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(71) Applicant: **SYNGENTA CROP PROTECTION AG** [CH/CH]; Rosentalstrasse 67, 4058 Basel (CH).

(72) Inventors: **SCUTT, James, Nicholas**; Syngenta Limited Syngenta, Jealott's Hill International Research Centre, Bracknell Berkshire RG42 6EY (GB). **WILLETTS, Nigel, James**; Syngenta Limited Syngenta, Jealott's Hill International Research Centre, Bracknell Berkshire RG42 6EY (GB).

(74) Agent: **SYNGENTA IP**; Rosentalstrasse 67, 4058 Basel (CH).

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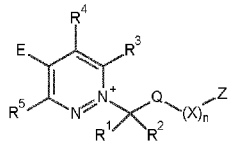
(54) Title: HERBICIDAL COMPOUNDS

(57) Abstract: Compounds of the formula (I) wherein the substituents are as defined in claim 1, useful as a pesticides, especially as herbicides.

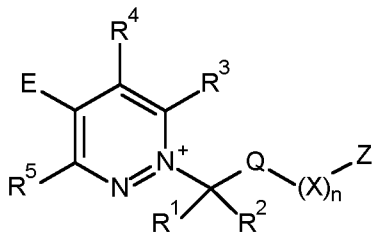


(I)

Herbicidal Compounds

The present invention relates to herbicidally active pyridazine derivatives, as well as to processes and intermediates used for the preparation of such derivatives. The invention further extends to herbicidal compositions comprising such derivatives, as well as to the use of such compounds and compositions for controlling undesirable plant growth: in particular the use for controlling weeds, in crops of useful plants.

The present invention is based on the finding that pyridazine derivatives of formula (I) as defined herein, exhibit surprisingly good herbicidal activity. Thus, according to the present invention there is provided use as a herbicide of a compound of formula (I) or an agronomically acceptable salt or zwitterionic species thereof:



(I)

wherein

R^1 is selected from the group consisting of hydrogen, halogen, C_1-C_6alkyl, C_2-C_6alkenyl, C_2-C_6alkynyl, C_3-C_6cycloalkyl, C_1-C_6haloalkyl, -OR^7, -OR^{15a}, -$N(R^6)S(O)_2R^{15}$, -$N(R^6)C(O)R^{15}$, -$N(R^6)C(O)OR^{15}$, –$N(R^6)C(O)NR^{16}R^{17}$, -$N(R^6)CHO$, -$N(R^{7a})_2$ and –$S(O)_rR^{15}$;

R^2 is selected from the group consisting of hydrogen, halogen, C_1-C_6alkyl and C_1-C_6haloalkyl;

and wherein when R^1 is selected from the group consisting of –OR^7, -OR^{15a}, -$N(R^6)S(O)_2R^{15}$, -$N(R^6)C(O)R^{15}$, -$N(R^6)C(O)OR^{15}$, –$N(R^6)C(O)NR^{16}R^{17}$, -$N(R^6)CHO$, -$N(R^{7a})_2$ and –$S(O)_rR^{15}$, R^2 is selected from the group consisting of hydrogen and C_1-C_6alkyl; or

R^1 and R^2 together with the carbon atom to which they are attached form a C_3-C_6cycloalkyl ring or a 3- to 6- membered heterocyclyl, which comprises 1 or 2 heteroatoms individually selected from N and O;

Q is $(CR^{1a}R^{2b})_m$;

m is 0, 1, 2 or 3;

each R^{1a} and R^{2b} are independently selected from the group consisting of hydrogen, halogen, C_1-C_6alkyl, C_1-C_6haloalkyl, -OH, -OR^7, -OR^{15a}, -NH_2, -NHR^7, -NHR^{15a}, -$N(R^6)CHO$, -$NR^{7b}R^{7c}$ and –$S(O)_rR^{15}$; or

each R^{1a} and R^{2b} together with the carbon atom to which they are attached form a C_3-C_6cycloalkyl ring or a 3- to 6- membered heterocyclyl, which comprises 1 or 2 heteroatoms individually selected from N and O;

R^3, R^4 and R^5 are independently selected from the group consisting of hydrogen, halogen, nitro, cyano, -NH_2, -NR^6R^7, -OH, -OR^7, -$S(O)_rR^{12}$, -$NR^6S(O)_rR^{12}$, C_1-C_6alkyl, C_1-C_6haloalkyl, C_3-C_6cycloalkyl, C_3-C_6halocycloalkyl, C_3-C_6cycloalkoxy, C_2-C_6alkenyl, C_2-C_6haloalkenyl, C_2-C_6alkynyl, C_1-C_3alkoxyC_1-

C_3alkyl-, hydroxyC_1-C_6alkyl-, C_1-C_6haloalkoxy, C_1-C_3haloalkoxyC_1-C_3alkyl-, C_1-C_6alkoxycarbonyl, C_3-C_6alkenyloxy, C_3-C_6alkynyloxy, C_1-C_6alkylcarbonyl, C_1-C_6alkylaminocarbonyl, di-C_1-C_6alkylaminocarbonyl, -$C(R^8)$=NOR^8, phenyl and heteroaryl, wherein the heteroaryl moiety is a 5- or 6-membered monocyclic aromatic ring which comprises 1, 2, 3 or 4 heteroatoms individually selected from N, O and S, and wherein any of said phenyl or heteroaryl moieties are optionally substituted by 1, 2 or 3 substituents R^9, which may be the same or different;

each R^6 is independently selected from hydrogen and C_1-C_6alkyl;

each R^7 is independently selected from the group consisting of C_1-C_6alkyl, -$S(O)_2R^{15}$, -$C(O)R^{15}$, -$C(O)OR^{15}$ and –$C(O)NR^{16}R^{17}$;

each R^{7a} is independently selected from the group consisting of -$S(O)_2R^{15}$, -$C(O)R^{15}$, -$C(O)OR^{15}$ –$C(O)NR^{16}R^{17}$ and –$C(O)NR^6R^{15a}$;

R^{7b} and R^{7c} are independently selected from the group consisting of C_1-C_6alkyl, -$S(O)_2R^{15}$, -$C(O)R^{15}$, -$C(O)OR^{15}$, –$C(O)NR^{16}R^{17}$ and phenyl, and wherein said phenyl is optionally substituted by 1, 2 or 3 R^9 substituents, which may be the same or different; or

R^{7b} and R^{7c} together with the nitrogen atom to which they are attached form a 4- to 6-membered heterocyclyl ring which optionally comprises one additional heteroatom individually selected from N, O and S; and

each R^9 is independently selected from the group consisting of halogen, cyano, -OH, -$N(R^6)_2$, C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4haloalkyl and C_1-C_4haloalkoxy;

E is selected from the group consisting of of –$C(O)OR^{10}$, -CHO, -$C(O)R^{24}$, -$C(O)NHOR^{11}$, -C(O)NHCN, -$C(O)NHR^{25}$, -$S(O)_2NHR^{25}$, -$C(O)NR^6(CR^6_2)_qC(O)(OR^{10})$, -$C(O)NR^6(CR^6_2)_qS(O)_2(OR^{10})$, -$C(O)NR^6(CR^6_2)_qP(O)(R^{13})(OR^{10})$, -$(CR^6_2)_qC(O)OR^{10}$, -$(CR^6_2)_qS(O)_2(OR^{10})$, -$(CR^6_2)_qP(O)(R^{13})(OR^{10})$, -$OC(O)NHOR^{11}$, -$O(CR^6_2)_qC(O)OR^{10}$, -OC(O)NHCN, -$O(CR^6_2)_qS(O)_2(OR^{10})$, -$O(CR^6_2)_qP(O)(R^{13})(OR^{10})$, -$NR^6C(O)NHOR^{11}$, -$NR^6C(O)NHCN$, -$C(O)NHS(O)_2R^{12}$, -$OC(O)NHS(O)_2R^{12}$, -$NR^6C(O)NHS(O)_2R^{12}$, -$S(O)_2OR^{10}$, -$OS(O)_2OR^{10}$, -$NR^6S(O)_2OR^{10}$, -$NR^6S(O)OR^{10}$, -$NHS(O)_2R^{14}$, -$S(O)OR^{10}$, -$S(CR^6_2)_qC(O)OR^{10}$, -$S(CR^6_2)_qS(O)_2(OR^{10})$, -$S(CR^6_2)_qP(O)(R^{13})(OR^{10})$, -$OS(O)OR^{10}$, -$S(O)_2NHCN$, -$S(O)_2NHC(O)R^{18}$, -$S(O)_2NHS(O)_2R^{12}$, -$OS(O)_2NHCN$, -$OS(O)_2NHS(O)_2R^{12}$, -$OS(O)_2NHC(O)R^{18}$, -$NR^6S(O)_2NHCN$, -$NR^6S(O)_2NHC(O)R^{18}$, –$N(OH)C(O)R^{15}$, –$ONHC(O)R^{15}$, -$NR^6S(O)_2NHS(O)_2R^{12}$, -$P(O)(R^{13})(OR^{10})$, -$P(O)H(OR^{10})$, -$OP(O)(R^{13})(OR^{10})$, -$NR^6P(O)(R^{13})(OR^{10})$ and tetrazole;

q is 1-3

X is selected from the group consisting of C_3-C_6cycloalkyl, phenyl, a 5- or 6- membered heteroaryl, which comprises 1, 2, 3 or 4 heteroatoms individually selected from N, O and S, and a 4- to 6- membered heterocyclyl, which comprises 1, 2 or 3 heteroatoms individually selected from N, O and S, and wherein said cycloalkyl, phenyl, heteroaryl or heterocyclyl moieties are optionally substituted by 1 or 2 substituents, which may be the same or different, selected from R^9, and wherein the aforementioned CR^1R^2, Q and Z moieties may be attached at any position of said cycloalkyl, phenyl, heteroaryl or heterocyclyl moieties;

n is 0 or 1;

Z is selected from the group consisting of hydrogen, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_6alkoxyC_1-C_6alkyl, nitro, halo, haloalkoxy, cyano, $-NH_2$, -OH, $-OR^7$, $-C(O)R^{15}$, $-C(O)NR^{16}R^{17}$, $-C(O)OR^{10}$, -CHO, $-C(O)NHOR^{11}$, -C(O)NHCN, $-OC(O)NHOR^{11}$, -OC(O)NHCN, $-NR^6C(O)NHOR^{11}$, $-NR^6C(O)NHCN$, $-C(O)NHS(O)_2R^{12}$, $-OC(O)NHS(O)_2R^{12}$, $-NHR^7$, $-N(R^7)_2$, $-NR^6C(O)NHS(O)_2R^{12}$, $-NR^6S(O)_2R^{15}$, $-S(O)_2OR^{10}$, $-OS(O)_2OR^{10}$, $-NR^6S(O)_2OR^{10}$, $-NR^6S(O)OR^{10}$, $-NHS(O)_2R^{14}$, $-S(O)_rR^{15}$, $-S(O)OR^{10}$, $-S(O)_2NR^{16}R^{17}$ $-OS(O)OR^{10}$, $-S(O)_2NHCN$, $-S(O)_2NHC(O)R^{18}$, $-S(O)_2NHS(O)_2R^{12}$, $-OS(O)_2NHCN$, $-OS(O)_2NHS(O)_2R^{12}$, $-OS(O)_2NHC(O)R^{18}$, $-NR^6S(O)_2NHCN$, $-NR^6S(O)_2NHC(O)R^{18}$, $-N(OH)C(O)R^{15}$, $-ONHC(O)R^{15}$, $-NR^6S(O)_2NHS(O)_2R^{12}$, $-P(O)(R^{13})(OR^{10})$, $-P(O)H(OR^{10})$, $-OP(O)(R^{13})(OR^{10})$, $-NR^6P(O)(R^{13})(OR^{10})$, tetrazole;

R^{10} is selected from the group consisting of hydrogen, C_1-C_6alkyl, phenyl and benzyl, and wherein said phenyl or benzyl are optionally substituted by 1, 2 or 3 R^9 substituents, which may be the same or different;

R^{11} is selected from the group consisting of hydrogen, C_1-C_6alkyl and phenyl, and wherein said phenyl is optionally substituted by 1, 2 or 3 R^9 substituents, which may be the same or different;

R^{12} is selected from the group consisting of C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, -OH, $-N(R^6)_2$ and phenyl, and wherein said phenyl is optionally substituted by 1, 2 or 3 R^9 substituents, which may be the same or different;

R^{13} is selected from the group consisting of -OH, C_1-C_6alkyl, C_1-C_6alkoxy, C_1-C_6haloalkoxy, -O-propargyl, –O-allyl and phenyl;

R^{14} is C_1-C_6haloalkyl;

R^{15} is selected from the group consisting of C_1-C_6alkyl and phenyl, and wherein said phenyl is optionally substituted by 1, 2 or 3 R^9 substituents, which may be the same or different;

R^{15a} is phenyl, wherein said phenyl is optionally substituted by 1, 2 or 3 R^9 substituents, which may be the same or different;

R^{16} and R^{17} are independently selected from the group consisting of hydrogen and C_1-C_6alkyl; or

R^{16} and R^{17} together with the nitrogen atom to which they are attached form a 4- to 6-membered heterocyclyl ring which optionally comprises one additional heteroatom individually selected from N, O and S;

R^{18} is selected from the group consisting of hydrogen, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, $-N(R^6)_2$ and phenyl, and wherein said phenyl is optionally substituted by 1, 2 or 3 R^9 substituents, which may be the same or different;

R^{24} is a peptide moiety comprising one, two or three amino acid moieties independently selected from the group consisting of Ala, Cys, Asp, Glu, Phe, Gly, His, Ile, Lys, Leu, Met, Asn, Pro, Gln, Arg, Ser, Thr, Val, Trp and Tyr, wherein said peptide moiety is bonded to the rest of the molecule via a nitrogen atom in the amino acid moiety;

R^{25} is selected from the group consisting of 5- or 6- membered heteroaromatic moieties, optionally substituted with one or more groups independently selected from R^2 or;

R^{25} is selected from the group consisting of 5- or 6- membered heteroaromatic moieties, containing at least two N atoms, optionally substituted with one or more groups independently selected from R^9;

and

r is 0, 1 or 2;

with the proviso that pyridazocidin is excluded.

According to a second aspect of the invention, there is provided a compound of formula (I) as defined above, wherein R^3, R^4 and R^5 are each independently hydrogen, C_1-C_6alkyl, or C_1-C_6alkoxy, with the proviso that said compound is not pyridazocidin

According to a third aspect of the invention, there is provided an agrochemical composition comprising a herbicidally effective amount of a compound of formula (I) and an agrochemically-acceptable diluent or carrier. Such an agricultural composition may further comprise at least one additional active ingredient.

According to a fourth aspect of the invention, there is provided a method of controlling or preventing undesirable plant growth, wherein a herbicidally effective amount of a compound of formula (I), or a composition comprising this compound as active ingredient, is applied to the plants, to parts thereof or the locus thereof.

According to a fifth aspect of the invention, there is provided the use of a compound of formula (I) as a herbicide.

According to a sixth aspect of the invention, there is provided a process for the preparation of compounds of formula (I).

As used herein, the term "halogen" or “halo” refers to fluorine (fluoro), chlorine (chloro), bromine (bromo) or iodine (iodo), preferably fluorine, chlorine or bromine.

As used herein, cyano means a -CN group.

As used herein, hydroxy means an -OH group.

As used herein, nitro means an $–NO_2$ group.

As used herein, the term "C_1-C_6alkyl" refers to a straight or branched hydrocarbon chain radical consisting solely of carbon and hydrogen atoms, containing no unsaturation, having from one to six carbon atoms, and which is attached to the rest of the molecule by a single bond. C_1-C_4alkyl and C_1-C_2alkyl are to be construed accordingly. Examples of C_1-C_6alkyl include, but are not limited to, methyl (Me), ethyl (Et), *n*-propyl, 1-methylethyl (iso-propyl), *n*-butyl, and 1-dimethylethyl (*t*-butyl).

As used herein, the term "C_1-C_6alkoxy" refers to a radical of the formula $-OR_a$ where R_a is a C_1-C_6alkyl radical as generally defined above. C_1-C_4alkoxy is to be construed accordingly. Examples of C_{1-4}alkoxy include, but are not limited to, methoxy, ethoxy, propoxy, iso-propoxy and *t*-butoxy.

As used herein, the term "C_1-C_6haloalkyl" refers to a C_1-C_6alkyl radical as generally defined above substituted by one or more of the same or different halogen atoms. C_1-C_4haloalkyl is to be construed

accordingly. Examples of C_1-C_6haloalkyl include, but are not limited to chloromethyl, fluoromethyl, fluoroethyl, difluoromethyl, trifluoromethyl and 2,2,2-trifluoroethyl.

As used herein, the term "C_2-C_6alkenyl" refers to a straight or branched hydrocarbon chain radical group consisting solely of carbon and hydrogen atoms, containing at least one double bond that can be of either the (*E*)- or (*Z*)-configuration, having from two to six carbon atoms, which is attached to the rest of the molecule by a single bond. C_2-C_4alkenyl is to be construed accordingly. Examples of C_2-C_6alkenyl include, but are not limited to, prop-1-enyl, allyl (prop-2-enyl) and but-1-enyl.

As used herein, the term "C_2-C_6haloalkenyl" refers to a C_2-C_6alkenyl radical as generally defined above substituted by one or more of the same or different halogen atoms. Examples of C_2-C_6haloalkenyl include, but are not limited to chloroethylene, fluoroethylene, 1,1-difluoroethylene, 1,1-dichloroethylene and 1,1,2-trichloroethylene.

As used herein, the term "C_2-C_6alkynyl" refers to a straight or branched hydrocarbon chain radical group consisting solely of carbon and hydrogen atoms, containing at least one triple bond, having from two to six carbon atoms, and which is attached to the rest of the molecule by a single bond. C_2-C_4alkynyl is to be construed accordingly. Examples of C_2-C_6alkynyl include, but are not limited to, prop-1-ynyl, propargyl (prop-2-ynyl) and but-1-ynyl.

As used herein, the term "C_1-C_6haloalkoxy" refers to a C_1-C_6alkoxy group as defined above substituted by one or more of the same or different halogen atoms. C_1-C_4haloalkoxy is to be construed accordingly. Examples of C_1-C_6haloalkoxy include, but are not limited to, fluoromethoxy, difluoromethoxy, fluoroethoxy, trifluoromethoxy and trifluoroethoxy.

As used herein, the term "C_1-C_3haloalkoxyC_1-C_3alkyl" refers to a radical of the formula R_b-O-R_a- where R_b is a C_1-C_3haloalkyl radical as generally defined above, and R_a is a C_1-C_3alkylene radical as generally defined above.

As used herein, the term "C_1-C_3alkoxyC_1-C_3alkyl" refers to a radical of the formula R_b-O-R_a- where R_b is a C_1-C_3alkyl radical as generally defined above, and R_a is a C_1-C_3alkylene radical as generally defined above.

As used herein, the term " C_1-C_3alkoxyC_1-C_3alkoxy-" refers to a radical of the formula R_b-O-R_a-O- where R_b is a C_1-C_3alkyl radical as generally defined above, and R_a is a C_1-C_3alkylene radical as generally defined above.

As used herein, the term "C_3-C_6alkenyloxy" refers to a radical of the formula -OR_a where R_a is a C_3-C_6alkenyl radical as generally defined above.

As used herein, the term "C_3-C_6alkynyloxy" refers to a radical of the formula -OR_a where R_a is a C_3-C_6alkynyl radical as generally defined above.

As used herein, the term "hydroxyC_1-C_6alkyl" refers to a C_1-C_6alkyl radical as generally defined above substituted by one or more hydroxy groups.

As used herein, the term "C_1-C_6alkylcarbonyl" refers to a radical of the formula -C(O)R_a where R_a is a C_1-C_6alkyl radical as generally defined above.

As used herein, the term "C_1-C_6alkoxycarbonyl" refers to a radical of the formula -C(O)OR_a where R_a is a C_1-C_6alkyl radical as generally defined above.

As used herein, the term “aminocarbonyl” refers to a radical of the formula -C(O)NH_2.

As used herein, the term "C_3-C_6cycloalkyl" refers to a stable, monocyclic ring radical which is saturated or partially unsaturated and contains 3 to 6 carbon atoms. C_3-C_4cycloalkyl is to be construed accordingly. Examples of C_3-C_6cycloalkyl include, but are not limited to, cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl.

As used herein, the term "C_3-C_6halocycloalkyl" refers to a C_3-C_6cycloalkyl radical as generally defined above substituted by one or more of the same or different halogen atoms. C_3-C_4halocycloalkyl is to be construed accordingly.

As used herein, the term "C_3-C_6cycloalkoxy" refers to a radical of the formula –OR_a where R_a is a C_3-C_6cycloalkyl radical as generally defined above.

As used herein, the term “N-C_3-C_6cycloalkylamino” refers to a radical of the formula -NHR_a where R_a is a C_3-C_6cycloalkyl radical as generally defined above.

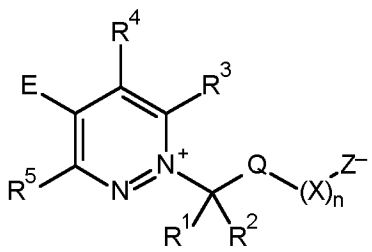
As used herein, except where explicitly stated otherwise, the term "heteroaryl" refers to a 5- or 6-membered monocyclic aromatic ring which comprises 1, 2, 3 or 4 heteroatoms individually selected from nitrogen, oxygen and sulfur. The heteroaryl radical may be bonded to the rest of the molecule *via* a carbon atom or heteroatom. Examples of heteroaryl include, furyl, pyrrolyl, imidazolyl, thienyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, triazolyl, tetrazolyl, pyrazinyl, pyridazinyl, pyrimidyl or pyridyl.

As used herein, except where explicitly stated otherwise, the term "heterocyclyl" or "heterocyclic" refers to a stable 4- to 6-membered non-aromatic monocyclic ring radical which comprises 1, 2, or 3 heteroatoms individually selected from nitrogen, oxygen and sulfur. The heterocyclyl radical may be bonded to the rest of the molecule via a carbon atom or heteroatom. Examples of heterocyclyl include, but are not limited to, pyrrolinyl, pyrrolidyl, tetrahydrofuryl, tetrahydrothienyl, tetrahydrothiopyranyl, piperidyl, piperazinyl, tetrahydropyranyl, dihydroisoxazolyl, dioxolanyl, morpholinyl or δ-lactamyl.

The presence of one or more possible asymmetric carbon atoms in a compound of formula (I) means that the compounds may occur in chiral isomeric forms, i.e., enantiomeric or diastereomeric forms. Also atropisomers may occur as a result of restricted rotation about a single bond. Formula (I) is intended to include all those possible isomeric forms and mixtures thereof. The present invention includes all those possible isomeric forms and mixtures thereof for a compound of formula (I). Likewise, formula (I) is intended to include all possible tautomers (including lactam-lactim tautomerism and keto-enol tautomerism) where present. The present invention includes all possible tautomeric forms for a compound of formula (I). Similarly, where there are di-substituted alkenes, these may be present in *E* or *Z* form or as mixtures of both in any proportion. The present invention includes all these possible isomeric forms and mixtures thereof for a compound of formula (I).

The compounds of formula (I) will typically be provided in the form of an agronomically acceptable salt, a zwitterion or an agronomically acceptable salt of a zwitterion. This invention covers all such agronomically acceptable salts, zwitterions and mixtures thereof in all proportions.

For example a compound of formula (I) wherein E or Z comprises an acidic proton, may exist as a zwitterion, a compound of formula (I-I) or formula (I-V), or as an agronomically acceptable salt, a compound of formula (I-II) or formula (I-VI)as shown below:



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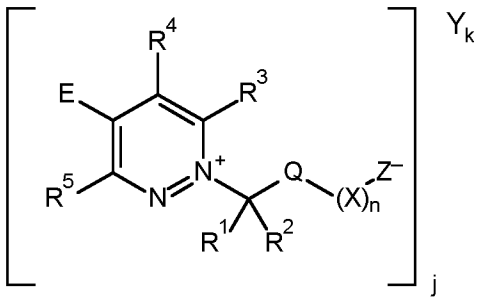
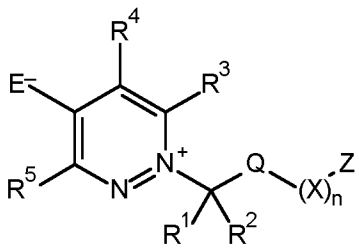
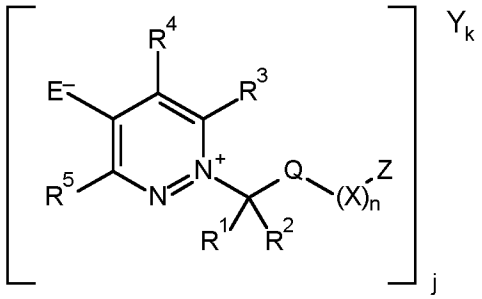


(I-II)



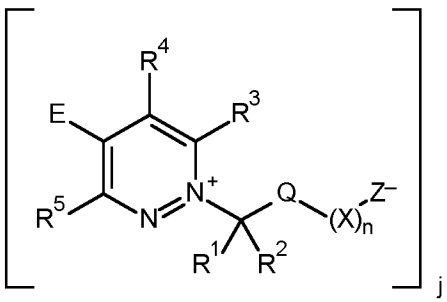
(I-V)



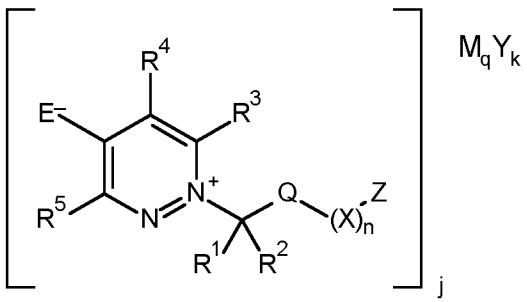
(I-VI)

wherein, Y represents an agronomically acceptable anion and j and k represent integers that may be selected from 1, 2 or 3, dependent upon the charge of the respective anion Y.

A compound of formula (I) may also exist as an agronomically acceptable salt of a zwitterion, a compound of formula (I-III) or formula (I-VII) as shown below:



(I-III)



(I-VII)

wherein, Y represents an agronomically acceptable anion, M represents an agronomically acceptable cation (in addition to the pyridazinium cation) and the integers j, k and q may be selected from 1, 2 or 3, dependent upon the charge of the respective anion Y and respective cation M.

Thus where a compound of formula (I) is drawn in protonated form herein, the skilled person would appreciate that it could equally be represented in unprotonated or salt form with one or more relevant counter ions.

In one embodiment of the invention there is provided a compound of formula (I-II) or formula (I-VI) wherein k is 2, j is 1 and Y is selected from the group consisting of halogen, trifluoroacetate and pentafluoropropionate. In this embodiment a nitrogen atom comprised in R^1, R^2, R^3, R^4, R^5, E, Q, Z or X may be protonated.

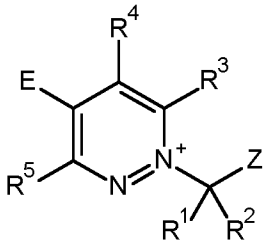
Suitable agronomically acceptable salts of the present invention, represented by an anion Y, include but are not limited chloride, bromide, iodide, fluoride, 2-naphthalenesulfonate, acetate, adipate, methoxide, ethoxide, propoxide, butoxide, aspartate, benzenesulfonate, benzoate, bicarbonate, bisulfate, bitartrate, butylsulfate, butylsulfonate, butyrate, camphorate, camsylate, caprate, caproate, caprylate, carbonate, citrate, diphosphate, edetate, edisylate, enanthate, ethanedisulfonate, ethanesulfonate, ethylsulfate, formate, fumarate, gluceptate, gluconate, glucoronate, glutamate, glycerophosphate, heptadecanoate, hexadecanoate, hydrogen sulfate, hydroxide, hydroxynaphthoate, isethionate, lactate, lactobionate, laurate, malate, maleate, mandelate, mesylate, methanedisulfonate, methylsulfate, mucate, myristate, napsylate, nitrate, nonadecanoate, octadecanoate, oxalate, pelargonate, pentadecanoate, pentafluoropropionate, perchlorate, phosphate, propionate, propylsulfate, propylsulfonate, succinate, sulfate, tartrate, tosylate, tridecylate, triflate, trifluoroacetate, undecylinate and valerate.

Suitable cations represented by M include, but are not limited to, metals, conjugate acids of amines and organic cations. Examples of suitable metals include aluminium, calcium, cesium, copper, lithium, magnesium, manganese, potassium, sodium, iron and zinc. Examples of suitable amines include allylamine, ammonia, amylamine, arginine, benethamine, benzathine, butenyl-2-amine, butylamine, butylethanolamine, cyclohexylamine, decylamine, diamylamine, dibutylamine, diethanolamine, diethylamine, diethylenetriamine, diheptylamine, dihexylamine, diisoamylamine, diisopropylamine, dimethylamine, dioctylamine, dipropanolamine, dipropargylamine, dipropylamine, dodecylamine, ethanolamine, ethylamine, ethylbutylamine, ethylenediamine, ethylheptylamine, ethyloctylamine, ethylpropanolamine, heptadecylamine, heptylamine, hexadecylamine, hexenyl-2-amine, hexylamine, hexylheptylamine, hexyloctylamine, histidine, indoline, isoamylamine, isobutanolamine, isobutylamine, isopropanolamine, isopropylamine, lysine, meglumine, methoxyethylamine, methylamine, methylbutylamine, methylethylamine, methylhexylamine, methylisopropylamine, methylnonylamine, methyloctadecylamine, methylpentadecylamine, morpholine, N,N-diethylethanolamine, N-methylpiperazine, nonylamine, octadecylamine, octylamine, oleylamine, pentadecylamine, pentenyl-2-amine, phenoxyethylamine, picoline, piperazine, piperidine, propanolamine, propylamine, propylenediamine, pyridine, pyrrolidine, sec-butylamine, stearylamine, tallowamine, tetradecylamine, tributylamine, tridecylamine, trimethylamine, triheptylamine, trihexylamine, triisobutylamine, triisodecylamine, triisopropylamine, trimethylamine, tripentylamine, tripropylamine, tris(hydroxymethyl)aminomethane, and undecylamine. Examples of suitable organic cations include benzyltributylammonium, benzyltrimethylammonium, benzyltriphenylphosphonium, choline, tetrabutylammonium, tetrabutylphosphonium, tetraethylammonium, tetraethylphosphonium, tetramethylammonium, tetramethylphosphonium, tetrapropylammonium, tetrapropylphosphonium, tributylsulfonium, tributylsulfoxonium, triethylsulfonium, triethylsulfoxonium, trimethylsulfonium, trimethylsulfoxonium, tripropylsulfonium and tripropylsulfoxonium.

Preferred compounds of formula (I), wherein E or Z comprises an acidic proton, can be represented as either (I-I), (I-V), (I-II) or (I-VI). For compounds of formula (I-II) or (I-VI) emphasis is given to salts when Y is chloride, bromide, iodide, hydroxide, bicarbonate, acetate, pentafluoropropionate, triflate, trifluoroacetate, methylsulfate, tosylate and nitrate, wherein j and k are 1. Preferably, Y is chloride, bromide, iodide, hydroxide, bicarbonate, acetate, trifluoroacetate, methylsulfate, tosylate and nitrate, wherein j and k are 1. For compounds of formula (I-II) or (I-VI) emphasis is also given to salts when Y is carbonate and sulfate, wherein j is 2 and k is 1, and when Y is phosphate, wherein j is 3 and k is 1.

Where appropriate compounds of formula (I) may also be in the form of (and/or be used as) an N-oxide.

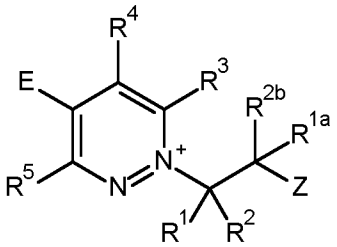
Compounds of formula (I) wherein m is 0 and n is 0 may be represented by a compound of formula (I-Ia) as shown below:



(I-Ia)

wherein R^1, R^2, R^3, R^4, R^5, E and Z are as defined for compounds of formula (I).

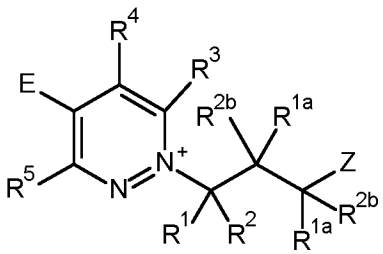
Compounds of formula (I) wherein m is 1 and n is 0 may be represented by a compound of formula (I-Ib) as shown below:



(I-Ib)

wherein R^1, R^2, R^{1a}, R^{2b}, R^3, R^4, R^5 , E and Z are as defined for compounds of formula (I).

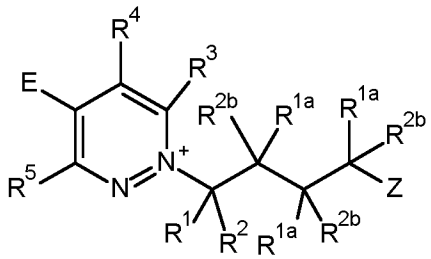
Compounds of formula (I) wherein m is 2 and n is 0 may be represented by a compound of formula (I-Ic) as shown below:



(I-Ic)

wherein R^1, R^2, R^{1a}, R^{2b}, R^3, R^4, R^5, E and Z are as defined for compounds of formula (I).

Compounds of formula (I) wherein m is 3 and n is 0 may be represented by a compound of formula (I-Id) as shown below:



(I-Id)

wherein R^1, R^2, R^{1a}, R^{2b}, R^3, R^4, R^5, E and Z are as defined for compounds of formula (I).

Pyridazocidin which is specifically excluded from compounds of the present invention is a compound of formula (I) in which R^1, R^2, R^3, R^4 and R^5 are hydrogen, E is –C(O)OH, Q is $–CH_2CH_2CH(NH_2)-$ and Z is –C(O)OH. Preferably also excluded are agrochemically acceptable salts of pyridazocidin.

The following are preferred definitions for formula (I). Any of the definitions given below may be combined with any definition of any other substituent given below or elsewhere in this document.

Preferably, R^1 is selected from the group consisting of hydrogen, halogen, C_1-C_6alkyl, C_1-C_6fluoroalkyl, $-OR^7$, $-NHS(O)_2R^{15}$, $-NHC(O)R^{15}$, $-NHC(O)OR^{15}$, $-NHC(O)NR^{16}R^{17}$, $-N(R^{7a})_2$ and $–S(O)_rR^{15}$. More preferably, R^1 is selected from the group consisting of hydrogen, halogen, C_1-C_6alkyl, C_1-C_6fluoroalkyl, $-OR^7$ and $-N(R^{7a})_2$. Even more preferably, R^1 is selected from the group consisting of hydrogen, C_1-C_6alkyl, $-OR^7$ and $-N(R^{7a})_2$. Even more preferably still, R^1 is hydrogen or C_1-C_6alkyl. Yet even more preferably still, R^1 is hydrogen or methyl. Most preferably R^1 is hydrogen.

R^2 is selected from the group consisting of hydrogen, halogen, C_1-C_6alkyl and C_1-C_6haloalkyl. Preferably, R^2 is selected from the group consisting of hydrogen, halogen, C_1-C_6alkyl and C_1-C_6fluoroalkyl. More preferably, R^2 is hydrogen or C_1-C_6alkyl. Even more preferably, R^2 is hydrogen or methyl. Most preferably R^2 is hydrogen.

Wherein when R^1 is selected from the group consisting of $–OR^7$, $-OR^{15a}$, $-N(R^6)S(O)_2R^{15}$, $-N(R^6)C(O)R^{15}$, $-N(R^6)C(O)OR^{15}$, $–N(R^6)C(O)NR^{16}R^{17}$, $-N(R^6)CHO$, $-N(R^{7a})_2$ and $–S(O)_rR^{15}$, then R^2 is selected from the group consisting of hydrogen and C_1-C_6alkyl. Preferably, when R^1 is selected from the group consisting of $–OR^7$, $-NHS(O)_2R^{15}$, $-NHC(O)R^{15}$, $-NHC(O)OR^{15}$, $-NHC(O)NR^{16}R^{17}$, $-N(R^{7a})_2$ and $–S(O)_rR^{15}$, then R^2 is selected from the group consisting of hydrogen and methyl.

Alternatively, R^1 and R^2 together with the carbon atom to which they are attached form a C_3-C_6cycloalkyl ring or a 3- to 6- membered heterocyclyl, which comprises 1 or 2 heteroatoms individually selected from N and O. Preferably, R^1 and R^2 together with the carbon atom to which they are attached form a C_3-C_6cycloalkyl ring. More preferably, R^1 and R^2 together with the carbon atom to which they are attached form a cyclopropyl ring.

In another embodiment R^1 is methyl and R^2 is hydrogen.

In another embodiment R^1 is methyl and R^2 is methyl.

In a preferred embodiment R^1 and R^2 are hydrogen

Q is $(CR^{1a}R^{2b})_m$.

m is 0, 1, 2 or 3. Preferably, m is 0,1 or 2. More preferably, m is 1 or 2. Most preferably, m is 0.

Each R^{1a} and R^{2b} are independently selected from the group consisting of hydrogen, halogen, C_1-C_6alkyl, C_1-C_6haloalkyl, -OH, -OR^7, -OR^{15a}, -NH_2, -NHR^7, -NHR^{15a}, -$N(R^6)CHO$, -$NR^{7b}R^{7c}$ and –$S(O)_rR^{15}$. Preferably, each R^{1a} and R^{2b} are independently selected from the group consisting of hydrogen, halogen, C_1-C_6alkyl, C_1-C_6fluoroalkyl, -OH, -NH_2 and -NHR^7. More preferably, each R^{1a} and R^{2b} are independently selected from the group consisting of hydrogen, C_1-C_6alkyl, –OH and –NH_2. Even more preferably, each R^{1a} and R^{2b} are independently selected from the group consisting of hydrogen, methyl, –OH and –NH_2. Even more preferably still, each R^{1a} and R^{2b} are independently selected from the group consisting of hydrogen and methyl. Most preferably R^{1a} and R^{2b} are hydrogen.

In another embodiment each R^{1a} and R^{2b} are independently selected from the group consisting of hydrogen and C_1-C_6alkyl.

Alternatively, each R^{1a} and R^{2b} together with the carbon atom to which they are attached form a C_3-C_6cycloalkyl ring or a 3- to 6- membered heterocyclyl, which comprises 1 or 2 heteroatoms individually selected from N and O. Preferably, each R^{1a} and R^{2b} together with the carbon atom to which they are attached form a C_3-C_6cycloalkyl ring. More preferably, each R^{1a} and R^{2b} together with the carbon atom to which they are attached form a cyclopropyl ring.

R^3 , R^4 , and R^5 are preferably independently hydrogen, C_1-C_6alkyl, or C_1-C_6alkoxy, most preferably hydrogen or methyl.

Each R^6 is independently selected from hydrogen and C_1-C_6alkyl. Preferably, each R^6 is independently selected from hydrogen and methyl.

Each R^7 is independently selected from the group consisting of C_1-C_6alkyl, -$S(O)_2R^{15}$, -$C(O)R^{15}$, -$C(O)OR^{15}$ and –$C(O)NR^{16}R^{17}$. Preferably, each R^7 is independently selected from the group consisting of C_1-C_6alkyl, -$C(O)R^{15}$ and –$C(O)NR^{16}R^{17}$. More preferably, each R^7 is C_1-C_6alkyl. Most preferably, each R^7 is methyl.

Each R^{7a} is independently selected from the group consisting of -$S(O)_2R^{15}$, -$C(O)R^{15}$, -$C(O)OR^{15}$ –$C(O)NR^{16}R^{17}$ and –$C(O)NR^6R^{15a}$. Preferably, each R^{7a} is independently -$C(O)R^{15}$ or –$C(O)NR^{16}R^{17}$.

R^{7b} and R^{7c} are independently selected from the group consisting of C_1-C_6alkyl, -$S(O)_2R^{15}$, -$C(O)R^{15}$, -$C(O)OR^{15}$, –$C(O)NR^{16}R^{17}$ and phenyl, and wherein said phenyl is optionally substituted by 1, 2 or 3 R^9 substituents, which may be the same or different. Preferably, R^{7b} and R^{7c} are independently selected from the group consisting of C_1-C_6alkyl, -$C(O)R^{15}$ and –$C(O)NR^{16}R^{17}$. More preferably, R^{7b} and R^{7c} are C_1-C_6alkyl. Most preferably, R^{7b} and R^{7c} are methyl.

Alternatively, R^{7b} and R^{7c} together with the nitrogen atom to which they are attached form a 4- to 6-membered heterocyclyl ring which optionally comprises one additional heteroatom individually selected from N, O and S. Preferably, R^{7b} and R^{7c} together with the nitrogen atom to which they are attached

form a 5- to 6-membered heterocyclyl ring which optionally comprises one additional heteroatom individually selected from N and O. More preferably, R^{7b} and R^{7c} together with the nitrogen atom to which they are attached form an pyrrolidyl, oxazolidinyl, imidazolidinyl, piperidyl, piperazinyl or morpholinyl group.

Each R^9 is independently selected from the group consisting of halogen, cyano, -OH, -$N(R^6)_2$, C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4haloalkyl and C_1-C_4haloalkoxy. Preferably, each R^9 is independently selected from the group consisting of halogen, cyano, -$N(R^6)_2$, C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4haloalkyl and C_1-C_4haloalkoxy. More preferably, each R^9 is independently selected from the group consisting of halogen, C_1-C_4alkyl, C_1-C_4alkoxy and C_1-C_4haloalkyl. Even more preferably, each R^9 is independently selected from the group consisting of halogen and C_1-C_4alkyl.

Preferably E is -$C(O)OR^{10}$, -$C(O)NHS(O)_2R^{12}$, -$C(O)R^{24}$, -$P(O)(R^{13})(OR^{10})$; or $C(O)NR^6(CR^6_2)_qC(O)(OR^{10})$.

X is selected from the group consisting of C_3-C_6cycloalkyl, phenyl, a 5- or 6- membered heteroaryl, which comprises 1, 2, 3 or 4 heteroatoms individually selected from N, O and S, and a 4- to 6- membered heterocyclyl, which comprises 1, 2 or 3 heteroatoms individually selected from N, O and S, and wherein said cycloalkyl, phenyl, heteroaryl or heterocyclyl moieties are optionally substituted by 1 or 2 substituents, which may be the same or different, selected from R^9, and wherein the aforementioned CR^1R^2, Q and Z moieties may be attached at any position of said cycloalkyl, phenyl, heteroaryl or heterocyclyl moieties.

Preferably, X is selected from the group consisting of phenyl and a 4- to 6- membered heterocyclyl, which comprises 1 or 2 heteroatoms individually selected from N and O, and wherein said phenyl or heterocyclyl moieties are optionally substituted by 1 or 2 substituents, which may be the same or different, selected from R^9, and wherein the aforementioned CR^1R^2, Q and Z moieties may be attached at any position of said phenyl or heterocyclyl moieties.

More preferably, X is a 4- to 6- membered heterocyclyl, which comprises 1 or 2 heteroatoms individually selected from N and O, and wherein said heterocyclyl moieties is optionally substituted by 1 or 2 substituents, which may be the same or different, selected from R^9, and wherein the aforementioned CR^1R^2, Q and Z moieties may be attached at any position of said heterocyclyl moiety.

In one embodiment, X is a 5-membered heterocyclyl, which comprises 1 heteroatom, wherein said heteroatom is N, and wherein the aforementioned CR^1R^2, Q and Z moieties may be attached at any position of said heterocyclyl moiety. Preferably, X is a 5-membered heterocyclyl, which comprises 1 heteroatom, wherein said heteroatom is N, and wherein the aforementioned CR^1R^2 and Q moieties are attached adjacent to the N atom and the Z moiety is attached to the N atom

In another embodiment, X is phenyl optionally substituted by 1 or 2 substituents, which may be the same or different, selected from R^9, and wherein the aforementioned CR^1R^2, Q and Z moieties may be attached at any position of said phenyl moiety. Preferably, X is phenyl and the aforementioned CR^1R^2 and Q moieties are attached in a postion *para* to the Z moiety.

n is 0 or 1. Preferably, n is 0.

Preferably, Z is selected from the group consisting of hydrogen, OH, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, –C(O)OR^{10}, -C(O)NHOR^{11}, -OC(O)NHOR^{11}, -NR^6C(O)NHOR^{11}, -C(O)NHS$(O)_2R^{12}$, -OC(O)NHS$(O)_2R^{12}$, -NR^6C(O)NHS$(O)_2R^{12}$, -S$(O)_2OR^{10}$, -OS$(O)_2OR^{10}$, -NR^6S$(O)_2OR^{10}$, -NR^6S(O)OR^{10}, -NHS$(O)_2R^{14}$, -S(O)OR^{10}, -OS(O)OR^{10}, -S$(O)_2$NHC(O)R^{18}, -S$(O)_2$NHS$(O)_2R^{12}$, -OS$(O)_2$NHS$(O)_2R^{12}$, -OS$(O)_2$NHC(O)R^{18}, -NR^6S$(O)_2$NHC(O)R^{18}, –N(OH)C(O)R^{15}, –ONHC(O)R^{15}, -NR^6S$(O)_2$NHS$(O)_2R^{12}$, -P(O)$(R^{13})(OR^{10})$, -P(O)H(OR^{10}), -OP(O)$(R^{13})(OR^{10})$ and -NR^6P(O)$(R^{13})(OR^{10})$.

More preferably, Z is selected from the group consisting of hydrogen, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_6alkoxy, –C(O)OR^{10}, -C(O)NHOR^{11}, -C(O)NHS$(O)_2R^{12}$, -S$(O)_2OR^{10}$, -OS$(O)_2OR^{10}$, -NR^6S$(O)_2OR^{10}$, -NHS$(O)_2R^{14}$, -S(O)OR^{10} and -P(O)$(R^{13})(OR^{10})$.

Even more preferably Z is selected from the group consisting of hydrogen, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_6alkoxy, -C(O)OR^{10}, -C(O)NHS$(O)_2R^{12}$, -S$(O)_2OR^{10}$, and -P(O)$(R^{13})(OR^{10})$.

Even more preferably still Z is selected from the group consisting of hydrogen, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl and C_1-C_6alkoxy,.

Most preferably Z is hydrogen, C_1-C_6alkyl or C_1-C_6hydroxyalkyl, especially hydrogen, methyl or CH_2OH.

R^{10} is selected from the group consisting of hydrogen, C_1-C_6alkyl, phenyl and benzyl, and wherein said phenyl or benzyl are optionally substituted by 1, 2 or 3 R^9 substituents, which may be the same or different. Preferably, R^{10} is selected from the group consisting of hydrogen, C_1-C_6alkyl, phenyl and benzyl. More preferably, R^{10} is selected from the group consisting of hydrogen and C_1-C_6alkyl. Most preferably, R^{10} is hydrogen.

R^{11} is selected from the group consisting of hydrogen, C_1-C_6alkyl and phenyl, and wherein said phenyl is optionally substituted by 1, 2 or 3 R^9 substituents, which may be the same or different. Preferably, R^{11} is selected from the group consisting of hydrogen, C_1-C_6alkyl and phenyl. More preferably, R^{11} is selected from the group consisting of hydrogen and C_1-C_6alkyl. Even more preferably, R^{11} is C_1-C_6alkyl. Most preferably, R^{11} is methyl.

R^{12} is selected from the group consisting of C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, -OH, -N$(R^6)_2$ and phenyl, and wherein said phenyl is optionally substituted by 1, 2 or 3 R^9 substituents, which may be the same or different. Preferably, R^{12} is selected from the group consisting of C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, -OH, -N$(R^6)_2$ and phenyl. More preferably, R^{12} is selected from the group consisting of C_1-C_6alkyl, C_1-C_6haloalkyl and -N$(R^6)_2$. Even more preferably, R^{12} is selected from the group consisting of methyl, -N$(Me)_2$ and trifluoromethyl. Most preferably, R^{12} is methyl.

R^{13} is selected from the group consisting of -OH, C_1-C_6alkyl, C_1-C_6alkoxy, C_1-C_6haloalkoxy, -O-propargyl, –O-allyl and phenyl. Preferably R^{13} is selected from the group consisting of C_1-C_6alkyl, C_1-C_6alkoxy, C_1-C_6haloalkoxy, -O-propargyl or –O-allyl. More preferably, R^{13} is selected from the group consisting of –OH and C_1-C_6alkoxy. Even more preferably, R^{13} is selected from the group consisting of methyl, ethyl, propyl, isopropyl, isobutyl, -O propargyl and –O-allyl.

R^{14} is C_1-C_6haloalkyl. Preferably, R^{14} is trifluoromethyl.

R^{15} is selected from the group consisting of C_1-C_6alkyl and phenyl, and wherein said phenyl is optionally substituted by 1, 2 or 3 R^9 substituents, which may be the same or different. Preferably, R^{15} is selected

from the group consisting of C_1-C_6alkyl and phenyl. More preferably, R^{15} is C_1-C_6alkyl. Most preferably R^{15} is methyl.

R^{15a} is phenyl, wherein said phenyl is optionally substituted by 1, 2 or 3 R^9 substituents, which may be the same or different. Preferably, R^{15a} is phenyl optionally substituted by 1 R^9 substituent. More preferably, R^{15a} is phenyl.

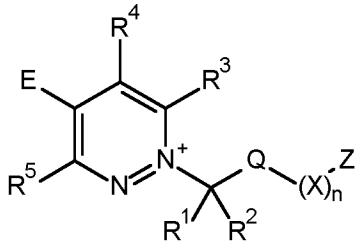
R^{16} and R^{17} are independently selected from the group consisting of hydrogen and C_1-C_6alkyl. Preferably, R^{16} and R^{17} are independently selected from the group consisting of hydrogen and methyl.

Alternatively, R^{16} and R^{17} together with the nitrogen atom to which they are attached form a 4- to 6-membered heterocyclyl ring which optionally comprises one additional heteroatom individually selected from N, O and S. Preferably, R^{16} and R^{17} together with the nitrogen atom to which they are attached form a 5- to 6-membered heterocyclyl ring which optionally comprises one additional heteroatom individually selected from N and O. More preferably, R^{16} and R^{17} together with the nitrogen atom to which they are attached form an pyrrolidyl, oxazolidinyl, imidazolidinyl, piperidyl, piperazinyl or morpholinyl group.

R^{18} is selected from the group consisting of hydrogen, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, $-N(R^6)_2$ and phenyl, and wherein said phenyl is optionally substituted by 1, 2 or 3 R^9 substituents, which may be the same or different. Preferably, R^{18} is selected from the group consisting of hydrogen, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, $-N(R^6)_2$ and phenyl. More preferably, R^{18} is selected from the group consisting of hydrogen, C_1-C_6alkyl and C_1-C_6haloalkyl. Further more preferably, R^{18} is selected from the group consisting of C_1-C_6alkyl and C_1-C_6haloalkyl. Most preferably, R^{18} is methyl or trifluoromethyl.

r is 0, 1 or 2. Preferably, r is 0 or 2.

There is also provided a process for the preparation of compounds of formula (I):

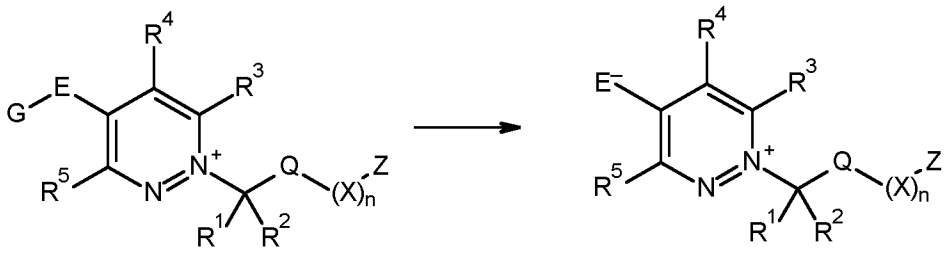


(I)

Wherein Q, Z, X, n, R^1, R^2, R^3, R^4, R^5 and E are as defined herein;

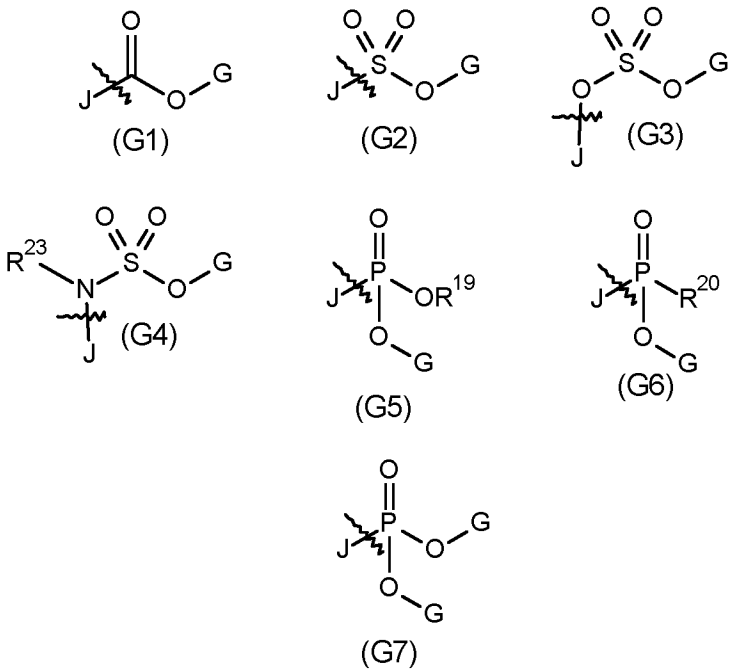
It should be understood that compounds of formula (I) may exist/be manufactured in 'procidal form', wherein they comprise a group 'G'. Such compounds are referred to herein as compounds of formula (I-IV).

G is a group which may be removed in a plant by any appropriate mechanism including, but not limited to, metabolism and chemical degradation to give a compound of formula (I-I), (I-V) or (I-VI) wherein E contains an acidic proton, for example see the scheme below:



(I-IV) (I-I)

Whilst such G groups may be considered as 'procidal', and thus yield active herbicidal compounds once removed, compounds comprising such groups may also exhibit herbicidal activity in their own right. In such cases in a compound of formula (I-IV), E-G may include but is not limited to, any one of (G1) to (G7) below and J indicates the point of attachment to the remaining part of a compound of formula (I):



In embodiments where E-G is (G1) to (G7), G, R^{19}, R^{20}, R^{21}, R^{22} and R^{23} are defined as follows:

G is C_1-C_6alkyl, C_2-C_6alkenyl, C_2-C_6alkynyl, -$C(R^{21}R^{22})OC(O)R^{19}$, phenyl or phenyl-$C_1$-$C_4$alkyl-, wherein said phenyl moiety is optionally substituted by 1 to 5 substituents independently selected from halo, cyano, nitro, C_1-C_6alkyl, C_1-C_6haloalkyl or C_1-C_6alkoxy.

R^{19} is C_1-C_6alkyl or phenyl,

R^{20} is hydroxy, C_1-C_6alkyl, C_1-C_6alkoxy or phenyl,

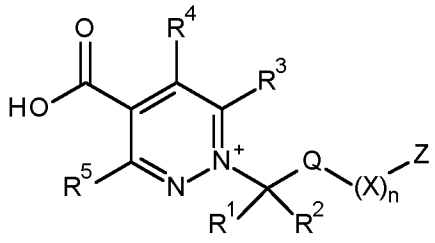
R^{21} is hydrogen or methyl,

R^{22} is hydrogen or methyl,

R^{23} is hydrogen or C_1-C_6alkyl.

The compounds in Tables 1 to 9 below illustrate the compounds of the invention. The skilled person would understand that the compounds of formula (I) may exist as an agronomically acceptable salt, a zwitterion or an agronomically acceptable salt of a zwitterion as described hereinbefore.

Table 1:
This table discloses 3 specific compounds of the formula (T-1):

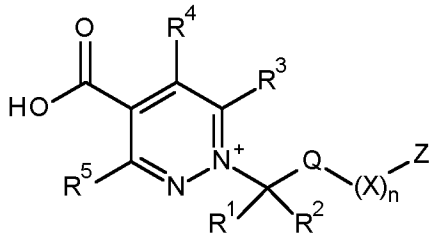


(T-1)

Wherein m, Q, R^3, R^4, R^5 and Z are as defined in Table 1, R^1 and R^2 are hydrogen and n is 0.

Compound number	R^3	R^4	R^5	Z	m	Q
1.001	H	H	H	-H	0	-
1.002	H	H	H	$-CH_2OH$	0	-
1.003	H	H	H	$-CH_2OMe$	0	-

Table 2:
This table discloses 3 specific compounds of the formula (T-2):

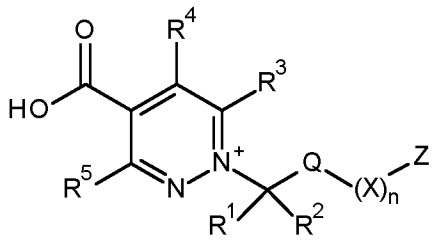


(T-2)

Wherein m, Q, R^3, R^4, R^5 and Z are as defined in Table 2, R^1 and R^2 are hydrogen and n is 0.

Compound number	R^3	R^4	R^5	Z	m	Q
2.001	H	H	H	-H	1	CH_2
2.002	H	H	H	$-CH_2OH$	1	CH_2
2.003	H	H	H	$-CH_2OMe$	1	CH_2

Table 3:
This table discloses 3 specific compounds of the formula (T-3):



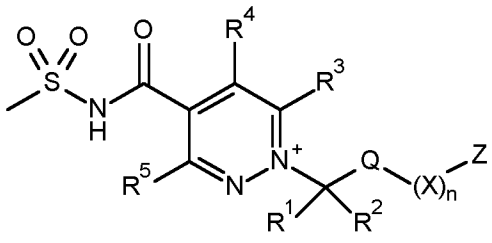
(T-3)

wherein m, Q, R^3, R^4, R^5 and Z are as defined in Table 3, R^1 and R^2 are hydrogen and n is 0.

Compound number	R^3	R^4	R^5	Z	m	Q
3.001	H	H	H	-H	2	CH_2CH_2
3.002	H	H	H	$-CH_2OH$	2	CH_2CH_2

Compound number	R^3	R^4	R^5	Z	m	Q
3.003	H	H	H	$-CH_2OMe$	2	CH_2CH_2

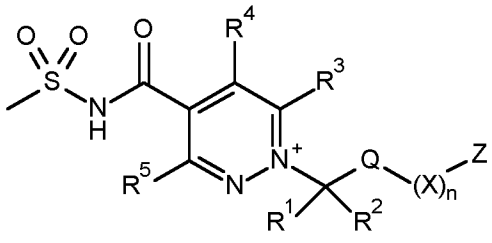
Table 4:
This table discloses 3 specific compounds of the formula (T-4):



(T-4)

wherein m, Q, R^3, R^4, R^5 and Z are as defined above in Table 1, R^1 and R^2 are hydrogen and n is 0.

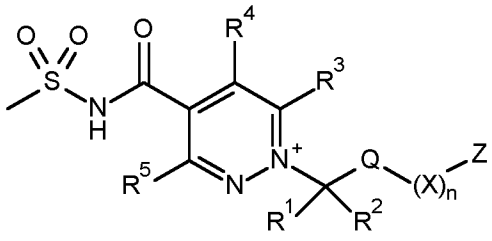
Table 5:
This table discloses 3 specific compounds of the formula (T-5):



(T-5)

wherein m, Q, R^3, R^4, R^5 and Z are as defined above in Table 2, R^1 and R^2 are hydrogen and n is 0.

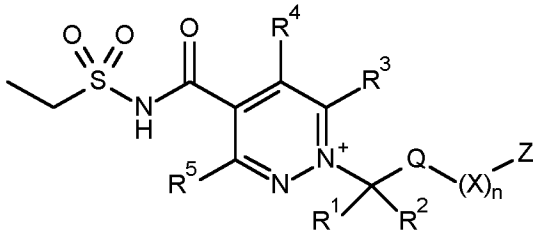
Table 6:
This table discloses 3 specific compounds of the formula (T-6):



(T-6)

wherein m, Q, R^3, R^4, R^5 and Z are as defined above in Table 3, R^1 and R^2 are hydrogen and n is 0.

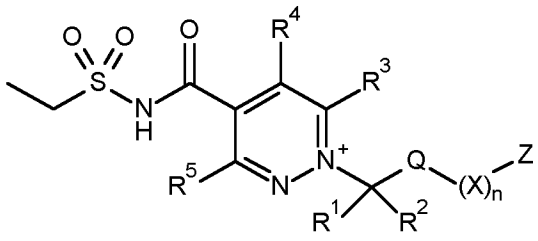
Table 7:
This table discloses 3 specific compounds of the formula (T-7):



(T-7)

wherein m, Q, R^3, R^4, R^5 and Z are as defined above in Table 1, R^1 and R^2 are hydrogen and n is 0.

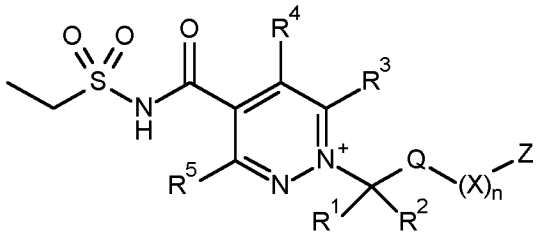
Table 8:
This table discloses 3 specific compounds of the formula (T-8):



(T-8)

wherein m, Q, R^3, R^4, R^5 and Z are as defined above in Table 2, R^1 and R^2 are hydrogen and n is 0.

Table 9:
This table discloses 3 specific compounds of the formula (T-9):



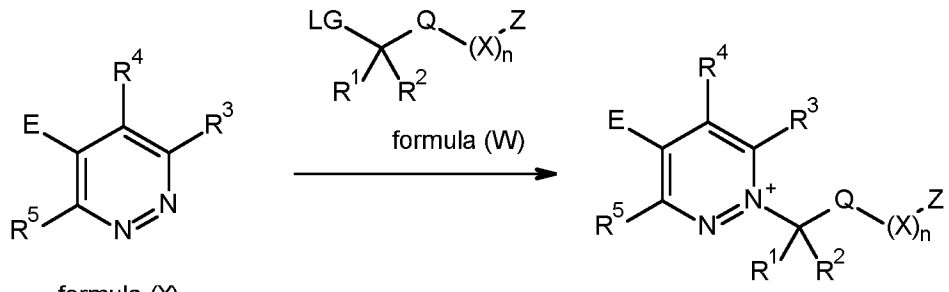
(T-9)

wherein m, Q, R^3, R^4, R^5 and Z are as defined above in Table 3, R^1 and R^2 are hydrogen and n is 0.

The compounds of formula (I) may be prepared by the alkylation of compounds of formula (X), wherein R^3, R^4, R^5 and E are as defined for compounds of formula (I), with a suitable alkylating agent of formula (W), wherein R^1, R^2, Q, X, n and Z are as defined for compounds of formula (I) and LG is a suitable leaving group, for example, halide or pseudohalide such as triflate, mesylate or tosylate, in a suitable solvent at a suitable temperature, as described in reaction scheme 1. Example conditions include stirring a compound of formula (X) with an alkylating agent of formula (W) in a solvent, or mixture of solvents, such as acetone, dichloromethane, dichloroethane, *N,N*-dimethylformamide, acetonitrile, 1,4-dioxane, water, acetic acid or trifluoroacetic acid at a temperature between -78ºC and 150ºC. Alkylating agents of formula (W) are commercially avaialable or are known in the literature and may include, but are not limited to, iodomethane, bromomethane, chloromethane, dimethylsulfate, iodoethane, bromoethane, chloroethane, diethylsulfate, 2-methoxyethyl trifluoromethanesulfonate, 2-bromoethyl methyl ether, 2-iodoethyl methyl ether, benzyl bromide, benzyl chloride, benzyl iodide, 2-bromoethanol, 2-iodoethanol, 2,2-difluoroethyl trifluoromethanesulfonate, 2-bromoethylamine hydrobromide, bromoacetic acid, methyl bromoacetate, 3-bromopropionoic acid, methyl 3-bromopropionate, 2-bromo-*N*-methoxyacetamide, sodium 2-bromoethanesulphonate, 2,2-dimethylpropyl 2-(trifluoromethylsulfonyloxy)ethanesulfonate, 2-bromo-*N*-methanesulfonylacetamide, 3-bromo-*N*-methanesulfonylpropanamide, dimethoxyphosphorylmethyl trifluoromethanesulfonate, dimethyl 3-bromopropylphosphonate, 3-chloro-2,2-dimethyl-propanoic acid and diethyl 2-bromoethylphosphonate. Such alkylating agents and related compounds are either known in the literature or may be prepared by known literature methods. Compounds of formula (I) which may be described as esters of *N*-alkyl acids, which include, but are not limited to, esters of carboxylic acids, phosphonic acids, phosphinic acids, sulfonic acids and sulfinic acids, may optionally be subsequently partially or fully hydrolysed by treament

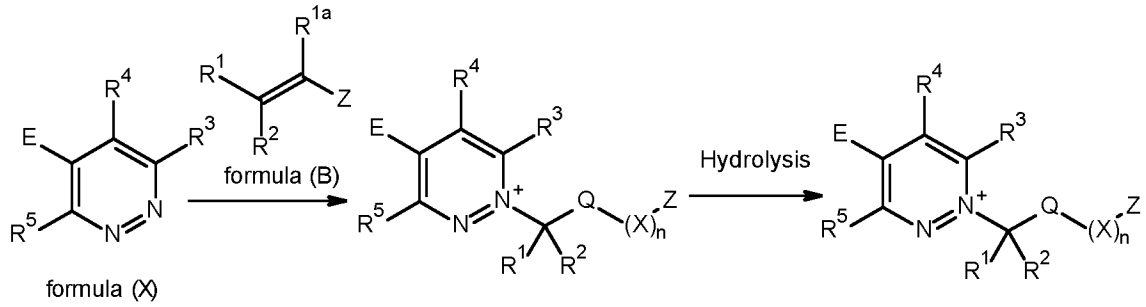
with a suitable reagent, for example, aqueous hydrochloric acid or trimethylsilyl bromide, in a suitable solvent at a suitable temperature between 0ºC and 100ºC.

Reaction scheme 1



Additonally, compounds of formula (I) may be prepared by reacting compounds of formula (X), wherein R^3, R^4, R^5 and E are as defined for compounds of formula (I), with a suitably activated electrophilic alkene of formula (B), wherein Z is -C(O)R^{15}, -C(O)N$R^{16}R^{17}$, –C(O)OR^{10}, -CHO, nitro, cyano, -S(O)$_2$OR^{10}, -S(O)$_2$N$R^{16}R^{17}$, -S(O)$_r R^{15}$, -P(O)(R^{13})(OR^{10}) and R^1, R^2, R^{1a}, R^{10}, R^{13}, R^{15}, R^{16} and R^{17} are as defined for compounds of formula (I), in a suitable solvent at a suitable temperature. Compounds of formula (B) are known in the literature, or may be prepared by known methods. Example reagents include, but are not limited to, acrylic acid, methacrylic acid, crotonic acid, 3,3-dimethylacrylic acid, methyl acrylate, ethene sulfonic acid, isopropyl ethylenesulfonate, 2,2-dimethylpropyl ethenesulfonate and dimethyl vinylphosphonate. The direct products of these reactions, which may be described as esters of N-alkyl acids, which include, but are not limited to, esters of carboxylic acids, phosphonic acids, phosphinic acids, sulfonic acids and sulfinic acids, may optionally be subsequently partially or fully hydrolysed by treament with a suitable reagent in a suitable solvent at a suitable temperature, as described in reaction scheme 2.

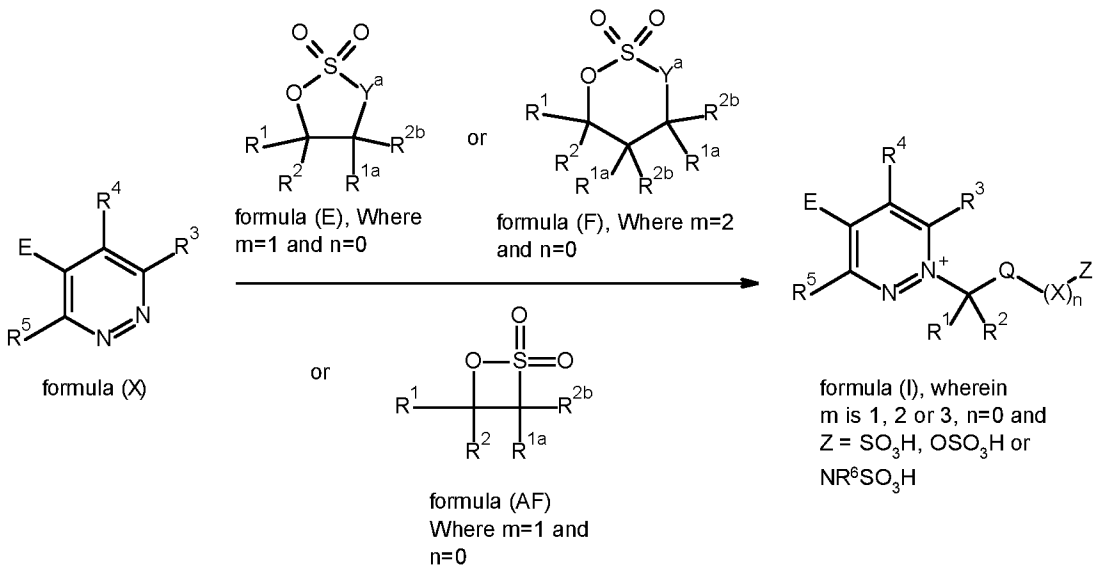
Reaction scheme 2



In a related reaction compounds of formula (I), wherein Q is C($R^{1a}R^{2b}$), m is 1, 2 or 3, n=0 and Z is -S(O)$_2$OH, -OS(O)$_2$OH or -NR^6S(O)$_2$OH, may be prepared by the reaction of compounds of formula (X), wherein R^3, R^4, R^5 and E are as defined for compounds of formula (I), with a cyclic alkylating agent of

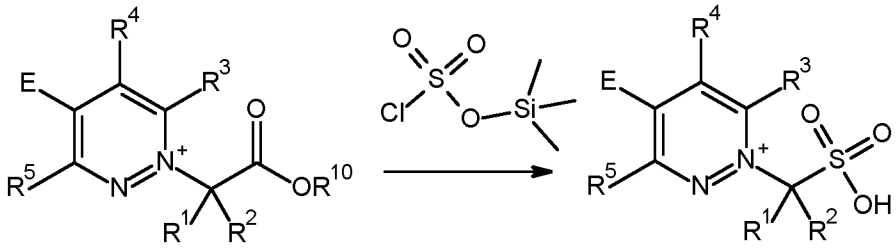
formula (E), (F) or (AF), wherein Y^a is $C(R^{1a}R^{2b})$, O or NR^6 and R^1, R^2, R^{1a}, R^{2b} and R^6 are as defined for compounds of formula (I), in a suitable solvent at a suitable temperature, as described in reaction scheme 3. Suitable solvents and suitable temperatures are as previously described. An alkylating agent of formula (E) or (F) may include, but is not limited to, 1,3-propanesultone, 1,4-butanesultone, ethylenesulfate, 1,3-propylene sulfate and 1,2,3-oxathiazolidine 2,2-dioxide. Such alkylating agents and related compounds are either known in the literature or may be prepared by known literature methods.

Reaction scheme 3



A compound of formula (I), wherein m is 0, n is 0 and Z is $-S(O)_2OH$, may be prepared from a compound of formula (I), wherein m is 0, n is 0 and Z is $C(O)OR^{10}$, by treatment with trimethylsilylchlorosulfonate in a suitable solvent at a suitable temperature, as described in reaction scheme 4. Preferred conditions include heating the carboxylate precursor in neat trimethylsilylchlorosulfonate at a temperature between 25ºC and 150ºC.

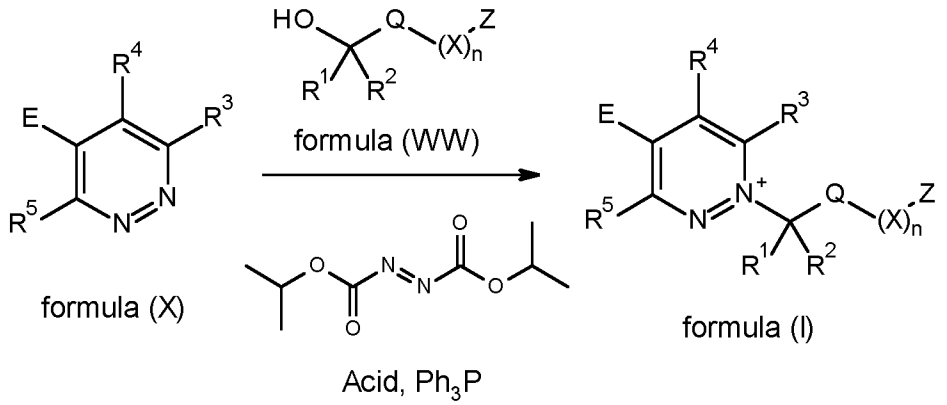
Reaction scheme 4



Furthermore, compounds of formula (I) may be prepared by reacting compounds of formula (X), wherein R^3, R^4, R^5 and E are as defined for compounds of formula (I), with a suitable alcohol of formula (WW), wherein R^1, R^2, Q, X, n and Z are as defined for compounds of formula (I), under Mitsunobu-type conditions such as those reported by Petit et al, Tet. Lett. 2008, 49 (22), 3663. Suitable phosphines include triphenylphosphine, suitable azodicarboxylates include diisopropylazodicarboxylate and suitable

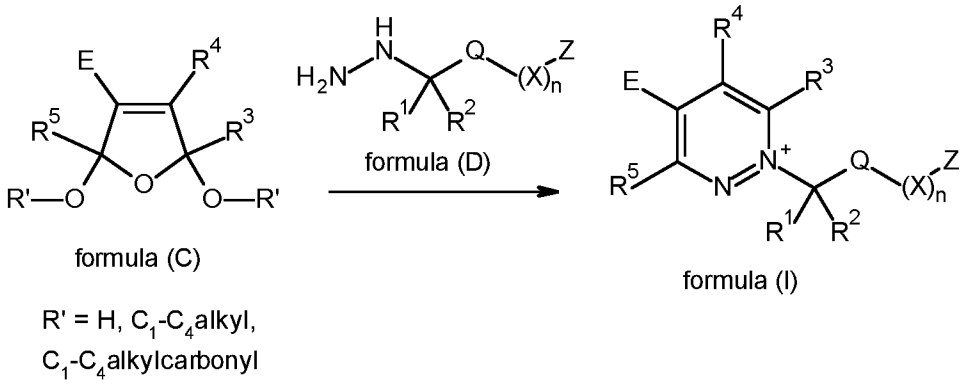
acids include fluoroboric acid, triflic acid and bis(trifluoromethylsulfonyl)amine, as described in reaction scheme 5. Alcohols of formula (WW) are either known in the literature or may be prepared by known literature methods.

Reaction scheme 5



Compounds of formula (I) may also be prepared by reacting compounds of formula (C), wherein R^3, R^4, R^5 and E are as defined for compounds of formula (I), with a hydrazine of formula (D), wherein R^1, R^2, Q, X, n and Z are as defined for compounds of formula (I), in a suitable solvent or mixture of solvents, in the presence of a suitable acid at a suitable temperature, between -78ºC and 150ºC, as described in reaction scheme 6. Suitable solvents, or mixtures thereof, include, but are not limited to, alcohols, such as methanol, ethanol and isopropanol, water, aqueous hydrochloric acid, aqueous sulfuric acid, acetic acid and trifluoroacetic acid. Hydrazine compounds of formula (D), for example 2,2-dimethylpropyl 2-hydrazinoethanesulfonate, are either known in the literature or may be prepared by known literature procedures.

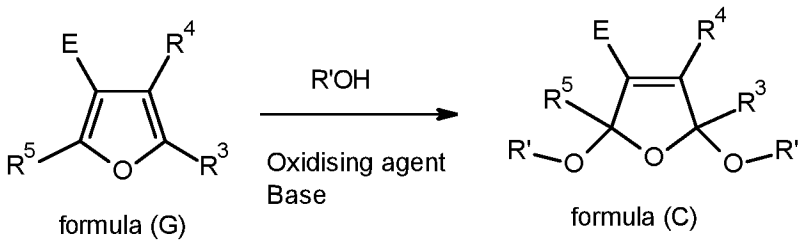
Reaction scheme 6



Compounds of formula (C) may be prepared by reacting compounds of formula (G), wherein R^3, R^4, R^5 and E are as defined for compounds of formula (I), with an oxidising agent in a suitable solvent at a suitable temperature, between -78ºC and 150ºC, optionally in the presence of a suitable base, as described in reaction scheme 7. Suitable oxidising agents include, but are not limited to, bromine and suitable solvents include, but are not limited to alcohols such as methanol, ethanol and isopropanol. Suitable bases include, but are not limited to, sodium bicarbonate, sodium carbonate, potassium bicarbonate, potassium carbonate and potassium acetate. Similar reactions are known in the literature

(for example Hufford, D. L.; Tarbell, D. S.; Koszalka, T. R. J. Amer. Chem. Soc., 1952, 3014). Furans of formula (G) are known in the literature or may be prepared using literature methods.

Reaction scheme 7



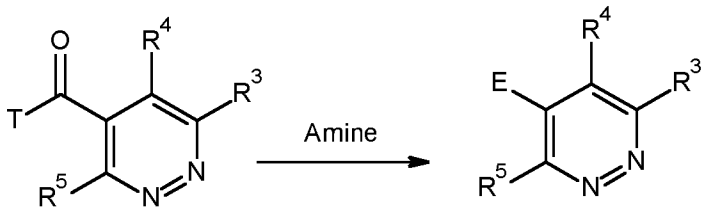
formula (G) formula (C)

R' = H, C_1-C_4alkyl, C_1-C_4alkyl carbonyl

Compounds of formula (X), wherein E is a carboxylic acid and R^3, R^4 and R^5 are as defined previously, are well known in the literature, or may be prepared by known methods. See, for example, Atkinson, C. M., Rodway, R. E., J. Chem. Soc., 1, 1959, Fischer et al, WO 2006000333, Guiles et al, WO 2009015208, O'Hara, F., Blackmond, D. G., Baran, P. S., J. Am. Chem. Soc., 135(32), 2013, 12122, Labelle et al, WO 2015153498, Johnston, A. J. S., Ling, K. B., Sale, D., Lebrasseur, N., Larrosa, I., Org. Lett., 18(23), 6094, 2016, Elbert, B. L., Farley, A. J. M., Gorman, T. W., Johnson, T. C., Genicot, C., Lallemand, B., Pasau, P., Flasz, J., Castro, J. L., MacCoss, M., Paton, R. S., Schofield, C. J., Smith, M. D., Willis, M. C., Dixon, D. J., Chem. Eur. J., 23(59), 14733, 2017, Beaumier et al, WO 2018096159 and Sparks et al, WO 2018125800.

Compounds of formula (X), wherein E is $-C(O)R^{24}$, $-C(O)NHOR^{11}$, -C(O)NHCN, $-C(O)NR^6(CR^6_2)_qZ$, $-C(O)NHS(O)_2R^{12}$, and R^3, R^4, R^5, R^6, R^{11}, R^{12}, R^{24}, q and Z are as defined previously, may be prepared from a compound of formula (J), wherein T is a halogen or T is an ester or activated ester, for example $-OC_1$-C_6alkyl, pentafluorophenol, *p*-nitrophenol, 2,4,6-trichlorophenol, $-OC(O)R'''$ or $-OS(O)_2R'''$, and R''' is, for example, C_1-C_6alkyl, C_1-C_6haloalkyl or optionally substituted phenyl and R^3, R^4 and R^5 are as defined previously, by reacting with an amine, for example but not limited to, of formula $-R^{24}$, NH_2OR^{11}, NH_2CN, $NHR^6(CR^6_2)_qZ$, $NH_2S(O)_2R^{12}$, in a suitable solvent or mixture of solvents, optionally in the presence of a suitable base at a suitable temperature between -78ºC and 200ºC, as described in reaction scheme 8. Suitable bases include, but are not limited to, triethylamine, pyridine, *N,N*-diisopropylethylamine, an alkali metal carbonate, such as sodium carbonate, potassium carbonate or cesium carbonate, or an alkali metal alkoxide, such as sodium methoxide. Suitable solvents include, but are not limited to, dichloromethane, *N,N*-dimethylformamide, THF or toluene. Compounds of formula (J) are either known in the literature or may be prepared by known literature methods or may be commercially available.

Reaction scheme 8

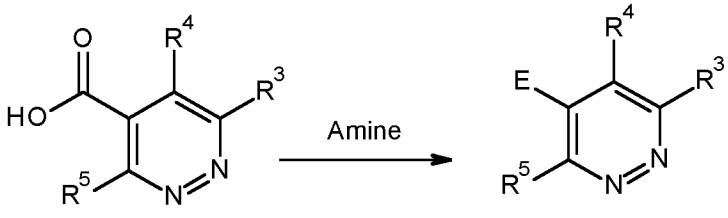


formula (J)

formula (X), wherein E is $-C(O)R^{24}$, $-C(O)NHOR^{11}$, $-C(O)NHCN$, $-C(O)NR^6(CR^6{}_2)_qZ$, $-C(O)NHS(O)_2R^{12}$

Compounds of formula (X), wherein E is $-C(O)R^{24}$, $-C(O)NHOR^{11}$, $-C(O)NHCN$, $-C(O)NR^6(CR^6{}_2)_qZ$, $-C(O)NHS(O)_2R^{12}$, and R^3, R^4, R^5, R^6, R^{11}, R^{12}, R^{24}, q and Z are as defined previously, may be prepared from a carboxylic acid of formula (L) by classical amide bond forming reactions which are very well known in the literature, as described in reaction scheme 9. Such reactions include, but are not limited to, reacting a carboxylic acid of formula (L) with an amine, for example, of formula $-R^{24}$, NH_2OR^{11}, NH_2CN, $NHR^6(CR^6{}_2)_qZ$ or $NH_2S(O)_2R^{12}$, wherein R^6, R^{11}, R^{12}, R^{24}, q and Z are as defined for compounds of formula (I), in the presence of a suitable coupling agent in a suitable solvent or mixture of solvents, at a suitable temperature between -78ºC and 200ºC, and optionally in the presence of a suitable base. Suitable coupling reagents include, but are not limited to, a carbodiimide, for example dicyclohexylcarbodiimide or 1-ethyl-3-[3-dimethylaminopropyl]carbodiimide hydrochloride, a phosphonic anhydride, for example 2,4,6-tripropyl-1,3,5,2,4,6-trioxatriphosphorinane-2,4,6-trioxide, or a phosphonium salt, for example benzotriazol-1-yloxy(tripyrrolidin-1-yl)phosphonium hexafluorophosphate. Suitable solvents include, but are not limited to, dichloromethane, *N,N*-dimethylformamide, THF or toluene, and suitable bases include, but are not limited to, triethylamine, pyridine and *N,N*-diisopropylethylamine. Compounds of formula (L) are either known in the literature or may be prepared by known literature methods or may be commercially available.

Reaction scheme 9

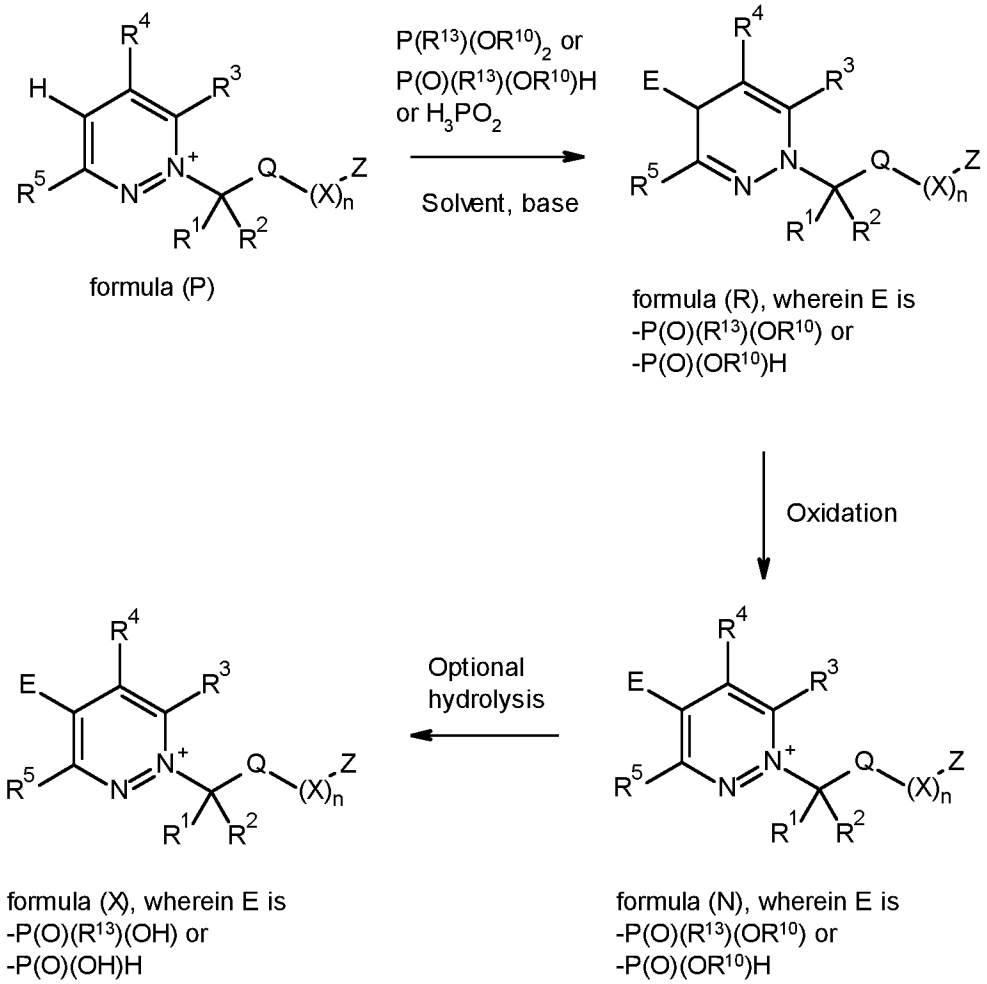


formula (L)

formula (X), wherein E is $-C(O)R^{24}$, $-C(O)NHOR^{11}$, $-C(O)NHCN$, $-C(O)NR^6(CR^6{}_2)_qZ$, $-C(O)NHS(O)_2R^{12}$

Compounds of formula (X), wherein E is -P(O)(R^{13})(OR^{10}) or -P(O)H(OR^{10}) and R^3, R^4 and R^5 are as defined previously, may be prepared by reacting a compound of formula (P) with a reagent of formula P(R^{13})(OR^{10})$_2$, P(O)(R^{13})(OR^{10})H and H_3PO_2 in an appropriate solvent, at an appropriate temperature, and optionally in the presence of an appropriate base and/or reagent such as tetrabutyl ammonium iodide, as described in reaction scheme 10. The direct product of this reaction may then be oxidised to a compound of formula (N) and, optionally, subsequently or partially hydrolysed to afford compounds of formula (X). Example oxidants include, but are not limited to, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, tetrachloro-p-benzoquinone, potassium permanganate, manganese dioxide, 2,2,6,6-tetramethyl-1-piperidinyloxy and bromine, and example hydrolysis conditions include treatment with aqueous hydrochloric acid or trimethylsilyl bromide, in a suitable solvent at a suitable temperature between 0ºC and 100ºC. Similar reactions are known in the literature, see for example Butkevicha, A. N., Sednevb, M. V., Shojaeia, H., Belova, V. N., Hella, S. W., Org. Lett., 20, 1261, 2018.

Reaction scheme 10



The compounds according to the invention can be used as herbicidal agents in unmodified form, but they are generally formulated into compositions in various ways using formulation adjuvants, such as carriers, solvents and surface-active substances. The formulations can be in various physical forms,

e.g. in the form of dusting powders, gels, wettable powders, water-dispersible granules, water-dispersible tablets, effervescent pellets, emulsifiable concentrates, microemulsifiable concentrates, oil-in-water emulsions, oil-flowables, aqueous dispersions, oily dispersions, suspo-emulsions, capsule suspensions, emulsifiable granules, soluble liquids, water-soluble concentrates (with water or a water-miscible organic solvent as carrier), impregnated polymer films or in other forms known e.g. from the Manual on Development and Use of FAO and WHO Specifications for Pesticides, United Nations, First Edition, Second Revision (2010). For water-soluble compounds, soluble liquids, water-soluble concentrates or water soluble granules are preferred. Such formulations can either be used directly or diluted prior to use. The dilutions can be made, for example, with water, liquid fertilisers, micronutrients, biological organisms, oil or solvents.

The formulations can be prepared e.g. by mixing the active ingredient with the formulation adjuvants in order to obtain compositions in the form of finely divided solids, granules, solutions, dispersions or emulsions. The active ingredients can also be formulated with other adjuvants, such as finely divided solids, mineral oils, oils of vegetable or animal origin, modified oils of vegetable or animal origin, organic solvents, water, surface-active substances or combinations thereof.

The active ingredients can also be contained in very fine microcapsules. Microcapsules contain the active ingredients in a porous carrier. This enables the active ingredients to be released into the environment in controlled amounts (e.g. slow-release). Microcapsules usually have a diameter of from 0.1 to 500 microns. They contain active ingredients in an amount of about from 25 to 95 % by weight of the capsule weight. The active ingredients can be in the form of a monolithic solid, in the form of fine particles in solid or liquid dispersion or in the form of a suitable solution. The encapsulating membranes can comprise, for example, natural or synthetic rubbers, cellulose, styrene/butadiene copolymers, polyacrylonitrile, polyacrylate, polyesters, polyamides, polyureas, polyurethane or chemically modified polymers and starch xanthates or other polymers that are known to the person skilled in the art. Alternatively, very fine microcapsules can be formed in which the active ingredient is contained in the form of finely divided particles in a solid matrix of base substance, but the microcapsules are not themselves encapsulated.

The formulation adjuvants that are suitable for the preparation of the compositions according to the invention are known *per se*. As liquid carriers there may be used: water, toluene, xylene, petroleum ether, vegetable oils, acetone, methyl ethyl ketone, cyclohexanone, acid anhydrides, acetonitrile, acetophenone, amyl acetate, 2-butanone, butylene carbonate, chlorobenzene, cyclohexane, cyclohexanol, alkyl esters of acetic acid, diacetone alcohol, 1,2-dichloropropane, diethanolamine, p-diethylbenzene, diethylene glycol, diethylene glycol abietate, diethylene glycol butyl ether, diethylene glycol ethyl ether, diethylene glycol methyl ether, *N,N*-dimethylformamide, dimethyl sulfoxide, 1,4-dioxane, dipropylene glycol, dipropylene glycol methyl ether, dipropylene glycol dibenzoate, diproxitol, alkylpyrrolidone, ethyl acetate, 2-ethylhexanol, ethylene carbonate, 1,1,1-trichloroethane, 2-heptanone, alpha-pinene, d-limonene, ethyl lactate, ethylene glycol, ethylene glycol butyl ether, ethylene glycol methyl ether, gamma-butyrolactone, glycerol, glycerol acetate, glycerol diacetate, glycerol triacetate, hexadecane, hexylene glycol, isoamyl acetate, isobornyl acetate, isooctane, isophorone, isopropylbenzene, isopropyl myristate, lactic acid, laurylamine, mesityl oxide, methoxypropanol, methyl

isoamyl ketone, methyl isobutyl ketone, methyl laurate, methyl octanoate, methyl oleate, methylene chloride, m-xylene, *n*-hexane, *n*-octylamine, octadecanoic acid, octylamine acetate, oleic acid, oleylamine, o-xylene, phenol, polyethylene glycol, propionic acid, propyl lactate, propylene carbonate, propylene glycol, propylene glycol methyl ether, p-xylene, toluene, triethyl phosphate, triethylene glycol, xylenesulfonic acid, paraffin, mineral oil, trichloroethylene, perchloroethylene, ethyl acetate, amyl acetate, butyl acetate, propylene glycol methyl ether, diethylene glycol methyl ether, methanol, ethanol, isopropanol, and alcohols of higher molecular weight, such as amyl alcohol, tetrahydrofurfuryl alcohol, hexanol, octanol, ethylene glycol, propylene glycol, glycerol, *N*-methyl-2-pyrrolidone and the like.

Suitable solid carriers are, for example, talc, titanium dioxide, pyrophyllite clay, silica, attapulgite clay, kieselguhr, limestone, calcium carbonate, bentonite, calcium montmorillonite, cottonseed husks, wheat flour, soybean flour, pumice, wood flour, ground walnut shells, lignin and similar substances.

A large number of surface-active substances can advantageously be used in both solid and liquid formulations, especially in those formulations which can be diluted with a carrier prior to use. Surface-active substances may be anionic, cationic, non-ionic or polymeric and they can be used as emulsifiers, wetting agents or suspending agents or for other purposes. Typical surface-active substances include, for example, salts of alkyl sulfates, such as diethanolammonium lauryl sulfate; salts of alkylarylsulfonates, such as calcium dodecylbenzenesulfonate; alkylphenol/alkylene oxide addition products, such as nonylphenol ethoxylate; alcohol/alkylene oxide addition products, such as tridecylalcohol ethoxylate; soaps, such as sodium stearate; salts of alkylnaphthalenesulfonates, such as sodium dibutylnaphthalenesulfonate; dialkyl esters of sulfosuccinate salts, such as sodium di(2-ethylhexyl)sulfosuccinate; sorbitol esters, such as sorbitol oleate; quaternary amines, such as lauryltrimethylammonium 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 di-alkylphosphate esters; and also further substances described e.g. in McCutcheon's Detergents and Emulsifiers Annual, MC Publishing Corp., Ridgewood New Jersey (1981).

Further adjuvants that can be used in pesticidal formulations include crystallisation inhibitors, viscosity modifiers, suspending agents, dyes, anti-oxidants, foaming agents, light absorbers, mixing auxiliaries, antifoams, complexing agents, neutralising or pH-modifying substances and buffers, corrosion inhibitors, fragrances, wetting agents, take-up enhancers, micronutrients, plasticisers, glidants, lubricants, dispersants, thickeners, antifreezes, microbicides, and liquid and solid fertilisers.

The compositions according to the invention can include an additive comprising an oil of vegetable or animal origin, a mineral oil, alkyl esters of such oils or mixtures of such oils and oil derivatives. The amount of oil additive in the composition according to the invention is generally from 0.01 to 10 %, based on the mixture to be applied. For example, the oil additive can be added to a spray tank in the desired concentration after a spray mixture has been prepared. Preferred oil additives comprise mineral oils or an oil of vegetable origin, for example rapeseed oil, olive oil or sunflower oil, emulsified vegetable oil, alkyl esters of oils of vegetable origin, for example the methyl derivatives, or an oil of animal origin, such as fish oil or beef tallow. Preferred oil additives comprise alkyl esters of C_8-C_{22} fatty acids, especially the methyl derivatives of C_{12}-C_{18} fatty acids, for example the methyl esters of lauric acid, palmitic acid and

oleic acid (methyl laurate, methyl palmitate and methyl oleate, respectively). Many oil derivatives are known from the Compendium of Herbicide Adjuvants, 10th Edition, Southern Illinois University, 2010.

The herbicidal compositions generally comprise from 0.1 to 99 % by weight, especially from 0.1 to 95 % by weight, compounds of formula (I) and from 1 to 99.9 % by weight of a formulation adjuvant which preferably includes from 0 to 25 % by weight of a surface-active substance. The inventive compositions generally comprise from 0.1 to 99 % by weight, especially from 0.1 to 95 % by weight, of compounds of the present invention and from 1 to 99.9 % by weight of a formulation adjuvant which preferably includes from 0 to 25 % by weight of a surface-active substance. Whereas commercial products may preferably be formulated as concentrates, the end user will normally employ dilute formulations.

The rates of application vary within wide limits and depend on the nature of the soil, the method of application, the crop plant, the pest to be controlled, the prevailing climatic conditions, and other factors governed by the method of application, the time of application and the target crop. As a general guideline compounds may be applied at a rate of from 1 to 2000 l/ha, especially from 10 to 1000 l/ha.

Preferred formulations can have the following compositions (weight %):

Emulsifiable concentrates:

active ingredient:	1 to 95 %, preferably 60 to 90 %
surface-active agent:	1 to 30 %, preferably 5 to 20 %
liquid carrier:	1 to 80 %, preferably 1 to 35 %

Dusts:

active ingredient:	0.1 to 10 %, preferably 0.1 to 5 %
solid carrier:	99.9 to 90 %, preferably 99.9 to 99 %

Suspension concentrates:

active ingredient:	5 to 75 %, preferably 10 to 50 %
water:	94 to 24 %, preferably 88 to 30 %
surface-active agent:	1 to 40 %, preferably 2 to 30 %

Wettable powders:

active ingredient:	0.5 to 90 %, preferably 1 to 80 %
surface-active agent:	0.5 to 20 %, preferably 1 to 15 %
solid carrier:	5 to 95 %, preferably 15 to 90 %

Granules:

active ingredient:	0.1 to 30 %, preferably 0.1 to 15 %
solid carrier:	99.5 to 70 %, preferably 97 to 85 %

The composition of the present may further comprise at least one additional pesticide. For example, the compounds according to the invention can also be used in combination with other herbicides or plant

growth regulators. In a preferred embodiment the additional pesticide is a herbicide and/or herbicide safener.

Thus, compounds of formula (I) can be used in combination with one or more other herbicides to provide various herbicidal mixtures. Specific examples of such mixtures include (wherein "I" represents a compound of formula (I)):- I + acetochlor; I + acifluorfen (including acifluorfen-sodium); I + aclonifen; I + alachlor; I + alloxydim; I + ametryn; I + amicarbazone; I + amidosulfuron; I + aminocyclopyrachlor ; I + aminopyralid; I + amitrole; I + asulam; I + atrazine; I + bensulfuron (including bensulfuron-methyl); I + bentazone; I + bicyclopyrone; I + bilanafos; I + bifenox; I + bispyribac-sodium; I + bixlozone; I + bromacil; I + bromoxynil; I + butachlor; I + butafenacil; I + cafenstrole; I + carfentrazone (including carfentrazone-ethyl); cloransulam (including cloransulam-methyl); I + chlorimuron (including chlorimuron-ethyl); I + chlorotoluron; I + cinosulfuron; I + chlorsulfuron; I + cinmethylin; I + clacyfos; I + clethodim; I + clodinafop (including clodinafop-propargyl); I + clomazone; I + clopyralid; I + cyclopyranil; I + cyclopyrimorate; I + cyclosulfamuron; I + cyhalofop (including cyhalofop-butyl); I + 2,4-D (including the choline salt and 2-ethylhexyl ester thereof); I + 2,4-DB; I + daimuron; I + desmedipham; I + dicamba (including the aluminum, aminopropyl, bis-aminopropylmethyl, choline, dichloroprop, diglycolamine, dimethylamine, dimethylammonium, potassium and sodium salts thereof); I + diclofop-methyl; I + diclosulam; I + diflufenican; I + difenzoquat; I + diflufenican; I + diflufenzopyr; I + dimethachlor; I + dimethenamid-P; I + diquat dibromide; I + diuron; I + esprocarb; I + ethalfluralin; I + ethofumesate; I + fenoxaprop (including fenoxaprop-P-ethyl); I + fenoxasulfone; I + fenquinotrione; I + fentrazamide; I + flazasulfuron; I + florasulam; I + florpyrauxifen; I + fluazifop (including fluazifop-P-butyl); I + flucarbazone (including flucarbazone-sodium);; I + flufenacet; I + flumetralin; I + flumetsulam; I + flumioxazin; I + flupyrsulfuron (including flupyrsulfuron-methyl-sodium);; I + fluroxypyr (including fluroxypyr-meptyl);; I + fluthiacet-methyl; I + fomesafen; I + foramsulfuron; I + glufosinate (including the ammonium salt thereof); I + glyphosate (including the diammonium, isopropylammonium and potassium salts thereof); I + halauxifen (including halauxifen-methyl); I + halosulfuron-methyl; I + haloxyfop (including haloxyfop-methyl); I + hexazinone; I + hydantocidin; I + imazamox; I + imazapic; I + imazapyr; I + imazaquin; I + imazethapyr; I + indaziflam; I + iodosulfuron (including iodosulfuron-methyl-sodium); I + iofensulfuron; I + iofensulfuron-sodium; I + ioxynil; I + ipfencarbazone; I + isoproturon; I + isoxaben; I + isoxaflutole; I + lactofen; I + lancotrione; I + linuron; I + MCPA; I + MCPB; I + mecoprop-P; I + mefenacet; I + mesosulfuron; I + mesosulfuron-methyl; I + mesotrione; I + metamitron; I + metazachlor; I + methiozolin; I + metobromuron; I + metolachlor; I + metosulam; I + metoxuron; I + metribuzin; I + metsulfuron; I + molinate; I + napropamide; I + nicosulfuron; I + norflurazon; I + orthosulfamuron; I + oxadiargyl; I + oxadiazon; I + oxasulfuron; I + oxyfluorfen; I + paraquat dichloride; I + pendimethalin; I + penoxsulam; I + phenmedipham; I + picloram; I + picolinafen; I + pinoxaden; I + pretilachlor; I + primisulfuron-methyl; I + prodiamine; I + prometryn; I + propachlor; I + propanil; I + propaquizafop; I + propham; I + propyrisulfuron, I + propyzamide; I + prosulfocarb; I + prosulfuron; I + pyraclonil; I + pyraflufen (including pyraflufen-ethyl): I + pyrasulfotole; I + pyrazolynate, I + pyrazosulfuron-ethyl; I + pyribenzoxim; I + pyridate; I + pyriftalid; I + pyrimisulfan, I + pyrithiobac-sodium; I + pyroxasulfone; I + pyroxsulam ; I + quinclorac; I + quinmerac; I + quizalofop (including quizalofop-P-ethyl and quizalofop-P-tefuryl),; I + rimsulfuron; I + saflufenacil; I + sethoxydim; I + simazine; I + *S*-metolachlor; I + sulcotrione; I + sulfentrazone; I + sulfosulfuron; I + tebuthiuron; I + tefuryltrione; I + tembotrione; I + terbuthylazine; I +

terbutryn; I + thiencarbazone; I + thifensulfuron; I + tiafenacil; I + tolpyralate; I + topramezone; I + tralkoxydim; I + triafamone; I + triallate; I + triasulfuron; I + tribenuron (including tribenuron-methyl); I + triclopyr; I + trifloxysulfuron (including trifloxysulfuron-sodium); I + trifludimoxazin; I + trifluralin; I + triflusulfuron; I + tritosulfuron; I + 4-hydroxy-1-methoxy-5-methyl-3-[4-(trifluoromethyl)-2-pyridyl]imidazolidin-2-one; I + 4-hydroxy-1,5-dimethyl-3-[4-(trifluoromethyl)-2-pyridyl]imidazolidin-2-one; I + 5-ethoxy-4-hydroxy-1-methyl-3-[4-(trifluoromethyl)-2-pyridyl]imidazolidin-2-one; I + 4-hydroxy-1-methyl-3-[4-(trifluoromethyl)-2-pyridyl]imidazolidin-2-one; I + 4-hydroxy-1,5-dimethyl-3-[1-methyl-5-(trifluoromethyl)pyrazol-3-yl]imidazolidin-2-one; I + (4R)1-(5-tert-butylisoxazol-3-yl)-4-ethoxy-5-hydroxy-3-methyl-imidazolidin-2-one; I + 3-[2-(3,4-dimethoxyphenyl)-6-methyl-3-oxo-pyridazine-4-carbonyl]bicyclo[3.2.1]octane-2,4-dione; I + 2-[2-(3,4-dimethoxyphenyl)-6-methyl-3-oxo-pyridazine-4-carbonyl]-5-methyl-cyclohexane-1,3-dione; I + 2-[2-(3,4-dimethoxyphenyl)-6-methyl-3-oxo-pyridazine-4-carbonyl]cyclohexane-1,3-dione; I + 2-[2-(3,4-dimethoxyphenyl)-6-methyl-3-oxo-pyridazine-4-carbonyl]-5,5-dimethyl-cyclohexane-1,3-dione; I + 6-[2-(3,4-dimethoxyphenyl)-6-methyl-3-oxo-pyridazine-4-carbonyl]-2,2,4,4-tetramethyl-cyclohexane-1,3,5-trione; I + 2-[2-(3,4-dimethoxyphenyl)-6-methyl-3-oxo-pyridazine-4-carbonyl]-5-ethyl-cyclohexane-1,3-dione; I + 2-[2-(3,4-dimethoxyphenyl)-6-methyl-3-oxo-pyridazine-4-carbonyl]-4,4,6,6-tetramethyl-cyclohexane-1,3-dione; I + 2-[6-cyclopropyl-2-(3,4-dimethoxyphenyl)-3-oxo-pyridazine-4-carbonyl]-5-methyl-cyclohexane-1,3-dione; I + 3-[6-cyclopropyl-2-(3,4-dimethoxyphenyl)-3-oxo-pyridazine-4-carbonyl]bicyclo[3.2.1]octane-2,4-dione; I + 2-[6-cyclopropyl-2-(3,4-dimethoxyphenyl)-3-oxo-pyridazine-4-carbonyl]-5,5-dimethyl-cyclohexane-1,3-dione; I + 6-[6-cyclopropyl-2-(3,4-dimethoxyphenyl)-3-oxo-pyridazine-4-carbonyl]-2,2,4,4-tetramethyl-cyclohexane-1,3,5-trione; I + 2-[6-cyclopropyl-2-(3,4-dimethoxyphenyl)-3-oxo-pyridazine-4-carbonyl]cyclohexane-1,3-dione; I + 4-[2-(3,4-dimethoxyphenyl)-6-methyl-3-oxo-pyridazine-4-carbonyl]-2,2,6,6-tetramethyl-tetrahydropyran-3,5-dione and I + 4-[6-cyclopropyl-2-(3,4-dimethoxyphenyl)-3-oxo-pyridazine-4-carbonyl]-2,2,6,6-tetramethyl-tetrahydropyran-3,5-dione.

The mixing partners of the compound of formula (I) may also be in the form of esters or salts, as mentioned e.g. in The Pesticide Manual, Fourteenth Edition, British Crop Protection Council, 2006.

The compound of formula (I) can also be used in mixtures with other agrochemicals such as fungicides, nematicides or insecticides, examples of which are given in The Pesticide Manual.

The mixing ratio of the compound of formula (I) to the mixing partner is preferably from 1: 100 to 1000:1.

The mixtures can advantageously be used in the above-mentioned formulations (in which case "active ingredient" relates to the respective mixture of compound of formula (I) with the mixing partner).

Compounds of formula (I) of the present invention may also be combined with herbicide safeners. Preferred combinations (wherein “I” represents a compound of formula (I)) include:- I + benoxacor, I + cloquintocet (including cloquintocet-mexyl); I + cyprosulfamide; I + dichlormid; I + fenchlorazole (including fenchlorazole-ethyl); I + fenclorim; I + fluxofenim; I+ furilazole I + isoxadifen (including isoxadifen-ethyl); I + mefenpyr (including mefenpyr-diethyl); I + metcamifen; I + N-(2-methoxybenzoyl)-4-[(methylaminocarbonyl)amino] benzenesulfonamide and I + oxabetrinil.

Particularly preferred are mixtures of a compound of formula (I) with cyprosulfamide, isoxadifen (including isoxadifen-ethyl), cloquintocet (including cloquintocet-mexyl) and/or N-(2-methoxybenzoyl)-4-[(methyl-aminocarbonyl)amino]benzenesulfonamide.

The safeners of the compound of formula (I) may also be in the form of esters or salts, as mentioned e.g. in The Pesticide Manual, 14th Edition (BCPC), 2006. The reference to cloquintocet-mexyl also applies to a lithium, sodium, potassium, calcium, magnesium, aluminium, iron, ammonium, quaternary ammonium, sulfonium or phosphonium salt thereof as disclosed in WO 02/34048, and the reference to fenchlorazole-ethyl also applies to fenchlorazole, etc.

Preferably the mixing ratio of compound of formula (I) to safener is from 100:1 to 1:10, especially from 20:1 to 1:1.

The mixtures can advantageously be used in the above-mentioned formulations (in which case "active ingredient" relates to the respective mixture of compound of formula (I) with the safener).

The compounds of formula (I) of this invention are useful as herbicides. The present invention therefore further comprises a method for controlling unwanted plants comprising applying to the said plants or a locus comprising them, an effective amount of a compound of the invention or a herbicidal composition containing said compound. 'Controlling' means killing, reducing or retarding growth or preventing or reducing germination. Generally the plants to be controlled are unwanted plants (weeds). 'Locus' means the area in which the plants are growing or will grow.

The rates of application of compounds of formula (I) may vary within wide limits and depend on the nature of the soil, the method of application (pre-emergence; post-emergence; application to the seed furrow; no tillage application etc.), the crop plant, the weed(s) to be controlled, the prevailing climatic conditions, and other factors governed by the method of application, the time of application and the target crop. The compounds of formula (I) according to the invention are generally applied at a rate of from 10 to 2000 g/ha, especially from 50 to 1000 g/ha.

The application is generally made by spraying the composition, typically by tractor mounted sprayer for large areas, but other methods such as dusting (for powders), drip or drench can also be used.

Useful plants in which the composition according to the invention can be used include crops such as cereals, for example barley and wheat, cotton, oilseed rape, sunflower, maize, rice, soybeans, sugar beet, sugar cane and turf.

Crop plants can also include trees, such as fruit trees, palm trees, coconut trees or other nuts. Also included are vines such as grapes, fruit bushes, fruit plants and vegetables.

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

Crops are also to be understood as being those which have been rendered resistant to harmful insects by genetic engineering methods, for example Bt maize (resistant to European corn borer), Bt cotton (resistant to cotton boll weevil) and also Bt potatoes (resistant to Colorado beetle). Examples of Bt maize are the Bt 176 maize hybrids of NK® (Syngenta Seeds). The Bt toxin is a protein that is formed naturally by *Bacillus thuringiensis* soil bacteria. Examples of toxins, or transgenic plants able to synthesise such toxins, are described in EP-A-451 878, EP-A-374 753, WO 93/07278, WO 95/34656, WO 03/052073 and EP-A-427 529. Examples of transgenic plants comprising one or more genes that code for an insecticidal resistance and express one or more toxins are KnockOut® (maize), Yield Gard® (maize), NuCOTIN33B® (cotton), Bollgard® (cotton), NewLeaf® (potatoes), NatureGard® and Protexcta®. Plant crops or seed material thereof can be both resistant to herbicides and, at the same time, resistant to insect feeding ("stacked" transgenic events). For example, seed can have the ability to express an insecticidal Cry3 protein while at the same time being tolerant to glyphosate.

Crops are also to be understood to include those which are obtained by conventional methods of breeding or genetic engineering and contain so-called output traits (e.g. improved storage stability, higher nutritional value and improved flavour).

Other useful plants include turf grass for example in golf-courses, lawns, parks and roadsides, or grown commercially for sod, and ornamental plants such as flowers or bushes.

Compounds of formula (I) and compositions of the invention can typically be used to control a wide variety of monocotyledonous and dicotyledonous weed species. Examples of monocotyledonous species that can typically be controlled include *Alopecurus myosuroides, Avena fatua, Brachiaria plantaginea, Bromus tectorum, Cyperus esculentus, Digitaria sanguinalis, Echinochloa crus-galli, Lolium perenne, Lolium multiflorum, Panicum miliaceum, Poa annua, Setaria viridis, Setaria faberi and Sorghum bicolor.* Examples of dicotyledonous species that can be controlled include *Abutilon theophrasti, Amaranthus retroflexus, Bidens pilosa, Chenopodium album, Euphorbia heterophylla, Galium aparine, Ipomoea hederacea, Kochia scoparia, Polygonum convolvulus, Sida spinosa, Sinapis arvensis, Solanum nigrum, Stellaria media, Veronica persica and Xanthium strumarium.*

The compounds of formula (I) are also useful for pre-harvest desiccation in crops, for example, but not limited to, potatoes, soybean, sunflowers and cotton. Pre-harvest desiccation is used to desiccate crop foliage without significant damage to the crop itself to aid harvesting.

Compounds/compositions of the invention are particularly useful in non-selective burn-down applications, and as such may also be used to control volunteer or escape crop plants.

Various aspects and embodiments of the present invention will now be illustrated in more detail by way of example. It will be appreciated that modification of detail may be made without departing from the scope of the invention.

EXAMPLES

The Examples which follow serve to illustrate, but do not limit, the invention.

Formulation Examples

Wettable powders	**a)**	**b)**	**c)**
active ingredients	25 %	50 %	75 %
sodium lignosulfonate	5 %	5 %	-
sodium lauryl sulfate	3 %	-	5 %
sodium diisobutylnaphthalenesulfonate	-	6 %	10 %
phenol polyethylene glycol ether (7-8 mol of ethylene oxide)	-	2 %	-
highly dispersed silicic acid	5 %	10 %	10 %
Kaolin	62 %	27 %	-

The combination is thoroughly mixed with the adjuvants and the mixture is thoroughly ground in a suitable mill, affording wettable powders that can be diluted with water to give suspensions of the desired concentration.

Emulsifiable concentrate	
active ingredients	10 %
octylphenol polyethylene glycol ether (4-5 mol of ethylene oxide)	3 %
calcium dodecylbenzenesulfonate	3 %
castor oil polyglycol ether (35 mol of ethylene oxide)	4 %
Cyclohexanone	30 %
xylene mixture	50 %

Emulsions of any required dilution, which can be used in plant protection, can be obtained from this concentrate by dilution with water.

Dusts	**a)**	**b)**	**c)**
Active ingredients	5 %	6 %	4 %
Talcum	95 %	-	-
Kaolin	-	94 %	-
mineral filler	-	-	96 %

Ready-for-use dusts are obtained by mixing the combination with the carrier and grinding the mixture in a suitable mill.

Extruded granules	
Active ingredients	15 %

sodium lignosulfonate	2 %
carboxymethylcellulose	1 %
Kaolin	82 %

The combination is mixed and ground with the adjuvants, and the mixture is moistened with water. The mixture is extruded and then dried in a stream of air.

Coated granules

Active ingredients	8 %
polyethylene glycol (mol. wt. 200)	3 %
Kaolin	89 %

The finely ground combination is uniformly applied, in a mixer, to the kaolin moistened with polyethylene glycol. Non-dusty coated granules are obtained in this manner.

Suspension concentrate

active ingredients	40 %
propylene glycol	10 %
nonylphenol polyethylene glycol ether (15 mol of ethylene oxide)	6 %
Sodium lignosulfonate	10 %
carboxymethylcellulose	1 %
silicone oil (in the form of a 75 % emulsion in water)	1 %
Water	32 %

The finely ground combination is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired dilution can be obtained by dilution with water.

Slow Release Capsule Suspension

28 parts of the combination are mixed with 2 parts of an aromatic solvent and 7 parts of toluene diisocyanate/polymethylene-polyphenylisocyanate-mixture (8:1). This mixture is emulsified in a mixture of 1.2 parts of polyvinylalcohol, 0.05 parts of a defoamer and 51.6 parts of water until the desired particle size is achieved. To this emulsion a mixture of 2.8 parts 1,6-diaminohexane in 5.3 parts of water is added. The mixture is agitated until the polymerization reaction is completed.

The obtained capsule suspension is stabilized by adding 0.25 parts of a thickener and 3 parts of a dispersing agent. The capsule suspension formulation contains 28% of the active ingredients. The medium capsule diameter is 8-15 microns.

The resulting formulation is applied to seeds as an aqueous suspension in an apparatus suitable for that purpose.

List of Abbreviations:

Boc = *tert*-butyloxycarbonyl

br = broad

$CDCl_3$ = chloroform-d

CD_3OD = methanol-d

°C = degrees Celsius

D_2O = water-d

DCM = dichloromethane

d = doublet

dd = double doublet

dt = double triplet

DMSO = dimethylsulfoxide

EtOAc = ethyl acetate

h = hour(s)

HCl = hydrochloric acid

HPLC = high-performance liquid chromatography (description of the apparatus and the methods used for HPLC are given below)

m = multiplet

M = molar

min = minutes

MHz = mega hertz

mL = millilitre

mp = melting point

ppm = parts per million

q = quartet

quin = quintet

rt = room temperature

s = singlet

t = triplet

THF = tetrahydrofuran

LC/MS = Liquid Chromatography Mass Spectrometry

Preparative Reverse Phase HPLC Method:

Compounds purified by mass directed preparative HPLC using ES+/ES- on a Waters FractionLynx Autopurification system comprising a 2767 injector/collector with a 2545 gradient pump, two 515 isocratic pumps, SFO, 2998 photodiode array (Wavelength range (nm): 210 to 400), 2424 ELSD and QDa mass spectrometer. A Waters Atlantis T3 5micron 19x10mm guard column was used with a Waters Atlantis T3 OBD, 5micron 30x100mm prep column.

Ionisation method: Electrospray positive and negative: Cone (V) 20.00, Source Temperature (°C) 120, Cone Gas Flow (L/Hr.) 50

Mass range (Da): positive 100 to 800, negative 115 to 800.

The preparative HPLC was conducted using an 11.4 minute run time (not using at column dilution, bypassed with the column selector), according to the following gradient table:

Time (mins)	Solvent A (%)	Solvent B (%)	Flow (ml / min)
0.00	100	0	35
2.00	100	0	35
2.01	100	0	35
7.0	90	10	35
7.3	0	100	35
9.2	0	100	35
9.8	99	1	35
11.35	99	1	35
11.40	99	1	35

515 pump 0ml/min Acetonitrile (ACD)

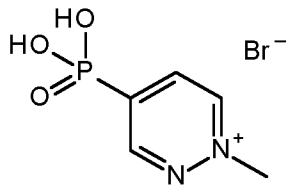
515 pump 1ml/min 90% Methanol/10% Water (make up pump)

Solvent A: Water with 0.05% Trifluoroacetic Acid

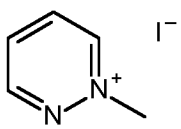
Solvent B: Acetonitrile with 0.05% Trifluoroacetic Acid

PREPARATION EXAMPLES

Example 1: Preparation of (1-methylpyridazin-1-ium-4-yl)phosphonic acid bromide A2



Step 1: Preparation of 1-methylpyridazin-1-ium iodide



Methyl iodide (2.33 mL) was added drop wise over 30 minutes to pyridazine (2 g) and stirred at room temperature for 1 hour. The resulting solid was filtered off and washed with iso-hexane to give 1-methylpyridazin-1-ium iodide as a hygroscopic orange solid.

^{1}H NMR (400MHz, CD_3OD) 9.87 (d, 1H), 9.54 (d, 1H), 8.72-8.64 (m, 1H), 8.61-8.53 (m, 1H), 4.70 (s,

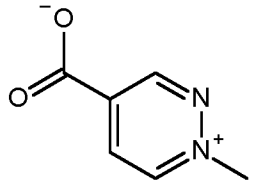
3H)

Step 2: Preparation of (1-methylpyridazin-1-ium-4-yl)phosphonic acid bromide A2

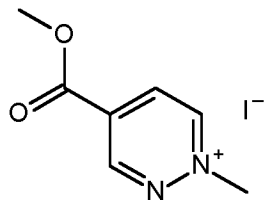
To a solution of 1-methylpyridazin-1-ium iodide (0.5 g) in acetonitrile (11 mL) at 0°C was added trimethyl phosphite (0.29 mL) followed by sodium iodide (0.37 g). This mixture was heated at 40°C for 1 hour. After cooling to room temperature the reaction mixture was quenched with water and extracted twice with dichloromethane. The combined organic extracts were dried over magnesium sulfate and concentrated. The residue was dissolved in chloroform (4.5 mL), cooled to 0°C and bromine (0.128 mL) was added drop wise. The reaction mixture was slowly warmed to room temperature, concentrated and purified by preparative reverse phase HPLC to afford a 5:1 mixture of (1-methylpyridazin-1-ium-4-yl)phosphonic acid and methoxy-(1-methylpyridazin-1-ium-4-yl)phosphinate which was used directly in the next step. The 5:1 mixture of (1-methylpyridazin-1-ium-4-yl)phosphonic acid and methoxy-(1-methylpyridazin-1-ium-4-yl)phosphinate (0.2 g) was dissolved in dichloromethane (2 mL) and bromotrimethylsilane (0.43 mL) was added drop wise at room temperature. The reaction mixture was stirred for a further 3 hours at this temperature then concentrated to afford (1-methylpyridazin-1-ium-4-yl)phosphonic acid bromide as an orange gum.

^{1}H NMR (400MHz, CD_3OD) 9.90 (d, 1H), 9.64 (d, 1H), 8.81 (dd, 1H), 4.71 (s, 3H) (2 x P(OH) protons missing)

Example 2: Preparation of 1-methylpyridazin-1-ium-4-carboxylate A3



Step 1: Preparation of methyl 1-methylpyridazin-1-ium-4-carboxylate iodide A1



To a solution of methyl pyridazine-4-carboxylate (1 g) in dichloromethane (10 mL) was added iodomethane (2.26 mL) and the reaction mixture was stirred at room temperature for 2 days. The resulting solid was filtered off and recrystallised from dichloromethane and acetone (2:1 ratio) to afford methyl 1-methylpyridazin-1-ium-4-carboxylate iodide which was used directly in the next step.

^{1}H NMR (400 MHz, D_2O) 9.82 (d, 1H), 9.75 (d, 1H), 8.90 (dd, 1H), 4.63 (s, 3H), 3.99 (s, 3H)

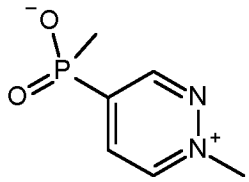
Step 2: Preparation of 1-methylpyridazin-1-ium-4-carboxylate A3

A solution of methyl 1-methylpyridazin-1-ium-4-carboxylate iodide (0.2 g) in concentrated hydrochloric acid (4 mL) was heated at 80°C for 3 hours. After cooling to room temperature the reaction mixture

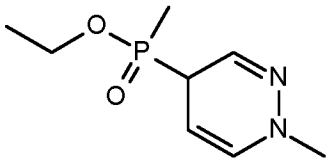
was concentrated and the crude product was triturated with acetone to afford 1-methylpyridazin-1-ium-4-carboxylate as a tan solid.

^{1}H NMR (400MHz, CD_3OD) 9.98 (d, 1H), 9.85 (d, 1H), 8.99 (dd, 1H), 4.74 (s, 3H)

Example 3: Preparation of methyl-(1-methylpyridazin-1-ium-4-yl)phosphinate A10

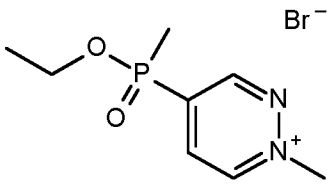


Step 1: Preparation of 4-[ethoxy(methyl)phosphoryl]-1-methyl-4H-pyridazine



To a solution of 1-methylpyridazin-1-ium iodide (0.5 g) in acetonitrile (11 mL) was added diethoxy(methyl)phosphane (0.304 mL) followed by sodium iodide (0.371 g). The reaction mixture was heated at 40°C for 60 minutes. After cooling to room temperature the reaction mixture was quenched with water and extracted twice with dichloromethane. The combined organic extracts were dried over sodium sulfate, filtered and the filtrate concentrated to afford crude 4-[ethoxy(methyl)phosphoryl]-1-methyl-4H-pyridazine which was used in the next step without further purification.

Step 2: Preparation of 4-[ethoxy(methyl)phosphoryl]-1-methyl-pyridazin-1-ium bromide A63



To a solution of 4-[ethoxy(methyl)phosphoryl]-1-methyl-4H-pyridazine (0.2 g) in chloroform (5 mL) was added bromine (0.133 mL) drop wise at 0°C. The reaction mixture was warmed to room temperature, stirred for a further hour, then concentrated to afford crude 4-[ethoxy(methyl)phosphoryl]-1-methyl-pyridazin-1-ium bromide which was used in the next step without further purification.

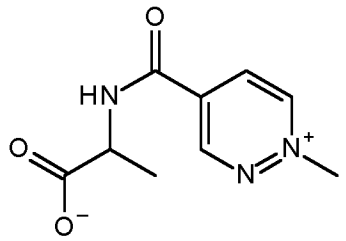
^{1}H NMR (400 MHz, CD_3OD) 10.03 (d, 1H), 9.83-9.78 (m, 1H), 9.04-8.97 (m, 1H), 4.79-4.77 (m, 3H), 4.17-4.01 (m, 2H), 2.05-1.98 (m, 3H), 1.41-1.36 (m, 3H)

Step 3: Preparation of methyl-(1-methylpyridazin-1-ium-4-yl)phosphinate A10

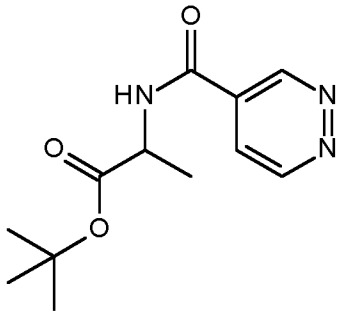
A solution of 4-[ethoxy(methyl)phosphoryl]-1-methyl-pyridazin-1-ium bromide (0.1 g) in concentrated aqueous hydrochloric acid (2 mL) was heated at reflux for 5 hours. After cooling to room temperature the rection mixture was concentrated to afford methyl-(1-methylpyridazin-1-ium-4-yl)phosphinate as a brown gum.

^{1}H NMR (400 MHz, D_2O) 9.61 (d, 1H), 9.47 (d, 1H), 8.52 - 8.64 (m, 1H), 4.57 (s, 3H), 1.53 (d, 3H)

Example 4: Preparation of 2-[(1-methylpyridazin-1-ium-4-carbonyl)amino]propanoate A19

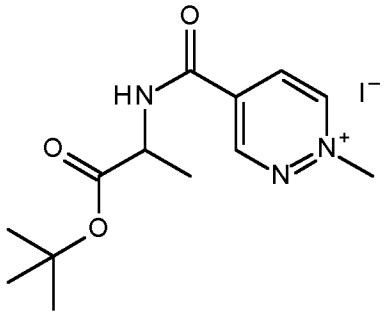


Step 1: Preparation of *tert*-butyl 2-(pyridazine-4-carbonylamino)propanoate



To a mixture of pyridazine-4-carboxylic acid (0.25 g), O-(Benzotriazol-1-yl)-*N,N,N',N'*-tetramethyluronium tetrafluoroborate (0.726 g) and *tert*-butyl 2-aminopropanoate hydrochloride (0.403 g) in acetonitrile (10 mL) was added trimethylamine (0.709 mL). After stirring at room temperature for 2 hours the reaction mixture was concentrated, dilluted with 2M aqueous hydrochloric acid and extracted twice with dichloromethane. The combined organic phases were dried over sodium sulfate and concentrated. The crude product was purified by silica gel chromatography eluting with 0-100% ethyl acetate in hexanes to afford crude *tert*-butyl 2-(pyridazine-4-carbonylamino)propanoate which was used directly in the next step.

Step 2: Preparation of *tert*-butyl 2-[(1-methylpyridazin-1-ium-4-carbonyl)amino]propanoate A65



To a solution of *tert*-butyl 2-(pyridazine-4-carbonylamino)propanoate (0.37 g) in dichloromethane (0.5 mL) was added iodomethane (0.302 mL) drop wise. The reaction mixture was stirred at room temperature for 5 days. The crude product was purified by preparative reverse phase HPLC to afford *tert*-butyl 2-[(1-methylpyridazin-1-ium-4-carbonyl)amino]propanoate iodide which was used directly in the next step.

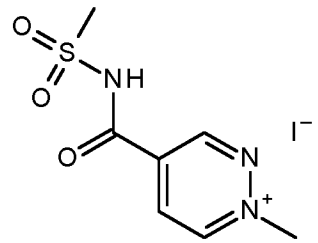
^{1}H NMR (400 MHz, CD_3OD) 9.97 (d, 1H), 9.82 - 9.77 (m, 1H), 8.96 - 8.90 (m, 1H), 4.73 (s, 3H), 4.53 (d, 1H), 1.59 - 1.50 (m, 3H), 1.49 (s, 9H) (NH proton missing)

Step 3: Preparation of 2-[(1-methylpyridazin-1-ium-4-carbonyl)amino]propanoate A19

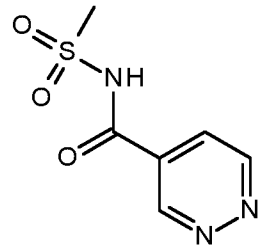
A solution of *tert*-butyl 2-[(1-methylpyridazin-1-ium-4-carbonyl)amino]propanoate (0.104 g) in formic acid (5 mL) was stirred at room temperature for 48 hours. The reaction mixture was concentrated to afford 2-[(1-methylpyridazin-1-ium-4-carbonyl)amino]propanoate.

^{1}H NMR (400 MHz, CD_3OD) 9.96 (d, 1H), 9.80 (d, 1H), 8.94 (dd, 1H), 4.73 (s, 3H), 4.57 (q, 1H), 1.54 (d, 3H) (NH proton missing)

Example 5: Preparation of 1-methyl-*N*-methylsulfonyl-pyridazin-1-ium-4-carboxamide iodide A28



Step 1: Preparation of *N*-methylsulfonylpyridazine-4-carboxamide



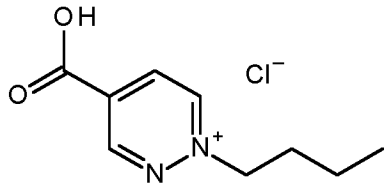
A mixture of pyridazine-4-carboxylic acid (0.5 g), 4-dimethylaminopyridine (0.646 g), methanesulfonamide (0.508 g) and *N,N'*-dicyclohexylmethanediimine (1.025 g) in dichloromethane (28 mL) was stirred at room temperature for 6 days. The reaction mixture was filtered, concentrated and purified by silica gel chromatography eluting with 0-10% methanol in dichloromethane to afford crude *N*-methylsulfonylpyridazine-4-carboxamide which was used without further purification in the next step.

Step 2: Preparation of 1-methyl-*N*-methylsulfonyl-pyridazin-1-ium-4-carboxamide iodide A28

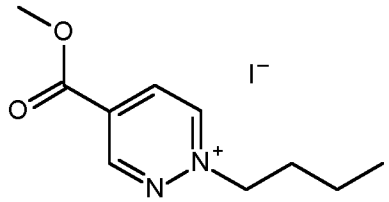
To a solution of *N*-methylsulfonylpyridazine-4-carboxamide (0.3 g) in acetone (2 mL) was added iodomethane (0.26 mL). After stirring at 40°C for 6 hours the reaction mixture was cooled to room temperature and concentrated. The crude product was triturated with methanol to afford 1-methyl-*N*-methylsulfonyl-pyridazin-1-ium-4-carboxamide iodide as an off white solid.

^{1}H NMR (400 MHz, CD_3OD) 8.27 (s, 1H), 8.26 (d, 1H), 7.35 (dd, 1H), 3.20 (s, 3H), 1.71 (s, 3H) (NH proton missing)

Example 6: Preparation of 1-butylpyridazin-1-ium-4-carboxylic acid chloride A33



Step 1: Preparation of methyl 1-butylpyridazin-1-ium-4-carboxylate iodide A64



To a solution of methyl pyridazine-4-carboxylate (0.7 g) in acetone (20 mL) was added 1-iodobutane (1.86 g) at room temperature. The mixture was stirred for 72 hours then concentrated and partititoned between dichloromethane (20 mL) and water (20 mL). The aqueous phase was concentrated and purified by preparative reverse phase HPLC to afford methyl 1-butylpyridazin-1-ium-4-carboxylate iodide.

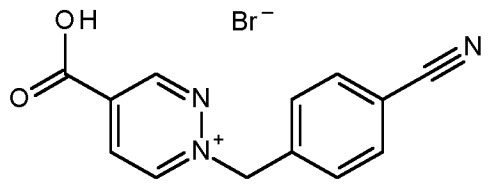
^{1}H NMR (400 MHz, D_2O) 9.89 (d, 1H), 9.82 (s, 1H), 8.95 (m, 1H), 4.89 (t, 2H), 4.04 (s, 3H), 2.09-2.00 (m, 2H), 1.37-1.32 (m, 2H), 0.90 (t, 3H)

Step 2: Preparation of 1-butylpyridazin-1-ium-4-carboxylic acid chloride A33

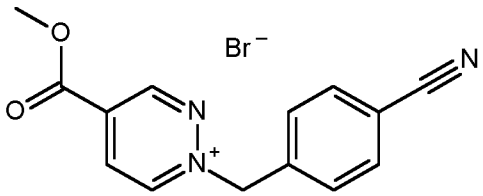
A suspension of methyl 1-butylpyridazin-1-ium-4-carboxylate iodide (0.4 g) in concentrated aqueous hydrochloric acid (60 mL) was heated at 60°C for 24 hours. After cooling to room temperature the reaction mixture was concentrated and purified by preparative reverse phase HPLC to afford 1-butylpyridazin-1-ium-4-carboxylic acid chloride as brown liquid.

^{1}H NMR (400 MHz, D_2O) 9.71 (d, 1H), 9.61 (s, 1H), 8.64 (dd, 1H), 4.76 (t, 2H), 2.07-2.00 (m, 2H), 1.36-1.31 (m, 2H), 0.91 (t, 3H) (CO_2H proton missing)

Example 7: Preparation of 1-[(4-cyanophenyl)methyl]pyridazin-1-ium-4-carboxylic acid bromide A38



Step 1: Preparation of methyl 1-[(4-cyanophenyl)methyl]pyridazin-1-ium-4-carboxylate bromide



To a solution of methyl pyridazine-4-carboxylate (0.7 g) in acetone (15 mL) was added 4-bromomethylbenzonitrile (1.95 g) at room temperature and the reaction mixture was heated at reflux for 24 hours. The reaction mixture was concentrated and partitioned between water (20 mL) and dichloromethane (20 mL). The aqueous phase was concentrated and purified by preparative reverse phase HPLC to afford methyl 1-[(4-cyanophenyl)methyl]pyridazin-1-ium-4-carboxylate bromide as a white solid.

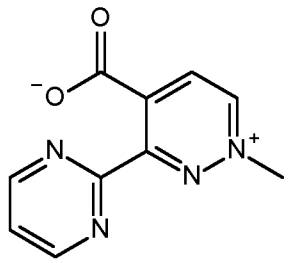
^{1}H NMR (400 MHz, D_2O) 10.01 (d, 1H), 9.75 (d, 1H), 9.94 (dd, 1H), 7.76 (d, 2H), 7.63 (d, 2H), 6.11 (s, 2H), 3.97 (s, 3H)

Step 2: Preparation of 1-[(4-cyanophenyl)methyl]pyridazin-1-ium-4-carboxylic acid bromide A38

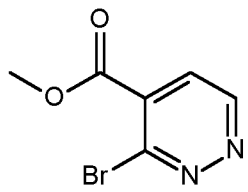
To a suspension of 1-[(4-cyanophenyl)methyl]pyridazin-1-ium-4-carboxylate bromide (0.3 g) in acetonitrile (3 mL) was added bromotrimethylsilane (0.41 g) drop wise at room temperature. The reaction mixture was stirred for 4 days at this temperature and concentrated. The crude product was purified by preparative reverse phase HPLC to afford 1-[(4-cyanophenyl)methyl]pyridazin-1-ium-4-carboxylic acid bromide as brown solid.

^{1}H NMR (400 MHz, D_2O) 9.84 (d, 1H), 9.58 (s, 1H), 8.68 (dd, 1H), 7.76 (d, 2H), 7.61 (d, 2H), 6.06 (s, 2H) (CO_2H proton missing)

Example 8: Preparation of 1-methyl-3-pyrimidin-2-yl-pyridazin-1-ium-4-carboxylate A43



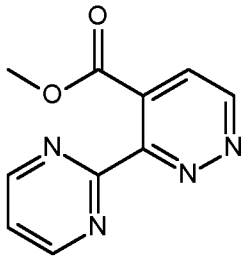
Step 1: Preparation of methyl 3-bromopyridazine-4-carboxylate



To a solution of methyl 3-hydroxypyridazine-4-carboxylate (0.5 g) in acetonitrile (20 mL) was added phosphoryl bromide (1.02 g) potionwise at 0°C, followed by heating at 100°C for 1 hour. After cooling to room temperature the reaction mixture was quenched with crushed ice and basified with saturated aqueous sodium bicarbonate. The aqueous phase was extracted with dichloromethane (3 x 50 mL),

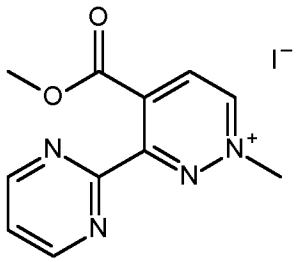
dried over sodium sulfate and concentrated to afford crude methyl 3-bromopyridazine-4-carboxylate which was used in the next step without further purification.

Step 2: Preparation of methyl 3-pyrimidin-2-ylpyridazine-4-carboxylate



To a solution of methyl 3-bromopyridazine-4-carboxylate (0.4 g) in 1,4-dioxane was added 2-(tributylstannyl)pyrimidine (0.748 g), copper(I) iodide (0.052 g) and cesium fluoride (0.56 g). The reaction mixture was purged with argon for 10 minutes and tetrakis(triphenylphosphine)palladium(0) (0.212 g) was added. After purging with argon for a further 10 minutes the reaction mixture was heated at 90°C for 16 hours. After cooling to room temperature the reaction mixture was filtered through diatomaceous earth and washed through with 10% methanol in dichloromethane (2 x 50 mL). The filtrate was concentrated and purified by silica gel chromatography eluting with 3% methanol in dichloromethane to afford methyl 3-pyrimidin-2-ylpyridazine-4-carboxylate which was used in the next step without further purification.

Step 3: Preparation of methyl 1-methyl-3-pyrimidin-2-yl-pyridazin-1-ium-4-carboxylate iodide A48



To a solution of 3-pyrimidin-2-yl-pyridazine-4-carboxylic acid methyl ester (0.28 g) in acetone (20 mL) was added iodomethane (1 mL) drop wise at room temperature. The reaction mixture was stirred at room temperature for 72 hours and the resulting precipitate was filtered off and washed with acetone (20 mL) to afford methyl 1-methyl-3-pyrimidin-2-yl-pyridazin-1-ium-4-carboxylate iodide as a brown solid.

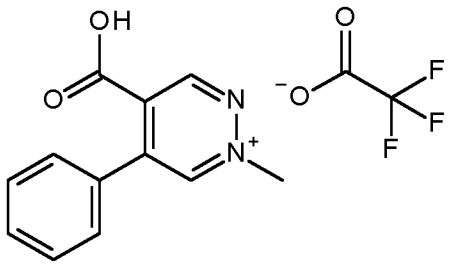
^{1}H NMR (400 MHz, D_2O) 9.96-9.94 (d, 1H), 8.98-8.96 (d, 2H), 8.91-8.89 (d, 1H), 7.73-7.70 (t, 1H), 4.74 (s, 3H), 3.86 (s, 3H)

Step 4: Preparation of 1-methyl-3-pyrimidin-2-yl-pyridazin-1-ium-4-carboxylate A43

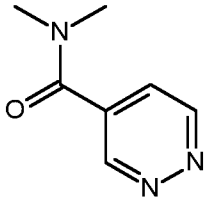
A mixture of methyl 1-methyl-3-pyrimidin-2-yl-pyridazin-1-ium-4-carboxylate iodide (0.1 g), concentrated aqueous hydrochloric acid (2.5 mL) and water (2.5 mL) was heated at 50°C for 16 hours. The reaction mixture was concentrated and triturated with methyl *tert*-butyl ether (20 mL) to afford 1-methyl-3-pyrimidin-2-yl-pyridazin-1-ium-4-carboxylate as a grey solid.

^{1}H NMR (400 MHz, D_2O) 9.70 (d, 1H), 8.92 (t, 2H), 8.51 (d, 1H), 7.65 (m, 1H), 4.64 (s, 3H)

Example 9: Preparation of 1-methyl-5-phenyl-pyridazin-1-ium-4-carboxylic acid 2,2,2-trifluoroacetate A44



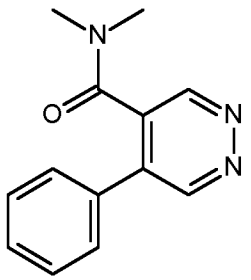
Step 1: Preparation of *N,N*-dimethylpyridazine-4-carboxamide



A solution of methyl pyridazine-4-carboxylate (1.5 g) in dimethyl amine (10 mL, 33% in ethanol) was stirred at 100°C for 3 hours in a sealed vessel. The reaction mixture was cooled, concentrated and purified by silica gel chromatography eluting with 80% ethyl acetate in hexane to afford *N,N*-dimethylpyridazine-4-carboxamide as a off white solid.

^{1}H NMR (400MHz, $CDCl_3$) 9.32 (dd, 1H), 9.24 (dd, 1H), 7.51 (dd, 1H), 3.16 (s, 3H) 3.01 (s, 3H)

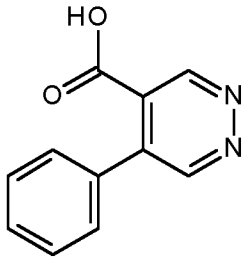
Step 2: Preparation of *N,N*-dimethyl-5-phenyl-pyridazine-4-carboxamide



To a solution of *N,N*-dimethylpyridazine-4-carboxamide (1 g) in tetrahydrofuran (20 mL) was added phenylmagnesium bromide (7.9 mL, 1M in tetrahydrofuran) drop wise. The reaction mixture was stirred at room temperature for 18 hours. After cooling to 0°C, the reaction mixture was quenched with saturated aqueous ammonium chloride (10 mL), diluted with water (150 mL) and extracted with ethyl acetate (3 x 150 mL). The combined organic phases were washed with brine, dried over anhydrous sodium sulfate and concentrated. To a solution of this crude poduct in tetrahydrofuran (20 mL) was added 2,3,5,6-tetrachloro-1,4-benzoquinone (1.07 g) and the reaction mixture was heated at 70°C for 18 hours. The reaction mixture was cooled to room temperature, concentrated and purified by silica gel chromatography eluting with 70% ethyl acetate in hexane to afford *N,N*-dimethyl-5-phenyl-pyridazine-4-carboxamide as off white solid.

^{1}H NMR (400 MHz, $CDCl_3$) 9.37 (s, 1H) 9.22 (s, 1H) 7.50-7.56 (m, 5H) 2.97 (s, 3H) 2.45 (s, 3H)

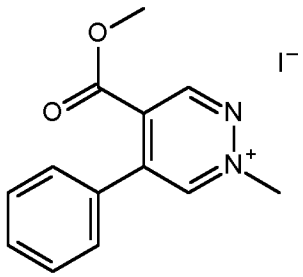
Step 3: Preparation of 5-phenylpyridazine-4-carboxylic acid



To *N,N*-dimethyl-5-phenyl-pyridazine-4-carboxamide (0.35 g) was added a solution of sodium hydroxide (0.25 g) in water (7 mL) and the reaction mixture was heated at 100°C for 72 hours. The reaction mixture was cooled to room temperature, concentrated and extracted with acetone (2 x 20 mL). The combined organic phases were concentrated to afford 5-phenylpyridazine-4-carboxylic acid as a white solid.

^{1}H NMR (400MHz, d_6-DMSO) 9.09 (s, 1 H), 8.89 (s, 1H), 7.71 (dd, 2 H), 7.39-7.48 (m, 3H) (CO_2H proton missing)

Step 4: Preparation of methyl 1-methyl-5-phenyl-pyridazin-1-ium-4-carboxylate iodide



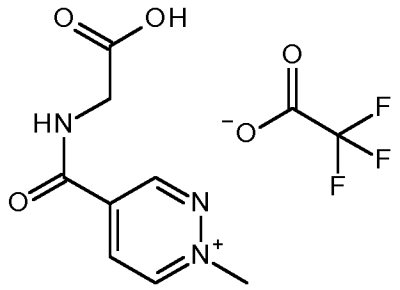
To a solution of 5-phenylpyridazine-4-carboxylic acid (0.3 g) in acetone (3 mL) at 0°C was added iodomethane (0.47 mL) drop wise. After warming to room temperature the reaction mixture was stirred for 40 hours. The reaction mixture was concentrated and washed methyl *tert*-butyl ether (2 x 10 mL). The crude product was dried under vacuum to afford methyl 1-methyl-5-phenyl-pyridazin-1-ium-4-carboxylate iodide which was used in the next step without further purification.

Step 5: Preparation of 1-methyl-5-phenyl-pyridazin-1-ium-4-carboxylic acid 2,2,2-trifluoroacetate A44

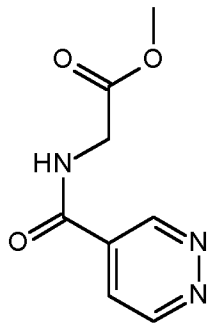
A solution of methyl 1-methyl-5-phenyl-pyridazin-1-ium-4-carboxylate iodide (0.34 g) in 2M aqueous hydrochloric acid (6.8 mL) was heated at 80°C for 40 hours. The reaction mixture was concentrated and purified by preparative reverse phase HPLC (trifluoroacetic acid is present in the eluent) to afford 1-methyl-5-phenyl-pyridazin-1-ium-4-carboxylic acid 2,2,2-trifluoroacetate.

^{1}H NMR (400MHz, D_2O) 9.63 (s, 1H), 9.48 (s, 1H), 7.75-7.52 (m, 5H), 4.60 (s, 3H) (CO_2H proton missing)

Example 10: Preparation of 2-[(1-methylpyridazin-1-ium-4-carbonyl)amino]acetic acid 2,2,2-trifluoroacetate A46



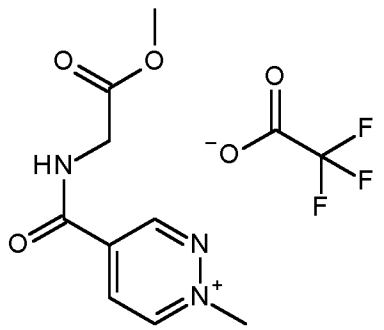
Step 1: Preparation of methyl 2-(pyridazine-4-carbonylamino)acetate



To a mixture of pyridazine-4-carboxylic acid (200 mg), methyl 2-aminoacetate hydrochloride (0.243 g), 3-(ethyliminomethyleneamino)-*N,N*-dimethyl-propan-1-amine hydrochloride (0.37 g), 1-hydroxybenzotriazole (0.022 g) in dichloromethane (4.03 mL) was added Hunig's Base (0.87 mL). The reaction mixture was stirred at room temperature overnight. The reaction mixture was diluted with chloroform and washed with water (3 x 20 mL). The organic layer was dried over sodium sulfate, concentrated and purified by silica gel chromatography eluting with 90 to 100% ethyl acetate in iso-hexane to give methyl 2-(pyridazine-4-carbonylamino)acetate.

^{1}H NMR (400MHz, d-DMSO) 9.52-9.59 (m, 2H) 9.47 (dd, 1H) 8.02 (dd, 1H) 4.10 (d, 2H) 3.68 (s, 3H)

Step 2: Preparation of methyl 2-[(1-methylpyridazin-1-ium-4-carbonyl)amino]acetate 2,2,2-trifluoroacetate A45



A solution of methyl 2-(pyridazine-4-carbonylamino)acetate (0.5 g) in acetone (5 mL) was cooled to 0°C and iodomethane (0.8 mL) was added drop wise. The solution was warmed to room temperature and stirred for 40 hours. The reaction mass was concentrated, washed with methyl *tert*-butyl ether and

purified by preparative reverse phase HPLC (trifluoroacetic acid is present in the eluent) to afford methyl 2-[(1-methylpyridazin-1-ium-4-carbonyl)amino]acetate 2,2,2-trifluoroacetate.

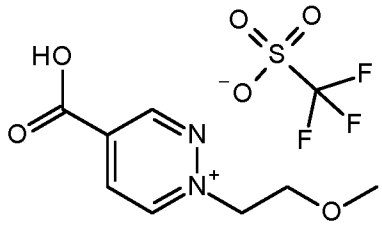
^{1}H NMR (400 MHz, D_2O) 9.87 (d, 1H), 9.74 (d, 1H), 8.87 (dd, 1H), 4.71 (s, 3H), 4.30 (s, 2H), 3.79 (s, 3H) (NH proton missing)

Step 3: Preparation of 2-[(1-methylpyridazin-1-ium-4-carbonyl)amino]acetic acid 2,2,2-trifluoroacetate A46

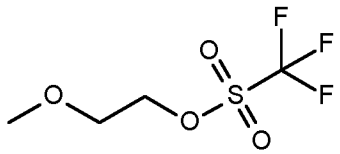
A solution of methyl 2-[(1-methylpyridazin-1-ium-4-carbonyl)amino]acetate 2,2,2-trifluoroacetate (0.40 g) in 2M aqueous hydrochloric acid (8 mL) was stirred at room temperature for 24 hours. The reaction mixture was concentrated and purified by preparative reverse phase HPLC (trifluoroacetic acid is present in the eluent) to afford 2 2-[(1-methylpyridazin-1-ium-4-carbonyl)amino]acetic acid 2,2,2-trifluoroacetate.

^{1}H NMR (400MHz, D_2O) 9.85 (d, 1H), 9.73 (d, 1H), 8.86 (dd, 1H), 4.70 (s, 3H), 4.25 (s, 2H) (NH and CO_2H protons missing)

Example 11: Preparation of 1-(2-methoxyethyl)pyridazin-1-ium-4-carboxylate trifluoromethanesulfonate A5



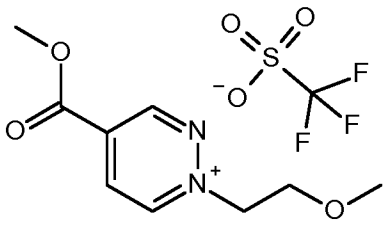
Step 1: Preparation of 2-methoxyethyl trifluoromethanesulfonate



A mixture of 2-methoxyethanol (0.518 mL), pyridine (0.635 mL) and dry dichloromethane (15 mL) was cooled to ~0°C and trifluoromethylsulfonyl trifluoromethanesulfonate (1.22 mL) was added dropwise. The reaction was stirred for 20 minutes. The mixture was partitioned between ethyl acetate and water. The organic phase was washed with brine, dried over magnesium sulfate and concentrated with care to give 2-methoxyethyl trifluoromethanesulfonate, which was used without further purification.

^{1}H NMR (500 MHz, $CDCl_3$) 4.64-4.60 (m, 2H), 3.73-3.69 (m, 2H), 3.42 (s, 3H) (ethyl acetate also present)

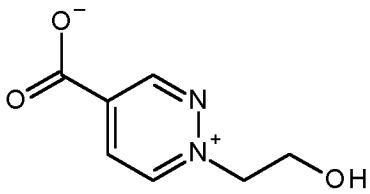
Step 2: Preparation of methyl 1-(2-methoxyethyl)pyridazin-1-ium-4-carboxylate trifluoromethanesulfonate A6



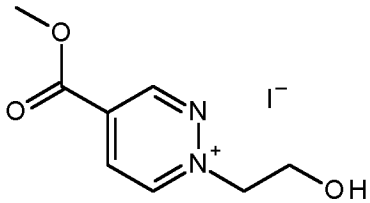
To a solution of methyl pyridazine-4-carboxylate (0.16 g) in dichloromethane (2 mL) was added 2-methoxyethyl trifluoromethanesulfonate (1.218 g) and the reaction was stirred at room temperature for 18 hours. The reaction mixture was partitioned between ethyl acetate and water. The aqueous phase was washed with further ethyl acetate, concentrated and purified by preparative reverse phase HPLC to give methyl 1-(2-methoxyethyl)pyridazin-1-ium-4-carboxylate trifluoromethanesulfonate.
^{1}H NMR (400 MHz, CD_3OD) 9.97 (d, 1H), 9.93-9.88 (m, 1H), 9.01 (dd, 1H), 5.16-5.09 (m, 2H), 4.10 (s, 3H), 4.04-3.95 (m, 2H), 3.35-3.33 (m, 3H)

Step 3: Preparation of 1-(2-methoxyethyl)pyridazin-1-ium-4-carboxylate trifluoromethanesulfonate A5
A mixture of methyl 1-(2-methoxyethyl)pyridazin-1-ium-4-carboxylate trifluoromethanesulfonate (0.04 g) and concentrated hydrochloric acid (2 mL) was heated at 80°C for 4 hours. The mixture was concentrated to give 1-(2-methoxyethyl)pyridazin-1-ium-4-carboxylate trifluoromethanesulfonate.
^{1}H NMR (400 MHz, CD_3OD) 9.97 (d, 1H), 9.89 (d, 1H), 8.99 (dd, 1H), 5.13 (s, 2H), 3.98-4.03 (m, 2H), 3.35 (s, 3H) (CO_2H proton missing)

Example 12: Preparation of 1-(2-hydroxyethyl)pyridazin-1-ium-4-carboxylate A9



Step 1 Preparation of methyl 1-(2-hydroxyethyl)pyridazin-1-ium-4-carboxylate iodide



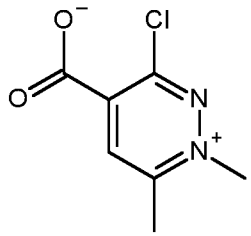
A mixture of methyl pyridazine-4-carboxylate (1 g) and 2-iodoethanol (1.413 mL) was heated at 70°C for 5 hours. The reaction mixture was partitioned between ethyl acetate and water. The aqueous phase was concentrated to give crude methyl 1-(2-hydroxyethyl)pyridazin-1-ium-4-carboxylate iodide, which was used without further purification. The major impurity is methyl 2-(2-hydroxyethyl)pyridazin-2-ium-4-carboxylate iodide.

Step 2: Preparation of 1-(2-hydroxyethyl)pyridazin-1-ium-4-carboxylate A9
Crude methyl 1-(2-hydroxyethyl)pyridazin-1-ium-4-carboxylate iodide (0.8 g) was heated at 80°C in 2M

aqueous hydrochloric acid (8 mL) for 3 hours. The reaction was concentrated and purified by preparative reverse phase HPLC to give 1-(2-hydroxyethyl)pyridazin-1-ium-4-carboxylate as a brown solid.

^{1}H NMR (400 MHz, CD_3OD) 9.73 (s, 2H), 8.69-8.75 (m, 1H), 4.90-4.96 (m, 2H), 4.06-4.13 (m, 2H) (OH proton missing)

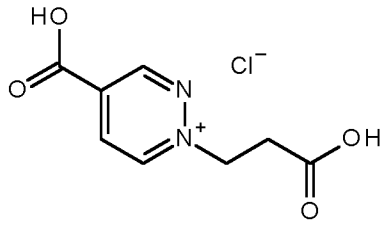
Example 13: Preparation of 3-chloro-1,6-dimethyl-pyridazin-1-ium-4-carboxylate A8



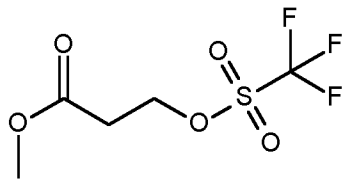
To a mixture of 3-chloro-6-methyl-pyridazine-4-carboxylic acid (0.1 g) and toluene (3 mL) was added dimethyl sulfate (0.548 mL) and the mixture was stirred at reflux for 6 hours. The reaction was concentrated and partitioned between water and dichloromethane. The aqueous layer was concentrated and purified by preparative reverse phase HPLC to give 3-chloro-1,6-dimethyl-pyridazin-1-ium-4-carboxylate as a tan solid.

^{1}H NMR (400 MHz, CD_3OD) 8.32 (s, 1H), 4.47 (s, 3H), 2.92 (s, 3H)

Example 14: Preparation of 1-(2-carboxyethyl)pyridazin-1-ium-4-carboxylic acid chloride A21



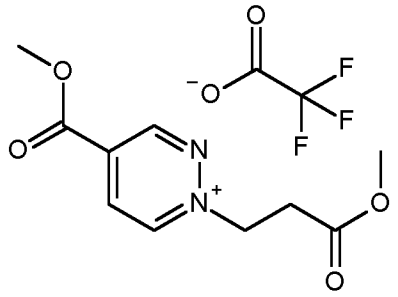
Step 1: Preparation of methyl 3-(trifluoromethylsulfonyloxy)propanoate



A solution of methyl 3-hydroxypropanoate (0.518 mL), pyridine (0.635 mL) in dry dichloromethane (15 mL) was cooled to ~0°C and trifluoromethylsulfonyl trifluoromethanesulfonate (1.22 mL) was added dropwise. After stirring for 20 minutes the reaction mixture was diluted with dichloromethane and washed with water. The organic phase was dried over sodium sulfate and concentrated with care to give methyl 3-(trifluoromethylsulfonyloxy)propanoate, which was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) 4.79 (t, 2H), 3.78 - 3.72 (m, 3H), 2.86 (t, 2H)

Step 2: Preparation of methyl 1-(3-methoxy-3-oxo-propyl)pyridazin-1-ium-4-carboxylate 2,2,2-trifluoroacetate A23



To a solution of methyl pyridazine-4-carboxylate (0.43 g) in dichloromethane (1 mL) was added methyl 3-(trifluoromethylsulfonyloxy)propanoate (3.4 g) and the reaction was stirred at room temperature for 18 hours. The reaction mixture was concentrated and purified by preparative reverse phase HPLC (trifluoroacetic acid is present in the eluent) to give methyl 1-(3-methoxy-3-oxo-propyl)pyridazin-1-ium-4-carboxylate 2,2,2-trifluoroacetate as a brown oil.

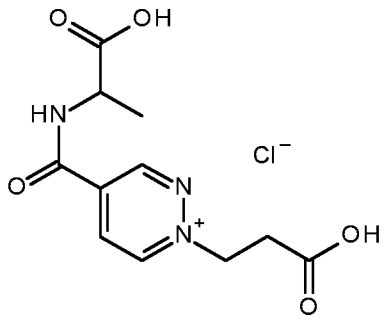
^{1}H NMR (400 MHz, CD_3OD) 10.12 (d, 1H), 9.89 (d, 1H), 9.02 (dd, 1H), 5.21 (t, 2H), 4.10 (s, 3H), 3.67 (s, 3H), 3.28 (t, 2H)

Step 3: Preparation of 1-(2-carboxyethyl)pyridazin-1-ium-4-carboxylic acid chloride A21

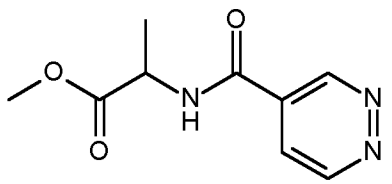
Methyl 1-(3-methoxy-3-oxo-propyl)pyridazin-1-ium-4-carboxylate 2,2,2-trifluoroacetate (0.06 g) was heated at 80°C in 2M aqueous hydrochloric acid (2 mL) for 4 hours. The reaction was concentrated to give 1-(2-carboxyethyl)pyridazin-1-ium-4-carboxylic acid chloride.

^{1}H NMR (400 MHz, CD_3OD) 10.11 (d, 1H), 9.87 (d, 1H), 8.99 (dd, 1H), 5.19 (t, 2H), 3.26 (t, 2H) (CO_2H protons missing)

Example 15: Preparation of 2-[[1-(2-carboxyethyl)pyridazin-1-ium-4-carbonyl]amino]propanoic acid chloride A50



Step 1: Preparation of methyl 2-(pyridazine-4-carbonylamino)propanoate

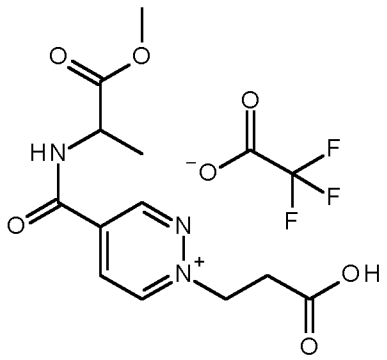


To a mixture of pyridazine-4-carboxylic acid (2 g) in acetonitrile (64.5 mL) was added triethylamine (6.81 mL), 2,4,6-tripropyl-1,3,5,2,4,6-trioxatriphosphorinane-2,4,6-trioxide (50% solution in ethyl acetate, 19.19 mL) followed by methyl 2-aminopropanoate hydrochloride (2.525 g) and the mixture

was stirred at room temperature for 16 hours. The reaction was concentrated and partitioned between ice cold water and ethyl acetate. The organic layer was washed with saturated aqueous sodium bicarbonate, dried over sodium sulfate, concentrated and purified by silica gel chromatography eluting with a mixture of ethyl acetate and cyclohexane to give methyl 2-(pyridazine-4-carbonylamino)propanoate.

^{1}H NMR (400 MHz, $CDCl_3$) 9.58 (s, 1H), 9.37 (d, 1H), 7.88 (dd, 1H), 4.75-4.85 (m, 1H), 3.80(s, 3H), 1.54(d, 3H) (NH proton missing)

Step 2: Preparation of 3-[4-[(2-methoxy-1-methyl-2-oxo-ethyl)carbamoyl]pyridazin-1-ium-1-yl]propanoic acid 2,2,2-trifluoroacetate A51



To a mixture of methyl 2-(pyridazine-4-carbonylamino)propanoate (0.7 g) and acetonitrile (10.5 mL) was added 3-bromopropanoic acid (0.54 g) and the mixture was heated at 60°C for 16 hours. The reaction was concentrated and purified by preparative reverse phase HPLC (trifluoroacetic acid is present in the eluent) to give 3-[4-[(2-methoxy-1-methyl-2-oxo-ethyl)carbamoyl]pyridazin-1-ium-1-yl]propanoic acid 2,2,2-trifluoroacetate.

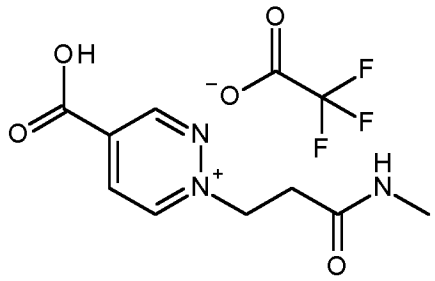
^{1}H NMR (400 MHz, D_2O) 9.93-10.05 (m, 1H), 9.71-9.82 (m, 1H), 8.80-8.94 (m, 1H), 5.10-5.25 (m, 2H), 4.64-4.74 (m, 1H), 3.76-3.83(m, 3H), 3.26-3.35 (m, 2H), 1.43-1.60 (m, 3H) (NH and CO_2H protons missing)

Step 3: Preparation of 2-[[1-(2-carboxyethyl)pyridazin-1-ium-4-carbonyl]amino]propanoic acid chloride A50

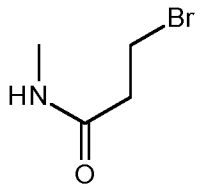
A mixture of 3-[4-[(2-methoxy-1-methyl-2-oxo-ethyl)carbamoyl]pyridazin-1-ium-1-yl]propanoic acid (0.1 g) and 2M aqueous hydrochloric acid (2 mL) was stirred at room temperature for 24 hours. The reaction was concentrated and the resulting residue was washed with cyclohexane followed by methyl *tert*-butyl ether and dried to give 2-[[1-(2-carboxyethyl)pyridazin-1-ium-4-carbonyl]amino]propanoic acid chloride.

^{1}H NMR (400 MHz, D_2O) 9.89 (d, 1H), 9.66 (d, 1H), 8.79 (dd, 1H), 5.09 (t, 2H), 4.53 (q, 1H), 3.19 (t, 2H), 1.44 (d, 3H) (NH and CO_2H protons missing)

Example 16: Preparation of 1-[3-(methylamino)-3-oxo-propyl]pyridazin-1-ium-4-carboxylic acid 2,2,2-trifluoroacetate A56



Step 1: Preparation of 3-bromo-N-methyl-propanamide



A solution of 3-bromopropanoyl chloride (2 g) in dichloromethane (35 mL) was cooled to ~5°C and methanamine (2M in tetrahydrofuran, 11.7 mL) was added dropwise. The mixture was allowed to warm to room temperature and was stirred for 18 hours. The reaction mixture was concentrated and partitioned between dichloromethane and saturated aqueous sodium bicarbonate. The organic layer was washed with further saturated aqueous sodium bicarbonate, dried over sodium sulfate and concentrated to give 3-bromo-N-methyl-propanamide as a white solid, which was used without further purification.

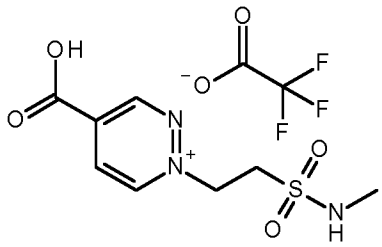
^{1}H NMR (400 MHz, $CDCl_3$) 5.61 (brs, 1H), 3.64 (t, 2H), 2.85 (d, 3H), 2.75 (t, 2H)

Step 2: Preparation of 1-[3-(methylamino)-3-oxo-propyl]pyridazin-1-ium-4-carboxylic acid 2,2,2-trifluoroacetate A56

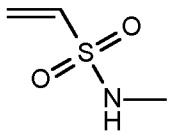
To a mixture of pyridazine-4-carboxylic acid (0.25 g) and acetonitrile (5 mL) was added 3-bromo-N-methyl-propanamide (0.502 g) and the mixture was heated at 80°C for 16 hours. Water (2.5 mL) was added and heating was continued at 80°C for 16 hours. The reaction was concentrated, triturated with methyl *tert*-butyl ether and purified by preparative reverse phase HPLC (trifluoroacetic acid is present in the eluent) to give 1-[3-(methylamino)-3-oxo-propyl]pyridazin-1-ium-4-carboxylic acid 2,2,2-trifluoroacetate.

^{1}H NMR (400 MHz, D_2O) 9.78 (d, 1H), 9.64 (d, 1H), 8.72 (dd, 1H), 5.11 - 5.04 (m, 2H), 3.08 - 3.01 (m, 2H), 2.59 - 2.54 (m, 3H) (NH and CO_2H protons missing)

Example 17: Preparation of 1-[2-(methylsulfamoyl)ethyl]pyridazin-1-ium-4-carboxylic acid 2,2,2-trifluoroacetate A55



Step 1: Preparation of N-methylethenesulfonamide



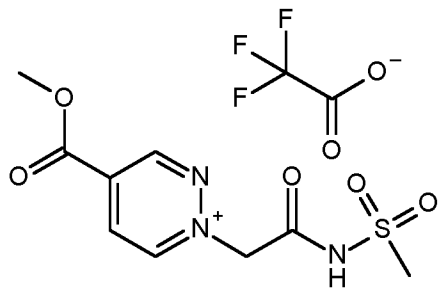
A solution of 2-chloroethanesulfonyl chloride (1.28 mL) in dichloromethane (35.3 mL) was cooled to ~5°C and methanamine (2M in tetrahydrofuran, 11.7 mL) was added dropwise. The mixture was allowed to warm to room temperature and was stirred for 18 hours. The reaction mixture was concentrated and partitioned between dichloromethane and saturated aqueous sodium bicarbonate. The organic layer was washed with further saturated aqueous sodium bicarbonate, dried over sodium sulfate and concentrated to give N-methylethenesulfonamide, which was used without further purification.

Step 2: Preparation of 1-[2-(methylsulfamoyl)ethyl]pyridazin-1-ium-4-carboxylic acid 2,2,2-trifluoroacetate A55

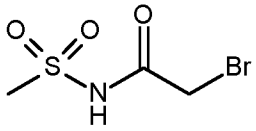
A mixture of pyridazine-4-carboxylic acid (0.2 g), 2,2,2-trifluoroacetic acid (1 mL), water (1 mL) and N-methylethenesulfonamide (0.234 g) was heated at 100°C for 16 hours. The reaction was concentrated, triturated with methyl *tert*-butyl ether and purified by preparative reverse phase HPLC (trifluoroacetic acid is present in the eluent) to give 1-[2-(methylsulfamoyl)ethyl]pyridazin-1-ium-4-carboxylic acid 2,2,2-trifluoroacetate.

^{1}H NMR (400 MHz, D_2O) 9.89 (d, 1H), 9.75 - 9.71 (m, 1H), 8.81 (dd, 1H), 5.27 (t, 2H), 4.00 - 3.94 (m, 2H), 2.62 - 2.59 (m, 3H) (NH and CO_2H protons missing)

Example 18: Preparation of methyl 1-[2-(methanesulfonamido)-2-oxo-ethyl]pyridazin-1-ium-4-carboxylate 2,2,2-trifluoroacetate A25



Step 1: Preparation of 2-bromo-N-methylsulfonyl-acetamide



To a solution of methanesulfonamide (1 g) in toluene (63 mL) was added 2-bromoacetyl bromide (3.7 mL) drop wise at room temperature. The reaction mixture was then heated at 110°C for 5 hours. The reaction was cooled to room temperature and then placed in an ice bath. The resulting precipitate was filtered off, washed with cold toluene and dried under vacuum to give 2-bromo-N-methylsulfonyl-acetamide as a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) 8.81 (br s, 1H), 3.95 (s, 2H), 3.35 (s, 3H)

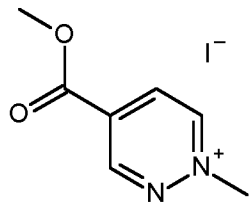
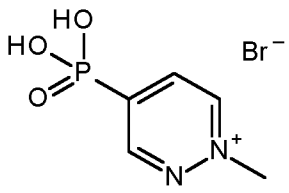
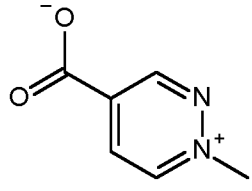
Step 2: Preparation of methyl 1-[2-(methanesulfonamido)-2-oxo-ethyl]pyridazin-1-ium-4-carboxylate 2,2,2-trifluoroacetate A25

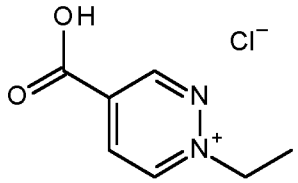
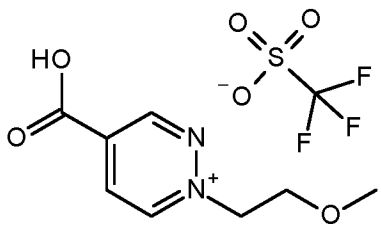
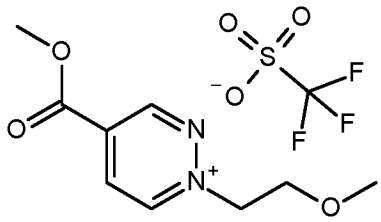
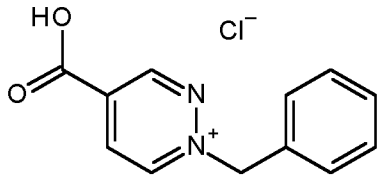
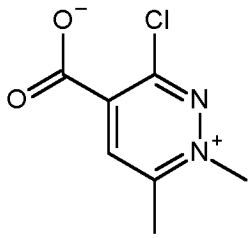
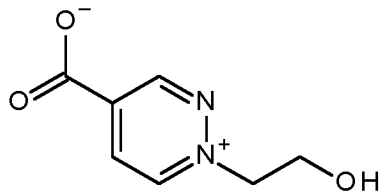
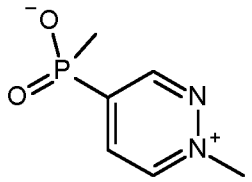
A mixture of methyl pyridazine-4-carboxylate (0.5 g), 2-bromo-N-methylsulfonyl-acetamide (0.939 g) and acetone (3 mL) was stirred at room temperature for 120 hours. The reaction was concentrated and purified by preparative reverse phase HPLC (trifluoroacetic acid is present in the eluent) to give methyl 1-[2-(methanesulfonamido)-2-oxo-ethyl]pyridazin-1-ium-4-carboxylate 2,2,2-trifluoroacetate.

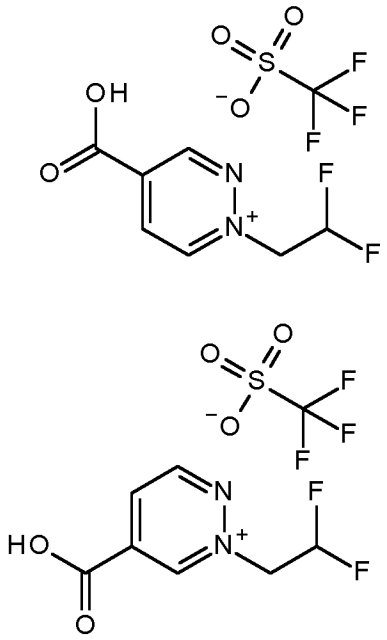
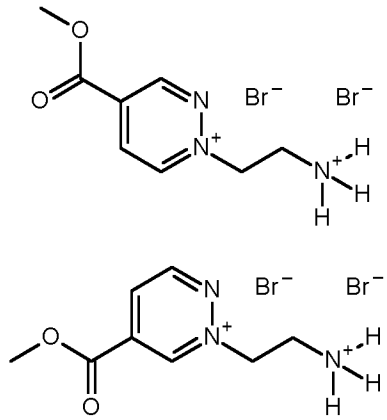
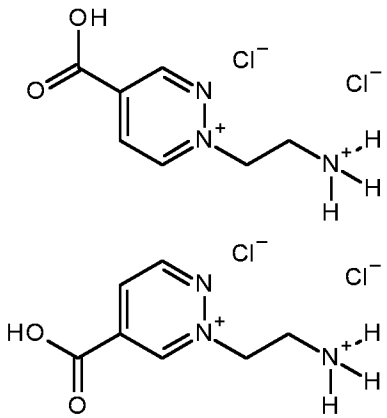
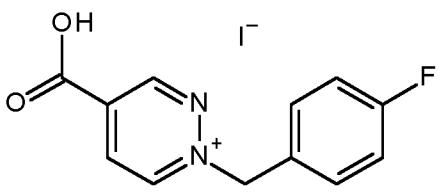
^{1}H NMR (400 MHz, D_2O) 9.87 (d, 1H), 9.81 (d, 1H), 9.01 (dd, 1H), 5.64 (s, 1H), 4.01 (s, 3H), 3.03 (s, 3H)(NH and one CH_2 protons missing)

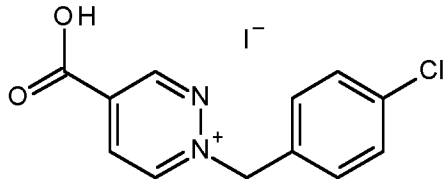
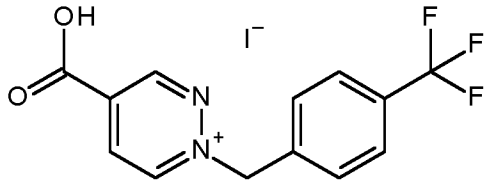
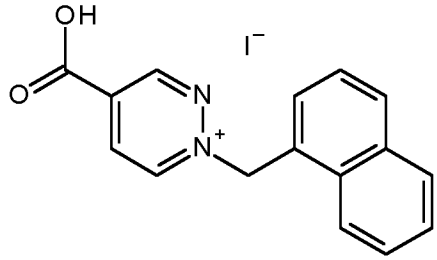
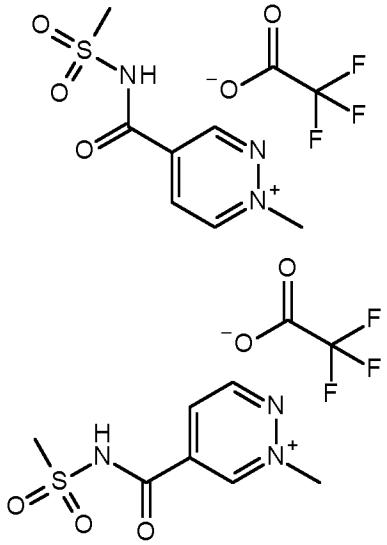
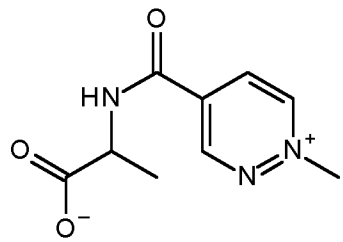
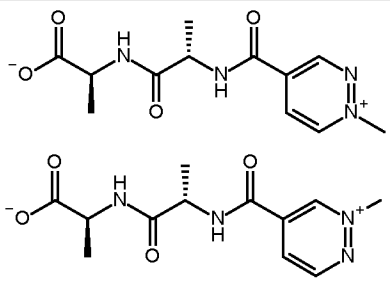
Additional compounds in Table A were prepared by analogous procedures, from appropriate starting materials.

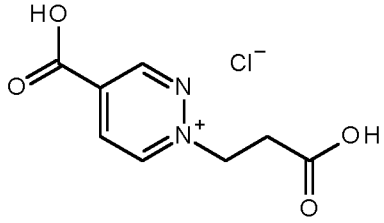
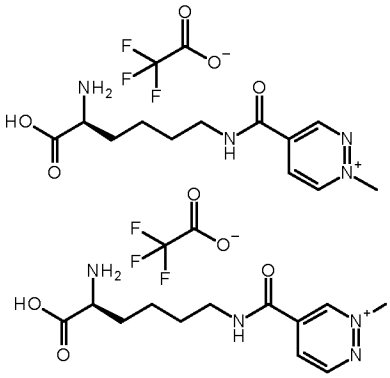
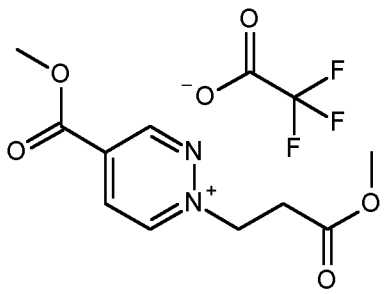
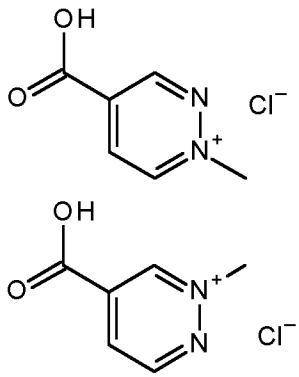
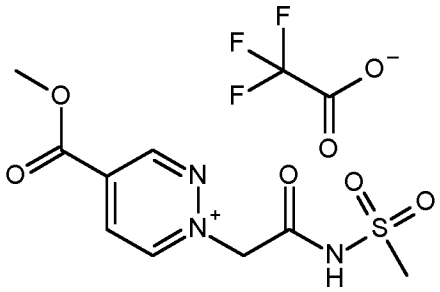
Table A

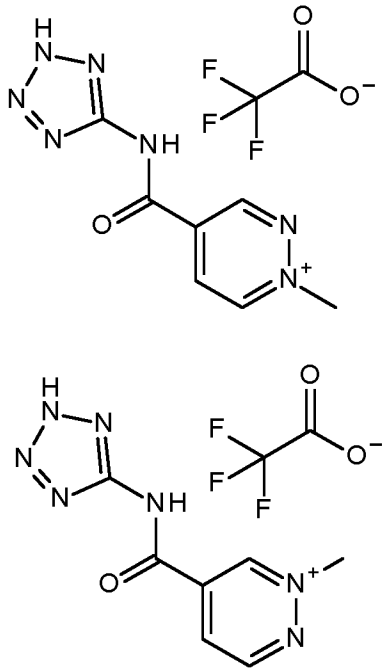
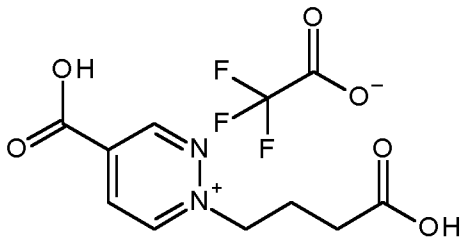
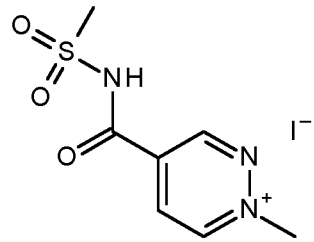
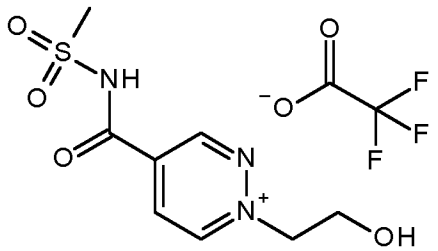
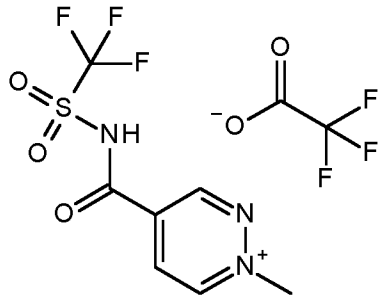
Cmpd. No.	Structure	^{1}H NMR
A1		(400 MHz, D_2O) 9.82 (d, 1H), 9.75 (d, 1H), 8.90 (dd, 1H), 4.63 (s, 3H), 3.99 (s, 3H)
A2		(400MHz, CD_3OD) 9.90 (d, 1H), 9.64 (d, 1H), 8.81 (dd, 1H), 4.71 (s, 3H) (P(OH) protons missing)
A3		(400MHz, CD_3OD) 9.98 (d, 1H), 9.85 (d, 1H), 8.99 (dd, 1H), 4.74 (s, 3H)

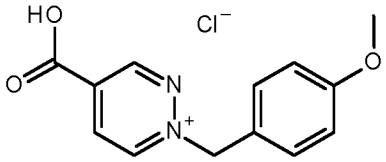
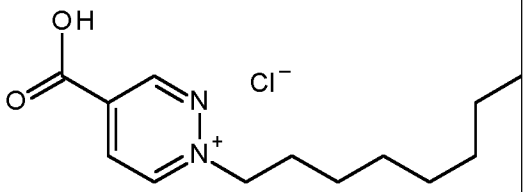
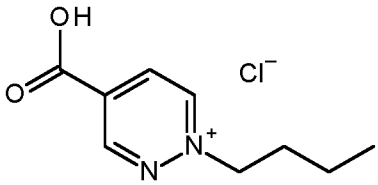
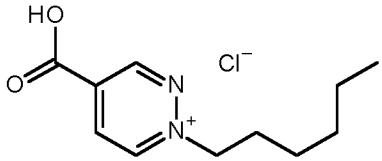
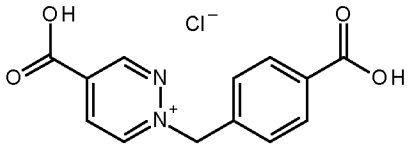
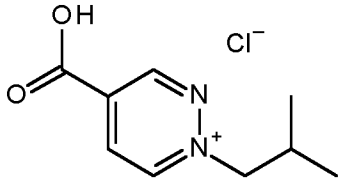
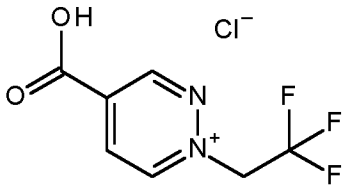
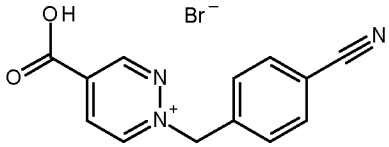
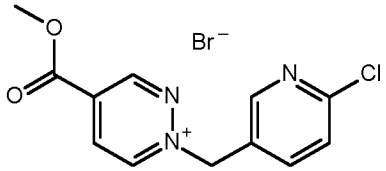
Cmpd. No.	Structure	^{1}H NMR
A4		(400 MHz, CD_3OD) 10.13 (d, 1H), 9.89 (d, 1H), 9.02 (dd, 1H), 5.04 (q, 2H), 1.78 (t, 3H) (CO_2H proton missing)
A5		(400 MHz, CD_3OD) 9.97 (d, 1H), 9.89 (d, 1H), 8.99 (dd, 1H), 5.13 (s, 2H), 3.98-4.03 (m, 2H), 3.35 (s, 3H) (CO_2H proton missing)
A6		(400 MHz, CD_3OD) 9.97 (d, 1H), 9.93-9.88 (m, 1H), 9.01 (dd, 1H), 5.16-5.09 (m, 2H), 4.10 (s, 3H), 4.04-3.95 (m, 2H), 3.35-3.33 (m, 3H)
A7		(400 MHz, CD_3OD) 10.26 (d, 1H), 9.83 (d, 1H), 9.00 (dd, 1H), 7.61-7.69 (m, 2H), 7.40-7.50 (m, 3H), 6.18 (s, 2H) (CO_2H missing)
A8		(400 MHz, CD_3OD) 8.32 (s, 1H), 4.47 (s, 3H), 2.92 (s, 3H)
A9		(400 MHz, CD_3OD) 9.73 (s, 2H), 8.69-8.75 (m, 1H), 4.90-4.96 (m, 2H), 4.06-4.13 (m, 2H) (OH proton missing)
A10		(400 MHz, D_2O) 9.61 (d, 1H), 9.47 (d, 1H), 8.52-8.64 (m, 1H), 4.57 (s, 3H), 1.53 (d, 3H)

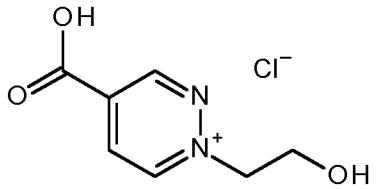
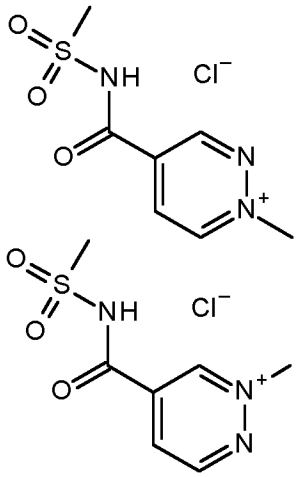
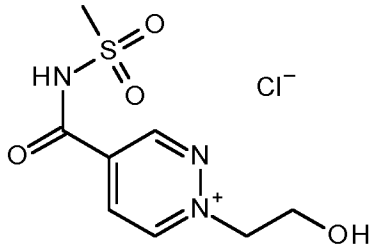
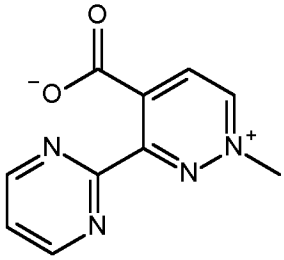
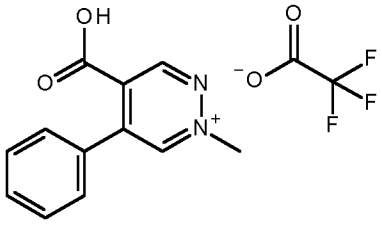
Cmpd. No.	Structure	^{1}H NMR
A11		(400 MHz, CD_3OD) 10.13 (d, 1H), 9.95 (br s, 1H), 9.12-9.07 (m, 1H), 6.77-6.44 (m, 1H), 5.55-5.43 (m, 2H) (CO_2H proton missing) [isolated as a 1:1 mixture of isomers with: 10.42 (s, 1H), 9.79 (d, 1H), 9.07-9.01 (m, 1H), 6.77-6.44 (m, 1H), 5.55-5.43 (m, 2H) (CO_2H proton missing)]
A12		(400 MHz, D_2O) 10.05-10.01 (m, 1H), 9.90-9.86 (m, 1H), 9.05-9.00 (m, 1H), 5.31-5.23 (m, 2H), 4.01 (s, 3H), 3.83-3.75 (m, 2H) [isolated as a 1:1 mixture of isomers with: 10.32-10.29 (m, 1H), 9.74-9.69 (m, 1H), 8.99-8.96 (m, 1H), 5.30-5.24 (m, 2H), 4.01 (s, 3H), 3.82-3.74 (m, 2H)]
A13		(400 MHz, CD_3OD) 10.28 (d, 1H), 9.94 (d, 1H), 9.10 (dd, 1H), 5.39 (dt, 2H), 3.90-3.84 (m, 2H) (NH and CO_2H protons missing) [isolated as a 1:1 mixture of isomers with: 10.46 (s, 1H), 9.85-9.80 (m, 1H), 9.03 (dd, 1H), 5.39 (dt, 2H), 3.90-3.84 (m, 2H) (NH and CO_2H protons missing)]
A14		(300 MHz, D_2O) 9.79 (d, 1H), 9.61 (s, 1H), 8.69 (d, 1H), 7.57-7.52 (m, 2H), 7.16 (t, 2H), 5.99 (s, 2H) (CO_2H proton missing)

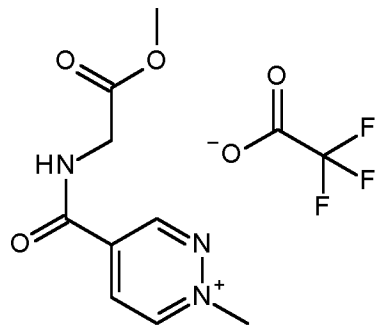
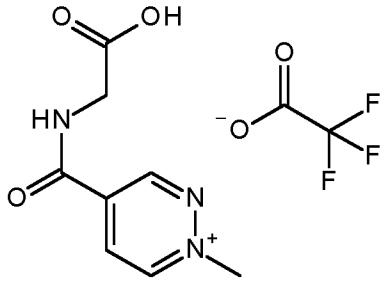
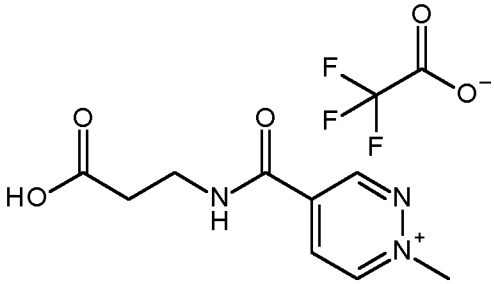
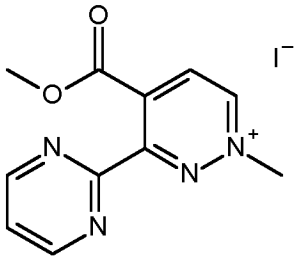
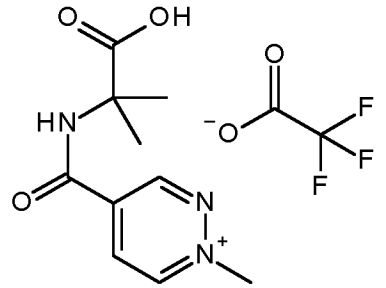
Cmpd. No.	Structure	^{1}H NMR
A15		(300 MHz, D_2O) 9.75 (d, 1H), 9.55 (s, 1H), 8.62 (dd, 1H), 7.43 (d, 2H), 7.38 (d, 2H), 5.94 (s, 2H) (CO_2H proton missing)
A16		(400 MHz, D_2O) 9.86 (dd, 1H), 9.62 (d, 1H), 8.71 (dd, 1H), 7.76 (d, 2H), 7.67 (d, 2H), 6.11 (s, 2H) (CO_2H proton missing)
A17		(300 MHz, D_2O) 9.56 (d, 1H), 9.49 (s, 1H), 8.48 (dd, 1H), 7.95 (d, 1H), 7.90-7.87 (m, 2H), 7.68 (d, 1H), 7.53-7.47 (m, 3H), 6.41 (s, 2H) (CO_2H proton missing)
A18		(400 MHz, CD_3OD) 9.85-9.82 (m, 1H), 9.81-9.78 (m, 1H), 8.91-8.86 (m, 1H), 4.72-4.67 (m, 3H), 3.20-3.13 (m, 3H) (NH proton missing) [isolated as a 1:1 mixture of isomers with: 10.12 (s, 1H), 9.55 (d, 1H), 8.85-8.81 (m, 1H), 4.72-4.67 (m, 3H), 3.20-3.13 (m, 3H) (NH proton missing)]
A19		(400 MHz, CD_3OD) 9.96 (d, 1H), 9.80 (d, 1H), 8.94 (dd, 1H), 4.73 (s, 3H), 4.57 (q, 1H), 1.54 (d, 3H) (NH proton missing)
A20		(400 MHz, CD_3OD) 9.94 (d, 1H), 9.82-9.79 (m, 1H), 8.97-8.92 (m, 1H), 4.77-4.69 (m, 3H), 4.64-4.56 (m, 1H), 4.23-4.13 (m, 1H), 1.54-1.50 (m, 3H), 1.38-1.32 (m, 3H) (NH protons missing) [isolated as a 1:1 mixture of isomers with: 10.22 (s, 1H), 9.64 (d, 1H), 8.91-8.87 (m, 1H), 4.77-4.69 (m, 3H), 4.64-4.56 (m, 1H), 4.23-4.13 (m, 1H), 1.54-1.50

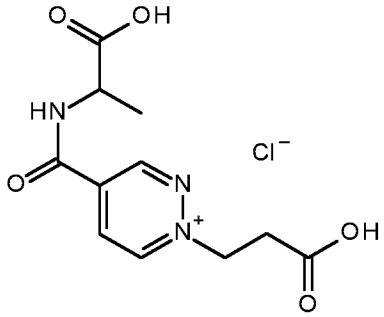
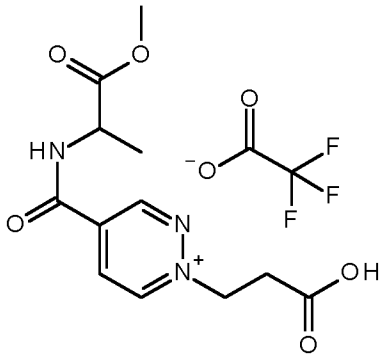
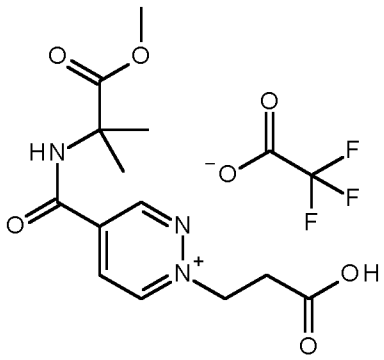
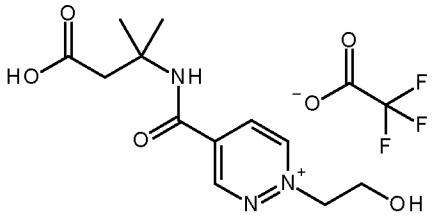
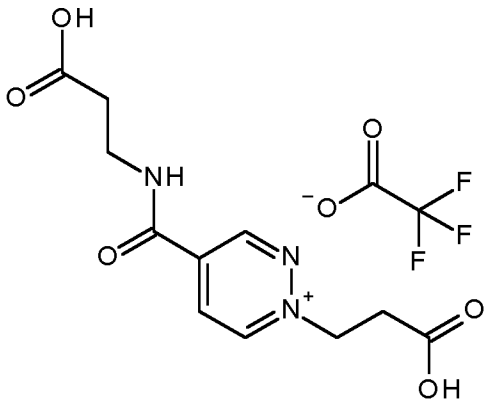
Cmpd. No.	Structure	^{1}H NMR
		(m, 3H), 1.38-1.32 (m, 3H) (NH protons missing)]
A21		(400 MHz, CD_3OD) 10.11 (d, 1H), 9.87 (d, 1H), 8.99 (dd, 1H), 5.19 (t, 2H), 3.26 (t, 2H) (CO_2H protons missing)
A22		(400 MHz, CD_3OD) 9.92-9.98 (m, 1H), 9.78-9.82 (m, 1H), 8.88-8.95 (m, 1H), 4.73 (s, 3H), 3.58-3.65 (m, 1H), 3.46-3.53 (m, 2H), 1.82-1.99 (m, 2H), 1.72 (br. s., 2H), 1.43-1.64 (m, 2H) (NH and CO_2H protons missing) [isolated as a 2:3 mixture of isomers with: 10.17-10.23 (m, 1H), 9.60-9.65 (m, 1H), 8.82-8.87 (m, 1H), 4.73 (s, 3H), 3.58-3.65 (m, 1H), 3.46-3.53 (m, 2H), 1.82-1.99 (m, 2H), 1.72 (br. s., 2H), 1.43-1.64 (m, 2H) (NH and CO_2H protons missing)]
A23		(400 MHz, CD_3OD) 10.12 (d, 1H), 9.92-9.86 (m, 1H), 9.02 (dd, 1H), 5.24-5.16 (m, 2H), 4.10 (s, 3H), 3.68 (s, 3H), 3.31-3.25 (m, 2H)
A24		(400 MHz, CD_3OD) 10.07 (d, 1H), 9.86-9.82 (m, 1H), 9.01 (dd, 1H), 5.09 (s, 3H) (CO2H proton missing) [isolated as a 1:1 mixture of isomers with: 10.26 (s, 1H), 9.72 (d, 1H), 8.93 (dd, 1H), 5.09 (s, 3H) (CO_2H proton missing)]
A25		(400 MHz, D_2O) 9.87 (d, 1H), 9.81 (d, 1H), 9.01 (dd, 1H), 5.64 (s, 1H), 4.01 (s, 3H), 3.03 (s, 3H) (NH and one CH_2 protons missing)

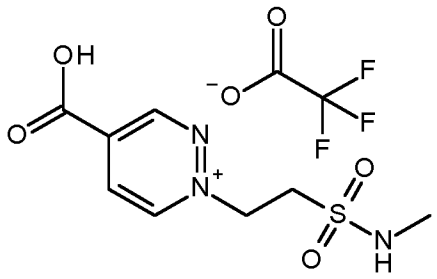
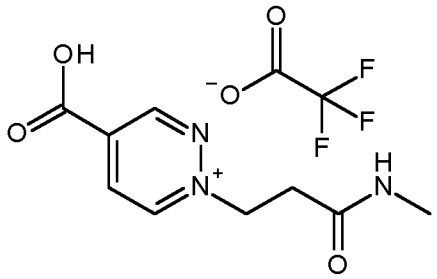
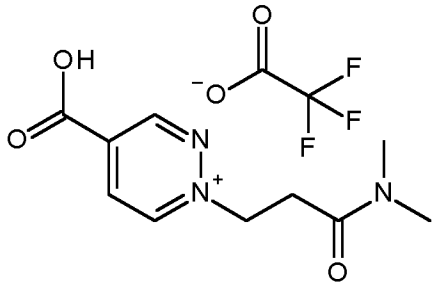
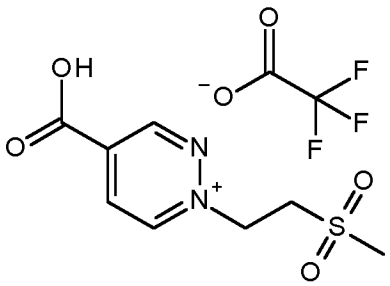
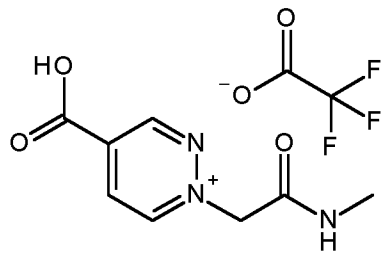
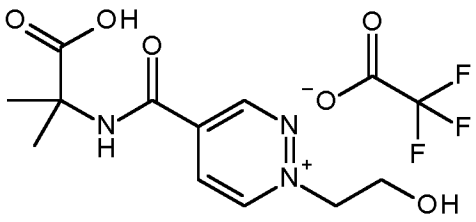
Cmpd. No.	Structure	^{1}H NMR
A26		(400 MHz, D_2O) 9.87 (br d, 1H), 9.82-9.73 (m, 1H), 8.99-8.94 (m, 1H), 4.67 (s, 3H) (NH protons missing) [isolated as a 1:1 mixture of isomers with: 10.15 (s, 1H), 9.62 (br d, 1H), 8.94-8.89 (m, 1H), 4.65 (s, 3H) (NH protons missing)]
A27		(400 MHz, CD_3OD) 10.01 (d, 1H), 9.88 (d, 1H), 8.98 (dd, 1H), 5.01-5.07 (m, 2H), 2.55-2.66 (m, 2H), 2.40-2.50 (m, 2H) (CO_2H protons missing)
A28		(400 MHz, CD_3OD) 8.27 (s, 1H), 8.26 (d, 1H), 7.35 (dd, 1H), 3.20 (s, 3H), 1.71 (s, 3H) (NH proton missing)
A29		(400 MHz, CD_3OD) 9.84-9.90 (m, 2H), 8.91-8.97 (m, 1H), 4.99 (m, 2H), 4.09-4.15 (m, 2H), 3.22 (s, 3H) (NH and OH missing)
A30		(400 MHz, D_2O) 9.71-9.79 (m, 2H), 8.86 (dd, 1H), 4.66 (s, 3H) (NH proton missing)

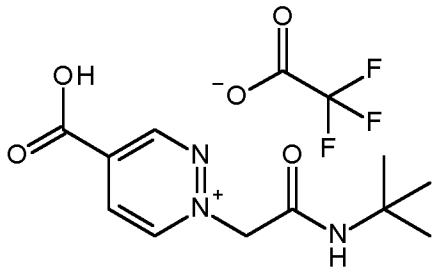
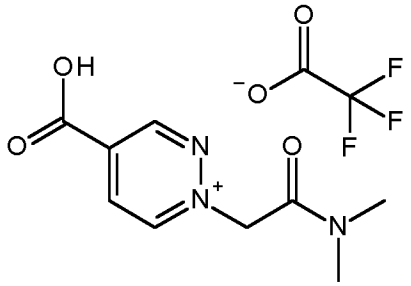
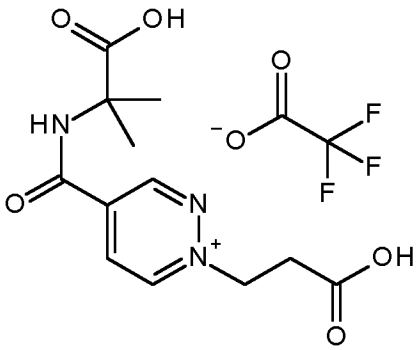
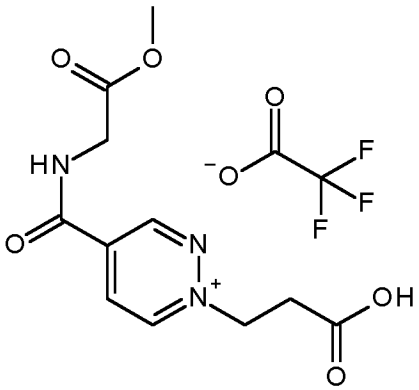
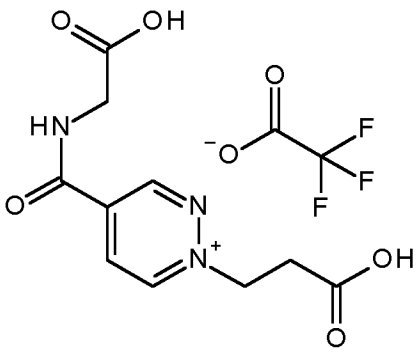
Cmpd. No.	Structure	^{1}H NMR
A31		(300 MHz, D_2O) 9.66 (d, 1H), 9.53 (s, 1H), 8.58 (dd, 1H), 7.44 (d, 2H), 6.96 (d, 2H), 5.89 (s, 2H), 3.74 (s, 3H) (CO_2H proton missing)
A32		(400 MHz, D_2O) 9.71 (d, 1H), 9.63 (d, 1H), 8.69 (dd, 1H), 4.80 (t, 2H), 2.05-2.03 (m, 2H), 1.27-1.17 (m, 10H), 0.75 (t, 3H) (CO_2H proton missing)
A33		(400 MHz, D_2O) 9.71 (d, 1H), 9.61 (s, 1H), 8.64 (dd, 1H), 4.76 (t, 2H), 2.07-2.00 (m, 2H), 1.36-1.31 (m, 2H), 0.91 (t, 3H) (CO_2H proton missing)
A34		(300 MHz, D_2O) 9.71 (d, 1H), 9.62 (s, 1H), 8.68 (dd, 1H), 4.81 (t, 2H), 2.08-1.99 (m, 2H), 1.26-1.18 (m, 6H), 0.77 (t, 3H) (CO_2H proton missing)
A35		(300 MHz, D_2O) 9.80 (d, 1H), 9.56 (s, 1H), 8.65 (dd, 1H), 7.95 (d, 2H), 7.53 (d, 2H), 6.03 (s, 2H) (CO_2H protons missing)
A36		(400 MHz, D_2O) 9.68 (d, 1H), 9.62 (s, 1H), 8.65 (dd, 1H), 4.64 (t, 2H), 2.38 (m, 1H), 0.92-0.90 (m, 6H) (CO_2H proton missing)
A37		(400 MHz, D_2O) 9.97 (d, 1H), 9.71 (d, 1H), 8.81 (dd, 1H), 5.75 (q, 2H) (CO_2H proton missing)
A38		(400 MHz, D_2O) 9.84 (d, 1H), 9.58 (s, 1H), 8.68 (dd, 1H), 7.76 (d, 2H), 7.61 (d, 2H), 6.06 (s, 2H) (CO_2H proton missing)
A39		(400 MHz, D_2O) 10.15 (d, 1H), 9.51 (d, 1H), 8.95 (dd, 1H), 8.54 (d, 1H), 7.96 (dd, 1H), 7.46 (d, 1H), 6.09 (s, 2H), 3.99 (s, 3H)

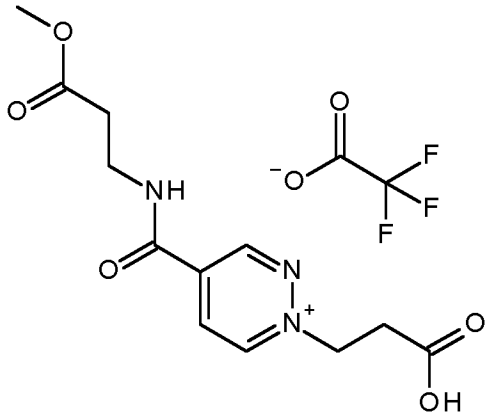
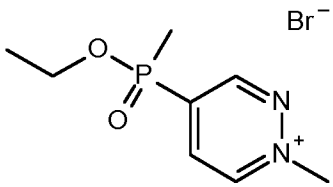
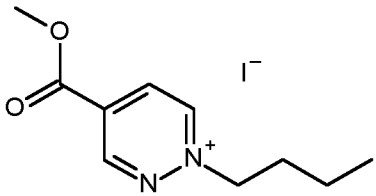
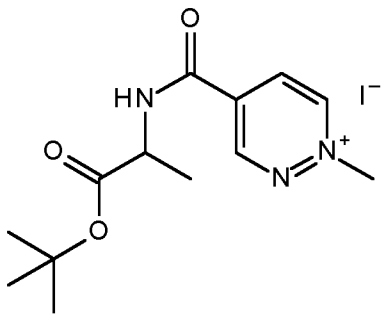
Cmpd. No.	Structure	^{1}H NMR
A40		(400 MHz, CD_3OD) 10.02 (br d, 1H), 9.90 (s, 1H), 9.08-8.96 (m, 1H), 5.08-5.03 (m, 2H), 4.20-4.09 (m, 2H) (CO_2H and OH protons missing)
A41		(400 MHz, CD_3OD) 9.83 - 9.80 (m, 1H), 9.80 - 9.76 (m, 1H), 8.91 - 8.86 (m, 1H), 4.74-4.70 (m, 3H), 3.34-3.18 (m, 3H) (NH proton missing) [isolated as a 7:3 mixture of isomers with: 10.07-10.04 (m, 1H), 9.60-9.55 (m, 1H), 8.86-8.83 (m, 1H), 4.74-4.70 (m, 3H), 3.34-3.18 (m, 3H) (NH proton missing)]
A42		(400 MHz, CD_3OD) 10.01 (d, 1H), 9.88 (d, 1H), 8.98 (dd, 1H), 5.04 (q, 2H), 4.14 (q, 2H), 3.41 (s, 3H) (OH and NH protons missing)
A43		(400 MHz, D_2O) 9.70 (d, 1H), 8.92 (t, 2H), 8.51 (d, 1H), 7.65 (m, 1H), 4.64 (s, 3H)
A44		(400 MHz, D_2O) 9.63 (s, 1H), 9.48 (s, 1H), 7.75-7.52 (m, 5H), 4.60 (s, 3H) (CO_2H proton missing)

Cmpd. No.	Structure	^{1}H NMR
A45		(400 MHz, D_2O) 9.87 (d, 1H), 9.74 (d, 1H), 8.87 (dd, 1H), 4.71 (s, 3H), 4.30 (s, 2H), 3.79 (s, 3H) (NH proton missing)
A46		(400 MHz, D_2O) 9.85 (d, 1H), 9.73 (d, 1H), 8.86 (dd, 1H), 4.70 (s, 3H), 4.25 (s, 2H) (NH and CO_2H protons missing)
A47		(400 MHz, D_2O) 9.86 (m, 1H), 9.71 (m, 1H), 8.82 (m, 1H), 4.72 (m, 3H), 3.74 (m, 2H), 2.76 (m, 2H) (NH and CO_2H protons missing)
A48		(400 MHz, D_2O) 9.96-9.94 (d, 1H), 8.98-8.96 (d, 2H), 8.91-8.89 (d, 1H), 7.73-7.70 (t, 1H), 4.74 (s, 3H), 3.86 (s, 3H)
A49		(400 MHz, D_2O) 9.80 (d, 1H), 9.66 (d, 1H), 8.80 (dd, 1H), 4.66 (s, 3H), 1.56 (s, 6H) (NH and CO_2H protons missing)

Cmpd. No.	Structure	^{1}H NMR
A50		(400 MHz, D_2O) 9.89 (d, 1H), 9.66 (d, 1H), 8.79 (dd, 1H), 5.09 (t, 2H), 4.53 (q, 1H), 3.19 (t, 2H), 1.44 (d, 3H) (NH and CO_2H protons missing)
A51		(400 MHz, D_2O) 9.93-10.05 (m, 1H), 9.71-9.82 (m, 1H), 8.80-8.94 (m, 1H), 5.10-5.25 (m, 2H), 4.64-4.74 (m, 1H), 3.76-3.83(m, 3H), 3.26-3.35 (m, 2H), 1.43-1.60 (m, 3H) (NH and CO_2H protons missing)
A52		(400 MHz, D_2O) 9.94 (d, 1H), 9.69 (d, 1H), 8.82 (dd, 1H), 5.14 (t, 2H), 3.73 (s, 3H), 3.25 (t, 2H), 1.56 (s, 6H) (NH and CO_2H protons missing)
A53		(400 MHz, D_2O) 9.81 (dd, 1H), 9.66 (d, 1H), 8.73 (dd, 1H), 4.95-5.00 (m, 2H), 4.11 - 4.19 (m, 2H), 2.92 (s, 2H), 1.50 (s, 6H) (NH, OH and CO_2H protons missing)
A54		(400 MHz, D_2O) 9.88 (d, 1H), 9.65 - 9.61 (m, 1H), 8.71 (dd, 1H), 5.09 (t, 2H), 3.63 (t, 2H), 3.20 (t, 2H), 2.66 (t, 2H) (NH and CO_2H protons missing)

Cmpd. No.	Structure	^{1}H NMR
A55		(400 MHz, D_2O) 9.89 (d, 1H), 9.75 - 9.71 (m, 1H), 8.81 (dd, 1H), 5.27 (t, 2H), 4.00 - 3.94 (m, 2H), 2.62 - 2.59 (m, 3H) (NH and CO_2H protons missing)
A56		(400 MHz, D_2O) 9.78 (d, 1H), 9.64 (d, 1H), 8.72 (dd, 1H), 5.11 - 5.04 (m, 2H), 3.08 - 3.01 (m, 2H), 2.59 - 2.54 (m, 3H) (NH and CO_2H protons missing)
A57		(400 MHz, D_2O) 9.84 (d, 1H), 9.67 - 9.62 (m, 1H), 8.75 (dd, 1H), 5.06 (t, 2H), 3.31 - 3.24 (m, 2H), 2.93 (s, 3H), 2.75 (s, 3H) (CO_2H proton missing)
A58		(400 MHz, D_2O) 9.94 (d, 1H), 9.76 - 9.71 (m, 1H), 8.82 (dd, 1H), 5.38 (t, 2H), 4.15 - 4.09 (m, 2H), 3.14 - 3.10 (m, 3H) (CO_2H proton missing)
A59		(400 MHz, D_2O) 9.78 - 9.81 (m, 1H), 9.68 (d, 1H), 8.81 (dd, 1H), 5.69 (s, 2H), 2.79 (s, 3H) (NH and CO_2H protons missing)
A60		(400 MHz, D_2O) 9.82 (d, 1H), 9.72 (d, 1H), 8.83 (dd, 1H), 4.98 (t, 2H), 4.13 (t, 2H), 1.55 (s, 6H) (NH, OH and CO_2H protons missing)

Cmpd. No.	Structure	^{1}H NMR
A61		(400 MHz, D_2O) 9.75 (dd, 1H), 9.69 (d, 1H), 8.82 (dd, 1H), 5.61 (s, 2H), 1.30 (s, 9H) (NH and CO_2H protons missing)
A62		(400 MHz, D_2O) 9.62 - 9.70 (m, 2H), 8.74 - 8.80 (m, 1H), 5.94 (s, 2H), 3.07 (s, 3H), 2.90 (s, 3H) (CO_2H proton missing)
A63		(400 MHz, D_2O) 9.93 (d, 1H), 9.70 (d, 1H), 8.82 (dd, 1H), 5.14 (t, 2H), 3.24 (t, 2H), 1.56 (s, 6H) (NH and CO_2H protons missing)
A64		(400 MHz, D_2O) 9.98-10.06 (m, 1H), 9.74-9.81 (m, 1H), 8.83-8.93 (m, 1H), 5.17-5.24 (m, 2H), 4.27-4.32 (m, 2H), 3.79 (s, 3H), 3.26-3.34 (m, 2H) (NH and CO_2H protons missing)
A65		(400 MHz, D_2O) 9.92 (d, 1H), 9.70 (d, 1H), 8.81 (dd, 1H), 5.11 (t, 2H), 4.17 (s, 2H), 3.21 (t, 2H) (NH and CO_2H protons missing)

Cmpd. No.	Structure	^{1}H NMR
A66		(400 MHz, D_2O) 9.93 (d, 1H), 9.68 (d, 1H), 8.76 (dd, 1H), 5.14 (t, 2H), 3.71 - 3.64 (m, 5H), 3.25 (t, 2H), 2.71 (t, 2H) (NH and CO_2H protons missing)
A67		(400 MHz, CD_3OD) 10.03 (d, 1H), 9.83-9.78 (m, 1H), 9.04-8.97 (m, 1H), 4.79-4.77 (m, 3H), 4.17-4.01 (m, 2H), 2.05-1.98 (m, 3H), 1.41-1.36 (m, 3H)
A68		(400 MHz, D_2O) 9.89 (d, 1H), 9.82 (s, 1H), 8.95 (m, 1H), 4.89 (t, 2H), 4.04 (s, 3H), 2.09-2.00 (m, 2H), 1.37-1.32 (m, 2H), 0.90 (t, 3H)
A69		(400 MHz, CD_3OD) 9.97 (d, 1H), 9.82 - 9.77 (m, 1H), 8.96 - 8.90 (m, 1H), 4.73 (s, 3H), 4.53 (d, 1H), 1.59 - 1.50 (m, 3H), 1.49 (s, 9H) (NH proton missing)

BIOLOGICAL EXAMPLES

Post-emergence efficacy

Seeds of a variety of test species were sown in standard soil in pots. After cultivation for 14 days (post-emergence) under controlled conditions in a glasshouse (at 24/16°C, day/night; 14 hours light; 65 % humidity), the plants were sprayed with an aqueous spray solution derived from the dissolution of the technical active ingredient formula (I) in a small amount of acetone and a special solvent and emulsifier mixture referred to as IF50 (11.12% Emulsogen EL360 TM + 44.44% N-methylpyrrolidone + 44.44% Dowanol DPM glycol ether), to create a 50g/l solution which was then diluted to required concentration using 0.25% or 1% Empicol ESC70 (Sodium lauryl ether sulphate) + 1% ammonium sulphate as diluent.

The test plants were then grown in a glasshouse under controlled conditions (at 24/16°C, day/night; 14 hours light; 65 % humidity) and watered twice daily. After 13 days the test was evaluated (100 = total damage to plant; 0 = no damage to plant).

Test plants:

Ipomoea hederacea (IPOHE), *Euphorbia heterophylla* (EPHHL), *Chenopodium album* (CHEAL), *Amaranthus palmeri* (AMAPA), *Lolium perenne* (LOLPE), *Digitaria sanguinalis* (DIGSA), *Eleusine indica* (ELEIN), *Echinochloa crus-galli* (ECHCG), *Setaria faberi* (SETFA)

The results are shown in Table B (below). A value of n/a indicates that this combination of weed and test compound was not tested/assessed.

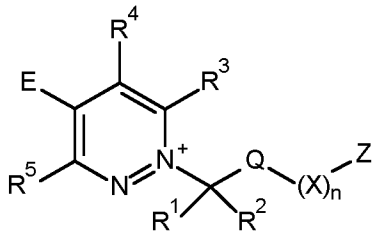
Table B – Control of weed species by compounds of formula (I) after post-emergence application

Compound Number	Application Rate g/Ha	AMAPA	CHEAL	EPHHL	IPOHE	ELEIN	LOLPE	DIGSA	SETFA	ECHCG
A1	1000	50	30	60	50	70	80	80	80	80
A2	1000	20	30	40	20	40	10	30	10	10
A3	1000	50	60	80	70	90	90	90	90	100
A4	1000	90	70	70	70	70	70	80	90	90
A5	1000	70	60	70	90	90	70	90	70	100
A6	1000	20	40	20	20	80	30	60	60	60
A7	1000	20	20	50	60	30	20	30	10	10
A8	500	40	30	20	10	30	10	20	10	10
A9	1000	80	70	70	100	90	90	90	90	90
A10	1000	50	10	50	40	20	10	30	50	40
A11	1000	60	60	50	50	40	30	30	20	40
A12	1000	40	20	40	30	10	0	20	20	20
A13	1000	20	20	10	10	40	40	50	30	40
A14	1000	10	10	20	10	20	0	20	30	30
A15	1000	10	10	40	30	20	0	20	30	10
A16	1000	10	20	20	20	10	0	30	30	20
A17	1000	30	20	30	10	20	0	30	20	20
A18	1000	60	60	70	80	70	30	70	70	70
A19	1000	50	80	40	70	50	30	60	70	50
A20	1000	10	40	40	10	20	10	10	0	10
A21	1000	30	50	30	40	60	0	50	30	20
A22	1000	30	40	10	10	20	0	30	10	10
A23	1000	30	30	50	30	50	10	40	20	40
A24	1000	50	60	40	50	10	30	30	80	80
A25	1000	20	40	40	20	10	0	20	30	50
A26	1000	10	10	20	30	30	20	30	50	30
A27	500	30	30	20	20	10	10	20	0	10
A28	1000	100	90	90	90	90	40	90	90	60
A29	1000	50	90	50	90	70	40	80	70	30
A30	1000	30	50	60	30	10	0	20	40	20
A31	1000	60	30	20	10	10	20	10	10	10
A32	1000	20	0	20	0	0	0	20	0	0
A33	1000	50	20	50	10	10	10	10	30	20
A34	1000	70	60	40	30	10	10	20	20	20
A35	1000	0	0	10	10	0	0	10	0	10
A36	1000	30	10	20	20	20	20	50	10	20
A37	1000	0	0	20	10	10	20	20	10	70

Compound Number	Application Rate g/Ha	AMAPA	CHEAL	EPHHL	IPOHE	ELEIN	LOLPE	DIGSA	SETFA	ECHCG
A38	1000	20	30	30	20	10	20	20	10	30
A39	1000	0	0	0	30	10	10	10	0	10
A40	1000	100	70	80	100	90	60	50	90	70
A41	1000	40	100	80	90	60	20	80	80	50
A42	1000	20	90	40	70	50	20	60	80	50
A44	500	40	70	30	20	10	0	20	10	10
A46	500	60	10	-	70	-	60	90	90	90
A47	500	40	60	-	50	70	30	50	10	40
A48	500	20	40	30	20	10	10	10	0	10
A49	500	90	80	90	100	100	70	100	90	100
A50	500	100	70	80	70	80	30	90	90	90
A51	500	90	90	80	20	40	50	80	80	70
A52	500	100	100	90	20	100	70	100	100	70
A53	500	100	100	60	100	90	60	90	90	40
A54	500	100	30	40	10	60	40	90	100	80
A55	500	40	30	70	50	30	60	100	80	60
A56	500	100	40	0	0	90	100	70	60	100
A57	500	10	30	10	0	80	80	90	60	60
A58	500	60	60	20	30	80	80	80	40	70
A59	130	0	10	20	10	10	10	30	60	40
A60	500	70	90	40	70	100	70	90	100	70
A61	500	70	20	40	40	80	50	50	70	60
A63	500	90	30	60	20	90	10	90	90	90
A64	500	90	70	80	40	90	60	90	90	80
A65	500	100	60	70	40	90	20	90	90	90
A66	500	100	100	20	40	100	50	100	90	40

CLAIMS

1. Use as a herbicide, of a compound of formula (I) or an agronomically acceptable salt or zwitterionic species thereof:



(I)

wherein

R^1 is selected from the group consisting of hydrogen, halogen, C_1-C_6alkyl, C_2-C_6alkenyl, C_2-C_6alkynyl, C_3-C_6cycloalkyl, C_1-C_6haloalkyl, -OR^7, -OR^{15a}, -$N(R^6)S(O)_2R^{15}$, -$N(R^6)C(O)R^{15}$, -$N(R^6)C(O)OR^{15}$, –$N(R^6)C(O)NR^{16}R^{17}$, -$N(R^6)CHO$, -$N(R^{7a})_2$ and –$S(O)_rR^{15}$;

R^2 is selected from the group consisting of hydrogen, halogen, C_1-C_6alkyl and C_1-C_6haloalkyl;

and wherein when R^1 is selected from the group consisting of –OR^7, -OR^{15a}, -$N(R^6)S(O)_2R^{15}$, -$N(R^6)C(O)R^{15}$, -$N(R^6)C(O)OR^{15}$, –$N(R^6)C(O)NR^{16}R^{17}$, -$N(R^6)CHO$, -$N(R^{7a})_2$ and –$S(O)_rR^{15}$, R^2 is selected from the group consisting of hydrogen and C_1-C_6alkyl; or

R^1 and R^2 together with the carbon atom to which they are attached form a C_3-C_6cycloalkyl ring or a 3- to 6- membered heterocyclyl, which comprises 1 or 2 heteroatoms individually selected from N and O;

Q is $(CR^{1a}R^{2b})_m$;

m is 0, 1, 2 or 3;

each R^{1a} and R^{2b} are independently selected from the group consisting of hydrogen, halogen, C_1-C_6alkyl, C_1-C_6haloalkyl, -OH, -OR^7, -OR^{15a}, -NH_2, -NHR^7, -NHR^{15a}, -$N(R^6)CHO$, -$NR^{7b}R^{7c}$ and –$S(O)_rR^{15}$; or

each R^{1a} and R^{2b} together with the carbon atom to which they are attached form a C_3-C_6cycloalkyl ring or a 3- to 6- membered heterocyclyl, which comprises 1 or 2 heteroatoms individually selected from N and O;

R^3, R^4 and R^5 are independently selected from the group consisting of hydrogen, halogen, nitro, cyano, -NH_2, -NR^6R^7, -OH, -OR^7, -$S(O)_rR^{12}$, -$NR^6S(O)_rR^{12}$, C_1-C_6alkyl, C_1-C_6haloalkyl, C_3-C_6cycloalkyl, C_3-C_6halocycloalkyl, C_3-C_6cycloalkoxy, C_2-C_6alkenyl, C_2-C_6haloalkenyl, C_2-C_6alkynyl, C_1-C_3alkoxyC_1-C_3alkyl-, hydroxyC_1-C_6alkyl-, C_1-C_6haloalkoxy, C_1-C_3haloalkoxyC_1-C_3alkyl-, C_1-C_6alkoxycarbonyl, C_3-C_6alkenyloxy, C_3-C_6alkynyloxy, C_1-C_6alkylcarbonyl, C_1-C_6alkylaminocarbonyl, di-C_1-C_6alkylaminocarbonyl, -$C(R^8)$=NOR^8, phenyl and heteroaryl,

wherein the heteroaryl moiety is a 5- or 6-membered monocyclic aromatic ring which comprises 1, 2, 3 or 4 heteroatoms individually selected from N, O and S, and wherein any of said phenyl or heteroaryl moieties are optionally substituted by 1, 2 or 3 substituents R^9, which may be the same or different;

each R^6 is independently selected from hydrogen and C_1-C_6alkyl;

each R^7 is independently selected from the group consisting of C_1-C_6alkyl, $-S(O)_2R^{15}$, $-C(O)R^{15}$, $-C(O)OR^{15}$ and $–C(O)NR^{16}R^{17}$;

each R^{7a} is independently selected from the group consisting of $-S(O)_2R^{15}$, $-C(O)R^{15}$, $-C(O)OR^{15}$ $–C(O)NR^{16}R^{17}$ and $–C(O)NR^6R^{15a}$;

R^{7b} and R^{7c} are independently selected from the group consisting of C_1-C_6alkyl, $-S(O)_2R^{15}$, $-C(O)R^{15}$, $-C(O)OR^{15}$, $–C(O)NR^{16}R^{17}$ and phenyl, and wherein said phenyl is optionally substituted by 1, 2 or 3 R^9 substituents, which may be the same or different; or

R^{7b} and R^{7c} together with the nitrogen atom to which they are attached form a 4- to 6-membered heterocyclyl ring which optionally comprises one additional heteroatom individually selected from N, O and S; and

each R^9 is independently selected from the group consisting of halogen, cyano, -OH, $-N(R^6)_2$, C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4haloalkyl and C_1-C_4haloalkoxy;

E is selected from the group consisting of of $–C(O)OR^{10}$, -CHO, $-C(O)R^{24}$, $-C(O)NHOR^{11}$, -C(O)NHCN, $-C(O)NHR^{25}$, $-S(O)_2NHR^{25}$, $-C(O)NR^6(CR^6_2)_qC(O)(OR^{10})$, $-C(O)NR^6(CR^6_2)_qS(O)_2(OR^{10})$ and $-C(O)NR^6(CR^6_2)_qP(O)(R^{13})(OR^{10})$, $-(CR^6_2)_qC(O)OR^{10}$, $-(CR^6_2)_qS(O)_2(OR^{10})$, $-(CR^6_2)_qP(O)(R^{13})(OR^{10})$, $-OC(O)NHOR^{11}$, $-O(CR^6_2)_qC(O)OR^{10}$, -OC(O)NHCN, $-O(CR^6_2)_qS(O)_2(OR^{10})$, $-O(CR^6_2)_qP(O)(R^{13})(OR^{10})$, $-NR^6C(O)NHOR^{11}$, $-NR^6C(O)NHCN$, $-C(O)NHS(O)_2R^{12}$, $-OC(O)NHS(O)_2R^{12}$, $-NR^6C(O)NHS(O)_2R^{12}$, $-S(O)_2OR^{10}$, $-OS(O)_2OR^{10}$, $-NR^6S(O)_2OR^{10}$, $-NR^6S(O)OR^{10}$, $-NHS(O)_2R^{14}$, $-S(O)OR^{10}$, $-S(CR^6_2)_qC(O)OR^{10}$, $-S(CR^6_2)_qS(O)_2(OR^{10})$, $-S(CR^6_2)_qP(O)(R^{13})(OR^{10})$, $-OS(O)OR^{10}$, $-S(O)_2NHCN$, $-S(O)_2NHC(O)R^{18}$, $-S(O)_2NHS(O)_2R^{12}$, $-OS(O)_2NHCN$, $-OS(O)_2NHS(O)_2R^{12}$, $-OS(O)_2NHC(O)R^{18}$, $-NR^6S(O)_2NHCN$, $-NR^6S(O)_2NHC(O)R^{18}$, $–N(OH)C(O)R^{15}$, $–ONHC(O)R^{15}$, $-NR^6S(O)_2NHS(O)_2R^{12}$, $-P(O)(R^{13})(OR^{10})$, $-P(O)H(OR^{10})$, $-OP(O)(R^{13})(OR^{10})$, $-NR^6P(O)(R^{13})(OR^{10})$ and tetrazole;

q is 1-3

X is selected from the group consisting of C_3-C_6cycloalkyl, phenyl, a 5- or 6- membered heteroaryl, which comprises 1, 2, 3 or 4 heteroatoms individually selected from N, O and S, and a 4- to 6- membered heterocyclyl, which comprises 1, 2 or 3 heteroatoms individually selected from N, O and S, and wherein said cycloalkyl, phenyl, heteroaryl or heterocyclyl moieties are optionally substituted by 1 or 2 substituents, which may be the same or different, selected from R^9, and wherein the aforementioned CR^1R^2, Q and Z moieties may be attached at any position of said cycloalkyl, phenyl, heteroaryl or heterocyclyl moieties;

n is 0 or 1;

Z is selected from the group consisting of hydrogen, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_6alkoxyC_1-C_6alkyl, nitro, halo, haloalkoxy, cyano, $-NH_2$, -OH, $-OR^7$, $-C(O)R^{15}$, $-C(O)NR^{16}R^{17}$, $-C(O)OR^{10}$, -CHO, $-C(O)NHOR^{11}$, -C(O)NHCN, $-OC(O)NHOR^{11}$, -OC(O)NHCN, $-NR^6C(O)NHOR^{11}$, $-NR^6C(O)NHCN$, $-C(O)NHS(O)_2R^{12}$, $-OC(O)NHS(O)_2R^{12}$, $-NHR^7$, $-N(R^7)_2$, $-NR^6C(O)NHS(O)_2R^{12}$, $-NR^6S(O)_2R^{15}$, $-S(O)_2OR^{10}$, $-OS(O)_2OR^{10}$, $-NR^6S(O)_2OR^{10}$, $-NR^6S(O)OR^{10}$, $-NHS(O)_2R^{14}$, $-S(O)_rR^{15}$, $-S(O)OR^{10}$, $-S(O)_2NR^{16}R^{17}$, $-OS(O)OR^{10}$, $-S(O)_2NHCN$, $-S(O)_2NHC(O)R^{18}$, $-S(O)_2NHS(O)_2R^{12}$, $-OS(O)_2NHCN$, $-OS(O)_2NHS(O)_2R^{12}$, $-OS(O)_2NHC(O)R^{18}$, $-NR^6S(O)_2NHCN$, $-NR^6S(O)_2NHC(O)R^{18}$, $-N(OH)C(O)R^{15}$, $-ONHC(O)R^{15}$, $-NR^6S(O)_2NHS(O)_2R^{12}$, $-P(O)(R^{13})(OR^{10})$, $-P(O)H(OR^{10})$, $-OP(O)(R^{13})(OR^{10})$, $-NR^6P(O)(R^{13})(OR^{10})$, tetrazole;

R^{10} is selected from the group consisting of hydrogen, C_1-C_6alkyl, phenyl and benzyl, and wherein said phenyl or benzyl are optionally substituted by 1, 2 or 3 R^9 substituents, which may be the same or different;

R^{11} is selected from the group consisting of hydrogen, C_1-C_6alkyl and phenyl, and wherein said phenyl is optionally substituted by 1, 2 or 3 R^9 substituents, which may be the same or different;

R^{12} is selected from the group consisting of C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, -OH, $-N(R^6)_2$ and phenyl, and wherein said phenyl is optionally substituted by 1, 2 or 3 R^9 substituents, which may be the same or different;

R^{13} is selected from the group consisting of -OH, C_1-C_6alkyl, C_1-C_6alkoxy, C_1-C_6haloalkoxy, -O-propargyl, –O-allyl and phenyl;

R^{14} is C_1-C_6haloalkyl;

R^{15} is selected from the group consisting of C_1-C_6alkyl and phenyl, and wherein said phenyl is optionally substituted by 1, 2 or 3 R^9 substituents, which may be the same or different;

R^{15a} is phenyl, wherein said phenyl is optionally substituted by 1, 2 or 3 R^9 substituents, which may be the same or different;

R^{16} and R^{17} are independently selected from the group consisting of hydrogen and C_1-C_6alkyl; or

R^{16} and R^{17} together with the nitrogen atom to which they are attached form a 4- to 6-membered heterocyclyl ring which optionally comprises one additional heteroatom individually selected from N, O and S;

R^{18} is selected from the group consisting of hydrogen, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, $-N(R^6)_2$ and phenyl, and wherein said phenyl is optionally substituted by 1, 2 or 3 R^9 substituents, which may be the same or different;

R^{24} is a peptide moiety comprising one, two or three amino acid moieties independently selected from the group consisting of Ala, Cys, Asp, Glu, Phe, Gly, His, Ile, Lys, Leu, Met, Asn, Pro, Gln, Arg, Ser, Thr, Val, Trp and Tyr, wherein said peptide moiety is bonded to the rest of the molecule via a nitrogen atom in the amino acid moiety;

R^{25} is selected from the group consisting of 5- or 6- membered heteroaromatic moieties, optionally substituted with one or more groups independently selected from R^2 or;

R^{25} is selected from the group consisting of 5- or 6- membered heteroaromatic moieties, containing at least two N atoms, optionally substituted with one or more groups independently selected from R^9;

and

r is 0, 1 or 2;

with the proviso that the use of pyridazocidin as herbicide is excluded.

2. A compound of formula (I) as defined in claim 1, wherein R^3, R^4 and R^5 are each independently hydrogen, C_1-C_6alkyl, or C_1-C_6alkoxy, with the proviso that said compound is not pyridazocidin.

3. The compound of claim 2, wherein R^1 and R^2 are independently selected from the group consisting of hydrogen and C_1-C_6alkyl.

4. The compound according to claim 2 or claim 3, wherein each R^{1a} and R^{2b} are independently selected from the group consisting of hydrogen, C_1-C_6alkyl, –OH and $–NH_2$

5. The compound according to any one of claims 2 to 4, wherein m is 0.

6. The compound according to any one of claims 2 to 5, wherein R^3 and R^4 are independently selected from the group consisting of hydrogen, C_1-C_6alkyl, and C_1-C_6alkoxy.

7. The compound according to any one of claims 2 to 6, wherein R^3 , R^4 and R^5 are independently hydrogen or methyl.

8. The compound according to any one of claims 2 to 7, wherein E is $-C(O)OR^{10}$, $-C(O)NHS(O)_2R^{12}$, $-C(O)R^{24}$, $-P(O)(R^{13})(OR^{10})$; or $C(O)NR^6(CR^6{}_2)_qC(O)(OR^{10})$.

9. A compound according to any one of claims 2 to 8, wherein Z is selected from the group consisting of hydrogen, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_6alkoxy, $-C(O)OR^{10}$, $-C(O)NHS(O)_2R^{12}$, $-S(O)_2OR^{10}$, and $-P(O)(R^{13})(OR^{10})$.

10. The compound according to claim 9, wherein Z is hydrogen, C_1-C_6alkyl or C_1-C_6hydroxyalkyl.

11. The compound according to any one of claims 2 to 10, wherein n is 0.

12. Use of a compound as defined in any one of claims 2 to 11 as a herbicide.

13. An agrochemical composition comprising a herbicidally effective amount of a compound of formula (I) as defined in any one of claims 1 to 11 and an agrochemically-acceptable diluent or carrier.

14. A method of controlling or preventing undesirable plant growth, wherein a herbicidally effective amount of a compound of formula (I) as defined in any one of claims 1 to 11, or a herbicidal composition according to claim 13, is applied to the plants, to parts thereof or to the locus thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/053008

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D237/24 C07D403/04 A01N43/58 C07F9/38
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D A01N C07F

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

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

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 2019/185875 A1 (SYNGENTA PARTICIPATIONS AG [CH]) 3 October 2019 (2019-10-03) claims 1-15; tables A,B; compounds A12,A28	1-14
A	B. CLIFFORD GERWICK ET AL: "Pyridazocidin, a new microbial phytotoxin with activity in the Mehler reaction", WEED SCIENCE., vol. 45, no. 5, 1 January 1997 (1997-01-01), pages 654-657, XP55657976, US ISSN: 0043-1745, DOI: 10.1017/S004317450009328 the whole document	1-14

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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

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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	Date of mailing of the international search report
13 May 2020	25/05/2020

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

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/053008

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2006/000333 A1 (BAYER CROPSCIENCE AG [DE]; FISCHER RUEDIGER [DE] ET AL.) 5 January 2006 (2006-01-05) cited in the application claims 1-15 -----	1-14

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2020/053008

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