



(51) International Patent Classification:

C07D 333/24 (2006.01) C07D 333/28 (2006.01)

A01N 43/10 (2006.01) C07D 333/38 (2006.01)

EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(21) International Application Number:

PCT/EP2022/062923

(22) International Filing Date:

12 May 2022 (12.05.2022)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

21174852.0 19 May 2021 (19.05.2021) EP

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,

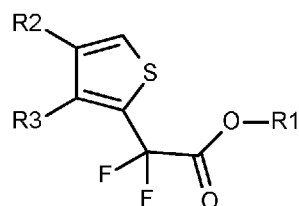
Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report (Art. 21(3))

(54) Title: THIOPHENE DERIVATIVES AND WEED CONTROL METHOD



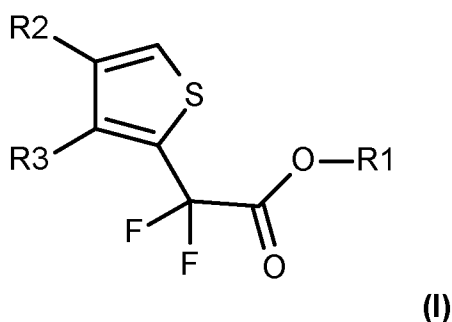
(57) Abstract: The present invention relates to a compound of Formula (I), (I) wherein R¹, R² and R³ are as defined herein and its use as a herbicide. The invention further relates to herbicidal compositions which comprise a compound of Formula (I) and to the use of (I) compounds of Formula (I) for controlling weeds, in particular in crops of useful plants.



THIOPHENE DERIVATIVES AND WEED CONTROL METHOD

The present invention relates to the use of certain compounds as herbicides, to herbicidal compositions which comprise the compounds, and to their use for controlling weeds, in particular in crops of useful plants, or for inhibiting plant growth.

The present invention is based on the finding that certain difluoro phenylacetic acids of formula (I) as defined herein, exhibit surprisingly good herbicidal activity. Thus, according to the present invention there is provided the use of a compound of Formula (I),



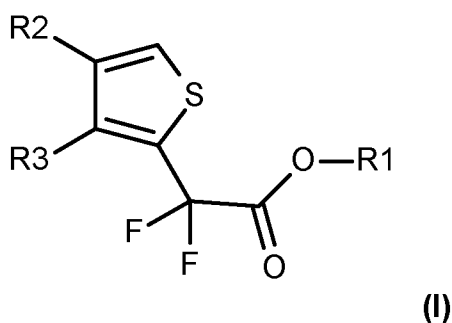
wherein

R_1 is selected from the group consisting of hydrogen, C1-C3alkyl and benzyl; and

each R_2 and R_3 is independently selected from the group consisting of hydrogen, halogen, methyl, cyano and C₁-haloalkyl, with the proviso that R_2 and R_3 are not both hydrogen,

or an agronomically acceptable salt of said compound, as a herbicide.

According to a second aspect of the present invention, there is provided a compound of formula (I) or an agronomically acceptable salt thereof:



wherein

R_1 is selected from the group consisting of hydrogen, C1-C3alkyl and benzyl;

each R2 and R3 is independently selected from the group consisting of hydrogen, halogen, methyl, cyano and C₁-haloalkyl, with the proviso that

when R1 is hydrogen, R3 is hydrogen, R2 is not Chlorine, Bromine, cyano or methyl;

when R1 is hydrogen, R2 is hydrogen, R3 is not Chlorine, Bromine, Iodine or methyl;

when R1 is hydrogen, R2 is methyl, R3 is not Chlorine, Bromine or Iodine; and

when R1 is ethyl, R2 is hydrogen, R3 is not hydrogen, Chlorine, Bromine or methyl.

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.

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, the term "C₁-C₃alkyl" refers to a straight or branched hydrocarbon chain radical consisting solely of carbon and hydrogen atoms, containing no unsaturation, having from one to five carbon atoms, and which is attached to the rest of the molecule by a single bond. Examples of C₁-C₃alkyl include, but are not limited to, methyl (Me), ethyl (Et), *n*-propyl, 1-methylethyl (iso-propyl).

As used herein, the term "C₁haloalkyl" refers to a methyl radical substituted by one or more of the same or different halogen atoms. Examples of C₁haloalkyl include, but are not limited to chloromethyl, fluoromethyl, difluoromethyl and trifluoromethyl.

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.

Suitable agronomically acceptable salts of the present invention can be with cations that 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.

In a preferred embodiment, the agrochemically acceptable salt is selected from the group consisting of sodium, potassium, aluminium, dimethylamine (DMA), diglycolamine (DGA) and choline salt. In an especially preferred embodiment, the agrochemically acceptable salt is choline salt.

The following list provides definitions, including preferred definitions, for substituents R^1 , R^2 and R^3 with reference to the compounds of formula (I) according to the invention. For any one of these substituents, 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 and C1-C2alkyl, more preferably hydrogen.

Preferably R^2 is selected from the group consisting of hydrogen and halogen, more preferably halogen, most preferably chlorine.

Preferably R^3 is selected from the group consisting of hydrogen and halogen, more preferably halogen, most preferably chlorine.

A preferred subset of compounds is one in which R^1 is selected from the group consisting of hydrogen and C1-C2alkyl; and each of R^2 and R^3 is selected from the group consisting of hydrogen and halogen

A more preferred subset of compounds is one in which R^1 is hydrogen; and each of R^2 and R^3 is halogen. A preferred embodiment in this subset is a compound (I) in which R^1 is hydrogen; and each of R^2 and R^3 is Chlorine.

Table of Examples

Table 1 below discloses 48 compounds designated compound numbers 1-1 to 1-48 respectively, of formula (I), wherein R^1 is hydrogen and wherein the values of R^2 and R^3 are as given in Table 1.

Table 1

Compound Number	R^2	R^3
1-1	F	H
1-2	Cl	H
1-3	Br	H
1-4	CN	H
1-5	Me	H
1-6	CF ₃	H
1-7	H	F
1-8	F	F
1-9	Cl	F
1-10	Br	F
1-11	CN	F
1-12	Me	F
1-13	CF ₃	F
1-14	H	Cl
1-15	F	Cl
1-16	Cl	Cl
1-17	Br	Cl
1-18	CN	Cl
1-19	Me	Cl
1-20	CF ₃	Cl
1-21	H	Br
1-22	F	Br
1-23	Cl	Br

Compound Number	R ²	R ³
1-24	Br	Br
1-25	CN	Br
1-26	Me	Br
1-27	CF ₃	Br
1-28	H	CN
1-29	F	CN
1-30	Cl	CN
1-31	Br	CN
1-32	CN	CN
1-33	Me	CN
1-34	CF ₃	CN
1-35	H	Me
1-36	F	Me
1-37	Cl	Me
1-38	Br	Me
1-39	CN	Me
1-40	Me	Me
1-41	CF ₃	Me
1-42	H	CF ₃
1-43	F	CF ₃
1-44	Cl	CF ₃
1-45	Br	CF ₃
1-46	CN	CF ₃
1-47	Me	CF ₃
1-48	CF ₃	CF ₃

48 compounds of formula (I), wherein R¹ is methyl and the values of R² and R³ are as given in Table 1 for compounds 1-1 to 1-48, are designated as compound numbers 2-1 to 2-48 respectively.

48 compounds of formula (I), wherein R^1 is ethyl and the values of R^2 and R^3 are as given in Table 1 for compounds 1-1 to 1-48, are designated as compound numbers 3-1 to 3-48 respectively.

48 compounds of formula (I), wherein R^1 is benzyl and the values of R^2 and R^3 are as given in Table 1 for compounds 1-1 to 1-48, are designated as compound numbers 4-1 to 4-48 respectively.

48 compounds of formula (I), wherein R^1 is lithium and the values of R^2 and R^3 are as given in Table 1 for compounds 1-1 to 1-48, are designated as compound numbers 5-1 to 5-48 respectively.

48 compounds of formula (I), wherein R^1 is sodium and the values of R^2 and R^3 are as given in Table 1 for compounds 1-1 to 1-48, are designated as compound numbers 6-1 to 6-48 respectively.

48 compounds of formula (I), wherein R^1 is ammonium and the values of R^2 and R^3 are as given in Table 1 for compounds 1-1 to 1-48, are designated as compound numbers 7-1 to 7-48 respectively.

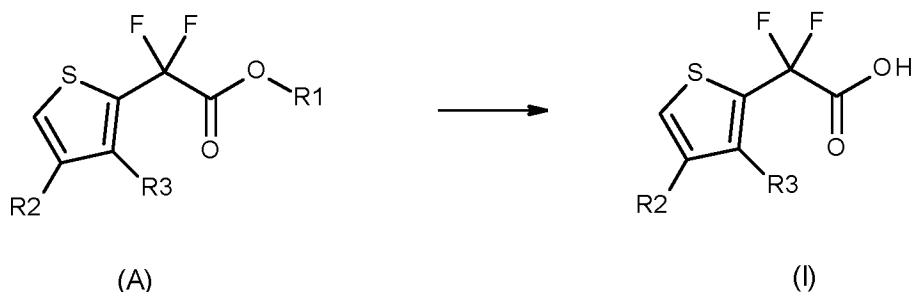
48 compounds of formula (I), wherein R^1 is diisopropylammonium and the values of R^2 and R^3 are as given in Table 1 for compounds 1-1 to 1-48, are designated as compound numbers 8-1 to 8-48 respectively.

48 compounds of formula (I), wherein R^1 is N,N,N-trimethylethanolammonium and the values of R^2 and R^3 are as given in Table 1 for compounds 1-1 to 1-48, are designated as compound numbers 9-1 to 9-48 respectively.

Compounds of the invention may be prepared by techniques known to the person skilled in the art of organic chemistry. General methods for the production of compounds of formula (I) are described below. Unless otherwise stated in the text, the substituents R^1 , R^2 and R^3 are as defined hereinbefore. The starting materials used for the preparation of the compounds of the invention may be purchased from usual commercial suppliers or may be prepared by known methods. The starting materials as well as the intermediates may be purified before use in the next step by state of the art methodologies such as chromatography, crystallization, distillation and filtration.

Compounds of formula (I) may be prepared from esters of formula (A) as shown in reaction scheme 1.

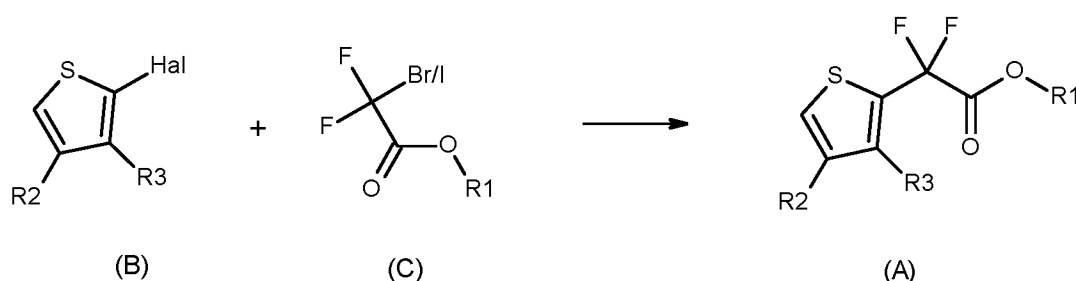
Reaction scheme 1



For example, a compound of formula (A), wherein R1 represents methyl or ethyl, may be treated with a base, such as lithium hydroxide, in a suitable solvent such as a mixture of ethanol and water.

Compounds of formula (A) may be prepared from aryl halides of formula (B) and alkyl halides of formula (C) as shown in reaction scheme 2.

Reaction scheme 2



For example, a mixture of a compound of formula (B), wherein Hal represents a halogen atom, for example a chlorine, bromine or iodine atom, and a compound of formula (C), wherein R¹ represents methyl or ethyl, may be treated with a metal, such as copper, in a suitable solvent such as dimethyl sulfoxide.

Thiophene halides of formula (B) are commercially available or may be prepared by methods well known in the literature.

Alkyl bromides or alkyl iodides of formula (C) are available or can be prepared by methods known in the literature.

One skilled in the art will realise that it is often possible to alter the order in which the transformations described above are conducted, or to combine them in alternative ways to prepare a wide range of compounds of formula (I). Multiple steps may also be combined in a single reaction. All such variations are contemplated within the scope of the invention.

The skilled person will also be aware that some reagents will be incompatible with certain values or combinations of the substituents R¹, R² and R³ as defined herein, and any additional steps, such as protection and/or deprotection steps, which are necessary to achieve the desired transformation will be clear to the skilled person.

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 dibutyl naphthalenesulfonate; 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 C₈-C₂₂ fatty acids, especially the methyl derivatives of C₁₂-C₁₈ 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.

The compounds of present invention can also be used in mixture with one or more additional herbicides and/or plant growth regulators. Examples of such additional herbicides or plant growth regulators include acetochlor, acifluorfen (including acifluorfen-sodium), aclonifen, ametryn, amicarbazone, aminopyralid, aminotriazole, atrazine, beflubutamid-M, benquitrione, bensulfuron (including bensulfuron-methyl), bentazone, bicyclopyrone, bilanafos, bipyrazone, bispyribac-sodium, bixlozone, bromacil, bromoxynil, butachlor, butafenacil, carfentrazone (including carfentrazone-ethyl), cloransulam (including

cloransulam-methyl), chlorimuron (including chlorimuron-ethyl), chlorotoluron, chlorsulfuron, cinmethylin, clacyfos, clethodim, clodinafop (including clodinafop-propargyl), clomazone, clopyralid, cyclopyranil, cyclopyrimorate, cyclosulfamuron, cyhalofop (including cyhalofop-butyl), 2,4-D (including the choline salt and 2-ethylhexyl ester thereof), 2,4-DB, desmedipham, dicamba (including the aluminium, aminopropyl, bis-aminopropylmethyl, choline, dichloroprop, diglycolamine, dimethylamine, dimethylammonium, potassium and sodium salts thereof) diclosulam, diflufenican, diflufenzopyr, dimethachlor, dimethenamid-P, dioxopyrithione, diquat dibromide, diuron, epyrifenacil, ethalfluralin, ethofumesate, fenoxaprop (including fenoxaprop-P-ethyl), fenoxasulfone, fenpyrazone, fenquinotrione, fentrazamide, flazasulfuron, florasulam, florpyrauxifen (including florpyrauxifen-benzyl), fluazifop (including fluazifop-P-butyl), flucarbazone (including flucarbazone-sodium), flufenacet, flumetsulam, flumioxazin, fluometuron, flupyrsulfuron (including flupyrsulfuron-methyl-sodium), fluroxypyr (including fluroxypyr-meptyl), fomesafen, foramsulfuron, glufosinate (including L-glufosinate and the ammonium salts of both), glyphosate (including the diammonium, isopropylammonium and potassium salts thereof), halauxifen (including halauxifen-methyl), haloxyfop (including haloxyfop-methyl), hexazinone, hydantocidin, imazamox (including R-imazamox), imazapic, imazapyr, imazethapyr, indaziflam, iodosulfuron (including iodosulfuron-methyl-sodium), iofensulfuron (including iofensulfuron-sodium), ioxynil, isoproturon, isoxaflutole, lancotrione, MCPA, MCPB, mecoprop-P, mesosulfuron (including mesosulfuron-methyl), mesotrione, metamitron, metazachlor, methiozolin, metolachlor, metosulam, metribuzin, metsulfuron, napropamide, nicosulfuron, norflurazon, oxadiazon, oxasulfuron, oxyfluorfen, paraquat dichloride, pendimethalin, penoxsulam, phenmedipham, picloram, pinoxaden, pretilachlor, primisulfuron-methyl, prometryne, propanil, propaquizafop, propyrisulfuron, propyzamide, prosulfocarb, prosulfuron, pyraclonil, pyraflufen (including pyraflufen-ethyl), pyrasulfotole, pyridate, pyriftalid, pyrimisulfan, pyroxasulfone, pyroxsulam, quinclorac, quinmerac, quizalofop (including quizalofop-P-ethyl and quizalofop-P-tefuryl), rimisoxafen, rimsulfuron, saflufenacil, sethoxydim, simazine, S-metalochlor, sulfentrazone, sulfosulfuron, tebuthiuron, tefuryltrione, tembotrione, terbuthylazine, terbutryn, tetflupyrolimet, thiencarbazone, thifensulfuron, tiafenacil, tolypyralate, topramezone, tralkoxydim, triafamone, triallate, triasulfuron, tribenuron (including tribenuron-methyl), triclopyr, trifloxysulfuron (including trifloxysulfuron-sodium), trifludimoxazin, trifluralin, triflusulfuron, tripyrasulfone, 3-(2-chloro-4-fluoro-5-(3-methyl-2,6-dioxo-4-trifluoromethyl-3,6-dihydropyrimidin-1(2H)-yl)phenyl)-5-methyl-4,5-dihydroisoxazole-5-carboxylic acid ethyl ester, 4-hydroxy-1-methoxy-5-methyl-3-[4-(trifluoromethyl)-2-pyridyl]imidazolidin-2-one, 4-hydroxy-1,5-dimethyl-3-[4-(trifluoromethyl)-2-pyridyl]imidazolidin-2-one, 5-ethoxy-4-hydroxy-1-methyl-3-[4-(trifluoromethyl)-2-pyridyl]imidazolidin-2-one, 4-hydroxy-1-methyl-3-[4-(trifluoromethyl)-2-pyridyl]imidazolidin-2-one, 4-hydroxy-1,5-dimethyl-3-[1-methyl-5-(trifluoromethyl)pyrazol-3-yl]imidazolidin-2-one, (4R)-1-(5-tert-butylisoxazol-3-yl)-4-ethoxy-5-hydroxy-3-methyl-imidazolidin-2-one, 4-amino-3-chloro-5-fluoro-6-(7-fluoro-1H-indol-6-yl)pyridine-2-carboxylic acid (including agrochemically acceptable esters thereof, for example, methyl 4-amino-3-chloro-5-fluoro-6-(7-fluoro-1H-indol-6-yl)pyridine-2-carboxylate, prop-2-ynyl 4-amino-3-chloro-5-fluoro-6-(7-fluoro-1H-indol-6-yl)pyridine-2-carboxylate and cyanomethyl 4-amino-3-chloro-5-fluoro-6-(7-fluoro-1H-indol-6-yl)pyridine-2-carboxylate), 3-ethylsulfanyl-N-(1,3,4-oxadiazol-2-yl)-5-(trifluoromethyl)-[1,2,4]triazolo[4,3-a]pyridine-8-carboxamide, 3-(isopropylsulfanylmethyl)-N-(5-methyl-1,3,4-oxadiazol-2-yl)-5-(trifluoromethyl)-[1,2,4]triazolo[4,3-a]pyridine-8-carboxamide, 3-(isopropylsulfonylmethyl)-N-(5-methyl-1,3,4-oxadiazol-2-yl)-5-(trifluoromethyl)-[1,2,4]triazolo[4,3-a]pyridine-8-carboxamide, 3-(ethylsulfonylmethyl)-N-(5-methyl-1,3,4-oxadiazol-2-yl)-5-(trifluoromethyl)-[1,2,4]triazolo[4,3-a]pyridine-8-carboxamide, ethyl 2-[[3-[[3-chloro-5-fluoro-6-[3-methyl-2,6-dioxo-4-(trifluoromethyl)pyrimidin-1-yl]-2-pyridyl]oxy]acetate and 6-chloro-4-(2,7-dimethyl-1-naphthyl)-5-hydroxy-2-methyl-pyridazin-3-one.

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, nematocides 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. Examples of such safeners include benoxacor, cloquintocet (including cloquintocetmexyl), cyprosulfamide, dichlormid, fenchlorazole (including fenchlorazoleethyl), fenclorim, fluxofenim, furilazole, isoxadifen (including isoxadifenethyl), mefenpr (including mefenpyr-diethyl), metcamifen and 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. A preferred range is 10-200g/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.

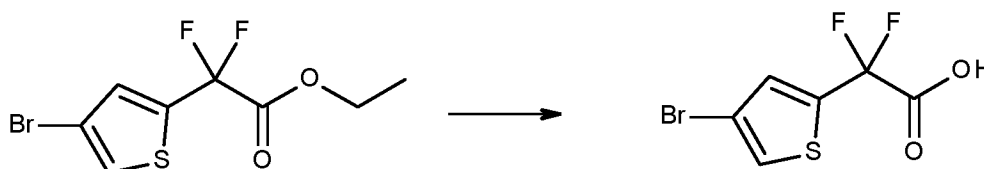
Various aspects and embodiments of the present invention will now be illustrated in more detail by way of example. It will be appreciated that modification of detail may be made without departing from the scope of the invention.

EXAMPLES

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

SYNTHESIS EXAMPLES

Example 1 Preparation of 2-(4-bromo-2-thienyl)-2,2-difluoro-acetic acid (Compound 1-3)



To a mixture of ethyl 2-(4-bromo-2-thienyl)-2,2-difluoro-acetate (1.00 g, 3.51 mmol) in methanol (5 mL) and water (5 mL) was added potassium carbonate (533 mg, 3.51 mmol). The reaction mixture was stirred at room temperature for 2 hours. The mixture was poured into water and extracted with ethyl acetate. The ethyl acetate solution was dried over anhydrous magnesium sulfate, filtered and evaporated to dryness to give 2-(4-bromo-2-thienyl)-2,2-difluoro-acetic acid (Compound 1-3) (820 mg, 3.19 mmol, 90%).

^1H NMR (400MHz, DMSO- d_6): δ 7.83 (s, 1H), 7.34 (s, 1H) ppm

Also prepared by this general method were:

2-(3,4-Dichloro-2-thienyl)-2,2-difluoro-acetic acid (Compound 1-16)

^1H NMR (400MHz, DMSO- d_6): δ 8.13 (s, 1H) ppm

2-(3-Bromo-2-thienyl)-2,2-difluoro-acetic acid (Compound 1-21)

^1H NMR (400MHz, DMSO- d_6): δ 7.72 (s, 1H), 7.21 (s, 1H), 7.11 (br s, 1H) ppm

2-(3-Chlorothiophen-2-yl)-2,2-difluoro-acetic acid (Compound 1-14)

^1H NMR (400MHz, DMSO- d_6): δ 7.45 (br s, 1H), 6.99 (dt, 1H) ppm

2-(4-Chlorothiophen-2-yl)-2,2-difluoro-acetic acid (Compound 1-2)

^1H NMR (400MHz, DMSO- d_6): δ 7.90 (s, 1H), 7.50 (s, 1H) ppm

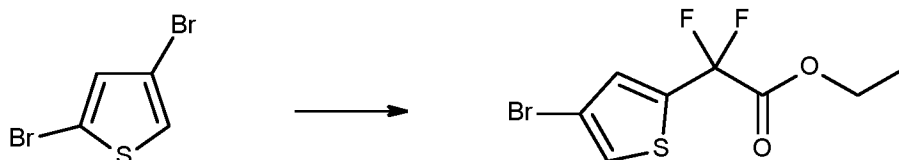
2,2-Difluoro-2-(3-fluoro-2-thienyl)-acetic acid ammonium salt (Compound 7-7)

^1H NMR (400MHz, DMSO- d_6): δ 7.57 (m, 1H), 7.20 (m, 4H), 6.93 (m, 1H) ppm

2-(3-Chloro-4-methyl-2-thienyl)-2,2-difluoro-acetic acid ammonium salt (Compound 7-

^1H NMR (400MHz, DMSO- d_6): δ 7.37 (s, 1H), 7.23 (m, 4H), 2.12 (s, 3H) ppm.

Example 2 Preparation of ethyl 2-(4-bromo-2-thienyl)-2,2-difluoro-acetate (Compound 3-3)



A mixture of ethyl 2-bromo-2,2-difluoro-acetate (812 mg, 4.00 mmol) and copper powder (512 mg, 8.00 mmol) in DMSO (10 mL) was stirred at room temperature for 1 hour. Then 2,4-dibromothiophene (484 mg, 2.00 mmol) was added to the mixture and it was stirred at 40°C overnight. The mixture was added to aqueous ammonium chloride and extracted with ethyl acetate. The combined organic layers were concentrated and purified by flash chromatography on silica gel (petroleum ether:ethyl acetate, 100:1) to give ethyl 2-(4-bromo-2-thienyl)-2,2-difluoro-acetate (Compound 3-3) (120 mg, 0.421 mmol, 21%).

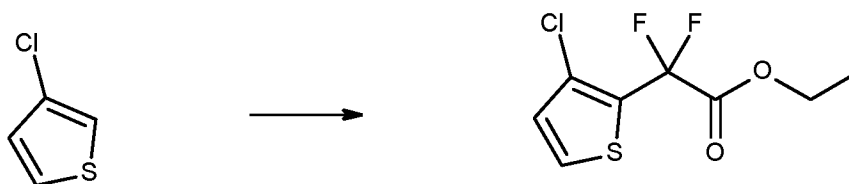
^1H NMR (400MHz, DMSO- d_6): δ 8.02 (s, 1H), 7.57 (s, 1H), 4.46 – 4.20 (m, 2H), 1.38 – 1.12 (m, 3H) ppm

Also prepared by this general method was:

Ethyl 2-(3,4-dichloro-2-thienyl)-2,2-difluoro-acetate (Compound 3-16)

^1H NMR (400MHz, CDCl_3): δ 7.32 (s, 1H), 4.32 (q, 2H), 1.29 (t, 3H) ppm

Example 3 Preparation of ethyl 2-(3-chloro-2-thienyl)-2,2-difluoro-acetate (Compound 3-14)



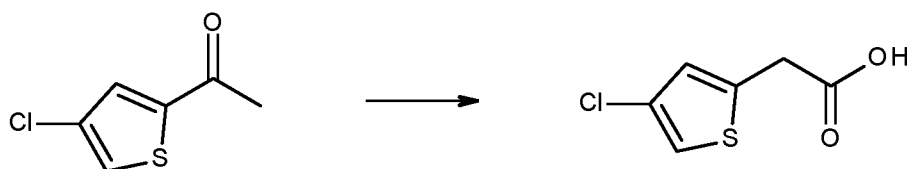
3-Chlorothiophene (1.00 g, 8.40 mmol) in DMSO (20.0 mL) was charged with ethyl 2,2-difluoro-2-iodoacetate (2.48 mL, 16.8 mmol) and Cu powder (2.66 g, 42.0 mmol). The reaction mixture was sealed and heated in a microwave irradiator at 60°C for 1 h. After this time, the reaction mass was cooled, diluted with water (50.0 mL) and filtered through a celite pad. The aqueous layer was extracted with tertiary butyl methyl ether (2 × 20.0 mL). The combined layers were washed with brine (10.0 mL), dried over anhydrous sodium sulphate and concentrated under reduced pressure to obtain the crude material, which was purified by

chromatography to provide ethyl 2-(3-chlorothiophen-2-yl)-2,2-difluoroacetate (Compound 3-14) (400 mg) as a colourless liquid.

^1H NMR (400MHz, CDCl_3): δ 7.43 (d, 1H), 6.97 (dt, 1H), 4.38 (q, 2H), 1.35 (t, 3H) ppm.

Example 4 Preparation of methyl 2-(4-chloro-2-thienyl)-2,2-difluoro-acetic acid (Compound 2-2)

Step 1 Synthesis of 2-(4-chloro-2-thienyl)-acetic acid



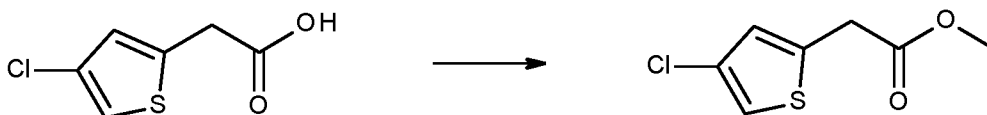
A cooled mixture of 1-(4-chloro-2-thienyl)-ethanone (2.00 g, 12.5 mmol), boron trifluoride etherate (7.33 g, 51.6 mmol) and methanol (3.5 ml) was added in one portion to a stirred suspension of lead tetraacetate (5.90 g, 18.1 mmol) in toluene (33 ml). The reaction mixture was stirred at room temperature for 24 h, then cold water (280 ml) added, and the mixture extracted with dichloromethane (3 X 50 ml). The combined organic extracts were washed sequentially with saturated aqueous sodium bicarbonate solution and brine, and then dried over sodium sulphate. After evaporating the solvent, the residue treated with a solution of sodium hydroxide (1.73 g) in water (16 ml) and MeOH (2 ml). After continuous stirring at room temperature for 2 h, the reaction mixture was washed with tert-butyl methyl ether. The aqueous layer was acidified with 6N HCl solution. The precipitated crystals were collected by suction, and the filtrate was extracted with ethyl acetate, dried, evaporated, and the residue was combined with the above-obtained precipitates. The crude was purified by chromatography to provide 2-(4-chlorothiophen-2-yl)-acetic acid (0.09 g) as a light yellow solid.

Also prepared by this general method was:

Methyl 2-(3-chloro-4-methyl-2-thienyl)-acetate

^1H NMR (400MHz, CDCl_3): δ 6.90 (s, 1H), 3.82 (s, 2H), 3.74 (s, 3H), 2.19 (s, 3H) ppm.

Step 2 Synthesis of methyl 2-(4-chloro-2-thienyl)-acetate

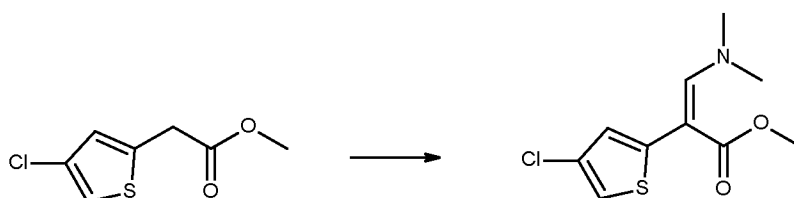


Iodomethane (0.24 g, 1.7 mmol) was added to a stirred mixture of 2-(4-chloro-2-thienyl)-acetic acid (200 mg, 1.13 mmol) and potassium carbonate (173 mg, 1.24 mmol) in

dimethylformamide (3 mL). After stirring for two hours, water was added and the mixture extracted with dichloromethane. The combined organic extracts were dried over sodium sulphate, filtered and evaporated under reduced pressure to provide methyl 2-(4-chloro-2-thienyl)-acetate (196 mg).

^1H NMR (400MHz, DMSO- d_6): δ 7.45 (d, 1H), 6.97 (d, 1H), 4.02 (s, 2H), 3.65 (s, 3H) ppm.

Step 3 Synthesis of methyl (E)-2-(4-chloro-2-thienyl)-3-(dimethylamino)-prop-2-enoate



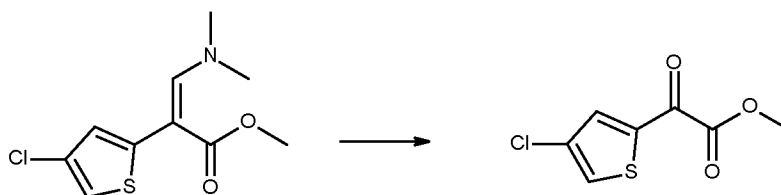
To a stirred solution of methyl 2-(4-chloro-2-thienyl)-acetate (300 mg, 1.57 mmol) in DMF (5 mL) was added dropwise 1,1-dimethoxy-N,N-dimethylmethanamine (0.563 g, 4.72 mmol) at room temperature. The reaction was stirred at 80°C for 3 hours. After cooling, the reaction mixture was quenched with water (15 mL) and extracted with dichloromethane (5 mL x 3). The combined organic layers were washed with brine, dried over anhydrous sodium sulphate, filtered, evaporated under reduced pressure to provide methyl (E)-2-(4-chloro-2-thienyl)-3-(dimethylamino)-prop-2-enoate (330 mg, 1.34 mmol, 85%) as a yellow oil. The crude product was directly used for next step without further purification.

Also prepared by this method were:

Methyl (E)-2-(3-chloro-4-methyl-2-thienyl)-3-(dimethylamino)-prop-2-enoate

Methyl (E)-3-(dimethylamino)-2-(3-fluoro-2-thienyl)-prop-2-enoate

Step 4 Synthesis of methyl 2-(4-chloro-2-thienyl)-2-oxo-acetate



To a stirred solution of methyl (E)-2-(4-chloro-2-thienyl)-3-(dimethylamino)-prop-2-enoate (0.330 g, 1.34 mmol) in THF/water (3 mL, 1:1) was added sodium periodate (0.862 g, 4.03 mmol) portionwise. The mixture was stirred for 3 hours. After completion, the reaction mixture was diluted with water (10 mL) and concentrated in vacuum to remove THF, then the residue was extracted with dichloromethane (25 mL x 3). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography to give methyl 2-(4-chloro-2-thienyl)-2-oxo-acetate (0.160 g, 0.782 mmol, 58%) as a yellow oil.

^1H NMR (400 MHz, DMSO- d_6): δ 8.25 (s, 1H), 8.10 (s, 1H), 3.90 (s, 3H) ppm

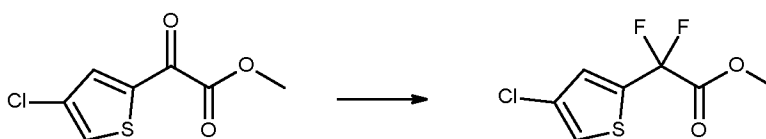
Also prepared by this general method were:

Methyl 2-(3-chloro-4-methyl-2-thienyl)-2-oxo-acetate

^1H NMR (400MHz, CDCl_3): δ 7.47 (s, 1H), 3.97 (s, 3H), 2.26 (s, 3H) ppm

Methyl 2-(3-fluoro-2-thienyl)-2-oxo-acetate

Step 5 Synthesis of methyl 2-(4-chloro-2-thienyl)-2,2-difluoro-acetate (Compound 2-2)



To a stirred solution of methyl 2-(4-chloro-2-thienyl)-2-oxo-acetate (159 mg, 0.834 mmol) in dichloromethane (4 mL) was added diethylaminosulfur trifluoride (0.471 g, 2.92 mmol) dropwise at 0°C . The mixture was stirred at room temperature for 16 h. Ice water (20 mL) was added to the reaction. The resulting mixture was extracted with dichloromethane (20 mL x 3). The combined organic phases were washed with brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to give methyl 2-(4-chloro-2-thienyl)-2,2-difluoro-acetate (Compound 2-2) (80 mg, 0.353 mmol, 42%) as a light-yellow oil.

^1H NMR (400 MHz, DMSO- d_6): δ 7.96 (s, 1H), 7.60 (s, 1H), 3.92 (s, 3H) ppm

Also prepared by this general method were:

Methyl 2-(3-chloro-4-methyl-2-thienyl)-2,2-difluoro-acetate (Compound 2-19)

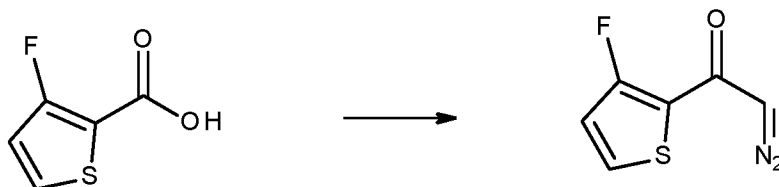
^1H NMR (400 MHz, DMSO- d_6): δ 7.71 (s, 1H), 3.91 (s, 3H), 2.18 (s, 3H) ppm

Methyl 2-(3-fluoro-2-thienyl)-2,2-difluoro-acetate (Compound 2-7)

^1H NMR (400MHz, CDCl_3): δ 7.37 (dd, 1H), 6.83 (d, 1H), 3.94 (s, 3H) ppm

Example 5 Preparation of methyl 2-(3-fluoro-2-thienyl)-acetate

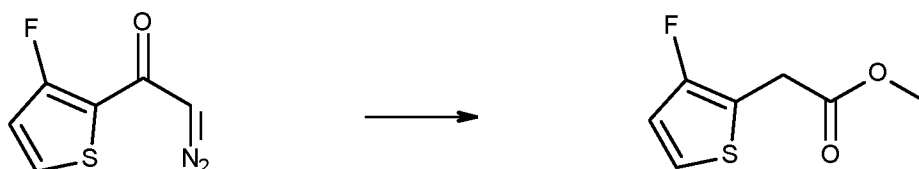
Step 1 Synthesis of 2-diazo-1-(3-fluoro-2-thienyl)-ethanone



Oxalyl chloride (1.17 mL, 13.9 mmol) was added dropwise to a solution of 3-fluorothiophene-2-carboxylic acid (1.69 g, 11.6 mmol) in dichloromethane (20 mL) and

dimethylformamide (drop) at 0 °C. The resulting mixture was stirred for 6 hours, then allowed to warm to ambient temperature and the solvent removed under reduced pressure to leave a white solid, which was dissolved in acetonitrile (10 ml). To this solution, cooled to 0 °C, were added triethylamine (1.40 g, 13.9 mmol) and trimethylsilyldiazomethane (3.96 g, 34.7 mmol). The resulting mixture was stirred at 0 °C for 1 hour, then allowed to warm to ambient temperature over 18 hours. Acetic acid was added and the solvent removed under reduced pressure. The residue was dissolved in ethyl acetate and water, the phases separated and the organic phase washed with aqueous sodium bicarbonate and brine, dried over sodium sulphate, filtered and evaporated under reduced pressure to leave a residue which was purified by chromatography to provide 2-diazo-1-(3-fluoro-2-thienyl)-ethanone as a yellow solid (700 mg).

Step 2 Synthesis of methyl 2-(3-fluoro-2-thienyl)-acetate



Silver benzoate (175 mg, 0.75 mmol) was added portionwise to a stirred mixture of 2-diazo-1-(3-fluoro-2-thienyl)-ethanone (170 mg, 1.0 mmol) and triethylamine (300 mg, 3.0 mmol) in methanol (3 ml). After stirring for two hours, iced water (10 ml) was added and the mixture extracted with ethyl acetate (3 x 20 ml). The combined organic extracts were washed with brine, dried over sodium sulphate, filtered and evaporated under reduced pressure to leave a residue which was purified by chromatography to provide methyl 2-(3-fluoro-2-thienyl)-acetate (45 mg) as a pale yellow liquid.

FORMULATION EXAMPLES

Wettable powders	a)	b)	c)
active ingredients	25 %	50 %	75 %
sodium lignosulfonate	5 %	5 %	-
sodium lauryl sulfate	3 %	-	5 %
sodium diisobutyl naphthalenesulfonate	-	6 %	10 %
phenol polyethylene glycol ether	-	2 %	-
(7-8 mol of ethylene oxide)			
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.

Extruder 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.

BIOLOGICAL EXAMPLES

Biological efficacy

Seeds of a variety of test species were sown in unsterilised compost in small pots. After cultivation for one day (pre-emergence) or seven days (post-emergence) in controlled conditions in the glasshouse (at 24/16°C, day/night; 14 hours light; 65 % humidity) the plants were sprayed with 1 mg of the active ingredient, formulated in 466µl of a acetone / water / Tween 20 (49.75:49.75:0.5) solution, which is equivalent to 1000 g/ha. Once the foliage was dry, the pots were kept in the glasshouse (at 24/16°C, day/night; 14 hours light; 65 % humidity), and were watered twice daily. After 12 days the test was evaluated and scored (100 = total damage to plant, 0 = no damage to plant). The results are shown in Table 2 below.

Table 2

Compound	Rate (g/ha)	Species							
		Post-Emergence				Pre-Emergence			
		AMAR E	LOLP E	STEM E	DIGS A	AMAR E	LOLP E	STEM E	DIGS A
1-3	1000	60	0	0	20	0	0	50	20

Pre-emergence biological efficacy

Seeds of weeds and/or crops were sown in standard soil in pots. After cultivation for one day under controlled conditions in a glasshouse (at 24/19°C, day/night; 16 hours light), the plants were sprayed with an aqueous spray solution derived from the formulation of the

technical active ingredient 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 using 0.2% Genapol XO80 as diluent to give the desired final dose of test compound.

The test plants were then grown under controlled conditions in the glasshouse (at 24/18°C, day/night; 15 hours light; 50 % humidity) and watered twice daily. After 13 days the test was evaluated (100 = total damage to plant; 0 = no damage to plant). The results are shown in Table 3 below.

Table 3

Compound	Rate (g/ha)	Species							
		AMAR E	AMAP A	STEM E	ABUT H	SETF A	ECHC G	ZEAM X	IPOH E
1-2	1000	40	30	-	-	30	0	0	30
1-14	1000	0	-	30	0	-	-	0	0
1-16	1000	90	-	90	100	-	20	30	90
1-21	1000	20	-	20	70	-	-	10	60

Post-emergence biological efficacy

Seeds of weeds and/or crops were sown in standard soil in pots. After cultivation for 14 days under controlled conditions in a glasshouse (at 24/19°C, day/night; 16 hours light), the plants were sprayed with an aqueous spray solution derived from the formulation of the technical active ingredient 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 using 0.2% Genapol XO80 as diluent to give the desired final dose of test compound.

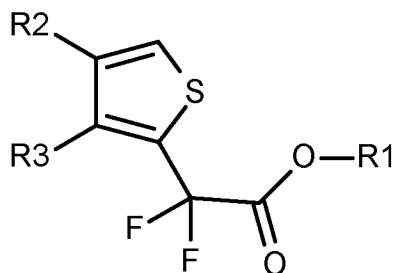
The test plants were then grown under controlled conditions in the glasshouse (at 24/18°C, day/night; 15 hours light; 50 % humidity) and watered twice daily. After 13 days the test was evaluated (100 = total damage to plant; 0 = no damage to plant). The results are shown in Table 4 below.

Table 4

Compound	Rate (g/ha)	Species							
		AMAR E	AMAP A	STEM E	ABUT H	SETF A	ECHC G	ZEAM X	IPOH E
1-2	1000	20	30	-	-	10	10	10	70
1-14	1000	30	-	10	10	-	-	20	30
1-16	1000	90	-	100	90	-	0	20	100
1-21	1000	30	-	70	80	-	-	40	70

Claims

1. Use of a compound of formula (I),



(I)

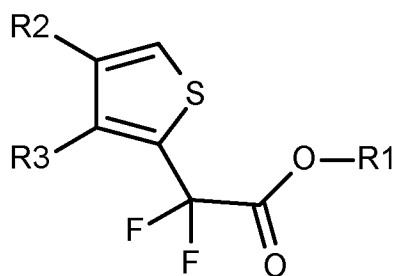
wherein

R₁ is selected from the group consisting of hydrogen, C₁-C₃alkyl and benzyl; and

each R₂ and R₃ is independently selected from the group consisting of hydrogen, halogen, methyl, cyano and C₁-haloalkyl, with the proviso that R₂ and R₃ are not both hydrogen,

or an agronomically acceptable salt of said compound, as a herbicide.

2. Use according to claim 1, wherein in the compound of Formula (I) R₁ is hydrogen.
3. Use according to claim 1 or claim 2, wherein in the compound of Formula (I) each R₂ and R₃ is independently selected from the group consisting of hydrogen and halogen.
4. Use according to claim 1 or claim 2, wherein in the compound of Formula (I) each R₂ and R₃ is halogen.
5. A compound of formula (I) or an agronomically acceptable salt thereof:



(I)

wherein

R₁ is selected from the group consisting of hydrogen, C₁-C₃alkyl and benzyl; and

each R2 and R3 is independently selected from the group consisting of hydrogen, halogen, methyl, cyano and C₁-haloalkyl, with the proviso that

when R1 is hydrogen, R3 is hydrogen, R2 is not Chlorine, Bromine, cyano or methyl;

when R1 is hydrogen, R2 is hydrogen, R3 is not Chlorine, Bromine, Iodine or methyl;

when R1 is hydrogen, R2 is methyl, R3 is not Chlorine, Bromine or Iodine; and

when R1 is ethyl, R2 is hydrogen, R3 is not hydrogen, Chlorine, Bromine or methyl.

6. A compound or an agronomically acceptable salt thereof according to claim 5, wherein R1 is hydrogen.
7. A compound or an agronomically acceptable salt thereof according to claim 5 or 6, wherein each R2 and R3 is independently selected from the group consisting of hydrogen and halogen.
8. A compound or an agronomically acceptable salt thereof according to any one of claims 5 to 7, wherein each R2 and R3 is halogen.
9. A compound or an agronomically acceptable salt thereof according to any one of claims 5 to 8, wherein each R2 and R3 is Chlorine.
10. An agrochemically acceptable salt according to any one of claims 5 to 8, wherein said salt is selected from the group consisting of sodium, potassium, aluminium, dimethylamine, diglycolamine and choline salt.
11. Use of a compound or an agronomically acceptable salt thereof according to any one of claims 5 to 10 as a herbicide.
12. A herbicidal composition comprising (i) a compound of Formula (I) or an agronomically acceptable salt thereof as defined in any one of claims 1 to 10 and (ii) an agriculturally acceptable formulation adjuvant.
13. A herbicidal composition according to claim 12, further comprising at least one additional pesticide.
14. A herbicidal composition according to claim 13, wherein the additional pesticide is a herbicide or herbicide safener.
15. A method of controlling weeds at a locus comprising application to the locus of a weed controlling amount of a compound of Formula (I) or an agrochemically acceptable salt according to any one of claims 1 to 10 or a herbicidal composition according to any one of claims 12 to 14.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2022/062923

A. CLASSIFICATION OF SUBJECT MATTER INV. C07D333/24 A01N43/10 C07D333/28 C07D333/38 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		
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	HONG GUANGFENG ET AL: "Transition-metal-free decarboxylative C3-difluoroarylmethylation of quinoxalin-2(1 H)-ones with [alpha],[alpha]-difluoroarylacetic acids", ORGANIC CHEMISTRY FRONTIERS , vol. 6, no. 8 9 April 2019 (2019-04-09), pages 1173-1182, XP055850295, DOI: 10.1039/C9QO00105K Retrieved from the Internet: URL:https://pubs.rsc.org/en/content/article epdf/2019/qo/c9qo00105k page 1175, right-hand column; compound 2o ----- -/--	5-7
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
1 August 2022		09/08/2022
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Johnson, Claire

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2022/062923

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GAO YANHUI ET AL: "Photoinitiated decarboxylative C3-difluoroarylmethylation of quinoxalin-2(1 H)-ones with potassium 2,2-difluoro-2-arylacetaes in water", RSC ADVANCES , vol. 10, no. 18 12 March 2020 (2020-03-12), pages 10559-10568, XP055850305, DOI: 10.1039/D0RA02059A Retrieved from the Internet: URL:https://pubs.rsc.org/en/content/articlepdf/2020/ra/d0ra02059a Scheme 3: the reactant 2 used to prepare compound 3ah -----	5, 7, 10
X	Kizi A.: "Azepine Product List" In: "Azepine Product List", 1 March 2019 (2019-03-01), Chemcats, Basingstoke, XP055850425, The compound of Registry No. 1784362-95-3 -----	5, 7
A	WO 2011/073098 A1 (BAYER CROPSCIENCE AG [DE]; JAKOBI HARALD [DE] ET AL.) 23 June 2011 (2011-06-23) claims 1, 12 -----	1-15
A	US 3 134 808 A (WEIL EDWARD D ET AL) 26 May 1964 (1964-05-26) column 3, line 14 - column 4, line 37 -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2022/062923

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		US 2011257014 A1	20-10-2011
		WO 2011073098 A1	23-06-2011
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