

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

24 August 2023 (24.08.2023)



(10) International Publication Number

WO 2023/156323 A1

(51) International Patent Classification:

C07D 215/22 (2006.01) A01N 43/42 (2006.01)

C07D 215/56 (2006.01)

(21) International Application Number:

PCT/EP2023/053441

(22) International Filing Date:

13 February 2023 (13.02.2023)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

22157289.4 17 February 2022 (17.02.2022) EP

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

(72) Inventors: **MORRIS, James Alan**; Syngenta, Jealott's Hill International Research Centre, Bracknell Berkshire RG42 6EY (GB). **ANDERSON, Zoe Jane**; Syngenta Jealott's Hill International Research Centre, Bracknell Berkshire RG42 6EY (GB). **SEDEN, Peter Timothy**; Syngenta Jealott's Hill International Research Centre, Bracknell RG42 6EY (GB). **EMMETT, Edward John**; Syngenta Jealott's Hill International Research Centre, Bracknell RG42 6EY (GB). **DALE, Suzanna**; Syngenta, Jealott's Hill International Research Centre, Bracknell Berkshire RG42 6EY (GB). **MUNNS, Gordon Richard**; Syngenta Jealott's Hill International Research Centre, Bracknell RG42 6EY (GB).

(74) Agent: SYNGENTA IP; Rosentalstrasse 67, 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, CV, 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, 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, CV, 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, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, 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).

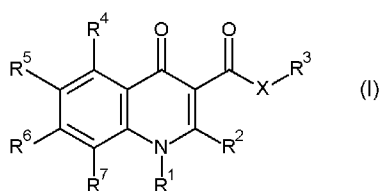
Declarations under Rule 4.17:

- 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))
- in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE

(54) Title: HERBICIDAL QUINOLONE DERIVATIVES



(57) Abstract: Compounds of Formula (I), (I.) wherein the substituents are as defined in claim 1. The invention further relates to herbicidal compositions which comprise a compound of Formula (I) and to the use of compounds of Formula (I) for controlling weeds, in particular in crops of useful plants.



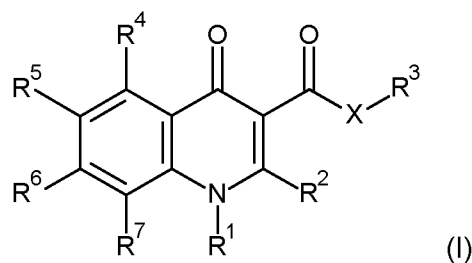
WO 2023/156323 A1

HERBICIDAL QUINOLONE DERIVATIVES

The present invention relates to herbicidal quinolone derivatives, e.g., as active ingredients, which have herbicidal activity. The invention also relates to agrochemical compositions which comprise at least one of the quinolone derivatives, to processes of preparation of these compounds and to uses of the quinolone derivatives or compositions in agriculture or horticulture for controlling weeds, in particular in crops of useful plants.

US 4,670,444, *Med Chem Res* (2016) 25,1861–1876, and *J. Chem. Soc., Perkin Trans. 1*, 2002, 1232–1235 describe quinolone derivatives as antibacterial agents. Further to this, CN108617661 and CN101643468 disclose the use of quinolone derivatives as agricultural agents, e.g. for use as insecticides, bactericides, or herbicides. In addition, *Chem. Commun.*, 2018, 54, 1869 discloses fluoroquinolone analogues with herbicidal activity.

According to the present invention, there is provided a compound of Formula (I):



wherein

X is O;

R¹ is C₁-C₆alkyl or phenyl optionally substituted with 1 or 2 groups, which may be the same or different, represented by R¹⁰;

R² is hydrogen, phenyl or heteroaryl, wherein the heteroaryl moiety is a 5- or 6-membered aromatic ring which comprises 1, 2, 3 or 4 heteroatoms individually selected from N, O and S, and wherein each phenyl and heteroaryl moiety may be optionally substituted with 1, 2, 3, or 4 groups, which may be the same or different, represented by R⁸;

R³ is hydrogen or C₁-C₆alkyl;

R⁴, R⁵, R⁶, and R⁷, are each independently selected from hydrogen, halogen, cyano, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆haloalkoxy, C₁-C₆alkylcarbonyl, C₁-C₆alkylsulfanyl, C₁-C₆alkylsulfinyl, C₁-C₆alkylsulfonyl, C₁-C₆alkylaminocarbonyl, aminocarbonyl, and phenyl, wherein each phenyl moiety may be optionally substituted with 1, 2, 3, or 4 groups, which may be the same or different, represented by R⁹;

R⁸ is cyano, nitro, halogen, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆haloalkoxy, C₁-C₆alkoxyC₁-C₆alkyl, C₁-C₆alkylsulfanyl, C₁-C₆alkylsulfinyl, C₁-C₆alkylsulfonyl, C₁-C₆alkylsulfonamido,

C₁-C₆alkylcarbonyl, C₁-C₆alkoxycarbonyl, C₁-C₆alkylaminocarbonyl, C₃-C₆cycloalkyl, C₃-C₆cycloalkylaminocarbonyl, or N,N-di(C₁-C₄alkyl)aminocarbonyl;

R⁹ is cyano, nitro, halogen, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆haloalkoxy, C₁-C₆alkoxyC₁-C₆alkyl, C₁-C₆alkylsulfanyl, C₁-C₆alkylsulfinyl, C₁-C₆alkylsulfonyl, C₁-C₆alkylsulfonamido,
5 C₁-C₆alkylcarbonyl, C₁-C₆alkoxycarbonyl, C₁-C₆alkylaminocarbonyl, C₃-C₆cycloalkyl, C₃-C₆cycloalkylaminocarbonyl, or N,N-di(C₁-C₄alkyl)aminocarbonyl; and

R¹⁰ is halogen, cyano, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆haloalkoxy, C₁-C₆alkylsulfanyl, or C₁-C₆alkylsulfonyl;

or a salt or an N-oxide thereof.

10

Surprisingly, it has been found that the novel compounds of Formula (I) have, for practical purposes, a very advantageous level of herbicidal activity.

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

According to a third aspect of the invention, there is provided a method of controlling weeds at a locus comprising applying to the locus a weed controlling amount of a composition comprising a compound of Formula (I).

20 According to a fourth aspect of the invention, there is provided the use of a compound of Formula (I) as a herbicide.

Where substituents are indicated as being "optionally substituted", this means that they may or may not carry one or more identical or different substituents, e.g., one, two or three R⁸ substituents. For example, C₁-C₆alkyl substituted by 1, 2 or 3 halogens, may include, but not be limited to, -CH₂Cl, -CHCl₂,
25 -CCl₃, -CH₂F, -CHF₂, -CF₃, -CH₂CF₃ or -CF₂CH₃ groups. As another example, C₁-C₆alkoxy substituted by 1, 2 or 3 halogens, may include, but not limited to, CH₂ClO-, CHCl₂O-, CCl₃O-, CH₂FO-, CHF₂O-, CF₃O-, CF₃CH₂O- or CH₃CF₂O- groups.

As used herein, the term "cyano" means a -CN group.

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

As used herein, the term "nitro" means an -NO₂ group.

As used herein, the term "C₁-C₆alkyl" refers to a straight or branched hydrocarbon chain radical consisting solely of carbon and hydrogen atoms, containing no unsaturation, having from one to six carbon atoms, and which is attached to the rest of the molecule by a single bond. "C₁-C₄alkyl" and "C₁-
35 C₃alkyl" are to be construed accordingly. Examples of C₁-C₆alkyl include, but are not limited to, methyl, ethyl, n-propyl, and the isomers thereof, for example, iso-propyl. A "C₁-C₆alkylene" group refers to the corresponding definition of C₁-C₆alkyl, except that such radical is attached to the rest of the molecule by two single bonds. The term "C₁-C₂alkylene" is to be construed accordingly. Examples of C₁-C₆alkylene, include, but are not limited to, -CH₂-, -CH₂CH₂- and -(CH₂)₃-.

As used herein, the term "C₁-C₆haloalkyl" refers a C₁-C₆alkyl radical as generally defined above substituted by one or more of the same or different halogen atoms. The terms "C₁-C₄haloalkyl" and "C₁-C₃haloalkyl", are to be construed accordingly. Examples of C₁-C₆haloalkyl include, but are not limited to trifluoromethyl.

5 As used herein, the term "C₁-C₆alkoxy" refers to a radical of the formula -OR_a where R_a is a C₁-C₆alkyl radical as generally defined above. The terms "C₁-C₄alkoxy" and "C₁-C₃alkoxy" are to be construed accordingly. Examples of C₁-C₆alkoxy include, but are not limited to, methoxy, ethoxy, 1-methylethoxy (iso-propoxy), and propoxy.

10 As used herein, the term "C₁-C₆haloalkoxy" refers to a C₁-C₆alkoxy radical as generally defined above substituted by one or more of the same or different halogen atoms. The terms "C₁-C₄haloalkoxy" and "C₁-C₃haloalkoxy", are to be construed accordingly. Examples of C₁-C₆haloalkoxy include, but are not limited to trifluoromethoxy.

15 As used herein, the term "C₁-C₆alkoxyC₁-C₆alkyl" refers to a radical of the formula R_bOR_a- wherein R_b is a C₁-C₆alkyl radical as generally defined above, and R_a is a C₁-C₆alkylene radical as generally defined above.

As used herein, the term "C₁-C₆alkoxycarbonyl" refers to a radical of the formula -C(O)OR_a, where R_a is a C₁-C₆alkyl radical as generally defined above.

20 As used herein, the term "C₃-C₆cycloalkyl" refers to a radical which is a monocyclic saturated ring system and which contains 3 to 6 carbon atoms. The terms "C₃-C₅cycloalkyl" and "C₃-C₄cycloalkyl" are to be construed accordingly. Examples of C₃-C₆cycloalkyl include, but are not limited to, cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl.

25 As used herein, the term "heteroaryl" refers to a 5- or 6-membered aromatic monocyclic ring radical which comprises 1, 2, 3 or 4 heteroatoms individually selected from nitrogen, oxygen and sulfur. Examples of heteroaryl include, but are not limited to, furanyl, pyrrolyl, thienyl, pyrazolyl, imidazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, triazolyl, tetrazolyl, pyrazinyl, pyridazinyl, pyrimidyl or pyridyl.

As used herein, the term "C₁-C₆alkylcarbonyl" refers to a radical of the formula -C(O)R_a, where R_a is a C₁-C₆alkyl radical as generally defined above. Examples of C₁-C₆alkylcarbonyl include, but are not limited to, acetyl.

30 As used herein, the term "C₁-C₆alkylsulfanyl" refers to a radical of the formula -SR_a, where R_a is a C₁-C₆alkyl radical as generally defined above. The terms "C₁-C₄alkylsulfanyl" and "C₁-C₃alkylsulfanyl", are to be construed accordingly. Examples of C₁-C₆alkylsulfanyl include, but are not limited to methylsulfanyl.

35 As used herein, the term "C₁-C₆alkylsulfinyl" refers to a radical of the formula -S(O)R_a, where R_a is a C₁-C₆alkyl radical as generally defined above. The terms "C₁-C₄alkylsulfinyl" and "C₁-C₃alkylsulfinyl", are to be construed accordingly. Examples of C₁-C₆alkylsulfinyl include, but are not limited to methylsulfinyl.

40 As used herein, the term "C₁-C₆alkylsulfonyl" refers to a radical of the formula -S(O)₂R_a, where R_a is a C₁-C₆alkyl radical as generally defined above. The terms "C₁-C₄alkylsulfonyl" and "C₁-C₃alkylsulfonyl", are to be construed accordingly. Examples of C₁-C₆alkylsulfonyl include, but are not limited to methylsulfonyl.

As used herein, the term "C₁-C₆alkylsulfonamido" refers to a radical of the formula -NHS(O)₂R_a, wherein R_a is a C₁-C₆alkyl radical as generally defined above.

As used herein, the term "aminocarbonyl" refers to a radical of the formula -C(O)NH₂.

As used herein, the term "C₁-C₆alkylaminocarbonyl" refers to a radical of the formula -C(O)NHR_a,
5 wherein R_a is a C₁-C₆alkyl radical as generally defined above.

As used herein, the term "N,N-di(C₁-C₄alkyl)aminocarbonyl" refers to a radical of the formula -C(O)N(R_a)(R_b), wherein R_a and R_b are each individually a C₁-C₄alkyl radical as generally defined above. The term "N,N-di(C₁-C₃alkyl)aminocarbonyl" is to be construed accordingly.

As used herein, the term "C₃-C₆cycloalkylaminocarbonyl" refers to a C₃-C₆cycloalkyl ring attached
10 to the rest of the molecule through an -NHC(O)- linker.

The presence of one or more possible stereogenic elements in a compound of formula (I) means that the compounds may occur in optically 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
15 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. The present invention includes all possible tautomeric forms for a compound of formula (I).

In each case, the compounds of formula (I) according to the invention are in free form or in salt form, e.g., an agronomically usable salt form. Salts that the compounds of Formula (I) may form with
20 amines, including primary, secondary and tertiary amines (for example ammonia, dimethylamine and triethylamine), alkali metal and alkaline earth metal bases, transition metals or quaternary ammonium bases are preferred.

The following list provides definitions, including preferred definitions, for substituents X, R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, and R¹⁰ with reference to compounds of formula (I). For any one of these
25 substituents, any of the definitions given below may be combined with any definition of any other substituent given below or elsewhere in this document.

X is O.

R¹ is C₁-C₆alkyl or phenyl optionally substituted with 1 or 2 groups, which may be the same or different, represented by R¹⁰. Preferably, R¹ is C₁-C₄alkyl or phenyl optionally substituted with a single
30 group, represented by R¹⁰. More preferably, R¹ is C₁-C₃alkyl or phenyl optionally substituted with a single group, represented by R¹⁰. More preferably still, R¹ is ethyl or 4-trifluoromethoxyphenyl. In one embodiment, R¹ is ethyl.

In one set of embodiments, R¹ is C₁-C₆alkyl. Preferably, R¹ is C₁-C₄alkyl. More preferably, R¹ is C₁-C₃alkyl. More preferably still, R¹ is methyl, ethyl, n-propyl, or isopropyl. Even more preferably, R¹ is
35 methyl or ethyl. Most preferably, R¹ is ethyl.

R² is hydrogen, phenyl or heteroaryl, wherein the heteroaryl moiety is a 5- or 6-membered aromatic ring which comprises 1, 2, 3 or 4 heteroatoms individually selected from N, O and S, and

wherein each phenyl and heteroaryl moiety may be optionally substituted with 1, 2, 3, or 4 groups, which may be the same or different, represented by R^8 .

Preferably, R^2 is hydrogen, phenyl or heteroaryl, wherein the heteroaryl moiety is a 5- or 6-membered aromatic ring which comprises 1, 2, or 3 heteroatoms individually selected from N, O and S, and wherein each phenyl and heteroaryl moiety may be optionally substituted with 1, 2, or 3 groups, which may be the same or different, represented by R^8 .

More preferably, R^2 is hydrogen, phenyl or heteroaryl, wherein the heteroaryl moiety is a 5- or 6-membered aromatic ring which comprises 1 or 2 heteroatoms individually selected from N and O, and wherein each phenyl and heteroaryl moiety may be optionally substituted with 1, 2, or 3 groups, which may be the same or different, represented by R^8 .

More preferably still, R^2 is hydrogen, phenyl or heteroaryl, wherein the heteroaryl moiety is a 5- or 6-membered aromatic ring which comprises 1 or 2 heteroatoms individually selected from N and O, and wherein each phenyl and heteroaryl moiety may be optionally substituted with 1 or 2 groups, which may be the same or different, represented by R^8 .

Even more preferably, R^2 is hydrogen, or phenyl substituted with 1 or 2 groups, which may be the same or different, represented by R^8 . In one set of embodiments, R^2 is hydrogen, 3,4-dichlorophenyl, 3-chloro-4-cyanophenyl, 4-chloro-3-cyanophenyl, 4-chloro-3-fluorophenyl, or 4-fluorophenyl. In a preferred set of embodiments, R^2 is hydrogen, 3,4-dichlorophenyl or 4-fluorophenyl.

In one set of embodiments, R^2 is phenyl or heteroaryl, wherein the heteroaryl moiety is a 5- or 6-membered aromatic ring which comprises 1, 2, 3 or 4 heteroatoms individually selected from N, O and S, and wherein each phenyl and heteroaryl moiety may be optionally substituted with 1, 2, 3, or 4 groups, which may be the same or different, represented by R^8 .

Preferably, R^2 is phenyl or heteroaryl, wherein the heteroaryl moiety is a 5- or 6-membered aromatic ring which comprises 1, 2, or 3 heteroatoms individually selected from N, O and S, and wherein each phenyl and heteroaryl moiety may be optionally substituted with 1, 2, or 3 groups, which may be the same or different, represented by R^8 .

More preferably, R^2 is phenyl or heteroaryl, wherein the heteroaryl moiety is a 5- or 6-membered aromatic ring which comprises 1 or 2 heteroatoms individually selected from N and O, and wherein each phenyl and heteroaryl moiety may be optionally substituted with 1, 2, or 3 groups, which may be the same or different, represented by R^8 .

More preferably still, R^2 is phenyl or heteroaryl, wherein the heteroaryl moiety is a 5- or 6-membered aromatic ring which comprises 1 or 2 heteroatoms individually selected from N and O, and wherein each phenyl and heteroaryl moiety may be optionally substituted with 1 or 2 groups, which may be the same or different, represented by R^8 .

Even more preferably, R^2 is phenyl optionally substituted with 1 or 2 groups, which may be the same or different, represented by R^8 . More preferably still, R^2 is phenyl substituted with 1 or 2 groups, which may be the same or different, represented by R^8 . In one set of embodiments, R^2 is 3,4-dichlorophenyl, 3-chloro-4-cyanophenyl, 4-chloro-3-cyanophenyl, 4-chloro-3-fluorophenyl, or 4-fluorophenyl. In a preferred set of embodiments, R^2 is 3,4-dichlorophenyl or 4-fluorophenyl. Preferably, R^2 is 3,4-dichlorophenyl.

R³ is hydrogen or C₁-C₆alkyl. Preferably, R³ is hydrogen or C₁-C₄alkyl, more preferably, hydrogen or C₁-C₃alkyl. Even more preferably, R³ is hydrogen, methyl, or ethyl. More preferably still, R³ is hydrogen.

R⁴, R⁵, R⁶, and R⁷, are each independently selected from hydrogen, halogen, cyano, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆haloalkoxy, C₁-C₆alkylcarbonyl, C₁-C₆alkylsulfanyl, C₁-C₆alkylsulfinyl, C₁-C₆alkylsulfonyl, C₁-C₆alkylaminocarbonyl, aminocarbonyl, and phenyl, wherein each phenyl moiety may be optionally substituted with 1, 2, 3, or 4 groups, which may be the same or different, represented by R⁹.

Preferably, R⁴ is hydrogen, halogen, cyano, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆haloalkoxy, C₁-C₆alkylcarbonyl, C₁-C₆alkylsulfanyl, C₁-C₆alkylsulfinyl, C₁-C₆alkylsulfonyl, C₁-C₆alkylaminocarbonyl, aminocarbonyl, or phenyl, wherein each phenyl moiety may be optionally substituted with 1, 2, 3, or 4 groups, which may be the same or different, represented by R⁹.

More preferably, R⁴ is hydrogen, halogen, cyano, C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkylcarbonyl, C₁-C₄alkylsulfanyl, C₁-C₄alkylsulfinyl, C₁-C₄alkylsulfonyl, C₁-C₄alkylaminocarbonyl, aminocarbonyl, or phenyl, wherein each phenyl moiety may be optionally substituted with 1, 2, or 3 groups, which may be the same or different, represented by R⁹.

More preferably still, R⁴ is hydrogen, halogen, cyano, C₁-C₃alkyl, C₁-C₃alkoxy, C₁-C₃haloalkyl, C₁-C₃haloalkoxy, C₁-C₃alkylcarbonyl, C₁-C₃alkylsulfanyl, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃alkylaminocarbonyl, aminocarbonyl, or phenyl, wherein each phenyl moiety may be optionally substituted with 1 or 2 groups, which may be the same or different, represented by R⁹.

Even more preferably, R⁴ is hydrogen, halogen, cyano, acetyl, or C₁-C₃haloalkyl. In another set of embodiments, R⁴ is hydrogen, halogen, cyano, acetyl, or trifluoromethyl. In a further set of embodiments, R⁴ is hydrogen, chloro, bromo, cyano, acetyl, or trifluoromethyl.

In one set of embodiments, R⁴ is hydrogen, halogen, cyano, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆haloalkoxy, C₁-C₆alkylsulfanyl, C₁-C₆alkylsulfinyl, C₁-C₆alkylsulfonyl, C₁-C₆alkylaminocarbonyl, aminocarbonyl, or phenyl, wherein each phenyl moiety may be optionally substituted with 1, 2, 3, or 4 groups, which may be the same or different, represented by R⁹.

Preferably, R⁴ is hydrogen, halogen, cyano, C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkylsulfanyl, C₁-C₄alkylsulfinyl, C₁-C₄alkylsulfonyl, C₁-C₄alkylaminocarbonyl, aminocarbonyl, or phenyl, wherein each phenyl moiety may be optionally substituted with 1, 2, or 3 groups, which may be the same or different, represented by R⁹.

More preferably, R⁴ is hydrogen, halogen, cyano, C₁-C₃alkyl, C₁-C₃alkoxy, C₁-C₃haloalkyl, C₁-C₃haloalkoxy, C₁-C₃alkylsulfanyl, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃alkylaminocarbonyl, aminocarbonyl, or phenyl, wherein each phenyl moiety may be optionally substituted with 1 or 2 groups, which may be the same or different, represented by R⁹.

In one set of embodiments, R⁴ is hydrogen, halogen, cyano, or C₁-C₃haloalkyl. In another set of embodiments, R⁴ is hydrogen, halogen, cyano, or trifluoromethyl. In a further set of embodiments, R⁴ is hydrogen, chloro, bromo, cyano, or trifluoromethyl.

R⁵ is hydrogen, halogen, cyano, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆haloalkoxy, C₁-C₆alkylsulfanyl, C₁-C₆alkylsulfinyl, C₁-C₆alkylsulfonyl, C₁-C₆alkylaminocarbonyl, aminocarbonyl, or

phenyl, wherein each phenyl moiety may be optionally substituted with 1, 2, 3, or 4 groups, which may be the same or different, represented by R⁹.

Preferably, R⁵ is hydrogen, halogen, cyano, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₄haloalkoxy, C₁-C₆alkylsulfanyl, C₁-C₄alkylsulfinyl, C₁-C₆alkylsulfonyl, C₁-C₄alkylaminocarbonyl, aminocarbonyl, or phenyl, wherein each phenyl moiety may be optionally substituted with 1, 2, or 3 groups, which may be the same or different, represented by R⁹.

More preferably, R⁵ is hydrogen, halogen, cyano, C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄haloalkyl, C₁-C₃haloalkoxy, C₁-C₄alkylsulfanyl, C₁-C₃alkylsulfinyl, C₁-C₄alkylsulfonyl, C₁-C₃alkylaminocarbonyl, aminocarbonyl, or phenyl, wherein each phenyl moiety may be optionally substituted with 1 or 2 groups, which may be the same or different, represented by R⁹.

In one set of embodiments, R⁵ is hydrogen, halogen, cyano, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆alkylsulfanyl, C₁-C₆alkylsulfonyl, aminocarbonyl, or phenyl, wherein each phenyl moiety may be optionally substituted with 1, or 2 groups, which may be the same or different, represented by R⁹. In a preferred set of embodiments, R⁵ is hydrogen, halogen, cyano, C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄haloalkyl, C₁-C₄alkylsulfanyl, C₁-C₄alkylsulfonyl, aminocarbonyl, or phenyl, wherein each phenyl moiety may be optionally substituted with a single R⁹ group. In a particularly preferred set of embodiments, R⁵ is hydrogen, halogen, cyano, C₁-C₃alkyl, C₁-C₃alkoxy, C₁-C₃haloalkyl, C₁-C₃alkylsulfanyl, C₁-C₃alkylsulfonyl, aminocarbonyl, or phenyl, wherein each phenyl moiety may be optionally substituted with a single R⁹ group. In an even more preferable set of embodiments, R⁵ is hydrogen, chloro, fluoro, bromo, cyano, methyl, methoxy, trifluoromethyl, methylsulfanyl, methylsulfonyl, aminocarbonyl, or 4-fluorophenyl.

R⁶ is hydrogen, halogen, cyano, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆haloalkoxy, C₁-C₆alkylsulfanyl, C₁-C₆alkylsulfinyl, C₁-C₆alkylsulfonyl, C₁-C₆alkylaminocarbonyl, aminocarbonyl, or phenyl, wherein each phenyl moiety may be optionally substituted with 1, 2, 3, or 4 groups, which may be the same or different, represented by R⁹.

Preferably, R⁶ is hydrogen, halogen, cyano, C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkylsulfanyl, C₁-C₄alkylsulfinyl, C₁-C₄alkylsulfonyl, C₁-C₄alkylaminocarbonyl, aminocarbonyl, or phenyl, wherein each phenyl moiety may be optionally substituted with 1, 2, or 3 groups, which may be the same or different, represented by R⁹.

More preferably, R⁶ is hydrogen, halogen, cyano, C₁-C₃alkyl, C₁-C₃alkoxy, C₁-C₃haloalkyl, C₁-C₃haloalkoxy, C₁-C₃alkylsulfanyl, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃alkylaminocarbonyl, aminocarbonyl, or phenyl, wherein each phenyl moiety may be optionally substituted with 1 or 2 groups, which may be the same or different, represented by R⁹.

In one set of embodiments, R⁶ is hydrogen, halogen, cyano, C₁-C₃alkoxy, or C₁-C₃haloalkyl. In another set of embodiments, R⁶ is hydrogen, halogen, cyano, methoxy, or trifluoromethyl. In a further set of embodiments, R⁶ is hydrogen, chloro, cyano, methoxy, or trifluoromethyl.

R⁷ is hydrogen, halogen, cyano, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆haloalkoxy, C₁-C₆alkylsulfanyl, C₁-C₆alkylsulfinyl, C₁-C₆alkylsulfonyl, C₁-C₆alkylaminocarbonyl, aminocarbonyl, or phenyl, wherein each phenyl moiety may be optionally substituted with 1, 2, 3, or 4 groups, which may be the same or different, represented by R⁹.

Preferably, R⁷ is hydrogen, halogen, cyano, C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkylsulfanyl, C₁-C₄alkylsulfinyl, C₁-C₄alkylsulfonyl, C₁-C₄alkylaminocarbonyl, aminocarbonyl, or phenyl, wherein each phenyl moiety may be optionally substituted with 1, 2, or 3 groups, which may be the same or different, represented by R⁹.

5 More preferably, R⁷ is hydrogen, halogen, cyano, C₁-C₃alkyl, C₁-C₃alkoxy, C₁-C₃haloalkyl, C₁-C₃haloalkoxy, C₁-C₃alkylsulfanyl, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃alkylaminocarbonyl, aminocarbonyl, or phenyl, wherein each phenyl moiety may be optionally substituted with 1 or 2 groups, which may be the same or different, represented by R⁹.

In one set of embodiments, R⁷ is hydrogen, halogen, cyano, C₁-C₃alkyl, C₁-C₃alkoxy, or C₁-
10 C₃haloalkyl. In a preferred set of embodiments, R⁷ is hydrogen.

In one set of embodiments, when R⁴, R⁶, and R⁷, are each independently selected from hydrogen, halogen, cyano, C₁-C₃alkoxy, and C₁-C₃haloalkyl, R⁵ is hydrogen, halogen, cyano, C₁-C₃alkyl, C₁-C₃alkoxy, C₁-C₃haloalkyl, C₁-C₃alkylsulfanyl, C₁-C₃alkylsulfonyl, aminocarbonyl, or phenyl, wherein the phenyl moiety may be optionally substituted with a single R⁹ group. In another set of embodiments,
15 when R⁴, R⁶, and R⁷, are each independently selected from hydrogen, halogen, cyano, methoxy, and trifluoromethyl, R⁵ is hydrogen, halogen, cyano, C₁-C₃alkyl, C₁-C₃alkoxy, C₁-C₃haloalkyl, C₁-C₃alkylsulfanyl, C₁-C₃alkylsulfonyl, aminocarbonyl, or phenyl, wherein the phenyl moiety may be optionally substituted with a single R⁹ group.

R⁸ is cyano, nitro, halogen, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆haloalkoxy, C₁-
20 C₆alkoxyC₁-C₆alkyl, C₁-C₆alkylsulfanyl, C₁-C₆alkylsulfinyl, C₁-C₆alkylsulfonyl, C₁-C₆alkylsulfonamido, C₁-C₆alkylcarbonyl, C₁-C₆alkoxycarbonyl, C₁-C₆alkylaminocarbonyl, C₃-C₆cycloalkyl, C₃-C₆cycloalkylaminocarbonyl, or N,N-di(C₁-C₄alkyl)aminocarbonyl.

Preferably, R⁸ is cyano, nitro, halogen, C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkoxyC₁-C₃alkyl, C₁-C₄alkylsulfanyl, C₁-C₄alkylsulfinyl, C₁-C₄alkylsulfonyl, C₁-C₄alkylsulfonamido,
25 C₁-C₄alkylcarbonyl, C₁-C₄alkoxycarbonyl, C₁-C₄alkylaminocarbonyl, C₃-C₆cycloalkyl, C₃-C₆cycloalkylaminocarbonyl, or N,N-di(C₁-C₃alkyl)aminocarbonyl.

More preferably, R⁸ is cyano, nitro, halogen, C₁-C₃alkyl, C₁-C₃alkoxy, C₁-C₃haloalkyl, C₁-C₃haloalkoxy, C₁-C₃alkoxyC₁-C₂alkyl, C₁-C₃alkylsulfanyl, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃alkylsulfonamido, C₁-C₃alkylcarbonyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylaminocarbonyl, C₃-
30 C₄cycloalkyl, C₃-C₄cycloalkylaminocarbonyl, or N,N-di(C₁-C₂alkyl)aminocarbonyl.

In a preferred set of embodiments, R⁸ is cyano or halogen. In a particularly preferred set of embodiments R⁸ is halogen, preferably chloro or fluoro. Most preferably, R⁸ is fluoro.

R⁹ is cyano, nitro, halogen, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆haloalkoxy, C₁-C₆alkoxyC₁-C₆alkyl, C₁-C₆alkylsulfanyl, C₁-C₆alkylsulfinyl, C₁-C₆alkylsulfonyl, C₁-C₆alkylsulfonamido,
35 C₁-C₆alkylcarbonyl, C₁-C₆alkoxycarbonyl, C₁-C₆alkylaminocarbonyl, C₃-C₆cycloalkyl, C₃-C₆cycloalkylaminocarbonyl, or N,N-di(C₁-C₄alkyl)aminocarbonyl.

Preferably, R⁹ is cyano, nitro, halogen, C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkoxyC₁-C₃alkyl, C₁-C₄alkylsulfanyl, C₁-C₄alkylsulfinyl, C₁-C₄alkylsulfonyl, C₁-C₄alkylsulfonamido,

C₁-C₄alkylcarbonyl, C₁-C₄alkoxycarbonyl, C₁-C₄alkylaminocarbonyl, C₃-C₆cycloalkyl, C₃-C₆cycloalkylaminocarbonyl, or N,N-di(C₁-C₃alkyl)aminocarbonyl.

More preferably, R⁹ is cyano, nitro, halogen, C₁-C₃alkyl, C₁-C₃alkoxy, C₁-C₃haloalkyl, C₁-C₃haloalkoxy, C₁-C₃alkoxyC₁-C₂alkyl, C₁-C₃alkylsulfanyl, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃alkylsulfonamido, C₁-C₃alkylcarbonyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylaminocarbonyl, C₃-C₄cycloalkyl, C₃-C₄cycloalkylaminocarbonyl, or N,N-di(C₁-C₂alkyl)aminocarbonyl.

In a preferred set of embodiments, R⁹ is halogen. In a particularly preferred set of embodiments R⁹ is chloro, fluoro, or bromo, and preferably fluoro.

10 R¹⁰ is halogen, cyano, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆haloalkoxy, C₁-C₆alkylsulfanyl, or C₁-C₆alkylsulfonyl. Preferably, R¹⁰ is halogen, cyano, C₁-C₃alkyl, C₁-C₃alkoxy, C₁-C₃haloalkyl, C₁-C₃haloalkoxy, C₁-C₃alkylsulfanyl, or C₁-C₃alkylsulfonyl. More preferably, R¹⁰ is halogen, cyano, methyl, ethyl, isopropyl, methoxy, ethoxy, isopropoxy, trifluoromethyl, trifluoromethoxy, methylsulfanyl, or methylsulfonyl. More preferably still, R¹⁰ is trifluoromethoxy.

15

In a compound of formula (I) according to the present invention, preferably:

X is O;

R¹ is ethyl or phenyl substituted with a single group represented by R¹⁰;

20 R² is hydrogen or phenyl substituted with 1 or 2 groups, which may be the same or different, represented by R⁸;

R³ is hydrogen;

R⁴, R⁵, R⁶, and R⁷ are each independently selected from hydrogen, halogen, cyano, methyl, methoxy, trifluoromethyl, methylsulfanyl, methylsulfonyl, aminocarbonyl, and 4-fluorophenyl;

R⁸ is halogen; and

25 R¹⁰ is C₁-C₃haloalkoxy.

In one embodiment, in a compound of formula (I) according to the present invention, preferably:

X is O;

R¹ is ethyl or 4-trifluoromethoxyphenyl;

30 R² is hydrogen, 3,4-dichlorophenyl or 4-fluorophenyl;

R³ is hydrogen; and

R⁴, R⁵, R⁶, and R⁷ are each independently selected from hydrogen, halogen, cyano, methyl, methoxy, trifluoromethyl, methylsulfanyl, methylsulfonyl, aminocarbonyl, and 4-fluorophenyl.

35 In one embodiment, in a compound of formula (I) according to the present invention, preferably:

X is O;

R¹ is ethyl or 4-trifluoromethoxyphenyl;

R² is hydrogen, 3,4-dichlorophenyl or 4-fluorophenyl;

R³ is hydrogen;

40 R⁴ is hydrogen, halogen, cyano, or trifluoromethyl;

R⁵ is hydrogen, halogen, cyano, methyl, methoxy, trifluoromethyl, methylsulfanyl, methylsulfonyl, aminocarbonyl, or 4-fluorophenyl;

R⁶ is hydrogen, chloro, cyano, methoxy, or trifluoromethyl; and

R⁷ is hydrogen.

5

In another embodiment, in a compound of formula (I) according to the present invention, preferably:

X is O;

R¹ is ethyl or 4-trifluoromethoxyphenyl;

10

R² is hydrogen, 3,4-dichlorophenyl or 4-fluorophenyl;

R³ is hydrogen;

R⁴ is hydrogen, trifluoromethyl, bromo, cyano, or acetyl;

R⁵ is hydrogen, bromo, chloro, fluoro, cyano, methyl, methoxy, trifluoromethyl, aminocarbonyl, methylsulfanyl, or methylsulfonyl;

15

R⁶ is hydrogen, methoxy, or trifluoromethyl; and

R⁷ is hydrogen.

In another embodiment, in a compound of formula (I) according to the present invention, preferably:

20

X is O;

R¹ is ethyl;

R² is 3,4-dichlorophenyl or 4-fluorophenyl;

R³ is hydrogen;

R⁴ is hydrogen, trifluoromethyl, bromo, or cyano;

25

R⁵ is hydrogen, bromo, chloro, fluoro, cyano, methyl, methoxy, trifluoromethyl, aminocarbonyl, methylsulfanyl, or methylsulfonyl;

R⁶ is hydrogen, methoxy, or trifluoromethyl; and

R⁷ is hydrogen.

30

In another embodiment, in a compound of formula (I) according to the present invention, preferably:

X is O;

R¹ is ethyl;

R² is 3,4-dichlorophenyl;

35

R³ is hydrogen;

R⁴ is hydrogen, trifluoromethyl, bromo, or cyano;

R⁵ is hydrogen, bromo, chloro, fluoro, cyano, methyl, methoxy, trifluoromethyl, aminocarbonyl, methylsulfanyl, or methylsulfonyl;

R⁶ is hydrogen, methoxy, or trifluoromethyl; and

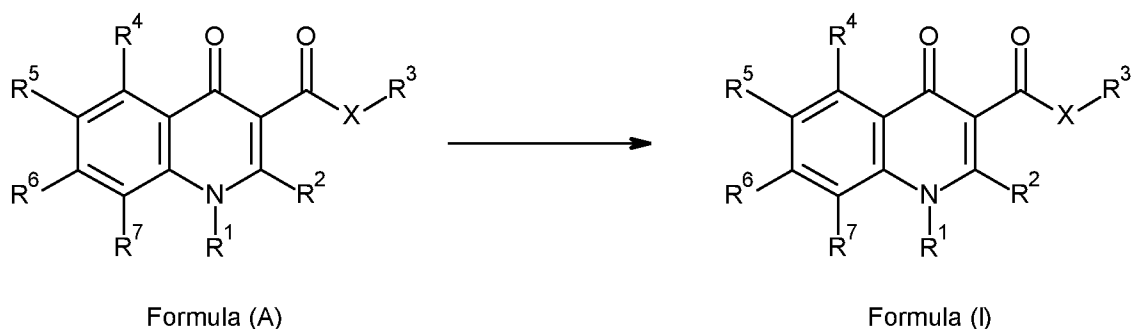
40

R⁷ is hydrogen.

Compounds of the invention can be made as shown in the following schemes, in which, unless otherwise stated, the definition of each variable is as defined above for a compound of Formula (I). General methods for the production of compounds of Formula (I) are described below. Unless otherwise stated in the text, R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and X are as defined hereinbefore. The starting materials
5 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, crystallisation, distillation and filtration.

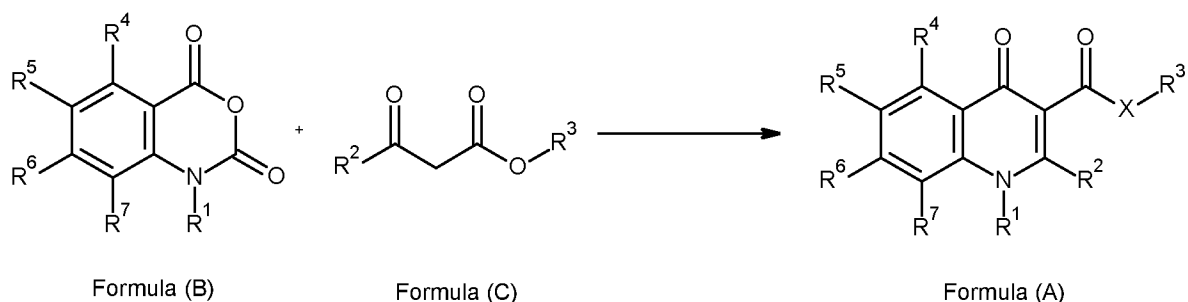
10 The compounds of Formula (I) of the present invention may be prepared from compounds of Formula (A) as shown in Scheme 1.

Scheme 1:

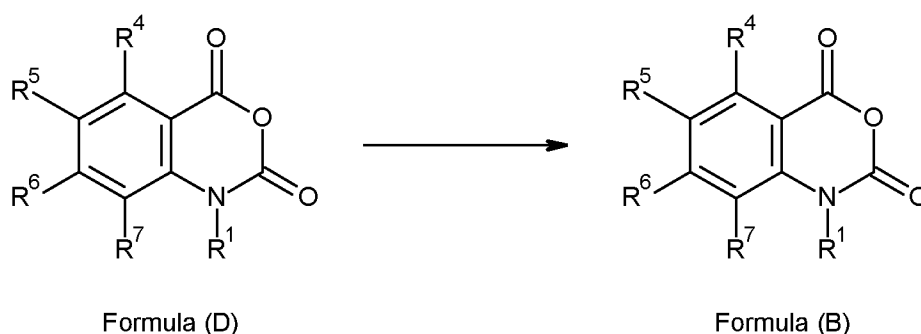


15 Compounds of Formula (I) wherein X is O and R^3 is H may be prepared by hydrolysis of a compound of Formula (A) wherein X is O and R^3 is not H but any other R^3 group as defined above, with a suitable base (such as sodium hydroxide or lithium hydroxide) or with a suitable acid (such as trifluoroacetic acid, hydrochloric acid, formic acid or sulfuric acid) in a suitable solvent (such as methanol, ethanol, dichloromethane, chloroform, ethyl acetate or tetrahydrofuran) with an optional co-solvent (such
20 as water). In the cases where a base was used, the product was obtained following acidification with a suitable acid (such as hydrochloric acid). This is shown in Scheme 1 above.

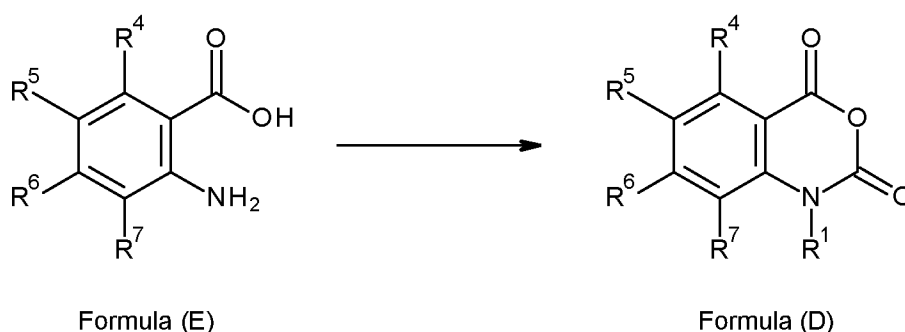
Compounds of Formula (A) wherein R^4 , R^5 , R^6 or R^7 are halogen (for example wherein R^4 , R^5 , R^6 or R^7 are Cl , Br or I) may be converted to a new compound of Formula (A) wherein R^4 , R^5 , R^6 or R^7 are
25 not halogen (for example, wherein R^4 , R^5 , R^6 or R^7 are C_1 - C_6 alkyl, phenyl, or cyano) by metal-catalysed cross coupling reactions, for example by Suzuki cross-coupling. In an additional transformation, compounds of Formula (A) wherein R^4 , R^5 , R^6 or R^7 are halogen (for example wherein R^4 , R^5 , R^6 or R^7 are Cl , Br or I) may be converted to a new compound of Formula (A) wherein R^4 , R^5 , R^6 or R^7 are C_1 - C_6 alkylcarbonyl by cross-coupling with an alkenyl stannane reagent under Stille coupling conditions,
30 followed by hydrolysis. The aforementioned and related C-Hal to C-R transformations are known to persons skilled in the art.

Scheme 2:

Compounds of Formula (A) wherein R³ is not H but any other R³ group as defined above, may be prepared from reaction of a compound of Formula (B) with a compound of Formula (C), with a suitable base (such as 1,8-diazabicyclo[5.4.0]undec-7-ene, potassium bis(trimethylsilyl)amide, potassium carbonate or sodium hydride) in a suitable solvent (such as tetrahydrofuran, *N,N*-dimethylformamide, dimethyl acetamide or water) at a given temperature (from -80 °C to reflux). This is shown in Scheme 2 above.

10 Scheme 3:

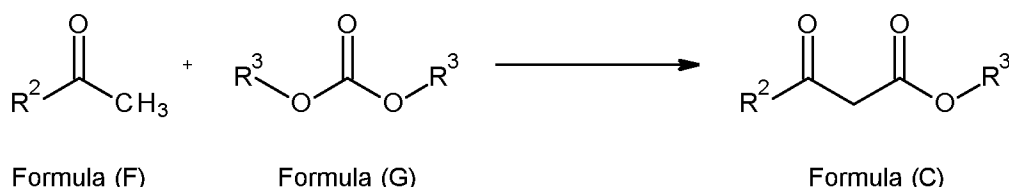
Compounds of Formula (B) wherein R¹ is not H but any other R¹ group as defined above may be prepared from a compound of Formula (D) wherein R³ is H, by alkylation with a suitable alkylating agent (such as an alkyl halide or dialkyl sulfate), in the presence of a suitable base (such as 1,8-diazabicyclo[5.4.0]undec-7-ene, diisopropyl ethylamine, sodium carbonate, potassium hydroxide or sodium hydride) in a suitable solvent (such as tetrahydrofuran, dimethyl acetamide or *N,N*-dimethylformamide) at a given temperature (such as room temperature to 50 °C). Such transformations are described in the scientific literature. This is shown in Scheme 3 above.

20 Scheme 4:

Compounds of Formula D may be prepared by reaction of a compound of Formula E with a suitable source of CO²⁺ such as triphosgene (bis(trichloromethyl) carbonate, phosgene, diphosgene, di-*tert*-butyl dicarbonate or ethyl chloroformate in a suitable solvent (such as tetrahydrofuran, toluene, 1,4-dioxane, acetonitrile or dichloromethane) optionally in the presence of a base (such as pyridine, triethylamine or sodium hydroxide) and optionally in the presence of a catalyst (such as 4-dimethylaminopyridine). These reactions may be performed at room temperature or at elevated temperature. This is shown in Scheme 4 above.

Alternatively, compounds of Formula (D) may be obtained from compounds of Formula (E) by reaction with a CO source (such as carbon monoxide) in the presence of a palladium catalyst (such as palladium (II) acetate) and a copper source (such as copper (II) acetate) in the presence of potassium iodide in a suitable solvent (such as acetonitrile) at elevated temperature (such as 60 °C). Compounds of Formula (E) are commercially available or may be prepared by methods reported in the literature.

15 Scheme 5:



Compounds of Formula (C) may be prepared by treatment of ketones of Formula (F) with a base (such as sodium hydride) in the presence of dialkyl carbonates of Formula (G) (such as dimethyl carbonate). Compounds of Formula (F) and Formula (G) are commercially available or may be prepared by methods familiar to persons skilled in the art. This is shown in Scheme 5 above.

The present invention still further provides a method of controlling weeds at a locus said method comprising application to the locus of a weed controlling amount of a composition comprising a compound of Formula (I). Moreover, the present invention may further provide a method of selectively controlling weeds at a locus comprising useful (crop) plants and weeds, wherein the method comprises application to the locus of a weed controlling amount of a composition according to the present invention. 'Controlling' means killing, reducing or retarding growth or preventing or reducing germination. It is noted that the compounds of the present invention show a much improved selectivity compared to known, structurally similar compounds. Generally the plants to be controlled are unwanted plants (weeds). 'Locus' means the area in which the plants are growing or will grow. The application may be applied to the locus pre-emergence and/or postemergence of the crop plant. Preferably, the compounds of the present invention are applied to the locus post-emergence of the crop. Some crop plants may be inherently tolerant to herbicidal effects of compounds of Formula (I).

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- 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 applied at a rate of from 10 to 2500 g/ha, especially from 25 to 1000 g/ha, more especially from 25 to 250 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
5 used.

The term "useful plants" is to be understood as also including useful plants that have been rendered tolerant to herbicides like bromoxynil or classes of herbicides such as, for example, 4-Hydroxyphenylpyruvate dioxygenase (HPPD) inhibitors, ALS inhibitors, for example primisulfuron, prosulfuron and trifloxysulfuron, 5-enol-pyrovyl-shikimate-3-phosphate-synthase (EPSPS) inhibitors,
10 glutamine synthetase (GS) inhibitors or protoporphyrinogen-oxidase (PPO) inhibitors as a result of conventional methods of breeding or genetic engineering. An example of a crop that has been rendered tolerant to imidazolinones, e.g. imazamox, by conventional methods of breeding (mutagenesis) is Clearfield® summer rape (Canola). Examples of crops that have been rendered tolerant to herbicides or classes of herbicides by genetic engineering methods include glyphosate- and glufosinate-resistant
15 maize varieties commercially available under the trade names RoundupReady®, Herculex I® and LibertyLink®.

The term "useful plants" is to be understood as also including useful plants which have been so transformed by the use of recombinant DNA techniques that they are capable of synthesising one or more selectively acting toxins, such as are known, for example, from toxin-producing bacteria, especially
20 those of the genus *Bacillus*.

Examples of such plants are: YieldGard® (maize variety that expresses a CryIA(b) toxin); YieldGard Rootworm® (maize variety that expresses a CryIIIB(b1) toxin); YieldGard Plus® (maize variety that expresses a CryIA(b) and a CryIIIB(b1) toxin); Starlink® (maize variety that expresses a Cry9(c) toxin); Herculex I® (maize variety that expresses a CryIF(a2) toxin and the enzyme
25 phosphinothricine N-acetyltransferase (PAT) to achieve tolerance to the herbicide glufosinate ammonium); NuCOTN 33B® (cotton variety that expresses a CryIA(c) toxin); Bollgard I® (cotton variety that expresses a CryIA(c) toxin); Bollgard II® (cotton variety that expresses a CryIA(c) and a CryIIA(b) toxin); VIPCOT® (cotton variety that expresses a VIP toxin); NewLeaf® (potato variety that expresses a CryIIIA toxin); NatureGard® Agrisure® GT Advantage (GA21 glyphosate-tolerant trait), Agrisure® CB
30 Advantage (Bt11 corn borer (CB) trait), Agrisure® RW (corn rootworm trait) and Protecta®.

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.

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

The compounds of Formula (I) (or compositions comprising such) 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*,
40 *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*.

Compounds of Formula (I) may be used in unmodified form or, preferably, together with the adjuvants conventionally employed in the art of formulation to provide herbicidal compositions, using formulation adjuvants, such as carriers, solvents and surface-active agents (SAA). The invention therefore further provides a herbicidal composition, comprising at least one compound Formula (I) and an agriculturally acceptable carrier and optionally an adjuvant. An agricultural acceptable carrier is for example a carrier that is suitable for agricultural use. Agricultural carriers are well known in the art.

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 compositions can be chosen from a number of formulation types. These include an emulsion concentrate (EC), a suspension concentrate (SC), a suspo-emulsion (SE), a capsule suspension (CS), a water dispersible granule (WG), an emulsifiable granule (EG), an emulsion, water in oil (EO), an emulsion, oil in water (EW), a micro-emulsion (ME), an oil dispersion (OD), an oil miscible flowable (OF), an oil miscible liquid (OL), a soluble concentrate (SL), an ultra-low volume suspension (SU), an ultra-low volume liquid (UL), a technical concentrate (TK), a dispersible concentrate (DC), a soluble powder (SP), a wettable powder (WP) and a soluble granule (SG). 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).

Soluble powders (SP) may be prepared by mixing a compound of Formula (I) 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, dextrans, 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
5 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
10 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 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
15 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 solvent) and then emulsifying the resultant liquid or solution into water containing one or more SAAs, 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 alkylnaphthalenes) and other appropriate organic solvents which
20 have a low solubility in water.

Microemulsions (ME) may be prepared by mixing water with a blend of one or more solvents with one or more SAAs, to produce spontaneously a thermodynamically stable isotropic liquid formulation. A compound of Formula (I) is present initially in either the water or the solvent/SAA blend. Suitable solvents for use in MEs include those hereinbefore described for use in ECs or in EWs. An ME may be
25 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.

Suspension concentrates (SC) may comprise aqueous or non-aqueous suspensions of finely
30 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 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,
35 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.

40 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
5 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
10 active agents (SAAs), spray additives based on oils, for example certain mineral oils or natural plant oils (such as soy bean and rape seed oil), modified plant oils such as methylated rape seed oil (MRSO), 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 SAAs of the cationic, anionic,
15 amphoteric or non-ionic type.

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

Suitable anionic SAAs 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
20 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
25 (predominately di-esters), for example the reaction between lauryl alcohol and tetraphosphoric acid; additionally these products may be ethoxylated), sulphosuccinamates, paraffin or olefine sulphonates, taurates, lignosulphonates and phosphates / sulphates of tristyrylphenols.

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

Suitable SAAs of the non-ionic type include condensation products of alkylene oxides, such as
30 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); alkanolamides; simple esters (for example fatty acid polyethylene glycol esters); amine oxides (for
35 example lauryl dimethyl amine oxide); lecithins and sorbitans and esters thereof, alkyl polyglycosides and tristyrylphenols. Suitable suspending agents include hydrophilic colloids (such as polysaccharides, polyvinylpyrrolidone or sodium carboxymethylcellulose) and swelling clays (such as bentonite or attapulgite).

The compounds of present invention can also be used in mixture with one or more additional
40 herbicides and/or plant growth regulators. Examples of such additional herbicides or plant growth regulators include acetochlor, acifluorfen (including acifluorfen-sodium), acetonifene, ametryn,

amicarbazone, aminopyralid, aminotriazole, atrazine, beflubutamid-M, benquitrione, bensulfuron (including bensulfuron-methyl), bentazone, bicyclopiron, bilanafos, bipyrazone, bispyribac-sodium, bixlozone, bromacil, bromoxynil, butachlor, butafenacil, carfentrazone (including carfentrazone-ethyl), cloransulam (including cloransulam-methyl), chlorimuron (including chlorimuron-ethyl), chlorotoluron,

5 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,

10 diflufenzopyr, dimethachlor, dimethenamid-P, dioxopyritrione, diquat dibromide, diuron, epyrifenacil, ethalfluralin, ethofumesate, fenoxaprop (including fenoxaprop-P-ethyl), fenoxasulfone, fenpyrazone, fenquitrione, fentrazamide, flazasulfuron, florasulam, florypyrauxifen (including florypyrauxifen-benzyl), fluazifop (including fluazifop-P-butyl), flucarbazone (including flucarbazone-sodium), flufenacet, flumetsulam, flumioxazin, fluometuron, fomesafen flupyr-sulfuron (including flupyr-sulfuron-methyl-

15 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

20 (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,

25 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,

30 tiafenacil, tolpyralate, topramezone, tralkoxydim, triafamone, triallate, triasulfuron, tribenuron (including tribenuron-methyl), triclopyr, trifloxysulfuron (including trifloxysulfuron-sodium), trifludimoxazin, trifluralin, triflusulfuron, tripyrasulfone, [(E)-[2-(trifluoromethyl)phenyl]methyleneamino] 2,6-bis[(4,6-dimethoxypyrimidin-2-yl)oxy]benzoate, 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-

35 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,

40 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, 6-chloro-4-(2,7-dimethyl-1-naphthyl)-5-hydroxy-2-methyl-pyridazin-3-one, tetrahydrofuran-2-ylmethyl (2R)-2-[(4-amino-3,5-dichloro-6-fluoro-2-pyridyl)oxy]propanoate, (2R)-2-[(4-amino-3,5-dichloro-6-fluoro-2-pyridyl)oxy]propanoic acid, tetrahydrofuran-2-ylmethyl 2-[(4-amino-3,5-dichloro-6-fluoro-2-pyridyl)oxy]propanoate, 2-[(4-amino-3,5-dichloro-6-fluoro-2-pyridyl)oxy]propanoic acid, 2-fluoro-N-(5-methyl-1,3,4-oxadiazol-2-yl)-3-[(R)-propylsulfinyl]-4-(trifluoromethyl)benzamide, 2-fluoro-N-(5-methyl-1,3,4-oxadiazol-2-yl)-3-propylsulfinyl-4-(trifluoromethyl)benzamide, (2-fluorophenyl)methyl 6-amino-5-chloro-2-(4-chloro-2-fluoro-3-methoxy-phenyl)pyrimidine-4-carboxylate, 6-amino-5-chloro-2-(4-chloro-2-fluoro-3-methoxy-phenyl)pyrimidine-4-carboxylic acid, 3-(3-chlorophenyl)-6-(5-hydroxy-1,3-dimethylpyrazole-4-carbonyl)-1,5-dimethyl-quinazoline-2,4-dione and [4-[3-(3-chlorophenyl)-1,5-dimethyl-2,4-dioxo-quinazoline-6-carbonyl]-2,5-dimethyl-pyrazol-3-yl] N,N-diethylcarbamate, methyl 2-[(E)-[2-chloro-4-fluoro-5-[3-methyl-2,6-dioxo-4-(trifluoromethyl)pyrimidin-1-yl]phenyl] methyleneamino]oxypropanoate and methyl (2R)-2-[(E)-[2-chloro-4-fluoro-5-[3-methyl-2,6-dioxo-4-(trifluoromethyl)pyrimidin-1-yl]phenyl]methyleneamino] oxypropanoate.

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, Sixteenth Edition, British Crop Protection Council, 2012. 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).

The compounds or mixtures of the present invention can also be used in combination with one or more herbicide safeners. Examples of such safeners include benoxacor, cloquintocet (including cloquintocet-mexyl), cyprosulfamide, dichlormid, fenchlorazole (including fenchlorazole-ethyl), fencloirim, fluxofenim, furilazole, isoxadifen (including isoxadifen-ethyl), mefenpyr (including mefenpyr-diethyl), metcamifen and oxabetrinil. Particularly preferred are mixtures of a compound of Formula (I) with cyprosulfamide, isoxadifen-ethyl, cloquintocet-mexyl and/or metcamifen.

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, 16th Edition (BCPC), 2012. 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.

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 compounds of Formula (I) are normally used in the form of agrochemical compositions and can be applied to the crop area or plant to be treated, simultaneously or in succession with further compounds. These further compounds can be e.g. fertilizers or micronutrient donors or other

preparations, which influence the growth of plants. They can also be selective herbicides or non-selective herbicides as well as insecticides, fungicides, bactericides, nematocides, molluscicides or mixtures of several of these preparations, if desired together with further carriers, surfactants or application promoting adjuvants customarily employed in the art of formulation.

- 5 The term "locus" as used herein means fields in or on which plants are growing, or where seeds of cultivated plants are sown, or where seed will be placed into the soil. It includes soil, seeds, and seedlings, as well as established vegetation.

The term "plants" refers to all physical parts of a plant, including seeds, seedlings, saplings, roots, tubers, stems, stalks, foliage, and fruits.

- 10 The term "plant propagation material" is understood to denote generative parts of the plant, such as seeds, which can be used for the multiplication of the latter, and vegetative material, such as cuttings or tubers, for example potatoes. There may be mentioned for example seeds (in the strict sense), roots, fruits, tubers, bulbs, rhizomes and parts of plants. Germinated plants and young plants which are to be transplanted after germination or after emergence from the soil, may also be mentioned. These young
15 plants may be protected before transplantation by a total or partial treatment by immersion. Preferably "plant propagation material" is understood to denote seeds.

Pesticidal agents referred to herein using their common name are known, for example, from "The Pesticide Manual", 15th Ed., British Crop Protection Council 2009.

- The compounds of formula (I) may be used in unmodified form or, preferably, together with the
20 adjuvants conventionally employed in the art of formulation. To this end, they may be conveniently formulated in known manner to emulsifiable concentrates, coatable pastes, directly sprayable or dilutable solutions or suspensions, dilute emulsions, wettable powders, soluble powders, dusts, granulates, and also encapsulations e.g. in polymeric substances. As with the type of the compositions, the methods of application, such as spraying, atomising, dusting, scattering, coating or pouring, are
25 chosen in accordance with the intended objectives and the prevailing circumstances. The compositions may also contain further adjuvants such as stabilizers, antifoams, viscosity regulators, binders or tackifiers as well as fertilizers, micronutrient donors or other formulations for obtaining special effects.

- Suitable carriers and adjuvants, e.g., for agricultural use, can be solid or liquid and are substances useful in formulation technology, e.g. natural or regenerated mineral substances, solvents, dispersants,
30 wetting agents, tackifiers, thickeners, binders or fertilizers. Such carriers are for example described in WO 97/33890.

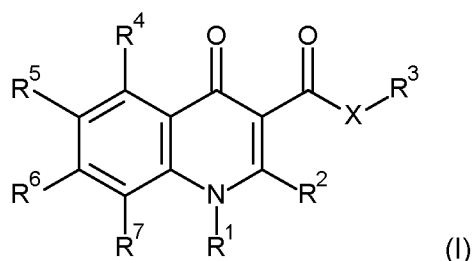
- The compounds of Formula (I) are normally used in the form of compositions and can be applied to the crop area or plant to be treated, simultaneously or in succession with further compounds. These further compounds can be, e.g., fertilizers or micronutrient donors or other preparations, which influence
35 the growth of plants. They can also be selective herbicides or non-selective herbicides as well as insecticides, fungicides, bactericides, nematocides, molluscicides or mixtures of several of these preparations, if desired together with further carriers, surfactants or application promoting adjuvants customarily employed in the art of formulation.

- The compound of Formula (I) may be the sole active ingredient of a composition or it may be
40 admixed with one or more additional active ingredients such as a pesticide, fungicide, synergist,

herbicide or plant growth regulator where appropriate. An additional active ingredient may, in some cases, result in unexpected synergistic activities.

In general, the formulations include from 0.01 to 90% by weight of active agent, from 0 to 20% agriculturally acceptable surfactant and 10 to 99.99% solid or liquid formulation inerts and adjuvant(s),
 5 the active agent consisting of at least the compound of formula (I) together with component (B) and (C), and optionally other active agents, particularly microbiocides or conservatives or the like. Concentrated forms of compositions generally contain in between about 2 and 80%, preferably between about 5 and 70% by weight of active agent. Application forms of formulation may for example contain from 0.01 to 20% by weight, preferably from 0.01 to 5% by weight of active agent. Whereas commercial products will
 10 preferably be formulated as concentrates, the end user will normally employ diluted formulations.

The tables below illustrate examples of individual compounds of Formula (I) according to the invention:



15 **Table 1: Individual compounds of formula (I) according to the invention**

Cpd No.	R ¹	R ²	R ⁴	R ⁵	R ⁶
001	Et	(3,4-dichlorophenyl)	CF ₃	CF ₃	H
002	Et	(3,4-dichlorophenyl)	CF ₃	Cl	H
003	Et	(3,4-dichlorophenyl)	CF ₃	CN	H
004	Et	(3,4-dichlorophenyl)	Cl	CF ₃	H
005	Et	(3,4-dichlorophenyl)	Cl	Cl	H
006	Et	(3,4-dichlorophenyl)	Cl	CN	H
007	Et	(3,4-dichlorophenyl)	CN	Cl	H
008	Et	(3,4-dichlorophenyl)	CN	CF ₃	H
009	Et	(3,4-dichlorophenyl)	CN	CN	H
010	Et	(3,4-dichlorophenyl)	H	CF ₃	CF ₃
011	Et	(3,4-dichlorophenyl)	H	CF ₃	Cl
012	Et	(3,4-dichlorophenyl)	H	CF ₃	CN
013	Et	(3,4-dichlorophenyl)	H	Cl	CF ₃
014	Et	(3,4-dichlorophenyl)	H	Cl	Cl
015	Et	(3,4-dichlorophenyl)	H	Cl	CN
016	Et	(3,4-dichlorophenyl)	H	CN	CF ₃
017	Et	(3,4-dichlorophenyl)	H	CN	Cl
018	Et	(3,4-dichlorophenyl)	H	CN	CN
019	Et	(3-chloro-4-cyano-phenyl)	H	CF ₃	H

Cpd No.	R ¹	R ²	R ⁴	R ⁵	R ⁶
020	Et	(3-chloro-4-cyano-phenyl)	H	Cl	H
021	Et	(3-chloro-4-cyano-phenyl)	H	CN	H
022	Et	(3-chloro-4-cyano-phenyl)	CF ₃	CF ₃	H
023	Et	(3-chloro-4-cyano-phenyl)	H	CF ₃	CF ₃
024	Et	(4-chloro-3-cyano-phenyl)	H	CF ₃	H
025	Et	(4-chloro-3-cyano-phenyl)	H	Cl	H
026	Et	(4-chloro-3-cyano-phenyl)	H	CN	H
027	Et	(4-chloro-3-cyano-phenyl)	CF ₃	CF ₃	H
028	Et	(4-chloro-3-cyano-phenyl)	H	CF ₃	CF ₃
029	Et	(4-chloro-3-fluoro-phenyl)	H	CF ₃	H
030	Et	(4-chloro-3-fluoro-phenyl)	H	Cl	H
031	Et	(4-chloro-3-fluoro-phenyl)	H	CN	H
032	Et	(4-chloro-3-fluoro-phenyl)	CF ₃	CF ₃	H
033	Et	(4-chloro-3-fluoro-phenyl)	H	CF ₃	CF ₃
034	Me	(3,4-dichlorophenyl)	H	CF ₃	H

Table A-1 provides 34 compounds A-1.001 to A.1.034 of Formula (I) wherein X is oxygen, R³ and R⁷ are hydrogen, and R¹, R², R⁴, R⁵, and R⁶ are as defined in Table 1.

5 Formulation Examples

Wettable powders

	a)	b)	c)
active ingredient [compound of formula (I)]	25 %	50 %	75 %
sodium lignosulfonate	5 %	5 %	-
sodium lauryl sulfate	3 %	-	5 %
sodium diisobutyl naphthalenesulfonate	-	6 %	10 %
phenol polyethylene glycol ether (7-8 mol of ethylene oxide)	-	2 %	-
highly dispersed silicic acid	5 %	10 %	10 %
Kaolin	62 %	27 %	-

The active ingredient 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.

10

Powders for dry seed treatment

	a)	b)	c)
active ingredient [compound of formula (I)]	25 %	50 %	75 %
light mineral oil	5 %	5 %	5 %
highly dispersed silicic acid	5 %	5 %	-
Kaolin	65 %	40 %	-

Talcum	-	20 %
--------	---	------

The active ingredient is thoroughly mixed with the adjuvants and the mixture is thoroughly ground in a suitable mill, affording powders that can be used directly for seed treatment.

Emulsifiable concentrate

active ingredient [compound of formula (I)]	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 %

5

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

<u>Dusts</u>	a)	b)	c)
Active ingredient [compound of formula (I)]	5 %	6 %	4 %
talcum	95 %	-	-
Kaolin	-	94 %	-
mineral filler	-	-	96 %

- 10 Ready-for-use dusts are obtained by mixing the active ingredient with the carrier and grinding the mixture in a suitable mill. Such powders can also be used for dry dressings for seed.

Extruder granules

Active ingredient [compound of formula (I)]	15 %
sodium lignosulfonate	2 %
carboxymethylcellulose	1 %
Kaolin	82 %

The active ingredient is mixed and ground with the adjuvants, and the mixture is moistened with water.

- 15 The mixture is extruded and then dried in a stream of air.

Coated granules

Active ingredient [compound of formula (I)]	8 %
polyethylene glycol (mol. wt. 200)	3 %
Kaolin	89 %

The finely ground active ingredient 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 ingredient [compound of formula (I)]	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 %

5

The finely ground active ingredient is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired dilution can be obtained by dilution with water. Using such dilutions, living plants as well as plant propagation material can be treated and protected against infestation by microorganisms, by spraying, pouring or immersion.

10

Flowable concentrate for seed treatment

active ingredient [compound of formula (I)]	40 %
propylene glycol	5 %
copolymer butanol PO/EO	2 %
tristyrenephenole with 10-20 moles EO	2 %
1,2-benzisothiazolin-3-one (in the form of a 20% solution in water)	0.5 %
monoazo-pigment calcium salt	5 %
Silicone oil (in the form of a 75 % emulsion in water)	0.2 %
Water	45.3 %

The finely ground active ingredient is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired dilution can be obtained by dilution with water. Using such dilutions, living plants as well as plant propagation material can be treated and protected against infestation by microorganisms, by spraying, pouring or immersion.

15

Slow Release Capsule Suspension

28 parts of a combination of the compound of formula (I) 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 polyvinyl alcohol, 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

20

25

diameter is 8-15 microns. The resulting formulation is applied to seeds as an aqueous suspension in an apparatus suitable for that purpose.

Examples

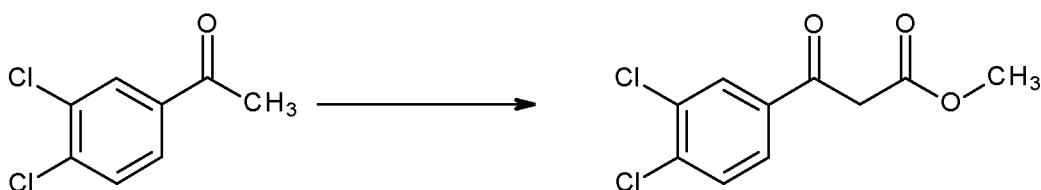
- 5 The following non-limiting examples provide specific synthesis methods for representative compounds of the present invention, as referred to in Table 2 below.

List of Abbreviations

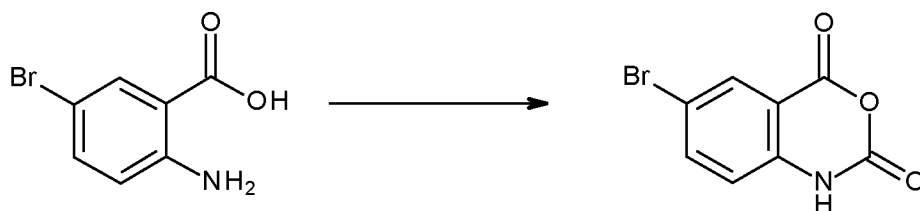
°C = degrees Celsius, d = doublet, dd = doublet of doublets, DMSO = dimethyl sulfoxide, M = molar, m
10 = multiplet, MHz = megahertz, q = quartet, s = singlet, t = triplet.

Example 1: Synthesis of 6-bromo-2-(3,4-dichlorophenyl)-1-ethyl-4-oxo-quinoline-3-carboxylic acid (Compound 8)

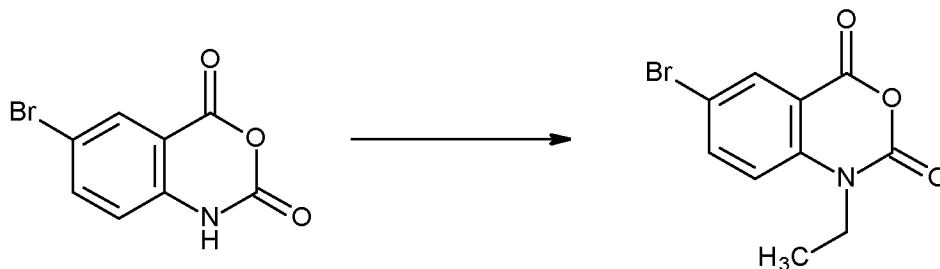
15 Step 1: Synthesis of methyl 3-(3,4-dichlorophenyl)-3-oxo-propanoate



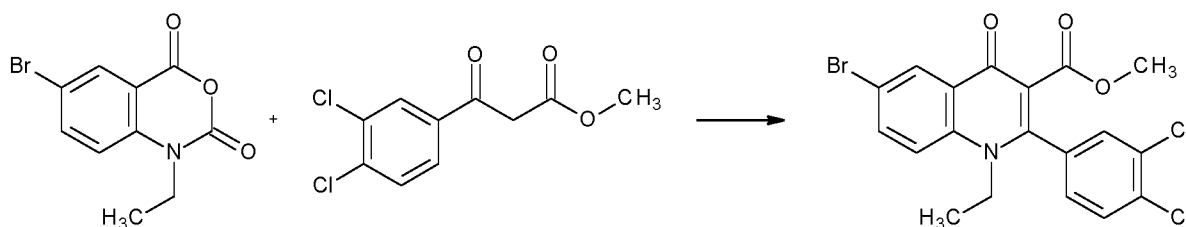
To a solution of 3,4-dichlorobenzoic acid (10.0 g, 52 mmol) in tetrahydrofuran (40 mL) at 0 °C and under nitrogen was added 1,1'-carbonyldiimidazole (9.3 g, 57 mmol) portion-wise, maintaining the internal temperature at <10 °C. On completion of addition, the cooling bath was removed and the reaction
20 mixture was stirred at room temperature for 1 hour to afford a yellow solution. This solution was added dropwise to a suspension of potassium;3-methoxy-3-oxo-propanoic acid (12.2 g, 77.6 mmol) and magnesium chloride (7.4 g, 78 mmol) in tetrahydrofuran (30 mL) at room temperature to afford a dense precipitate. The mixture was heated at 70 °C for 2 hours and then at 50 °C for a further 2 hours. The cooled reaction mixture was partitioned between aqueous hydrogen chloride solution (2M)
25 and diethyl ether. The organic extracts were washed with saturated aqueous sodium chloride solution, then dried over anhydrous magnesium sulfate and evaporated to dryness under reduced pressure. The crude product was purified by flash chromatography on silica gel using a gradient of 0-20% ethyl acetate in cyclohexane as eluent to give methyl 3-(3,4-dichlorophenyl)-3-oxo-propanoate (mixture of tautomers) as a colourless liquid (10.0 g, 40.5 mmol). Enol: ¹H NMR (400 MHz, chloroform) δ = 12.47 (s, 1H), 7.87 (d, 1H), 7.59 (m, 3H), 7.49 (d, 1H), 5.65 (s, 1H), 3.82 (s, 3H). Keto: ¹H NMR (400 MHz, chloroform) δ =
30 8.03 (d, 1H), 7.77 (m, 1H), 7.58 (d, 2H), 3.97 (s, 2H), 3.76 (s, 3H).

Step 1': Synthesis of 6-bromo-1H-3,1-benzoxazine-2,4-dione

A solution of 2-amino-5-bromo-benzoic acid (1.00 g, 4.6 mmol) in tetrahydrofuran (20 mL) was cooled to 0 °C and triphosgene (bis(trichloromethyl) carbonate (1.6 g, 5.2 mmol) was added portion-wise to afford a cloudy suspension. After 0.25 hours, the reaction mixture was allowed to warm to room temperature upon which the suspension dissolved. The resultant reaction mixture was stirred at room temperature for 2 hours after which time it was poured into water and extracted into dichloromethane. The organic extracts were dried over anhydrous magnesium sulfate and evaporated to dryness under reduced pressure to afford 6-bromo-1H-3,1-benzoxazine-2,4-dione as a pale grey solid (1.11 g, 4.59 mmol). ¹H NMR (400 MHz, methanol) δ = 8.15 (d, 1H), 7.81 (dd, 1H), 7.09 (d, 1H).

Step 2: Synthesis of 6-bromo-1-ethyl-3,1-benzoxazine-2,4-dione

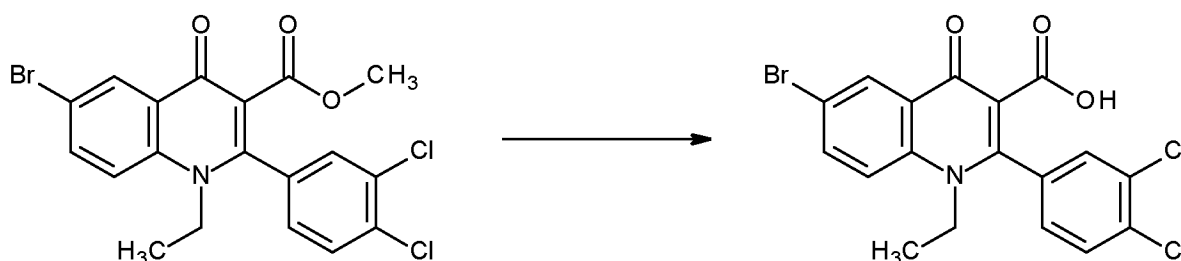
To a solution of 6-bromo-1H-3,1-benzoxazine-2,4-dione (2.22 g, 9.17 mmol) in tetrahydrofuran (50 mL) was added iodoethane (1.5 mL, 19 mmol) followed by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1.6 mL, 10 mmol). The resultant solution was stirred at room temperature for 0.25 hours and then heated at 50 °C for 3 hours. The resultant reaction mixture was poured into aqueous hydrogen chloride solution (2M), extracted into dichloromethane and evaporated to dryness under reduced pressure. The crude product was purified by reverse phase flash chromatography on C-18 silica gel using a gradient of acetonitrile in water to afford 6-bromo-1-ethyl-3,1-benzoxazine-2,4-dione as a tan solid (2.15 g, 7.96 mmol). ¹H NMR (400 MHz, chloroform) δ = 8.28 (d, 1H), 7.85 (dd, 1H), 7.09 (d, 1H), 4.13 (q, 2H), 1.38 (t, 3H).

Step 2': Synthesis of methyl 6-bromo-2-(3,4-dichlorophenyl)-1-ethyl-4-oxo-quinoline-3-carboxylate

To a solution of 6-bromo-1-ethyl-3,1-benzoxazine-2,4-dione (2.15 g, 7.96 mmol) and methyl 3-(3,4-dichlorophenyl)-3-oxo-propanoate (2.2 g, 8.9 mmol) in tetrahydrofuran (50 mL) at 0 °C was added dropwise 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 2.7 mL, 18 mmol). After 5 minutes, cooling was removed and the reaction mixture was heated at 50 °C for 3 hours. The cooled reaction mixture was evaporated to dryness under reduced pressure. The crude product was purified by flash chromatography on silica gel using a gradient of 0-80% ethyl acetate in cyclohexane as eluent to give methyl 6-bromo-2-(3,4-dichlorophenyl)-1-ethyl-4-oxo-quinoline-3-carboxylate as a cream solid (1.77 g, 3.89 mmol). ¹H NMR (400 MHz, chloroform) δ = 8.64 (d, 1H), 7.81 (dd, 1H), 7.60 (d, 1H), 7.54 (d, 1H), 7.44 (d, 1H), 7.28 (dd, 1H), 4.01 (q, 2H), 3.59 (s, 3H), 1.28 (t, 3H).

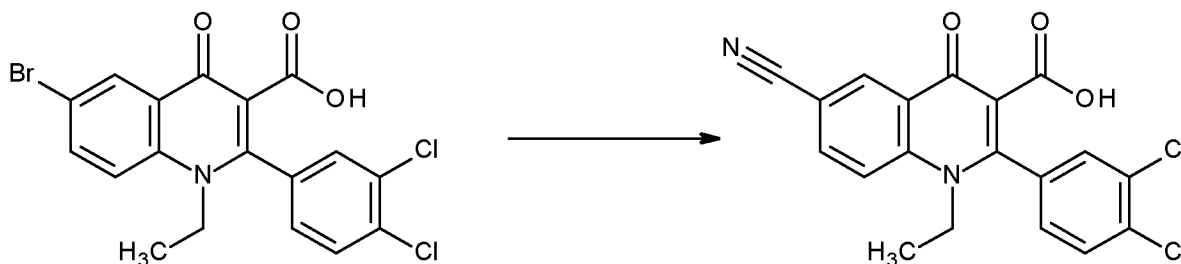
10

Step 3: Synthesis of 6-bromo-2-(3,4-dichlorophenyl)-1-ethyl-4-oxo-quinoline-3-carboxylic acid (Compound 8)



To a solution of methyl 6-bromo-2-(3,4-dichlorophenyl)-1-ethyl-4-oxo-quinoline-3-carboxylate (0.80 g, 1.8 mmol) in a mixture of methanol (10 mL) and water (5 mL) was added lithium hydroxide (0.30 g, 7.1 mmol). The resultant reaction mixture was heated at 90 °C for 3 hours. The cooled reaction mixture was evaporated to dryness under reduced pressure and the crude product was suspended in water. The mixture was acidified to pH 1 using dilute aqueous hydrogen chloride solution (2M) and the precipitated solid was extracted into dichloromethane and evaporated to dryness under reduced pressure to give 6-bromo-2-(3,4-dichlorophenyl)-1-ethyl-4-oxo-quinoline-3-carboxylic acid as a cream solid (0.71 g, 1.6 mmol). ¹H NMR (400 MHz, chloroform) δ = 15.54 (brs, 1H), 8.77 (d, 1H), 7.96 (dd, 1H), 7.64 (d, 1H), 7.61 (d, 1H), 7.39 (d, 1H), 7.15 (dd, 1H), 4.14 (q, 2H), 1.33 (t, 3H).

Example 2: Synthesis of 6-cyano-2-(3,4-dichlorophenyl)-1-ethyl-4-oxo-quinoline-3-carboxylic acid (Compound 7)



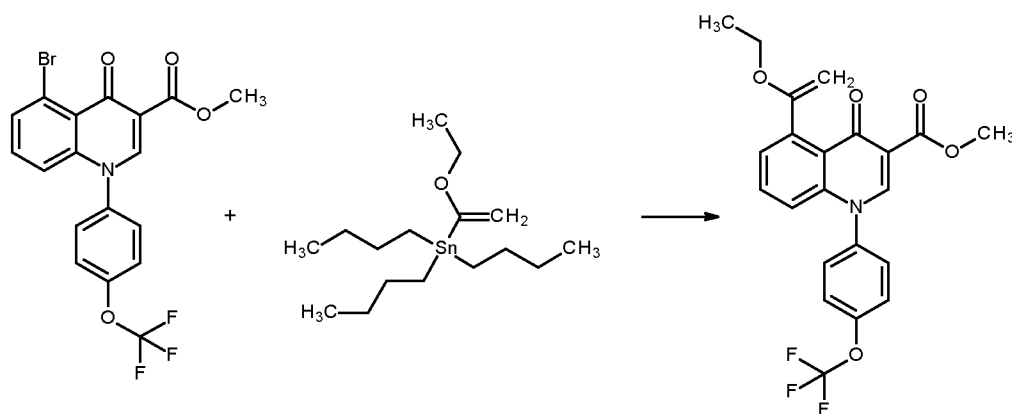
To a solution of 6-bromo-2-(3,4-dichlorophenyl)-1-ethyl-4-oxo-quinoline-3-carboxylic acid (0.200 g, 0.45 mmol) in *N,N*-dimethylformamide (10 mL) was added zinc cyanide (0.105 g, 0.894 mmol) and tetrakis(triphenyl- λ^5 -phosphanyl)palladium (0.050 g, 0.043 mmol) and the reaction mixture was heated under microwave irradiation at 160 °C for 0.75 hours. The cooled reaction mixture was

30

partitioned between water and dichloromethane. The organic extract was evaporated to dryness under reduced pressure and the crude residue was purified by flash chromatography on silica gel using a gradient of 0-100% ethyl acetate in cyclohexane as eluent to give 6-cyano-2-(3,4-dichlorophenyl)-1-ethyl-4-oxo-quinoline-3-carboxylic acid as a cream solid (0.060 g, 0.15 mmol). ¹H NMR (400 MHz, chloroform) δ = 15.12 (brd, 1H), 8.96 (d, 1H), 8.07 (dd, 1H), 7.83 (d, 1H), 7.66 (d, 1H), 7.40 (d, 1H), 7.16 (dd, 1H), 4.18 (q, 2H), 1.36 (t, 3H).

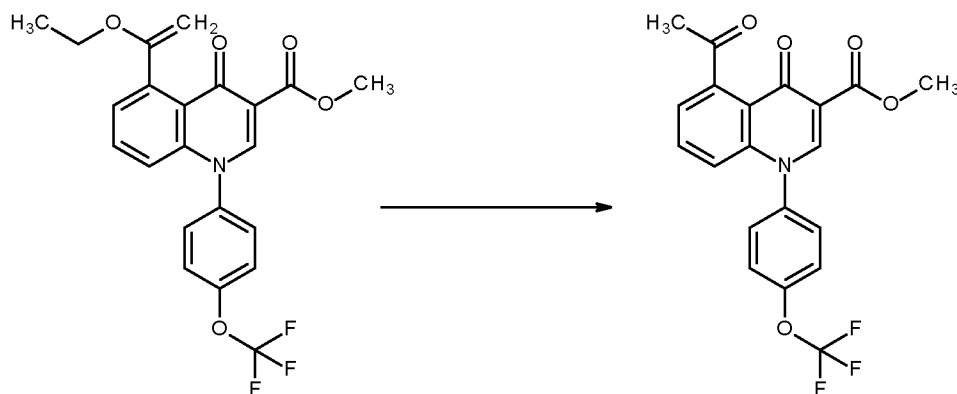
Example 3: Synthesis of 5-acetyl-4-oxo-1-[4-(trifluoromethoxy)phenyl]quinoline-3-carboxylic acid (Compound 19)

10 Step 1: Synthesis of methyl 5-(1-ethoxyvinyl)-4-oxo-1-[4-(trifluoromethoxy)phenyl]quinoline-3-carboxylate



To a stirred solution of methyl 5-bromo-4-oxo-1-[4-(trifluoromethoxy)phenyl]quinoline-3-carboxylate (500 mg, 1.07 mmol) in toluene (15 mL) was added tributyl(1-ethoxyvinyl)stannane (0.55 mL, 1.6 mmol) at room temperature. The resultant reaction mixture was purged with argon for 5 minutes followed by addition of bis(triphenylphosphine)palladium (II) chloride (0.078 g, 0.11 mmol). The resultant reaction mixture was purged with argon and then heated with stirring at 100 °C for 1 hour. The cooled reaction mixture was filtered through diatomaceous earth and the filtrate was evaporated to dryness under reduced pressure. The crude residue was purified by flash chromatography on silica gel using 10% ethyl acetate in hexanes as eluent to give methyl 5-(1-ethoxyvinyl)-4-oxo-1-[4-(trifluoromethoxy)phenyl]quinoline-3-carboxylate as a yellow solid. ¹H NMR (400 MHz, DMSO-d₆) δ = 8.40 (s, 1H), 7.81 (d, 2H), 7.68 (d, 2H), 7.57 (t, 1H), 7.26 (d, 1H), 6.92 (d, 1H), 4.26 (s, 1H), 4.05 (s, 1H), 3.94 - 3.89 (m, 2H), 3.72 (s, 3H), 1.21 (t, 3H).

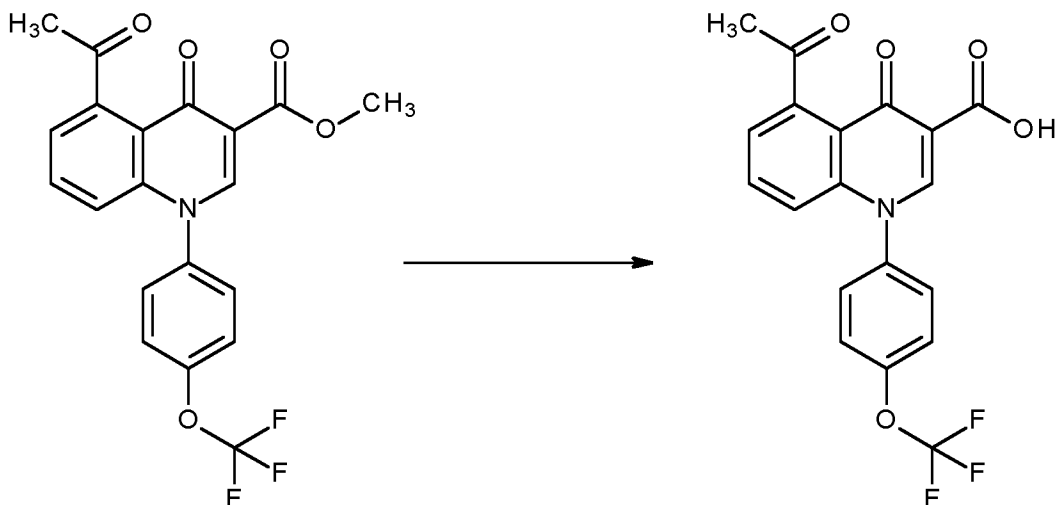
25 Step 2: Synthesis of methyl 5-acetyl-4-oxo-1-[4-(trifluoromethoxy)phenyl]quinoline-3-carboxylate



To a stirred solution of methyl 5-(1-ethoxyvinyl)-4-oxo-1-[4-(trifluoromethoxy)phenyl]quinoline-3-carboxylate (890 mg, 2.05 mmol) in acetone (15 mL) at room temperature was added dilute aqueous hydrogen chloride solution (2M, 5 mL). The resultant reaction mixture was stirred at room temperature for 16 hours. The reaction mixture was evaporated under reduced pressure and the crude residue was purified by flash chromatography on silica gel using a gradient of 0-75% ethyl acetate in hexanes as eluent to give methyl 5-acetyl-4-oxo-1-[4-(trifluoromethoxy)phenyl]quinoline-3-carboxylate as an off-white solid. ¹H NMR (400 MHz, DMSO-d₆) δ = 8.64 (s, 1H), 7.86 (d, 2H), 7.71 (t, 3H), 7.26 (d, 1H), 7.04 (d, 1H), 3.72 (s, 3H), 2.39 (s, 3H)

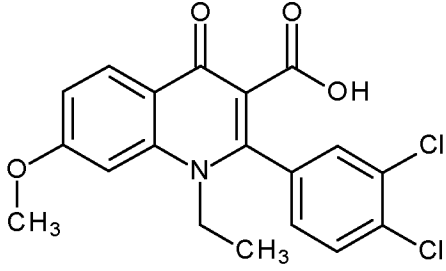
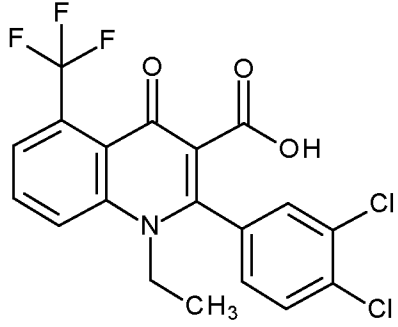
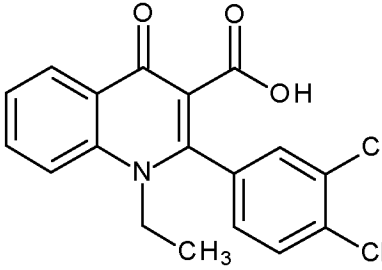
10

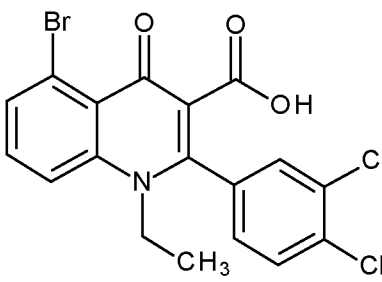
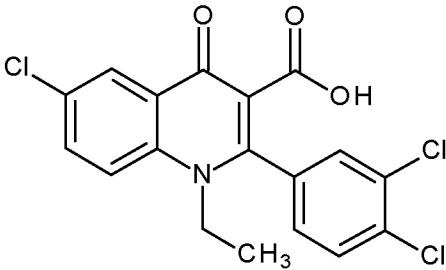
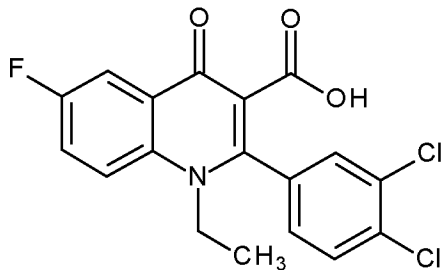
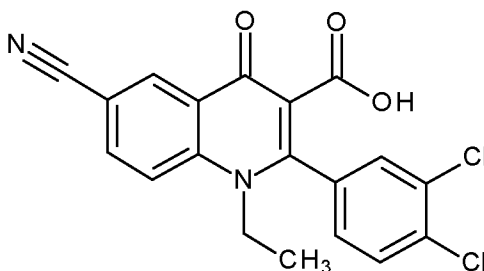
Step 3: Synthesis of 5-acetyl-4-oxo-1-[4-(trifluoromethoxy)phenyl]quinoline-3-carboxylic acid (Compound 19)

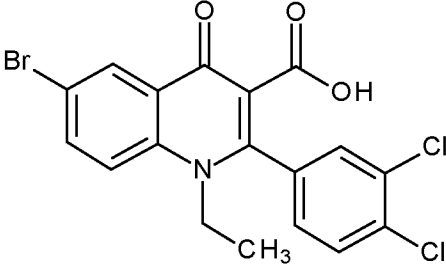
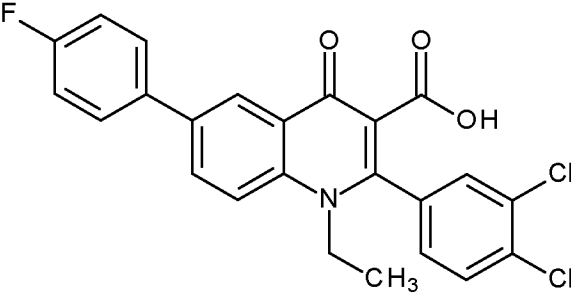
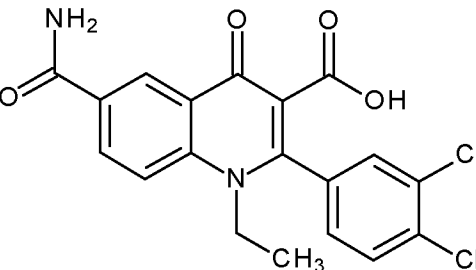
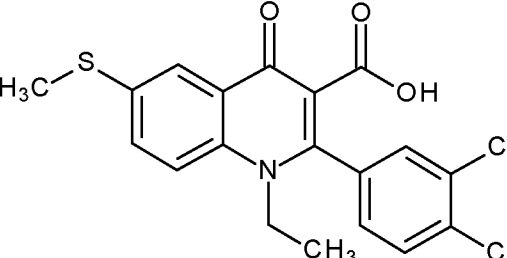


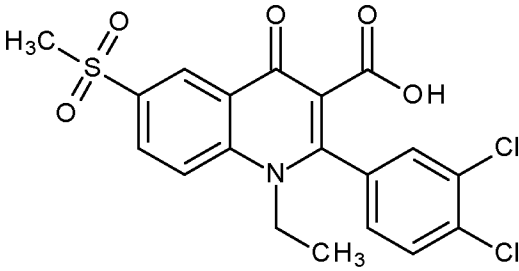
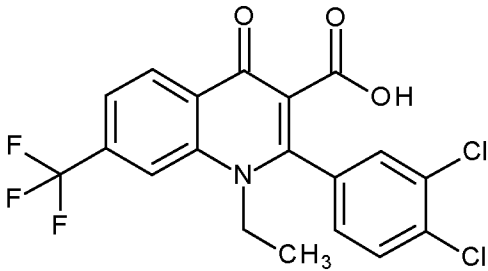
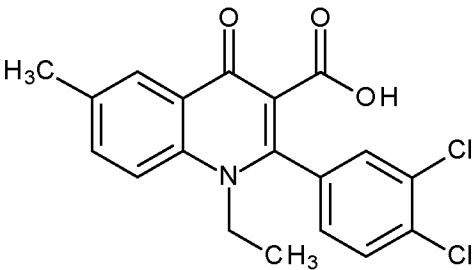
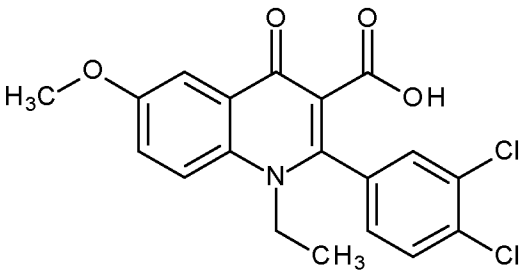
To a stirred solution of methyl 5-acetyl-4-oxo-1-[4-(trifluoromethoxy)phenyl]quinoline-3-carboxylate (100 mg, 0.22 mmol) in tetrahydrofuran (5 mL) at room temperature was added solution of lithium hydroxide hydrate (0.019 g, 0.44 mmol) in water (1 mL). The resultant reaction mixture was stirred at room temperature for 1 hour. The reaction mixture was evaporated to dryness under reduced pressure and the crude product was suspended in water (20 mL). The mixture was neutralised by addition of dilute aqueous hydrogen chloride solution (2M, 5 mL) and the precipitated solid was filtered and dried under reduced pressure to give 5-acetyl-4-oxo-1-[4-(trifluoromethoxy)phenyl]quinoline-3-carboxylic acid. ¹H NMR (400 MHz, chloroform) δ = 14.01 (s, 1H), 8.78 (s, 1H), 7.74 - 7.70 (m, 1H), 7.56 - 7.51 (m, 4H), 7.33 - 7.31 (dd, 1H), 7.17 - 7.14 (dd, 1H), 2.61 (s, 3H)

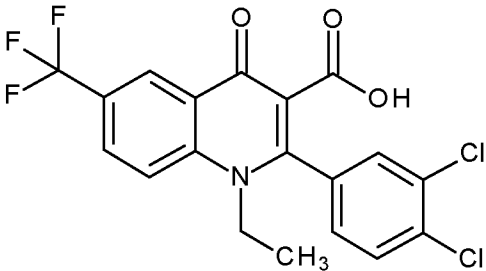
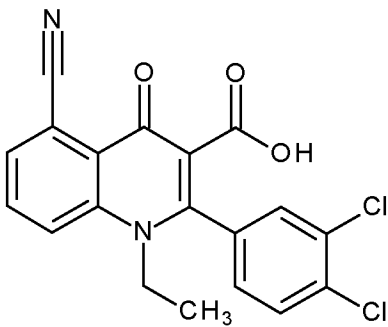
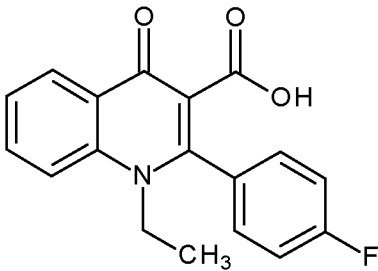
Table 2: ¹H NMR Data for selected compounds according to the invention.

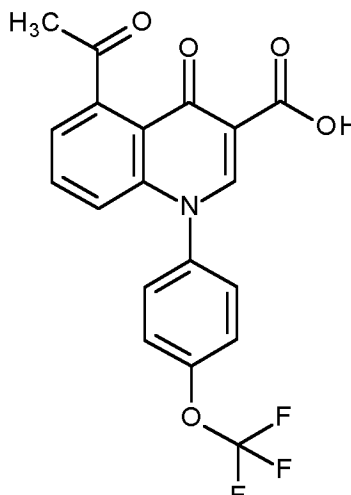
Compound Number	Compound Name	Structure & ¹ H NMR Data
1	2-(3,4-dichlorophenyl)-1-ethyl-7-methoxy-4-oxo-quinoline-3-carboxylic acid	 ¹H NMR (400 MHz, methanol) δ = 8.50 (d, 1H), 7.70 (d, 1H), 7.53 (d, 1H), 7.34 - 7.21 (m, 3H), 4.21 (q, 2H), 4.04 (s, 3H), 1.35 (t, 3H)
2	2-(3,4-dichlorophenyl)-1-ethyl-4-oxo-5-(trifluoromethyl)quinoline-3-carboxylic acid	 ¹H NMR (400 MHz, chloroform) δ = 8.09 - 8.03 (m, 1H), 8.01 - 7.90 (m, 2H), 7.68 - 7.59 (m, 1H), 7.42 - 7.37 (m, 1H), 7.20 - 7.07 (m, 1H), 4.27 - 4.12 (m, 2H), 1.38 - 1.26 (m, 3H)
3	2-(3,4-dichlorophenyl)-1-ethyl-4-oxo-quinoline-3-carboxylic acid	 ¹H NMR (400MHz, chloroform) δ = 15.90 (brs, 1H), 8.64 (dd, 1H), 7.91 (ddd, 1H), 7.74 (dd, 1H), 7.63 (d, 1H), 7.64 (ddd, 1H), 7.40 (d, 1H), 7.16 (dd, 1H), 4.17 (d, 2H), 1.35 (t, 3H)

Compound Number	Compound Name	Structure & ¹ H NMR Data
4	5-bromo-2-(3,4-dichlorophenyl)-1-ethyl-4-oxo-quinoline-3-carboxylic acid	 ¹H NMR (400 MHz, methanol) δ = 7.92 (dd, 1H), 7.80 (d, 1H), 7.70 - 7.64 (m, 2H), 7.45 (d, 1H), 7.20 (dd, 1H), 4.219 (q, 2H), 1.34 (t, 3H)
5	6-chloro-2-(3,4-dichlorophenyl)-1-ethyl-4-oxo-quinoline-3-carboxylic acid	 ¹H NMR (400 MHz, chloroform) δ = 15.55 (brs, 1H), 8.60 (d, 1H), 7.83 (dd, 1H), 7.68 (d, 1H), 7.64 (d, 1H), 7.39 (d, 1H), 7.15 (dd, 1H), 4.15 (q, 2H), 1.34 (t, 3H)
6	2-(3,4-dichlorophenyl)-1-ethyl-6-fluoro-4-oxo-quinoline-3-carboxylic acid	 ¹H NMR (400 MHz, chloroform) δ = 15.61 (brs, 1H), 8.26 (dd, 1H), 7.77 (dd, 1H), 7.68 - 7.59 (m, 2H), 7.39 (d, 1H), 7.15 (dd, 1H), 4.17 (q, 2H), 1.35 (t, 3H)
7	6-cyano-2-(3,4-dichlorophenyl)-1-ethyl-4-oxo-quinoline-3-carboxylic acid	 ¹H NMR (400 MHz, chloroform) δ = 15.12 (brd, 1H), 8.96 (d, 1H), 8.07 (dd, 1H), 7.83 (d, 1H), 7.66 (d, 1H), 7.40 (d, 1H), 7.16 (dd, 1H), 4.18 (q, 2H), 1.36 (t, 3H)

Compound Number	Compound Name	Structure & ¹ H NMR Data
8	6-bromo-2-(3,4-dichlorophenyl)-1-ethyl-4-oxo-quinoline-3-carboxylic acid	 ¹H NMR (400 MHz, chloroform) δ = 15.55 (brs, 1H), 8.77 (d, 1H), 7.97 (dd, 1H), 7.64 (d, 1H), 7.61 (d, 1H), 7.39 (d, 1H), 7.15 (dd, 1H), 4.14 (q, 2H), 1.34 (t, 3H)
9	2-(3,4-dichlorophenyl)-1-ethyl-6-(4-fluorophenyl)-4-oxo-quinoline-3-carboxylic acid	 ¹H NMR (400 MHz, DMSO-d₆) δ = 8.72 (d, 1H), 8.19 (brd, 1H), 8.02 (brd, 1H), 7.78 (dd, 2H), 7.69 (d, 1H), 7.57 (d, 1H), 7.32 (dd, 1H), 7.25 (t, 2H), 4.25 (q, 2H), 1.36 (t, 3H)
10	6-carbamoyl-2-(3,4-dichlorophenyl)-1-ethyl-4-oxo-quinoline-3-carboxylic acid	 ¹H NMR (400 MHz, DMSO-d₆) δ = 15.31 (brs, 1H), 8.97 (brd, 1H), 8.45 - 8.35 (m, 2H), 8.18 (brd, 1H), 7.88 (s, 1H), 7.84 (brd, 1H), 7.65 (brs, 1H), 7.52 (dd, 1H), 4.16 (brd, 2H), 1.21 (brt, 3H)
11	2-(3,4-dichlorophenyl)-1-ethyl-6-methylsulfanyl-4-oxo-quinoline-3-carboxylic acid	

Compound Number	Compound Name	Structure & ¹ H NMR Data
		¹ H NMR (400 MHz, chloroform) δ = 8.33 (d, 1H), 7.73 (dd, 1H), 7.65 - 7.59 (m, 2H), 7.40 (d, 1H), 7.16 (dd, 1H), 4.15 (q, 2H), 2.65 (s, 3H), 1.33 (t, 3H)
12	2-(3,4-dichlorophenyl)-1-ethyl-6-methylsulfonyl-4-oxo-quinoline-3-carboxylic acid	 ¹ H NMR (400 MHz, DMSO-d ₆) δ = 14.35 (brs, 1H), 8.85 (d, 1H), 8.41 - 8.27 (m, 2H), 7.91 - 7.83 (m, 2H), 7.54 (dd, 1H), 4.20 - 4.11 (m, 2H), 3.37 (s, 3H), 1.21 (brt, 3H)
13	2-(3,4-dichlorophenyl)-1-ethyl-4-oxo-7-(trifluoromethyl)quinoline-3-carboxylic acid	 ¹ H NMR (400 MHz, chloroform) δ = 15.38 (brs, 1H), 8.79 (d, 1H), 7.96 (s, 1H), 7.86 (dd, 1H), 7.66 (d, 1H), 7.40 (d, 1H), 7.16 (dd, 1H), 4.21 (q, 2H), 1.38 (t, 3H)
14	2-(3,4-dichlorophenyl)-1-ethyl-6-methyl-4-oxo-quinoline-3-carboxylic acid	 ¹ H NMR (400 MHz, chloroform) δ = 8.43 (d, 1H), 7.74 - 7.69 (m, 1H), 7.66 - 7.60 (m, 2H), 7.40 (d, 1H), 7.16 (dd, 1H), 4.15 (q, 2H), 2.57 (s, 3H), 1.33 (t, 3H)
15	2-(3,4-dichlorophenyl)-1-ethyl-6-methoxy-4-oxo-quinoline-3-carboxylic acid	

Compound Number	Compound Name	Structure & ¹ H NMR Data
		¹ H NMR (400 MHz, chloroform) δ = 7.97 (d, 1H), 7.67 (d, 1H), 7.63 (d, 1H), 7.49 (dd, 1H), 7.40 (d, 1H), 7.16 (dd, 1H), 4.16 (q, 2H), 4.00 (s, 3H), 1.34 (t, 3H)
16	2-(3,4-dichlorophenyl)-1-ethyl-4-oxo-6-(trifluoromethyl)quinoline-3-carboxylic acid	 ¹ H NMR (400 MHz, chloroform) δ = 15.37 (brs, 1H), 8.93 (d, 1H), 8.09 (dd, 1H), 7.85 (d, 1H), 7.65 (d, 1H), 7.40 (d, 1H), 7.16 (dd, 1H), 4.19 (q, 2H), 1.36 (t, 3H)
17	5-cyano-2-(3,4-dichlorophenyl)-1-ethyl-4-oxo-quinoline-3-carboxylic acid	 ¹ H NMR (400 MHz, DMSO-d ₆) δ = 14.12 (brs, 1H), 8.53 - 8.33 (m, 1H), 8.21 - 8.00 (m, 2H), 7.88 (brs, 1H), 7.69 - 7.50 (m, 2H), 4.14 (brd, 2H), 1.19 (brs, 3H)
18	1-ethyl-2-(4-fluorophenyl)-4-oxo-quinoline-3-carboxylic acid	 ¹ H NMR (400 MHz, acetonitrile) δ = 8.58 (dt, 1H), 7.98 (d, 2H), 7.72 - 7.65 (m, 1H), 7.43 - 7.38 (m, 2H), 7.35 - 7.28 (m, 2H), 4.17 (q, 2H), 1.26 (t, 3H)

Compound Number	Compound Name	Structure & ¹ H NMR Data
19	5-acetyl-4-oxo-1-[4-(trifluoromethoxy)phenyl]quinoline-3-carboxylic acid	 ¹H NMR (400 MHz, chloroform) δ = 14.01 (s, 1H), 8.78 (s, 1H), 7.74 - 7.70 (m, 1H), 7.56 - 7.51 (m, 4H), 7.33 - 7.31 (dd, 1H), 7.17 - 7.14 (dd, 1H), 2.61 (s, 3H)

Biological examples

Seeds of a variety of test species are sown in standard soil in pots (*Abutilon theophrasti* (ABUTH), *Ipomoea hederacea* (IPOHE), *Setaria faberi* (SETFA), *Echinochloa crus-galli* (ECHCG), *Zea mays* (ZEAMX), *Amaranthus retroflexus* (AMARE), *Solanum nigrum* (SOLNI), *Lolium perenne* (LOLPE), *Amaranthus palmeri* (AMAPA)). After 8 days cultivation under controlled conditions in a glasshouse (at 24 °C /16 °C, day/night; 14 hours light; 65 % humidity), the plants are sprayed with an aqueous spray solution 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/ha unless otherwise stated. The test plants are then grown in a glasshouse under controlled conditions in a glasshouse (at 24 °C/16 °C, day/night; 14 hours light; 65 % humidity) and watered twice daily. After 13 days 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 = 81-100%; 4 = 61-80%; 3=41-60%; 2=21-40%; 1=0-20%; - = not tested).

TABLE B1: Pre-emergence Test

Cpd No.	ABUTH	IPHE	SETFA	ECHCG	ZEAMX	AMARE	SOLNI	LOLPE	AMAPA
1	3	2	2	1	1	0	-	-	-
2	2	2	5	5	1	2	2	0	-
3	1	3	5	5	3	2	4	3	-
4	-	1	5	5	3	1	-	-	2
5	-	0	2	0	1	0	-	-	0
6	-	0	5	5	0	0	-	-	0

7	-	1	5	5	3	0	-	-	0
8	-	1	5	5	2	1	-	-	2
9	-	1	4	3	1	0	-	-	0
10	-	0	0	0	2	0	-	-	0
11	-	1	5	5	2	1	-	-	3
12	-	1	5	5	1	3	-	-	3
13	-	0	0	0	0	0	-	-	0
14	-	2	4	4	2	5	-	-	5
15	-	2	5	4	1	3	-	-	3
16	-	1	5	5	1	1	-	-	0
17	-	1*	-	-	-	1*	-	-	1*
18		0	3	2	0	1	-	-	1
19	-	0	3	3	0	0	-	-	0

* Compounds are applied at 250 g/ha

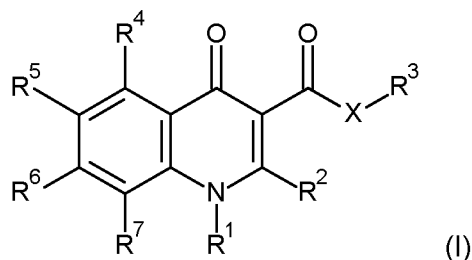
TABLE B2: Post-emergence Test

Cpd No.	ABUTH	IPOHE	SETFA	ECHCG	ZEAMX	AMARE	SOLNI	LOLPE	AMAPA
1	-	3	2	1	0	0	-	-	-
2	3	3	4	5	3	2	2	1	-
3	2	4	4	3	1	3	4	2	-
4	-	1	1	1	1	0	-	-	0
5	-	1	4	-	2	1	-	-	1
6	-	3	4	4	4	1	-	-	3
7	-	2	4	-	3	3	-	-	4
8	-	4	4	4	4	0	-	-	1
9	-	2	0	0	0	2	-	-	2
10	-	1	4	-	2	2	-	-	4
11	-	1	3	4	2	2	-	-	3
12	-	2	3	4	1	3	-	-	2
13	-	0	1	2	1	2	-	-	1
14	-	3	3	3	2	5	-	-	5
15	-	2	2	3	1	2	-	-	2
16	-	2	4	4	3	0	-	-	0
17	-	2*	1*	1*	0*	2*	-	-	2*
18	-	0	1	1	1	1	-	-	1
19	-	1	3	4	3	0	-	-	2

* Compounds are applied at 250 g/ha

CLAIMS

1. A compound of Formula (I):



5 wherein

X is O;

R¹ is C₁-C₆alkyl or phenyl optionally substituted with 1 or 2 groups, which may be the same or different, represented by R¹⁰;

10 R² is hydrogen, phenyl or heteroaryl, wherein the heteroaryl moiety is a 5- or 6-membered aromatic ring which comprises 1, 2, 3 or 4 heteroatoms individually selected from N, O and S, and wherein each phenyl and heteroaryl moiety may be optionally substituted with 1, 2, 3, or 4 groups, which may be the same or different, represented by R⁸;

R³ is hydrogen or C₁-C₆alkyl;

15 R⁴, R⁵, R⁶, and R⁷, are each independently selected from hydrogen, halogen, cyano, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆haloalkoxy, C₁-C₆alkylcarbonyl, C₁-C₆alkylsulfanyl, C₁-C₆alkylsulfinyl, C₁-C₆alkylsulfonyl, C₁-C₆alkylaminocarbonyl, aminocarbonyl, and phenyl, wherein each phenyl moiety may be optionally substituted with 1, 2, 3, or 4 groups, which may be the same or different, represented by R⁹;

20 R⁸ is cyano, nitro, halogen, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆haloalkoxy, C₁-C₆alkoxyC₁-C₆alkyl, C₁-C₆alkylsulfanyl, C₁-C₆alkylsulfinyl, C₁-C₆alkylsulfonyl, C₁-C₆alkylsulfonamido, C₁-C₆alkylcarbonyl, C₁-C₆alkoxycarbonyl, C₁-C₆alkylaminocarbonyl, C₃-C₆cycloalkyl, C₃-C₆cycloalkylaminocarbonyl, or N,N-di(C₁-C₄alkyl)aminocarbonyl;

25 R⁹ is cyano, nitro, halogen, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆haloalkoxy, C₁-C₆alkoxyC₁-C₆alkyl, C₁-C₆alkylsulfanyl, C₁-C₆alkylsulfinyl, C₁-C₆alkylsulfonyl, C₁-C₆alkylsulfonamido, C₁-C₆alkylcarbonyl, C₁-C₆alkoxycarbonyl, C₁-C₆alkylaminocarbonyl, C₃-C₆cycloalkyl, C₃-C₆cycloalkylaminocarbonyl, or N,N-di(C₁-C₄alkyl)aminocarbonyl; and

R¹⁰ is halogen, cyano, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆haloalkoxy, C₁-C₆alkylsulfanyl, or C₁-C₆alkylsulfonyl;

or a salt or an N-oxide thereof.

2. The compound according to claim 1, wherein R^1 is C_1 - C_3 alkyl or phenyl optionally substituted with a single group, represented by R^{10} .
3. The compound according to claim 1 or claim 2, wherein R^2 is hydrogen, or phenyl substituted with 1 or 2 groups, which may be the same or different, represented by R^8 .
4. The compound according to any one of claims 1 to 3, wherein R^2 is phenyl substituted with 1 or 2 groups, which may be the same or different, represented by R^8 .
5. The compound according to any one of claims 1 to 4, wherein R^3 is hydrogen.
6. The compound according to any one of claims 1 to 5, wherein R^5 is hydrogen, halogen, cyano, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkyl, C_1 - C_3 haloalkoxy, C_1 - C_4 alkylsulfanyl, C_1 - C_3 alkylsulfinyl, C_1 - C_4 alkylsulfonyl, C_1 - C_3 alkylaminocarbonyl, aminocarbonyl, or phenyl, wherein each phenyl moiety may be optionally substituted with 1 or 2 groups, which may be the same or different, represented by R^9 .
7. The compound according to any one of claims 1 to 6, wherein when R^4 , R^6 , and R^7 , are each independently selected from hydrogen, halogen, cyano, C_1 - C_3 alkoxy, and C_1 - C_3 haloalkyl, R^5 is hydrogen, halogen, cyano, C_1 - C_3 alkyl, C_1 - C_3 alkoxy, C_1 - C_3 haloalkyl, C_1 - C_3 alkylsulfanyl, C_1 - C_3 alkylsulfonyl, aminocarbonyl, or phenyl, wherein the phenyl moiety may be optionally substituted with a single R^9 group.
8. The compound according to any one of claims 1 to 7, wherein R^4 is hydrogen, halogen, cyano, acetyl, or trifluoromethyl.
9. The compound according to any one of claims 1 to 8, wherein R^8 is halogen.
10. The compound according to any one of claims 1 to 9, wherein
X is O;
 R^1 is ethyl or 4-trifluoromethoxyphenyl;
 R^2 is hydrogen, 3,4-dichlorophenyl or 4-fluorophenyl;
 R^3 is hydrogen; and
 R^4 , R^5 , R^6 , and R^7 are each independently selected from hydrogen, halogen, cyano, methyl, methoxy, trifluoromethyl, methylsulfanyl, methylsulfonyl, aminocarbonyl, and 4-fluorophenyl.
11. A herbicidal composition comprising a compound according to any one of the previous claims and an agriculturally acceptable formulation adjuvant.
12. A herbicidal composition according to claim 11, further comprising at least one additional pesticide.

13. A herbicidal composition according to claim 12, wherein the additional pesticide is a herbicide or herbicide safener.
14. A method of controlling unwanted plant growth, comprising applying a compound of Formula (I)
5 as defined in any one of claims 1 to 10, or a herbicidal composition according to any one of claims 11 to 13, to the unwanted plants or to the locus thereof.
15. Use of a compound of Formula (I) according to any one of claims 1 to 10 as a herbicide.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2023/053441

A. CLASSIFICATION OF SUBJECT MATTER INV. C07D215/22 C07D215/56 A01N43/42 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, WPI Data, CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 108 617 661 A (OCEAN UNIV CHINA) 9 October 2018 (2018-10-09) cited in the application Compound X has been tested according to [0068]; page 5; compounds IV, X -----	1-15
X	CN 113 735 769 A (UNIV TAIYUAN TECHNOLOGY) 3 December 2021 (2021-12-03) CAS RN 195988-50-2 Same technical field; page 6, paragraph 0028 - paragraph 0029 -----	1-15
X	WO 2022/010150 A1 (ILAB [KR]) 13 January 2022 (2022-01-13) several compounds; page 38, paragraph 421 page 26; compound 2a -----	1-10
-/-		
☒ 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
23 February 2023		03/03/2023
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 Goss, Ilaria

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2023/053441

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	COPPOLA G M ET AL: "THE CHEMISTRY OF 2H-3,1-BENZOXAZINE-2,4(1H)DIONE (ISATOIC ANHYDRIDE). 7. REACTIONS WITH ANIONS OF ACTIVE METHYLENES TO FORM QUINOLINES", JOURNAL OF HETEROCYCLIC CHEMISTRY, WILEY-BLACKWELL PUBLISHING, INC, US, vol. 16, 1 January 1979 (1979-01-01), pages 1605-1610, XP002270881, ISSN: 0022-152X, DOI: 10.1002/JHET.5570160817 Table III, several compounds Table IV, compound 85; page 1609 - page 1610 -----	1-10
X	CN 108 623 563 A (OCEAN UNIV CHINA) 9 October 2018 (2018-10-09) VI, XII; page 5 -----	1-10
X	JIAN-PING LIN ET AL: "Transition metal-free one-pot synthesis of 2-substituted 3-carboxy-4-quinolone and chromone derivatives", CHEMICAL COMMUNICATIONS, vol. 49, no. 46, 1 January 2013 (2013-01-01), pages 5313-5315, XP055597047, UK ISSN: 1359-7345, DOI: 10.1039/c3cc41690a Table 1 and Table 2, Compound 4a, 4b-4j and few other compounds; page 5314 -----	1-10
X	HUANG PEI-QIANG ET AL: EUROPEAN JOURNAL OF ORGANIC CHEMISTRY , vol. 2017, no. 3 18 January 2017 (2017-01-18), pages 582-592, XP055938306, DE ISSN: 1434-193X, DOI: 10.1002/ejoc.201601326 Retrieved from the Internet: URL:https://api.wiley.com/onlinelibrary/tdm/v1/articles/10.1002%2Fejoc.201601326 Synthesis of 4-quinolone Compound 11; page 585 -----	1-10
4	A CN 108 623 562 A (OCEAN UNIV CHINA) 9 October 2018 (2018-10-09) Reference to a relevant agricultural insecticides; page 13, paragraph [0006] ----- -/--	1-15

1

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2023/053441

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2021/008045 A1 (SHAO CHANGLUN [CN] ET AL) 14 January 2021 (2021-01-14) Last general formula of intermediates The difference resides in present R1 being in that formula always H; page 48 -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2023/053441

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
CN 108617661	A	09-10-2018	NONE	
CN 113735769	A	03-12-2021	NONE	
WO 2022010150	A1	13-01-2022	KR 20220005991 A WO 2022010150 A1	14-01-2022 13-01-2022
CN 108623563	A	09-10-2018	NONE	
CN 108623562	A	09-10-2018	NONE	
US 2021008045	A1	14-01-2021	CN 108929323 A US 2021008045 A1 WO 2018171740 A1	04-12-2018 14-01-2021 27-09-2018