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(54) Benævnelse: **4-AMINO-6-(HETEROCYKLISKE)PICOLINATER OG 6-AMINO-2-(HETEROCYKLISKE)PYRIMIDIN-4-CARBOXYLATER OG DERES ANVENDELSE SOM HERBICIDER**

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WO-A1-2013/014165

DESCRIPTION

Field

[0001] The invention relates to herbicidal compounds and compositions and to methods for controlling undesirable vegetation.

Background

[0002] The occurrence of undesirable vegetation, e.g., weeds, is a constant problem facing famers in crops, pasture, and other settings. Weeds compete with crops and negatively impact crop yield. The use of chemical herbicides is an important tool in controlling undesirable vegetation.

[0003] Substituted picolinic acids and pyrimidine-4-carboxylic acids and their use as herbicides are discussed e.g. in WO 2013/014165 A1.

[0004] There remains a need for new chemical herbicides that offer a broader spectrum of weed control, selectivity, minimal crop damage, storage stability, ease of handling, higher activity against weeds, and/or a means to address herbicide-tolerance that develops with respect to herbicides currently in use.

Summary of the Invention

[0005] Provided herein are compounds defined by the formula of claim 1 and N-oxides and agriculturally acceptable salts thereof.

[0006] In one embodiment, the compound is 4-amino-3-chloro-5-fluoro-6-(7-fluoro-1*H*-indol-6-yl) picolinic acid. In one embodiment, the compound is methyl 4-amino-3-chloro-5-fluoro-6-(7-fluoro-1*H*-indol-6-yl) picolinate.

[0007] Also provided are methods of controlling undesirable vegetation comprising (a) contacting the undesirable vegetation or area adjacent to the undesirable vegetation or (b) pre-emergently contacting soil or water a herbicidally effective amount of at least one compound of the formula of claim 1 or agriculturally acceptable derivative thereof.

Detailed Description

DEFINITIONS

[0008] As used herein, herbicide and herbicidal active ingredient mean a compound that controls undesirable vegetation when applied in an appropriate amount.

[0009] As used herein, control of or controlling undesirable vegetation means killing or preventing the vegetation, or causing some other adversely modifying effect to the vegetation e.g., deviations from natural growth or development, regulation, desiccation, retardation, and the like.

[0010] As used herein, a herbicidally effective or vegetation controlling amount is an amount of herbicidal active ingredient the application of which controls the relevant undesirable vegetation.

[0011] As used herein, applying a herbicide or herbicidal composition means delivering it directly to the targeted vegetation or to the locus thereof or to the area where control of undesired vegetation is desired. Methods of application include, but are not limited to pre-emergently contacting soil or water, post-emergently contacting the undesirable vegetation or area adjacent to the undesirable vegetation.

[0012] As used herein, plants and vegetation include, but are not limited to, dormant seeds, germinant seeds, emerging seedlings, plants emerging from vegetative propagules, immature vegetation, and established vegetation.

[0013] As used herein, agriculturally acceptable salts and esters refer to salts and esters that exhibit herbicidal activity, or that are or can be converted in plants, water, or soil to the referenced herbicide. Exemplary agriculturally acceptable esters are those that are or can by hydrolyzed, oxidized, metabolized, or otherwise converted, *e.g.*, in plants, water, or soil, to the corresponding carboxylic acid which, depending on the pH, may be in the dissociated or undissociated form.

[0014] Suitable salts include those derived from alkali or alkaline earth metals and those derived from ammonia and amines. Preferred cations include sodium, potassium, magnesium, and aminium cations of the formula:

$$R^{13}R^{14}R^{15}R^{16}N^{+}$$

wherein R^{13}, R^{14}, R^{15} and R^{16} each, independently represents hydrogen or C_1-C_{12} alkyl, C_3-C_{12} alkenyl or C_3-C_{12} alkynyl, each of which is optionally substituted by one or more hydroxy, C_1-C_4 alkoxy, C_1-C_4 alkylthio or phenyl groups, provided that R^{13}, R^{14}, R^{15} and R^{16} are sterically compatible. Additionally, any two R^{13}, R^{14}, R^{15} and R^{16} together may represent an aliphatic difunctional moiety containing one to twelve carbon atoms and up to two oxygen or sulfur atoms. Salts of the compounds of Formula I can be prepared by treatment of compounds of Formula I with a metal hydroxide, such as sodium hydroxide, with an amine, such as ammonia, trimethylamine, diethanolamine, 2-methylthiopropylamine, bisallylamine, 2-butoxyethylamine, morpholine, cyclododecylamine, or benzylamine or with a tetraalkylammonium hydroxide, such as tetramethylammonium hydroxide or choline hydroxide. Amine salts are often preferred forms of the compounds of Formula I because they are water-soluble and lend themselves to the preparation of desirable aqueous based herbicidal compositions.

[0015] Compounds of the formula (I) include N-oxides. Pyridine N-oxides can be obtained by oxidation of the corresponding pyridines. Suitable oxidation methods are described, for example, in Houben-Weyl, Methoden der organischen Chemie [Methods in organic chemistry], expanded and subsequent volumes to the 4th edition, volume E 7b, p. 565 f.

[0016] As used herein, unless otherwise specified, acyl refers to formyl, C_1-C_3 alkylcarbonyl, and C_1-C_3 haloalkylcarbonyl. C_1-C_6 acyl refers to formyl, C_1-C_5 alkylcarbonyl, and C_1-C_5 haloalkylcarbonyl (the group contains a total of 1 to 6 carbon atoms).

[0017] As used herein, alkyl refers to saturated, straight-chained or branched saturated hydrocarbon moieties. Unless otherwise specified, C_1-C_{10} alkyl groups are intended. Examples include methyl, ethyl, propyl, 1-methyl-ethyl, butyl, 1-methyl-propyl, 2-methyl-propyl, 1,1-dimethyl-ethyl, pentyl, 1-methyl-butyl, 2-methyl-butyl, 3-methyl-butyl, 2,2-dimethyl-propyl, 1-ethyl-propyl, hexyl, 1,1-dimethyl-propyl, 1,2-dimethyl-propyl, 1-methyl-pentyl, 2-methyl-pentyl, 3-methyl-pentyl, 4-methyl-pentyl, 1,1-dimethyl-butyl, 1,2-dimethyl-butyl, 1,3-dimethyl-butyl, 2,2-dimethyl-butyl, 2,3-dimethyl-butyl, 3,3-dimethyl-butyl, 1-ethyl-butyl, 2-ethyl-butyl, 1,1,2-trimethyl-propyl, 1,2,2-trimethyl-propyl, 1-ethyl-1-methyl-propyl, and 1-ethyl-2-methyl-propyl.

[0018] As used herein, "haloalkyl" refers to straight-chained or branched alkyl groups, wherein these groups the hydrogen atoms may partially or entirely be substituted with halogen atoms. Unless otherwise specified, C_1-C_8 groups are intended. Examples include chloromethyl, bromomethyl, dichloromethyl, trichloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, chlorofluoromethyl, dichlorofluoromethyl, chlorodifluoromethyl, 1-chloroethyl, 1-bromoethyl, 1-fluoroethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2-chloro-2-fluoroethyl, 2-chloro-2-difluoroethyl, 2,2-dichloro-2-fluoroethyl, 2,2,2-trichloroethyl, pentafluoroethyl, and 1,1,1-trifluoroprop-2-yl.

[0019] As used herein, alkenyl refers to unsaturated, straight-chained, or branched hydrocarbon moieties containing a double bond. Unless otherwise specified, C_2-C_8 alkenyl are intended. Alkenyl groups may contain more than one unsaturated bond. Examples include ethenyl, 1-propenyl, 2-propenyl, 1-methylethenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl, 1-methyl-2-propenyl, 2-methyl-2-propenyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1-methyl-1-butenyl, 2-methyl-1-butenyl, 3-methyl-1-butenyl, 1-methyl-2-butenyl, 2-methyl-2-butenyl, 3-methyl-2-butenyl, 1-methyl-3-butenyl, 2-methyl-3-butenyl, 3-methyl-3-butenyl, 1,1-dimethyl-2-propenyl, 1,2-dimethyl-1-propenyl, 1,2-dimethyl-2-propenyl, 1-ethyl-1-propenyl, 1-ethyl-2-propenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 4-hexenyl, 5-hexenyl, 1-methyl-1-pentenyl, 2-methyl-1-pentenyl, 3-methyl-1-pentenyl, 4-methyl-1-pentenyl, 1-methyl-2-pentenyl, 2-methyl-2-pentenyl, 3-methyl-2-pentenyl, 4-methyl-2-pentenyl, 1-methyl-3-pentenyl, 2-methyl-3-pentenyl, 3-methyl-3-pentenyl, 4-methyl-3-pentenyl, 1-methyl-4-pentenyl, 2-methyl-4-pentenyl, 3-methyl-4-pentenyl, 4-methyl-4-pentenyl, 1,1-dimethyl-2-butenyl, 1,1-dimethyl-3-butenyl, 1,2-dimethyl-1-butenyl, 1,2-dimethyl-2-butenyl, 1,2-dimethyl-3-butenyl, 1,3-dimethyl-1-

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[0020] As used herein, alkynyl represents straight-chained or branched hydrocarbon moieties containing a triple bond. Unless otherwise specified, C_2-C_8 alkynyl groups are intended. Alkynyl groups may contain more than one unsaturated bond. Examples include C_2-C_6-alkynyl, such as ethynyl, 1-propynyl, 2-propynyl (or propargyl), 1-butynyl, 2-butynyl, 3-butynyl, 1-methyl-2-propynyl, 1-pentynyl, 2-pentynyl, 3-pentynyl, 4-pentynyl, 3-methyl-1-butynyl, 1-methyl-2-butynyl, 1-methyl-3-butinyul, 2-methyl-3-butynyl, 1,1-dimethyl-2-propynyl, 1-ethyl-2-propynyl, 1-hexynyl, 2-hexynyl, 3-hexynyl, 4-hexynyl, 5-hexynyl, 3-methyl-1-pentynyl, 4-methyl-1-pentynyl, 1-methyl-2-pentynyl, 4-methyl-2-pentynyl, 1-methyl-3-pentynyl, 2-methyl-3-pentynyl, 1-methyl-4-pentynyl, 2-methyl-4-pentynyl, 3-methyl-4-pentynyl, 1,1-dimethyl-2-butynyl, 1,1-dimethyl-3-butynyl, 1,2-dimethyl-3-butynyl, 2,2-dimethyl-3-butynyl, 3,3-dimethyl-1-butynyl, 1-ethyl-2-butynyl, 1-ethyl-3-butynyl, 2-ethyl-3-butynyl, and 1-ethyl-1-methyl-2-propynyl.

[0021] As used herein, alkoxy refers to a group of the formula R-O-, where R is alkyl as defined above. Unless otherwise specified, alkoxy groups wherein R is a C_1-C_8 alkyl group are intended. Examples include methoxy, ethoxy, propoxy, 1-methyl-ethoxy, butoxy, 1-methyl-propoxy, 2-methyl-propoxy, 1,1-dimethyl-ethoxy, pentoxy, 1-methyl-butyloxy, 2-methyl-butoxy, 3-methyl-butoxy, 2,2-di-methyl-propoxy, 1-ethyl-propoxy, hexoxy, 1,1-dimethyl-propoxy, 1,2-dimethyl-propoxy, 1-methyl-pentoxy, 2-methyl-pentoxy, 3-methyl-pentoxy, 4-methyl-penoxy, 1,1-dimethyl-butoxy, 1,2-dimethyl-butoxy, 1,3-dimethyl-butoxy, 2,2-dimethyl-butoxy, 2,3-dimethyl-butoxy, 3,3-dimethyl-butoxy, 1-ethyl-butoxy, 2-ethylbutoxy, 1,1,2-trimethyl-propoxy, 1,2,2-trimethyl-propoxy, 1-ethyl-1-methyl-propoxy, and 1-ethyl-2-methyl-propoxy.

[0022] As used herein, haloalkoxy refers to a group of the formula R-O-, where R is haloalkyl as defined above. Unless otherwise specified, haloalkoxy groups wherein R is a C_1-C_8 alkyl group are intended. Examples include chloromethoxy, bromomethoxy, dichloromethoxy, trichloromethoxy, fluoromethoxy, difluoromethoxy, trifluoromethoxy, chlorofluoromethoxy, dichlorofluoromethoxy, chlorodifluoromethoxy, 1-chloroethoxy, 1-bromoethoxy, 1-fluoroethoxy, 2-fluoroethoxy, 2,2-difluoroethoxy, 2,2,2-trifluoroethoxy, 2-chloro-2-fluoroethoxy, 2-chloro,2-difluoroethoxy, 2,2-dichloro-2-fluoroethoxy, 2,2,2-trichloroethoxy, pentafluoroethoxy, and 1,1,1-trifluoroprop-2-oxy.

[0023] As used herein, alkylthio refers to a group of the formula R-S- where R is alkyl as defined above. Unless otherwise specified, alkylthio groups wherein R is a C_1-C_8 alkyl group are intended. Examples include methylthio, ethylthio, propylthio, 1-methylethylthio, butylthio, 1-methyl-propylthio, 2-methylpropylthio, 1,1-dimethylethylthio, pentylthio, 1-methylbutylthio, 2-methylbutylthio, 3-methylbutylthio, 2,2-dimethylpropylthio, 1-ethylpropylthio, hexylthio, 1,1-dimethyl propylthio, 1,2-dimethyl propylthio, 1-methylpentylthio, 2-methylpentylthio, 3-methyl-pentylthio, 4-methyl-pentylthio, 1,1-dimethyl butylthio, 1,2-dimethyl-butylthio, 1,3-dimethyl-butylthio, 2,2-dimethyl butylthio, 2,3-dimethyl butylthio, 3,3-dimethylbutylthio, 1-ethylbutylthio, 2-ethylbutylthio, 1,1,2-trimethyl propylthio, 1,2,2-trimethyl propylthio, 1-ethyl-1-methyl propylthio, and 1-ethyl-2-methylpropylthio.

[0024] As used herein, haloalkylthio refers to an alkylthio group as defined above wherein the carbon atoms are partially or entirely substituted with halogen atoms. Unless otherwise specified, haloalkylthio groups wherein R is a C_1-C_8 alkyl group are intended. Examples include chloromethylthio, bromomethylthio, dichloromethylthio, trichloromethylthio, fluoromethylthio, difluoromethylthio, trifluoromethylthio, chlorofluoromethylthio, dichlorofluoro-methylthio, chlorodifluoromethylthio, 1-chloroethylthio, 1-bromoethylthio, 1-fluoroethylthio, 2-fluoroethylthio, 2,2-difluoroethylthio, 2,2,2-trifluoroethylthio, 2-chloro-2-fluoroethylthio, 2-chloro-2-difluoroethylthio, 2,2-dichloro-2-fluoroethylthio, 2,2,2-trichloroethylthio, pentafluoroethylthio, and 1,1,1-trifluoroprop-2-ylthio.

[0025] As used herein, aryl, as well as derivative terms such as aryloxy, refers to a phenyl, indanyl or naphthyl group with phenyl being preferred. The term "heteroaryl", as well as derivative terms such as "heteroaryloxy", refers to a 5- or 6-membered aromatic ring containing one or more heteroatoms, viz., N, O or S; these heteroaromatic rings may be fused to other aromatic systems. The aryl or heteroaryl substituents may be unsubstituted or substituted with one or more substituents selected from halogen, hydroxy, nitro, cyano, formyl, C_1-C_6 alkyl, C_2-C_6 alkenyl, C_2-C_6 alkynyl, C_1-C_6 alkoxy, C_1-C_6 haloalkyl, C_1-C_6 haloalkoxy, C_1-C_6 acyl, C_1-C_6 alkylthio, C_1-C_6 alkylsulfinyl, C_1-C_6 alkylsulfonyl, C_1-C_6 alkoxycarbonyl, C_1-C_6 carbamoyl, hydroxycarbonyl, C_1-C_6 alkylcarbonyl, aminocarbonyl, C_1-C_6 alkylaminocarbonyl, C_1-C_6 dialkylaminocarbonyl,

provided that the substituents are sterically compatible and the rules of chemical bonding and strain energy are satisfied. Preferred substituents include halogen, C_1-C_2 alkyl and C_1-C_2 haloalkyl.

[0026] As used herein alkylcarbonyl refers to an alkyl group bonded to a carbonyl group. C_1-C_3 alkylcarbonyl and C_1-C_3 haloalkylcarbonyl refer to groups wherein a C_1-C_3 alkyl group is bonded to a carbonyl group (the group contains a total of 2 to 4 carbon atoms).

[0027] As used herein, alkoxycarbonyl refers to a group of the formula

wherein R is alkyl.

[0028] As used herein, arylalkyl refers to an alkyl group substituted with an aryl group. C_7-C_{10} arylalkyl refers to a group wherein the total number of carbon atoms in the group is 7 to 10.

[0029] As used herein alkylamino refers to an amino group substituted with one or two alkyl groups, which may be the same or different.

[0030] As used herein haloalkylamino refers to an alkylamino group wherein the alkyl carbon atoms are partially or entirely substituted with halogen atoms.

[0031] As used herein, C_1-C_6 alkylaminocarbonyl refers to a group of the formula RNHC(O)- wherein R is C_1-C_6 alkyl, and C_1-C_6 dialkylaminocarbonyl refers to a group of the formula $R_2NC(O)$- wherein each R is independently C_1-C_6 alkyl.

[0032] As used herein alkylcarbamyl refers to a carbamyl group substituted on the nitrogen with an alkyl group.

[0033] As used herein alkylsulfonyl refers to a group of the formula

where R is alkyl.

[0034] As used herein carbamyl (also referred to as carbamoyl and aminocarbonyl) refers to a group of the formula

[0035] As used herein dialkylphosphonyl refers to a group of the formula

where R is independently alkyl in each occurrence.

[0036] As used herein, C_1-C_6 trialkylsilyl refers to a group of the formula -SiR_3 wherein each R is independently a C_1-C_6 alkyl group (the group contains a total of 3 to 18 carbon atoms).

[0037] As used herein Me refers to a methyl group; OMe refers to a methoxy group; i-Pr refers to an isopropyl group.

[0038] As used herein, the term "halogen" including derivative terms such as "halo" refers to fluorine, chlorine, bromine and iodine.

[0039] As used herein, plants and vegetation include, but are not limited to, germinant seeds, emerging seedlings, plants emerging from vegetative propagules, immature vegetation, and established vegetation.

COMPOUNDS OF THE FORMULA DEFINED IN CLAIM 1

[0040] The invention provides compounds of the formula defined in claim 1 and N-oxides and agriculturally acceptable salts thereof.

[0041] In some embodiments, the compound is the carboxylic acid or an agriculturally acceptable ester or salt. In some embodiments, the compound is the carboxylic acid or its methyl ester.

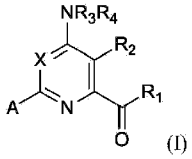
[0042] In some embodiments, $R^{1'}$ is hydrogen or C_1-C_8 alkyl. In some embodiments, $R^{1'}$ is hydrogen.

[0043] In some embodiments, R^2 is Cl. In some embodiments, R^2 is OMe. In some embodiments, R^2 is vinyl or 1-propenyl.

[0044] In some embodiments, R^6 is hydrogen, halogen, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_3 alkoxy, or C_1-C_3 haloalkoxy. In some embodiments, R^6 is hydrogen or fluorine. In some embodiments, R^6 is hydrogen. In some embodiments, R^6 is fluorine.

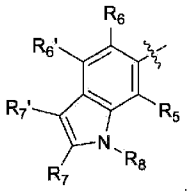
[0045] In some embodiments, $R^{6'}$ is hydrogen or halogen. In some embodiments, $R^{6'}$ is hydrogen, F, or Cl. In some embodiments, $R^{6'}$ is hydrogen or F. In some embodiments, $R^{6'}$ is hydrogen.

[0046] It is particularly noteworthy that the present compounds, which can be represented by Formula (I) below, exhibit a significant increase in activity because X is CF. This is demonstrated by comparing the activity of Compounds 1.21 and 1.22 (wherein X is CH) with that of Compounds 1.08 and 1.09 (wherein X is CF). It is also demonstrated by comparing the activity of Compounds 1.23 and 1.24 (wherein X is CH) with that of inventive Compounds 1.15 and 1.16 (wherein X is CF). The increased activity is further enhanced because R^5 is F



(I)

with A being

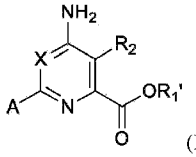


[0047] In some embodiments, R^6 is hydrogen or F. In certain embodiments, R^6 is F. In certain embodiments, R^6 is H.

[0048] In one embodiment, the compound is 4-amino-3-chloro-5-fluoro-6-(7-fluoro-1*H*-indol-6-yl) picolinic acid. In one embodiment, the compound is methyl 4-amino-3-chloro-5-fluoro-6-(7-fluoro-1*H*-indol-6-yl) picolinate.

EXEMPLARY COMPOUNDS

[0049] The following Table 1 describes exemplary compounds of Formula (I')



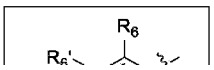
(I')

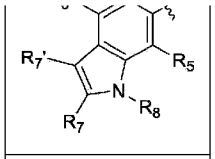
Table 2 sets forth the structure, appearance, preparation method, and precursor(s) used in synthesis of the exemplary compounds. Table 3 sets forth physical data for each of the exemplary compounds.

[0050] Blank spaces in compound tables herein indicate hydrogen, or that for the A group indicated in a particular row the column in which the blank occurs is not relevant.

Table 1: Compounds of Formula (I') with indolyl tails

A is A15:





A15

C.No.	$R^{1'}$	R^2	X	A	R^5	R^6	$R^{6'}$	$R^{6''}$	R^7	$R^{7'}$	R^8
1.08*	Me	Cl	CF	A15							
1.09*	H	Cl	CF	A15							
1.10*	Me	Cl	CF	A15							Me
1.11*	H	Cl	CF	A15							Me
1.12	Me	Cl	CF	A15	F						$Si(i\text{-}Pr)_3$
1.13*	Me	Cl	CF	A15		F					
1.14*	H	Cl	CF	A15		F					
1.15	Me	Cl	CF	A15	F						
1.16	H	Cl	CF	A15	F						
1.17	H	OMe	CF	A15	F						
1.18	Me	vinyl	CF	A15	F						
1.19	H	vinyl	CF	A15	F						
1.20	Me	OMe	CF	A15	F						
1.21*	Me	Cl	CH	A15							
1.22*	H	Cl	CH	A15							
1.23*	Me	Cl	CH	A15	F						
1.24*	H	Cl	CH	A15	F						

* Comparative compound

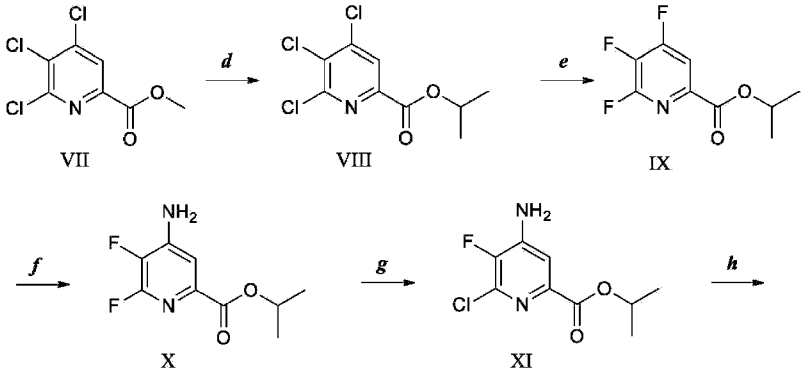
METHODS OF PREPARING THE COMPOUNDS

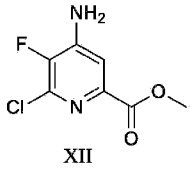
[0051] Exemplary procedures to synthesize compounds of Formula (I) are provided below.

[0052] The 4-amino-6-(heterocyclic)picolinic acids of Formula (I) can be prepared in a number of ways.

[0053] As depicted in Scheme II, the 4,5,6-trichloropicolinate of Formula (VII) can be converted to the corresponding isopropyl ester of Formula (VIII), via a reaction with isopropyl alcohol and concentrated sulfuric acid, *e.g.,* at reflux temperature under Dean-Stark conditions (reaction *d*). The isopropyl ester of Formula (VIII) can be reacted with a fluoride ion source, such as cesium fluoride, in a polar, aprotic solvent, such as dimethyl sulfoxide (DMSO), at a temperature, such as 80 °C, under Dean-Stark conditions, to yield the isopropyl 4,5,6-trifluoropicolinate of Formula (IX) (reaction *e*). The isopropyl 4,5,6-trifluoropicolinate of Formula (IX) can be aminated with a nitrogen source, such as ammonia, in a polar, aprotic solvent, such as DMSO, to produce a 4-amino-5,6-difluoropicolinate of Formula (X) (reaction *f*). The fluoro substituent in the 6-position of the 4-amino-5,6-difluoropicolinate of Formula (X) can be exchanged with a chloro substituent by treatment with a chloride source, such as hydrogen chloride, *e.g.*, in dioxane, in a Parr reactor, at a temperature, such as 100 °C, to produce a 4-amino-5-fluoro-6-chloro-picolinate of Formula (XI) (reaction *g*). The 4-amino-5-fluoro-6-chloropicolinate of Formula (XI) can be transesterified to the corresponding methyl ester of Formula (XII) by reaction with titanium(IV) isopropoxide in methyl alcohol at reflux temperature (reaction *h*).

Scheme II



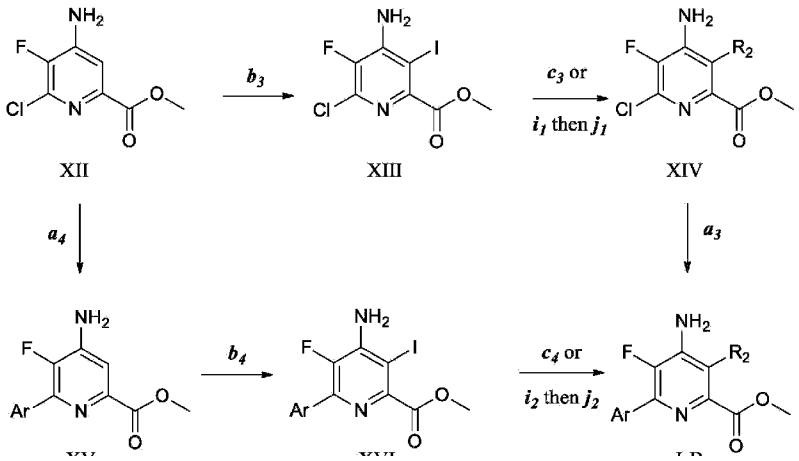


XII

[0054] As depicted in Scheme III, the 4-amino-5-fluoro-6-chloropicolinate of Formula (XII) can be transformed into the 3-iodo-4-amino-5-fluoro-6-chloropicolinate of Formula (XIII) via reaction with iodinating reagents, such as periodic acid and iodine, in a polar, protic solvent, such as methyl alcohol (reaction b_3). Stille coupling of the 3-iodo-4-amino-5-fluoro-6-chloropicolinates of Formula (XIII) with a stannane, such as tributyl(vinyl)stannane, in the presence of a catalyst, such as bis(triphenylphosphine)-palladium(II) dichloride, in a non-reactive solvent, such as 1,2-dichloroethane, at a temperature, such as 120-130 °C, e.g., in a microwave reactor, provides 3-(substituted)-4-amino-5-fluoro-6-chloropicolinates of Formula (XIV), wherein R^2 is alkyl, alkenyl, alkynyl, haloalkenyl and alkylthio (reaction c_3). Alternatively, the 3-iodo-4-amino-5-fluoro-6-chloropicolinates of Formula (XIII) can be treated with cesium carbonate and a catalytic amount of both copper(I) iodide and 1,10-phenanthroline in the presence of a polar, protic solvent, such as methyl alcohol, at a temperature, such as 65 °C, to provide a 3-(substituted)-4-amino-5-fluoro-6-chloropicolinic acids of Formula (XIV), wherein R^2 is alkoxy or haloalkoxy (reaction i_1), which can be esterified to the methyl esters, *e.g.*, by treatment with hydrogen chloride (gas) and methyl alcohol at 50 °C (reaction j_1). The 3-(substituted)-4-amino-5-fluoro-6-chloropicolinates of Formula (XIV) can be converted to the 4-amino-6-substituted-picolinates of Formula (I-B), wherein Ar is as herein defined, via Suzuki coupling with a boronic acid or ester, in the presence of a base, such as potassium fluoride, and a catalyst, such as bis(triphenylphosphine)-palladium(II) dichloride, in a polar, protic solvent mixture, such as acetonitrile-water, at a temperature, such as 110 °C, *e.g.*, in a microwave reactor (reaction a_3).

[0055] Alternatively, the 4-amino-5-fluoro-6-chloropicolinates of Formula (XII) can be converted to the 4-amino-5-fluoro-6-substituted-picolinates of Formula (XV), wherein Ar is as herein defined, via Suzuki coupling with a boronic acid or ester, in the presence of a base, such as potassium fluoride, and a catalyst, such as bis(triphenylphosphine)-palladium(II) dichloride, in a polar, protic solvent mixture, such as acetonitrile-water, at a temperature, such as 110 °C, *e.g.*, in a microwave reactor (reaction a_4). The 4-amino-5-fluoro-6-substituted-picolinates of Formula (XV) can be transformed into the 3-iodo-4-amino-5-fluoro-6-substituted-picolinates of Formula (XVI) via reaction with iodinating reagents, such as periodic acid and iodine, in a polar, protic solvent, such as methyl alcohol (reaction b_4). Stille coupling of the 3-iodo-4-amino-5-fluoro-6-substituted-picolinates of Formula (XVI) with a stannane, such as tributyl(vinyl)stannane, in the presence of a catalyst, such as bis(triphenylphosphine)-palladium(II) dichloride, in a non-reactive solvent, such as 1,2-dichloroethane, at a temperature, such as 120-130 °C, *e.g.*, in a microwave reactor, provides 3-(substituted)-4-amino-5-fluoro-6-substituted-picolinates of Formula (I-B), wherein R^2 is alkyl, alkenyl, alkynyl, haloalkenyl and alkylthio (reaction c_4). Alternatively, the 3-iodo-4-amino-5-fluoro-6-substituted-picolinates of Formula (XVI) can be treated with cesium carbonate and a catalytic amount of both copper(I) iodide and 1,10-phenanthroline in the presence of a polar, protic solvent, such as methyl alcohol, at a temperature, such as 65 °C, to provide a 3-(substituted)-4-amino-5-fluoro-6-substituted-picolinic acids of Formula (I-B), wherein R^2 is alkoxy or haloalkoxy (reaction i_2), which can be esterified to the methyl esters, *e.g.*, by treatment with hydrogen chloride (gas) and methyl alcohol, at a temperature, such as 50 °C (reaction j_2).

Scheme III



XV XVI I-B

[0056] The compounds of Formulae I-B obtained by any of these processes, can be recovered by conventional means and purified by standard procedures, such as by recrystallization or chromatography. The compounds defined by the formula in claim 1 can be prepared from compounds of Formulae I-B using standard methods well known in the art.

COMPOSITIONS AND METHODS

[0057] In some embodiments, the compounds provided herein are employed in mixtures containing a herbicidally effective amount of the compound along with at least one agriculturally acceptable adjuvant or carrier. Exemplary adjuvants or carriers include those that are not phytotoxic or significantly phytotoxic to valuable crops, e.g., at the concentrations employed in applying the compositions for selective weed control in the presence of crops, and/or do not react or significantly react chemically with the compounds provided herein or other composition ingredients. Such mixtures can be designed for application directly to weeds or their locus or can be concentrates or formulations that are diluted with additional carriers and adjuvants before application. They can be solids, such as, for example, dusts, granules, water dispersible granules, or wettable powders, or liquids, such as, and for example, emulsifiable concentrates, solutions, emulsions or suspensions. They can also be provided as a pre-mix or tank-mixed.

[0058] Suitable agricultural adjuvants and carriers that are useful in preparing the herbicidal mixtures of the disclosure are well known to those skilled in the art. Some of these adjuvants include, but are not limited to, crop oil concentrate (mineral oil (85%) + emulsifiers (15%)); nonylphenol ethoxylate; benzylcocoalkyldimethyl quaternary ammonium salt; blend of petroleum hydrocarbon, alkyl esters, organic acid, and anionic surfactant; C_9-C_{11} alkylpolyglycoside; phosphated alcohol ethoxylate; natural primary alcohol (C_{12}-C_{16}) ethoxylate; di-sec-butylphenol EO-PO block copolymer; polysiloxane-methyl cap; nonylphenol ethoxylate + urea ammonium nitrate; emulsified methylated seed oil; tridecyl alcohol (synthetic) ethoxylate (8EO); tallow amine ethoxylate (15 EO); PEG(400) dioleate-99.

[0059] Liquid carriers that can be employed include water and organic solvents. The organic solvents typically used include, but are not limited to, petroleum fractions or hydrocarbons such as mineral oil, aromatic solvents, paraffinic oils, and the like; vegetable oils such as soybean oil, rapeseed oil, olive oil, castor oil, sunflower seed oil, coconut oil, corn oil, cottonseed oil, linseed oil, palm oil, peanut oil, safflower oil, sesame oil, tung oil and the like; esters of the above vegetable oils; esters of monoalcohols or dihydric, trihydric, or other lower polyalcohols (4-6 hydroxy containing), such as 2-ethylhexyl stearate, *n*-butyl oleate, isopropyl myristate, propylene glycol dioleate, di-octyl succinate, di-butyl adipate, di-octyl phthalate and the like; esters of mono-, di- and poly-carboxylic acids and the like. Specific organic solvents include toluene, xylene, petroleum naphtha, crop oil, acetone, methyl ethyl ketone, cyclohexanone, trichloroethylene, perchloroethylene, ethyl acetate, amyl acetate, butyl acetate, propylene glycol monomethyl ether and diethylene glycol monomethyl ether, methyl alcohol, ethyl alcohol, isopropyl alcohol, amyl alcohol, ethylene glycol, propylene glycol, glycerine, *N*-methyl-2-pyrrolidinone, *N,N*-dimethyl alkylamides, dimethyl sulfoxide, liquid fertilizers, and the like. In some embodiments, water is the carrier for the dilution of concentrates.

[0060] Suitable solid carriers include talc, pyrophyllite clay, silica, attapulgus clay, kaolin clay, kieselguhr, chalk, diatomaceous earth, lime, calcium carbonate, bentonite clay, Fuller's earth, cottonseed hulls, wheat flour, soybean flour, pumice, wood flour, walnut shell flour, lignin, and the like.

[0061] In some embodiments, one or more surface-active agents are utilized in the compositions of the present disclosure. Such surface-active agents are, in some embodiments, employed in both solid and liquid compositions, *e.g.*, those designed to be diluted with carrier before application. The surface-active agents can be anionic, cationic or nonionic in character and can be employed as emulsifying agents, wetting agents, suspending agents, or for other purposes. Surfactants conventionally used in the art of formulation and which may also be used in the present formulations are described, *inter alia,* in McCutcheon's Detergents and Emulsifiers Annual, MC Publishing Corp., Ridgewood, New Jersey, 1998, and in Encyclopedia of Surfactants, Vol. I-III, Chemical Publishing Co., New York, 1980-81. Typical surface-active agents include salts of alkyl sulfates, such as diethanolammonium lauryl sulfate; alkylarylsulfonate salts, such as calcium dodecylbenzenesulfonate; alkylphenol-alkylene oxide addition products, such as nonylphenol-C_{18} ethoxylate; alcohol-alkylene oxide addition products, such as tridecyl alcohol-C_{16} ethoxylate; soaps, such as sodium stearate; alkylnaphthalene-sulfonate salts, such as sodium dibutylnaphthalenesulfonate; dialkyl esters of sulfosuccinate salts, such as sodium di(2-ethylhexyl) sulfosuccinate; sorbitol esters, such as sorbitol oleate; quaternary amines, such as lauryl trimethylammonium chloride; polyethylene glycol esters of fatty acids, such as polyethylene glycol stearate; block copolymers of ethylene oxide

and propylene oxide; salts of mono- and dialkyl phosphate esters; vegetable or seed oils such as soybean oil, rapeseed/canola oil, olive oil, castor oil, sunflower seed oil, coconut oil, corn oil, cottonseed oil, linseed oil, palm oil, peanut oil, safflower oil, sesame oil, tung oil and the like; and esters of the above vegetable oils, e.g., methyl esters.

[0062] Oftentimes, some of these materials, such as vegetable or seed oils and their esters, can be used interchangeably as an agricultural adjuvant, as a liquid carrier or as a surface active agent.

[0063] Other adjuvants commonly used in agricultural compositions include compatibilizing agents, antifoam agents, sequestering agents, neutralizing agents and buffers, corrosion inhibitors, dyes, odorants, spreading agents, penetration aids, sticking agents, dispersing agents, thickening agents, freezing point depressants, antimicrobial agents, and the like. The compositions may also contain other compatible components, for example, other herbicides, plant growth regulants, fungicides, insecticides, and the like and can be formulated with liquid fertilizers or solid, particulate fertilizer carriers such as ammonium nitrate, urea and the like.

[0064] The concentration of the active ingredients in the herbicidal compositions of this disclosure is generally from about 0.001 to about 98 percent by weight. Concentrations from about 0.01 to about 90 percent by weight are often employed. In compositions designed to be employed as concentrates, the active ingredient is generally present in a concentration from about 5 to about 98 weight percent, preferably about 10 to about 90 weight percent. Such compositions are typically diluted with an inert carrier, such as water, before application. The diluted compositions usually applied to weeds or the locus of weeds generally contain about 0.0001 to about 1 weight percent active ingredient and preferably contain about 0.001 to about 0.05 weight percent.

[0065] The present compositions can be applied to weeds or their locus by the use of conventional ground or aerial dusters, sprayers, and granule applicators, by addition to irrigation or flood water, and by other conventional means known to those skilled in the art.

[0066] In some embodiments, the compounds and compositions described herein are applied as a post-emergence application, pre-emergence application, in-water application to flooded paddy rice or water bodies (e.g., ponds, lakes and streams), or burn-down application.

[0067] In some embodiments, the compounds and compositions provided herein are utilized to control weeds in crops, including but not limited to citrus, apple, rubber, oil, palm, forestry, direct-seeded, water-seeded and transplanted rice, wheat, barley, oats, rye, sorghum, corn/maize, pastures, grasslands, rangelands, fallowland, turf, tree and vine orchards, aquatics, or row-crops, as well as non-crop settings, e.g., industrial vegetation management (IVM) or rights-of-way. In some embodiments, the compounds and compositions are used to control woody plants, broadleaf and grass weeds, or sedges.

[0068] In some embodiments, the compounds and compositions provided herein are utilized to control undesirable vegetation in rice. In certain embodiments, the undesirable vegetation is *Brachiaria platyphylla* (Groseb.) Nash (broadleaf signalgrass, BRAPP), *Digitaria sanguinalis* (L.) Scop. (large crabgrass, DIGSA), *Echinochloa crus-galli* (L.) P. Beauv. (barnyardgrass, ECHCG), *Echinochloa colonum* (L.) LINK (junglerice, ECHCO), *Echinochloa oryzoides* (Ard.) Fritsch (early watergrass, ECHOR), *Echinochloa oryzicola* (Vasinger) Vasinger (late watergrass, ECHPH), *Ischaemum rugosum* Salisb. (saramollagrass, ISCRU), *Leptochloa chinensis* (L.) Nees (Chinese sprangletop, LEFCH), *Leptochloa fascicularis* (Lam.) Gray (bearded sprangletop, LEFFA), *Leptochloa panicoides* (Presl.) Hitchc. (Amazon sprangletop, LEFPA), *Panicum dichotomiflorum* (L.) Michx. (fall panicum, PANDI), *Paspalum dilatatum* Poir. (dallisgrass, PASDI), *Cyperus difformis* L. (smallflower flatsedge, CYPDI), *Cyperus esculentus* L. (yellow nutsedge, CYPES), *Cyperus iria* L. (rice flatsedge, CYPIR), *Cyperus rotundus* L. (purple nutsedge, CYPRO), *Eleocharis* species (ELOSS), *Fimbristylis miliacea* (L.) Vahl (globe fringerush, FIMMI), *Schoenoplectus juncoides* Roxb. (Japanese bulrush, SPCJU), *Schoenoplectus maritimus* L. (sea clubrush, SCPMA), *Schoenoplectus mucronatus* L. (ricefield bulrush, SCPMU), *Aeschynomene* species, (jointvetch, AESSS), *Alternantheraphiloxeroides* (Mart.) Griseb. (alligatorweed, ALRPH), *Alisma plantago-aquatica* L. (common waterplantain, ALSPA), *Amaranthus* species, (pigweeds and amaranths, AMASS), *Ammannia coccinea* Rottb. (redstem, AMMCO), *Eclipta alba* (L.) Hassk. (American false daisy, ECLAL), *Heteranthera limosa* (SW.) Willd./Vahl (ducksalad, HETLI), *Heteranthera reniformis* R. & P. (roundleaf mudplantain, HETRE), *Ipomoea hederacea* (L.) Jacq. (ivyleaf morningglory, IPOHE), *Lindernia dubia* (L.) Pennell (low false pimpernel, LIDDU), *Monochoria korsakowii* Regel & Maack (monochoria, MOOKO), *Monochoria vaginalis* (Burm. F.) C. Presl ex Kuhth, (monochoria, MOOVA), *Murdannia nudiflora* (L.) Brenan (doveweed, MUDNU), *Polygonum pensylvanicum* L., (Pennsylvania smartweed, POLPY), *Polygonum persicaria* L. (ladysthumb, POLPE), *Polygonum hydropiperoides* Michx. (POLHP, mild smartweed), *Rotala indica* (Willd.) Koehne (Indian toothcup, ROTIN), *Sagittaria* species, (arrowhead, SAGSS), *Sesbania exaltata* (Raf.) Cory/Rydb. Ex Hill (hemp sesbania, SEBEX), or *Sphenoclea zeylanica* Gaertn. (gooseweed, SPDZE).

[0069] In some embodiments, the compounds and compositions provided herein are utilized to control undesirable vegetation in cereals. In certain embodiments, the undesirable vegetation is *Alopecurus myosuroides* Huds. (blackgrass, ALOMY), *Apera spica-venti* (L.) Beauv. (windgrass, APESV), *Avena fatua* L. (wild oat, AVEFA), *Bromus tectorum* L. (downy brome, BROTE), *Lolium multiflorum* Lam. (Italian ryegrass, LOLMU), *Phalaris minor* Retz. (littleseed canarygrass, PHAMI), *Poa annua* L. (annual bluegrass, POANN), *Setaria pumila* (Poir.) Roemer & J.A. Schultes (yellow foxtail, SETPU), *Setaria viridis* (L.) Beauv. (green foxtail, SETVI), *Cirsium arvense* (L.) Scop. (Canada thistle, CIRAR), *Galium aparine* L. (catchweed bedstraw, GALAP), *Kochia scoparia* (L.) Schrad. (kochia, KCHSC), *Lamium purpureum* L. (purple deadnettle , LAMPU), *Matricaria recutita* L. (wild chamomile, MATCH), *Matricaria matricarioides* (Less.) Porter (pineappleweed, MATMT), *Papaver rhoeas* L. (common poppy, PAPRH), *Polygonum convolvulus* L. (wild buckwheat, POLCO), *Salsola tragus* L. (Russian thistle, SASKR), *Stellaria media* (L.) Vill. (common chickweed, STEME), *Veronica persica* Poir. (Persian speedwell, VERPE), *Viola arvensis* Murr. (field violet, VIOAR), or *Viola tricolor* L. (wild violet, VIOTR).

[0070] In some embodiments, the compounds and compostions provided herein are utilized to control undesirable vegetation in range and pasture. In certain embodiments, the undesirable vegetation is *Ambrosia artemisiifolia* L. (common ragweed, AMBEL), *Cassia obtusifolia* (sickle pod, CASOB), *Centaurea maculosa* auct. non Lam. (spotted knapweed, CENMA), *Cirsium arvense* (L.) Scop. (Canada thistle, CIRAR), *Convolvulus arvensis* L. (field bindweed, CONAR), *Euphorbia esula* L. (leafy spurge, EPHES), *Lactuca serriola* L./Torn. (prickly lettuce, LACSE), *Plantago lanceolata* L. (buckhorn plantain, PLALA), *Rumex obtusifolius* L. (broadleaf dock, RUMOB), *Sida spinosa* L. (prickly sida, SIDSP), *Sinapis arvensis* L. (wild mustard, SINAR), *Sonchus arvensis* L. (perennial sowthistle, SONAR), *Solidago* species (goldenrod, SOOSS), *Taraxacum officinale* G.H. Weber ex Wiggers (dandelion, TAROF), *Trifolium repens* L. (white clover, TRFRE), or *Urtica dioica* L. (common nettle, URTDI).

[0071] In some embodiments, the compounds and compositions provided herein are utilized to control undesirable vegetation found in row crops. In certain embodiments, the undesirable vegetation is *Alopecurus myosuroides* Huds. (blackgrass, ALOMY), *Avena fatua* L. (wild oat, AVEFA), *Brachiaria platyphylla* (Groseb.) Nash (broadleaf signalgrass, BRAPP), *Digitaria sanguinalis* (L.) Scop. (large crabgrass, DIGSA), *Echinochloa crus-galli* (L.) P. Beauv. (barnyardgrass, ECHCG), *Echinochloa colonum* (L.) Link (junglerice, ECHCO), *Lolium multiflorum* Lam. (Italian ryegrass, LOLMU), *Panicum dichotomiflorum* Michx. (fall panicum, PANDI), *Panicum miliaceum* L. (wild-proso millet, PANMI), *Setaria faberi* Herrm. (giant foxtail, SETFA), *Setaria viridis* (L.) Beauv. (green foxtail, SETVI), *Sorghum halepense* (L.) Pers. (Johnsongrass, SORHA), *Sorghum bicolor* (L.) Moench ssp. *Arundinaceum* (shattercane, SORVU), *Cyperus esculentus* L. (yellow nutsedge, CYPES), *Cyperus rotundus* L. (purple nutsedge, CYPRO), *Abutilon theophrasti* Medik. (velvetleaf, ABUTH), *Amaranthus* species (pigweeds and amaranths, AMASS), *Ambrosia artemisiifolia* L. (common ragweed, AMBEL), *Ambrosia psilostachya* DC. (western ragweed, AMBPS), *Ambrosia trifida* L. (giant ragweed, AMBTR), *Asclepias syriaca* L. (common milkweed, ASCSY), *Chenopodium album* L. (common lambsquarters, CHEAL), *Cirsium arvense* (L.) Scop. (Canada thistle, CIRAR), *Commelina benghalensis* L. (tropical spiderwort, COMBE), *Datura stramonium* L. (jimsonweed, DATST), *Daucus carota* L. (wild carrot, DAUCA), *Euphorbia heterophylla* L. (wild poinsettia, EPHHL), *Erigeron bonariensis* L. (hairy fleabane, ERIBO), *Erigeron canadensis* L. (Canadian fleabane, ERICA), *Helianthus annuus* L. (common sunflower, HELAN), *Jacquemontia tamnifolia* (L.) Griseb. (smallflower morningglory, IAQTA), *Ipomoea hederacea* (L.) Jacq. (ivyleaf morningglory, IPOHE), *Ipomoea lacunosa* L. (white morningglory, IPOLA), *Lactuca serriola* L./Torn. (prickly lettuce, LACSE), *Portulaca oleracea* L. (common purslane, POROL), *Sida spinosa* L. (prickly sida, SIDSP), *Sinapis arvensis* L. (wild mustard, SINAR), *Solanum ptychanthum* Dunal (eastern black nightshade, SOLPT), or *Xanthium strumarium* L. (common cocklebur, XANST).

[0072] In some embodiments, application rates of about 1 to about 4,000 grams/hectare (g/ha) are employed in post-emergence operations. In some embodiments, rates of about 1 to about 4,000 g/ha are employed in pre-emergence operations.

[0073] In some embodiments, the compounds, compositions, and methods provided herein are used in conjunction with one or more other herbicides to control a wider variety of undesirable vegetation. When used in conjunction with other herbicides, the presently claimed compounds can be formulated with the other herbicide or herbicides, tank-mixed with the other herbicide or herbicides or applied sequentially with the other herbicide or herbicides. Some of the herbicides that can be employed in conjunction with the compounds of the present disclosure include: 4-CPA, 4-CPB, 4-CPP, 2,4-D, 2,4-D choline salt, 2,4-D esters and amines, 2,4-DB, 3,4-DA, 3,4-DB, 2,4-DEB, 2,4-DEP, 3,4-DP, 2,3,6-TBA, 2,4,5-T, 2,4,5-TB, acetochlor, acifluorfen, aclonifen, acrolein, alachlor, allidochlor, alloxydim, allyl alcohol, alorac, ametridione, ametryn, amibuzin, amicarbazone, amidosulfuron, aminocyclopyrachlor, aminopyralid, amiprofos-methyl, amitrole, ammonium sulfamate, anilofos, anisuron, asulam, atraton, atrazine, azafenidin, azimsulfuron, aziprotryne, barban, BCPC, beflubutamid, benazolin, bencarbazone, benfluralin, benfuresate, bensulfuron-methyl, bensulide, benthiocarb, bentazon-sodium, benzadox, benzfendizone, benzipram, benzobicyclon, benzofenap, benzofluor, benzoylprop, benzthiazuron, bicyclopyrone, bifenox,

bilanafos, bispyribac-sodium, borax, bromacil, bromobonil, bromobutide, bromofenoxim, bromoxynil, brompyrazon, butachlor, butafenacil, butamifos, butenachlor, buthidazole, buthiuron, butralin, butroxydim, buturon, butylate, cacodylic acid, cafenstrole, calcium chlorate, calcium cyanamide, cambendichlor, carbasulam, carbetamide, carboxazole, chlorprocarb, carfentrazone-ethyl, CDEA, CEPC, chlomethoxyfen, chloramben, chloranocryl, chlorazifop, chlorazine, chlorbromuron, chlorbufam, chloreturon, chlorfenac, chlorfenprop, chlorflurazole, chlorflurenol, chloridazon, chlorimuron, chlornitrofen, chloropon, chlorotoluron, chloroxuron, chloroxynil, chlorpropham, chlorsulfuron, chlorthal, chlorthiamid, cinidon-ethyl, cinmethylin, cinosulfuron, cisanilide, clethodim, cliodinate, clodinafop-propargyl, clofop, clomazone, clomeprop, cloprop, cloproxydim, clopyralid, cloransulam-methyl, CMA, copper sulfate, CPMF, CPPC, credazine, cresol, cumyluron, cyanatryn, cyanazine, cycloate, cyclosulfamuron, cycloxydim, cycluron, cyhalofop-butyl, cyperquat, cyprazine, cyprazole, cypromid, daimuron, dalapon, dazomet, delachlor, desmedipham, desmetryn, di-allate, dicamba, dichlobenil, dichloralurea, dichlormate, dichlorprop, dichlorprop-P, diclofop, diclosulam, diethamquat, diethatyl, difenopenten, difenoxuron, difenzoquat, diflufenican, diflufenzopyr, dimefuron, dimepiperate, dimethachlor, dimethametryn, dimethenamid, dimethenamid-P, dimexano, dimidazon, dinitramine, dinofenate, dinoprop, dinosam, dinoseb, dinoterb, diphenamid, dipropetryn, diquat, disul, dithiopyr, diuron, DMPA, DNOC, DSMA, EBEP, eglinazine, endothal, epronaz, EPTC, erbon, esprocarb, ethalfluralin, ethbenzamide, ethametsulfuron, ethidimuron, ethiolate, ethobenzamid, etobenzamid, ethofumesate, ethoxyfen, ethoxysulfuron, etinofen, etnipromid, etobenzanid, EXD, fenasulam, fenoprop, fenoxaprop, fenoxaprop-P-ethyl, fenoxaprop-P-ethyl + isoxadifen-ethyl, fenoxasulfone, fenteracol, fenthiaprop, fentrazamide, fenuron, ferrous sulfate, flamprop, flamprop-M, flazasulfuron, florasulam, fluazifop, fluazifop-P-butyl, fluazolate, flucarbazone, flucetosulfuron, fluchloralin, flufenacet, flufenican, flufenpyr-ethyl, flumetsulam, flumezin, flumiclorac-pentyl, flumioxazin, flumipropyn, fluometuron, fluorodifen, fluoroglycofen, fluoromidine, fluoronitrofen, fluothiuron, flupoxam, flupropacil, flupropanate, flupyrsulfuron, fluridone, flurochloridone, fluroxypyr, flurtamone, fluthiacet, fomesafen, foramsulfuron, fosamine, furyloxyfen, glufosinate, glufosinate-ammonium, glyphosate, halosafen, halosulfuron-methyl, haloxydine, haloxyfop-methyl, haloxyfop-P-methyl, halauxifen-methyl, hexachloroacetone, hexaflurate, hexazinone, imazamethabenz, imazamox, imazapic, imazapyr, imazaquin, imazethapyr, imazosulfuron, indanofan, indaziflam, iodobonil, iodomethane, iodosulfuron, iofensulfuron, ioxynil, ipazine, ipfencarbazone, iprymidam, isocarbamid, isocil, isomethiozin, isonoruron, isopolinate, isopropalin, isoproturon, isouron, 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quizalofop-P-ethyl, rhodethanil, rimsulfuron, saflufenacil, S-metolachlor, sebuthylazine, secbumeton, sethoxydim, siduron, simazine, simeton, simetryn, SMA, sodium arsenite, sodium azide, sodium chlorate, sulcotrione, sulfallate, sulfentrazone, sulfometuron, sulfosate, sulfosulfuron, sulfuric acid, sulglycapin, swep, TCA, tebutam, tebuthiuron, tefuryltrione, tembotrione, tepraloxydim, terbacil, terbucarb, terbuchlor, terbumeton, terbuthylazine, terbutryn, tetrafluron, thenylchlor, thiazafluron, thiazopyr, thidiazimin, thidiazuron, thiencarbazone-methyl, thifensulfuron, thiobencarb, tiocarbazil, tioclorim, topramezone, tralkoxydim, triafamone, tri-allate, triasulfuron, triaziflam, tribenuron, tricamba, triclopyr esters and amines, tridiphane, trietazine, trifloxysulfuron, trifluralin, triflusulfuron, trifop, trifopsime, trihydroxytriazine, trimeturon, tripropindan, tritac, tritosulfuron, vernolate and xylachlor.

[0074] The compounds and compositions of the present disclosure can generally be employed in combination with known herbicide safeners, such as benoxacor, benthiocarb, brassinolide, cloquintocet (e.g., mexyl), cyometrinil, daimuron, dichlormid, dicyclonon, dimepiperate, disulfoton, fenchlorazole-ethyl, fenclorim, flurazole, fluxofenim, furilazole, harpin proteins, isoxadifen-ethyl, mefenpyr-diethyl, MG 191, MON 4660, naphthalic anhydride (NA), oxabetrinil, R29148 and N-phenylsulfonylbenzoic acid amides, to enhance their selectivity.

[0075] The compounds, compositions, and methods described herein be used to control undesirable vegetation on glyphosate-tolerant-, glufosinate-tolerant-, dicamba-tolerant-, phenoxy auxin-tolerant-, pyridyloxy auxin-tolerant-,

aryloxyphenoxypropionate-tolerant-, acetyl CoA carboxylase (ACCase) inhibitor-tolerant-, imidazolinone-tolerant-, acetolactate synthase (ALS) inhibitor-tolerant-, 4-hydroxyphenyl-pyruvate dioxygenase (HPPD) inhibitor-tolerant-, protoporphyrinogen oxidase (PPO) inhibitor-tolerant-, triazine-tolerant-, and bromoxynil-tolerant- crops (such as, but not limited to, soybean, cotton, canola/oilseed rape, rice, cereals, corn, turf, etc), for example, in conjunction with glyphosate, glufosinate, dicamba, phenoxy auxins, pyridyloxy auxins, aryloxyphenoxypropionates, ACCase inhibitors, imidazolinones, ALS inhibitors, HPPD inhibitors, PPO inhibitors, triazines, and bromoxynil. The compositions and methods may be used in controlling undesirable vegetation in crops possessing multiple or stacked traits conferring tolerance to multiple chemistries and/or inhibitors of multiple modes-of-action.

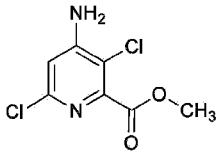
[0076] The compounds and compositions provided herein may also be employed to control herbicide resistant or tolerant weeds. Exemplary resistant or tolerant weeds include, but are not limited to, biotypes resistant or tolerant to acetolactate synthase (ALS) inhibitors, photosystem II inhibitors, acetyl CoA carboxylase (ACCase) inhibitors, synthetic auxins, photosystem I inhibitors, 5-enolpyruvylshikimate-3-phosphate (EPSP) synthase inhibitors, microtubule assembly inhibitors, lipid synthesis inhibitors, protoporphyrinogen oxidase (PPO) inhibitors, carotenoid biosynthesis inhibitors, very long chain fatty acid (VLCFA) inhibitors, phytoene desaturase (PDS) inhibitors, glutamine synthetase inhibitors, 4-hydroxyphenyl-pyruvate-dioxygenase (HPPD) inhibitors, mitosis inhibitors, cellulose biosynthesis inhibitors, herbicides with multiple modes-of-action such as quinclorac, and unclassified herbicides such as arylaminopropionic acids, difenzoquat, endothall, and organoarsenicals. Exemplary resistant or tolerant weeds include, but are not limited to, biotypes with resistance or tolerance to multiple herbicides, multiple chemical classes, and multiple herbicide modes-of-action.

[0077] The described embodiments and following examples are for illustrative purposes.

SYNTHESIS OF PRECURSORS

Preparation 1: Methyl 4-amino-3,6-dichloropicolinate (Head A)

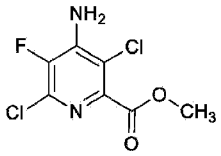
[0078]



[0079] Prepared as described in Fields et al., WO 2001051468 A1.

Preparation 2: Methyl 4-amino-3,6-dichloro-5-fluoropicolinate (Head B)

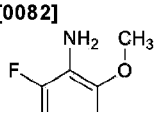
[0080]

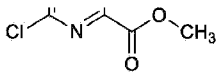


[0081] Prepared as described in Fields et al., Tetrahedron Letters 2010, 511, 79-81.

Preparation 3: Methyl 4-amino-6-chloro-5-fluoro-3-methoxypicolinate (Head F)

[0082]

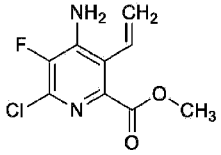




[0083] Prepared as described in Epp et al., WO 2013003740 A1.

Preparation 4: Methyl 4-amino-6-chloro-5-fluoro-3-vinylpicolinate (Head G)

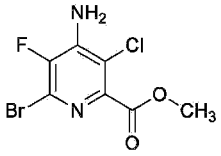
[0084]



[0085] Methyl 4-amino-6-chloro-5-fluoro-3-iodopicolinate (7.05 g, 21.33 mmol, prepared as described in Epp et al., WO 2013003740 A1) and vinyltri-n-butyltin (7.52 mL, 25.6 mmol) were suspended in dichloroethane (71.1 mL) and the mixture was degassed with Argon for 10 min. Bis(triphenylphosphine)palladium(II) chloride (1.497 g, 2.133 mmol) was then added, and the reaction mixture was stirred at 70 °C overnight (clear orange solution). The reaction was monitored by gas chromatography-mass spectrometry (GC-MS). After 20 h, the reaction mixture was concentrated, adsorbed onto Celite, and purified by column chromatography (silica gel (SiO_2), hexanes/ethyl acetate gradient) to afford the title compound (3.23 g, 65.7 %) as a light brown solid: mp 99-100°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (dd, *J* = 18.1, 11.6 Hz, 1H), 5.72 (dd, *J* = 11.5, 1.3 Hz, 1H), 5.52 (dd, *J* = 18.2, 1.3 Hz, 1H), 4.79 (s, 2H), 3.91 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -138.79 (s); EIMS *m/z* 230.

Preparation 5: Methyl 4-amino-6-bromo-3-chloro-5-fluoropicolinate (Head I)

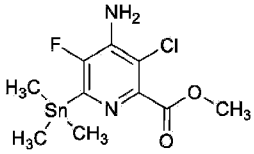
[0086]



[0087] Prepared as described in Arndt et al., US 20120190857 A1.

Preparation 6: Methyl 4-amino-3-chloro-5-fluoro-6-(trimethylstannyl)picolinate (Head J)

[0088]

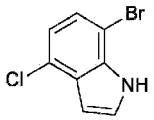


[0089] Methyl 4-amino-6-bromo-3-chloro-5-fluoropicolinate (500 mg, 1.8 mmol), 1,1,1,2,2,2-hexamethyldistannane (580 mg, 1.8 mmol) and bis(triphenylphosphine)-palladium(II) chloride (120 mg, 0.18 mmol) were combined in dry dioxane (6 mL), sparged with a stream of nitrogen for 10 min and then heated to 80 °C for 2 h. The cooled mixture was stirred with ethyl acetate (25 mL) and saturated NaCl (25 mL) for 15 min. The organic phase was separated, filtered through diatomaceous earth, dried (Na_2SO_4) and evaporated. The residue was taken up in ethyl acetate (4 mL), stirred and treated in portions with hexane (15 mL). The milky white solution was decanted from any solids produced, filtered through glass wool and

evaporated to give the title compound as an off-white solid (660 mg, 100%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.63 (d, *J* = 29.1 Hz, 1H), 3.97 (s, 2H), 0.39 (s, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -130.28; EIMS *m/z* 366.

Preparation 7: 7-Bromo-4-chloro-1*H*-indole

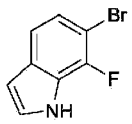
[0090]



[0091] To a solution of 1-bromo-4-chloro-2-nitrobenzene (932 mg, 3.95 mmol) in tetrahydrofuran (10 mL), vinylmagnesium bromide (0.7 M in tetrahydrofuran; 12 mmol) in tetrahydrofuran (15 mL) was added drop wise at -40 °C. After 1 h the reaction mixture was poured into saturated ammonium chloride (NH_4Cl). The resulting organic layer was concentrated. The resulting residue was purified using a Teledyne ISCO chromatography system with a gradient eluent system of 2% ethyl acetate in hexane to yield the title compound (400 mg, 44%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.73 (t, *J* = 2.8 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 7.19 - 7.39 (m, 2H), 8.43 (s, 1H).

Preparation 8: 6-Bromo-7-fluoro-1H indole

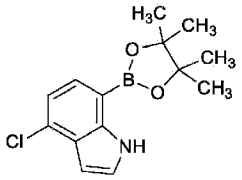
[0092]



[0093] 6-Bromo-7-fluoro-1*H*-indole was prepared from 1-bromo-2-fluoro-3-nitrobenzene as described in Preparation 7 (250 mg, 25.2%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.52 - 6.62 (m, 1H), 7.13 - 7.34 (m, 3H), 8.38 (s, 1H); ESIMS *m/z* 215.0 ($[M+H]^+$).

Preparation 9 (Precursor Example 1): 4-Chloro-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole

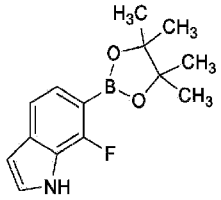
[0094]



[0095] To a solution of 7-bromo-4-chloro-1*H*-indole (8 g, 0.03 mol) in dioxane, KOAc (9.8 g, 0.1 mol), dichloro[1,1'-bis(diphenylphosphino)ferrocene]-palladium(II) (2.19 g, 0.003 mol), and 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (13.2 g, 0.052 mol) were charged as solids. The reaction mixture was placed under inert atmosphere and the flask was sealed. The reaction was heated to 100 °C for 16 h. The reaction mixture was then treated with H_2O and extracted with ethyl acetate. The organic layer was partitioned and concentrated. The resulting residue was purfied using a Teledyne ISCO chromatography system with a gradient eluent system of ethyl acetate in hexane to yield the title compound (1.3 g, 15.6%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 12H), 6.58 - 6.73 (m, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.28 - 7.36 (m, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 9.34 (s, 1H).

Preparation 10 (Precursor Example 2): 7-Fluoro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole

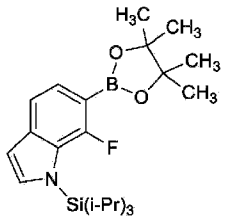
[0096]



[0097] 7-Fluoro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole was prepared as described in Preparation 9 from 6-bromo-7-fluoro-1*H*-indole (150 mg, 45.5%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (s, 25H), 1.39 (s, 24H), 7.27 (d, *J* = 4.5 Hz, 2H), 7.40 (d, *J* = 2.6 Hz, 2H), 8.43 (s, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -124.52; ^{13}C NMR (101 MHz, $CDCl_3$) δ 24.87 (d, *J* = 15.9 Hz), 77.30 , 83.49 (d, *J*= 6.9 Hz), 103.25, 115.98 (d, *J* = 3.3 Hz), 126.08 (d, *J* = 7.7 Hz).

Preparation 11 (Precursor Example 3): 7-Fluoro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(triisopropylsilyl)-1*H*-indole

[0098]

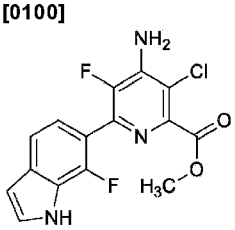


[0099] 7-Fluoro-1-(triisopropylsilyl)-1*H*-indole (4.0 g, 14 mmol) (Prepared according to M. Schlosser, et al., Eur. J. Org. Chem. 2006, 2956-2969) was dissolved in 30 mL dry THF, cooled to -75 °C, treated in portions with sec-butyl lithium (10 mL, 1.4 M, 14 mmol) and stirred for 2 h at -75 °C. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.0 mL, 2.7 g, 14 mmol) was added in portions and the mixture was stirred for 1 h at -75 °C. The cooling bath was removed and the temperature was allowed to rise to 5 °C over 30 min. The reaction was quenched by addition of 5 mL saturated NH_4Cl and partitioned between ethyl acetate and water. The organic phase was washed with saturated sodium chloride (NaCl), dried (Na_2SO_4), evaporated onto silica gel, and purified by flash chromatography (SiO_2; eluting with hexanes) to give the title compound as a thick oil (4.2 g, 73%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 7.9, 4.6 Hz, 1H), 7.38 (m, 2H), 1.75 (m, 3H), 1.38 (s, 12H), 1.13 (d, *J* = 7.6 Hz, 18H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.07; EIMS *m/z* 417.

EXAMPLES OF SYNTHESIS OF COMPOUNDS OF THE CLAIMED FORMULA

Example 1. Methyl 4-amino-3-chloro-5-fluoro-6-(7-fluoro-1H-indol-6-yl)picolinate (Compound No. 1.15)

[0100]



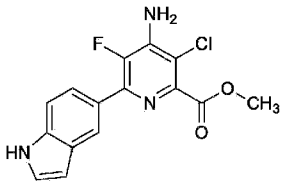
[0101] Methyl 4-amino-3,6-dichloro-5-fluoropicolinate (0.650 g, 2.72 mmol), 7-fluoro-6-(4,4,5,5-tetramethyl-1,3,2-

dioxaborolan-2-yl)-1*H*-indole (0.817 g, 3.13 mmol), bis(triphenylphosphine)palladium(II) chloride (0.191 g, 0.272 mmol), and cesium fluoride (0.826 g, 5.44 mmol) were combined in acetonitrile (4.53 mL) and water (4.53 mL). The reaction mixture was irradiated in a Biotage Initiator microwave at 110 °C in a sealed vial for 30 min. The cooled reaction mixture was partitioned between ethyl acetate and water. The organic phase was dried and concentrated. The product was purified by flash chromatography (SiO_2; eluting with 5-40% ethyl acetate in hexanes) to provide the title compound as an white solid (0.517 g, 52.4 % yield). Note: Potassium fluoride replaced cesium fluoride in some examples that refer to this particular example.

[0102] The preparation method used in this example is referred to in Table 2 as "Coupling 1".

Example 2: Methyl 4-amino-3-chloro-5-fluoro-6-(1*H*-indol-5-yl)picolinate (Compound No. 1.2)

[0103]

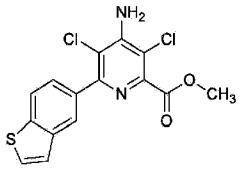


[0104] 1*H*-Indol-5-ylboronic acid (220 mg, 1.4 mmol, 1.1 equiv) and methyl 4-amino-3,6-dichloro-5-fluoropicolinate (300 mg, 1.3 mmol, 1.0 equiv) were sequentially added to a 5 mL Biotage microwave vessel, followed by cesium fluoride (380 mg, 2.5 mmol, 2.0 equiv), palladium(II) acetate (14 mg, 0.063 mmol, 0.05 equiv), and sodium 3,3',3"-phosphinetriyltribenzenesulfonate (71 mg, 0.13 mmol, 0.10 equiv). A 3:1 mixture of water:acetonitrile (2.5 mL) was added and the resulting dark brown mixture was placed in a Biotage microwave and heated to 150 °C for 5 min, with external IR-sensor temperature monitoring from the side of the vessel. The cooled reaction mixture was diluted with water (50 mL) and extracted with dichloromethane (15 x 30 mL). The combined organic layers were dried (sodium sulfate), gravity filtered, and concentrated by rotary evaporation. The residue was purified by reverse phase column chromatography (5% acetonitrile to 100% acetonitrile gradient) to yield the title compound as a tan powder (290 mg, 73%).

[0105] The preparation method used in this example is referred to in Table 2 as "Coupling 2".

Example 3: Methyl 4-amino-6-(benzo[6]thiophenyl-5-yl)-3,5-dichloropicolinate (Compound No. 3.01- not according to the claimed formula)

[0106]

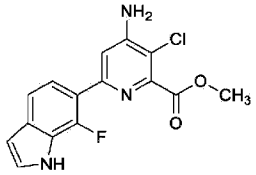


[0107] To a 5 mL microwave vial was added methyl 4-amino-3,5,6-trichloropicolinate (0.232 g, 0.909 mmol), 2-(benzo[*b*]thiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.260 g, 0.999 mmol), cesium fluoride (0.276 g, 1.817 mmol) and $(PPh_3)_2PdCl_2$ (0.064 g, 0.091 mmol). The reaction vial was then sealed and placed under inert atmosphere. Subsequently, dioxane (4.0 mL) and H_2O (1.0 mL) were added and the reaction mixture was heated in a Biotage microwave at 120 °C for 60 min, with external IR-sensor temperature monitoring from the side of the vessel. The reaction mixture was cooled to room temperature and diluted with ethyl acetate (5 mL) and poured into brine solution. The layers were separated and the aqueous phase was extracted with ethyl acetate (3 x 10 mL). The organic extracts were combined, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude product was purified using a Teledyne ISCO purification system with a gradient eluent system of ethyl acetate and hexanes. Further purification was performed, as needed, using a Teledyne ISCO reverse phase system with a gradient eluent system of acetonitrile and H_2O to yield the title compound as a white solid.

[0108] The preparation method used in this example is referred to in Table 2 as "Coupling 4".

Example 4: Methyl 4-amino-3-chloro-6-(7-fluoro-1H indol-6-yl)picolinate (Compound No. 1.23 - comparative example, not according to the claimed formula)

[0109]

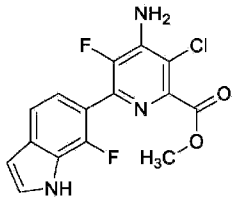


[0110] Methyl 4-acetamido-3,6-dichloropicolinate (400 mg, 1.520 mmol),7-fluoro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (437 mg, 1.673 mmol), cesium fluoride (462 mg, 3.04 mmol), and $(PPh_3)_2PdCl_2$ (107 mg, 0.152 mmol) were charged as solids into a microwave reaction vessel and dioxane (4 mL) and water (1 mL) were added. The reaction vessel was sealed and irradiated in a Biotage Initiator microwave at 110 °C for 2 h, with external IR-sensor temperature monitoring from the side. The reaction mixture was partitioned between ethyl acetate and water. The organic phase was filtered and concentrated. The intermediate product was purified by flash chromatography (ISCO 40 g silica 10-75% EtOAc: Hexanes 16 CV). Fractions containing product were combined and concentrated to give 524 mg of a white solid intermediate methyl 4-acetamido-3-chloro-6-(7-fluoro-1*H*-indol-6-yl)picolinate (0.524 g, 1.448 mmol) which was subsequently diluted with methanol (10.0 mL). Then acetyl chloride (0.725 mL, 10.20 mmol) was added. The reaction mixture was allowed to stir at room temperature for 18 h. The reaction mixture was concentrated to dryness. The resulting residue was dissolved in ethyl acetate and poured into saturated $NaHCO_3$ solution. The layers were partitioned and the aqueous layer was extracted with ethyl acetate (3 x 15 mL). The organic extracts were combined, washed with saturated NaCl solution, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was purified using a Teledyne ISCO purification system with a gradient eluent system of ethyl acetate and hexanes to yield the title compound as a white solid (365 mg, 79%).

[0111] The preparation method used in this example is referred to in Table 2 as "Coupling 6".

Example 5: Methyl 4-amino-3-chloro-5-fluoro-6-(7-fluoro-1*H*-indol-6-yl)picolinate (Compound No. 1.15)

[0112]

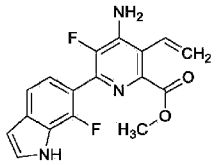


[0113] 7-Fluoro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(triisopropylsilyl)-1*H*-indole (500 mg, 1.2 mmol), methyl 4-amino-3,6-dichloro-5-fluoropicolinate (290 mg, 1.2 mmol), cesium fluoride (360 mg, 2.4 mmol) and bis(triphenylphosphine)palladium(II) chloride (84 mg, 0.12 mmol) were combined in 4 mL of a 1:1 v/v acetonitrile-water mixture and heated at 115 °C for 25 min in a Biotage Initiator microwave reactor. The mixture was partitoned between ethyl acetate and saturated NaCl and the organic phase was dried and evaporated. Purification by flash chromatography (SiO_2; eluting with 0-20% ethyl acetate in dichloromethane) provided impure product. The material was purified by flash chromatography again (SiO_2; eluting with 0-30% ethyl acetate in hexanes) to provide the title compound as a white solid (220 mg, 52%).

[0114] The preparation method used in this example is referred to in Table 2 as "Coupling 8".

Example 6: Methyl 4-amino-5-fluoro-6-(7-fluoro-1*H*-indol-6-yl)-3-vinylpicolinate (Compound No. 1.18)

[0115]

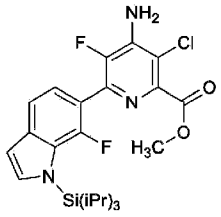


[0116] 7-Fluoro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(triisopropylsilyl)-1*H*-indole (320 mg, 0.77 mmol), methyl 4-amino-6-chloro-5-fluoro-3-vinylpicolinate (190 mg,0.84 mmol), sodium carbonate (81 mg, 0.77 mmol) and bis(triphenylphosphine)palladium(II) chloride (54 mg, 0.08 mmol) were combined in 4 mL of a 1:1 v/v acetonitrile-water mixture and heated to 115 °C for 30 min in a Biotage Initiator microwave reactor. The mixture was partitioned between ethyl acetate and water. The organic phase was washed with saturated NaCl, dried (Na_2SO_4), and evaporated. Purification by flash chromatography (SiO_2; eluting with 0-20% ethyl acetate in hexanes) provided 220 mg of the TIPS protected product. This material was dissolved in 10 mL of THF, treated with tetrabutylammonium fluoride hydrate (260 mg, 1.0 mmol) and stirred for 1 h. The mixture was partitioned between saturated NaCl and ethyl acetate. The organic phase was washed with saturated NaCl, dried (Na_2SO_4), and evaporated. Purification by flash chromatography (SiO_2; eluting with 0-20% ethyl acetate in hexanes) provided the title compound as a white solid (100 mg, 37%).

[0117] The preparation method used in this example is referred to in Table 2 as "Coupling 9".

Example 7: Preparation of methyl 4-amino-3-chloro-5-fluoro-6-(7-fluoro-1-(triisopropylsilyl)-1*H*-indol-6-yl)picolinate (Compound 1.12)

[0118]

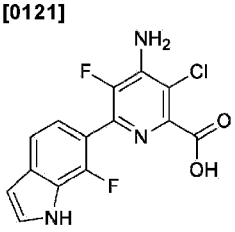


[0119] 7-Fluoro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(triisopropylsilyl)-1*H*-indole (1.0 g, 2.4 mmol), methyl 4-amino-3,6-dichloro-5-fluoropicolinate (630 mg, 2.6 mmol), sodium carbonate (250 mg, 2.4 mmol) and with bis(triphenylphosphine)palladium(II) chloride (170 mg, 0.24 mmol) were combined in 10 mL of 1:1 v/v acetonitrile-water and heated at 110 °C for 30 min in a Biotage Initiator microwave reactor. The mixture was stirred with 30 mL ethyl acetate and 20 mL water and filtered through glass wool to remove dark solids. The organic phase was washed with saturated NaCl, dried (Na_2SO_4), and evaporated. Purification by flash chromatography (SiO_2; eluting with 0-30% ethyl acetate in hexanes) provided the title compound as a white solid (520 mg; 42%).

[0120] The preparation method used in this example is referred to in Table 2 as "Coupling 10".

Example 8: 4-Amino-3-chloro-5-fluoro-6-(7-fluoro-1H indol-6-yl)picolinic acid (Compound 1.16)

[0121]

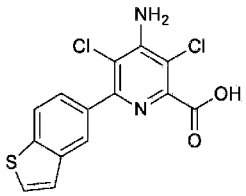


[0122] To a reaction vessel containing methyl 4-amino-3-chloro-5-fluoro-6-(7-fluoro-1*H*-indol-6-yl)picolinate (0.500 g, 1.481 mmol) was added methanol (14.81 mL) and sodium hydroxide (2.96 mL, 5.92 mmol). The reaction mixture was stirred overnight at RT then acidfied by adding a slight excess of 2 N HCl. The mixture was concentrated and the precipitate that formed was washed with water and dried under vacuum to provide 4-amino-3-chloro-5-fluoro-6-(7-fluoro-1*H*-indol-6-yl)picolinic acid (0.400 g, 79% yield) as an off-white solid.

[0123] The preparation method used in this example is referred to in Table 2 as "Hydrolysis 1".

Example 9: 4-Amino-6-(benzo[b]thiophen-5-yl)-3,5-dichloropicolinic acid (Compound 3.02 - not according to the claimed formula)

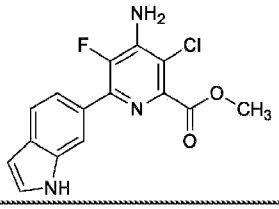
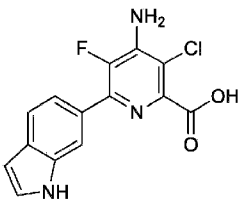
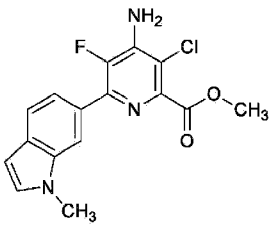
[0124]

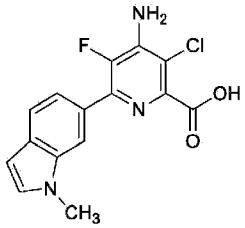
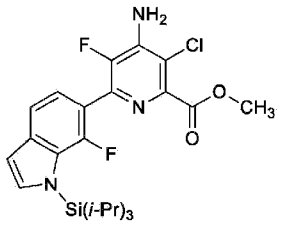
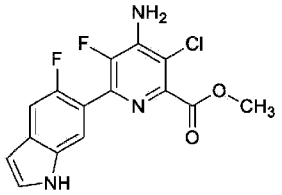
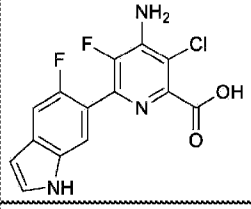
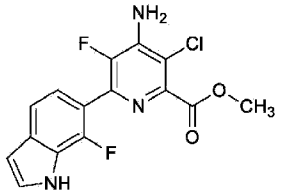
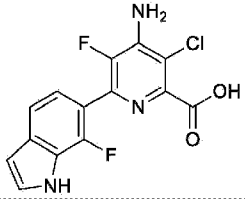
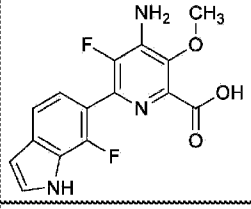
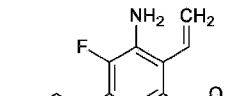


[0125] In a 100 mL round bottom flask, methyl 4-amino-6-(benzo[b]thiophen-5-yl)-3,5-dichloropicolinate (210 mg, 0.595 mmol) was dissolved in methanol (2.3 mL), tetrahydrofuran (2.3 mL), and H_2O (1.2 mL). Lithium hydroxide hydrate (74.8 mg, 1.784 mmol) was added as a solid. The reaction mixture was stirred at room temperature until complete. The reaction mixture was concentrated to dryness. The resulting residue was dissolved in H_2O (2.0 mL) and 1 N HCl was used to adjust the pH to 3.0, causing a precipitate to form. This suspension was extracted with ethyl acetate (3 x 15 mL). The organic extracts were combined, washed with saturated NaCl solution, dried ($MgSO_4$), filtered and concentrated. Additional purification of the resulting solid was performed, as needed, using a Teledyne ISCO reverse phase system with a gradient eluent system of acetonitrile and H_2O to yield the title compound as a white solid (110 mg, 55%).

[0126] The preparation method used in this example is referred to in Table 2 as "Hydrolysis 2".

Table 2. Compound Number, Structure, Appearance, and Preparation Method

Compound Number	Structure	Appearance	Preparation Method:	Precursor(s)
1.08*		Off-White Foam	Coupling 2	Head B; 1*H*-Indol-6-ylboronic acid
1.09*		White Powder	Hydrolysis 1	Compound 1.08
1.10*		Tan Powder	Coupling 2	Head B; 1-Methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole

Compound Number	Structure	Appearance	Preparation Method:	Precursor(s)
1.11*		Pale Yellow Powder	Hydrolysis 1	Compound 1.10
1.12		White Solid	Coupling 10	Head B
1.13*		Off-White Solid	Coupling 4	Head B; 5-fluoro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole
1.14*		Tan Solid	Hydrolysis 2	Compound 1.13
1.15		White Solid	Coupling 4	Head B; 7-fluoro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole
1.16		Tan Solid	Hydrolysis 2	Compound 1.15
1.17		White Solid	Hydrolysis 1	Compound 1.20
1.18		White Solid	Coupling 9	Head G

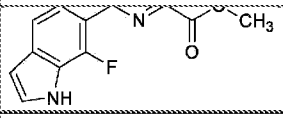
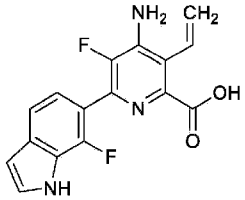
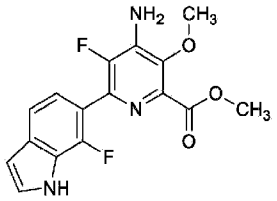
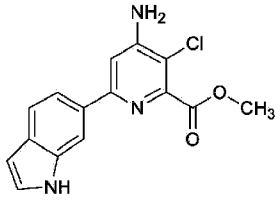
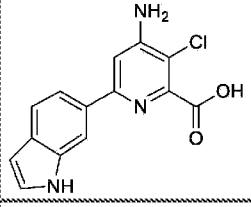
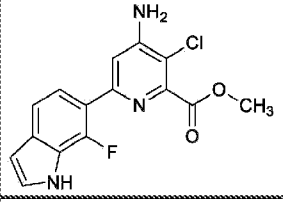
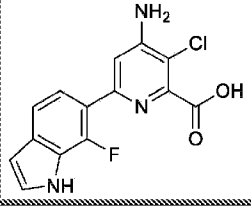
Compound Number	Structure	Appearance	Preparation Method:	Precursor(s)
				
1.19		Tan Solid	Hydrolysis 1	Compound 1.18
1.20		White Solid	Coupling 8	Head F
1.21*		White Solid	Coupling 1	Head A, (1H-indol-6-yl)boronic acid
1.22*		Orange Solid	Hydrolysis 1	Compound 1.21
1.23*		White Solid	Coupling 6	As described
1.24*		Yellow Solid	Hydrolysis 2	Compound 1.23
* Comparative Example				

Table 3. Analytical Data for Compounds in Table 1

C. No.	MP (°C)	^{1}H NMR
1.08*	66-69	^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (br s, 1H), 8.02 (s, 1H), 7.71 (s, 2H), 7.29 (t, *J* = 3 Hz, 1H), 6.58 (m, 1H), 4.86 (br s, 2H), 3.99 (s, 3H)
1.09	138-140	^{1}H NMR (300 MHz, DMSO-d_6) δ 7.95 (s, 1H), 7.63 (d, *J* = 8 Hz, 1H), 7.54 (dt, *J* = 8, 2 Hz, 1H), 7.47 (t, *J* = 3 Hz, 1H), 6.79 (br s, 2H), 6.48 (m, 1H)

C. No.	MP (°C)	^{1}H NMR
1.10*	116-119	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (t, *J* = 1 Hz, 1H), 7.69 (br s, 2H), 7.13 (d, *J* = 3 Hz, 1H), 6.50 (dd, *J* = 3, 1 Hz, 1H), 4.85 (br s, 2H), 3.99 (s, 3H), 3.84 (s, 3H)
1.11*	173-176	^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93 (s, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.46 (d, *J* = 3 Hz, 1H), 6.50 (d, *J* = 3 Hz, 1H), 6.37 (br s, 2H), 3.87 (s, 3H)
1.12	181-182	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.1 Hz, 1H), 7.40 (d, *J* = 3.2 Hz, 1H), 7.29 (dd, *J* = 8.1, 5.9 Hz, 1H), 4.90 (s, 2H), 3.98 (s, 3H), 1.68 (m, 3H), 1.14 (d, *J* = 7.6 Hz, 18H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.55, - 124.65, -136.90, -137.00. ESIMS *m/z* 492 [$(M-H)^-$].
1.13*		^{1}H NMR (DMSO-d_6) δ 3.88 (s, 3H), 6.49 (ddd, *J* = 2.9, 1.9, 0.8 Hz, 1H), 6.96 (s, 2H), 7.43 (d, *J* = 11.1 Hz, 1H), 7.50 (d, *J* = 6.0 Hz, 1H), 7.54 (t, *J* = 2.8 Hz, 1H), 11.32 (s, 1H)
1.14*		^{1}H NMR (DMSO-d_6) δ 6.46 - 6.52 (m, 1H), 6.88 (s, 2H), 7.42 (d, *J*= 11.1 Hz, 1H), 7.49 - 7.56 (m, 2H), 11.33 (s, 1H), 13.56 (s, 1H)
1.15		^{1}H NMR (DMSO-d_6) δ 3.88 (s, 3H), 6.59 (td, *J* = 3.2, 1.9 Hz, 1H), 6.99 (s, 2H), 7.08 (dd, *J* = 8.2, 6.2 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.52 (t, *J* = 2.8 Hz, 1H), 11.82 (t, *J* = 2.2 Hz, 1H)
1.16		^{1}H NMR (DMSO-d_6) δ 6.59 (td, *J* = 3.2, 1.9 Hz, 1H), 6.90 (s, 2H), 7.10 (dd, *J* = 8.2, 6.2 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.51 (t, *J* = 2.8 Hz, 1H), 11.81 (s, 1H), 13.57 (s, 1H)
1.17	133-140	^{1}H NMR (400 MHz, DMSO-d_6) δ 11.76 (s, 1H), 7.49 (dd, *J* = 3.0, 2.5 Hz, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.09 (dd, *J* = 8.2, 6.2 Hz, 1H), 6.57 (td, *J* = 3.3, 1.9 Hz, 1H), 6.41 (s, 2H), 3.80 (s, 3H). ^{19}F NMR (376 MHz, DMSOd_6) δ -134.66, -134.73. ESIMS *m/z* 320 [$(M+H)^+$].
1.18	164-166	^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.49 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.35 - 7.28 (m, 2H), 6.94 (dd, *J* = 18.1, 11.5 Hz, 1H), 6.61 (td, *J* = 3.4, 2.1 Hz, 1H), 5.72 (dd, *J* = 11.5, 1.5 Hz, 1H), 5.60 (dd, *J* = 18.1, 1.5 Hz, 1H), 4.72 (s, 2H), 3.91 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -135.79, -135.87, -140.98, -141.07. ESIMS *m/z* 330 [$(M+H)^+$].
1.19		^{1}H NMR (400 MHz, DMSO-d_6) δ 11.76 (d, *J* = 16.4 Hz, 1H), 7.48 (m, 1H), 7.11 (dd, *J* = 8.2, 6.2 Hz, 1H), 6.79 (dd, *J* = 17.8, 11.5 Hz, 1H), 6.58 (dd, *J* = 5.1, 3.2 Hz, 1H), 6.38 (s, 1H), 5.56 (m, 1H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -134.07, -134.15, -143.26, -143.34. ESIMS *m/z* 316 [$(M+H)^+$].
1.20	203-205	^{1}H NMR (400 MHz, DMSO-d_6) δ 11.76 (s, 1H), 7.49 (dd, *J* = 6.0, 3.3 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.05 (dd, *J* = 8.1, 6.3 Hz, 1H), 6.57 (m, 1H), 6.49 (s, 2H), 3.84 (s, 3H), 3.79 (s, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ - 134.75, -134.82, -138.34, -138.42. ESIMS *m/z* 334 [$(M+H)^+$].
1.21*	83-85	^{1}H NMR (400 MHz, DMSO-d_6) δ 11.20 (s, 1H), 8.00 (m, 1H), 7.59 (m, 1H), 7.53 (m, 1H), 7.43 (dd, *J* = 3.1, 2.4 Hz, 1H), 7.32 (s, 1H), 6.61 (s, 2H), 6.45 (s, 1H), 3.91 (s, 3H)
1.22*	172-174	^{1}H NMR (400 MHz, DMSO-d_6) δ 11.47 (s, 1H), 7.94 (d, *J* = 1.2 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.52 (t, *J* = 2.8 Hz, 1H), 7.46 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.51 (t, *J* = 2.5 Hz, 1H), NaN (m, 2H)
1.23*		^{1}H NMR (DMSO-d_6) δ 3.89 (s, 3H), 6.54 (td, *J* = 3.4, 1.9 Hz, 1H), 6.75 (s, 2H), 7.31 (d, *J* = 1.5 Hz, 1H), 7.37 - 7.52 (m, 3H), 11.76 (s, 1H)
1.24*		^{1}H NMR (DMSO-d_6) δ 6.50 - 6.62 (m, 1H), 6.71 (s, 2H), 7.27 (d, *J*= 1.5 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.45 - 7.53 (m, 2H), 11.76 (d, *J*= 2.4 Hz, 1H), 13.48 (s, 1H)
* Comparative Example		

Table 4: Percent Control Rating Conversion Table

Rating	% Visual Growth Reduction
A	95-100
B	85-94
C	75-84
D	60-74
E	45-59
F	30-44
G	0-29

Example C. Evaluation of Postemergent Herbicidal Activity

[0127] Post-emergent Test II: Seeds or nutlets of the desired test plant species were planted in Sun Gro Metro-Mix® 360 planting mixture, which typically has a pH of 6.0 to 6.8 and an organic matter content of about 30 percent, in plastic pots with a surface area of 64 square centimeters (cm^2). When required to ensure good germination and healthy plants, a fungicide treatment and/or other chemical or physical treatment was applied. The plants were grown for 7-21 d in a greenhouse with an approximate 15 h photoperiod which was maintained at about 23-29 °C during the day and 22-28 °C during the night. Nutrients and water were added on a regular basis and supplemental lighting was provided with overhead metal halide 1000-Watt lamps as necessary. The plants were employed for testing when they reached the first or second true leaf stage.

[0128] A weighed amount, determined by the highest rate to be tested, of each test compound was placed in a 25 mL glass vial and was dissolved in 4 mL of a 97:3 v/v mixture of acetone and DMSO to obtain concentrated stock solutions. If the test compound did not dissolve readily, the mixture was warmed and/or sonicated. The concentrated stock solutions obtained were diluted with 20 mL of an aqueous mixture containing acetone, water, isopropyl alcohol, DMSO, Atplus 411F crop oil concentrate, and Triton® X-155 surfactant in a 48.5:39:10:1.5:1.0:0.02 v/v ratio to obtain spray solutions containing the highest application rates. Additional application rates were obtained by serial dilution of 12 mL of the high rate solution into a solution containing 2 mL of 97:3 v/v mixture of acetone and DMSO and 10 mL of an aqueous mixture containing acetone, water, isopropyl alcohol, DMSO, Atplus 411F crop oil concentrate, and Triton X-155 surfactant in a 48.5:39:10:1.5:1.0:0.02 v/v ratio to obtain 1/2X, 1/4X, 1/8X and 1/16X rates of the high rate. Compound requirements are based upon a 12 mL application volume at a rate of 187 liters per hectare (L/ha). Formulated compounds were applied to the plant material with an overhead Mandel track sprayer equipped with 8002E nozzles calibrated to deliver 187 L/ha over an application area of 0.503 square meters at a spray height of 18 inches (43 cm) above the average plant canopy height. Control plants were sprayed in the same manner with the solvent blank.

[0129] The treated plants and control plants were placed in a greenhouse as described above and watered by subirrigation to prevent wash-off of the test compounds. After 14 d, the condition of the test plants as compared with that of the untreated plants was determined visually and scored on a scale of 0 to 100 percent where 0 corresponds to no injury and 100 corresponds to complete kill. Some of the compounds tested, application rates employed, plant species tested, and results are given in Tables 5 and 6.

Table 5. Post-emergent Test II Herbicidal Activity on Key Broadleaf Weed and Crop Species

C.No.	Application Rate (g ai/ha)	Visual Growth Reduction (%) 14 Days After Application					
		ABUTH	AMARE	BRSNN	CHEAL	EPHHL	HELAN
1.08*	35	B	A	E	A	A	B
	70	A	A	C	A	A	A
	140	A	A	B	A	A	A
1.09*	35	A	A	A	A	B	A
	70	A	A	A	A	A	A
	140	A	A	A	A	A	A
1.10*	35	G	G	G	A	G	G
	70	G	B	G	A	G	G
	140	G	A	G	A	G	E

C.No.	Application Rate (g ai/ha)	Visual Growth Reduction (%) 14 Days After Application					
		ABUTH	AMARE	BRSNN	CHEAL	EPHHL	HELAN
1.13*	35	G	G	G	D	G	E
	70	G	F	G	C	G	D
	140	G	F	F	B	F	D
1.14*	35	G	C	E	D	G	D
	70	G	B	D	D	G	C
	140	G	B	C	C	D	C
1.15	35	A	A	C	A	A	A
	70	A	A	A	A	A	A
	140	A	A	A	A	A	A
1.16	35	B	A	A	A	A	A
	70	A	A	A	A	A	A
	140	A	A	A	A	A	B
1.17	35	E	A	A	A	A	A
	70	E	A	A	A	A	A
	140	D	A	A	A	A	A
1.19	35	A	A	A	A	A	D
	70	A	A	A	A	A	C
	140	A	A	A	A	A	A
1.20	35	E	C	A	A	A	A
	70	D	B	A	A	A	A
	140	D	A	A	A	A	A
1.21*	35	D	G	G	E	C	E
	70	D	G	G	B	B	C
	140	D	E	D	B	A	C
1.22*	35	G	C	E	G	E	C
	70	G	C	D	G	C	B
	140	G	B	D	G	B	B
1.23*	35	A	A	D	A	A	D
	70	A	A	C	A	A	C
	140	A	A	B	A	A	B
1.24*	35	B	A	B	B	A	D
	70	A	A	E	A	A	C
	140	A	A	A	A	A	B

* Comparative Example
ABUTH: velvetleaf (*Abutilon theophrasti*)
AMARE: redroot pigweed (*Amaranthus retroflexus*)
BRSNN: oilseed rape, canola (*Brassica napus)*
CHEAL: lambsquarters (*Chenopodium album*)
EPHHL: wild poinsettia (*Euphorbia heterophylla*)
HELAN: sunflower (*Helianthus annuus*)
g ai/ha: grams active ingredient per hectare
n/t: not tested

Table 6. Post-emergent Test II Herbicidal Activity on Key Grass and Sedge Weeds as well as Grass Crops

C. No.	Application Rate (g ai/ha)	Visual Growth Reduction (%) 14 Days After Application					
		CYPES	ECHCG	SETFA	ORYSA	TRZAS	ZEAMX
1.08*	35	G	B	G	G	G	E
	70	G	A	D	G	G	C

C. No.	Application Rate (g ai/ha)	Visual Growth Reduction (%) 14 Days After Application					
		CYPES	ECHCG	SETFA	ORYSA	TRZAS	ZEAMX
	140	G	A	C	G	F	B
1.09*	35	F	A	B	G	G	D
	70	C	A	B	G	G	C
	140	B	A	B	G	G	C
1.10*	35	G	G	G	G	G	G
	70	G	G	G	G	G	G
	140	G	G	G	G	G	G
1.12	35	G	G	C	G	E	G
	70	G	G	D	G	G	G
	140	G	B	C	G	G	G
1.13*	35	G	G	G	G	G	G
	70	G	G	G	G	G	G
	140	G	G	G	G	G	G
1.14*	35	G	G	G	G	G	G
	70	G	G	G	G	G	G
	140	G	G	G	G	G	G
1.15	35	G	C	D	G	E	G
	70	D	B	D	G	D	F
	140	E	A	B	F	D	D
1.16	35	G	C	D	F	F	G
	70	D	B	C	D	D	F
	140	B	A	B	D	D	D
1.17	35	E	B	C	G	D	D
	70	E	B	B	G	D	C
	140	E	B	B	G	D	C
1.19	35	B	B	D	F	D	D
	70	C	B	C	E	C	D
	140	A	A	B	D	C	B
1.20	35	G	G	E	G	G	F
	70	G	D	C	G	E	E
	140	G	C	B	G	D	D
1.21*	35	G	G	n/t	G	G	G
	70	G	G	n/t	G	G	G
	140	G	G	n/t	G	G	G
1.22*	35	G	G	G	G	G	G
	70	G	G	D	G	G	G
	140	G	G	B	G	G	G
1.23*	35	G	G	G	G	G	G
	70	G	G	G	G	G	G
	140	G	D	D	G	F	G
1.24*	35	G	G	G	G	G	G
	70	G	G	E	G	F	G
	140	G	G	D	G	E	G

ECHCG: barnyardgrass (*Echinochloa crus-galli*)
CYPES: yellow nutsedge (*Cyperus esculentus*)

ORYSA: rice (*Oryza sativa*)
SETFA: giant foxtail (*Setaria faberi*)
TRZAS: wheat, spring (*Triticum aestivum*)
ZEAMX: maize, corn (*Zea mays*)
g ai/ha: grams active ingredient per hectare
n/t: not tested

Example D. Evaluation of Postemergent Herbicidal Activity in Wheat and Barley

[0130] Post-emergent Test III. Seeds of the desired test plant species were planted in Sun Gro MetroMix® 306 planting mixture, which typically has a pH of 6.0 to 6.8 and an organic matter content of about 30 percent, in plastic pots with a surface area of 103.2 square centimeters (cm^2). When required to ensure good germination and healthy plants, a fungicide treatment and/or other chemical or physical treatment was applied. The plants were grown for 7-36 days (d) in a greenhouse with an approximate 14 hour (h) photoperiod which was maintained at about 18 °C during the day and 17 °C during the night. Nutrients and water were added on a regular basis and supplemental lighting was provided with overhead metal halide 1000-Watt lamps as necessary. The plants were employed for testing when they reached the second or third true leaf stage.

[0131] A weighed amount, determined by the highest rate to be tested, of each test compound was placed in a 25 mL glass vial and was dissolved in 4 mL of a 97:3 v/v mixture of acetone and DMSO to obtain concentrated stock solutions. If the test compound did not dissolve readily, the mixture was warmed and/or sonicated. The concentrated stock solutions obtained were diluted with 20 mL of an aqueous mixture containing acetone, water, isopropyl alcohol, DMSO, Agri-Dex crop oil concentrate, and X-77 surfactant in a 48:39:10:1.5:1.5:0.02 v/v ratio to obtain spray solutions containing the highest application rates. Additional application rates were obtained by serial dilution of 12 mL of the high rate solution into a solution containing 2 mL of 97:3 v/v mixture of acetone and DMSO and 10 mL of an aqueous mixture containing acetone, water, isopropyl alcohol, DMSO, Agri-Dex crop oil concentrate, and X-77 surfactant in a 48:39:10:1.5:1.5:0.02 v/v ratio to obtain 1/2X, 1/4X, 1/8X and 1/16X rates of the high rate. Compound requirements are based upon a 12 mL application volume at a rate of 187 liters per hectare (L/ha). Formulated compounds were applied to the plant material with an overhead Mandel track sprayer equipped with 8002E nozzles calibrated to deliver 187 L/ha over an application area of 0.503 square meters at a spray height of 18 inches (43 cm) above the average plant canopy height. Control plants were sprayed in the same manner with the solvent blank.

[0132] The treated plants and control plants were placed in a greenhouse as described above and watered by subirrigation to prevent wash-off of the test compounds. After 21 d, the condition of the test plants as compared with that of the untreated plants was determined visually and scored on a scale of 0 to 100 percent where 0 corresponds to no injury and 100 corresponds to complete kill.

[0133] By applying the well-accepted probit analysis as described by J. Berkson in Journal of the American Statistical Society, 48, 565 (1953) and by D. Finney in "Probit Analysis" Cambridge University Press (1952), the above data can be used to calculate GR_{20}, GR_{50}, GR_{80} and GR_{90} values, which are defined as growth reduction factors that correspond to the effective dose of herbicide required to kill or control 20 percent, 50 percent, 80 percent or 90 percent, respectively, of a target plant.

[0134] Some of the compounds tested, application rates employed, plant species tested, and results are given in Table 7.

Table 7: Activity of Herbicidal Compounds in Wheat and Barley

Compound No.	Application Rate (g ai/ha)	Visual growth Reduction (%) 21 Days After Application											
		HORVS	TRZAS	CIRAR	GALAP	KCHSC	LAMPU	MATCH	PAPRH	SASKR	SINAR	VERPE	VIOTR
	17.5	F	F	F	D	D	A	F	A	C	A	A	E
	35	E	E	D	B	B	A	E	A	C	A	A	D
	70	E	D	C	A	B	A	D	A	B	A	A	C
	GR20	8	13	--	--	--	--	--	--	--	--	--	--
	GR50	--	--	30	9	6	0.1	45	0.06	7	4	0.28	22
	GR80	--	--	70	23	28	1	>140	1	30	8	2	63

Compound No.	Application Rate (g ai/ha)	Visual growth Reduction (%) 21 Days After Application											
		HORVS	TRZAS	CIRAR	GALAP	KCHSC	LAMPU	MATCH	PAPRH	SASKR	SINAR	VERPE	VIOTR
1.15	GR90	--	--	109	37	67	2	>140	2	95	12	6	111
	17.5	G	G	D	F	C	C	B	A	D	B	A	E
	35	G	G	B	E	B	A	A	A	C	A	A	D
	70	F	F	A	A	A	A	A	A	B	A	A	C
	GR20	44	41	--	--	--	--	--	--	--	--	--	--
	GR50	--	--	9	26	7	3	3	0.0004	10	5	0.0004	19
	GR80	--	--	25	34	20	10	9	0.0004	28	11	0.05	56
1.16	GR90	--	--	43	40	39	19	16	0.0004	78	17	1	99
	17.5	G	G	G	A	F	B	G	D	F	C	B	G
	35	G	G	G	A	E	A	G	A	E	C	B	E
	70	G	G	G	A	D	A	G	A	C	A	A	D
	GR20	>140	66	--	--	--	--	--	--	--	--	--	--
	GR50	--	--	>140	1	35	3	>140	11	29	3	1	44
	GR80	--	--	>140	4	110	6	>140	17	90	14	8	119
1.23*	GR90	--	-	>140	7	>140	9	>140	22	>140	32	21	>140
	17.5	G	G	D	D	D	E	G	D	D	B	F	E
	35	G	G	C	B	C	D	G	D	B	A	D	D
	70	G	F	B	B	B	C	G	C	B	A	C	C
	GR20	66	52	--	--	--	--	--	--	--	--	--	--
	GR50	--	--	14	7	4	15	114	24	3	6	30	24
	GR80	--	--	35	23	33	93	>140	52	28	13	66	78
1.24*	GR90	--	--	57	44	103	>140	>140	77	95	19	100	>140
*Comparative Example													

REFERENCES CITED IN THE DESCRIPTION

Cited references

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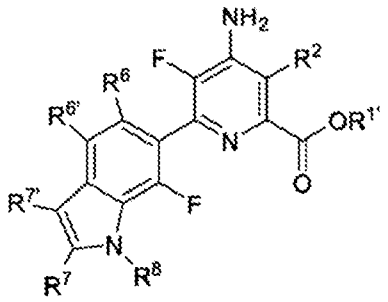
- **D. FINNEY**Probit AnalysisCambridge University Press19520000 [0133]

PATENTKRAV

1. Forbindelse defineret ved følgende formel:



hvor

$R^{1'}$ er hydrogen, C_1-C_8alkyl eller C_7-C_{10}arylalkyl;

R^2 er Cl, methoxy, vinyl eller 1-propenyl;

R^6 og $R^{6'}$ uafhængigt er hydrogen, halogen, C_1-C_4alkyl, C_1-C_4halogenalkyl, cyclopropyl, halogencyclopropyl, C_2-C_4alkenyl, C_2-C_4halogenalkenyl, C_2-C_4alkynyl, C_1-C_3alkoxy, C_1-C_3halogenalkoxy, C_1-C_3alkylthio, C_1-C_3halogenalkylthio, amino, C_1-C_4alkylamino eller C_2-C_4halogenalkylamino, OH, CN eller NO_2;

R^7 og $R^{7'}$ uafhængigt er hydrogen, halogen, C_1-C_4alkyl, C_1-C_4halogenalkyl, cyclopropyl, halogencyclopropyl, C_2-C_4alkenyl, C_2-C_4halogenalkenyl, C_2-C_4alkynyl, C_1-C_3alkoxy, C_1-C_3halogenalkoxy, C_1-C_3alkylthio, C_1-C_3halogenalkylthio, amino, C_1-C_4alkylamino, C_2-C_4halogenalkylamino eller phenyl;

R^8 er hydrogen, C_1-C_6alkyl, C_1-C_6halogenalkyl, C_3-C_6alkenyl, C_3-C_6halogenalkenyl, C_3-C_6alkynyl, formyl, C_1-C_3alkylcarbonyl, C_1-C_3halogenalkylcarbonyl, C_1-C_6alkoxycarbonyl, C_1-C_6alkylcarbamyl, C_1-C_6alkylsulfonyl, C_1-C_6trialkylsilyl eller phenyl;

eller en N-oxid eller et agrikulturelt acceptabelt salt deraf.

2. Forbindelse ifølge krav 1, hvor R^2 er Cl.

3. Forbindelse ifølge et hvilket som helst af kravene 1-2, hvor R^6 og $R^{6'}$ uafhængigt er hydrogen eller halogen.

4. Forbindelse ifølge et hvilket som helst af kravene 1-3,

hvor R^6 og $R^{6'}$ begge er hydrogen.

5. Forbindelse ifølge et hvilket som helst af kravene 1-4, hvor R^7 og $R^{7'}$ uafhængigt er hydrogen eller halogen.

6. Forbindelse ifølge et hvilket som helst af kravene 1-5, hvor R^8 er C_1-C_6alkyl, C_1-C_6halogenalkyl, C_3-C_6alkenyl, C_3-C_6halogenalkenyl, C_3-C_6alkynyl, formyl, C_1-C_3alkylcarbonyl, C_1-C_3halogenalkylcarbonyl, C_1-C_6alkoxycarbonyl, C_1-C_6alkylcarbamyl, C_1-C_6alkylsulfonyl, C_1-C_6trialkylsilyl eller phenyl.

7. Forbindelse ifølge et hvilket som helst af kravene 1-6, hvor R^6, $R^{6'}$ R^7, $R^{7'}$ og R^8 hver er hydrogen.

8. Forbindelse ifølge et hvilket som helst af kravene 1-7, hvor $R^{1'}$ er hydrogen eller C_1-C_8alkyl, fortrinsvis hvor $R^{1'}$ er hydrogen.

9. Herbicid sammensætning, som omfatter en forbindelse ifølge et hvilket som helst af kravene 1-8 og et agrikulturelt acceptabelt adjuvans eller bæremateriale.

10. Sammensætning ifølge krav 9, som endvidere omfatter et yderligere pesticid.

11. Sammensætning ifølge krav 9 eller 10, som endvidere omfatter en herbicid safener.

12. Fremgangsmåde til bekæmpelse af uønsket vegetation, som omfatter påføring på vegetationen eller et område tilstødende vegetationen eller påføring på jord eller tilsætning i vand til forebyggelse af fremspiring eller vækst af vegetationen af en herbicid effektiv mængde af en forbindelse ifølge et hvilket som helst af kravene 1-8 eller en sammensætning ifølge et hvilket som helst af kravene 9-11.

13. Fremgangsmåde til bekæmpelse af uønsket vegetation, som omfatter (a) etablering af kontakt mellem den uønskede

vegetation eller et område tilstødende den uønskede vegetation eller (b) før-spirings-etablering af kontakt mellem jord eller vand og en herbicid effektiv mængde af mindst én forbindelse ifølge et hvilket som helst af kravene 1-8 eller en sammensætning ifølge et hvilket som helst af kravene 9-11.