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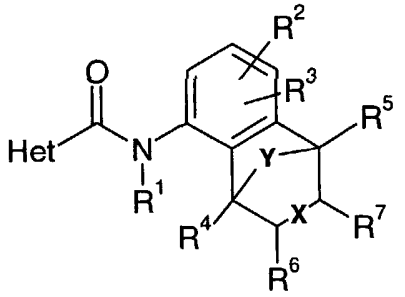
(54) Title: HETEROCYCLOCARBOXAMIDE DERIVATIVES



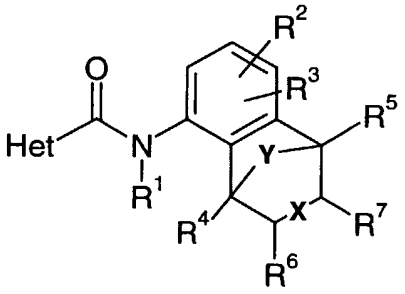
(I)

(57) Abstract: The invention relates to a fungicidally active compound of formula (I): where Het is a 5- or 6-membered heterocyclic ring containing one to three heteroatoms, each independently selected from oxygen, nitrogen and sulphur, provided that the ring is not 1,2,3-triazole, the ring being substituted by groups R^8, R^9 and R^{10}; X is a single or double bond; Y is O, S, $N(R^{11})$ or $(CR^{12}R^{13})(CR^{14}R^{15})_m(CR^{16}R^{17})_n$; m is 0 or 1; n is 0 or 1; and R^1 to R^{17} each, independently, have a range of values; to the preparation of these compounds, to novel intermediates used in the preparation of these compounds, to agrochemical compositions which comprise at least one of the novel compounds as active ingredient, to the preparation of the compositions mentioned and to the use of the active ingredients or compositions in agriculture or horticulture for controlling or preventing infestation of plants by phytopathogenic microorganisms, preferably fungi.

HETEROCYCLOCARBOXAMIDE DERIVATIVES

The present invention relates to novel tricyclic amine derivatives which have microbiocidal activity, in particular fungicidal activity. The invention also relates to the preparation of these compounds, to novel intermediates used in the preparation of these compounds, to agrochemical compositions which comprise at least one of the novel compounds as active ingredient, to the preparation of the compositions mentioned and to the use of the active ingredients or compositions in agriculture or horticulture for controlling or preventing infestation of plants by phytopathogenic microorganisms, preferably fungi.

The present invention provides a compound of formula (I):



(I)

where Het is a 5- or 6-membered heterocyclic ring containing one to three heteroatoms, each independently selected from oxygen, nitrogen and sulphur, provided that the ring is not 1,2,3-triazole, the ring being substituted by groups R^8, R^9 and R^{10}; X is a single or double bond; Y is O, S, $N(R^{11})$ or $(CR^{12}R^{13})(CR^{14}R^{15})_m(CR^{16}R^{17})_n$; m is 0 or 1; n is 0 or 1; R^1 is hydrogen, C_{1-4} alkyl, C_{1-4} haloalkyl, C_{1-4} alkoxy, C_{1-4} haloalkoxy, $CH_2C{\equiv}CR^{18}$, $CH_2CR^{19}{=}CHR^{20}$, $CH{=}C{=}CH_2$ or COR^{21}; R^2 and R^3 are each, independently, hydrogen, halogen, C_{1-4} alkyl, C_{1-4} alkoxy or C_{1-4} haloalkoxy; R^4, R^5, R^6 and R^7 are each, independently, hydrogen, halogen, C_{1-4} alkyl, C_{1-4} haloalkyl, C_{1-4} alkoxy, C_{1-4} haloalkoxy, C_{1-4} alkylthio, C_{1-4} haloalkylthio, hydroxymethyl, C_{1-4} alkoxymethyl, $C(O)CH_3$ or $C(O)OCH_3$; R^8, R^9 and R^{10} are each, independently, hydrogen, halogen, cyano, nitro, C_{1-4} alkyl, C_{1-4} haloalkyl, C_{1-4} alkoxy(C_{1-4})alkylene or C_{1-4} haloalkoxy(C_{1-4})alkylene, provided that at least one of R^8, R^9 and R^{10} is not hydrogen; R^{11} is hydrogen, C_{1-4} alkyl, benzyl (in which the phenyl group is optionally substituted with up to three substituents, each independently selected from halogen, C_{1-4} alkyl, C_{1-4} haloalkyl and C_{1-4} alkoxy),

formyl, $C(O)C_{1-4}$ alkyl (optionally substituted by halogen or C_{1-4} alkoxy), $C(=O)O$-C_{1-6} alkyl (optionally substituted by halogen, C_{1-4} alkoxy or cyano) or C_{1-4} alkoxy(C_{1-4})alkylene; R^{12}, R^{13}, R^{14}, R^{15}, R^{16} and R^{17} are each, independently, hydrogen, halogen, hydroxy, C_{1-6} alkyl, C_{2-6} alkenyl [both optionally substituted by halogen, hydroxy, C_{1-4} alkoxy, =O, aryl or O-C(O)-C_{1-4} alkyl or a 3-7 membered carboxylic ring (itself optionally substituted by up to three methyl groups)], a 3-7 membered saturated ring (optionally substituted by up to three methyl groups and optionally containing one heteroatom selected from nitrogen and oxygen) or C_{1-4} alkoxy; or R^{12} and R^{13} together with the carbon atom to which they are attached form the group C=O or a 3-5 membered carbocyclic ring (optionally substituted by up to three methyl groups and optionally with up to 2 heteroatoms each independently selected from O and N); or R^{12} and R^{13} together form a C_{1-6} alkylidene (optionally substituted by up to three methyl groups) or a C_{3-6} cycloalkylidene group (optionally substituted by up to three methyl groups); R^{18}, R^{19} and R^{20} are each, independently, hydrogen, halogen, C_{1-4} alkyl, C_{1-4} haloalkyl or C_{1-4} alkoxy(C_{1-4})alkylene; and R^{21} is hydrogen, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-4} alkoxy(C_{1-4})alkylene, C_{1-4} alkyl-S-(C_{1-4})alkylene, C_{1-4} alkoxy or aryl.

Halogen is fluoro, chloro, bromo or iodo; preferably fluoro, chloro or bromo.

Each alkyl moiety is a straight or branched chain and is, for example, methyl, ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, *n*-hexyl, *iso*-propyl, *sec*-butyl, *iso*-butyl, *tert*-butyl, *neo*-pentyl, *n*-heptyl, 1,3-dimethylbutyl, 1,3-dimethylpentyl, 1-methyl-3-ethyl-butyl or 1,3,3-trimethylbutyl. Likewise, each alkylene moiety is a straight or branched chain.

Haloalkyl moieties are alkyl moieties which are substituted by one or more of the same or different halogen atoms and are, for example, CF_3, CF_2Cl, CHF_2, CH_2F, CCl_3, CF_3CH_2, CHF_2CH_2, CH_2FCH_2, CH_3CHF or CH_3CF_2.

Alkenyl and alkynyl moieties can be in the form of straight or branched chains.

Each alkenyl moiety, where appropriate, may be of either the (E)- or (Z)-configuration.

A 3-5 membered carbocyclic ring includes a spiro-three or five membered ring.

Aryl includes phenyl, naphthyl, anthracyl, fluorenyl and indanyl but is preferably phenyl.

Alkylidene moieties may be in the form of straight or branched chains. Alkylidene includes methylidene [CH_2=], ethylidene [$CH_3C(H)$=], *n*-propylidene, *i*-propylidene

[$(CH_3)_2C$=], *n*-butylidene, *i*-butylidene, 2-butylidene, *n*-pentylidene, *i*-pentylidene, *neo*-pentylidene, 2-pentylidene, *n*-hexylidene, 2-hexylidene, 3-hexylidene, *i*-hexylidene and *neo*-hexylidene.

Cycloalkyl includes cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl.

Cycloalkenyl includes cyclobutenyl, cyclopentenyl, cyclohexenyl and cycloheptenyl.

Cycloalkylidene includes cyclopropylidene [$c(C_3H_4)$=], cyclobutylidene, cyclopentylidene and cyclohexylidene.

In one aspect of the invention, R^{11} is hydrogen, C_{1-4} alkyl, benzyl (in which the phenyl group is optionally substituted with up to three substituents, each independently selected from halogen, C_{1-4} alkyl, C_{1-4} haloalkyl and C_{1-4} alkoxy), formyl, $C(O)C_{1-4}$ alkyl or C_{1-4} alkoxy(C_{1-4})alkylene.

In another aspect of the invention, R^{12}, R^{13}, R^{14}, R^{15}, R^{16} and R^{17} are each, independently, hydrogen, C_{1-4} alkyl or C_{1-4} alkoxy.

Het is preferably pyrrolyl, pyrazolyl, thiazolyl, oxazolyl, pyridinyl, pyrimidyl, pyridazinyl, 2,3-dihydro-[1,4]oxathiine-6-yl, oxazinyl, thiazinyl or triazinyl.

Het is more preferably pyrrolyl, pyrazolyl, thiazolyl, oxazolyl, pyridinyl or 2,3-dihydro-[1,4]oxathiine-yl.

Het is even more preferably pyrrolyl, pyrazolyl, thiazolyl or pyridinyl.

Het is most preferably pyrrolyl or pyrazolyl.

Preferably X is a single bond.

In one aspect, Y is O, S, $N(R^{11})$, CH_2, CH_2CH_2, $CH_2CH_2CH_2$, $C(CH_3)_2$, $CH(CH_3)$, $CH(C_2H_5)$, $C(CH_3)(C_2H_5)$, $CH(OCH_3)$ or $C(OCH_3)_2$; more preferably $N(R^{11})$, O, S, CH_2, CH_2CH_2, $CH_2CH_2CH_2$, $C(CH_3)_2$, $CH(CH_3)$ or $CH(C_2H_5)$; even more preferably $N(R^{11})$, O, S, CH_2 or CH_2CH_2; and still more preferably O, CH_2 or $N(R^{11})$.

Preferably Y is O, $N(R^{11})$ or $(CR^{12}R^{13})(CR^{14}R^{15})_m(CR^{16}R^{17})_n$.

More preferably Y is O or $(CR^{12}R^{13})(CR^{14}R^{15})_m(CR^{16}R^{17})_n$.

Even more preferably Y is $(CR^{12}R^{13})(CR^{14}R^{15})_m(CR^{16}R^{17})_n$.

Still more preferably Y is $(CR^{12}R^{13})$.

Preferably n is 0.

Preferably m is 0.

Preferably R^1 is hydrogen, $CH_2C{\equiv}CR^{18}$, $CH{=}C{=}CH_2$ or COR^{21}.

More preferably R^1 is hydrogen, $CH_2C{\equiv}CH$, $CH{=}C{=}CH_2$, C(O)H or $C(O)CH_3$.

Yet more preferably R^1 is hydrogen, $CH_2C{\equiv}CH$, $CH{=}C{=}CH_2$ or $C(O)CH_3$.

Even more preferably R^1 is hydrogen, $CH_2C{\equiv}CH$ or $CH{=}C{=}CH_2$.

Most preferably R^1 is hydrogen.

Preferably R^2 is hydrogen, halogen or C_{1-4} alkyl.

More preferably R^2 is hydrogen or halogen.

Most preferably R^2 is hydrogen.

Preferably R^3 is hydrogen or methyl.

More preferably R^3 is hydrogen.

Preferably R^4 is hydrogen, C_{1-4} alkyl, halogen, C_{1-4} haloalkyl, C_{1-4} alkoxy, $C(O)CH_3$ or $C(O)OCH_3$.

More preferably R^4 is hydrogen, C_{1-2} alkyl, halogen, CF_3, methoxy, $C(O)CH_3$ or $C(O)OCH_3$.

Even more preferably R^4 is hydrogen, methyl, chlorine, CF_3 or methoxy.

Most preferably R^4 is hydrogen or methyl.

Preferably R^5 is hydrogen, C_{1-4} alkyl, halogen, C_{1-4} haloalkyl, C_{1-4} alkoxy, $C(O)CH_3$ or $C(O)OCH_3$.

More preferably R^5 is hydrogen, C_{1-2} alkyl, chlorine, CF_3, methoxy, $C(O)CH_3$ or $C(O)OCH_3$.

Most preferably R^5 is hydrogen or methyl.

Preferably R^6 is hydrogen, C_{1-4} alkyl, C_{1-4} alkoxy or $C(O)CH_3$.

More preferably R^6 is hydrogen, methyl, methoxy or $C(O)CH_3$.

Most preferably R^6 is hydrogen or methyl.

Preferably R^7 is hydrogen, C_{1-4} alkyl, C_{1-4} alkoxy or $C(O)CH_3$.

More preferably R^7 is hydrogen, methyl, methoxy or $C(O)CH_3$.

Most preferably R^7 is hydrogen or methyl.

Preferably R^8 is hydrogen, halogen, C_{1-4} alkyl, C_{1-4} haloalkyl or methoxymethylene.

More preferably R^8 is hydrogen, chloro, fluoro, bromo, C_{1-2} alkyl, CF_3, CF_2Cl, CHF_2, CH_2F or methoxymethylene.

Even more preferably R^8 is hydrogen, chloro, fluoro, C_{1-2} alkyl, CF_3, CF_2Cl, CHF_2, CH_2F or methoxymethylene.

Most preferably R^8 is hydrogen, chloro, fluoro, methyl, CF_3, CHF_2 or CH_2F.

Preferably R^9 is hydrogen, halogen, C_{1-4} alkyl or C_{1-4} haloalkyl or methoxymethylene.

More preferably R^9 is hydrogen, chloro, fluoro, bromo, C_{1-2} alkyl, CF_3, CF_2Cl, CHF_2, CH_2F or methoxymethylene.

Even more preferably R^9 is hydrogen, chloro, fluoro, C_{1-2} alkyl, CF_3, CF_2Cl, CHF_2, CH_2F or methoxymethylene.

Most preferably R^9 is hydrogen, chloro, fluoro, methyl, CF_3, CHF_2 or CH_2F.

Preferably R^{10} is hydrogen, halogen, C_{1-4} alkyl, C_{1-4} haloalkyl or methoxymethylene.

More preferably R^{10} is hydrogen, chloro, fluoro, bromo, C_{1-2} alkyl, CF_3, CF_2Cl, CHF_2, CH_2F or methoxymethylene.

Even more preferably R^{10} is hydrogen, chloro, fluoro, C_{1-2} alkyl, CF_3, CF_2Cl, CHF_2, CH_2F or methoxymethylene.

Most preferably R^{10} is hydrogen, chloro, fluoro, methyl, CF_3, CHF_2 or CH_2F.

In one aspect of the invention R^{11} is hydrogen, C_{1-4} alkyl, benzyl, formyl, $C(O)CH_3$ or $C(O)OC(CH_3)_3$; more preferably hydrogen or C_{1-2} alkyl.

Preferably R^{11} is C_{1-4} alkyl, formyl, $C(O)CH_3$ or $C(O)OC_{1-6}$ alkyl (optionally substituted by halogen, CN or C_{1-4} alkoxy).

More preferably R^{11} is $C(O)OC_{1-4}$ alkyl.

In one aspect of the invention R^{12}, R^{13}, R^{14}, R^{15}, R^{16} and R^{17} are each, independently, hydrogen, C_{1-2} alkyl or methoxy.

Preferably R^{12} and R^{13} are each, independently, hydrogen, halogen, C_{1-5} alkyl, C_{1-3} alkoxy, CH_2OH, CH(O), C_{3-6} cycloalkyl, CH_2O-$C(=O)CH_3$, CH_2-C_{3-6} cycloalkyl or benzyl; or R^{12} and R^{13} together with the carbon atom to which they are attached form the group C=O or a 3-5 membered carbocyclic ring; or R^{12} and R^{13} together form C_{1-5} alkylidene or C_{3-6} cycloalkylidene.

More preferably R^{12} and R^{13} are, independently, H, CH_3, C_2H_5, *n*-C_3H_7, *i*-C_3H_7, *n*-C_4H_9, *sec*-C_4H_9, *i*-C_4H_9, $CH(C_2H_5)_2$, CH_2-cyclopropyl or cyclopentyl; or R^{12} and R^{13} together with the carbon atom to which they are attached form a 3-membered or 5-membered carbocyclic ring.

Preferably R^{14} is H or CH_3.

Preferably R^{15} is H or CH_3.

Preferably R^{16} is H or CH_3.

Preferably R^{17} is H or CH_3.

Preferably R^{18} is hydrogen, chloro, bromo, methyl or methoxy.

More preferably R^{18} is hydrogen, chloro or methyl.

Most preferably R^{18} is hydrogen.

Preferably R^{19} is hydrogen, chloro, bromo, methyl or methoxy.

More preferably R^{19} is hydrogen, chloro or methyl.

Most preferably R^{19} is hydrogen.

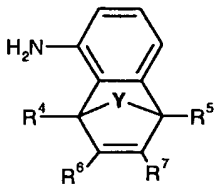
Preferably R^{20} is hydrogen, chloro, bromo, methyl or methoxy.

More preferably R^{20} is hydrogen, chloro or methyl.

Most preferably R^{20} is hydrogen.

Preferably R^{21} is hydrogen, methyl, $OC(CH_3)_3$ or CH_3OCH_2.

Compounds of formula (C):

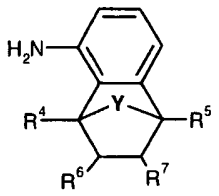


(C)

where Y, R^4, R^5, R^6 and R^7 are as defined above for a compound of formula (I) are useful as intermediates in the preparation of compounds of formula (I). Some Compounds of formula (C) are novel but some are already known.

Therefore, in another aspect, the present invention provides a compound of formula (C) where Y is O or S; and R^4, R^5, R^6 and R^7 are each $C(O)OCH_3$; or Y is $N(R^{11})$ or $(CR^{12}R^{13})(CR^{14}R^{15})_m(CR^{16}R^{17})_n$; R^4, R^5, R^6, R^7, R^{14}, R^{15}, R^{16}, R^{17}, m and n are each as defined above for a compound of formula (I); R^{11} is benzyl (in which the phenyl group is optionally substituted with up to three substituents, each independently selected from halogen, C_{1-4} alkyl, C_{1-4} haloalkyl and C_{1-4} alkoxy); and R^{12} and R^{13} together with the carbon atom to which they are attached form a 3-5 membered carbocyclic ring (optionally substituted by up to three methyl groups and containing 1 or 2 heteroatoms each independently selected from O and N).

Compounds of formula (D):



(D)

where Y, R^4, R^5, R^6 and R^7 are as defined above for a compound of formula (I) are also useful as intermediates in the preparation of compounds of formula (I). Some Compounds of formula (D) are novel but some are already known.

Therefore, in another aspect, the present invention provides a compound of formula (D) where Y is O or S; and R^4, R^5, R^6 and R^7 are each $C(O)OCH_3$; or Y is $N(R^{11})$ or $(CR^{12}R^{13})(CR^{14}R^{15})_m(CR^{16}R^{17})_n$; R^4, R^5, R^6, R^7, R^{14}, R^{15}, R^{16}, R^{17}, m and n are each as defined above for a compound of formula (I); R^{11} is benzyl (in which the phenyl group is optionally substituted with up to three substituents, each independently selected from halogen, C_{1-4} alkyl, C_{1-4} haloalkyl and C_{1-4} alkoxy) ; and R^{12} and R^{13} together with the carbon atom to which they are attached form a 3-5 membered carbocyclic ring (optionally substituted by up to three methyl groups and containing 1 or 2 heteroatoms each independently selected from O and N).

The compounds of formula (I), (C) and (D) may exist as different geometric or optical isomers or in different tautomeric forms. This invention covers, for each formula, all such isomers and tautomers and mixtures thereof in all proportions as well as isotopic forms such as deuterated compounds.

The compounds in Tables 1 to 29 below illustrate compounds of the invention.

Table 1 provides 94 compounds of formula (C) wherein Y, R^4, R^5, R^6 and R^7 are as defined in Table 1.

Table 1

Compound Number	R^4	R^5	R^6	R^7	Y
1.01	CH_3	CH_3	H	H	O
1.02	CH_3	H	H	H	O
1.03	H	CH_3	H	H	O
1.04	CH_3	CH_3	$C(O)CH_3$	H	O
1.05	CH_3	CH_3	H	$C(O)CH_3$	O
1.06	CH_3	$C(O)CH_3$	H	H	O
1.07	$C(O)CH_3$	CH_3	H	H	O
1.08	$C(O)OCH_3$	H	H	H	O
1.09	H	$C(O)OCH_3$	H	H	O
1.10	H	H	H	H	O

1.11	CF_3	CF_3	H	H	O
1.12	OCH_3	OCH_3	H	H	O
1.13	H	H	CH_3	CH_3	O
1.14	C_2H_5	C_2H_5	H	H	O
1.15	CH3	H	CH_3	H	O
1.16	H	CH3	H	CH_3	O
1.17	CH_3	H	CH_3	H	CH_2
1.18	H	CH_3	H	CH_3	CH_2
1.19	CH_3	CH_3	CH_3	CH_3	CH_2
1.20	CH_3	CH_3	CH_3	CH_3	$CH(CH_3)$
1.21	H	H	H	H	$CH(CH_3)$
1.22	CH_3	CH_3	H	H	CH_2CH_2
1.23	H	H	CH_3	CH_3	CH_2CH_2
1.24	H	H	H	H	$CH_2CH_2CH_2$
1.25	H	H	CH_3	CH_3	$C(CH_3)_2$
1.26	CH_3	CH_3	CH_3	CH_3	$C(CH_3)_2$
1.27	CH_3	H	CH_3	H	$C(CH_3)_2$
1.28	H	CH_3	H	CH_3	$C(CH_3)_2$
1.29	H	H	H	H	$C(CH_3)_2$
1.30	CH_3	CH_3	H	H	$C(CH_3)_2$
1.31	H	H	H	H	$C(OCH_3)_2$
1.32	H	H	H	H	S
1.33	CH_3	CH_3	H	H	S
1.34	H	H	CH_3	CH_3	S
1.35	OCH_3	OCH_3	H	H	S
1.36	H	CH_3	H	H	S
1.37	CH_3	H	H	H	S
1.38	CH_3	H	CH_3	H	S
1.39	H	CH_3	H	CH_3	S
1.40	H	OCH_3	H	H	S
1.41	OCH_3	H	H	H	S
1.42	CH_3	H	CH_3	CH_3	S
1.43	H	CH_3	CH_3	CH_3	S
1.44	H	H	CH_3	H	S
1.45	H	H	H	CH_3	S
1.46	H	H	OCH_3	H	S
1.47	H	H	H	OCH_3	S
1.48	H	H	H	H	$N(CH_3)$
1.49	CH_3	CH_3	H	H	$N(CH_3)$
1.50	H	H	H	H	$N(C_2H_5)$
1.51	H	H	H	H	NCH_2Ph
1.52	H	H	H	H	$NC(O)CH_3$
1.53	H	H	H	H	$NC(O)OC(CH_3)_3$
1.54	H	H	H	H	NH
1.55	H	H	H	H	NC(O)H
1.56	CH_3	CH_3	H	H	NC(O)H
1.57	CH_3	CH_3	H	H	NH
1.58	CH_3	CH_3	H	H	$NC(O)CH_3$
1.58	CH_3	CH_3	H	H	$NC(O)OC(CH_3)_3$
1.59	CH_3	CH_3	H	H	NCH_2Ph
1.60	Cl	Cl	H	H	O
1.61	H	H	H	H	$NC(O)OCH_3$
1.62	H	H	H	H	NCH_2-4-Cl-Ph
1.63	H	H	H	H	NCH_2-4-CH_3-Ph

1.64	H	H	H	H	NCH_2-3-Cl-Ph
1.65	H	H	H	H	NCH_2-3-CF_3-Ph
1.66	H	H	H	H	NCH_2-3-OCH_3-Ph
1.67	CH_3	CH_3	H	H	$NC(O)OCH_3$
1.68	CH_3	CH_3	H	H	$NC(O)OC_2H_5$
1.69	H	H	H	H	$NC(O)OC_2H_5$
1.70	CH_3	CH_3	H	H	$NC(O)OCH_2CH_2Cl$
1.71	H	H	H	H	$NC(O)OCH_2CH_2Cl$
1.72	CH_3	CH_3	H	H	$NC(O)OC_4H_9$-(*n*)
1.73	H	H	H	H	$NC(O)OC_4H_9$-(*n*)
1.74	CH_3	CH_3	H	H	$NC(O)OC_4H_9$-(*i*)
1.75	H	H	H	H	$NC(O)OC_4H_9$-(*i*)
1.76	H	H	H	H	$CH(C_3H_7$-(*i*)) syn or anti
1.77	H	H	H	H	$CH(C_3H_7$-(*n*)) syn or anti
1.78	H	H	H	H	$CH(C_4H_9$-(*i*)) syn or anti
1.79	H	H	H	H	$CH(C_4H_9$-(*n*)) syn or anti
1.80	H	H	H	H	$C(C_2H_4$-(*c*))
1.81	H	H	H	H	$C(C_4H_8$-(*c*))
1.82	H	H	H	H	$CHCH(C_2H_5)_2$ syn or anti
1.83	H	H	H	H	$CHCH_2(C_3H_5$-(*c*) syn or anti
1.84	H	H	H	H	$CH(C_5H_9$-(*c*) syn or anti
1.85	H	H	H	H	$CHCH_2OAc$ syn or anti
1.86	H	H	H	H	CHCHO syn or anti
1.87	H	H	H	H	$CHCH_2OH$ syn or anti
1.88	H	H	H	H	$CHCH_2$-C_6H_5 syn or anti
1.89	H	H	H	H	C=O
1.90	H	H	H	H	$C(O$-C_3H_7-(*n*))$_2$
1.91	H	H	H	H	$C(O$-C_2H_5-)$_2$
1.92	H	H	H	H	$CH(C_2H_5)$ syn or anti
1.93	H	H	H	H	CF_2
1.94	H	H	H	H	CH(Cl) syn or anti

Table 2 provides 111 compounds of formula (D) wherein Y, R^4, R^5, R^6 and R^7 are as defined in Table 2.

Table 2

Cmpd. No.	R^4	R^5	R^6	R^7	Y
2.01	CH_3	CH_3	H	H	O
2.02	CH_3	H	H	H	O
2.03	H	CH_3	H	H	O
2.04	CH_3	CH_3	$C(O)CH_3$	H	O
2.05	CH_3	CH_3	H	$C(O)CH_3$	O
2.06	CH_3	$C(O)CH_3$	H	H	O
2.07	$C(O)CH_3$	CH_3	H	H	O
2.08	$C(O)OCH_3$	H	H	H	O
2.09	H	$C(O)OCH_3$	H	H	O
2.10	H	H	H	H	O
2.11	CF_3	CF_3	H	H	O
2.12	OCH_3	OCH_3	H	H	O
2.13	H	H	CH_3	CH_3	O
2.14	C_2H_5	C_2H_5	H	H	O

2.15	CH_3	H	CH_3	H	O
2.16	H	H	H	H	CH_2
2.17	CH_3	H	CH_3	H	CH_2
2.18	H	CH_3	H	CH_3	CH_2
2.19	CH_3	CH_3	CH_3	CH_3	CH_2
2.20	CH_3	CH_3	CH_3	CH_3	$CH(CH_3)$ syn or anti
2.21	H	H	H	H	$CH(CH_3)$ syn or anti
2.22	H	H	H	H	$CH(C_2H_5)$ syn or anti
2.23	H	H	H	H	CH_2CH_2
2.24	CH_3	CH_3	H	H	CH_2CH_2
2.25	H	H	CH_3	CH_3	CH_2CH_2
2.26	H	H	OCH_3	H	CH_2CH_2
2.27	H	H	H	OCH_3	CH_2CH_2
2.28	H	H	H	H	$CH_2CH_2CH_2$
2.29	H	H	CH_3	CH_3	$C(CH_3)_2$
2.30	CH_3	CH_3	CH_3	CH_3	$C(CH_3)_2$
2.31	CH_3	H	CH_3	H	$C(CH_3)_2$
2.32	H	CH_3	H	CH_3	$C(CH_3)_2$
2.33	CH_3	CH_3	CH_3	CH_3	$C(CH_3)(C_2H_5)$
2.34	H	H	H	H	$C(CH_3)_2$
2.35	CH_3	CH_3	H	H	$C(CH_3)_2$
2.36	H	H	H	H	$CH(OCH_3)$ syn or anti
2.37	H	H	H	H	S
2.38	CH_3	CH_3	H	H	S
2.39	H	H	CH_3	CH_3	S
2.40	OCH_3	OCH_3	H	H	S
2.41	H	CH_3	H	H	S
2.42	CH_3	H	H	H	S
2.43	CH_3	H	CH_3	H	S
2.44	H	CH_3	H	CH_3	S
2.45	H	OCH_3	H	H	S
2.46	OCH_3	H	H	H	S
2.47	CH_3	H	CH_3	CH_3	S
2.48	H	CH_3	CH_3	CH_3	S
2.49	H	H	CH_3	H	S
2.50	H	H	H	CH_3	S
2.51	H	H	OCH_3	H	S
2.52	H	H	H	OCH_3	S
2.53	H	H	H	H	$N(CH_3)$
2.54	CH_3	CH_3	H	H	$N(CH_3)$
2.55	H	H	H	H	$N(C_2H_5)$
2.56	H	H	H	H	NCH_2Ph
2.57	H	H	H	H	$NC(O)CH_3$
2.58	H	H	H	H	$NC(O)OC(CH_3)_3$
2.59	H	H	H	H	NH
2.60	Cl	Cl	H	H	O
2.61	H	H	H	H	NC(O)H
2.62	CH_3	CH_3	H	H	NC(O)H
2.63	CH_3	CH_3	H	H	NH
2.64	CH_3	CH_3	H	H	$NC(O)CH_3$
2.65	CH_3	CH_3	H	H	$NC(O)OC(CH_3)_3$
2.66	CH_3	CH_3	H	H	NCH_2Ph
2.67	H	H	H	H	$NC(O)OCH_3$
2.68	H	H	H	H	NCH_2-4-Cl-Ph

2.69	H	H	H	H	NCH_2-4-CH_3-Ph
2.70	H	H	H	H	NCH_2-3-Cl-Ph
2.71	H	H	H	H	NCH_2-3-CF_3-Ph
2.72	H	H	H	H	NCH_2-3-OCH_3-Ph
2.73	CH_3	CH_3	H	H	$NC(O)OCH_3$
2.74	CH_3	CH_3	H	H	$NC(O)OC_2H_5$
2.75	H	H	H	H	$NC(O)OC_2H_5$
2.76	CH_3	CH_3	H	H	$NC(O)OCH_2CH_2Cl$
2.77	H	H	H	H	$NC(O)OCH_2CH_2Cl$
2.78	CH_3	CH_3	H	H	$NC(O)OC_4H_9$-(*n*)
2.79	H	H	H	H	$NC(O)OC_4H_9$-(*n*)
2.80	CH_3	CH_3	H	H	$NC(O)OC_4H_9$-(*i*)
2.81	H	H	H	H	$NC(O)OC_4H_9$-(*i*)
2.82	H	H	H	H	$CH(C_3H_7$-(*i*)) syn or anti
2.83	H	H	H	H	$CH(C_3H_7$-(*n*)) syn or anti
2.84	H	H	H	H	$CH(C_4H_9$-(*i*)) syn or anti
2.85	H	H	H	H	$CH(C_4H_9$-(*n*)) syn or anti
2.86	H	H	H	H	$C(C_2H_4$-(*c*))
2.87	H	H	H	H	$C(C_4H_8$-(*c*))
2.88	H	H	H	H	$CHCH(C_2H_5)_2$ syn or anti
2.89	H	H	H	H	$CHCH_2(C_3H_5$-(*c*) syn or anti
2.90	H	H	H	H	$CH(C_5H_9$-(*c*) syn or anti
2.91	H	H	H	H	$CHCH_2OAc$ syn or anti
2.92	H	H	H	H	CHCHO syn or anti
2.93	H	H	H	H	$CHCH_2OH$ syn or anti
2.94	H	H	H	H	$CHCH_2$-C_6H_5 syn or anti
2.95	H	H	H	H	C=O
2.96	H	H	H	H	$C(O$-C_3H_7-(*n*))$_2$
2.97	H	H	H	H	$C(O$-$C_2H_5)_2$
2.98	H	H	H	H	$C(O$-C_3H_7-(*i*))$_2$
2.99	H	H	H	H	$C(O$-$CH_3)_2$
2.100	H	H	H	H	$C(OH)CH_3$ syn or anti
2.101	H	H	H	H	$C(OH)C_2H_5$ syn or anti
2.102	H	H	H	H	
2.103	H	H	H	H	CF_2
2.104	H	H	H	H	CH(F) syn or anti
2.105	H	H	H	H	$C(CH_3)$ (C_2H_5) syn or anti
2.106	H	H	H	H	$C=C(CH_3)_2$
2.107	H	H	H	H	$C=C(C_2H_5)_2$
2.108	H	H	H	H	$C=cC_5H_8$
2.109	H	H	H	H	$C=CH(CH_3)$
2.110	H	H	H	H	$C=CH(C_2H_5)$
2.111	H	H	H	H	$C=cC_3H_4$

Table Z represents Table 3 [when Z is 3], Table 4 [when Z is 4], Table 5 [when Z is 5], Table 6 [when Z is 6] , Table 7 [when Z is 7], Table 8 [when Z is 8], Table 9 [when Z is 9], Table 10 [when Z is 10], Table 11 [when Z is 11], Table 12 [when Z is 12] , Table 13 [when Z is 13], Table 14 [when Z is 14], Table 15 [when Z is 15], Table 16 [when Z is 16], Table 17 [when Z is 17], Table 18 [when Z is 18], Table 19 [when Z is 19], Table 20 [when Z is 20], Table 21 [when Z is 21], Table 22 [when Z is 22], Table 23

[when Z is 23], Table 24 [when Z is 24], Table 25 [when Z is 25], Table 26 [when Z is 26], Table 27 [when Z is 27], Table 28 [when Z is 28] and represents Table 29 [when Z is 29]. X is either a single bond (-) or a double bond (=).

Table Z

Cpd. No.	R^1	R^4	R^5	R^6	R^7	X	Y
Z.001	H	CH_3	CH_3	H	H	=	O
Z.002	$CH_2C{\equiv}CH$	CH_3	CH_3	H	H	=	O
Z.003	$CH{=}C{=}CH_2$	CH_3	CH_3	H	H	=	O
Z.004	$C(O)CH_3$	CH_3	CH_3	H	H	=	O
Z.005	H	CH_3	H	H	H	=	O
Z.006	H	H	CH_3	H	H	=	O
Z.007	H	CH_3	CH_3	$C(O)CH_3$	H	=	O
Z.008	H	CH_3	CH_3	H	$C(O)CH_3$	=	O
Z.009	H	CH_3	$C(O)CH_3$	H	H	=	O
Z.010	H	$C(O)CH_3$	CH_3	H	H	=	O
Z.011	H	$COOCH_3$	H	H	H	=	O
Z.012	H	H	$COOCH_3$	H	H	=	O
Z.013	H	H	H	H	H	=	O
Z.014	$CH_2C{\equiv}CH$	H	H	H	H	=	O
Z.015	$CH{=}C{=}CH_2$	H	H	H	H	=	O
Z.016	$COCH_3$	H	H	H	H	=	O
Z.017	H	CF_3	CF_3	H	H	=	O
Z.018	H	OCH_3	OCH_3	H	H	=	O
Z.019	H	H	H	CH_3	CH_3	=	O
Z.020	H	C_2H_5	C_2H_5	H	H	=	O
Z.021	H	CH3	H	CH_3	H	=	O
Z.022	H	H	CH3	H	CH_3	=	O
Z.023	H	CH_3	CH_3	H	H	–	O
Z.024	$CH_2C{\equiv}CH$	CH_3	CH_3	H	H	–	O
Z.025	$CH{=}C{=}CH_2$	CH_3	CH_3	H	H	–	O
Z.026	$COCH_3$	CH_3	CH_3	H	H	–	O
Z.027	H	CH_3	H	H	H	–	O
Z.028	H	H	CH_3	H	H	–	O
Z.029	H	CH_3	CH_3	$C(O)CH_3$	H	–	O
Z.030	H	CH_3	CH_3	H	$C(O)CH_3$	–	O
Z.031	H	CH_3	C(O)CH3	H	H	–	O
Z.032	H	$C(O)CH_3$	CH_3	H	H	–	O
Z.033	H	$COOCH_3$	H	H	H	–	O
Z.034	H	H	$COOCH_3$	H	H	–	O
Z.035	H	H	H	H	H	–	O
Z.036	$CH_2C{\equiv}CH$	H	H	H	H	–	O
Z.037	$CH{=}C{=}CH_2$	H	H	H	H	–	O
Z.038	$COCH_3$	H	H	H	H	–	O
Z.039	H	H	H	H	H	–	O
Z.040	H	CF_3	CF_3	H	H	–	O
Z.041	H	OCH_3	OCH_3	H	H	–	O
Z.042	H	H	H	CH_3	CH_3	–	O
Z.043	$CH_2C{\equiv}CH$	H	H	CH_3	CH_3	–	O
Z.044	$CH{=}C{=}CH_2$	H	H	CH_3	CH_3	–	O
Z.045	$COCH_3$	H	H	CH_3	CH_3	–	O

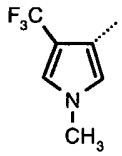
Z.046	H	C_2H_5	C_2H_5	H	H	–	O
Z.047	H	CH_3	H	CH_3	H	–	O
Z.048	H	H	H	H	H	–	CH_2
Z.049	$CH_2C{\equiv}CH$	H	H	H	H	–	CH_2
Z.050	$CH{=}C{=}CH_2$	H	H	H	H	–	CH_2
Z.051	$COCH_3$	H	H	H	H	–	CH_2
Z.052	H	H	H	H	H	=	CH_2
Z.053	$CH_2C{\equiv}CH$	H	H	H	H	=	CH_2
Z.054	$CH{=}C{=}CH_2$	H	H	H	H	=	CH_2
Z.055	$COCH_3$	H	H	H	H	=	CH_2
Z.056	H	CH_3	H	CH_3	H	–	CH_2
Z.057	H	CH_3	H	CH_3	H	=	CH_2
Z.058	H	H	CH_3	H	CH_3	–	CH_2
Z.059	H	H	CH_3	H	CH_3	=	CH_2
Z.060	H	CH_3	CH_3	CH_3	CH_3	=	CH_2
Z.061	H	CH_3	CH_3	CH_3	CH_3	–	CH_2
Z.062	$CH_2C{\equiv}CH$	CH_3	CH_3	CH_3	CH_3	–	CH_2
Z.063	$CH{=}C{=}CH_2$	CH_3	CH_3	CH_3	CH_3	–	CH_2
Z.064	$COCH_3$	CH_3	CH_3	CH_3	CH_3	–	CH_2
Z.065	H	CH_3	CH_3	CH_3	CH_3	=	$CH(CH_3)$ syn or anti
Z.066	H	CH_3	CH_3	CH_3	CH_3	–	$CH(CH_3)$ syn or anti
Z.067	$CH_2C{\equiv}CH$	CH_3	CH_3	CH_3	CH_3	–	$CH(CH_3)$ syn or anti
Z.068	$CH{=}C{=}CH_2$	CH_3	CH_3	CH_3	CH_3	–	$CH(CH_3)$ syn or anti
Z.069	$COCH_3$	CH_3	CH_3	CH_3	CH_3	–	$CH(CH_3)$ syn or anti
Z.070	H	H	H	H	H	=	$CH(CH_3)$ syn or anti
Z.071	H	H	H	H	H	–	$CH(CH_3)$ syn or anti
Z.072	$CH_2C{\equiv}CH$	H	H	H	H	–	$CH(CH_3)$ syn or anti
Z.073	$CH{=}C{=}CH_2$	H	H	H	H	–	$CH(CH_3)$ syn or anti
Z.074	$COCH_3$	H	H	H	H	–	$CH(CH_3)$ syn or anti
Z.075	H	H	H	H	H	–	$CH(C_2H_5)$ syn or anti
Z.076	H	H	H	H	H	–	CH_2CH_2
Z.077	$CH_2C{\equiv}CH$	H	H	H	H	–	CH_2CH_2
Z.078	$CH{=}C{=}CH_2$	H	H	H	H	–	CH_2CH_2
Z.079	$COCH_3$	H	H	H	H	–	CH_2CH_2
Z.080	H	CH_3	CH_3	H	H	=	CH_2CH_2
Z.081	H	CH_3	CH_3	H	H	–	CH_2CH_2
Z.082	H	H	H	CH_3	CH_3	=	CH_2CH_2
Z.083	H	H	H	CH_3	CH_3	–	CH_2CH_2
Z.084	H	H	H	OCH_3	H	–	CH_2CH_2
Z.085	H	H	H	H	OCH_3	–	CH_2CH_2
Z.086	H	H	H	H	H	–	$CH_2CH_2CH_2$
Z.087	H	H	H	H	H	=	$CH_2CH_2CH_2$
Z.088	H	H	H	CH_3	CH_3	=	$C(CH_3)_2$
Z.089	H	H	H	CH_3	CH_3	–	$C(CH_3)_2$
Z.090	$CH_2C{\equiv}CH$	H	H	CH_3	CH_3	–	$C(CH_3)_2$
Z.091	$CH{=}C{=}CH_2$	H	H	CH_3	CH_3	–	$C(CH_3)_2$
Z.092	$COCH_3$	H	H	CH_3	CH_3	–	$C(CH_3)_2$
Z.093	H	CH_3	CH_3	CH_3	CH_3	=	$C(CH_3)_2$
Z.094	H	CH_3	CH_3	CH_3	CH_3	–	$C(CH_3)_2$
Z.095	H	CH_3	H	CH_3	H	–	$C(CH_3)_2$
Z.096	H	H	CH_3	H	CH_3	–	$C(CH_3)_2$
Z.097	H	CH_3	H	CH_3	H	=	$C(CH_3)_2$
Z.098	H	H	CH_3	H	CH_3	=	$C(CH_3)_2$
Z.099	H	CH_3	CH_3	CH_3	CH_3	–	$C(CH_3)(C_2H_5)$

Z.100	H	H	H	H	H	–	$C(CH_3)_2$
Z.101	$CH_2C{\equiv}CH$	H	H	H	H	–	$C(CH_3)_2$
Z.102	H	H	H	H	H	=	$C(CH_3)_2$
Z.103	H	CH_3	CH_3	H	H	–	$C(CH_3)_2$
Z.104	H	CH_3	CH_3	H	H	=	$C(CH_3)_2$
Z.105	H	H	H	H	H	=	$C(OCH_3)_2$
Z.106	H	H	H	H	H	–	$CH(OCH_3)$ syn or anti
Z.107	H	H	H	H	H	=	S
Z.108	$CH_2C{\equiv}CH$	H	H	H	H	=	S
Z.109	$CH{=}C{=}CH_2$	H	H	H	H	=	S
Z.110	$COCH_3$	H	H	H	H	=	S
Z.111	H	H	H	H	H	–	S
Z.112	$CH_2C{\equiv}CH$	H	H	H	H	–	S
Z.113	$CH{=}C{=}CH_2$	H	H	H	H	–	S
Z.114	$COCH_3$	H	H	H	H	–	S
Z.115	H	CH_3	CH_3	H	H	=	S
Z.116	H	CH_3	CH_3	H	H	–	S
Z.117	$CH_2C{\equiv}CH$	CH_3	CH_3	H	H	–	S
Z.118	$CH{=}C{=}CH_2$	CH_3	CH_3	H	H	–	S
Z.119	$COCH_3$	CH_3	CH_3	H	H	–	S
Z.120	H	H	H	CH_3	CH_3	=	S
Z.121	H	H	H	CH_3	CH_3	–	S
Z.122	$CH_2C{\equiv}CH$	H	H	CH_3	CH_3	–	S
Z.123	$CH{=}C{=}CH_2$	H	H	CH_3	CH_3	–	S
Z.124	$COCH_3$	H	H	CH_3	CH_3	–	S
Z.125	H	OCH_3	OCH_3	H	H	=	S
Z.126	H	OCH_3	OCH_3	H	H	–	S
Z.127	H	H	CH_3	H	H	=	S
Z.128	H	H	CH_3	H	H	–	S
Z.129	H	CH_3	H	H	H	=	S
Z.130	H	CH_3	H	H	H	–	S
Z.131	H	CH_3	H	CH_3	H	=	S
Z.132	H	CH_3	H	CH_3	H	–	S
Z.133	H	H	CH_3	H	CH_3	=	S
Z.134	H	H	CH_3	H	CH_3	–	S
Z.135	H	H	OCH_3	H	H	=	S
Z.136	H	H	OCH_3	H	H	–	S
Z.137	H	OCH_3	H	H	H	=	S
Z.138	H	OCH_3	H	H	H	–	S
Z.139	H	CH_3	H	CH_3	CH_3	=	S
Z.140	H	CH_3	H	CH_3	CH_3	–	S
Z.141	H	H	CH_3	CH_3	CH_3	=	S
Z.142	H	H	CH_3	CH_3	CH_3	–	S
Z.143	H	H	H	CH_3	H	=	S
Z.144	H	H	H	CH_3	H	–	S
Z.145	H	H	H	H	CH_3	=	S
Z.146	H	H	H	H	CH_3	–	S
Z.147	H	H	H	OCH_3	H	=	S
Z.148	H	H	H	OCH_3	H	–	S
Z.149	H	H	H	H	OCH_3	=	S
Z.150	H	H	H	H	OCH_3	–	S
Z.151	H	H	H	H	H	=	$N(CH_3)$
Z.152	H	H	H	H	H	–	$N(CH_3)$
Z.153	$CH_2C{\equiv}CH$	H	H	H	H	–	$N(CH_3)$

Z.154	$CH=C=CH_2$	H	H	H	H	–	$N(CH_3)$
Z.155	$COCH_3$	H	H	H	H	–	$N(CH_3)$
Z.156	H	CH_3	CH_3	H	H	=	$N(CH_3)$
Z.157	H	CH_3	CH_3	H	H	–	$N(CH_3)$
Z.158	$CH_2C\equiv CH$	CH_3	CH_3	H	H	–	$N(CH_3)$
Z.159	$CH=C=CH_2$	CH_3	CH_3	H	H	–	$N(CH_3)$
Z.160	$COCH_3$	CH_3	CH_3	H	H	–	$N(CH_3)$
Z.161	H	H	H	H	H	=	$N(C_2H_5)$
Z.162	H	H	H	H	H	–	$N(C_2H_5)$
Z.163	H	H	H	H	H	=	NCH_2Ph
Z.164	H	H	H	H	H	–	NCH_2Ph
Z.165	H	H	H	H	H	=	$NC(O)CH_3$
Z.166	H	H	H	H	H	–	$NC(O)CH_3$
Z.167	H	H	H	H	H	=	$NC(O)OC(CH_3)_3$
Z.168	H	H	H	H	H	–	$NC(O)OC(CH_3)_3$
Z.169	H	H	H	H	H	=	NH
Z.170	H	H	H	H	H	–	NH
Z.171	H	H	H	H	H	=	NC(O)H
Z.172	H	H	H	H	H	–	NC(O)H
Z.173	H	CH_3	CH_3	H	H	=	NCH_2Ph
Z.174	H	CH_3	CH_3	H	H	–	NCH_2Ph
Z.175	H	CH_3	CH_3	H	H	=	$NC(O)CH_3$
Z.176	H	CH_3	CH_3	H	H	–	$NC(O)CH_3$
Z.177	H	CH_3	CH_3	H	H	=	$NC(O)OC(CH_3)_3$
Z.178	H	CH_3	CH_3	H	H	–	$NC(O)OC(CH_3)_3$
Z.179	H	CH_3	CH_3	H	H	=	NH
Z.180	H	CH_3	CH_3	H	H	–	NH
Z.181	H	CH_3	CH_3	H	H	=	NC(O)H
Z.182	H	CH_3	CH_3	H	H	–	NC(O)H
Z.183	H	H	H	H	H	–	$NC(O)OCH_3$
Z.184	H	H	H	H	H	–	NCH_2-4-Cl-Ph
Z.185	H	H	H	H	H	–	NCH_2-4-CH_3-Ph
Z.186	H	H	H	H	H	–	NCH_2-3-Cl-Ph
Z.187	H	H	H	H	H	–	NCH_2-3-CF_3-Ph
Z.188	H	H	H	H	H	–	NCH_2-3-OCH_3-Ph
Z.189	H	CH_3	CH_3	H	H	–	$NC(O)OCH_3$
Z.190	H	CH_3	CH_3	H	H	–	$NC(O)OC_2H_5$
Z.191	H	H	H	H	H	–	$NC(O)OC_2H_5$
Z.192	H	CH_3	CH_3	H	H	–	$NC(O)OCH_2CH_2Cl$
Z.193	H	H	H	H	H	–	$NC(O)OCH_2CH_2Cl$
Z.194	H	CH_3	CH_3	H	H	–	$NC(O)OC_4H_9$-(*n*)
Z.195	H	H	H	H	H	–	$NC(O)OC_4H_9$-(*n*)
Z.196	H	CH_3	CH_3	H	H	–	$NC(O)OC_4H_9$-(*i*)
Z.197	H	H	H	H	H	–	$NC(O)OC_4H_9$-(*i*)
Z.198	H	CH_3	CH_3	H	H	–	$NC(O)OC_3H_7$-(*n*)
Z.199	H	H	H	H	H	–	$NC(O)OC_3H_7$-(*n*)
Z.200	H	CH_3	CH_3	H	H	–	$NC(O)OC_3H_7$-(*i*)
Z.201	H	H	H	H	H	–	$NC(O)OC_3H_7$-(i)
Z.202	H	H	H	H	H	–	$CH(C_7H_7$-(*i*)) syn or anti
Z.203	$CH_2C\equiv CH$	H	H	H	H	–	$CH(C_3H_7$-(*i*)) syn or anti
Z.204	$CH=C=CH_2$	H	H	H	H	–	$CH(C_3H_7$-(*i*)) syn or anti
Z.205	$COCH_3$	H	H	H	H	–	$CH(C_3H_7$-(*i*)) syn or anti
Z.206	H	H	H	H	H	=	$CH(C_3H_7$-(*i*)) syn or anti
Z.207	H	H	H	H	H	–	$CH(C_3H_7$-(*n*)) syn or anti

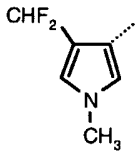
Z.208	H	H	H	H	H	–	CH(C_4H_9-(*i*)) syn or anti
Z.209	H	H	H	H	H	–	CH(C_4H_9-(*n*)) syn or anti
Z.210	H	H	H	H	H	–	C(C_2H_4-(*c*))
Z.211	H	H	H	H	H	–	C(C_4H_8-(*c*))
Z.212	H	H	H	H	H	–	CHCH(C_2H_5)$_2$ syn or anti
Z.213	H	H	H	H	H	–	CHCH$_2$(C_3H_5-(*c*) syn or anti
Z.214	H	H	H	H	H	–	CH(C_5H_9-(*c*) syn or anti
Z.215	H	H	H	H	H	–	CHCH$_2$OAc syn or anti
Z.216	H	H	H	H	H	–	CHCHO syn or anti
Z.217	H	H	H	H	H	–	CHCH$_2$OH syn or anti
Z.218	H	H	H	H	H	–	CHCH$_2$-C_6H_5 syn or anti
Z.219	H	H	H	H	H	–	C=O
Z.220	H	H	H	H	H	–	C(O-C_3H_7-(*n*))$_2$
Z.221	H	H	H	H	H	–	C(O-C_2H_5)$_2$
Z.222	H	H	H	H	H	–	C(OH)CH_3 syn or anti
Z.223	H	H	H	H	H	–	C(OH)C_2H_5 syn or anti
Z.224	H	H	H	H	H	–	
Z.225	H	H	H	H	H	–	CHCH(Ph)$_2$ syn or anti
Z.226	H	H	H	H	H	–	CF_2
Z.227	H	H	H	H	H	–	CH(F) syn or anti
Z.228	H	H	H	H	H	–	C(C_2H_5)(CH_3) syn or anti
Z.229	H	H	H	H	H	–	CH(*sec*-C_4H_9) syn or anti
Z.230	H	H	H	H	H	–	C=C(CH_3)$_2$
Z.231	H	H	H	H	H	–	C=C(C_2H_5)$_2$
Z.232	H	H	H	H	H	–	C=cC_5H_8
Z.233	H	H	H	H	H	–	C=CH(CH_3)
Z.234	H	H	H	H	H	–	C=CH(C_2H_5)
Z.235	H	H	H	H	H	–	C=cC_3H_4

Table 3 provides 235 compounds of formula (I) where Het is



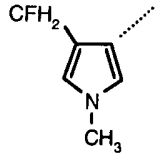
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 3.

Table 4 provides 235 compounds of formula (I) where Het is



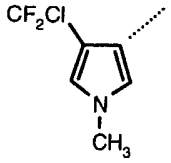
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 4.

Table 5 provides 235 compounds of formula (I) where Het is



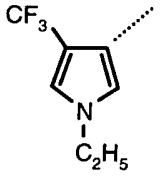
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 5.

Table 6 provides 235 compounds of formula (I) where Het is



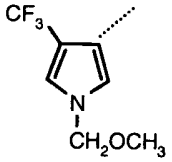
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 6.

Table 7 provides 235 compounds of formula (I) where Het is



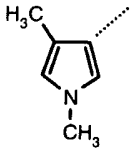
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 7.

Table 8 provides 235 compounds of formula (I) where Het is



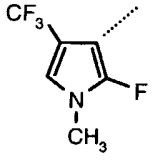
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 8.

Table 9 provides 235 compounds of formula (I) where Het is



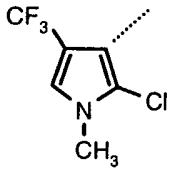
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 9.

Table 10 provides 235 compounds of formula (I) where Het is



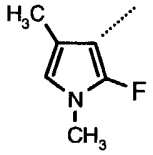
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 10.

Table 11 provides 235 compounds of formula (I) where Het is



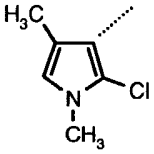
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 11.

Table 12 provides 235 compounds of formula (I) where Het is



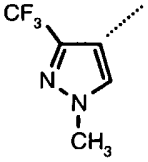
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 12.

Table 13 provides 235 compounds of formula (I) where Het is



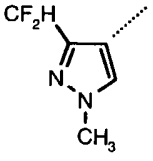
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 13.

Table 14 provides 235 compounds of formula (I) where Het is



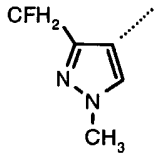
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 14.

Table 15 provides 235 compounds of formula (I) where Het is



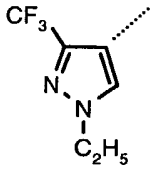
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 15.

Table 16 provides 235 compounds of formula (I) where Het is



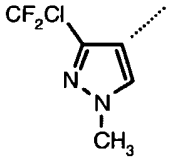
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 16.

Table 17 provides 235 compounds of formula (I) where Het is



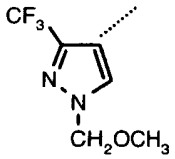
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 17.

Table 18 provides 235 compounds of formula (I) where Het is



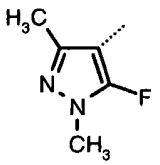
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 18.

Table 19 provides 235 compounds of formula (I) where Het is



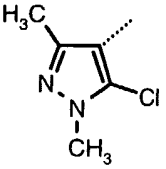
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 19.

Table 20 provides 235 compounds of formula (I) where Het is



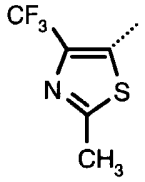
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 20.

Table 21 provides 235 compounds of formula (I) where Het is



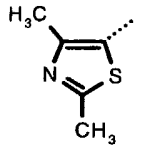
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 21.

Table 22 provides 235 compounds of formula (I) where Het is



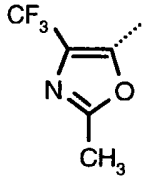
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 22.

Table 23 provides 235 compounds of formula (I) where Het is



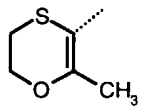
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 23.

Table 24 provides 235 compounds of formula (I) where Het is



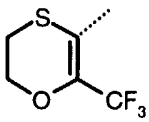
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 24.

Table 25 provides 235 compounds of formula (I) where Het is



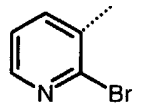
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 25.

Table 26 provides 235 compounds of formula (I) where Het is



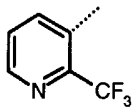
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 26.

Table 27 provides 235 compounds of formula (I) where Het is



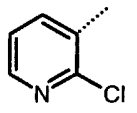
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 27.

Table 28 provides 235 compounds of formula (I) where Het is



R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 28.

Table 29 provides 235 compounds of formula (I) where Het is



R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 29.

Throughout this description, temperatures are given in degrees Celsius; "NMR" means nuclear magnetic resonance spectrum; MS stands for mass spectrum; and "%" is percent by weight, unless corresponding concentrations are indicated in other units; "syn" refers to a syn configuration of the relevant substituent with respect to the annellated benzene ring; and "anti" refers to an anti configuration of the relevant substituent with respect to the annellated benzene ring.

The following abbreviations are used throughout this description:

m.p. =	melting point	b.p.=	boiling point.
s =	singlet	br =	broad
d =	doublet	dd =	doublet of doublets
t =	triplet	q =	quartet
m =	multiplet	ppm =	parts per million

Table 30 shows selected melting point and selected NMR data, all with $CDCl_3$ as the solvent (unless otherwise stated; if a mixture of solvents is present, this is indicated as, for example, [$CDCl_3$ / d_6-DMSO]), (no attempt is made to list all characterising data in all cases) for compounds of Tables 1 to 29.

Table 30

Compund No.	m.p (/°C)	NMR proton shifts (/ppm) ($CDCl_3$ unless otherwise stated)
1.01	92-96	6.85 and 6.7(two m,2 x 2H), 6.47(t,1H), ca.5-3(br.,exchangeable with D_2O, 2H), 2.07(s,3H), 1.85(s,3H).
1.10	121-124	

2.01	92-93	7.05(t,1H), 6.7(t,2H), ca.5(brd,exchangeable with D_2O,2H), 2.0(s,3H), 1.9(m,2H), 1.8(s,3H), 1.7(m,1H), 1.5(m,1H).
2.02	92-93	
2.03	112-114	
2.10	75-76	
2.16	63-64	6.90(dd (~t), J_1= 7.3 Hz, J_2 = 8.2 Hz, 1H), 6.65(d,J=7.3Hz,1H), 6.46(d,J = 8.2 Hz,1H), 3.46 (br.,exchangeable with D_2O,2H), 3.35(br.s,1H), 3.31(br.s,1H), 1.87(m,2H), 1.70(m,1H), 1.50(m,1H), 1.18(m,1H).
2.23	74-75	6.99 (t, 1H), 6.63(d overlapped by a t, 2H), 4.0-3.5(br, exchangeable with D_2O, 2H), 3.08(br. s, 1H), 2.94(br.s, 1H), 1.76(m, 4H), 1.40(m, 4H).
2.53	139-140	6.97(t, 1H), 6.69(d, 1H), 6.51(d, 1H), 4.12(br s, 1H), 4.03(br s, 1H), 3.9-3.1(br, exchangeable with D_2O, 2H), 2.06(s, 3H) overlapped by a m at 2.12-2.05(2H), 1.26-1.19 (m, 2H).
2.55	viscous	6.95(t, 1H), 6.68(d, 1H), 6.51(d, 1H), 4.26(d, 1H), 4.18(d, 1H), 3.56(br, exchangeable with D_2O, 2H), 2.22(br d, 2H), 2.10(br, 2H), 1.22(m, 2+2H), 1.03(t,3H).
2.58	89-90	6.94(dd (~t), J_1= 7.3Hz, J_2= 7.9Hz,1H), 6.68(d,J=7.3Hz,1H), 6.49 (d, J= 7.9Hz,1H), 5.11(br,1H), 5.04(br,1H), 3.5-3.0(br,2H, exchangeable with D_2O), 2.07(m,2H), 1.40(s,9H), 1.30(m,2H).
2.59	oil	6.91(dd (~t), J_1= 7.3Hz, J_2= 7.9Hz,1H), 6.66(d,J=7.3Hz,1H), 6.44(d, J=7.9Hz,1H), 4.55(d, J=~1 Hz,1H)), 4.48(d,J=~1 Hz,1H), 4.0-3.0(br, exchangeable with D_2O, H), 2.02(m,2H), 1.25(m,2H).
2.61	176-177	syn-anti-mixture: 8.00 & 7.98(s, 1H), 6.96(t, 1H), 6.71 & 6.67(d, 1H), 6.50(d, 1H), 5.55 & 5.48(br s, 1H), 5.09 & 5.02(br s, 1H), 4.0-3.0(br, exchangeable with D_2O, 2H), 2.06(m, 2H), 1.37-1.47(m, 2H).
2.64	110-111	6.96(t, 1H), 6.58(d, 1H), 6.47(d, 1H), 3.79(br, 2H), 2.29(s, 3H), 2.01(s, 6H), 1.98(m, 2H), 1.54(m, 1H), 1.32(m, 1H).
2.65	94-95	6.96(t, 1H), 6.59(d, 1H), 6.47(d, 1H), ca 3.7(br, exchangeable with D_2O, 2H), 2.18(s, 3H), 1.95(m, 2H), 1.93(s, 3H), 1.49(m, 1H), 1.37(s, 9H), 1.25(m, 1H).
2.67	104-105	6.96(t, 1H), 6.69(d), 1H), 6.50(d, 1H), 5.20(br, 1H), 5.13(br, 1H), 3.64(s, 3H), 2.10(m, 2H), 1.33(m, 2H).
2.73	114-115	6.97(t. 1H),6.60(d, 1H), 3.80(br, 2H), 3.55(s, 3H), 2.20(s, 3H), 1.97(m, 2H),1.95(s, 3H), 1.50(m, 1H), 1.29(m, 1H).

2.75	viscous	6.95(t, 1H), 6.70(d, 1H), 6.50(d, 1H), 5.20(br, 1H), 5.13(br, 1H), 4.07(q, 2H), 3.33(br, 2H),2.10(m, 2H), 1.32(m, 2H), 1.22(t, 3H).
2.77	viscous	6.97(t, 1H), 6.72(d, 1H), 6.53(d, 1H), 5.24(m, 1H), 5.16(m, 1H), 4.27(br, 2H), 3.64(t, 2H), 3.18(br, 2H), 2.12(m, 2H), 1.35(m, 2H).
2.79	viscous	6.96(t, 1H), 6.71(d, 1H), 6.52(d, 1H), 5.20(br, 1H), 5.12(br, 1H), 4.02(t, 2H), 3.19(br, 2H), 2.09(m, 2H), 1.57(m, 2H), 1.34(m, 4H), 0.91(t, 3H).
2.81	viscous	6.96(t, 1H), 6.71(d, 1H), 6.52(d, 1H), 5.21(br, 1H), 5.13(br, 1H), 3.80(d, 2H), 3.25(br, 2H), 2.10(m, 2H), 1.88(m,1H), 1.33(m, 2H), 0.89(d, 6H).
2.82 syn:anti = 86:14	waxy solid	data for the syn component: 6.91(t, 1H), 6.65(d, 1H), 6.49(d, 1H), 3.5(br, 2H), 3.20(br, 1H), 3.15(br, 1H), 1.92(m, 2H), 1.54(d, 1H), 1.19(m, 2H), 1.03(m, 1H), 0.81(d, 6H).
2.82 syn:anti = 35:65	oil	data for the syn-anti mixture: 6.94-6.87(m, 1H), 6.65(m, 1H), 6.52 and 6.46(d, 1H), 3.52(br, 2H), 3.21, 3.16 and 3.14(three m, 2H), 1.96-1.84(m, 2H), 1.55 and 1.49(two d, 1H), 1.43 and 1.03(m, 1H), 1.22-1.12(m, 2H), 0.92 and 0.82(two m, 6H).
2.84 syn:anti = 12:88	viscous	data for the anti component: 6.89(t, 1H), 6.64(d, 1H), 6.48(d, 1H), ca 4.0-3.75(br, 2H), 3.03(br, 1H), 3.00(br, 1H), 1.96-1.87(m, 3H), 1.58(m, 1H), 1.12(m, 3H), 0.91(d, 6H).
2.84 syn:anti = 82:18	viscous	data for the syn component: 6.92(t, 1H), 6.64(d, 1H), 6.50(t, 1H), 3.53(br, 2H), 3.08(m, 1H), 3.03(m, 1H), 2.02(t, 1H), 1.90(m, 2H), 1.46(m, 1H), 1.16(m, 2H), 0.92(m, 2H), 0.81(d, 6H).
2.86	viscous	6.92(t, 1H), 6.66(d, 1H), 6.49(d, 1H), 3.52(br, 2H), 2.62(m, 1H), 2.59(m, 1H), 2.07(m, 2H), 1.27(m, 2H), 0.54(m, 2H), 0.45(m, 2H).
2.88 syn:anti = 46:54	viscous	data for the syn-anti-(1:1) mixture: 6.91 and 6.89(two t, 1H), 6.63(d, 1H), 6.48 and 6.46(two d, 1H), 3.52(br, 2H), 3.20, 3.16 and 3.13(three, m, 2H), 1.93-1.86(m, 2H), 1.78 and 1.72(two d, 1H), 1.45(m, 1H), 1.37-1.11(m, 6H), 0.85 and 0.76(two m, 6H).
2.89 syn:anti = 84:16	viscous	data for the syn component: 6.90(t, 1H), 6.64(d, 1H), 6.48(d, 1H), 3.51(br, 2H), 3.19(br s, 1H), 3.13(br s, 1H), 2.08(t, 1H), 1.94(m, 2H), 1.20(m, 2H), 0.97(m, 1H), 0.90(m, 1H), 0.57(1H), 0.35(m, 2H), 0.13(m, 2H).

2.90 syn:anti = 74:26	viscous	data for the syn component: 6.91(t, 1H), 6.64(d, 1H), 6.49(d, 1H), 3.52(br, 2H), 3.12(br s, 1H), 3.08(br s, 1H), 1.91(m, 2H), 1.8-1.0(m, 12H).
2.94 syn:anti = 74:26	viscous	data for the syn component: 7.28(m, 2H), 7.17(m, 1H), 7.04(d, 2H), 6.99(t, 1H), 6.72(d, 1H), 6.57(d, 1H), 3.6(br, 2H), 3.06(m, 2H), 2.35(m, 2H), 2.20(m,1H), 1.89(m, 2H), 1.20(m, 2H).
2.106	81-82	6.90(t, 1H),6.67(d, 1H), 6.47(d, 1H), 3.77(m, 1H), 3.73(m, 1H), 3.56(br, 2H), 1.88(m, 2H), 1.63(s,6H), 1.26(m, 2H).
2.107	viscous	6.89(t, 1H), 6.65(d, 1H), 6.46(d, 1H), 3.76(m, 1H), 3.72(m, 1H), 3.56(br, 2H), 2.12-1.90(m, 4H), 1.88(m, 2H), 1.26(m, 2H), 0.94(m, 6H).
3.001	150-154	
3.002	163-165	
3.023	129-133 [as a mixture of rotational isomers]	7.62(br), 7.44(d,*J* ~ 1 Hz), 7.32(d,*J* ~ 1 Hz), 7.2(m), 7.0(m); these signals account for 6 protons. Further signals at 3.7(s,3H), 1.84(s,3H), 1.82(s,3H), 2.0-1.5(m,4H).
3.024	172-176	7.5–7.0(m) and 6.8(br.s) accounting for 5H, 5.7–4.8 (two sets of AB systems,2H), 4.1(m,1H), 3.35 and 3.3(two s, accounting for 3H), 1.85, 1.75, 1.70(three s, accounting for 6H), 2.0–1.4(m,4H).
3.027	amorphous solid	7.60 br.s,1H), 7.34(br.s,1H), 7.22-7.07(m,3H), 7.01(br.s,1H), 5.27(d,1H), 3.71(s,3H), 2.19(m,1H), 1.91(m,1H), 1.83(s,3H), 1.71(m,1H), 1.49(m,1H).
3.028	amorphous solid	7.68(br.,1H), 7.53(d,1H), 7.37(br.s,1H), 7.17(t,1H), 7.00(br.s,1H), 6.96(d,1H), 5.39(d,1H), 3.70(s,3H), 2.25(m,1H), 1.83(s,3H), 1.83-1.66(m,2H), 1.48(m,1H).
3.035	amorphous solid	
3.048	amorphous solid	7.85(d,1H), 7.72(br.,1H), 7.48(br.s,1H), 7.60(t,1H), 7.0(br s,1H), 9.95(d,1H), 3.73(s,3H), 3.43(br.s,1H), 3.37(br.s,1H), 1.9(m,2H), 1.75(m,1H), 1.55(m,1H), 1.2(m,2H).
3.052	136-138	
3.076	154-155	
3.152	amorphous solid	7.71(br, 1H), 7.69(d, 1H), 7.39(br s, 1H), 7.18(t, 1H), 7.06(d, 1H), 6.99(br s, 1H), 4.30(br s, 1H), 4.18(br s, 1H), 3.71(s, 3H), 2.20(m, 2H), 2.12(s, 3H), 1.42-1.21(m, 2H)..
3.162	amorphous solid	7.71(d, 1H), 7.68(br, 1H), 7.39(br s, 1H), 7.17(t, 1H), 7.05(d, 1H), 7.01(br s, 1H), 4.40(br s, 1H), 4.28(br s, 1H), 3.72(s, 3H), 2.24(br, 2H), 2.17(br, 2H), 1.37(t, 1H), 1.25(t, 1H), 1.04(t, 3H).

3.168	amorphous solid	7.71 (br,2H), 7.37 (br.s,1H), 7.14(t,1H), 7.05(d,1H), 7.00(br.s,1H), 5.18(br,1H), 5.11(br,1H), 3.71(s,3H), 2.14(m,2H), 1.50(m,1H), 1.38(s,9H), 1.30(m,1H).
3.172	amorphous solid	syn-anti mixture: 8.00(s, 1H), 7.72(br, 1H), 7.58 & 7..31(d, 1H), 7.38 & 7.36(br s, 1H), 7.16(t, 1H), 7.11 & 7.09(d, 1H), 7.01(br s, 1H), 5.61 & 5.53 (br s, 1H), 5.19 & 5.09(br s, 1H), 3.71(s, 3H), 2.11(m, 2H), 1.75-1.61(m, 1H), 1.50-1.39(m, 1H).
3.176	231-232	7.48(br, 1H), 7.22(t, 1H), 7.09(br, 1H), 7.06(d, 1H), 6.96(br s, 1H), 5.91(br s, 1H), 3.69(s, 3H), 2.87(m, 1H), 2.22(m, 2H), 1.97(s, 3H), ca 1.9(m, 1H), 1.66(s, 3H), 1.49(s, 3H).
3.183	amorphous solid	7.71(br, 1H), 7.3(br d, 1H), 7.38(br s, 1H), 7.16(t, 1H), 7.06(d, 1H), 7.02(br s, 1H), 5.25(m, 1H), 5.18(m, 1H), 3.72(s, 3H), 3.62(s, 3H), 2.16(m, 2H), 1.55(m, 1H), 1.35(m, 1H).
3.189	amorphous	7.65(br, 1H), 7.31(d, 1H), 7.30(br s, 1H), 7.17(t, 1H), 7.02(d, 1H), 7.01(br s, 1H), 3.72(s, 3H), 3.54(s, 3H), 2.08(s, 3H), 1.99(s, 3H), 1.94(m, 2H), 1.76(m, 1H), 1.33(m, 1H).
3.191	amorphous	7.72(br, 1H), 7.64(d, 1H), 7.38(br s, 1H), 7.16(t, 1H), 7.07(d, 1H), 7.02(br s, 1H), 5.26(m, 1H), 5.20(m, 1H), 4.05(q, 1H), 3.72(s, 3H), 2.15(m, 2H), 1.55(m, 1H), 1.35(m, 1H), 1.20(t, 3H).
3.193	amorphous	7.72(br, 1H), 7.60(d, 1H), 7.38(br s, 1H), 7.16(t, 1H), 7.08(d, 1H), 7.02(br s, 1H), 5.29(m, 1H), 5.22(m, 1H), 4.24(m, 2H), 3.73(s, 3H), 3.61(t, 2H), 2.18(m, 2H), 1.59(m, 1H), 1.37(m, 1H).
3.195	amorphous	7.72(br, 1H), 7.65(d, 1H), 7.38(br s, 1H), 7.15(t, 1H), 7.06(d, 1H), 7.01(br s, 1H), 5.26(m, 1H), 5.18(m, 1H), 4.00(t, 2H), 3.72(s, 3H), 2.15(m, 2H), 1.55(m, 3H), 1.34(m, 3H), 0.89(t, 3H).
3.197	amorphous	7.72(br, 1H), 7.66(d, 1H), 7.38(br s, 1H), 7.16(t, 1H), 7.07(d, 1H), 7.01(br s, 1H), 5.27(m, 1H), 5.19(m, 1H), 3.78(dd , 2H), 3.73(s, 3H), 2.16(m, 2H), 1.87(m, 1H), 1.55(m, 1H), 1.35(m, 1H).
3.202 syn:anti = 90:10	121-125	data for the syn component: 7.91(d, 1H), 7.72(br, 1H), 7.38(br s, 1H), 7.10(t, 1H), 7.00(br s, 1H), 6.97(d, 1H), 3.72(s, 3H), 3.32(m, 1H), 3.22(m, 1H), 1.95(m, 2H), 1.58(d, 1H), 1.20(m, 2H), 0.90(m, 1H), 0.81(m, 6H).
3.202 syn:anti = 34:66	amorphous	data for the syn-anti mixture: 7.91 and 7.85(two d, 1H), 7.72(br,1H), 7.37(m, 1H), 7.12-7.05(m, 1H), 6.99(m, 1H), 6.98-6.94(m, 1H), 3.71(s, 3H), 3.32, 3.25. 3.22 and 3.19(four m, 2H), 1.96-1.88(m, 2H), 1.58 and 1.51(two d, 1H), 1.44 and

		0.98(two m, 1H), 1.26-1.12(m, 2H). 0.91 and 0.81(two m, 6H).
3.208 syn:anti = 10:90	130-131	data for the anti component: 7.85(d, 1H), 7.70(br, 1H), 7.38(br s, 1H), 7.08(t, 1H), 6.99(br s, 1H), 6.95(d, 1H), 3.71(s, 3H), 3.12(m, 1H), 3.06(m, 1H), 2.0-1.9(m, 3H), 1.6-1.5(m, 2H), 1.22-1.11(m, 3H), 0.92(d, 6H).
3.208 syn:anti = 85:15	amorphous	data for the syn component: 7.92(d, 1H), 7.70(br, 1H), 7.38(br s, 1H), 7.11(t, 1H), 6.99(br s, 1H), 6.96(d, 1H), 3.71(s, 1H), 3.19(m, 1H), 3.10(m, 1H), 2.06(t, 1H), 1,97(m, 2H), 1.44(m, 1H), 1.27-1.11(m, 2H), 0.90(m, 2H), 0.79(d, 6H).
3.210	155-157	7.84(d, 1H), 7.68(br, 1H), 7.37(br s, 1H), 7.11(t, 1H), 6.98(d, 1H), 3.71(s, 3H),2.69(m, 1H), 2.65(m, 1H), 2.09(m, 2H), 1.33(m, 1H), 1.32(m, 1H), 0.49(m, 4H).
3.212	amorphous	data for the syn-anti mixture: 7.92 and 7.85(two d, 1H), 7.72(br, 1H), 7.38(m, 1H), 7.13-7.06(m, 1H), 7.00(m, 1H), 6.96(m, 1H), 3.72(s, 3H), 3.32, 3.25, 3.22 and 3.19(four m, 2H), 1.92(m, 2H), 1.82 and 1.72(two d, 1H), 1.43(m, 1H), 1.35-1.05(m, 6H), 0.84 and 0.73(two t, 6H).
3.213 syn:anti = 95:05	115-117	data for the syn component: 7.90(d, 1H), 7.71br, 1H), 7.38(br s, 1H), 7.10(t, 1H), 6.99(br s, 1H), 6.96(d, 1H), 3.71(s, 3H), 3.31(m, 1H), 3.18(m, 1H), 2.12(t, 1H), 1.98(m, 2H), 1.28-1.14(m, 3H), 1.0-0.78(m, 2H), 0.55(m, 1H), 0.34(m, 2H), 0.16(m, 2H).
3.214 syn:anti = 74:26	amorphous	data for the syn component: 7.93(d, 1H), 7.72(br, 1H), 7.38(br s, 1H), 7.11(t, 1H), 7.00(br s, 1H), 6.95(d, 1H), 3.71(s, 3H), 3.24(m, 1H), 3.14(m, 1H), 1.94(m, 2H), 1.8-0.88(m, 12H).
3.218 syn:anti = 92:08	143-146	data for for the syn component: 7.96(d, 1H), 7.70(br, 1H), 7.37(br s, 1H), 7.30-6.95(m, 8H), 3.72(s, 3H), 3.18(m, 1H), 3.12(m, 1H), 2.37-2.07(m, 3H), 1.93(m, 2H), 1.25(m, 2H).
3.230	amorphous	7.82(d, 1H), 7.75(br, 1H), 7.39(br s, 1H), 7.08(t, 1H), 7.01(br s, 1H), 6.98(d, 1H), 3.83(m, 1H), 3.78(m, 1H), 3.72(s, 3H), 1.90(m, 2H), 1.61(s, 6H), 1.35-1.21(m, 2H).
3.231	amorphous	7.81(d, 1H), 7.75(br, 1H), 7.38(br s, 1H), 7.08(t, 1H), 7.00(br s, 1H), 6.97(d, 1H), 3.85(m, 1H), 3.77(m, 1H), 3.72(s, 3H), 2.1-1.9(m, 6H), 1.38-1.21(m, 2H), 0.93(m, 6H).
4.048	viscous oil	7.87(br, 1H), 7.80(d, 1H), 7.27(m, 1H), 7.07(t, 1H), 6.96(d, 1H), 6.95(t,*J*=56 Hz, 1H), 6.87(m, 1H), 3.68(s, 3H), 3.47(br.s, 1H), 3.36(br.s, 1H), 1.90(m, 2H), 1.74(m, 1H), 1.50(m, 1H), 1.16–1.24(m, 2H).
8.048	viscous oil	7.83(br d, 1H), 7.76(br, 1H), 7.55(br s, 1H), 7.12(br s,

		1H), 7.09(t, 1H), 6.98(d, 1H), 5.19(s, 2H), 3.45(br s, 1H), 3.37(br s, 1H), 3.32(s, 3H), 1.92(m, 2H), 1.77(m, 1H), 1.52(m, 1H), 1.22(m, 2H).
11.048	viscous oil	7.90(br d, 1H), 7.73(br, 1H), 7.09(t, 1H), 7.04(br s, 1H), 6.98(d, 1H), 3.68(s, 3H), 3.43(br s, 1H), 3.38(be s, 1H), 1.90(m, 2H), 1.77(m, 1H), 1.52(m, 1H), 1.24(m, 2H).
14.002	148-151	
14.023	162-166	
14.024	148-150	
14.027	182-184	
14.028	amorphous solid	8.04(s,1H), 7.66(br.,1H), 7.45(d,1H), 7.19(t,1H), 6.99(d,1H), 5.37(d,1H), 3.98(s,3H), 2.25(m,1H), 1.83(s,3H), 1.83-1.65(m,2H), 1.47(m,1H).
14.035	144-146	
14.048	amorphous solid	8.05(s,1H), 7.8(d,1H), 7.7(br.s,1H), 7.6(t,1H), 7.0(d,1H), 3.98(s,3H), 3.43(br.s,1H), 3.39(br.s,1H), 1.9(m,2H), 1.75(m,1H), 1.54(m,1H), 1.2(m,2H).
14.052	121-122	
14.076	127-130	
14.152	amorphous solid	8.09(s, 1H), 7.75(br, 1H), 7.62(d, 1H), 7.19(t, 1H), 7.09(d, 1H), 4.30(br, 1H), 4.20(br s, 1H), 3.98(s, 3H), 2.2-2.1(m, 2H), 2.11(br s, 3H), 1.4-1.2(m, 2H).
14.162	142-147	8.09(s, 1H), 7.74(br, 1H), 7.63(d, 1H), 7.19(t, 1H), 7.08(d, 1H), 4.40(br s, 1H), 4.31(br s, 1H), 4.00(s, 3H), 2.26(br, 2H), 2.15(br, 2H), 1.38(t, 1H), 1.26(t, 1H), 1.05(t, 3H).
14.168	amorphous solid	8.04(s,1H), 7.72(br,1H), 7.60(d,1H), 7.16(t,1H), 7.08(d,1H), 5.15(br,1H), 5.12(br,1H), 3.99(s,3H), 2.13(m,2H), 1.49(m,1H), 1.38(s,9H), 1.32(m,1H).
14.172	123-124	syn-anti mixture; DMSO: 9.97 (s, 1H), 8.45 & 8.43(br, 1H), 7.87(br s, 1H), 7.21 & 7.12(d, 1H), 7.06(m, 2H), 5.42 & 5.29(br, 1H), 5.24(m, 1H), 3.88(s, 3H), 1.87(m, 2H), 1.45 & 1.39(m, 1H), 1.21(m, 1H).
14.176	232-233	8.12(br, 1H), 7.23(t, 1H), 7.09-7.05(m, 2H), 5.93(s, 1H), 3.97(s, 3H), 2.90(m, 1H), 2.32-2.20(m, 2H), 1.97(s, 3H), 1.90(m, 1H), 1.67(s, 3H), 1.48(s, 3H).
14.178	148-150	7.98(br, 1H), 7.67(br, 1H), 7.30(d, 1H), 7.19(t, 1H), 7.04(d, 1H), 3.99(s, 3H), 2.05(s, 3H), 1.97(s, 3H) overlapped by a m (2.00-1.89, 2H), 1.68(m, 1H), 1.35(s, 9H), 1.31(m, 1H).
14.183	amorphous solid	8.05(s, 1H), 7.74(br, 1H), 7.53(d, 1H), 7.17(t, 1H), 7.10(d, 1H),5.23(m, 1H), 5.19(m, 1H), 4.00(s, 3H), 3.62(s, 3H), 2.14(m, 2H), 1.55(m, 1H), 1.35(1H).
14.189	amorphous	7.99(br s, 1H), 7.68(br, 1H), 7.28(d, 1H), 7.19(t, 1H), 7.06(d, 1H), 3.99(s, 3H), 3.54(s, 3H), 2.06(s, 3H), 2.02-1.91(m, 2H), 1.72(m, 1H), 1.35(m, 1H).
14.191	amorphous	8.05(s, 1H), 7.75(br, 1H), 7.55(d, 1H), 7.17(t, 1H),

		7.11(d, 1H), 5.23(m, 1H), 5.20(m, 1H), 4.05(q, 2H), 4.00(s, 3H), 2.15(m, 2H), 1.54(m, 1H), 1.35(m, 1H), 1.20(t, 3H).
14.193	amorphous	8.05(s, 1H), 7.72(br, 1H), 7.52(d, 1H), 7.18(t, 1H), 7.12(d, 1H), 5.27(m, 1H), 5.23(m, 1H), 4.24(m, 2H), 4.00(s, 3H), 3.61(t, 2H), 2.19(m, 2H), 1.58(m, 1H), 1.38(m, 1H).
14.195	amorphous	8.05(s, 1H), 7.75(br, 1H), 7.55(d, 1H), 7.17(t, 1H), 7.10(d, 1H), 5.23(m, 1H), 5.20(m, 1H), 4.00(s, 3H), 4.00(t, 2H), 2.15(m, 2H), 1.55(m, 3H), 1.35(m, 3H), 0.89(t, 3H).
14.197	amorphous	8.05(s, 1H), 7.77(br, 1H), 7.55(d, 1H), 5.24(m, 1H), 5.20(m, 1H), 3.99(s, 3H), 3.78(dd, 2H), 2.17(m, 2H), 1.86(m, 1H), 1.55(m, 1H), 1.36(m, 1H), 0.87(d, 6H).
14.202 syn:anti = 90:10	145-150	data for the syn component: 8.06(s, 1H), 7.84(d, 1H), 7.70(br, 1H), 7.12(t, 1H), 7.01(d, 1H), 3.99(s, 3H), 3.29(m, 1H), 3.23(m, 1H), 1.96(m, 2H), 1.60(d, 1H), 1.20(m, 2H), 0.96(m, 1H), 0.80(m, 6H).
14.202 syn:anti = 28:72	amorphous	data for the syn-anti mixture: 8.05(br, 1H), 7.83 and 7.78(two d, 1H), 7.70(br, 1H), 7.14-7.07(m, 1H), 7.01-6.98(m, 1H), 3.99(s, 3H), 3.30 and 3.21(two m, 2H), 1.97-1.90(m, 2H), 1.60 and 1.51(two d, 1H), 1.43 and 0.98(two m, 1H), 1.26-1.12(m, 2H), 0.91 and 0.82(two m, 6H).
14.208 syn:anti = 10:90	132-133	data for the anti component: 8.04(s, 1H), 7.77(d, 1H), 7.68(br, 1H), 7.09(t, 1H), 6.99(d, 1H), 3.99(s, 3H), 3.08(m, 2H), 2.0-1.91(m, 3H), 1.63-1.55(m, 2H), 1.22-1.10(m, 3H), 0.91(d, 6H).
14.208 syn:anti = 85:15	130-133	data for the syn component: 8.05(br s, 1H), 7.84(d, 1H), 7.68(br, 1H), 7.12(t, 1H), 7.00(d, 1H), 3.99(s, 3H), 3.16(m, 1H), 3.12(m, 1H), 2.10(t, 1H), 1.97(m, 2H), 1.44(m, 1H), 1.22(m, 2H), 0.91(m, 2H), 0.80(d, 6H).
14.210	151-153	8.04(br, 1H), 7.76(d, 1H), 7.65(br, 1H), 7.12(t, 1H), 7.02(d, 1H), 3.98(s, 3H), 2.66(m, 2H), 2.10(m, 2H), 1.29(m, 2H), 0.49(m, 4H).
14.212 syn:anti = 48:52	amorphous	data for the syn-anti mixture: 8.05(br, 1H), 7.84 and 7.78(two d, 1H), 7.69(br, 1H), 7.14-7.08(m, 1H), 6.99(m, 1H), 3.99(s, 3H), 3.29, 3.24 and 3.20(three m, 2H), 1.95(m, 2H), 1.83 and 1.74(two d, 1H), 1.44(m, 1H), 1.35-1.11(m, 6H), 0.85 and 0.74(two t, 6H).
14.213 syn:anti = 90:10	amorphous	data for the syn component: 8.05(s, 1H), 7.83(d, 1H), 7.70(br, 1H), 7.12(t, 1H), 7.00(d, 1H), 3.99(s, 3H), 3.29(m, 1H), 3.20(m, 1H), 2.14(t, 1H), 2.00(m, 2H), 1.16(m, 2H), 1.02-0.78(m,

		2H), 0.55(m, 1H), 0.35(m, 2H), -016(m, 2H).
14.214 syn:anti = 74:26	amorphous	data for the syn component: 8.05(s, 1H), 7.85(d, 1H), 7.69(br, 1H), 7.12(t, 1H), 7.00(d, 1H), 3.99(s, 3H), 3.21(m, 1H), 3.16(m, 1H), 1.96(m, 2H), 1.80-0.0.9(m, 12H).
14.218 syn:anti = 78:22	amorphous	data for the syn component: 8.05(s, 1H), 7.89(d, 1H), 7.68(br, 1H), 7.30-6.92(m, 7H), 4.00(s, 3H), 3.14(m, 2H), 2.60-2.10(m, 3H), 1.94(m, 2H), 1.29-1.15(m, 2H).
14.230	183-187	8.06(br s, 1H), 7.74(d, overlapped by br, 2H), 7.09(t, 1H), 7.02(d, 1H), 4.00(s, 3H), 3.83(m, 1H), 3.80(m, 1H), 1.92(m, 2H), 1.62(s, 6H), 1.35-1.11(m, 2H).
14.231	amorphous	8.05(br s, 1H), 7.73(d, overlapped by br, 2H), 7.09(t, 1H), 7.01(d, 1H), 3.99(s, 3H), 3.82(m, 1H), 3.79(m, 1H), 2.1-1.95(m, 4H), 1.92(m, 2H), 1.38-1.23(m, 2H), 0.93(m, 6H).
15.013	139-140	
15.023	amorphous solid	7.99(s,1H), 7.93(br.,1H), 7.22-7.16(m,2H), 7.03(d,1H), 6.88(t,J_{HF}=54Hz,1H), 3.93(s,3H), 1.90(m,2H), 1.82(s,3H), 1.80(s,3H), 1.55(m,2H).
15.027	168-169	
15.028	145-147	
15.035	136-139	
15.048	132-134	8.11(br.,1H), 8.03(s,1H), 7.83(d,1H), 7.08(t,1H), 6.98(d,1H), 6.88(t,J_{HF}=54Hz,1H), 3.93(s,3H), 3.49(br.s,1H), 3.37(br.s,1H), 1.91(m,2H), 1.74(m,1H), 1.51(m,1H), 1.22(m,2H).
15.049	107-108	
15.050	115-117	
15.052	118-122	
15.076	148-150	
15.086	amorphous solid	8.00(s. 1H), 7.97(br, 1H), 7.64(d, 1H), 7.15(t, 1H), 6.94(d, 1H), 6.86(t,J_{HF}=54.3Hz, 1H), 3.92(s, 3H), 3.25(br. s, 1H), 3.03(br. s, 1H), 1.94(d, 2H), 1.8-1.6(m, 8H).
15.152	141-147(dec.)	8.07(br, 1H), 8.05(s, 1H), 7.76(d, 1H), 7.18(t, 1H), 7.06(d, 1H), 6.87(t, J_{HF}=54.2Hz, 1H), 4.26(br s, 1H), 4.12(br s, 1H), 3.95(s, 3H), 2.16(m, 2H), 2.07(s, 3H), 1.37-1.19(m, 2H).
15.162	amorphous solid	8.17(br, 1H), 8.09(s, 1H), 7.72(d, 1H), 7.20(t, 1H), 7.07(d, 1H), 6.90(t, J_{HF}=54.2Hz, 1H), 4.56(br s, 1H), 4.38(br s, 1H), 3.96(s, 3H), 2.32(br, 2H), 2.23(br, 2H), 1.42(t, 1H), 1.30(t, 1H), 1.08(t, 3H).
15.168	viscous	8.12 (br,1H), 8.04(s,1H), 7.72(d,1H), 7.15(t,1H), 7.06 (d,1H), 6.89(t,J_{HF}=54Hz,1H), 5.22(br,1H), 5.11(br,1H), 3.05(s,3H), 2.12(m,2H), 1.53-1.24(m,2H), 1.37(s,9H).
15.172	amorphous solid	syn-anti mixture: 8.22 & 8.16(br, 1H), 8.06(br s, 1H),

		8.00(s, 1H), 7.58 & 7.42(d, 1H), 7.17(t, 1H), 7.10(d, 1H), 6.93 & 6.91(t, J_{HF}= 54Hz, 1H), 5.64 & 5.53(br s, 1H), 5.21 & 5.10(br s, 1H), 3.95(s, 3H), 2.10(m, 2H), 1.63(m, 1H), 1.43(m, 1H).
15.176	223-224	
15.183	amorphous solid	8.13(br, 1H), 8.05(s, 1H), 7.65(d, 1H), 7.17(t, 1H), 7.08(d, 1H), 6.91(t, J_{HF}= 54Hz, 1H), 5.29(br s, 1H), 5.19(br s, 1H), 3.96(s, 3H), 3.62(s, 3H), 2.15(m, 2H). 1.53(m, 1H), 1.35(m, 1H).
15.189	amorphous	7.95(br, 2H), 7.25(d, 1H), 7.19(t, 1H), 7.06(d, 1H), 6.94(t, J_{HF}= 54Hz, 1H), 3.94(s, 3H), 3.54(s, 3H), 2.07(s, 3H), 1.99(s, 3H), 1.98(m, 2H), 1.72(m, 1H), 1.35(m, 1H) .
15.191	amorphous	8.15(br, 1H), 8.05(s, 1H), 7.66(d, 1H), 7.17(t, 1H), 7.08(d, 1H), (6.91(t, J_{HF}= 54Hz, 1H), 5.30(m, 1H), 5.20(m, 1H), 4.05(q, 2H), 3.95(s, 3H), 2.14(m, 2H), 1.52(m, 1H), 1.35(m, 1H), 1.20(t, 3H).
15.193	amorphous	8.12(br, 1H), 8.05(s, 1H), 7.64(d, 1H), 7.18(t, 1H), 7.09(d, 1H), 6.91(t, J_{HF}= 54Hz, 1H), 5.32(m, 1H), 5.23(m, 1H), 4.24(m, 2H), 3.96(s, 3H), 3.61(t, 2H), 2.18(m, 2H), 1.55(m, 1H), 1.37(m, 1H).
15.195	amorphous	8.13(br, 1H), 8.05(s, 1H), 7.67(d, 1H), 7.16(t, 1H), 7.07(d, 1H), 6.91(t, J_{HF}= 54Hz, 1H), 5.29(M, 1H), 5.18(m, 1H), 4.01(t, 2H), 3.95(s, 3H), 2.16(m, 2H), 1.53(m, 3H), 1.33(m, 3H), 0.88(t, 3H).
15.197	amorphous	8.14(br, 1H), 8.05(s, 1H), 7.69(d, 1H), 7.15(t, 1H), 7.08(d, 1H), 6.91(t, J_{HF}= 54Hz, 1H), 5.30(m, 1H), 5.20(m, 1H), 3.96(s, 3H), 3.79(dd, 2H), 2.16(m, 2H), 1.86(m, 1H), 1.53(m, 1H), 1.35(m, 1H), 0.87(d, 6H).
15.202 syn:anti = 90:10	110-112	data for the syn component: 8.10(br, 1H), 8.05(br s, 1H), 7.92(d, 1H), 7.11(t, 1H), 6.98(d, 1H), 6.87(t, J_{HF}= 54Hz, 1H), 3.95(s, 3H), 3.37(m, 1H), 3.22(m, 1H), 1.95(m, 2H), 1.58(d, 1H), 1.19(m, 2H), 0.98(m, 1H), 0.81(m, 6H).
15.202 syn:anti = 35:65	amorphous	data for the syn-anti mixture: 8.09(br, 1H), 8.04(br, 1H), 7.91 and 7.84(two d, 1H), 7.13-7.06(m, 1H), 7.02-6.96(m, 1H), 6.88 and 6.87 (two t, J_{HF}= 54Hz, 1H), 3.95(s, 3H), 3.38, 3.30, 3.23 and 3.20(four m, 2H), 1.96-1.89(m, 2H), 1.58 and 1.50(two d, 1H), 1.44 and 0.97(two m, 1H), 1.20-1.12(m, 2H), 0.91 and 0.82(two m, 6H).
15.208 syn:anti = 12:88	viscous	data for the anti component: 8.07(br, 1H), 8.03(br s, 1H), 7.84(d, 1H), 7.08(t, 1H), 6.97(d, 1H), 6.88(t, J_{HF}= 54Hz, 1H), 3.94(s, 3H), 3.17(m, 1H), 3.07(m, 1H), 1.93(m, 3H), 1.59(m, 1H), 1.28-1.12(m, 4H), 0.91(d, 6H).
15.208	117-119	data for the syn component:

syn:anti = 93:7		8.08(br, 1H), 8.04(br s, 1H), 7.91(d, 1H), 7.12(t, 1H), 6.98(d, 1H), 6.87(t, J_{HF}= 54Hz, 1H), 3.94(s, 3H), 3.25(m, 1H), 3.11(m, 1H), 2.07(t, 1H), 1.96(m, 2H), 1.45(m, 1H), 1.19(m, 2H), 0.89(m, 2H), 0.80(d, 6H).
15.210	158-160	8.04(br, 2H), 7.84(d, 1H), 7.12(t, 1H), 7.00(d, 1H), 6.86(t, J_{HF}= 54Hz, 1H), 3.94(s, 3H), 2.74(m, 1H), 2.66(m, 1H), 2.11(m, 2H), 1.33(m, 1H), 1.26(m, 1H), 0.48(m, 4H).
15.212 syn:anti = 46:54	amorphous	data for the syn-anti mixture: 8.09(br, 1H), 8.04(br s, 1H), 7.92 and 7.85(two d, 1H), 7.13-7.07(m, 1H), 6.98(m, 1H), 6.88 and 6.87(two t, J_{HF}= 54Hz, 1H), 3.95(s, 3H), 3.37, 3.31, 3.23 and 3.20(four m, 2H), 1.95(m, 2H), 1.82 and 1.73(two d, 1H), 1.46(m, 1H), 1.37-1.10(m, 6H), 0.85 and 0.74(two t, 6H).
15.213 syn:anti = 90:10	131-135	data for the syn component: 8.08(br, 1H), 8.04(s, 1H), 7.90(d, 1H), 7.11(t, 1H), 6.98(d, 1H), 6.87(t, J_{HF}= 54Hz, 1H), 3.95(s, 3H), 3.37(m, 1H), 3.19(m, 1H), 2.13(t, 1H), 1.98(m, 2H), 1.24(m, 2H), 1.1-0,78(m, 2H), 0.55(m, 1H), 0.35(m, 2H), -0.16(m, 2H).
15.214 syn:anti = 74:26	amorphous	data for the syn component: 8.09(br, 1H), 8.04(s, 1H), 7.92(d, 1H), 7.12(t, 1H), 6.98(d, 1H), 6.87(t, J_{HF}= 54Hz, 1H), 3.95(s, 3H), 3.29(m, 1H), 3.15(m, 1H), 1.95(m, 2H), 1.80-0.90(m, 12H).
15.218 syn:anti = 74:26	amorphous	data for the syn component: 8.08(br, 1H), 8.05(s, 1H), 7.96(d, 1H), 7.3-6.9(m, 7H), 6.85(t, J_{HF}= 54Hz, 1H), 3.96(s, 3H), 3.23(m, 1H), 3.13(m, 1H), 2.4-2.07(m, 3H), 1.95(m, 2H), 1.3-1.1(m, 2H).
15.230	amorphous	8.15(br, 1H), 8.05(br s,1H), 7.83(d, 1H), 7.09(t, 1H), 7.00(d, 1H), 6.90(t, J_{HF}= 54Hz, 1H), 3.94(s, 3H), 3.92(m, 1H), 3.80(m, 1H), 1.91(m, 2H), 1.61(s, 6H), 1.35-1.22(m, 2H).
15.231	amorphous	8.13(br, 1H), 8.04(br s, 1H), 7.82(d, 1H), 7.09(t, 1H), 6.99(d, 1H), 6.90(t, J_{HF}= 54Hz, 1H), 3.94(s, 3H), 3.91(m, 1H), 3.78(m, 1H), 2.1-1.95(m, 4H), 1.91(m, 2H), 1.39-1.21(m, 2H), 0.93(m, 6H).
16.048	amorphous solid	8.16(brd d, 1H), 7.98(brd s, 1H), 7.85(d, 1H), 7.10(t, 1H), 6.99(d, 1H), 5.72(AB-signal, 1H), 5.59(AB-signal, 1H), 3.94(s, 3H), 3.47(br s, 1H), 3.38(brd s, 1H), 1.91(m, 2H), 1.76(m, 1H), 1.52(m, 1H), 1.23(m, 2H).
16.076	viscous	8.13(brd, 1H), 7.95(brd s, 1H), 7.70(d, 1H), 7.19(t, 1H), 7.02(d, 1H), 5.64(d, J_{HF}=48.7Hz, 2H), 3.92(s, 3H), 3.15(br s, 1H), 3.02(brd s, 1H), 1.77(d, 4H), 1.39(d, 4H).

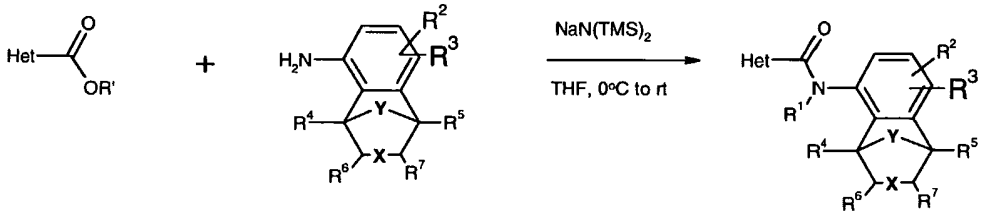
21.023	161-165	
20.048	132-133	
21.048	136-138	
22.048	viscous oil	7.78(br.,1H), 7.68(d,1H), 7.12–7.03(m,2H), 3.39(br.s,2H), 2.76(s,3H), 1.92(m,2H), 1.76(m,1H), 1.53(m,1H), 1.20(m,2H).
23.048	viscous oil	7.60(br d, 1H), 7.38(br, 1H), 7.10(t, 1H), 7.03(d, 1H), 3.39(m, 2H), 2.76(s, 3H), 1.93(m, 2H), 1.78(m, 1H), 1.55(m, 1H), 1.23(m, 2H).
24.048	viscous oil	7.85(br.,1H), 7.72(d,1H), 7.12–7.02(m,2H), 3.43(br.s,1H), 3.40(br.s,1H), 2.63(s,3H), 1.93(m,2H), 1.78(m,1H), 1.55(m,1H), 1.23(m,2H).
29.048	158-160	
29.052	151-152	
29.202 syn:anti = 90:10	146-147	data for the syn component: 8.53(m, 1H), 8.28(d, 1H), 8.17(br, 1H), 7.82(d, 1H), 7.42(d, 1H), 7.15(t, 1H), 7.05(d, 1H), 3.37(m, 1H), 3.26(m, 1H), 1.98(m, 2H), 1.62(d, 1H), 1.24(m, 2H), 0.97(m, 1H), 0.82(d, 6H).
29.202 syn:anti = 34:66	amorphous	data for the syn-anti mixture: 8.53(m, 1H), 8.27(m, 1H), 8.15(br, 1H), 7.82-7.77(m, 1H), 7.42(m, 1H), 7.17-7.10(m, 1H), 7.06-7.02(m, 1H), 3.38, 3.30, 3.26 and 3.23(four m, 2H), 1.99-1.90(m, 2H), 1.62 and 1.54(two d, 1H), 1.46 and 0.99(two m, 1H), 1.30-1.10(m, 2H), 0.91 and 0.83(two m, 6H).
29.208 syn:anti = 82:18	amorphous	
29.213 syn:anti = 90:10	amorphous	data for the syn component: 8.52(m, 1H), 8.29(d, 1H), 8.20(br, 1H), 7.81(d, 1H), 7.43(d, 1H), 7.15(t, 1H), 7.04(d, 1H), 3.36(m, 1H), 3.23(m, 1H), 2.16(t, 1H), 2.00(m, 2H), 1.29(m, 3H), 0.98(m, 1H), 0.86(m, 1H), 0.57(m, 1H), 0.35(m, 2H), -0.15(m, 2H).
29.208 syn:anti = 15:85	amorphous	data for the anti component: 8.52(m, 1H), 8.28(d, 1H), 8.16(br, 1H), 7.78(d, 1H), 7.41(d, 1H), 7.12(t, 1H), 7.02(d, 1H), 3.17(m, 1H), 3.10(m, 1H), 1.96(m, 3H), 1.59(m, 1H), 1.26-1.1(m 4H), 0.91(d, 6H).
29.212 syn:anti = 47:53	amorphous	data for the syn-anti mixture: 8.52(m, 1H), 8.26(m, 1H), 8.15(br, 1H), 7.83 and 7.78(two d, 1H), 7.42(m, 1H), 7.17-7.10(m, 1H), 7.04(m, 1H), 3.37. 3.30, 3.27 and 3.23(four m, 2H), 1.95(m, 2H), 1.86 and 1.77(two d, 1H), 1.45(m, 1H), 1.38-1.10(m, 6H), 0.85 and 0.74(two t, 6H).
29.214 syn:anti =	amorphous	data for the syn component: 8.52(m, 1H), 8.29(d, 1H), 8.16(br, 1H), 7.83(d, 1H),

74:26		7.43(d, 1H), 7.16(t, 1H), 7.05(d, 1H), 3.30(m, 1H), 3.19(m, 1H), 1.98(m, 2H), 1.80-0.8(m, 12H).
29.218 syn:anti = 88:12	amorphous	
29.230	amorphous	8.53(m, 1H), 8.29(d, 1H), 8.17(br, 1H), 7.71(d, 1H), 7.43(m, 1H), 7.13(t, 1H), 7.06(d, 1H), 3.91(m, 1H), 3.82(m, 1H), 1.93(m, 2H), 1.63(s, 6H), 1.40-1.23(m, 2H).
29.231	amorphous	8.53(m, 1H), 8.26(d, 1H), 8.16(br, 1H), 7.73(d, 1H), 7.43(m, 1H), 7.13(t, 1H), 7.05(d, 1H), 3.91(m, 1H), 3.81(m, 1H), 2.1-1.89(m, 6H), 1.40-1.23(m, 2H), 0.93(m, 6H).

The compounds according to formula (I) may be prepared according to the following reaction schemes.

Preparation of a compound of formula (I)

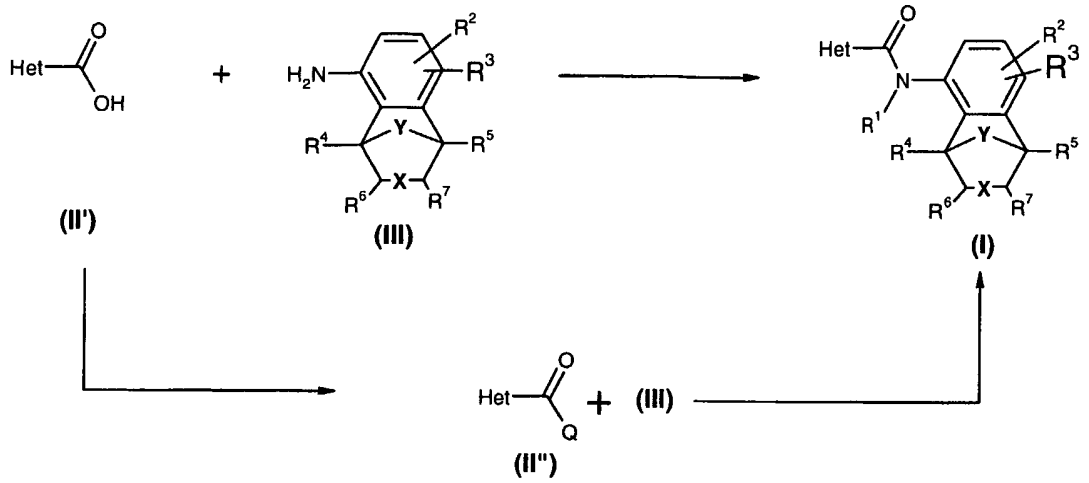
Scheme 1



(II) (III) (I)

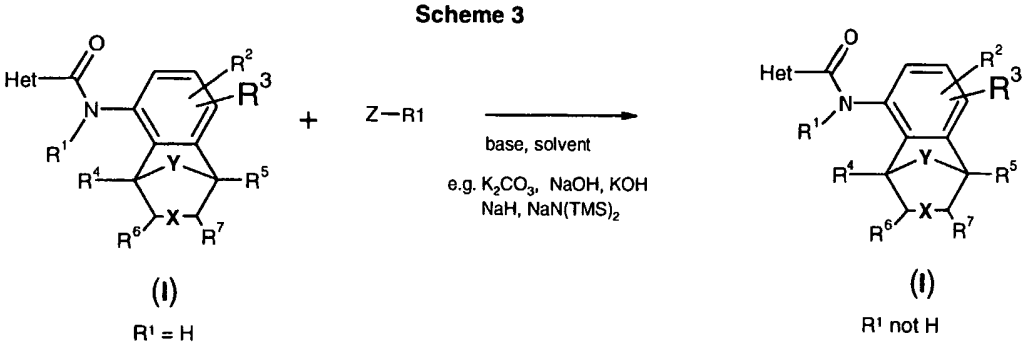
A compound of formula (I) [where R^1 is hydrogen; and Het, R^2, R^3, R^4, R^5, R^6, R^7, X and Y are as defined above for a compound of formula (I)] may be synthesized by reacting a compound of (II) [where Het is as defined above for a compound of formula (I) and R' is C_{1-5} alkyl] with an aniline of formula (III) [where R^2, R^3, R^4, R^5, R^6, R^7, X and Y are as defined above for a compound of formula (I)] in the presence of $NaN(TMS)_2$ at -10°C to ambient temperature, preferably in dry THF, as described by *J.Wang et al. Synlett*, 2001, 1485.

Scheme 2



Alternatively, a compound of formula (I) [where R^1 is hydrogen; and Het, R^2, R^3, R^4, R^5, R^6, R^7, X and Y are as defined above for a compound of formula (I)] may be prepared by reacting a compound of formula (II') [where Het is as defined above for a compound of formula (I)] with an aniline of formula (III) [where R^2, R^3, R^4, R^5, R^6, R^7, X and Y are as defined above for a compound of formula (I)] in the presence of an activating agent [such as BOP-Cl] and two equivalents of a base [such as triethylamine] or by reacting a compound of formula (II") [where Het is as defined above for a compound of formula (I); and Q is Cl, F or Br] which is obtained from a compound of formula (II') by treatment with a halogenating agent such as thionyl chloride, oxalyl chloride, phosgene, SF_4, DAST, Deoxofluor or thionlylbromide, with an aniline of formula (III) [where R^2, R^3, R^4, R^5, R^6, R^7, X and Y are as defined above for a compound of formula (I)] in the presence of one equivalent of base [such as NEt_3, $NaHCO_3$, $KHCO_3$, Na_2CO_3 or K_2CO_3] in a solvent [such as dichloromethane, ethyl acetate or DMF] preferably at -10 to 30°C.

Scheme 3



Furthermore a compound of formula (I) [where R^1 is hydrogen; and Het, R^2 to R^7, X and Y are as defined for a compound of formula (I)] is reacted with a species Z-R^1 [where R^1 is as defined for formula (I), except that it is not hydrogen; and Z is preferably Cl, Br or I; or Z is such that Z-R^1 is an anhydride, that is, when R^1 is COR*, Z is OCOR*] in the presence of a base [for example NaH, NEt_3, $NaHCO_3$ or K_2CO_3] in an appropriate solvent [such as ethyl acetate] or in a biphasic mixture [such as dichloromethane /water mixture], at –10 to 30°C.

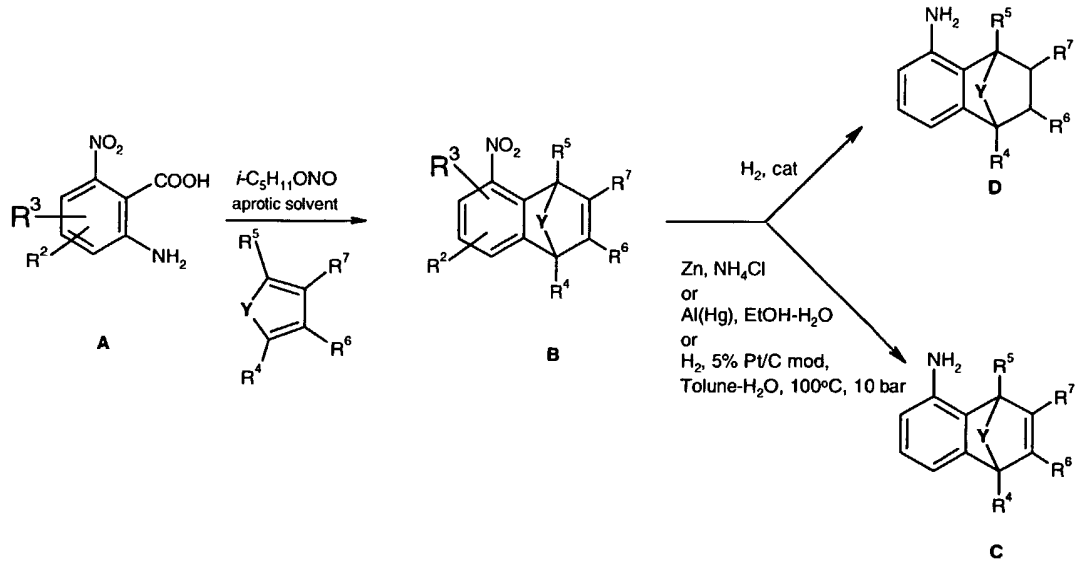
Starting Materials

Heterocyclic acids and esters [that is, compounds of formula (II') or (II)] are generally known from the literature or may be synthesized according to known methods. *Ortho*-substituted aminobenzonorbonenes (including homologues) of formula (C) or (D) (scheme 4) may be accomplished through *Diels-Alder* addition of an *in situ* generated benzyne [for example starting from a 6-nitroanthranilic acid of formula (A), as described by L.Paquette et al, *J. Amer. Chem. Soc. 99*, 3734 (**1977**) or from other suitable precursers (see H. Pellissier et al. *Tetrahedron, 59*, 701 (**2003**)] to a 5-7 membered cyclic 1,4-diene to give a nitro-benzonorbornadiene of formula (B) according to or by analogy to L.Paquette et al, *J. Amer. Chem. Soc. 99*, 3734 (**1977**), D. Gravel et al. *Can. J. Chem. 69*, 1193 (**1991**), J.R. Malpass et al. *Tetrahedron , 48*, 861 (**1992**), D.E. Lewis et al. *Synthetic Communications, 23*, 993 (**1993**), R.N. Warrener et al. *Molecules, 6*, 353 (**2001**), R.N. Warrener et al. *Molecules, 6*, 194 (**2001**) or I. Fleming et al. *J. Chem. Soc., Perkin Trans.1*, 2645 (**1998**). Suitable aprotic solvents for this step include ethyl acetate, dichloromethane, acetone, THF and dimethoxyethane. Reaction temperatures range from room temperature to 100°C, preferably 40-80°C.

Subsequent selective reduction of the nitro-group in a compound of formula (B) to give an amino-benzonorbornadiene of formula (C) requires mild conditions [for example, either metallic zinc in the presence of ammonium chloride, or aluminium amalgam]. Both methods work in protic solvents such as ethanol, water or mixtures thereof. Alternatively a compound of formula (C) may also be obtained from a compound of formula (B) by catalytic hydrogen reduction with a modified 5% Pt/C catalyst at elevated pressure (~10bar) and elevated temperature (~100°C) in toluene-water. Catalytic reduction under standard conditions (for example 5% Pd/C or 5% Ra/Ni or 5% Rh/C) in

a solvent [such as methanol, ethanol, THF or ethyl acetate] reduces both the nitro-group and the double bond to furnish a benzonorbornene of formula (D). Preferred reaction conditions are ambient temperature and normal pressure.

Scheme 4



Some of the compounds of formulae (B), (C) and (D) are described in the literature [see, for example, L. A Paquette et al., *J. Amer. Chem Soc. 99*, 3734 (1977); D. Gravel et al., *Canad. J. Chem. 69*, 1193 (1991); T. Nishiyama et al., *Rikagaku-hen, 28*, 37 (2000); H. Plieninger et al., *Chem. Ber. 109*, 2121 (1976); and A. J. Kirby et al., *J. Chem. Soc., Perkin Trans. 2*, 1997, 1081].

Novel starting materials of formulae (C) or (D) may be synthesized by analogy to scheme 4 or according to the literature cited above.

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

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

useful plants, while at the same time protecting also those parts of the plants that grow later e.g. from phytopathogenic microorganisms.

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

Furthermore the compounds according to present invention may be used for controlling fungi in related areas, for example in the protection of technical materials, including wood and wood related technical products, in food storage, in hygiene management, etc.

The compounds of formula (I) are, for example, effective against the phytopathogenic fungi of the following classes: Fungi imperfecti (e.g. Botrytis, Pyricularia, Helminthosporium, Fusarium, Septoria, Cercospora and Alternaria) and Basidiomycetes (e.g. Rhizoctonia, Hemileia, Puccinia). Additionally, they are also effective against the Ascomycetes classes (e.g. Venturia and Erysiphe, Podosphaera, Monilinia, Uncinula) and of the Oomycetes classes (e.g. Phytophthora, Pythium, Plasmopara). Outstanding activity has been observed against powdery mildew (Erysiphe spp.). Furthermore, the novel compounds of formula I are effective against phytopathogenic bacteria and viruses (e.g. against Xanthomonas spp, Pseudomonas spp, Erwinia amylovora as well as against the tobacco mosaic virus).

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

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

Suitable carriers and adjuvants can be solid or liquid and are substances useful in formulation technology, e.g. natural or regenerated mineral substances, solvents, dispersants, wetting agents, tackifiers, thickeners, binders or fertilizers. Such carriers are for example described in WO97/33890.

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

The compounds of formula (I) can be mixed with other fungicides, resulting in some cases in unexpected synergistic activities. Mixing components which are particularly preferred are azoles, such as azaconazole, BAY 14120, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazalil, imibenconazole, ipconazole, metconazole, myclobutanil, pefurazoate, penconazole, pyrifenox, prochloraz, propiconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triflumizole, triticonazole; pyrimidinyl carbinole, such as ancymidol, fenarimol, nuarimol; 2-amino-pyrimidines, such as bupirimate, dimethirimol, ethirimol; morpholines, such as dodemorph, fenpropidine, fenpropimorph, spiroxamine, tridemorph;

anilinopyrimidines, such as cyprodinil, mepanipyrim, pyrimethanil; pyrroles, such as fenpiclonil, fludioxonil; phenylamides, such as benalaxyl, furalaxyl, metalaxyl, R-metalaxyl, ofurace, oxadixyl; benzimidazoles, such as benomyl, carbendazim, debacarb, fuberidazole, thiabendazole; dicarboximides, such as chlozolinate, dichlozoline, iprodione, myclozoline, procymidone, vinclozoline; carboxamides, such as carboxin, fenfuram, flutolanil, mepronil, oxycarboxin, thifluzamide; guanidines, such as guazatine, dodine, iminoctadine; strobilurines, such as azoxystrobin, kresoxim-methyl, metominostrobin, SSF-129, trifloxystrobin, picoxystrobin, BAS 500F (proposed name pyraclostrobin), BAS 520; dithiocarbamates, such as ferbam, mancozeb, maneb, metiram, propineb, thiram, zineb, ziram; N-halomethylthiotetrahydrophthalimides, such as captafol, captan, dichlofluanid, fluoromides, folpet, tolyfluanid; Cu-compounds, such as Bordeaux mixture, copper hydroxide, copper oxychloride, copper sulfate, cuprous oxide, mancopper, oxine-copper; nitrophenol-derivatives, such as dinocap, nitrothal-isopropyl; organo-p-derivatives, such as edifenphos, iprobenphos, isoprothiolane, phosdiphen, pyrazophos, tolclofos-methyl; various others, such as acibenzolar-S-methyl, anilazine, benthiavalicarb, blasticidin-S, chinomethionate, chloroneb, chlorothalonil, cyflufenamid, cymoxanil, dichlone, diclomezine, dicloran, diethofencarb, dimethomorph, SYP-LI90 (proposed name: flumorph), dithianon, ethaboxam, etridiazole, famoxadone, fenamidone, fenoxanil, fentin, ferimzone, fluazinam, flusulfamide, fenhexamid, fosetyl-aluminium, hymexazol, iprovalicarb, IKF-916 (cyazofamid), kasugamycin, methasulfocarb, metrafenone, nicobifen, pencycuron, phthalide, polyoxins, probenazole, propamocarb, pyroquilon, quinoxyfen, quintozene, sulfur, triazoxide, tricyclazole, triforine, validamycin, zoxamide (RH7281).

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

be applied to seeds (coating) by impregnating the seeds or tubers either with a liquid formulation of the fungicide or coating them with a solid formulation.

A formulation [that is, a composition containing the compound of formula (I)] and, if desired, a solid or liquid adjuvant, is prepared in a known manner, typically by intimately mixing and/or grinding the compound with extenders, for example solvents, solid carriers and, optionally, surface active compounds (surfactants).

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

Advantageous rates of application are normally from 5g to 2kg of active ingredient (a.i.) per hectare (ha), preferably from 10g to 1kg a.i./ha, most preferably from 20g to 600g a.i./ha. When used as seed drenching agent, convenient dosages are from 10mg to 1g of active substance per kg of seeds.

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

The following non-limiting Examples illustrate the above-described invention in more detail.

EXAMPLE 1

This Example illustrates the preparation of Compound No. 2.01.

A solution of 1,4-dimethyl-5-nitro-1,4-dihydro-1,4-epoxynaphthalene (5.49g; 25.27mmol) (see T. Nishiyama et al., *Rikagaku-hen*, *28*, 37-43 (2000)) in THF (55ml) was hydrogenated in the presence of RaNi (1.1g) at ambient temparature. Hydrogen uptake was 2.23litres (97%) after 18hours. After filtering off the catalyst the filtrate was evaporated and taken up into ether, washed with an aqueous $NaHCO_3$-solution and dried ($NaSO_4$) to give 4.60g of crude product as an oil. Trituration with hexane and a trace of ether furnished a total of 4.51g (94%) of reddish crystalline product.

EXAMPLE 2

This Example illustrates the preparation of Compound No. 1.01.

To 1,4-dimethyl-5-nitro-1,4-dihydro-1,4-epoxynaphthalene (4.22g; 19.43mmol) (see Example 1) in ethanol (60ml) was added a solution of ammoniumchloride (2.08g) in water (5.2ml) at 47°C. Under vigorous stirring, zinc powder (9.10g; 0.14mol) was added

in portions over a period of 5minutes. The suspension was heated to reflux for 5½hours followed by filtration through Hyflo™ to give a clear yellow filtrate. After evaporation the crude product amounted 4.57g of a viscous oil. Column chromatography on silica gel in ethyl acetate-hexane (1:4) gave 1.24g (34%) of the desired product as brownish crystals.

EXAMPLE 3

This Example illustrates the preparation of Compound No. 2.16.

A solution of 5-nitrobenzonorbornadiene (L.A. Paquette et al., *J. Amer. Chem. Soc. 99*, 3734 (1977)) (2.52g; 13.46mmol) in methanol (100ml) was hydrogenated in the presence of 5% Pd/C (0.5g) at ambient temperature. H_2-uptake was 1.14litres (95%) after 11minutes. The solution was filtered from the catalyst and evaporated to give pure product (1.86g; 87%) as a yellow oil, which solidified on standing at room temperature (m.p. 63-64°C).

EXAMPLE 4

This Example illustrates the preparation of Compound No. 3.023.

A solution of 1-methyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid (1.02g; 5.3mmol) and a catalytic amount of DMF (3drops) in dichloromethane (20ml) was reacted under initial ice cooling with oxalyl chloride (0.805g; 1.2eq.) for 2hours. Within 15minutes, the reaction mixture was then added dropwise to a solution of 1,8-dimethyl-11-oxa-tricyclo[6.2.1.0*2,7*]undeca-2,4,6-trien-3-ylamine (Compound No. 2.01; see preparation above) (1.0g; 5.284mmol) and triethylamine (1.07g; 10.57mmol) in 20ml dichloromethane under cooling (3-7°C) with subsequent stirring at ambient temperature for 3¼hours. The reaction mixture was then poured on to ice water and extracted with dichloromethane to give 2.26g of crude product. Purification on silica gel in ethyl acetate-hexane (1:1) followed by trituration with ether-hexane furnished a solid (1.14g; 59%) as a mixture of isomers.

EXAMPLE 5

This Example illustrates the preparation of Compound No.3.024.

A suspension of NaH (0.107g; 60% oil dispersion, ~2.7mmol) in DMF (5ml) was reacted with a solution of 1-methyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid(1,8-dimethyl-11-oxa-tricyclo[6.2.1.0*2,7*]undeca-2,4,6-trien-3-yl)-amide (Compound No.

3.023; see preparation above) (0.65g; 1.784mmol) in 5ml DMF at 10-15°C for 30minutes. 3-Bromo-1-propyne (0.276g; 2.32mmol) was added and the mixture was further reacted overnight at ambient temperature. After aqueous work up with ice water and ethyl acetate and purification on silica gel 0.36g (50%) of the desired product as a mixture of isomers were obtained.

FORMULATION EXAMPLES FOR COMPOUNDS OF FORMULA (I)

Working procedures for preparing formulations of the compounds of formula I such as Emulsifiable Concentrates, Solutions, Granules, Dusts and Wettable Powders are described in WO97/33890.

BIOLOGICAL EXAMPLES: FUNGICIDAL ACTIONS

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

1 week old wheat plants cv. Arina are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application, the wheat plants are inoculated by spraying a spore suspension ($1x10^5$uredospores/ml) on the test plants. After an incubation period of 2 days at 20°C and 95%r.h. the plants are kept in a greenhouse for 8days at 20°C and 60%r.h. The disease incidence is assessed 10 days after inoculation.

Infestation is prevented virtually completely (0-5% infestation) with each of Compounds 3.048, 14.048, 29.048, 15.048, 20.048, 3.028, 22.048, 21.048, 15.023, 15.027, 15.028, 3.035, 14.035, 15.035, 15.052, 14.210, 15.210, 14.202 and 15.202.

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

5 week old apple seedlings cv. McIntosh are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after, the application apple plants are inoculated by shaking plants infected with apple powdery mildew above the test plants. After an incubation period of 12 days at 22°C and 60%r.h. under a light regime of 14/10hours (light/dark) the disease incidence is assessed.

Compounds 3.048, 14,048, 15.048, 22.048, 14.210, 15.210, 14.202, 15.202 and 15.023 each exhibit strong efficacy (<20% infestation).

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

4 week old apple seedlings cv. McIntosh are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application, the

apple plants are inoculated by spraying a spore suspension ($4x10^5$conidia/ml) on the test plants. After an incubation period of 4 days at 21°C and 95%r.h. the plants are placed for 4 days at 21°C and 60%r.h. in a greenhouse. After another 4 day incubation period at 21°C and 95%r.h. the disease incidence is assessed.

Compounds 3.048, 14.048, 14.210, 15.210, 14.202, 15.202 and 15.048 each exhibit strong efficacy (<20% infestation).

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

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

Compounds 3.023, 14.023, 3.048, 14.048, 15.048, 3.027, 3.028, 15.023, 14.210, 15.210, 14.202, 15.202 and 15.027 each exhibit strong efficacy (<20% infestation).

Example B-5: Action against Botrytis cinerea / grape (Botrytis on grapes)

5 week old grape seedlings cv. Gutedel are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. Two days after application, the grape plants are inoculated by spraying a spore suspension ($1x10^6$ conidia/ml) on the test plants. After an incubation period of 4 days at 21°C and 95%r.h. in a greenhouse the disease incidence is assessed.

Compounds 14.048, 15.048, 3.028, 14.210, 15.210, 14.202, 15.202 and 15.027 each show good activity in this test (<50% disease incidence).

Example B-6: Action against Botrytis cinerea / tomato (Botrytis on tomatoes)

4 week old tomato plants cv. Roter Gnom are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. Two days after application, the tomato plants are inoculated by spraying a spore suspension ($1x10^5$conidia/ml) on the test plants. After an incubation period of 4 days at 20°C and 95%r.h. in a growth chamber the disease incidence is assessed.

Compounds 3.048, 3.052, 14.052, 15.048, 14.210, 15.210, 14.202, 15.202 and 15.023 each exhibit good efficacy (<50% disease incidence).

Example B-7: Action against Septoria nodorum / wheat (Septoria leaf spot on wheat)

1 week old wheat plants cv. Arina are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application, the wheat plants are inoculated by spraying a spore suspension ($5x10^5$conidia/ml) on the test plants. After an incubation period of 1 day at 20°C and 95%r.h. the plants are kept for 10 days at 20°C and 60%r.h. in a greenhouse. The disease incidence is assessed 11 days after inoculation.

Compounds 3.002, 3.048, 14.048, 14.210, 15.210, 14.202, 15.202 and 15.048 each show good activity in this test (<50% disease incidence).

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

1 week old barley plants cv. Regina are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. Two days after application, the barley plants are inoculated by spraying a spore suspension ($3x10^4$conidia/ml) on the test plants. After an incubation period of 4 days at 20°C and 95%r.h. in a greenhouse the disease incidence is assessed.

Compounds 3.023, 14.023, 3.048, 14.048, 15.048, 3.027, 15.023, 15.027, 14.210, 15.210, 14.202, 15.202 and 15.028 each show good activity in this test (<20% disease incidence).

Example B-9: Action against Alternaria solani / tomato (Early blight on tomatoes)

4 week old tomato plants cv. Roter Gnom are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. Two days after application, the tomato plants are inoculated by spraying a spore suspension ($2x10^5$conidia/ml) on the test plants. After an incubation period of 3days at 20°C and 95%r.h. in a growth chamber the disease incidence is assessed.

Compounds 3.023, 14.023, 3.048, 14.048, 14.210, 15.210, 14.202, 15.202 and 15.048 each show good activity in this test (<20% disease incidence).

Example B-10: Action against Uncinula necator / grape (Powdery mildew on grapes)

5week old grape seedlings cv. Gutedel are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application, the grape plants are inoculated by shaking plants infected with grape powdery mildew above the test plants. After an incubation period of 7days at 26°C and 60%r.h. under a light regime of 14/10hours (light/dark) the disease incidence is assessed.

Compounds 14.048, 15.048, 14.028 and 15.023 each show good activity in this test (<20% disease incidence).

Example B-11: Systemic Action against Erysiphe graminis / barley (Powdery mildew on barley) (Pouch test)

The formulated test compound (0.002% active ingredient) is applied into a pouch which was previously equipped with a filter paper. After the application barley seeds (cv.Express) are sown into the upper fault of the filter paper. The prepared pouches are then incubated at 23°C/18°C (day/night) and 80%r.h. One week after sowing barley plants were inoculated by shaking powdery mildew infected plants above the test plants. After an incubation period of 6days the disease incidence was assessed. The efficacy of each test compound is used as an indicator for systemic activity.

Compounds 14.024, 3.002, 3.048, 29.048, 3.027, 22.048, 21.048, 15.023, 15.027, 15.028 and 15.035 each show good activity in this test (<50% disease incidence).

Example B-12: Action against Fusarium culmorum / wheat (Fusarium head blight on wheat) (Pouch test)

A conidia suspension of F. culmorum ($7x10^5$conidia/ml) is mixed with the formulated test compound (0.002% active ingredient). The mixture is applied into a pouch which was previously equipped with a filter paper. After the application wheat seeds (cv.Orestis) are sown into the upper fault of the filter paper. The prepared pouches are then incubated for 11days at ca.10-18° C and 100%r.h. with a daily light period of 14hours. The evaluation is made by assessing the degree of disease occurrence in the form of brown lesions on the roots.

Compounds 14.024, 15.048, 20.048, 14.027, 24.048 and 3.035 each show good activity in this test (<50% disease incidence).

Example B-13: Action Gaeumannomyces graminis / wheat (Take-all on wheat) (pouch test)

A defined amount of mycelium of G. graminis is mixed with water. The formulated test compound (0.002% active ingredient) is added to the mycelium suspension. The mixture is applied into a pouch which was previously equipped with a filter paper. After the application wheat seeds (cv.Orestis) are sown into the upper fault of the filter paper. The prepared pouches are then incubated for 14days at 18°C/16°C (day/night) and 80%r.h. with a daily light period of 14hours. The evaluation is made by assessing the degree of root browning.

Compounds 15.048, 20.048, 21.048, 15.028 and 15.052 each show good activity in this test (<50% disease incidence).

Example B-14: Action against Puccinia recondita / wheat (Brownrust on wheat) (Pouch test)

Formulated test compound (0.002% active ingredient) is applied into a pouch which was previously equipped with a filter paper. After the application wheat seeds (cv.Arina) are sown into the upper fault of the filter paper. The prepared pouches are then incubated at 23°C/18°C (day/night) and 80%r.h. One week after sowing, the wheat plants were inoculated by spraying a spore suspension ($1x10^5$uredospores/ml) on the test plants. After an incubation period of 1day at 23°C and 95%r.h. the plants were kept for 9days at 20°C/18°C (day/night) and 80%r.h . The disease incidence was assessed 10days after inoculation. The efficacy of each test compound is used as an indicator for systemic activity.

Compounds 14.024, 3.002, 14.002, 15.048, 20.048, 3.027, 22.048, 15.023, 15.027, 15.028, 3.035, 14.035 and 15.035 each show good activity in this test (<50% disease incidence).

Example B-15: Action against Rhizoctonia solani / rice (Sheath blight on rice) (Pouch test)

A defined amount of mycelium of R.solani is mixed with water. The formulated test compound (0.002% active ingredient) is added to the mycelium suspension. The mixture is applied into a pouch which was previously equipped with a filter paper. After the application rice seeds (cv.Koshihikari) are sown into the upper fault of the filter paper. The prepared pouches are then incubated for 10days at 23°C/21°C (day/night) and 100%r.h. with a daily light period of 14hours. The evaluation is made by assessing the degree of disease occurrence in the form of brown lesions on the roots.

Compounds 3.048, 14.048, 29.048, 3.052, 29.052, 14.052, 15.048, 20.048, 3.027, 14.028, 22.048, 21.048, 4.048, 15.023, 3.035, 14.035 and 15.035 each show good activity in this test (<50% disease incidence).

Example B-16: Action against Septoria nodorum / wheat (Septoria leaf spot on wheat) (Pouch test)

The formulated test compound (0.002% active ingredient) was applied into a pouch which was previously equipped with a filter paper. After the application, wheat

seeds (cv. Arina) were sown into the upper fault of the filter paper. The prepared pouches were then incubated at 23°C/18°C (day/night) and 80%r.h. One week after sowing, the wheat plants were inoculated by spraying a spore suspension ($5x10^5$conidia/ml) on the test plants. After an incubation period of 1day at 23°C and 95%r.h. the plants were kept for 9days at 20°C/18°C (day/night) and 80%r.h. The disease incidence was assessed 8days after inoculation. The efficacy of each test compound is used as an indicator for systemic activity.

Compounds 3.048, 29.048, 15.048, 14.027, 15.023 and 15.027 each show good activity in this test (<50% disease incidence).

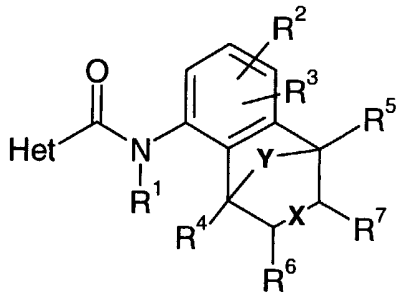
Example B-17: Action against Septoria tritici / wheat (Septoria leaf spot on wheat)

2 week old wheat plants cv. Riband are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application, wheat plants are inoculated by spraying a spore suspension ($10x10^5$conidia/ml) on the test plants. After an incubation period of 1 day at 23°C and 95% r.h., the plants are kept for 16 days at 23°C and 60% r.h. in a greenhouse. The disease incidence is assessed 18 days after inoculation.

Compounds 14.202 or 14.210 each show good activity in this test (<20% disease incidence).

CLAIMS

1. A compound of formula (I):



(I)

where Het is a 5- or 6-membered heterocyclic ring containing one to three heteroatoms, each independently selected from oxygen, nitrogen and sulphur, provided that the ring is not 1,2,3-triazole, the ring being substituted by groups R^8, R^9 and R^{10}; X is a single or double bond; Y is O, S, $N(R^{11})$ or $(CR^{12}R^{13})(CR^{14}R^{15})_m(CR^{16}R^{17})_n$; m is 0 or 1; n is 0 or 1; R^1 is hydrogen, C_{1-4} alkyl, C_{1-4} haloalkyl, C_{1-4} alkoxy, C_{1-4} haloalkoxy, $CH_2C{\equiv}CR^{18}$, $CH_2CR^{19}{=}CHR^{20}$, $CH{=}C{=}CH_2$ or COR^{21}; R^2 and R^3 are each, independently, hydrogen, halogen, C_{1-4} alkyl, C_{1-4} alkoxy or C_{1-4} haloalkoxy; R^4, R^5, R^6 and R^7 are each, independently, hydrogen, halogen, C_{1-4} alkyl, C_{1-4} haloalkyl, C_{1-4} alkoxy, C_{1-4} haloalkoxy, C_{1-4} alkylthio, C_{1-4} haloalkylthio, hydroxymethyl, C_{1-4} alkoxymethyl, $C(O)CH_3$ or $C(O)OCH_3$; R^8, R^9 and R^{10} are each, independently, hydrogen, halogen, cyano, nitro, C_{1-4} alkyl, C_{1-4} haloalkyl, C_{1-4} alkoxy(C_{1-4})alkylene or C_{1-4} haloalkoxy(C_{1-4})alkylene, provided that at least one of R^8, R^9 and R^{10} is not hydrogen; R^{11} is hydrogen, C_{1-4} alkyl, benzyl (in which the phenyl group is optionally substituted with up to three substituents, each independently selected from halogen, C_{1-4} alkyl, C_{1-4} haloalkyl and C_{1-4} alkoxy), formyl, $C(O)C_{1-4}$ alkyl (optionally substituted by halogen or C_{1-4} alkoxy), $C(=O)O\text{-}C_{1-6}$ alkyl (optionally substituted by halogen, C_{1-4} alkoxy or cyano) or C_{1-4} alkoxy(C_{1-4})alkylene; R^{12}, R^{13}, R^{14}, R^{15}, R^{16} and R^{17} are each, independently, hydrogen, halogen, hydroxy, C_{1-6} alkyl, C_{2-6} alkenyl [both optionally substituted by halogen, hydroxy, C_{1-4} alkoxy, =O, aryl or $O\text{-}C(O\text{-}C_{1-4}$ alkyl or a 3-7 membered carboxylic ring (itself optionally substituted by up to three methyl groups)], a 3-7 membered saturated ring (optionally

substituted by up to three methyl groups and optionally containing one heteroatom selected from nitrogen and oxygen) or C_{1-4} alkoxy; or R^{12} and R^{13} together with the carbon atom to which they are attached form the group C=O or a 3-5 membered carbocyclic ring (optionally substituted by up to three methyl groups and optionally with up to 2 heteroatoms each independently selected from O and N); or R^{12} and R^{13} together form a C_{1-6} alkylidene (optionally substituted by up to three methyl groups) or a C_{3-6} cycloalkylidene group (optionally substituted by up to three methyl groups); R^{18}, R^{19} and R^{20} are each, independently, hydrogen, halogen, C_{1-4} alkyl, C_{1-4} haloalkyl or C_{1-4} alkoxy(C_{1-4})alkylene; and R^{21} is hydrogen, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-4} alkoxy(C_{1-4})alkylene, C_{1-4} alkyl-S-(C_{1-4})alkylene, C_{1-4} alkoxy or aryl.

2. A compound of formula (I) as claimed in claim 1 where Het is pyrrolyl, pyrazolyl, thiazolyl, oxazolyl, pyridinyl, pyrimidyl, pyridazinyl, 2,3-dihydro-[1,4]oxathiine-6-yl, oxazinyl, thiazinyl or triazinyl.

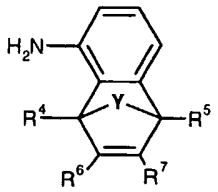
3. A compound of formula (I) as claimed in claim 1 or 2 where Y is O, $N(R^{11})$ or $(CR^{12}R^{13})(CR^{14}R^{15})_m(CR^{16}R^{17})_n$.

4. A compound of formula (I) as claimed in claim 1, 2 or 3 where R^1 is hydrogen, $CH_2C{\equiv}CR^{18}$, $CH{=}C{=}CH_2$ or COR^{21}.

5. A compound of formula (I) as claimed in claim 1, 2, 3 or 4 where R^2 is hydrogen, halogen or C_{1-4} alkyl.

6. A compound of formula (I) as claimed in claim 1, 2, 3, 4 or 5 where R^3 is hydrogen or methyl.

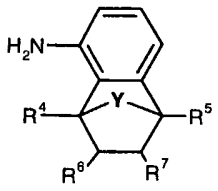
7. A compound of formula (C):



(C)

where Y is O or S; and R^4, R^5, R^6 and R^7 are each $C(O)OCH_3$; or Y is $N(R^{11})$ or $(CR^{12}R^{13})(CR^{14}R^{15})_m(CR^{16}R^{17})_n$; R^4, R^5, R^6, R^7, R^{14}, R^{15}, R^{16}, R^{17}, m and n are each as defined in claim 1; R^{11} is benzyl (in which the phenyl group is optionally substituted with up to three substituents, each independently selected from halogen, C_{1-4} alkyl, C_{1-4} haloalkyl and C_{1-4} alkoxy); and R^{12} and R^{13} together with the carbon atom to which they are attached form a 3-5 membered carbocyclic ring (optionally substituted by up to three methyl groups and containing 1 or 2 heteroatoms each independently selected from O and N).

8. A compound of formula (D):



(D)

where Y is O or S; and R^4, R^5, R^6 and R^7 are each $C(O)OCH_3$; or Y is $N(R^{11})$ or $(CR^{12}R^{13})(CR^{14}R^{15})_m(CR^{16}R^{17})_n$; R^4, R^5, R^6, R^7, R^{14}, R^{15}, R^{16}, R^{17}, m and n are each as defined in claim 1; R^{11} is benzyl (in which the phenyl group is optionally substituted with up to three substituents, each independently selected from halogen, C_{1-4} alkyl, C_{1-4} haloalkyl and C_{1-4} alkoxy); and R^{12} and R^{13} together with the carbon atom to which they are attached form a 3-5 membered carbocyclic ring (optionally substituted by up to three methyl groups and containing 1 or 2 heteroatoms each independently selected from O and N).

9. A composition for controlling microorganisms and preventing attack and infestation of plants therewith, wherein the active ingredient is a compound of formula (I) as claimed in claim 1 together with a suitable carrier.

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

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/11388

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07D487/08 C07D493/08 C07D495/08 C07D207/34 C07D231/14
C07D213/78 C07D277/56 C07D263/34 C07D327/06 A01N43/36
A01N43/32 A01N43/50

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

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, BEILSTEIN Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 00 09482 A (NOVARTIS ERFIND VERWALT GMBH ;EBERLE MARTIN (CH); NOVARTIS AG (CH)) 24 February 2000 (2000-02-24) examples 66-69 ---	1-10
Y	WO 01 49664 A (WALTER HARALD ;SYNGENTA PARTICIPATIONS AG (CH); SCHNEIDER HERMANN) 12 July 2001 (2001-07-12) table 9 ---	1-10
Y	WO 01 53259 A (WALTER HARALD ;SYNGENTA PARTICIPATIONS AG (CH); SCHNEIDER HERMANN) 26 July 2001 (2001-07-26) table 9 ---	1-10
A	WO 02 066470 A (AMGEN INC) 29 August 2002 (2002-08-29) examples 87,333,306,362,646 --- -/--	1-10

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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

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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 March 2004	12/03/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Menegaki, F

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/11388

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	A.J.KIRBY ET AL.: CHEMICAL SOCIETY, PERKIN TRANSACTIONS, no. 2, - 1997 pages 1081-1093, XP009026772 cited in the application example 30 ---	7,8
A	ODA, MASATSUGU ET.AL.: "structure activity relationships of 2-Chloropyridine-3-carboxamide fungicides" JOURNAL OF PESTICIDE SCIENCE (INT.ED.), no. 18, - 1993 pages 49-57, XP009026800 cited in the application examples 36,37 ---	1-10
A	DATABASE CROSSFIRE BEILSTEIN 'Online! Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; Database accession no. 7269102 (BRN) XP002271778 cited in the application abstract	7,8
A	& PLIENINGER, H. ET AL.: CHEMISCHE BERICHTE, no. 109, - 1976 pages 2126-2139, cited in the application examples ---	7,8
A	DATABASE CROSSFIRE BEILSTEIN 'Online! Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; Database accession no. 4803445 (BRN) XP002271779 abstract	7,8
A	& GRAVEL, D. ET AL.: CANADIAN JOURNAL OF CHEMISTRY, vol. 69, no. 8, - 1991 pages 1193-1200, cited in the application examples ---	7,8
A	ROBERT A. SNOW ET AL: "Analysis of bridging regioselectivity operative in photorearrangement of ortho-substituted benzonorbornadienes" JOURNAL OF THE AMERICAN CHEM. SOCIETY, vol. 99, no. 11, - 1977 pages 3734-3744, XP002271785 cited in the application example 23 ---	7,8

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/11388

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	H.PLIENINGER ET AL: "Synthese von benz'c,d!indol-derivaten" CHEMISCHE BERICHTE, vol. 109, - 1976 pages 2121-2125, XP009026773 cited in the application examples 9,10 -----	7,8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 03/11388

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

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1(part),7/8 (part)
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

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

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1(part),7/8 (part)

Present claims 1, 7, 8 relate to an extremely large number of possible compounds. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compounds claimed. In the present case, Claim 1, in part, as well as claims 7,8 (partly), lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely, with regard to claim 1, those parts relating to the compounds wherein Het is as defined in Claim 2; with regard to claims 7,8 for the exemplified intermediate compounds falling under the definition of formulas (C)/(D) in said claims.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 03/11388

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0009482 A	24-02-2000	AU 756140 B2	02-01-2003
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		US 2003225106 A1	04-12-2003