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(71) Applicant: **DOW AGROSCIENCES LLC** [US/US];
9330 Zionsville Road, Indianapolis, IN 46268 (US).(72) Inventors: **CORREA DA SILVA, Olavo**; 9330 Zionsville Road, Indianapolis, IN 46268 (US). **MATHIESON, Todd**; 9330 Zionsville Road, Indianapolis, IN 46268 (US). **SLEUGH, Byron B.**; 9330 Zionsville Road, Indianapolis, IN 46268 (US). **STUHR, Garrick W.**; 9330 Zionsville

Road, Indianapolis, IN 46268 (IN). **HOPKINS, Bradley**; 9330 Zionsville Road, Indianapolis, IN 46268 (US). **RUSHTON, Mary E.**; 9330 Zionsville Road, Indianapolis, IN 46268 (US).

(74) Agent: **LEE, Yung-Hui**; Dow AgroSciences LLC, 9330 Zionsville Road, Indianapolis, IN 46268 (US).

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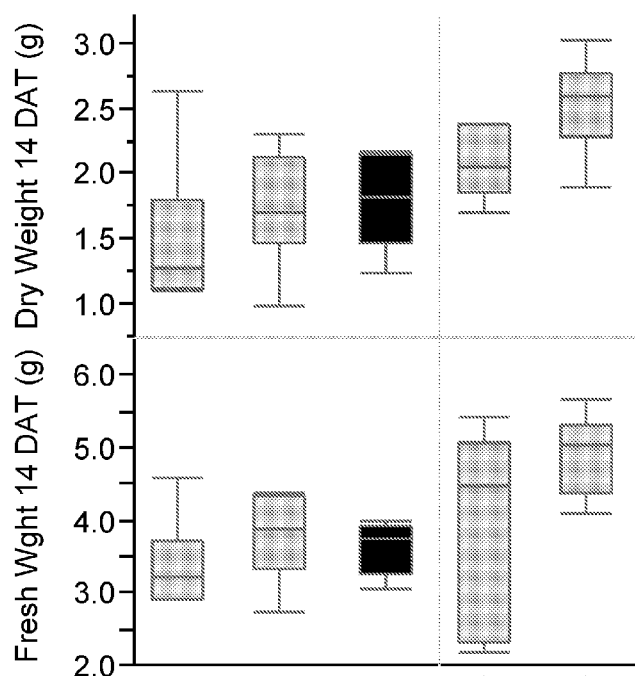


FIG. 6

(57) **Abstract:** This invention is based on the discovery that a combination of certain pesticide and a cyclopropene compound can greatly enhance plant health and/or tolerance to stress. The combination provided herein can be performed in a compositional mixture, or a simultaneous or sequential application with one or more compounds of Compound A and Compound B as provided herein. In one embodiment, the stress is associated with vegetable transplants from a green house/nursery into an open field. In another embodiment, the stress is associated with heat, cold, and/or drought.



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COMPOSITIONS AND METHODS FOR ENHANCING PLANT HEALTH AND/OR TOLERANCE TO STRESS

BACKGROUND

5 Plants are often treated by contacting them with compositions. For example, US
Patent Publication 2006/0160704 discloses treating non-citrus plants with compositions that
contain at least one cyclopropene and that contain at least one plant growth regulator that is
not a cyclopropene. It may be desired to provide methods that involve treating certain
specific crop plants at developmental stage or stages appropriate for those specific crop
10 plants. Further, it may also be desired to provide methods of treating plants that result in an
increase in the yield of the crop produced by those plants.

 In addition to yield enhancement, reducing adverse effects from various stresses may
be at least partially mitigated by application(s) of certain plant growth regulator(s). Sources
of stress may be from heat, cold, drought, or other chemicals. One particular stress occurs
15 during transplant of vegetables from a green house/nursery into an open field. Therefore,
there remains a need for compositions and/or methods for enhancing plant health and/or
tolerance to stress, in particular for vegetable transplants.

SUMMARY OF INVENTION

 This invention is based on the discovery that a combination of certain pesticide and a
20 cyclopropene compound can greatly enhance plant health and/or tolerance to stress. In one
embodiment, the stress is associated with vegetable transplants from a green house/nursery
into an open field. In another embodiment, the stress is associated with heat, cold, and/or
drought. In one embodiment, the stress comprises abiotic stress. Abiotic stress may include
dehydration or other osmotic stress, salinity, high or low light intensity, high or low
25 temperatures, submergence, exposure to heavy metals, and oxidative stress. In another
embodiment, the stress comprises an environmental stress. In a further embodiment, the
environmental stress comprises drought and/or heat. In another embodiment, the stress
comprises mechanical stress.

 In one aspect, provided is a composition comprising a mixture comprising (i) an
30 effective amount of Compound A according to Formula One, or an agriculturally acceptable
salt, ester, or amide thereof, as described herein, and (ii) a Compound B according to
Formula Two, or an agriculturally acceptable salt, ester, or amide thereof, as described
herein.

In one embodiment, weight ratio of Compound A to Compound B can be between 1:10 and 1000:1; between 1:10 and 1:1; between 1:1 and 1:100; or between 1:10 and 1:1000.

In another embodiment, the mixture comprises a synergistic combination of Compound A and Compound B for enhancing plant health and/or tolerance to stress. In one embodiment,

5 the composition further comprises a Compound C, or an agriculturally acceptable salt, ester, or amide thereof, as described herein. In a further embodiment, the Compound C is selected from the group consisting of spinosyn natural factor, semi-synthetic derivative, butenyl-spinosyn natural factor, or semi-synthetic derivative. In another further embodiment, the

Compound C comprises spinetoram. In another embodiment, the Compound C is selected

10 from the group consisting of azoxystrobin, sulfoxaflor, spinetoram, and combinations thereof.

In another aspect, provided is a method for enhancing plant health and/or tolerance to stress for plants. The method comprises (i) first applying an effective amount of Compound A according to Formula One, or an agriculturally acceptable salt, ester, or amide thereof, as described herein, to a plant or plant part; and (ii) second applying a Compound B according

15 to Formula Two, or an agriculturally acceptable salt, ester, or amide thereof, as described herein, to the plant or plant part; wherein the first applying and the second applying steps can be performed in either order or simultaneously.

In one embodiment, weight ratio of Compound A to Compound B can be between 1:10 and 1000:1; between 1:10 and 1:1; between 1:1 and 1:100; or between 1:10 and 1:1000.

20 In another embodiment, the combination of Compound A and Compound B is synergistic. In another embodiment, the first applying step is performed in an enclosed space, for example a green house or nursery. In another embodiment, the second applying step is performed in an enclosed space, for example a green house or nursery. In another embodiment, the first applying step is performed in an open space, for example an open field. In another

25 embodiment, the second applying step is performed in an open space, for example an open field.

In one embodiment, the plant comprises a vegetable. In a further embodiment, the vegetable is selected from the group consisting of tomato, peppers, celery, lettuce, broccoli, cabbage, cauliflower, artichokes, leeks, and combinations thereof. In another further

30 embodiment, the vegetable is selected from the group consisting of tomato, potato, sweet potato, cassava, pepper, bell pepper, carrot, celery, squash, eggplant, cabbage, cauliflower, broccoli, asparagus, mushroom, onion, garlic, leek, and snap bean.

In another embodiment, the method provided further comprises third applying a Compound C, or an agriculturally acceptable salt, ester, or amide thereof, as described herein,

to the plant or plant part. In a further embodiment, the Compound C is selected from the group consisting of spinosyn natural factor, semi-synthetic derivative, butenyl-spinosyn natural factor, or semi-synthetic derivative. In another further embodiment, the Compound C comprises spinetoram. In another embodiment, the Compound C is selected from the group consisting of azoxystrobin, sulfoxaflor, spinetoram, and combinations thereof.

In another aspect, provided is a method for enhancing plant health and/or tolerance to stress for plants. The method comprises applying the composition as described herein, to a plant or plant part.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 shows exemplary results of enhancing plant health (leaf length at day 12, plant height at day 12, and dry weight at day 14) during transplant of tomato seedlings after applications of: (1) 1-MCP at 50 ppm; (2) Compound A at 25 ppm and 1-MCP at 25 ppm; (3) Compound A at 25 ppm, 1-MCP at 25 ppm, and spinetoram at 25 ppm; and (4) untreated tomato seedlings.

FIG. 2 shows exemplary results of % plant vigor at day 4, day 13, and day 28 during transplant of broccoli seedlings after application of: (1) untreated broccoli seedlings; (2) 1-MCP at 50 ppm; (3) Compound A at 50 ppm and 1-MCP at 25 ppm; (4) Compound A at 25 ppm, 1-MCP at 25 ppm, and spinetoram at 25 ppm.

FIG. 3 shows exemplary results of enhancing plant health (leaf area at day 13 and plant height at day 13) during transplant of broccoli seedlings after application of: (1) untreated broccoli seedlings; (2) 1-MCP at 50 ppm; (3) Compound A at 50 ppm and 1-MCP at 25 ppm; (4) Compound A at 25 ppm, 1-MCP at 25 ppm, and spinetoram at 25 ppm.

FIG. 4 shows exemplary results of plant biomass at day 14 and day 28 during transplant of broccoli seedlings after application of: (1) untreated broccoli seedlings; (2) 1-MCP at 50 ppm; (3) Compound A at 50 ppm and 1-MCP at 25 ppm; (4) Compound A at 25 ppm, 1-MCP at 25 ppm, and spinetoram at 25 ppm.

FIG. 5 shows exemplary results of enhancing plant health (leaf area at day 28 and plant height at day 29) during transplant of tomato seedling after applications of: (1) untreated tomato seedlings; (2) 1-MCP at 50 ppm; (3) Compound A at 25 ppm and 1-MCP at 50 ppm; and (4) Compound A at 25 ppm, 1-MCP at 25 ppm, and spinetoram at 25 ppm.

FIG. 6 shows exemplary results of prolonged treatments for enhancing plant health (dry weight at day 14 and fresh weight at day 14) during transplant of tomato seedlings after applications of: (1) Compound A at 25 ppm and 1-MCP at 50 ppm treatment for one day; (2) Compound A at 25 ppm, 1-MCP at 50 ppm, and spinetoram at 25 ppm treatment for one day;

(3) untreated tomato seedlings; (4) Compound A at 25 ppm and 1-MCP at 50 ppm treatment for six days; and (5) Compound A at 25 ppm, 1-MCP at 50 ppm, and spinetoram at 25 ppm treatment for six days.

DETAILED DESCRIPTION OF THE INVENTION

5 This invention is based on the discovery that a combination of certain pesticide and a cyclopropene compound can greatly enhance plant health and/or tolerance to stress. The combination provided herein can be applied in a compositional mixture, or a simultaneous or sequential application with one or more compounds of Compound A and Compound B as provided herein. The combination described herein provides greater efficacy as compared to
10 Compound B alone. Although cyclopropene compounds are known to be plant growth regulators, the combination described herein is unexpected because Compound A according to Formula One has been previously disclosed as pesticide, in particular insecticide. Examples of Compound A according to Formula One have been disclosed in U.S. Patent No. 8,901,153; U.S. Patent Publication Nos. 2014/0213448 and 2013/0291227; and International
15 PCT Publication Nos. WO 2013/162716 and WO 2013/162715, the contents of which are hereby incorporated by reference in their entireties.

Definitions

 The examples given in the definitions are generally non-exhaustive and must not be construed as limiting the invention disclosed in this document. It is understood that a
20 substituent should comply with chemical bonding rules and steric compatibility constraints in relation to the particular molecule to which it is attached.

 “**Alkenyl**” means an acyclic, unsaturated (at least one carbon-carbon double bond), branched or unbranched, substituent consisting of carbon and hydrogen, for example, vinyl, allyl, butenyl, pentenyl, and hexenyl.

25 “**Alkenyloxy**” means an alkenyl further consisting of a carbon-oxygen single bond, for example, allyloxy, butenyloxy, pentenyloxy, hexenyloxy.

 “**Alkoxy**” means an alkyl further consisting of a carbon-oxygen single bond, for example, methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, and *tert*-butoxy.

 “**Alkyl**” means an acyclic, saturated, branched or unbranched, substituent consisting
30 of carbon and hydrogen, for example, methyl, ethyl, (C₃)alkyl which represents *n*-propyl and isopropyl, (C₄)alkyl which represents *n*-butyl, *sec*-butyl, isobutyl, and *tert*-butyl.

 “**Alkynyl**” means an acyclic, unsaturated (at least one carbon-carbon triple bond), branched or unbranched, substituent consisting of carbon and hydrogen, for example, ethynyl, propargyl, butynyl, and pentynyl.

“**Alkynyloxy**” means an alkynyl further consisting of a carbon-oxygen single bond, for example, pentynyloxy, hexynyloxy, heptynyloxy, and octynyloxy.

“**Aryl**” means a cyclic, aromatic substituent consisting of hydrogen and carbon, for example, phenyl, naphthyl, and biphenyl.

5 “**(C_x-C_y)**” where the subscripts “x” and “y” are integers such as 1, 2, or 3, means the range of carbon atoms for a substituent – for example, (C₁-C₄)alkyl means methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, isobutyl, and *tert*-butyl, each individually.

“**Cycloalkenyl**” means a monocyclic or polycyclic, unsaturated (at least one carbon-carbon double bond) substituent consisting of carbon and hydrogen, for example,
10 cyclobutenyl, cyclopentenyl, cyclohexenyl, norbornenyl, bicyclo[2.2.2]octenyl, tetrahydronaphthyl, hexahydronaphthyl, and octahydronaphthyl.

“**Cycloalkenyloxy**” means a cycloalkenyl further consisting of a carbon-oxygen single bond, for example, cyclobutenyloxy, cyclopentenyl, norbornenyloxy, and bicyclo[2.2.2]octenyloxy.

15 “**Cycloalkyl**” means a monocyclic or polycyclic, saturated substituent consisting of carbon and hydrogen, for example, cyclopropyl, cyclobutyl, cyclopentyl, norbornyl, bicyclo[2.2.2]octyl, and decahydronaphthyl.

“**Cycloalkoxy**” means a cycloalkyl further consisting of a carbon-oxygen single bond, for example, cyclopropyloxy, cyclobutyloxy, cyclopentyloxy, norbornyloxy, and
20 bicyclo[2.2.2]octyloxy.

“**Halo**” means fluoro, chloro, bromo, and iodo.

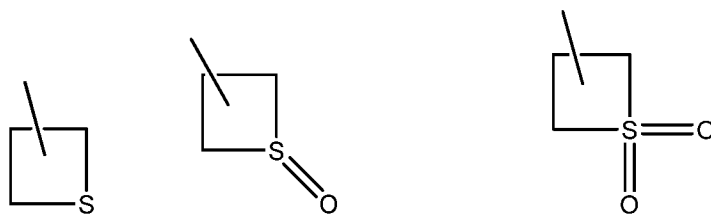
“**Haloalkoxy**” means an alkoxy further consisting of, from one to the maximum possible number of identical or different, halos, for example, fluoromethoxy, trifluoromethoxy, 2,2-difluoropropoxy, chloromethoxy, trichloromethoxy, 1,1,2,2-
25 tetrafluoroethoxy, and pentafluoroethoxy.

“**Haloalkyl**” means an alkyl further consisting of, from one to the maximum possible number of, identical or different, halos, for example, fluoromethyl, trifluoromethyl, 2,2-difluoropropyl, chloromethyl, trichloromethyl, and 1,1,2,2-tetrafluoroethyl.

“**Heterocyclyl**” means a cyclic substituent that may be fully saturated, partially
30 unsaturated, or fully unsaturated, where the cyclic structure contains at least one carbon and at least one heteroatom, where said heteroatom is nitrogen, sulfur, or oxygen. In the case of sulfur, that atom can be in other oxidation states such as a sulfoxide and sulfone. Examples of aromatic heterocyclyls include, but are not limited to, benzofuranyl, benzoisothiazolyl, benzoisoxazolyl, benzoxazolyl, benzothienyl, benzothiazolyl, cinnolinyl, furanyl, imidazolyl,

indazolyl, indolyl, isoindolyl, isoquinolinyl, isothiazolyl, isoxazolyl, oxadiazolyl, oxazolyl, oxazolyl, phthalazinyl, pyrazinyl, pyrazolinyl, pyrazolyl, pyridazinyl, pyridyl, pyrimidinyl, pyrrolyl, quinazolinyl, quinolinyl, quinoxalinyl, tetrazolyl, thiazolinyl, thiazolyl, thienyl, triazinyl, and triazolyl. Examples of fully saturated heterocyclyls include, but are not limited to, piperazinyl, piperidiny, morpholinyl, pyrrolidinyl, oxetanyl, tetrahydrofuranyl, tetrahydrothienyl and tetrahydropyranyl. Examples of partially unsaturated heterocyclyls include, but are not limited to, 1,2,3,4-tetrahydroquinolinyl, 4,5-dihydro-oxazolyl, 4,5-dihydro-1*H*-pyrazolyl, 4,5-dihydro-isoxazolyl, and 2,3-dihydro-[1,3,4]-oxadiazolyl.

Additional examples include the following



thietanyl

thietanyl-oxide

thietanyl-dioxide.

As used herein, the phrase “plant health” and/or “tolerance to stress” may be measured according to one or more of criteria including, but not limited to, biomass, plant height, leaf length, leaf area, root growth, root length, greenness or chlorophyll content, growth rate, harvest index, root dry weight, shoot dry weight, total dry weight, specific oil or protein content, nutrient content, total yield, number of leaves, days to maturity, vigor (1-9), canopy % coverage, plant survival rate, stem diameter, root/shoot ratio, and combinations thereof. In addition, enhancing “tolerance to stress” may include one or more of criteria including, but not limited to, enhanced water use efficiency, enhanced cold tolerance, enhanced heat tolerance, enhanced salt tolerance, increased yield, enhanced nitrogen use efficiency, enhanced seed protein, enhanced seed oil, and combinations thereof.

As used herein, the phrase “plant” includes dicotyledonous plants and monocotyledonous plants. Examples of dicotyledonous plants include tobacco, Arabidopsis, soybean, tomato, papaya, canola, sunflower, cotton, alfalfa, potato, grapevine, pigeon pea, pea, Brassica, chickpea, sugar beet, rapeseed, watermelon, melon, pepper, peanut, pumpkin, radish, spinach, squash, broccoli, cabbage, carrot, cauliflower, celery, Chinese cabbage, cucumber, eggplant, and lettuce. Examples of monocotyledonous plants include corn, rice, wheat, sugarcane, barley, rye, sorghum, orchids, bamboo, banana, cattails, lilies, oat, onion, millet, and triticale. Examples of fruit include banana, pineapple, oranges, grapes, grapefruit, watermelon, melon, apples, peaches, pears, kiwifruit, mango, nectarines, guava, persimmon,

avocado, lemon, fig, and berries. Examples of flowers include baby's breath, carnation, dahlia, daffodil, geranium, gerbera, lily, orchid, peony, Queen Anne's lace, rose, snapdragon, or other cut-flowers or ornamental flowers, potted-flowers, and flower bulbs.

As used herein, plants include, but are not limited to, germinant seeds, emerging
5 seedlings, plants emerging from vegetative propagules, immature vegetation, and established vegetation.

As used herein, the phrase "vegetable" include, but not limited to, tomato, peppers, celery, lettuce, broccoli, cabbage, cauliflower, artichokes, and leeks.

As used herein, agriculturally acceptable salts and esters refer to salts and esters that
10 exhibit herbicidal activity, or that are or can be converted in plants, water, or soil to the referenced herbicide. Exemplary agriculturally acceptable esters are those that are or can be hydrolyzed, oxidized, metabolized, or otherwise converted, *e.g.*, in plants, water, or soil, to the corresponding carboxylic acid which, depending on the pH, may be in the dissociated or undissociated form.

15 In some embodiment, synergism may be defined as "an interaction of two or more factors such that the effect when combined is greater than the predicted effect based on the response of each factor applied separately." Senseman, S., Ed. Herbicide Handbook. 9th ed. Lawrence: Weed Science Society of America, 2007. In some embodiments, the compositions exhibit synergy as determined by the Colby's equation (Colby, S. R. Calculation of the
20 synergistic and antagonistic response of herbicide combinations. Weeds 1967, 15, 20-22.

As used herein, to "treat" a plant or plant part means to bring the plant or plant part into contact with a material.

Among embodiments in which plants are treated using methods involving a composition of the present invention, the plants that are treated may be any plants that
25 produce a useful product. Among embodiments in which plant parts are treated using methods involving a composition of the present invention, the plant parts that are treated may be any part of the plant that produces a useful product. In some embodiments, useful plant parts are treated with a method involving use of a composition of the present invention.

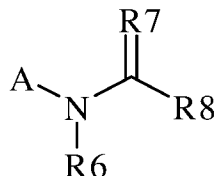
In embodiments of the present invention in which a plant or plant part is treated, a
30 composition of the present invention is used in a way that brings Compound A and/or Compound B into contact with the plant or plant part. In some embodiments, the method involves using a composition of the present invention in a way that releases Compound B from the cyclopropene molecular encapsulating agent complex under conditions in which the cyclopropene compound then comes into contact with the plant or plant part.

All patents and patent applications cited in this document are hereby incorporated by reference by their entireties.

Compound A

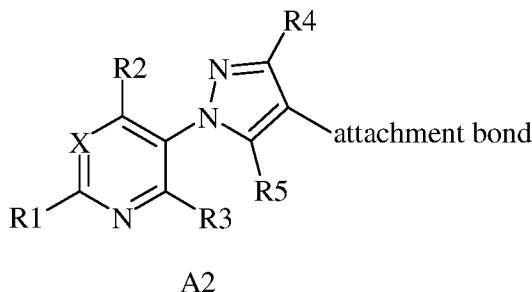
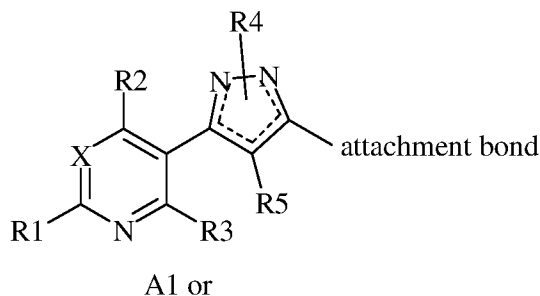
This document discloses molecules of Compound A having the following formula

5 (“Formula One”):



wherein

(a) A is either



;

- 10 (b) R1 is H, F, Cl, Br, I, CN, NO₂, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, OR₉, C(=X₁)R₉, C(=X₁)OR₉,
 15 C(=X₁)N(R₉)₂, N(R₉)₂, N(R₉)C(=X₁)R₉, S(O)_nR₉, S(O)_nOR₉, S(O)_nN(R₉)₂, or R₉S(O)_nR₉,

wherein each said R1, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, C₆-C₂₀ aryl,

or C₁-C₂₀ heterocyclyl, (each of which that can be substituted, may optionally be substituted with R₉);

(c) R₂ is H, F, Cl, Br, I, CN, NO₂, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, OR₉, C(=X₁)R₉, C(=X₁)OR₉, C(=X₁)N(R₉)₂, N(R₉)₂, N(R₉)C(=X₁)R₉, SR₉, S(O)_nOR₉, or R₉S(O)_nR₉,

wherein each said R₂, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, (each of which that can be substituted, may optionally be substituted with R₉);

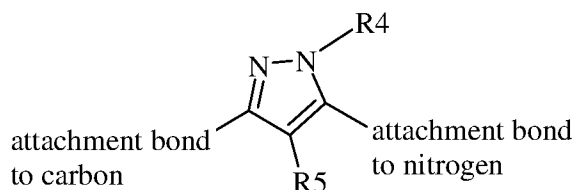
(d) R₃ is H, F, Cl, Br, I, CN, NO₂, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, OR₉, C(=X₁)R₉, C(=X₁)OR₉, C(=X₁)N(R₉)₂, N(R₉)₂, N(R₉)C(=X₁)R₉, SR₉, S(O)_nOR₉, or R₉S(O)_nR₉,

wherein each said R₃, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, (each of which that can be substituted, may optionally be substituted with R₉);

(e) when A is

(1) A₁ then A₁ is either

(a) A₁₁

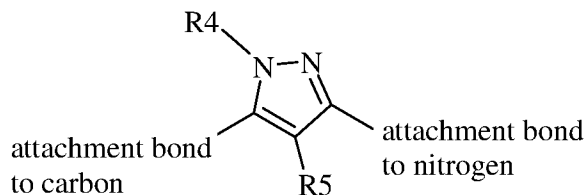


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where R4 is H, NO₂, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, C(=X1)R9, C(=X1)OR9, C(=X1)N(R9)₂, N(R9)₂, N(R9)C(=X1)R9, S(O)_nOR9, or R9S(O)_nR9,

wherein each said R4, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR9, S(O)_nOR9, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, (each of which that can be substituted, may optionally be substituted with R9), or

(b) A12



A12

where R4 is a C₁-C₆ alkyl,

(2) A2 then R4 is H, F, Cl, Br, I, CN, NO₂, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, OR9, C(=X1)R9, C(=X1)OR9, C(=X1)N(R9)₂, N(R9)₂, N(R9)C(=X1)R9, SR9, S(O)_nOR9, or R9S(O)_nR9,

wherein each said R4, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, (each of which that can be substituted, may optionally be substituted with R₉);

(f) R₅ is H, F, Cl, Br, I, CN, NO₂, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, OR₉, C(=X₁)R₉, C(=X₁)OR₉, C(=X₁)N(R₉)₂, N(R₉)₂, N(R₉)C(=X₁)R₉, SR₉, S(O)_nOR₉, or R₉S(O)_nR₉,

wherein each said R₅, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, or C₆-C₂₀ aryl, (each of which that can be substituted, may optionally be substituted with R₉);

(g)

(1) when A is A₁ then R₆ is R₁₁, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, OR₉, C(=X₁)R₉, C(=X₁)OR₉, C(=X₁)N(R₉)₂, N(R₉)₂, N(R₉)C(=X₁)R₉, SR₉, S(O)_nOR₉, R₉S(O)_nR₉, C₁-C₆ alkyl C₆-C₂₀ aryl (wherein the alkyl and aryl can independently be substituted or unsubstituted), C(=X₂)R₉, C(=X₁)X₂R₉, R₉X₂C(=X₁)R₉, R₉X₂R₉, C(=O)(C₁-C₆ alkyl)S(O)_n(C₁-C₆ alkyl), C(=O)(C₁-C₆ alkyl)C(=O)O(C₁-C₆ alkyl), (C₁-C₆ alkyl)OC(=O)(C₆-C₂₀ aryl), (C₁-C₆ alkyl)OC(=O)(C₁-C₆ alkyl), C₁-C₆ alkyl-(C₃-C₁₀ cyclohaloalkyl), or (C₁-C₆ alkenyl)C(=O)O(C₁-C₆ alkyl), or R₉X₂C(=X₁)X₂R₉,

wherein each said R₆ (except R₁₁), which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, C₆-

C₂₀ aryl, or C₁-C₂₀ heterocyclyl, R₉aryl, (each of which that can be substituted, may optionally be substituted with R₉),

optionally R₆ (except R₁₁) and R₈ can be connected in a cyclic arrangement, where optionally such arrangement can have one or more heteroatoms selected from O, S, or N, in the cyclic structure connecting R₆ and R₈, and

- (2) when A is A₂ then R₆ is R₁₁, H, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, OR₉, C(=X₁)R₉, C(=X₁)OR₉, C(=X₁)N(R₉)₂, N(R₉)₂, N(R₉)C(=X₁)R₉, SR₉, S(O)_nOR₉, R₉S(O)_nR₉, C₁-C₆ alkyl C₆-C₂₀ aryl (wherein the alkyl and aryl can independently be substituted or unsubstituted), C(=X₂)R₉, C(=X₁)X₂R₉, R₉X₂C(=X₁)R₉, R₉X₂R₉, C(=O)(C₁-C₆ alkyl)S(O)_n(C₁-C₆ alkyl), C(=O)(C₁-C₆ alkyl)C(=O)O(C₁-C₆ alkyl), (C₁-C₆ alkyl)OC(=O)(C₆-C₂₀ aryl), (C₁-C₆ alkyl)OC(=O)(C₁-C₆ alkyl), C₁-C₆ alkyl-(C₃-C₁₀ cyclohaloalkyl), or (C₁-C₆ alkenyl)C(=O)O(C₁-C₆ alkyl), or R₉X₂C(=X₁)X₂R₉,

wherein each said R₆ (except R₁₁), which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, R₉aryl, (each of which that can be substituted, may optionally be substituted with R₉),

optionally R₆ (except R₁₁) and R₈ can be connected in a cyclic arrangement, where optionally such arrangement can have one or more heteroatoms selected from O, S, or N, in the cyclic structure connecting R₆ and R₈;

(h) R₇ is O, S, NR₉, or NOR₉;

(i) R₈ is substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, OR₉, OR₉S(O)_nR₉, C(=X₁)R₉, C(=X₁)OR₉, R₉C(=X₁)OR₉, R₉X₂C(=X₁)R₉X₂R₉, C(=X₁)N(R₉)₂, N(R₉)₂, N(R₉)(R₉S(O)_nR₉), N(R₉)C(=X₁)R₉, SR₉, S(O)_nOR₉, R₉S(O)_nR₉, or R₉S(O)_n(NZ)R₉,

wherein each said R8, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkoxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, N(R9)S(O)_nR9, oxo, OR9,
 5 S(O)_nOR9, R9S(O)_nR9, S(O)_nR9, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, (each of which that can be substituted, may optionally be substituted with R9)

alternatively R8 is R13-S(O)_n-R13 wherein each R13 is independently selected from substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, substituted or unsubstituted S(O)_nC₁-C₆ alkyl, substituted or unsubstituted N(C₁-C₆alkyl)₂, wherein each said substituted alkyl, substituted alkenyl, substituted alkoxy, substituted alkenyloxy, substituted cycloalkyl, substituted cycloalkenyl, substituted aryl,
 10 substituted heterocyclyl, has one or more substituents independently selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkoxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OC₁-C₆ alkyl, OC₁-C₆ haloalkyl, S(O)_nC₁-C₆alkyl, S(O)_nOC₁-C₆ alkyl, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, C₂-C₆ alkynyl, C₁-C₆ alkoxy,
 15 N(R9)S(O)_nR9, OR9, N(R9)₂, R9OR9, R9N(R9)₂, R9C(=X1)R9, R9C(=X1)N(R9)₂, N(R9)C(=X1)R9, R9N(R9)C(=X1)R9, S(O)_nOR9, R9C(=X1)OR9, R9OC(=X1)R9, R9S(O)_nR9, S(O)_nR9, oxo, (each of which that can be substituted, may optionally be substituted with R9);

(j) R9 is (each independently) H, CN, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, substituted or unsubstituted S(O)_nC₁-C₆ alkyl, substituted or unsubstituted N(C₁-C₆alkyl)₂,
 25

wherein each said R9, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkoxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OC₁-C₆ alkyl, OC₁-C₆ haloalkyl, S(O)_nC₁-C₆alkyl, S(O)_nOC₁-C₆ alkyl, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl;
 30

(k) n is 0, 1, or 2;

(l) X is N or CR_{n1} where R_{n1} is H, F, Cl, Br, I, CN, NO₂, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, OR₉, C(=X1)R₉, C(=X1)OR₉, C(=X1)N(R₉)₂, N(R₉)₂, N(R₉)C(=X1)R₉, SR₉, S(O)_nR₉, S(O)_nOR₉, or R₉S(O)_nR₉,

wherein each said R_{n1} which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, (each of which that can be substituted, may optionally be substituted with R₉);

(m) X1 is (each independently) O or S;

(n) X2 is (each independently) O, S, =NR₉, or =NOR₉;

(o) Z is CN, NO₂, C₁-C₆ alkyl(R₉), C(=X1)N(R₉)₂;

(p) R11 is Q₁(C≡C)R12, wherein Q₁ is a bond, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₂-C₆ alkynyl, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₂-C₁₀ cycloalkoxy, substituted or unsubstituted C₁-C₆ alkylOR₉, substituted or unsubstituted C₁-C₆ alkylS(O)_nR₉, substituted or unsubstituted C₁-C₆ alkylS(O)_n(=NR₉), substituted or unsubstituted C₁-C₆ alkylN(R₉) (where (C≡C) is attached directly to the N by a bond), substituted or unsubstituted C₁-C₆ alkylN(R₉)₂, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₀-C₆ alkylC(=R7)C₀-C₆ alkylR₉, substituted or unsubstituted C₀-C₆ alkylC(=R7)OR₉, substituted or unsubstituted C₁-C₆ alkylOC₀-C₆ alkylC(=R7)R₉, substituted or unsubstituted C₁-C₆ alkylN(R₉)(C(=R7)R₉), substituted or unsubstituted C₁-C₆ alkylN(R₉)(C(=R7)OR₉), substituted or unsubstituted C₀-C₆ alkyl C(=R7)C₀-C₆ alkylN(R₉) (where (C≡C) is attached directly to the N by a bond), substituted or unsubstituted C₀-C₆alkylC(=R7)C₀-C₆ alkylN(R₉)₂, OR₉, S(O)_nR₉, N(R₉)R₉, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl,

wherein each said Q₁, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₂-C₆ alkynyl, C₁-C₆

haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, SR₉, S(O)_nR₉, S(O)_nOR₉, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, R₉aryl, C₁-C₆alkylOR₉, C₁-C₆alkylS(O)_nR₉, (each of which that can be substituted, may optionally be substituted with R₉)

5 optionally Q₁ and R₈ can be connected in a cyclic arrangement, where optionally such arrangement can have one or more heteroatoms selected from O, S, or N, in the cyclic structure connecting Q₁ and R₈;

(q) R₁₂ is Q₁ (except where Q₁ is a bond), F, Cl, Br, I, Si(R₉)₃ (where each R₉ is independently selected), or R₉; and

10 (r) with the following provisos

(1) that R₆ and R₈ cannot both be C(=O)CH₃,

(2) that when A₁ is A₁₁ then R₆ and R₈ together do not form fused ring systems,

(3) that R₆ and R₈ are not linked in a cyclic arrangement with only -CH₂-,

15 (4) that when A is A₂ then R₅ is not C(=O)OH,

(5) that when A is A₂ and R₆ is H then R₈ is not a -(C₁-C₆ alkyl)-O-(substituted aryl), and

(6) that when A is A₂ then R₆ is not -(C₁alkyl)(substituted aryl).

20 In another embodiment of this invention A is A₁.

In another embodiment of this invention A is A₂.

In another embodiment of this invention R₁ is H.

In another embodiment of this invention R₂ is H.

25 In another embodiment of this invention R₃ is selected from H, or substituted or unsubstituted C₁-C₆ alkyl.

In another embodiment of this invention R₃ is selected from H or CH₃.

In another embodiment of the invention when A is A₁ then A₁ is A₁₁.

30 In another embodiment of the invention when A is A₁, and A₁ is A₁₁, then R₄ is selected from H, or substituted or unsubstituted C₁-C₆ alkyl, or substituted or unsubstituted C₆-C₂₀ aryl.

In another embodiment of the invention when A is A₁, and A₁ is A₁₁ then R₄ is selected from CH₃, CH(CH₃)₂, or phenyl.

In another embodiment of the invention when A is A₁, and A₁ is A₁₂, then R₄ is CH₃.

In another embodiment of this invention when A is A2 then R4 is selected from H, or substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₆-C₂₀ aryl, wherein each said R4, which is substituted, has one or more substituents selected from F, Cl, Br, or I.

In another embodiment of this invention when A is A2 then R4 is H or C₁-C₆ alkyl.

In another embodiment of this invention when A is A2 then R4 is H, CH₃, CH₂CH₃, CH=CH₂, cyclopropyl, CH₂Cl, CF₃, or phenyl.

In another embodiment of this invention when A is A2 then R4 is Br or Cl.

In another embodiment of this invention R5 is H, F, Cl, Br, I, or substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₁-C₆ alkoxy.

In another embodiment of this invention R5 is H, OCH₂CH₃, F, Cl, Br, or CH₃.

In another embodiment of this invention, when A is A1 then R6 is substituted or unsubstituted C₁-C₆ alkyl.

In another embodiment of this invention when A is A2 then R6 is selected from substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₃-C₁₀ cycloalkyl, C(=X1)R9, C(=X1)X2R9, R9X2R9, C(=O)(C₁-C₆ alkyl)S(O)_n(C₁-C₆ alkyl), (C₁-C₆ alkyl)OC(=O)(C₆-C₂₀ aryl), (C₁-C₆ alkyl)OC(=O)(C₁-C₆ alkyl), or R9X2C(=X1)X2R9.

In another embodiment of this invention when A is A2 then R6 and R8 are connected in a cyclic arrangement, where optionally such arrangement can have one or more heteroatoms selected from O, S, or, N, in the cyclic structure connecting R6 and R8.

In another embodiment of this invention R6 is C₁-C₆ alkyl, or C₁-C₆ alkyl-phenyl.

In another embodiment of this invention R6 is H, CH₃, CH₂CH₃, CH₂CH₂CH₃, CH(CH₃)₂, CH₂phenyl, CH₂CH(CH₃)₂, CH₂cyclopropyl, C(=O)CH₂CH₂SCH₃, C(=O)OC(CH₃)₃, CH₂CH=CH₂, C(=O)OCH₂CH₃, C(=O)CH(CH₃)CH₂SCH₃, cyclopropyl, CD₃, CH₂OC(=O)phenyl, C(=O)CH₃, C(=O)CH(CH₃)₂, CH₂OC(=O)CH(CH₃)₂, CH₂OC(=O)CH₃, C(=O)phenyl, CH₂OCH₃, CH₂OC(=O)CH₂OCH₂CH₃, CH₂CH₂OCH₃, CH₂OC(=O)OCH(CH₃)₂, CH₂CH₂OCH₂OCH₃, CH₂CH₂OCH₃, CH₂CH₂OC(=O)CH₃, CH₂CN.

In another embodiment of this invention R6 is methyl or ethyl.

In another embodiment of this invention R7 is O or S.

In another embodiment of this invention R8 is selected from substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or

unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, R⁹C(=X¹)OR⁹, SR⁹, S(O)_nOR⁹, R⁹S(O)_nR⁹, or R⁹S(O)_n(NZ)R⁹.

In another embodiment of this invention R⁸ is CH(CH₃)CH₂SCH₃, CH(CH₃)₂,
 5 C(CH₃)₂CH₂SCH₃, CH₂CH₂SCH₃, CH₂CF₃, CH₂CH₂C(=O)OCH₃, N(H)(CH₂CH₂SCH₃),
 OCH₂CH₂SCH₃, CH(CH₂SCH₃)(CH₂phenyl), thiazolyl, oxazolyl, isothiazolyl, substituted-
 furanyl, CH₃, C(CH₃)₃, phenyl, CH₂CH₂OCH₃, pyridyl, CH₂CH(CH₃)SCH₃, OC(CH₃)₃,
 C(CH₃)₂CH₂SCH₃, CH(CH₃)CH(CH₃)SCH₃, CH(CH₃)CF₃, CH₂CH₂-thienyl,
 CH(CH₃)SCF₃, CH₂CH₂Cl, CH₂CH₂CH₂CF₃, CH₂CH₂S(=O)CH₃, CH(CH₃)CH₂S(=O)CH₃,
 10 CH₂CH₂S(=O)₂CH₃, CH(CH₃)CH₂S(=O)₂CH₃, NCH₂CH₃, N(H)(CH₂CH₂CH₃),
 C(CH₃)=C(H)(CH₃), N(H)(CH₂CH=CH₂), CH₂CH(CF₃)SCH₃, CH(CF₃)CH₂SCH₃, thietanyl,
 CH₂CH(CF₃)₂, CH₂CH₂CF(OCF₃)CF₃, CH₂CH₂CF(CF₃)CF₃, CF(CH₃)₂, CH(CH₃)phenyl-Cl,
 CH(CH₃)phenyl-F, CH(CH₃)phenyl-OCF₃, CH₂N(CH₃)(S(=O)₂N(CH₃)₂),
 CH(CH₃)OCH₂CH₂SCH₃, CH(CH₃)OCH₂CH₂OCH₃, OCH₃, CH(CH₃)SCH₃, CH₂SCH₃,
 15 N(H)CH₃, CH(Br)CH₂Br, or CH(CH₃)CH₂SCD₃.

In another more preferred embodiment of this invention R⁸ is preferably R¹³-S(O)_n-
 R¹³ wherein each R¹³ is independently selected from substituted or unsubstituted C₁-C₆
 alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy,
 substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl,
 20 substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl,
 substituted or unsubstituted C₁-C₂₀ heterocyclyl, substituted or unsubstituted S(O)_nC₁-C₆
 alkyl, substituted or unsubstituted N(C₁-C₆alkyl)₂, wherein each said substituted alkyl,
 substituted alkenyl, substituted alkoxy, substituted alkenyloxy, substituted cycloalkyl,
 substituted cycloalkenyl, substituted aryl, substituted heterocyclyl, has one or more
 25 substituents independently selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl,
 C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀
 cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OC₁-C₆
 alkyl, OC₁-C₆ haloalkyl, S(O)_nC₁-C₆alkyl, S(O)_nOC₁-C₆ alkyl, C₆-C₂₀ aryl, or C₁-C₂₀
 heterocyclyl, C₂-C₆ alkynyl, C₁-C₆ alkoxy, N(R⁹)S(O)_nR⁹, OR⁹, N(R⁹)₂, R⁹OR⁹, R⁹N(R⁹)₂,
 30 R⁹C(=X¹)R⁹, R⁹C(=X¹)N(R⁹)₂, N(R⁹)C(=X¹)R⁹, R⁹N(R⁹)C(=X¹)R⁹, S(O)_nOR⁹,
 R⁹C(=X¹)OR⁹, R⁹OC(=X¹)R⁹, R⁹S(O)_nR⁹, S(O)_nR⁹, oxo, (each of which that can be
 substituted, may optionally be substituted with R⁹).

In another embodiment of this invention R⁸ is (substituted or unsubstituted C₁-C₆
 alkyl)-S(O)_n-(substituted or unsubstituted C₁-C₆ alkyl) wherein said substituents on said

substituted alkyls are independently selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OC₁-C₆ alkyl, OC₁-C₆ haloalkyl, S(O)_nC₁-C₆alkyl, S(O)_nOC₁-C₆ alkyl, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, C₂-C₆ alkynyl, C₁-C₆ alkoxy, N(R₉)S(O)_nR₉, OR₉, N(R₉)₂, R₉OR₉, R₉N(R₉)₂, R₉C(=X₁)R₉, R₉C(=X₁)N(R₉)₂, N(R₉)C(=X₁)R₉, R₉N(R₉)C(=X₁)R₉, S(O)_nOR₉, R₉C(=X₁)OR₉, R₉OC(=X₁)R₉, R₉S(O)_nR₉, S(O)_nR₉, oxo, (each of which that can be substituted, may optionally be substituted with R₉).

In another embodiment of this invention R₈ is selected from CH(CH₃)SCH₂CF₃, CH₂CH₂SCH₂CF₃, CH₂SCH₂CF₃, CH₂SCHClCF₃, CH(CH₂CH₃)SCH₂CF₃, CH(CH₃)SCH₂CHF₂, CH(CH₃)SCH₂CH₂F, CH₂CH₂SCH₂CH₂F, CH(CH₃)S(=O)₂CH₂CF₃, CH(CH₃)S(=O)CH₂CF₃, CH(CH₃)CH₂SCF₃, CH(CH₃)CH₂SCF₃, CH(CH₃)SCH₂CH₂CF₃, and CH₂CH₂SCH₂CH₂CF₃.

In another embodiment of this invention R₈ is (substituted or unsubstituted C₁-C₆ alkyl)-S(O)_n-(substituted or unsubstituted C₁-C₆ alkyl)-(substituted or unsubstituted C₃-C₁₀ cycloalkyl) wherein said substituents on said substituted alkyls and said substituted cycloalkyls are independently selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OC₁-C₆ alkyl, OC₁-C₆ haloalkyl, S(O)_nC₁-C₆alkyl, S(O)_nOC₁-C₆ alkyl, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, C₂-C₆ alkynyl, C₁-C₆ alkoxy, N(R₉)S(O)_nR₉, OR₉, N(R₉)₂, R₉OR₉, R₉N(R₉)₂, R₉C(=X₁)R₉, R₉C(=X₁)N(R₉)₂, N(R₉)C(=X₁)R₉, R₉N(R₉)C(=X₁)R₉, S(O)_nOR₉, R₉C(=X₁)OR₉, R₉OC(=X₁)R₉, R₉S(O)_nR₉, S(O)_nR₉, oxo, (each of which that can be substituted, may optionally be substituted with R₉).

In another embodiment of this invention R₈ is selected from CH(CH₃)CH₂SCH₂(2,2 difluorocyclopropyl), CH₂CH₂SCH₂(2,2 difluorocyclopropyl), CH₂CH₂S(=O)CH₂(2,2 difluorocyclopropyl), CH₂CH₂S(=O)₂CH₂CH₂(2,2 difluorocyclopropyl), and CH₂CH(CF₃)SCH₂(2,2 difluorocyclopropyl).

In another embodiment of this invention R₈ is (substituted or unsubstituted C₁-C₆ alkyl)-S(O)_n-(substituted or unsubstituted C₂-C₆ alkenyl) wherein said substituents on said substituted alkyls and substituted alkenyls are independently selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OC₁-C₆ alkyl, OC₁-C₆ haloalkyl, S(O)_nC₁-C₆alkyl, S(O)_nOC₁-C₆ alkyl, C₆-

C₂₀ aryl, or C₁-C₂₀ heterocyclyl, C₂-C₆ alkynyl, C₁-C₆ alkoxy, N(R₉)S(O)_nR₉, OR₉, N(R₉)₂, R₉OR₉, R₉N(R₉)₂, R₉C(=X₁)R₉, R₉C(=X₁)N(R₉)₂, N(R₉)C(=X₁)R₉, R₉N(R₉)C(=X₁)R₉, S(O)_nOR₉, R₉C(=X₁)OR₉, R₉OC(=X₁)R₉, R₉S(O)_nR₉, S(O)_nR₉, oxo, (each of which that can be substituted, may optionally be substituted with R₉).

- 5 In another embodiment of this invention R₈ is selected from CH₂CH₂SCH₂CH=CCl₂, CH₂SCH₂CH=CCl₂, CH(CH₃)SCH₂CH=CCl₂, CH(CH₃)SCH=CHF, CH₂CH₂S(=O)CH₂CH₂CF₃, and CH₂CH₂S(=O)₂CH₂CH₂CF₃.

In another embodiment of this invention X is CR_{n1} where R_{n1} is H or halo.

In another embodiment of this invention X is CR_{n1} where R_{n1} is H or F.

- 10 In another embodiment of this invention X₁ is O.

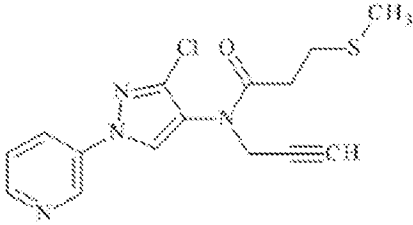
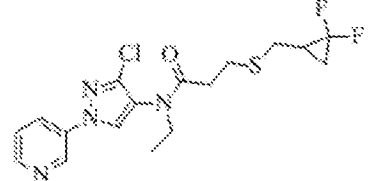
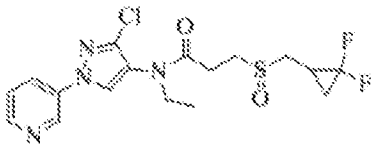
In another embodiment of this invention X₂ is O.

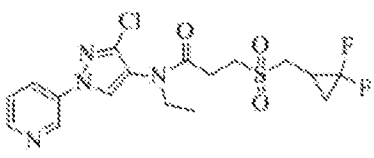
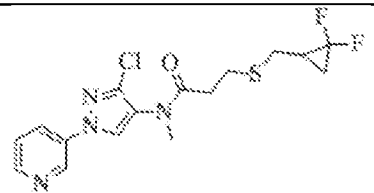
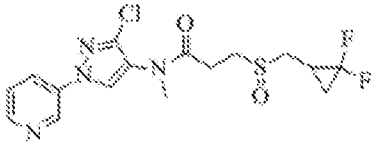
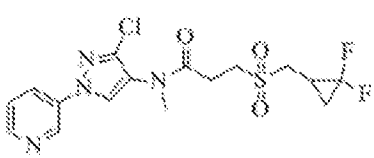
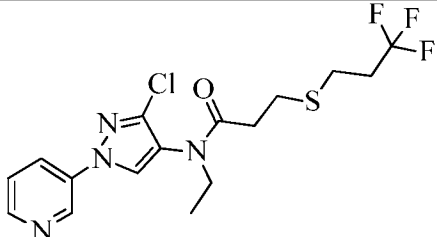
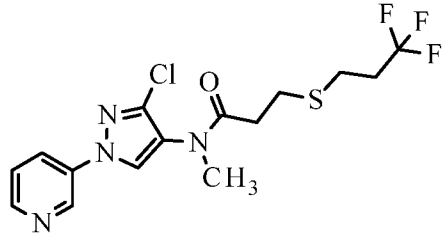
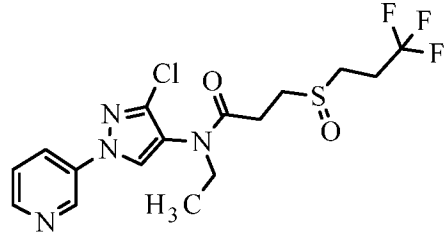
In another embodiment of this invention R₁₁ is substituted or unsubstituted C₁-C₆ alkylC≡CR₁₂.

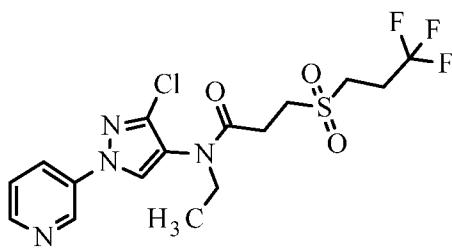
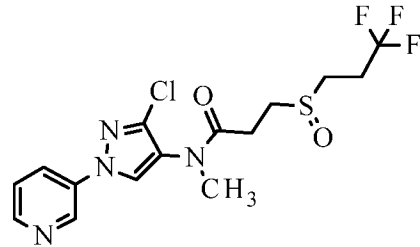
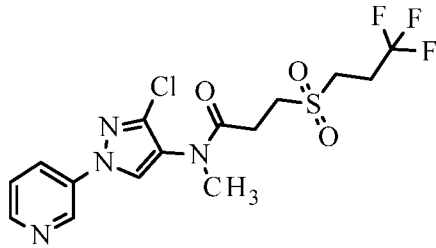
In another embodiment of this invention R₁₁ is CH₂C≡CH.

- 15 The molecules of Formula One will generally have a molecular mass of about 100 Daltons to about 1200 Daltons. However, it is generally preferred if the molecular mass is from about 120 Daltons to about 900 Daltons, and it is even more generally preferred if the molecular mass is from about 140 Daltons to about 600 Daltons.

Non-limiting examples of Compound A including the following:

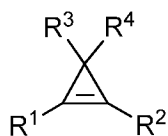
607	
626	
627	

628	
629	
630	
631	
653	
860	
861	

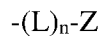
862	
924	
932	

Compound B

This document discloses molecules of Compound B representing cyclopropene compounds having the following formula (“**Formula Two**”):



where each R^1 , R^2 , R^3 and R^4 is independently selected from the group consisting of H and a chemical group of the formula:



where n is an integer from 0 to 12. Each L is a bivalent radical. Suitable L groups include, for example, radicals containing one or more atoms selected from B, C, N, O, P, S, Si, or mixtures thereof. The atoms within an L group may be connected to each other by single bonds, double bonds, triple bonds, or mixtures thereof. Each L group may be linear, branched, cyclic, or a combination thereof. In any one R group (*i.e.*, any one of R^1 , R^2 , R^3

and R⁴) the total number of heteroatoms (*i.e.*, atoms that are neither H nor C) is from 0 to 6. Independently, in any one R group the total number of non-hydrogen atoms is 50 or less.

Each Z is a monovalent radical. Each Z is independently selected from the group consisting of a C₁-C₈ alkyl, hydrogen, halo, cyano, nitro, nitroso, azido, chlorate, bromate, iodate, isocyanato, isocyanido, isothiocyanato, pentafluorothio, and a chemical group G, wherein G is a 3- to 14-membered ring system.

The R¹, R², R³, and R⁴ groups are independently selected from the suitable groups. Among the groups that are suitable for use as one or more of R¹, R², R³, and R⁴ are, for example, aliphatic groups, aliphatic-oxy groups, alkylphosphonato groups, cycloaliphatic groups, cycloalkylsulfonyl groups, cycloalkylamino groups, heterocyclic groups, aryl groups, heteroaryl groups, halogens, silyl groups, and mixtures and combinations thereof. Groups that are suitable for use as one or more of R¹, R², R³, and R⁴ may be substituted or unsubstituted.

Among the suitable R¹, R², R³, and R⁴ groups are, for example, aliphatic groups. Some suitable aliphatic groups include, for example, alkyl, alkenyl, and alkynyl groups. Suitable aliphatic groups may be linear, branched, cyclic, or a combination thereof. Independently, suitable aliphatic groups may be substituted or unsubstituted.

As used herein, a chemical group of interest is said to be “substituted” if one or more hydrogen atoms of the chemical group of interest is replaced by a substituent.

Also among the suitable R¹, R², R³, and R⁴ groups are, for example, substituted and unsubstituted heterocyclyl groups that are connected to the cyclopropene compound through an intervening oxy group, amino group, carbonyl group, or sulfonyl group; examples of such R¹, R², R³, and R⁴ groups are heterocycloxy, heterocyclylcarbonyl, diheterocyclylamino, and diheterocyclylaminosulfonyl.

Also among the suitable R¹, R², R³, and R⁴ groups are, for example, substituted and unsubstituted heterocyclic groups that are connected to the cyclopropene compound through an intervening oxy group, amino group, carbonyl group, sulfonyl group, thioalkyl group, or aminosulfonyl group; examples of such R¹, R², R³, and R⁴ groups are diheteroarylamino, heteroarylthioalkyl, and diheteroarylaminosulfonyl.

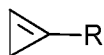
Also among the suitable R¹, R², R³, and R⁴ groups are, for example, hydrogen, fluoro, chloro, bromo, iodo, cyano, nitro, nitroso, azido, chlorate, bromate, iodate, isocyanato, isocyanido, isothiocyanato, pentafluorothio, acetoxo, carboethoxy, cyanato, nitrato, nitrito, perchlorato, allenyl, butylmercapto, diethylphosphonato, dimethylphenylsilyl, isoquinolyl,

mercapto, naphthyl, phenoxy, phenyl, piperidino, pyridyl, quinolyl, triethylsilyl, trimethylsilyl, and substituted analogs thereof.

As used herein, the chemical group G is a 3- to 14-membered ring system. Ring systems suitable as chemical group G may be substituted or unsubstituted; they may be aromatic (including, for example, phenyl and naphthyl) or aliphatic (including unsaturated aliphatic, partially saturated aliphatic, or saturated aliphatic); and they may be carbocyclic or heterocyclic. Among heterocyclic G groups, some suitable heteroatoms are, for example, nitrogen, sulfur, oxygen, and combinations thereof. Ring systems suitable as chemical group G may be monocyclic, bicyclic, tricyclic, polycyclic, spiro, or fused; among suitable chemical group G ring systems that are bicyclic, tricyclic, or fused, the various rings in a single chemical group G may be all the same type or may be of two or more types (for example, an aromatic ring may be fused with an aliphatic ring).

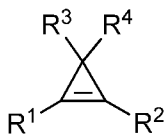
In one embodiment, one or more of R^1 , R^2 , R^3 , and R^4 is hydrogen or C_1 - C_{10} alkyl. In another embodiment, each of R^1 , R^2 , R^3 , and R^4 is hydrogen or C_1 - C_8 alkyl. In another embodiment, each of R^1 , R^2 , R^3 , and R^4 is hydrogen or C_1 - C_4 alkyl. In another embodiment, each of R^1 , R^2 , R^3 , and R^4 is hydrogen or methyl. In another embodiment, R^1 is C_1 - C_4 alkyl and each of R^2 , R^3 , and R^4 is hydrogen. In another embodiment, R^1 is methyl and each of R^2 , R^3 , and R^4 is hydrogen, and the cyclopropene compound is known herein as 1-methylcyclopropene or "1-MCP."

In one embodiment, the Compound B (cyclopropene compound) is of the formula:



wherein R is a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkylalkyl, phenyl, or naphthyl group; wherein the substituents are independently halogen, alkoxy, or substituted or unsubstituted phenoxy. In one embodiment, R is C_1 - C_8 alkyl. In another embodiment, R is methyl.

In another embodiment, the Compound B (cyclopropene compound) is of the formula:



wherein R^1 is a substituted or unsubstituted C_1 - C_4 alkyl, C_2 - C_4 alkenyl, C_2 - C_4 alkynyl, C_3 - C_6 cycloalkyl, cycloalkylalkyl, phenyl, or naphthyl group; and R^2 , R^3 , and R^4 are hydrogen.

In another embodiment, the cyclopropene comprises 1-methylcyclopropene (1-MCP).

In some embodiments, a cyclopropene is used that has boiling point at one atmosphere pressure of 50 °C or lower; or 25 °C or lower; or 15 °C or lower. Independently, in some embodiments, a cyclopropene is used that has boiling point at one atmosphere pressure of -100 °C or higher; -50 °C or higher; or -25 °C or higher; or 0 °C or higher.

5 The cyclopropenes applicable to this invention may be prepared by any method. Some suitable methods of preparation of cyclopropenes are the processes disclosed in U.S. Patents No. 5,518,988 and 6,017,849. Any compound that is not a cyclopropene is known herein as a "non-cyclopropene."

10 When a cyclopropene compound is used, in some embodiments the concentration of the cyclopropene compound as used in the compositions and/or methods provided is 0.5 ppb or higher; 1 ppb or higher; 10 ppb or higher; or 100 ppb or higher. In some embodiments, the concentration of the cyclopropene compound is 100 ppm or lower; 50 ppm or lower; 10 ppm or lower; or 5 ppm or lower. In some embodiments, the concentration of the cyclopropene compound is between 5 ppm and 250 ppm; between 25 ppm and 100 ppm; between 45 ppm
15 and 150 ppm; or between 15 ppm and 100 ppm.

 In some embodiments, one or more composition of the present invention includes at least one ionic complexing reagent. An ionic complexing reagent interacts with a cyclopropene to form a complex that is stable in water. Some suitable ionic complexing reagents, for example, include lithium ion. In some embodiments, no ionic complexing
20 reagent is used.

 In some embodiments, no composition of the present invention includes any molecular encapsulating agent. In other embodiments, one or more composition of the present invention includes at least one molecular encapsulating agent. In another embodiment, the molecular encapsulating agent is selected from the group consisting of
25 substituted cyclodextrins, unsubstituted cyclodextrins, and combinations thereof. In a further embodiment, the molecular encapsulating agent comprises alpha-cyclodextrin.

 When a molecular encapsulating agent is used, suitable molecular encapsulating agents include, for example, organic and inorganic molecular encapsulating agents. Suitable organic molecular encapsulating agents include, for example, substituted cyclodextrins,
30 unsubstituted cyclodextrins, and crown ethers. Suitable inorganic molecular encapsulating agents include, for example, zeolites. Mixtures of suitable molecular encapsulating agents are also suitable. In some embodiments of the invention, the encapsulating agent is alpha-cyclodextrin, beta-cyclodextrin, gamma-cyclodextrin, or a mixture thereof. In some embodiments of the invention, particularly when the cyclopropene is 1-methylcyclopropene,

the encapsulating agent is alpha-cyclodextrin. The preferred encapsulating agent will vary depending upon the structure of the cyclopropene or cyclopropenes being used. Any cyclodextrin or mixture of cyclodextrins, cyclodextrin polymers, modified cyclodextrins, or mixtures thereof can also be utilized pursuant to the present invention. Some cyclodextrins are available, for example, from Wacker Biochem Inc., Adrian, MI or Cerestar USA, Hammond, IN, as well as other vendors.

In some of the embodiments in which a molecular encapsulating agent is present, at least one molecular encapsulating agent encapsulates one or more cyclopropenes. A cyclopropene or substituted cyclopropene molecule encapsulated in a molecule of a molecular encapsulating agent is known herein as a "cyclopropene molecular encapsulating agent complex." The cyclopropene molecular encapsulation agent complexes can be prepared by any means. In one method of preparation, for example, such complexes are prepared by contacting the cyclopropene with a solution or slurry of the molecular encapsulation agent and then isolating the complex, using, for example, processes disclosed in U. S. Patent No. 6,017,849. For example, in one method of making a complex in which 1-MCP is encapsulated in a molecular encapsulating agent, the 1-MCP gas is bubbled through a solution of alpha-cyclodextrin in water, from which the complex first precipitates and is then isolated by filtration. In some embodiments, complexes are made by the above method and, after isolation, are dried and stored in solid form, for example as a powder, for later addition to useful compositions.

In some embodiments, one or more molecular encapsulating agent and one or more cyclopropenes are both present in a composition; in some of such embodiments, the amount of molecular encapsulating agent can usefully be characterized by the ratio of moles of molecular encapsulating agent to moles of cyclopropene. In some embodiments, the ratio of moles of molecular encapsulating agent to moles of cyclopropene is 0.1 or larger; or 0.2 or larger; or 0.5 or larger; or 0.9 or larger. Independently, in some of such embodiments, the ratio of moles of molecular encapsulating agent to moles of cyclopropene is 2 or lower; or 1.5 or lower.

Compound C

In one embodiment, the combination of Compound A and Compound B may further comprises a spinosyn natural factor or semi-synthetic derivative or butenyl-spinosyn natural factor or semi-synthetic derivative as Compound C. Examples of specific spinosyns that can be used include spinosad and spinetoram.

Saccharopolyspora spinosa produces a mixture of nine closely related compounds collectively called “spinosyns.” Within the mixture, spinosyn A and D, known as spinosad, are the major components and have the highest activity against key insect targets. Spinosyn J and L, two of the minor components within the spinosyn mixture, are the precursors for spinetoram, the second generation spinosyn insecticide.

Spinosad comprises approximately 85% spinosyn A and approximately 15% spinosyn D. Spinosyns A and D are natural products produced by fermentation of *Saccharopolyspora spinosa*, as disclosed in U.S. Pat. No. 5,362,634. The spinosyn compounds consist of a 5,6,5-tricyclic ring system, fused to a 12-membered macrocyclic lactone, a neutral sugar (rhamnose), and an amino sugar (forosamine). Spinosyn compounds are also disclosed in U.S. Patent Nos. 5,496,931; 5,670,364; 5,591,606; 5,571,901; 5,202,242; 5,767,253; 5,840,861; 5,670,486 and 5,631,155. As used herein, the term “spinosyn” includes natural factors and semi-synthetic derivatives of the naturally produced factors. A large number of chemical modifications to these spinosyn compounds have been made, as disclosed in U.S. Patent No. 6,001,981.

Spinetoram is a mixture of 5,6-dihydro-3'-ethoxy spinosyn J (major component) and 3'-ethoxy spinosyn L. The mixture can be prepared by ethoxylating a mixture of spinosyn J and spinosyn L, followed by hydrogenation. Accordingly, spinetoram is a semi-synthetic spinosyn mixture of 50-90% (2*R*,3*aR*,5*aR*,5*bS*,9*S*,13*S*,14*R*,16*aS*,16*bR*)-2-(6-deoxy-3-*O*-ethyl-2,4-di-*O*-methyl- α -L-mannopyranosyloxy)-13-[(2*R*,5*S*,6*R*)-5-(dimethylamino)tetrahydro-6-methylpyran-2-yloxy]-9-ethyl-2,3,3*a*,4,5,5*a*,5*b*,6,9,10,11,12,13,14,16*a*,16*b*-hexadecahydro-14-methy-1*H*-*as*-indaceno[3,2-*d*]oxacyclododecine-7,15-dione, and 50-10% (2*R*,3*aR*,5*aS*,5*bS*,9*S*,13*S*,14*R*,16*aS*,16*bS*)-2-(6-deoxy-3-*O*-ethyl-2,4-di-*O*-methyl- α -L-mannopyranosyloxy)-13-[(2*R*,5*S*,6*R*)-5-(dimethylamino)tetrahydro-6-methylpyran-2-yloxy]-9-ethyl-2,3,3*a*,5*a*,5*b*,6,9,10,11,12,13,14,16*a*,16*b*-tetradecahydro-4,14-dimethyl-1*H*-*as*-indaceno[3,2-*d*]oxacyclododecine-7,15-dione. Synthesis of the components of spinetoram is described in U.S. Patent No. 6,001,981.

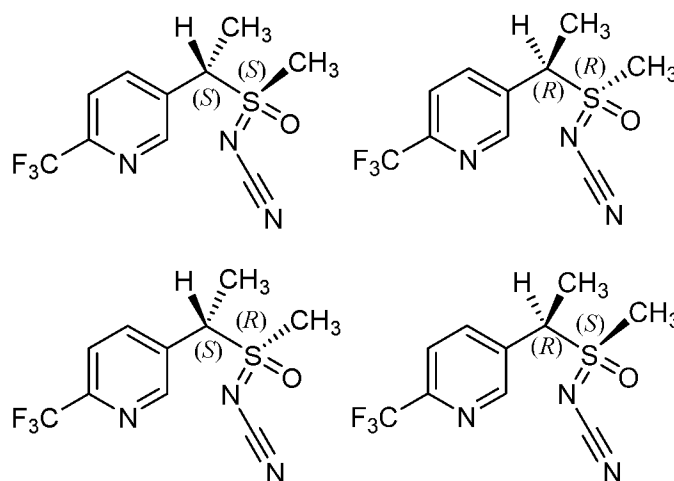
In another embodiment, Compound C may comprise a macrolide insecticide, which has been disclosed in U.S. Pat. No. 6,800,614. These compounds are characterized by the presence of reactive functional groups that make further modifications possible at locations where such modifications were not feasible in previously disclosed spinosyns. Natural and semi-synthetic derivatives of the butenyl spinosyns are disclosed in U.S. Pat. No. 6,919,464. The term “butenyl-spinosyn” as used herein is intended to include natural factors and semi-synthetic derivatives of the naturally produced factors.

The spinosyn compound may be a naturally produced or synthetic polyketide-derived tetracyclic macrolide. The spinosyn compound may be a fermentation product including at least one of the compounds produced by *Saccharopolyspora spinosa* and disclosed in U.S. Pat. No. 5,362,634. Other spinosyn compounds are also disclosed in U.S. Patent Nos.

5 5,496,931, 5,670,364, 5,591,606, 5,571,901, 5,202,242, 5,767,253, 5,840,861, 5,670,486, 5,631,155, and 6,001,981.

In another embodiment, the combination of Compound A and Compound B may further comprises sulfoxaflor as Compound C. Sulfoxaflor is the common name for [methyl(oxo){1-[6-(trifluoromethyl)-3-pyridyl]ethyl}- λ^6 -sulfanylidene]cyanamide (IUPAC designation) which is also known as *N*-[methyloxido[1-[6-(trifluoromethyl)-3-pyridinyl]ethyl]- λ^4 -sulfanylidene]cyanamide (CAS Name, CAS registry number 946578-00-3). Sulfoxaflor is described in U.S. Patent No. 7,687,634 B2. Sulfoxaflor may be synthesized using methods such as those described in International Patent Publication No. WO2007/095229. Sulfoxaflor is a mixture of four possible stereoisomers, the chemical

15 structures of which are as follows:



In one embodiment, the combination of Compound A and Compound B may further comprise azoxystrobin as Compound C. Azoxystrobin is the common name for methyl (α E)-2-[[6-(2-cyanophenoxy)-4-pyrimidinyl]oxy]- α -(methoxymethylene)benzeneacetate. Its fungicidal activity is described in The Pesticide Manual, Fourteenth Edition, 2006, and its synthesis has been described in U.S. Patent Nos. 5,145,856, 5,264,440, and 5,395,837.

20

In another aspect, provided is a composition comprising a mixture comprising (i) an effective amount of Compound B according to Formula Two, or an agriculturally acceptable salt, ester, or amide thereof, as described herein, and (ii) a Compound C, or an agriculturally acceptable salt, ester, or amide thereof, as described herein.

25

In one embodiment, weight ratio of Compound B to Compound C can be between 1:10 and 1000:1; between 1:10 and 1:1; between 1:1 and 1:100; or between 1:10 and 1:1000. In another embodiment, the mixture comprises a synergistic combination for Compound B and Compound C for enhancing plant health and/or tolerance to stress. In a further
5 embodiment, the Compound C is selected from the group consisting of spinosyn natural factor, semi-synthetic derivative, butenyl-spinosyn natural factor, or semi-synthetic derivative. In another further embodiment, the Compound C comprises spinetoram. In another embodiment, the Compound C is selected from the group consisting of azoxystrobin, sulfoxaflor, spinetoram, and combinations thereof.

10 In another aspect, provided is a method for enhancing plant health and/or tolerance to stress for plants. The method comprises (i) first applying an effective amount of Compound B according to Formula Two, or an agriculturally acceptable salt, ester, or amide thereof, as described herein, to a plant or plant part; and (ii) second applying a Compound C, or an agriculturally acceptable salt, ester, or amide thereof, as described herein, to the plant or plant
15 part; wherein the first applying and the second applying steps can be performed in either order or simultaneously.

In one embodiment, weight ratio of Compound B and Compound C are between 1:10 and 1000:1; between 1:10 and 1:1; between 1:1 and 1:100; or between 1:10 and 1:1000. In another embodiment, the combination of Compound B and Compound C is synergistic. In
20 another embodiment, the first applying step is performed in an enclosed space, for example a green house or nursery. In another embodiment, the second applying step is performed in an enclosed space, for example a green house or nursery. In another embodiment, the first applying step is performed in an open space, for example an open field. In another embodiment, the second applying step is performed in an open space, for example an open
25 field.

Stereoisomers

Molecules of Formula One may exist as one or more stereoisomers. Thus, certain molecules can be produced as racemic mixtures. It will be appreciated by those skilled in the art that one stereoisomer may be more active than the other stereoisomers. Individual
30 stereoisomers may be obtained by known selective synthetic procedures, by conventional synthetic procedures using resolved starting materials, or by conventional resolution procedures. Certain molecules disclosed in this document can exist as two or more isomers. The various isomers include geometric isomers, diastereomers, and enantiomers. Thus, the molecules disclosed in this document include geometric isomers, racemic mixtures,

individual stereoisomers, and optically active mixtures. It will be appreciated by those skilled in the art that one isomer may be more active than the others. The structures disclosed in the present disclosure are drawn in only one geometric form for clarity, but are intended to represent all geometric forms of the molecule.

5 Formulations

A pesticide is rarely suitable for application in its pure form. It is usually necessary to add other substances so that the pesticide can be used at the required concentration and in an appropriate form, permitting ease of application, handling, transportation, storage, and maximum pesticide activity. Thus, pesticides are formulated into, for example, baits, concentrated emulsions, dusts, emulsifiable concentrates, fumigants, gels, granules, microencapsulations, seed treatments, suspension concentrates, suspoemulsions, tablets, water soluble liquids, water dispersible granules or dry flowables, wettable powders, and ultra low volume solutions. For further information on formulation types see "Catalogue of Pesticide Formulation Types and International Coding System" Technical Monograph n°2, 5th Edition by CropLife International (2002).

Pesticides are applied most often as aqueous suspensions or emulsions prepared from concentrated formulations of such pesticides. Such water-soluble, water-suspendable, or emulsifiable formulations are either solids, usually known as wettable powders, or water dispersible granules, or liquids usually known as emulsifiable concentrates, or aqueous suspensions. Wettable powders, which may be compacted to form water dispersible granules, comprise an intimate mixture of the pesticide, a carrier, and surfactants. The concentration of the pesticide is usually from about 10% to about 90% by weight. The carrier is usually selected from among the attapulgite clays, the montmorillonite clays, the diatomaceous earths, or the purified silicates. Effective surfactants, comprising from about 0.5% to about 10% of the wettable powder, are found among sulfonated lignins, condensed naphthalenesulfonates, naphthalenesulfonates, alkylbenzenesulfonates, alkyl sulfates, and non-ionic surfactants such as ethylene oxide adducts of alkyl phenols.

Emulsifiable concentrates of pesticides comprise a convenient concentration of a pesticide, such as from about 50 to about 500 grams per liter of liquid dissolved in a carrier that is either a water miscible solvent or a mixture of water-immiscible organic solvent and emulsifiers. Useful organic solvents include aromatics, especially xylenes and petroleum fractions, especially the high-boiling naphthalenic and olefinic portions of petroleum such as heavy aromatic naphtha. Other organic solvents may also be used, such as the terpenic solvents including rosin derivatives, aliphatic ketones such as cyclohexanone, and complex

alcohols such as 2-ethoxyethanol. Suitable emulsifiers for emulsifiable concentrates are selected from conventional anionic and non-ionic surfactants.

Aqueous suspensions comprise suspensions of water-insoluble pesticides dispersed in an aqueous carrier at a concentration in the range from about 5% to about 50% by weight.

5 Suspensions are prepared by finely grinding the pesticide and vigorously mixing it into a carrier comprised of water and surfactants. Ingredients, such as inorganic salts and synthetic or natural gums may also be added, to increase the density and viscosity of the aqueous carrier. It is often most effective to grind and mix the pesticide at the same time by preparing the aqueous mixture and homogenizing it in an implement such as a sand mill, ball mill, or
10 piston-type homogenizer.

Pesticides may also be applied as granular compositions that are particularly useful for applications to the soil. Granular compositions usually contain from about 0.5% to about 10% by weight of the pesticide, dispersed in a carrier that comprises clay or a similar substance. Such compositions are usually prepared by dissolving the pesticide in a suitable
15 solvent and applying it to a granular carrier which has been pre-formed to the appropriate particle size, in the range of from about 0.5 to about 3 mm. Such compositions may also be formulated by making a dough or paste of the carrier and compound and crushing and drying to obtain the desired granular particle size.

Dusts containing a pesticide are prepared by intimately mixing the pesticide in
20 powdered form with a suitable dusty agricultural carrier, such as kaolin clay, ground volcanic rock, and the like. Dusts can suitably contain from about 1% to about 10% of the pesticide. They can be applied as a seed dressing or as a foliage application with a dust blower machine.

It is equally practical to apply a pesticide in the form of a solution in an appropriate organic solvent, usually petroleum oil, such as the spray oils, which are widely used in
25 agricultural chemistry.

Pesticides can also be applied in the form of an aerosol composition. In such compositions the pesticide is dissolved or dispersed in a carrier, which is a pressure-generating propellant mixture. The aerosol composition is packaged in a container from which the mixture is dispensed through an atomizing valve.

30 Pesticide baits are formed when the pesticide is mixed with food or an attractant or both. When the pests eat the bait they also consume the pesticide. Baits may take the form of granules, gels, flowable powders, liquids, or solids. They can be used in pest harborages.

Fumigants are pesticides that have a relatively high vapor pressure and hence can exist as a gas in sufficient concentrations to kill pests in soil or enclosed spaces. The toxicity

of the fumigant is proportional to its concentration and the exposure time. They are characterized by a good capacity for diffusion and act by penetrating the pest's respiratory system or being absorbed through the pest's cuticle. Fumigants are applied to control stored product pests under gas proof sheets, in gas sealed rooms or buildings or in special chambers.

5 Pesticides can be microencapsulated by suspending the pesticide particles or droplets in plastic polymers of various types. By altering the chemistry of the polymer or by changing factors in the processing, microcapsules can be formed of various sizes, solubility, wall thicknesses, and degrees of penetrability. These factors govern the speed with which the active ingredient within is released, which in turn, affects the residual performance, speed of
10 action, and odor of the product.

Oil solution concentrates are made by dissolving pesticide in a solvent that will hold the pesticide in solution. Oil solutions of a pesticide usually provide faster knockdown and kill of pests than other formulations due to the solvents themselves having pesticidal action and the dissolution of the waxy covering of the integument increasing the speed of uptake of
15 the pesticide. Other advantages of oil solutions include better storage stability, better penetration of crevices, and better adhesion to greasy surfaces.

Another embodiment is an oil-in-water emulsion, wherein the emulsion comprises oily globules which are each provided with a lamellar liquid crystal coating and are dispersed in an aqueous phase, wherein each oily globule comprises at least one compound which is
20 agriculturally active, and is individually coated with a monolamellar or oligolamellar layer comprising: (1) at least one non-ionic lipophilic surface-active agent, (2) at least one non-ionic hydrophilic surface-active agent and (3) at least one ionic surface-active agent, wherein the globules having a mean particle diameter of less than 800 nanometers. Further information on the embodiment is disclosed in U.S. patent publication 20070027034
25 published February 1, 2007, having Patent Application serial number 11/495,228. For ease of use, this embodiment will be referred to as "OIWE".

For further information consult "Insect Pest Management" 2nd Edition by D. Dent, copyright CAB International (2000). Additionally, for more detailed information consult "Handbook of Pest Control – The Behavior, Life History, and Control of Household Pests"
30 by Arnold Mallis, 9th Edition, copyright 2004 by GIE Media Inc.

Other Formulation Components

Generally, when the molecules disclosed in Formula One are used in a formulation, such formulation can also contain other components. These components include, but are not limited to, (this is a non-exhaustive and non-mutually exclusive list) wetters, spreaders,

stickers, penetrants, buffers, sequestering agents, drift reduction agents, compatibility agents, anti-foam agents, cleaning agents, and emulsifiers. A few components are described forthwith.

A wetting agent is a substance that when added to a liquid increases the spreading or penetration power of the liquid by reducing the interfacial tension between the liquid and the surface on which it is spreading. Wetting agents are used for two main functions in agrochemical formulations: during processing and manufacture to increase the rate of wetting of powders in water to make concentrates for soluble liquids or suspension concentrates; and during mixing of a product with water in a spray tank to reduce the wetting time of wettable powders and to improve the penetration of water into water-dispersible granules. Examples of wetting agents used in wettable powder, suspension concentrate, and water-dispersible granule formulations are: sodium lauryl sulfate; sodium dioctyl sulfosuccinate; alkyl phenol ethoxylates; and aliphatic alcohol ethoxylates.

A dispersing agent is a substance which adsorbs onto the surface of particles and helps to preserve the state of dispersion of the particles and prevents them from reaggregating. Dispersing agents are added to agrochemical formulations to facilitate dispersion and suspension during manufacture, and to ensure the particles redisperse into water in a spray tank. They are widely used in wettable powders, suspension concentrates and water-dispersible granules. Surfactants that are used as dispersing agents have the ability to adsorb strongly onto a particle surface and provide a charged or steric barrier to reaggregation of particles. The most commonly used surfactants are anionic, non-ionic, or mixtures of the two types. For wettable powder formulations, the most common dispersing agents are sodium lignosulfonates. For suspension concentrates, very good adsorption and stabilization are obtained using polyelectrolytes, such as sodium naphthalene sulfonate formaldehyde condensates. Tristyrylphenol ethoxylate phosphate esters are also used. Non-ionics such as alkylarylethylene oxide condensates and EO-PO block copolymers are sometimes combined with anionics as dispersing agents for suspension concentrates. In recent years, new types of very high molecular weight polymeric surfactants have been developed as dispersing agents. These have very long hydrophobic 'backbones' and a large number of ethylene oxide chains forming the 'teeth' of a 'comb' surfactant. These high molecular weight polymers can give very good long-term stability to suspension concentrates because the hydrophobic backbones have many anchoring points onto the particle surfaces. Examples of dispersing agents used in agrochemical formulations are: sodium lignosulfonates; sodium naphthalene sulfonate

formaldehyde condensates; tristyrylphenol ethoxylate phosphate esters; aliphatic alcohol ethoxylates; alkyl ethoxylates; EO-PO block copolymers; and graft copolymers.

An emulsifying agent is a substance which stabilizes a suspension of droplets of one liquid phase in another liquid phase. Without the emulsifying agent the two liquids would
5 separate into two immiscible liquid phases. The most commonly used emulsifier blends contain alkylphenol or aliphatic alcohol with twelve or more ethylene oxide units and the oil-soluble calcium salt of dodecylbenzenesulfonic acid. A range of hydrophile-lipophile balance (“HLB”) values from 8 to 18 will normally provide good stable emulsions. Emulsion stability can sometimes be improved by the addition of a small amount of an EO-PO block copolymer
10 surfactant.

A solubilizing agent is a surfactant which will form micelles in water at concentrations above the critical micelle concentration. The micelles are then able to dissolve or solubilize water-insoluble materials inside the hydrophobic part of the micelle. The types of surfactants usually used for solubilization are non-ionics, sorbitan monooleates, sorbitan
15 monooleate ethoxylates, and methyl oleate esters.

Surfactants are sometimes used, either alone or with other additives such as mineral or vegetable oils as adjuvants to spray-tank mixes to improve the biological performance of the pesticide on the target. The types of surfactants used for bioenhancement depend generally on the nature and mode of action of the pesticide. However, they are often non-ionics such as:
20 alkyl ethoxylates; linear aliphatic alcohol ethoxylates; aliphatic amine ethoxylates.

A carrier or diluent in an agricultural formulation is a material added to the pesticide to give a product of the required strength. Carriers are usually materials with high absorptive capacities, while diluents are usually materials with low absorptive capacities. Carriers and diluents are used in the formulation of dusts, wettable powders, granules and water-
25 dispersible granules.

Organic solvents are used mainly in the formulation of emulsifiable concentrates, oil-in-water emulsions, suspoemulsions, and ultra low volume formulations, and to a lesser extent, granular formulations. Sometimes mixtures of solvents are used. The first main groups of solvents are aliphatic paraffinic oils such as kerosene or refined paraffins. The
30 second main group (and the most common) comprises the aromatic solvents such as xylene and higher molecular weight fractions of C9 and C10 aromatic solvents. Chlorinated hydrocarbons are useful as cosolvents to prevent crystallization of pesticides when the formulation is emulsified into water. Alcohols are sometimes used as cosolvents to increase

solvent power. Other solvents may include vegetable oils, seed oils, and esters of vegetable and seed oils.

Thickeners or gelling agents are used mainly in the formulation of suspension concentrates, emulsions and suspoemulsions to modify the rheology or flow properties of the liquid and to prevent separation and settling of the dispersed particles or droplets.

Thickening, gelling, and anti-settling agents generally fall into two categories, namely water-insoluble particulates and water-soluble polymers. It is possible to produce suspension concentrate formulations using clays and silicas. Examples of these types of materials, include, but are not limited to, montmorillonite, bentonite, magnesium aluminum silicate, and attapulgite. Water-soluble polysaccharides have been used as thickening-gelling agents for many years. The types of polysaccharides most commonly used are natural extracts of seeds and seaweeds or are synthetic derivatives of cellulose. Examples of these types of materials include, but are not limited to, guar gum; locust bean gum; carrageenan; alginates; methyl cellulose; sodium carboxymethyl cellulose (SCMC); hydroxyethyl cellulose (HEC). Other types of anti-settling agents are based on modified starches, polyacrylates, polyvinyl alcohol and polyethylene oxide. Another good anti-settling agent is xanthan gum.

Microorganisms can cause spoilage of formulated products. Therefore preservation agents are used to eliminate or reduce their effect. Examples of such agents include, but are not limited to: propionic acid and its sodium salt; sorbic acid and its sodium or potassium salts; benzoic acid and its sodium salt; *p*-hydroxybenzoic acid sodium salt; methyl *p*-hydroxybenzoate; and 1,2-benzisothiazolin-3-one (BIT).

The presence of surfactants often causes water-based formulations to foam during mixing operations in production and in application through a spray tank. In order to reduce the tendency to foam, anti-foam agents are often added either during the production stage or before filling into bottles. Generally, there are two types of anti-foam agents, namely silicones and non-silicones. Silicones are usually aqueous emulsions of dimethyl polysiloxane, while the non-silicone anti-foam agents are water-insoluble oils, such as octanol and nonanol, or silica. In both cases, the function of the anti-foam agent is to displace the surfactant from the air-water interface.

“Green” agents (*e.g.*, adjuvants, surfactants, solvents) can reduce the overall environmental footprint of crop protection formulations. Green agents are biodegradable and generally derived from natural and/or sustainable sources, *e.g.* plant and animal sources. Specific examples are: vegetable oils, seed oils, and esters thereof, also alkoxylated alkyl polyglucosides.

Applications

The combination or composition provided may be used in an area where plants, such as crops, are growing (*e.g.* pre-planting, planting, pre-harvesting). The use of the combination or composition provided to benefit the plants being grown in the area. Such benefits, may include, but are not limited to, improving the health of a plant, improving the yield of a plant (*e.g.* increased biomass and/or increased content of valuable ingredients), improving the vigor of a plant (*e.g.* improved plant growth and/or greener leaves), improving the quality of a plant (*e.g.* improved content or composition of certain ingredients), and improving the tolerance to abiotic and/or biotic stress of the plant.

In the practice of the present invention, the composition may be contacted with a plant in a variety of ways. For example, the composition of the present invention may be a solid, a liquid, a gas, or a mixture thereof.

EXAMPLES

Example 1

Tomato seedlings are treated with various compositions during transplant. The treatments are performed in a green house using chemigation (injection) right before transplant (day 1). FIG. 1 shows exemplary results of enhancing plant health (leaf length at day 12, plant height at day 12, and dry weight at day 14) after applications of: (1) untreated broccoli seedlings; (2) 1-MCP at 50 ppm; (3) Compound A at 50 ppm and 1-MCP at 25 ppm; (4) Compound A at 25 ppm, 1-MCP at 25 ppm, and spinetoram at 25 ppm.

Example 2

A similar study is performed as Example 1 where % plant vigor of broccoli seedlings is measured. FIG. 2 shows exemplary results of % plant vigor at day 4, day 13, and day 28 during transplant of broccoli seedlings after application of: (1) untreated broccoli seedlings; (2) 1-MCP at 50 ppm; (3) Compound A at 50 ppm and 1-MCP at 25 ppm; (4) Compound A at 25 ppm, 1-MCP at 25 ppm, and spinetoram at 25 ppm. The % plant vigor is measured based on visual inspection of the seedlings where untreated and un-transplanted seedlings are used as 100% during the same time periods.

Example 3

Another similar study is performed as Example 2 where measurements of leaf area, plant height, and biomass are performed for broccoli seedlings. FIG. 3 shows exemplary results of enhancing plant health (leaf area at day 13 and plant height at day 13) during transplant of broccoli seedlings after application of: (1) untreated broccoli seedlings; (2) 1-

MCP at 50 ppm; (3) Compound A at 50 ppm and 1-MCP at 25 ppm; (4) Compound A at 25 ppm, 1-MCP at 25 ppm, and spinetoram at 25 ppm.

In addition, FIG. 4 shows exemplary results of plant biomass at day 14 and day 28 during transplant of broccoli seedlings after application of: (1) untreated broccoli seedlings; (2) 1-MCP at 50 ppm; (3) Compound A at 50 ppm and 1-MCP at 25 ppm; (4) Compound A at 25 ppm, 1-MCP at 25 ppm, and spinetoram at 25 ppm.

Example 4

A similar study is performed as Example 1 where measurements of leaf area, plant height, and biomass are performed for tomato seedlings. FIG. 5 shows exemplary results of enhancing plant health (leaf area at day 28 and plant height at day 29) during transplant of tomato seedling after applications of: (1) untreated tomato seedlings; (2) 1-MCP at 50 ppm; (3) Compound A at 25 ppm and 1-MCP at 50 ppm; and (4) Compound A at 25 ppm, 1-MCP at 25 ppm, and spinetoram at 25 ppm.

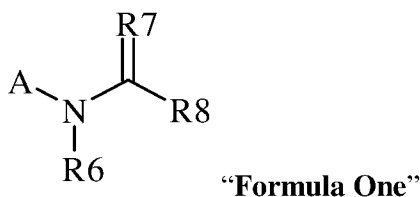
Example 5

A similar study is performed as Example 1 where prolonged treatments up to six days are performed. FIG. 5 shows exemplary results of enhancing plant health (leaf area at day 28 and plant height at day 29) during transplant of tomato seedling after applications of: (1) untreated tomato seedlings; (2) 1-MCP at 50 ppm; (3) Compound A at 25 ppm and 1-MCP at 50 ppm; and (4) Compound A at 25 ppm, 1-MCP at 25 ppm, and spinetoram at 25 ppm.

WE CLAIM

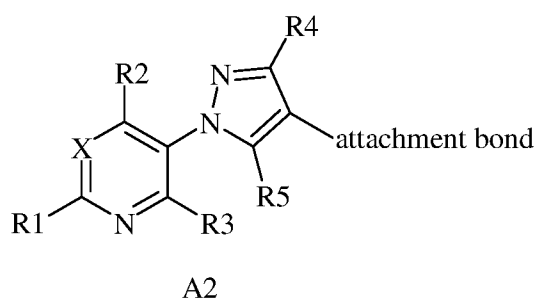
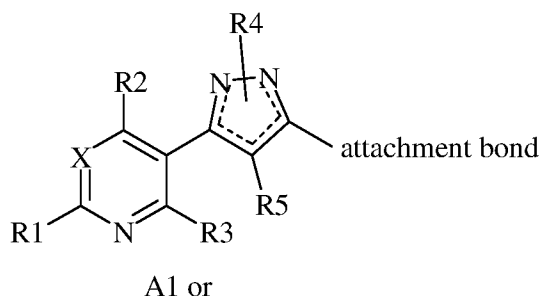
1. A composition comprising a mixture comprising:

(i) an effective amount of a Compound A according to Formula One, or an agriculturally acceptable salt, ester, or amide thereof:



wherein

(a) A is either



(b) R1 is H, F, Cl, Br, I, CN, NO₂, substituted or unsubstituted C₁-C₆ alkyl,

10 substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy,
substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl,
substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl,
substituted or unsubstituted C₁-C₂₀ heterocyclyl, OR₉, C(=X1)R₉, C(=X1)OR₉,
C(=X1)N(R₉)₂, N(R₉)₂, N(R₉)C(=X1)R₉, S(O)_nR₉, S(O)_nOR₉, S(O)_nN(R₉)₂, or R₉S(O)_nR₉,

15 wherein each said R1, which is substituted, has one or more substituents
selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆
haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀
cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, C₆-C₂₀ aryl,

or C₁-C₂₀ heterocyclyl, (each of which that can be substituted, may optionally be substituted with R₉);

(c) R₂ is H, F, Cl, Br, I, CN, NO₂, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, OR₉, C(=X₁)R₉, C(=X₁)OR₉, C(=X₁)N(R₉)₂, N(R₉)₂, N(R₉)C(=X₁)R₉, SR₉, S(O)_nOR₉, or R₉S(O)_nR₉,

wherein each said R₂, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, (each of which that can be substituted, may optionally be substituted with R₉);

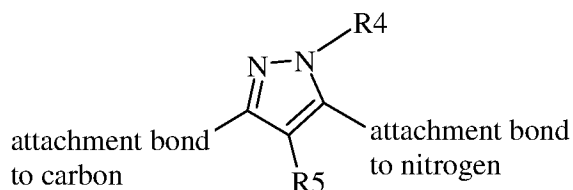
(d) R₃ is H, F, Cl, Br, I, CN, NO₂, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, OR₉, C(=X₁)R₉, C(=X₁)OR₉, C(=X₁)N(R₉)₂, N(R₉)₂, N(R₉)C(=X₁)R₉, SR₉, S(O)_nOR₉, or R₉S(O)_nR₉,

wherein each said R₃, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, (each of which that can be substituted, may optionally be substituted with R₉);

(e) when A is

(1) A₁ then A₁ is either

(a) A₁₁

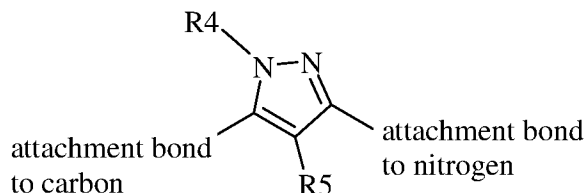


A11

where R4 is H, NO₂, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, C(=X1)R₉, C(=X1)OR₉, C(=X1)N(R₉)₂, N(R₉)₂, N(R₉)C(=X1)R₉, S(O)_nOR₉, or R₉S(O)_nR₉,

wherein each said R4, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkoxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, (each of which that can be substituted, may optionally be substituted with R₉), or

(b) A12



A12

where R4 is a C₁-C₆ alkyl,

(2) A2 then R4 is H, F, Cl, Br, I, CN, NO₂, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, OR₉, C(=X1)R₉, C(=X1)OR₉, C(=X1)N(R₉)₂, N(R₉)₂, N(R₉)C(=X1)R₉, SR₉, S(O)_nOR₉, or R₉S(O)_nR₉,

wherein each said R4, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl,

C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, (each of which that can be substituted, may optionally be substituted with R₉);

- 5 (f) R₅ is H, F, Cl, Br, I, CN, NO₂, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, OR₉, C(=X₁)R₉, C(=X₁)OR₉, C(=X₁)N(R₉)₂, N(R₉)₂, N(R₉)C(=X₁)R₉, SR₉, S(O)_nOR₉,
10 or R₉S(O)_nR₉,

wherein each said R₅, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, or C₆-C₂₀
15 aryl, (each of which that can be substituted, may optionally be substituted with R₉);

(g)

- (1) when A is A₁ then R₆ is R₁₁, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, OR₉, C(=X₁)R₉, C(=X₁)OR₉, C(=X₁)N(R₉)₂, N(R₉)₂, N(R₉)C(=X₁)R₉, SR₉, S(O)_nOR₉, R₉S(O)_nR₉, C₁-C₆ alkyl C₆-C₂₀ aryl (wherein the alkyl and aryl can independently be substituted or unsubstituted), C(=X₂)R₉, C(=X₁)X₂R₉, R₉X₂C(=X₁)R₉, R₉X₂R₉, C(=O)(C₁-C₆ alkyl)S(O)_n(C₁-C₆ alkyl), C(=O)(C₁-C₆ alkyl)C(=O)O(C₁-C₆ alkyl), (C₁-C₆ alkyl)OC(=O)(C₆-C₂₀ aryl), (C₁-C₆ alkyl)OC(=O)(C₁-C₆ alkyl), C₁-C₆ alkyl-(C₃-C₁₀ cyclohaloalkyl), or (C₁-C₆ alkenyl)C(=O)O(C₁-C₆ alkyl), or R₉X₂C(=X₁)X₂R₉,
25

wherein each said R₆ (except R₁₁), which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, R₉aryl, (each of which that can be substituted, may optionally be substituted with R₉),
30

optionally R₆ (except R₁₁) and R₈ can be connected in a cyclic

arrangement, where optionally such arrangement can have one or more heteroatoms selected from O, S, or N, in the cyclic structure connecting R6 and R8, and

- (2) when A is A2 then R6 is R11, H, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, OR9, C(=X1)R9, C(=X1)OR9, C(=X1)N(R9)₂, N(R9)₂, N(R9)C(=X1)R9, SR9, S(O)_nOR9, R9S(O)_nR9, C₁-C₆ alkyl C₆-C₂₀ aryl (wherein the alkyl and aryl can independently be substituted or unsubstituted), C(=X2)R9, C(=X1)X2R9, R9X2C(=X1)R9, R9X2R9, C(=O)(C₁-C₆ alkyl)S(O)_n(C₁-C₆ alkyl), C(=O)(C₁-C₆ alkyl)C(=O)O(C₁-C₆ alkyl), (C₁-C₆ alkyl)OC(=O)(C₆-C₂₀ aryl), (C₁-C₆ alkyl)OC(=O)(C₁-C₆ alkyl), C₁-C₆ alkyl-(C₃-C₁₀ cyclohaloalkyl), or (C₁-C₆ alkenyl)C(=O)O(C₁-C₆ alkyl), or R9X2C(=X1)X2R9,

wherein each said R6 (except R11), which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR9, S(O)_nOR9, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, R9aryl, (each of which that can be substituted, may optionally be substituted with R9),

optionally R6 (except R11) and R8 can be connected in a cyclic arrangement, where optionally such arrangement can have one or more heteroatoms selected from O, S, or N, in the cyclic structure connecting R6 and R8;

(h) R7 is O, S, NR9, or NOR9;

(i) R8 is R13-S(O)_n-R13 wherein each R13 is independently selected from substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, substituted or unsubstituted S(O)_nC₁-C₆ alkyl, substituted or unsubstituted N(C₁-C₆alkyl)₂, wherein each said substituted alkyl, substituted alkenyl, substituted alkoxy, substituted alkenyloxy, substituted cycloalkyl, substituted cycloalkenyl, substituted aryl, substituted heterocyclyl, has one or more substituents independently selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀

halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OC₁-C₆ alkyl, OC₁-C₆ haloalkyl, S(O)_nC₁-C₆alkyl, S(O)_nOC₁-C₆ alkyl, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, C₂-C₆ alkynyl, C₁-C₆ alkoxy, N(R₉)S(O)_nR₉, OR₉, N(R₉)₂, R₉OR₉, R₉N(R₉)₂, R₉C(=X₁)R₉, R₉C(=X₁)N(R₉)₂, N(R₉)C(=X₁)R₉, R₉N(R₉)C(=X₁)R₉, S(O)_nOR₉, R₉C(=X₁)OR₉, R₉OC(=X₁)R₉,
 5 R₉S(O)_nR₉, S(O)_nR₉, oxo, (each of which that can be substituted, may optionally be substituted with R₉);

(j) R₉ is (each independently) H, CN, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl,
 10 substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, substituted or unsubstituted S(O)_nC₁-C₆ alkyl, substituted or unsubstituted N(C₁-C₆alkyl)₂,

wherein each said R₉, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OC₁-C₆ alkyl, OC₁-C₆ haloalkyl, S(O)_nC₁-C₆alkyl, S(O)_nOC₁-C₆ alkyl, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl;

(k) n is 0, 1, or 2;

(l) X is N or CR_{n1} where R_{n1} is H, F, Cl, Br, I, CN, NO₂, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, OR₉, C(=X₁)R₉, C(=X₁)OR₉, C(=X₁)N(R₉)₂, N(R₉)₂, N(R₉)C(=X₁)R₉, SR₉, S(O)_nR₉,
 20 S(O)_nOR₉, or R₉S(O)_nR₉,

wherein each said R_{n1} which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, (each of which that can be substituted, may optionally be substituted with R₉);

(m) X₁ is (each independently) O or S;

(n) X₂ is (each independently) O, S, =NR₉, or =NOR₉;

(o) Z is CN, NO₂, C₁-C₆ alkyl(R₉), C(=X₁)N(R₉)₂;

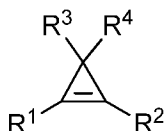
(p) R11 is $Q_1(C\equiv C)R_{12}$, wherein Q_1 is a bond, substituted or unsubstituted C_1-C_6 alkyl, substituted or unsubstituted C_2-C_6 alkenyl, substituted or unsubstituted C_2-C_6 alkynyl, substituted or unsubstituted C_3-C_{10} cycloalkyl, substituted or unsubstituted C_2-C_{10} cycloalkoxy, substituted or unsubstituted C_1-C_6 alkylOR9, substituted or unsubstituted C_1-C_6 alkylS(O)_nR9, substituted or unsubstituted C_1-C_6 alkylS(O)_n(=NR9), substituted or unsubstituted C_1-C_6 alkylN(R9) (where $(C\equiv C)$ is attached directly to the N by a bond), substituted or unsubstituted C_1-C_6 alkylN(R9)₂, substituted or unsubstituted C_2-C_6 alkenyloxy, substituted or unsubstituted C_3-C_{10} cycloalkenyl, substituted or unsubstituted C_0-C_6 alkylC(=R7)C₀-C₆ alkylR9, substituted or unsubstituted C_0-C_6 alkylC(=R7)OR9, substituted or unsubstituted C_1-C_6 alkylOC₀-C₆ alkylC(=R7)R9, substituted or unsubstituted C_1-C_6 alkylN(R9)(C(=R7)R9), substituted or unsubstituted C_1-C_6 alkylN(R9)(C(=R7)OR9), substituted or unsubstituted C_0-C_6 alkyl C(=R7)C₀-C₆ alkylN(R9) (where $(C\equiv C)$ is attached directly to the N by a bond), substituted or unsubstituted C_0-C_6 alkylC(=R7)C₀-C₆ alkylN(R9)₂, OR9, S(O)_nR9, N(R9)R9, substituted or unsubstituted C_6-C_{20} aryl, substituted or unsubstituted C_1-C_{20} heterocyclyl,

wherein each said Q_1 , which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C_1-C_6 alkyl, C_2-C_6 alkenyl, C_2-C_6 alkynyl, C_1-C_6 haloalkyl, C_2-C_6 haloalkenyl, C_1-C_6 haloalkyloxy, C_2-C_6 haloalkenyloxy, C_3-C_{10} cycloalkyl, C_3-C_{10} cycloalkenyl, C_3-C_{10} halocycloalkyl, C_3-C_{10} halocycloalkenyl, OR9, SR9, S(O)_nR9, S(O)_nOR9, C_6-C_{20} aryl, or C_1-C_{20} heterocyclyl, R9aryl, C_1-C_6 alkylOR9, C_1-C_6 alkylS(O)_nR9, (each of which that can be substituted, may optionally be substituted with R9)

optionally Q_1 and R8 can be connected in a cyclic arrangement, where optionally such arrangement can have one or more heteroatoms selected from O, S, or N, in the cyclic structure connecting Q_1 and R8;

(q) R12 is Q_1 (except where Q_1 is a bond), F, Cl, Br, I, Si(R9)₃ (where each R9 is independently selected), or R9; and

(ii) a Compound B according to Formula Two, or an agriculturally acceptable salt, ester, or amide thereof:



“Formula Two”

where each R¹, R², R³ and R⁴ is independently selected from the group consisting of H and a chemical group of the formula:



n is an integer from 0 to 12;

each L is a bivalent radical selected from B, C, N, O, P, S, Si, or mixtures thereof;

each Z is a monovalent radical selected from the group consisting of a C₁-C₈ alkyl, hydrogen, halo, cyano, nitro, nitroso, azido, chlorate, bromate, iodate, isocyanato, isocyanido, isothiocyanato, pentafluorothio, and a chemical group G, wherein G is a 3- to 14-membered ring system.

2. The composition of claim 1, wherein said A of Compound A is A1.

10 3. The composition of claim 1, wherein said A of Compound A is A2.

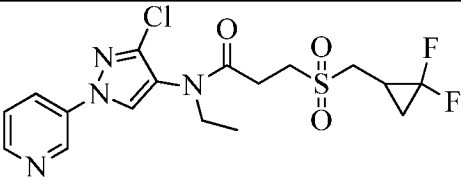
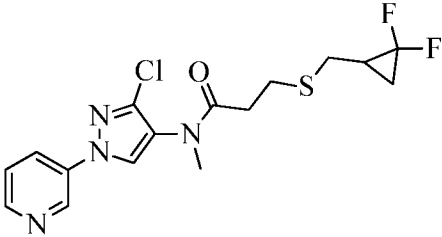
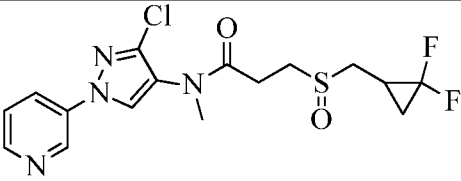
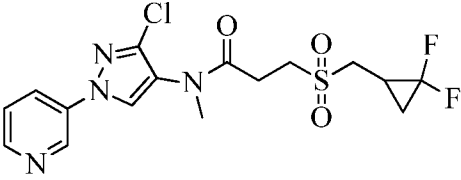
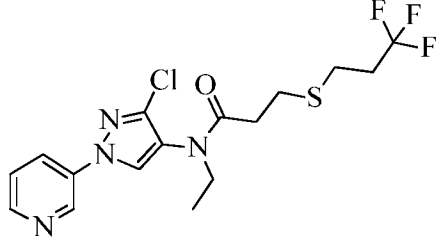
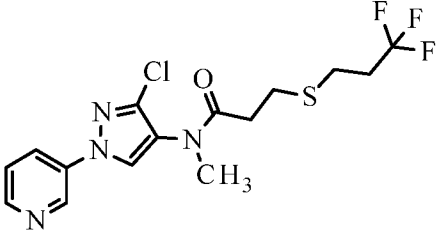
4. The composition of claim 1, wherein said R1 of of Compound A is H.

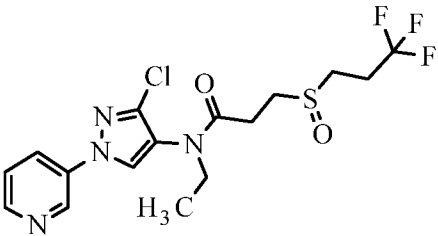
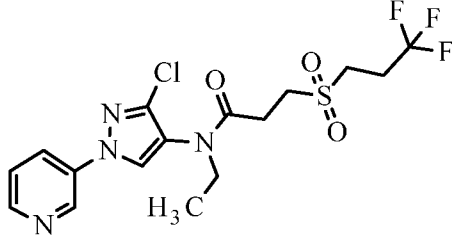
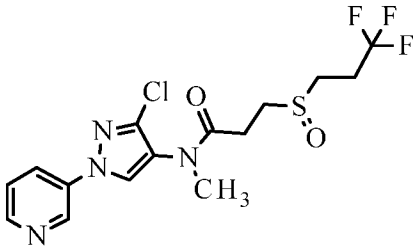
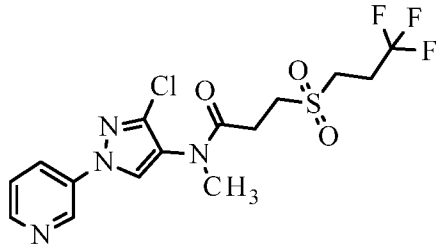
5. The composition of claim 1, wherein said R2 of of Compound A is H.

15

6. The composition of claim 1, wherein said Compound A has one of the following structures

607	
626	
627	

628	
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631	
653	
860	

861	
862	
924	
932	

7. The composition of claim 1, wherein the composition is a liquid.

8. The composition of claim 1, wherein the Compound B comprises 1-methylcyclopropene (1-MCP).

9. The composition of claim 1, wherein the composition comprises a complex of a cyclopropene compound of Compound B and a molecular encapsulating agent.

10. The composition of claim 9, wherein the molecular encapsulating agent is selected from alpha-cyclodextrin, beta-cyclodextrin, gamma-cyclodextrin, or combinations thereof.

5 11. The composition of claim 1, wherein weight ratio of Compound A to Compound B is between 1:10 and 1000:1.

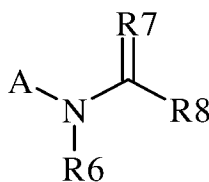
12. The composition of claim 1, further comprising a Compound C selected from the group consisting of azoxystrobin, sulfoxaflor, spinetoram, and combinations thereof.

10

13. The composition of claim 1, wherein the mixture comprises a synergistic combination of Compound A and Compound B for enhancing plant health and/or tolerance to stress.

14. A method for enhancing plant health and/or tolerance to stress, comprising:

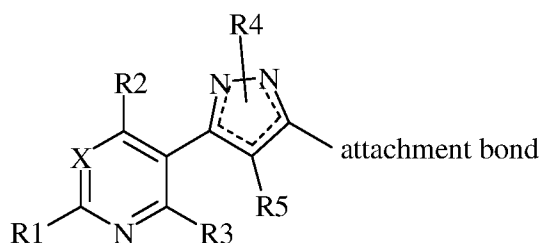
15 (i) first applying an effective amount of Compound A according to Formula One, or an agriculturally acceptable salt, ester, or amide thereof, to a plant or plant part:



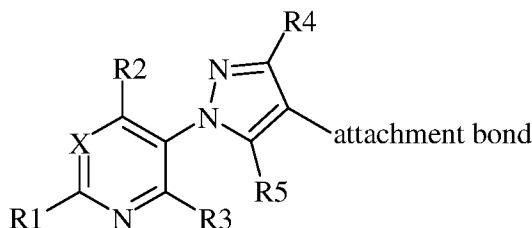
“Formula One”

wherein

(a) A is either



A1 or



A2

;

(b) R1 is H, F, Cl, Br, I, CN, NO₂, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, OR₉, C(=X1)R₉, C(=X1)OR₉, C(=X1)N(R₉)₂, N(R₉)₂, N(R₉)C(=X1)R₉, S(O)_nR₉, S(O)_nOR₉, S(O)_nN(R₉)₂, or R₉S(O)_nR₉,

wherein each said R1, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, (each of which that can be substituted, may optionally be substituted with R₉);

(c) R2 is H, F, Cl, Br, I, CN, NO₂, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, OR₉, C(=X1)R₉, C(=X1)OR₉, C(=X1)N(R₉)₂, N(R₉)₂, N(R₉)C(=X1)R₉, SR₉, S(O)_nOR₉, or R₉S(O)_nR₉,

wherein each said R2, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀

cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, (each of which that can be substituted, may optionally be substituted with R₉);

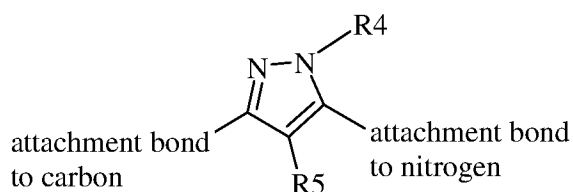
(d) R₃ is H, F, Cl, Br, I, CN, NO₂, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, OR₉, C(=X₁)R₉, C(=X₁)OR₉, C(=X₁)N(R₉)₂, N(R₉)₂, N(R₉)C(=X₁)R₉, SR₉, S(O)_nOR₉, or R₉S(O)_nR₉,

wherein each said R₃, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, (each of which that can be substituted, may optionally be substituted with R₉);

(e) when A is

(1) A₁ then A₁ is either

(a) A₁₁



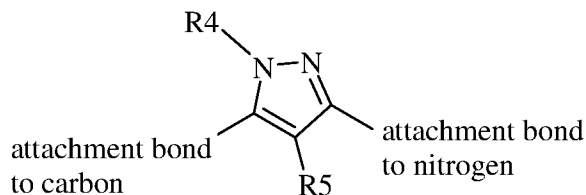
A₁₁

where R₄ is H, NO₂, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, C(=X₁)R₉, C(=X₁)OR₉, C(=X₁)N(R₉)₂, N(R₉)₂, N(R₉)C(=X₁)R₉, S(O)_nOR₉, or R₉S(O)_nR₉,

wherein each said R₄, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, C₆-C₂₀ aryl,

or C₁-C₂₀ heterocyclyl, (each of which that can be substituted, may optionally be substituted with R₉), or

(b) A12



A12

5 where R₄ is a C₁-C₆ alkyl,

(2) A2 then R₄ is H, F, Cl, Br, I, CN, NO₂, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, OR₉, C(=X₁)R₉, C(=X₁)OR₉, C(=X₁)N(R₉)₂, N(R₉)₂, N(R₉)C(=X₁)R₉, SR₉, S(O)_nOR₉, or R₉S(O)_nR₉,

15 wherein each said R₄, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, (each of which that can be substituted, may optionally be substituted with R₉);

(f) R₅ is H, F, Cl, Br, I, CN, NO₂, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, OR₉, C(=X₁)R₉, C(=X₁)OR₉, C(=X₁)N(R₉)₂, N(R₉)₂, N(R₉)C(=X₁)R₉, SR₉, S(O)_nOR₉, or R₉S(O)_nR₉,

25 wherein each said R₅, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, or C₆-C₂₀ aryl, (each of which that can be substituted, may optionally be substituted with R₉);

(g)

(1) when A is A1 then R6 is R11, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, OR9, C(=X1)R9, C(=X1)OR9, C(=X1)N(R9)₂, N(R9)₂, N(R9)C(=X1)R9, SR9, S(O)_nOR9, R9S(O)_nR9, C₁-C₆ alkyl C₆-C₂₀ aryl (wherein the alkyl and aryl can independently be substituted or unsubstituted), C(=X2)R9, C(=X1)X2R9, R9X2C(=X1)R9, R9X2R9, C(=O)(C₁-C₆ alkyl)S(O)_n(C₁-C₆ alkyl), C(=O)(C₁-C₆ alkyl)C(=O)O(C₁-C₆ alkyl), (C₁-C₆ alkyl)OC(=O)(C₆-C₂₀ aryl), (C₁-C₆ alkyl)OC(=O)(C₁-C₆ alkyl), C₁-C₆ alkyl-(C₃-C₁₀ cyclohaloalkyl), or (C₁-C₆ alkenyl)C(=O)O(C₁-C₆ alkyl), or R9X2C(=X1)X2R9,

wherein each said R6 (except R11), which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR9, S(O)_nOR9, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, R9aryl, (each of which that can be substituted, may optionally be substituted with R9),

optionally R6 (except R11) and R8 can be connected in a cyclic arrangement, where optionally such arrangement can have one or more heteroatoms selected from O, S, or, N, in the cyclic structure connecting R6 and R8, and

(2) when A is A2 then R6 is R11, H, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, OR9, C(=X1)R9, C(=X1)OR9, C(=X1)N(R9)₂, N(R9)₂, N(R9)C(=X1)R9, SR9, S(O)_nOR9, R9S(O)_nR9, C₁-C₆ alkyl C₆-C₂₀ aryl (wherein the alkyl and aryl can independently be substituted or unsubstituted), C(=X2)R9, C(=X1)X2R9, R9X2C(=X1)R9, R9X2R9, C(=O)(C₁-C₆ alkyl)S(O)_n(C₁-C₆ alkyl), C(=O)(C₁-C₆ alkyl)C(=O)O(C₁-C₆ alkyl), (C₁-C₆ alkyl)OC(=O)(C₆-C₂₀ aryl), (C₁-C₆ alkyl)OC(=O)(C₁-C₆ alkyl), C₁-C₆ alkyl-(C₃-C₁₀ cyclohaloalkyl), or (C₁-C₆ alkenyl)C(=O)O(C₁-C₆ alkyl), or R9X2C(=X1)X2R9,

wherein each said R6 (except R11), which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆

haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, R₉aryl, (each of which that can be substituted, may optionally be substituted with R₉),

5 optionally R₆ (except R₁₁) and R₈ can be connected in a cyclic arrangement, where optionally such arrangement can have one or more heteroatoms selected from O, S, or N, in the cyclic structure connecting R₆ and R₈;

(h) R₇ is O, S, NR₉, or NOR₉;

(i) R₈ is R₁₃-S(O)_n-R₁₃ wherein each R₁₃ is independently selected from
 10 substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, substituted or unsubstituted S(O)_nC₁-C₆ alkyl, substituted or unsubstituted
 15 N(C₁-C₆alkyl)₂, wherein each said substituted alkyl, substituted alkenyl, substituted alkoxy, substituted alkenyloxy, substituted cycloalkyl, substituted cycloalkenyl, substituted aryl, substituted heterocyclyl, has one or more substituents independently selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OC₁-C₆ alkyl, OC₁-C₆ haloalkyl, S(O)_nC₁-C₆alkyl, S(O)_nOC₁-C₆ alkyl, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, C₂-C₆ alkynyl, C₁-C₆ alkoxy, N(R₉)S(O)_nR₉, OR₉, N(R₉)₂, R₉OR₉, R₉N(R₉)₂, R₉C(=X₁)R₉, R₉C(=X₁)N(R₉)₂, N(R₉)C(=X₁)R₉, R₉N(R₉)C(=X₁)R₉, S(O)_nOR₉, R₉C(=X₁)OR₉, R₉OC(=X₁)R₉, R₉S(O)_nR₉, S(O)_nR₉, oxo, (each of which that can be substituted, may optionally be
 20 substituted with R₉);

(j) R₉ is (each independently) H, CN, substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, substituted or unsubstituted S(O)_nC₁-C₆ alkyl, substituted or unsubstituted N(C₁-C₆alkyl)₂,
 30

wherein each said R₉, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀

cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OC₁-C₆ alkyl, OC₁-C₆ haloalkyl, S(O)_nC₁-C₆alkyl, S(O)_nOC₁-C₆ alkyl, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl;

(k) n is 0, 1, or 2;

(l) X is N or CR_{n1} where R_{n1} is H, F, Cl, Br, I, CN, NO₂, substituted or
 5 unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or
 unsubstituted C₁-C₆ alkoxy, substituted or unsubstituted C₂-C₆ alkenyloxy, substituted or
 unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted
 or unsubstituted C₆-C₂₀ aryl, substituted or unsubstituted C₁-C₂₀ heterocyclyl, OR₉,
 C(=X₁)R₉, C(=X₁)OR₉, C(=X₁)N(R₉)₂, N(R₉)₂, N(R₉)C(=X₁)R₉, SR₉, S(O)_nR₉,
 10 S(O)_nOR₉, or R₉S(O)_nR₉,

wherein each said R_{n1} which is substituted, has one or more substituents
 selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆
 haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀
 cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, S(O)_nOR₉, C₆-C₂₀ aryl,
 15 or C₁-C₂₀ heterocyclyl, (each of which that can be substituted, may optionally be substituted
 with R₉);

(m) X₁ is (each independently) O or S;

(n) X₂ is (each independently) O, S, =NR₉, or =NOR₉;

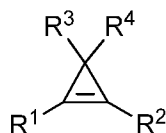
(o) Z is CN, NO₂, C₁-C₆ alkyl(R₉), C(=X₁)N(R₉)₂;

(p) R₁₁ is Q₁(C≡C)R₁₂, wherein Q₁ is a bond, substituted or unsubstituted C₁ –
 C₆ alkyl, substituted or unsubstituted C₂-C₆ alkenyl, substituted or unsubstituted C₂-C₆
 alkynyl, substituted or unsubstituted C₃-C₁₀ cycloalkyl, substituted or unsubstituted C₂-C₁₀
 cycloalkoxy, substituted or unsubstituted C₁-C₆ alkylOR₉, substituted or unsubstituted C₁-C₆
 alkylS(O)_nR₉, substituted or unsubstituted C₁-C₆ alkylS(O)_n(=NR₉), substituted or
 25 unsubstituted C₁-C₆ alkylN(R₉) (where (C≡C) is attached directly to the N by a bond),
 substituted or unsubstituted C₁-C₆ alkylN(R₉)₂, substituted or unsubstituted C₂-C₆
 alkenyloxy, substituted or unsubstituted C₃-C₁₀ cycloalkenyl, substituted or unsubstituted C₀-
 C₆ alkylC(=R₇)C₀-C₆ alkylR₉, substituted or unsubstituted C₀-C₆ alkylC(=R₇)OR₉,
 substituted or unsubstituted C₁-C₆ alkylOC₀-C₆ alkylC(=R₇)R₉, substituted or unsubstituted
 30 C₁-C₆ alkylN(R₉)(C(=R₇)R₉), substituted or unsubstituted C₁-C₆ alkylN(R₉)(C(=R₇)OR₉),
 substituted or unsubstituted C₀-C₆ alkyl C(=R₇)C₀-C₆ alkylN(R₉) (where (C≡C) is attached
 directly to the N by a bond), substituted or unsubstituted C₀-C₆alkylC(=R₇)C₀-C₆
 alkylN(R₉)₂, OR₉, S(O)_nR₉, N(R₉)R₉, substituted or unsubstituted C₆-C₂₀ aryl, substituted or
 unsubstituted C₁-C₂₀ heterocyclyl,

wherein each said Q₁, which is substituted, has one or more substituents selected from F, Cl, Br, I, CN, NO₂, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₂-C₆ alkynyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl, C₁-C₆ haloalkyloxy, C₂-C₆ haloalkenyloxy, C₃-C₁₀ cycloalkyl, C₃-C₁₀ cycloalkenyl, C₃-C₁₀ halocycloalkyl, C₃-C₁₀ halocycloalkenyl, OR₉, SR₉, S(O)_nR₉, S(O)_nOR₉, C₆-C₂₀ aryl, or C₁-C₂₀ heterocyclyl, R₉aryl, C₁-C₆alkylOR₉, C₁-C₆alkylS(O)_nR₉, (each of which that can be substituted, may optionally be substituted with R₉)

optionally Q₁ and R₈ can be connected in a cyclic arrangement, where optionally such arrangement can have one or more heteroatoms selected from O, S, or N, in the cyclic structure connecting Q₁ and R₈;

- 10 (q) R₁₂ is Q₁ (except where Q₁ is a bond), F, Cl, Br, I, Si(R₉)₃ (where each R₉ is independently selected), or R₉; and
- (ii) second applying a Compound B according to Formula Two, or an agriculturally acceptable salt, ester, or amide thereof, to the plant or plant part:



“Formula Two”

- 15 where each R¹, R², R³ and R⁴ is independently selected from the group consisting of H and a chemical group of the formula:



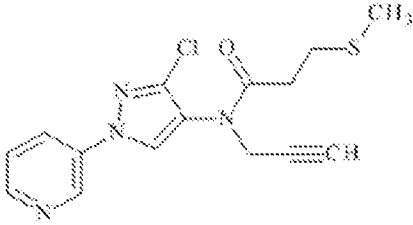
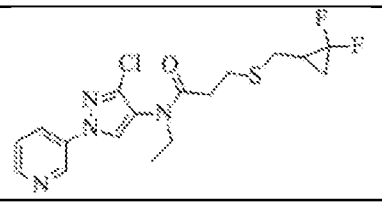
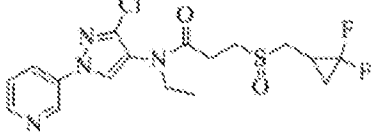
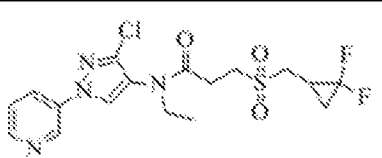
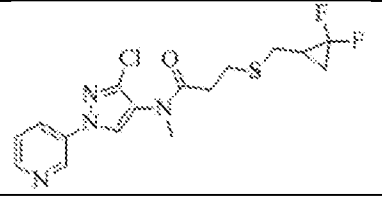
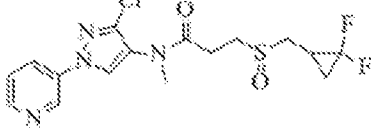
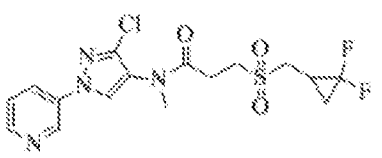
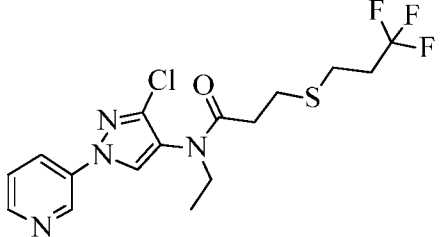
n is an integer from 0 to 12;

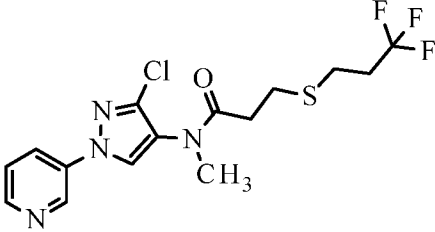
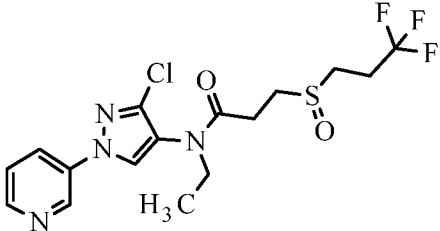
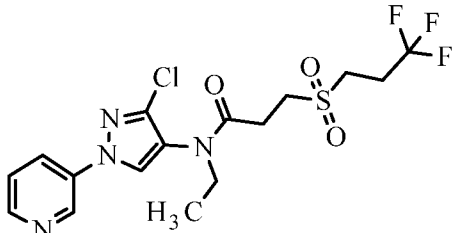
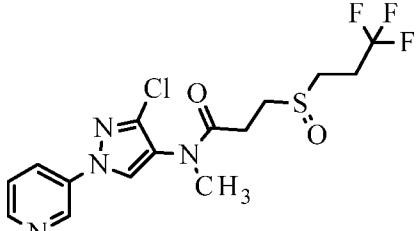
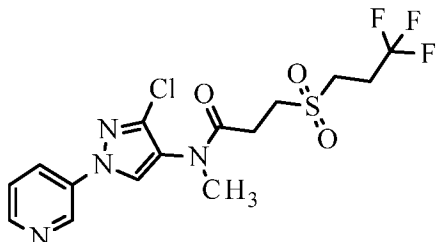
each L is a bivalent radical selected from B, C, N, O, P, S, Si, or mixtures thereof;

- 20 each Z is a monovalent radical selected from the group consisting of a C₁-C₈ alkyl, hydrogen, halo, cyano, nitro, nitroso, azido, chlorate, bromate, iodate, isocyanato, isocyanido, isothiocyanato, pentafluorothio, and a chemical group G, wherein G is a 3- to 14-membered ring system;

- wherein the first applying and the second applying steps can be performed in either order or simultaneously.
- 25

15. The method of claim 14, wherein said Compound A has one of the following structures

607	
626	
627	
628	
629	
630	
631	
653	

860	
861	
862	
924	
932	

16. The method of claim 14, wherein the Compound B comprises 1-methylcyclopropene (1-MCP).

17. The method of claim 14, wherein weight ratio of Compound A to Compound B is
5 between 1:10 and 1000:1.

18. The method of claim 14, wherein the combination of Compound A and Compound B is synergistic.

10 19. The method of claim 14, wherein the first applying step or the second applying step is performed in an enclosed space.

20. The method of claim 14, wherein the first applying step or the second applying step is performed in an open space.

15

21. The method of claim 14, wherein the plant comprises a vegetable.

22. The method of claim 21, wherein the vegetable is selected from the group consisting of tomato, peppers, celery, lettuce, broccoli, cabbage, cauliflower, artichokes, leeks, and
20 combinations thereof.

23. The method of claim 14, further comprising third applying a Compound C selected from the group consisting of azoxystrobin, sulfoxaflor, spinetoram, and combinations thereof, to the plant or plant part.

25

24. A method for enhancing plant health and/or tolerance to stress for plants, comprising applying the composition of claim 1 to a plant or plant part.

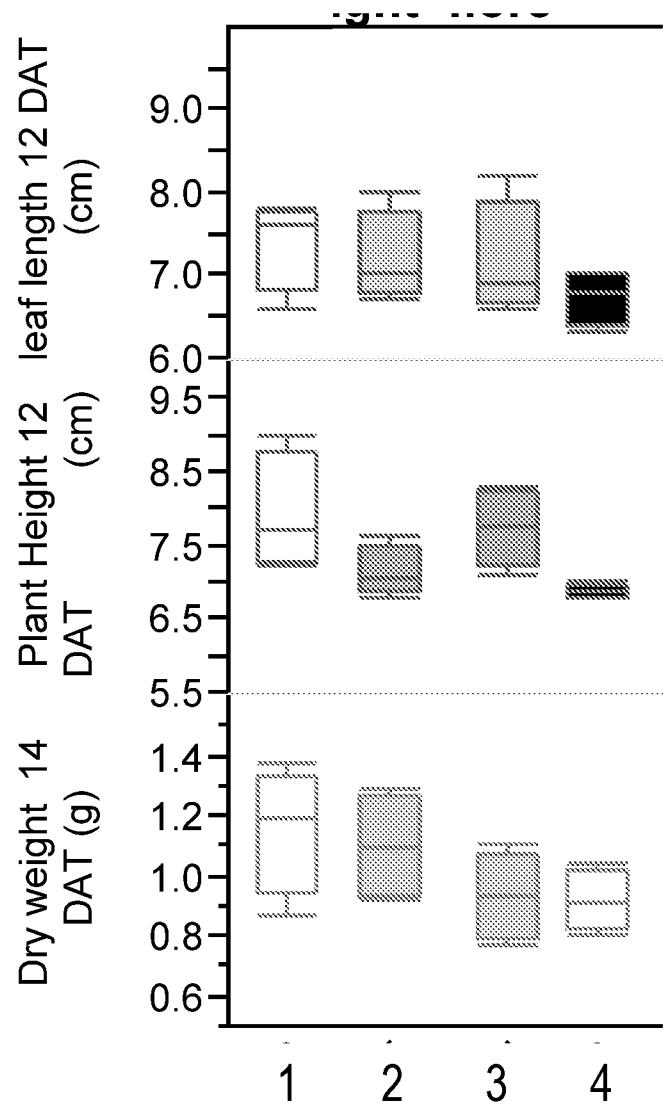


FIG. 1.

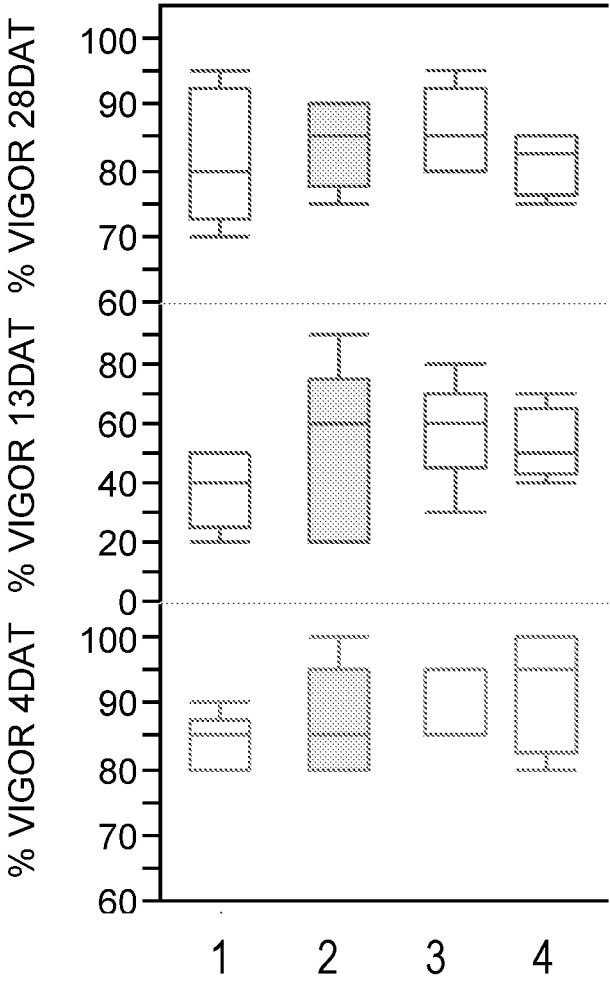


FIG. 2

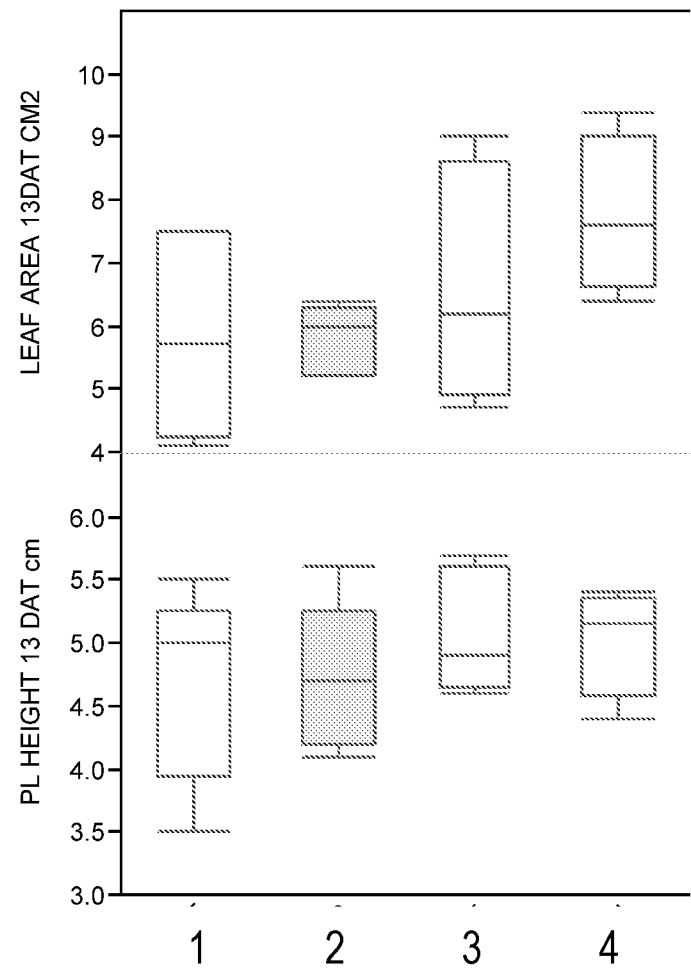


FIG. 3

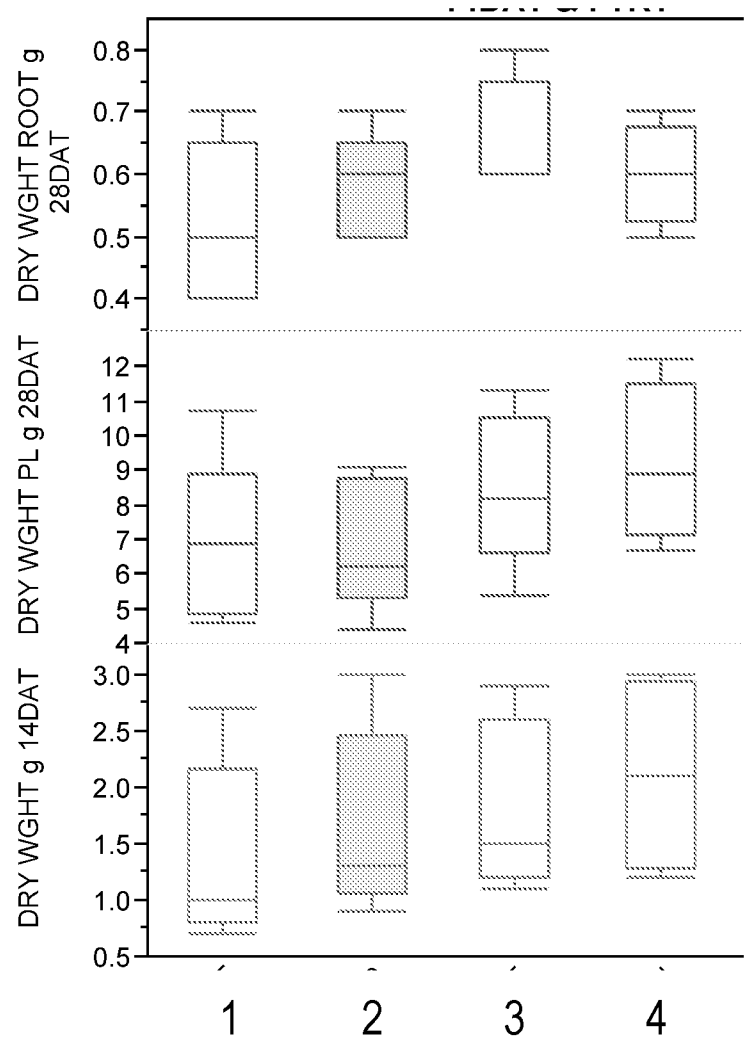


FIG. 4

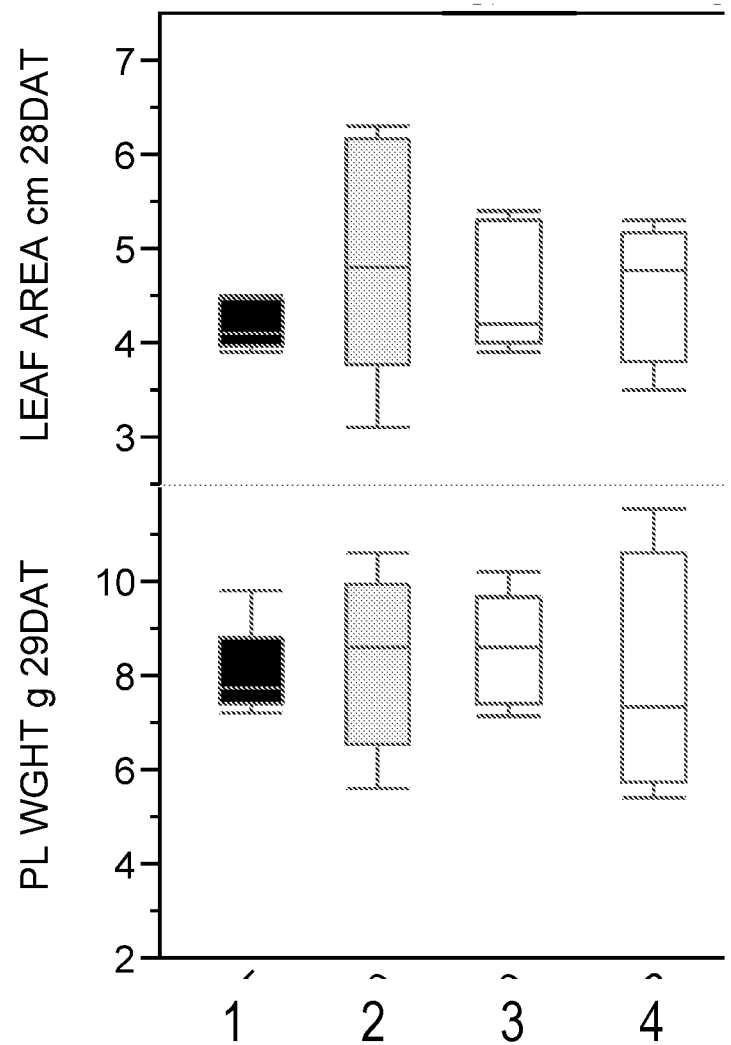


FIG. 5

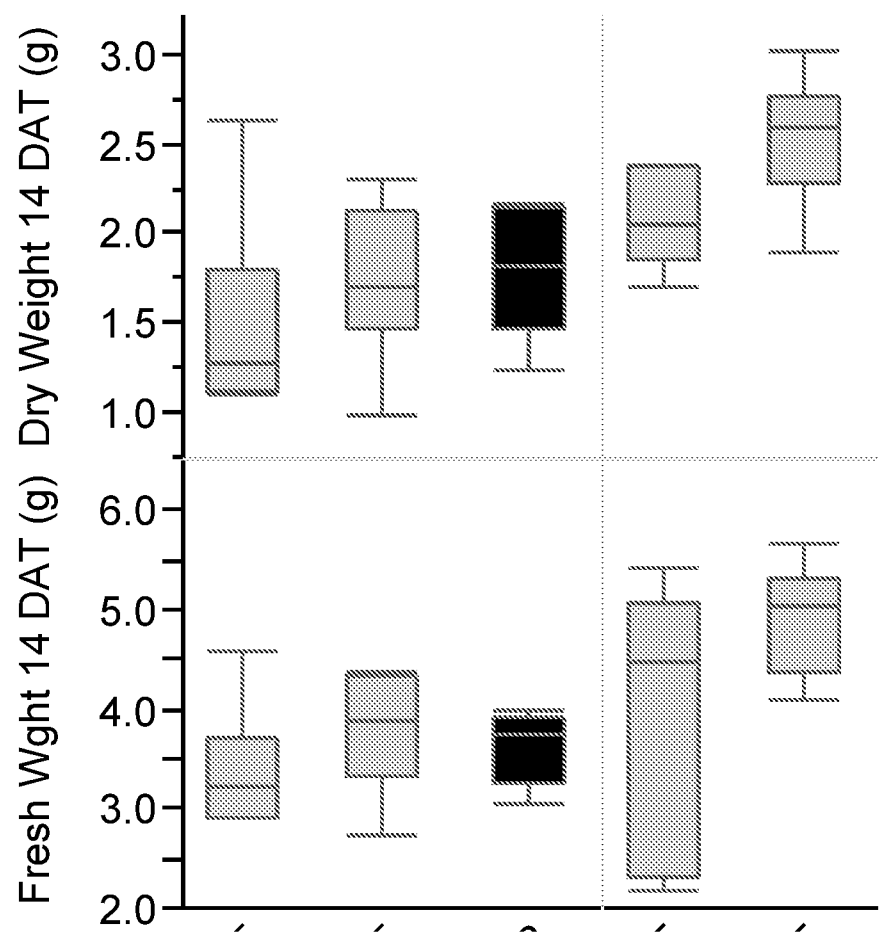


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2016/021291

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - A01N 43/56; A01N 27/00; A01N 43/54; C07D 231/10; C07D 401/02; C07D 401/04 (2016.01)

CPC - A01N 27/00; A01N 43/54; A01N 43/56; C07D 231/10; C07D 401/02; C07D 401/04 (2016.05)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8) - A01N 27/00; A01N 43/54; A01N 43/56; C07D 231/10; C07D 401/02; C07D 401/04 (2016.01)

CPC - A01N 27/00; A01N 43/54; A01N 43/56; C07D 231/10; C07D 401/02; C07D 401/04 (2016.05)

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

USPC - 504/105; 504/106; 504/177; 504/181; IPC(8) - A01N 27/00; A01N 43/54; A01N 43/56; C07D 231/10; C07D 401/02 (2016.01);

CPC - A01N 27/00; A01N 43/54; A01N 43/56; C07D 231/10; C07D 401/02; C07D 401/04 (2016.05) (keyword delimited)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatBase, Google Patents, STN, Google Scholar

Search terms used: pesticides, pyrazolopyrimidine, pyrimidine, pyrazole, MCP or methylcyclopropene, plant, stress, tolerance, encapsulating, azoxystrobin, sulfoxaflor, spinetoram, fluoromethyl

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2013/0109566 A1 (DOW AGROSCIENCES LLC) 02 May 2013 (02.05.2013) entire document	1, 2, 4, 5, 7, 9-13
A	US 2008/0318775 A1 (BASEL et al) 25 December 2008 (25.12.2008) entire document	1, 2, 4, 5, 7, 9-13
A	US 2013/0298290 A1 (HAAS et al) 07 November 2013 (07.11.2013) entire document	1, 2, 4, 5, 7, 9-13
A	US 5,556,873 A (HUANG et al) 17 September 1996 (17.09.1996) entire document	1, 2, 4, 5, 7, 9-13

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

23 June 2016

Date of mailing of the international search report

29 JUL 2016

Name and mailing address of the ISA/

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, VA 22313-1450

Facsimile No. 571-273-8300

Authorized officer

Blaine R. Copenheaver

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2016/021291

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Extra Sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1, 2, 4, 5, 7, 9-13

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

Continued from Box No. III Observations where unity of invention is lacking

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees need to be paid.

Group I+: claims 1-13 are drawn to compositions.

Group II+: claims 14-24 are drawn to methods for enhancing plant health and/or tolerance.

The first invention of Group I+ is restricted to a composition comprising a mixture comprising: (i) an effective amount of a Compound A according to Formula One, wherein A is A1, wherein A1 is A11; R1 is H; R2 is H; R3 is H, R4 is H; R5 is H; R6 is R11, wherein R11 is Q1(C=C)R12, wherein Q1 is a bond and R12 is F; R7 is O; R8 is R13-S(O)n-R13, wherein each R13 is independently substituted C1 alkyl, wherein each substituted alkyl has one substituent selected as F, and wherein n is 0; and X is N; or an agriculturally acceptable salt, ester, or amide thereof; and (ii) a Compound B according to Formula Two, where each R1, R2, R3, and R4 are independently selected as H, or an agriculturally acceptable salt, ester, or amide thereof. It is believed that claims 1, 2, 4, 5, 7, and 9-13 read on this first named invention and thus these claims will be searched without fee to the extent that they read on the above embodiment.

The first invention of Group II+ is restricted to a method for enhancing plant health and/or tolerance to stress, comprising: (i) first applying an effective amount of Compound A according to Formula One, wherein A is A1, wherein A1 is A11; R1 is H; R2 is H; R3 is H, R4 is H; R5 is H; R6 is R11, wherein R11 is Q1(C=C)R12, wherein Q1 is a bond and R12 is F; R7 is O; R8 is R13-S(O)n-R13, wherein each R13 is independently substituted C1 alkyl, wherein each substituted alkyl has one substituent selected as F, and wherein n is 0; and X is N; or an agriculturally acceptable salt, ester, or amide thereof; to a plant or plant part; (ii) second applying a Compound B according to Formula Two, where each R1, R2, R3, and R4 are independently selected as H, or an agriculturally acceptable salt, ester, or amide thereof, to the plant or plant part: wherein the first applying and the second applying steps can be performed in either order or simultaneously.

Applicant is invited to elect additional formula(e) for each additional compound to be searched in a specific combination by paying an additional fee for each set of election. Each additional elected formula(e) requires the selection of a single definition for each compound variable. An exemplary election would be a mixture comprising: (i) an effective amount of a Compound A according to Formula One, wherein A is A2; R1 is substituted C6 aryl, wherein R1 has two substituents selected as CN and NO2; R2 is F; R3 is unsubstituted C3 cycloalkenyl, R4 is OR9, wherein R9 is unsubstituted C18 heterocyclyl; R5 is H; R6 is unsubstituted C6 aryl; R7 is O; R8 is R13-S(O)n-R13, wherein each R13 is independently substituted C2 alkoxy, wherein each substituted alkyl has one substituent selected as F, and wherein n is 1; and X is CRn1, wherein Rn1 is NO2; or an agriculturally acceptable salt, ester, or amide thereof; and (ii) a Compound B according to Formula Two, where each R1, R2, R3, and R4 are independently selected as H, or an agriculturally acceptable salt, ester, or amide thereof. Additional formula(e) will be searched upon the payment of additional fees. Applicants must specify the claims that read on any additional elected inventions. Applicants must further indicate, if applicable, the claims which read on the first named invention if different than what was indicated above for this group. Failure to clearly identify how any paid additional invention fees are to be applied to the "+" group(s) will result in only the first claimed invention to be searched/examined.

The inventions listed in Groups I+ and II+ do not relate to a single general inventive concept under PCT Rule 13.1, because under PCT Rule 13.2 they lack the same or corresponding special technical features for the following reasons:

The special technical features of Group I+, compositions, are not present in Group II+, and the special technical features of Group II+, methods for enhancing plant health and/or tolerance, are not present in Group I+.

The Groups I+ and II+ formulae do not share a significant structural element requiring the selection of alternatives for the compound variables A, R1, R2, R3, R4, R6, R7, and R8.

The Groups I+ and II+ share the technical features of a composition comprising a mixture comprising: (i) an effective amount of a Compound A according to Formula One, or an agriculturally acceptable salt, ester, or amide thereof (ii) a Compound B according to Formula Two, or an agriculturally acceptable salt, ester, or amide thereof; a method for enhancing plant health and/or tolerance to stress, comprising: (i) first applying an effective amount of Compound A according to Formula One, or an agriculturally acceptable salt, ester, or amide thereof, to a plant or plant part; (ii) second applying a Compound B according to Formula Two, or an agriculturally acceptable salt, ester, or amide thereof, to the plant or plant part: wherein the first applying and the second applying steps can be performed in either order or simultaneously; and a method for enhancing plant health and/or tolerance to stress for plants, comprising applying the composition to a plant or plant part. However, these shared technical features do not represent a contribution over the prior art.

Specifically, US 2013/0109566 A1 to Dow AgroSciences LLC teaches a composition comprising a mixture comprising: (i) an effective amount of a Compound A, according to Formula One, wherein A is A2; R1 is H; R2 is H; R3 is H; R4 is unsubstituted C1-alkyl; R5 is H; R6 is R11, wherein R11 is Q1(C=C)R12, wherein Q1 is unsubstituted C1-alkyl, and R12 is R9, wherein R9 is H; R7 is O; R8 is R13-S(O)n-R13, wherein the R13 which shares a carbon with R7 is unsubstituted C2-alkyl, the terminal R13 is unsubstituted C1-alkyl, and n is 0; and X is CRn1, wherein Rn1 is F; or an agriculturally acceptable salt, ester, or amide thereof (Para. [0433], N-(1-(5-fluoropyridin-3-yl)-3-methyl-1H-pyrazol-4-yl)-3-(methylthio)-N-(prop-2-ynyl)propanamide, see shown structure) (ii) a Compound B according to Formula Two, where R1 is H; R2 is -(L)n-Z, wherein n is 0 and Z is a monovalent radical selected as C1 alkyl; R3 is H; and R4 is H, or an agriculturally acceptable salt, ester, or amide thereof (Para. [0556]). The molecules of Formula One may be used in mixtures, applied simultaneously or sequentially, alone or with other compounds to enhance plant vigor (e.g. to grow a better root system, to better withstand stressful growing conditions). Such other compounds are, for example, compounds that modulate plant ethylene receptors, most notably 1-methylcyclopropene (also known as 1-MCP.); a method for enhancing plant health and/or tolerance to stress (Paras. [0556]-[0569]), comprising: (i) first applying an effective amount of Compound A according to Formula One, wherein A is A2; R1 is H; R2 is H; R3 is H; R4 is unsubstituted C1-alkyl; R5 is H; R6 is R11, wherein R11 is Q1(C=C)R12, wherein Q1 is unsubstituted C1-alkyl, and R12 is R9, wherein R9 is H; R7 is O; R8 is R13-S(O)n-R13, wherein the R13 which shares a carbon with R7 is unsubstituted C2-alkyl, the terminal R13 is unsubstituted C1-alkyl, and n is 0; and X is CRn1, wherein Rn1 is F; or an agriculturally acceptable salt, ester, or amide thereof (Para. [0433], N-(1-(5-fluoropyridin-3-yl)-3-methyl-1H-pyrazol-4-yl)-3-(methylthio)-N-(prop-2-ynyl)propanamide, see shown structure) to a plant or plant part (Paras. [0557]; [0561]);

(ii) second applying a Compound B according to Formula Two, where R1 is H; R2 is $-(L)_n-Z$, wherein n is 0 and Z is a monovalent radical selected as C1 alkyl; R3 is H; and R4 is H, or an agriculturally acceptable salt, ester, or amide thereof (Para. [0556], The molecules of Formula One may be used in mixtures, applied simultaneously or sequentially, alone or with other compounds to enhance plant vigor (e.g. to grow a better root system, to better withstand stressful growing conditions). Such other compounds are, for example, compounds that modulate plant ethylene receptors, most notably 1-methylcyclopropene (also known as 1-MCP).); wherein the first applying and the second applying steps can be performed in either order or simultaneously (Para. [0556], The molecules of Formula One may be used in mixtures, applied simultaneously or sequentially, alone or with other compounds to enhance plant vigor); and a method for enhancing plant health and/or tolerance to stress for plants (Paras. [0556]-[0569]), comprising applying the composition (Para. [0433],[0556]) to a plant or plant part (Paras. [0557]; [0561]).

The inventions listed in Groups I+ and II+ therefore lack unity under Rule 13 because they do not share a same or corresponding special technical feature.