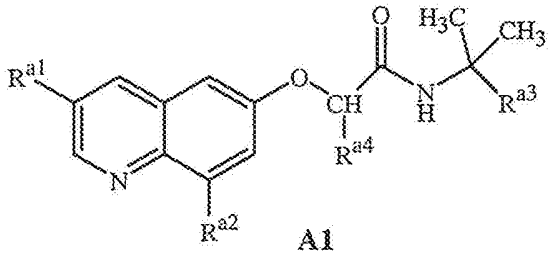
ethyl-6-octyl-[1,2,4]triazolo[1,5-a]pyrimidin-7-ylamine, pentyl *N*-[4-[[[[(1-methyl-1*H*-tetrazol-5-yl)phenylmethylene]amino]oxy]methyl]-2-thiazolyl]carbamate and pentyl *N*-[6-[[[[(1-methyl-1*H*-tetrazol-5-yl)phenylmethylene]amino]oxy]methyl]-2-pyridinyl]carbamate.

9. The composition of any one of Claims 1 to 8, wherein (b) includes at least one compound selected from chlorothalonil, metconazole, prothioconazole and penthiopyrad.

10. The composition of any one of Claims 1 to 6, wherein component (b) includes at least one fungicidal compound selected from compounds of Formula **A1** and salts thereof



A1

wherein

R^{a1} is halogen, C_1–C_4 alkoxy or C_1–C_4 alkynyl;

R^{a2} is H, halogen or C_1–C_4 alkyl;

R^{a3} 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^{a4} is methyl or Y^{a1}-R^{a5};

R^{a5} is C_1–C_2 alkyl; and

Y^{a1} is CH_2, O or S.

11. A composition comprising: (a) at least one compound selected from the compounds of Formula **1** as defined in Claim 1, *N*-oxides, and salts thereof; and at least one invertebrate pest control compound or agent.

12. A composition comprising the composition of any one of Claims 1 to 11 and at least one additional component selected from the group consisting of surfactants, solid diluents and liquid diluents.

13. A method for protecting a plant or plant seed from diseases caused by fungal pathogens comprising applying a fungicidally effective amount of the composition of any one of Claims 1 to 12 to the plant or plant seed.

14. A method for protecting a plant from a powdery mildew disease comprising applying to the plant a fungicidally effective amount of the composition of any one of Claims 1 to 5, wherein component (b) includes at least one fungicidal compound selected from (b11) quinone outside inhibitor fungicides.

15. A method for protecting a plant from a *Septoria* disease comprising applying to the plant a fungicidally effective amount of the composition of Claim 10.

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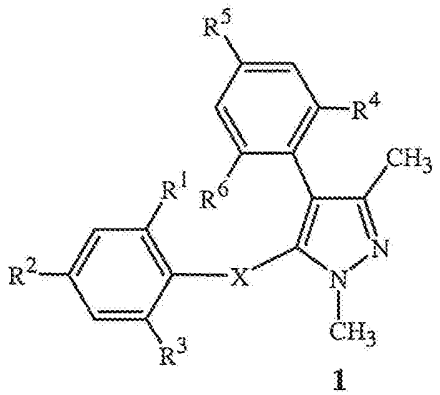
16. A compound of Formula **1** or an *N*-oxide or salt thereof,



1

wherein

X is NH;

R^1 is halogen;

R^2 is H;

R^3 is halogen;

R^4 is halogen;

R^5 is H, cyano, halogen or C_1–C_2 alkoxy; and

R^6 is H or halogen;

provided that when R^1 is F, then R^3 is Cl, and when R^1 is Cl, then R^3 is F.

17. A compound of Claim 16, wherein

R^3 is F or Cl.

18. A compound of Claim 17, wherein

R^1 is Cl or Br; and

R^3 is F.

19. A compound of Claim 16 selected from the group consisting of

4-(2-chloro-4-fluorophenyl)-*N*-(2-chloro-6-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine,

4-(2-bromo-4-fluorophenyl)-*N*-(2-chloro-6-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine, and

N-(2-bromo-6-fluorophenyl)-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5-amine.

20. A compound of Claim 16 which is 4-(2-bromo-4-fluorophenyl)-N-(2-chloro-6-fluorophenyl)-1,3-dimethyl-1*H*-pyrazol-5- amine.

21. A fungicidal composition comprising: (1) a compound of any one of Claims 16 to 20; and (2) at least one additional component selected from the group consisting of surfactants, solid diluents and liquid diluents.

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22. A method for protecting a plant or plant seed from diseases caused by fungal pathogens comprising applying a fungicidally effective amount of the compound of any one of Claims 16 to 20 to the plant or plant seed.