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(71) Applicants: **THE REGENTS OF THE UNIVERSI¬TY OF CALIFORNIA** [US/US]; 1111 Franklin Street, Twelfth Floor, Oakland, CA 94607-5200 (US). **SYNGENTA PARTICIPATIONS AG** [CH/CH]; Schwarzwaldallee 215, CH-4058 Basel (CH).

(72) Inventors: **CUTLER, Sean, R.;** c/o University of California, Riverside, Institute/Integrative Genome Bio., 3119A Genomics Bldg., Riverside, CA 92521 (US). **LACHIA, Mathilde, Denise;** c/o Syngenta Crop Protection AG, Schaffhauserstrasse, 4332 Stein (CH). **WENDEBORN, Sebastian, Volker;** c/o Syngenta Crop Protection AG, Schaffhauserstrasse, 4332 Stein (CH). **GODFREY, Christopher, Richard Ayles;** c/o Syngenta Crop Protection AG, Schaffhauserstrasse, 4332 Stein (CH). **SABBADIN, Davide;** c/o Syngenta Crop Protection AG, Schaffhauserstrasse, 4332 Stein (CH).

(74) Agent: **MANN, Jeffry, S.** et al; Morgan, Lewis & Bockius LLP, One Market, Spear Street Tower, San Francisco, CA 94105 (US).

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(54) Title: CARBAMATE QUINABACTIN

(57) Abstract: The present invention relates to novel sulfonamide derivatives, to processes and intermediates for preparing them, to plant growth regulator compositions comprising them and to methods of using them for controlling the growth of plants, improving plant tolerance to abiotic stress (including environmental and chemical stresses), inhibiting seed germination and/or safening a plant against phytotoxic effects of chemicals.

CARBAMATE QUINABACTIN

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application No. 62/363,549 filed on July 18, 2016, which is incorporated herein by reference in its entirety for all purposes.

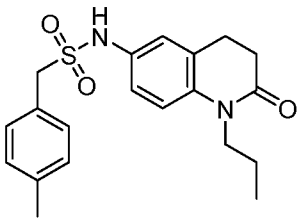
FIELD OF THE INVENTION

[0002] The present invention relates to novel sulfonamide derivatives, to processes and intermediates for preparing them, to plant growth regulator compositions comprising them and to methods of using them for controlling the growth of plants, improving plant tolerance to abiotic stress (including environmental and chemical stresses), inhibiting seed germination and/or safening a plant against phytotoxic effects of chemicals.

BACKGROUND OF THE INVENTION

[0003] Abscisic acid (ABA) is a plant hormone that plays a major role in plant growth, development and response to abiotic stress. ABA causes many of its cellular responses by binding to a soluble family of receptors called PYR/PYL proteins, which contain a ligand-binding pocket for ABA and other agonists. Direct application of ABA to plants has been shown to improve their water use efficiency. However, ABA is difficult and expensive to prepare and itself unstable to environmental conditions and therefor unsuitable for large scale agricultural applications. It is therefore desirable to search for ABA agonists that may be useful for improving plant tolerance to environment stress such as drought, inhibit seed germination, regulate plant growth and improve crop yield.

[0004] Park *et al.* (2009, Science, vol. 324(5930), 1068-1071) reported that ABA agonist pyrabactin activates ABA responses in seeds, but does not trigger significant responses in vegetative tissues. Okamoto *et al.* (PNAS, 2013, 110(29), 12132-12137; and WO2013/148339) reported a new ABA agonist, quinabactin, which binds to the PYR/PRL receptor proteins and causes an abscisic acid response *in vivo.* Quinabactin has been shown to induce stomatal closure, suppress of water loss and promote drought tolerance.



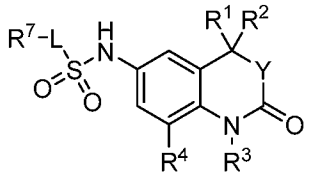
quinabactin

[0005] There is a need to identify improved agonists of abscisic acid for improving plant growth and development, and plant tolerance to environmental stresses. The present invention relates to novel analogs of quinabactin that have improved properties. Benefits of the compounds of the present invention include enhanced tolerance to abiotic stress, improved inhibition of seed germination, better regulation of crop growth, improved crop yield, and/or improved physical properties resulting in better plant uptake, water solubility, chemical stability or physical stability.

SUMMARY OF THE INVENTION

[0006] The present invention provides novel sulfonamide derivatives, processes and intermediates for preparing them, compositions comprising them and methods of using them.

[0007] In one aspect, the invention provides a compound of Formula (I):



I

or salts or N-oxides thereof, and isomers, tautomers, enantiomers or diastereomers of these compounds. R^1 and R^2 are independently selected from hydrogen and alkyl; or R^1 and R^2, together with the atom to which they are attached, are joined to form a cycloalkyl. Y is O or NR^6. R^6 is selected from hydrogen, alkyl, alkenyl, alkynyl, alkoxy, and heteroalkyl, wherein said alkyl, alkenyl, alkynyl, alkoxy, and heteroalkyl is optionally substituted with one to five R^y. Each R^y is independently selected from halogen, hydroxy, alkoxy, cyano, and alkoxycarbonyl. R^3 is selected from alkyl, alkenyl, alkynyl, heteroalkyl, cycloalkyl, aryl, and heteroaryl, each optionally substituted with one to five R^x. Each R^x is independently selected from halogen, hydroxy, alkoxy, cyano, alkoxycarbonyl, cycloalkyl, and aryl, wherein said cycloalkyl and aryl is optionally substituted with one to five moieties independently selected

from halogen, alkyl, and haloalkyl. R^4 is selected from hydrogen, alkyl, fluoro, and chloro. L is selected from a bond and alkyl. R^7 is selected from aryl and heteroaryl, each optionally substituted with one to five R^5. Each R^5 is independently selected from alkyl, alkenyl, alkynyl, alkoxy, haloalkyl, haloalkoxy, heteroalkyl, cycloalkyl, cyano, and halogen.

[0008] In further aspects, the invention provides formulations of these compounds formulated appropriately for administration to plants and methods of using the compounds and formulations.

[0009] Other objects, advantages and aspects of the present invention will be apparent from the detailed description below.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

[0010] Before the invention is described in greater detail, it is to be understood that the invention is not limited to particular embodiments described herein as such embodiments may vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and the terminology is not intended to be limiting. The scope of the invention will be limited only by the appended claims. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between the upper and lower limit of that range and any other stated or intervening value in that stated range, is encompassed within the invention. The upper and lower limits of these smaller ranges may independently be included in the smaller ranges and are also encompassed within the invention, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the invention. Certain ranges are presented herein with numerical values being preceded by the term "about." The term "about" is used herein to provide literal support for the exact number that it precedes, as well as a number that is near to or approximately the number that the term precedes. In determining whether a number is near to or approximately a specifically recited number, the near or approximating unrecited number may be a number, which, in the context in which it is presented, provides the

substantial equivalent of the specifically recited number. All publications, patents, and patent applications cited in this specification are incorporated herein by reference to the same extent as if each individual publication, patent, or patent application were specifically and individually indicated to be incorporated by reference. Furthermore, each cited publication, patent, or patent application is incorporated herein by reference to disclose and describe the subject matter in connection with which the publications are cited. The citation of any publication is for its disclosure prior to the filing date and should not be construed as an admission that the invention described herein is not entitled to antedate such publication by virtue of prior invention. Further, the dates of publication provided might be different from the actual publication dates, which may need to be independently confirmed.

[0011] It is noted that the claims may be drafted to exclude any optional element. As such, this statement is intended to serve as antecedent basis for use of such exclusive terminology as "solely," "only," and the like in connection with the recitation of claim elements, or use of a "negative" limitation. As will be apparent to those of skill in the art upon reading this disclosure, each of the individual embodiments described and illustrated herein has discrete components and features which may be readily separated from or combined with the features of any of the other several embodiments without departing from the scope or spirit of the invention. Any recited method may be carried out in the order of events recited or in any other order that is logically possible. Although any methods and materials similar or equivalent to those described herein may also be used in the practice or testing of the invention, representative illustrative methods and materials are now described.

[0012] The following definitions are broadly applicable to each of the embodiments of the present invention set forth herein below. Unless defined otherwise, all technical and scientific terms used herein generally have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Generally, the nomenclature used herein and the laboratory procedures in analytical chemistry, and organic synthesis are those well-known and commonly employed in the art. Standard techniques, or modifications thereof, are used for chemical syntheses and chemical analyses.

[0013] The term "alkyl," by itself or as part of another substituent, means, unless otherwise stated, a straight- or branched-chain, or cyclic hydrocarbon radical, or combination thereof, which is fully saturated and can include mono-, di-, tri- and tetra-valent radicals, having the number of carbon atoms designated *(i.e.* Ci-Cio means one to ten carbons). Examples of

saturated hydrocarbon radicals include, but are not limited to, groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, isobutyl, sec-butyl, cyclohexyl, (cyclohexyl)methyl, cyclopropylmethyl, homologs and isomers of, for example, n-pentyl, n-hexyl, n-heptyl, n-octyl, and the like. The term "alkyl", as used herein refers to alkyl moieties, which can be mono-, di- or polyvalent species as appropriate to satisfy valence requirements.

[0014] The term "alkenyl," by itself or as part of another substituent, means, unless otherwise stated, a straight- or branched-chain, or cyclic alkyl radical, or combination thereof, having one or more carbon-carbon double bonds. Examples of alkenyl groups include, but are not limited to, vinyl, 2-propenyl, crotyl, isopenten-2-yl, butadien-2-yl, 2,4-pentadienyl, l,4-pentadien-3-yl, and the higher homologs and isomers.

[0015] The term "alkynyl," by itself or as part of another substituent, means, unless otherwise stated, a straight- or branched-chain, or cyclic alkyl radical, or combination thereof, having one or more carbon-carbon triple bonds. Examples of alkynyl groups include, but are not limited to, ethynyl, 1- and 3-propynyl, 3-butynyl, and the higher homologs and isomers.

[0016] The term "alkylene," by itself or as part of another substituent, means a divalent radical derived from an alkyl moiety, as exemplified, but not limited, by **-CH2CH2CH2CH2-** Typically, an alkyl (or alkylene) group will have from 1 to 24 carbon atoms, with those groups having 10 or fewer carbon atoms being preferred in the present invention. For alkylene and heteroalkylene linker groups, it is optional that no orientation of the linker group is implied by the direction in which the formula of the linker group is written. For example, the formula -C(0) $_2$R'- represents -C(0) $_2$R'- and, optionally, -R'C(0) $_2$- . A "lower alkyl" or "lower alkylene" is a shorter chain alkyl or alkylene group, generally having eight, seven, six, five or fewer carbon atoms.

[0017] The terms "alkoxy," "alkylamino" and "alkylthio" (or thioalkoxy) are used in their conventional sense, and refer to those alkyl groups attached to the remainder of the molecule via an oxygen atom, an amino group, or a sulfur atom, respectively.

[0018] The term "heteroalkyl," by itself or in combination with another term, means, unless otherwise stated, a stable straight- or branched-chain, or cyclic alkyl radical consisting of the stated number of carbon atoms and at least one heteroatom selected from the group consisting of B, **O,** N, Si and S, wherein the heteroatom may optionally be oxidized and the nitrogen atom may optionally be quatemized. The heteroatom(s) may be placed at any internal

position of the heteroalkyl group or at a terminus, *e.g.,* the position through which the alkyl group is attached to the remainder of the molecule. Examples of "heteroalkyl" groups include, but are not limited to, $-CH_2-CH_2-0-CH_3$, $-CH_2-CH_2-NH-CH_3$, $-CH_2-CH_2-N(CH_3)-CH_3$, $-CH_2-S-CH_2-CH_3$, $-CH_2-CH_2$,-S(0)-CH_3, $-CH_2-CH_2-S(0)_2-CH_3$, $-Si(CH_3)_3$, and $-CH_2-CH=N-OCH_3$. Two or more heteroatoms may be consecutive, such as, for example, $-CH_2-NH-OCH_3$ and $-CH_2-0-Si(CH_3)_3$. Similarly, the term "heteroalkylene" by itself or as part of another substituent refers to a divalent heteroalkyl radical, as exemplified, but not limited by, $-CH_2-CH_2-S-CH_2-CH_2-$ and $-CH_2-S-CH_2-CH_2-NH-CH_2-$. For heteroalkylene groups, heteroatoms can also occupy either or both of the termini *(e.g.,* alkyleneoxy, alkylenedioxy, alkyleneamino, alkylenediamino, and the like).

[0019] The terms "cycloalkyl" and "heterocycloalkyl", by themselves or in combination with other terms, represent, unless otherwise stated, cyclic versions of "alkyl" and "heteroalkyl", respectively. Additionally, for heterocycloalkyl, a heteroatom can occupy the position at which the heterocycle is attached to the remainder of the molecule. Examples of cycloalkyl include, but are not limited to, 3-, 4-, 5-, and 6-membered cycloalkyl rings. Examples of cycloalkyl include, but are not limited to, C_{3-C6} cycloalkyl, C_{3-C5} cycloalkyl, C_{3-C4} cycloalkyl, and C_{5-C6} cycloalkyl. Examples of cycloalkyl include, but are not limited to, cyclopentyl, cyclohexyl, cycloheptyl, and the like. Examples of heterocycloalkyl include, but are not limited to, 3-, 4-, 5-, and 6-membered heterocycloalkyl rings. Examples of heterocycloalkyl include, but are not limited to, 1-piperidinyl, 2-piperidinyl, 3-piperidinyl, 4-morpholinyl, 3-morpholinyl, tetrahydrofuran-2-yl, tetrahydrofuran-3-yl, tetrahydrothien-2-yl, tetrahydrothien-3-yl, 1-piperazinyl, 2-piperazinyl, and the like.

[0020] In some embodiments, any of the alkyl, alkenyl, alkynyl, alkylene, heteroalkylene, alkoxy, alkylamino, alkylthio, heteroalkyl, cycloalkyl and heterocycloalkyl groups is optionally substituted, *e.g.,* with one or more groups referred to herein as an "alkyl group substituent."

[0021] The terms "halo" or "halogen," by themselves or as part of another substituent, mean, unless otherwise stated, a fluorine, chlorine, bromine, or iodine atom. Additionally, terms such as "haloalkyl," are meant to include monohaloalkyl and polyhaloalkyl. For example, the term "halo(Ci-C4)alkyl" is meant to include, but not be limited to, trifluoromethyl, 2,2,2-trifluoroethyl, 4-chlorobutyl, 3-bromopropyl, and the like.

[0022] The term "aryl" means, unless otherwise stated, a polyunsaturated, aromatic substituent that can be a single ring or multiple rings (preferably from 1 to 3 rings), which are fused together. The term "heteroaryl" refers to aryl groups (or rings) that contain from one to four heteroatoms selected from N, O, and S, wherein the nitrogen and sulfur atoms are optionally oxidized, and the nitrogen atom(s) are optionally quatemized. A heteroaryl group can be attached to the remainder of the molecule through a heteroatom. Examples of heteroaryl include, but are not limited to, 5- and 6-membered, monocyclic heteroaryl rings. Further examples of heteroaryl include, but are not limited to, 9- and 10-membered, bicyclic heteroaryl ring systems. Non-limiting examples of aryl and heteroaryl groups include phenyl, 1-naphthyl, 2-naphthyl, 1-pyrrolyl, 2-pyrrolyl, 3-pyrrolyl, 3-pyrazolyl, 2-imidazolyl, 4-imidazolyl, pyrazinyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-furyl, 3-furyl, 2-thienyl, 3-thienyl, 2-pyridyl, 3-pyridyl, 4-pyridyl, 2-pyrimidyl, 4-pyrimidyl, 5-benzothiazolyl, purinyl, 2-benzimidazolyl, 5-indolyl, 1-isoquinolyl, 5-isoquinolyl, 2-quinoxalinyl, 5-quinoxalinyl, 3-quinolyl, and 6-quinolyl. In some embodiments, any of the aryl and heteroaryl groups is optionally substituted, *e.g.,* with one or more groups referred to herein as an "aryl group substituent."

[0023] The term "arylalkyl" includes those radicals in which an aryl group is attached to an alkyl group (e.g., benzyl, phenethyl, and the like).

[0024] Substituents for the alkyl and heteroalkyl radicals as well as those groups often referred to as alkylene, heteroalkylene, alkenyl, heteroalkenyl, alkynyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, and heterocycloalkenyl are generically referred to as "alkyl group substituents," and they can be one or more of a variety of groups selected from, but not limited to: -OR', =0, =NR', =N-OR\ -NR'R", -SR.', -halogen, -SiR'R"R"', -OC(0)R', -C(0)R', -C0 $_2$R', -CONR'R", -OC(0)NR'R", -NR"C(0)R', -NR'-C(0)NR"R"', -NR"C(0) $_2$R', -NR-C(NR'R"R")=NR"", -NR-C(NR'R")=NR"', -S(0)R', -S(0) $_2$R', -S(0) $_2$NR'R", -NRS0 $_2$R', -CN and -N0 $_2$ in a number ranging from zero to (2m'+l), where m' is the total number of carbon atoms in such radical. R', R", R"' and R"" each preferably independently refer to hydrogen, substituted or unsubstituted heteroalkyl, substituted or unsubstituted aryl, *e.g.,* aryl substituted with 1-3 halogens, substituted or unsubstituted alkyl, alkoxy or thioalkoxy groups, or arylalkyl groups. When a compound of the invention includes more than one R group, for example, each of the R groups is independently selected

as are each R', R", R'" and R"" groups when more than one of these groups is present. When R' and R" are attached to the same nitrogen atom, they can be combined with the nitrogen atom to form a 5-, 6-, or 7-membered ring. For example, -NR'R" is meant to include, but not be limited to, 1-pyrrolidinyl and 4-morpholinyl. From the above discussion of substituents, one of skill in the art will understand that the term "substituted alkyl" includes groups with carbon atoms bound to groups other than hydrogen, such as haloalkyl *(e.g.,* -CF_3 and -CH2CF3) and acyl *(e.g.,* -C(0)CH_3, -C(0)CF_3, -C(0)CH_2OCH_3, and the like).

[0025] Similar to the substituents described for the alkyl radical, substituents for the aryl and heteroaryl groups are generically referred to as "aryl group substituents." Exemplary substituents are selected from the list of alkyl group substituents and others, for example: halogen, -OR', =0, =NR', =N-OR\ -NR'R", -SR.', -SiR'R"R'", -OC(0)R\ -C(0)R\ **-CO2R',** -CONR'R", -OC(0)NR'R", -NR"C(0)R', -NR'-C(0)NR"R'", -NR"C(0)$_2$R', -NR-C(NR'R"R'")=NR"", -NR-C(NR'R")=NR'", -S(0)R', -S(0)$_2$R', -S(0)$_2$NR'R", **-NRSO2R',** -CN and **-NO2,** -R', -N_3, -CH(Ph)$_2$, fluoro(Ci-C_4)alkoxy, and fluoro(Ci-C_4)alkyl, in a number ranging from zero to the total number of open valences on the aromatic ring system; and where R', R", R'" and R"" are preferably independently selected from hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted heteroalkyl, substituted or unsubstituted aryl and substituted or unsubstituted heteroaryl. When a compound of the invention includes more than one R group, for example, each of the R groups is independently selected as are each R', R", R'" and R"" groups when more than one of these groups is present.

[0026] Two of the substituents on an aryl or heteroaryl ring, together with the atom to which they are attached, may optionally be joined to form a ring *(e.g.,* a cycloalkyl or heterocycloalkyl ring) that is fused to the aryl or heteroaryl ring.

[0027] Two of the substituents on adjacent atoms of the aryl or heteroaryl ring may optionally be replaced with a substituent of the formula -T-C(0)-(CRR')$_q$-U-, wherein T and U are independently -NR-, -0-, -CRR'- or a single bond, and q is an integer from 0 to 3. Alternatively, two of the substituents on adjacent atoms of the aryl or heteroaryl ring may optionally be replaced with a substituent of the formula -A-(CH$_2$)$_r$-B-, wherein A and B are independently -CRR'-, -0-, -NR-, *S ~, S(0)-,* -S(0)$_2$-, -S(0)$_2$NR'- or a single bond, and r is an integer of from 1 to 4. One of the single bonds of the new ring so formed may optionally be replaced with a double bond. Alternatively, two of the substituents on adjacent

atoms of the aryl or heteroaryl ring may optionally be replaced with a substituent of the formula -(CRR')s –X– (CR"R"')d–, where s and d are independently integers of from 0 to 3, and X is **-0-,** -NR'-, *S* –, **- S(0)-** , **- S(0) $_2$-** , or - S**(0** $)_2$NR'-. The substituents R, R', R" and R"' are preferably independently selected from hydrogen or substituted or unsubstituted (Ci-Ci $_6$)alkyl.

[0028] As used herein, the term "heteroatom" includes oxygen (O), nitrogen (N), sulfur (S) and silicon (Si).

[0029] The symbol "R" is a general abbreviation that represents a substituent group that is selected from H, substituted or unsubstituted alkyl, substituted or unsubstituted heteroalkyl, substituted or unsubstituted aryl, substituted or unsubstituted heteroaryl, and substituted or unsubstituted heterocyclyl groups. R can also refer to alkyl group substituents and aryl group substituents.

[0030] The term "salt(s)" includes salts of the compounds which are prepared with relatively nontoxic acids or bases, depending on the particular substituents found on the compounds described herein. When compounds of the present invention contain relatively acidic functionalities, base addition salts can be obtained by contacting the neutral form of such compounds with a sufficient amount of the desired base, either neat or in a suitable inert solvent. Examples of base addition salts include sodium, potassium, calcium, ammonium, organic amino, or magnesium salt, or a similar salt. When compounds of the present invention contain relatively basic functionalities, acid addition salts can be obtained by contacting the neutral form of such compounds with a sufficient amount of the desired acid, either neat or in a suitable inert solvent. Examples of acid addition salts include those derived from inorganic acids like hydrochloric, hydrobromic, nitric, carbonic, monohydrogencarbonic, phosphoric, monohydrogenphosphoric, dihydrogenphosphoric, sulfuric, monohydrogensulfuric, hydriodic, or phosphorous acids, and the like, as well as the salts derived from relatively nontoxic organic acids like acetic, propionic, isobutyric, butyric, maleic, malic, malonic, benzoic, succinic, suberic, fumaric, lactic, mandelic, phthalic, benzenesulfonic, p-tolylsulfonic, citric, tartaric, methanesulfonic, and the like. Also included are salts of amino acids such as arginate, and the like, and salts of organic acids like glucuronic or galactunoric acids and the like (see, for example, Berge *et al, Journal of Pharmaceutical Science,* **66:** 1-19 (1977)). Certain specific compounds of the present

invention contain both basic and acidic functionalities that allow the compounds to be converted into either base or acid addition salts. Hydrates of the salts are also included.

[0031] The symbol ~, displayed perpendicular to a bond, indicates the point at which the displayed moiety is attached to the remainder of the molecule.

[0032] The compounds herein described may have one or more asymmetric centers or planes. Compounds of the present invention containing an asymmetrically substituted atom may be isolated in optically active or racemic forms. It is well known in the art how to prepare optically active forms, such as by resolution of racemic forms (racemates), by asymmetric synthesis, or by synthesis from optically active starting materials. Resolution of the racemates can be accomplished, for example, by conventional methods such as crystallization in the presence of a resolving agent, or chromatography, using, for example a chiral HPLC column. Many geometric isomers of olefins, C=N double bonds, and the like can also be present in the compounds described herein, and all such stable isomers are contemplated in the present invention. Cis and trans geometric isomers of the compounds of the present invention are described and may be isolated as a mixture of isomers or as separated isomeric forms. All chiral (enantiomeric and diastereomeric), and racemic forms, as well as all geometric isomeric forms of a structure are intended, unless the specific stereochemistry or isomeric form is specifically indicated.

[0033] The graphic representations of racemic, ambiscalemic and scalemic or enantiomerically pure compounds used herein are taken from Maehr, *J. Chem. Ed.,* 62: 114-120 (1985): solid and broken wedges are used to denote the absolute configuration of a chiral element; wavy lines indicate disavowal of any stereochemical implication which the bond it represents could generate; solid and broken bold lines are geometric descriptors indicating the relative configuration shown but not implying any absolute stereochemistry; and wedge outlines and dotted or broken lines denote enantiomerically pure compounds of indeterminate absolute configuration.

[0034] The term "charged group" refers to a group that bears a negative charge or a positive charge. The negative charge or positive charge can have a charge number that is an integer selected from 1, 2, 3 or higher or that is a fractional number. Exemplary charged groups include for example **-OP0 $_3^{2-}$,**–OP**0 $_2^-$**, –P^+Ph_3, - N^+R'R''R''', - S^+R and - **C(0)0 $^-$.**

It is understood that charged groups are accompanied by counterions of opposite charge, whether or not such counterions are expressly represented in the formulae provided herein.

[0035] The compounds herein described may have one or more charged groups. For example, the compounds may be zwitterionic, but may be neutral overall. Other embodiments may have one or more charged groups, depending on the pH and other factors. In these embodiments, the compound may be associated with a suitable counter-ion. It is well known in the art how to prepare salts or exchange counter-ions. Generally, such salts can be prepared by reacting free acid forms of these compounds with a stoichiometric amount of the appropriate base (such as Na, Ca, Mg, or K hydroxide, carbonate, bicarbonate, or the like), or by reacting free base forms of these compounds with a stoichiometric amount of the appropriate acid. Such reactions are typically carried out in water or in an organic solvent, or in a mixture of the two. Counter-ions may be changed, for example, by ion-exchange techniques such as ion-exchange chromatography. All zwitterions, salts and counter-ions are intended, unless the counter-ion or salt is specifically indicated.

[0036] In some embodiments, the definition of terms used herein is according to IUPAC.

[0037] According to the present invention, "regulating or improving the growth of a crop" means an improvement in plant vigour, an improvement in plant quality, improved tolerance to stress factors, and/or improved input use efficiency.

[0038] An 'improvement in plant vigour' means that certain traits are improved qualitatively or quantitatively when compared with the same trait in a control plant which has been grown under the same conditions in the absence of the method of the invention. Such traits include, but are not limited to, early and/or improved germination, improved emergence, the ability to use less seeds, increased root growth, a more developed root system, increased root nodulation, increased shoot growth, increased tillering, stronger tillers, more productive tillers, increased or improved plant stand, less plant verse (lodging), an increase and/or improvement in plant height, an increase in plant weight (fresh or dry), bigger leaf blades, greener leaf colour, increased pigment content, increased photosynthetic activity, earlier flowering, longer panicles, early grain maturity, increased seed, fruit or pod size, increased pod or ear number, increased seed number per pod or ear, increased seed mass, enhanced seed filling, less dead basal leaves, delay of senescence, improved vitality of the plant, increased levels of amino acids in storage tissues and/or less inputs needed (e.g., less

fertiliser, water and/or labour needed). A plant with improved vigour may have an increase in any of the aforementioned traits or any combination or two or more of the aforementioned traits.

[0039] An 'improvement in plant quality' means that certain traits are improved qualitatively or quantitatively when compared with the same trait in a control plant which has been grown under the same conditions in the absence of the method of the invention. Such traits include, but are not limited to, improved visual appearance of the plant, reduced ethylene (reduced production and/or inhibition of reception), improved quality of harvested material, *e.g.,* seeds, fruits, leaves, vegetables (such improved quality may manifest as improved visual appearance of the harvested material), improved carbohydrate content **(e**.**g**., increased quantities of sugar and/or starch, improved sugar acid ratio, reduction of reducing sugars, increased rate of development of sugar), improved protein content, improved oil content and composition, improved nutritional value, reduction in anti-nutritional compounds, improved organoleptic properties **(e**.**g**., improved taste) and/or improved consumer health benefits **(e**.g., increased levels of vitamins and anti-oxidants)), improved post-harvest characteristics **(e**.g., enhanced shelf-life and/or storage stability, easier processability, easier extraction of compounds), more homogenous crop development **(e**.g., synchronised germination, flowering and/or fruiting of plants), and/or improved seed quality **(e**.g., for use in following seasons). A plant with improved quality may have an increase in any of the aforementioned traits or any combination or two or more of the aforementioned traits.

[0040] An 'improved tolerance to stress factors' means that certain traits are improved qualitatively or quantitatively when compared with the same trait in a control plant which has been grown under the same conditions in the absence of the method of the invention. Such traits include, but are not limited to, an increased tolerance and/or resistance to abiotic stress factors which cause sub-optimal growing conditions such as drought **(e**.**g**., any stress which leads to a lack of water content in plants, a lack of water uptake potential or a reduction in the water supply to plants), cold exposure, heat exposure, osmotic stress, UV stress, flooding, increased salinity **(e**.g., in the soil), increased mineral exposure, ozone exposure, high light exposure and/or limited availability of nutrients **(e**.**g**., nitrogen and/or phosphorus nutrients). A plant with improved tolerance to stress factors may have an increase in any of the aforementioned traits or any combination or two or more of the aforementioned traits. In the

case of drought and nutrient stress, such improved tolerances may be due to, for example, more efficient uptake, use or retention of water and nutrients. In particular, the compounds or compositions of the present invention are useful to improve tolerance to drought stress.

[0041] An 'improved input use efficiency' means that the plants are able to grow more effectively using given levels of inputs compared to the grown of control plants which are grown under the same conditions in the absence of the method of the invention. In particular, the inputs include, but are not limited to fertiliser (such as nitrogen, phosphorous, potassium, micronutrients), light and water. A plant with improved input use efficiency may have an improved use of any of the aforementioned inputs or any combination of two or more of the aforementioned inputs.

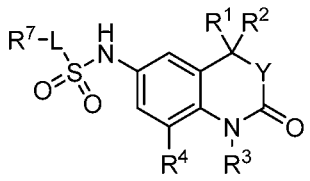
[0042] The term "plants" refers to all physical parts of a plant, including seeds, seedlings, saplings, roots, tubers, stems, stalks, foliage, and fruits.

[0043] The term "locus" as used herein means fields in or on which plants are growing, or where seeds of cultivated plants are sown, or where seed will be placed into the soil. It includes soil, seeds, and seedlings, as well as established vegetation.

[0044] The term "plant propagation material" denotes all generative parts of a plant, for example seeds or vegetative parts of plants such as cuttings and tubers. It includes seeds in the strict sense, as well as roots, fruits, tubers, bulbs, rhizomes, and parts of plants.

Compounds

[0045] In one aspect, the invention provides a compound of Formula (I):



I

or salts or N-oxides thereof, and isomers, tautomers, enantiomers or diastereomers of these compounds. R^1, R^2, Y, R^3, R^4, L, and R^7 are as defined herein. Any combination of R^1, R^2, Y, R^3, R^4, L, and R^7 is encompassed by this disclosure and specifically provided by the invention.

[0046] In some embodiments, R^1 and R^2 are independently selected from hydrogen and alkyl. In some embodiments, R^1 and R^2 are independently selected from hydrogen and **C1-C4**

(i.e., Ci, C_2, C_3, or C_4) alkyl. In some embodiments, R^1 and R^2 are independently selected from hydrogen and methyl. In some embodiments, R^1 and R^2 are hydrogen. In some embodiments, R^1 is hydrogen; and R^2 is alkyl. In some embodiments, R^1 is hydrogen; and R^2 is C1-C4 alkyl. In some embodiments, R^1 is hydrogen; and R^2 is methyl. In some embodiments, R^1 and R^2 are alkyl. In some embodiments, R^1 and R^2 are C1-C4 alkyl. In some embodiments, R^1 and R^2 are methyl. In some embodiments, R^1 and R^2, together with the atom to which they are attached, are joined to form a cycloalkyl. In some embodiments, R^1 and R^2, together with the atom to which they are attached, are joined to form a C3-C4 cycloalkyl. In some embodiments, R^1 and R^2, together with the atom to which they are attached, are joined to form a cyclopropyl. In an exemplary embodiment, one of R^1 or R^2 is methyl but both R^1 and R^2 are not methyl.

[0047] In some embodiments, Y is O or NR^6. R^6 is as defined herein. In some embodiments, Y is O. In some embodiments, Y is NR^6.

[0048] In some embodiments, R^6 is selected from hydrogen, alkyl, alkenyl, alkynyl, alkoxy, and heteroalkyl, wherein said alkyl, alkenyl, alkynyl, alkoxy, and heteroalkyl is optionally substituted with one to five *(i.e.,* one, two, three, four, or five) R^y. R^y is as defined herein. In some embodiments, R^6 is selected from hydrogen, C1-C4 alkyl, C2-C4 alkenyl, C2-C4 alkynyl, C1-C4 alkoxy, C1-C4 heteroalkyl, each optionally substituted with one to five R^y. In some embodiments, R^6 is hydrogen. In some embodiments, R^6 is C1-C4 *(i.e.,* C_1, C_2, C3, or C_4) alkyl. In some embodiments, R^6 is methyl.

[0049] In some embodiments, each R^y is independently selected from halogen, hydroxy, alkoxy, cyano, and alkoxycarbonyl. In some embodiments, each R^y is independently selected from halogen, hydroxy, C1-C4 alkoxy, cyano, and (C1-C3 alkoxy)-carbonyl.

[0050] In some embodiments, R^3 is selected from alkyl, alkenyl, alkynyl, heteroalkyl, cycloalkyl, aryl, and heteroaryl, each optionally substituted with one to five *(i.e.,* one, two, three, four, or five) R^x. R^x is as defined herein. In some embodiments, R^3 is selected from C_1-C_6 alkyl, C2-C6 alkenyl, C2-C6 alkynyl, C1-C6 heteroalkyl, C3-C6 cycloalkyl, phenyl, and 5- or 6-membered heteroaryl, each optionally substituted with one to five R^x. In some embodiments, R^3 is selected from C1-C6 alkyl, C2-C6 alkenyl, (C3-C4 cycloalkyl)-Ci-C3 alkyl, C1-C6 haloalkyl, and (C1-C3 alkoxy)-Ci-C3 alkyl. In some embodiments, R^3 is selected from ethyl, n-propyl, isopropyl, allyl, cyclopropylmethyl, 2,2,2-trifluoroethyl, 2,2-difluoroethyl

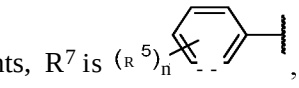
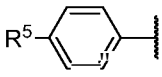
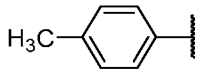
and 2-methoxy ethyl. In some embodiments, R^3 is $C_{1\text{-}C6}$ *(i.e.,* C_1, C_2, C_3, C_4, C_5, or C_6) alkyl. In some embodiments, the alkyl group is linear or branched. In some embodiments, R^3 is Ci alkyl *(i.e.,* methyl). In some embodiments, R^3 is C_2 alkyl *(i.e.,* ethyl). In some embodiments, R^3 is C_3 alkyl *(i.e.,* n-propyl or iso-propyl). In some embodiments, R^3 is C_4 alkyl *(i.e.,* n-butyl, sec-butyl, iso-butyl, or tert-butyl). In some embodiments, R^3 is selected from ethyl and n-propyl. In some embodiments, R^3 is ethyl. In some embodiments, R^3 is n-propyl. In some embodiments, R^3 is $C_{2\text{-}C6}$ *(i.e.,* C_2, C_3, C_4, C_5, or C_6) alkenyl. In some embodiments, R^3 is allyl ($-CH_2-CH=CH_2$).

[0051] In some embodiments, each R^x is independently selected from halogen, hydroxy, alkoxy, cyano, alkoxycarbonyl, cycloalkyl, and aryl. In some embodiments, each R^x is independently selected from halogen, hydroxy, $C_{1\text{-}C4}$ alkoxy, cyano, ($C_{1\text{-}C3}$ alkoxy)-carbonyl, $C_{3\text{-}C4}$ cycloalkyl, and phenyl. In some embodiments, the cycloalkyl (of R^x) is optionally substituted with one to five *(i.e.,* one, two, three, four, or five) moieties independently selected from halogen, alkyl, and haloalkyl. In some embodiments, the cycloalkyl (of R^x) is optionally substituted with one to five moieties independently selected from halogen, $C_{1\text{-}C3}$ alkyl, and $C_{1\text{-}C3}$ haloalkyl. In some embodiments, the aryl (of R^x) is optionally substituted with one to five *(i.e.,* one, two, three, four, or five) moieties independently selected from halogen, alkyl, and haloalkyl. In some embodiments, the aryl (of R^x) is optionally substituted with one to five moieties independently selected from halogen, $C_{1\text{-}C3}$ alkyl, and $C_{1\text{-}C3}$ haloalkyl.

[0052] In some embodiments, R^4 is selected from hydrogen, alkyl, fluoro, and chloro. In some embodiments, R^4 is selected from hydrogen, $C_{1\text{-}C4}$ alkyl, fluoro, and chloro. In some embodiments, R^4 is selected from hydrogen and fluoro. In some embodiments, R^4 is hydrogen. In some embodiments, R^4 is fluoro.

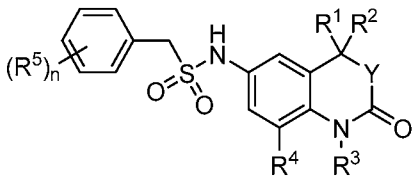
[0053] In some embodiments, L is selected from a bond and alkyl. In some embodiments, L is selected from a bond and C_1-C_2 alkyl. In some embodiments, L is a bond. In some embodiments, L is C1-C2 alkyl. In some embodiments, L is $-CH_2-$.

[0054] In some embodiments, R^7 is selected from aryl and heteroaryl, each optionally substituted with one to five *(i.e.,* one, two, three, four, or five) R^5. R^5 is as defined herein. In some embodiments, R^7 is selected from phenyl and 5-, 6-, 9-, or 10-membered heteroaryl, each optionally substituted with one to five R^5. In some embodiments, R^7 is selected from

phenyl, thienyl (such as 2- and 3-thienyl), pyridyl (such as 2-, 3-, and 4-pyridyl) and benzo[cf]thiazolyl (such as benzo[cf]thiazol-5-yl), each optionally substituted with one to five *(e.g.,* one to three) R^5. In some embodiments, R^7 is phenyl, optionally substituted with one to five R^5. In some embodiments, R^7 is  , wherein n is selected from 0, 1, 2, 3, 4, and 5. In some embodiments, n is selected from 0, 1, and 2. In some embodiments, n is 1. In some embodiments, R^7 is  . In some embodiments, R^7 is ^-alkyl-phenyl. In some embodiments, R^7 is *p*-(C_1-C_4 alkyl)-phenyl. In some embodiments, R^7 is />-tolyl:  . In some embodiments, R^7 is ^-cycloalkyl-phenyl. In some embodiments, R^7 is *p*-(C_3-C_5 cycloalkyl)-phenyl.

[0055] In some embodiments, each R^5 is independently selected from alkyl, alkenyl, alkynyl, alkoxy, haloalkyl, haloalkoxy, heteroalkyl, cycloalkyl, cyano, and halogen. In some embodiments, each R^5 is independently selected from C1-C4 alkyl, C2-C4 alkenyl, C2-C4 alkynyl, C1-C4 alkoxy, C1-C4 haloalkyl, C1-C4 haloalkoxy, C1-C4 heteroalkyl, C3-C5 cycloalkyl, cyano, and halogen. In some embodiments, each R^5 is independently selected from C1-C4 alkyl, C1-C4 haloalkyl, C1-C4 heteroalkyl, C3-C5 cycloalkyl, and halogen. In some embodiments, each R^5 is independently selected from C1-C4 alkyl, C_{3-C5} cycloalkyl, and halogen. In some embodiments, each R^5 is independently selected from methyl, ethyl, n-propyl, cyclopropyl, fluorine, and chlorine. In some embodiments, each R^5 is independently selected from C1-C4 alkyl. In some embodiments, each R^5 is methyl.

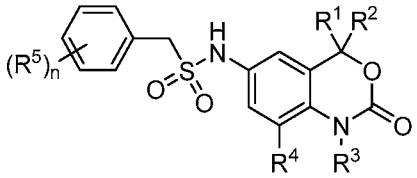
[0056] In some embodiments, the invention provides a compound of Formula (II):



II

or salts or N-oxides thereof, and isomers, tautomers, enantiomers or diastereomers of these compounds. R^1, R^2, Y, R^3, R^4, n, and R^5 are as defined herein. Any combination of R^1, R^2, Y, R^3, R^4, n, and R^5 is encompassed by this disclosure and specifically provided by the invention.

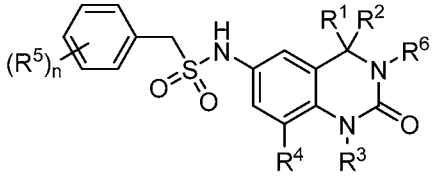
[0057] In some embodiments, the invention provides a compound of Formula (IIa):



IIa

or salts or N-oxides thereof, and isomers, tautomers, enantiomers or diastereomers of these compounds. R^1, R^2, R^3, R^4, n, and R^5 are as defined herein. Any combination of R^1, R^2, R^3, R^4, n, and R^5 is encompassed by this disclosure and specifically provided by the invention.

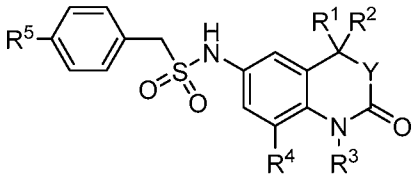
[0058] In some embodiments, the invention provides a compound of Formula (lib):



IIb

or salts or N-oxides thereof, and isomers, tautomers, enantiomers or diastereomers of these compounds. R^1, R^2, R^6, R^3, R^4, n, and R^5 are as defined herein. Any combination of R^1, R^2, R^6, R^3, R^4, n, and R^5 is encompassed by this disclosure and specifically provided by the invention.

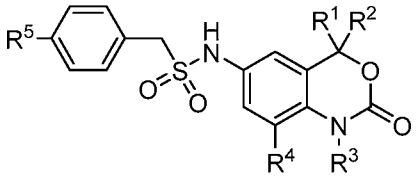
[0059] In some embodiments, the invention provides a compound of Formula (III):



III

or salts or N-oxides thereof, and isomers, tautomers, enantiomers or diastereomers of these compounds. R^1, R^2, Y, R^3, R^4, and R^5 are as defined herein. Any combination of R^1, R^2, Y, R^3, R^4, and R^5 is encompassed by this disclosure and specifically provided by the invention.

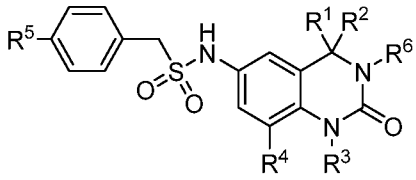
[0060] In some embodiments, the invention provides a compound of Formula (IIia):



IIia

or salts or N-oxides thereof, and isomers, tautomers, enantiomers or diastereomers of these compounds. R^1, R^2, R^3, R^4, and R^5 are as defined herein. Any combination of R^1, R^2, R^3, R^4, and R^5 is encompassed by this disclosure and specifically provided by the invention.

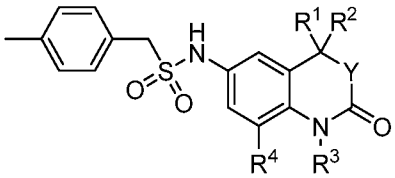
[0061] In some embodiments, the invention provides a compound of Formula (IIIb):



IIIb

or salts or N-oxides thereof, and isomers, tautomers, enantiomers or diastereomers of these compounds. R^1, R^2, R^6, R^3, R^4, and R^5 are as defined herein. Any combination of R^1, R^2, R^6, R^3, R^4, and R^5 is encompassed by this disclosure and specifically provided by the invention.

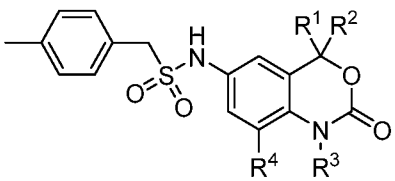
[0062] In some embodiments, the invention provides a compound of Formula (IV):



IV

or salts or N-oxides thereof, and isomers, tautomers, enantiomers or diastereomers of these compounds. R^1, R^2, Y, R^3, and R^4 are as defined herein. Any combination of R^1, R^2, Y, R^3, and R^4 is encompassed by this disclosure and specifically provided by the invention.

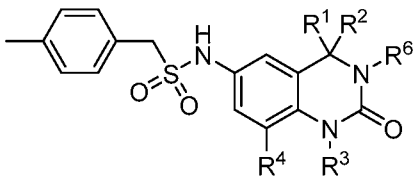
[0063] In some embodiments, the invention provides a compound of Formula (IVa):



IVa

or salts or N-oxides thereof, and isomers, tautomers, enantiomers or diastereomers of these compounds. R^1, R^2, R^3, and R^4 are as defined herein. Any combination of R^1, R^2, R^3, and R^4 is encompassed by this disclosure and specifically provided by the invention.

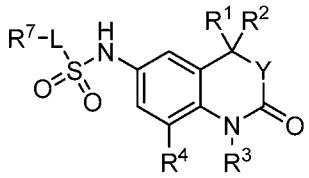
[0064] In some embodiments, the invention provides a compound of Formula (IVb):



IVb

or salts or N-oxides thereof, and isomers, tautomers, enantiomers or diastereomers of these compounds. R^1, R^2, R^6, R^3, and R^4 are as defined herein. Any combination of R^1, R^2, R^6, R^3, and R^4 is encompassed by this disclosure and specifically provided by the invention.

[0065] In some embodiments, the invention provides a compound of Formula (I):

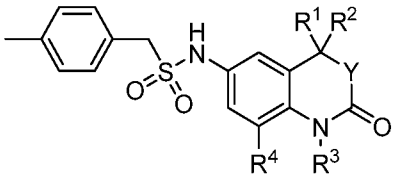


I

wherein R^1 and R^2 are independently selected from hydrogen and **C1-C4** alkyl; or R^1 and R^2, together with the atom to which they are attached, are joined to form a **C3-C4** cycloalkyl; Y is O or NR^6; R^6 is selected from hydrogen **C1-C4** alkyl, C_2-C_4 alkenyl, C_2-C_4 alkynyl, **C1-C4** alkoxy, and **C1-C4** heteroalkyl, wherein said **C1-C4** alkyl, **C2-C4** alkenyl, **C2-C4** alkynyl, **C1-C4** alkoxy, and **C1-C4** heteroalkyl is optionally substituted with one to five R^y; each R^y is independently selected from halogen, hydroxy, **C1-C4** alkoxy, cyano, and **(C1-C3** alkoxy)-carbonyl; R^3 is selected from **C1-C6** alkyl, **C2-C6** alkenyl, **C2-C6** alkynyl, **C1-C6** heteroalkyl, **C3-C6** cycloalkyl, phenyl, and 5- or 6-membered heteroaryl, each optionally substituted with one to five R^x; each R^x is independently selected from halogen, hydroxy, **C1-C4** alkoxy, cyano, **(C1-C3** alkoxy)-carbonyl, **C3-C4** cycloalkyl, and phenyl, wherein said **C3-C4** cycloalkyl and phenyl is optionally substituted with one to five moieties independently selected from halogen, **C1-C3** alkyl, and **C1-C3** haloalkyl; R^4 is -selected from hydrogen, **C1-C4** alkyl, fluoro, and chloro; L is selected from a bond and **C1-C2** alkyl; R^7 is selected from phenyl and 5-, 6-, 9-, or 10-membered heteroaryl, each optionally substituted with one to five R^5; each R^5 is independently selected from **C1-C4** alkyl, **C2-C4** alkenyl, **C2-C4** alkynyl, **C1-C4** alkoxy, **C1-C4**

haloalkyl, C1-C4 haloalkoxy, C1-C4 heteroalkyl, C3-C5 cycloalkyl, cyano, and halogen. In an exemplary embodiment, in which R_7 is phenyl, it is not substituted at the para-position with CF_3. In some embodiments, the invention provides salts or N-oxides of a compound as defined in this paragraph, and isomers, tautomers, enantiomers or diastereomers of these compounds.

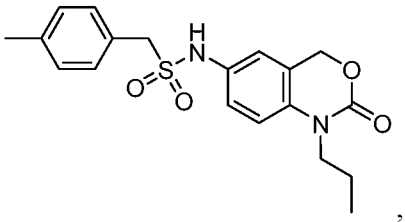
[0066] In some embodiments, the invention provides a compound of Formula (IV):



IV

wherein R^1 and R^2 are independently selected from hydrogen and methyl; or R^1 and R^2, together with the atom to which they are attached, are joined to form a cyclopropyl; Y is O or NR^6; R^6 is selected from hydrogen and methyl; R^3 is selected from ethyl, n-propyl, isopropyl, allyl, cyclopropylmethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, and 2-methoxyethyl; R^4 is selected from hydrogen and fluoro. In some embodiments, the invention provides salts or N-oxides of a compound as defined in this paragraph, and isomers, tautomers, enantiomers or diastereomers of these compounds.

[0067] Exemplary compounds of the invention are shown in the Examples and Scheme A below.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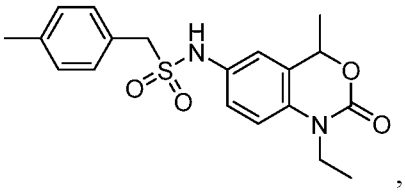
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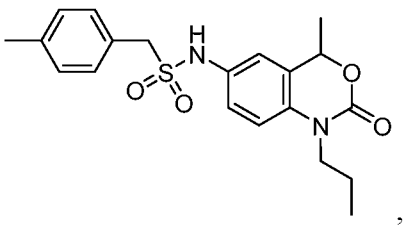
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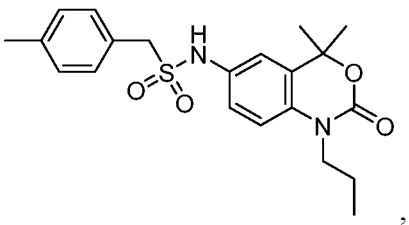
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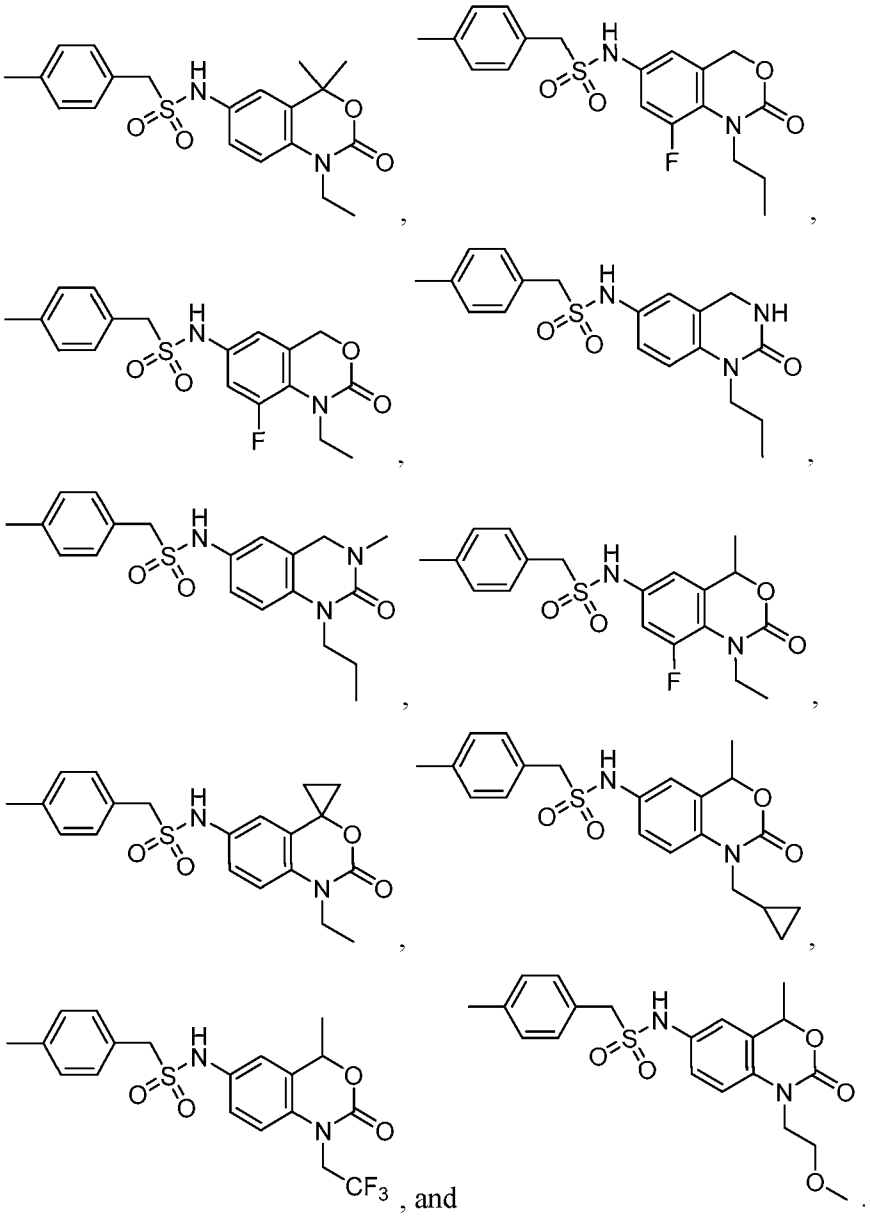
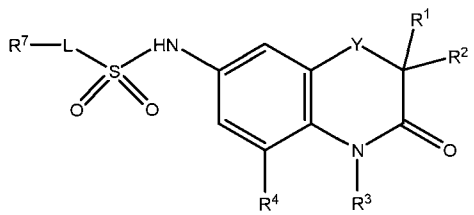


Scheme A. Exemplary compounds of the invention.

[0068] In various embodiments, the compound of the invention has greater activity against PYLl and/or PYL2 and/or PYL3 and/or PYL5 than a compound according to Formula V:

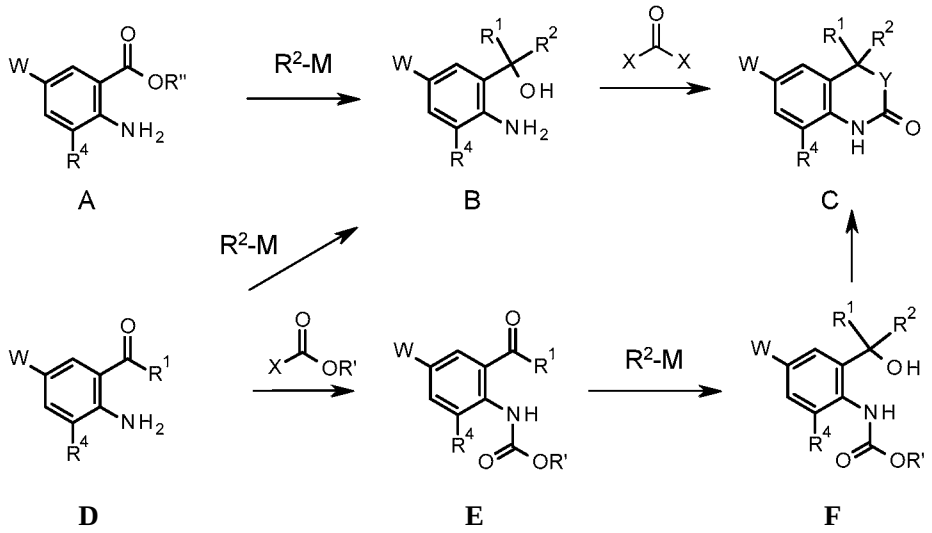


V

in which the variable substituents have the identity set forth above in the context of Formulae I-IV, above. Applicants have thus demonstrated that the favorable activity of the compounds of the invention is at least partially due to the selection of the position of the intra-annular heteroatom in the compounds of the invention.

[0069] Compounds of the invention are generally conventionally synthesized. The synthetic methods known in the art and described herein can be used to synthesize compounds of the invention, using appropriate precursors. Schemes 1-5 provide exemplary methods of preparing the compounds of Formula (I). R^1, R^2, Y, R^3, R^4, R^6, L, Y and R^7 are as defined above.

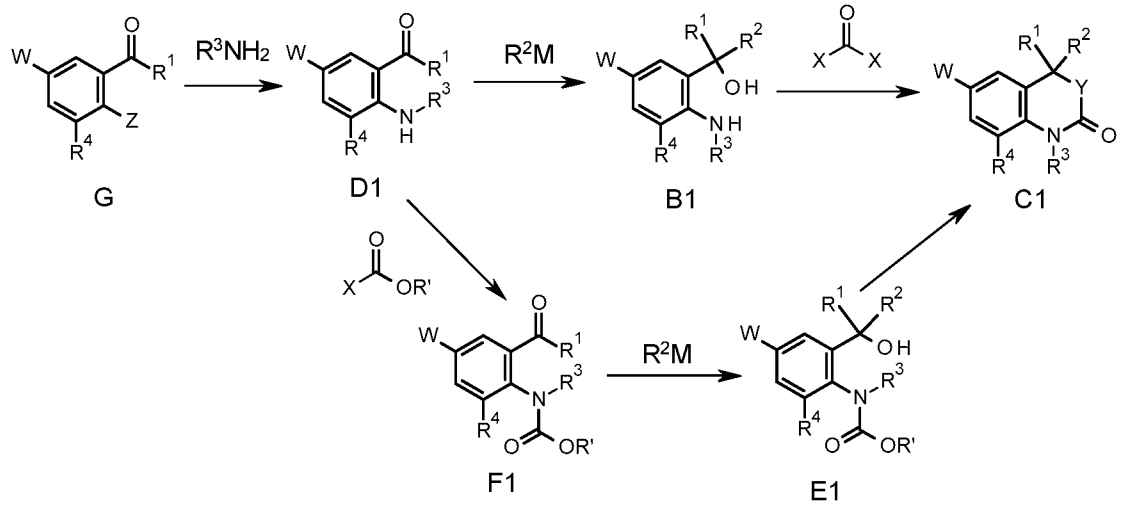
SCHEME 1:



[0070] A compound of Formula (C), wherein W is hydrogen, halogen or nitro and Y is oxygen, can be prepared from a compound of Formula (B) by reaction with an acylation compound of formula CO(X)2 wherein X is a leaving group such as halogen, imidazol, methoxide or trichloromethyl (triphosgene), eventually in the presence of a base. Compound of Formula (B), wherein R^1 and R^2 are hydrogen can be obtained from a compound or Formula (A), wherein R" is hydrogen or alkyl group by a reduction with a reducing agent such as BH_3, $LiAlH_4$ or DIBALH. Compound of Formula (B), wherein R^2 is hydrogen can be obtained from compound of formula (D) by reduction with $NaBH_4$. Compound of Formula (B), wherein R^2 is alkyl can be obtained from a compound of formula (D) by addition of an organometallic reagent of formula R^2M wherein M can be for example Mg, Zn, or Li.

[0071] Alternatively, a compound of Formula (C), wherein W is hydrogen or halogen or nitro, can be obtained from a compound of Formula (E), wherein R' is alkyl, by reaction with a base such as potassium carbonate or potassium *tert*-butoxide. Compound of Formula (F), wherein R^2 is hydrogen can be obtained from a compound of Formula (E) by reaction with $NaBH_4$. Compound of Formula (F), wherein R^2 is alkyl can be obtained from a compound of Formula (E) by addition of an organometallic reagent of formula R^2M wherein M can be for example Mg, Zn, or Li. Compound of Formula E can be made from compound of Formula (D) by reaction with an acylating agent of formula X(CO)OR', wherein R' is alkyl and X is halogen or an alkoxygroup, in the presence of a organic base such as pyridine or triethyl amine.

SCHEME 2:



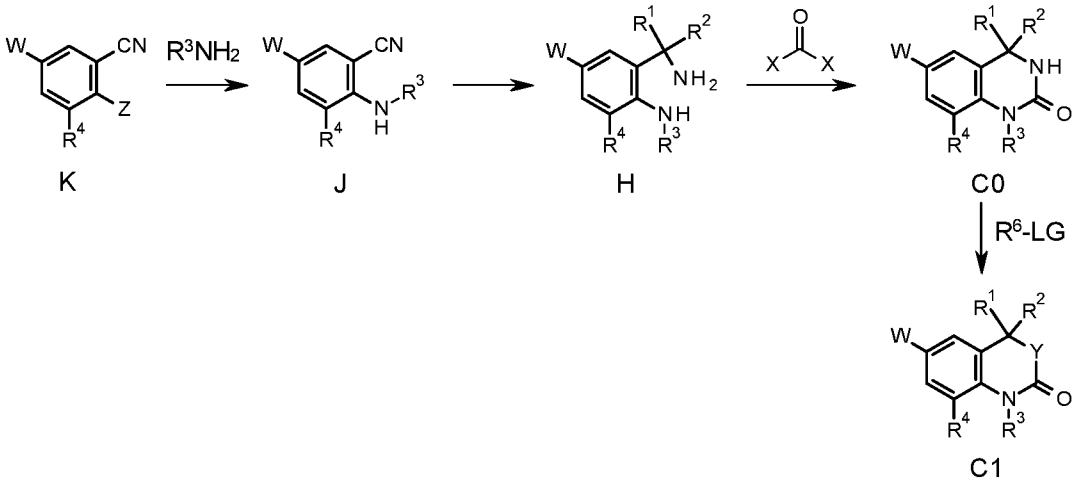
[0072] A compound of Formula (CI), wherein W is hydrogen or halogen or nitro and Y is oxygen, can be prepared from a compound of Formula (Bl) by reaction with an acylating compound of formula CO(X)2 wherein X is a leaving group such as halogen, imidazol, methoxide or trichloromethyl (triphosgene), eventually in the presence of a base. Compound of Formula (Bl), wherein R^2 is hydrogen can be obtained from compound of formula (Dl) by reduction with $NaBH_4$. Compound of Formula (Bl), wherein R^2 is alkyl can be obtained from a compound of Formula (Dl) by addition of an organometallic reagent of formula R^2M wherein M can be for example Mg, Zn, or Li.

[0073] Alternatively, a compound of Formula (CI), wherein W is hydrogen or halogen or nitro, can be obtained from a compound of Formula (El), wherein R' is alkyl group, by reaction with a base such as potassium carbonate. Compound of Formula (Fl), wherein R^2 is

hydrogen can be obtained from a compound of Formula (El) by reaction with $NaBH_4$. Compound of Formula (Fl), wherein R^2 is alkyl can be obtained from a compound of Formula (El) by addition of an organometallic reagent of formula R^2M wherein M can be for example Mg, Zn, or Li. Compound of formula E can be made from compound of Formula (Dl) by reaction with an acylating agent of formula X(CO)OR', wherein R' is alkyl and X is halogen or an alkoxygroup, in the presence of a organic base such as pyridine or triethyl amine.

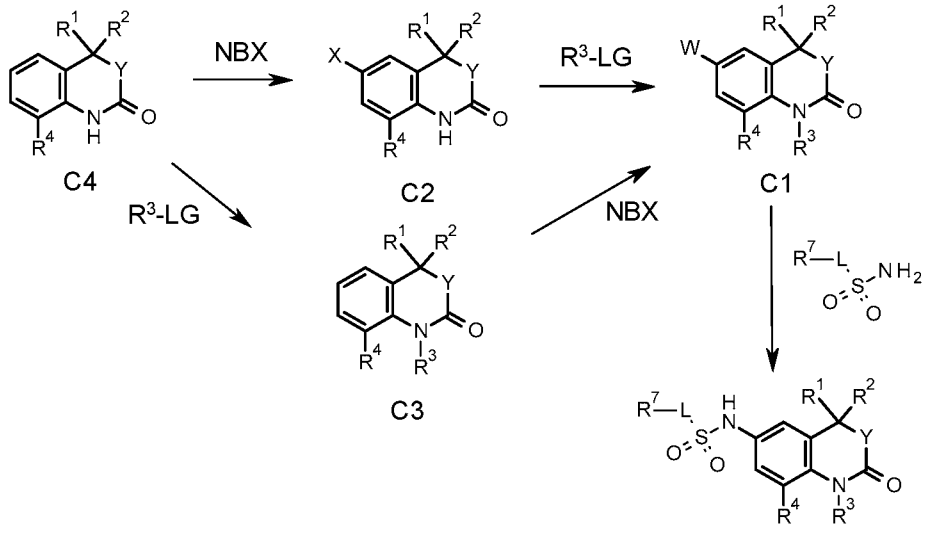
[0074] Compound of Formula (Dl) can be obtained from compound of Formula (G), wherein Z is a leaving group such as halogen by reaction with an amine or formula R^3NH_2.

SCHEME 3:



[0075] A compound of Formula (CI), wherein W is hydrogen or halogen or nitro and Y is N-R^6, can be obtained from a compound of Formula (CO) by reation with R^6-LG, wherein LG is a leaving group such as halogen or tosylate in the presence of a base such as sodium hydride. The compound of Formula (CO) can be obtained from a compound of Formula (H) by reaction with an acylating compound of formula $CO(X)_2$ wherein X is a leaving group such as halogen, imidazol, methoxide or trichloromethyl (triphosgene), eventually in the presence of a base. A compound of Formula (H) can be obtained from a compound of Formula (J) by reduction with $LiAlH_4$ or by hydrogenation in the presence of a catalyst such as Pd/C or Raney Ni. A compound of Formula (J) can be obtained from a compound of Formula (K), wherein Z is a leaving group such as fluoride, by reaction with an amine of formula R^3NH_2.

SCHEME 4:



[0076] A compound of Formula **(I)** can be prepared from a reaction between a compound of Formula (CI), wherein W is an halogen such as bromine, and a sulfonamide of formula R^7-L-S0 $_2NH_2$ in the presence of a catalyst such as a Pd(0) catalyst, a phosphine ligand and a base such as potassium carbonate as in Organic Letters, 2000, 2(8), 1101-1104 or Organic Letters, 2011, 13(10), 2564-2567. This reaction can also be done in the presence of a copper catalyst as in Tetrahedron Letters, 2005, 46(43), 7295-7298.

[0077] Compounds of Formula (CI) can be prepared as described in Schemes 2 and 3.

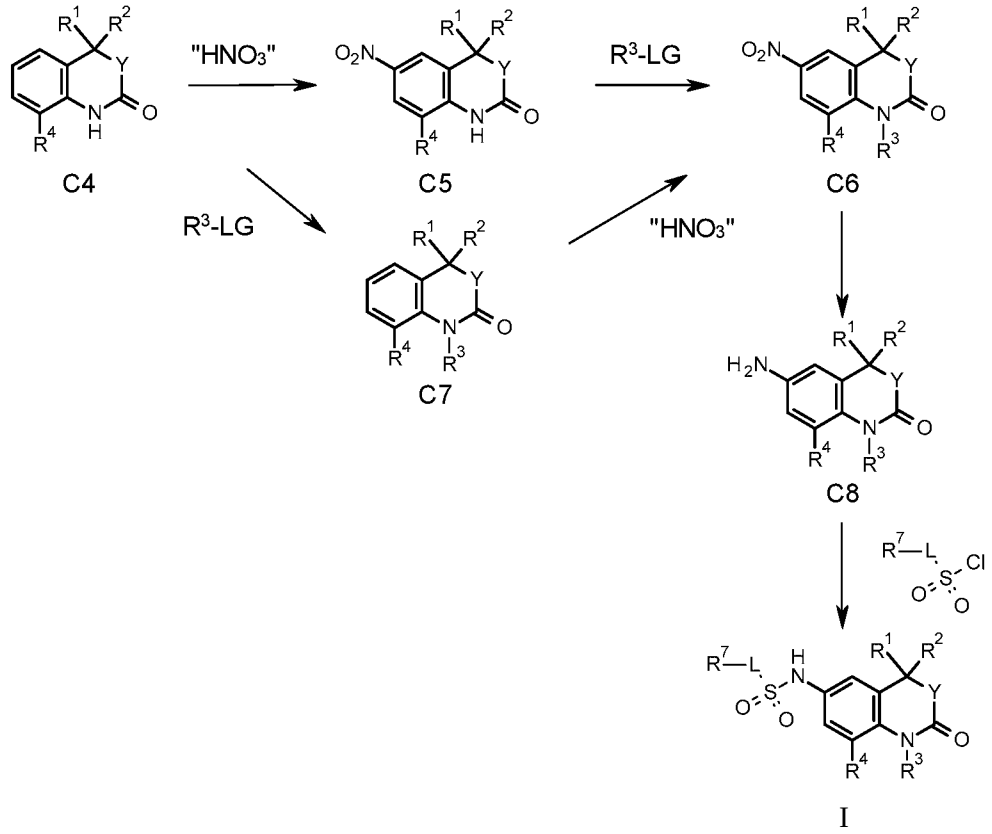
[0078] Alternatively, a compound of Formula (CI) can be prepared from compound of Formula (C2), wherein X is an halogen, by reaction with a an alkylating agent of Formula R^3-LG, wherein LG is a leaving group such as halogen, tosylate, mesylate or triflate and a base such as potassium carbotane or sodium hydride. Compound of Formula (C2), wherein X is a halogen, can be prepared from compound of Formula (C4) by reaction with a succinimide of Formula NBX, such as N-bromo-succinimide.

[0079] Alternatively, a compound of Formula (CI) can be prepared from compound of Formula (C3) by reaction with a succinimide of Formula NBX, such as N-bromo-succinimide. A compound of Formula (C3) can be obtained from a compound of Formula (C4) by reaction with an alkylating agent of Formula R^3-LG, wherein LG is a leaving group such as halogen, tosylate, or mesylate and a base such as potassium carbonate, potassium tert-

butoxide or sodium hydride. Compound of Formula (C3) can be also be prepared as described in Scheme 2 or 3.

[0080] Compounds of Formula (C2), and (C4) can be also be prepared as described in Scheme 1.

SCHEME 5:



[0081] Compounds of Formula (I) can be prepared from a compound of Formula (C8) and a sulfonyl chloride of formula R^7-L-S0 $_2$C1 in the presence of an organic base such as triethyl amine.

[0082] A compound of Formula (C8) can be prepared by reduction of a compound of Formula (C6) using a metal such as tin chloride, iron or zinc chloride in the presence of ammonium chloride or by hydrogenation with hydrogen in the presence of a catalyst such as Pd/C.

[0083] Compounds of Formula (C6) can be prepared as described in Schemes 2 and 3.

[0084] Alternatively, a compound of Formula (C6) can be prepared through nitration of a compound of Formula (C7) by reaction with nitric acid in the presence of an acid such as

sulphuric acid, acetic acid or trifluoroacetic acid. A compound of Formula (C7) can be prepared from a compound of Formula (CI) by reaction with a compound of formula R^3-LG wherein LG is a leaving group such as halogen or tosylate, and a base such as potassium carbonate, potassium tert-butoxide or sodium hydride in a polar solvent such as DMF or THF. Compounds of Formula (C7) can also be prepared as in Schemes 2 and 3.

[0085] Alternatively, a compound of Formula (C6) can be prepared from a compound of Formula (C5) by reaction with a compound of formula R^3-LG wherein LG is a leaving group such as halogen or tosylate, and a base such as potassium carbonate, potassium tert-butoxide or sodium hydride in a polar solvent such as DMF or THF. A compound of Formula (C5) can be obtained from a compound of Formula (CI) by reaction with nitric acid in the presence of an acid such as sulphuric acid, acetic acid or trifluoroacetic acid.

[0086] Compounds of Formula (C4) and (C5) can also be prepared as described in Scheme 1.

[0087] Sulfonyl chlorides of formula R^7-L-S0 $_2$C 1 are either commercially available or can be prepared by a person skilled in the art following known procedures from the literature.

[0088] Exemplary syntheses of various compounds of the invention are set forth in Example 1.

Compositions and Uses

[0089] In one embodiment, the compounds of the present invention are applied in combination with an agriculturally acceptable adjuvant. In particular, there is provided a composition comprising a compound of the present invention and an agriculturally acceptable adjuvant. There may also be mentioned an agrochemical composition comprising a compound of the present invention.

[0090] The present invention provides a method of improving the tolerance of a plant to abiotic stress, wherein the method comprises applying to the plant, plant part, plant propagation material, or plant growing locus a compound, composition or mixture according to the present invention.

[0091] The present invention provides a method for regulating or improving the growth of a plant, wherein the method comprises applying to the plant, plant part, plant propagation material, or plant growing locus a compound, composition or mixture according to the

present invention. In one embodiment, plant growth is regulated or improved when the plant is subject to abiotic stress conditions.

[0092] The present invention also provides a method for inhibiting seed germination of a plant, comprising applying to the seed, or a locus containing seeds, a compound, composition or mixture according to the present invention.

[0093] The present invention also provides a method for safening a plant against phytotoxic effects of chemicals, comprising applying to the plant, plant part, plant propagation material, or plant growing locus a compound, composition or mixture according to the present invention.

[0094] Suitably the compound or composition is applied in an amount sufficient to elicit the desired response.

[0095] Other effects of regulating or improving the growth of a crop include a decrease in plant height, or reduction in tillering, which are beneficial features in crops or conditions where it is desirable to have less biomass and fewer tillers.

[0096] Any or all of the above crop enhancements may lead to an improved yield by improving *e.g.,* plant physiology, plant growth and development and/or plant architecture. In the context of the present invention 'yield' includes, but is not limited to, (i) an increase in biomass production, grain yield, starch content, oil content and/or protein content, which may result from (a) an increase in the amount produced by the plant *per se* or (b) an improved ability to harvest plant matter, (ii) an improvement in the composition of the harvested material *(e.g.,* improved sugar acid ratios, improved oil composition, increased nutritional value, reduction of anti-nutritional compounds, increased consumer health benefits) and/or (iii) an increased/facilitated ability to harvest the crop, improved processability of the crop and/or better storage stability/shelf life. Increased yield of an agricultural plant means that, where it is possible to take a quantitative measurement, the yield of a product of the respective plant is increased by a measurable amount over the yield of the same product of the plant produced under the same conditions, but without application of the present invention. According to the present invention, it is preferred that the yield be increased by at least 0.5%, more preferred at least 1%, even more preferred at least 2%, still more preferred at least 4% , preferably 5% or even more.

[0097] Any or all of the above crop enhancements may also lead to an improved utilisation of land, i.e. land which was previously unavailable or sub-optimal for cultivation may become available. For example, plants which show an increased ability to survive in drought conditions, may be able to be cultivated in areas of sub-optimal rainfall, *e.g.,* perhaps on the fringe of a desert or even the desert itself.

[0098] In one aspect of the present invention, crop enhancements are made in the substantial absence of pressure from pests and/or diseases and/or abiotic stress. In a further aspect of the present invention, improvements in plant vigour, stress tolerance, quality and/or yield are made in the substantial absence of pressure from pests and/or diseases. For example pests and/or diseases may be controlled by a pesticidal treatment that is applied prior to, or at the same time as, the method of the present invention. In a still further aspect of the present invention, improvements in plant vigour, stress tolerance, quality and/or yield are made in the absence of pest and/or disease pressure. In a further embodiment, improvements in plant vigour, quality and/or yield are made in the absence, or substantial absence, of abiotic stress.

[0099] The compounds of the present invention can be used alone, but are generally formulated into compositions using formulation adjuvants, such as carriers, solvents and surface-active agents (SFAs). Thus, the present invention further provides a composition comprising a compound of the present invention and an agriculturally acceptable formulation adjuvant. There is also provided a composition consisting essentially of a compound of the present invention and an agriculturally acceptable formulation adjuvant. There is also provided a composition consisting of a compound of the present invention and an agriculturally acceptable formulation adjuvant.

[0100] The present invention further provides a plant growth regulator composition comprising a compound of the present invention and an agriculturally acceptable formulation adjuvant. There is also provided a plant growth regulator composition consisting essentially of a compound of the present invention and an agriculturally acceptable formulation adjuvant. There is also provided a plant growth regulator composition consisting of a compound of the present invention and an agriculturally acceptable formulation adjuvant.

[0101] The present invention further provides a plant abiotic stress management composition comprising a compound of the present invention and an agriculturally acceptable formulation adjuvant. There is also provided a plant abiotic stress management composition

consisting essentially of a compound of the present invention and an agriculturally acceptable formulation adjuvant. There is also provided a plant abiotic stress management composition consisting of a compound of the present invention and an agriculturally acceptable formulation adjuvant.

[0102] The present invention further provides a seed germination inhibitor composition comprising a compound of the present invention and an agriculturally acceptable formulation adjuvant. There is also provided a seed germination inhibitor composition consisting essentially of a compound of the present invention and an agriculturally acceptable formulation adjuvant. There is also provided a seed germination inhibitor composition consisting of a compound of the present invention and an agriculturally acceptable formulation adjuvant.

[0103] The composition can be in the form of concentrates which are diluted prior to use, although ready-to-use compositions can also be made. The final dilution is usually made with water, but can be made instead of, or in addition to, water, with, for example, liquid fertilisers, micronutrients, biological organisms, oil or solvents.

[0104] The compositions generally comprise from 0.1 to 99 % by weight, especially from 0.1 to 95 % by weight, compounds of the present invention and from 1 to 99.9 % by weight of a formulation adjuvant which preferably includes from 0 to 25 % by weight of a surface-active substance.

[0105] The compositions can be chosen from a number of formulation types, many of which are known from the Manual on Development and Use of FAO Specifications for Plant Protection Products, 5th Edition, 1999. These include dustable powders (DP), soluble powders (SP), water soluble granules (SG), water dispersible granules (WG), wettable powders (WP), granules (GR) (slow or fast release), soluble concentrates (SL), oil miscible liquids (OL), ultralow volume liquids (UL), emulsifiable concentrates (EC), dispersible concentrates (DC), emulsions (both oil in water (EW) and water in oil (EO)), micro-emulsions (ME), suspension concentrates (SC), aerosols, capsule suspensions (CS) and seed treatment formulations. The formulation type chosen in any instance will depend upon the particular purpose envisaged and the physical, chemical and biological properties of the compound of the present invention.

[0106] Dustable powders (DP) may be prepared by mixing a compound of the present invention with one or more solid diluents (for example natural clays, kaolin, pyrophyllite, bentonite, alumina, montmorillonite, kieselguhr, chalk, diatomaceous earths, calcium phosphates, calcium and magnesium carbonates, sulphur, lime, flours, talc and other organic and inorganic solid carriers) and mechanically grinding the mixture to a fine powder.

[0107] Soluble powders (SP) may be prepared by mixing a compound of the present invention with one or more water-soluble inorganic salts (such as sodium bicarbonate, sodium carbonate or magnesium sulphate) or one or more water-soluble organic solids (such as a polysaccharide) and, optionally, one or more wetting agents, one or more dispersing agents or a mixture of these agents to improve water dispersibility/solubility. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water soluble granules (SG).

[0108] Wettable powders (WP) may be prepared by mixing a compound of the present invention with one or more solid diluents or carriers, one or more wetting agents and, preferably, one or more dispersing agents and, optionally, one or more suspending agents to facilitate the dispersion in liquids. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water dispersible granules (WG).

[0109] Granules (GR) may be formed either by granulating a mixture of a compound of the present invention and one or more powdered solid diluents or carriers, or from pre-formed blank granules by absorbing a compound of the present invention (or a solution thereof, in a suitable agent) in a porous granular material (such as pumice, attapulgite clays, fuller's earth, kieselguhr, diatomaceous earths or ground com cobs) or by adsorbing a compound of the present invention (or a solution thereof, in a suitable agent) on to a hard core material (such as sands, silicates, mineral carbonates, sulphates or phosphates) and drying if necessary. Agents which are commonly used to aid absorption or adsorption include solvents (such as aliphatic and aromatic petroleum solvents, alcohols, ethers, ketones and esters) and sticking agents (such as polyvinyl acetates, polyvinyl alcohols, dextrins, sugars and vegetable oils). One or more other additives may also be included in granules (for example an emulsifying agent, wetting agent or dispersing agent).

[0110] Dispersible Concentrates (DC) may be prepared by dissolving a compound of the present invention in water or an organic solvent, such as a ketone, alcohol or glycol ether.

These solutions may contain a surface active agent (for example to improve water dilution or prevent crystallisation in a spray tank).

[0111] Emulsifiable concentrates (EC) or oil-in-water emulsions (EW) may be prepared by dissolving a compound of the present invention in an organic solvent (optionally containing one or more wetting agents, one or more emulsifying agents or a mixture of these agents). Suitable organic solvents for use in ECs include aromatic hydrocarbons (such as alkylbenzenes or alkylnaphthalenes, exemplified by SOLVESSO 100, SOLVESSO 150 and SOLVESSO 200; SOLVESSO is a Registered Trade Mark), ketones (such as cyclohexanone or methylcyclohexanone) and alcohols (such as benzyl alcohol, furfuryl alcohol or butanol), N-alkylpyrrolidones (such as N-methylpyrrolidone or N-octylpyrrolidone), dimethyl amides of fatty acids (such as Cg-Cio fatty acid dimethylamide) and chlorinated hydrocarbons. An EC product may spontaneously emulsify on addition to water, to produce an emulsion with sufficient stability to allow spray application through appropriate equipment.

[0112] Preparation of an EW involves obtaining a compound of the present invention either as a liquid (if it is not a liquid at room temperature, it may be melted at a reasonable temperature, typically below 70°C) or in solution (by dissolving it in an appropriate solvent) and then emulsifying the resultant liquid or solution into water containing one or more SFAs, under high shear, to produce an emulsion. Suitable solvents for use in EWs include vegetable oils, chlorinated hydrocarbons (such as chlorobenzenes), aromatic solvents (such as alkylbenzenes or alkylnaphthalenes) and other appropriate organic solvents which have a low solubility in water.

[0113] Microemulsions (ME) may be prepared by mixing water with a blend of one or more solvents with one or more SFAs, to produce spontaneously a thermodynamically stable isotropic liquid formulation. A compound of the present invention is present initially in either the water or the solvent/SFA blend. Suitable solvents for use in MEs include those hereinbefore described for use in ECs or in EWs. An ME may be either an oil-in-water or a water-in-oil system (which system is present may be determined by conductivity measurements) and may be suitable for mixing water-soluble and oil-soluble pesticides in the same formulation. An ME is suitable for dilution into water, either remaining as a microemulsion or forming a conventional oil-in-water emulsion.

[0114] Suspension concentrates (SC) may comprise aqueous or non-aqueous suspensions of finely divided insoluble solid particles of a compound of the present invention. SCs may be prepared by ball or bead milling the solid compound of the present invention in a suitable medium, optionally with one or more dispersing agents, to produce a fine particle suspension of the compound. One or more wetting agents may be included in the composition and a suspending agent may be included to reduce the rate at which the particles settle. Alternatively, a compound of the present invention may be dry milled and added to water, containing agents hereinbefore described, to produce the desired end product.

[0115] Aerosol formulations comprise a compound of the present invention and a suitable propellant (for example w-butane). A compound of the present invention may also be dissolved or dispersed in a suitable medium (for example water or a water miscible liquid, such as ft-propanol) to provide compositions for use in non-pressurised, hand-actuated spray pumps.

[0116] Capsule suspensions (CS) may be prepared in a manner similar to the preparation of EW formulations but with an additional polymerisation stage such that an aqueous dispersion of oil droplets is obtained, in which each oil droplet is encapsulated by a polymeric shell and contains a compound of the present invention and, optionally, a carrier or diluent therefor. The polymeric shell may be produced by either an interfacial polycondensation reaction or by a coacervation procedure. The compositions may provide for controlled release of the compound of the present invention and they may be used for seed treatment. A compound of the present invention may also be formulated in a biodegradable polymeric matrix to provide a slow, controlled release of the compound.

[0117] The composition may include one or more additives to improve the biological performance of the composition, for example by improving wetting, retention or distribution on surfaces; resistance to rain on treated surfaces; or uptake or mobility of a compound of the present invention. Such additives include surface active agents (SFAs), spray additives based on oils, for example certain mineral oils or natural plant oils (such as soy bean and rape seed oil), and blends of these with other bio-enhancing adjuvants (ingredients which may aid or modify the action of a compound of the present invention).

[0118] Wetting agents, dispersing agents and emulsifying agents may be SFAs of the cationic, anionic, amphoteric or non-ionic type.

[0119] Suitable SFAs of the cationic type include quaternary ammonium compounds (for example cetyltrimethyl ammonium bromide), imidazolines and amine salts.

[0120] Suitable anionic SFAs include alkali metals salts of fatty acids, salts of aliphatic monoesters of sulphuric acid (for example sodium lauryl sulphate), salts of sulphonated aromatic compounds (for example sodium dodecylbenzenesulphonate, calcium dodecylbenzenesulphonate, butylnaphthalene sulphonate and mixtures of sodium di-wopropyl- and tri-wopropyl-naphthalene sulphonates), ether sulphates, alcohol ether sulphates (for example sodium laureth-3-sulphate), ether carboxylates (for example sodium laureth-3-carboxylate), phosphate esters (products from the reaction between one or more fatty alcohols and phosphoric acid (predominately mono-esters) or phosphorus pentoxide (predominately di-esters), for example the reaction between lauryl alcohol and tetraphosphoric acid; additionally these products may be ethoxylated), sulphosuccinamates, paraffin or olefine sulphonates, taurates and lignosulphonates.

[0121] Suitable SFAs of the amphoteric type include betaines, propionates and glycinates.

[0122] Suitable SFAs of the non-ionic type include condensation products of alkylene oxides, such as ethylene oxide, propylene oxide, butylene oxide or mixtures thereof, with fatty alcohols (such as oleyl alcohol or cetyl alcohol) or with alkylphenols (such as octylphenol, nonylphenol or octylcresol); partial esters derived from long chain fatty acids or hexitol anhydrides; condensation products of the partial esters with ethylene oxide; block polymers (comprising ethylene oxide and propylene oxide); alkanolamides; simple esters (for example fatty acid polyethylene glycol esters); amine oxides (for example lauryl dimethyl amine oxide); and lecithins.

[0123] Suitable suspending agents include hydrophilic colloids (such as polysaccharides, polyvinylpyrrolidone or sodium carboxymethylcellulose) and swelling clays (such as bentonite or attapulgite).

[0124] The compound or composition of the present invention may be applied to a plant, part of the plant, plant organ, plant propagation material or a plant growing locus.

[0125] The application is generally made by spraying the composition, typically by tractor mounted sprayer for large areas, but other methods such as dusting (for powders), drip or drench can also be used. Alternatively the composition may be applied in furrow or directly to a seed before or at the time of planting.

[0126] The compound or composition of the present invention may be applied pre-emergence or post-emergence. Suitably, where the composition is used to regulate the growth of crop plants or enhance the tolerance to abiotic stress, it may be applied post-emergence of the crop. Where the composition is used to inhibit or delay the germination of seeds, it may be applied pre-emergence.

[0127] The present invention envisages application of the compounds or compositions of the invention to plant propagation material prior to, during, or after planting, or any combination of these.

[0128] Although active ingredients can be applied to plant propagation material in any physiological state, a common approach is to use seeds in a sufficiently durable state to incur no damage during the treatment process. Typically, seed would have been harvested from the field; removed from the plant; and separated from any cob, stalk, outer husk, and surrounding pulp or other non-seed plant material. Seed would preferably also be biologically stable to the extent that treatment would not cause biological damage to the seed. It is believed that treatment can be applied to seed at any time between seed harvest and sowing of seed including during the sowing process.

[0129] Methods for applying or treating active ingredients on to plant propagation material or to the locus of planting are known in the art and include dressing, coating, pelleting and soaking as well as nursery tray application, in furrow application, soil drenching, soil injection, drip irrigation, application through sprinklers or central pivot, or incorporation into soil (broad cast or in band). Alternatively or in addition active ingredients may be applied on a suitable substrate sown together with the plant propagation material.

[0130] The rates of application of compounds of the present invention may vary within wide limits and depend on the nature of the soil, the method of application (pre- or post-emergence; seed dressing; application to the seed furrow; no tillage application etc.), the crop plant, the prevailing climatic conditions, and other factors governed by the method of application, the time of application and the target crop. For foliar or drench application, the compounds of the present invention according to the invention are generally applied at a rate of from about 1 to about 2000 g/ha, especially from about 5 to about 1000 g/ha. For seed treatment the rate of application is generally from about 0.0005 to about 150 g per 100 kg of seed.

[0131] The compounds and compositions of the present invention may be applied to dicotyledonous or monocotyledonous crops.

[0132] Crops of useful plants in which the composition according to the invention can be used include perennial and annual crops, such as berry plants for example blackberries, blueberries, cranberries, raspberries and strawberries; cereals for example barley, maize (corn), millet, oats, rice, rye, sorghum triticale and wheat; fibre plants for example cotton, flax, hemp, jute and sisal; field crops for example sugar and fodder beet, coffee, hops, mustard, oilseed rape (canola), poppy, sugar cane, sunflower, tea and tobacco; fruit trees for example apple, apricot, avocado, banana, cherry, citrus, nectarine, peach, pear and plum; grasses for example Bermuda grass, bluegrass, bentgrass, centipede grass, fescue, ryegrass, St. Augustine grass and Zoysia grass; herbs such as basil, borage, chives, coriander, lavender, lovage, mint, oregano, parsley, rosemary, sage and thyme; legumes for example beans, lentils, peas and soya beans; nuts for example almond, cashew, ground nut, hazelnut, peanut, pecan, pistachio and walnut; palms for example oil palm; ornamentals for example flowers, shrubs and trees; other trees, for example cacao, coconut, olive and rubber; vegetables for example asparagus, aubergine, broccoli, cabbage, carrot, cucumber, garlic, lettuce, marrow, melon, okra, onion, pepper, potato, pumpkin, rhubarb, spinach and tomato; and vines for example grapes.

[0133] Crops are to be understood as being those which are naturally occurring, obtained by conventional methods of breeding, or obtained by genetic engineering. They include crops which contain so-called output traits (e.g., improved storage stability, higher nutritional value and improved flavour).

[0134] Crops are to be understood as also including those crops which have been rendered tolerant to herbicides like bromoxynil or classes of herbicides such as ALS-, EPSPS-, GS-, HPPD- and PPO-inhibitors. An example of a crop that has been rendered tolerant to imidazolinones, *e.g.,* imazamox, by conventional methods of breeding is Clearfield® summer canola. Examples of crops that have been rendered tolerant to herbicides by genetic engineering methods include *e.g.,* glyphosate- and glufosinate-resistant maize varieties commercially available under the trade names RoundupReady®, Herculex I® and LibertyLink®.

[0135] Crops are also to be understood as being those which naturally are or have been rendered resistant to harmful insects. This includes plants transformed by the use of recombinant DNA techniques, for example, to be capable of synthesising one or more selectively acting toxins, such as are known, for example, from toxin-producing bacteria. Examples of toxins which can be expressed include δ-endotoxins, vegetative insecticidal proteins (Vip), insecticidal proteins of bacteria colonising nematodes, and toxins produced by scorpions, arachnids, wasps and fungi.

[0136] An example of a crop that has been modified to express the Bacillus thuringiensis toxin is the Bt maize KnockOut® (Syngenta Seeds). An example of a crop comprising more than one gene that codes for insecticidal resistance and thus expresses more than one toxin is VipCot® (Syngenta Seeds). Crops or seed material thereof can also be resistant to multiple types of pests (so-called stacked transgenic events when created by genetic modification). For example, a plant can have the ability to express an insecticidal protein while at the same time being herbicide tolerant, for example Herculex I® (Dow AgroSciences, Pioneer Hi-Bred International).

[0137] Compounds of the present invention may also be used to inhibit or delay the germination of seeds of non-crop plants, for example as part of an integrated weed control program. A delay in germination of weed seeds may provide a crop seedling with a stronger start by reducing competition with weeds.

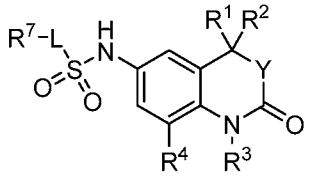
[0138] Alternatively compounds of the present invention may be used to delay the germination of seeds of crop plants, for example to increase the flexibility of timing of planting for the grower.

[0139] Normally, in the management of a crop a grower would use one or more other agronomic chemicals or biologicals in addition to the compound or composition of the present invention. There is also provided a mixture comprising a compound or composition of the present invention, and a further active ingredient.

[0140] Examples of agronomic chemicals or biologicals include pesticides, such as acaricides, bactericides, fungicides, herbicides, insecticides, nematicides, plant growth regulators, crop enhancing agents, safeners as well as plant nutrients and plant fertilizers. Examples of suitable mixing partners may be found in the Pesticide Manual, 15th edition (published by the British Crop Protection Council). Such mixtures may be applied to a plant,

plant propagation material or plant growing locus either simultaneously (for example as a pre-formulated mixture or a tank mix), or sequentially in a suitable timescale. Co-application of pesticides with the present invention has the added benefit of minimising farmer time spent applying products to crops. The combination may also encompass specific plant traits incorporated into the plant using any means, for example conventional breeding or genetic modification.

[0141] The present invention also provides the use of a compound of Formula (I):



I

wherein R^1, R^2, Y, R^3, R^4, L, and R^7 are as defined herein; or salts or N-oxides thereof, and isomers, tautomers, enantiomers or diastereomers of these compounds; or a composition comprising a compound according to Formula (I) and an agriculturally acceptable formulation adjuvant, for improving the tolerance of a plant to abiotic stress, regulating or improving the growth of a plant, inhibiting seed germination and/or safening a plant against phytotoxic effects of chemicals.

[0142] There is also provided the use of a compound, composition or mixture of the present invention, for improving the tolerance of a plant to abiotic stress, regulating or improving the growth of a plant, inhibiting seed germination and/or safening a plant against phytotoxic effects of chemicals.

[0143] The materials and methods of the present invention are further illustrated by the examples which follow. These examples are offered to illustrate, but not to limit the claimed invention.

EXAMPLES

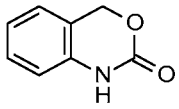
[0144] LCMS spectra were recorded on a Mass Spectrometer from Waters (SQD or ZQ Single quadrupole mass spectrometer) equipped with an electrospray source (Polarity: positive or negative ions, Capillary: 3.00 kV, Cone range: 30-60 V, Extractor: 2.00 V, Source Temperature: 150°C, Desolvation Temperature: 350°C, Cone Gas Flow: 0 L/Hr, Desolvation Gas Flow: 650 L/Hr, Mass range: 100 to 900 Da) and an Acquity UPLC from Waters: Binary

pump, heated column compartment and diode-array detector. Solvent degasser, binary pump, heated column compartment and diode-array detector. Column: Waters UPLC HSS T3 , 1.8 μm, 30 x 2.1 mm, Temp: 60 °C, DAD Wavelength range (nm): 210 to 500, Solvent Gradient: A = water + 5% MeOH + 0.05 % HCOOH, B= Acetonitrile + 0.05 % HCOOH: gradient: 0 min 0% B, 100%A; 1.2-1.5min 100% B; Flow (mL/min) 0.85

Example 1: Syntheses

Preparation of N-(2-oxo- 1-propyl-4H-3. 1-benzoxazin-6-yl)- 1-(p-tolyl)methanesulfonamide (Compound CQ1)

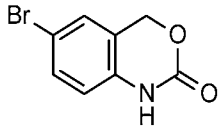
Step 1: 1.4-dihydro-3.1-benzoxazin-2-one



[0145] 2-amino-5-bromo-3-fluoro-benzoic acid (2.00 g, 16.2 mmol) was dissolved in acetonitrile (16 mL). Ethyl chloroformate (1.55 mL, 16.2 mmol) and pyridine (1.31 mL, 16.2 mmol) were then added dropwise. The reaction mixture was then stirred at room temperature for 1 h. Water was added and the reaction mixture was extracted with ethyl acetate, dried and concentrated to give ethyl N-[2-(hydroxymethyl)phenyl] carbamate as a pale orange oil. The crude oil was taken up in EtOH (20 mL) and potassium carbonate (1.64 g, 16.2 mmol) was added. The reaction mixture was heated to 60 °C for 1 h and the ethanol was removed. The solid was partitioned between water and ethyl acetate and the organic layer was dried and concentrated to give l,4-dihydro-3,l-benzoxazin-2-one (2.42 g, 16.2 mmol, 99.9%) as a white powder. The compound was used as such for the next step.

[0146] LCMS: 0.52 min; ES+ 150 (M+H+); ^{1}H NMR (CHLOROFORM-d, 400MHz): δ (ppm) 7.27 (t, 1H), 7.12 (d, 1H), 7.05 (t, 1H), 6.88 (d, 1H), 5.34 (s, 2H)

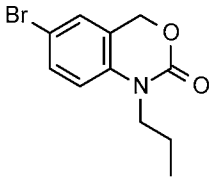
Step 2: 6-bromo-1.4-dihydro-3.1-benzoxazin-2-one



[0147] l,4-dihydro-3,l-benzoxazin-2-one (1.00 g, 6.70 mmol) was dissolved in DMF (13 mL) and cooled to 0°C. NBS (1.33 g, 7.38 mmol) was added in portions at 0 °C. The reaction mixture was stirred at 40 °C for 3 h. The reaction mixture was poured on water and the solid was filtered, washed with water and dried via suction to give 6-bromo-l,4-dihydro-3,l-benzoxazin-2-one as a white powder (1.44 g, 94%). The compound was used as such for the next step.

[0148] LCMS: 0.72 min; ES+ 228/230 (M+H+); ^{1}H NMR (CHLOROFORM-d, 400MHz): δ (ppm) 8.61-8.84 (s, 1H), 7.38 (dd, H), 7.26 (s, 2H), 6.77 (d, 1H), 5.30 (s, 2H).

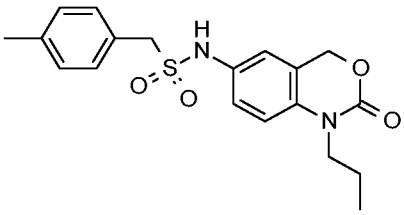
Step 3. 6-bromo-l-propyl-4H-3.1-benzoxazin-2-one



[0149] 6-bromo-l,4-dihydro-3,l-benzoxazin-2-one (500 mg, 2.19 mmol) was dissolved in DMF (11 mL) and potassium carbonate (0.459 g, 3.28 mmol) was added. The suspension was stirred for 10 min and then 1-bromopropane (0.400 mL, 4.38 mmol) was added dropwise. The reaction mixture was heated to 60 °C and stirred for 4 hours. The reaction mixture was poured into ice/water and extracted with ethyl acetate (2x20 mL). The combined organic layers were washed with brine (3x20 mL), dried over Na_2SO_4 and concentrated. The crude oil was purified by flash chromatography to give 6-bromo-l,4-dihydro-3,l-benzoxazin-2-one (390 mg, 1.4438 mmol, 66% Yield) as a colourless solid.

[0150] LCMS: 0.97 min; ES+ 270/272 (M+H+); ^{1}H NMR (CHLOROFORM-d, 400MHz): δ (ppm) 7.45 (dd, 1H), 7.25-7.29 (s, 1H), 6.82 (d, 1H), 5.15 (s, 2H), 3.80-3.88 (m, 2H), 1.55-1.79 (m, 4H), 1.00 (t, 3H).

Step 4: N-(2-oxo-l-propyl-4H-3.1-benzoxazin-6-yl)-l-(p-tolyl)methanesulfonamide CQ1

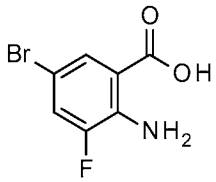


[0151] 6-bromo-l-propyl-4H-3,l-benzoxazin-2-one (200 mg, 0.740 mmol) , p-tolylmethanesulfonamide (0.151 g, 0.777 mmol) and potassium carbonate (0.206 g, 1.480 mmol) were suspended in toluene (3 mL) and purged with argon. tBuBrettPhos Pd G3 (0.016 g, 0.018 mmol) was added and the reaction mixture was heated to reflux for 1 h. The reaction mixture was cooled down to room temperature and the reaction mixture was diluted with ethyl acetate (20 mL) and water (20 mL). The aqueous layer was extracted with ethyl acetate (2x20 mL) and the combined organic layers were washed with brine, dried and concentrated. The crude brown gum was purified by flash chromatography to give the desired product as a white solid (200 mg, 76%).

[0152] LCMS: 0.96 min; ES+ 375 (M+H+); ^{1}H NMR (CHLOROFORM-d, 400MHz): δ (ppm) 7.14-7.25 (m, 4H), 7.03 (d, 1H), 6.93 (s, 1H), 6.89 (d, 1H), 6.25 (s, 1H), 5.13 (s, 2H), 4.30 (s, 2H), 3.85 (m, 2H), 2.37 (s, 3H), 1.77 (sxt, 2H), 1.01 (t, 3H)

Preparation of N-(8-fluoro-2-oxo- 1-propyl-4H-3 .1-benzoxazin-6-yl)- 1-(p-tolvDmethanesulfonamide (Compound CQ2)

Step 1: 2-amino-5-bromo-3-fluoro-benzoic acid

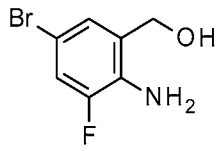


[0153] 2-Amino-3-fluoro-benzoic acid (2.00 g, 12.9 mmol) was suspended in dichloromethane (34.0 mL) and N-bromosuccinimide (2.39 g, 12.9 mmol) was added in small portions at 0 °C. The reaction mixture was stirred at room temperature for 1 hour. The reaction mixture was filtered and the solid was washed with dichloromethane (30 mL) and

dried in air for 15 min to give the desired product as a white solid (2.46 g, 10.5 mmol, 82% Yield).

[0154] LCMS: 0.82 min; ES+ 234/236 (M+H+); ^{1}H NMR (DMSO-d$_6$, 400MHz): δ (ppm) 7.62-7.66 (s, 1H), 7.52 (d, 1H).

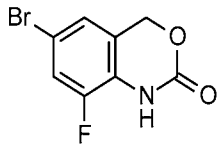
Step 2: (2-amino-5-bromo-3-fluoro-phenyl)methanol



[0155] To a solution of 2-amino-5-bromo-3-fluoro-benzoic acid (1.00 g4.27 mmol) in tetrahydrofuran (10 mL) was added borane (1.0 mol/L in THF, 13 mL, 12.8 mmol). The reaction mixture was stirred ovemight at room temperature. After 12 h, the reaction was not complete and the reaction was heated to 45 °C for 6 h. The reaction mixture was cooled to room temperature and MeOH (1 mL) was slowly added. After 30 min, the reaction mixture concentrated to a volume of ~ 5 mL and a saturated solution of NaHCCb and water were added. The reaction mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, dried and concentrated. The crude white solid was purified by flash chromatography to give the desired product as a white solid (0.600 g, 64%).

[0156] LCMS= 0.73 min; ES+ 202/204 (M-OH-); ^{1}H NMR (DMSO-d$_6$, 400MHz): δ (ppm) 7.18 (d, 1H), 7.12 (s, 1H), 5.26 (br s, 1H), 5.06 (br s, 2H), 4.40 (s, 2H).

Step 3: 6-bromo-8-fluoro-1 .4-dihydro-3. 1-benzoxazin-2-one

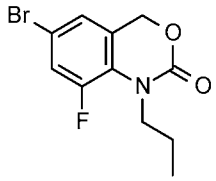


[0157] 2-Amino-5-bromo-3-fluoro-phenyl)methanol (600 mg, 2.73 mmol) was dissolved in acetonitrile (3 mL) and ethyl chloroformate (0.269 mL, 2.72 mmol) was added. The reaction mixture was cooled to 0 °C and pyridine (0.242 mL, 3.00 mmol) was then added dropwise.The reaction mixture was then stirred at room temperature for 1 h. Water was added and the reaction mixture was extracted with ethyl acetate, dried and concentrated to give a

pale white solid. The crude compound was taken up in ethanol (20 mL) and potassium carbonate (0.574 g, 4.11 mmol) was added. The reaction mixture was heated to 60 °C for 1 h and the reaction mixture was cooled to room temperature. The reaction mixture was partitioned between ethyl acetate and water. The organic layer was dried and concentrated to give the desired product as a white solid (585 mg, 83%).

[0158] LCMS= 0.74 min; ES+ 246/248 (M+H+); ^{1}H NMR (DMSO-d$_6$, 400MHz): δ (ppm) 10.53 (s, 1H), 7.52 (d, 1H), 7.32 (s, 1H), 5.32 (s, 2H).

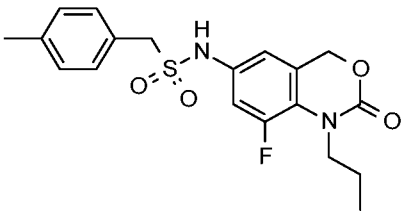
Step 4: 6-bromo-8-fluoro-l-propyl-4H-3.1-benzoxazin-2-one



[0159] To a solution of 6-bromo-8-fluoro-l,4-dihydro-3,l-benzoxazin-2-one (375 mg, 1.524 mmol) in dimethylformamide (8 mL) was added potassium carbonate (0.319 g, 2.28 mmol) and 1-bromopropane (0.278 mL, 3.05 mmol). The reaction mixture was stirred at 50 °C for 3 h, cooled down to room temperature and poured into ice/water. The aqueous layer was extracted with ethyl acetate (2x20 mL). The combined organic layers were washed with brine (3x20 mL), dried and concentrated. The crude oil was purified by flash chromatography to give 6-bromo-8-fluoro-l-propyl-4H-3,l-benzoxazin-2-one as a white solid (215 mg, 0.74 mmol, 49%).

[0160] LCMS= 1.03 min; ES+ 288/280 (M+H+); ^{1}H NMR (CHLOROFORM-d, 400MHz): δ (ppm) 7.23-7.30 (d, 1H), 7.10 (s, 1H), 5.08 (s, 2H), 3.88-4.03 (m, 2H), 1.72 (sxt, 2H), 0.94 (t, 3H)

Step 5: N-(2-oxo-8-fluoro-l-propyl-4H-3.1-benzoxazin-6-yl)-l-(p-tolyl)methanesulfonamide CQ2

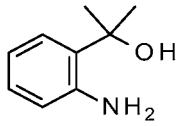


[0161] 6-Bromo-8-fluoro-l-propyl-4H-3,l-benzoxazin-2-one (0.520 mmol, 0.150 g), p-tolylmethanesulfonamide (0.494 mmol, 0.096 g) and potassium carbonate (1.04 mmol, 0.145 g) were suspended in toluene (2 mL) and the flask was purged with argon for 15min. tBuBrettPhos Pd G3 (0.026 mmol, 0.022 g) and the reaction mixture was heated to 100° for 2 h. The reaction mixture was cooled to room temperature and diluted with ethyl acetate and water/brine. The aqueous layer was extracted twice with ethyl acetate. The organic layers were combined, dried and concentrated. The crude compound was purified by flash chromatography to give the desired product (90 mg, 44%) as a colorless solid;

[0162] m.p. : 137-140 °C; LCMS: 0.98 min; ES+ 393 (M+H+); ^{1}H NMR (CHLOROFORM-d, 400MHz): δ (ppm) 7.18 (s, 4H), 6.82 (d, IH), 6.66 (s, IH), 6.50 (s, IH), 5.03 (s, 2H), 4.33 (s, 2H), 3.90-4.01 (m, 2H), 2.36 (s, 3H), 1.74 (sxt, 2H), 0.95 (t, 3H)

Preparation of N-(l -ethyl-4.4-dimethyl-2-oxo-3 .1-benzoxazin-6-yl)- 1-(p-tolvDmethanesulfonamide (Compound CQ3)

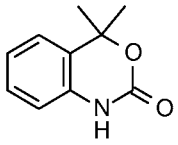
Step 1: 2-(2-aminophenyl)propan-2-ol



[0163] To a solution of l-(2-aminophenyl)ethanone (1.50 g, 11.1 mmol) in THF (11 mL, cooled at 0 °C and under a small flow of Ar was added slowly methylmagnesium bromide (1.0 mol/L in THF, 28 mL, 27.7 mmol). The reaction mixture was warmed to room temperature. The reaction mixture was quenched carefully with sat. ammonium chloride aqueous solution and and the reaction mixture was extracted with ethyl acetate (3*20 mL), dried and concentrated. The crude brown oil was purified by flash chromatography to give 2-(2-aminophenyl)propan-2-ol as a pale oil (1.20 g, 72%).

[0164] LCMS: 0.24 min; ES+ 134 (M-OH-); ^{1}H NMR (CHLOROFORM-d, 400MHz): δ (ppm) 7.15 (d, IH), 7.06 (t, IH), 6.72 (t, IH), 6.65 (d, IH), 3.65 (br s, IH), 1.67 (s, 6H).

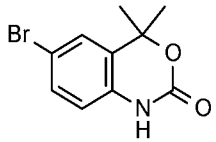
Step 2: 4.4-dimethyl-lH-3.1-benzoxazin-2-one



[0165] 2-(2-aminophenyl)propan-2-ol (1.19 g, 7.87 mmol) was suspend in dioxane (10 mL) and added carbonyldiimidazole (1.53 g, 9.44 mmol) and stirred for 2 h at room temperature. Aqueous HCl (I N, 15 mL) was added and the reaction was extracted with ethyl acetate (3x20 mL). The combined organic layers were washed with IN HCl and brine, dried and concentrated to give 4,4-dimethyl-lH-3,l-benzoxazin-2-one as a pale solid (1.34 g, 7.56 mmol, 96%). The product was used as such without further purification in the next step.

[0166] LCMS: 0.70 min; ES+ 178 (M+H+); ^{1}H NMR (CHLOROFORM-d, 400MHz): δ (ppm) 9.08 (br s, 1H), 7.24 (t, 1H), 7.14 (d, 1H), 7.07 (t, 1H), 6.89 (d, 1H), 1.73 (s, 6H)

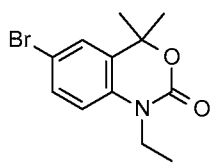
Step 3: 6-bromo-4.4-dimethyl-lH-3.1-benzoxazin-2-one



[0167] 4,4-dimethyl-lH-3,l-benzoxazin-2-one (1.00 g, 5.64 mmol) was dissolved in dimethylformamide (11 mL) and cooled to 0°C. NBS (1.12 g, 6.21 mmol) was added. The reaction mixture was stirred at room temperature for 4 h.The reaction mixture was poured on water and the white precipitate was filtered and washed with water to give 6-bromo-4,4-dimethyl-lH-3,l-benzoxazin-2-one as a white powder (1.29 g, 89% yield).

[0168] LCMS: 0.83 min; ES+ 256/258 (M+H+); ^{1}H NMR (CHLOROFORM-d, 400MHz): δ (ppm) 9.13 (br s, 1H), 7.36 (d, 1H), 7.27 (s, 1H), 6.77 (d, 1H), 1.73 (s, 6H).

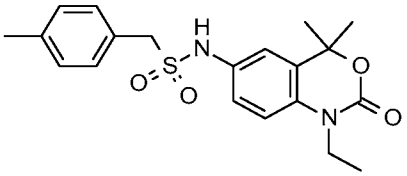
Step 4: 6-bromo-4.4-dimethyl-l-ethyl-3.1-benzoxazin-2-one



[0169] 6-bromo-4,4-dimethyl-lH-3,l-benzoxazin-2-one (250 mg, 0.976 mmol) was dissolved in dimethylformamide (5 mL) and potassium carbonate (0.204 g, 1.46 mmol) was added. The suspension was stirred for 10 min and then iodoethane (0.158 mL, 1.95 mmol) was added. The reaction mixture was heated to 60°C and stirred for 4 h. The reaction mixture was poured into ice/water and then extracted with ethyl acetate (3x20 mL). The combined organic layers were washed with brine (2x20 mL). dried and concentrated. The crude oil was purified by flash chromatography to give the desired compound (0.275 g, 99%) as a colorless oil.

[0170] LCMS: 0.98 min; ES+ 284/286 (M+H+); ^{1}H NMR (CHLOROFORM-d, 400MHz): δ (ppm) 7.43 (d,lH), 7.28 (s, 1H), 6.86 (d, 1H), 3.98 (q, 2H), 1.67 (s, 6H), 1.32 (t, 3H)

Step 5: N-(l-ethyl-4^-dimethyl-2-oxo-3J-benzoxazin-6-yl)-l-(p4olyl)methanesulfonamide CQ3

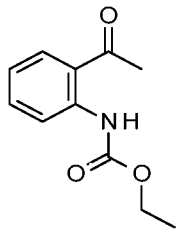


[0171] 6-bromo-4,4-dimethyl-l-ethyl-3,l-benzoxazin-2-one (100 mg, 0.352 mmol), p-tolylmethanesulfonamide (65 mg, 0.334 mmol) and potassium carbonate (98 mg, 0.703 mmol) were suspend in toluene (1.5 mL) and the suspension is purged with argon. tBuBrettPhos Pd G3 (15 mg, 0.017 mmol) was added and the reaction mixture was heated to 90° for 30min. The reaction mixture was cooled to room temperature and diluted with ethyl acetate and water. The aqueous layer was extracted twice with ethyl acetate, the combined organic layers were combined, dried and concentrated. The crude product was purified by flash chromatography over silica to give the desired product as a beige solid (103 mg, 75%).

[0172] LCMS: 0.93 min; ES+ 389 (M+H+); ^{1}H NMR (CHLOROFORM-d, 400MHz): δ (ppm) 7.16-7.22 (m, 4H), 7.10 (d, 1H), 6.93 (d, 1H), 6.89 (s, 1 H), 6.22 (s, 1H), 4.30 (s, 2H), 3.99 (q, 2H), 2.37 (s, 3H), 1.65 (s, 6H), 1.34 (t, 3H)

Preparation of N-(1-ethyl-4-methyl-2-oxo-4H-3. 1-benzoxazin-6-yl)- 1-(p-tolvDmethanesulfonamide (Compound CQ4)

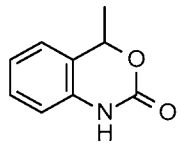
Step 1: ethyl N-(2-acetylphenyl)carbamate



[0173] 2-Acetylaniline (10.0 g, 72.5 mmol) was dissolved in ethyl acetate (72 mL) and cooled to 0°. Ethyl chloroformate (7.86 mL, 79.8 mmol) was added followed by pyridine dropwise (6.22 mL, 76. 1 mmol). Water was added and the reaction was extracted with ethyl acetate. The organic layers were washed with IN HCl, dried and concentrated to give ethyl N-(2-acetylphenyl)carbamate (15.0 g, quant.) as an orange solid.

[0174] LCMS: 0.97 min; ES+ 208 (M+H+); ^{1}H NMR (CHLOROFORM-d, 400MHz): δ (ppm) 11.15 (br s, 1H), 8.49 (d, 1H), 7.88 (d, 1H), 7.55 (t, 1H), 7.06 (t, 1H), 4.23 (q, 2H), 2.66 (s, 3H), 1.33 (t, 3H)

Step 2: 4-methyl-1.4-dihydro-3.1-benzoxazin-2-one

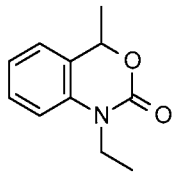


[0175] Ethyl N-(2-acetylphenyl)carbamate (1.00 g, 4.83 mmol) was solved in THF (25 mL) and added sodium borohydride (0.369 g, 9.65 mmol). The reaction mixture was stirred over 5 h at room temperature. The reaction mixture was quenched with water (10 mL) and then lOmL of HCl (1 M) were added very slowly. The reaction mixture was then extracted with ethyl acetate (3x25 mL) and washed with brine, dried and concentrated to give a crude oil of ethyl N-[2-(l-hydroxyethyl)phenyl]carbamate and 4-methyl-l,4-dihydro-3,l-benzoxazin-2-one. The crude mixture was taken up in acetonitrile (20 mL) and potassium carbonate (0.667 g, 4.83 mmol) was added. The suspension was heated to reflux for 5 h, cooled down to rt, filtered and concentrated. The crude solid was purified by flash

chromatography to give 4-methyl-l,4-dihydro-3,l-benzoxazin-2-one (0.727 g, 92%) as a white solid.

[0176] LCMS: 0.64 min; ES+ 164 (M+H+); ^{1}H NMR (CHLOROFORM-d, 400MHz): δ (ppm) 8.79 (br s, 1H), 7.44 (t, 1H), 7.19-7.31 (m, 2H), 7.09 (d, 1H), 5.65-5.76 (q, 1H), 1.90 (d, 3H)

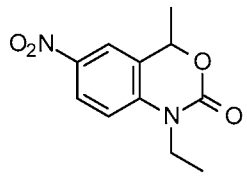
Step 3: l-ethyl-4-methyl-4-H-3.1-benzoxazin-2-one



[0177] 4-Methyl-l,4-dihydro-3,l-benzoxazin-2-one (0.149 g, 0.913 mmol) was dissolved in dimethylformamide (5 mL) and added potassium carbonate (0.378 g, 2.74 mmol) and bromoethane (0.200 g, 1.82 mmol) were added. The reaction mixture was stirred over 24h at room temperature. The reaction mixture was quenched with water and extracted with ethyl acetate (3x50 mL). The combined organic layer were washed with water (2xl00mL), dried and concentrated to give l-ethyl-4-methyl-3,l-benzoxazin-2-one as a colourless oil (0.140 g, 80%)

[0178] LCMS: 0.82 min; ES+ 192 (M+H+); ^{1}H NMR (CHLOROFORM-d, 400MHz): δ (ppm) 7.34 (t, 1H), 7.06-7.18 (m, 2H), 6.99 (d, 1H), 5.36 (q, 1H), 3.92-4.05 (m, 2H), 1.68 (d, 3H), 1.35 (t, 3H)

Step 4: l-ethyl-4-methyl-6-nitro-4H-3.1-benzoxazin-2-one

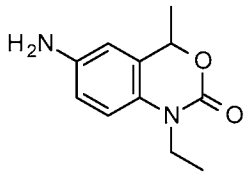


[0179] l-Ethyl-4-methyl-4-H-3,l-benzoxazin-2-one (0.140 g, 0.732 mmol) was dissolved in trifluoroacetic acid (2 mL) and sodium nitrate (0.093 g, 1.01 mmol) was added. The reaction mixture was heated to 60 °C and stirred for lh. The reaction mixture was cooled down to room temperature and poured into ice/water. The white solid was filtered, washed

with water and collected to give l-ethyl-4-methyl-6-nitro-4H-3,l-benzoxazin-2-one (0.138 g, 80%).

[0180] LCMS: 0.83 min; ES+ 237 (M+H+); IH NMR (CHLOROFORM-d, 400MHz): δ (ppm) 8.27 (d, IH), 8.05 (s, IH), 7.09 (d, IH), 5.44 (q, IH), 3.97-4.11 (m, 2H), 1.77 (d, 3H), 1.38 (t, 3H)

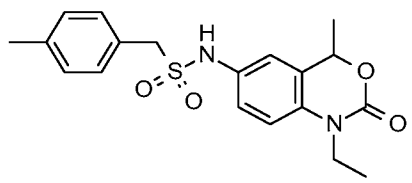
Step 5: 6-amino-l-ethyl-4-methyl-4H-3.1-benzoxazin-2-one



[0181] To a solution of l-ethyl-4-methyl-6-nitro-4H-3,l-benzoxazin-2-one (0. 138 g, 0.584 mmol) in EtOH/water (1/1, 5 mL) was added iron (0.163 g, 2.92 mmol) and ammonium chloride (0.313 g, 5.84 mmol). The reaction mixture was heated to 80 °C, stirred for 1 h and cooled down to room temperature. It was then with water and ethyl acetate, filtered over celite, the filtrate was extracted with ethyl acetate (2x50ml). The combined organic layers were washed with brine, dried and concentrated to give the desired product (0.140 g, 100%) as a brown oil.

[0182] LCMS: 0.29 min; ES+ 207 (M+H+); ^{1}H NMR (CHLOROFORM-d, 400MHz): δ (ppm) 6.78 (d, IH), 6.65 (d, IH), 6.47 (s, IH), 5.25 (q, IH), 3.91 (q, 2H), 3.39-3.75 (brs, 2H), 1.62 (d, 3H), 1.30 (t, 3H)

Step 6: N-(l-ethyl-4-methyl-2-oxo-4H-3.1-benzoxazin-6-yl)-l-(p-tolyl)methanesulfonamide CQ4

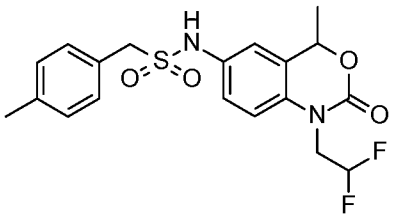


[0183] To a solution of 6-Amino-l-ethyl-4-methyl-4H-3,l-benzoxazin-2-one (0. 140 g, 0.678 mmol) in ethyl acetate (5 mL) was added *N N*-diisopropylethylamine (0.175 g, 1.35 mmol) and p-tolylmethanesulfonyl chloride (0.180 g, 0.882 mmol). The reaction mixture was

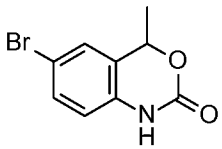
stirred for 15 min, concentrated and purified by flash chromatography to give the desired product as a pale solid (54 mg, 21%).

[0184] LCMS: 0.92 min; ES+ 375 (M+H+); ^{1}H NMR (CHLOROFORM-d, 400MHz): δ (ppm) 7.12-7.20 (m, 4H), 7.09 (d, IH), 6.92 (d,lH), 6.89 (s, IH), 6.65 (s, IH), 5.29 (q, lH), 4.28 (s, 2H), 3.95 (q, 2H), 2.34 (s, 3H), 1.63 (d, 3H), 1.34 (t, 3H)

Preparation of N-[1-(2.2-difluoroethyl)-4-methyl-2-oxo-4H-3 .1-benzoxazin-6-vH-1-(p-tolvDmethanesulfonamide (Compound CQ32)



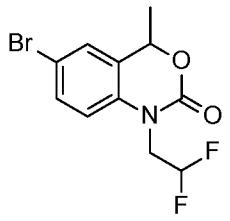
Step 1: 6-bromo-4-methyl-1 .4-dihvdro-3. 1-benzoxazin-2-one



[0185] 4-methyl-l ,4-dihydro-3, l-benzoxazin-2-one (13.7 g, 84.0 mmol) was dissolved in dimethylformamide (340 mL) and cooled to 0 °C. N-Bromosuccinimide (19.6 g, 109 mmol) was added in portions at 0 °C. Reaction was warmed up to room temperature and stirred for 15 h. The reaction mixture was poured on water/ice and a suspension was formed. It was filtered and washed with water, and dried to give the crude 6-bromo-4-methyl-l ,4-dihydro-3,l -benzoxazin-2-one (18.7 g, 92%) as a beige powder.

[0186] LCMS: 0.79 min; ES+ 243 (M+H+); IH NMR (400 MHz, CHLOROFORM-d) d ppm 1.68 - (d, 3 H), 5.45 (q, 1 H), 6.72 (d, 1 H), 7.22 (s, 1 H), 7.35 (d, 1 H), 8.52 (brs, 1 H).

Step 2: 6-bromo-l -(2.2-difluoroethyl)-4-methyl-4H-3.1 -benzoxazin-2-one



[0187] 6-Bromo-4-methyl-4H-3,l-benzoxazin-2-one (250 mg, 1.033 mmol) was dissolved in N,N-dimethylformamide (5.2 mL) under argon and cooled to 0 °C. Sodium hydride (55 mass% in oil, 54 mg, 1.24 mmol) was added and it was stirred for 15min. Then 2,2-difiuoroethyl triflate (0.316 g, 1.45 mmol) was added dropwise and the reaction mixture was warmed up to rt and stirred for 2.5 h. The reaction mixture was poured into water/ice and extracted with ethyl acetate twice. The combined organic layers were washed with aqueous LiCl solution (10%) twice and once with brine, then dried over Na2SC>4 and concentrated to give the crude (325mg) which was purified by flash chromatography to give 6-bromo-l-(2,2-difluoroethyl)-4-methyl-4H-3,l-benzoxazin-2-one (183 mg, 58%) as a brown oil.

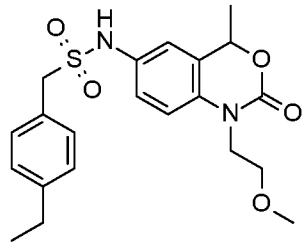
[0188] LCMS: 0.94 min; ES+ 306/308 ($M+H^+$); 1H NMR (400 MHz, CHLOROFORM-d) δ ppm 1.65 1.70 (t, 3 H), 4.12 (m, 2 H), 5.31 (q, 1 H), 5.95-6-28 (m, 1H), 6.90 (d, 1 H) 7.21 (s, 1 H) 7.38 (d, 1 H).

Step 3: N-r 1-(2.2-difluoroethyl)-4-methyl-2-oxo-4H-3. 1-benzoxazin-6-vH -1-(p-tolvDmethanesulfonamide (Compound CQ32)

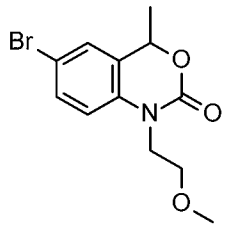
[0189] 6-bromo-l-(2,2-difluoroethyl)-4-methyl-4H-3,l-benzoxazin-2-one (0.100 g, 0.33 mmol), 4-methylbenzylsulfonamide (0.060 g, 0.314 mmol) and potassium carbonate (fine powder) (0.087 g, 0.63 mmol) were suspended in toluene (2.1 mL) and purged with argon for 10 min. tBuBrettPhos Pd G3 (134 mg, 0.0156 mmol) was added and the reaction mixture was heated to 100 °C for 3 h. The reaction mixture was cooled to room temperature and diluted with ethyl acetate and water. The aqueous layer was extracted with ethyl acetate, the organic layers were combined, dried over Na2S04 and the solvent was evaporated to give the crude (210mg) as a brown foam which was purified by flash chromatography to give N-[l-(2,2-difluoroethyl)-4-methyl-2-oxo-4H-3,l-benzoxazin-6-yl]-l-(p-tolyl)methanesulfonamide (120 mg, 1.44 mmol, 66%) as a beige foam.

[0190] LCMS: 0.91 min; ES+ 411 (M+H+); 1H NMR (400 MHz, CHLOROFORM-d) δ ppm l.56 - 1.61 (m, 3 H) 2.26 - 2.30 (m, 3 H) 4.11 - 4.21 (m, 2 H) 4.21 - 4.24 (m, 2 H) 5.22 - 5.32 (m, 1 H) 5.96 - 6.32 (m, 2 H) 6.82 - 6.86 (m, 1 H) 6.92 - 6.99 (m, 2 H) 7.07 - 7.13 (m, 4 H) 7.18 - 7.21 (m, 1 H).

Preparation of l-(4-ethylphenyl)-N -**ri** -(2-methoxyethyl)-4-methyl-2-oxo-4H-3.1-benzoxazin-6-vHmethanesulfonamide (Compound CQ24)



Step 1: 6-bromo-l-(2-methoxyethyl)-4-methyl-4H-3.1-benzoxazin-2-one



[0191] 6-bromo-4-methyl-l,4-dihydro-3,l-benzoxazin-2-one (1 g, 4.13 mmol) was dissolved in dimethylformamide (17 mL) and potassium carbonate (1.44 g, 10.32 mmol) was added. l-bromo-2-methoxy-ethane (0.613 mL, 6.19 mmol) was added dropwise and the reaction mixture was heated to 50°C and stirred on. l-Bromo-2-methoxy-ethane (0.5 eq, 0.205 mL) were added and it was stirred for further 4 h. Water and ethyl acetate were added and it was extracted with ethyl acetate. The organic layers were combined, washed twice with a 5% LiCl-solution and once with brine, dried over Na2S04 and the solvent was evaporated to give the crude (1. 29 g) as a yellow oily solid which was purified by combiflash to give 6-bromo-l-(2-methoxyethyl)-4-methyl-4H-3,l-benzoxazin-2-one (1.02 g, 83%) as a colourless foam.

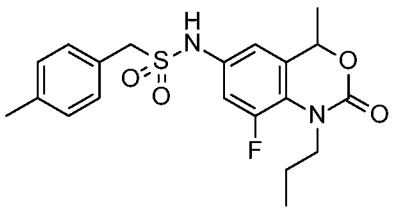
[0192] LCMS: 0.92 min; ES+ 302 ($M+H^+$); 1H NMR (400 MHz, CHLOROFORM-d) d ppm 1.65 (d, 3 H), 3.32 (s, 3 H), 3.68 (dd, 2 H), 4.01 (m, 2 H), 5.33 (q, 1 H), 7.06 (d, 1 H), 7.21 (s, 1 H), 7.43 (dd, 1 H).

Step 2: 1-(4-ethylphenyl)-N-[1-(2-methoxyethyl)-4-methyl-2-oxo-4H-3. 1-benzoxazin-6-yllmethanesulfonamide (Compound CQ24)

[0193] 6-bromo-l-(2-methoxyethyl)-4-methyl-4H-3,l-benzoxazin-2-one (0.1 g, 0.33 mmol), (4-ethylphenyl)methanesulfonamide (0.063 g, 0.3165 mmol) and potassium carbonate (0.092 g, 0.66 mmol) were suspend in toluene (4 mL) and it was purged with argon for 15min. tBuBrettPhos Pd G3 (0.015 g, 0.016 mmol) was added and the mixture was heated up to 100°C for 2 h at this temperature. Reaction mixture was cooled down to room temperature and mixture diluted with ethyl acetate and water. The mixture was extracted three times with ethyl acetate. Afterwards the organic layers were combined, dried over Na2SC>4, filtered and evaporated to give 153 mg of a brownish liquid. The mixture was purified by flash chromatography 5% cyclohexane / ethyl acetate 45 % to give l-(4-ethylphenyl)-N-[l-(2-methoxyethyl)-4-methyl-2-oxo-4H-3,l-benzoxazin-6-yl]methanesulfonamide (104 mg, 45 %) as a yellowish solid.

[0194] LCMS: 0.94 min; ES+ 419 (M+H+); 1H NMR (400 MHz, CHLOROFORM-d) δ ppm 1.21 (t, 3 H), 1.62 (d, 3 H), 2.62 (m, 2 H), 3.36 (s, 3 H), 3.65 - 3.75 (m, 2 H), 3.99 - 4.15 (m, 2 H) 4.28 (s, 2 H), 5.31 (q, 1 H), 6.60 (brs, 1 H), 6.91 (s, 1 H), 7.05 (dd, 1 H), 7.11 (d, 1 H), 7.15 - 7.23 (m, 4 H).

Preparation of N-(8-fluoro-4-methyl-2-oxo- 1-propyl-4H-3 .1-benzoxazin-6-yl)- 1-(p-tolvDmethanesulfonamide (Compound CO12)



Step 1: l-r3-fluoro-2-(propylamino)phenvHethanone

[0195] A solution of l-(2,3-difluorophenyl)ethanone (7.81g, 50 mmol), K_2C0_3 (10.4g, 75 mmol) and propylamine (12.3 mL. 150 mmol) in DMF (55 mL) was heated at 50 °C for 42 h. The reaction mixture was then poured into ice water and extracted 3 times with a 1/1 mixture of ethyl acetate and cyclohexane. The combined organic layer were washed with brine and

concentrated under vacuo to give l-[3-fluoro-2-(propylamino)phenyl]ethanone (9.38g, 96%) as a pale green oil.

LCMS: 1.09 min; ES+ 196 ($M+H^+$); ¾NMR (400 MHz, CHLOROFORM-d) 8.78 (s, 1H), 7.52 (d, 1H), 7.08 (dd, 1 H), 6.51 (m, 1H), 3.42 (m, 2 H), 2.52 (s, 3H), 1.61 (m, 2H), 0.94 (t, 3H).

Step 2: 8-fluoro-4-methyl-l-propyl-4H-3.1-benzoxazin-2-one

[0196] To a solution of l-[3-fluoro-2-(propylamino)phenyl]ethanone (9.35 g, 47 mmol) in dioxane (95 mL) was added K2CO3 (7.74g, 57.5 mmol) and ethyl chloroformate (5.67 mL, 57.5 mmol). The suspension was stirred at 85 °C for 5 h, cooled down to room temperature and filtered. The solvent were evaporated and the crude oil was purified by flash chromatography to give ethyl N-(2-acetyl-6-fluoro-phenyl)-N-propyl-carbamate (11.28g, 88%) as an oil.

[0197] To a solution of ethyl N-(2-acetyl-6-fluoro-phenyl)-N-propyl-carbamate (4.01 g, 15.0 mmol) in methanol (38 mL was added portionwise sodium borohydride (567 mg, 15.0 mmol) at 0 °C. The solution was stirred for 30 min and then quenched with a saturated solution of NH4CI. The solution was extracted two times with ethyl acetate and the organic layers were washed with water, brine, dried over Na2SC>4, filtered and evaporated to give ethyl N-[2-fluoro-6-(l-hydroxyethyl)phenyl]-N-propyl-carbamate (4.06 g, quant) as an oil which was used directly in the next step.

[0198] To a solution of ethyl N-[2-fluoro-6-(l-hydroxyethyl)phenyl]-N-propyl-carbamate (4.04g, 15.0 mmol) in THF (75 mL) under Ar cooled at -20 °C was added NaH (55% in mineral oil, 654 mg, 15.0 mmol) and the solution was stirred for 15 min at 0 °C. The reaction mixture was then quenched with iPrOH (1 mL) followed by a saturated solution of NH_4C1. The solution was extracted two times with ethyl acetate and the organic layers were washed with water, brine, dried over Na2SC>4, filtered and evaporated. The crude compound was crystallized from pentane to give 8-fluoro-4-methyl-l-propyl-4H-3,l-benzoxazin-2-one (2.57 g, 77%).

[0199] LCMS: 0.96 min; ES+ 224 ($M+H^+$); ^1H NMR (400 MHz, CHLOROFORM-d) 7.10-7.15 (m, 2 H), 6.91 (m, 1H), 5.25 (q, 1H), 3.98 (m, 2 H), 1.75 (m, 2H), 1.66 (d, 3H), 0.94 (t, 3H).

Step 3: 6-Bromo-8-fluoro-4-methyl-l-propyl-4H-3.1-benzoxazin-2-one

[0200] To a solution of 8-fluoro-4-methyl-l-propyl-4H-3,l-benzoxazin-2-one (1.10 g, 4.93 mmol) in trifluoroacetic acid (11 mL) was added at room temperature N-bromosuccinimide (1.33g. 7.39 mmol) and the reaction mixture was heated to 60°C for 16 h. The reaction mixture was then cooled down to room temperature and poured into a cold aqueous solution of NaOH (2 M) and sodium thiosulfate was added. The solution was extracted two times with ethyl acetate and the organic layers were washed with water, brine, dried over Na2S04, filtered and evaporated. The crude compound was crystallized from dichloromethane and petrolether to give 6-Bromo-8-fluoro-4-methyl-l-propyl-4H-3,l-benzoxazin-2-one (780 mg, 52%).

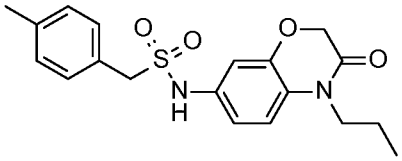
[0201] LCMS: 1.08 min; ES+ 302/304 (M+H+); ^{1}H NMR (400 MHz, CHLOROFORM-d) 7.22 (s, 1 H), 7.07 (s, 1H), 5.21 (q, 1H), 3.96 (m, 2 H), 1.71 (m, 2H), 1.65 (d, 3H), 0.93 (t, 3H).

Step 4: N-(8-fluoro-4-methyl-2-oxo- 1-propyl-4H-3. 1-benzoxazin-6-yl)- 1-(p-tolvDmethanesulfonamide (Compound CO12)

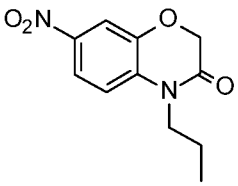
[0202] 6-Bromo-8-fluoro-4-methyl-l-propyl-4H-3,l-benzoxazin-2-one (150 mg, 0.495 mmol), p-tolylmethanesulfonamide (84 mg, 0.450 mmol) and potassium carbonate (127 mg, 0.900 mmol) were suspended in toluene (2.25 mL) and purged with argon for 15min. tBuBrettPhos Pd G3 was added and the mixture was heated up to 100°C for overnight. A mixture of ice/water was added and product was extracted with ethyl acetate. Organic phase was isolated and dried on magnesium sulfate then concentrated on vaccumn. The crude product was purified by combifiash to giveN-(8-fluoro-4-methyl-2-oxo-l-propyl-4H-3,l-benzoxazin-6-yl)-l-(p-tolyl)methanesulfonamide (80 mg, 43.7% Yield) as a beige cristal. LCMS: 1.01 min; ES+ 407 (M+H+); ^{1}H NMR (CHLOROFORM-d, 400MHz): δ (ppm) 7.18 (m, 4 H), 6.78 - 6.90 (d, 1 H), 6.60 (s, 1 H), 6.28 (s, 1 H), 5.19 (q, 1 H), 4.33 (s, 2 H), 3.81 - 4.09 (m, 2 H), 2.36 (s, 3 H), 1.66 - 1.83 (m, 2 H), 1.63 (d, 3 H), 0.95 (t, 3 H).

[0203] Compounds CQ5-CQ39 (see Table 1) were prepared using a similar method to the one described above.

Preparation of N-(3-oxo-4-propyl-1.4-benzoxazin-7-yl)-l -(p-tolyl)methanesulfonamide (CO40)

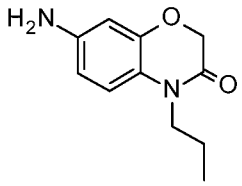


Step 1: 7-nitro-4-propyl-1,4-benzoxazin-3-one



[0204] 7-Nitro-4H-l,4-benzoxazin-3-one (5.00 g) was dissolved in DMF (37 mL). Potassium carbonate (10.8 g) was added followed by 1-bromopropane (9.50 g, 7.03 mL) dropwise. The reaction mixture was stirred overnight and ice-water (200 mL) was added. The yellow suspension was filtrated, the filter cake was washed with water and dried to give 7-nitro-4-propyl-l ,4-benzoxazin-3-one as a yellow solid (6.01 g, 98%); ¾ NMR (CHLOROFORM-d, 400MHz): δ (ppm) 7.96 (d, IH), 7.84 (s, IH), 7.04 (d, IH), 4.20 (s, 2H), 3.92 (t, 2H), 1.69 (m, 2H), 0.95 (t, 3H).

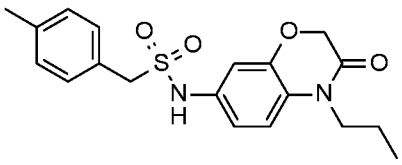
Step 2: 7-amino-4-propyl-1.4-benzoxazin-3-one



[0205] Pd-C (5%, 0.770 g) was suspended in EtOH (10 mL). A solution of 7-nitro-4-propyl-l,4-benzoxazin-3-one (5.70 g) in EtOH (100 mL) was added. The flask was purged with Ar and the reaction mixture was stirred at room temperature under H_2 atmosphere overnight. The flask was purged with Ar and the suspension was filtrated over Celite®, and the filter cake was washed with EtOH. The filtrate was evaporated to give 7-amino-4-propyl-l ,4-benzoxazin-3-one as a pale beige solid (4.8g, 96%) .

LCMS: 0.52 min; ES+ 207 (M+H+); ¾NMR (CHLOROFORM-d, 400MHz): δ (ppm) δ (ppm) 6.75 (d, 1H), 6.35 (m, 2H), 4.50 (s, 2H), 3.82 (t, 2H), 3.52 (brs, 2H), 1.62 (m, 2H), 0.95 (t, 3H).

Step 3: N-(3-oxo-4-propyl-1.4-benzoxazin-7-yl)-l-(p-tolyl)methanesulfonamide (CQ4

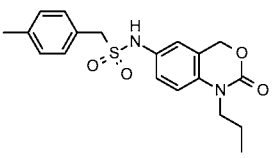
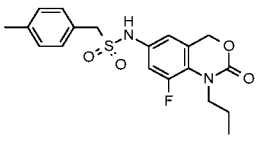


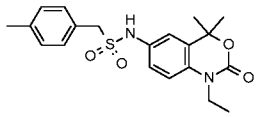
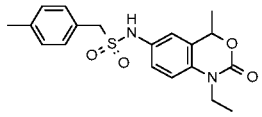
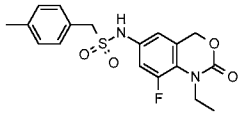
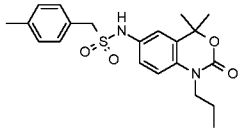
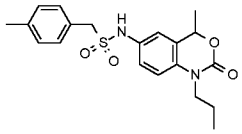
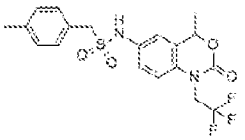
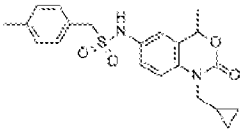
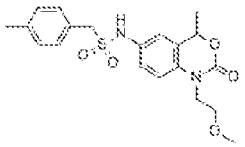
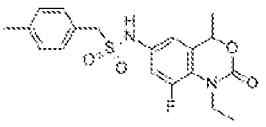
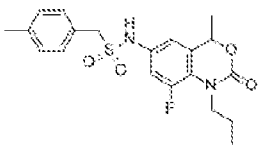
[0206] 7-Amino-4-propyl-l,4-benzoxazin-3-one (0.040 g) was dissolved in ethyl acetate (4 niL) and the solution was cooled on an ice bath. Diisopropylethylamine (0.063 g, 0.085 mL) was added followed by p-tolylmethanesulfonyl chloride (0.052 g). The reaction mixture was stirred 1 h at room temperature, water was added and the aqueous layer was extracted with ethyl acetate three times. The combined organic layers were washed with aqueous HCl (IN, 10 mL), saturated NaHCCb, brine, dried with Na_2SO_4 and concentrated. The crude product was purified by flash chromatography to giveN-(3-oxo-4-propyl-l,4-benzoxazin-7-yl)-l-(p-tolyl)methanesulfonamide (54 mg, 74%) as a white solid.

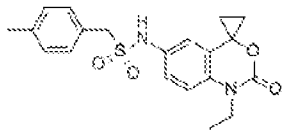
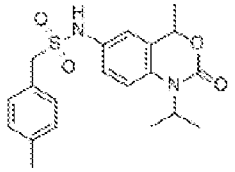
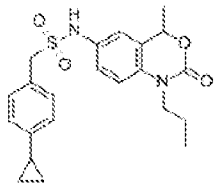
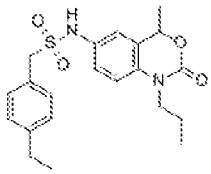
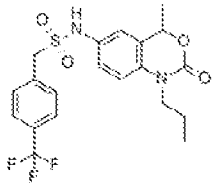
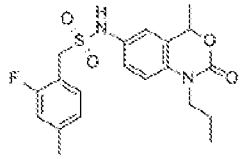
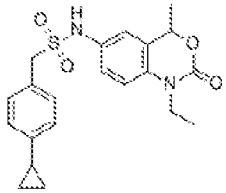
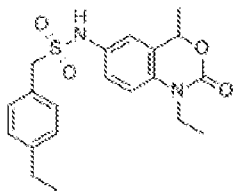
[0207] LCMS: 0.96 min; ES+ 375 (M+H+); ^1H NMR (CHLOROFORM-d, 400MHz): δ (ppm) δ (ppm) 7.20-7.30 (4H, m). 6.92 (d, 1H), 6.83 (m, 2H), 6.59 (m, 2H), 4.59 (s, 2H), 4.25 (s, 2H), 3.82 (t, 2H), 3.31 (s, 3H), 1.62 (m, 2H), 0.97 (t, 3H).

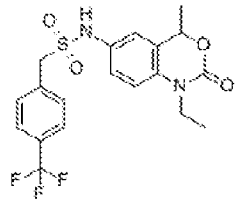
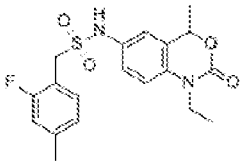
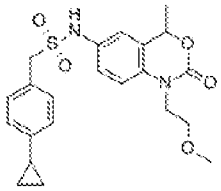
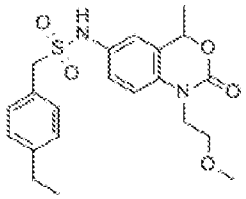
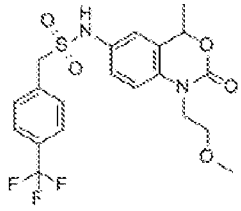
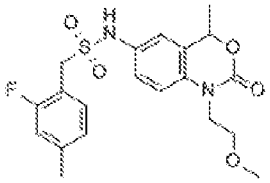
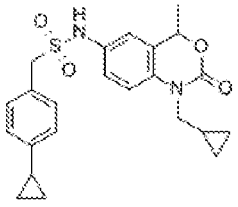
[0208] Compounds CQ41-CQ60 were prepared using a method similar to the one set forth above.

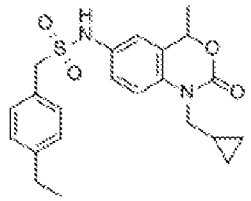
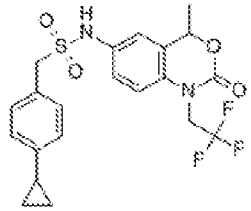
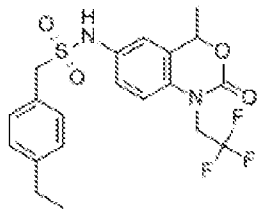
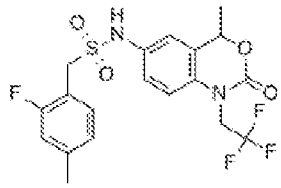
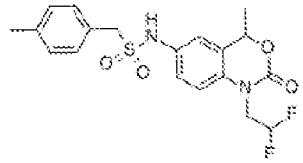
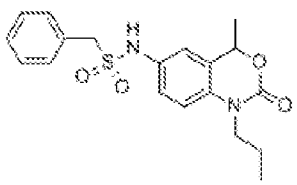
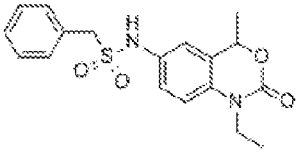
Table 1. Synthesized compounds.

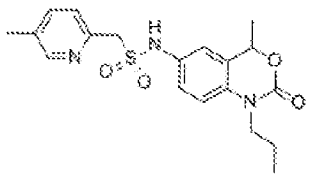
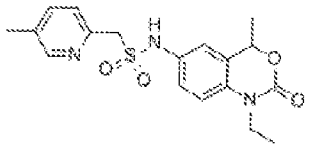
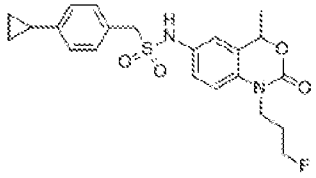
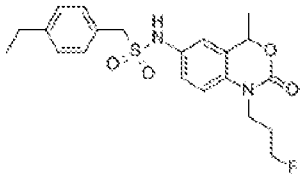
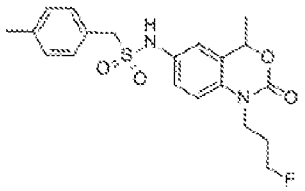
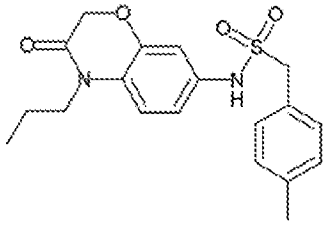
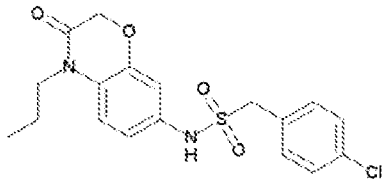
Structure	Compound	RT	Mass
	CQ1	0.96	375
	CQ2	0.98	393

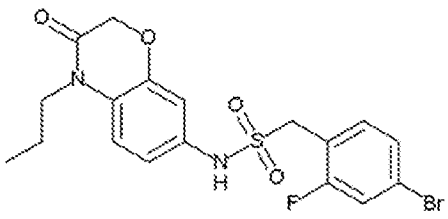
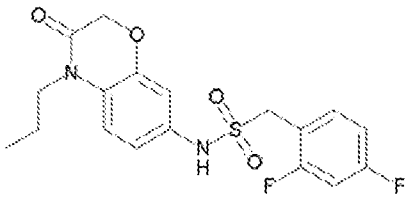
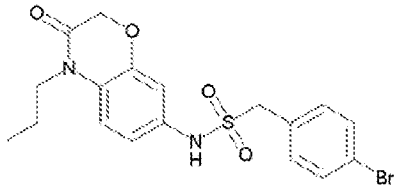
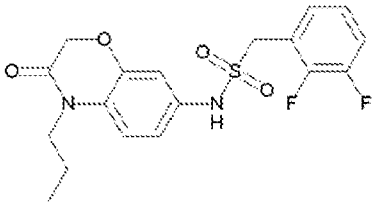
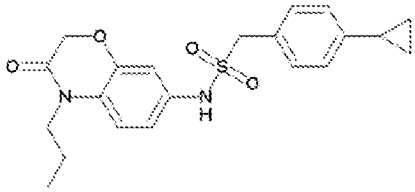
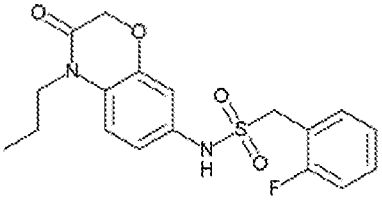
Structure	Compound	RT	Mass
	CQ3	0.93	389
	CQ4	0.92	375
	CQ5	0.94	379
	CQ6	0.98	403
	CQ7	0.96	389
	CQ8	0.98	429
	CQ9	0.88	406
	CQ10	0.90	406
	CQ11	0.97	393
	CQ12	1,01	407

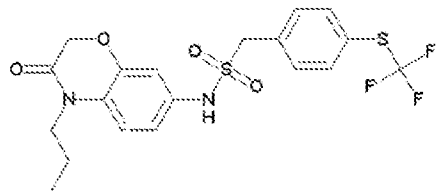
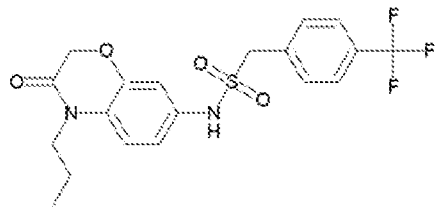
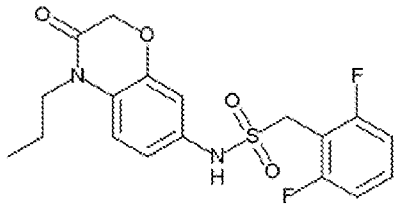
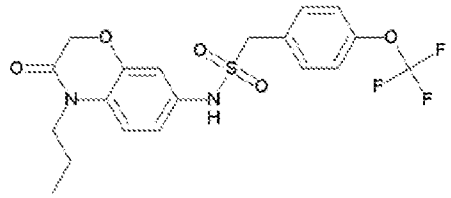
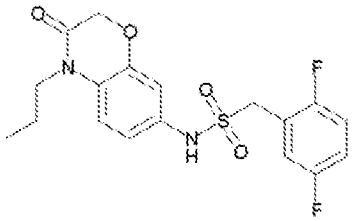
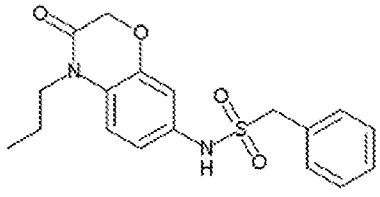
Structure	Compound	RT	Mass
	CQ13	0.95	387
	CQ14	0.95	389
	CQ15	0.99	416
	CQ16	1.00	404
	CQ17	0.98	443
	CQ18	0.98	407
	CQ19	0.97	401
	CQ20	0.95	389

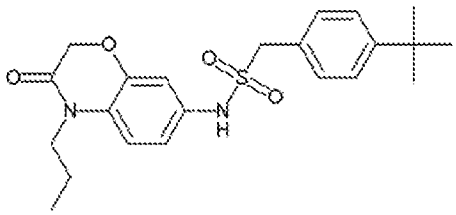
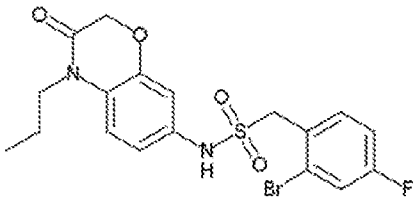
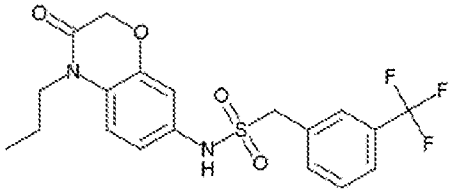
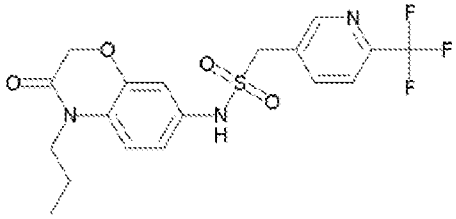
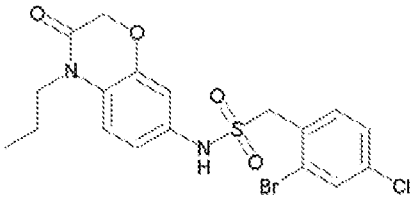
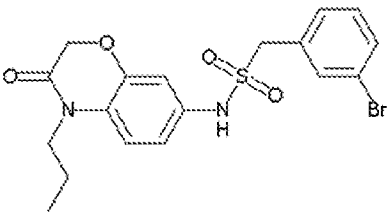
Structure	Compound	RT	Mass
	CQ21	0.94	429
	CQ22	0.93	393
	CQ23	0.94	431
	CQ24	0.94	419
	CQ25	0.94	459
	CQ26	0.91	421
	CQ27	1,03	427

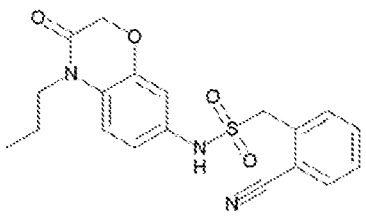
Structure	Compound	RT	Mass
	CQ28	1.01	415
	CQ29	0.99	455
	CQ30	1.00	443
	CQ31	0.97	447
	CQ32	0.91	411
	CQ33	0.91	375
	CQ34	0.86	361

Structure	Compound	RT	Mass
	CQ35	0.84	391
	CQ36	0.75	376
	CQ37	0,95	433
	CQ38	0.96	421
	CQ39	0.91	407
	CQ40		
	CQ41		

Structure	Compound	RT	Mass
	CQ42		
	CQ43		
	CQ44		
	CQ45		
	CQ46		
	CQ47		

Structure	Compound	RT	Mass
	CQ48		
	CQ49		
	CQ50		
	CQ51		
	CQ52		
	CQ53		

Structure	Compound	RT	Mass
	CQ54		
	CQ55		
	CQ56		
	CQ57		
	CQ58		
	CQ59		

Structure	Compound	RT	Mass
	CQ60		

Example 2: *In Vitro* Activity

[0209] Phosphatase activity assays using recombinant Arabidopsis hexahistidine tagged PYR1 or PYL2 receptors, and the GST-tagged type 2C protein phosphatase HAB1. Recombinant PYR1 and PYL2 receptor proteins were prepared as previously described (Okamoto *et al.* 2013). Briefly, receptors cloned in the vector pET28 were expressed in BL21[DE3]pLysS *E. coli* host cells at 18°C overnight, and subsequently purified from sonicated lysates using Ni-NTA agarose (Qiagen, USA), according to the manufacturer's instructions. Recombinant GST-HAB1 was expressed and purified as described previously (Park *et al,* 2009). Enzymatic assays were carried out as follows: purified proteins were pre-incubated at 22°C for 30 minutes in 160 μï assay buffer containing 100 mM Tris-HCl -pH7.9, lOOmM NaCl, 3 μg bovine serum albumin, and 0.1% 2-mercaptoethanol, 1 mM MnC^, and the different compounds of the present invention or carrier-only solvent controls. Reactions were started by adding 40 μL of a reaction solution containing 25 mM 4-nitrophenyl phosphate dissolved in assay buffer after which absorbance measurements were immediately collected at 405 nm on a Tecan plate reader. Reactions contained 100 nM GST-HAB1 and 200 nM 6x-His-PYRl or 6x-His-PYL2. For $IC5_0$ calculations the specified compounds were tested in PP2C assays in concentrations ranging from 50μM to 4nM. The dose response data was fitted to a log (inhibitor) vs response-(variable slope) model using non-linear regression to infer the $IC5_0$ values, using Graph Pad Prism 6.0. Assays were conducted in triplicate. The data reported are the means of the three technical replicates.

Table 2. Inhibition of PYR1-HAB1 and PYL2-HAB 1.

Compound	PYR1 IC50 (nM)	PYL2 IC50 (nM)
Quinabactin	104	262
CQ1	45	156
CQ3	148	347

Compound	PYRl IC50 (nM)	PYL2 IC50 (nM)
CQ4	33	29
CQ6	140	145
CQ5	637	2322
CQ2	537	1161
CQ7	222	79
CQ8	179	96
CQ9	142	79
CQ10	366	132
CQ11	606	144
CQ12	290	101
CQ14	514	152
CQ15	185	157
CQ16	141	47
CQ17	494	234
CQ18	82	74
CQ19	126	163
CQ20	70	46
CQ21	840	335
CQ22	38	46
CQ23	306	243
CQ24	211	69
CQ25	953	357
CQ26	112	98
CQ27	342	202
CQ28	446	125
CQ29	244	257
CQ30	242	94
CQ31	77	93
CQ32	248	104
CQ33	195	97
CQ34	197	153
CQ35	27	49

Compound	PYR1 IC50 (nM)	PYL2 IC50 (nM)
CQ36	20	58

Table 3: PP2C Activity on PYLl, PYL2, PYL3 and PYL5 (% activity compared to DMSO Control)

Compound	PYL1	PYL2	PYL3	PYL5
	200 nM	200 nM	500 nM	500 nM
DMSO	100	100	100	100
Quinabactin	23	44	73	21
CQ40	65.59	88.33	87	72.5
CQ41	53.67	90.74	95.8	69.3
CQ42	74.29	88.91	93.4	73.8
CQ43	68.59	91.48	89.9	72.6
CQ44	70.66	89.59	93.3	80.9
CQ45	53.41	92.15	94.3	86.2
CQ46	84.63	94.83	93.9	85
CQ47	70.88	96.27	94.4	89.8
CQ48	77.83	91.7	92.4	78.5
CQ49	84.81	94.46	100.2	89.3
CQ50	85.41	93.32	92.4	88
CQ51	86.41	90.31	93.1	80.1
CQ52	89.1	94.79	91.1	89.7
CQ53	92.46	93.73	91.3	97.4
CQ54	93.7	94.6	95	95.1
CQ55	94.31	95.36	93.4	95.5
CQ56	97.22	97.3	95	97.5
CQ57	93.73	95.98	95.1	99
CQ58	95.24	95.05	90.7	92.6
CQ59	88.6	99.26	100	97
CQ60	91.18	95.81	90.5	90.8

Example 3: *In Vivo* Activity

Germination inhibition assay

[0210] To examine if the compounds of the present invention possess bioactivity *in vivo,* we examined their effects *on Arabidopsis* seed germination. Surface sterilized seeds were plated in 0.1% top agar on to 0.7% agar petri plates containing ½ x strength Murashige and Skoog salts and stratified for 4 days at 4 °C, after which they were transferred to a light-tight germination chamber at 22 °C and 99% humidity. Germination was scored 3 days post imbibition by radical emergence.

Table 4. Percent germination of Arabidopsis seeds.

Compound	% germination at 1uM
Quinabactin	85
CQ1	6
ABA	3
DMSO	100

Plant water use in soybean

[0211] Compounds were tested for their effect on reducing plant water use as follows. Each compound was dissolved in a blank emulsifiable concentrate (EC) formulation that was then diluted to the desired concentration with water containing additional surfactant (EXTRAVON lg/20L). The compounds were applied by foliar spray to 12 day old soybean plants (variety S20-G7) grown in controlled environment plant growth chambers. Plant water use during the day was assessed by repeated weighing of the pots in which the plants were grown before and after application of the compounds at the indicated times (expressed in days after application (DAA)). The water use data before application was used to correct any differences in water use arising due to non-treatment effects (e.g. due to differences in plant size). The untransformed water use values were subjected to an analysis of covariance, fitting the effect of treatment and using the baseline water use 1 day before application as a covariate.

[0212] The results are expressed compared to negative control treatment (diluted EC formulation without active ingredient but with EXTRAVON lg/20L).

[0213] Application of the chemicals (0 DAA) takes place approximately between 08:00 and 09:30 a.m. WU is measured within day time (chamber light is on 06:00 to 20:00) at these timepoints: 0 DAA a.m. (10:30-12:50), 0 DAA p.m. (14:00-19:50), 1 DAA a.m. (7:30-12:50), 1 DAA p.m. (14:00-19:50), 2 DAA a.m. (07:30-12:50) and 2 DAA p.m. (14:00-19:50). The culmulative total WU 0-2 DAA is calculated by summing the WU data mentioned above.

[0214] The percent of increase or decrease of water use (WU) during day time compared to a negative control treatment (blank formulation) are shown. 0 = identical to negative control; -8.5 = 8.5% decrease in water use compared to negative control treatment. Average WU values of 6 pots (each with three plants) per treatment are shown.

Table 5. Water use data for soybean plants after administration of the indicated compounds at 500 μM.

Compounds	0 DAA AM	0DAA PM	1DAA AM	1DAA PM	2 DAA AM	2 DAA PM	Total 0 to 2 DAA
Control	0	0	0	0	0	0	0
quinabactin	-41.8	-39.8	-19.3	-9.9	-1.7	1.8	-9.5
CQ1	-51.4	-43.9	-35	-24.5	-19.4	-28.5	-46.7

Table 6. Separate experiment: Water use data for soybean plants after administration of the indicated compounds at 500 μM

Compounds	0 DAA AM	0DAA PM	1DAA AM	1DAA PM	2 DAA AM	2 DAA PM	Total 0 to 2 DAA
Control	0	0	0	0	0	0	0
quinabactin	-45.1	-42.-2	-20.2	-10.8	-3	-2.2	-17
CQ40	-10	-4	-5	-4	-6	-4	-5

The data show that this compound is less active than quinabactin at reducing transpiration in soybean.

Table 7. Water use data for soybean plants after administration of the indicated compounds at 125 μM.

Compounds	0 DAA AM	0DAA PM	1DAA AM	1DAA PM	2 DAA AM	2 DAA PM	Total 0 to 2 DAA
Control	0	0	0	0	0	0	0
Quinabactin (500 μM)	-41.8	-39.8	-19.3	-9.9	-1.7	1.8	-9.5
CQ7	-50	-51.4	-48.5	-41.2	-32.9	-30.7	-41.2
CQ12	-52.8	-57.2	-58.8	-54.2	-52.5	-47.4	-53.7
CQ16	-52.8	-57.2	-58.8	-54.2	-52.5	-47.4	-53.7

Plant water use in corn

[0215] Compounds were tested for their effect on reducing plant water use as follows. The compounds were applied by foliar spray to 12 day old corn plants (variety NK OCTET)

grown in controlled environment plant growth chambers. All compounds were applied using an emulsifiable concentrate (EC) formulation that was diluted to the desired concentrations with water containing 0.4% of the adjuvant rape seed methyl ester. Plant water use during the day was assessed by repeated weighing of the pots in which the plants were grown before and after application of the compounds at the indicated times (expressed in days after application (DAA)). The water use data before application was used to correct any differences in water use arising due to non-treatment effects (e.g. due to differences in plant size). The untransformed water use values were subjected to an analysis of covariance, fitting the effect of treatment and using the baseline water use 1 day before application as a covariate.

[0216] Application of the chemicals (0 DAA) takes place approximately between 08:00 and 09:30 a.m. WU is measured within day time (chamber light is on 06:00 to 20:00) at these timepoints: 0 DAA a.m. (10:30-12:50), 0 DAA p.m. (14:00-19:50), 1 DAA a.m. (07:30-12:50), 1 DAA p.m. (14:00-19:50), 2 DAA a.m. (07:30-12:50) and 2 DAA p.m. (14:00-19:50). The culmulative total WU (0-2.5 DAA) is calculated by summing the WU data mentioned above.

[0217] The percent of increase or decrease of water use (WU) during day time compared to a negative control treatment (blank formulation) are shown. 0 = identical to negative control; -8.5 = 8.5% decrease in water use compared to negative control treatment. Average WU values of 6 pots (each with three plants) per treatment are shown.

Table 8. Water use data for com plants after administration of the indicated compounds at 500 μM.

Compounds	0 DAA AM	0DAA PM	1DAA AM	1DAA PM	2 DAA AM	2 DAA PM	Total 0 to 2 DAA
Control	0	0	0	0	0	0	0
quinabactin	-19.9	-15.1	-10.9	-5.3	-8.9	-8.2	-10.4
CQ1	-28.6	-28.4	-13.6	-6.3	-9.6	-9.3	-13.6
CQ4	-39.4	-36.2	-12.1	-4.7	-7.2	-5.9	-13.2

Table 9. Water use data for corn plants after administration of the indicated compounds at 500 μM.

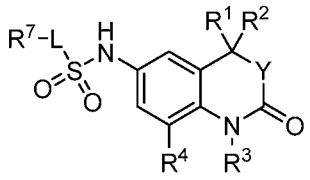
Compounds	0 DAA AM	0DAA PM	1DAA AM	1DAA PM	2 DAA AM	2 DAA PM	Total 0 to 2 DAA
Control	0	0	0	0	0	0	0
quinabactin	-19.9	-15.1	-10.9	-5.3	-8.9	-8.2	-10.4
CQ2	-28.3	-33.4	-15.9	-4.8	-6.8	-2.6	-12.9
CQ3	-4.6	0.7	1.3	-1.7	-0.3	-0.4	-0.6
CQ6	-9.8	2.6	-1.6	1.1	-3.4	1.7	-1.3
CQ7	-47.3	-51.6	-17.8	-7	-7	-5.2	-19.2
CQ8	-15.1	-16.6	-13.3	-8.4	-7.7	-3.7	-10.1
CQ9	-32.4	-38.8	-13.7	-4.2	-5.8	-1.9	-13
CQ10	-29.8	-31.9	-17	-4.3	-8.1	1.1	-12.7
CQ12	-47.4	-46.7	-16.6	-0.1	-1.9	2.7	-13.4
CQ14	-15.2	-10.7	-10.7	-0.4	-3.8	2.7	-5.3
CQ15	-26.4	-28.9	-11.7	-4	-3.5	-1.5	-10.4
CQ16	-40	-48.5	-17.4	-5.2	-5.2	1.2	-14.6
CQ17	-16.8	-15.7	-11.1	-3.2	-7.3	-1.3	-8.5
CQ18	-29.2	-28.8	-7.2	-0.3	-4.6	-0.3	-9
CQ19	-20.3	-12.7	-13.8	-3.5	-8.3	-0.1	-9
CQ20	-33.3	-40.1	-13.2	-4.7	-5.1	-1.5	-13
CQ21	-14.6	-7.6	-9	-4.4	-6.3	-1	-6.2
CQ22	-43	-33.9	-14.1	-8.4	-7	-5.9	-15.1
CQ23	-23.2	-15.5	-10.5	-2.9	-4.1	-2.1	-8.1
CQ24	-31.5	-36.9	-12.7	-6.8	-4.9	-4.6	-13.9

CQ25	-15.6	-10.1	-8	-4.5	-5	-3.7	-7
CQ26	-39.5	-47.1	-19.3	-10.4	-10.2	-8.2	-19.9
CQ27	-26.3	-23.2	-10.8	-3.5	-4.5	-1.8	-9.9
CQ28	-33	-35.6	-10.8	-3.5	-3.1	-1.7	-12
CQ30	-24.5	-23	-13.4	-5.1	-7	-5.1	-11.4
CQ31	-30.3	-30.1	-18.1	-11.5	-12.7	-10.8	-17.4
CQ32	-20.3	-9.3	-12.9	-2.5	-7.7	-0.1	-7.8
CQ33	-48.9	-51.7	-28.9	-22.4	-17	-17.8	-28.1
CQ35	-50.5	-52.8	-27.7	-20.5	-15.8	-14.9	-26.8
CQ36	-39.1	-33.2	-20.6	-16.9	-15.9	-14.9	-21
CQ37	-46.2	-51.7	-28.2	-21	-15.1	-15	-26.4
CQ38	-53.6	-54.3	-37.1	-25.3	-15.6	-14.2	-29.7
CQ39	-57.5	-59.8	-51.9	-42.9	-22.4	-21.9	-39.6

[0218] It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are included within the spirit and purview of this application and are considered within the scope of the appended claims. All publications, patents, and patent applications cited herein are hereby incorporated by reference in their entirety for all purposes.

WHAT IS CLAIMED IS;

1. A compound of Formula (I):



I

wherein

R^1 and R^2 are independently selected from hydrogen and alkyl; or R^1 and R^2, together with the atom to which they are attached, are joined to form a cycloalkyl;

Y is O or NR^6;

R^6 is selected from hydrogen, alkyl, alkenyl, alkynyl, alkoxy, and heteroalkyl, wherein said alkyl, alkenyl, alkynyl, alkoxy, and heteroalkyl is optionally substituted with one to five R^y;

each R^y is independently selected from halogen, hydroxy, alkoxy, cyano, and alkoxycarbonyl;

R^3 is selected from alkyl, alkenyl, alkynyl, heteroalkyl, cycloalkyl, aryl, and heteroaryl, each optionally substituted with one to five R^x;

each R^x is independently selected from halogen, hydroxy, alkoxy, cyano, alkoxycarbonyl, cycloalkyl, and aryl, wherein said cycloalkyl and aryl is optionally substituted with one to five moieties independently selected from halogen, alkyl, and haloalkyl;

R^4 is selected from hydrogen, alkyl, fluoro, and chloro;

L is selected from a bond and alkyl; and

R^7 is selected from aryl and heteroaryl, each optionally substituted with one to five R^5;

each R^5 is independently selected from alkyl, alkenyl, alkynyl, alkoxy, haloalkyl, haloalkoxy, heteroalkyl, cycloalkyl, cyano, and halogen;

or salts or N-oxides thereof,

and isomers, tautomers, enantiomers or diastereomers of these compounds.

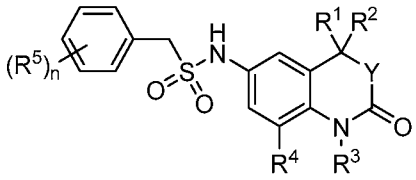
2. The compound according to claim **1,** wherein L is selected from a bond and **C1-C2** alkyl.

3. The compound according to any preceding claim, wherein L is $-CH_2-$.

4. The compound according to any preceding claim, wherein R^7 is selected from phenyl and 5-, 6-, 9-, or 10-membered heteroaryl, each optionally substituted with one to five R^5.

5. The compound according to any preceding claim, wherein R^7 is selected from phenyl, thienyl, pyridyl, and benzo[cf]thiazolyl, each optionally substituted with one to five R^5.

6. The compound according to any preceding claim, wherein the compound is of Formula (II):

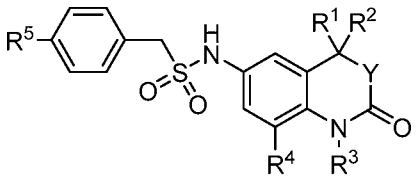


II

wherein n is selected from 0, 1, 2, 3, 4, and 5.

7. The compound according to claim **6,** wherein n is selected from 0, 1, and 2.

8. The compound according to any preceding claim, wherein the compound is of Formula (III):



III.

9. The compound according to any preceding claim, wherein each R^5 is independently selected from C1-C4 alkyl, C2-C4 alkenyl, C2-C4 alkynyl, C1-C4 alkoxy, C1-C4 haloalkyl, Ci-$_{C4}$ haloalkoxy, C1-C4 heteroalkyl, $_{C3-C5}$ cycloalkyl, cyano, and halogen.

10. The compound according to any preceding claim, wherein each R^5 is independently selected from C1-C4 alkyl, C1-C4 haloalkyl, C1-C4 heteroalkyl, C_{3-C5} cycloalkyl, and halogen.

11. The compound according to any preceding claim, wherein each R^5 is independently selected from methyl, ethyl, n-propyl, cyclopropyl, fluorine, and chlorine.

12. The compound according to any preceding claim, wherein each R^5 is methyl.

13. The compound according to any preceding claim, wherein Y is O.

14. The compound according to any one of claims **1-12,** wherein Y is NR^6.

15. The compound according to claim **14,** wherein each R^y is independently selected from halogen, hydroxy, C1-C4 alkoxy, cyano, and (C1-C3 alkoxy)-carbonyl.

16. The compound according to claim **14** or claim **15,** wherein R^6 is selected from hydrogen, C1-C4 alkyl, C2-C4 alkenyl, C2-C4 alkynyl, C1-C4 alkoxy, and C1-C4 heteroalkyl, wherein said C1-C4 alkyl, C2-C4 alkenyl, C2-C4 alkynyl, C1-C4 alkoxy, and C1-C4 heteroalkyl is optionally substituted with one to five R^y.

17. The compound according to claim **14,** wherein R^6 is selected from hydrogen and Ci-C_4 alkyl.

18. The compound according to claim **17,** wherein R^6 is selected from hydrogen and methyl.

19. The compound according to any preceding claim, wherein
R^1 and R^2 are independently selected from hydrogen and C1-C4 alkyl; or
R^1 and R^2, together with the atom to which they are attached, are joined to form a C3-C4 cycloalkyl.

20. The compound according to any preceding claim, wherein R^1 and R^2 are independently selected from hydrogen and methyl.

21. The compound according to any one of claims **1-19,** wherein R^1 and R^2, together with the atom to which they are attached, are joined to form a cyclopropyl.

22. The compound according to any preceding claim, wherein R^4 is selected from hydrogen, C1-C4 alkyl, fluoro, and chloro.

23. The compound according to any preceding claim, wherein R^4 is selected from hydrogen and fluoro.

24. The compound according to any preceding claim, wherein each R^x is independently selected from halogen, hydroxy, C1-C4 alkoxy, cyano, (C1-C3 alkoxy)-carbonyl, C3-C4 cycloalkyl, and phenyl, wherein said C3-C4 cycloalkyl and phenyl is optionally substituted with one to five moieties independently selected from halogen, C1-C3 alkyl, and C1-C3 haloalkyl.

25. The compound according to any preceding claim, wherein R^3 is selected from C1-C6 alkyl, C2-C6 alkenyl, C2-C6 alkynyl, C1-C6 heteroalkyl, C3-C6 cycloalkyl, phenyl, and 5- or 6-membered heteroaryl, each optionally substituted with one to five R^x.

26. The compound according to any preceding claim, wherein $\mathbf{R^3}$ is selected from C1-C6 alkyl, C_2-C_6 alkenyl, (C_3-C_4 cycloalkyl)-Ci-C_3 alkyl, Ci-C_6 haloalkyl, and (C1-C3 alkoxy)-C_1-C_3 alkyl.

27. The compound according to any preceding claim, wherein $\mathbf{R^3}$ is selected from ethyl, n-propyl, isopropyl, allyl, cyclopropylmethyl, **2,2**-difluoroethyl, **2,2,2**-trifluoroethyl, and **2**-methoxyethyl.

28. A composition comprising a compound as defined in any preceding claim, and an agriculturally acceptable formulation adjuvant.

29. A mixture comprising a compound as defined in any of claims **1-27,** and a further active ingredient.

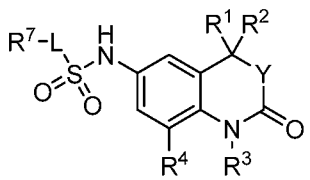
30. A method for improving the tolerance of a plant to abiotic stress, wherein the method comprises applying to the plant, plant part, plant propagation material, or plant growing locus a compound according to any of claims **1-27,** a composition according to claim **28,** or a mixture according to claim **29.**

31. A method for inhibiting seed germination of a plant, wherein the method comprises applying to the seed or a locus containing seeds a compound according to any one of claims **1-27,** a composition according to claim **28,** or a mixture according to claim **29.**

32. A method for regulating or improving the growth of a plant, wherein the method comprises applying to the plant, plant part, plant propagation material, or plant growing locus a compound according to any one of claims **1-27,** a composition according to claim **28,** or a mixture according to claim **29.**

33. A method for safening a plant against phytotoxic effects of chemicals, comprising applying to the plant, plant part, plant propagation material, or plant growing locus a compound, according to any one of claims **1-27,** a composition according to claim **28,** or a mixture according to claim **29.**

34. Use of a compound of Formula **(I):**



I

wherein

R^1 and R^2 are independently selected from hydrogen and alkyl; or R^1 and R^2, together with the atom to which they are attached, are joined to form a cycloalkyl;

Y is O or NR^6;

R^6 is selected from hydrogen, alkyl, alkenyl, alkynyl, alkoxy, and heteroalkyl, wherein said alkyl, alkenyl, alkynyl, alkoxy, and heteroalkyl is optionally substituted with one to five R^y;

each R^y is independently selected from halogen, hydroxy, alkoxy, cyano, and alkoxycarbonyl;

R^3 is selected from alkyl, alkenyl, alkynyl, heteroalkyl, cycloalkyl, aryl, and heteroaryl, each optionally substituted with one to five R^x;

each R^x is independently selected from halogen, hydroxy, alkoxy, cyano, alkoxycarbonyl, cycloalkyl, and aryl, wherein said cycloalkyl and aryl is optionally substituted with one to five moieties independently selected from halogen, alkyl, and haloalkyl;

R^4 is selected from hydrogen, alkyl, fluoro, and chloro;

L is selected from a bond and alkyl; and

R^7 is selected from aryl and heteroaryl, each optionally substituted with one to five R^5;

each R^5 is independently selected from alkyl, alkenyl, alkynyl, alkoxy, haloalkyl, haloalkoxy, heteroalkyl, cycloalkyl, cyano, and halogen;

or salts or N-oxides thereof,

and isomers, tautomers, enantiomers or diastereomers of these compounds;

or a composition comprising a compound according to Formula (I) and an agriculturally acceptable formulation adjuvant, for improving the tolerance of a plant to abiotic stress, regulating or improving the growth of a plant, inhibiting seed germination and/or safening a plant against phytotoxic effects of chemicals.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/042417

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D265/18 C07D265/36 A01N43/86
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D 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 practicable, search terms used)
EPO-Internal , WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005/085470 Al (ZHANG PUWEN [US] ET AL) 21 Apri l 2005 (2005-04-21) Progesterone receptor modul ators ; page 26; cl aims ; exampl e 74 --- -/- ·	1,2,4,5 , 9-11 , 13 , 19 ,20, 22-26

[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 application or patent but published on or after the international filing date

"L" documentwhich may throw doubts on priority claim(s) orwhich 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
19 September 2017	27/09/2017

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	Bedel , Chri sti an

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

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ACHIM SCHLAPBACH ET AL: "A novel Pd-catalyzed cyclization reaction of ureas for the synthesis of dihydroquinazolinone p38 kinase inhibitors" , BIOORGANIC & MEDICINAL CHEMISTRY LETTERS, vol . 14, no. 2, 1 January 2004 (2004-01-01) , pages 357-360, XP055405602 , AMSTERDAM, NL ISSN: 0960-894X, DOI: 10.1016/j .bmcl .2003 .11.006 P38 kinase inhibitors as pharmaceutical ; page 358; table 2; compounds 8, 10-15	1,2,4,5 , 9-12 , 14-20, 22-25
X, P	WO 2017/114052 Al (SHANGHAI INST FOR BIOLOGICAL SCIENCES CHINESE ACAD OF SCIENCES [CN]) 6 July 2017 (2017-07-06) high-stress resistance plant growth regulator; claims ; examples	1-34
A	M. 0KAM0T0 ET AL: "Activation of dimeric ABA receptors elicits guard cell closure, ABA-regulated gene expression, and drought tolerance" , PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES, vol . 110, no. 29, 1 July 2013 (2013-07-01) , pages 12132-12137 , XP055139599 , ISSN: 0027-8424, DOI: 10.1073/pnas .1305919110 agonist that active ABA receptors- reduce abiotic stress in plants	1-34
A	WO 2013/148339 Al (UNIV CALIFORNIA [US]) 3 October 2013 (2013-10-03) cited in the application the whole document	1-34

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2017/042417

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2005085470 Al	21-04-2005	US 2005085470 Al	21-04-2005
		US 2007225281 Al	27-09-2007
W0 2017114052 Al	06-07-2017	CN 106749080 A	31-05-2017
		WO 2017114052 Al	06-07-2017
W0 2013148339 Al	03-10-2013	AR 090513 Al	19-11-2014
		AU 2013240193 Al	23-10-2014
		CA 2868803 Al	03-10-2013
		CN 104363760 A	18-02-2015
		EA 201401067 Al	30-01-2015
		EP 2830422 Al	04-02-2015
		JP 6166349 B2	19-07-2017
		JP 2015512915 A	30-04-2015
		KR 20140144216 A	18-12-2014
		US 2015047073 Al	12-02-2015
		W0 2013148339 Al	03-10-2013