



Industria y Comercio
SUPERINTENDENCIA

PCT

SOLICITUD

PATENTE DE INVENCION

03-38176

21. EXPEDIENTE N°

24. TÍTULO

PIRROCARBOXTANIDAS Y PIRROCARBOXTANIDAS Y SUS DER.

ASIMÉTRICAS

25. CLASIFICACIÓN INTERNACIONAL **AOI N 43/46; CO7D 207/327**

71. SOLICITANTE

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Basilea, Suiza.

74. APODERADO

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Cédula No. 1092

22. BOGOTÁ, D. C.

**Industria y Comercio**

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SUPERINTENDENCIA Y COMERCIO

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Dependencia: 2000 DIVISION DE NUEVAS CREACIONES

**FORMULARIO UNICO DE SOLICITUD DE PATENTE
PCT
ENTRADA EN FASE NACIONAL**

1

SOLICITUD DE:



Patente de Invención.



Patente de Modelo de Utilidad.



Capítulo I.



Capítulo II.

2

**SOLICITANTE
(71)****Nombre: SYNGENTA PARTICIPATIONS
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Suiza

Domicilio: Basilea, Suiza.

IDENTIFICACION

C.C.



NIT



C.E.



Otro



Cual _____

Número: _____

3

**REPRESENTANTE
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IDENTIFICACION

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NIT



C.E.



Otro



Cual _____

Número: 438.019 T.P. 31.929

4

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5

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6

**Título (54) PIRROLCARBOXIAMIDAS Y PIRROLCARBOTIOAMIDAS Y SUS USOS
AGROQUIMICOS**

7

Clasificación Internacional (51) C07D 207/327 ; A01N 43/36

8

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GB.GB.

(32) Fecha

8 de noviembre de 200012 de diciembre de 2000

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9

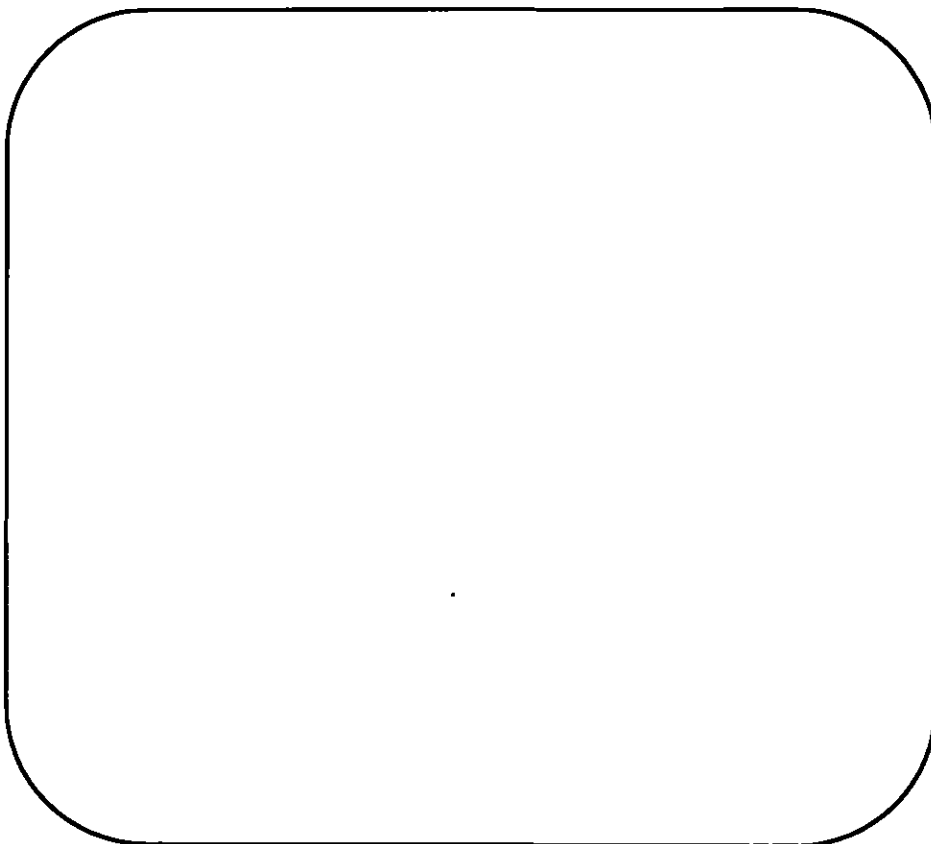
Comprobante de pago No.: 03-27.658 Fecha: 22 de abril de 2003

10

Anexos:

- ☒ Comprobante de pago de la tasa de presentación de la solicitud por 400.000.00.
- ☐ Comprobante de pago por reivindicación de prioridad.
- ☐ Documento que acredita la existencia y representación legal cuando el solicitante sea persona jurídica.
- ☐ Poderes, si fuere el caso.
- ☐ Documento de cesión del inventor al solicitante o a su causante.
- ☐ Declaraciones.
- ☒ Copia de la solicitud internacional. (Resumen, descripción, reivindicaciones, dibujos)
- ☒ Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicaciones, dibujos)
- ☒ Copia del examen preliminar efectuado por la IPEA.
- ☐ Traducción del examen preliminar efectuado por la IPEA.
- ☐ De ser el caso, copia del contrato de acceso.
- ☐ De ser el caso, documento que acredite la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas.
- ☐ De ser el caso, certificado de depósito del material biológico.
- ☐ Arte final 12x12
- ☐ De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionadas parcial o totalmente con la invención de esta solicitud.
- ☐ Otros

11

FIGURA CARACTERISTICA:

12

Solicito la concesión de la patente,

NOMBRE: EMILIO FERRERO

FIRMA : 
C.C. 438.019 de Usaquén T.P. 31.929

(19) World Intellectual Property Organization
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GENTA PARTICIPATIONS AG [CH/CH]; Schwarzwald-
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(72) Inventor; and

(75) Inventor/Applicant (for US only): WALTER, Harald
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Intellectual Property, P.O.Box, CH-4002 Basel (CH).

(81) Designated States (national): AB, AG, AL, AM, AT, AU,
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GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI,
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TG).

Published:

- with International search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: PYRROLCARBOXAMIDES AND PYRROLCARBOTHIOAMIDES AND THEIR AGROCHEMICAL USES

(57) Abstract: The invention relates to novel pesticidal pyrrolcarboxamide of the formula (I), wherein X is oxygen or sulfur; R₁ is CF₃, CF₃H or C₂H₅; R₂ is C₁-C₃alkyl, C₁-C₃haloalkyl, C₁-C₃alkoxy-C₁-C₃alkyl or C₁-C₃haloalkoxy-C₁-C₃alkyl; R₃ is hydrogen, methyl, CF₃ or fluoro; Q is (Q1), (Q2), (Q3), (Q4); R₄ is C₆-C₁₄bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF₃; C₆-C₁₄bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF₃; C₆-C₁₄bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF₃; a group of the form (a) wherein R₇, R₈, R₉ are independently of each other C₁-C₃alkyl or C₁-C₃haloalkyl; or a group (b) wherein R₁₀ and R₁₁ are independently of each other hydrogen or halogen and n=1 or 2; and R₅ and R₆ are independently of each other hydrogen or halogen. The novel compounds have plant-protecting properties and are suitable for protecting plants against infestation by phytopathogenic microorganisms.

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07D207/327 C07D409/12 C07D207/32 A01N43/36 C07C211/46

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)

IPC 7 C07D C07C

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 practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 09482 A (NOVARTIS ERFIND VERWALT GMBH ; EBERLE MARTIN (CH); NOVARTIS AG (CH)) 24 February 2000 (2000-02-24) page 1 -page 3; claim 1	1-21
A	EP 0 737 682 A (MITSUI TOATSU CHEMICALS) 16 October 1996 (1996-10-16) page 2, line 35 -page 3, line 29; claim 1	1-21
A	EP 0 841 336 A (MITSUI TOATSU CHEMICALS) 13 May 1998 (1998-05-13) page 2, line 10 -page 3, line 29; claim 1	1-21
A	EP 0 824 099 A (MITSUI TOATSU CHEMICALS) 18 February 1998 (1998-02-18) page 4, line 5 -page 5, line 12; claim 1	1-21
	-/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in 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 document 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 relating 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
- "Z" document member of the same patent family

Date of the actual completion of the international search

6 February 2002

Date of mailing of the international search report

12 2 04 03

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Authorized officer:

Uselli, A

INTERNATIONAL SEARCH REPORT

International Application No

/EP 01/12830

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 01 49664 A (WALTER HARALD ;SYNGENTA PARTICIPATIONS AG (CH); SCHNEIDER HERMANN) 12 July 2001 (2001-07-12) page 1 -page 11; claim 1; tables 1,2	1-21

INTERNATIONAL SEARCH REPORT

national application No.
PCT/EP 01/12830

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-21

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 219

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-21

Compounds of formula (I)

2. Claims: 22 (part)- 24(part), 25, 27, 29, 30

Intermediates of formula (IV) in which Q is Q1

3. Claims: 22(part)-24(part), 26,28

Intermediates of formula (IV) in which Q is Q2, Q3 or Q4

INTERNATIONAL SEARCH REPORT

Information on patent family members

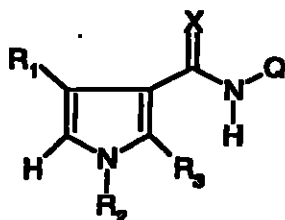
Patent Application No
P. 01/12830

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0009482	A	24-02-2000	AU 5513899 A BR 9912962 A CN 1311774 T WO 0009482 A1 EP 1105375 A1 PL 345823 A1 US 2002019541 A1	06-03-2000 08-05-2001 05-09-2001 24-02-2000 13-06-2001 14-01-2002 14-02-2002
EP 0737682	A	16-10-1996	CA 2173788 A1 CN 1146993 A ,B DE 69618370 D1 EP 0737682 A1 JP 3164762 B2 JP 9235282 A JP 2001151770 A KR 201426 B1 US 5747518 A	12-10-1996 09-04-1997 14-02-2002 16-10-1996 08-05-2001 09-09-1997 05-06-2001 15-06-1999 05-05-1998
EP 0841336	A	13-05-1998	CA 2220276 A1 CN 1185437 A ,B EP 0841336 A1 JP 10182642 A KR 269420 B1 US 5869427 A	06-05-1998 24-06-1998 13-05-1998 07-07-1998 16-10-2000 09-02-1999
EP 0824099	A	18-02-1998	CA 2213111 A1 CN 1338452 A CN 1178791 A ,B DE 69708004 D1 EP 0824099 A1 ES 2164972 T3 JP 10310577 A US 5965774 A US 5914344 A	15-02-1998 06-03-2002 15-04-1998 13-12-2001 18-02-1998 01-03-2002 24-11-1998 12-10-1999 22-06-1999
WO 0149664	A	12-07-2001	AU 2157901 A WO 0149664 A1	16-07-2001 12-07-2001

PYRROLCARBOXYAMIDES AND PYRROLCARBOTHIOAMIDES AND THEIR AGROCHEMICAL USES

The present invention relates to novel pyrrolicarboxylic acid amides and pyrrolicarbothioic acid amides which have microbicidal activity, in particular fungicidal activity. The invention also relates to the preparation of these substances, to agrochemical compositions which comprise at least one of the novel compounds as active ingredient, to the preparation of the compositions mentioned and to the use of the active ingredients or compositions in agriculture and horticulture for controlling or preventing infestation of plants by phytopathogenic microorganisms, preferably fungi.

The 3-pyrrolicarboxylic acid amides and 3-pyrrolicarbothioic acid amides of the present invention have the general formula (1),



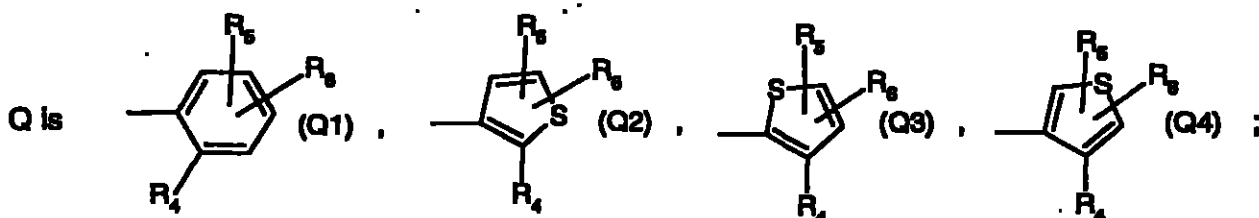
wherein

X is oxygen or sulfur;

R₁ is CF₃, CF₂H or CFH₂;

R₂ is C₁-C₃alkyl, C₁-C₃haloalkyl, C₁-C₃alkoxy-C₁-C₃alkyl or C₁-C₃haloalkoxy-C₁-C₃alkyl;

R₃ is hydrogen, methyl, CF₃ or fluoro;

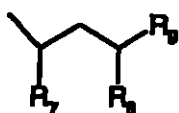


R₄ is C₆-C₁₄bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF₃;

C₆-C₁₄bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF₃;

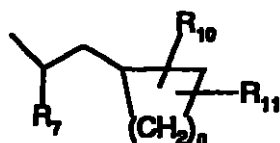
C₆-C₁₄bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF₃; or a group of the form

- 2 -



wherein R_7 , R_8 and R_9 are independently of each other C_1 - C_3 alkyl or

C_1 - C_3 haloalkyl; or a group



wherein R_{10} and R_{11} are independently of each other hydrogen or

halogen and $n = 1$ or 2 ; and

R_5 and R_6 are independently of each other hydrogen or halogen.

Surprisingly, it has now been found that the compounds of formula I exhibit improved biological properties which render them more suitable for the practical use in agriculture and horticulture.

Where asymmetrical carbon atoms are present in the compounds of formula I, these compounds are in optically active form. The invention relates to the pure isomers, such as enantiomers and diastereomers, as well as to all possible mixtures of isomers, e.g. mixtures of diastereomers, racemates or mixture of racemates.

Within the present specification alkyl denotes methyl, ethyl, n-propyl and isopropyl. Non-branched alkyl is preferred. Alkyl as part of other radicals such as alkoxy, haloalkyl, etc. is understood in an analogous way. Halogen will be understood generally as meaning fluoro, chloro, bromo or iodo. Fluoro, chloro or bromo are preferred meanings. Halogen as part of other radicals such as haloalkyl, haloalkoxy, etc. is understood in an analogous way.

Bicycloalkyl is, depending on the ring size, bicyclo[2.1.1]hexane, bicyclo[2.2.1]heptane, bicyclo[2.2.2]octane, bicyclo[3.2.1]octane, bicyclo[3.2.2]nonane, bicyclo[4.2.2]decane, bicyclo[4.3.2]undecane, adamantane and the like.

Bicycloalkenyl is bicyclo[2.1.1]hex-4-ene, bicyclo[2.2.1]hept-2-ene, bicyclo[2.2.2]oct-2-ene and the like.

Bicycloalkadienyl is bicyclo[2.2.1]hepta-2,5-diene, bicyclo[2.2.2]octa-2,5-diene, and the like.

One specific subgroup of the compounds of formula I is the group wherein X is oxygen.

Another specific subgroup of the compounds of formula I is the group wherein X is sulfur.

Preferred subgroups of compounds of formula I are those wherein

X is oxygen; or

X is sulfur; or

R₁ is CF₃; or

R₁ is CF₂H; or

R₁ is CFH₂; or

R₂ is C₁-C₃alkyl; or

R₂ is C₁-C₃haloalkyl; or

R₂ is C₁-C₃alkoxy-C₁-C₃alkyl; or

R₂ is C₁-C₃haloalkoxy-C₁-C₃alkyl; or

R₂ is C₁-C₃alkyl or C₁-C₃haloalkyl; or

R₂ is C₁-C₃alkyl, C₁-C₃haloalkyl or C₁-C₃alkoxy-C₁-C₃alkyl; or

R₂ is methyl or CH₂OCH₃; or

R₂ is methyl; or

R₃ is hydrogen; or

R₃ is methyl; or

R₃ is CF₃; or

R₃ is fluoro; or

R₃ is hydrogen or fluoro; or

Q is Q1; or

Q is Q2, Q3 or Q4; or

Q is Q2; or

Q is Q3; or

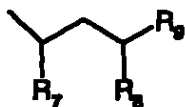
Q is Q4; or

R₄ is C₈-C₁₀bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF₃; or

C₈-C₁₀bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF₃; or

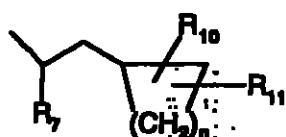
C₈-C₁₀bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF₃; or

a group of the form



wherein R₇, R₈ and R₉ are independently of each other C₁-C₃alkyl or

C₁-C₃haloalkyl; or a group



wherein R₁₀ and R₁₁ are independently of each other hydrogen or

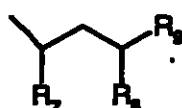
halogen and n = 1 or 2; or

R₄ is C₆-C₁₀bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF₃ ,

C₆-C₁₀bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF₃ ,

C₆-C₁₀bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF₃ , or

a group of the form



wherein R₇, R₈ and R₉ are independently of each other C₁-C₃alkyl or

C₁-C₃haloalkyl; and

R₅ and R₆ are independently of each other hydrogen, chloro, bromo or fluoro; or

R₅ and R₆ are independently of each other hydrogen, chloro or fluoro; or

R₅ is hydrogen and R₆ is chloro or fluoro.

Further preferred subgroups are those wherein

a) X is oxygen;

R₁ is CF₃;

R₂ is C₁-C₃alkyl or C₁-C₃alkoxy-C₁-C₃alkyl;

R₃ is hydrogen or fluoro;

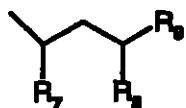
Q is Q1;

R₄ is C₆-C₁₀bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF₃; or

C₆-C₁₀bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF₃; or

C₆-C₁₀bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF₃; or

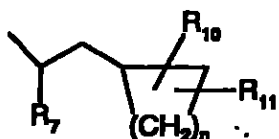
a group of the form



wherein R₇, R₈ and R₉ are independently of each other C₁-C₃alkyl or

C₁-C₃haloalkyl; or a group

- 5 -



wherein R_{10} and R_{11} are independently of each other hydrogen or

halogen and $n = 1$ or 2 ; and

R_5 and R_6 are independently of each other hydrogen, fluoro, chloro or bromo; or

b) X is oxygen;

R_1 is CF_3 ;

R_2 is C_1 - C_3 alkyl or C_1 - C_3 haloalkyl;

R_3 is hydrogen or fluoro;

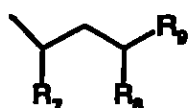
Q is Q2, Q3 or Q4;

R_4 is C_6 - C_{10} bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3 ; or

C_6 - C_{10} bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3 ; or

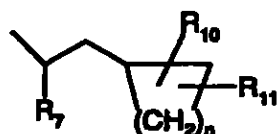
C_6 - C_{10} bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3 ; or

a group of the form



wherein R_7 , R_8 and R_9 are independently of each other C_1 - C_3 alkyl or

C_1 - C_3 haloalkyl; or a group



wherein R_{10} and R_{11} are independently of each other hydrogen or

halogen and $n = 1$ or 2 ; and

R_5 and R_6 are independently of each other hydrogen, fluoro, chloro or bromo; and among this subgroup Q = Q2 is preferred; or

ab) X is oxygen;

R_1 is CF_3 ;

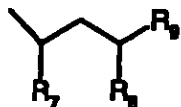
R_2 is methyl or CH_2OCH_3 ;

R_3 is hydrogen or fluoro;

Q is Q1;

R_4 is a group of the form

- 6 -



wherein R₇, R₈ and R₉ are independently of each other C₁-C₃alkyl or

C₁-C₃haloalkyl; and

R₅ and R₆ are independently of each other hydrogen, fluoro, chloro or bromo; or

c) X is oxygen;

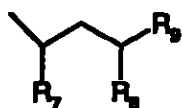
R₁ is CF₃;

R₂ is methyl;

R₃ is hydrogen or fluoro;

Q is Q1;

R₄ is a group of the form



wherein R₇, R₈ and R₉ are independently of each other CF₃, methyl or

ethyl, preferably methyl; and

R₅ and R₆ are independently of each other hydrogen, fluoro or chloro; or

d) X is oxygen;

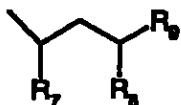
R₁ is CF₃;

R₂ is methyl;

R₃ is hydrogen;

Q is Q1;

R₄ is a group of the form



wherein R₇, R₈ and R₉ are independently of each other methyl or ethyl,

preferably methyl; and

R₅ and R₆ are independently of each other hydrogen, fluoro or chloro; or

e) X is oxygen;

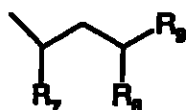
R₁ is CF₃;

R₂ is methyl;

R₃ is fluoro;

Q is Q1;

R₄ is a group of the form



wherein R_7 , R_8 and R_9 are independently of each other methyl or ethyl,

preferably methyl; and

R_5 and R_6 are independently of each other hydrogen, fluoro or chloro.

Other preferred subgroups are those wherein

f) X is sulfur;

R_1 is CF_3 ;

R_2 is C_1 - C_3 alkyl or C_1 - C_3 haloalkyl;

R_3 is hydrogen or fluoro;

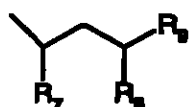
Q is Q1;

R_4 is C_6 - C_{10} bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3 ; or

C_6 - C_{10} bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3 ; or

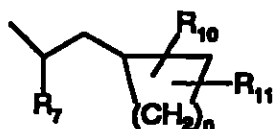
C_6 - C_{10} bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3 ; or

a group of the form



wherein R_7 , R_8 and R_9 are independently of each other C_1 - C_3 alkyl or

C_1 - C_3 haloalkyl; or a group



wherein R_{10} and R_{11} are independently of each other hydrogen or

halogen and $n = 1$ or 2 ; and

R_5 and R_6 are independently of each other hydrogen, fluoro, chloro or bromo; or

g) X is sulfur;

R_1 is CF_3 ;

R_2 is C_1 - C_3 alkyl or C_1 - C_3 haloalkyl;

R_3 is hydrogen or fluoro;

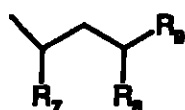
Q is Q2, Q3 or Q4;

R_4 is C_6 - C_{10} bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3 ; or

C_6 - C_{10} bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3 ; or

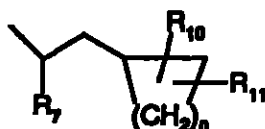
C_6 - C_{10} bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3 ; or

a group of the form



wherein R_7 , R_8 and R_9 are independently of each other C_1 - C_3 alkyl or

C_1 - C_3 haloalkyl; or a group



wherein R_{10} and R_{11} are independently of each other hydrogen or

halogen and $n = 1$ or 2 ; and

R_5 and R_6 are independently of each other hydrogen, fluoro, chloro or bromo.

Other subgroups of compounds of formula I are those wherein

h) X is oxygen or sulfur;

R_1 is CF_3 ;

R_2 is C_1 - C_3 alkyl, C_1 - C_3 haloalkyl or C_1 - C_3 alkoxy- C_1 - C_3 alkyl ;

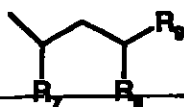
R_3 is hydrogen or fluoro;

Q is Q1;

R_4 is C_6 - C_{10} bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3 ;

C_6 - C_{10} bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3 ;

C_6 - C_{10} bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3 ; a group of the form



wherein R_7 , R_8 and R_9 are independently of each other C_1 - C_3 alkyl or

C_1 - C_3 haloalkyl; and

R_5 and R_6 are independently of each other hydrogen, chloro or fluoro; or

i) X is oxygen or sulfur;

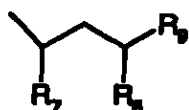
R_1 is CF_3 ;

R_2 is C_1 - C_3 alkyl, C_1 - C_3 haloalkyl or C_1 - C_3 alkoxy- C_1 - C_3 alkyl ;

R_3 is hydrogen or fluoro;

Q is Q1;

R_4 is a group of the form



wherein R₇, R₈ and R₉ are independently of each other C₁-C₃alkyl or

C₁-C₃haloalkyl; and

R₈ and R₉ are independently of each other hydrogen, chloro or fluoro; or

j) X is oxygen or sulfur;

R₁ is CF₃;

R₂ is C₁-C₃alkyl, C₁-C₃haloalkyl or C₁-C₃alkoxy-C₁-C₃alkyl;

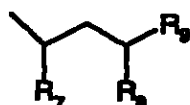
R₃ is hydrogen or fluoro;

Q is Q2, Q3 or Q4;

R₄ is C₆-C₁₀bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF₃;

C₆-C₁₀bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF₃;

C₆-C₁₀bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF₃; a group of the form



wherein R₇, R₈ and R₉ are independently of each other C₁-C₃alkyl or

C₁-C₃haloalkyl; and

R₈ and R₉ are independently of each other hydrogen, chloro or fluoro; or

k) X is oxygen or sulfur;

R₁ is CF₃;

R₂ is C₁-C₃alkyl, C₁-C₃haloalkyl or C₁-C₃alkoxy-C₁-C₃alkyl;

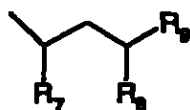
R₃ is hydrogen or fluoro;

Q is Q2;

R₄ is C₆-C₁₀bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF₃;

C₆-C₁₀bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF₃;

C₆-C₁₀bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF₃; a group of the form



wherein R₇, R₈ and R₉ are independently of each other C₁-C₃alkyl or

C₁-C₃haloalkyl; and

R₈ and R₉ are independently of each other hydrogen, chloro or fluoro; or

- 10 -

l) X is oxygen or sulfur;

R₁ is CH₂F or CF₂H;

R₂ is C₁-C₃alkyl, C₁-C₃haloalkyl or C₁-C₃alkoxy-C₁-C₃alkyl;

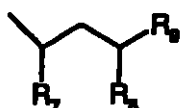
R₃ is hydrogen or fluoro;

Q is Q1;

R₄ is C₆-C₁₀bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF₃;

C₆-C₁₀bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF₃;

C₆-C₁₀bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF₃; a group of the form



wherein R₇, R₈ and R₉ are independently of each other C₁-C₃alkyl or

C₁-C₃haloalkyl; and

R₅ and R₆ are independently of each other hydrogen, chloro or fluoro; or

m) X is oxygen;

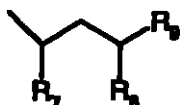
R₁ is CH₂F or CF₂H;

R₂ is methyl or CH₂OCH₃;

R₃ is hydrogen or fluoro;

Q is Q1;

R₄ is a group of the form



wherein R₇, R₈ and R₉ are independently of each other C₁-C₃alkyl or

C₁-C₃haloalkyl; and

R₅ and R₆ are independently of each other hydrogen, chloro or fluoro; or

n) X is oxygen or sulfur;

R₁ is CH₂F or CF₂H;

R₂ is C₁-C₃alkyl, C₁-C₃haloalkyl or C₁-C₃alkoxy-C₁-C₃alkyl;

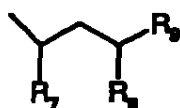
R₃ is hydrogen or fluoro;

Q is Q2, Q3 or Q4;

R₄ is C₆-C₁₀bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF₃;

C₆-C₁₀bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF₃;

C₆-C₁₀bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF₃; a group of the form



wherein R₇, R₈ and R₉ are independently of each other C₁-C₃alkyl or

C₁-C₃haloalkyl; and

R₅ and R₆ are independently of each other hydrogen, chloro or fluoro; or

o) X is oxygen;

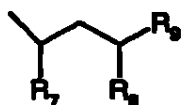
R₁ is CH₂F or CF₂H;

R₂ is methyl or CH₂OCH₃;

R₃ is hydrogen or fluoro;

Q is Q2, Q3 or Q4;

R₄ is a group of the form



wherein R₇, R₈ and R₉ are independently of each other C₁-C₃alkyl or

C₁-C₃haloalkyl; and

R₅ and R₆ are independently of each other hydrogen, chloro or fluoro.

Preferred individual compounds are :

1-methyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid [2-(1,3-dimethylbutyl)phenyl]amide;

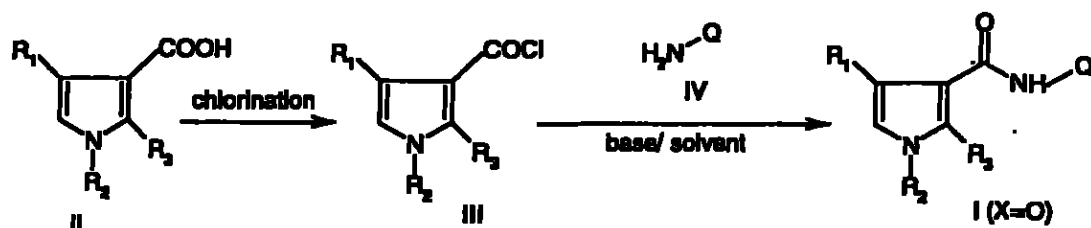
1-methoxymethyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid [2-(1,3-dimethylbutyl)phenyl]amide;

1-methyl-2-fluoro-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid [2-(1,3-dimethylbutyl)phenyl]amide;

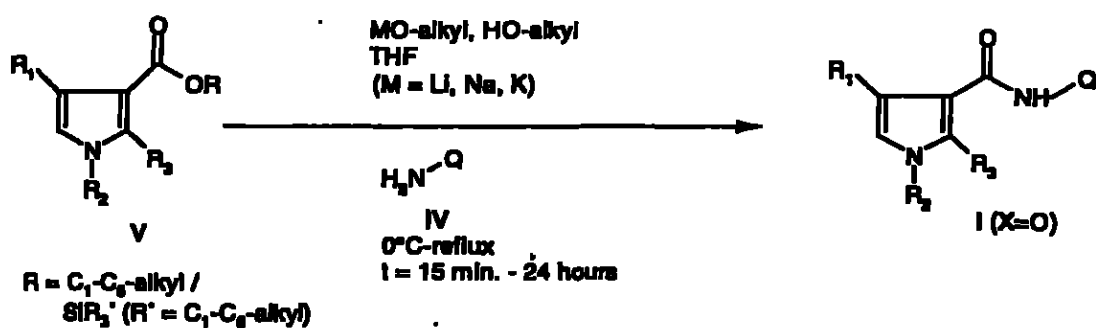
1-methoxymethyl-2-fluoro-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid [2-(1,3-dimethylbutyl)phenyl]amide;

1-methyl-4-trifluoromethyl-1H-pyrrole-3-carbothioic acid [2-(1,3-dimethylbutyl)phenyl] amide.

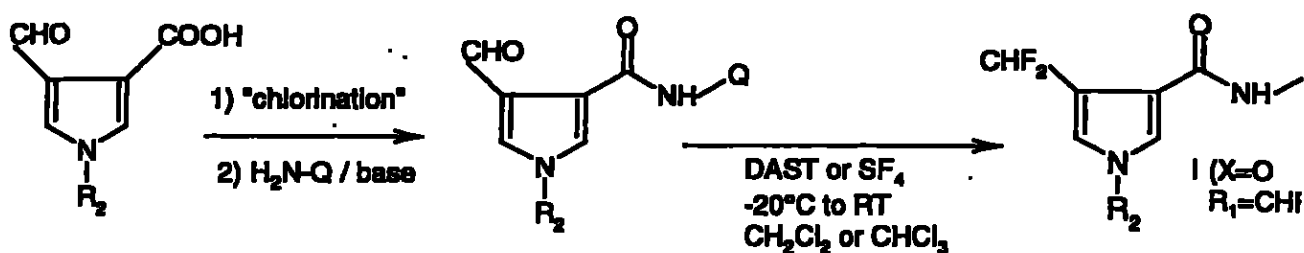
The compounds according to formula I wherein X is oxygen may be prepared according to the following reaction Scheme 1A.

Scheme 1A

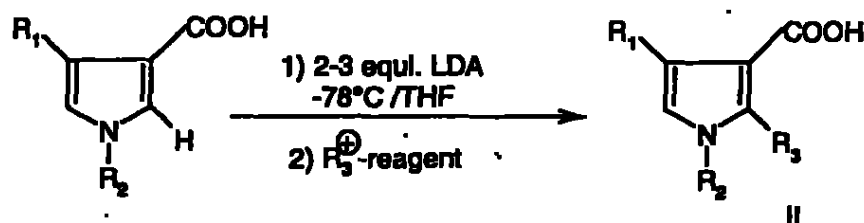
The compounds of the formula I wherein X is oxygen may also be prepared from the corresponding esters according to reaction Scheme 1B.

Scheme 1B

A further method for the synthesis of compounds of the formula I is outlined in Scheme 1C.

Scheme 1C

The synthesis of the pyrrole carboxylic acids of formula II wherein R_3 is not hydrogen may be conducted according to Scheme 2A.

Scheme 2A

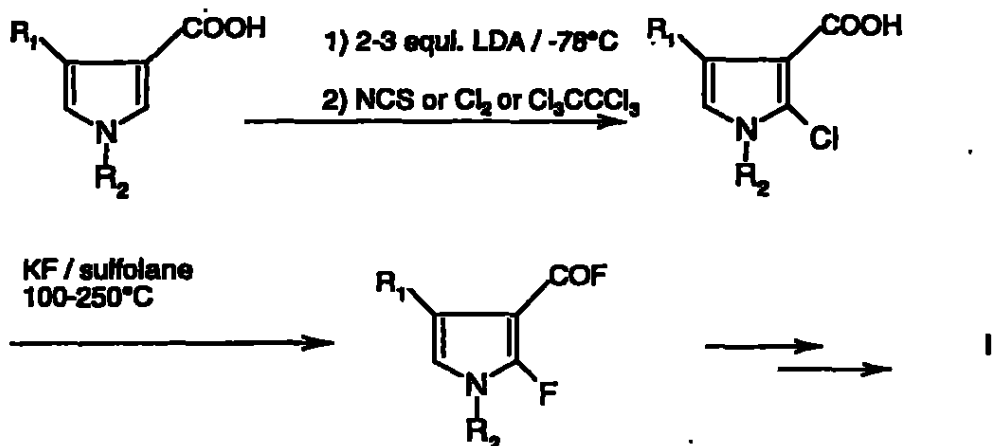
R_3^+ -reagents : P^+ = N-fluoro-bis(phenylsulfonyl)amine, N-fluoro-N-methyl-toluene-4-sulfonamide,
2-fluoro-3,3-dimethyl-2,3-dihydro-1,2-benzisothiazole-1,1-dioxide,
1-fluoro-sym.-collidiniumtetrafluoroborate

M^+ = MeI, MeBr, DMS (dimethylsulfate)
 Cl^+ = NCS, Cl_2 , hexachloroethane

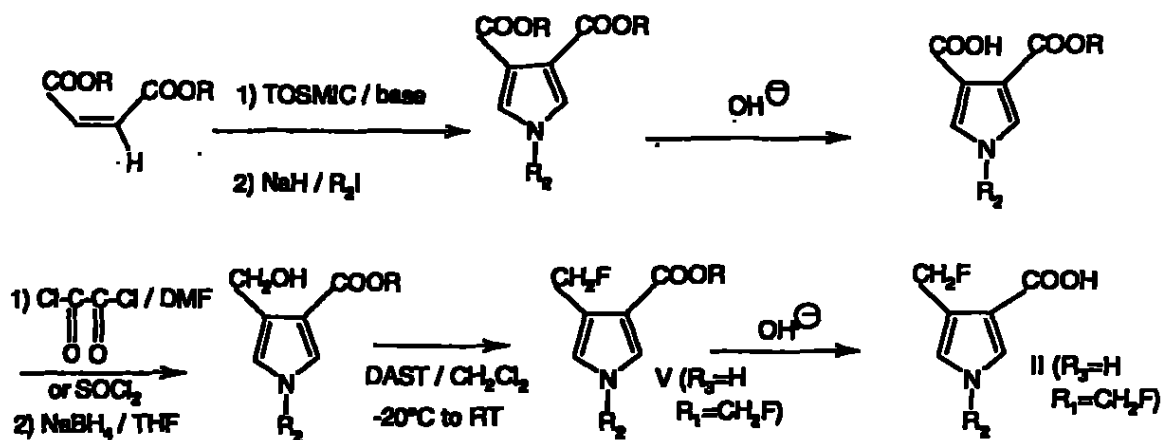
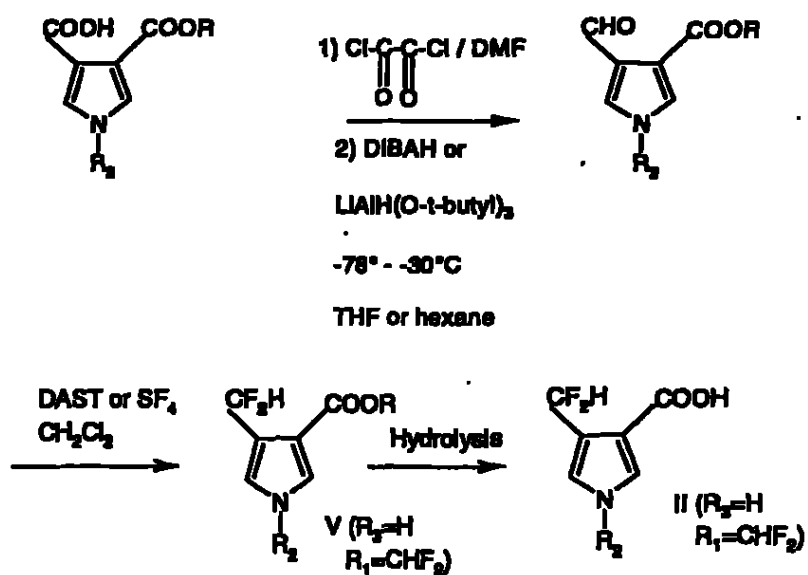
LDA = lithiumdiisopropylamide

The synthesis of the pyrrole carboxylic acids of formula II wherein $R_3 = H$ is described in WO-00/09482.

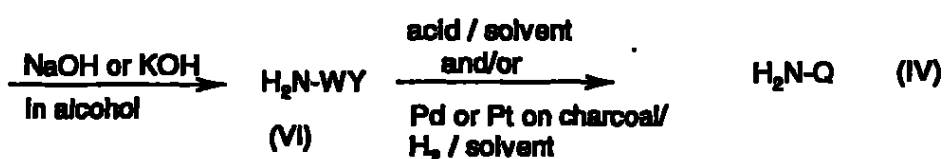
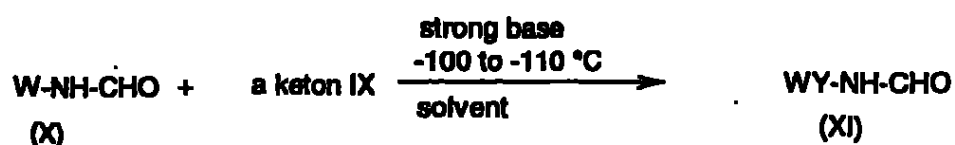
Alternatively the pyrrole carboxylic acid fluorides wherein R_3 is fluoro may be obtained as outlined in Scheme 2B.

Scheme 2B

The synthesis of the pyrrole carboxylic acids II may also be conducted according to the Schemes 2C or 2D.

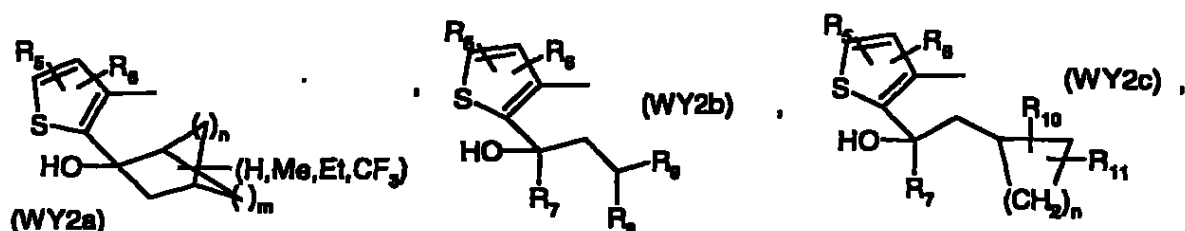
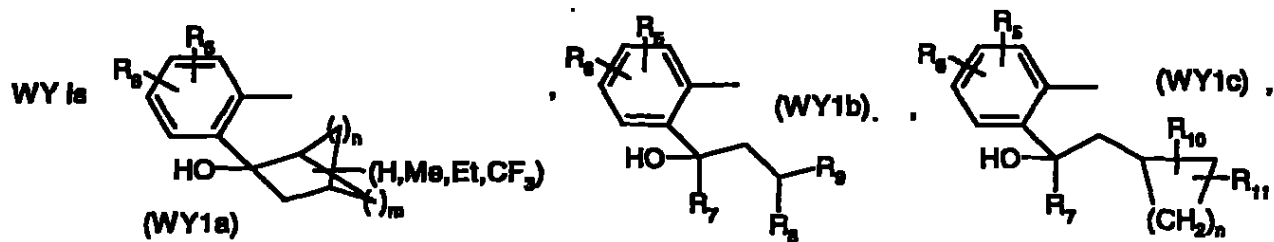
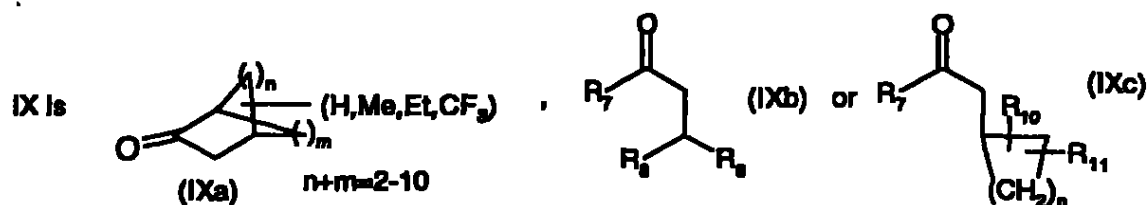
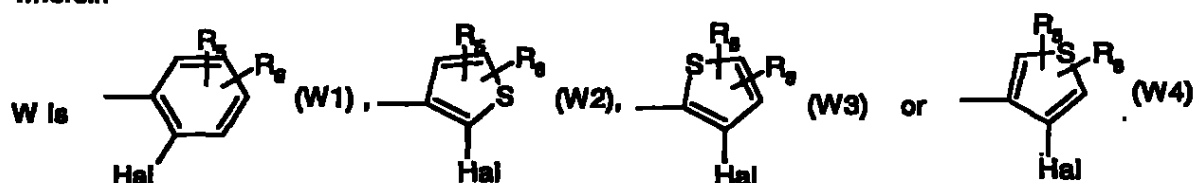
Scheme 2C**Scheme 2D**

The amine Intermediates NH₂-Q of formula IV may be prepared according to the following reactions as outlined in Scheme 3.

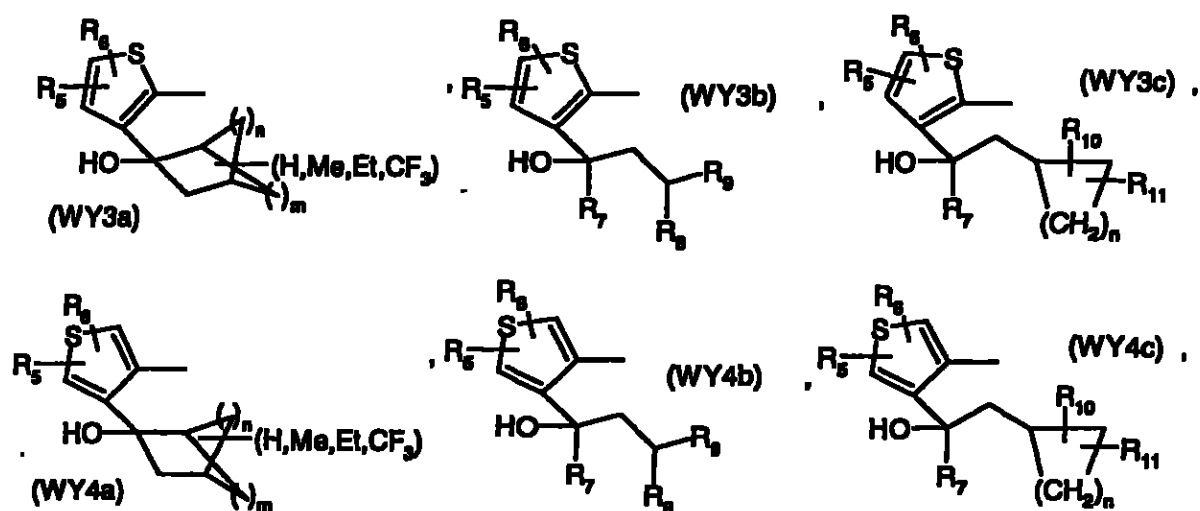
Scheme 3**Route a)**

wherein Q, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁ and n are as described for the compounds of formula I, Hal is Br or I; strong base is n-BuLi, sec-BuLi, tert-BuLi, PhLi; and

wherein

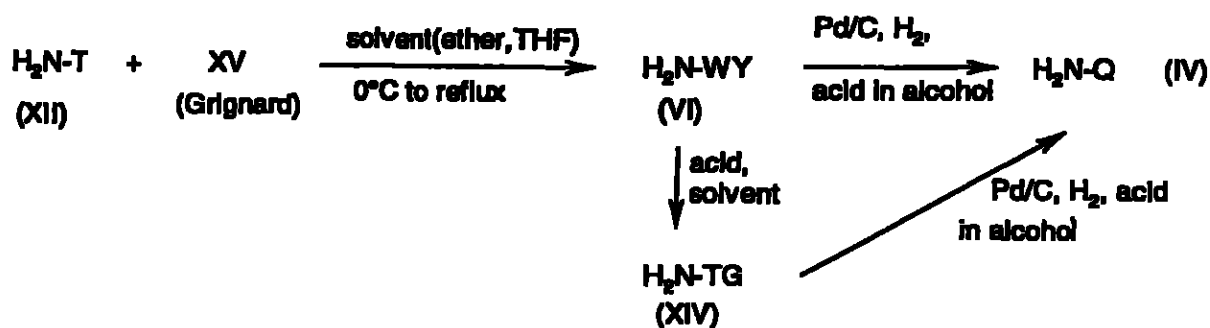


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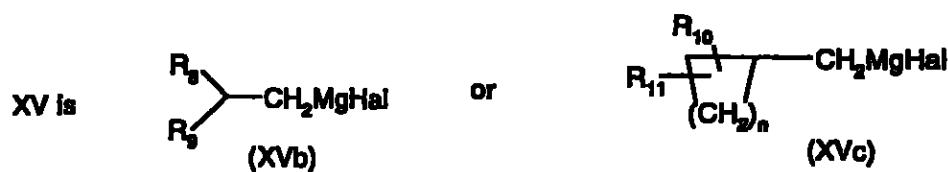
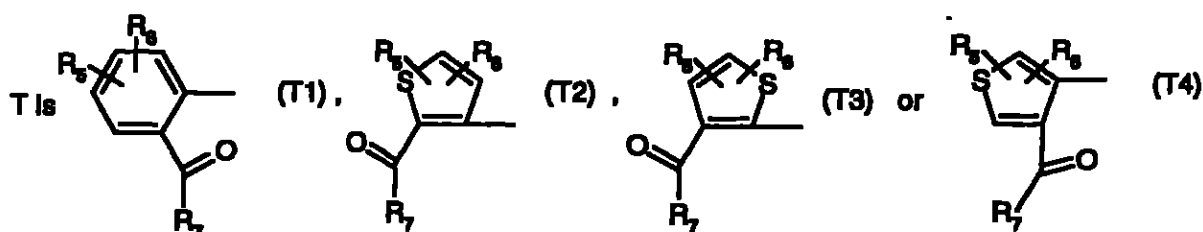
and $n+m=2-10$

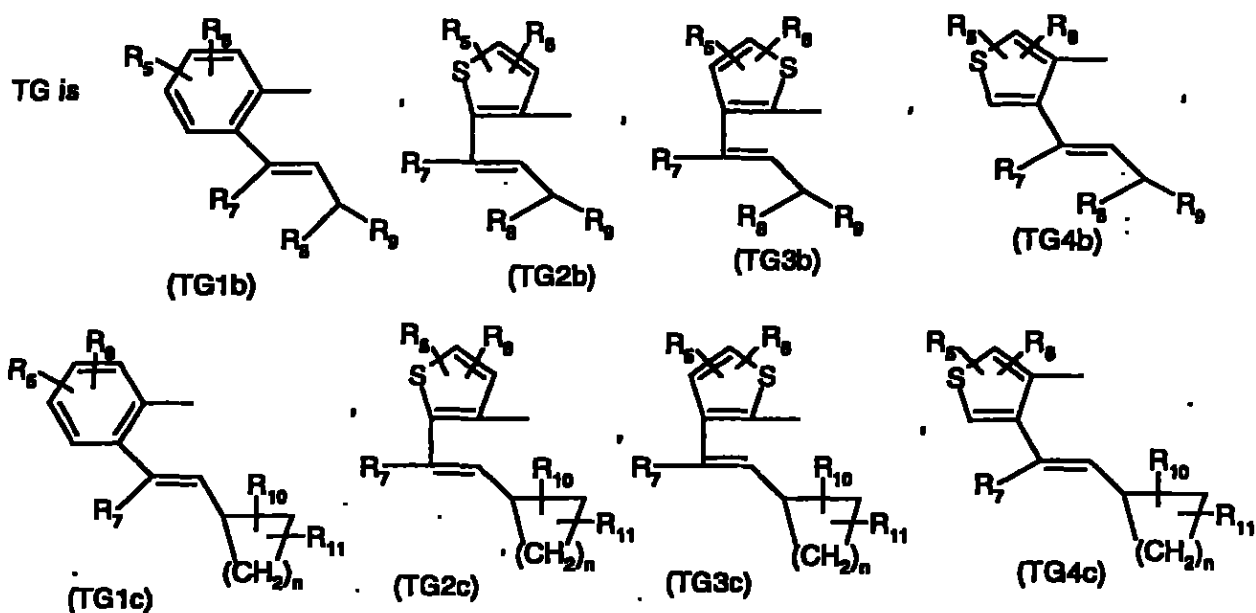
or

Route b)



wherein

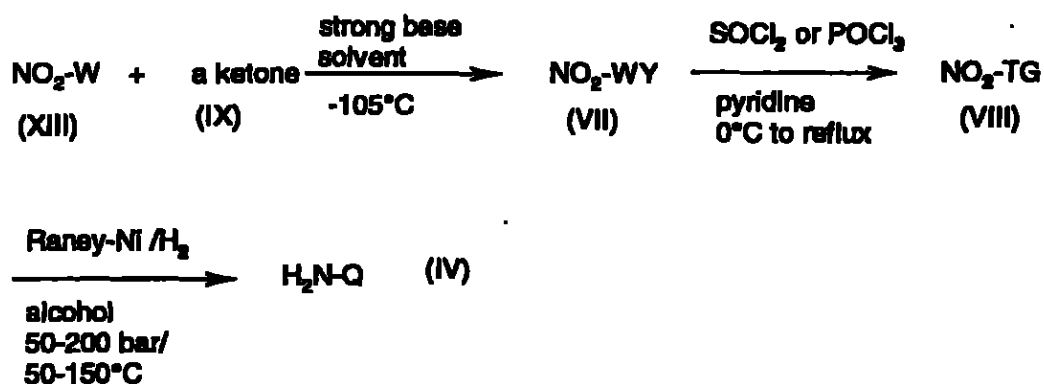




and wherein isomeric mixtures are possible at the double bond

or

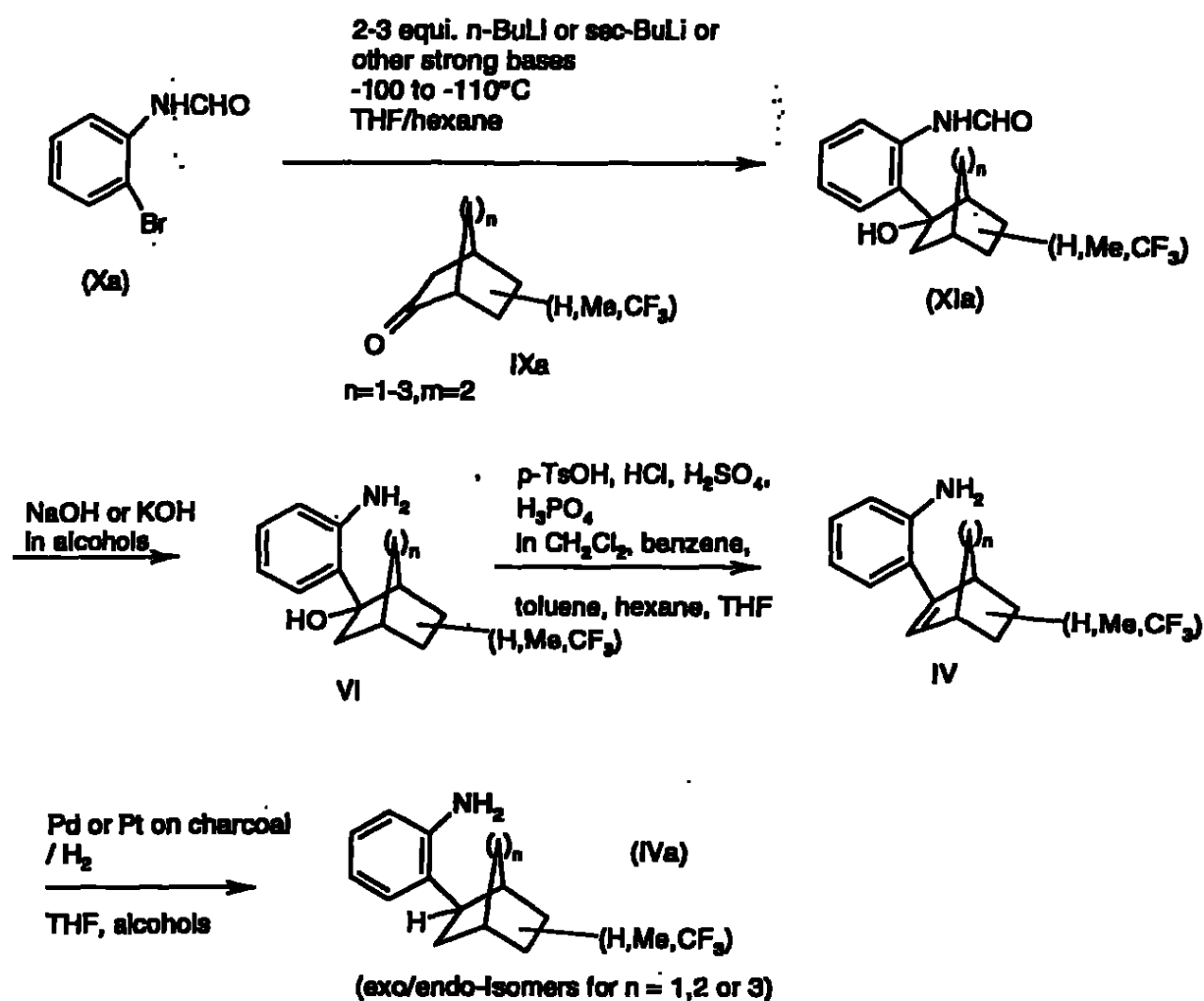
Route c)



Specific amines of the formula IV can be prepared as follows:

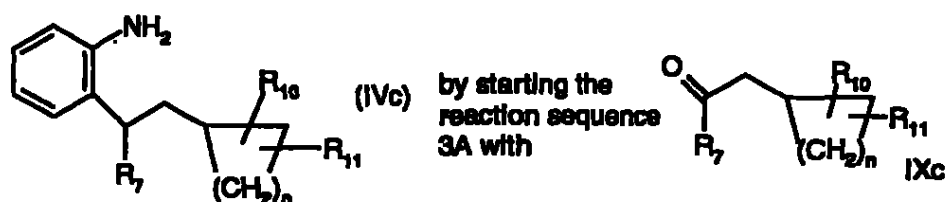
-- The amines $\text{H}_2\text{N-Q}$ of formula IV, wherein $\text{Q} = \text{Q1}$ as defined in formula I and R_4 is bicycloalkyl, bicycloalkenyl or bicycloalkadienyl and R_5 and R_6 are hydrogen may be obtained according to Scheme 3A (Route a).

Scheme 3A



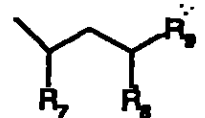
For the synthesis of 2-bicyclo[2.2.1]hept-2-yl phenylamine and other bicyclic systems see for example EP-116044.

According to Scheme 3A the following compounds are also available :



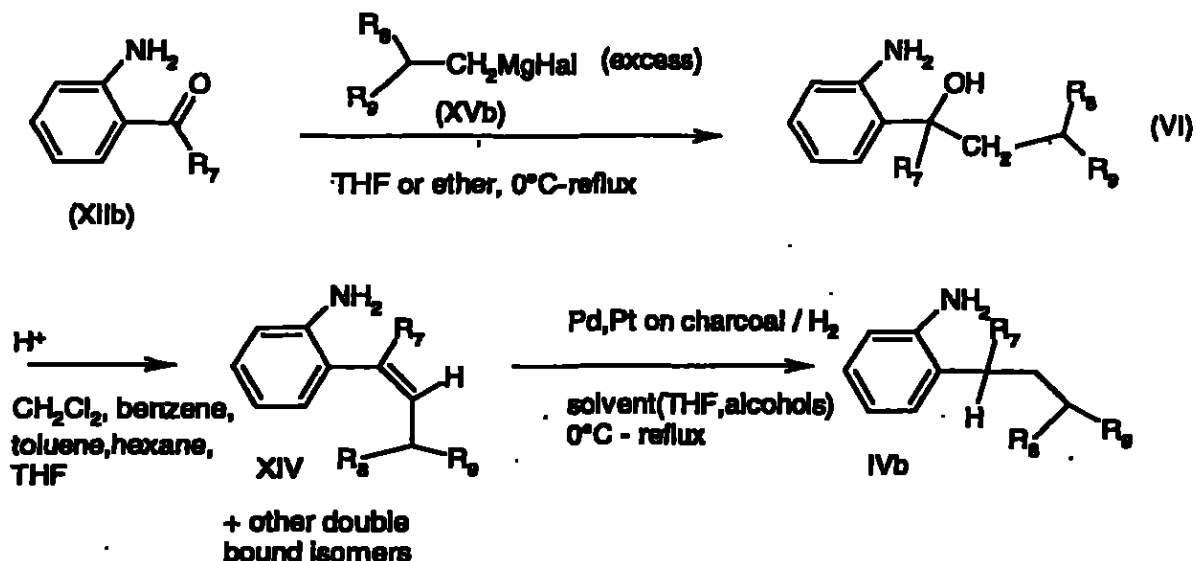
wherein *R*₅ and *R*₆ are hydrogen and *R*₇, *R*₁₀, *R*₁₁ and *n* are as defined for formula I.

-- The amines H_2N-Q wherein Q is Q1 and R_4 is a group of the form



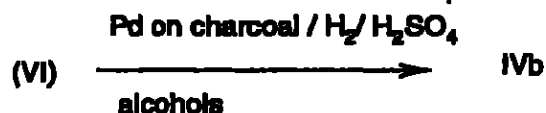
R_5 and R_6 are hydrogen and R_7 , R_8 and R_9 are as defined for formula I may be obtained according to Scheme 3B (Route b).

Scheme 3B



(other syntheses of ortho-alkylsubstituted anilines are also described in EP-824099)

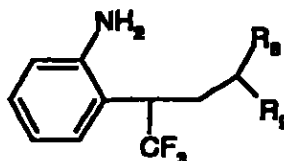
or in a one step hydrogenation of the OH-group of compounds of formula VI



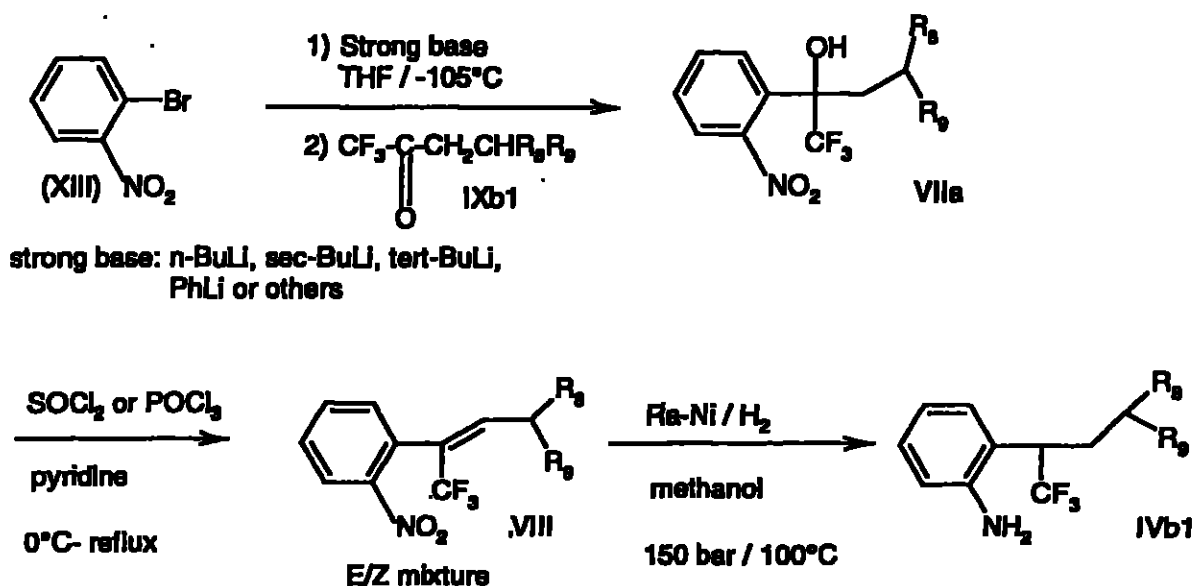
— Another synthesis of the amine intermediates is outlined in Scheme 3C (Route c).

Scheme 3C

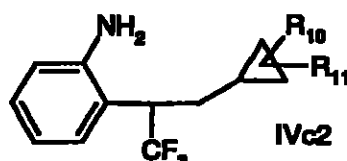
for compounds of formula IVb1



wherein R_7 is CF_3 , R_6 and R_8 are hydrogen and R_5 and R_9 are as defined for formula I

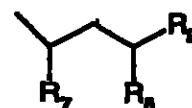


Using the reaction sequence outlined in Scheme 3C the compounds of formula IVc2 wherein R₈ and R₉ are hydrogen, R₇ is CF₃, n=1 and R₁₀ and R₁₁ are as defined for formula I are also available



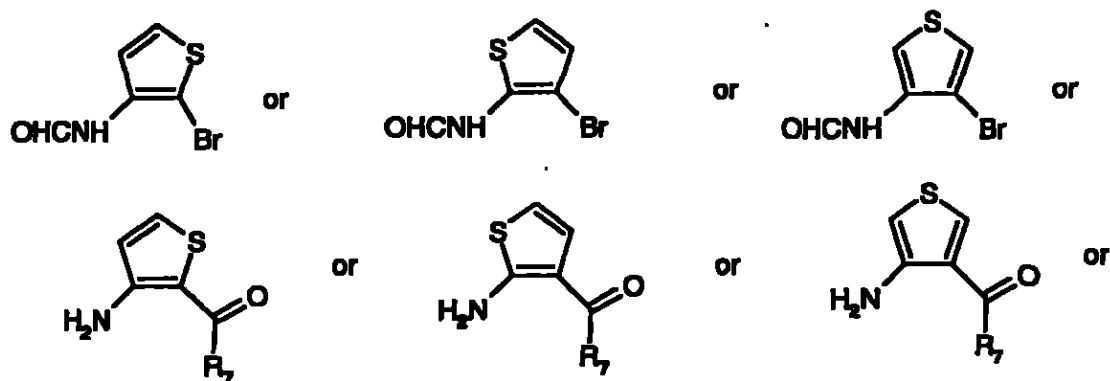
-- The synthesis of the amines IV wherein Q is Q2, Q3 or Q4, R₅ and R₆ are hydrogen and

R₄ is bicycloalkyl, bicycloalkenyl, bicycloalkadienyl or a group of the form

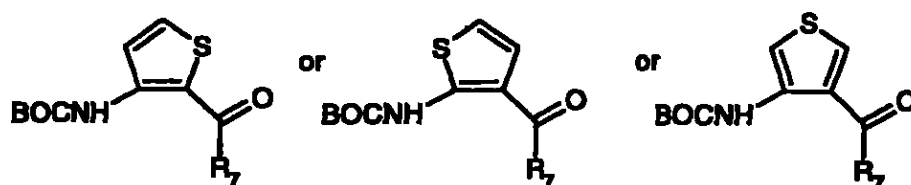


and wherein R₇, R₈ and R₉ are as defined for formula I may be obtained according to scheme 3A) or 3B) starting from the following corresponding thienyl derivatives

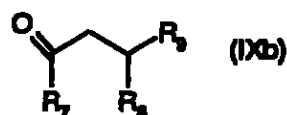
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(protected aminothiophenes)

BOC = $-\text{C}(\text{O})\text{OC}(\text{CH}_3)_3$

and reacting either with the ketone IXa or IXb

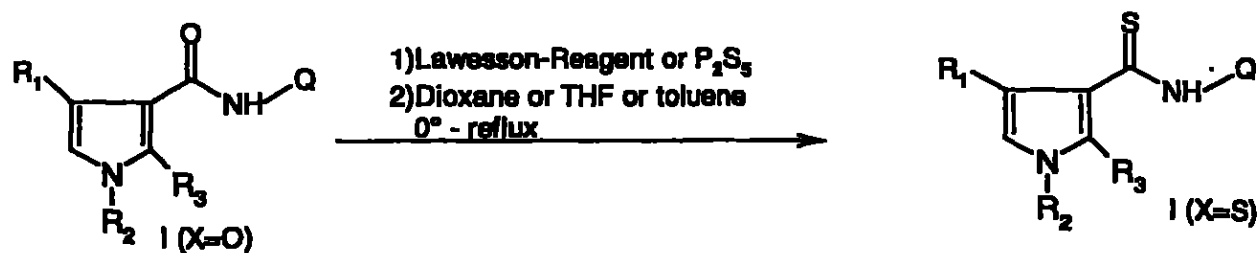


or the Grignard-reagent XVb



The present invention also relates to novel ketones of formula IX.

The carbothioic acid amides of formula I, wherein X=S may be obtained from the compounds of formula I wherein X=O according to Scheme 4.

Scheme 4

The following phenylamine derivatives of formula IV are new and part of the invention :

2-bicyclo[2.2.2]oct-2-yl-phenylamine;
2-bicyclo[2.2.2]oct-2-en-2-yl-phenylamine;
2-bicyclo[2.2.2]octa-2,5-dien-2-yl-phenylamine;
2-(2-aminophenyl)-1,1,1-trifluoromethyl-4-methyl-pentan-2-ol;
2-(2-aminophenyl)-1-cyclopropyl-propan-2-ol;
2-(2-aminophenyl)-1-cyclopropyl-butan-2-ol;
2-(3-methyl-1-trifluoromethyl-but-1-enyl)-phenylamine;
2-(3-methyl-1-trifluoromethyl-butyl)phenylamine;
2-(2-cyclopropyl-1-methyl-ethyl)phenylamine; and
2-(1-cyclopropylmethyl-propyl)phenylamine.

Surprisingly, it has now been found that the novel compounds of formula I have, for practical purposes, a very advantageous spectrum of activities for protecting plants against diseases that are caused by fungi as well as by bacteria and viruses.

The compounds of formula I can be used in the agricultural sector and related fields of use as active ingredients for controlling plant pests. The novel compounds are distinguished by excellent activity at low rates of application, by being well tolerated by plants and by being environmentally safe. They have very useful curative, preventive and systemic properties and are used for protecting numerous cultivated plants. The compounds of formula I can be used to inhibit or destroy the pests that occur on plants or parts of plants (fruit, blossoms, leaves, stems, tubers, roots) of different crops of useful plants, while at the same time protecting also those parts of the plants that grow later e.g. from phytopathogenic micro-organisms.

It is also possible to use compounds of formula I as dressing agents for the treatment of plant propagation material, in particular of seeds (fruit, tubers, grains) and plant cuttings (e.g. rice), for the protection against fungal infections as well as against phytopathogenic fungi occurring in the soil.

The compounds I are, for example, effective against the phytopathogenic fungi of the following classes: Fungi imperfecti (e.g. Botrytis, Pyricularia, Helminthosporium, Fusarium, Septoria, Cercospora and Alternaria) and Basidiomycetes (e.g. Rhizoctonia, Hemileia, Puccinia). Additionally, they are also effective against the Ascomycetes classes (e.g. Ven-

turia and Erysiphe, Podosphaera, Monilinia, Uncinula) and of the Oomycetes classes (e.g. Phytophthora, Pythium, Plasmopara). Outstanding activity has been observed against powdery mildew (Erysiphe spp.). Furthermore, the novel compounds of formula I are effective against phytopathogenic bacteria and viruses (e.g. against Xanthomonas spp, Pseudomonas spp, Erwinia amylovora as well as against the tobacco mosaic virus).

Within the scope of present invention, target crops to be protected typically comprise the following species of plants: cereal (wheat, barley, rye, oat, rice, maize, sorghum and related species); beet (sugar beet and fodder beet); pomes, drupes and soft fruit (apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries and blackberries); leguminous plants (beans, lentils, peas, soybeans); oil plants (rape, mustard, poppy, olives, sunflowers, coconut, castor oil plants, cocoa beans, groundnuts); cucumber plants (pumpkins, cucumbers, melons); fibre plants (cotton, flax, hemp, jute); citrus fruit (oranges, lemons, grapefruit, mandarins); vegetables (spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, paprika); lauraceae (avocado, cinnamomum, camphor) or plants such as tobacco, nuts, coffee, eggplants, sugar cane, tea, pepper, vines, hops, bananas and natural rubber plants, as well as ornamentals.

The compounds of formula I are used in unmodified form or, preferably, together with the adjuvants conventionally employed in the art of formulation. To this end they are conveniently formulated in known manner to emulsifiable concentrates, coatable pastes, directly sprayable or dilutable solutions, 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, atomizing, dusting, scattering, coating or pouring, are 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 can be solid or liquid and are substances useful in formulation technology, e.g. natural or regenerated mineral substances, solvents, dispersants, 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 the growth of plants. They can also be 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 compounds of formula I can be mixed with other fungicides, resulting in some cases in unexpected synergistic activities.

Mixing components which are particularly preferred are azoles such as azaconazole, blitertanol, propiconazole, difenoconazole, diniconazole, cyproconazole, epoxiconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazalil, imibenconazole, ipconazole, tebuconazole, tetraconazole, fenbuconazole, metconazole, myclobutanil, perfurazoate, penconazole, bromuconazole, pyrifenoxy, prochloraz, triadimefon, triadimenol, triflumizole or triticonazole; pyrimidinyl carbinoles such as ancymidol, fenarimol or nuarimol; 2-amino-pyrimidine such as bupirimate, dimethirimol or ethirimol; morpholines such as dodemorph, fenpropidin, fenpropimorph, spiroxamin or tridemorph; anilinopyrimidines such as cyprodinil, pyrimethanil or mepanipyrim; pyrroles such as fenpiclonil or fludioxonil; phenylamides such as benalaxyl, furalaxyl, metalaxyl, R-metalaxyl, ofurace or oxadixyl; benzimidazoles such as benomyl, carbendazim, debacarb, fuberidazole or thiaabendazole; dicarboximides such as chlozolinate, dichlozoline, iprodione, myclozoline, procymidone or vinclozolin; carboxamides such as carboxin, fenfuram, flutolanil, mepronil, oxycarboxin or thifluzamide; guanidines such as guazatine, dodine or iminoctadine; strobilurines such as azoxystrobin, kresoxim-methyl, metominostrobin, SSF-129, methyl 2-[(2-trifluoromethyl)-pyrid-6-yloxy-methyl]-3-methoxyacrylate or 2-[α [(α -methyl-3-trifluoromethyl-benzyl)imino]-oxy]-o-tolyl-glyoxylic acid-methylester-O-methyloxime (trifloxystrobin); dithiocarbamates such as ferbam, mancozeb, maneb, metiram, propineb, thiram, zineb or ziram; N-halomethylthio-dicarboximides such as captan, captan, dichlofluanid, fluoromide, folpet or tolyfluanid; copper compounds such as Bordeaux mixture, copper hydroxide, copper oxychloride, copper sulfate, cuprous oxide, mancozeb or oxine-copper; nitrophenol derivatives such as dinocap or nitrothal-isopropyl; organo phosphorous derivatives such as edifenphos, lprobenphos, isoprothiolane, phosdiphen, pyrazophos or toclofos-methyl; and other compounds of diverse structures such as acibenzolar-S-methyl, anilazine, blastidil-S,

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chinomethionat, chloroneb, chlorothalonil, cymoxanil, dichlone, diclomezine, dicloran, diehofencarb, dimethomorph, dithianon, etridiazole, famoxadone, fenamidone, fentin, ferimzone, fluazinam, flusulfamide, fenhexamid, fosetyl-aluminium, hymexazol, kasugamycin, methasulfocarb, pencycuron, phthalide, polyoxins, probenazole, propamocarb, pyroquilon, quinoxifen, quintozone, sulfur, triazoxide, tricyclazole, triforine, validamycin, (S)-5-methyl-2-methylthio-5-phenyl-3-phenyl-amino-3,5-dihydroimidazol-4-one (RPA 407213), 3,5-dichloro-N-(3-chloro-1-ethyl-1-methyl-2-oxopropyl)-4-methylbenzamide (RH-7281), N-allyl-4,5-dimethyl-2-trimethylsilylthiophene-3-carboxamide (MON 65500), 4-chloro-4-cyano-N,N-dimethyl-5-p-tolylimidazole-1-sulfonamide (IKF-916), N-(1-cyano-1,2-dimethylpropyl)-2-(2,4-dichlorophenoxy)-propionamide (AC 382042), or Iprovalcarb (SZX 722).

A preferred method of applying a compound of formula I, or an agrochemical composition which contains at least one of said compounds, is foliar application. The frequency of application and the rate of application will depend on the risk of infestation by the corresponding pathogen. However, the compounds of formula I can also penetrate the plant through the roots via the soil (systemic action) by drenching the locus of the plant with a liquid formulation, or by applying the compounds in solid form to the soil, e.g. in granular form (soil application). In crops of water rice such granulates can be applied to the flooded rice field. The compounds of formula I may also be applied to seeds (coating) by impregnating the seeds or tubers either with a liquid formulation of the fungicide or coating them with a solid formulation.

The formulation, i.e. the compositions containing the compound of formula I and, if desired, a solid or liquid adjuvant, are prepared in known manner, typically by intimately mixing and/or grinding the compound with extenders, e.g. solvents, solid carriers and, optionally, surface active compounds (surfactants).

The agrochemical formulations will usually contain from 0.1 to 99 % by weight, preferably from 0.1 to 95 % by weight, of the compound of formula I, 99.9 to 1 % by weight, preferably 99.8 to 5 % by weight, of a solid or liquid adjuvant, and from 0 to 25 % by weight, preferably from 0.1 to 25 % by weight, of a surfactant.

Advantageous rates of application are normally from 5 g to 2 kg of active ingredient (a.i.) per hectare (ha), preferably from 10 g to 1 kg a.i./ha, most preferably from 20 g to 600 g

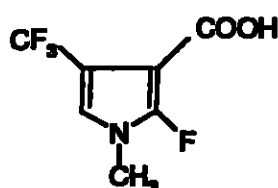
a.i./ha. When used as seed drenching agent, convenient dosages are from 10 mg to 1 g of active substance per kg of seeds.

Whereas it is preferred to formulate commercial products as concentrates, the end user will normally use dilute formulations.

The following non-limiting examples illustrate the above-described invention in more detail. Temperatures are given in degrees Celsius. The following abbreviations are used: m.p.= melting point; b.p.= boiling point. "NMR" means nuclear magnetic resonance spectrum. MS stands for mass spectrum. "%" is percent by weight, unless corresponding concentrations are indicated in other units.

Example 1

2-Fluoro-1-methyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid

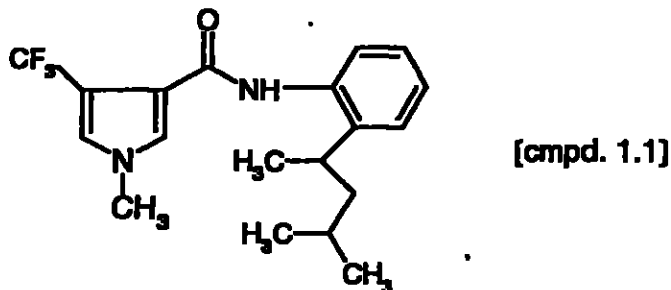


A solution of 1.25g (11mmol) lithiumdiisopropylamide (LDA) in 95% in 20ml absolute THF is dropwise added to a solution of 1.0g (5.2mmol) 1-methyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid in 60ml THF in such a manner that the temperature remains constant at -75°C. After 3 hours stirring at -75°C, a solution of 1.95g (6.2mmol) N-fluoro-bis(phenylsulfonyl)amine in 20ml absolute THF is added in ca. 30 minutes at a constant temperature of -75°C. Then the cooling is stopped and the reaction mixture is stirred for 16 hours, thereby slowly warming up to room temperature. Then the solvent is removed in a water jet vacuum and the residue is solved in water. After addition of 1N hydrochloric acid (pH = 1) ethylacetate is added and the organic phase extracted twice with additional water. After separation of the organic phase, drying over sodium sulfate and evaporation of the solvent in a water jet vacuum the raw material is obtained. The crude product is purified by column chromatography over silica-gel (eluant : hexane/ethylacetate = 1:1). Yield : 0.65g 2-Fluoro-1-methyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid in the form of white crystals; m.p. : 190-191°C.

2-Chloro-1-methyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid can be obtained in analogous manner using for example N-chlorosuccinimide as halogenation agent in the reaction described above, m.p. 197-198°C.

Example 2

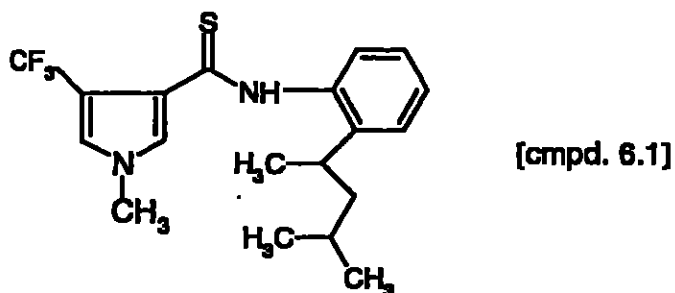
1-Methyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid[2-(1,3-dimethylbutyl)phenyl]amide



A solution of 0.5g (2.6mmol) 1-methyl-4-trifluoromethylpyrrole-3-carboxylic acid and 0.37g (2.85mmol) oxalylchloride in 20ml methylene chloride is stirred for 3 hours at room temperature in the presence of a catalytic amount of DMF. Then the acid chloride solution is slowly added to a solution of 0.46g (2.6mmol) 2-(1,3-dimethylbutyl)phenylamine, 0.33g (3.4mmol) triethylamine and 15ml methylene chloride. The resulting mixture is then stirred for 16 hours at room temperature. After removal of the solvent in a water jet vacuum, the raw material is taken up in ethylacetate. The ethylacetate phase is washed twice with water and then the organic phase is dried over sodium sulfate. After evaporation of the solvent in a water jet vacuum, the obtained residue is purified by column chromatography over silica-gel (eluant: hexane/ethylacetate = 3:1). Yield: 0.45g 1-Methyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid[2-(1,3-dimethylbutyl)phenyl]amide in the form of brownish crystals; m.p. : 83-85°C.

Example 3

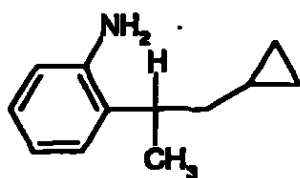
1-Methyl-4-trifluoromethyl-1H-pyrrole-3-carbothioic acid[2-(1,3-dimethylbutyl)phenyl]amide



In a sulfonation flask a mixture of 0.6 g 1-Methyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid[2-(1,3-dimethylbutyl)phenyl]amide, 0.45 g P_2S_5 and 30 ml dioxane is heated at 70-75°C for 3 hours. After filtration, the solvent is removed in a water jet vacuum and the residue taken up in ethylacetate. The organic phase is washed twice with water and ethylacetate is removed in a water jet vacuum. The crude material is purified by column chromatography over silica gel (eluant: ethylacetate/n-hexane = 1:1). Yield: 0.53 g 1-Methyl-4-trifluoromethyl-1H-pyrrole-3-carbothioic acid[2-(1,3-dimethylbutyl)phenyl]amide in the form of a reddish resin (^1H -NMR).

Example 4 (amine intermediate)

2-(2-cyclopropyl-1-methyl-ethyl)phenylamine

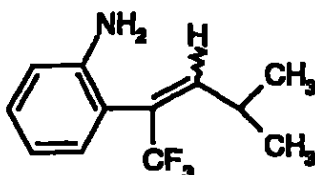


[compd. 7.6]

To a solution of 2.96 g (15.5 mmol) of 2-(2-aminophenyl)-1-cyclopropyl-propan-2-ol in 70 ml methanol is added 4.43 g (43.4 mmol) conc. sulfuric acid (98%). The resulting mixture is hydrogenated over 600 mg Pd/C(10%) for 20 hours at 30-35°C. After that time no more hydrogen uptake is detected. The catalyst is filtered off and the solvent removed in a water-jet vacuum. The residue is taken up in ethylacetate/water and the water phase is neutralised by the addition of sodium carbonate. The water phase is extracted twice with ethylacetate, then the combined organic phase is dried over sodium sulfate. After removal of the solvent in a water-jet vacuum, the crude amine is obtained. The obtained raw material is purified by column chromatography over silica gel (eluant: hexane/ether = 5:1). Yield: 2.1 g 2-(2-cyclopropyl-1-methyl-ethyl)phenylamine in the form of a brown oil (^1H -NMR).

Example 5 (amine intermediate)

2-(3-methyl-1-trifluoromethyl-but-1-enyl)phenylamine, E/Z-isomeric mixture

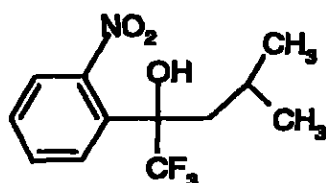


[compd. 7.4]

A solution of 1.14 g (4.4 mmol) 1-(3-methyl-1-trifluoromethyl-but-1-enyl)-2-nitrobenzene in 20 ml methanol is hydrogenated over 10% Pd/C (230 mg) at room temperature for 20 minutes. Then the catalyst is filtered off and the solvent removed in a water-jet vacuum. The crude product is purified by column chromatography over silica gel (eluant: methylenechloride/hexane = 2:1). Yield: 0.6 g ((sum E + Z isomer) 2-(3-methyl-1-trifluoromethyl-but-1-enyl)phenylamine in the form of a brown oil. After column chromatography both isomers are obtained in pure form (¹H-NMR).

Example 6

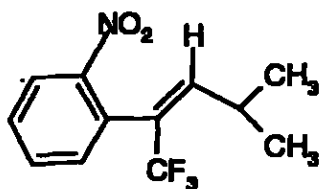
1,1,1-trifluoromethyl-4-methyl-2-(2-nitrophenyl)pentan-2-ol



To a solution of 20.2 g (0.1 mol) 2-bromonitrobenzene in 300 ml abs. tetrahydrofuran is added 81 ml of sec. BuLi (0.105 mol) over a period of 30 minutes in such a manner that the internal temperature remains constant at -103 to -107°C. After stirring for 70 minutes at -103 to -107°C a solution of 20.0 g (0.13 mol) of trifluoromethylisobutylketone in 150 ml abs. tetrahydrofuran is added over a period of 20 minutes in such a manner that the temperature remains constant at -105°C (± 2°C). After stirring for 4 hours at -105°C the temperature is raised to -20°C and a solution of 150 ml of saturated ammoniumchloride solution is added. Then 1 l of ethylacetate is added and the organic phase is washed 3 times with water. After drying the organic phase over sodium sulfate and distilling off the solvent in a water-jet vacuum the raw-material is obtained. Purification is achieved by column chromatography over silica gel (eluant: hexane/ethylacetate = 5:1). Yield: 8.2 g 1,1,1-trifluoromethyl-4-methyl-2-(2-nitrophenyl)pentan-2-ol in the form of a brownish powder, m.p.: 103-105°C.

Example 7

1-(3-methyl-1-trifluoromethyl-but-1-enyl)-2-nitrobenzene (E/Z-mixture)

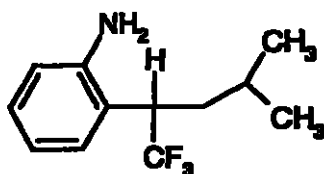


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To a solution of 10.8 g (39 mmol) 1,1,1-trifluoromethyl-4-methyl-2-(2-nitrophenyl)pentan-2-ol in 110 ml of abs. pyridine is added slowly 13.9 g (117 mmol) thionylchloride at a temperature of 0-5°C. Then the mixture is heated at 90-95°C for 1 hour. After cooling the reaction mixture is added to ice water. The resulting solution is extracted carefully with ethylacetate and after drying of the organic phase over sodium sulfate and distilling off the solvent in a water-jet vacuum, the crude product is obtained. Purification is achieved by column chromatography over silica gel (eluant: methylene chloride/hexane = 1:1). Yield: 5.2 g 1-(3-methyl-1-trifluoromethyl-but-1-enyl)-2-nitrobenzene in the form of a brownish oil (¹H-NMR).

Example 8 (amine intermediate)

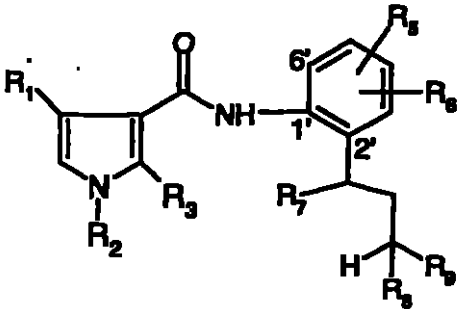
2-(3-methyl-1-trifluoromethyl-butyl)phenylamine



[compd. 7.5]

A solution of 2.98 g (12.9 mmol) 1-(3-methyl-1-trifluoromethyl-but-1-enyl)-2-nitrobenzene in 30 ml methanol is hydrogenated over Raney-Nickel (ethanol) at 100°C and 150 bar for 10 hours. Then the catalyst is filtered off and the solvent removed in a water-jet vacuum. The obtained crude product is purified by column chromatography over silica gel (eluant: hexane/methylene chloride = 1:2). Yield: 1.9 g 2-(3-methyl-1-trifluoromethyl-butyl)phenylamine in the form of a brown oil (¹H-NMR).

Table 1

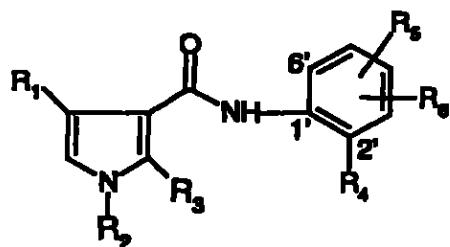


1a (md = mixture of diastereoisomers)

Cmpd. no.	R ₁	R ₂	R ₃	R ₅	R	R ₇	R ₈	R ₉	phys. data m.p.°C
1.1	CF ₃	Me	H	H	H	Me	Me	Me	83-85
1.2	CF ₃	CH ₂ OMe	H	H	H	Me	Me	Me	75-77
1.3	CF ₃	Me	H	H	H	CF ₃	Me	Me	98-100
1.4	CF ₃	Me	H	H	H	Me	CF ₃	CF ₃	
1.5	CF ₃	Me	H	H	H	Me	Me	Et	93-97 (md)
1.6	CF ₃	CH ₂ OMe	H	H	H	Me	Me	Et	
1.7	CF ₃	Me	H	6'-F	H	Me	Me	Me	
1.8	CF ₃	Me	H	5'-F	H	Me	Me	Me	
1.9	CF ₃	Me	H	H	H	Me	Et	Et	84-86
1.10	CF ₃	Me	F	H	H	Me	Me	Me	
1.11	CF ₃	CH ₂ OMe	F	H	H	Me	Me	Me	
1.12	CF ₃	Me	F	H	H	Me	Me	Et	resin; ¹ H-NMR, MS
1.13	CF ₃	Me	F	H	H	CF ₃	Me	Me	resin; ¹ H-NMR, MS
1.14	CF ₃	Me	F	H	H	CF ₃	Me	Et	
1.15	CF ₂ H	Me	H	H	H	Me	Me	Me	
1.16	CF ₂ H	Me	H	H	H	Me	Me	Et	
1.17	CF ₂ H	Me	H	H	H	CF ₃	Me	Me	Resin
1.18	CF ₂ H	Me	H	H	H	Me	CF ₃	CF ₃	
1.19	CF ₂ H	Me	H	H	H	CF ₂ H	Me	Me	
1.20	CF ₂ H	CH ₂ OMe	H	H	H	Me	Me	Me	

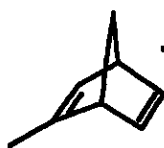
1.21	CF ₃ H	CH ₂ OMe	H	H	H	Me	Me	Et	
1.22	CF ₃ H	Me	F	H	H	Me	Me	Me	
1.23	CF ₃ H	Me	F	H	H	Me	Me	Et	
1.24	CFH ₂	Me	H	H	H	Me	Me	Me	
1.25	CFH ₂	Me	H	H	H	Me	Me	Et	
1.26	CFH ₂	Me	F	H	H	Me	Me	Me	
1.27	CFH ₂	Me	F	H	H	Me	Me	Et	
1.28	CF ₃	Me	H	H	H	Et	Me	Me	Resin; ¹ H-NMR, M ⁺ = 366
1.29	CF ₃	Me	H	H	H	Et	Me	Et	oil; M ⁺ = 380
1.30	CF ₃	Me	F	H	H	Et	Me	Me	
1.31	CF ₃	Me	F	H	H	Et	Me	Et	
1.32	CF ₃ H	Me	H	H	H	Et	Me	Me	
1.33	CF ₃ H	Me	H	H	H	Et	Me	Et	
1.34	CF ₃ H	Me	F	H	H	Et	Me	Me	
1.35	CFH ₂	Me	H	H	H	Et	Me	Me	

Table 2

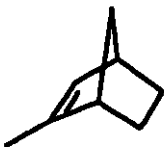
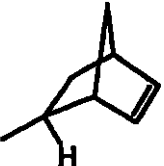
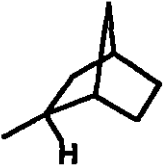
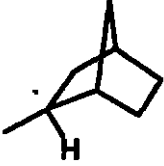
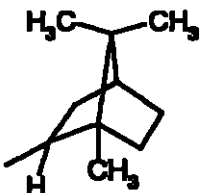
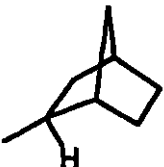
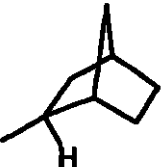


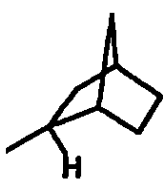
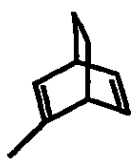
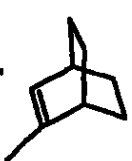
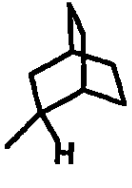
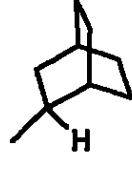
1b

Cmpd. no.	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	Phys.data m.p.°C
2.1	CF ₃	Me	H		H	H	



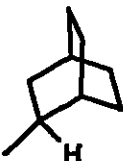
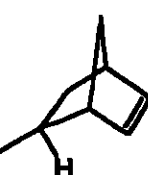
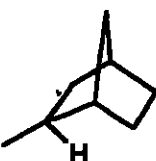
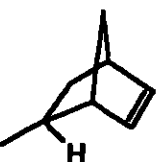
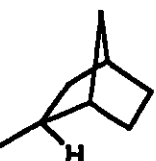
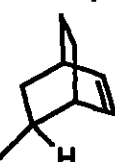
- 33 -

2.2	CF ₃	Me	H		H	H	Resin (¹ H-NMR, MS)
2.3	CF ₃	Me	H		H	H	
2.4	CF ₃	Me	H		H	H	.136-137
2.5	CF ₃	Me	H		6'-F	H	
2.6	CF ₃	Me	H		H	H	
2.7	CF ₃	CH ₂ OMe	H		H	H	
2.8	CF ₂ H	Me	H		H	H	

2.9	CF ₂ H	Me	H		H	H	
2.10	CF ₃	Me	H		H	H	105-107
2.11	CF ₃	Me	H		H	H	110-112
2.12	CF ₃	Me	H		H	H	
2.13	CF ₃	Me	H		H	H	127-129
2.14	CF ₃	CH ₂ OMe	H		H	H	
2.15	CF ₃	Me	H		4'-F	H	

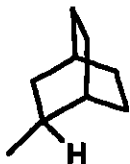
25

- 35 -

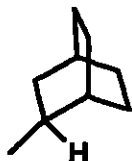
2.16	CF ₃	CH ₂ OMe	H		4'-F	H
2.17	CF ₂ H	Me	H		H	H
2.18	CF ₃	Me	F		H	H
2.19	CF ₃	Me	F		H	H
2.20	CF ₃	CH ₂ OMe	F		H	H
2.21	CF ₃	CH ₂ OMe	F		H	H
2.22	CF ₃	Me	F		H	H

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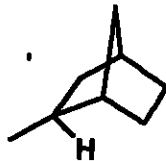
2.23 CF₃ Me F H H 176-178



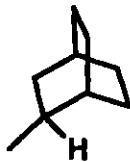
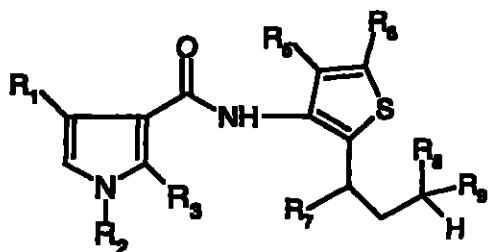
2.24 CF₃ CH₂OMe F H H



2.25 CF₃ Me Me H H



2.26 CF₃ Me Me H H

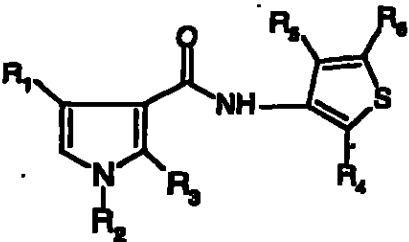
**Table 3**

lc

Cmpd. no.	R ₁	R ₂	R ₃	R ₅	R ₆	R ₇	R ₈	R ₉	Phys. data m.p.°C
3.1	CF ₃	Me	H	H	H	Me	Me	Me	92-93
3.2	CF ₃	CH ₂ OMe	H	H	H	Me	Me	Me	
3.3	CF ₃	Me	H	H	H	CF ₃	Me	Me	
3.4	CF ₃	Me	H	H	H	Me	CF ₃	CF ₃	
3.5	CF ₃	Me	H	H	H	Me	Me	Et	

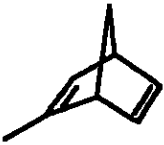
3.6	CF ₃	CH ₂ OMe	H	H	H	Me	Me	Et	
3.7	CF ₃	Me	H	6'-F	H	Me	Me	Me	
3.8	CF ₃	Me	H	5'-F	H	Me	Me	Me	
3.9	CF ₃	Me	H	H	H	Me	Et	Et	
3.10	CF ₃	Me	F	H	H	Me	Me	Me	Oil
3.11	CF ₃	CH ₂ OMe	F	H	H	Me	Me	Me	
3.12	CF ₃	Me	F	H	H	Me	Me	Et	
3.13	CF ₃	Me	F	H	H	CF ₃	Me	Me	
3.14	CF ₃	Me	F	H	H	CF ₃	Me	Et	
3.15	CF ₂ H	Me	H	H	H	Me	Me	Me	Oil
3.16	CF ₂ H	Me	H	H	H	Me	Me	Et	
3.17	CF ₂ H	Me	H	H	H	CF ₃	Me	Me	
3.18	CF ₂ H	Me	H	H	H	Me	Me	Me	
3.19	CFH ₂	Me	H	H	H	Me	Me	Me	
3.20	CFH ₂	Me	H	H	H	Me	Me	Et	
3.21	CFH ₂	Me	H	H	H	CF ₃	Me	Me	
3.22	CFH ₂	Me	H	H	H	Me	Me	Me	

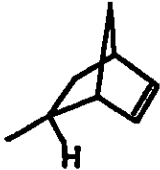
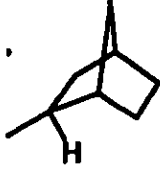
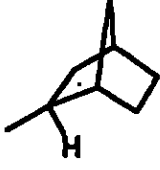
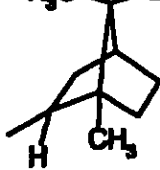
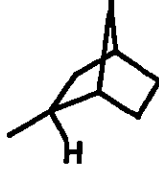
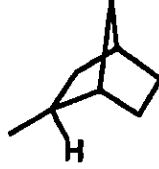
Table 4



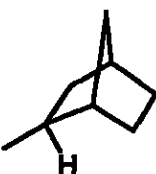
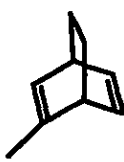
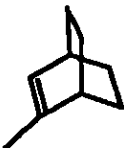
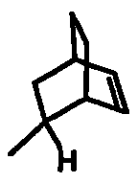
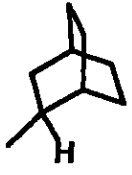
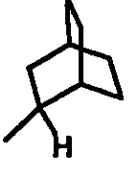
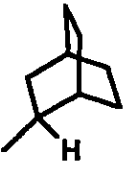
Id

Cmpd. no.	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	phys.data m.p.°C
4.1	CF ₃	Me	H		H	H	

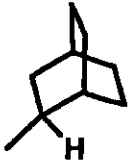
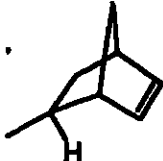
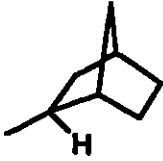
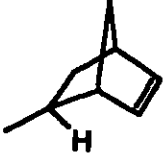
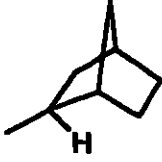
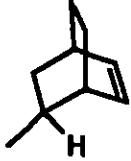


4.2	CF ₃	Me	H		H	H	Resin
4.3	CF ₃	Me	H		H	H	
4.4	CF ₂	Me	H		H	H	Resin
4.5	CF ₃	Me	H		6'-F	H	
4.6	CF ₃	Me	H		H	H	
4.7	CF ₃	CH ₂ OMe	H		H	H	
4.8	CF ₂ H	Me	H		H	H	

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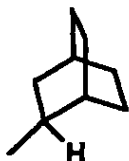
4.9	CF ₂ H	Me	H		H	H
4.10	CF ₃	Me	H		H	H
4.11	CF ₃	Me	H		H	H
4.12	CF ₃	Me	H		H	H
4.13	CF ₃	Me	H		H	H
4.14	CF ₃	CH ₂ OMe	H		H	H
4.15	CF ₃	Me	H		4'-F	H

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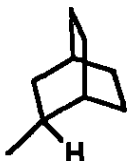
4.16	CF ₃	CH ₂ OMe	H		4'-F	H
4.17	CF ₂ H	Me	H		H	H
4.18	CF ₃	Me	F		H	H
4.19	CF ₃	Me	F		H	H
4.20	CF ₃	CH ₂ OMe	F		H	H
4.21	CF ₃	CH ₂ OMe	F		H	H
4.22	CF ₃	Me	F		H	H

- 41 -

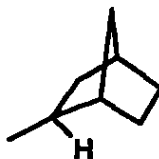
4.23 CF₃ Me F H H



4.24 CF₃ CH₂OMe F H H



4.25 CF₃ Me Me H H



4.26 CF₃ Me Me H H

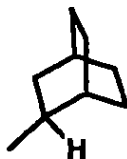
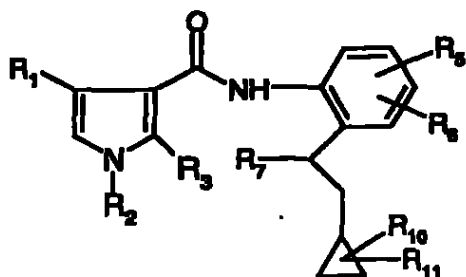


Table 5



Id

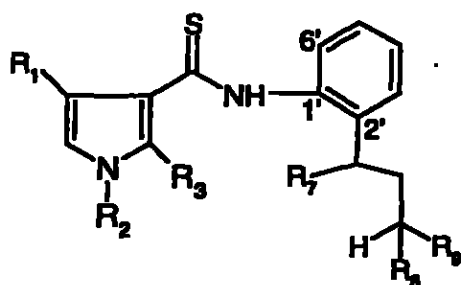
Cmpd. no.	R ₁	R ₂	R ₃	R ₅	R ₆	R ₇	R ₁₀	R ₁₁	phys.data m.p.°C
5.1	CF ₃	Me	H	H	H	Me	H	H	109-110
5.2	CF ₃	CH ₂ OMe	H	H	H	Me	H	H	
5.3	CF ₃	Me	H	H	H	CF ₃	H	H	
5.4	CF ₃	Me	H	H	H	Me	Cl	Cl	
5.5	CF ₃	CH ₂ OMe	H	H	H	CF ₃	H	H	

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5.6	CF ₃	Me	F	H	H	Me	H	H
5.7	CF ₃	CH ₂ OMe	F	H	H	Me	H	H
5.8	CF ₃	Me	F	H	H	CF ₃	H	H
5.9	CF ₃	CH ₂ OMe	F	H	H	Me	H	H
5.10	CF ₃	CH ₂ OMe	F	H	H	CF ₃	H	H
5.11	CF ₃	Me	F	H	H	Me	Cl	Cl
5.12	CF ₂ H	Me	H	H	H	Me	H	H
5.13	CF ₂ H	Me	H	H	H	CF ₃	H	H
5.14	CF ₂ H	CH ₂ OMe	H	H	H	Me	H	H
5.15	CF ₂ H	CH ₂ OMe	H	H	H	CF ₃	H	H
5.16	CF ₂ H	Me	F	H	H	Me	H	H
5.17	CF ₂ H	Me	F	H	H	CF ₃	H	H
5.18	CF ₂ H	CH ₂ OMe	F	H	H	Me	H	H
5.19	CF ₂ H	CH ₂ OMe	F	H	H	CF ₃	H	H
5.20	CF ₂ H	Me	H	H	H	Me	Cl	Cl
5.21	CF ₂ H	CH ₂ OMe	H	H	H	Me	Cl	Cl
5.22	CFH ₂	Me	H	H	H	Me	H	H
5.23	CFH ₂	Me	H	H	H	Et	H	H
5.24	CF ₂ H	Me	F	H	H	Me	H	H
5.25	CF ₃	Me	H	H	H	Et	H	H
5.26	CF ₃	Me	F	H	H	Et	H	H
5.27	CF ₂ H	Me	H	H	H	Et	H	H
5.28	CF ₂ H	Me	F	H	H	Et	H	H

59-61

Table 6

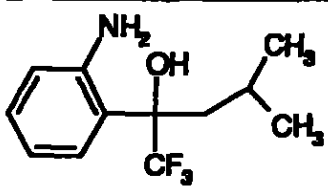
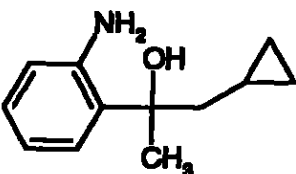
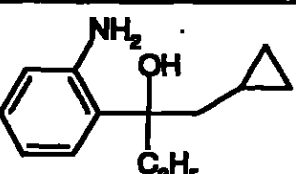
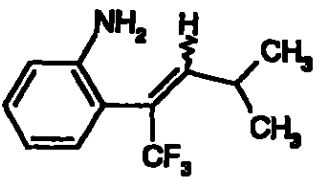
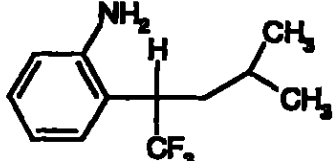
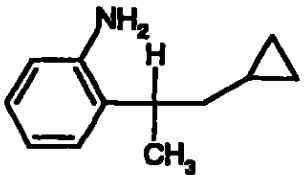
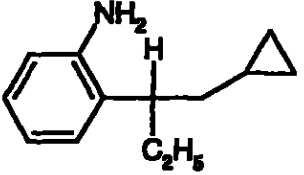


1e

(md = mixture of diastereoisomers)

Cmpd. no.	R ₁	R ₂	R ₃	R ₇	R ₈	R ₉	Phys. Data m.p. °C
6.1	CF ₃	Me	H	Me	Me	Me	resin; ¹ H-NMR; M ⁺ =368
6.2	CF ₃	CH ₂ OMe	H	Me	Me	Me	
6.3	CF ₃	Me	H	CF ₃	Me	Me	
6.4	CF ₃	Me	H	Me	CF ₃	CF ₃	
6.5	CF ₃	Me	H	Me	Me	Et	md; resin; ¹ H-NMR; M ⁺ =382
6.6	CF ₃	CH ₂ OMe	H	Me	Me	Et	
6.7	CF ₃	Me	H	Me	Et	Et	
6.8	CF ₃	Me	F	Me	Me	Me	Resin; M ⁺ = 386
6.9	CF ₃	CH ₂ OMe	F	Me	Me	Me	
6.10	CF ₃	Me	F	Me	Me	Et	
6.11	CF ₃	Me	F	CF ₃	Me	Me	
6.12	CF ₃	Me	F	CF ₃	Me	Et	
6.13	CF ₂ H	Me	H	Me	Me	Me	
6.14	CF ₂ H	Me	H	Me	Me	Et	
6.15	CF ₂ H	Me	H	CF ₃	Me	Me	
6.16	CF ₂ H	Me	H	Me	Me	Me	

Table 7: Amine-Intermediates

Cmpd.No.		Phys.data (m.p. °C or NMR)
7.1		84-86
7.2		Oil; ¹ H-NMR
7.3		Oil; ¹ H-NMR
7.4 7.4.1: E-isomer 7.4.2: Z-isomer E/Z-mixture		Oil; ¹ H-NMR
7.5		Oil; ¹ H-NMR
7.6		Oil; ¹ H-NMR
7.7		Oil; ¹ H-NMR

¹H-NMR Table

Compd. No.	¹ H-NMR-data (ppm/multiplicity/number of protons; solvent CDCl ₃)
6.1	0.82/2xd/6H; 1.19/d/3H; 1.35-1.60/m/1H; 3.70/s/3H; 6.99/d/1H; 7.2-7.4/m/4H; 7.61/d/1H; 8.70/s(broad)/1H
6.5	0.75-0.88/m/12H; 1.0-1.65/m/6H; 1.18/d/3H; 1.20/d/3H; 3.0/m/2H; 3.70/s/6H; 7.0/d/2H; 7.2-7.4/m/8H; 7.61/d/2H; 8.7/s/2H
7.2	0.1/m/2H; 0.45/m/2H; 0.65/m/1H; 1.69/s/3H; 1.80/m/1H; 2.0/m/1H; 3.7/s(broad)/3H(OH+NH ₂); 6.60-6.70/m/2H; 6.98-7.11/m/2H
7.3	0.01/m/2H; 0.35/m/2H; 0.55/m/2H; 0.75/t/3H; 1.51/m/1H; 1.8-2.05/m/3H; 3.72/s(broad)/3H(OH+NH ₂); 6.47-6.59/m/2H; 6.91/m/2H
7.4.1 (E-isomer)	1.09/d/6H; 3.02/m/1H; 3.60/s(broad)/2H(NH ₂); 5.81/d/1H; 6.72/m/2H; 6.99/dxd/1H; 7.15/txd/1H
7.4.2 (Z-isomer)	0.91/d/3H; 1.03/d/3H; 2.25/m/1H; 3.58/s(broad)/2H; 6.36/dxd/1H; 6.78/m/2H; 6.99/dxd/1H; 7.18/txd/1H
7.5	0.83/d/3H; 0.87/d/3H; 1.40/m/1H; 1.69/m/1H; 1.99/m/1H; 3.6/m/3H(NH ₂ +H-benzyllic); 6.75/dxd/1H; 6.85/t/1H; 7.09-7.2/m/2H
7.6	0.05/m/2H; 0.4/m/2H; 0.69/m/1H; 1.29/d/3H; 1.35/m/1H; 1.60/m/1H; 2.88/m/1H; 3.65/s(broad)/2H(NH ₂); 6.68/d/1H; 6.85/t/1H; 7.0/txd/1H; 7.1/dxd/1H
7.7	0.01/m/2H; 0.38/m/2H; 0.60/m/1H; 0.82/t/3H; 1.32/m/1H; 1.52-1.80/m/3H; 2.68/m/1H; 3.65/s(broad)/2H(NH ₂); 6.69/d/1H; 6.78/t/1H; 7.0/txd/1H; 7.08/dxd/1H
1.28	0.78-0.85/t+d/9H; 1.35-1.69/m/5H; 2.85/m/1H; 3.70/s/3H; 7.0/d/1H; 7.20/m/3H; 7.37/d/1H; 7.58/s(broad)/1H; 7.7/m/1H

Formulation Examples for compounds of formula I

Working procedures for preparing formulations of the compounds of formula I such as Emulsifiable concentrates, Solutions, Granulates, Dusts and Wettable powders are described in WO 97/33890.

Biological Examples: Fungicidal actions

Example B-1: Action against *Puccinia recondita* / wheat (Brownrust on wheat)

1 week old wheat plants cv. Arina are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application wheat plants are inoculated by spraying a spore suspension (1×10^5 uredospores/ml) on the test plants. After an incubation period of 2 days at 20° C and 95% r. h. plants are kept in a greenhouse for 8 days at 20° C and 60% r.h. The disease incidence is assessed 10 days after inoculation.

Compounds of Tables 1 to 6 show good activity in these tests (< 20% infestation).

Example B-2: Action against *Podosphaera leucotricha* / apple (Powdery mildew on apple)

5 week old apple seedlings cv. McIntosh are treated with the formulated test compound (0.002% active ingredient) in a spray chamber. One day after application apple plants are inoculated by shaking plants infected with apple powdery mildew above the test plants. After an incubation period of 12 days at 22° C and 60% r. h. under a light regime of 14/10 h (light/dark) the disease incidence is assessed.

Compounds of Tables 1 to 6 show good activity in this test.

Example B-3: Action against *Venturia inaequalis* / apple (Scab on apple)

4 week old apple seedlings cv. McIntosh are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application apple plants are inoculated by spraying a spore suspension (4×10^5 conidia/ml) on the test plants. After an incubation period of 4 days at 21° C and 95% r. h. the plants are placed for 4 days at 21° C and 60% r. h. in a greenhouse. After another 4 day incubation period at 21° C and 95% r. h. the disease incidence is assessed.

Compounds of Tables 1 to 6 show good activity in this test.

Example B-4: Action against *Erysiphe graminis* / barley (Powdery mildew on barley)

1 week old barley plants cv. Express are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application barley plants are inoculated by shaking powdery mildew infected plants above the test plants. After an incubation period of 6 days at 20° C / 18° C (day/night) and 60% r. h. in a greenhouse the disease incidence is assessed.

Compounds of Tables 1 to 6 show good activity in this test.

Example B-5: Action against *Botrytis cinerea* / apple (Botrytis on apple fruits)

In an apple fruit cv. Golden Delicious 3 holes are drilled and each filled with 30 µl droplets of the formulated test compound (0.002% active ingredient). Two hours after application 50 µl of a spore suspension of *B. cinerea* (4×10^5 conidia/ml) are pipetted on the application sites. After an incubation period of 7 days at 22° C in a growth chamber the disease incidence is assessed.

Compounds of Tables 1 to 6 show good activity in this test.

Example B-6: Action against *Botrytis cinerea* / grape (Botrytis on grapes)

5 week old grape seedlings cv. Gutedel are treated with the formulated test compound (0.002% active ingredient) in a spray chamber. Two days after application grape plants are inoculated by spraying a spore suspension (1×10^8 conidia/ml) on the test plants. After an incubation period of 4 days at 21° C and 95% r. h. in a greenhouse the disease incidence is assessed.

Compounds of Tables 1 to 6 show good activity in this test.

Example B-7: Action against *Botrytis cinerea* / tomato (Botrytis on tomatoes)

4 week old tomato plants cv. Roter Gnom are treated with the formulated test compound (0.002% active ingredient) in a spray chamber. Two days after application tomato plants are inoculated by spraying a spore suspension (1×10^5 conidia/ml) on the test plants. After an incubation period of 4 days at 20° C and 95% r. h. in a growth chamber the disease incidence is assessed.

Compounds of Tables 1 to 6 show good activity in this test.

Example B-8: Action against *Pyrenophora teres* / barley (Net blotch on barley)

1 week old barley plants cv. Express are treated with the formulated test compound (0.002% active ingredient) in a spray chamber. Two days after application barley plants are inoculated by spraying a spore suspension (3×10^4 conidia/ml) on the test plants. After an incubation period of 2 days at 20° C and 95% r. h. plants are kept for 2 days at 20° C and 60% r.h. in a greenhouse. The disease incidence is assessed 4 days after inoculation.

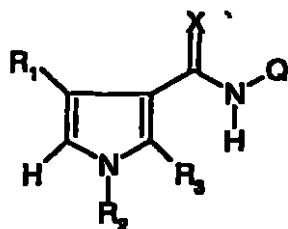
Compounds of Tables 1 to 6 show good activity in this test.

Example B-9: Action against *Septoria nodorum* / wheat (Septoria leaf spot on wheat)

1 week old wheat plants cv. Arina are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application wheat plants are inoculated by spraying a spore suspension (5×10^5 conidia/ml) on the test plants. After an incubation period of 1 day at 20° C and 95% r. h. plants are kept for 10 days at 20° C and 60% r.h. in a greenhouse. The disease incidence is assessed 11 days after inoculation. Compounds of Tables 1 to 6 show good activity in this test.

What is claimed is

1. A pyrrolicarboxylic acid amide or pyrrolicarbothioic acid amide of the formula I



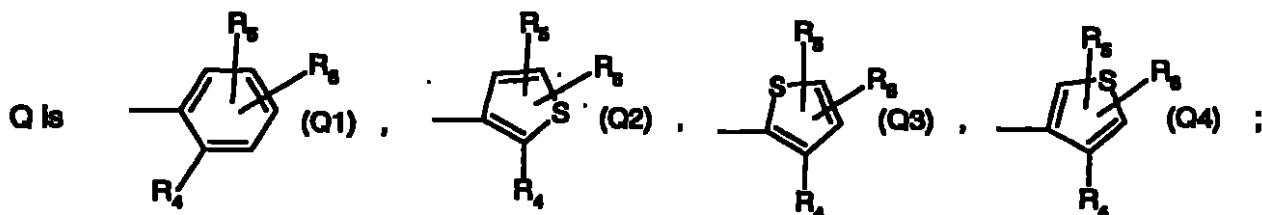
wherein

X is oxygen or sulfur;

R₁ is CF₃, CF₂H or CFH₂;

R₂ is C₁-C₃alkyl, C₁-C₃haloalkyl, C₁-C₃alkoxy-C₁-C₃alkyl or C₁-C₃haloalkoxy-C₁-C₃alkyl;

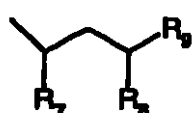
R₃ is hydrogen, methyl, CF₃ or fluoro;



R₄ is C₆-C₁₄bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF₃;

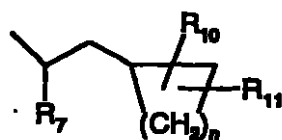
C₆-C₁₄bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF₃;

C₆-C₁₄bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF₃; a group of the form



wherein R₇, R₈ and R₉ are independently of each other C₁-C₃alkyl or

C₁-C₃haloalkyl; or a group



wherein R₁₀ and R₁₁ are independently of each other hydrogen or

halogen and n = 1 or 2; and

R₅ and R₆ are independently of each other hydrogen or halogen.

2. A compound of formula I according to claim 1, wherein X is oxygen.

3. A compound of formula I according to claim 1, wherein X is sulfur.

4. A compound of formula I according to claim 1, wherein R_1 is CF_3 ;

R_2 is C_1 - C_3 alkyl, C_1 - C_3 haloalkyl or C_1 - C_3 alkoxy- C_1 - C_3 alkyl ;

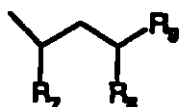
R_3 is hydrogen or fluoro;

Q is Q1;

R_4 is C_8 - C_{10} bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3 ;

C_8 - C_{10} bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3 ;

C_8 - C_{10} bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3 ; a group of the form

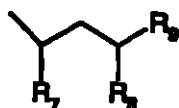


wherein R_7 , R_8 and R_9 are independently of each other C_1 - C_3 alkyl or

C_1 - C_3 haloalkyl; and

R_5 and R_6 are independently of each other hydrogen, chloro or fluoro.

5. A compound of formula I according to claim 4, wherein R_4 is a group of the form



wherein R_7 , R_8 and R_9 are independently of each other C_1 - C_3 alkyl or

C_1 - C_3 haloalkyl.

6. A compound of formula I according to claim 1, wherein R_1 is CF_3 ;

R_2 is C_1 - C_3 alkyl, C_1 - C_3 haloalkyl or C_1 - C_3 alkoxy- C_1 - C_3 alkyl;

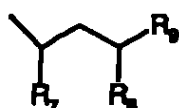
R_3 is hydrogen or fluoro;

Q is Q2, Q3 or Q4;

R_4 is C_6 - C_{10} bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3 ;

C_6 - C_{10} bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3 ;

C_6 - C_{10} bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3 ; a group of the form



wherein R_7 , R_8 and R_9 are independently of each other C_1 - C_3 alkyl or

C_1 - C_3 haloalkyl; and

R_5 and R_6 are independently of each other hydrogen, chloro or fluoro.

7. A compound of formula I according to claim 6, wherein Q is Q2.

8. A compound of formula I according to claim 2, wherein

R_1 is CF_3 ;

R_2 is C_1 - C_3 alkyl or C_1 - C_3 alkoxy- C_1 - C_3 alkyl;

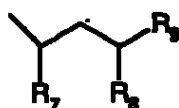
R_3 is hydrogen or fluoro;

Q is Q1;

R_4 is C_6 - C_{10} bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3 ;

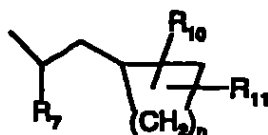
C_6 - C_{10} bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3 ;

C_6 - C_{10} bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3 ; a group of the form



wherein R_7 , R_8 and R_9 are independently of each other C_1 - C_3 alkyl or

C_1 - C_3 haloalkyl; or a group



wherein R_{10} and R_{11} are independently of each other hydrogen or

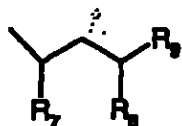
halogen and $n = 1$ or 2 ; and

R_5 and R_6 are independently of each other hydrogen, chloro or fluoro.

9. A compound of formula I according to claim 8, wherein

R_2 is methyl or CH_2OCH_3 ;

R_4 is a group of the form



wherein R_7 , R_8 and R_9 are independently of each other CF_3 , methyl or

ethyl, preferably methyl; and

R_5 and R_6 are independently of each other hydrogen, fluoro or chloro.

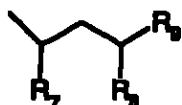
10. A compound of formula I according to claim 9, wherein
 R_2 is methyl.

11. A compound of formula I according to claim 9, wherein

R_2 is methyl;

R_3 is hydrogen;

R_4 is a group of the form



wherein R_7 , R_8 and R_9 are independently of each other methyl or ethyl,

preferably methyl; and

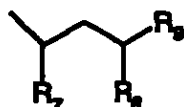
R_5 and R_6 are independently of each other hydrogen, fluoro or chloro.

12. A compound of formula I according to claim 9, wherein

R_2 is methyl;

R_3 is fluoro;

R_4 is a group of the form



wherein R_7 , R_8 and R_9 are independently of each other methyl or ethyl,

preferably methyl; and

R_5 and R_6 are independently of each other hydrogen, fluoro or chloro.

13. A compound of formula I according to claim 1, wherein

R_1 is CF_2H or CFH_2 ;

- 53 -

R_2 is C_1 - C_3 alkyl, C_1 - C_3 haloalkyl or C_1 - C_3 alkoxy- C_1 - C_3 alkyl;

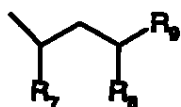
R_3 is hydrogen or fluoro;

Q is Q1;

R_4 is C_8 - C_{10} bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3 ;

C_8 - C_{10} bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3 ;

C_8 - C_{10} bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3 ; a group of the form



wherein R_7 , R_8 and R_9 are independently of each other C_1 - C_3 alkyl or

C_1 - C_3 haloalkyl; and

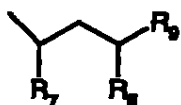
R_8 and R_9 are independently of each other hydrogen, chloro or fluoro.

14. A compound of formula I according to claim 13, wherein

X is oxygen;

R_2 is methyl or CH_2OCH_3 ;

R_4 is a group of the form



wherein R_7 , R_8 and R_9 are independently of each other C_1 - C_3 alkyl or

C_1 - C_3 haloalkyl.

15. A compound of formula I according to claim 1, wherein

R_1 is CF_2H or CFH_2 ;

R_2 is C_1 - C_3 alkyl, C_1 - C_3 haloalkyl or C_1 - C_3 alkoxy- C_1 - C_3 alkyl;

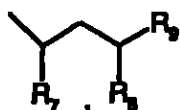
R_3 is hydrogen or fluoro;

Q is Q2, Q3 or Q4;

R_4 is C_8 - C_{10} bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3 ;

C_8 - C_{10} bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3 ;

C_8 - C_{10} bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3 ; a group of the form



wherein R_7 , R_8 and R_9 are independently of each other C_1 - C_3 alkyl or

C_1 - C_3 haloalkyl; and

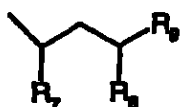
R_8 and R_9 are independently of each other hydrogen, chloro or fluoro.

16. A compound of formula I according to claim 15, wherein

X is oxygen;

R_2 is methyl or CH_2OCH_3 ;

R_4 is a group of the form



wherein R_7 , R_8 and R_9 are independently of each other C_1 - C_3 alkyl or

C_1 - C_3 haloalkyl.

17. A compound of formula I according to claim 1 selected from

1-methyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid [2-(1,3-dimethylbutyl)phenyl]amid ;

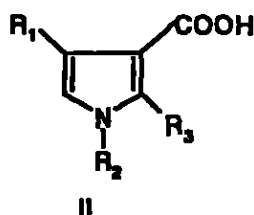
1-methoxymethyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid [2-(1,3-dimethylbutyl)phenyl]amide;

1-methyl-2-fluoro-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid [2-(1,3-dimethylbutyl)phenyl]amide;

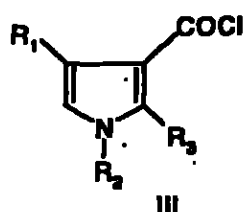
1-methoxymethyl-2-fluoro-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid [2-(1,3-dimethylbutyl)phenyl]amide;

1-methyl-4-trifluoromethyl-1H-pyrrole-3-carbothioic acid [2-(1,3-dimethylbutyl)phenyl]amide.

18. A process for the preparation of compounds of formula I, which comprises in a first step preparing the compounds of formula I wherein $X=O$ by converting the pyrrolecarboxylic acid II



to the acid chloride III

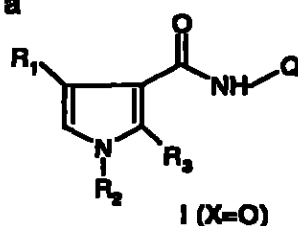


and by reacting the pyrrole acid chloride III with the amine IV

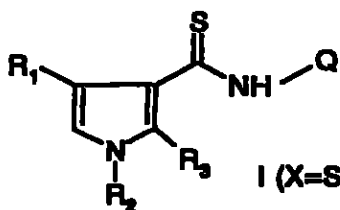
H_2N-Q IV

to the compounds of formula I

a



and optionally converting these compounds to the compounds of formula I wherein X=S by reacting with Lawesson-Reagent or P_2S_5 in dioxane, tetrahydrofurane or toluene at a temperature of 0° - reflux to



and wherein R_1 , R_2 , R_3 and Q are as defined for formula I in claim 1.

19. A composition for controlling microorganisms and preventing attack and Infestation of plants, wherein the active ingredient is a compound as claimed in claim 1 together with a suitable carrier.

20. Use of a compound of formula I according to claim 1 for protecting plants against infestation by phytopathogenic microorganisms.

21. A method of controlling or preventing infestation of cultivated plants by phytopathogenic microorganisms by application of a compound of formula I as claimed in claim 1 to plants, to parts thereof or the locus thereof.

22. The amine intermediates of formula IV H_2N-Q wherein Q and R_4 , R_5 , R_6 , R_7 , R_8 , R_9 , R_{10} and R_{11} are as defined in claim 1.

23. A compound of formula IV according to claim 22 selected from

2-bicyclo[2.2.2]oct-2-yl-phenylamine;

2-bicyclo[2.2.2]oct-2-en-2-yl-phenylamine;

2-bicyclo[2.2.2]octa-2,5-dien-2-yl-phenylamine;

2-(2-aminophenyl)-1,1,1-trifluoromethyl-4-methyl-pentan-2-ol;

2-(2-aminophenyl)-1-cyclopropyl-propan-2-ol;

2-(2-aminophenyl)-1-cyclopropyl-butan-2-ol;

2-(3-methyl-1-trifluoromethyl-but-1-enyl)-phenylamine;

2-(3-methyl-1-trifluoromethyl-butyl)phenylamine;

2-(2-cyclopropyl-1-methyl-ethyl)phenylamine; and

2-(1-cyclopropylmethyl-propyl)phenylamine.

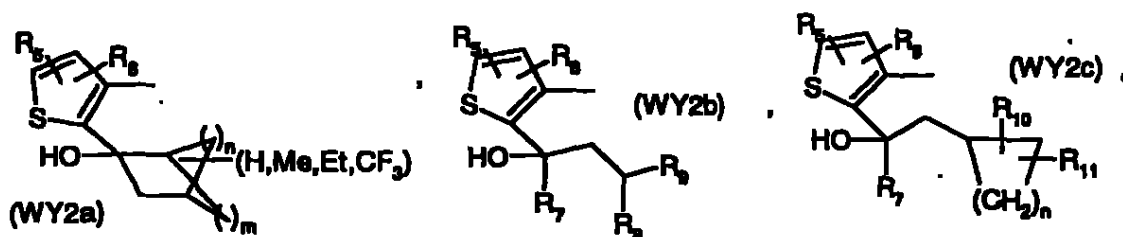
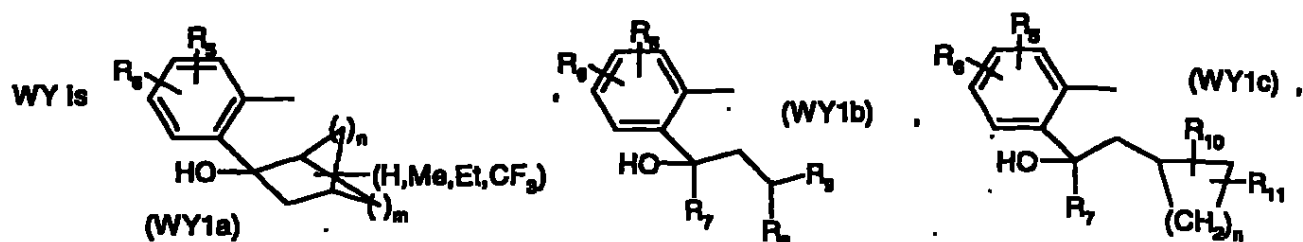
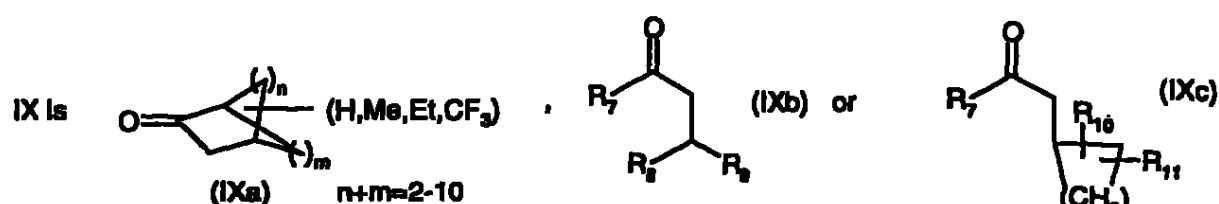
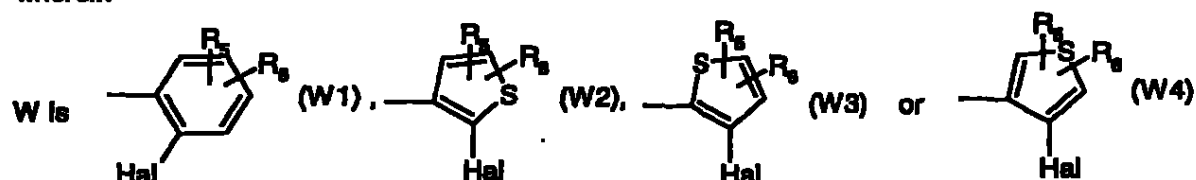
24. A process for the preparation of compounds of the formula IV according to claim 22, characterized by

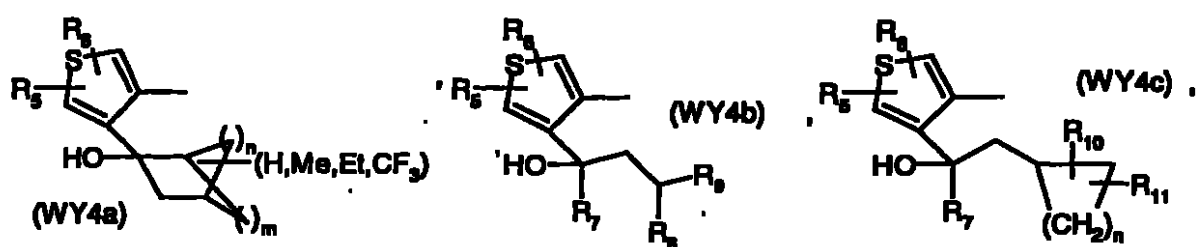
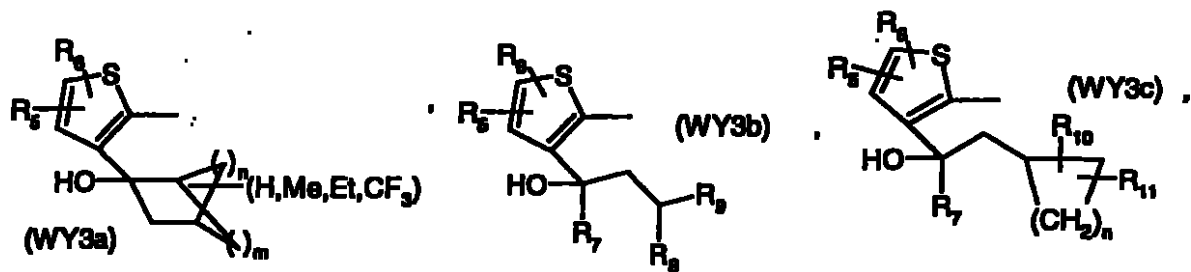
Route a) reacting the formyl derivate $W-NHCHO$ of formula X with a ketone of formula IX in the presence of 2-3 equivalents of $n-BuLi$ or $sec-BuLi$ or another strong base in a solvent at a temperature of -100 to $-110^\circ C$ providing the compounds of formula XI ($WY-NHCHO$); converting the formyl derivative of formula XI to the amine compounds of formula VI (H_2N-WY) in a basic hydrolysis by reacting with $NaOH$ or KOH in alcohols; and hydrogenation the amine VI to the compounds IV (H_2N-Q) with $Pd/charcoal$ in the presence of a strong acid (i.e. sulfuric acid) or alternatively elimination of water and then hydrogenation; or

Route b) reacting the amine of formula XII (H_2N-T) with an excess of the Grignard reagent of formula XV in a solvent like THF or ether at a temperature $0^\circ C$ to reflux to the amine of formula VI; and

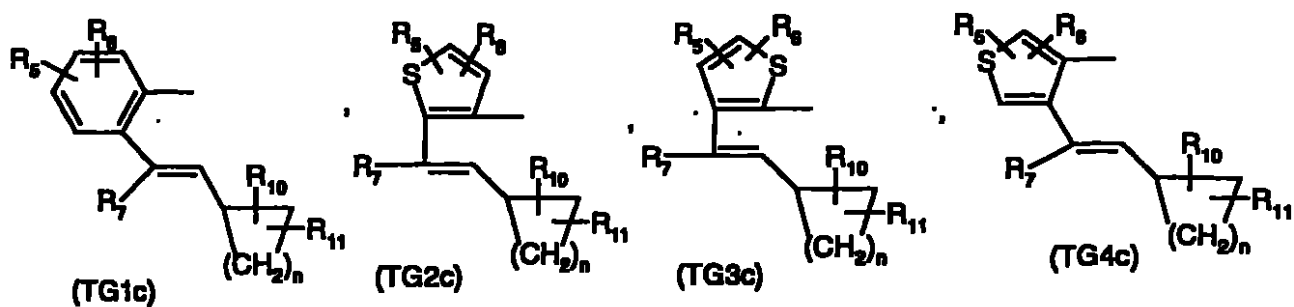
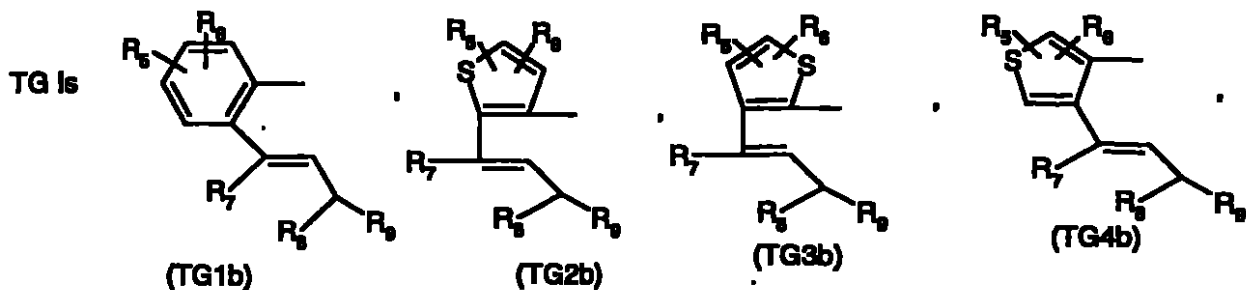
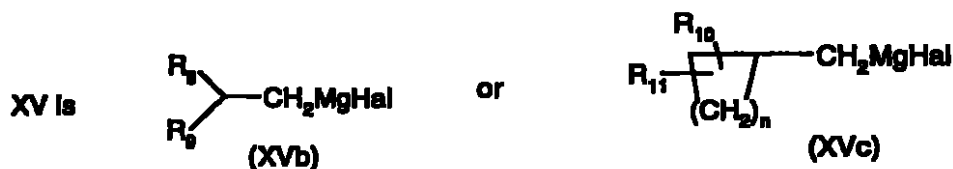
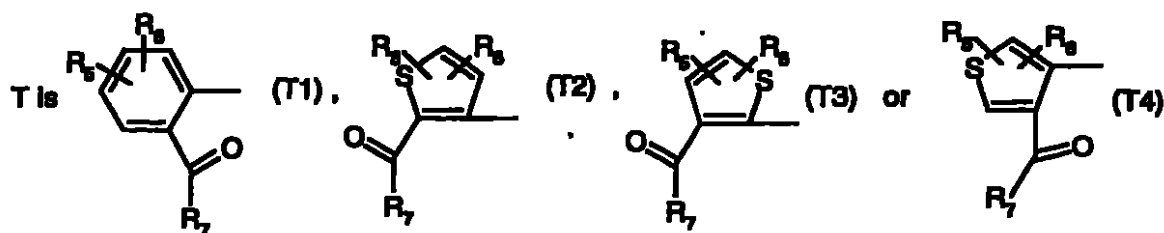
converting the amine VI to the amine XIV (H_2N-TG) by elimination of water; the hydrogenation of XIV with Pd or Pt on charcoal in a solvent like THF or alcohols at temperatures of $0^\circ C$ to reflux provides the compounds of formula IV; or directly the compounds of formula VI by hydrogenation with Pd on charcoal in the presence of sulfuric acid in a solvent like an alcohol provides the amines IV; or
 Route c) reacting the nitro derivative NO_2-W (formula XIII) with a ketone of formula IX providing the nitro derivative NO_2-WY of formula VII; transforming the compound of formula VII by reaction with $SOCl_2$ or $POCl_3$ in pyridine at a temperature of $0^\circ C$ to reflux to the derivative VIII (NO_2-TG); and hydrogenation of the compound of formula VIII with Raney-Ni in alcohol at a pressure of 50-200 bar and a temperature of $50-150^\circ C$ to the compound of formula IV; wherein Q, R_5 , R_6 , R_7 , R_8 , R_9 , R_{10} , R_{11} are as defined in claim 1 for compounds of the formula I, Hal is Br or I and

wherein





and wherein $n+m=2-10$

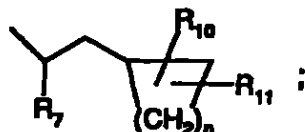


25. A process according to claim 24, Route a), for compounds of formula IV wherein Q is Q1; and

R₄ is C₇-C₈bicycloalkyl unsubstituted or substituted by methyl or CF₃;

C₇-C₈bicycloalkenyl unsubstituted or substituted by methyl or CF₃;

C₇-C₈bicycloalkadienyl unsubstituted or substituted by methyl or CF₃; or a group



R₅ and R₆ are hydrogen; and wherein R₇, R₁₀, R₁₁ and n are as defined in claim 1.

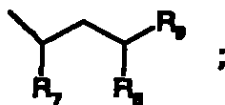
26. A process according to claim 24, Route a), wherein

Q is Q2, Q3 or Q4; and

R₄ is C₇-C₁₀bicycloalkyl unsubstituted or substituted by methyl or CF₃;

C₇-C₁₀bicycloalkenyl unsubstituted or substituted by methyl or CF₃;

C₇-C₁₀bicycloalkadienyl unsubstituted or substituted by methyl or CF₃; or a group



R₅ and R₆ are hydrogen; and wherein R₇, R₈, R₉ and n are as defined in claim 1.

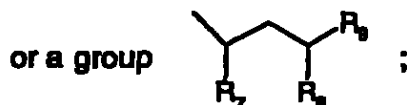
27. A process according to claim 24, Route b), wherein

Q is Q1; and

R₄ is C₇-C₁₀bicycloalkyl unsubstituted or substituted by methyl or CF₃;

C₇-C₁₀bicycloalkenyl unsubstituted or substituted by methyl or CF₃;

C₇-C₁₀bicycloalkadienyl unsubstituted or substituted by methyl or CF₃;



R₅ and R₆ are hydrogen; and wherein R₇, R₈, R₉ and n are as defined in claim 1.

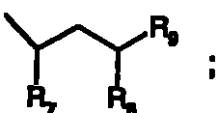
28. A process according to claim 24; Route b), wherein

Q is Q2, Q3 or Q4; and

R₄ is C₇-C₁₀bicycloalkyl unsubstituted or substituted by methyl or CF₃;

C_7-C_{10} bicycloalkenyl unsubstituted or substituted by methyl or CF_3 ;

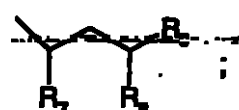
C_7-C_{10} bicycloalkadienyl unsubstituted or substituted by methyl or CF_3 ;

or a group  ;

R_5 and R_6 are hydrogen; and wherein R_7 , R_8 , R_9 and n are as defined in claim 1.

29. A process according to claim 24, Route c), wherein

Q is Q1; and

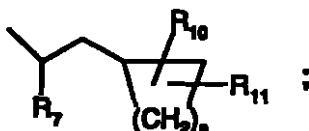
R_4 is a group  ;

R_5 and R_6 are hydrogen;

R_7 is CF_3 ; and wherein R_8 , R_9 and n are as described in claim 1.

30. A process according to claim 24, Route c), wherein

Q is Q1;

R_4 is a group  ;

R_5 and R_6 are hydrogen;

n is 1;

R_7 is CF_3 ; and wherein R_{10} and R_{11} are as defined in claim 1.

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

1281-92138

PCT/EP 0 1 / 1 28 3 0 ✓	
International Application No.	
06 NOV 2001	(08. 11. 2001) ✓
International Filing Date	
EUROPEAN PATENT OFFICE PCT INTERNATIONAL APPLICATION	
Name of receiving Office and "PCT International Application"	
Applicant's or agent's file reference (if desired) (12 characters maximum)	PF/5 -50034A

Box No. I TITLE OF INVENTION

PYRROLCARBOXAMIDES AND PYRROLCARBOTHIOAMIDES

Box No. II APPLICANT

☐ This person is also inventor

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence (if no State of residence is indicated below.)

Syngenta Participations AG
Schwarzwaldallee 215
4058 Basel
CH

Telephone No. +41 61 323 11 11

Facsimile No. +41 61 323 50 44

Teleprinter No.

Applicant's registration No. with the Office

State (that is, country) of nationality: CH

State (that is, country) of residence: CH

This person is applicant
for the purposes of:

☐all designated
States☒all designated States except
the United States of America☐the United States
of America only☐the States indicated in
the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence (if no State of residence is indicated below.)

WALTER, Harald
Syngenta Crop Protection AG
Schwarzwaldallee 215
4058 Basel
CH

This person is:

☐

applicant only

☒

applicant and inventor

☐inventor only (If this check-box is
marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality: DE

State (that is, country) of residence: CH

This person is applicant
for the purposes of:

☐all designated
States☐all designated States except
the United States of America☒the United States
of America only☐the States indicated in
the Supplemental Box☒

Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf
of the applicant(s) before the competent International Authorities as:

☒

agent

☐

common representative

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

BASTIAN, Werner
c/o Syngenta Participations AG
Intellectual Property
P.O. Box
CH-4002 Basel
Switzerland

Telephone No. +41 61 323 11 11

Facsimile No. +41 61 323 50 44

Teleprinter No.

☐

Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Along Form PCT/RO/101

See Notes to the request form

Box No.V DESIGNATION OF STATES mark the applicable check-boxes below; at least one must be marked.

The following designations are hereby made under Rule 4.9(a)

Regional Patent

- ☒ AP ARIPO Patent: GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, MZ Mozambique, SD Sudan, SL Sierra Leone, SZ Swaziland, TZ United Republic of Tanzania, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☒ EA Eurasian Patent: AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ EP European Patent: AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, TR Turkey, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☒ OA OAPI Patent: BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

National Patent (if other kind of protection or treatment desired, specify on dotted line)

- | | | |
|---|--|--|
| ☒ AE United Arab Emirates | ☒ GE Georgia | ☒ MW Malawi |
| ☒ AG Antigua and Barbuda | ☒ GH Ghana | ☒ MX Mexico |
| ☒ AL Albania | ☒ GM Gambia | ☒ MZ Mozambique |
| ☒ AM Armenia | ☒ HR Croatia | ☒ NO Norway |
| ☒ AT Austria | ☒ HU Hungary | ☒ NZ New Zealand |
| ☒ AU Australia | ☒ ID Indonesia | ☒ PL Poland |
| ☒ AZ Azerbaijan | ☒ IL Israel | ☒ PT Portugal |
| ☒ BA Bosnia and Herzegovina | ☒ IN India | ☒ RO Romania |
| ☒ BB Barbados | ☒ IS Iceland | ☒ RU Russian Federation |
| ☒ BG Bulgaria | ☒ JP Japan | ☒ SD Sudan |
| ☒ BR Brazil | ☒ KE Kenya | ☒ SE Sweden |
| ☒ BY Belarus | ☒ KG Kyrgyzstan | ☒ SG Singapore |
| ☒ BZ Belize | ☒ KP Democratic People's Republic of Korea | ☒ SI Slovenia |
| ☒ CA Canada | ☒ KR Republic of Korea | ☒ SK Slovakia |
| ☒ CH & LI Switzerland and Liechtenstein | ☒ KZ Kazakhstan | ☒ SL Sierra Leone |
| ☒ CN China | ☒ LC Saint Lucia | ☒ TJ Tajikistan |
| ☒ CO Colombia | ☒ LK Sri Lanka | ☒ TM Turkmenistan |
| ☒ CR Costa Rica | ☒ LR Liberia | ☒ TR Turkey |
| ☒ CU Cuba | ☒ LS Lesotho | ☒ TT Trinidad and Tobago |
| ☒ CZ Czech Republic | ☒ LT Lithuania | ☒ TZ United Republic of Tanzania |
| ☒ DE Germany | ☒ LU Luxembourg | ☒ UA Ukraine |
| ☒ DK Denmark | ☒ LV Latvia | ☒ UG Uganda |
| ☒ DM Dominica | ☒ MA Morocco | ☒ US United States of America |
| ☒ DZ Algeria | ☒ MD Republic of Moldova | ☒ UZ Uzbekistan |
| ☒ EE Estonia | ☒ MG Madagascar | ☒ VN Viet Nam |
| ☒ ES Spain | ☒ MK The former Yugoslav Republic of Macedonia | ☒ YU Yugoslavia |
| ☒ FI Finland | ☒ MN Mongolia | ☒ ZA South Africa |
| ☒ GB United Kingdom | | ☒ ZW Zimbabwe |
| ☒ GD Grenada | | |

Check-box reserved for designating States which have become party to the PCT after issuance of this sheet

- ☒ EC Ecuador ☐
- ☒ PH Philippines (from 17th August 01) ☐

Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation (including fees) must reach the receiving Office within the 15-month time limit.)

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See Notes to the request form

Box No. VI PRIORITY CLAIM

The priority of the following earlier application(s) is hereby claimed:

Filing Date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application: regional Office	international application: receiving Office
Item (1) 08 November 2000 (08.11.00) ✓	0027284.9 ✓	GB ✓		
Item (2) 12 December 2000 (12.12.00) ✓	0030268.7 ✓	GB ✓		
Item (3)				
Item (4)				
Item (5)				

☐ Further priority claims are indicated in the Supplemental Box.

The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as:

☐ all items ☐ item (1) ☐ item (2) ☐ item (3) ☐ item (4) ☐ item (5) ☐ other, see Suppl. Box

* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)).

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) (If two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA /

Request to use results of earlier search; reference to that search (If an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year)

Number

Country (or regional Office)

Box No. VIII DECLARATIONS

The following declarations are contained in Boxes Nos. VIII(i) to (v) (mark the applicable check-boxes below and indicate in the right column the number of each type of declaration):

Number of
declarations

- ☐ Box No. VIII (i) Declaration as to the identity of the inventor :
- ☐ Box No. VIII (ii) Declaration as to the applicant's entitlement, as at the international filing date, to apply for and being granted a patent :
- ☐ Box No. VIII (iii) Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application :
- ☐ Box No. VIII (iv) Declaration of inventorship (only for the purposes of designation of the United States of America) :
- ☐ Box No. VIII (v) Declaration as to non-prejudicial disclosures or exceptions to lack of novelty :

Box No. IX CHECK LIST: LANGUAGE OF FILING

This international application contains:

(a) the following number of sheets in paper form:

request : 4
description (excluding
sequence listing part) : 48
claims : 12
abstract : 1
drawings : 0
Sub-total number of sheets : 65

sequence listing part of
description (actual number
of sheets if filed in paper
form, whether or not also
filed in computer readable
form: see (b) below) : 0

Total number of sheets : 65

(b) sequence listing part of description filed in computer readable form

- (i) ☐ only (under Section 801(a)(i))
(ii) ☐ in addition to being filed in paper form (under Section 801(a)(ii))

Type and number of carrier (diskette,
CD-ROM, CD-R or other) on which the
sequence listing part is contained (additional
copies to be indicated under item 9(II), in if
right column):

This international application is accompanied by the following item(s) (mark the applicable check-boxes below and indicate in right column the number of each item):

Number
of items

1. ☒ fee calculation sheet : 1
2. ☒ original separate power of attorney : 1
3. ☐ original general power of attorney :
4. ☒ copy of general power of attorney; reference number, if any: AV 42789 : 1
5. ☐ statement explaining lack of signature :
6. ☒ priority document(s) identified in Box No VI as item(s): (1) : 1
7. ☐ translation of international application into (language): :
8. ☐ separate indications concerning deposited microorganism or other biological material :
9. ☐ sequence listing in computer readable form (indicate also type and number of carriers (diskette, CD-ROM, CD-R or other)) :
(i) ☐ copy submitted for the purposes of international search under rule 13ter only (and not as part of the international application) :
(ii) ☐ (only where check-box (b)(i) or (b)(ii) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under rule 13ter :
(iii) ☐ together with relevant statement as to the identity of the copy or copies with the sequence listing part mentioned in left column :
10. ☐ other (specify) :

Figure of the drawings which should accompany the abstract: —

Language of filing of the international application:

English

Box No. X SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request)

in the name of the applicants
The representative

29.10.2001

ZWICKL, Markus, AV 42789

For receiving Office use only	
1. Date of actual receipt of the purported international application:	06 NOV 2001
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:	
4. Date of timely receipt of the required corrections under PCT Article 11(2):	
5. International Searching Authority ISA/	6. ☐ Transmittal of search copy delayed until search fee is paid

(C.E. 11. 01)

2. Drawings:
☐ received
☐ not received

Date of receipt of the record copy by the International Bureau:

For International Bureau use only

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See Notes to the request form

PATENT COOPERATION TREATY

RECEIVED AT INTELLECTUAL PROPERTY R&T 2.0 BASEL				
27. Jan. 2003				
ASSIGN	APPL	CATA	REN	
INVOICE	PS	TS	ARCHIVE	CIRC

VERIFY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

Bastian, Werner
SYNGENTA PARTICIPATIONS AG
Intellectual Property
P.O. Box
CH-4002 Basel
SUISSE

IPD AGROCHEMICALS
ATTORNEY GENERAL
Date of receipt 28 JAN 2003
PAGES

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing
(day/month/year) 23.01.2003

Applicant's or agent's file reference
PF/5-50034A

IMPORTANT NOTIFICATION

International application No.
PCT/EP01/12830

International filing date (day/month/year)
08/11/2001

Priority date (day/month/year)
08/11/2000

Applicant
SYNGENTA PARTICIPATIONS AG et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the International application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the International application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

For the purpose of deciding whether the claimed invention is patentable or not, the elected Offices may apply criteria additional to or different from the criteria on which the international preliminary examination report is based (see Articles 27(5), 33(5)). Additional criteria may include e.g. exemptions from patentability and the requirements of enabling disclosure and of clarity and support of claims.

Name and mailing address of the IPEA/

European Patent Office
D-80288 Munich
Tel. +49 89 2399 - 0 Tlx 523656 epmu d
Fax +49 89 2399 - 4485

Authorized officer

Ambrosia, J.F.

Tel. +49 89 2399-8012



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PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PF/5-50034A		FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/EP01/12830	International filing date (day/month/year) 06/11/2001	Priority date (day/month/year) 08/11/2000	
International Patent Classification (IPC) or national classification and IPC C07D207/327			
Applicant SYNGENTA PARTICIPATIONS AG et al.			
1. This International preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36. 2. This REPORT consists of a total of 7 sheets, including this cover sheet. ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 807 of the Administrative Instructions under the PCT). These annexes consist of a total of 1 sheets.			
3. This report contains indications relating to the following items: - I ☒ Basis of the report - II ☐ Priority - III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability - IV ☐ Lack of unity of invention - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement - VI ☐ Certain documents cited - VII ☐ Certain defects in the international application - VIII ☐ Certain observations on the international application			
Date of submission of the demand 23/05/2002		Date of completion of this report 23.01.2003	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2369 - 0 Tx: 523656 epmu d Fax: +49 89 2369 - 4485		Authorized officer Usuelli, A Telephone No. +49 89 2369 7368 	

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP01/12830

I. Basis of the report

1. With regard to the elements of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-36,38-48 as originally filed

37 as received on 15/02/2002 with letter of 11/02/2002

Claims, No.:

1-30 as originally filed

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP01/12830

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

- 6. Additional observations, if necessary:**

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

- 1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:**

- ☐ the entire international application.

- ☒ **claims Nos. 22-30.**

because:

- ☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):

- ☐ the description, claims or drawings (indicate particular elements below) or said claims Nos. are so unclear that no meaningful opinion could be formed (specify):

- ☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.

- ☒ no international search report has been established for the said claims Nos. 22-30.

- 2. A meaningful international preliminary examination cannot be carried out due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:**

- ☐
- the written form has not been furnished or does not comply with the standard.

- ☐ the computer readable form has not been furnished or does not comply with the standard.

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

- ## 1. Statement

Novelty (N) **Yes: Claims 1-21**
 No: Claims

Inventive step (IS)	Yes:	Claims
---------------------	------	--------

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP01/12830

	No:	Claims	1-21
Industrial applicability (IA)	Yes:	Claims	1-21
	No:	Claims	

2. Citations and explanations
see separate sheet

Re Item III

Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The International Preliminary Examination Report is carried out only in respect of those parts of the application for which a search report has been established, namely claims 1-21

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

In the present report reference is made to the following documents:

d1: WO 00 09482 A

d2: EP 0 737 682 A

d3: EP 0 841 336 A

d4: EP 0 824 099 A

1- Novelty

The subject matter of the present application is considered to comply with the requirements of novelty (Art. 33.2 PCT).

Document d(1) discloses a general class of pyrrolcarboxamides derivatives which overlaps with present formula (I) in which R4 is the group containing the radicals R7-R9, when (in d3) A is a phenyl or thiopenyl group and R3 is a C1-C6 alkyl.

However, d1 does not disclose neither subclasses of preferred compounds nor specific examples in which R3 is an alkyl chain containing at least 2 tertiary carbon atoms.

Thus, this feature which is present in the radical R4 of the present compounds, can be regarded as the new technical teaching upon which the novelty of present formula (I) can be acknowledged.

Present compounds are novel vis-à-vis d2-d4 on account of the pyrrole ring.

2- Inventive step

2.1- Document d(1) which discloses pyrrolcarboxamide derivatives having microbicidal

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP01/12830

activity is considered to represent the closest state of the art.

The technical problem underlying the present invention can be seen in the provision of further microbicides.

For the purpose of assessing the inventive step in the international preliminary examination it is accepted that present compounds of formula (I) indeed represent a solution of the above defined technical problem, i.e. possess the microbicidal activity.

2.2- As already referred above, the formula (I) disclosed in d1, encompasses, at least in part, present formula (I).

Accordingly, it appears that the skilled person faced with the problem of providing further agents having microbicidal activity, would arrive in an obvious manner to the present compounds of formula (I) since d(1) clearly teaches that this class of compounds possess microbicidal activity.

Additionally, heterocyclic or carbocyclic amides, having microbicidal/fungicidal activity are disclosed also in d2-d4.

These compounds differ from present compounds of formula (I) in that they lack the pyrrole ring. However, the amine portion of these molecules correspond to present group Q in that it includes thiopenyl (d2 and d3) or aryl (d4) rings substituted by alkyl or cycloalkyl radicals (cf. for instance, compounds 1.10 -1.19 and 1.41 of d2, compounds 1.7-1.9 of d3 and example 1 of d4). Thus, it appears that the selection of present radical R4, which is the feature determining the novelty of present compounds vis-à-vis d1, cannot be considered to involve an inventive activity since this feature appears to be commonly present in the compounds of the prior art possessing the same activity and having similar structures.

In this context it is observed that the comparative tests between present compound 3.1 and the compounds 1.4 and 1.5 of d1, cannot be regarded as an evidence of the presence of an inventive activity. In present compound 3.1 the group R4 is a 1,3-dimethylbutyl radical. In the compounds 1.4 and 1.5 of d1, the corresponding radicals are the substituents 4-fluorophenyl and 4-chlorophenyl. However, d1 encompasses compounds in which R3 (corresponding to present group R4) is a C1-C6 alkyl (cf. also the paragraph "Novelty"). Thus, the closest prior art is represented by those compounds of d1 containing these radicals, such as for instance the compounds 57-62.

Accordingly, in the absence of unexpected properties vis-à-vis the molecules of d1 representing the closest state of the art, present compounds of formula (I), their

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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP01/12830

compositions and their uses for protecting plant are not considered inventive in the sense of Art. 33.3 PCT.

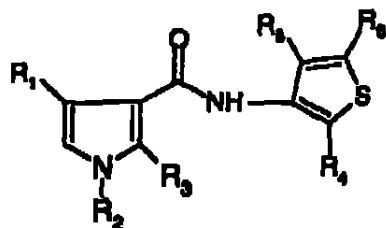
Present process of claim 18 correspond to the last two steps of the process of scheme (1) of d1. Accordingly, also claim 18 does not comply with the requirements of Art. 33.3 PCT.

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- 37 -

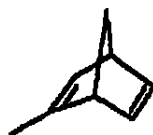
3.6	CF ₃	CH ₂ OMe	H	H	H	Me	Me	Et	
3.7	CF ₃	Me	H	6'-F	H	Me	Me	Me	
3.8	CF ₃	Me	H	5'-F	H	Me	Me	Me	
3.9	CF ₃	Me	H	H	H	Me	Et	Et	
3.10	CF ₃	Me	F	H	H	Me	Me	Me	Oil
3.11	CF ₃	CH ₂ OMe	F	H	H	Me	Me	Me	
3.12	CF ₃	Me	F	H	H	Me	Me	Et	
3.13	CF ₃	Me	F	H	H	CF ₃	Me	Me	
3.14	CF ₃	Me	F	H	H	CF ₃	Me	Et	
3.15	CF ₂ H	Me	H	H	H	Me	Me	Me	Oil
3.16	CF ₂ H	Me	H	H	H	Me	Me	Et	
3.17	CF ₂ H	Me	H	H	H	CF ₃	Me	Me	
3.18	CF ₂ H	Me	H	H	H	Me	Me	Me	
3.19	CFH ₂	Me	H	H	H	Me	Me	Me	
3.20	CFH ₂	Me	H	H	H	Me	Me	Et	
3.21	CFH ₂	Me	H	H	H	CF ₃	Me	Me	
3.22	CFH ₂	Me	H	H	H	Me	Me	Me	

Table 4



Id

Cmpd. no.	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	phys.data m.p. °C
4.1	CF ₃	Me	H		H	H	



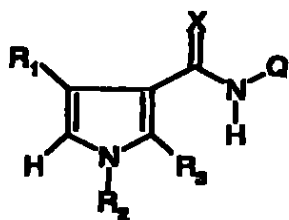
AMENDED SHEET

PIRROLCARBOXIAMIDAS Y PIRROLCARBOTIOAMIDAS Y SUS USOS

AGROQUIMICOS

La presente invención se relaciona con amidas de ácido pirrolcarboxílico novedosas y amidas de ácido pirrolcarbotioico que tienen actividad microbici da, en particular actividad fungici da. La invención también se relaciona con la preparación de estas sustancias, con composiciones agroquímicas que comprenden al menos uno de los compuestos novedosos como ingrediente activo, con la preparación de las composiciones mencionadas y con el uso de los ingredientes activos o composiciones en agricultura y horticultura para controlar o prevenir la infestación de plantas por microorganismos fitopatogénicos, preferiblemente hongos.

Las amidas de ácido 3-pirrolcarboxílico y las amidas de ácido 3-pirrolcarbotioico de la presente invención tienen la fórmula general (I),



En donde

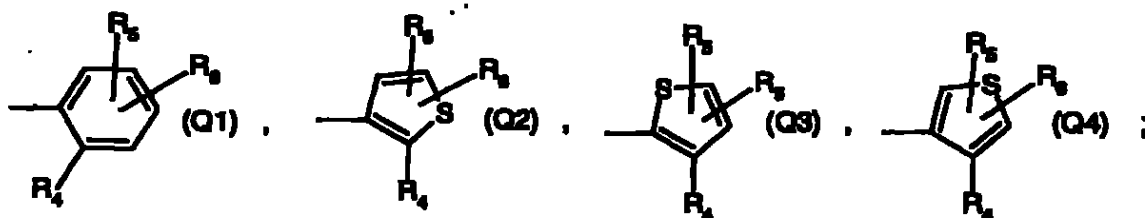
X es oxígeno o azufre;

R₁ es CF₃, CF₂H o CFH₂;

R₂ es alquilo C₁-C₃, haloalquilo C₁-C₃, alcoxi C₁-C₃ alquilo -C₁-C₃ o haloalcoxi C₁-C₃- alquilo C₁-C₃;

R₃ es hidrógeno, metilo, CF₃ o flúor;

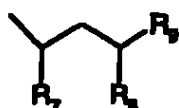
Q es



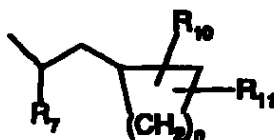
R₄ es bicicloalquilo C₆-C₁₄ no sustituido o sustituido por metilo, etilo o CF₃;

bicicloalquenilo C₆-C₁₄ no sustituido o sustituido por metilo, etilo o CF₃;

bícicloalcadienilo C_6-C_{14} no sustituido o sustituido por metilo, etilo o CF_3 ; o un grupo de la forma



Donde R_7 , R_8 y R_9 son independientemente uno del otro alquilo C_1-C_3 o haloalquilo C_1-C_3 ; o un grupo



En donde R_{10} y R_{11} son independientemente uno del otro hidrógeno o halógeno y $n = 1$ o 2 ; y

R_5 y R_6 son independientemente uno del otro hidrógeno o halógeno.

Sorprendentemente, se ha encontrado ahora que los compuestos de fórmula I exhiben propiedades biológicas

mejoradas que los hacen más adecuados para el uso práctico de la agricultura y horticultura.

Donde están presentes átomos de carbono asimétricos en los compuestos de la fórmula 1, estos compuestos están en forma ópticamente activa. La invención se relaciona con isómeros puros, tales como enantiómeros y diastereómeros, así como también con todas las mezclas posibles de isómeros, por ejemplo, mezclas de diastereómeros, racematos o mezclas de racematos.

Dentro de la presente especificación alquilo denota metilo, etilo, n-propilo e isopropilo. El alquilo no ramificado es el preferido. El alquilo como parte de otro radical es tales como alcoxi, alquilo, etc. se entiende en una forma análoga. El halógeno se entenderá generalmente como significando flúor, cloro, bromo, o yodo. Flúor, cloro o bromo son los significados preferidos. El halógeno como parte de otros radicales tales como haloalquilo, haloalcoxi, etc.; se entiende de manera análoga.

El bicicloalquilo es, dependiendo el tamaño del anillo, biciclo[2.1.1]hexano, biciclo[2.2.1]heptano,

biciclo [2.2.2]octano, biciclo[3.2.1]octano,
biciclo[3.2.2]nonano, biciclo[4.2.2]decano,
biciclo[4.3.2]undecano, adamantano y similares.

Bicicloalquenilo es biciclo [2.1.1]hex-4-eno,
biciclo[2.2.1]hept-2-eno, biciclo[2.2.2]oct-2-eno y
similares.

Bicicloalcadienilo es biciclo[2.2.1]hepta -2,5-
dieno, biciclo[2.2.2]octa-2,5-dieno, y similares.

Un subgrupo específico de los compuestos de fórmula
I es el grupo donde X es oxígeno.

Otro subgrupo específico de los compuestos de
fórmula I es el grupo donde X es azufre.

Los subgrupos preferidos de compuestos de fórmula 1
son aquellos en donde

X es oxígeno: o

X es azufre; o

R₁ es CF₃; O

R₁ es CF₂H; o

R_1 es CFH_2 ; o

R_2 es alquilo $\text{C}_1\text{-C}_3$; o

R_2 es haloalquilo $\text{C}_1\text{-C}_3$; o

R_2 es alcoxi $\text{C}_1\text{-C}_3$ alquilo- $\text{C}_1\text{-C}_3$; o

R_2 es haloalcoxi $\text{C}_1\text{-C}_3$ alquilo- $\text{C}_1\text{-C}_3$.o

R_2 es alquilo $\text{C}_1\text{-C}_3$ o haloalquilo $\text{C}_1\text{-C}_3$; o

R_2 es alquilo $\text{C}_1\text{-C}_3$, haloalquilo $\text{C}_1\text{-C}_3$ o alcoxi
 $\text{C}_1\text{-C}_3$ alquilo- $\text{C}_1\text{-C}_3$; o

R_2 es metilo o CH_2OCH_3 ; o

R_2 es metilo; o

R_3 es hidrógeno; o

R_3 es metilo; o

R_3 es CF_3 ; o

R_3 es flúor; o

R_3 es hidrógeno o flúor; o

Q es Q1; o

Q es Q2, Q3 o Q4; o

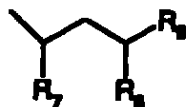
Q es Q2; o

Q es Q3; o

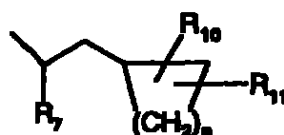
Q es Q4; o

R_4 es bicicloalquilo $\text{C}_6\text{-C}_{10}$ no sustituido o
sustituido por metilo, etilo o CF_3 ; o
bicicloalquenilo $\text{C}_6\text{-C}_{10}$ no sustituido o sustituido por
metilo, etilo o CF_3 ; o bicicloalcadienilo $\text{C}_6\text{-C}_{10}$ no

sustituido o sustituido por metilo, etilo o CF_3 ; o un grupo de la forma



Donde R_7 , R_8 y R_9 son independientemente uno del otro alquilo $\text{C}_1\text{-C}_3$ o haloalquilo $\text{C}_1\text{-C}_3$; o un grupo

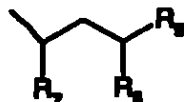


Donde R_{10} y R_{11} son independientemente uno del otro hidrógeno o halógeno y $n = 1$ o 2 ; o

R_4 es bicicloalquilo $\text{C}_6\text{-C}_{10}$ no sustituido o sustituido por metilo, etilo o CF_3 ,

Bicicloalquenilo $\text{C}_6\text{-C}_{10}$ no sustituido o sustituido por metilo, etilo CF_3 ,

bicicloalcadieniloC₆-C₁₀ no sustituido o sustituido por metilo, etilo o CF₃, o un grupo de la forma



Donde R₇, R₈ y R₉ son independientemente uno del otro alquiloC₁-C₃ o haloalquiloC₁-C₃; y

R₅ y R₆ son independientemente uno del otro hidrógeno, cloro, bromo o flúor; o

R₅ y R₆ son independientemente uno del otro hidrógeno, cloro o flúor; o

R₅ es hidrógeno y R₆ es cloro o flúor.

Los subgrupos adicionalmente preferidos son aquellos donde

a) X es oxígeno;

R₁ es CF₃;

R₂ es alquilo C₁-C₃ o alcoxi C₁-C₃ alquilo C₁-C₃;

R_3 es hidrógeno o flúor;

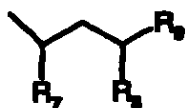
Q es Q_1 ;

R_4 es bicicloalquilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

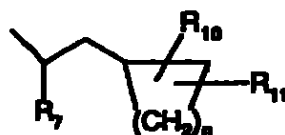
Bicicloalquenilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

Bicicloalcadienilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

un grupo de la fórmula



donde R_7 , R_8 y R_9 son independientemente uno del otro alquilo C_1-C_3 o haloalquilo C_1-C_3 ; o un grupo



Donde R_{10} y R_{11} son independientemente uno del otro hidrógeno o halógeno y $n = 1$ o 2 ; y

R_5 y R_6 son independientemente uno del otro hidrógeno flúor, cloro o bromo; o

b) X es oxígeno;

R_1 es CF_3 ;

R_2 es alquilo C_1-C_3 o haloalquilo C_1-C_3 ;

R_3 es hidrógeno o flúor;

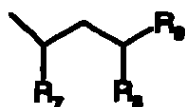
Q es Q2, Q3 o Q4;

R_4 es bicicloalquilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

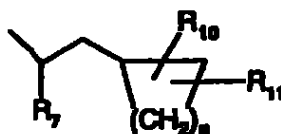
Bicicloalquenilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

Bicicloalcadienilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

un grupo de la forma



donde R_7 , R_8 y R_9 son independientemente uno del otro alquilo C_1-C_3 o haloalquilo C_1-C_3 ; o un grupo



Donde R_{10} y R_{11} son independientemente uno del otro hidrógeno o halógeno y $n = 1$ o 2 ; y

R_5 y R_6 son independientemente uno del otro hidrógeno, flúor, cloro, o bromo; y entre este subgrupo $Q = Q2$ es preferido; o

ab) X es oxígeno;

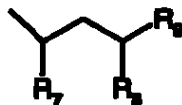
R_1 es CF_3 ;

R_2 es metilo o CH_2OCH_3 ;

R_3 es hidrógeno o flúor;

Q es Q1;

R_4 es un grupo de la forma



donde R_7 , R_8 y R_9 son independientemente uno del otro alquilo C_1-C_3 o haloalquilo C_1-C_3 ; y

R_5 y R_6 son independientemente uno del otro hidrógeno, flúor, cloro o bromo; o

c) X es oxígeno;

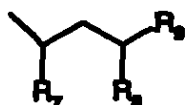
R_1 es CF_3 ;

R_2 es metilo;

R_3 es hidrógeno o flúor;

Q es Q1;

R_4 es un grupo de la forma



donde R_7 , R_8 y R_9 son independientemente uno del otro CF_3 , metilo o etilo, preferiblemente metilo; y

R_5 y R_6 son independientemente uno del otro hidrógeno, flúor, o cloro; o

d) X es oxígeno;

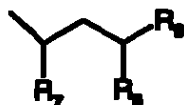
R_1 es CF_3 ;

R_2 es metilo;

R_3 es hidrógeno;

Q es $Q1$;

R_4 es un grupo de la forma



donde R_7 , R_8 y R_9 son independientemente uno del otro metilo o etilo, preferiblemente metilo; y

R_5 y R_6 son independientemente uno del otro hidrógeno, flúor, o cloro; o

e) X es oxígeno;

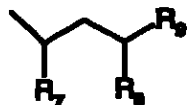
R_1 es CF_3 ;

R_2 es metilo;

R_3 es flúor;

Q es $Q1$;

R_4 es un grupo de la forma



donde R_7 , R_8 y R_9 son independientemente uno del otro metilo o etilo, preferiblemente metilo; y

R_5 y R_6 son independientemente uno del otro hidrógeno, flúor, o cloro o.

f) X es azufre;

R_1 es CF_3 ;

R_2 es alquilo C_1-C_3 o haloalquilo C_1-C_3 ;

R_3 es hidrógeno o flúor;

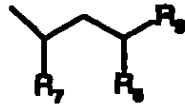
Q es Q1;

R_4 es bicicloalquilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

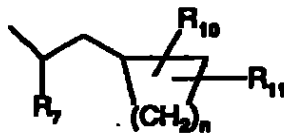
Bicicloalquenilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

Bicicloalcadienilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

un grupo de la forma



donde R_7 , R_8 y R_9 son independientemente uno del otro alquilo C_1-C_3 o haloalquilo C_1-C_3 ; o un grupo



Donde R_{10} y R_{11} son independientemente uno del otro hidrógeno o halógeno y $n = 1$ o 2 ; y

R_5 y R_6 son independientemente uno del otro hidrógeno, flúor, cloro, o bromo; o

g) X es azufre;

R_1 es CF_3 ;

R_2 es alquilo C_1-C_3 o haloalquilo C_1-C_3 ;

R_3 es hidrógeno o flúor;

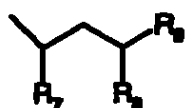
Q es Q2, Q3 o Q4;

R_4 es bicicloalquilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

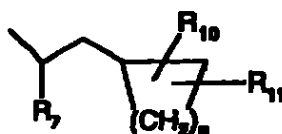
Bicicloalquenilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

Bicicloalcadienilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

un grupo de la forma



donde R_7 , R_8 y R_9 son independientemente uno del otro alquilo C_1-C_3 o haloalquilo C_1-C_3 ; o un grupo



Donde R_{10} y R_{11} son independientemente uno del otro hidrógeno o halógeno y $n = 1$ o 2 ; y

R_5 y R_6 son independientemente uno del otro hidrógeno, flúor, cloro, o bromo.

Otros subgrupos de compuestos de fórmula I son aquellos en donde

h) X es oxígeno o azufre;

R_1 es CF_3 ;

R_2 es alquilo C_1-C_3 o haloalquilo C_1-C_3 o alcoxi C_1-C_3
- alquilo C_1-C_3 ;

R_3 es hidrógeno o flúor;

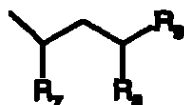
Q es Q_1 ;

R_4 es bicicloalquilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

Bicicloalquenilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

Bicicloalcadienilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ;

un grupo de la forma



donde R_7 , R_8 y R_9 son independientemente uno del otro alquilo C_1-C_3 o haloalquilo C_1-C_3 ; y

R_5 y R_6 son independientemente uno del otro hidrógeno, cloro, o flúor; o

i) X es oxígeno o azufre;

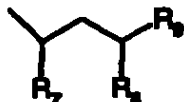
R_1 es CF_3 ;

R_2 es alquilo C_1-C_3 , haloalquilo C_1-C_3 o alcoxi C_1-C_3 - alquilo C_1-C_3 ;

R_3 es hidrógeno o flúor;

Q es Q_1 ;

R_4 es un grupo de la forma



donde R_7 , R_8 y R_9 son independientemente uno del otro alquilo C_1-C_3 o haloalquilo C_1-C_3 ; y

R_5 y R_6 son independientemente uno del otro hidrógeno, cloro, o flúor; o

j) X es oxígeno o azufre;

R₁ es CF₃;

R₂ es alquilo C₁-C₃, haloalquilo C₁-C₃ o alcoxi C₁-C₃ -
alquilo C₁-C₃;

R₃ es hidrógeno o flúor;

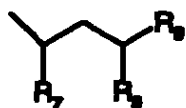
Q es Q₂, Q₃ o Q₄;

R₄ es bicicloalquilo C₆-C₁₀ no sustituido o
sustituido por metilo, etilo o CF₃; o

Bicicloalquenilo C₆-C₁₀ no sustituido o sustituido
por metilo, etilo o CF₃; o

Bicicloalcadienilo C₆-C₁₀ no sustituido o sustituido
por metilo, etilo o CF₃;

un grupo de la forma



donde R₇, R₈ y R₉ son independientemente uno del otro
alquilo C₁-C₃ o haloalquilo C₁-C₃; y

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70

R_5 y R_6 son independientemente uno del otro hidrógeno, cloro, o flúor; o

K) X es oxígeno o azufre;

R_1 es CF_3 ;

R_2 es alquilo C_1-C_3 , haloalquilo C_1-C_3 o alcoxi C_1-C_3 - alquilo C_1-C_3 ;

R_3 es hidrógeno o flúor;

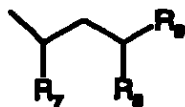
Q es Q2;

R_4 es bicicloalquilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

Bicicloalquenilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

Bicicloalcadienilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ;

un grupo de la forma



donde R_7 , R_8 y R_9 son independientemente uno del otro alquilo C_1-C_3 o haloalquilo C_1-C_3 ; y

R_5 y R_6 son independientemente uno del otro hidrógeno, cloro, o flúor; o

1) X es oxígeno o azufre;

R_1 es CF_3 ;

R_2 es alquilo C_1-C_3 , haloalquilo C_1-C_3 o alcoxi C_1-C_3 - alquilo C_1-C_3 ;

R_3 es hidrógeno o flúor;

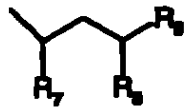
Q es Q_1 ;

R_4 es bicicloalquilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

Bicicloalquenilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

Bicicloalcadienilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ;

un grupo de la forma



donde R₇, R₈ y R₉ son independientemente uno del otro alquilo C₁-C₃ o haloalquilo C₁-C₃; y

R₅ y R₆ son independientemente uno del otro hidrógeno, cloro, o flúor; o

m) X es oxígeno;

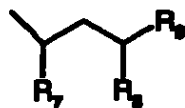
R₁ es CH₂F o CF₂H;

R₂ es metilo o CH₂OCH₃;

R₃ es hidrógeno o flúor;

Q es Q₁;

R₄ es un grupo de la forma



donde R₇, R₈ y R₉ son independientemente uno del otro alquilo C₁-C₃ o haloalquilo C₁-C₃; y

R_5 y R_6 son independientemente uno del otro hidrógeno, cloro, o flúor; o

n) X es oxígeno o azufre;

R_1 es CH_2F o CF_2H ;

R_2 es alquilo $\text{C}_1\text{-C}_3$, haloalquilo $\text{C}_1\text{-C}_3$ o alcoxi $\text{C}_1\text{-C}_3$ - alquilo $\text{C}_1\text{-C}_3$;

R_3 es hidrógeno o flúor;

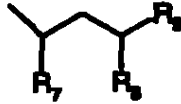
Q es Q2, Q3 o Q4;

R_4 es bicicloalquilo $\text{C}_6\text{-C}_{10}$ no sustituido o sustituido por metilo, etilo o CF_3 ; o

Bicicloalquenilo $\text{C}_6\text{-C}_{10}$ no sustituido o sustituido por metilo, etilo o CF_3 ; o

Bicicloalcadienilo $\text{C}_6\text{-C}_{10}$ no sustituido o sustituido por metilo, etilo o CF_3 ;

un grupo de la forma



donde R₇, R₈ y R₉ son independientemente uno del otro alquilo C₁-C₃ o haloalquilo C₁-C₃; y .

R₅ y R₆ son independientemente uno del otro hidrógeno, cloro, o flúor; o

o) X es oxígeno;

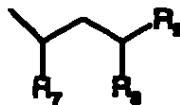
R₁ es CH₂F o CF₂H;

R₂ es metilo o CH₂OCH₃;

R₃ es hidrógeno o flúor;

Q es Q₂, Q₃ o Q₄;

R₄ es un grupo de la forma



donde R₇, R₈ y R₉ son independientemente uno del otro alquilo C₁-C₃ o haloalquilo C₁-C₃; y

R₅ y R₆ son independientemente uno del otro hidrógeno, cloro, o flúor. Compuestos individuales preferidos son:

Ácido 1-metil-4-trifluorometil-1H-pirrol-3-carboxílico [2-(1,3-dimetilbutil)fenil]amida;

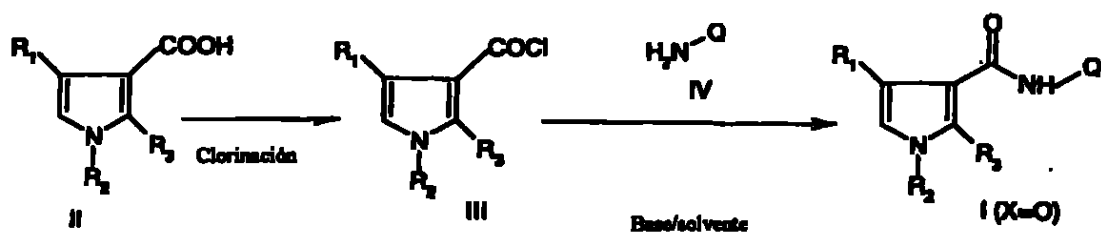
Ácido 1-metoximetil-4-trifluorometil-1H-pirrol-3-carboxílico [2-(1,3-dimetilbutil)fenil]amida;

Ácido 1-metil-2-fluoro-trifluorometil-1H-pirrol-3-carboxílico [2-(1,3-dimetilbutil)fenil]amida;

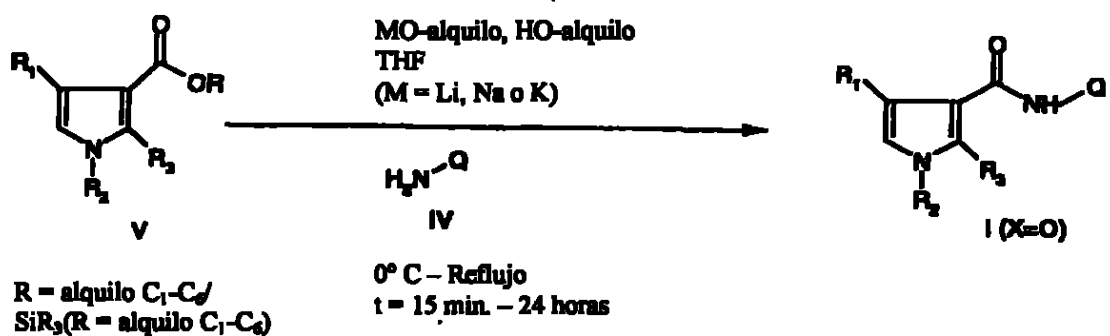
Ácido 1-metoximetil-2-fluoro-4-trifluorometil-1H-pirrol-3-carboxílico [2-(1,3-dimetilbutil)fenil]amida;

Ácido 1-metil-4-trifluorometil-1H-pirrol-3-carboxílico [2-(1,3-dimetilbutil)fenil]amida.

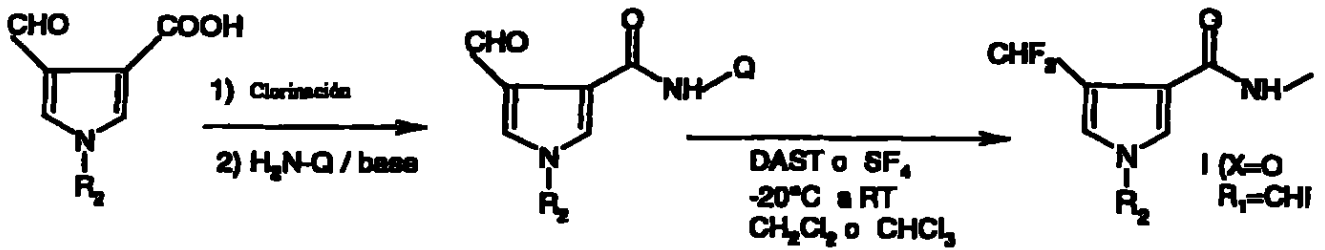
Los compuestos de acuerdo con la fórmula I en donde X es oxígeno se pueden preparar de acuerdo al siguiente esquema de reacción 1A.

ESQUEMA 1A

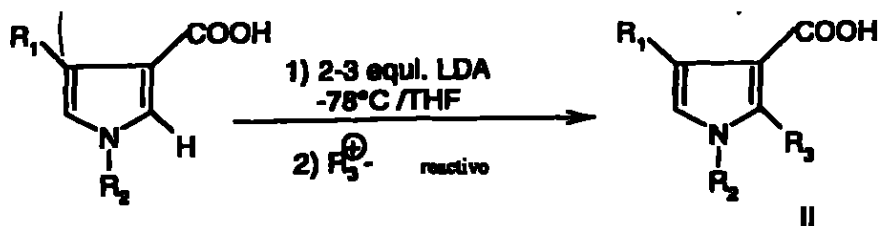
Los compuestos de acuerdo con la fórmula I en donde X es oxígeno también se pueden preparar a partir de los ésteres correspondientes de acuerdo al esquema de reacción 1B.

ESQUEMA 1B

Un método adicional para la síntesis de los compuestos de la fórmula I se bosqueja en el esquema 1C.

ESQUEMA 1C

La síntesis de pirrol de ácidos carboxílicos de fórmula II en donde R_3 no es hidrógeno puede ser conducido de acuerdo al esquema 2A.

ESQUEMA 2A

R_3^+ - reactivos: $\text{F}^+=\text{N}$ -fluoro-bis(fenilsulfonil)amina,

N-fluoro-N-metil-tolueno-4-sulfonamida, 2-fluoro-3,3-dimetil-2,3-dihidro-1,2-benzisotiazol-1,1-dióxido, 1-fluoro-sym.-colidiniotetrafluoroborato

28

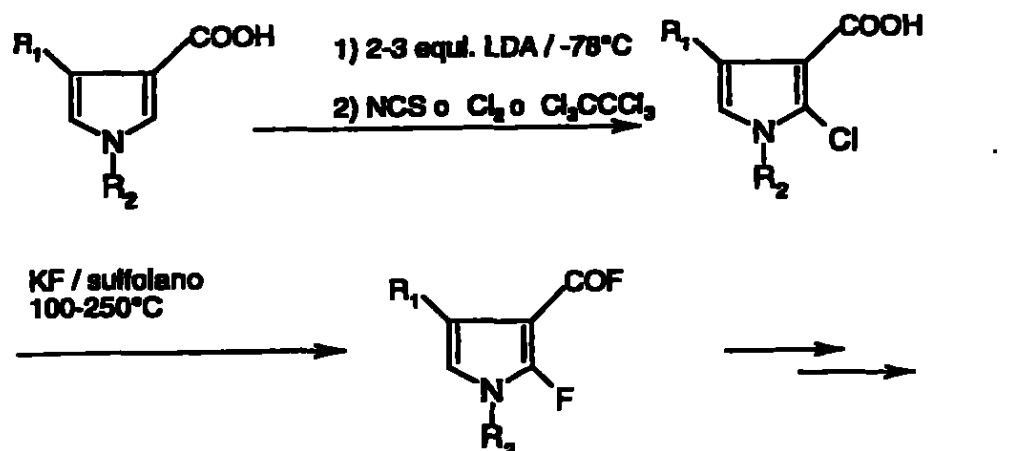
$\text{Me}^{\oplus} = \text{MeI}, \text{MeBr}, \text{DMS (dimetilsulfato)}$

$\text{Cl}^{\oplus} = \text{NCS}, \text{Cl}_2, \text{hexacloroetano}$

$\text{LDA} = \text{litioldiisopropilamida}$

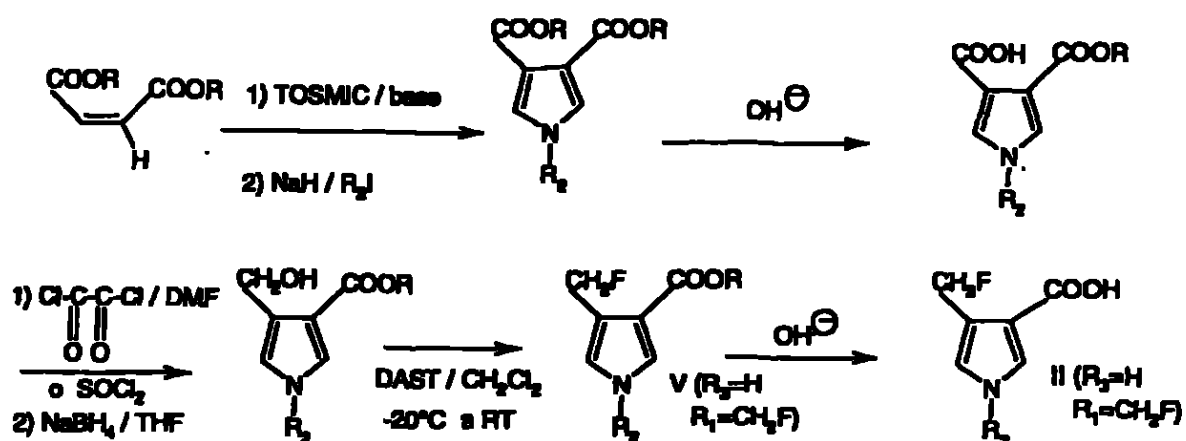
La síntesis de los ácidos carboxílicos de pirrol de la fórmula II en donde $\text{R}_3 = \text{H}$ se describen en WO-00/09482.

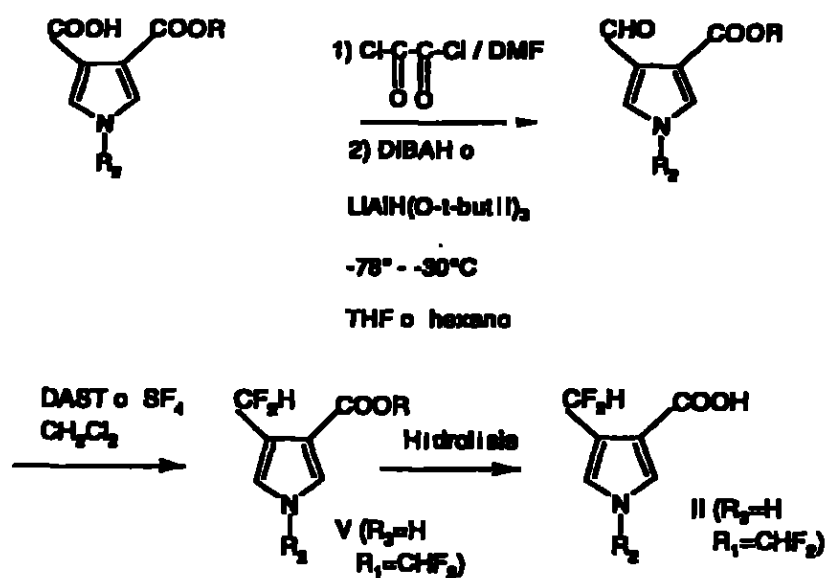
Alternativamente el fluoruro de ácido carboxílico de pirrol en donde R_3 es flúor puede ser obtenido como se bosqueja en el esquema 2B



La síntesis de ácidos carboxílicos de pirrol II también pueden ser conducidos de acuerdo a los esquemas 2C o 2D.

ESQUEMA 2C

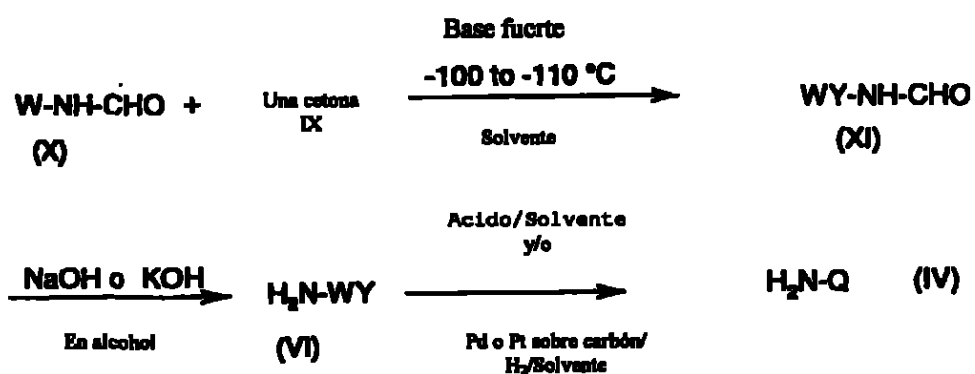


ESQUEMA 2D

Los Intermedios de amina $\text{NH}_2\text{-Q}$ de la fórmula IV se pueden preparar de acuerdo a las siguientes reacciones como se bosqueja en el esquema 3.

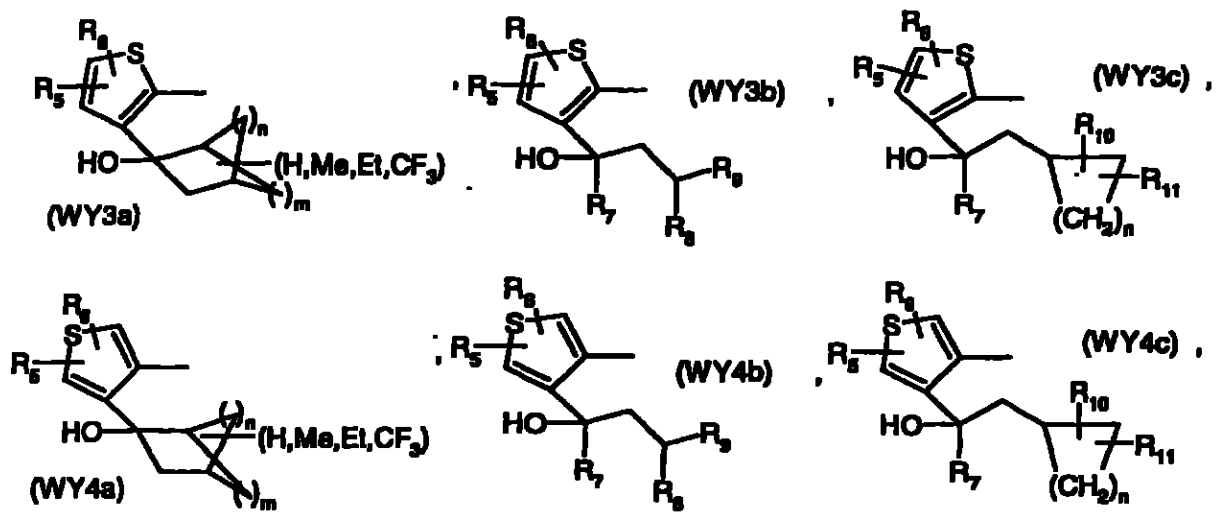
ESQUEMA 3

Ruta a)



En donde Q, R5, R6, R7, R8, R9, R10, R11 y n son como se describió para los compuestos de fórmula I, Hal es Br o I; base fuerte e n-BuLi, tert.-BuLi, PhLi; y

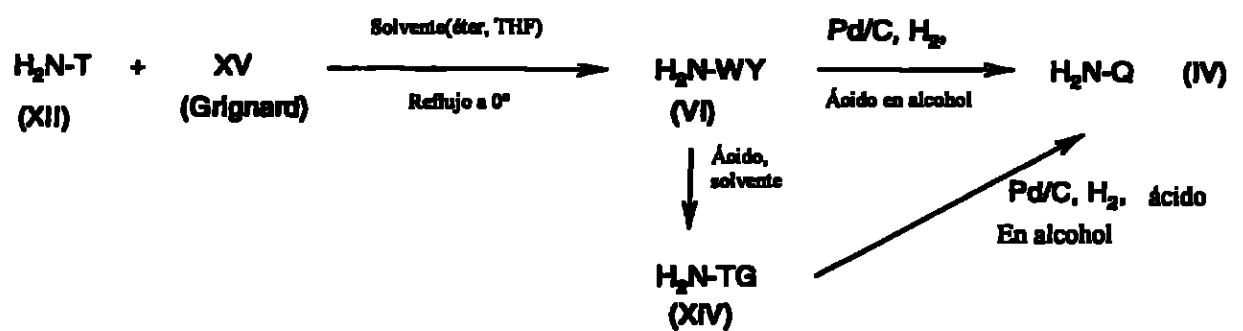
En donde



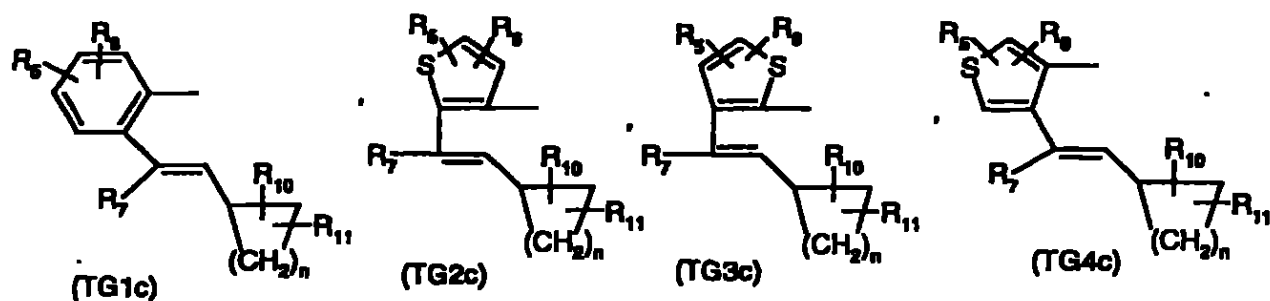
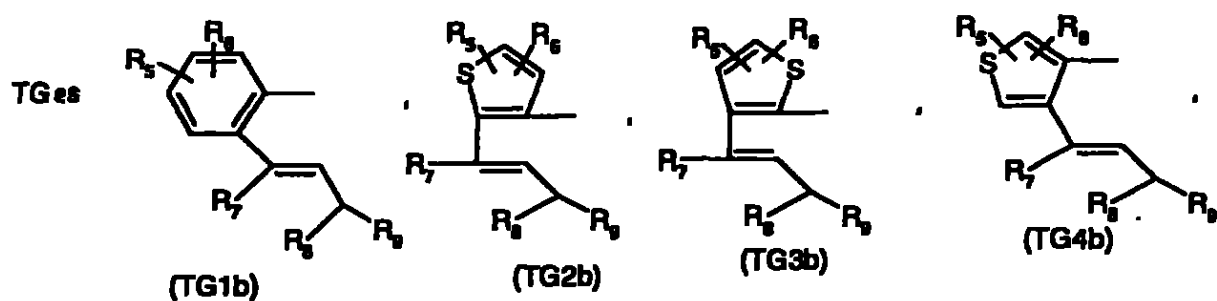
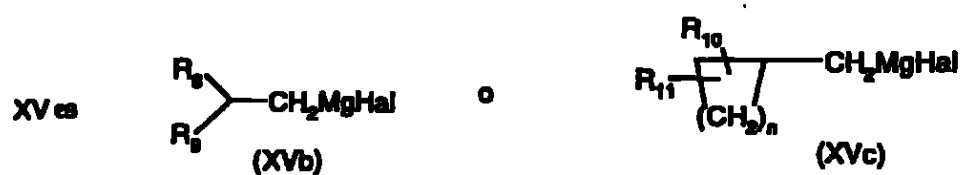
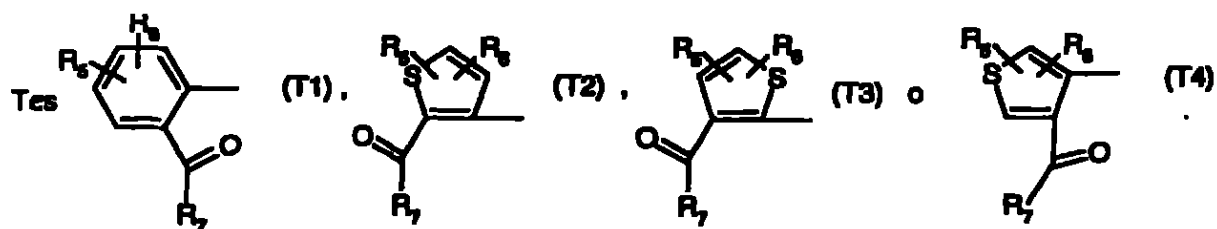
$$y + n + m = 2 - 10$$

o

Ruta b)



En donde

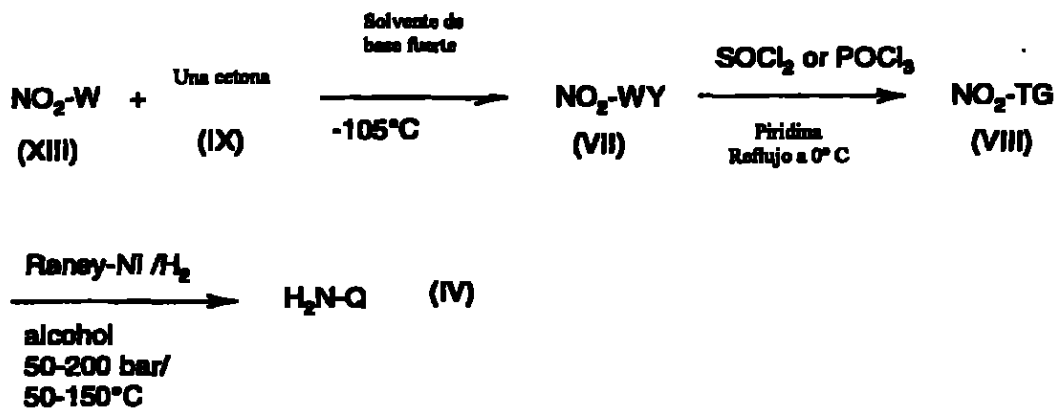


Y donde las mezclas isoméricas son posibles en el enlace doble.

85

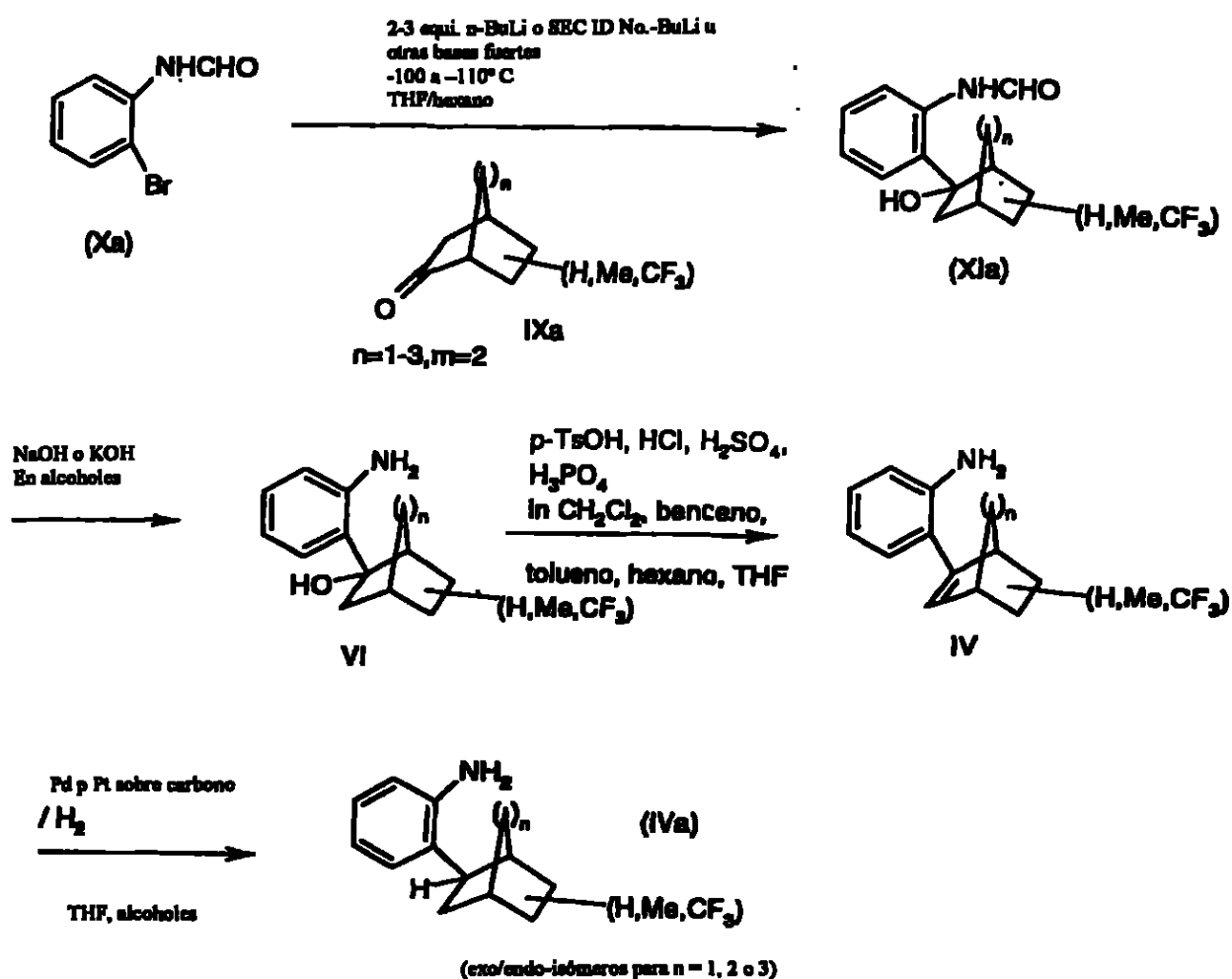
O

Ruta c)



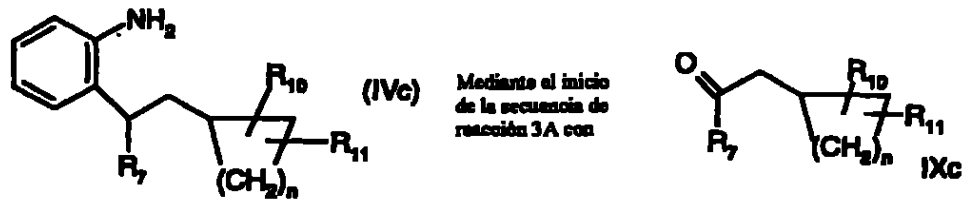
Aminas específicas de la fórmula IV pueden ser preparadas como sigue:

-- Las aminas $\text{H}_2\text{N-Q}$ de la fórmula IV, en donde Q = Q1 como se definió en la fórmula I y R4 es bicicloalquilo o bicicloalcadienilo y R5 y R6 son hidrógeno se pueden obtener de acuerdo al esquema 3A (Ruta a).



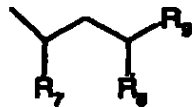
Para la síntesis de 2-biciclo[2.2.1]hept-2-il fenilamina y otros biciclosistemas ver por ejemplo EP-116044.

De acuerdo al esquema 3^a los siguientes compuestos también están disponibles:

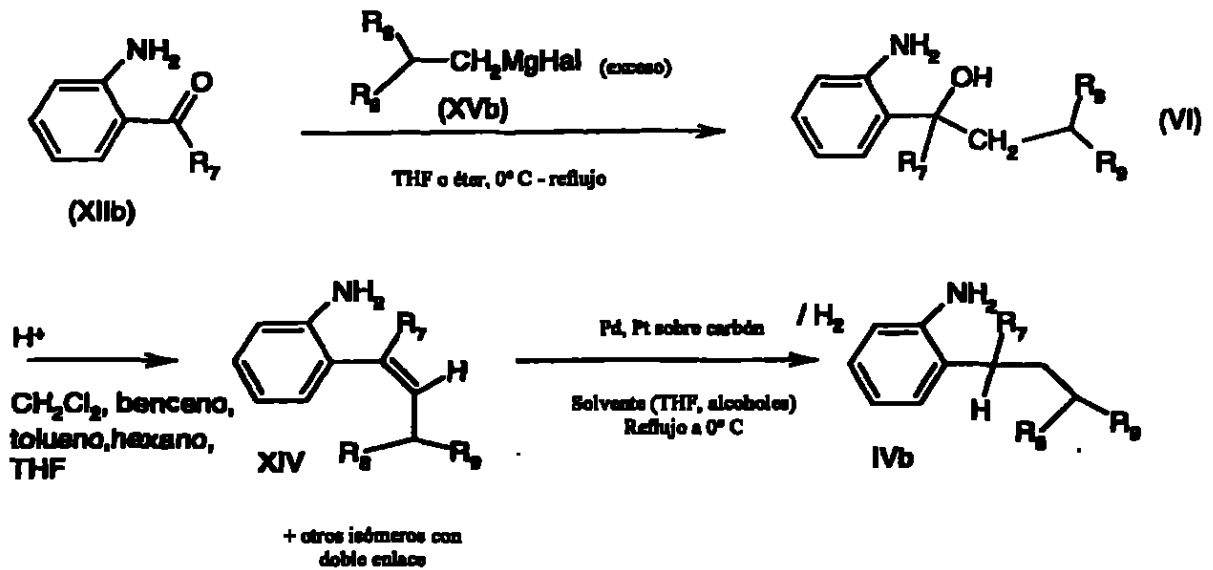


En donde R_5 y R_6 son hidrógeno y R_7 , R_{10} , R_{11} y n son como se definió para la fórmula I.

-- Las aminas H_2N-Q en donde Q es Q_1 y R_4 es un grupo de la forma

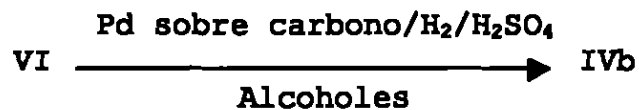


R_5 y R_7 son hidrógeno y R_7 , R_8 y R_9 son como se definió para la fórmula I se pueden obtener de acuerdo al esquema 3B (ruta b).

ESQUEMA 3B

(otras síntesis o anilinas orto-alquil sustituidas también se describen en la EP-824099)

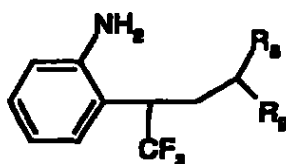
o en una etapa de hidrogenación del grupo OH de los compuestos de fórmula VI



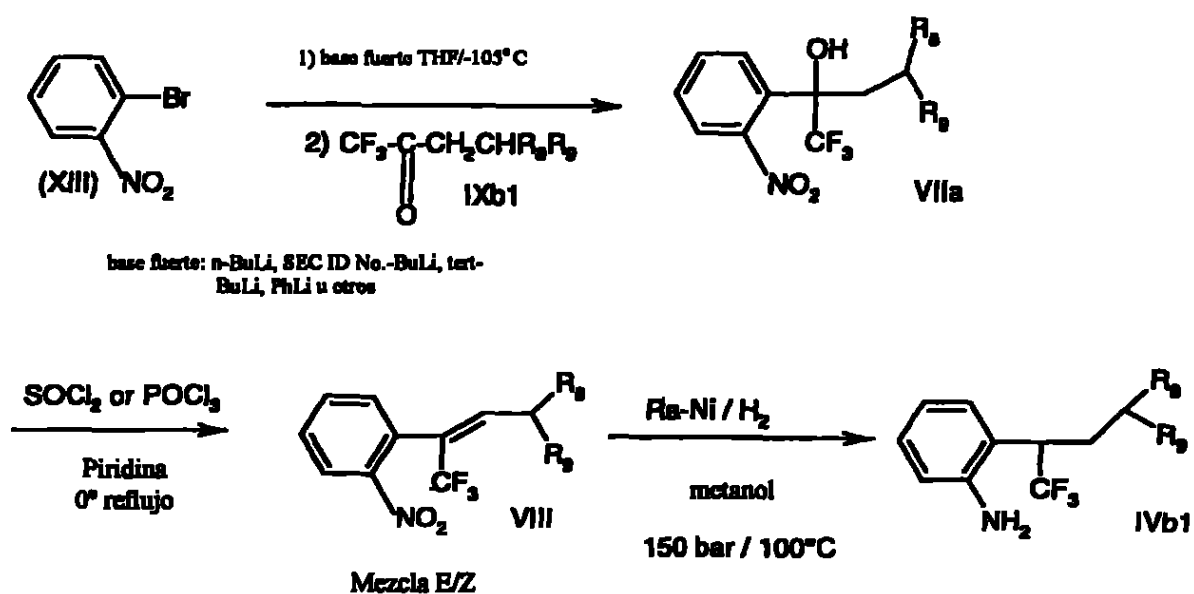
Otras síntesis de los intermedios de amina se resaltan en el esquema 3C (ruta c).

ESQUEMA 3C

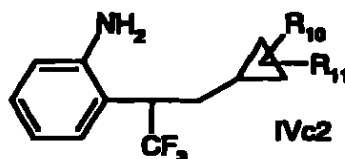
Para los compuestos de fórmula IVb1



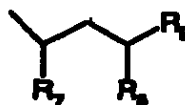
Donde R_7 es CF_3 , R_8 y R_9 son hidrógeno y R_8 y R_9 son como se definió para la fórmula I



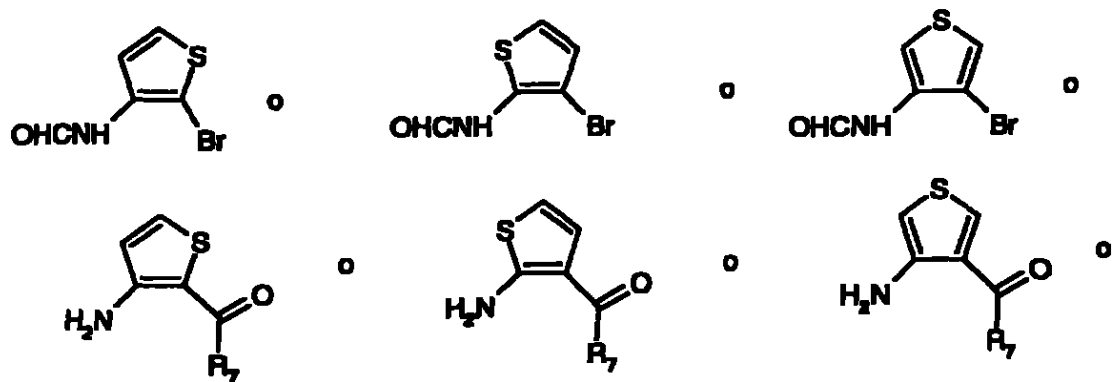
utilizando la secuencia de reacción destacada en el esquema 3C de los compuestos de fórmula IVc2 en donde R_5 y R_6 son hidrógeno, R_7 CF_3 , $n=1$ y R_{10} y R_{11} son como se definió para la fórmula I también están disponibles



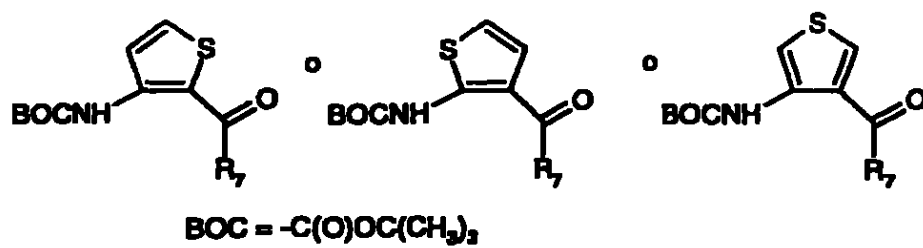
- la síntesis de las aminas IV en donde Q es Q2, Q3 o Q4, R_5 y R_6 son hidrógeno y R_4 es bicicloalquilo, bicicloalquenilo, bicicloalcadienilo o un grupo de la fórmula



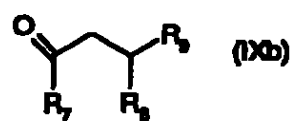
y en donde R_7 , R_8 y R_9 son como se definió para la fórmula I se pueden obtener de acuerdo al esquema 3A) o 3B) iniciando desde los siguientes correspondientes derivados tienilo



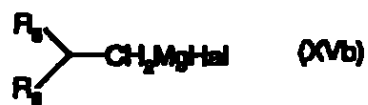
(Aminotiofenos protegidos)



y reaccionan con la cetona IXa o IXb



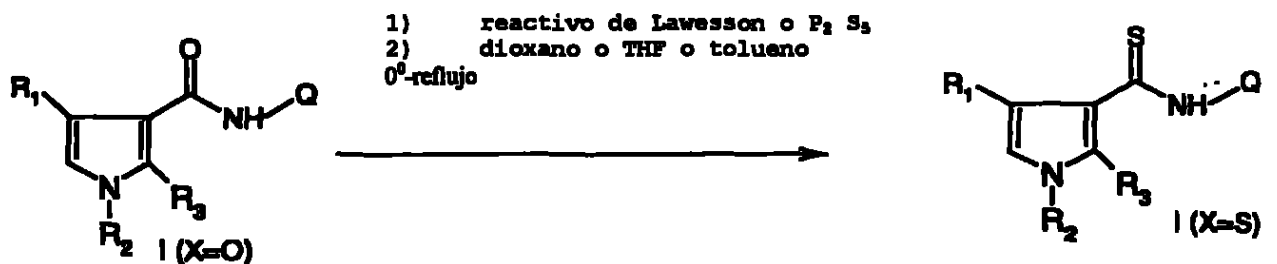
o el reactivo de Grignard XVb



La presente invención también se relaciona con cetonas novedosas de la fórmula IX.

Las amidas de ácido carbotioico de la fórmula I, donde X=S se pueden obtener de los compuestos de fórmula I en donde X=O de acuerdo al esquema 4.

ESQUEMA 4



Los siguientes derivados de fenilamina de la fórmula IV son nuevos y parte de la invención:

2-biciclo[2.2.2]oct-2-il-fenilamina;

2-biciclo[2.2.2]oct-2-en-2-il-fenilamina;

2-biciclo[2.2.2]octa-2,5-dien-2-il-fenilamina;

2-(2-aminofenil)-1,1,1-trifluorometil-4-metil-pentan-2-ol;

2-(2-aminofenil)-1-ciclopropil-propan-2-ol;

2-(2-aminofenil)-1-ciclopropil-butan-2-ol;

2-(3-metil-1-trifluorometil-but-1-enil)-fenilamina;

2-(3-metil-1-trifluorometil-butil)fenilamina;

2-(2-ciclopropil-1-metil-etil)fenilamina; y

2-(1-ciclopropilmetil-propil)fenilamina.

Sorprendentemente, se ha encontrado ahora que los compuestos novedosos de la fórmula I tienen, para propósitos prácticos, un espectro muy ventajoso de actividades para proteger plantas contra enfermedades que son causadas por hongos así como también bacteria y virus.

Los compuestos de la fórmula I se pueden utilizar en el sector agrícola y campos relacionados de uso como ingredientes activos para controlar plagas de plantas. Los compuestos novedosos se distinguen por la excelente actividad a bajas proporciones de aplicación, siendo bien toleradas por la plantas y siendo ambientalmente seguras. Ellas tienen propiedades muy útiles curativas, preventivas y sistémicas y se utilizan para proteger

numerosas plantas cultivadas. Los compuestos de fórmula I se pueden utilizar inhibir o destruir las plagas que se presentan en las plantas o partes de las plantas (frutas, flores, hojas, tallos, tubérculos, raíces) o diferentes cultivos de plantas útiles, mientras que a la vez se protegen también aquellas partes de las plantas que crecen posteriormente por ejemplo de microorganismos patógenos.

También es posible utilizar compuestos de fórmula I como agentes de recubrimiento para el tratamiento de material de propagación vegetal, en particular de semillas (frutas, tubérculos, granos) y plantas cortadas (por ejemplo arroz), para la protección contra infecciones fungosas así como también contra la ocurrencia de hongos fitopatógenos en el suelo.

Los compuestos I son, por ejemplo, efectivos contra los hongos fitopatógenos de las siguientes clases: hongos imperfectos (por ejemplo Botritis, Piricularia, Helminthosporium, Fusarium, Septoria, Cercospora y Alternaria) y basidiomicetes (por ejemplo rizoctonia, hemileia, puccinia). Adicionalmente, ellos también son efectivos contra las clases de ascomicetes (por ejemplo

Venturia y Erisite, Podosfera, Monilinia, Uncinula) y de las clases Oomicetes (por ejemplo fitoptora, fitiun, plasmopara). La actividad restante se ha observado contra mildew pulverulento (Erisife spp.). Adicionalmente, los compuestos novedosos de la fórmula I son efectivos contra bacterias fitopatógenas y virus (por ejemplo contra Xantomonas spp, Seudomonas spp, Erwinia amilovora así como también contra el virus del mosaico del tabaco).

Dentro del alcance de la presente invención, los cultivos objeto a ser protegidos típicamente comprende las siguientes especies de plantas: cereales (trigo, cebada, centeno, avena, arroz, maíz, sorgo y especies relacionadas); remolacha (remolacha dulce y remolacha forragera); pomos, drupas y frutas suaves (manzanas, peras, ciruelos, melocotones, almendras; cerezas, fresas, frambuesas y zarzamora); plantas leguminosas (frijoles, lentejas, arvejas, soya); plantas de aceite (colza, mostaza, haba, olivas, girasoles, coco, plantas de aceite de castor, semillas de cacao, cacahuete); plantas de cocombro (calabazas, cocombros, melones); plantas de fibra (algodón, lino, cáñamo, yute); frutas cítricas (naranjas, limones, toronjas, mandarinas); vegetales (espinaca, lechuga, espárragos, repollos, zanahorias,

cebollas, tomates, papas, papricas); lauraceas (aguacate, canela, alcanfor) o plantas tales como tabaco, nueces, café, plantas huevo, caña de azúcar, te, pimienta, vides, lúpulo, bananas, y plantas de caucho natural, así como también ornamentales.

Los compuestos de fórmula I son utilizados en forma no modificada o, preferiblemente, junto ayudantes convencionalmente empleados en la técnica de formulación. Para este fin ellos son convenientemente formulados de maneras conocidas para concentrados emulsificables, pastas recubribles, soluciones directamente rociables o diluibles, emulsiones diluidas, polvos humectables, polvos solubles, polvos granulados, y también encapsulaciones, por ejemplo en sustancias poliméricas. Como con el tipo de composiciones, los métodos de aplicación, tales como rociado, atomización, espolvoreado, dispersión, recubrimiento o vertimientos, se escogen de acuerdo con los objetivos pretendidos y las circunstancias prevalentes. Las composiciones también pueden contener ayudantes adicionales tales como estabilizadores, antiespumantes, reguladores de viscosidad, ligadores o elementos que producen pegajosidad así como también fertilizantes, donadores de

micronutrientes gotas formulaciones para obtener efectos especiales.

Los portadores adecuados y ayudantes pueden ser sólidos o líquidos y son sustancias útiles en la tecnología de formulación, por ejemplo sustancias minerales naturales o regeneradas, solventes, dispersantes, agentes humectantes, elementos que producen pegajosidad, espesantes, ligadores o fertilizantes. Tales portadores son por ejemplo descritos en WO 97/33890.

Compuestos de fórmula I son normalmente utilizados en la forma de composiciones y se pueden aplicar al área de cultivo o la planta a ser tratada, simultáneamente o en sucesión con compuestos adicionales. Estos compuestos adicionales también pueden ser por ejemplo fertilizantes o donadores de micronutrientes o u otras preparaciones que influyen el crecimiento de las plantas. Ellas también se pueden ser herbicidas selectivos así como también insecticidas, fungicidas, bactericidas, nematocidas, moluscicidas, y mezclas de varias de estas preparaciones, si se desea junto con portadores adicionales, tensoactivos o ayudantes que pongan la

aplicación empleados de costumbre en la técnica de formulación. Los compuestos de la fórmula I se pueden mezclar con otros fungicidas, dando como resultado en algunos casos actividades sinérgicas inesperadas.

Componentes mezclados que son particularmente preferidos son los azoles tales como azaconazol, bitertanol, propiconazol, difenoconazol, diniconazol, ciproconazol, epoxiconazol, fluquinconazol, flusilazol, flutriafol, hexaconazol, imizalil, imibenconazol, ipconazol, tebuconazol, tetraconazol, fenbuconazol, metconazol, miclobutanilo, perfurazoato, penconazol, bromuconazol, pirifenox, procloraz, triadimefon, triadimenol, triflumisol o triticonazol; pirimidil carbinos tales como ansimidol, fenamirol o nuarimol; 2-amino-pirimidina tales como bupirimato, dimetirimol o etirimol, morfolinas tales como dodemor, fenpropidina, fenpropimor, expirosamina o tridermor; anilinopiridimina tales como ciprodinilo pirimetanilo o mepanipirin; pirroles tales como fenciclonil, o fludioxonil; fenilamidas tales como benalaxilo, furalaxilo, metalaxilo, R-metalaxilo, ofurace u oxadixilo; benzimidazoles tales como benomilo, carbendazim, debacarb, fuberidazola o tiabendazol; dicarboximidas tales como clozolinato,

diclozolina, iprodina, miclozolina, procimidona o vinclozolina; carboxamidas tales como carboxina, fenfuram, flutolanil, nepronil, oxicarboxin o tifluzamida; guanidinas tales como guazatina, dodina o iminoctadina; estrobilurinas tales como azoxistrobina, cresoximetil, metominostrobin, SSF-129, metil 2-[(2-trifluorometil)-pirid-6-iloximetil]-3-metoxiacrilato ácido 2-[α{[(α-metil-3-trifluorometil-benzil)imino]-oxi]-o-tolil]-glioxílico-metiléster-O-metiloxioma (trifloxistrobina); ditiocarbamatos tales como ferbam, mancozeb, maneb, metiram, propineb, tiram, zineb o ziram; N-halometiltio-dicarboximidas tales como captafol, captan, diclofuanid, fluoromida, folteb o toliflunamid; compuestos de cobre tales como mezclas de Bordeaux, hidróxido de cobre, oxiclórico de cobre, sulfato de cobre, óxido cuproso, "mancopper" u oxina-cobre; derivados de nitrofenol tales como dinocap o nitrofenol isopropilo; derivados organofosforados tales como edifendos, iprobenfos, isoprothiolano, fosdifen, pirazofos o toclofos-metilo; y otros compuestos de estructuras diversas tales como acibenzolar-S-metilo, anilazina, blastocidín-S, quinometionat, cloroneb, clorotalonilo, cimoxanilo, diclona, diclomezina, dicloran, diclofencarb,

100

dimetomor, ditianon, etridiazol, famoxadona, fenamidona, fentina, ferimzona, fluacinan, flusulfamida, fenhexamida, fosetil-aluminio, himezasol, kasugamisina, metasulfocar, pencicuron, eftalamida, polioxinas, probenazol, propamorcar, piroquilon, quinoxifen, quintozene, azufre, triazoxido, trisiclason, triforina, validamicina, (S)-5-metil-2-metiltio-5-fenil-3-fenil-amino-3,5-dihidroimidazol-4-one (RPA 407213), 3,5-dicloro-N-(3-cloro-1-etil-1-metil-2-oxopropil)-4-metilbenzamida (RH-7281), N-allyl-4,5-dimetil-2-trimetilsililtiofeno-3-carboxamida (MON 65500), 4-cloro-4-ciano-N,N-dimetil-5-p-tolilimidazol-1-sulfon-amida (IKF-916), N-(1-ciano-1,2-dimetil-propil)-2-(2,4-diclorofenoxi)-propionamida (AC 382042), o iprovalicarb (SZX 722).

Un método preferido de aplicar un compuesto de fórmula I, o una composición agroquímica que contiene al menos uno de dichos compuestos, es aplicación foliar. La frecuencia de aplicación y la proporción de aplicación dependerá del riesgo de infestación por el patógeno correspondiente. Sin embargo, los compuestos de fórmula I también pueden penetrar la planta a través de las raíces por vía del suelo (acción sistémica) al remojar el locus de la planta con una formulación líquida, o al aplicar

DA

los compuestos en forma sólida al suelo, por ejemplo, en forma granular (aplicación al suelo). En los cultivos de arroz de agua tales granulados se pueden aplicar al campo de arroz fluido. Los compuestos de la fórmula I también se pueden aplicar a semillas (recubrimiento) mediante impregnación de las semillas o los tubérculos o con una formulación líquida del fungicida o recubriéndolos con una formulación sólida.

La formulación, es decir, las composiciones que contienen los compuestos de fórmula I y, si se desea, un ayudante sólido o líquido, se preparan de manera conocida, típicamente al mezclar íntimamente y/o moler los compuestos con extendedores, por ejemplo, solventes, portadores sólidos y, opcionalmente, compuestos de superficie activa (tensoactivos).

Las formulaciones agroquímicas usualmente contendrán de 0,1 a 99% en peso, preferiblemente de 0,1 a 95% en peso, del compuesto de la fórmula I, 99,9 a 1% en peso, preferiblemente 99,8 a 5% en peso de un ayudante sólido o líquido, y desde 0 a 25% en peso, preferiblemente desde 0,1 a 25%, de un tensoactivo.

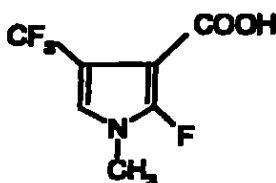
Las razones ventajosas de aplicación son normalmente de 5 a 2 Kg de ingrediente activo (a.i.) por hectárea (ha), preferiblemente de 10g a 1 Kg a.i./ha, más preferiblemente desde 20g a 600 g a.i/ha. Cuando se utilizan como agentes remojantes de semilla, las dosis convenientes van desde 10 mg a 1 g de sustancia activa por Kg de semillas.

Mientras que se prefiere formular productos comerciales como concentrados, el usuario final o normalmente utilizara formulaciones diluidas.

Los siguientes ejemplos no limitativos ilustran la invención anteriormente descrita con más detalle. Las temperatura se dan en grados Celsius. Las siguientes abreviaturas se utilizan: m.p = punto de fusión; b.p. = punto de ebullición. "RMN" significa espectro de resonancia magnética nuclear. MS se establece para espectro de masa. "%" es el porcentaje del peso, a menos que las concentraciones correspondientes se indiquen en otras unidades.

EJEMPLO 1

Ácido 2-fluoro-1-metil-4-trifluorometil-1H-pirrol-3-carboxílico



Una solución de 1,25 g (11 mmol) de litiodiisopropilamida (LDA) á 95% en 20 ml THF absoluto se agrega gota a gota a una solución de 1,0 g (5,2 mmol) ácido 1-metil-4-trifluorometil-1H-pirrol-3-carboxílico en 60 ml de THF de tal manera que la temperatura permanece constante a -75°C . después de 3 horas de agitar a -75°C , una solución de 1.95 g (6,2 mmol) N-fluoro-bis(fenilsulfonil)amina en 20 ml THF absoluto se agrega en ca. 30 minutos a una temperatura constante de -75°C . luego el enfriamiento se detiene y la mezcla de reacción se agita durante 16 horas, calentando de esta forma lentamente hasta temperatura ambiente. Luego el solvente se remueve en un vacío de chorro de agua y el residuo es disuelto en agua. Después de la adición de ácido

04

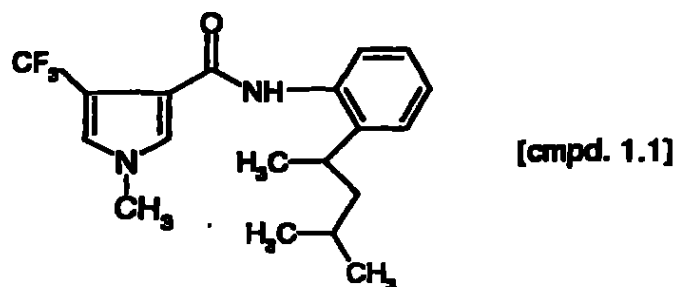
clorhídrico 1N (pH = 1) el etilacetato se agrega y la fase orgánica se extrae dos veces con agua adicional. Después de la separación de la fase orgánica, se obtiene la materia prima, secando sobre sulfato de sodio y la evaporación de solvente en un vacío de chorro de agua. El producto crudo se purifica mediante, cromatografía de columnas sobre sílica gel (eluante: hexano/etilacetato = 1:1). Rendimiento: 0,65 g ácido 2-fluoro-1-metil-4-trifluorometil-1H-pirrol-3-carboxílico en la forma de cristales blancos; m.p.: 190.191°C.

El ácido 2-cloro-1-metil-4-trifluorometil-1H-pirrol-3-carboxílico se puede obtener de manera análoga utilizando por ejemplo N-clorsucinimida como agente de halogenación en la reacción escrita anteriormente, m.p. 197-198°C.

EJEMPLO 2

Ácido 1-metil-4-trifluorometil-1H-pirrol-3-carboxílico [2-(1,3-dimetilbutil)fenil]amida

25

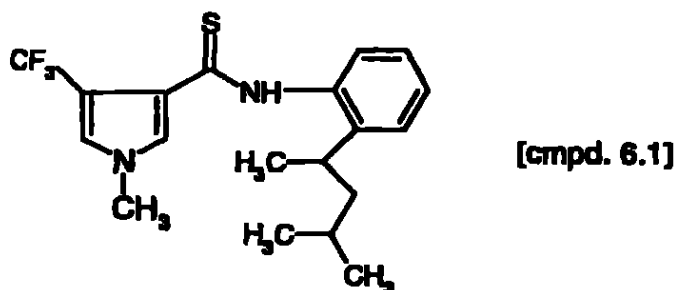


Una solución de 0,5 g (2,6 mmol) ácido 1-metil-4-trifluorometilpirrol-3-carboxílico y 0,37 g (2,85 mmol) de oxalilcloruro en 20 ml de cloruro de metileno se agita durante 3 horas a temperatura ambiente en la presencia de una cantidad catalítica de DMF. Entonces la solución de cloruro ácida es lentamente agregada a una solución de 0,46 g (2,6 mmol) 2-(1,3-dimetilbutil)fenilamina, 0,33 g (3,4 mmol) trietilamina y 15 ml de cloruro de metileno. Para esta resultante se agita entonces durante 16 horas a temperatura ambiente. Después de la remoción del solvente un vacío de chorro de agua, la materia prima se toma en etilacetato. La fase de etilacetato se lava dos veces con agua y luego la fase orgánica se seca sobre sulfato de sodio. Después de la evaporación del solvente en un vacío de chorro de agua, el residuo obtenido se purifica mediante cromatografía de columna sobre sílica gel (eluante: hexano/etilacetato = 3:1). Rendido: 0,45 g ácido 1-Metil-4-trifluorometil-1H-pirrol-3-carboxílico

[2-(1,3-dimetilbutil)fenil]amida en la forma de cristales
café; m.p.: 83-85°C.

EJEMPLO 3

Ácido 1-metil-4-trifluorometil-1H-pirrol-3-
carbotioico [2-(1,3-dimetilbutil)fenil]amida



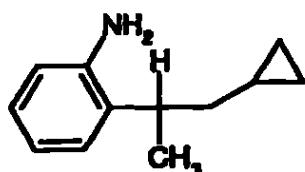
Un frasco de sulfonación una mezcla de 0,6 g de
ácido 1-Metil-4-trifluorometil-1H-pirrol-3-carboxílico
[2-(1,3-dimetilbutil)fenil]amida, 0,45 g P_2S_5 y 30 ml de
dioxano se calienta a 70-75°C durante 3 horas. Después de
la filtración, el solvente se remueve en un vacío de
chorro de agua y el residuo se toma en etilacetato. La
fase orgánica se lava dos veces con agua y el etilacetato
se remueve en un vacío de chorro de agua. El material
crudo se purifica mediante cromatografía de columna sobre
sílica gel (eluante: etilacetato/n-hexano = 1:1).

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Rendimiento: 0,53 g ácido 1-Metil-4-trifluorometil-1H-pirrol-3-carbotioico [2-(1,3-dimetilbutil)fenil]amida en la forma de una resina rojiza (^1H -RMN).

EJEMPLO 4 (Intermedio de amina)

2-(2-ciclopropil-1-metil-etil)fenilamina



[compd. 7.6]

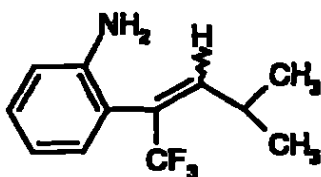
A una solución de 2,96 g (15,5 mmol) de 2-(2-aminofenil)-1-ciclopropil-propan-2-ol en 70 ml de metanol se agrega 4,43 g (43,4 mmol) ácido sulfúrico conc. (96%). La mezcla resultante se hidrogena sobre 600 mg Pd/C(10%) durante 20 horas a 30-35°C. después de ese tiempo no se detecta más tomas de hidrogeno. El catalizador se filtra y el solvente se remueve en un vacío de chorro de agua. El residuo se toma en el etilacetato/agua en la fase acuosa se neutraliza mediante la adición de carbonato de sodio. La fase de agua se extrae dos veces con etilacetato, entonces la fase orgánica combinada se seca

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sobre sulfato de sodio. Después de la remoción del solvente en un vacío de chorro de agua, el crudo de amina se obtiene. La materia prima obtenida se purifica mediante cromatografía de columnas sobre sílica gel (eluante: hexano/éter = 5:1). Rendimiento: 2,1 g 2-(2-ciclopropil-1-metil-etil)fenilamina en la forma de un aceite café (^1H -RMN).

EJEMPLO 5 (intermedio de amina)

Mezcla E/Z-isomerica 2-(3-metil-1-trifluorometil-but-1-enil)fenilamina



[compd. 7.4]

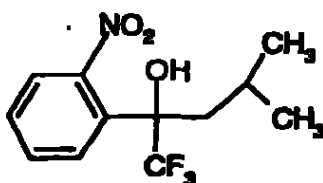
Una solución de 1,14 g (4,4 mmol) 1-(3-metil-1-trifluorometil-but-1-enil)-2-nitrobenceno en 20 ml de metanol se hidrogena sobre 10% Pd/C (230 mg) a temperatura ambiente durante 20 minutos. luego el catalizador se filtra y el solvente se remueve en un vacío de chorro de agua. El producto crudo se purifica

JP

mediante cromatografía de columnas sobre sílica gel (eluant: metilenecloruro/hexano = 2:1). Rendimiento: 0,6 g (suma E+Z isómero) 2-(3-metil-1-trifluorometil-but-1-enil)fenilamina de la forma de un aceite café. Después de la cromatografía de columna ambos isómeros se obtienen en forma pura (^1H -RMN).

EJEMPLO 6

1,1,1-trifluorometil-4-metil-2-(2-nitrofenil)-
pentan-2-ol

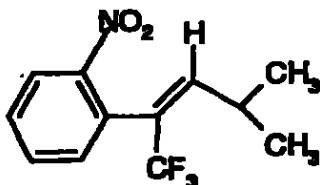


A una solución de 20,2 g (0,1 mol) 2-bromonitrobenceno en 300 ml tetrahidrofurano absorbente. Se agrega 81 ml de SEC ID No. BuLi (0,105 mol) durante un periodo de 30 minutos de tal manera que la temperatura interna permanece constante a -103 a -107°C . después de agitar durante 70 minutos a -103 a -107°C una solución de 20,0 g (0,13 mol) de triflorometilisobutilcetona en 150 ml de tetrahidrofurano a ese punto se agrega durante un

periodo de 20 minutos de tal manera que la temperatura permanece constante a -105°C ($\pm 2^{\circ}\text{C}$). Después de agitar durante 4 horas a -105°C la temperatura se eleva a -20°C y se agrega una solución de 150 ml de aminocloruro saturado. Luego se agrega un l de etilacetato y la fase orgánica se lava tres veces con agua. Después de secar la fase orgánica con el sulfato de sodio y destilar el solvente en un vacío de chorro de agua se obtienen la materia prima. La purificación se logra mediante cromatografía de columna sobre sílica gel (eluante: hexano/etilacetato = 5:1). Rendimiento: 8,2 g 1,1,1-trifluorometil-4-metil-2-(2-nitrofenil)pentan-2-ol en la forma de un polvo café; m.p.: $103-105^{\circ}\text{C}$.

EJEMPLO 7

1-(3-metil-1-trifluorometil-but-1-enil)-2-nitrobenceno (Mezcla E/Z)



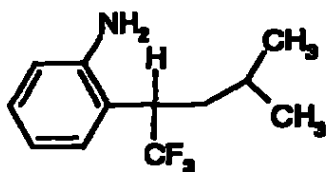
A una solución de 10,8 g (39 mmol) 1,1,1-trifluorometil-4-metil-2-(2-nitrofenil)pentan-2-ol en 110 ml de piridina abs. Se agrega lentamente 13,9 g (117 mmol) de tionilcloruro a una temperatura de 0,5°C. luego la mezcla se calienta a 90-95°C durante 1 hora. Después de enfriar la mezcla de reacción se agrega agua helada. La solución resultante se extrae cuidadosamente con etilacetato y después se seca la fase orgánica sobre sulfato de sodio y se destila el solvente en un vacío de chorro de agua, se obtiene el producto crudo. Se logra la purificación mediante cromatografía de columnas sobre sílica gel (eluante: cloruro de metileno/hexano = 1:1). Rendimiento: 5,2 g 1-(3-metil-1-trifluorometil-but-1-enil)-2-nitrobenceno en la forma de un aceite café (¹H-RMN).

EJEMPLO 8

(amina intermedia)

2-(3-metil-1-trifluorometil-butil)fenilamina

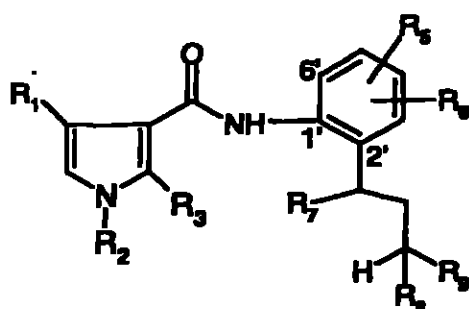
112



[compd. 7.5]

Una solución de 2,98 g (12,9 mmol) 1-(3-metil-1-trifluorometil-but-1-enil)-2-nitrobenceno en 30 ml de metanol se hidrogena sobre Raney-Nickel (etanol) a 100°C y 150 bar durante 10 horas. Luego el catalizador filtra y el solvente se remueve en un vacío de chorro de agua. El producto crudo obtenido se purifica mediante cromatografía de columna sobre sílica gel (eluante: hexano/cloruro de metileno = 1:2). Rendimiento: 1,9 g 2-(3-metil-1-trifluorometil-butil)fenilamina de la forma de un aceite café (^1H -RMN).

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TABLA 1

1a

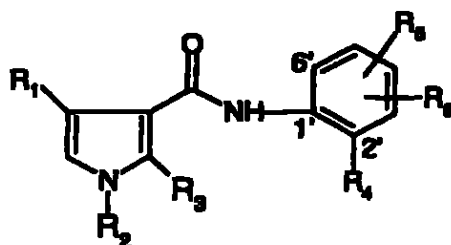
(Md = mezcla de diastereómeros)

Cmpd. no.	R ₁	R ₂	R ₃	R ₅	R	R ₇	R ₈	R ₉	phys. data m.p. °C
1.1	CF ₃	Me	H	H	H	Me	Me	Me	83-85
1.2	CF ₃	CH ₂ OMe	H	H	H	Me	Me	Me	75-77
1.3	CF ₃	Me	H	H	H	CF ₃	Me	Me	98-100
1.4	CF ₃	Me	H	H	H	Me	CF ₃	CF ₃	
1.5	CF ₃	Me	H	H	H	Me	Me	Et	93-97 (md)
1.6	CF ₃	CH ₂ OMe	H	H	H	Me	Me	Et	
1.7	CF ₃	Me	H	6'-F	H	Me	Me	Me	
1.8	CF ₃	Me	H	5'-F	H	Me	Me	Me	
1.9	CF ₃	Me	H	H	H	Me	Et	Et	84-86
1.10	CF ₃	Me	F	H	H	Me	Me	Me	
1.11	CF ₃	CH ₂ OMe	F	H	H	Me	Me	Me	
1.12	CF ₃	Me	F	H	H	Me	Me	Et	resin; ¹ H-NMR, MS
1.13	CF ₃	Me	F	H	H	CF ₃	Me	Me	resin; ¹ H-NMR, MS
1.14	CF ₃	Me	F	H	H	CF ₃	Me	Et	
1.15	CF ₂ H	Me	H	H	H	Me	Me	Me	
1.16	CF ₂ H	Me	H	H	H	Me	Me	Et	
1.17	CF ₂ H	Me	H	H	H	CF ₃	Me	Me	Resina
1.18	CF ₂ H	Me	H	H	H	Me	CF ₃	CF ₃	
1.19	CF ₂ H	Me	H	H	H	CF ₂ H	Me	Me	
1.20	CF ₂ H	CH ₂ OMe	H	H	H	Me	Me	Me	

1.21	CF ₂ H	CH ₂ OMe	H	H	H	Me	Me	Et
1.22	CF ₂ H	Me	F	H	H	Me	Me	Me
1.23	CF ₂ H	Me	F	H	H	Me	Me	Et
1.24	CFH ₂	Me	H	H	H	Me	Me	Me
1.25	CFH ₂	Me	H	H	H	Me	Me	Et
1.26	CFH ₂	Me	F	H	H	Me	Me	Me
1.27	CFH ₂	Me	F	H	H	Me	Me	Et
1.28	CF ₃	Me	H	H	H	Et	Me	Me
1.29	CF ₃	Me	H	H	H	Et	Me	Et
1.30	CF ₃	Me	F	H	H	Et	Me	Me
1.31	CF ₃	Me	F	H	H	Et	Me	Et
1.32	CF ₂ H	Me	H	H	H	Et	Me	Me
1.33	CF ₂ H	Me	H	H	H	Et	Me	Et
1.34	CF ₂ H	Me	F	H	H	Et	Me	Me
1.35	CFH ₂	Me	H	H	H	Et	Me	Me

Resin; ¹H-NMR,
M⁺ = 366
oil; M⁺ = 380 ,

Tabla 2



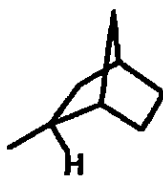
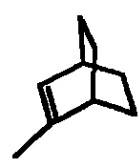
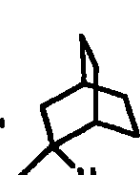
1b

Cmpd. no.	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	Phys.data m.p. °C
2.1	CF ₃	Me	H		H	H	

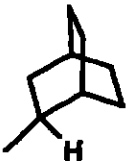
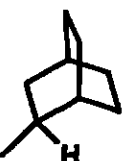
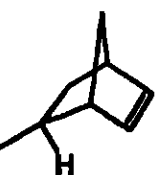
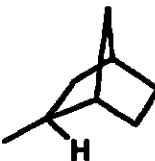
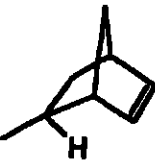
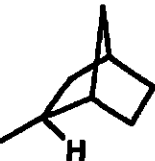
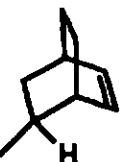


2.2	CF ₃	Me	H		H	H	Resina (¹ H-NMR, MS)
2.3	CF ₃	Me	H		H	H	
2.4	CF ₃	Me	H		H	H	136-137
2.5	CF ₃	Me	H		6'-F	H	
2.6	CF ₃	Me	H		H	H	
2.7	CF ₃	CH ₂ OMe	H		H	H	
2.8	CF ₂ H	Me	H		H	H	

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2.9	CF_2H	Me	H		H	H	
2.10	CF_3	Me	H		H	H	105-107
2.11	CF_3	Me	H		H	H	110-112
2.12	CF_3	Me	H		H	H	
2.13	CF_3	Me	H		H	H	127-129
2.14	CF_3	CH_2OMe	H		H	H	
2.15	CF_3	Me	H		4'-F	H	

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2.16	CF ₃	CH ₂ OMe	H		4'-F	H
2.17	CF ₂ H	Me	H		H	H
2.18	CF ₃	Me	F		H	H
2.19	CF ₃	Me	F		H	H
2.20	CF ₃	CH ₂ OMe	F		H	H
2.21	CF ₃	CH ₂ OMe	F		H	H
2.22	CF ₃	Me	F		H	H

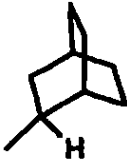
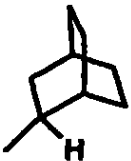
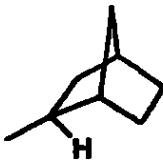
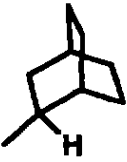
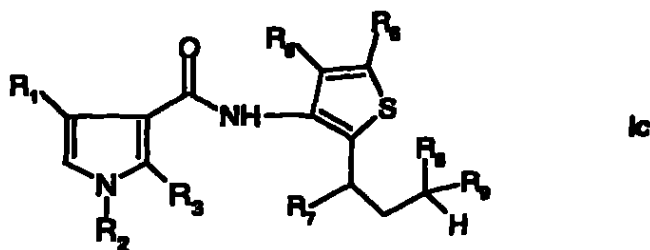
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2.24	CF ₃	CH ₂ OMe	F		H	H	
2.25	CF ₃	Me	Me		H	H	
2.26	CF ₃	Me	Me		H	H	

Tabla 3

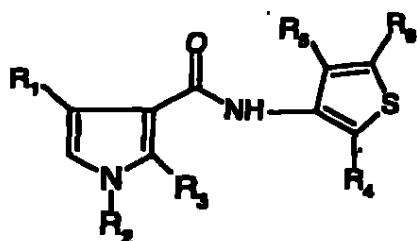


Cmpd. no.	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	R ₈	R ₉	Phys. data m.p. °C
3.1	CF ₃	Me	H	H	H	Me	Me	Me	Me	92-93
3.2	CF ₃	CH ₂ OMe	H	H	H	Me	Me	Me	Me	
3.3	CF ₃	Me	H	H	H	CF ₃	Me	Me	Me	
3.4	CF ₃	Me	H	H	H	Me	CF ₃	CF ₃	CF ₃	
3.5	CF ₃	Me	H	H	H	Me	Me	Et	Et	

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3.6	CF ₃	CH ₂ OMe	H	H	H	Me	Me	Et	
3.7	CF ₃	Me	H	6'-F	H	Me	Me	Me	
3.8	CF ₃	Me	H	5'-F	H	Me	Me	Me	
3.9	CF ₃	Me	H	H	H	Me	Et	Et	
3.10	CF ₃	Me	F	H	H	Me	Me	Me	Acetic
3.11	CF ₃	CH ₂ OMe	F	H	H	Me	Me	Me	
3.12	CF ₃	Me	F	H	H	Me	Me	Et	
3.13	CF ₃	Me	F	H	H	CF ₃	Me	Me	
3.14	CF ₃	Me	F	H	H	CF ₃	Me	Et	
3.15	CF ₂ H	Me	H	H	H	Me	Me	Me	Acetic
3.16	CF ₂ H	Me	H	H	H	Me	Me	Et	
3.17	CF ₂ H	Me	H	H	H	CF ₃	Me	Me	
3.18	CF ₂ H	Me	H	H	H	Me	Me	Me	
3.19	CFH ₂	Me	H	H	H	Me	Me	Me	
3.20	CFH ₂	Me	H	H	H	Me	Me	Et	
3.21	CFH ₂	Me	H	H	H	CF ₃	Me	Me	
3.22	CFH ₂	Me	H	H	H	Me	Me	Me	

Tabla 4

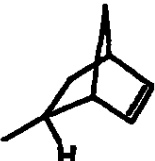
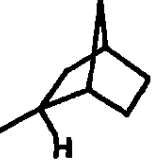
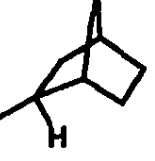
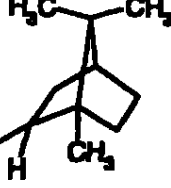
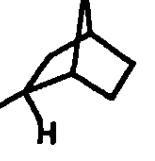
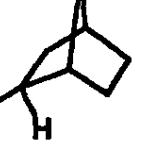


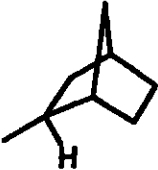
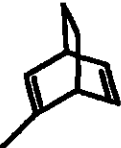
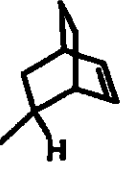
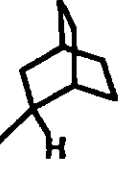
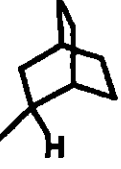
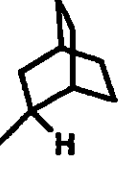
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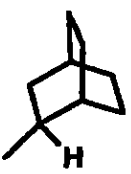
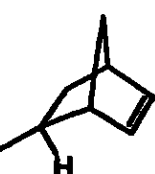
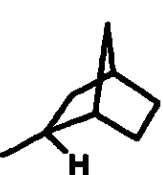
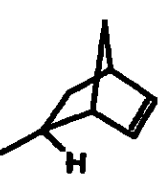
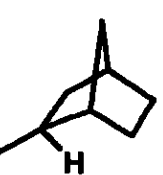
Cmpd. no.	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	phys.data m.p. °C
4.1	CF ₃	Me	H		H	H	



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4.2	CF ₃	Me	H		H	H	Resina
4.3	CF ₃	Me	H		H	H	
4.4	CF ₃	Me	H		H	H	Resina
4.5	CF ₃	Me	H		6'-F	H	
4.6	CF ₃	Me	H		H	H	
4.7	CF ₃	CH ₂ OMe	H		H	H	
4.8	CF ₂ H	Me	H		H	H	

4.9	CF_2H	Me	H		H	H
4.10	CF_3	Me	H		H	H
4.11	CF_3	Me	H		H	H
4.12	CF_3	Me	H		H	H
4.13	CF_3	Me	H		H	H
4.14	CF_3	CH_2OMe	H		H	H
4.15	CF_3	Me	H		4'-F	H

4.16	CF ₃	CH ₂ OMe	H		4'-F	H
4.17	CF ₂ H	Me	H		H	H
4.18	CF ₃	Me	F		H	H
4.19	CF ₃	Me	F		H	H
4.20	CF ₃	CH ₂ OMe	F		H	H
4.21	CF ₃	CH ₂ OMe	F		H	H
4.22	CF ₃	Me	F		H	H

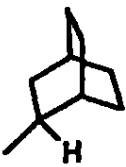
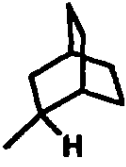
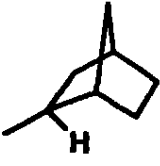
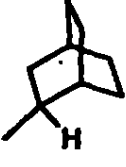
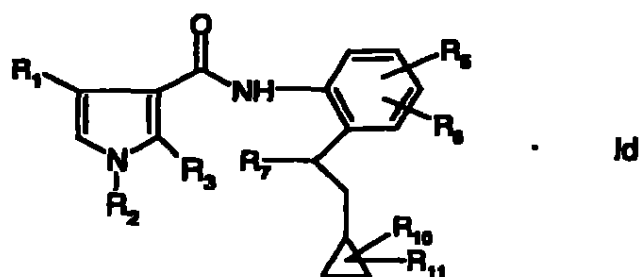
4.23	CF ₃	Me	F		H	H
4.24	CF ₃	CH ₂ OMe	F		H	H
4.25	CF ₃	Me	Me		H	H
4.26	CF ₃	Me	Me		H	H

Tabla 5

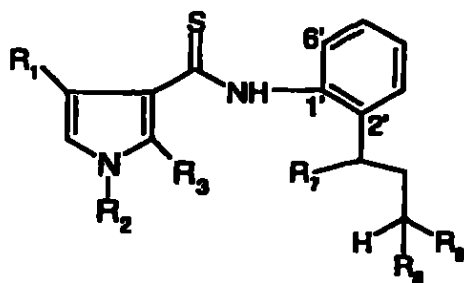
Cmpd. no.	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	R ₁₀	R ₁₁	phys.data m.p. °C
5.1	CF ₃	Me	H	H	H	Me	H	H		109-110
5.2	CF ₃	CH ₂ OMe	H	H	H	Me	H	H		
5.3	CF ₃	Me	H	H	H	CF ₃	H	H		
5.4	CF ₃	Me	H	H	H	Me	Cl	Cl		
5.5	CF ₃	CH ₂ OMe	H	H	H	CF ₃	H	H		

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5.6	CF ₃	Me	F	H	H	Me	H	H
5.7	CF ₃	CH ₂ OMe	F	H	H	Me	H	H
5.8	CF ₃	Me	F	H	H	CF ₃	H	H
5.9	CF ₃	CH ₂ OMe	F	H	H	Me	H	H
5.10	CF ₃	CH ₂ OMe	F	H	H	CF ₃	H	H
5.11	CF ₃	Me	F	H	H	Me	Cl	Cl
5.12	CF ₂ H	Me	H	H	H	Me	H	H
5.13	CF ₂ H	Me	H	H	H	CF ₃	H	H
5.14	CF ₂ H	CH ₂ OMe	H	H	H	Me	H	H
5.15	CF ₂ H	CH ₂ OMe	H	H	H	CF ₃	H	H
5.16	CF ₂ H	Me	F	H	H	Me	H	H
5.17	CF ₂ H	Me	F	H	H	CF ₃	H	H
5.18	CF ₂ H	CH ₂ OMe	F	H	H	Me	H	H
5.19	CF ₂ H	CH ₂ OMe	F	H	H	CF ₃	H	H
5.20	CF ₂ H	Me	H	H	H	Me	Cl	Cl
5.21	CF ₂ H	CH ₂ OMe	H	H	H	Me	Cl	Cl
5.22	CFH ₂	Me	H	H	H	Me	H	H
5.23	CFH ₂	Me	H	H	H	Et	H	H
5.24	CF ₂ H	Me	F	H	H	Me	H	H
5.25	CF ₃	Me	H	H	H	Et	H	H
5.26	CF ₃	Me	F	H	H	Et	H	H
5.27	CF ₂ H	Me	H	H	H	Et	H	H
5.28	CF ₂ H	Me	F	H	H	Et	H	H

59-61

125

Tabla 6

1a

(md = mezcla de diastereoisómeros)

Cmpd. no.	R ₁	R ₂	R ₃	R ₇	R ₈	R ₉	Phys. Data m.p. °C
6.1	CF ₃	Me	H	Me	Me	Me	resin; ¹ H-NMR; M ⁺ =368
6.2	CF ₃	CH ₂ OMe	H	Me	Me	Me	
6.3	CF ₃	Me	H	CF ₃	Me	Me	
6.4	CF ₃	Me	H	Me	CF ₃	CF ₃	
6.5	CF ₃	Me	H	Me	Me	Et	md; resin; ¹ H-NMR; M ⁺ =382
6.6	CF ₃	CH ₂ OMe	H	Me	Me	Et	
6.7	CF ₃	Me	H	Me	Et	Et	
6.8	CF ₃	Me	F	Me	Me	Me	Resin; M ⁺ = 386
6.9	CF ₃	CH ₂ OMe	F	Me	Me	Me	
6.10	CF ₃	Me	F	Me	Me	Et	
6.11	CF ₃	Me	F	CF ₃	Me	Me	
6.12	CF ₃	Me	F	CF ₃	Me	Et	
6.13	CF ₂ H	Me	H	Me	Me	Me	
6.14	CF ₂ H	Me	H	Me	Me	Et	
6.15	CF ₂ H	Me	H	CF ₃	Me	Me	
6.16	CF ₂ H	Me	H	Me	Me	Me	

Tabla 7: Intermedios de Amina

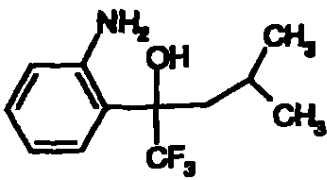
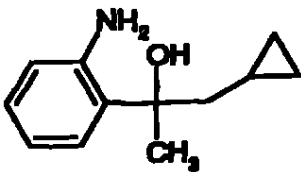
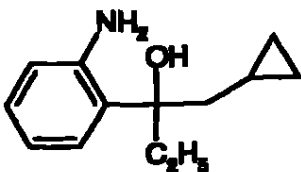
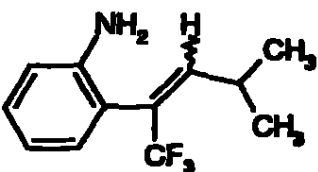
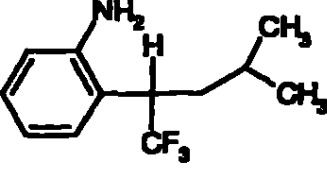
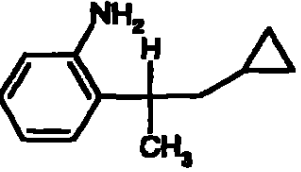
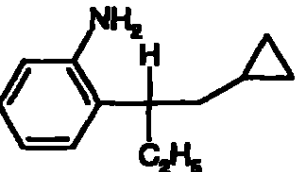
Cmpd.No.		Phys.data (m.p.°C or NMR)
7.1		84-86
7.2		Oil; ¹ H-NMR
7.3		Oil; ¹ H-NMR
7.4 7.4.1: E- isomero 7.4.2: Z- isomero Mezcla E/Z		Oil; ¹ H-NMR
7.5		Oil; ¹ H-NMR
7.6		Oil; ¹ H-NMR
7.7		Oil; ¹ H-NMR

Tabla ^1H -RMN

Comp No.	Datos ^1H -RMN (ppm/multiplicidad/número de protones; solvente CDCl_3)
6.1	0.82/2xd/6H; 1.19/d/3H; 1.35-1.60/m/1H; 3.70/s/3H; 6.99/d/1H; 7.2-7.4/m/4H; 7.61/d/1H; 8.70/s(broad)/1H
6.6	0.75-0.88/m/12H; 1.0-1.65/m/6H; 1.18/d/3H; 1.20/d/3H; 3.0/m/2H; 3.70/s/6H; 7.0/d/2H; 7.2-7.4/m/8H; 7.61/d/2H; 8.7/s/2H
7.2	0.1/m/2H; 0.45/m/2H; 0.65/m/1H; 1.69/s/3H; 1.80/m/1H; 2.0/m/1H; 3.7/s(broad)/3H(OH+NH ₂); 6.60-6.70/m/2H; 6.98-7.11/m/2H
7.3	0.01/m/2H; 0.35/m/2H; 0.55/m/2H; 0.75/v/3H; 1.51/m/1H; 1.8-2.05/m/3H; 3.72/s(broad)/3H(OH+NH ₂); 6.47-6.59/m/2H; 6.91/m/2H
7.4.1 (E-isomer)	1.09/d/6H; 3.02/m/1H; 3.60/s(broad)/2H(NH ₂); 5.81/d/1H; 6.72/m/2H; 6.99/dxd/1H; 7.15/bxd/1H
7.4.2 (Z-isomer)	0.91/d/3H; 1.03/d/3H; 2.25/m/1H; 3.58/s(broad)/2H; 6.36/dxd/1H; 6.78/m/2H; 6.99/dxd/1H; 7.18/bxd/1H
7.5	0.83/d/3H; 0.87/d/3H; 1.40/m/1H; 1.69/m/1H; 1.99/m/1H; 3.6/m/3H(NH ₂ +H-benzylic); 6.75/dxd/1H; 6.85/v/1H; 7.09-7.2/m/2H
7.6	0.05/m/2H; 0.4/m/2H; 0.69/m/1H; 1.29/d/3H; 1.35/m/1H; 1.60/m/1H; 2.88/m/1H; 3.65/s(broad)/2H(NH ₂); 6.68/d/1H; 6.85/v/1H; 7.0/bxd/1H; 7.1/dxd/1H
7.7	0.01/m/2H; 0.38/m/2H; 0.60/m/1H; 0.82/v/3H; 1.32/m/1H; 1.52-1.80/m/3H; 2.68/m/1H; 3.65/s(broad)/2H(NH ₂); 6.69/d/1H; 6.78/v/1H; 7.0/bxd/1H; 7.08/dxd/1H
1.28	0.78-0.85/v+d/9H; 1.35-1.69/m/5H; 2.85/m/1H; 3.70/s/3H; 7.0/d/1H; 7.20/m/3H; 7.37/d/1H; 7.58/s(broad)/1H; 7.7/m/1H

**Ejemplos de Formulación para los Compuestos de
fórmula I**

Los procedimientos de trabajo para preparar las formulaciones de los compuestos de fórmula I tales como concentrados emulsificables, soluciones, granulados, polvos y polvos humectantes se describen en la WO 97/33890.

Ejemplos Biológicos: Acciones Fungicidas

**Ejemplo B-1: Acción contra la Puccinia
recondita/trigo (la roya del trigo)**

Plantas de trigo de una semana de nacidos cv. "Arina" son tratados con el compuesto de ensayo formulado (0,02% de ingrediente activo en una cámara de rociado. Un día después de la aplicación las plantas de trigo son inoculadas por rociado con una suspensión de esporas (1×10^5 uredosporas/ml) sobre las plantas de ensayo. Después de un periodo de incubación de dos días a 20° C y 95% de humedad relativa las plantas son mantenidas en un invernadero durante 28 días a 20° C y 60% de humedad

relativa. La incidencia de enfermedad se logra 10 días después de la inoculación.

Los compuestos de las tablas 1 a 6 muestran una buena actividad en estos ensayos (<20% de infestación).

Ejemplo B-2: acción contra la Podosphaera leucotricha/manzana (mildew polvoriento sobre la manzana)

Semillas de manzana de 5 semanas cv. McIntosh son tratadas con el compuesto de ensayo formulado (0,002% de ingrediente activo) en una cámara de rociado. Un día después de la aplicación las plantas de manzana son inoculadas por medio de inocular las plantas infectadas con mildew polvoriento de manzana por encima de las plantas de ensayo. Después de un periodo de incubación de 12 día a 22° C y 60% de humedad relativa bajo un régimen de luz de 14/10 horas (luz/oscuridad) la incidencia de la enfermedad se determina.

Los compuestos de las tablas 1 a 6 muestran una buena actividad en este ensayo.

Ejemplo B.3: Acción contra Venturia
inaequalis/manzana (Costra sobre la manzana)

Plántulas de manzana de 4 semanas cv. McIntosh son tratadas con el compuesto de ensayo formulado (0,02% de ingrediente activo) en una cámara de rociado. Un día después de la aplicación las plantas de manzana son inoculadas por rociado de una suspensión de espora (4×10^5 conidia/ml) sobre las plantas de ensayo. Después de un periodo de incubación de 4 días a 21° C y 95% de humedad relativa las plantas son colocadas durante 4 días a 21° C y 60% de humedad relativa en un invernadero. Después de otros 4 días de periodo de incubación a 21° C y 95% de humedad relativa la incidencia de la enfermedad se determina.

Los compuestos de las tablas 1 a 6 muestran una buena actividad en este ensayo.

Ejemplo B-4: acción contra Erisipe graminis /cebada
(mildew polvoroso sobre la cebada)

Plantas de cebada de una semana de nacida cv. Express son tratadas con el compuesto de ensayo formulado

(0,02% de ingrediente efectivo) en una cámara de rociado. Un día después de la aplicación las plantas de cebada son inoculadas por medio de agitar plantas infectadas con mildew polvoroso por encima de las plantas de ensayo. Después de un periodo de incubación de 6 días a 20° C/18° C (día/noche) y 60% de humedad relativa en un invernadero la incidencia de la enfermedad fue determinada.

Los compuestos de las tablas 1 a 6 muestran una buena actividad en este ensayo.

Ejemplo B-5: Acción contra Botritis cinerea /
manzana (Botritis sobre frutos de manzana)

En un fruto de manzana cv. Golden Delicious 3 agujeros son taladrados y cada uno es llenado con 30 µl de goticas del compuesto de ensayo formulado (0,002% de ingrediente activo). Dos horas después de la aplicación 50 µl de una suspensión de esporas de B. cinerea (4×10^5 conidia/ml) son pipeteadas sobre los sitios de aplicación. Después de un periodo de incubación de 7 días a 22° C en una cámara de crecimiento la incidencia de la enfermedad es determinada.

Los compuestos de la tabla 1 a 6 muestran buena actividad en este ensayo.

Ejemplo B-6: acción contra Botritis cinerea/uva
(botritis sobre uvas)

Plántulas de uva de 5 semanas cv. Gutedel son tratadas con el compuesto de ensayo formulado (0,002% de ingrediente activo) en una cámara de rociado. Dos días después de la aplicación las plantas de uva son inoculadas por rociado con una suspensión de esporas (1×10^6 conidia/ml) sobre las plantas de ensayo. Después de un periodo de incubación de 4 días a 21° C y 95% de humedad relativa en un invernadero la incidencia de la enfermedad es determinada.

Los compuestos de las tablas 1 a 6 muestran buena actividad en este ensayo.

Ejemplo B-7: acción contra Botritis cinerea/tomate
(Botritis sobre tomates)

Plantas de tomate de cuatro semanas cv. Roter Gnom son tratadas con el compuesto de ensayo formulado (0,002% de ingrediente activo) en una cámara de rociado. Dos días después de la aplicación las plantas de tomate son inoculadas con una suspensión de esporas (1×10^5 conidia/ml) sobre las plantas de ensayo. Después de un periodo de incubación de 4 días a 20° C y 95% de humedad relativa en una cámara de crecimiento la incidencia de la enfermedad es determinada.

Los compuestos de las tablas 1 a 6 muestran una buena actividad en este ensayo.

Ejemplo B-8: acción contra pirenofora teres/cebada
(mancha en red sobre cebada)

Plantas de cebada en una semana cv. Express son tratadas con el compuesto de ensayo formulado (0,002% de ingrediente activo) en una cámara de rociado. Dos días después de la aplicación las plantas de cebada son inoculadas por rociado con una suspensión de esporas (3×10^4 conidia/ml) sobre las plantas de ensayo. Después de un periodo de incubación de dos días a 20° C y 95% de humedad relativa las plantas son mantenidas durante dos

días a 20° C y 60% de humedad relativa en un invernadero. La incidencia de la enfermedad es determinada cuatro días después de la inoculación.

Los compuestos de las tablas 1 a 6 muestra una buena actividad de este ensayo.

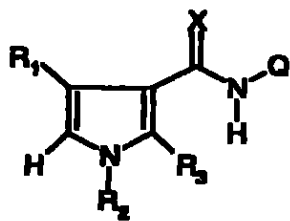
Ejemplo B-9: acción contra Septoria nodorum/trigo
(manchas de hoja de septoria sobre el trigo)

Plantas de trigo de una semana cv. "Arina" son tratadas con el compuesto de ensayo formulado (0,02% de ingrediente activo) en una cámara de rociado. Un día después de la aplicación las plantas de trigo son inoculadas por rociado con una suspensión de esporas (5 x 10⁶ conidia/ml) sobre las plantas de ensayo. Después de un periodo de incubación de un día a 20° C y 95% de humedad relativa las plantas son mantenidas durante 10 días a 20° C y 60% de humedad relativa en un invernadero. La incidencia de la enfermedad es determinada 11 días después de la inoculación. Los compuestos de las tablas 1 a 6 muestran una buena actividad en este ensayo.

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REIVINDICACIONES

1. Una amida de ácido pirrolcarboxílico o pirrolcarbotioico de la fórmula (I),



En donde

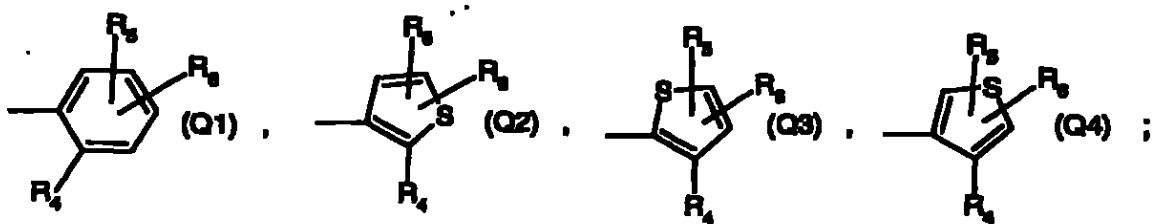
X es oxígeno o azufre;

R_1 es CF_3 , CF_2H o CFH_2 ;

R_2 es alquilo C_1-C_3 , haloalquilo C_1-C_3 , alcoxi C_1-C_3 alquilo $-C_1-C_3$ o haloalcoxi C_1-C_3 - alquilo C_1-C_3 ;

R_3 es hidrógeno, metilo, CF_3 o flúor;

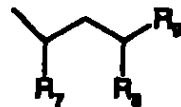
Q es



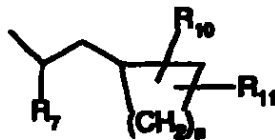
R_4 es bicicloalquilo C_6-C_{14} no sustituido o sustituido por metilo, etilo o CF_3 ;

bicicloalquenilo C_6-C_{14} no sustituido o sustituido por metilo, etilo o CF_3 ;

bicicloalcadienilo C_6-C_{14} no sustituido o sustituido por metilo, etilo o CF_3 ; o un grupo de la forma



Donde R_7 , R_8 y R_9 son independientemente uno del otro alquilo C_1-C_3 o haloalquilo C_1-C_3 ; o un grupo



En donde R_{10} y R_{11} son independientemente uno del otro hidrógeno o halógeno y $n = 1$ o 2 ; y

R_5 y R_6 son independientemente uno del otro hidrógeno o halógeno.

2. Un compuesto de fórmula I de acuerdo a la reivindicación 1, en donde X es oxígeno.

3. Un compuesto de fórmula I de acuerdo a la reivindicación 1, en donde X es azufre.

4. Un compuesto de fórmula I de acuerdo a la reivindicación 1, en donde

R_1 es CF_3 ;

R_2 es alquilo C_1-C_3 , haloalquilo C_1-C_3 , o alcoxi C_1-C_3 alquilo C_1-C_3 ;

R_3 es hidrógeno o flúor;

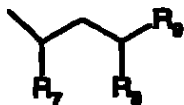
Q es Q_1 ;

R_4 es bicicloalquilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

Bicicloalquenilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

Bicicloalcadienilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ;

un grupo de la fórmula

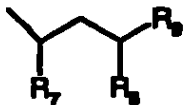


donde R_7 , R_8 y R_9 son independientemente uno del otro alquilo C_1-C_3 o haloalquilo C_1-C_3 ; y

R_5 y R_6 son independientemente el uno del otro hidrógeno, cloro o flúor.

5. Un compuesto de la fórmula I de acuerdo a la reivindicación 1, en donde

R_4 es un grupo de la forma



En donde R_7 , R_8 y R_9 son independientemente uno del otro alquilo C_1-C_3 o haloalquilo C_1-C_3 .

6. Un compuesto de la fórmula I e acuerdo a la reivindicación 1, en donde

R_1 es CF_3 ;

R_2 es alquilo C_1-C_3 , haloalquilo C_1-C_3 , o alcoxi C_1-C_3 alquilo C_1-C_3 ;

R_3 es hidrógeno o flúor;

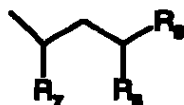
Q es Q_2 , Q_3 o Q_4 ;

R_4 es bicicloalquilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

Bicicloalquenilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

Bicicloalcadienilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ;

un grupo de la forma



donde R_7 , R_8 y R_9 son independientemente uno del otro alquilo C_1-C_3 o haloalquilo C_1-C_3 ; y

R_5 y R_6 son independientemente el uno del otro hidrógeno, cloro o flúor.

7. Un compuesto de la fórmula I de acuerdo a la reivindicación 6, en donde

Q es Q2.

8. Un compuesto de la fórmula I de acuerdo a la reivindicación 2, en donde

R₁ es CF₃;

R₂ es alquilo C₁-C₃ o alcoxi C₁-C₃ alquilo C₁-C₃;

R₃ es hidrógeno o flúor;

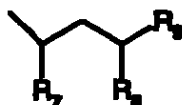
Q es Q1;

R₄ es bicicloalquilo C₆-C₁₀ no sustituido o sustituido por metilo, etilo o CF₃; o

Bicicloalquenilo C₆-C₁₀ no sustituido o sustituido por metilo, etilo o CF₃; o

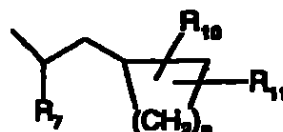
Bicicloalcadienilo C₆-C₁₀ no sustituido o sustituido por metilo, etilo o CF₃; o

un grupo de la fórmula



M/

donde R_7 , R_8 y R_9 son independientemente uno del otro alquilo C_1-C_3 o haloalquilo C_1-C_3 ; o un grupo



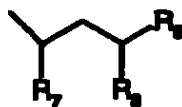
Donde R_{10} y R_{11} son independientemente uno del otro hidrógeno o halógeno y $n = 1$ o 2 ; y

R_5 y R_6 son independientemente uno del otro hidrógeno, cloro o flúor.

9. Un compuesto de fórmula I de acuerdo a la reivindicación 8, en donde

R_2 es metilo o CH_2OCH_3 ;

R_4 es un grupo de la forma



donde R_7 , R_8 y R_9 son independientemente uno del otro CF_3 , metilo o etilo, preferiblemente metilo; y

R_5 y R_6 son independientemente uno del otro hidrógeno, flúor, o cloro.

10. Un compuesto de la fórmula I de acuerdo a la reivindicación 9, en donde

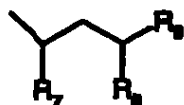
R_2 es metilo.

11. Un compuesto de la fórmula I de acuerdo a la reivindicación 9, en donde

R_2 es metilo;

R_3 es hidrógeno;

R_4 es un grupo de la forma



donde R_7 , R_8 y R_9 son independientemente uno del otro metilo o etilo, preferiblemente metilo; y

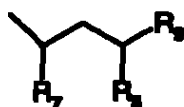
R_5 y R_6 son independientemente uno del otro hidrógeno, flúor, o cloro.

12. Un compuesto de la fórmula I de acuerdo a la reivindicación 9, en donde

R_2 es metilo;

R_3 es flúor;

R_4 es un grupo de la forma



donde R_7 , R_8 y R_9 son independientemente uno del otro metilo o etilo, preferiblemente metilo; y

R_5 y R_6 son independientemente uno del otro hidrógeno, flúor, o cloro.

13. Un compuesto de fórmula I de acuerdo a la reivindicación 1, en donde

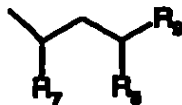
R_1 es CF_2H o CHF_2 ;

R_2 es alquilo C_1-C_3 , haloalquilo C_1-C_3 o alcoxi C_1-C_3 - alquilo C_1-C_3 ;

R_3 es hidrógeno o flúor;

Q es $Q1$;

R_4 es un grupo de la forma



donde R_7 , R_8 y R_9 son independientemente uno del otro alquilo C_1-C_3 o haloalquilo C_1-C_3 ; y

R_5 y R_6 son independientemente uno del otro hidrógeno, cloro o flúor.

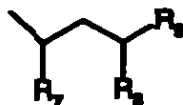
14. Un compuesto de la fórmula I de acuerdo a la reivindicación 13, en donde

X es oxígeno;

R_2 es metilo o CH_2OCH_3 ;

R_4 es un grupo de la forma

MS



donde R_7 , R_8 y R_9 son independientemente uno del otro alquilo C_1-C_3 o haloalquilo C_1-C_3 .

15. Un compuesto de fórmula I de acuerdo con la reivindicación 1, en donde

R_1 es CF_2H o CFH_2 ;

R_2 es alquilo C_1-C_3 , haloalquilo C_1-C_3 o alcoxi C_1-C_3 - alquilo C_1-C_3 ;

R_3 es hidrógeno o flúor;

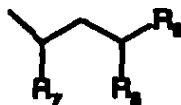
Q es Q_2 , Q_3 o Q_4 ;

R_4 es bicicloalquilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

Bicicloalquenilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ; o

Bicicloalcadienilo C_6-C_{10} no sustituido o sustituido por metilo, etilo o CF_3 ;

un grupo de la forma



donde R_7 , R_8 y R_9 son independientemente uno del otro alquilo C_1-C_3 o haloalquilo C_1-C_3 ; y

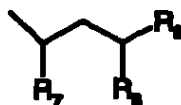
R_5 y R_6 son independientemente uno del otro hidrógeno, cloro o flúor.

16. Un compuesto de la fórmula I de acuerdo con la reivindicación 15, en donde

X es oxígeno;

R_2 es metilo o CH_2OCH_3 ;

R_4 es un grupo de la forma



donde R_7 , R_8 y R_9 son independientemente uno del otro alquilo C_1-C_3 o haloalquilo C_1-C_3 .

17. Un compuesto de la fórmula I de acuerdo con la reivindicación 1, seleccionado de

Ácido 1-metil-4-trifluorometil-1H-pirrol-3-carboxílico [2-(1,3-dimetilbutil)fenil]amida;

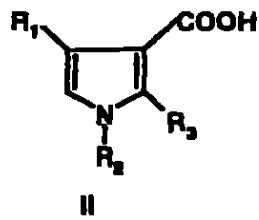
Ácido 1-metoximetil-4-trifluorometil-1H-pirrol-3-carboxílico [2-(1,3-dimetilbutil)fenil]amida;

Ácido 1-metil-2-fluoro-trifluorometil-1H-pirrol-3-carboxílico [2-(1,3-dimetilbutil)fenil]amida;

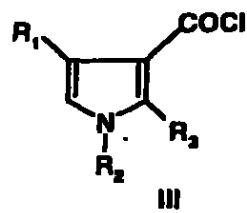
Ácido 1-metoximetil-2-fluoro-4-trifluorometil-1H-pirrol-3-carboxílico [2-(1,3-dimetilbutil)fenil]amida;

Ácido 1-metil-4-trifluorometil-1H-pirrol-3-carboxílico [2-(1,3-dimetilbutil)fenil]amida.

18. Un proceso de preparación de los compuestos de fórmula I, el cual comprende en una primera etapa preparar los compuestos de fórmula I en donde X = O por medio de convertir el ácido pirrolcarboxílico II



a el ácido clorhídrico III

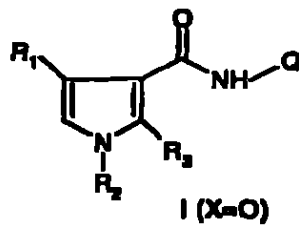


y por medio de hacer reaccionar el ácido clorhídrico
pirrol III con la amina IV

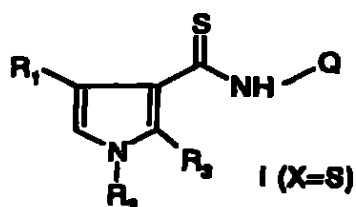
$\text{H}_2\text{N-Q}$ IV

A los compuestos de fórmula I

Un



Y opcionalmente convertir estos compuestos en los compuestos de fórmula I en donde $X = S$ por medio de hacer reaccionar el reactivo Lawesson o P_2S_5 en dioxano, tetrahidrofurano o tolueno a una temperatura de 0° en reflujo a



Y en donde R_1 , R_2 , R_3 y Q son como se definió para la fórmula I en la reivindicación 1.

19. Una composición para controlar microorganismos e impedir el ataque e infestación de las plantas, en donde el ingrediente activo es un compuesto según la reivindicación 1 junto con un portador adecuado.

20. El uso de un compuesto de fórmula I de acuerdo con la reivindicación 1 para proteger las plantas contra la infestación con microorganismos fitopatógenicos.

21. Un método para controlar o impedir la infestación de plantas cultivadas por microorganismos

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fitopatogénicos por medio de la aplicación de un compuesto de fórmula I según la reivindicación 1 a las plantas, las partes de ellas o el locus de la misma.

22. Intermedios de aminas de fórmula IV H_2N-Q

en donde Q y R_4 , R_5 , R_6 , R_7 , R_8 , R_9 , R_{10} y R_{11} son como se definió en la reivindicación 1.

23. Un compuesto de fórmula IV de acuerdo con la reivindicación 22 seleccionado a partir de

- 2-biciclo[2.2.2]oct-2-il-fenilamina;
- 2-biciclo[2.2.2]oct-2-en-2-il-fenilamina;
- 2-biciclo[2.2.2]octa-2,5-dien-2-il-fenilamina;
- 2-(2-aminofenil)-1,1,1-trifluorometil-4-metil-pentan-2-ol;
- 2-(2-aminofenil)-1-ciclopropil-propan-2-ol;
- 2-(2-aminofenil)-1-ciclopropil-butan-2-ol;
- 2-(3-metil-1-trifluorometil-but-1-enil)-fenilamina;
- 2-(3-metil-1-trifluorometil-butil)fenilamina;
- 2-(2-ciclopropil-1-metil-etil)fenilamina; y
- 2-(1-ciclopropilmetil-propil)fenilamina.

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24. Un proceso para la preparación de compuestos de la fórmula IVB de acuerdo a la reivindicación 22, caracterizado por

ruta a) reaccionar el derivado de formilo W-NHCHO de fórmula X con una cetona de fórmula IX en la presencia de 2-3 equivalentes de n-BuLi o SEC ID No.-BuLi u otra base fuerte en un solvente en una temperatura de -100 a -110° C suministrando los compuestos de fórmula XI (WY-NHCHO);

convertir el derivado de formilo de fórmula XI en compuestos de amina de fórmula VI (H₂N-WY) en una hidrólisis básica por medio de hacer reaccionar con NaOH o KOH en alcoholes; e hidrogenar la amina VI en los compuestos IV (H₂N-Q) con Pd/carbón en la presencia de un ácido fuerte (por ejemplo ácido sulfúrico) o alternativamente la eliminación del agua y luego la hidrogenación; o

ruta b) hacer reaccionar la amina de fórmula XII (H₂N-T) con un exceso del reactivo Grignard de fórmula XV en un disolvente como THF o éter a una temperatura de 0° C a reflujo a la amina de fórmula VI; y

convertir la amina VI a la amina XIV ($\text{H}_2\text{N-TG}$) por la eliminación de agua; la hidrogenación de XIV con PD o Pt sobre carbón en un disolvente como el THF o alcoholes a temperaturas a 0°C a reflujo suministra los compuestos de fórmula IV; o directamente los compuestos de la fórmula VI por hidrogenación con PD sobre carbón en la presencia de ácido sulfúrico en un disolvente similar a un alcohol que suministra las aminas IV; o

ruta c) hacer reaccionar el derivado ($\text{NO}_2\text{-W}$ (fórmula XIII)) con una cetona de fórmula IX suministrando el derivado nitro $\text{NO}_2\text{-WY}$ de fórmula VII; o

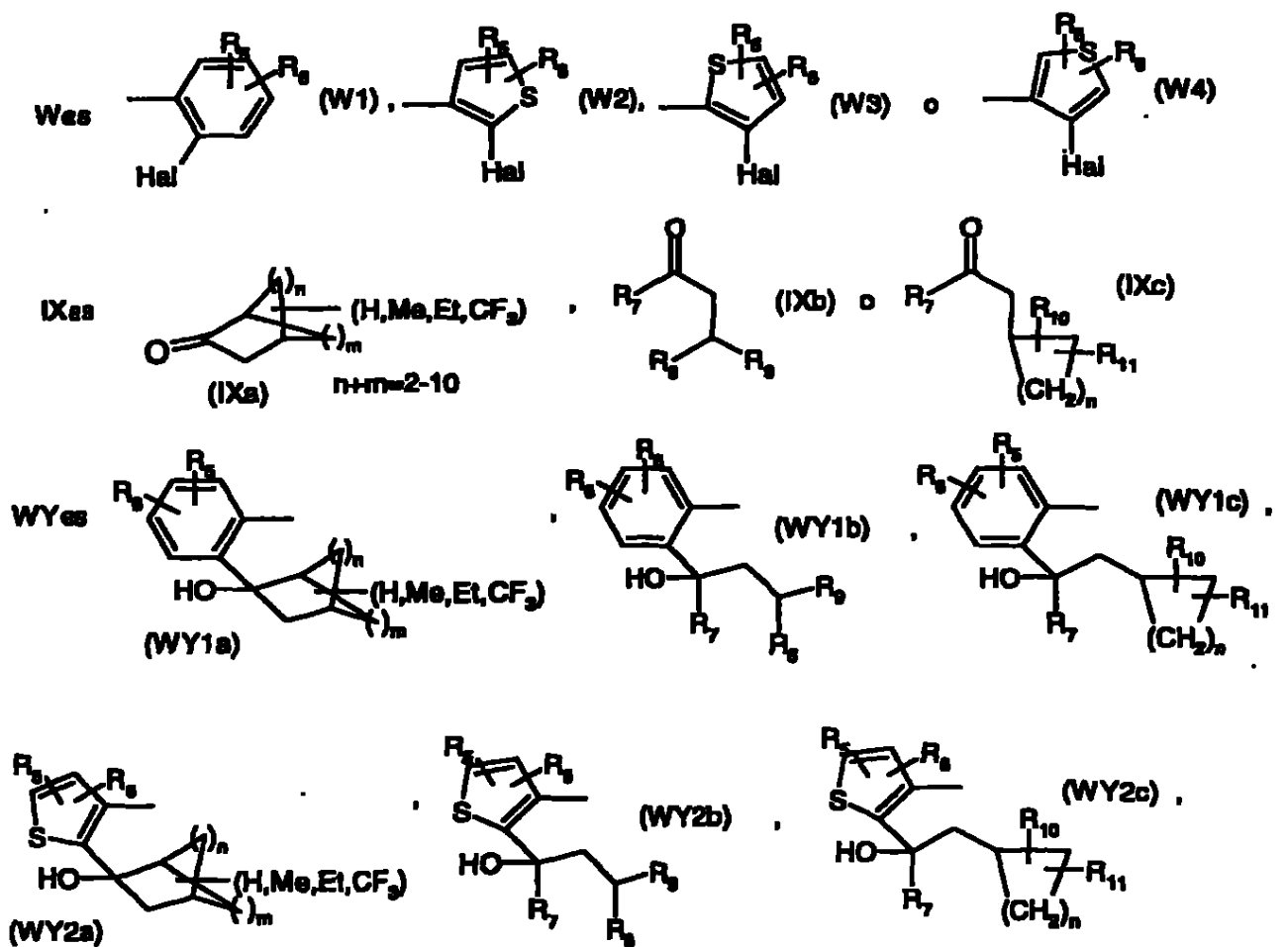
transformar el compuesto de fórmula VII por medio de la reacción con SOCl_2 o POCl_3 en piridina a una temperatura de 0° a reflujo en el derivado VIII ($\text{NO}_2\text{-TG}$);
y

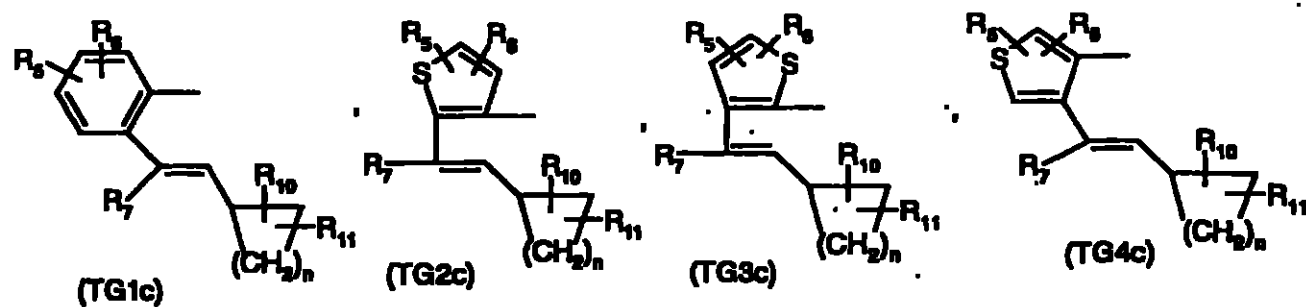
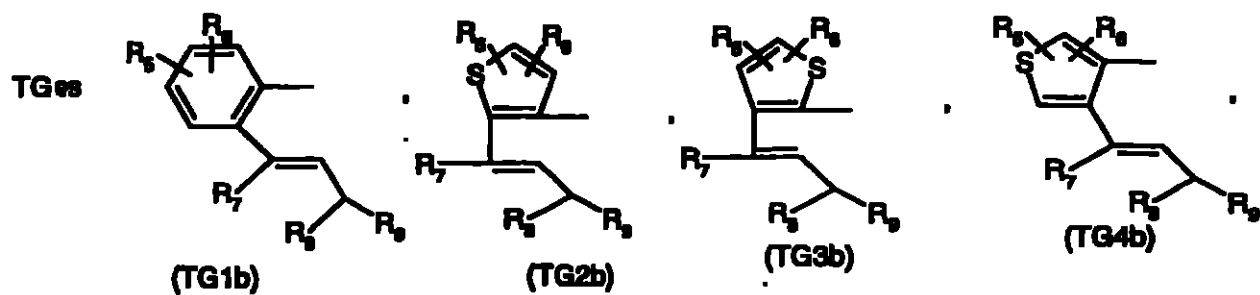
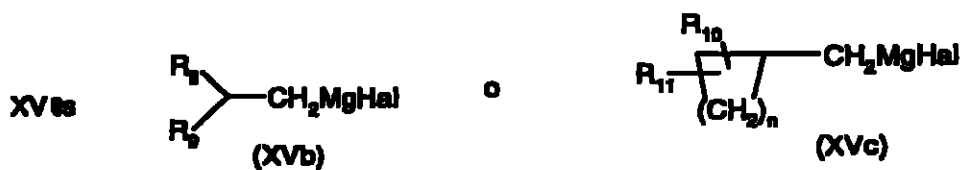
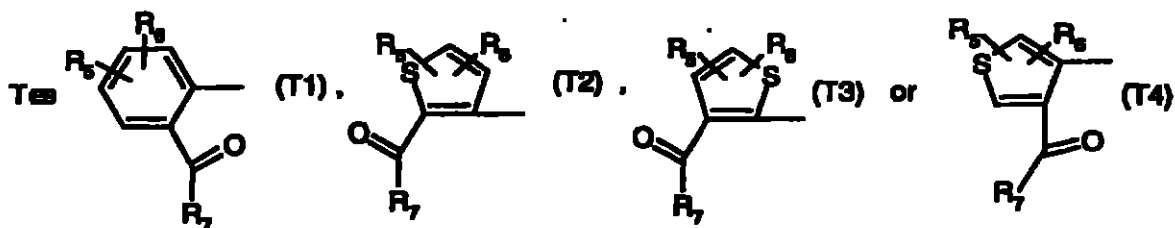
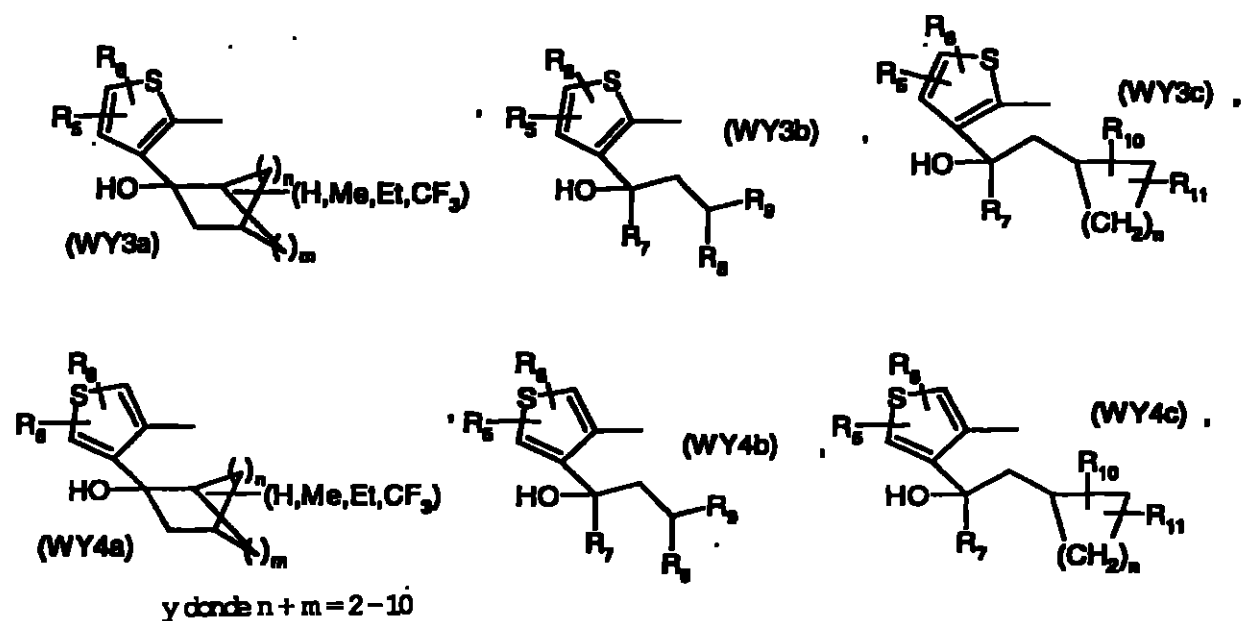
la hidrogenación del compuesto de fórmula VIII con Raney-Ni en alcohol a una presión de 50 - 200 bar y a una temperatura de 50 a 150°C en el compuesto de fórmula IV;

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en donde Q, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁ son como se definió en la reivindicación 1 para los compuestos de la fórmula I, Hal es Br o I y

en donde



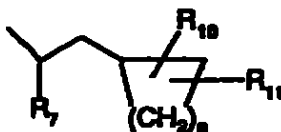


25. Un proceso de acuerdo a la reivindicación 24, ruta a) para compuestos de fórmula IV en donde Q es Q1; y

R_4 es bicicloalquilo C_7-C_{19} , no sustituido o sustituido por metilo, o CF_3 ;

bicicloalquenilo C_7-C_9 , no sustituido o sustituido por metilo, o CF_3 ;

bicicloalcadienilo C_7-C_9 , no sustituido o sustituido por metilo, o CF_3 ; o un grupo



R_5 y R_6 son hidrógeno; y donde R_7 , R_{10} , R_{11} y n son como se definió en la reivindicación 1.

26. Un proceso de acuerdo a la reivindicación 24, ruta a), en donde

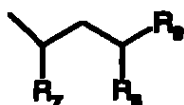
Q es Q2, Q3 o Q4; y

R_4 es bicicloalquilo C_7-C_{10} no sustituido o sustituido por metilo, o CF_3 ;

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bicicloalquenilo C₇-C₁₀ no sustituido o sustituido por metilo, o CF₃;

bicicloalcadienilo C₇-C₁₀ no sustituido o sustituido por metilo, o CF₃; o un grupo .



R₅ y R₆ son hidrógeno; y donde R₇, R₈, R₉ y n son como se definió en la reivindicación 1.

27. Un proceso de acuerdo a la reivindicación 24, ruta b), en donde

Q es Q1; y

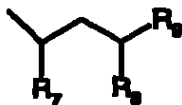
R₄ es bicicloalquilo C₇-C₁₀ no sustituido o sustituido por metilo, o CF₃;

bicicloalquenilo C₇-C₁₀ no sustituido o sustituido por metilo, o CF₃;

bicicloalcadienilo C₇-C₁₀ no sustituido o sustituido por metilo, o CF₃;

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o un grupo



R_5 y R_6 son hidrógeno; y donde R_7 , R_8 , R_9 y n son como se definió en la reivindicación 1.

28. Un proceso de acuerdo a la reivindicación 24, ruta b), en donde

Q es Q_2 , Q_3 o Q_4 ; y

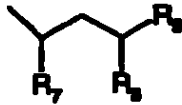
R_4 es bicicloalquilo C_7-C_{10} no sustituido o sustituido por metilo, o CF_3 ;

bicicloalquenilo C_7-C_{10} no sustituido o sustituido por metilo, o CF_3 ;

bicicloalcadienilo C_7-C_{10} no sustituido o sustituido por metilo, o CF_3 ;

o un grupo

/FB

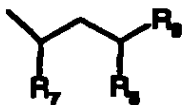


R₅ y R₆ son hidrógeno; y donde R₇, R₈, R₉ y n son como se definió en la reivindicación 1.

29. Un proceso de acuerdo a la reivindicación 24, ruta c), en donde

Q es Q1; y

R₄ es un grupo



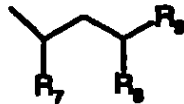
R₅ y R₆ son hidrógeno; y donde R₇, R₈, R₉ y n son como se definió en la reivindicación 1.

29. Un proceso de acuerdo a la reivindicación 24, ruta c), en donde

Q es Q1; y

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R_4 es un grupo



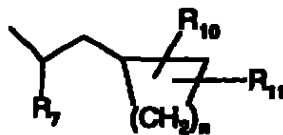
R_5 y R_6 son hidrógeno;

R_7 es CF_3 ; y en donde R_8 , R_9 y n son como se definió en la reivindicación 1.

30. Un proceso de acuerdo a la reivindicación 24, ruta c), en donde

Q es $Q1$; y

R_4 es un grupo



R_5 y R_6 son hidrógeno;

n es 1;

R_7 es CF_3 ; y en donde R_{10} R_{11} son como se definió en la reivindicación 1.

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SUBINDUSTRIA Y COMERCIO
Aduana : 0000176 0000000 Folios: 160
Fecha (CIB): 2003-05-07 16:53:42
Tramite : 611 PCT-PATENT 379 CASE 3821 411 PRESENTAC
Dependencia: 2000 DIVISION DE MARCA COMERCIAL

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 03 - 27,658
FECHA : ABRIL 22 DE 2003

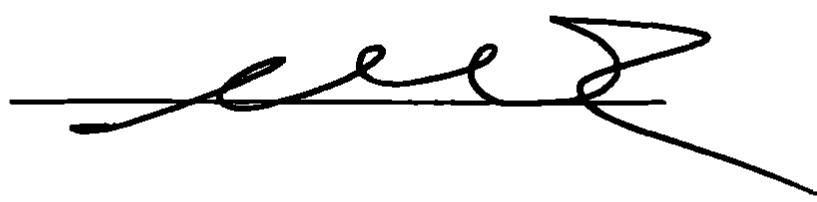
***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	9003691	22/04/2003	23,079,000.00

***** CONCEPTO *****

CANT. RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1 50005-01-01 SOLICITUDES	7 TRAMITES DE SOL. DE DISENOS INDUS	400,000.00
	TOTAL :	400,000.00

SOM: CUATROCIENTOS MIL PESOS

RESPONSABLE : 

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

020 13602-84/-002-7

REQUISITOS NECESARIOS PARA PRESENTACION Y AGILIZACION DEL TRAMITE

	USUARIO	RADICADOR
PATENTE DE INVENCION ☒ MODELO DE UTILIDAD	()	()
- Indicación de que se solicita la concesión de una patente	()	()
- Datos de identificación del solicitante o de la persona que se presenta la solicitud	()	()
- Descripción de la invención	()	()
- Dibujos de ser estos pertinentes	()	()
- Comprobante de Pago de las tasas establecidas	()	()

COMPLETA () INCOMPLETA ()

DISEÑO INDUSTRIAL ()

- Indicación de que se solicita el registro de Diseño Industrial () ()
- Datos de identificación del solicitante o de la persona que presenta la solicitud. () ()
- Representación gráfica y fotográfica del Diseño Industrial o muestra del Material que incorpora el diseño () ()
- Comprobante de pago de las tasas establecidas () ()

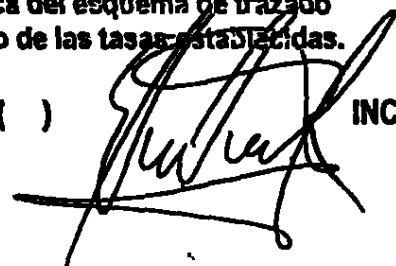
COMPLETA () INCOMPLETA ()

ESQUEMA DE TRAZADO ()

- Indicación de que solicita el registro de un Esquema de trazado. () ()
- Datos de identificación del solicitante o de la persona que presenta La solicitud. () ()
- Representación gráfica del esquema de trazado () ()
- Comprobante de pago de las tasas establecidas. () ()

COMPLETA () INCOMPLETA ()

Firma Responsable:



SECRETARIA Y COMERCIO

Radicación : 23826176 00000002 F.L. 30- 300

Fecha: 2023-05-27 16:53:40

Trámite : 011 FCI-GENE 379 FASE INCI 411 PRESENTAC

Dependencia: 2020 DIVISION DE NUEVAS OPERACIONES