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(54) Title: NOVEL DERIVATIVES OF NON-CODED AMINO ACIDS AND THEIR USE AS HERBICIDES

(57) Abstract: Novel chemical compounds having herbicidal activity, agricultural compositions, process for their manufacture and their use in crop protection are provided.



Novel Derivatives of Non-coded Amino Acids and Their Use as Herbicides

FIELD OF THE INVENTION

The invention relates to novel chemical compounds having
5 herbicidal activity, process for their manufacture and their use
in crop protection.

BACKGROUND OF THE INVENTION

Amino acids and their derivatives are involved in a plethora of
cellular reactions and therefore they influence on a number of
10 physiological processes such as plant growth and development,
intracellular pH control, generation of metabolic energy or
redox power, and resistance to both abiotic and biotic stress.
Pools of all amino acids are induced during stress. For example,
proline significantly increases in stress response in several
15 plants and considered as a compatible osmolyte. In addition,
branched-chain amino acids are also dramatically induced during
various stress conditions.

The role of amino acids in signaling in plants is being recently
discussed. In this context, regulation of amino acid content,
20 fluxes, and transport through the plant are critical for plant
adaptation to carbon and nitrogen status, development, and
defense.

Mechanisms underlying regulation of amino acids pools require
further elucidations. Local amino acid concentrations depend on
25 the synthesis and degradation rates of proteins as well as amino
acids and on transport processes. These processes rather modify
the total pool size, which is especially relevant when bulk
degradation takes place such as during germination and
senescence.

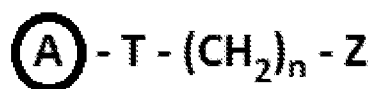
30 New compounds effective for controlling the growth of undesired
vegetation are in constant demand. In the most common situation,
such compounds are sought to selectively control the growth of

weeds in useful crops such as cotton, rice, corn, wheat and soybeans, to name a few. Unchecked weed growth in such crops can cause significant losses, reducing profit to the farmer and increasing costs to the consumer. In other situations, herbicides are desired which will control all plant growth. Examples of areas in which complete control of all vegetation is desired are areas around railroad tracks, storage tanks and industrial storage areas. Identifying new compounds having herbicidal activity, which are more effective, less costly and environmentally safe, remains long and unmet need.

SUMMARY OF THE INVENTION

It is a principal object of the present invention to provide novel, safe and potent herbicides.

The invention provides an agricultural composition comprising a compound having the structure



or a salt thereof, wherein:

A is cyclopentadiene, benzene and indene scaffold comprising from 1 to 4 heteroatoms; wherein each of the heteroatoms is independently selected from the group consisting of N, S, Se, and O; and wherein one or more of the carbon atoms of the ring are optionally chemically attached to at least one of the groups consisting of: $-\text{SO}_2\text{CF}_3$, $-\text{O}-\text{SO}_2\text{CF}_3$, $-\text{NR}_3^+$, $-\text{SO}_2\text{R}$, $-\text{C}\equiv\text{N}$, $-\text{CX}_3$, CX_2R , $-\text{COX}$, $-\text{CHO}$, $-\text{COR}$, $-\text{CO}_2\text{R}$, $-\text{CONH}_2$, $-\text{CONHR}$, $-\text{CONR}_2$, $-\text{N}=\text{O}$, $-\text{N}\equiv\text{N}^+$, $-\text{N}=\text{NR}$, $-\text{CR}=\text{NR}$, $-\text{N}=\text{CR}_2$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, and $-\text{I}$, and wherein X is selected from F, Cl, Br and I;

n is 0 to 5;

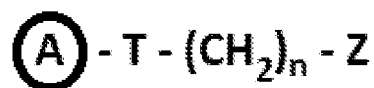
T is unsubstituted or substituted methylene group with one or two halides, oxygen, $-\text{SO}_2\text{CF}_3$, $-\text{O}-\text{SO}_2\text{CF}_3$, $-\text{NR}_3^+$, $-\text{SO}_2\text{R}$, $-\text{C}\equiv\text{N}$, -

CX₃, CX₂R-COX, -CHO, -COR, -CO₂R, -CONH₂, -CONHR, -CONR₂, -F, -N=O, -N≡N⁺, -N=NR, -CR=NR, -N=CR₂, and wherein X is selected from -F, -Cl, -Br and -I; and,

Z is -COOH, COO⁻, OH, -O-R, COOR with saturated or non-saturated alcohol residues with straight, branched, cyclic, aromatic or heteroaromatic chain; -O-(CH₂CH₂O)_nR (n≥1); -O-(CHMeCH₂O)_nR (n≥1)); sulfonyl group, carbamoyl group, primary amine, secondary amine, tertiary amine, carboxamide, -NR-O-R, -O-NR₂, hydrazine, -NH-COR, and methanimidamide moiety or a salt thereof;

wherein R is selected from H, substituted or non-substituted alkyl, and substituted or non-substituted aryl group; and, wherein the composition comprises at least one agriculturally acceptable carrier.

The invention further provides a method of controlling undesired plant growth, comprising applying to the locus of the undesired plant growth a herbicidally effective amount of a compound having the structure



or a salt thereof, wherein:

A is cyclopentadiene, benzene and indene scaffold comprising from 1 to 4 heteroatoms; wherein each of the heteroatoms is independently selected from the group consisting of N, S, Se, and O; and wherein one or more of the carbon atoms of the ring are optionally chemically attached to at least one of the groups consisting of: -SO₂CF₃, -O-SO₂CF₃, -NR₃⁺, -SO₂R, -C≡N, -CX₃, CX₂R, -COX, -CHO, -COR, -CO₂R, -CONH₂, -CONHR, -CONR₂, -N=O, -N≡N⁺, -N=NR, -CR=NR, -N=CR₂, -F, -Cl, -Br, and -I; and wherein X is selected from F, Cl, Br and I;

n is 0 to 5;

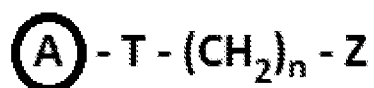
T is unsubstituted or substituted methylene group with one or two halides, oxygen, $-\text{SO}_2\text{CF}_3$, $-\text{O}-\text{SO}_2\text{CF}_3$, $-\text{NR}_3^+$, $-\text{SO}_2\text{R}$, $-\text{C}\equiv\text{N}$, $-\text{CX}_3$, CX_2R , $-\text{COX}$, $-\text{CHO}$, $-\text{COR}$, $-\text{CO}_2\text{R}$, $-\text{CONH}_2$, $-\text{CONHR}$, $-\text{CONR}_2$, $-\text{F}$, $-\text{N}=\text{O}$, $-\text{N}\equiv\text{N}^+$, $-\text{N}=\text{NR}$, $-\text{CR}=\text{NR}$, $-\text{N}=\text{CR}_2$, and wherein X is selected from F, Cl, Br and I; and,

Z is $-\text{COOH}$, COO^- , OH , $-\text{O}-\text{R}$, COOR with saturated or non-saturated alcohol residues with straight, branched, cyclic, aromatic or heteroaromatic chain; $-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n\text{R}$ ($n\geq 1$); $-\text{O}-(\text{CHMeCH}_2\text{O})_n\text{R}$ ($n\geq 1$); sulfonyl group, carbamoyl group, primary amine, secondary amine, tertiary amine, carboxamide, $-\text{NR}-\text{O}-\text{R}$, $-\text{O}-\text{NR}_2$, hydrazine, $-\text{NH}-\text{COR}$, and methanimidamide moiety or a salt thereof;

wherein R is selected from H, substituted or non-substituted alkyl, and substituted or non-substituted aryl group.

The invention further provides a method of controlling undesired plant growth comprising applying to the locus of the undesired plant growth:

a. A first herbicide having the structure



or a salt thereof, wherein:

A is cyclopentadiene, benzene and indene scaffold comprising from 1 to 4 heteroatoms; wherein each of the heteroatoms is independently selected from the group consisting of N, S, Se, and O; and wherein one or more of the carbon atoms of the ring are optionally chemically attached to at least one of the groups consisting of: $-\text{SO}_2\text{CF}_3$, $-\text{O}-\text{SO}_2\text{CF}_3$, $-\text{NR}_3^+$, $-\text{SO}_2\text{R}$, $-\text{C}\equiv\text{N}$, $-\text{CX}_3$, $\text{CX}_2\text{R}-\text{COX}$, $-\text{CHO}$, $-\text{COR}$, $-\text{CO}_2\text{R}$, $-\text{CONH}_2$, $-\text{CONHR}$, $-\text{CONR}_2$, $-\text{F}$, $-\text{N}=\text{O}$, $-\text{N}\equiv\text{N}^+$, $-\text{N}=\text{NR}$, $-\text{CR}=\text{NR}$, $-\text{N}=\text{CR}_2$, $-\text{Cl}$, $-\text{Br}$, and $-\text{I}$; and wherein X is selected from F, Cl, Br and I;

n is 0 to 5;

T is unsubstituted or substituted methylene group with one or two halides, oxygen, $-\text{SO}_2\text{CF}_3$, $-\text{O}-\text{SO}_2\text{CF}_3$, $-\text{NR}_3^+$, $-\text{SO}_2\text{R}$, $-\text{C}\equiv\text{N}$, $-\text{CX}_3$, CX_2R , $-\text{COX}$, $-\text{CHO}$, $-\text{COR}$, $-\text{CO}_2\text{R}$, $-\text{CONH}_2$, $-\text{CONHR}$,
 5 $-\text{CONR}_2$, $-\text{F}$, $-\text{N}=\text{O}$, $-\text{N}\equiv\text{N}^+$, $-\text{N}=\text{NR}$, $-\text{CR}=\text{NR}$, $-\text{N}=\text{CR}_2$, and wherein X is selected from F, Cl, Br and I; and,

Z is $-\text{COOH}$, COO^- , OH , $-\text{O}-\text{R}$, COOR with saturated or non-saturated alcohol residues with straight, branched, cyclic, aromatic or heteroaromatic chain; $-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n\text{R}$
 10 $(n\geq 1)$; $-\text{O}-(\text{CHMeCH}_2\text{O})_n\text{R}$ $(n\geq 1)$; sulfonyl group, carbamoyl group, primary amine, secondary amine, tertiary amine, carboxamide, $-\text{NR}-\text{O}-\text{R}$, $-\text{O}-\text{NR}_2$, hydrazine, $-\text{NH}-\text{COR}$, and methanimidamide moiety or a salt thereof;

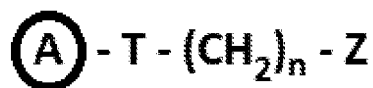
wherein R is selected from H, substituted or non-substituted alkyl, and substituted or non-substituted aryl group,
 15

b. A second herbicide,

to thereby effectively control the undesired plant growth.

The invention further provides a composition for controlling
 20 undesired plant growth comprising a mixture of:

a. a compound having the structure



or a salt thereof, wherein:

A is cyclopentadiene, benzene and indene scaffold
 25 comprising from 1 to 4 heteroatoms; wherein each of the heteroatoms is independently selected from the group consisting of N, S, Se, and O; and wherein one or more of the carbon atoms of the ring are optionally chemically attached to at least one of the groups consisting of: -

SO₂CF₃, -O-SO₂CF₃, -NR₃⁺, -SO₂R, -C≡N, -CX₃, CX₂R, -COX, -CHO, -COR, -CO₂R, -CONH₂, -CONHR, -CONR₂, -F, -N=O, -N≡N⁺, -N=NR, -CR=NR, -N=CR₂, -Cl, -Br, and -I; and wherein X is selected from F, Cl, Br and I;

5 n is 0 to 5;

T is unsubstituted or substituted methylene group with one or two halides, oxygen, -SO₂CF₃, -O-SO₂CF₃, -NR₃⁺, -SO₂R, -C≡N, -CX₃, CX₂R-COX, -CHO, -COR, -CO₂R, -CONH₂, -CONHR, -CONR₂, -F, -N=O, -N≡N⁺, -N=NR, -CR=NR, -N=CR₂, and
10 wherein X is selected from F, Cl, Br and I; and,

Z is -COOH, COO⁻, OH, -O-R, COOR with saturated or non-saturated alcohol residues with straight, branched, cyclic, aromatic or heteroaromatic chain; -O-(CH₂CH₂O)_nR (n≥1); -O-(CHMeCH₂O)_nR (n≥1)); sulfonyl group, carbamoyl
15 group, primary amine, secondary amine, tertiary amine, carboxamide, -NR-O-R, -O-NR₂, hydrazine, -NH-COR, and methanimidamide moiety or a salt thereof;

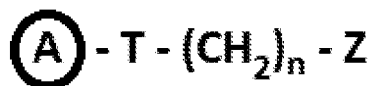
wherein R is selected from H, substituted or non-substituted alkyl, and substituted or non-substituted aryl group;

20 b. at least one herbicide selected from the group consisting of atrazine, terbuthylazine, (S)-metolachlor, metolachlor, terbutryn, simazine, dimethenamid, (S)-dimethenamid, flufenacet, acetochlor, alachlor, isoxaflutole, isoxachlortole, mesotrione, sulcotrione, metosulam,
25 flumetsulam, pendimethalin, bromoxynil, bentazone, carfentrazone-ethyl, clomazone, nicosulfuron, rimsulfuron, halosulfuron-methyl, metribuzin, flumiclorac-pentyl, prosulfuron, primisulfuron-methyl, dicamba, fluthiacet-methyl, pyridate, 2,4-D, clopyralide, diflufenzopyr,
30 fluroxypyr, MCPA, MCPB, mecoprop (MCP), metobenzuron, thifensulfuron-methyl, aclonifen, EPTC, glyphosate, glufosinate, sulfosate, cyanazine, propaquizafop,

- metamitron, pyramin, phenmedipham, desmedipham, ethofumesate, triasulfuron, chloridazon, lenacil, triallate, fluazifop, sethoxydim, quizalofop, clopyralide, clethodim, oxasulfuron, acifluorfen, benazolin-ethyl, sulfentrazone, chlorimuron-ethyl, cloransulam-methyl, fomesafen, imazamox, imazaquin, imazethapyr, imazapyr, lactofen, fenoxaprop(P-ethyl), thidiazuron, tribufos, trifluralin, dimethachlor, napropamide, quinmerac, metazachlor, carbetamide, dimefuron, propyzamide, ethametsulfuron-methyl, tebutam, fluometuron, prometryn, norflurazon, pyriithiobac-sodium, MSMA, DSMA, diuron, flurochloridone, dithiopyr, thiazopyr, oxyfluorfen, ethalfluralin, clodinafop, amidosulfuron, diclofop-methyl, diflufenican, ethoxysulfuron, fentrazamide, flazasulfuron, florasulam, fluazolate, flucarbazone, flupyralsulfuron-methyl sodium, flurtamone, iodosulfuron, isoproturon, chlortoluron, chlorsulfuron, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, 2,4-DB, 2,4-DP, bifenox, flamprop-M, imazamethabenz-methyl, ioxynil, tralkoxydim, fluoroglycofen-ethyl, methabenzthiazuron, isoxaben, prosulfocarb, difenzoquat-metilsulfate, pretilachlor, cinosulfuron, fenclorim, bensulfuron-methyl, imazosulfuron, pyrazosulfuron-ethyl, azimsulfuron, esprocarb, mefenacet, molinate, propanil, pyrazolate, cyhalofop-butyl, bispyribac-sodium, pyriminobac-methyl, cafenstrole, oxadiargyl, oxadiazon, bromobutide, MY-100, dymron, NB 061, MK243, HW-52, AC 014, ametryn, hexazinone, asulam, azafenidin, tebuthiuron, ethametsulfuron-methyl, or a combination thereof; and,
- c. at least one agriculturally acceptable carrier.

The invention further provides a composition for controlling undesired plant growth comprising a mixture of:

- a. a compound having the structure



or a salt thereof, wherein:

A is cyclopentadiene, benzene and indene scaffold comprising from 1 to 4 heteroatoms; wherein each of the heteroatoms is independently selected from the group consisting of N, S, Se, and O; and wherein one or more of the carbon atoms of the ring are optionally chemically attached to at least one of the groups consisting of: -SO₂CF₃, -O-SO₂CF₃, -NR₃⁺, -SO₂R, -C≡N, -CX₃, CX₂R-COX, -CHO, -COR, -CO₂R, -CONH₂, -CONHR, -CONR₂, -F, -N=O, -N≡N⁺, -N=NR, -CR=NR, -N=CR₂, -Cl, -Br, and -I; and wherein X is selected from F, Cl, Br and I;

n is 0 to 5;

T is unsubstituted or substituted methylene group with one or two halide atoms, oxygen, -SO₂CF₃, -O-SO₂CF₃, -NR₃⁺, -SO₂R, -C≡N, -CX₃, -COX, -CHO, -COR, -CO₂R, -CONH₂, -CONHR, -CONR₂, -F, -N=O, -N≡N⁺, -N=NR, -CR=NR, -N=CR₂, and wherein X is selected from F, Cl, Br and I; and,

Z is -COOH, COO⁻, OH, -O-R, COOR with saturated or non-saturated alcohol residues with straight, branched, cyclic, aromatic or heteroaromatic chain; -O-(CH₂CH₂O)_nR (n≥1); -O-(CHMeCH₂O)_nR (n≥1)); sulfonyl group, carbamoyl group, primary amine, secondary amine, tertiary amine, carboxamide, -NR-O-R, -O-NR₂, hydrazine, -NH-COR, and methanimidamide moiety or a salt thereof;

wherein R is selected from H, substituted or non-substituted alkyl, and substituted or non-substituted aryl group;

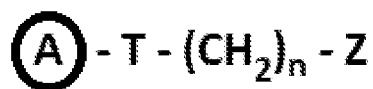
b. at least one plant growth regulator; and,

c. at least one agriculturally acceptable carrier.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is now described more fully hereinafter with reference to the accompanying examples, in which embodiments of the invention are shown. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather these embodiments are provided so that this disclosure will be thorough and complete and will fully convey the scope of the invention to those skilled in the art.

10 In one embodiment, the invention provides an agricultural composition comprising a compound or a salt thereof having the structure



15

or a salt thereof, wherein:

A is cyclopentadiene, benzene and indene scaffold comprising from 1 to 4 heteroatoms; wherein each of the heteroatoms is independently selected from the group consisting of N, S, Se, and O; and wherein one or more of the carbon atoms of the ring are optionally chemically attached to at least one of the groups consisting of: $-\text{SO}_2\text{CF}_3$, $-\text{O}-\text{SO}_2\text{CF}_3$, $-\text{NR}_3^+$, $-\text{SO}_2\text{R}$, $-\text{C}\equiv\text{N}$, $-\text{CX}_3$, CX_2R , $-\text{COX}$, $-\text{CHO}$, $-\text{COR}$, $-\text{CO}_2\text{R}$, $-\text{CONH}_2$, $-\text{CONHR}$, $-\text{CONR}_2$, $-\text{N}=\text{O}$, $-\text{N}\equiv\text{N}^+$, $-\text{N}=\text{NR}$, $-\text{CR}=\text{NR}$, $-\text{N}=\text{CR}_2$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, and $-\text{I}$, and wherein X is selected from F, Cl, Br and I;

25

n is 0 to 5;

T is unsubstituted or substituted methylene group with one or two halides, oxygen, $-\text{SO}_2\text{CF}_3$, $-\text{O}-\text{SO}_2\text{CF}_3$, $-\text{NR}_3^+$, $-\text{SO}_2\text{R}$, $-\text{C}\equiv\text{N}$, $-\text{CX}_3$, $\text{CX}_2\text{R}-\text{COX}$, $-\text{CHO}$, $-\text{COR}$, $-\text{CO}_2\text{R}$, $-\text{CONH}_2$, $-\text{CONHR}$, $-\text{CONR}_2$, $-\text{F}$,

-N=O, -N≡N⁺, -N=NR, -CR=NR, -N=CR₂, and wherein X is selected from -F, -Cl, -Br and -I; and,

Z is -COOH, COO⁻, OH, -O-R, COOR with saturated or non-saturated alcohol residues with straight, branched, cyclic, aromatic or heteroaromatic chain; -O-(CH₂CH₂O)_nR (n≥1); -O-(CHMeCH₂O)_nR (n≥1)); sulfonyl group, carbamoyl group, primary amine, secondary amine, tertiary amine, carboxamide, -NR-O-R, -O-NR₂, hydrazine, -NH-COR, and methanimidamide moiety or a salt thereof;

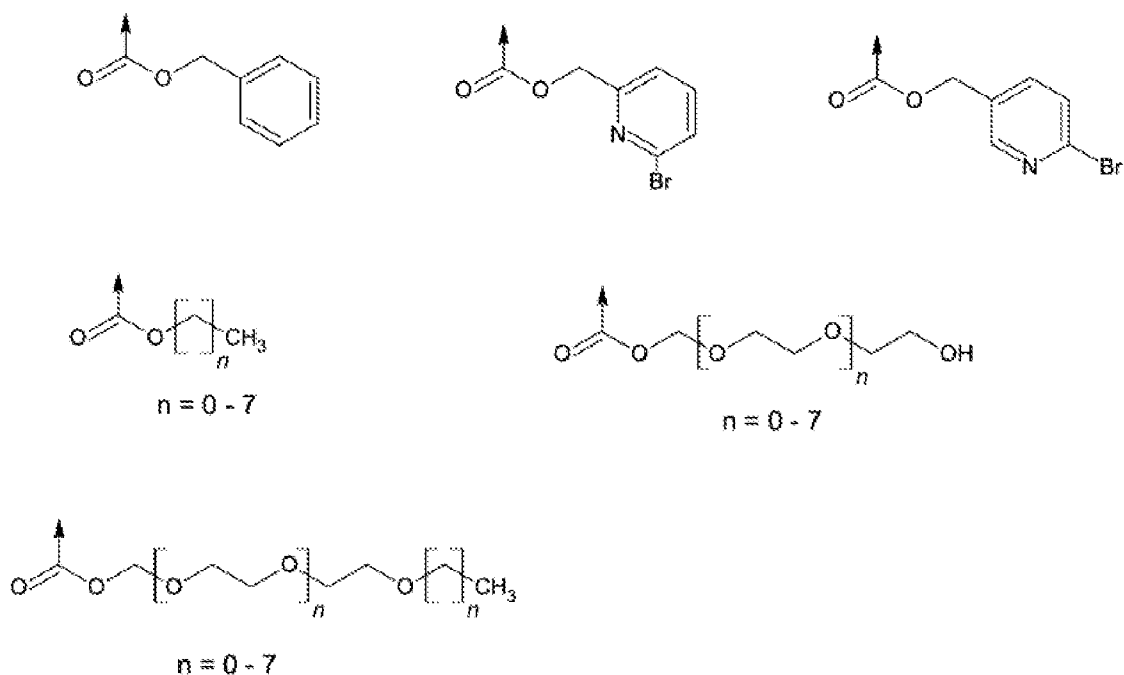
wherein R is selected from H, substituted or non-substituted alkyl, and substituted or non-substituted aryl group; and, wherein the composition comprises at least one agriculturally acceptable carrier.

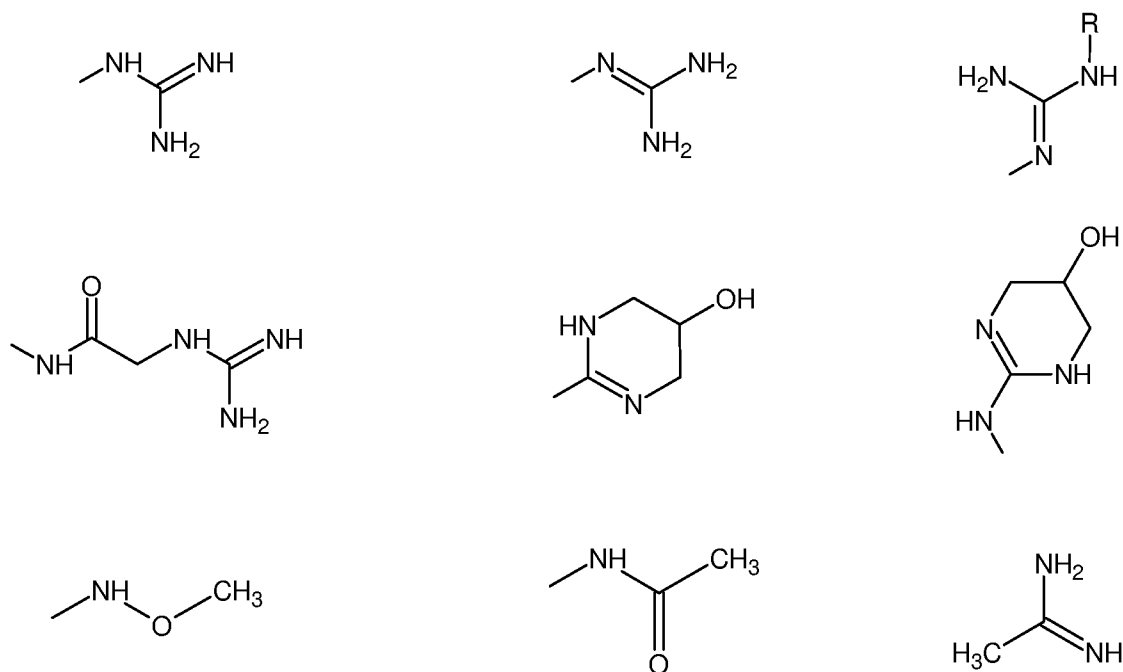
According to some embodiments of the composition of the invention, A is heterocyclic aromatic ring substituted with one or more Electron Withdrawing Group (EWG). As used herein, the term "electron withdrawing group" (EWG) refers, without limitation, to an atom or a group that draws electron density from neighboring atoms or aromatic ring, usually by resonance and/or inductive effects. In the context of the invention, the non-limiting list of the EWG of the invention includes: trifluoromethanesulfonyl and triflate groups; substituted ammonium groups, such as, without limitation, -NR₃⁺ (R is alkyl/s or H); nitro and nitroso groups, -NO₂, -N=O; sulfonic acids and sulfonyl groups (-O)-SO₃H, -SO₂R; cyano group, trihalomethyl groups -CX₃ (X is F, Cl, Br, I); haloformyl groups -COX (X is F, Cl, Br, I); formyl and acyl groups -CHO, -COR; (substituted) aminocarbonyl groups -CONH₂, -CONHR, -CONR₂; halo groups -F, -Cl, -Br, -I; Azo groups -N≡N⁺ or -N=NR; imino group -CR=NR or -N=CR₂.

According to some embodiments of the above composition, Z may be, without limitation, carboxyl or salts thereof -COOH or COO⁻, hydroxyl -OH, ether -O-R, ester COOR with saturated or non-

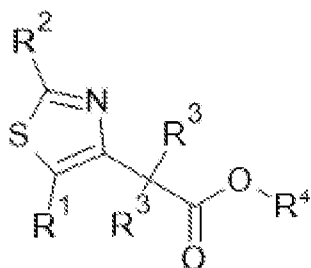
saturated alcohol groups with straight, branched, cyclic chain
 or aromatic/heteroaromatic chain, ethylene- and polyethylene
 glycol $-O-(CH_2CH_2O)_nR$ ($n \geq 1$, R is H or alkyl), propylene and
 polypropylene glycol $-O-(CHMeCH_2O)_nR$ ($n \geq 1$, R is H or alkyl),
 5 phosphates (substituted and non-substituted), sulfate/sulfonyl,
 carbamoyl group that consists of primary, secondary, and
 tertiary amide substituted with straight, branched, cyclic
 aliphatic chain, cyclic aromatic/heteroaromatic chain, ethylene
 glycol and polyethylene glycol (as above), propylene glycol,
 10 polypropylene glycol (as above), primary amine, secondary amine,
 tertiary amine, carboxamide, alkoxyamine groups of type $-NR-O-$
 R and $-O-NR_2$, hydrazine, acetamide group $-NH-COR$, and
 methanimidamide moiety, or salts thereof.

According to some embodiments, of the above composition, Z might
 15 be, without limitation:

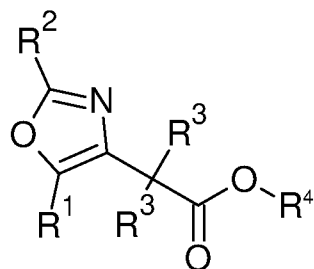




According to some embodiments, the above composition comprises a compound having the structure

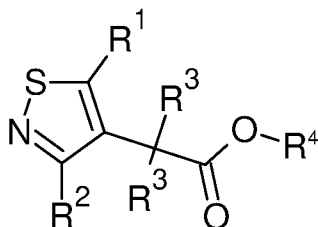


- 5 or a salt thereof, wherein each R^1 and R^2 is independently selected from H, Cl; Br; I; $-\text{CF}_3$; and $-\text{CN}$, where at least one of them is not H; R^3 is H, $-\text{COH}$, $-\text{CN}$, O or F; and R^4 is selected from H, saturated or non-saturated aliphatic straight, branched, cyclic or aromatic chain; ethylene glycol; polyethylene glycol; propylene glycol, polypropylene glycol, ethylpyridine, ethylbenzene, 1-(bromophenyl)ethan-1-one, 1-(1H-inden-3-yl)ethan-1-one, 1-(2,3-dihydro-1H-inden-1-yl)ethan-1-one; 1-(2,3-dihydro-1H-inden-1-yl)propan-1-one; and 1-(1H-inden-3-yl)propan-1-one.
- 10
- 15 According to some embodiments, the above composition comprises a compound having the structure



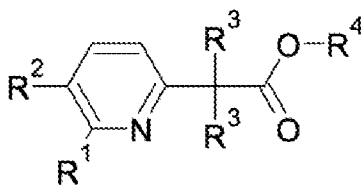
Wherein R¹ and R² is selected from H, Cl; Br; I; -CF₃; and -CN where at least one of them is not H; R³ is H, -COH, -CN, O or F; and R⁴ is selected from H, saturated or non-saturated aliphatic straight, branched, cyclic or aromatic chain; ethylene glycol; polyethylene glycol; propylene glycol, polypropylene glycol, ethylpyridine, ethylbenzene, 1-(bromophenyl)ethan-1-one, 1-(1H-inden-3-yl)ethan-1-one, 1-(2,3-dihydro-1H-inden-1-yl)ethan-1-one; 1-(2,3-dihydro-1H-inden-1-yl)propan-1-one; and 1-(1H-inden-3-yl)propan-1-one.

According to some embodiments, the above composition comprises a compound having the structure



Wherein R¹ and R² is selected from H, Cl; Br; I; -CF₃; and -CN where at least one of them is not H; R³ is H, -COH, -CN, O or F; R⁴ is selected from H, saturated or non-saturated aliphatic straight, branched, cyclic or aromatic chain; ethylene glycol; polyethylene glycol; propylene glycol, polypropylene glycol, ethylpyridine, ethylbenzene, 1-(bromophenyl)ethan-1-one, 1-(1H-inden-3-yl)ethan-1-one, 1-(2,3-dihydro-1H-inden-1-yl)ethan-1-one; 1-(2,3-dihydro-1H-inden-1-yl)propan-1-one; and 1-(1H-inden-3-yl)propan-1-one.

According to some embodiments, the above composition comprises a compound having the structure

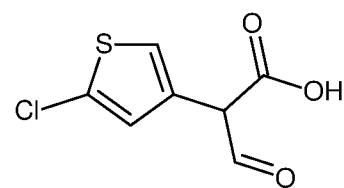
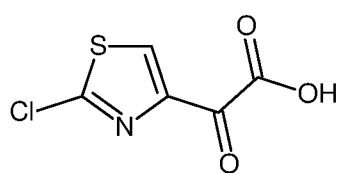
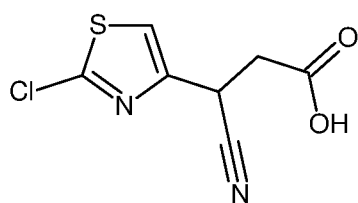
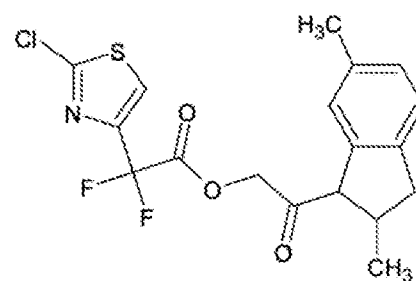
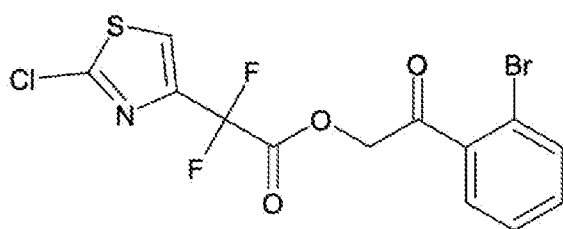
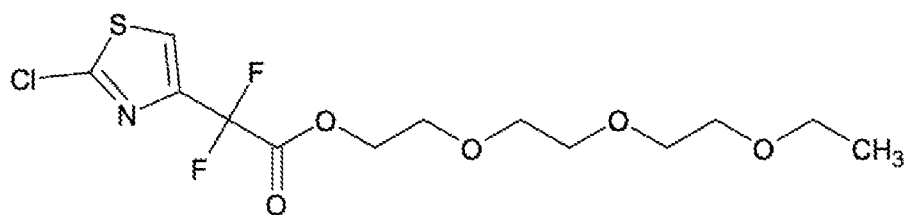
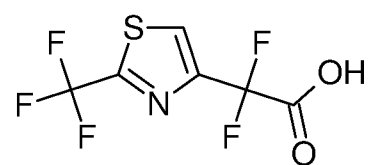
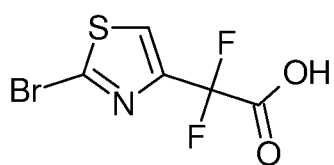
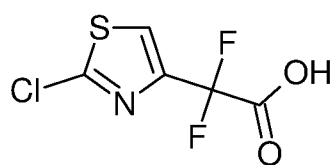


wherein R^1 is selected from Cl; Br; I; $-CF_3$; R^2 and R^3 is H or F; and R^4 is selected from H, saturated or non-saturated aliphatic straight, branched, cyclic or aromatic chain; ethylene glycol; polyethylene glycol; propylene glycol, polypropylene glycol, ethylpyridine, ethylbenzene, 1-(bromophenyl)ethan-1-one, 1-(1H-inden-3-yl)ethan-1-one, 1-(2,3-dihydro-1H-inden-1-yl)ethan-1-one; 1-(2,3-dihydro-1H-inden-1-yl)propan-1-one; and 1-(1H-inden-3-yl)propan-1-one.

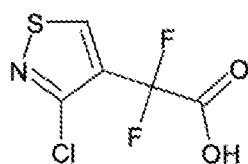
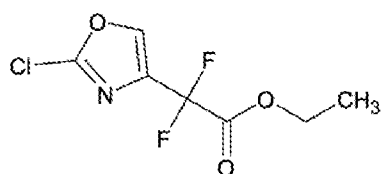
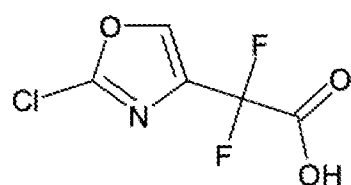
- 10 According to some embodiments, the above composition comprises a compound selected from (2-bromo-1,3-thiazol-4-yl)(difluoro)acetic acid; difluoro[2-(trifluoromethyl)-1,3-thiazol-4-yl]acetic acid; (2-cyano-1,3-thiazol-4-yl)(difluoro)acetic acid; (2-chloro-1,3-thiazol-4-yl)(difluoro)acetic acid; 2-[2-(2-ethoxyethoxy)ethoxy]ethyl (2-chloro-1,3-thiazol-4-yl)(difluoro)acetate; 2-(2-bromophenyl)-2-oxoethyl (2-chloro-1,3-thiazol-4-yl)(difluoro)acetate; 2-(2,7-methyl-2,3-dihydro-1H-inden-1-yl)-2-oxoethyl (2-chloro-1,3-thiazol-4-yl)(difluoro)acetate; (2-chloro-1,3-oxazol-4-yl)(difluoro)acetic acid; ethyl (2-chloro-1,3-oxazol-4-yl)(difluoro)acetate; difluoro(1,2,3-thiadiazol-4-yl)acetic acid; (1,2,3-thiadiazol-4-yl)acetic acid; (3-chloro-1,2-thiazol-4-yl)(difluoro)acetic acid.
- 15
- 20

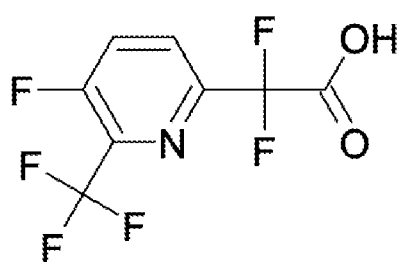
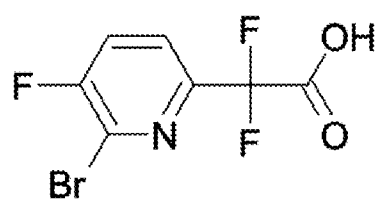
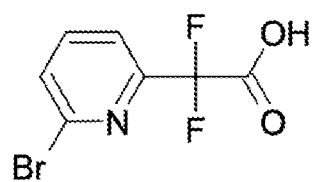
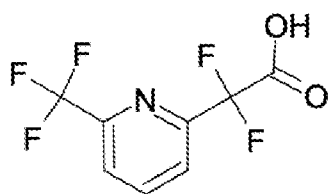
According to some embodiments of the above composition, the non-limiting list of compounds or agriculturally acceptable salts includes:

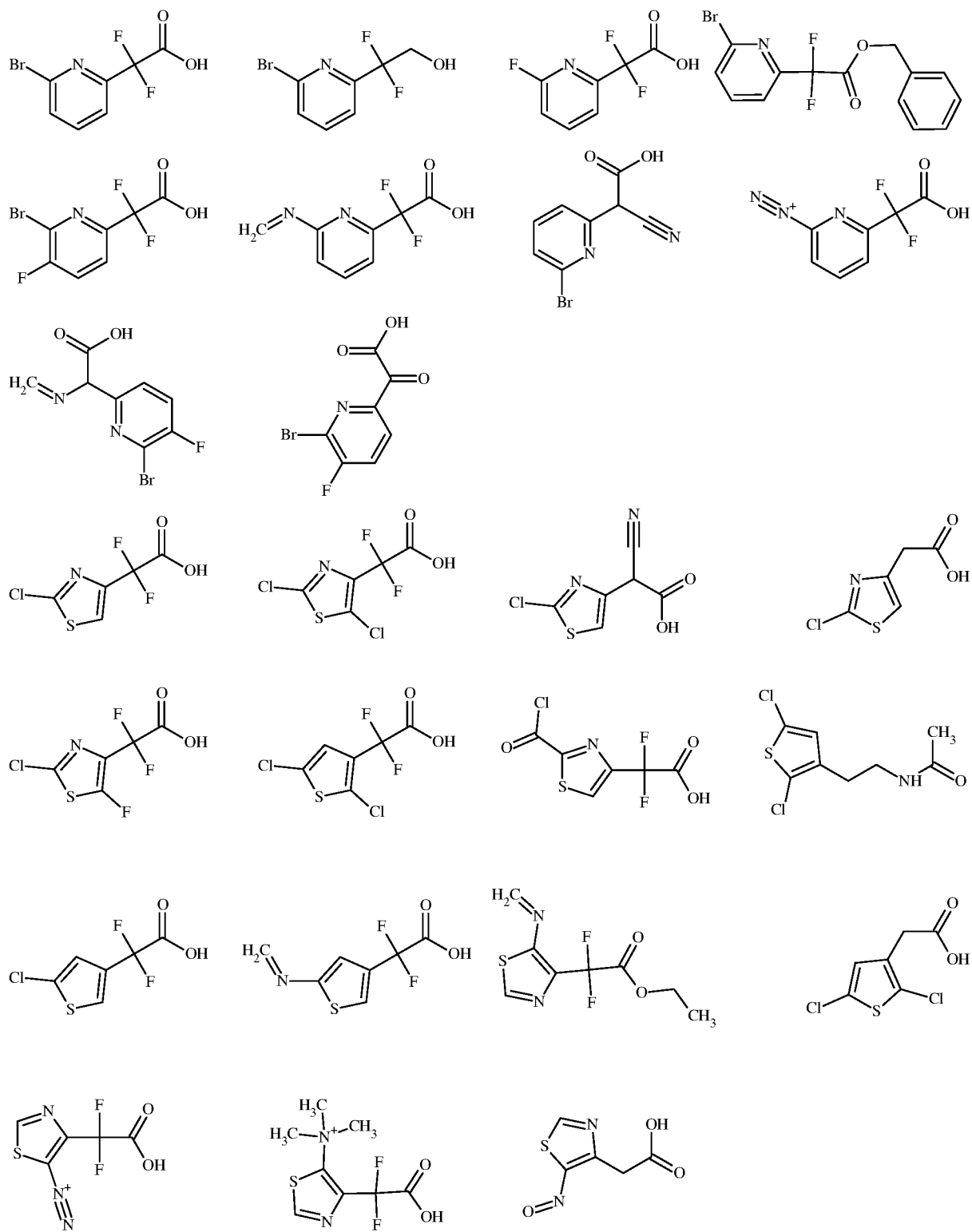
25



5







According to some embodiments of the above composition, the agricultural composition further comprises at least one crop protection agent. In one embodiment, the at least one crop protection agent is selected from the group consisting of

5 fungicide, insecticide, herbicide, and plant growth regulator. In one embodiment, the crop protection agent is herbicide. In another embodiment, the crop protection agent is plant growth regulator. In one embodiment, the at least one crop protection agent is selected from the group consisting of

10 terbutylazine, (S)-metolachlor, metolachlor, terbutryn, simazine, dimethenamid, (S)-dimethenamid, flufenacet, acetochlor, alachlor, isoxaflutole, isoxachlortole, mesotrione, sulcotrione, metosulam, flumetsulam, pendimethalin, bromoxynil, bentazone, carfentrazone-ethyl, clomazone, nicosulfuron,

15 rimsulfuron, halosulfuron-methyl, metribuzin, flumiclorac-pentyl, prosulfuron, primisulfuron-methyl, dicamba, fluthiacet-methyl, pyridate, 2,4-D, clopyralide, diflufenzopyr, fluroxypyr, MCPA, MCPB, mecoprop (MCP), metobenzuron, thifensulfuron-methyl, aclonifen, EPTC, glyphosate,

20 glufosinate, sulfosate, cyanazine, propaquizafop, metamitron, pyramin, phenmedipham, desmedipham, ethofumesate, triasulfuron, chloridazon, lenacil, triallate, fluazifop, sethoxydim, quizalofop, clopyralide, clethodim, oxasulfuron, acifluorfen, benazolin-ethyl, sulfentrazone, chlorimuron-ethyl, cloransulam-

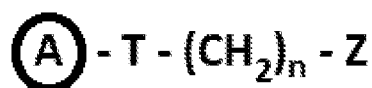
25 methyl, fomesafen, imazamox, imazaquin, imazethapyr, imazapyr, lactofen, fenoxaprop (P-ethyl), thidiazuron, tribufos, trifluralin, dimethachlor, napropamide, quinmerac, metazachlor, carbetamide, dimefuron, propyzamide, ethametsulfuron-methyl, tebutam, fluometuron, prometryn, norflurazon, pyriithiobac-

30 sodium, MSMA, DSMA, diuron, flurochloridone, dithiopyr, thiazopyr, oxyfluorfen, ethalfluralin, clodinafop, amidosulfuron, diclofop-methyl, diflufenican, ethoxysulfuron, fentrazamide, flazasulfuron, florasulam, fluazolate, flucarbazone, flupyrsulfuron-methyl sodium, flurtamone,

iodosulfuron, isoproturon, chlortoluron, chlorsulfuron, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, 2,4-DB, 2,4-DP, bifenox, flamprop-M, imazamethabenz-methyl, ioxynil, tralkoxydim, fluoroglycofen-ethyl, methabenzthiazuron, isoxaben, prosulfocarb, difenzoquat-metilsulfate, pretilachlor, 5 cinosulfuron, fenclorim, bensulfuron-methyl, imazosulfuron, pyrazosulfuron-ethyl, azimsulfuron, esprocarb, mefenacet, molinate, propanil, pyrazolate, cyhalofop-butyl, bispyribac-sodium, pyriminobac-methyl, cafenstrole, oxadiargyl, oxadiazon, 10 bromobutide, MY-100, dymron, NB 061, MK243, HW-52, AC 014, ametryn, hexazinone, asulam, azafenidin, tebuthiuron, ethametsulfuron-methyl, or a combination thereof.

According to some embodiments, the invention provides a method of controlling undesired plant growth comprising applying to the 15 locus of said undesired plant growth the agricultural composition according to one or more embodiments of the above composition.

According to some embodiments, the invention provides a method of controlling undesired plant growth comprising applying to the 20 locus of the undesired plant growth a herbicidally effective amount of a compound having the structure



or a salt thereof, wherein:

A is cyclopentadiene, benzene and indene scaffold comprising 25 from 1 to 4 heteroatoms; wherein each of the heteroatoms is independently selected from the group consisting of N, S, Se, and O; and wherein one or more of the carbon atoms of the ring are optionally chemically attached to at least one of the groups consisting of: -SO₂CF₃, -O-SO₂CF₃, -NR₃⁺, -SO₂R, 30 -C≡N, -CX₃, CX₂R, -COX, -CHO, -COR, -CO₂R, -CONH₂, -CONHR, -

CONR₂, -N=O, -N≡N⁺, -N=NR, -CR=NR, -N=CR₂, -F, -Cl, -Br, and -I; and wherein X is selected from F, Cl, Br and I;

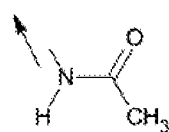
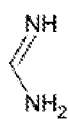
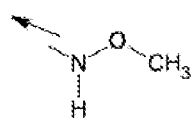
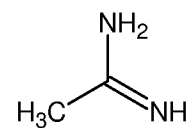
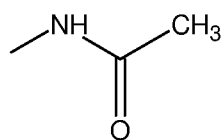
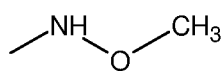
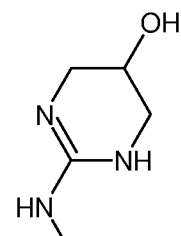
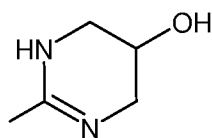
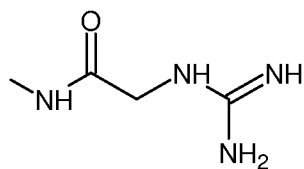
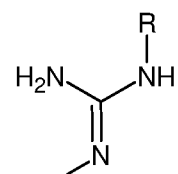
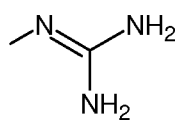
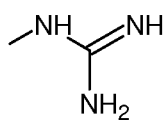
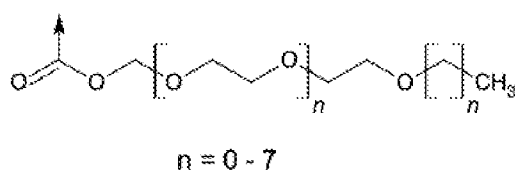
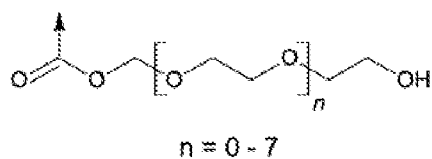
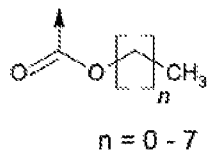
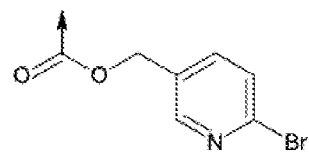
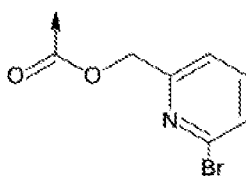
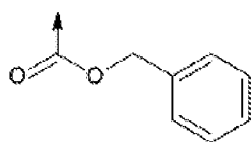
n is 0 to 5;

T is unsubstituted or substituted methylene group with one or two halides, oxygen, -SO₂CF₃, -O-SO₂CF₃, -NR₃⁺, -SO₂R, -C≡N, -CX₃, CX₂R, -COX, -CHO, -COR, -CO₂R, -CONH₂, -CONHR, -CONR₂, -F, -N=O, -N≡N⁺, -N=NR, -CR=NR, -N=CR₂, and wherein X is selected from F, Cl, Br and I; and,

Z is -COOH, COO⁻, OH, -O-R, COOR with saturated or non-saturated alcohol residues with straight, branched, cyclic, aromatic or heteroaromatic chain; -O-(CH₂CH₂O)_nR (n≥1); -O-(CHMeCH₂O)_nR (n≥1)); sulfonyl group, carbamoyl group, primary amine, secondary amine, tertiary amine, carboxamide, -NR-O-R, -O-NR₂, hydrazine, -NH-COR, and methanimidamide moiety or a salt thereof;

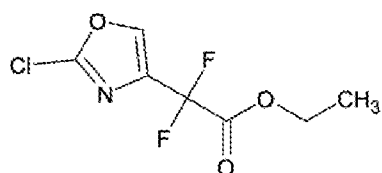
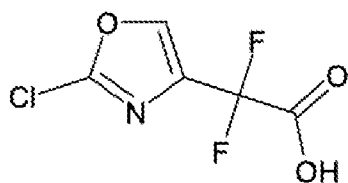
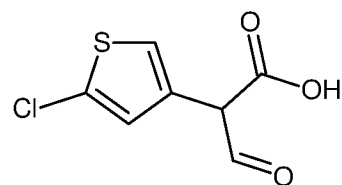
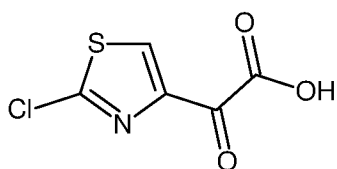
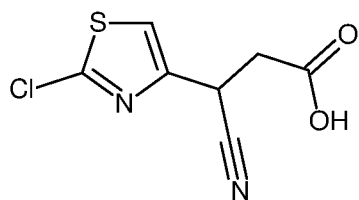
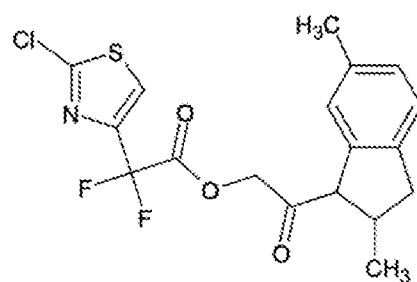
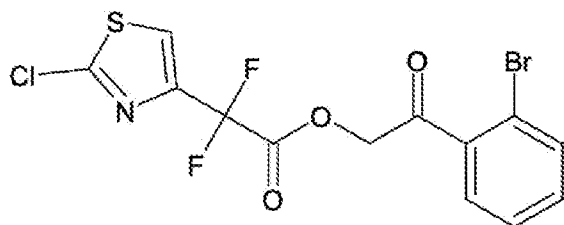
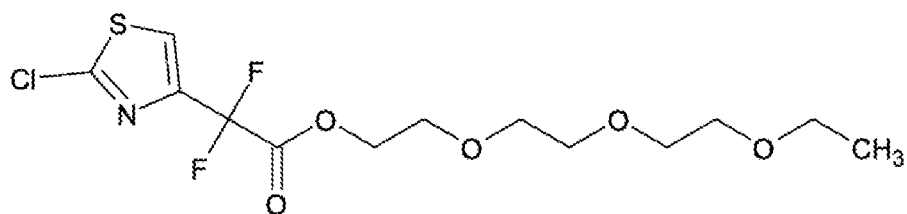
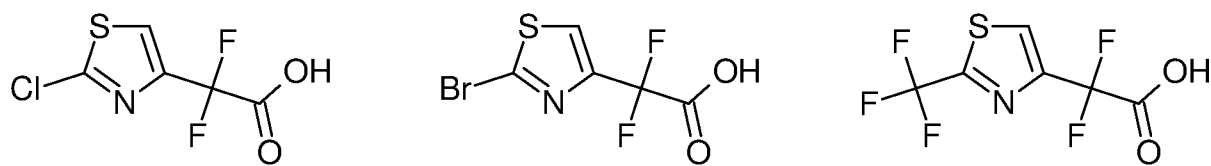
wherein R is selected from H, substituted or non-substituted alkyl, and substituted or non-substituted aryl group.

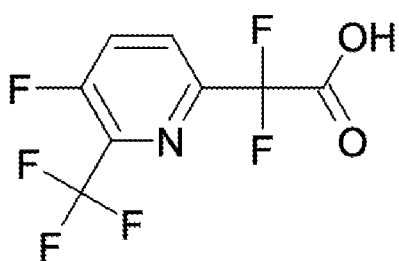
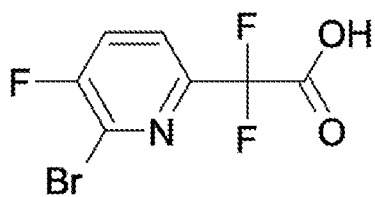
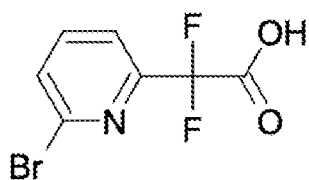
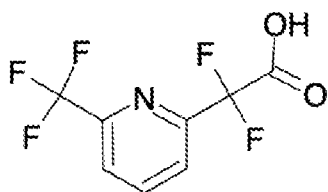
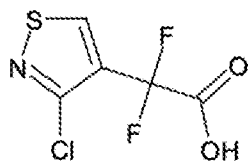
According to some embodiments, Z might be selected, without limitation, from the group including:

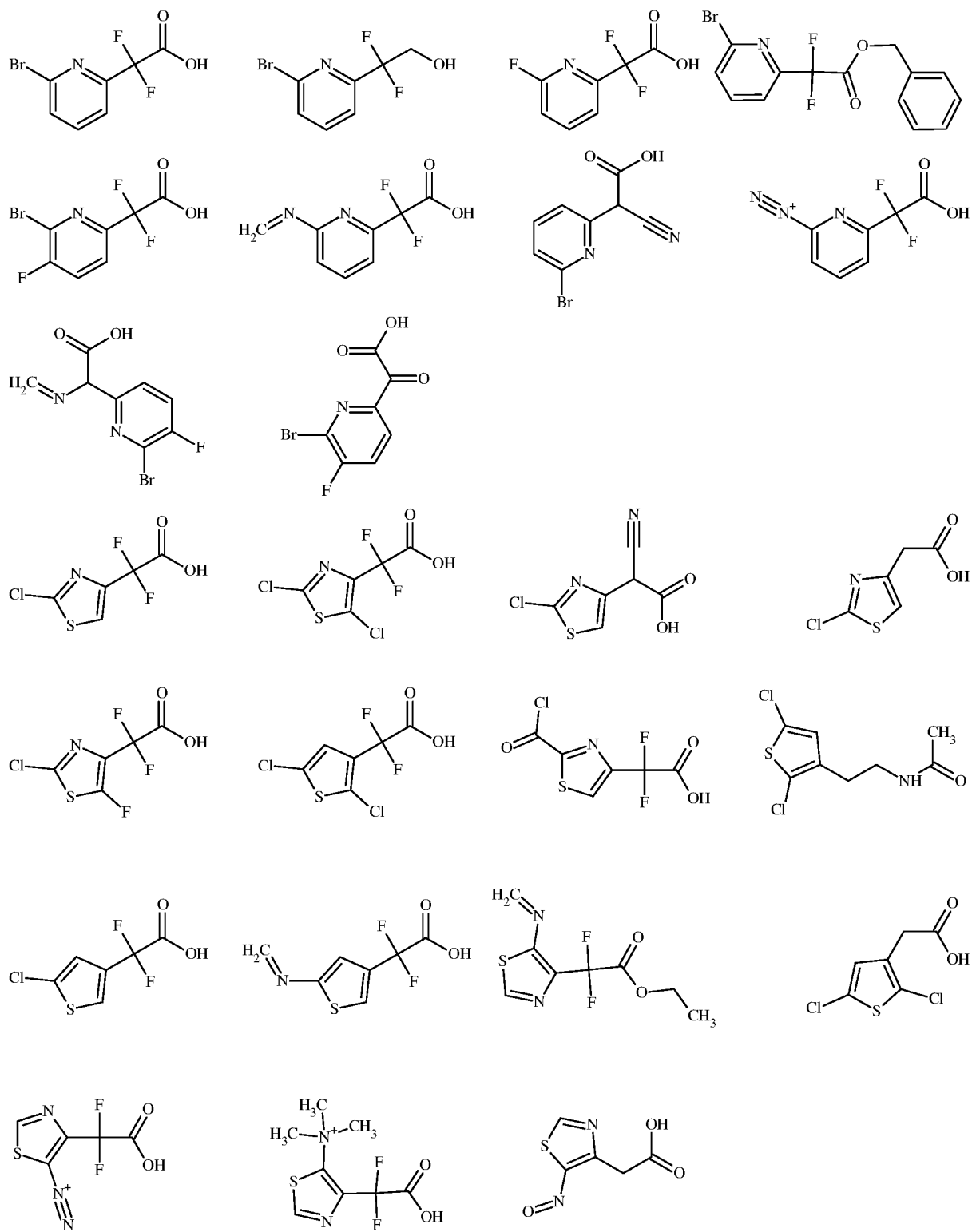


According to some embodiments of the above method, the
 5 unlimiting list of compounds, or agriculturally acceptable salts
 includes:

According to some embodiments of the above composition, the non-limiting list of compounds or agriculturally acceptable salts includes:





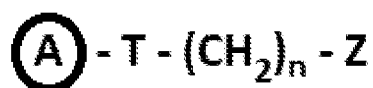


According to some embodiments of the above method, the method further comprises applying to the locus of the undesired plant growth at least one crop protection agent. In one embodiment, the crop protection agent is selected from the group consisting of herbicide, fungicide, insecticide and plant growth regulator. According to some embodiments of the above method, the crop protection agent is herbicide. In one embodiment, the crop protection agent is amino acid synthesis inhibitor herbicide. In one embodiment, the non-limiting list of amino acid synthesis inhibitor herbicides of the invention includes: sulfonylurea herbicide, imidazolinone herbicide, sulfonamide herbicide, amino acid derivatives, imazamox, imazapic, imazethapyr, imazaquin, imazapyr and imazamethabenz, Chlorimuron, Primisulfuron, Thifensulfuron, Triasulfuron, Nicosulfuron, Metsulfuron, Tribenuron, Rimsulfuron, Triflusulfuron, glyphosate or any combination thereof.

According to some embodiments of the above method, the crop protection agent is a plant growth regulator. In one embodiment, the non-limiting list of plant growth regulators of the invention includes: dicamba, 2,4-D, clopyralid and fluroxypyr.

According to some embodiments, the invention provides a method of controlling undesired plant growth comprising applying to the locus of the undesired plant growth:

a. a first herbicide having the structure



or a salt thereof, wherein:

A is cyclopentadiene, benzene and indene scaffold comprising from 1 to 4 heteroatoms; wherein each of the heteroatoms is independently selected from the group consisting of N, S, Se, and O; and wherein one or more of the carbon atoms of the ring are optionally chemically attached to at least one

of the groups consisting of: $-\text{SO}_2\text{CF}_3$, $-\text{O}-\text{SO}_2\text{CF}_3$, $-\text{NR}_3^+$, $-\text{SO}_2\text{R}$, $-\text{C}\equiv\text{N}$, $-\text{CX}_3$, $\text{CX}_2\text{R}-\text{COX}$, $-\text{CHO}$, $-\text{COR}$, $-\text{CO}_2\text{R}$, $-\text{CONH}_2$, $-\text{CONHR}$, $-\text{CONR}_2$, $-\text{F}$, $-\text{N}=\text{O}$, $-\text{N}\equiv\text{N}^+$, $-\text{N}=\text{NR}$, $-\text{CR}=\text{NR}$, $-\text{N}=\text{CR}_2$, $-\text{Cl}$, $-\text{Br}$, and $-\text{I}$; and wherein X is selected from F, Cl, Br and I;

5 n is 0 to 5;

T is unsubstituted or substituted methylene group with one or two halides, oxygen, $-\text{SO}_2\text{CF}_3$, $-\text{O}-\text{SO}_2\text{CF}_3$, $-\text{NR}_3^+$, $-\text{SO}_2\text{R}$, $-\text{C}\equiv\text{N}$, $-\text{CX}_3$, CX_2R , $-\text{COX}$, $-\text{CHO}$, $-\text{COR}$, $-\text{CO}_2\text{R}$, $-\text{CONH}_2$, $-\text{CONHR}$, $-\text{CONR}_2$, $-\text{F}$, $-\text{N}=\text{O}$, $-\text{N}\equiv\text{N}^+$, $-\text{N}=\text{NR}$, $-\text{CR}=\text{NR}$, $-\text{N}=\text{CR}_2$, and
10 wherein X is selected from F, Cl, Br and I; and,

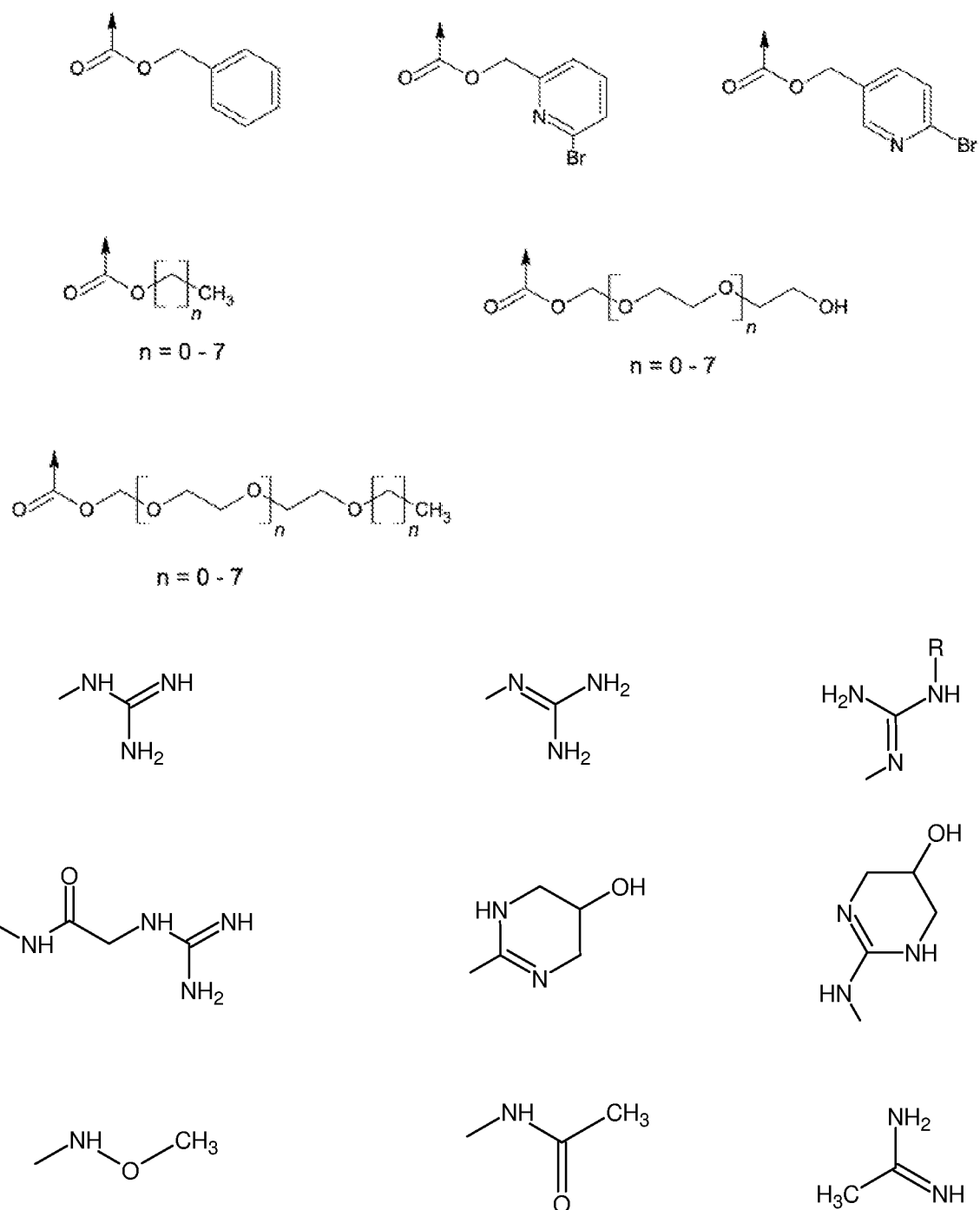
Z is $-\text{COOH}$, COO^- , OH , $-\text{O}-\text{R}$, COOR with saturated or non-saturated alcohol residues with straight, branched, cyclic, aromatic or heteroaromatic chain; $-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n\text{R}$ ($n\geq 1$); $-\text{O}-(\text{CHMeCH}_2\text{O})_n\text{R}$ ($n\geq 1$); sulfonyl group, carbamoyl
15 group, primary amine, secondary amine, tertiary amine, carboxamide, $-\text{NR}-\text{O}-\text{R}$, $-\text{O}-\text{NR}_2$, hydrazine, $-\text{NH}-\text{COR}$, and methanimidamide moiety or a salt thereof;

wherein R is selected from H, substituted or non-substituted alkyl, and substituted or non-substituted aryl group;

20 b. a second herbicide, to effectively control the undesired plant growth.

to thereby effectively control the undesired plant growth.

According to some embodiments of the above method, Z might be, without limitation:



According to some embodiments of the above method, the second herbicide is amino acid synthesis inhibitor herbicide.

- 5 According to some embodiments of the above method, the second herbicide is selected from the group consisting of sulfonylurea herbicide, imidazolinone herbicide, sulfonamide herbicide, and amino acid derivative.

According to some embodiments of the above method, the non-limiting list of the second herbicides of the invention includes: imazamox, imazapic, imazethapyr, imazaquin, imazapyr, imazamethabenz, Chlorimuron, Primisulfuron, Thifensulfuron,

5 Triasulfuron, Nicosulfuron, Metsulfuron, Tribenuron, Rimsulfuron, Triflusulfuron, Glyphosate, atrazine, terbuthylazine, (S)-metolachlor, metolachlor, terbutryn, simazine, dimethenamid, (S)-dimethenamid, flufenacet, acetochlor, alachlor, isoxaflutole, isoxachlortole, mesotrione,

10 sulcotrione, metosulam, flumetsulam, pendimethalin, bromoxynil, bentazone, carfentrazone-ethyl, clomazone, nicosulfuron, rimsulfuron, halosulfuron-methyl, metribuzin, flumiclorac-pentyl, prosulfuron, primisulfuron-methyl, dicamba, fluthiacet-methyl, pyridate, 2,4-D, clopyralide, diflufenzopyr,

15 fluroxypyr, MCPA, MCPB, mecoprop (MCP), metobenzuron, thifensulfuron-methyl, aclonifen, EPTC, glyphosate, glufosinate, sulfosate, cyanazine, propaquizafop, metamitron, pyramin, phenmedipham, desmedipham, ethofumesate, triasulfuron, chloridazon, lenacil, triallate, fluazifop, sethoxydim,

20 quizalofop, clopyralide, clethodim, oxasulfuron, acifluorfen, benazolin-ethyl, sulfentrazone, chlorimuron-ethyl, cloransulam-methyl, fomesafen, imazamox, imazaquin, imazethapyr, imazapyr, lactofen, fenoxaprop(P-ethyl), thidiazuron, tribufos, trifluralin, dimethachlor, napropamide, quinmerac, metazachlor,

25 carbetamide, dimefuron, propyzamide, ethametsulfuron-methyl, tebutam, fluometuron, prometryn, norflurazon, pyriithiobac-sodium, MSMA, DSMA, diuron, flurochloridone, dithiopyr, thiazopyr, oxyfluorfen, ethalfluralin, clodinafop, amidosulfuron, diclofop-methyl, diflufenican, ethoxysulfuron,

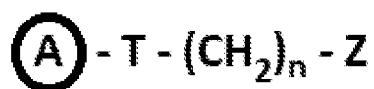
30 fentrazamide, flazasulfuron, florasulam, fluazolate, flucarbazone, flupyrsulfuron-methyl sodium, flurtamone, iodosulfuron, isoproturon, chlortoluron, chlorsulfuron, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, 2,4-DB, 2,4-DP, bifenox, flamprop-M, imazamethabenz-methyl, ioxynil,

tralkoxydim, fluoroglycofen-ethyl, methabenzthiazuron, isoxaben, prosulfocarb, difenzoquat-metilsulfate, pretilachlor, cinosulfuron, fenclorim, bensulfuron-methyl, imazosulfuron, pyrazosulfuron-ethyl, azimsulfuron, esprocarb, mefenacet, 5 molinate, propanil, pyrazolate, cyhalofop-butyl, bispyribac-sodium, pyriminobac-methyl, cafenstrole, oxadiargyl, oxadiazon, bromobutide, MY-100, dymron, NB 061, MK243, HW-52, AC 014, ametryn, hexazinone, asulam, azafenidin, tebuthiuron, and ethametsulfuron-methyl.

10 According to some embodiments of the above method, the method further comprises applying a third herbicide or a plant growth regulator.

According to some embodiments, the invention provides a composition for controlling undesired plant growth comprising a 15 mixture of:

a. a compound or a salt thereof having the structure



or a salt thereof, wherein:

20 A is cyclopentadiene, benzene and indene scaffold comprising from 1 to 4 heteroatoms; wherein each of the heteroatoms is independently selected from the group consisting of N, S, Se, and O; and wherein one or more of the carbon atoms of the ring are optionally chemically attached to at least one of the groups consisting of: -
25 SO₂CF₃, -O-SO₂CF₃, -NR₃⁺, -SO₂R, -C≡N, -CX₃, CX₂R-COX, -CHO, -COR, -CO₂R, -CONH₂, -CONHR, -CONR₂, -F, -N=O, -N≡N⁺, -N=NR, -CR=NR, -N=CR₂, -Cl, -Br, and -I; and wherein X is selected from F, Cl, Br and I;

n is 0 to 5;

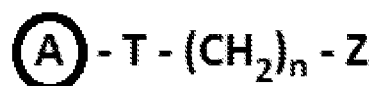
- T is unsubstituted or substituted methylene group with one or two halides, oxygen, $-\text{SO}_2\text{CF}_3$, $-\text{O}-\text{SO}_2\text{CF}_3$, $-\text{NR}_3^+$, $-\text{SO}_2\text{R}$, $-\text{C}\equiv\text{N}$, $-\text{CX}_3$, CX_2R , $-\text{COX}$, $-\text{CHO}$, $-\text{COR}$, $-\text{CO}_2\text{R}$, $-\text{CONH}_2$, $-\text{CONHR}$, $-\text{CONR}_2$, $-\text{F}$, $-\text{N}=\text{O}$, $-\text{N}\equiv\text{N}^+$, $-\text{N}=\text{NR}$, $-\text{CR}=\text{NR}$, $-\text{N}=\text{CR}_2$, and
 5 wherein X is selected from F, Cl, Br and I; and,
- Z is $-\text{COOH}$, COO^- , OH , $-\text{O}-\text{R}$, COOR with saturated or non-saturated alcohol residues with straight, branched, cyclic, aromatic or heteroaromatic chain; $-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n\text{R}$ ($n\geq 1$); $-\text{O}-(\text{CHMeCH}_2\text{O})_n\text{R}$ ($n\geq 1$); sulfonyl group, carbamoyl
 10 group, primary amine, secondary amine, tertiary amine, carboxamide, $-\text{NR}-\text{O}-\text{R}$, $-\text{O}-\text{NR}_2$, hydrazine, $-\text{NH}-\text{COR}$, and methanimidamide moiety or a salt thereof;
- wherein R is selected from H, substituted or non-substituted alkyl, and substituted or non-substituted aryl group;
- 15 b. at least one herbicide selected from the group consisting of atrazine, terbuthylazine, (S)-metolachlor, metolachlor, terbutryn, simazine, dimethenamid, (S)-dimethenamid, flufenacet, acetochlor, alachlor, isoxaflutole, isoxachlortole, mesotrione, sulcotrione, metosulam,
 20 flumetsulam, pendimethalin, bromoxynil, bentazone, carfentrazone-ethyl, clomazone, nicosulfuron, rimsulfuron, halosulfuron-methyl, metribuzin, flumiclorac-pentyl, prosulfuron, primisulfuron-methyl, dicamba, fluthiacet-methyl, pyridate, 2,4-D, clopyralide, diflufenzopyr,
 25 fluroxypyr, MCPA, MCPB, mecoprop (MCP), metobenzuron, thifensulfuron-methyl, aclonifen, EPTC, glyphosate, glufosinate, sulfosate, cyanazine, propaquizafop, metamitron, pyramin, phenmedipham, desmedipham, ethofumesate, triasulfuron, chloridazon, lenacil,
 30 triallate, fluazifop, sethoxydim, quizalofop, clopyralide, clethodim, oxasulfuron, acifluorfen, benazolin-ethyl, sulfentrazone, chlorimuron-ethyl, cloransulam-methyl, fomesafen, imazamox, imazaquin, imazethapyr, imazapyr,

lactofen, fenoxaprop(P-ethyl), thidiazuron, tribufos, trifluralin, dimethachlor, napropamide, quinmerac, metazachlor, carbetamide, dimefuron, propyzamide, ethametsulfuron-methyl, tebutam, fluometuron, prometryn, norflurazon, pyriithiobac-sodium, MSMA, DSMA, diuron, flurochloridone, dithiopyr, thiazopyr, oxyfluorfen, ethalfluralin, clodinafop, amidosulfuron, diclofop-methyl, diflufenican, ethoxysulfuron, fentrazamide, flazasulfuron, florasulam, fluazolate, flucarbazone, flupyrsulfuron-methyl sodium, flurtamone, iodosulfuron, isoproturon, chlortoluron, chlorsulfuron, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, 2,4-DB, 2,4-DP, bifenox, flamprop-M, imazamethabenz-methyl, ioxynil, tralkoxydim, fluoroglycofen-ethyl, methabenzthiazuron, isoxaben, prosulfocarb, difenzoquat-metilsulfate, pretilachlor, cinosulfuron, fenclorim, bensulfuron-methyl, imazosulfuron, pyrazosulfuron-ethyl, azimsulfuron, esprocarb, mefenacet, molinate, propanil, pyrazolate, cyhalofop-butyl, bispyribac-sodium, pyriminobac-methyl, cafenstrole, oxadiargyl, oxadiazon, bromobutide, MY-100, dymron, NB 061, MK243, HW-52, AC 014, ametryn, hexazinone, asulam, azafenidin, tebuthiuron, ethametsulfuron-methyl, or a combination thereof; and,

c. at least one agriculturally acceptable carrier.

According to some embodiments, the invention provides a composition for controlling undesired plant growth comprising a mixture of:

a. a compound having the structure



or a salt thereof, wherein:

A is cyclopentadiene, benzene and indene scaffold comprising from 1 to 4 heteroatoms; wherein each of the heteroatoms is independently selected from the group consisting of N, S, Se, and O; and wherein one or more of the carbon atoms of the ring are optionally chemically attached to at least one of the groups consisting of: -SO₂CF₃, -O-SO₂CF₃, -NR₃⁺, -SO₂R, -C≡N, -CX₃, CX₂R-COX, -CHO, -COR, -CO₂R, -CONH₂, -CONHR, -CONR₂, -F, -N=O, -N≡N⁺, -N=NR, -CR=NR, -N=CR₂, -Cl, -Br, and -I; and wherein X is selected from F, Cl, Br and I;

n is 0 to 5;

T is unsubstituted or substituted methylene group with one or two halides, oxygen, -SO₂CF₃, -O-SO₂CF₃, -NR₃⁺, -SO₂R, -C≡N, -CX₃, CX₂R, -COX, -CHO, -COR, -CO₂R, -CONH₂, -CONHR, -CONR₂, -F, -N=O, -N≡N⁺, -N=NR, -CR=NR, -N=CR₂, and wherein X is selected from F, Cl, Br and I; and,

Z is -COOH, COO⁻, OH, -O-R, COOR with saturated or non-saturated alcohol residues with straight, branched, cyclic, aromatic or heteroaromatic chain; -O-(CH₂CH₂O)_nR (n≥1); -O-(CHMeCH₂O)_nR (n≥1)); sulfonyl group, carbamoyl group, primary amine, secondary amine, tertiary amine, carboxamide, -NR-O-R, -O-NR₂, hydrazine, -NH-COR, and methanimidamide moiety or a salt thereof;

wherein R is selected from H, substituted or non-substituted alkyl, and substituted or non-substituted aryl group;

b. at least one plant growth regulator; and

c. at least one agriculturally acceptable carrier.

According to some embodiments, method of controlling amino acid content in a plant or a plant part thereof, comprising applying an effective amount of the agricultural composition according to the above embodiments of the invention.

According to some embodiments, the invention provides a method of controlling amino acid content in a plant or a plant part thereof, comprising applying an effective amount of the agricultural composition according to the above embodiments of the invention.

According to some embodiments, the invention provides a method of controlling plant growth comprising applying to the plant or a plant part thereof, an effective amount of the agricultural composition according to the above embodiments of the invention.

According to some embodiments, the invention provides a method of controlling growth of plants at least partially resistant to herbicides selected from the HPAC 9 group (Inhibitors of EPSP synthesis), 2 (Acetolactate Synthase (ALS) inhibitors), and 4 (Plant growth regulators or synthetic auxins), comprising applying to the plant or a plant part thereof, an effective amount of the agricultural composition according to the above embodiments of the invention.

According to some embodiments, the invention provides an agricultural composition comprising one or more compounds listed in Tables 2, 3, 4 and 5, and at least one agriculturally acceptable carrier.

According to some embodiments, the invention provides method of controlling undesired plant growth comprising applying one or more compounds listed in Tables 2, 3, 4 and 5.

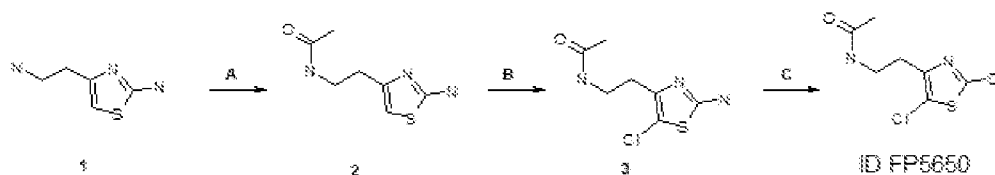
According to some embodiments, the invention provides method of controlling undesired plant growth comprising applying an agricultural composition comprising one or more compounds listed in Tables 2, 3, 4 and 5, and at least one agriculturally acceptable carrier.

Examples

In the examples below, if an abbreviation is not defined above, it has its generally accepted meaning. Further, all temperatures

are in degrees Celsius (unless otherwise indicated). The following methods were used to prepare the compounds set forth below as indicated.

Example 1: Synthesis of N-[2-(2,5-dichloro-1,3-thiazol-4-yl)ethyl]acetamide (ID FP5650)



- 5 Step A: 4-(2-aminoethyl)thiazol-2-amine dihydrochloride (5 g, 23.3 mmol) was suspended in DCM and cooled to 0°C, following by the consequent addition of TEA (7g, 70 mmol) and acetic anhydride (2.4g, 24 mmol) in a dropwise manner. After the reaction was complete, the mixture was evaporated to dryness and re-
- 10 evaporated with toluene 3 times to give crude N-(2-(2-aminothiazol-4-yl)ethyl)acetamide (4.5g, crude) which was used in the next step without purification.

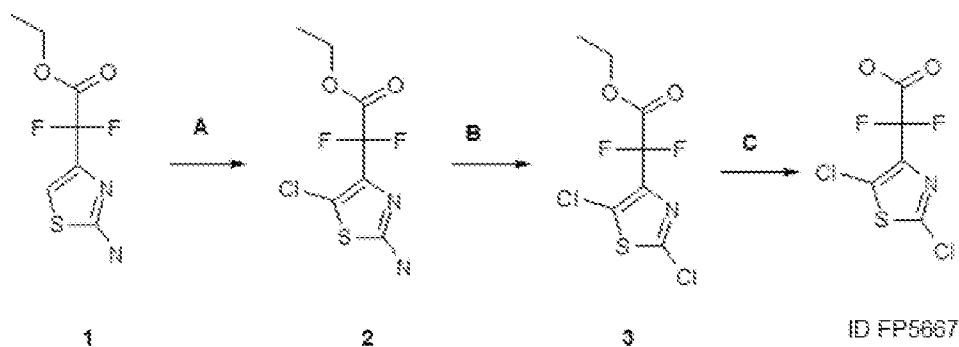
- Step B: N-(2-(2-aminothiazol-4-yl)ethyl)acetamide (4.5 g, 24.2 mmol) was dissolved in CH₃CN (50 mL), cooled to 0°C and NCS
- 15 (3.33 g, 25 mmol) was added in one portion. After the reaction was complete (concluded by HNMR) the organic solvent was evaporated to dryness and the crude mixture was partitioned between EtOAc (50 mL) and H₂O (50mL). The organic layer was washed with H₂O and brine, dried over Na₂SO₄ and evaporated under
- 20 reduced pressure to give ethyl N-(2-(2-amino-5-chlorothiazol-4-yl)ethyl)acetamide (3.7 g, 17.0 mmol, 70% yield) as yellow oil.

- Step C: To the pre-cooled to 0°C solution of N-(2-(2-amino-5-chlorothiazol-4-yl)ethyl)acetamide (3.7 g, 17.0 mmol) in CH₃CN (50 mL) anhydrous CuCl₂ (2.3g, 17 mmol) was added in one portion.
- 25 After 10 min, tert-butyl nitrite (1.8g, 17.5 mmol) was added in a dropwise manner (reaction starts after addition of about 10% of the reagent; the start can be identified by the beginning of

vigorous gas evolution). After the reaction was complete (concluded by HNMR) the volume of the reaction mixture was carefully reduced under reduced pressure to a half; the resulted crude mixture was dissolved in EtOAc (100 mL) and thoroughly washed with 5% aq HCl and brine. The organic layer was dried over Na₂SO₄ and evaporated under reduced pressure to give crude product, which was purified by FCC to give N-(2-(2,5-dichlorothiazol-4-yl)ethyl)acetamide (1.22g, 5.1mmol, 30% yield).

¹H NMR (500 MHz, DMSO-d₆) δ 7.94 (s, 1H), 3.29 (q, J = 6.4 Hz, 2H), 2.76 (t, J = 6.8 Hz, 2H), 1.76 (s, 3H). LCMS 239 [M+H]⁺. MW 239.12; Melting point 87°C, Purity 90%.

Example 2: Synthesis of 2-(2,5-dichloro-1,3-thiazol-4-yl)-2,2-difluoroacetic acid (ID FP5667)



Step A: Ethyl 2-(2-aminothiazol-4-yl)-2,2-difluoroacetate (350 g, 1.58 mol) was dissolved in CH₃CN (3 L), cooled to 0°C and NCS (215 g, 1.6 mol) was added in one portion. After the reaction was complete (concluded by HNMR) the organic solvent was evaporated to dryness and the crude mixture was partitioned between EtOAc (3 L) and H₂O (1 L). The organic layer was washed with H₂O and brine, dried over Na₂SO₄ and evaporated under reduced pressure to give ethyl 2-(2-amino-5-chlorothiazol-4-yl)-2,2-difluoroacetate (283 g, 1.1 mol, 70% yield) as yellow solid.

Step B: To the pre-cooled to 0°C solution of ethyl 2-(2-amino-5-chlorothiazol-4-yl)-2,2-difluoroacetate (283 g, 1.1 mol) in

CH₃CN (3 L) anhydrous CuCl₂ (155 g, 1.15 mol) was added in one portion. After 10 min, tert-butyl nitrite (121 g, 1.16 mol) was added in a dropwise manner (reaction starts after addition of about 10% of the reagent; the start can be identified by the beginning of vigorous gas evolution). After the reaction was complete (concluded by HNMR) the volume of the reaction mixture was carefully reduced under reduced pressure to a half; the resulted crude mixture was dissolved in EtOAc (3 L) and thoroughly washed with 5% aq HCl and brine. The organic layer was dried over Na₂SO₄ and evaporated under reduced pressure to give crude ethyl 2-(2,5-dichlorothiazol-4-yl)-2,2-difluoroacetate (210 g, crude) as dark brown oil, which was used in the next step without purification.

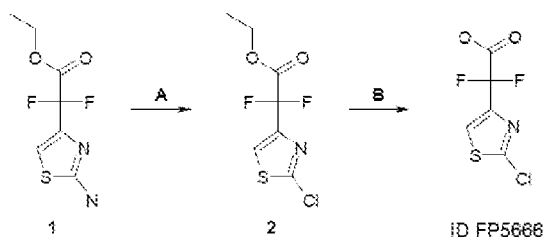
Step C: Crude ethyl 2-(2,5-dichlorothiazol-4-yl)-2,2-difluoroacetate (210 g, crude) from the previous step was dissolved in EtOH (2 L), and the 20% aq K₂CO₃ (0.5 L) was added in one portion. After the reaction was complete (typically 3 hrs) the solvents were evaporated to dryness, and the crude mixture was dissolved in H₂O (0.5 L); the clear solution was washed with CHCl₃ (3*200 mL) and MTBE (100 mL). The water layer was acidified with NaHSO₄ to pH = 4 and extracted with diethyl ether (3*150 mL). Combined organic layer was washed with brine, dried over Na₂SO₄ and evaporated under reduced pressure to give oily product. After column chromatography and trituration with pentane pure 2-(2,5-dichlorothiazol-4-yl)-2,2-difluoroacetic acid was obtained (113 g, 0.46 mol, 27% yield on 3 steps) as yellow solid.

¹H NMR (500 MHz, cdcl₃) δ 10.38 (s, 1H).

¹³C NMR (126 MHz, cdcl₃) δ 165.29 (t, J = 33.4 Hz), 149.86 (s), 140.45 (t, J = 29.7 Hz), 129.24 (s), 109.64 (t, J = 253.2 Hz).

¹⁹F NMR (470 MHz, cdcl₃) δ -102.57 (s).

LCMS 248 [M+H]⁺. Purity >95%

Example 3: Synthesis of 2-chloro-1,3-thiazol-4-yl)-2,2-difluoroacetic acid (ID FP5666)

Step A: To the pre-cooled to 0°C solution of ethyl 2-(2-aminothiazol-4-yl)-2,2-difluoroacetate (250 g, 1.12 mol) in CH₃CN (3 L) anhydrous CuCl₂ (155 g, 1.15 mol) was added in one portion (Caution! Exothermic effect is observed! Heating up to 10°C). After 10 min, tert-butyl nitrite (121 g, 1.16 mol) was added in a dropwise manner (reaction starts after addition of about 10% of the reagent; the start can be identified by the beginning of vigorous gas evolution). After the reaction was complete (concluded by HNMR) the volume of the reaction mixture was carefully reduced under reduced pressure to a half; the resulted crude mixture was dissolved in EtOAc (3 L) and thoroughly washed with 5% aq HCl and brine. The organic layer was dried over Na₂SO₄ and evaporated under reduced pressure to give crude ethyl 2-(2-chlorothiazol-4-yl)-2,2-difluoroacetate (205 g, crude) which was used in the next step without purification.

Step B: Crude ethyl 2-(2-chlorothiazol-4-yl)-2,2-difluoroacetate (205 g, crude) from the previous step was dissolved in EtOH (1.5 L), and the 20% aq K₂CO₃ (0.5 L) was added in one portion. After the reaction was complete (typically 3 hrs) the solvents were evaporated to dryness, and the crude mixture was dissolved in H₂O (500 mL); the clear solution was washed with CHCl₃ (3* 200 mL) and MTBE (100 mL). The water layer was acidified with NaHSO₄ to pH = 4 and extracted with diethyl ether (3*150 mL). Combined organic layer was washed with brine, dried over Na₂SO₄ and evaporated under reduced pressure to give oily product. After

column chromatography and trituration with pentane pure 2-(2-chlorothiazol-4-yl)-2,2-difluoroacetic acid (108 g, 0.5 mol, 45% yield on 2 steps) was obtained as yellow solid.

^1H NMR (400 MHz, CDCl_3) δ 11.61 (s, 1H), 7.70 (s, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 165.10 (t, $J = 33.6$ Hz), 154.53 (s), 145.63 (t, $J = 30.9$ Hz), 122.62 (t, $J = 4.7$ Hz), 109.40 (t, $J = 251.0$ Hz).

^{19}F NMR (376 MHz, CDCl_3) δ -103.92 (s).

LCMS 214 $[\text{M}+\text{H}]^+$. MP 92°C; Purity >95%

Example 4: Effect of derivatives of heterocyclic amino acids on germination & early plants development.

Materials: Seeds of Lettuce R. (Super-Jericho, non-sterilized) were obtained from Ben Shazar Moshe Ltd., 99% purity. The test compounds listed in the Table 2 below were synthesized de novo or purchased from different vendors.

Filter Paper Bioassays with Lettuce seeds: The protocol is following Bertin et al. 2009 and Movellan et al. 2014 with specified modifications as described below.

Seeds were placed on Whatman no. 1 filter paper (Whatman, Middlesex, U.K.) in Petri dishes (10 seeds per plate) with 2.0 ml of aqueous solution of a test material in concentration ranged from 0 (control) to 1 mmol/l were placed in a tray tilted at 45°. The trays were kept in dark for 48 hours and then transferred to the growth chamber with 6/18 dark/ light cycle for 4 days. Each experiment was performed at least with two repeats.

The development of plants' radicle and shoots were visually assessed 6 days after the beginning of the test to determine Minimal Effective Concentration (MEC) of a test material. In the context of the invention, MEC is defined as the lowest concentration level of a test material that caused deviation (absence of germination or malformation of radicle or shoots)

from the plant's development in the Control group. MEC is expressed in an arbitrary unit as activity score, as presented in Table 1:

MEC	Activity score
Higher than 0.1 mM	Weak
0.1 mM	Moderate
0.01 mM	Strong
0.001 mM and less	Very strong

Herbicidal activity of selected compounds on seeds germination and early plant development are summarized in Table 2:

ID	Chemical name	Score
584	2-(2,5-dichlorothiophen-3-yl) ethan-1-amine	moderate
585	3-(2,5-dichlorothiophen-3-yl)-2-hydroxypropanoic acid	moderate
586	2-(2,5-dichlorothiophen-3-yl) acetic acid	strong
587	1-(2,5-dichlorothiophen-3-yl)methanamine	weak
588	2-(thiophen-3-yl)ethan-1-amine	weak
589	2-(thiophen-3-yl)ethan-1-ol	strong
590	2-amino-1-(thiophen-3-yl)ethan-1-ol	weak
591	2-(thiophen-3-yl)acetamide	moderate
592	2-(1H-1,2,4-triazol-5-yl)ethan-1-amine	weak

593	3-(thiophen-3-yl)propan-1-amine	weak
596	2,5-dichloro-1,3-thiazole-4-carboxylic acid	Weak
597	4-(2,5-dichlorothiophen-3-yl)butanoic acid	Moderate
598	ethyl 3-[5-(chloromethyl)-1,3,4-thiadiazol-2-yl]-2-acetamido-3,3-difluoropropanoate	Weak
599	2-amino-3-(1H-indazol-3-yl)propanoic acid hydrochloride[HCl]	Moderate
678	(2-bromopyridin-4-yl)acetic acid	Strong
680	3-(2-bromopyridin-4-yl)-2-hydroxypropanoic acid	Weak
686	bis[(2-bromopyridin-4-yl)methyl]amine	Weak
688	2-(2-bromopyridin-4-yl)ethan-1-amine	Weak
689	2-(2,6-dibromopyridin-4-yl)acetic acid	Moderate
690	2-bromo-4-(2-bromoethyl)pyridine	Weak
691	naphthalene-2-carboxylic acid	Weak
692	2-bromopyridine-4-carboxylic acid	Weak
694	(2E)-3-(2,6-dichloropyridin-3-yl)prop-2-enoic acid	Moderate
5600	4-(2,5-dichlorothiophen-3-yl)butanamide	Weak
5601	2-(thiophen-3-yl)ethane-1-thiol	Moderate
5602	(2-aminoethyl)[(2,5-dichlorothiophen-3-yl)methyl]amine	Moderate

5603	2-([2-(thiophen-3-yl)ethyl]sulfanyl)ethan-1-amine	Weak
5604	3-(thiophen-3-yl)propane-1,2-diol	Moderate
5605	3-[(2,5-dichlorothiophen-3-yl)formamido]-2,2-difluoropropanoic acid	Weak
5606	3-(2,5-dichlorothiophen-3-yl)propanoic acid	Moderate
5607	(2E)-3-(5-chlorothiophen-2-yl)prop-2-enoic acid	Moderate
5608	(2E)-3-(1,3-thiazol-5-yl)prop-2-enoic acid	Weak
5609	2-(2,5-dichlorothiophen-3-yl)acetamide	Strong
5610	[(2,5-dichlorothiophen-3-yl)methyl]hydrazine	Weak
5612	3-(2,5-dichlorothiophen-3-yl)-2-oxopropanoic acid	Strong
5613	2,5-dichloro-1,3-thiazole-4-carbonylchloride	Weak
5614	2-bromo-N-[(2,5-dichlorothiophen-3-yl)methyl]pyridine-4-carboxamide	Moderate
5615	2-([(2,5-dichlorothiophen-3-yl)methyl]amino)acetic acid	Weak
5616	dichloro-1,3-thiazole-4-carboxamide	Moderate
5618	N-(2,5-dichloro-1,3-thiazol-4-yl)acetamide	Moderate

5620	(3E)-4-(2,5-dichlorothiophen-3-yl)-2-oxobut-3-enoic acid	Weak
5621	(2E)-3-(3-chloro-1H-1,2,4-triazol-5-yl)prop-2-enoic acid	Weak
5622	(2E)-3-(2,4-dichloro-1,3-thiazol-5-yl)prop-2-enoic acid	Moderate
5623	2-(2-chlorothiophen-3-yl)-2,2-difluoroacetic acid	Strong
5624	3-([(2,5-dichlorothiophen-3-yl)methyl]amino)-2,2-difluoropropanoic acid	Weak
5625	2-(5-chlorothiophen-3-yl)-2,2-difluoroacetic acid	Strong
5626	3-{4-[(2,5-dichlorothiophen-3-yl)methyl]piperazin-1-yl}propanoic acid	Weak
5628	3-(1H-1,2,4-triazol-1-yl)propanoic acid	Weak
5631	2-(2,5-dichlorothiophen-3-yl)-2-oxoacetic acid	Weak
5632	4-(2,5-dichlorothiophen-3-yl)-4,4-difluorobutanoic acid	Moderate
5633	2-amino-3-(1H-1,2,4-triazol-1-yl)propanoic acid dihydrochloride[HCl]	Strong
5636	2-(2,5-dichlorothiophen-3-yl)-2,2-difluoroacetamide	Strong
5637	2-(2,5-dichloro-1,3-thiazol-4-yl)acetic acid	Strong

5640	(2,5-dichlorothiophen-3-yl) (difluoro)acetic acid	Strong
5643	ethyl (2,5-dichlorothiophen-3-yl) (difluoro)acetate	Moderate
5644	[2-(2,5-dichlorothiophen-3-yl) (difluoro)acetamido]acetic acid	Strong
5645	2-oxo-2-(2,4,5-trichlorothiophen-3-yl)acetic acid	Strong
5654	2,2-difluoro-2-(2-oxo-2,3-dihydro-1H-1,3-benzodiazol-5-yl)acetic acid	Weak
5655	ethyl (2,5-dichloro-1,3-thiazol-4-yl) (difluoro)acetate	Strong
5657	4-(2,5-dichlorothiophen-3-yl)butan-1-amine	Moderate
5659	2-amino-2-(2,5-dichlorothiophen-3-yl)acetic acid	Weak
5660	propyl [2-(1H-1,2,4-triazol-3-yl)ethyl]amine	Weak
5661	ethyl 2-(2-bromo-5-methyl-1,3-thiazol-4-yl)acetate	Moderate
5662	ethyl 2-bromo-2-(2-bromo-5-methyl-1,3-thiazol-4-yl)acetate	Moderate
5663	ethyl 2-(2-bromo-1,3-thiazol-4-yl)acetate	Moderate
5666	sodium(2-chloro-1,3-thiazol-4-yl) (difluoro)acetate	very strong

5667	2-(2,5-dichloro-1,3-thiazol-4-yl)-2,2-difluoroacetic acid	very strong
5670	2-(2,5-dichlorothiophen-3-yl)-N-methoxyethan-1-amine	Moderate
5673	2-amino-4567-tetrahydro-1,3-benzothiazole-4-carboxylic acid hydrochloride	<moderate
5679	2,2-difluoro-2-[2-(trifluoromethyl)-1,3-thiazol-4-yl]acetic acid	very strong
5680	2-(2,5-dichloro-1,3-thiazol-4-yl)-NNN-trimethylethan-1-aminium	Weak
5683	2-chloro[1,3]thiazolo[5,4-b]pyridine-6-carboxylic acid	Moderate
5691	2-(2,5-dichloro-1,3-thiazol-4-yl)ethan-1-amine	Strong
5694	benzyl[2-(2,5-dichlorothiophen-3-yl)ethyl]amine	Moderate
5697	4-[difluoro(phenyl)methyl]-1,3-thiazol-2-amine	Strong
5700	2,2-difluoro[2-(trifluoromethyl)-1,3-thiazol-5-yl]acetic acid	Moderate
5702	2-chloro-4-(2-hydrazinyethyl)-1,3-thiazole	Moderate
5704	2-(2-chloro-1,3-thiazol-4-yl)acetohydrazide	Moderate
5705	[2-(2,5-dichlorothiophen-3-yl)ethyl]hydrazine	Moderate

5707	ethyl difluoro[5-(trifluoromethyl)thiophen-3-yl]acetate	Weak
5708	N-[2-(2,5-dichlorothiophen-3-yl)ethyl]-2-phenylacetamide	Moderate
5709	benzyl (2,5-dichlorothiophen-3-yl) (difluoro) acetate	very strong
5710	2,2-difluoro-2-[5-(trifluoromethyl)-1,3-thiazol-2-yl]acetic acid	Strong
5715	2-(2-chloro-1,3-thiazol-4-yl)-N'-methyl acetohydrazide	Moderate
5716	2-[2-(5-chloro-3-fluoropyridin-2-yl)-1,3-thiazol-4-yl]acetic acid	Moderate
5717	2,2-difluoro-2-[5-methyl-2-(trifluoromethyl)-1,3-thiazol-4-yl]acetic acid	Strong
5719	2,2-difluoro-2-(2-nitro-1,3-thiazol-4-yl)acetic acid	Moderate
5721	sodium 2-(2-chloro-1,3-thiazol-5-yl)-2,2-difluoroacetate	Moderate
5722	(2,4-dichloro-1,3-thiazol-5-yl) (difluoro) acetic acid	Weak
5723	N-(2-{[2-(2,5-dichlorothiophen-3-yl)ethyl]amino}ethyl)methane sulfonamide	Strong
5724	2-(2-chloro-1,3-thiazol-4-yl)-2,2-difluoroethan-1-ol	Moderate

5725	N'-[2-(2,5-dichlorothiophen-3-yl)ethyl]-N-(3-hydroxypropyl)guanidine	Moderate
5726	2-carbamimidamido-N-[2-(2,5-dichlorothiophen-3-yl)ethyl]acetamide	Moderate
5727	N-[2-(2,5-dichlorothiophen-3-yl)ethyl]-N'-(2-hydroxypropyl)guanidine	Moderate
5728	difluoro[2-(trifluoromethyl)thiophen-3-yl]acetic acid	Strong
5729	ethyl 2-(2-amino-5-chloro-1,3-thiazol-4-yl)-2,2-difluoroacetate	Weak
5730	2-(2-bromo-1,3-thiazol-4-yl)-2,2-difluoroacetic acid	very strong
5732	N-{2-[3-(2,5-dichlorothiophen-3-yl)propoxy]phenyl}guanidine	Moderate
5734	2-[2-(4-chloro-2-fluorophenyl)-1,3-thiazol-4-yl]-2,2-difluoroacetic acid	Moderate
5735	(4-bromophenyl)methyl(2,5-dichlorothiophen-3-yl)acetate	strong.strong
5736	2,2-difluoro-2-{2-[3-fluoro-5-(trifluoromethyl)pyridin-2-yl]-1,3-thiazol-4-yl}acetic acid	Moderate
5737	[(2-bromo-1,3-thiazol-4-yl)(difluoro)methyl]phosphonic acid	Weak
5738	2-(4-methylphenyl)-2-oxoethyl(2-chloro-1,3-thiazol-4-yl)(difluoro)acetate	very strong

5740	2-oxo-2-(pyridin-2-yl)ethyl (2-chloro-1,3-thiazol-4-yl) (difluoro) acetate	very strong
5741	2-oxo-2-phenylethyl (2-chloro-1,3-thiazol-4-yl) (difluoro) acetate	very strong
5742	2-(2-{[2-(2,5-dichlorothiophen-3-yl)ethyl]amino}-45-dihydro-1H-imidazol-1-yl)ethan-1-ol	Moderate
5743	3-acetyl-1-[2-(2,5-dichlorothiophen-3-yl)ethyl]piperidin-4-one	Moderate
5744	[2,5-bis(trifluoromethyl)-1,3-thiazol-4-yl] (difluoro) acetic acid	Moderate
5745	2-[2-(benzyloxy)ethoxy]ethyl 2-(2-chloro-1,3-thiazol-4-yl)-2,2-difluoroacetate	very strong
5746	2-(2-methoxyethoxy)ethyl (2-chloro-1,3-thiazol-4-yl) (difluoro) acetate	very strong
5747	(2-bromophenyl)methyl (2,5-dichlorothiophen-3-yl) (difluoro) acetate	very strong
5748	2-(1,2,3-thiadiazol-4-yl) acetic acid	Moderate
5750	5H,6H-thieno[3,2-d][1,2,3]thiadiazole-5-carboxylic acid	Moderate
5751	(2-chloro-5-fluoro-1,3-thiazol-4-yl) (difluoro) acetic acid	strong.strong
5752	{2-[(6-amino-9H-purin-9-yl)methoxy]ethoxy}methyl (2-chloro-1,3-thiazol-4-yl) acetate	Moderate

5756	3-(4-bromophenyl)-1-(2-chloro-1,3-thiazol-4-yl)-1,1-difluoropropan-2-one	very strong
5757	(6-bromopyridin-2-yl)methyl 2-(2,5-dichlorothiophen-3-yl)-2,2-difluoroacetate	Strong
5758	benzyl 2-(2-chloro-1,3-thiazol-4-yl)acetate	Strong
5759	(6-bromopyridin-2-yl)methyl 2-(2,5-dichlorothiophen-3-yl)acetate	very strong
5760	difluoro[4-(trifluoromethyl)-1,3-thiazol-2-yl]acetic acid	Moderate
5761	3-(2-chlorothiophen-3-yl)-3,3-difluoro-2-hydroxypropanenitrile	Strong
5762	benzyl 2-(2-chloro-1,3-thiazol-4-yl)(difluoro)acetate	very strong
5763	2,2-difluoro-2-{2-[2-fluoro-4-(trifluoromethyl)phenyl]-1,3-thiazol-4-yl}acetic acid	Moderate
5764	difluoro[4-(trifluoromethyl)thiophen-3-yl]acetic acid	Strong
5765	N''-[3-(2,5-dichlorothiophen-3-yl)propyl]guanidine	Strong
5766	N-[2-(2,5-dichlorothiophen-3-yl)ethyl]-N'-(4-hydroxyphenyl)guanidine	Moderate
5768	(4-bromophenyl)methyl 2-(2,5-dichlorothiophen-3-yl)(difluoro)acetate	Strong

5769	N''-[2-(2,5-dichlorothiophen-3-yl)ethyl]guanidine	Strong
5770	2-{2-[3-fluoro-5-(trifluoromethyl)pyridin-2-yl]-1,3-thiazol-4-yl}acetic acid	Weak
5771	2-(2-methoxyethoxy)ethyl (2-chloro-1,3-thiazol-4-yl) (difluoro) acetate	very strong
5772	(2-bromophenyl)methyl (2,5-dichlorothiophen-3-yl) (difluoro) acetate	Strong
5773	2-(3-chloro-1,2-thiazol-4-yl)-2,2-difluoroacetic acid	Moderate
5774	[3-(2-bromo-1,3-thiazol-4-yl)propyl]phosphonic acid	Weak
5776	lithium(1+) 2-(1,2,5-thiadiazol-3-yl) acetate[Li+]	Moderate
5777	2-[2-(2,5-dichlorothiophen-3-yl)ethyl]-1,4,5,6-tetrahydropyrimidin-5-ol	Weak
5778	2,5,8,11,14-pentaoxahexadecan-16-yl 2-(2-chloro-1,3-thiazol-4-yl)-2,2-difluoroacetate	very strong
5779	(4-cyanothiophen-3-yl) (difluoro) acetic acid	Strong
5781	ethyl 2,2-difluoro-2-[2-(trifluoromethyl)-1,3-thiazol-4-yl]acetate	Strong
5783	ethyl 2-(2-chlorooxazol-4-yl)-2,2-difluoroacetate	Moderate

5784	ethyl 2-(2-chloro-1,3-thiazol-4-yl)-2,2-difluoroacetate	very strong
5785	(4-methyl-1,2,5-thiadiazol-3-yl)acetic acid	Moderate
5786	2-(2-chloro-1,3-benzothiazol-4-yl)-2,2-difluoroacetic acid	Moderate
5791	2-[5-chloro-2-(trifluoromethyl)-1,3-thiazol-4-yl]-2,2-difluoroacetic acid	Strong
5795	2-(4-methylphenyl)-2-oxoethyl (2-chloro-1,3-thiazol-4-yl)acetate	Moderate
5796	ethyl (5-chlorothiophen-3-yl)acetate	Moderate
5799	difluoro(1H-tetrazol-5-yl)acetic acid	Moderate
5800	2-(2-ethoxyethoxy)ethyl (2-chloro-1,3-thiazol-4-yl)acetate	Strong
5801	2-(6-bromopyridin-2-yl)-2-oxoethyl 2-(2-chloro-1,3-thiazol-4-yl)acetate	Moderate
5802	(6-bromopyridin-2-yl)methyl 2-(2-chlorothiophen-3-yl)acetate	Moderate
6600	2-bromopyridine-4-carboxamide	Weak
6602	(2-bromopyridin-4-yl)urea	Weak
6603	(2E)-3-(6-chloropyridin-2-yl)prop-2-enoic acid	Weak
6604	(2E)-3-(2-chloropyridin-3-yl)prop-2-enoic acid	Moderate

6605	(2E)-3-(2-bromopyridin-3-yl)prop-2-enoic acid	Strong
6606	(2E)-3-(2-bromopyridin-4-yl)prop-2-enoic acid	Weak
6607	2-bromo-N-(2-bromopyridin-4-yl)pyridine-4-carboxamide	Strong
6608	(2E)-3-(2-bromo-strong-nitropyridin-4-yl)prop-2-enoic acid	Moderate
6609	2-(6-bromopyridin-3-yl)-2-oxoacetic acid	Weak
6610	(2E)-3-(2-bromopyridin-4-yl)-N-(4-hydroxyphenyl)prop-2-enamide	Moderate
6611	3-(2-bromopyridin-4-yl)-2-oxopropanoic acid	Weak
6612	2-(2,6-dibromopyridin-4-yl)ethan-1-amine	Moderate
6614	2,2-difluoro-2-(pyridin-4-yl)acetic acid	Weak
6615	2-[4-(pyridin-4-yloxy)phenyl]acetic acid	Weak
6616	3-amino-3-(2-bromopyridin-4-yl)propanamide	Weak
6617	2-(6-bromopyridin-2-yl)-2,2-difluoroacetic acid	Strong
6618	3-[(2-bromopyridin-4-yl)formamido]-2,2-difluoropropanoic acid	Strong
6619	2,2-difluoro-2-(pyrimidin-2-yl)acetic acid	Weak
6620	2-(6-bromopyridin-3-yl)-2,2-difluoroacetic acid	Strong

6621	2-(6-bromopyrimidin-4-yl)ethan-1-amine	Strong
6625	2-(2-phenoxy pyridin-4-yl)ethan-1-amine	Weak
6626	(2-bromopyridin-4-yl)(oxo)acetic acid	Moderate
6627	1-chloroisoquinoline-7-carboxylic acid	Moderate
6628	2-(2,6-dichloropyridin-4-yl)-2,2-difluoroacetic acid	Weak
6629	methyl 2-(2-bromopyridin-4-yl)-2,2-difluoroacetate	Moderate
6631	(2E)-3-(2-bromo-3-nitropyridin-4-yl)prop-2-enoic acid	Moderate
6632	(2,6-dibromopyridin-4-yl)-2,2-difluoroacetic acid	Weak
6634	6-bromopyridine-2-carboximidamide hydrochloride[HCl]	Weak
6635	ethyl 2-(6-bromopyridin-2-yl)acetate	Moderate
6636	N-[(6-bromopyridin-2-yl)methyl]guanidine	Moderate
6637	N-(6-bromopyridin-2-yl)guanidine hydrochloride	Weak
6638	(2E)-3-(6-bromopyridin-3-yl)-2,3-difluoroprop-2-enoic acid	Moderate
6640	ethyl 2-(6-bromopyridin-2-yl)-2,2-difluoroacetate	Strong
6643	2-(6-bromopyridin-2-yl)-2,2-difluoroethan-1-ol	Moderate

6645	2-bromo-6-phenoxy pyridine	Strong
6646	benzyl (6-bromopyridin-2-yl) (difluoro) acetate	Strong
6649	3-(2-bromopyridin-4-yl)propan-1-amine	Moderate
6651	2,2-difluoro-2-[6-(trifluoromethyl)pyridin-2-yl]acetic acid	Strong
6652	2,2-difluoro-2-[4-(trifluoromethyl)pyrimidin-2-yl]acetic acid	Moderate
6658	2,2-difluoro-2-{6-[2-(trifluoromethyl)-1,3-thiazol-4-yl]pyridin-2-yl}acetic acid	Moderate
6659	2,2-difluoro-2-{6-[2-fluoro-4-(trifluoromethyl)phenyl]pyridin-2-yl}acetic acid	Moderate
6660	difluoro(3,5,6-trifluoropyridin-2-yl)acetic acid	Moderate
6661	2-fluoro-2-(3,5,6-trifluoropyridin-2-yl)acetic acid	Moderate
6664	difluoro(6-fluoropyridin-2-yl)acetic acid	Strong
6667	(6-chloropyridin-2-yl) (difluoro) acetic acid	Strong
6669	2-amino-3-(3-bromophenyl)propanoic acid	Moderate
6670	6-bromopyridine-2-carbonitrile	Weak
6671	[6-chloro-5-(trifluoromethyl)pyridin-2-yl] (difluoro) acetic acid	Strong

6681	(6-bromo-5-fluoropyridin-2-yl) (difluoro)acetic acid	very strong
6682	[6-bromo-5-(trifluoromethyl)pyridin-2-yl] (difluoro)acetic acid	Strong

Example 6: Post-emergence herbicidal activity of selected derivatives of non-coded amino acids (DNAA).

The tests were performed on Romaine lettuce (*Lactuca sativa* L.) plants at the stage 2 to 3 leaves. The plants were grown in mini-pots packed with soil, dimensions 2 X 2 X 5 cm, one plant per mini-pot. Test compounds were dissolved in 0.1% aqueous solution water solution of Silwet adjuvant to final concentrations ranging from 0 (Control) to 0.0001%. The test compounds were applied on soil (1 ml per pot) or foliar with airbrush (0.1 ml per pot). Each concentration was tested on 20 plants. Two weeks after the treatment the herbicidal effects of the respective test material were visually evaluated (aboveground part and roots. Then the aboveground part of the plants was neatly cut and weighed (wet weight) to assess the growth inhibition caused by the test compound. The growth inhibition (GI) was calculated as following:

$$GI = 1 - Mt * 100\% / Mc$$

Where Mt and Mc are median wet weight of treated and control plants, respectively. In the context of the invention, the herbicidal effect was assessed by concentration of the compound causing more than 85% of Growth Inhibition (GI) or irreversible damage of the plants (Table 3). Herbicidal activity of selected DHAAAs is summarized in Table 4 (soil application) and Table 5 (Foliar application).

Table 3. The success criteria (Scores of herbicidal activity)

Test material causing more than 85% of Growth Inhibition (GI) or irreversible plant damage, (milligram per pot)	Score
<0.01	very strong
0.01 to 0.05	strong
0.5	moderate
1.0	weak

Table 4: Herbicidal activity of selected DNAA's (Soil application)

ID	Chemical name	Score
584	2-(2,5-dichlorothiophen-3-yl)ethan-1-amine	weak
586	2-(2,5-dichlorothiophen-3-yl)acetic acid	moderate
678	(2-bromopyridin-4-yl)acetic acid	weak
689	2-(2,6-dibromopyridin-4-yl)acetic acid	moderate
5600	4-(2,5-dichlorothiophen-3-yl)butanamide	moderate
5623	2-(2-chlorothiophen-3-yl)-2,2-difluoroacetic acid	strong
5625	2-(5-chlorothiophen-3-yl)-2,2-difluoroacetic acid	strong
5629	N-[2-(2,5-dichlorothiophen-3-yl)ethyl]acetamide	moderate
5637	2-(2,5-dichloro-1,3-thiazol-4-yl)acetic acid	strong
5640	(2,5-dichlorothiophen-3-yl) (difluoro)acetic acid	strong
5650	N-[2-(2,5-dichloro-1,3-thiazol-4-yl)ethyl]acetamide	moderate
5655	ethyl (2,5-dichloro-1,3-thiazol-4-yl) (difluoro)acetate	strong

5656	methyl 2-chloro-2-(2,5-dichlorothiophen-3-yl) acetate	moderate
5661	ethyl 2-(2-bromo-5-methyl-1,3-thiazol-4-yl) acetate	moderate
5663	ethyl 2-(2-bromo-1,3-thiazol-4-yl) acetate	moderate
5666	sodium (2-chloro-1,3-thiazol-4-yl) (difluoro) acetate	strong
5667	2-(2,5-dichloro-1,3-thiazol-4-yl)-2,2-difluoroacetic acid	strong
5668	ethyl (2,5-dichlorothiophen-3-yl) acetate	strong
5669	benzyl 2-(2,5-dichlorothiophen-3-yl) acetate	strong
5670	2-(2,5-dichlorothiophen-3-yl)-N-methoxyethan-1-amine	moderate
5679	2,2-difluoro-2-[2-(trifluoromethyl)-1,3-thiazol-4-yl]acetic acid	strong
5724	2-(2-chloro-1,3-thiazol-4-yl)-2,2-difluoroethan-1-ol	strong
5728	difluoro[2-(trifluoromethyl)thiophen-3-yl]acetic acid	strong
5730	2-(2-bromo-1,3-thiazol-4-yl)-2,2-difluoroacetic acid	strong
5738	2-(4-methylphenyl)-2-oxoethyl (2-chloro-1,3-thiazol-4-yl) (difluoro) acetate	strong
5745	2-[2-(benzyloxy)ethoxy]ethyl 2-(2-chloro-1,3-thiazol-4-yl)-2,2-difluoroacetate	strong
5746	2-(2-methoxyethoxy)ethyl (2-chloro-1,3-thiazol-4-yl) (difluoro) acetate	strong
5747	(2-bromophenyl)methyl (2,5-dichlorothiophen-3-yl) (difluoro) acetate	moderate
5757	(6-bromopyridin-2-yl)methyl 2-(2,5-dichlorothiophen-3-yl)-2,2-difluoroacetate	strong
5759	(6-bromopyridin-2-yl)methyl (2,5-dichlorothiophen-3-yl) acetate	strong

5761	3-(2-chlorothiophen-3-yl)-3,3-difluoro-2-hydroxypropanenitrile	strong
5768	(4-bromophenyl)methyl (2,5-dichlorothiophen-3-yl) (difluoro)acetate	moderate
5771	2-(2-methoxyethoxy)ethyl (2-chloro-1,3-thiazol-4-yl) (difluoro)acetate	very strong
5772	(2-bromophenyl)methyl (2,5-dichlorothiophen-3-yl) (difluoro)acetate	strong
5778	2,5,8,11,14-pentaoxahexadecan-16-yl 2-(2-chloro-1,3-thiazol-4-yl)-2,2-difluoroacetate	very strong
5781	ethyl 2,2-difluoro-2-[2-(trifluoromethyl)-1,3-thiazol-4-yl]acetate	very strong
6610	(2E)-3-(2-bromopyridin-4-yl)-N-(4-hydroxyphenyl)prop-2-enamide	moderate
6617	2-(6-bromopyridin-2-yl)-2,2-difluoroacetic acid	strong
6635	ethyl 2-(6-bromopyridin-2-yl)acetate	moderate
6638	(2E)-3-(6-bromopyridin-3-yl)-2,3-difluoroprop-2-enoic acid	moderate
6640	ethyl 2-(6-bromopyridin-2-yl)-2,2-difluoroacetate	moderate
6643	2-(6-bromopyridin-2-yl)-2,2-difluoroethan-1-ol	moderate
6646	benzyl (6-bromopyridin-2-yl) (difluoro)acetate	strong
6651	2,2-difluoro-2-[6-(trifluoromethyl)pyridin-2-yl]acetic acid	moderate
6664	difluoro(6-fluoropyridin-2-yl)acetic acid	strong
6667	(6-chloropyridin-2-yl) (difluoro)acetic acid	strong
6671	[6-chloro-5-(trifluoromethyl)pyridin-2-yl] (difluoro)acetic acid	strong

Table 5. Herbicidal activity of selected DNAAs (foliar application).

ID	Chemical name	Score
586	2-(2,5-dichlorothiophen-3-yl)acetic acid	moderate
5623	2-(2-chlorothiophen-3-yl)-2,2-difluoroacetic acid	strong
5625	2-(5-chlorothiophen-3-yl)-2,2-difluoroacetic acid	strong
5637	2-(2,5-dichloro-1,3-thiazol-4-yl)acetic acid	moderate
5640	(2,5-dichlorothiophen-3-yl)(difluoro)acetic acid	strong
5655	ethyl (2,5-dichloro-1,3-thiazol-4-yl)(difluoro)acetate	strong
5661	ethyl 2-(2-bromo-5-methyl-1,3-thiazol-4-yl)acetate	moderate
5663	ethyl 2-(2-bromo-1,3-thiazol-4-yl)acetate	strong
5666	sodium (2-chloro-1,3-thiazol-4-yl)(difluoro)acetate	strong
5667	2-(2,5-dichloro-1,3-thiazol-4-yl)-2,2-difluoroacetic acid	strong
5669	benzyl 2-(2,5-dichlorothiophen-3-yl)acetate	strong
5679	2,2-difluoro-2-[2-(trifluoromethyl)-1,3-thiazol-4-yl]acetic acid	strong
5709	benzyl (2,5-dichlorothiophen-3-yl)(difluoro)acetate	moderate
5728	difluoro[2-(trifluoromethyl)thiophen-3-yl]acetic acid	strong
5730	2-(2-bromo-1,3-thiazol-4-yl)-2,2-difluoroacetic acid	strong
5738	2-(4-methylphenyl)-2-oxoethyl (2-chloro-1,3-thiazol-4-yl)(difluoro)acetate	moderate
5745	2-[2-(benzyloxy)ethoxy]ethyl 2-(2-chloro-1,3-thiazol-4-yl)-2,2-difluoroacetate	moderate
5746	2-(2-methoxyethoxy)ethyl (2-chloro-1,3-thiazol-4-yl)(difluoro)acetate	strong

5747	(2-bromophenyl)methyl (2,5-dichlorothiophen-3-yl) (difluoro)acetate	moderate
5759	(6-bromopyridin-2-yl)methyl (2,5-dichlorothiophen-3-yl)acetate	strong
5768	(4-bromophenyl)methyl (2,5-dichlorothiophen-3-yl) (difluoro)acetate	strong
5771	2-(2-methoxyethoxy)ethyl (2-chloro-1,3-thiazol-4-yl) (difluoro)acetate	strong
5772	(2-bromophenyl)methyl (2,5-dichlorothiophen-3-yl) (difluoro)acetate	moderate
5778	2,5,8,11,14-pentaoxahexadecan-16-yl 2-(2-chloro-1,3-thiazol-4-yl)-2,2-difluoroacetate	moderate
5781	ethyl 2,2-difluoro-2-[2-(trifluoromethyl)-1,3-thiazol-4-yl]acetate	strong
6617	2-(6-bromopyridin-2-yl)-2,2-difluoroacetic acid	moderate

Example 7: Herbicidal activity of selected DNAAs on the development of weeds.

Weed seeds were sown in 0.3-liter pots, containing medium-heavy clay-loam soil from organic fields (55% clay, 23% silt, 20% sand, 2% organic matter, pH 7.1). The experiment was conducted in a completely randomized design. Each treatment was replicated 3 times (3 pots). Each compound was typically tested on crops (Corn, Wheat, Soy, Cotton, Oat, Chickpea) and weeds (Amaranth, Chenopodium, Lentils, Sinapis, Silybum).

The herbicides were applied at dose from 0 (control) to 5 mg/pot. The treatment was performed at the day of sown (pre-emergence treatment). Then the pots were transferred to a mesh house 24 hours after herbicide application and were sprinkler irrigated to field capacity of the soil. Alternatively, the herbicides were applied on grown plants at stage 2 - 3 true leaves (post-emergence treatment).

The plants were grown in the mesh house during the entire experiment. Plant development at 6, 12, 19, 26 and 32 days after

application (DAA) were evaluated on a scale of 0 to 5, in which 0 represents dead plants and 5 represents healthy plants similar or not different from Control. In the context of the invention, the herbicidal effect was expressed as a score calculated as an average of assessments of plants vigor, height, and leaf color.

Table 6. Average Herbicidal Effect of DHAA's on potted weeds

Soil application 1 mg/pot.	Weeds, pre-emergence				
ID	Amaranth	Silybum	Lentils	Sinapis	Chenopodium
586	2.0	1.0	0.5	5.0	1.5
5637	1.5	0.5	0.0	3.5	1.5
5640	4.0	2.5	0.0	-	5.0
5643	0.5	0.0	5.0	5.0	4.0
5666	1.0	0.5	0.0	1.0	0.0
5667	2.0	3.5	0.0	2.0	0.0
5668	3.0	5.0	4.0	5.0	2.0
5679	4.5	2.0	0.0	2.0	1.5
6617	4.5	5.0	2.0	3.5	4.5
6635	4.0	3.0	0.0	3.0	0.5
6643	0.0	2.5	0.0	4.0	3.0
6651	5.0	4.0	-	4.0	1.5

Soil application 1 mg/pot.	Weeds, post-emergence				
ID	Amaranth	Silybum	Lentils	Sinapis	Chenopodium
586	3.3	3.7	3.2	-	4.5
5637	3.3	1.0	1.7	0.0	2.2
5640	2.0	2.0	2.1	-	3.4
5643	4.0	3.0	4.0	5.0	5.0
5666	1.2	0.0	0.0	0.0	1.5
5667	3.0	0.0	0.0	0.0	2.4
5679	1.0	2.0	0.5	1.0	1.0
6617	2.0	4.5	1.0	2.0	0.5

6635	4.0	2.5	0.0	2.0	3.0
6640	4.0	3.0	2.0	3.0	1.0
6643	1.0	2.0	0.0	4.0	4.0
6651	0.5	2.0	-	2.0	0.5

Example 8: Effect of derivatives of heterocyclic amino acids on germination

Materials: Seeds of Lettuce R. (Super-Jericho, non-sterilized) were obtained from Ben Shahar Moshe Ltd., 99% purity. The test compounds listed in the Table 2 below were synthesized de novo or purchased from different vendors.

Filter Paper Bioassays with Lettuce seeds: The protocol is following Bertin et al. 2009 and Movellan et al. 2014 with specified modifications as described below.

Seeds were placed on Whatman no. 1 filter paper (Whatman, Middlesex, U.K.) in Petri dishes (10 seeds per plate) with 2.0 ml of aqueous solution of a test material in concentration ranged from 0 (control) to 1 mmol/l were placed in a tray tilted at 45°. The trays were kept in dark for 48 hours and then transferred to the growth chamber with 6/18 dark/ light cycle for 4 days. Each experiment was performed at least with two repeats.

The development of plants' radicle and shoots were visually assessed 6 days after the beginning of the test to determine Fully Effective Concentration (FEC) of a test material. In the context of the invention, FED is defined as the lowest concentration level of a test material that mostly preventing seeds germination.

Inhibitory effect of selected compounds on seeds germination are summarized in Table 7.

Table 7. Fully Effective Concentration (FEC) of selected compounds

ID	Chemical name	FEC (mM)
584	2-(2,5-dichlorothiophen-3-yl)ethan-1-amine	0.500
586	2-(2,5-dichlorothiophen-3-yl)acetic acid	0.050
5602	(2-aminoethyl)[(2,5-dichlorothiophen-3-yl)methyl]amine, 95%	2.000
5609	2-(2,5-dichlorothiophen-3-yl)acetamide	1.000
5612	3-(2,5-dichlorothiophen-3-yl)-2-oxopropanoic acid	0.100
5622	(2E)-3-(2,4-dichloro-1,3-thiazol-5-yl)prop-2-enoic acid	1.000
5623	2-(2-chlorothiophen-3-yl)-2,2-difluoroacetic acid	1.000
5636	2-(2,5-dichlorothiophen-3-yl)-2,2-difluoroacetamide	0.100
5637	2-(2,5-dichloro-1,3-thiazol-4-yl)acetic acid	0.050
5640	(2,5-dichlorothiophen-3-yl)(difluoro)acetic acid	0.100
5644	[2-(2,5-dichlorothiophen-3-yl)(difluoro)acetamido]acetic acid	1.000
5655	ethyl (2,5-dichloro-1,3-thiazol-4-yl)(difluoro)acetate	1.000
5657	4-(2,5-dichlorothiophen-3-yl)butan-1-amine	0.100
5666	sodium (2-chloro-1,3-thiazol-4-yl)(difluoro)acetate	0.010
5700	2,2-difluoro[2-(trifluoromethyl)-1,3-thiazol-5-yl]acetic acid	2.000
5702	2-chloro-4-(2-hydrazinylethyl)-1,3-thiazole	2.000
5709	benzyl (2,5-dichlorothiophen-3-yl)(difluoro)acetate	0.100
5710	2,2-difluoro-2-[5-(trifluoromethyl)-1,3-thiazol-2-yl]acetic acid	0.100

5717	2,2-difluoro-2-[5-methyl-2-(trifluoromethyl)-1,3-thiazol-4-yl]acetic acid	0.100
5728	difluoro[2-(trifluoromethyl)thiophen-3-yl]acetic acid	1.000
5730	2-(2-bromo-1,3-thiazol-4-yl)-2,2-difluoroacetic acid	0.010
5735	(4-bromophenyl)methyl (2,5-dichlorothiophen-3-yl)acetate	0.500
5738	2-(4-methylphenyl)-2-oxoethyl (2-chloro-1,3-thiazol-4-yl) (difluoro)acetate	0.010
5740	2-oxo-2-(pyridin-2-yl)ethyl (2-chloro-1,3-thiazol-4-yl) (difluoro)acetate	0.050
5741	2-oxo-2-phenylethyl (2-chloro-1,3-thiazol-4-yl) (difluoro)acetate	0.050
5742	2-(2-{[2-(2,5-dichlorothiophen-3-yl)ethyl]amino}-4,5-dihydro-1H-imidazol-1-yl)ethan-1-ol	1.000
5745	, 2-[2-(benzyloxy)ethoxy]ethyl 2-(2-chloro-1,3-thiazol-4-yl)-2,2-difluoroacetate	0.010
5746	2-(2-methoxyethoxy)ethyl (2-chloro-1,3-thiazol-4-yl) (difluoro)acetate	0.001
5747	(2-bromophenyl)methyl (2,5-dichlorothiophen-3-yl) (difluoro)acetate	0.500
5751	(2-chloro-5-fluoro-1,3-thiazol-4-yl) (difluoro)acetic acid	0.100
5756	3-(4-bromophenyl)-1-(2-chloro-1,3-thiazol-4-yl)-1,1-difluoropropan-2-one	0.010
5757	(6-bromopyridin-2-yl)methyl 2-(2,5-dichlorothiophen-3-yl)-2,2-difluoroacetate	0.100
5758	benzyl 2-(2-chloro-1,3-thiazol-4-yl)acetate	0.100
5759	(6-bromopyridin-2-yl)methyl (2,5-dichlorothiophen-3-yl)acetate	0.010

5761	3-(2-chlorothiophen-3-yl)-3,3-difluoro-2-hydroxypropanenitrile	0.100
5762	benzyl (2-chloro-1,3-thiazol-4-yl) (difluoro)acetate	0.010
5768	(4-bromophenyl)methyl (2,5-dichlorothiophen-3-yl) (difluoro)acetate	0.500
5769	N'-[2-(2,5-dichlorothiophen-3-yl)ethyl]guanidine	0.100
5771	2-(2-methoxyethoxy)ethyl (2-chloro-1,3-thiazol-4-yl) (difluoro)acetate	0.050
5772	(2-bromophenyl)methyl (2,5-dichlorothiophen-3-yl) (difluoro)acetate	0.500
5778	2,5,8,11,14-pentaoxahexadecan-16-yl 2-(2-chloro-1,3-thiazol-4-yl)-2,2-difluoroacetate	5.000
5779	(4-cyanothiophen-3-yl) (difluoro)acetic acid	1.000
5784	ethyl 2-(2-chloro-1,3-thiazol-4-yl)-2,2-difluoroacetate	0.050
5791	2-[5-chloro-2-(trifluoromethyl)-1,3-thiazol-4-yl]-2,2-difluoroacetic acid	0.010

Example 9: Comparison of herbicidal activity of selected derivatives of non-coded amino acids (DNAA) with structurally related non-coded amino acids

The tests were performed on Romaine lettuce (*Lactuca sativa* L.) plants at the stage 2 to 3 leaves. The plants were grown in mini-pots packed with soil, dimensions 2 X 2 X 5 cm, one plant per mini-pot. Test compounds were dissolved in 0.1% aqueous solution water solution of Silwet adjuvant. The test material where applied in rate 0 (Control), 0.01, 0.05, and 0.5 mg/pot. The test compounds were applied on soil or foliar with airbrush (0.1 ml per pot). Each concentration was tested on 20 plants. Two weeks after the treatment the herbicidal effects of the respective test material were visually evaluated (aboveground

part and roots. Then the aboveground part of the plants was neatly cut and weighed (wet weight) to assess the growth inhibition caused by the test compound. The growth inhibition (GI) was calculated as following:

$$GI = 1 - Mt * 100\% / Mc$$

Where Mt and Mc are median wet weight of treated and control plants, respectively. Compounds selected for the comparison of inhibitory effects are listed in the Table 8. Comparison of the herbicidal effects of non-coded amino acids (NAA) and their structural analogues, DNAA is summarized in the Table 9.

Table 8. List of selected NAA and structurally related DNAA

ID	Chemical name
517	2-amino-3-(2,5-dichlorothiophen-3-yl)propanoic acid
5640	(2,5-dichlorothiophen-3-yl)(difluoro)acetic acid
527	2-amino-3-(2,5-dichloro-1,3-thiazol-4-yl)propanoic acid
5667	(2,5-dichloro-1,3-thiazol-4-yl)(difluoro)acetic acid
586	2-(2,5-dichlorothiophen-3-yl)acetic acid
516	2-amino-3-(2-chlorothiophen-3-yl)propanoic acid
5623	2-(2-chlorothiophen-3-yl)-2,2-difluoroacetic acid
632	2-amino-3-(2-bromopyridin-4-yl)propanoic acid
6617	2-(6-bromopyridin-2-yl)-2,2-difluoroacetic acid

Table 9: Comparison of Herbicidal effects of selected NAAs and structurally related DNAA, growth application (% soil application)

Test mg/pot	Compounds' ID			
	NAA/ DNAA			
	517/ 5640	527/ 5667	516/ 5623	632/ 6617
0.50	75%/ 100%	90%/ 100%	38%/ 98%	21%/ 91%
0.05	25%/ 100%	11%/ 91%	0%/ 79%	13%/ 92%
0.01	0%/ 5%	0%/ 90%	0%/ 34%	0%/ 52%

Table 10: Comparison of Herbicidal effects of selected NAAs and structurally related DNAA, growth application (% , foliar application)

Test mg/pot	Compounds' ID			
	NAA/ DNAA			
Foliar	517/ 5640	527/ 5667	516/ 5623	632/ 6617
0.50	29%/ 100%	44%/ 100%	0%/ 97%	8%/ 100%
0.05	0%/ 100%	0%/ 92%	0%/ 91%	0%/ 88%

Discussion:

It was established that aminoacyl-tRNA synthetases may acylate tRNA with selected non-coded amino acids thus facilitated inclusion of these molecules in nascent peptides. It was also suggested in the past that herbicidal activity of selected non-coded amino acids is based on its ability to acylate tRNA, be included in peptides and thus change 3D structure of cell proteins.

NCAADs of the invention lack either carboxy or amino group. Given that, aminoacyl-tRNA synthetases cannot acylate tRNA with NCAADs lacking carboxyl as well as NCAADs lacking the amino group cannot link to the nascent peptide. Therefore, none of the NCAADs of the invention can be incorporated into peptide and exert the anticipated effect on the 3D structure of cellular proteins.

As appears from the experimental data above, NCAADs of the invention have strong herbicidal activity. This is as opposed to initial assumption that these compounds can only act as inert

structural analogues of herbicidal non-coded AAs (NCAAs). Moreover, surprisingly, the NCAADs of the invention demonstrate 10 to 100 times higher herbicidal activity than corresponding NCAAs.

- 5 Numerous NCAADs showing herbicidal activity both in foliar and soil applications suggesting effective absorption by leaves, shoots, and roots. This is opposite to the corresponding NCAAs, exhibiting herbicidal activity only in soil application.

Unless otherwise defined, all technical and/or scientific terms
10 used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the invention pertains. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of
15 embodiments of the invention, exemplary methods and/or materials are described below. In case of conflict, the patent specification, including definitions, will prevail. In addition, the materials, methods, and examples are illustrative only and are not intended to be necessarily limiting.

As used herein the terms "comprises", "comprising", "includes",
20 "including", "having" and their conjugates mean "including but not limited to".

The term "consisting of" means "including and limited to".

As used herein, the singular form "a", "an" and "the" include plural references unless the context clearly dictates otherwise.
25 For example, the term "a compound" or "at least one compound" may include a plurality of compounds, including mixtures thereof.

It will be understood that when an element is referred to as being "on," "attached" to, "connected" to, "coupled" with,
30 "contacting," etc., another element, it can be directly on, attached to, connected to, coupled with and/or contacting the other element or intervening elements can also be present. In

contrast, when an element is referred to as being, for example, "directly on," "directly attached" to, "directly connected" to, "directly coupled" with or "directly contacting" another element, there are no intervening elements present. It will also
5 be appreciated by those of skill in the art that references to a structure or feature that is disposed "adjacent" another feature can have portions that overlap or underlie the adjacent feature.

It will be understood that, although the terms first, second,
10 etc., may be used herein to describe various elements, components, regions, layers and/or sections, these elements, components, regions, layers and/or sections should not be limited by these terms. Rather, these terms are only used to distinguish one element, component, region, layer and/or
15 section, from another element, component, region, layer and/or section.

As will be appreciated by those of skill in the art, the compounds of the various formulas disclosed herein may contain chiral centers, e.g., asymmetric carbon atoms. Thus, the present
20 disclosure is concerned with the synthesis of both: (i) racemic mixtures of the active compounds, and (ii) enantiomeric forms of the active compounds. The resolution of racemates into enantiomeric forms and racemization of optically active enantiomeric form can be done in accordance with known
25 procedures in the art. Geometric isomers of double bonds and the like may also be present in the compounds disclosed herein, and all such stable isomers are included within the present disclosure unless otherwise specified. Also included in the compounds of the disclosure are tautomers (e.g., tautomers of
30 triazole and/or imidazole) and rotamers. All chains defined by the formulas herein which include three or more carbons may be saturated or unsaturated unless otherwise indicated.

It is understood that substituents and substitution patterns on the compounds used in the method of the present invention can be selected by one of ordinary skill in the art to provide compounds that are chemically stable and that can be readily synthesized by techniques known in the art from readily available starting materials. If a substituent is itself substituted with more than one group, it is understood that these multiple groups may be on the same carbon or on different carbons, so long as a stable structure results.

An "optionally substituted" group refers to a functional group in which one or more bonds to a hydrogen atom contained therein are replaced by a bond to non-hydrogen or non-carbon atoms, provided that normal valences are maintained and that the substitution results in a stable compound. Substituted groups also include groups in which one or more bonds to a carbon(s) or hydrogen(s) atom are replaced by one or more bonds, including double or triple bonds, to a heteroatom. Where multiple substituent moieties are disclosed or claimed, the substituted compound can be independently substituted by one or more of the disclosed or claimed substituent moieties, singly or pluraly. By independently substituted, it is meant that the (two or more) substituents can be the same or different. In choosing the compounds of the present invention, one of ordinary skill in the art will recognize that the various substituents are to be chosen in conformity with well-known principles of chemical structure connectivity.

As used herein, "H" refers to a hydrogen atom. "C" refers to a carbon atom. "N" refers to a nitrogen atom. "O" refers to an oxygen atom. "Halo" refers to F, Cl, Br or I. The term "hydroxy," as used herein, refers to an -OH moiety. "Br" refers to a bromine atom. "Cl" refers to a chlorine atom. "I" refers to an iodine atom. "F" refers to a fluorine atom. An "acyl group" is intended to mean a group -C(O)-R, where R is a suitable substituent, for

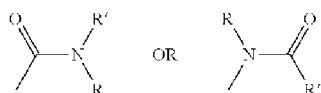
example, an acetyl group, a propionyl group, a butyryl group, a benzoyl group, or an alkylbenzoyl group. "Alkyl," as used herein, refers to a straight or branched chain hydrocarbon containing from 1 or 2 to 10 or 20 or more carbon atoms (e.g., C2, C3, C4, C5, C6, C7, C8, C9, C10, C11, C12, C13, C14, C15, etc.). In some embodiments the alkyl can be a lower alkyl. "Lower alkyl" refers to straight or branched chain alkyl having from 1 to 3, or from 1 to 5, or from 1 to 8 carbon atoms. Representative examples of alkyl include, but are not limited to, methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, n-pentyl, isopentyl, neopentyl, n-hexyl, 3-methylhexyl, 2,2-dimethylpentyl, 2,3-dimethylpentyl, n-heptyl, n-octyl, n-nonyl, n-decyl, and the like. As used herein, the identification of a carbon number range, e.g., C1-C12 alkyl, is intended to include each of the component carbon number moieties within such range, so that each intervening carbon number and any other stated or intervening carbon number value in that stated range is encompassed, such that sub-ranges of carbon number within specified carbon number ranges may independently be specified. For example, C1-C12 alkyl is intended to include methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl, including straight chain as well as branched groups, as noted above, and the carbon number range C1-C12 alkyl may also be more restrictively specified as sub-ranges such as C1-C4 alkyl, C2-C8 alkyl, C2-C4 alkyl, C3-C5 alkyl, or any other sub-range within the broader carbon number range. In addition, ranges of carbon numbers specifically excluding a carbon number or numbers are contemplated, as are sub-ranges excluding either or both of carbon number limits of specified ranges. As generally understood by those of ordinary skill in the art, "saturation" refers to the state in which all available valence bonds of an atom (e.g., carbon) are attached to other atoms. Similarly, "unsaturation" refers to the state in which not all the available valence bonds are attached to other atoms;

in such compounds the extra bonds usually take the form of double or triple bonds (usually with carbon). For example, a carbon chain is "saturated" when there are no double or triple bonds present along the chain or directly connected to the chain (e.g., a carbonyl), and is "unsaturated" when at least one double or triple bond is present along the chain or directly connected to the chain (e.g., a carbonyl). Further, the presence or absence of a substituent depending upon chain saturation will be understood by those of ordinary skill in the art to depend upon the valence requirement of the atom or atoms to which the substituent binds (e.g., carbon). "Alkenyl," as used herein, refers to a straight or branched chain hydrocarbon containing from 1 or 2 to 10 or 20 or more carbons, and containing at least one carbon-carbon double bond, formed structurally, for example, by the replacement of two hydrogens. Representative examples of "alkenyl" include, but are not limited to, ethenyl, 2-propenyl, 2-methyl-2-propenyl, 3-butenyl, 4-pentenyl, 5-hexenyl, 2-heptenyl, 2-methyl-1-heptenyl, 3-decenyl and the like. "Alkynyl," as used herein, refers to a straight or branched chain hydrocarbon group containing from 1 or 2 to 10 or 20 or more carbon atoms, and containing at least one carbon-carbon triple bond. Representative examples of alkynyl include, but are not limited, to acetylenyl, 1-propynyl, 2-propynyl, 3-butylnyl, 2-pentylnyl, 1-butylnyl and the like. The term "cycloalkyl," as used herein, refers to a saturated cyclic hydrocarbon group containing from 3 to 8 carbons or more.

As understood in the art, the term "optionally substituted" indicates that the specified group is either unsubstituted or substituted by one or more suitable substituents. A "substituent" that is "substituted" is an atom or group which takes the place of a hydrogen atom on the parent chain or cycle of an organic molecule. "Heterocycle," as used herein, refers to a monocyclic, bicyclic or tricyclic ring system. Monocyclic heterocycle ring systems are exemplified by any 5 to 9-membered

ring containing 1, 2, 3, or 4 heteroatoms independently selected from the group consisting of: O, N, and S. "Aryl" as used herein refers to a ring system having one or more aromatic rings. Representative examples of aryl include azulenyl, indanyl, indenyl, naphthyl, phenyl, tetrahydronaphthyl, and the like. "Heteroaryl" means a cyclic, aromatic hydrocarbon in which one or more carbon atoms have been replaced with heteroatoms (e.g., N, O or S). If the heteroaryl group contains more than one heteroatom, the heteroatoms may be the same or different.

"Alkoxy," as used herein, refers to an alkyl group, as defined herein, appended to the parent molecular moiety through an oxy group, as defined herein. An "amine" or "amino" is intended to mean the group -NH_2 . "Primary amines" have one of three hydrogen atoms replaced by an alkyl or aromatic group. "Secondary amines" have two organic substituents bound to the nitrogen together with one hydrogen. "Tertiary amines" have three organic substituents bound to the nitrogen. An "amide" as used herein, refers to a functional group having a carbonyl group (C=O) linked to a nitrogen atom (N), or an organic compound that contains this group, generally depicted as:



wherein, R and R' can independently be any covalently linked atom or atoms. The term "oxo," as used herein, refers to a $=\text{O}$ moiety. The term "oxy," as used herein, refers to a $-\text{O}-$ moiety. "Nitro" refers to the organic compound functional group $-\text{NO}_2$. "Carbonyl" is a functional group having a carbon atom double-bonded to an oxygen atom ($-\text{C=O}$). "Carboxy" as used herein refers to a $-\text{COOH}$ functional group, also written as $-\text{CO}_2\text{H}$ or $-(\text{C=O})-\text{OH}$.

It will be understood that the compounds, compositions and methods provided herein may be further specified in some

embodiments by provisos or limitations excluding specific substituents, groups, moieties, structures, ingredients, steps, or conditions, as applicable, in relation to various broader specifications and exemplifications set forth herein.

5 "Agriculturally acceptable carriers" of the invention include, without limitation, adjuvants, mixers, enhancers, etc. beneficial for application of the chemical formula. Suitable carriers should not be phytotoxic to valuable crops, particularly at the concentrations employed in applying the
10 compositions for selective weed control in the presence of crops and should not react chemically with the compounds of the chemical formula herein or other composition ingredients. Such mixtures can be designed for application directly to weeds or their locus or can be concentrates or formulations which are
15 normally diluted with additional carriers and adjuvants before application. They may include inert or active components and can be solids, such as, for example, dusts, granules, water dispersible granules, or wettable powders, or liquids, such as, for example, emulsifiable concentrates, solutions, emulsions or
20 suspensions. Suitable agricultural carriers useful in preparing agricultural compositions of the present invention are well known to those skilled in the art. For example, liquid carriers that can be employed include water, toluene, xylene, petroleum naphtha, crop oil, acetone, methyl ethyl ketone, cyclohexanone,
25 trichloroethylene, perchloroethylene, ethyl acetate, amyl acetate, butyl acetate, propylene glycol monomethyl ether and diethylene glycol monomethyl ether, methanol, ethanol, isopropanol, amyl alcohol, ethylene glycol, propylene glycol, glycerine, and the like. Water is generally the carrier of choice
30 for the dilution of concentrates. Suitable solid carriers include talc, pyrophyllite clay, silica, attapulgius clay, kieselguhr, chalk, diatomaceous earth, lime, calcium carbonate, bentonite clay, Fuller's earth, cotton seed hulls, wheat flour,

soybean flour, pumice, wood flour, walnut shell flour, lignin, and the like.

It is frequently desirable to incorporate one or more surface-active agents into the compositions of the present invention.

- 5 Such surface-active agents are advantageously employed in both solid and liquid compositions, especially 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
- 10 agents, or for other purposes. 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.sub.18 ethoxylate; alcohol-
- 15 alkylene oxide addition products, such as tridecyl alcohol-C.sub.16 ethorylate; soaps, such as sodium stearate; alkylnaphthalenesulfonate salts, such as sodium dibutylnaphthalenesulfonate; dialkyl esters of sulfosuccinate salts, such as sodium di(2-ethylhexyl) sulfosuccinate; sorbitol
- 20 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; and salts of mono and dialkyl phosphate esters.
- 25 Other adjuvants commonly utilized in agricultural compositions include antifoam agents, compatibilizing agents, sequestering agents, neutralizing agents and buffers, corrosion inhibitors, dyes, odorants, penetrations aids, spreading agents, sticking agents, dispersing agents, thickening agents, freeze point
- 30 depressants, antimicrobial agents, and the like. The compositions can 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.

"Agriculturally acceptable salt" is intended to mean a salt that retains the biological effectiveness of the free acids and
5 bases of a specified compound and that is not biologically or otherwise undesirable. Examples of agriculturally acceptable salts include sulfates, pyrosulfates, bisulfates, sulfites, bisulfites, phosphates, monohydrogenphosphates, dihydrogenphosphates, metaphosphates, pyrophosphates,
10 chlorides, bromides, iodides, acetates, propionates, decanoates, caprylates, acrylates, formates, isobutyrate, caproates, heptanoates, propiolates, oxalates, malonates, succinates, suberates, sebacates, fumarates, maleates, butyne-1,4-dioates, hexyne-1,6-dioates, benzoates, chlorobenzoates,
15 methylbenzoates, dinitrobenzoates, hydroxybenzoates, methoxybenzoates, phthalates, sulfonates, xylenesulfonates, phenylacetates, phenylpropionates, phenylbutyrates, citrates, lactates, γ -hydroxybutyrates, glycollates, tartrates, methane-sulfonates, propanesulfonates, naphthalene-1-sulfonates,
20 naphthalene-2-sulfonates, and mandelates.

Throughout this application, various embodiments of this invention may be presented in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an
25 inflexible limitation on the scope of the invention. Accordingly, the description of a range should be considered to have specifically disclosed all the possible subranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered
30 to have specifically disclosed subranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for

example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Whenever a numerical range is indicated herein, it is meant to include any cited numeral (fractional or integral) within the indicated range. The phrases "ranging/ranges between" a first indicate number and a second indicate number and "ranging/ranges from" a first indicate number "to" a second indicate number are used herein interchangeably and are meant to include the first and second indicated numbers and all the fractional and integral numerals therebetween.

Certain features of the invention, which are, for clarity, described in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention, which are, for brevity, described in the context of a single embodiment, may also be provided separately or in any suitable sub-combination or as suitable in any other described embodiment of the invention. Certain features described in the context of various embodiments are not to be considered essential features of those embodiments, unless the embodiment is inoperative without those elements.

As used herein the term "method" refers to manners, means, techniques and procedures for accomplishing a given task including, but not limited to, those manners, means, techniques and procedures either known to, or readily developed from known manners, means, techniques and procedures by practitioners of the chemical, agricultural, biological, and biochemical arts.

As used herein the term "plant growth regulator" refers but not limited to a compound, either natural or synthetic, that modifies or controls one or more specific physiological processes within a plant.

As used herein the term "plant" refers but not limited to whole plants, ancestors and progeny of the plants and plant parts,

including seeds, shoots, stems, roots (including tubers), and plant cells, tissues and organs. The plant may be in any form including suspension cultures, embryos, meristematic regions, callus tissue, leaves, gametophytes, sporophytes, pollen, and
5 microspores.

As used herein the term "crop protection agent" refers but not limited to an agent which is a pesticide (or a mixture of more than one pesticide) or a plant growth regulator.

As used herein the term "pesticide" refers to, but not limited
10 to a chemical or biological agent that deters, incapacitates, kills, or otherwise discourages pests.

Compounds of this invention will generally be used as a herbicidal active ingredient in a composition. As used herein the term "composition" refers but not limited to a formulation,
15 with at least one additional component selected from the group consisting of surfactants, solid diluents and liquid diluents, which serves as a carrier. The formulation or composition ingredients are selected to be consistent with the physical properties of the active ingredient, mode of application and
20 environmental factors such as oil type, moisture and temperature. Useful compositions may include both liquid and solid formulation. Liquid formulations may include solutions (including emulsifiable concentrates), suspensions, emulsions (including microemulsions, oil-in-water emulsions, flowable
25 concentrates and/or suspensions) and alike, which optionally can be thickened into gels. The general types of aqueous liquid compositions are soluble concentrate, suspension concentrate, capsule suspension, concentrated emulsion, microemulsion, oil-in-water emulsion, flowable concentrate and suspension. The
30 general types of nonaqueous liquid compositions are emulsifiable concentrate, microemulsifiable concentrate, dispersible concentrate and oil dispersion.

The general types of solid formulations are dusts, powders, granules, pellets, prills, astilles, tablets, filled films (including seed coatings) and the like, which can be water-dispersible ("wetttable") or water-soluble. Films and coatings formed from film-forming solutions or flowable suspensions are particularly useful for seed treatment. Active ingredient can be (micro)encapsulated and further formed into a suspension or solid formulation; alternatively, the entire formulation of active ingredient can be encapsulated (or "overcoated"). Encapsulation can control or delay release of the active ingredient. Sprayable formulations are typically extended in a suitable medium before spraying. Such liquid and solid formulations are formulated to be readily diluted in the spray medium, usually water, but occasionally another suitable medium like an aromatic or paraffinic hydrocarbon or vegetable oil. Spray volumes can range from about one to several thousand liters per hectare, but more typically are in the range from about ten to several hundred liters per hectare. Sprayable formulations can be tank mixed with water or another suitable medium for foliar treatment by aerial or ground application, or for application to the growing medium of the plant. Liquid and dry formulations can be metered directly into drip irrigation systems or metered into the furrow during planting.

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

The compounds of the invention have (both preemergent and postemergent) herbicidal activity. As used herein the term "controlling undesired plant growth" refers to killing or injuring the vegetation or reducing its growth.

The compounds and compositions of the invention can be usefully applied by a variety of methods involving contacting a herbicidally effective amount of a compound of the invention,

or a composition comprising said compound and at least one of a surfactant, a solid diluent or a liquid diluent, to the foliage or other part of the undesired plant or to the environment of the undesired plant growth such as the soil or water in which the undesired plant is growing or which surrounds the seed or other propagule of the undesired plant.

A herbicidally effective amount of the compounds of this invention is determined by a number of factors: formulation selected, method of application, amount and type of undesired plant growth present, growing conditions, etc. In general, a herbicidally effective amount of compounds of this invention is about 0.001 to 20 kg/ha with a preferred range of about 0.004 to 1 kg/ha. One skilled in the art can easily determine the herbicidally effective amount necessary for the desired level of weed control.

The compounds of the invention are applied, typically in a form of formulated composition, to a locus comprising desired vegetation (e.g., crops) and undesired plant growth (i.e. weeds), both of which may be seeds, seedlings and/or larger plants, in contact with a growth medium (e.g., soil). In this locus, a composition comprising the compounds of the invention can be directly applied to a plant or any part of a plant thereof, particularly of the undesired plant growth, and/or to the growth medium in contact with the plant.

Compounds of this invention can also be mixed with one or more other biologically active compounds or agents including herbicides, herbicide safeners, fungicides, insecticides, nematocides, bactericides, acaricides, plant growth regulators such as insect molting inhibitors and rooting stimulants, chemosterilants, semiochemicals, repellents, attractants, pheromones, feeding stimulants, plant nutrients, other biologically active compounds or bacteria, virus or fungi to form a multi-component pesticide giving broader spectrum of

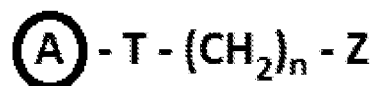
agricultural protection. Mixtures of the compounds of the invention with other herbicides can broaden the spectrum of activity against additional weed species and suppress the proliferation of any resistant biotypes.

5 Throughout this application various publications, published patent applications and published patents are referenced. The disclosures of these publications in their entirety are hereby incorporated by reference into this application in order to more fully describe the state of the art to which this invention
10 pertains.

Certain features of the invention, which are, for clarity, described in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention, which are, for brevity,
15 described in the context of a single embodiment, may also be provided separately or in any suitable subcombination or as suitable in any other described embodiment of the invention. Certain features described in the context of various embodiments are not to be considered essential features of those
20 embodiments, unless the embodiment is inoperative without those elements.

Claims:

1. An agricultural composition comprising a compound or a salt thereof having the structure



or a salt thereof, wherein:

A is cyclopentadiene, benzene and indene scaffold comprising from 1 to 4 heteroatoms; wherein each of the heteroatoms is independently selected from the group consisting of N, S, Se, and O; and wherein one or more of the carbon atoms of the ring are optionally chemically attached to at least one of the groups consisting of: $-\text{SO}_2\text{CF}_3$, $-\text{O}-\text{SO}_2\text{CF}_3$, $-\text{NR}_3^+$, $-\text{SO}_2\text{R}$, $-\text{C}\equiv\text{N}$, $-\text{CX}_3$, CX_2R , $-\text{COX}$, $-\text{CHO}$, $-\text{COR}$, $-\text{CO}_2\text{R}$, $-\text{CONH}_2$, $-\text{CONHR}$, $-\text{CONR}_2$, $-\text{N}=\text{O}$, $-\text{N}\equiv\text{N}^+$, $-\text{N}=\text{NR}$, $-\text{CR}=\text{NR}$, $-\text{N}=\text{CR}_2$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, and $-\text{I}$, and wherein X is selected from F, Cl, Br and I;

n is 0 to 5;

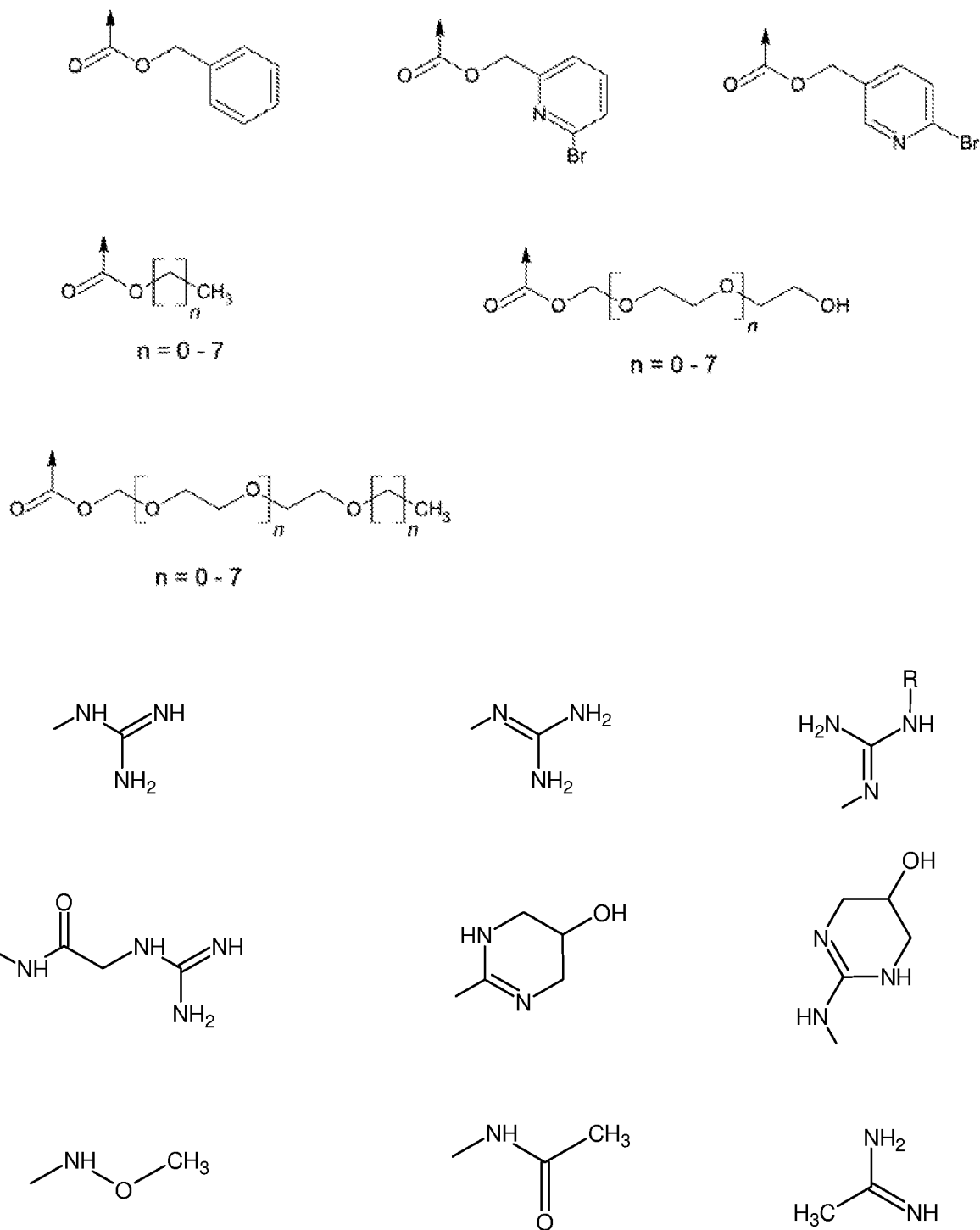
T is unsubstituted or substituted methylene group with one or two halides, oxygen, $-\text{SO}_2\text{CF}_3$, $-\text{O}-\text{SO}_2\text{CF}_3$, $-\text{NR}_3^+$, $-\text{SO}_2\text{R}$, $-\text{C}\equiv\text{N}$, $-\text{CX}_3$, $\text{CX}_2\text{R}-\text{COX}$, $-\text{CHO}$, $-\text{COR}$, $-\text{CO}_2\text{R}$, $-\text{CONH}_2$, $-\text{CONHR}$, $-\text{CONR}_2$, $-\text{F}$, $-\text{N}=\text{O}$, $-\text{N}\equiv\text{N}^+$, $-\text{N}=\text{NR}$, $-\text{CR}=\text{NR}$, $-\text{N}=\text{CR}_2$, and wherein X is selected from $-\text{F}$, $-\text{Cl}$, $-\text{Br}$ and $-\text{I}$; and,

Z is $-\text{COOH}$, $\text{COO}-$, OH , $-\text{O}-\text{R}$, COOR with saturated or non-saturated alcohol residues with straight, branched, cyclic, aromatic or heteroaromatic chain; $-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n\text{R}$ ($n\geq 1$); $-\text{O}-(\text{CHMeCH}_2\text{O})_n\text{R}$ ($n\geq 1$)); sulfonyl group, carbamoyl group, primary amine, secondary amine, tertiary amine, carboxamide, $-\text{NR}-\text{O}-\text{R}$, $-\text{O}-\text{NR}_2$, hydrazine, $-\text{NH}-\text{COR}$, and methanimidamide moiety or a salt thereof;

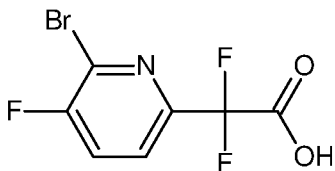
wherein R is selected from H, substituted or non-substituted alkyl, and substituted or non-substituted aryl group; and,

wherein the composition comprises at least one agriculturally acceptable carrier.

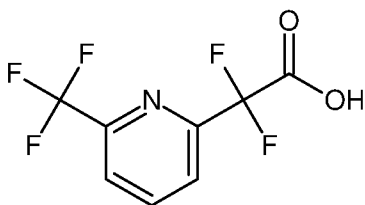
2. The composition of claim 1, wherein Z is selected from



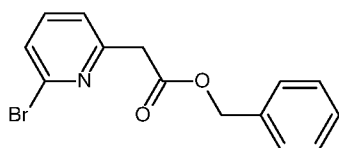
3. The composition of claim 1 or 2, comprising the compound having the structure



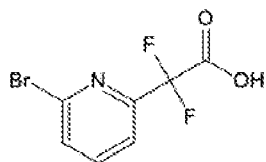
4. The composition of claim 1 or 2, comprising the compound having the structure



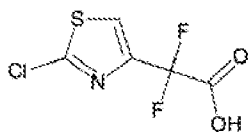
5. The composition of claim 1 or 2, comprising the compound having the structure



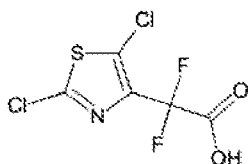
6. The composition of claim 1 or 2, comprising the compound having the structure



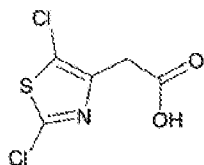
7. The composition of claim 1 or 2, comprising the compound having the structure



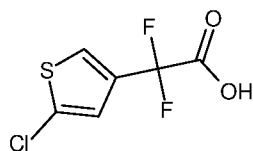
8. The composition of claim 1 or 2, comprising the compound having the structure



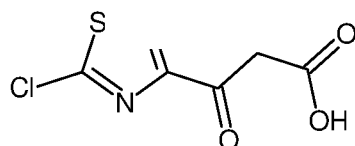
9. The composition of claim 1 or 2, comprising the compound having the structure



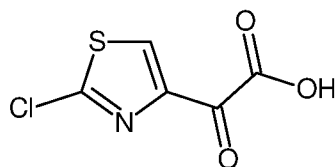
10. The composition of claim 1 or 2, comprising the compound having the structure



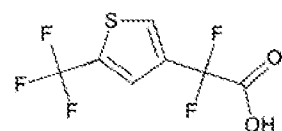
11. The composition of claim 1 or 2, comprising the compound having the structure



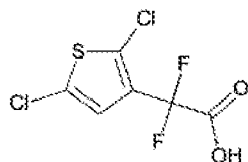
12. The composition of claim 1 or 2, comprising the compound having the structure



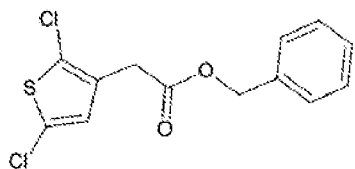
13. The composition of claim 1 or 2, comprising the compound having the structure



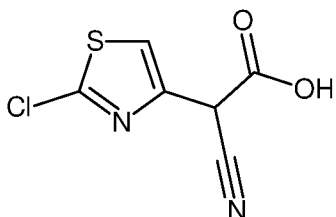
14. The composition of claim 1 or 2, comprising the compound having the structure



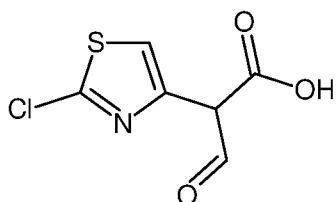
15. The composition of claim 1 or 2, comprising the compound having the structure



16. The composition of claim 1 or 2, comprising the compound having the structure



17. The composition of claim 1 or 2, comprising the compound having the structure

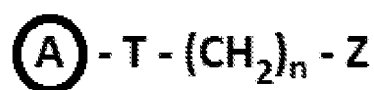


18. The composition of any one of claims 1 to 17, further comprising at least one crop protection agent.
19. The composition of claim 18, wherein the at least one crop protection agent is selected from the group consisting of fungicide, insecticide, herbicide, and plant growth regulator.
20. The agricultural composition of claim 19, wherein the crop protection agent is herbicide.
21. The agricultural composition of claim 19, wherein the crop protection agent is plant growth regulator.
22. The agricultural composition of claim 19, wherein the at least one crop protection agent is selected from the group consisting of atrazine, terbutylazine, (S)-metolachlor, metolachlor, terbutryn, simazine, dimethenamid, (S)-dimethenamid, flufenacet, acetochlor, alachlor, isoxaflutole, isoxachlortole, mesotrione, sulcotrione, metosulam, flumetsulam, pendimethalin, bromoxynil, bentazone, carfentrazone-ethyl, clomazone, nicosulfuron,

rimsulfuron, halosulfuron-methyl, metribuzin, flumiclorac-pentyl, prosulfuron, primisulfuron-methyl, dicamba, fluthiacet-methyl, pyridate, 2,4-D, clopyralide, diflufenzopyr, fluroxypyr, MCPA, MCPB, mecoprop (MCP), metobenzuron, thifensulfuron-methyl, aclonifen, EPTC, glyphosate, glufosinate, sulfosate, cyanazine, propaquizafop, metamitron, pyramin, phenmedipham, desmedipham, ethofumesate, triasulfuron, chloridazon, lenacil, triallate, fluazifop, sethoxydim, quizalofop, clopyralide, clethodim, oxasulfuron, acifluorfen, benazolin-ethyl, sulfentrazone, chlorimuron-ethyl, cloransulam-methyl, fomesafen, imazamox, imazaquin, imazethapyr, imazapyr, lactofen, fenoxaprop (P-ethyl), thidiazuron, tribufos, trifluralin, dimethachlor, napropamide, quinmerac, metazachlor, carbetamide, dimefuron, propyzamide, ethametsulfuron-methyl, tebutam, fluometuron, prometryn, norflurazon, pyriithiobac-sodium, MSMA, DSMA, diuron, flurochloridone, dithiopyr, thiazopyr, oxyfluorfen, ethalfluralin, clodinafop, amidosulfuron, diclofop-methyl, diflufenican, ethoxysulfuron, fentrazamide, flazasulfuron, florasulam, fluazolate, flucarbazone, flupyrsulfuron-methyl sodium, flurtamone, iodosulfuron, isoproturon, chlortoluron, chlorsulfuron, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, 2,4-DB, 2,4-DP, bifenox, flamprop-M, imazamethabenz-methyl, ioxynil, tralkoxydim, fluoroglycofen-ethyl, methabenzthiazuron, isoxaben, prosulfocarb, difenzoquat-metilsulfate, pretilachlor, cinosulfuron, fenclorim, bensulfuron-methyl, imazosulfuron, pyrazosulfuron-ethyl, azimsulfuron, esprocarb, mefenacet, molinate, propanil, pyrazolate, cyhalofop-butyl, bispyribac-sodium, pyriminobac-methyl, cafenstrole, oxadiargyl, oxadiazon, bromobutide, MY-100, dymron, NB 061, MK243, HW-52, AC 014,

ametryn, hexazinone, asulam, azafenidin, tebuthiuron, ethametsulfuron-methyl, or a combination thereof.

23. A method of controlling undesired plant growth comprising applying to the locus of said undesired plant growth the agricultural composition of any one of claims 1 to 22.
24. A method of controlling undesired plant growth, comprising applying to the locus of the undesired plant growth a herbicidally effective amount of a compound having the structure



or a salt thereof, wherein:

A is cyclopentadiene, benzene and indene scaffold comprising from 1 to 4 heteroatoms; wherein each of the heteroatoms is independently selected from the group consisting of N, S, Se, and O; and wherein one or more of the carbon atoms of the ring are optionally chemically attached to at least one of the groups consisting of: -SO₂CF₃, -O-SO₂CF₃, -NR₃⁺, -SO₂R, -C≡N, -CX₃, CX₂R, -COX, -CHO, -COR, -CO₂R, -CONH₂, -CONHR, -CONR₂, -N=O, -N≡N⁺, -N=NR, -CR=NR, -N=CR₂, -F, -Cl, -Br, and -I; and wherein X is selected from F, Cl, Br and I;

n is 0 to 5;

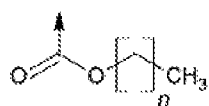
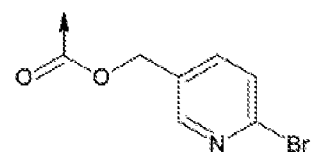
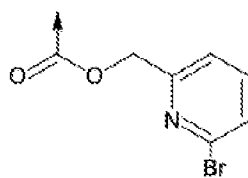
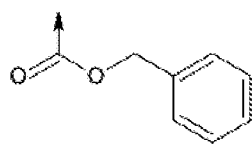
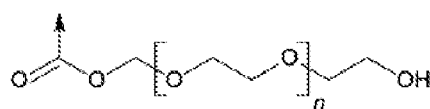
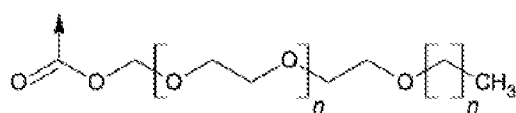
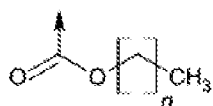
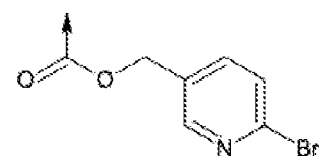
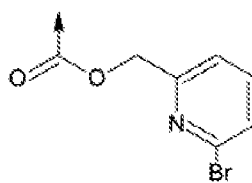
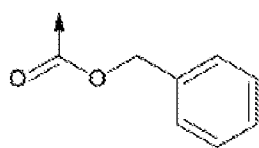
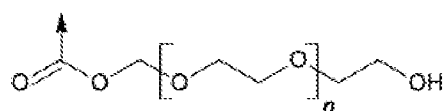
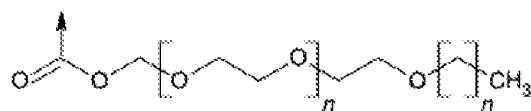
T is unsubstituted or substituted methylene group with one or two halides, oxygene, -SO₂CF₃, -O-SO₂CF₃, -NR₃⁺, -SO₂R, -C≡N, -CX₃, CX₂R, -COX, -CHO, -COR, -CO₂R, -CONH₂, -CONHR, -CONR₂, -F, -N=O, -N≡N⁺, -N=NR, -CR=NR, -N=CR₂, and wherein X is selected from F, Cl, Br and I; and,

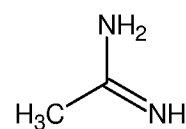
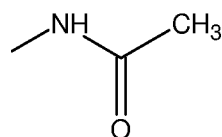
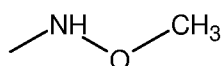
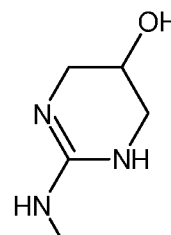
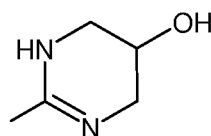
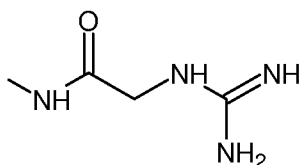
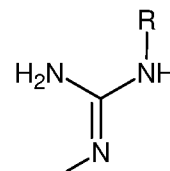
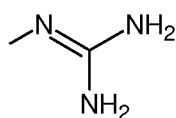
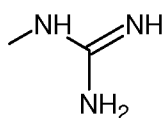
Z is -COOH, COO⁻, OH, -O-R, COOR with saturated or non-saturated alcohol residues with straight, branched,

cyclic, aromatic or heteroaromatic chain; $-O-(CH_2CH_2O)_nR$ ($n \geq 1$); $-O-(CHMeCH_2O)_nR$ ($n \geq 1$); carbamoyl group, primary amine, secondary amine, tertiary amine, carboxamide, $-NR-O-R$, $-O-NR_2$, hydrazine, $-NH-COR$, and methanimidamide moiety or a salt thereof;

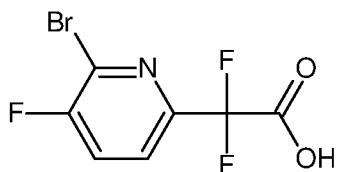
wherein R is selected from H, substituted or non-substituted alkyl, and substituted or non-substituted aryl group.

25. The method of claim 24, wherein Z is selected from

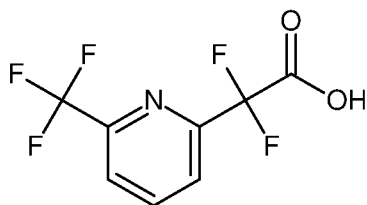
 $n = 0 - 7$  $n = 0 - 7$  $n = 0 - 7$  $n = 0 - 7$  $n = 0 - 7$  $n = 0 - 7$



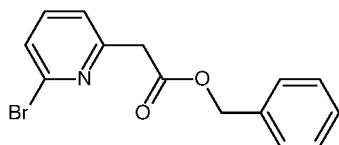
26. The method of claim 24 or 25, comprising applying to the locus of the undesired plant growth a herbicidally effective amount of a compound, having the structure



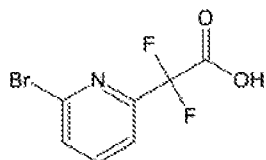
27. The method of claim 24 or 25, comprising applying to the locus of the undesired plant growth a herbicidally effective amount of a compound, having the structure



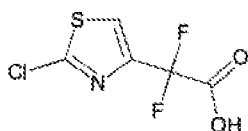
28. The method of claim 24 or 25, comprising applying to the locus of the undesired plant growth a herbicidally effective amount of a compound, having the structure



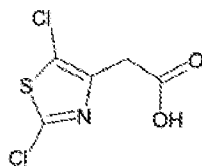
29. The method of claim 24 or 25, comprising applying to the locus of the undesired plant growth a herbicidally effective amount of a compound, having the structure



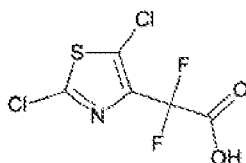
30. The method of claim 24 or 25, comprising applying to the locus of the undesired plant growth a herbicidally effective amount of a compound, having the structure



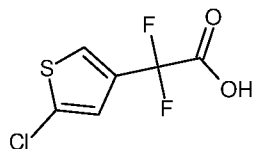
31. The method of claim 24 or 25, comprising applying to the locus of the undesired plant growth a herbicidally effective amount of a compound, having the structure



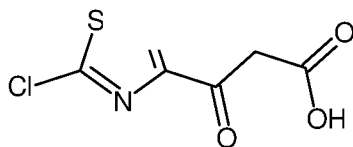
32. The method of claim 24 or 25, comprising applying to the locus of the undesired plant growth a herbicidally effective amount of a compound, having the structure



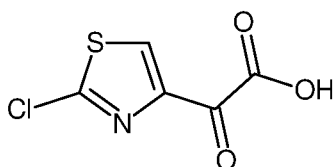
33. The method of claim 24 or 25, comprising applying to the locus of the undesired plant growth a herbicidally effective amount of a compound, having the structure



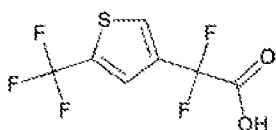
34. The method of claim 24 or 25, comprising applying to the locus of the undesired plant growth a herbicidally effective amount of a compound, having the structure



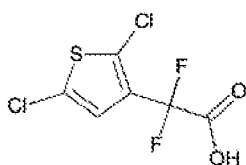
35. The method of claim 24 or 25, comprising applying to the locus of the undesired plant growth a herbicidally effective amount of a compound, having the structure



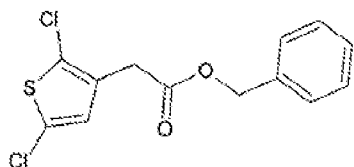
36. The method of claim 24 or 25, comprising applying to the locus of the undesired plant growth a herbicidally effective amount of a compound, having the structure



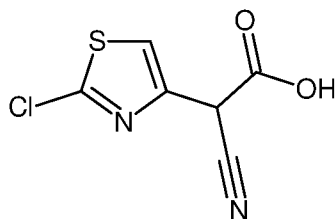
37. The method of claim 24 or 25, comprising applying to the locus of the undesired plant growth a herbicidally effective amount of a compound, having the structure



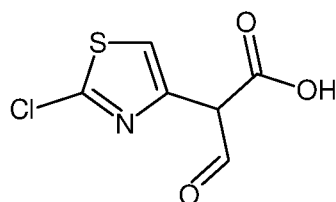
38. The method of claim 24 or 25, comprising applying to the locus of the undesired plant growth a herbicidally effective amount of a compound, having the structure



39. The method of claim 24 or 25, comprising applying to the locus of the undesired plant growth a herbicidally effective amount of a compound, having the structure

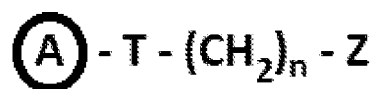


40. The method of claim 24 or 25, comprising applying to the locus of the undesired plant growth a herbicidally effective amount of a compound, having the structure



41. The method of any one of claims 24 to 40, further comprising applying to the locus of the undesired plant growth at least one crop protection agent.
42. The method of claim 41, wherein the crop protection agent is selected from the group consisting of herbicides, fungicides, insecticides and plant growth regulators.
43. The method of claim 42, wherein the crop protection agent is herbicide.
44. The method of claim 43, wherein the crop protection agent is amino acid synthesis inhibitor herbicide.
45. The method of claim 44, wherein the amino acid synthesis inhibitor herbicide is selected from the group consisting of sulfonylurea herbicide, imidazolinone herbicide, sulfonamide herbicide and amino acid derivatives, or a combination thereof.
46. The method of claim 44, wherein the amino acid synthesis inhibitor herbicide is selected from the group consisting of imazamox, imazapic, imazethapyr, imazaquin, imazapyr and imazamethabenz, or a combination thereof.

47. The method of claim 44, wherein the amino acid synthesis inhibitor herbicide is selected from the group consisting of Chlorimuron, Primisulfuron, Thifensulfuron, Triasulfuron, Nicosulfuron, Metsulfuron, Tribenuron, Rimsulfuron and Triflusulfuron or a combination thereof.
48. The method of claim 44, wherein the amino acid synthesis inhibitor herbicide is glyphosate.
49. The method of claim 42, wherein the crop protection agent is a plant growth regulator.
50. The method of claim 49, wherein the plant growth regulator is selected from the group consisting of dicamba, 2,4-D, clopyralid and fluroxypyr.
51. A method of controlling undesired plant growth comprising applying to the locus of the undesired plant growth:
- a. A first herbicide having the structure



or a salt thereof, wherein:

A is cyclopentadiene, benzene and indene scaffold comprising from 1 to 4 heteroatoms; wherein each of the heteroatoms is independently selected from the group consisting of N, S, Se, and O; and wherein one or more of the carbon atoms of the ring are optionally chemically attached to at least one of the groups consisting of: $-\text{SO}_2\text{CF}_3$, $-\text{O}-\text{SO}_2\text{CF}_3$, $-\text{NR}_3^+$, $-\text{SO}_2\text{R}$, $-\text{C}\equiv\text{N}$, $-\text{CX}_3$, $\text{CX}_2\text{R}-\text{COX}$, $-\text{CHO}$, $-\text{COR}$, $-\text{CO}_2\text{R}$, $-\text{CONH}_2$, $-\text{CONHR}$, $-\text{CONR}_2$, $-\text{F}$, $-\text{N}=\text{O}$, $-\text{N}\equiv\text{N}^+$, $-\text{N}=\text{NR}$, $-\text{CR}=\text{NR}$, $-\text{N}=\text{CR}_2$, $-\text{Cl}$, $-\text{Br}$, and $-\text{I}$; and wherein X is selected from F, Cl, Br and I;

n is 0 to 5;

T is unsubstituted or substituted methylene group with one or two halides, oxygen, $-\text{SO}_2\text{CF}_3$, $-\text{O}-\text{SO}_2\text{CF}_3$, $-\text{NR}_3^+$, $-\text{SO}_2\text{R}$, $-\text{C}\equiv\text{N}$, $-\text{CX}_3$, CX_2R , $-\text{COX}$, $-\text{CHO}$, $-\text{COR}$, $-\text{CO}_2\text{R}$, $-\text{CONH}_2$, $-\text{CONHR}$, $-\text{CONR}_2$, $-\text{F}$, $-\text{N}=\text{O}$, $-\text{N}\equiv\text{N}^+$, $-\text{N}=\text{NR}$, $-\text{CR}=\text{NR}$, $-\text{N}=\text{CR}_2$, and wherein X is selected from F, Cl, Br and I; and,

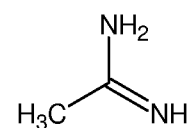
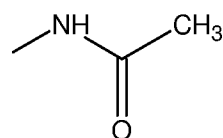
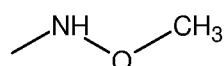
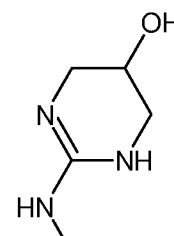
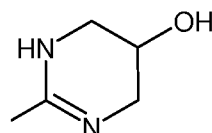
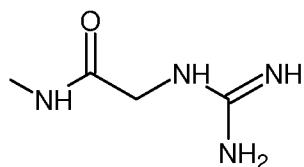
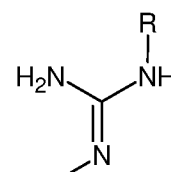
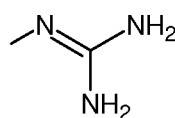
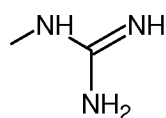
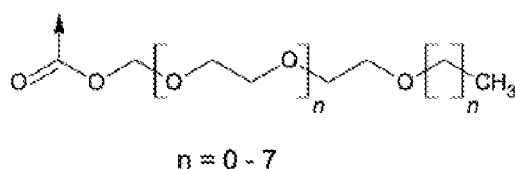
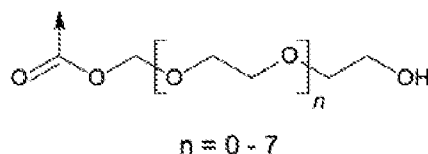
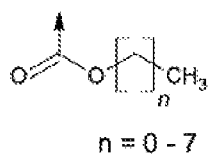
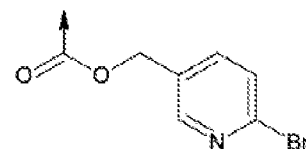
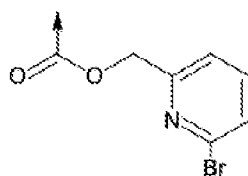
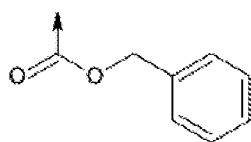
Z is $-\text{COOH}$, COO^- , OH , $-\text{O}-\text{R}$, COOR with saturated or non-saturated alcohol residues with straight, branched, cyclic, aromatic or heteroaromatic chain; $-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n\text{R}$ ($n\geq 1$); $-\text{O}-(\text{CHMeCH}_2\text{O})_n\text{R}$ ($n\geq 1$); sulfonyl group, carbamoyl group, primary amine, secondary amine, tertiary amine, carboxamide, $-\text{NR}-\text{O}-\text{R}$, $-\text{O}-\text{NR}_2$, hydrazine, $-\text{NH}-\text{COR}$, and methanimidamide moiety or a salt thereof;

wherein R is selected from H, substituted or non-substituted alkyl, and substituted or non-substituted aryl group; and,

b. A second herbicide,

to thereby effectively control the undesired plant growth.

52. The method of claim 51, wherein Z is selected from

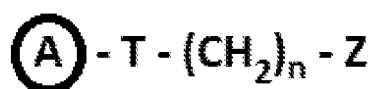


53. The method of claim 51 or 52, wherein the second herbicide is amino acid synthesis inhibitor herbicide.
54. The method of claim 53, wherein the second herbicide is selected from the group consisting of sulfonylurea herbicide, imidazolinone herbicide, sulfonamide herbicide and amino acid derivative.

55. The method of claim 53, wherein the second herbicide is selected from the group consisting of imazamox, imazapic, imazethapyr, imazaquin, imazapyr, imazamethabenz, Chlorimuron, Primisulfuron, Thifensulfuron, Triasulfuron, Nicosulfuron, Metsulfuron, Tribenuron, Rimsulfuron, Triflusulfuron and Glyphosate.
56. The method of claim 51, wherein the second herbicide is selected from the group consisting of atrazine, terbuthylazine, (S)-metolachlor, metolachlor, terbutryn, simazine, dimethenamid, (S)-dimethenamid, flufenacet, acetochlor, alachlor, isoxaflutole, isoxachlortole, mesotrione, sulcotrione, metosulam, flumetsulam, pendimethalin, bromoxynil, bentazone, carfentrazone-ethyl, clomazone, nicosulfuron, rimsulfuron, halosulfuron-methyl, metribuzin, flumiclorac-pentyl, prosulfuron, primisulfuron-methyl, dicamba, fluthiacet-methyl, pyridate, 2,4-D, clopyralide, diflufenzopyr, fluroxypyr, MCPA, MCPB, mecoprop (MCP), metobenzuron, thifensulfuron-methyl, aclonifen, EPTC, glyphosate, glufosinate, sulfosate, cyanazine, propaquizafop, metamitron, pyramin, phenmedipham, desmedipham, ethofumesate, triasulfuron, chloridazon, lenacil, triallate, fluazifop, sethoxydim, quizalofop, clopyralide, clethodim, oxasulfuron, acifluorfen, benazolin-ethyl, sulfentrazone, chlorimuron-ethyl, cloransulam-methyl, fomesafen, imazamox, imazaquin, imazethapyr, imazapyr, lactofen, fenoxaprop (P-ethyl), thidiazuron, tribufos, trifluralin, dimethachlor, napropamide, quinmerac, metazachlor, carbetamide, dimefuron, propyzamide, ethametsulfuron-methyl, tebutam, fluometuron, prometryn, norflurazon, pyriithiobac-sodium, MSMA, DSMA, diuron, flurochloridone, dithiopyr, thiazopyr, oxyfluorfen, ethalfluralin, clodinafop, amidosulfuron, diclofop-methyl, diflufenican, ethoxysulfuron, fentrazamide, flazasulfuron, florasulam, fluazolate,

flucarbazone, flupyrsulfuron-methyl sodium, flurtamone, iodosulfuron, isoproturon, chlortoluron, chlorsulfuron, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, 2,4-DB, 2,4-DP, bifenox, flamprop-M, imazamethabenz-methyl, ioxynil, tralkoxydim, fluoroglycofen-ethyl, methabenzthiazuron, isoxaben, prosulfocarb, difenzoquat-metilsulfate, pretilachlor, cinosulfuron, fenclorim, bensulfuron-methyl, imazosulfuron, pyrazosulfuron-ethyl, azimsulfuron, esprocarb, mefenacet, molinate, propanil, pyrazolate, cyhalofop-butyl, bispyribac-sodium, pyriminobac-methyl, cafenstrole, oxadiargyl, oxadiazon, bromobutide, MY-100, dymron, NB 061, MK243, HW-52, AC 014, ametryn, hexazinone, asulam, azafenidin, tebuthiuron, and ethametsulfuron-methyl.

57. The method of any one of claims 51 to 56 further comprising applying a third herbicide or a plant growth regulator.
58. A composition for controlling undesired plant growth comprising a mixture of:
- a. a compound or a salt thereof having the structure



wherein:

A is cyclopentadiene, benzene and indene scaffold comprising from 1 to 4 heteroatoms; wherein each of the heteroatoms is independently selected from the group consisting of N, S, Se, and O; and wherein one or more of the carbon atoms of the ring are optionally chemically attached to at least one of the groups consisting of: $-\text{SO}_2\text{CF}_3$, $-\text{O}-\text{SO}_2\text{CF}_3$, $-\text{NR}_3^+$, $-\text{SO}_2\text{R}$, $-\text{C}\equiv\text{N}$, $-\text{CX}_3$, CX_2R , $-\text{COX}$, $-\text{CHO}$, $-\text{COR}$, $-\text{CO}_2\text{R}$, $-\text{CONH}_2$, $-\text{CONHR}$, $-\text{CONR}_2$, $-\text{F}$, $-\text{N}=\text{O}$, $-\text{N}\equiv\text{N}^+$, $-\text{N}=\text{NR}$, $-\text{CR}=\text{NR}$, $-$

$N=CR_2$, -Cl, -Br, and -I; and wherein X is selected from F, Cl, Br and I;

n is 0 to 5;

T is unsubstituted or substituted methylene group with one or two halides, oxygene, $-SO_2CF_3$, $-O-SO_2CF_3$, $-NR_3^+$, $-SO_2R$, $-C\equiv N$, $-CX_3$, CX_2R-COX , $-CHO$, $-COR$, $-CO_2R$, $-CONH_2$, $-CONHR$, $-CONR_2$, $-F$, $-N=O$, $-N\equiv N^+$, $-N=NR$, $-CR=NR$, $-N=CR_2$, and wherein X is selected from F, Cl, Br and I; and,

Z is $-COOH$, COO^- , OH , $-O-R$, $COOR$ with saturated or non-saturated alcohol residues with straight, branched, cyclic, aromatic or heteroaromatic chain; $-O-(CH_2CH_2O)_nR$ ($n\geq 1$); $-O-(CHMeCH_2O)_nR$ ($n\geq 1$); sulfonyl group, carbamoyl group, primary amine, secondary amine, tertiary amine, carboxamide, $-NR-O-R$, $-O-NR_2$, hydrazine, $-NH-COR$, and methanimidamide moiety or a salt thereof;

wherein R is selected from H, substituted or non-substituted alkyl, and substituted or non-substituted aryl group;

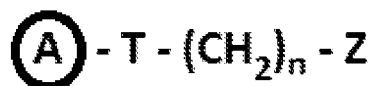
- b. at least one herbicide selected from the group consisting of atrazine, terbuthylazine, (S)-metolachlor, metolachlor, terbutryn, simazine, dimethenamid, (S)-dimethenamid, flufenacet, acetochlor, alachlor, isoxaflutole, isoxachlortole, mesotrione, sulcotrione, metosulam, flumetsulam, pendimethalin, bromoxynil, bentazone, carfentrazone-ethyl, clomazone, nicosulfuron, rimsulfuron, halosulfuron-methyl, metribuzin, flumiclorac-pentyl, prosulfuron, primisulfuron-methyl, dicamba, fluthiacet-methyl, pyridate, 2,4-D, clopyralide, diflufenzopyr, fluroxypyr, MCPA, MCPB, mecoprop (MCP), metobenzuron, thifensulfuron-methyl, aclonifen, EPTC, glyphosate, glufosinate, sulfosate, cyanazine, propaquizafop,

metamitron, pyramin, phenmedipham, desmedipham, ethofumesate, triasulfuron, chloridazon, lenacil, triallate, fluazifop, sethoxydim, quizalofop, clopyralide, clethodim, oxasulfuron, acifluorfen, benazolin-ethyl, sulfentrazone, chlorimuron-ethyl, cloransulam-methyl, fomesafen, imazamox, imazaquin, imazethapyr, imazapyr, lactofen, fenoxaprop(P-ethyl), thidiazuron, tribufos, trifluralin, dimethachlor, napropamide, quinmerac, metazachlor, carbetamide, dimefuron, propyzamide, ethametsulfuron-methyl, tebutam, fluometuron, prometryn, norflurazon, pyriithiobac-sodium, MSMA, DSMA, diuron, flurochloridone, dithiopyr, thiazopyr, oxyfluorfen, ethalfluralin, clodinafop, amidosulfuron, diclofop-methyl, diflufenican, ethoxysulfuron, fentrazamide, flazasulfuron, florasulam, fluazolate, flucarbazone, flupyrsulfuron-methyl sodium, flurtamone, iodosulfuron, isoproturon, chlortoluron, chlorsulfuron, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, 2,4-DB, 2,4-DP, bifenox, flamprop-M, imazamethabenz-methyl, ioxynil, tralkoxydim, fluoroglycofen-ethyl, methabenzthiazuron, isoxaben, prosulfocarb, difenzoquat-metilsulfate, pretilachlor, cinosulfuron, fenclozim, bensulfuron-methyl, imazosulfuron, pyrazosulfuron-ethyl, azimsulfuron, esprocarb, mefenacet, molinate, propanil, pyrazolate, cyhalofop-butyl, bispyribac-sodium, pyriminobac-methyl, cafenstrole, oxadiargyl, oxadiazon, bromobutide, MY-100, dymron, NB 061, MK243, HW-52, AC 014, ametryn, hexazinone, asulam, azafenidin, tebuthiuron, ethametsulfuron-methyl, or a combination thereof; and,

c. at least one agriculturally acceptable carrier.

59. A composition for controlling undesired plant growth comprising a mixture of:

a. a compound having the structure



or a salt thereof, wherein:

A is cyclopentadiene, benzene and indene scaffold comprising from 1 to 4 heteroatoms; wherein each of the heteroatoms is independently selected from the group consisting of N, S, Se, and O; and wherein one or more of the carbon atoms of the ring are optionally chemically attached to at least one of the groups consisting of: $-\text{SO}_2\text{CF}_3$, $-\text{O}-\text{SO}_2\text{CF}_3$, $-\text{NR}_3^+$, $-\text{SO}_2\text{R}$, $-\text{C}\equiv\text{N}$, $-\text{CX}_3$, $\text{CX}_2\text{R}-\text{COX}$, $-\text{CHO}$, $-\text{COR}$, $-\text{CO}_2\text{R}$, $-\text{CONH}_2$, $-\text{CONHR}$, $-\text{CONR}_2$, $-\text{F}$, $-\text{N}=\text{O}$, $-\text{N}\equiv\text{N}^+$, $-\text{N}=\text{NR}$, $-\text{CR}=\text{NR}$, $-\text{N}=\text{CR}_2$, $-\text{Cl}$, $-\text{Br}$, and $-\text{I}$; and wherein X is selected from F, Cl, Br and I;

n is 0 to 5;

T is unsubstituted or substituted methylene group with one or two halide atoms, oxygen, $-\text{SO}_2\text{CF}_3$, $-\text{O}-\text{SO}_2\text{CF}_3$, $-\text{NR}_3^+$, $-\text{SO}_2\text{R}$, $-\text{C}\equiv\text{N}$, $-\text{CX}_3$, $-\text{COX}$, $-\text{CHO}$, $-\text{COR}$, $-\text{CO}_2\text{R}$, $-\text{CONH}_2$, $-\text{CONHR}$, $-\text{CONR}_2$, $-\text{F}$, $-\text{N}=\text{O}$, $-\text{N}\equiv\text{N}^+$, $-\text{N}=\text{NR}$, $-\text{CR}=\text{NR}$, $-\text{N}=\text{CR}_2$, and wherein X is selected from F, Cl, Br and I; and,

Z is $-\text{COOH}$, $\text{COO}-$, OH , $-\text{O}-\text{R}$, COOR with saturated or non-saturated alcohol residues with straight, branched, cyclic, aromatic or heteroaromatic chain; $-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n\text{R}$ ($n\geq 1$); $-\text{O}-(\text{CHMeCH}_2\text{O})_n\text{R}$ ($n\geq 1$); sulfonyl group, carbamoyl group, primary amine, secondary amine, tertiary amine, carboxamide, $-\text{NR}-\text{O}-\text{R}$, $-\text{O}-\text{NR}_2$, hydrazine, $-\text{NH}-\text{COR}$, and methanimidamide moiety or a salt thereof;

wherein R is selected from H, substituted or non-substituted alkyl, and substituted or non-substituted aryl group;

- b. at least one plant growth regulator; and,
- c. at least one agriculturally acceptable carrier.

60. A method of controlling amino acid content in a plant or a plant part thereof, comprising applying an effective amount of the agricultural composition of any one of claims 1 to 22.
61. A method of controlling plant growth comprising applying to the plant or a plant part thereof, an effective amount of the agricultural composition of any one of claims 1 to 22.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IL2022/050749

A. CLASSIFICATION OF SUBJECT MATTER

A01N 43/00(2022.01)i; **A01N 43/10**(2022.01)i; **A01N 43/28**(2022.01)i; **A01N 43/40**(2022.01)i; **A01N 43/78**(2022.01)i;
C07D 213/16(2022.01)i; **C07D 213/44**(2022.01)i; **C07D 213/54**(2022.01)i; **C07D 213/61**(2022.01)i; **C07D 277/24**(2022.01)i;
C07D 277/30(2022.01)i; **C07D 333/06**(2022.01)i; **C07D 333/24**(2022.01)i; **C07D 333/28**(2022.01)i
CPC:A01N 43/00; A01N 2300/00; A01N 43/10; A01N 43/28; A01N 43/40; A01N 43/78; C07D 213/16; C07D 213/44; C07D 213/54; C07D 213/61; C07D 277/24; C07D 277/30; C07D 333/06; C07D 333/24; C07D 333/28

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A01N 43/00; A01N 43/10; A01N 43/28; A01N 43/40; A01N 43/78; C07D 213/16; C07D 213/44; C07D 213/54; C07D 213/61;
C07D 277/24; C07D 277/30; C07D 333/06; C07D 333/24; C07D 333/28
CPC:A01N 43/00; A01N 2300/00; A01N 43/10; A01N 43/28; A01N 43/40; A01N 43/78; C07D 213/16; C07D 213/44; C07D 213/54; C07D 213/61; C07D 277/24; C07D 277/30; C07D 333/06; C07D 333/24; C07D 333/28

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

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

Databases consulted: Google Patents, CAPLUS, BIOSIS, EMBASE, REGISTRY, Google Scholar Search terms used: Structures, agriculture, herbicide, fungicide, plant grow

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 2009025397 A1 (SUMITOMO CHEMICAL CO [JP]; KUMAMOTO KOJI [JP]; MIYAZAKI HIROYUKI [JP]) 26 February 2009 (2009-02-26) page 1 line 17 –p.4 l. 19, p. 6 l. 1-6, pages 93, 94, 98, 101-105, 11-160, cl. 1-3, 5, 7, 8-9	1,3-6,18-21 7-17,22
X Y	WO 0039094 A1 (NOVARTIS AG [CH]; NOVARTIS ERFIND VERWALT GMBH [AT]; EDMUNDS ANDREW [CH]; LUETHY CHRISTOPH [CH]; SECKINGER KARL [DE]) 06 July 2000 (2000-07-06) pp. 1-2, p.37 para. 2, p. 3, p. 38 para.1,2, p.39 para. 3, table 1, comp. XVIId: A8, A9, A29, A61, A100, A101, A121, A130, A131, A151, A160, A161, A537, A538, A557, A834, A835, A1099, A1100, A1102, A1231, A1232, A1234, claims 1, 2, 8, 11, 13-17	1-6,23-29,52,61 7-17,30-40,46,48

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

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance
“E” earlier application or patent but published on or after the international filing date
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“O” document referring to an oral disclosure, use, exhibition or other means
“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
“&” document member of the same patent family

Date of the actual completion of the international search

19 September 2022

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/IL2022/050749

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 2004016088 A2 (BAYER CROPSCIENCE SA [FR]; MANSFIELD DARREN JAMES [FR]; COOKE TRACEY [GB]; THOMAS PETER STANLEY [GB]; COQUERON PIERRE-YVES [FR]; VORS JEAN-PIERRE [FR]; BRIGGS GEOFFREY GOWER [GB]; LACHAISE HELENE [FR]; RIECK HEIKO [FR]; DESBORDES PHILIPPE [FR]; GROSJEAN-COURNOYER MARIE-CLAIR [FR]) 26 February 2004 (2004-02-26) p. 1 lines 1-6, 20-30, p. 5 lines. 20-25, p. 7 lines 10-20, Tables A, B, cl. 1-8, 13, 16	1,3-6,18,19,23, 24,26-29,52,61 7-17,30-40,46,48
X Y	WO 9222203 A1 (DU PONT [US]) 23 December 1992 (1992-12-23) abstract, p.1 lines 7-14, p. 2 lines 14-30, p.4 lines 12-14, p. 91, p. 96 line 19-p.99	1,3-6,18-24,26- 29,41-45,47,49-51 7-17,30-40,46,48
X Y	US 6806230 B1 (KUMIAI CHEMICAL INDUSTRY CO [JP]; IHARA CHEMICAL IND CO [JP]) 19 October 2004 (2004-10-19) abstract, tables 1-17, 27-33, col. 1 l. 28- col. 5 l. 43, col. 94 l. 24-35, 47-49, col 95 lines 1-4, col. 116 l. 35-53, claims, examples	1,3-6,18-21,23,24,26- 29,41-43,51,52,59,61 7-17,30-40,46,48
Y	US 2007135630 A1 (BAYER CROPSCIENCE AG) 14 June 2007 (2007-06-14) [0377], [0379], [0381], [0388], [0633], [0634], [0701], [0837], [0867], [0872], [0880], [0881], [0910], [0916], Ex. II Ex. XIV	7-17,30-40,46,48
A	Synthesis and antifungal activity of the derivatives of novel pyrazole carboxamide and isoxazolol pyrazole carboxylate. Molecules, 2015, 20.3: 4383-4394 SUN, Jialong; ZHOU, Yuanming (2015/03/09) 2.2 Antifungal activity, Table 1, Conclusions	1-17

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