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(54) **POLYENYLCYCLOPROPANECARBOXYLIC ESTERS WITH HIGH INSECTICIDAL ACTIVITY**
STARK INSEKTIZIDWIRKENDE POLYENYLCYCLOPROPANCARBONSÄUREESTER
ESTERS POLYÉNYLCYCLOPROPANECARBOXYLIQUES À HAUTE ACTIVITÉ INSECTICIDE

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(56) References cited:
EP-A- 0 939 073 DE-A1- 2 113 124
DE-A1- 2 231 436

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- **ELLIOTT M ET AL: "INSECTICIDAL ACTIVITY OF THE PYRETHRINS AND RELATED COMPOUNDS X. ALPHA 5-BENZYL-3-FURYL METHYL 2,2-DIMETHYLCYCLOPROPANECARBOXYLATES WITH ETHYLENIC SUBSTITUENTS AT POSITION 3 ON THE CYCLOPROPANE RING" PESTICIDE SCIENCE, ELSEVIER APPLIED SCIENCE PUBLISHER. BARKING, GB, vol. 7, 1 January 1976 (1976-01-01), pages 499-502, XP009048947 ISSN: 0031-613X cited in the application**

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EP 2 203 064 B9

Description

FIELD OF THE INVENTION

[0001] The present invention relates to the field of insecticides derived from chrysanthemic acid.

STATE OF THE ART

[0002] 2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxylic acid (chrysanthemic acid) is a starting material for the synthesis of a number of pyrethroid insecticides, widely used in agriculture and the domestic field for controlling ants, spiders, mosquitoes, flies and other unwanted insects. The esters of said acid and their derivatives in position 3 of the cyclopropane ring are of particular interest. Included among them are the 3-dichlorovinyl derivative esterified with 2,3,5,6 tetrafluorobenzyl alcohol (transfluthrin), and (2,3,5,6-tetrafluoro-4-methoxymethyl)benzyl-2,2-dimethyl-3-prop-1-enylcyclopropanecarboxylate (metofluthrin); metofluthrin and other similar compounds are described in EP-A-939 073. Other 3-vinyl-2,2-dimethylcyclopropanecarboxylic derivatives esterified with furyl or thienyl alcohols are known from DE-A-2 113 124. In EP-A-31 041 phenoxybenzyl esters of cyclopropanecarboxylic acid, containing in position 3 a mono/poly-halogenated diene substituent are described. Pestic.Sci., 1976,7,p.499-502 describes 3-alkadienylcyclopropanecarboxylic derivatives, in which the carboxyl is esterified with 5-benzyl-3-furanmethanol. Similar derivatives are known from DE-A-2 231 436.

[0003] Despite the introduction of the different aforementioned insecticides, the need was however felt for new higher strength insecticidal compounds, with a wide spectrum of action and well tolerated by man and animals.

DESCRIPTION OF THE FIGURES

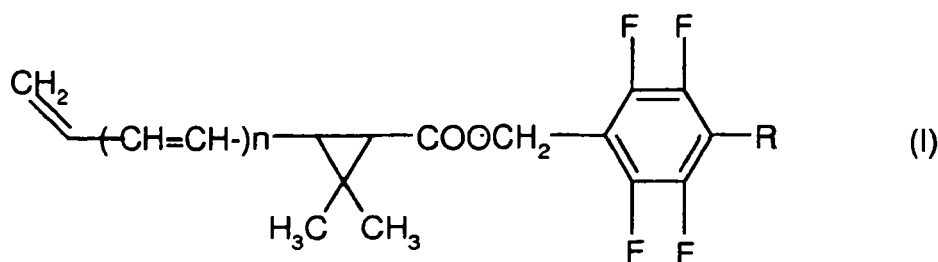
[0004]

Figure 1: Structure of the compounds of examples 1-3 of the invention with stereochemical indicators;

Figure 2: Structure of the compounds of examples 4 and 8 of the invention and of comparative compound of example 7 with stereochemical indicators.

SUMMARY

[0005] It has now been found that compounds of structural formula (I)



wherein n is chosen from 1 and 2 and R is chosen from -H, -CH₃, C₂H₅, -OCH₃, -OC₂H₅, and -CH₂-OCH₃ exhibit an unexpectedly high insecticidal activity.

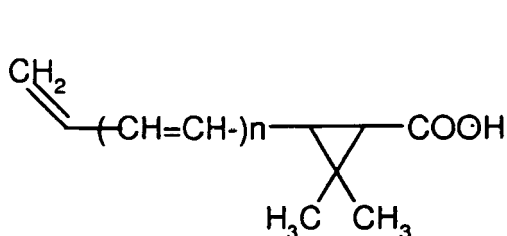
DETAILED DESCRIPTION

[0006] The preferred compounds according to the invention are those having formula (I) wherein R is H or -CH₂-OCH₃. Particularly preferred are the following compounds:

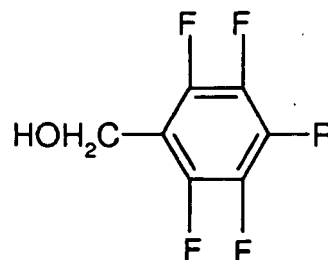
2,3,5,6-tetrafluorobenzyl-(1RS,3RS)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylate;
 2,3,5,6-tetrafluorobenzyl-(1R,3R)-3-((E)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylate;
 2,3,5,6-tetrafluorobenzyl-(1R,3R)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylate;
 2,3,5,6-tetrafluorobenzyl-(1R,3R)-3-(Hexa-1,3(E)-5(E/Z)-1,3,5-trienyl)-2,2-dimethylcyclopropane-1-carboxylate;
 2,3,5,6-tetrafluoro-4-methoxymethyl benzyl (1R,3R)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylate.

[0007] The compounds of formula (I), compared to other commonly used 2,3,5,6 tetrafluorobenzyl esters of 2,2-dimethylcyclopropanecarboxylic acid derivatives, such as transfluthrin and metofluthrin, are found to be surprisingly more active. The spectrum of action is wide-ranging and includes common flying and crawling insects; preferred among the flying insects is the mosquito; preferred among the crawling insects are arthropods, for example the Blattellidae.

[0008] The invention comprises a process for the synthesis of the aforesaid compounds of formula (I). They can be produced by esterification of an acid of formula (II) with an alcohol of formula (III) where, in said formulas, n and R have the aforesaid meanings.



(II)

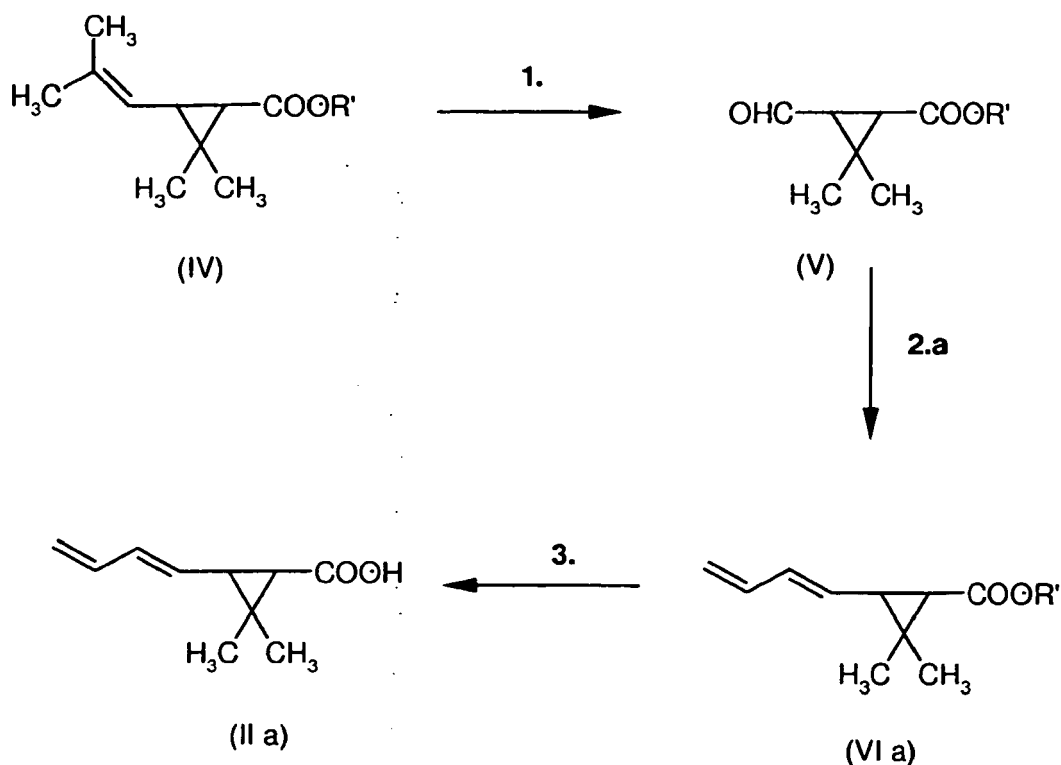


(III)

[0009] The esterification preferably takes place after activation of the COOH group of compound (II). Activation methods are known from the chemical literature, such as conversion of carboxyl to acyl halide; this latter is easily obtained for example by reacting compound (II) with an acyl chloride such as tosyl chloride, in the presence of a suitable amine such as N-methylimidazole, in acetonitrile as the solvent. The activated carboxyl, in the presence of alkaline catalysis, reacts at high yield with the alcohol (III) to provide the desired compound (I).

[0010] The precursor compounds of formula (III) are commercially available or can be produced by methods described in the literature.

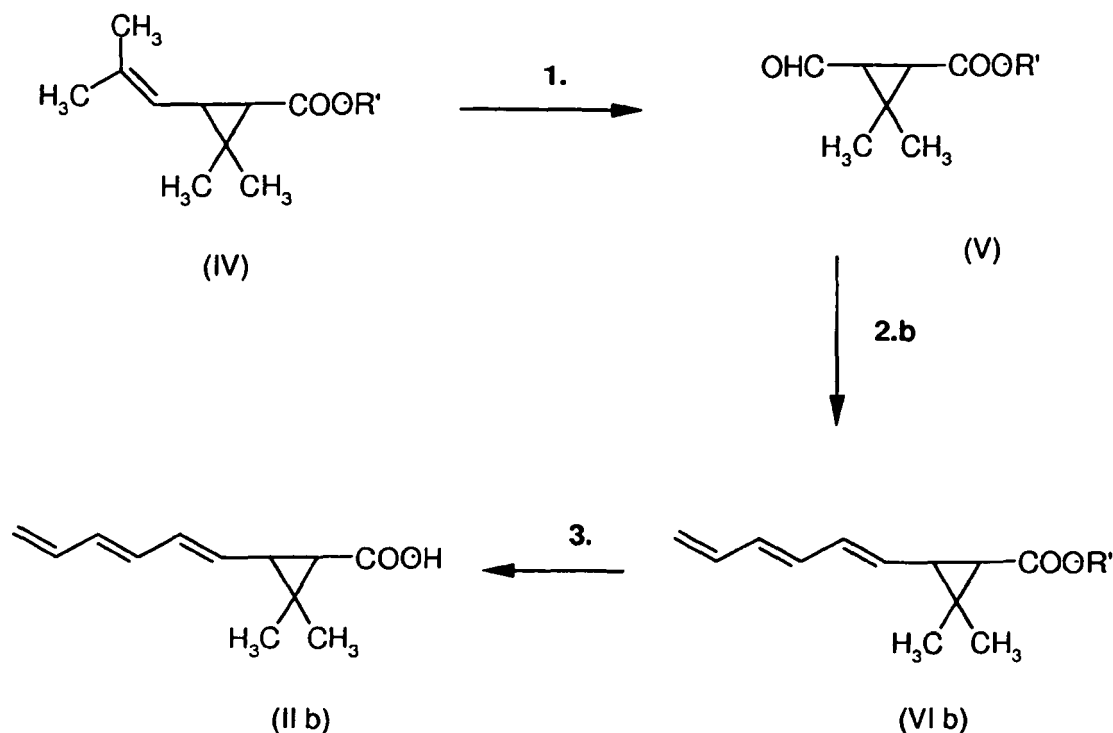
[0011] The precursor compound of formula (IIa), (i.e. those of formula (II) with n=1) are obtainable on the basis of the following reaction scheme, where R' is a C₁-C₃ alkyl, preferably ethyl.



[0012] Step 1 is an ozonolysis reaction, achievable under conditions known from the chemical literature (P.J. Dijkstra

et al. JOC 1987,52,2433-2442). Step 2.a is a Wittig reaction, carried out with an allyltriphenylphosphonium halide under conditions known to the skilled person of the art (cf. J.Chem.Soc. (C), 1970, p.1076; Vedejs E. JOC 1984,49,210-212). The reaction can also be undertaken with diethyl allyl phosphonate (Wang J. et al. in Synthesis 2002,99-103) (Horner Emmons reaction).

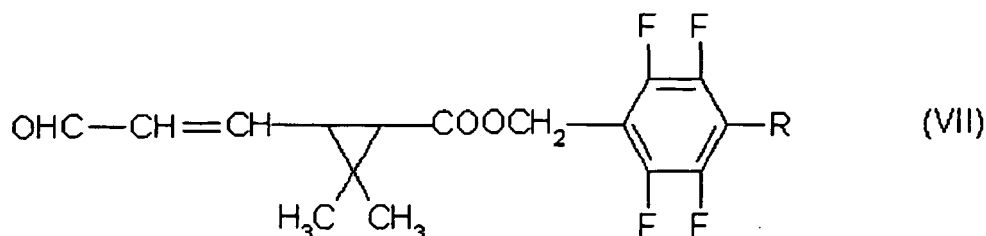
[0013] Step 3 is a hydrolysis with alkaline catalysis carried out under standard conditions. The compounds of formula (IIb) (i.e. those of formula (II) in which n=2) are obtainable on the basis of the following reaction scheme, where R' is a C1-C3 alkyl, preferably ethyl.



[0014] This scheme differs from the preceding in that at point 2.b two addition reactions are carried out: the first with a formylmethyltriphenylphosphonium halide (this reaction typically takes place in an aromatic solvent such as benzene, in the presence of triethylamine, at ambient temperature); the product obtained is then reacted with an allyltriphenylphosphonium halide, under the aforegiven conditions for this reagent.

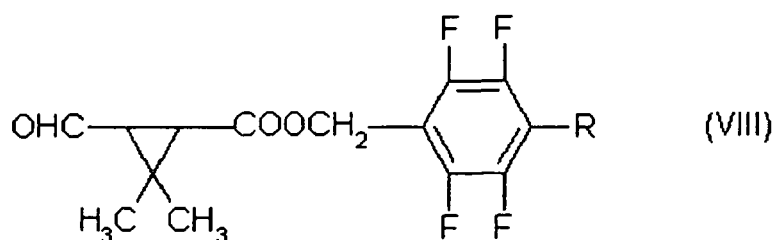
[0015] The precursor compounds of formula (IV) (esters of chrysanthemic acid) are commercially available or can be produced by methods described in the literature as reported for example by Wakasugi et al. in Adv.Synth.Catal. 2003,345,1209-1214.

[0016] A particularly effective synthesis path for obtaining the compounds of formula (I) where n=2, with high yield and purity, comprises the formation of an aldehyde ester of formula (VII) where R has the meanings defined in formula (I).



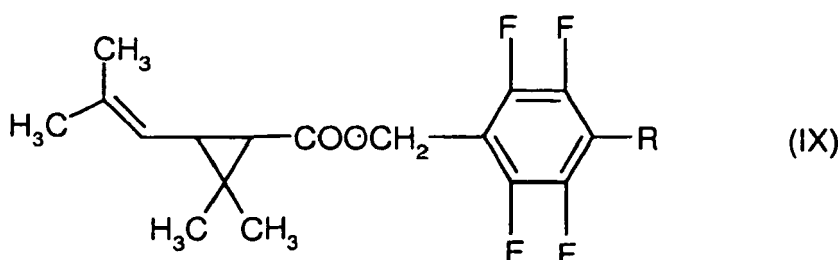
[0017] By converting the -CHO group of compound (VII) into an allyl group, the desired compounds of formula (I), with n=2, are obtained. The conversion into an allyl group is obtained by treating compound (VII) with an allyltriphenylphosphonium halide, under the aforestated conditions for this reagent.

[0018] The intermediates of formula (VII) are new, and as such constitute a further aspect of the invention. They can be themselves synthesized by treating a compound of formula (VIII) with a formylmethyltriphenylphosphonium halide, where R has the previously defined meanings.



10 **[0019]** The reaction of compound (VIII) with the formylmethyltriphenylphosphonium halide takes place under the aforegiven conditions for this reagent.

[0020] The compound (VIII) can itself be obtained by ozonolysis starting from the corresponding ester of chrysanthemic acid having formula (IX).



25 **[0021]** The compound (IX) is easily obtained by esterification of chrysanthemic acid with the suitable 2,3,5,6 tetrafluorobenzyl alcohol (Wakasugi et al. in Adv.Synth.Catal. 2003,345,1209-1214).

[0022] The compounds of formula (I) of the invention are chiral, containing centres of asymmetry, and are optically active: they can be present in eight stereoisomeric forms for n=1 and in sixteen stereoisomeric forms for n=2 characterized by different geometric and optical isomery, and in their respective mixtures. The present invention therefore extends to the individual optical and geometric isomers having formula (I), and to mixtures thereof in any proportion.

[0023] The aforesaid optical and geometric isomers are obtained by applying the aforescribed process on derivatives of formula (IV), (V), (VI a/b), (II a/b) having a specific optical and geometric configuration; said configuration is reproduced in the final compound (I). Specifically, to obtain the 1R,3R stereoisomer of compound (I), the corresponding 1 R,3R stereoisomers of the intermediates (IV), (V), (VI a/b), (II a/b) are used. In order to obtain the 1 S,3S stereoisomer of compound (I), the corresponding 1S,3S stereoisomers of the intermediates (IV), (V), (VI a/b), (II a/b) are used.

[0024] By working with enantiomeric mixtures (racemic or enantiomerically enriched) of the aforesaid precursor intermediates, the compounds of formula (I) are obtained in the corresponding mixtures.

[0025] Similarly, compounds of formula (I) with diastereoisomeric configuration (Z) or (E) are obtained starting from the intermediates (VI) and (II) having the same configuration, which are themselves obtainable from the aldehyde of formula (V) in a suitable configuration by Horner Emmons reaction with diethylallyl phosphonate.

[0026] The E/Z diastereoisomeric mixtures of the compounds of formula (I) are obtained starting from the corresponding diastereoisomeric mixtures of the aforesaid precursor intermediates.

[0027] A further aspect of the present application is an insecticidal composition comprising one or more compounds of formula (I) as previously defined. Optionally, to complement and/or increase the spectrum of action, said compositions can contain, in addition to the compounds of formula (I), further insecticidal compounds chosen from those commonly available and more indicated for the chosen treatment. Synergistic compounds, i.e. not themselves insecticides but which contribute to increasing the activity of the compounds of formula (I), can be included in the compositions; synergistic compounds such as, e.g. ,piperonyl butoxide and 1-(3,4-dimethoxyphenyl)ethyl 2-butyn-1-yl ether, known as Verbutin, are well known in the insecticide field.

[0028] The insecticidal composition can be produced in solid form (e.g. powders, granules) or liquid form (solutions, suspensions, emulsions, microemulsions) using techniques known in the art. The formulation can also be encapsulated to achieve modulated release over time. In the present insecticidal compositions, the compound of formula (I) is contained in a weight/weight percentage comprised between 0.001% and 95%, preferably between 0.001% and 50%, and more preferably between 0.001% and 5%. If two or more compounds of formula (I) are used, the aforesaid weight percentages would refer to the overall sum of the compounds of formula (I) present in the composition. In addition to the aforementioned active principles, adjuvants chosen from those commonly used in insecticidal compositions can be present. These include emulsifiers, UV stabilizers, antioxidants and other additives that are non-specific for insecticidal activity but useful for the specific application. Examples of emulsifiers are dodecylbenzenesulphonate, lignosulphonates, phospholipids, pol-

ethylene glycols. Examples of UV stabilizers are 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-octyloxy-benzophenone, 4-hydroxy-2,2,6,6-tetramethylpiperidine sebacate. An example of an antioxidant is 2,6-di-tert-butyl-1-hydroxytoluene.

[0029] A further aspect of the present application is a process for preparing the aforesaid insecticidal compositions comprising mixing one or more compounds of formula (I) as previously defined with one or more excipients useful for insecticidal formulations, and optionally other active principles with insecticidal activity, and synergistic compounds.

[0030] The invention also includes a method for eliminating insects, characterized by bringing into contact a substrate containing said insects with one or more of the aforesaid suitably formulated compounds of formula (I); the substrate can be an enclosed environment (house, school, office and other public premises, etc) or an open environment (gardens, parks, surfaces of agricultural use, etc); the substrate can be an article, e.g. fabrics, mattresses, carpets containing the insects to be eliminated; the substrate can be the air present in one of said environments or one of the surfaces that comprise said environments; the substrate can also be the surface of an animal contaminated by insects; in this latter case the compounds of formula (I) can be applied directly onto the animal after suitably formulating with suitable excipients for veterinary use. The compound of formula (I) is dispensed at the times and in amounts determined on the basis of the volume of the environment to be treated, and the degree of its infestation. The compounds of formula (I) present a low toxicity to man and animals and can therefore be used with a wide safety margin.

[0031] The following examples serve to illustrate the invention.

EXAMPLE 1: 2,3,5,6-tetrafluorobenzyl-(1RS,3RS)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylate

a. Synthesis of (1RS,3RS)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-7-carboxylic acid

[0032] (1RS,3RS)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylic acid is prepared from the corresponding ethyl (1 RS,3RS)-3-carboxyaldehyde-2,2-dimethylcyclopropane-1-carboxylate, obtained by ozonolysis of racemic 80:20 trans/cis chrysanthemic acid ethyl ester; the ozonolysis product is then subjected to a Wittig reaction with allyl triphenylphosphonium bromide as described in *J.Chem. Soc. (C)*,1076, (1970), followed by alkaline hydrolysis of the ester, after purification on silica gel column with 100/1 (v/v) petroleum ether/ethyl ether as eluent. The resulting acid, obtained by acidification of the corresponding salt, is used in the crude form for the subsequent reaction.

b. Synthesis of 2,3,5,6-tetrafluorobenzyl-(1RS,3RS)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-7-carboxylate

[0033] 3.4 ml (43 mmol) of N-methylimidazole, CH₃CN (43 ml) and finally 2.38 g (14.3 mmol) of (1 RS,3RS)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylic acid are introduced into a flask under nitrogen atmosphere. The mixture is cooled to 0°C and a solution of 3.26 g (17.2 mmol) of tosyl chloride dissolved in 19 ml of CH₃CN is added. At the end of the addition, the mixture is left at ambient temperature for 45 minutes, then cooled again to 0°C and 2.6 ml (14.3 mmol) of 2,3,5,6-tetrafluorobenzyl alcohol dissolved in 16 ml of CH₃CN are added. The mixture is agitated at ambient temperature for 4 hours, diluted with H₂O and transferred into a separating funnel. The reaction mixture is extracted 3 times with ethyl ether and the organic phases washed with water and with a saturated NaCl solution. The ether phase is separated, dried over Na₂SO₄ and filtered. Following evaporation at 21 mbar/30°C, the crude reaction product is taken up in 100/1 (v/v) petroleum ether/ethyl ether and purified on a silica gel chromatography column using the same eluent. By evaporation of the solvent, 4.61 g of an oily product with a purity equal to 97.0% is obtained.

IR (CHCl₃, cm⁻¹) 3200, 3086, 2925, 1725, 1178.

¹H NMR (CDCl₃) δ 7.13-7.04 (m, 1 H, CHAr), 6.75-6.65 (m, 1 H, CH=(Z)), 6.33-6.08 (m, 4 vinyl CH (E)+(Z)), 5.45-5.39 (m, 1 H, vinyl CH (Z)), 5.26-5.10+4.99-4.97 (m, 8 H, 2 vinyl-CH₂ + 2CH₂O (E)+(Z)), 2.36-2.32 (m, 1H, CH-cyclopropane (Z)), 2.10-2.07. (m, 1H, CH-cyclopropane (E)), 1.58 (d, 1H, J = 7.5 Hz, CH-cyclopropane (Z)), 1.54 (d, 1H, J=5.2 Hz, CH-cyclopropane (E)), 1.28 (s, 3 H, Me, (Z)), 1.26 (s, 3 H, Me, (E)), 1.1 (s, 6 H, 2Me, (Z)+(E)).

¹³C NMR (CDCl₃) δ 171.16, 171.07, 147.12-146.84 (m, aromatic C-F), 146.56-146.37 (m, aromatic C-F), 144.65-144.37 (m, aromatic C-F), 144.07-143.84 (m, aromatic C-F), 136.44, 133.15, 132.23, 131.77, 130.95, 128.32, 118.16, 115.75, 115.37 (t, J=18Hz, aromatic-C), 106.61 (t, J=22Hz, aromatic-CH), 53.59, 36.62, 35.04, 34.03, 32.43, 29.81, 29.68, 22.0, 21.91, 20.26, 20.23

EXAMPLE 2: 2,3,5,6-tetrafluorobenzyl-(1R,3R)-3-((E)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylate

a. Synthesis of (1R,3R)-3-((E)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylic acid

[0034] (1R,3R)-3-((E)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylic acid is prepared from the correspond-

ing ethyl (1R,3R)-3-carboxyaldehyde-2,2-dimethylcyclopropane-1-carboxylate, obtained by ozonolysis of (1R,3R) chrysanthemic acid ethyl ester by reaction with diethylallyl phosphonate according to the following reaction scheme:

[0035] 5.02 ml (28.8 mmol) of diethylallyl phosphonate are dissolved in 43 ml of anhydrous tetrahydrofuran in a flask under nitrogen atmosphere. The mixture is cooled to -78°C and 18 ml of a solution of 1.6 M butyllithium in n-hexane are added slowly. The mixture is left under agitation at -78°C for 1 hour, then 30 ml of hexamethylphosphotriamide are added followed by 3.5 g (20.6 mmol) of ethyl (1R,3R)-3-carboxyaldehyde-2,2-dimethylcyclopropane-1-carboxylate. The mixture is agitated for 12 hours at ambient temperature, then 45 ml of a saturated ammonium chloride solution are added. Extraction is then carried out three times with 50 ml of ethyl ether. After drying over anhydrous sodium sulphate, the solution is evaporated under vacuum (21 mbar/30°C) and the crude product purified on silica gel column, with 95/5 (v/v) petroleum ether/ethyl ether as eluent, to obtain an oily product with an E/Z ratio of 97/3.

b. Synthesis of 2,3,5,6-tetrafluorobenzyl (1R,3R)-3-((E)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-7-carboxylate

[0036] In a similar way to that described in example 1 part b., 2.38 g (14.3 mmol) of (1R,3R)-3-((E)-buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylic acid are added with 3.4 ml (43 mmol) of N-methyl imidazole dissolved in 43 ml of CH₃CN, and reacted with 3.26 g (17.2 mmol) of tosyl chloride dissolved in 19 ml of CH₃CN then with 2.6 ml (14.3 mmol) of 2,3,5,6-tetrafluorobenzyl alcohol dissolved in 16 ml of CH₃CN. After purification on silica gel column with 100/1 (v/v) petroleum ether/ethyl ether as eluent, 4.58 g of an oily product with an E/Z ratio of 97/3 and a purity equal to 96.1 % are obtained.

IR (CHCl₃, cm⁻¹) 3201, 3085, 2930, 1725, 1176.

¹H NMR (CDCl₃) δ 7.15-7.07 (m, 1 H, CHAr), 6.37-6.18 (m, 2H, 2CH=), 5.38-5.45 (m, 1 H, vinyl CH), 5.28-5.20 (m, 2H, CH₂O), 5.18 (dd, J₁=2Hz, J₂=12Hz, CH₂=), 4.98 (dd, J₁=2Hz, J₂=12Hz, CH₂=), 2.16-2.07 (m, 1H, CH-cyclopropane), 1.58 (d, 1H, J=7.5 Hz, CH-cyclopropane), 1.36 (s, 3 H, Me), 1.18 (s, 3H, Me).

¹³C NMR (CDCl₃) δ 171.05, 147.11-146.36 (m, 2 Aromatic C-F), 144.6-143.88 (m, 2 Aromatic C-F), 136.44, 136.43, 133.15, 130.93, 115.72, 115.68 (t, J=18Hz, Aromatic-C), 106.59 (t, J=22Hz, Aromatic-CH), 53.55, 36.61, 34.02, 29.79, 21.89, 20.21.

EXAMPLE 3: 2,3,5,6-tetrafluorobenzyl (1R,3R)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylate

a. Synthesis of (1R,3R)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylic acid

[0037] In a similar way to that described in example 1 part a., (1R,3R)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylic acid is prepared from the corresponding ethyl (1R,3R)-3-carboxyaldehyde-2,2-dimethylcyclopropane-1-carboxylate, obtained by ozonolysis of (1R,3R) chrysanthemic acid methyl ester; the ozonolysis product is then subjected to a Wittig reaction with allyl triphenylphosphonium bromide as described in *J.Chem. Soc. (C)*, 1076, (1970), followed by alkaline hydrolysis of the ester, after purification on silica gel column with 100/1 (v/v) petroleum ether/ethyl ether as eluent. The resulting acid, obtained by acidification of the corresponding salt, is used in the crude form for the subsequent reaction.

b. Synthesis of 2,3,5,6-tetrafluorobenzyl (1R,3R)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylate

[0038] In a similar way to that described in example 1 part b., 2.38 g (14.3 mmol) of (1R,3R)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylic acid are added with 3.4 ml (43 mmol) of N-methyl imidazole dissolved in 43 ml of CH₃CN, and reacted with 3.26 g (17.2 mmol) of tosyl chloride dissolved in 19 ml of CH₃CN, then with 2.6 ml (14.3 mmol) of 2,3,5,6-tetrafluorobenzyl alcohol dissolved in 16 ml of CH₃CN. After purification on silica gel column with 100/1 (v/v) petroleum ether/ethyl ether as eluent, 4.64 g of an oily product with a purity equal to 94% are obtained.

IR (CHCl₃, cm⁻¹) 3200, 3086, 2925, 1725, 1178.

¹H NMR (CDCl₃) δ 7.13-7.04 (m, 1 H, CHAr), 6.80-6.65 (m, 1 H, CH=(Z)), 6.33-6.08 (m, 4 vinyl CH (E)+(Z)), 5.45-5.39 (m, 1 H, vinyl CH (Z)), 5.26-5.10+4.99-4.97 (m, 8 H, 2 vinyl-CH₂ + 2CH₂O (E)+(Z)), 2.36-2.32 (m, 1H, CH-cyclopropane (Z)), 2.10-2.07 (m, 1H, CH-cyclopropane (E)), 1.58 (d, 1H, J = 7.5 Hz, CH-cyclopropane (Z)), 1.54 (d, 1H, J=5.2 Hz, CH-cyclopropane (E)), 1.28 (s, 3 H, Me, (Z)), 1.26 (s, 3 H, Me, (E)), 1.1 (s, 6 H, 2Me, (Z)+(E)).

¹³C NMR (CDCl₃) δ 171.16, 171.07, 147.12-146.84 (m, Aromatic C-F), 146.56-146.37 (m, Aromatic C-F), 144.65-144.37 (m, Aromatic C-F), 144.07-143.84 (m, Aromatic C-F), 136.44, 133.15, 132.23, 131.77, 130.95, 128.32, 118.16, 115.75, 115.37 (t, J=18Hz, Aromatic-C), 106.61 (t, J=22Hz, Aromatic-CH), 53.59, 36.62, 35.04, 34.03, 32.43, 29.81, 29.68, 22.0, 21.91, 20.26, 20.23.

EXAMPLE 4: 2,3,5,6-tetrafluorobenzyl (1R,3R)-3-(Hexa-1,3(E)-5(E/Z)-trienyl)-2,2-dimethylcyclopropane-1-carboxylate

[0039] The compound is prepared from (1R,3R)-3-carboxyaldehyde-2,2-dimethylcyclopropane-1-carboxylate of 2,3,5,6 tetrafluorobenzyl alcohol, obtained by ozonolysis of the corresponding chrysanthemic acid ester. Then 30.4 g (100 mmol) of aldehyde are reacted under nitrogen atmosphere with 40.9 g (120 mmol) of formylmethyltriphenyl phosphonium chloride in 500 ml of benzene in the presence of 15.15 g (150 mmol) of triethylamine at ambient temperature for 28 hours. The crude (1R,3R)-3-(3(E)-oxopropenyl)-2,2-dimethylcyclopropane-1-carboxylate of 2,3,5,6 tetrafluorobenzyl alcohol thus obtained, is purified after evaporation of the solvent at 25°C/21 mbar on silica gel chromatography column with 2/1 (v/v) petroleum ether/ethyl acetate as eluent, to obtain 26.7 g of product.

¹H NMR (CDCl₃) δ 9.40 (d, 1 H, J=8 Hz, CHO), 7.11-7.03 (m, 1 H, CHAr), 6.49-6.42 (m, 1 H, vinyl-CH), 6.24-6.17 (m, 1 H, vinyl CH), 5.24-5.16 (m, 2H, CH₂O), 2.25 (q, 1H, J= 4.8Hz, CH), 1.86 (d, 1H, J = 5.6 Hz, CH), 1.27 (s, 3 H, Me), 1.22 (s, 3 H, Me).

¹³C NMR (CDCl₃) δ 192.5, 169.8, 154.9, 147.1-146.3 (m, Aromatic C-F), 144.6-143.8 (m, Aromatic C-F), 134.0, 114.9 (t, J=16.6 Hz, Aromatic-C), 106.8 (t, J=22Hz, Aromatic-CH), 60.2, 53.9, 36.0, 35.8, 31.5, 21.9, 20.2, 14.1.

[0040] The product obtained is added slowly at 0°C to an ether solution (ethyl ether) of 45.7 g (118 mmol) of allyltriphenylphosphonium bromide in 300 ml of anhydrous ethyl ether, pre-cooled to 0°C, to which are added 11.1 ml of 1.6 M butyllithium solution in n-hexane. At the end of the addition the mixture is left for 1 hour at 0°C then for 3 hours at ambient temperature. The solution is then filtered and concentrated at 20°C/21 mbar, to obtain an oil which is purified on silica gel column with 100/1 petroleum ether/ethyl ether as eluent. 27.2 g of an oily product with 96% purity are obtained.

IR (CHCl₃, cm⁻¹) 3203, 3083, 2919, 2530, 1721, 1172.

¹H NMR (CDCl₃) δ 7.11-7.07 (m, 1 H, CHAr), 6.34-6.16 (m, 4 H, vinyl CH), 5.49-5.41 (m, 1 H, vinyl CH), 5.23-5.05 (m, 4 H, 2 vinyl-CH + 2CH₂O), 2.13-2.01 (m, 1H, CH-cyclopropane), 1.63-1.56 (m, 1 H, CH-cyclopropane), 1.27 (s, 3 H, Me), 1.12 (s, 3 H, Me).

¹³C NMR (CDCl₃) δ 171.88, 171.08, 137.0, 136.93, 132.8, 132.6, 132.4, 131.9, 131.7, 131.3, 129.6, 129.2, 117.0, 116.8, 106.6 (t, J=22Hz, Aromatic-CH), 64.3, 38.3, 38.1, 34.8, 33.5, 29.7, 28.8, 21.9, 21.4.

EXAMPLE 5: Effectiveness of insecticide in the vapour phase against mosquitoes of the species *Aedes aegypti* and *Culex quinquefasciatus*

[0041] Test units consisting of a paper support 20 cm x 10 cm in size were impregnated with the compound of example 3 and, for comparative purposes, with the reference compounds transfluthrin and metofluthrin, at an amount of 5.00 mg/unit for each compound (pure).

[0042] Using a common laboratory stand, the test unit was placed at a height of about 30 cm from the ground along one side of a 20 m³ room (L 3.00 m x D 2.49 m x H 2.69 m). In order to homogenize the insecticidal air within the room, a small electric fan was placed on the floor diagonal to the surface of the unit, in the nearest corner at a distance of about 50 cm from the unit. Three metal cages (L 8.4cm x Ø 8.0cm x mesh 1.0 mm) for every mosquito species, each containing 20 3-4 day old individuals of mixed sex, were placed along the other three sides of the room, at a height of 1.80 m from the ground and at a distance of 0.45 m from the respective walls. During the test the room was kept closed and temperature and humidity were controlled (T 23-26°C, RH 49-61%).

[0043] The fan was switched on and left on for 8 continuous hours. The times needed to reach 10%, 50% and 90% insect knock-down (KT10, KT50 and KT90, respectively) were recorded.

[0044] Every 2 hours and up to the 6th hour after the fan was switched on, new cages were introduced containing insects (set of 3 cages for each species).

[0045] At the end of the 8th hour, the percentage of insects knocked down in all the cages was determined, then the insects were removed from the room and transferred into an uncontaminated atmosphere within closed containers containing a sugary solution. The percentage mortality was recorded at the 24th hour from the start of the test.

[0046] The results obtained are summarized in tables 1 and 2 and the data are averages for the 3 cages.

Table 1

Tested species: <i>Aedes aegypti</i>						
Compound	Insect exposure after the following hours	Knock-down (minutes) time			% knock-down 8 h	% mortality 24 h
		KT10	KT50	KT90		
Example 3 5mg/unit	0	16	19	25	100	100
	2	4	6	9	100	100
	4	4	6	11	100	100
Transfluthrin 5mg/unit	0	21	26	36	100	100
	2	5	9	12	100	100
	4	4	7	10	100	100
Metofluthrin 5mg/unit	0	23	30	39	100	100
	2	7	9	15	100	100
	4	6	8	14	100	100

Table 2

Tested species: <i>Culex quinquefasciatus</i>						
Compound	Insect exposure after the following hours	Knock-down (minutes) time			% knock-down 8h	% mortality 24h
		KT10	KT50	KT90		
Example 3 5mg/unit	0	20	23	31	100	100
	2	6	8	12	100	100
	4	6	10	18	100	100
Transfluthrin 5mg/unit	0	27	37	44	100	100
	2	7	14	20	100	100
	4	9	17	22	100	100
Metofluthrin 5mg/unit	0	26	30	35	100	100
	2	11	16	24	100	100
	4	11	16	20	100	100

EXAMPLE 6: Effectiveness of residual insecticide on surfaces against cockroaches of the species *Blattella germanica*

[0047] Solutions of the compound of example 3 in acetone and, for comparison, of the reference compounds Trans-

fluthrin and Metofluthrin were applied from a distance of 12 cm onto glazed tiles (Ostara model, 15 x 15 cm = 225 cm²) by means of a suitable glass sprayer, so as to obtain an applied amount of pure compound equal to 50 mg/m². After treatment the tiles were transferred to and maintained in a closed test room at controlled temperature and humidity (24-25°C, RH 50-60%). Glass rings (H 5.5 cm x Ø 9.5 cm), with their internal surface treated with talc, and each containing 5 cockroaches, were positioned at the centre of the tiles for each of the assessment times of 24 hours, 3, 7, 10 and 14 days following treatment. For each assessment day, the insects were maintained on the surface for 24 hours and the time (hours, minutes) necessary to attain 100% knock-down followed by death, or percentage knock-down at the end of 24 hours, were recorded. The results obtained are summarized in table 3:

Table 3

Tested species: <i>Blattella germanica</i>						
Compound	Amount applied (mg/m ²)	Time (hours, minutes) to reach 100% knock-down followed by death, or percentage knock-down after 24 hours				
		1 day	3 days	7 days	10 days	14 days
EXAMPLE 3	50	15'	15'	15'	15'	15'
TRANSFLUTHRIN	50	24 h 60%	24 h 0%	24 h 0%	---	---
METOFLUTHRIN	50	2 h (24 h 80% *)	24 h 40%	24 h 0%	24 h 0%	---
UNTREATED CONTROL	---	24 h 0%	24 h 0%	24 h 0%	24 h 0%	24 h 0%

(*) one of the 5 individuals recovered within 24 hours from initial exposure.

[0048] The activity data presented in tables 1-3 show, for the compound of example 3 in accordance with formula (I) of the invention, a marked reduction in knock-down time for the different species tested. In particular, a very obvious increase in activity compared with the reference insecticides is observed with *Blattella germanica* (arthropod). In this respect, table 3 shows a total knock-down (100%) within 15 minutes of exposure for the compound of the invention; vice-versa, the reference insecticides, transfluthrin and metofluthrin, achieved only a partial knock-down i.e. between 60 and 80%, at 24 hours after exposure. The compounds of the invention hence demonstrate a decidedly superior strength; the diversity of the species on which activity is found also confirms the wide spectrum of action.

EXAMPLE 7: (2-benzyl-4-hydroxymethylfuryl) (1R,3R)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylate- (comparative)

a. Synthesis of (1R,3R)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylic acid

[0049] In a similar way to that described in example 1 part a., (1 R,3R)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylic acid is prepared from the corresponding ethyl (1R,3R)-3-carboxyaldehyde-2,2-dimethylcyclopropane-1-carboxylate, obtained by ozonolysis of (1 R,3R) chrysanthemic acid methyl ester; the ozonolysis product is then subjected to a Wittig reaction with allyl triphenylphosphonium bromide as described in J.Chem. Soc. (C),1076, (1970), followed by alkaline hydrolysis of the ester, after purification on silica gel column with 100/1 (v/v) petroleum ether/ethyl ether as eluent. The resulting acid, obtained by acidification of the corresponding salt, is used in the crude form for the subsequent reaction.

b. Synthesis of (2-benzyl-4-hydroxymethylfuryl) (1R,3R)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylate

[0050] In a similar way to that described in example 1 part b., 4.76 g (28.6 mmol) of (1R,3R)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylic acid are added with 6.8 ml (86 mmol) of N-methyl imidazole dissolved in 86 ml of CH₃CN, and reacted with 6.52 g (34.4 mmol) of tosyl chloride dissolved in 38 ml of CH₃CN, then with 5.38 g (28.6 mmol) of 2-benzyl-4-hydroxymethyl-furan dissolved in 32 ml of CH₃CN. After purification on silica gel column with 100/1 (v/v) petroleum ether/ethyl ether as eluent, 9.1 g of an oily product with a purity equal to 96% are obtained.

IR (CDCl₃, cm⁻¹) 3200, 3086, 2925, 1725, 1178.

¹H NMR (CHCl₃ 400 MHz) δ 7.39-7.20 (m, 12 H, (E+Z), Arom-CH+CH= (furan)) 6.80-6.68 (m, 1 H, CH=; Z), 6.39-6.05 (m, 4H (E+Z), 4CH=), 6.02 (s, 1 H, CH= (furan); E), 5.50-5.40 (m, 1 H, CH=; E), 5.30-5.05 (m, 4H(E+Z), CH=), 5.02-4.81 (m, 5H, (E+Z), 2CH₂+CH=), 3.95 (s, 2H, CH₂ (E)); 2.38-2.32 (m, 1H(Z), CH cyclopropane); 2.11-2.03 (m, 1H(E), CH cyclopropane); 1.60 (d, 1H(E), J=7.1 Hz, CH), 1.58 (d, 1H(Z), J=7.2 Hz, CH), 1.31 (s, 3H (Z), CH₃) 1.29 (s, 3H (E), CH₃), 1.19 (s, 6 H(E+Z) CH₃).

¹³C NMR (CDCl₃, 100MHz) δ(E+Z) 171.74, 171.67, 155.58, 140.35, 137.70, 136.52, 132.35, 131.52, 131-34, 128.72, 128.51, 126.57, 121.21, 117.00, 115.57, 107.27, 77.21, 65.83, 57.97, 57.94, 36.28, 35.43, 34.53, 34.42, 34.10, 32.09, 29.45, 29.33, 22.60, 22.32, 22.10, 22.01, 20.32, 20.28, 15.26, 14.04.

EXAMPLE 8: 2,3,5,6-tetrafluoro-4-methoxymethyl benzyl (1R,3R)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylate**a. Synthesis of (1R,3R)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylic acid**

[0051] In a similar way to that described in example 1 part a., (1R,3R)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylic acid is prepared from the corresponding ethyl (1R,3R)-3-carboxyaldehyde-2,2-dimethylcyclopropane-1-carboxylate, obtained by ozonolysis of (1 R,3R) chrysanthemic acid methyl ester; the ozonolysis product is then subjected to a Wittig reaction with allyl triphenylphosphonium bromide as described in *J.Chem. Soc. (C)*,1076, (1970), followed by alkaline hydrolysis of the ester, after purification on silica gel column with 100/1 (v/v) petroleum ether/ethyl ether as eluent. The resulting acid, obtained by acidification of the corresponding salt, is used in the crude form for the subsequent reaction.

b. Synthesis of 2,3,5,6-tetrafluoro-4-methoxymethyl benzyl (1R,3R)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylate

[0052] In a similar way to that described in example 1 part b., 4.76 g (28.6 mmol) of (1R,3R)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylic acid are added with 6.8 ml (86 mmol) of N-methyl imidazole dissolved in 86 ml of CH₃CN, and reacted with 6.52 g (34.4 mmol) of tosyl chloride dissolved in 38 ml of CH₃CN, then with 6.41 g (28.6 mmol) of 2,3,5,6-tetrafluoro-4-methoxymethyl benzyl alcohol dissolved in 32 ml of CH₃CN. After purification on silica gel column with 100/1 (v/v) petroleum ether/ethyl ether as eluent, 9.5 g of an oily product with a purity equal to 96% are obtained.

IR (CHCl₃, cm⁻¹) 3200, 3095, 2932, 1732, 1178.

¹H NMR (CDCl₃ 400 MHz) δ 6.78-6.63 (m, 1H, CH=) 6.38-6.16 (m, 3H, CH=; Z+E), 5.38-5.46 (m, 1H CH=,E), 4.95-5.25 (m, 9H, 5CH= + 2CH=; E+Z), 4.58 (m, 4H, (E+Z), 2CH₂), 3.41 (s, 6H(E+Z), OCH₃), 2.38-2.31 (m, 1H (Z), CH cyclopropane), 2.15-2.05 (m, 1H (E) CH cyclopropane); 1.58 (d, 1H(E), J=7.3 Hz, CH); 1.55 (d, 1H(Z), J=7.2 Hz, CH); 1.50 (s, 3H(Z), CH₃), 1.47 (s, 3H(Z), CH₃), 1.18 (s, 6 H, 2CH₃).

¹³C NMR (CDCl₃, 100MHz) δ (E+Z) 171.10, 171.02, 146.45, 146.39, 146.31, 146.27, 146.23, 146.17, 143.99, 143.93, 143.87, 143.79, 143.75, 143.69, 136.42, 133.14, 132.22, 131.74, 130.92, 128.30, 118.12, 117.01, 116.83, 116.66, 115.71, 114.99, 114.82, 114.65, 65.78, 61.35, 59.43, 53.48, 36.60, 35.02, 34.02, 32.40, 9.77, 29.65, 21.97, 21.88, 20.25, 20.22, 15.21.

EXAMPLE 9: Effectiveness of insecticide in the vapour phase against mosquitoes of the species *Aedes aegypti* and *Culex quinquefasciatus*

[0053] Test units consisting of a paper support 20 cm x 10 cm in size were impregnated with the compound of examples 3, 7 and 8 and, for comparative purposes, with the reference compounds transfluthrin and metofluthrin, at an amount of 5.00 mg/unit for each compound (pure). Using a common laboratory stand, the test unit was placed at a height of about 30 cm from the ground along one side of a 20 m³ room (L 3.00 m x D 2.49 m x H 2.69 m). In order to homogenize the insecticidal air within the room, a small electric fan was placed on the floor diagonal to the surface of the unit, in the

nearest corner at a distance of about 50 cm from the unit. Three metal cages (L 8.4cm x Ø 8.0cm x mesh 1.0 mm) for every mosquito species, each containing 20 3-4 day old individuals of mixed sex, were placed along the other three sides of the room, at a height of 1.80 m from the ground and at a distance of 0.45 m from the respective walls. During the test the room was kept closed and temperature and humidity were controlled (T 23-26°C, RH 49-61%). The fan was switched on and left on for 8 continuous hours. The times needed to reach 10%, 50% and 90% insect knock-down (KT10, KT50 and KT90, respectively) were recorded.

[0054] Every 2 hours and up to the 6th hour after the fan was switched on, new cages were introduced containing insects (set of 3 cages for each species).

[0055] At the end of the 8th hour, the percentage of insects knocked down in all the cages was determined, then the insects were removed from the room and transferred into an uncontaminated atmosphere within closed containers containing a sugary solution. The percentage mortality was recorded at the 24th hour from the start of the test.

[0056] The results obtained are summarized in tables 1 and 2 and the data are averages for the 3 cages.

Table 1

Tested species: <i>Aedes aegypti</i>						
Compound	Insect exposure after the following hours	Knock-down (minutes) time			% Knock-down 8h	% mortality 24h
		KT10	KT50	KT90		
Example 3 5mg/unit	0	16	20	26	100	100
	2	5	8	11	100	100
	4	5	8	12	100	100
Example 7 5 mg/unit	0	n.a.	n.a.	n.a.	5	79
	2	n.a.	n.a.	n.a.	0	79
	4	n.a.	n.a.	n.a.	0	65
Example 8 5 mg/unit	0	22	31	40	100	100
	2	12	29	41	100	100
	4	18	32	50	100	100
Transfluthrin 5mg/unit	0	21	26	35	100	100
	2	7	9	12	100	100

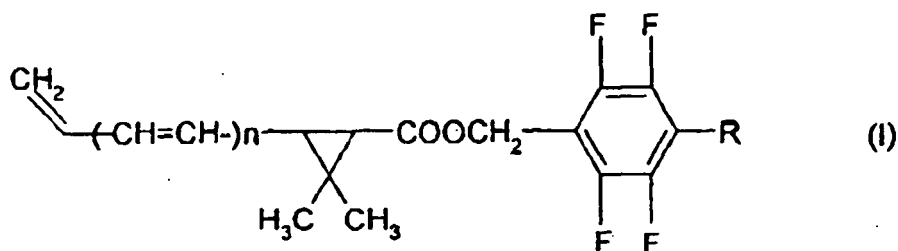
	4	6	9	14	100	100
Metofluthrin 5mg/unit	0	16	25	34	100	100
	2	7	9	15	100	100
	4	6	8	14	100	100

Tabella 2

Tested species: <i>Culex quinquefasciatus</i>						
Compound	Insect exposure after the following hours	Knock-down time (minutes)			% Knock-down 8h	% mortality 24h
		KT1	KT5	KT9		
		0	0	0		
Example 3 5mg/unit	0	23	28	35	100	100
	2	7	11	15	100	100
	4	8	10	14	100	100
Example 7 5 mg/unit	0	n.a.	n.a.	n.a.	8	70
	2	n.a.	n.a.	n.a.	2	35
	4	n.a.	n.a.	n.a.	0	23
Example 8 5 mg/unit	0	35	44	70	100	83
	2	39	50	68	100	70
	4	39	53	66	100	61
Transfluthrin 5mg/unit	0	31	42	55	100	100
	2	16	25	34	100	100
	4	11	16	24	100	100
Metofluthrin 5mg/unit	0	22	32	36	100	100
	2	11	16	22	100	100
	4	10	14	20	100	100

Claims

1. Compounds of formula (I)



in which n is chosen from 1 and 2 and R is chosen from -H, -CH₃, C₂H₅, -OCH₃, -OC₂H₅, and -CH₂-OCH₃, their enantiomers and diastereoisomers and mixtures thereof.

2. Compounds according to claim 1, chosen from:

- 2,3,5,6-tetrafluorobenzyl-(1RS,3RS)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylate;
 2,3,5,6-tetrafluorobenzyl-(1R,3R)-3-((E)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylate;
 2,3,5,6-tetrafluorobenzyl-(1R,3R)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylate;
 2,3,5,6-tetrafluorobenzyl-(1R,3R)-3-(Hexa-1,3(E)-5(E/Z)-1,3,5-trienyl)-2,2-dimethylcyclopropane-1-carboxylate;
 2,3,5,6-tetrafluoro-4-methoxymethyl benzyl (1R,3R)-3-((E/Z)-Buta-1,3-dienyl)-2,2-dimethylcyclopropane-1-carboxylate.

3. Compounds of formula (I) as defined in claims 1-2 for use as insecticides.

4. Compounds according to claim 3 for use in the insect decontamination of domestic environments and their surfaces, public premises and their surfaces, parks, gardens, and for agricultural surfaces.

5. Method for the elimination of insects from a substrate requiring it, **characterized by** bringing said substrate into contact with an effective amount of one or more compounds of formula (I) as defined in claims 1-2.

6. Method according to claim 5 wherein said substrate is a domestic environment or a surface thereof, public premises or a surface thereof, a park, a garden, an agricultural surface.

7. Use of one or more compounds of formula (I) as defined in claims 1-2, in the preparation of a veterinary product with insecticidal activity.

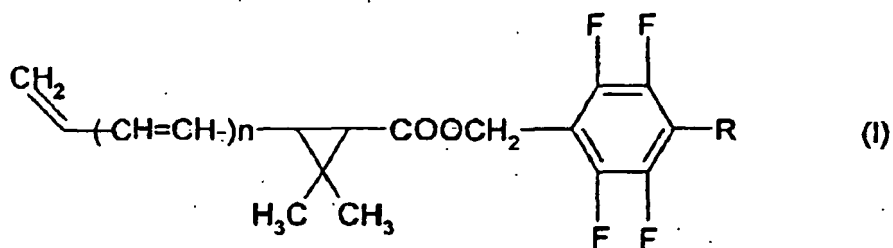
8. Insecticidal composition **characterized by** comprising one or more compounds of formula (I) as defined in claims 1-2 in combination with excipients for insecticidal compositions.

9. Composition according to claim 8 containing a w/w percentage of compound (I), comprised between 0.001 and 95%.

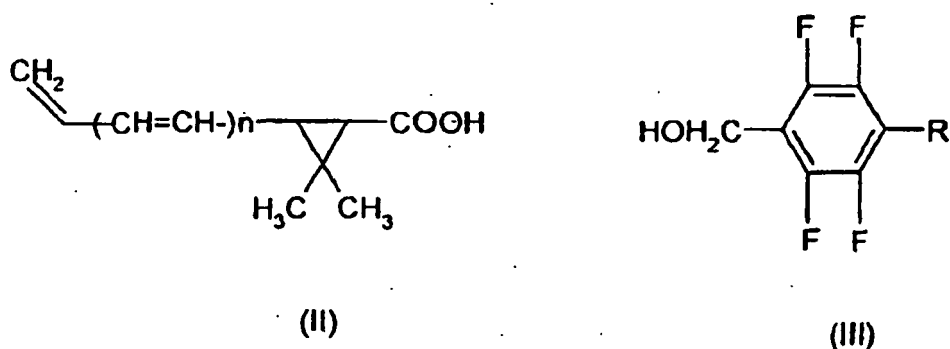
10. Composition according to claim 8 containing a w/w percentage of compound (I), comprised between 0.001 and 50%.

11. Composition according to claim 8 containing a w/w percentage of compound (I), comprised between 0.001 and 5%.

12. Process for the synthesis of compounds of formula (I)

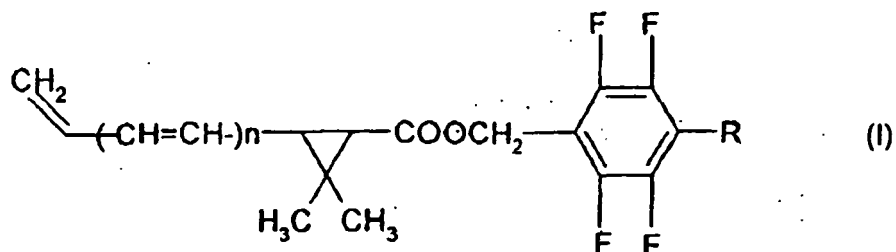


in which n is chosen from 1 and 2 and R is chosen from -H, -CH₃, C₂H₅, -OCH₃, -OC₂H₅, and -CH₂-OCH₃, their enantiomers and diastereoisomers and mixtures thereof, comprising reacting a compound of formula (II), optionally activated at the -COOH group, with an alcohol of formula (III), where n and R have the meanings described for formula (I).

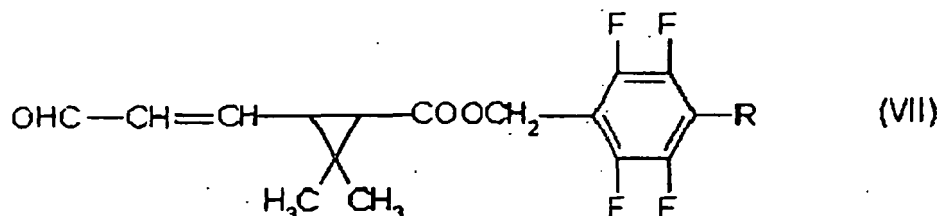


13. Process according to claim 12 where the -COOH group is activated by formation of the corresponding acyl halide.

14. Process for the synthesis of compounds of formula (I)

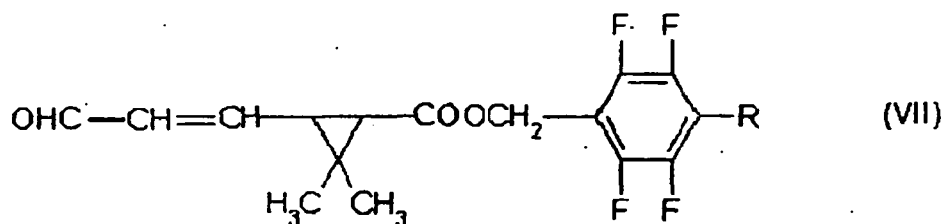


in which n is 2 and R is chosen from -H, -CH₃, C₂H₅, -OCH₃, -OC₂H₅, and -CH₂-OCH₃, their enantiomers and diastereoisomers and mixtures thereof, comprising the treatment of a compound of formula (VII)



with an allyltriphenylphosphonium halide.

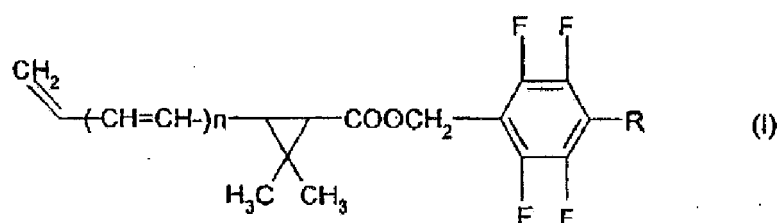
15. Compound of formula (VII)



10 in which R is chosen from -H, -CH₃, C₂H₅, -OCH₃, -OC₂H₅, and -CH₂-OCH₃, their enantiomers and diastereoisomers and mixtures thereof.

Patentansprüche

1. Verbindungen mit der Formel (I)



25 worin n aus 1 und 2 ausgewählt ist und R aus -H, -CH₃, -C₂H₅, -OCH₃, -OC₂H₅ und -CH₂-OCH₃, deren Enantiomeren und Diastereoisomeren und Mischungen hiervon ausgewählt ist.

2. Verbindungen nach Anspruch 1, welche ausgewählt sind aus:

2,3,5,6-Tetrafluorobenzyl-(1RS,3RS)-3-((E/Z)-buta-1,3-dienyl)-2,2-dimethylcyclopropan-1-carboxylat;
 2,3,5,6-Tetrafluorobenzyl-(1R,3R)-3-((E)-buta-1,3-dienyl)-2,2-dimethylcyclopropan-1-carboxylat;
 2,3,5,6-Tetrafluorobenzyl-(1R,3R)-3-((E/Z)-buta-1,3-dienyl)-2,2-dimethylcyclopropan-1-carboxylat;
 2,3,5,6-Tetrafluorobenzyl-(1R,3R)-3-(hexa-1,3(E)-5(E/Z)-1,3,5-trienyl)-2,2-dimethylcyclopropan-1-carboxylat;
 2,3,5,6-Tetrafluoro-4-methoxymethylbenzyl-(1R,3R)-3-((E/Z)-buta-1,3-dienyl)-2,2-dimethylcyclopropan-1-carboxylat.

3. Verbindungen mit der Formel (I) nach Anspruch 1 oder 2 zur Verwendung als Insektizide.

4. Verbindungen nach Anspruch 3 zur Verwendung bei der Insektendekontamination von häuslichen Umgebungen und ihren Oberflächen, öffentlichen Gebäuden und ihren Oberflächen, Parks, Gärten und landwirtschaftlichen Flächen.

5. Verfahren zur Eliminierung von Insekten von einem Substrat, welches dies benötigt, **dadurch gekennzeichnet, dass** das Substrat in Kontakt mit einer wirksamen Menge einer oder mehrerer Verbindungen mit der Formel (I) nach Anspruch 1 oder 2 gebracht wird.

6. Verfahren nach Anspruch 5, wobei das Substrat eine häusliche Umgebung oder eine Oberfläche hiervon, ein öffentliches Gebäude oder eine Oberfläche hiervon, ein Park, ein Garten oder eine landwirtschaftliche Fläche ist.

7. Verwendung einer oder mehrerer Verbindungen mit der Formel (I) nach Anspruch 1 oder 2 bei der Herstellung eines tiermedizinischen Produkts mit insektizider Aktivität.

8. Insektizide Zusammensetzung, **dadurch gekennzeichnet, dass** diese eine oder mehrere Verbindungen mit der Formel (I) nach Anspruch 1 oder 2 in Mischung mit Hilfsmitteln für insektizide Zusammensetzungen enthält.

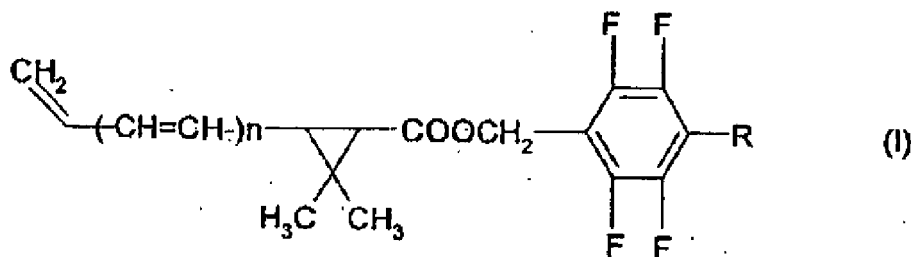
9. Zusammensetzung nach Anspruch 8, welche zwischen 0,001 und 95 Gewichtsprozent der Verbindung mit der

Formel (I) enthält.

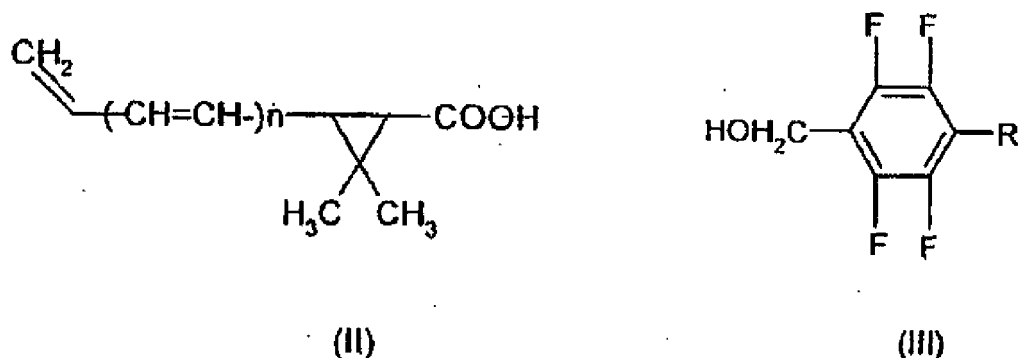
10. Zusammensetzung nach Anspruch 8, welche zwischen 0,001 und 50 Gewichtsprozent der Verbindung mit der Formel (I) enthält.

11. Zusammensetzung nach Anspruch 8, welche zwischen 0,001 und 5 Gewichtsprozent der Verbindung mit der Formel (I) enthält.

12. Verfahren zur Synthese von Verbindungen mit der Formel (I)

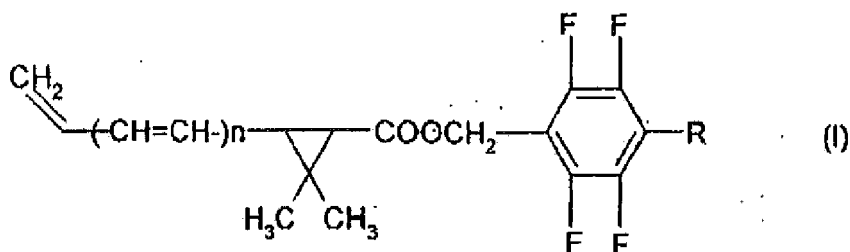


worin n aus 1 und 2 gewählt ist und R aus $-\text{H}$, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{OCH}_3$, $-\text{OC}_2\text{H}_5$ und $-\text{CH}_2-\text{OCH}_3$, deren Enantiomeren und Diastereoisomeren und Mischungen hiervon ausgewählt wird, umfassend das Reagieren einer Verbindung mit der Formel (II), welche optional an der $-\text{COOH}$ -Gruppe aktiviert ist, mit einem Alkohol mit der Formel (III), worin n und R die für die Formel (I) beschriebenen Bedeutungen aufweisen.

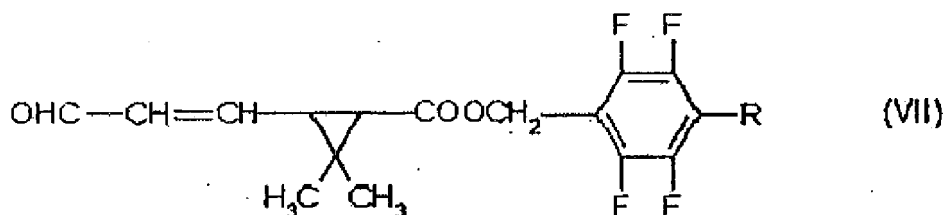


13. Verfahren nach Anspruch 12, wobei die $-\text{COOH}$ -Gruppe durch die Bildung des entsprechenden Acylhalogenids aktiviert wird.

14. Verfahren zur Synthese von Verbindungen mit der Formel (I)

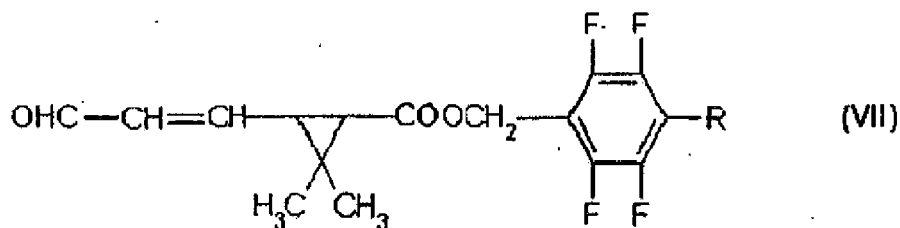


worin n 2 ist und R aus $-\text{H}$, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{OCH}_3$, $-\text{OC}_2\text{H}_5$ und $-\text{CH}_2-\text{OCH}_3$, deren Enantiomeren und Diastereoisomeren und Mischungen hiervon ausgewählt wird, umfassend die Behandlung einer Verbindung mit der Formel (VII)



mit einem Allyltriphenylphosphoniumhalogenid.

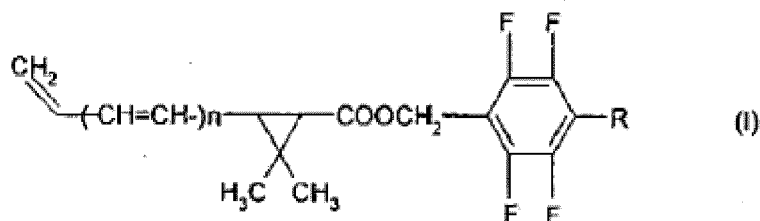
15. Verbindung mit der Formel (VII)



25 worin R aus -H, -CH₃, -C₂H₅, -OCH₃, -OC₂H₅ und -CH₂-OCH₃, deren Enantiomeren und Diastereoisomeren und Mischungen hiervon ausgewählt wird.

Revendications

30 1. Composés de formule (I)



dans laquelle n est choisi parmi 1 et 2 et R est choisi parmi -H, -CH₃, -C₂H₅, -OCH₃, -OC₂H₅ et -CH₂-OCH₃, leurs énantiomères et diastéréoisomères et des mélanges de ceux-ci.

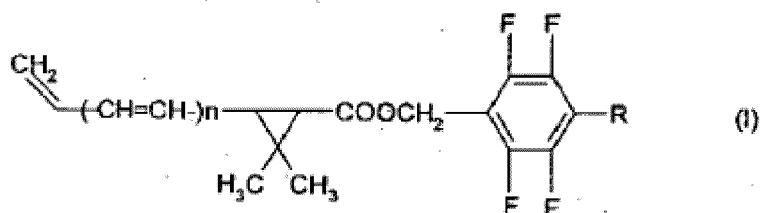
45 2. Composés selon la revendication 1, choisis parmi :

- le 2,3,5,6-tétrafluorobenzyl-(1R,3R)-3-((E/Z)-buta-1,3-diényl)-2,2-diméthylcyclopropane-1-carboxylate;
 le 2,3,5,6-tétrafluorobenzyl-(1R,3R)-3-((E)-buta-1,3-diényl)-2,2-diméthylcyclopropane-1-carboxylate;
 le 2,3,5,6-tétrafluorobenzyl-(1R,3R)-3-((E/Z)-buta-1,3-diényl)-2,2-diméthylcyclopropane-1-carboxylate;
 le 2,3,5,6-tétrafluorobenzyl-(1R,3R)-3-(hexa-1,3(E)-5(E/Z)-buta-1,3,5-triényl)-2,2-diméthylcyclopropane-1-carboxylate ;
 le 2,3,5,6-tétrafluoro-4-méthoxyméthylbenzyl-(1R,3R)-3-((E/Z)-buta-1,3-diényl)-2,2-diméthylcyclopropane-1-carboxylate.

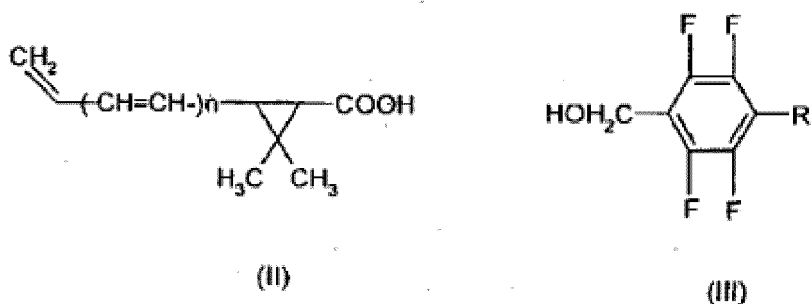
55 3. Composés de formule (I) définis dans les revendications 1 et 2, pour une utilisation en tant qu'insecticides.

4. Composés selon la revendication 3, pour une utilisation dans la décontamination des insectes d'environnements domestiques et de leurs surfaces, lieux publics et de leurs surfaces, parcs, jardins, et pour des surfaces agricoles.

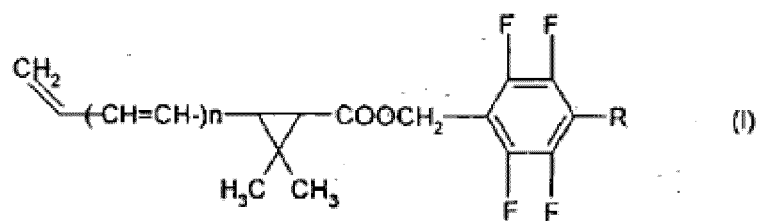
5. Procédé d'élimination des insectes d'un substrat en ayant besoin, **caractérisé par** la mise en contact dudit substrat avec une quantité efficace d'un ou plusieurs composés de formule (I) tels que définis dans les revendications 1 et 2.
6. Procédé selon la revendication 5, dans lequel ledit substrat est un environnement domestique ou une surface de celui-ci, un lieu public ou une surface de celui-ci, un parc, un jardin, une surface agricole.
7. Utilisation d'un ou plusieurs composés de formule (I) tels que définis dans les revendications 1 et 2, dans la préparation d'un produit vétérinaire ayant une activité insecticide.
8. Composition insecticide **caractérisée en ce qu'**elle comprend un ou plusieurs composés de formule (I) tels que définis dans les revendications 1 et 2 en combinaison avec des excipients pour des compositions insecticides.
9. Composition selon la revendication 8, contenant un pourcentage m/m de composé (I), compris entre 0,001 et 95 %.
10. Composition selon la revendication 8, contenant un pourcentage m/m de composé (I), compris entre 0,001 et 50 %.
11. Composition selon la revendication 8, contenant un pourcentage m/m de composé (I), compris entre 0,001 et 5 %.
12. Procédé de synthèse des composés de formule (I)



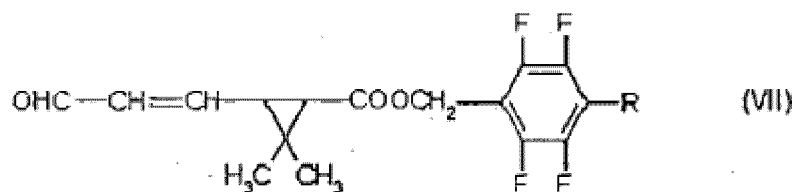
dans laquelle n est choisi parmi 1 et 2 et R est choisi parmi -H, -CH₃, -C₂H₅, -OCH₃, -OC₂H₅ et -CH₂-OCH₃, leurs énantiomères et diastéréoisomères et des mélanges de ceux-ci, comprenant la mise en réaction d'un composé de formule (II), facultativement activé au niveau du groupe -COOH, avec un alcool de formule (III), où n et R ont les significations décrites pour la formule (I)



13. Procédé selon la revendication 12, dans lequel le groupe -COOH est activé par la formation de l'halogénure d'acyle correspondant.
14. Procédé de synthèse des composés de formule (I)

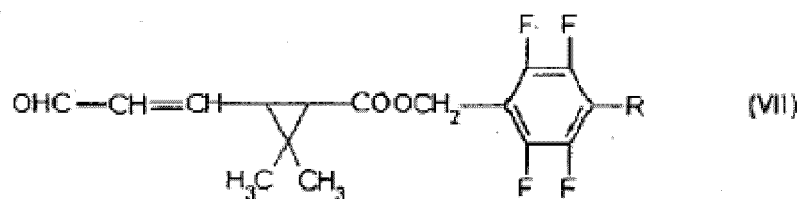


10 dans laquelle n vaut 2 et R est choisi parmi -H, -CH₃, -C₂H₅, -OCH₃, -OC₂H₅ et -CH₂-OCH₃, leurs énantiomères et diastéréoisomères et des mélanges de ceux-ci, comprenant le traitement d'un composé de formule (VII)



20 avec un halogénure d'allyltriphénylphosphonium.

15. Composé de formule (VII)



35 dans laquelle R est choisi parmi -H, -CH₃, -C₂H₅, -OCH₃, -OC₂H₅ et -CH₂-OCH₃, leurs énantiomères et diastéréoisomères et des mélanges de ceux-ci.

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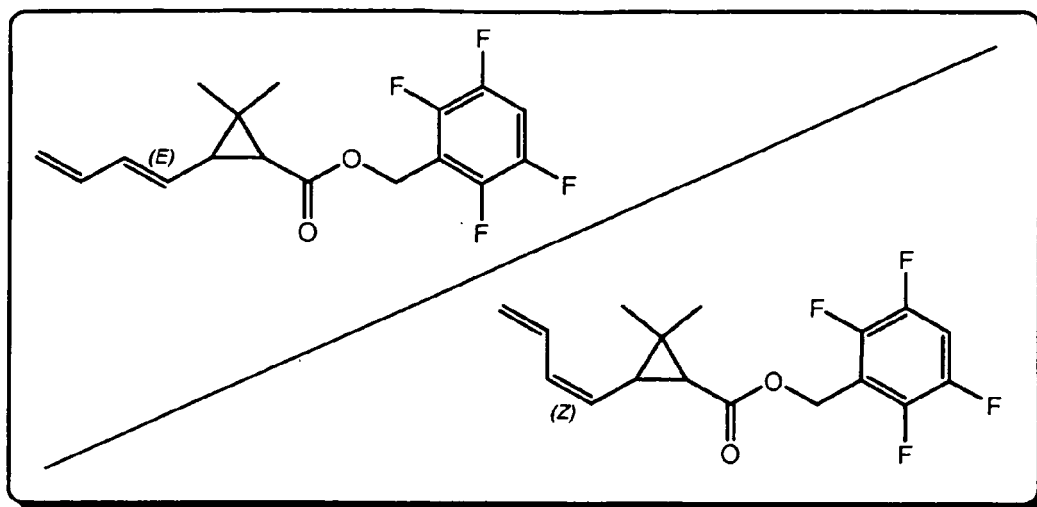
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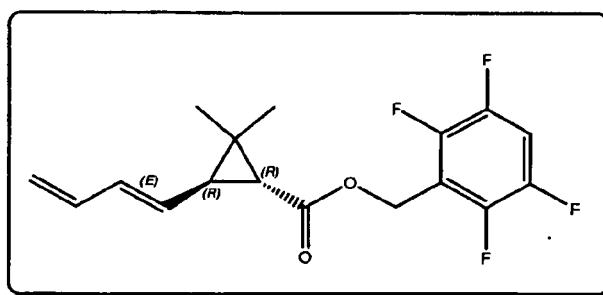
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FIGURE 1

Compound of example 1



Compound of example 2



Compound of example 3

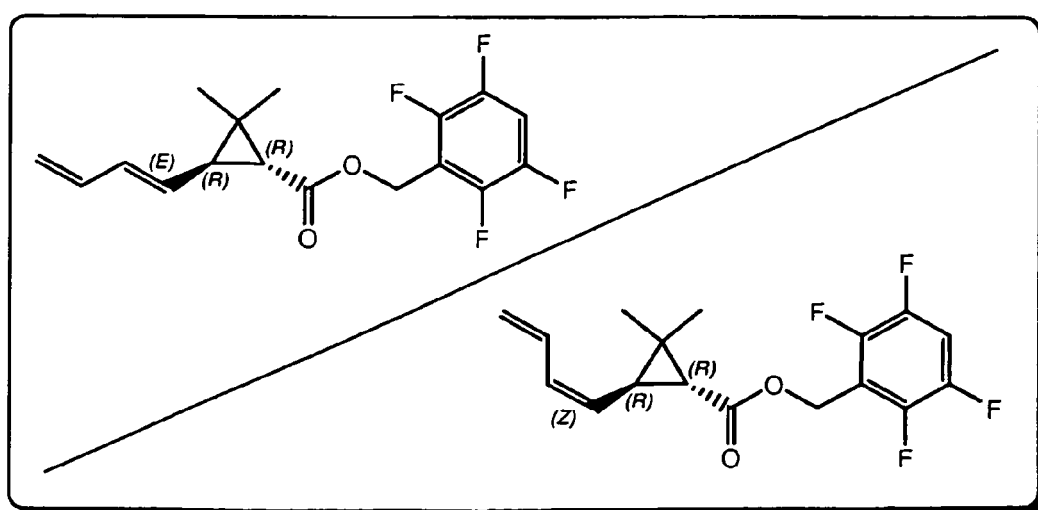
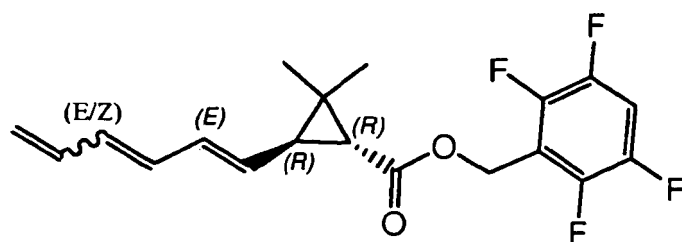
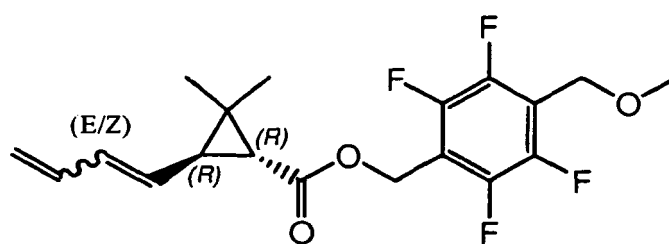


FIGURE 2

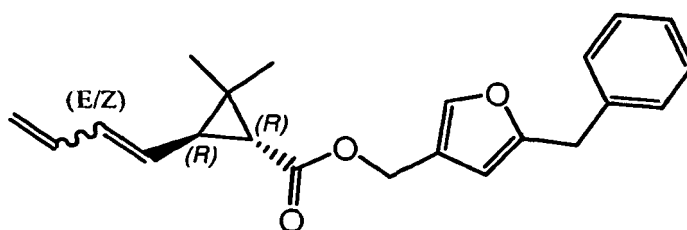
Compound of example 4



Compound of example 8



Comparative compound of example 7



REFERENCES CITED IN THE DESCRIPTION

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