

COMMONWEALTH OF AUSTRALIA
Patents Act 1952-1977

Declaration in Support of an Application for a Patent

(Combined Form - Convention and ~~Non-Convention~~)

* Strike out for
non-convention

In support of the *Convention* application made for a patent ~~patent~~ for an
invention entitled INSECTICIDAL PYRAZOLINES

Insert full
name and address
of declarant

I, James Joseph Flynn, Asst. Secretary - Patent Board of
E. I. DU PONT DE NEMOURS AND COMPANY, 2604 Montchanin Bldg.,
Wilmington, Delaware 19898, United States of America

do solemnly and sincerely declare as follows:-

1. ~~I am the applicant (or one of the applicants) for the patent.~~
~~Where the application is made by two or more persons, I am one of the applicants.~~

1. I am authorised by E. I. DU PONT DE NEMOURS AND COMPANY
the applicant for the ~~patent~~ to make this declaration on its behalf.

Strike out Para. 2,
for non-convention

2. The basic application(s) as defined by section 141 of the Act ~~was~~ made in
the United States of America
on the 5th day of January 1987, No. 000,326,
by Thomas Martin STEVENSON, and
on the 28th day of October 1987, No. 113,530,
by Thomas Martin STEVENSON, and
on the day of 19 , No. ,
by

Insert full
name(s) and
address(es) of
inventor(s)

3. ~~I am the actual inventor (or one of the actual inventors) of the invention.~~
~~Where the invention is made by two or more persons, I am one of the actual inventors.~~
3. Thomas Martin STEVENSON
of 103 Iroquois Court
Newark, Delaware 19702
United States of America

~~is~~ the actual inventor(s) of the invention and the facts upon which ~~the~~ the
~~are~~ said Corporation is entitled to make the application are as
follows:- E. I. DU PONT DE NEMOURS AND COMPANY is the assignee
of the invention and of the priority right from the said
actual inventor(s)

Strike out Para. 4,
for non-convention

4. The basic application(s) referred to in paragraph 2 of this Declaration ~~was~~ the
first application(s) made in a Convention country in respect of the invention the subject of the
application

DECLARED AT Wilmington, Delaware, U.S.A.

this 9th day of June 1988.

(12) PATENT ABRIDGMENT (11) Document No. AU-B-11544/88
 (19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 598633

(54) Title
 1-SUB-PHENYL-3-SUB-PHENYLAMINO(THIO) CARBONYL-PYRAZOLINES AS
 INSECTICIDES

International Patent Classification(s)
 (51)^a C07D 231/06 A01N 043/56

(21) Application No. : 11544/88 (22) Application Date : 14.12.87

(87) WIPO Number : WO88/06583

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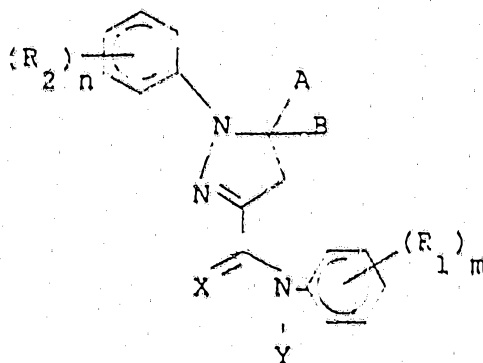
(71) Applicant(s)
 E.I. DU PONT DE NEMOURS AND COMPANY

(72) Inventor(s)
 THOMAS MARTIN STEVENSON

(74) Attorney or Agent
 CALLINAN LAWRIE

(57) Claim

1. A compound having the following formula, and agriculturally suitable salts thereof:



wherein:

X is O or S;

Y is H, C₁ to C₄ alkyl, C₂ to C₄ alkoxyalkyl, C₁ to C₄ alkylthio, C₁ to C₄ haloalkylthio, phenylthio, or phenylthio substituted with 1 to 3 substituents independently selected from W, C₂ to C₄

- alkoxycarbonyl, $C(O)H$, C_2 to C_4
alkylcarbonyl or C_2 to C_4 haloalkylcarbonyl;
A is H, C_1 to C_6 alkyl, phenyl, phenyl substituted by $(R_5)_p$, CN, CO_2R_3 , $C(O)R_3$,
 $C(O)NR_3R_4$, $C(S)NR_3R_4$, $C(S)R_3$, or $C(S)SR_3$;
B is H, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl,
 C_2 to C_6 alkoxyalkyl, C_2 to C_6 cyanoalkyl,
 C_3 to C_8 alkoxycarbonylalkyl, C_2 to C_6 alkenyl,
 C_2 to C_6 alkynyl, C_2 to C_6 alkoxycarbonyl,
phenyl, phenyl substituted with 1 to 3 substituents independently selected from W,
benzyl or benzyl substituted with 1 to 3 substituents independently selected from W;
W is halogen, CN, NO_2 , C_1 to C_2 alkyl, C_1 to C_2 haloalkyl, C_1 to C_2 alkoxy, C_1 to C_2 haloalkoxy, C_1 to C_2 alkylthio, C_1 to C_2 haloalkylthio, C_1 to C_2 alkylsulfonyl or C_1 to C_2 haloalkylsulfonyl;
 R_1 , R_2 and R_5 are independently R_3 , halogen, CN, N_3 , SCN, NO_2 , OR_3 , SR_3 , $S(O)R_3$, $S(O)_2R_3$, $OC(O)R_3$, $OS(O)_2R_3$, CO_2R_3 , $C(O)R_3$, $C(O)NR_3R_4$, $S(O)_2NR_3R_4$, NR_3R_4 , $NR_4C(O)R_3$, $OC(O)NHR_3$, $NR_4C(O)NHR_3$, $NR_4S(O)_2R_3$, or when m, n or p is 2, R_1 , R_2 or R_5 can be taken together as $-OCH_2O-$, $-OCF_2O-$, $-OCH_2CH_2O-$, $-CH_2C(CH_3)_2O-$, $-OCF_2CF_2O-$, or $-CF_2CF_2O-$ to form a cyclic bridge; provided R_1 is other than H;
 R_3 is H, C_1 to C_4 alkyl, C_1 to C_4 haloalkyl, C_2 to C_4 alkenyl, C_2 to C_4 haloalkenyl, C_2 to C_4 alkynyl, C_2 to C_4 haloalkynyl, C_2 to C_4 alkoxyalkyl, C_2 to C_4 alkylthioalkyl, C_1 to C_4 nitroalkyl, C_2 to C_4 cyanoalkyl, C_3 to C_6 alkoxycarbonylalkyl, C_3 to C_6 cycloalkyl, C_3 to C_6 halocycloalkyl, phenyl, benzyl, or phenyl or benzyl substituted with 1 to 3 substituents independently selected from W;

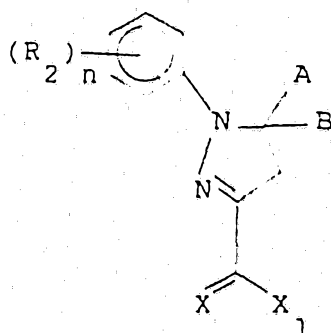
R_4 is H or C_1 to C_4 alkyl, or when R_3 and R_4 are attached to a single nitrogen atom, they can be taken together as $(CH_2)_4$, $(CH_2)_5$ or $(CH_2CH_2OCH_2CH_2)$;

m is 1 to 3;

n is 0 to 3; and

p is 0 to 3.

10. A compound of the formula:



wherein:

X is O or S;

X_1 is OH, Cl or C_1 to C_6 alkoxy;

A is H, C_1 to C_6 alkyl, phenyl, phenyl substituted by $(R_5)_p$, CN, CO_2R_3 , $C(O)R_3$, $C(O)NR_3R_4$, $C(S)NR_3R_4$, $C(S)R_3$ or $C(S)SR_3$;

B is H, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl, C_2 to C_6 alkoxyalkyl, C_2 to C_6 cyanoalkyl, C_3 to C_8 alkoxy carbonylalkyl, C_2 to C_6 alkenyl, C_2 to C_6 alkynyl, C_2 to C_6 alkoxy carbonyl, phenyl, or phenyl substituted with 1 to 3 substituents independently selected from W, benzyl, benzyl substituted with 1 to 3 substituents independently selected from W;

W is halogen, CN, NO_2 , C_1 to C_2 alkyl, C_1 to C_2 haloalkyl, C_1 to C_2 alkoxy, C_1 to C_2 haloalkoxy, C_1 to C_2 alkylthio, C_1 to C_2 halo-

alkylthio, C_1 to C_2 alkylsulfonyl or C_1 to C_2 haloalkylsulfonyl;
 R_2 and R_5 are independently R_3 , halogen, CN, N_3 , SCN, NO_2 , OR_3 , SR_3 , $S(O)R_3$, $S(O)_2R_3$, $OC(O)R_3$, $OS(O)_2R_3$, CO_2R_3 , $C(O)R_3$, $C(O)NR_3R_4$, $S(O)_2NR_3R_4$, NR_3R_4 , $NR_4C(O)R_3$, $OC(O)NHR_3$, $NR_4C(O)NHR_3$, $NR_4S(O)_2R_3$, or, when n or p is 2, R_2 or R_5 can be taken together as $-OCH_2O-$, $-OCF_2O-$, $-OCH_2CH_2O-$, $-CH_2C(CH_3)_2O-$, $-OCF_2CF_2O-$ or $-CF_2CF_2O-$ to form a cyclic bridge; except that both R_2 and R_5 are not H;
 R_3 is H, C_1 to C_4 alkyl, C_1 to C_4 haloalkyl, C_2 to C_4 alkenyl, C_2 to C_4 haloalkenyl, C_2 to C_4 alkynyl, C_2 to C_4 haloalkynyl, C_2 to C_4 alkoxyalkyl, C_2 to C_4 alkylthioalkyl, C_1 to C_4 nitroalkyl, C_2 to C_4 cyanoalkyl, C_3 to C_6 alkoxycarbonylalkyl, C_3 to C_6 cycloalkyl, C_3 to C_6 halocycloalkyl, phenyl, benzyl, or phenyl or benzyl substituted with 1 to 3 substituents independently selected from W;
 R_4 is H or C_1 to C_4 alkyl, or when R_3 and R_4 are attached to a single nitrogen atom, they can be taken together as $\{CH_2\}_4$, $\{CH_2\}_5$ or $\{CH_2CH_2OCH_2CH_2\}_2$;
n is 0 to 3; and
p is 0 to 3.

16. A method of controlling insects comprising contacting them with an effective amount of a compound according to Claim 1.

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁴ : C07D 231/06, A10N 43/56	A1	(11) International Publication Number: WO 88/ 06583 (43) International Publication Date: 7 September 1988 (07.09.88)
(21) International Application Number: PCT/US87/03235 (22) International Filing Date: 14 December 1987 (14.12.87) (31) Priority Application Numbers: 000,326 113,530 (32) Priority Dates: 5 January 1987 (05.01.87) 28 October 1987 (28.10.87) (33) Priority Country: US (71) Applicant: E.I. DUPONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventor: STEVENSON, Thomas, Martin ; 103 Iroquois Court, Newark, DE 19702 (US). (74) Agent: COSTELLO, James, A.; E.I. du Pont de Nemours and Company, Legal Department, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> A.O.J.P. 27 OCT 1988 AUSTRALIAN 26 SEP 1988 PATENT OFFICE This document contains the amendments made under Section 49 and is correct for printing.
(54) Title: INSECTICIDAL PYRAZOLINES (57) Abstract Pyrazolines and their intermediates, including all geometric and stereoisomers of the pyrazolines and intermediates, agricultural compositions containing the pyrazolines, and methods for use as insecticides.		

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Title

INSECTICIDAL PYRAZOLINES

Cross-Reference To Related Application

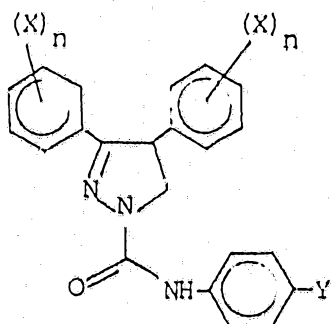
This is a continuation-in-part of copending
5 application bearing U.S. Serial No. 000,326, filed on
January 5, 1987.

Background of the Invention

Vaughan, J. Org. Chem., 20 (1955), pages 1619 to
1626, discloses 1,5-diphenyl-2-pyrazoline-3-
10 carboxamide. No utility is given for the disclosed
compound which, in any event, does not suggest a
compound of the instant invention.

U.S. 4,070,365 discloses insecticidal compounds
of the formula

15



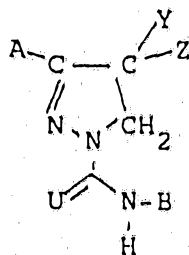
20

wherein X is halogen,
and Y is halogen, NO₂
or alkyl.

25

EP 153,127 discloses insecticidal compounds of
the formula

30



35

wherein

A is unsubstituted or substituted phenyl;

B is unsubstituted or substituted phenyl;

U is O, S or NR;

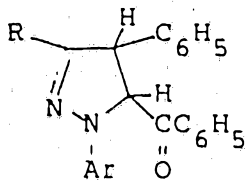
5 Y is alkyl, unsubstituted or substituted phenyl, or C(X)G;

Z is H, cycloalkyl, unsubstituted or substituted phenyl R⁴-Q;

X is O or S; and

10 G and R⁴-Q are broadly defined.

Harhash et al., J. Heterocyclic Chem., 21 (1984),
at page 1013, discloses the preparation of five
pyrazoline compounds, none of which is disclosed in the
instant application. No utility is given for any of
15 said compounds:



where R/Ar are

C₆H₅/C₆H₅;

CO₂C₂H₅/C₆H₅;

C(O)NHC₆H₅/C₆H₅;

CH=CHC₆H₅/C₆H₅; and

CH₃/4-NO₂-C₆H₄.

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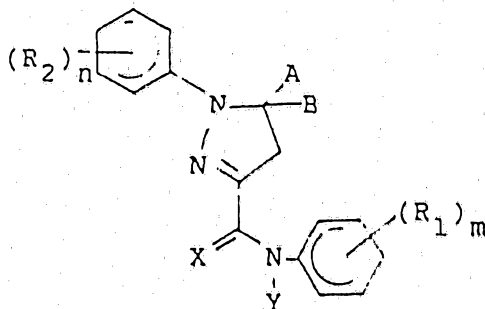
Summary of the Invention

5 This invention concerns certain 4,5-dihydro-1H-pyrazole-3-carboxamides (hereinafter referred to as pyrazolines) and intermediates to said compounds, including all geometric and stereoisomers of the pyrazolines and the intermediates. This invention
 10 also concerns agricultural compositions comprising at least one of said pyrazolines as active ingredient and an agriculturally suitable carrier therefor. This invention also concerns a method for controlling insects comprising contacting them or their
 15 environment with an effective amount of a pyrazoline of this invention.

More specifically, this invention pertains to pyrazolines of Formula I and agriculturally suitable salts thereof:

20

25

Formula I

wherein:

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X is O or S;

Y is H, C₁ to C₄ alkyl, C₂ to C₄ alkoxyalkyl, C₁ to C₄ alkylthio, C₁ to C₄ haloalkylthio, phenylthio, or phenylthio substituted with 1 to 3 substituents independently selected
 35 from W, C₂ to C₄ alkoxycarbonyl, C(O)H, C₂ to C₄ alkylcarbonyl or C₂ to C₄ haloalkylcarbonyl;

- 5 A is H, C₁ to C₆ alkyl, phenyl, phenyl substituted by (R₅)_p, CN, CO₂R₃, C(O)R₃, C(O)NR₃R₄, C(S)NR₃R₄, C(S)R₃ or C(S)SR₃;
- 10 B is H, C₁ to C₆ alkyl, C₁ to C₆ haloalkyl, C₂ to C₆ alkoxyalkyl, C₂ to C₆ cyanoalkyl, C₃ to C₈ alkoxycarbonylalkyl, C₂ to C₆ alkenyl, C₂ to C₆ alkynyl, C₂ to C₆ alkoxycarbonyl, phenyl, phenyl substituted with 1 to 3 substituents independently selected from W, benzyl or benzyl substituted with 1 to 3 substituents independently selected from W;
- 15 W is halogen, CN, NO₂, C₁ to C₂ alkyl, C₁ to C₂ haloalkyl, C₁ to C₂ alkoxy, C₁ to C₂ haloalkoxy, C₁ to C₂ alkylthio, C₁ to C₂ haloalkylthio, C₁ to C₂ alkylsulfonyl or C₁ to C₂ haloalkylsulfonyl;
- 20 R₁, R₂ and R₅ are independently R₃, halogen, CN, N₃, SCN, NO₂, OR₃, SR₃, S(O)R₃, S(O)₂R₃, OC(O)R₃, OS(O)₂R₃, CO₂R₃, C(O)R₃, C(O)NR₃R₄, S(O)₂NR₃R₄, NR₃R₄, NR₄C(O)R₃, OC(O)NHR₃, NR₄C(O)NHR₃, NR₄S(O)₂R₃, or when m, n or p is 2, R₁, R₂ or R₅
- 25 can be taken together as -OCH₂O-, -OCF₂O-, -OCH₂CH₂O-, -CH₂C(CH₃)₂O-, -OCF₂CF₂O-, or -CF₂CF₂O- to form a cyclic bridge; provided R₁ is other than H;
- 30 R₃ is H, C₁ to C₄ alkyl, C₁ to C₄ haloalkyl, C₂ to C₄ alkenyl, C₂ to C₄ haloalkenyl, C₂ to C₄ alkynyl, C₂ to C₄ haloalkynyl, C₂ to C₄ alkoxyalkyl, C₂ to C₄ alkylthioalkyl, C₁ to C₄ nitroalkyl, C₂ to C₄ cyanoalkyl, C₃ to C₆ alkoxycarbonylalkyl, C₃ to C₆ cycloalkyl, C₃ to C₆ halocycloalkyl, phenyl, benzyl, or
- 35 phenyl or benzyl substituted with 1 to 3 substituents independently selected from W;

5

R_4 is H or C_1 to C_4 alkyl, or when R_3 and R_4 are attached to a single nitrogen atom, they can be taken together as $\{CH_2\}_4$, $\{CH_2\}_5$ or $\{CH_2CH_2OCH_2CH_2\}$;

m is 1 to 3;

10

n is 0 to 3; and

p is 0 to 3.

In the above definitions, the term "alkyl", used either alone or in compound words such as "alkylthio" or 15 "haloalkyl", means straight chain or branched alkyl such as methyl, ethyl, n-propyl, isopropyl or the different butyl, pentyl, hexyl isomers.

Alkoxy includes methoxy, ethoxy, n-propyloxy, isopropyloxy and the different butoxy or pentoxy isomers.

20

Alkenyl includes straight chain or branched alkenes, such as vinyl, 1-propenyl, 2-propenyl, 3-propenyl and the different butenyl, pentenyl and hexenyl isomers.

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Alkynyl includes straight chain or branched alkynes, such as ethynyl, 1-propynyl, 2-propynyl and the different butynyl, pentynyl and hexynyl isomers.

Alkylthio includes methylthio, ethylthio and the different propylthio and butylthio isomers.

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Alkylsulfonyl and the like are used analogously to the above examples.

Cycloalkyl includes cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl.

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The term "halogen", either alone or in compound words such as "haloalkyl", means fluorine, chlorine, bromine or iodine. Further, when used in compound words

such as "haloalkyl" said alkyl can be partially or fully substituted with halogen atoms, which may be the same or different. Examples of haloalkyl include $\text{CH}_2\text{CH}_2\text{F}$, $\text{CF}_2\text{CF}_2\text{H}$ and CH_2CHFCl . The terms "halocycloalkyl", "haloalkenyl" and "haloalkynyl" are used analogously to "haloalkyl".

The total number of carbon atoms in a substituent group is indicated by the " C_i to C_j " prefix where i and j are numbers from 1 to 8. For example, C_1 to C_3 alkylsulfonyl would designate methylsulfonyl through propylsulfonyl; C_2 alkoxyalkoxy would designate OCH_2OCH_3 ; C_4 alkoxyalkoxy would designate the various isomers of an alkoxy group substituted with a second alkoxy group containing a total of 4 carbon atoms, examples including $\text{OCH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$ and $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$; C_2 cyanoalkyl would designate CH_2CN and C_3 cyanoalkyl would designate $\text{CH}_2\text{CH}_2\text{CN}$ and $\text{CH}(\text{CN})\text{CH}_3$; C_2 alkylcarbonyl would designate $\text{C}(\text{O})\text{CH}_3$ and C_4 alkylcarbonyl would include $\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{C}(\text{O})\text{CH}(\text{CH}_3)_2$; and as a final example, C_3 alkoxy-carbonylalkyl would designate $\text{CH}_2\text{CO}_2\text{CH}_3$ and C_4 alkoxy-carbonylalkyl would include $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$, $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ and $\text{CH}(\text{CH}_3)\text{CO}_2\text{CH}_3$.

Preferred compounds (A) are those of Formula I wherein

- 30 X is O;
 Y is H, CH_3 , SCH_3 , CCl_3 , SC_6H_5 ,
 $2-(\text{NO}_2)\text{C}_6\text{H}_4\text{S}$, $\text{C}(\text{O})\text{CH}_3$, $\text{C}(\text{O})\text{H}$, $\text{C}(\text{O})\text{CF}_3$,
 CO_2CH_3 or $\text{CO}_2\text{C}_2\text{H}_5$;
 35 R_3 is C_1 to C_4 alkyl, C_1 to C_2 haloalkyl,
 C_2 to C_4 alkenyl, C_2 to C_4 haloalkenyl,

propargyl, phenyl, benzyl, or phenyl or benzyl
 5 substituted with one of F, Cl, Br, CF_3 , OCF_2H ,
 OCF_3 or NO_2 ;

n is 0 to 2;

p is 0 to 2; and

m is 1 to 2.

10

Preferred compounds (B) are preferred compounds
 (A) wherein

R_1 is halogen, CN, SCN, NO_2 , R_3 , OR_3 , SR_3 ,
 $\text{S}(\text{O})_2\text{R}_3$, CO_2R_3 or $\text{C}(\text{O})\text{R}_3$, or when m is 2,

15

R_1 can be taken together as $-\text{OCF}_2\text{O}-$,
 $-\text{CH}_2\text{C}(\text{CH}_3)_2\text{O}-$, $-\text{OCF}_2\text{CF}_2\text{O}-$ or $-\text{CF}_2\text{CF}_2\text{O}-$;

R_2 and R_5 are independently halogen, CN, SCN,
 NO_2 , R_3 , OR_3 , SR_3 , $\text{S}(\text{O})_2\text{R}_3$, $\text{OC}(\text{O})\text{R}_3$,
 $\text{OS}(\text{O})_2\text{R}_3$, CO_2R_3 , $\text{C}(\text{O})\text{R}_3$, $\text{C}(\text{O})\text{NR}_3\text{R}_4$,
 20 $\text{S}(\text{O})_2\text{NR}_3\text{R}_4$ or NR_3R_4 ;

R_3 is C_1 to C_4 alkyl, C_1 to C_2 haloalkyl,
 C_2 to C_4 alkenyl, C_2 to C_4 haloalkenyl or
 propargyl;

R_4 is H or C_1 to C_2 alkyl;

25

A is C_1 to C_4 alkyl, phenyl, phenyl substituted
 with $(R_5)_p$, CO_2R_3 , $\text{C}(\text{O})\text{R}_3$, $\text{C}(\text{O})\text{NR}_3\text{R}_4$
 or $\text{C}(\text{O})\text{NR}_4$ phenyl said phenyl optionally
 substituted with F, Cl, Br, CF_3 , OCF_2H , OCF_3
 or NO_2 ; and

30

B is H, C_1 to C_4 alkyl, C_1 to C_4 haloalkyl,
 or C_3 to C_4 alkenyl.

Preferred compounds (C) are preferred compounds
 (B) wherein

35

Y is H, CH_3 , $\text{C}(\text{O})\text{CH}_3$ or CO_2CH_3 ;

m is 1 or 2 and one substituent is in the
 4-position of the phenyl ring;

n is 1 or 2 and one substituent is in the
 4-position of the phenyl ring;

- 5 p is 1 or 2 and one substituent is in the
 3 or 4-position of the phenyl ring;
 R_1 is F, Cl, Br, CF_3 , OCF_2H , OCF_3 or CN,
 or when m is 2, R_1 can be taken together
 as $-CH_2C(CH_3)_2O-$ or $-CF_2CF_2O-$;
 10 R_2 is F, Cl, Br, CN, NO_2 , CF_3 , CH_3 , OCH_3 , OCF_2H ,
 OCF_3 , SCH_3 , SCF_2H , $S(O)_2CH_3$ or $N(CH_3)_2$;
 R_5 is F, Cl, Br, CN, NO_2 , CF_3 , CH_3 , OCH_3 , OCF_2H ,
 OCF_3 , SCH_3 , SCF_2H , $S(O)_2CH_3$, $S(O)_2CF_2H$,
 CO_2CH_3 , $C(O)NHCH_3$, $C(O)N(CH_3)_2$, $S(O)_2N(CH_3)_2$
 or $N(CH_3)_2$;
 15 A is phenyl or phenyl substituted with $(R_5)_p$; and
 B is H or CH_3 .

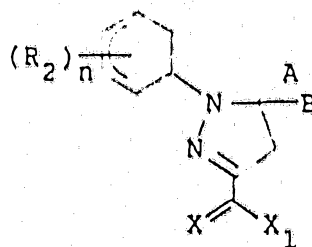
Preferred compounds (D) are preferred compounds
(B) wherein

- 20 Y is H, CH_3 , $C(O)CH_3$ or CO_2CH_3 ;
 m is 1 or 2 and one substituent is in the
 4-position of the phenyl ring;
 n is 1 or 2 and one substituent is in the
 4-position of the phenyl ring;
 25 R_1 is F, Cl, Br, CF_3 , OCF_2H , OCF_3 or CN,
 or when m is 2, R_1 can be taken together
 as $-CH_2C(CH_3)_2O-$ or $-CF_2CF_2O-$;
 R_2 is F, Cl, Br, CN, NO_2 , CF_3 , CH_3 , OCH_3 , OCF_2H ,
 OCF_3 , SCH_3 , SCF_2H , $S(O)_2CH_3$, $S(O)_2CF_2H$,
 30 CO_2CH_3 , $C(O)NHCH_3$, $C(O)N(CH_3)_2$, $S(O)_2N(CH_3)_2$
 or $N(CH_3)_2$;
 A is CO_2CH_3 , $CO_2C_2H_5$, $C(O)NHCH_3$ or
 $C(O)N(CH_3)_2$; and
 B is CH_3 .

Especially preferred compounds are:

- 5 (E) A compound of (D):
Methyl 1-(4-chlorophenyl)-4,5-dihydro-
5-methyl-3-[[4-(trifluoromethyl)phenyl]-
aminocarbonyl]-1H-pyrazole-5-carboxylate.
- 10 (F) A compound of (C):
1-(4-chlorophenyl)-5-(4-fluorophenyl)-4,5-
dihydro-N-[4-(trifluoromethyl)phenyl]-1H-
pyrazole-3-carboxamide.
- (G) A compound of (C):
1,5-bis(4-chlorophenyl)-4,5-dihydro-N-[4-
(trifluoromethyl)phenyl]-1H-pyrazole-3-
carboxamide.
- 15 (H) A compound of (C):
1-(4-chlorophenyl)-5-(4-cyanophenyl)-4,5-
dihydro-N-[4-(trifluoromethyl)phenyl]-1H-
pyrazole-3-carboxamide.

This invention also pertains to compounds of
20 Formula II which are useful as intermediates to prepare
compounds of Formula I. The intermediates of this
invention are:



30 Formula II

wherein:

- X is O or S;
X₁ is OH, Cl or C₁ to C₆ alkoxy;
A is H, C₁ to C₆ alkyl, phenyl, phenyl substituted
35 by (R₅)_p, CN, CO₂R₃, C(O)R₃, C(O)NR₃R₄,
C(S)NR₃R₄, C(S)R₃ or C(S)SR₃;
B is H, C₁ to C₆ alkyl, C₁ to C₆ haloalkyl, C₂
to C₆ alkoxyalkyl, G₂ to C₆ cyanoalkyl, C₃ to

5 C_8 alkoxy carbonyl alkyl, C_2 to C_6 alkenyl, C_2 to C_6 alkynyl, C_2 to C_6 alkoxy carbonyl, phenyl, or phenyl substituted with 1 to 3 substituents independently selected from W, benzyl, benzyl substituted with 1 to 3 substituents independently selected from W;

10 W is halogen, CN, NO_2 , C_1 to C_2 alkyl, C_1 to C_2 haloalkyl, C_1 to C_2 alkoxy, C_1 to C_2 haloalkoxy, C_1 to C_2 alkylthio, C_1 to C_2 haloalkylthio, C_1 to C_2 alkylsulfonyl or C_1 to C_2 haloalkylsulfonyl;

15 R_2 and R_5 are independently R_3 , halogen, CN, N_3 , SCN, NO_2 , OR_3 , SR_3 , $S(O)R_3$, $S(O)_2R_3$, $OC(O)R_3$, $OS(O)_2R_3$, CO_2R_3 , $C(O)R_3$, $C(O)NR_3R_4$, $S(O)_2NR_3R_4$, NR_3R_4 , $NR_4C(O)R_3$, $OC(O)NHR_3$, $NR_4C(O)NHR_3$, $NR_4S(O)_2R_3$, or, when n or p is 2, R_2 or R_5 can be taken together as $-OCH_2O-$, $-OCF_2O-$, $-OCH_2CH_2O-$, $-CH_2C(CH_3)_2O-$, $-OCF_2CF_2O-$ or $-CF_2CF_2O-$ to form a cyclic bridge; except that both R_2 and R_5 are not H;

20 R_3 is H, C_1 to C_4 alkyl, C_1 to C_4 haloalkyl, C_2 to C_4 alkenyl, C_2 to C_4 haloalkenyl, C_2 to C_4 alkynyl, C_2 to C_4 haloalkynyl, C_2 to C_4 alkoxyalkyl, C_2 to C_4 alkylthioalkyl, C_1 to C_4 nitroalkyl, C_2 to C_4 cyanoalkyl, C_3 to C_6 alkoxy carbonyl alkyl, C_3 to C_6 cycloalkyl, C_3 to C_6 halocycloalkyl, phenyl, benzyl, or phenyl or benzyl substituted with 1 to 3 substituents independently selected from W;

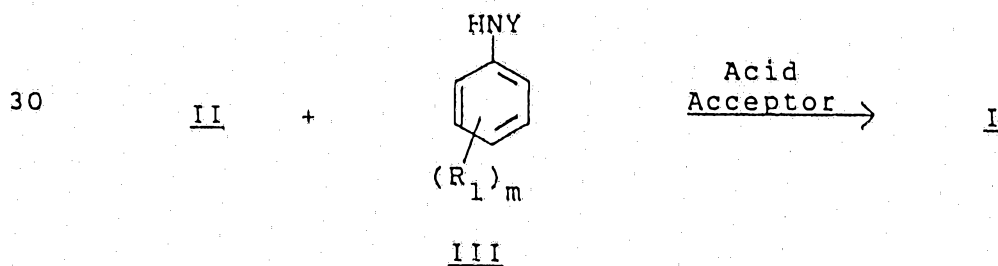
25 R_4 is H or C_1 to C_4 alkyl, or when R_3 and R_4 are attached to a single nitrogen atom, they can be taken together as $\{CH_2\}_4$, $\{CH_2\}_5$ or $\{CH_2CH_2OCH_2CH_2\}$;

30 n is 0 to 3; and

35 p is 0 to 3.



One particularly useful method involves the chlorination of an acid derivative (II, $X_1 = OH$) with thionyl chloride or another chlorinating agent followed by treatment with an aniline (III) in the presence of an acid acceptor such as an amine base, preferably triethylamine. Suitable solvents for the chlorination reaction are inert to hydrogen chloride and include benzene, toluene, and dichloromethane. Preferred temperatures for this process are from 20° to 100°C with temperatures between 20° and 80°C being particularly preferred. The latter reaction can be carried out in many different inert solvents such as dialkylethers, chlorinated hydrocarbons, and aromatic hydrocarbons. While temperatures at or below 25°C are preferred, higher temperatures can also be employed. These reactions are normally run at atmospheric pressure, but can also be carried out at elevated pressures.



35

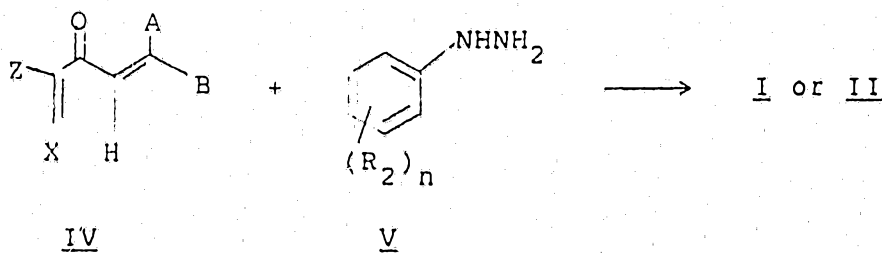
Esters of Formula II ($X_1 = C_1$ to C_6 alkoxy)
5 can be converted directly to compounds of Formula I in several ways. In the presence of Lewis acids such as $AlMe_3$, anilines react readily with esters of Formula II. The reaction is best carried out at room temperature to 120°C. Suitable solvents include
10 dichloromethane, 1,2-dichloroethane, and toluene. The method described by Weinreb et al., Organic Synthesis, 59, 49, (1982), proceeds best with esters of lower alcohols such as methanol or ethanol.

Acids of Formula II ($X_1 = OH$) can be converted
15 directly to compounds of Formula I by use of coupling agents known in the peptide art in conjunction with anilines. Coupling agents include dicyclohexylcarbodiimide (DCC), N-hydroxysuccinimide, 2-chloro-N-methylpyridinium iodide, carbonyl diimidazole, or
20 other agents capable of activating an acid function or acting as a dehydrating agent. These and other methods are described in Gross et al., "The Peptides," 3 Vols., Academic Press, New York, 1979 to 1981.

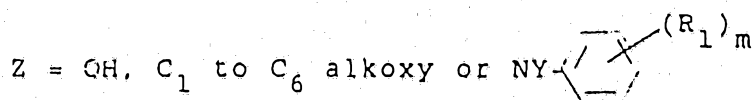
Compounds of Formula I can also be obtained from
25 the cyclization of appropriate phenylhydrazines (V) with keto-acid derivatives (IV). It will be appreciated by those skilled in the art that this process applies equally to acids, esters, and anilides and further that the interconversion of these groups as
30 discussed in the sequence (II→I) can be carried out after the cyclization reaction. The conditions for these reactions are well known in the art and described by Hill et al., Trans. Illinois Acad. Sci., 33 (1940), 112 and by Vaughan, J. Org. Chem., 20 (1955), 1619.
35 The cyclization reaction is best carried out on an unsaturated keto-acid derivative (IV) in refluxing alcoholic media, in refluxing lower carboxylic

acids, or in polar aprotic solvents such as
 5 dimethylformamide or dimethyl sulfoxide. Ethanol
 containing acetic acid or acetic acid alone are the
 preferred solvents although other protic or aprotic
 solvents and mixtures are also applicable. In some
 cases, phenyl hydrazones can be isolated prior to final
 10 cyclization and these can be refluxed further in order
 to complete the cyclization. While the unsaturated
 acid derivatives (IV) are preferred, saturated com-
 pounds with a reactive group such as a halogen beta to
 the carbonyl can be employed in certain instances.

15



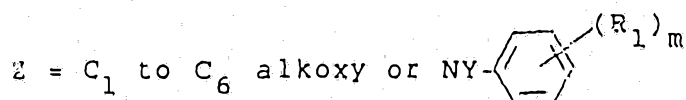
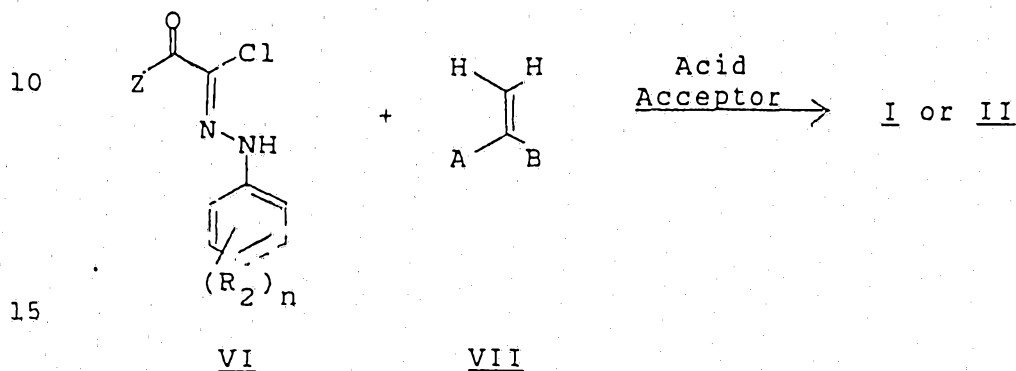
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25

Compounds of Formula I and intermediates of
 Formula II can also be obtained by the dipolar cyclo-
 addition reaction of nitrile-imines, generated from
 substituted phenylhydrazones of Formula VI, with
 appropriately substituted alkenes. The presence of an
 30 acid acceptor (generally an amine base, for example,
 triethylamine) is necessary for the formation of the
 nitrile-imine. In a typical reaction, the alkene is
 used in a two- to five-fold molar excess and the amine
 base in a three- to five-fold excess based on the
 35 hydrazone (VI). Suitable solvents include but are not
 restricted to benzene, toluene, 1,2-dichloro-
 ethane, chloroform, and tetrahydrofuran. The reaction
 can be carried out at temperatures ranging from 20° to
 120°C with the relative reactivity of the alkene (VII)
 governing the required temperature for a given example.

The required hydrazones (VI) for the synthesis of compounds of Formula I and II can be prepared by methods known in the art or by modifications thereof; see, e.g., Shawali et al., Tetrahedron, 20 (1971), 2517.



Some compounds of Formula I (Y=H) can be converted to other compounds of Formula I by alkylation, acylation, and sulphenylation reactions (Y=H). Reaction of compounds of Formula I in the presence of an acid acceptor with electrophilic agents (Y-leaving group) results in substitution on nitrogen. Strong bases such as sodium hydride, potassium t-butoxide, potassium hydride, and other bases known in the art to deprotonate amides are preferred in the process. Suitable electrophiles include, but are not restricted to alkyl halides, acyl halides, acid anhydrides, carbonates, chloroformates, disulphides, and sulphenyl halides. This reaction is normally run in the temperature range of 0-25°C, but can be run at temperatures up to 120°C if unreactive electrophiles are used. Solvents not deprotonated

15

under the reactions conditions such as tetrahydrofuran, dimethylformamide, dimethoxyethane, and diethyl ether are preferred.

Compounds of Formula I (X=O) can be converted to
5 compounds of Formula I (X=S) by means of thiating agents. Conversion of amides to thioamides is well known in the art. Phosphorous pentasulfide either alone or in combination with organic or inorganic bases is a preferred reagent to effect this
10 conversion. When phosphorous pentasulfide is used alone, organic bases such as pyridine are the preferred solvents. When it is used in conjunction with inorganic bases such as sodium bicarbonate, the preferred solvents are ethers such as diglyme.
15 Temperatures between 20° to 160°C can be employed successfully with temperatures between 90° to 120°C preferred. These and other means to convert amides to thioamides are described by Lapucha, Synthesis (1987), 256.

20 It will be appreciated by those skilled in the art that, regardless of the method of synthesis, compounds of Formula II can be converted to compounds of the instant invention by the methods described above. Many functional group transformations known to those
25 skilled in the art can be employed to convert compounds of Formula I to new compounds of Formula I and that this will overcome any incompatibility of certain such groups with reagents and conditions disclosed above with respect to typical reaction
30 mechanisms.

Example 1

5 N-(4-Chlorophenyl)-2-[(4-chlorophenyl)amino]-2-oxo-
ethanehydrazonoyl chloride

The compound, 4-chloroaniline (7.8 gm), was diazotized in 30 ml of 6N hydrochloric acid with sodium nitrite (4.5 gm) at 0 to 5°C. The resulting
10 solution was added over twenty minutes by means of an insulated dropping funnel to a vigorously stirred mixture of 2,4'-dichloroacetoacetanilide (10 gm) and sodium acetate (15.1 gm) in ethanol (260 ml) held at 0 to 5°C. The suspension was stirred for 2 hours
15 (temperature 20°C) and filtered. The solid was dried by dissolution in dichloromethane and addition of magnesium sulfate. Filtration, evaporation of the solvent and trituration with butyl chloride provided the title compound (15.2 gm), m.p.: 180° to 181°C.
20 NMR(CDCl₃) 8.5 (br, NH), 8.3 (br, NH), 7.6-7.1 (m, 8H).

Example 2

N-(4-Chlorophenyl)-2-[4-(trifluoromethyl)phenyl]-
amino-2-oxoethanehydrazonoyl chloride

25 Similarly prepared by the method of Example 1, 2-chloro-4'-trifluoromethylacetoacetanilide (8.6 gm) gave the title compound (3.8 gm), m.p.: 167° to 168.5°C. NMR (CDCl₃) 8.6 (br, NH), 8.3 (br, NH), 7.7-7.1 (m, 8H, ArH).
30

Example 3

Methyl 1-(4-chlorophenyl)-3-[(4-chlorophenyl)aminocar-
bonyl]-4,5-dihydro-5-methyl-1H-pyrazole-5-carboxylate

A sample of the compound of Example 1 (0.82 gm)
35 was heated in refluxing benzene (15 ml) containing methyl methacrylate (4 ml). The resulting solution was treated dropwise with a solution of triethylamine (1.5 ml) in benzene (10 ml) and heated an additional

2 hours. The mixture was partitioned between ethyl
5 acetate (50 ml) and 1N hydrochloric acid and the
organic layer dried with magnesium sulfate. The
organic residue was purified by silica gel chroma-
tography with 20% ethyl acetate/hexanes followed by
recrystallization from methanol to afford the title
10 compound (0.62 gm); m.p.: 138° to 140°C. ¹H NMR
(CDCl₃) 8.4 (br, NH), 7.6-6.9 (m, ArH, 8H), 3.8
(s, CH₃, 3H); 3.7 (d, 1H, CH), 3.3 (d, 1H, CH),
1.7 (s, 3H, CH₃).

15

Example 4

Methyl 1-(4-chlorophenyl)-4,5-dihydro-5-methyl-3-
[[[4-(trifluoromethyl)phenyl]amino]carbonyl]-1H-
pyrazole-5-carboxylate

Analogous treatment of the compound of Example 2
(3.0 gm) under the conditions of Example 3 gave the
20 title compound (2.0 gm); m.p. (MeOH): 178.5° to 180°C.
NMR (CDCl₃) 8.5 (NH, br), 7.6-7.0 (m, 8H, ArH), 3.8
(s, CH₃, 3H), 3.7 (d, 1H, CH), 3.3 (d, 1H, CH), 1.7
(s, CH₃, 3H).

25

Example 5

N,1-bis(4-chlorophenyl)-5-(4-cyanophenyl)-4,5-dihydro-
1H-pyrazole-3-carboxamide

Repetition of Example 3 with 4-cyanostyrene (1.5
ml) on one-fifth the original scale gave the title
30 compound (0.21 gm); m.p. (Ethanol): 183° to 186°C.
NMR (CDCl₃) 8.5 (br, NH), 7.6-6.9 (m, 12H, ArH), 5.4
(dd, 1H, CH), 3.8 (dd, 1H, CH), 3.1 (dd, 1H, CH).

Example 6

35 Ethyl chloro[2-(4-chlorophenyl)hydrazono]acetate

The compound, 4-chloroaniline (15.6 gm), was
diazotized as described in Example 1 and repetition of
that experiment with ethyl-2-chloroacetoacetate (16.5

18

ml) and sodium acetate (32 gm) gave the title compound (22.7 gm) as reddish needles after recrystallization from benzene; m.p.: 145° to 147.5°C. NMR (CDCl₃) 8.3 (1H, NH, br), 7.3-7.1 (m, 4H, ArH), 4.4 (q, 2H, OCH₂), 1.4 (t, 3H, CH₃).

Example 7

Methyl chloro[2-(4-chlorophenyl)hydrazono]acetate

Similarly obtained by the method of Example 6 from methyl-2-chloroacetoacetate (29.5 gm), 4-chloro-aniline (25 gm), and sodium acetate (51 gm) was the title compound (36.4 gm); m.p.: 149° to 150°C. NMR (CDCl₃) 8.3 (br, NH), 7.3 (m, 2H), 7.1 (m, 2H), 3.9 (s, 3H, CH₃).

Example 8

Methyl chloro[2-(4-fluorophenyl)hydrazono]acetate

The title compound (16.4 gm) was obtained on repeating the procedure of Example 7 at 2/3 scale with 4-fluoroaniline (13.3 gm); m.p.: 110° to 113°C. NMR (CDCl₃) 8.34 (br, NH), 7.3-7.0 (m, ArH, 4H), 3.93 (s, CH₃, 3H).

Example 9

Ethyl 1,5-bis(4-chlorophenyl)-4,5-dihydro-1H-pyrazole-3-carboxylate

The compound of Example 6 (5.0 gm) was heated in refluxing benzene (30 ml) containing 4-chlorostyrene (7.0 ml). Addition of a benzene (10 ml) solution of triethylamine (7.5 ml) was followed by one hour of continued heating. The cooled mixture was filtered, rotovapped, and dried on the vacuum pump to remove excess styrene. The residual solid was recrystallized from hexane/benzene (charcoal) to give the title compound (6.3 gm); m.p.: 128° to 130°C. NMR (CDCl₃)

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7.3-6.9 (m, 8H, ArH), 5.4 (dd, 1H, CH), 4.3 (q, 2H, OCH₂), 3.8 (m, 1H, CH), 3.0 (m, 1H, CH), 1.38 (t, 3H, CH₃).

5

Example 10

Ethyl 1,5-bis(4-Chlorophenyl)-4,5-dihydro-5-methyl-1H-pyrazole-3-carboxylate

The compound of Example 6 (1.0 gm) was converted to the title compound (0.6 gm) by adaptation of the procedure of Example 9 to 4-chloro- α -methyl styrene (2.5 ml). The product was a yellow oil. NMR (CDCl₃) 7.3-6.8 (m, ArH, 8H), 4.3 (q, 2H, CH₂), 3.3 (m, 2H, CH₂), 1.8 (s, 3H, CH₃), 1.3 (t, 3H, CH₃).

15

Example 11

Dimethyl 1-(4-fluorophenyl)-4,5-dihydro-5-methyl-1H-pyrazole-3,5-dicarboxylate

A solution of the compound of Example 8 (5 gm) in ethyl acetate (30 ml) was treated with methyl methacrylate (10 ml) and triethylamine (6 ml). After stirring for 4 hours the reaction was partitioned between ethyl acetate (100 ml) and water (100 ml). The organic layer was washed with aqueous HCl (1N 100 ml), dried, and concentrated to leave the title compound (5 g): m.p.: 114-118°C. NMR (CDCl₃) 7.26-7.0 (m, ArH, 4H) 3.88 (s, OMe, 3H), 3.77 (s, OMe, 3H), 3.5 (d, CH 1H), 3.2 (d, CH, 1H), 1.7 (s, Me, 3H).

25

Example 12

1,5-bis(4-Chlorophenyl)-N-(4-fluorophenyl)-4,5-dihydro-1H-pyrazole-3-carboxamide

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The product of Example 9 (0.72 gm) was refluxed with 50% sodium hydroxide (1 ml) in 85% aqueous methanol (10 ml) for 2 hours. The mixture was acidified with 6N aqueous hydrochloric acid and partitioned

35

between ethyl acetate and water. The ethyl acetate
5 layer was dried with magnesium sulfate and concentrated
to a yellow solid. The solid was suspended in benzene
(20 ml) containing thionyl chloride (1.5 ml) and heated
at reflux for 1.5 hour. The mixture was concentrated
and azeotroped with toluene (10 ml) to give the oily
10 acid chloride which was dissolved in tetrahydrofuran
(15 ml) and treated dropwise with a benzene solution
(10 ml) of triethylamine (1.0 ml) and 4-fluoroaniline
(0.3 ml). The reaction mixture was stirred for 18
hours and partitioned between ethyl acetate and 1N
15 hydrochloric acid. The organic layer was washed with
sodium bicarbonate and brine. The dried organic layer
(magnesium sulfate) was concentrated to leave a residue
that could be purified by column chromatography or
recrystallization from methanol. The title compound
20 (0.46 g) was a yellow solid; m.p.: 194° to 195.5°C.
NMR (CDCl₃) 8.5 (br, NH), 7.7-7.0 (m, 12H, ArH), 5.4
(m, 1H, CH), 3.8 (m, 1H, CH), 3.2 (m, 1H, CH).

Example 13

25 1,5-Bis(4-chlorophenyl)-4,5-dihydro-N-[(4-trifluoro-
methyl)phenyl]-1H-pyrazole-3-carboxamide

The title compound (6.3 g) was prepared by the
method of Example 12 using 4-aminobenzotrifluoride
(3.2 ml) and the compound of Example 9 (6.5 g). The
30 compound was more conveniently prepared by omitting
the acidification and extraction of the
tetrahydrofuran solution. Simply evaporating the
solvent and triturating the residue with methanol
provided pure product as a powder; m.p.: 212.5
35 -214°C. NMR (CDCl₃) 8.6 (br, NH), 7.8-7.0 (m, ArH,
12H), 5.4 (dd, CH, 1H), 3.8 (dd, CH, 1H), 3.2 (dd, CH,
1H).

Example 14

5 1,5-bis(4-Chlorophenyl)-4,5-dihydro-5-methyl-N-[(4-4-trifluoromethyl)phenyl]-1H-pyrazole-3-carboxamide

Application of the procedure of Example 12 to the compound of Example 10 (0.60 g) and 4-trifluoromethylaniline (0.4 ml) gave the title compound (0.51 g) after silica gel chromatography in 20% ethyl acetate/hexanes and subsequent recrystallization from hexanes/butyl chloride; m.p.: 205° to 206°C. NMR (CDCl₃) 8.6 (br, NH), 7.8-6.9 (m, 12H, ArH), 3.4 (m, 2H, CH₂), 1.8 (s, 3H, CH₃).

15

Example 15

Methyl 1-(4-fluorophenyl)-4,5-dihydro-3-[(4-iodophenyl)-aminocarbonyl]-5-methyl-1H-pyrazole-5-carboxylate

The compound of Example 11 (0.5 g) was dissolved in dichloromethane (5 ml) and added to a mixture of trimethylaluminum (2M in toluene, 1.68 ml) and 4-iodoaniline (0.7 g) in dichloromethane (10 ml). The mixture was stirred at room temperature for 16 hours and partitioned between 1N HCl (100 ml) and dichloromethane (100 ml). The organic layer was dried and evaporated to leave a solid. Recrystallization from ether/hexanes gave the title compound (0.73 g); m.p.: 84-85°C. NMR (CDCl₃) 8.4 (br, NH), 7.7-6.9 (m, ArH, 12H), 3.8 (s, OMe, 3H), 3.8 (d, CH, 1H), 3.3 (d, CH, 1H), 1.7 (s, Me, 3H).

30

Example 16

Potassium 4-(4-fluorophenyl)-2-oxo-3-butenolate

35

A solution of pyruvic acid and p-fluorobenzaldehyde (24.8 g) in methanol (20 ml) was cooled to 15°C and treated with a solution of potassium

hydroxide (16.8 g) in (50 ml) methanol. After 2/3 of
5 the addition was complete, the cooling bath was
removed and the temperature was allowed to rise to
40°C. A yellow precipitate appeared and was filtered
after standing overnight. The solid was washed well
with methanol and ether. The title compound (34.5 g)
10 was used without further purification.

Example 17

15 1-(3,4-Dichlorophenyl)-5-(4-fluorophenyl)-4,5-dihydro-
N-[4-(trifluoromethyl)phenyl]-1H-pyrazole-3-carboxamide

The compound of Example 16 (9.0 g) was treated
with a solution of 3,4-dichlorophenylhydrazene
hydrochloride (9.5 g) in water (100 ml). The orange
solid was filtered and air dried. It was suspended in
20 glacial acetic acid (150 ml) and refluxed for 3 hr.
On cooling the pyrazoline acid crystallized (3.3 g).
A second crop was also collected (1.1 g). The acid
was suspended in benzene (100 ml) and treated with
thionyl chloride (6 ml). The mixture was refluxed for
25 2 hr. and evaporated. The residue was dissolved in
dry tetrahydrofuran (50 ml) and separated into five
equal portions. One aliquot was added to a solution
of 4-aminobenzotrifluoride (0.35 ml) and triethylamine
(0.9 ml) in tetrahydrofuran (10 ml). The mixture was
30 stirred for 30 min. and evaporated. The residue was
trituated with methanol (10 ml) to give the title
compound (0.9 g). m.p.: 241.5-243°C. NMR (CDCl₃),
8.6 (m, NH), 7.8-6.7 (m, ArH, 11H), 5.4 (dd, 1H, CH),
3.8 (dd, 1H, CH), 3.2 (dd, 1H, CH).

5

Example 184-(4-Fluorophenyl)-2-oxo-N-[4-(trifluoromethyl)phenyl]-3-butenamide

The compound of Example 16 was converted to the corresponding carboxylic acid by the general method of Stecher (J. Am. Chem. Soc., 1952, 74, 4392). The free acid (8.5 g) was treated with dichloromethylmethylether (10 ml) in 30 ml CH_2Cl_2 . The mixture was heated at reflux with the evolution of HCl. Evaporation after 2 hr. gave the acid chloride which was dissolved in tetrahydrofuran (100 ml) and treated dropwise with a mixture of triethylamine (8 ml) and 4-aminobenzotrifluoride (4 ml) in tetrahydrofuran (25 ml). After 1 hr. the mixture was partitioned between 1N HCl and ethyl acetate. On standing overnight the ethyl acetate layer deposited the title compound (5 g). m.p.: 200-201°C. NMR (CDCl_3), 9.2 (br, NH), 8.0-7.1 (m, Ar and CH_2 , 10H).

25

Example 194,5-Dihydro-4-(4-fluorophenyl)-1-phenyl-N-[4-(trifluoromethyl)phenyl]-1H-pyrazole-3-carboxamide

The title compound (0.4 g) was obtained by heating the compound of Example 18 (0.6 g) and phenylhydrazine (0.2 ml) in dimethylformamide (5 ml) at reflux for 1 hr. The residue was purified by chromatography on silica gel (50 g) with hexanes/ethyl acetate (3:1) as eluent. m.p.: 183.5-184.5°C. NMR (CDCl_3) 8.6 (br, NH), 7.8-7.0 (m, ArH, 13 H), 5.4 (m, 1H, CH), 3.8 (m, 1H, CH) 3.2 (m, 1H, CH).

Example 20

5 1,5-Bis(4-chlorophenyl)-4,5-dihydro-N-methyl-N-[4-(tri-
fluoromethyl)phenyl]-1H-pyrazole-3-carboxamide

The compound of Example 13 (2.1 g) was added to
a suspension of sodium hydride (60% in oil; 0.2 g) in
dry tetrahydrofuran (25 ml). After 30 min. methyl
10 iodide (0.9 g) was added in three separate portions.
The mixture was stirred for 18 hr. and quenched with
ammonium chloride solution. The mixture was extracted
with ethyl acetate and the organic layer was dried
and evaporated. The oily residue was chromatographed
15 on silica gel with hexanes/ethyl acetate (3:1) as
eluent to give the title compound (1.4 g); m.p.:
181-183°C. NMR (CDCl₃) 7.8-6.9 (m, ArH, 10H), 6.26
(d, ArH, 2H), 5.15 (dd, CH, 1H), 3.8 (dd, CH, 1H), 3.5
(s, NMe, 3H), 3.15 (dd, CH, 1H).

20

Example 21

N-acetyl-1,5-bis(4-chlorophenyl)-4,5-dihydro-N-[4-(tri-
fluoromethyl)phenyl]-1H-pyrazole-3-carboxamide

The title compound (0.8 g) was prepared by the
method of Example 20 at 1/2 scale using acetic
25 anhydride (0.5 ml) in place of methyl iodide.
Purification by silica gel chromatography using
hexanes/ethyl acetate (5:1) as eluent gave a solid
which crystallized as bright yellow needles from
methanol: m.p.: 158-160°C. NMR (CDCl₃) 7.7-6.9
30 (m, ArH, 10H), 6.5 (d, ArH, 2H), 5.3 (dd, CH, 1H), 3.7
(dd, CH, 1H), 3.05 (dd, CH, 1H), 2.5 (s, COMe, 3H).

Example 22

35 Methyl 1-(4-chlorophenyl)-4,5-dihydro-5-methyl-3-[[[4-
(trifluoromethyl)phenyl]amino]thioxomethyl]-1H-pyrazole-
5-carboxylate

The compound of Example 4 (0.67 g) was heated
under reflux with phosphorous pentasulfide (1.1 g) and

pyridine (3 ml) for 1 hr. The mixture was cooled and
5 poured into saturated sodium bicarbonate solution (100
ml) and ethyl acetate (100 ml). The organic layer was
washed with 1N hydrochloric acid (100 ml) and the
aqueous layer was reextracted with ethyl acetate. The
combined organic layers were dried, evaporated and
10 chromatographed on silica gel with hexanes/ethyl
acetate (1:1) to give an oil. The title compound
(0.46 g) solidified on standing: m.p.: 76-80°C
(dec.). NMR (CDCl_3) 8.1-7.0 (m, ArH, 8H), 3.8 (s,
Me, 3H), 3.8 (d, CH, 1H), 3.5 (d, CH, 1H), 1.7 (s, Me,
15 3H).

Using the procedures of Examples 1 to 22 and the
methods described herein, the following compounds of
Tables 1 to 7 can be prepared.

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Structures for Tables

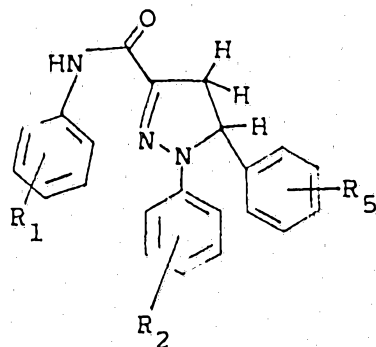
5

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Table 1

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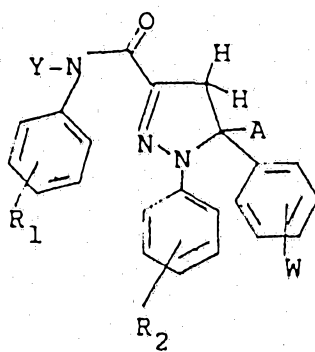
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Table 2

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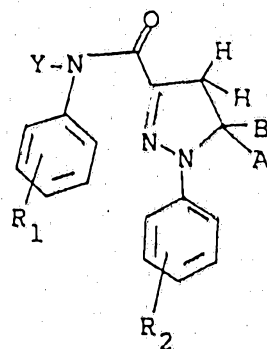
25

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Table 3

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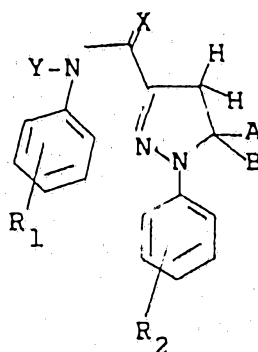
35

Structures (continued)

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Table 4

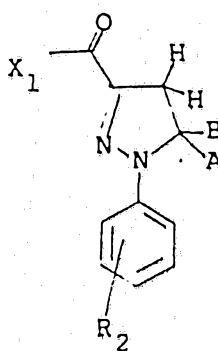
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Table 5

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Table 1

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p.(°C)</u>
5	4-CF ₃	4-Cl	4-CN	160 to 164
	4-CF ₃	4-F	4-CN	188 to 190
	4-CF ₃	4-H	4-CN	194 to 195
	4-CF ₃	4-Br	4-CN	
	4-CF ₃	4-I	4-CN	
10	4-CF ₃	4-OCF ₃	4-CN	
	4-CF ₃	4-CF ₃	4-CN	
	4-CF ₃	4-OCF ₂ H	4-CN	
	4-CF ₃	4-CF ₂ H	4-CN	
	4-CF ₃	4-Cl	4-Cl	212 to 214.5
15	4-CF ₃	4-F	4-Cl	161 to 162.5
	4-CF ₃	4-H	4-Cl	200 to 201
	4-CF ₃	4-Br	4-Cl	227 to 229
	4-CF ₃	4-I	4-Cl	
	4-CF ₃	4-OCF ₃	4-Cl	
20	4-CF ₃	4-CF ₃	4-Cl	218 to 220
	4-CF ₃	4-OCF ₂ H	4-Cl	187 to 188
	4-CF ₃	4-CF ₂ H	4-Cl	
	4-CF ₃	4-Cl	4-F	213 to 214.5
	4-CF ₃	4-F	4-F	180.5 to 183
25	4-CF ₃	4-H	4-F	183.5 to 184.5
	4-CF ₃	4-Br	4-F	
	4-CF ₃	4-I	4-F	
	4-CF ₃	4-OCF ₃	4-F	179 to 180
	4-CF ₃	4-CF ₃	4-F	201 to 202
30	4-CF ₃	4-OCF ₂ H	4-F	176 to 178
	4-CF ₃	4-CF ₂ H	4-F	
	4-CF ₃	4-CN	4-CN	186 to 188
	4-CF ₃	4-CN	4-Cl	
	4-CF ₃	4-CN	4-F	221 to 222
35	4-CF ₃	4-Cl	4-H	

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-CF ₃	4-F	4-H	171 to 173
	4-CF ₃	4-H	4-H	213 to 214
	4-CF ₃	4-Br	4-H	
	4-CF ₃	4-CN	4-H	
	4-CF ₃	4-I	4-H	
10	4-CF ₃	4-OCF ₃	4-H	176 to 178
	4-CF ₃	4-CF ₃	4-H	
	4-CF ₃	4-OCF ₂ H	4-H	
	4-CF ₃	4-CF ₂ H	4-H	
	4-CF ₃	4-Cl	4-CH ₃	185 to 186
15	4-CF ₃	4-F	4-CH ₃	
	4-CF ₃	4-H	4-CH ₃	
	4-CF ₃	4-Br	4-CH ₃	
	4-CF ₃	4-CN	4-CH ₃	
	4-CF ₃	4-I	4-CH ₃	
20	4-CF ₃	4-Cl	3-Cl	200 to 201
	4-CF ₃	4-F	3-Cl	
	4-CF ₃	4-H	3-Cl	
	4-CF ₃	4-Br	3-Cl	
	4-CF ₃	4-CN	3-Cl	
25	4-CF ₃	4-OCF ₃	3-Cl	
	4-CF ₃	4-OCF ₂ H	3-Cl	
	4-CF ₃	4-CF ₃	3-Cl	
	4-CF ₃	4-CF ₂ H	3-Cl	
	4-CF ₃	4-Cl	3,4-di-F	193.5 to 195
30	4-CF ₃	4-F	3,4-di-F	171 to 173
	4-CF ₃	4-Br	3,4-di-F	
	4-CF ₃	4-H	3,4-di-F	
	4-CF ₃	4-CN	3,4-di-F	
	4-CF ₃	4-OCF ₃	3,4-di-F	

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-CF ₃	4-OCF ₂ H	3,4-di-F	
	4-CF ₃	4-CF ₃	3,4-di-F	
	4-CF ₃	4-CF ₂ H	3,4-di-F	
	4-CF ₃	4-Cl	3,4-di-Cl	225 to 226
	4-CF ₃	4-F	3,4-di-Cl	
10	4-CF ₃	4-Br	3,4-di-Cl	
	4-CF ₃	4-H	3,4-di-Cl	
	4-CF ₃	4-CN	3,4-di-Cl	
	4-CF ₃	4-OCF ₃	3,4-di-Cl	
	4-CF ₃	4-CF ₃	3,4-di-Cl	
15	4-CF ₃	4-OCF ₂ H	3,4-di-Cl	
	4-CF ₃	4-CF ₂ H	3,4-di-Cl	
	4-CF ₃	4-Cl	3-CN	
	4-CF ₃	4-F	3-CN	
	4-CF ₃	4-Br	3-CN	
20	4-CF ₃	4-H	3-CN	
	4-CF ₃	4-CN	3-CN	171 to 173
	4-CF ₃	4-CF ₃	3-CN	
	4-CF ₃	4-OCF ₃	3-CN	
	4-CF ₃	4-OCF ₂ H	3-CN	
25	4-CF ₃	4-CF ₂ H	3-CN	
	4-CF ₃	4-Cl	4-CO ₂ Me	199 to 200
	4-CF ₃	4-F	4-CO ₂ Me	174 to 179
	4-CF ₃	4-Br	4-CO ₂ Me	
	4-CF ₃	4-H	4-CO ₂ Me	
30	4-CF ₃	4-CN	4-CO ₂ Me	
	4-CF ₃	4-CF ₃	4-CO ₂ Me	208 to 210
	4-CF ₃	4-OCF ₃	4-CO ₂ Me	
	4-CF ₃	4-OCF ₂ H	4-CO ₂ Me	
	4-CF ₃	4-CF ₂ H	4-CO ₂ Me	

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-CF ₃	4-Cl	4-CF ₃	194 to 196
	4-CF ₃	4-F	4-CF ₃	
	4-CF ₃	4-Br	4-CF ₃	
	4-CF ₃	4-H	4-CF ₃	
	4-CF ₃	4-Cl	4-CF ₃	
10	4-CF ₃	4-CF ₃	4-CF ₃	218 to 219
	4-CF ₃	4-OCF ₃	4-CF ₃	
	4-CF ₃	4-OCF ₂ H	4-CF ₃	
	4-CF ₃	4-CF ₂ H	4-CF ₃	
	4-CF ₃	4-Cl	4-Br	
15	4-CF ₃	4-F	4-Br	207 to 208
	4-CF ₃	4-CN	4-Br	
	4-CF ₃	4-CF ₃	4-Br	
	4-CF ₃	4-H	4-Br	
	4-CF ₃	4-Cl	3-Br	
20	4-CF ₃	4-F	3-Br	238 to 240
	4-CF ₃	4-CF ₃	3-Br	
	4-CF ₃	4-CN	3-Br	
	4-CF ₃	4-H	3-Br	
	4-OCF ₃	4-Cl	4-CN	
25	4-OCF ₃	4-F	4-CN	224 to 225
	4-OCF ₃	4-Br	4-CN	
	4-OCF ₃	4-H	4-CN	
	4-OCF ₃	4-CN	4-CN	
	4-OCF ₃	4-CF ₃	4-CN	
30	4-OCF ₃	4-OCF ₃	4-CN	165 to 167
	4-OCF ₃	4-OCF ₂ H	4-CN	
	4-OCF ₃	4-CF ₂ H	4-CN	
	4-OCF ₃	4-Cl	4-F	
	4-OCF ₃	4-F	4-F	
35	4-OCF ₃	4-Br	4-F	

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₃</u>	<u>m.p. (°C)</u>
5	4-OCF ₃	4-H	4-F	
	4-OCF ₃	4-CN	4-F	
	4-OCF ₃	4-CF ₃	4-F	
10	4-OCF ₃	4-OCF ₃	4-F	140.5 to 142
	4-OCF ₃	4-OCF ₂ H	4-F	120 to 124
	4-OCF ₃	4-CF ₂ H	4-F	
	4-OCF ₃	4-Cl	4-Cl	170 to 172
	4-OCF ₃	4-F	4-Cl	
15	4-OCF ₃	4-Br	4-Cl	
	4-OCF ₃	4-CN	4-Cl	
	4-OCF ₃	4-H	4-Cl	
	4-OCF ₃	4-CF ₃	4-Cl	
20	4-OCF ₃	4-OCF ₃	4-Cl	
	4-OCF ₃	4-OCF ₂ H	4-Cl	
	4-OCF ₃	4-CF ₂ H	4-Cl	
	4-OCF ₃	4-Cl	3-Cl	
	4-OCF ₃	4-F	3-Cl	
	4-OCF ₃	4-Br	3-Cl	
25	4-OCF ₃	4-H	3-Cl	
	4-OCF ₃	4-CN	3-Cl	
	4-OCF ₃	4-CF ₃	3-Cl	
	4-OCF ₃	4-OCF ₃	3-Cl	
	4-OCF ₃	4-OCF ₂ H	3-Cl	
30	4-OCF ₃	4-CF ₂ H	3-Cl	
	4-OCF ₃	4-Cl	4-H	
	4-OCF ₃	4-F	4-H	
	4-OCF ₃	4-Br	4-H	
	4-OCF ₃	4-H	4-H	
35	4-OCF ₃	4-CN	4-H	
	4-OCF ₃	4-CF ₃	4-H	
	4-OCF ₃	4-OCF ₃	4-H	

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-OCF ₃	4-OCF ₂ H	4-H	
	4-OCF ₃	4-CF ₂ H	4-H	
	4-OCF ₃	4-Cl	3,4-di-F	134.5 to 135.5
	4-OCF ₃	4-F	3,4-di-F	162.5 to 164
	4-OCF ₃	4-Br	3,4-di-F	
10	4-OCF ₃	4-H	3,4-di-F	
	4-OCF ₃	4-CN	3,4-di-F	
	4-OCF ₃	4-CF ₃	3,4-di-F	
	4-OCF ₃	4-OCF ₃	3,4-di-F	
	4-OCF ₃	4-OCF ₂ H	3,4-di-F	
15	4-OCF ₃	4-CF ₂ H	3,4-di-F	
	4-OCF ₃	4-Cl	4-CO ₂ Me	
	4-OCF ₃	4-F	4-CO ₂ Me	
	4-OCF ₃	4-Br	4-CO ₂ Me	
	4-OCF ₃	4-H	4-CO ₂ Me	
20	4-OCF ₃	4-CN	4-CO ₂ Me	
	4-OCF ₃	4-CF ₃	4-CO ₂ Me	
	4-OCF ₃	4-OCF ₃	4-CO ₂ Me	
	4-OCF ₃	4-OCF ₂ H	4-CO ₂ Me	
	4-OCF ₃	4-CF ₂ H	4-CO ₂ Me	
25	4-OCF ₃	4-Cl	4-CF ₃	
	4-OCF ₃	4-F	4-CF ₃	
	4-OCF ₃	4-Br	4-CF ₃	
	4-OCF ₃	4-H	4-CF ₃	
	4-OCF ₃	4-CN	4-CF ₃	
30	4-OCF ₃	4-CF ₃	4-CF ₃	
	4-OCF ₃	4-OCF ₃	4-CF ₃	
	4-OCF ₃	4-OCF ₂ H	4-CF ₃	
	4-OCF ₃	4-CF ₂ H	4-CF ₃	
	4-OCF ₃	4-CF ₂ H	4-CF ₃	

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-F	4-Cl	4-CN	
	4-F	4-F	4-CN	174 to 175
	4-F	4-H	4-CN	204 to 207
	4-F	4-Br	4-CN	
	4-F	4-I	4-CN	
10	4-F	4-CN	4-CN	
	4-F	4-Cl	4-Cl	194 to 195.5
	4-F	4-F	4-Cl	181 to 182
	4-F	4-H	4-Cl	201 to 202
	4-F	4-Br	4-Cl	
15	4-F	4-I	4-Cl	
	4-F	4-CN	4-Cl	
	4-F	4-Cl	4-F	203 to 204
	4-F	4-F	4-F	157 to 158.5
	4-F	4-H	4-F	
20	4-F	4-Br	4-F	
	4-F	4-I	4-F	
	4-F	4-CN	4-F	204 to 206
	4-F	4-Cl	4-H	
	4-F	4-F	4-H	168 to 169
25	4-F	4-H	4-H	
	4-F	4-Br	4-H	
	4-F	4-I	4-H	
	4-F	4-CN	4-H	190 to 192
	4-F	4-Cl	4-CH ₃	170 to 171
30	4-F	4-F	4-CH ₃	
	4-F	4-H	4-CH ₃	
	4-F	4-Br	4-CH ₃	
	4-F	4-I	4-CH ₃	
	4-F	4-CN	4-CH ₃	

Table 1 (continued)

5	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
	4-Cl	4-Cl	4-CN	180 to 183
	4-Cl	4-F	4-CN	169 to 170
	4-Cl	4-H	4-CN	178 to 179
10	4-Cl	4-Br	4-CN	
	4-Cl	4-I	4-CN	
	4-Cl	4-CN	4-CN	solid (a)
	4-Cl	4-CF ₃	4-CN	
	4-Cl	4-OCF ₃	4-CN	
15	4-Cl	4-OCF ₂ H	4-CN	
	4-Cl	4-CF ₂ H	4-CN	
	4-Cl	4-Cl	4-Cl	186 to 188
	4-Cl	4-F	4-Cl	137 to 139.5
	4-Cl	4-H	4-Cl	
20	4-Cl	4-Br	4-Cl	
	4-Cl	4-I	4-Cl	
	4-Cl	4-CN	4-Cl	
	4-Cl	4-CF ₃	4-Cl	206 to 208
	4-Cl	4-OCF ₃	4-Cl	
25	4-Cl	4-OCF ₂ H	4-Cl	173 to 175
	4-Cl	4-CF ₂ H	4-Cl	
	4-Cl	4-Cl	4-F	208 to 209.5
	4-Cl	4-F	4-F	
	4-Cl	4-H	4-F	
30	4-Cl	4-Br	4-F	
	4-Cl	4-I	4-F	
	4-Cl	4-CN	4-F	215 to 218
	4-Cl	4-CF ₃	4-F	
	4-Cl	4-OCF ₃	4-F	181 to 183
35	4-Cl	4-OCF ₂ H	4-F	175 to 176
	4-Cl	4-CF ₂ H	4-F	
	4-Cl	4-Cl	4-H	

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-Cl	4-F	4-H	140 to 142
	4-Cl	4-H	4-H	
	4-Cl	4-Br	4-H	
	4-Cl	4-I	4-H	
	4-Cl	4-CN	4-H	
10	4-Cl	4-CF ₃	4-H	202 to 203
	4-Cl	4-OCF ₃	4-H	
	4-Cl	4-OCF ₂ H	4-H	
	4-Cl	4-CF ₂ H	4-H	
	4-Cl	4-Cl	4-CH ₃	
15	4-Cl	4-F	4-CH ₃	188 to 190
	4-Cl	4-H	4-CH ₃	
	4-Cl	4-Br	4-CH ₃	
	4-Cl	4-I	4-CH ₃	
	4-Cl	4-CN	4-CH ₃	
20	4-Cl	4-CF ₃	4-Cl	206 to 208
	4-Cl	4-Cl	3-Cl	
	4-Cl	4-F	3-Cl	
	4-Cl	4-H	3-Cl	
	4-Cl	4-Br	3-Cl	
25	4-Cl	4-CN	3-Cl	188 to 191
	4-Cl	4-OCF ₃	3-Cl	
	4-Cl	4-OCF ₂ H	3-Cl	
	4-Cl	4-CF ₃	3-Cl	
	4-Cl	4-CF ₂ H	3-Cl	
30	4-Cl	4-Cl	3,4-di-F	148.5 to 151
	4-Cl	4-F	3,4-di-F	
	4-Cl	4-Br	3,4-di-F	
	4-Cl	4-H	3,4-di-F	
	4-Cl	4-CN	3,4-di-F	
35	4-Cl	4-OCF ₃	3,4-di-F	170 to 171
	4-Cl	4-OCF ₂ H	3,4-di-F	
	4-Cl	4-CF ₃	3,4-di-F	
	4-Cl	4-CF ₂ H	3,4-di-F	
	4-Cl	4-Cl	3,4-di-F	

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-Cl	4-Cl	3,4-di-Cl	
	4-Cl	4-F	3,4-di-Cl	
	4-Cl	4-Br	3,4-di-Cl	
	4-Cl	4-H	3,4-di-Cl	
	4-Cl	4-CN	3,4-di-Cl	
	4-Cl	4-OCF ₃	3,4-di-Cl	
	4-Cl	4-CF ₃	3,4-di-Cl	
10	4-Cl	4-OCF ₂ H	3,4-di-Cl	
	4-Cl	4-CF ₂ H	3,4-di-Cl	
	4-Cl	4-Cl	3-CN	
	4-Cl	4-F	3-CN	
	4-Cl	4-Br	3-CN	
	4-Cl	4-H	3-CN	
	4-Cl	4-CN	3-CN	
15	4-Cl	4-CF ₃	3-CN	168 to 170
	4-Cl	4-OCF ₃	3-CN	
	4-Cl	4-OCF ₂ H	3-CN	
	4-Cl	4-CF ₂ H	3-CN	
	4-Cl	4-Cl	4-CO ₂ Me	202 to 205
	4-Cl	4-F	4-CO ₂ Me	170 to 176
	4-Cl	4-Br	4-CO ₂ Me	
20	4-Cl	4-H	4-CO ₂ Me	
	4-Cl	4-CN	4-CO ₂ Me	
	4-Cl	4-CF ₃	4-CO ₂ Me	175 to 178
	4-Cl	4-OCF ₃	4-CO ₂ Me	
	4-Cl	4-OCF ₂ H	4-CO ₂ Me	
	4-Cl	4-CF ₂ H	4-CO ₂ Me	
	4-Cl	4-Cl	4-CF ₃	
25	4-Cl	4-F	4-CF ₃	
	4-Cl	4-Br	4-CF ₃	
	4-Cl	4-H	4-CF ₃	
	4-Cl	4-CN	4-CF ₃	
	4-Cl	4-CF ₃	4-CF ₃	177 to 178
	4-Cl	4-OCF ₃	4-CF ₃	
	4-Cl	4-OCF ₃	4-CF ₃	
30	4-Cl	4-Cl	4-CF ₃	
	4-Cl	4-F	4-CF ₃	
	4-Cl	4-Br	4-CF ₃	
	4-Cl	4-H	4-CF ₃	
	4-Cl	4-CN	4-CF ₃	
	4-Cl	4-CF ₃	4-CF ₃	
	4-Cl	4-OCF ₃	4-CF ₃	
35				

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-Cl	4-OCF ₂ H	4-CF ₃	
	4-Cl	4-CF ₂ H	4-CF ₃	
	4-Cl	4-Cl	4-Br	191 to 193.5
	4-Cl	4-F	4-Br	
	4-Cl	4-CN	4-Br	246 to 248
10	4-Cl	4-CF ₃	4-Br	
	4-Cl	4-H	4-Br	
	4-Cl	4-Cl	3-Br	
	4-Cl	4-F	3-Br	
	4-Cl	4-CF ₃	3-Br	
15	4-Cl	4-CN	3-Br	
	4-Cl	4-H	3-Br	
	4-Br	4-F	4-CN	
	4-Br	4-Cl	4-CN	197.5 to 198.5
	4-Br	4-H	4-CN	
20	4-Br	4-F	4-Cl	
	4-Br	4-Cl	4-Cl	190 to 192
	4-Br	4-H	4-Cl	
	4-I	4-F	4-CN	
	4-I	4-Cl	4-CN	
25	4-I	4-H	4-CN	
	4-I	4-F	4-Cl	
	4-I	4-Cl	4-Cl	207.5 to 209
	4-I	4-H	4-Cl	
	4-(4'-chloro- phenoxy)	4-Cl	4-Cl	214 to 215.5
30	4-(4'-chloro- phenoxy)	4-F	4-CN	
	4-OCH ₃	4-Cl	4-CN	
	4-NO ₂	4-Cl	4-CN	222 to 223
	4-CO ₂ Et	4-Cl	4-CN	
	4-SMe	4-Cl	4-CN	
35	4-SO ₂ Me	4-Cl	4-CN	
	4-Me	4-Cl	4-CN	

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-CH=CH ₂	4-Cl	4-CN	
	4-C≡CH	4-Cl	4-CN	
	4-CONMe ₂	4-Cl	4-CN	
	4-SCF ₃	4-Cl	4-CN	
	4-OCH(CH ₃) ₂	4-Cl	4-CN	
10	4-OSO ₂ CH ₃	4-Cl	4-CN	
	4-OCOCH ₃	4-Cl	4-CN	
	4-NMe ₂	4-Cl	4-CN	
	4-NHCOCH ₃	4-Cl	4-CN	
	4-OCONHMe	4-Cl	4-CN	
15	4-NHCONH ₂	4-Cl	4-CN	
	4-COCH ₃	4-Cl	4-CN	
	4-OCH ₃	4-Cl	4-Cl	177 to 178
	4-NO ₂	4-Cl	4-Cl	223 to 225
	4-CO ₂ Et	4-Cl	4-Cl	
20	4-SMe	4-Cl	4-Cl	
	4-SO ₂ Me	4-Cl	4-Cl	
	4-Me	4-Cl	4-Cl	153 to 155
	4-CH=CH ₂	4-Cl	4-Cl	
	4-C≡CH	4-Cl	4-Cl	
25	4-CONMe ₂	4-Cl	4-Cl	
	4-SGF ₃	4-Cl	4-Cl	
	4-OCH(CH ₃) ₂	4-Cl	4-Cl	
	4-OSO ₂ CH ₃	4-Cl	4-Cl	
	4-OCOCH ₃	4-Cl	4-Cl	
30	4-NMe ₂	4-Cl	4-Cl	
	4-NHCOCH ₃	4-Cl	4-Cl	
	4-OCONHMe	4-Cl	4-Cl	
	4-NHCONH ₂	4-Cl	4-Cl	
	4-COCH ₃	4-Cl	4-Cl	193 to 195

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Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-OCH ₃	4-F	4-CN	
	4-NO ₂	4-F	4-CN	
	4-CO ₂ Et	4-F	4-CN	
	4-SMe	4-F	4-CN	
	4-SO ₂ Me	4-F	4-CN	
10	4-Me	4-F	4-CN	
	4-CH=CH ₂	4-F	4-CN	
	4-C≡CH	4-F	4-CN	
	4-CONMe ₂	4-F	4-CN	
	4-SCF ₃	4-F	4-CN	
15	4-OCH(CH ₃) ₂	4-F	4-CN	
	4-OSO ₂ CH ₃	4-F	4-CN	
	4-OCOCH ₃	4-F	4-CN	
	4-NMe ₂	4-F	4-CN	
	4-NHCOCH ₃	4-F	4-CN	
20	4-CONHMe	4-F	4-CN	
	4-NHCONH ₂	4-F	4-CN	
	4-COCH ₃	4-F	4-CN	
	4-OCH ₃	4-F	4-Cl	
	4-NO ₂	4-F	4-Cl	180 to 185
25	4-CO ₂ Et	4-F	4-Cl	
	4-SMe	4-F	4-Cl	
	4-SO ₂ Me	4-F	4-Cl	
	4-Me	4-F	4-Cl	
	4-CH=CH ₂	4-F	4-Cl	
30	4-C≡CH	4-F	4-Cl	
	4-CONMe ₂	4-F	4-Cl	
	4-SCF ₃	4-F	4-Cl	
	4-OCH(CH ₃) ₂	4-F	4-Cl	
	4-OSO ₂ CH ₃	4-F	4-Cl	
35	4-OCOCH ₃	4-F	4-Cl	

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Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-NMe ₂	4-F	4-Cl	
	4-NHCOCH ₃	4-F	4-Cl	
	4-OCNHMe	4-F	4-Cl	
	4-NHCONH ₂	4-F	4-Cl	
	4-COCH ₃	4-F	4-Cl	
10	4-CF ₃	4-F	3-Cl, 4-CN	
	4-CF ₃	4-Cl	3-Cl, 4-CN	
	4-CF ₃	4-F	3-CN, 4-F	
	4-CF ₃	4-Cl	3-CN, 4-F	
	4-CF ₃	4-F	3-CN, 4-Cl	
15	4-CF ₃	4-Cl	3-CN, 4-Cl	
	4-CF ₃	4-F	2-F, 4-CN	
	4-CF ₃	4-Cl	2-F, 4-CN	
	4-CF ₃	4-F	2-F, 4-Cl	
	4-CF ₃	4-Cl	2-F, 4-Cl	
20	4-CF ₃	4-F	2,4-di-F	
	4-CF ₃	4-Cl	2,4-di-F	
	4-CF ₃	4-F	3,5-di-F	
	4-CF ₃	4-Cl	3,5-di-F	
	4-CF ₃	4-F	2-Cl	
25	4-CF ₃	4-Cl	2-Cl	190 to 192
	4-CF ₃	4-F	3-F	
	4-CF ₃	4-Cl	3-F	
	4-CF ₃	4-F	2-F	
	4-CF ₃	4-Cl	2-F	
30	4-CF ₃	4-F	2-CN	
	4-CF ₃	4-Cl	2-CN	
	4-CF ₃	4-F	3-CF ₃	
	4-CF ₃	4-Cl	3-CF ₃	
	4-CF ₃	4-F	2-CF ₃	
35	4-CF ₃	4-Cl	2-CF ₃	

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-CF ₃	4-F	3,4-di-CN	
	4-CF ₃	4-Cl	3,4-di-CN	
	4-CF ₃	4-F	3-F, 4-Cl	
	4-CF ₃	4-Cl	3-F, 4-Cl	
	4-CF ₃	4-F	3-Cl, 4-F	
10	4-CF ₃	4-Cl	3-Cl, 4-F	
	4-CF ₃	4-F	3-F, 4-CN	
	4-CF ₃	4-Cl	3-F, 4-CN	
	4-CF ₃	4-F	3,5-di-Cl	
	4-CF ₃	4-Cl	3,5-di-Cl	
15	4-CF ₃	4-F	3-Cl, 5-F	
	4-CF ₃	4-Cl	3-Cl, 5-F	
	4-CF ₃	4-OCH ₃	4-CN	
	4-CF ₃	4-NO ₂	4-CN	
	4-CF ₃	4-CO ₂ Et	4-CN	
20	4-CF ₃	4-SMe	4-CN	
	4-CF ₃	4-SO ₂ Me	4-CN	
	4-CF ₃	4-Me	4-CN	
	4-CF ₃	4-CH=CH ₂	4-CN	
	4-CF ₃	4-C≡CH	4-CN	
25	4-CF ₃	4-CONMe ₂	4-CN	
	4-CF ₃	4-SGF ₃	4-CN	
	4-CF ₃	4-OCH(CH ₃) ₂	4-CN	
	4-CF ₃	4-OSO ₂ CH ₃	4-CN	
	4-CF ₃	4-OCOCH ₃	4-CN	
30	4-CF ₃	4-NMe ₂	4-CN	
	4-CF ₃	4-NHCOCH ₃	4-CN	
	4-CF ₃	4-OCONHMe	4-CN	
	4-CF ₃	4-NHCONH ₂	4-CN	
	4-CF ₃	4-COCH ₃	4-CN	

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-CF ₃	4-OCH ₃	4-F	
	4-CF ₃	4-NO ₂	4-F	232 to 234
	4-CF ₃	4-CO ₂ Et	4-F	
	4-CF ₃	4-SMe	4-F	
	4-CF ₃	4-SO ₂ Me	4-F	242 to 244
10	4-CF ₃	4-Me	4-F	
	4-CF ₃	4-CH=CH ₂	4-F	
	4-CF ₃	4-C≡CH	4-F	
	4-CF ₃	4-CONMe ₂	4-F	
	4-CF ₃	4-SCF ₃	4-F	
15	4-CF ₃	4-OCH(CH ₃) ₂	4-F	
	4-CF ₃	4-OSO ₂ CH ₃	4-F	
	4-CF ₃	4-OCOCH ₃	4-F	
	4-CF ₃	4-NMe ₂	4-F	
	4-CF ₃	4-NHCOCH ₃	4-F	
20	4-CF ₃	4-OCONHMe	4-F	
	4-CF ₃	4-NHCONH ₂	4-F	
	4-CF ₃	4-COCH ₃	4-F	
	4-CF ₃	4-OCH ₃	4-Cl	
	4-CF ₃	4-NO ₂	4-Cl	
25	4-CF ₃	4-CO ₂ Et	4-Cl	
	4-CF ₃	4-SMe	4-Cl	
	4-CF ₃	4-SO ₂ Me	4-Cl	
	4-CF ₃	4-Me	4-Cl	201.5 to 203.5
	4-CF ₃	4-CH=CH ₂	4-Cl	
30	4-CF ₃	4-C≡CH	4-Cl	
	4-CF ₃	4-CONMe ₂	4-Cl	
	4-CF ₃	4-SCF ₃	4-Cl	
	4-CF ₃	4-OCH(CH ₃) ₂	4-Cl	
	4-CF ₃	4-OSO ₂ CH ₃	4-Cl	
35	4-CF ₃	4-OCOCH ₃	4-Cl	

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-CF ₃	4-NMe ₂	4-Cl	
	4-CF ₃	4-NHCOCH ₃	4-Cl	
	4-CF ₃	4-OCONHMe	4-Cl	
	4-CF ₃	4-NHCONH ₂	4-Cl	
	4-CF ₃	4-COCH ₃	4-Cl	
10	4-Cl	4-OCH ₃	4-CN	
	4-Cl	4-NO ₂	4-CN	
	4-Cl	4-CO ₂ Et	4-CN	
	4-Cl	4-SMe	4-CN	
	4-Cl	4-SO ₂ Me	4-CN	
15	4-Cl	4-Me	4-CN	
	4-Cl	4-CH=CH ₂	4-CN	
	4-Cl	4-C≡CH	4-CN	
	4-Cl	4-CONMe ₂	4-CN	
	4-Cl	4-SCF ₃	4-CN	
20	4-Cl	4-OCH(CH ₃) ₂	4-CN	
	4-Cl	4-OSO ₂ CH ₃	4-CN	
	4-Cl	4-OCOCH ₃	4-CN	
	4-Cl	4-NMe ₂	4-CN	
	4-Cl	4-NHCOCH ₃	4-CN	
25	4-Cl	4-OCONHMe	4-CN	
	4-Cl	4-NHCONH ₂	4-CN	
	4-Cl	4-COCH ₃	4-CN	
	4-Cl	4-OCH ₃	4-Cl	188 to 189
	4-Cl	4-NO ₂	4-Cl	
30	4-Cl	4-CO ₂ Et	4-Cl	
	4-Cl	4-SMe	4-Cl	
	4-Cl	4-SO ₂ Me	4-Cl	
	4-Cl	4-Me	4-Cl	
	4-Cl	4-CH=CH ₂	4-Cl	
35	4-Cl	4-C≡CH	4-Cl	

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-Cl	4-CONMe ₂	4-Cl	
	4-Cl	4-SCF ₃	4-Cl	
	4-Cl	4-OCH(CH ₃) ₂	4-Cl	
	4-Cl	4-OSO ₂ CH ₃	4-Cl	
	4-Cl	4-OCOCH ₃	4-Cl	
10	4-Cl	4-NMe ₂	4-Cl	
	4-Cl	4-NHCOCH ₃	4-Cl	
	4-Cl	4-OCONHMe	4-Cl	
	4-Cl	4-NHCONH ₂	4-Cl	
	4-Cl	4-COCH ₃	4-Cl	
15	4-Cl	4-OCH ₃	4-F	
	4-Cl	4-NO ₂	4-F	
	4-Cl	4-CO ₂ Et	4-F	
	4-Cl	4-SMe	4-F	
	4-Cl	4-SO ₂ Me	4-F	
20	4-Cl	4-Me	4-F	
	4-Cl	4-CH=CH ₂	4-F	
	4-Cl	4-C≡CH	4-F	
	4-Cl	4-CONMe ₂	4-F	
	4-Cl	4-SCF ₃	4-F	
25	4-Cl	4-OCH(CH ₃) ₂	4-F	
	4-Cl	4-OSO ₂ CH ₃	4-F	
	4-Cl	4-OCOCH ₃	4-F	
	4-Cl	4-NMe ₂	4-F	
	4-Cl	4-NHCOCH ₃	4-F	
30	4-Cl	4-OCONHMe	4-F	
	4-Cl	4-NHCONH ₂	4-F	
	4-Cl	4-COCH ₃	4-F	

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-CF ₃	4-Cl	4-OCH ₃	163 to 164
	4-CF ₃	4-Cl	4-NO ₂	
	4-CF ₃	4-Cl	4-CO ₂ Et	
	4-CF ₃	4-Cl	4-SMe	
	4-CF ₃	4-Cl	4-SO ₂ Me	
10	4-CF ₃	4-Cl	4-Me	
	4-CF ₃	4-Cl	4-CH=CH ₂	
	4-CF ₃	4-Cl	4-C≡CH	
	4-CF ₃	4-Cl	4-CONMe ₂	
	4-CF ₃	4-Cl	4-SCF ₃	
15	4-CF ₃	4-Cl	4-OCH(CH ₃) ₂	
	4-CF ₃	4-Cl	4-OSO ₂ CH ₃	
	4-CF ₃	4-Cl	4-OCOCH ₃	
	4-CF ₃	4-Cl	4-NMe ₂	
	4-CF ₃	4-Cl	4-NHCOCH ₃	
20	4-CF ₃	4-Cl	4-OCONHMe	
	4-CF ₃	4-Cl	4-NHCONH ₂	
	4-CF ₃	4-Cl	4-COCH ₃	
	4-F	4-F	4-OCH ₃	
	4-F	4-F	4-NO ₂	
25	4-F	4-F	4-CO ₂ Et	
	4-F	4-F	4-SMe	
	4-F	4-F	4-SO ₂ Me	
	4-F	4-F	4-Me	
	4-F	4-F	4-CH=CH ₂	
30	4-F	4-F	4-C≡CH	
	4-F	4-F	4-CONMe ₂	
	4-F	4-F	4-SCF ₃	
	4-F	4-F	4-OCH(CH ₃) ₂	
	4-F	4-F	4-OSO ₂ CH ₃	
35	4-F	4-F	4-OCOCH ₃	
	4-F	4-F	4-NMe ₂	

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-F	4-F	4-NHCOCH ₃	
	4-F	4-F	4-CONHMe	
	4-F	4-F	4-NHCONH ₂	
10	4-F	4-F	4-COCH ₃	
	4-Cl	4-Cl	4-OCH ₃	166 to 168
	4-Cl	4-Cl	4-NO ₂	
	4-Cl	4-Cl	4-CO ₂ Et	
	4-Cl	4-Cl	4-SMe	
15	4-Cl	4-Cl	4-SO ₂ Me	
	4-Cl	4-Cl	4-Me	
	4-Cl	4-Cl	4-CH=CH ₂	
	4-Cl	4-Cl	4-C≡CH	
20	4-Cl	4-Cl	4-CONMe ₂	
	4-Cl	4-Cl	4-SCF ₃	
	4-Cl	4-Cl	4-OCH(CH ₃) ₂	
	4-Cl	4-Cl	4-OSO ₂ CH ₃	
	4-Cl	4-Cl	4-OCOCH ₃	
25	4-Cl	4-Cl	4-NMe ₂	
	4-Cl	4-Cl	4-NHCOCH ₃	
	4-Cl	4-Cl	4-CONHMe	
	4-Cl	4-Cl	4-NHCONH ₂	
	4-Cl	4-Cl	4-COCH ₃	
30	3-F, 4-CF ₃	4-Cl	4-CN	
	3-Cl, 4-CF ₃	4-Cl	4-CN	
	2-F, 4-CF ₃	4-Cl	4-CN	
	2-Cl, 4-CF ₃	4-Cl	4-CN	
	3-F, 4-Cl	4-Cl	4-CN	
	3,4-di-F	4-Cl	4-CN	
35	3-Cl, 4-F	4-Cl	4-CN	
	3,4-di-Cl	4-Cl	4-CN	
	4-F, 3-CF ₃	4-Cl	4-CN	
	4-Cl, 3-CF ₃	4-Cl	4-CN	

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	5-F, 3-CF ₃	4-F	4-CN	
	5-Cl, 3-CF ₃	4-F	4-CN	
	3,5-di-F	4-F	4-CN	
	3,5-di-Cl	4-F	4-CN	
	3-F, 5-Cl	4-F	4-CN	
10	3-CF ₃	4-F	4-CN	
	3-CF ₃	4-Cl	4-CN	
	3-Cl	4-F	4-CN	
	3-Cl	4-Cl	4-CN	
	3-F	4-F	4-CN	
15	3-F	4-Cl	4-CN	
	4-CF ₃	3-F	4-CN	
	4-CF ₃	3-Cl	4-CN	
	4-CF ₃	3-F, 4-Cl	4-CN	
	4-CF ₃	3-Cl, 4-F	4-CN	
20	4-CF ₃	3,4-di-F	4-CN	
	4-CF ₃	3,4-di-Cl	4-CN	
	4-CF ₃	3,5-di-F	4-CN	
	4-CF ₃	3,5-di-Cl	4-CN	
	4-CF ₃	3-F, 5-Cl	4-CN	
25	4-CF ₃	3,4,5-trifluoro	4-CN	
	4-CF ₃	3,4,5-trichloro	4-CN	
	4-CF ₃	2-F	4-CN	
	4-CF ₃	2-Cl	4-CN	
	4-CF ₃	2-F, 4-Cl	4-CN	
30	4-CF ₃	2-Cl, 4-F	4-CN	
	4-CF ₃	2,4-di-F	4-CN	
	4-CF ₃	2,4-di-Cl	4-CN	
	4-CF ₃	3-F	4-F	
	4-CF ₃	3-Cl	4-F	
35	4-CF ₃	3-F, 4-Cl	4-F	

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-CF ₃	3-Cl, 4-F	4-F	
	4-CF ₃	3,5-di-F	4-F	
	4-CF ₃	3,5-di-Cl	4-F	
	4-CF ₃	3-F, 5-Cl	4-F	
	4-CF ₃	3,4,5-trifluoro	4-F	
10	4-CF ₃	3,4,5-trichloro	4-F	
	4-CF ₃	2-F	4-F	
	4-CF ₃	2-Cl	4-F	
	4-CF ₃	2-F, 4-Cl	4-F	
	4-CF ₃	2-Cl, 4-F	4-F	
15	4-CF ₃	2,4-di-F	4-F	
	4-CF ₃	2,4-di-Cl	4-F	
	4-CF ₃	3-F	4-Cl	
	4-CF ₃	3-F, 4-Cl	4-CN	
	4-CF ₃	3-Cl, 4-F	4-Cl	
20	4-CF ₃	3,4-di-F	4-Cl	
	4-CF ₃	3,5-di-F	4-Cl	
	4-CF ₃	3,5-di-Cl	4-Cl	
	4-CF ₃	3-F, 5-Cl	4-Cl	
	4-CF ₃	3,4,5-trifluoro	4-Cl	
25	4-CF ₃	3,4,5-trichloro	4-Cl	
	4-CF ₃	2-F	4-Cl	
	4-CF ₃	2-F, 4-Cl	4-Cl	
	4-CF ₃	2-Cl, 4-F	4-Cl	
	4-CF ₃	2,4-di-F	4-Cl	
30	4-CF ₃	2,4-di-Cl	4-Cl	
	4-Cl	4-CF ₃	4-Cl	206 to 208
	4-Cl	4-Cl	4-Br	191 to 193.5
	4-CF ₃	4-Cl	4-Br	207 to 208
	4-CN	4-Cl	4-Cl	247 to 249

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Table 1. (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	3-CF ₃	4-Cl	4-Cl	131 to 139
	4-Cl	4-Cl	3-Cl	188 to 191
	4-Cl	4-Cl	2-Cl	192 to 195
	4-CF ₃	4-OMe	4-Cl	204 to 205
	4-F	4-Cl	3,4-di-Cl	185 to 186
10	4-CF ₃	3-Cl	4-Cl	187 to 189
	4-F	3-Cl	4-Cl	177 to 179
	4-CF ₃	2-Cl	4-Cl	125 to 126
	4-F	2-Cl	4-Cl	107 to 111
	4-CF ₃	4-F	4-SCH ₃	170 to 172.5
15	4-CF ₃	4-F	4-OCF ₂ H	
	4-CF ₃	4-Cl	4-OCF ₂ H	
	4-CF ₃	4-F	4-OCF ₃	
	4-CF ₃	4-Cl	4-OCF ₃	
	3,4-OCF ₂ CF ₂ O	4-F	4-CN	
20	4-CF ₃	3,4-OCF ₂ CF ₂ O	4-CN	
	4-CF ₃	4-F	3,4-OCF ₂ CF ₂ O	
	3,4-OCH ₂ O	4-F	4-CN	
	3,4-OCH ₂ CH ₂ O	4-F	4-CN	
	4-CF ₃	3,4-OCH ₂ O	4-CN	
25	4-N ₃	4-F	4-CN	
	4-SCN	4-F	4-CN	
	4-NHSO ₂ Me	4-F	4-CN	
	4-CF ₃	4-N ₃	4-CN	
	4-CF ₃	4-SCN	4-CN	
30	4-CF ₃	4-NHSO ₂ Me	4-CN	
	4-CF ₃	4-F	4-N ₃	
	4-CF ₃	4-F	4-SCN	
	4-CF ₃	4-F	4-NHSO ₂ Me	
	4-Cl	4-Cl	4-CH ₂ CN	143 to 145

35

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-CF ₃	4-iPr	4-Cl	194 to 195
	4-Cl	4-iPr	4-Cl	207 to 209
	4-OMe	4-iPr	4-Cl	162 to 163.5
10	4-Cl	4-Me	4-Cl	201.5 to 203.5
	4-OMe	4-Me	4-Cl	183 to 184.5
	4-iPr	4-Me	4-Cl	172 to 174
	4-NO ₂	4-iPr	4-Cl	242 to 244
	4-iPr	4-iPr	4-Cl	122 to 126
15	2,5-di-F	4-CN	4-F	149 to 150
	3,5-di-NO ₂	4-CN	4-F	132 to 134
	4-Et	4-CN	4-F	215 to 216
	3-CF ₃ , 4-F	4-CN	4-F	175 to 176
	4-OC ₆ H ₅	4-CN	4-F	226 to 227
20	4-tBu	4-CN	4-H	126 to 128.5
	4-Cl	4-CN	4-H	202 to 203
	4-CN	4-CN	4-H	218.5 to 220.5
	2,3,4-tri-Cl	4-CN	4-F	155 to 158
	3-CF ₃	4-CN	4-F	175 to 177
25	3-Cl	4-CN	4-F	189 to 190
	2-Cl	4-CN	4-F	194 to 196
	3-F	4-CN	4-F	184 to 185
	2-F	4-CN	4-F	172 to 173
	2,3,4-tri-Cl	4-CF ₃	4-OC ₆ H ₅	196 to 198
30	3-CF ₃ , 4-F	4-CF ₃	4-OC ₆ H ₅	161 to 163
	4-OC ₆ H ₅	4-CF ₃	4-OC ₆ H ₅	185 to 186
	4-CF ₃	4-CF ₃	4-OC ₆ H ₅	141 to 143
	3-CF ₃	4-CF ₃	4-OC ₆ H ₅	169 to 171
	4-CN	4-CF ₃	4-OC ₆ H ₅	157 to 160
35	3-CN	4-CF ₃	4-OC ₆ H ₅	178 to 180
	4-Cl	4-CF ₃	4-OC ₆ H ₅	150 to 152
	3-Cl	4-CF ₃	4-OC ₆ H ₅	179 to 180
	4-F	4-CF ₃	4-OC ₆ H ₅	140 to 142

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p.(°C)</u>
5	4-Cl	3-Cl	4-Cl	160 to 161
	3-Cl	3-Cl	4-Cl	173 to 175
	4-iPr	4-Cl	4-Cl	190 to 191
10	4-OCF ₂ CF ₂ H	4-Cl	4-Cl	172 to 173
	3-Cl,4-Cl	4-Cl	4-Cl	227 to 229
	2-F,4-Cl	4-Cl	4-Cl	184 to 185
	2,5-di-F	4-CN	4-Br	178 to 180
	3,5-di-NO ₂	4-CN	4-Br	259 to 264
15	2,4,4-tri-Cl	4-CN	4-Br	239 to 241
	4-Et	4-CN	4-Br	226 to 228
	3-CF ₃ ,4-F	4-CN	4-Br	171 to 172
	4-OC ₆ H ₅	4-CN	4-Br	216 to 217
	4-C ₆ H ₅	4-CN	4-Br	227 to 228
20	3-CF ₃	4-CN	4-Br	129 to 132
	2-CF ₃	4-CN	4-Br	175 to 180
	4-CN	4-CN	4-Br	150 to 151
	3-CN	4-CN	4-Br	210 to 212
	2-CN	4-CN	4-Br	237 to 239
25	3-Cl	4-CN	4-Br	180 to 182
	2-Cl	4-CN	4-Br	224 to 226
	4-F	4-CN	4-Br	208 to 209
	3-F	4-CN	4-Br	202 to 203
	2-F	4-CN	4-Br	191 to 192
30	3-CF ₃	4-CF ₃	4-F	123 to 129
	4-CN	4-CF ₃	4-F	253 to 254
	3-CN	4-CF ₃	4-F	161 to 171
	4-F	4-CF ₃	4-F	168 to 176
	3-F	4-CF ₃	4-F	148 to 153
35	3-Cl	4-Cl	4-OMe	167 to 169
	3-CF ₃	4-Cl	4-OMe	179 to 180
	3-CF ₃ ,4-F	4-Cl	4-OMe	135 to 136

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-F	4-Cl	4-OMe	158 to 159
	4-CN	4-Cl	4-OMe	222 to 224
	3-CN	4-Cl	4-OMe	205 to 208
	4-C ₆ H ₅	4-Cl	4-Cl	200.5 to 203
	4-O-s-Bu	4-Cl	4-Cl	176.5 to 178
10	3,4-OCH ₂ O-	4-Cl	4-Cl	221.5 to 223
	3,5-di-F	4-Cl	4-Cl	200.5 to 202
	2,3,4-tri-Cl	4-CF ₃	3-CN	243 to 246
	3-CF ₃ , 4-F	4-CF ₃	3-CN	195 to 197
	4-OC ₆ H ₅	4-CF ₃	3-CN	209 to 211
15	3-CF ₃	4-CF ₃	3-CN	179 to 180
	4-CN	4-CF ₃	3-CN	182 to 184
	3-CN	4-CF ₃	3-CN	182 to 184
	3-Cl	4-CF ₃	3-CN	215 to 216
	4-F	4-CF ₃	3-CN	175 to 177
20	4-CF ₃	4-OCF ₂ CF ₂ H	4-Cl	198 to 199
	4-Cl	4-OCF ₂ CF ₂ H	4-Cl	186 to 187
	4-OCF ₂ CF ₂ H	4-OCF ₂ CF ₂ H	4-Cl	137 to 138
	4-iPr	4-OCF ₂ CF ₂ H	4-Cl	126 to 122.5
	4-CF ₃	4-OCF ₂ CF ₂ H	4-H	166 to 168.5
25	4-Br	4-OCF ₂ CF ₂ H	4-H	183.5 to 185
	4-CF ₃	2-Me, 4-Cl	4-Cl	151 to 152
	3-CF ₃	2-Me, 4-Cl	4-Cl	98 to 101
	4-CN	2-Me, 4-Cl	4-Cl	163 to 169
	3-CN	2-Me, 4-Cl	4-Cl	177 to 178
30	4-Cl	2-Me, 4-Cl	4-Cl	152 to 153
	3-Cl	2-Me, 4-Cl	4-Cl	111 to 113
	4-F	2-Me, 4-Cl	4-Cl	142 to 148
	3-CF ₃ , 4-F	2-Me, 4-Cl	4-Cl	121 to 123
	2-Me, 4-Cl	2-Me, 4-Cl	4-Cl	105 to 109
35	3-Cl, 4-F	2-Me, 4-Cl	4-Cl	125 to 128

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-CN	4-CF ₃	4-H	219 to 221
	2-CN	4-CF ₃	4-H	187 to 188
	3-Cl	4-CF ₃	4-H	157 to 159
10	2-Cl	4-CF ₃	4-H	210 to 212
	4-F	4-CF ₃	4-H	170 to 172
	2-F	4-CF ₃	4-H	178 to 179
	3-CF ₃	4-F	4-H	151 to 152
	4-CN	4-F	4-H	204 to 206
15	3-CN	4-F	4-H	195 to 196
	3-Cl	4-F	4-H	170 to 172
	3-F	4-F	4-H	143 to 144
	3-CF ₃ , 4-F	4-F	4-H	178 to 180
	3-Cl, 4-F	4-F	4-H	187 to 189
20	4-NHCOMe	4-F	4-Cl	278 to 280
	4-OEt	4-F	4-Cl	199 to 200.5
	4-C ₆ H ₅	4-F	4-Cl	188 to 191
	3-Cl, 4-Br	4-F	4-Cl	211 to 212.5
	2,4-di-F	4-F	4-Cl	137 to 140
25	4-OMe	4-CN	4-OMe	190 to 191
	4-t-Bu	4-CN	4-OMe	127 to 129
	4-NO ₂	4-CN	4-OMe	230 to 232
	4-CN	4-CN	4-OMe	221 to 223
	4-Cl	4-CN	4-OMe	194 to 196
30	4-CF ₃	4-CN	4-OMe	189 to 191
	4-CF ₃	4-CF ₃	4-C ₆ H ₅	183 to 184
	4-CN	4-CF ₃	4-C ₆ H ₅	229 to 231
	4-Cl	4-CF ₃	4-C ₆ H ₅	224 to 226
	4-F	4-CF ₃	4-C ₆ H ₅	206 to 208
35	4-t-Bu	4-CF ₃	4-C ₆ H ₅	206 to 208
	3-F, 4-CF ₃	4-CF ₃	4-C ₆ H ₅	166 to 167
	2-OMe	4-Cl	2 Cl	158 to 160

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p.(°C)</u>
5	3-OMe	4-Cl	2-Cl	168 to 169
	4-OMe	4-Cl	2-Cl	153 to 155
10	2-Cl	4-Cl	2-Cl	182 to 184
	3-Cl	4-Cl	2-Cl	197 to 198
	4-CF ₃	4-CF ₃	4-CONEt ₂	195 to 196
	4-CN	4-CF ₃	4-CONEt ₂	238 to 241
	4-Cl	4-CF ₃	4-CONEt ₂	219 to 223
	4-F	4-CF ₃	4-CONEt ₂	163 to 165
15	4-CF ₃	4-CO ₂ Me	4-F	172 to 176
	4-CN	4-CO ₂ Me	4-F	193 to 195
	4-Cl	4-CO ₂ Me	4-F	191 to 193
	4-F	4-CO ₂ Me	4-F	188 to 189
20	4-CF ₃	4-CO ₂ Me	4-Cl	237 to 238
	4-CN	4-CO ₂ Me	4-Cl	261 to 263
	4-Cl	4-CO ₂ Me	4-Cl	216 to 218
	4-t-Bu	4-CO ₂ Me	4-Cl	183 to 185
	2-CN	4-Cl	2-Cl	186 to 187
	3-CN	4-Cl	2-Cl	200 to 202
25	4-CN	4-Cl	2-Cl	232 to 234
	4-Cl	4-Cl	2-Cl	190 to 192
	4-t-Bu	4-Cl	2-Cl	195 to 197
	4-CH ₂ C ₆ H ₅	4-Cl	2-Cl	154 to 157
	4-F	4-Cl	2-Cl	148 to 150
30	4-CF ₃	4-Cl	2-Cl	189 to 190
	3-OMe	2-Cl	4-F	128 to 130
	4-OMe	2-Cl	4-F	154 to 155
	4-Cl	2-Cl	4-F	165 to 166
	3-SO ₂ NH ₂	2-Cl	4-F	98 to 101
35	4-SO ₂ NH ₂	2-Cl	4-F	195 to 197
	3-CN	2-Cl	4-F	153 to 154
	4-CN	2-Cl	4-F	160 to 163

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-t-Bu	2-Cl	4-F	92 to 94
	2-OMe	3-Cl	4-F	153 to 155
	3-OMe	3-Cl	4-F	146 to 147
10	4-OMe	3-Cl	4-F	200 to 201
	2-Cl	3-Cl	4-F	137 to 139
	3-Cl	3-Cl	4-F	151 to 152
	4-Cl	3-Cl	4-F	192 to 194
	4-SO ₂ NH ₂	3-Cl	4-F	273 to 278
15	2-CN	3-Cl	4-F	153 to 155
	3-CN	3-Cl	4-F	195 to 196
	4-CN	3-Cl	4-F	219 to 220
	4-t-Bu	3-Cl	4-F	176 to 177
	4-CH ₂ C ₆ H ₅	3-Cl	4-F	159 to 163
20	4-CF ₃	4-t-Bu	4-C ₆ H ₅	202 to 204
	4-Cl	4-t-Bu	4-C ₆ H ₅	solid (b)
	4-Cl	4-t-Bu	4-t-Bu	164 to 166
	4-CF ₃	4-t-Bu	4-t-Bu	161 to 164
	4-NO ₂	4-t-Bu	4-t-Bu	202 to 205
25	4-CN	4-t-Bu	4-t-Bu	234 to 237
	4-OMe	4-t-Bu	4-t-Bu	194 to 196
	4-OMe	4-CN	4-CN	209 to 211
	3,4,5-tri-Cl	4-Cl	4-F	190 to 192
	4-SCH ₃	4-Cl	4-F	183 to 185
30	4-CO ₂ Et	4-Cl	4-F	183 to 184
	4-CF ₃	3,4-di-Cl	4-F	241 to 243
	4-OCF ₃	3,4-di-Cl	4-F	219 to 221
	4-C ₆ H ₅	3,4-di-Cl	4-F	193 to 194
	4-SO ₂ NH ₂	3,4-di-Cl	4-F	261 to 264
35	4-OEt	3,4-di-Cl	4-F	226 to 227
	4-CF ₃	4-CF ₃	4-COCF ₃	164 to 166
	4-CN	4-CF ₃	4-COCF ₃	110 to 113

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-Cl	4-CF ₃	4-COCF ₃	122 to 125
	4-F	4-CF ₃	4-COCF ₃	74 to 76
	4-t-Bu	4-CF ₃	4-COCF ₃	95 to 98
10	4-CO ₂ Me	4-CF ₃	4-COCF ₃	104 to 108
	4-SO ₂ NH ₂	4-Cl	2-Cl	276 to 283
	4-F	3-Cl	4-F	167 to 168
	4-CF ₃	3-Cl	4-F	181 to 183
	3-SO ₂ NH ₂	4-Cl	2-Cl	186 to 189
15	3-OMe	2-Cl	4-F	101 to 105
	4-OMe	2-Cl	4-F	101 to 105
	2-SO ₂ NH ₂	4-Cl	2-Cl	242 to 246
	3-OMe	2-CN	4-F	167 to 168
	4-OMe	2-CN	4-F	202 to 205
20	2-Cl	2-CN	4-F	141 to 142
	3-Cl	2-CN	4-F	173 to 174
	4-Cl	2-CN	4-F	181 to 182
	3-SO ₂ NH ₂	2-CN	4-F	149 to 153
	4-SO ₂ NH ₂	2-CN	4-F	170 to 174
25	2-CN	2-CN	4-F	159 to 161
	3-CN	2-CN	4-F	184 to 186
	4-CN	2-CN	4-F	258 to 259
	4-t-Bu	2-CN	4-F	206 to 207
	4-CF ₃	2-CN	4-F	206 to 207
30	2-OMe	4-Cl	3-Cl	131 to 133
	3-OMe	4-Cl	3-Cl	149 to 150
	4-OMe	4-Cl	3-Cl	201 to 202
	2-Cl	4-Cl	3-Cl	171 to 173
	3-Cl	4-Cl	3-Cl	143 to 146
35	2-SO ₂ NH ₂	4-Cl	3-Cl	205 to 207
	4-SO ₂ NH ₂	4-Cl	3-Cl	275 to 280
	2-CN	4-Cl	3-Cl	146 to 149

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₃</u>	<u>m.p. (°C)</u>
5	3-CN	4-Cl	3-Cl	155 to 157
	4-t-Bu	4-Cl	3-Cl	106 to 107
10	4-CH ₂ C ₆ H ₅	4-Cl	3-Cl	119 to 125
	4-CN	4-Cl	3-Cl	179 to 185
	4-CO ₂ -n-Pr	4-Cl	3-Cl	166 to 168
	3,5-di-Cl	4-Cl	3-Cl	184 to 187
	4-CO ₂ -n-Pr	4-Cl	4-F	183.5 to 184.5
15	4-CF ₃	4-CF ₃	4-CO ₂ H	261 to 265
	4-CN	4-CF ₃	4-CO ₂ H	137 to 141
	4-Cl	4-CF ₃	4-CO ₂ H	228 to 230
	4-F	4-CF ₃	4-CO ₂ H	154 to 160
	4-t-Bu	4-CF ₃	4-CO ₂ H	146 to 153
20	4-CF ₃	4-CF ₃	4-C ₂ H ₅	131 to 133
	4-CF ₃	4-NH ₂	4-F	195 to 197
	3-SO ₂ NH ₂	4-Cl	3-Cl	130 to 138
	4-CN	2-OMe	4-F	173 to 176
	2-CH ₂ C ₆ H ₅	2-OMe	4-F	117 to 121
25	4-CF ₃	2-OMe	4-F	154 to 159
	2-OMe	2-OMe	4-F	107 to 111
	4-OMe	2-OMe	4-F	109 to 111
	2-Cl	2-OMe	4-F	90 to 97
	4-Cl	2-OMe	4-F	105 to 157
30	4-SO ₂ NH ₂	2-OMe	4-F	141 to 144
	2-CN	2-OMe	4-F	179 to 181
	3-OMe	2-OMe	4-F	oil (c)
	3-Cl	2-OMe	4-F	oil (d)
	3-OMe	4-Cl	2-OMe	112 to 114
35	4-t-Bu	2-OMe	4-F	76 to 83
	3-CN	2-OMe	4-F	80 to 81
	4-OMe	4-Cl	2-OMe	149 to 153
	2-Cl	4-Cl	2-OMe	130 to 132

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	3-Cl	4-Cl	2-OMe	139 to 141
	4-Cl	4-Cl	2-OMe	155 to 157
	2-SO ₂ NH ₂	4-Cl	2-OMe	123 to 127
10	4-SO ₂ NH ₂	4-Cl	2-OMe	248 to 256
	2-OMe	4-Cl	2-OMe	124 to 126
	2-CN	4-Cl	2-OMe	163 to 165
	3-CN	4-Cl	2-OMe	154 to 160
	4-CN	4-Cl	2-OMe	153 to 159
15	2-CH ₂ C ₆ H ₅	4-Cl	2-OMe	148 to 150
	4-CF ₃	4-Cl	2-OMe	172 to 173
	3-SO ₂ NH ₂	4-Cl	2-OMe	118 to 123
	4-t-Bu	4-Cl	2-OMe	87 to 92
	2-SO ₂ NH ₂	3-Cl	4-F	114 to 121
20	3-SO ₂ NH ₂	3-Cl	4-F	118 to 123
	2-SO ₂ NH ₂	2-OMe	4-F	oil (e)
	3-SO ₂ NH ₂	2-OMe	4-F	oil (f)
	4-OMe	2-CH ₂ C ₆ H ₅	4-F	153 to 154
	4-Br	4-F	3,4-di-F	175.5 to 177.5
25	4-CN	4-CN	4-CN	173 to 176
	4-t-Bu	4-CN	4-CN	143 to 142
	4-OMe	4-Cl	4-OMe	174 to 175
	4-NO ₂	4-Cl	4-OMe	238 to 239
	4-Br	4-OCF ₃	4-F	187.5 to 189
30	4-OCF ₂ CF ₂ H	4-Cl	3,4-di-F	145 to 146
	3,4,5-tri-Cl	4-Cl	4-Cl	>250°
	4-CN	2-CH ₂ C ₆ H ₅	4-F	156 to 161
	4-t-Bu	2-CH ₂ C ₆ H ₅	4-F	182 to 184
	4-CF ₃	2-CH ₂ C ₆ H ₅	4-F	85 to 87
35	4-CF ₃	3,4-di-F	4-F	193.5 to 195
	4-OCF ₃	3,4-di-F	4-F	205 to 206
	4-SMe	3,4-di-F	4-F	208.5 to 210

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-Br	3,4-di-F	4-F	195 to 196
	4-SO ₂ NH ₂	3,4-di-F	4-F	>250°
	4-C ₆ H ₅	3,4-di-F	4-F	>140°
10	4-Cl	3,4-di-F	4-F	172 to 174
	4-OEt	3,4-di-F	4-F	220.5 to 221.5
	4-F	4-Cl	4-NO ₂	167 to 176
	4-Cl	4-Cl	4-t-Bu	195 to 197
	4-OMe	4-Cl	4-t-Bu	173 to 175
15	4-CN	4-Cl	4-t-Bu	151 to 155
	4-CF ₃	4-Cl	4-t-Bu	150 to 153
	4-t-Bu	4-Cl	4-t-Bu	201 to 202
	4-NO ₂	4-Cl	4-t-Bu	246 to 252
	4-Cl	4-Cl	4-C ₆ H ₅	211 to 213
20	4-OMe	4-Cl	4-C ₆ H ₅	206 to 208
	4-CN	4-Cl	4-C ₆ H ₅	220 to 222
	4-CF ₃	4-Cl	4-C ₆ H ₅	195 to 197
	4-t-Bu	4-Cl	4-C ₆ H ₅	211 to 213
	4-NO ₂	4-Cl	4-C ₆ H ₅	220 to 225
25	4-CN	4-CF ₃	4-Br	255 to 257
	4-Cl	4-CF ₃	4-Br	206 to 207
	4-F	4-CF ₃	4-Br	209 to 210
	4-NO ₂	4-CF ₃	4-Br	239 to 242
	4-CN	4-F	4-CO ₂ Me	164 to 168
30	4-F	4-F	4-CO ₂ Me	164 to 167
	4-t-Bu	4-F	4-CO ₂ Me	198 to 202
	3-CF ₃ , 4-F	4-F	4-CO ₂ Me	113 to 118
	4-CN	4-CF ₃	4-CO ₂ Me	191 to 192
	4-F	4-CF ₃	4-CO ₂ Me	156 to 157
35	4-CO ₂ Me	4-CF ₃	4-CO ₂ Me	170 to 172
	4-CF ₃	4-NO ₂	4-Cl	240 to 242

Table 1 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
5	4-CF ₃	4-CF ₃	4-CONH(p-C ₆ H ₄ -CF ₃)	>275
	4-Cl	4-CF ₃	4-CONH(p-C ₆ H ₄ -Cl)	276 to 279
	4-F	4-Cl	4-CO ₂ Me	195 to 197
10	4-CF ₃	4-NH ₂	4-Cl	155 to 160
	4-C ₆ H ₄ S(p-C ₆ H ₄ Cl)	3-CN	4-F	205 to 209
	2-CN, 2-CF ₃	3-CN	4-F	210 to 215
	2-OCH ₃	3-OCH ₃	4-F	75 to 78
	3-OCH ₃	3-OCH ₃	4-F	87 to 90
15	4-OCH ₃	3-OCH ₃	4-F	174 to 176
	2-Cl	3-OCH ₃	4-F	143 to 145
	3-Cl	3-OCH ₃	4-F	141 to 143
	4-Cl	3-OCH ₃	4-F	163 to 165
	2-SO ₂ NH ₂	3-OCH ₃	4-F	100 to 105
20	3-SO ₂ NH ₂	3-OCH ₃	4-F	105 to 110
	4-SO ₂ NH ₂	3-OCH ₃	4-F	255 to 257
	2-CN	3-OCH ₃	4-F	
	4-t-Bu	3-OCH ₃	4-F	136 to 138
	2-CH ₂ C ₆ H ₅	3-OCH ₃	4-F	149 to 150
25	4-CF ₃	3-OCH ₃	4-F	166 to 170
	4-OCH ₃	4-Cl	3-CN	107 to 109
	3-Cl	4-Cl	3-CN	96 to 99
	4-Cl	4-Cl	3-CN	102 to 105
	2-SO ₂ NH ₂	4-Cl	3-CN	134 to 138
30	3-SO ₂ NH ₂	4-Cl	3-CN	135 to 142
	4-SO ₂ NH ₂	4-Cl	3-CN	229 to 231
	4-CN	4-Cl	3-CN	195 to 198
	4-t-Bu	4-Cl	3-CN	122 to 126
	4-CF ₃	4-Cl	3-CN	188 to 190
35	4-CN	3-OCH ₃	4-F	127 to 135
	2-OCH ₃	4-Cl	2-CN	196 to 198
	2-Cl	4-Cl	2-CN	201 to 202

Table 1 (continued)

5	<u>R₁</u>	<u>R₂</u>	<u>R₅</u>	<u>m.p. (°C)</u>
	3-Cl	4-Cl	2-CN	198 to 200
	4-Cl	4-Cl	2-CN	150 to 153
	2-SO ₂ NH ₂	4-Cl	2-CN	181 to 185
10	3-SO ₂ NH ₂	4-Cl	2-CN	125 to 130
	4-SO ₂ NH ₂	4-Cl	2-CN	258 to 260
	2-CN	4-Cl	2-CN	190 to 192
	3-CN	4-Cl	2-CN	186 to 189
	4-CN	4-Cl	2-CN	237 to 241
15	4-t-Bu	4-Cl	2-CN	203 to 205
	2-CH ₂ C ₆ H ₅	4-Cl	2-CN	186 to 188
	4-CF ₃	4-Cl	2-CN	194 to 196
	4-F	4-Cl	2-CN	200 to 202
	4-Br	4-OCHF ₂	4-F	181 to 182.5
20	H ¹ NMR spectra (δ):			
		(a)	8.55(NH)	
		(b)	8.5 (NH)	
		(c)	8.50(NH)	
		(d)	8.55(NH)	
		(e)	10.35(NH)	
		(f)	8.75(NH)	

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Table 2

	<u>R₁</u>	<u>R₂</u>	<u>W</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-CF ₃	4-F	4-CN	CH ₃	H	
	4-CF ₃	4-F	4-CN	CH ₂ CH ₃	H	
	4-CF ₃	4-F	4-CN	CO ₂ CH ₃	H	
10	4-CF ₃	4-F	4-CN	CO ₂ CH ₂ CH ₃	H	
	4-CF ₃	4-F	4-CN	COCH ₃	H	
	4-CF ₃	4-F	4-CN	COCF ₃	H	
	4-CF ₃	4-F	4-Cl	CH ₃	H	
	4-CF ₃	4-F	4-CF ₃	CH ₃	H	
15	4-CF ₃	4-F	4-F	CH ₃	H	
	4-CF ₃	4-F	3,4-di-F	CH ₃	H	
	4-CF ₃	4-F	3-Cl	CH ₃	H	
	4-CF ₃	4-F	4-CO ₂ Me	CH ₃	H	
	4-CF ₃	4-F	3-CN	CH ₃	H	
20	4-CF ₃	4-Cl	4-Cl	CH ₃	H	205 to 206
	4-CF ₃	4-Cl	4-F	CH ₃	H	195 to 197
	4-CF ₃	4-Cl	4-CF ₃	CH ₃	H	
	4-CF ₃	4-Cl	3,4-di-F	CH ₃	H	
	4-CF ₃	4-Cl	3-Cl	CH ₃	H	
25	4-CF ₃	4-Cl	4-CO ₂ Me	CH ₃	H	
	4-CF ₃	4-Cl	3-CN	CH ₃	H	
	4-CF ₃	4-CF ₃	4-Cl	CH ₃	H	136 to 139
	4-CF ₃	4-CF ₃	4-F	CH ₃	H	149 to 150

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Table 2 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>W</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-CF ₃	4-CF ₃	4-CF ₃	CH ₃	H	
	4-CF ₃	4-CF ₃	3,4-di-F	CH ₃	H	
	4-CF ₃	4-CF ₃	3-Cl	CH ₃	H	
	4-CF ₃	4-CF ₃	4-CO ₂ Me	CH ₃	H	
	4-CF ₃	4-CF ₃	3-CN	CH ₃	H	
10	4-CF ₃	4-OCF ₃	4-Cl	CH ₃	H	136 to 139
	4-CF ₃	4-OCF ₃	4-F	CH ₃	H	149 to 150
	4-CF ₃	4-OCF ₃	4-CF ₃	CH ₃	H	
	4-CF ₃	4-OCF ₃	4-CO ₂ Me	CH ₃	H	
	4-CF ₃	4-OCF ₃	3-Cl	CH ₃	H	
15	4-CF ₃	4-OCF ₃	3,4-di-F	CH ₃	H	
	4-CF ₃	4-OCF ₃	4-CN	CH ₃	H	
	4-CF ₃	4-OCF ₃	3-CN	CH ₃	H	
	4-CF ₃	4-OCF ₂ H	4-Cl	CH ₃	H	
	4-CF ₃	4-OCF ₂ H	4-F	CH ₃	H	
20	4-CF ₃	4-OCF ₂ H	4-CF ₃	CH ₃	H	
	4-CF ₃	4-OCF ₂ H	4-CO ₂ Me	CH ₃	H	
	4-CF ₃	4-OCF ₂ H	3-Cl	CH ₃	H	
	4-CF ₃	4-OCF ₂ H	3,4-di-F	CH ₃	H	
	4-CF ₃	4-OCF ₂ H	4-CN	CH ₃	H	
25	4-CF ₃	4-OCF ₂ H	3-CN	CH ₃	H	
	4-CF ₃	4-CN	4-Cl	CH ₃	H	
	4-CF ₃	4-CN	4-F	CH ₃	H	
	4-CF ₃	4-CN	4-CF ₃	CH ₃	H	
	4-CF ₃	4-CN	4-CO ₂ Me	CH ₃	H	
30	4-CF ₃	4-CN	3-Cl	CH ₃	H	
	4-CF ₃	4-CN	3,4-di-F	CH ₃	H	
	4-CF ₃	4-CN	4-CN	CH ₃	H	
	4-CF ₃	4-CN	3-CN	CH ₃	H	
	4-CF ₃	4-H	4-Cl	CH ₃	H	
35	4-CF ₃	4-H	4-F	CH ₃	H	

Table 2 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>W</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-CF ₃	4-H	4-CF ₃	CH ₃	H	
	4-CF ₃	4-H	4-CO ₂ Me	CH ₃	H	
	4-CF ₃	4-H	3-Cl	CH ₃	H	
	4-CF ₃	4-H	3,4-di-F	CH ₃	H	
	4-CF ₃	4-H	4-CN	CH ₃	H	
10	4-CF ₃	4-H	3-CN	CH ₃	H	
	4-CF ₃	4-Br	4-Cl	CH ₃	H	
	4-CF ₃	4-Br	4-F	CH ₃	H	
	4-CF ₃	4-Br	4-CF ₃	CH ₃	H	
	4-CF ₃	4-Br	4-CO ₂ Me	CH ₃	H	
15	4-CF ₃	4-Br	3-Cl	CH ₃	H	
	4-CF ₃	4-Br	3,4-di-F	CH ₃	H	
	4-CF ₃	4-Br	4-CN	CH ₃	H	
	4-OCF ₃	4-F	4-Cl	CH ₃	H	
	4-OCF ₃	4-F	4-OCF ₃	CH ₃	H	
20	4-OCF ₃	4-F	4-F	CH ₃	H	
	4-OCF ₃	4-F	3,4-di-F	CH ₃	H	
	4-OCF ₃	4-F	3-Cl	CH ₃	H	
	4-OCF ₃	4-F	4-CO ₂ Me	CH ₃	H	
	4-OCF ₃	4-F	3-CN	CH ₃	H	
25	4-OCF ₃	4-Cl	4-Cl	CH ₃	H	
	4-OCF ₃	4-Cl	4-F	CH ₃	H	
	4-OCF ₃	4-Cl	4-CF ₃	CH ₃	H	
	4-OCF ₃	4-Cl	3,4-di-F	CH ₃	H	
	4-OCF ₃	4-Cl	3-Cl	CH ₃	H	
30	4-OCF ₃	4-Cl	4-CO ₂ Me	CH ₃	H	
	4-OCF ₃	4-Cl	3-CN	CH ₃	H	
	4-OCF ₃	4-CF ₃	4-Cl	CH ₃	H	
	4-OCF ₃	4-CF ₃	4-F	CH ₃	H	
	4-OCF ₃	4-CF ₃	4-CF ₃	CH ₃	H	
35	4-OCF ₃	4-CF ₃	3,4-di-F	CH ₃	H	

Table 2 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>W</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-OCF ₃	4-CF ₃	3-Cl	CH ₃	H	
	4-OCF ₃	4-CF ₃	4-CO ₂ Me	CH ₃	H	
	4-OCF ₃	4-CF ₃	3-CN	CH ₃	H	
	4-OCF ₃	4-OCF ₃	4-Cl	CH ₃	H	
	4-OCF ₃	4-OCF ₃	4-F	CH ₃	H	
10	4-OCF ₃	4-OCF ₃	4-CF ₃	CH ₃	H	
	4-OCF ₃	4-OCF ₃	4-CO ₂ Me	CH ₃	H	
	4-OCF ₃	4-OCF ₃	3-Cl	CH ₃	H	
	4-OCF ₃	4-OCF ₃	3,4-di-F	CH ₃	H	
	4-OCF ₃	4-OCF ₃	4-CN	CH ₃	H	
15	4-OCF ₃	4-OCF ₃	3-CN	CH ₃	H	
	4-OCF ₃	4-OCF ₂ H	4-Cl	CH ₃	H	
	4-OCF ₃	4-OCF ₂ H	4-F	CH ₃	H	
	4-OCF ₃	4-OCF ₂ H	4-CF ₃	CH ₃	H	
	4-OCF ₃	4-OCF ₂ H	4-CO ₂ Me	CH ₃	H	
20	4-OCF ₃	4-OCF ₂ H	3-Cl	CH ₃	H	
	4-OCF ₃	4-OCF ₂ H	3,4-di-F	CH ₃	H	
	4-OCF ₃	4-OCF ₂ H	4-CN	CH ₃	H	
	4-OCF ₃	4-OCF ₂ H	3-CN	CH ₃	H	
	4-OCF ₃	4-CN	4-Cl	CH ₃	H	
25	4-OCF ₃	4-CN	4-F	CH ₃	H	
	4-OCF ₃	4-CN	4-CF ₃	CH ₃	H	
	4-OCF ₃	4-CN	4-CO ₂ Me	CH ₃	H	
	4-OCF ₃	4-CN	3-Cl	CH ₃	H	
	4-OCF ₃	4-CN	3,4-di-F	CH ₃	H	
30	4-OCF ₃	4-CN	4-CN	CH ₃	H	
	4-OCF ₃	4-CN	3-CN	CH ₃	H	
	4-OCF ₃	4-H	4-Cl	CH ₃	H	
	4-OCF ₃	4-H	4-F	CH ₃	H	
	4-OCF ₃	4-H	4-CF ₃	CH ₃	H	
35	4-OCF ₃	4-H	4-CO ₂ Me	CH ₃	H	

Table 2 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>W</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-OCF ₃	4-H	3-Cl	CH ₃	H	
	4-OCF ₃	4-H	3,4-di-F	CH ₃	H	
	4-OCF ₃	4-H	4-CN	CH ₃	H	
	4-OCF ₃	4-H	3-CN	CH ₃	H	
	4-OCF ₃	4-Br	4-Cl	CH ₃	H	
10	4-OCF ₃	4-Br	4-F	CH ₃	H	
	4-OCF ₃	4-Br	4-CF ₃	CH ₃	H	
	4-OCF ₃	4-Br	4-CO ₂ Me	CH ₃	H	
	4-OCF ₃	4-Br	3-Cl	CH ₃	H	
	4-OCF ₃	4-Br	3,4-di-F	CH ₃	H	
15	4-OCF ₃	4-Br	4-CN	CH ₃	H	
	4-Cl	4-F	4-Cl	CH ₃	H	195 to 197.5
	4-Cl	4-F	4-CF ₃	CH ₃	H	
	4-Cl	4-F	4-F	CH ₃	H	
	4-Cl	4-F	3,4-di-F	CH ₃	H	
20	4-Cl	4-F	3-Cl	CH ₃	H	
	4-Cl	4-F	4-CO ₂ Me	CH ₃	H	
	4-Cl	4-F	3-CN	CH ₃	H	
	4-Cl	4-Cl	4-Cl	CH ₃	H	189 to 190
	4-Cl	4-Cl	4-F	CH ₃	H	
25	4-Cl	4-Cl	4-CF ₃	CH ₃	H	
	4-Cl	4-Cl	3,4-di-F	CH ₃	H	
	4-Cl	4-Cl	3-Cl	CH ₃	H	
	4-Cl	4-Cl	4-CO ₂ Me	CH ₃	H	
	4-Cl	4-Cl	3-CN	CH ₃	H	
30	4-Cl	4-CF ₃	4-Cl	CH ₃	H	132 to 134
	4-Cl	4-CF ₃	4-F	CH ₃	H	108 to 111
	4-Cl	4-CF ₃	4-CF ₃	CH ₃	H	
	4-Cl	4-CF ₃	3,4-di-F	CH ₃	H	
	4-Cl	4-CF ₃	3-Cl	CH ₃	H	
35	4-Cl	4-CF ₃	4-CO ₂ Me	CH ₃	H	

Table 2 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>W</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-Cl	4-CF ₃	3-CN	CH ₃	H	
	4-Cl	4-OCF ₃	4-Cl	CH ₃	H	
	4-Cl	4-OCF ₃	4-F	CH ₃	H	
	4-Cl	4-OCF ₃	4-CF ₃	CH ₃	H	
	4-Cl	4-OCF ₃	3,4-di-F	CH ₃	H	
10	4-Cl	4-OCF ₃	3-Cl	CH ₃	H	
	4-Cl	4-OCF ₃	4-CO ₂ Me	CH ₃	H	
	4-Cl	4-OCF ₃	3-CN	CH ₃	H	
	4-Cl	4-OCF ₂ H	4-Cl	CH ₃	H	
	4-Cl	4-OCF ₂ H	4-F	CH ₃	H	
15	4-Cl	4-OCF ₂ H	4-CF ₃	CH ₃	H	
	4-Cl	4-OCF ₂ H	4-CO ₂ Me	CH ₃	H	
	4-Cl	4-OCF ₂ H	3-Cl	CH ₃	H	
	4-Cl	4-OCF ₂ H	3,4-di-F	CH ₃	H	
	4-Cl	4-OCF ₂ H	4-CN	CH ₃	H	
20	4-Cl	4-OCF ₂ H	3-CN	CH ₃	H	
	4-Cl	4-CN	4-Cl	CH ₃	H	
	4-Cl	4-CN	4-F	CH ₃	H	
	4-Cl	4-CN	4-CF ₃	CH ₃	H	
	4-Cl	4-CN	4-CO ₂ Me	CH ₃	H	
25	4-Cl	4-CN	3-Cl	CH ₃	H	
	4-Cl	4-CN	3,4-di-F	CH ₃	H	
	4-Cl	4-CN	4-CN	CH ₃	H	
	4-Cl	4-CN	3-CN	CH ₃	H	
	4-Cl	4-H	4-Cl	CH ₃	H	
30	4-Cl	4-H	4-F	CH ₃	H	
	4-Cl	4-H	4-CF ₃	CH ₃	H	
	4-Cl	4-H	4-CO ₂ Me	CH ₃	H	
	4-Cl	4-H	3-Cl	CH ₃	H	
	4-Cl	4-H	3,4-di-F	CH ₃	H	
35	4-Cl	4-H	4-CN	CH ₃	H	

Table 2 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>W</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
	4-Cl	4-H	3-CN	CH ₃	H	
5	4-Cl	4-Br	4-Cl	CH ₃	H	
	4-Cl	4-Br	4-F	CH ₃	H	
	4-Cl	4-Br	4-CF ₃	CH ₃	H	
	4-Cl	4-Br	4-CO ₂ Me	CH ₃	H	
	4-Cl	4-Br	3-Cl	CH ₃	H	
10	4-Cl	4-Br	3,4-di-F	CH ₃	H	
	4-Cl	4-Br	4-CN	CH ₃	H	
	4-Cl	4-Br	3-CN	CH ₃	H	
	4-Br	4-F	4-Cl	CH ₃	H	
	4-Br	4-F	4-CF ₃	CH ₃	H	
15	4-Br	4-F	4-F	CH ₃	H	
	4-Br	4-F	3,4-di-F	CH ₃	H	
	4-Br	4-F	3-Cl	CH ₃	H	
	4-Br	4-F	4-CO ₂ Me	CH ₃	H	
	4-Br	4-F	3-CN	CH ₃	H	
20	4-Br	4-Cl	4-Cl	CH ₃	H	
	4-Br	4-Cl	4-F	CH ₃	H	
	4-Br	4-Cl	4-CF ₃	CH ₃	H	
	4-Br	4-Cl	3,4-di-F	CH ₃	H	
	4-Br	4-Cl	3-Cl	CH ₃	H	
25	4-Br	4-Cl	4-CO ₂ Me	CH ₃	H	
	4-Br	4-Cl	3-CN	CH ₃	H	
	4-Br	4-CF ₃	4-Cl	CH ₃	H	
	4-Br	4-CF ₃	4-F	CH ₃	H	
	4-Br	4-CF ₃	4-CF ₃	CH ₃	H	
30	4-Br	4-CF ₃	3,4-di-F	CH ₃	H	
	4-Br	4-CF ₃	3-Cl	CH ₃	H	
	4-Br	4-CF ₃	4-CO ₂ Me	CH ₃	H	
	4-Br	4-CF ₃	3-CN	CH ₃	H	
	4-Br	4-OCF ₃	4-Cl	CH ₃	H	
35						

Table 2 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>W</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-Br	4-OCF ₃	4-F	CH ₃	H	
	4-Br	4-OCF ₃	4-CF ₃	CH ₃	H	
	4-Br	4-OCF ₃	4-CO ₂ Me	CH ₃	H	
	4-Br	4-OCF ₃	3-Cl	CH ₃	H	
	4-Br	4-OCF ₃	3,4-di-F	CH ₃	H	
10	4-Br	4-OCF ₃	4-CN	CH ₃	H	
	4-Br	4-OCF ₃	3-CN	CH ₃	H	
	4-Br	4-OCF ₂ H	4-Cl	CH ₃	H	
	4-Br	4-OCF ₂ H	4-F	CH ₃	H	
	4-Br	4-OCF ₂ H	4-CF ₃	CH ₃	H	
15	4-Br	4-OCF ₂ H	4-CO ₂ Me	CH ₃	H	
	4-Br	4-OCF ₂ H	3-Cl	CH ₃	H	
	4-Br	4-OCF ₂ H	3,4-di-F	CH ₃	H	
	4-Br	4-OCF ₂ H	4-CN	CH ₃	H	
	4-Br	4-OCF ₂ H	3-CN	CH ₃	H	
20	4-Br	4-CN	4-Cl	CH ₃	H	
	4-Br	4-CN	4-F	CH ₃	H	
	4-Br	4-CN	4-CF ₃	CH ₃	H	
	4-Br	4-CN	4-CO ₂ Me	CH ₃	H	
	4-Br	4-CN	3-Cl	CH ₃	H	
25	4-Br	4-CN	3,4-di-F	CH ₃	H	
	4-Br	4-CN	4-CN	CH ₃	H	
	4-Br	4-CN	3-CN	CH ₃	H	
	4-Br	4-H	4-Cl	CH ₃	H	
	4-Br	4-H	4-F	CH ₃	H	
30	4-Br	4-H	4-CF ₃	CH ₃	H	
	4-Br	4-H	4-CO ₂ Me	CH ₃	H	
	4-Br	4-H	3-Cl	CH ₃	H	
	4-Br	4-H	3,4-di-F	CH ₃	H	
	4-Br	4-H	4-CN	CH ₃	H	
35	4-Br	4-H	3-CN	CH ₃	H	

Table 2 (continued)¹

	<u>R₁</u>	<u>R₂</u>	<u>W</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-Br	4-Br	4-Cl	CH ₃	H	
	4-Br	4-Br	4-F	CH ₃	H	
	4-Br	4-Br	4-CF ₃	CH ₃	H	
10	4-Br	4-Br	4-CO ₂ Me	CH ₃	H	
	4-Br	4-Br	3-Cl	CH ₃	H	
	4-Br	4-Br	3,4-di-F	CH ₃	H	
	4-Br	4-Br	4-CN	CH ₃	H	
	4-CF ₃	4-F	4-CN	H	CH ₂ CH ₃	
15	4-CF ₃	4-F	4-CN	H	CO ₂ Me	
	4-CF ₃	4-F	4-CN	H	CO ₂ Et	
	4-CF ₃	4-F	4-CN	H	COCF ₃	
	4-CF ₃	4-F	4-CN	H	COCH ₂ Cl	
	4-CF ₃	4-F	4-CN	H	COCO ₂ Me	
20	4-CF ₃	4-F	4-CN	H	-SCCl ₃	
	4-CF ₃	4-F	4-CN	H	-SC ₆ H ₅	
	4-CF ₃	4-Cl	4-F	H	-CO ₂ Et	
	4-CF ₃	4-Cl	4-F	H	-CH ₂ CH ₃	
	4-CF ₃	4-Cl	4-F	H	-COCH ₂ Cl	
25	4-CF ₃	4-Cl	4-F	H	-COCH ₂ CH ₃	
	4-CF ₃	4-Cl	4-F	H	-S-CCl ₃	
	4-CF ₃	4-Cl	4-F	H	-S-C ₆ H ₅	

30

35

Table 2 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>W</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-CF ₃	4-Cl	4-F	H	propyl	
	4-CF ₃	4-Cl	4-F	H	butyl	
10	4-CF ₃	4-F	4-Cl	CH ₃	H	
	4-CF ₃	4-F	4-F	CH ₃	H	
	4-CF ₃	4-Cl	4-CN	CH ₃	H	
	4-CF ₃	4-Cl	4-F	CH ₃	H	
	4-CF ₃	4-Cl	4-Cl	CH ₃	H	205 to 206
	4-CF ₃	4-H	4-CN	CH ₃	H	
15	4-CF ₃	4-H	4-F	CH ₃	H	
	4-CF ₃	4-H	4-Cl	CH ₃	H	
	4-F	4-F	4-F	CH ₃	H	
	4-F	4-F	4-CN	CH ₃	H	
20	4-F	4-F	4-Cl	CH ₃	H	
	4-F	4-Cl	4-CN	CH ₃	H	
	4-F	4-Cl	4-F	CH ₃	H	
	4-F	4-Cl	4-Cl	CH ₃	H	
	4-F	4-H	4-CN	CH ₃	H	
	4-F	4-H	4-F	CH ₃	H	
25	4-I	4-H	4-Cl	CH ₃	H	
	4-Cl	4-F	4-CN	CH ₃	H	
	4-Cl	4-Cl	4-CN	CH ₃	H	
	4-CF ₃	4-Cl	4-F	H	CH ₃	164 to 167
	4-CF ₃	4-Cl	4-Cl	H	CH ₃	181 to 183
30	4-CF ₃	4-Cl	4-CN	H	CH ₃	
	4-CF ₃	4-Cl	3-CN	H	CH ₃	
	4-CF ₃	4-Cl	4-CO ₂ Me	H	CH ₃	
	4-CF ₃	4-Cl	3,4-di-F	H	CH ₃	
	4-CF ₃	4-Cl	3-Cl	H	CH ₃	
35	4-CF ₃	4-F	4-F	H	CH ₃	

Table 2 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>W</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-CF ₃	4-F	4-Cl	H	CH ₃	
	4-CF ₃	4-F	4-CN	H	CH ₃	
	4-CF ₃	4-F	4-CO ₂ Me	H	CH ₃	
	4-CF ₃	4-F	3-Cl	H	CH ₃	
	4-CF ₃	4-F	3-CN	H	CH ₃	
10	4-CF ₃	4-F	3,4-di-F	H	CH ₃	
	4-CF ₃	4-CF ₃	4-F	H	CH ₃	
	4-CF ₃	4-CF ₃	4-Cl	H	CH ₃	
	4-CF ₃	4-CF ₃	4-CN	H	CH ₃	
	4-CF ₃	4-CF ₃	4-CO ₂ Me	H	CH ₃	
15	4-CF ₃	4-CF ₃	3-Cl	H	CH ₃	
	4-CF ₃	4-CF ₃	3-CN	H	CH ₃	
	4-CF ₃	4-CF ₃	3,4-di-F	H	CH ₃	
	4-CF ₃	4-H	4-F	H	CH ₃	
	4-CF ₃	4-H	4-Cl	H	CH ₃	
20	4-CF ₃	4-H	4-CN	H	CH ₃	
	4-CF ₃	4-H	4-CO ₂ Me	H	CH ₃	
	4-CF ₃	4-H	3-Cl	H	CH ₃	
	4-CF ₃	4-H	3-CN	H	CH ₃	
	4-CF ₃	4-H	3,4-di-F	H	CH ₃	
25	4-CF ₃	4-CN	4-F	H	CH ₃	
	4-CF ₃	4-CN	4-Cl	H	CH ₃	
	4-CF ₃	4-CN	4-CN	H	CH ₃	
	4-CF ₃	4-CN	4-CO ₂ Me	H	CH ₃	
	4-CF ₃	4-Cl	3-Cl	H	CH ₃	
30	4-CF ₃	4-CN	3-CN	H	CH ₃	
	4-CF ₃	4-CN	3,4-di-F	H	CH ₃	
	4-OCF ₃	4-Cl	4-F	H	CH ₃	
	4-OCF ₃	4-Cl	4-Cl	H	CH ₃	
	4-OCF ₃	4-Cl	4-CN	H	CH ₃	
35	4-OCF ₃	4-Cl	3-CN	H	CH ₃	

Table 2 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>W</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-OCF ₃	4-Cl	4-CO ₂ Me	H	CH ₃	
	4-OCF ₃	4-Cl	3,4-di-F	H	CH ₃	
	4-OCF ₃	4-Cl	3-Cl	H	CH ₃	
	4-OCF ₃	4-F	4-F	H	CH ₃	
	4-OCF ₃	4-F	4-Cl	H	CH ₃	
10	4-OCF ₃	4-F	4-CN	H	CH ₃	
	4-OCF ₃	4-F	4-CO ₂ Me	H	CH ₃	
	4-OCF ₃	4-F	3-Cl	H	CH ₃	
	4-OCF ₃	4-F	3-CN	H	CH ₃	
	4-OCF ₃	4-F	3,4-di-F	H	CH ₃	
15	4-OCF ₃	4-CF ₃	4-F	H	CH ₃	
	4-OCF ₃	4-CF ₃	4-Cl	H	CH ₃	
	4-OCF ₃	4-CF ₃	4-CN	H	CH ₃	
	4-OCF ₃	4-CF ₃	4-CO ₂ Me	H	CH ₃	
	4-OCF ₃	4-CF ₃	3-Cl	H	CH ₃	
20	4-OCF ₃	4-CF ₃	3-CN	H	CH ₃	
	4-OCF ₃	4-CF ₃	3,4-di-F	H	CH ₃	
	4-OCF ₃	4-H	4-F	H	CH ₃	
	4-OCF ₃	4-H	4-Cl	H	CH ₃	
	4-OCF ₃	4-H	4-CN	H	CH ₃	
25	4-OCF ₃	4-H	4-CO ₂ Me	H	CH ₃	
	4-OCF ₃	4-H	3-Cl	H	CH ₃	
	4-OCF ₃	4-H	3-CN	H	CH ₃	
	4-OCF ₃	4-H	3,4-di-F	H	CH ₃	
	4-OCF ₃	4-CN	4-F	H	CH ₃	
30	4-OCF ₃	4-CN	4-Cl	H	CH ₃	
	4-OCF ₃	4-CN	4-CN	H	CH ₃	
	4-OCF ₃	4-CN	4-CO ₂ Me	H	CH ₃	
	4-OCF ₃	4-CN	3-Cl	H	CH ₃	
	4-OCF ₃	4-CN	3-CN	H	CH ₃	
35	4-OCF ₃	4-CN	3,4-di-F	H	CH ₃	

Table 2 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>W</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-Cl	4-Cl	4-F	H	CH ₃	
	4-Cl	4-Cl	4-Cl	H	CH ₃	
	4-Cl	4-Cl	4-CN	H	CH ₃	
	4-Cl	4-Cl	3-CN	H	CH ₃	
	4-Cl	4-Cl	4-CO ₂ Me	H	CH ₃	
10	4-Cl	4-Cl	3,4-di-F	H	CH ₃	
	4-Cl	4-Cl	3-Cl	H	CH ₃	
	4-Cl	4-F	4-F	H	CH ₃	
	4-Cl	4-F	4-Cl	H	CH ₃	
	4-Cl	4-F	4-CN	H	CH ₃	
15	4-Cl	4-F	4-CO ₂ Me	H	CH ₃	
	4-Cl	4-F	3-Cl	H	CH ₃	
	4-Cl	4-F	3-CN	H	CH ₃	
	4-Cl	4-F	3,4-di-F	H	CH ₃	
	4-Cl	4-CF ₃	4-F	H	CH ₃	
20	4-Cl	4-CF ₃	4-Cl	H	CH ₃	
	4-Cl	4-CF ₃	4-CN	H	CH ₃	
	4-Cl	4-CF ₃	4-CO ₂ Me	H	CH ₃	
	4-Cl	4-CF ₃	3-Cl	H	CH ₃	
	4-Cl	4-CF ₃	3-CN	H	CH ₃	
25	4-Cl	4-CF ₃	3,4-di-F	H	CH ₃	
	4-Cl	4-H	4-F	H	CH ₃	
	4-Cl	4-H	4-Cl	H	CH ₃	
	4-Cl	4-H	4-CN	H	CH ₃	
	4-Cl	4-H	4-CO ₂ Me	H	CH ₃	
30	4-Cl	4-H	3-Cl	H	CH ₃	
	4-Cl	4-H	3-CN	H	CH ₃	
	4-Cl	4-H	3,4-di-F	H	CH ₃	
	4-Cl	4-CN	4-F	H	CH ₃	
	4-Cl	4-CN	4-Cl	H	CH ₃	
35	4-Cl	4-CN	4-CN	H	CH ₃	

Table 2 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>W</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-Cl	4-CN	4-CO ₂ Me	H	CH ₃	
	4-Cl	4-CN	3-Cl	H	CH ₃	
	4-Cl	4-CN	3-CN	H	CH ₃	
	4-Cl	4-CN	3,4-di-F	H	CH ₃	
10	4-CF ₃	4-F	4-Cl	H	COCF ₃	
	4-CF ₃	4-F	4-F	H	COCF ₃	
	4-CF ₃	4-Cl	4-CN	H	COCF ₃	
	4-CF ₃	4-Cl	4-F	H	COCF ₃	
	4-CF ₃	4-Cl	4-Cl	H	COCF ₃	
	4-F	4-F	4-F	H	COCF ₃	
15	4-F	4-F	4-CN	H	COCF ₃	
	4-F	4-F	4-Cl	H	COCF ₃	
	4-F	4-Cl	4-CN	H	COCF ₃	
	4-F	4-Cl	4-F	H	COCF ₃	
	4-F	4-Cl	4-Cl	H	COCF ₃	
	4-Cl	4-F	4-CN	H	COCF ₃	
20	4-Cl	4-Cl	4-CN	H	COCF ₃	
	4-Cl	4-F	4-Cl	H	COCF ₃	
	4-CF ₃	4-F	4-Cl	H	CO ₂ Me	
	4-CF ₃	4-F	4-CN	H	CO ₂ Me	
	4-CF ₃	4-F	4-F	H	Me	
	4-CF ₃	4-Cl	4-CN	H	Me	
25	4-CF ₃	4-Cl	4-F	H	CO ₂ Me	75 to 78
	4-CF ₃	4-Cl	4-Cl	H	CO ₂ Me	120 to 124
	4-CF ₃	4-CF ₃	4-CN	H	CO ₂ Me	
	4-CF ₃	4-CF ₃	4-F	H	CO ₂ Me	
	4-CF ₃	4-CF ₃	4-Cl	H	CO ₂ Me	
	4-CF ₃	4-OCF ₃	4-CN	H	CO ₂ Me	
30	4-CF ₃	4-OCF ₃	4-Cl	H	CO ₂ Me	
	4-CF ₃	4-H	4-CN	H	CO ₂ Me	
	4-CF ₃	4-H	4-F	H	CO ₂ Me	
	4-CF ₃	4-H	4-F	H	CO ₂ Me	

Table 2 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>W</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-CF ₃	4-H	4-Cl	H	CO ₂ Me	
	4-OCF ₃	4-F	4-F	H	CO ₂ Me	
	4-OCF ₃	4-F	4-Cl	H	CO ₂ Me	
	4-OCF ₃	4-Cl	4-F	H	CO ₂ Me	
	4-OCF ₃	4-Cl	4-Cl	H	CO ₂ Me	
10	4-OCF ₃	CF ₃	4-F	H	CO ₂ Me	
	4-OCF ₃	CF ₃	4-Cl	H	CO ₂ Me	
	4-F	4-F	4-F	H	CO ₂ Me	
	4-F	4-F	4-CN	H	CO ₂ Me	
	4-F	4-F	4-Cl	H	CO ₂ Me	
15	4-F	4-Cl	4-CN	H	CO ₂ Me	
	4-F	4-Cl	4-F	H	CO ₂ Me	
	4-F	4-Cl	4-Cl	H	CO ₂ Me	
	4-Cl	4-F	4-CN	H	CO ₂ Me	
	4-Cl	4-Cl	4-CN	H	CO ₂ Me	
20	4-Cl	4-F	4-Cl	H	CO ₂ Me	
	4-CF ₃	4-F	4-Cl	H	CHO	
	4-CF ₃	4-F	4-F	H	CHO	
	4-CF ₃	4-Cl	4-CN	H	CHO	
	4-CF ₃	4-Cl	4-F	H	CHO	
25	4-CF ₃	4-Cl	4-Cl	H	CHO	
	4-F	4-F	4-F	H	CHO	
	4-F	4-F	4-CN	H	CHO	
	4-F	4-F	4-Cl	H	CHO	
	4-F	4-Cl	4-CN	H	CHO	
30	4-F	4-Cl	4-F	H	CHO	
	4-F	4-Cl	4-Cl	H	CHO	
	4-Cl	4-F	4-CN	H	CHO	
	4-Cl	4-Cl	4-CN	H	CHO	
	4-Cl	4-F	4-Cl	H	CHO	
35	4-Cl	4-F	4-Cl	H	CHO	
	4-CF ₃	4-F	4-Cl	H	COCH ₃	

Table 2 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>W</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-CF ₃	4-F	4-F	H	COCH ₃	
	4-CF ₃	4-Cl	4-CN	H	COCH ₃	
	4-CF ₃	4-Cl	4-F	H	COCH ₃	153 to 155
	4-CF ₃	4-Cl	4-Cl	H	COCH ₃	158 to 160
	4-CF ₃	4-CF ₃	4-F	H	COCH ₃	
10	4-CF ₃	4-CF ₃	4-Cl	H	COCH ₃	
	4-CF ₃	4-CF ₃	4-CN	H	COCH ₃	
	4-CF ₃	4-CN	4-F	H	COCH ₃	
	4-CF ₃	4-CN	4-Cl	H	COCH ₃	
	4-CF ₃	4-CN	4-CN	H	COCH ₃	
15	4-CF ₃	4-H	4-F	H	COCH ₃	
	4-CF ₃	4-H	4-Cl	H	COCH ₃	
	4-CF ₃	4-H	4-CN	H	COCH ₃	
	4-OCF ₃	4-F	4-F	H	COCH ₃	
	4-OCF ₃	4-F	4-Cl	H	COCH ₃	
20	4-OCF ₃	4-F	4-CN	H	COCH ₃	
	4-OCF ₃	4-Cl	4-F	H	COCH ₃	
	4-OCF ₃	4-Cl	4-Cl	H	COCH ₃	
	4-OCF ₃	4-Cl	4-CN	H	COCH ₃	
	4-OCF ₃	4-CF ₃	4-F	H	COCH ₃	
25	4-OCF ₃	4-CF ₃	4-Cl	H	COCH ₃	
	4-OCF ₃	4-CF ₃	4-CN	H	COCH ₃	
	4-OCF ₃	4-H	4-F	H	COCH ₃	
	4-OCF ₃	4-H	4-Cl	H	COCH ₃	
	4-OCF ₃	4-H	4-CN	H	COCH ₃	
30	4-OCF ₃	4-CN	4-F	H	COCH ₃	
	4-OCF ₃	4-CN	4-Cl	H	COCH ₃	
	4-OCF ₃	4-CN	4-CN	H	COCH ₃	
	4-F	4-F	4-F	H	COCH ₃	
	4-F	4-F	4-CN	H	COCH ₃	
35	4-F	4-F	4-Cl	H	COCH ₃	

Table 2 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>W</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-F	4-Cl	4-CN	H	COCH ₃	
	4-F	4-Cl	4-F	H	COCH ₃	
	4-F	4-Cl	4-Cl	H	COCH ₃	
10	4-Cl	4-F	4-CN	H	COCH ₃	
	4-Cl	4-Cl	4-CN	H	COCH ₃	
	4-Cl	4-F	4-Cl	H	COCH ₃	
	4-CF ₃	4-Cl	4-Cl	H	CH ₂ CH ₃	
	4-CF ₃	4-Cl	4-Cl	H	CH ₂ CO ₂ Me	
15	4-CF ₃	4-Cl	4-Cl	H	CO ₂ Me	
	2,5-di-F	4-Cl	4-Cl	CH ₃	H	158 to 159.5
	3,5-di-NO ₂	4-Cl	4-Cl	CH ₃	H	252.5 to 255
	2,3,4-tri-Cl	4-Cl	4-Cl	CH ₃	H	242 to 246
	4-Et	4-Cl	4-Cl	CH ₃	H	180 to 181
20	3-CF ₃ , 4-F	4-Cl	4-Cl	CH ₃	H	165 to 166
	4-C ₆ H ₁₁	4-Cl	4-Cl	CH ₃	H	181 to 182
	3-CN	4-Cl	4-Cl	CH ₃	H	112 to 116
	2-CN	4-Cl	4-Cl	CH ₃	H	143 to 148
	2-Cl	4-Cl	4-Cl	CH ₃	H	157 to 159
25	4-F	4-Cl	4-Cl	CH ₃	H	141.5 to 142.5
	3-F	4-Cl	4-Cl	CH ₃	H	149 to 150
	2-F	4-Cl	4-Cl	CH ₃	H	129 to 135
	2,3,4-tri-Cl	3-CF ₃	4-Cl	CH ₃	H	191 to 192
	3-CF ₃ , 4-F	3-CF ₃	4-Cl	CH ₃	H	188 to 189
30	4-OC ₆ H ₅	3-CF ₃	4-Cl	CH ₃	H	110 to 114
	4-CF ₃	3-CF ₃	4-Cl	CH ₃	H	211 to 213

35

Table 2 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>W</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
10	3-CF ₃	3-CF ₃	4-Cl	CH ₃	H	146 to 148
	4-CN	3-CF ₃	4-Cl	CH ₃	H	161 to 163
	3-CN	3-CF ₃	4-Cl	CH ₃	H	189 to 191
	4-Cl	3-CF ₃	4-Cl	CH ₃	H	178 to 181
	3-Cl	3-CF ₃	4-Cl	CH ₃	H	122 to 125
15	4-F	3-CF ₃	4-Cl	CH ₃	H	184 to 186
	4-CF ₃	2-Me, 4-Cl	4-Cl	CH ₃	H	oil (a)
	3-CF ₃	2-Me, 4-Cl	4-Cl	CH ₃	H	oil (b)
	4-CN	2-Me, 4-Cl	4-Cl	CH ₃	H	oil (c)
	3-CN	2-Me, 4-Cl	4-Cl	CH ₃	H	80 to 82
20	4-Cl	2-Me, 4-Cl	4-Cl	CH ₃	H	82 to 84
	3-Cl	2-Me, 4-Cl	4-Cl	CH ₃	H	68 to 70
	4-F	2-Me, 4-Cl	4-Cl	CH ₃	H	82 to 84
	3-CF ₃ , 4-F	2-Me, 4-Cl	4-Cl	CH ₃	H	oil (d)
	4-CN	4-CF ₃	4-F	CH ₃	H	94 to 96
25	4-F	4-CF ₃	4-F	CH ₃	H	98 to 100
	4-CF ₃	4-F	4-H	H	COCH ₃	156 to 158
	4-CF ₃	4-Cl	4-F	H	COCH ₂ CH ₃	132 to 134
	4-CF ₃	4-OCF ₂ H	4-F	H	CH ₃	oil (e)

¹H NMR spectra (δ):

(a) 8.60(NH)

(b) 8.52(NH)

(c) 8.60(NH)

(d) 8.54(NH)

(e) 3.5(NMe)

8.1

Table 3

	<u>R₁</u>	<u>R₂</u>	<u>B</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-CF ₃	4-F	CH ₃	CO ₂ Me	H	163 to 164
	4-CF ₃	4-H	CH ₃	CO ₂ Me	H	
	4-CF ₃	4-Cl	CH ₃	CO ₂ Me	H	178.5 to 180
	4-CF ₃	4-Br	CH ₃	CO ₂ Me	H	186 to 188
	4-CF ₃	4-I	CH ₃	CO ₂ Me	H	
10	4-CF ₃	4-CN	CH ₃	CO ₂ Me	H	198 to 203
	4-CF ₃	4-OCF ₂ H	CH ₃	CO ₂ Me	H	
	4-CF ₃	4-OCF ₃	CH ₃	CO ₂ Me	H	
	4-CF ₃	4-CF ₃	CH ₃	CO ₂ Me	H	198 to 199
	4-F	4-F	CH ₃	CO ₂ Me	H	
15	4-F	4-H	CH ₃	CO ₂ Me	H	
	4-F	4-Cl	CH ₃	CO ₂ Me	H	
	4-F	4-Br	CH ₃	CO ₂ Me	H	
	4-F	4-I	CH ₃	CO ₂ Me	H	
	4-F	4-CN	CH ₃	CO ₂ Me	H	
20	4-Cl	4-F	CH ₃	CO ₂ Me	H	
	4-Cl	4-H	CH ₃	CO ₂ Me	H	
	4-Cl	4-Cl	CH ₃	CO ₂ Me	H	138 to 140
	4-Cl	4-Br	CH ₃	CO ₂ Me	H	132 to 136
	4-Cl	4-I	CH ₃	CO ₂ Me	H	
25	4-Cl	4-CN	CH ₃	CO ₂ Me	H	187 to 192
	4-Cl	4-CF ₃	CH ₃	CO ₂ Me	H	
	4-Cl	4-OCF ₃	CH ₃	CO ₂ Me	H	162 to 165
	4-OCF ₃	4-CF ₃	CH ₃	CO ₂ Me	H	
	4-OCF ₃	4-OCF ₃	CH ₃	CO ₂ Me	H	
30	4-OCF ₃	4-Cl	CH ₃	CO ₂ Me	H	
	4-OCF ₃	4-Br	CH ₃	CO ₂ Me	H	gum (oo)
	4-OCF ₃	4-H	CH ₃	CO ₂ Me	H	
	4-OCF ₃	4-CN	CH ₃	CO ₂ Me	H	
	4-OCF ₃	4-F	CH ₃	CO ₂ Me	H	

35

Table 3 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>B</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-CF ₃	4-F	CH ₃	CO ₂ Et	H	
	4-CF ₃	4-H	CH ₃	CO ₂ Et	H	
	4-CF ₃	4-Cl	CH ₃	CO ₂ Et	H	
	4-CF ₃	4-Br	CH ₃	CO ₂ Et	H	
	4-CF ₃	4-I	CH ₃	CO ₂ Et	H	
10	4-CF ₃	4-CN	CH ₃	CO ₂ Et	H	
	4-F	4-F	CH ₃	CO ₂ Et	H	
	4-F	4-H	CH ₃	CO ₂ Et	H	
	4-F	4-Cl	CH ₃	CO ₂ Et	H	
	4-F	4-Br	CH ₃	CO ₂ Et	H	
15	4-F	4-I	CH ₃	CO ₂ Et	H	
	4-F	4-CN	CH ₃	CO ₂ Et	H	
	4-Cl	4-F	CH ₃	CO ₂ Et	H	112.5 to 114
	4-Cl	4-H	CH ₃	CO ₂ Et	H	
	4-Cl	4-Cl	CH ₃	CO ₂ Et	H	
20	4-Cl	4-Br	CH ₃	CO ₂ Et	H	
	4-Cl	4-I	CH ₃	CO ₂ Et	H	
	4-Cl	4-CN	CH ₃	CO ₂ Et	H	
	4-CF ₃	4-F	CH ₃	CONMe ₂	H	
	4-CF ₃	4-H	CH ₃	CONMe ₂	H	
25	4-CF ₃	4-Cl	CH ₃	CONMe ₂	H	
	4-CF ₃	4-Br	CH ₃	CONMe ₂	H	
	4-CF ₃	4-I	CH ₃	CONMe ₂	H	
	4-CF ₃	4-CN	CH ₃	CONMe ₂	H	
	4-F	4-F	CH ₃	CONMe ₂	H	
30	4-F	4-H	CH ₃	CONMe ₂	H	
	4-F	4-Cl	CH ₃	CONMe ₂	H	
	4-F	4-Br	CH ₃	CONMe ₂	H	
	4-F	4-I	CH ₃	CONMe ₂	H	
	4-F	4-CN	CH ₃	CONMe ₂	H	
35	4-Cl	4-F	CH ₃	CONMe ₂	H	

Table 3 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>B</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-Cl	4-H	CH ₃	CONMe ₂	H	
	4-Cl	4-Cl	CH ₃	CONMe ₂	H	
	4-Cl	4-Br	CH ₃	CONMe ₂	H	
	4-Cl	4-I	CH ₃	CONMe ₂	H	
	4-Cl	4-CN	CH ₃	CONMe ₂	H	
10	4-CF ₃	4-OCH ₃	CH ₃	CO ₂ Me	H	
	4-CF ₃	4-NO ₂	CH ₃	CO ₂ Me	H	
	4-CF ₃	4-CO ₂ Et	CH ₃	CO ₂ Me	H	
	4-CF ₃	4-SMe	CH ₃	CO ₂ Me	H	
	4-CF ₃	4-SO ₂ Me	CH ₃	CO ₂ Me	H	
	4-CF ₃	4-Me	CH ₃	CO ₂ Me	H	
15	4-CF ₃	4-CH=CH ₂	CH ₃	CO ₂ Me	H	
	4-CF ₃	4-C≡CH	CH ₃	CO ₂ Me	H	
	4-CF ₃	4-CONMe ₂	CH ₃	CO ₂ Me	H	
	4-CF ₃	4-SCF ₃	CH ₃	CO ₂ Me	H	
	4-CF ₃	4-OCH(CH ₃) ₂	CH ₃	CO ₂ Me	H	
	4-CF ₃	4-OSO ₂ CH ₃	CH ₃	CO ₂ Me	H	
20	4-CF ₃	4-OCOCH ₃	CH ₃	CO ₂ Me	H	
	4-CF ₃	4-NMe ₂	CH ₃	CO ₂ Me	H	
	4-CF ₃	4-NHCOCH ₃	CH ₃	CO ₂ Me	H	
	4-CF ₃	4-OCONHMe	CH ₃	CO ₂ Me	H	
	4-CF ₃	4-NHCONH ₂	CH ₃	CO ₂ Me	H	
	4-CF ₃	4-COCH ₃	CH ₃	CO ₂ Me	H	
25	4-F	4-OCH ₃	CH ₃	CO ₂ Me	H	
	4-F	4-NO ₂	CH ₃	CO ₂ Me	H	
	4-F	4-CO ₂ Et	CH ₃	CO ₂ Me	H	
	4-F	4-SMe	CH ₃	CO ₂ Me	H	
	4-F	4-SO ₂ Me	CH ₃	CO ₂ Me	H	
	4-F	4-Me	CH ₃	CO ₂ Me	H	
30	4-F	4-CH=CH ₂	CH ₃	CO ₂ Me	H	
	4-F	4-C≡CH	CH ₃	CO ₂ Me	H	
	4-F	4-CH=CH ₂	CH ₃	CO ₂ Me	H	
	4-F	4-C≡CH	CH ₃	CO ₂ Me	H	
	4-F	4-CH=CH ₂	CH ₃	CO ₂ Me	H	
	4-F	4-C≡CH	CH ₃	CO ₂ Me	H	
35						

Table 3 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>B</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-F	4-CONMe ₂	CH ₃	CO ₂ Me	H	
	4-F	4-SCF ₃	CH ₃	CO ₂ Me	H	
	4-F	4-OCH(CH ₃) ₂	CH ₃	CO ₂ Me	H	
	4-F	4-OSO ₂ CH ₃	CH ₃	CO ₂ Me	H	
	4-F	4-OCOCH ₃	CH ₃	CO ₂ Me	H	
10	4-F	4-NMe ₂	CH ₃	CO ₂ Me	H	
	4-F	4-NHCOCH ₃	CH ₃	CO ₂ Me	H	
	4-F	4-OCONHMe	CH ₃	CO ₂ Me	H	
	4-F	4-NHCONH ₂	CH ₃	CO ₂ Me	H	
	4-F	4-COCH ₃	CH ₃	CO ₂ Me	H	
15	4-OCH ₃	4-F	CH ₃	CO ₂ Me	H	
	4-NO ₂	4-F	CH ₃	CO ₂ Me	H	
	4-CO ₂ Et	4-F	CH ₃	CO ₂ Me	H	
	4-SMe	4-F	CH ₃	CO ₂ Me	H	
	4-SO ₂ Me	4-F	CH ₃	CO ₂ Me	H	
20	4-Me	4-F	CH ₃	CO ₂ Me	H	
	4-CH=CH ₂	4-F	CH ₃	CO ₂ Me	H	
	4-C≡CH	4-F	CH ₃	CO ₂ Me	H	
	4-CONMe ₂	4-F	CH ₃	CO ₂ Me	H	
	4-SCF ₃	4-F	CH ₃	CO ₂ Me	H	
25	4-OCH(CH ₃) ₂	4-F	CH ₃	CO ₂ Me	H	
	4-OSO ₂ CH ₃	4-F	CH ₃	CO ₂ Me	H	
	4-OCOCH ₃	4-F	CH ₃	CO ₂ Me	H	
	4-NMe ₂	4-F	CH ₃	CO ₂ Me	H	
	4-NHCOCH ₃	4-F	CH ₃	CO ₂ Me	H	
30	4-OCONHMe	4-F	CH ₃	CO ₂ Me	H	
	4-NHCONH ₂	4-F	CH ₃	CO ₂ Me	H	
	4-COCH ₃	4-F	CH ₃	CO ₂ Me	H	
	4-OCH ₃	4-Cl	CH ₃	CO ₂ Me	H	
	4-NO ₂	4-Cl	CH ₃	CO ₂ Me	H	
35	4-CO ₂ Et	4-Cl	CH ₃	CO ₂ Me	H	

Table 3 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>B</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-SMe	4-Cl	CH ₃	CO ₂ Me	H	
	4-SO ₂ Me	4-Cl	CH ₃	CO ₂ Me	H	
	4-Me	4-Cl	CH ₃	CO ₂ Me	H	
	4-CH=CH ₂	4-Cl	CH ₃	CO ₂ Me	H	
	4-C≡CH	4-Cl	CH ₃	CO ₂ Me	H	
10	4-CONMe ₂	4-Cl	CH ₃	CO ₂ Me	H	
	4-SCF ₃	4-Cl	CH ₃	CO ₂ Me	H	
	4-OCH(CH ₃) ₂	4-Cl	CH ₃	CO ₂ Me	H	
	4-OSO ₂ CH ₃	4-Cl	CH ₃	CO ₂ Me	H	
	4-OCOCH ₃	4-Cl	CH ₃	CO ₂ Me	H	
15	4-NMe ₂	4-Cl	CH ₃	CO ₂ Me	H	
	4-NHCOCH ₃	4-Cl	CH ₃	CO ₂ Me	H	
	4-OCNHMe	4-Cl	CH ₃	CO ₂ Me	H	
	4-NHCONH ₂	4-Cl	CH ₃	CO ₂ Me	H	
	4-COCH ₃	4-Cl	CH ₃	CO ₂ Me	H	
20	4-CF ₃	4-F	CH ₃	CO ₂ H	H	
	4-CF ₃	4-F	CH ₃	COCH ₃	H	
	4-CF ₃	4-F	CH ₃	COCH ₂ CH ₃	H	
	4-CF ₃	4-F	CH ₃	CO ₂ CH ₂ CH ₂ CH ₃	H	
	4-CF ₃	4-F	CH ₃	CO ₂ CH(CH ₃) ₂	H	
25	4-CF ₃	4-F	CH ₃	CO ₂ C ₆ H ₅	H	
	4-CF ₃	4-F	CH ₃	COC ₆ H ₅	H	
	4-CF ₃	4-F	CH ₂ CH ₃	CO ₂ Me	H	
	4-CF ₃	4-F	CH ₂ CH ₃	CO ₂ Et	H	
	4-CF ₃	4-F	CH ₂ CH ₃	COCH ₃	H	
30	4-CF ₃	4-F	C ₆ H ₅	CO ₂ Me	H	
	4-CF ₃	4-F	C ₆ H ₅	CO ₂ Et	H	
	4-CF ₃	4-F	H	CO ₂ Me	H	
	4-CF ₃	4-F	H	COCH ₃	H	
	4-CF ₃	4-F	H	CO ₂ Et	H	

Table 3 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>B</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-CF ₃	4-F	H	CONMe ₂	H	
	4-CF ₃	4-F	CH ₂ CH ₃	CONMe ₂	H	
	4-CF ₃	4-Cl	H	CO ₂ Et	H	
	4-CF ₃	4-Cl	H	CO ₂ Me	H	200 to 204
	4-F	4-Cl	H	CO ₂ Me	H	
10	4-Cl	4-Cl	H	CO ₂ Me	H	
	4-Cl	4-CF ₃	H	CO ₂ Me	H	162 to 164.5
	4-F	4-F	H	CO ₂ Me	H	
	4-Cl	4-F	H	CO ₂ Me	H	147 to 148
	4-Cl	4-F	CH ₃	CO ₂ C ₆ H ₅	H	161 to 163.5
15	4-Cl	4-CF ₃	CH ₂ CO ₂ Me	CO ₂ Me	H	138 to 142
	4-CF ₃	4-F	CH ₂ CO ₂ Me	CO ₂ Me	H	155 to 156
	4-CF ₃	4-Cl	CH ₂ CO ₂ Me	CO ₂ Me	H	
	4-CF ₃	4-Cl	CH ₂ CN	CO ₂ Me	H	
	4-Br	4-Cl	H	CO ₂ Me	H	174 to 177
20	4-Cl	4-Cl	H	COCH ₂ CH ₃	H	198 to 199
	4-CF ₃	4-F	CH ₃	CO ₂ Me	CHO	
	4-CF ₃	4-H	CH ₃	CO ₂ Me	CHO	
	4-CF ₃	4-Cl	CH ₃	CO ₂ Me	CHO	
	4-CF ₃	4-Br	CH ₃	CO ₂ Me	CHO	
25	4-CF ₃	4-I	CH ₃	CO ₂ Me	CHO	
	4-CF ₃	4-CN	CH ₃	CO ₂ Me	CHO	
	4-F	4-F	CH ₃	CO ₂ Me	CHO	
	4-F	4-H	CH ₃	CO ₂ Me	CHO	
	4-F	4-Cl	CH ₃	CO ₂ Me	CHO	
30	4-F	4-Br	CH ₃	CO ₂ Me	CHO	
	4-F	4-I	CH ₃	CO ₂ Me	CHO	
	4-F	4-CN	CH ₃	CO ₂ Me	CHO	
	4-Cl	4-F	CH ₃	CO ₂ Me	CHO	
	4-Cl	4-H	CH ₃	CO ₂ Me	CHO	

35

Table 3 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>B</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-Cl	4-Cl	CH ₃	CO ₂ Me	CHO	
	4-Cl	4-Br	CH ₃	CO ₂ Me	CHO	
	4-Cl	4-I	CH ₃	CO ₂ Me	CHO	
	4-Cl	4-CN	CH ₃	CO ₂ Me	CHO	
10	4-CF ₃	4-F	CH ₃	CO ₂ Me	COCH ₃	
	4-CF ₃	4-H	CH ₃	CO ₂ Me	COCH ₃	
	4-CF ₃	4-Cl	CH ₃	CO ₂ Me	COCH ₃	
	4-CF ₃	4-Br	CH ₃	CO ₂ Me	COCH ₃	
	4-CF ₃	4-I	CH ₃	CO ₂ Me	COCH ₃	
	4-CF ₃	4-CN	CH ₃	CO ₂ Me	COCH ₃	
15	4-F	4-F	CH ₃	CO ₂ Me	COCH ₃	
	4-F	4-H	CH ₃	CO ₂ Me	COCH ₃	
	4-F	4-Cl	CH ₃	CO ₂ Me	COCH ₃	
	4-F	4-Br	CH ₃	CO ₂ Me	COCH ₃	
	4-F	4-I	CH ₃	CO ₂ Me	COCH ₃	
	4-F	4-CN	CH ₃	CO ₂ Me	COCH ₃	
20	4-Cl	4-F	CH ₃	CO ₂ Me	COCH ₃	
	4-Cl	4-H	CH ₃	CO ₂ Me	COCH ₃	
	4-Cl	4-Cl	CH ₃	CO ₂ Me	COCH ₃	
	4-Cl	4-Br	CH ₃	CO ₂ Me	COCH ₃	
	4-Cl	4-I	CH ₃	CO ₂ Me	COCH ₃	
25	4-Cl	4-CN	CH ₃	CO ₂ Me	COCH ₃	
	4-CF ₃	4-F	CH ₃	CO ₂ Me	CO ₂ Me	
	4-CF ₃	4-H	CH ₃	CO ₂ Me	CO ₂ Me	
	4-CF ₃	4-Cl	CH ₃	CO ₂ Me	CO ₂ Me	
	4-CF ₃	4-Br	CH ₃	CO ₂ Me	CO ₂ Me	
	4-CF ₃	4-I	CH ₃	CO ₂ Me	CO ₂ Me	
30	4-CF ₃	4-CN	CH ₃	CO ₂ Me	CO ₂ Me	
	4-F	4-F	CH ₃	CO ₂ Me	CO ₂ Me	
	4-F	4-H	CH ₃	CO ₂ Me	CO ₂ Me	

Table 3 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>B</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-F	4-Cl	CH ₃	CO ₂ Me	CO ₂ Me	
	4-F	4-Br	CH ₃	CO ₂ Me	CO ₂ Me	
	4-F	4-I	CH ₃	CO ₂ Me	CO ₂ Me	
	4-F	4-CN	CH ₃	CO ₂ Me	CO ₂ Me	
	4-Cl	4-F	CH ₃	CO ₂ Me	CO ₂ Me	
10	4-Cl	4-H	CH ₃	CO ₂ Me	CO ₂ Me	
	4-Cl	4-Cl	CH ₃	CO ₂ Me	CO ₂ Me	
	4-Cl	4-Br	CH ₃	CO ₂ Me	CO ₂ Me	
	4-Cl	4-I	CH ₃	CO ₂ Me	CO ₂ Me	
	4-Cl	4-CN	CH ₃	CO ₂ Me	CO ₂ Me	
15	4-CF ₃	4-Cl	CH ₃	CO ₂ Me	CH ₃	oil (a)
	4-CF ₃	4-F	CH ₃	CO ₂ Me	CH ₃	91 to 95
	4-CF ₃	4-CN	CH ₃	CO ₂ Me	CH ₃	145 to 149
	4-CF ₃	4-CF ₃	CH ₃	CO ₂ Me	CH ₃	114 to 116
	4-CF ₃	4-Br	CH ₃	CO ₂ Me	CH ₃	126 to 130
20	4-CF ₃	4-OCF ₃	CH ₃	CO ₂ Me	CH ₃	78 to 82
	4-CF ₃	4-H	CH ₃	CO ₂ Me	CH ₃	
	4-CF ₃	4-Cl	CH ₃	CO ₂ Me	CH ₂ CH ₃	
	4-CF ₃	4-F	CH ₃	CO ₂ Me	CH ₂ CH ₃	
	4-CF ₃	4-CN	CH ₃	CO ₂ Me	CH ₂ CH ₃	
25	4-CF ₃	4-CF ₃	CH ₃	CO ₂ Me	CH ₂ CH ₃	
	4-CF ₃	4-Br	CH ₃	CO ₂ Me	CH ₂ CH ₃	
	4-CF ₃	4-OCF ₃	CH ₃	CO ₂ Me	CH ₂ CH ₃	
	4-CF ₃	4-H	CH ₃	CO ₂ Me	CH ₂ CH ₃	
	4-CF ₃	4-Cl	CH ₃	CO ₂ Me	CH ₂ CH ₂ CH ₃	
30	4-CF ₃	4-F	CH ₃	CO ₂ Me	CH ₂ CH ₂ CH ₃	oil (b)
	4-CF ₃	4-CF ₃	CH ₃	CO ₂ Me	CH ₂ CH ₂ CH ₃	oil (c)
	4-CF ₃	4-OCF ₃	CH ₃	CO ₂ Me	CH ₂ CH ₂ CH ₃	oil (d)
	4-CF ₃	4-CN	CH ₃	CO ₂ Me	CH ₂ CH ₂ CH ₃	
	4-CF ₃	4-Br	CH ₃	CO ₂ Me	CH ₂ CH ₂ CH ₃	
35	4-OCF ₃	4-Cl	CH ₃	CO ₂ Me	CH ₃	

Table 3 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>B</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-OCF ₃	4-F	CH ₃	CO ₂ Me	CH ₃	
	4-OCF ₃	4-CF ₃	CH ₃	CO ₂ Me	CH ₃	
	4-OCF ₃	4-CN	CH ₃	CO ₂ Me	CH ₃	
	4-OCF ₃	4-Br	CH ₃	CO ₂ Me	CH ₃	
	4-OCF ₃	4-OCF ₃	CH ₃	CO ₂ Me	CH ₃	
10	4-Cl	4-Cl	CH ₃	CO ₂ Me	CH ₃	
	4-Cl	4-F	CH ₃	CO ₂ Me	CH ₃	
	4-Cl	4-CF ₃	CH ₃	CO ₂ Me	CH ₃	
	4-Cl	4-CN	CH ₃	CO ₂ Me	CH ₃	
	4-Cl	4-Br	CH ₃	CO ₂ Me	CH ₃	
15	4-Cl	4-OCF ₃	CH ₃	CO ₂ Me	CH ₃	
	4-Br	4-Cl	CH ₃	CO ₂ Me	CH ₃	141 to 142
	4-Br	4-F	CH ₃	CO ₂ Me	CH ₃	151 to 154
	4-Br	4-CF ₃	CH ₃	CO ₂ Me	CH ₃	
	4-Br	4-CN	CH ₃	CO ₂ Me	CH ₃	
20	4-Br	4-Br	CH ₃	CO ₂ Me	CH ₃	
	4-Br	4-OCF ₃	CH ₃	CO ₂ Me	CH ₃	oil (e)
	4-CF ₃	4-Cl	H	H	H	167 to 168
	4-CF ₃	4-F	H	H	H	
	4-CF ₃	4-CF ₃	H	H	H	
25	4-CF ₃	4-CN	H	H	H	
	4-CF ₃	4-H	H	H	H	
	4-CF ₃	4-OCF ₃	H	H	H	
	4-CF ₃	4-Cl	H	H	CH ₃	
	4-CF ₃	4-Cl	H	H	COCH ₃	
30	4-CF ₃	4-Cl	H	H	CO ₂ CH ₃	
	4-OCF ₃	4-Cl	H	H	H	
	4-OCF ₃	4-CF ₃	H	H	H	
	4-OCF ₃	4-CN	H	H	H	
	4-Cl	4-Cl	H	H	H	
35	4-Cl	4-CF ₃	H	H	H	

Table 3 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>B</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
	4-Cl	4-CN	H	H	H	
5	4-CF ₃	4-Cl	4-F-Benzyl	H	H	
	4-CF ₃	4-Cl	4-Cl-Benzyl	H	H	
	4-CF ₃	4-Cl	4-CN-Benzyl	H	H	
	4-CF ₃	4-F	4-F-Benzyl	H	H	
	4-CF ₃	4-F	4-Cl-Benzyl	H	H	
10	4-CF ₃	4-F	4-CN-Benzyl	H	H	
	4-CF ₃	4-CF ₃	4-F-Benzyl	H	H	
	4-CF ₃	4-CF ₃	4-Cl-Benzyl	H	H	
	4-CF ₃	4-CF ₃	4-CN-Benzyl	H	H	
15	4-CF ₃	4-Cl	CH ₂ CH ₂ CH ₃	CH ₃	H	
	4-CF ₃	4-F	CH ₂ CH ₂ CH ₃	CH ₃	H	122 to 125
	4-CF ₃	4-CF ₃	CH ₂ CH ₂ CH ₃	CH ₃	H	
	4-CF ₃	4-Cl	CH ₂ CH ₂ CH ₂ CH ₃	CH ₃	H	
	4-CF ₃	4-F	CH ₂ CH ₂ CH ₂ CH ₃	CH ₃	H	
	4-CF ₃	4-CF ₃	CH ₂ CH ₃	CH ₃	H	
20	4-CF ₃	4-Cl	CH ₂ CH ₂ CN	H	H	
	4-CF ₃	4-Cl	CH ₂ CH ₂ CH ₂ CN	H	H	
	4-CF ₃	4-Cl	CH ₂ CH ₂ CN	CH ₃	H	
	4-CN	4-Cl	H	CO ₂ Me	H	192 to 197
	4-Cl	4-Cl	H	CO ₂ Me	H	166 to 168
25	2-F,4-Cl	4-Cl	H	CO ₂ Me	H	160 to 170
	4-Cl	4-CN	H	CO ₂ Me	H	187 to 190
	4-CN	4-CN	H	CO ₂ Me	H	182 to 185
	4-CN	4-CN	CH ₃	CO ₂ Me	H	205 to 215
	2-F,4-Cl	4-CN	CH ₃	CO ₂ Me	H	195 to 197
30	4-CN	4-Cl	CH ₃	CONHMe	H	>250
	4-Cl	4-Cl	H	CONHMe	H	>250

Table 3 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>B</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-F	4-CN	CH ₃	CN	H	200 to 202
	2-F, 4-Cl	4-CN	H	CONH-n-Bu	H	205 to 210
	4-CN	2-F, 4-Cl	CH ₃	CO ₂ Me	H	oil (f)
	4-CN	4-F	CH ₃	CHO	H	116 to 121
	4-F	4-F	CH ₃	CHO	H	122 to 125
10	2,4-di-Cl	4-F	CH ₃	CHO	H	104 to 113
	4-CF ₃	4-F	i-Pr	CHO	H	128 to 131
	4-CN	4-F	i-Pr	CHO	H	182 to 185
	4-F	4-F	i-Pr	CHO	H	124 to 129
	2-F, 4-Cl	4-F	i-Pr	CHO	H	108 to 115
15	4-CF ₃	4-CF ₃	i-Pr	CHO	H	133 to 138
	4-CN	4-CF ₃	i-Pr	CHO	H	foam (g)
	4-CF ₃	4-Cl	i-Pr	CHO	H	145 to 149
	4-CN	4-Cl	i-Pr	CHO	H	160 to 164
	4-CF ₃	4-CN	CH ₃	CO ₂ Me	CH ₃	129 to 130
20	4-Br	4-CF ₃	CH ₃	CO ₂ Me	H	128 to 182
	4-Br	4-CN	CH ₃	CO ₂ Me	H	170 to 173
	4-Br	4-Cl	CH ₃	CO ₂ Me	H	147 to 148
	4-Br	4-Cl	CH ₃	CONHC ₆ H ₄ (p-Br)	H	glass (h)
	4-Br	4-F	CH ₃	CO ₂ Me	H	153 to 157
25	2,4-di-Cl	4-Cl	i-Pr	CHO	H	glass (i)
	4-CF ₃	4-CF ₃	Me	CONHC ₆ H ₄ (p-CF ₃)	H	foam (j)
	4-CN	4-CN	i-Pr	CHO	H	oil (k)
	4-F	4-CN	i-Pr	CHO	H	oil (l)
	4-CF ₃	4-F	n-Bu	CO ₂ Me	CH ₃	oil (m)
30	4-CF ₃	4-Cl	n-Bu	CO ₂ Me	CH ₃	oil (n)
	4-CF ₃	4-CF ₃	n-Bu	CO ₂ Me	CH ₃	oil (o)
	4-I	4-F	CH ₃	CO ₂ Me	H	84 to 85
	4-OCF ₃	2-F, 4-Cl	CH ₃	CO ₂ Me	H	110 to 115
	4-CF ₃	2,4-di-Cl	CH ₃	CO ₂ Me	H	89 to 92
35	4-CF ₃	2,4-di-Cl	CH ₂ C ₆ H ₅	CO ₂ Me	H	oil (p)
	4-F	2,4-di-Cl	CH ₂ C ₆ H ₅	CO ₂ Me	H	oil (q)

Table 3 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>B</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u>
5	4-CF ₃	2,4-di-Cl	CH ₃	CO ₂ Me	H	145 to 146
	4-Br	2,4-di-Cl	CH ₂ C ₆ H ₅	CO ₂ Me	H	oil (r)
	4-CF ₃	2,4-di-Cl	CH ₂ C ₆ H ₅	CO ₂ n-Bu	H	oil (s)
	4-CF ₃	2-F,4-Cl	CH ₃	CO ₂ n-Bu	H	129 to 131
10	4-CF ₃	2-F,4-Cl	CH ₃	CO ₂ Me	H	156 to 160
	4-OCF ₃	2-F,4-Cl	CH ₃	CO ₂ n-Bu	H	123 to 124
	4-CF ₃	2,4-di-Cl	CH ₃	CO ₂ n-Bu	CH ₃	oil (t)
	4-CF ₃	4-F	CH ₃	CO ₂ n-Bu	H	132 to 140
	4-OCF ₃	4-F	CH ₃	CO ₂ n-Bu	H	109 to 111
	4-CO ₂ Me	4-F	CH ₃	CO ₂ n-Bu	H	112 to 114
	4-Br	4-F	CH ₃	CO ₂ n-Bu	H	137 to 139
	4-CF ₃	4-F	CH ₃	CO ₂ n-Bu	CH ₃	oil (u)
15	4-CN	4-F	CH ₃	CO ₂ n-Bu	CH	151 to 153
	4-OCF ₃	4-F	n-Bu	CO ₂ Me	H	84 to 87
	4-Br	4-F	n-Bu	CO ₂ Me	H	125 to 128
	4-Br	4-OCF ₃	CH ₃	CO ₂ Me	H	oil (v)
	4-I	4-F	n-Bu	CO ₂ Me	H	153 to 155
	4-CN	4-F	n-Bu	CO ₂ Me	H	168 to 170
	4-SMe	4-F	n-Bu	CO ₂ Me	H	113 to 115
	4-CF ₃	4-F	n-Bu	CO ₂ Me	H	124 to 126
20	4-CN	4-OCF ₃	CH ₃	CO ₂ Me	H	146 to 149
	4-Br	4-Cl	CH ₂ C ₆ H ₅	CO ₂ Me	H	185 to 187
	4-F	4-Cl	CH ₂ C ₆ H ₅	CO ₂ Me	H	180 to 181
	4-OCF ₃	4-Cl	CH ₂ C ₆ H ₅	CO ₂ Me	H	151 to 155
	4-Br	4-Br	CH ₃	CO ₂ Me	CH ₃	144 to 149
	4-CN	4-Br	CH ₃	CO ₂ Me	CH ₃	foam (w)
25	4-Br	4-Br	CH ₃	CO ₂ Me	H	80 to 83
	4-CF ₃	4-Cl	CH ₃	CO ₂ -t-Bu	CH ₃	131 to 132
	4-CF ₃	4-Br	CH ₃	CONHC ₆ H ₅ (p-CF ₃)	H	foam (x)

Table 3 (continued)

	<u>R₁</u>	<u>R₂</u>	<u>B</u>	<u>A</u>	<u>Y</u>	<u>m.p. (°C)</u> <u>glass (y)</u>
	4-Br	4-Br	CH ₃	CONHC ₆ H ₅ (p-Br)	H	
5	4-OCF ₃	4-Br	CH ₃	CONHC ₆ H ₅ (p-CF ₃)	H	foam (z)
	4-CN	4-Cl	allyl	CO ₂ Me	H	172 to 175.5
	4-SMe	4-Cl	allyl	CO ₂ Me	H	105 to 108.5
	4-CF ₃	4-Cl	allyl	CO ₂ Me	H	oil (aa)
	4-CF ₃	4-Cl	allyl	CO ₂ Me	CH ₃	oil (bb)
10	4-CF ₃	4-Cl	allyl	CO ₂ Me	n-Pr	oil (cc)
	4-Br	4-Cl	allyl	CO ₂ Me	CH ₃	125
	4-CF ₃	4-F	CH ₃	CO ₂ Me	n-Pr	oil (dd)
	4-CF ₃	4-Cl	CH ₃	CO ₂ Me	n-Pr	solid (ee)
	4-Br	4-Cl	allyl	CO ₂ Me	H	oil (ff)
15	4-I	4-Cl	CH ₃	CO ₂ Me	H	
	4-OCF ₃	4-OCF ₃	CH ₃	CO ₂ -t-Bu	H	oil (gg)
	4-CF ₃	4-OCF ₃	CH ₃	CO ₂ -t-Bu	H	oil (hh)
	4-CF ₃	4-Br	CH ₃	CO ₂ -t-Bu	CH ₃	oil (ii)
	4-Br	4-Br	CH ₃	CO ₂ -t-Bu	H	oil (jj)
20	4-OCF ₃	4-Br	CH ₃	CO ₂ -t-Bu	H	oil (kk)
	4-Br	4-OCF ₃	CH ₃	CO ₂ -t-Bu	H	oil (ll)
	4-CF ₃	4-Br	CH ₃	CO ₂ -t-Bu	H	oil (mm)
	4-OCF ₃	4-Br	CH ₃	CO ₂ -t-Bu	H	oil (nn)
	4-Cl	4-Cl	CH ₃	CHO	H	203 to 205
25	4-CF ₃	4-F	CH ₃	CHO	H	178 to 180

Infrared spectra ν_{CO} (CM⁻¹):

	(a)	1740, 1640	(b)	1740, 1635
	(c)	1745, 1640	(d)	1745, 1640
	(e)	1740, 1640	(f)	1745, 1680
30	(g)	1735, 1680	(h)	1670, 1660
	(i)	1730, 1680	(j)	1705, 1685
	(k)	1730, 1670	(l)	1730, 1665
	(m)	1740, 1640	(n)	1740, 1640
	(o)	1745, 1642	(p)	1740, 1675
	(q)	1735, 1670	(r)	1735, 1670
	(s)	1735, 1675	(t)	1740, 1645
	(u)	1740, 1640	(v)	1740, 1665
35	(w)	1740, 1675	(x)	1690, 1670
	(y)	1680, 1660	(z)	1675, 1665
	(aa)	1740, 1680	(bb)	1740, 1640
	(cc)	1740, 1640	(dd)	1740, 1635
	(ee)	1740, 1630	(ff)	1740, 1670
	(gg)	1740, 1675	(hh)	1740, 1675
	(ii)	1740, 1640	(jj)	1730, 1670
	(kk)	1740, 1670	(ll)	1740, 1670
	(mm)	1740, 1670	(nn)	1740, 1670
			(oo)	1740, 1665

	<u>R₁</u>	<u>R₂</u>	<u>A</u>	<u>B</u>	<u>Y</u>	<u>X</u>	<u>m.p. (°C)</u>
	4-CF ₃	4-Cl	4-F-phenyl	H	H	S	169 to 171
5	4-CF ₃	4-Cl	4-F-phenyl	CH ₃	H	S	
	4-CF ₃	4-Cl	4-F-phenyl	H	CH ₃	S	
	4-CF ₃	4-Cl	4-F-phenyl	CH ₃	CH ₃	S	
	4-CF ₃	4-Cl	4-Cl-phenyl	H	H	S	
	4-CF ₃	4-CN	4-Cl-phenyl	H	H	S	
10	4-CF ₃	4-F	4-F-phenyl	H	H	S	
	4-CF ₃	4-F	4-Cl-phenyl	H	H	S	
	4-CF ₃	4-F	4-CN-phenyl	H	H	S	
	4-CF ₃	4-CF ₃	4-F-phenyl	H	H	S	
	4-CF ₃	4-CF ₃	4-Cl-phenyl	H	H	S	
15	4-CF ₃	4-CF ₃	4-CN-phenyl	H	H	S	
	4-CF ₃	4-OCF ₃	4-F-phenyl	H	H	S	
	4-CF ₃	4-OCF ₃	4-Cl-phenyl	H	H	S	
	4-CF ₃	4-OCF ₃	4-CN-phenyl	H	H	S	
20	4-CF ₃	4-H	4-F-phenyl	H	H	S	
	4-CF ₃	4-H	4-Cl-phenyl	H	H	S	
	4-CF ₃	4-H	4-CN-phenyl	H	H	S	
	4-CF ₃	4-CN	4-F-phenyl	H	H	S	
	4-CF ₃	4-CN	4-Cl-phenyl	H	H	S	
	4-CF ₃	4-CN	4-F-phenyl	H	H	S	
25	4-OCF ₃	4-Cl	4-F-phenyl	H	H	S	
	4-OCF ₃	4-Cl	4-Cl-phenyl	H	H	S	
	4-OCF ₃	4-F	4-F-phenyl	H	H	S	
	4-OCF ₃	4-I	4-Cl-phenyl	H	H	S	
	4-OCF ₃	4-CF ₃	4-F-phenyl	H	H	S	
30	4-OCF ₃	4-CF ₃	4-Cl-phenyl	H	H	S	
	4-OCF ₃	4-OCF ₃	4-F-phenyl	H	H	S	
	4-OCF ₃	4-OCF ₃	4-Cl-phenyl	H	H	S	
	4-Cl	4-Cl	4-F-phenyl	H	H	S	
	4-Cl	4-Cl	4-Cl-phenyl	H	H	S	
35	4-Cl	4-F	4-F-phenyl	H	H	S	

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NOT TO BE CONSIDERED
FOR THE PURPOSES OF INTERNATIONAL PROCESSING

see Administrative Instructions

Section 410 (b)

Table 5

	<u>R₂</u>	<u>A</u>	<u>B</u>	<u>X₁</u>	<u>Physical Properties</u>
	4-F	4-Cl-phenyl	H	OH	solid
5	4-F	4-Cl-phenyl	H	Cl	
	4-F	4-F-phenyl	H	OH	
	4-F	4-F-phenyl	H	Cl	
	4-F	4-CN-phenyl	H	OH	$\nu_{CO} = 1680 \text{ cm}^{-1}$
10	4-F	4-CN-phenyl	H	Cl	
	4-Cl	4-Cl-phenyl	H	OH	
	4-Cl	4-Cl-phenyl	H	Cl	
	4-Cl	4-F-phenyl	H	OH	m.p.: 188 to 191°C
	4-Cl	4-F-phenyl	H	Cl	$\nu_{CO} = 1720 \text{ cm}^{-1}$
15	4-Cl	4-CN-phenyl	H	OH	
	4-Cl	4-CN-phenyl	Cl		
	4-Cl	3,4-di-F-phenyl	H	OH	m.p.: 216 to 217°C
	4-Cl	3,4-di-F-phenyl	H	Cl	
	4-Cl	3-Cl-phenyl	H	OH	
20	4-Cl	3-Cl-phenyl	H	Cl	
	4-CF ₃	4-Cl-phenyl	H	OH	
	4-CF ₃	4-Cl-phenyl	H	Cl	
	4-CF ₃	4-F-phenyl	H	OH	
	4-CF ₃	4-F-phenyl	H	Cl	
25	4-Cl	CO ₂ Me	CH ₃	OH	
	4-F	CO ₂ Me	CH ₃	OH	
	4-Cl	4-Cl-phenyl	CH ₃	OH	
	4-Cl	4-Cl-phenyl	CH ₃	Cl	
	4-Cl	4-F-phenyl	CH ₃	OH	
30	4-Cl	4-F-phenyl	CH ₃	Cl	
	4-Cl	4-Cl-phenyl	H	OMe	m.p.: 103 to 106
	4-Cl	4-Cl-phenyl	H	OEt	m.p.: 128 to 130°C
	4-Cl	4-F-phenyl	H	OMe	m.p.: 121 to 123°C
	4-Cl	4-CN-phenyl	H	OMe	m.p.: 134 to 135.5°C
35	4-Cl	4-CF ₃ -phenyl	H	OMe	NMR: 3.8 (OMe)

Table 5 (continued)

	<u>R₂</u>	<u>A</u>	<u>B</u>	<u>X₁</u>	<u>Physical Properties</u>
5	4-Cl	3,4-di-Cl-phenyl	H	OMe	m.p.: 128 to 129°C
	4-Cl	3,4-di-F-phenyl	H	OMe	m.p.: 154 to 156°C
	4-Cl	3-Cl-phenyl	H	OMe	NMR: 3.8 (OMe)
	4-Cl	4-Cl-phenyl	CH ₃	OMe	NMR: 3.8 (OMe)
	4-Cl	4-F-phenyl	CH ₃	OMe	
10	4-F	4-Cl-phenyl	H	OMe	NMR: 3.8 (OMe)
	4-F	4-F-phenyl	H	OMe	m.p.: 88 to 90.5°C
	4-F	4-CN-phenyl	H	OMe	m.p.: 144.5 to 145.5°C
	4-F	3,4-di-F-phenyl	H	OMe	m.p.: 120 to 121.5°C

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Formulation and Use

The compounds of this invention will generally be used in formulation with a carrier comprising a liquid or solid diluent or an organic solvent. Useful formulations of the compounds of Formula I can be prepared in conventional ways. They include dusts, granules, pellets, solutions, suspensions, emulsions, wettable powders, emulsifiable concentrates, dry flowables and the like. Many of these can be applied directly. Sprayable formulations can be extended in suitable media and used at spray volumes of from about one to several hundred liters per hectare. High strength compositions are primarily used as intermediates for further formulation. The formulations, broadly, contain about 1% to 99% by weight of active ingredient(s) and at least one of a) about 0.1% to 20% surfactant(s) and b) about 5% to 99% solid or liquid diluent(s). More specifically, they will contain these ingredients in the following approximate proportions:

	Active Ingredient	<u>Percent by Weight</u>	
		<u>Diluent(s)</u>	<u>Surfactant(s)</u>
Wettable Powders	25-90	0-74	1-10
Oil Suspensions, Emulsions, Solutions, (including Emulsifiable Concentrates)	1-50	40-95	0-35
Dusts	1-25	70-99	0-5
Granules and Pellets	1-95	5-99	0-15
High Strength Compositions	90-99	0-10	0-2

Lower or higher levels of active ingredient can, of course, be present depending on the intended use and the physical properties of the compound. Higher ratios of surfactant to active ingredient are some-

times desirable, and are achieved by incorporation into the formulation or by tank mixing.

Typical solid diluents are described in Watkins, et al., "Handbook of Insecticide Dust Diluents and Carriers", 2nd Ed., Dorland Books, Caldwell, New Jersey. The more absorptive diluents are preferred for wettable powders and the denser ones for dusts. Typical liquid diluents and solvents are described in Marsden, "Solvents Guide," 2nd Ed., Interscience, New York, 1950. Solubility under 0.1% is preferred for suspension concentrates; solution concentrates are preferably stable against phase separation at 0°C. "McCutcheon's Detergents and Emulsifiers Annual", Allured Publ. Corp., Ridgewood, New Jersey, as well as Sisely and Wood, "Encyclopedia of Surface Active Agents", Chemical Publ. Co., Inc., New York, 1964, list surfactants and recommended uses. All formulations can contain minor amounts of additives to reduce foam, caking, corrosion, microbiological growth, etc. Preferably, ingredients should be approved by the U.S. Environmental Protection Agency for the use intended.

The methods of making such compositions are well known. Solutions are prepared by simply mixing the ingredients. Fine solid compositions are made by blending and, usually, grinding as in a hammer or fluid energy mill. Suspensions are prepared by wet milling (see, for example, U.S. 3,060,084). Granules and pellets can be made by spraying the active material upon preformed granular carriers or by agglomeration techniques. See Browning, "Agglomeration", Chemical Engineering, December 4, 1967, pages 147 and following, and "Perry's Chemical Engineer's Handbook", 4th Ed., McGraw-Hill, New York, 1963, pages 8 to 59 and following.

Many of the compounds of the invention are most efficacious when applied in the form of an emulsifiable concentrate mixed with a spray oil or spray oil concentrate. Although any oil can be used as a spray oil, spray oils usually have these characteristics: they are not phytotoxic to the crop sprayed, and they have appropriate viscosity. Petroleum based oils are commonly used for spraying. In some areas, crop oils are preferred such as the following:

Common Crop Oils Used as Spray Oils

	Corn Oil	Linseed Oil
	Cottonseed Oil	Soybean Oil
	Coconut Oil	Sunflower Oil
	Rapeseed Oil	Olive Oil
15	Peanut Oil	Palm Oil
	Safflower Oil	Sesame Oil
	Mustardseed Oil	Caster Oil

The following oils also meet the criteria for a spray oil: mineral, fish and cod liver oil.

Spray oil concentrates comprise a spray oil together with one or more additional ingredients such as emulsifiers and wetting agents. A number of useful spray oil and spray oil concentrates can be found in "A Guide to Agricultural Spray Adjuvants Used in the United States" by Thomson, Thomson Publications, California, 1986.

Examples of useful formulations of compounds of the present invention are as follows:

Example 23

Emulsifiable Concentrate

	N,5-bis(4-chlorophenyl)-1-(4-fluorophenyl)-4,5-dihydro-1H-pyrazole-3-carboxamide	20%
	blend of oil soluble sulfonates	
	and polyoxyethylene ethers	10%
35	isophorone	70%

101

The ingredients are combined and stirred with gentle warming to speed solution. A fine screen filter is included in packaging operation to insure the absence of any extraneous undissolved material in the product.

Example 24

Wettable Powder

10	Methyl 1-(4-chlorophenyl)-4,5-dihydro-5-methyl-3- [[4-(trifluoromethyl)phenyl]aminocarbonyl]-1H- pyrazole-5-carboxylate	30%
	sodium alkyl naphthalenesulfonate	2%
	sodium ligninsulfonate	2%
15	synthetic amorphous silica	3%
	kaolinite	63%

The active ingredient is mixed with the inert materials in a blender. After grinding in a hammer-mill, the material is re-blended and sifted through a 50 mesh screen.

Example 25

Dust

	Wettable powder of Example 24	10%
	pyrophyllite (powder)	90%

The wettable powder and the pyrophyllite diluent are thoroughly blended and then packaged. The product is suitable for use as a dust.

Example 26

Granule

30	1,5-bis(4-chlorophenyl)-4,5-dihydro-N-[4-(trifluoro- methyl)phenyl]-1H-pyrazole-3-carboxamide	10%
	attapulgit granules (low volatile matter, 0.71/0.30 mm; U.S.S. No. 25-50 sieves)	90%

The active ingredient is dissolved in a volatile solvent such as acetone and sprayed upon dedusted and pre-warmed attapulgit granules in a double cone blender. The acetone is then driven off by heating. The granules are then allowed to cool and are packaged.

Example 27Granule

5	Wettable powder of Example 24	15%
	gypsum	69%
	potassium sulfate	16%

The ingredients are blended in a rotating mixer and water sprayed on to accomplish granulation. When most of the material has reached the desired range of 0.1 to 0.42 mm (U.S.S. No. 18 to 40 sieves), the granules are removed, dried, and screened. Oversize material is crushed to produce additional material in the desired range. These granules contain 4.5% active ingredient.

Example 28Solution

	N,5-bis(4-chlorophenyl)-1-(4-fluorophenyl)-4,5-dihydro-1H-pyrazole-3-carboxamide	25%
20	N-methyl-pyrrolidone	75%

The ingredients are combined and stirred to produce a solution suitable for direct, low volume application.

Example 29Aqueous Suspension

25	Methyl 1-(4-chlorophenyl)-4,5-dihydro-5-methyl-3-[[4-(trifluoromethyl)phenyl]aminocarbonyl]-1H-pyrazole-5-carboxylate	40%
30	polyacrylic acid thickener	0.3%
	dodecyclophenol polyethylene glycol ether	0.5%
	disodium phosphate	1.0%
	monosodium phosphate	0.5%
35	polyvinyl alcohol	1.0%
	water	56.7%

The ingredients are blended and ground together in a sand mill to produce particles essentially all under 5 microns in size.

Example 30

Oil Suspension

	Methyl 1-(4-chlorophenyl)-4,5-dihydro-5-methyl-3-[[4-(trifluoromethyl)phenyl]aminocarbonyl]-1H-pyrazole-5-carboxylate	35.0%
10	blend of polyalcohol carboxylic esters and oil soluble petroleum sulfonates	6.0%
15	xylene range solvent	59.0%

The ingredients are combined and ground together in a sand mill to produce particles essentially all below 5 microns. The product can be used directly, extended with oils, or emulsified in water.

Example 31

20

Bait Granules

	Methyl 1-(4-chlorophenyl)-4,5-dihydro-5-methyl-3-[[4-(trifluoromethyl)phenyl]aminocarbonyl]-1H-pyrazole-5-carboxylate	3.0%
25	blend of polyethoxylated nonylphenols and sodium dodecylbenzene sulfonates	9.0%
	ground up corn cobs	88.0%

30 The active ingredient and surfactant blend are dissolved in a suitable solvent such as acetone and sprayed onto the ground corn cobs. The granules are then dried and packaged.

35 Compounds of Formula I can also be mixed with one or more other insecticides, fungicides, nematocides, bactericides, acaricides, or other biologically active compounds to form a multi-component pesticide giving

an even broader spectrum of effective agricultural protection. Examples of other agricultural protectants with which compounds of the present invention can be mixed or formulated are:

5 Insecticides:

- 3-hydroxy-N-methylcrotonamide(dimethylphosphate)ester
(monocrotophos)
methylcarbamic acid, ester with 2,3-dihydro-2,2-
dimethyl-7-benzofuranol (carbofuran)
10 O-[2,4,5-trichloro- α -(chloromethyl)benzyl]phosphoric
acid, O',O'-dimethyl ester (tetrachlorvinphos)
2-mercaptosuccinic acid, diethyl ester, S-ester with
thionophosphoric acid, dimethyl ester (malathion)
phosphorothioic acid, O,O-dimethyl, O-p-nitrophenyl
15 ester (methyl parathion)
methylcarbamic acid, ester with α -naphthol (carbaryl)
methyl O-(methylcarbamoyl)thiolacetohydroxamate
(methomyl)
N'-(4-chloro-o-tolyl)-N,N-dimethylformamidine
20 (chlordimeform)
O,O-diethyl-O-(2-isopropyl-4-methyl-6-pyrimidylphos-
phorothioate (diazinon)
octachlorocamphene (toxaphene)
O-ethyl O-p-nitrophenyl phenylphosphonothioate (EPN)
25 (S)- α -cyano-m-phenoxybenzyl(1R,3R)-3-(2,2-dibromo-
vinyl)-2,2-dimethylcyclopropanecarboxylate (delta-
methrin)
Methyl N',N'-dimethyl-N-[(methylcarbamoyl)oxy]-1-thio-
oxamimidate (oxamyl)
30 cyano(3-phenoxyphenyl)-methyl-4-chloro- α -(1-methyl-
ethyl)benzeneacetate (fenvalerate)
(3-phenoxyphenyl)methyl(+)-cis,trans-3-(2,2-dichloro-
ethenyl)-2,2-dimethylcyclopropanecarboxylate
(permethrin)
35 α -cyano-3-phenoxybenzyl 3-(2,2-dichloro-yl)-2,2-
dimethylcyclopropane carboxylate (cyflumethrin)

O-ethyl-S-(p-chlorophenyl)ethylphosphonodithioate
(profenofos)
phosphorothiolothionic acid, O-ethyl-O-[4-(methylthio)-
phenyl]-S-n-propyl ester (sulprofos).

- 5 Additional insecticides are listed hereafter by their
common names: triflumuron, diflubenzuron, methoprene,
buprofezin, thiodicarb, acephate, azinphos-methyl,
chlorpyrifos, dimethoate, fonophos, isofenphos,
methidathion, methamidophos, monocrotophos, phosmet,
10 phosphamidon, phosalone, pirimicarb, phorate,
profenofos, terbufos, trichlorfon, methoxychlor,
bifenthrin, biphenate, cyfluthrin, fenpropathrin,
fluvalinate, flucythrinate, tralomethrin, metaldehyde
and rotenone.

15 Fungicides:

- methyl 2-benzimidazolecarbamate (carbendazim)
tetramethylthiuram disulfide (thiuram)
n-dodecylguanidine acetate (dodine)
manganese ethylenebisdithiocarbamate (maneb)
20 1,4-dichloro-2,5-dimethoxybenzene (chloroneb)
methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate
(benomyl)
1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-
ylmethyl]-1H-1,2,4-triazole (propiconazole)
25 2-cyano-N-ethylcarbamoyl-2-methoxyiminoacetamide
(cymoxanil)
1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-
1-yl)-2-butanone (triadimefon)
N-(trichloromethylthio)tetrahydrophthalimide (captan)
30 N-(trichloromethylthio)phthalimide (folpet)
1-[[[bis(4-fluorophenyl)][methylsilyl]methyl]-1H-
1,2,4-triazole.

Nematocides:

- S-methyl 1-(dimethylcarbamoyl)-N-(methylcarbamoyloxy)-
35 thioformimidate

S-methyl 1-carbamoyl-N-(methylcarbamoyloxy)thioformimide

- 5 N-isopropylphosphoramidic acid, O-ethyl O'-[4-(methylthio)-m-tolyl]diester (fenamiphos).

Bactericides:

tribasic copper sulfate
streptomycin sulfate.

- 10 Acaricides:

senecioic acid, ester with 2-sec-butyl-4,6-dinitrophenol (binapacryl)

6-methyl-1,3-dithiolo[4,5- β]quinoxalin-2-one
(oxythioquinox)

- 15 ethyl 4,4'-dichlorobenzilate (chlorobenzilate)
1,1-bis(p-chlorophenyl)-2,2,2-trichloroethanol
(dicofol)

bis(pentachloro-2,4-cyclopentadien-1-yl) (dienochlor)
tricyclohexyltin hydroxide (cyhexatin)

- 20 trans-5-(4-chlorophenyl)-N-cyclohexyl-4-methyl-2-oxo-
thiazolidine-3-carboxamide (hexythiazox)

amitraz

propargite

fenbutatin-oxide

- 25 biscalofentezin.

Biological

Bacillus thuringiensis

Avermectin B.

- 30 Utility

The compounds of the present invention exhibit activity against a wide spectrum of foliar and soil inhabiting insects. Those skilled in the art will recognize that not all compounds are equally effective against all insects, but the compounds of this invention display activity against economically

35

important pest species, such as grasshoppers and cockroaches; thrips; hemipterans: plant bugs (Miridae), such as tarnished plant bug, lace bugs (Tingidae), seed bugs (Lygaeidae) such as cinch bugs, stink bugs (Pentatomidae), leaf-footed bugs (Coreidae), such as squash bug, and red bugs and stainers (Pyrrhocoridae) such as cotton stainer; also homopterans such as whiteflies, leafhoppers, spittlebugs and planthoppers such as aster leafhopper, potato leafhopper and rice planthoppers, psyllids such as pear psylla, scales (coccids and diaspidids) and mealybugs; coleopterans including weevils, such as boll weevil and rice water weevil, grain borers, chrysomellid beetles, such as Colorado potato beetle, flea beetles and other leaf beetles, coccinellid beetles such as Mexican bean beetle, and soil insects such as southern corn rootworm and wireworm; lepidopterous larvae including noctuids such as fall armyworm, beet armyworm, other Spodoptera spp., Heliothis virescens, Heliothis zea, cabbage looper, green cloverworm, velvetbean caterpillar, cotton leafworm, black cutworm, and other noctuid cutworms and including pyralids such as European corn borer, navel orangeworm, and stalk/stem borers and including tortricids like codling moth and grape berry moth as well as pink bollworm and diamondback moth; and dipterans such as leafminers, soil maggots, midges, tephritid fruit flies. The specific species, for which control is exemplified below, are: fall armyworm, Spodoptera frugiperda; tobacco budworm, Heliothis virescens; boll weevil, Anthonomus grandis; European corn borer, Ostrinia nubilalis; southern corn rootworm, Diabrotica undecimpunctata howardi; and

aster leafhopper, Macrosteles fascifrons. The pest control afforded by the compounds of the present invention is not limited, however, to these species.

Application

Insects are controlled and agricultural crops are protected by applying one or more of the Formula I compounds of this invention, in an effective amount, to the locus of infestation, to the area to be protected, or directly on the pests to be controlled. A preferred method of application is by spraying with spray equipment that distributes the compound on the foliage, in the soil, or to the plant part that is infested or needs to be protected. Alternatively, granular formulations of these compounds can be applied to soil or foliage or, optionally, incorporated into the soil. Either aerial or ground application can be used.

The pyrazoline compound(s) of this invention can be applied directly, but most often application will be of a formulation comprising one or more compounds of this invention, in an agriculturally suitable carrier or diluent. A most preferred method of application involves spraying a water dispersion or refined oil solution of the compounds. Combinations with spray oils and spray oil concentrates often enhance the efficacy of the compounds of Formula I.

The rate of application of the Formula I compounds required for effective control will depend on such factors as the species of insect to be controlled, the pest's life stage, its size, its location, the host crop, time of year of application, ambient moisture, temperature conditions, and the like. In general, application rates of 0.05 to 2 kg

of active ingredient per hectare are sufficient to provide effective control in large scale field operations under normal circumstances, but as little as 0.01 kg/hectare may be sufficient or as much as 8 kg/hectare may be required, depending upon the factors listed above. The addition of a compound such as piperonyl butoxide, can enhance the insecticidal activity of the compounds of Formula I.

The following Examples demonstrate the control efficacy of compounds of Formula I on specific insect pests wherein Compounds 1 through 476 and Compounds 1A through 132A are described in Tables 6 and 7, respectively.

Structures for Biological Tables

Table 6

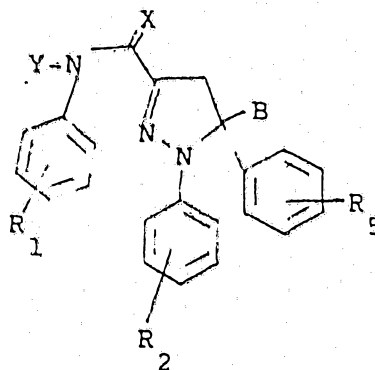


Table 7

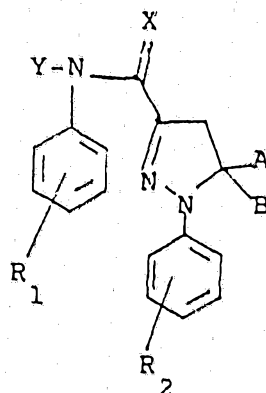


Table 6

5	Compound #	R ₂	R ₅	R ₁	B	Y	X
	1	4-F	4-Cl	4-Cl	H	H	O
	2	4-Cl	4-OMe	H	H	H	O
	3	4-CF ₃	4-Cl	4-Cl	H	H	O
10	4	4-Cl	4-Cl	4-Cl	H	H	O
	5	4-Cl	4-Cl	4-CF ₃	H	H	O
	6	4-Cl	4-CN	4-Cl	H	H	O
	7	4-Cl	4-Br	4-Cl	H	H	O
	8	4-Cl	4-Br	4-CF ₃	H	H	O
15	9	4-Cl	4-OMe	4-Cl	H	H	O
	10	4-Cl	4-Cl	4-COOEt	H	H	O
	11	4-Cl	4-Cl	4-I	H	H	O
	12	4-Cl	4-Cl	4-F	H	H	O
	13	4-Cl	4-Cl	4-OC ₆ H ₄ p-Cl	H	H	O
20	14	4-Cl	4-Cl	4-CN	H	H	O
	15	4-Cl	4-Cl	3-CF ₃	H	H	O
	16	4-Cl	4-Cl	4-CF ₃	Me	H	O
	17	4-Cl	3-Cl	4-Cl	H	H	O
	18	4-Cl	3-Cl	4-CF ₃	H	H	O
25	19	4-Cl	2-Cl	4-Cl	H	H	O
	20	4-Cl	2-Cl	4-CF ₃	H	H	O
	21	4-OMe	4-Cl	4-CF ₃	H	H	O
	22	4-OMe	4-Cl	4-Cl	H	H	O
	23	4-Cl	4-CN	4-CF ₃	H	H	O
30	24	4-Cl	4-Me	4-CF ₃	H	H	O
	25	4-Cl	4-Me	4-F	H	H	O
	26	4-Cl	4-CF ₃	4-CF ₃	H	H	O
	27	4-Cl	4-CF ₃	4-F	H	H	O
	28	4-Cl	3,4-di-Cl	4-CF ₃	H	H	O
35	29	4-Cl	3,4-di-Cl	4-F	H	H	O
	30	4-Cl	4-F	4-CF ₃	H	H	O

Table 6 (continued)

5	Compound #	R ₂	R ₅	R ₁	B	Y	X
	31	4-Cl	4-F	4-F	H	H	O
	32	4-F	4-Cl	4-CF ₃	H	H	O
	33	4-F	4-Cl	4-F	H	H	O
10	34	H	4-Cl	4-CF ₃	H	H	O
	35	H	4-Cl	4-F	H	H	O
	36	3-Cl	4-Cl	4-CF ₃	H	H	O
	37	3-Cl	4-Cl	4-F	H	H	O
	38	2-Cl	4-Cl	4-CF ₃	H	H	O
15	39	2-Cl	4-Cl	4-F	H	H	O
	40	4-F	4-SMe	4-CF ₃	H	H	O
	41	4-F	4-F	4-CF ₃	H	H	O
	42	4-F	4-F	4-F	H	H	O
	43	4-F	4-CN	4-CF ₃	H	H	O
20	44	4-F	4-CN	4-F	H	H	O
	45	4-F	4-CN	4-Cl	H	H	O
	46	H	4-CN	4-CF ₃	H	H	O
	47	H	4-CN	4-F	H	H	O
	48	H	4-CN	4-Cl	H	H	O
25	49	4-Cl	4-CH ₂ CN	4-Cl	H	H	O
	50	4-F	H	4-Cl	H	H	O
	51	4-Cl	4-Cl	4-CF ₃	H	COMe	O
	52	4-Cl	4-Cl	4-CF ₃	H	Me	O
	54	4-CF ₃	4-Cl	4-Cl	Me	H	O
30	55	4-CF ₃	4-Cl	4-F	Me	H	O
	56	4-F	4-Cl	4-Cl	Me	H	O
	57	3-Cl	4-Cl	4-Cl	Me	H	O
	58	3-Cl	4-Cl	3-Cl	Me	H	O
	59	4-Cl	4-Cl	4-CF ₃	H	COOMe	O
35	60	4-Cl	4-Cl	4-CF ₃	H	Et	O

Table 6 (continued)

5	Compound #	R ₂	R ₅	R ₁	B	Y	X
	61	4-Cl	4-Cl	4-CF ₃	H	CH ₂ COOMe	O
	62	4-Cl	4-Cl	4-OMe	H	H	O
	63	4-Cl	4-Cl	4-i-Pr	H	H	O
10	64	4-Cl	4-Cl	4-Me	H	H	O
	65	4-Cl	4-Cl	4-OCF ₂ CF ₂ H	H	H	O
	66	4-Cl	4-Cl	3,4-di-Cl	H	H	O
	67	4-Cl	4-Cl	2-F,4-Cl	H	H	O
	68	4-Cl	4-Cl	4-NO ₂	H	H	O
15	69	4-Cl	4-Cl	4-Br	H	H	O
	70	4-CN	4-Br	2,5-di-F	H	H	O
	71	4-CN	4-Br	3,5-di-NO ₂	H	H	O
	72	4-CN	4-Br	2,3,4-tri-Cl	H	H	O
	73	4-CN	4-Br	4-Et	H	H	O
20	74	4-CN	4-Br	3-CF ₃ ,4-F	H	H	O
	75	4-CN	4-Br	4-C ₆ H ₅	H	H	O
	76	4-CN	4-Br	4-cyclohexyl	H	H	O
	77	4-CN	4-Br	4-CF ₃	H	H	O
	78	4-CN	4-Br	3-CF ₃	H	H	O
25	79	4-CN	4-Br	2-CF ₃	H	H	O
	80	4-CN	4-Br	4-CN	H	H	O
	81	4-CN	4-Br	3-CN	H	H	O
	82	4-CN	4-Br	2-CN	H	H	O
30	83	4-CN	4-Br	4-Cl	H	H	O
	84	4-CN	4-Br	3-Cl	H	H	O
	85	4-CN	4-Br	2-Cl	H	H	O
	86	4-CN	4-Br	4-F	H	H	O
	87	4-CN	4-Br	3-F	H	H	O
35	88	4-CN	4-Br	2-F	H	H	O
	89	4-CF ₃	4-F	4-CF ₃	H	H	O
	90	4-CF ₃	4-F	3-CF ₃	H	H	O

Table 6 (continued)

5	Compound #	<u>R₂</u>	<u>R₅</u>	<u>R₁</u>	<u>B</u>	<u>Y</u>	<u>X</u>
	91	4-CF ₃	4-F	4-CN	H	H	O
	92	4-CF ₃	4-F	3-CN	H	H	O
	93	4-CF ₃	4-F	4-F	H	H	O
10	94	4-CF ₃	4-F	3-F	H	H	O
	95	4-Cl	4-CN	4-NO ₂	H	H	O
	96	4-Cl	4-CN	4-Br	H	H	O
	97	4-Cl	4-OMe	3-Cl	H	H	O
	98	4-Cl	4-OMe	3-CF ₃	H	H	O
15	99	4-Cl	4-OMe	3-CF ₃ , 4-F	H	H	O
	100	4-Cl	4-OMe	4-F	H	H	O
	101	4-Cl	4-OMe	4-CN	H	H	O
	102	4-Cl	4-OMe	3-CN	H	H	O
	103	4-Cl	4-OMe	2,5-di-F	Me	H	O
20	104	4-Cl	4-Cl	3,5-di-NO ₂	Me	H	O
	105	4-Cl	4-Cl	2,3,4-tri-Cl	Me	H	O
	106	4-Cl	4-Cl	4-Et	Me	H	O
	107	4-Cl	4-Cl	3-CF ₃ , 4-F	Me	H	O
	108	4-Cl	4-Cl	4-cyclohexyl	Me	H	O
25	109	4-Cl	4-Cl	3-CN	Me	H	O
	110	4-Cl	4-Cl	2-CN	Me	H	O
	111	4-Cl	4-Cl	4-Cl	Me	H	O
	112	4-Cl	4-Cl	2-Cl	Me	H	O
	113	4-i-Pr	4-Cl	4-CF ₃	H	H	O
30	114	4-i-Pr	4-Cl	4-Cl	H	H	O
	115	4-i-Pr	4-Cl	4-OMe	H	H	O
	116	4-Me	4-Cl	4-CF ₃	H	H	O
	117	4-Me	4-Cl	4-Cl	H	H	O
	118	4-Me	4-Cl	4-OMe	H	H	O
35	119	4-Me	4-Cl	4-i-Pr	H	H	O
	120	4-i-Pr	4-Cl	4-NO ₂	H	H	O
	121	4-i-Pr	4-Cl	4-i-Pr	H	H	O

Table 6 (continued)

5	Compound #	R ₂	R ₅	R ₁	B	Y	X
	122	4-Cl	4-Cl	4-F	Me	H	O
	123	4-Cl	4-Cl	3-F	Me	H	O
	124	4-Cl	4-Cl	2-F	Me	H	O
10	125	4-Cl	4-Cl	2-Me, 4-Cl	Me	H	O
	126	4-CN	4-F	2,5-di-F	H	H	O
	127	4-CN	4-F	3,5-di-NO ₂	H	H	O
	128	4-CN	4-F	4-Et	H	H	O
	129	4-CN	4-F	3-CF ₃ , 4-F	H	H	O
15	130	4-CN	4-F	4-OC ₆ H ₅	H	H	O
	131	4-CN	4-F	4-CF ₃	H	H	O
	132	4-CN	H	4-CF ₃	H	H	O
	133	4-CN	H	4-t-Bu	H	H	O
	134	4-CN	H	4-Cl	H	H	O
20	135	4-CN	H	4-CN	H	H	O
	136	4-CN	4-F	2,3,4-tri-Cl	H	H	O
	137	4-CN	4-F	3-CF ₃	H	H	O
	138	4-CN	4-F	4-Cl	H	H	O
	139	4-CN	4-F	3-Cl	H	H	O
25	140	4-CN	4-F	2-Cl	H	H	O
	141	4-CN	4-F	4-F	H	H	O
	142	4-CN	4-F	3-F	H	H	O
	143	4-CN	4-F	2-F	H	H	O
	144	4-CF ₃	4-OC ₆ H ₅	2,3,4-tri-Cl	H	H	O
30	145	4-CF ₃	4-OC ₆ H ₅	3-CF ₃ , 4-F	H	H	O
	146	4-CF ₃	4-OC ₆ H ₅	4-OC ₆ H ₅	H	H	O
	147	4-CF ₃	4-OC ₆ H ₅	4-CF ₃	H	H	O
	148	4-CF ₃	4-OC ₆ H ₅	3-CF ₃	H	H	O
	149	4-CF ₃	4-OC ₆ H ₅	4-CN	H	H	O
35	150	4-CF ₃	4-OC ₆ H ₅	3-CN	H	H	O
	151	4-CF ₃	4-OC ₆ H ₅	4-Cl	H	H	O
	152	4-CF ₃	4-OC ₆ H ₅	3-Cl	H	H	O

Table 6 (continued)

5	Compound #	R ₂	R ₅	R ₁	B	Y	X
	153	4-CF ₃	4-OC ₆ H ₅	4-F	H	H	O
	154	4-Cl	4-Cl	4-COMe	H	H	O
	155	4-Cl	4-Cl	4-C ₆ H ₅	H	H	O
10	156	4-Cl	4-Cl	4-O-s-Bu	H	H	O
	157	4-Cl	4-Cl	3,4-OCH ₂ O	H	H	O
	158	4-Cl	4-Cl	3-F,5-F	H	H	O
	159	3-CF ₃	4-Cl	2,3,4-tri-Cl	Me	H	O
	160	3-CF ₃	4-Cl	3-CF ₃ ,4-F	Me	H	O
15	161	3-CF ₃	4-Cl	4-OC ₆ H ₅	Me	H	O
	162	3-CF ₃	4-Cl	4-CF ₃	Me	H	O
	163	3-CF ₃	4-Cl	3-CF ₃	Me	H	O
	164	3-CF ₃	4-Cl	4-CN	Me	H	O
	165	3-CF ₃	4-Cl	3-CN	Me	H	O
20	166	3-CF ₃	4-Cl	4-Cl	Me	H	O
	167	3-CF ₃	4-Cl	3-Cl	Me	H	O
	168	3-CF ₃	4-Cl	4-F	Me	H	O
	169	4-CF ₃	3-CN	2,3,4-tri-Cl	H	H	O
	170	4-CF ₃	3-CN	3-CF ₃ ,4-F	H	H	O
25	171	4-CF ₃	3-CN	4-OC ₆ H ₅	H	H	O
	172	4-CF ₃	3-CN	4-CF ₃	H	H	O
	173	4-CF ₃	3-CN	3-CF ₃	H	H	O
	174	4-CF ₃	3-CN	4-CN	H	H	O
	175	4-CF ₃	3-CN	3-CN	H	H	O
30	176	4-CF ₃	3-CN	4-Cl	H	H	O
	177	4-CF ₃	3-CN	3-Cl	H	H	O
	178	4-CF ₃	3-CN	4-F	H	H	O
	179	4-OCF ₂ CF ₂ H	4-Cl	4-CF ₃	H	H	O
	180	4-OCF ₂ CF ₂ H	4-Cl	4-Cl	H	H	O
35	181	4-OCF ₂ CF ₂ H	4-Cl	4-OCF ₂ CF ₂ H	H	H	O
	182	4-OCF ₂ CF ₂ H	4-Cl	4-i-Pr	H	H	O

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NOT TO BE CONSIDERED
FOR THE PURPOSES OF INTERNATIONAL PROCESSING

see Administrative Instructions

Section 410 (b)

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NOT TO BE CONSIDERED
FOR THE PURPOSES OF INTERNATIONAL PROCESSING

see Administrative Instructions

Section 410 (b)

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NOT TO BE CONSIDERED
FOR THE PURPOSES OF INTERNATIONAL PROCESSING

see Administrative Instructions

Section 410 (b)

Table 6 (continued)

5	Compound	<u>R₂</u>	<u>R₅</u>	<u>R₁</u>	<u>B</u>	<u>Y</u>	<u>X</u>
	303	4-Cl	4-F	4-Cl	H	H	0
	304	4-Cl	4-F	4-OCF ₃	H	H	0
	305	4-Cl	4-F	4-SCH ₃	H	H	0
10	306	4-Cl	4-F	4-COOEt	H	H	0
	307	3,4-di-Cl	4-F	4-CF ₃	H	H	0
	308	3,4-di-Cl	4-F	4-OCF ₃	H	H	0
	309	3,4-di-Cl	4-F	4-C ₆ H ₅	H	H	0
	310	3,4-di-Cl	4-F	4-SO ₂ NH ₂	H	H	0
15	311	3,4-di-Cl	4-F	4-OEt	H	H	0
	312	4-CF ₃	4-COCF ₃	4-CF ₃	H	H	0
	313	4-CF ₃	4-COCF ₃	4-CH ₃	H	H	0
	314	4-CF ₃	4-COCF ₃	4-Cl	H	H	0
	315	4-CF ₃	4-COCF ₃	4-F	H	H	0
20	316	4-CF ₃	4-COCF ₃	4-t-Bu	H	H	0
	317	4-CF ₃	4-COCF ₃	4-COMe	H	H	0
	318	4-Cl	2-Cl	4-SO ₂ NH ₂	H	H	0
	319	3-Cl	4-F	4-F	H	H	0
	320	3-Cl	4-F	4-CF ₃	H	H	0
25	321	4-Cl	2-Cl	3-SO ₂ NH ₂	H	H	0
	322	2-Cl	4-F	3-Cl	H	H	0
	323	2-Cl	4-F	2-CN	H	H	0
	324	4-Cl	2-Cl	2-SO ₂ NH ₂	H	H	0
	325	2-CN	4-F	3-OMe	H	H	0
30	326	2-CN	4-F	4-OMe	H	H	0
	327	2-CN	4-F	2-Cl	H	H	0
	328	2-CN	4-F	3-Cl	H	H	0
	329	2-CN	4-F	4-Cl	H	H	0
	330	2-CN	4-F	3-SO ₂ NH ₂	H	H	0
35	331	2-CN	4-F	4-SO ₂ NH ₂	H	H	0
	332	2-CN	4-F	2-CN	H	H	0

Table 6 (continued)

5	Compound #	R_2	R_5	R_1	$\underline{B}$	$\underline{Y}$	$\underline{Z}$
	333	2-CN	4-F	3-CN	H	H	O
	334	2-CN	4-F	4-CN	H	H	O
	335	2-CN	4-F	4-t-Bu	H	H	O
10	336	2-CN	4-F	4-CF ₃	H	H	O
	337	4-Cl	3-Cl	2-OMe	H	H	O
	338	4-Cl	3-Cl	3-OMe	H	H	O
	339	4-Cl	3-Cl	4-OMe	H	H	O
	340	4-Cl	3-Cl	2-Cl	H	H	O
15	341	4-Cl	3-Cl	3-Cl	H	H	O
	342	4-Cl	3-Cl	2-SO ₂ NH ₂	H	H	O
	343	4-Cl	3-Cl	3-SO ₂ NH ₂	H	H	O
	344	4-Cl	3-Cl	2-CN	H	H	O
	345	4-Cl	3-Cl	3-CN	H	H	O
20	346	4-Cl	3-Cl	4-t-Bu	H	H	O
	347	4-Cl	3-Cl	2-CH ₂ C ₆ H ₅	H	H	O
	348	4-Cl	3-Cl	4-CN	H	H	O
	349	4-Cl	3-Cl	4-COO-n-Pr	H	H	O
	350	4-Cl	3-Cl	3,5-Cl	H	H	O
25	351	4-Cl	4-F	4-CF ₃	H	COOMe	O
	352	4-Cl	4-F	4-CF ₃	H	Me	O
	353	4-Cl	4-F	4-COO-n-Pr	H	H	O
	354	4-Cl	4-F	4-CF ₃	H	H	S
	355	4-CF ₃	4-COOH	4-CF ₃	H	H	O
30	356	4-CF ₃	4-COOH	4-CN	H	H	O
	357	4-CF ₃	4-COOH	4-Cl	H	H	O
	358	4-CF ₃	4-COOH	4-F	H	H	O
	359	4-CF ₃	4-COOH	4-t-Bu	H	H	O
	360	4-CF ₃	4-CF ₃	4-CF ₃	H	H	O
35	361	4-CF ₃	4-CF ₃	4-Cl	H	H	O
	362	4-CF ₃	C ₂ H ₃	4-CF ₃	H	H	O

Table 6 (continued)

5	Compound #	R_2	R_5	R_1	B	Y	X
	363	4-NO ₂	4-F	4-CF ₃	H	H	O
	364	4-NH ₂	4-F	4-CF ₃	H	H	O
	365	4-SO ₂ CH ₃	4-F	4-CF ₃	H	H	O
10	366	4-Cl	3-Cl	3-SO ₂ NH ₂	H	H	O
	367	2-OMe	4-F	4-CN	H	H	O
	368	2-OMe	4-F	2-CH ₂ C ₆ H ₅	H	H	O
	369	2-OMe	4-F	4-CF ₃	H	H	O
	370	2-OMe	4-F	2-OMe	H	H	O
15	371	2-OMe	4-F	4-OMe	H	H	O
	372	2-OMe	4-F	2-Cl	H	H	O
	373	2-OMe	4-F	4-Cl	H	H	O
	374	2-OMe	4-F	4-SO ₂ NH ₂	H	H	O
	375	2-OMe	4-F	2-CN	H	H	O
20	376	2-OMe	4-F	3-OMe	H	H	O
	377	2-OMe	4-F	3-Cl	H	H	O
	378	4-Cl	2-OMe	3-OMe	H	H	O
	379	2-OMe	4-F	4-t-Bu	H	H	O
	380	2-OMe	4-F	3-CH	H	H	O
25	381	4-Cl	2-OMe	4-OMe	H	H	O
	382	4-Cl	2-OMe	2-Cl	H	H	O
	383	4-Cl	2-OMe	3-Cl	H	H	O
	384	4-Cl	2-OMe	4-Cl	H	H	O
	385	4-Cl	2-OMe	2-CO ₂ NH ₂	H	H	O
30	386	4-Cl	2-OMe	2-SO ₂ NH ₂	H	H	O
	387	4-Cl	2-OMe	2-OMe	H	H	O
	388	4-Cl	2-OMe	2-CN	H	H	O
	389	4-Cl	2-OMe	3-CN	H	H	O
	390	4-Cl	2-OMe	4-CN	H	H	O
35	391	4-Cl	2-OMe	2-CH ₂ C ₆ H ₅	H	H	O
	392	4-Cl	2-OMe	4-CF ₃	H	H	O
	393	4-Cl	2-OMe	3-SO ₂ NH ₂	H	H	O

Table 6 (continued)

5	Compound #	R ₂	R ₅	R ₁	B	Y	X
	394	4-Cl	2-OMe	4-t-Bu	H	H	O
	395	3-Cl	4-F	2-SO ₂ NH ₂	H	H	O
	396	3-Cl	4-F	3-SO ₂ NH ₂	H	H	O
10	397	2-OMe	4-F	2-SO ₂ NH ₂	H	H	O
	398	2-OMe	4-F	3-SO ₂ NH ₂	H	H	O
	399	2-CH ₂ C ₆ H ₅	4-F	4-OMe	H	H	O
	400	4-F	3,4-F	4-CF ₃	H	H	O
	401	4-F	3,4-F	4-OCF ₃	H	H	O
15	402	4-F	3,4-F	4-Cl	H	H	O
	403	4-F	3,4-F	4-Br	H	H	O
	404	4-CN	4-CN	4-CN	H	H	O
	405	4-CN	4-CN	4-t-Bu	H	H	O
	406	4-Cl	4-OMe	4-OMe	H	H	O
20	407	4-Cl	4-OMe	4-NO ₂	H	H	O
	408	4-Cl	4-OMe	4-CF ₃	H	H	O
	409	4-Cl	4-OMe	4-t-Bu	H	H	O
	410	4-OCF ₃	4-F	4-CF ₃	H	H	O
	411	4-OCF ₃	4-F	4-OCF ₃	H	H	O
25	412	4-OCF ₃	4-F	4-Cl	H	H	O
	413	4-OCF ₃	4-F	4-Br	H	H	O
	414	4-Cl	3,4-F	4-CF ₃	H	H	O
	415	4-Cl	3,4-F	4-OCF ₃	H	H	O
	416	4-Cl	3,4-F	4-OCF ₂ CF ₂ H	H	H	O
30	417	4-Cl	3,4-F	4-Cl	H	H	O
	418	4-Cl	4-Cl	3,4,5-tri-Cl	H	H	O
	419	4-Cl	4-Cl	4-OCF ₃	H	H	O
	420	4-CF ₃	4-F	4-CF ₃	H	H	O
	421	2-CH ₂ C ₆ H ₅	4-F	4-CN	H	H	O
35	422	2-CH ₂ C ₆ H ₅	4-F	4-t-Bu	H	H	O
	423	2-CH ₂ C ₆ H ₅	4-F	4-CF ₃	H	H	O

Table 6 (continued)

5	Compound #	R ₂	R ₅	R ₁	B	Y	X
	424	3,4-di-F	4-F	4-CF ₃	H	H	O
	425	3,4-di-F	4-F	4-OCF ₃	H	H	O
	426	3,4-di-F	4-F	4-SMe	H	H	O
10	427	3,4-di-F	4-F	4-Br	H	H	O
	428	3,4-di-F	4-F	4-SO ₂ NH	H	H	O
	429	3,4-di-F	4-F	4-C ₆ H ₅	H	H	O
	430	3,4-di-F	4-F	4-Cl	H	H	O
	431	3,4-di-F	4-F	4-OEt	H	H	O
15	432	4-F	H	4-CF ₃	H	Ac	O
	433	4-NO ₂	4-Cl	4-F	H	H	O
	434	4-CF ₃	4-Cl	4-CF ₃	Me	H	O
	435	4-Cl	4-t-Bu	4-Cl	H	H	O
	436	4-Cl	4-t-Bu	4-OMe	H	H	O
20	437	4-Cl	4-t-Bu	4-CN	H	H	O
	438	4-Cl	4-t-Bu	4-CF ₃	H	H	O
	439	4-Cl	4-t-Bu	4-t-Bu	H	H	O
	440	4-Cl	4-t-Bu	4-NO ₂	H	H	O
	441	4-Cl	4-C ₆ H ₅	4-Cl	H	H	O
25	442	4-Cl	4-C ₆ H ₅	4-OMe	H	H	O
	443	4-Cl	4-C ₆ H ₅	4-CN	H	H	O
	444	4-Cl	4-C ₆ H ₅	4-CF ₃	H	H	O
	445	4-Cl	4-C ₆ H ₅	4-t-Bu	H	H	O
	446	4-Cl	4-C ₆ H ₅	4-NO ₂	H	H	O
30	447	4-CF ₃	4-Br	4-CF ₃	H	H	O
	448	4-CF ₃	4-Br	4-CN	H	H	O
	449	4-CF ₃	4-Br	4-Cl	H	H	O
	450	4-CF ₃	4-Br	4-F	H	H	O
	451	4-CF ₃	4-Br	4-NO ₂	H	H	O
35	452	4-F	4-COOMe	4-CF ₃	H	H	O
	453	4-F	4-COOMe	4-CN	H	H	O

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Table 6 (continued)

5	Compound #	R ₂	R ₅	R ₁	B	Y	X
	454	4-F	4-COOMe	4-Cl	H	H	O
	455	4-F	4-COOMe	4-F	H	H	O
	456	4-F	4-COOMe	4-t-Bu	H	H	O
10	457	4-F	4-COOMe	3-CF ₃ , 4-F	H	H	O
	458	4-Cl	4-F	4-CF ₃	Me	H	O
	459	4-CF ₃	4-COOMe	4-CF ₃	H	H	O
	460	4-CF ₃	4-COOMe	4-CN	H	H	O
	461	4-CF ₃	4-COOMe	4-Cl	H	H	O
15	462	4-CF ₃	4-COOMe	4-F	H	H	O
	463	4-CF ₃	4-COOMe	4-COOMe	H	H	O
	464	4-NO ₂	4-Cl	4-CF ₃	H	H	O
	465	4-Cl	4-F	4-CF ₃	H	COEt	O
	466	4-CF ₃	4-Br	4-NH ₂	H	H	O
20	467	4-Cl	4-COOMe	4-CF ₃	H	H	O
	468	4-CF	4-CONHC ₆ H ₄ (p-CF ₃)	4-CF ₃	H	H	O
	469	4-Cl	4-COOMe	4-Cl	H	H	O
	470	4-Cl	4-CONHC ₆ H ₄ (p-Cl)	4-Cl	H	H	O
	471	4-Cl	4-COOMe	4-F	H	H	O
25	472	4-NH ₂	4-Cl	4-CF	H	H	O
	473	4-Br	4-F	4-CF	H	H	O
	474	4-Br	4-F	4-Cl	H	H	O
	475	4-Br	4-F	4-F	H	H	O

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5	Compound	R ₂	R ₁	B	A	X	Y
	1A	4-F	4-Cl	H	COOMe	O	H
	2A	4-F	4-Cl	Me	COOEt	O	H
	3A	4-Cl	H	H	COOMe	O	H
	4A	4-CF ₃	4-Cl	H	COOMe	O	H
10	5A	4-CF ₃	4-Cl	CH ₂ COOMe	COOMe	O	H
	6A	4-Cl	4-CF ₃	H	COOMe	O	H
	7A	4-Cl	4-CF ₃	Me	COOMe	O	H
	8A	4-F	4-Cl	Me	COOC ₆ H ₅	O	H
	9A	4-Cl	4-Cl	Me	COOMe	O	H
15	10A	4-Cl	4-Cl	Me	CN	O	H
	11A	4-Cl	4-Cl	Me	CHO	O	H
	12A	4-Cl	4-Cl	H	COEt	O	H
	13A	4-F	4-CF ₃	Me	COOMe	O	H
	14A	4-F	4-CF ₃	Me	CHO	O	H
20	15A	4-F	4-CF ₃	CH ₂ COOMe	COOMe	O	H
	16A	4-Cl	4-Br	H	COOMe	O	H
	17A	4-Cl	4-CN	H	COOMe	O	H
	18A	4-Cl	4-Cl	H	COOMe	O	H
	19A	4-Cl	2-F, 4-Cl	H	COOMe	O	H
25	20A	4-CN	4-Cl	H	COOMe	O	H
	21A	4-CN	4-CN	H	COOMe	O	H
	22A	4-CN	4-Cl	Me	COOMe	O	H
	23A	4-CN	4-CN	Me	COOMe	O	H
	24A	4-CN	2-F, 4-Cl	Me	COOMe	O	H
30	25A	4-F	4-CF ₃	Me	CHO	O	H
	26A	4-Cl	4-CN	Me	CONHMe	O	H
	27A	4-Cl	4-Cl	H	CONHMe	O	H
	28A	4-CN	4-F	Me	CN	O	H
	29A	4-Cl	2-F, 4-Cl	H	CONHnBu	O	H
35	30A	2-F, 4-Cl	4-CN	Me	COOMe	O	H

Table 7 (continued)

5	Compound	R ₂	R ₁	B	A	X	Y
	31A	4-F	4-CN	Me	CHO	O	H
	32A	4-F	4-F	Me	CHO	O	H
	33A	4-F	2,4-di-Cl	Me	CHO	O	H
	34A	4-Cl	4-CF ₃	H	H	O	H
10	35A	4-CN	4-CF ₃	Me	COOMe	O	H
	36A	4-F	4-CF ₃	i-Pr	CHO	O	H
	37A	4-F	4-CN	i-Pr	CHO	O	H
	38A	4-F	4-F	i-Pr	CHO	O	H
	39A	4-F	2-F, 4-Cl	i-Pr	CHO	O	H
15	40A	4-CF ₃	4-CF ₃	i-Pr	CHO	O	H
	41A	4-CF ₃	4-CN	i-Pr	CHO	O	H
	42A	4-CN	4-CF ₃	i-Pr	CHO	O	H
	43A	4-Cl	4-CF ₃	i-Pr	CHO	O	H
	44A	4-Cl	4-CN	i-Pr	CHO	O	H
20	45A	4-CF ₃	4-CF ₃	Me	COOMe	O	H
	46A	4-CF ₃	4-CF ₃	Me	COOMe	O	H
	47A	4-CN	4-CF ₃	Me	COOMe	O	H
	48A	4-F	4-CF ₃	Me	COOMe	O	H
	49A	4-CF ₃	4-Br	Me	COOMe	O	H
25	50A	4-CN	4-Br	Me	COOMe	O	H
	51A	4-Cl	4-Br	Me	COOMe	O	H
	52A	4-Cl	4-Br	Me	CONHC ₆ H ₄ Br	O	H
	53A	4-F	4-Br	Me	COOMe	O	H
	54A	4-Cl	4-CF ₃	Me	COOMe	O	Me
30	55A	4-Cl	2,4-di-Cl	i-Pr	CHO	O	H
	56A	4-CF ₃	4-CF ₃	Me	CONHC ₆ H ₄ CF ₃	O	H
	57A	4-CN	4-CN	i-Pr	CHO	O	H
	58A	4-CN	4-F	i-Pr	CHO	O	H
	59A	4-F	4-CF ₃	n-Bu	COOMe	O	Me
35	60A	4-Cl	4-CF ₃	n-Bu	COOMe	O	Me

Table 7 (continued)

5	Compound	R ₂	R ₁	B	A	X	Y
	61A	4-CF ₃	4-CF ₃	n-Bu	COOMe	O	Me
	62A	4-F	4-I	Me	COOMe	O	H
	63A	2,4-di-Cl	4-OCF ₃	Me	COOMe	O	H
	64A	2,4-di-Cl	4-OCF ₃	Me	COOMe	O	H
10	65A	2,4-di-Cl	4-CF ₃	CH ₂ C ₆ H ₅	COOMe	O	H
	66A	2,4-di-Cl	4-F	CH ₂ C ₆ H ₅	COOMe	O	H
	67A	2,4-di-Cl	4-CF ₃	Me	COOMe	O	H
	68A	2,4-di-Cl	4-Br	CH ₂ C ₆ H ₅	COOn-Bu	O	H
	69A	2,4-di-Cl	4-CF ₃	Me	COOn-Bu	O	H
15	70A	2-F,4-Cl	4-CF ₃	Me	COOn-Bu	O	H
	71A	2-F,4-Cl	4-CF ₃	Me	COOnMe	O	H
	72A	2-F,4-Cl	4-OCF ₃	Me	COOn-Bu	O	H
	73A	2-F,4-Cl	4-CF ₃	Me	COOn-Bu	O	H
	74A	4-F	4-CF ₃	Me	n-Pr	O	H
20	75A	4-F	4-CF ₃	Me	COOn-Bu	O	H
	76A	4-F	4-OCF ₃	Me	COOn-Bu	O	H
	77A	4-F	4-COOMe	Me	COOn-Bu	O	H
	78A	4-F	4-Br	Me	COOn-Bu	O	H
	79A	4-F	4-CF ₃	Me	COOn-Bu	O	H
25	80A	4-F	4-CN	Me	COOn-Bu	O	H
	81A	4-F	4-OCF ₃	n-Bu	COOMe	O	H
	82A	4-F	4-Br	n-Bu	COOMe	O	H
	83A	4-OCF ₃	4-Br	Me	COOMe	O	H
	84A	4-F	4-I	n-Bu	COOMe	O	H
30	85A	4-F	4-CN	n-Bu	COOMe	O	H
	86A	4-OCF ₃	4-Cl	Me	COOMe	O	H
	87A	4-F	4-SMe	n-Bu	COOMe	O	H
	88A	4-F	4-CF ₃	n-Bu	COOMe	O	H
	89A	4-F	4-Br	Me	COOMe	O	H
35	90A	4-Cl	4-Br	Me	COOMe	O	H

Table 7 (continued)

5	Compound #	R ₂	R ₁	B	A	X	Y
	91A	4-OCF ₃	4-CF ₃	Me	COMe	O	H
	92A	4-OCF ₃	4-Br	Me	COOMe	O	H
	93A	4-OCF ₃	4-CN	Me	COOMe	O	H
	94A	4-Cl	4-Br	CH ₂ C ₆ H ₅	COOMe	O	H
10	95A	4-Cl	4-F	CH ₂ C ₆ H ₅	COOMe	O	H
	96A	4-Cl	4-OCF ₃	CH ₂ C ₆ H ₅	COOMe	O	H
	97A	4-Br	4-Br	Me	COOMe	O	H
	98A	4-Br	4-CF ₃	Me	COOMe	O	H
	99A	4-Br	4-CN	Me	COOMe	O	H
15	100A	4-Br	4-CF ₃	Me	COOMe	O	H
	101A	4-Br	4-Br	Me	COOMe	O	H
	102A	4-Br	4-OCF ₃	Me	COOMe	O	H
	103A	4-Br	4-Cl	Me	COOMe	O	H
	104A	4-Cl	4-CF ₃	Me	COOt-Bu	O	Me
	105A	4-OCF ₃	4-CF ₃	Me	COOMe	O	n-Pr
20	106A	4-CF ₃	4-CF ₃	Me	COOMe	O	n-Pr
	107A	4-Br	4-CF ₃	Me	CONHC ₆ H ₄ (p-CF ₃)	O	H
	108A	4-Br	4-Br	Me	CONHC ₆ H ₄ (p-Br)	O	H
	109A	4-Br	4-OCF ₃	Me	CONC ₆ H ₄ (p-OCF ₃)	O	H
	110A	4-Cl	4-CN	allyl	COOMe	O	H
25	111A	4-Cl	4-SMe	allyl	COOMe	O	H
	112A	4-Cl	4-CF ₃	allyl	COOMe	O	H
	113A	4-Cl	4-CF ₃	allyl	COOMe	O	Me
	114A	4-Cl	4-CF ₃	allyl	COOMe	O	n-Pr
	115A	4-Cl	4-Br	allyl	COOMe	O	Me
30	116A	4-F	4-CF ₃	Me	COOMe	S	H
	117A	4-Cl	4-CF ₃	Me	COOMe	S	H
	118A	4-Cl	4-CF ₃	Me	COOMe	S	Me
	119A	4-F	4-OCF ₃	n-Bu	COOMe	S	H
	120A	4-F	4-CF ₃	Me	COOMe	O	n-Pr
35	121A	4-Cl	4-CF ₃	Me	COOMe	O	n-Pr

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Table 7 (continued)

5	Compound #	R_2	R_1	B	A	X	Y
	122A	4-Cl	4-Br	allyl	COOEt	O	H
	123A	4-Cl	4-OCF ₃	Me	COOMe	O	Me
	124A	4-Cl	4-I	Me	COOMe	O	H
10	125A	4-OCF ₃	4-OCF ₃	Me	COOt-Bu	O	H
	126A	4-OCF ₃	4-CF ₃	Me	COOt-Bu	O	Me
	127A	4-Br	4-CF ₃	Me	COOt-Bu	O	Me
	128A	4-Br	4-Br	Me	COOt-Bu	O	H
	129A	4-Br	4-OCF ₃	Me	COOt-Bu	O	H
15	130A	4-OCF ₃	4-Br	Me	COOt-Bu	O	H
	131A	4-Br	4-CF ₃	Me	COOt-Bu	O	H
	132A	4-Br	4-OCF	Me	COOt-Bu	O	H

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Example 32Fall Armyworm

5 Test units, each consisting of an 8-ounce plastic cup containing a layer of wheat germ diet, approximately 0.5 cm thick, were prepared. Ten third-instar larvae of fall armyworm (Spodoptera frugiperda) were placed into each cup. Solutions of each of the test compounds (acetone/distilled water 75/25 solvent) were
10 sprayed onto the cups, a single solution per set of three cups. Spraying was accomplished by passing the cups, on a conveyer belt, directly beneath a flat fan hydraulic nozzle which discharged the spray at a rate of 0.5 pounds of active ingredient per acre (about
15 0.55 kg/ha) at 30 p.s.i. The cups were then covered and held at 27°C and 50% relative humidity for 72 hours, after which time mortality readings were taken.

Of the compounds tested on fall armyworm, the
20 following resulted in greater than or equal to 80% mortality:

1, 3, 4, 5, 6, 10, 11, 12, 14, 16, 17, 18,
20, 23, 26, 27, 29, 30, 31, 32, 33, 34, 36, 40, 41,
42, 44, 45, 46, 47, 48, 50, 51, 54, 59, 65, 67, 68,
25 69, 71, 74, 77, 86, 89, 90, 95, 96, 113, 116, 119,
132, 134, 135, 137, 138, 141, 162, 164, 166, 170, 172,
174, 176, 180, 184, 193, 195, 197, 200, 202, 203, 206,
221, 222, 223, 224, 225, 229, 231, 249, 253, 254, 255,
270, 303, 304, 305, 306, 307, 351, 352, 354, 357, 363,
30 364, 410, 411, 412, 414, 415, 417, 427, 430 from Table
6 and 7A, 9A, 13A, 46A, 50A, 51A 53A 61A, 62A, 83A,
100A, 102A, 103A from Table 7.

Example 33Tobacco Budworm

35 The test procedure of Example 32 was repeated for efficacy against third-instar larvae of the

tobacco budworm (Heliothis virescens) except that mortality was assessed at 48 hours. Of the compounds tested on tobacco budworm, the following resulted in greater than or equal to 80% mortality:

1, 4, 5, 6, 11, 15, 23, 26, 27, 29, 30, 32, 41, 43, 45, 51, 54, 59, 65, 68, 69, 77, 96, 138, 172, 221, 222, 223, 225, 229, 249, 253, 303, 304, 305, 351, 352, 356, 358, 410, 411, 412, 414, 415, 417, 427, 430, from Table 6 and 7A, 40A, 46A, 54A, 62A, 83A, 100A, 102A, 103A from Table 7.

Example 34

European Corn Borer

Test units, each consisting of an 8-ounce plastic cup containing a one-inch square of wheat germ/soyflour diet were prepared. Five third-instar larvae of the European corn borer (Ostrinia nubilalis) were placed into each cup. Sets of three test units were sprayed as described in Example 32 with individual solutions of the test compounds. The cups were then covered and held at 27°C and 50% relative humidity for 48 hours, after which time mortality readings were taken. Of the compounds tested on European corn borer, the following resulted in greater than or equal to 80% mortality:

1, 5, 6, 18, 23, 30, 32, 33, 34, 40, 41, 42, 43, 44, 45, 46, 48, 50, 51, 59, 65, 68, 74, 86, 89, 95, 96, 116, 132, 134, 135, 138, 141, 164, 172, 176, 178, 197, 203, 211, 222, 224, 225, 227, 229, 231, 237, 249, 251, 254, 303, 304, 305, 351, 352, 354, 364, 410, 411, 412, 414, 415, 417, 427, 430, from Table 6 and 1A, 2A, 7A, 13A, 18A, 40A, 43A, 46A, 51A, 53A, 54A, 74A, 100A, 102A, 103A from Table 7.

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Example 35Southern Corn Rootworm

5 Test units, each consisting of an 8-ounce plastic cup containing 1 sprouted corn seed, were prepared. Sets of three test units were sprayed as described in Example 32 with individual solutions of the test compounds. After the spray on the cups had dried, five third-instar larvae of the southern corn rootworm (Diabrotica undecimpunctata howardi) were placed into each cup. A moistened dental wick was inserted into each cup to prevent drying and the cups were then covered. The cups were then held at 27°C and 50% relative humidity for 48 hours, after which time mortality readings were taken.

Of the compounds tested on southern corn rootworm, the following resulted in greater than or equal to 80% mortality:

20 5, 6, 11, 12, 16, 17, 18, 23, 26, 29, 30, 31, 32, 34, 41, 43, 44, 45, 46, 48, 51, 74, 77, 86, 89, 90, 96, 132, 138, 141, 172, 221, 225, 303, 304, 351, 352, 354, 364, 410, 412, 414, 415, 417, 427, 430 from Table 6 and 7A, 9A, 13A, 17A, 34A, 46A, 50A, 51A, 53A, 54A, 62A, 74A, 83A, 100A, 102A, 103A, from Table 7.

Example 36Boll Weevil

Five adult boll weevils (Anthonomus grandis) were placed into each of a series of 9-ounce cups. The test procedure employed was then otherwise the same as in Example 32 with three cups per treatment. Mortality readings were taken 48 hours after treatment.

Of the compounds tested on boll weevil, the following resulted in greater than or equal to 80% mortality:

35 5, 6, 11, 12, 18, 22, 23, 24, 26, 30, 31, 32, 33, 34, 40, 41, 42, 43, 44, 45, 46, 51, 54, 59, 63,

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66, 67, 68, 77, 89, 90, 95, 96, 116, 117, 132, 134,
137, 138, 139, 141, 162, 166, 172, 174, 176, 179, 181,
183, 203, 206, 217, 221, 222, 225, 227, 229, 249, 253,
270, 302, 303, 304, 305, 307, 351, 352, 410, 412, 414,
415, 417, 430 from Table 6 and 2A, 6A, 7A, 9A, 13A,
34A, 46A, 50A, 51A, 54A, 62A, 71A, 100A, 102A, 103A,
from Table 7.

Example 37Aster Leafhopper

Test units were prepared from a series of
12-ounce cups, each containing oat (Avena sativa)
seedlings in a 1-inch layer of sterilized soil. Sets
of three test units were sprayed as described in
Example 32 with individual solutions of the test
compounds. After the oats had dried from the
spraying, between 10 and 15 adult aster leafhoppers
(Mascrosteles fascifrons) were aspirated into each of
the covered cups. The cups were held at 27°C and 50%
relative humidity for 48 hours, after which time
mortality readings were taken.

Of the compounds tested on aster leafhopper, the
following resulted in greater than or equal to 80%
mortality:

5, 6, 23, 32, 34, 41, 43, 45, 50, 69, 96,
221, 303, 304, 351, 352, 410, 415, 417, from Table 6
and 7A, 13A, 46A, 51A, 53A, 54A, 62A, 74A, 100A, 102A,
103A from Table 7.

Example 38Combinations with Spray Oils

5 Both short-term and residual insecticidal activity of the tested compound (Compound 30) against fall armyworm, Spodoptera frugiperda, was improved when the emulsifiable concentrate formulation of the compound was combined with spray oils or spray oil
10 concentrates.

The test compound was diluted in 5 ml of acetone and then mixed with distilled water to 100 and 50 ppm. Spray oil or spray oil concentrate was added to the solutions in the ratio 10:1 oil:active
15 ingredient. The spray oil was a paraffinic petroleum-based oil having a median distillation temperature at atmospheric pressure of 377°C. The spray oil concentrate consisted of 83% isoparaffinic oil and 17% of a mixture of sorbitol ester and
20 epoxylated sorbitol ester. Test units consisted of 3 week-old soybean plants growing in 4 inch pots. Three plants were sprayed to runoff on a turntable sprayer at 10 rpm with an atomizing nozzle for each treatment.

After the spray dried, treated leaflets were cut
25 in half and each piece was placed in one well of a 6-cell tissue culture plate. One third instar larva was placed in each cell. The entire unit was then capped with a piece of moistened blotter paper. Four such units were set up for each treatment. Test units
30 were held at 27°C and 50% relative humidity. Mortality was assessed at 72 hours. Treated plants were held at 27°C and 50% relative humidity and the test was repeated at 7 and 14 days to determine residual activity.

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The results are recorded in Table 8.

Table 8

Compound 30 With and Without Spray Oil
or Spray Oil Concentrate

			<u>% MORTALITY</u>		
10	<u>TREATMENT</u>	<u>RATE (PPM)</u>	<u>DAY 0</u>	<u>DAY 7</u>	<u>DAY 14</u>
	Compound 30 +	100	100	100	100
	Spray Oil	50	100	96	96
	Concentrate				
15	Compound 30 +	100	100	100	100
	Spray Oil	50	100	100	100
	Compound 30	100	100	83	50
	(without oil)	50	100	83	46

20 Example 39

Improved Activity with Synergists

Test units were prepared as described in Example 32 using 5 fall armyworm larvae, Spodoptera frugiperda. Prior to treatment with the test compound (Compound 30), the units were oversprayed with the piperonyl butoxide (PBO) at a rate 5X the concentration to be used for the test compound, using the technique described in Example 32. After 2.5 hours, the units were oversprayed with the test compound at 10, 5, 2.5, 1.0, 0.5 and 0.1 ppm. The test units were covered and held for 72 hours at 27°C and 50% relative humidity after which time mortality was assessed. The results are recorded in Table 9.

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Table 9Effect of Adding Piperonyl Butoxide

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% MORTALITY

	<u>RATE (PPM)</u>	<u>WITHOUT PBO</u>	<u>WITH PBO 5:1</u>
	10	100	100
10	5	100	100
	2.5	96	100
	1.0	96	96
	0.5	44	80
15	0.1	20	80

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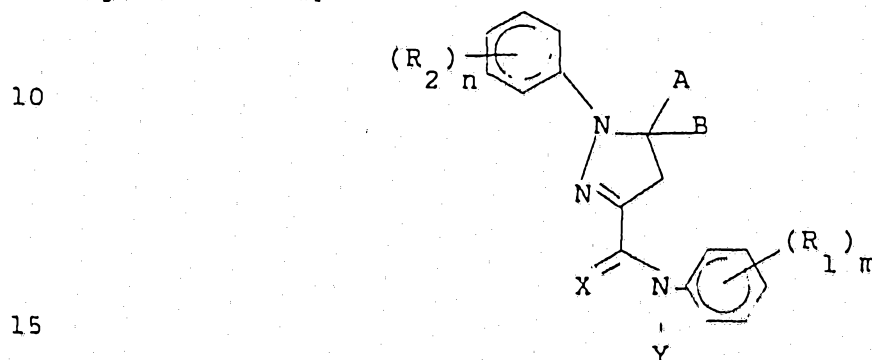
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WHAT IS CLAIMED:

The embodiments of the invention in which an
 5 exclusive property or privilege is claimed are defined
 as follows:

1. A compound having the following formula, and
 agriculturally suitable salts thereof:



wherein:

X is O or S;

Y is H, C₁ to C₄ alkyl, C₂ to C₄
 20 alkoxyalkyl, C₁ to C₄ alkylthio, C₁ to C₄
 haloalkylthio, phenylthio, or phenylthio
 substituted with 1 to 3 substituents
 independently selected from W, C₂ to C₄
 alkoxy carbonyl, C(O)H, C₂ to C₄
 alkyl carbonyl or C₂ to C₄ haloalkyl carbonyl;

A is H, C₁ to C₆ alkyl, phenyl, phenyl substi-
 25 tuted by (R₅)_p, CN, CO₂R₃, C(O)R₃,
 C(O)NR₃R₄, C(S)NR₃R₄, C(S)R₃ or C(S)SR₃;

B is H, C₁ to C₆ alkyl, C₁ to C₆ haloalkyl,
 30 C₂ to C₆ alkoxyalkyl, C₂ to C₆ cyanoalkyl,
 C₃ to C₈ alkoxy carbonyl alkyl, C₂ to C₆ alkenyl,
 C₂ to C₆ alkynyl, C₂ to C₆ alkoxy carbonyl,
 phenyl, phenyl substituted with 1 to 3 sub-
 stituents independently selected from W,
 benzyl or benzyl substituted with 1 to 3 sub-
 35 stituents independently selected from W;

W is halogen, CN, NO₂, C₁ to C₂ alkyl, C₁ to C₂
 haloalkyl, C₁ to C₂ alkoxy, C₁ to C₂ halo-

alkoxy, C_1 to C_2 alkylthio, C_1 to C_2 haloalkylthio, C_1 to C_2 alkylsulfonyl or C_1 to C_2 haloalkylsulfonyl;

R_1 , R_2 and R_5 are independently R_3 , halogen, CN, N_3 , SCN, NO_2 , OR_3 , SR_3 , $S(O)R_3$, $S(O)_2R_3$, $OC(O)R_3$, $OS(O)_2R_3$, CO_2R_3 , $C(O)R_3$, $C(O)NR_3R_4$, $S(O)_2NR_3R_4$, NR_3R_4 , $NR_4C(O)R_3$, $OC(O)NHR_3$, $NR_4C(O)NHR_3$, $NR_4S(O)_2R_3$, or when m, n or p is 2, R_1 , R_2 or R_5 can be taken together as $-OCH_2O-$, $-OCF_2O-$, $-OCH_2CH_2O-$, $-CH_2C(CH_3)_2O-$, $-OCF_2CF_2O-$, or $-CF_2CF_2O-$ to form a cyclic bridge; provided R_1 is other than H;

R_3 is H, C_1 to C_4 alkyl, C_1 to C_4 haloalkyl, C_2 to C_4 alkenyl, C_2 to C_4 haloalkenyl, C_2 to C_4 alkynyl, C_2 to C_4 haloalkynyl, C_2 to C_4 alkoxyalkyl, C_2 to C_4 alkylthioalkyl, C_1 to C_4 nitroalkyl, C_2 to C_4 cyanoalkyl, C_3 to C_6 alkoxy carbonylalkyl, C_3 to C_6 cycloalkyl, C_3 to C_6 halocycloalkyl, phenyl, benzyl, or phenyl or benzyl substituted with 1 to 3 substituents independently selected from W;

R_4 is H or C_1 to C_4 alkyl, or when R_3 and R_4 are attached to a single nitrogen atom, they can be taken together as $(CH_2)_4$, $(CH_2)_5$ or $(CH_2CH_2OCH_2CH_2)$;

m is 1 to 3;

n is 0 to 3; and

p is 0 to 3.

2. A compound according to Claim 1 wherein

X is O;

Y is H, CH_3 , SCH_3 , $SCCl_3$, SC_6H_5 , 2- $(NO_2)C_6H_4S$, $C(O)CH_3$, $C(O)H$, $C(O)CF_3$, CO_2CH_3 or $CO_2C_2H_5$;

R_3 is C_1 to C_4 alkyl, C_1 to C_2 haloalkyl, C_2 to C_4 alkenyl, C_2 to C_4 haloalkenyl,

propargyl, phenyl, benzyl, or phenyl or benzyl substituted with one of F, Cl, Br, CF_3 , OCF_2H , OCF_3 or NO_2 ;

n is 0 to 2;

p is 0 to 2; and

m is 1 to 2.

3. A compound according to Claim 2 wherein

R_1 is halogen, CN, SCN, NO_2 , R_3 , OR_3 , SR_3 , $\text{S(O)}_2\text{R}_3$, CO_2R_3 or C(O)R_3 , or when m is 2, R_1 can be taken together as $-\text{OCF}_2\text{O}-$,

$-\text{CH}_2\text{C(CH}_3)_2\text{O}-$, $-\text{OCF}_2\text{CF}_2\text{O}-$ or $-\text{CF}_2\text{CF}_2\text{O}-$;

R_2 and R_5 are independently halogen, CN, SCN, NO_2 , R_3 , OR_3 , SR_3 , $\text{S(O)}_2\text{R}_3$, OC(O)R_3 , $\text{OS(O)}_2\text{R}_3$, CO_2R_3 , C(O)R_3 , $\text{C(O)NR}_3\text{R}_4$, $\text{S(O)}_2\text{NR}_3\text{R}_4$ or NR_3R_4 ;

R_3 is C_1 to C_4 alkyl, C_1 to C_2 haloalkyl, C_2 to C_4 alkenyl, C_2 to C_4 haloalkenyl or propargyl;

R_4 is H or C_1 to C_2 alkyl;

A is C_1 to C_4 alkyl, phenyl, phenyl substituted with $(\text{R}_5)_p$, CO_2R_3 , C(O)R_3 , $\text{C(O)NR}_3\text{R}_4$ or C(O)NR_4 phenyl said phenyl optionally substituted with F, Cl, Br, CF_3 , OCF_2H , OCF_3 or NO_2); and

B is H, C_1 to C_4 alkyl, C_1 to C_4 haloalkyl, or C_3 to C_4 alkenyl.

4. A compound according to Claim 3 wherein

Y is H, CH_3 , C(O)CH_3 or CO_2CH_3 ;

m is 1 or 2 and one substituent is in the 4-position of the phenyl ring;

n is 1 or 2 and one substituent is in the 4-position of the phenyl ring;

p is 1 or 2 and one substituent is in the 3 or 4-position of the phenyl ring;

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R_1 is F, Cl, Br, CF_3 , OCF_2H , OCF_3 or CN, or
when m is 2, R_1 can be taken together as
- $CH_2C(CH_3)_2O$ - or - CF_2CF_2O -;

R_2 is F, Cl, Br, CN, NO_2 , CF_3 , CH_3 , OCH_3 , OCF_2H ,
 OCF_3 , SCH_3 , SCF_2H , $S(O)_2CH_3$ or $N(CH_3)_2$;

R_5 is F, Cl, Br, CN, NO_2 , CF_3 , CH_3 , OCH_3 , OCF_2H ,
 OCF_3 , SCH_3 , SCF_2H , $S(O)_2CH_3$, $S(O)_2CF_2H$,
 CO_2CH_3 , $C(O)NHCH_3$, $C(O)N(CH_3)_2$, $S(O)_2N(CH_3)_2$
or $N(CH_3)_2$;

A is phenyl or phenyl substituted with $(R_5)_p$; and
B is H or CH_3 .

5. A compound according to Claim 3 wherein

Y is H, CH_3 , $C(O)CH_3$ or CO_2CH_3 ;

m is 1 or 2 and one substituent is in the
4-position of the phenyl ring;

n is 1 or 2 and one substituent is in the
4-position of the phenyl ring;

R_1 is F, Cl, Br, CF_3 , OCF_2H , OCF_3 or CN, or
when m is 2, R_1 can be taken together as
- $CH_2(CH_3)_2O$ - or CF_2CF_2O -;

R_2 is F, Cl, Br, CN, NO_2 , CF_3 , CH_3 , OCH_3 , OCF_2H ,
 OCF_3 , SCH_3 , SCF_2H , $S(O)_2CH_3$, $S(O)_2CF_2H$,
 CO_2CH_3 , $C(O)CH_3$, $C(O)N(CH_3)_2$, $S(O)_2N(CH_3)_2$
or $N(CH_3)_2$;

A is CO_2CH_3 , $CO_2C_2H_5$, $C(O)NHCH_3$ or
 $C(O)N(CH_3)_2$; and

B is CH_3 .

6. A compound according to Claim 5: methyl

1-(4-chlorophenyl)-4,5-dihydro-5-methyl-3-[[4-(tri-
fluoromethyl)phenyl]aminocarbonyl]-1H-pyrazole-5-car-
boxylate.

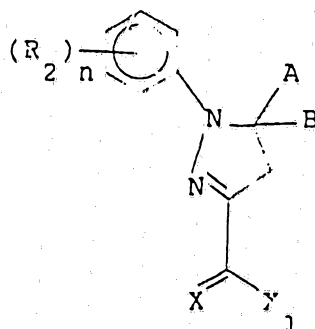
7. A compound according to Claim 4: 1-(4-chlorophenyl)-5-(4-fluorophenyl)-4,5-dihydro-N-[4-(trifluoromethyl)phenyl]-1H-pyrazole-3-carboxamide.

8. A compound according to Claim 4: 1,5-bis(4-chlorophenyl)-4,5-dihydro-N-[4-(trifluoromethyl)phenyl]-1H-pyrazole-3-carboxamide.

9. A compound of according to Claim 4:
1-(4-chlorophenyl)-5-(4-cyanophenyl)-4,5-dihydro-N-[4-(trifluoromethyl)phenyl]-1H-pyrazole-3-carboxamide.

10. A compound of the formula:

15



20

wherein:

- X is O or S;
- 25 X_1 is OH, Cl or C_1 to C_6 alkoxy;
- A is H, C_1 to C_6 alkyl, phenyl, phenyl substituted by $(R_5)_p$, CN, CO_2R_3 , $C(O)R_3$, $C(O)NR_3R_4$, $C(S)NR_3R_4$, $C(S)R_3$ or $C(S)SR_3$;
- 30 B is H, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl, C_2 to C_6 alkoxyalkyl, C_2 to C_6 cyanoalkyl, C_3 to C_8 alkoxyalkyl, C_2 to C_6 alkenyl, C_2 to C_6 alkynyl, C_2 to C_6 alkoxyalkyl, phenyl, or phenyl substituted with 1 to 3 substituents independently selected from W, benzyl, benzyl substituted with 1 to 3 substituents independently selected from W;
- 35 W is halogen, CN, NO_2 , C_1 to C_2 alkyl, C_1 to C_2 haloalkyl, C_1 to C_2 alkoxy, C_1 to C_2 haloalkoxy, C_1 to C_2 alkylthio, C_1 to C_2 halo-



alkylthio, C_1 to C_2 alkylsulfonyl or C_1 to C_2 haloalkylsulfonyl;

- 5 R_2 and R_5 are independently R_3 , halogen, CN, N_3 , SCN, NO_2 , OR_3 , SR_3 , $S(O)R_3$, $S(O)_2R_3$, $OC(O)R_3$, $OS(O)_2R_3$, CO_2R_3 , $C(O)R_3$, $C(O)NR_3R_4$, $S(O)_2NR_3R_4$, NR_3R_4 , $NR_4C(O)R_3$, $OC(O)NHR_3$, $NR_4C(O)NHR_3$, $NR_4S(O)_2R_3$, or, when n or p is 2, R_2 or R_5 can be taken together as $-OCH_2O-$, $-OCF_2O-$, $-OCH_2CH_2O-$, $-CH_2C(CH_3)_2O-$, $-OCF_2CF_2O-$ or $-CF_2CF_2O-$ to form a cyclic bridge; except that both R_2 and R_5 are not H;
- 10 R_3 is H, C_1 to C_4 alkyl, C_1 to C_4 haloalkyl, C_2 to C_4 alkenyl, C_2 to C_4 haloalkenyl, C_2 to C_4 alkynyl, C_2 to C_4 haloalkynyl, C_2 to C_4 alkoxyalkyl, C_2 to C_4 alkylthioalkyl, C_1 to C_4 nitroalkyl, C_2 to C_4 cyanoalkyl, C_3 to C_6 alkoxycarbonylalkyl, C_3 to C_6 cycloalkyl, C_3 to C_6 halocycloalkyl, phenyl, benzyl, or phenyl or benzyl substituted with 1 to 3 substituents independently selected from W;
- 15 R_4 is H or C_1 to C_4 alkyl, or when R_3 and R_4 are attached to a single nitrogen atom, they can be taken together as $\{CH_2\}_{2,4}$, $\{CH_2\}_{2,5}$ or $\{CH_2CH_2OCH_2CH_2\}$;
- 20 n is 0 to 3; and
 p is 0 to 3.
- 25

30 11. A composition comprising an insecticidally effective amount of a compound according to Claim 1 and an agriculturally suitable carrier therefor.

12. A composition comprising an insecticidally effective amount of a compound according to Claim 2 and an agriculturally suitable carrier therefor.

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13. A composition comprising an insecticidally effective amount of a compound according to Claim 3 and an agriculturally suitable carrier therefor.

14. A composition comprising an insecticidally effective amount of a compound according to Claim 4 and an agriculturally suitable carrier therefor.

15. A composition comprising an insecticidally effective amount of a compound according to Claim 5 and an agriculturally suitable carrier therefor.

16. A method of controlling insects comprising contacting them with an effective amount of a compound according to Claim 1.

17. A method of controlling insects comprising contacting them with an effective amount of a compound according to Claim 2.

18. A method of controlling insects comprising contacting them with an effective amount of a compound according to Claim 3.

19. A method of controlling insects comprising contacting them with an effective amount of a compound according to Claim 4.

20. A method of controlling insects comprising contacting them with an effective amount of a compound according to Claim 5.

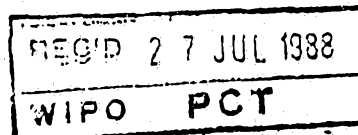
21. A composition according to Claim 11 comprising additionally a spray oil or spray oil concentrate.

22. A method for controlling insects comprising contacting them with an effective amount of a formulation according to Claim 21.

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**PATENT COOPERATION TREATY
INTERNATIONAL SEARCH REPORT**



IDENTIFICATION OF INTERNATIONAL APPLICATION		Applicant's or Agent's File Reference BA-8707-A
International Application No. PCT/US 87/03235	International Filing Date 14th December 1987	
Receiving Office RO/US	Priority Date Claimed 28th October 1987 5th January 1987	
Applicant E. I. DU PONT DE NEMOURS AND COMPANY		
I. ☐ CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹ (Observations on supplemental sheet (2))		
II. ☐ UNITY OF INVENTION IS LACKING ² (Observations on supplemental sheet (2))		
III. TITLE, ABSTRACT AND FIGURE OF DRAWING		
1. The following indicated items are approved as submitted by the applicant: ³ ☒ Title. ☒ Abstract.		
2. The texts established by this International Searching Authority of the following indicated items are set forth below: ☐ Title. ☐ Abstract.		
☐ Text of the abstract continued on supplemental sheet (1)		
3. a. ☐ The definitive contents of the abstract are established by this International Searching Authority as proposed in form PCT/ISA/204 previously sent to the applicant. b. ☐ This report is incomplete as far as the abstract is concerned as the time limit for comments by the applicant on the draft prepared by this International Searching Authority has not expired. ⁴		
4. Figure to be published with the abstract: ⁵ Figure No. _____ ☐ None of the figures ☐ as suggested by the applicant ☐ because the applicant failed to suggest a figure ☐ because this figure better characterizes the invention		

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 87/03235

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁴ : C 07 D 231/06; A 10 N 43/56		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁴	C 07 D 231/00, A 01 N 43/00	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT *		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	Journal of Heterocyclin Chemistry, volume 21, no. 4, 1 August 1984, (Tampa, US), H.M. Hassaneen et al.: "The regio-selectivity in the formation of pyrazolines and pyrazoles from nitrile imines", pages 1013-1016 see the whole document cited in the application	
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A	The Journal of Organic Chemistry, volume 20, no. 12, 1 December 1955, The American Chemical Society, (Washington, DC, US), W.R. Vaughan: "2,3-Pyrrolidinediones. VI. Reactions with phenylhydrazine", pages 1619-1626 see the whole document cited in the application	

* Special categories of cited documents: ¹⁰ "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 doubt 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 "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. "A" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
3rd July 1988	25 JUL, 1988	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	M. VAN MOL 