

W.P.



Industria y Comercio
SUPERINTENDENCIA

12

PCT

SOLICITUD

PATENTE DE INVENCION

EXPEDIENTE N°

04-2809

TÍTULO

6-(2-TOLIL) - TRIAZOLOPIRIDINAS SUSTITUIDAS COMO FUNGICIDAS

1. CLASIFICACIÓN INTERNACIONAL **C07D487/04**

71. SOLICITANTE **BASF AKTIENGESELLSCHAFT**

DOMICILIO **Ludwigshafen, República Federal de Alemania.**

74 APODERADO **EMILIO FERRERO**

Código 1092

22 BOGOTÁ, D. C. **16-01-04**

97



Industria y Comercio

SUPERINTENDENCIA



04 002809 00

PETITORIO

SUPERINTENDENCIA Y COMERCIO

Radicación : 04083099 00000000

Folios: 204

Fecha (MM): 2004-01-16 17:13:42

Trámite : 011 PCI-PATENT 2/3 FASE NACI 411 PRESENTAC

Dependencia: 2628 DIVISION DE MARCAS COMERCIALES

lón

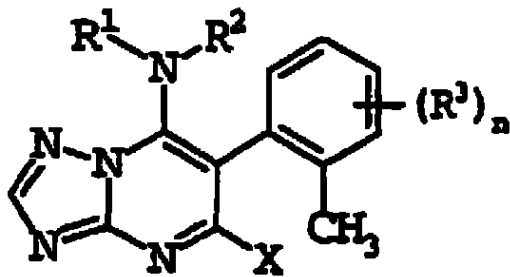
FORMULARIO UNICO DE SOLICITUD DE PATENTE PCT ENTRADA EN FASE NACIONAL

1	SOLICITUD DE:	
	☒ Patente de Invención.	☐ Patente de Modelo de Utilidad.
	☐ Capítulo I.	☒ Capítulo II.
2	SOLICITANTE (71) Nombre: BASF AKTIENGESSELLSCHAFT sociedad constituida y existente bajo las leyes de la Republica Federal de Alemania. Dirección: 67056 Ludwigshafen Republica Federal de Alemania. Domicilio: Ludwigshafen, Republica Federal de Alemania. IDENTIFICACION C.C. ☐ NIT ☐ C.E. ☐ Otro ☐ Cual _____ Número: _____	
3	REPRESENTANTE O APODERADO Nombre: EMILIO FERRERO Dirección: Carrera 4ª. No. 72-35 Teléfono: 347 36 11 Fax:: 217 92 11 E-mail: <u>clientes@camyp.com.</u> Domicilio: Bogotá, Colombia. IDENTIFICACION C.C. ☒ NIT ☐ C.E. ☐ Otro ☐ Cual _____ Número: <u>438.019</u> T.P. <u>31.929</u>	
4	INVENTOR (ES) (72) 1. Jordi TORMO I BLASCO Mühlweg 47, 67117 Limburgshafen, República Federal de Alemania 2. Hubert SAUTER Neckarpromenade 20, 68167 Mannheim, República Federal de Alemania 3. Bernd MÜLLER Jean-Ganss-Strasse 21, 67227 Frankenthal, República Federal de Alemania 4. Markus GEWEHR Goethestrasse 21, 56288 Kastellaun, República Federal de Alemania 5. Wassilos GRAMMENOS Samuel-Hahnemann-Weg 9, 67071 Ludwigshafen, República Federal de Alemania 6. Thomas GROTE Im Hoehnhausen 18, 67157 Wachenheim, República Federal de Alemania 9. Ingo ROSE C2, 19, 68159 Mannheim, República Federal de Alemania 10. Peter SCHÄFER Römerstrasse 1, 67308 Ottersheim, República Federal de Alemania 11. Frank SCHIEWECK Lindenweg 4, 67258 Hessheim, República Federal de Alemania 12. Michael RACK Sandwingert 67 69123 Heidelberg, República Federal de Alemania 13. Eberhard MERMANN Von-Gagern-Strasse 2, 64646 Heppenheim, República Federal de Alemania 14. Siegfried STRATHMANN Donnersbergstrasse 9, 67117 Limburgerhof, República Federal de Alemania	

	7. Andreas GYPSE B 4,4, 68159 Mannheim, República Federal de Alemania 8. Joachim RHEINHEIMER Merziger Str. 24, 67063 Ludwigshafen, República Federal de Alemania	15. Gisela LORENZ Erlenweg 13, 67434 Hambach, República Federal de Alemania 16. Reinhard STIERL Ginsterstr 17, 67112 Mutterstadt, República Federal de Alemania						
5	PCT (86) Solicitud Internacional No. <u>PCT/EP/02/07578</u> Fecha: <u>Julio 8 de 2002</u> Publicación Internacional No. <u>WO 03/008417</u> Fecha: <u>Enero 30 de 2003</u>							
6	Título (54) <u>6-(2-TOLIL) -TRIAZOLOPIRIMIDINAS SUSTITUIDAS COMO FUNGICIDAS</u>							
7	Clasificación Internacional (51) <u>C07D 487/04</u>							
8	Prioridad SI ☒ NO ☐	<table border="1"><thead><tr><th>(33) País de Origen</th><th>(32) Fecha</th><th>(31) Número de Solicitud</th></tr></thead><tbody><tr><td><u>EP</u></td><td><u>Julio 18 de 2001</u></td><td><u>01117402.6</u></td></tr></tbody></table>	(33) País de Origen	(32) Fecha	(31) Número de Solicitud	<u>EP</u>	<u>Julio 18 de 2001</u>	<u>01117402.6</u>
(33) País de Origen	(32) Fecha	(31) Número de Solicitud						
<u>EP</u>	<u>Julio 18 de 2001</u>	<u>01117402.6</u>						
9	Comprobante de pago No.: <u>04-689</u> Fecha: <u>Enero 6 de 2004</u>							
10	Anexos: ☒ Comprobante de pago de la tasa de presentación de la solicitud por \$ 422.000.00. ☐ 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 acredita 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:



(I)

12

Solicito la concesión de la patente,

NOMBRE: EMILIO FERREROFIRMA: 

C.C. 438.019 de Usaquén T.P. 31.929

MRE/lms

CARRERA
BOGOTÁ, COLOMBIA

REPRESENTACION Y PODER

Yo (nosotros), abajo firmado (s)
BASF Aktiengesellschaft

domicillado(s) en ..Ludwigshafen, República
Federal de Alemania

por el presente nombramos a GERMAN CAVELIER, tpa. 832; GONZALO PERDOMO, tpa. 831; ERNESTO CAVELIER, tpa. 11519; y EMILIO FERRERO, tpa. 31929; domiciliados en la Carrera 4ª N° 72-35, Bogotá, Colombia, en obediencia a lo dispuesto en el párrafo 1º del Artículo 543 del Código de Comercio, el primero como principal y los demás como suplentes, en su orden, como nuestros representantes en todos los asuntos de propiedad industrial con facultad para recibir notificaciones y nombrar apoderados judiciales o extrajudiciales. El primer representante suplente reemplazará al principal en caso de ausencia o impedimento temporal o definitivo de aquél. La misma regla se aplicará cuando el segundo representante suplente haya de reemplazar al primero, o el tercero al segundo. En tales casos, el representante principal, o el primero, o segundo suplente, en su caso, o ambos, declararán su intención de no ejercer la representación mediante declaración autenticada por Notario Público en Colombia, o por Notario u otro Funcionario Público, o Cónsul de Colombia, en el extranjero; y si se tratare de impedimento, con el certificado respectivo. Si alguno de los nombrados faltare definitivamente, el siguiente tomará su lugar. Cuando cesare la ausencia o impedimento del representante principal, o de su primero o segundo suplente, en su caso, podrán ejercer la representación, en su orden, uno u otros según el caso, asumiéndola por el solo hecho de ejercerla, cesando en ese momento el ejercicio de la representación por el primero, segundo o tercer suplente en su caso.

Además, y bajo las mismas reglas, conferimos poder a los abogados arriba nombrados, para obtener la protección de mi (nuestra) propiedad industrial y contra la competencia desleal, a cuyo efecto autorizo (amos) a los dichos apoderados para que me (nos) representen ante cualesquiera entidades o personas, ejerzan o no jurisdicción, especialmente ante las del orden administrativo, contencioso-administrativo y judicial, en todo lo concerniente a los siguientes asuntos: a) Obtención de patentes de invención, modelos y dibujos industriales; el registro de marcas de fábrica, colectivas, defensivas y de servicios; el depósito de nombres comerciales y enseñas; su renovación, traspaso, cambio de nombre o domicilio, cancelación voluntaria; y el registro de licencias de uso de esos derechos; b) Las acciones de oposición, cancelación, nulidad, medidas cautelares, concesión de licencias y en general los juicios civiles, penales, administrativos o contencioso-administrativos relacionados con estos derechos; acciones y juicios que promovamos o se nos promuevan. Y para que en todos los asuntos arriba determinados, puedan sustituir este mandato, transcribir, desistír, cancelar, recibir, renunciar, y ratificar los actos hechos por agentes oficiales.

Dado y firmado hoy ..17 de marzo de 1989

en D-6700 Ludwigshafen

BASF Aktiengesellschaft

ppa. Welzel

(Für Patente, Modelle und Zeichnungen; Warenzeichen und Servicemarken; Handelsnamen und -zeichen).

VERTRETUNG UND VOLLMACHT

Ich (wir) unten Unterzeichnender (de)
BASF Aktiengesellschaft

wohnhaft in Ludwigshafen, República Federal de Alemania

verleihen durch dieses Schreiben an GERMAN CAVELIER, tpa. 832; GONZALO PERDOMO, tpa. 831; ERNESTO CAVELIER, tpa. 11519; und EMILIO FERRERO, tpa. 31929; wohnhaft in der Carrera 4ª N° 72-35, Bogotá, Kolumbien, um die Verfügung des Absatzes 1 im Artikel 543 des Handelsgesetzbuch zu beachten, der erste als Hauptvertreter und die übrigen als Stellvertreter, beziehungsweise, als unsere Vertreter in allen was sich auf das industrielle Eigentum bezieht, berechtigt Meldungen zu empfangen und gerichtliche und aussergerichtliche Bevollmächtigte zu ernennen. Der erste Stellvertreter wird den Hauptvertreter ersetzen wegen zeitweiliger oder definitiver Abwesenheit oder Hindernisses des ersten. Dieselbe Regel wird angewandt werden wenn der zweite Stellvertreter den ersten ersetzen muss, oder der dritte den zweiten. In solchen Fällen der Hauptvertreter, oder der erste oder der zweite Stellvertreter, beziehungsweise, oder beide, werden ihre Absicht aussprechen um nicht die Vertretung auszuüben mittelst Aussage notariell beglaubigt in Kolumbien, oder vor Notar oder vor einem anderen öffentlichen Beamten, oder kolumbianischen Konsul im Auslande; und wenn es ein Hindernis sei, mittels der betreffenden Beglaubigung. Wenn einer der Genannten immerfort abwesend wäre, der Folgende wird ihn ersetzen. Im Falle dass die Abwesenheit oder das Hindernis des Hauptvertreters, oder diejenigen seines ersten, zweiten oder dritten Vertreters, beziehungsweise, besonders, einer oder anderen, ordnungsgemäss werden die Vertretung ausüben und sie zu sich nehmen nur auf Grund sie auszuüben, mit Aufheben zur Zeit der Ausübung der Vertretung durch den ersten, den zweiten oder den dritten Stellvertreter beziehungsweise.

Ausserdem, und unter diesen Regeln, wir verleihen den genannten Rechtsanwälte die Vollmacht, und um den Schutz meines (unseres) industriellen Eigentums zu erhalten und gegen den unlauteren Wettbewerb zu diesem Zweck ich (wir) die genannten Bevollmächtigten ernenne (n) damit sie (s) vor staatlichen Institutionen oder Personen, die die Rechtsprechung ausüben oder nicht vor allem vor denen mit Verwaltungs, streitigem Verwaltung, [?] Charakter, in allen was sich auf folgende Angelegenheiten bezieht, zu vertreten: a) Erlangung von Patenten, Modellen und Zeichnungen; Registrierung von Waren; Spatzen-Defensive- und Service-marken; Aufbewahrung von Handelsnamen und -zeichen; ihre Erneuerung und Übertragung; Namen und Wohnsitzänderung; freiwillige Annullierung und die Registrierung von Vertragssachen; b) Die Oppositionsklagen, Annullierung, Ungültigkeit, Vorsichtmassnahmen, Lizenzen und im allgemeinen die Zivil-, Straf-, Verwaltungs- oder streitigen Verwaltungsprozesse, die mit diesen Rechten verbunden sind, Aktionen und Verhandlungen, die wir vorantreiben oder die man uns vorantreibt und; c) damit sie in allen oben bestimmten Angelegenheiten dieses Mandat ersetzen, regeln, davon Abstand nehmen, annullieren, empfangen, verzichten, Meldungen annehmen und gerichtliche und aussergerichtliche Bevollmächtigte ernennen, und die Handlungen der halbamtlichen Vertreter bestätigen.

Unterschrift heute am 17. März 1989

in D-6700 Ludwigshafen

ppa. Richters

GENERAL DE COI

GO. GENERAL DE COLOMBIA

SULLO

U.R.Nr. 1407/89

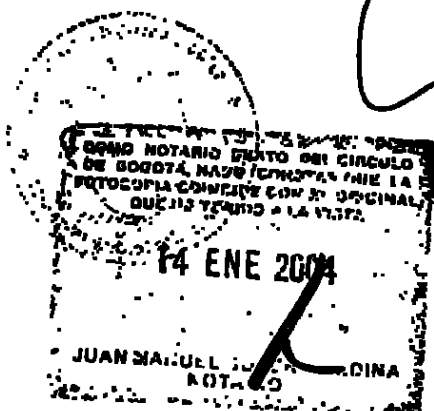
Ich beglaubige hiermit die Echtheit der vorst.
eigenhändig vor mir vollzogenen Unterschriften der für
die Firma BASF Aktiengesellschaft Ludwigshafen am Rhein
handelnden Herren:

1. Dr. Gunther W e l z e l , Chemiker in
Ludwigshafen am Rhein,
2. Dr. Peter R i c h t e r s , Chemiker in
Ludwigshafen am Rhein.

Die Herren Dr. Welzel und Dr. Richters sind mir persönlich
bekannt.

Aufgrund heutiger Einsichtnahme in das Handelsregister
beim Amtsgericht Ludwigshafen am Rhein HR B 3000 be-
scheinige ich, daß die Herren Dr. Welzel und Dr. Richters
als Prokuristen gemeinschaftlich zur Vertretung und
Zeichnung der Firma BASF Aktiengesellschaft mit dem
Sitz in Ludwigshafen am Rhein berechtigt sind.

Ludwigshafen am Rhein, den 17. März 1989



Th. Walter
Notarassessor
als amtlich bestellter Vertreter
des Notars Dr. Gerhard Kohler

Die Echtheit vorstehender Unterschrift des Notarassessors

Thomas Walter

als amtlich bestellter Vertreter des Notars Justizrat Dr. Kohler
in Ludwigshafen am Rhein und die Echtheit des beigedruckten
Dienststempels werden hiermit bestätigt. Zugleich wird bescheinigt,
daß der Vorgenannte zur Vornahme der Amtshandlung befugt war.

Frankenthal (Pfalz), den einundzwanzigsten März neunzehnhundert-
neunundachtzig

Präsident des Landgerichts

Franz Serfas
(Franz Serfas)



Kostenvermerk: Gebühr 20.-- DM



RECEIVED
MAY 11 1989
NOTARY
THOMAS WALTER
FRANKENTHAL (PFALZ)

El suscrito Cónsul General de Colombia en Frankfurt
am Main, República Federal de Alemania, vistos los
documentos presentados por los interesados,

C E R T I F I C A:

Que el señor Thomas Walter-----
quien como Notario en Ludwigshafen am Rhein-----
autenticó la(s) firma(s) del(os) signatario(s) del
Poder precedente, ejercía las funciones indicadas y
su firma corresponde a la registrada ante el Tribunal Re-
gional de Frankenthal (Pfalz)-----
que la compañía BASF Aktiengesellschaft-----
es una sociedad constituida de acuerdo con las leyes
de la República Federal de Alemania y cumple su objeto
conforme a las mismas; que el(los) señor(es) Dr. Gunther
WELZEL y el Dr. Peter RICHTERS-----
quien(es) en sus carácter(es) de apoderados-----
----- y cuya(s) firma(s) fué
(fueron) autenticada(s) ante el Notario Thomas Walter-----
----- es(son) su(s) representan-----
te(s) legal(es) en este país.

El Cónsul General no asume responsabilidad por el con-
tenido del documento.

Esta Certificación se expide en Frankfurt am Main,
el seis de Abril de mil novecientos ochenta y nueve.

Frankfurt a. M 06 APR 1989

PAGADO IMPUESTO DE TIMBRE

Por 4 U.S. \$ de Ley E. S. N. N.



№-0077

14 FEB 2004
JUAN LAA... DINA...
COMO NOTARIO SEYTO DEL CIRCULO
DE BOGOTA, HAGO CONSTAR QUE LA
FOTOCOPIA COINCIDE CON EL ORIGINAL
QUE HE TENIDO A LA VISTA

GENERAL

124 APR 1964 No. 85061

di Antonia Nino
cuyo firma aparece al pie del presente
documento, declarando en ora fecha
las personas que interviene.

Chavez

MONTE EMERENCIOSO ACUNA

Monte de Emerencias Generales

COMO NOTARIO SEATO DEL CIRCULO
DE BOGOTA, HAGO CONSTAR QUE LA
FOTOCOPIA COINCIDE CON EL ORIGINAL
QUE HE TENIDO A LA VISTA

14 ENE 2004

JUAN MANUEL S. LIT. L. LINA
NOTARIO



6

SOMOS NOTARIO DEL CIRCULO
DE BOBOTA, MAGD GUNETAH QUE LA
FOTOCOPIA COINCIDE CON EL ORIGINAL
QUE HE TENIDO A LA OPORTA
14 ENE 2004
JUAN D. L. JINA

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COMO NOTARIO SE
DE BOGOTA, HAGO CONSTAR QUE LA
FOTOCOPIA CONCORDA CON EL ORIGINAL
QUE HE TENIDO EN VISTA
14 ENE 2004
JUAN MANUEL

Die konsularische Legalisierung ist notwendig.

NOTA PARA EL SEÑOR CONSUL COLOMBIANO: Según los artículos 65 del C. de P. C. y 480 del C. Co., si el poderdante es una sociedad, el señor Cónsul debe certificar que tuvo a la vista las pruebas de su existencia, que ejerce su objeto social, que quien confiere el poder es su representante y puede otorgar poder, seguidamente autenticar la firma de éste.

8

TRADUCCION OFICIAL NO. 2056

de un documento escrito en Alemán, el cual para su identificación se sella con el sello de la traductora, lo mismo que la presente.-

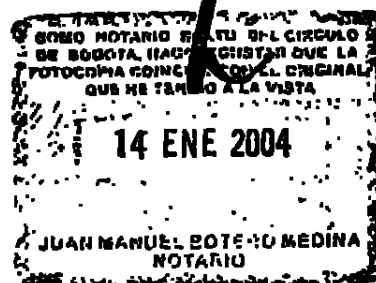
(A continuación del poder conferido a GERMAN CAVELIER, GONZALO PERDOMO, ERNESTO CAVELIER y EMILIO FERRERO, domiciliados en la Cra. 4 No. 72-35, Bogotá, el 17 de marzo de 1989, por la sociedad BASF Aktiengesellschaft, domiciliada en Ludwigshafen, RFA:)

Protocolo notarial No. 1407/89

Certifico la autenticidad de las firmas anteriores puestas ante mí, por los señores:

1. Dr. Gunther W e l z e l , químico, domiciliado en Ludwigshafen am Rhein,
2. Dr. Peter R i c h t e r s , químico, domiciliado en Ludwigshafen am Rhein.

A los doctores Walzel y Richters los conozco en persona.



LUZ ARIAGA DE HERDAN
TRADUCTORA E INTERPRETE OFICIAL
C.C. No. 599 Miliuteña

Certifico, por haber tenido a la vista el registro de comercio HR B 3000, del juzgado de Ludwigshafen, que los doctores Wlzel y Richters, en su calidad de apoderados, están facultados para representar conjuntamente y firmar por la sociedad BASF Aktiengesellschaft, con sede en Ludwigshafen.

Ludwigshafen am Rhein, 17 de marzo de 1989

(sello redondo:)

Dr. Siegfried Kohler

Fdo.: firma ilegible

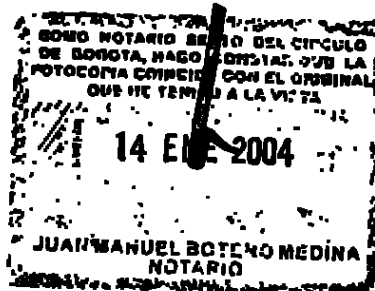
Notario de Ludwigshafen

Th. Walter

Asesor del notario como representante oficialmente designado del notario Dr. Siegfried Kohler

Se certifica la autenticidad de la firma anterior del asesor del notario, consejero de justicia Dr. Kohler, domiciliado en Ludwigshafen am Rhein, y la del sello oficial que la acompaña. Al mismo tiempo se certifica que el mencionado notario estaba facultado para realizar ese acto oficial.

Frankenthal (Pfalz), veintiuno de marzo de mil novecientos ochenta y nueve



LUZ ARRIAGA DE HERCER
TASACIONES E INGENIERIA S.A.
Calle 100 No. 595 Monterrey

El Presidente del Tribunal Regional

Fdm.: firma ilegible (sello redondo:)

(Franz Serfas)

El Presidente del Tribunal Regional
de Frankenthal (Pfalz)

Nota: Derrechos 20,-- DM

EN ESPAÑOL: La legalización de las firmas anteriores por el
Consulado de General de Colombia en Frankfurt, bajo el No.
0077 (Certificación consular) del 6 de abril de 1989 y del
Ministerio de Relaciones Exteriores de Colombia bajo el No.
85061 del 24 de abril de 1989.

Pagado impuesto de timbre US\$ 6,00

ES TRADUCCION FIEL Y COMPLETA, de la cual se deja copia en
los archivos de estas oficinas para su confrontación.

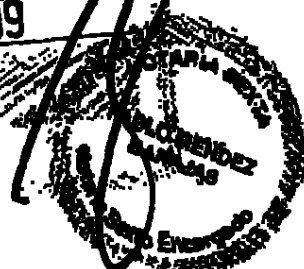
Bogotá, 26 de abril de 1989

LUZ ARRIAGA DE HERBEN
TRADUCTORA E INTERPRETE OFICIAL

Regulación No. 599 Minjusticia

COLOMBIA - REPUBLICA DE
BOGOTÁ, D. C.
MAYO 1989
LUZ Arriaga de Herben
CERTIFICACIONES CONSULARES NO. (2)
05 AGO. 1999
SANTAFE DE BOGOTÁ

COMO NOTARIO BERTO DEL CIRCULO
DE BOGOTÁ, NAGO CONSTAN QUE LA
FOTOCOPIA CONCIDE CON EL ORIGINAL
QUE HE TENIDO A LA VISTA
14 ENE 2004
JUAN CARLOS MEDINA
NOTARIO



MINISTERIO DE RELACIONES EXTERIORES
LEGALIZACIONES
Bogotá 28 MAR 1955 No. 88045
HACE CONSTAR
Que el señor
Luz DE Heredia
cuya firma aparece al pie del presente
documento, desempeña en esa fecha
las funciones allí indicadas.

14 ENE 2004
JUAN MANUEL SOTERO MEDINA
NOTARIO
División Consular
Encargado

881051599954

B. C. C. 18
SUCURSAL CORPORATIVA



DECLARACION Y PAGO DEL
IMPUESTO D
TIMBR
NACION

16 013 01 000045 1

RECIBO DE IMPUESTOS

16 013 01 000045 1

DATOS GENERALES	① Administración de impuestos de: BOGOTA		Código: 0.3	② Teléfono: 2120100
	③ Documento de identificación (marque X) C.C. & T.I. ☐ C ☐ NIT. ☐ A ☒ Y No. 860041367		④ Apellidos y Nombres o Razón Social de las partes (máximo 60 caracteres). CAVELIER ABOGADOS	
	⑤ C.C. & T.I. ☐ C ☒ X NIT. ☐ A ☐ Y No. 19'301.629		⑥ Apellidos y Nombres o Razón Social de las partes (máximo 60 caracteres). BORENO ROCHA JAIME	
	⑦ Dirección (de la persona o entidad identificada en la casilla 4) Cra. 4a. No. 72-35		Municipio: BOGOTA	Departamento: CUNDINAMARCA
	⑧ Relación(es) tipa(s) de documento(s), indicando número, fecha, valor y naturaleza de la transacción. TIMBRE TRADUCCION OFICIAL No. 2056 DE ABRIL 26 DE 1989 PAGO DERECHOS TRADUCCION DE UN PODER COLO 0361-52-218-8			

REVISADO
SECCION DE NEGOCIOS GENERALES
DIRECCION DE ASUNTOS CONSULARES
DE RELACIONES EXTERIORES

FIRMA	Responsable del pago
	Nombre: 19301629

1 VALOR DEL IMPUESTO A PAGAR	750
2 Sanciones	0
3 Intereses de mora	0
4 TOTAL PAGAR (sumando 1 + 2 + 3)	750

1 037 *** 750.00

DEM-31-V-88

CONTRIBUYENTE

CON PAGO
NOTARIO DE CUNDINAMARCA
DE SUJETA, PAGO CON LA
FOTOCOPIA CONCIERDE CON EL ORIGINAL
DUE HE TENIDO A VISTA
14 ENE 2004
JUAN MANUEL BOTENO MEDINA
NOTARIO

CAVELIER

ABOGADOS

EDIFICIO SISKI

CARRERA 49, No. 72-35
BOGOTA 8, COLOMBIA

CORREO ELECTRONICO MUNDIAL: CAVE

TELEFONO (57) (1) 2120100

CABLES: CAVELEYES

TELEX:
(23)741

CAVE UC

Señor Jefe de la
DIVISION DE NUEVAS CREACIONES
Superintendencia de Industria y Comercio
E. S. D.

Poderdante: BASF AKTIENGESELLSCHAFT

Poder conferido el: 17-03-89

Yo, GERMAN CAVELIER, obrando en mi calidad de apoderado principal del poderdante arriba mencionado, atentamente manifiesto a Usted que sustituyo el poder conferido en el doctor EMILIO FERRERO, Abogado con Tarjeta Profesional No. 31.929, con todas las facultades que me fueron conferidas.

Hago la anterior sustitución conforme al artículo 66 del Código de Procedimiento Civil ya que los otros sustitutos faltan en este momento.

Señor Jefe,

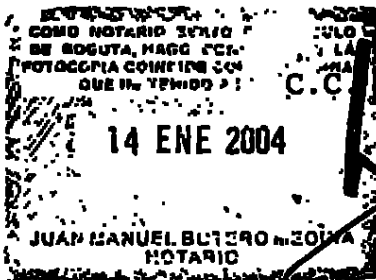
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C.C. No. 2.877.924 de Bogotá

14 ENE 2004

Acepto:



EMILIO FERRERO

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DILIGENCIA DE AUTENTICACION DE FIRMA
CON PRESENTACION PERSONAL

(Art. 1ro. del Decreto 2282 de 1989)

Ante el Notario Cincuenta (50) del Circulo de Santafé de
Bogotá-c.mparecio, el Doctor EMILIO FERNANDEZ

quien exhibió la cédula de ciudadanía número 6728-91
expedida en UAGUAY y la tarjeta profesional
número 31.929 del Ministerio de Justicia, con
el presente documento dirigido a: D. P. MUÑOZ (ASISTENTE)
y declaró que la firma que aparece en el: uya.

FIRMA AUTOGRAFA DEL DECLARANTE

- 6 OCT. 1993

Santafé de Bogotá, D. C.

AUTORIZO LA ANTERIOR



DILIGENCIA DE AUTENTICACION DE FIRMA
CON PRESENTACION PERSONAL

(Art. 1ro. del Decreto 2282 de 1989)

Ante el Notario Cincuenta (50) del Circulo de Santafé de
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quien exhibió la cédula de ciudadanía número 207724
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FIRMA AUTOGRAFA DEL DECLARANTE

01 OCT. 1993

Santafé de Bogotá, D. C.

AUTORIZO LA ANTERIOR

COMO NOTARIO JEFE DEL CIRCULO
DE BOGOTA, HACE CONSTAR QUE LA
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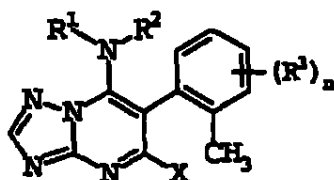
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(54) Title: SUBSTITUTED 6-(2-TOLYL)-TRIAZOLOPYRIMIDINES AS FUNGICIDES



(1)

(57) Abstract: Substituted 6-(2-tolyl)-triazolopyrimidines of formula (I) in which R¹ and R² independently denote hydrogen or alkyl, alkenyl, alkynyl, or alkyldienyl, haloalkyl, haloalkenyl, cycloalkyl, phenyl, naphthyl, or 5- or 6-membered heterocyclyl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or 5- or 6-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or where R¹ and R² radicals may be unsubstituted or substituted asdefined in the description, or R¹ and R² together with the interjacent nitrogen atom represent a 5- or 6-membered heterocyclic ring, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, which may be substituted; R³ is halogen, cyano, alkyl, alkoxy, haloalkyl, or C(=O)A, wherein A is hydrogen, hydroxy, alkyl, amino, or mono- or dialkyl-amino; n is an integer from 1 to 4; and X is halogen, cyano, alkyl, alkoxy, haloalkoxy or alkenyloxy; processes for their preparation, compositions containing them and to their use for combating phytopathogenic fungi.

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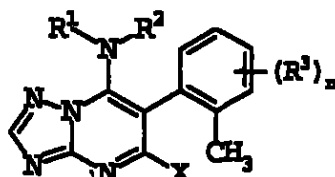
SUBSTITUTED 6-(2-TOLYL)-TRIAZOLOPYRIMIDINES AS FUNGICIDES

Description

5

The invention relates to substituted 6-(2-tolyl)-triazolopyrimidines of formula I

10



I

in which

15

R^1 and R^2 independently denote hydrogen or C_1 - C_{10} -alkyl, C_2 - C_{10} -alkenyl, C_2 - C_{10} -alkynyl, or C_4 - C_{10} -alkadienyl, C_1 - C_{10} -haloalkyl, C_2 - C_{10} -haloalkenyl, C_3 - C_{10} -cycloalkyl, phenyl, naphthyl, or

20

5- or 6-membered heterocyclyl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or

5- or 6-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or

25

where R^1 and R^2 radicals may be unsubstituted or partly or fully halogenated or may carry one to three groups R^a ,

30

R^a is cyano, nitro, hydroxyl, C_1 - C_6 -alkyl, C_3 - C_6 -cycloalkyl, C_1 - C_6 -alkoxy, C_1 - C_6 -alkylthio, C_1 - C_6 -alkylamino, di- C_1 - C_6 -alkylamino, C_2 - C_6 -alkenyl, C_2 - C_6 -alkenyloxy, C_2 - C_6 -alkynyl, C_3 - C_6 -alkynyloxy and C_1 - C_4 -alkylenedioxy; or

35

R^1 and R^2 together with the interjacent nitrogen atom represent a 5- or 6-membered heterocyclic ring, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, which may be substituted by one to three R^a radicals;

40

R^3 is halogen, cyano, C_1 - C_{10} -alkyl, C_1 - C_{10} -alkoxy, C_1 - C_{10} -haloalkyl, or $C(=O)A$, wherein

45

A is hydrogen, hydroxy, C_1 - C_8 -alkyl, C_1 - C_8 -alkoxy, amino, C_1 - C_8 -alkylamino, or di- $(C_1$ - C_8 -alkyl)-amino;

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n is an integer from 1 to 4; and

X is halogen, cyano, C₁-C₆-alkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy or C₃-C₆-alkenyloxy.

5

Moreover, the invention relates to processes for their preparation, compositions containing them and to their use for combating phytopathogenic fungi.

10 6-Phenyl-7-amino-triazolopyrimidines are generally known from US 4,567,262 and US 5,593,996.

Triazolopyrimidines with a trifluorophenyl group in 6-position are disclosed in WO-A 98/46607 and EP-A 945 453.

15

From WO-A 98/46608 diverse 6-phenyl-triazolopyrimidines are known, which are substituted in the 7-position by fluorinated alkylamines.

20 The compounds disclosed in the documents discussed above are said to be active against various phytopathogenic fungi.

It is an object of the present invention to provide compounds having improved fungicidal activity.

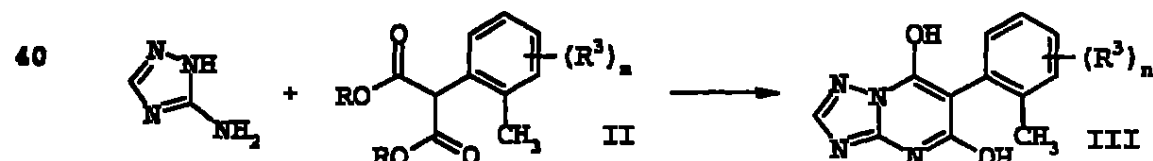
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We have found that this object is achieved by the compounds defined at the outset. Furthermore, we have found processes for their preparation, compositions comprising them and methods for controlling phytopathogenic fungi using the compounds I.

30

The compounds of the formula I differ from the compounds known from closest prior art WO-A 98/46608 in the 2-tolyl group, which is further substituted.

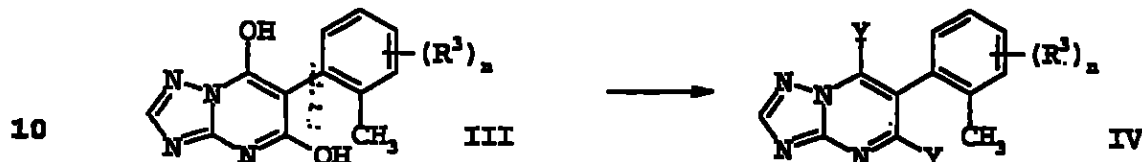
35 The present invention further provides a process for the preparation of compounds of formula I as defined above which comprises reacting 5-amino-triazole with 2-(2-tolyl)-substituted malonic acid ester of formula II, in which



R represents alkyl, preferably C₁-C₆-alkyl, in particular methyl or ethyl, under alkaline conditions, preferably using high boiling tertiary amines as for example tri-n-butylamine as disclosed for example by EP-A 770 615 to yield compounds of formula III.

45

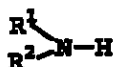
The resulting 5,7-dihydroxy-6-phenyl-triazolopyrimidine of formula III, wherein R^3 and n are as defined for formula I, is subsequently treated with a halogenating agent, preferably with a brominating or chlorinating agent, such as phosphorus oxybromide or phosphorus oxychloride, neat or in the presence of a solvent to give IV.



The reaction is suitably carried out at a temperature in the range from 0 °C to 150 °C, the preferred reaction temperature being from 80 °C to 125 °C as disclosed for example by EP-A 15 770 615.

Dihalotriazolopyrimidine IV is further reacted with an amine of formula V

20



in which R^1 and R^2 are as defined in formula I to produce compounds of formula I in which X is halogen.

25

The reaction between the 5,7-dihalo compound IV and the amine of formula V can be carried out under conditions known from WO-A 98/46608. The reaction is preferably carried out in the presence of a solvent. Suitable solvents include ethers, such as dioxane, diethyl ether and, especially, tetrahydrofuran, halogenated hydrocarbons such as dichloromethane and aromatic hydrocarbons, for example toluene.

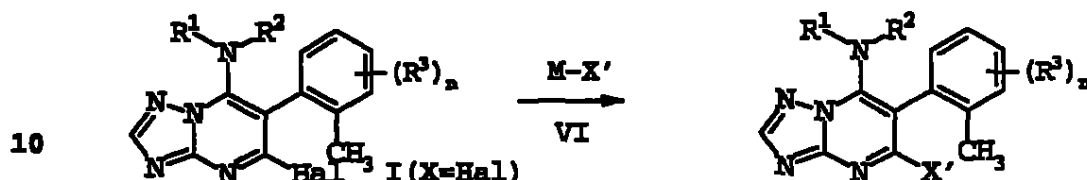
The reaction is suitably carried out at a temperature in the range from 0°C to 70°C, the preferred reaction temperature being from 10°C to 35°C.

It is also preferred that the reaction is carried out in the presence of a base. Suitable bases include tertiary amines, such as triethylamine, and inorganic bases, such as potassium carbonate or sodium carbonate. Alternatively, an excess of the compound of formula V may serve as a base.

Compounds of formula I in which X denotes cyano, C_1-C_6 -alkoxy, C_1-C_6 -haloalkoxy or C_3-C_8 -alkenyloxy can be prepared by reacting compounds I in which X is halogen, preferably chloro, with compounds of formula VI, which are, dependent from the value of X'

45

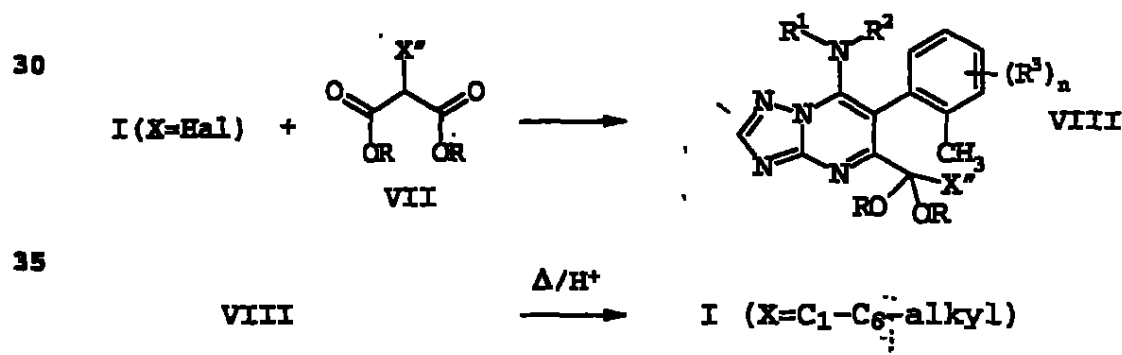
to be introduced to yield formula I compounds, an anorganic cyano salt, an alkoxylate, haloalkoxylate or an alkenyloxylate, respectively, preferably in the presence of a solvent. The cation M in formula VI has minor influence; for practical and economical reasons usually ammonium-, tetraalkylammonium- or alkali metal- and earth metal salts are preferred.



The reaction is suitably carried out at a temperature in the range from 0 to 120°C, the preferred reaction temperature being from 10 to 40°C [cf. J. Heterocycl. Chem., Vol.12, p. 861-863 (1975)].

Suitable solvents include ethers, such as dioxane, diethyl ether and, especially, tetrahydrofuran, halogenated hydrocarbons such as dichloromethane and aromatic hydrocarbons, for example toluene.

Compounds of formula I in which X denotes C₁-C₆-alkyl can be prepared by reacting compounds I in which X is halogen, preferably chloro, with malonic acid esters of formula VII, wherein X' denotes H or C₁-C₅-alkyl and R denotes C₁-C₄-alkyl, to compounds of formula VIII and decarboxylation under conditions described in US 5,994,360.



Accordingly, the invention relates to the novel intermediates of formulae II, III and IV.

The compounds of formula II are preferably prepared by reaction of the corresponding substituted bromobenzenes with sodium dialkylmalonates in the presence of a copper(I) salt [cf. Chemistry Letters, pp. 367-370, 1981; EP-A 10 02 788].

The compounds of formula II may also be prepared by reaction of an alkyl 2-(2-tolyl)-acetate with dialkylcarbonate in the presence of a strong base, preferably sodium ethoxide and sodium hydride (cf. Heterocycles, pp. 1031-1047, 1996).

5

The substituted phenylacetates which are the starting compounds for compounds of formula II are known and commercially available, and/or they are obtainable by generally known methods.

- 10 The reaction mixtures are worked up in a customary manner, for example by mixing with water, phase separation and, if required, chromatographic purification of the crude products. Some of the end products are obtained in the form of colorless or slightly brownish, viscous oils, which are purified or freed from volatile
- 15 components under reduced pressure and at moderately elevated temperatures. If the end products are obtained as solids, purification can also be carried out by recrystallization or digestion.

- If individual compounds I are not obtainable by the routes described above, they can be prepared by derivatization of other compounds I.

- In the symbol definitions given in the formulae above, collective terms were used which generally represent the following substituents:

- halogen: fluorine, chlorine, bromine and iodine;
- C₁-C₁₀-alkyl: saturated, straight-chain or branched hydrocarbon radicals having 1 to 10, especially 1 to 6 carbon atoms, for example C₁-C₄-alkyl as mentioned above or pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-di-methylpropyl, 1-ethylpropyl, hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methylpropyl and 1-ethyl-2-methylpropyl;
- 40 - C₂-C₁₀-alkenyl: unsaturated, straight-chain or branched hydrocarbon radicals having 2 to 10, especially 2 to 6 carbon atoms and a double bond in any position, for example ethenyl, 1-propenyl, 2-propenyl, 1-methylethenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl,
- 45 1-methyl-2-propenyl and 2-methyl-2-propenyl;

C₂-C₁₀-alkynyl: straight-chain or branched hydrocarbon radicals having 2 to 10, especially 2 to 4 carbon atoms and a triple bond in any position, for example ethynyl, 1-propynyl, 2-propynyl, 1-butylnyl, 2-butylnyl, 3-butylnyl and 1-methyl-2-propynyl;

5

- C₁-C₁₀-haloalkyl and haloalkyl moieties of C₁-C₆-haloalkoxy: straight-chain or branched alkyl groups having 1 to 6 or 10, preferably 1 to 4 carbon atoms (as mentioned above), where the hydrogen atoms in these groups may be partially or fully replaced
 10 by halogen atoms as mentioned above, for example C₁-C₂-haloalkoxy, such as chloromethoxy, bromomethoxy, dichloromethoxy, trichloromethoxy, fluoromethoxy, difluoromethoxy, trifluoromethoxy, chlorofluoromethoxy, dichlorofluoromethoxy, chlorodifluoromethoxy, 1-chloroethoxy, 1-bromoethoxy,
 15 1-fluoroethoxy, 2-fluoroethoxy, 2,2-difluoroethoxy, 2,2,2-trifluoroethoxy, 2-chloro-2-fluoroethoxy, 2-chloro-2,2-difluoroethoxy, 2,2-dichloro-2-fluoroethoxy, 2,2,2-trichloroethoxy and pentafluoroethoxy;

20 C₃-C₁₀-cycloalkyl: mono- or bicyclic cycloalkyl groups having 3 to 10 carbon atoms; monocyclic groups preferably have 3 to 8, especially 3 to 6 ring members, bicyclic groups preferably have 8 to 10 ring members.

25 A 5- or 6-membered heterocyclyl group, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, preferably one oxygen atom, for example 1-pyrimidinyl, 2-pyrimidinyl, morpholin-4-yl.

30 5-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom: 5-membered heteroaryl groups which, in addition to carbon atoms, may contain one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom as ring members, for example
 35 2-furyl, 3-furyl, 2-thienyl, 3-thienyl, 2-pyrrolyl, 3-pyrrolyl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 3-isothiazolyl, 4-isothiazolyl, 5-isothiazolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-imidazolyl, 4-imidazolyl, 1,2,4-oxa-
 40 diazol-3-yl, 1,2,4-oxadiazol-5-yl, 1,2,4-thiadiazol-3-yl, 1,2,4-thiadiazol-5-yl, 1,2,4-triazol-3-yl, 1,3,4-oxadiazol-2-yl, 1,3,4-thiadiazol-2-yl and 1,3,4-triazol-2-yl;

6-membered heteroaryl, containing one to four nitrogen atoms:

45 6-membered heteroaryl groups which, in addition to carbon atoms, may contain one to three or one to four nitrogen atoms as ring members, for example 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, 3-py-

ridaziny1, 4-pyridaziny1, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl, 2-pyraziny1, 1,3,5-triazin-2-yl and 1,2,4-triazin-3-yl.

With respect to their intended use, preference is given to
5 triazolopyrimidines of the formula I having the following substituents, where the preference is valid in each case on its own or in combination:

A preferred cycloalkyl moiety is cyclopentyl being optionally
10 substituted by one or more nitro, cyano, C₁-C₆-alkyl, C₁-C₆-alkoxy groups.

A preferred heteroaryl moiety is pyridyl, pyrimidyl, pyrazolyl or
thienyl.

15 Preference is given to compounds of formula I in which any alkyl or haloalkyl part of the groups R¹ or R², which may be straight chained or branched, contains up to 10 carbon atoms, preferably 1 to 9 carbon atoms, more preferably 2 to 6 carbon atoms, any
20 alkenyl or alkynyl part of the substituents R¹ or R² contains up to 10 carbon atoms, preferably 2 to 9 carbon atoms, more preferably 3 to 6 carbon atoms, any cycloalkyl part of the substituents R¹ or R² contains from 3 to 10 carbon atoms, preferably from 3 to 8 carbon atoms, more preferably from 3 to 6 carbon atoms, and any
25 bicycloalkyl part of the substituents R¹ or R² contains from 5 to 9 carbon atoms, preferably from 7 to 9 carbon atoms. Any alkyl, alkenyl or alkynyl group may be linear or branched.

Likewise, preference is given to compounds of formula I wherein R¹
30 is not hydrogen.

Compounds of formula I are preferred in which R¹ represents a straight-chained or branched C₁-C₁₀-alkyl, in particular a branched C₃-C₁₀-alkyl group, a C₃-C₈-cycloalkyl, a C₅-C₉-bicycloalkyl,
35 a C₃-C₈-cycloalkyl-C₁-C₆-alkyl, C₁-C₁₀-alkoxy-C₁-C₆-alkyl, a C₁-C₁₀-haloalkyl or a phenyl group being optionally substituted by one to three halogen atoms or C₁-C₁₀-alkyl or C₁-C₁₀-alkoxy groups.

Particular preference is given to compounds I in which R² represents hydrogen, C₁-C₁₀-alkyl or C₁-C₁₀-haloalkyl, in particular hydrogen.
40

Besides, particular preference is given to compounds I in which R² is hydrogen.

Moreover, particular preference is given to compounds I in which R² is methyl.

Furthermore, particular preference is given to compounds I in which R² is ethyl.

If R¹ denotes C₁-C₁₀-haloalkyl, preferably polyfluorinated alkyl, in particular 2,2,2-trifluoroethyl, 2-(1,1,1-trifluoropropyl) or 2-(1,1,1-trifluorobutyl), R² preferably represents hydrogen.

10

If R¹ denotes optionally substituted C₃-C₈-cycloalkyl, preferably cyclopentyl or cyclohexyl, R² preferably represents hydrogen or C₁-C₆-alkyl.

15 Moreover, particular preference is given to compounds I in which R¹ and R² together with the interjacent nitrogen atom form an optionally substituted heterocyclic ring, preferably an optionally substituted C₃-C₇-heterocyclic ring, in particular pyrrolidine, piperidine, tetrahydropyridine, in particular 1,2,3,6-tetrahydro-
20 pyridine or azepane which is optionally substituted by one or more C₁-C₁₀-alkyl groups.

Preference is given to compounds of formula I in which any alkyl part of the groups R¹ or R², which may be straight chained or
25 branched, contains 1 to 9 carbon atoms, more preferably 2 to 6 carbon atoms, any alkenyl or alkynyl part of the substituents R¹ or R² contains 2 to 9 carbon atoms, more preferably 3 to 6 carbon atoms, any cycloalkyl part of the substituents R¹ or R² contains from 3 to 10 carbon atoms, preferably from 3 to 8 carbon atoms,
30 more preferably from 3 to 6 carbon atoms, and any bicycloalkyl part of the substituents R¹ or R² contains from 7 to 9 carbon atoms. Any alkyl, alkenyl or alkynyl moiety may be linear or branched.

35 Compounds of formula I are preferred in which R¹ represents a straight-chained or branched C₁-C₁₀-alkyl, in particular branched C₃-C₁₀-alkyl, a C₃-C₈-cycloalkyl, C₅-C₉-bicycloalkyl, C₃-C₈-cycloalkyl-C₁-C₆-alkyl, C₁-C₁₀-alkoxy-C₁-C₆-alkyl, or phenyl being optionally substituted by one to three C₁-C₁₀-alkyl or C₁-C₁₀-alkoxy
40 groups.

Particular preference is given to compounds I in which R² represents hydrogen or C₁-C₁₀-alkyl, in particular hydrogen.

45 Moreover, particular preference is given to compounds I in which R² is methyl or ethyl.

If R^1 denotes an optionally substituted C_3 - C_8 -cycloalkyl group, preferably cyclopentyl or cyclohexyl, R^2 preferably represents hydrogen or C_1 - C_6 -alkyl.

5 Moreover, particular preference is given to compounds I in which R^1 and R^2 together with the interjacent nitrogen atom form an optionally substituted heterocyclic ring, preferably an optionally substituted C_3 - C_7 -heterocyclic ring, in particular a pyrrolidine, piperidine, tetrahydropyridine, in particular 1,2,3,6-tetrahydro-
10 pyridine or azepane ring which is optionally substituted by one or more C_1 - C_{10} -alkyl groups.

Likewise, particular preference is given to compounds I in which R^2 is hydrogen.

15

Particular preference is also given to compounds I in which n has the value 2 and R^3 groups are in 4- and 6-position.

Moreover, preference is given to compounds I in which a R^3 group
20 is in para-position.

Furthermore, particular preference is given to compounds I in which $(R^3)_n$ is 4,6-dimethyl.

25 Likewise, particular preference is given to compounds I in which $(R^3)_n$ is 4- $(C_1$ - C_8 -alkoxy)carbonyl, especially 4-methoxycarbonyl.

Besides, particular preference is given to compounds I in which $(R^3)_n$ is 4-methoxy-6-methyl, or 4-fluoro-6-methyl.

30

Particular preference is also given to compounds I in which $(R^3)_n$ is 4-fluoro, 6-fluoro, or 4-chloro.

Besides, particular preference is given to compounds I in which X
35 is chloro or bromo, especially chloro.

Moreover, preference is given to compounds I in which X is cyano or methyl.

40 Furthermore, particular preference is given to compounds I in which X is methoxy, ethoxy, n -propoxy, iso-propoxy, allyloxy, or 3-methylallyloxy.

The particularly preferred embodiments of the intermediates with
45 respect to the variables correspond to those of the radicals X , R^1 , R^2 and R^3 of formula I.

Included in the scope of the present invention are (R) and (S) isomers of compounds of general formula I having a chiral center and the racemates thereof, and salts, N-oxides and acid addition compounds.

5

With respect to their use, particular preference is given to the compounds I compiled in the tables below. The groups mentioned in the tables for a substituent are furthermore for their part, independently of the combination in which they are mentioned, a

10 particularly preferred embodiment of the respective substituents.

Table 1

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 4-chloro and R^1 and R^2 correspond to one row in Table A

15

Table 2

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 5-chloro and R^1 and R^2 correspond to one row in Table A

20 Table 3

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 6-chloro and R^1 and R^2 correspond to one row in Table A

Table 4

25

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 3-fluoro and R^1 and R^2 correspond to one row in Table A

Table 5

30

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 4-fluoro and R^1 and R^2 correspond to one row in Table A

Table 6

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 5-fluoro and R^1 and R^2 correspond to one row in Table A

35

Table 7

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 6-fluoro and R^1 and R^2 correspond to one row in Table A

40 Table 8

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 3-methyl and R^1 and R^2 correspond to one row in Table A

Table 9

45

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 4-methyl and R^1 and R^2 correspond to one row in Table A

Table 10

Compounds of formula I, in which X is chloro, (R³)_n is 5-methyl and R¹ and R² correspond to one row in Table A

5 Table 11

Compounds of formula I, in which X is chloro, (R³)_n is 6-methyl and R¹ and R² correspond to one row in Table A

Table 12

10 Compounds of formula I, in which X is chloro, (R³)_n is 4-methoxy and R¹ and R² correspond to one row in Table A

Table 13

15 Compounds of formula I, in which X is chloro, (R³)_n is 5-methoxy and R¹ and R² correspond to one row in Table A

Table 14

20 Compounds of formula I, in which X is chloro, (R³)_n is 6-methoxy and R¹ and R² correspond to one row in Table A

Table 15

Compounds of formula I, in which X is chloro, (R³)_n is 4-trifluoromethyl and R¹ and R² correspond to one row in Table A

25 Table 16

Compounds of formula I, in which X is chloro, (R³)_n is 5-trifluoromethyl and R¹ and R² correspond to one row in Table A

Table 17

30 Compounds of formula I, in which X is chloro, (R³)_n is 6-trifluoromethyl and R¹ and R² correspond to one row in Table A

Table 18

35 Compounds of formula I, in which X is chloro, (R³)_n is 4,6-dimethyl and R¹ and R² correspond to one row in Table A

Table 19

40 Compounds of formula I, in which X is chloro, (R³)_n is 4-methoxy-6-methyl and R¹ and R² correspond to one row in Table A

Table 20

45 Compounds of formula I, in which X is chloro, (R³)_n is 4-fluoro-6-methyl and R¹ and R² correspond to one row in Table A

Table 21

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 4-methoxycarbonyl and R^1 and R^2 correspond to one row in Table A

5 Table 22

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 4-cyano and R^1 and R^2 correspond to one row in Table A

Table 23

10 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-chloro and R^1 and R^2 correspond to one row in Table A

Table 24

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 5-chloro and
15 R^1 and R^2 correspond to one row in Table A

Table 25

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 6-chloro and
20 R^1 and R^2 correspond to one row in Table A

Table 26

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 3-fluoro and
 R^1 and R^2 correspond to one row in Table A

25 Table 27

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-fluoro and
 R^1 and R^2 correspond to one row in Table A

Table 28

30 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 5-fluoro and
 R^1 and R^2 correspond to one row in Table A

Table 29

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 6-fluoro and
35 R^1 and R^2 correspond to one row in Table A

Table 30

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 3-methyl and
40 R^1 and R^2 correspond to one row in Table A

Table 31

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-methyl and
 R^1 and R^2 correspond to one row in Table A

Table 32

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 5-methyl and R^1 and R^2 correspond to one row in Table A

5 Table 33

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 6-methyl and R^1 and R^2 correspond to one row in Table A

Table 34

10 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-methoxy and R^1 and R^2 correspond to one row in Table A

Table 35

15 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 5-methoxy and R^1 and R^2 correspond to one row in Table A

Table 36

20 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 6-methoxy and R^1 and R^2 correspond to one row in Table A

Table 37

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

25 Table 38

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 5-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 39

30 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 6-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 40

35 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4,6-dimethyl and R^1 and R^2 correspond to one row in Table A

Table 41

40 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-methoxy-6-methyl and R^1 and R^2 correspond to one row in Table A

Table 42

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-fluoro-6-methyl and R^1 and R^2 correspond to one row in Table A

Table 43

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-methoxycarbonyl and R^1 and R^2 correspond to one row in Table A

5 Table 44

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-cyano and R^1 and R^2 correspond to one row in Table A

Table 45

10 Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-chloro and R^1 and R^2 correspond to one row in Table A

Table 46

15 Compounds of formula I, in which X is cyano, $(R^3)_n$ is 5-chloro and R^1 and R^2 correspond to one row in Table A

Table 47

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 6-chloro and R^1 and R^2 correspond to one row in Table A

20

Table 48

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 3-fluoro and R^1 and R^2 correspond to one row in Table A

25 Table 49

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-fluoro and R^1 and R^2 correspond to one row in Table A

Table 50

30 Compounds of formula I, in which X is cyano, $(R^3)_n$ is 5-fluoro and R^1 and R^2 correspond to one row in Table A

Table 51

35 Compounds of formula I, in which X is cyano, $(R^3)_n$ is 6-fluoro and R^1 and R^2 correspond to one row in Table A

Table 52

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 3-methyl and R^1 and R^2 correspond to one row in Table A

40

Table 53

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-methyl and R^1 and R^2 correspond to one row in Table A

45

Table 54

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 5-methyl and R^1 and R^2 correspond to one row in Table A

5 Table 55

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 6-methyl and R^1 and R^2 correspond to one row in Table A

Table 56

10 Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-methoxy and R^1 and R^2 correspond to one row in Table A

Table 57

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 5-methoxy and R^1 and R^2 correspond to one row in Table A

Table 58

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 6-methoxy and R^1 and R^2 correspond to one row in Table A

20

Table 59

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

25 Table 60

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 5-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 61

30 Compounds of formula I, in which X is cyano, $(R^3)_n$ is 6-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 62

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4,6-dimethyl and R^1 and R^2 correspond to one row in Table A

35

Table 63

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-methoxy-6-methyl and R^1 and R^2 correspond to one row in Table A

40

Table 64

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-fluoro-6-methyl and R^1 and R^2 correspond to one row in Table A

45

Table 65

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-methoxycarbonyl and R^1 and R^2 correspond to one row in Table A

5 Table 66

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-cyano and R^1 and R^2 correspond to one row in Table A

Table 67

10 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-chloro and R^1 and R^2 correspond to one row in Table A

Table 68

15 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 5-chloro and R^1 and R^2 correspond to one row in Table A

Table 69

20 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 6-chloro and R^1 and R^2 correspond to one row in Table A

Table 70

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 3-fluoro and R^1 and R^2 correspond to one row in Table A

25 Table 71

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-fluoro and R^1 and R^2 correspond to one row in Table A

Table 72

30 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 5-fluoro and R^1 and R^2 correspond to one row in Table A

Table 73

35 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 6-fluoro and R^1 and R^2 correspond to one row in Table A

Table 74

40 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 3-methyl and R^1 and R^2 correspond to one row in Table A

Table 75

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-methyl and R^1 and R^2 correspond to one row in Table A

17

Table 76

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 5-methyl and R^1 and R^2 correspond to one row in Table A

5 Table 77

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 6-methyl and R^1 and R^2 correspond to one row in Table A

Table 78

10 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-methoxy and R^1 and R^2 correspond to one row in Table A

Table 79

15 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 5-methoxy and R^1 and R^2 correspond to one row in Table A

Table 80

20 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 6-methoxy and R^1 and R^2 correspond to one row in Table A

Table 81

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

25 Table 82

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 5-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 83

30 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 6-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 84

35 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4,6-dimethyl and R^1 and R^2 correspond to one row in Table A

Table 85

40 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-methoxy-6-methyl and R^1 and R^2 correspond to one row in Table A

Table 86

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-fluoro-6-methyl and R^1 and R^2 correspond to one row in Table A

Table 87

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-methoxycarbonyl and R^1 and R^2 correspond to one row in Table A

5 Table 88

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-cyano and R^1 and R^2 correspond to one row in Table A

Table 89

10 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-chloro and R^1 and R^2 correspond to one row in Table A

Table 90

15 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 5-chloro and R^1 and R^2 correspond to one row in Table A

Table 91

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 6-chloro and R^1 and R^2 correspond to one row in Table A

20

Table 92

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 3-fluoro and R^1 and R^2 correspond to one row in Table A

25 Table 93

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-fluoro and R^1 and R^2 correspond to one row in Table A

Table 94

30 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 5-fluoro and R^1 and R^2 correspond to one row in Table A

Table 95

35 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 6-fluoro and R^1 and R^2 correspond to one row in Table A

Table 96

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 3-methyl and R^1 and R^2 correspond to one row in Table A

40

Table 97

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-methyl and R^1 and R^2 correspond to one row in Table A

45

Table 98

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 5-methyl and R^1 and R^2 correspond to one row in Table A

5 Table 99

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 6-methyl and R^1 and R^2 correspond to one row in Table A

Table 100

10 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-methoxy and R^1 and R^2 correspond to one row in Table A

Table 101

15 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 5-methoxy and R^1 and R^2 correspond to one row in Table A

Table 102

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 6-methoxy and R^1 and R^2 correspond to one row in Table A

20

Table 103

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

25 Table 104

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 5-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 105

30 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 6-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 106

35 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4,6-dimethyl and R^1 and R^2 correspond to one row in Table A

Table 107

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-methoxy-6-methyl and R^1 and R^2 correspond to one row in Table A

40

Table 108

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-fluoro-6-methyl and R^1 and R^2 correspond to one row in Table A

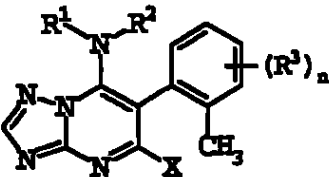
45

Table 109
Compounds of formula I, in which X is methyl, (R³)_n is 4-methoxycarbonyl and R¹ and R² correspond to one row in Table A

5 Table 110
Compounds of formula I, in which X is methyl, (R³)_n is 4-cyano and R¹ and R² correspond to one row in Table A

Table A

10



I

15

No.	R ¹	R ²
A-1	H	H
A-2	CH ₂ CH ₃	H
20 A-3	CH ₂ CH ₃	CH ₃
A-4	CH ₂ CH ₃	CH ₂ CH ₃
A-5	CH ₂ CF ₃	H
A-6	CH ₂ CF ₃	CH ₃
25 A-7	CH ₂ CF ₃	CH ₂ CH ₃
A-8	CH ₂ CCl ₃	H
A-9	CH ₂ CCl ₃	CH ₃
A-10	CH ₂ CCl ₃	CH ₂ CH ₃
30 A-11	CH ₂ CH ₂ CH ₃	H
A-12	CH ₂ CH ₂ CH ₃	CH ₃
A-13	CH ₂ CH ₂ CH ₃	CH ₂ CH ₃
A-14	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃
A-15	CH(CH ₃) ₂	H
35 A-16	CH(CH ₃) ₂	CH ₃
A-17	CH(CH ₃) ₂	CH ₂ CH ₃
A-18	(±) CH(CH ₃) - CH ₂ CH ₃	H
A-19	(±) CH(CH ₃) - CH ₂ CH ₃	CH ₃
40 A-20	(±) CH(CH ₃) - CH ₂ CH ₃	CH ₂ CH ₃
A-21	(S) CH(CH ₃) - CH ₂ CH ₃	H
A-22	(S) CH(CH ₃) - CH ₂ CH ₃	CH ₃
A-23	(S) CH(CH ₃) - CH ₂ CH ₃	CH ₂ CH ₃
45 A-24	(R) CH(CH ₃) - CH ₂ CH ₃	H
A-25	(R) CH(CH ₃) - CH ₂ CH ₃	CH ₃
A-26	(R) CH(CH ₃) - CH ₂ CH ₃	CH ₂ CH ₃

No.	R ¹	R ²
A-27	(±) CH(CH ₃)-CH(CH ₃) ₂	H
A-28	(±) CH(CH ₃)-CH(CH ₃) ₂	CH ₃
5 A-29	(±) CH(CH ₃)-CH(CH ₃) ₂	CH ₂ CH ₃
A-30	(S) CH(CH ₃)-CH(CH ₃) ₂	H
A-31	(S) CH(CH ₃)-CH(CH ₃) ₂	CH ₃
A-32	(S) CH(CH ₃)-CH(CH ₃) ₂	CH ₂ CH ₃
10 A-33	(R) CH(CH ₃)-CH(CH ₃) ₂	H
A-34	(R) CH(CH ₃)-CH(CH ₃) ₂	CH ₃
A-35	(R) CH(CH ₃)-CH(CH ₃) ₂	CH ₂ CH ₃
A-36	(±) CH(CH ₃)-C(CH ₃) ₃	H
A-37	(±) CH(CH ₃)-C(CH ₃) ₃	CH ₃
15 A-38	(±) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
A-39	(S) CH(CH ₃)-C(CH ₃) ₃	H
A-40	(S) CH(CH ₃)-C(CH ₃) ₃	CH ₃
A-41	(S) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
20 A-42	(R) CH(CH ₃)-C(CH ₃) ₃	H
A-43	(R) CH(CH ₃)-C(CH ₃) ₃	CH ₃
A-44	(R) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
A-45	(±) CH(CH ₃)-CF ₃	H
25 A-46	(±) CH(CH ₃)-CF ₃	CH ₃
A-47	(±) CH(CH ₃)-CF ₃	CH ₂ CH ₃
A-48	(S) CH(CH ₃)-CF ₃	H
A-49	(S) CH(CH ₃)-CF ₃	CH ₃
A-50	(S) CH(CH ₃)-CF ₃	CH ₂ CH ₃
30 A-51	(R) CH(CH ₃)-CF ₃	H
A-52	(R) CH(CH ₃)-CF ₃	CH ₃
A-53	(R) CH(CH ₃)-CF ₃	CH ₂ CH ₃
A-54	(±) CH(CH ₃)-CCl ₃	H
35 A-55	(±) CH(CH ₃)-CCl ₃	CH ₃
A-56	(±) CH(CH ₃)-CCl ₃	CH ₂ CH ₃
A-57	(S) CH(CH ₃)-CCl ₃	H
A-58	(S) CH(CH ₃)-CCl ₃	CH ₃
40 A-59	(S) CH(CH ₃)-CCl ₃	CH ₂ CH ₃
A-60	(R) CH(CH ₃)-CCl ₃	H
A-61	(R) CH(CH ₃)-CCl ₃	CH ₃
A-62	(R) CH(CH ₃)-CCl ₃	CH ₂ CH ₃
45 A-63	CH ₂ C(CH ₃)=CH ₂	H
A-64	CH ₂ C(CH ₃)=CH ₂	CH ₃
A-65	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃

No.	R ¹	R ²
A-66	cyclopentyl	H
A-67	cyclopentyl	CH ₃
A-68	cyclopentyl	CH ₂ CH ₃
A-69	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -	
A-70	CH ₂ CF ₂ CF ₃	H
A-71	CH ₂ CF ₂ CF ₃	CH ₃
A-72	CH ₂ CF ₂ CF ₃	CH ₂ CH ₃
A-73	CH ₂ CF ₂ CF ₂ CF ₃	H
A-74	CH ₂ CF ₂ CF ₂ CF ₃	CH ₃
A-75	CH ₂ CF ₂ CF ₂ CF ₃	CH ₂ CH ₃

- 15 The compounds I are suitable as fungicides. They have outstanding activity against a broad spectrum of phytopathogenic fungi, in particular from the classes of the *Ascomycetes*, *Deuteromycetes*, *Phycomycetes* and *Basidiomycetes*. Some of them act systemically, and they can be employed in crop protection as foliar- and soil-
20 acting fungicides.

They are especially important for controlling a large number of fungi on a variety of crop plants such as wheat, rye, barley, oats, rice, maize, grass, bananas, cotton, soya, coffee, sugar
25 cane, grapevines, fruit species, ornamentals and vegetables such as cucumbers, beans, tomatoes, potatoes and cucurbits, and on the seeds of these plants.

Specifically, they are suitable for controlling the following
30 plant diseases:

- *Alternaria* species, *Podosphaera* species, *Sclerotinia* species, *Physalospora* canker on vegetables and fruit,
- *Botrytis cinerea* (gray mold) on strawberries, vegetables, ornamentals and grapevines,
- 35 • *Corynespora cassicola* on cucumbers,
- *Colletotrichum* species on fruit and vegetables,
- *Diplocarpon rosae* on roses,
- *Elsinoe fawcetti* and *Diaporthe citri* on citrus fruit,
- *Sphaerotheca* species on cucurbits, strawberries and roses,
- 40 • *Cercospora* species on peanuts, sugar beets and aubergines,
- *Erysiphe cichoracearum* on cucurbits,
- *Leveillula taurica* on paprika, tomatoes and aubergines,
- *Mycosphaerella* species on apples and japanese apricot,
- *Phyllactinia kakicola*, *Gloeosporium kaki* on japanese apricot,
- 45 • *Gymnosporangium yamadae*, *Leptothyrium pomi*, *Podosphaera leucotricha* and *Gloeodes pomigena* on apples,
- *Cladosporium carpophilum* on pears and japanese apricot,

- *Phomopsis* species on pears,
- *Phytophthora* species on citrus fruit, potatoes, onions, especially *Phytophthora infestans* on potatoes and tomatoes,
- *Blumeria graminis* (powdery mildew) on cereals,
- 5 • *Fusarium*- and *Verticillium* species on various plants,
- *Glomerella cingulata* on tee,
- *Drechslera*- and *Bipolaris* species on cereals and rice,
- *Mycosphaerella* species on bananas and peanuts,
- *Plasmopara viticola* on grapevines,
- 10 • *Peronospora* species on onions, spinach and chrysanthemum,
- *Phaeoisariopsis vitis* and *Sphaceloma ampelina* on grapefruits,
- *Pseudocercospora herpotrichoides* on wheat and barley,
- *Pseudoperonospora* species on hop and cucumbers,
- *Puccinia* species and *Typhula* species on cereals and turf,
- 15 • *Pyricularia oryzae* on rice,
- *Rhizoctonia* species on cotton, rice and turf,
- *Stagonospora nodorum* and *Septoria tritici* on wheat,
- *Uncinula necator* on grapevines,
- *Ustilago* species on cereals and sugar cane, and
- 20 • *Venturia* species (scab) on apples and pears.

Moreover, the compounds I are suitable for controlling harmful fungi such as *Paecilomyces variotii* in the protection of materials (e.g. wood, paper, paint dispersions, fibers and tissues) and
25 in the protection of stored products.

The compounds I are applied by treating the fungi, or the plants, seeds, materials or the soil to be protected against fungal infection, with a fungicidally active amount of the active ingredients. Application can be effected both before and after infection of the materials, plants or seeds by the fungi.
30

In general, the fungicidal compositions comprise from 0.1 to 95, preferably 0.5 to 90, % by weight of active ingredient.

35

When used in crop protection, the rates of application are from 0.01 to 2.0 kg of active ingredient per ha, depending on the nature of the effect desired.

40 In the treatment of seed, amounts of active ingredient of from 0.001 to 0.1 g, preferably 0.01 to 0.05 g, are generally required per kilogram of seed.

When used in the protection of materials or stored products, the
45 rate of application of active ingredient depends on the nature of the field of application and on the effect desired. Rates of application conventionally used in the protection of materials are,

for example, from 0.001 g to 2 kg, preferably 0.005 g to 1 kg, of active ingredient per cubic meter of material treated.

The compounds I can be converted into the customary formulations, e.g. solutions, emulsions, suspensions, dusts, powders, pastes and granules. The use form depends on the particular purpose; in any case, it should guarantee a fine and uniform distribution of the compound according to the invention.

10 The formulations are prepared in a known manner, e.g. by extending the active ingredient with solvents and/or carriers, if desired using emulsifiers and dispersants, it also being possible to use other organic solvents as auxiliary solvents if water is used as the diluent. Auxiliaries which are suitable are essentially: solvents such as aromatics (e.g. xylene), chlorinated aromatics (e.g. chlorobenzenes), paraffins (e.g. mineral oil fractions), alcohols (e.g. methanol, butanol), ketones (e.g. cyclohexanone), amines (e.g. ethanolamine, dimethylformamide) and water; carriers such as ground natural minerals (e.g. kaolins, 15 clays, talc, chalk) and ground synthetic minerals (e.g. highly-disperse silica, silicates); emulsifiers such as non-ionic and anionic emulsifiers (e.g. polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates) and dispersants such as lignin-sulfite waste liquors and methylcellulose.

25 Suitable surfactants are alkali metal, alkaline earth metal and ammonium salts of lignosulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid, dibutyl-naphthalenesulfonic acid, alkylaryl-sulfonates, alkyl sulfates, alkylsulfonates, fatty alcohol sulfates and fatty acids and their alkali metal and alkaline earth metal salts, salts of sulfated fatty alcohol glycol ether, condensates of sulfonated naphthalene and naphthalene derivatives with formaldehyde, condensates of naphthalene or of naphthalenesulfonic acid with phenol or formaldehyde, polyoxyethylene octylphenyl 30 ether, ethoxylated isooctylphenol, octylphenol, nonylphenol, alkylphenol polyglycol ethers, tributylphenyl polyglycol ethers, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl alcohol 40 polyglycol ether acetal, sorbitol esters, lignin-sulfite waste liquors and methylcellulose.

Substances which are suitable for the preparation of directly sprayable solutions, emulsions, pastes or oil dispersions are mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, furthermore coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocar-

25

bons, e.g. benzene, toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes or their derivatives, methanol, ethanol, propanol, butanol, chloroform, carbon tetrachloride, cyclohexanol, cyclohexanone, chlorobenzene, isophorone, strongly
5 polar solvents, e.g. dimethylformamide, dimethyl sulfoxide, N-methylpyrrolidone and water.

Powders, materials for scattering and dusts can be prepared by mixing or concomitantly grinding the active substances with a solid carrier.
10

Granules, e.g. coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active ingredients to solid carriers. Examples of solid carriers are mineral earths, such as silicas, silica gels, silicates, talc, kaolin, attaclay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers, e.g. ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders and other solid carriers.
15
20

In general, the formulations comprise of from 0.01 to 95% by weight, preferably from 0.1 to 90% by weight, of the active ingredient. The active ingredients are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR spectrum).
25

The following are exemplary formulations:

- 30 I. 5 parts by weight of a compound according to the invention are mixed intimately with 95 parts by weight of finely divided kaolin. This gives a dust which comprises 5% by weight of the active ingredient.
- 35 II. 30 parts by weight of a compound according to the invention are mixed intimately with a mixture of 92 parts by weight of pulverulent silica gel and 8 parts by weight of paraffin oil which had been sprayed onto the surface of this silica gel. This gives a formulation of the active ingredient with good
40 adhesion properties (comprises 23% by weight of active ingredient).
- III. 10 parts by weight of a compound according to the invention are dissolved in a mixture composed of 90 parts by weight of xylene, 6 parts by weight of the adduct of 8 to 10 mol of ethylene oxide and 1 mol of oleic acid N-monoethanolamide, 2
45 parts by weight of calcium dodecylbenzenesulfonate and 2

parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil (comprises 9% by weight of active ingredient).

- 5 IV. 20 parts by weight of a compound according to the invention are dissolved in a mixture composed of 60 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 5 parts by weight of the adduct of 7 mol of ethylene oxide and 1 mol of isooctylphenol and 5 parts by weight of the adduct of 40 mol
10 of ethylene oxide and 1 mol of castor oil (comprises 16% by weight of active ingredient).
- V. 80 parts by weight of a compound according to the invention are mixed thoroughly with 3 parts by weight of sodium diisobutyl
15 naphthalene- α -sulfonate, 10 parts by weight of the sodium salt of a lignosulfonic acid from a sulfite waste liquor and 7 parts by weight of pulverulent silica gel, and the mixture is ground in a hammer mill (comprises 80% by weight of active ingredient).
- 20 VI. 90 parts by weight of a compound according to the invention are mixed with 10 parts by weight of N-methyl- α -pyrrolidone, which gives a solution which is suitable for use in the form of microdrops (comprises 90% by weight of active ingre-
25 dient).
- VII. 20 parts by weight of a compound according to the invention are dissolved in a mixture composed of 40 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 20 parts by
30 weight of the adduct of 7 mol of ethylene oxide and 1 mol of isooctylphenol and 10 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil. Pouring the solution into 100,000 parts by weight of water and finally distributing it therein gives an aqueous dispersion which
35 comprises 0.02% by weight of the active ingredient.
- VIII. 20 parts by weight of a compound according to the invention are mixed thoroughly with 3 parts by weight of sodium diisobutyl
40 naphthalene- α -sulfonate, 17 parts by weight of the sodium salt of a lignosulfonic acid from a sulfite waste liquor and 60 parts by weight of pulverulent silica gel, and the mixture is ground in a hammer mill. Finely distributing the mixture in 20,000 parts by weight of water gives a spray
45 mixture which comprises 0.1% by weight of the active ingredient.

The active ingredients can be used as such, in the form of their formulations or the use forms prepared therefrom, e.g. in the form of directly sprayable solutions, powders, suspensions or dispersions, emulsions, oil dispersions, pastes, dusts, materials for spreading, or granules, by means of spraying, atomizing, dusting, scattering or pouring. The use forms depend entirely on the intended purposes; in any case, this is intended to guarantee the finest possible distribution of the active ingredients according to the invention.

10

Aqueous use forms can be prepared from emulsion concentrates, pastes or wettable powders (sprayable powders, oil dispersions) by adding water. To prepare emulsions, pastes or oil dispersions, the substances as such or dissolved in an oil or solvent, can be homogenized in water by means of wetter, tackifier, dispersant or emulsifier. Alternatively, it is possible to prepare concentrates composed of active substance, wetter, tackifier, dispersant or emulsifier and, if appropriate, solvent or oil, and such concentrates are suitable for dilution with water.

20

The active ingredient concentrations in the ready-to-use products can be varied within substantial ranges. In general, they are from 0.0001 to 10%, preferably from 0.01 to 1%.

25 The active ingredients may also be used successfully in the ultra-low-volume process (ULV), it being possible to apply formulations comprising over 95% by weight of active ingredient, or even the active ingredient without additives.

30 Various types of oils, herbicides, fungicides, other pesticides, or bactericides may be added to the active ingredients, if appropriate also only immediately prior to use (tank mix). These agents can be admixed with the agents according to the invention in a weight ratio of 1:10 to 10:1.

35

In the use form as fungicides, the compositions according to the invention can also be present together with other active ingredients, e.g. with herbicides, insecticides, growth regulators, fungicides or else with fertilizers. Mixing the compounds I or the compositions comprising them in the use form as fungicides with other fungicides frequently results in a broader fungicidal spectrum of action.

45 The following list of fungicides, together with which the compounds according to the invention can be used, is intended to illustrate the possible combinations, but not to impose any limitation:

- sulfur, dithiocarbamates and their derivatives, such as iron(III) dimethyldithiocarbamate, zinc dimethyldithiocarbamate, zinc ethylenebisdithiocarbamate, manganese ethylenebisdithiocarbamate, manganese zinc ethylenediaminebisdithiocarbamate, tetramethylthiuram disulfide, ammonia complex of zinc (N,N-ethylenebisdithiocarbamate), ammonia complex of zinc (N,N'-propylenebisdithiocarbamate), zinc (N,N'-propylenebisdithiocarbamate), N,N'-polypropylenebis(thiocarbamoyl)disulfide;
- nitro derivatives, such as dinitro(1-methylheptyl)phenyl crotonate, 2-sec-butyl-4,6-dinitrophenyl 3,3-dimethylacrylate, 2-sec-butyl-4,6-dinitrophenylisopropyl carbonate, diisopropyl 5-nitro-isophthalate;
- heterocyclic substances, such as 2-heptadecyl-2-imidazoline acetate, 2,4-dichloro-6-(o-chloroanilino)-s-triazine, O,O-diethyl phthalimidophosphonothioate, 5-amino-1-[bis(dimethylamino)phosphinyl]-3-phenyl-1,2,4-triazole, 2,3-dicyano-1,4-dithioanthraquinone, 2-thio-1,3-dithiolo[4,5-b]quinoxaline, methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate, 2-methoxycarbonylaminobenzimidazole, 2-(2-furyl)benzimidazole, 2-(4-thiazolyl)benzimidazole, N-(1,1,2,2-tetrachloroethylthio)tetrahydrophthalimide, N-trichloromethylthiotetrahydrophthalimide, N-trichloromethylthiophthalimide, 5-Chloro-2-cyano-4-p-tolyl-imidazole-1-sulfonic acid dimethylamide, N-dichlorofluoromethylthio-N',N'-dimethyl-N-phenylsulfo-diamide, 5-ethoxy-3-trichloromethyl-1,2,3-thiadiazole, 2-thiocyanatomethylthiobenzothiazole, 1,4-dichloro-2,5-dimethoxybenzene, 4-(2-chlorophenylhydrazono)-3-methyl-5-isoxazolone, pyridine-2-thiol 1-oxide, 8-hydroxyquinoline or its copper salt, 2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiine, 2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiine 4,4-dioxide, 2-methyl-5,6-dihydro-4H-pyran-3-carboxanilide, 2-methylfuran-3-carboxanilide, 2,5-dimethylfuran-3-carboxanilide, 2-Chloro-N-(4'-chloro-biphenyl-2-yl)-nicotinamide, 2,4,5-trimethylfuran-3-carboxanilide, N-cyclohexyl-2,5-dimethylfuran-3-carboxamide, N-cyclohexyl-N-methoxy-2,5-dimethylfuran-3-carboxamide, 2-methylbenzanilide, 2-iodobenzanilide, N-formyl-N-morpholine-2,2,2-trichloroethyl acetal, piperazine-1,4-diylbis-1-(2,2,2-trichloroethyl)formamide, 1-(3,4-dichloroanilino)-1-formylamino-2,2,2-trichloroethane; 2,6-dimethyl-N-tridecylmorpholine or its salts, 2,6-dimethyl-N-cyclododecylmorpholine or its salts, N-[3-(p-tert-butylphenyl)-2-methylpropyl]-cis-2,6-dimethyl-morpholine, N-[3-(p-tert-butylphenyl)-2-methylpropyl]-piperidine, 1-[2-(2,4-dichlorophenyl)-4-ethyl-1,3-dioxolan-2-yl-ethyl]-1H-1,2,4-triazole, 1-[2-(2,4-dichlorophenyl)-4-n-propyl-1,3-dioxolan-2-yl-ethyl]-1H-1,2,4-triazole,

N-(n-propyl)-N-(2,4,6-trichlorophenoxyethyl)-N'-imidazolyl-urea, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanone, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanol, (2RS,3RS)-1-[3-(2-chlorophenyl)-2-(4-fluorophenyl)-oxiran-2-ylmethyl]-1H-1,2,4-triazole, α -(2-chlorophenyl)- α -(4-chlorophenyl)-5-pyrimidinemethanol, 5-butyl-2-dimethylamino-4-hydroxy-6-methylpyrimidine, bis(p-chlorophenyl)-3-pyridinemethanol, 1,2-bis(3-ethoxycarbonyl-2-thioureido)benzene, 1,2-bis(3-methoxycarbonyl-2-thioureido)benzene, strobilurines such as azoxystrobin, kresoxim methyl, methyl-E-methoxyimino-[α -(2-phenoxyphenyl)]-acetamide, methyl E-methoxyimino-[α -(2,5-dimethylphenoxy)-o-tolyl]acetamide, picoxystrobin, pyraclostrobin, trifloxystrobin, anilinopyrimidines such as N-(4,6-dimethylpyrimidin-2-yl)aniline, N-[4-methyl-6-(1-propynyl)pyrimidin-2-yl]aniline, N-[4-methyl-6-cyclopropylpyrimidin-2-yl]aniline, phenylpyrroles such as 4-(2,2-difluoro-1,3-benzodioxol-4-yl)pyrrole-3-carbonitrile, cinnamamides such as 3-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)acryloylmorpholine, 3-(4-fluorophenyl)-3-(3,4-dimethoxyphenyl)acryloylmorpholine, and a variety of fungicides such as dodecylguanidine acetate, 3-[3-(3,5-dimethyl-2-oxycyclohexyl)-2-hydroxyethyl]glutarimide, hexachlorobenzene, methyl N-(2,6-dimethylphenyl)-N-(2-furoyl)-DL-alaninate, DL-N-(2,6-dimethylphenyl)-N-(2'-methoxyacetyl)-alanine methyl ester, N-(2,6-dimethylphenyl)-N-chloroacetyl-D,L-2-amino-butylolactone, DL-N-(2,6-dimethylphenyl)-N-(phenylacetyl)alanine methyl ester, 5-methyl-5-vinyl-3-(3,5-dichlorophenyl)-2,4-dioxo-1,3-oxazolidine, 3-[3,5-dichlorophenyl(5-methyl-5-methoxymethyl)-1,3-oxazolidine-2,4-dione, 3-(3,5-dichlorophenyl)-1-isopropylcarbamoylhydantoin, N-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide, 2-cyano-[N-(ethylaminocarbonyl)-2-methoximino]acetamide, 3,5-Dichloro-N-(3-chloro-1-ethyl-1-methyl-2-oxo-propyl)-4-methyl-benzamide, 1-(3-Bromo-6-methoxy-2-methyl-phenyl)-1-(2,3,4-trimethoxy-6-methyl-phenyl)-methanone, 1-[2-(2,4-dichloro-phenyl)pentyl]-1H-1,2,4-triazole, 2,4-difluoro- α -(1H-1,2,4-triazolyl-1-methyl)benzhydrol alcohol, N-(3-chloro-2,6-dinitro-4-trifluoromethylphenyl)-5-trifluoromethyl-3-chloro-2-aminopyridine, 1-((bis(4-fluorophenyl)methylsilyl)methyl)-1H-1,2,4-triazole.

Synthesis Examples

With due modification of the starting compounds, the protocols shown in the synthesis examples below were used for obtaining 5 further compounds I. The resulting compounds I, together with physical data, are listed in Table I which follows.

Example 1 Preparation of diethyl (2-fluoro-6-methylphenyl)-malonate

10

Diethyl malonate (0.49 mol) was added to a mixture of sodium hydride (0.51 mol) and 1,4-dioxane (140 ml) at 60°C within 2 hours. The mixture was stirred for 10 minutes at 60°C and copper (I) bromide (0.05 mol) was added. After 15 minutes, a solution of 15 2-bromo-3-fluorotoluene (0.25 mol) in 10 ml 1,4-dioxane was added. The reaction mixture was kept at 100°C for about 15 hours and after cooling to about 15°C 35 ml of 12N Hydrochloric acid were added. The precipitate was filtered off, the filtrate was extracted with diethyl ether. The organic phase was separated, 20 dried and filtered. The filtrate was evaporated to yield 42 g of the title compound.

Example 2 Preparation of 5,7-dihydroxy-6-(2-fluoro-6-methylphenyl)-[1,2,4]-triazolo-[1,5- α]pyrimidine

25

A mixture of 3-amino-1,2,4-triazole (14 g), diethyl (2-fluoro-6-methylphenyl)-malonate (0.17 mol, Ex. 1) and tributylamine (50 ml) is heated at 180°C for six hours; after cooling to 70°C a solution of 21g sodium hydroxide in 200 ml water was 30 added and the reaction mixture was stirred for 30 minutes. The organic phase was separated off and the aqueous phase was extracted with diethyl ether. The aqueous phase was acidified with concentrated hydrochloric acid. The precipitate was collected by filtration and dried to yield 41 g of the title compound.

35

Example 3 Preparation of 5,7-dichloro-6-(2-fluoro-6-methylphenyl)-[1,2,4]-triazolo-[1,5- α]pyrimidine

A mixture of the compound from Ex. 2 (30 g) and phosphorous oxychloride (50 ml) was refluxed for eight hours. Phosphorous oxychloride was partly distilled off. The residue was poured into a mixture of dichloromethane and water. The organic layer was separated, dried and filtered. The filtrate was concentrated in vacuo to yield 27 g of the title compound of mp. 130°C.

45

29

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Example 4 Preparation of 5-chloro-6-(2-fluoro-6-methylphenyl)-7-isopropylamino-[1,2,4]-triazolo[1,5-a]pyrimidine [I-8]

5 A mixture of isopropylamine (1.5 mmol), triethylamine (1.5 mmol) and dichloromethane (10 ml) was added to a solution of 1.5 mmol of the product from Ex. 3 in 20 ml dichloromethane under stirring. The reaction mixture was stirred for about 16 hours at about 20 to 25°C and subsequently washed with 5 % hydrochloric
10 acid. The organic layer was separated, dried and filtered. The filtrate was evaporated and the residue was chromatographed to yield 0.46 g of the title compound of mp. 128°C.

Example 5 Preparation of 5-cyano-6-(2-fluoro-6-methylphenyl)-7-(4-methylpiperidin-1-yl)-[1,2,4]-triazolo[1,5-a]pyrimidine [I-49]
15

A mixture of 0.1 mol compound I-9 and tetraethylammonium cyanide (0.25 mol) in 750 ml Dimethylformamide (DMF) was stirred for
20 16 hours at about 20 to 25°C. To this mixture was added water and methyl-tert.butyl ether (MTBE), the organic phase was separated, washed with water, dried and filtered. The filtrate was evaporated and the residue was chromatographed to yield 6.51 g of the title compound of mp. 211°C.

25

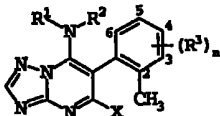
Example 6 Preparation of 5-methoxy-6-(2-fluoro-6-methylphenyl)-7-(4-methylpiperidin-1-yl)-[1,2,4]-triazolo[1,5-a]pyrimidine [I-50]

30 After having added a solution of sodium methanolate (30%, 71.5 mmol) to a solution of 65 mmol of compound I-9 in 400 ml dry methanol was added this mixture was stirred for about 16 hours at about 20 to 25°C. Methanol was evaporated and the residue was dissolved with dichloromethane. The organic phase was washed with
35 water, dried and filtered. The filtrate was evaporated and the residue was chromatographed to yield 4.32 g of the title compound of mp. 142°C.

40

45

Table I



I

No.	R ¹	R ²	(R ³) _n	X	phys. data
					(m.p. [°C], ¹ H-NMR δ [ppm])
I-1	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	4, 6-(CH ₃) ₂	Cl	131
I-2	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		4, 6-(CH ₃) ₂	Cl	138
I-3	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	4-OCH ₃ -6-CH ₃	Cl	74
I-4	(±) CH(CH ₃)-CH(CH ₃) ₃	H	4-OCH ₃ -6-CH ₃	Cl	163
I-5	CH ₂ CF ₃	H	4-OCH ₃ -6-CH ₃	Cl	191
I-6	H	H	6-F	Cl	250
I-7	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	6-F	Cl	124
I-8	CH(CH ₃) ₂	H	6-F	Cl	128
I-9	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		6-F	Cl	142
I-10	cyclopentyl	H	6-F	Cl	159
I-11	CH ₂ CH ₃	CH ₂ CH ₃	6-F	Cl	147
I-12	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃	6-F	Cl	124
I-13	CH(CH ₃) ₂	CH ₃	6-F	Cl	159

32

No.	R ¹	R ²	(R ²) _n	X	phys. data (m.p. [°C], ¹ H-NMR δ [ppm])
I-14	(±) CH(CH ₃)-CH ₂ CH ₃	H	6-F	Cl	115
I-15	(S) CH(CH ₃)-CH ₂ CH ₃	H	6-F	Cl	123
I-16	(R) CH(CH ₃)-CH ₂ CH ₃	H	6-F	Cl	129
I-17	(±) CH(CH ₃)-CH(CH ₃) ₂	H	6-F	Cl	A) 133 / B) 138
I-18	(S) CH(CH ₃)-CH(CH ₃) ₂	H	6-F	Cl	A) 120 / B) 130
I-19	(R) CH(CH ₃)-CH(CH ₃) ₂	H	6-F	Cl	A) 119 / B) 131
I-20	(±) CH(CH ₃)-CH(CH ₃) ₃	H	6-F	Cl	A) 148 / B) 174
I-21	(S) CH(CH ₃)-CH(CH ₃) ₃	H	6-F	Cl	A) 160 / B) 203
I-22	(R) CH(CH ₃)-CH(CH ₃) ₃	H	6-F	Cl	A) 159 / B) 203
I-23	(±) CH(CH ₃)-CF ₃	H	6-F	Cl	A) 149 / B) 56
I-24	(S) CH(CH ₃)-CF ₃	H	6-F	Cl	A) 166 / B) 70
I-25	(R) CH(CH ₃)-CF ₃	H	6-F	Cl	A) 167 / B) 70
I-26	CH ₂ CF ₃	H	6-F	Cl	173
I-27	H	H	4-F	Cl	281
I-28	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	4-F	Cl	115
I-29	CH(CH ₃) ₂	H	4-F	Cl	94
I-30	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		4-F	Cl	168
I-31	cyclopentyl	H	4-F	Cl	141
I-32	CH ₂ CH ₃	CH ₂ CH ₃	4-F	Cl	156
I-33	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃	4-F	Cl	121

No.	R ¹	R ²	(R ³) _n	X	phys. data (m.p. [°C], ¹ H-NMR δ (ppm))
I-34	CH(CH ₃) ₂	CH ₃	4-F	Cl	153
I-35	(±) CH(CH ₃)-CH ₂ CH ₃	H	4-F	Cl	118
I-36	(S) CH(CH ₃)-CH ₂ CH ₃	H	4-F	Cl	125
I-37	(R) CH(CH ₃)-CH ₂ CH ₃	H	4-F	Cl	126
I-38	(±) CH(CH ₃)-CH(CH ₃) ₂	H	4-F	Cl	132
I-39	(S) CH(CH ₃)-CH(CH ₃) ₂	H	4-F	Cl	124
I-40	(R) CH(CH ₃)-CH(CH ₃) ₂	H	4-F	Cl	124
I-41	(±) CH(CH ₃)-CH(CH ₃) ₃	H	4-F	Cl	162
I-42	(S) CH(CH ₃)-CH(CH ₃) ₃	H	4-F	Cl	156
I-43	(R) CH(CH ₃)-CH(CH ₃) ₃	H	4-F	Cl	156
I-44	(±) CH(CH ₃)-CF ₃	H	4-F	Cl	163
I-45	(S) CH(CH ₃)-CF ₃	H	4-F	Cl	145
I-46	(R) CH(CH ₃)-CF ₃	H	4-F	Cl	145
I-47	CH ₂ CF ₃	H	4-F	Cl	167
I-48	CH ₂ CF ₃	H	4-F-6-CH ₃	Cl	220
I-49	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		6-F	CN	211
I-50	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		6-F	OCH ₃	142
I-51	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		6-F	CH ₃	145
I-52	cyclopentyl	H	4,6-(CH ₃) ₂	Cl	200
I-53	CH ₂ CH ₃	CH ₂ CH ₃	4,6-(CH ₃) ₂	Cl	105

No.	R ¹	R ²	(R ³) _n	X	phys. data (m.p. [°C], ¹ H-NMR δ [ppm])
I-54	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃	4,6-(CH ₃) ₂	Cl	99
I-55	(±) CH(CH ₃)-CH ₂ CH ₃	H	4,6-(CH ₃) ₂	Cl	191
I-56	(S) CH(CH ₃)-CH ₂ CH ₃	H	4,6-(CH ₃) ₂	Cl	184
I-57	(R) CH(CH ₃)-CH ₂ CH ₃	H	4,6-(CH ₃) ₂	Cl	184
I-58	(±) CH(CH ₃)-CH(CH ₃) ₂	H	4,6-(CH ₃) ₂	Cl	107
I-59	(S) CH(CH ₃)-CH(CH ₃) ₂	H	4,6-(CH ₃) ₂	Cl	87
I-60	(R) CH(CH ₃)-CH(CH ₃) ₂	H	4,6-(CH ₃) ₂	Cl	87
I-61	(±) CH(CH ₃)-CH(CH ₃) ₃	H	4,6-(CH ₃) ₂	Cl	79
I-62	(S) CH(CH ₃)-CH(CH ₃) ₃	H	4,6-(CH ₃) ₂	Cl	81
I-63	(R) CH(CH ₃)-CH(CH ₃) ₃	H	4,6-(CH ₃) ₂	Cl	81
I-64	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	4-Cl	Cl	137
I-65	CH(CH ₃) ₂	H	4-Cl	Cl	136
I-66	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		4-Cl	Cl	173
I-67	cyclopentyl	H	4-Cl	Cl	147
I-68	CH ₂ CH ₃	CH ₂ CH ₃	4-Cl	Cl	167
I-69	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃	4-Cl	Cl	149
I-70	CH(CH ₃) ₂	CH ₃	4-Cl	Cl	159
I-71	(±) CH(CH ₃)-CH ₂ CH ₃	H	4-Cl	Cl	128
I-72	(S) CH(CH ₃)-CH ₂ CH ₃	H	4-Cl	Cl	114
I-73	(R) CH(CH ₃)-CH ₂ CH ₃	H	4-Cl	Cl	114

No.	R ¹	R ²	(R ³) _n	X	phys. data (m.p. [°C], ¹ H-NMR δ [ppm])
I-74	(±) CH(CH ₃)-CH(CH ₃) ₂	H	4-Cl	Cl	116
I-75	(S) CH(CH ₃)-CH(CH ₃) ₂	H	4-Cl	Cl	130
I-76	(R) CH(CH ₃)-CH(CH ₃) ₂	H	4-Cl	Cl	130
I-77	(±) CH(CH ₃)-CH(CH ₃) ₃	H	4-Cl	Cl	159
I-78	(S) CH(CH ₃)-CH(CH ₃) ₃	H	4-Cl	Cl	159
I-79	(R) CH(CH ₃)-CH(CH ₃) ₃	H	4-Cl	Cl	159
I-80	(±) CH(CH ₃)-CF ₃	H	4-Cl	Cl	184
I-81	(S) CH(CH ₃)-CF ₃	H	4-Cl	Cl	143
I-82	(R) CH(CH ₃)-CF ₃	H	4-Cl	Cl	143
I-83	CH ₂ CF ₃	H	4-Cl	Cl	206
I-84	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	4-CH ₃	Cl	158
I-85	CH(CH ₃) ₂	H	4-CH ₃	Cl	145
I-86	CH ₂ CH ₃	CH ₂ CH ₃	4-CH ₃	Cl	141
I-87	(±) CH(CH ₃)-CH ₂ CH ₃	H	4-CH ₃	Cl	122
I-88	(S) CH(CH ₃)-CH(CH ₃) ₃	H	4-CH ₃	Cl	108
I-89	(R) CH(CH ₃)-CH(CH ₃) ₃	H	4-CH ₃	Cl	108
I-90	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		4-COOCH ₃	Cl	8.45(s); 8.05(s); 7.95(d); 7.25(d); 4.0(s); 3.85(d); 3.45(d); 2.7(t); 2.65(t); 2.25(s); 1.55(m); 1.45(m); 1.25(m); 0.9(d)

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No.	R ¹	R ²	(R ³) _n	X	phys. data (m.p. [°C], ¹ H-NMR δ [ppm])
I-91	(R) CH(CH ₃)-CH(CH ₃) ₂	H	4-COOCH ₃	Cl	8.35 (s); 8.1 (s); 8.0 (d); 7.35 (d); 6.2 (m); 3.95 (s); 3.1 (m); 2.25 (s); 1.55 (sept); 1.2 (d); 0.95 (d); 0.9 (d)
I-92	(S) CH(CH ₃)-CF ₃	H	4-COOCH ₃	Cl	8.4 (s); 8.15 (s); 8.05 (d); 7.35 (m); 5.7 (m); 4.6 (m); 3.95 (s); 2.3 (s); 2.25 (s); 1.4 (d); 1.3 (d)
I-93	CH ₂ CF ₂ CF ₃	H	6-F	Cl	162
I-94	CH ₂ CF ₂ CF ₂ CF ₃	H	6-F	Cl	165
I-95	CH ₂ CF ₂ CF ₃	H	4-F	Cl	176
I-96	CH ₂ CF ₂ CF ₂ CF ₃	H	4-F	Cl	138
I-97	CH ₂ CF ₂ CF ₃	H	4-Cl	Cl	164
I-98	CH ₂ CF ₂ CF ₂ CF ₃	H	4-Cl	Cl	126
I-99	H	H	4-Cl	Cl	276

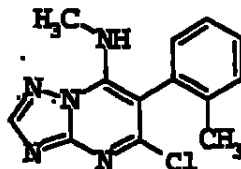
In some cases of chiral groups R¹ and due to the hindered rotation of the phenyl group two diastereomers A) and B) exist which may differ in their physical properties.

Examples of the action against harmful fungi

The fungicidal action of the compounds of the formula I was demonstrated by the following experiments:

The active compounds, separately or together, were formulated as a 10% emulsion in a mixture of 70% by weight of cyclohexanone, 20% by weight of Nekanil® LN (Lutensol® AP6, wetting agent having emulsifying and dispersant action based on ethoxylated alkylphenols) and 10% by weight of Wettol® EM (nonionic emulsifier based on ethoxylated castor oil) and diluted with water to the desired concentration.

Compound A known from WO-A 98/46608 (No. 9) served as comparative active compound:



Comparison trial 1 - Fungicidal control of early blight on tomato toes (*Alternaria solani*)

Young seedlings of tomato plants of the variety "Große Fleischtomate St. Pierre" were grown in pots to the 2 to 4 leaf stage. These plants were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient mentioned in the table below, prepared from a stock solution containing 10 % of the active ingredient, 85 % cyclohexanone and 5 % emulsifier. The next day, the treated plants were inoculated with an aqueous suspension of *Alternaria solani* containing 0.2×10^6 spores per ml. Then the trial plants were immediately transferred to a humid chamber. After 6 days at 20 to 23°C and a relative humidity close to 100 %, the extent of fungal attack on the leaves was visually assessed as % diseased leaf area.

In this test, the plants which had been treated with 63 ppm of compounds I-23 and I-24, resp., showed an infection of not more than 3%, whereas the the plants treated with 63 ppm of the comparison compound A were infected to 15%, and the untreated plants were infected to 90%.

Comparison trial 2 - Fungicidal control of powdery mildew on wheat caused by *Blumeria graminis* f. sp. *tritici*

The first fully developed leaves of pot grown wheat of the variety "Kanzler" were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient or their mixture mentioned in the table below, prepared from a stock solution containing 10 % of the active ingredient, 85 % cyclohexanone and 5 % emulsifier. The next day the treated plants were inoculated with spores of *Blumeria graminis* f. sp. *tritici* by shaking heavily infested stock plants over the treated pots. After cultivation in the greenhouse for 7 days at 22-26°C and a relative humidity between 60 to 90 % the extent of fungal attack on the leaves was visually assessed as % diseased leaf area.

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In this test, the plants which had been treated with 63 ppm of compounds I-23 and I-24, resp., showed an infection of not more than 3%, whereas the the plants treated with 63 ppm of the comparison compound A were infected to 30%, and the untreated plants were infected to 85%.

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Comparison trial 3 - Fungicidal control of grape downy mildew (*Plasmopara viticola*)

Grape cuttings of the cultivar "Müller-Thurgau" were grown in pots to the 4 to 5 leaf stage. These plants were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient or their mixture mentioned in the table below, prepared from a stock solution containing 10 % of the active ingredient, 85 % cyclohexanone and 5 % emulsifier. The plants were allowed to air-dry. The next day they were inoculated with an aqueous spore suspension of *Plasmopara viticola* by spraying it at the lower leaf-side. Then the trial plants were immediately transferred for 24 h to a humid chamber with 22 - 24°C and a relative humidity close to 100 %. For a period of 5 days, cultivation followed in a greenhouse at 20 - 25°C and a relative humidity about 50-80 %. To stimulate the outbreak of the disease symptoms, the plants were transferred to a humid chamber again for 24 hours. Then the extent of fungal attack on the lower leaf surface was visually assessed as % diseased leaf area.

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In this test, the plants which had been treated with 250 ppm of compounds I-23 and I-24, resp., showed an infection of not more than 7%, whereas the the plants treated with 250 ppm of the comparison compound A, and the untreated plants were infected to 80%.

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Use Example 1 - Fungicidal control of early blight on tomatoes (*Alternaria solani*)

The test was conducted as described in Comparison trial 1.

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In this test, the plants which have been treated with 250 ppm of compounds I-7, I-9, I-10, I-28, I-30, I-35, I-38, I-41, I-44, I-66, and I-83, resp., showed no infection, whereas the untreated plants were infected to 90%.

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Use Example 2 - Fungicidal control of powdery mildew on wheat caused by *Blumeria graminis* f. sp. *tritici*

The test was conducted as described in Comparison trial 2.

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In this test, the plants which have been treated with 250 ppm of compounds I-14, I-28, I-30, I-35, I-38, I-41, and I-44, resp., showed an infection of not more than 5%, whereas the untreated plants were infected to 85%.

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Use Example 3 - Fungicidal control of grape downy mildew (*Plasmopara viticola*)

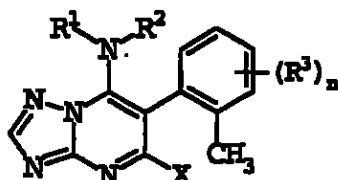
Leaves of potted vines of the "Müller Thurgau" variety were
25 sprayed with aqueous liquors made from a stock solution consisting of 10% of active ingredient, 85% of cyclohexanone, and 5% of emulsifier. To assess the duration of action, the plants were set up, after the sprayed-on layer had dried, in the greenhouse for 8 days. Then the leaves were infected with a zoospore suspension of the fungus *Plasmopara viticola*, first placed in a vapour-saturated chamber at 24°C, and then kept for 5 days in a greenhouse at 20 to 30°C. To accelerate and intensify the sporangio-
30 phore discharge, the plants were then again placed in the moist chamber for 16 hours. The extent of fungus attack was then assessed on the undersides of the leaves.
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In this test, the plants which have been treated with 250 ppm of compounds I-7, I-9, I-10, I-35, I-38, and I-44, resp., showed an infection of 3 to 40%, whereas the untreated plants were infected
40 to 80%.

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Claims:

1. Substituted 6-(2-tolyl)-triazolopyrimidines of formula I



I

in which

R^1 and R^2 independently denote hydrogen or

C_1 - C_{10} -alkyl, C_2 - C_{10} -alkenyl, C_2 - C_{10} -alkynyl, or C_4 - C_{10} -alkadienyl, C_1 - C_{10} -haloalkyl, C_2 - C_{10} -haloalkenyl, C_3 - C_{10} -cycloalkyl, phenyl, naphthyl, or

C_3 - C_{10} -cycloalkyl, phenyl, naphthyl, or

5- or 6-membered heterocyclyl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or

5- or 6-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or

where R^1 and R^2 radicals may be unsubstituted or partly or fully halogenated or may carry one to three groups R^a ,

R^a is cyano, nitro, hydroxyl, C_1 - C_6 -alkyl, C_1 - C_6 -haloalkyl, C_3 - C_6 -cycloalkyl, C_1 - C_6 -alkoxy, C_1 - C_6 -haloalkoxy, C_1 - C_6 -alkylthio, C_1 - C_6 -alkylamino, di- C_1 - C_6 -alkylamino, C_2 - C_6 -alkenyl, C_2 - C_6 -alkenyloxy, C_2 - C_6 -alkynyl, C_3 - C_6 -alkynyloxy and C_1 - C_4 -alkylenedioxy; or

R^1 and R^2 together with the interjacent nitrogen atom represent a 5- or 6-membered heterocyclic ring, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, which may be substituted by one to three R^a radicals;

R^3 is halogen, cyano, C_1 - C_{10} -alkyl, C_1 - C_{10} -alkoxy, C_1 - C_{10} -haloalkyl, or $C(=O)A$, wherein

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A is hydrogen, hydroxy, C₁-C₈-alkyl, C₁-C₈-alkoxy, amino, C₁-C₈-alkylamino, or di-(C₁-C₈-alkyl)amino;

n is an integer from 1 to 4; and

X is halogen, cyano, C₁-C₆-alkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy or C₃-C₈-alkenyloxy.

2. Compounds of formula I according to claim 1, in which

R¹ is straight chained or branched C₁-C₆-alkyl, C₂-C₆-alkenyl, C₃-C₉-cycloalkyl, or C₁-C₁₀-haloalkyl, and

R² is hydrogen or C₁-C₆-alkyl, or

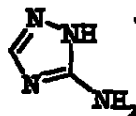
R¹ and R² together with the interjacent nitrogen atom represent a heterocyclic ring with 5 or 6 carbon atoms being optionally substituted with one or two C₁-C₆-alkyl groups.

3. Compounds of formula I according to claims 1 or 2 in which R² is hydrogen.

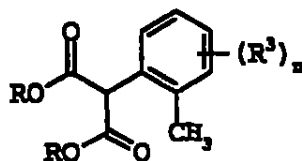
4. Compounds of formula I according to claims 1 to 3 in which X is halogen.

5. Compounds of formula I according to claims 1 to 4 in which (R³)_n is 4-(C₁-C₈-alkoxy-carbonyl) or 4-cyano.

6. A process for the preparation of compounds of formula I as defined in claim 4 which comprises reacting 5-amino-1,2,4-triazole



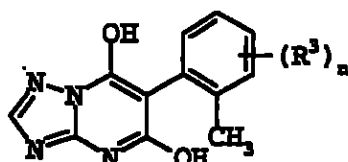
with 2-phenyl-substituted malonic acid ester of formula II,



II

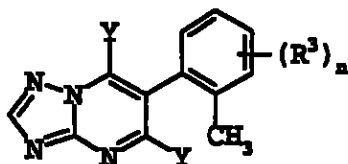
wherein R³ and n are as defined in formula I, and R denotes C₁-C₆-alkyl, under alkaline conditions, to yield compounds of formula III,

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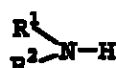
III

which are subsequently treated with a halogenating agent to give 5,7-dihalogen-6-phenyl-triazolopyrimidines of formula IV



IV

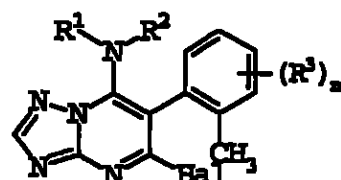
in which Y is halogen, with an amine of formula V



V

in which R¹ and R² are as defined in formula I to produce compounds of formula I.

7. A process for the preparation of compounds of formula I according to claim 1 wherein X is cyano, C₁-C₁₀-alkoxy, or C₁-C₁₀-haloalkyl, which comprises reacting 5-halogen-triazolopyrimidine of formula I



I (X=Hal)

with compounds of formula VI,

M-X'

VI

which are, dependent from the value of X' to be introduced, an anorganic cyano salt, an alkoxylate, haloalkoxylate or an alkenyloxylate, resp., wherein M is ammonium-, tetraalkylammonium-, alkalimetal- or earth metal cation, to produce compounds of formula I.

8. Intermediates of formulae II, III, and IV as defined in claim 6.

9. A composition suitable for controlling phytopathogenic fungi, comprising a solid or liquid carrier and a compound of the formula I as claimed in claim 1.

10. A method for controlling phytopathogenic fungi, which comprises treating the fungi or the materials, plants, the soil or the seed to be protected against fungal attack with an effective amount of a compound of the formula I as claimed in claim 1.

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07D487/04 A01N43/90 //(C07D487/04,249:00,239:00)

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 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6 204 269 B1 (W. PFRENGLE ET AL.) 20 March 2001 (2001-03-20) column 3, line 50 -column 3, line 55; claims 1-10; example 7	1-9
P,Y	WO 02 46195 A (BASF AG) 13 June 2002 (2002-06-13) claims 1-10	1-9
Y	US 5 948 783 A (K.-J. PEES ET AL.) 7 September 1999 (1999-09-07) claims 1-8	1-9
Y	FR 2 795 073 A (AMERICAN CYANAMID CO.) 22 December 2000 (2000-12-22) claims 1-5	1-9
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"Z" document member of the same patent family

Date of the actual completion of the international search

29 October 2002

Date of mailing of the international search report

07/11/2002

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Authorized officer

Herz, C

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/07578

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 02 38565 A (BASF AG) 16 May 2002 (2002-05-16) claims 1-9; table A	1-9
P,Y	WO 02 50077 A (BAYER AG) 27 June 2002 (2002-06-27) claims 1-9	1-9
X	EP 0 071 792 A (BASF AG) 16 February 1983 (1983-02-16) page 10, line 23; claims 1-8	1-9
Y	WO 98 46608 A (AMERICAN CYANAMID CO.) 22 October 1998 (1998-10-22) cited in the application claims 1-10	1-9
Y	EP 0 550 113 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 7 July 1993 (1993-07-07) claims 1-10	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 02/07578

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6204269	B1	20-03-2001	US 5986135 A BR 9904354 A CN 1250052 A EP 0989130 A1 JP 2000119275 A ZA 9905673 A	16-11-1999 12-09-2000 12-04-2000 29-03-2000 25-04-2000 30-03-2000
WO 0246195	A	13-06-2002	WO 0246195 A1 AU 2362901 A	13-06-2002 18-06-2002
US 5948783	A	07-09-1999	NONE	
FR 2795073	A	22-12-2000	FR 2795073 A1	22-12-2000
WO 0238565	A	16-05-2002	AU 2183102 A WO 0238565 A2	21-05-2002 16-05-2002
WO 0250077	A	27-06-2002	DE 10063115 A1 AU 3167602 A WO 0250077 A2	27-06-2002 01-07-2002 27-06-2002
EP 71792	A	16-02-1983	DE 3130633 A1 AT 11539 T AU 553663 B2 AU 8665982 A CA 1180329 A1 CS 226748 B2 DD 202093 A5 DE 3262143 D1 DK 341682 A ,B, EP 0071792 A2 GR 76193 A1 HU 188325 B IE 53269 B1 JP 1634879 C JP 2061955 B JP 58043974 A US 4567263 A ZA 8205498 A	17-02-1983 15-02-1985 24-07-1986 10-02-1983 01-01-1985 16-04-1984 31-08-1983 14-03-1985 02-02-1983 16-02-1983 03-08-1984 28-04-1986 28-09-1988 20-01-1992 21-12-1990 14-03-1983 28-01-1986 27-07-1983
WO 9846608	A	22-10-1998	AU 735730 B2 AU 6867198 A BG 103805 A BR 9808531 A CN 1257502 T EE 9900486 A EP 0975635 A1 HU 0001993 A2 JP 2001520650 T NO 994973 A NZ 500143 A PL 336164 A1 SK 141499 A3 TR 9902552 T2 TW 460476 B WO 9846608 A1 ZA 9803054 A	12-07-2001 11-11-1998 30-06-2000 23-05-2000 21-06-2000 15-06-2000 02-02-2000 28-10-2000 30-10-2001 13-10-1999 29-06-2001 05-06-2000 11-09-2001 22-05-2000 21-10-2001 22-10-1998 11-10-1999

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/07578

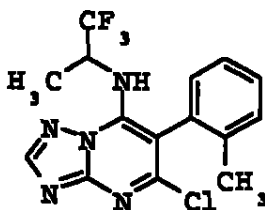
Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 550113 A	07-07-1993	EP 0550113 A2	07-07-1993
		EP 0782997 A2	09-07-1997
		GR 3033916 T3	30-11-2000
		AT 159256 T	15-11-1997
		AT 192154 T	15-05-2000
		AU 667204 B2	14-03-1996
		AU 3043592 A	01-07-1993
		BR 9205172 A	06-07-1993
		CA 2086404 A1	01-07-1993
		CN 1075144 A ,B	11-08-1993
		CN 1141119 A ,B	29-01-1997
		DE 69222746 D1	20-11-1997
		DE 69222746 T2	12-02-1998
		DE 69230977 D1	31-05-2000
		DE 69230977 T2	09-11-2000
		DK 550113 T3	09-02-1998
		DK 782997 T3	07-08-2000
		ES 2108727 T3	01-01-1998
		ES 2147411 T3	01-09-2000
		GR 3025920 T3	30-04-1998
		HK 1010105 A1	23-06-2000
		HU 217349 B	28-01-2000
		IL 104244 A	13-07-1997
		JP 5271234 A	19-10-1993
		NZ 245581 A	26-07-1995
		PL 297160 A1	06-09-1993
		PL 171579 B1	30-05-1997
		PT 782997 T	29-09-2000
		RU 2089552 C1	10-09-1997
		SG 47563 A1	17-04-1998
		US 5593996 A	14-01-1997
		ZA 9210043 A	28-07-1993

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Compound A known from WO-A 98/46608 (No. 9) served as comparative active compound:



Comparison trial 1 - Fungicidal control of early blight on tomatoes (*Alternaria solani*)

Young seedlings of tomato plants of the variety "Große Fleischtomate St. Pierre" were grown in pots to the 2 to 4 leaf stage. These plants were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient mentioned in the table below, prepared from a stock solution containing 10 % of the active ingredient, 85 % cyclohexanone and 5 % emulsifier. The next day, the treated plants were inoculated with an aqueous suspension of *Alternaria solani* containing 0.2×10^6 spores per ml. Then the trial plants were immediately transferred to a humid chamber. After 6 days at 20 to 23°C and a relative humidity close to 100 %, the extent of fungal attack on the leaves was visually assessed as % diseased leaf area.

In this test, the plants which had been treated with 63 ppm of compounds I-23 and I-24, resp., showed an infection of not more than 3%, whereas the the plants treated with 63 ppm of the comparison compound A were infected to 15%, and the untreated plants were infected to 90%.

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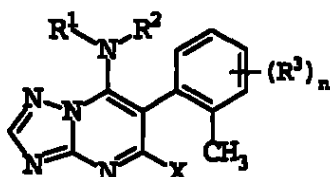
Substituted 6-(2-tolyl)-triazolopyrimidines

Description

5

The invention relates to substituted 6-(2-tolyl)-triazolopyrimidines of formula I

10



I

in which

15

R^1 and R^2 independently denote hydrogen or C_1 - C_{10} -alkyl, C_2 - C_{10} -alkenyl, C_2 - C_{10} -alkynyl, or C_4 - C_{10} -alkadienyl, C_1 - C_{10} -haloalkyl, C_2 - C_{10} -haloalkenyl, C_3 - C_{10} -cycloalkyl, phenyl, naphthyl, or

20

5- or 6-membered heterocyclyl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or

5- or 6-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or

25

where R^1 and R^2 radicals may be unsubstituted or partly or fully halogenated or may carry one to three groups R^a ,

30

R^a is cyano, nitro, hydroxyl, C_1 - C_6 -alkyl, C_3 - C_6 -cycloalkyl, C_1 - C_6 -alkoxy, C_1 - C_6 -alkylthio, C_1 - C_6 -alkylamino, di- C_1 - C_6 -alkylamino, C_2 - C_6 -alkenyl, C_2 - C_6 -alkenyloxy, C_2 - C_6 -alkynyl, C_3 - C_6 -alkynyloxy and C_1 - C_4 -alkylenedioxy; or

35

R^1 and R^2 together with the interjacent nitrogen atom represent a 5- or 6-membered heterocyclic ring, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, which may be substituted by one to three R^a radicals;

40

R^3 is halogen, cyano, C_1 - C_{10} -alkyl, C_1 - C_{10} -alkoxy, C_1 - C_{10} -haloalkyl, or $C(=O)A$, wherein

45

A is hydrogen, hydroxy, C_1 - C_8 -alkyl, C_1 - C_8 -alkoxy, amino, C_1 - C_8 -alkylamino, or di- $(C_1$ - C_8 -alkyl)-amino;

2

n is an integer from 1 to 4; and

X is halogen, cyano, C₁-C₆-alkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy or C₃-C₈-alkenyloxy.

5

Moreover, the invention relates to processes for their preparation, compositions containing them and to their use for combating phytopathogenic fungi.

10 6-Phenyl-7-amino-triazolopyrimidines are generally known from US 4,567,262 and US 5,593,996.

Triazolopyrimidines with a trifluorophenyl group in 6-position are disclosed in WO-A 98/46607 and EP-A 945 453.

15

From WO-A 98/46608 diverse 6-phenyl-triazolopyrimidines are known, which are substituted in the 7-position by fluorinated alkylamines.

20 The compounds disclosed in the documents discussed above are said to be active against various phytopathogenic fungi.

It is an object of the present invention to provide compounds having improved fungicidal activity.

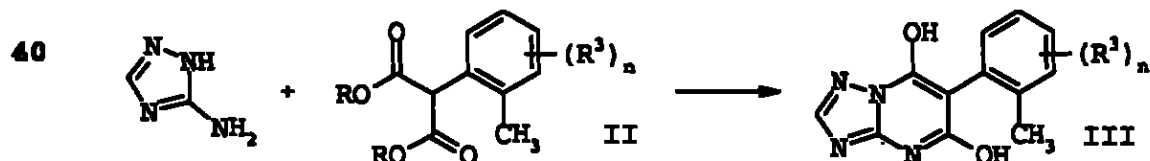
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We have found that this object is achieved by the compounds defined at the outset. Furthermore, we have found processes for their preparation, compositions comprising them and methods for controlling phytopathogenic fungi using the compounds I.

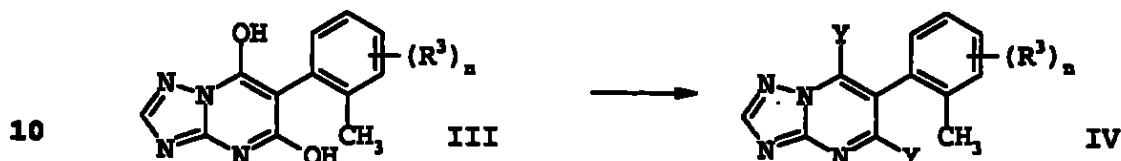
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The compounds of the formula I differ from the compounds known from closest prior art WO-A 98/46608 in the 2-tolyl group, which is further substituted.

35 The present invention further provides a process for the preparation of compounds of formula I as defined above which comprises reacting 5-amino-triazole with 2-(2-tolyl)-substituted malonic acid ester of formula II, in which



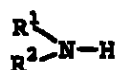
The resulting 5,7-dihydroxy-6-phenyl-triazolopyrimidine of formula III, wherein R^3 and n are as defined for formula I, is subsequently treated with a halogenating agent, preferably with a brominating or chlorinating agent, such as phosphorus oxybromide or phosphorus oxychloride, neat or in the presence of a solvent to give IV.



The reaction is suitably carried out at a temperature in the range from 0 °C to 150 °C, the preferred reaction temperature being from 80 °C to 125 °C as disclosed for example by EP-A 15 770 615.

Dihalotriazolopyrimidine IV is further reacted with an amine of formula V

20



V

in which R^1 and R^2 are as defined in formula I to produce compounds of formula I in which X is halogen.

25

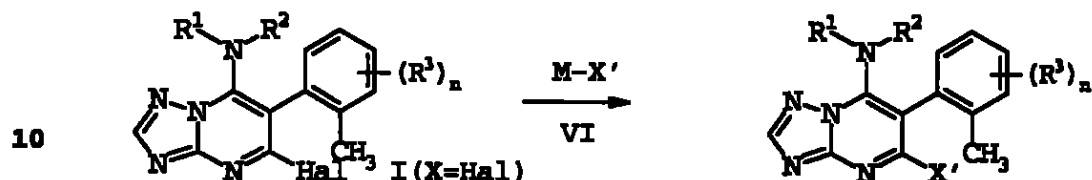
The reaction between the 5,7-dihalo compound IV and the amine of formula V can be carried out under conditions known from WO-A 98/46608. The reaction is preferably carried out in the presence of a solvent. Suitable solvents include ethers, such as dioxane, diethyl ether and, especially, tetrahydrofuran, halogenated hydrocarbons such as dichloromethane and aromatic hydrocarbons, for example toluene.

The reaction is suitably carried out at a temperature in the range from 0°C to 70°C, the preferred reaction temperature being from 10°C to 35°C.

It is also preferred that the reaction is carried out in the presence of a base. Suitable bases include tertiary amines, such as triethylamine, and inorganic bases, such as potassium carbonate or sodium carbonate. Alternatively, an excess of the compound of formula V may serve as a base.

Compounds of formula I in which X denotes cyano, C_1-C_6 -alkoxy, C_1-C_6 -haloalkoxy or C_3-C_8 -alkenyloxy can be prepared by reacting compounds I in which X is halogen, preferably chloro, with compounds of formula VI, which are, dependent from the value of X'

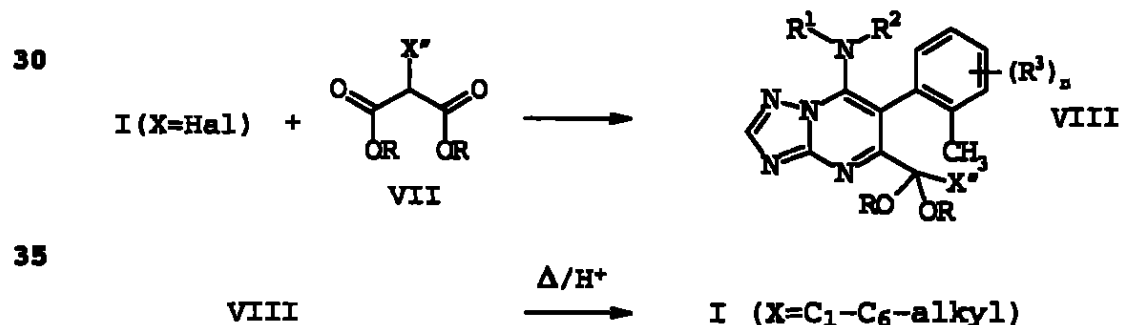
to be introduced to yield formula I compounds, an anorganic cyano salt, an alkoxylate, haloalkoxylate or an alkenyloxylate, respectively, preferably in the presence of a solvent. The cation M in formula VI has minor influence; for practical and economical reasons usually ammonium-, tetraalkylammonium- or alkali metal- and earth metal salts are preferred.



The reaction is suitably carried out at a temperature in the range from 0 to 120°C, the preferred reaction temperature being from 10 to 40°C [cf. J. Heterocycl. Chem., Vol.12, p. 861-863 (1975)].

Suitable solvents include ethers, such as dioxane, diethyl ether and, especially, tetrahydrofuran, halogenated hydrocarbons such as dichloromethane and aromatic hydrocarbons, for example toluene.

Compounds of formula I in which X denotes C₁-C₆-alkyl can be prepared by reacting compounds I in which X is halogen, preferably chloro, with malonic acid esters of formula VII, wherein X' denotes H or C₁-C₅-alkyl and R denotes C₁-C₄-alkyl, to compounds of formula VIII and decarboxylation under conditions described in US 5,994,360.



Accordingly, the invention relates to the novel intermediates of formulae II, III and IV.

The compounds of formula II are preferably prepared by reaction of the corresponding substituted bromobenzenes with sodium dialkylmalonates in the presence of a copper(I) salt [cf. Chemistry Letters, pp. 367-370, 1981; EP-A 10 02 788].

29

5

The compounds of formula II may also be prepared by reaction of an alkyl 2-(2-tolyl)-acetate with dialkylcarbonate in the presence of a strong base, preferably sodium ethoxide and sodium hydride (cf. Heterocycles, pp. 1031-1047, 1996).

5

The substituted phenylacetates which are the starting compounds for compounds of formula II are known and commercially available, and/or they are obtainable by generally known methods.

- 10 The reaction mixtures are worked up in a customary manner, for example by mixing with water, phase separation and, if required, chromatographic purification of the crude products. Some of the end products are obtained in the form of colorless or slightly brownish, viscous oils, which are purified or freed from volatile
- 15 components under reduced pressure and at moderately elevated temperatures. If the end products are obtained as solids, purification can also be carried out by recrystallization or digestion.

If individual compounds I are not obtainable by the routes described above, they can be prepared by derivatization of other compounds I.

In the symbol definitions given in the formulae above, collective terms were used which generally represent the following substituents:

- halogen: fluorine, chlorine, bromine and iodine;
- C₁-C₁₀-alkyl: saturated, straight-chain or branched hydrocarbon radicals having 1 to 10, especially 1 to 6 carbon atoms, for example C₁-C₄-alkyl as mentioned above or pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-di-methylpropyl, 1-ethylpropyl, hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethyl-
- 35 butyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methylpropyl and 1-ethyl-2-methylpropyl;
- 40 - C₂-C₁₀-alkenyl: unsaturated, straight-chain or branched hydrocarbon radicals having 2 to 10, especially 2 to 6 carbon atoms and a double bond in any position, for example ethenyl, 1-propenyl, 2-propenyl, 1-methylethenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl,
- 45 1-methyl-2-propenyl and 2-methyl-2-propenyl;

C₂-C₁₀-alkynyl: straight-chain or branched hydrocarbon radicals having 2 to 10, especially 2 to 4 carbon atoms and a triple bond in any position, for example ethynyl, 1-propynyl, 2-propynyl, 1-butyne, 2-butyne, 3-butyne and 1-methyl-2-propynyl;

5

- C₁-C₁₀-haloalkyl and haloalkyl moieties of C₁-C₆-haloalkoxy: straight-chain or branched alkyl groups having 1 to 6 or 10, preferably 1 to 4 carbon atoms (as mentioned above), where the hydrogen atoms in these groups may be partially or fully replaced

10 by halogen atoms as mentioned above, for example C₁-C₂-haloalkoxy, such as chloromethoxy, bromomethoxy, dichloromethoxy, trichloromethoxy, fluoromethoxy, difluoromethoxy, trifluoromethoxy, chlorofluoromethoxy, dichlorofluoromethoxy, chlorodifluoromethoxy, 1-chloroethoxy, 1-bromoethoxy,

15 1-fluoroethoxy, 2-fluoroethoxy, 2,2-difluoroethoxy, 2,2,2-trifluoroethoxy, 2-chloro-2-fluoroethoxy, 2-chloro-2,2-difluoroethoxy, 2,2-dichloro-2-fluoroethoxy, 2,2,2-trichloroethoxy and pentafluoroethoxy;

20 C₃-C₁₀-cycloalkyl: mono- or bicyclic cycloalkyl groups having 3 to 10 carbon atoms; monocyclic groups preferably have 3 to 8, especially 3 to 6 ring members, bicyclic groups preferably have 8 to 10 ring members.

25 A 5- or 6-membered heterocyclyl group, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, preferably one oxygen atom, for example 1-pyrimidinyl, 2-pyrimidinyl, morpholin-4-yl.

30 5-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom: 5-membered heteroaryl groups which, in addition to carbon atoms, may contain one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom as ring members, for example

35 2-furyl, 3-furyl, 2-thienyl, 3-thienyl, 2-pyrrolyl, 3-pyrrolyl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 3-isothiazolyl, 4-isothiazolyl, 5-isothiazolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-imidazolyl, 4-imidazolyl, 1,2,4-oxa-
40 diazol-3-yl, 1,2,4-oxadiazol-5-yl, 1,2,4-thiadiazol-3-yl, 1,2,4-thiadiazol-5-yl, 1,2,4-triazol-3-yl, 1,3,4-oxadiazol-2-yl, 1,3,4-thiadiazol-2-yl and 1,3,4-triazol-2-yl;

6-membered heteroaryl, containing one to four nitrogen atoms:

45 6-membered heteroaryl groups which, in addition to carbon atoms, may contain one to three or one to four nitrogen atoms as ring members, for example 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, 3-py-

7

ridaziny1, 4-pyridaziny1, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl, 2-pyraziny1, 1,3,5-triazin-2-yl and 1,2,4-triazin-3-yl.

With respect to their intended use, preference is given to
5 triazolopyrimidines of the formula I having the following substituents, where the preference is valid in each case on its own or in combination:

A preferred cycloalkyl moiety is cyclopentyl being optionally
10 substituted by one or more nitro, cyano, C₁-C₆-alkyl, C₁-C₆-alkoxy groups.

A preferred heteroaryl moiety is pyridyl, pyrimidyl, pyrazolyl or thienyl.

15

Preference is given to compounds of formula I in which any alkyl or haloalkyl part of the groups R¹ or R², which may be straight chained or branched, contains up to 10 carbon atoms, preferably 1 to 9 carbon atoms, more preferably 2 to 6 carbon atoms, any
20 alkenyl or alkynyl part of the substituents R¹ or R² contains up to 10 carbon atoms, preferably 2 to 9 carbon atoms, more preferably 3 to 6 carbon atoms, any cycloalkyl part of the substituents R¹ or R² contains from 3 to 10 carbon atoms, preferably from 3 to 8 carbon atoms, more preferably from 3 to 6 carbon atoms, and any
25 bicycloalkyl part of the substituents R¹ or R² contains from 5 to 9 carbon atoms, preferably from 7 to 9 carbon atoms. Any alkyl, alkenyl or alkynyl group may be linear or branched.

Likewise, preference is given to compounds of formula I wherein R¹
30 is not hydrogen.

Compounds of formula I are preferred in which R¹ represents a straight-chained or branched C₁-C₁₀-alkyl, in particular a branched C₃-C₁₀-alkyl group, a C₃-C₈-cycloalkyl, a C₅-C₉-bicycloalkyl,
35 a C₃-C₈-cycloalkyl-C₁-C₆-alkyl, C₁-C₁₀-alkoxy-C₁-C₆-alkyl, a C₁-C₁₀-haloalkyl or a phenyl group being optionally substituted by one to three halogen atoms or C₁-C₁₀-alkyl or C₁-C₁₀-alkoxy groups.

Particular preference is given to compounds I in which R² represents hydrogen, C₁-C₁₀-alkyl or C₁-C₁₀-haloalkyl, in particular hydrogen.
40

Besides, particular preference is given to compounds I in which R² is hydrogen.

45

8

Moreover, particular preference is given to compounds I in which R² is methyl.

Furthermore, particular preference is given to compounds I in which R² is ethyl.

If R¹ denotes C₁-C₁₀-haloalkyl, preferably polyfluorinated alkyl, in particular 2,2,2-trifluoroethyl, 2-(1,1,1-trifluoropropyl) or 2-(1,1,1-trifluorobutyl), R² preferably represents hydrogen.

10

If R¹ denotes optionally substituted C₃-C₈-cycloalkyl, preferably cyclopentyl or cyclohexyl, R² preferably represents hydrogen or C₁-C₆-alkyl.

15 Moreover, particular preference is given to compounds I in which R¹ and R² together with the interjacent nitrogen atom form an optionally substituted heterocyclic ring, preferably an optionally substituted C₃-C₇-heterocyclic ring, in particular pyrrolidine, piperidine, tetrahydropyridine, in particular 1,2,3,6-tetrahydro-
20 pyridine or azepane which is optionally substituted by one or more C₁-C₁₀-alkyl groups.

Preference is given to compounds of formula I in which any alkyl part of the groups R¹ or R², which may be straight chained or
25 branched, contains 1 to 9 carbon atoms, more preferably 2 to 6 carbon atoms, any alkenyl or alkynyl part of the substituents R¹ or R² contains 2 to 9 carbon atoms, more preferably 3 to 6 carbon atoms, any cycloalkyl part of the substituents R¹ or R² contains from 3 to 10 carbon atoms, preferably from 3 to 8 carbon atoms,
30 more preferably from 3 to 6 carbon atoms, and any bicycloalkyl part of the substituents R¹ or R² contains from 7 to 9 carbon atoms. Any alkyl, alkenyl or alkynyl moiety may be linear or branched.

35 Compounds of formula I are preferred in which R¹ represents a straight-chained or branched C₁-C₁₀-alkyl, in particular branched C₃-C₁₀-alkyl, a C₃-C₈-cycloalkyl, C₅-C₉-bicycloalkyl, C₃-C₈-cycloalkyl-C₁-C₆-alkyl, C₁-C₁₀-alkoxy-C₁-C₆-alkyl, or phenyl being optionally substituted by one to three C₁-C₁₀-alkyl or C₁-C₁₀-alkoxy
40 groups.

Particular preference is given to compounds I in which R² represents hydrogen or C₁-C₁₀-alkyl, in particular hydrogen.

45 Moreover, particular preference is given to compounds I in which R² is methyl or ethyl.

9

If R^1 denotes an optionally substituted C_3 - C_8 -cycloalkyl group, preferably cyclopentyl or cyclohexyl, R^2 preferably represents hydrogen or C_1 - C_6 -alkyl.

- 5 Moreover, particular preference is given to compounds I in which R^1 and R^2 together with the interjacent nitrogen atom form an optionally substituted heterocyclic ring, preferably an optionally substituted C_3 - C_7 -heterocyclic ring, in particular a pyrrolidine, piperidine, tetrahydropyridine, in particular 1,2,3,6-tetrahydro-
10 pyridine or azepane ring which is optionally substituted by one or more C_1 - C_{10} -alkyl groups.

Likewise, particular preference is given to compounds I in which R^2 is hydrogen.

15

Particular preference is also given to compounds I in which n has the value 2 and R^3 groups are in 4- and 6-position.

- Moreover, preference is given to compounds I in which a R^3 group
20 is in para-position.

Furthermore, particular preference is given to compounds I in which $(R^3)_n$ is 4,6-dimethyl.

- 25 Likewise, particular preference is given to compounds I in which $(R^3)_n$ is 4-(C_1 - C_8 -alkoxy)carbonyl, especially 4-methoxycarbonyl.

Besides, particular preference is given to compounds I in which $(R^3)_n$ is 4-methoxy-6-methyl, or 4-fluoro-6-methyl.

30

Particular preference is also given to compounds I in which $(R^3)_n$ is 4-fluoro, 6-fluoro, or 4-chloro.

- Besides, particular preference is given to compounds I in which X
35 is chloro or bromo, especially chloro.

Moreover, preference is given to compounds I in which X is cyano or methyl.

- 40 Furthermore, particular preference is given to compounds I in which X is methoxy, ethoxy, n -propoxy, iso-propoxy, allyloxy, or 3-methylallyloxy.

- The particularly preferred embodiments of the intermediates with
45 respect to the variables correspond to those of the radicals X , R^1 , R^2 and R^3 of formula I.

10

Included in the scope of the present invention are (R) and (S) isomers of compounds of general formula I having a chiral center and the racemates thereof, and salts, N-oxides and acid addition compounds.

5

With respect to their use, particular preference is given to the compounds I compiled in the tables below. The groups mentioned in the tables for a substituent are furthermore for their part, independently of the combination in which they are mentioned, a

10 particularly preferred embodiment of the respective substituents.

Table 1

Compounds of formula I, in which X is chloro, (R³)_n is 4-chloro and R¹ and R² correspond to one row in Table A

15

Table 2

Compounds of formula I, in which X is chloro, (R³)_n is 5-chloro and R¹ and R² correspond to one row in Table A

20 Table 3

Compounds of formula I, in which X is chloro, (R³)_n is 6-chloro and R¹ and R² correspond to one row in Table A

Table 4

25 Compounds of formula I, in which X is chloro, (R³)_n is 3-fluoro and R¹ and R² correspond to one row in Table A

Table 5

Compounds of formula I, in which X is chloro, (R³)_n is 4-fluoro and R¹ and R² correspond to one row in Table A

30

Table 6

Compounds of formula I, in which X is chloro, (R³)_n is 5-fluoro and R¹ and R² correspond to one row in Table A

35

Table 7

Compounds of formula I, in which X is chloro, (R³)_n is 6-fluoro and R¹ and R² correspond to one row in Table A

40 Table 8

Compounds of formula I, in which X is chloro, (R³)_n is 3-methyl and R¹ and R² correspond to one row in Table A

Table 9

45 Compounds of formula I, in which X is chloro, (R³)_n is 4-methyl and R¹ and R² correspond to one row in Table A

11

Table 10

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 5-methyl and R^1 and R^2 correspond to one row in Table A

5 Table 11

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 6-methyl and R^1 and R^2 correspond to one row in Table A

Table 12

10 Compounds of formula I, in which X is chloro, $(R^3)_n$ is 4-methoxy and R^1 and R^2 correspond to one row in Table A

Table 13

15 Compounds of formula I, in which X is chloro, $(R^3)_n$ is 5-methoxy and R^1 and R^2 correspond to one row in Table A

Table 14

20 Compounds of formula I, in which X is chloro, $(R^3)_n$ is 6-methoxy and R^1 and R^2 correspond to one row in Table A

Table 15

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 4-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

25 Table 16

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 5-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 17

30 Compounds of formula I, in which X is chloro, $(R^3)_n$ is 6-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 18

35 Compounds of formula I, in which X is chloro, $(R^3)_n$ is 4,6-dimethyl and R^1 and R^2 correspond to one row in Table A

Table 19

40 Compounds of formula I, in which X is chloro, $(R^3)_n$ is 4-methoxy-6-methyl and R^1 and R^2 correspond to one row in Table A

Table 20

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 4-fluoro-6-methyl and R^1 and R^2 correspond to one row in Table A

12

Table 21

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 4-methoxycarbonyl and R^1 and R^2 correspond to one row in Table A

5 Table 22

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 4-cyano and R^1 and R^2 correspond to one row in Table A

Table 23

10 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-chloro and R^1 and R^2 correspond to one row in Table A

Table 24

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 5-chloro and
15 R^1 and R^2 correspond to one row in Table A

Table 25

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 6-chloro and
20 R^1 and R^2 correspond to one row in Table A

Table 26

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 3-fluoro and
 R^1 and R^2 correspond to one row in Table A

25 Table 27

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-fluoro and
 R^1 and R^2 correspond to one row in Table A

Table 28

30 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 5-fluoro and
 R^1 and R^2 correspond to one row in Table A

Table 29

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 6-fluoro and
35 R^1 and R^2 correspond to one row in Table A

Table 30

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 3-methyl and
 R^1 and R^2 correspond to one row in Table A

40

Table 31

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-methyl and
 R^1 and R^2 correspond to one row in Table A

45

Table 32

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 5-methyl and R^1 and R^2 correspond to one row in Table A

5 Table 33

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 6-methyl and R^1 and R^2 correspond to one row in Table A

Table 34

10 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-methoxy and R^1 and R^2 correspond to one row in Table A

Table 35

15 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 5-methoxy and R^1 and R^2 correspond to one row in Table A

Table 36

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 6-methoxy and R^1 and R^2 correspond to one row in Table A

20

Table 37

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

25 Table 38

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 5-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 39

30 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 6-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 40

35 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4,6-dimethyl and R^1 and R^2 correspond to one row in Table A

Table 41

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-methoxy-6-methyl and R^1 and R^2 correspond to one row in Table A

40

Table 42

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-fluoro-6-methyl and R^1 and R^2 correspond to one row in Table A

45

52

Table 43

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-methoxycarbonyl and R^1 and R^2 correspond to one row in Table A

5 Table 44

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-cyano and R^1 and R^2 correspond to one row in Table A

Table 45

10 Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-chloro and R^1 and R^2 correspond to one row in Table A

Table 46

15 Compounds of formula I, in which X is cyano, $(R^3)_n$ is 5-chloro and R^1 and R^2 correspond to one row in Table A

Table 47

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 6-chloro and R^1 and R^2 correspond to one row in Table A

20

Table 48

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 3-fluoro and R^1 and R^2 correspond to one row in Table A

25 Table 49

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-fluoro and R^1 and R^2 correspond to one row in Table A

Table 50

30 Compounds of formula I, in which X is cyano, $(R^3)_n$ is 5-fluoro and R^1 and R^2 correspond to one row in Table A

Table 51

35 Compounds of formula I, in which X is cyano, $(R^3)_n$ is 6-fluoro and R^1 and R^2 correspond to one row in Table A

Table 52

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 3-methyl and R^1 and R^2 correspond to one row in Table A

40

Table 53

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-methyl and R^1 and R^2 correspond to one row in Table A

45

Table 54

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 5-methyl and R^1 and R^2 correspond to one row in Table A

5 Table 55

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 6-methyl and R^1 and R^2 correspond to one row in Table A

Table 56

10 Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-methoxy and R^1 and R^2 correspond to one row in Table A

Table 57

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 5-methoxy
15 and R^1 and R^2 correspond to one row in Table A

Table 58

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 6-methoxy and R^1 and R^2 correspond to one row in Table A

20

Table 59

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

25 Table 60

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 5-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 61

30 Compounds of formula I, in which X is cyano, $(R^3)_n$ is 6-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 62

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4,6-dimethyl
35 and R^1 and R^2 correspond to one row in Table A

Table 63

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-methoxy-6-methyl and R^1 and R^2 correspond to one row in Table A

40

Table 64

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-fluoro-6-methyl and R^1 and R^2 correspond to one row in Table A

45

Table 65

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-methoxycarbonyl and R^1 and R^2 correspond to one row in Table A

5 Table 66

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-cyano and R^1 and R^2 correspond to one row in Table A

Table 67

10 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-chloro and R^1 and R^2 correspond to one row in Table A

Table 68

15 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 5-chloro and R^1 and R^2 correspond to one row in Table A

Table 69

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 6-chloro and R^1 and R^2 correspond to one row in Table A

20

Table 70

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 3-fluoro and R^1 and R^2 correspond to one row in Table A

25 Table 71

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-fluoro and R^1 and R^2 correspond to one row in Table A

Table 72

30 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 5-fluoro and R^1 and R^2 correspond to one row in Table A

Table 73

35 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 6-fluoro and R^1 and R^2 correspond to one row in Table A

Table 74

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 3-methyl and R^1 and R^2 correspond to one row in Table A

40

Table 75

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-methyl and R^1 and R^2 correspond to one row in Table A

45

Table 76

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 5-methyl and R^1 and R^2 correspond to one row in Table A

5 Table 77

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 6-methyl and R^1 and R^2 correspond to one row in Table A

Table 78

10 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-methoxy and R^1 and R^2 correspond to one row in Table A

Table 79

15 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 5-methoxy and R^1 and R^2 correspond to one row in Table A

Table 80

20 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 6-methoxy and R^1 and R^2 correspond to one row in Table A

Table 81

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

25 Table 82

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 5-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 83

30 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 6-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 84

35 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4,6-dimethyl and R^1 and R^2 correspond to one row in Table A

Table 85

40 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-methoxy-6-methyl and R^1 and R^2 correspond to one row in Table A

Table 86

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-fluoro-6-methyl and R^1 and R^2 correspond to one row in Table A

Table 87

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-methoxycarbonyl and R^1 and R^2 correspond to one row in Table A

5 Table 88

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-cyano and R^1 and R^2 correspond to one row in Table A

Table 89

10 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-chloro and R^1 and R^2 correspond to one row in Table A

Table 90

15 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 5-chloro and R^1 and R^2 correspond to one row in Table A

Table 91

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 6-chloro and R^1 and R^2 correspond to one row in Table A

20

Table 92

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 3-fluoro and R^1 and R^2 correspond to one row in Table A

25 Table 93

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-fluoro and R^1 and R^2 correspond to one row in Table A

Table 94

30 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 5-fluoro and R^1 and R^2 correspond to one row in Table A

Table 95

35 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 6-fluoro and R^1 and R^2 correspond to one row in Table A

Table 96

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 3-methyl and R^1 and R^2 correspond to one row in Table A

40

Table 97

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-methyl and R^1 and R^2 correspond to one row in Table A

45

5X

Table 98

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 5-methyl and R^1 and R^2 correspond to one row in Table A

5 Table 99

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 6-methyl and R^1 and R^2 correspond to one row in Table A

Table 100

10 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-methoxy and R^1 and R^2 correspond to one row in Table A

Table 101

15 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 5-methoxy and R^1 and R^2 correspond to one row in Table A

Table 102

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 6-methoxy and R^1 and R^2 correspond to one row in Table A

20

Table 103

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

25 Table 104

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 5-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 105

30 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 6-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 106

35 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4,6-dimethyl and R^1 and R^2 correspond to one row in Table A

Table 107

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-methoxy-6-methyl and R^1 and R^2 correspond to one row in Table A

40

Table 108

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-fluoro-6-methyl and R^1 and R^2 correspond to one row in Table A

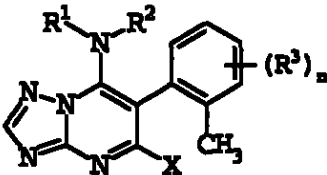
45

Table 109
Compounds of formula I, in which X is methyl, (R³)_n is 4-methoxycarbonyl and R¹ and R² correspond to one row in Table A

5 Table 110
Compounds of formula I, in which X is methyl, (R³)_n is 4-cyano and R¹ and R² correspond to one row in Table A

Table A

10



I

15

No.	R ¹	R ²
A-1	H	H
A-2	CH ₂ CH ₃	H
20 A-3	CH ₂ CH ₃	CH ₃
A-4	CH ₂ CH ₃	CH ₂ CH ₃
A-5	CH ₂ CF ₃	H
A-6	CH ₂ CF ₃	CH ₃
25 A-7	CH ₂ CF ₃	CH ₂ CH ₃
A-8	CH ₂ CCl ₃	H
A-9	CH ₂ CCl ₃	CH ₃
A-10	CH ₂ CCl ₃	CH ₂ CH ₃
30 A-11	CH ₂ CH ₂ CH ₃	H
A-12	CH ₂ CH ₂ CH ₃	CH ₃
A-13	CH ₂ CH ₂ CH ₃	CH ₂ CH ₃
A-14	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃
A-15	CH(CH ₃) ₂	H
35 A-16	CH(CH ₃) ₂	CH ₃
A-17	CH(CH ₃) ₂	CH ₂ CH ₃
A-18	(±) CH(CH ₃)-CH ₂ CH ₃	H
A-19	(±) CH(CH ₃)-CH ₂ CH ₃	CH ₃
40 A-20	(±) CH(CH ₃)-CH ₂ CH ₃	CH ₂ CH ₃
A-21	(S) CH(CH ₃)-CH ₂ CH ₃	H
A-22	(S) CH(CH ₃)-CH ₂ CH ₃	CH ₃
A-23	(S) CH(CH ₃)-CH ₂ CH ₃	CH ₂ CH ₃
45 A-24	(R) CH(CH ₃)-CH ₂ CH ₃	H
A-25	(R) CH(CH ₃)-CH ₂ CH ₃	CH ₃
A-26	(R) CH(CH ₃)-CH ₂ CH ₃	CH ₂ CH ₃

No.	R ¹	R ²
5	A-27 (±) CH(CH ₃)-CH(CH ₃) ₂	H
	A-28 (±) CH(CH ₃)-CH(CH ₃) ₂	CH ₃
	A-29 (±) CH(CH ₃)-CH(CH ₃) ₂	CH ₂ CH ₃
	A-30 (S) CH(CH ₃)-CH(CH ₃) ₂	H
	A-31 (S) CH(CH ₃)-CH(CH ₃) ₂	CH ₃
10	A-32 (S) CH(CH ₃)-CH(CH ₃) ₂	CH ₂ CH ₃
	A-33 (R) CH(CH ₃)-CH(CH ₃) ₂	H
	A-34 (R) CH(CH ₃)-CH(CH ₃) ₂	CH ₃
	A-35 (R) CH(CH ₃)-CH(CH ₃) ₂	CH ₂ CH ₃
	A-36 (±) CH(CH ₃)-C(CH ₃) ₃	H
15	A-37 (±) CH(CH ₃)-C(CH ₃) ₃	CH ₃
	A-38 (±) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
	A-39 (S) CH(CH ₃)-C(CH ₃) ₃	H
	A-40 (S) CH(CH ₃)-C(CH ₃) ₃	CH ₃
	A-41 (S) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
20	A-42 (R) CH(CH ₃)-C(CH ₃) ₃	H
	A-43 (R) CH(CH ₃)-C(CH ₃) ₃	CH ₃
	A-44 (R) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
	A-45 (±) CH(CH ₃)-CF ₃	H
	A-46 (±) CH(CH ₃)-CF ₃	CH ₃
25	A-47 (±) CH(CH ₃)-CF ₃	CH ₂ CH ₃
	A-48 (S) CH(CH ₃)-CF ₃	H
	A-49 (S) CH(CH ₃)-CF ₃	CH ₃
	A-50 (S) CH(CH ₃)-CF ₃	CH ₂ CH ₃
	A-51 (R) CH(CH ₃)-CF ₃	H
30	A-52 (R) CH(CH ₃)-CF ₃	CH ₃
	A-53 (R) CH(CH ₃)-CF ₃	CH ₂ CH ₃
	A-54 (±) CH(CH ₃)-CCl ₃	H
	A-55 (±) CH(CH ₃)-CCl ₃	CH ₃
	A-56 (±) CH(CH ₃)-CCl ₃	CH ₂ CH ₃
35	A-57 (S) CH(CH ₃)-CCl ₃	H
	A-58 (S) CH(CH ₃)-CCl ₃	CH ₃
	A-59 (S) CH(CH ₃)-CCl ₃	CH ₂ CH ₃
	A-60 (R) CH(CH ₃)-CCl ₃	H
	A-61 (R) CH(CH ₃)-CCl ₃	CH ₃
40	A-62 (R) CH(CH ₃)-CCl ₃	CH ₂ CH ₃
	A-63 CH ₂ C(CH ₃)=CH ₂	H
	A-64 CH ₂ C(CH ₃)=CH ₂	CH ₃
	A-65 CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃
	A-65 CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃

No.	R ¹	R ²
A-66	cyclopentyl	H
A-67	cyclopentyl	CH ₃
5 A-68	cyclopentyl	CH ₂ CH ₃
A-69	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -	
A-70	CH ₂ CF ₂ CF ₃	H
A-71	CH ₂ CF ₂ CF ₃	CH ₃
10 A-72	CH ₂ CF ₂ CF ₃	CH ₂ CH ₃
A-73	CH ₂ CF ₂ CF ₂ CF ₃	H
A-74	CH ₂ CF ₂ CF ₂ CF ₃	CH ₃
A-75	CH ₂ CF ₂ CF ₂ CF ₃	CH ₂ CH ₃

- 15 The compounds I are suitable as fungicides. They have outstanding activity against a broad spectrum of phytopathogenic fungi, in particular from the classes of the *Ascomycetes*, *Deuteromycetes*, *Phycomycetes* and *Basidiomycetes*. Some of them act systemically, and they can be employed in crop protection as foliar- and soil-
20 acting fungicides.

They are especially important for controlling a large number of fungi on a variety of crop plants such as wheat, rye, barley, oats, rice, maize, grass, bananas, cotton, soya, coffee, sugar
25 cane, grapevines, fruit species, ornamentals and vegetables such as cucumbers, beans, tomatoes, potatoes and cucurbits, and on the seeds of these plants.

Specifically, they are suitable for controlling the following
30 plant diseases:

- *Alternaria* species, *Podosphaera* species, *Sclerotinia* species, *Physalospora* canker on vegetables and fruit,
- *Botrytis cinerea* (gray mold) on strawberries, vegetables, ornamentals and grapevines,
- 35 • *Corynespora cassiicola* on cucumbers,
- *Colletotrichum* species on fruit and vegetables,
- *Diplocarpon rosae* on roses,
- *Elsinoe fawcetti* and *Diaporthe citri* on citrus fruit,
- *Sphaerotheca* species on cucurbits, strawberries and roses,
- 40 • *Cercospora* species on peanuts, sugar beets and aubergines,
- *Erysiphe cichoracearum* on cucurbits,
- *Leveillula taurica* on paprika, tomatoes and aubergines,
- *Mycosphaerella* species on apples and japanese apricot,
- *Phyllactinia kakicola*, *Gloesporium kaki* on japanese apricot,
- 45 • *Gymnosporangium yamadai*, *Leptothyrium pomi*, *Podosphaera leucotricha* and *Gloeodes pomigena* on apples,
- *Cladosporium carpophilum* on pears and japanese apricot,

23

- *Phomopsis* species on pears,
- *Phytophthora* species on citrus fruit, potatoes, onions, especially *Phytophthora infestans* on potatoes and tomatoes,
- *Blumeria graminis* (powdery mildew) on cereals,
- 5 • *Fusarium*- and *Verticillium* species on various plants,
- *Glomerella cingulata* on tee,
- *Drechslera*- and *Bipolaris* species on cereals and rice,
- *Mycosphaerella* species on bananas and peanuts,
- *Plasmopara viticola* on grapevines,
- 10 • *Personospora* species on onions, spinach and chrysanthemum,
- *Phaeoisariopsis vitis* and *Sphaceloma ampelina* on grapefruits,
- *Pseudocercospora herpotrichoides* on wheat and barley,
- *Pseudoperonospora* species on hop and cucumbers,
- *Puccinia* species and *Typhula* species on cereals and turf,
- 15 • *Pyricularia oryzae* on rice,
- *Rhizoctonia* species on cotton, rice and turf,
- *Stagonospora nodorum* and *Septoria tritici* on wheat,
- *Uncinula necator* on grapevines,
- *Ustilago* species on cereals and sugar cane, and
- 20 • *Venturia* species (scab) on apples and pears.

Moreover, the compounds I are suitable for controlling harmful fungi such as *Paecilomyces variotii* in the protection of materials (e.g. wood, paper, paint dispersions, fibers and tissues) and
25 in the protection of stored products.

The compounds I are applied by treating the fungi, or the plants, seeds, materials or the soil to be protected against fungal infection, with a fungicidally active amount of the active ingredients. Application can be effected both before and after infection of the materials, plants or seeds by the fungi.
30

In general, the fungicidal compositions comprise from 0.1 to 95, preferably 0.5 to 90, % by weight of active ingredient.
35

When used in crop protection, the rates of application are from 0.01 to 2.0 kg of active ingredient per ha, depending on the nature of the effect desired.

40 In the treatment of seed, amounts of active ingredient of from 0.001 to 0.1 g, preferably 0.01 to 0.05 g, are generally required per kilogram of seed.

When used in the protection of materials or stored products, the
45 rate of application of active ingredient depends on the nature of the field of application and on the effect desired. Rates of application conventionally used in the protection of materials are,

for example, from 0.001 g to 2 kg, preferably 0.005 g to 1 kg, of active ingredient per cubic meter of material treated.

The compounds I can be converted into the customary formulations, e.g. solutions, emulsions, suspensions, dusts, powders, pastes and granules. The use form depends on the particular purpose; in any case, it should guarantee a fine and uniform distribution of the compound according to the invention.

- 10 The formulations are prepared in a known manner, e.g. by extending the active ingredient with solvents and/or carriers, if desired using emulsifiers and dispersants, it also being possible to use other organic solvents as auxiliary solvents if water is used as the diluent. Auxiliaries which are suitable are essentially:
- 15 solvents such as aromatics (e.g. xylene), chlorinated aromatics (e.g. chlorobenzenes), paraffins (e.g. mineral oil fractions), alcohols (e.g. methanol, butanol), ketones (e.g. cyclohexanone), amines (e.g. ethanolamine, dimethylformamide) and water; carriers such as ground natural minerals (e.g. kaolins, clays, talc, chalk) and ground synthetic minerals (e.g. highly-disperse silica, silicates); emulsifiers such as non-ionic and anionic emulsifiers (e.g. polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates) and dispersants such as lignin-sulfite waste liquors and methylcellulose.
- 25 Suitable surfactants are alkali metal, alkaline earth metal and ammonium salts of lignosulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid, dibutyl-naphthalenesulfonic acid, alkylaryl-sulfonates, alkyl sulfates, alkylsulfonates, fatty alcohol sulfates and fatty acids and their alkali metal and alkaline earth metal salts, salts of sulfated fatty alcohol glycol ether, condensates of sulfonated naphthalene and naphthalene derivatives with formaldehyde, condensates of naphthalene or of naphthalenesulfonic acid with phenol or formaldehyde, polyoxyethylene octylphenyl
- 30 ether, ethoxylated isooctylphenol, octylphenol, nonylphenol, alkylphenol polyglycol ethers, tributylphenyl polyglycol ethers, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl alcohol
- 40 polyglycol ether acetal, sorbitol esters, lignin-sulfite waste liquors and methylcellulose.

Substances which are suitable for the preparation of directly sprayable solutions, emulsions, pastes or oil dispersions are mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, furthermore coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocar-

25

bons, e.g. benzene, toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes or their derivatives, methanol, ethanol, propanol, butanol, chloroform, carbon tetrachloride, cyclohexanol, cyclohexanone, chlorobenzene, isophorone, strongly
5 polar solvents, e.g. dimethylformamide, dimethyl sulfoxide, N-methylpyrrolidone and water.

Powders, materials for scattering and dusts can be prepared by mixing or concomitantly grinding the active substances with a solid
10 carrier.

Granules, e.g. coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active ingredients to solid carriers. Examples of solid carriers are mineral earths,
15 such as silicas, silica gels, silicates, talc, kaolin, attaclay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers, e.g. ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable
20 origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders and other solid carriers.

In general, the formulations comprise of from 0.01 to 95% by weight, preferably from 0.1 to 90% by weight, of the active ingredient. The active ingredients are employed in a purity of from
25 90% to 100%, preferably 95% to 100% (according to NMR spectrum).

The following are exemplary formulations:

30 I. 5 parts by weight of a compound according to the invention are mixed intimately with 95 parts by weight of finely divided kaolin. This gives a dust which comprises 5% by weight of the active ingredient.

35 II. 30 parts by weight of a compound according to the invention are mixed intimately with a mixture of 92 parts by weight of pulverulent silica gel and 8 parts by weight of paraffin oil which had been sprayed onto the surface of this silica gel. This gives a formulation of the active ingredient with good
40 adhesion properties (comprises 23% by weight of active ingredient).

III. 10 parts by weight of a compound according to the invention are dissolved in a mixture composed of 90 parts by weight of xylene, 6 parts by weight of the adduct of 8 to 10 mol of
45 ethylene oxide and 1 mol of oleic acid N-monoethanolamide, 2 parts by weight of calcium dodecylbenzenesulfonate and 2

26

parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil (comprises 9% by weight of active ingredient).

- 5 IV. 20 parts by weight of a compound according to the invention are dissolved in a mixture composed of 60 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 5 parts by weight of the adduct of 7 mol of ethylene oxide and 1 mol of isooctylphenol and 5 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil (comprises 16% by weight of active ingredient).
- 10
- V. 80 parts by weight of a compound according to the invention are mixed thoroughly with 3 parts by weight of sodium diisobutylnaphthalene- α -sulfonate, 10 parts by weight of the sodium salt of a lignosulfonic acid from a sulfite waste liquor and 7 parts by weight of pulverulent silica gel, and the mixture is ground in a hammer mill (comprises 80% by weight of active ingredient).
- 15
- 20
- VI. 90 parts by weight of a compound according to the invention are mixed with 10 parts by weight of N-methyl- α -pyrrolidone, which gives a solution which is suitable for use in the form of microdrops (comprises 90% by weight of active ingredient).
- 25
- VII. 20 parts by weight of a compound according to the invention are dissolved in a mixture composed of 40 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 20 parts by weight of the adduct of 7 mol of ethylene oxide and 1 mol of isooctylphenol and 10 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil. Pouring the solution into 100,000 parts by weight of water and finely distributing it therein gives an aqueous dispersion which comprises 0.02% by weight of the active ingredient.
- 30
- 35
- VIII. 20 parts by weight of a compound according to the invention are mixed thoroughly with 3 parts by weight of sodium diisobutylnaphthalene- α -sulfonate, 17 parts by weight of the sodium salt of a lignosulfonic acid from a sulfite waste liquor and 60 parts by weight of pulverulent silica gel, and the mixture is ground in a hammer mill. Finely distributing the mixture in 20,000 parts by weight of water gives a spray mixture which comprises 0.1% by weight of the active ingredient.
- 40
- 45

The active ingredients can be used as such, in the form of their formulations or the use forms prepared therefrom, e.g. in the form of directly sprayable solutions, powders, suspensions or dispersions, emulsions, oil dispersions, pastes, dusts, materials for spreading, or granules, by means of spraying, atomizing, dusting, scattering or pouring. The use forms depend entirely on the intended purposes; in any case, this is intended to guarantee the finest possible distribution of the active ingredients according to the invention.

10

Aqueous use forms can be prepared from emulsion concentrates, pastes or wettable powders (sprayable powders, oil dispersions) by adding water. To prepare emulsions, pastes or oil dispersions, the substances as such or dissolved in an oil or solvent, can be homogenized in water by means of wetter, tackifier, dispersant or emulsifier. Alternatively, it is possible to prepare concentrates composed of active substance, wetter, tackifier, dispersant or emulsifier and, if appropriate, solvent or oil, and such concentrates are suitable for dilution with water.

20

The active ingredient concentrations in the ready-to-use products can be varied within substantial ranges. In general, they are from 0.0001 to 10%, preferably from 0.01 to 1%.

25 The active ingredients may also be used successfully in the ultra-low-volume process (ULV), it being possible to apply formulations comprising over 95% by weight of active ingredient, or even the active ingredient without additives.

30 Various types of oils, herbicides, fungicides, other pesticides, or bactericides may be added to the active ingredients, if appropriate also only immediately prior to use (tank mix). These agents can be admixed with the agents according to the invention in a weight ratio of 1:10 to 10:1.

35

In the use form as fungicides, the compositions according to the invention can also be present together with other active ingredients, e.g. with herbicides, insecticides, growth regulators, fungicides or else with fertilizers. Mixing the compounds I or the compositions comprising them in the use form as fungicides with other fungicides frequently results in a broader fungicidal spectrum of action.

45 The following list of fungicides, together with which the compounds according to the invention can be used, is intended to illustrate the possible combinations, but not to impose any limitation:

- sulfur, dithiocarbamates and their derivatives; such as iron(III) dimethyldithiocarbamate, zinc dimethyldithiocarbamate, zinc ethylenebisdithiocarbamate, manganese ethylenebisdithiocarbamate, manganese zinc ethylenediaminebisdithiocarbamate, tetramethylthiuram disulfide, ammonia complex of zinc (N,N-ethylenebisdithiocarbamate), ammonia complex of zinc (N,N'-propylenebisdithiocarbamate), zinc (N,N'-propylenebisdithiocarbamate), N,N'-polypropylenebis(thiocarbamoyl)disulfide;
- nitro derivatives, such as dinitro(1-methylheptyl)phenyl crotonate, 2-sec-butyl-4,6-dinitrophenyl 3,3-dimethylacrylate, 2-sec-butyl-4,6-dinitrophenylisopropyl carbonate, diisopropyl 5-nitro-isophthalate;
- heterocyclic substances, such as 2-heptadecyl-2-imidazoline acetate, 2,4-dichloro-6-(o-chloroanilino)-s-triazine, 0,0-diethyl phthalimidophosphonothioate, 5-amino-1-[bis(dimethylamino)phosphinyl]-3-phenyl-1,2,4-triazole, 2,3-dicyano-1,4-dithioanthraquinone, 2-thio-1,3-dithiolo[4,5-b]quinoxaline, methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate, 2-methoxycarbonylaminobenzimidazole, 2-(2-furyl)benzimidazole, 2-(4-thiazolyl)benzimidazole, N-(1,1,2,2-tetrachloroethylthio)tetrahydrophthalimide, N-trichloromethylthiotetrahydrophthalimide, N-trichloromethylthiophthalimide, 5-Chloro-2-cyano-4-p-tolyl-imidazole-1-sulfonic acid dimethylamide, N-dichlorofluoromethylthio-N',N'-dimethyl-N-phenylsulfo-diamide, 5-ethoxy-3-trichloromethyl-1,2,3-thiadiazole, 2-thiocyanatomethylthiobenzothiazole, 1,4-dichloro-2,5-dimethoxybenzene, 4-(2-chlorophenylhydrazono)-3-methyl-5-isoxazolone, pyridine-2-thiol 1-oxide, 8-hydroxyquinoline or its copper salt, 2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiine, 2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiine 4,4-dioxide, 2-methyl-5,6-dihydro-4H-pyran-3-carboxanilide, 2-methylfuran-3-carboxanilide, 2,5-dimethylfuran-3-carboxanilide, 2-Chloro-N-(4'-chloro-biphenyl-2-yl)-nicotinamide, 2,4,5-trimethylfuran-3-carboxanilide, N-cyclohexyl-2,5-dimethylfuran-3-carboxamide, N-cyclohexyl-N-methoxy-2,5-dimethylfuran-3-carboxamide, 2-methylbenzanilide, 2-iodobenzanilide, N-formyl-N-morpholine-2,2,2-trichloroethyl acetal, piperazine-1,4-diylbis-1-(2,2,2-trichloroethyl)formamide, 1-(3,4-dichloroanilino)-1-formylamino-2,2,2-trichloroethane; 2,6-dimethyl-N-tridecylmorpholine or its salts, 2,6-dimethyl-N-cyclododecylmorpholine or its salts, N-[3-(p-tert-butylphenyl)-2-methylpropyl]-cis-2,6-dimethyl-morpholine, N-[3-(p-tert-butylphenyl)-2-methylpropyl]-piperidine, 1-[2-(2,4-dichlorophenyl)-4-ethyl-1,3-dioxolan-2-yl-ethyl]-1H-1,2,4-triazole, 1-[2-(2,4-dichlorophenyl)-4-n-propyl-1,3-dioxolan-2-yl-ethyl]-1H-1,2,4-triazole,

N-(n-propyl)-N-(2,4,6-trichlorophenoxyethyl)-N'-imidazo-
 lyl-urea, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-tri-
 azol-1-yl)-2-butanone, 1-(4-chlorophenoxy)-3,3-dimethyl-
 1-(1H-1,2,4-triazol-1-yl)-2-butanol, (2RS,3RS)-1-[3-(2-chlo-
 5 rophenyl)-2-(4-fluorophenyl)-oxiran-2-ylmethyl]-1H-1,2,4-tri-
 azole, α -(2-chlorophenyl)- α -(4-chlorophenyl)-5-pyrimidineme-
 thanol, 5-butyl-2-dimethylamino-4-hydroxy-6-methylpyrimidine,
 bis(p-chlorophenyl)-3-pyridinemethanol, 1,2-bis(3-ethoxycar-
 10 bonyl-2-thioureido)benzene, 1,2-bis(3-methoxycarbonyl-2-thio-
 ureido)benzene,
 strobilurines such as azoxystrobin, kresoxim methyl,
 methyl-E-methoxyimino-[α -(2-phenoxyphenyl)]-acetamide, methyl
 E-methoxyimino-[α -(2,5-dimethylphenoxy)-o-tolyl]acetamide,
 15 picoxystrobin, pyraclostrobin, trifloxystrobin,
 anilinopyrimidines such as N-(4,6-dimethylpyrimidin-2-yl)an-
 iline, N-[4-methyl-6-(1-propynyl)pyrimidin-2-yl]-aniline,
 N-[4-methyl-6-cyclopropylpyrimidin-2-yl]aniline,
 phenylpyrroles such as 4-(2,2-difluoro-1,3-benzodioxol-4-
 20 yl)pyrrole-3-carbonitrile,
 cinnamamides such as 3-(4-chlorophenyl)-3-(3,4-dimethoxy-
 phenyl)acryloylmorpholine, 3-(4-fluorophenyl)-3-(3,4-di-
 methoxy-phenyl)acryloylmorpholine,
 and a variety of fungicides such as dodecylguanidine acetate,
 25 3-[3-(3,5-dimethyl-2-oxycyclohexyl)-2-hydroxyethyl]glutar-
 imide, hexachlorobenzene, methyl N-(2,6-dimethylphe-
 nyl)-N-(2-furoyl)-DL-alaninate, DL-N-(2,6-dimethylphe-
 nyl)-N-(2'-methoxyacetyl)-alanine methyl ester, N-(2,6-dime-
 thylphenyl)-N-chloroacetyl-D,L-2-amino- butyrolactone,
 30 DL-N-(2,6-dimethylphenyl)-N-(phenylacetyl)alanine methyl
 ester, 5-methyl-5-vinyl-3-(3,5-dichlorophenyl)-2,4-di-
 oxo-1,3-oxazolidine, 3-[3,5-dichlorophenyl(5-methyl-5-me-
 thoxymethyl)-1,3-oxazolidine-2,4-dione, 3-(3,5-dichlorophe-
 nyl)-1-isopropylcarbamoylethylhydantoin, N-(3,5-dichlorophe-
 35 nyl)-1,2-dimethylcyclopropane-1,2-dicarboximide, 2-cya-
 no-[N-(ethylaminocarbonyl)-2-methoximino]acetamide,
 3,5-Dichloro-N-(3-chloro-1-ethyl-1-methyl-2-oxo-propyl)-4-
 methyl-benzamide, 1-(3-Bromo-6-methoxy-2-methyl-phenyl)-
 1-(2,3,4-trimethoxy-6-methyl-phenyl)-methanone, 1-[2-(2,4-di-
 40 chloro-phenyl)pentyl]-1H-1,2,4-triazole, 2,4-difluoro-
 α -(1H-1,2,4-triazolyl-1-methyl)benzhydryl alcohol, N-(3-chlo-
 ro-2,6-dinitro-4-trifluoromethylphenyl)-5-trifluorome-
 thyl-3-chloro-2-aminopyridine, 1-((bis(4-fluorophenyl)methyl-
 silyl)methyl)-1H-1,2,4-triazole.

Synthesis Examples

With due modification of the starting compounds, the protocols shown in the synthesis examples below were used for obtaining 5 further compounds I. The resulting compounds I, together with physical data, are listed in Table I which follows.

Example 1 Preparation of diethyl (2-fluoro-6-methylphenyl)-malonate

10

Diethyl malonate (0.49 mol) was added to a mixture of sodium hydride (0.51 mol) and 1,4-dioxane (140 ml) at 60°C within 2 hours. The mixture was stirred for 10 minutes at 60°C and copper (I) bromide (0.05 mol) was added. After 15 minutes, a solution of 15 2-bromo-3-fluorotoluene (0.25 mol) in 10 ml 1,4-dioxane was added. The reaction mixture was kept at 100°C for about 15 hours and after cooling to about 15°C 35 ml of 12N Hydrochloric acid were added. The precipitate was filtered off, the filtrate was extracted with diethyl ether. The organic phase was separated, 20 dried and filtered. The filtrate was evaporated to yield 42 g of the title compound.

Example 2 Preparation of 5,7-dihydroxy-6-(2-fluoro-6-methylphenyl)-[1,2,4]-triazolo-[1,5-a]pyrimidine

25

A mixture of 3-amino-1,2,4-triazole (14 g), diethyl (2-fluoro-6-methylphenyl)-malonate (0.17 mol, Ex. 1) and tributylamine (50 ml) is heated at 180°C for six hours; after cooling to 70°C a solution of 21g sodium hydroxide in 200 ml water was 30 added and the reaction mixture was stirred for 30 minutes. The organic phase was separated off and the aqueous phase was extracted with diethyl ether. The aqueous phase was acidified with concentrated hydrochloric acid. The precipitate was collected by filtration and dried to yield 41 g of the title compound.

35

Example 3 Preparation of 5,7-dichloro-6-(2-fluoro-6-methylphenyl)-[1,2,4]-triazolo-[1,5-a]pyrimidine

A mixture of the compound from Ex. 2 (30 g) and phosphorous oxy- 40 chloride (50 ml) was refluxed for eight hours. Phosphorous oxychloride was partly distilled off. The residue was poured into a mixture of dichloromethane and water. The organic layer was separated, dried and filtered. The filtrate was concentrated in vacuo to yield 27 g of the title compound of mp. 130°C.

45

31

Example 4 Preparation of 5-chloro-6-(2-fluoro-6-methylphenyl)-7-isopropylamino-[1,2,4]-triazolo[1,5-a]pyrimidine [I-8]

5 A mixture of isopropylamine (1.5 mmol), triethylamine (1.5 mmol) and dichloromethane (10 ml) was added to a solution of 1.5 mmol of the product from Ex. 3 in 20 ml dichloromethane under stirring. The reaction mixture was stirred for about 16 hours at about 20 to 25°C and subsequently washed with 5 % hydrochloric
10 acid. The organic layer was separated, dried and filtered. The filtrate was evaporated and the residue was chromatographed to yield 0.46 g of the title compound of mp. 128°C.

Example 5 Preparation of 5-cyano-6-(2-fluoro-6-methylphenyl)-7-(4-methylpiperidin-1-yl)-[1,2,4]-triazolo[1,5-a]pyrimidine [I-49]
15

A mixture of 0.1 mol compound I-9 and tetraethylammonium cyanide (0.25 mol) in 750 ml Dimethylformamide (DMF) was stirred for
20 16 hours at about 20 to 25°C. To this mixture was added water and methyl-tert.butyl ether (MTBE), the organic phase was separated, washed with water, dried and filtered. The filtrate was evaporated and the residue was chromatographed to yield 6.51 g of the title compound of mp. 211°C.

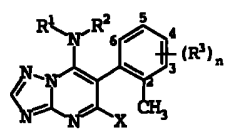
25 Example 6 Preparation of 5-methoxy-6-(2-fluoro-6-methylphenyl)-7-(4-methylpiperidin-1-yl)-[1,2,4]-triazolo[1,5-a]pyrimidine [I-50]

30 After having added a solution of sodium methanolate (30%, 71.5 mmol) to a solution of 65 mmol of compound I-9 in 400 ml dry methanol was added this mixture was stirred for about 16 hours at about 20 to 25°C. Methanol was evaporated and the residue was dissolved with dichloromethane. The organic phase was washed with
35 water, dried and filtered. The filtrate was evaporated and the residue was chromatographed to yield 4.32 g of the title compound of mp. 142°C.

40

45

Table I



I

No.	R ¹	R ²	(R ³) _n	X	phys. data
					(m.p. [°C]; ¹ H-NMR δ [ppm])
I-1	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	4, 6-(CH ₃) ₂	Cl	131
I-2	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		4, 6-(CH ₃) ₂	Cl	138
I-3	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	4-OCH ₃ -6-CH ₃	Cl	74
I-4	(±) CH(CH ₃)-CH(CH ₃) ₃	H	4-OCH ₃ -6-CH ₃	Cl	163
I-5	CH ₂ CF ₃	H	4-OCH ₃ -6-CH ₃	Cl	191
I-6	H	H	6-F	Cl	250
I-7	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	6-F	Cl	124
I-8	CH(CH ₃) ₂	H	6-F	Cl	128
I-9	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		6-F	Cl	142
I-10	cyclopentyl	H	6-F	Cl	159
I-11	CH ₂ CH ₃	CH ₂ CH ₃	6-F	Cl	147
I-12	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃	6-F	Cl	124
I-13	CH(CH ₃) ₂	CH ₃	6-F	Cl	159

32

78

No.	R ¹	R ²	(R ³) _n	X	phys. data
					(m.p. [°C], ¹ H-NMR δ [ppm])
I-14	(±) CH(CH ₃)-CH ₂ CH ₃	H	6-F	Cl	115
I-15	(S) CH(CH ₃)-CH ₂ CH ₃	H	6-F	Cl	123
I-16	(R) CH(CH ₃)-CH ₂ CH ₃	H	6-F	Cl	129
I-17	(±) CH(CH ₃)-CH(CH ₃) ₂	H	6-F	Cl	A) 133 / B) 138
I-18	(S) CH(CH ₃)-CH(CH ₃) ₂	H	6-F	Cl	A) 120 / B) 130
I-19	(R) CH(CH ₃)-CH(CH ₃) ₂	H	6-F	Cl	A) 119 / B) 131
I-20	(±) CH(CH ₃)-CH(CH ₃) ₃	H	6-F	Cl	A) 148 / B) 174
I-21	(S) CH(CH ₃)-CH(CH ₃) ₃	H	6-F	Cl	A) 160 / B) 203
I-22	(R) CH(CH ₃)-CH(CH ₃) ₃	H	6-F	Cl	A) 159 / B) 203
I-23	(±) CH(CH ₃)-CF ₃	H	6-F	Cl	A) 149 / B) 56
I-24	(S) CH(CH ₃)-CF ₃	H	6-F	Cl	A) 166 / B) 70
I-25	(R) CH(CH ₃)-CF ₃	H	6-F	Cl	A) 167 / B) 70
I-26	CH ₂ CF ₃	H	6-F	Cl	173
I-27	H	H	4-F	Cl	281
I-28	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	4-F	Cl	115
I-29	CH(CH ₃) ₂	H	4-F	Cl	94
I-30	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		4-F	Cl	168
I-31	cyclopentyl	H	4-F	Cl	141
I-32	CH ₂ CH ₃	CH ₂ CH ₃	4-F	Cl	156
I-33	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃	4-F	Cl	121

23

No.	R ¹	R ²	(R ³) _n	X	phys. data (m.p. [°C], ¹ H-NMR δ [ppm])
I-34	CH(CH ₃) ₂	CH ₃	4-F	Cl	153
I-35	(±) CH(CH ₃)-CH ₂ CH ₃	H	4-F	Cl	118
I-36	(S) CH(CH ₃)-CH ₂ CH ₃	H	4-F	Cl	125
I-37	(R) CH(CH ₃)-CH ₂ CH ₃	H	4-F	Cl	126
I-38	(±) CH(CH ₃)-CH(CH ₃) ₂	H	4-F	Cl	132
I-39	(S) CH(CH ₃)-CH(CH ₃) ₂	H	4-F	Cl	124
I-40	(R) CH(CH ₃)-CH(CH ₃) ₂	H	4-F	Cl	124
I-41	(±) CH(CH ₃)-CH(CH ₃) ₃	H	4-F	Cl	162
I-42	(S) CH(CH ₃)-CH(CH ₃) ₃	H	4-F	Cl	156
I-43	(R) CH(CH ₃)-CH(CH ₃) ₃	H	4-F	Cl	156
I-44	(±) CH(CH ₃)-CF ₃	H	4-F	Cl	163
I-45	(S) CH(CH ₃)-CF ₃	H	4-F	Cl	145
I-46	(R) CH(CH ₃)-CF ₃	H	4-F	Cl	145
I-47	CH ₂ CF ₃	H	4-F	Cl	167
I-48	CH ₂ CF ₃	H	4-F-6-CH ₃	Cl	220
I-49	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		6-F	CN	211
I-50	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		6-F	OCH ₃	142
I-51	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		6-F	CH ₃	145
I-52	cyclopentyl	H	4,6-(CH ₃) ₂	Cl	200
I-53	CH ₂ CH ₃	CH ₂ CH ₃	4,6-(CH ₃) ₂	Cl	105

No.	R ¹	R ²	(R ³) _n	X	phys. data
					(m.p. [°C]; ¹ H-NMR δ [ppm])
I-54	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃	4, 6-(CH ₃) ₂	Cl	99
I-55	(±) CH(CH ₃)-CH ₂ CH ₃	H	4, 6-(CH ₃) ₂	Cl	191
I-56	(S) CH(CH ₃)-CH ₂ CH ₃	H	4, 6-(CH ₃) ₂	Cl	184
I-57	(R) CH(CH ₃)-CH ₂ CH ₃	H	4, 6-(CH ₃) ₂	Cl	184
I-58	(±) CH(CH ₃)-CH(CH ₃) ₂	H	4, 6-(CH ₃) ₂	Cl	107
I-59	(S) CH(CH ₃)-CH(CH ₃) ₂	H	4, 6-(CH ₃) ₂	Cl	87
I-60	(R) CH(CH ₃)-CH(CH ₃) ₂	H	4, 6-(CH ₃) ₂	Cl	87
I-61	(±) CH(CH ₃)-CH(CH ₃) ₃	H	4, 6-(CH ₃) ₂	Cl	79
I-62	(S) CH(CH ₃)-CH(CH ₃) ₃	H	4, 6-(CH ₃) ₂	Cl	81
I-63	(R) CH(CH ₃)-CH(CH ₃) ₃	H	4, 6-(CH ₃) ₂	Cl	81
I-64	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	4-Cl	Cl	137
I-65	CH(CH ₃) ₂	H	4-Cl	Cl	136
I-66	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		4-Cl	Cl	173
I-67	cyclopentyl	H	4-Cl	Cl	147
I-68	CH ₂ CH ₃	CH ₂ CH ₃	4-Cl	Cl	167
I-69	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃	4-Cl	Cl	149
I-70	CH(CH ₃) ₂	CH ₃	4-Cl	Cl	159
I-71	(±) CH(CH ₃)-CH ₂ CH ₃	H	4-Cl	Cl	128
I-72	(S) CH(CH ₃)-CH ₂ CH ₃	H	4-Cl	Cl	114
I-73	(R) CH(CH ₃)-CH ₂ CH ₃	H	4-Cl	Cl	114

No.	R ¹	R ²	(R ³) ₂	X	phys. data (m.p. [°C], ¹ H-NMR δ [ppm])
I-74	(±) CH(CH ₃)-CH(CH ₃) ₂	H	4-Cl	Cl	116
I-75	(S) CH(CH ₃)-CH(CH ₃) ₂	H	4-Cl	Cl	130
I-76	(R) CH(CH ₃)-CH(CH ₃) ₂	H	4-Cl	Cl	130
I-77	(±) CH(CH ₃)-CH(CH ₃) ₃	H	4-Cl	Cl	159
I-78	(S) CH(CH ₃)-CH(CH ₃) ₃	H	4-Cl	Cl	159
I-79	(R) CH(CH ₃)-CH(CH ₃) ₃	H	4-Cl	Cl	159
I-80	(±) CH(CH ₃)-CF ₃	H	4-Cl	Cl	184
I-81	(S) CH(CH ₃)-CF ₃	H	4-Cl	Cl	143
I-82	(R) CH(CH ₃)-CF ₃	H	4-Cl	Cl	143
I-83	CH ₂ CF ₃	H	4-Cl	Cl	206
I-84	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	4-CH ₃	Cl	158
I-85	CH(CH ₃) ₂	H	4-CH ₃	Cl	145
I-86	CH ₂ CH ₃	CH ₂ CH ₃	4-CH ₃	Cl	141
I-87	(±) CH(CH ₃)-CH ₂ CH ₃	H	4-CH ₃	Cl	122
I-88	(S) CH(CH ₃)-CH(CH ₃) ₃	H	4-CH ₃	Cl	108
I-89	(R) CH(CH ₃)-CH(CH ₃) ₃	H	4-CH ₃	Cl	108
I-90	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		4-COOCH ₃	Cl	8.45(s); 8.05(s); 7.95(d); 7.25(d); 4.0(s); 3.85(d); 3.45(d); 2.7(t); 2.65(t); 2.25(s); 1.55(m); 1.45(m); 1.25(m); 0.9(d)

36

No.	R ¹	R ²	(R ³) _n	X	phys. data
					(m.p. [°C], ¹ H-NMR δ [ppm])
I-91	(R) CH(CH ₃)-CH(CH ₃) ₂	H	4-COOCH ₃	Cl	8.35(s); 8.1(s); 8.0(d); 7.35(d); 6.2(m); 3.95(s); 3.1(m); 2.25(s); 1.55(sept); 1.2(d); 0.95(d); 0.9(d)
I-92	(S) CH(CH ₃)-CF ₃	H	4-COOCH ₃	Cl	8.4(s); 8.15(s); 8.05(d); 7.35(m); 5.7(m); 4.6(m); 3.95(s); 2.3(s); 2.25(s); 1.4(d); 1.3(d)
I-93	CH ₂ CF ₂ CF ₃	H	6-F	Cl	162
I-94	CH ₂ CF ₂ CF ₂ CF ₃	H	6-F	Cl	165
I-95	CH ₂ CF ₂ CF ₃	H	4-F	Cl	176
I-96	CH ₂ CF ₂ CF ₂ CF ₃	H	4-F	Cl	138
I-97	CH ₂ CF ₂ CF ₃	H	4-Cl	Cl	164
I-98	CH ₂ CF ₂ CF ₂ CF ₃	H	4-Cl	Cl	126
I-99	H	H	4-Cl	Cl	276

37

In some cases of chiral groups R¹ and due to the hindered rotation of the phenyl group two diastereomers A) and B) exist which may differ in their physical properties.

Examples of the action against harmful fungi

The fungicidal action of the compounds of the formula I was demonstrated by the following experiments:

The active compounds, separately or together, were formulated as a 10% emulsion in a mixture of 70% by weight of cyclohexanone, 20% by weight of Nekanil® LN (Lutensol® AP6, wetting agent having emulsifying and dispersant action based on ethoxylated alkylphenols) and 10% by weight of Wettol® EM (nonionic emulsifier based on ethoxylated castor oil) and diluted with water to the desired concentration.

Compound A known from WO-A 98/46608 (No. 9) served as comparative active compound:



Comparison trial 1 - Fungicidal control of early blight on tomatoes (*Alternaria solani*)

Young seedlings of tomato plants of the variety "Große Fleischtomate St. Pierre" were grown in pots to the 2 to 4 leaf stage. These plants were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient mentioned in the table below, prepared from a stock solution containing 10 % of the active ingredient, 85 % cyclohexanone and 5 % emulsifier. The next day, the treated plants were inoculated with an aqueous suspension of *Alternaria solani* containing 0.2×10^6 spores per ml. Then the trial plants were immediately transferred to a humid chamber. After 6 days at 20 to 23°C and a relative humidity close to 100 %, the extent of fungal attack on the leaves was visually assessed as % diseased leaf area.

In this test, the plants which had been treated with 63 ppm of compounds I-23 and I-24, resp., showed an infection of not more than 3%, whereas the the plants treated with 63 ppm of the comparison compound A were infected to 15%, and the untreated plants were infected to 90%.

39

Comparison trial 2 - Fungicidal control of powdery mildew on wheat caused by *Blumeria graminis* f. sp. *tritici*

The first fully developed leaves of pot grown wheat of the variety "Kanzler" were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient or their mixture mentioned in the table below, prepared from a stock solution containing 10 % of the active ingredient, 85 % cyclohexanone and 5 % emulsifier. The next day the treated plants were inoculated with spores of *Blumeria graminis* f. sp. *tritici* by shaking heavily infested stock plants over the treated pots. After cultivation in the greenhouse for 7 days at 22-26°C and a relative humidity between 60 to 90 % the extent of fungal attack on the leaves was visually assessed as % diseased leaf area.

15

In this test, the plants which had been treated with 63 ppm of compounds I-23 and I-24, resp., showed an infection of not more than 3%, whereas the the plants treated with 63 ppm of the comparison compound A were infected to 30%, and the untreated plants were infected to 85%.

20

Comparison trial 3 - Fungicidal control of grape downy mildew (*Plasmopara viticola*)

Grape cuttings of the cultivar "Müller-Thurgau" were grown in pots to the 4 to 5 leaf stage. These plants were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient or their mixture mentioned in the table below, prepared from a stock solution containing 10 % of the active ingredient, 85 % cyclohexanone and 5 % emulsifier. The plants were allowed to air-dry. The next day they were inoculated with an aqueous spore suspension of *Plasmopara viticola* by spraying it at the lower leaf-side. Then the trial plants were immediately transferred for 24 h to a humid chamber with 22 - 24°C and a relative humidity close to 100 %. For a period of 5 days, cultivation followed in a greenhouse at 20 - 25°C and a relative humidity about 50-80 %. To stimulate the outbreak of the disease symptoms, the plants were transferred to a humid chamber again for 24 hours. Then the extent of fungal attack on the lower leaf surface was visually assessed as % diseased leaf area.

25

In this test, the plants which had been treated with 250 ppm of compounds I-23 and I-24, resp., showed an infection of not more than 7%, whereas the the plants treated with 250 ppm of the comparison compound A, and the untreated plants were infected to 80%.

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Use Example 1 - Fungicidal control of early blight on tomatoes (*Alternaria solani*)

The test was conducted as described in Comparison trial 1.

5

In this test, the plants which have been treated with 250 ppm of compounds I-7, I-9, I-10, I-28, I-30, I-35, I-38, I-41, I-44, I-66, and I-83, resp., showed no infection, whereas the untreated plants were infected to 90%.

10

Use Example 2 - Fungicidal control of powdery mildew on wheat caused by *Blumeria graminis* f. sp. *tritici*

The test was conducted as described in Comparison trial 2.

15

In this test, the plants which have been treated with 250 ppm of compounds I-14, I-28, I-30, I-35, I-38, I-41, and I-44, resp., showed an infection of not more than 5%, whereas the untreated plants were infected to 85%.

20

Use Example 3 - Fungicidal control of grape downy mildew (*Plasmopara viticola*)

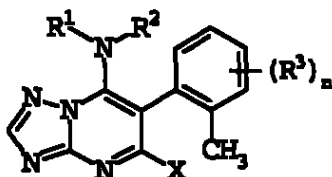
Leaves of potted vines of the "Müller Thurgau" variety were
25 sprayed with aqueous liquors made from a stock solution consisting of 10% of active ingredient, 85% of cyclohexanone, and 5% of emulsifier. To assess the duration of action, the plants were set up, after the sprayed-on layer had dried, in the greenhouse for 8 days. Then the leaves were infected with a zoospore suspension of the fungus *Plasmopara viticola*, first placed in a vapour-saturated chamber at 24°C, and then kept for 5 days in a greenhouse at 20 to 30°C. To accelerate and intensify the sporangio-
30 phore discharge, the plants were then again placed in the moist chamber for 16 hours. The extent of fungus attack was then assessed on the undersides of the leaves.
35

In this test, the plants which have been treated with 250 ppm of compounds I-7, I-9, I-10, I-35, I-38, and I-44, resp., showed an infection of 3 to 40%, whereas the untreated plants were infected
40 to 80%.

45

Claims:

1. Substituted 6-(2-tolyl)-triazolopyrimidines of formula I



I

in which

R^1 and R^2 independently denote hydrogen or

C_1 - C_{10} -alkyl, C_2 - C_{10} -alkenyl, C_2 - C_{10} -alkynyl, or C_4 - C_{10} -alkadienyl, C_1 - C_{10} -haloalkyl, C_2 - C_{10} -haloalkenyl, C_3 - C_{10} -cycloalkyl, phenyl, naphthyl, or

C_3 - C_{10} -cycloalkyl, phenyl, naphthyl, or

5- or 6-membered heterocyclyl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or

5- or 6-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or

where R^1 and R^2 radicals may be unsubstituted or partly or fully halogenated or may carry one to three groups R^a ,

R^a is cyano, nitro, hydroxyl, C_1 - C_6 -alkyl, C_1 - C_6 -haloalkyl, C_3 - C_6 -cycloalkyl, C_1 - C_6 -alkoxy, C_1 - C_6 -haloalkoxy, C_1 - C_6 -alkylthio, C_1 - C_6 -alkylamino, di- C_1 - C_6 -alkylamino, C_2 - C_6 -alkenyl, C_2 - C_6 -alkenyloxy, C_2 - C_6 -alkynyl, C_3 - C_6 -alkynyloxy and C_1 - C_4 -alkylenedioxy; or

R^1 and R^2 together with the interjacent nitrogen atom represent a 5- or 6-membered heterocyclic ring, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, which may be substituted by one to three R^a radicals;

R^3 is halogen, cyano, C_1 - C_{10} -alkyl, C_1 - C_{10} -alkoxy, C_1 - C_{10} -haloalkyl, or $C(=O)A$, wherein

80
20

42

A is hydrogen, hydroxy, C₁-C₈-alkyl, C₁-C₈-alkoxy, amino, C₁-C₈-alkylamino, or di-(C₁-C₈-alkyl)amino;

n is an integer from 1 to 4; and

5

X is halogen, cyano, C₁-C₆-alkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy or C₃-C₈-alkenyloxy.

2. Compounds of formula I according to claim 1, in which

10

R¹ is straight chained or branched C₁-C₆-alkyl, C₂-C₆-alkenyl, C₃-C₉-cycloalkyl, or C₁-C₁₀-haloalkyl, and

R² is hydrogen or C₁-C₆-alkyl, or

15

R¹ and R² together with the interjacent nitrogen atom represent a heterocyclic ring with 5 or 6 carbon atoms being optionally substituted with one or two C₁-C₆-alkyl groups.

20

3. Compounds of formula I according to claims 1 or 2 in which R² is hydrogen.

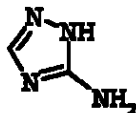
4. Compounds of formula I according to claims 1 to 3 in which X is halogen.

25

5. Compounds of formula I according to claims 1 to 4 in which (R³)_n is 4-(C₁-C₈-alkoxy-carbonyl) or 4-cyano.

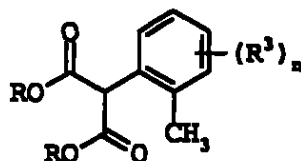
6. A process for the preparation of compounds of formula I as defined in claim 4 which comprises reacting 5-amino-1,2,4-triazole

35



with 2-phenyl-substituted malonic acid ester of formula II,

40

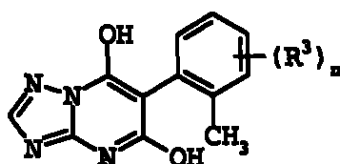


II

wherein R³ and n are as defined in formula I, and R denotes C₁-C₆-alkyl, under alkaline conditions, to yield compounds of formula III,

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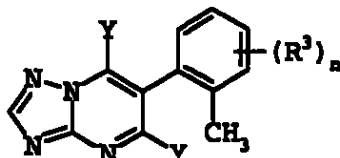
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III

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which are subsequently treated with a halogenating agent to give 5,7-dihalogen-6-phenyl-triazolopyrimidines of formula IV

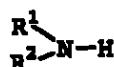


IV

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in which Y is halogen with an amine of formula V

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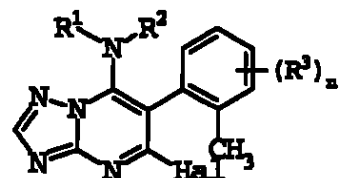
V

in which R¹ and R² are as defined in formula I to produce compounds of formula I.

20

7. A process for the preparation of compounds of formula I according to claim 1 wherein X is cyano, C₁-C₁₀-alkoxy, or C₁-C₁₀-haloalkyl, which comprises reacting 5-halogen-triazolopyrimidine of formula I

25



I (X=Hal)

30

with compounds of formula VI,

M-X'

VI

35

which are, dependent from the value of X' to be introduced, an anorganic cyano salt, an alkoxylate, haloalkoxylate or an alkenyloxylate, resp., wherein M is ammonium-, tetraalkylammonium-, alkalimetal- or earth metal cation, to produce compounds of formula I.

40

8. Intermediates of formulae II, III, and IV as defined in claim 6.

45

9. A composition suitable for controlling phytopathogenic fungi, comprising a solid or liquid carrier and a compound of the formula I as claimed in claim 1.

44

10. A method for controlling phytopathogenic fungi; which comprises treating the fungi or the materials, plants, the soil or the seed to be protected against fungal attack with an effective amount of a compound of the formula I as claimed in claim 1.

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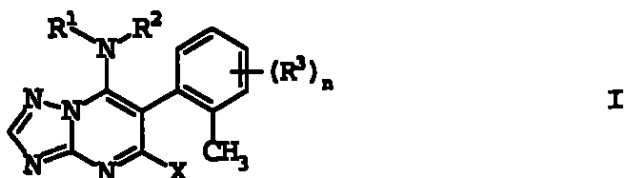
Substituted 6-(2-tolyl)-triazolopyrimidines

Abstract

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Substituted 6-(2-tolyl)-triazolopyrimidines of formula I

10



in which

15 R^1 and R^2 independently denote hydrogen or alkyl, alkenyl, alky-
nyl, or alkadienyl, haloalkyl, haloalkenyl, cycloalkyl, phe-
nyl, naphthyl, or 5- or 6-membered heterocyclyl, containing
one to four nitrogen atoms or one to three nitrogen atoms and
one sulfur or oxygen atom, or 5- or 6-membered heteroaryl,
20 containing one to four nitrogen atoms or one to three
nitrogen atoms and one sulfur or oxygen atom, or

where R^1 and R^2 radicals may be unsubstituted or substituted
as defined in the description, or

25

R^1 and R^2 together with the interjacent nitrogen atom represent a
5- or 6-membered heterocyclic ring, containing one to four
nitrogen atoms or one to three nitrogen atoms and one sulfur
or oxygen atom, which may be substituted ;

30

R^3 is halogen, cyano, alkyl, alkoxy, haloalkyl, or $C(=O)A$,
wherein

A is hydrogen, hydroxy, alkyl, amino, or mono- or dialkyl-
35 amino;

n is an integer from 1 to 4; and

X is halogen, cyano, alkyl, alkoxy, haloalkoxy or alkenyloxy;

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processes for their preparation, compositions containing them and
to their use for combating phytopathogenic fungi.

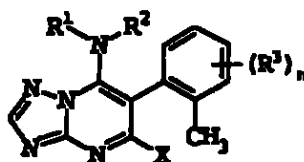
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6-(2-TOLIL)-TRIAZOLOPIRIMIDINAS SUSTITUIDAS

COMO FUNGICIDAS

Descripción

La invención se relaciona con 6-(2-tolil)-triazolopirimidinas sustituidas en la fórmula I



I

En la cual

R¹ y R² independientemente significan hidrogeno o alquilo C₁-C₁₀, alquenilo C₂-C₁₀, alquenilo C₂-C₁₀, o alcadienilo C₄-C₁₀, haloalquilo C₂-C₁₀, haloalquenilo C₂-C₁₀, cicloalquilo C₃-C₁₀, fenilo, naftilo, o

heterociclilo de 5 o 6 miembros, que contiene de 1 a 4 átomos de nitrógeno o 1 a 3 átomos de nitrógeno y un átomo de azufre u oxígeno, o

heteroarilo 5 o 6 miembros que contiene 1 a 4 átomos de nitrógeno o 1 a 3 átomos de nitrógeno y un átomo de azufre u oxígeno, o

donde los radicales R^1 y R^2 pueden ser no sustituidos o parcial o completamente halogenados o pueden llevar 1 a 3 grupos R^a ,

R^a es ciano, nitro, hidroxilo, alquilo C_1-C_6 , cicloalquilo C_3-C_6 , alcoxi C_1-C_6 , alquiltio C_1-C_6 , alquilamino C_1-C_6 , di- C_1-C_6 alquilamino, alquenilo C_2-C_6 , alqueniloxi C_2-C_6 , alquinilo C_2-C_6 , alquiniloxi C_3-C_6 y alquilenodioxí C_1-C_4 ;

R^1 y R^2 juntos con el átomo de nitrógeno interyacente representan un anillo heterocíclico de 5 o 6 miembros, que contiene 1 a 4 átomos de nitrógeno o 1 a 3 átomos de nitrógeno y un átomo de azufre u oxígeno, que puede ser sustituido por 1 a 3 radicales R^a ;

R^3 es halógeno, ciano, alquilo C_1-C_{10} , alcoxi C_1-C_{10} , haloalquilo C_1-C_{10} , o $C(=O)A$, en donde

A es hidrogeno, hidróxi, alquilo C_1-C_8 , alcoxi C_1-C_8 , amino, alquilamino C_1-C_8 , o di-(alquil C_1-C_8)-amino; n es un entero de 1 a 4; y

X es halógeno, ciano, alquilo C_1-C_6 , alcoxi C_1-C_6 , haloalcoxi C_1-C_6 o alquenciloxi C_3-C_8 .

Más aun, la invención se relaciona con procesos para su preparación, composiciones que los contienen y su uso para combatir hongo fitopatógenos.

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Las 6-fenil-7-amino-triazolopirimidinas son generalmente conocidas de la US 4,567,262 y la US 5,593,996.

Las triazolopirimidinas con un grupo trifluorofenilo en la posición 6 se describe en la WO-A 98/46607 y EP-A 945 453.

De la WO-A 98/46608 diversos 6-fenil-triazolopirimidinas son conocidas, las cuales son sustituidas en la posición 7 por alquilaminas fluorinadas.

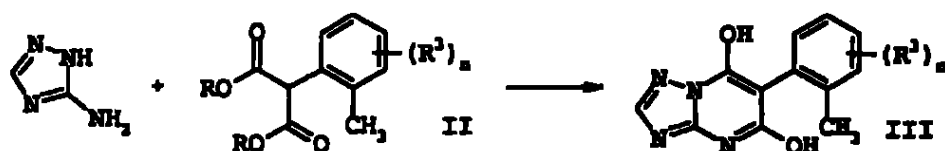
Los compuestos descritos en los documentos discutidos anteriormente se dicen que son activos contra varios hongos fitopatógenos.

Es objeto de la presente invención suministrar compuestos que tienen una actividad fungicida mejorada.

Hemos encontrado que este objeto se logra por medio de los compuestos definidos al principio. Adicionalmente, hemos encontrado procesos para su preparación, composiciones que las comprendan y métodos para controlar hongos fitopatógenos utilizando los compuestos I.

Los compuestos de la fórmula I difieren de los compuestos conocidos de la técnica anterior más cercana WO-A 98/46608 en el grupo 2-tolilo, el cual es adicionalmente sustituido.

La presente invención suministra además un proceso para la preparación de compuesto de fórmula I como se definió anteriormente que comprenden hacer reaccionar 5-amino-triazol con éster de ácido malónico 2-(2-tolil)-sustituido de la fórmula II, en la cual



R representa alquilo, preferiblemente alquilo C₁-C₆, en particular metilo o etilo, bajo condiciones alcalinas, preferiblemente utilizando aminas terciarias de alto punto de ebullición como por ejemplo tri-n-butilamina

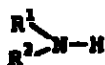
como se describió en la EP-A 770 615 para producir compuestos de la fórmula III.

Los 5,7-dihidroxi-6-fenil-triazolopirimidinas resultantes de la fórmula III, en donde R^3 y n son como se definió para la fórmula I, son subsecuentemente tratados con un agente halogenante, preferiblemente con un agente brominante o clorinante, tal como oxibromuro de fósforo o oxicloruro de fósforo puros o en la presencia de un solvente para dar IV.



La reacción es adecuadamente llevada a cabo a una temperatura en el rango de 0° C a 150° C, la temperatura de reacción preferida es de 80° C a 125° C como se describió por ejemplo en la EP-A 770 615.

La dihalotriazolopirimidina IV reacciona adicionalmente con una amina de la fórmula V.



V

En donde R^1 y R^2 son como se definió en la fórmula I para producir compuestos de fórmula I en la cual X es halógeno.

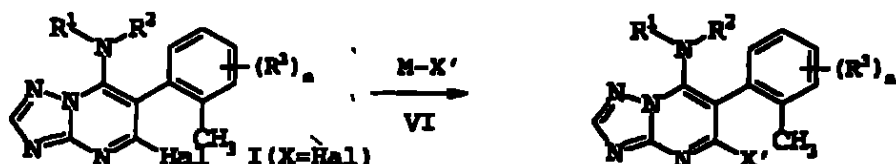
La reacción entre el compuesto 5,7-dihalo IV y la amina de la fórmula V se puede llevar a cabo bajo condiciones conocidas de la WO-A 98/46608. La reacción se lleva a cabo preferiblemente en la presencia de un solvente. Los solventes adecuados incluyen éteres, tales como dioxano, dietil éter y, especialmente, tetrahidrofurano, hidrocarburos halogenados tales como diclorometano e hidrocarburos aromáticos, por ejemplo tolueno.

La reacción es adecuadamente llevada a cabo a una temperatura en el rango de 0° C a 70° C, la temperatura de reacción preferida es de 10° C a 35° C.

También se prefiere que la reacción se lleve a cabo en la presencia de una base. Las bases adecuadas incluyen aminas terciarias, tales como trietilamina, y bases inorgánicas, tales como carbonato de potasio o carbonato de sodio. Alternativamente, un exceso del compuesto de la fórmula V puede servir como una base.

Los compuestos de fórmula I en los cuales X denota ciano, alcoxi C₁-C₆, haloalcoxi C₁-C₆ o alqueniloxi C₃-C₈ se pueden preparar al hacer reaccionar compuestos I en los cuales X es halógeno, preferiblemente cloro, con compuestos de la fórmula VI, que son, dependientes del valor de X' para ser introducidos para producir compuestos de fórmula I, una sal ciano inorgánica, un alcóxilato, haloalcóxilato o un alqueniloxilato, respectivamente, preferiblemente en la presencia de un solvente. El catión M en la fórmula VI tiene influencia menor; por razones prácticas y económicas usualmente se

prefieren las sales de amonio, tetraalquilamonio o metales alcalinos y alcalinotérreos.

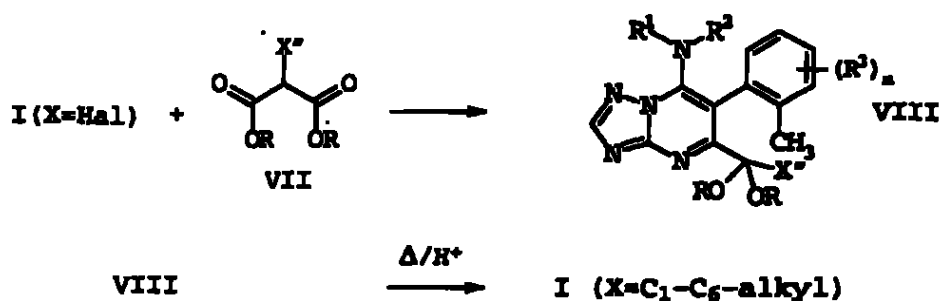


La reacción es adecuadamente llevada a cabo a una temperatura en el rango de 0 a 120° C, la temperatura de reacción preferida va de 10 a 40° C [cf. J. Heterocicl. chem., vol. 12, p. 861-863 (1975)].

Los solventes adecuados incluyen éteres tales como dioxano, dietil éter y, especialmente, tetrahidrofurano, hidrocarburos halogenados tales como diclorometano e hidrocarburos aromáticos, por ejemplo tolueno.

Los compuestos de fórmula I en los cuales X denota alquilo C₁-C₆ se pueden preparar al hacer reaccionar

compuestos I en los cuales X es halógeno, preferiblemente cloro, con estrés de ácido malónico de la fórmula IV, en donde X'' denota H o alquilo C₁-C₅ y R denota alquilo C₁-C₄, a los compuestos de fórmula de VIII y des carboxilación bajo condiciones descritas en la US 5,994, 360.



De acuerdo con esto, la invención se relaciona con intermedios novedosos de las fórmulas II, III y IV.

Los compuestos de fórmula II son preferiblemente preparados por medio de la reacción de las correspondientes bromobencenos sustituidos con

dialquilmalonatos (I) [cf. chemistry letters, pp. 367-370, 1981; EP-A 10 02 788].

Los compuestos de fórmula II también pueden ser preparados mediante la reacción de 2-(2-tolilo)-acetato de alquilo con dialquílcarbonato en la presencia de una base fuerte, preferiblemente etóxido de sodio e hidróxido de sodio (cf. Heterociclos, pp. 1031-1047, 1996).

Los fenilacetatos sustituidos que son los compuestos de partida para los compuestos de la fórmula II son conocidos y disponibles comercialmente, y/o ellos son obtenibles por métodos conocidos generalmente.

Las mezclas de reacción se trabajan en la forma acostumbrada, por ejemplo al mezclar con agua, fase de separación y, si se requiere, purificación cromatográfica de los productos crudos. Algunos de los productos terminados se obtienen en la forma de aceites incoloros o algo marrones y viscosos, que son purificados o liberados de los componentes volátiles bajo presión reducida y a temperaturas moderadamente elevadas. Si los productos terminados son obtenidos como sólidos, la purificación

también puede ser llevada a cabo mediante recristalización o digestión.

Si los compuestos individuales I no son obtenibles por las rutas descritas anteriormente, ellas se pueden preparar mediante la derivación de otros compuestos I.

En las definiciones de símbolo dadas en la fórmula anterior, se utilizaron términos colectivos que generalmente representan los siguientes sustituyentes:

- halógeno : flúor, cloro, bromo y yodo;

- alquilo- C_1-C_{10} : saturado, radicales de hidrocarbano de cadena recta o ramificada que tienen 1 a 10, especialmente 1 a 6 átomos de carbono, por ejemplo alquilo- C_1-C_4 como se mencionó anteriormente o pentilo, 1-metilbutilo, 2-metilbutilo, 3-metilbutilo, 2,2-dimetilpropilo, 1-etilpropilo, hexilo, 1,1-dimetilpropilo, 1,2-dimetilpropilo, 1-metilpentilo, 2-metilpentilo, 3-metilpentilo, 4-metilpentilo, 1,1-dimetilbutilo, 1,2-dimetilbutilo, 1,3-dimetilbutilo, 2,2-dimetilbutilo, 2,3-dimetilbutilo, 3,3-dimetilbutilo, 1-etilbutilo, 2-

etilbutilo, 1,1, 2-trimetilpropilo, 1,2, 2-trimetilpropilo, 1-etil-1-metilpropilo y 1-etil-2-metilpropilo; alqueniolo- C_2-C_{10} : no saturado, radicales hidrocarbón de cadena recta o ramificada que tienen 2 a 10, especialmente 2 a 6 átomos de carbono y un doble enlace en cualquier posición, por ejemplo etenilo, 1-propenilo, 2-propenilo, 1-metiletenilo, 1-butenilo, 2-butenilo, 3-butenilo, 1-metil-1-propenilo, 2-metil-1-propenilo, 1-metil-2-propenilo y 2-metil-2-propenilo;

- alquiniolo C_2-C_{10} : radicales hidrocarbón de cadena recta o ramificada que tienen 2 a 10, especialmente 2 a 4 átomos de carbono y un triple enlace en cualquier posición, por ejemplo etinilo, 1-propinilo, 2-propinilo, 1-butinilo, 2-butinilo, 3-butinilo y 1-metil-2-propinilo;

- haloalquilo- C_1-C_{10} y porciones de haloalquilo de haloalcoxi C_1-C_6 : grupos alquilo de cadena recta o ramificada que tienen 1 a 6 o 10, preferiblemente 1 a 4 átomos de carbono (como se mencionó anteriormente), donde los átomos de hidrógeno en estos grupos puede ser parcialmente o completamente reemplazados por átomos

halógeno como se mencionó anteriormente, por ejemplo haloalcoxi- C_1-C_2 , tales como clorometoxi, bromometoxi, diclorometoxi, triclorometoxi, fluorometoxi, difluorometoxi, trifluorometoxi, clorofluorometoxi, diclorofluorometoxi, clorodifluorometoxi, 1-cloroetoxi, 1-bromoetoxi, 1-fluoroetoxi, 2-fluoroetoxi, 2,2-difluoroetoxi, 2,2,2-tri-fluoroetoxi, 2-cloro-2-fluoroetoxi, 2-cloro-2,2-difluoro- etoxi, 2,2-dicloro-2-fluoroetoxi, 2,2, 2-tricloroetoxi y pentafluoroetoxi;

- cicloalquilo C_3-C_{10} : grupos cicloalquilo mono- o bicíclicos que tienen 3 a 10 átomos de carbono; grupos monocíclicos que tienen preferiblemente 3 a 8, especialmente 3 a 6 miembros de anillo, grupos bicíclicos que tienen preferiblemente 8 a 10 miembros de anillo.

Un grupo heterociclilo de 5- o 6- miembros, contienen uno a cuatro átomos de nitrógeno o uno a tres átomos de nitrógeno y un azufre o átomo de oxígeno, preferiblemente un átomo de oxígeno, por ejemplo 1-pirimidinilo, 2-pirimidinilo, morfolin-4-ilo.

Un heteroarilo de 5 miembros, contienen uno a cuatro átomos de nitrógeno o uno a tres átomos de nitrógeno y un azufre o átomo de oxígeno: grupos heteroarilo de 5 miembros que, en adición a los átomos de carbono, puede contener uno a cuatro átomos de nitrógeno o uno a tres átomos de nitrógeno y un azufre o átomo de oxígeno como miembros de anillo, por ejemplo 2-furilo, 3-furilo, 2-tienilo, 3-tienilo, 2-pirrolilo, 3-pirrolilo, 3-isoxazolilo, 4-isoxazolilo, 5-isoxazolilo, 3-isotiazolilo, 4-isotiazolilo, 5-isotiazolilo, 3-pirazolilo, 4-pirazolilo, 5-pirazolilo, 2-oxazolilo, 4-oxazolilo, 5-oxazolilo, 2-tiazolilo, 4-tiazolilo, 5-tiazolilo, 2-imidazolilo, 4-imidazolilo, 1,2, 4-oxadiazol-3-ilo, 1, 2,4-oxadiazol-5-ilo, 1, 2,4-tiadiazol-3-ilo, 1,2, 4-tiadiazol-5-ilo, 1,2, 4-triazol-3-ilo, 1,3, 4-oxadiazol-2-ilo, 1, 3,4-tiadiazol-2-il y 1, 3,4-triazol-2-ilo;

- heteroarilo de 6- miembros, contienen uno a cuatro átomos de nitrógeno: grupos heteroarilo de 6 miembros que, en adición a los átomos de carbono, puede contener uno a tres o uno a cuatro átomos de nitrógeno como miembros de anillo, por ejemplo 2-piridinilo, 3-

piridinilo, 4-piridinilo, 3-piridazinilo, 4-piridazinilo, 2-pirimidinilo, 4-pirimidinilo, 5-pirimidinilo, 2-pirazinilo, 1, 3,5-triazin-2-ilo y 1, 2,4-triazin-3-ilo.

Con respecto al uso propuesto, se da preferencia a las triazolopirimidinas de la fórmula I que tiene los siguientes sustituyentes, donde la preferencia es válida en cada caso propio o en combinación:

Una porción cicloalquilo preferida es ciclopentilo siendo opcionalmente sustituido por uno o más nitro, ciano, alquilo-C₁-C₆, alcoxi-C₁-C₆ grupos.

Una porción heteroarilo es piridilo, pirimidilo, pirazolilo o tienilo.

Se da preferencia a los compuestos de la fórmula I en los cuales cualquier parte alquilo o haloalquilo de los grupos R¹ o R², que pueden ser de cadena recta o ramificada, contienen más de 10 átomos de carbono,

preferiblemente 1 a 9 átomos de carbono, más preferiblemente 2 a 6 átomos de carbono, cualquier parte alqueno o alquino de los sustituyentes R^1 o R^2 contiene más de 10 átomos de carbono, preferiblemente 2 a 9 átomos de carbono, más preferiblemente 3 a 6 átomos de carbono, cualquier parte cicloalquilo de los sustituyentes R^1 o R^2 contiene de 3 a 10 átomos de carbono, preferiblemente de 3 a 8 átomos de carbono, más preferiblemente de 3 a 6 átomos de carbono, y cualquier parte bicicloalquilo de los sustituyentes R^1 o R^2 contiene de 5 a 9 átomos de carbono, preferiblemente de 7 a 9 átomos de carbono. Cualquier grupo alquilo, alqueno o alquino puede ser lineal o ramificado.

Así mismo, se da particular preferencia a los compuestos de la fórmula I en donde R^1 no es hidrógeno.

Compuestos de fórmula I se prefieren en los cuales R^1 representa un alquilo- C_1-C_{10} de cadena recta o ramificada, en particular un grupo alquilo C_3-C_{10} ramificado, un grupo cicloalquilo C_3-C_8 -, un bicicloalquilo C_5-C_9 -, un cicloalquilo- C_3-C_8 -alquilo- C_1-C_6 , alcoxi- C_1-C_{10} -alquilo- C_1-C_6 , un haloalquilo- C_1-C_{10} o un grupo fenilo que está

opcionalmente sustituido por uno o tres átomos de halógeno o grupos alquilo-C₁-C₁₀ o alcoxi-C₁-C₁₀.

Se da particular preferencia a los compuestos I en los cuales R² representa hidrógeno, alquilo C₁-C₁₀ o haloalquilo C₁-C₁₀, en particular hidrógeno.

Además, se da particular preferencia a los compuestos I en los que R² es hidrógeno.

Por otra parte, se da particular preferencia a los compuestos I en los que R² es metilo.

Adicionalmente, se da particular preferencia a los compuestos I en los que R² es etilo.

Si R¹ denota haloalquilo-C₁-C₁₀, preferiblemente alquilo polifluorinado, en particular 2,2, 2-trifluoroetil, 2-(1, 1,1-trifluoropropil) o 2-(1,1,1-trifluorobutil), R² preferiblemente representa hidrógeno.

Si R^1 denota cicloalquilo- C_3-C_8 opcionalmente sustituido, preferiblemente ciclopentilo o ciclohexilo, R^2 preferiblemente representa hidrógeno o alquilo- C_1-C_6 .

Por otra parte, se da particular preferencia a los compuestos I en los cuales R^1 y R^2 junto con el átomo de nitrógeno interyacente forma un anillo heterocíclico opcionalmente sustituido, preferiblemente un anillo heterocíclico- C_3-C_7 , en particular pirrolidina, piperidina, tetrahidropiridina, en particular 1,2,3,6-tetrahidro- piridina o azepan que está opcionalmente sustituido por uno o más grupos alquilo- C_1-C_{10} .

Se da preferencia a los compuestos de fórmula I en los cuales cualquier parte alquilo de los grupos R^1 o R^2 , que pueden ser de cadena recta o ramificada, contienen 1 a 9 átomos de carbono, más preferiblemente 2 a 6 átomos de carbono, cualquier parte alquenilo o alquinilo de los sustituyentes R^1 o R^2 contienen 2 a 9 átomos de carbono, más preferiblemente 3 a 6 átomos de carbono, cualquier parte cicloalquilo de los sustituyentes R^1 o R^2 contiene

de 3 a 10 átomos de carbono, preferiblemente de 3 a 8 átomos de carbono, más preferiblemente de 3 a 6 átomos de carbono, y cualquier parte bicicloalquilo de los sustituyentes R^1 o R^2 contiene de 7 a 9 átomos de carbono. Cualquier parte alquilo, alquenoilo o alquinoilo puede ser lineal o ramificada.

Compuestos de la fórmula I son preferidos en los cuales R^1 representa un alquilo- C_1-C_{10} de cadena recta o ramificada, en particular alquilo- C_3-C_{10} , un cicloalquilo- C_3-C_8 , bicicloalquilo- C_5-C_9 , cicloalquilo- C_3-C_8 -alquilo- C_1-C_6 , alcoxi- C_1-C_{10} -alquilo- C_1-C_6 , o fenilo está opcionalmente sustituido por uno o tres grupos alquilo- C_1-C_{10} o alcoxi- C_1-C_{10} .

Se da particular preferencia a los compuestos I en los cuales R^2 representa hidrógeno o alquilo- C_1-C_{10} , en particular hidrógeno.

Por otra parte, se da particular preferencia a los compuestos I en los cuales R^2 es metilo o etilo

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Si R^1 denota un grupo cicloalquilo C_3-C_8 opcionalmente sustituido, preferiblemente ciclopentilo o ciclohexilo, R^2 preferiblemente representa hidrógeno o alquilo- C_1-C_6 .

Por otra parte, se da particular preferencia a los compuestos I en los cuales R^1 y R^2 juntos con el átomo de nitrógeno interyacente forman un anillo heterocíclico opcionalmente sustituido, preferiblemente un anillo heterocíclico- C_3-C_7 opcionalmente sustituido, in particular a pirrolidina, piperidina, tetrahidropiridina, en particular 1,2,3,6-tetrahidro-piridino o anillo azepan el cual se sustituye opcionalmente por uno o más grupos alquilo- C_1-C_{10} .

Así mismo, se da particular preferencia a los compuestos I en los cuales R^2 es hidrógeno.

También se da particular preferencia a los compuestos I en los cuales n tiene el valor 2 y los grupos R^3 están en la posición 4 y 6.

Por otra parte, se da preferencia a los compuestos I en los cuales el grupo R^3 está en una porción para.

Adicionalmente, se da particular preferencia a los compuestos I en los cuales $(R^3)_n$ es 4,6-dimetilo.

Así mismo, se da particular preferencia a los compuestos I en los cuales $(R^3)_n$ es carbonilo 4-(alcoxi- C_1-C_8), especialmente 4-metoxycarbonilo.

Además, se da particular preferencia a los compuestos I en los cuales $(R^3)_n$ es 4-metoxi-6-metilo, o 4-fluoro-6-metilo.

También se da particular preferencia a los compuestos I en los cuales $(R^3)_n$ es 4-fluoro, 6-fluoro, o 4-cloro.

Además, se da particular preferencia a los compuestos I en los cuales X es cloro o bromo, especialmente cloro.

Por otra parte, preference is given to compounds I in which X es ciano o metilo.

Adicionalmente, se da particular preferencia a los compuestos I en los cuales X es metoxi, etoxi, n-propoxi, iso-propoxi, aliloxi, o 3-metilaliloxi.

Las modalidades particularmente preferidas de los intermedios con respecto a las variables corresponde a aquellas de los radicales X, R¹, R² y R³ de la fórmula I

Incluidos en el alcance la presente invención están los isómeros (R) y (S) de los compuestos de la fórmula general I que tiene un centro quiral y los racematos de estos, y sales, N-óxidos y de adición ácida.

Con respecto a su uso, se da particular preferencia a los compuestos I compilados en las tablas adelante. Los grupos mencionados en las tablas para un sustituyente

adicionalmente son parte de este, independientemente de la combinación en la que ellos se mencionen, una modalidad particularmente preferida de los respectivos sustituyentes.

Tabla 1

Compuestos de fórmula I, en el cual X es cloro, $(R^3)_n$ es 4-cloro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla

2 Compuestos de fórmula I, en el cual X es cloro, $(R^3)_n$ es 5-cloro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 3

Compuestos de fórmula I, en el cual X es cloro, $(R^3)_n$ es 6-cloro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 4

Compuestos de fórmula I, en el cual X es cloro, $(R^3)_n$ es 3-fluoro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 5

Compuestos de fórmula I, en el cual X es cloro, $(R^3)_n$ es 4-fluoro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 6

Compuestos de fórmula I, en el cual X es cloro, $(R^3)_n$ es 5-fluoro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 7

Compuestos de fórmula I, en el cual X es cloro, $(R^3)_n$ es 6-fluoro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 8

Compuestos de fórmula I, en el cual X es cloro, $(R^3)_n$ es 3-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 9

Compuestos de fórmula I, en el cual X es cloro, $(R^3)_n$ es 4-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 10

Compuestos de fórmula I, en el cual X es cloro, $(R^3)_n$ es 5-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 11

Compuestos de fórmula I, en el cual X es cloro, $(R^3)_n$ es 6-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 12

Compuestos de fórmula I, en el cual X es cloro, $(R^3)_n$ es 4-metoxi y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 13

Compuestos de fórmula I, en el cual X es cloro, $(R^3)_n$ es 5-metoxi y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 14

Compuestos de fórmula I, en el cual X es cloro, $(R^3)_n$ es 6-metoxi y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 15

Compuestos de fórmula I, en el cual X es cloro, $(R^3)_n$ es 4-trifluorometilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 16

Compuestos de fórmula I, en el cual X es cloro, $(R^3)_n$ es 5-trifluorometilo y R^1 y R^2 corresponden a una fila en la Tabla A

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Tabla 17

Compuestos de fórmula I, en el cual X es cloro, $(R^3)_n$ es 6-trifluorometilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 18

Compuestos de fórmula I, en el cual X es cloro, $(R^3)_n$ es 4,6-dimetilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 19

Compuestos de fórmula I, en el cual X es cloro, $(R^3)_n$ es 4-metoxi-6-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 20

Compuestos de fórmula I, en el cual X es cloro, $(R^3)_n$ es 4-fluoro-6-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

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Tabla 21

Compuestos de fórmula I, en el cual X es cloro, $(R^3)_n$ es 4-metoxicarbonilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 22

Compuestos de fórmula I, en el cual X es cloro, $(R^3)_n$ es 4-ciano y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 23

Compuestos de fórmula I, en los cuales X es bromo, $(R^3)_n$ es 4-cloro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 24

Compuestos de fórmula I, en los cuales X es bromo, $(R^3)_n$ es 5-cloro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 25

Compuestos de fórmula I, en los cuales X es bromo, $(R^3)_n$ es 6-cloro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 26

Compuestos de fórmula I, en los cuales X es bromo, $(R^3)_n$ es 3-fluoro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 27

Compuestos de fórmula I, en los cuales X es bromo, $(R^3)_n$ es 4-fluoro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 28

Compuestos de fórmula I, en los cuales X es bromo, $(R^3)_n$ es 5-fluoro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 29

Compuestos de fórmula I, en los cuales X es bromo, $(R^3)_n$ es 6-fluoro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 30

Compuestos de fórmula I, en los cuales X es bromo, $(R^3)_n$ es 3-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 31

Compuestos de fórmula I, en los cuales X es bromo, $(R^3)_n$ es 4-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 32

Compuestos de fórmula I, en los cuales X es bromo, $(R^3)_n$ es 5-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 33

Compuestos de fórmula I, en los cuales X es bromo, $(R^3)_n$ es 6-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 34

Compuestos de fórmula I, en los cuales X es bromo, $(R^3)_n$ es 4-metoxi y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 35

Compuestos de fórmula I, en los cuales X es bromo, $(R^3)_n$ es 5-metoxi y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 36

Compuestos de fórmula I, en los cuales X es bromo, $(R^3)_n$ es 6-metoxi y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 37

Compuestos de fórmula I, en los cuales X es bromo, $(R^3)_n$ es 4-trifluorometilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 38

Compuestos de fórmula I, en los cuales X es bromo, $(R^3)_n$ es 5-trifluorometilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 39

Compuestos de fórmula I, en los cuales X es bromo, $(R^3)_n$ es 6-trifluorometilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 40

Compuestos de fórmula I, en los cuales X es bromo, $(R^3)_n$ es 4,6-dimetilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 41

Compuestos de fórmula I, en los cuales X es bromo, $(R^3)_n$ es 4-metoxi-6-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 42

Compuestos de fórmula I, en los cuales X es bromo, $(R^3)_n$ es 4-fluoro-6-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 43

Compuestos de fórmula I, en los cuales X es bromo, $(R^3)_n$ es 4-metoxycarbonilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 44

Compuestos de fórmula I, en los cuales X es bromo, $(R^3)_n$ es 4-ciano y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 45

Compuestos de fórmula I, en los cuales X es ciano, $(R^3)_n$ es 4-cloro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 46

Compuestos de fórmula I, en los cuales X es ciano, $(R^3)_n$ es 5-cloro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 47

Compuestos de fórmula I, en los cuales X es ciano, $(R^3)_n$ es 6-cloro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 48

Compuestos de fórmula I, en los cuales X es ciano, $(R^3)_n$ es 3-fluoro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 49

Compuestos de fórmula I, en los cuales X es ciano, $(R^3)_n$ es 4-fluoro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 50

Compuestos de fórmula I, en los cuales X es ciano, $(R^3)_n$ es 5-fluoro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 51

Compuestos de fórmula I, en los cuales X es ciano, $(R^3)_n$ es 6-fluoro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 52

Compuestos de fórmula I, en los cuales X es ciano, $(R^3)_n$ es 3-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 53

Compuestos de fórmula I, en los cuales X es ciano, $(R^3)_n$ es 4-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 54

Compuestos de fórmula I, en los cuales X es ciano, $(R^3)_n$ es 5-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

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Tabla 55

Compuestos de fórmula I, en los cuales X es ciano, $(R^3)_n$ es 6-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 56

Compuestos de fórmula I, en los cuales X es ciano, $(R^3)_n$ es 4-metoxi y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 57

Compuestos de fórmula I, en los cuales X es ciano, $(R^3)_n$ es 5-metoxi y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 58

Compuestos de fórmula I, en los cuales X es ciano, $(R^3)_n$ es 6-metoxi y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 59

Compuestos de fórmula I, en los cuales X es ciano, $(R^3)_n$ es 4-trifluorometilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 60

Compuestos de fórmula I, en los cuales X es ciano, $(R^3)_n$ es 5-trifluorometilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 61

Compuestos de fórmula I, en los cuales X es ciano, $(R^3)_n$ es 6-trifluorometilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 62

Compuestos de fórmula I, en los cuales X es ciano, $(R^3)_n$ es 4,6-dimetilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 63

Compuestos de fórmula I, en los cuales X es ciano, $(R^3)_n$ es 4-metoxi-6-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 64

Compuestos de fórmula I, en los cuales X es ciano, $(R^3)_n$ es 4-fluoro-6-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 65

Compuestos de fórmula I, en los cuales X es ciano, $(R^3)_n$ es 4-metoxycarbonilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 66

Compuestos de fórmula I, en los cuales X es ciano, $(R^3)_n$ es 4-ciano y R^1 y R^2 corresponden a una fila en la Tabla A

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Tabla 67

Compuestos de fórmula I, en los cuales X es metoxi, $(R^3)_n$ es 4-cloro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 68

Compuestos de fórmula I, en los cuales X es metoxi, $(R^3)_n$ es 5-cloro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 69

Compuestos de fórmula I, en los cuales X es metoxi, $(R^3)_n$ es 6-cloro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 70

Compuestos de fórmula I, en los cuales X es metoxi, $(R^3)_n$ es 3-fluoro y R^1 y R^2 corresponde a una fila en la Tabla A

Tabla 71

Compuestos de fórmula I, en los cuales X es metoxi, $(R^3)_n$ es 4-fluoro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 72

Compuestos de fórmula I, en los cuales X es metoxi, $(R^3)_n$ es 5-fluoro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 73

Compuestos de fórmula I, en los cuales X es metoxi, $(R^3)_n$ es 6-fluoro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 74

Compuestos de fórmula I, en los cuales X es metoxi, $(R^3)_n$ es 3-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 75

Compuestos de fórmula I, en los cuales X es metoxi, $(R^3)_n$ es 4-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 76

Compuestos de fórmula I, en los cuales X es metoxi, $(R^3)_n$ es 5-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 77

Compuestos de fórmula I, en los cuales X es metoxi, $(R^3)_n$ es 6-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 78

Compuestos de fórmula I, en los cuales X es metoxi, $(R^3)_n$ es 4-metoxi y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 79

Compuestos de fórmula I, en los cuales X es metoxi, $(R^3)_n$ es 5-metoxi y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 80

Compuestos de fórmula I, en los cuales X es metoxi, $(R^3)_n$ es 6-metoxi y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 81

Compuestos de fórmula I, en los cuales X es metoxi, $(R^3)_n$ es 4-trifluorometilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 82

Compuestos de fórmula I, en los cuales X es metoxi, $(R^3)_n$ es 5-trifluorometilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 83

Compuestos de fórmula I, en los cuales X es metoxi, $(R^3)_n$ es 6-trifluorometilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 84

Compuestos de fórmula I, en los cuales X es metoxi, $(R^3)_n$ es 4,6-dimetilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 85

Compuestos de fórmula I, en los cuales X es metoxi, $(R^3)_n$ es 4-metoxi-6-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 86

Compuestos de fórmula I, en los cuales X es metoxi, $(R^3)_n$ es 4-fluoro-6-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 87

Compuestos de fórmula I, en los cuales X es metoxi, $(R^3)_n$ es 4-metoxicarbonilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 88

Compuestos de fórmula I, en los cuales X es metoxi, $(R^3)_n$ es 4-ciano y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 89 Compuestos de fórmula I, en los cuales X es metil, $(R^3)_n$ es 4-cloro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 90

Compuestos de fórmula I, en los cuales X es metil, $(R^3)_n$ es 5-cloro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 91

Compuestos de fórmula I, en los cuales X es metil, $(R^3)_n$ es 6-cloro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 92

Compuestos de fórmula I, en los cuales X es metil, $(R^3)_n$ es 3-fluoro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 93

Compuestos de fórmula I, en los cuales X es metil, $(R^3)_n$ es 4-fluoro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 94

Compuestos de fórmula I, en los cuales X es metil, $(R^3)_n$ es 5-fluoro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 95

Compuestos de fórmula I, en los cuales X es metil, $(R^3)_n$ es 6-fluoro y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 96

Compuestos de fórmula I, en los cuales X es metil, $(R^3)_n$ es 3-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 97

Compuestos de fórmula I, en los cuales X es metil, $(R^3)_n$ es 4-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 98

Compuestos de fórmula I, en los cuales X es metil, $(R^3)_n$ es 5-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 99

Compuestos de fórmula I, en los cuales X es metil, $(R^3)_n$ es 6-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 100

Compuestos de fórmula I, en los cuales X es metil, $(R^3)_n$ es 4-metoxi y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 101

Compuestos de fórmula I, en los cuales X es metil, $(R^3)_n$ es 5-metoxi y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 102

Compuestos de fórmula I, en los cuales X es metil, $(R^3)_n$ es 6-metoxi y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 103

Compuestos de fórmula I, en los cuales X es metil, $(R^3)_n$ es 4-trifluorometilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 104

Compuestos de fórmula I, en los cuales X es metil, $(R^3)_n$ es 5-trifluorometilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 105

Compuestos de fórmula I, en los cuales X es metil, $(R^3)_n$ es 6-trifluorometilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 106

Compuestos de fórmula I, en los cuales X es metil, $(R^3)_n$ es 4,6-dimetilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 107

Compuestos de fórmula I, en los cuales X es metil, $(R^3)_n$ es 4-metoxi-6-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 108

Compuestos de fórmula I, en los cuales X es metil, $(R^3)_n$ es 4-fluoro-6-metilo y R^1 y R^2 corresponden a una fila en la Tabla A

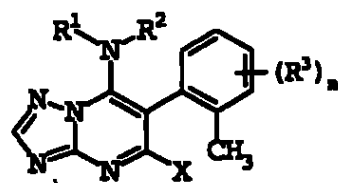
Tabla 109

Compuestos de fórmula I, en los cuales X es metil, $(R^3)_n$ es 4-metoxicarbonilo y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla 110

Compuestos de fórmula I, en los cuales X es metil, $(R^3)_n$ es 4-ciano y R^1 y R^2 corresponden a una fila en la Tabla A

Tabla A



I

No.	R ¹	R ²
A-1	H	H
A-2	CH ₂ CH ₃	H
A-3	CH ₂ CH ₃	CH ₃
A-4	CH ₂ CH ₃	CH ₂ CH ₃
A-5	CH ₂ CF ₃	H
A-6	CH ₂ CF ₃	CH ₃
A-7	CH ₂ CF ₃	CH ₂ CH ₃
A-8	CH ₂ CH ₂ CH ₃	H
A-9	CH ₂ CH ₂ CH ₃	CH ₃
A-10	CH ₂ CH ₂ CH ₃	CH ₂ CH ₃
A-11	CH ₂ CH ₂ CH ₃	H
A-12	CH ₂ CH ₂ CH ₃	CH ₃
A-13	CH ₂ CH ₂ CH ₃	CH ₂ CH ₃
A-14	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃

A-15	$\text{CH}(\text{CH}_3)_2$	H
A-16	$\text{CH}(\text{CH}_3)_2$	CH_3
A-17	$\text{CH}(\text{CH}_3)_2$	CH_2CH_3
A-18	$(\pm) \text{CH}(\text{CH}_3) - \text{CH}_2\text{CH}_3$	H
A-19	$(\pm) \text{CH}(\text{CH}_3) - \text{CH}_2\text{CH}_3$	CH_3
A-20	$(\pm) \text{CH}(\text{CH}_3) - \text{CH}_2\text{CH}_3$	CH_2CH_3
A-21	$(S) \text{CH}(\text{CH}_3) - \text{CH}_2\text{CH}_3$	H
A-22	$(S) \text{CH}(\text{CH}_3) - \text{CH}_2\text{CH}_3$	CH_3
A-23	$(S) \text{CH}(\text{CH}_3) - \text{CH}_2\text{CH}_3$	CH_2CH_3
A-24	$(R) \text{CH}(\text{CH}_3) - \text{CH}_2\text{CH}_3$	H
A-25	$(R) \text{CH}(\text{CH}_3) - \text{CH}_2\text{CH}_3$	CH_3
A-26	$(R) \text{CH}(\text{CH}_3) - \text{CH}_2\text{CH}_3$	CH_2CH_3
A-27	$(\pm) \text{CH}(\text{CH}_3) - \text{CH}(\text{CH}_3)_2$	H
A-28	$(\pm) \text{CH}(\text{CH}_3) - \text{CH}(\text{CH}_3)_2$	CH_3
A-29	$(\pm) \text{CH}(\text{CH}_3) - \text{CH}(\text{CH}_3)_2$	CH_2CH_3
A-30	$(S) \text{CH}(\text{CH}_3) - \text{CH}(\text{CH}_3)_2$	H
A-31	$(S) \text{CH}(\text{CH}_3) - \text{CH}(\text{CH}_3)_2$	CH_3
A-32	$(S) \text{CH}(\text{CH}_3) - \text{CH}(\text{CH}_3)_2$	CH_2CH_3
A-33	$(R) \text{CH}(\text{CH}_3) - \text{CH}(\text{CH}_3)_2$	H
A-34	$(R) \text{CH}(\text{CH}_3) - \text{CH}(\text{CH}_3)_2$	CH_3
A-35	$(R) \text{CH}(\text{CH}_3) - \text{CH}(\text{CH}_3)_2$	CH_2CH_3
A-36	$(\pm) \text{CH}(\text{CH}_3) - \text{C}(\text{CH}_3)_3$	H

A-37	$(\pm) \text{CH}(\text{CH}_3) - \text{C}(\text{CH}_3)_3$	CH_3
A-38	$(\pm) \text{CH}(\text{CH}_3) - \text{C}(\text{CH}_3)_3$	CH_2CH_3
A-39	$(S) \text{CH}(\text{CH}_3) - \text{C}(\text{CH}_3)_3$	H
A-40	$(S) \text{CH}(\text{CH}_3) - \text{C}(\text{CH}_3)_3$	CH_3
A-41	$(S) \text{CH}(\text{CH}_3) - \text{C}(\text{CH}_3)_3$	CH_2CH_3
A-42	$(R) \text{CH}(\text{CH}_3) - \text{C}(\text{CH}_3)_3$	H
A-43	$(R) \text{CH}(\text{CH}_3) - \text{C}(\text{CH}_3)_3$	CH_3
A-44	$(R) \text{CH}(\text{CH}_3) - \text{C}(\text{CH}_3)_3$	CH_2CH_3
A-45	$(\pm) \text{CH}(\text{CH}_3) - \text{CF}_3$	H
A-46	$(\pm) \text{CH}(\text{CH}_3) - \text{CF}_3$	CH_3
A-47	$(\pm) \text{CH}(\text{CH}_3) - \text{CF}_3$	CH_2CH_3
A-48	$(S) \text{CH}(\text{CH}_3) - \text{CF}_3$	H
A-49	$(S) \text{CH}(\text{CH}_3) - \text{CF}_3$	CH_3
A-50	$(S) \text{CH}(\text{CH}_3) - \text{CF}_3$	CH_2CH_3
A-51	$(R) \text{CH}(\text{CH}_3) - \text{CF}_3$	H
A-52	$(R) \text{CH}(\text{CH}_3) - \text{CF}_3$	CH_3
A-53	$(R) \text{CH}(\text{CH}_3) - \text{CF}_3$	CH_2CH_3
A-54	$(\pm) \text{CH}(\text{CH}_3) - \text{CCl}_3$	H
A-55	$(\pm) \text{CH}(\text{CH}_3) - \text{CCl}_3$	CH_3
A-56	$(\pm) \text{CH}(\text{CH}_3) - \text{CCl}_3$	CH_2CH_3
A-57	$(S) \text{CH}(\text{CH}_3) - \text{CCl}_3$	H

A-58	(S) $\text{CH}(\text{CH}_3) - \text{CCl}_3$	CH_3
A-59	(S) $\text{CH}(\text{CH}_3) - \text{CCl}_3$	CH_2CH_3
A-60	(R) $\text{CH}(\text{CH}_3) - \text{CCl}_3$	H
A-61	(R) $\text{CH}(\text{CH}_3) - \text{CCl}_3$	CH_3
A-62	(R) $\text{CH}(\text{CH}_3) - \text{CCl}_3$	CH_2CH_3
A-63	$\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$	H
A-64	$\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$	CH_3
A-65	$\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$	CH_2CH_3
A-66	ciclopentilo	H
A-67	ciclopentilo	CH_3
A-68	ciclopentilo	CH_2CH_3
A-69	$-(\text{CH}_2)_2\text{CH}(\text{CH}_3)(\text{CH}_2)_2-$	
A-70	$\text{CH}_2\text{CF}_2\text{CF}_3$	H
A-71	$\text{CH}_2\text{CF}_2\text{CF}_3$	CH_3
A-72	$\text{CH}_2\text{CF}_2\text{CF}_3$	CH_2CH_3
A-73	$\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_3$	H
A-74	$\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_3$	CH_3
A-75	$\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_3$	CH_2CH_3

Los compuestos I son adecuados como fungicidas. Ellos tienen actividad importante contra un amplio espectro de hongos fitopatogénicos, en particular de las clases

Ascomicetes, Deuteromycetes, Phycomicetes y Basidiomicetes. Algunos de ellos actúan sistemáticamente y pueden ser empleados en la protección de cultivos como fungicidas de acción foliar y del suelo.

Ellos son especialmente importante para controlar un gran número de hongos sobre una variedad de plantas de cultivo tales como trigo, centeno, cebada, avena, arroz, maíz, pasto, bananas, algodón, soja, café caña de azúcar, viñedos, especies frutales, ornamentales y vegetales tales como cucurbitáceas, habichuela, tomates, papas y cucurbitáceas, y sobre las semillas de estas plantas.

Especialmente, ellas son adecuadas para controlar las siguientes enfermedades de las plantas:

- *Alternaria Species*, *Podosphaera species*, *Sclerotinia species*, *Physalospora canker* sobre vegetales y fruta,
- *Botrytis cinerea* (moho gris) en fresas, vegetales, ornamentales y viñedo,
- *Corynespora cassiicola* sobre cucurbitáceas,

- Colletotrichum species sobre fruta y vegetales,
- Diplocarpon rosae sobre rosas,
- Elsinoe fawcetti y Diaporthe citri sobre frutos cítricos,
- Sphaeroteca species sobre cucurbitáceas, fresas y rosas
- Cercospora species sobre cacahuete, caña de azúcar, auberginas,
- Erysiphe cichoracearum sobre cucurbitáceas
- Leveillula tarurica sobre paprika, tomates y auberginas,
- Mycosphaerella species sobre manzanas y albaricoque Japonés,
- Gymnosporangium yamadae, Leptotthyrium pomi, Podosphaera leucotricha y Gloedes pomigena sobre manzanas,
- Cladosporium carpophilum sobre peras y albaricoque japonés,
- Especies de fomopsis sobre peras,

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- Especies de fitoftora sobre frutos cítricos, papas, cebollas, especialmente fitoftora infestans sobre papas y tomates,
- Blumeria graminis. (mildew de polvo) sobre cereales,
- Especies fusarium y verticilium sobre varias plantas,
- Glomerela cingulata sobre tee,
- Especies drechslera y bipolaris sobre cereales y arroz,
- Especies de micosphaerella sobre bananos y maní,
- Plasmopara viticola sobre vides,
- Especies de peronospora sobre cebollas, espinacas y crisantemo,
- Faeoisariopsis vitis y sfaceloma ampelina sobre frutos de uvas, pseudocercospora herpotricoides sobre trigo y cebada,
- Especies de pseudoperonospora sobre lúpulo y cohombro,

- Especies de puccinia y especies tifula sobre cereales y césped,
- Piricularia oryzae sobre arroz, especies rhizoctonia sobre algodón, arroz y césped,
- Stagonospora nodorum y septoria tritici sobre trigo,
- Uncinula necator sobre vides,
- Especies de ustilago sobre cereales y caña de azúcar, y
- Especies de venturia (costra) sobre manzanas y peras.

Más aún, los compuestos I son adecuados para controlar hongos dañinos tales como paecilomices variotii en la protección de materiales (por ejemplo, madera, papel, dispersiones de pintura, fibras y tejidos) y en la protección de productos almacenados.

Los compuestos son aplicados al tratar los hongos, y las plantas, semillas, materiales o el suelo a ser protegido contra infección por hongos, con una cantidad

fungicidamente activa de los ingredientes activos. La aplicación se puede efectuar tanto antes como después de la infección de los materiales, plantas o semillas por los hongos.

En general, las composiciones fungicidas comprenden de 0,1 a 95, preferiblemente 0,5 a 90, % en peso de ingrediente activo.

Cuando se utiliza en protección de cultivos, los índices de aplicación van de 0,01 a 2,0 kg de ingrediente activo por ha, dependiendo de la naturaleza del efecto deseado.

En el tratamiento de semillas, las cantidades de ingrediente activo van de 0,001 a 0.1 g, preferiblemente 0,01 a 0,05 g, son generalmente requeridas por kilogramo de semilla.

Cuando se utilizan en la protección de materiales o productos almacenados, el índice de aplicación de ingrediente activo depende de la naturaleza del campo de

aplicación y del efecto deseado. Los índices de aplicación convencionalmente utilizados en la protección de materiales son, por ejemplo, 0,001 g a 2 kg, preferiblemente 0,005 g a 1 kg, de ingrediente activo por metro cúbico de material tratado.

Los compuestos I se pueden convertir en formulaciones habituales, por ejemplo, soluciones, emulsiones, suspensiones, polvos, talcos, pastas y gránulos. La forma de uso depende del propósito particular; en cualquier caso, se debe garantizar una distribución final y uniforme del compuesto de acuerdo con la invención.

Las formulaciones se preparan de manera conocida, por ejemplo, al extender el ingrediente activo con solvente y/o portadores, si se desea utilizando emulsificadores y dispersantes, también es posible utilizar otros solventes orgánicos como solventes auxiliares si se utiliza agua como diluyente los auxiliares que son adecuados son esencialmente: solventes tales como aromáticas (por ejemplo xileno), aromáticos clorinados (por ejemplo clorobenzenos), parafinas (por ejemplo fracciones de

aceite mineral), alcoholes (por ejemplo metanol, butanol), cetonas (por ejemplo ciclohexanona), aminas (por ejemplo etanolamina, dimetilformamida) y agua; portadores tales como minerales naturales del suelo (por ejemplo caolines, arcillas, talco, yeso) y minerales sintéticos del suelo (por ejemplo sílice altamente disperso, silicato); emulsificadores no iónicos y aniónicos (por ejemplo éteres de alcohol graso de polioxietileno, alquilsulfonatos y arilsulfonatos) y dispersantes tales como licores de desperdicio de lignina- sulfito y metilcelulosa.

Los tenso activos adecuados son metales alcalino, metales alcalinotérreos y sales de amonio de ácido lignosulfónico, ácido naftalenesulfónico, ácido fenolsulfónico, ácido dibutilnaftalenesulfónico, alquilaril-sulfonates, alquil sulfatos, alquilsulfonatos, sulfatos y ácidos grasos de alcohol graso y sus sales de metal alcalino y alcalinoterreo, sales de éter de glicol alcohol graso sulfatado, condensados de naftaleno sulfonatado y derivados de naftaleno o de ácidonaftalenesulfónico con fenol o formaldehído, polioxietileno octifenil éter, isooctilfenol etoxilado,

octilfenol, nonilfenol, alquilfenol poliglicol éteres, tributilfenil poliglicol éteres, alcoholes de alquilaril polieter, alcohol isotridecilo, alcohol graso /condensados de oxido de etileno, aceite etoxilado de castor, éteres de alquilo de polioxietileno, polioxipropileno etoxilado, lauril alcohol poliglicol éter acetal, esteres de sorbitol, licores de desperdicio de lignina-sulfito y metilcelulosa.

Las sustancias que son adecuadas para la preparación de soluciones directamente pulverizables, emulsiones, pastas o dispersiones en aceite son fracciones de aceite mineral de punto de ebullición medio a alto, tales como aceite de kerosene o diesel, adicionalmente aceites de alquitrán de hulla y aceites de origen vegetal o animal, hidrocarburos alifáticos, cíclicos y aromáticos, por ejemplo benceno, tolueno, xileno, parafina, tetrahidronaftaleno, naftalenos alquilatados o sus derivados, metanol, etanol, propanol, butanol, cloroformo, tetracloruro de carbono, ciclohexanol, ciclohexanona, clorobenceno, isoforona, solventes fuertemente polares, por ejemplo, dimetilformamida, dimetil sulfóxido, N-metilpirrolidona y agua.

Los polvos, materiales para esparcimiento y polvos se pueden preparar al mezclar o moler concomitantemente las sustancias activas con un portador sólido.

Los gránulos, por ejemplo, gránulos recubiertos, gránulos impregnados y gránulos homogéneos, se pueden preparar al unir los ingredientes activos aportadores sólidos. Ejemplos de portadores sólidos son tierras minerales, tales como sílices, sílica gel, silicatos, talco, kaolin, arcilla de atapulgita, piedra caliza, cal, yeso, bolo, loess, arcilla, dolomite, tierra de diatomaceas, sulfato de calcio, sulfato de magnesio, oxido de magnesio, materiales sintéticos del suelo, fertilizante, por ejemplo, sulfato de amonio, fosfato de amonio, nitrato de amonio, ureas, y productos de origen vegetal, tales como harinas de cereal, harinas de corteza de árbol, harinas de madera y harinas de cáscara de nuez, polvos de celulosa y otros portadores sólidos.

En general, las formulaciones comprenden desde 0,01 a 95% en peso, preferiblemente desde 0,1 a 90% en peso,

del ingrediente activo. Los ingredientes activos son empleados en una pureza que va desde 90% a 100%, preferiblemente 95% a 100% (de acuerdo al espectro RMN).

Las siguientes son formulaciones de ejemplos:

- I. 5 partes en peso de un compuesto de acuerdo con la invención son mezcladas íntimamente con 95 partes en peso de un caolín finamente dividido. Esto da un polvo que comprende 5% en peso del ingrediente activo.
- II. 30 partes en peso de un compuesto de acuerdo con la invención son mezcladas íntimamente con una mezcla de 92 partes en peso de sílica gel pulverulenta y 8 partes en peso de aceite de parafina que ha sido pulverizado sobre la superficie de esta sílica gel. Esto da una formulación del ingrediente activo con buenas

propiedades de adhesión (comprende 23% en peso del ingrediente activo).

III. 10 partes en peso de un compuesto de acuerdo con la invención son disueltas en una mezcla compuesta de 90 partes en peso xileno, 6 partes en peso de aducto de 8 a 10 moles de oxido de etileno y 1 mol de N-monoetanolamida de ácido oleico, 2 partes en peso de dodecilbenzenesulfonato de calcio y 2 partes en peso de aducto de 40 mol de oxido de etileno y 1 mol de aceite de castor (comprende 9% en peso del ingrediente activo).

IV. 20 partes en peso de un compuesto de acuerdo con la invención se disuelven en una mezcla compuesta de 60 partes en peso de ciclohexanona, 30 partes en peso de isobutanol, 5 partes en peso del aducto de 7 molde oxido de etileno y 1 mol isooctilfenol y 5 partes en peso del aducto de 40 moles de oxido de etileno y 1 mol de aceite de

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castor (comprende 16% en peso del ingrediente activo).

- V. 80 partes en peso de un compuesto de acuerdo con la invención se mezclan completamente con 3 partes en peso de disobutilnaftaleno-alfa-sulfonato de sodio, 10 partes en peso de la sal de sodio de un ácidolignosulfónico de desperdicio de sulfito y 7 partes en peso de sílica gel pulverulenta, y la mezcla se muele en un molino de martillo (comprende 80% en peso del ingrediente activo).

- VI. 90 partes en peso de a compuesto de acuerdo con la invención se mezclan con 10 partes en peso de N-metil- α -pirrolidona, que da una solución que es adecuada para usar en la forma de micro gotas (comprende 90% en peso de del ingrediente activo).

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VII. 20 partes en peso de un compuesto de acuerdo con la invención se disuelven en una mezcla compuesta de 40 partes en peso de ciclohexanona, 30 partes en peso de isobutanol, 20 partes en peso del aducto de 7 moles de oxido de etileno y 1 mol de isooctilfenol y 10 partes en peso del aducto de 40 mol oxido de etileno y 1 mol de aceite de castor. Vertiendo la solución en 100.000 partes en peso de agua y distribuyendo finamente allí da una dispersión acuosa que comprende 0,02% en peso del ingrediente activo.

VIII. 20 partes en peso de un compuesto de acuerdo con la invención se mezclan completamente con 3 partes en peso de diisobutilnaftaleno- α -sulfonato de sodio, 17 partes en peso de la sal de sodio de un ácido lignosulfónico de un licor de desperdicio de sulfito y 60 partes en peso de sílica gel pulverulenta, y la mezcla se muele en un molino de martillo. Distribuyendo finamente la mezcla en 20,000 partes en peso de agua da una mezcla de pulverizado que comprende 0,1% en peso del ingrediente activo.

Los ingredientes activos se pueden utilizar como tales, en la forma de sus formulaciones o las formas de uso preparadas de estos, por ejemplo, en la forma de soluciones directamente pulverizables, polvos, suspensiones, o dispersiones, emulsiones, dispersiones de aceite, pastas, polvos, materiales para pulverizar, o gránulos, por medio de rociantes, atomizantes, pulverizantes, dispersándolos o vertiéndolos. Las formas de uso dependen completamente de los propósitos pretendidos; en cualquier caso, se pretende garantizar la distribución más fina posible del ingrediente activo de acuerdo con la invención.

Las formas de uso acuosas se pueden preparar de concentrados de emulsión, pastas o polvos humectables (polvos rociables, dispersiones de aceite) al agregar agua. Para preparar emulsiones como pastas o dispersiones de aceite, las sustancias como tales o disueltas en un aceite o solvente, se pueden homogenizar en agua por medio de humectantes, sustancias inductoras de pegajosidad, dispersantes o emulsificadores y, si es

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apropiado, solvente o aceite, y tales concentrados son adecuados para disolución con agua.

Las concentraciones de ingrediente activo en los productos listos para usar se pueden variar dentro de rangos sustanciales. En general, ellos van de 0,0001 a 10%, preferiblemente de 0,01 a 1%.

Los ingredientes activos también se pueden utilizar exitosamente en los procesos de volumen ultra bajo (UVL), es posible aplicar formulaciones que comprenden más del 95% en peso de ingrediente activo, o aún el ingrediente activo sin aditivos.

Varios tipos de aceites, herbicidas, fungicidas, otros pesticidas, o bactericidas se pueden agregar a los ingredientes activos, si es apropiado también solo inmediatamente antes del uso (mezcla en el tanque). Estos agentes se pueden mezclar con los agentes de acuerdo con la invención en una proporción en peso de 1: 10 a 10: 1.

En la forma de uso como fungicidas, las composiciones de acuerdo con la invención también pueden estar presentes junto con otros ingredientes activos, por ejemplo, herbicidas, insecticidas, reguladores del crecimiento, fungicidas o u otros con fertilizantes. La mezcla de los compuestos I o las composiciones que los comprenden en la forma de uso como fungicidas con otros fungicidas frecuentemente da como resultado un espectro de acción fungicida más amplio.

La siguiente lista de fungicidas, junto con los cuales los compuestos de acuerdo con la invención se pueden utilizar, pretende ilustrar las posibles combinaciones, pero no imponer ninguna limitación:

Azufre, ditiocarbamatos y sus derivados, tales como hierro (III) dimetilditiocarbamato, dimetilditiocarbamato de zinc, etilenebisditiocarbamato de zinc, etilenebisditiocarbamato de manganeso,

etilenodiaminobisditiocarbamato de zinc manganeso,
 disulfuro tetrametiltiuram, complejo de amonio de
 zinc (N,N-etilenebisditiocarbamato), complejo de amonio de
 zinc (N,N'-propilenebisditiocarbamato), zinc (N,N'-
 propilenebis- ditiocarbamato), N,N'-polipropilenebis
 (tiocarbamoil) disulfuro; nitro derivados, tales como
 dinitro (1-metilheptil) fenilo crotonato, 2-sec-butil-
 4,6-dinitrofenilo 3,3-dimetilacrilato, 2-sec-butil-4,6-
 dinitrofenilisopropilo carbonato, diisopropilo 5-nitro-
 isoftalato; sustancias heterocíclicas, tales como 2-
 heptadecil-2-imidazolino acetato, 2,4-dicloro-6-(o-
 cloroanilino)-s-triazina, O,O-dietil
 ftalimidofosfonotioato, 5-amino-1-[bis(dimetilamino)
 fosfinil]-3-fenilo-1,2,4-triazol, 2,3-diciano-1,4-
 ditioantraquinona, 2-tio-1,3-ditiolo[4,5-b]quinoxalino,
 metilo 1-(butilcarbamoil)-2-benzimidazolcarbamato, 2-
 metoxicarboniloaminobenzimidazol, 2-(2-furil)
 benzimidazol, 2-(4-tiazolil)benzimidazol, N-(1,1,2,2-
 tetracloroetiltio) tetrahidroftalimida, N-
 triclorometiltiotetrahidroftalimida, N-
 triclorometiltioftalimida, ácido 5-cloro-2-ciano-4-p-
 tolil-imidazol-1-sulfonico dimetilamida, N-
 diclorofluorometiltio-N',N'-dimetil-N-fenilosulfo-
 diamida, 5-etoxi-3-triclorometil-1,2,3-tiadiazol, 2-

tiocianatometiltiobenzotiazol, 1,4-dicloro-2,5-
 dimetoxibenceno, 4-(2-clorofenilohidrazono)-3-metil-5-
 isoxazolona, piridine-2-tiol 1-oxida, 8-hidroxiquinolino
 o su sal de cobre, 2,3-dihidro-5-carboxanilido-6-metil-1,
 4-oxatiino, 2,3-dihidro-5-carboxanilido-6-metil-1,4-
 oxatiino 4,4-dioxida, 2-metil-5,6-dihidro-4H-piran-3-
 carboxanilida, 2-metilfuran-3-carboxanilida, 2,5-
 dimetilfuran-3-carboxanilida, 2-cloro-N-(4'-cloro-
 bifenilo-2-il)-nicotinamida, 2,4,5-trimetilfuran-3-
 carboxanilida, N-ciclohexil-2,5-dimetilfuran-3-
 carboxamida, N-ciclohexil-N-metoxi-2,5-dimetilfuran-3-
 carboxamida, 2-metilbenzanilida, 2-yodobenzanilida, N-
 formil-N-morfolino-2,2,2-tricloroetil acetal, piperazin-
 1,4-diilbis-1-(2,2,2-tricloro-etil) formamida, 1-(3,4-
 dicloroanilino)-1-formilamino-2,2,2-tricloroetano; 2,6-
 dimetil-N-tridecilmorfolino o sus sales, 2,6-dimetil-N-
 ciclododecilmorfolino o sus sales, N-[3-(p-tert-
 butilfenilo)-2-metilpropil]-cis-2,6-dimetil-morfolino, N-
 3-[(p-tert-butilfenilo)-2-metilpropil]-piperidino, 1-[2-
 (2,4-diclorofenilo)-4-etil]-1,3-dioxolan-2-il-etil-1H-
 1,2,4-triazol, 1-[2-(2,4-diclorofenilo)-4-N-propil-1, 3-
 dioxolan-2-il-etil]-1H-1,2,4-triazol, N-(N-propil)-N-(2,
 4,6-triclorofenoxietil)-N'-imidazolil-urea, 1-(4-
 clorofenoxi)-3,3-dimetil-1-(1H-1,2,4-triazol-1-il) -2-

butanona, 1-(4-clorofenoxi)-3,3-dimetil-1-(1H-1,2,4-triazol-1-il)-2-butanol, (2RS,3RS)-1-[3-(2-clorofenilo)-2-(4-fluorofenilo)-oxiran-2-ilmetil]-1H-1,2,4-triazol, α -(2-clorofenilo)- α -(4-clorofenilo)-5-pirimidinemetanol, 5-butil-2-dimetilamino-4-hidroxi-6-metilpirimidina, bis(p-clorofenilo)-3-piridinemetanol, 1,2-bis(3-etoxicarbonilo-2-tioureido)benceno, 1,2-bis(3-metoxicarbonilo-2-tioureido)benceno, estrobilurinas tales como azoxistrobina, cresoxim metil, metil-e-metoxiimino- $[\alpha$ -(2-fenoxifenil)-acetamida, metilo E-metoxiimino- $[\alpha$ -(2,5-dimetilfenoxi)-o-tolil]acetamida, picoxistrobin, piraclostrobin, trifloxistrobin, anilinopirimidinas tales como N-(4,6-dimetilpirimidin-2-il)anilina, N-4-metil-6-(1-propinilo) pirimidin-2-il-aniline, N-[4-metil-6-ciclopropilpirimidin-2-il]-anilina, fenilpirroles tales como 4-(2,2-difluoro-1,3-benzodioxol-4-il)pirrol-3-carbonitrilo, cinnamamidas tales como 3-(4-clorofenilo)-3-(3,4-dimetoxifenil)acriloilmorfolino, 3-(4-fluorofenilo)-3-(3,4-di-metoxi-fenilo) acriloilmorfoline, y una variedad de fungicidas tales como acetato de dodecilguanidina, 3-3-(3,5-dimetil-2-oxiciclohexil)-2-hidroxietil glutarimida, hexaclorobenceno, metilo N-(2,6-dimetilfenilo)-N-(2-furoil)-DL-alaninato, DL-N-(2,6-

dimetilfenilo)-N-(2'-metoxiacetil)-alanina metil ester,
 N-(2,6-dimetilfenilo)-N-cloroacetil-D,L-2-amino-
 butirolactona, DL-N-(2,6-dimetilfenilo)-N-(fenilacetil)
 alanino metil ester, 5-metil-5-vinilo-3-(3,5-
 diclorofenilo)-2,4-dioxo-1,3-oxazolidino, 3-[3,5-
 diclorofenilo (5-metil-5-metoximetil)-1,3-oxazolidin-2,4-
 diona, 3-(3,5-diclorofenil)-1-
 isopropilcarbamoilhidantoin, N-(3,5-diclorofenil)-1,2-
 dimetilciclopropano-1,2-dicarboximida, 2-ciano-[N-
 (etilaminocarbonilo)-2-metoximino]acetamida, 3,5-dicloro-
 N-(3-cloro-1-etil-1-metil-2-oxo-propil)-4-metil-
 benzamida, 1-(3-bromo-6-metoxi-2-metil-fenilo)-1-(2, 3,4-
 trimetoxi-6-metil-fenilo)-metanona, 1-[2-(2,4-di-cloro-
 fenilo)pentil]-1H-1,2,4-triazol, 2,4-difluoro- α -(1H-1,2,
 4-triazolil-1-metil)benzhidril alcohol, N-(3-cloro-2,6-
 dinitro-4-trifluorometilfenilo)-5-trifluorometil-3-cloro-
 2-aminopiridina, 1-((bis(4-fluorofenilo)metil-silil)
 metil)-1H-1,2,4-triazol.

Ejemplos de Síntesis

Con la debida modificación de los compuestos de partida, los protocolos mostrados en los ejemplos de síntesis adelante fueron utilizados para obtener compuestos I adicionales. Los compuestos resultantes I, junto con los datos físicos son listados en la tabla I que sigue.

Ejemplo I

Preparación de dietil (2-fluoro-6-metilfenil)-malonato.

Se agregó dietilmalonato (0.49 moles) a una mezcla de hidruro de sodio (0,51 mol) y 1,4-dioxano (140 ml) a 60° C durante dos horas. La mezcla se agitó durante 10 minutos a 60° C y se agregó bromuro de cobre (I) (0,05 mol). Después de 15 minutos, se agregó a una solución de 2-bromo-3-fluorotolueno (0,25 mol) en 10 ml de 1,4-dioxano. La mezcla de reacción se mantuvo a 100° C durante aproximadamente 15 horas y después se enfrió hasta aproximadamente 15° C 35 ml de ácido clorhídrico 12 N se agregó. El precipitado se filtró, el filtrado se extrajo con dietiléter. La fase orgánica se separó, se

secó y se filtró. El filtrado se evaporó para producir 42 g del compuesto del título.

Ejemplo 2

Preparación de 5,7-dihidroxi-6-(2-fluoro-6-metilfenil)-[1,2,4]-triazolo-[1,5- α]pirimidina

Una mezcla de 3-amino-1,2,4-triazol (14 g), dietil (2-fluoro-6-metilfenil)-malonato (0,17 mol, Ej. 1) y tributilamina (50 ml) se calienta a 180° C durante 6 horas; después de enfriar a 70° C una solución de 21 g de hidróxido de sodio en 200 ml de agua se agregó y la mezcla de reacción se agitó durante 30 minutos. La fase orgánica se separó y la fase acuosa se extrajo con dietiéter. La fase acuosa se acidificó con ácido clorhídrico concentrado. El precipitado se recolectó por filtración y se secó para producir 41 g del compuesto del título.

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Ejemplo 3

Preparación de 5,7-dicloro-6-(2-fluoro-6-metilfenil)-[1,2,4]-triazolo-[1,5- α]pirimidina

Una mezcla del compuesto en el ejemplo 2 (30 g) de oxicloruro de fósforo (50 ml) se reflujo durante 8 horas. El oxicloruro de fósforo fue parcialmente destilado. El residuo se vertió en una mezcla de diclorometano y agua. La capa orgánica se separó, se secó y se filtró. El filtrado se concentró in vacuo para producir 27 g del compuesto del título de un p.f. de 130° C.

Ejemplo 4

Preparación de 5-cloro-6-(2-fluoro-6-metilfenil)-7-isopropilamino-[1,2,4]-triazolo[1,5- α]pirimidina [I-8]

Una mezcla de isopropilamina (1,5 mmol), trietilamina (1,5 mmol) y diclorometano (10 ml) se agregó a una solución de 1,5 mmol del producto del ejemplo 3 en 20 ml de diclorometano bajo agitación. La mezcla de reacción se agitó durante aproximadamente 16 horas a aproximadamente

20 a 25° C y subsecuentemente se lavó con ácido clorhídrico al 5%. La capa orgánica se separó. Se secó, y se filtró. El filtrado se evaporó y el residuo se cromatografió para producir 0,46 g del compuesto del título de p.f. 128° C.

Ejemplo 5

Preparación de 5-ciano-6-(2-fluoro-6-metilfenil)-7-(4-metilpiperidin-1-il)-[1,2,4]-triazolo[1,5- α]pirimidina
[I-49]

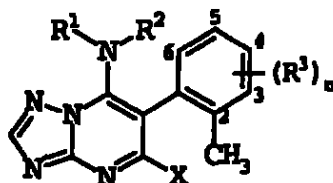
Una mezcla de 0,1 mol de uu compuesto I-9 y cianuro de t etrametilamonio (0,25 mol) en 750 ml de dimetilformamida (DMF) se agitó durante 16 horas a aproximadamente 20 a 25° C. a esta mezcla se agregó agua y metil-terc-butiléter (MTBE), la fase orgánica se separó, se lavó con agua, se secó y se filtró. El filtrado se evaporó y el residuo se cromatografió para producir 6,51 g del compuesto del título de p.f. 211° C.

Ejemplo 6

Preparación de 5-metoxi-6-(2-fluoro-6-metilfenil)-7-(4-metilpiperidin-1-il)-[1,2,4]-triazolo[1,5- α]pirimidina [I-59]

Después de haber agregado una solución de metanolato de sodio (30%, 71,5 mmol) a una solución de 65 mmol del compuesto I-9 en 400 ml de metanol seco se agregó esta mezcla que fue agitada durante aproximadamente 16 horas a aproximadamente 20 a 25° C. el metanol se evaporó y el residuo se disolvió en diclorometano. La fase orgánica se lavó con agua, se secó y se filtró. El filtrado se evaporó y el residuo se cromatografió para producir 4,32 g del compuesto del título de p.f. 142° C.

Tabla I



I

No.	R ¹	R ²	(R ³) _n	Cl	Datos físicos (p.f.[°C]; ¹ H-RMN δ [ppm])
I-1	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	4, 6-(CH ₃) ₂	Cl	131
I-2	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		4, 6-(CH ₃) ₂	Cl	138
I-3	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	4-OCH ₃ -6-CH ₃	Cl	74
I-4	(±)CH(CH ₃)-CH(CH ₃) ₃	H	4-OCH ₃ -6-CH ₃	Cl	163
I-5	CH ₂ CF ₃	H	4-OCH ₃ -6-CH ₃	Cl	191
I-6	H	H	6-F	Cl	250
I-7	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	6-F	Cl	124
I-8	CH(CH ₃) ₂	H	6-F	Cl	128
I-9	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		6-F	6-F	142
I-10	ciclopentilo	H	6-F	Cl	159

I-11	CH_2CH_3	CH_2CH_3	6-F	Cl	147
I-12	$\text{CH}_2\text{CH}_2\text{CH}_3$	$\text{CH}_2\text{CH}_2\text{CH}_3$	6-F	Cl	124
I-13	$\text{CH}(\text{CH}_3)_2$	CH_3	6-F	Cl	159
I-14	$(\pm)\text{CH}(\text{CH}_3)-\text{CH}_2\text{CH}_3$	H	6-F	Cl	115
I-15	$(S)\text{CH}(\text{CH}_3)-\text{CH}_2\text{CH}_3$	H	6-F	Cl	123
I-16	$(R)\text{CH}(\text{CH}_3)-\text{CH}_2\text{CH}_3$	H	6-F	Cl	129
I-17	$(\pm)\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_2$	H	6-F	Cl	A) 133 / B) 138
I-18	$(S)\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_2$	H	6-F	Cl	A) 120 / B) 130
I-19	$(R)\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_2$	H	6-F	Cl	A) 119 / B) 131
I-20	$(\pm)\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_3$	H	6-F	Cl	A) 148 / B) 174
I-21	$(S)\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_3$	H	6-F	Cl	A) 160 / B) 203
I-22	$(R)\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_3$	H	6-F	Cl	A) 159 / B) 203
I-23	$(\pm)\text{CH}(\text{CH}_3)-\text{CF}_3$	H	6-F	Cl	A) 149 / B) 56
I-24	$(S)\text{CH}(\text{CH}_3)-\text{CF}_3$	H	6-F	Cl	A) 166 / B) 70

I-25	(R) CH(CH ₃)-CF ₃	H	6-F	Cl	A) 167 / B) 70
I-26	CH ₂ CF ₃	H	6-F	Cl	173
I-27	H	H	4-F	Cl	281
I-28	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	4-F	Cl	115
I-29	CH(CH ₃) ₂	H	4-F	Cl	94
I-30	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		4-F	Cl	168
I-31	ciclopentilo	CH ₂ CH ₃	4-F	Cl	141
I-32	CH ₂ CH ₃	CH ₂ CH ₂ CH ₃	4-F	Cl	156
I-33	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃	4-F	Cl	121
I-34	CH(CH ₃) ₂	CH ₃	4-F	Cl	153
I-35	(±) CH(CH ₃)-CH ₂ CH ₃	H	4-F	Cl	118
I-36	(S) CH(CH ₃)-CH ₂ CH ₃	H	4-F	Cl	125
I-37	(R) CH(CH ₃)-CH ₂ CH ₃	H	4-F	Cl	126
I-38	(±) CH(CH ₃)-CH ₃) ₂	H	4-F	Cl	132

I-39	(S) CH(CH ₃) -CH ₃) ₂	H	4-F	Cl	124
I-40	(R) CH(CH ₃) -CH ₃) ₂	H	4-F	Cl	124
I-41	(±) CH(CH ₃) -CH ₃) ₃	H	4-F	Cl	162
I-42	(S) CH(CH ₃) -CH ₃) ₃	H	4-F	Cl	156
I-43	(R) CH(CH ₃) -CH ₃) ₃	H	4-F	Cl	156
I-44	(±) CH(CH ₃) CF ₃	H	4-F	Cl	163
I-45	(S) CH(CH ₃) CF ₃	H	4-F	Cl	145
I-46	(R) CH(CH ₃) CF ₃	H	4-F	Cl	145
I-47	CH ₂ CF ₃	H	4-F	Cl	167
I-48	CH ₂ CF ₃	H	4-F-6-CH ₃	Cl	220
I-49	-(CH ₂) ₂ CH(CH ₃) (CH ₂) ₂ -		6-F	CN	211
I-50	-(CH ₂) ₂ CH(CH ₃) (CH ₂) ₂ -		6-F	OCH ₃	142
I-51	-(CH ₂) ₂ CH(CH ₃) (CH ₂) ₂ -		6-F	CH ₃	145
I-52	Ciclopentilo	H	4, 6-(CH ₃) ₂	Cl	200

I-53	CH_2CH_3	CH_2CH_3	4, 6- $(\text{CH}_3)_2$	Cl	105
I-54	$\text{CH}_2\text{CH}_2\text{CH}_3$	$\text{CH}_2\text{CH}_2\text{CH}_3$	4, 6- $(\text{CH}_3)_2$	Cl	99
I-55	($\pm$) $\text{CH}(\text{CH}_3)-\text{CH}_2\text{CH}_3$	H	4, 6- $(\text{CH}_3)_2$	Cl	191
I-56	(S) $\text{CH}(\text{CH}_3)-\text{CH}_2\text{CH}_3$	H	4, 6- $(\text{CH}_3)_2$	Cl	184
I-57	(R) $\text{CH}(\text{CH}_3)-\text{CH}_2\text{CH}_3$	H	4, 6- $(\text{CH}_3)_2$	Cl	184
I-58	($\pm$) $\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_2$	H	4, 6- $(\text{CH}_3)_2$	Cl	107
I-59	(S) $\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_2$	H	4, 6- $(\text{CH}_3)_2$	Cl	87
I-60	(R) $\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_2$	H	4, 6- $(\text{CH}_3)_2$	Cl	87
I-61	($\pm$) $\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_3$	H	4, 6- $(\text{CH}_3)_2$	Cl	79
I-62	(S) $\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_3$	H	4, 6- $(\text{CH}_3)_2$	Cl	81
I-63	(R) $\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_3$	H	4, 6- $(\text{CH}_3)_2$	Cl	81
I-64	$\text{CH}_2\text{C}(\text{CH}_3)_2$	CH_2CH_3	4-Cl	Cl	137
I-65	$\text{CH}(\text{CH}_3)_2$	H	4-Cl	Cl	136
I-66	$-(\text{CH}_2)_2\text{CH}(\text{CH}_3)(\text{CH}_2)_2-$		4-Cl	Cl	173

I-67	ciclopentilo	H	4-Cl	Cl	147
I-68	CH_2CH_3	CH_2CH_3	4-Cl	Cl	167
I-69	$\text{CH}_2\text{CH}_2\text{CH}_3$	$\text{CH}_2\text{CH}_2\text{CH}_3$	4-Cl	Cl	149
I-70	$\text{CH}(\text{CH}_3)_2$	CH_3	4-Cl	Cl	159
I-71	$(\pm) \text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_3$	H	4-Cl	Cl	128
I-72	$(S) \text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_3$	H	4-Cl	Cl	114
I-73	$(R) \text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_3$	H	4-Cl	Cl	114
I-74	$(\pm) \text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_2$	H	4-Cl	Cl	116
I-75	$(S) \text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_2$	H	4-Cl	Cl	130
I-76	$(R) \text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_2$	H	4-Cl	Cl	130
I-77	$(\pm) \text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_3$	H	4-Cl	Cl	159
I-78	$(S) \text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_3$	H	4-Cl	Cl	159
I-79	$(R) \text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_3$	H	4-Cl	Cl	159
I-80	$(\pm) \text{CH}(\text{CH}_3)-\text{CF}_3$	H	4-Cl	Cl	184

I-81	(S) CH (CH ₃) -CF ₃	H	4-Cl	Cl	143
I-82	(R) CH (CH ₃) -CF ₃	H	4-Cl	Cl	143
I-83	CH ₂ CH ₃	H	4-Cl	Cl	206
I-84	CH ₂ C (CH ₃) =CH ₂	CH ₂ CH ₃	4-CH ₃	Cl	158
I-85	CH (CH ₃) ₂	H	4-CH ₃	Cl	145
I-86	CH ₂ CH ₃	CH ₂ CH ₃	4-CH ₃	Cl	141
I-87	(±) CH (CH ₃) -CH ₂ CH ₃	H	4-CH ₃	Cl	122
I-88	(S) CH (CH ₃) -CH (CH ₃) ₃	H	4-CH ₃	Cl	108
I-89	(R) CH (CH ₃) -CH (CH ₃) ₃	H	4-CH ₃	Cl	108
I-90	- (CH ₂) ₂ CH (CH ₃) (CH ₂) ₂ -		4-COOH ₃	Cl	8,45 (s) ; 8.05 (s) ; 7,95 (d) ; 7,25 (d) ; 4,0 (s) ; 3,85 (d) ; 3,45 (d) 2, 7 (t) ; 2,65 (t) ; 2,25 (s) ; 1,55 (m) ; 1,25 (m) ; 0,9 (d)

I-91	(R) CH(CH ₃)-CH(CH ₃) ₂	H	4-COOH ₃	Cl	8,35(s); 8,1(S); 8,0(d); 7,35(d); 6,2(m); 3,95(s) 3,1(m); 2,25(s); 1,55(sept); 1,2(d); 0,95(d); 0,9(d)
I-92	(S) CH(CH ₃)-CF ₃	H	4-COOH ₃	Cl	8,4(s); 8,15(s); 8,0(d); 7,35(m); 5,7(m); 4,6(m); 3,95(s); 2,3(s); 2,25(s); 1.4(d); 1,3(d)
I-93	CH ₂ CF ₂ CF ₃	H	6-F	Cl	162
I-94	CH ₂ CF ₂ CF ₂ CF ₃	H	6-F	Cl	165
I-95	CH ₂ CF ₂ CF ₃	H	4-F	Cl	176
I-96	CH ₂ CF ₂ CF ₂ CF ₃	H	4-F	Cl	138
I-97	CH ₂ CF ₂ CF ₃	H	4-Cl	Cl	164
I-98	CH ₂ CF ₂ CF ₂ CF ₃	H	4-F	Cl	126
I-99	H	H	4-F	Cl	176

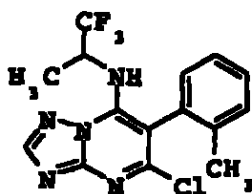
En algunos casos de grupos quirales R₁ debido a la rotación impedida del grupo fenilo existe dos diastereómeros A) y B) que pueden diferir en sus propiedades físicas.

Ejemplos de acción contra hongos dañinos

La acción fungicida de los compuestos de la fórmula I se demostró mediante los siguientes experimentos:

Los compuestos activos, separadamente o juntos, fueron formulados como una emulsión al 10% en una mezcla de 70% en peso de ciclohexanona, 20% en peso de Nekanil® LN (Lutensol® AP6, agente humectante que tiene acción emulsificante y dispersante basado en alquilfenoles etoxilados y 10% en peso de Wettol® EM (emulsificador no iónico basado en aceite de castor etoxilado) y diluido con agua a la concentración deseada.

El Compuesto A conocido de la WO-A-98/46608 (No. 9) sirvió como compuesto activo comparativo



Ensayo de comparación 1 - Control fungicida de añublo temprano en tomates (*Alternaria Solani*)

Plántulas jóvenes de plantas de tomate de la variedad "Grosse Fleischtomate St. Pierre" crecieron en materas hasta la etapa de 2 a 4 hojas. Estas plantas fueron rociadas para escurrir con una suspensión acuosa, que contiene la concentración del ingrediente activo mencionado en la tabla de adelante, preparada de una solución de almacenamiento que contiene 10% del ingrediente activo, 85% de ciclohexanona y 5% de emulsificador. Al siguiente día, las plantas tratadas fueron inoculadas con una suspensión acuosa de *Alternaria Solana* que contiene $0,2 \times 10^6$ esporas por ml. Luego las plantas del ensayo fueron transferidas inmediatamente a una cámara húmeda. Después de 6 días con de 20 a 23° C y una humedad relativa cercana al 100%, la extensión del

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ataque fungoso sobre las hojas fue visualmente evaluada como un porcentaje del área enferma de la hoja.

En este texto, las plantas que han sido tratadas con 63 ppm de los compuestos I-23 y I-24, respectivamente, mostraron una infección de no más del 3%, mientras que las plantas tratadas con 63 ppm del compuesto A de comparación fueron efectuadas con el 15%, y las plantas no tratadas fueron infectadas con el 90%.

Ensayo de comparación 2, control fungicida de Midew polvoroso sobre trigo causado por *Blumeria graminis* f. sp. *Tritici*

Las primeras hojas completamente desarrolladas del trigo crecido en la materia de la variedad "Kanzler" se rociaron para escurrir con una suspensión acuosa, que contiene la concentración del ingrediente activo o su mezcla mencionada en la tabla de adelante, preparada de una solución de almacenamiento que contiene 10% del ingrediente activo, 85% de ciclohexanona y 5% de

emulsificador. Al siguiente día, las plantas tratadas fueron inoculadas con esporas de *Blumeria graminis* f. sp. *Tritici* al agitar plantas de almacenamiento fuertemente infectadas sobre las materas tratadas. Después de cultivo en el invernadero durante 7 días a 22-26° C y una humedad relativa entre el 60 y el 90% la extensión del ataque fungoso sobre las hojas se evaluó visualmente como porcentaje del área enferma de la hoja.

En este ensayo, las plantas que habían sido tratadas con 63 ppm del compuesto 1-23 y 1-24, respectivamente, mostraron una infección de no más del 3%, mientras que las mismas plantas tratadas con 63 ppm del compuesto A de comparación fueron infectadas por un 30%, y las plantas no tratadas se infectaron con un 85%.

Ensayo de comparación 3 - control fungicida mildew bajo de uva (*Plasmopara viticola*)

Cortes de uva del cultivo "Müller-Thurgau" crecieron en materas hasta la etapa de 4 a 5 hojas. Estas plantas

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fueron rociadas para escurrir con una suspensión acuosa, que contenía la concentración del ingrediente activo o su mezcla mencionada en la tabla de adelante, preparada de una solución de almacenamiento que contiene 10% del ingrediente activo, 85% de ciclohexanona y 5% de emulsificador. Las plantas se les permitió secarse al aire. Al siguiente día ellas se inocularon con una suspensión acuosa de esporas de *Plasmopara viticola* al rociar estas por el lado de las hojas más bajas. Luego las plantas de ensayo fueron transferidas inmediatamente durante 24 h a una cámara húmeda con 22-24° C y una humedad relativa cercana al 100%. Durante un periodo de cinco días, el cultivo siguió en un invernadero a 20 - 25° C y la humedad relativa aproximadamente 50-80%. Para estimular el surgimiento de los síntomas de la enfermedad, las plantas fueron transferidas a una cámara húmeda de nuevo durante 24 horas. Luego la extensión del ataque fungicida sobre la superficie de las hojas inferiores fue visualmente evaluada como un porcentaje del área enferma de la hoja.

En este ensayo, las plantas que habían sido tratadas con 250 ppm de los compuestos 1-23 y 1-24, respectivamente

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mostraron una infección de no más del 7%, mientras que las plantas tratadas con 250 ppm del compuesto A de comparación, y las plantas no tratadas fueron infectadas con el 80%.

Ejemplo de Uso 1 - control fungicida de añublo temprano en tomates (*Alternaria solani*)

El ensayo se condujo como se describió en el ensayo de comparación 1.

En este ensayo, las plantas que habían sido tratadas con 250 ppm de los compuestos I - 7, I - 9, I - 10, I - 28, I - 30, I - 35, I - 38, I - 41, I - 44, I - 66, y I - 83, respectivamente, no mostraron infección, mientras que las plantas no tratadas se infectaron hasta un 90%.

Ejemplo de uso 2 - Control fungicida de mildew polvoroso sobre trigo causado por *Blumeria graminis* f. sp. *Tritici*

El ensayo fue conducido como se describió en el ensayo de comparación 2

En este ensayo, las plantas que habían sido tratadas con 250 ppm de los compuestos I - 14, I - 28, I - 30, I - 35, I - 38, I - 41, I - 44, respectivamente, mostraron una infección de no más del 5%, mientras que las plantas no tratadas fueron infectadas con un 85%.

Ejemplo de uso 3 - Control de fungicida de mildew bajo de uva (*Plasmopara viticola*)

Las hojas de las vides en materia de la variedad "Müller Thurgau" se rociaron con licores acuosos hechos de la solución de almacenamiento que consiste de 10% de ingrediente activo, 85% de ciclohexanona y 5% de emulsificador. Para evaluar la duración de la acción, las plantas fueron levantadas, después de que la capa rociada había secado, en el invernadero durante 8 días. Luego las hojas fueron infectadas con suspensión de zoosporas del hongo *Plasmopara viticola*, ubicado en una cámara saturada

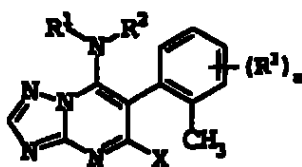
de vapor a 24° C, y luego mantenida durante 5 días en un invernadero con 20 a 30° C. para acelerar e intensificar la descarga de esporangioforas, las plantas fueron entonces de nuevo ubicadas en la cámara de humedad durante 16 horas. La extensión del ataque fungoso fue entonces evaluada sobre los lados interiores de las hojas.

En este ensayo, las plantas que habían sido tratadas con 250 ppm de los compuestos I - 7, I - 9, I - 10, I - 35, I - 38, y I - 44, respectivamente, mostraron una infección de 3 al 40%, mientras que las plantas no tratadas fueron infectadas hasta un 80%.

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REIVINDICACIONES

1. 6-(2-tolil)-triazolopirimidinas sustituidas de la fórmula I



I

En la cual

R^1 y R^2 independientemente significan hidrogeno o alquilo C_1-C_{10} , alquenilo C_2-C_{10} , alquenilo C_2-C_{10} , o alcadienilo C_4-C_{10} , haloalquilo C_2-C_{10} , haloalquenilo C_2-C_{10} , o

cicloalquilo C_3-C_{10} , fenilo, naftilo, o

heterociclilo de 5 o 6 miembros, que contiene de 1 a 4 átomos de nitrógeno o 1 a 3 átomos de nitrógeno y un átomo de azufre u oxígeno, o

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1A

heteroarilo 5 o 6 miembros que contiene 1 a 4 átomos de nitrógeno o 1 a 3 átomos de nitrógeno y un átomo de azufre u oxígeno, o

donde los radicales R^1 y R^2 pueden ser no sustituidos o parcial o completamente halogenados o pueden llevar 1 a 3 grupos R^a ,

R^a es ciano, nitro, hidroxilo, alquilo C_1-C_6 , cicloalquilo C_3-C_6 , alcoxi C_1-C_6 , alquiltio C_1-C_6 , alquilamino C_1-C_6 , di- C_1-C_6 alquilamino, alquenilo C_2-C_6 , alqueniloxi C_2-C_6 , alquinilo C_2-C_6 , alquiniloxi C_3-C_6 y alquilenedioxi C_1-C_4 ; o

R^1 y R^2 juntos con el átomo de nitrógeno interyacente representan un anillo heterocíclico de 5 o 6 miembros, que contiene 1 a 4 átomos de nitrógeno o 1 a 3 átomos de nitrógeno y un átomo de azufre u oxígeno, que puede ser sustituido por 1 a 3 radicales R^a ;

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R³ es halógeno, ciano, alquilo C₁-C₁₀, alcoxi C₁-C₁₀, haloalquilo C₁-C₁₀, o C(=O)A, en donde

A es halógeno, hidroxil, alquilo C₁-C₈, alcoxi C₁-C₈, amino, alquilamino C₁-C₈, o di-(alquil C₁-C₈)-amino;

n es un entero de 1 a 4; y

X es halógeno, ciano, alquilo C₁-C₆, alcoxi C₁-C₆, haloalcoxi C₁-C₆ o alqueniloxi C₃-C₈.

2. Compuestos de fórmula I de acuerdo con la reivindicación 1, en la cual

R¹ es alquilo C₁-C₆ de cadena recta o ramificada, alquenilo C₂-C₆, cicloalquilo C₃-C₉, o haloalquilo C₁-C₁₀, y

R² es hidrógeno o alquilo C₁-C₆, o

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R1 y R2 junto con el átomo de hidrógeno interyacente representan un anillo heterocíclico con 5 a 6 átomos de carbono siendo opcionalmente sustituidos con 1 o 2 grupos alquilo C₁-C₆.

3. Compuestos de fórmula I de acuerdo a la reivindicación 1 o 2 en los cuales R² es hidrógeno.

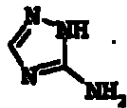
4. Compuestos de fórmula I de acuerdo a la reivindicación 1 a 3 en los cuales X es halógeno.

5. Compuestos de fórmula I de acuerdo a la reivindicación 1 a 4 en los cuales (R³)_n es 4-(C₁-C₆-alcoxi-carbonilo) o 4-ciano.

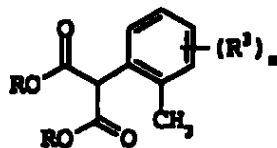
6. Un proceso para la preparación de compuestos de fórmula I como se definió en la reivindicación 4

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que comprende hacer reaccionar 5-amino-1,2,4-triazol



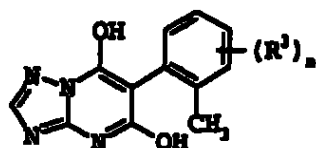
Con éster de ácido masónico 2-fenil-sustituido de fórmula II,



II

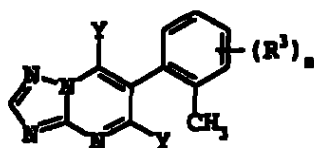
En donde R^3 y n son como se definió en la fórmula I, y R denota alquilo C_1-C_6 , bajo condicione alcalina para producir compuestos de fórmula III,

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1



III

Que son subsecuentemente tratados con un agente halogenante para dar 5,7-dihalogen-6-fenil-triazolopirimidina de fórmula IV



IV

En la cual Y es halógeno con una amina de fórmula V

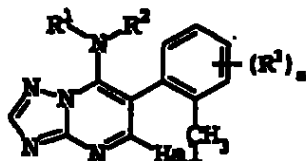


V

En la cual R¹ y R² son como se definió en la fórmula I para producir compuestos de fórmula I.

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7. Un proceso para la preparación de compuestos de fórmula I de acuerdo a la reivindicación 1 en donde X es ciano, alcoxi C₁-C₁₀, o haloalquilo C₁-C₁₀, que comprenden hacer reaccionar 5-halogenotriazolo pirimidina de fórmula I



I (X=Hal)

Con los compuestos de fórmula VI,



VI

Que son, dependientes, del valor de X' a ser introducido, una sal ciano orgánica, un alcoxilato, haloalcoxilato o un alqueniloxilato, respectivamente, en donde M es catión amonio, tetraalquilamonio, alcalimetal o metal alcalinotérreo para producir compuestos de la fórmula I.

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8. Intermedio de las fórmulas II, III, y IV, como se definió en la reivindicación 6.
9. Una composición adecuada para controlar hongos fitopatógenos, que comprende un portador sólido o líquido y un compuesto de la fórmula 1 como se reivindicó en la reivindicación 1.
10. Un método para controlar hongos fitopatógenos, que comprende tratar el hongo o los materiales, plantas, el suelo o la semilla a ser protegida contra ataques fungosos con una cantidad efectiva de un compuesto de la fórmula I como se reivindicó en la reivindicación 1.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Article 36 and Rule 70)

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Applicant's or agent's file reference 0000052858	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA418)	
International application No. PCT/EP0207578	International filing date (day/month/year) 08.07.2002	Priority date (day/month/year) 18.07.2001
International Patent Classification (IPC) or both national classification and IPC C07D487/04		
Applicant BASF AKTIENGESELLSCHAFT 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 4 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 607 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 opinion 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 Rule 66.2(a)(ii) 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 21.11.2002	Date of completion of this report 06.10.2003	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tlx 523856 epmu d Fax +49 89 2399 - 4465	Authorized Officer Herz, C Telephone No. +49 89 2399-8275 	

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/EP0207578**

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

1-37, 39, 40

as originally filed

38

received on 06.11.2002 with letter of 05.11.2002

Claims, Numbers

1-10

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:

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:

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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/EP02/07578**

**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	1-10
	No: Claims	
Inventive step (IS)	Yes: Claims	1-10
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-10
	No: Claims	

2. Citations and explanations

see separate sheet

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INTERNATIONAL PRELIMINARY

International application No. PCT/EP02/07578

EXAMINATION REPORT - SEPARATE SHEET

1. Due to the specific substitution pattern of the phenyl ring at position 6 of the triazolopyrimidine core the compounds claimed are considered to be (a) novel (selection) vis-à-vis the state of the art as represented by the documents cited in the International Search Report (ISER) (Art. 33 (2) PCT).
2. With regard to the results of comparative tests submitted with Applicant's letter dated 31/07/03 and already included with the specification (p. 38), respectively, against compounds disclosed in the closest prior art, US-A-6 204 269 (D1), US-A-5 948 783 (D3), and FR-A-2 795 073 (D4), which are closely related in structure to those presently claimed, a surprising improvement has been demonstrated being indicative of an inventive solution of the technical problem of providing compounds exhibiting a significantly improved antifungal activity (Art. 33 (3) PCT).

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TRATADO DE COOPERACIÓN DE PATENTES**PCT****REPORTE DE EXAMEN PRELIMINAR INTERNACIONAL****(Artículo 36 y Regla 70 PCT)****Archivo de referencia del agente o solicitante****0000052658****PARA ACCIÓN COMPLEMENTARIA****Ver Notificación de Reporte de Examen Preliminar
Internacional (del PCT/IPEA/416)****Solicitud Internacional No.****PCT/EP02/07578****Fecha de presentación internacional (día/mes/año)****08.07.2002****Fecha de Prioridad (día/mes/año)****18.07.2001****Clasificación de Patente Internacional (IPC) o
clasificación nacional e IPC****C07D487/04****SOLICITANTE****BASF AKTIENGESELLSCHAFT et al.**

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1. Este Reporte de Examen Preliminar Internacional ha sido preparado por esta Autoridad Examinadora Preliminar Internacional y se remite al solicitante de acuerdo con el Artículo 36.

2. Este REPORTE consiste de un total de 4 hojas, incluyendo esta hoja de portada.

☒ Este reporte también se acompaña por ANEXOS, es decir hojas de la descripción, reivindicaciones y/o dibujos que han sido corregidos y son la base para este reporte y/o hojas que contienen rectificaciones hechas antes a esta Autoridad (ver Regla 70.16 y Sección 607 de las Instrucciones Administrativas de acuerdo con el PCT).

Estos anexos consisten de un total de 1 hojas.

3. Este Reporte contiene indicaciones relacionadas con los siguientes ítems:

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- I ☒ Base del Reporte
- II ☐ Prioridad
- III ☐ Concepto de sin fundamento con respecto a novedad, nivel inventivo y aplicabilidad industrial
- IV ☐ Falta de unidad de invención
- V ☒ Declaración motivada de acuerdo con la regla 62.2(a)(ii) con respecto a novedad, nivel inventivo o aplicabilidad industrial; las citaciones y explicaciones ayudan a dicha declaración
- VI ☐ Ciertos documentos citados
- VII ☐ Ciertos defectos en la solicitud internacional
- VIII ☐ Ciertas observaciones sobre la solicitud internacional

Fecha de presentación de la petición

21.11.2002

Fecha de terminación de este reporte

06.10.2003

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Nombre y dirección de correspondencia de la autoridad
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Oficial autorizado

Herz, C

Tel. +49 89 2399-8275

(aparece sello de la Oficina de Patentes Europea)

Del PCT/IPEA409 (hoja de portada) (Enero 1994)

**REPORTE DE EXAMEN
PRELIMINAR INTERNACIONAL**

Solicitud Internacional No.
PCT/EP02/07578

I. Bases del Reporte

1. Con respecto a los elementos de la solicitud internacional: (reemplazo de las hojas que han sido suministradas a la Oficina de recepción en respuesta a una invitación de acuerdo con el Artículo 14 se refieren a en este reporte como "presentadas originalmente" y no se anexan a este reporte ya que ellas no contienen correcciones (Reglas 70.16 y 70.17)):

Descripción, páginas:

1-37, 39, 40	como se presentó originalmente
38	recibida en 06.11.2002 con carta de 05.11.2002

Reivindicaciones, Números:

1-10	como se presentó originalmente
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198
1976

2. Con respecto al idioma, todos los elementos marcados anteriormente estuvieron disponibles o fueron suministrados a esta Autoridad en el idioma en el que la solicitud internacional se presentó, a menos que se indique lo contrario de acuerdo con este ítem.

Estos elementos estuvieron disponibles o fueron suministrados a esta Autoridad en el siguiente idioma:

, que es:

☐ el idioma de una traducción suministrada para propósitos de búsqueda internacional (de acuerdo con la regla 23.1(b)).

☐ el idioma de publicación de la solicitud internacional (de acuerdo con la regla 48.3(b)).

☐ el idioma de la traducción suministrado para propósitos de examen preliminar internacional (de acuerdo con la regla 55.2 y/o 55.3).

3. Con respecto a cualquier secuencia de ácido amino y/o nucleótido descrito en la solicitud internacional, el concepto escrito se emitió sobre la base de la lista de secuencia:

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- ☐ Contenida en la solicitud internacional en forma impresa
 - ☐ Presentada junto con la solicitud internacional en forma legible por computador
 - ☐ Suministrada posteriormente a esta Autoridad en forma escrita
 - ☐ Suministrada posteriormente a esta Autoridad en forma escrita forma legible por computador
 - ☐ La declaración de que el listado de secuencias escrito suministrado posteriormente no va más allá de la descripción en la solicitud internacional como se presentó se ha suministrado.
 - ☐ La declaración de que la información registrada en forma legible por computador es idéntica al listado de secuencias escrito que se ha suministrado.
4. Las correcciones han dado como resultado la cancelación de:
- ☐ la descripción, páginas:
 - ☐ las reivindicaciones, Nos.:
 - ☐ Los dibujos, hojas:
5. ☐ Este reporte ha sido emitido como si (algunas de) las correcciones no hubieran sido hechas, ya que

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ellas han sido consideradas que van más allá de la descripción como se presentó, como se indicó en la casilla complementaria (Regla 70.2(c)):

(Cualquier reemplazo de hojas que contengan dichas correcciones se debe referir de acuerdo al ítem 1 y anexadas a este reporte)

6. Observaciones adicionales, si es necesario:

Del PCT/IPEA/409 (Julio 1999)

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199**REPORTE DE EXAMEN****PRELIMINAR INTERNACIONAL**

Solicitud Internacional No.
PCT/EP02/003829

V. Declaración motivada de acuerdo con el Artículo 35(2) con respecto a novedad, nivel inventivo o aplicabilidad industrial; las citaciones y explicaciones ayudan a dicha declaración

1. Declaración

Novedad (N)

Si: Reivindicaciones 1-10

No: Reivindicaciones

Nivel inventivo (IS)

Si: Reivindicaciones 1-10

No: Reivindicaciones

Aplicabilidad Industrial (IA)

Si: Reivindicaciones 1-10

No: Reivindicaciones

2. Citaciones y Explicaciones

Ver hoja separada

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REPORTE DE EXAMEN**PRELIMINAR INTERNACIONAL - HOJA SEPARADA**

Solicitud Internacional No.

PCT/EP02/07578

1. Debido al modelo de sustitución específico del anillo fenilo en la posición 6 del núcleo triazolopirimidina los compuestos reivindicados se consideran novedosos frente al estado de la técnica como se representa por los documentos citados en el Reporte de búsqueda Internacional (ISR) (Art.33(2)PCT).

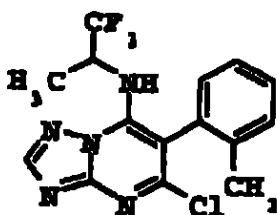
2. con respecto a los resultados de los ensayos comparativos presentados con la carta del Solicitante fechada 31/07/03 y ya incluida con la especificación (p. 38), respectivamente, contra compuestos descritos en la técnica anterior más cercana, US-A-6 204 269 (D1), US-A-5 948 783 (D3), y FR-A-2 795 073 (D4), que se relaciona cercanamente en estructura a aquellas reivindicadas actualmente, una mejora sorprendente se ha demostrado es indicativo de una solución inventiva de el problema técnico de suministrar compuestos que exhiban una actividad antifungosa mejorada significativamente (Artículo. 33(3) PCT).

Ejemplos de la acción contra hongos dañinos

La acción fungicida de los compuestos de fórmula I se demostró mediante los siguientes experimentos:

Los compuestos activos, junto o por separado, se formularon como una emulsión al 10% en una mezcla de 70% en peso de ciclohexanona, 20% en peso de Nekali® LN (Lutensol® AP6 agente humectante que tiene acción emulsificante y dispersante basada en alquifenoles etoxilados) y 10% en peso de Wettol® EM (emulsificador no iónico basado en aceite de castor etoxilado) y diluido con agua a la concentración deseada

El Compuesto A conocido de la WO-A- 98/46608 (No. 9) sirvió como compuesto activo comparativo:



Ensayo de comparación 1 - Control fungicida de añublo temprano sobre tomates (*Alternaria solani*)

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Plántulas jóvenes de plantas de tomate de la variedad "Grosse Fleischtomate St. Pierre" crecieron en materas hasta la etapa de 2 a 4 hojas. Estas plantas se rociaron con una corriente de una suspensión acuosa, que contiene la concentración del ingrediente activo mencionado en la tabla adelante, preparado de una solución que contiene 10% de ingrediente activo, 85% de ciclohexanona, y 5% de emulsificador. El siguiente día, las plantas tratadas se inocularon con una suspensión acuosa de *Alternaria solani* que contiene $0,2 \times 10^6$ esporas por ml. Luego las plantas de ensayo se transplantaron inmediatamente a una cámara de humedad. Después de 6 días a $20 - 23^{\circ} \text{C}$ y humedad relativa cercana al 100%, el alcance del ataque del hongo sobre las hojas fue evaluado visualmente como % de área de hoja enferma.

En este ensayo, las plantas que han sido tratadas con 63 ppm de los compuestos I-23 y I-24, respectivamente, mostraron una infección de no más del 3%, mientras que las plantas tratadas con 63 ppm de la comparación del compuesto A se infectó al 15%, y las plantas no tratadas se infectaron al 90%.

Item	Expediente No	04002809	No de Folia
		No de unidades	295.
1	CD		
2	DVD		
3	REVISTA		
4	LIBRO		
5	PERIODICO		
6	DISQUETES		
7	SOBRE DE MANILA		
8	SOBRE BLANCO TAMAÑO CARTA	↓	
9	SOBRE BLANCO TAMAÑO OFICIO		
10	OTROS:		

Observaciones:
Artes finales
contiene 2 figuras

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SUBDIRECCION Y COMERCIO

Folio: 893

Radicacion : 011-PCJ-COMER
Fecha (MMDD) : 2004-01-16 17:13:42
Tramite : 011 PCI-MRLEM / 379 FASE NÚM 411 PRESENTAC
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

ADMINISTRACIÓN Y COMERCIO

Folien 283

4.11 线性规划

4023

REFERENCES

Mr. PAGO

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: 

Fecha:



2020
Bogotá, D.C.,

Doctor:
EMILIO FERRERO
Apoderado
BASF AKTIENGESELLSCHAFT.

Oficio N°
04220

ASUNTO:	Radicación N°	04-2809
	Solicitud Internacional	PCT/EP02/07578
	Fecha inicio fase nacional	18/02/2004
	Trámite	011
	Evento	379
	Actuación	430
	Folios	001

Como resultado del examen de forma, realizado con fundamento en el artículo 38 de la Decisión 486 de la Comisión de la Comunidad Andina, artículo 27 del Tratado de Cooperación en Materia de Patentes (PCT), regla 51 bis del Reglamento y Circular Única de la Superintendencia de Industria y Comercio, se le comunica que:

□ La solicitud no contiene la copia del documento en que consta la cesión del derecho a la patente del inventor al solicitante o a su causante. (Art. 26-k) Decisión 486).

En cumplimiento de lo dispuesto por el artículo 39 de la Decisión 486, se le requiere para que dentro del término de dos meses siguientes a la fecha de notificación del presente oficio, complete los requisitos anteriormente enunciados. En caso de no dar cumplimiento al presente requerimiento, la solicitud se considerará abandonada y perderá su prelación.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única N° 10 de 2001.


ALIX CARMENZA CESPEDES DE VERGEL
Jefe de la División de Nuevas Creaciones.

El anterior requerimiento fue notificado por fijación en lista de fecha, 23 de marzo de 2004.

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