



- (51) **International Patent Classification:**
C07D 403/04 (2006.01) *A01N 43/64* (2006.01)
- (21) **International Application Number:**
PCT/EP2014/056211
- (22) **International Filing Date:**
27 March 2014 (27.03.2014)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
1305759.1 28 March 2013 (28.03.2013) GB
- (71) **Applicant:** SYNGENTA LIMITED [GB/GB]; Priestley Road, Surrey Research Park, Guildford Surrey GU2 7YH (GB).
- (72) **Inventors:** VINER, Russell Colin; Syngenta Limited, Jealott's Hill International Research Centre, Bracknell Berkshire RG42 6EY (GB). RZEPA, Paula Rocha; Syngenta Limited, Jealott's Hill International Research Centre, Bracknell Berkshire RG42 6EY (GB). MITCHELL, Glynn; Syngenta Limited, Jealott's Hill International Research Centre, Bracknell Berkshire RG42 6EY (GB).
- (74) **Agent:** SYNGENTA INTERNATIONAL AG; Intellectual Property, WRO 1008-Z1-26, Schwarzwaldallee 215, CH-4058 Basel (CH).

(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, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, 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, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, 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, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, 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).

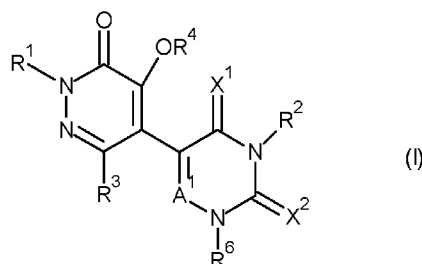
Declarations under Rule 4.17:

— of inventorship (Rule 4.17(iv))

Published:

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

(54) **Title:** PYRIDAZINONE DERIVATIVES AS HERBICIDES

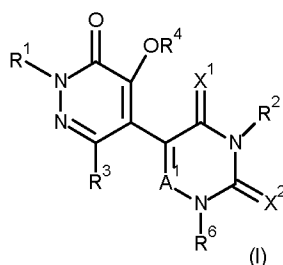


(57) **Abstract:** The present invention relates to compounds of Formula (I), or an agronomically acceptable salt of said compounds wherein A¹, X¹, X², R¹, R², R³, R⁴ and R⁶ are as defined herein. The invention further relates to herbicidal compositions which comprise a compound of Formula (I), and to their use for controlling weeds, in particular in crops of useful plants.

PYRIDAZINONE DERIVATIVES AS HERBICIDES

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

Herbicidal 6-acyl-1,2,4-triazine-3,5-dione derivatives are disclosed in WO2012/002096. The present invention relates to alternative herbicidal 1,2,4-triazine-3,5-dione derivatives. Thus, according to the present invention there is provided a compound of Formula (I):



or an agronomically acceptable salt thereof,
wherein:-

X^1 and X^2 are independently selected from the group consisting of O and S;

A^1 is N or CR^5 ;

R^1 is selected from the group consisting of hydrogen, C_1 - C_6 alkyl, C_3 - C_6 cycloalkyl, C_2 - C_6 alkenyl, C_2 - C_6 alkynyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy- C_1 - C_3 -alkyl and C_3 - C_6 cycloalkyl- C_1 - C_3 -alkyl;

R^2 is selected from the group consisting of C_1 - C_6 alkyl-, C_1 - C_6 haloalkyl-, C_2 - C_6 alkenyl, C_2 - C_6 alkynyl, C_3 - C_6 cycloalkyl, C_1 - C_6 alkoxy- C_1 - C_3 -alkyl-, C_1 - C_3 alkoxy- C_3 - C_6 cycloalkyl-, C_1 - C_3 alkyl-S(O)_p- C_3 - C_6 cycloalkyl-, C_1 - C_3 alkoxy- C_1 - C_3 alkyl-, C_1 - C_6 alkylcarbonyl- C_1 - C_3 alkyl-, tetrahydropyranyl- C_1 - C_3 alkyl-, benzyl-, pyridyl and phenyl-, the benzyl, pyridyl and phenyl groups being

optionally substituted by one or more substituents selected from the group consisting of cyano, nitro, halogen, C₁-C₃alkyl-, C₁-C₃haloalkyl-, C₂-C₃alkenyl-, C₁-C₃alkoxy-, C₁-C₃alkoxy-C₁-C₃-alkoxy-, C₁-C₃alkyl-S(O)_p-, C₁-C₃haloalkyl-S(O)_p- and C₁-C₃haloalkoxy-;

5

R³ is selected from the group consisting of hydrogen, hydroxyl, halogen, nitro, amino, cyano, C₁-C₆alkyl, C₁-C₃alkoxy-, C₃-C₆cycloalkyl, C₂-C₆alkenyl, C₂-C₆alkynyl, C₁-C₆haloalkyl, C₁-C₆alkoxy-C₁-C₃-alkyl, C₃-C₆cycloalkyl-C₁-C₃-alkyl, C₁-C₆alkyl-S(O)_p-, C₁-C₆alkyl-S(O)_p- C₁-C₃-alkyl, C₁-C₆haloalkyl-S(O)_p-, C₁-C₃alkylamino, C₁-C₃dialkylamino and C₁-C₆haloalkyl-S(O)_p-C₁-C₃-alkyl;

10

R⁴ is selected from the group consisting of hydrogen, C₁-C₆alkylcarbonyl-, arylcarbonyl-, C₁-C₆alkoxycarbonyl-, C₁-C₆alkyl-S(O)_p-, C₁-C₆alkyl-S(O)_pcarbonyl- and aryl-S(O)_p- (e.g phenyl-S(O)_p-), wherein said aryl groups may be optionally substituted by one or more R⁷;

15

R⁵ is selected from the group consisting of hydrogen, hydroxyl, C₁-C₆ alkyl, C₁-C₆ haloalkyl and C₁-C₆alkoxy-C₁-C₃alkyl;

20

R⁶ is selected from the group consisting of hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy-C₁-C₆alkyl, C₁-C₆haloalkoxy-C₁-C₆alkyl, C₁-C₆alkoxy-C₁-C₆alkoxy-C₁-C₆alkyl, C₂-C₆alkenyl, C₂-C₆haloalkenyl, C₂-C₆alkynyl, C₂-C₆haloalkynyl and C₃-C₆ cycloalkyl;

25

R⁷ is selected from the group consisting of halo-, C₁-C₃alkyl, C₁-C₃ haloalkyl and C₁-C₆alkoxy; and

p = 0, 1 or 2.

30

Halogen (or halo) encompasses fluorine, chlorine, bromine or iodine. The same correspondingly applies to halogen in the context of other definitions, such as haloalkyl or halophenyl.

Haloalkyl groups having a chain length of from 1 to 6 carbon atoms are, for example, fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, 2,2,2-trifluoroethyl, 2-fluoroethyl, 2-chloroethyl, pentafluoroethyl, 1,1-difluoro-2,2,2-trichloroethyl, 2,2,3,3-tetrafluoroethyl and 2,2,2-trichloroethyl, heptafluoro-n-propyl and perfluoro-n-hexyl.

Alkoxy groups preferably have a chain length of from 1 to 6 carbon atoms. Alkoxy is, for example, methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy, sec-butoxy or tert-butoxy or a pentyloxy or hexyloxy isomer, preferably methoxy and ethoxy. It should also be appreciated that two alkoxy substituents present on the same carbon atom may be joined to form a spiro group. Thus, the methyl groups present in two methoxy substituents may be joined to form a spiro 1,3 dioxolane substituent, for example. Such a possibility is within the scope of the present invention.

Haloalkoxy is, for example, fluoromethoxy, difluoromethoxy, trifluoromethoxy, 2,2,2-trifluoroethoxy, 1,1,2,2-tetrafluoroethoxy, 2-fluoroethoxy, 2-chloroethoxy, 2,2-difluoroethoxy or 2,2,2-trichloroethoxy, preferably difluoromethoxy, 2-chloroethoxy or trifluoromethoxy.

C₁-C₆alkyl-S- (alkylthio) is, for example, methylthio, ethylthio, propylthio, isopropylthio, n-butylthio, isobutylthio, sec-butylthio or tert-butylthio, preferably methylthio or ethylthio.

C₁-C₆alkyl-S(O)- (alkylsulfinyl) is, for example, methylsulfinyl, ethylsulfinyl, propylsulfinyl, isopropylsulfinyl, n-butylsulfinyl, isobutylsulfinyl, sec-butylsulfinyl or tert-butylsulfinyl, preferably methylsulfinyl or ethylsulfinyl.

C₁-C₆alkyl-S(O)₂- (alkylsulfonyl) is, for example, methylsulfonyl, ethylsulfonyl, propylsulfonyl, isopropylsulfonyl, n-butylsulfonyl, isobutylsulfonyl, sec-butylsulfonyl or tert-butylsulfonyl, preferably methylsulfonyl or ethylsulfonyl.

Alkylamino is, for example, methylamino, ethylamino, n-propylamino, isopropylamino or a butylamino isomer. Dialkylamino is, for example, dimethylamino, methylethylamino, diethylamino, n-propylmethylamino, dibutylamino or

diisopropylamino. Preference is given to alkylamino groups having a chain length of from 1 to 4 carbon atoms.

Alkoxyalkyl groups preferably have from 1 to 6 carbon atoms. Alkoxyalkyl is, for example, methoxymethyl, methoxyethyl, ethoxymethyl, ethoxyethyl, n-propoxymethyl, n-propoxyethyl, isopropoxymethyl or isopropoxyethyl.

In a particular aspect of the present invention there is provided a compound of Formula (I), wherein A^1 is N.

10

In another aspect of the present invention there is provided a compound of Formula (I), wherein A^1 is CR^5 .

In a preferred embodiment of the invention is a compound of Formula (I) wherein X^1 and X^2 are O.

15

In a more preferred embodiment of the invention R^1 is selected from the group consisting of C_1 - C_4 alkyl, cyclopropyl, difluoromethyl, cyclopropylmethyl-, vinyl and propargyl with methyl being particularly preferred.

20

In another preferred embodiment, R^2 is selected from the group consisting of C_1 - C_6 alkyl- (preferably methyl), C_1 - C_3 alkoxy- C_1 - C_3 alkyl-, C_1 - C_6 alkylcarbonyl- C_1 - C_3 alkyl-, benzyl-, pyridyl- and phenyl-, the benzyl-, pyridyl- and phenyl- groups being optionally substituted by one or more substituents selected from the group consisting of cyano, halogen, C_1 - C_3 alkyl-, C_1 - C_3 haloalkyl-, C_2 - C_3 alkenyl-, C_1 - C_3 alkoxy- and C_1 - C_3 haloalkoxy-.

25

Preferably, R^3 is selected from the group consisting of hydrogen, halogen, cyano, C_1 - C_6 alkyl, C_2 - C_6 alkenyl, C_2 - C_6 alkynyl, C_1 - C_6 haloalkyl and C_1 - C_6 alkyl-S(O)_p-.

More preferably, R^3 is selected from the group consisting of hydrogen, halogen and C_1 - C_6 alkyl, most preferred being hydrogen or methyl.

30

Preferably, R^4 is hydrogen.

Preferably, R⁵ is hydrogen or methyl, preferably hydrogen.

Preferably, R⁶ is selected from the group consisting of hydrogen, methyl and halogen.

5

Compounds of Formula I may contain asymmetric centres and may be present as a single enantiomer, pairs of enantiomers in any proportion or, where more than one asymmetric centre are present, contain diastereoisomers in all possible ratios. Typically one of the enantiomers has enhanced biological activity compared to the other possibilities.

10

Similarly, where there are disubstituted alkenes, these may be present in E or Z form or as mixtures of both in any proportion.

15

Furthermore, compounds of Formula I may be in equilibrium with alternative tautomeric forms. It should be appreciated that all tautomeric forms (single tautomer or mixtures thereof), racemic mixtures and single isomers are included within the scope of the present invention.

20

The present invention also includes agronomically acceptable salts that the compounds of Formula I may form with amines (for example ammonia, dimethylamine and triethylamine), alkali metal and alkaline earth metal bases or quaternary ammonium bases. Among the alkali metal and alkaline earth metal hydroxides, oxides, alkoxides and hydrogen carbonates and carbonates used as salt formers, emphasis is to be given to the hydroxides, alkoxides, oxides and carbonates of lithium, sodium, potassium, magnesium and calcium, but especially those of sodium, magnesium and calcium. The corresponding trimethylsulfonium salt may also be used.

25

30

The compounds of Formula (I) according to the invention can be used as herbicides by themselves, but they are generally formulated into herbicidal compositions using formulation adjuvants, such as carriers, solvents and surface-active agents (SFAs). Thus, the present invention further provides a herbicidal composition comprising a herbicidal compound according to any one of the previous

claims and an agriculturally acceptable formulation adjuvant. The composition can be in the form of concentrates which are diluted prior to use, although ready-to-use compositions can also be made. The final dilution is usually made with water, but can be made instead of, or in addition to, water, with, for example, liquid fertilisers,
5 micronutrients, biological organisms, oil or solvents.

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
10 weight of a surface-active substance.

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

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

30 Soluble powders (SP) may be prepared by mixing a compound of Formula (I) or (II) with one or more water-soluble inorganic salts (such as sodium bicarbonate, sodium carbonate or magnesium sulphate) or one or more water-soluble organic solids (such as a polysaccharide) and, optionally, one or more wetting agents, one or more

dispersing agents or a mixture of said agents to improve water dispersibility/solubility. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water soluble granules (SG).

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

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

Dispersible Concentrates (DC) may be prepared by dissolving a compound of Formula (I) in water or an organic solvent, such as a ketone, alcohol or glycol ether. These solutions may contain a surface active agent (for example to improve water dilution or prevent crystallisation in a spray tank).

Emulsifiable concentrates (EC) or oil-in-water emulsions (EW) may be prepared by dissolving a compound of Formula (I) in an organic solvent (optionally containing one or more wetting agents, one or more emulsifying agents or a mixture of said agents). Suitable organic solvents for use in ECs include aromatic hydrocarbons (such as alkylbenzenes or alkylnaphthalenes, exemplified by SOLVESSO 100, SOLVESSO 150 and SOLVESSO 200; SOLVESSO is a Registered

Trade Mark), ketones (such as cyclohexanone or methylcyclohexanone) and alcohols (such as benzyl alcohol, furfuryl alcohol or butanol), N-alkylpyrrolidones (such as N-methylpyrrolidone or N-octylpyrrolidone), dimethyl amides of fatty acids (such as C₈-C₁₀ fatty acid dimethylamide) and chlorinated hydrocarbons. An EC product may
5 spontaneously emulsify on addition to water, to produce an emulsion with sufficient stability to allow spray application through appropriate equipment.

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

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

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

Aerosol formulations comprise a compound of Formula (I) and a suitable propellant (for example *n*-butane). A compound of Formula (I) may also be dissolved or dispersed in a suitable medium (for example water or a water miscible liquid, such as *n*-propanol) to provide compositions for use in non-pressurised, hand-actuated spray pumps.

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

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

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

Suitable anionic SFAs include alkali metals salts of fatty acids, salts of aliphatic monoesters of sulphuric acid (for example sodium lauryl sulphate), salts of sulphonated aromatic compounds (for example sodium dodecylbenzenesulphonate, calcium dodecylbenzenesulphonate, butyl-naphthalene sulphonate and mixtures of sodium di-*isopropyl*- and tri-*isopropyl*-naphthalene sulphonates), ether sulphates, alcohol ether sulphates (for example sodium laureth-3-sulphate), ether carboxylates

(for example sodium laureth-3-carboxylate), phosphate esters (products from the reaction between one or more fatty alcohols and phosphoric acid (predominately mono-esters) or phosphorus pentoxide (predominately di-esters), for example the reaction between lauryl alcohol and tetraphosphoric acid; additionally these products
5 may be ethoxylated), sulphosuccinamates, paraffin or olefine sulphonates, taurates and lignosulphonates.

Suitable SFAs of the amphoteric type include betaines, propionates and glycines.

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

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

20

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. Examples
25 of such mixtures are (in which 'I' represents a compound of Formula I). I + acetochlor, I + acifluorfen, I + acifluorfen-sodium, I + acetonifene, I + acrolein, I + alachlor, I + alloxymid, I + ametryn, I + amicarbazone, I + amidosulfuron, I + aminopyralid, I + amitrole, I + anilofos, I + asulam, I + atrazine, I + azafenidin, I + azimsulfuron, I + BCPC, I + beflubutamid, I + benazolin, I + bencarbazone, I + benfluralin, I +
30 benfuresate, I + bensulfuron, I + bensulfuron-methyl, I + bensulide, I + bentazone, I + benzfendazole, I + benzobicyclon, I + benzofenap, I + bicyclopyrone, I + bifenox, I + bilanafos, I + bispyribac, I + bispyribac-sodium, I + borax, I + bromacil, I + bromobutide, I + bromoxynil, I + butachlor, I + butamifos, I + butralin, I +

butroxydim, I + butylate, I + cacodylic acid, I + calcium chlorate, I + cafenstrole, I + carbetamide, I + carfentrazone, I + carfentrazone-ethyl, I + chlorflurenol, I + chlorflurenol-methyl, I + chloridazon, I + chlorimuron, I + chlorimuron-ethyl, I + chloroacetic acid, I + chlorotoluron, I + chlorpropham, I + chlorsulfuron, I + chlorthal, I + chlorthal-dimethyl, I + cinidon-ethyl, I + cinmethylin, I + cinosulfuron, I + cisanilide, I + clethodim, I + clodinafop, I + clodinafop-propargyl, I + clomazone, I + clomeprop, I + clopyralid, I + cloransulam, I + cloransulam-methyl, I + cyanazine, I + cycloate, I + cyclosulfamuron, I + cycloxydim, I + cyhalofop, I + cyhalofop-butyl, I + 2,4-D, I + daimuron, I + dalapon, I + dazomet, I + 2,4-DB, I + I + desmedipham, I + dicamba, I + dichlobenil, I + dichlorprop, I + dichlorprop-P, I + diclofop, I + diclofop-methyl, I + diclosulam, I + difenzoquat, I + difenzoquat metilsulfate, I + diflufenican, I + diflufenzopyr, I + dimefuron, I + dimepiperate, I + dimethachlor, I + dimethametryn, I + dimethenamid, I + dimethenamid-P, I + dimethipin, I + dimethylarsinic acid, I + dinitramine, I + dinoterb, I + diphenamid, I + dipropetryn, I + diquat, I + diquat dibromide, I + dithiopyr, I + diuron, I + endothal, I + EPTC, I + esprocarb, I + ethalfluralin, I + ethametsulfuron, I + ethametsulfuron-methyl, I + ethephon, I + ethofumesate, I + ethoxyfen, I + ethoxysulfuron, I + etobenzanid, I + fenoxaprop-P, I + fenoxaprop-P-ethyl, I + fentrazamide, I + ferrous sulfate, I + flamprop-M, I + flazasulfuron, I + florasulam, I + fluazifop, I + fluazifop-butyl, I + fluazifop-P, I + fluazifop-P-butyl, I + fluazolate, I + flucarbazone, I + flucarbazone-sodium, I + flucetosulfuron, I + fluchloralin, I + flufenacet, I + flufenpyr, I + flufenpyr-ethyl, I + flumetralin, I + flumetsulam, I + flumiclorac, I + flumiclorac-pentyl, I + flumioxazin, I + flumipropin, I + fluometuron, I + fluoroglycofen, I + fluoroglycofen-ethyl, I + fluoxaprop, I + flupoxam, I + flupropacil, I + flupropanate, I + flupyrsulfuron, I + flupyrsulfuron-methyl-sodium, I + flurenol, I + fluridone, I + flurochloridone, I + fluroxypyr, I + flurtamone, I + fluthiacet, I + fluthiacet-methyl, I + fomesafen, I + foramsulfuron, I + fosamine, I + glufosinate, I + glufosinate-ammonium, I + glyphosate, I + halauxifen, I + halosulfuron, I + halosulfuron-methyl, I + haloxyfop, I + haloxyfop-P, I + hexazinone, I + imazamethabenz, I + imazamethabenz-methyl, I + imazamox, I + imazapic, I + imazapyr, I + imazaquin, I + imazethapyr, I + imazosulfuron, I + indanofan, I + indaziflam, I + iodomethane, I + iodosulfuron, I + iodosulfuron-methyl-sodium, I + ioxynil, I + isoproturon, I + isouron, I + isoxaben, I + isoxachlortole, I + isoxaflutole, I + isoxapyrifop, I + karbutilate, I + lactofen, I + lenacil, I + linuron, I + mecoprop, I + mecoprop-P, I +

mefenacet, I + mefluidide, I + mesosulfuron, I + mesosulfuron-methyl, I + mesotrione, I + metam, I + metamifop, I + metamidron, I + metazachlor, I + methabenzthiazuron, I + methazole, I + methylarsonic acid, I + methylidymron, I + methyl isothiocyanate, I + metolachlor, I + S-metolachlor, I + metosulam, I + metoxuron, I + metribuzin, I +
5 metsulfuron, I + metsulfuron-methyl, I + molinate, I + monolinuron, I + naproanilide, I + napropamide, I + naptalam, I + neburon, I + nicosulfuron, I + n-methyl glyphosate, I + nonanoic acid, I + norflurazon, I + oleic acid (fatty acids), I + orbencarb, I + orthosulfamuron, I + oryzalin, I + oxadiargyl, I + oxadiazon, I + oxasulfuron, I + oxaziclomefone, I + oxyfluorfen, I + paraquat, I + paraquat dichloride, I + pebulate, I +
10 + pendimethalin, I + penoxsulam, I + pentachlorophenol, I + pentanochlor, I + pentoxazone, I + pethoxamid, I + phenmedipham, I + picloram, I + picolinafen, I + pinoxaden, I + piperophos, I + pretilachlor, I + primisulfuron, I + primisulfuron-methyl, I + prodiamine, I + profoxydim, I + prohexadione-calcium, I + prometon, I + prometryn, I + propachlor, I + propanil, I + propaquizafop, I + propazine, I + propham,
15 I + propisochlor, I + propoxycarbazone, I + propoxycarbazone-sodium, I + propyzamide, I + prosulfocarb, I + prosulfuron, I + pyraclonil, I + pyraflufen, I + pyraflufen-ethyl, I + pyrasulfotole, I + pyrazolynate, I + pyrazosulfuron, I + pyrazosulfuron-ethyl, I + pyrazoxyfen, I + pyribenzoxim, I + pyributicarb, I + pyridafol, I + pyridate, I + pyriftalid, I + pyriminobac, I + pyriminobac-methyl, I +
20 pyrimisulfan, I + pyrithiobac, I + pyrithiobac-sodium, I + pyroxasulfone, I + pyroxsulam, I + quinclorac, I + quinmerac, I + quinclamine, I + quizalofop, I + quizalofop-P, I + rimsulfuron, I + saflufenacil, I + sethoxydim, I + siduron, I + simazine, I + simetryn, I + sodium chlorate, I + sulcotrione, I + sulfentrazone, I + sulfometuron, I + sulfometuron-methyl, I + sulfosate, I + sulfosulfuron, I + sulfuric
25 acid, I + tebuthiuron, I + tefuryltrione, I + tembotrione, I + tepraloxymid, I + terbacil, I + terbumeton, I + terbuthylazine, I + terbutryn, I + thenylchlor, I + thiazopyr, I + thifensulfuron, I + thiencarbazone, I + thifensulfuron-methyl, I + thiobencarb, I + topramezone, I + tralkoxydim, I + tri-allate, I + triasulfuron, I + triaziflam, I + tribenuron, I + tribenuron-methyl, I + triclopyr, I + trietazine, I + trifloxysulfuron, I +
30 trifloxysulfuron-sodium, I + trifluralin, I + triflusulfuron, I + triflusulfuron-methyl, I + trihydroxytriazine, I + trinexapac-ethyl, I + tritosulfuron, I + [3-[2-chloro-4-fluoro-5-(1-methyl-6-trifluoromethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-3-yl)phenoxy]-2-pyridyloxy]acetic acid ethyl ester (CAS RN 353292-31-6). The compounds of the

present invention may also be combined with herbicidal compounds disclosed in WO06/024820 and/or WO07/096576.

5 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.

10 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).

15 The compounds of Formula I according to the invention can also be used in combination with one or more safeners. Likewise, mixtures of a compound of Formula I according to the invention with one or more further herbicides can also be used in combination with one or more safeners. The safeners can be AD 67 (MON 4660), benoxacor, cloquintocet-mexyl, cyprosulfamide (CAS RN 221667-31-8),
20 dichlormid, fenchlorazole-ethyl, fenclorim, fluxofenim, furilazole and the corresponding R isomer, isoxadifen-ethyl, mefenpyr-diethyl, oxabetrinil, N-isopropyl-4-(2-methoxy-benzoylsulfamoyl)-benzamide (CAS RN 221668-34-4). Other possibilities include safener compounds disclosed in, for example, EP0365484 e.g. N-(2-methoxybenzoyl)-4-[(methylaminocarbonyl)amino]benzenesulfonamide.

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

30 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
5 compound of Formula I with the safener).

The present invention still further provides a method of selectively controlling weeds at a locus comprising crop plants and weeds, wherein the method comprises application to the locus of a weed controlling amount of a composition according to
10 the present invention. '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
15 limits and depend on the nature of the soil, the method of application (pre- or post-emergence; seed dressing; application to the seed furrow; no tillage application etc.), the crop plant, the 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
20 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
25 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
30 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®.

In a preferred embodiment the crop plant is rendered tolerant to HPPD-inhibitors via genetic engineering. Methods of rendering crop plants tolerant to HPPD-inhibitors are known, for example from WO0246387. Thus in an even more preferred embodiment the crop plant is transgenic in respect of a polynucleotide comprising a DNA sequence which encodes an HPPD-inhibitor resistant HPPD enzyme derived from a bacterium, more particularly from *Pseudomonas fluorescens* or *Shewanella colwelliana*, or from a plant, more particularly, derived from a monocot plant or, yet more particularly, from a barley, maize, wheat, rice, *Brachiaria*, *Cenchrus*, *Lolium*, *Festuca*, *Setaria*, *Eleusine*, *Sorghum* or *Avena* species.

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.

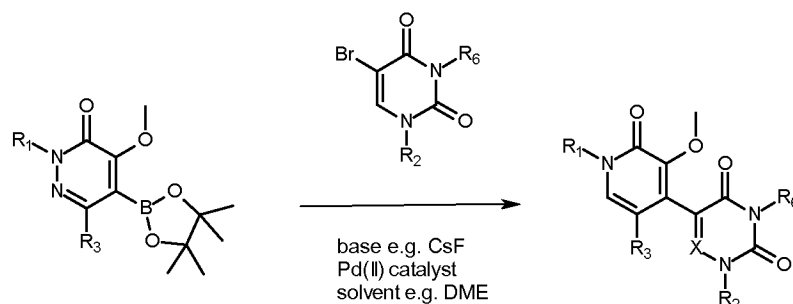
Crops are also to be understood to include those which are obtained by conventional methods of breeding or genetic engineering and contain so-called output traits (e.g. improved storage stability, higher nutritional value and improved flavour).

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.

The compositions can be used to control unwanted plants (collectively, 'weeds'). The weeds to be controlled may be both monocotyledonous species, for example *Agrostis*, *Alopecurus*, *Avena*, *Brachiaria*, *Bromus*, *Cenchrus*, *Cyperus*, *Digitaria*, *Echinochloa*, *Eleusine*, *Lolium*, *Monochoria*, *Rottboellia*, *Sagittaria*, *Scirpus*, *Setaria* and *Sorghum*, and dicotyledonous species, for example *Abutilon*, *Amaranthus*, *Ambrosia*, *Chenopodium*, *Chrysanthemum*, *Conyza*, *Galium*, *Ipomoea*, *Nasturtium*, *Sida*, *Sinapis*, *Solanum*, *Stellaria*, *Veronica*, *Viola* and *Xanthium*. Weeds can also include plants which may be considered crop plants but which are growing outside a crop area ('escapes'), or which grow from seed left over from a previous planting of a different crop ('volunteers'). Such volunteers or escapes may be tolerant to certain other herbicides.

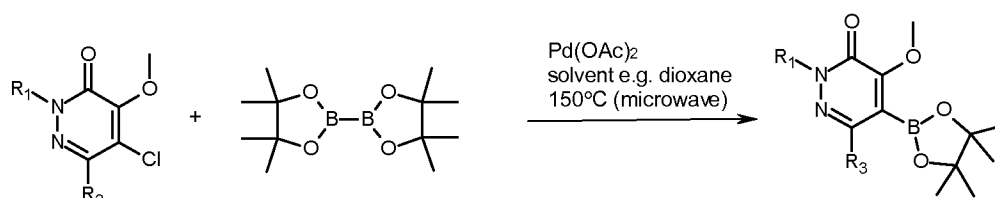
The compounds of the present invention can be prepared according to the following schemes.

- 5 **Scheme 1.** Reaction of a triazinedione or pyrimidinedione bromide with a boronic ester



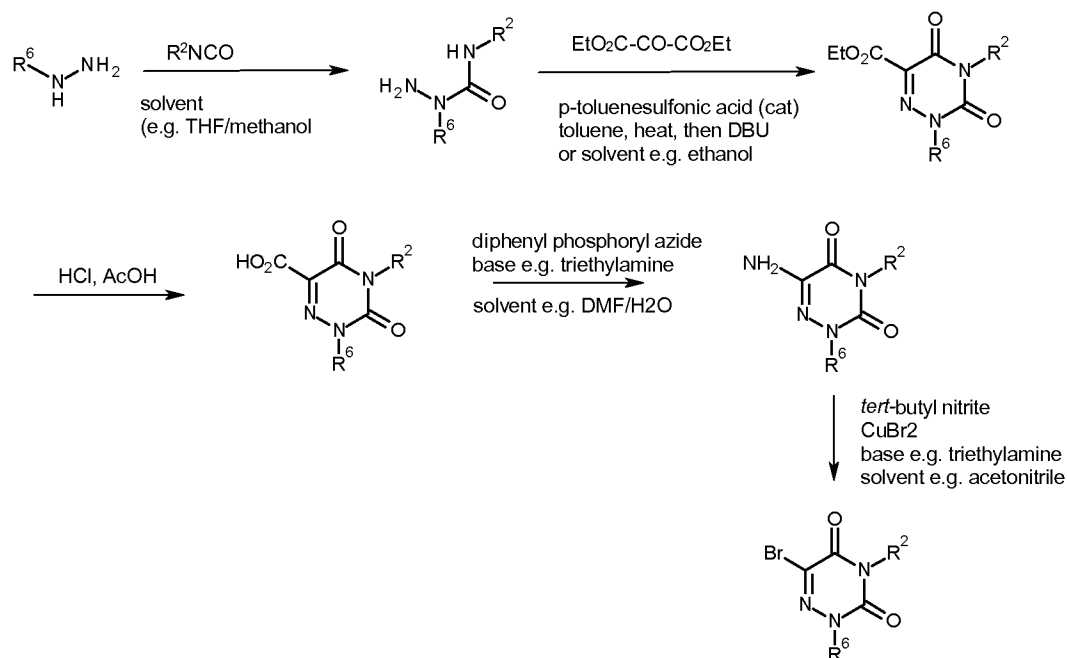
- 10 The boronic esters can be prepared by known methods or methods analogous to known methods, for example as shown in Scheme 2.

Scheme 2. Formation of pyridazinone boronic esters:



15

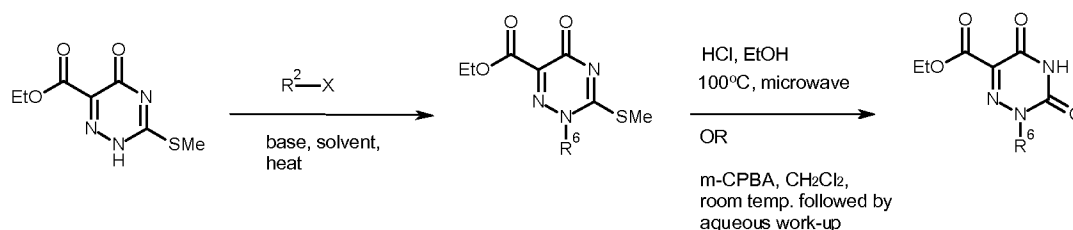
The heterocyclic bromides can be prepared by ring synthesis, by known methods or methods analogous to known methods. In cases where A¹=N, the triazinedione bromides can be prepared by ring synthesis by the method shown in Scheme 3.

Scheme 3. Formation of triazinedione bromides – construction of triazinedione ring:

5 wherein DBU is diazabicyclo[5.4.0]undec-7-ene.

In cases where $\text{A}^1 = \text{N}$ and R^6 is an alkyl group, the R^6 group can be installed via a selective alkylation reaction as shown in Scheme 4.

10

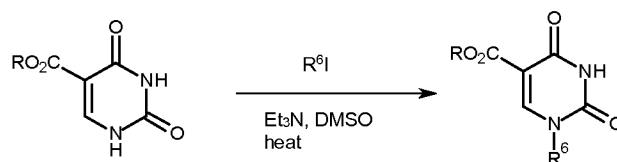
Scheme 4. Introduction of R^6 into triazinediones by selective alkylation:

Wherein X is a halogen such as chlorine, bromine or iodine, the base is an inorganic base such as potassium carbonate, the solvent is a non-protic organic solvent such as toluene, and m-CPBA is *meta*-chloroperbenzoic acid.

15

In cases where $\text{A} = \text{C}$ and R^6 is an alkyl group, the R^6 group can be installed via a selective alkylation reaction as shown in Scheme 5.

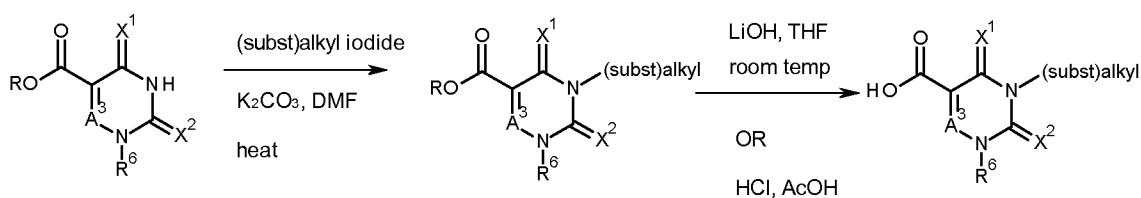
20

Scheme 5. Selective alkylation of heterocyclic diones:

5

In cases where R^2 is alkyl, the carboxylic acid can be prepared by N-alkylation of the NH ester followed by de-esterification as shown in Scheme 6.

Scheme 6. Formation of heterocyclic carboxylic ester and acid - N-alkylation of heterocycle (i.e. $R^2 = (\text{substituted})\text{alkyl}$):



15

The aryl or heteroarylboronic acids are known or are readily available using established procedures.

Example 1: Preparation of 6-Bromo-4-butyl-2-methyl-1,2,4-triazine-3,5-dione

Step 1: To a cold solution of methyl hydrazine (20g) in tetrahydrofuran (100ml) on an ice-water bath is added trimethylsilyl isocyanate under a nitrogen atmosphere over a period of 20 minutes and stirred at same temperature for an hour. The reaction mixture is then slowly warmed to room temperature, then methanol (70ml) is added, warmed to 40°C and stirred at the same temperature for 5 hours. The reaction mixture was then concentrated under reduced pressure to afford 1-amino-1,3-dimethyl-urea (23g, 60%)

¹H NMR (400 MHz, d₆-DMSO) δ ppm = 0.91 (3 H, s), 4.46 (3 H, bs), 5.95 (2 H, bs)

Step 2: A solution of 1-amino-1,3-dimethyl-urea (23g) and diethylketomalonate (45g) in ethanol (250ml) is refluxed for 36 hours under a nitrogen atmosphere. The reaction mixture is concentrated to afford the crude product. This material is purified by column chromatography, eluting with 20% ethyl acetate in hexane, to give ethyl 2-methyl-3,5-dioxo-1,2,4-triazine-6-carboxylate (20g).

¹H NMR (400 MHz, d₆-DMSO) δ ppm = 1.26 (3 H, t), 3.49 (3 H, s), 4.27 (2 H, q), 12.37 (1 H, bs)

Step 3: To a solution of ethyl 2-methyl-3,5-dioxo-1,2,4-triazine-6-carboxylate (20g) in N,N-dimethylformamide (200ml) under a nitrogen atmosphere is added potassium carbonate (41g) followed by dropwise addition of *n*-butyl iodide (28g) over a period of 15 minutes at room temperature. The resulting reaction mixture is then warmed to 60°C for 2 hours, monitoring the reaction by TLC. The reaction mixture is then quenched with ice cold water (300ml) and extracted with dichloromethane (500ml X 3); the combined dichloromethane extracts are dried (sodium sulphate), filtered and concentrated under reduced pressure. The crude product is purified by column chromatography, eluting with 20% ethyl acetate in hexane, to give ethyl 4-butyl-2-methyl-3,5-dioxo-1,2,4-triazine-6-carboxylate (18g).

¹H NMR (400 MHz, CDCl₃) δ ppm = 0.93 (3H, t), 1.37 (2H, dq), 1.38 (3H, t), 1.62 (2H, dq), 3.70 (3H, s), 3.94 (2H, t), 4.41 (2H, q)

Step 4: To a cold solution of ethyl 4-butyl-2-methyl-3,5-dioxo-1,2,4-triazine-6-carboxylate (18g) in acetic acid (180ml) on an ice-water bath is added dropwise hydrochloric acid (conc., 180ml), then the reaction mixture is stirred at room temperature for 24 hours. All volatiles are removed from the reaction mixture under reduced pressure and the residue is triturated with diethyl ether (50ml) to afford 4-butyl-2-methyl-3,5-dioxo-1,2,4-triazine-6-carboxylic acid as a white solid (12g).

¹H NMR (400 MHz, d₆-DMSO) δ ppm = 0.89 (3H, t), 1.29 (2H, dq), 1.51 (2H, dq), 3.54 (3H, s), 3.76 (2H, t)

Step 5: To a solution of 4-butyl-2-methyl-3,5-dioxo-1,2,4-triazine-6-carboxylic acid (5g) in N,N-dimethylformamide (50ml) under a nitrogen atmosphere is added triethylamine (4.5g), followed by dropwise addition of diphenyl phosphoryl azide (9.1g) over a period of 10 minutes. The reaction mixture is stirred at room temperature for 3 hours, then water (5ml) is added and the reaction mixture is heated at 100°C for a further 1 hour. The reaction mixture is cooled and all volatiles are removed under reduced pressure. The residue is dissolved in ethyl acetate (500ml) and washed with a saturated aqueous solution of sodium hydrogen carbonate (200ml), followed by water (200ml) and brine (200ml). The ethyl acetate layer is dried (sodium sulphate), filtered and concentrated under reduced pressure. The crude product is purified by column chromatography on silica, eluting with 20% ethyl acetate in hexane, to give 6-amino-4-butyl-2-methyl-1,2,4-triazine-3,5-dione (2.5g).

¹H NMR (400 MHz, CDCl₃) δ ppm = 0.94 (3H, t), 1.36 (2H, dq), 1.63 (2H, dq), 3.46 (3H, s), 3.94 (2H, t), 4.65 (2H, bs)

Step 6: To a solution of *tert*-butyl nitrite (6.8g) and copper (II) bromide (11g) in acetonitrile (70ml) at 65°C under a nitrogen atmosphere, is added portion wise 6-amino-4-butyl-2-methyl-1,2,4-triazine-3,5-dione (6.5g). The reaction mixture is stirred at this temperature for an hour, monitoring by TLC, then cooled to room temperature, poured onto 1N aqueous hydrochloric acid and extracted with ethyl

acetate (250 ml x 2); the combined organic extracts are dried (sodium sulphate), filtered and concentrated under reduced pressure. The crude product is purified by column chromatography on silica, eluting with 20% ethyl acetate in hexane to give 6-bromo-4-butyl-2-methyl-1,2,4-triazine-3,5-dione (4.8g).

5

^1H NMR (400 MHz, CDCl_3) δ ppm = 0.94 (3H, t), 1.36 (2H, dq), 1.61 (2H, dq), 3.64 (3H, s), 3.96 (2H, t)

Example 2: Preparation of 4-Butyl-2-methyl-6-(1-methyl-5,6-dioxo-4H-pyridazin-4-yl)-1,2,4-triazine-3,5-dione (Compound 1.002)

10

Step 1: Preparation of 4-Butyl-6-(5-methoxy-1-methyl-6-oxo-pyridazin-4-yl)-2-methyl-1,2,4-triazine-3,5-dione

15 5-chloro-4-methoxy-2-methyl-pyridazin-3-one (500mg), bis(pinacolato)diboron (1.1g), potassium acetate (0.43g), tricyclohexyl phosphine (0.13g) and palladium(II) acetate (0.5g) are dissolved in 1,4-dioxane (10ml). The mixture is heated to 150°C in the microwave for 18 minutes. The reaction mixture is filtered through celite and washed with ethyl acetate and then the solvent is concentrated *in vacuo*.

20

In a second microwave vial, 6-bromo-4-butyl-2-methyl-1,2,4-triazine-3,5-dione (1.01g), cesium fluoride (1.74g) and [1,1'-bis(diphenylphosphino)-ferrocene]palladium(II) dichloride dichloromethane adduct (0.19g) are combined. Then 4-methoxy-2-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridazin-
25 3-one (0.76g) in dimethoxyethane (10ml) is added and the mixture heated to 150°C in the microwave. The reaction mixture is filtered through celite and washed with ethyl acetate.

The crude product is dry-loaded onto a 40g silica cartridge, eluting with a gradient of
30 iso-hexane:ethyl acetate. Fractions containing product are combined and concentrated *in vacuo* to yield an orange oil (480.0mg). This is dissolved in iso-hexane (15.0ml) and sonicated, after which a solid appeared. The solid was collected by filtration to

yield 4-butyl-6-(5-methoxy-1-methyl-6-oxo-pyridazin-4-yl)-2-methyl-1,2,4-triazine-3,5-dione as a beige solid (188.0mg).

¹H NMR (400 MHz, CDCl₃) δ ppm = 0.96 (3 H, t, *J*=7.5 Hz) 1.40 (2 H, dd, *J*=15.6, 7.5 Hz) 1.61 - 1.71 (2 H, m) 3.70 (3 H, s) 3.81 (3 H, s) 3.95 - 4.03 (2 H, m) 4.22 (3 H, s) 7.67 (1 H, s)

Step 2: 4-Butyl-2-methyl-6-(1-methyl-5,6-dioxo-4H-pyridazin-4-yl)-1,2,4-triazine-3,5-dione

4-butyl-6-(5-methoxy-1-methyl-6-oxo-pyridazin-4-yl)-2-methyl-1,2,4-triazine-3,5-dione (180.0mg) is dissolved in morpholine (2.0ml). The reaction is stirred at 100°C for 90 minutes.

The reaction mixture is carefully added to aqueous hydrochloric acid (2.0M, 30.0ml) and stirred for 10 minutes. The solid formed is collected by filtration then dissolved again in 20.0ml dichloromethane, which is washed with another portion of hydrochloric acid (2.0M, 15.0ml). The dichloromethane layer is separated and concentrated *in vacuo*. The crude product is triturated with acetonitrile (5.0ml) then sonicated; the resulting solid was collected by filtration to yield 4-butyl-2-methyl-6-(1-methyl-5,6-dioxo-4H-pyridazin-4-yl)-1,2,4-triazine-3,5-dione as an off-white solid (88.0mg).

Example 3: Preparation of 2-Methyl-6-(1-methyl-5,6-dioxo-4H-pyridazin-4-yl)-4-phenyl-1,2,4-triazine-3,5-dione (Compound 1.001)

Step 1: Preparation of 6-(5-Methoxy-1-methyl-6-oxo-pyridazin-4-yl)-2-methyl-4-phenyl-1,2,4-triazine-3,5-dione

5-chloro-4-methoxy-2-methyl-pyridazin-3-one (500.0mg), bis(pinacolato)diboron (1.1g), potassium acetate (0.43g), tricyclohexylphosphine (0.13g) and palladium(II) acetate (0.05g) are dissolved in 1,4-dioxane (10 ml). The mixture is heated to 150°C in the microwave for 18 minutes. The mixture is then filtered through celite and washed with ethyl acetate, then the solvent is concentrated *in vacuo*.

In a second microwave vial, 6-bromo-2-methyl-4-phenyl-1,2,4-triazine-3,5-dione (1.2g - prepared from methyl hydrazine and phenylisocyanate analogously to the synthesis of 6-bromo-4-butyl-2-methyl-1,2,4-triazine-3,5-dione described in Example 1), cesium fluoride (1.74g) and [1,1'-bis(diphenylphosphino)ferrocene]-palladium(ii) dichloride dichloromethane adduct (0.19g) are combined. Then 4-methoxy-2-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridazin-3-one (0.76g) in dimethoxyethane (10 ml) is added and the mixture is heated to 160°C in a microwave for 18 minutes. The reaction mixture is filtered over celite and washed with ethyl acetate.

The crude product is dry-loaded onto a 40g silica cartridge, eluting with a gradient of iso-hexane:ethyl acetate. Fractions containing product are combined and concentrated *in vacuo* to yield an orange solid (280.0mg). The solid is triturated with methanol (10ml) and the resulting solid is collected by filtration to yield 6-(5-methoxy-1-methyl-6-oxo-pyridazin-4-yl)-2-methyl-4-phenyl-1,2,4-triazine-3,5-dione as a beige solid (203.0mg).

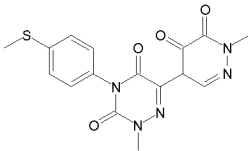
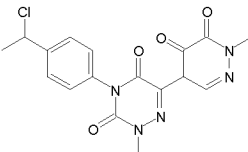
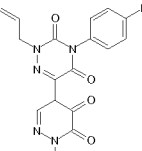
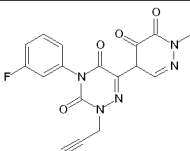
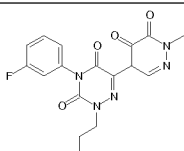
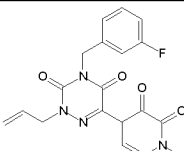
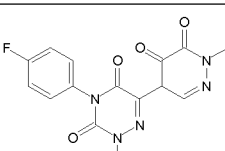
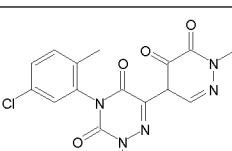
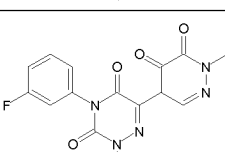
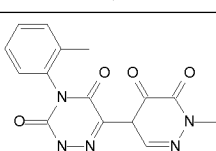
¹H NMR (400 MHz, CDCl₃) δ ppm = 3.76 (3 H, s) 3.81 (3 H, s) 4.21 (3 H, s) 7.22 - 7.30 (2 H, m) 7.44 - 7.58 (3 H, m) 7.74 (1 H, s)

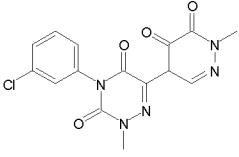
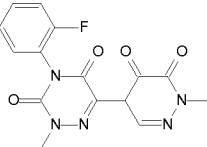
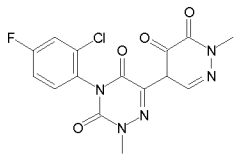
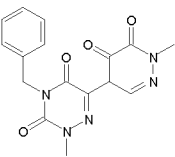
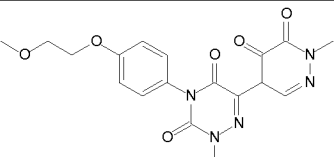
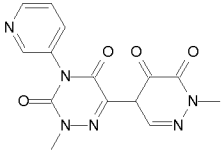
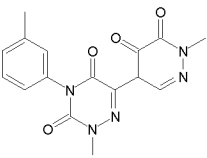
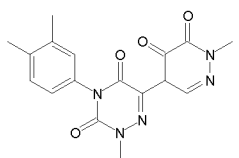
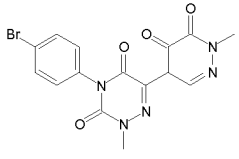
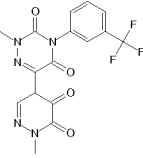
Step 2: Preparation of 2-Methyl-6-(1-methyl-5,6-dioxo-4H-pyridazin-4-yl)-4-phenyl-1,2,4-triazine-3,5-dione

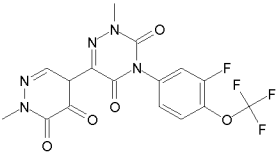
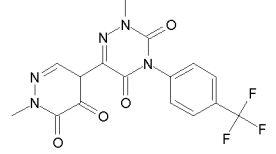
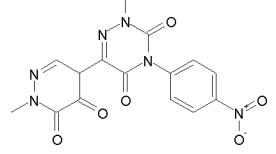
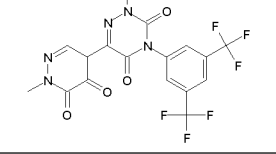
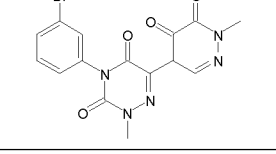
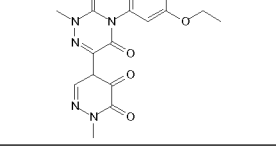
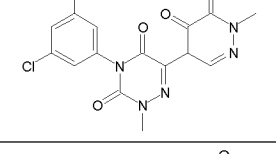
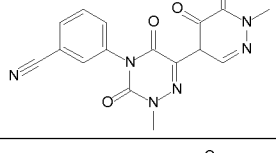
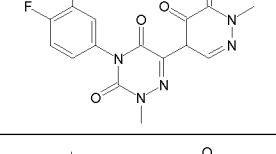
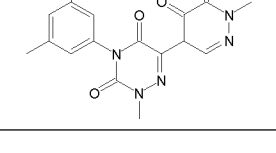
6-(5-methoxy-1-methyl-6-oxo-pyridazin-4-yl)-2-methyl-4-phenyl-1,2,4-triazine-3,5-dione (203.0 mg) is dissolved in morpholine (2.0ml). The reaction is stirred at 100°C for 90 minutes. The reaction mixture is then added to water (30.0ml) and stirred; the aqueous layer is extracted with dichloromethane (2 x 15ml) and the organic layer separated. The aqueous layer is acidified with aqueous hydrochloric acid (2.0 M, 30.0ml) and is then extracted with dichloromethane (3 x 15ml). The organic layers are combined and concentrated *in vacuo*. The crude product is triturated with acetonitrile (5ml) and the resulting solid is collected by filtration to yield 2-methyl-6-(1-methyl-5,6-dioxo-4H-pyridazin-4-yl)-4-phenyl-1,2,4-triazine-3,5-dione as a pale yellow solid (76.0 mg).

TABLE 1 – Examples of herbicidal compounds of the present invention.

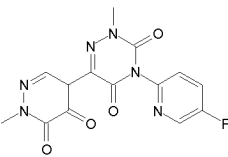
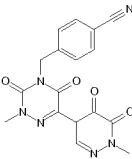
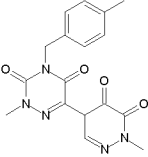
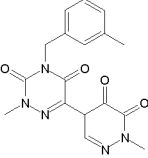
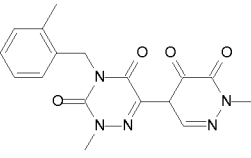
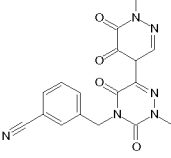
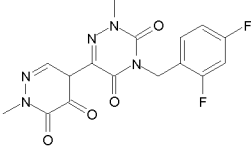
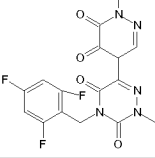
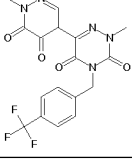
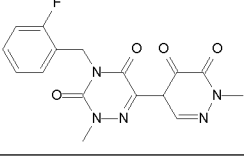
Compound Number	Structure	NMR
1.001		
1.002		CDCl ₃ : δ ppm = 0.93 - 1.00 (3 H, m) 1.40 (2 H, dd, <i>J</i> =15.0, 7.5 Hz) 1.62 - 1.71 (2 H, m) 3.74 (3 H, s) 3.84 (3 H, s) 3.97 - 4.04 (2 H, m) 7.98 (1 H, s)
1.003		CDCl ₃ : δ ppm = 3.80 (3 H, s) 3.85 (3 H, s) 7.26 - 7.29 (1 H, m) 7.46 - 7.58 (4 H, m) 8.01 (1 H, s)
1.004		
1.005		
1.006		
1.007		
1.008		
1.009		

Compound Number	Structure	NMR
1.010		
1.011		
1.012		
1.013		
1.014		
1.015		
1.016		
1.017		
1.018		
1.019		

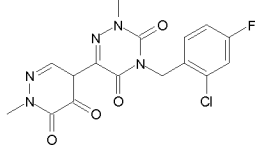
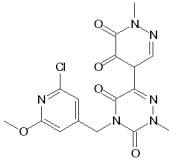
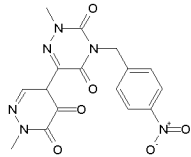
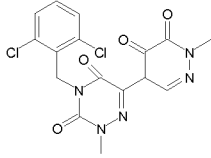
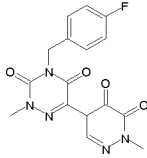
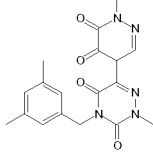
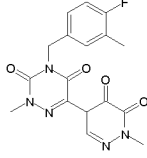
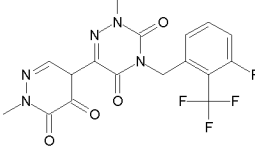
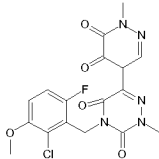
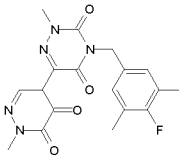
Compound Number	Structure	NMR
1.020		
1.021		
1.022		
1.023		
1.024		
1.025		
1.026		
1.027		
1.028		
1.029		

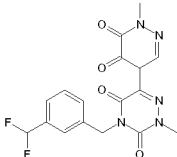
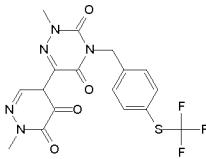
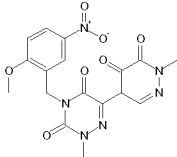
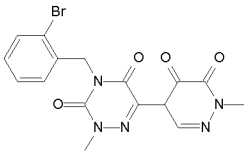
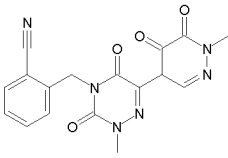
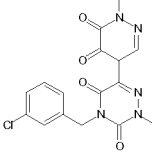
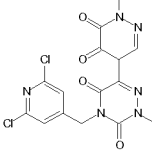
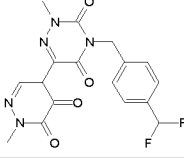
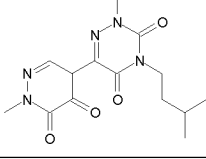
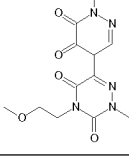
Compound Number	Structure	NMR
1.030		
1.031		
1.032		
1.033		
1.034		
1.035		
1.036		
1.037		
1.038		
1.039		

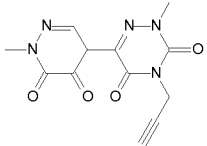
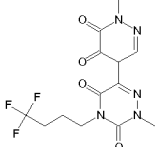
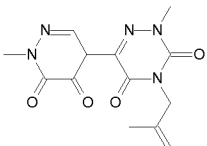
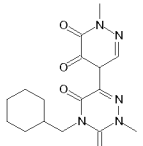
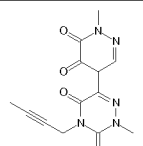
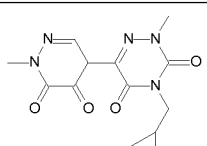
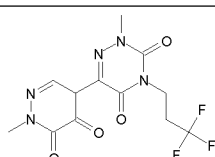
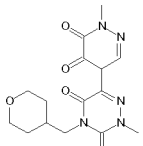
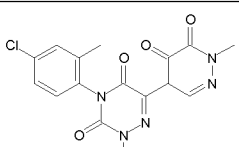
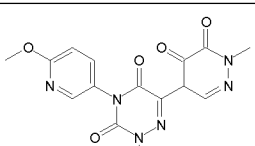
Compound Number	Structure	NMR
1.040		
1.041		
1.042		
1.043		
1.044		
1.045		
1.046		
1.047		
1.048		
1.049		

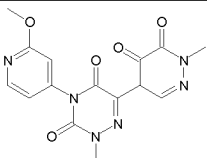
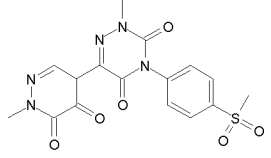
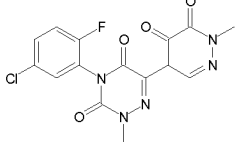
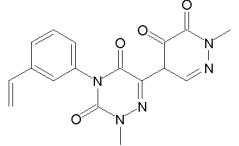
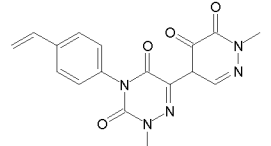
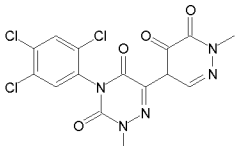
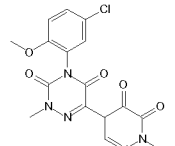
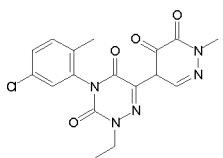
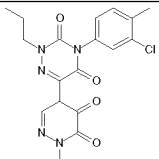
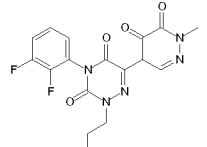
Compound Number	Structure	NMR
1.050		
1.051		
1.052		
1.053		
1.054		
1.055		
1.056		
1.057		
1.058		
1.059		

Compound Number	Structure	NMR
1.060		
1.061		
1.062		
1.063		
1.064		
1.065		
1.066		
1.067		
1.068		
1.069		

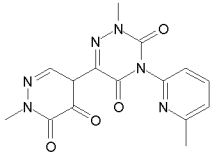
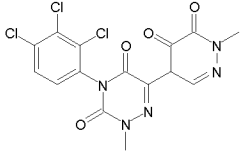
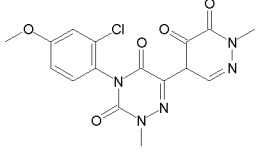
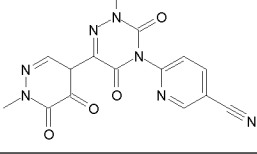
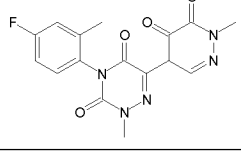
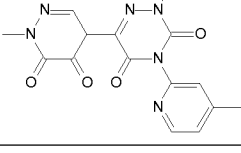
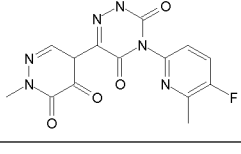
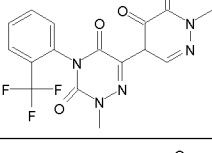
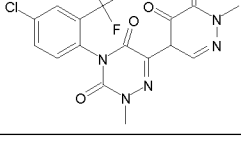
Compound Number	Structure	NMR
1.070		
1.071		
1.072		
1.073		
1.074		
1.075		
1.076		
1.077		
1.078		
1.079		

Compound Number	Structure	NMR
1.080		
1.081		
1.082		
1.083		
1.084		
1.085		
1.086		
1.087		
1.088		
1.089		

Compound Number	Structure	NMR
1.090		
1.019		
1.092		
1.093		
1.094		
1.095		
1.096		
1.097		
1.098		
1.099		

Compound Number	Structure	NMR
1.100		
1.101		
1.102		
1.103		
1.104		
1.105		
1.106		
1.107		
1.108		
1.109		

Compound Number	Structure	NMR
1.110		
1.111		
1.112		
1.113		
1.114		
1.115		
1.116		
1.117		
1.118		
1.119		

Compound Number	Structure	NMR
1.120		
1.121		
1.122		
1.123		
1.124		
1.125		
1.126		
1.127		
1.128		

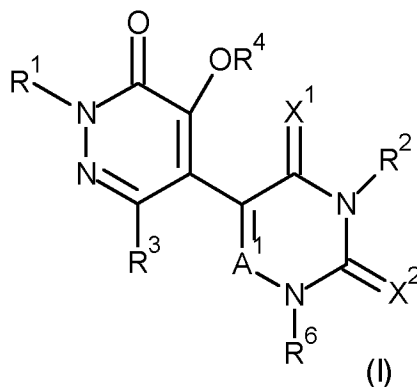
Biological Examples

Seeds of a variety of test species are sown in standard soil in pots (*Alopecurus*
 5 *myosuroides* (ALOMY), *Setaria faberi* (SETFA), *Echinochloa crus-galli* (ECHCG),
Solanum nigrum (SOLNI), *Amaranthus retroflexus* (AMARE), *Ipomoea hederacea*
 (IPOHE)). After cultivation for one day (pre-emergence) or after 8 days cultivation
 (post-emergence) under controlled conditions in a glasshouse (at 24/16°C, day/night;
 14 hours light; 65 % humidity), the plants are sprayed with an aqueous spray solution
 10 derived from the formulation of the technical active ingredient in acetone / water
 (50:50) solution containing 0.5% Tween 20 (polyoxyethelyene sorbitan monolaurate,
 CAS RN 9005-64-5). Compounds are applied at 1000 g/h. The test plants are then
 grown in a glasshouse under controlled conditions in a glasshouse (at 24/16°C,
 day/night; 14 hours light; 65 % humidity) and watered twice daily. After 13 days for
 15 pre and post-emergence, the test is evaluated for the percentage damage caused to the
 plant. The biological activities are shown in the following table on a five point scale
 (5 = 80-100%; 4 = 60-79%; 3=40-59%; 2=20-39%; 1=0-19%).

Compound	POST Application						PRE Application					
	SOLNI	AMARE	SETFA	ALOMY	ECHCG	IPOHE	SOLNI	AMARE	SETFA	ALOMY	ECHCG	IPOHE
1.002	5	5	3	1	5	5	2	3	3	1	3	1
1.003	5	5	4	2	5	5	3	5	1	1	3	1

Claims

1. A compound of Formula (I):



or an agronomically acceptable salt thereof,
wherein:-

- 10 X^1 and X^2 are independently selected from the group consisting of O and S;

A^1 is N or CR^5 ;

- 15 R^1 is selected from the group consisting of hydrogen, C_1 - C_6 alkyl, C_3 - C_6 cycloalkyl, C_2 - C_6 alkenyl, C_2 - C_6 alkynyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy- C_1 - C_3 -alkyl and C_3 - C_6 cycloalkyl- C_1 - C_3 -alkyl;

- 20 R^2 is selected from the group consisting of C_1 - C_6 alkyl-, C_1 - C_6 haloalkyl-, C_2 - C_6 alkenyl, C_2 - C_6 alkynyl, C_3 - C_6 cycloalkyl, C_1 - C_6 alkoxy- C_1 - C_3 -alkyl-, C_1 - C_3 alkoxy- C_3 - C_6 cycloalkyl-, C_1 - C_3 alkyl- $S(O)_p$ - C_3 - C_6 cycloalkyl-, C_1 - C_3 alkoxy- C_1 - C_3 alkyl-, C_1 - C_6 alkylcarbonyl- C_1 - C_3 alkyl-, tetrahydropyranyl- C_1 - C_3 alkyl-, benzyl-, pyridyl and phenyl-, the benzyl, pyridyl and phenyl groups being optionally substituted by one or more substituents selected from the group consisting of cyano, nitro, halogen, C_1 - C_3 alkyl-, C_1 - C_3 haloalkyl-, C_2 - C_3 alkenyl-, C_1 - C_3 alkoxy-, C_1 - C_3 alkoxy- C_1 - C_3 -alkoxy-, C_1 - C_3 alkyl- $S(O)_p$ -, C_1 - C_3 haloalkyl- $S(O)_p$ - and C_1 - C_3 haloalkoxy-;
- 25

R^3 is selected from the group consisting of hydrogen, hydroxyl, halogen, nitro, amino, cyano, C_1 - C_6 alkyl, C_1 - C_3 alkoxy-, C_3 - C_6 cycloalkyl, C_2 - C_6 alkenyl, C_2 - C_6 alkynyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy- C_1 - C_3 -alkyl, C_3 - C_6 cycloalkyl- C_1 - C_3 -alkyl, C_1 - C_6 alkyl- $S(O)_p$ -, C_1 - C_6 alkyl- $S(O)_p$ - C_1 - C_3 -alkyl, C_1 - C_6 haloalkyl- $S(O)_p$ -, C_1 - C_3 alkylamino, C_1 - C_3 dialkylamino and C_1 - C_6 haloalkyl- $S(O)_p$ - C_1 - C_3 -alkyl;

R^4 is selected from the group consisting of hydrogen, C_1 - C_6 alkylcarbonyl-, arylcarbonyl-, C_1 - C_6 alkoxycarbonyl-, C_1 - C_6 alkyl- $S(O)_p$ -, C_1 - C_6 alkyl- $S(O)_p$ carbonyl- and aryl- $S(O)_p$ -, wherein said aryl groups may be optionally substituted by one or more R^7 ;

R^5 is selected from the group consisting of hydrogen, hydroxyl, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl and C_1 - C_6 alkoxy- C_1 - C_3 alkyl;

R^6 is selected from the group consisting of hydrogen, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy- C_1 - C_6 alkyl, C_1 - C_6 haloalkoxy- C_1 - C_6 alkyl, C_1 - C_6 alkoxy- C_1 - C_6 alkoxy- C_1 - C_6 alkyl, C_1 - C_6 alkyl C_2 - C_6 alkenyl, C_2 - C_6 haloalkenyl, C_2 - C_6 alkynyl, C_2 - C_6 haloalkynyl and C_3 - C_6 cycloalkyl;

R^7 is selected from the group consisting of halo-, C_1 - C_3 alkyl, C_1 - C_3 haloalkyl and C_1 - C_6 alkoxy; and

$p = 0, 1$ or 2 .

2. A compound of Formula (I) according to claim 1, wherein A^1 is N.
3. A compound of Formula (I) according to any one of the previous claims, wherein X^1 and X^2 are oxygen.
4. A compound according to any one of the previous claims, wherein R^1 is methyl or ethyl.

5. A compound according to any one of the previous claims, wherein R² is selected from the group consisting of C₁-C₆alkyl-, C₁-C₃alkoxy-C₁-C₃alkyl-, C₁-C₆alkylcarbonyl-C₁-C₃alkyl-, benzyl-, pyridyl- and phenyl-, the benzyl-, pyridyl- and phenyl- groups being optionally substituted by one or more substituents selected from the group consisting of cyano, halogen, C₁-C₃alkyl-, C₁-C₃haloalkyl-, C₂-C₃alkenyl-, C₁-C₃alkoxy- and C₁-C₃haloalkoxy-.
6. A compound according to any one of the previous claims, wherein R³ is selected from the group consisting of hydrogen, halogen, cyano, C₁-C₆alkyl-, C₂-C₆alkenyl-, C₂-C₆alkynyl-, C₁-C₆haloalkyl and C₁-C₆alkyl-S(O)_p-.
7. A compound according to any one of the previous claims, wherein R⁴ is hydrogen.
8. A compound according to any one of the previous claims, wherein R⁵ is hydrogen or methyl.
9. A compound according to any one of the previous claims, wherein R⁶ is selected from the group consisting of hydrogen, methyl and halogen.
10. A herbicidal composition comprising a compound according to any one of the previous claims and an agriculturally acceptable formulation adjuvant.
11. A herbicidal composition according to claim 10, further comprising at least one additional pesticide.
12. A herbicidal composition according to claim 11, wherein the additional pesticide is a herbicide or herbicide safener.
13. A method of controlling weeds at a locus comprising application to the locus of a weed controlling amount of a composition according to any one of claims 10 to 12.
14. Use of a compound of Formula (I) as defined in claim 1 as a herbicide.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/056211A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D403/04
ADD. A01N43/64

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

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.
A	DE 10 2007 020690 A1 (BAYER HEALTHCARE AG [DE]) 6 November 2008 (2008-11-06) examples -----	1-14
A	GB 2 399 754 A (SYNGENTA PARTICIPATIONS AG [CH]) 29 September 2004 (2004-09-29) examples -----	1-14
A	WO 2004/093896 A1 (PHARMACIA CORP [US]; STEPHENSON DIANE T [US]; TAYLOR DUNCAN P [US]) 4 November 2004 (2004-11-04) compounds 58, ID92 -----	1-14
A,P	WO 2013/050421 A1 (SYNGENTA LTD [GB]; BHONOA H YUNAS [GB]; ELLIOTT ALISON CLARE [GB]; GAUL) 11 April 2013 (2013-04-11) pages 32,52,55; examples; table C8 ----- -/-	1-14



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

10 June 2014

Date of mailing of the international search report

26/06/2014

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

Menegaki, Fotini

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/056211

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A, P	WO 2013/083774 A1 (SYNGENTA LTD [GB]) 13 June 2013 (2013-06-13) examples	1-14
A	----- JP H11 152273 A (OTSUKA CHEMICAL CO LTD) 8 June 1999 (1999-06-08) table Table 1 -----	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2014/056211

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 102007020690 A1	06-11-2008	DE 102007020690 A1	06-11-2008
		WO 2008135152 A1	13-11-2008

GB 2399754 A	29-09-2004	NONE	

WO 2004093896 A1	04-11-2004	US 2005009733 A1	13-01-2005
		WO 2004093896 A1	04-11-2004

WO 2013050421 A1	11-04-2013	AR 088097 A1	07-05-2014
		AU 2012320565 A1	24-04-2014
		CA 2850013 A1	11-04-2013
		WO 2013050421 A1	11-04-2013

WO 2013083774 A1	13-06-2013	UY 34494 A	31-07-2013
		WO 2013083774 A1	13-06-2013

JP H11152273 A	08-06-1999	NONE	
