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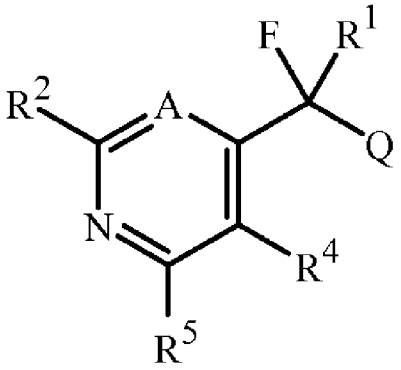
(54) **Title**: PYRIDINE AND PYRIMIDINE COMPOUNDS FOR CONTROLLING INVERTEBRATE

(57) **Abstract**: Disclosed are compounds of Formula 1, *N*-oxides, and salts thereof, wherein A is N or CR^3; R^1, R^2, R^3, R^4, R^5 and Q are as defined in the disclosure. Also disclosed are compositions containing the compounds of Formula 1 and methods for controlling an invertebrate pest comprising contacting the invertebrate pest or its environment with a biologically effective amount of a compound or a composition of the invention.



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PYRIDINE AND PYRIMIDINE COMPOUNDS FOR CONTROLLING INVERTEBRATE PESTS

FIELD OF THE INVENTION

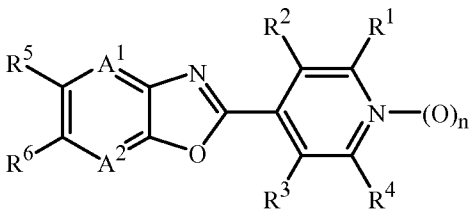
This invention relates to certain substituted pyridine compounds, their *N*-oxides, salts and their compositions suitable for agronomic, nonagronomic and animal health uses, methods of their use for controlling invertebrate pests such as arthropods in both agronomic and nonagronomic environments, and for treatment of parasite infections in animals or infestations in the general environment.

BACKGROUND OF THE INVENTION

The control of invertebrate pests is extremely important in achieving high crop efficiency. Damage by invertebrate pests to growing and stored agronomic crops can cause significant reduction in productivity and thereby result in increased costs to the consumer. The control of invertebrate pests in forestry, greenhouse crops, ornamentals, nursery crops, stored food and fiber products, livestock, household, turf, wood products, and public health is also important. Many products are commercially available for these purposes, but the need continues for new compounds that are more effective, less costly, less toxic, environmentally safer or have different sites of action.

The control of animal parasites in animal health is essential, especially in the areas of food production and companion animals. Existing methods of treatment and parasite control are being compromised due to growing resistance to many current commercial parasiticides. The discovery of more effective ways to control animal parasites is therefore imperative.

World Patent Publication WO 2009/131237 discloses pyridinium compounds of Formula **i** for harmful anthropod control.



i

The pyridinium compounds of the present invention are not disclosed in this publication.

SUMMARY OF THE INVENTION

This invention is directed to compounds of Formula **1** (including all stereoisomers), *N*-oxides, and salts thereof, and compositions containing them and their use for controlling invertebrate pests:

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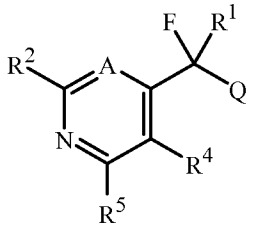


1

wherein

A is N or CR^3;

R^1 is hydrogen, halogen, hydroxyl, cyano, SF_5, C_1–C_4 alkyl, C_2–C_4 alkenyl, C_2–C_4 alkynyl, C_1–C_4 haloalkyl, C_2–C_4 haloalkenyl, C_2–C_4 haloalkynyl, C_3–C_4 cycloalkyl, C_3–C_4 halocycloalkyl, C_1–C_4 alkoxy, C_1–C_4 haloalkoxy, C_2–C_4 alkylthio, C_2–C_4 alkylsulfinyl, C_2–C_4 alkylsulfonyl, C_2–C_4 haloalkylthio C_2–C_4 cyanoalkyl, C_2–C_4 alkylcarbonyl or C_2–C_4 alkoxycarbonyl;

R^2 and R^5 are each independently selected from hydrogen and fluorine;

$R^3$and R^4 are each independently selected from hydrogen, halogen, cyano, amino, nitro, SF_5, -CHO, 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_2–C_6 haloalkynyl, C_3–C_6 cycloalkyl, C_3–C_6 halocycloalkyl, C_4–C_8 alkylcycloalkyl, C_4–C_8 cycloalkylalkyl, C_3–C_6 cycloalkenyl, C_2–C_6 alkoxyalkyl, C_2–C_6 alkylthioalkyl, C_2–C_6 alkylcarbonyl, C_2–C_6 haloalkylcarbonyl, C_2–C_6 alkoxycarbonyl, C_2–C_6 alkylaminocarbonyl, C_3–C_8 dialkylaminocarbonyl, C_2–C_6 cyanoalkyl, C_1–C_6 alkoxy, C_1–C_6 haloalkoxy, C_2–C_6 alkoxyalkoxy, C_1–C_6 alkylthio, C_1–C_6 haloalkylthio, C_1–C_6 alkylsulfinyl, C_1–C_6 haloalkylsulfinyl, C_1–C_6 alkylsulfonyl, C_1–C_6 haloalkylsulfonyl, C_3–C_9 trialkylsilyl, C_1–C_6 alkylamino, C_2–C_6 dialkylamino, C_2–C_6 haloalkylamino, C_2–C_6 halodialkylamino or C_2–C_6 alkylcarbonylamino; or Q^1, OQ^1 or SQ^1;

Q is phenyl or naphthalenyl each optionally substituted on carbon atom ring members with up to 5 substituents independently selected from R^{9a}; or

Q is a 5- to 6-membered heteroaromatic ring provided that the 5- to 6-membered heteroaromatic ring is not imidazole or pyridazine, or an 8- to 11-membered heteroaromatic bicyclic ring system provided that the 8- to 11-membered heteroaromatic bicyclic ring system does not contain a pyridazine ring; each ring or ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members; or

Q is a 3- to 7-membered nonaromatic carbocyclic ring, a 5- to 7-membered nonaromatic heterocyclic ring provided that the 5- to 7-membered nonaromatic heterocyclic ring is not piperidine, or an 8- to 11-membered nonaromatic bicyclic ring system provided that the 8- to 11-membered nonaromatic bicyclic ring system does not contain a piperidine ring; each ring or ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S, up to 4 N and up to 2 Si atoms, wherein up to 3 carbon atom ring members are independently selected from C(=O) and C(=S), the sulfur atom ring members are independently selected from $S(=O)_s(=NR^{17})_f$, and the silicon atom ring members are independently selected from $SiR^{10}R^{11}$, each ring or ring system optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members;

each R^{9a} is independently halogen, hydroxy, amino, cyano, nitro, SF_5, C_1–C_6 alkyl, C_2–C_6 alkenyl, C_2–C_6 alkynyl, C_3–C_6 cycloalkyl, C_4–C_{10} cycloalkylalkyl, C_4–C_{10} alkylcycloalkyl, C_5–C_{10} alkylcycloalkylalkyl, C_6–C_{14} cycloalkylcycloalkyl, C_1–C_6 haloalkyl, C_2–C_6 haloalkenyl, C_2–C_6 haloalkynyl, C_3–C_6 halocycloalkyl, C_1–C_4 alkoxy, C_1–C_4 haloalkoxy, C_2–C_4 alkoxyalkoxy, C_1–C_4 alkylthio, C_1–C_4 alkylsulfinyl, C_1–C_4 alkylsulfonyl, C_1–C_4 haloalkylthio, C_1–C_4 haloalkylsulfinyl, C_1–C_4 haloalkylsulfonyl, C_1–C_4 alkylamino, C_2–C_8 dialkylamino, C_3–C_6 cycloalkylamino, C_2–C_4 alkoxyalkyl, C_1–C_4 hydroxyalkyl, C_2–C_4 alkylcarbonyl, C_2–C_6 alkoxycarbonyl, C_2–C_6 alkylcarbonyloxy, C_2–C_6 alkylcarbonylthio, C_2–C_6 alkylaminocarbonyl, C_3–C_8 dialkylaminocarbonyl, C_3–C_6 haloalkylcarbonylamino, C_3–C_6 haloalkylcarbonyl(alkyl)amino or C_3–C_6 trialkylsilyl; or phenyl, phenoxy or naphthalenyl optionally substituted with up to 3 substituents independently selected from halogen, cyano, C_1–C_2 alkyl, C_1–C_2 haloalkyl, C_1–C_2 alkoxy and C_1–C_2 haloalkoxy; or a 5- to 6-membered heteroaromatic ring containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 3 substituents independently selected from halogen, cyano, C_1–C_2 alkyl, C_1–C_2 haloalkyl, C_1–C_2 alkoxy and C_1–C_2 haloalkoxy on carbon atom ring members and cyano, C_1–C_2 alkyl and C_1–C_2 alkoxy on nitrogen atom ring members; or a 3- to 7-membered nonaromatic ring containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, wherein up to 3 carbon atom ring members are independently selected from C(=O) and C(=S), the ring optionally substituted with up to 3 substituents independently selected from halogen, cyano, C_1–C_2 alkyl, C_1–C_2 haloalkyl, C_1–C_2 alkoxy and

C_1–C_2 haloalkoxy on carbon atom ring members and cyano, C_1–C_2 alkyl and C_1–C_2 alkoxy on nitrogen atom ring members;

each R^{9b} is independently hydrogen, cyano, C_1–C_3 alkyl, C_1–C_3 haloalkyl, C_1–C_3 alkoxy, C_2–C_3 alkylcarbonyl, C_2–C_3 alkoxycarbonyl or C_3–C_6 cycloalkyl;

Q^1 is phenyl or naphthalenyl each optionally substituted on carbon atom ring members with up to 5 substituents independently selected from R^{9a}; or

Q^1 is a 5- to 6-membered heteroaromatic ring or an 8- to 11-membered heteroaromatic bicyclic ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members; or

Q^1 is a 3- to 7-membered nonaromatic carbocyclic ring, a 5- to 7-membered nonaromatic heterocyclic ring or an 8- to 11-membered nonaromatic bicyclic ring system, each ring or ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S, up to 4 N and up to 2 Si atoms, wherein up to 3 carbon atom ring members are independently selected from C(=O) and C(=S), the sulfur atom ring members are independently selected from $S(=O)_s(=NR^{17})_f$, and the silicon atom ring members are independently selected from $SiR^{10}R^{11}$, each ring or ring system optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members;

each R^{10} and R^{11} is independently C_1–C_5 alkyl, C_2–C_5 alkenyl, C_2–C_5 alkynyl, C_3–C_5 cycloalkyl, C_3–C_6 halocycloalkyl, C_4–C_{10} cycloalkylalkyl, C_4–C_7 alkylcycloalkyl, C_5–C_7 alkylcycloalkylalkyl, C_1–C_5 haloalkyl, C_1–C_5 alkoxy or C_1–C_5 haloalkoxy;

each R^{17} is independently hydrogen, cyano, C_1–C_6 alkyl, C_1–C_6 haloalkyl, C_3–C_8 cycloalkyl, C_3–C_8 halocycloalkyl, C_1–C_6 alkoxy, C_1–C_6 haloalkoxy, C_1–C_6 alkylamino, C_2–C_8 dialkylamino, C_1–C_6 haloalkylamino or phenyl; and

s and f are independently 0, 1 or 2 in each instance of $S(=O)_s(=NR^{17})_f$, provided that the sum of s and f is 0, 1 or 2;

provided that

the compound of Formula **1** is other than 4,4'-(1,2,2,2-tetrafluoroethylidene)-bis[pyridine] or 4,4'-(1,2,2,2-tetrafluoroethylidene)bis[2,3,5,6-tetrafluoropyridine].

This invention is also directed to such compounds of Formula **1** (including all stereoisomers), *N*-oxides, and salts thereof, and compositions containing them and their use for controlling invertebrate pests.

This invention also provides a composition comprising a compound of Formula **1**, an *N*-oxide, or a salt thereof, and at least one additional component selected from the group consisting of surfactants, solid diluents and liquid diluents. In one embodiment, this invention also provides a composition for controlling an invertebrate pest comprising a compound of Formula **1**, an *N*-oxide, or a salt thereof, and at least one additional component selected from the group consisting of surfactants, solid diluents and liquid diluents, said composition further comprising at least one additional biologically active compound or agent.

This invention provides a method for controlling an invertebrate pest comprising contacting the invertebrate pest or its environment with a biologically effective amount of a compound of Formula **1**, an *N*-oxide, or a salt thereof (e.g., as a composition described herein). This invention also relates to such method wherein the invertebrate pest or its environment is contacted with a composition comprising a biologically effective amount of a compound of Formula **1**, an *N*-oxide, or a salt thereof, and at least one additional component selected from the group consisting of surfactants, solid diluents and liquid diluents, said composition optionally further comprising a biologically effective amount of at least one additional biologically active compound or agent.

This invention also provides a method for controlling an invertebrate pest comprising contacting the invertebrate pest or its environment with a biologically effective amount of any of the aforesaid compositions wherein the environment is a plant.

This invention also provides a method for controlling an invertebrate pest comprising contacting the invertebrate pest or its environment with a biologically effective amount of any of the aforesaid compositions wherein the environment is an animal.

This invention also provides a method for controlling an invertebrate pest comprising contacting the invertebrate pest or its environment with a biologically effective amount of any of the aforesaid compositions wherein the environment is a seed.

This invention also provides a method for protecting a seed from an invertebrate pest comprising contacting the seed with a biologically effective amount of a compound of Formula **1**, an *N*-oxide, or a salt thereof (e.g., as a composition described herein). This invention also relates to the treated seed.

This invention further provides a composition for protecting an animal from an invertebrate parasitic pest comprising a parasiticidally effective amount of a compound of Formula **1**, an *N*-oxide, or a salt thereof, and at least one carrier.

This invention further provides a method for treating, preventing, inhibiting and/or killing ecto and/or endoparasites comprising administering to and/or on an animal a parasiticidally effective amount of a compound of Formula **1**, an *N*-oxide, or a salt thereof (e.g., as a composition described herein). This invention also relates to such method wherein a parasiticidally effective amount of a compound of Formula **1**, an *N*-oxide, or a salt thereof,

(e.g., as a composition described herein) is administered to an environment (e.g., a stall or blanket) in which an animal resides.

DETAILS OF THE INVENTION

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

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

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

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

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

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

As referred to in this disclosure, the term "invertebrate pest" includes arthropods, gastropods, nematodes and helminths of economic importance as pests. The term "arthropod" includes insects, mites, spiders, scorpions, centipedes, millipedes, pill bugs and symphylans. The term "gastropod" includes snails, slugs and other Stylommatophora. The

term "nematode" includes members of the phylum Nematoda, such as phytophagous nematodes and helminth nematodes parasitizing animals. The term "helminth" includes all of the parasitic worms, such as roundworms (phylum Nematoda), heartworms (phylum Nematoda, class Secernentea), flukes (phylum Platyhelminthes, class Tematoda), acanthocephalans (phylum Acanthocephala), and tapeworms (phylum Platyhelminthes, class Cestoda).

In the context of this disclosure "invertebrate pest control" means inhibition of invertebrate pest development (including mortality, feeding reduction, and/or mating disruption), and related expressions are defined analogously.

The term "agronomic" refers to the production of field crops such as for food and fiber and includes the growth of corn, soybeans and other legumes, rice, cereal (e.g., wheat, oats, barley, rye, rice, maize), leafy vegetables (e.g., lettuce, cabbage, and other cole crops), fruiting vegetables (e.g., tomatoes, pepper, eggplant, crucifers and cucurbits), potatoes, sweet potatoes, grapes, cotton, tree fruits (e.g., pome, stone and citrus), small fruit (berries, cherries) and other specialty crops (e.g., canola, sunflower, olives).

The term "nonagronomic" refers to other than field crops, such as horticultural crops (e.g., greenhouse, nursery or ornamental plants not grown in a field), residential, agricultural, commercial and industrial structures, turf (e.g., sod farm, pasture, golf course, lawn, sports field, etc.), wood products, stored product, agro-forestry and vegetation management, public health (i.e. human) and animal health (e.g., domesticated animals such as pets, livestock and poultry, undomesticated animals such as wildlife) applications.

Nonagronomic applications include protecting an animal from an invertebrate parasitic pest by administering a parasiticidally effective (i.e. biologically effective) amount of a compound of the invention, typically in the form of a composition formulated for veterinary use, to the animal to be protected. As referred to in the present disclosure and claims, the terms "parasiticidal" and "parasiticidally" refers to observable effects on an invertebrate parasite pest to provide protection of an animal from the pest. Parasiticidal effects typically relate to diminishing the occurrence or activity of the target invertebrate parasitic pest. Such effects on the pest include necrosis, death, retarded growth, diminished mobility or lessened ability to remain on or in the host animal, reduced feeding and inhibition of reproduction. These effects on invertebrate parasite pests provide control (including prevention, reduction or elimination) of parasitic infestation or infection of the animal.

In the above recitations, the term "alkyl", used either alone or in compound words such as "haloalkyl" includes straight-chain or branched alkyl, such as, methyl, ethyl, *n*-propyl, *i*-propyl, or the different butyl, pentyl or hexyl isomers. "Alkenyl" includes straight-chain or branched alkenes such as ethenyl, 1-propenyl, 2-propenyl, and the different butenyl, pentenyl and hexenyl isomers. "Alkenyl" also includes polyenes such as 1,2-propadienyl and 2,4-hexadienyl. "Alkynyl" includes straight-chain or branched alkynes such as ethynyl,

1-propynyl, 2-propynyl and the different butynyl, pentynyl and hexynyl isomers. "Alkynyl" can also include moieties comprised of multiple triple bonds such as 2,5-hexadiynyl.

"Cycloalkyl" includes, for example, cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl. The term "cycloalkylalkyl" denotes cycloalkyl substitution on an alkyl moiety. Examples of "cycloalkylalkyl" include cyclopropylmethyl, cyclopentylethyl, and other cycloalkyl moieties bonded to straight-chain or branched alkyl groups. "Cycloalkenyl" includes groups such as cyclopentenyl and cyclohexenyl as well as groups with more than one double bond such as 1,3- and 1,4-cyclohexadienyl. The term "cycloalkoxy" denotes cycloalkyl attached to and linked through an oxygen atom such as cyclopentyloxy and cyclohexyloxy. "Alkylcycloalkylalkyl" denotes an alkyl group substituted with alkylcycloalkyl. Examples of "alkylcycloalkylalkyl" include 1-, 2-, 3- or 4-methyl or -ethyl cyclohexylmethyl. The term "cycloalkylcycloalkyl" denotes cycloalkyl substitution on another cycloalkyl ring, wherein each cycloalkyl ring independently has from 3 to 7 carbon atom ring members. Examples of cycloalkylcycloalkyl include cyclopropylcyclopropyl (such as 1,1'-bicyclopropyl-1-yl, 1,1'-bicyclopropyl-2-yl), cyclohexylcyclopentyl (such as 4-cyclopentylcyclohexyl) and cyclohexylcyclohexyl (such as 1,1'-bicyclohexyl-1-yl), and the different *cis*- and *trans*-cycloalkylcycloalkyl isomers, (such as (1*R*,2*S*)-1,1'-bicyclopropyl-2-yl and (1*R*,2*R*)-1,1'-bicyclopropyl-2-yl). "Cycloalkylamino" denotes an NH radical substituted with cycloalkyl. Examples of "cycloalkylamino" include cyclopropylamino and cyclohexylamino. The term "cycloalkylaminoalkyl" denotes cycloalkylamino substitution on an alkyl group. Examples of "cycloalkylaminoalkyl" include cyclopropylaminomethyl, cyclopentylaminoethyl, and other cycloalkylamino moieties bonded to straight-chain or branched alkyl groups.

The term "halogen", either alone or in compound words such as "haloalkyl", or when used in descriptions such as "alkyl substituted with halogen" includes fluorine, chlorine, bromine or iodine. Further, when used in compound words such as "haloalkyl", or when used in descriptions such as "alkyl substituted with halogen" said alkyl may be partially or fully substituted with halogen atoms which may be the same or different. Examples of "haloalkyl" or "alkyl substituted with halogen" include CF_3, CH_2Cl, CH_2CF_3 and CCl_2CF_3. The terms "haloalkenyl", "haloalkynyl" "haloalkoxy", "haloalkylthio", "haloalkylamino", "haloalkylsulfinyl", "haloalkylsulfonyl", "halocycloalkyl", and the like, are defined analogously to the term "haloalkyl". Examples of "haloalkenyl" include $(Cl)_2C{=}CHCH_2$ and $CF_3CH_2CH{=}CHCH_2$. Examples of "haloalkynyl" include $HC{\equiv}CCHCl$, $CF_3C{\equiv}C$, $CCl_3C{\equiv}C$ and $FCH_2C{\equiv}CCH_2$. Examples of "haloalkoxy" include CF_3O, CCl_3CH_2O, $HCF_2CH_2CH_2O$ and CF_3CH_2O. Examples of "haloalkylthio" include CCl_3S, CF_3S, CCl_3CH_2S and $ClCH_2CH_2CH_2S$. Examples of "haloalkylamino" include $CF_3(CH_3)CHNH$, $(CF_3)_2CHNH$ and CH_2ClCH_2NH. Examples of "haloalkylsulfinyl" include $CF_3S(=O)$, $CCl_3S(=O)$, $CF_3CH_2S(=O)$ and $CF_3CF_2S(=O)$. Examples of "haloalkylsulfonyl" include

$CF_3S(=O)_2$, $CCl_3S(=O)_2$, $CF_3CH_2S(=O)_2$ and $CF_3CF_2S(=O)_2$. Examples of "halocycloalkyl" include 2-chlorocyclopropyl, 2-fluorocyclobutyl, 3-bromocyclopentyl and 4-chlorocyclohexyl. The term "halodialkyl", either alone or in compound words such as "halodialkylamino", means at least one of the two alkyl groups is substituted with at least one halogen atom, and independently each halogenated alkyl group may be partially or fully substituted with halogen atoms which may be the same or different. Examples of "halodialkylamino" include $(BrCH_2CH_2)_2N$ and $BrCH_2CH_2(ClCH_2CH_2)N$.

"Alkoxy" includes, for example, methoxy, ethoxy, *n*-propoxy, isopropoxy and the different butoxy, pentoxy and hexyloxy isomers. "Alkoxyalkyl" denotes alkoxy substitution on alkyl. Examples of "alkoxyalkyl" include CH_2OCH_3, $CH_2CH_2OCH_3$, $CH_2OCH_2CH_3$, $CH_2OCH_2CH_2CH_2CH_3$ and $CH_2CH_2OCH_2CH_3$. "Alkenyloxy" includes straight-chain or branched alkenyl attached to and linked through an oxygen atom. Examples of "alkenyloxy" include $H_2C=CHCH_2O$, $(CH_3)_2C=CHCH_2O$, $(CH_3)CH=CHCH_2O$, $(CH_3)CH=C(CH_3)CH_2O$ and $CH_2=CHCH_2CH_2O$. "Alkynyloxy" includes straight-chain or branched alkynyloxy moieties. Examples of "alkynyloxy" include $HC\equiv CCH_2O$, $CH_3C\equiv CCH_2O$ and $CH_3C\equiv CCH_2CH_2O$.

The term "alkylthio" includes straight-chain or branched alkylthio moieties such as methylthio, ethylthio, and the different propylthio, butylthio, pentylthio and hexylthio isomers. "Alkylsulfinyl" includes both enantiomers of an alkylsulfinyl group. Examples of "alkylsulfinyl" include $CH_3S(=O)$, $CH_3CH_2S(=O)$, $CH_3CH_2CH_2S(=O)$, $(CH_3)_2CHS(=O)$ and the different butylsulfinyl, pentylsulfinyl and hexylsulfinyl isomers. Examples of "alkylsulfonyl" include $CH_3S(=O)_2$, $CH_3CH_2S(=O)_2$, $CH_3CH_2CH_2S(=O)_2$, $(CH_3)_2CHS(=O)_2$, and the different butylsulfonyl, pentylsulfonyl and hexylsulfonyl isomers. The chemical abbreviations S(O) and S(=O) as used herein represent a sulfinyl moiety. The chemical abbreviations SO_2, $S(O)_2$ and $S(=O)_2$ as used herein represent a sulfonyl moiety.

"Alkylamino" denotes an NH radical substituted with straight-chain or branched alkyl. Examples of "alkylamino" include $NHCH_2CH_3$, $NHCH_2CH_2CH_3$, and $NHCH_2CH(CH_3)_2$. "Dialkylamino" denotes an N radical substituted independently with two straight-chain or branched alkyl groups. Examples of "dialkylamino" include $N(CH_3)_2$, $N(CH_3CH_2CH_2)_2$ and $N(CH_3)CH_2CH_3$. "Halodialkylamino" denotes one straight-chain or branched alkyl moiety and one straight-chain or branched haloalkyl moiety bonded to an N radical, or two independent straight-chain or branched haloalkyl moieties bonded to an N radical, wherein "haloalkyl" is as defined above. Examples of "halodialkylamino" include $N(CH_2CH_3)(CH_2CH_2Cl)$ and $N(CF_2CF_3)_2$. An example of haloalkylcarbonylamino is $NHC(O)CF_3$ and an example of haloalkylcarbonyl(alkyl)amino is $N(CH_3)C(O)CF_3$.

"Alkylcarbonyl" denotes a straight-chain or branched alkyl moiety bonded to a C(O) moiety. The chemical abbreviations C(O) and C(=O) as used herein represent a carbonyl moiety. Examples of "alkylcarbonyl" include $C(O)CH_3$, $C(O)CH_2CH_2CH_3$ and

$C(O)CH(CH_3)_2$. Examples of "haloalkylcarbonyl" include $C(O)CF_3$, $C(O)CCl_3$, $C(O)CH_2CF_3$ and $C(O)CF_2CF_3$.

"Alkoxycarbonyl" denotes a straight-chain or branched alkyl moiety bonded to a CO_2 moiety. The chemical abbreviations CO_2, C(O)O and C(=O)O as used herein represent an oxycarbonyl moiety. Examples of "alkoxycarbonyl" include $C(O)OCH_3$, $C(O)OCH_2CH_3$, $C(O)OCH_2CH_2CH_3$ and $C(O)OCH(CH_3)_2$.

"Alkylaminocarbonyl" denotes a straight-chain or branched alkyl moiety bonded to a C(O)NH moiety. The chemical abbreviations C(O)NH, and C(O)N as used herein represent an amide moiety (i.e. an aminocarbonyl group). Examples of "alkylaminocarbonyl" include $C(O)NHCH_3$, $C(O)NHCH_2CH_2CH_3$ and $C(O)NHCH(CH_3)_2$. "Dialkylaminocarbonyl" denotes two independent straight-chain or branched alkyl moieties bonded to a C(O)N moiety. Examples of "dialkylaminocarbonyl" include $C(O)N(CH_3)_2$ and $C(O)N(CH_3)(CH_2CH_3)$.

"Trialkylsilyl" includes 3 branched and/or straight-chain alkyl radicals attached to and linked through a silicon atom, such as trimethylsilyl, triethylsilyl and *tert*-butyldimethylsilyl.

"-CHO" means formyl.

The total number of carbon atoms in a substituent group is indicated by the "C_i–C_j" prefix where i and j are numbers from 1 to 14. For example, C_1–C_4 alkyl designates methyl through butyl; C_2 alkoxyalkyl designates CH_2OCH_3; C_3 alkoxyalkyl designates, for example, $CH_3CH(OCH_3)$, $CH_2CH_2OCH_3$ or $CH_2OCH_2CH_3$; and C_4 alkoxyalkyl designates the various isomers of an alkyl group substituted with an alkoxy group containing a total of four carbon atoms, examples including $CH_2OCH_2CH_2CH_3$ and $CH_2CH_2OCH_2CH_3$.

When a group contains a substituent which can be hydrogen, for example R^2, then when this substituent is taken as hydrogen, it is recognized that this is equivalent to said group being unsubstituted. When a variable group is shown to be optionally attached to a position, for example $(R^v)_r$ in U-36 of Exhibit 1 wherein r may be 0, then hydrogen can be at the position even if not recited in the variable group definition. When one or more positions on a group are said to be "not substituted" or "unsubstituted", then hydrogen atoms are attached to take up any free valency.

The phrase "an 8- to 11-membered heteroaromatic bicyclic ring system provided that the 8- to 11-membered heteroaromatic bicyclic ring system does not contain a pyridazine ring" is meant to indicate that any heteroaromatic bicyclic ring system that includes the pyridazine ring is excluded. Examples of excluded ring systems are pyridazine fused to a benzene ring phthalazine) and pyridazine fused to a pyridine ring (pyrido[2,3-d]pyridazine). The phrase "an 8- to 11-membered nonaromatic bicyclic ring system provided that the 8- to 11-membered nonaromatic bicyclic ring system does not contain a piperidine ring" is meant to indicate that any nonaromatic bicyclic ring system that includes the piperidine ring is

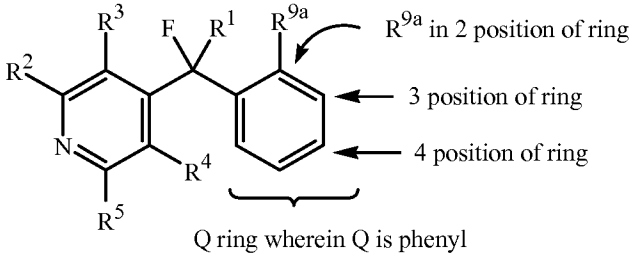
excluded. Examples of excluded ring systems are piperidine fused to a cyclohexane (decahydroquinoline) and a bridged piperidine ring system (9-aza-bicyclo[3.3.1]nonane).

Unless otherwise indicated, a "ring" or "ring system" as a component of Formula **1** is carbocyclic or heterocyclic. The term "ring system" denotes two or more connected rings. The term "bicyclic ring system" denotes a ring system consisting of two rings sharing two or more common atoms.

A ring or a bicyclic ring system can be part of an extended ring system containing more than two rings wherein substituents on the ring or bicyclic ring system are taken together to form the additional rings, which may be in bicyclic relationships with other rings in the extended ring system.

The term "ring member" refers to an atom (e.g., C, O, N or S) or other moiety (e.g., C(=O), C(=S) or $S(=O)_s(=NR^{17})_f$) forming the backbone of a ring or ring system. The term "aromatic" indicates that each of the ring atoms is essentially in the same plane and has a *p*-orbital perpendicular to the ring plane, and that (4n + 2) π electrons, where n is a positive integer, are associated with the ring or ring system to comply with Hückel's rule.

The term "2-position" in a ring refers to the position in a ring relative to the point of attachment of the ring to the rest of the compound of Formula **1**. For example when it is stated that "Q is a phenyl or a 6-membered heteroaromatic ring substituted with R^{9a} in the 2 position", the position of the R^{9a} group is indicated in the structure below:



1

"Partially saturated" and "partially unsaturated" with reference to a ring or ring system means that the ring or ring system contains at least one double bond but the ring or ring system is not aromatic. A ring system is aromatic if at least one component ring is aromatic.

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

The terms "heterocyclic ring" or "heterocycle" denotes a ring wherein at least one of the atoms forming the ring backbone is other than carbon. Unless otherwise indicated, a heterocyclic ring can be a saturated, partially unsaturated, or fully unsaturated ring. "Saturated heterocyclic ring" refers to a heterocyclic ring containing only single bonds between ring members. "Partially saturated heterocyclic ring" refers a heterocyclic ring containing at least one double bond but which is not aromatic. The term "heteroaromatic ring" denotes a fully unsaturated aromatic ring in which at least one atom forming the ring backbone is not carbon. Typically a heteroaromatic ring contains no more than 4 nitrogens, no more than 1 oxygen and no more than 1 sulfur. Unless otherwise indicated, heteroaromatic rings can be attached through any available carbon or nitrogen by replacement of a hydrogen on said carbon or nitrogen. The term "heteroaromatic bicyclic ring system" denotes a ring system consisting of two fused rings, in which at least one of the two rings is a heteroaromatic ring as defined above.

When a radical (e.g., a 3- to 10-membered ring in the definition of Q) is optionally substituted with listed substituents with the number of substituents stated (e.g., "up to 5"), then the radical may be unsubstituted or substituted with a number of substituents ranging up to the high number stated (e.g., "5"), and the attached substituents are independently selected from the substituents listed.

When a substituent (e.g., Q) is a ring or ring system, it can be attached to the remainder of Formula **1** through any available ring member, unless otherwise described.

As noted above, Q is, *inter alia*, a 3- to 7-membered ring or a 8- to 11-membered ring system, each ring or ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S, up to 4 N and up to 2 Si atoms wherein up to 3 carbon atom ring members are independently selected from C(=O) and C(=S), the sulfur atom ring members are independently selected from $S(=O)_s(=NR^{17})_f$, and the silicon atom ring members are independently selected from $SiR^{10}R^{11}$. In this definition the ring members selected from up to 2 O, up to 2 S, up to 4 N and up to 2 Si atoms are optional, because the number of heteroatom ring members may be zero. When no heteroatom ring members are present, the ring or ring system is carbocyclic. If at least one heteroatom ring member is present, the ring or ring system is heterocyclic. The definition of $S(=O)_s(=NR^{17})_f$ allows up to 2 sulfur ring members, which can be oxidized sulfur moieties (e.g., S(=O) or $S(=O)_2$) or unoxidized sulfur atoms (i.e. when s and f are both zero). The nitrogen atom ring members may be oxidized as *N*-oxides, because compounds relating to Formula **1** also include *N*-oxide derivatives. The up to 3 carbon atom ring members selected from C(=O) and C(=S) are in addition to the up to 4 heteroatoms selected from up to 2 O, up to 2 S, up to 4 N and up to 2 Si atoms. As the R^{9a} and R^{9b} substituents are optional, 0 to 5 substituents may be present, limited only by the number of available points of attachment.

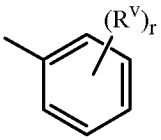
The term "unsubstituted" in connection with a group such as a ring or ring system means the group does not have any substituents other than its one or more attachments to the remainder of Formula **1**. The term "optionally substituted" means that the number of substituents can be zero. Unless otherwise indicated, optionally substituted groups may be substituted with as many optional substituents as can be accommodated by replacing a hydrogen atom with a non-hydrogen substituent on any available carbon or nitrogen atom. Commonly, the number of optional substituents (when present) ranges from 1 to 3.

The number of optional substituents may be restricted by an expressed limitation. For example, the phrase "optionally substituted with up to 5 substituents independently selected from R^{9a}" means that 0, 1, 2, 3, 4 or 5 substituents can be present (if the number of potential connection points allows). When a range specified for the number of substituents exceeds the number of positions available for substituents on a ring, the actual higher end of the range is recognized to be the number of available positions.

When the number of optional substituents is not restricted by an expressed limitation (e.g., the phrases "optionally substituted with halogen" or "unsubstituted or substituted with at least one substituent independently selected from"), it is understood to mean that the number of optional substituents can range from 0 up to the number of positions available. One skilled in the art will appreciate that while some substituents such as halogen can be present at every available position (for example, the C_2F_5 substituent is a C_2 alkyl group substituted with the maximum number of 5 fluorine atoms), practical factors such as cost and synthetic accessibility can limit the number of occurences of other substituents. These limitations are part of the general synthetic knowledge known to those skilled in the art. Of note are embodiments wherein in the absence of expressed limitation of number of optional substituents, the number of optional substituents is up to 3 (i.e. 0, 1, 2 or 3) if accommodated by the number of available positions.

As noted above, substituents such as Q can be (among others) a 5- or 6-membered heteroaromatic ring [provided that the 5- to 6-membered heteroaromatic ring is not imidazole (U-15 through U-18) or pyridazine (U-52 and U-53)], optionally substituted with one or more substituents selected from a group of substituents as defined in the Summary of Invention. Examples of a 5- or 6-membered heteroaromatic ring optionally substituted with one or more substituents include the rings U-2 through U-61 illustrated in Exhibit 1 wherein R^v is any substituent as defined in the Summary of the Invention for Q (e.g., R^{9a} and R^{9b}) and r is an integer from 0 to 5, limited by the number of available positions on each U group. As U-29, U-30, U-36, U-37, U-38, U-39, U-40, U-41, U-42 and U-43 have only one available position, for these U groups r is limited to the integers 0 or 1, and r being 0 means that the U group is unsubstituted and a hydrogen is present at the position indicated by $(R^v)_r$.

Exhibit 1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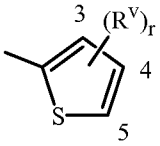
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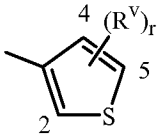
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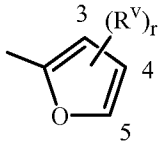
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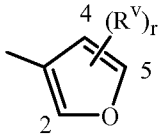
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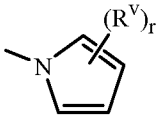
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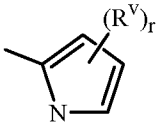
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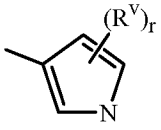
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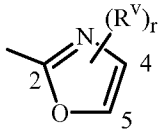
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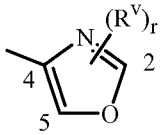
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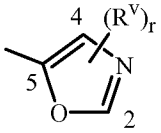
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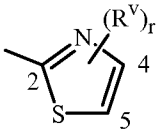
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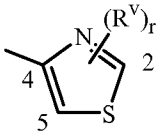
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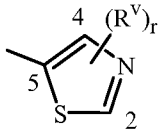
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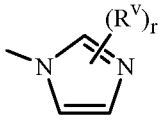
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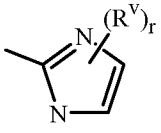
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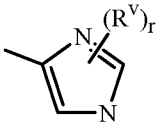
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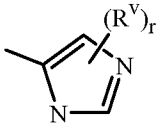
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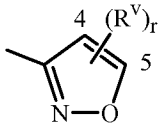
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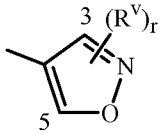
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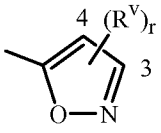
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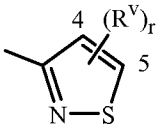
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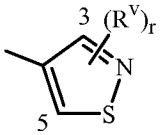
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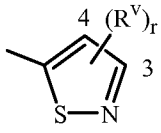
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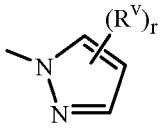
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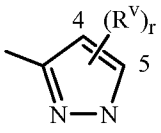
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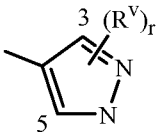
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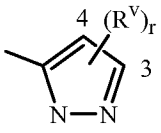
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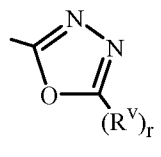
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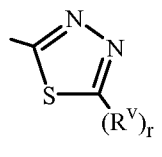
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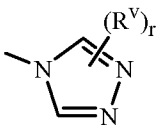
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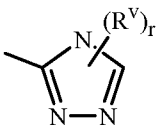
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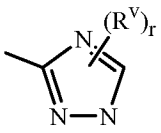
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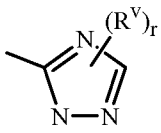
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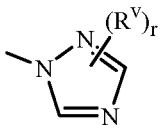
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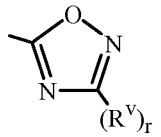
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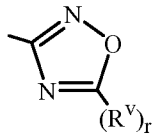
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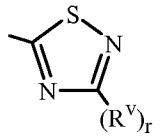
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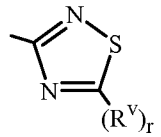
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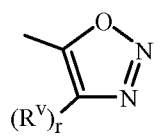
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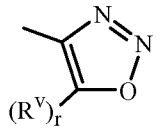
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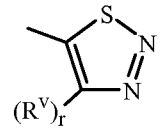
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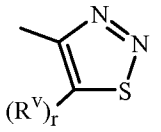
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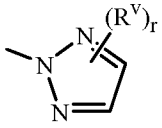
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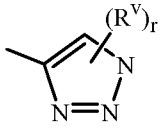
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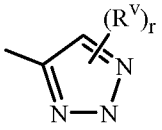
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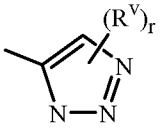
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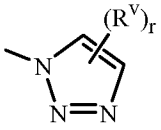
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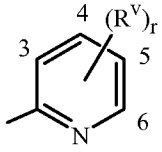
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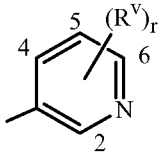
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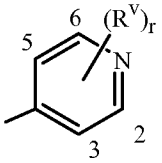
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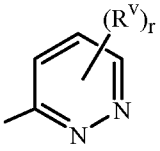
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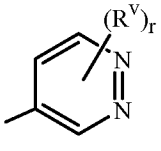
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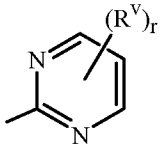
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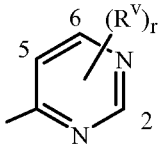
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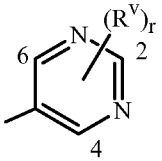
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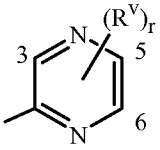
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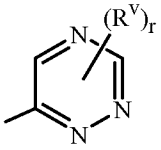
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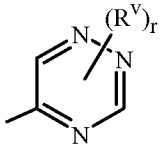
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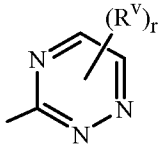
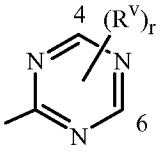

U-60 and

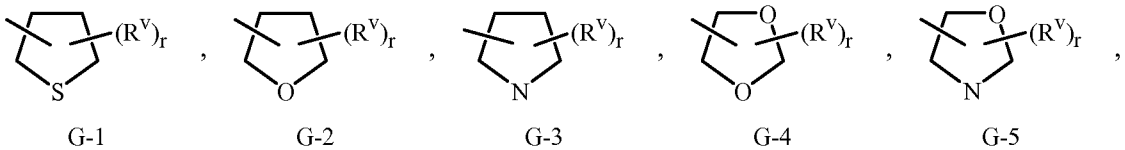

U-61 .

Note that when Q is a 5- to 7-membered saturated or unsaturated non-aromatic heterocyclic ring [provided that the 5- to 7-membered nonaromatic heterocyclic ring is not piperidine (G-8)] optionally substituted with one or more substituents selected from the group of substituents as defined in the Summary of Invention for Q, one or two carbon ring members of the heterocycle can optionally be in the oxidized form of a carbonyl moiety.

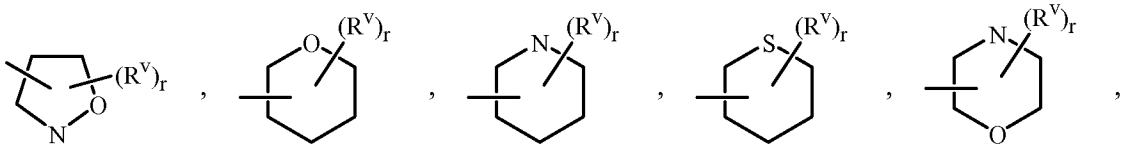
Examples of a 5- to 7-membered saturated or non-aromatic unsaturated heterocyclic ring include the rings G-1 through G-35 as illustrated in Exhibit 2. Note that when the attachment point on the G group is illustrated as floating, the G group can be attached to the remainder of Formula **1** through any available carbon or nitrogen of the G group by replacement of a hydrogen atom. The optional substituents corresponding to R^V can be attached to any available carbon or nitrogen by replacing a hydrogen atom. For these G rings, r is typically an integer from 0 to 4, limited by the number of available positions on each G group.

Note that when Q comprises a ring selected from G-28 through G-35, G^2 is selected from O, S or N. Note that when G^2 is N, the nitrogen atom can complete its valence by substitution with either H or the substituents corresponding to R^v as defined in the Summary of Invention for Q (i.e. R^{9b}).

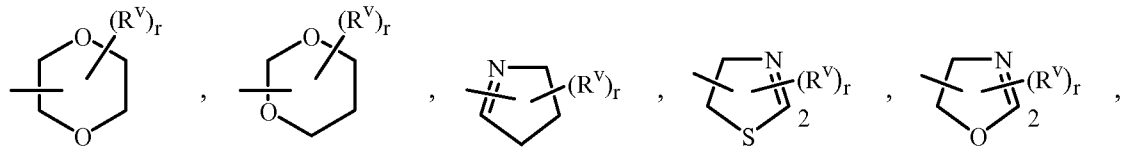
Exhibit 2



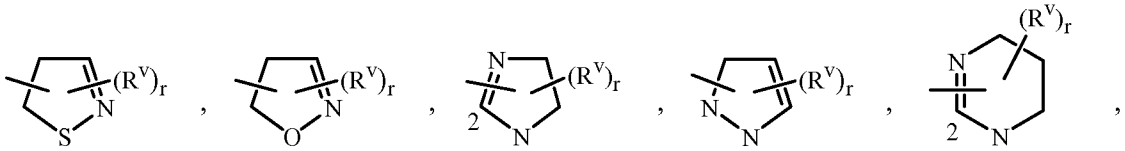
G-1 , G-2 , G-3 , G-4 , G-5 ,



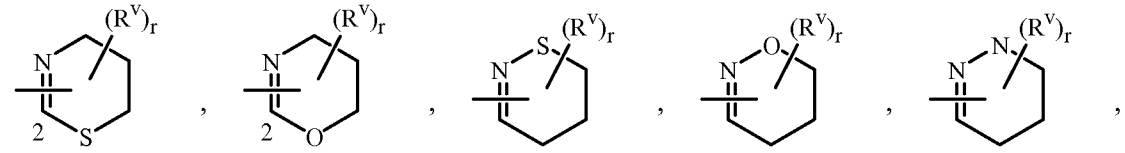
G-6 , G-7 , G-8 , G-9 , G-10 ,



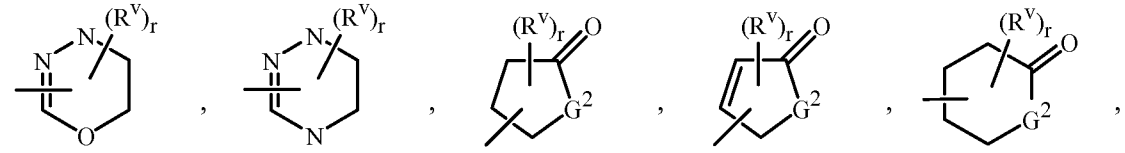
G-11 , G-12 , G-13 , G-14 , G-15 ,



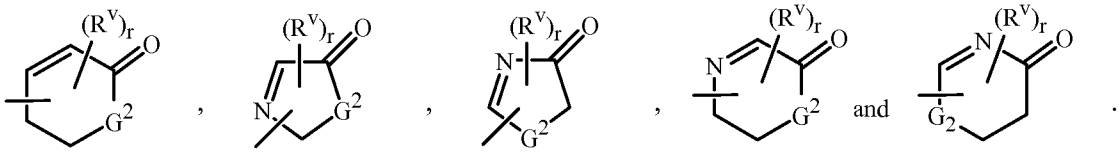
G-16 , G-17 , G-18 , G-19 , G-20 ,



G-21 , G-22 , G-23 , G-24 , G-25 ,



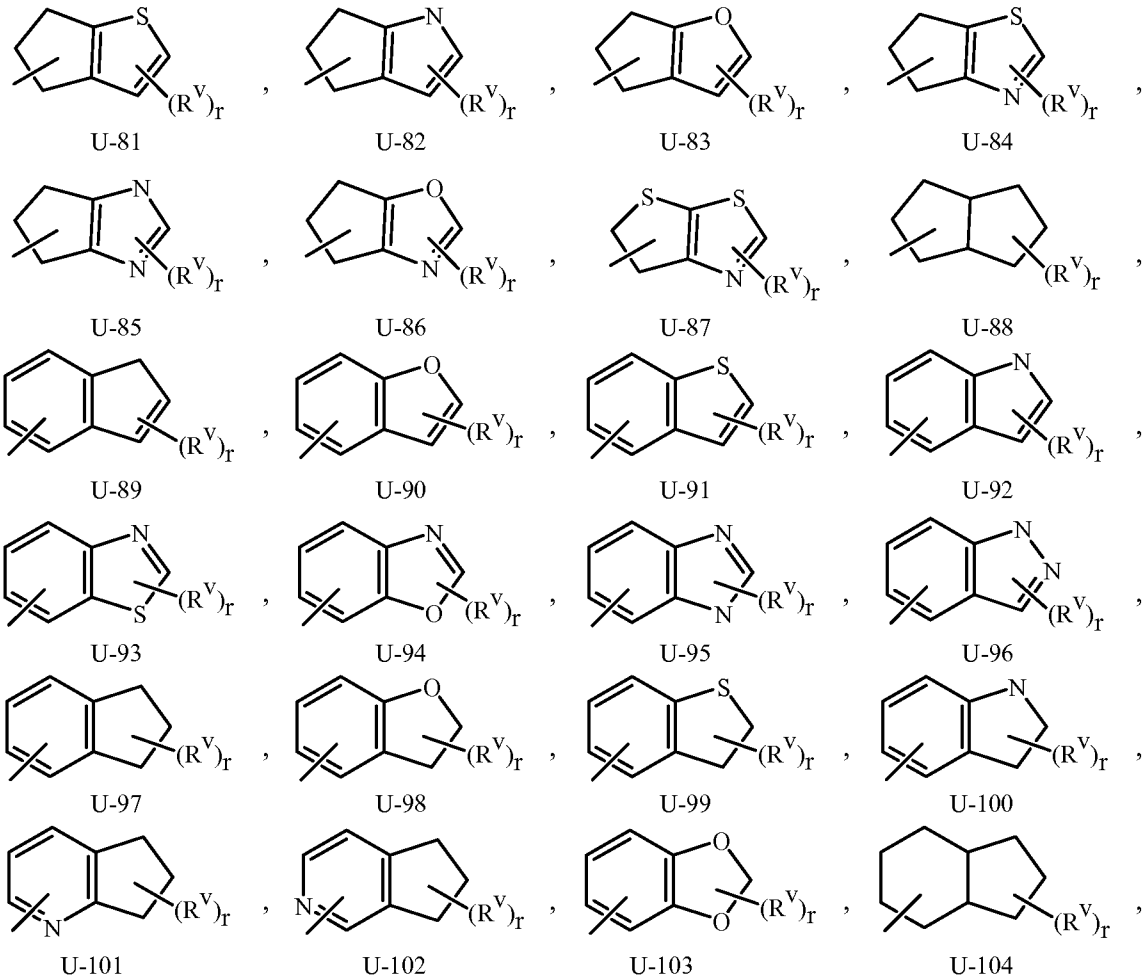
G-26 , G-27 , G-28 , G-29 , G-30 ,



G-31 G-32 G-33 G-34 G-35

As noted above, Q can be (among others) an 8- to 11-membered heteroaromatic bicyclic ring system [provided that the 8- to 11-membered heteroaromatic bicyclic ring system does not contain a pyridazine ring (U-121 and U-122)] or an 8- to 11-membered nonaromatic bicyclic ring system [provided that the 8- to 11-membered nonaromatic bicyclic ring system does not contain a piperidine ring (U-109 and U-110)] optionally substituted with one or more substituents selected from a group of substituents as defined in the Summary of Invention (i.e. R^{9a} and R^{9b}). Examples of 8- to 11-membered fused bicyclic ring systems optionally substituted with one or more substituents include the rings U-81 through U-123 illustrated in Exhibit 3 wherein R^v is any substituent as defined in the Summary of the Invention for Q (i.e. R^{9a} and R^{9b}), and r is typically an integer from 0 to 5.

Exhibit 3



U-81 U-82 U-83 U-84

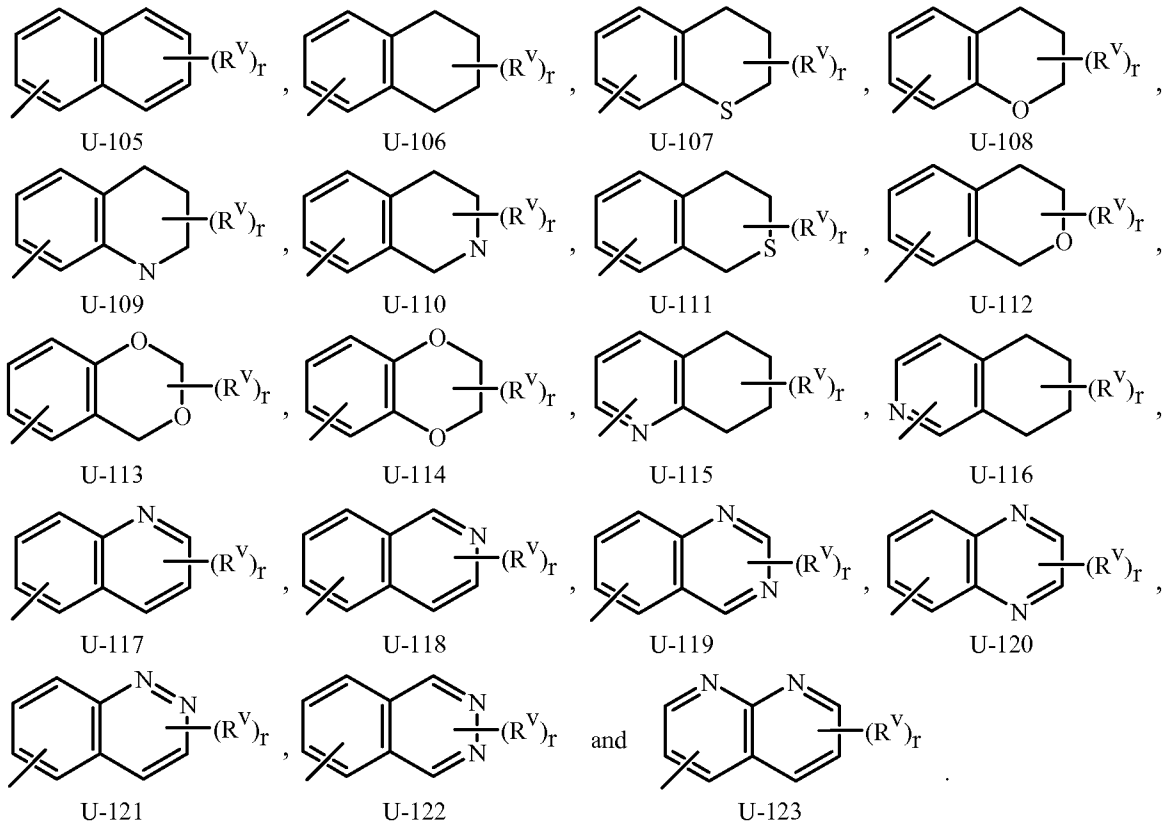
U-85 U-86 U-87 U-88

U-89 U-90 U-91 U-92

U-93 U-94 U-95 U-96

U-97 U-98 U-99 U-100

U-101 U-102 U-103 U-104

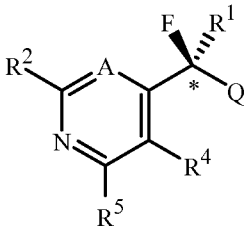


Although R^v groups are shown in the structures of Exhibits 1, 2 and 3, it is noted that they do not need to be present since they are optional substituents. Note that when R^v is H when attached to an atom, this is the same as if said atom is unsubstituted. The nitrogen atoms that require substitution to fill their valence are substituted with H or R^v. Note that when the attachment point between $(R^v)_r$ and the ring is illustrated as floating, $(R^v)_r$ can be attached to any available carbon atom or nitrogen atom of the ring. Note that when the attachment point on the ring is illustrated as floating, the ring can be attached to the remainder of Formula **1** through any available carbon or nitrogen of the ring by replacement of a hydrogen atom.

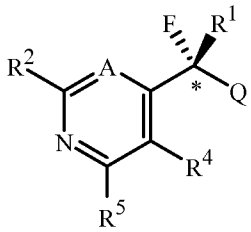
A wide variety of synthetic methods are known in the art to enable preparation of aromatic and nonaromatic heterocyclic rings and ring systems; for extensive reviews see the eight volume set of *Comprehensive Heterocyclic Chemistry*, A. R. Katritzky and C. W. Rees editors-in-chief, Pergamon Press, Oxford, 1984 and the twelve volume set of *Comprehensive Heterocyclic Chemistry II*, A. R. Katritzky, C. W. Rees and E. F. V. Scriven editors-in-chief, Pergamon Press, Oxford, 1996.

Compounds of this invention can exist as one or more stereoisomers. The various stereoisomers include enantiomers, diastereomers and atropisomers. One skilled in the art will appreciate that one stereoisomer may be more active and/or may exhibit beneficial effects when enriched relative to the other stereoisomer(s) or when separated from the other

stereoisomer(s). Additionally, the skilled artisan knows how to separate, enrich, and/or to selectively prepare said stereoisomers. The compounds of the invention may be present as a mixture of stereoisomers, individual stereoisomers or as an optically active form. For example, two possible enantiomers of Formula **1** are depicted as Formula **1a** and Formula **1b** involving the chiral center identified with an asterisk (*). Analogously, other chiral centers are possible in other groups, for example in R^4 or Q.



1a



1b

Molecular depictions drawn herein follow standard conventions for depicting stereochemistry. To indicate stereoconfiguration, bonds rising from the plane of the drawing and towards the viewer are denoted by solid wedges wherein the broad end of the wedge is attached to the atom rising from the plane of the drawing towards the viewer. Bonds going below the plane of the drawing and away from the viewer are denoted by dashed wedges wherein the narrow end of the wedge is attached to the atom further away from the viewer. Constant width lines indicate bonds with a direction opposite or neutral relative to bonds shown with solid or dashed wedges; constant width lines also depict bonds in molecules or parts of molecules in which no particular stereoconfiguration is intended to be specified.

This invention comprises racemic mixtures, for example, equal amounts of the enantiomers of Formulae **1a** and **1b**. In addition, this invention includes compounds that are enriched compared to the racemic mixture in an enantiomer of Formula **1**. Also included are the essentially pure enantiomers of compounds of Formula **1**, for example, Formula **1a** and Formula **1b**.

When enantiomerically enriched, one enantiomer is present in greater amounts than the other, and the extent of enrichment can be defined by an expression of enantiomeric excess ("ee"), which is defined as $(2x-1)\cdot 100$ %, where x is the mole fraction of the dominant enantiomer in the mixture (e.g., an ee of 20 % corresponds to a 60:40 ratio of enantiomers).

Preferably the compositions of this invention have at least a 50 % enantiomeric excess; more preferably at least a 75 % enantiomeric excess; still more preferably at least a 90 % enantiomeric excess; and the most preferably at least a 94 % enantiomeric excess of the more active isomer. Of particular note are enantiomerically pure embodiments of the more active isomer.

Compounds of Formula **1** can comprise additional chiral centers. For example, substituents and other molecular constituents such as R^4 may themselves contain chiral

centers (e.g., methylsulfoxide moiety in compounds 161 and 162). This invention comprises racemic mixtures as well as enriched and essentially pure stereoconfigurations at these additional chiral centers.

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

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

Ed., Academic Press; M. Tisler and B. Stanovnik in *Advances in Heterocyclic Chemistry*, vol. 9, pp 285–291, A. R. Katritzky and A. J. Boulton, Eds., Academic Press; and G. W. H. Cheeseman and E. S. G. Werstiuk in *Advances in Heterocyclic Chemistry*, vol. 22, pp 390–392, A. R. Katritzky and A. J. Boulton, Eds., Academic Press.

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

Embodiments of the present invention as described in the Summary of the Invention include those described below. In the following Embodiments Formula **1** includes stereoisomers, *N*-oxides, and salts thereof, and reference to "a compound of Formula **1**" includes the definitions of substituents specified in the Summary of the Invention unless further defined in the Embodiments.

Embodiment 1. A compound of Formula **1** wherein R^1 is hydrogen, halogen or C_1–C_4 alkyl.

Embodiment 1a. A compound of Embodiment 1 wherein R^1 is hydrogen, halogen or methyl.

Embodiment 1b. A compound of Embodiment 1a wherein R^1 is hydrogen or fluoro.

Embodiment 2. A compound of Formula **1** or any one of Embodiments 1 through 1b, either alone or in combination, wherein R^2 and R^5 are each independently selected from hydrogen or halogen.

Embodiment 2a. A compound of Embodiment 2 wherein R^2 and R^5 are each independently selected from hydrogen, fluoro or chloro.

Embodiment 2b. A compound of Embodiment 2a wherein R^2 and R^5 are each independently selected from hydrogen or fluoro.

Embodiment 2c. A compound of Embodiment 2a wherein R^2 and R^5 are each hydrogen.

Embodiment 3. A compound of Formula **1** or any one of Embodiments 1 through 2b, either alone or in combination, wherein R^3 and R^4 are each independently

selected from hydrogen, halogen, cyano, amino, nitro, SF_5, -CHO, 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_2–C_6 haloalkynyl, C_3–C_6 cycloalkyl, C_3–C_6 halocycloalkyl, C_4–C_8 alkylcycloalkyl, C_4–C_8 cycloalkylalkyl, C_3–C_6 cycloalkenyl, C_2–C_6 alkoxyalkyl, C_2–C_6 alkylthioalkyl, C_2–C_6 alkylcarbonyl, C_2–C_6 haloalkylcarbonyl, C_2–C_6 alkoxycarbonyl, C_2–C_6 alkylaminocarbonyl, C_3–C_8 dialkylaminocarbonyl, C_2–C_6 cyanoalkyl, C_1–C_6 alkoxy, C_1–C_6 haloalkoxy, C_2–C_6 alkoxyalkoxy, C_1–C_6 alkylthio, C_1–C_6 haloalkylthio, C_1–C_6 alkylsulfinyl, C_1–C_6 haloalkylsulfinyl, C_1–C_6 alkylsulfonyl, C_1–C_6 haloalkylsulfonyl, C_3–C_9 trialkylsilyl, C_1–C_6 alkylamino, C_2–C_6 dialkylamino, C_2–C_6 haloalkylamino, C_2–C_6 halodialkylamino or C_2–C_6 alkylcarbonylamino; or Q^1.

Embodiment 3a. A compound of Embodiment 3 wherein R^3 and R^4 are each independently selected from hydrogen, halogen, C_1–C_6 alkyl, C_1–C_6 haloalkyl, C_1–C_6 alkoxy, C_1–C_6 haloalkoxy, C_1–C_6 alkylthio, C_1–C_6 alkylsulfinyl or C_1–C_6 alkylsulfonyl.

Embodiment 3b. A compound of Embodiment 3a wherein R^3 and R^4 are each independently selected from hydrogen, halogen, C_1–C_6 alkyl, C_1–C_6 alkoxy, C_1–C_6 alkylthio, C_1–C_6 alkylsulfinyl or C_1–C_6 alkylsulfonyl.

Embodiment 3c. A compound of Embodiment 3b wherein R^3 and R^4 are each independently selected from hydrogen, fluoro, chloro, methoxy, methylthio, methylsulfinyl or methylsulfonyl.

Embodiment 3d. A compound of Embodiment 3c wherein R^3 and R^4 are each independently selected from hydrogen, fluoro, chloro, methoxy or methylthio.

Embodiment 3e. A compound of Embodiment 3 wherein R^3 and R^4 are other than hydrogen, C_2–C_6 alkoxycarbonyl, C_2–C_6 alkylaminocarbonyl and C_3–C_8 dialkylaminocarbonyl.

Embodiment 3f. A compound of Embodiments 3 through 3e wherein R^3 and R^4 are other than hydrogen.

Embodiment 4. A compound of Formula **1** or any one of Embodiments 1 through 3e, either alone or in combination, wherein one of R^3 or R^4 is Q^1, OQ^1 or SQ^1.

Embodiment 5. A compound of Formula **1** or any one of Embodiments 1 through 4, either alone or in combination, wherein Q^1 is phenyl or naphthalenyl each optionally substituted on carbon atom ring members with up to 5 substituents independently selected from R^{9a}; or a 5- to 6-membered heteroaromatic ring or an 8- to 11-membered heteroaromatic bicyclic ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally

substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members.

Embodiment 5a. A compound of Embodiment 5 wherein Q^1 is phenyl or naphthalenyl each optionally substituted on carbon atom ring members with up to 5 substituents independently selected from R^{9a}; or a 5- to 6-membered heteroaromatic ring containing ring members selected from carbon atoms and up to 3 heteroatoms independently selected from up to 2 O, up to 2 S and up to 3 N atoms, and optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members.

Embodiment 5b. A compound of Embodiment 5a wherein Q^1 is phenyl optionally substituted on carbon atom ring members with up to 5 substituents independently selected from R^{9a}.

Embodiment 5c. A compound of Embodiment 5a wherein Q^1 is a 5- to 6-membered heteroaromatic ring containing ring members selected from carbon atoms and up to 3 heteroatoms independently selected from up to 2 O, up to 2 S and up to 3 N atoms, and optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members.

Embodiment 6. A compound of Formula **1** or any one of Embodiments 1 through 5c either alone or in combination, wherein Q is phenyl or naphthalenyl each optionally substituted on carbon atom ring members with up to 5 substituents independently selected from R^{9a}; or a 5- to 6-membered heteroaromatic ring or an 8- to 11-membered heteroaromatic bicyclic ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members.

Embodiment 6a. A compound of Formula **1** or any one of Embodiments 1 through 5c either alone or in combination, wherein Q is phenyl or naphthalenyl each optionally substituted on carbon atom ring members with up to 5 substituents independently selected from R^{9a}; or a 5- to 6-membered heteroaromatic ring provided that the 5- to 6-membered heteroaromatic ring is not imidazole or pyridazine, or an 8- to 11-membered heteroaromatic bicyclic ring system provided that the 8- to 11-membered heteroaromatic bicyclic ring system does not contain a pyridazine ring; each ring or ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 5

substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members.

Embodiment 6b. A compound of Embodiment 6 wherein Q is phenyl or naphthalenyl each optionally substituted on carbon atom ring members with up to 5 substituents independently selected from R^{9a}; or a 5- to 6-membered heteroaromatic ring containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members.

Embodiment 6c. A compound of Embodiment 6a wherein Q is phenyl optionally substituted on carbon atom ring members with up to 5 substituents independently selected from R^{9a}; or a 5- to 6-membered heteroaromatic ring provided that the 5- to 6-membered heteroaromatic ring is not imidazole or pyridazine, or an 8- to 11-membered heteroaromatic bicyclic ring system provided that the 8- to 11-membered heteroaromatic bicyclic ring system does not contain a pyridazine ring; each ring or ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members.

Embodiment 6d. A compound of Embodiment 6b wherein Q is phenyl optionally substituted on carbon atom ring members with up to 5 substituents independently selected from R^{9a}; or a 6-membered heteroaromatic ring containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members.

Embodiment 6e. A compound of Embodiment 6c wherein Q is phenyl optionally substituted on carbon atom ring members with up to 5 substituents independently selected from R^{9a}; or a 6-membered heteroaromatic ring provided that the 6-membered heteroaromatic ring is not pyridazine; each ring containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members.

Embodiment 6f. A compound of Embodiment 6d wherein Q is a 6-membered heteroaromatic ring containing ring members selected from carbon atoms and up

to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members.

Embodiment 6g. A compound of Embodiment 6e wherein Q is a 6-membered heteroaromatic ring provided that the 6-membered heteroaromatic ring is not pyridazine; each ring containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members.

Embodiment 6h. A compound of Embodiment 6f or 6g wherein Q is other than 2-pyridinyl or 6-pyrimidinyl.

Embodiment 6i. A compound of Embodiment 6 or 6a wherein Q is phenyl, pyridinyl, benzoxazole or benzimidazole optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members.

Embodiment 6j. A compound of Embodiment 6 or 6a wherein Q is phenyl, 3- or 4-pyridinyl, benzoxazole or benzimidazole optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members.

Embodiment 6k. A compound of Embodiment 6d or 6e wherein Q is a phenyl ring or a 6-membered heteroaromatic ring each ring substituted with R^{9a} in the 2 position, optionally substituted with R^{9a} in the 3 or 4 position and optionally substituted with R^{9b} on nitrogen atom ring members.

Embodiment 6l. A compound of Embodiment 6 or 6a wherein Q is phenyl, optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members.

Embodiment 6m. A compound of Embodiment 6 wherein Q an 8- to 11-membered heteroaromatic bicyclic ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring member.

Embodiment 6n. A compound of Embodiment 6a wherein Q an 8- to 11-membered heteroaromatic bicyclic ring system provided that the 8- to 11-membered heteroaromatic bicyclic ring system does not contain a pyridazine ring; each ring system containing ring members selected from carbon atoms and up to 4

heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring member.

Embodiment 6o. A compound of Embodiment 6m or 6n wherein Q is other than 1-phthalazinyl or 4-isoquinolinyl.

Embodiment 7. A compound of Formula **1** or any one of Embodiments 1 through 6o, either alone or in combination, wherein each R^{9a} is independently halogen, hydroxy, amino, cyano, nitro, C_1–C_6 alkyl, C_2–C_6 alkenyl, C_2–C_6 alkynyl, C_3–C_6 cycloalkyl, C_4–C_{10} cycloalkylalkyl, C_4–C_{10} alkylcycloalkyl, C_5–C_{10} alkylcycloalkylalkyl, C_6–C_{14} cycloalkylcycloalkyl, C_1–C_6 haloalkyl, C_2–C_6 haloalkenyl, C_2–C_6 haloalkynyl, C_3–C_6 halocycloalkyl, C_1–C_4 alkoxy, C_1–C_4 haloalkoxy, C_2–C_4 alkoxyalkoxy, C_1–C_4 alkylthio, C_1–C_4 alkylsulfinyl, C_1–C_4 alkylsulfonyl, C_1–C_4 haloalkylthio, C_1–C_4 haloalkylsulfinyl, C_1–C_4 haloalkylsulfonyl, C_1–C_4 alkylamino, C_2–C_8 dialkylamino, C_3–C_6 cycloalkylamino, C_2–C_4 alkoxyalkyl, C_1–C_4 hydroxyalkyl, C_2–C_4 alkylcarbonyl, C_2–C_6 alkoxycarbonyl, C_2–C_6 alkylcarbonyloxy, C_2–C_6 alkylcarbonylthio, C_2–C_6 alkylaminocarbonyl, C_3–C_8 dialkylaminocarbonyl, C_3–C_6 haloalkylcarbonylamino, C_3–C_6 haloalkylcarbonyl(alkyl)amino or C_3–C_6 trialkylsilyl; or phenyl.

Embodiment 7a. A compound of Formula **1** or any one of Embodiments 1 through 6j, either alone or in combination, wherein each R^{9a} is independently halogen, hydroxy, amino, cyano, nitro, SF_5, C_1–C_6 alkyl, C_2–C_6 alkenyl, C_2–C_6 alkynyl, C_3–C_6 cycloalkyl, C_4–C_{10} cycloalkylalkyl, C_4–C_{10} alkylcycloalkyl, C_5–C_{10} alkylcycloalkylalkyl, C_6–C_{14} cycloalkylcycloalkyl, C_1–C_6 haloalkyl, C_2–C_6 haloalkenyl, C_2–C_6 haloalkynyl, C_3–C_6 halocycloalkyl, C_1–C_4 alkoxy, C_1–C_4 haloalkoxy, C_2–C_4 alkoxyalkoxy, C_1–C_4 alkylthio, C_1–C_4 alkylsulfinyl, C_1–C_4 alkylsulfonyl, C_1–C_4 haloalkylthio, C_1–C_4 haloalkylsulfinyl, C_1–C_4 haloalkylsulfonyl, C_1–C_4 alkylamino, C_2–C_8 dialkylamino, C_3–C_6 cycloalkylamino, C_2–C_4 alkoxyalkyl, C_1–C_4 hydroxyalkyl, C_2–C_4 alkylcarbonyl, C_2–C_6 alkoxycarbonyl, C_2–C_6 alkylcarbonyloxy, C_2–C_6 alkylcarbonylthio, C_2–C_6 alkylaminocarbonyl, C_3–C_8 dialkylaminocarbonyl, C_3–C_6 haloalkylcarbonylamino, C_3–C_6 haloalkylcarbonyl(alkyl)amino or C_3–C_6 trialkylsilyl; or phenyl.

Embodiment 7b. A compound of Embodiment 7 wherein R^{9a} in the 2 position is present and is halogen, hydroxy, amino, cyano, nitro, C_1–C_6 alkyl, C_2–C_6 alkenyl, C_2–C_6 alkynyl, C_3–C_6 cycloalkyl, C_4–C_{10} cycloalkylalkyl, C_4–C_{10} alkylcycloalkyl, C_5–C_{10} alkylcycloalkylalkyl, C_6–C_{14} cycloalkylcycloalkyl, C_1–

C_6 haloalkyl, C_2–C_6 haloalkenyl, C_2–C_6 haloalkynyl, C_3–C_6 halocycloalkyl, C_1–C_4 alkoxy, C_1–C_4 haloalkoxy, C_1–C_4 alkylthio, C_1–C_4 alkylsulfinyl, C_1–C_4 alkylsulfonyl, C_1–C_4 haloalkylthio, C_1–C_4 haloalkylsulfinyl, C_1–C_4 haloalkylsulfonyl, C_1–C_4 alkylamino, C_2–C_8 dialkylamino, C_3–C_6 cycloalkylamino, C_2–C_4 alkoxyalkyl, C_1–C_4 hydroxyalkyl, C_2–C_4 alkylcarbonyl, C_2–C_6 alkylcarbonyloxy, C_2–C_6 alkylcarbonylthio, or C_3–C_6 trialkylsilyl; or phenyl.

Embodiment 7c. A compound of Embodiment 7a wherein R^{9a} in the 2 position is present and is halogen, hydroxy, amino, cyano, nitro, SF_5, C_1–C_6 alkyl, C_2–C_6 alkenyl, C_2–C_6 alkynyl, C_3–C_6 cycloalkyl, C_4–C_{10} cycloalkylalkyl, C_4–C_{10} alkylcycloalkyl, C_5–C_{10} alkylcycloalkylalkyl, C_6–C_{14} cycloalkylcycloalkyl, C_1–C_6 haloalkyl, C_2–C_6 haloalkenyl, C_2–C_6 haloalkynyl, C_3–C_6 halocycloalkyl, C_1–C_4 alkoxy, C_1–C_4 haloalkoxy, C_1–C_4 alkylthio, C_1–C_4 alkylsulfinyl, C_1–C_4 alkylsulfonyl, C_1–C_4 haloalkylthio, C_1–C_4 haloalkylsulfinyl, C_1–C_4 haloalkylsulfonyl, C_1–C_4 alkylamino, C_2–C_8 dialkylamino, C_3–C_6 cycloalkylamino, C_2–C_4 alkoxyalkyl, C_1–C_4 hydroxyalkyl, C_2–C_4 alkylcarbonyl, C_2–C_6 alkylcarbonyloxy, C_2–C_6 alkylcarbonylthio, or C_3–C_6 trialkylsilyl; or phenyl.

Embodiment 7d. A compound of any one of Embodiments 7 through 7c wherein each R^{9a} is independently halogen, SF_5, C_1–C_6 alkyl, C_1–C_6 haloalkyl, C_1–C_4 alkoxy, C_1–C_4 haloalkoxy, C_1–C_4 alkylthio, C_1–C_4 alkylsulfinyl, C_1–C_4 alkylsulfonyl, C_1–C_4 haloalkylthio, C_1–C_4 haloalkylsulfinyl, C_1–C_4 haloalkylsulfonyl or C_3–C_6 trialkylsilyl.

Embodiment 7e. A compound of any one of Embodiments 7 through 7d wherein each R^{9a} is independently halogen, C_1–C_6 alkyl, C_1–C_6 haloalkyl, C_1–C_4 alkoxy, C_1–C_4 haloalkoxy or C_3–C_6 trialkylsilyl.

Embodiment 7f. A compound of any one of Embodiments 7 through 7e wherein each R^{9a} is independently halogen, SF_5, *tert*-butyl, CF_3, OCF_3, CF_2CF_3 or SCF_3.

Embodiment 7g. A compound of any one of Embodiments 7 through 7f wherein each R^{9a} is independently halogen, *tert*-butyl, CF_3 or OCF_3.

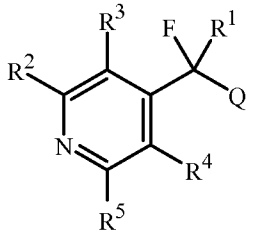
Embodiment 8. A compound of Formula **1** or any one of Embodiments 1 through 7c, either alone or in combination, wherein R^{9b} is hydrogen, C_1–C_3 alkyl, C_1–C_3 haloalkyl or C_1–C_3 alkoxy.

Embodiment 8a. A compound of Embodiment 8 wherein R^{9b} is hydrogen or methyl.

Embodiment 9. A compound of Formula **1** or any one of Embodiments 1 through 8a, either alone or in combination, wherein A is N.

Embodiment 9a. A compound of Formula **1** or any one of Embodiments 1 through 8a, either alone or in combination, wherein A is CR^3.

Also of note is a compound of Formula **1A**



1A

Embodiment AAA. A compound of Formula **1A** wherein

R^1 is hydrogen, halogen, hydroxyl, cyano, SF_5, C_1–C_4 alkyl, C_2–C_4 alkenyl, C_2–C_4 alkynyl, C_1–C_4 haloalkyl, C_2–C_4 haloalkenyl, C_2–C_4 haloalkynyl, C_3–C_4 cycloalkyl, C_3–C_4 halocycloalkyl, C_1–C_4 alkoxy, C_1–C_4 haloalkoxy, C_2–C_4 alkylthio, C_2–C_4 alkylsulfinyl, C_2–C_4 alkylsulfonyl, C_2–C_4 haloalkylthio C_2–C_4 cyanoalkyl, C_2–C_4 alkylcarbonyl or C_2–C_4 alkoxycarbonyl;

R^2, R^3, R^4 and R^5 are each independently selected from hydrogen, halogen, cyano, amino, nitro, SF_5, -CHO, 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_2–C_6 haloalkynyl, C_3–C_6 cycloalkyl, C_3–C_6 halocycloalkyl, C_4–C_8 alkylcycloalkyl, C_4–C_8 cycloalkylalkyl, C_3–C_6 cycloalkenyl, C_2–C_6 alkoxyalkyl, C_2–C_6 alkylthioalkyl, C_2–C_6 alkylcarbonyl, C_2–C_6 haloalkylcarbonyl, C_2–C_6 alkoxycarbonyl, C_2–C_6 alkylaminocarbonyl, C_3–C_8 dialkylaminocarbonyl, C_2–C_6 cyanoalkyl, C_1–C_6 alkoxy, C_1–C_6 haloalkoxy, C_2–C_6 alkoxyalkoxy, C_1–C_6 alkylthio, C_1–C_6 haloalkylthio, C_1–C_6 alkylsulfinyl, C_1–C_6 haloalkylsulfinyl, C_1–C_6 alkylsulfonyl, C_1–C_6 haloalkylsulfonyl, C_3–C_9 trialkylsilyl, C_1–C_6 alkylamino, C_2–C_6 dialkylamino, C_2–C_6 haloalkylamino, C_2–C_6 halodialkylamino or C_2–C_6 alkylcarbonylamino; or Q^1, OQ^1 or SQ^1;

Q is phenyl or naphthalenyl each optionally substituted on carbon atom ring members with up to 5 substituents independently selected from R^{9a}; or

Q is a 5- to 6-membered heteroaromatic ring or an 8- to 11-membered heteroaromatic bicyclic ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members; or

Q is a 3- to 7-membered nonaromatic carbocyclic ring, a 5- to 7-membered nonaromatic heterocyclic ring or an 8- to 11-membered nonaromatic bicyclic ring system, each ring or ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S,

up to 4 N and up to 2 Si atoms, wherein up to 3 carbon atom ring members are independently selected from C(=O) and C(=S), the sulfur atom ring members are independently selected from $S(=O)_s(=NR^{17})_f$, and the silicon atom ring members are independently selected from $SiR^{10}R^{11}$, each ring or ring system optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members;

each R^{9a} is independently halogen, hydroxy, amino, cyano, nitro, C_1–C_6 alkyl, C_2–C_6 alkenyl, C_2–C_6 alkynyl, C_3–C_6 cycloalkyl, C_4–C_{10} cycloalkylalkyl, C_4–C_{10} alkylcycloalkyl, C_5–C_{10} alkylcycloalkylalkyl, C_6–C_{14} cycloalkylcycloalkyl, C_1–C_6 haloalkyl, C_2–C_6 haloalkenyl, C_2–C_6 haloalkynyl, C_3–C_6 halocycloalkyl, C_1–C_4 alkoxy, C_1–C_4 haloalkoxy, C_2–C_4 alkoxyalkoxy, C_1–C_4 alkylthio, C_1–C_4 alkylsulfinyl, C_1–C_4 alkylsulfonyl, C_1–C_4 haloalkylthio, C_1–C_4 haloalkylsulfinyl, C_1–C_4 haloalkylsulfonyl, C_1–C_4 alkylamino, C_2–C_8 dialkylamino, C_3–C_6 cycloalkylamino, C_2–C_4 alkoxyalkyl, C_1–C_4 hydroxyalkyl, C_2–C_4 alkylcarbonyl, C_2–C_6 alkoxycarbonyl, C_2–C_6 alkylcarbonyloxy, C_2–C_6 alkylcarbonylthio, C_2–C_6 alkylaminocarbonyl, C_3–C_8 dialkylaminocarbonyl, C_3–C_6 haloalkylcarbonylamino, C_3–C_6 haloalkylcarbonyl(alkyl)amino or C_3–C_6 trialkylsilyl; or phenyl, phenoxy or naphthalenyl optionally substituted with up to 3 substituents independently selected from halogen, cyano, C_1–C_2 alkyl, C_1–C_2 haloalkyl, C_1–C_2 alkoxy and C_1–C_2 haloalkoxy; or a 5- to 6-membered heteroaromatic ring containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 3 substituents independently selected from halogen, cyano, C_1–C_2 alkyl, C_1–C_2 haloalkyl, C_1–C_2 alkoxy and C_1–C_2 haloalkoxy on carbon atom ring members and cyano, C_1–C_2 alkyl and C_1–C_2 alkoxy on nitrogen atom ring members; or a 3- to 7-membered nonaromatic ring containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, wherein up to 3 carbon atom ring members are independently selected from C(=O) and C(=S), the ring optionally substituted with up to 3 substituents independently selected from halogen, cyano, C_1–C_2 alkyl, C_1–C_2 haloalkyl, C_1–C_2 alkoxy and C_1–C_2 haloalkoxy on carbon atom ring members and cyano, C_1–C_2 alkyl and C_1–C_2 alkoxy on nitrogen atom ring members;

each R^{9b} is independently hydrogen, cyano, C_1–C_3 alkyl, C_1–C_3 haloalkyl, C_1–C_3 alkoxy, C_2–C_3 alkylcarbonyl, C_2–C_3 alkoxycarbonyl or C_3–C_6 cycloalkyl;

Q^1 is phenyl or naphthalenyl each optionally substituted on carbon atom ring members with up to 5 substituents independently selected from R^{9a}; or

Q^1 is a 5- to 6-membered heteroaromatic ring or an 8- to 11-membered heteroaromatic bicyclic ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members; or

Q^1 is a 3- to 7-membered nonaromatic carbocyclic ring, a 5- to 7-membered nonaromatic heterocyclic ring or an 8- to 11-membered nonaromatic bicyclic ring system, each ring or ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S, up to 4 N and up to 2 Si atoms, wherein up to 3 carbon atom ring members are independently selected from C(=O) and C(=S), the sulfur atom ring members are independently selected from $S(=O)_s(=NR^{17})_f$, and the silicon atom ring members are independently selected from $SiR^{10}R^{11}$, each ring or ring system optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members;

each R^{10} and R^{11} is independently C_1–C_5 alkyl, C_2–C_5 alkenyl, C_2–C_5 alkynyl, C_3–C_5 cycloalkyl, C_3–C_6 halocycloalkyl, C_4–C_{10} cycloalkylalkyl, C_4–C_7 alkylcycloalkyl, C_5–C_7 alkylcycloalkylalkyl, C_1–C_5 haloalkyl, C_1–C_5 alkoxy or C_1–C_5 haloalkoxy;

each R^{17} is independently hydrogen, cyano, C_1–C_6 alkyl, C_1–C_6 haloalkyl, C_3–C_8 cycloalkyl, C_3–C_8 halocycloalkyl, C_1–C_6 alkoxy, C_1–C_6 haloalkoxy, C_1–C_6 alkylamino, C_2–C_8 dialkylamino, C_1–C_6 haloalkylamino or phenyl; and

s and f are independently 0, 1 or 2 in each instance of $S(=O)_s(=NR^{17})_f$, provided that the sum of s and f is 0, 1 or 2;

provided that

the compound of Formula **1** is other than 4,4'-(1,2,2,2-tetrafluoroethylidene)-bispyridine or 4,4'-(tetrafluoroethylidene)bis[2,3,5,6-tetrafluoropyridine].

Embodiments of this invention, including Embodiments 1–9a and AAA above, as well as any other embodiments described herein, can be combined in any manner, and the descriptions of variables in the embodiments pertain not only to the compounds of Formula **1** and Formula **1A** but also to the starting compounds and intermediate compounds useful for preparing the compounds of Formula **1** and Formula **1A**. In addition, embodiments of this invention, including Embodiments 1–9a and AAA above as well as any other embodiments described herein, and any combination thereof, pertain to the compositions and methods of the present invention.

Combinations of Embodiments 1–9a and AAA are illustrated by:

Embodiment AA. A compound of of Formula **1** as described in the invention wherein

A is N or CR^3;

R^1 is hydrogen, halogen, hydroxyl, cyano, SF_5, C_1–C_4 alkyl, C_2–C_4 alkenyl, C_2–C_4 alkynyl, C_1–C_4 haloalkyl, C_2–C_4 haloalkenyl, C_2–C_4 haloalkynyl, C_3–C_4 cycloalkyl, C_3–C_4 halocycloalkyl, C_1–C_4 alkoxy, C_1–C_4 haloalkoxy, C_2–C_4 alkylthio, C_2–C_4 alkylsulfinyl, C_2–C_4 alkylsulfonyl, C_2–C_4 haloalkylthio C_2–C_4 cyanoalkyl, C_2–C_4 alkylcarbonyl or C_2–C_4 alkoxycarbonyl;

R^2 and R^5 are each independently selected from hydrogen and fluorine;

$R^3$and R^4 are each independently selected from hydrogen, halogen, cyano, amino, nitro, SF_5, -CHO, 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_2–C_6 haloalkynyl, C_3–C_6 cycloalkyl, C_3–C_6 halocycloalkyl, C_4–C_8 alkylcycloalkyl, C_4–C_8 cycloalkylalkyl, C_3–C_6 cycloalkenyl, C_2–C_6 alkoxyalkyl, C_2–C_6 alkylthioalkyl, C_2–C_6 alkylcarbonyl, C_2–C_6 haloalkylcarbonyl, C_2–C_6 alkoxycarbonyl, C_2–C_6 alkylaminocarbonyl, C_3–C_8 dialkylaminocarbonyl, C_2–C_6 cyanoalkyl, C_1–C_6 alkoxy, C_1–C_6 haloalkoxy, C_2–C_6 alkoxyalkoxy, C_1–C_6 alkylthio, C_1–C_6 haloalkylthio, C_1–C_6 alkylsulfinyl, C_1–C_6 haloalkylsulfinyl, C_1–C_6 alkylsulfonyl, C_1–C_6 haloalkylsulfonyl, C_3–C_9 trialkylsilyl, C_1–C_6 alkylamino, C_2–C_6 dialkylamino, C_2–C_6 haloalkylamino, C_2–C_6 halodialkylamino or C_2–C_6 alkylcarbonylamino; or Q^1, OQ^1 or SQ^1;

Q is phenyl or naphthalenyl each optionally substituted on carbon atom ring members with up to 5 substituents independently selected from R^{9a}; or

Q is a 5- to 6-membered heteroaromatic ring provided that the 5- to 6-membered heteroaromatic ring is not imidazole or pyridazine, or an 8- to 11-membered heteroaromatic bicyclic ring system provided that the 8- to 11-membered heteroaromatic bicyclic ring system does not contain a pyridazine ring; each ring or ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members; or

Q is a 3- to 7-membered nonaromatic carbocyclic ring, a 5- to 7-membered nonaromatic heterocyclic ring provided that the 5- to 7-membered nonaromatic heterocyclic ring is not piperidine, or an 8- to 11-membered nonaromatic bicyclic ring system provided that the 8- to 11-membered nonaromatic bicyclic ring system does not contain a piperidine ring; each ring or ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S, up to 4 N and up to 2 Si atoms, wherein up to 3 carbon atom ring members are independently selected from C(=O) and C(=S),

the sulfur atom ring members are independently selected from $S(=O)_s(=NR^{17})_f$, and the silicon atom ring members are independently selected from $SiR^{10}R^{11}$, each ring or ring system optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members;

each R^{9a} is independently halogen, hydroxy, amino, cyano, nitro, SF_5, C_1–C_6 alkyl, C_2–C_6 alkenyl, C_2–C_6 alkynyl, C_3–C_6 cycloalkyl, C_4–C_{10} cycloalkylalkyl, C_4–C_{10} alkylcycloalkyl, C_5–C_{10} alkylcycloalkylalkyl, C_6–C_{14} cycloalkylcycloalkyl, C_1–C_6 haloalkyl, C_2–C_6 haloalkenyl, C_2–C_6 haloalkynyl, C_3–C_6 halocycloalkyl, C_1–C_4 alkoxy, C_1–C_4 haloalkoxy, C_2–C_4 alkoxyalkoxy, C_1–C_4 alkylthio, C_1–C_4 alkylsulfinyl, C_1–C_4 alkylsulfonyl, C_1–C_4 haloalkylthio, C_1–C_4 haloalkylsulfinyl, C_1–C_4 haloalkylsulfonyl, C_1–C_4 alkylamino, C_2–C_8 dialkylamino, C_3–C_6 cycloalkylamino, C_2–C_4 alkoxyalkyl, C_1–C_4 hydroxyalkyl, C_2–C_4 alkylcarbonyl, C_2–C_6 alkoxycarbonyl, C_2–C_6 alkylcarbonyloxy, C_2–C_6 alkylcarbonylthio, C_2–C_6 alkylaminocarbonyl, C_3–C_8 dialkylaminocarbonyl, C_3–C_6 haloalkylcarbonylamino, C_3–C_6 haloalkylcarbonyl(alkyl)amino or C_3–C_6 trialkylsilyl; or phenyl, phenoxy or naphthalenyl optionally substituted with up to 3 substituents independently selected from halogen, cyano, C_1–C_2 alkyl, C_1–C_2 haloalkyl, C_1–C_2 alkoxy and C_1–C_2 haloalkoxy; or a 5- to 6-membered heteroaromatic ring containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 3 substituents independently selected from halogen, cyano, C_1–C_2 alkyl, C_1–C_2 haloalkyl, C_1–C_2 alkoxy and C_1–C_2 haloalkoxy on carbon atom ring members and cyano, C_1–C_2 alkyl and C_1–C_2 alkoxy on nitrogen atom ring members; or a 3- to 7-membered nonaromatic ring containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, wherein up to 3 carbon atom ring members are independently selected from C(=O) and C(=S), the ring optionally substituted with up to 3 substituents independently selected from halogen, cyano, C_1–C_2 alkyl, C_1–C_2 haloalkyl, C_1–C_2 alkoxy and C_1–C_2 haloalkoxy on carbon atom ring members and cyano, C_1–C_2 alkyl and C_1–C_2 alkoxy on nitrogen atom ring members;

each R^{9b} is independently hydrogen, cyano, C_1–C_3 alkyl, C_1–C_3 haloalkyl, C_1–C_3 alkoxy, C_2–C_3 alkylcarbonyl, C_2–C_3 alkoxycarbonyl or C_3–C_6 cycloalkyl;

Q^1 is phenyl or naphthalenyl each optionally substituted on carbon atom ring members with up to 5 substituents independently selected from R^{9a}; or

Q^1 is a 5- to 6-membered heteroaromatic ring or an 8- to 11-membered heteroaromatic bicyclic ring system containing ring members selected from carbon atoms and up

to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members; or

Q^1 is a 3- to 7-membered nonaromatic carbocyclic ring, a 5- to 7-membered nonaromatic heterocyclic ring or an 8- to 11-membered nonaromatic bicyclic ring system, each ring or ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S, up to 4 N and up to 2 Si atoms, wherein up to 3 carbon atom ring members are independently selected from C(=O) and C(=S), the sulfur atom ring members are independently selected from $S(=O)_s(=NR^{17})_f$, and the silicon atom ring members are independently selected from $SiR^{10}R^{11}$, each ring or ring system optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members;

each R^{10} and R^{11} is independently C_1–C_5 alkyl, C_2–C_5 alkenyl, C_2–C_5 alkynyl, C_3–C_5 cycloalkyl, C_3–C_6 halocycloalkyl, C_4–C_{10} cycloalkylalkyl, C_4–C_7 alkylcycloalkyl, C_5–C_7 alkylcycloalkylalkyl, C_1–C_5 haloalkyl, C_1–C_5 alkoxy or C_1–C_5 haloalkoxy;

each R^{17} is independently hydrogen, cyano, C_1–C_6 alkyl, C_1–C_6 haloalkyl, C_3–C_8 cycloalkyl, C_3–C_8 halocycloalkyl, C_1–C_6 alkoxy, C_1–C_6 haloalkoxy, C_1–C_6 alkylamino, C_2–C_8 dialkylamino, C_1–C_6 haloalkylamino or phenyl; and

s and f are independently 0, 1 or 2 in each instance of $S(=O)_s(=NR^{17})_f$, provided that the sum of s and f is 0, 1 or 2;

provided that

the compound of Formula **1** is other than 4,4'-(1,2,2,2-tetrafluoroethylidene)-bis[pyridine] or 4,4'-(1,2,2,2-tetrafluoroethylidene)bis[2,3,5,6-tetrafluoropyridine].

Embodiment A. A compound of Embodiment AAA wherein

R^1 is hydrogen, halogen or C_1–C_4 alkyl;

R^2 and R^5 are each independently selected from hydrogen or halogen;

R^3 and R^4 are each independently selected from hydrogen, halogen, C_1–C_6 alkyl, C_1–C_6 haloalkyl, C_1–C_6 alkoxy, C_1–C_6 haloalkoxy, C_1–C_6 alkylthio, C_1–C_6 alkylsulfinyl or C_1–C_6 alkylsulfonyl;

Q is phenyl optionally substituted on carbon atom ring members with up to 5 substituents independently selected from R^{9a}; or a 5- to 6-membered heteroaromatic ring or an 8- to 11-membered heteroaromatic bicyclic ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S

and up to 4 N atoms, and optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members; and

each R^{9a} is independently halogen, C_1–C_6 alkyl, C_1–C_6 haloalkyl, C_1–C_4 alkoxy, C_1–C_4 haloalkoxy or C_3–C_6 trialkylsilyl.

Embodiment A1. A compound of Embodiment AA wherein

A is CR^3;

R^1 is hydrogen, halogen or C_1–C_4 alkyl;

R^2 and R^5 are each hydrogen;

R^3 and R^4 are each independently selected from hydrogen, halogen, C_1–C_6 alkyl, C_1–C_6 haloalkyl, C_1–C_6 alkoxy, C_1–C_6 haloalkoxy, C_1–C_6 alkylthio, C_1–C_6 alkylsulfinyl or C_1–C_6 alkylsulfonyl;

Q is phenyl optionally substituted on carbon atom ring members with up to 5 substituents independently selected from R^{9a}; or a 5- to 6-membered heteroaromatic ring provided that the 5- to 6-membered heteroaromatic ring is not imidazole or pyridazine, or an 8- to 11-membered heteroaromatic bicyclic ring system provided that the 8- to 11-membered heteroaromatic bicyclic ring system does not contain a pyridazine ring; each ring or ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members; and

each R^{9a} is independently halogen, SF_5, C_1–C_6 alkyl, C_1–C_6 haloalkyl, C_1–C_4 alkoxy, C_1–C_4 haloalkoxy, C_1–C_4 alkylthio, C_1–C_4 alkylsulfinyl, C_1–C_4 alkylsulfonyl, C_1–C_4 haloalkylthio, C_1–C_4 haloalkylsulfinyl, C_1–C_4 haloalkylsulfonyl or C_3–C_6 trialkylsilyl.

Embodiment B. A compound of Embodiment A wherein

R^1 is hydrogen, halogen or methyl;

R^2 and R^5 are hydrogen;

R^3 and R^4 are each independently selected from hydrogen, halogen, C_1–C_6 alkyl, C_1–C_6 alkoxy, C_1–C_6 alkylthio, C_1–C_6 alkylsulfinyl or C_1–C_6 alkylsulfonyl; and

Q is phenyl, pyridinyl, benzoxazole or benzimidazole optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members.

Embodiment B1. A compound of Embodiment A1 wherein

R^1 is hydrogen, halogen or methyl; and

Q is phenyl, pyridinyl, benzoxazole or benzimidazole optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members.

Embodiment C. A compound of Embodiment B wherein

R^1 is hydrogen or fluoro;

R^3 and R^4 are each independently selected from hydrogen, fluoro, chloro, methoxy or methylthio.

Q is phenyl, optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members; and

each R^{9a} is independently halogen, *tert*-butyl, CF_3 or OCF_3.

Embodiment C1. A compound of Embodiment B1 wherein

R^1 is hydrogen or fluoro;

R^3 and R^4 are each independently selected from hydrogen, fluoro, chloro, methoxy, methylthio, methylsulfinyl or methylsulfonyl.

Q is phenyl, optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members; and

each R^{9a} is independently halogen, SF_5, *tert*-butyl, CF_3, OCF_3, CF_2CF_3 or SCF_3.

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

5-chloro-2-(difluoro-4-pyridinylmethyl)benzoxazole;

4-[difluoro[4-(trifluoromethyl)phenyl]methyl]pyridine;

4-[[4-(1,1-dimethylethyl)phenyl]fluoromethyl]-3,5-difluoropyridine;

4-[[4-(1,1-dimethylethyl)phenyl]fluoromethyl]-3-fluoropyridine; and

3,5-dichloro-4-[fluoro[4-(trifluoromethoxy)phenyl]methyl]pyridine.

Additional specific embodiments include compounds of Formula **1** selected from the group consisting of:

3,5-dichloro-4-[[4-(1,1-dimethylethyl)phenyl]fluoromethyl]pyridine

3-fluoro-4-[fluoro[4-(trifluoromethoxy)phenyl]methyl]-5-(methylthio)pyridine

3-chloro-4-[fluoro[4-(trifluoromethoxy)phenyl]methyl]-5-(methylthio)pyridine

4-[[4-(1,1-dimethylethyl)phenyl]fluoromethyl]pyridine

3-chloro-5-(ethylthio)-4-[fluoro[4-(trifluoromethoxy)phenyl]methyl]pyridine

3-fluoro-4-[fluoro[4-[(trifluoromethyl)thio]phenyl]methyl]-5-(methylthio)pyridine

3-fluoro-4-[fluoro[4-(trifluoromethyl)phenyl]methyl]-5-(methylthio)pyridine

3-fluoro-4-[[4-(1,1-dimethylethyl)phenyl]fluoromethyl]pyridine

Of note is that compounds of this invention are characterized by favorable metabolic and/or soil residual patterns and exhibit activity controlling a spectrum of agronomic and nonagronomic invertebrate pests.

Of particular note, for reasons of invertebrate pest control spectrum and economic importance, protection of agronomic crops from damage or injury caused by invertebrate pests by controlling invertebrate pests are embodiments of the invention. Compounds of this invention because of their favorable translocation properties or systemicity in plants also protect foliar or other plant parts which are not directly contacted with a compound of Formula **1** or a composition comprising the compound.

Also noteworthy as embodiments of the present invention are compositions comprising a compound of any of the preceding Embodiments, as well as any other embodiments described herein, and any combinations thereof, and at least one additional component selected from the group consisting of a surfactant, a solid diluent and a liquid diluent, said compositions optionally further comprising at least one additional biologically active compound or agent.

Further noteworthy as embodiments of the present invention are compositions for controlling an invertebrate pest comprising a compound (i.e. in a biologically effective amount) of any of the preceding Embodiments, as well as any other embodiments described herein, and any combinations thereof, and at least one additional component selected from the group consisting of a surfactant, a solid diluent and a liquid diluent, said compositions optionally further comprising at least one additional biologically active compound or agent (i.e. in a biologically effective amount).

Embodiments of the invention also include a composition for protecting an animal comprising a compound (i.e. in a parasiticidally effective amount) of any of the preceding Embodiments, either alone or in combination, and a carrier.

Embodiments of the invention further include methods for controlling an invertebrate pest comprising contacting the invertebrate pest or its environment with a biologically effective amount of a compound of any of the preceding Embodiments, either alone or in combination, (e.g., as a composition described herein). Of particular note is a method for protecting an animal comprising administering to the animal a parasiticidally effective amount of a compound of any of the preceding Embodiments, either alone or in combination, (e.g., as a composition described herein).

Embodiments of the invention also include a composition comprising a compound of any of the preceding Embodiments, either alone or in combination, in the form of a soil drench liquid formulation. Embodiments of the invention further include methods for controlling an invertebrate pest comprising contacting the soil with a liquid composition as a soil drench comprising a biologically effective amount of a compound of any of the preceding Embodiments, either alone or in combination.

Embodiments of the invention also include a spray composition for controlling an invertebrate pest comprising a compound (i.e. in a biologically effective amount) of any of the preceding Embodiments, either alone or in combination, and a propellant. Embodiments of the invention further include a bait composition for controlling an invertebrate pest comprising a compound (i.e. in a biologically effective amount) of any of the preceding Embodiments, either alone or in combination, one or more food materials, optionally an attractant, and optionally a humectant. Embodiments of the invention also include a device for controlling an invertebrate pest comprising said bait composition and a housing adapted to receive said bait composition, wherein the housing has at least one opening sized to permit the invertebrate pest to pass through the opening so the invertebrate pest can gain access to said bait composition from a location outside the housing, and wherein the housing is further adapted to be placed in or near a locus of potential or known activity for the invertebrate pest.

Embodiments of the invention also include a method for protecting a seed from an invertebrate pest comprising contacting the seed with a biologically effective amount of a compound of any of the preceding Embodiments, either alone or in combination, (e.g., as a composition described herein).

Embodiments of the invention also include methods for protecting an animal from an invertebrate parasitic pest comprising administering to the animal a parasiticidally effective amount of a compound of any of the preceding Embodiments, either alone or in combination.

Embodiments of the invention also include methods for controlling an invertebrate pest comprising contacting the invertebrate pest or its environment with a biologically effective amount of a compound of Formula **1**, an *N*-oxide, or a salt thereof, (e.g., as a composition described herein), provided that the methods are not methods of medical treatment of a human or animal body by therapy.

Embodiments of the invention also include any of the preceding embodiments, either alone or in combination, wherein the invertebrate pest is an arthropod. Embodiments of the invention also include any of the preceding embodiments, either alone or in combination, wherein the arthropod is selected from the group consisting of insects, mites, spiders, scorpions, centipedes, millipedes, pill bugs and symphylans. Embodiments of the invention also include any of the preceding embodiments, either alone or in combination, wherein the arthropod is an insect.

Embodiments of the invention also include any of the preceding embodiments, either alone or in combination, wherein the invertebrate pest is a gastropod. Embodiments of the invention also include any of the preceding embodiments, either alone or in combination, wherein the gastropod is selected from the group consisting of snails, slugs and other Stylommatophora.

Embodiments of the invention also include any of the preceding embodiments, either alone or in combination, wherein the invertebrate pest is a nematode. Embodiments of the invention also include any of the preceding embodiments, either alone or in combination, wherein the nematode is selected from phytophagous nematodes.

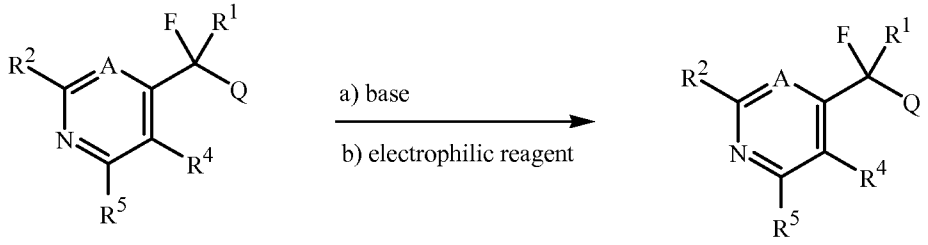
Embodiments of the invention also include any of the preceding embodiments, either alone or in combination, wherein the invertebrate pest is a helminth. Embodiments of the invention also include any of the preceding embodiments, either alone or in combination, wherein the helminth is selected from the group consisting of roundworms, heartworms, flukes, acanthocephalans and tapeworms.

This invention also relates to such methods wherein the invertebrate pest or its environment is contacted with a composition comprising a biologically effective amount of a compound of Formula **1**, an *N*-oxide, or a salt thereof, and at least one additional component selected from the group consisting of surfactants, solid diluents and liquid diluents, said composition optionally further comprising a biologically effective amount of at least one additional biologically active compound or agent, provided that the methods are not methods of medical treatment of a human or animal body by therapy.

One or more of the following methods and variations as described in Schemes 1–11 can be used to prepare the compounds of Formula **1** or the compounds of Formula **1A**. The definitions of R^1, R^2, R^3, R^4, R^5 and Q in the compounds of Formulae **1**–**11** below are as defined above in the Summary of the Invention unless otherwise noted. Formulae **1a**–**1g** are various subsets of Formula **1**, and all substituents for Formulae **1a**–**1g** are as defined above for Formula **1** unless otherwise indicated. Ambient or room temperature is defined as about 20–25 °C.

As shown in Scheme 1, compounds of Formula **1b** (compounds of Formula **1** wherein R^1 is F, Cl, Me etc.) can be prepared by treatment of corresponding mono fluoro compounds of Formula **1a** (compounds of Formula 1 wherein R^1 is H) with a base, useful bases include, for example *n*-BuLi (*n*-butyllithium), KHMDS (potassium hexamethyldisilazane or potassium bis(trimethylsilyl)amide), LHMDS (lithium hexamethyldisilazane or lithium bis(trimethylsilyl)amide) at a temperature between about –100 and about –20 °C, in ethereal solvents, such as diethyl ether or tetrahydrofuran, followed by addition of an electrophilic reagent such as $F(SO_2Ph)_2$, CCl_3CCl_3 or methyl iodide If the electrophilic reagent is a solid, it is dissolved in an inert solvent, such as THF, diethyl ether, before adding to the cold solution of the organometallic intermediate. The method of Scheme 1 is illustrated by synthesis Example 1, Step C.

Scheme 1

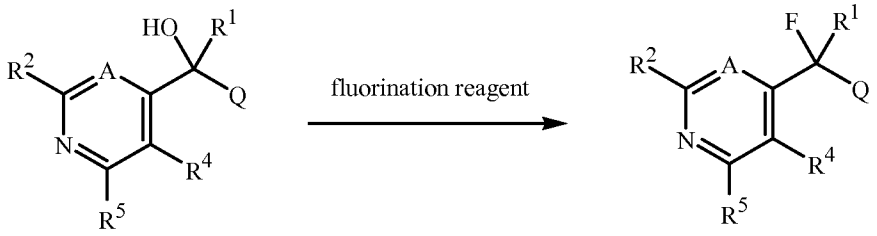


1a
wherein R^1 is H

1b
wherein R^1 is other than H

As shown in Scheme 2, compounds of Formula **1a** can be prepared by contacting the corresponding alcohols of Formula **2a** with fluorination reagents such as (diethylamino)sulfur trifluoride (DAST) or bis(2-methoxyethyl)aminosulfur trifluoride (Deoxo-Fluor) in haloalkane solvents, such as dichloromethane or trichloromethane from -78 °C to room temperature. A general procedure is known in the art, for example, see, Lal, G. S. et al. *J. Org. Chem.* **1999**, *64*, 7048. The method of Scheme 2 is illustrated by synthesis Example 1, Step B and Example 5, Step B.

Scheme 2



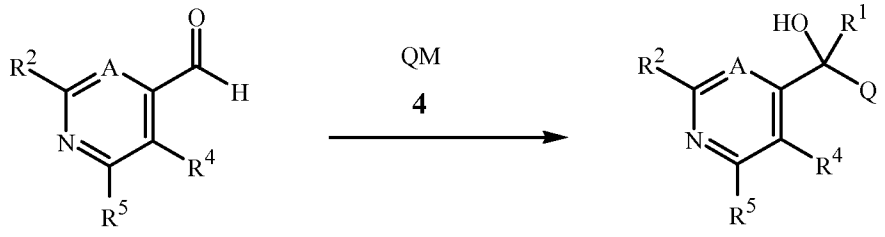
2a
wherein R^1 is H

1a
wherein R^1 is H

As shown in Scheme 3, compounds of Formula **2a** are readily available from nucleophilic addition of compounds of Formula **4** with the corresponding aldehydes of Formula **3**. The nucleophiles of Formula **4** can be generated by various chemical approaches. For example, the metal–halogen exchange reaction of a haloaromatic ring (QX, wherein X is preferred to be Br or I) with *n*-butyllithium or *i*-propylmagnesium bromide typically at a temperature between about –100 and about –20 °C can generate the nucleophiles of Formula **4** *in situ*. A wide variety of general procedures for conducting metal halogen exchange followed by reaction with electrophiles are known in the art and can be readily adapted for the present method. For related general procedures see, for example, M. Schlosser, *Angew. Chem. Int. Ed.* **2004**, *43*, 2 and P. Knochel et al., *Synthesis*, **2002**, 565. In addition, the nucleophiles of Formula **4** can be prepared via Grinard reaction of the corresponding QX with magnesium or are available directly from commercially sources, for

example, 4-tert-butylphenylmagnesium bromide or 4-(trifluoromethoxy)phenylmagnesium bromide. Most of the aldehydes of Formula **3** are commercially available or are known compounds in the chemical literature. The method of Scheme 3 is illustrated by synthesis Example 1, Step A.

Scheme 3



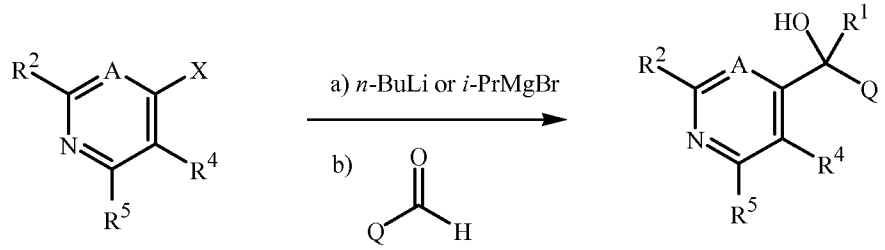
3 wherein M is Li or MgX **2a**

wherein R^1 is H

Compounds of Formula **4** can also be prepared by treating QH (wherein QH is benzoxazole or benzothiazole derivatives) with *n*-butyllithium at a temperature of about -78 °C in solvent, such as diethyl ether or THF. For a related reference see, for example: Bushey, et al. *J. Org. Chem.* **1985**, *50*, 2091-2095. This method is illustrated by synthesis Example 5, Step A.

As shown in Scheme 4, compounds of Formula **2a** can also be prepared by reaction of nucleophiles generated from compounds of Formula **6** with aldehydes of Formula **5**. For example, metal-halogen exchange (wherein X is Br or I) of compounds of Formula **6** with *n*-butyllithium or *i*-propylmagnesium bromide in ether solvents, such as THF, diethyl ether or dioxanes at temperatures between -100 °C to -40 °C will generate the desired 4-pyridyl anions *in situ*. The compounds of Formula **2a** can be prepared by trapping those anions with various aldehydes of Formula **5**. This method is well known in literature, see, for example: T. Francois, et al. *Tetrahedron*, **2000,** *56*, 1349. Another approach to obtain the 4-pyridyl anions is from 3-*t*-butylamidepyridine derivatives. Treatment of compounds of Formula **6** (wherein X is H, A is CR^3 and R^3 is $NHCOCMe_3$) with 2.5 to 3 equivalents of *n*-butyllithium or *n*-butyllithium/tetramethylethylene diamine complex at temperature between -78 °C to -10 °C in ether solvents (such as diether ether or THF) followed by quenching with aldehydes of Formula **5** affords alcohols of Formula 2a. This method is also known in the literature, see, L. Estel, et al., *J. Heterocyclic Chem.* **1989** *26*, 105.

Scheme 4



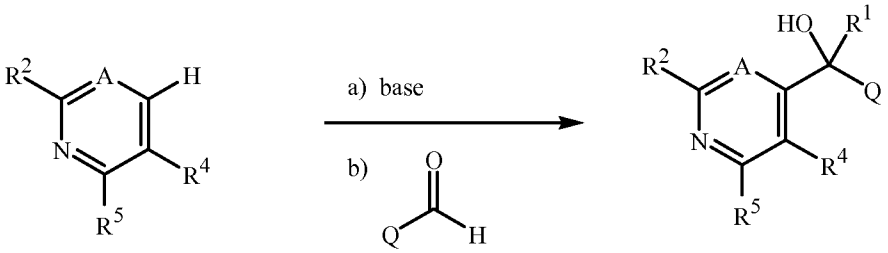
6
wherein X is Br or I

5

2a
wherein R^1 is H

As shown in Scheme 5, treating compounds of Formula **7** with base, such as lithium diisopropylamide, 2,2,6,6-tetramethylpiperidinyl magnesium chloride lithium chloride complex etc. in ether solvents, such as THF, diethyl ether or dioxanes at temperatures between -100 °C to -10 °C will generate the desired anions *in situ*. By quenching the above anion with aldehydes of Formula **5,** compounds of Formula **2a** can be prepared. This method is well known in literature, see, for example: R. J. Mattson, et al. *J. Org. Chem.*, **1990,** *55*, 3410. The method of Scheme 5 is illustrated by synthesis Example 6, Step A.

Scheme 5



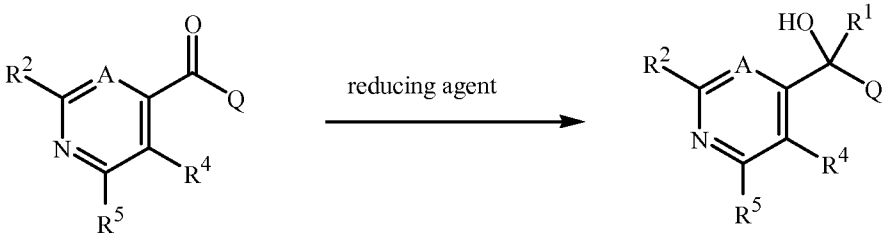
7

5

2a
wherein R^1 is H

As shown in Scheme 6, compounds of Formula **2a** can also be prepared from the corresponding carbonyl compounds of Formula **8**. By treating compounds of Formula **8** in solvents, such as methanol, ethanol or ethers (such as tetrahydrofuran) with a variety of reducing agents, such as sodium borohydride or borane-dimethylsulfide or reducing conditions like catalytic hydrogenation, compounds of Formula **2a** can be prepared. Several general procedures of this type of transformation are known in the art; see, for example, D. Douglas, et al., *J. Med. Chem* **2009**, *52*, 4694; M. Moriyasu, et al., *Synlett* **1997**, *3*, 273.

Scheme 6

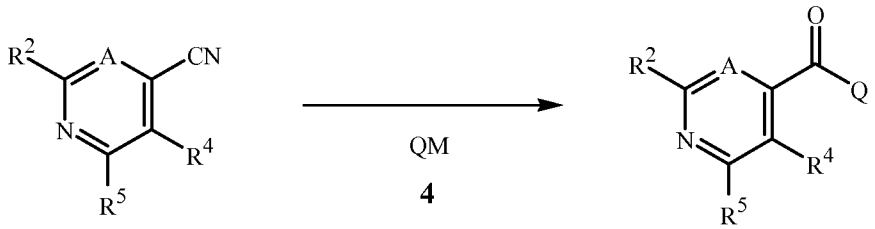


8 **2a**

wherein R^1 is H

As shown in Scheme 7, compounds of Formula **8** can be prepared from cyano-pyridine or cyano-pyrimidine derivatives of Formula **9**. Reaction of compounds of Formula **4** (similar chemistry discussed in Scheme 3) from halogen-metal exchange of QX with nitrile compounds of Formula **9** can provide carbonyl compounds of Formula **8**. For related references see, for example: U.S. Patent Application Publication US 2008/280891 and Bela. et al. *European J. Org. Chem.* **2004** *17*, 3623-3632. Many of the compounds of Formula **9** are commercially available or readily available from literature synthetic methods.

Scheme 7

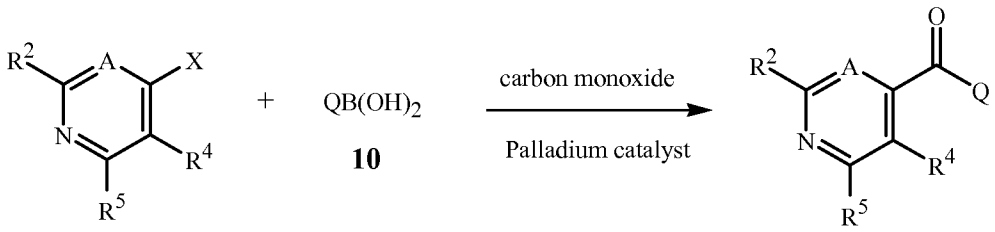


9 **8**

As shown in Scheme 8, compounds of Formula **8** can also be prepared from compounds of Formula **6** (wherein X is preferred to be Br or I) derivatives. The palladium-catalyzed cross-coupling reaction of a 4-halopyridine or pyrimidine of Formula **6**, carbon monoxide and boronic acids of Formula **10** (wherein Q is a substituted phenyl) provide an alternative way to prepare compounds of Formula **8**. By treating a mixture of 4-halopyridine or pyrimidine of Formula **6** and boronic acids of Formula **10** in the presence of palladium catalyst (such as bis(triphenylphosphine)palladium(II) dichloride, or tetrakis(triphenylphosphine)-palladium(0)) and base (such as potassium carbonate, sodium carbonate or cesium carbonate) at a temperature of about 80 to 150 °C in ethereal solvents (such as tetrahydrofuran or dioxane) under pressurized carbon monoxide atmosphere from 1 to 50 bar will provide the desired carbonyl compounds of Formula **8**. A detailed experimental procedure is given in Couve-Bonnair et. al., *Tetrahedron Lett.* **2001**, *42*, 3689-

3691. Most of the compounds of Formula **6** and boronic acids of Formula **10** are commercially available or readily available from the chemical literature.

Scheme 8

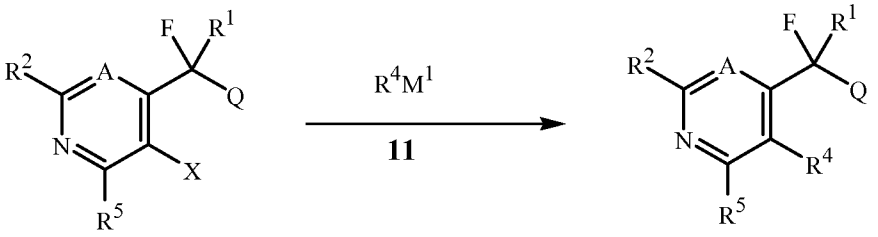


6 **10** **8**

wherein X is Br or I

As shown in Scheme 9, compounds of Formula **1c** wherein R^4 is phenyl, methyl or vinyl can be prepared by contacting compounds of Formula **1d** wherein X is Cl, Br or I with a compound of Formula **11** (a boronic acid or an organotin compound wherein R^4 is phenyl, methyl or vinyl) in the presence of a palladium catalyst. A wide variety of palladium-containing compounds and complexes are useful as catalysts for the present method. Examples of palladium-containing compounds and complexes useful as catalysts in the method of Scheme 9 include $Pd(OAc)_2$ (palladium(II) acetate), $PdCl_2$ (palladium(II) chloride), $PdCl_2(PPh_3)_2$ bis(triphenylphosphine)palladium(II) dichloride, $Pd(PPh_3)_4$ (tetrakis(triphenylphosphine)palladium(0), $Pd(C_5H_7O_2)_2$ (palladium(II) acetylacetonate) and $Pd_2(dba)_3$ tris (dibenzylideneacetone)dipalladium(0). Coupling reactions with boronic acids or derivatives or organotin compounds in the presence of palladium catalysts can be conducted over a wide range of temperatures, including from about 25 to about 150 °C. Of note are temperatures from about 80 and about 110 °C, which typically provide fast reaction rates and high product yields. Useful solvents include, for example, ethers such as 1,2-dimethoxyethane, amides such as *N*,*N*-dimethylacetamide, and nonhalogenated aromatic hydrocarbons such as toluene. A wide variety of known general procedures are reasonably believed to be readily adaptable by one skilled in the art to the method of Scheme 9. For recent review articles and books about this type of functional group transformation; see, for example, F. Bellina et al., *Synthesis* **2004**, *15*, 2419–2440; P. Espinet and A. M. Echavarren, *Angewandte Chemie, International Edition* **2004**, *43*, 4704–4734; and J. J. Li, G. W. Gribble, editors, Palladium in Heterocyclic Chemistry: A Guide for the Synthetic Chemist. 2000. The method of Scheme 9 is illustrated by synthesis Example 2.

Scheme 9



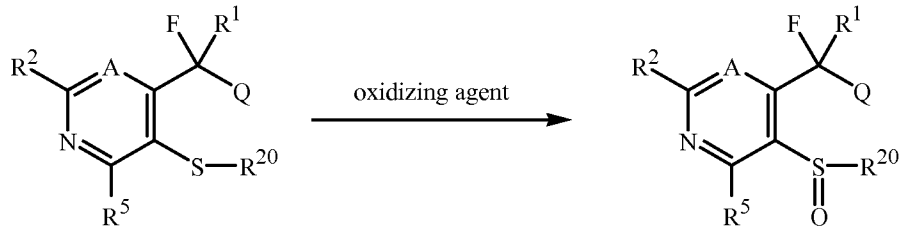
1d
wherein X is Cl, Br or I

wherein M^1 is $B(OH)_2$ or $Sn(Bu)_3$

1c
wherein R^4 is phenyl, methyl or vinyl

As shown in Scheme 10, compounds of Formula **1e** can be prepared by the oxidation of the corresponding thio compounds of Formula **1f** (wherein R^4 is SR^{20} and prepared according to methods in previous Schemes 2 and 3). The oxidation of compounds of Formula **1f** with sodium periodate ($NaIO_4$) in alcohol and water mixed solvents at room temperature will provide sulfinyl compounds of Formula **1e**. This method is known in the literature, for example, see, Ponticello et al. *J. Org. Chem.* **1979**, *44*, 3080-3082. The method of Scheme 10 is illustrated by synthesis Example 3.

Scheme 10

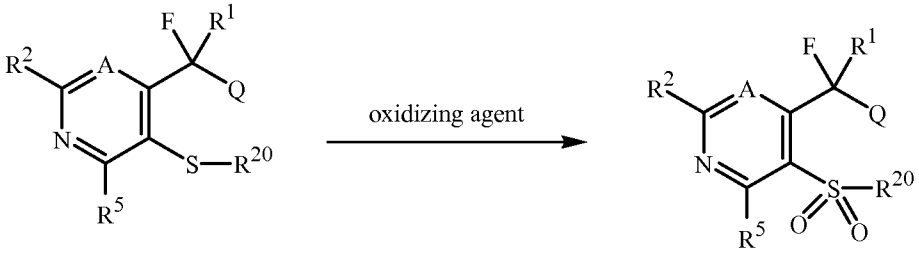


1f
wherein R^{20} is C_1-C_6 alkyl

1e

As shown in Scheme 11, compounds of Formula **1g** can be prepared by the oxidation of the corresponding thio compounds of Formula **1f**. The oxidation of compounds of Formula **1f** with 2 to 3 equivalents of *meta*-chloroperbenzoic acid in haloalkane solvents, such as dichloromethane or chloroform at temperatures of about 0 °C to room temperature will provide sulfonyl compounds of Formula **1g**. For a related reference see, for example: World Patent Publication WO 2010/125985. The method of Scheme 11 is illustrated by synthesis Example 4.

Scheme 11



1f

wherein R^{20} is C_1-C_6 alkyl

1g

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

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

Without further elaboration, it is believed that one skilled in the art using the preceding description can utilize the present invention to its fullest extent. The following Synthesis Examples are, therefore, to be construed as merely illustrative, and not limiting of the disclosure in any way whatsoever. Steps in the following Synthesis Examples illustrate a procedure for each step in an overall synthetic transformation, and the starting material for each step may not have necessarily been prepared by a particular preparative run whose procedure is described in other Examples or Steps. Ambient or room temperature is defined as about 20–25 °C. Percentages are by weight except for chromatographic solvent mixtures or where otherwise indicated. Parts and percentages for chromatographic solvent mixtures are by volume unless otherwise indicated. MPLC refers to medium pressure liquid chromatography on silica gel. ^{1}H NMR spectra are reported in ppm downfield from tetramethylsilane; “s” means singlet, “d” means doublet, “dd” means doublet of doublets,

"ddd" means doublet of doublet of doublets, "t" means triplet, "m" means multiplet, and "br s" means broad singlet. For mass spectral data, the numerical value reported is the molecular weight of the parent molecular ion (M) formed by addition of H^+ (molecular weight of 1) to the molecule to give a M+1 peak observed by mass spectrometry using atmospheric pressure chemical ionization (AP^+).

SYNTHESIS EXAMPLE 1

Preparation of 3-chloro-4-[[4-(1,1-dimethylethyl)phenyl]fluoromethyl]pyridine (compound number 7)and 3-chloro-4-[[4-(1,1-dimethylethyl)phenyl]difluoromethyl]pyridine (compound number 9)

Step A: Preparation of 3-chloro-α-[4-(1,1-dimethylethyl)phenyl]-4-pyridinemethanol

To a stirred solution of 3-chloro-4-pyridinecarboxaldehyde (1.10 g, 7.8 mmol) in tetrahydrofuran (20 mL) was added a solution of 4-*tert*-butylphenylmagnesium bromide (4.68 mL, 2.0 M in diethyl ether) at 0 °C. After stirring for 2 hrs, the reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic phases were washed with water and saturated aqueous NaCl solution, dried with anhydrous sodium sulfate and concentrated. The residue was purified by column chromatography on silica gel using hexanes/ethyl acetate (50:50 to 5:95) as eluent to afford the title product as a pale yellow solid (1.08 g).

^{1}H NMR ($CDCl_3$) δ 8.52 (d, 1H), 8.47 (s, 1H), 7.71 (d, 1H), 7.36 (d, 2H), 7.29 (d, 2H), 6.10 (d, 1H), 2.58 (s, br. 1H), 1.30 (s, 9H).

Step B: Preparation of 3-chloro-4-[[4-(1,1-dimethylethyl)phenyl]fluoromethyl]-pyridine

To a stirred solution of 3-chloro-α-[4-(1,1-dimethylethyl)phenyl]-4-pyridinemethanol (i.e. the product of Step A) (650 mg, 2.36 mmol) in dichloromethane (25 mL) was added bis(2-methoxyethyl)aminosulfur trifluoride (0.57 mL, 3.07 mmol) at -78 °C. After stirring for 2 hrs, the reaction mixture was diluted with saturated aqueous $NaHCO_3$ solution and extracted with dichloromethane. The combined organic phases were washed with water and saturated aqueous NaCl solution, dried with anhydrous sodium sulfate and concentrated. The residue was purified by column chromatography on silica gel using hexanes/ethyl acetate (80:20 to 40:60) as eluent to afford the title compound, a compound of the present invention, as a colorless oil (390 mg).

^{1}H NMR ($CDCl_3$) δ 8.58 (d, 1H), 8.55 (s, 1H), 7.60 (d, 1H), 7.39 (d, 2H), 7.27 (d, 2H), 6.66 (d, 1H), 2.58 (s, br. 1H), 1.30 (s, 9H).

Step C: Preparation of 3-chloro-4-[[4-(1,1-dimethylethyl)phenyl]difluoromethyl]-pyridine

To a stirred solution of 3-chloro-4-[[4-(1,1-dimethylethyl)phenyl]fluoromethyl]-pyridine (i.e. the product of Step B) (400 mg, 1.44 mmol) in tetrahydrofuran (10 mL) was added potassium bis(trimethylsilyl)amide (8.6 mL, 0.5 M in toluene) at -78 °C. After stirring for 0.5 hr at -78 °C, N-fluorobenzenesulfonimide (910 mg, 2.88 mmol) was added to the reaction mixture. The reaction mixture was allowed to warm to room temperature slowly over 3 hrs, and then was diluted with water and extracted with ethyl acetate. The combined organic phases were washed with water and saturated aqueous NaCl solution, dried with anhydrous sodium sulfate and concentrated. The residue was purified by column chromatography on silica gel using hexanes/ethyl acetate (80:20 to 40:60) as eluent to afford the title compound, a compound of the present invention, as a colorless oil (65 mg).

^{1}H NMR ($CDCl_3$) δ 8.64 (d, 1H), 8.63 (s, 1H), 7.67 (d, 1H), 7.43 (d, 2H), 7.38 (d, 2H), 1.32 (s, 9H).

SYNTHESIS EXAMPLE 2

Preparation of 4-[[4-(1,1-dimethylethyl)phenyl]fluoromethyl]-3-phenylpyridine (compound number 25)

To a stirred mixture of 3-bromo-4-[[4-(1,1-dimethylethyl)phenyl]fluoromethyl]-pyridine (prepared in a similar manner as Synthesis Example 1, Steps A and B) (210 mg, 0.65 mmol, 5,5-dimethyl phenylboronic acid 1,3-propanediol ester (186 mg, 0.98 mmol), and potassium carbonate (270 mg, 1.96 mmol) in dioxane/water (12 mL / 4 mL) was added $Pd(PPh_3)_4$ (37 mg, 0.03 mmol) at room temperature. The reaction mixture was stirred at 80 °C for 4 hrs, then cooled to room temperature, diluted with water, and extracted with ethyl acetate. The combined organic phases were washed with water and saturated aqueous NaCl solution, dried with anhydrous sodium sulfate and concentrated. The residue was purified by column chromatography on silica gel using hexanes/ethyl acetate (90:10 to 60:40) as eluent to afford the title compound, a compound of the present invention, as a pale yellow oil (160 mg).

^{1}H NMR ($CDCl_3$) δ 8.67 (d, 1H), 8.52 (s, 1H), 7.56 (d, 1H), 7.31 (m, 5H), 7.15 (d, 2H), 6.99 (d, 2H), 6.46 (d, 1H), 1.27 (s, 9H).

SYNTHESIS EXAMPLE 3

Preparation of 4-[fluoro[4-(trifluoromethoxy)phenyl]methyl]-3-(methylsulfinyl)pyridine (compound number 39)

To a mixture of 4-[fluoro[4-(trifluoromethoxy)phenyl]methyl]-3-(methylthio)-pyridine (prepared in a similar manner as Synthesis Example 1, Steps A and B) (200 mg, 0.63 mmol) in methanol/water (2 mL / 4 mL) was added sodium periodate (270 mg, 1.26 mmol). The resulting mixture was stirred at 40 °C for 1.5 hrs, then treated with an aqueous solution of

$Na_2S_2O_3$ and extracted with chloroform. The combined organic phases were washed with water and saturated aqueous NaCl solution, dried with anhydrous sodium sulfate and concentrated. The residue was purified by column chromatography on silica gel using hexanes/ethyl acetate (50:50 to 5:95) as eluent to afford the title compound, a compound of the present invention, as a colorless oil (100 mg).

^1H NMR ($CDCl_3$) δ 8.54 (m, 2H), 7.49 (d, 1H), 7.39 (d, 2H), 7.22 (d, 2H), 6.73 (d, 1H), 2.44 (s, 3H).

SYNTHESIS EXAMPLE 4

Preparation of 4-[fluoro[4-(trifluoromethoxy)phenyl]methyl]-3-(methylsulfonyl)pyridine (compound number 40)

To a stirred solution of 4-[fluoro[4-(trifluoromethoxy)phenyl]methyl]-3-(methylthio)-pyridine (prepared in a similar manner as Synthesis Example 1, Steps A and B) (200 mg, 0.63 mmol) in chloroform (3 mL) was added *meta*-chloroperbenzoic acid (282 mg, 1.26 mmol in 77% purity) at 0 °C. The reaction mixture was allowed to warm to room temperature, stir for 3 hrs, and then treated with saturated aqueous $NaHCO_3$ solution, and extracted with chloroform. The combined organic phases were washed with water and saturated aqueous NaCl solution, dried with anhydrous sodium sulfate and concentrated. The residue was purified by column chromatography on silica gel using hexanes/ethyl acetate (50:50 to 10:90) as eluent to afford the title compound, a compound of the present invention, as a colorless oil (105 mg).

^1H NMR ($CDCl_3$) δ 9.23 (s, 1H), 8.98 (d, 1H), 7.72 (d, 1H), 7.48 (d, 1H), 7.45 (d, 2H), 7.27 (d, 2H), 2.70 (s, 3H).

SYNTHESIS EXAMPLE 5

Preparation of 2-[(3-chloro-4-pyridinyl)fluoromethyl]benzothiazole (compound number 4)

Step A: Preparation of α-(3-chloro-4-pyridinyl)-2-benzothiazolemethanol

To a stirred solution of benzothiazole (780 mg, 5.78 mmol) in tetrahydrofuran (25 mL) was added *n*-butyllithium (3.6 mL, 2.0 M in hexanes) dropwise at -78 °C. After stirring at -78 °C for 0.5 hr, a solution of 3-chloro-4-pyridinecarboxaldehyde (900 mg, 6.36 mmol) in tetrahydrofuran (5 mL) was added slowly at –78 °C to the reaction mixture. The reaction mixture was stirred for another 5 hrs at -78 °C, then was treated with water and extracted with ethyl acetate. The combined organic phases were washed with water and saturated aqueous NaCl solution, dried with anhydrous sodium sulfate and concentrated. The residue was purified by column chromatography on silica gel using hexanes/ethyl acetate (60:40 to 10:90) as eluent to afford the title product as a pale yellow solid (120 mg).

^1H NMR ($CDCl_3$) δ 8.62 (s, 1H), 8.55 (d, 1H), 8.06 (d, 1H), 7.88 (d, 1H), 7.60 (d, 1H), 7.24 (m, 2H), 6.32 (s, 1H).

Step B: Preparation of 2-[(3-chloro-4-pyridinyl)fluoromethyl]benzothiazole

To a stirred mixture of α-(3-chloro-4-pyridinyl)-2-benzothiazolemethanol (i.e. the product of Step A) (110 mg, 0.40 mmol) in dichloromethane (4 mL) was added bis(2-methoxyethyl)aminosulfur trifluoride (0.20 mL, 1.08 mmol) at -78 °C. After stirring for 2 hrs, the reaction mixture was treated with saturated aqueous $NaHCO_3$ solution and extracted with dichloromethane. The combined organic phases were washed with water and saturated aqueous NaCl solution, dried with anhydrous sodium sulfate and concentrated. The residue was purified by column chromatography on silica gel using hexanes/ethyl acetate (80:20 to 40:60) as eluent to afford the title compound, a compound of the present invention, as a colorless oil (60 mg).

^{1}H NMR ($CD_3C(O)CD_3$) δ 8.66 (s, 1H), 8.64 (d, 1H), 8.07 (d, 1H), 7.92 (d, 1H), 7.62 (d, 1H), 7.52 (dd, 1H), 7.45 (dd, 1H), 7.08 (d, 1H).

SYNTHESIS EXAMPLE 6

Preparation of 4-[fluoro[4-(trifluoromethoxy)phenyl]methyl]-5-methoxypyrimidine (compound number 43)

Step A: Preparation of 5-methoxy-α-[4-(trifluoromethoxy)phenyl]-4-pyrimidinemethanol

A solution of 2,2,6,6-tetramethylpiperidinyl magnesium chloride lithium chloride complex solution (3.8 mL, 1.0 M in toluene/tetrahydrofuran) was slowly added to a stirred solution of 5-methoxy-pyrimidine (320 mg, 2.9 mmol) in tetrahydrofuran (10 mL) at –78 °C. After stirring at –40 °C to –20 °C for 1 hr, the reaction mixture was treated with 4-(trifluoromethoxy)benzyaldehyde (610 mg, 3.2 mmol) at –78 °C. After stirring for another 1hr at –78 °C, the reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic phases were washed with water and saturated aqueous NaCl solution, dried with anhydrous sodium sulfate and concentrated. The residue was purified by column chromatography on silica gel using hexanes/ethyl acetate (70:30 to 20:80) as eluent to afford the title product (260 mg).

^{1}H NMR ($CDCl_3$) δ 8.88 (s, 1H), 8.30 (s, 1H), 7.41 (d, 2H), 7.15 (d, 2H), 5.97 (s, 1H), 5.08 (s, br. 1H), 3.89 (s, 3H).

Step B: Preparation of 4-[fluoro[4-(trifluoromethoxy)phenyl]methyl]-5-methoxypyrimidine

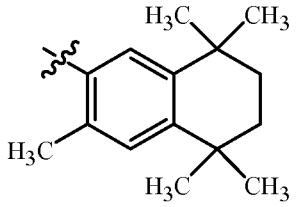
To a stirred solution of 5-methoxy-α-[4-(trifluoromethoxy)phenyl]-4-pyrimidinemethanol (i.e. the product of Step A) (150 mg, 0.5 mmol) in dichloromethane (10 mL) was added bis(2-methoxyethyl)aminosulfur trifluoride (0.2 mL) at -78 °C. After stirring for 1 hr, the reaction mixture was diluted with saturated aqueous $NaHCO_3$solution and extracted with dichloromethane. The combined organic phases were washed with water and saturated aqueous NaCl solution, dried with anhydrous sodium sulfate and concentrated.

The residue was purified by column chromatography on silica gel using hexanes/ethyl acetate (80:20 to 40:60) as eluent to afford the title compound, a compound of the present invention, as a colorless oil (110 mg).

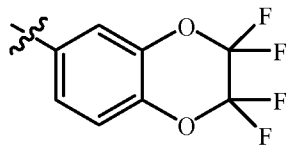
^{1}H NMR ($CDCl_3$) δ 8.93 (s, 1H), 8.41 (s, 1H), 7.55 (d, 1H), 7.21 (d, 2H), 6.79 (d, 1H), 3.96 (s, 3H).

By the procedures described herein together with methods known in the art, the following compounds of Tables 1A to 98I can be prepared. The following abbreviations are used in Tables 1A to 98I which follow: *t* is tertiary, *s* is secondary, *n* is normal, *i* is iso, Me is methyl, Et is ethyl, Pr is propyl, Bu is butyl, Ph is phenyl, OMe is methoxy, OEt is ethoxy, SMe is methylthio, S(O)Me is methylsulfinyl and SO_2Me is methylsulfonyl.

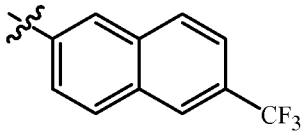
Fragments Q-1 through Q-15 shown below are referred to in Tables 1A to 98I. The wavy line denotes the attachment point of the fragment to the remainder of the molecule.



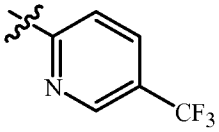
Q-1



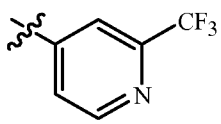
Q-2



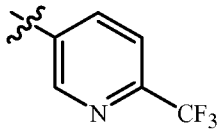
Q-3



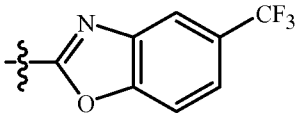
Q-4



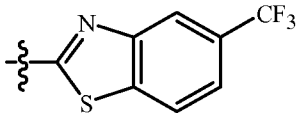
Q-5



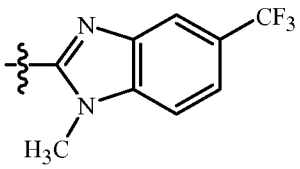
Q-6



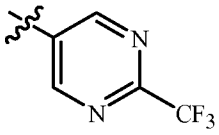
Q-7



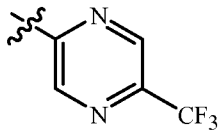
Q-8



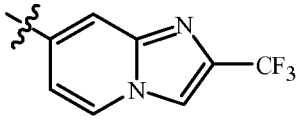
Q-9



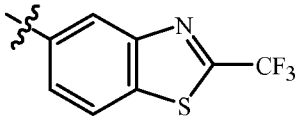
Q-10



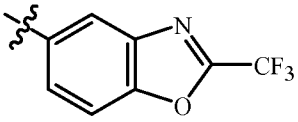
Q-11



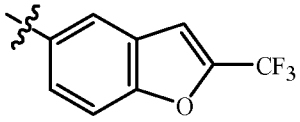
Q-12



Q-13



Q-14



Q-15

Tables 1A–98A pertain to the structure shown below.

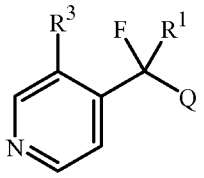


TABLE 1A

R^1 is H and R^3 is H

Q	Q	Q
4-chlorophenyl	3-(CF_3)phenyl	3-F, 4-(CF_3)phenyl
4-bromophenyl	3-(OCF_3)phenyl	3-Cl, 4-(CF_3)phenyl
4-iodophenyl	3-(*s*-Bu)phenyl	3-Br, 4-(CF_3)phenyl
4-nitrophenyl	3-(*t*-Bu)phenyl	3-Me, 4-(CF_3)phenyl
4-cyanophenyl	3-($CMe_2CH_2CH_3$)phenyl	2,6-diF, 4-(CF_3)phenyl
4-(CO_2CH_3)phenyl	3-($SiMe_3$)phenyl	2,6-diCl, 4-(CF_3)phenyl
4-(CF_3)phenyl	3-(O-*i*-Pr))phenyl	2-F, 4-(OCF_3)phenyl
4-(OCF_3)phenyl	3-(O-*t*-Bu)phenyl	2-Cl, 4-(OCF_3)phenyl
4-(*s*-Bu)phenyl	3-(OCH_2OCH_3)phenyl	2-Me, 4-(OCF_3)phenyl
4-(*t*-Bu)phenyl	3-($OCMe_2CO_2Et$)phenyl	3-F, 4-(OCF_3)phenyl
4-($CMe_2CH_2CH_3$)phenyl	3-(S-*i*-Pr)phenyl	3-Cl, 4-(OCF_3)phenyl
4-($SiMe_3$)phenyl	3-(SCH_2CF_3)phenyl	3-Br, 4-(OCF_3)phenyl
4-(O-*i*-Pr))phenyl	3-($NMeCOCF_3$)phenyl	3-Me, 4-(OCF_3)phenyl
4-(O-*t*-Bu)phenyl	3-($CF(CF_3)_2$)phenyl	2,6-diF, 4-(OCF_3)phenyl
4-(OCH_2OCH_3)phenyl	3-(O-Ph)phenyl	2,6-diCl, 4-(OCF_3)phenyl
4-($OCMe_2CO_2Et$)phenyl	2-F, 4-(*t*-Bu)phenyl	2,6-diMe, 4-($CF(CF_3)_2$)phenyl
4-(S-*i*-Pr)phenyl	2-Cl, 4-(*t*-Bu)phenyl	2,6-diF, 4-($CF(CF_3)_2$)phenyl
4-((SCH_2CF_3)phenyl	2-Me, 4-(*t*-Bu)phenyl	2,6-diCl, 4-($CF(CF_3)_2$)phenyl
4-($NMeCOCF_3$)phenyl	3-F, 4-(*t*-Bu)phenyl	2-F, 4-(CF_2CF_3)phenyl
4-($CF(CF_3)_2$)phenyl	3-Cl, 4-(*t*-Bu)phenyl	2-Cl, 4-(CF_2CF_3)phenyl
4-(O-Ph)phenyl	3-Br, 4-(*t*-Bu)phenyl	2-Me, 4-(CF_2CF_3)phenyl
3-chlorophenyl	3-Me, 4-(*t*-Bu)phenyl	3-F, 4-(CF_2CF_3)phenyl
3-bromophenyl	2,6-diF, 4-(*t*-Bu)phenyl	3-Cl, 4-(CF_2CF_3)phenyl
3-iodophenyl	2,6-diCl, 4-(*t*-Bu)phenyl	3-Br, 4-(CF_2CF_3)phenyl
3-nitrophenyl	2-F, 4-(CF_3)phenyl	3-Me, 4-(CF_2CF_3)phenyl
3-cyanophenyl	2-Cl, 4-(CF_3)phenyl	2,6-diF, 4-(CF_2CF_3)phenyl
3-(CO_2CH_3)phenyl	2-Me, 4-(CF_3)phenyl	2,6-diCl, 4-(CF_2CF_3)phenyl
4-(SCF_3)phenyl	3-(SCF_3)phenyl	Q-1
4-(S(O)CF_3)phenyl	3-(S(O)CF_3)phenyl	Q-2

Q	Q	Q
4-(SO_2CF_3)phenyl	3-(SO_2CF_3)phenyl	Q-3
4-(CF_2CF_3)phenyl	3-(CF_2CF_3)phenyl	Q-4
4-($CF_2CF_2CF_3$)phenyl	3-($CF_2CF_2CF_3$)phenyl	Q-5
4-(SF_5)phenyl	3-(SF_5)phenyl	Q-6
4-(OCF_2CF_3)phenyl	3-(OCF_2CF_3)phenyl	Q-7
2-F, 4-(SCF_3)phenyl	2-F, 4-(OCF_2CF_3)phenyl	Q-8
2-Cl, 4-(SCF_3)phenyl	2-Cl, 4-(OCF_2CF_3)phenyl	Q-9
2-Me, 4-(SCF_3)phenyl	2-Me, 4-(OCF_2CF_3)phenyl	Q-10
3-F, 4-(SCF_3)phenyl	3-F, 4-(OCF_2CF_3)phenyl	Q-11
3-Cl, 4-(SCF_3)phenyl	3-Cl, 4-(OCF_2CF_3)phenyl	Q-12
3-Br, 4-(SCF_3)phenyl	3-Br, 4-(OCF_2CF_3)phenyl	Q-13
3-Me, 4-(SCF_3)phenyl	3-Me, 4-(OCF_2CF_3)phenyl	Q-14
2,6-diF, 4-(SCF_3)phenyl	2,6-diF, 4-(OCF_2CF_3)phenyl	Q-15
2,6-diCl, 4-(SCF_3)phenyl	2,6-diCl, 4-(OCF_2CF_3)phenyl	

The present disclosure also includes Tables 2A through 98A, each of which is constructed the same as Table 1A above except that the row heading in Table 1A (i.e. "R^1 is H, R^3 is H.") below the Markush structure is replaced with the respective row heading shown below. For example, in Table 2A the row heading is "R^1 is H, R^3 is F, and Q is as defined in Table 1A above. Thus, the first entry in Table 2A specifically discloses 4-[(4-chlorophenyl)fluoromethyl]-3-fluoropyridine.

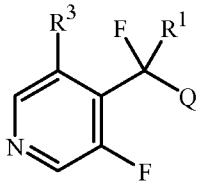
Table	Table Headings	Table	Table Headings
2A	R^1 is H and R^3 is F	50A	R^1 is F and R^3 is H
3A	R^1 is H and R^3 is Cl	51A	R^1 is F and R^3 is F
4A	R^1 is H and R^3 is Br	52A	R^1 is F and R^3 is Cl
5A	R^1 is H and R^3 is I	53A	R^1 is F and R^3 is Br
6A	R^1 is H and R^3 is Me	54A	R^1 is F and R^3 is I
7A	R^1 is H and R^3 is Et	55A	R^1 is F and R^3 is Me
8A	R^1 is H and R^3 is *n*-Pr	56A	R^1 is F and R^3 is Et
9A	R^1 is H and R^3 is *i*-Pr	57A	R^1 is F and R^3 is *n*-Pr
10A	R^1 is H and R^3 is *n*-Bu	58A	R^1 is F and R^3 is *i*-Pr
11A	R^1 is H and R^3 is *i*-Bu	59A	R^1 is F and R^3 is *n*-Bu
12A	R^1 is H and R^3 is *t*-Bu	60A	R^1 is F and R^3 is *i*-Bu
13A	R^1 is H and R^3 is C≡CH	61A	R^1 is F and R^3 is *t*-Bu
14A	R^1 is H and R^3 is CH=CH_2	62A	R^1 is F and R^3 is C≡CH

Table	Table Headings
15A	R^1 is H and R^3 is CF_3
16A	R^1 is H and R^3 is CF_2CF_3
17A	R^1 is H and R^3 is OMe
18A	R^1 is H and R^3 is OEt
19A	R^1 is H and R^3 is O-*n*-Pr
20A	R^1 is H and R^3 is O-*i*-Pr
21A	R^1 is H and R^3 is O-*t*-Bu
22A	R^1 is H and R^3 is OCH_2CF_3
23A	R^1 is H and R^3 is OCH_2CHF_2
24A	R^1 is H and R^3 is OCH_2CH_2F
25A	R^1 is H and R^3 is CH_2OMe
26A	R^1 is H and R^3 is CH_2OEt
27A	R^1 is H and R^3 is OCH_2CH_2OMe
28A	R^1 is H and R^3 is OCH_2CH_2OEt
29A	R^1 is H and R^3 is SMe
30A	R^1 is H and R^3 is S(O)Me
31A	R^1 is H and R^3 is SO_2Me
32A	R^1 is H and R^3 is SEt
33A	R^1 is H and R^3 is S(O)Et
34A	R^1 is H and R^3 is SO_2Et
35A	R^1 is H and R^3 is S-*n*-Pr
36A	R^1 is H and R^3 is S(O)-*n*-Pr
37A	R^1 is H and R^3 is SO_2-*n*-Pr
38A	R^1 is H and R^3 is S-*i*-Pr
39A	R^1 is H and R^3 is S(O)-*i*-Pr
40A	R^1 is H and R^3 is SO_2-*i*-Pr
41A	R^1 is H and R^3 is SCH_2CF_3
42A	R^1 is H and R^3 is S(O) CH_2CF_3
43A	R^1 is H and R^3 is SO_2 CH_2CF_3
44A	R^1 is H and R^3 is Ph
45A	R^1 is H and R^3 is 2-Pyridinyl
46A	R^1 is H and R^3 is 3-Pyridinyl
47A	R^1 is H and R^3 is 4-Pyridinyl
48A	R^1 is H and R^3 is O-Ph
49A	R^1 is H and R^3 is S-Ph

Table	Table Headings
63A	R^1 is F and R^3 is $CH=CH_2$
64A	R^1 is F and R^3 is CF_3
65A	R^1 is F and R^3 is CF_2CF_3
66A	R^1 is F and R^3 is OMe
67A	R^1 is F and R^3 is OEt
68A	R^1 is F and R^3 is O-*n*-Pr
69A	R^1 is F and R^3 is O-*i*-Pr
70A	R^1 is F and R^3 is O-*t*-Bu
71A	R^1 is F and R^3 is OCH_2CF_3
72A	R^1 is F and R^3 is OCH_2CHF_2
73A	R^1 is F and R^3 is OCH_2CH_2F
74A	R^1 is F and R^3 is CH_2OMe
75A	R^1 is F and R^3 is CH_2OEt
76A	R^1 is F and R^3 is OCH_2CH_2OMe
77A	R^1 is F and R^3 is OCH_2CH_2OEt
78A	R^1 is F and R^3 is SMe
79A	R^1 is F and R^3 is S(O)Me
80A	R^1 is F and R^3 is SO_2Me
81A	R^1 is F and R^3 is SEt
82A	R^1 is F and R^3 is S(O)Et
83A	R^1 is F and R^3 is SO_2Et
84A	R^1 is F and R^3 is S-*n*-Pr
85A	R^1 is F and R^3 is S(O)-*n*-Pr
86A	R^1 is F and R^3 is SO_2-*n*-Pr
87A	R^1 is F and R^3 is S-*i*-Pr
88A	R^1 is F and R^3 is S(O)-*i*-Pr
89A	R^1 is F and R^3 is SO_2-*i*-Pr
90A	R^1 is F and R^3 is SCH_2CF_3
91A	R^1 is F and R^3 is S(O) CH_2CF_3
92A	R^1 is F and R^3 is SO_2 CH_2CF_3
93A	R^1 is F and R^3 is Ph
94A	R^1 is F and R^3 is 2-Pyridinyl
95A	R^1 is F and R^3 is 3-Pyridinyl
96A	R^1 is F and R^3 is 4-Pyridinyl
97A	R^1 is F and R^3 is O-Ph
98A	R^1 is F and R^3 is S-Ph

TABLE 1B

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



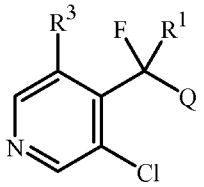
For example, the first compound in Table 1B is the structure shown immediately above wherein R^1 is H, R^3 is H and Q is 4-chlorophenyl.

TABLES 2B-98B

Tables 2B through 98B are constructed in a similar manner as Tables 2A through 98A.

TABLE 1C

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



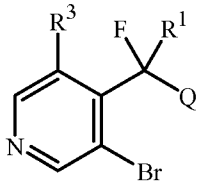
For example, the first compound in Table 1C is the structure shown immediately above wherein R^1 is H, R^3 is H and Q is 4-chlorophenyl.

TABLES 2C-98C

Tables 2C through 98C are constructed in a similar manner as Tables 2A through 98A.

TABLE 1D

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



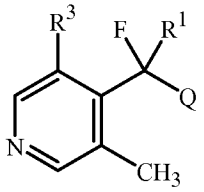
For example, the first compound in Table 1D is the structure shown immediately above wherein R^1 is H, R^3 is H and Q is 4-chlorophenyl.

TABLES 2D-98D

Tables 2D through 98D are constructed in a similar manner as Tables 2A through 98A.

TABLE 1E

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



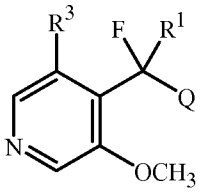
For example, the first compound in Table 1E is the structure shown immediately above wherein R^1 is H, R^3 is H and Q is 4-chlorophenyl.

TABLES 2E-98E

Tables 2E through 98E are constructed in a similar manner as Tables 2A through 98A.

TABLE 1F

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



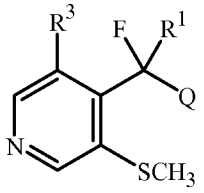
For example, the first compound in Table 1F is the structure shown immediately above wherein R^1 is H, R^3 is H and Q is 4-chlorophenyl.

TABLES 2F-98F

Tables 2F through 98F are constructed in a similar manner as Tables 2A through 98A.

TABLE 1G

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



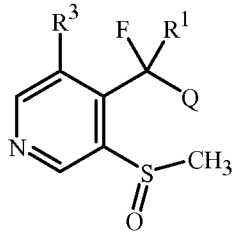
For example, the first compound in Table 1G is the structure shown immediately above wherein R^1 is H, R^3 is H and Q is 4-chlorophenyl.

TABLES 2G-98G

Tables 2G through 98G are constructed in a similar manner as Tables 2A through 98A.

TABLE 1H

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



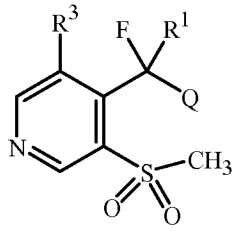
For example, the first compound in Table 1H is the structure shown immediately above wherein R^1 is H, R^3 is H and Q is 4-chlorophenyl.

TABLES 2H-98H

Tables 2H through 98H are constructed in a similar manner as Tables 2A through 98A.

TABLE 1I

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



For example, the first compound in Table 1I is the structure shown immediately above wherein R^1 is H, R^3 is H and Q is 4-chlorophenyl.

TABLES 2I-98I

Tables 2I through 98I are constructed in a similar manner as Tables 2A through 98A.

Examples of intermediates useful in the preparation of compounds of this invention are shown in Tables I1 through I42.

Tables I1–I21 pertain to the structure shown below.

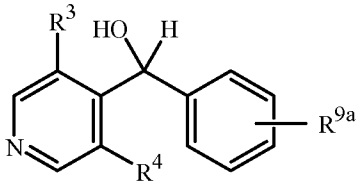


TABLE I1

R^3 is SMe and R^4 is H

R^{9a}	R^{9a}	R^{9a}
4-*t*-Bu	4-OCF_3	4-OCF_2CF_3
4-SCF_3	4-SF_5	4-CF_3
4-CF_2CF_3	3-F, 4-*t*-Bu	3-Cl, 4-*t*-Bu
3-F, 4-OCF_3	3-Cl, 4-OCF_3	3-F, 4-OCF_2CF_3
3-Cl, 4-OCF_2CF_3	3-F, 4-SCF_3	3-Cl, 4-SCF_3
3-F, 4-SF_5	3-Cl, 4-SF_5	3-F, 4-CF_3
3-Cl, 4-CF_3	3-F, 4-CF_2CF_3	3-Cl, 4-CF_2CF_3

The present disclosure also includes Tables I2 through I21, each of which is constructed the same as Table I1 above except that the row heading in Table I1 (i.e. "R^3 is SMe and R^4 is H.") below the Markush structure is replaced with the respective row heading shown below. For example, in Table I2 the row heading is "R^3 is SMe and R^4 is F, and R^{9a} is as defined in Table I1 above. Thus, the first entry in Table I2 specifically discloses α-[4-(1,1-dimethylethyl)phenyl]-3-fluoro-5-(methylthio)-4-pyridinemethanol.

Table	Table Headings	Table	Table Headings
I2	R^3 is SMe and R^4 is F	I12	R^3 is SEt and R^4 is Cl
I3	R^3 is SMe and R^4 is Cl	I13	R^3 is S(O)Et and R^4 is H
I4	R^3 is S(O)Me and R^4 is H	I14	R^3 is S(O)Et and R^4 is F
I5	R^3 is S(O)Me and R^4 is F	I15	R^3 is S(O)Et and R^4 is Cl
I6	R^3 is S(O)Me and R^4 is Cl	I16	R^3 is SO_2Et and R^4 is H
I7	R^3 is SO_2Me and R^4 is H	I17	R^3 is SO_2Et and R^4 is F
I8	R^3 is SO_2Me and R^4 is F	I18	R^3 is SO_2Et and R^4 is Cl
I9	R^3 is SO_2Me and R^4 is Cl	I19	R^3 is OMe and R^4 is H
I10	R^3 is SEt and R^4 is H	I20	R^3 is OMe and R^4 is F
I11	R^3 is SEt and R^4 is F	I21	R^3 is OMe and R^4 is Cl

Tables I22–I42 pertain to the structure shown below.

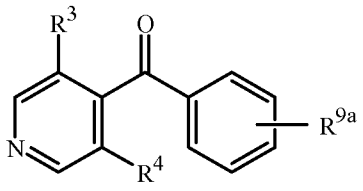


TABLE I22

R^3 is SMe and R^4 is H

R^{9a}	R^{9a}	R^{9a}
4-*t*-Bu	4-OCF_3	4-OCF_2CF_3
4-SCF_3	4-SF_5	4-CF_3
4-CF_2CF_3	3-F, 4-*t*-Bu	3-Cl, 4-*t*-Bu
3-F, 4-OCF_3	3-Cl, 4-OCF_3	3-F, 4-OCF_2CF_3
3-Cl, 4-OCF_2CF_3	3-F, 4-SCF_3	3-Cl, 4-SCF_3
3-F, 4-SF_5	3-Cl, 4-SF_5	3-F, 4-CF_3
3-Cl, 4-CF_3	3-F, 4-CF_2CF_3	3-Cl, 4-CF_2CF_3

The present disclosure also includes Tables I23 through I42, each of which is constructed the same as Table I22 above except that the row heading in Table I22 (i.e. "R^3 is SMe and R^4 is H.") below the Markush structure is replaced with the respective row heading shown below. For example, in Table I23 the row heading is "R^3 is SMe and R^4 is F, and R^{9a} is as defined in Table I22 above. Thus, the first entry in Table I23 specifically discloses [3-fluoro-5-(methylthio)-4-pyridinyl]-[4-(1,1-dimethylethyl)phenyl]methanone.

Table	Table Headings	Table	Table Headings
I23	R^3 is SMe and R^4 is F	I33	R^3 is SEt and R^4 is Cl
I24	R^3 is SMe and R^4 is Cl	I34	R^3 is S(O)Et and R^4 is H
I25	R^3 is S(O)Me and R^4 is H	I35	R^3 is S(O)Et and R^4 is F
I26	R^3 is S(O)Me and R^4 is F	I36	R^3 is S(O)Et and R^4 is Cl
I27	R^3 is S(O)Me and R^4 is Cl	I37	R^3 is SO_2Et and R^4 is H
I28	R^3 is SO_2Me and R^4 is H	I38	R^3 is SO_2Et and R^4 is F
I29	R^3 is SO_2Me and R^4 is F	I39	R^3 is SO_2Et and R^4 is Cl
I30	R^3 is SO_2Me and R^4 is Cl	I40	R^3 is OMe and R^4 is H
I31	R^3 is SEt and R^4 is H	I41	R^3 is OMe and R^4 is F
I32	R^3 is SEt and R^4 is F	I42	R^3 is OMe and R^4 is Cl

A compound of this invention will generally be used as an invertebrate pest control active ingredient in a composition, i.e. formulation, with at least one additional component selected from the group consisting of surfactants, solid diluents and liquid diluents, which serves as a carrier. The formulation or composition ingredients are selected to be consistent with the physical properties of the active ingredient, mode of application and environmental factors such as soil type, moisture and temperature.

Useful formulations include both liquid and solid compositions. Liquid compositions include solutions (including emulsifiable concentrates), suspensions, emulsions (including microemulsions and/or suspoemulsions) and the like, which optionally can be thickened into gels. The general types of aqueous liquid compositions are soluble concentrate, suspension

concentrate, capsule suspension, concentrated emulsion, microemulsion and suspo-emulsion. The general types of nonaqueous liquid compositions are emulsifiable concentrate, microemulsifiable concentrate, dispersible concentrate and oil dispersion.

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

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

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

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

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

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

methylated, ethylated, butylated) wherein the fatty acids can be obtained by hydrolysis of glycerol esters from plant and animal sources, and can be purified by distillation. Typical liquid diluents are described in Marsden, *Solvents Guide*, 2nd Ed., Interscience, New York, 1950.

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

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

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

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

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

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

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

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

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

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

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

Example A

High Strength Concentrate

compound 6	98.5%
silica aerogel	0.5%
synthetic amorphous fine silica	1.0%

Example B

Wettable Powder

compound 14	65.0%
dodecylphenol polyethylene glycol ether	2.0%
sodium ligninsulfonate	4.0%
sodium silicoaluminate	6.0%
montmorillonite (calcined)	23.0%

Example C

Granule

compound 20	10.0%
attapulgite granules (low volatile matter, 0.71/0.30 mm; U.S.S. No. 25–50 sieves)	90.0%

Example D

Extruded Pellet

compound 22	25.0%
anhydrous sodium sulfate	10.0%
crude calcium ligninsulfonate	5.0%
sodium alkylnaphthalenesulfonate	1.0%
calcium/magnesium bentonite	59.0%

Example E

Emulsifiable Concentrate

compound 31	10.0%
polyoxyethylene sorbitol hexoleate	20.0%
C_6–C_{10} fatty acid methyl ester	70.0%

Example F

Microemulsion

compound 6	5.0%
polyvinylpyrrolidone-vinyl acetate copolymer	30.0%
alkylpolyglycoside	30.0%
glyceryl monooleate	15.0%
water	20.0%

Example G

Seed Treatment

compound 14	20.00%
polyvinylpyrrolidone-vinyl acetate copolymer	5.00%
montan acid wax	5.00%
calcium ligninsulfonate	1.00%
polyoxyethylene/polyoxypropylene block copolymers	1.00%
stearyl alcohol (POE 20)	2.00%
polyorganosilane	0.20%
colorant red dye	0.05%
water	65.75%

Example H

Fertilizer Stick

compound 20	2.50%
pyrrolidone-styrene copolymer	4.80%
tristyrylphenyl 16-ethoxylate	2.30%
talc	0.80%
corn starch	5.00%
slow-release fertilizer	36.00%
kaolin	38.00%
water	10.60%

Example I

Suspension Concentrate

compound 22	35%
butyl polyoxyethylene/polypropylene block copolymer	4.0%
stearic acid/polyethylene glycol copolymer	1.0%
styrene acrylic polymer	1.0%
xanthan gum	0.1%
propylene glycol	5.0%
silicone based defoamer	0.1%
1,2-benzisothiazolin-3-one	0.1%
water	53.7%

Example J

Emulsion in Water

compound 31	10.0%
butyl polyoxyethylene/polypropylene block copolymer	4.0%
stearic acid/polyethylene glycol copolymer	1.0%

Emulsion in Water	
styrene acrylic polymer	1.0%
xanthan gum	0.1%
propylene glycol	5.0%
silicone based defoamer	0.1%
1,2-benzisothiazolin-3-one	0.1%
aromatic petroleum based hydrocarbon	20.0
water	58.7%

Example K

Oil Dispersion	
compound 6	25%
polyoxyethylene sorbitol hexaoleate	15%
organically modified bentonite clay	2.5%
fatty acid methyl ester	57.5%

Example L

Suspoemulsion	
compound 14	10.0%
imidacloprid	5.0%
butyl polyoxyethylene/polypropylene block copolymer	4.0%
stearic acid/polyethylene glycol copolymer	1.0%
styrene acrylic polymer	1.0%
xanthan gum	0.1%
propylene glycol	5.0%
silicone based defoamer	0.1%
1,2-benzisothiazolin-3-one	0.1%
aromatic petroleum based hydrocarbon	20.0%
water	53.7%

Compounds of this invention exhibit activity against a wide spectrum of invertebrate pests. These pests include invertebrates inhabiting a variety of environments such as, for example, plant foliage, roots, soil, harvested crops or other foodstuffs, building structures or animal integuments. These pests include, for example, invertebrates feeding on foliage (including leaves, stems, flowers and fruits), seeds, wood, textile fibers or animal blood or tissues, and thereby causing injury or damage to, for example, growing or stored agronomic crops, forests, greenhouse crops, ornamentals, nursery crops, stored foodstuffs or fiber products, or houses or other structures or their contents, or being harmful to animal health or public health. Those skilled in the art will appreciate that not all compounds are equally effective against all growth stages of all pests.

These present compounds and compositions are thus useful agronomically for protecting field crops from phytophagous invertebrate pests, and also nonagronomically for protecting other horticultural crops and plants from phytophagous invertebrate pests. This utility includes protecting crops and other plants (i.e. both agronomic and nonagronomic) that contain genetic material introduced by genetic engineering (i.e. transgenic) or modified by mutagenesis to provide advantageous traits. Examples of such traits include tolerance to herbicides, resistance to phytophagous pests (e.g., insects, mites, aphids, spiders, nematodes, snails, plant-pathogenic fungi, bacteria and viruses), improved plant growth, increased tolerance of adverse growing conditions such as high or low temperatures, low or high soil moisture, and high salinity, increased flowering or fruiting, greater harvest yields, more rapid maturation, higher quality and/or nutritional value of the harvested product, or improved storage or process properties of the harvested products. Transgenic plants can be modified to express multiple traits. Examples of plants containing traits provided by genetic engineering or mutagenesis include varieties of corn, cotton, soybean and potato expressing an insecticidal *Bacillus thuringiensis* toxin such as YIELD GARD®, KNOCKOUT®, STARLINK®, BOLLGARD®, NuCOTN® and NEWLEAF®, and herbicide-tolerant varieties of corn, cotton, soybean and rapeseed such as ROUNDUP READY®, LIBERTY LINK®, IMI®, STS® and CLEARFIELD®, as well as crops expressing *N*-acetyltransferase (GAT) to provide resistance to glyphosate herbicide, or crops containing the HRA gene providing resistance to herbicides inhibiting acetolactate synthase (ALS). The present compounds and compositions may interact synergistically with traits introduced by genetic engineering or modified by mutagenesis, thus enhancing phenotypic expression or effectiveness of the traits or increasing the invertebrate pest control effectiveness of the present compounds and compositions. In particular, the present compounds and compositions may interact synergistically with the phenotypic expression of proteins or other natural products toxic to invertebrate pests to provide greater-than-additive control of these pests.

Compositions of this invention can also optionally comprise plant nutrients, e.g., a fertilizer composition comprising at least one plant nutrient selected from nitrogen, phosphorus, potassium, sulfur, calcium, magnesium, iron, copper, boron, manganese, zinc, and molybdenum. Of note are compositions comprising at least one fertilizer composition comprising at least one plant nutrient selected from nitrogen, phosphorus, potassium, sulfur, calcium and magnesium. Compositions of the present invention which further comprise at least one plant nutrient can be in the form of liquids or solids. Of note are solid formulations in the form of granules, small sticks or tablets. Solid formulations comprising a fertilizer composition can be prepared by mixing the compound or composition of the present invention with the fertilizer composition together with formulating ingredients and then preparing the formulation by methods such as granulation or extrusion. Alternatively solid formulations can be prepared by spraying a solution or suspension of a compound or

composition of the present invention in a volatile solvent onto a previous prepared fertilizer composition in the form of dimensionally stable mixtures, e.g., granules, small sticks or tablets, and then evaporating the solvent.

Examples of agronomic or nonagronomic invertebrate pests include eggs, larvae and adults of the order Lepidoptera, such as armyworms, cutworms, loopers, and heliothines in the family Noctuidae (e.g., pink stem borer (*Sesamia inferens* Walker), corn stalk borer (*Sesamia nonagrioides* Lefebvre), southern armyworm (*Spodoptera eridania* Cramer), fall armyworm (*Spodoptera fugiperda* J. E. Smith), beet armyworm (*Spodoptera exigua* Hübner), cotton leafworm (*Spodoptera littoralis* Boisduval), yellowstriped armyworm (*Spodoptera ornithogalli* Guenée), black cutworm (*Agrotis ipsilon* Hufnagel), velvetbean caterpillar (*Anticarsia gemmatalis* Hübner), green fruitworm (*Lithophane antennata* Walker), cabbage armyworm (*Barathra brassicae* Linnaeus), soybean looper (*Pseudoplusia includens* Walker), cabbage looper (*Trichoplusia ni* Hübner), tobacco budworm (*Heliothis virescens* Fabricius)); borers, casebearers, webworms, coneworms, cabbageworms and skeletonizers from the family Pyralidae (e.g., European corn borer (*Ostrinia nubilalis* Hübner), navel orangeworm (*Amyelois transitella* Walker), corn root webworm (*Crambus caliginosellus* Clemens), sod webworms (Pyralidae: *Crambinae*) such as sod worm (*Herpetogramma licarsisalis* Walker), sugarcane stem borer (*Chilo infuscatellus* Snellen), tomato small borer (*Neoleucinodes elegantalis* Guenée), green leafroller (*Cnaphalocerus medinalis*), grape leaffolder (*Desmia funeralis* Hübner), melon worm (*Diaphania nitidalis* Stoll), cabbage center grub (*Helluala hydralis* Guenée), yellow stem borer (*Scirpophaga incertulas* Walker), early shoot borer (*Scirpophaga infuscatellus* Snellen), white stem borer (*Scirpophaga innotata* Walker), top shoot borer (*Scirpophaga nivella* Fabricius), dark-headed rice borer (*Chilo polychrysus* Meyrick), cabbage cluster caterpillar (*Crocidolomia binotalis* English)); leafrollers, budworms, seed worms, and fruit worms in the family Tortricidae (e.g., codling moth (*Cydia pomonella* Linnaeus), grape berry moth (*Endopiza viteana* Clemens), oriental fruit moth (*Grapholita molesta* Busck), citrus false codling moth (*Cryptophlebia leucotreta* Meyrick), citrus borer (*Ecdytolopha aurantiana* Lima), redbanded leafroller (*Argyrotaenia velutinana* Walker), obliquebanded leafroller (*Choristoneura rosaceana* Harris), light brown apple moth (*Epiphyas postvittana* Walker), European grape berry moth (*Eupoecilia ambiguella* Hübner), apple bud moth (*Pandemis pyrusana* Kearfott), omnivorous leafroller (*Platynota stultana* Walsingham), barred fruit-tree tortrix (*Pandemis cerasana* Hübner), apple brown tortrix (*Pandemis heparana* Denis & Schiffermüller)); and many other economically important lepidoptera (e.g., diamondback moth (*Plutella xylostella* Linnaeus), pink bollworm (*Pectinophora gossypiella* Saunders), gypsy moth (*Lymantria dispar* Linnaeus), peach fruit borer (*Carposina niponensis* Walsingham), peach twig borer (*Anarsia lineatella* Zeller), potato tuberworm (*Phthorimaea operculella* Zeller), spotted teniform leafminer (*Lithocolletis blancardella* Fabricius), Asiatic apple leafminer

(*Lithocolletis ringoniella* Matsumura), rice leaffolder (*Lerodea eufala* Edwards), apple leafminer (*Leucoptera scitella* Zeller)); eggs, nymphs and adults of the order Blattodea including cockroaches from the families Blattellidae and Blattidae (e.g., oriental cockroach (*Blatta orientalis* Linnaeus), Asian cockroach (*Blatella asahinai* Mizukubo), German cockroach (*Blattella germanica* Linnaeus), brownbanded cockroach (*Supella longipalpa* Fabricius), American cockroach (*Periplaneta americana* Linnaeus), brown cockroach (*Periplaneta brunnea* Burmeister), Madeira cockroach (*Leucophaea maderae* Fabricius)), smoky brown cockroach (*Periplaneta fuliginosa* Service), Australian Cockroach (*Periplaneta australasiae* Fabr.), lobster cockroach (*Nauphoeta cinerea* Olivier) and smooth cockroach (*Symploce pallens* Stephens)); eggs, foliar feeding, fruit feeding, root feeding, seed feeding and vesicular tissue feeding larvae and adults of the order Coleoptera including weevils from the families Anthribidae, Bruchidae, and Curculionidae (e.g., boll weevil (*Anthonomus grandis* Boheman), rice water weevil (*Lissorhoptrus oryzophilus* Kuschel), granary weevil (*Sitophilus granarius* Linnaeus), rice weevil (*Sitophilus oryzae* Linnaeus)), annual bluegrass weevil (*Listronotus maculicollis* Dietz), bluegrass billbug (*Sphenophorus parvulus* Gyllenhal), hunting billbug (*Sphenophorus venatus vestitus*), Denver billbug (*Sphenophorus cicatristriatus* Fahraeus)); flea beetles, cucumber beetles, rootworms, leaf beetles, potato beetles, and leafminers in the family Chrysomelidae (e.g., Colorado potato beetle (*Leptinotarsa decemlineata* Say), western corn rootworm (*Diabrotica virgifera virgifera* LeConte)); chafers and other beetles from the family Scarabaeidae (e.g., Japanese beetle (*Popillia japonica* Newman), oriental beetle (*Anomala orientalis* Waterhouse, *Exomala orientalis* (Waterhouse) Baraud), northern masked chafer (*Cyclocephala borealis* Arrow), southern masked chafer (*Cyclocephala immaculata* Olivier or *C. lurida* Bland), dung beetle and white grub (Aphodius spp.), black turfgrass ataenius (*Ataenius spretulus* Haldeman), green June beetle (*Cotinis nitida* Linnaeus), Asiatic garden beetle (*Maladera castanea* Arrow), May/June beetles (*Phyllophaga* spp.) and European chafer (*Rhizotrogus majalis* Razoumowsky)); carpet beetles from the family Dermestidae; wireworms from the family Elateridae; bark beetles from the family Scolytidae and flour beetles from the family Tenebrionidae.

In addition, agronomic and nonagronomic pests include: eggs, adults and larvae of the order Dermaptera including earwigs from the family Forficulidae (e.g., European earwig (*Forficula auricularia* Linnaeus), black earwig (*Chelisoches morio* Fabricius)); eggs, immatures, adults and nymphs of the orders Hemiptera and Homoptera such as, plant bugs from the family Miridae, cicadas from the family Cicadidae, leafhoppers (e.g. *Empoasca* spp.) from the family Cicadellidae, bed bugs (e.g., *Cimex lectularius* Linnaeus) from the family Cimicidae, planthoppers from the families Fulgoroidae and Delphacidae, treehoppers from the family Membracidae, psyllids from the family Psyllidae, whiteflies from the family Aleyrodidae, aphids from the family Aphididae, phylloxera from the family Phylloxeridae,

mealybugs from the family Pseudococcidae, scales from the families Coccidae, Diaspididae and Margarodidae, lace bugs from the family Tingidae, stink bugs from the family Pentatomidae, chinch bugs (e.g., hairy chinch bug (*Blissus leucopterus hirtus* Montandon) and southern chinch bug (*Blissus insularis* Barber)) and other seed bugs from the family Lygaeidae, spittlebugs from the family Cercopidae squash bugs from the family Coreidae, and red bugs and cotton stainers from the family Pyrrhocoridae.

Agronomic and nonagronomic pests also include: eggs, larvae, nymphs and adults of the order Acari (mites) such as spider mites and red mites in the family Tetranychidae (e.g., European red mite (*Panonychus ulmi* Koch), two spotted spider mite (*Tetranychus urticae* Koch), McDaniel mite (*Tetranychus mcdanieli* McGregor)); flat mites in the family Tenuipalpidae (e.g., citrus flat mite (*Brevipalpus lewisi* McGregor)); rust and bud mites in the family Eriophyidae and other foliar feeding mites and mites important in human and animal health, i.e. dust mites in the family Epidermoptidae, follicle mites in the family Demodicidae, grain mites in the family Glycyphagidae; ticks in the family Ixodidae, commonly known as hard ticks (e.g., deer tick (*Ixodes scapularis* Say), Australian paralysis tick (*Ixodes holocyclus* Neumann), American dog tick (*Dermacentor variabilis* Say), lone star tick (*Amblyomma americanum* Linnaeus)) and ticks in the family Argasidae, commonly known as soft ticks (e.g., relapsing fever tick (*Ornithodoros turicata*), common fowl tick (*Argas radiatus*)); scab and itch mites in the families Psoroptidae, Pyemotidae, and Sarcoptidae; eggs, adults and immatures of the order Orthoptera including grasshoppers, locusts and crickets (e.g., migratory grasshoppers (e.g., *Melanoplus sanguinipes* Fabricius, *M. differentialis* Thomas), American grasshoppers (e.g., *Schistocerca americana* Drury), desert locust (*Schistocerca gregaria* Forskal), migratory locust (*Locusta migratoria* Linnaeus), bush locust (*Zonocerus* spp.), house cricket (*Acheta domesticus* Linnaeus), mole crickets (e.g., tawny mole cricket (*Scapteriscus vicinus* Scudder) and southern mole cricket (*Scapteriscus borellii* Giglio-Tos)); eggs, adults and immatures of the order Diptera including leafminers (e.g., *Liriomyza* spp. such as serpentine vegetable leafminer (*Liriomyza sativae* Blanchard)), midges, fruit flies (Tephritidae), frit flies (e.g., *Oscinella frit* Linnaeus), soil maggots, house flies (e.g., *Musca domestica* Linnaeus), lesser house flies (e.g., *Fannia canicularis* Linnaeus, *F. femoralis* Stein), stable flies (e.g., *Stomoxys calcitrans* Linnaeus), face flies, horn flies, blow flies (e.g., *Chrysomya* spp., *Phormia* spp.), and other muscoid fly pests, horse flies (e.g., *Tabanus* spp.), bot flies (e.g., *Gastrophilus* spp., *Oestrus* spp.), cattle grubs (e.g., *Hypoderma* spp.), deer flies (e.g., *Chrysops* spp.), keds (e.g., *Melophagus ovinus* Linnaeus) and other Brachycera, mosquitoes (e.g., *Aedes* spp., *Anopheles* spp., *Culex* spp.), black flies (e.g., *Prosimulium* spp., *Simulium* spp.), biting midges, sand flies, sciarids, and other Nematocera; eggs, adults and immatures of the order Thysanoptera including onion thrips (*Thrips tabaci* Lindeman), flower thrips (*Frankliniella* spp.), and other foliar feeding thrips; insect pests of the order Hymenoptera including ants of the Family Formicidae

including the Florida carpenter ant (*Camponotus floridanus* Buckley), red carpenter ant (*Camponotus ferrugineus* Fabricius), black carpenter ant (*Camponotus pennsylvanicus* De Geer), white-footed ant (*Technomyrmex albipes* fr. Smith), big headed ants (*Pheidole* sp.), ghost ant (*Tapinoma melanocephalum* Fabricius); Pharaoh ant (*Monomorium pharaonis* Linnaeus), little fire ant (*Wasmannia auropunctata* Roger), fire ant (*Solenopsis geminata* Fabricius), red imported fire ant (*Solenopsis invicta* Buren), Argentine ant (*Iridomyrmex humilis* Mayr), crazy ant (*Paratrechina longicornis* Latreille), pavement ant (*Tetramorium caespitum* Linnaeus), cornfield ant (*Lasius alienus* Förster) and odorous house ant (*Tapinoma sessile* Say). Other Hymenoptera including bees (including carpenter bees), hornets, yellow jackets, wasps, and sawflies (*Neodiprion* spp.; *Cephus* spp.); insect pests of the order Isoptera including termites in the Termitidae (e.g., *Macrotermes* sp., *Odontotermes obesus* Rambur), Kalotermitidae (e.g., *Cryptotermes* sp.), and Rhinotermitidae (e.g., *Reticulitermes* sp., *Coptotermes* sp., *Heterotermes tenuis* Hagen) families, the eastern subterranean termite (*Reticulitermes flavipes* Kollar), western subterranean termite (*Reticulitermes hesperus* Banks), Formosan subterranean termite (*Coptotermes formosanus* Shiraki), West Indian drywood termite (*Incisitermes immigrans* Snyder), powder post termite (*Cryptotermes brevis* Walker), drywood termite (*Incisitermes snyderi* Light), southeastern subterranean termite (*Reticulitermes virginicus* Banks), western drywood termite (*Incisitermes minor* Hagen), arboreal termites such as *Nasutitermes* sp. and other termites of economic importance; insect pests of the order Thysanura such as silverfish (*Lepisma saccharina* Linnaeus) and firebrat (*Thermobia domestica* Packard); insect pests of the order Mallophaga and including the head louse (*Pediculus humanus capitis* De Geer), body louse (*Pediculus humanus* Linnaeus), chicken body louse (*Menacanthus stramineus* Nitszch), dog biting louse (*Trichodectes canis* De Geer), fluff louse (*Goniocotes gallinae* De Geer), sheep body louse (*Bovicola ovis* Schrank), short-nosed cattle louse (*Haematopinus eurysternus* Nitzsch), long-nosed cattle louse (*Linognathus vituli* Linnaeus) and other sucking and chewing parasitic lice that attack man and animals; insect pests of the order Siphonoptera including the oriental rat flea (*Xenopsylla cheopis* Rothschild), cat flea (*Ctenocephalides felis* Bouche), dog flea (*Ctenocephalides canis* Curtis), hen flea (*Ceratophyllus gallinae* Schrank), sticktight flea (*Echidnophaga gallinacea* Westwood), human flea (*Pulex irritans* Linnaeus) and other fleas afflicting mammals and birds. Additional arthropod pests covered include: spiders in the order Araneae such as the brown recluse spider (*Loxosceles reclusa* Gertsch & Mulaik) and the black widow spider (*Latrodectus mactans* Fabricius), and centipedes in the order Scutigeromorpha such as the house centipede (*Scutigera coleoptrata* Linnaeus).

Examples of invertebrate pests of stored grain include larger grain borer (*Prostephanus truncatus*), lesser grain borer (*Rhyzopertha dominica*), rice weevil (*Stiophilus oryzae*), maize weevil (*Stiophilus zeamais*), cowpea weevil (*Callosobruchus maculatus*), red flour beetle

(*Tribolium castaneum*), granary weevil (*Stiophilus granarius*), Indian meal moth (*Plodia interpunctella*), Mediterranean flour beetle (*Ephestia kuhniella*) and flat or rusty grain beetle (*Cryptolestis ferrugineus*).

Compounds of the invention show particularly high activity against pests in the order Lepidoptera (e.g., *Alabama argillacea* Hübner (cotton leaf worm), *Archips argyrospila* Walker (fruit tree leaf roller), *A. rosana* Linnaeus (European leaf roller) and other *Archips* species, *Chilo suppressalis* Walker (rice stem borer), *Cnaphalocrosis medinalis* Guenée (rice leaf roller), *Crambus caliginosellus* Clemens (corn root webworm), *Crambus teterrellus* Zincken (bluegrass webworm), *Cydia pomonella* Linnaeus (codling moth), *Earias insulana* Boisduval (spiny bollworm), *Earias vittella* Fabricius (spotted bollworm), *Helicoverpa armigera* Hübner (American bollworm), *Helicoverpa zea* Boddie (corn earworm), *Heliothis virescens* Fabricius (tobacco budworm), *Herpetogramma licarsisalis* Walker (sod webworm), *Lobesia botrana* Denis & Schiffermüller (grape berry moth), *Pectinophora gossypiella* Saunders (pink bollworm), *Phyllocnistis citrella* Stainton (citrus leafminer), *Pieris brassicae* Linnaeus (large white butterfly), *Pieris rapae* Linnaeus (small white butterfly), *Plutella xylostella* Linnaeus (diamondback moth), *Spodoptera exigua* Hübner (beet armyworm), *Spodoptera litura* Fabricius (tobacco cutworm, cluster caterpillar), *Spodoptera frugiperda* J. E. Smith (fall armyworm), *Trichoplusia ni* Hübner (cabbage looper) and *Tuta absoluta* Meyrick (tomato leafminer)).

Compounds of the invention also have significant activity on members from the order Homoptera including: *Acyrthosiphon pisum* Harris (pea aphid), *Aphis craccivora* Koch (cowpea aphid), *Aphis fabae* Scopoli (black bean aphid), *Aphis gossypii* Glover (cotton aphid, melon aphid), *Aphis pomi* De Geer (apple aphid), *Aphis spiraecola* Patch (spirea aphid), *Aulacorthum solani* Kaltenbach (foxglove aphid), *Chaetosiphon fragaefolii* Cockerell (strawberry aphid), *Diuraphis noxia* Kurdjumov/Mordvilko (Russian wheat aphid), *Dysaphis plantaginea* Paaserini (rosy apple aphid), *Eriosoma lanigerum* Hausmann (woolly apple aphid), *Hyalopterus pruni* Geoffroy (mealy plum aphid), *Lipaphis erysimi* Kaltenbach (turnip aphid), *Metopolophium dirrhodum* Walker (cereal aphid), *Macrosiphum euphorbiae* Thomas (potato aphid), *Myzus persicae* Sulzer (peach-potato aphid, green peach aphid), *Nasonovia ribisnigri* Mosley (lettuce aphid), *Pemphigus* spp. (root aphids and gall aphids), *Rhopalosiphum maidis* Fitch (corn leaf aphid), *Rhopalosiphum padi* Linnaeus (bird cherry-oat aphid), *Schizaphis graminum* Rondani (greenbug), *Sitobion avenae* Fabricius (English grain aphid), *Therioaphis maculata* Buckton (spotted alfalfa aphid), *Toxoptera aurantii* Boyer de Fonscolombe (black citrus aphid), and *Toxoptera citricida* Kirkaldy (brown citrus aphid); *Adelges* spp. (adelgids); *Phylloxera devastatrix* Pergande (pecan phylloxera); *Bemisia tabaci* Gennadius (tobacco whitefly, sweetpotato whitefly), *Bemisia argentifolii* Bellows & Perring (silverleaf whitefly), *Dialeurodes citri* Ashmead (citrus whitefly) and *Trialeurodes vaporariorum* Westwood (greenhouse whitefly); *Empoasca*

fabae Harris (potato leafhopper), *Laodelphax striatellus* Fallen (smaller brown planthopper), *Macrolestes quadrilineatus* Forbes (aster leafhopper), *Nephotettix cinticeps* Uhler (green leafhopper), *Nephotettix nigropictus* Stål (rice leafhopper), *Nilaparvata lugens* Stål (brown planthopper), *Peregrinus maidis* Ashmead (corn planthopper), *Sogatella furcifera* Horvath (white-backed planthopper), *Sogatodes orizicola* Muir (rice delphacid), *Typhlocyba pomaria* McAtee white apple leafhopper, *Erythroneoura* spp. (grape leafhoppers); *Magicidada septendecim* Linnaeus (periodical cicada); *Icerya purchasi* Maskell (cottony cushion scale), *Quadraspidiotus perniciosus* Comstock (San Jose scale); *Planococcus citri* Risso (citrus mealybug); *Pseudococcus* spp. (other mealybug complex); *Cacopsylla pyricola* Foerster (pear psylla), *Trioza diospyri* Ashmead (persimmon psylla).

Compounds of this invention may also have activity on members from the order Hemiptera including: *Acrosternum hilare* Say (green stink bug), *Anasa tristis* De Geer (squash bug), *Blissus leucopterus leucopterus* Say (chinch bug), *Cimex lectularius* Linnaeus (bed bug) *Corythuca gossypii* Fabricius (cotton lace bug), *Cyrtopeltis modesta* Distant (tomato bug), *Dysdercus suturellus* Herrich-Schäffer (cotton stainer), *Euchistus servus* Say (brown stink bug), *Euchistus variolarius* Palisot de Beauvois (one-spotted stink bug), *Graptosthetus* spp. (complex of seed bugs), *Leptoglossus corculus* Say (leaf-footed pine seed bug), *Lygus lineolaris* Palisot de Beauvois (tarnished plant bug), *Nezara viridula* Linnaeus (southern green stink bug), *Oebalus pugnax* Fabricius (rice stink bug), *Oncopeltus fasciatus* Dallas (large milkweed bug), *Pseudatomoscelis seriatus* Reuter (cotton fleahopper). Other insect orders controlled by compounds of the invention include Thysanoptera (e.g., *Frankliniella occidentalis* Pergande (western flower thrips), *Scirthothrips citri* Moulton (citrus thrips), *Sericothrips variabilis* Beach (soybean thrips), and *Thrips tabaci* Lindeman (onion thrips); and the order Coleoptera (e.g., *Leptinotarsa decemlineata* Say (Colorado potato beetle), *Epilachna varivestis* Mulsant (Mexican bean beetle) and wireworms of the genera *Agriotes*, *Athous* or *Limonius*).

Compounds of the present invention also have activity on members of the Classes Nematoda, Cestoda, Trematoda, and Acanthocephala including economically important members of the orders Strongylida, Ascaridida, Oxyurida, Rhabditida, Spirurida, and Enoplida such as but not limited to economically important agricultural pests (i.e. root knot nematodes in the genus *Meloidogyne*, lesion nematodes in the genus *Pratylenchus*, stubby root nematodes in the genus *Trichodorus*, etc.) and animal and human health pests (i.e. all economically important flukes, tapeworms, and roundworms, such as *Strongylus vulgaris* in horses, *Toxocara canis* in dogs, *Haemonchus contortus* in sheep, *Dirofilaria immitis* Leidy in dogs, *Anoplocephala perfoliata* in horses, *Fasciola hepatica* Linnaeus in ruminants, etc.).

Note that some contemporary classification systems place Homoptera as a suborder within the order Hemiptera.

Of note is use of compounds of this invention for controlling potato leafhopper (*Empoasca fabae*). Of note is use of compounds of this invention for controlling corn planthopper (*Peregrinus maidis*). Of note is use of compounds of this invention for controlling cotton melon aphid (*Aphis gossypii*). Of note is use of compounds of this invention for controlling green peach aphid (*Myzus persicae*). Of note is use of compounds of this invention for controlling diamondback moth (*Plutella xylostella*). Of note is use of compounds of this invention for controlling fall armyworm (*Spodoptera frugiperda*).

Of note is use of compounds of this invention for controlling southern green stink bug (*Nezara viridula*), western tarnished plant bug (*Lygus hesperus*), rice water weevil (*Lissorhoptrus oryzophilus*), rice brown planthopper (*Nilaparvata lugens*), rice green leafhopper (*Nephotettix virescens*) and striped rice borer (*Chilo suppressalis*).

Compounds of this invention can also be mixed with one or more other biologically active compounds or agents including insecticides, fungicides, nematocides, bactericides, acaricides, herbicides, herbicide safeners, growth regulators such as insect molting inhibitors and rooting stimulants, chemosterilants, semiochemicals, repellents, attractants, pheromones, feeding stimulants, other biologically active compounds or entomopathogenic bacteria, virus or fungi to form a multi-component pesticide giving an even broader spectrum of agronomic and nonagronomic utility. Thus the present invention also pertains to a composition comprising a biologically effective amount of a compound of Formula **1**, an *N*-oxide, or salt thereof, at least one additional component selected from the group consisting of surfactants, solid diluents and liquid diluents, and at least one additional biologically active compound or agent. For mixtures of the present invention, the other biologically active compounds or agents can be formulated together with the present compounds, including the compounds of Formula **1**, to form a premix, or the other biologically active compounds or agents can be formulated separately from the present compounds, including the compounds of Formula **1**, and the two formulations combined together before application (e.g., in a spray tank) or, alternatively, applied in succession.

Examples of such biologically active compounds or agents with which compounds of this invention can be formulated are insecticides such as abamectin, acephate, acequinocyl, acetamiprid, acrinathrin, amidoflumet, amitraz, avermectin, azadirachtin, azinphos-methyl, bensultap, bifenthrin, bifenazate, bistrifluron, borate, buprofezin, cadusafos, carbaryl, carbofuran, cartap, carzol, chlorantraniliprole, chlorfenapyr, chlorfluazuron, chlorpyrifos, chlorpyrifos-methyl, chromafenozide, clofentezin, clothianidin, cyantraniliprole, cyflumetofen, cyfluthrin, beta-cyfluthrin, cyhalothrin, gamma-cyhalothrin, lambda-cyhalothrin, cypermethrin, alpha-cypermethrin, zeta-cypermethrin, cyromazine, deltamethrin, diafenthiuron, diazinon, dieldrin, diflubenzuron, dimefluthrin, dimehypo, dimethoate, dinotefuran, diofenolan, emamectin, endosulfan, esfenvalerate, ethiprole, etofenprox, etoxazole, fenbutatin oxide, fenothiocarb, fenoxycarb, fenpropathrin,

fenvalerate, fipronil, flonicamid, flubendiamide, flucythrinate, flufenerim, flufenoxuron, fluvalinate, tau-fluvalinate, fonophos, formetanate, fosthiazate, halofenozide, hexaflumuron, hexythiazox, hydramethylnon, imidacloprid, indoxacarb, insecticidal soaps, isofenphos, lufenuron, malathion, meperfluthrin, metaflumizone, metaldehyde, methamidophos, methidathion, methiodicarb, methomyl, methoprene, methoxychlor, metofluthrin, monocrotophos, methoxyfenozide, nitenpyram, nithiazine, novaluron, noviflumuron, oxamyl, parathion, parathion-methyl, permethrin, phorate, phosalone, phosmet, phosphamidon, pirimicarb, profenofos, profluthrin, propargite, protrifenbute, pymetrozine, pyrafluprole, pyrethrin, pyridaben, pyridalyl, pyrifluquinazon, pyriprole, pyriproxyfen, rotenone, ryanodine, spinetoram, spinosad, spirodiclofen, spiromesifen, spirotetramat, sulprofos, sulfoxaflor, tebufenozide, tebufenpyrad, teflubenzuron, tefluthrin, terbufos, tetrachlorvinphos, tetramethrin, tetramethylfluthrin, thiacloprid, thiamethoxam, thiodicarb, thiosultap-sodium, tolfenpyrad, tralomethrin, triazamate, trichlorfon, triflumuron, *Bacillus thuringiensis* delta-endotoxins, entomopathogenic bacteria, entomopathogenic viruses and entomopathogenic fungi.

Of note are insecticides such as abamectin, acetamiprid, acrinathrin, amitraz, avermectin, azadirachtin, bensultap, bifenthrin, buprofezin, cadusafos, carbaryl, cartap, chlorantraniliprole, chlorfenapyr, chlorpyrifos, clothianidin, cyantraniliprole, cyfluthrin, beta-cyfluthrin, cyhalothrin, gamma-cyhalothrin, lambda-cyhalothrin, cypermethrin, alpha-cypermethrin, zeta-cypermethrin, cyromazine, deltamethrin, dieldrin, dinotefuran, diofenolan, emamectin, endosulfan, esfenvalerate, ethiprole, etofenprox, etoxazole, fenothiocarb, fenoxycarb, fenvalerate, fipronil, flonicamid, flubendiamide, flufenoxuron, fluvalinate, formetanate, fosthiazate, hexaflumuron, hydramethylnon, imidacloprid, indoxacarb, lufenuron, metaflumizone, methiodicarb, methomyl, methoprene, methoxyfenozide, nitenpyram, nithiazine, novaluron, oxamyl, pymetrozine, pyrethrin, pyridaben, pyridalyl, pyriproxyfen, ryanodine, spinetoram, spinosad, spirodiclofen, spiromesifen, spirotetramat, tebufenozide, tetramethrin, thiacloprid, thiamethoxam, thiodicarb, thiosultap-sodium, tralomethrin, triazamate, triflumuron, *Bacillus thuringiensis* delta-endotoxins, all strains of *Bacillus thuringiensis* and all strains of *Nucleo polyhydrosis* viruses.

One embodiment of biological agents for mixing with compounds of this invention include entomopathogenic bacteria such as *Bacillus thuringiensis,* and the encapsulated delta-endotoxins of *Bacillus thuringiensis* such as MVP® and MVPII® bioinsecticides prepared by the CellCap® process (CellCap®, MVP® and MVPII® are trademarks of Mycogen Corporation, Indianapolis, Indiana, USA); entomopathogenic fungi such as green muscardine fungus; and entomopathogenic (both naturally occurring and genetically modified) viruses including baculovirus, nucleopolyhedro virus (NPV) such as *Helicoverpa*

zea nucleopolyhedrovirus (HzNPV), *Anagrapha falcifera* nucleopolyhedrovirus (AfNPV); and granulosis virus (GV) such as *Cydia pomonella* granulosis virus (CpGV).

Of particular note is such a combination where the other invertebrate pest control active ingredient belongs to a different chemical class or has a different site of action than the compound of Formula **1**. In certain instances, a combination with at least one other invertebrate pest control active ingredient having a similar spectrum of control but a different site of action will be particularly advantageous for resistance management. Thus, a composition of the present invention can further comprise a biologically effective amount of at least one additional invertebrate pest control active ingredient having a similar spectrum of control but belonging to a different chemical class or having a different site of action. These additional biologically active compounds or agents include, but are not limited to, sodium channel modulators such as bifenthrin, cypermethrin, cyhalothrin, lambda-cyhalothrin, cyfluthrin, beta-cyfluthrin, deltamethrin, dimefluthrin, esfenvalerate, fenvalerate, indoxacarb, metofluthrin, profluthrin, pyrethrin and tralomethrin; cholinesterase inhibitors such as chlorpyrifos, methomyl, oxamyl, thiodicarb and triazamate; neonicotinoids such as acetamiprid, clothianidin, dinotefuran, imidacloprid, nitenpyram, nithiazine, thiacloprid and thiamethoxam; insecticidal macrocyclic lactones such as spinetoram, spinosad, abamectin, avermectin and emamectin; GABA (γ–aminobutyric acid)-gated chloride channel antagonists such as avermectin or blockers such as ethiprole and fipronil; chitin synthesis inhibitors such as buprofezin, cyromazine, flufenoxuron, hexaflumuron, lufenuron, novaluron, noviflumuron and triflumuron; juvenile hormone mimics such as diofenolan, fenoxycarb, methoprene and pyriproxyfen; octopamine receptor ligands such as amitraz; molting inhibitors and ecdysone agonists such as azadirachtin, methoxyfenozide and tebufenozide; ryanodine receptor ligands such as ryanodine, anthranilic diamides such as chlorantraniliprole, cyantraniliprole and flubendiamide; nereistoxin analogs such as cartap; mitochondrial electron transport inhibitors such as chlorfenapyr, hydramethylnon and pyridaben; lipid biosynthesis inhibitors such as spirodiclofen and spiromesifen; cyclodiene insecticides such as dieldrin or endosulfan; pyrethroids; carbamates; insecticidal ureas; and biological agents including nucleopolyhedro viruses (NPV), members of *Bacillus thuringiensis*, encapsulated delta-endotoxins of *Bacillus thuringiensis*, and other naturally occurring or genetically modified insecticidal viruses.

Further examples of biologically active compounds or agents with which compounds of this invention can be formulated are: fungicides such as 1-[4-[4-[5-(2,6-difluorophenyl)-4,5-dihydro-3-isoxazolyl]-2-thiazolyl]-1-piperidinyl]-2-[5-methyl-3-(trifluoromethyl)-1*H*-pyrazol-1-yl]ethanone, acibenzolar, aldimorph, amisulbrom, azaconazole, azoxystrobin, benalaxyl, benomyl, benthiavalicarb, benthiavalicarb-isopropyl, binomial, biphenyl, bitertanol, blasticidin-S, Bordeaux mixture (Tribasic copper sulfate), boscalid/nicobifen, bromuconazole, bupirimate, buthiobate, carboxin, carpropamid, captafol, captan,

carbendazim, chloroneb, chlorothalonil, chlozolinate, clotrimazole, copper oxychloride, copper salts such as copper sulfate and copper hydroxide, cyazofamid, cyflunamid, cymoxanil, cyproconazole, cyprodinil, dichlofluanid, diclocymet, diclomezine, dicloran, diethofencarb, difenoconazole, dimethomorph, dimoxystrobin, diniconazole, diniconazole-M, dinocap, discostrobin, dithianon, dodemorph, dodine, econazole, etaconazole, edifenphos, epoxiconazole, ethaboxam, ethirimol, ethridiazole, famoxadone, fenamidone, fenarimol, fenbuconazole, fencaramid, fenfuram, fenhexamide, fenoxanil, fenpiclonil, fenpropidin, fenpropimorph, fentin acetate, fentin hydroxide, ferbam, ferfurazoate, ferimzone, fluazinam, fludioxonil, flumetover, fluopicolide, fluoxastrobin, fluquinconazole, fluquinconazole, flusilazole, flusulfamide, flutolanil, flutriafol, fluxapyroxad, folpet, fosetyl-aluminum, fthalide, fuberidazole, furalaxyl, furametpyr, hexaconazole, hymexazole, guazatine, imazalil, imibenconazole, iminoctadine, iodicarb, ipconazole, iprobenfos, iprodione, iprovalicarb, isoconazole, isoprothiolane, isotianil, kasugamycin, kresoxim-methyl, mancozeb, mandipropamid, maneb, mapanipyrin, mefenoxam, mepronil, metalaxyl, metconazole, methasulfocarb, metiram, metominostrobin/fenominostrobin, mepanipyrim, metrafenone, miconazole, myclobutanil, neo-asozin (ferric methanearsonate), nuarimol, octhilinone, ofurace, orysastrobin, oxadixyl, oxolinic acid, oxpoconazole, oxycarboxin, paclobutrazol, penconazole, pencycuron, penflufen, penthiopyrad, perfurazoate, phosphonic acid, phthalide, picobenzamid, picoxystrobin, polyoxin, probenazole, prochloraz, procymidone, propamocarb, propamocarb-hydrochloride, propiconazole, propineb, proquinazid, prothioconazole, pyraclostrobin, pyrametostrobin, pyraoxystrobin, pryazophos, pyrifenox, pyrimethanil, pyrifenox, pyriofenone, pyrolnitrine, pyroquilon, quinconazole, quinoxyfen, quintozene, silthiofam, simeconazole, spiroxamine, streptomycin, sulfur, tebuconazole, tebufloquin, techrazene, tecloftalam, tecnazene, tetraconazole, thiabendazole, thifluzamide, thiophanate, thiophanate-methyl, thiram, tiadinil, tolclofos-methyl, tolyfluanid, triadimefon, triadimenol, triarimol, triazoxide, tridemorph, trimorphamide, tricyclazole, trifloxystrobin, triforine, triticonazole, uniconazole, validamycin, valifenalate, vinclozolin, zineb, ziram, and zoxamide; nematocides such as aldicarb, imicyafos, oxamyl and fenamiphos; bactericides such as streptomycin; acaricides such as amitraz, chinomethionat, chlorobenzilate, cyhexatin, dicofol, dienochlor, etoxazole, fenazaquin, fenbutatin oxide, fenpropathrin, fenpyroximate, hexythiazox, propargite, pyridaben and tebufenpyrad.

Of note are fungicides and compositions comprising fungicides such as 1-[4-[4-[5-(2,6-difluorophenyl)-4,5-dihydro-3-isoxazolyl]-2-thiazolyl]-1-piperidinyl]-2-[5-methyl-3-(trifluoromethyl)-1*H*-pyrazol-1-yl]ethanone, azoxystrobin, copper hydroxide, cymoxanil, cyproconazole, difenoconazole, famoxadone, fenoxanil, ferimzone, flusilazole, flutolanil, fthalide, furametpyr, hexaconazole, isoprothiolane, isotianil, kasugamycin, mancozeb, metominostrobin, orysastrobin, pencycuron, penthiopyrad, picoxystrobin, probenazole,

propiconazole, proquinazid, pyroquilon, simeconazole, tiadinil, tricyclazole, trifloxystrobin and validamycin.

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

Compounds of this invention and compositions thereof can be applied to plants genetically transformed to express proteins toxic to invertebrate pests (such as *Bacillus thuringiensis* delta-endotoxins). Such an application may provide a broader spectrum of plant protection and be advantageous for resistance management. The effect of the exogenously applied invertebrate pest control compounds of this invention may be synergistic with the expressed toxin proteins.

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

For embodiments where one or more of these various mixing partners are used, the weight ratio of these various mixing partners (in total) to the compound of Formula **1**, an *N*-oxide, or salt thereof, is typically between about 1:3000 and about 3000:1. Of note are weight ratios between about 1:300 and about 300:1 (for example ratios between about 1:30 and about 30:1). One skilled in the art can easily determine through simple experimentation the biologically effective amounts of active ingredients necessary for the desired spectrum of biological activity. It will be evident that including these additional components can expand the spectrum of invertebrate pests controlled beyond the spectrum controlled by the compound of Formula **1** alone.

Table A lists specific combinations of a compound of Formula **1** with other invertebrate pest control agents illustrative of the mixtures, compositions and methods of the present invention. The first column of Table A lists the specific invertebrate pest control agents (e.g., "Abamectin" in the first line). The second column of Table A lists the mode of action (if known) or chemical class of the invertebrate pest control agents. The third column of Table A lists embodiment(s) of ranges of weight ratios for rates at which a compound of Formula **1** can be applied relative to an invertebrate pest control agent (e.g., "50:1 to 1:50" of a compound of Formula **1** relative to abamectin by weight). Thus, for example, the first

line of Table A specifically discloses the combination of a compound of Formula **1** with abamectin can be applied in a weight ratio between 50:1 to 1:50. The remaining lines of Table A are to be construed similarly. Of further note Table A lists specific combinations of a compound of Formula **1** with other invertebrate pest control agents illustrative of the mixtures, compositions and methods of the present invention and includes additional embodiments of weight ratio ranges for application rates.

Table A

Invertebrate Pest Control Agent	Mode of Action or Chemical Class	Typical Weight Ratio
Abamectin	macrocyclic lactones	50:1 to 1:50
Acetamiprid	neonicotinoids	150:1 to 1:200
Amitraz	octopamine receptor ligands	200:1 to 1:100
Avermectin	macrocyclic lactones	50:1 to 1:50
Azadirachtin	ecdysone agonists	100:1 to 1:120
Beta-cyfluthrin	sodium channel modulators	150:1 to 1:200
Bifenthrin	sodium channel modulators	100:1 to 1:10
Buprofezin	chitin synthesis inhibitors	500:1 to 1:50
Cartap	nereistoxin analogs	100:1 to 1:200
Chlorantraniliprole	ryanodine receptor ligands	100:1 to 1:120
Chlorfenapyr	mitochondrial electron transport inhibitors	300:1 to 1:200
Chlorpyrifos	cholinesterase inhibitors	500:1 to 1:200
Clothianidin	neonicotinoids	100:1 to 1:400
Cyantraniliprole	ryanodine receptor ligands	100:1 to 1:120
Cyfluthrin	sodium channel modulators	150:1 to 1:200
Cyhalothrin	sodium channel modulators	150:1 to 1:200
Cypermethrin	sodium channel modulators	150:1 to 1:200
Cyromazine	chitin synthesis inhibitors	400:1 to 1:50
Deltamethrin	sodium channel modulators	50:1 to 1:400
Dieldrin	cyclodiene insecticides	200:1 to 1:100
Dinotefuran	neonicotinoids	150:1 to 1:200
Diofenolan	molting inhibitor	150:1 to 1:200
Emamectin	macrocyclic lactones	50:1 to 1:10
Endosulfan	cyclodiene insecticides	200:1 to 1:100
Esfenvalerate	sodium channel modulators	100:1 to 1:400
Ethiprole	GABA-regulated chloride channel blockers	200:1 to 1:100
Fenothiocarb		150:1 to 1:200
Fenoxycarb	juvenile hormone mimics	500:1 to 1:100

Invertebrate Pest Control Agent	Mode of Action or Chemical Class	Typical Weight Ratio
Fenvalerate	sodium channel modulators	150:1 to 1:200
Fipronil	GABA-regulated chloride channel blockers	150:1 to 1:100
Flonicamid		200:1 to 1:100
Flubendiamide	ryanodine receptor ligands	100:1 to 1:120
Flufenoxuron	chitin synthesis inhibitors	200:1 to 1:100
Hexaflumuron	chitin synthesis inhibitors	300:1 to 1:50
Hydramethylnon	mitochondrial electron transport inhibitors	150:1 to 1:250
Imidacloprid	neonicotinoids	1000:1 to 1:1000
Indoxacarb	sodium channel modulators	200:1 to 1:50
Lambda-cyhalothrin	sodium channel modulators	50:1 to 1:250
Lufenuron	chitin synthesis inhibitors	500:1 to 1:250
Metaflumizone		200:1 to 1:200
Methomyl	cholinesterase inhibitors	500:1 to 1:100
Methoprene	juvenile hormone mimics	500:1 to 1:100
Methoxyfenozide	ecdysone agonists	50:1 to 1:50
Nitenpyram	neonicotinoids	150:1 to 1:200
Nithiazine	neonicotinoids	150:1 to 1:200
Novaluron	chitin synthesis inhibitors	500:1 to 1:150
Oxamyl	cholinesterase inhibitors	200:1 to 1:200
Pymetrozine		200:1 to 1:100
Pyrethrin	sodium channel modulators	100:1 to 1:10
Pyridaben	mitochondrial electron transport inhibitors	200:1 to 1:100
Pyridalyl		200:1 to 1:100
Pyriproxyfen	juvenile hormone mimics	500:1 to 1:100
Ryanodine	ryanodine receptor ligands	100:1 to 1:120
Spinetoram	macrocyclic lactones	150:1 to 1:100
Spinosad	macrocyclic lactones	500:1 to 1:10
Spirodiclofen	lipid biosynthesis inhibitors	200:1 to 1:200
Spiromesifen	lipid biosynthesis inhibitors	200:1 to 1:200
Tebufenozide	ecdysone agonists	500:1 to 1:250
Thiacloprid	neonicotinoids	100:1 to 1:200
Thiamethoxam	neonicotinoids	1250:1 to 1:1000
Thiodicarb	cholinesterase inhibitors	500:1 to 1:400
Thiosultap-sodium		150:1 to 1:100

Invertebrate Pest Control Agent	Mode of Action or Chemical Class	Typical Weight Ratio
Tralomethrin	sodium channel modulators	150:1 to 1:200
Triazamate	cholinesterase inhibitors	250:1 to 1:100
Triflumuron	chitin synthesis inhibitors	200:1 to 1:100
Bacillus thuringiensis	biological agents	50:1 to 1:10
Bacillus thuringiensis delta-endotoxin	biological agents	50:1 to 1:10
NPV (e.g., Gemstar)	biological agents	50:1 to 1:10

Of note is the composition of the present invention wherein the at least one additional biologically active compound or agent is selected from the Invertebrate Pest Control Agents listed in Table A above.

The weight ratios of a compound, including a compound of Formula **1**, an *N*-oxide, or salt thereof, to the additional invertebrate pest control agent typically are between 1000:1 and 1:1000, with one embodiment being between 500:1 and 1:500, another embodiment being between 250:1 and 1:200 and another embodiment being between 100:1 and 1:50.

Listed below in Tables B1 to B12 are embodiments of specific compositions comprising a compound of Formula **1** (compound numbers (Cmpd. No.) refer to compounds in Index Tables A–D) and an additional invertebrate pest control agent.

Table B1

Mixture No.	Cmpd. No.	and	Invertebrate Pest Control Agent	Mixture No.	Cmpd. No.	and	Invertebrate Pest Control Agent
B1-1	20	and	Abamectin	B1-36	20	and	Imidacloprid
B1-2	20	and	Acetamiprid	B1-37	20	and	Indoxacarb
B1-3	20	and	Amitraz	B1-38	20	and	Lambda-cyhalothrin
B1-4	20	and	Avermectin	B1-39	20	and	Lufenuron
B1-5	20	and	Azadirachtin	B1-40	20	and	Metaflumizone
B1-5a	20	and	Bensultap	B1-41	20	and	Methomyl
B1-6	20	and	Beta-cyfluthrin	B1-42	20	and	Methoprene
B1-7	20	and	Bifenthrin	B1-43	20	and	Methoxyfenozide
B1-8	20	and	Buprofezin	B1-44	20	and	Nitenpyram
B1-9	20	and	Cartap	B1-45	20	and	Nithiazine
B1-10	20	and	Chlorantraniliprole	B1-46	20	and	Novaluron
B1-11	20	and	Chlorfenapyr	B1-47	20	and	Oxamyl
B1-12	20	and	Chlorpyrifos	B1-48	20	and	Phosmet
B1-13	20	and	Clothianidin	B1-49	20	and	Pymetrozine
B1-14	20	and	Cyantraniliprole	B1-50	20	and	Pyrethrin
B1-15	20	and	Cyfluthrin	B1-51	20	and	Pyridaben

Mixture No.	Cmpd. No.	and	Invertebrate Pest Control Agent	Mixture No.	Cmpd. No.	and	Invertebrate Pest Control Agent
B1-16	20	and	Cyhalothrin	B1-52	20	and	Pyridalyl
B1-17	20	and	Cypermethrin	B1-53	20	and	Pyriproxyfen
B1-18	20	and	Cyromazine	B1-54	20	and	Ryanodine
B1-19	20	and	Deltamethrin	B1-55	20	and	Spinetoram
B1-20	20	and	Dieldrin	B1-56	20	and	Spinosad
B1-21	20	and	Dinotefuran	B1-57	20	and	Spirodiclofen
B1-22	20	and	Diofenolan	B1-58	20	and	Spiromesifen
B1-23	20	and	Emamectin	B1-59	20	and	Spirotetramat
B1-24	20	and	Endosulfan	B1-60	20	and	Tebufenozide
B1-25	20	and	Esfenvalerate	B1-61	20	and	Thiacloprid
B1-26	20	and	Ethiprole	B1-62	20	and	Thiamethoxam
B1-27	20	and	Fenothiocarb	B1-63	20	and	Thiodicarb
B1-28	20	and	Fenoxycarb	B1-64	20	and	Thiosultap-sodium
B1-29	20	and	Fenvalerate	B1-65	20	and	Tolfenpyrad
B1-30	20	and	Fipronil	B1-66	20	and	Tralomethrin
B1-31	20	and	Flonicamid	B1-67	20	and	Triazamate
B1-32	20	and	Flubendiamide	B1-68	20	and	Triflumuron
B1-33	20	and	Flufenoxuron	B1-69	20	and	*Bacillus thuringiensis*
B1-34	20	and	Hexaflumuron	B1-70	20	and	*Bacillus thuringiensis* delta-endotoxin
B1-35	20	and	Hydramethylnon	B1-71	20	and	NPV (e.g., Gemstar)

Table B2

Table B2 is identical to Table B1, except that each reference to compound 20 in the column headed "Cmpd. No." is replaced by a reference to compound 14. For example, the first mixture in Table B2 is designated B2-1 and is a mixture of compound 14 and the additional invertebrate pest control agent abamectin.

Table B3

Table B3 is identical to Table B1, except that each reference to compound 20 in the column headed "Cmpd. No." is replaced by a reference to compound 22. For example, the first mixture in Table B3 is designated B3-1 and is a mixture of compound 22 and the additional invertebrate pest control agent abamectin.

Table B4

Table B4 is identical to Table B1, except that each reference to compound 20 in the column headed "Cmpd. No." is replaced by a reference to compound 6. For example, the first

mixture in Table B4 is designated B4-1 and is a mixture of compound 6 and the additional invertebrate pest control agent abamectin.

Table B5

Table B5 is identical to Table B1, except that each reference to compound 20 in the column headed "Cmpd. No." is replaced by a reference to compound 7. For example, the first mixture in Table B5 is designated B5-1 and is a mixture of compound 7 and the additional invertebrate pest control agent abamectin.

Table B6

Table B6 is identical to Table B1, except that each reference to compound 20 in the column headed "Cmpd. No." is replaced by a reference to compound 8. For example, the first mixture in Table B6 is designated B6-1 and is a mixture of compound 8 and the additional invertebrate pest control agent abamectin.

Table B7

Table B7 is identical to Table B1, except that each reference to compound 20 in the column headed "Cmpd. No." is replaced by a reference to compound 21. For example, the first mixture in Table B7 is designated B7-1 and is a mixture of compound 21 and the additional invertebrate pest control agent abamectin.

Table B8

Table B8 is identical to Table B1, except that each reference to compound 20 in the column headed "Cmpd. No." is replaced by a reference to compound 62. For example, the first mixture in Table B8 is designated B8-1 and is a mixture of compound 62 and the additional invertebrate pest control agent abamectin.

Table B9

Table B9 is identical to Table B1, except that each reference to compound 20 in the column headed "Cmpd. No." is replaced by a reference to compound 65. For example, the first mixture in Table B9 is designated B9-1 and is a mixture of compound 65 and the additional invertebrate pest control agent abamectin.

Table B10

Table B10 is identical to Table B1, except that each reference to compound 20 in the column headed "Cmpd. No." is replaced by a reference to compound 94. For example, the first mixture in Table B10 is designated B10-1 and is a mixture of compound 94 and the additional invertebrate pest control agent abamectin.

Table B11

Table B11 is identical to Table B1, except that each reference to compound 20 in the column headed "Cmpd. No." is replaced by a reference to compound 106. For example, the first

mixture in Table B11 is designated B11-1 and is a mixture of compound 106 and the additional invertebrate pest control agent abamectin.

Table B12

Table B12 is identical to Table B1, except that each reference to compound 20 in the column headed "Cmpd. No." is replaced by a reference to compound 118. For example, the first mixture in Table B12 is designated B12-1 and is a mixture of compound 118 and the additional invertebrate pest control agent abamectin.

Listed below in Tables C1 to C12 are embodiments of specific compositions comprising a compound of Formula **1** (compound numbers (Cmpd. No.) refer to compounds in Index Tables A–D) and an additional fungicide.

Table C1

Mixture No.	Cmpd. No.	and	Fungicide	Mixture No.	Cmpd. No.	and	Fungicide
C1-1	20	and	Probenazole	C1-17	20	and	Difenoconazole
C1-2	20	and	Tiadinil	C1-18	20	and	Cyproconazole
C1-3	20	and	Isotianil	C1-19	20	and	Propiconazole
C1-4	20	and	Pyroquilon	C1-20	20	and	Fenoxanil
C1-5	20	and	Metominostrobin	C1-21	20	and	Ferimzone
C1-6	20	and	Flutolanil	C1-22	20	and	Fthalide
C1-7	20	and	Validamycin	C1-23	20	and	Kasugamycin
C1-8	20	and	Furametpyr	C1-24	20	and	Picoxystrobin
C1-9	20	and	Pencycuron	C1-25	20	and	Penthiopyrad
C1-10	20	and	Simeconazole	C1-26	20	and	Famoxadone
C1-11	20	and	Orysastrobin	C1-27	20	and	Cymoxanil
C1-12	20	and	Trifloxystrobin	C1-28	20	and	Proquinazid
C1-13	20	and	Isoprothiolane	C1-29	20	and	Flusilazole
C1-14	20	and	Azoxystrobin	C1-30	20	and	Mancozeb
C1-15	20	and	Tricyclazole	C1-31	20	and	Copper hydroxide
C1-16	20	and	Hexaconazole	C1-32	20	and	(a)

(a) 1-[4-[4-[5-(2,6-difluorophenyl)-4,5-dihydro-3-isoxazolyl]-2-thiazolyl]-1-piperidinyl]-2-[5-methyl-3-(trifluoromethyl)-1*H*-pyrazol-1-yl]ethanone

Table C2

Table C2 is identical to Table C1, except that each reference to compound 20 in the column headed "Cmpd. No." is replaced by a reference to compound 14. For example, the first mixture in Table C2 is designated C2-1 and is a mixture of compound 14 and the additional fungicide probenazole.

Table C3

Table C3 is identical to Table C1, except that each reference to compound 20 in the column headed "Cmpd. No." is replaced by a reference to compound 22. For example, the first mixture in Table C3 is designated C3-1 and is a mixture of compound 22 and the additional fungicide probenazole.

Table C4

Table C4 is identical to Table C1, except that each reference to compound 20 in the column headed "Cmpd. No." is replaced by a reference to compound 6. For example, the first mixture in Table C4 is designated C4-1 and is a mixture of compound 6 and the additional fungicide probenazole.

Table C5

Table C5 is identical to Table C1, except that each reference to compound 20 in the column headed "Cmpd. No." is replaced by a reference to compound 7. For example, the first mixture in Table C5 is designated C5-1 and is a mixture of compound 7 and the additional fungicide probenazole.

Table C6

Table C6 is identical to Table C1, except that each reference to compound 20 in the column headed "Cmpd. No." is replaced by a reference to compound 8. For example, the first mixture in Table C6 is designated C6-1 and is a mixture of compound 8 and the additional fungicide probenazole.

Table C7

Table C7 is identical to Table C1, except that each reference to compound 20 in the column headed "Cmpd. No." is replaced by a reference to compound 21. For example, the first mixture in Table C7 is designated C7-1 and is a mixture of compound 21 and the additional fungicide probenazole.

Table C8

Table C8 is identical to Table C1, except that each reference to compound 20 in the column headed "Cmpd. No." is replaced by a reference to compound 62. For example, the first mixture in Table C8 is designated C8-1 and is a mixture of compound 62 and the additional fungicide probenazole.

Table C9

Table C9 is identical to Table C1, except that each reference to compound 20 in the column headed "Cmpd. No." is replaced by a reference to compound 65. For example, the first mixture in Table C9 is designated C9-1 and is a mixture of compound 65 and the additional fungicide probenazole.

Table C10

Table C10 is identical to Table C1, except that each reference to compound 20 in the column headed "Cmpd. No." is replaced by a reference to compound 94. For example, the first mixture in Table C10 is designated C10-1 and is a mixture of compound 694 and the additional fungicide probenazole.

Table C11

Table C11 is identical to Table C1, except that each reference to compound 20 in the column headed "Cmpd. No." is replaced by a reference to compound 106. For example, the first mixture in Table C11 is designated C11-1 and is a mixture of compound 106 and the additional fungicide probenazole.

Table C12

Table C12 is identical to Table C1, except that each reference to compound 20 in the column headed "Cmpd. No." is replaced by a reference to compound 118. For example, the first mixture in Table C12 is designated C12-1 and is a mixture of compound 118 and the additional fungicide probenazole.

Invertebrate pests are controlled in agronomic and nonagronomic applications by applying one or more compounds of this invention, typically in the form of a composition, in a biologically effective amount, to the environment of the pests, including the agronomic and/or nonagronomic locus of infestation, to the area to be protected, or directly on the pests to be controlled.

Thus the present invention comprises a method for controlling an invertebrate pest in agronomic and/or nonagronomic applications, comprising contacting the invertebrate pest or its environment with a biologically effective amount of one or more of the compounds of the invention, or with a composition comprising at least one such compound or a composition comprising at least one such compound and a biologically effective amount of at least one additional biologically active compound or agent. Examples of suitable compositions comprising a compound of the invention and a biologically effective amount of at least one additional biologically active compound or agent include granular compositions wherein the additional active compound is present on the same granule as the compound of the invention or on granules separate from those of the compound of the invention.

Embodiments of the method of this invention include contacting the environment. Of note is the method wherein the environment is a plant. Also of note is the method wherein the environment is an animal. Also of note is the method wherein the environment is a seed.

To achieve contact with a compound or composition of the invention to protect a field crop from invertebrate pests, the compound or composition is typically applied to the seed of

the crop before planting, to the foliage (e.g., leaves, stems, flowers, fruits) of crop plants, or to the soil or other growth medium before or after the crop is planted.

One embodiment of a method of contact is by spraying. Alternatively, a granular composition comprising a compound of the invention can be applied to the plant foliage or the soil. Compounds of this invention can also be effectively delivered through plant uptake by contacting the plant with a composition comprising a compound of this invention applied as a soil drench of a liquid formulation, a granular formulation to the soil, a nursery box treatment or a dip of transplants. Of note is a composition of the present invention in the form of a soil drench liquid formulation. Also of note is a method for controlling an invertebrate pest comprising contacting the invertebrate pest or its environment with a biologically effective amount of a compound of the present invention or with a composition comprising a biologically effective amount of a compound of the present invention. Of further note is this method wherein the environment is soil and the composition is applied to the soil as a soil drench formulation. Of further note is that compounds of this invention are also effective by localized application to the locus of infestation. Other methods of contact include application of a compound or a composition of the invention by direct and residual sprays, aerial sprays, gels, seed coatings, microencapsulations, systemic uptake, baits, ear tags, boluses, foggers, fumigants, aerosols, dusts and many others. One embodiment of a method of contact is a dimensionally stable fertilizer granule, stick or tablet comprising a compound or composition of the invention. The compounds of this invention can also be impregnated into materials for fabricating invertebrate control devices (e.g., insect netting).

Compounds of this invention are also useful in seed treatments for protecting seeds from invertebrate pests. In the context of the present disclosure and claims, treating a seed means contacting the seed with a biologically effective amount of a compound of this invention, which is typically formulated as a composition of the invention. This seed treatment protects the seed from invertebrate soil pests and generally can also protect roots and other plant parts in contact with the soil of the seedling developing from the germinating seed. The seed treatment may also provide protection of foliage by translocation of the compound of this invention or a second active ingredient within the developing plant. Seed treatments can be applied to all types of seeds, including those from which plants genetically transformed to express specialized traits will germinate. Representative examples include those expressing proteins toxic to invertebrate pests, such as *Bacillus thuringiensis* toxin or those expressing herbicide resistance such as glyphosate acetyltransferase, which provides resistance to glyphosate.

One method of seed treatment is by spraying or dusting the seed with a compound of the invention (i.e. as a formulated composition) before sowing the seeds. Compositions formulated for seed treatment generally comprise a film former or adhesive agent. Therefore typically a seed coating composition of the present invention comprises a biologically

effective amount of a compound of Formula **1**, an *N*-oxide, or salt thereof, and a film former or adhesive agent. Seed can be coated by spraying a flowable suspension concentrate directly into a tumbling bed of seeds and then drying the seeds. Alternatively, other formulation types such as wetted powders, solutions, suspoemulsions, emulsifiable concentrates and emulsions in water can be sprayed on the seed. This process is particularly useful for applying film coatings on seeds. Various coating machines and processes are available to one skilled in the art. Suitable processes include those listed in P. Kosters et al., *Seed Treatment: Progress and Prospects*, 1994 BCPC Mongraph No. 57, and references listed therein.

The treated seed typically comprises a compound of the present invention in an amount from about 0.1 g to 1 kg per 100 kg of seed (i.e. from about 0.0001 to 1% by weight of the seed before treatment). A flowable suspension formulated for seed treatment typically comprises from about 0.5 to about 70% of the active ingredient, from about 0.5 to about 30% of a film-forming adhesive, from about 0.5 to about 20% of a dispersing agent, from 0 to about 5% of a thickener, from 0 to about 5% of a pigment and/or dye, from 0 to about 2% of an antifoaming agent, from 0 to about 1% of a preservative, and from 0 to about 75% of a volatile liquid diluent.

The compounds of this invention can be incorporated into a bait composition that is consumed by an invertebrate pest or used within a device such as a trap, bait station, and the like. Such a bait composition can be in the form of granules which comprise (a) active ingredients, namely a biologically effective amount of a compound of Formula **1** an *N*-oxide, or salt thereof; (b) one or more food materials; optionally (c) an attractant, and optionally (d) one or more humectants. Of note are granules or bait compositions which comprise between about 0.001-5% active ingredients, about 40-99% food material and/or attractant; and optionally about 0.05-10% humectants, which are effective in controlling soil invertebrate pests at very low application rates, particularly at doses of active ingredient that are lethal by ingestion rather than by direct contact. Some food materials can function both as a food source and an attractant. Food materials include carbohydrates, proteins and lipids. Examples of food materials are vegetable flour, sugar, starches, animal fat, vegetable oil, yeast extracts and milk solids. Examples of attractants are odorants and flavorants, such as fruit or plant extracts, perfume, or other animal or plant component, pheromones or other agents known to attract a target invertebrate pest. Examples of humectants, i.e. moisture retaining agents, are glycols and other polyols, glycerine and sorbitol. Of note is a bait composition (and a method utilizing such a bait composition) used to control at least one invertebrate pest selected from the group consisting of ants, termites and cockroaches. A device for controlling an invertebrate pest can comprise the present bait composition and a housing adapted to receive the bait composition, wherein the housing has at least one opening sized to permit the invertebrate pest to pass through the opening so the invertebrate

pest can gain access to the bait composition from a location outside the housing, and wherein the housing is further adapted to be placed in or near a locus of potential or known activity for the invertebrate pest.

The compounds of this invention can be applied without other adjuvants, but most often application will be of a formulation comprising one or more active ingredients with suitable carriers, diluents, and surfactants and possibly in combination with a food depending on the contemplated end use. One method of application involves spraying a water dispersion or refined oil solution of a compound of the present invention. Combinations with spray oils, spray oil concentrations, spreader stickers, adjuvants, other solvents, and synergists such as piperonyl butoxide often enhance compound efficacy. For nonagronomic uses such sprays can be applied from spray containers such as a can, a bottle or other container, either by means of a pump or by releasing it from a pressurized container, e.g., a pressurized aerosol spray can. Such spray compositions can take various forms, for example, sprays, mists, foams, fumes or fog. Such spray compositions thus can further comprise propellants, foaming agents, etc. as needed for application. Of note is a spray composition comprising a biologically effective amount of a compound or a composition of the present invention and a carrier. One embodiment of such a spray composition comprises a biologically effective amount of a compound or a composition of the present invention and a propellant. Representative propellants include, but are not limited to, methane, ethane, propane, butane, isobutane, butene, pentane, isopentane, neopentane, pentene, hydrofluorocarbons, chlorofluorocarbons, dimethyl ether, and mixtures of the foregoing. Of note is a spray composition (and a method utilizing such a spray composition dispensed from a spray container) used to control at least one invertebrate pest selected from the group consisting of mosquitoes, black flies, stable flies, deer flies, horse flies, wasps, yellow jackets, hornets, ticks, spiders, ants, gnats, and the like, including individually or in combinations.

Nonagronomic uses refer to invertebrate pest control in the areas other than fields of crop plants. Nonagronomic uses of the present compounds and compositions include control of invertebrate pests in stored grains, beans and other foodstuffs, and in textiles such as clothing and carpets. Nonagronomic uses of the present compounds and compositions also include invertebrate pest control in ornamental plants, forests, in yards, along roadsides and railroad rights of way, and on turf such as lawns, golf courses and pastures. Nonagronomic uses of the present compounds and compositions also include invertebrate pest control in houses and other buildings which may be occupied by humans and/or companion, farm, ranch, zoo or other animals. Nonagronomic uses of the present compounds and compositions also include the control of pests such as termites that can damage wood or other structural materials used in buildings.

Nonagronomic uses of the present compounds and compositions also include protecting human and animal health by controlling invertebrate pests that are parasitic or transmit infectious diseases. The controlling of animal parasites includes controlling external parasites that are parasitic to the surface of the body of the host animal (e.g., shoulders, armpits, abdomen, inner part of the thighs) and internal parasites that are parasitic to the inside of the body of the host animal (e.g., stomach, intestine, lung, veins, under the skin, lymphatic tissue). External parasitic or disease transmitting pests include, for example, chiggers, ticks, lice, mosquitoes, flies, mites and fleas. Internal parasites include heartworms, hookworms and helminths. Compounds and compositions of the present invention are particularly suitable for combating external parasitic or disease transmitting pests. Compounds and compositions of the present invention are suitable for systemic and/or non-systemic control of infestation or infection by parasites on animals.

Compounds and compositions of the present invention are suitable for combating parasites that infest animal subjects including those in the wild, livestock and agricultural working animals such as cattle, sheep, goats, horses, pigs, donkeys, camels, bison, buffalos, rabbits, hens, turkeys, ducks, geese and bees (e.g., raised for meat, milk, butter, eggs, fur, leather, feathers and/or wool). By combating parasites, fatalities and performance reduction (in terms of meat, milk, wool, skins, eggs, honey, etc.) are reduced, so that applying a composition comprising a compound of the present invention allows more economic and simple husbandry of animals.

Compounds and compositions of the present invention are especially suitable for combating parasites that infest companion animals and pets (e.g., dogs, cats, pet birds and aquarium fish), research and experimental animals (e.g., hamsters, guinea pigs, rats and mice), as well as animals raised for/in zoos, wild habitats and/or circuses.

In an embodiment of this invention, the animal is preferably a vertebrate, and more preferably a mammal, avian or fish. In a particular embodiment, the animal subject is a mammal (including great apes, such as humans). Other mammalian subjects include primates (e.g., monkeys), bovine (e.g., cattle or dairy cows), porcine (e.g., hogs or pigs), ovine (e.g., goats or sheep), equine (e.g., horses), canine (e.g., dogs), feline (e.g., house cats), camels, deer, donkeys, bison, buffalos, antelopes, rabbits, and rodents (e.g., guinea pigs, squirrels, rats, mice, gerbils, and hamsters). Avians include Anatidae (swans, ducks and geese), Columbidae (e.g., doves and pigeons), Phasianidae (e.g., partridges, grouse and turkeys), Thesienidae (e.g., domestic chickens), Psittacines (e.g., parakeets, macaws, and parrots), game birds, and ratites (e.g., ostriches).

Birds treated or protected by the inventive compounds can be associated with either commercial or noncommercial aviculture. These include Anatidae, such as swans, geese, and ducks, Columbidae, such as doves and domestic pigeons, Phasianidae, such as partridge,

grouse and turkeys, Thesienidae, such as domestic chickens, and Psittacines, such as parakeets, macaws, and parrots raised for the pet or collector market, among others.

For purposes of the present invention, the term "fish" shall be understood to include without limitation, the Teleosti grouping of fish, i.e., teleosts. Both the Salmoniformes order (which includes the Salmonidae family) and the Perciformes order (which includes the Centrarchidae family) are contained within the Teleosti grouping. Examples of potential fish recipients include the Salmonidae, Serranidae, Sparidae, Cichlidae, and Centrarchidae, among others.

Other animals are also contemplated to benefit from the inventive methods, including marsupials (such as kangaroos), reptiles (such as farmed turtles), and other economically important domestic animals for which the inventive methods are safe and effective in treating or preventing parasite infection or infestation.

Examples of invertebrate parasitic pests controlled by administering a parasiticidally effective amount of a compound of this invention to an animal to be protected include ectoparasites (arthropods, acarines, etc) and endoparasites (helminths, e.g., nematodes, trematodes, cestodes, acanthocephalans, etc.).

The disease or group of diseases described generally as helminthiasis is due to infection of an animal host with parasitic worms known as helminths. The term 'helminths' is meant to include nematodes, trematodes, cestodes and acanthocephalans. Helminthiasis is a prevalent and serious economic problem with domesticated animals such as swine, sheep, horses, cattle, goats, dogs, cats and poultry.

Among the Helminths, the group of worms described as nematodes causes widespread and at times serious infection in various species of animals. Nematodes that are contemplated to be treated by the compounds of this invention and by the inventive methods include, without limitation, the following genera: *Acanthocheilonema*, *Aelurostrongylus*, *Ancylostoma*, *Angiostrongylus*, *Ascaridia*, *Ascaris*, *Brugia*, *Bunostomum*, *Capillaria*, *Chabertia*, *Cooperia*, *Crenosoma*, *Dictyocaulus*, *Dioctophyme*, *Dipetalonema*, *Diphyllobothrium*, *Dirofilaria*, *Dracunculus*, *Enterobius*, *Filaroides*, *Haemonchus*, *Heterakis*, *Lagochilascaris*, *Loa*, *Mansonella*, *Muellerius*, *Necator*, *Nematodirus*, *Oesophagostomum*, *Ostertagia*, *Oxyuris*, *Parafilaria*, *Parascaris*, *Physaloptera*, *Protostrongylus*, *Setaria*, *Spirocerca*, *Stephanofilaria*, *Strongyloides*, *Strongylus*, *Thelazia*, *Toxascaris*, *Toxocara*, *Trichinella*, *Trichonema*, *Trichostrongylus*, *Trichuris*, *Uncinaria* and *Wuchereria*.

Of the above, the most common genera of nematodes infecting the animals referred to above are *Haemonchus*, *Trichostrongylus*, *Ostertagia*, *Nematodirus*, *Cooperia*, *Ascaris*, *Bunostomum*, *Oesophagostomum*, *Chabertia*, *Trichuris*, *Strongylus*, *Trichonema*, *Dictyocaulus*, *Capillaria*, *Heterakis*, *Toxocara*, *Ascaridia*, *Oxyuris*, *Ancylostoma*, *Uncinaria*, *Toxascaris* and *Parascaris*. Certain of these, such as *Nematodirus*, *Cooperia* and

Oesophagostomum attack primarily the intestinal tract while others, such as *Haemonchus* and *Ostertagia*, are more prevalent in the stomach while others such as *Dictyocaulus* are found in the lungs. Still other parasites may be located in other tissues such as the heart and blood vessels, subcutaneous and lymphatic tissue and the like.

Trematodes that are contemplated to be treated by the compounds of this invention and by the inventive methods include, without limitation, the following genera: *Alaria*, *Fasciola*, *Nanophyetus*, *Opisthorchis*, *Paragonimus* and *Schistosoma*.

Cestodes that are contemplated to be treated by the compounds of this invention and by the inventive methods include, without limitation, the following genera: *Diphyllobothrium*, *Diplydium*, *Spirometra* and *Taenia*.

The most common genera of parasites of the gastrointestinal tract of humans are *Ancylostoma*, *Necator*, *Ascaris*, *Strongyloides*, *Trichinella*, *Capillaria*, *Trichuris* and *Enterobius*. Other medically important genera of parasites which are found in the blood or other tissues and organs outside the gastrointestinal tract are the filarial worms such as *Wuchereria*, *Brugia*, *Onchocerca* and *Loa*, as well as *Dracunculus* and extra intestinal stages of the intestinal worms *Strongyloides* and *Trichinella*.

Numerous other Helminth genera and species are known to the art, and are also contemplated to be treated by the compounds of the invention. These are enumerated in great detail in *Textbook of Veterinary Clinical Parasitology*, *Volume 1*, *Helminths*, E. J. L. Soulsby, F. A. Davis Co., Philadelphia, Pa.; *Helminths, Arthropods and Protozoa*, (*6th Edition of Monnig's Veterinary Helminthology and Entomology*), E. J. L. Soulsby, The Williams and Wilkins Co., Baltimore, Md.

It is also contemplated that the inventive compounds are effective against a number of ectoparasites of animals, e.g., arthropod ectoparasites of mammals and birds although it is also recognized that some arthropods can be endoparasites as well.

Thus, insect and acarine pests include, e.g., biting insects, such as flies and mosquitoes, mites, ticks, lice, fleas, true bugs, parasitic maggots, and the like.

Adult flies include, e.g., the horn fly or *Haematobia irritans*, the horse fly or *Tabanus* spp., the stable fly or *Stomoxys calcitrans*, the black fly or *Simulium* spp., the deer fly or *Chrysops* spp., the louse fly or *Melophagus ovinus*, the tsetse fly or *Glossina* spp. Parasitic fly maggots include, e.g., the bot fly (*Oestrus ovis* and *Cuterebra* spp.), the blow fly or *Phaenicia* spp., the screwworm or *Cochliomyia hominivorax*, the cattle grub or *Hypoderma* spp., the fleeceworm and the *Gastrophilus* of horses. Mosquitoes include, for example, *Culex* spp., *Anopheles* spp., and *Aedes* spp.

Mites include Mesostigmata spp. e.g., mesostigmatids such as the chicken mite, *Dermanyssus gallinae*; itch or scab mites such as Sarcoptidae spp. for example, *Sarcoptes scabiei*; mange mites such as Psoroptidae spp. including *Chorioptes bovis* and *Psoroptes*

ovis; chiggers e.g., Trombiculidae spp. for example the North American chigger, *Trombicula alfreddugesi*.

Ticks include, e.g., soft-bodied ticks including Argasidae spp. for example *Argas* spp. and *Ornithodoros* spp.; hard-bodied ticks including Ixodidae spp., for example *Rhipicephalus sanguineus*, *Dermacentor variabilis*, *Dermacentor andersoni*, *Amblyomma americanum*, *Ixodes scapularis* and *Boophilus* spp.

Lice include, e.g., sucking lice, e.g., *Menopon* spp. and *Bovicola* spp.; biting lice, e.g., *Haematopinus* spp., *Linognathus* spp. and *Solenopotes* spp.

Fleas include, e.g., *Ctenocephalides* spp., such as dog flea (*Ctenocephalides canis*) and cat flea (*Ctenocephalides felis*); *Xenopsylla* spp. such as oriental rat flea (*Xenopsylla cheopis*); and *Pulex* spp. such as human flea (*Pulex irritans*).

True bugs include, e.g., *Cimicidae* or e.g., the common bed bug (*Cimex lectularius*); Triatominae spp. including triatomid bugs also known as kissing bugs; for example *Rhodnius prolixus* and *Triatoma* spp.

Generally, flies, fleas, lice, mosquitoes, gnats, mites, ticks and helminths cause tremendous losses to the livestock and companion animal sectors. Arthropod parasites also are a nuisance to humans and can vector disease-causing organisms in humans and animals.

Numerous other arthropod pests and ectoparasites are known to the art, and are also contemplated to be treated by the compounds of the invention. These are enumerated in great detail in *Medical and Veterinary Entomology*, D. S. Kettle, John Wiley & Sons, New York and Toronto; *Control of Arthropod Pests of Livestock: A Review of Technology*, R. O. Drummand, J. E. George, and S. E. Kunz, CRC Press, Boca Raton, Fla.

The compounds and compositions of this invention may also be effective against a number of protozoa endoparasites of animals, such as those summarized by Table 1, as follows.

Table 1

Exemplary Parasitic Protozoa and Associated Human Diseases

Phylum	**Subphylum**	**Representative Genera**	**Human Disease or Disorder**
Sarcomastigophora (with flagella, pseudopodia, or both)	Mastigophora (Flagella)	*Leishmania*	Visceral, cutaneous and mucocutaneous Infection
		Trypansoma	Sleeping sickness
			Chagas' disease
		Giardia	Diarrhea
		Trichomonas	Vaginitis

Table 1

Exemplary Parasitic Protozoa and Associated Human Diseases

Phylum	**Subphylum**	**Representative Genera**	**Human Disease or Disorder**
	Sarcodina (pseudopodia)	*Entamoeba*	Dysentery, liver Abscess
		Dientamoeba	Colitis
		Naegleria and Acanthamoeba	Central nervous system and corneal ulcers
		Babesia	Babesiesis
Apicomplexa (apical complex)		*Plasmodium*	Malaria
		Isospora	Diarrhea
		Sarcocystis	Diarrhea
		Cryptosporidum	Diarrhea
		Toxoplasma	Toxoplasmosis
		Eimeria	Chicken coccidiosis
Microspora		*Enterocytozoon*	Diarrhea
Ciliaphora (with cilia)		*Balantidium*	Dysentery
Unclassified		*Pneumocystis*	Pneumonia

In particular, the compounds of this invention are effective against ectoparasites including fleas such as *Ctenocephalides felis* (cat flea) and *Ctenocephalides canis* (dog flea).

The compounds of this invention may also be effective against other ectoparasites including flies such as *Haematobia (Lyperosia) irritans* (horn fly), *Stomoxys calcitrans* (stable fly), *Simulium* spp. (blackfly), *Glossina* spp. (tsetse flies), *Hydrotaea irritans* (head fly), *Musca autumnalis* (face fly), *Musca domestica* (house fly), *Morellia simplex* (sweat fly), *Tabanus* spp. (horse fly), *Hypoderma bovis*, *Hypoderma lineatum*, *Lucilia sericata*, *Lucilia cuprina* (green blowfly), *Calliphora* spp. (blowfly), *Protophormia* spp., *Oestrus ovis* (nasal botfly), *Culicoides* spp. (midges), *Hippobosca equine*, *Gastrophilus instestinalis*, *Gastrophilus haemorrhoidalis* and *Gastrophilus naslis*; lice such as *Bovicola (Damalinia) bovis*, *Bovicola equi*, *Haematopinus asini*, *Felicola subrostratus*, *Heterodoxus spiniger*, *Lignonathus setosus* and *Trichodectes canis*; keds such as *Melophagus ovinus*; mites such as *Psoroptes* spp., *Sarcoptes scabei*, *Chorioptes bovis*, *Demodex equi*, *Cheyletiella* spp., *Notoedres cati*, *Trombicula* spp. and *Otodectes cyanotis* (ear mites); and ticks such as *Ixodes*

spp., *Boophilus* spp., *Rhipicephalus* spp., *Amblyomma* spp., *Dermacentor* spp., *Hyalomma* spp. and *Haemaphysalis* spp.

Biologically active compounds or agents useful in the compositions of the present invention include the organophosphate pesticides. This class of pesticides has very broad activity as insecticides and, in certain instances, anthelminitic activity. Organophosphate pesticides include, e.g., dicrotophos, terbufos, dimethoate, diazinon, disulfoton, trichlorfon, azinphos-methyl, chlorpyrifos, malathion, oxydemeton-methyl, methamidophos, acephate, ethyl parathion, methyl parathion, mevinphos, phorate, carbofenthion and phosalone. It is also contemplated to include combinations of the inventive methods and compounds with carbamate type pesticides, including, e.g., carbaryl, carbofuran, aldicarb, molinate, methomyl, carbofuran, etc., as well as combinations with the organochlorine type pesticides. It is further contemplated to include combinations with biological pesticides, including repellents, the pyrethrins (as well as synthetic variations thereof, e.g., allethrin, resmethrin, permethrin, tralomethrin), and nicotine, that is often employed as an acaricide. Other contemplated combinations are with miscellaneous pesticides including: bacillus thuringensis, chlorobenzilate, formamidines (e.g., amitraz), copper compounds (e.g., copper hydroxide and cupric oxychloride sulfate), cyfluthrin, cypermethrin, dicofol, endosulfan, esenfenvalerate, fenvalerate, lambda-cyhalothrin, methoxychlor and sulfur.

Of note are additional biologically active compounds or agents selected from art-known anthelmintics, such as, for example, avermectins (e.g., ivermectin, moxidectin, milbemycin), benzimidazoles (e.g., albendazole, triclabendazole), salicylanilides (e.g., closantel, oxyclozanide), substituted phenols (e.g., nitroxynil), pyrimidines (e.g., pyrantel), imidazothiazoles (e.g., levamisole) and praziquantel.

Other biologically active compounds or agents useful in the compositions of the present invention can be selected from Insect Growth Regulators (IGRs) and Juvenile Hormone Analogues (JHAs) such as diflubenzuron, triflumuron, fluazuron, cyromazine, methoprene, etc., thereby providing both initial and sustained control of parasites (at all stages of insect development, including eggs) on the animal subject, as well as within the environment of the animal subject.

Of note are biologically active compounds or agents useful in the compositions of the present invention selected from the antiparasitic class of avermectin compounds. As stated above, the avermectin family of compounds is a series of very potent antiparasitic agents known to be useful against a broad spectrum of endoparasites and ectoparasites in mammals.

A notable compound for use within the scope of the present invention is ivermectin. Ivermectin is a semi-synthetic derivative of avermectin and is generally produced as a mixture of at least 80% 22,23-dihydroavermectin B_{1a} and less than 20% 22,23-dihydroavermectin B_{1b}. Ivermectin is disclosed in U.S. 4,199,569.

Abamectin is an avermectin that is disclosed as Avermectin B_{1a}/B_{1b} in U.S. 4,310,519. Abamectin contains at least 80% of avermectin B_{1a} and not more than 20% of avermectin B_{1b}.

Another notable avermectin is Doramectin, also known as 25-cyclohexyl-avermectin B_1. The structure and preparation of Doramectin is disclosed in U.S. 5,089,480.

Another notable avermectin is Moxidectin. Moxidectin, also known as LL-F28249 alpha, is known from U.S. 4,916,154.

Another notable avermectin is Selamectin. Selamectin is 25-cyclohexyl-25-de(1-methylpropyl)-5-deoxy-22,23-dihydro-5-(hydroxyimino)-avermectin B_1 monosaccharide.

Milbemycin, or B41, is a substance which is isolated from the fermentation broth of a Milbemycin producing strain of Streptomyces. The microorganism, the fermentation conditions and the isolation procedures are more fully described in U.S. 3,950,360 and U.S. 3,984,564.

Emamectin (4"-deoxy-4"-epi-methylaminoavermectin B_1), which can be prepared as described in U.S. 5,288,710 or U.S. 5,399,717, is a mixture of two homologues, 4"-deoxy-4"-epi-methylaminoavermectin B_{1a} and 4"-deoxy-4"-epi-methylaminoavermectin B_{1b}. Preferably, a salt of Emamectin is used. Non-limiting examples of salts of Emamectin which can be used in the present invention include the salts described in U.S. 5,288,710, e.g., salts derived from benzoic acid, substituted benzoic acid, benzenesulfonic acid, citric acid, phosphoric acid, tartaric acid, maleic acid, and the like. Most preferably, the Emamectin salt used in the present invention is Emamectin benzoate.

Eprinomectin is chemically known as 4"-epi-acetylamino-4"-deoxy-avermectin B_1. Eprinomectin was specifically developed to be used in all cattle classes and age groups. It was the first avermectin to show broad-spectrum activity against both endo- and ecto-parasites while also leaving minimal residues in meat and milk. It has the additional advantage of being highly potent when delivered topically.

The composition of the present invention optionally comprises combinations of one or more of the following antiparasite compounds: imidazo[1,2-b]pyridazine compounds as described by U.S. application Ser. No. 11/019,597, filed on Dec. 22, 2004, and published on Aug. 18, 2005 as US 2005-0182059A1; 1-(4-mono and di-halomethylsulphonylphenyl)-2-acylamino-3-fluoropropanol compounds, as described by U.S. application Ser. No. 11/018,156, filed on Dec. 21, 2004, now US Patent 7,361,689; trifluoromethanesulfonanilide oxime ether derivatives, as described by U.S. application Ser. No. 11/231,423, filed on Sep. 21, 2005, now US Patent 7,312,248; and *n*-[(phenyloxy)phenyl]-1,1,1-trifluoromethanesulfonamide and *n*-[(phenylsulfanyl)phenyl]-1,1,1-trifluoromethanesulfonamide derivatives, as described by U.S. Provisional Application Ser. No. 60/688,898, filed on Jun. 9, 2005, and published as US 2006-0281695A1 on Dec. 14, 2006.

The compositions of the present invention can also further comprise a flukicide. Suitable flukicides include, for example, triclabendazole, fenbendazole, albendazole, Clorsulon and oxibendazole. It will be appreciated that the above combinations can further include combinations of antibiotic, antiparasitic and anti-fluke active compounds.

In addition to the above combinations, it is also contemplated to provide combinations of the inventive methods and compounds, as described herein, with other animal health remedies such as trace elements, anti-inflammatories, anti-infectives, hormones, dermatological preparations, including antiseptics and disinfectants, and immunobiologicals such as vaccines and antisera for the prevention of disease.

For example, such antinfectives include one or more antibiotics that are optionally co-administered during treatment using the inventive compounds or methods, e.g., in a combined composition and/or in separate dosage forms. Art-known antibiotics suitable for this purpose include, for example, those listed herein below.

One useful antibiotic is Florfenicol, also known as D-(threo)-1-(4-methylsulfonylphenyl)-2-dichloroacetamido-3-fluoro-1-propanol. Another notable antibiotic compound is D-(threo)-1-(4-methylsulfonyphenyl)-2-difluoroacetamido-3-fluoro-1-propanol. Another useful antibiotic is Thiamphenicol. Processes for the manufacture of these antibiotic compounds, and intermediates useful in such processes, are described in U.S. 4,311,857; U.S. 4,582,918; U.S. 4,973,750; U.S. 4,876,352; U.S. 5,227,494; U.S. 4,743,700; U.S. 5,567,844; U.S. 5,105,009; U.S. 5,382,673; U.S. 5,352,832; and U.S. 5,663,361. Other florfenicol analogs and/or prodrugs have been disclosed and such analogs also can be used in the compositions and methods of the present invention (see e.g., U.S. Patent Application Publication No: 2004/0082553, now US Patent 7,041,670, and U.S. patent application Ser. No. 11/016,794, now US Patent 7,153,842).

Another useful antibiotic compound is Tilmicosin. Tilmicosin is a macrolide antibiotic that is chemically defined as 20-dihydro-20-deoxy-20-(*cis*-3,5-dimethylpiperidin-1-yl)-desmycosin and which is reportedly disclosed in U.S. 4,820,695.

Another useful antibiotic for use in the present invention is tulathromycin. Tulathromycin is also identified as (2R,3S,4R,5R,8R,10R,11R,12S,13S,14R) 13-[(2,6-dideoxy-3-*C*-methyl-3-*O*-methyl-4-*C*-[(propylamino)methyl]-alpha-L-ribo-hexopyranosyl]-oxy]-2-ethyl-3,4,10-trihydroxy-3,5,8,10,12,14-hexamethyl-11-[[3,4,6-trideoxy-3-(dimethyl-amino)-beta-D-xylo-hexopyranosyl]oxy]-1-oxa-6-azacyclopentadecan-15-one. Tulathromycin can be prepared in accordance with the procedures set forth in U.S. Patent Publication No. 2003/0064939 A1.

Further antibiotics for use in the present invention include the cephalosporins such as, for example, ceftiofur, cefquinome, etc. The concentration of the cephalosporin in the formulation of the present invention optionally varies between about 1 mg/mL to 500 mg/mL.

Another useful antibiotic includes the fluoroquinolones, such as, for example, enrofloxacin, danofloxacin, difloxacin, orbifloxacin and marbofloxacin. Enrofloxacin is typically administered in a concentration of about 100 mg/mL. Danofloxacin is typically administered at a concentration of about 180 mg/mL.

Other useful macrolide antibiotics include compounds from the class of ketolides, or, more specifically, the azalides. Such compounds are described in, for example, U.S. 6,514,945, U.S. 6,472,371, U.S. 6,270,768, U.S. 6,437,151, U.S. 6,271,255, U.S. 6,239,112, U.S. 5,958,888, U.S. 6,339,063 and U.S. 6,054,434.

Other useful antibiotics include the tetracyclines, particularly chlortetracycline and oxytetracycline. Other antibiotics may include β-lactams such as penicillins, e.g., penicillin, ampicillin, amoxicillin, or a combination of amoxicillin with clavulanic acid or other beta lactamase inhibitors.

Nonagronomic applications in the veterinary sector are by conventional means such as by enteral administration in the form of, for example, tablets, capsules, drinks, drenching preparations, granulates, pastes, boli, feed-through procedures, or suppositories; or by parenteral administration, such as by injection (including intramuscular, subcutaneous, intravenous, intraperitoneal) or implants; by nasal administration; by topical administration, for example, in the form of immersion or dipping, spraying, washing, coating with powder, or application to a small area of the animal, and through articles such as neck collars, ear tags, tail bands, limb bands or halters which comprise compounds or compositions of the present invention.

Any of the compounds of the present invention, or a suitable combination of such compounds, may be administered directly to the animal subject and/or indirectly by applying it to the local environment in which the animal dwells (such as bedding, enclosures, or the like). Direct administration includes contacting the skin, fur or feathers of a subject animal with the compounds, or by feeding or injecting the compounds into the animal.

The compounds of the present invention may be administered in a controlled release form, e.g., in a subcutaneous slow release formulation, or in the form of a controlled release device affixed to an animal such as a fleacollar. Collars for the controlled release of an insecticide agent for long term protection against flea infestation in a companion animal are art-known, and are described, for example, by U.S. 3,852,416, U.S. 4,224,901, U.S. 5,555,848 and U.S. 5,184,573.

Typically a parasiticidal composition according to the present invention comprises a mixture of a compound of Formula **1**, an *N*-oxide, or salt thereof, with one or more pharmaceutically or veterinarily acceptable carriers comprising excipients and auxiliaries selected with regard to the intended route of administration (e.g., oral, topical or parenteral administration such as injection) and in accordance with standard practice. In addition, a suitable carrier is selected on the basis of compatibility with the one or more active

ingredients in the composition, including such considerations as stability relative to pH and moisture content. Therefore of note is a composition for protecting an animal from an invertebrate parasitic pest comprising a parasitically effective amount of a compound of the invention and at least one carrier.

For parenteral administration including intravenous, intramuscular and subcutaneous injection, a compound of the present invention can be formulated in suspension, solution or emulsion in oily or aqueous vehicles, and may contain adjuncts such as suspending, stabilizing and/or dispersing agents. The compounds of the present invention may also be formulated for bolus injection or continuous infusion. Pharmaceutical compositions for injection include aqueous solutions of water-soluble forms of active ingredients (e.g., a salt of an active compound), preferably in physiologically compatible buffers containing other excipients or auxiliaries as are known in the art of pharmaceutical formulation. Additionally, suspensions of the active compounds may be prepared in a lipophilic vehicle. Suitable lipophilic vehicles include fatty oils such as sesame oil, synthetic fatty acid esters such as ethyl oleate and triglycerides, or materials such as liposomes. Aqueous injection suspensions may contain substances that increase the viscosity of the suspension, such as sodium carboxymethyl cellulose, sorbitol, or dextran. Formulations for injection may be presented in unit dosage form, e.g., in ampoules or in multi-dose containers. Alternatively, the active ingredient may be in powder form for constitution with a suitable vehicle, e.g., sterile, pyrogen-free water, before use.

In addition to the formulations described supra, the compounds of the present invention may also be formulated as a depot preparation. Such long acting formulations may be administered by implantation (for example, subcutaneously or intramuscularly) or by intramuscular or subcutaneous injection. The compounds of the present invention may be formulated for this route of administration with suitable polymeric or hydrophobic materials (for instance, in an emulsion with a pharmacologically acceptable oil), with ion exchange resins, or as a sparingly soluble derivative such as, without limitation, a sparingly soluble salt.

For administration by inhalation, the compounds of the present invention can be delivered in the form of an aerosol spray using a pressurized pack or a nebulizer and a suitable propellant, e.g., without limitation, dichlorodifluoromethane, trichlorofluoromethane, dichlorotetrafluoroethane or carbon dioxide. In the case of a pressurized aerosol, the dosage unit may be controlled by providing a valve to deliver a metered amount. Capsules and cartridges of, for example, gelatin for use in an inhaler or insufflator may be formulated containing a powder mix of the compound and a suitable powder base such as lactose or starch.

Compounds of the present invention have been discovered to have favorable pharmacokinetic and pharmacodynamic properties providing systemic availability from oral

administration and ingestion. Therefore after ingestion by the animal to be protected, parasiticidally effective concentrations of compounds of the invention in the bloodstream protect the treated animal from blood-sucking pests such as fleas, ticks and lice. Therefore of note is a composition for protecting an animal from an invertebrate parasite pest in a form for oral administration (i.e. comprising, in addition to a parasiticidally effective amount of a compound of the invention, one or more carriers selected from binders and fillers suitable for oral administration and feed concentrate carriers).

For oral administration in the form of solutions (the most readily available form for absorption), emulsions, suspensions, pastes, gels, capsules, tablets, boluses, powders, granules, rumen-retention and feed/water/lick blocks, a compound of the present invention can be formulated with binders/fillers known in the art to be suitable for oral administration compositions, such as sugars and sugar derivatives (e.g., lactose, sucrose, mannitol, sorbitol), starch (e.g., maize starch, wheat starch, rice starch, potato starch), cellulose and derivatives (e.g., methylcellulose, carboxymethylcellulose, ethylhydroxycellulose), protein derivatives (e.g., zein, gelatin), and synthetic polymers (e.g., polyvinyl alcohol, polyvinylpyrrolidone). If desired, lubricants (e.g., magnesium stearate), disintegrating agents (e.g., cross-linked polyvinylpyrrolidinone, agar, alginic acid) and dyes or pigments can be added. Pastes and gels often also contain adhesives (e.g., acacia, alginic acid, bentonite, cellulose, xanthan gum, colloidal magnesium aluminum silicate) to aid in keeping the composition in contact with the oral cavity and not being easily ejected.

If the parasiticidal compositions are in the form of feed concentrates, the carrier is typically selected from high-performance feed, feed cereals or protein concentrates. Such feed concentrate-containing compositions can, in addition to the parasiticidal active ingredients, comprise additives promoting animal health or growth, improving quality of meat from animals for slaughter or otherwise useful to animal husbandry. These additives can include, for example, vitamins, antibiotics, chemotherapeutics, bacteriostats, fungistats, coccidiostats and hormones.

The compounds of Formula **1** may also be formulated in rectal compositions such as suppositories or retention enemas, using, e.g., conventional suppository bases such as cocoa butter or other glycerides.

Formulations for topical administration are typically in the form of a powder, cream, suspension, spray, emulsion, foam, paste, aerosol, ointment, salve or gel. More typically a topical formulation is a water-soluble solution, which can be in the form of a concentrate that is diluted before use. Parasiticidal compositions suitable for topical administration typically comprise a compound of the present invention and one or more topically suitable carriers. In applications of a parasiticidal composition topically to the exterior of an animal as a line or spot (i.e. “spot-on” treatment), the active ingredient migrates over the surface of the animal to cover most or all of its external surface area. As a result, the treated animal is particularly

protected from invertebrate pests that feed off the epidermis of the animal such as ticks, fleas and lice. Therefore formulations for topical localized administration often comprise at least one organic solvent to facilitate transport of the active ingredient over the skin and/or penetration into the epidermis of the animal. Carriers in such formulations include propylene glycol, paraffins, aromatics, esters such as isopropyl myristate, glycol ethers, alcohols such as ethanol, *n*-propanol, 2-octyl dodecanol or oleyl alcohol; solutions in esters of monocarboxylic acids, such as isopropyl myristate, isopropyl palmitate, lauric acid oxalic ester, oleic acid oleyl ester, oleic acid decyl ester, hexyl laurate, oleyl oleate, decyl oleate, caproic acid esters of saturated fatty alcohols of chain length C_{12}-C_{18}; solutions of esters of dicarboxylic acids, such as dibutyl phthalate, diisopropyl isophthalate, adipic acid diisopropyl ester, di-*n*-butyl adipate or solutions of esters of aliphatic acids, e.g., glycols. It may be advantageous for a crystallization inhibitor or a dispersant known from the pharmaceutical or cosmetic industry also to be present.

A pour-on formulation may also be prepared for control of parasites in an animal of agricultural worth. The pour-on formulations of this invention can be in the form of a liquid, powder, emulsion, foam, paste, aerosol, ointment, salve or gel. Typically, the pour-on formulation is liquid. These pour-on formulations can be effectively applied to sheep, cattle, goats, other ruminants, camelids, pigs and horses. The pour-on formulation is typically applied by pouring in one or several lines or in a spot-on the dorsal midline (back) or shoulder of an animal. More typically, the formulation is applied by pouring it along the back of the animal, following the spine. The formulation can also be applied to the animal by other conventional methods, including wiping an impregnated material over at least a small area of the animal, or applying it using a commercially available applicator, by means of a syringe, by spraying or by using a spray race. The pour-on formulations include a carrier and can also include one or more additional ingredients. Examples of suitable additional ingredients are stabilizers such as antioxidants, spreading agents, preservatives, adhesion promoters, active solubilisers such as oleic acid, viscosity modifiers, UV blockers or absorbers, and colourants. Surface active agents, including anionic, cationic, non-ionic and ampholytic surface active agents, can also be included in these formulations.

The formulations of this invention typically include an antioxidant, such as BHT (butylated hydroxytoluene). The antioxidant is generally present in amounts of at 0.1-5% (wt/vol). Some of the formulations require a solubilizer, such as oleic acid, to dissolve the active agent, particularly if spinosad is used. Common spreading agents used in these pour-on formulations are: IPM, IPP, caprylic/capric acid esters of saturated C_{12}–C_{18} fatty alcohols, oleic acid, oleyl ester, ethyl oleate, triglycerides, silicone oils and DPM. The pour-on formulations of this invention are prepared according to known techniques. Where the pour-on is a solution, the parasiticide/insecticide is mixed with the carrier or vehicle, using heat and stirring where required. Auxiliary or additional ingredients can be added to the

mixture of active agent and carrier, or they can be mixed with the active agent prior to the addition of the carrier. If the pour-on is an emulsion or suspension, these formulations are similarly prepared using known techniques.

Other delivery systems for relatively hydrophobic pharmaceutical compounds may be employed. Liposomes and emulsions are well-known examples of delivery vehicles or carriers for hydrophobic drugs. In addition, organic solvents such as dimethylsulfoxide may be used, if needed.

For agronomic applications, the rate of application required for effective control (i.e. "biologically effective amount") will depend on such factors as the species of invertebrate to be controlled, the pest's life cycle, life stage, its size, location, time of year, host crop or animal, feeding behavior, mating behavior, ambient moisture, temperature, and the like. Under normal circumstances, application rates of about 0.01 to 2 kg of active ingredients per hectare are sufficient to control pests in agronomic ecosystems, but as little as 0.0001 kg/hectare may be sufficient or as much as 8 kg/hectare may be required. For nonagronomic applications, effective use rates will range from about 1.0 to 50 mg/square meter but as little as 0.1 mg/square meter may be sufficient or as much as 150 mg/square meter may be required. One skilled in the art can easily determine the biologically effective amount necessary for the desired level of invertebrate pest control.

In general for veterinary use, a compound of Formula **1**, an *N*-oxide, or salt thereof, is administered in a parasiticidally effective amount to an animal to be protected from invertebrate parasite pests. A parasiticidally effective amount is the amount of active ingredient needed to achieve an observable effect diminishing the occurrence or activity of the target invertebrate parasite pest. One skilled in the art will appreciate that the parasitically effective dose can vary for the various compounds and compositions of the present invention, the desired parasitical effect and duration, the target invertebrate pest species, the animal to be protected, the mode of application and the like, and the amount needed to achieve a particular result can be determined through simple experimentation.

For oral administration to homeothermic animals, the daily dosage of a compound of the present invention typically ranges from about 0.01 mg/kg to about 100 mg/kg, more typically from about 0.5 mg/kg to about 100 mg/kg, of animal body weight. For topical (e.g., dermal) administration, dips and sprays typically contain from about 0.5 ppm to about 5000 ppm, more typically from about 1 ppm to about 3000 ppm, of a compound of the present invention.

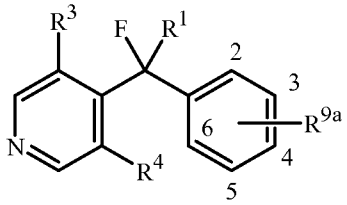
Representative compounds of this invention prepared by the methods described herein are shown in Index Tables A–C. See Index Table D for ^{1}H NMR data. For mass spectral data (AP^+ (M+1)), the numerical value reported is the molecular weight of the parent molecular ion (M) formed by addition of H^+ (molecular weight of 1) to the molecule to give a M+1 peak observed by mass spectrometry using atmospheric pressure chemical ionization

(AP+). The alternate molecular ion peaks (e.g., M+2 or M+4) that occur with compounds containing multiple halogens are not reported.

The following abbreviations are used in the Index Tables which follow: Cmpd means Compound, Me is methyl, Et is ethyl, *i*-Pr is isopropyl, n-Pr is *normal*-propyl, *c*-Pr is *cyclo*-propyl, *n*-Bu is *normal*-butyl, *t*-Bu is *tertiary*-butyl, *i*-Pn is *iso*-pentyl, Ph is phenyl, SMe is methylthio, S(O)Me is methylsulfinyl and SO_2Me is methylsulfonyl.

The wavy line denotes the attachment point of the fragment to the remainder of the molecule.

INDEX TABLE A



Cmpd	R^1	R^3	R^4	R^{9a}	AP+ (M+1)
7	H	Cl	H	4-$C(CH_3)_3$	278
8	H	H	H	4-$C(CH_3)_3$	244
9	F	Cl	H	4-$C(CH_3)_3$	296
10	H	H	H	3-$C(CH_3)_3$	244
11	H	H	H	4-CF_3	256
12	H	Cl	H	3-$C(CH_3)_3$	278
14	F	H	H	4-CF_3	274
15	H	H	H	4-OCF_3	272
16	F	H	H	3-$C(CH_3)_3$	262
17	H	Cl	H	4-OCF_3	306
18	H	H	H	4-F, 3-CF_3	*
19	F	H	H	4-F, 3-CF_3	292
20	H	F	F	4-$C(CH_3)_3$	280
21	H	Cl	Cl	4-$C(CH_3)_3$	*
22	H	F	H	4-$C(CH_3)_3$	262
23	H	Br	H	4-$C(CH_3)_3$	324
24	H	Br	Br	4-$C(CH_3)_3$	400
25	H	Ph	H	4-$C(CH_3)_3$	320
26	H	H	H	4-Ph	264
27	H	H	H	3-Ph	264

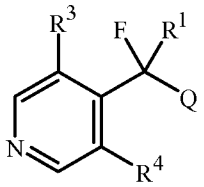
Cmpd	R^1	R^3	R^4	R^{9a}	AP+ (M+1)
29	H	F	H	4-OCF_3	290
30	H	F	F	4-OCF_3	*
31	H	Cl	Cl	4-OCF_3	340
32	H	H	H	4-$Si(CH_3)_3$	260
34	H	SCH_3	H	4-OCF_3	*
35	H	Cl	Cl	4-OCF_3	354
36	H	Cl	Cl	4-OCF_3	358
37	H	Cl	Cl	2-F, 5-OCF_3	358
39	H	S(O)Me	H	4-OCF_3	334
40	H	SO_2Me	H	4-OCF_3	350
57	H	Cl	Cl	4-CF_3	324
60	H	H	H	2-Cl, 4-CF_3	290
61	H	Me	H	4-$C(CH_3)_3$	258
62	H	SCH_3	Cl	4-OCF_3	352
63	H	SCH_3	SCH_3	4-OCF_3	364
64	H	Cl	Cl	2,6-diCl, 4-CF_3	392
65	H	SEt	Cl	4-OCF_3	366
66	H	SEt	SEt	4-OCF_3	392
67	H	Cl	Cl	4-OPh	348
68	H	SEt	H	4-OCF_3	332
69	H	Cl	Cl	4-OCF_3	328
70	H	F	H	4-$C(OMe)(CF_3)_2$	386
71	H	H	H	4-OCH_3	218
72	H	S(*i*-Pr)	H	4-OCF_3	346
73	H	S(*n*-Pr)	H	4-OCF_3	346
74	H	Cl	Cl	4-$OCH_2OCH_2CH_3$	330
77	H	Cl	H	4-CF_3	290
80	H	H	H	4-(*n*-Pr)	230
81	H	H	H	4-(*i*-Pr)	230
82	H	H	H	4-O(*n*-Pr)	246
83	H	F	H	4-$CF(CF_3)_2$	374
85	H	H	H	4-Cl	222
86	H	S(*n*-Pr)	Cl	4-OCF_3	380
87	H	Cl	H	4-CN	247
88	Me	Cl	H	4-OCF_3	320
89	H	Cl	H	4-Br	300

Cmpd	R^1	R^3	R^4	R^{9a}	AP+ (M+1)
90	H	SMe	Cl	4-$C(CH_3)_3$	324
91	H	SMe	Cl	4-OCH_2CF_3	366
92	H	SEt	Cl	4-$C(CH_3)_3$	338
93	H	OMe	OMe	4-$C(CH_3)_3$	304
94	H	SMe	F	4-OCF_3	336
95	H	SMe	F	4-$C(CH_3)_3$	308
96	H	SEt	F	4-$C(CH_3)_3$	322
97	Me	SMe	H	4-OCF_3	332
98	*c*-Pr	Cl	H	4-OCF_3	346
99	H	H	H	4-$CF(CF_3)_2$	406
100	H	SPh	Cl	4-OCF_3	414
101	H	Cl	Cl	4-SF_5	*
102	H	OMe	OMe	4-OCF_3	332
103	H	OCH_2CF_3	F	4-$C(CH_3)_3$	360
104	H	OPh	H	4-$C(CH_3)_3$	336
105	H	SEt	F	4-OCF_3	350
106	H	SMe	F	4-SCF_3	352
107	H	SEt	F	4-SCF_3	366
108	H	OCH_2CF_3	F	4-OCF_3	388
109	H	SMe	Cl	4-OPh	360
110	H	Cl	H	4-$CF(CF_3)(CF_2CF_3)$	440
111	H	SCH_2CF_3	F	4-$C(CH_3)_3$	376
112	H	SCH_2CF_3	F	4-OCF_3	404
113	Me	F	F	4-$C(CH_3)_3$	*
114	Me	SMe	F	4-$C(CH_3)_3$	*
115	H	H	H	2-SMe, 4-$CF(CF_3)(CF_2CF_3)$	452
116	H	Cl	H	2-SMe, 4-$CF(CF_3)(CF_2CF_3)$	486
117	H	F	F	4-CF_3	292
118	H	SMe	F	4-CF_3	320
119	H	OCH_2CF_3	F	4-CF_3	372
120	H	O(*i*-Bu)	F	4-$C(CH_3)_3$	334
121	H	SCH_2CF_3	F	4-CF_3	388
122	H	O(*i*-Bu)	F	4-CF_3	346
125	H	O(*i*-Bu)	F	4-OCF_3	362
126	H	Cl	H	2,6-diCl, 4-$CF(CF_3)(CF_2CF_3)$	508
127	H	H	H	2,6-diCl, 4-$CF(CF_3)(CF_2CF_3)$	474

Cmpd	R^1	R^3	R^4	R^{9a}	AP+ (M+1)
128	H	O(*i*-Pn)	F	4-OCF_3	376
129	H	H	H	2-S(O)Me, 4-$CF(CF_3)(CF_2CF_3)$	468
130	H	Cl	H	2-S(O)Me, 4-$CF(CF_3)(CF_2CF_3)$	502
131	H	OCH_2CF_3	Cl	4-OCF_3	404
132	H	Cl	H	2-SO_2Me, 4-$CF(CF_3)(CF_2CF_3)$	518
133	H	H	H	2-SO_2Me, 4-$CF(CF_3)(CF_2CF_3)$	484
134	H	SMe	Cl	3-I, 6-OCF_3	479
136	H	SMe	Cl	4-SCF_3	368
137	H	SMe	Cl	3-F, 4-CF_3	354
139	H	SMe	Cl	3-Cl, 4-CF_3	370
140	H	SMe	Cl	4-CF_3	336
141	H	SMe	Cl	3-F, 4-OCF_3	370
142	H	SMe	Cl	2-F, 3-CF_3	354
143	H	SMe	Cl	2-Br, 6-F, 5-CF_3	433
150	H	S(O)Me	Cl	3-F, 4-CF_3	370
155	H	F	F	4-SCF_3	324
157	H	F	H	4-SCF_3	306
160	H	SMe	H	4-SCF_3	334
164	H	F	H	4-SO_2CF_3	338
165	H	F	H	4-S(O)CF_3	322
166	H	SO_2Me	F	4-OCF_3	368
167	Et	F	F	4-SCF_3	352
169	H	OEt	F	4-OCF_3	334
170	H	OMe	F	4-OCF_3	320

* See Index Table E for ^{1}H NMR data.

INDEX TABLE B



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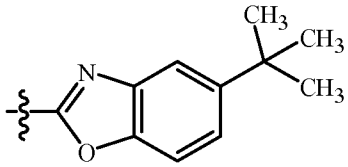
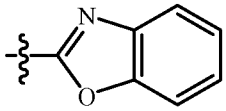
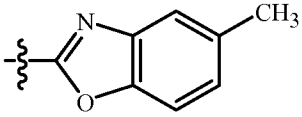
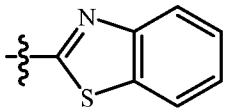
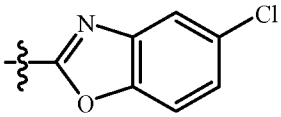
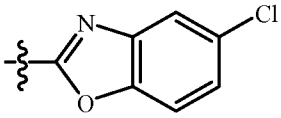
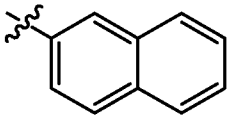
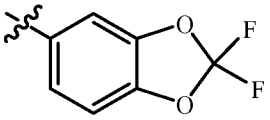
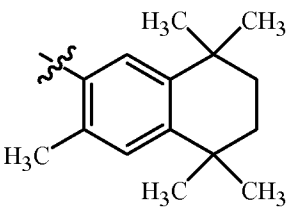
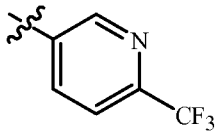
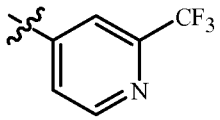
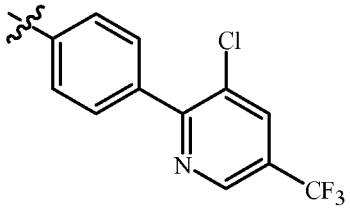
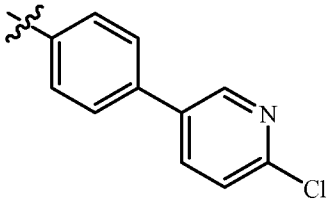
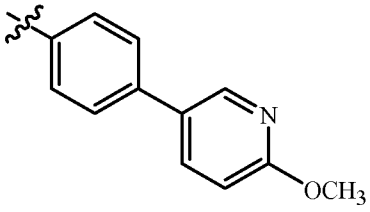
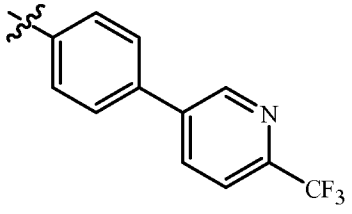
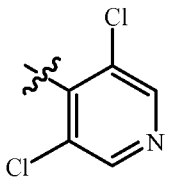
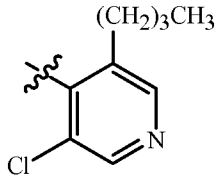
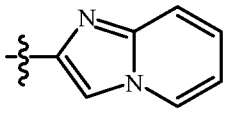
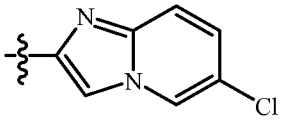
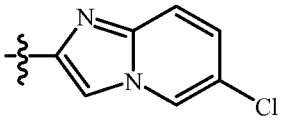
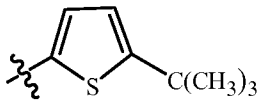
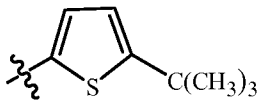
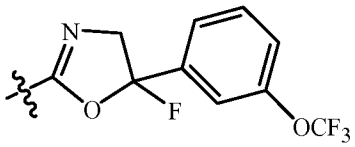
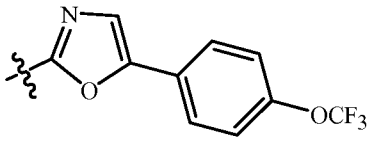
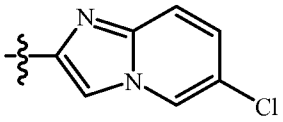
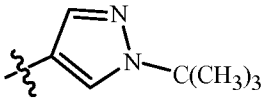
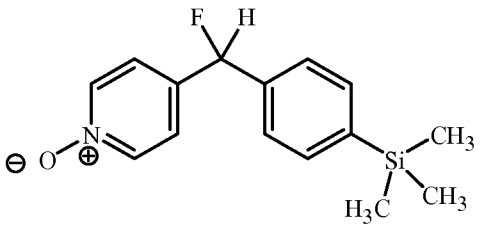
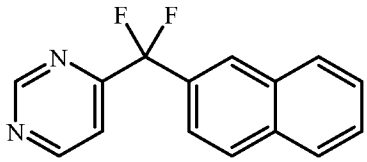
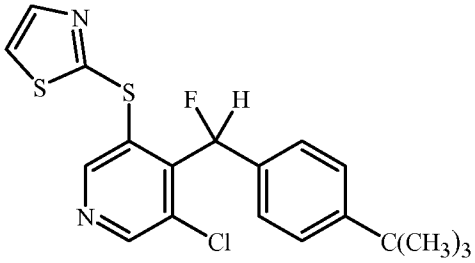
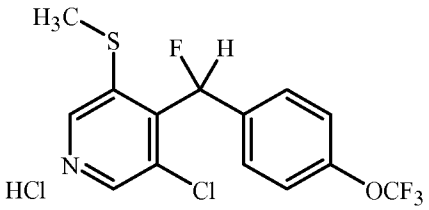
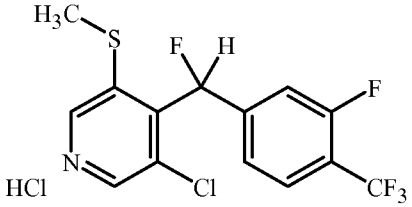
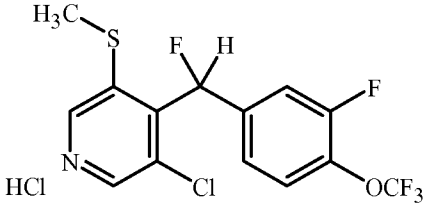
Cmpd	R^1	R^3	R^4	Q	AP+ (M+1)
1	H	Cl	H		*
2	H	Cl	H		*
3	H	Cl	H		*
4	H	Cl	H		279
5	H	H	H		263
6	F	H	H		281
13	H	H	H		238
28	H	H	H		*
38	H	Cl	Cl		*

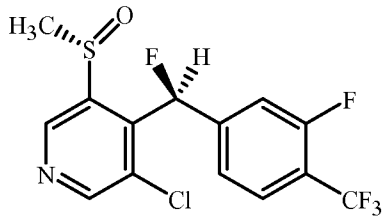
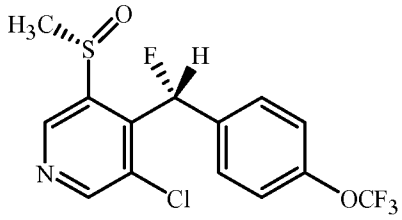
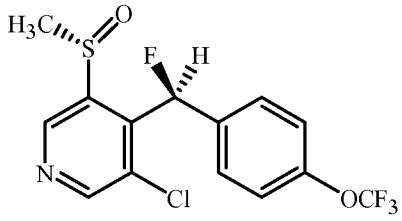
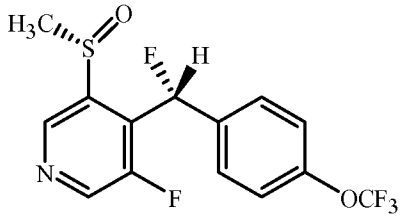
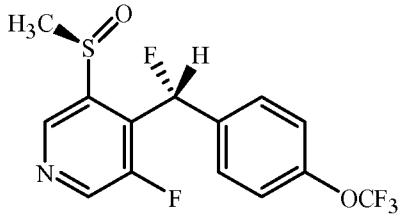
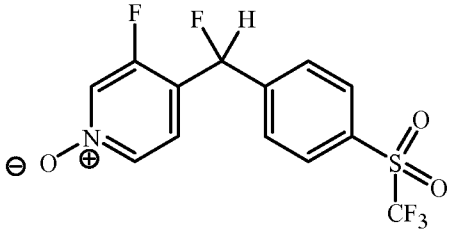
Cmpd	R^1	R^3	R^4	Q	AP+ (M+1)
58	H	Cl	Cl		325
59	H	Cl	Cl		325
75	H	Cl	H		402
76	H	Cl	H		333
78	H	Cl	H		329
79	H	Cl	H		367
123	H	Cl	Cl		327

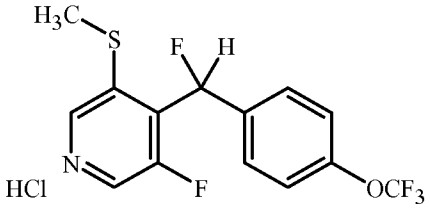
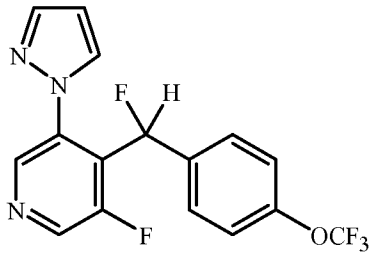
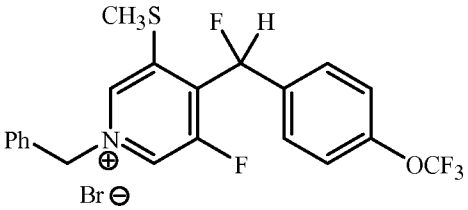
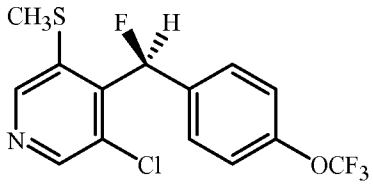
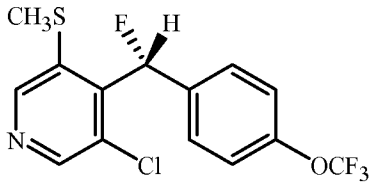
Cmpd	R^1	R^3	R^4	Q	AP+ (M+1)
124	H	Cl	Cl		347
145	H	Cl	Cl		297
146	H	Cl	Cl		331
147	H	F	H		280
148	H	Cl	Cl		*
149	H	SMe	F		*
151	H	Cl	Cl		*
152	H	Cl	Cl		*
153	H	F	F		297
154	H	SMe	F		*

* See Index Table E for ^{1}H NMR data.

INDEX TABLE C

Cmpd	Structure	AP+ (M+1)
33		276
55		*
84		393
135		352
138		354
144		370

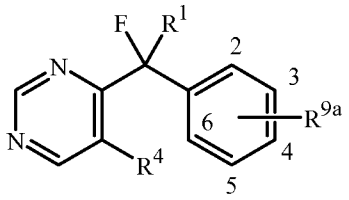
Cmpd	Structure	AP+ (M+1)
156		370
158		368
159		368
161		*
162		*
163		354

Cmpd	Structure	AP+ (M+1)
168		336
171		356
172		*
173		352#
174		352#

* See Index Table E for ^{1}H NMR data.

\# Absolute configuration is temporarily assigned.

INDEX TABLE D



Cmpd	R^1	R^4	R^{9a}	AP+ (M+1)
41	H	SCH_3	4-OCF_3	319
42	H	SCH_2CH_3	4-OCF_3	333
43	H	OCH_3	4-OCF_3	303
44	H	Br	4-CF_3	336
45	H	Br	4-OCF_3	352
46	H	OCH_2CH_3	4-OCF_3	317
47	H	SCH_2CH_3	4-$C(CH_3)_3$	305
48	H	SCH_3	4-$C(CH_3)_3$	291
49	H	$SO_2CH_2CH_3$	4-OCF_3	365
50	H	$S(O)CH_2CH_3$	4-OCF_3	349
51	H	SCH_2Ph	4-$C(CH_3)_3$	367
52	H	H	3-CF_3	*
53	F	H	4-Cl	*
54	F	H	3-Ph	*
56	F	H	3-OCF_3	*

* See Index Table E for ^{1}H NMR data.

INDEX TABLE E

Cmpd No.	^{1}H NMR Data [a]
1	δ 8.68 (d, 1H), 8.63(s, 1H), 7.792 (s, 1H), 7.75 (d,1H), 7.49 (s, 2H), 6.92 (d, 1H), 1.367 (s, 9H).
2	δ 8.70 (d, 1H), 8.64 (s,1H), 7.78 (d,1H), 7.76 (d,1H), 7.57 (d, 1H), 7.41 (m, 2H), 6.94 (d, 1H).
3	δ 8.68 (d, 1H), 8.63 (s, 1H), 7.74 (d, 1H), 7.55 (s, 1H), 7.43 (d, 1H), 7.23 (d, 1H), 6.90 (d, 1H), 2.47 (s, 3H).
18	δ 8.666 (d,2H), 7.65 (dd, 1H), 7.60 (dd,1H), 7.30 (dd,2H), 6.80 (d,1H).
21	δ 8.518 (s,2H), 7.39 (d,2H), 7.30 (d,2H), 7.12 (d, 1H).
28	δ 8.65 (d, 2H), 7.32 (d, 2H), 7.08 (m, 3H), 6.63 (d, 1H).

Cmpd No.	^{1}H NMR Data [a]
30	δ 8.396(s, 2H), 7.43 (d,2H), 7.263 (d, 2H), 6.85 (d, 1H).
34	δ 8.546 (s,2H), 7.48(d,1H),7.38 (d,2H),7.21(d,2H), 6.73(d,1H), 2.43 (s,3H).
38	δ 8.57 (s, 2H), 7.13(d,1H),6.98 (s,1H)2.39 (s,3H),1.64(m,4H),1.26 (s,6H),1.17(s,3H),1.04(s,3H).
52	δ 9.18 (s, 1H), 8.84 (d, 1H), 7.73 (s, 1H), 7.64-7.52 (m, 4H), 6.49 (d, 1H).
53	δ 9.28 (s, 1H), 8.93 (d, 1H), 7.73 (d, 1H), 7.55 (d, 2H), 7.43 (d, 2H).
54	δ 9.30 (s, 1H), 8.92 (s, 1H), 7.82 (s, 1H), 7.76-7.37 (m, 9H).
55	δ 9.30 (s, 1H), 8.93 (d, 1H), 8.13 (s, 1H), 7.92-7.55 (m, 7H).
56	δ 9.29 (s, 1H), 8.94 (d, 1H), 7.75 (d, 1H), 7.49 (m, 3H), 7.3 (m, 1H).
101	δ 8.57 (s, 2H), 8.78 (d, 2H), 7.46 (d, 2H), 7.20 (d, 1H).
109	δ 8.36 (s, 1H), 8.35 (s, 1H), 7.29-7.24 (m, 4H), 7.12-7.02 (m, 2H), 6.96-6.90 (m, 4H), 2.43 (s, 3H).
113	δ 8.30 (s, 2H), 7.45 (m, 4H), 2.18 (dt, 1H), 1.31 (s, 9H).
114	δ 8.23 (s, 1H), 8.18 (s, 1H), 7.35 (m, 4H), 2.43 (s, 3H), 2.18 (dd, 3H), 1.31 (s, 9H).
123	δ 8.46 (s, 4H), 7.22 (d, 1H).
124	δ 8.50 (s, 1H), 8.50 (s, 1H), 8.32 (s, 1H), 7.59 (s, 1H), 7.07 (d, 1H), 2.89-2.86 (m, 2H), 1.67-1.61 (m, 2H), 1.37-1.32 (m, 2H), 0.88 (t, 3H).
134	δ 8.49 (s, 1H), 8.45 (s, 1H), 7.93 (s, 1H), 7,74 (d, 1H), 7.33 (d, 1H), 7.01 (m, 1H), 2.50 (s, 3H).
148	δ 8.53 (s, 2H), 7.13 (d, 1H), 6.86 (t, 1H), 6.71 (dd, 1H), 1.37 (s, 9H)
149	δ 8.37 (s, 1H), 8.36 (s, 1H), 7.06 (d, 1H), 6.90 (t, 1H), 6.70 (dd, 1H), 2.53 (s, 3H), 1.36 (s, 9H)
151	δ 8.57 (s, 2H), 7.50 (t, 1H), 7.40 (d, 1H), 7.34 (d, 1H), 7.33 (s, 1H), 6.04 (dd, 1H), 4.27 (m, 2H).
152	δ 8.56 (s, 2H), 7.86 (s, 1H), 7.84 (d, 2H), 7.39 (m, 2H), 7.08 (d, 1H).
154	δ 8.36 (s, 1H), 8.35 (s, 1H), 7.61 (d, 1H), 7.58 (s, 1H), 6.94 (d, 1H), 2.54 (s, 3H), 1.57 (s, 9H).
161	δ 9.17 (s, 1H), 8.67 (s, 1H), 7.37 (d, 2H), 7.28 (d, 2H), 6.98 (d, 1H), 2.64 (s, 3H).
162	δ 9.22 (s, 1H), 8.66 (s, 1H), 7.46 (d, 2H), 7.26 (d, 2H), 6.99 (d, 1H), 2.93 (s, 3H).
172	δ 9.67 (s, 1H), 9.65 (m, 1H), 7.93 (m, 2H), 7.50 (d, 2H), 7.34 (m, 3H), 7.23 (d, 2H), 6.86 (d, 1H), 6.62 (s, 2H), 2.97 (s, 3H).

[a] ^{1}H NMR data are in ppm downfield from tetramethylsilane. $CDCl_3$ solution unless indicated otherwise. Couplings are designated by (s)-singlet, (d)-doublet, (t)-triplet, (m)-multiplet, (dd)-doublet of doublets, (br s)-broad singlet.

The following Tests demonstrate the control efficacy of compounds of this invention on specific pests. "Control efficacy" represents inhibition of invertebrate pest development (including mortality) that causes significantly reduced feeding. The pest control protection afforded by the compounds is not limited, however, to these species. Compound numbers refer to compounds in Index Tables A–C.

BIOLOGICAL EXAMPLES OF THE INVENTION

TEST A

For evaluating control of diamondback moth (*Plutella xylostella*) the test unit consisted of a small open container with a 12–14-day-old radish plant inside. This was pre-infested with ~50 neonate larvae that were dispensed into the test unit via corn cob grits using a bazooka inoculator. The larvae moved onto the test plant after being dispensed into the test unit.

Test compounds were formulated using a solution containing 10% acetone, 90% water and 300 ppm X-77® Spreader Lo-Foam Formula non-ionic surfactant containing alkylarylpolyoxyethylene, free fatty acids, glycols and isopropanol (Loveland Industries, Inc. Greeley, Colorado, USA). The formulated compounds were applied in 1 mL of liquid through a SUJ2 atomizer nozzle with 1/8 JJ custom body (Spraying Systems Co., Wheaton, Illinois, USA) positioned 1.27 cm (0.5 inches) above the top of each test unit. Test compounds were sprayed at 50 ppm and/or 10 ppm, and replicated three times. After spraying of the formulated test compound, each test unit was allowed to dry for 1 h and then a black, screened cap was placed on top. The test units were held for 6 days in a growth chamber at 25 °C and 70% relative humidity. Plant feeding damage was then visually assessed based on foliage consumed.

Of the compounds of Formula **1** tested at 250 ppm, the following provided very good to excellent levels of control efficacy (40% or less feeding damage and/or 100% mortality): 6, 7, 8, 10, 16, 18, 19, 23, 25, 27, 28, 41, 42, 44, 45, 46, 57, 58, 59, 60, 62, 64, 65, 68, 69, 70, 72, 73, 77, 81, 85, 88, 89, 94, 97, 98, 100, 101, 105, 106, 107, 108, 112, 113, 116, 118, 119, 121, 122, 125, 127, 131, 133, 135, 136, 137, 138, 139, 140, 142 and 143.

TEST B

For evaluating control of green peach aphid (*Myzus persicae*) through contact and/or systemic means, the test unit consisted of a small open container with a 12–15-day-old radish plant inside. This was pre-infested by placing on a leaf of the test plant 30–40 aphids on a piece of leaf excised from a culture plant (cut-leaf method). The aphids moved onto the test plant as the leaf piece desiccated. After pre-infestation, the soil of the test unit was covered with a layer of sand.

Test compounds were formulated and sprayed at 50 ppm and/or 10 ppm as described for Test A. The applications were replicated three times. After spraying of the formulated

test compound, each test unit was allowed to dry for 1 h and then a black, screened cap was placed on top. The test units were held for 6 days in a growth chamber at 19–21 °C and 50–70% relative humidity. Each test unit was then visually assessed for insect mortality.

Of the compounds of Formula **1** tested at 250 ppm, the following resulted in at least 80% mortality: 7, 8, 10, 14, 17, 20, 21, 22, 24, 41, 42, 43, 45, 46, 50, 57, 58, 62, 63, 65, 68, 70, 72, 81, 83, 85, 91, 94, 96, 97, 99, 101, 103, 105, 107, 108, 110, 118, 122, 125, 131, 135, 136, 137, 138, 139, 140 and 142.

TEST C

For evaluating control of cotton melon aphid (*Aphis gossypii*) through contact and/or systemic means, the test unit consisted of a small open container with a 6–7-day-old cotton plant inside. This was pre-infested with 30–40 insects on a piece of leaf according to the cut-leaf method described for Test C, and the soil of the test unit was covered with a layer of sand.

Test compounds were formulated and sprayed at 50 ppm and/or 10 ppm as described for Test C. The applications were replicated three times. After spraying, the test units were maintained in a growth chamber and then visually rated as described for Test C.

Of the compounds of Formula **1** tested at 250 ppm, the following resulted in at least 80% mortality: 7, 8, 9, 10, 14, 15, 16, 17, 20, 21, 22, 41, 42, 43, 44, 46, 57, 58, 62, 65, 69, 70, 72, 73, 77, 80, 81, 83, 88, 89, 91, 94, 102, 106, 107, 108, 112, 113, 118, 119, 121, 122, 131, 135, 136, 137, 139 and 140.

TEST D

For evaluating control of corn planthopper (*Peregrinus maidis*) through contact and/or systemic means, the test unit consisted of a small open container with a 3–4-day-old maize plant (spike) inside. White sand was added to the top of the soil prior to application. Test compounds were formulated and sprayed at 50 ppm and/or 10 ppm, and replicated three times as described for Test A. After spraying, the test units were allowed to dry for 1 h before they were post-infested with ~15-20 nymphs (18 to 21 day old) by sprinkling them onto the sand with a salt shaker. A black, screened cap was placed on the top of each test unit, and the test units were held for 6 days in a growth chamber at 22–24 °C and 50–70% relative humidity. Each test unit was then visually assessed for insect mortality.

Of the compounds of Formula **1** tested at 250 ppm the following provided very good to excellent levels of control efficacy (80% or more mortality): 1, 2, 3, 4, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 57, 58, 59, 60, 61, 62, 63, 65, 66, 67, 68, 69, 70, 72, 73, 74, 77, 80, 81, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 99, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 117, 118, 119, 120, 121, 122, 125, 127, 128, 131, 134, 135, 136, 137, 138, 139, 140, 142 and 149.

TEST E

For evaluating control of potato leafhopper (*Empoasca fabae*) through contact and/or systemic means, the test unit consisted of a small open container with a 5–6-day-old Soleil bean plant (primary leaves emerged) inside. White sand was added to the top of the soil and one of the primary leaves was excised prior to application.

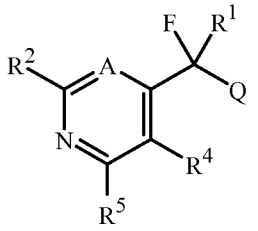
Test compounds were formulated and sprayed at 50 ppm and/or 10 ppm, and the tests were replicated three times as described for Test A. After spraying, the test units were allowed to dry for 1 h before they were post-infested with 5 potato leafhoppers (18–21-day-old adults). A black, screened cap was placed on the top of each test unit, and the test units were held for 6 days in a growth chamber at 24 °C and 70% relative humidity. Each test unit was then visually assessed for insect mortality.

Of the compounds of Formula **1** tested at 250 ppm the following provided very good to excellent levels of control efficacy (80% or more mortality): 1, 8, 10, 12, 20, 41, 42, 43, 44, 46, 57, 58, 59, 60, 62, 64, 65, 94, 105, 106, 107, 108, 112, 113, 116, 118, 119, 121, 137, 138, 139, 140 and 142.

CLAIMS

What is claimed is:

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



1

wherein

A is N or CR^3;

R^1 is hydrogen, halogen, hydroxyl, cyano, SF_5, C_1–C_4 alkyl, C_2–C_4 alkenyl, C_2–C_4 alkynyl, C_1–C_4 haloalkyl, C_2–C_4 haloalkenyl, C_2–C_4 haloalkynyl, C_3–C_4 cycloalkyl, C_3–C_4 halocycloalkyl, C_1–C_4 alkoxy, C_1–C_4 haloalkoxy, C_2–C_4 alkylthio, C_2–C_4 alkylsulfinyl, C_2–C_4 alkylsulfonyl, C_2–C_4 haloalkylthio C_2–C_4 cyanoalkyl, C_2–C_4 alkylcarbonyl or C_2–C_4 alkoxycarbonyl;

R^2 and R^5 are each independently selected from hydrogen and fluorine;

$R^3$and R^4 are each independently selected from hydrogen, halogen, cyano, amino, nitro, SF_5, -CHO, 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_2–C_6 haloalkynyl, C_3–C_6 cycloalkyl, C_3–C_6 halocycloalkyl, C_4–C_8 alkylcycloalkyl, C_4–C_8 cycloalkylalkyl, C_3–C_6 cycloalkenyl, C_2–C_6 alkoxyalkyl, C_2–C_6 alkylthioalkyl, C_2–C_6 alkylcarbonyl, C_2–C_6 haloalkylcarbonyl, C_2–C_6 alkoxycarbonyl, C_2–C_6 alkylaminocarbonyl, C_3–C_8 dialkylaminocarbonyl, C_2–C_6 cyanoalkyl, C_1–C_6 alkoxy, C_1–C_6 haloalkoxy, C_2–C_6 alkoxyalkoxy, C_1–C_6 alkylthio, C_1–C_6 haloalkylthio, C_1–C_6 alkylsulfinyl, C_1–C_6 haloalkylsulfinyl, C_1–C_6 alkylsulfonyl, C_1–C_6 haloalkylsulfonyl, C_3–C_9 trialkylsilyl, C_1–C_6 alkylamino, C_2–C_6 dialkylamino, C_2–C_6 haloalkylamino, C_2–C_6 halodialkylamino or C_2–C_6 alkylcarbonylamino; or Q^1, OQ^1 or SQ^1;

Q is phenyl or naphthalenyl each optionally substituted on carbon atom ring members with up to 5 substituents independently selected from R^{9a}; or

Q is a 5- to 6-membered heteroaromatic ring provided that the 5- to 6-membered heteroaromatic ring is not imidazole or pyridazine, or an 8- to 11-membered heteroaromatic bicyclic ring system provided that the 8- to 11-membered

heteroaromatic bicyclic ring system does not contain a pyridazine ring; each ring or ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members; or

Q is a 3- to 7-membered nonaromatic carbocyclic ring, a 5- to 7-membered nonaromatic heterocyclic ring provided that the 5- to 7-membered nonaromatic heterocyclic ring is not piperidine, or an 8- to 11-membered nonaromatic bicyclic ring system provided that the 8- to 11-membered nonaromatic bicyclic ring system does not contain a piperidine ring; each ring or ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S, up to 4 N and up to 2 Si atoms, wherein up to 3 carbon atom ring members are independently selected from C(=O) and C(=S), the sulfur atom ring members are independently selected from $S(=O)_s(=NR^{17})_f$, and the silicon atom ring members are independently selected from $SiR^{10}R^{11}$, each ring or ring system optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members;

each R^{9a} is independently halogen, hydroxy, amino, cyano, nitro, SF_5, C_1–C_6 alkyl, C_2–C_6 alkenyl, C_2–C_6 alkynyl, C_3–C_6 cycloalkyl, C_4–C_{10} cycloalkylalkyl, C_4–C_{10} alkylcycloalkyl, C_5–C_{10} alkylcycloalkylalkyl, C_6–C_{14} cycloalkylcycloalkyl, C_1–C_6 haloalkyl, C_2–C_6 haloalkenyl, C_2–C_6 haloalkynyl, C_3–C_6 halocycloalkyl, C_1–C_4 alkoxy, C_1–C_4 haloalkoxy, C_2–C_4 alkoxyalkoxy, C_1–C_4 alkylthio, C_1–C_4 alkylsulfinyl, C_1–C_4 alkylsulfonyl, C_1–C_4 haloalkylthio, C_1–C_4 haloalkylsulfinyl, C_1–C_4 haloalkylsulfonyl, C_1–C_4 alkylamino, C_2–C_8 dialkylamino, C_3–C_6 cycloalkylamino, C_2–C_4 alkoxyalkyl, C_1–C_4 hydroxyalkyl, C_2–C_4 alkylcarbonyl, C_2–C_6 alkoxycarbonyl, C_2–C_6 alkylcarbonyloxy, C_2–C_6 alkylcarbonylthio, C_2–C_6 alkylaminocarbonyl, C_3–C_8 dialkylaminocarbonyl, C_3–C_6 haloalkylcarbonylamino, C_3–C_6 haloalkylcarbonyl(alkyl)amino or C_3–C_6 trialkylsilyl; or phenyl, phenoxy or naphthalenyl optionally substituted with up to 3 substituents independently selected from halogen, cyano, C_1–C_2 alkyl, C_1–C_2 haloalkyl, C_1–C_2 alkoxy and C_1–C_2 haloalkoxy; or a 5- to 6-membered heteroaromatic ring containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 3 substituents independently selected

from halogen, cyano, C_1–C_2 alkyl, C_1–C_2 haloalkyl, C_1–C_2 alkoxy and C_1–C_2 haloalkoxy on carbon atom ring members and cyano, C_1–C_2 alkyl and C_1–C_2 alkoxy on nitrogen atom ring members; or a 3- to 7-membered nonaromatic ring containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, wherein up to 3 carbon atom ring members are independently selected from C(=O) and C(=S), the ring optionally substituted with up to 3 substituents independently selected from halogen, cyano, C_1–C_2 alkyl, C_1–C_2 haloalkyl, C_1–C_2 alkoxy and C_1–C_2 haloalkoxy on carbon atom ring members and cyano, C_1–C_2 alkyl and C_1–C_2 alkoxy on nitrogen atom ring members;

each R^{9b} is independently hydrogen, cyano, C_1–C_3 alkyl, C_1–C_3 haloalkyl, C_1–C_3 alkoxy, C_2–C_3 alkylcarbonyl, C_2–C_3 alkoxycarbonyl or C_3–C_6 cycloalkyl;

Q^1 is phenyl or naphthalenyl each optionally substituted on carbon atom ring members with up to 5 substituents independently selected from R^{9a}; or

Q^1 is a 5- to 6-membered heteroaromatic ring or an 8- to 11-membered heteroaromatic bicyclic ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members; or

Q^1 is a 3- to 7-membered nonaromatic carbocyclic ring, a 5- to 7-membered nonaromatic heterocyclic ring or an 8- to 11-membered nonaromatic bicyclic ring system, each ring or ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S, up to 4 N and up to 2 Si atoms, wherein up to 3 carbon atom ring members are independently selected from C(=O) and C(=S), the sulfur atom ring members are independently selected from $S(=O)_s(=NR^{17})_f$, and the silicon atom ring members are independently selected from $SiR^{10}R^{11}$, each ring or ring system optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members;

each R^{10} and R^{11} is independently C_1–C_5 alkyl, C_2–C_5 alkenyl, C_2–C_5 alkynyl, C_3–C_5 cycloalkyl, C_3–C_6 halocycloalkyl, C_4–C_{10} cycloalkylalkyl, C_4–C_7 alkylcycloalkyl, C_5–C_7 alkylcycloalkylalkyl, C_1–C_5 haloalkyl, C_1–C_5 alkoxy or C_1–C_5 haloalkoxy;

each R^{17} is independently hydrogen, cyano, C_1–C_6 alkyl, C_1–C_6 haloalkyl, C_3–C_8 cycloalkyl, C_3–C_8 halocycloalkyl, C_1–C_6 alkoxy, C_1–C_6 haloalkoxy, C_1–C_6 alkylamino, C_2–C_8 dialkylamino, C_1–C_6 haloalkylamino or phenyl; and

s and f are independently 0, 1 or 2 in each instance of $S(=O)_s(=NR^{17})_f$, provided that the sum of s and f is 0, 1 or 2;

provided that

the compound of Formula **1** is other than 4,4'-(1,2,2,2-tetrafluoroethylidene)-bis[pyridine] or 4,4'-(1,2,2,2-tetrafluoroethylidene)bis[2,3,5,6-tetrafluoropyridine].

2. A compound of Claim 1 wherein

A is CR^3;

R^1 is hydrogen, halogen or C_1–C_4 alkyl;

R^2 and R^5 are each hydrogen;

R^3 and R^4 are each independently selected from hydrogen, halogen, C_1–C_6 alkyl, C_1–C_6 haloalkyl, C_1–C_6 alkoxy, C_1–C_6 haloalkoxy, C_1–C_6 alkylthio, C_1–C_6 alkylsulfinyl or C_1–C_6 alkylsulfonyl;

Q is phenyl optionally substituted on carbon atom ring members with up to 5 substituents independently selected from R^{9a}; or a 5- to 6-membered heteroaromatic ring provided that the 5- to 6-membered heteroaromatic ring is not imidazole or pyridazine, or an 8- to 11-membered heteroaromatic bicyclic ring system provided that the 8- to 11-membered heteroaromatic bicyclic ring system does not contain a pyridazine ring; each ring or ring system containing ring members selected from carbon atoms and up to 4 heteroatoms independently selected from up to 2 O, up to 2 S and up to 4 N atoms, and optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members; and

each R^{9a} is independently halogen, SF_5, C_1–C_6 alkyl, C_1–C_6 haloalkyl, C_1–C_4 alkoxy, C_1–C_4 haloalkoxy, C_1–C_4 alkylthio, C_1–C_4 alkylsulfinyl, C_1–C_4 alkylsulfonyl, C_1–C_4 haloalkylthio, C_1–C_4 haloalkylsulfinyl, C_1–C_4 haloalkylsulfonyl or C_3–C_6 trialkylsilyl.

3. A compound of Claim 2 wherein

R^1 is hydrogen, halogen or methyl; and

Q is phenyl, pyridinyl, benzoxazole or benzimidazole optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members and R^{9b} on nitrogen atom ring members.

4. A compound of Claim 3 wherein

R^1 is hydrogen or fluoro;

R^3 and R^4 are each independently selected from hydrogen, fluoro, chloro, methoxy, methylthio, methylsulfinyl or methylsulfonyl.

Q is phenyl, optionally substituted with up to 5 substituents independently selected from R^{9a} on carbon atom ring members; and

each R^{9a} is independently halogen, SF_5, *tert*-butyl, CF_3, OCF_3, CF_2CF_3 or SCF_3.

5. A compound of Claim 1 that is selected from the group consisting of:

5-chloro-2-(difluoro-4-pyridinylmethyl)benzoxazole;

4-[difluoro[4-(trifluoromethyl)phenyl]methyl]pyridine;

4-[[4-(1,1-dimethylethyl)phenyl]fluoromethyl]-3,5-difluoropyridine;

4-[[4-(1,1-dimethylethyl)phenyl]fluoromethyl]-3-fluoropyridine; and

3,5-dichloro-4-[fluoro[4-(trifluoromethoxy)phenyl]methyl]pyridine.

3,5-dichloro-4-[[4-(1,1-dimethylethyl)phenyl]fluoromethyl]pyridine

3-fluoro-4-[fluoro[4-(trifluoromethoxy)phenyl]methyl]-5-(methylthio)pyridine

3-chloro-4-[fluoro[4-(trifluoromethoxy)phenyl]methyl]-5-(methylthio)pyridine

4-[[4-(1,1-dimethylethyl)phenyl]fluoromethyl]pyridine

3-chloro-5-(ethylthio)-4-[fluoro[4-(trifluoromethoxy)phenyl]methyl]pyridine

3-fluoro-4-[fluoro[4-[(trifluoromethyl)thio]phenyl]methyl]-5-(methylthio)pyridine

3-fluoro-4-[fluoro[4-(trifluoromethyl)phenyl]methyl]-5-(methylthio)pyridine

3-fluoro-4-[[4-(1,1-dimethylethyl)phenyl]fluoromethyl]pyridine

6. A composition comprising a compound of Claim 1 and at least one additional component selected from the group consisting of surfactants, solid diluents and liquid diluents.

7. The composition of Claim 6 further comprising at least one additional biologically active compound or agent.

8. The composition of Claim 7 wherein the at least one additional biologically active compound or agent is selected from the group consisting of abamectin, acephate, acequinocyl, acetamiprid, acrinathrin, amidoflumet, amitraz, avermectin, azadirachtin, azinphos-methyl, bensultap, bifenthrin, bifenazate, bistrifluron, borate, buprofezin, cadusafos, carbaryl, carbofuran, cartap, carzol, chlorantraniliprole, chlorfenapyr, chlorfluazuron, chlorpyrifos, chlorpyrifos-methyl, chromafenozide, clofentezin, clothianidin, cyantraniliprole, cyflumetofen, cyfluthrin, beta-cyfluthrin, cyhalothrin, gamma-cyhalothrin, lambda-cyhalothrin, cypermethrin, alpha-cypermethrin, zeta-cypermethrin, cyromazine,

deltamethrin, diafenthiuron, diazinon, dieldrin, diflubenzuron, dimefluthrin, dimehypo, dimethoate, dinotefuran, diofenolan, emamectin, endosulfan, esfenvalerate, ethiprole, etofenprox, etoxazole, fenbutatin oxide, fenothiocarb, fenoxycarb, fenpropathrin, fenvalerate, fipronil, flonicamid, flubendiamide, flucythrinate, flufenerim, flufenoxuron, fluvalinate, tau-fluvalinate, fonophos, formetanate, fosthiazate, halofenozide, hexaflumuron, hexythiazox, hydramethylnon, imidacloprid, indoxacarb, insecticidal soaps, isofenphos, lufenuron, malathion, metaflumizone, metaldehyde, methamidophos, methidathion, methiodicarb, methomyl, methoprene, methoxychlor, metofluthrin, monocrotophos, methoxyfenozide, nitenpyram, nithiazine, novaluron, noviflumuron, oxamyl, parathion, parathion-methyl, permethrin, phorate, phosalone, phosmet, phosphamidon, pirimicarb, profenofos, profluthrin, propargite, protrifenbute, pymetrozine, pyrafluprole, pyrethrin, pyridaben, pyridalyl, pyrifluquinazon, pyriprole, pyriproxyfen, rotenone, ryanodine, spinetoram, spinosad, spirodiclofen, spiromesifen, spirotetramat, sulprofos, sulfoxaflor, tebufenozide, tebufenpyrad, teflubenzuron, tefluthrin, terbufos, tetrachlorvinphos, tetramethrin, thiacloprid, thiamethoxam, thiodicarb, thiosultap-sodium, tolfenpyrad, tralomethrin, triazamate, trichlorfon, triflumuron, *Bacillus thuringiensis* delta-endotoxins, entomopathogenic bacteria, entomopathogenic viruses and entomopathogenic fungi.

9. A composition for protecting an animal from an invertebrate parasitic pest comprising a parasiticidally effective amount of a compound of Claim 1 and at least one carrier.

10. A method for controlling an invertebrate pest comprising contacting the invertebrate pest or its environment with a biologically effective amount of a compound of Claim 1.

11. A treated seed comprising a compound of Claim 1 in an amount of from about 0.0001 to 1 % by weight of the seed before treatment.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/064371

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D213/26 C07D213/61 C07D213/70 C07D239/34 C07D401/06
C07D405/06 C07D409/06 C07D413/06 C07D417/06 A61K31/44
A61K31/505 A01N43/40 A01N43/54

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D A61K A01N

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHAMBERS: "Reactions Involving Fluoride Ion. Part VII. Reactions of Polyfluoroethylenes with Pentafluoropyridine and Tetrafluoropyridazine", JOURNAL OF THE CHEMICAL SOCIETY, PERKIN TRANSACTIONS 1, CHEMICAL SOCIETY, LETCHWORTH; GB, 1 January 1973 (1973-01-01), pages 1411-1415, XP009156891, ISSN: 0300-922X page 1413; compound XVI	1-4
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[X] Further documents are listed in the continuation of Box C.

[X] 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 document 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	Date of mailing of the international search report
7 March 2012	02/04/2012

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

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/064371

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	WO 02/24663 A2 (SUMITOMO CHEMICAL CO [JP]; MIZUNO HAJIME [JP]; SAKAMOTO NORIYASU [JP];) 28 March 2002 (2002-03-28) claims 1-66	1-11
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International application No
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