



# Industria y Comercio

SUPERINTENDENCIA

PCT



*fundada*

SOLICITUD

**PATENTE DE INVENCION**

02-2821

EXPEDIENTE No.

TITULO

: ARIL Y HETEROARILCICLOPROPIL OXIM ETHERES Y SU USO COMO  
FUNGICIDAS

CLASIFICACION INTERNACIONAL

: C07C 251/60

SOLICITANTE

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CODIGO APODERADO : 1092

BOGOTA, D. C.

15-01-2002

102038

64

531


**Industria y Comercio**

SUPERINTENDENCIA

**PETITORIO**

SUPERINDUSTRIA Y COMERCIO

Radicación : 02002021 00000003

Folios: 84

Fecha (AND): 2002-01-15 16:20:37

Trámite : 333 TEMPORAL

411 PRESENTA

Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

Trámite 11 Act 378

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

1

**SOLICITUD DE:**


Patente de Invención.



Patente de Modelo de Utilidad.



Capítulo I.



Capítulo II.

2

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(71)

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sociedad constituida y existente bajo las leyes del Estado de Delaware, Estados Unidos de América

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NIT



C.E.



Otro



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**PCT (86)**

 Solicitud Internacional No. PCT/US01/15451

 Fecha 11 de mayo de 2001

 Publicación Internacional No. WO 01/87826 A1

 Fecha 22 de noviembre de 2001

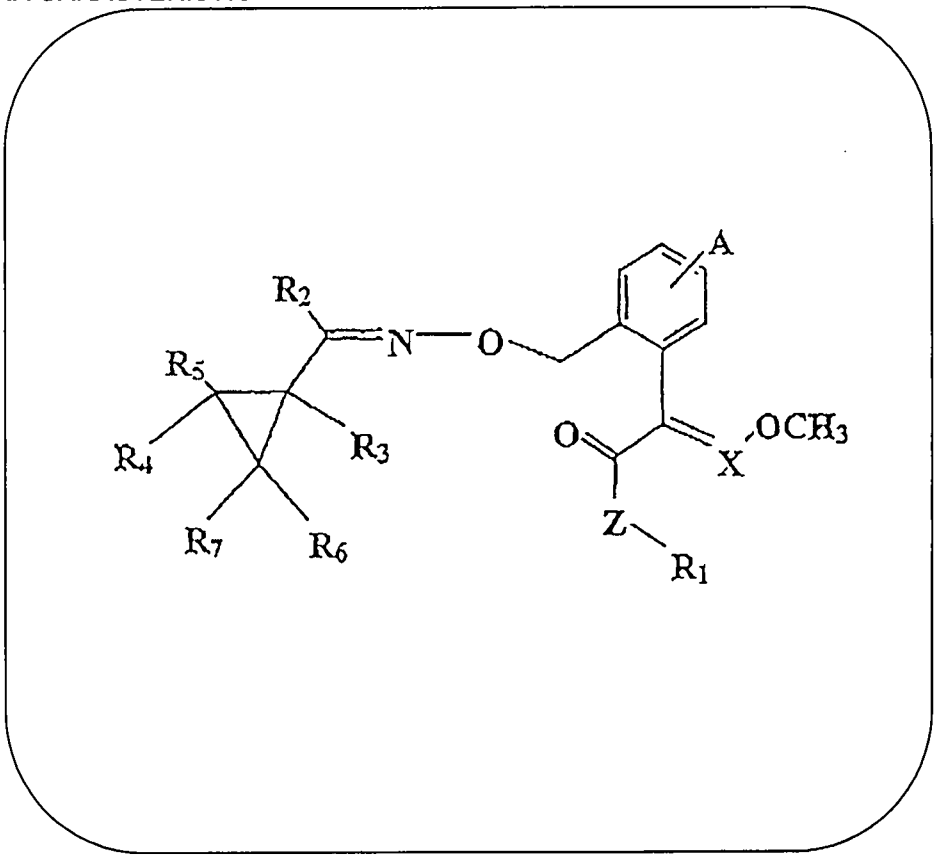
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**Título (54) ARIL Y HETEROARILCICLOPROPIL OXIM ETHERES Y SU USO COMO FUNGICIDAS**

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                     |                    |                          |
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| <div>7</div> <div>Clasificación Internacional (51)</div> <div>C07C 251/60</div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                     |                    |                          |
| <div>8</div> <div>Prioridad</div> <div>SI <input checked="" type="checkbox"/> NO <input type="checkbox"/></div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | (33) País de Origen | (32) Fecha         | (31) Número de Solicitud |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | US                  | 15 de mayo de 2000 | 09/572,487               |
| <div>9</div> <div>Comprobante de pago No.: 01-77,144 por valor de \$356,640 Fecha 10 de diciembre de 2001</div> <div>Comprobante de pago No.: 02-406 por valor de \$21,360 Fecha 8 de enero de 2002</div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                     |                    |                          |
| <div>10</div> <div>Anexos:</div> <div><div><input checked="" type="checkbox"/></div>Comprobante de pago de la tasa de presentación de la solicitud.</div> <div><div><input type="checkbox"/></div>Comprobante de pago por reivindicación de prioridad.</div> <div><div><input checked="" type="checkbox"/></div>Documento que acredita la existencia y representación legal cuando el solicitante sea persona jurídica.</div> <div><div><input checked="" type="checkbox"/></div>Poderes, si fuere el caso.</div> <div><div><input type="checkbox"/></div>Documento de cesión del inventor al solicitante o a su causante.</div> <div><div><input type="checkbox"/></div>Declaraciones.</div> <div><div><input checked="" type="checkbox"/></div>Copia de la solicitud internacional. (Resumen, descripción, reivindicaciones, dibujos)</div> <div><div><input type="checkbox"/></div>Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicaciones, dibujos)</div> <div><div><input type="checkbox"/></div>Copia del examen preliminar efectuado por la IPEA.</div> <div><div><input type="checkbox"/></div>Traducción del examen preliminar efectuado por la IPEA.</div> <div><div><input type="checkbox"/></div>De ser el caso, copia del contrato de acceso.</div> <div><div><input type="checkbox"/></div>De ser el caso, documento que acredite la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas.</div> <div><div><input type="checkbox"/></div>De ser el caso, certificado de depósito del material biológico.</div> <div><div><input checked="" type="checkbox"/></div>Arte final 12x12</div> <div><div><input type="checkbox"/></div>De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionadas parcial o totalmente con la invención de esta solicitud.</div> <div><div><input type="checkbox"/></div>Otros</div> |                     |                    |                          |

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FIGURA CARACTERISTICA:



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Solicito la concesión de la patente,

NOMBRE: EMILIO FERRERO

FIRMA: *Emilio Ferrero*

Instrucciones para la presentación de los anexos, ver reverso de esta página

(19) World Intellectual Property Organization  
International Bureau(43) International Publication Date  
22 November 2001 (22.11.2001)

PCT

(10) International Publication Number  
WO 01/87826 A1(51) International Patent Classification<sup>7</sup>: C07C 251/60,  
251/58, A01N 37/18, 37/50SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA,  
ZW.

(21) International Application Number: PCT/US01/15451

(84) Designated States (regional): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,  
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(22) International Filing Date: 11 May 2001 (11.05.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
09/572,487 15 May 2000 (15.05.2000) US(63) Related by continuation (CON) or continuation-in-part  
(CIP) to earlier application:  
US 09/572,487 (CIP)  
Filed on 15 May 2000 (15.05.2000)(71) Applicant (for all designated States except US): ROHM  
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AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,  
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,  
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,  
MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK,

## Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted  
a patent (Rule 4.17(ii)) for the following designations: AE,  
AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA,  
CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES,  
FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,  
KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG,  
MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE,  
SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU,  
ZA, ZW. ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL,  
SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ,  
MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE,  
DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR),  
OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML,  
MR, NE, SN, TD, TG)
- as to the applicant's entitlement to claim the priority of the  
earlier application (Rule 4.17(iii)) for the following desig-  
nations: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY,  
BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC,  
EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN,  
IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV,  
MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT,  
RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA,  
UG, UZ, VN, YU, ZA, ZW. ARIPO patent (GH, GM, KE, LS,  
MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM,  
AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT,  
BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,  
NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,  
GA, GN, GW, ML, MR, NE, SN, TD, TG)
- of inventorship (Rule 4.17(iv)) for US only

## Published:

- with international search report

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

(54) Title: ARYL AND HETEROARYLCYCLOPROPYL OXIME ETHERS AND THEIR USE AS FUNGICIDES

(57) Abstract: The present invention relates to certain aryl cyclopropyl oxime ether and oxime amide compounds, compositions  
containing these compounds, and methods for controlling fungi by the use of a fungitoxic amount of these compounds.

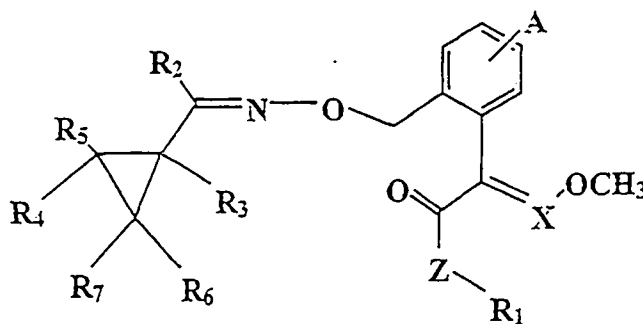
WO 01/87826 A1

# ARYL and HETEROARYLCYCLOPROPYL OXIME ETHERS AND THEIR USE AS FUNGICIDES

The present invention relates to certain aryl cyclopropyl oxime ether compounds, compositions containing these compounds, and methods for controlling fungi by the use of a fungitoxic amount of these compounds.

Compounds having certain oxime ether structures are disclosed in U.S. Patent Nos. 5,194,662, 5,292,759, and 6,063,956. The disclosed compounds provide control of a variety of fungal organisms. We have discovered a select group of such cyclopropyl oxime ethers containing specific substituted aryl and heterocyclic moieties which possess unexpectedly superior fungicidal properties when compared with the genus of compounds disclosed in the aforementioned patents.

The cyclopropyloxime ethers of the present invention have the Formula (I)



I

wherein X is N or CH; Z is O, S, or NR<sub>8</sub>;

A is hydrogen, halo, cyano, (C<sub>1</sub>-C<sub>12</sub>)alkyl, or (C<sub>1</sub>-C<sub>12</sub>)alkoxy;

R<sub>1</sub> and R<sub>8</sub> are independently hydrogen or (C<sub>1</sub>-C<sub>4</sub>)alkyl;

R<sub>2</sub> is hydrogen, (C<sub>1</sub>-C<sub>4</sub>)alkyl, halo(C<sub>1</sub>-C<sub>4</sub>)alkyl, (C<sub>3</sub>-C<sub>6</sub>)cycloalkyl, halo(C<sub>3</sub>-C<sub>6</sub>)cycloalkyl, (C<sub>2</sub>-C<sub>4</sub>)alkenyl, halo(C<sub>2</sub>-C<sub>4</sub>)alkenyl, (C<sub>2</sub>-C<sub>4</sub>)alkynyl, halo(C<sub>2</sub>-C<sub>4</sub>)alkynyl, or cyano;

R<sub>3</sub> is hydrogen, (C<sub>1</sub>-C<sub>4</sub>)alkyl, halo(C<sub>1</sub>-C<sub>4</sub>)alkyl, (C<sub>3</sub>-C<sub>6</sub>)cycloalkyl, halo(C<sub>3</sub>-C<sub>6</sub>)cycloalkyl, (C<sub>2</sub>-C<sub>4</sub>)alkenyl, halo(C<sub>2</sub>-C<sub>4</sub>)alkenyl, (C<sub>2</sub>-C<sub>4</sub>)alkynyl, or halo(C<sub>2</sub>-C<sub>4</sub>)alkynyl;

R<sub>4</sub> and R<sub>5</sub> are independently hydrogen, (C<sub>1</sub>-C<sub>4</sub>)alkyl, halo(C<sub>1</sub>-C<sub>4</sub>)alkyl, (C<sub>3</sub>-C<sub>6</sub>)cycloalkyl, halo(C<sub>3</sub>-C<sub>6</sub>)cycloalkyl, (C<sub>2</sub>-C<sub>4</sub>)alkenyl, halo(C<sub>2</sub>-C<sub>4</sub>)alkenyl, (C<sub>2</sub>-C<sub>4</sub>)alkynyl, halo(C<sub>2</sub>-C<sub>4</sub>)alkynyl, halo, cyano, or (C<sub>1</sub>-C<sub>4</sub>)alkoxycarbonyl;

and wherein

A) R<sub>7</sub> is aryl or heterocyclic ring wherein the aryl or heterocyclic ring is substituted with from 2 to 5 substituents and wherein the positions on the aryl or heterocyclic ring adjacent to the bond to the cyclopropyl ring are both substituted and R<sub>6</sub> is hydrogen, (C<sub>1</sub>-C<sub>4</sub>)alkyl, halo(C<sub>1</sub>-C<sub>4</sub>)alkyl, (C<sub>3</sub>-C<sub>6</sub>)cycloalkyl, halo(C<sub>3</sub>-C<sub>6</sub>)cycloalkyl, (C<sub>2</sub>-C<sub>4</sub>)alkenyl, halo(C<sub>2</sub>-C<sub>4</sub>)alkenyl, (C<sub>2</sub>-C<sub>4</sub>)alkynyl, halo(C<sub>2</sub>-C<sub>4</sub>)alkynyl, halo, cyano, or (C<sub>1</sub>-C<sub>4</sub>)alkoxycarbonyl;

or

B) R<sub>7</sub> is an aryl or heterocyclic ring wherein the aryl or heterocyclic ring is unsubstituted or substituted from 1 to 4 substituents wherein at least one of the positions on the aryl or heterocyclic ring adjacent to the bond to the cyclopropyl ring is a hydrogen and R<sub>6</sub> is selected from the group consisting of (C<sub>1</sub>-C<sub>4</sub>)alkyl, halo(C<sub>1</sub>-C<sub>4</sub>)alkyl, (C<sub>3</sub>-C<sub>6</sub>)cycloalkyl, halo(C<sub>3</sub>-C<sub>6</sub>)cycloalkyl, (C<sub>2</sub>-C<sub>4</sub>)alkenyl, halo(C<sub>2</sub>-C<sub>4</sub>)alkenyl, (C<sub>2</sub>-C<sub>4</sub>)alkynyl, halo(C<sub>2</sub>-C<sub>4</sub>)alkynyl, halo, cyano, or (C<sub>1</sub>-C<sub>4</sub>)alkoxycarbonyl;

and their salts, complexes, enantiomorphs, stereoisomers;

and mixtures thereof.

The biological activity of compounds of Formula I is greatly influenced by the interaction between the R<sub>6</sub> and R<sub>7</sub> groups, which are attached to the same carbon on the cyclopropyl ring, and, more specifically, by the number, type, and configuration of substituents on the aryl or heteroaryl R<sub>7</sub>, particularly those in the ortho position to the bond between the R<sub>7</sub> group and the cyclopropyl ring, while taking into account whether the R<sub>6</sub> group is a hydrogen or a different group.

The aforementioned alkyl, alkenyl, alkynyl and (C<sub>3</sub>-C<sub>6</sub>)cycloalkyl groups may be optionally and independently substituted with up to three substituents selected from nitro, halomethyl, (C<sub>1</sub>-C<sub>4</sub>)alkoxycarbonyl, and cyano.

Unless otherwise specified herein, the term alkyl includes both branched and straight chain alkyl groups from 1 to 4 carbon atoms. Typical alkyl groups are methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, isobutyl, t-butyl, n-pentyl, isopentyl, n-hexyl, n-heptyl, isooctyl, nonyl, decyl, undecyl, dodecyl and the like. The term haloalkyl refers to an alkyl group substituted with from 1 to 3 halogens.

Unless otherwise specified herein, the term alkenyl refers to an ethylenically unsaturated hydrocarbon group, straight or branched, having a chain length of from 2 to 4 carbon atoms and 1 ethylenic bonds. The term haloalkenyl refers to an alkenyl group substituted with from 1 to 3 halogen atoms. The term alkynyl refers to an unsaturated hydrocarbon group, straight or branched, having a chain length of from 2 to 4 carbon atoms and 1 acetylenic bonds.

Unless otherwise specified herein, the term aryl includes phenyl and naphthyl which maybe substituted with up to five substituents independently selected from halogen, cyano, nitro, trihalomethyl, trihalomethoxy, phenyl, phenoxy, (C<sub>1</sub>-C<sub>4</sub>)alkyl, (C<sub>3</sub>-C<sub>6</sub>)cycloalkyl, (C<sub>2</sub>-C<sub>4</sub>)alkenyl, (C<sub>1</sub>-C<sub>4</sub>)alkoxy, (C<sub>1</sub>-C<sub>4</sub>)alkylthio, (C<sub>1</sub>-C<sub>4</sub>)alkylsulfoxide, halo(C<sub>1</sub>-C<sub>4</sub>)alkyl, halo(C<sub>1</sub>-C<sub>4</sub>)alkoxy, halo(C<sub>3</sub>-C<sub>6</sub>)cycloalkyl, halo(C<sub>2</sub>-C<sub>4</sub>)alkenyl, or (C<sub>1</sub>-C<sub>4</sub>)alkoxycarbonyl. Typical phenyl substituents, wherein at least one of the positions on the phenyl ring adjacent to the bond to the cyclopropyl ring is substituted with hydrogen include but are not limited to 2-chloro, 3-chloro, 4-chloro, 2-fluoro, 3-fluoro, 4-fluoro, 2-bromo, 3-bromo, 4-bromo, 2-methyl, 3-methyl, 4-methyl, 2-trifluoromethyl, 3-trifluoromethyl, 4-trifluoromethyl, 2-methoxy, 3-methoxy, 4-methoxy, 2-trifluoromethoxy, 3-trifluoromethoxy, 4-trifluoromethoxy, 2-cyano, 3-cyano, 4-cyano, 2,3-dichloro, 2,3-difluoro, 2,3-dibromo, 2,3-dimethyl, 2,3-dimethoxy, 2,3-bis(trifluoromethyl), 2,3bis-(trifluoromethoxy), 2,4-difluoro, 2,4-dichloro, 2,4-dibromo, 2,4-dimethyl, 2,4-dimethoxy, 2,4-bis(trifluoromethyl), 2,4-bis(trifluoromethoxy), 2,5-difluoro, 2,5-dichloro, 2,5-dibromo, 2,5-dimethyl, 2,5-

dimethoxy, 2,5-bis(trifluoromethyl), 2,5-bis-(trifluoromethoxy), 3,4-difluoro, 3,4-dichloro, 3,4-dibromo, 3,4-dimethyl, 3,4-dimethoxy, 3,4-bis(trifluoromethyl), 3,4-bis(trifluoromethoxy), 3,5-difluoro, 3,5-dichloro, 3,5-dibromo, 3,5-dimethyl, 3,5-bis(trifluoromethyl), 3,5-bis(trifluoro-methoxy), 2,3,4-trifluoro, 2,3,4-trichloro, 2,3,4-tribromo, 2,3,4-trimethyl, 2,3,4-trimethoxy, 2,3,4-tris(trifluoromethyl), 2,3,4-tris(trifluoromethoxy), 2,3,5-trifluoro, 2,3,5-trichloro, 2,3,5-tribromo, 2,3,5-trimethyl, 2,3,5-tris(trifluoromethyl), 2,3,5-tris(trifluoromethoxy), 2,4,5-trifluoro, 2,4,5-trichloro, 2,4,5-tribromo, 2,4,5-trimethyl, 2,4,5-trimethoxy, 2,4,5-tris(trifluoromethyl), 2,4,5-tris(trifluoromethoxy), 3,4,5-trifluoro, 3,4,5-trichloro, 3,4,5-tribromo, 3,4,5-trimethyl, 3,4,5-trimethoxy, 3,4,5-tris(trifluoromethyl), 3,4,5-tris(trifluoromethoxy), 2,3,4,5-tetrafluoro, 2,3,4,5-tetrachloro, 2,3,4,5-tetrabromo, 2,3,4,5-tetramethyl, 2,3,4,5-tetramethoxy, 2,3,4,5-tetra(trifluoromethyl), and 2,3,4,5-tetra(tetrafluoromethoxy).

Typical phenyl substituents, where both positions on the phenyl ring adjacent to the bond to the cyclopropyl rings are substituted include but are not limited to 2,6-dichloro, 2,3,6-trichloro, 2,4,6-trichloro, 2,6-difluoro, 2,3,6-trifluoro, 2,4,6-trifluoro, 2,6-dibromo, 2,3,6-tribromo, 2,4,6-tribromo, 2,3,4,6-tetrachloro, 2,3,5,6-tetrachloro, 2,3,4,5,6-pentachloro, 2,3,4,6-tetrabromo, 2,3,5,6-tetrabromo, 2,3,4,5,6-pentabromo, 2,3,4,6-tetrafluoro, 2,3,5,6-tetrafluoro, 2,3,4,5,6-pentafluoro, 2,6-dimethyl, 2,3,6-trimethyl, 2,4,6-trimethyl, 2,6-dimethoxy, 2,3,6-trimethoxy, 2,4,6-trimethoxy, 2,6-diethoxy, 2,3,6-triethoxy, 2,4,6-triethoxy, 2,3,4,6-tetramethyl, 2,3,5,6-tetramethyl, 2,3,4,5,6-pentamethyl, 2,3,4,6-tetramethoxy, 2,3,5,6-tetramethoxy, 2,3,4,5,6-pentamethoxy, 2,3,4,6-tetraethoxy, 2,3,5,6-tetraethoxy, 2,3,4,5,6-pentaethoxy, 2,6-dicyano, 2,3,6-tricyano, 2,4,6-tricyano, 2,6-dinitro, 2,6-diphenyl, 2,6-diphenoxy, 2,6-dibenzyl, 2,6-bis(trifluoromethyl), 2,3,6-tris(trifluoromethyl), 2,4,6-tris-(trifluoro-methyl), 2,3,4,6-tetra(trifluoromethyl), 2,3,5,6-tetra(trifluoromethyl), 2,3,4,5,6-penta(trifluoromethyl), 2,6-bis-(trifluoromethoxy), 2,3,6-tris(trifluoromethoxy), 2,4,6-tris(trifluoromethoxy), 2,3,4,5-tetra(trifluoromethoxy), 2,3,4,6-tetra-(trifluoro-methoxy), 2,3,5,6-tetra(trifluoromethoxy), 2,3,4,5,6-penta(trifluoromethoxy), 2-bromo-6-chloro, 2-bromo-6-fluoro, 2-bromo-6-(trifluoromethyl), 2-bromo-6-methyl, 2-bromo-6-methoxy, 2-bromo-6-

(trifluoromethoxy), 2-bromo-6-cyano, 2-chloro-6-fluoro, 2-chloro-6-(trifluoromethyl), 2-chloro-6-methyl, 2-chloro-6-methoxy, 2-chloro-6-trifluoromethoxy, 2-chloro-6-cyano, 2-fluoro-6-(trifluoromethyl), 2-fluoro-6-methyl, 2-fluoro-6-methoxy, 2-fluoro-6-(trifluoromethoxy), 6-cyano-2-fluoro, 2-methyl-6-(trifluoromethyl), 6-methoxy-2-methyl, 2-methyl-6-(trifluoromethoxy), 6-cyano-2-methyl, 3,6-dichloro-2-fluoro, 3-chloro-2,6-difluoro, 4-chloro-2,6-difluoro, 2-bromo-3,6-dichloro, 2,3-dibromo-6-chloro, 3-chloro-2,6-dibromo, 2,6-dichloro-3-fluoro, 2,3-dichloro-6-fluoro, 2-chloro-3,6-difluoro, 3-bromo-2,6-dichloro, 3-bromo-2,6-fluoro, 3-bromo-6-chloro-2-fluoro, 2-bromo-5-chloro-6-fluoro, 2,6-dibromo-3-fluoro, 2,5-dibromo-6-fluoro, 2,4-dichloro-6-fluoro, 2,6-chloro-4-fluoro, 2,4-dichloro-6-bromo, 2,6-dichloro-4-bromo, 2,4-difluoro-6-chloro, 2,4-difluoro-6-bromo, 2,6-difluoro-4-bromo, 2,4-dibromo-6-fluoro, 2,4-dibromo-6-chloro, 2,6-dibromo-4-chloro, 2,6-dibromo-4-fluoro, 2,4-dichloro-6-methyl, 2,6-dichloro-4-methyl, 2-chloro-4,6-dimethyl, 4-chloro-2,6-dimethyl, 2,4-difluoro-6-methyl, 2,6-difluoro-4-methyl, 2-fluoro-4,6-dimethyl, 4-fluoro-2,6-dimethyl, 2,4-dibromo-6-methyl, 2,6-dibromo-4-methyl, 2-bromo-4,6-dimethyl, 4-bromo-2,6-dimethyl, 2,4-dichloro-6-methoxy, 2,6-dichloro-4-methoxy, 2-chloro-4,6-dimethoxy, 4-chloro-2,6-dimethoxy, 2,4-difluoro-6-methoxy, 2,6-difluoro-4-methoxy, 2-fluoro-4,6-dimethoxy, 4-fluoro-2,6-dimethoxy, 2,4-dibromo-6-methoxy, 2,6-dibromo-4-methoxy, 4-bromo-2,6-dimethoxy, 4-bromo-2,6-dimethoxy, 2,4-dichloro-6-(trifluoromethyl), 2,6-dichloro-4-(trifluoromethyl), 2-chloro-4,6-bis(trifluoromethyl), 4-chloro-2,6-bis(trifluoromethyl), 2,4-difluoro-6-(trifluoromethyl), 2,6-difluoro-4-(trifluoromethyl), 2-fluoro-4,6-bis(trifluoromethyl), 4-fluoro-2,6-bis(trifluoromethyl), 2,4-dibromo-6-(trifluoromethyl), 2,6-dibromo-4-(trifluoromethyl), 2-bromo-4,6-bis(trifluoromethyl), 4-bromo-2,6-bis(trifluoromethyl), 2-chloro-4,6-bis(trifluoromethoxy), 4-chloro-2,6-bis(trifluoromethoxy), 2,4-difluoro-6-(trifluoromethoxy), 2,6-difluoro-4-(trifluoromethoxy), 2-fluoro-4,6-bis(trifluoromethoxy), 4-fluoro-2,6-bis(trifluoromethoxy), 2,4-dibromo-6-(trifluoromethoxy), 2,6-dibromo-4-(trifluoromethoxy), 2-bromo-4,6-bis(trifluoromethoxy), 4-bromo-2,6-bis(trifluoromethoxy), 4,6-dichloro-2-nitro, 4,6-dibromo-2-nitro, 4,6-difluoro-2-nitro, 2,6-dichloro-4-nitro, 2-bromo-3,4,6-trichloro, 6-fluoro-2,4,5-trichloro, 6-

chloro-2,4,5-tribromo, 6-fluoro-2,4,5-tribromo, 2-bromo-3,4,6-trifluoro, 2-chloro-3,4,6-trifluoro, 6-methyl-2,4,5-trichloro, 6-methyl-2,4,5-tribromo, 6-methyl-2,4,5-trifluoro, 6-(trifluoromethyl)-2,4,5-trichloro, 6-(trifluoromethyl)-2,4,5-tribromo, 2-(trifluoro-methyl)-3,4,6-trifluoro, 6-(trifluoromethoxy)-2,4,5-tribromo, 2-(trifluoromethoxy)-3,4,6-trifluoro, 6-(trifluoromethoxy)-2,4,5-trichloro, 2-bromo-3,5,6-trichloro, 6-fluoro-2,3,5-trichloro, 6-chloro-2,3,5-tribromo, 6-fluoro-2,3,5-tribromo, 2-bromo-3,5,6-trifluoro, 2-chloro-3,5,6-trifluoro, 6-methyl-2,3,5-trichloro, 6-methyl-2,3,5-tribromo, 2-methyl-3,5,6-trifluoro, 6-(trifluoromethyl)-2,3,5-trichloro, 6-(trifluoro-methyl)-2,3,5-tribromo, 2-(trifluoromethyl)-3,5,6-trifluoro, 2-(trifluoromethoxy)-3,5,6-trichloro, 6-(trifluoromethoxy)-2,3,5-tribromo, 2-(trifluoromethoxy)-3,5,6-trifluoro, 4-bromo-2,3,5,6-tetrachloro, 4-fluoro-2,3,5,6-tetrachloro, 4-chloro-2,3,5,6-tetrabromo-, 4-fluoro-2,3,5,6-tetrabromo, 4-chloro-2,3,5,6-tetrafluoro, 4-bromo-2,3,5,6-tetrafluoro, 2-bromo-3,4,5,6-tetrachloro, 6-fluoro-2,3,4,5-tetrachloro-, 2-chloro-3,4,5,6-tetrafluoro, 2-bromo-3,4,5,6-tetrafluoro, 2-chloro-3,4,5,6-tetrabromo, 2-fluoro-3,4,5,6-tetrabromo, 4-methyl-2,3,5,6-tetrachloro, 4-methyl-2,3,5,6-tetrabromo, 4-methyl-2,3,5,6-tetrafluoro, 2,3,5,6-tetrachloro-4-(trifluoromethyl), 2,3,5,6-tetrabromo-4-(trifluoromethyl), 2,3,5,6-tetrafluoro-4-(trifluoromethyl), 2,3,5,6-tetrachloro-4-(trifluoromethoxy), 2,3,5,6-tetrabromo-4-(trifluoromethoxy, 2,3,5,6-tetrafluoro-4-(trifluoromethoxy), 6-methyl-2,3,4,5-tetrachloro, 6-methyl-2,3,4,5-tetrabromo, 2-methyl-3,4,5,6-tetrafluoro, 2,3,4,5-tetrachloro-6-(trifluoromethyl), 2,3,4,5-tetrabromo-6-(trifluoromethyl), 3,4,5,6-tetrafluoro-2-(trifluoromethyl), 2,3,4,5-tetrachloro-6-(trifluoromethoxy), 2,3,4,5-tetrabromo-6-(trifluoromethoxy), and 3,4,5,6-tetrafluoro-2-(trifluoromethoxy).

The term heterocyclic refers to a substituted 6 membered unsaturated ring selected from 3- or 4-pyridinyl, 5-pyrimidinyl, 3-pyridazinyl or a 5 membered unsaturated ring selected from 3-thienyl, 3-furyl, 3-pyrrolyl, 4-isoxazolyl, 4-isothiazolyl or 4-pyrazolyl wherein both the positions on the heterocyclic ring adjacent to the bond to the cyclopropyl ring are substituted and the ring is substituted with from 2 to 4 substituents independently selected from (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>3</sub>-C<sub>6</sub>)cycloalkyl, trihalomethyl, trihalomethoxy, halogen, cyano, (C<sub>1</sub>-C<sub>4</sub>)alkoxycarbonyl, nitro, phenyl, and phenoxy. The term heterocyclic also

refers to a substituted or unsubstituted 6 membered unsaturated ring containing one, two or three heteroatoms, preferably one, two or three heteroatoms independently selected from oxygen, nitrogen, and sulfur or a 5 membered unsaturated ring containing one, two or three heteroatoms, preferably one or two heteroatoms independently selected from oxygen, nitrogen, and sulfur wherein the heterocyclic ring is unsubstituted or is substituted with from 1 to 3 substituents wherein at least one of the positions of the heterocyclic ring adjacent to the bond to the cyclopropyl ring is a hydrogen substituent. Examples of heterocycles include but are not limited to 2-, 3- or 4-pyridinyl, pyrazinyl, 4-, or 5-pyrimidinyl, pyridazinyl, pyrazole, imidazolyl, 2 or 3-thienyl, 2 or 3-furyl, 3-pyrrolyl, oxazolyl, isoxazolyl, thiazolyl, isothiazolyl, oxadiazolyl, and thiadiazolyl. These rings may be optionally substituted with up from 1 to 3 substituents independently selected from (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>3</sub>-C<sub>7</sub>)cycloalkyl, trihalomethyl, halogen, cyano, (C<sub>1</sub>-C<sub>4</sub>)alkoxycarbonyl, nitro, phenyl, and phenoxy.

Halogen or halo includes iodo, fluoro, bromo and chloro moieties.

The compounds of the general Formula I may be obtained in preparation as E/Z isomeric mixtures. These isomers can be separated into individual components by conventional means. The substituted cyclopropanes of Formula I may be obtained in preparation as cis and trans isomeric mixtures which can also be separated into individual components by conventional means. Both the individual isomeric compounds as well as mixtures thereof form subjects of the invention and can be used as fungicides and insecticides.

One preferred embodiment of this invention includes the compounds, enantiomorphs, salts and complexes of Formula I wherein X is CH or N; Z is O or NH; A, R<sub>3</sub>, R<sub>4</sub>, and R<sub>5</sub> are each hydrogen; R<sub>1</sub> and R<sub>2</sub> are CH<sub>3</sub>; R<sub>7</sub> is 2,6-dichlorophenyl or 2,6-difluorophenyl; and R<sub>6</sub> is hydrogen.

Another preferred embodiment of this invention includes the compounds, enantiomorphs, salts and complexes of Formula I wherein X is CH or N; Z is O or NH; A, R<sub>3</sub>, R<sub>4</sub>, and R<sub>5</sub> are each hydrogen; R<sub>1</sub> and R<sub>2</sub> are CH<sub>3</sub>; R<sub>7</sub> is 2,6-dichlorophenyl or 2,6-difluorophenyl; and R<sub>6</sub> is halo, (C<sub>1</sub>-C<sub>4</sub>)alkyl, halo(C<sub>1</sub>-

C<sub>4</sub>)alkyl, cyclopropyl, halocyclopropyl, (C<sub>2</sub>-C<sub>4</sub>)alkenyl, halo(C<sub>2</sub>-C<sub>4</sub>)alkenyl, (C<sub>2</sub>-C<sub>4</sub>)alkynyl, or halo(C<sub>2</sub>-C<sub>4</sub>)alkynyl.

Another preferred embodiment of this invention is the compounds, enantiomorphs, salts and complexes of Formula I wherein X is CH or N; Z is O or NH; A is hydrogen; R<sub>1</sub> and R<sub>2</sub> are independently (C<sub>1</sub>-C<sub>4</sub>)alkyl; R<sub>3</sub>, R<sub>4</sub>, and R<sub>5</sub> are hydrogen; R<sub>7</sub> is phenyl other than 2,6-dichlorophenyl or 2,6-difluorophenyl such that the positions on the phenyl ring adjacent to the bond to the cyclopropyl rings are both substituted, and R<sub>6</sub> is selected from hydrogen, halo, (C<sub>1</sub>-C<sub>4</sub>)alkyl, halo(C<sub>1</sub>-C<sub>4</sub>)alkyl, cyclopropyl, halocyclopropyl, (C<sub>2</sub>-C<sub>4</sub>)alkenyl, halo(C<sub>2</sub>-C<sub>4</sub>)alkenyl, (C<sub>2</sub>-C<sub>4</sub>)alkynyl, and halo(C<sub>2</sub>-C<sub>4</sub>)alkynyl.

A more preferred embodiment of this invention is the compounds, enantiomorphs, salts and complexes of Formula I wherein X is CH or N; Z is O or NH; A is hydrogen; R<sub>1</sub> and R<sub>2</sub> are independently (C<sub>1</sub>-C<sub>4</sub>)alkyl; R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> are hydrogen; R<sub>6</sub> is hydrogen; and R<sub>7</sub> is 2,3,6-trisubstitutedphenyl, 2,4,6-trisubstitutedphenyl, 2,3,4,6-tetrasubstitutedphenyl, 2,3,5,6-tetrasubstituted, or 2,3,4,5,6-pentasubstitutedphenyl.

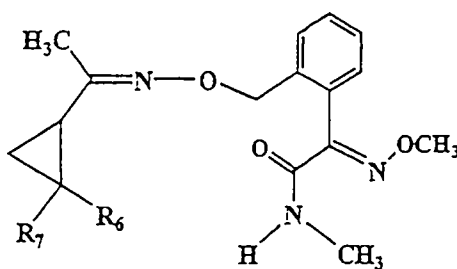
An even more preferred embodiment of this invention are the compounds, enantiomorphs, salts and complexes of Formula I wherein X is N; Z is NH; A is hydrogen; R<sub>1</sub> and R<sub>2</sub> are CH<sub>3</sub>; R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> are hydrogen; R<sub>6</sub> is hydrogen; and R<sub>7</sub> is 2,3,6-trihalophenyl, 2,4,6-trihalophenyl, 2,3,4,6-tetrahalophenyl, 2,3,5,6-tetrahalophenyl, or 2,3,4,5,6-pentahalophenyl.

Still another preferred embodiment of this invention is the compounds, enantiomorphs, salts and complexes of Formula I wherein X is CH or N; Z is O or NH; A is hydrogen; R<sub>1</sub> and R<sub>2</sub> are independently (C<sub>1</sub>-C<sub>4</sub>)alkyl; R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> are hydrogen; R<sub>7</sub> is a substituted or unsubstituted phenyl or heterocyclic wherein at least one of the positions on the phenyl or heterocyclic ring adjacent to the bond to the cyclopropyl ring is a hydrogen substituent; and R<sub>6</sub> is (C<sub>1</sub>-C<sub>4</sub>)alkyl, halo(C<sub>1</sub>-C<sub>4</sub>)alkyl, cyclopropyl, halocyclopropyl, (C<sub>2</sub>-C<sub>4</sub>)alkenyl, halo(C<sub>2</sub>-C<sub>4</sub>)alkenyl, (C<sub>2</sub>-C<sub>4</sub>)alkynyl, halo(C<sub>2</sub>-C<sub>4</sub>)alkynyl, halo or cyano.

Another more preferred embodiment of this invention is the compounds, enantiomorphs, salts and complexes of Formula I wherein X is N; Z is O or NH;

A is hydrogen;  $R_1$  and  $R_2$  is  $(CH_3)$ ;  $R_3$ ,  $R_4$  and  $R_5$  are hydrogen;  $R_7$  is phenyl, 2-substitutedphenyl, 3-substitutedphenyl, 4-substitutedphenyl, 2,3-disubstitutedphenyl, 2,4-disubstitutedphenyl, 2,5-disubstitutedphenyl, 3,4-disubstitutedphenyl, 3,5-disubstituted, 2,3,4-trisubstitutedphenyl, 2,3,5-trisubstitutedphenyl, 2,4,5-trisubstitutedphenyl, 3,4,5-trisubstitutedphenyl, or 2,3,4,5-tetrasubstitutedphenyl; and  $R_6$  is halo, cyano,  $(C_1-C_4)$ alkyl, or halo( $C_1-C_4$ )alkyl.

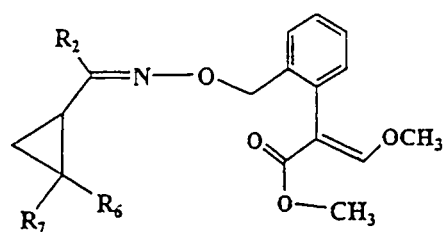
A second even more preferred embodiment of this invention is the compounds, enantiomorphs, salts and complexes of Formula II wherein  $R_7$  is phenyl, 2-halophenyl, 3-halophenyl, 4-halophenyl, 2,3-dihalophenyl, 2,4-dihalophenyl, 2,5-dihalophenyl, 3,4-dihalophenyl, 3,5-dihalophenyl, 2,3,4-trihalophenyl, 2,3,5-trihalophenyl, 2,4,5-trihalophenyl, 3,4,5-trihalophenyl, or 2,3,4,5-tetrahalophenyl, and  $R_6$  is  $(C_1-C_4)$ alkyl.



II

A most preferred embodiment of this invention is the compounds, enantiomorphs, salts and complexes of Formula II wherein  $R_7$  is phenyl, 2-chlorophenyl, 3-chlorophenyl, or 4-chlorophenyl, 2-fluorophenyl, 3-fluorophenyl, 4-fluorophenyl, 2,4-dichlorophenyl, 2,4-difluorophenyl, 2-chloro-4-fluorophenyl, 2-fluoro-4-chlorophenyl, and  $R_6$  is  $CH_3$ .

Typical compounds of Formula I encompassed by the present invention wherein A,  $R_3$ ,  $R_4$ , and  $R_5$  are hydrogen; X is CH and Z is O; and  $R_1$  is methyl include those compounds presented in Table 1 of Formula III where  $R_2$ ,  $R_6$ , and  $R_7$  are defined in Table 1. As used in Tables 1 to 12, Ph is phenyl.



Formula III

Table 1

| <u>Comp</u> | <u>R<sub>2</sub></u> | <u>R<sub>6</sub></u> | <u>R<sub>7</sub></u>    |
|-------------|----------------------|----------------------|-------------------------|
| 1.1         | H                    | CH <sub>3</sub>      | Ph                      |
| 1.2         | H                    | CH <sub>3</sub>      | 4-Cl(Ph)                |
| 1.3         | H                    | CH <sub>3</sub>      | 4-Br(Ph)                |
| 1.4         | H                    | CH <sub>3</sub>      | 4-F(Ph)                 |
| 1.5         | H                    | CH <sub>3</sub>      | 4-OCH <sub>3</sub> (Ph) |
| 1.6         | H                    | CH <sub>3</sub>      | 4-CF <sub>3</sub> (Ph)  |
| 1.7         | H                    | CH <sub>3</sub>      | 4-NO <sub>2</sub> (Ph)  |
| 1.8         | H                    | CH <sub>3</sub>      | 2,4-Cl(Ph)              |
| 1.9         | H                    | CH <sub>3</sub>      | 2,4-F(Ph)               |
| 1.10        | H                    | CH <sub>3</sub>      | 3,4-F(Ph)               |
| 1.11        | CH <sub>3</sub>      | CH <sub>3</sub>      | Ph                      |
| 1.12        | CH <sub>3</sub>      | CH <sub>3</sub>      | 2-Cl(Ph)                |
| 1.13        | CH <sub>3</sub>      | CH <sub>3</sub>      | 3-Cl(Ph)                |
| 1.14        | CH <sub>3</sub>      | CH <sub>3</sub>      | 4-Cl(Ph)                |
| 1.15        | CH <sub>3</sub>      | CH <sub>3</sub>      | 2-Br(Ph)                |
| 1.16        | CH <sub>3</sub>      | CH <sub>3</sub>      | 3-Br(Ph)                |
| 1.17        | CH <sub>3</sub>      | CH <sub>3</sub>      | 4-Br(Ph)                |
| 1.18        | CH <sub>3</sub>      | CH <sub>3</sub>      | 2-F(Ph)                 |
| 1.19        | CH <sub>3</sub>      | CH <sub>3</sub>      | 3-F(Ph)                 |
| 1.20        | CH <sub>3</sub>      | CH <sub>3</sub>      | 4-F(Ph)                 |
| 1.21        | CH <sub>3</sub>      | CH <sub>3</sub>      | 2-OCH <sub>3</sub> (Ph) |
| 1.22        | CH <sub>3</sub>      | CH <sub>3</sub>      | 3-OCH <sub>3</sub> (Ph) |
| 1.23        | CH <sub>3</sub>      | CH <sub>3</sub>      | 4-OCH <sub>3</sub> (Ph) |
| 1.24        | CH <sub>3</sub>      | CH <sub>3</sub>      | 2-CH <sub>3</sub> (Ph)  |
| 1.25        | CH <sub>3</sub>      | CH <sub>3</sub>      | 3-CH <sub>3</sub> (Ph)  |
| 1.26        | CH <sub>3</sub>      | CH <sub>3</sub>      | 4-CH <sub>3</sub> (Ph)  |
| 1.27        | CH <sub>3</sub>      | CH <sub>3</sub>      | 2-CF <sub>3</sub> (Ph)  |
| 1.28        | CH <sub>3</sub>      | CH <sub>3</sub>      | 3-CF <sub>3</sub> (Ph)  |
| 1.29        | CH <sub>3</sub>      | CH <sub>3</sub>      | 4-CF <sub>3</sub> (Ph)  |
| 1.30        | CH <sub>3</sub>      | CH <sub>3</sub>      | 2-NO <sub>2</sub> (Ph)  |
| 1.31        | CH <sub>3</sub>      | CH <sub>3</sub>      | 3-NO <sub>2</sub> (Ph)  |
| 1.32        | CH <sub>3</sub>      | CH <sub>3</sub>      | 4-NO <sub>2</sub> (Ph)  |
| 1.33        | CH <sub>3</sub>      | CH <sub>3</sub>      | 2,3-Cl(Ph)              |
| 1.34        | CH <sub>3</sub>      | CH <sub>3</sub>      | 2,4-Cl(Ph)              |
| 1.35        | CH <sub>3</sub>      | CH <sub>3</sub>      | 2,5-Cl(Ph)              |
| 1.36        | CH <sub>3</sub>      | CH <sub>3</sub>      | 3,4-Cl(Ph)              |
| 1.37        | CH <sub>3</sub>      | CH <sub>3</sub>      | 3,5-Cl(Ph)              |
| 1.38        | CH <sub>3</sub>      | CH <sub>3</sub>      | 2,3,5-Cl(Ph)            |
| 1.39        | CH <sub>3</sub>      | CH <sub>3</sub>      | 2,3-F(Ph)               |

|      |                                   |                 |                         |
|------|-----------------------------------|-----------------|-------------------------|
| 1.40 | CH <sub>3</sub>                   | CH <sub>3</sub> | 2,4-F(Ph)               |
| 1.41 | CH <sub>3</sub>                   | CH <sub>3</sub> | 2,5-F(Ph)               |
| 1.42 | CH <sub>3</sub>                   | CH <sub>3</sub> | 3,4-F(Ph)               |
| 1.43 | CH <sub>3</sub>                   | CH <sub>3</sub> | 3,5-F(Ph)               |
| 1.44 | CH <sub>3</sub>                   | CH <sub>3</sub> | 2,4,5-F(Ph)             |
| 1.45 | CH <sub>3</sub>                   | CH <sub>3</sub> | 2,4,5-Cl(Ph)            |
| 1.46 | CH <sub>3</sub>                   | CH <sub>3</sub> | 3,4,5-Cl(Ph)            |
| 1.47 | CH <sub>3</sub>                   | CH <sub>3</sub> | 2,3,4,5-Cl(Ph)          |
| 1.48 | CH <sub>3</sub>                   | CH <sub>3</sub> | 2,3,5-F(Ph)             |
| 1.49 | CH <sub>3</sub>                   | CH <sub>3</sub> | 3,4,5-F(Ph)             |
| 1.50 | CH <sub>3</sub>                   | CH <sub>3</sub> | 2,3,4,5-F(Ph)           |
| 1.51 | C <sub>2</sub> H <sub>5</sub>     | CH <sub>3</sub> | Ph                      |
| 1.52 | C <sub>2</sub> H <sub>5</sub>     | CH <sub>3</sub> | 2-Cl(Ph)                |
| 1.53 | C <sub>2</sub> H <sub>5</sub>     | CH <sub>3</sub> | 3-Cl(Ph)                |
| 1.54 | C <sub>2</sub> H <sub>5</sub>     | CH <sub>3</sub> | 4-Cl(Ph)                |
| 1.55 | C <sub>2</sub> H <sub>5</sub>     | CH <sub>3</sub> | 4-Br(Ph)                |
| 1.56 | C <sub>2</sub> H <sub>5</sub>     | CH <sub>3</sub> | 4-F(Ph)                 |
| 1.57 | C <sub>2</sub> H <sub>5</sub>     | CH <sub>3</sub> | 4-OCH <sub>3</sub> (Ph) |
| 1.58 | C <sub>2</sub> H <sub>5</sub>     | CH <sub>3</sub> | 4-CH <sub>3</sub> (Ph)  |
| 1.59 | C <sub>2</sub> H <sub>5</sub>     | CH <sub>3</sub> | 4-NO <sub>2</sub> (Ph)  |
| 1.60 | C <sub>2</sub> H <sub>5</sub>     | CH <sub>3</sub> | 2,4-Cl(Ph)              |
| 1.61 | C <sub>2</sub> H <sub>5</sub>     | CH <sub>3</sub> | 2,4-F(Ph)               |
| 1.62 | n-C <sub>3</sub> H <sub>7</sub>   | CH <sub>3</sub> | Ph                      |
| 1.63 | n-C <sub>3</sub> H <sub>7</sub>   | CH <sub>3</sub> | 2-Cl(Ph)                |
| 1.64 | n-C <sub>3</sub> H <sub>7</sub>   | CH <sub>3</sub> | 3-Cl(Ph)                |
| 1.65 | n-C <sub>3</sub> H <sub>7</sub>   | CH <sub>3</sub> | 4-Cl(Ph)                |
| 1.66 | n-C <sub>3</sub> H <sub>7</sub>   | CH <sub>3</sub> | 4-F(Ph)                 |
| 1.67 | n-C <sub>3</sub> H <sub>7</sub>   | CH <sub>3</sub> | 3-OCH <sub>3</sub> (Ph) |
| 1.68 | n-C <sub>3</sub> H <sub>7</sub>   | CH <sub>3</sub> | 4-OCH <sub>3</sub> (Ph) |
| 1.69 | n-C <sub>3</sub> H <sub>7</sub>   | CH <sub>3</sub> | 4-CH <sub>3</sub> (Ph)  |
| 1.70 | n-C <sub>3</sub> H <sub>7</sub>   | CH <sub>3</sub> | 4-NO <sub>2</sub> (Ph)  |
| 1.71 | n-C <sub>3</sub> H <sub>7</sub>   | CH <sub>3</sub> | 2,4-Cl(Ph)              |
| 1.72 | n-C <sub>3</sub> H <sub>7</sub>   | CH <sub>3</sub> | 2,4-F(Ph)               |
| 1.73 | iso-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub> | Ph                      |
| 1.74 | iso-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub> | 2-Cl(Ph)                |
| 1.75 | iso-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub> | 3-Cl(Ph)                |
| 1.76 | iso-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub> | 4-Cl(Ph)                |
| 1.77 | iso-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub> | 4-Br(Ph)                |
| 1.78 | iso-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub> | 4-F(Ph)                 |
| 1.79 | iso-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub> | 4-OCH <sub>3</sub> (Ph) |
| 1.80 | iso-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub> | 4-CH <sub>3</sub> (Ph)  |
| 1.81 | iso-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub> | 4-NO <sub>2</sub> (Ph)  |
| 1.82 | iso-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub> | 2,4-Cl(Ph)              |
| 1.83 | iso-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub> | 2,4-F(Ph)               |
| 1.84 | n-C <sub>4</sub> H <sub>9</sub>   | CH <sub>3</sub> | Ph                      |
| 1.85 | n-C <sub>4</sub> H <sub>9</sub>   | CH <sub>3</sub> | 2-Cl(Ph)                |
| 1.86 | n-C <sub>4</sub> H <sub>9</sub>   | CH <sub>3</sub> | 3-Cl(Ph)                |
| 1.87 | n-C <sub>4</sub> H <sub>9</sub>   | CH <sub>3</sub> | 4-Cl(Ph)                |
| 1.88 | n-C <sub>4</sub> H <sub>9</sub>   | CH <sub>3</sub> | 4-Br(Ph)                |

|       |                                   |                 |                         |
|-------|-----------------------------------|-----------------|-------------------------|
| 1.89  | n-C <sub>4</sub> H <sub>9</sub>   | CH <sub>3</sub> | 4-F(Ph)                 |
| 1.90  | n-C <sub>4</sub> H <sub>9</sub>   | CH <sub>3</sub> | 4-OCH <sub>3</sub> (Ph) |
| 1.91  | n-C <sub>4</sub> H <sub>9</sub>   | CH <sub>3</sub> | 4-CH <sub>3</sub> (Ph)  |
| 1.92  | n-C <sub>4</sub> H <sub>9</sub>   | CH <sub>3</sub> | 4-NO <sub>2</sub> (Ph)  |
| 1.93  | n-C <sub>4</sub> H <sub>9</sub>   | CH <sub>3</sub> | 2,4-Cl(Ph)              |
| 1.94  | n-C <sub>4</sub> H <sub>9</sub>   | CH <sub>3</sub> | 2,4-F(Ph)               |
| 1.95  | iso-C <sub>4</sub> H <sub>9</sub> | CH <sub>3</sub> | Ph                      |
| 1.96  | iso-C <sub>4</sub> H <sub>9</sub> | CH <sub>3</sub> | 2-Cl(Ph)                |
| 1.97  | iso-C <sub>4</sub> H <sub>9</sub> | CH <sub>3</sub> | 3-Cl(Ph)                |
| 1.98  | iso-C <sub>4</sub> H <sub>9</sub> | CH <sub>3</sub> | 4-Cl(Ph)                |
| 1.99  | iso-C <sub>4</sub> H <sub>9</sub> | CH <sub>3</sub> | 4-F(Ph)                 |
| 1.100 | iso-C <sub>4</sub> H <sub>9</sub> | CH <sub>3</sub> | 2-OCH <sub>3</sub> (Ph) |
| 1.101 | iso-C <sub>4</sub> H <sub>9</sub> | CH <sub>3</sub> | 3-OCH <sub>3</sub> (Ph) |
| 1.102 | iso-C <sub>4</sub> H <sub>9</sub> | CH <sub>3</sub> | 4-OCH <sub>3</sub> (Ph) |
| 1.103 | iso-C <sub>4</sub> H <sub>9</sub> | CH <sub>3</sub> | 4-CH <sub>3</sub> (Ph)  |
| 1.104 | iso-C <sub>4</sub> H <sub>9</sub> | CH <sub>3</sub> | 2,4-Cl(Ph)              |
| 1.105 | iso-C <sub>4</sub> H <sub>9</sub> | CH <sub>3</sub> | 2,4-F(Ph)               |
| 1.106 | cyclopropyl                       | CH <sub>3</sub> | Ph                      |
| 1.107 | cyclopropyl                       | CH <sub>3</sub> | 2-Cl(Ph)                |
| 1.108 | cyclopropyl                       | CH <sub>3</sub> | 3-Cl(Ph)                |
| 1.109 | cyclopropyl                       | CH <sub>3</sub> | 4-Cl(Ph)                |
| 1.110 | cyclopropyl                       | CH <sub>3</sub> | 4-F(Ph)                 |
| 1.111 | cyclopropyl                       | CH <sub>3</sub> | 3-OCH <sub>3</sub> (Ph) |
| 1.112 | cyclopropyl                       | CH <sub>3</sub> | 4-OCH <sub>3</sub> (Ph) |
| 1.113 | cyclopropyl                       | CH <sub>3</sub> | 4-CH <sub>3</sub> (Ph)  |
| 1.114 | cyclopropyl                       | CH <sub>3</sub> | 4-NO <sub>2</sub> (Ph)  |
| 1.115 | cyclopropyl                       | CH <sub>3</sub> | 2,4-Cl(Ph)              |
| 1.116 | cyclopropyl                       | CH <sub>3</sub> | 2,4-F(Ph)               |
| 1.117 | 1-CH <sub>3</sub> -cyclopropyl    | CH <sub>3</sub> | Ph                      |
| 1.118 | 1-CH <sub>3</sub> -cyclopropyl    | CH <sub>3</sub> | 2-Cl(Ph)                |
| 1.119 | 1-CH <sub>3</sub> -cyclopropyl    | CH <sub>3</sub> | 3-Cl(Ph)                |
| 1.120 | 1-CH <sub>3</sub> -cyclopropyl    | CH <sub>3</sub> | 4-Cl(Ph)                |
| 1.121 | 1-CH <sub>3</sub> -cyclopropyl    | CH <sub>3</sub> | 2-Br(Ph)                |
| 1.122 | CN                                | CH <sub>3</sub> | Ph                      |
| 1.123 | CN                                | CH <sub>3</sub> | 2-Cl(Ph)                |
| 1.124 | CN                                | CH <sub>3</sub> | 3-Cl(Ph)                |
| 1.125 | CN                                | CH <sub>3</sub> | 4-Cl(Ph)                |
| 1.126 | CN                                | CH <sub>3</sub> | 2-Br(Ph)                |
| 1.127 | CN                                | CH <sub>3</sub> | 3-Br(Ph)                |
| 1.128 | CN                                | CH <sub>3</sub> | 4-Br(Ph)                |
| 1.129 | CN                                | CH <sub>3</sub> | 2-F(Ph)                 |
| 1.130 | CN                                | CH <sub>3</sub> | 3-F(Ph)                 |
| 1.131 | CN                                | CH <sub>3</sub> | 4-F(Ph)                 |
| 1.132 | CN                                | CH <sub>3</sub> | 2-OCH <sub>3</sub> (Ph) |
| 1.133 | CN                                | CH <sub>3</sub> | 3-OCH <sub>3</sub> (Ph) |
| 1.134 | CN                                | CH <sub>3</sub> | 4-OCH <sub>3</sub> (Ph) |
| 1.135 | CN                                | CH <sub>3</sub> | 2-CH <sub>3</sub> (Ph)  |
| 1.136 | CN                                | CH <sub>3</sub> | 3-CH <sub>3</sub> (Ph)  |

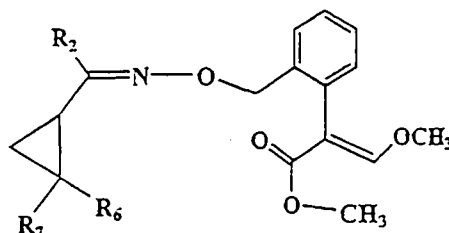
|       |                 |                                 |                         |
|-------|-----------------|---------------------------------|-------------------------|
| 1.137 | CN              | CH <sub>3</sub>                 | 4-CH <sub>3</sub> (Ph)  |
| 1.138 | CN              | CH <sub>3</sub>                 | 2-CF <sub>3</sub> (Ph)  |
| 1.139 | CN              | CH <sub>3</sub>                 | 3-CF <sub>3</sub> (Ph)  |
| 1.140 | CN              | CH <sub>3</sub>                 | 4-CF <sub>3</sub> (Ph)  |
| 1.141 | CN              | CH <sub>3</sub>                 | 2-NO <sub>2</sub> (Ph)  |
| 1.142 | CN              | CH <sub>3</sub>                 | 3-NO <sub>2</sub> (Ph)  |
| 1.143 | CN              | CH <sub>3</sub>                 | 4-NO <sub>2</sub> (Ph)  |
| 1.144 | CN              | CH <sub>3</sub>                 | 2,3-Cl(Ph)              |
| 1.145 | CN              | CH <sub>3</sub>                 | 2,4-Cl(Ph)              |
| 1.146 | CN              | CH <sub>3</sub>                 | 2,5-Cl(Ph)              |
| 1.147 | CN              | CH <sub>3</sub>                 | 3,4-Cl(Ph)              |
| 1.148 | CN              | CH <sub>3</sub>                 | 3,5-Cl(Ph)              |
| 1.149 | CN              | CH <sub>3</sub>                 | 2,3,5-Cl(Ph)            |
| 1.150 | CN              | CH <sub>3</sub>                 | 2,4,5-Cl(Ph)            |
| 1.151 | CN              | CH <sub>3</sub>                 | 3,4,5-Cl(Ph)            |
| 1.152 | CN              | CH <sub>3</sub>                 | 2,3-F(Ph)               |
| 1.153 | CN              | CH <sub>3</sub>                 | 2,4-F(Ph)               |
| 1.154 | CN              | CH <sub>3</sub>                 | 2,5-F(Ph)               |
| 1.155 | CN              | CH <sub>3</sub>                 | 3,4-F(Ph)               |
| 1.156 | CN              | CH <sub>3</sub>                 | 3,5-F(Ph)               |
| 1.157 | CN              | CH <sub>3</sub>                 | 2,3,5-F(Ph)             |
| 1.158 | CN              | CH <sub>3</sub>                 | 2,4,5-F(Ph)             |
| 1.159 | CN              | CH <sub>3</sub>                 | 3,4,5-F(Ph)             |
| 1.160 | CF <sub>3</sub> | CH <sub>3</sub>                 | Ph                      |
| 1.161 | CF <sub>3</sub> | CH <sub>3</sub>                 | 2-Cl(Ph)                |
| 1.162 | CF <sub>3</sub> | CH <sub>3</sub>                 | 3-Cl(Ph)                |
| 1.163 | CF <sub>3</sub> | CH <sub>3</sub>                 | 4-Cl(Ph)                |
| 1.164 | CF <sub>3</sub> | CH <sub>3</sub>                 | 4-F(Ph)                 |
| 1.165 | CF <sub>3</sub> | CH <sub>3</sub>                 | 4-CH <sub>3</sub> (Ph)  |
| 1.166 | CH <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>   | Ph                      |
| 1.167 | CH <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>   | 2-Cl(Ph)                |
| 1.168 | CH <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>   | 3-Cl(Ph)                |
| 1.169 | CH <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>   | 4-Cl(Ph)                |
| 1.170 | CH <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>   | 4-F(Ph)                 |
| 1.171 | CH <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>   | 2-OCH <sub>3</sub> (Ph) |
| 1.172 | CH <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>   | 3-OCH <sub>3</sub> (Ph) |
| 1.173 | CH <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>   | 4-OCH <sub>3</sub> (Ph) |
| 1.174 | CH <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>   | 4-CH <sub>3</sub> (Ph)  |
| 1.175 | CH <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>   | 4-NO <sub>2</sub> (Ph)  |
| 1.176 | CH <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>   | 2,4-Cl(Ph)              |
| 1.177 | CH <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>   | 2,4-F(Ph)               |
| 1.178 | CH <sub>3</sub> | n-C <sub>3</sub> H <sub>7</sub> | Ph                      |
| 1.179 | CH <sub>3</sub> | n-C <sub>3</sub> H <sub>7</sub> | 2-Cl(Ph)                |
| 1.180 | CH <sub>3</sub> | n-C <sub>3</sub> H <sub>7</sub> | 3-Cl(Ph)                |
| 1.181 | CH <sub>3</sub> | n-C <sub>3</sub> H <sub>7</sub> | 4-Cl(Ph)                |
| 1.182 | CH <sub>3</sub> | n-C <sub>3</sub> H <sub>7</sub> | 4-F(Ph)                 |
| 1.183 | CH <sub>3</sub> | n-C <sub>3</sub> H <sub>7</sub> | 3-OCH <sub>3</sub> (Ph) |
| 1.184 | CH <sub>3</sub> | n-C <sub>3</sub> H <sub>7</sub> | 4-OCH <sub>3</sub> (Ph) |
| 1.185 | CH <sub>3</sub> | n-C <sub>3</sub> H <sub>7</sub> | 4-CH <sub>3</sub> (Ph)  |

|       |                 |                                   |                        |
|-------|-----------------|-----------------------------------|------------------------|
| 1.186 | CH <sub>3</sub> | n-C <sub>3</sub> H <sub>7</sub>   | 4-NO <sub>2</sub> (Ph) |
| 1.187 | CH <sub>3</sub> | n-C <sub>3</sub> H <sub>7</sub>   | 2,4-Cl(Ph)             |
| 1.188 | CH <sub>3</sub> | n-C <sub>3</sub> H <sub>7</sub>   | 2,4-F(Ph)              |
| 1.189 | CH <sub>3</sub> | iso-C <sub>3</sub> H <sub>7</sub> | Ph                     |
| 1.190 | CH <sub>3</sub> | iso-C <sub>3</sub> H <sub>7</sub> | 4-Cl(Ph)               |
| 1.191 | CH <sub>3</sub> | n-C <sub>4</sub> H <sub>9</sub>   | Ph                     |
| 1.192 | CH <sub>3</sub> | n-C <sub>4</sub> H <sub>9</sub>   | 4-Cl(Ph)               |
| 1.193 | CH <sub>3</sub> | iso-C <sub>4</sub> H <sub>9</sub> | Ph                     |
| 1.194 | CH <sub>3</sub> | iso-C <sub>4</sub> H <sub>9</sub> | 4-Cl(Ph)               |
| 1.195 | CN              | C <sub>2</sub> H <sub>5</sub>     | Ph                     |
| 1.196 | CN              | n-C <sub>3</sub> H <sub>7</sub>   | Ph                     |
| 1.197 | CN              | iso-C <sub>3</sub> H <sub>7</sub> | Ph                     |
| 1.198 | CN              | n-C <sub>4</sub> H <sub>9</sub>   | Ph                     |
| 1.199 | CN              | iso-C <sub>4</sub> H <sub>9</sub> | Ph                     |
| 1.200 | CF <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>     | Ph                     |
| 1.201 | CF <sub>3</sub> | n-C <sub>3</sub> H <sub>7</sub>   | Ph                     |
| 1.202 | CF <sub>3</sub> | iso-C <sub>3</sub> H <sub>7</sub> | Ph                     |
| 1.203 | CF <sub>3</sub> | n-C <sub>4</sub> H <sub>9</sub>   | Ph                     |
| 1.204 | CF <sub>3</sub> | iso-C <sub>4</sub> H <sub>9</sub> | Ph                     |
| 1.205 | H               | CF <sub>3</sub>                   | Ph                     |
| 1.206 | CH <sub>3</sub> | CF <sub>3</sub>                   | Ph                     |
| 1.207 | CN              | CF <sub>3</sub>                   | Ph                     |
| 1.208 | CF <sub>3</sub> | CF <sub>3</sub>                   | Ph                     |
| 1.209 | H               | CH <sub>2</sub> =CH               | Ph                     |
| 1.210 | CH <sub>3</sub> | CH <sub>2</sub> =CH               | Ph                     |
| 1.211 | CN              | CH <sub>2</sub> =CH               | Ph                     |
| 1.212 | CF <sub>3</sub> | CH <sub>2</sub> =CH               | Ph                     |
| 1.213 | H               | CH <sub>3</sub> CH=CH             | Ph                     |
| 1.214 | CH <sub>3</sub> | CH <sub>3</sub> CH=CH             | Ph                     |
| 1.215 | CN              | CH <sub>3</sub> CH=CH             | Ph                     |
| 1.216 | CF <sub>3</sub> | CH <sub>3</sub> CH=CH             | Ph                     |
| 1.217 | CH <sub>3</sub> | CH <sub>3</sub>                   | 2-Cl,4-F(Ph)           |

Table 2: Compounds 2.1 to 2.217 are compounds of Formula I wherein A, R<sub>3</sub>, R<sub>4</sub>, and R<sub>5</sub> are hydrogen; X is N and Z is O; R<sub>1</sub> is methyl; and R<sub>2</sub>, R<sub>6</sub>, and R<sub>7</sub> are defined as in Table 1. The following compounds are all oils and possess either a trans cyclopropane or an enriched trans cyclopropane stereochemistry for R<sub>7</sub> and the iminoxy substituent, and the indicated A:B iminoxy isomer ratio is shown: 2.11, 2.12 (9:1 A:B isomers), 2.14A (7:3 trans:cis cyclopropane isomers), 2.17 (9:1 A:B isomers), 2.18A, 2.20 (4:1 A:B isomers), 2.20B, 2.34 (5:1 A:B isomers), 2.166 (4:1 A:B isomers), 2.170 (6:1 A:B isomers), 2.178 (4:1 A:B isomers), 2.189 (7:3 A:B isomers), and 2.217 (6:1 A:B isomers).

Table 3: Compounds 3.1 to 3.217 are compounds of Formula I wherein A, R<sub>3</sub>, R<sub>4</sub>, and R<sub>5</sub> are hydrogen; X is N and Z is NH, R<sub>1</sub> is methyl; and R<sub>2</sub>, R<sub>6</sub>, and R<sub>7</sub> are defined as in Table 1. The following compounds possess either a trans cyclopropane or an enriched trans cyclopropane stereochemistry for R<sub>7</sub> and the iminoxy substituent, and the indicated A:B iminoxy isomer ratio is shown: 3.11 (oil, 4:1 A:B isomers), 3.12A (mp. 100-103 °C), 3.14A (oil, 7:3 trans:cis cyclopropane isomers), 3.17 (oil, 9:1 A:B isomers), 3.18A (mp. 95-99 °C), 3.20 (oil, 4:1 A:B isomers), 3.20A (mp. 57-61 °C), 3.20B (oil), 3.34A (mp. 121-125 °C), 3.40A (oil), 3.166 (oil, 4:1 A:B isomers), 3.170A (mp. 74-77 °C), 3.178 (oil, 4:1 A:B isomers), 3.189 (oil, 7:3 A:B isomers), and 3.217A (mp 110-113 °C).

Typical compounds of Formula I encompassed by the present invention wherein A, R<sub>3</sub>, R<sub>4</sub>, and R<sub>5</sub> are hydrogen; X is CH and Z is O; and R<sub>1</sub> is methyl include those compounds presented in Table 4 of Formula III where R<sub>2</sub>, R<sub>6</sub>, and R<sub>7</sub> are defined in Table 4.



Formula III

Table 4

| Comp | R <sub>2</sub>  | R <sub>6</sub>  | R <sub>7</sub> |
|------|-----------------|-----------------|----------------|
| 4.1  | H               | CH <sub>3</sub> | 2-pyridyl      |
| 4.2  | H               | CH <sub>3</sub> | 3-pyridyl      |
| 4.3  | H               | CH <sub>3</sub> | 4-pyridyl      |
| 4.4  | H               | CH <sub>3</sub> | 2-pyrazinyl    |
| 4.5  | H               | CH <sub>3</sub> | 4-pyrimidinyl  |
| 4.6  | H               | CH <sub>3</sub> | 5-pyrimidinyl  |
| 4.7  | H               | CH <sub>3</sub> | 3-pyridazinyl  |
| 4.8  | H               | CH <sub>3</sub> | 4-pyridazinyl  |
| 4.9  | H               | CH <sub>3</sub> | 2-furyl        |
| 4.10 | H               | CH <sub>3</sub> | 3-furyl        |
| 4.11 | H               | CH <sub>3</sub> | 2-thienyl      |
| 4.12 | H               | CH <sub>3</sub> | 3-thienyl      |
| 4.13 | CH <sub>3</sub> | CH <sub>3</sub> | 2-pyridyl      |
| 4.14 | CH <sub>3</sub> | CH <sub>3</sub> | 3-pyridyl      |
| 4.15 | CH <sub>3</sub> | CH <sub>3</sub> | 4-pyridyl      |

|      |                                 |                 |                                     |
|------|---------------------------------|-----------------|-------------------------------------|
| 4.16 | CH <sub>3</sub>                 | CH <sub>3</sub> | 2-pyrazinyl                         |
| 4.17 | CH <sub>3</sub>                 | CH <sub>3</sub> | 4-pyrimidinyl                       |
| 4.18 | CH <sub>3</sub>                 | CH <sub>3</sub> | 5-pyrimidinyl                       |
| 4.19 | CH <sub>3</sub>                 | CH <sub>3</sub> | 3-pyridazinyl                       |
| 4.20 | CH <sub>3</sub>                 | CH <sub>3</sub> | 4-pyridazinyl                       |
| 4.21 | CH <sub>3</sub>                 | CH <sub>3</sub> | 2-furyl                             |
| 4.22 | CH <sub>3</sub>                 | CH <sub>3</sub> | 3-furyl                             |
| 4.23 | CH <sub>3</sub>                 | CH <sub>3</sub> | 2-thienyl                           |
| 4.24 | CH <sub>3</sub>                 | CH <sub>3</sub> | 3-thienyl                           |
| 4.25 | CH <sub>3</sub>                 | CH <sub>3</sub> | 1-CH <sub>3</sub> -3-(1H)-pyrazolyl |
| 4.26 | CH <sub>3</sub>                 | CH <sub>3</sub> | 1-CH <sub>3</sub> -4-(1H)-pyrazolyl |
| 4.27 | CH <sub>3</sub>                 | CH <sub>3</sub> | 5-(1H)-pyrazolyl                    |
| 4.28 | CH <sub>3</sub>                 | CH <sub>3</sub> | 4-(1H)-imidazolyl                   |
| 4.29 | CH <sub>3</sub>                 | CH <sub>3</sub> | 5-(1H)-imidazolyl                   |
| 4.30 | CH <sub>3</sub>                 | CH <sub>3</sub> | 5-(1H)-pyrazolyl                    |
| 4.31 | CH <sub>3</sub>                 | CH <sub>3</sub> | 3-isothiazolyl                      |
| 4.32 | CH <sub>3</sub>                 | CH <sub>3</sub> | 4-isothiazolyl                      |
| 4.33 | CH <sub>3</sub>                 | CH <sub>3</sub> | 5-isothiazolyl                      |
| 4.34 | CH <sub>3</sub>                 | CH <sub>3</sub> | 4-thiazolyl                         |
| 4.35 | CH <sub>3</sub>                 | CH <sub>3</sub> | 5-thiazolyl                         |
| 4.36 | CH <sub>3</sub>                 | CH <sub>3</sub> | 3-isooxazolyl                       |
| 4.37 | CH <sub>3</sub>                 | CH <sub>3</sub> | 4-isooxazolyl                       |
| 4.38 | CH <sub>3</sub>                 | CH <sub>3</sub> | 5-isooxazolyl                       |
| 4.39 | CH <sub>3</sub>                 | CH <sub>3</sub> | 4-oxazolyl                          |
| 4.40 | CH <sub>3</sub>                 | CH <sub>3</sub> | 5-oxazolyl                          |
| 4.41 | CH <sub>3</sub>                 | CH <sub>3</sub> | 1-methyl-2-(1H)-pyrrolyl            |
| 4.42 | CH <sub>3</sub>                 | CH <sub>3</sub> | 1-methyl-3-(1H)-pyrrolyl            |
| 4.43 | CH <sub>3</sub>                 | CH <sub>3</sub> | 2-quinolinyl                        |
| 4.44 | CH <sub>3</sub>                 | CH <sub>3</sub> | 3-quinolinyl                        |
| 4.45 | CH <sub>3</sub>                 | CH <sub>3</sub> | 4-quinolinyl                        |
| 4.46 | CH <sub>3</sub>                 | CH <sub>3</sub> | 3-Cl-pyrid-2-yl                     |
| 4.47 | CH <sub>3</sub>                 | CH <sub>3</sub> | 2-Cl-pyrid-3-yl                     |
| 4.48 | CH <sub>3</sub>                 | CH <sub>3</sub> | 2-Cl-pyrid-4-yl                     |
| 4.49 | CH <sub>3</sub>                 | CH <sub>3</sub> | 4-Cl-furan-2-yl                     |
| 4.50 | CH <sub>3</sub>                 | CH <sub>3</sub> | 2-Cl-furan-3-yl                     |
| 4.51 | C <sub>2</sub> H <sub>5</sub>   | CH <sub>3</sub> | 2-pyridyl                           |
| 4.52 | C <sub>2</sub> H <sub>5</sub>   | CH <sub>3</sub> | 3-pyridyl                           |
| 4.53 | C <sub>2</sub> H <sub>5</sub>   | CH <sub>3</sub> | 4-pyridyl                           |
| 4.54 | C <sub>2</sub> H <sub>5</sub>   | CH <sub>3</sub> | 2-furyl                             |
| 4.55 | C <sub>2</sub> H <sub>5</sub>   | CH <sub>3</sub> | 3-furyl                             |
| 4.56 | C <sub>2</sub> H <sub>5</sub>   | CH <sub>3</sub> | 2-thienyl                           |
| 4.57 | C <sub>2</sub> H <sub>5</sub>   | CH <sub>3</sub> | 3-thienyl                           |
| 4.58 | n-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub> | 2-pyridyl                           |
| 4.59 | n-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub> | 3-pyridyl                           |
| 4.60 | n-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub> | 4-pyridyl                           |
| 4.61 | n-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub> | 2-furyl                             |
| 4.62 | n-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub> | 3-furyl                             |
| 4.63 | n-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub> | 2-thienyl                           |
| 4.64 | n-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub> | 3-thienyl                           |

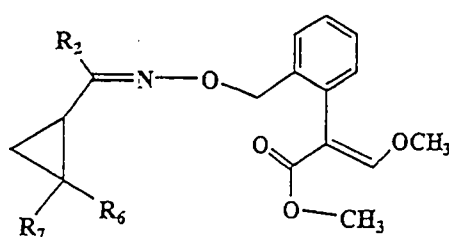
|       |                                   |                                 |           |
|-------|-----------------------------------|---------------------------------|-----------|
| 4.65  | iso-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub>                 | 2-pyridyl |
| 4.66  | iso-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub>                 | 3-pyridyl |
| 4.67  | iso-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub>                 | 4-pyridyl |
| 4.68  | iso-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub>                 | 2-furyl   |
| 4.69  | iso-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub>                 | 3-furyl   |
| 4.70  | iso-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub>                 | 2-thienyl |
| 4.71  | iso-C <sub>3</sub> H <sub>7</sub> | CH <sub>3</sub>                 | 3-thienyl |
| 4.72  | n-C <sub>4</sub> H <sub>9</sub>   | CH <sub>3</sub>                 | 2-pyridyl |
| 4.73  | n-C <sub>4</sub> H <sub>9</sub>   | CH <sub>3</sub>                 | 3-pyridyl |
| 4.74  | n-C <sub>4</sub> H <sub>9</sub>   | CH <sub>3</sub>                 | 4-pyridyl |
| 4.75  | n-C <sub>4</sub> H <sub>9</sub>   | CH <sub>3</sub>                 | 2-furyl   |
| 4.76  | n-C <sub>4</sub> H <sub>9</sub>   | CH <sub>3</sub>                 | 3-furyl   |
| 4.77  | n-C <sub>4</sub> H <sub>9</sub>   | CH <sub>3</sub>                 | 2-thienyl |
| 4.78  | n-C <sub>4</sub> H <sub>9</sub>   | CH <sub>3</sub>                 | 3-thienyl |
| 4.79  | iso-C <sub>4</sub> H <sub>9</sub> | CH <sub>3</sub>                 | 2-pyridyl |
| 4.80  | iso-C <sub>4</sub> H <sub>9</sub> | CH <sub>3</sub>                 | 3-pyridyl |
| 4.81  | iso-C <sub>4</sub> H <sub>9</sub> | CH <sub>3</sub>                 | 4-pyridyl |
| 4.82  | iso-C <sub>4</sub> H <sub>9</sub> | CH <sub>3</sub>                 | 2-furyl   |
| 4.83  | iso-C <sub>4</sub> H <sub>9</sub> | CH <sub>3</sub>                 | 3-furyl   |
| 4.84  | iso-C <sub>4</sub> H <sub>9</sub> | CH <sub>3</sub>                 | 2-thienyl |
| 4.85  | iso-C <sub>4</sub> H <sub>9</sub> | CH <sub>3</sub>                 | 3-thienyl |
| 4.86  | c-C <sub>3</sub> H <sub>5</sub>   | CH <sub>3</sub>                 | 2-pyridyl |
| 4.87  | c-C <sub>3</sub> H <sub>5</sub>   | CH <sub>3</sub>                 | 3-pyridyl |
| 4.88  | c-C <sub>3</sub> H <sub>5</sub>   | CH <sub>3</sub>                 | 4-pyridyl |
| 4.89  | c-C <sub>3</sub> H <sub>5</sub>   | CH <sub>3</sub>                 | 2-furyl   |
| 4.90  | c-C <sub>3</sub> H <sub>5</sub>   | CH <sub>3</sub>                 | 3-furyl   |
| 4.91  | c-C <sub>3</sub> H <sub>5</sub>   | CH <sub>3</sub>                 | 2-thienyl |
| 4.92  | c-C <sub>3</sub> H <sub>5</sub>   | CH <sub>3</sub>                 | 3-thienyl |
| 4.93  | CN                                | CH <sub>3</sub>                 | 2-pyridyl |
| 4.94  | CN                                | CH <sub>3</sub>                 | 3-pyridyl |
| 4.95  | CN                                | CH <sub>3</sub>                 | 4-pyridyl |
| 4.96  | CN                                | CH <sub>3</sub>                 | 2-furyl   |
| 4.97  | CN                                | CH <sub>3</sub>                 | 3-furyl   |
| 4.98  | CN                                | CH <sub>3</sub>                 | 2-thienyl |
| 4.99  | CN                                | CH <sub>3</sub>                 | 3-thienyl |
| 4.100 | CF <sub>3</sub>                   | CH <sub>3</sub>                 | 2-pyridyl |
| 4.101 | CF <sub>3</sub>                   | CH <sub>3</sub>                 | 3-pyridyl |
| 4.102 | CF <sub>3</sub>                   | CH <sub>3</sub>                 | 4-pyridyl |
| 4.105 | CF <sub>3</sub>                   | CH <sub>3</sub>                 | 2-thienyl |
| 4.106 | CF <sub>3</sub>                   | CH <sub>3</sub>                 | 3-thienyl |
| 4.107 | CH <sub>3</sub>                   | C <sub>2</sub> H <sub>5</sub>   | 2-pyridyl |
| 4.108 | CH <sub>3</sub>                   | C <sub>2</sub> H <sub>5</sub>   | 3-pyridyl |
| 4.109 | CH <sub>3</sub>                   | C <sub>2</sub> H <sub>5</sub>   | 4-pyridyl |
| 4.110 | CH <sub>3</sub>                   | C <sub>2</sub> H <sub>5</sub>   | 2-furyl   |
| 4.111 | CH <sub>3</sub>                   | C <sub>2</sub> H <sub>5</sub>   | 3-furyl   |
| 4.112 | CH <sub>3</sub>                   | C <sub>2</sub> H <sub>5</sub>   | 2-thienyl |
| 4.113 | CH <sub>3</sub>                   | C <sub>2</sub> H <sub>5</sub>   | 3-thienyl |
| 4.114 | CH <sub>3</sub>                   | n-C <sub>3</sub> H <sub>7</sub> | 2-pyridyl |
| 4.115 | CH <sub>3</sub>                   | n-C <sub>3</sub> H <sub>7</sub> | 3-pyridyl |

|       |                 |                                   |           |
|-------|-----------------|-----------------------------------|-----------|
| 4.116 | CH <sub>3</sub> | n-C <sub>3</sub> H <sub>7</sub>   | 4-pyridyl |
| 4.117 | CH <sub>3</sub> | n-C <sub>3</sub> H <sub>7</sub>   | 2-furyl   |
| 4.118 | CH <sub>3</sub> | n-C <sub>3</sub> H <sub>7</sub>   | 3-furyl   |
| 4.119 | CH <sub>3</sub> | n-C <sub>4</sub> H <sub>9</sub>   | 2-pyridyl |
| 4.120 | CH <sub>3</sub> | n-C <sub>4</sub> H <sub>9</sub>   | 3-pyridyl |
| 4.121 | CH <sub>3</sub> | n-C <sub>4</sub> H <sub>9</sub>   | 4-pyridyl |
| 4.122 | CH <sub>3</sub> | n-C <sub>4</sub> H <sub>9</sub>   | 2-thienyl |
| 4.123 | CH <sub>3</sub> | n-C <sub>4</sub> H <sub>9</sub>   | 3-thienyl |
| 4.124 | CH <sub>3</sub> | iso-C <sub>4</sub> H <sub>9</sub> | 2-pyridyl |
| 4.125 | CH <sub>3</sub> | iso-C <sub>4</sub> H <sub>9</sub> | 3-pyridyl |
| 4.126 | CH <sub>3</sub> | iso-C <sub>4</sub> H <sub>9</sub> | 4-pyridyl |
| 4.127 | CH <sub>3</sub> | iso-C <sub>4</sub> H <sub>9</sub> | 2-thienyl |
| 4.128 | CH <sub>3</sub> | iso-C <sub>4</sub> H <sub>9</sub> | 3-thienyl |
| 4.129 | CH <sub>3</sub> | cyclopropyl                       | 2-pyridyl |
| 4.130 | CH <sub>3</sub> | cyclopropyl                       | 3-pyridyl |
| 4.131 | CH <sub>3</sub> | cyclopropyl                       | 4-pyridyl |
| 4.132 | CH <sub>3</sub> | cyclopropyl                       | 2-thienyl |
| 4.133 | CH <sub>3</sub> | cyclopropyl                       | 3-thienyl |
| 4.134 | CF <sub>3</sub> | CH <sub>3</sub>                   | 2-pyridyl |
| 4.135 | CF <sub>3</sub> | CH <sub>3</sub>                   | 3-pyridyl |
| 4.136 | CF <sub>3</sub> | CH <sub>3</sub>                   | 4-pyridyl |
| 4.134 | CF <sub>3</sub> | CH <sub>3</sub>                   | 2-furyl   |
| 4.135 | CF <sub>3</sub> | CH <sub>3</sub>                   | 3-furyl   |
| 4.136 | CF <sub>3</sub> | CH <sub>3</sub>                   | 2-thienyl |
| 4.137 | CF <sub>3</sub> | CH <sub>3</sub>                   | 3-thienyl |
| 4.138 | CF <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>     | 2-pyridyl |
| 4.139 | CF <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>     | 3-pyridyl |
| 4.140 | CF <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>     | 4-pyridyl |
| 4.141 | CF <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>     | 2-furyl   |
| 4.142 | CF <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>     | 3-furyl   |
| 4.143 | CF <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>     | 2-thienyl |
| 4.144 | CF <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>     | 3-thienyl |
| 4.145 | CN              | CH <sub>3</sub>                   | 2-pyridyl |
| 4.146 | CN              | CH <sub>3</sub>                   | 3-pyridyl |
| 4.147 | CN              | CH <sub>3</sub>                   | 4-pyridyl |
| 4.148 | CN              | CH <sub>3</sub>                   | 2-furyl   |
| 4.149 | CN              | CH <sub>3</sub>                   | 3-furyl   |
| 4.150 | CN              | CH <sub>3</sub>                   | 2-thienyl |
| 4.151 | CN              | CH <sub>3</sub>                   | 3-thienyl |
| 4.152 | CN              | C <sub>2</sub> H <sub>5</sub>     | 2-pyridyl |
| 4.153 | CN              | C <sub>2</sub> H <sub>5</sub>     | 3-pyridyl |
| 4.154 | CN              | C <sub>2</sub> H <sub>5</sub>     | 4-pyridyl |
| 4.155 | CN              | C <sub>2</sub> H <sub>5</sub>     | 2-furyl   |
| 4.156 | CN              | C <sub>2</sub> H <sub>5</sub>     | 3-furyl   |
| 4.157 | CN              | C <sub>2</sub> H <sub>5</sub>     | 2-thienyl |
| 4.158 | CN              | C <sub>2</sub> H <sub>5</sub>     | 3-thienyl |

Table 5: Compounds 5.1 to 5.158 are compounds of Formula I wherein A, R<sub>3</sub>, R<sub>4</sub>, and R<sub>5</sub> are hydrogen; X is N and Z is O; R<sub>1</sub> is methyl; and R<sub>2</sub>, R<sub>6</sub>, and R<sub>7</sub> are defined as in Table 4.

Table 6: Compounds 6.1 to 6.158 are compounds of Formula I wherein A, R<sub>3</sub>, R<sub>4</sub>, and R<sub>5</sub> are hydrogen; X is N and Z is NH, R<sub>1</sub> is methyl; and R<sub>2</sub>, R<sub>6</sub>, and R<sub>7</sub> are defined as in Table 4.

Typical compounds of Formula I encompassed by the present invention wherein A, R<sub>3</sub>, R<sub>4</sub>, and R<sub>5</sub> are hydrogen; X is CH and Z is O; and R<sub>1</sub> is methyl include those compounds presented in Table 7 of Formula III where R<sub>2</sub>, R<sub>6</sub>, and R<sub>7</sub> are defined in Table 7



Formula III

Table 7

| Comp | R <sub>2</sub>  | R <sub>6</sub> | R <sub>7</sub>              |
|------|-----------------|----------------|-----------------------------|
| 7.1  | H               | H              | 2,6-Cl(Ph)                  |
| 7.2  | H               | H              | 2,3,6-Cl(Ph)                |
| 7.3  | H               | H              | 2,4,6-Cl(Ph)                |
| 7.4  | H               | H              | 2,6-Br(Ph)                  |
| 7.5  | H               | H              | 2,3,6-Br(Ph)                |
| 7.6  | H               | H              | 2,4,6-Br(Ph)                |
| 7.7  | H               | H              | 2,6-F(Ph)                   |
| 7.8  | H               | H              | 2,3,6-F(Ph)                 |
| 7.9  | H               | H              | 2,4,6-F(Ph)                 |
| 7.10 | H               | H              | 2,6-CH <sub>3</sub> (Ph)    |
| 7.11 | H               | H              | 2,3,6-CH <sub>3</sub> (Ph)  |
| 7.12 | H               | H              | 2,4,6-CH <sub>3</sub> (Ph)  |
| 7.13 | H               | H              | 2,6-CH <sub>3</sub> O(Ph)   |
| 7.14 | H               | H              | 2,3,6-CH <sub>3</sub> O(Ph) |
| 7.15 | H               | H              | 2,4,6-CH <sub>3</sub> O(Ph) |
| 7.16 | CH <sub>3</sub> | H              | 2,6-Cl(Ph)                  |
| 7.17 | CH <sub>3</sub> | H              | 2,3,6-Cl(Ph)                |
| 7.18 | CH <sub>3</sub> | H              | 2,4,6-Cl(Ph)                |
| 7.19 | CH <sub>3</sub> | H              | 2,6-Br(Ph)                  |
| 7.20 | CH <sub>3</sub> | H              | 2,3,6-Br(Ph)                |
| 7.21 | CH <sub>3</sub> | H              | 2,4,6-Br(Ph)                |
| 7.22 | CH <sub>3</sub> | H              | 2,6-F(Ph)                   |

|      |                 |   |                                              |
|------|-----------------|---|----------------------------------------------|
| 7.23 | CH <sub>3</sub> | H | 2,3,6-F(Ph)                                  |
| 7.24 | CH <sub>3</sub> | H | 2,4,6-F(Ph)                                  |
| 7.25 | CH <sub>3</sub> | H | 2,6-CH <sub>3</sub> (Ph)                     |
| 7.26 | CH <sub>3</sub> | H | 2,3,6-CH <sub>3</sub> (Ph)                   |
| 7.27 | CH <sub>3</sub> | H | 2,4,6-CH <sub>3</sub> (Ph)                   |
| 7.28 | CH <sub>3</sub> | H | 2,6-CH <sub>3</sub> O(Ph)                    |
| 7.29 | CH <sub>3</sub> | H | 2,3,6-CH <sub>3</sub> O(Ph)                  |
| 7.30 | CH <sub>3</sub> | H | 2,4,6-CH <sub>3</sub> O(Ph)                  |
| 7.31 | CH <sub>3</sub> | H | 2,6-NO <sub>2</sub> (Ph)                     |
| 7.32 | CH <sub>3</sub> | H | 2,6-CN(Ph)                                   |
| 7.33 | CH <sub>3</sub> | H | 2,3,6-CN(Ph)                                 |
| 7.34 | CH <sub>3</sub> | H | 2,4,6-CN(Ph)                                 |
| 7.35 | CH <sub>3</sub> | H | 2,6-Ph(Ph)                                   |
| 7.36 | CH <sub>3</sub> | H | 2,3,6-PhPh                                   |
| 7.37 | CH <sub>3</sub> | H | 2,4,6-Ph(Ph)                                 |
| 7.38 | CH <sub>3</sub> | H | 2,6-PhO(Ph)                                  |
| 7.39 | CH <sub>3</sub> | H | 2,3,6-PhO(Ph)                                |
| 7.40 | CH <sub>3</sub> | H | 2,4,6-PhO(Ph)                                |
| 7.41 | CH <sub>3</sub> | H | 2,6-CF <sub>3</sub> (Ph)                     |
| 7.42 | CH <sub>3</sub> | H | 2,3,6-CF <sub>3</sub> (Ph)                   |
| 7.43 | CH <sub>3</sub> | H | 2,4,6-CF <sub>3</sub> (Ph)                   |
| 7.44 | CH <sub>3</sub> | H | 2,6-CF <sub>3</sub> O(Ph)                    |
| 7.45 | CH <sub>3</sub> | H | 2,3,6-CF <sub>3</sub> O(Ph)                  |
| 7.46 | CH <sub>3</sub> | H | 2,4,6-CF <sub>3</sub> O(Ph)                  |
| 7.47 | CH <sub>3</sub> | H | 2,3,4,6-Cl(Ph)                               |
| 7.48 | CH <sub>3</sub> | H | 2,3,5,6-Cl(Ph)                               |
| 7.49 | CH <sub>3</sub> | H | 2,3,4,5,6-Cl(Ph)                             |
| 7.50 | CH <sub>3</sub> | H | 2,3,4,6-Ph(Ph)                               |
| 7.51 | CH <sub>3</sub> | H | 2,3,5,6-Ph(Ph)                               |
| 7.52 | CH <sub>3</sub> | H | 2,3,4,5,6-Ph(Ph)                             |
| 7.53 | CH <sub>3</sub> | H | 2,3,4,6-PhO(Ph)                              |
| 7.54 | CH <sub>3</sub> | H | 2,3,5,6-PhO(Ph)                              |
| 7.55 | CH <sub>3</sub> | H | 2,3,4,5,6-PhO(Ph)                            |
| 7.56 | CH <sub>3</sub> | H | 2,3,4,6-Br(Ph)                               |
| 7.57 | CH <sub>3</sub> | H | 2,3,5,6-Br(Ph)                               |
| 7.58 | CH <sub>3</sub> | H | 2,3,4,5,6-Br(Ph)                             |
| 7.59 | CH <sub>3</sub> | H | 2,3,4,6-F(Ph)                                |
| 7.60 | CH <sub>3</sub> | H | 2,3,5,6-F(Ph)                                |
| 7.61 | CH <sub>3</sub> | H | 2,3,4,5,6-F(Ph)                              |
| 7.62 | CH <sub>3</sub> | H | 2,3,4,6-CH <sub>3</sub> (Ph)                 |
| 7.63 | CH <sub>3</sub> | H | 2,3,5,6-CH <sub>3</sub> (Ph)                 |
| 7.64 | CH <sub>3</sub> | H | 2,3,4,5,6-CH <sub>3</sub> (Ph)               |
| 7.65 | CH <sub>3</sub> | H | 2,3,4,6-C <sub>2</sub> H <sub>5</sub> (Ph)   |
| 7.66 | CH <sub>3</sub> | H | 2,3,5,6-C <sub>2</sub> H <sub>5</sub> (Ph)   |
| 7.67 | CH <sub>3</sub> | H | 2,3,4,5,6-C <sub>2</sub> H <sub>5</sub> (Ph) |
| 7.68 | CH <sub>3</sub> | H | 2,3,4,6-CH <sub>3</sub> O(Ph)                |
| 7.69 | CH <sub>3</sub> | H | 2,3,5,6-CH <sub>3</sub> O(Ph)                |
| 7.70 | CH <sub>3</sub> | H | 2,3,4,5,6-CH <sub>3</sub> O(Ph)              |
| 7.71 | CH <sub>3</sub> | H | 2,3,4,6-CF <sub>3</sub> (Ph)                 |

|       |                 |   |                                            |
|-------|-----------------|---|--------------------------------------------|
| 7.72  | CH <sub>3</sub> | H | 2,3,5,6-CF <sub>3</sub> (Ph)               |
| 7.73  | CH <sub>3</sub> | H | 2,3,4,5,6-CF <sub>3</sub> (Ph)             |
| 7.74  | CH <sub>3</sub> | H | 2,3,4,6-CF <sub>3</sub> O(Ph)              |
| 7.75  | CH <sub>3</sub> | H | 2,3,5,6-CF <sub>3</sub> O(Ph)              |
| 7.76  | CH <sub>3</sub> | H | 2,3,4,5,6-CF <sub>3</sub> O(Ph)            |
| 7.77  | CH <sub>3</sub> | H | 2,3,4,6-CN(Ph)                             |
| 7.78  | CH <sub>3</sub> | H | 2,3,5,6-CN(Ph)                             |
| 7.79  | CH <sub>3</sub> | H | 2,3,4,5,6-CN(Ph)                           |
| 7.80  | CH <sub>3</sub> | H | 2-Br-6-Cl(Ph)                              |
| 7.81  | CH <sub>3</sub> | H | 2-Br-6-F(Ph)                               |
| 7.82  | CH <sub>3</sub> | H | 2-Br-6-CH <sub>3</sub> (Ph)                |
| 7.83  | CH <sub>3</sub> | H | 2-Br-6-CF <sub>3</sub> (Ph)                |
| 7.84  | CH <sub>3</sub> | H | 2-Br-6-CH <sub>3</sub> O(Ph)               |
| 7.85  | CH <sub>3</sub> | H | 2-Br-6-CF <sub>3</sub> O(Ph)               |
| 7.86  | CH <sub>3</sub> | H | 2-Br-6-CN(Ph)                              |
| 7.87  | CH <sub>3</sub> | H | 2-Cl-6-F(Ph)                               |
| 7.88  | CH <sub>3</sub> | H | 2-Cl-6-CH <sub>3</sub> (Ph)                |
| 7.89  | CH <sub>3</sub> | H | 2-Cl-6-CF <sub>3</sub> (Ph)                |
| 7.90  | CH <sub>3</sub> | H | 2-Cl-6-CH <sub>3</sub> O(Ph)               |
| 7.91  | CH <sub>3</sub> | H | 2-Cl-6-CF <sub>3</sub> O(Ph)               |
| 7.92  | CH <sub>3</sub> | H | 2-Cl-6-CN(Ph)                              |
| 7.93  | CH <sub>3</sub> | H | 2-F-6-CH <sub>3</sub> (Ph)                 |
| 7.94  | CH <sub>3</sub> | H | 2-F-6-CF <sub>3</sub> (Ph)                 |
| 7.95  | CH <sub>3</sub> | H | 2-F-6-CH <sub>3</sub> O(Ph)                |
| 7.96  | CH <sub>3</sub> | H | 2-F-6-CF <sub>3</sub> O(Ph)                |
| 7.97  | CH <sub>3</sub> | H | 6-CN-2F(Ph)                                |
| 7.98  | CH <sub>3</sub> | H | 2-CH <sub>3</sub> -6-CF <sub>3</sub> (Ph)  |
| 7.99  | CH <sub>3</sub> | H | 6-CH <sub>3</sub> O-2-CH <sub>3</sub> (Ph) |
| 7.100 | CH <sub>3</sub> | H | 2-CH <sub>3</sub> -6-CF <sub>3</sub> O(Ph) |
| 7.101 | CH <sub>3</sub> | H | 6-CN-2-OCH <sub>3</sub> (Ph)               |
| 7.102 | CH <sub>3</sub> | H | 6-CN-2-CH <sub>3</sub> (Ph)                |
| 7.103 | CH <sub>3</sub> | H | 3,6-Cl-2-F(Ph)                             |
| 7.104 | CH <sub>3</sub> | H | 3Cl-2,6-F(Ph)                              |
| 7.105 | CH <sub>3</sub> | H | 4-Cl-2,6-F(Ph)                             |
| 7.106 | CH <sub>3</sub> | H | 2-Br-3,6-Cl(Ph)                            |
| 7.107 | CH <sub>3</sub> | H | 2,3-Br-6-Cl(Ph)                            |
| 7.108 | CH <sub>3</sub> | H | 3-Cl-2,6Br(Ph)                             |
| 7.109 | CH <sub>3</sub> | H | 2,6-Cl-3-F(Ph)                             |
| 7.110 | CH <sub>3</sub> | H | 2,3-Cl-6-F(Ph)                             |
| 7.111 | CH <sub>3</sub> | H | 2-Cl-3,6-F(Ph)                             |
| 7.112 | CH <sub>3</sub> | H | 3-Br-2,6-Cl(Ph)                            |
| 7.113 | CH <sub>3</sub> | H | 3-Br-2,6-F(Ph)                             |
| 7.114 | CH <sub>3</sub> | H | 3-Br-6Cl-2-F(Ph)                           |
| 7.115 | CH <sub>3</sub> | H | 2-Br-5Cl-6-F(Ph)                           |
| 7.116 | CH <sub>3</sub> | H | 2,6-Br-3-F(Ph)                             |
| 7.117 | CH <sub>3</sub> | H | 2,5-Br-6-F(Ph)                             |
| 7.118 | CH <sub>3</sub> | H | 2,4-Cl-6F(Ph)                              |
| 7.119 | CH <sub>3</sub> | H | 2,6-Cl-4F(Ph)                              |
| 7.120 | CH <sub>3</sub> | H | 2,4-Cl-6Br(Ph)                             |

|       |                 |   |                                                |
|-------|-----------------|---|------------------------------------------------|
| 7.121 | CH <sub>3</sub> | H | 2,6-Cl-4Br(Ph)                                 |
| 7.122 | CH <sub>3</sub> | H | 2,4-F-6-Cl(Ph)                                 |
| 7.123 | CH <sub>3</sub> | H | 2,4-F-6-Br(Ph)                                 |
| 7.124 | CH <sub>3</sub> | H | 2,6-F-4-Br(Ph)                                 |
| 7.125 | CH <sub>3</sub> | H | 2,4-Br-6-F(Ph)                                 |
| 7.126 | CH <sub>3</sub> | H | 2,4-Br-6-Cl(Ph)                                |
| 7.127 | CH <sub>3</sub> | H | 2,6-Br-4-Cl(Ph)                                |
| 7.128 | CH <sub>3</sub> | H | 2,6-Br-4-F(Ph)                                 |
| 7.129 | CH <sub>3</sub> | H | 2,4-Cl-6-CH <sub>3</sub> (Ph)                  |
| 7.130 | CH <sub>3</sub> | H | 2,6-Cl-4-CH <sub>3</sub> (Ph)                  |
| 7.131 | CH <sub>3</sub> | H | 2-Cl-4,6-(CH <sub>3</sub> ) <sub>2</sub> (Ph)  |
| 7.132 | CH <sub>3</sub> | H | 4-Cl-2,6-(CH <sub>3</sub> ) <sub>2</sub> (Ph)  |
| 7.133 | CH <sub>3</sub> | H | 2,4-F-6-CH <sub>3</sub> (Ph)                   |
| 7.134 | CH <sub>3</sub> | H | 2,6-F-4-CH <sub>3</sub> (Ph)                   |
| 7.135 | CH <sub>3</sub> | H | 2-F-4,6-(CH <sub>3</sub> ) <sub>2</sub> (Ph)   |
| 7.136 | CH <sub>3</sub> | H | 4-F-2,6-(CH <sub>3</sub> ) <sub>2</sub> (Ph)   |
| 7.137 | CH <sub>3</sub> | H | 2,4-Br-6-CH <sub>3</sub> (Ph)                  |
| 7.138 | CH <sub>3</sub> | H | 2,6-Br-4-CH <sub>3</sub> (Ph)                  |
| 7.139 | CH <sub>3</sub> | H | 2-Br-4,6-(CH <sub>3</sub> ) <sub>2</sub> (Ph)  |
| 7.140 | CH <sub>3</sub> | H | 4-Br-2,6-(CH <sub>3</sub> ) <sub>2</sub> (Ph)  |
| 7.141 | CH <sub>3</sub> | H | 2,4-Cl-6-CF <sub>3</sub> (Ph)                  |
| 7.142 | CH <sub>3</sub> | H | 2,6-Cl-4-CF <sub>3</sub> (Ph)                  |
| 7.143 | CH <sub>3</sub> | H | 2-Cl-4,6-(CF <sub>3</sub> ) <sub>2</sub> (Ph)  |
| 7.144 | CH <sub>3</sub> | H | 4-Cl-2,6-(CF <sub>3</sub> ) <sub>2</sub> (Ph)  |
| 7.145 | CH <sub>3</sub> | H | 2,4-F-6-CF <sub>3</sub> (Ph)                   |
| 7.146 | CH <sub>3</sub> | H | 2,6-F-4-CF <sub>3</sub> (Ph)                   |
| 7.147 | CH <sub>3</sub> | H | 2-F-3,6-(CF <sub>3</sub> ) <sub>2</sub> (Ph)   |
| 7.148 | CH <sub>3</sub> | H | 3-F-2,6-(CF <sub>3</sub> ) <sub>2</sub> (Ph)   |
| 7.149 | CH <sub>3</sub> | H | 2,3-Br-6-CF <sub>3</sub> (Ph)                  |
| 7.150 | CH <sub>3</sub> | H | 2,6-Br-3-CF <sub>3</sub> (Ph)                  |
| 7.137 | CH <sub>3</sub> | H | 2-Br-4,6-(CF <sub>3</sub> ) <sub>2</sub> (Ph)  |
| 7.138 | CH <sub>3</sub> | H | 4-Br-2,6-(CF <sub>3</sub> ) <sub>2</sub> (Ph)  |
| 7.139 | CH <sub>3</sub> | H | 2,4-Cl-6-CF <sub>3</sub> O(Ph)                 |
| 7.140 | CH <sub>3</sub> | H | 2,6-Cl-4-CF <sub>3</sub> O(Ph)                 |
| 7.141 | CH <sub>3</sub> | H | 2-Cl-4,6-(CF <sub>3</sub> O) <sub>2</sub> (Ph) |
| 7.142 | CH <sub>3</sub> | H | 4-Cl-2,6-(CF <sub>3</sub> O) <sub>2</sub> (Ph) |
| 7.143 | CH <sub>3</sub> | H | 2,4-F-6-CF <sub>3</sub> O(Ph)                  |
| 7.144 | CH <sub>3</sub> | H | 2,6-F-4-CF <sub>3</sub> O(Ph)                  |
| 7.145 | CH <sub>3</sub> | H | 2-F-4,6-(CF <sub>3</sub> O) <sub>2</sub> (Ph)  |
| 7.146 | CH <sub>3</sub> | H | 4-F-2,6-(CF <sub>3</sub> O) <sub>2</sub> (Ph)  |
| 7.147 | CH <sub>3</sub> | H | 2,4-F-6-CF <sub>3</sub> O(Ph)                  |
| 7.148 | CH <sub>3</sub> | H | 2,6-F-4-CF <sub>3</sub> O(Ph)                  |
| 7.149 | CH <sub>3</sub> | H | 2-F-4,6-(CF <sub>3</sub> O) <sub>2</sub> (Ph)  |
| 7.150 | CH <sub>3</sub> | H | 4-F-2,6-(CF <sub>3</sub> O) <sub>2</sub> (Ph)  |
| 7.151 | CH <sub>3</sub> | H | 2-Br-3,4,6-Cl(Ph)                              |
| 7.152 | CH <sub>3</sub> | H | 6-F-2,4,5-Cl(Ph)                               |
| 7.153 | CH <sub>3</sub> | H | 6-Cl-2,4,5-Br(Ph)                              |
| 7.154 | CH <sub>3</sub> | H | 6-F-2,4,5-Br(Ph)                               |
| 7.155 | CH <sub>3</sub> | H | 2-Br-3,4,6-F(Ph)                               |

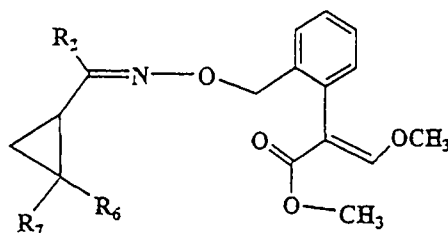
|       |                 |   |                                    |
|-------|-----------------|---|------------------------------------|
| 7.156 | CH <sub>3</sub> | H | 2-Cl-3,4,6-F(Ph)                   |
| 7.157 | CH <sub>3</sub> | H | 6-CH <sub>3</sub> -2,4,5-Cl(Ph)    |
| 7.158 | CH <sub>3</sub> | H | 6-CH <sub>3</sub> -2,4,5-Br(Ph)    |
| 7.159 | CH <sub>3</sub> | H | 6-CH <sub>3</sub> -2,4,5-F(Ph)     |
| 7.160 | CH <sub>3</sub> | H | 6-CF <sub>3</sub> -2,4,5-Cl(Ph)    |
| 7.161 | CH <sub>3</sub> | H | 6-CF <sub>3</sub> -2,4,5-Br(Ph)    |
| 7.162 | CH <sub>3</sub> | H | 6-CF <sub>3</sub> -2,4,5-F(Ph)     |
| 7.163 | CH <sub>3</sub> | H | 6-CF <sub>3</sub> O-2,4,5-Cl(Ph)   |
| 7.164 | CH <sub>3</sub> | H | 6-CF <sub>3</sub> O-2,4,5-Br(Ph)   |
| 7.165 | CH <sub>3</sub> | H | 6-CF <sub>3</sub> O-2,4,5-F(Ph)    |
| 7.166 | CH <sub>3</sub> | H | 2-Br-3,5,6-Cl(Ph)                  |
| 7.167 | CH <sub>3</sub> | H | 2-Br-3,5,6-F(Ph)                   |
| 7.168 | CH <sub>3</sub> | H | 2-Cl-3,5,6-F(Ph)                   |
| 7.169 | CH <sub>3</sub> | H | 6-F-2,3,5-Cl(Ph)                   |
| 7.170 | CH <sub>3</sub> | H | 6-Cl-2,3,5-Br(Ph)                  |
| 7.171 | CH <sub>3</sub> | H | 6-F-2,3,5-Br(Ph)                   |
| 7.172 | CH <sub>3</sub> | H | 6-CH <sub>3</sub> -2,3,5-Cl(Ph)    |
| 7.173 | CH <sub>3</sub> | H | 6-CH <sub>3</sub> -2,3,5-Br(Ph)    |
| 7.174 | CH <sub>3</sub> | H | 2-CH <sub>3</sub> -3,5,6-F(Ph)     |
| 7.175 | CH <sub>3</sub> | H | 6-CF <sub>3</sub> -2,3,5-Cl(Ph)    |
| 7.176 | CH <sub>3</sub> | H | 6-CF <sub>3</sub> -2,3,5-Br(Ph)    |
| 7.177 | CH <sub>3</sub> | H | 2-CF <sub>3</sub> -3,5,6-F(Ph)     |
| 7.178 | CH <sub>3</sub> | H | 6-CF <sub>3</sub> O-2,3,5-Cl(Ph)   |
| 7.179 | CH <sub>3</sub> | H | 6-CF <sub>3</sub> O-2,3,5-Br(Ph)   |
| 7.180 | CH <sub>3</sub> | H | 2-CF <sub>3</sub> O-3,5,6-F(Ph)    |
| 7.172 | CH <sub>3</sub> | H | 4-Br-2,3,5,6-Cl(Ph)                |
| 7.173 | CH <sub>3</sub> | H | 4-F-2,3,5,6-Cl(Ph)                 |
| 7.174 | CH <sub>3</sub> | H | 4-Cl-2,3,5,6-Br(Ph)                |
| 7.175 | CH <sub>3</sub> | H | 4-F-2,3,5,6-Br(Ph)                 |
| 7.176 | CH <sub>3</sub> | H | 4-Cl-2,3,5,6-F(Ph)                 |
| 7.177 | CH <sub>3</sub> | H | 4-Br-2,3,5,6-F(Ph)                 |
| 7.178 | CH <sub>3</sub> | H | 2-Br-3,4,5,6-Cl(Ph)                |
| 7.179 | CH <sub>3</sub> | H | 2-F-3,4,5,6-Cl(Ph)                 |
| 7.180 | CH <sub>3</sub> | H | 2-Cl-3,4,5,6-F(Ph)                 |
| 7.181 | CH <sub>3</sub> | H | 2-Br-3,4,5,6-F(Ph)                 |
| 7.182 | CH <sub>3</sub> | H | 6-Cl-2,3,4,5-Br(Ph)                |
| 7.183 | CH <sub>3</sub> | H | 6-F-2,3,4,5-Br(Ph)                 |
| 7.184 | CH <sub>3</sub> | H | 4-CH <sub>3</sub> -2,3,5,6-Cl(Ph)  |
| 7.185 | CH <sub>3</sub> | H | 4-CH <sub>3</sub> -2,3,5,6-Br(Ph)  |
| 7.186 | CH <sub>3</sub> | H | 4-CH <sub>3</sub> -2,3,5,6-F(Ph)   |
| 7.187 | CH <sub>3</sub> | H | 4-CF <sub>3</sub> -2,3,5,6-Cl(Ph)  |
| 7.188 | CH <sub>3</sub> | H | 4-CF <sub>3</sub> -2,3,5,6-Br(Ph)  |
| 7.189 | CH <sub>3</sub> | H | 4-CF <sub>3</sub> -2,3,5,6-F(Ph)   |
| 7.190 | CH <sub>3</sub> | H | 4-CH <sub>3</sub> O-2,3,5,6-Cl(Ph) |
| 7.191 | CH <sub>3</sub> | H | 4-CF <sub>3</sub> O-2,3,5,6-Br(Ph) |
| 7.192 | CH <sub>3</sub> | H | 4-CF <sub>3</sub> O-2,3,5,6-F(Ph)  |
| 7.193 | CH <sub>3</sub> | H | 4-CF <sub>3</sub> O-2,3,5,6-Cl(Ph) |
| 7.194 | CH <sub>3</sub> | H | 6-CH <sub>3</sub> -2,3,4,5-Cl(Ph)  |
| 7.195 | CH <sub>3</sub> | H | 6-CH <sub>3</sub> -2,3,4,5-Br(Ph)  |

|       |                 |                                   |                                    |
|-------|-----------------|-----------------------------------|------------------------------------|
| 7.196 | CH <sub>3</sub> | H                                 | 2-CH <sub>3</sub> -3,4,5,6-F(Ph)   |
| 7.197 | CH <sub>3</sub> | H                                 | 6-CF <sub>3</sub> O-2,3,4,5-Cl(Ph) |
| 7.198 | CH <sub>3</sub> | H                                 | 6-CF <sub>3</sub> O-2,3,4,5-BrPh   |
| 7.199 | CH <sub>3</sub> | H                                 | 2-CF <sub>3</sub> O-3,4,5,6-F(Ph)  |
| 7.200 | CH <sub>3</sub> | CH <sub>3</sub>                   | 2,6-Cl(Ph)                         |
| 7.201 | CH <sub>3</sub> | CH <sub>3</sub>                   | 2,3,6-Cl(Ph)                       |
| 7.202 | CH <sub>3</sub> | CH <sub>3</sub>                   | 2,4,6-Cl(Ph)                       |
| 7.203 | CH <sub>3</sub> | CH <sub>3</sub>                   | 2,6-Br(Ph)                         |
| 7.204 | CH <sub>3</sub> | CH <sub>3</sub>                   | 2,3,6-Br(Ph)                       |
| 7.205 | CH <sub>3</sub> | CH <sub>3</sub>                   | 2,4,6-Br(Ph)                       |
| 7.206 | CH <sub>3</sub> | CH <sub>3</sub>                   | 2,6-F(Ph)                          |
| 7.207 | CH <sub>3</sub> | CH <sub>3</sub>                   | 2,3,6-F(Ph)                        |
| 7.208 | CH <sub>3</sub> | CH <sub>3</sub>                   | 2,4,6-F(Ph)                        |
| 7.209 | CH <sub>3</sub> | CH <sub>3</sub>                   | 2,6-CH <sub>3</sub> (Ph)           |
| 7.210 | CH <sub>3</sub> | CH <sub>3</sub>                   | 2,3,6-CH <sub>3</sub> (Ph)         |
| 7.211 | CH <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>     | 2,4,6-CH <sub>3</sub> (Ph)         |
| 7.212 | CH <sub>3</sub> | n-C <sub>3</sub> H <sub>7</sub>   | 2,6-Cl(Ph)                         |
| 7.213 | CH <sub>3</sub> | iso-C <sub>3</sub> H <sub>7</sub> | 2,3,6-Cl(Ph)                       |
| 7.214 | CH <sub>3</sub> | n-C <sub>4</sub> H <sub>9</sub>   | 2,4,6-Cl(Ph)                       |
| 7.215 | CH <sub>3</sub> | iso-C <sub>4</sub> H <sub>9</sub> | 2,6-Cl(Ph)                         |
| 7.216 | CH <sub>3</sub> | CH <sub>2</sub> =CH               | 2,3,6-Cl(Ph)                       |
| 7.217 | CH <sub>3</sub> | CH <sub>3</sub> CH=CH             | 2,4,6-Cl(Ph)                       |
| 7.218 | CN              | H                                 | 2,6-Cl(Ph)                         |
| 7.219 | CN              | CH <sub>3</sub>                   | 2,3,6-Cl(Ph)                       |
| 7.220 | CN              | C <sub>2</sub> H <sub>5</sub>     | 2,4,6-Cl(Ph)                       |
| 7.221 | CN              | n-C <sub>3</sub> H <sub>7</sub>   | 2,6-Cl(Ph)                         |
| 7.222 | CN              | iso-C <sub>3</sub> H <sub>7</sub> | 2,3,6-Cl(Ph)                       |
| 7.223 | CN              | n-C <sub>4</sub> H <sub>9</sub>   | 2,4,6-Cl(Ph)                       |
| 7.224 | CN              | iso-C <sub>4</sub> H <sub>9</sub> | 2,6-Cl(Ph)                         |
| 7.225 | CN              | CH <sub>2</sub> =CH               | 2,3,6-Cl(Ph)                       |
| 7.226 | CN              | CH <sub>3</sub> CH=CH             | 2,4,6-Cl(Ph)                       |
| 7.227 | CF <sub>3</sub> | H                                 | 2,6-Cl(Ph)                         |
| 7.228 | CF <sub>3</sub> | CH <sub>3</sub>                   | 2,3,6-Cl(Ph)                       |
| 7.229 | CF <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>     | 2,4,6-Cl(Ph)                       |
| 7.230 | CF <sub>3</sub> | n-C <sub>3</sub> H <sub>7</sub>   | 2,6-Cl(Ph)                         |
| 7.231 | CF <sub>3</sub> | iso-C <sub>3</sub> H <sub>7</sub> | 2,3,6-Cl(Ph)                       |

Table 8: Compounds 8.1 to 8.231 are compounds of Formula I wherein A, R<sub>3</sub>, R<sub>4</sub>, and R<sub>5</sub> are hydrogen; X is N and Z is O; R<sub>1</sub> is methyl; and R<sub>2</sub>, R<sub>6</sub>, and R<sub>7</sub> are defined as in Table 7. The following compounds possess either a trans cyclopropane or an enriched trans cyclopropane stereochemistry for R<sub>7</sub> and the iminoxy substituent, and the indicated A:B iminoxy isomer ratio is shown: 8.16 (oil, 9:1 A:B isomers), 8.16A (oil), 8.16B (oil), 8.22 (oil, 7.9:2.1 A:B isomers), and 8.200 (oil, 4:1 A:B isomers).

Table 9: Compounds 9.1 to 9.231 are compounds of Formula I wherein A, R<sub>3</sub>, R<sub>4</sub>, and R<sub>5</sub> are hydrogen; X is N and Z is NH, R<sub>1</sub> is methyl; and R<sub>2</sub>, R<sub>6</sub>, and R<sub>7</sub> are defined as in Table 7. The following compounds possess either a trans cyclopropane or an enriched trans cyclopropane stereochemistry for R<sub>7</sub> and the iminoxy substituent, and the indicated A:B iminoxy isomer ratio is shown: 9.16 (oil, 9:1 A:B isomers), 9.16A (oil), 9.16B (mp. 140-146 °C), 9.22A (oil) and 9.22B (oil), and 9.200 (oil, 9:1 A:B isomers).

Typical compounds of Formula I encompassed by the present invention wherein A, R<sub>3</sub>, R<sub>4</sub>, and R<sub>5</sub> are hydrogen; X is CH and Z is O; and R<sub>1</sub> is methyl include those compounds presented in Table 10 of Formula III where R<sub>2</sub>, R<sub>6</sub>, and R<sub>7</sub> are defined in Table 10.



Formula III

Table 10

| Comp  | R <sub>2</sub>  | R <sub>6</sub> | R <sub>7</sub>                                      |
|-------|-----------------|----------------|-----------------------------------------------------|
| 10.1  | H               | H              | 2,4-Cl-pyrid-3-yl                                   |
| 10.2  | H               | H              | 2,4-F-pyrid-3-yl                                    |
| 10.3  | H               | H              | 2-Cl-4-F-pyrid-3-yl                                 |
| 10.4  | H               | H              | 2,4-(CH <sub>3</sub> ) <sub>2</sub> -pyrid-3-yl     |
| 10.5  | H               | H              | 3,5-Cl-pyrid-4-yl                                   |
| 10.6  | H               | H              | 3,5-F-pyrid-4-yl                                    |
| 10.7  | H               | H              | 3-Cl-5-F-pyrid-4-yl                                 |
| 10.8  | H               | H              | 3,5-(CH <sub>3</sub> ) <sub>2</sub> -pyrid-4-yl     |
| 10.9  | H               | H              | 4,6-Cl-pyrimidin-5-yl                               |
| 10.10 | H               | H              | 4,6-F-pyrimidin-5-yl                                |
| 10.11 | H               | H              | 4,6-(CH <sub>3</sub> ) <sub>2</sub> -pyrimidin-5-yl |
| 10.12 | H               | H              | 4-Cl-6-F-pyrimidin-5-yl                             |
| 10.13 | CH <sub>3</sub> | H              | 2,4-Cl-pyrid-3-yl                                   |
| 10.14 | CH <sub>3</sub> | H              | 2,4-F-pyrid-3-yl                                    |
| 10.15 | CH <sub>3</sub> | H              | 2-Cl-4-F-pyrid-3-yl                                 |
| 10.16 | CH <sub>3</sub> | H              | 2,4-(CH <sub>3</sub> ) <sub>2</sub> -pyrid-3-yl     |
| 10.17 | CH <sub>3</sub> | H              | 3,5-Cl-pyrid-4-yl                                   |
| 10.18 | CH <sub>3</sub> | H              | 3,5-F-pyrid-4-yl                                    |
| 10.19 | CH <sub>3</sub> | H              | 3-Cl-5-F-pyrid-4-yl                                 |
| 10.20 | CH <sub>3</sub> | H              | 3,5-(CH <sub>3</sub> ) <sub>2</sub> -pyrid-4-yl     |

|       |                 |                 |                                                     |
|-------|-----------------|-----------------|-----------------------------------------------------|
| 10.21 | CH <sub>3</sub> | H               | 4,6-Cl-pyrimidin-5-yl                               |
| 10.22 | CH <sub>3</sub> | H               | 4,6-F-pyrimidin-5-yl                                |
| 10.23 | CH <sub>3</sub> | H               | 4,6-(CH <sub>3</sub> ) <sub>2</sub> -pyrimidin-5-yl |
| 10.24 | CH <sub>3</sub> | H               | 4-Cl-6-F-pyrimidin-5-yl                             |
| 10.25 | CH <sub>3</sub> | H               | 3,5-Cl-pyridazin-4-yl                               |
| 10.26 | CH <sub>3</sub> | H               | 3,5-F-pyridazin-4-yl                                |
| 10.27 | CH <sub>3</sub> | H               | 3,5-Br-pyridazin-4-yl                               |
| 10.28 | CH <sub>3</sub> | H               | 3,5-(CH <sub>3</sub> ) <sub>2</sub> -pyridazin-4-yl |
| 10.29 | CH <sub>3</sub> | H               | 3-Cl-5-F-pyridazin-4-yl                             |
| 10.30 | CH <sub>3</sub> | H               | 5-Cl-3-F-pyridazin-4-yl                             |
| 10.31 | CH <sub>3</sub> | H               | 3-Br-5-Cl-pyridazin-4-yl                            |
| 10.32 | CH <sub>3</sub> | H               | 5-Br-3-Cl-pyridazin-4-yl                            |
| 10.33 | CH <sub>3</sub> | H               | 2,4-Cl-thien-3-yl                                   |
| 10.34 | CH <sub>3</sub> | H               | 2,4-F-thien-3-yl                                    |
| 10.35 | CH <sub>3</sub> | CH <sub>3</sub> | 2-Cl-4-F-thien-3-yl                                 |
| 10.36 | CH <sub>3</sub> | CH <sub>3</sub> | 2-F-4-Cl-thien-3-yl                                 |
| 10.37 | CH <sub>3</sub> | CH <sub>3</sub> | 2,4-(CH <sub>3</sub> ) <sub>2</sub> -thien-3-yl     |
| 10.38 | CH <sub>3</sub> | CH <sub>3</sub> | 2,4,5-Cl-thien-3-yl                                 |
| 10.39 | CH <sub>3</sub> | CH <sub>3</sub> | 2,4,5-F-thien-3-yl                                  |
| 10.40 | CH <sub>3</sub> | CH <sub>3</sub> | 2,4,5-CH <sub>3</sub> -thien-3-yl                   |
| 10.41 | CH <sub>3</sub> | CH <sub>3</sub> | 2,4-Cl-furan-3-yl                                   |
| 10.42 | CH <sub>3</sub> | CH <sub>3</sub> | 2,4-F-furan-3-yl                                    |
| 10.43 | CH <sub>3</sub> | CH <sub>3</sub> | 2-Cl-4F-furan-3-yl                                  |
| 10.44 | CH <sub>3</sub> | CH <sub>3</sub> | 2-F-4Cl-furan-3-yl                                  |
| 10.45 | CH <sub>3</sub> | CH <sub>3</sub> | 2,4-(CH <sub>3</sub> ) <sub>2</sub> -furan-3-yl     |
| 10.46 | CH <sub>3</sub> | CH <sub>3</sub> | 2,4,5-Cl-furan-3-yl                                 |
| 10.47 | CH <sub>3</sub> | CH <sub>3</sub> | 2,4,5-F-furan-3-yl                                  |
| 10.48 | CH <sub>3</sub> | CH <sub>3</sub> | 2,4,5-CH <sub>3</sub> -furan-3-yl                   |
| 10.49 | CH <sub>3</sub> | CH <sub>3</sub> | 2,4-Cl-1-CH <sub>3</sub> -1H-pyrrol-3-yl            |
| 10.50 | CH <sub>3</sub> | CH <sub>3</sub> | 2,4-F-1-CH <sub>3</sub> -1H-pyrrol-3-yl             |
| 10.51 | CH <sub>3</sub> | CH <sub>3</sub> | 2-Cl-4F-1-CH <sub>3</sub> -1H-pyrrol-3-yl           |
| 10.52 | CH <sub>3</sub> | CH <sub>3</sub> | 2-F-4Cl-1-CH <sub>3</sub> -1H-pyrrol-3-yl           |
| 10.53 | CH <sub>3</sub> | CH <sub>3</sub> | 3,5-Cl-isoxazol-4-yl                                |
| 10.54 | CH <sub>3</sub> | CH <sub>3</sub> | 3,5-F-isoxazol-4-yl                                 |
| 10.55 | CH <sub>3</sub> | CH <sub>3</sub> | 3,5-Br-isoxazol-4-yl                                |
| 10.56 | CH <sub>3</sub> | CH <sub>3</sub> | 3,5-CH <sub>3</sub> -isoxazol-4-yl                  |
| 10.57 | CH <sub>3</sub> | CH <sub>3</sub> | 3,5-CH <sub>3</sub> O-isoxazol-4-yl                 |
| 10.58 | CH <sub>3</sub> | CH <sub>3</sub> | 3,5-CF <sub>3</sub> O-isoxazol-4-yl                 |
| 10.50 | CH <sub>3</sub> | CH <sub>3</sub> | 3,5-Cl-isothiazol-4-yl                              |
| 10.60 | CH <sub>3</sub> | CH <sub>3</sub> | 3,5-F-isothiazol-4-yl                               |
| 10.61 | CH <sub>3</sub> | CH <sub>3</sub> | 3,5-Br-isothiazol-4-yl                              |
| 10.62 | CH <sub>3</sub> | CH <sub>3</sub> | 3,5-CH <sub>3</sub> -isothiazol-4-yl                |
| 10.63 | CH <sub>3</sub> | CH <sub>3</sub> | 3,5-CH <sub>3</sub> O-isothiazol-4-yl               |
| 10.64 | CH <sub>3</sub> | CH <sub>3</sub> | 3,5-CF <sub>3</sub> O-isothiazol-4-yl               |
| 10.66 | CH <sub>3</sub> | CH <sub>3</sub> | 3,5-Cl-1-CH <sub>3</sub> -1H-pyrazol-4-yl           |
| 10.67 | CH <sub>3</sub> | CH <sub>3</sub> | 3,5-F-1-CH <sub>3</sub> -1H-pyrazol-4-yl            |
| 10.68 | CH <sub>3</sub> | CH <sub>3</sub> | 3,5-Br-1-CH <sub>3</sub> -1H-pyrazol-4-yl           |
| 10.69 | CH <sub>3</sub> | CH <sub>3</sub> | 3-Cl-5F-1-CH <sub>3</sub> -1H-pyrazol-4-yl          |
| 10.70 | CH <sub>3</sub> | CH <sub>3</sub> | 2,4-Cl-pyrid-3-yl                                   |

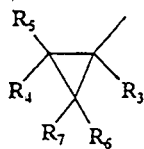
|        |                 |                                   |                                                 |
|--------|-----------------|-----------------------------------|-------------------------------------------------|
| 10.71  | CH <sub>3</sub> | C <sub>2</sub> H <sub>5</sub>     | 2,4-F-pyrid-3-yl                                |
| 10.72  | CH <sub>3</sub> | n-C <sub>3</sub> H <sub>7</sub>   | 2-Cl-4-F-pyrid-3-yl                             |
| 10.73  | CH <sub>3</sub> | iso-C <sub>3</sub> H <sub>7</sub> | 2,4-(CH <sub>3</sub> ) <sub>2</sub> -pyrid-3-yl |
| 10.74  | CH <sub>3</sub> | n-C <sub>4</sub> H <sub>9</sub>   | 3,5-Cl-pyrid-4-yl                               |
| 10.75  | CH <sub>3</sub> | iso-C <sub>4</sub> H <sub>9</sub> | 3,5-F-pyrid-4-yl                                |
| 10.76  | CH <sub>3</sub> | CH <sub>2</sub> =CH               | 3-Cl-5-F-pyrid-4-yl                             |
| 10.77  | CN              | CH <sub>3</sub> CH=CH             | 2,4-Cl-pyrid-3-yl                               |
| 10.78  | CN              | CH <sub>3</sub>                   | 2,4-F-pyrid-3-yl                                |
| 10.79  | CN              | CH <sub>3</sub>                   | 2-Cl-4-F-pyrid-3-yl                             |
| 10.80  | CN              | CH <sub>3</sub>                   | 2,4-(CH <sub>3</sub> ) <sub>2</sub> -pyrid-3-yl |
| 10.81  | CN              | CH <sub>3</sub>                   | 3,5-Cl-pyrid-4-yl                               |
| 10.82  | CN              | CH <sub>3</sub>                   | 3,5-F-pyrid-4-yl                                |
| 10.83  | CN              | CH <sub>3</sub>                   | 3-Cl-5-F-pyrid-4-yl                             |
| 10.84  | CN              | CH <sub>3</sub>                   | 4,6-Cl-pyrimidin-5-yl                           |
| 10.85  | CN              | CH <sub>3</sub>                   | 4,6-F-pyrimidin-5-yl                            |
| 10.86  | CN              | CH <sub>3</sub>                   | 2,4-Cl-thien-3-yl                               |
| 10.87  | CN              | CH <sub>3</sub>                   | 2,4-F-thien-3-yl                                |
| 10.88  | CN              | CH <sub>3</sub>                   | 2-Cl-4-F-thien-3-yl                             |
| 10.89  | CN              | CH <sub>3</sub>                   | 2-F-4-Cl-thien-3-yl                             |
| 10.90  | CN              | CH <sub>3</sub>                   | 2,4-(CH <sub>3</sub> ) <sub>2</sub> -thien-3-yl |
| 10.89  | CN              | CH <sub>3</sub>                   | 2,4,5-Cl-thien-3-yl                             |
| 10.90  | CN              | CH <sub>3</sub>                   | 2,4,5-F-thien-3-yl                              |
| 10.91  | CN              | CH <sub>3</sub>                   | 2,4,5-CH <sub>3</sub> -thien-3-yl               |
| 10.92  | CN              | C <sub>2</sub> H <sub>5</sub>     | 2,4-Cl-pyrid-3-yl                               |
| 10.93  | CN              | n-C <sub>3</sub> H <sub>7</sub>   | 2,4-Cl-pyrid-3-yl                               |
| 10.94  | CN              | iso-C <sub>3</sub> H <sub>7</sub> | 2,4-Cl-thien-3-yl                               |
| 10.95  | CN              | n-C <sub>4</sub> H <sub>9</sub>   | 2,4-F-thien-3-yl                                |
| 10.96  | CN              | iso-C <sub>4</sub> H <sub>9</sub> | 2-Cl-4-F-thien-3-yl                             |
| 10.97  | CN              | CH <sub>2</sub> =CH               | 2-F-4-Cl-thien-3-yl                             |
| 10.98  | CN              | CH <sub>3</sub> CH=CH             | 2,4-(CH <sub>3</sub> ) <sub>2</sub> -thien-3-yl |
| 10.99  | CF <sub>3</sub> | CH <sub>3</sub>                   | 2,4-Cl-pyrid-3-yl                               |
| 10.100 | CF <sub>3</sub> | CH <sub>3</sub>                   | 2,4-F-pyrid-3-yl                                |
| 10.101 | CF <sub>3</sub> | CH <sub>3</sub>                   | 2,4-Cl-thien-3-yl                               |
| 10.102 | CF <sub>3</sub> | CH <sub>3</sub>                   | 2,4-F-thien-3-yl                                |
| 10.103 | CF <sub>3</sub> | CH <sub>3</sub>                   | 2-Cl-4-F-thien-3-yl                             |
| 10.104 | CF <sub>3</sub> | CH <sub>3</sub>                   | 2-F-4-Cl-thien-3-yl                             |
| 10.105 | CF <sub>3</sub> | CH <sub>3</sub>                   | 2,4-(CH <sub>3</sub> ) <sub>2</sub> -thien-3-yl |
| 10.106 | CF <sub>3</sub> | CH <sub>3</sub>                   | 3,5-Cl-isothiazol-4-yl                          |
| 10.107 | CF <sub>3</sub> | CH <sub>3</sub>                   | 3,5-F-isothiazol-4-yl                           |
| 10.108 | CF <sub>3</sub> | n-C <sub>3</sub> H <sub>7</sub>   | 2,4-Cl-pyrid-3-yl                               |
| 10.109 | CF <sub>3</sub> | iso-C <sub>3</sub> H <sub>7</sub> | 2,4-F-pyrid-3-yl                                |
| 10.110 | CF <sub>3</sub> | n-C <sub>4</sub> H <sub>9</sub>   | 3,5-Cl-pyrid-4-yl                               |
| 10.111 | CF <sub>3</sub> | iso-C <sub>4</sub> H <sub>9</sub> | 3,5-F-pyrid-4-yl                                |
| 10.112 | CF <sub>3</sub> | CH <sub>2</sub> =CH               | 2,4-Cl-pyrid-3-yl                               |
| 10.113 | CF <sub>3</sub> | CH <sub>3</sub> CH=CH             | 2,4-F-pyrid-3-yl                                |

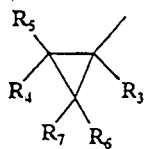
Table 11: Compounds 11.1 to 11.113 are compounds of Formula I wherein A, R<sub>3</sub>, R<sub>4</sub>, and R<sub>5</sub> are hydrogen; X is N and Z is O; R<sub>1</sub> is methyl; and R<sub>2</sub>, R<sub>6</sub>, and R<sub>7</sub> are defined as in Table 7.

Table 12: Compounds 12.1 to 12.113 are compounds of Formula I wherein A, R<sub>3</sub>, R<sub>4</sub>, and R<sub>5</sub> are hydrogen; X is N and Z is NH, R<sub>1</sub> is methyl; and R<sub>2</sub>, R<sub>6</sub>, and R<sub>7</sub> are defined as in Table 7.

Compounds of the present invention are prepared according to the following synthetic schemes. Scheme A describes the preparation of compounds of the Formula (I) where A and R<sub>2</sub> to R<sub>7</sub> are as defined in Tables 1-2, 4-5, 7-8, and 10-11; X is CH or N, and Z is O (compounds of Formula VI and VII). The cyclopropyl oximes (V) are reacted with the appropriately substituted benzyl derivatives (IV), where Z is a halogen, such as bromo, chloro or iodo, preferably a benzyl bromide. A cyclopropyl substituted oxime represented by the general formula (V) is treated, at room temperature, with an appropriate base to form an anion, followed by the addition of the benzyl bromide (IV). Typical bases employed are metal hydrides such as sodium hydride, alkoxides such as sodium methoxide and hydroxide bases such as sodium or potassium hydroxide and alkali bases such as sodium or potassium carbonate. Typical solvents employed with hydride bases are N,N-dimethylformamide (DMF) and tetrahydrofuran (THF); with hydroxide bases DMF, THF, methyl ethyl ketone (MEK) and acetone and with alkali bases solvents such as DMF, acetone, and MEK.

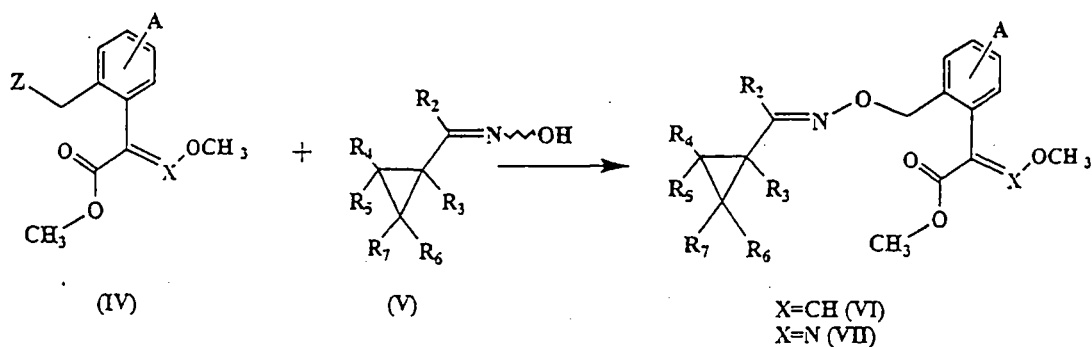
As shown in Scheme A, the N-O bond in C(R<sub>2</sub>)=N-O-, appears in the E



position (assuming  is the larger substituent), It should be recognized that the Z isomer can also be produced as well as mixtures. When isomers are produced they are designated isomer A (higher R<sub>f</sub> on thin layer chromatography) and isomer B (lower R<sub>f</sub> on thin layer chromatography). The determination of which isomer, A or B possesses the E or Z geometry can be made by such conventional techniques as X ray crystallography or by spectroscopic means such as nuclear magnetic resonance spectroscopy. For the compounds of the present

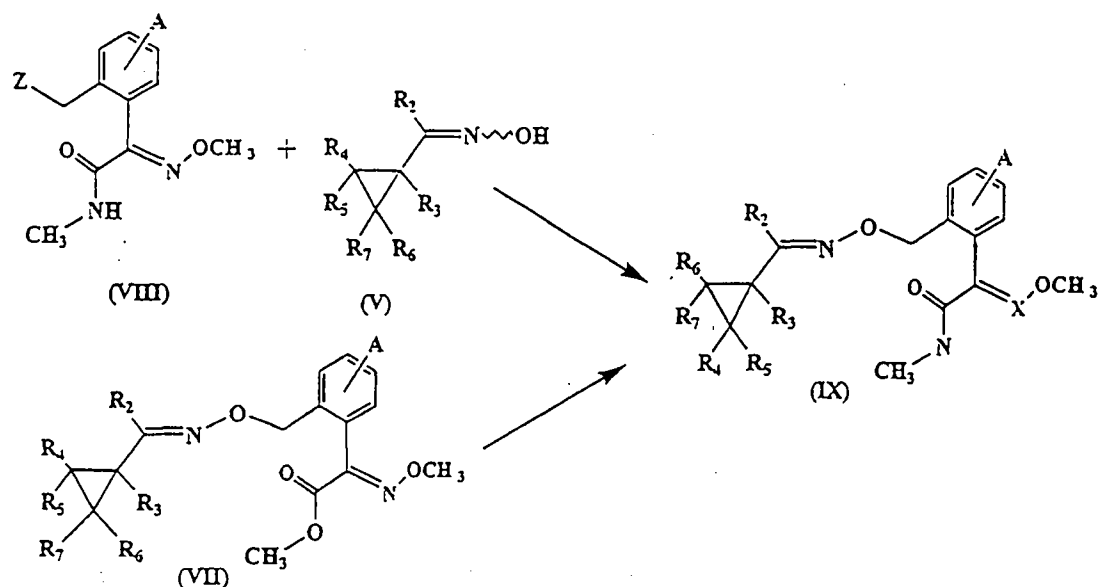
invention isomer A has been assigned the E iminoxy configuration and isomer B, the Z iminoxy configuration.

### Scheme A



Compounds of formula VI (X is CH) are prepared by alkylation with methyl E- $\alpha$ -(2-bromomethylphenyl)- $\beta$ -methoxyacrylate in the presence of a base, preferably NaOH or KOH, in a solvent, preferably acetone or methyl ethyl ketone. Methyl E- $\alpha$ -(2-bromomethylphenyl)- $\beta$ -methoxyacrylate, as a single E isomer, can be prepared in two steps from 2-methylphenylacetate as described previously in US Patent Number 4,914,128, columns 3-4. Compounds of formula VII (X=N) are prepared by the reaction with methyl E-2-(bromomethyl)phenylglyoxylate O-methyloxime in the presence of a base, preferably NaOH or KOH, in a solvent, preferably acetone or methyl ethyl ketone. Methyl 2-(bromomethyl)phenylglyoxylate O-methyloxime can be prepared as described in US Patent Numbers 4,999,042, columns 17-18 and 5,157,144, columns 17-18. Methyl 2-(bromomethyl)phenylglyoxylate O-methyloxime is prepared from methyl 2-methylphenylacetate by treatment with an alkyl nitrite under basic conditions to provide after methylation, methyl 2-methylphenyl-glyoxalate O-methyl oxime which can also be prepared from methyl 2-methylphenylglyoxalate by treatment with 2-hydroxylamine hydrochloride and methylation or by treatment with methoxylamine hydrochloride.

### Scheme B

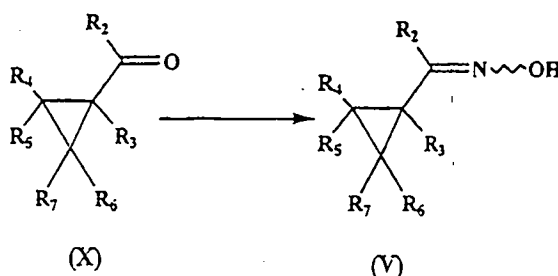


As shown in scheme B compounds of formula IX (X is N) and of Tables 3, 6, 9, and 12 can be prepared by the aminolysis of oximinoacetate (VII). The aminolysis of oximinoacetate to oximinoacetamides has been described in US Patent Numbers 5,185,342, cols. 22, 48 and 57, 5,221,691, cols. 26-27 and 5,407,902, col. 8. For example, compounds of formula VII and of Table 2 are treated with 40% aqueous methylamine in methanol to provide compounds of formula IX and of Table 3 of formula I where Z is NH. Alternatively, as is shown in scheme B intermediate unsaturated oximes (V) are reacted with N-methyl (E)-2-methoxyimino-2-[2-(bromomethyl)phenyl]acetamide VIII in the presence of a base such as an hydroxide base preferably in a solvent such as acetone or methyl ethyl ketone to provide compounds of formula (IX). N-methyl (E)-2-methoxy-imino-2-[2-(bromomethyl)phenyl]acetamide is described in US Patent Number 5,387,714, col. 13.

The oximes of the general formula (V) can be obtained, as shown in Scheme C, by reacting the corresponding cyclopropyl aldehyde or ketone (X) with hydroxylamine hydrochloride from room temperature to reflux, preferably at room temperature, in an appropriate solvent such as methanol or ethanol in the presence of an appropriate alkali such as sodium hydroxide, potassium carbonate or pyridine. A general description of the synthesis of oximes with hydroxylamine is described in March, *Advanced Organic Chemistry*, 4th Ed, pp. 906-907 and references therein. The oximes of the general formula (III) when obtained as a mixture of syn or anti oxime isomers can be separated into

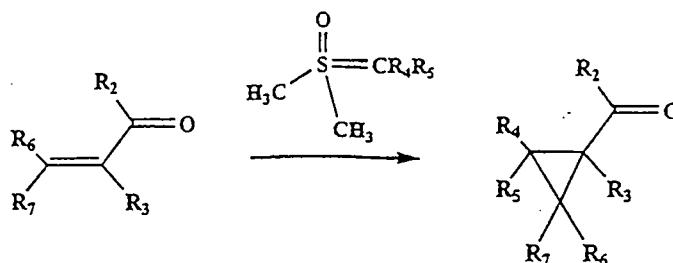
individual isomers and alkylated as described in scheme A and B. When a mixture of oximes of the general formula (III) are used in Schemes A and B the compounds of the formula VI, VII and IX can be separated into their individual isomers by conventional chromatographic techniques.

### Scheme C



The cyclopropyl aldehydes or ketones (X) are prepared by conventional techniques. The unsaturated intermediate XI (Scheme D) is reacted with a sulfur ylide, prepared from a dimethylsulfoxonium salt in the presence of a base, resulting in the substituted acyl cyclopropanes, X, as shown in Scheme D. The chemistry of sulfur ylides is described in Trost and Melvin, Sulfur Ylids, Academic Press, New York, NY 1975 and in Block, Reactions of Organosulfur Compounds, pp. 91-123, Academic Press, New York, NY 1978. Typical reaction conditions for sulfur ylide formation from a dimethylsulfoxonium salt utilizes bases such as hydroxides, metal hydrides and alkoxides in solvents such as dimethoxyethane, dimethylsulfoxide and water depending on the base employed. The reactions are conducted from 0 to 20°C preferably from 10-15°C and preferably with alkali metal hydroxides in dimethylsulfoxide. Typically dimethylsulfoxonium methylide is prepared from trimethylsulfoxonium iodide in dimethylsulfoxide in the presence of powdered sodium hydroxide at room temperature. The unsaturated aldehydes or ketones (XI) are added dropwise to the ylide and stirred at room temperature.

### Scheme D

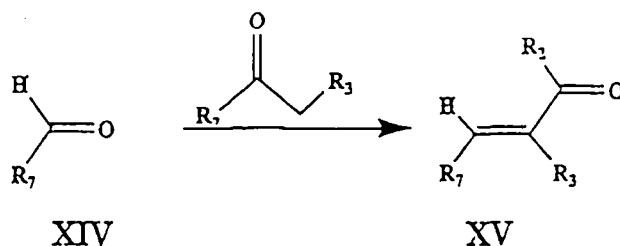


## XI

## X

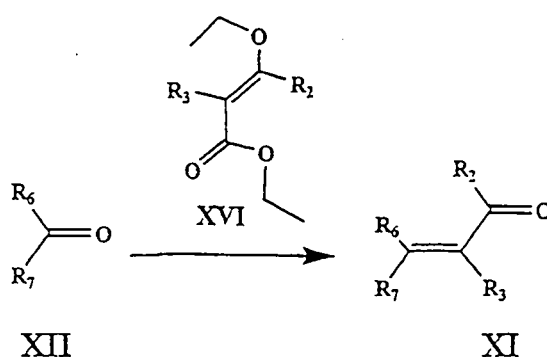
The  $\alpha,\beta$ -unsaturated aldehydes or ketones XI can be prepared by conventional condensation techniques. A extensive description of the synthesis of  $\alpha,\beta$ -unsaturated aldehydes or ketones (enones) is described in March, Advanced Organic Chemistry, 4th Ed, pp. 937-955 and references therein. For example Organic Reactions, Volume 16 describes the general aldol condensation of ketones and aldehydes. For intermediates of formula XI of this invention, in general the ketones and aldehydes are  $R_7COR_6$  (XII) and  $R_2COCH_2R_3$  (XIII) where  $R_2$ ,  $R_3$ ,  $R_6$ , and  $R_7$  are defined previously. When  $R_6$  is hydrogen, the aldehydes  $R_7CHO$  (XIV), are for example benzaldehydes (arylCHO) or heterocyclic aldehydes substituted with from 2 to 5 substituents wherein the positions on the aryl and heterocyclic ring adjacent to the bond to the cyclopropyl ring, in Formula I, are both substituted. These substituted benzaldehydes or heterocyclic aldehydes are commercially available or prepared by conventional techniques. The aldehydes  $R_7CHO$  (XIV) are reacted with the ketones  $R_2COCH_2R_3$ , XIII, (as shown in Scheme E) to provide the intermediates enones XV. Typically the ketone,  $R_2COCH_2R_3$ , is dissolved in a hydroxylic solvent, such as methanol or ethanol, to which is added dropwise the aldehyde  $R_7CHO$  followed by the base or alternatively a solution of the aldehyde in an aqueous basic solution is added. The typical bases used can be alkali metal hydroxides, such as barium, potassium or sodium hydroxide and the dropwise addition is conducted from 0°C to 35°C preferably at ambient temperature. When the enone is derived from acetone ( $R_2$  is methyl and  $R_3$  is hydrogen) the solvent can be acetone to which is added  $R_7COR_6$  followed by the aqueous hydroxide solution. Preferably the aldehyde is dissolved in a solvent mixture of acetone:water (1:5) to which is added the base while stirring at room temperature.

## Scheme E



When  $R_6$  is not hydrogen,  $R_7\text{COR}_6$  (XII) are the ketones  $\text{arylCOR}_6$  or heterocyclic ketones, substituted with from 2 to 5 substituents wherein the positions on the aryl and heterocyclic rings adjacent to the bond to the cyclopropyl ring, in Formula I, are both substituted or aryl or heterocyclic ring is unsubstituted or substituted from 1 to 4 substituents wherein at least one of the positions on the aryl or heterocyclic rings adjacent to the bond to the cyclopropyl ring, in Formula I, is a hydrogen. For the compounds of formula I where  $R_6$  is not hydrogen the intermediate unsaturated aldehydes and ketones XI are prepared, as shown in Scheme F, according to the procedures described in US Patent Number 3,950,427, col. 17 line 20, to provide after purification the E diastereoisomer ( $R_7$  is trans to  $R_2\text{CO}$  in XI). In a typical preparation a ketone such as  $R_7\text{COR}_6$  is reacted with an ethyl trans 3-ethoxycrotonate in dimethylformamide in the presence of potassium t-butoxide followed by acidic hydrolysis and decarboxylation to give XI. The crotonates, XVI, can be prepared from substituted ethyl acetoketones by conventional techniques

Scheme F

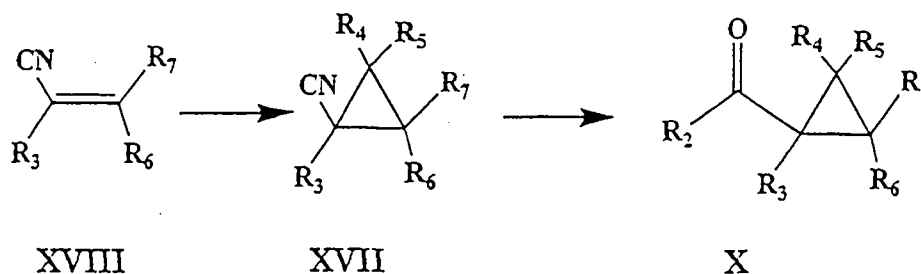


Alternatively the  $\alpha,\beta$ -unsaturated cyclopropyl ketones X can be prepared from cyclopropyl nitriles XIV which are prepared via cyclopropanation of the acrylonitriles XVIII as is described in Scheme G. The acrylonitriles XVIII starting materials, shown in Scheme G can be prepared by conventional

synthetic methods as described in March, Advanced Organic Chemistry, 4th Ed, pp. 937-955 and references therein. For example the nitrile derivative  $R_3CH_2CN$  is condensed with the ketone or aldehyde  $R_7COR_6$  in the presence of a base to provide the acrylonitriles XIII. Typically the a nitrile is dissolved in a solvent such as ethanol and water to which is added the aldehyde or ketone followed by a base. Typical bases used can be alkali metal hydroxides, such as barium, potassium or sodium hydroxide and the mixture is stirred typically at ambient temperature.

The acrylonitrile XVIII is treated as is described in Scheme D with a sulfur ylide to provide the cyclopropyl nitriles XVII. The cyclopropyl nitrile XVII is transformed to the cyclopropyl ketone by organometallic addition to the nitrile followed by hydrolysis. For example the standard Grignard reagents  $R_2MgX$  or organolithium reagents,  $R_2Li$ , add to the nitrile functionality to provide the ketone X. The addition reaction to nitriles is described in March, Advanced Organic Chemistry, 4th Ed, pp.935-936 and references cited therein. The cyclopropyl nitrile XVII can be transformed to the cyclopropyl aldehyde X' (where  $R_2$  is H) by standard reductive methods such as with diisobutylaluminum hydride (DiBAL). The formation of aldehydes from the reduction of nitriles is described in March, Advanced Organic Chemistry, 4th Ed, pp.919-920 and references cited therein.

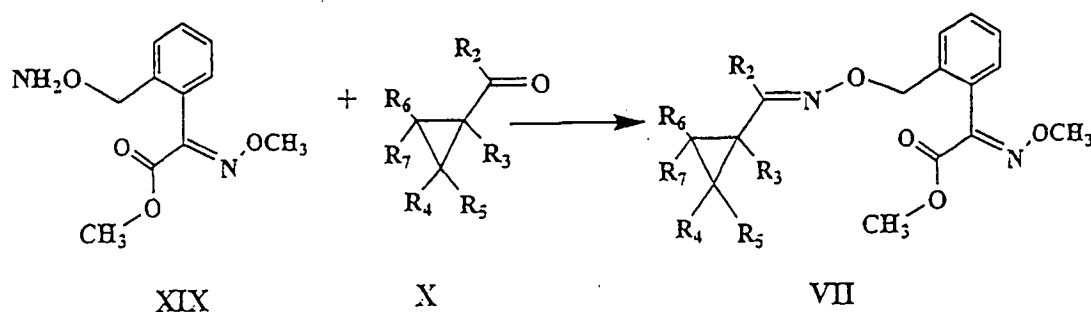
Scheme G



A direct synthesis of compounds of the formula VII or IX is shown in Scheme H. Compounds of the Formula VII or IX can be prepared directly from the functionalized cyclopropyl ketones or aldehydes, X, by condensation with the aminoxy intermediate XIX. The preparation of aminoxy intermediate XIX is described in US Patent Number 5,194,662. The aminoxy intermediate XIX is

prepared in a two step sequence by the alkylation of IV (where X is N) with N-hydroxyphthalimide which is treated with hydrazine to provide XIX. The aminoxy intermediate XIX is condensed with ketones or aldehydes X to provide VII which are treated as shown in scheme B to provide IX.

Scheme H



The compounds of this invention can be made according to the following procedures:

#### Example 1

Preparation of E and Z imine isomers: (E,E) and (Z,E) Methyl 2-[2-((trans-1-(2-(2',6'-dichlorophenyl)cyclopropyl)ethylidene)-aminooxymethyl)phenyl]-2-methoxyiminoacetate Compound 8.16, 8.16A and 8.16B of Table 8

#### Preparation of 4-(2,6-dichlorophenyl)-3-buten-2-one

To a 1000 ml round bottom flask equipped with mechanical stirrer, and nitrogen inlet were charged 26.5 g (0.15 moles) of 2,6-dichlorobenzaldehyde, 125 mls of acetone, 600 mls of water, and 9.3 g (0.23 moles) of sodium hydroxide. The mixture was stirred for 12 hours at room temperature. Analysis of an aliquot by GC indicated complete reaction. The resulting solid was collected by vacuum filtration, and washed with 100 mls of water, 100 mls of hexane, and dried *in vacuo* at 40°C for 3 hours. 31.4 g of the title compound, 4-(2,6-dichlorophenyl)-3-buten-2-one, was isolated as a pale yellow solid in 98% isolated yield.

NMR 300 MHz  $^1\text{H}$   $\text{CDCl}_3$  2.43 (s, 3H); 6.80 (d, 1H); 7.18-7.38 (m, 1H); 7.4 (d, 2H); 7.6 (d, 1H).

#### Preparation of trans-1-(2,6 dichlorophenyl)-2-acetyl-cyclopropane

To a 1000 ml round bottom flask equipped with magnetic stirrer, nitrogen inlet and addition funnel were charged 33.2 g (0.151 moles) of trimethyl

40  
sulfoxonium iodide, 6.1 g (0.151 moles) of powdered sodium hydroxide, and 300 mls DMSO. The mixture was stirred at room temperature for 1 hour, followed by the rapid addition of the 4-(2,6-dichlorophenyl)-3-buten-2-one (32.3 g, 0.151 moles) in one portion. The reaction was then stirred for 10 minutes at ambient temperature, then poured into 200 mls of ice water and extracted with 3 x 100 ml of ethyl ether. The ether extract was washed with 2 x 100 mls of water, 100mls of brine, dried over anhydrous  $\text{MgSO}_4$ , filtered through 2" of silica gel, and concentrated *in vacuo* on a rotary evaporator to afford 31.7 g of a thick pale yellow oil which was chromatographed on silica gel with 90% hexane, 10% ethyl acetate. The pure fractions were combined and concentrated *in vacuo* on a rotary evaporator to afford 27.9 g of trans-1-(2,6 dichlorophenyl)-2-acetyl-cyclopropane as a free flowing pale yellow liquid.in 81% yield.

NMR 300 MHz  $^1\text{H}$   $\text{CDCl}_3$  1.4-1.48 (m, 1H); 1.78-1.86 (m, 1H); 2.21-2.30 (m, 1H); 2.34-2.4 (m, 1H); 2.41 (s, 3H), 7.2 (m, 1H), 7.3 (d, 2H).

Preparation of E and Z imine isomers: (E,E) and (Z,E) Methyl 2-[2-((trans-1-(2-(2',6'-dichlorophenyl)cyclopropyl)ethylidene)aminooxymethyl)phenyl]-2-methoxyiminoacetate

To a 100 ml round bottom flask equipped with magnetic stirrer were charged 1.0 g (0.0044 moles) of the trans-1-(2,6 dichlorophenyl)-2-acetyl-cyclopropane, 1.1 g (0.0044 moles) of the methyl (E)-2-(aminooxymethyl)phenyl glyoxylate O-methyloxime, and 50 mls of anhydrous methanol. The reaction was stirred overnight at room temperature. Analysis of an aliquot by GC indicated no starting material and two new products. The reaction was then poured into 100 mls of water and extracted with 3 x 50 ml of ethyl ether. The ether extract was washed with 100 mls of water, 100 mls of 0.1N HCl, and 100mls of brine, dried over anhydrous magnesium sulfate, filtered, and concentrated *in vacuo* on a rotary evaporator to afford 2.0g of a thick yellow oil which was chromatographed on silica with 20 % ethyl acetate/ 80% hexane. The pure fractions were combined and concentrated *in vacuo* on a rotary evaporator to afford 1.4 g of the methyl 2-[2-((trans-1-(2-(2',6'-dichlorophenyl)cyclopropyl)-ethylidene)aminooxymethyl)phenyl]-2-methoxyiminoacetate as a pale yellow oil as a 90/10 A:B (E,E:E,Z) isomer ratio in 72% isolated yield.

NMR 300 MHz  $^1\text{H}$   $\text{CDCl}_3$  1.3 (m, 1H); 1.7 (m, 1H); 1.85 (s, 3H); 1.95 (m, 1H); 2.2 (m, 1H); 3.85 (s, 3H), 4.1 (s, 3H); 5.0 (s, 2H); 7.1 (m, 1H), 7.2 (m, 1H); 7.3 (d, 2H); 7.4-7.6 (m, 3H).

An additional 10.0g of the crude product as an orange oil (85% chemically pure and 2:1 A:B isomers) was chromatographed on silica with 20 % ethyl acetate/ 80% hexane. 5.02 grams of isomer A as a pale yellow oil was collected (E:E)- methyl 2-[2-((trans-1-(2-(2',6'-dichlorophenyl)cyclopropyl)ethylidene)-aminooxymethyl)phenyl]-2-methoxyiminoacetate. Compound 6A, Isomer A, E imine, NMR (300MHz.,  $^1\text{H}$   $\text{CDCl}_3$ ): 1.19-1.30 (1H, m), 1.50-1.58 (1H, m), 1.75-1.85 (1H, m) 1.84 (3H, s), 2.06-2.14 (1H, m), 3.85 (3H, s), 4.05 (3H, s), 4.98 (2H, s), 7.03-7.49 (7H, m). 0.825 grams of isomer B as a pale yellow oil was collected (E:Z)-methyl 2-[2-((trans-1-(2-(2',6'-dichlorophenyl)cyclopropyl)ethylidene)-aminooxymethyl)phenyl]-2-methoxyiminoacetate. Compound 8.16B, Isomer B, Z imine, NMR (300MHz.,  $^1\text{H}$   $\text{CDCl}_3$ ): 1.21-1.28 (1H, m), 1.40-1.52 (1H, m), 1.70 (3H, s), 2.18-2.23 (1H, m) 2.61-2.70 (1H, m), 3.80 (3H, s), 4.00 (3H, s), 4.97 (2H, s), 7.05-7.52 (7H, m).

Preparation of methyl (E)-2-(aminooxymethyl)phenyl glyoxylate O-methyloxime  
Methyl (E)-2-(O-phthalimidoxymethyl)phenyl glyoxylate O-methyloxime

To a dry 500 ml round bottom flask equipped with magnetic stirrer, and nitrogen inlet were charged 5.1 g (0.0315 moles) of N-hydroxyphthalimide, 1.3 g (0.0315 moles) of sodium hydroxide, and 300 ml of anhydrous dimethylformamide. The dark red solution was stirred at ambient temperature for 20 min., followed by the addition of the methyl 2-(bromomethyl)-phenylglyoxylate-O-methyloxime (15 g, 60% pure, 0.0315 moles) in one portion. The reaction was stirred at ambient temperature over the weekend, then poured into 800 mls of water and stirred for 1 hour to afford a white solid which was collected by vacuum filtration and washed with water, hexane, and dried under vacuum at 40°C overnight. Isolated 11.5g of a white solid (98% isolated yield) which was consistent with the desired product, methyl (E)-2-(O-phthalimidoxymethyl)phenyl glyoxylate O-methyloxime, upon analysis by 300 MHz  $^1\text{H}$  NMR (300 MHz,  $^1\text{H}$ ,  $\text{CDCl}_3$ , TMS=0 ppm) 3.8 (s, 3H), 3.95 (s, 3H), 5.0 (s, 2H), 7.1 (d, 1H), 7.5 (m, 2H), 7.7-7.9 (m, 5H).

Preparation of methyl (E)-2-(aminooxymethyl)phenyl glyoxylate O-methyloxime.

To a 250ml round-bottom flask equipped with magnetic stirrer were charged 11.4 g (0.031 moles) of methyl (E)-2-(O-phthalimidoxymethyl)phenyl glyoxylate O-methyloxime 100 mls of anhydrous methanol, and 1.9 g (0.034 moles) of hydrazine monohydrate. The flask was stoppered, and the reaction was stirred at ambient temperature for 2 hours. The resulting solid was removed by filtration and the filtrate was concentrated on the rotary evaporator. The residue was dissolved in 100 mls of ether, filtered, and stripped to afford 7.4 g of a thick yellow oil (100% isolated yield). which was consistent with the desired product methyl (E)-2-(aminooxymethyl)phenyl glyoxylate O-methyloxime upon analysis by 300 MHz <sup>1</sup>H NMR. Stored at -20°C until needed for future synthesis.

NMR (300 MHz, 1H, CDCl<sub>3</sub>, TMS=0 ppm) 3.87 (s, 3H), 4.03 (s, 3H), 4.6 (s, 2H), 4.9-5.4 (bs, 2H), 7.2 (m, 1H), 7.4-7.5 (m, 3H).

**Example 2**

Preparation of E and Z imine isomers: (E,E) and (Z,E)-N-Methyl 2-[2-((trans-1-(2-(2',6'-dichlorophenyl)cyclopropyl)ethylidene)aminooxymethyl)phenyl]-2-methoxyiminoacetamide Compounds 9.16, 9.16A, 9.16B of Table 9.

To a 100 ml flask equipped with magnetic stirrer and were charged 0.7 g (0.00115 moles) of (E,E:Z,E)-methyl 2-[2-((trans-1-(2-(2',6'-dichlorophenyl)cyclopropyl) ethylidene)aminooxymethyl)phenyl]-2-methoxyiminoacetate, 50 mls of methanol, and 2 mls (0.026 moles) of 40% aqueous methyl amine solution. The mixture stirred at ambient temperature overnight. then poured into 200 mls of water and extracted with 3 x 100 ml of ethyl ether. The ether extract was washed with 2 x 100 mls of water, 100 mls of 0.1 N HCl, and 100mls of brine, dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated *in vacuo* on a rotary evaporator to afford 0.6g of N-Methyl 2-[2-((trans-1-(2-(2',6'-dichlorophenyl)cyclopropyl)ethylidene)aminooxymethyl)-phenyl]-2-methoxyiminoacetamide as a thick viscous pale yellow oil. 90/10 A:B (E,E:Z,E) isomers ratio in 88% isolated yield.

NMR 300 MHz,  $^1\text{H}$   $\text{CDCl}_3$  1.2 (m, 1H); 1.6 (m, 1H); 1.8 (s, 3H); 1.9 (m, 1H); 2.2 (m, 1H); 2.9 (d, 3H); 3.95 (s, 3H), 5.0 (s, 2H); 6.7 (bs, 1H); 7.1 (m, 1H), 7.2 (m, 1H); 7.3 (d, 2H); 7.4-7.6 (m, 3H).

Additionally each of 8.16A and 8.16B oxime esters was separately treated as above with methylamine.

Aminolysis of 5.01 grams of 8.16A (E,E isomer) gave 5.02 grams (100% yield) of (E,E)-N-methyl 2-[2-((trans-1-(2-(2',6'-dichlorophenyl)cyclopropyl)ethylidene)aminooxymethyl)phenyl]-2-methoxyiminoacetamide as an oil. The oil was treated with ether, concentrated and cooled in dry ice followed by the addition of hexane to complete the crystallization. The resulting crystals were filtered to give a solid mpt. 94-97°C. Compound 9.16A, Isomer A, E,E isomer, NMR (300MHz,  $^1\text{H}$   $\text{CDCl}_3$ ): 1.20-1.30 (1H, m), 1.51-1.58 (1H, m), 1.80-1.89 (1H, m), 1.82 (3H, s), 2.2 (1H, m), 2.89 (3H, d), 3.96 (3H, s), 4.98 (2H, s), 6.70 (1H, br), 7.05-7.48 (7H, m).

Aminolysis of 0.825grams of 8.16B (Z,E isomer) gave 0.825 grams (100% yield) of (Z,E)-N-methyl 2-[2-((trans-1-(2-(2',6'-dichlorophenyl)cyclopropyl)ethylidene)aminooxymethyl)phenyl]-2-methoxyiminoacetamide as solid, mpt. 140-146°C. Compound 9.16B, Isomer B, Z,E isomer, NMR (300MHz,  $^1\text{H}$   $\text{CDCl}_3$ ): 1.22-1.30 (1H, m), 1.40-1.51 (1H, m), 1.70 (3H, s), 2.15-2.23 (1H, m), 2.60-2.69 (1H, m), 2.85 (3H, d), 3.90 (3H, s), 4.97 (2H, s), 6.70 (1H, br), 7.09-7.51 (7H, m).

### Example 3

Preparation of E and Z imine isomers: (E,E) and (Z,E) Methyl 2-[2-((trans-1-(2-(2',6'-difluorophenyl)cyclopropyl)ethylidene)aminooxymethyl)phenyl]-2-methoxyiminoacetate Compound 8.22 of Table 8

### Preparation of 4-(2,6-difluorophenyl)-3-buten-2-one

To a 100ml reaction bottle equipped with magnetic stir bar were charged 5.0g (35.2mmole) 2,6-difluorobenzaldehyde in 20 ml acetone, added 50% NaOH (42 mmole) in 60ml water (exothermic) and stirred room temperature. The reaction was monitored by GLC and after 2 hours worked up. The reaction mixture was extracted with 50ml  $\text{CHCl}_3$ , washed with 50ml  $\text{H}_2\text{O}$ , dried over

anhydrous  $\text{MgSO}_4$ , filtered, and removed solvent *in vacuo* on a rotary evaporator to afford 5.7g of 4-(2,6-difluoro-phenyl)-3-buten-2-one as a yellow oil (81% purity by GC) in 89.5% isolated yield.

NMR (300 MHz  $^1\text{H}$   $\text{CDCl}_3$ ): 2.4 (s, 3H); 6.9 (m, 3H); 7.3 (m, 1H); 7.6 (d, 1H).

Preparation of trans-1-(2,6 difluorophenyl)-2-acetyl-cyclopropane

To a 500 ml round bottom flask equipped with magnetic stirrer, nitrogen inlet and addition funnel was charged 2.47 g (11.2 mmoles) of trimethyl sulfoxonium iodide, 0.448g (11.2mmole) of powdered sodium hydroxide, and 50 mls DMSO. The mixture was stirred at room temperature for 0.5 hour, followed by the rapid addition of 2.04g (11.2mmole) 2,6-difluoro-phenyl-3-buten-2-one in 25ml DMSO in one portion. The reaction was stirred for 15 minutes at ambient temperature, poured into 200 mls of ice water, and then extracted with 150 ml of ethyl ether. The ether extract was washed with 4 x 100 mls of water, dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo* on a rotary evaporator to afford 1.3 g crude product as a yellow oil. This was combined with 1.6g from a similar reaction and the total crude of 2.9g was chromatographed on silica with  $\text{CH}_2\text{Cl}_2$ . Fractions (#5-9) were combined and concentrated *in vacuo* on a rotary evaporator to afford 1.5g (92% purity by GC) of trans-1-(2,6 difluorophenyl)-2-acetylcyclopropane as a free flowing pale yellow liquid. in 28.8% yield.

NMR (300 MHz  $^1\text{H}$   $\text{CDCl}_3$ ): 1.6 (m, 2H); 2.3 (s, 3H); 2.4 (m, 2H); 6.8 (m, 2H), 7.1 (m, 1H).

Preparation of E and Z imine isomers: (E,E) and (Z,E) Methyl 2-[2-((trans-1-(2,6'-difluorophenyl)cyclopropyl)ethylidene)aminooxymethyl]phenyl]-2-methoxyiminoacetate

To a 25ml reaction vial equipped with magnetic stirrer were charged 1.0 g (0.0051 moles) of the trans-1-(2,6 difluorophenyl)-2-acetyl-cyclopropane and 1.33 g (0.0056 moles) of the methyl (E)-2-(aminooxymethyl)phenyl glyoxylate O-methyloxime in 5 mls of anhydrous methanol and 5 drops glacial acetic acid. The reaction was stirred 4 hours at room temperature with formation of precipitate. The sample was refrigerated overnight and then worked up. The white precipitate was filtered *in vacuo*, washed with 2 x 10ml hexane, and

dried in the vacuum oven at ambient to afford 1.1g of the methyl 2-[2-((trans-1-(2-(2',6'-difluorophenyl)cyclopropyl)ethylidene)aminoxy-methyl)phenyl]-2-methoxyiminoacetate as a white solid, mpt. 81-88°C, as a 79:21 A:B (E:E,Z:E) isomer ratio in 51.9% isolated yield.

NMR (300 MHz <sup>1</sup>H CDCl<sub>3</sub>): 1.4 (t, 2H); 1.65-1.8 (d, 3H); 2.1 (m, 2H); 3.8 (d, 3H); 4.0 (d, 3H); 5.0 (s, 2H); 6.8 (m, 2H), 7-7.2 (m, 2H); 7.3-7.5 (m, 3H).

#### Example 4

Preparation of E and Z imine isomers: (E,E) and (Z,E)-N-Methyl 2-[2-((trans-1-(2-(2',6'-difluorophenyl)cyclopropyl)ethylidene)aminoxymethyl)phenyl]-2-methoxyiminoacetamide Compounds 9.22A, 9.22B of Table 9.

To a 25ml reaction test tube under nitrogen atmosphere were charged 0.95g of (E,E:Z,E)-methyl 2-[2-((trans-1-(2-(2',6'-difluorophenyl)cyclopropyl)ethylidene)- aminooxymethyl)phenyl]-2-methoxyiminoacetate (2.3mmole) in 7ml MeOH and 1.8g 40% aqueous methyl amine (23mmole) which was heated at 55-60°C. The reaction was monitored by TLC and worked up after 1.5 hours. Removed the methanol *in vacuo* on the rotary evaporator at 30°C. To the residue was added 125ml ethyl acetate and 50ml water, partitioned, further washed the organic phase with 2 x 50ml water, dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated *in vacuo* on the rotary evaporator at 40°C to give 1g of (E,E:Z,E)-N-methyl 2-[2-((trans-1-(2-(2',6'-difluorophenyl)cyclopropyl)ethylidene)aminoxymethyl)phenyl]-2-methoxyiminoacetamide as a 76:24 A:B (E,E:Z,E) isomer ratio. This mixture was chromatographed on silica with 1:2 ethyl acetate:hexane to afford both (E,E) and (Z,E) isomers of the N-methyl 2-[2-((trans-1-(2-(2',6'-difluorophenyl)cyclopropyl)ethylidene)aminoxy-methyl)phenyl]-2-methoxyiminoacetamide. 700mg of isomer-A (E,E) was isolated as a clear oil and 150mg isomer B (Z,E) was isolated also as a pale yellow oil. The chromatographed combined isolated yield was 89.5%. Compound 9.7A, Isomer A, E,E isomer: NMR (300 MHz <sup>1</sup>H CDCl<sub>3</sub>) 1.4 (t, 2H); 1.8 (s, 3H); 2.1 (m, 2H); 2.9 (d, 3H); 3.9 (s, 3H); 4.9 (s, 2H); 6.7 (bs, 1H); 6.8 (t, 2H); 7-7.2 (m, 2H); 7.3-7.5 (m, 3H). Compound 9.7B, Isomer B, Z,E isomer NMR (300 MHz <sup>1</sup>H CDCl<sub>3</sub>) 1.3 (m, 1H); 1.6 (m, 4H); 2.1 (m, 1H); 2.8

(m, 4H); 3.9 (s, 3H); 4.9 (s, 2H); 6.7 (bs, 1H); 6.8 (t, 2H); 7-7.2 (m, 2H); 7.3-7.5 (m, 3H).

#### Example 5.

#### Preparation of Methyl 2-[2-((1-(2-(4'-chlorophenyl)-2-methylcyclopropyl)-ethylidene)aminooxymethyl)phenyl]-2-methoxyiminoacetate

Compound 2.14A of Table 2.

#### Preparation of E and Z enone isomers of 4-(4-chlorophenyl)-3-penten-2-one

To a 500 ml round bottom flask equipped with magnetic stirrer, nitrogen inlet and addition funnel were charged 10g (0.065 moles) of 4'-chloroacetophenone, 10.2g (0.065 moles) of ethyl-trans-3-ethoxycrotonate, and 150 mls of dry dimethylformamide. To this solution was then added 7.3 g (0.065 moles) of potassium t-butoxide in one portion. The reaction was stirred at ambient temperature under nitrogen for a total of three days. The reaction mixture was then poured into 200 mls of water and the aqueous was extracted with 3 x 50 mls of ethyl ether to remove any unreacted starting material. The aqueous fraction was acidified to pH 2 with 1 N aqueous HCl, and extracted with 3 x 100 mls of ethyl ether. The ether extract was washed with 2 x 100 mls of water and 100 mls of saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated on a rotary evaporator to afford 12.4 g of a tan solid. This solid was then stirred in 50 mls of conc. HCl for 2 hours at ambient temperature, then poured into 100 g of crushed ice, and extracted with 3 x 100 ml of ethyl ether. The ether extract was washed with 2 x 100 mls of water, 100mls of brine, dried over anhydrous magnesium sulfate, filtered, and concentrated on a rotary evaporator to afford 7.6 g of a yellow liquid, 4-(4-chlorophenyl)-3-penten-2-one, which appeared to be a mixture of the E and Z enones, with some minor chemical impurities, in 59.3 % crude yield. The product was used in the next step without further purification.

300 MHz <sup>1</sup>H NMR (tms=0 ppm) 2.3 (s, 3H); 2.5 (s, 3H); 6.5 (s, 1H); 7.3-7.5 (m, 4H).

#### Preparation of trans and cis-1-(4-chlorophenyl)-1-methyl-2-acetylcyclopropane

To a 250 ml round bottom flask equipped with magnetic stirrer, nitrogen inlet and addition funnel were charged the trimethyl sulfoxonium iodide (8.5 g, 0.0386 moles), powdered sodium hydroxide (1.6 g, 0.0386 moles) and 100 mls of dry DMSO. The mixture was stirred at room temperature for 1 hour, followed by the rapid addition of the (E > Z)-4-(4-chlorophenyl)-3-penten-2-one (7.5 g, 0.0386 moles) in 10 mls DMSO. The reaction was stirred for 3 days at ambient temperature, then poured into 200 mls of ice water and extracted with 3 x 100 ml of ethyl ether. The ether extract was washed with 2 x 100 mls of water, 100 mls of brine, dried over anhydrous  $\text{MgSO}_4$ , filtered through 2" of silica gel, and concentrated on a rotary evaporator to afford 3.2 g of a thick pale yellow oil which was chromatographed on silica gel with 10 % ethyl acetate, 90% hexane. The pure fractions were combined and concentrated on the rotary evaporator to afford 1.4 g (17.2% isolated yield) of a pale yellow liquid which was consistent with trans and cis-1-(4-chlorophenyl)-1-methyl-2-acetylcyclopropane upon analysis by 300Mz  $^1\text{H}$  NMR.

300 MHz  $^1\text{H}$  NMR (tms=0 ppm) 1.2 (m, 1H); 1.4 (s, 3H); 1.6 (m, 1H); 2.2 (m, 1H); 2.35 (s, 3H); 7.1-7.4 (m, 4H).

Preparation of Methyl 2-[(1-(2-(4'-chlorophenyl)-2-methylcyclopropyl)-ethylidene)aminoxymethyl]phenyl]-2-methoxviminoacetate

To a 20 ml glass vial equipped with magnetic stirrer were charged the 1.0 g (0.0048 moles) of the trans and cis-1-(4-chlorophenyl)-1-methyl-2-acetylcyclopropane, 1.2 g (0.0048 moles) of the methyl (E)-2-(aminooxymethyl)phenyl glyoxylate O-methyloxime, and 10 mls of dry methanol. The vial was capped, and stirred overnight at ambient temperature. The reaction mixture was then poured into 100 mls of water and extracted with 3 x 100 ml of ethyl ether. The ether extract was washed with 2 x 100 mls of water, 100 mls of 1 N HCl, and 100 mls of saturated sodium chloride solution, dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated on a rotary evaporator to afford 1.6 g of a thick orange oil which was chromatographed on silica gel with 20% ethyl acetate, 80% hexane. The pure fractions after chromatography were combined and concentrated on a rotary evaporator to afford 0.75 g of a clear colorless

viscous oil (36.5% isolated yield) which was consistent with isomer A, (E,E)-methyl 2-[2-((1-(2-(4'-chlorophenyl)-2-methylcyclopropyl)ethylidene)aminooxymethyl)phenyl]-2-methoxyiminoacetate upon analysis by 300 MHz  $^1\text{H}$  NMR with a 70:30 ratio of cyclopropane isomers.

300 MHz  $^1\text{H}$  NMR (tms=0 ppm) 1.15 (s, 3H) 1.2 (m, 1H); 1.4 (m, 1H); 1.6 (m, 1H); 2.0 (s, 3H); 3.85 (s, 3H); 4.0 (s, 3H); 5.0 (s, 2H); 7.1-7.3 (m, 5H); 7.35-7.6 (m, 3H)

#### Example 6

#### Preparation of (E,E)-N-Methyl 2-[2-((1-(2-(4'-chlorophenyl)-2-methylcyclopropyl)ethylidene)aminooxymethyl)phenyl]-2-methoxyiminoacetamide

Compound 3.14A of Table 3.

To a 100 ml round bottom flask equipped with magnetic stirrer were charged 0.7 g (0.00163 moles) of the (E,E)-methyl 2-[2-((1-(2-(4'-dichlorophenyl)-2-methylcyclopropyl)ethylidene)aminooxymethyl)phenyl]-2-methoxyiminoacetate, 25mls of anhydrous methanol, and 1 ml (0.0129 moles) of 40% methyl amine in water. The flask was stoppered, and stirred overnight at ambient temperature. The reaction mixture was then poured into 100 mls of water and extracted with 3 x 50 ml of ethyl ether. The ether extract was washed with 2 x 50 mls of water, 50 mls of 1 N HCl, 50mls of saturated sodium chloride solution, dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated on a rotary evaporator to afford 0.7 g of a yellow viscous oil which was chromatographed on silica gel with 20% ethyl acetate, 80% hexane. The pure fractions were combined and concentrated on a rotary evaporator to afford 0.55 g of a clear colorless viscous oil (79% isolated yield) which was consistent with isomer A (E,E)-N-methyl 2-[2-((1-(2-(4'-chlorophenyl)-2-methylcyclopropyl)ethylidene)aminooxymethyl)phenyl]-2-methoxyiminoacetamide upon analysis by 300Mz  $^1\text{H}$  NMR and as 70:30 mixture of cyclopropane isomers

300 MHz  $^1\text{H}$  NMR (tms=0 ppm) 1.15 (s, 3H) 1.2 (m, 1H); 1.4 (m, 1H); 1.65 (m, 1H); 2.0 (s, 3H); 2.9 (d, 3H); 4.0 (s, 3H); 5.0 (s, 2H); 6.8 (bs, 1H); 7.1-7.3 (m, 5H); 7.35-7.6 (m, 3H).

#### Example 7

Preparation of Methyl 2-[2-((trans-1-(2-phenyl-2-methylcyclopropyl)ethylidene)aminooxymethyl)phenyl]-2-methoxyiminoacetate

Compound 2.11 of Table 2.

To a 25ml reaction vial equipped with magnetic stirrer were charged 217mg (1.25 mmole) of the trans-1-phenyl-1-methyl-2-acetylcyclopropane and 298 mg (1.25 mmole) of the methyl (E)-2-(aminooxymethyl)phenyl glyoxylate O-methyloxime in 5 ml of anhydrous methanol and 1 drop glacial acetic acid. The reaction was monitored by GC and after 3 hours 90mg more of the methyl 2-(bromomethyl)phenyl glyoxylate O-methyloxime was added and 5 drops of glacial acetic acid. After stirring 20 hours no more starting material ketone remained and the reaction was worked up. The methanol was removed *in vacuo* on the rotary evaporator. To the residue was added 100ml ethyl acetate and 50ml water, partitioned, further washed the organic phase with 3 x 50ml water, dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated *in vacuo* on the rotary evaporator to give 0.6g of yellow oil with solid which was chromatographed on silica with 30:70 ethyl acetate:hexane. The pure fractions were combined to afford 260mg of a clear oil (isolated yield 52.8%) whose NMR was consistent with methyl 2-[2-((trans-1-(2-phenyl-2-methylcyclopropyl)ethylidene)aminooxymethyl)phenyl]-2-methoxyiminoacetate as a mixture of isomers, A>B.

NMR (300 MHz <sup>1</sup>H CDCl<sub>3</sub>): 1.1-1.4 (m, 5H); 1.75 (m, 1H); 2.0 (s, 3H); 3.85 (s, 3H); 4.05 (s, 3H); 5.0 (s, 2H); 7.1-7.5 (m, 9H).

Example 8

Preparation of (E,E and Z,E)-N-Methyl 2-[2-((trans-1-(2-phenyl-2-methylcyclopropyl)ethylidene)aminooxymethyl)phenyl]-2-methoxyiminoacetamide

Compound 3.11 of Table 3.

To a 25ml reaction test tube under nitrogen atmosphere were charged 160 mg of the methyl 2-[2-((trans-1-(2-phenyl-2-methylcyclopropyl)ethylidene)aminooxy-methyl)phenyl]-2-methoxyiminoacetate (0.41 mmole) in 3ml MeOH and 315 mg 40% aqueous methyl amine (4.1 mmole) which was heated at 55-60C. Monitored by TLC and worked up after 1.5 hours.

Removed the methanol *in vacuo* on the rotary evaporator at 30C. To the residue was added 125ml ethyl acetate and 50ml water, partitioned, further washed the organic phase with 2 x 50ml water, dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated *in vacuo* on the rotary evaporator at 40C to afford 130 mg (isolated yield 80.7%) of (E,E and Z,E)-N-methyl 2-[2-((trans-1-(2-phenyl-2-methyl-cyclopropyl)ethylidene)aminooxymethyl)phenyl]-2-methoxyiminoacetamide as a clear oil in a 4:1 ratio of isomers A to B (E,E:Z,E). NMR (300 MHz <sup>1</sup>H CDCl<sub>3</sub>): 1.1-1.4 (m, 5H); 1.75 (m, 1H); 1.95 (s, 3H); 2.9 (d, 3H); 3.95 (s, 3H); 5.0 (s, 2H); 6.7 (bs, 1H); 7.1-7.5 (m, 9H).

Proton NMR data (300MHz) are provided in Table 13 for typical examples of Tables 1 to 12 and are illustrative of the present invention\*

Table 13

| Compd | NMR DATA                                                                                                                              |
|-------|---------------------------------------------------------------------------------------------------------------------------------------|
| 2.11  | 1.1-1.4 (m, 5H); 1.75 (m, 1H); 2.0 (s, 3H); 3.85 (s, 3H); 4.05 (s, 3H); 5.0 (s, 2H); 7.1-7.5(m,9H).                                   |
| 2.12  | 1.1(m, 1H); 1.2(s, 3H); 1.4(m, 1H); 1.7(m, 1H); 2.1(s, 3H); 3.86(s, 3H); 4.05(s, 3H); 5.0(s, 2H); 7.0-7.6(m, 8H)                      |
| 2.14A | 1.15(s,3H), 1.2(m,1H), 1.4(m,1H); 1.6 (m, 1H); 2.0(s, 3H); 3.85 (s, 3H); 4.0 (s, 3H); 5.0 (s, 2H); 7.1-7.3 (m, 5H); 7.35-7.6 (m, 3H). |
| 2.17  | 1.1(m, 1H); 1.2(s, 3H); 1.4(m, 1H); 1.8(m, 1H); 2.0(s, 3H); 3.85(s, 3H); 4.05(s, 3H); 5.0(s, 2H); 7.1-7.5(m, 8H)                      |
| 2.18A | 1.05(m, 1H); 1.15(s, 3H); 1.3(m, 1H); 1.7(m, 1H); 2.05(s, 3H); 3.86(s, 3H);4.05(s, 3H); 4.99(s, 2H); 6.9-7.5(m, 8H).                  |
| 2.20  | 1.1(m, 1H); 1.2(s, 3H); 1.35(m, 1H); 1.8(m, 1H); 2.0(s, 3H); 3.85(s, 3H); 4.05(s, 3H); 5.0(s, 2H); 7.0(t, 2H); 7.1-7.4(m, 6H).        |
| 2.20B | 0.95(m, 1H); 1.2(s, 3H); 1.85(s, 3H); 1.9-2.1(m, 2H); 3.75(s, 3H); 3.95(s, 3H); 5.0(s, 2H); 6.9(t, 2H); 7.1-7.5(m, 6H).               |
| 2.34  | 1.1(m, 1H); 1.15(s, 3H); 1.4(m, 1H); 1.7(m, 1H); 2.07(s, 3H); 3.87(s, 3H); 4.05(s, 3H); 4.98(s, 2H); 7.1-7.5(m, 7H).                  |
| 2.166 | 0.8(m, 3H); 1.1(m, 1H); 1.2(m, 2H); 1.4(m, 1H); 1.8(m, 1H); 2.05(s, 3H); 3.85(s, 3H); 4.05(s, 3H); 5.0(s, 2H); 7.1-7.4(m, 9H).        |
| 2.170 | 0.69(t, 3H); 1.05(m, 1H); 1.3(m, 2H); 1.5-1.7(m, 2H); 2.02(s, 3H); 3.87(s, 3H); 4.05(s, 3H); 4.98(s, 2H); 6.9-7.5(m, 8H)              |
| 2.178 | 0.85(m, 3H); 1.1-1.4(m, 4H); 1.6(m, 3H); 2.0(s, 3H); 3.85(s, 3H); 4.05(s, 3H); 5.0(s, 2H); 7.1-7.4(m, 9H).                            |
| 2.189 | 0.8(d, 6H); 0.95(s, 4H); 1.25(s, 4H); 1.35(m, 1H); 1.9(m, 1H); 3.8(s, 3H); 4.0(s, 3H); 4.9(q, 2H); 7.1-7.4(m, 9H).                    |
| 2.217 | 1.05(m, 1H); 1.15(s, 3H); 1.4(m, 1H); 1.7(m, 1H); 2.07(s, 3H); 3.86(s, 3H); 4.05(s, 3H); 4.98(s, 2H); 6.9-7.6(m, 7H).                 |
| 3.11  | 1.1-1.4 (m, 5H); 1.75 (m, 1H); 1.95 (s, 3H); 2.9 (d, 3H); 3.95 (s, 3H); 5.0                                                           |

|        |                                                                                                                                                                                |
|--------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|        | (s, 2H); 6.7 (bs, 1H); 7.1-7.5 (m, 9H).                                                                                                                                        |
| 3.12A  | 1.1(m, 1H); 1.18(s, 3H); 1.4(m, 1H); 1.7(m, 1H); 2.1(s, 3H); 2.91(d, 3H); 3.96(s, 3H); 5.0(s, 2H); 6.75(b, 1H); 7.1-7.5(m, 8H)                                                 |
| 3.14A  | 1.15 (s, 3H) 1.2 (m, 1H); 1.4 (m, 1H); 1.65 (m, 1H); 2.0(s, 3H); 2.9 (d, 3H); 4.0 (s, 3H); 5.0 (s, 2H); 6.8 (bs, 1H); 7.1-7.3 (m, 5H); 7.35-7.6 (m, 3H).                       |
| 3.17   | 1.1(m, 1H); 1.2(s, 3H); 1.3(m, 1H); 1.7(m, 1H); 2.0(s, 3H); 2.9(d, 3H); 4.0(s, 3H); 5.0(s, 2H); 6.8(bs, 1H); 7.1-7.5(m, 8H).                                                   |
| 3.18A  | 1.1(m, 1H); 1.15(s, 3H); 1.35(m, 1H); 1.7(m, 1H); 2.05(s, 3H); 2.91(d, 3H); 3.96(s, 3H); 4.99(s, 2H); 6.75(b, 1H); 6.9-7.5(m, 8H).                                             |
| 3.20   | 1.1(m, 1H); 1.2(s, 3H); 1.3(m, 1H); 1.7(m, 1H); 2.0(s, 3H); 2.95(d, 3H); 4.0(s, 3H); 5.0(s, 2H); 6.8(bs, 1H); 7.0(t, 2H); 7.1-7.5(m, 6H).                                      |
| 3.20B  | 0.95(m, 1H); 1.2(s, 3H); 1.9(s, 3H); 2.0-2.2(m, 2H); 2.85(d, 3H); 3.9(s, 3H); 5.0(s, 2H); 6.8(bs, 1H); 6.9(t, 2H); 7.1-7.5(m, 6H)                                              |
| 3.34A  | 1.0(m, 1H); 1.15(s, 3H); 1.4(m, 1H); 1.7(m, 1H); 2.07(s, 3H); 2.91(d, 3H); 3.96(s, 3H); 4.98(s, 2H); 6.75(b, 1H); 7.1-7.5(m, 7H)                                               |
| 3.40A  | 1.05(m, 1H); 1.12(s, 3H); 1.3(m, 1H); 1.65(m, 1H); 2.03(s, 3H); 2.91(d, 3H); 3.96(s, 3H); 4.98(s, 2H); 6.77(m, 3H); 7.1-7.5(m, 5H)                                             |
| 3.166  | 0.8(m, 3H); 1.1(m, 1H); 1.2(m, 2H); 1.4-1.7(m, 2H); 2.1(s, 3H); 2.85(d, 3H); 4.1(s, 3H); 5.0(s, 2H); 6.8(bs, 1H); 7.1-7.4(m, 9H)                                               |
| 3.170A | 0.69(t, 3H); 1.05(m, 1H); 1.25(m, 2H); 1.5-1.7(m, 2H); 2.02(s, 3H); 2.91(d, 3H); 3.96(s, 3H); 4.98(s, 2H); 6.75(b, 1H); 6.9-7.5(m, 8H)                                         |
| 3.178  | 0.85(m, 3H); 1.1-1.4(m, 4H); 1.6(m, 3H); 2.05(s, 3H); 2.95(d, 3H); 4.0(s, 3H); 5.0(s, 2H); 6.8(bs, 1H); 7.1-7.4(m, 9H)                                                         |
| 3.189  | 0.8(d, 6H); 1.0(s, 4H); 1.2(s, 4H); 1.3(m, 1H); 1.9(m, 1H); 2.9(d, 3H); 4.0(s, 3H); 4.85(q, 2H); 6.8(bs 1H); 7.1-7.4(m, 9H)                                                    |
| 3.217A | 1.05(m, 1H); 1.15(s, 3H); 1.4(m, 1H); 1.7(m, 1H); 2.07(s, 3H); 2.91(d, 3H); 3.96(s, 3H); 4.98(s, 2H); 6.75(b, 1H); 6.9-7.6(m, 7H)                                              |
| 8.16   | 1.3 (m, 1H); 1.7 (m, 1H); 1.85 (s, 3H); 1.95 (m, 1H); 2.2 (m, 1H); 3.85 (s, 3H), 4.1 (s, 3H); 5.0 (s, 2H); 7.1 (m, 1H), 7.2 (m, 1H); 7.3 (d, 2H); 7.4-7.6 (m, 3H).             |
| 8.16A  | 1.19-1.30 (1H, m), 1.50-1.58 (1H, m), 1.75-1.85 (1H, m) 1.84 (3H, s), 2.06-2.14 (1H, m), 3.85 (3H, s), 4.05 (3H, s), 4.98 (2H, s), 7.03-7.49 (7H, m).                          |
| 8.16B  | 1.21-1.28 (1H, m), 1.40-1.52 (1H, m), 1.70 (3H, s), 2.18-2.23 (1H, m) 2.61-2.70 (1H, m), 3.80 (3H, s), 4.00 (3H, s), 4.97 (2H, s), 7.05-7.52 (7H, m).                          |
| 8.22   | 1.4 (t, 2H); 1.65-1.8 (d, 3H); 2.1 (m, 2H); 3.8 (d, 3H); 4.0 (d, 3H); 5.0 (s, 2H); 6.8 (m, 2H), 7-7.2 (m, 2H); 7.3-7.5 (m, 3H).                                                |
| 8.200  | 1.1(m, 1H); 1.2(s, 3H); 1.4(m, 1H); 1.8(m, 1H); 2.1(s, 3H); 3.9(s, 3H); 4.1(s, 3H); 5.0(s, 2H); 7.1-7.6(m, 7H)                                                                 |
| 9.16   | 1.2 (m, 1H); 1.6 (m, 1H); 1.8 (s, 3H); 1.9 (m, 1H); 2.2 (m, 1H); 2.9 (d, 3H); 3.95 (s, 3H), 5.0 (s, 2H); 6.7 (bs, 1H); 7.1 (m, 1H), 7.2 (m, 1H); 7.3 (d, 2H); 7.4-7.6 (m, 3H). |
| 9.16A  | 1.20-1.30 (1H, m), 1.51-1.58 (1H, m), 1.80-1.89 (1H, m), 1.82 (3H, s), 2.2 (1H, m), 2.89 (3H, d), 3.96 (3H, s), 4.98 (2H, s), 6.70 (1H, br), 7.05-                             |

|       |                                                                                                                                                                       |
|-------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|       | 7.48 (7H, m).                                                                                                                                                         |
| 9.16B | 1.22-1.30 (1H, m), 1.40-1.51 (1H, m), 1.70 (3H, s), 2.15-2.23 (1H, m), 2.60-2.69 (1H, m), 2.85 (3H, d), 3.90 (3H, s), 4.97 (2H, s), 6.70 (1H, br), 7.09-7.51 (7H, m). |
| 9.22A | 1.4 (t, 2H); 1.8 (s, 3H); 2.1 (m, 2H); 2.9 (d, 3H); 3.9 (s, 3H); 4.9 (s, 2H); 6.7 (bs, 1H); 6.8 (t, 2H); 7-7.2 (m, 2H); 7.3-7.5 (m, 3H).                              |
| 9.22B | 1.3 (m, 1H); 1.6 (m, 4H); 2.1 (m, 1H); 2.8 (m, 4H); 3.9 (s, 3H); 4.9 (s, 2H); 6.7 (bs, 1H); 6.8 (t, 2H); 7-7.2 (m, 2H); 7.3-7.5 (m, 3H).                              |
| 9.200 | 1.1(m, 1H); 1.2(s, 3H); 1.4(m, 1H); 1.8(m, 1H); 2.1(s, 3H); 2.85(d, 3H); 3.9(s, 3H); 5.0(s, 2H); 6.8(bs, 1H); 7.1-7.5(m, 7H)                                          |

\*NMR data for compounds designated by A or B are data for one single stereoisomer for  $R_2C=N-O$ . Compounds without designation are a mixture of stereoisomers and the data provided is for the major isomer.

### Example 9

Numerous compounds of this invention were tested for fungicidal activity in vivo against the diseases described below. The compounds were dissolved in a 1:1 mixture of acetone and methanol and then diluted with a 2:1:1 mixture of water, acetone and methanol (by volume) to achieve the appropriate concentration. The solution was sprayed onto the plants and allowed to dry for two hours. Then the plants were inoculated with fungal spores. Each test utilized control plants which were sprayed with the appropriate solvent and inoculated. For these protective tests, the plants were inoculated one day after treating the plants with the compounds of this invention. The remainder of the technique of each of the tests is given below along with the results for various compounds described herein by the Compound # against the various fungi at a dose of 150 grams per hectare or 38 grams per hectare. The results are percent disease control as compared to the untreated check wherein one hundred was rated as complete disease control and zero as no disease control. The application of the test fungal spores to the test plants was as follows:

#### Wheat Leaf Rust (WLR)

*Puccinia recondita* (f. sp. *tritici*) was cultured on 7-day old wheat (cultivar Fielder) over a 12-day period in the greenhouse. Spores were collected from the leaves by settling on aluminum foil. The spores were cleaned by sieving through a 250-micron opening screen and stored dry. The dried spores were used within

one month.. A spore suspension was prepared from dry uredia by adding 20 mg (9.5 million spores) per ml of Soltrol oil. The suspension was dispensed into gelatin capsules (0.7 ml capacity) which attach to the oil atomizers. One capsule is used per flat of twenty 2-inch square pots of 7-day old plants, cultivar Fielder. After waiting for at least 15 minutes for the oil to evaporate from the wheat leaves, the plants were placed in a dark mist chamber (18-20°C and 100% relative humidity) for 24 hours. The plants were then placed in the greenhouse and evaluated after 12 days for disease.

#### Wheat Leaf Blotch (SNW)

Cultures of *Septoria nodorum* was maintained on Czapek-Dox V-8 juice agar plates in an incubator at 20°C with alternating periods of 12 hours of light and 12 hours of darkness for 2 weeks. A water suspension of the spores was obtained by shaking the portion of the plate with fungal material in deionized water and filtering through cheesecloth. The spore-containing water suspension was diluted to a spore concentration of  $3.0 \times 10^6$  spores per ml. The inoculum was dispersed by a DeVilbiss atomizer over one-week old Fielder wheat plants which had been previously sprayed with the fungicide compound. The inoculated plants were placed in a humidity cabinet at 20°C with alternating 12 hours of light and 12 hours of darkness for 7 days. The inoculated seedlings were then moved to a controlled environment room at 20°C for 2 days of incubation.

Disease control values were recorded as percent control.

#### Wheat Powdery Mildew (WPM)

*Erysiphe graminis* (f. sp. *tritici*) was cultured on wheat seedlings, cultivar Fielder, in a controlled temperature room at 18°C. Mildew spores were shaken from the culture plants onto 7-day old wheat seedlings which had been previously sprayed with the fungicide compound. The inoculated seedlings were kept in a controlled temperature room at 18°C and subirrigated. The percent disease control was rated 7 days after the inoculation. Disease control values were recorded as percent control.

#### Cucumber Powdery Mildew (CPM)

*Sphaerotheca fulginea* was maintained on cucumber plants, cultivar Bush Champion, in the greenhouse. Inoculum was prepared by placing five to ten

heavily mildewed leaves in a glass jar with 500ml of water containing 1 drop of Tween 80 (polyoxyethylene monooleate) per 100 ml. After shaking the liquid and leaves, the inoculum was filtered through cheese cloth and misted onto the plants with a squirt bottle mister. The spore count was 100,000 spores/ml. The plants were then placed in the greenhouse for infection and incubation. The plants were scored seven days after inoculation. Disease control values were recorded as percent control.

#### Tomato Late Blight (TLB)

Cultures of *Phytophthora infestans* were maintained on green pea-amended agar for two to three weeks. The spores were washed from the agar with water and dispersed with a DeVilbiss atomizer over the leaves of 3-week old Pixie tomato plants which had been previously treated with compound of the present invention. The inoculated plants were placed in a humidity cabinet at 20°C for 24 hours for infection. The plants were then removed to a controlled environment room at 20°C and 90% humidity. The plants were scored for disease control after five days.

#### Grape Downy Mildew (GDM)

*Plasmopara viticola* was maintained. leaves of grape plants, cultivar Delaware, in a controlled temperature chamber at 20°C in humid air with moderate light intensity for 7 to 8 days. A water suspension of the spores from infested leaves was obtained and the spore concentration was adjusted to about  $3 \times 10^5$  per ml of water. Delaware grape plants were inoculated by spraying the underside of leaves with a De Vilbiss atomizer until small drops were observed on the leaves. The inoculated plants were incubated in a mist chamber for 24 hours at 20°C. The plants were then removed to a controlled environmental room at 20°C. Disease control values were recorded as percent control seven days after inoculation.

#### Rice Blast (RB)

Cultures of *Pyricularia oryzae* were maintained on potato dextrose agar for two to three week. The spores were washed from the agar with water containing 1 drop of Tween 80 per 100ml. After filtering the spore suspension through two layers of cheese cloth, the spore count was adjusted to  $5 \times 10^5$  per

ml of water. The spore suspension was sprayed onto 12-day old rice plants, cultivar M-1, using a DeVilbiss atomizer. The inoculated plants were placed in a humidity at chamber 20°C for 36 hours to allow for infection.. After the infection period the plants were placed in the greenhouse. After 6 days, the plants were scored for disease control. Disease control values were recorded as percent control.

#### Cucumber Downy Mildew (CDM)

The cultures of *Pseudoperonospora cubensis* were maintained on cucumber plants. Leaves showing excellent sporulation were frozen in glass jars at -40°C. After extracting the spores by shaking the leaves in water, the lower surface of the treated cucumber leaves were sprayed with a spore concentration of 100,000 spores per ml of water. The cucumber plants were placed in a Dew Chamber at 20°C for 24 hr. After this infection period, the plants were placed in a growth chamber at 20°C and 90% humidity for 5 days. After severe infection was observed, the leaves were examined for disease development. Disease control values were recorded as percent control.

#### Cucumber Anthracnose (CA)

The fungal pathogen *Colletotrichum lagenarium* was cultured on potato dextrose agar (PDA) in the dark at 22 C for a period of 8 to 14 days. Spores of *C. lagenarium* were removed from the PDA plates by flooding the plate surface with distilled water, amended with 0.5% v/w of yeast extract. The upper surface of the fungal colony was scraped with a blunt instrument until most of the spores were released into the aqueous environment. The spore suspension was filtered through cheesecloth, and the spore count was adjusted by adding more water, containing the yeast extract, until  $3.0 \times 10^6$  spores per ml of water was achieved.

#### Tomato Early Blight (TEB)

Cultures of *Alternaria solani* were grown on V-8 juice agar plates at room temperature under fluorescent lights (12 hr light, 12 hr dark) for 2 weeks. A suspension of the spores was obtained flooding the surface of the agar plate with a 0.5% solution of yeast extract in distilled water. The surface of the agar plate was scraped lightly with a blunt plastic instrument to release the spores into the liquid. The spore suspension was filtered through cheesecloth, and the spore

concentration was adjusted to approximately 80,000 spores per ml. Tomato plants (cv. Patio hybrid) were approximately 18-days old at time of treatment with experimental compounds. Following treatment, the plants were placed in the greenhouse for 1 day. After this period, the plants were inoculated with freshly prepared spore suspension using a DeVilbiss atomizer. The spore suspension was applied to the upper surface of the leaves. After inoculation, the plants were placed in a Dew Chamber at 20°C for 24 hr to allow for infection. The plants were then transferred to a growth chamber at 22°C and 80% humidity for three days. Disease control values were recorded as percent control.

The chemically-treated cucumber plants were 15-days old, cultivar Bush Champion. The upper leaf surface of the plants were sprayed with the spore suspension until runoff, using a hand-held pump spray bottle. The plants were placed in a fluorescent-lighted mist chamber (12 hr light, 12 hr dark) for 48 hours. After that infection period, the plants were placed in a growth chamber for 3 days at 25 C and 90% humidity. The treated plants were then evaluated for disease control. Disease control values were recorded as percent control.

#### Wheat Helminthosporium (HEL)

The fungal pathogen, *Helminthosporium sativum* (also known as *Bipolaris sorokiniana*), was cultured on V8 agar media at room temperature under fluorescent lights (12 hr on, 12 hr off) for a period of two to four weeks. Spores of *H. sativum* were removed from the V8 agar plates by flooding the plate surface with distilled water, amended with 0.5% v/w of yeast extract and 1 drop of Tween-80 per 100 ml. The upper surface of the fungal colonies were rubbed lightly with a plastic instrument until most of the spores were released into the aqueous environment. The spore suspension was filtered through cheesecloth, and the spore count was adjusted by adding additional water containing the yeast extract and Tween-80, until a spore count of 60,000 to 80,000 spores per ml was achieved.

Chemically-treated wheat plants were sprayed with the spore suspension until runoff, using a hand-held pump spray bottle. The plants were placed in a fluorescent-lighted mist chamber for 24 hours. After that infection period, the plants were placed in a growth chamber for 1-2 days at 24 °C with 14 hour

photoperiod and 20 °C at night. The treated plants were then evaluated for disease control. Disease control values were recorded as percent control.

When tested against wheat leaf rust at 150 grams per hectare compounds 2.11, 2.166, 3.11, 3.14A, 3.166, 3.178, 9.16 and 9.22A exhibited 100% control and when tested at 38 grams per hectare compounds 2.12, 2.14A, 2.18A, 2.34, 2.70, 2.217, 3.12A, 3.17, 3.18A, 3.20, 3.34A, 3.40A, 3.70A and 9.200 exhibited 95% or better control.

When tested against wheat leaf blotch at 150 grams per hectare compounds 3.11, 3.14A, 9.16 and 9.22A exhibited 90% or better control and when tested at 38 grams per hectare compounds 2.11, 2.12, 2.17, 2.18A, 2.166, 2.217, 3.12A, 3.17, 3.18A, 3.20, 3.34A, 3.70A, and 3.217A exhibited 90% or better control.

When tested against wheat powdery mildew at 150 grams per hectare compounds 2.11, 2.166, 9.16, and 9.22A exhibited 90% or better control and when tested at 38 grams per hectare compounds 2.18A, 2.20, 2.70, 2.217, 3.20, 3.40A, and 3.217A exhibited 90% or better control.

When tested against cucumber powdery mildew at a dose of 150 grams per hectare compounds 3.11, 3.14A, 8.16, 9.16 and 9.22A exhibited 100% control and when tested at 38 grams per hectare compounds 2.18A, 2.34, 2.217, 3.12, 3.17, 3.18A, 3.20, 3.34A, 3.40A and 3.217A exhibited 99% or better control.

When tested against tomato late blight at 150 grams per hectare compounds 3.11, 3.14A, 8.16, 9.16 and 9.22A exhibited 95% or better control and when tested at 38 grams per hectare compounds 2.14A, 2.17, 2.18A, 2.20, 3.12A, 3.17, 3.18A, 3.20, 3.40A, 3.70A and 3.217A exhibited 95% or better control.

When tested against grape downy mildew at 150 grams per hectare compounds 3.11, 9.16, and 9.22A exhibited 100% control.

When tested against rice blast at 150 grams per hectare compounds 3.11, 3.14A, 8.16, 9.16, and 9.22A exhibited 95% or better control and when tested at 38 grams per hectare compounds 2.12, 2.14A, 2.18A, 2.20, 2.20B, 3.12A, 3.17, 3.18A, 3.20, 3.40A and 3.217A exhibited 90% or better control.

When tested against cucumber downy mildew at 150 grams per hectare compounds 3.11, 3.14A and 9.16 exhibited 95% or better control and when

tested at 38 grams per hectare compounds 2.14A, 2.17, 2.20, 3.17 and 3.20 exhibited 90% or better control and when tested at 9 grams per hectare compound 9.22A exhibited 100% control.

When tested against cucumber anthracnose at 150 grams per hectare compounds compounds 3.11, 3.14A, 9.16 and 9.22A exhibited 100% control and when tested at 38 grams per hectare compounds 2.12, 2.14A, 2.17, 2.18A, 2.20, 2.34, 2.70, 2.166, 2.217, 3.12A, 3.17, 3.18A, 3.20, 3.34A, 3.40A, 3.70A, 3.166, 3.178, 3.217A, 8.16, 8.200 and 9.200 exhibited 95% or better control.

When tested against tomato early blight at 38 grams per hectare compounds compounds 2.14A, 2.17, 2.20, 3.11, 3.14A, 3.17, 3.20, 3.166, 8.16, 9.16 and 9.200 exhibited 95% or better control.

The surprising activity of the compounds of this invention is demonstrated through comparison of these compounds with similarly substituted compounds in tests as described above. The following table provides data for Example compound 9.16 (wherein R<sub>7</sub> is 2,6-dichlorophenyl and R<sub>6</sub> is hydrogen) in a side-by-side compared to a similar compound wherein R<sub>7</sub> is 4-fluorophenyl and R<sub>6</sub> is hydrogen (comparison example 1 - CE-1) and a compound wherein R<sub>7</sub> is 4-chlorophenyl and R<sub>6</sub> is hydrogen (CE-2):

| Compound | Dose<br>g/ha | CA  | CPM | RB | SNW | TEB | WLR | WPM |
|----------|--------------|-----|-----|----|-----|-----|-----|-----|
| 9.16     | 25           | 100 | 100 | 98 | 95  | 95  | 95  | 85  |
| 9.16     | 6            | 99  | 95  | 90 | 95  | 85  | 90  | 0   |
| CE-1     | 25           | 99  | 100 | 95 | 80  | 95  | 95  | 80  |
| CE-1     | 6            | 85  | 80  | 85 | 75  | 95  | 90  | 80  |
| CE-2     | 25           | 90  | 99  | 90 | 95  | 95  | 90  | 50  |
| CE-2     | 6            | 80  | 85  | 85 | 85  | 95  | 85  | 0   |

The following table provides data for Example compound 9.16 (wherein R<sub>7</sub> is 2,6-dichlorophenyl and R<sub>6</sub> is hydrogen) in a different side-by-side test compared to CE-1 and a similar compound wherein R<sub>7</sub> is phenyl and R<sub>6</sub> is hydrogen (CE-3):

| Compound | Dose<br>g/ha | CA | CPM | SNW | TEB | WLR | WPM |
|----------|--------------|----|-----|-----|-----|-----|-----|
| 9.16     | 38           | 99 | 100 | 90  | 100 | 98  | 85  |
| 9.16     | 9            | 98 | 95  | 90  | 95  | 90  | 75  |

|      |     |    |    |    |    |    |    |
|------|-----|----|----|----|----|----|----|
| 9.16 | 2   | 85 | 75 | 80 | 80 | 90 | 50 |
| 9.16 | 0.5 | 0  | 0  | 0  | 75 | 50 | 0  |
| CE-1 | 38  | 75 | 90 | 90 | 85 | 98 | 85 |
| CE-1 | 9   | 75 | 75 | 80 | 90 | 85 | 50 |
| CE-1 | 2   | 0  | 0  | 50 | 0  | 80 | 0  |
| CE-1 | 0.5 | 0  | 0  | 0  | 0  | 50 | 0  |
| CE-3 | 38  | 75 | 50 | 80 | 95 | 85 | 0  |
| CE-3 | 9   | 50 | 0  | 50 | 75 | 80 | 0  |
| CE-3 | 2   | 0  | 0  | 50 | 0  | 50 | 0  |
| CE-3 | 0.5 | 0  | 0  | 0  | 0  | 0  | 0  |

The following table provides data for Example compound 9.16 (wherein R<sub>7</sub> is 2,6-dichlorophenyl and R<sub>6</sub> is hydrogen and) in another side-by-side test compared to CE-2 (R<sub>7</sub> is 4-chlorophenyl and R<sub>6</sub> is hydrogen):

| Compound | Dose<br>g/ha | CA  | CDM | CPM | RB | SNW | TLB | WLR | WPM |
|----------|--------------|-----|-----|-----|----|-----|-----|-----|-----|
| 9.16     | 38           | 100 | 100 | 100 | 98 | 99  | 100 | 99  | 90  |
| 9.16     | 9            | 95  | 99  | 100 | 95 | 95  | 90  | 99  | 85  |
| 9.16     | 2            | 85  | 100 | 80  | 80 | 95  | 80  | 99  | 50  |
| 9.16     | 0.5          | 50  | 75  | 0   | 80 | 90  | 50  | 90  | 0   |
| CE-2     | 38           | 85  | 100 | 100 | 95 | 90  | 100 | 100 | 90  |
| CE-2     | 9            | 75  | 100 | 90  | 85 | 95  | 100 | 99  | 80  |
| CE-2     | 2            | 0   | 100 | 50  | 50 | 80  | 85  | 85  | 50  |
| CE-2     | 0.5          | 0   | 75  | 0   | 0  | 75  | 50  | 75  | 0   |

The following table provides data for Example compound 3.11 (wherein R<sub>6</sub> is methyl and R<sub>7</sub> is phenyl) in a side-by-side test compared to CE-3 (R<sub>6</sub> is hydrogen and R<sub>7</sub> is phenyl):

| Compound | Dose<br>g/ha | CA | CPM | HEL | SNW | TEB | WLR | WPM |
|----------|--------------|----|-----|-----|-----|-----|-----|-----|
| 3.11     | 150          | -  | 95  | 80  | 99  | 100 | 98  | 85  |
| 3.11     | 38           | 99 | 85  | 80  | 95  | 100 | 99  | 75  |
| 3.11     | 9            | 98 | 75  | 0   | 85  | 90  | 95  | 50  |
| 3.11     | 2            | 90 | 0   | 0   | 80  | 80  | 85  | 0   |
| 3.11     | 0.5          | 0  | 0   | 0   | 50  | 0   | 75  | 0   |
| CE-3     | 150          | 85 | 85  | 50  | 85  | 100 | 98  | 75  |
| CE-3     | 38           | 75 | 50  | 0   | 80  | 95  | 85  | 0   |
| CE-3     | 9            | 50 | 0   | 0   | 50  | 75  | 80  | 0   |
| CE-3     | 2            | 0  | 0   | 0   | 50  | 0   | 50  | 0   |
| CE-3     | 0.5          | 0  | 0   | 0   | 0   | 0   | 0   | 0   |

The following table provides data for Example compound 3.20 (wherein R<sub>6</sub> is methyl and R<sub>7</sub> is 4-fluorophenyl) in a side-by-side test compared to CE-1 (wherein R<sub>6</sub> is hydrogen and R<sub>7</sub> is 4-fluorophenyl):

| Compound | Dose<br>g/ha | CA | CPM | HEL | SNW | TEB | WLR | WPM |
|----------|--------------|----|-----|-----|-----|-----|-----|-----|
| 3.20     | 150          | 99 | 100 | 85  | 99  | 95  | 100 | 90  |
| 3.20     | 38           | 98 | 90  | 80  | 99  | 95  | 100 | 85  |
| 3.20     | 9            | 99 | 80  | 80  | 95  | 100 | 99  | 80  |
| 3.20     | 2            | 75 | 50  | 75  | 90  | 80  | 90  | 75  |
| 3.20     | 0.5          | 0  | 0   | 0   | 80  | 0   | 80  | 0   |
| CE-1     | 150          | 95 | 100 | 75  | /P  | 90  | 98  | 85  |
| CE-1     | 38           | 75 | 90  | 50  | 90  | 85  | 98  | 85  |
| CE-1     | 9            | 75 | 75  | 0   | 80  | 90  | 85  | 50  |
| CE-1     | 2            | 0  | 0   | 0   | 50  | 0   | 80  | 0   |
| CE-1     | 0.5          | 0  | 0   | 0   | 0   | 0   | 50  | 0   |

The compounds of this invention are useful as agricultural fungicides and, as such, can be applied to various loci such as the seed, the soil or the foliage of plants to be protected.

The compounds of this invention can be applied as fungicidal sprays by methods commonly employed, such as conventional high-volume hydraulic sprays, low-volume sprays, air-blast spray, aerial sprays and dusts. The dilution and rate of application will depend upon the type of equipment employed, the method of application, plants to be treated and diseases to be controlled. Generally, the compounds of this invention will be applied in amount of from about 0.005 kilogram to about 50 kilograms per hectare and preferably from about 0.025 to about 25 kilograms per hectare of the active ingredient.

As a seed protectant, the amount of toxicant coated on the seed is usually at a dosage rate of from about 0.05 to about 20, preferably from about 0.05 to about 4, and more preferably from about 0.1 to about 1 grams per hundred kilograms of seed. As a soil fungicide the chemical can be incorporated in the soil or applied to the surface usually at a rate of from about 0.02 to about 20, preferably from about 0.05 to about 10, and more preferably from about 0.1 to about 5 kilograms per hectare. As a foliar fungicide, the toxicant is usually applied to growing plants at a rate of from about 0.01 to about 10, preferably

from about 0.02 to 5, and more preferably from about 0.25 to about 1 kilograms per hectare.

Inasmuch as the compounds of this invention display fungicidal activity, these compounds can be combined with other known fungicides to provide broad spectrum activity. Suitable fungicides include, but are not limited to, those compounds listed in U.S. Patent Number 5,252,594 (see in particular columns 14 and 15). Other known fungicides which can be combined with the compounds of this invention are dimethomorph, cymoxanil, thifluzamide, furalaxyl, ofurace, benalaxyl, oxadixyl, propamocarb, cyprofuram, fenpiclonil, fludioxonil, pyrimethanil, cyprodinil, triticonazole, fluquinconazole, metconazole, spiroxamine, carpropamid, azoxystrobin, kresoxim-methyl, metominostrobin and trifloxystrobin.

The compounds of this invention can be advantageously employed in various ways. Since these compounds possess broad spectrum fungicidal activity, they can be employed in the storage of cereal grain. These compounds can also be employed as fungicides in cereals including wheat, barley and rye, in rice, peanuts, beans and grapes, on turf, in fruit, nut and vegetable orchards, and for golf course applications.

Examples of diseases against which the compounds of the invention are useful include helminthosporium of corn and barley, wheat and barley powdery mildew, wheat leaf and stem rusts, barley stripe and leaf rust, tomato early blight, tomato late blight, peanut early leaf spot, grape powdery mildew, grape black rot, apple scab, apple powdery mildew, cucumber powdery mildew, brown rot of fruits, botrytis, bean powdery mildew, cucumber anthracnose, wheat septoria nodorum, rice sheath blight and rice blast

Compositions and formulations according to the present invention may also include known pesticidal compounds. This expands the spectrum of activity of the preparation and may give rise to synergism. Suitable insecticides known in the art include those listed in U.S. Patent 5,075,471, see in particular columns 14 and 15.

The compounds of the present invention can be used in the form of compositions or formulations. Examples of the preparation of compositions and

formulations can be found in the American Chemical Society publication "Pesticidal Formulation Research," (1969), Advances in Chemistry Series No. 86, written by Wade Van Valkenburg; and the Marcel Dekker, Inc. publication "Pesticide Formulations", (1973) edited by Wade Van Valkenburg. In these compositions and formulations, the active substance is mixed with conventional inert agronomically acceptable (i.e., plant compatible and/or pesticidally inert) pesticide diluents or extenders such as solid carrier material or liquid carrier material, of the type usable in conventional pesticide compositions or formulations. By "agronomically acceptable carrier" is meant any substance which can be used to dissolve, disperse or diffuse the active ingredient in the composition without impairing the active ingredient's effectiveness and which by itself has no significant detrimental effect on the soil, equipment, desirable plants, or agronomic environment. If desired, adjuvants such as surfactants, stabilizers, antifoam agents and anti-drift agents may also be combined.

Examples of compositions and formulations according to the invention are aqueous solutions and dispersions, oily solutions and oil dispersions, pastes, dusting powders, wettable powders, emulsifiable concentrates, flowables, granules, baits, invert emulsions, aerosol compositions and fumigating candles. Wettable powders, pastes, flowables and emulsifiable concentrates are concentrated preparations which are diluted with water before or during use. In such formulations, the compounds are extended with a liquid or solid carrier and, when desired, suitable surfactants are incorporated. Baits are preparations generally comprising a food or other substance attractive to insects, that includes at least one compound of the instant invention.

It is usually desirable, particularly in the case of foliar spray formulations, to include adjuvants, such as wetting agents, spreading agents, dispersing agents, stickers, adhesive and the like in accordance with agricultural practices. A listing of such adjuvants commonly used in the art, and a discussion of adjuvants, can be found in many references, such as in the John W. McCutcheon, Inc. publication "Detergents and Emulsifiers, Annual."

The active compounds of the present invention may be employed alone or in the form of mixtures with one another and/or with such solid and/or liquid

dispersible carrier vehicles and/or with other known compatible active agents, especially plant protection agents, such as other insecticides, arthropodicides, nematocides, fungicides, bactericides, rodenticides, herbicides, fertilizers, growth-regulating agents, synergists.

In the compositions of the invention, the active compound is present in an amount substantially between about 0.0001 (1:999,999) -99 (99:1) % by weight. For compositions suitable for storage or transportation, the amount of active ingredient is preferably between about 0.5 (1:199) -90 (9:1) % by weight, and more preferably between about 1 (1:99) -75 (3:1) % by weight of the mixture. Compositions suitable for direct application or field application generally contain the active compound in an amount substantially between about 0.0001 (1:999,999) -95 (19:1) %, preferably between about 0.0005 (1:199,999) -90 (9:1) % by weight, and more preferably between about 0.001 (1:99,999) -75 (3:1) % by weight of the mixture. The composition can also be stated as a ratio of the compound to the carrier. In the present invention the weight ratio of these materials (active compound/carrier) can vary from 99:1 (99%) to 1:4 (20%) and more preferably from 10:1 (91%) to 1:3 (25%).

In general, the compounds of this invention can be dissolved in certain solvents such as acetone, methanol, ethanol, dimethylformamide, pyridine or dimethyl sulfoxide and such solutions can be diluted with water. The concentrations of the solution can vary from about 1% to about 90% with a preferred range being from about 5% to about 50%.

For the preparation of emulsifiable concentrates, the compound can be dissolved in suitable organic solvents, or a mixture of solvents, together with an emulsifying agent to enhance dispersion of the compound in water. The concentration of the active ingredient in emulsifiable concentrates is usually from about 10% to about 90%, and in flowable emulsion concentrates, can be as high as about 75%.

Wettable powders suitable for spraying, can be prepared by admixing the compound with a finely divided solid, such as clay, inorganic silicate and carbonate, and silica and incorporating wetting agents, sticking agents, and/or dispersing agents in such mixtures. The concentration of active ingredients in

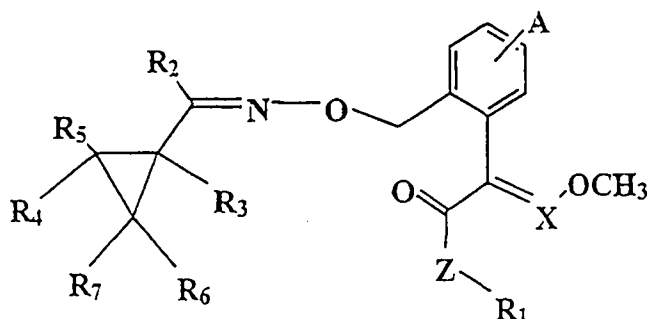
such formulations is usually in the range of from about 20% to about 99%, preferably from about 40% to about 75%. A typical wettable powder is made by blending 50 parts of a compound of Formula I, 45 parts of a synthetic precipitated hydrated silicon dioxide and 5 parts of sodium lignosulfonate. In another preparation a kaolin type (Barden) clay is used in place of the synthetic precipitated hydrated silicon dioxide in the above wettable powder, and in another such preparation 25% of the silicon dioxide is replaced with a synthetic sodium silicoaluminate.

Dusts are prepared by mixing compounds of Formula I, or the enantiomorphs, salts and complexes thereof with finely divided inert solids which can be organic or inorganic in nature. Materials useful for this purpose include botanical flours, silicas, silicates, carbonates and clays. One convenient method of preparing a dust is to dilute a wettable powder with a finely divided carrier. Dust concentrates containing from about 20% to about 80% of the active ingredient are commonly made and are subsequently diluted to from about 1% to about 10% use concentration.

In addition to the aforementioned ingredients the preparations according to the invention may also contain other substances commonly used in preparations of this kind. For example, a lubricant, such as calcium stearate or magnesium stearate, may be added to a wettable powder or to a mixture to be granulated. Furthermore there may, for example, be added "adhesives" such as polyvinylalcohol-cellulose derivatives or other colloidal materials, such as casein, to improve the adherence of the pesticide to the surface to be protected.

## WE CLAIM:

1. A compound of the formula:



wherein X is N or CH; Z is O, S, or NR<sub>8</sub>;

A is hydrogen, halo, cyano, (C<sub>1</sub>-C<sub>12</sub>)alkyl, or (C<sub>1</sub>-C<sub>12</sub>)alkoxy;

R<sub>1</sub> and R<sub>8</sub> are independently hydrogen or (C<sub>1</sub>-C<sub>4</sub>)alkyl;

R<sub>2</sub> is hydrogen, (C<sub>1</sub>-C<sub>4</sub>)alkyl, halo(C<sub>1</sub>-C<sub>4</sub>)alkyl, (C<sub>3</sub>-C<sub>6</sub>)cycloalkyl, halo(C<sub>3</sub>-C<sub>6</sub>)cycloalkyl, (C<sub>2</sub>-C<sub>4</sub>)alkenyl, halo(C<sub>2</sub>-C<sub>4</sub>)alkenyl, (C<sub>2</sub>-C<sub>4</sub>)alkynyl, halo(C<sub>2</sub>-C<sub>4</sub>)alkynyl, or cyano;

R<sub>3</sub> is hydrogen, (C<sub>1</sub>-C<sub>4</sub>)alkyl, halo(C<sub>1</sub>-C<sub>4</sub>)alkyl, (C<sub>3</sub>-C<sub>6</sub>)cycloalkyl, halo(C<sub>3</sub>-C<sub>6</sub>)cycloalkyl, (C<sub>2</sub>-C<sub>4</sub>)alkenyl, halo(C<sub>2</sub>-C<sub>4</sub>)alkenyl, (C<sub>2</sub>-C<sub>4</sub>)alkynyl, or halo(C<sub>2</sub>-C<sub>4</sub>)alkynyl;

R<sub>4</sub> and R<sub>5</sub> are independently hydrogen, (C<sub>1</sub>-C<sub>4</sub>)alkyl, halo(C<sub>1</sub>-C<sub>4</sub>)alkyl, (C<sub>3</sub>-C<sub>6</sub>)cycloalkyl, halo(C<sub>3</sub>-C<sub>6</sub>)cycloalkyl, (C<sub>2</sub>-C<sub>4</sub>)alkenyl, halo(C<sub>2</sub>-C<sub>4</sub>)alkenyl, (C<sub>2</sub>-C<sub>4</sub>)alkynyl, halo(C<sub>2</sub>-C<sub>4</sub>)alkynyl, halo, cyano, or (C<sub>1</sub>-C<sub>4</sub>)alkoxycarbonyl;

and wherein

- A) R<sub>7</sub> is aryl or heterocyclic ring wherein the aryl or heterocyclic ring is substituted with from 2 to 5 substituents and wherein the positions on the aryl or heterocyclic ring adjacent to the bond to the cyclopropyl ring are both substituted and R<sub>6</sub> is hydrogen, (C<sub>1</sub>-C<sub>4</sub>)alkyl, halo(C<sub>1</sub>-C<sub>4</sub>)alkyl, (C<sub>3</sub>-C<sub>6</sub>)cycloalkyl, halo(C<sub>3</sub>-C<sub>6</sub>)cycloalkyl, (C<sub>2</sub>-C<sub>4</sub>)alkenyl, halo(C<sub>2</sub>-C<sub>4</sub>)alkenyl, (C<sub>2</sub>-C<sub>4</sub>)alkynyl, halo(C<sub>2</sub>-C<sub>4</sub>)alkynyl, halo, cyano, or (C<sub>1</sub>-C<sub>4</sub>)alkoxycarbonyl;

or

B)  $R_7$  is an aryl or heterocyclic ring wherein the aryl or heterocyclic ring is unsubstituted or substituted from 1 to 4 substituents wherein at least one of the positions on the aryl or heterocyclic ring adjacent to the bond to the cyclopropyl ring is a hydrogen and  $R_6$  is selected from the group consisting of  $(C_1-C_4)$ alkyl, halo $(C_1-C_4)$ alkyl,  $(C_3-C_6)$ cycloalkyl, halo $(C_3-C_6)$ cycloalkyl,  $(C_2-C_4)$ alkenyl, halo $(C_2-C_4)$ alkenyl,  $(C_2-C_4)$ alkynyl, halo $(C_2-C_4)$ alkynyl, halo, cyano, or  $(C_1-C_4)$ alkoxycarbonyl;

and their salts, complexes, enantiomorphs, stereoisomers;  
and mixtures thereof.

2. The compound of claim 1, wherein X is CH, Z is O,  $R_2$  is  $(C_1-C_4)$ alkyl, and  $R_3$  is H.
3. The compound of claim 2, wherein  $R_7$  is 2,6-dichlorophenyl, 2,6-difluorophenyl, 2,6-dibromophenyl, 2,6-bis(trifluoromethyl)phenyl, 2,3,6-trichlorophenyl, 2,3,6-trifluorophenyl, 2,3,6-tribromophenyl, 2,3,6-tris(trifluoromethyl)phenyl, 2,4,6-trichlorophenyl, 2,4,6-trifluorophenyl, 2,4,6-tribromophenyl, or 2,4,6-tris(trifluoromethyl)phenyl.
4. The compound of claim 2, wherein  $R_7$  is 2,6-difluorophenyl or 2,6-dichlorophenyl.
5. The compound of claim 1, wherein X is N, Z is O or NH,  $R_2$  is  $(C_1-C_4)$ alkyl and  $R_3$  is H.
6. The compound of claim 5, wherein  $R_7$  is 2,6-dichlorophenyl, 2,6-difluorophenyl, 2,6-dibromophenyl, 2,6-bis(trifluoromethyl)phenyl, 2,3,6-trichlorophenyl, 2,3,6-trifluorophenyl, 2,3,6-tribromophenyl, 2,3,6-tris(trifluoromethyl)phenyl, 2,4,6-trichlorophenyl, 2,4,6-trifluorophenyl, 2,4,6-tribromophenyl, or 2,4,6-tris(trifluoromethyl)phenyl.

7. The compound of claim 5, wherein  $R_7$  is 2,6-difluorophenyl or 2,6-dichlorophenyl.
8. The compound of claim 1, wherein the compound is N-methyl-2-[2-((trans-1-(2-(2',6'-dichlorophenyl)cyclopropyl)ethylidene)aminooxymethyl)phenyl]-2-methoxyiminoacetamide.
9. The compound of claim 2, wherein  $R_6$  is ( $C_1$ - $C_4$ )alkyl and  $R_7$  is phenyl, 2-chlorophenyl, 3-chlorophenyl, 4-chlorophenyl, 4-fluorophenyl, 4-bromophenyl, 2-(trifluoromethyl)phenyl, 2,4-dichlorophenyl, 2,4-difluorophenyl, 2,4-dibromophenyl, 2,4-bis(trifluoromethyl)phenyl, 2-chloro-4-fluorophenyl, or 2-fluoro-4-chlorophenyl.
10. The compound of claim 5, wherein  $R_6$  is ( $C_1$ - $C_4$ )alkyl and  $R_7$  is phenyl, 2-chlorophenyl, 3-chlorophenyl, 4-chlorophenyl, 4-fluorophenyl, 4-bromophenyl, 2-(trifluoromethyl)phenyl, 2,4-dichlorophenyl, 2,4-diifluorophenyl, 2,4-dibromophenyl, 2,4-bis(trifluoromethyl)phenyl, 2-chloro-4-fluorophenyl, or 2-fluoro-4-chlorophenyl.
11. The compound of claim 1 where the compound is N-methyl 2-[2-((trans-1-(2-(4'-fluorophenyl)-2-methylcyclopropyl)ethylidene)aminooxymethyl)phenyl]-2-methoxyiminoacetamide, N-methyl 2-[2-((trans-1-(2-(2',4'-difluorophenyl)-2-methylcyclopropyl)ethylidene)aminooxymethyl)phenyl]-2-methoxyiminoacetamide, methyl 2-[2-((trans-1-(2-(2',4'-difluorophenyl)-2-methylcyclopropyl)ethylidene)aminooxymethyl)phenyl]-2-methoxyiminoacetate.
12. A method of preparation of the compounds of claim 4 wherein X is N, Z is O, and  $R_6$  is ( $C_1$ - $C_4$ )alkyl comprising the step of reacting methyl (E)-2-(aminooxymethyl)phenyl glyoxylate O-methyloxime with a 1-aryl or 1-heteroaryl-1-( $C_1$ - $C_4$ )alkyl-2-((C=O)( $C_1$ - $C_4$ )alkyl)cyclopropane.

13. A fungicidal composition comprising an agronomically acceptable carrier and the compound of claim 1, wherein the ratio of the carrier to the compound is between 99:1 and 1:4.
14. A method for controlling phytopathogenic fungi which comprises applying the compound of claim 1 to the locus where control is desired, at a rate of from 0.005 to 50 kilograms per hectare.

## INTERNATIONAL SEARCH REPORT

In national Application No

PCT/US 01/15451

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C251/60 C07C251/58 A01N37/18 A01N37/50

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C A01N

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

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

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

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                            | Relevant to claim No. |
|------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X          | DE 197 16 237 A (BASF AG)<br>22 October 1998 (1998-10-22)<br>page 10, line 1 - line 14; table 6<br>example 7<br>pages 48-50, Table B, compounds with R4 =<br>aryl<br>page 57; examples 5-8; table 1<br>claims | 1-14                  |
| P,A        | US 6 063 956 A (ROSS RONALD ET AL)<br>16 May 2000 (2000-05-16)<br>cited in the application<br>column 3, line 41 - line 60<br>claims<br>tables 1,2                                                             | 1-14                  |
|            | — — — — —<br>-/-                                                                                                                                                                                              |                       |

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

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

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

\*g\* document member of the same patent family

Date of the actual completion of the international search

22 August 2001

Date of mailing of the international search report

30/08/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

O'Sullivan; P

INTERNATIONAL SEARCH REPORT

|                           |
|---------------------------|
| Inventor's Application No |
| PCT/US 01/15451           |

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                                       |                       |
|------------------------------------------------------|-------------------------------------------------------------------------------------------------------|-----------------------|
| Category *                                           | Citation of document, with indication, where appropriate, of the relevant passages                    | Relevant to claim No. |
| A                                                    | US 5 998 455 A (KUENG RUTH BEATRICE ET AL) 7 December 1999 (1999-12-07)<br>column 1, line 5 - line 27 | 1-14                  |

INTERNATIONAL SEARCH REPORT  
Information on patent family members

International Application No  
PCT/US 01/15451

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s)                                                                                                                                                                                    | Publication<br>date                                                                                                                                                                |
|-------------------------------------------|---------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| DE 19716237 A                             | 22-10-1998          | AU 6832498 A<br>WO 9847886 A<br>EP 0975616 A                                                                                                                                                                  | 13-11-1998<br>29-10-1998<br>02-02-2000                                                                                                                                             |
| US 6063956 A                              | 16-05-2000          | AU 1007500 A<br>BR 0000194 A<br>CN 1262269 A<br>EP 1026151 A<br>JP 2000212148 A                                                                                                                               | 03-08-2000<br>19-09-2000<br>09-08-2000<br>09-08-2000<br>02-08-2000                                                                                                                 |
| US 5998455 A                              | 07-12-1999          | AU 690464 B<br>AU 6125196 A<br>BR 9608358 A<br>CA 2224977 A<br>CZ 9704040 A<br>WO 9700012 A<br>EP 0831698 A<br>HU 9802198 A, B<br>JP 11507655 T<br>NZ 310452 A<br>PL 323945 A<br>TR 9701619 T<br>ZA 9605080 A | 23-04-1998<br>15-01-1997<br>18-08-1998<br>03-01-1997<br>13-05-1998<br>03-01-1997<br>01-04-1998<br>28-01-1999<br>06-07-1999<br>29-09-1999<br>27-04-1998<br>21-05-1998<br>17-12-1996 |

CAVELIER  
ABOGADOS  
EDIFICIO SISKI  
CARRERA 4ª N° 72-35  
BOGOTÁ, 6 - COLOMBIA

REPRESENTACION, RATIFICACION Y PODER

For patents, utility models, industrial designs, trademarks, commercial names, trade emblems, slogans.

Para patentes, modelos de utilidad, diseños industriales, marcas de fábrica, nombres comerciales, enseñanzas, lemas comerciales.

REPRESENTATION, RATIFICATION AND  
POWER OF ATTORNEY

I (we), the undersigned/Yo (nosotros), abajo firmado (s)

Dow AgroSciences LLC

of/domiciliado (s) en 9330 Zionsville Road,  
Indianapolis, Indiana 46268, United  
States of America,

por el presente ratificamos la  
presentada por  
como agente oficioso ante  
en

el  
y por el presente nombramos a GERMAN CAVELIER, tpa. 832; GONZALO PERDOMO, tpa. 831; EMILIO FERRERO, tpa. 31929; y LUZ CLEMENCIA DE PAEZ, tpa. 23555; domiciliados en la Carrera 4ª N° 72-35, Bogotá, Colombia, en obediencia a lo dispuesto en el parágrafo 1º del Artículo 543 del Código de Comercio, el primero como principal y los demás como suplentes, en su orden, como mis (nuestros) representantes en todos los asuntos de propiedad industrial con facultad para recibir notificaciones y nombrar apoderados judiciales o extrajudiciales. El primer representante suplente reemplazará al principal en caso de ausencia o impedimento temporal o definitivo de aquél. La misma regla se aplicará cuando el segundo representante suplente haya de reemplazar al primero, o el tercero al segundo. En tales casos, el representante principal, o el primero, o segundo suplente, en su caso, o ambos, declararán su intención de no ejercer la representación mediante declaración autenticada por Notario Público en Colombia, o por Notario u otro Funcionario Público, o Cónsul de Colombia, en el extranjero; y si se tratare de impedimento, con el certificado respectivo. Si alguno de los nombrados faltare definitivamente, el siguiente tomará su lugar. Cuando cesare la ausencia o impedimento del representante principal, o de su primero o segundo suplentes, en su caso, podrán ejercer la representación, en su orden, uno u otros según el caso, asumiéndola por el solo hecho de ejercerla, cesando en ese momento el ejercicio de la representación por el primero, segundo o tercer suplente en su caso.

Además, confiero (conferimos) poder a los abogados arriba nombrados, para obtener la protección de mi (nuestra) propiedad industrial y contra la competencia desleal, a cuyo efecto autorizo (amos) a los dichos apoderados para que me (nos) representen ante cualesquiera entidades o personas, ejerzan o no jurisdicción, especialmente ante las del orden administrativo, contencioso-administrativo y judicial, así como los tribunales de arbitramento, en todo lo concerniente a los siguientes asuntos: a) Obtención de patentes de invención, modelos de utilidad y diseños industriales; el registro de marcas de fábrica, colectivas, defensivas, de servicio, lemas comerciales, nombres comerciales, enseñanzas, variedades vegetales y denominaciones de origen; su renovación, traspaso, cambio de nombre o domicilio, cancelación voluntaria; y el registro de licencias de uso de esos derechos; b) Las acciones de competencia desleal, protección del consumidor, oposiciones u observaciones, cancelación administrativa o judicial, nulidad,

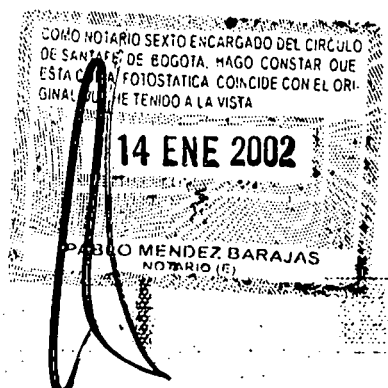
hereby ratify the  
filed without a Power of Attorney by  
before  
in

on  
and do hereby appoint GERMAN CAVELIER, tpa. 832; GONZALO PERDOMO, tpa. 831; EMILIO FERRERO, tpa. 31929; and LUZ CLEMENCIA DE PAEZ, tpa. 23555; domiciled at Carrera 4ª N° 72-35, Bogotá, Colombia, in due compliance with the terms of Paragraph 1st. of Article 543 of the Commercial Code, the first as principal and the others as alternates, in the order of their appointment, as our representatives for all industrial property matters with faculty to receive notifications and to appoint attorneys in and out of Court. The first alternate shall replace the principal in case of his absence or of temporal or definitive impediment. The same rule will apply when the second alternate representative is to replace the first one, or when the third is to replace the first or second alternates in their turn, or both of them, second. In such cases, the principal representative, or the shall state their intention not to act as representatives through a declaration given before a Notary Public in Colombia, or before a Notary or another Public Official or a Colombian Consul abroad; and in case of impediment, the appropriate certificate shall suffice. If any of the appointees were to be definitely absent, the following alternate shall take his place. When the absence or impediment of the principal representative, or of the first or second alternate in their turn ceases, the representation can be taken again in their sequence, by the principal, the first or second alternate depending on case, and the mere fact or its exercise will suffice. The exercise of the representation by the first, second or third alternates in their turn shall end at such time.

In addition, we grant a Power of Attorney in favor of the above-named attorneys-at-law so that they may obtain the protection of my (our) industrial property and against the unfair competition, for which purpose I (we) authorize the said attorneys to represent me (us) before any authorities or persons, with or without jurisdiction, specially those administrative, administrative contentious and judicial, as well as before Arbitration Court, in all matters concerning the following: a) Obtainment of patents, utility models and industrial designs; the registration of trademarks, collective, defensive and service marks, slogans, commercial names, trade emblems, vegetal varieties and denominations of origin; its renewal, assignment, change of name or domicile, voluntary cancellation; and the registration of licenses of use of the above rights; b) Actions of

A la vuelta →

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medidas cautelares, concesión de licencias, la tutela, la protección de secretos industriales, y en general los juicios civiles, penales, administrativos o contencioso-administrativos relacionados con estos derechos; acciones y procesos que promovamos o se nos promuevan. Y para que en todos los asuntos arriba determinados, puedan sustituir este mandato, transigir, conciliar, admitir los hechos del proceso, desistir, cancelar, recibir, renunciar, y ratificar los actos de agentes oficiosos.

73

unfair competition, protection to the consumer, oppositions or observations, administrative or Court cancellation, nullity, infringement, granting of licenses, the action for writ mandamus, the protection of trade secrets, and in general the civil, penal, and administrative suits relating to those rights; actions and suits instituted by me (us) or against me (us). And that in all the above matters they may substitute this Power of Attorney, compromise, conciliate, admit the facts of the case, desist, cancel, receive, resign, and ratify acts done by representatives without a power of attorney.

Given and signed this/Dado y firmado hoy \_\_\_\_\_

February 6, 1998

In/en Indianapolis, Indiana 46268

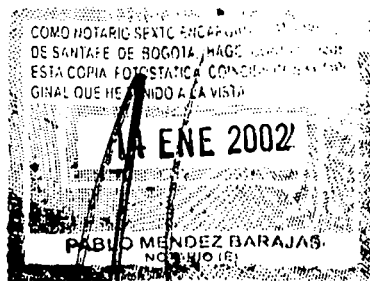
United States of America

Kenneth L. Loertscher

Signature

Firma

Kenneth L. Loertscher  
Assistant Secretary  
& General Patent Counsel





# Consulado General de Colombia

500 NORTH MICHIGAN AVENUE, SUITE 2040  
CHICAGO, ILLINOIS 60611

TEL (312)923-1196 FAX(312)923-1197

No. 254

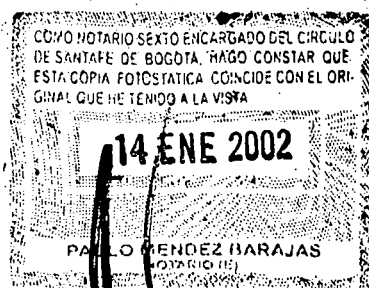
Chicago, FEB 20 1998

El suscrito Cónsul General de Colombia, CERTIFICA, que el señor (a) MARY REEVER, quien como SECRETARIA DELEGADA ESTADO, IN., autenticó la firma del signatario del poder precedente, ejercía en la fecha las funciones indicadas y su firma corresponde a la registrada en este Consulado; que la compañía DOW AGROSCIENCES LLC es una sociedad constituida de acuerdo con las leyes de DELAWARE y cumple su objeto conforme a las mismas; que el (a) señor (a) KENNETH L. WERTSCHER, quien en su carácter de REPRESENTANTE LEGAL de la citada compañía confiere el poder precedente, es su representante legal en este país.

El Cónsul General no asume responsabilidad alguna por el contenido del documento.

PAGADO IMPUESTO DE TIMBRE Y DERECHOS CONSULARES  
US\$56.00 (Cincuenta y seis dólares)

  
CARLOS ALFONSO NEGRETE  
Cónsul General



MINISTERIO DE RELACIONES  
EXTERIORES

NO SE ASUME  
RESPONSABILIDAD DEL TEXTO

1998 MAR 11 11:55

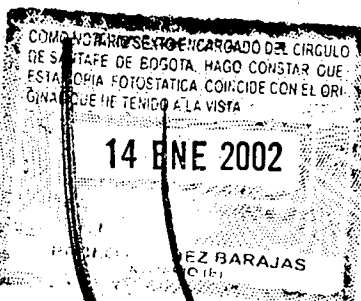
CLIA FIRMADA EN EL  
MINISTERIO DE SEMPENA  
FUNCIONES INDICADAS

JEFE DE LEGALIZACIONES  
SANTAFE DE BOGOTA D.C.

Bernarda R. de Martinez

Traductora e Interprete Oficial

Resolución 683 Minjusticia 1999



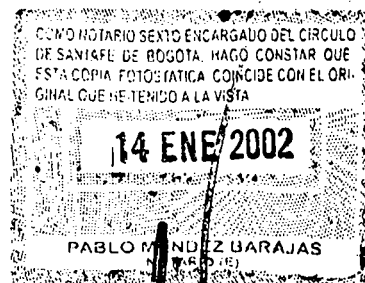
UNITED STATES OF AMERICA  
CERTIFICATE OF OFFICE  
STATE OF INDIANA

I, Sue Anne Gilroy, Secretary of State of Indiana, DO HEREBY CERTIFY: That,  
according to records on file in my office, Lydia S. Owens was duly elected  
or appointed to the office of Notary Public in and for Hendricks County  
and that the term of said office included the date of February 6, 1998: that to all his/her official acts as said offi-

cial, full faith and credit ought to be given in all Courts of  
Justice and elsewhere. In testimony whereof, I have here unto  
set my hand and affixed the Great Seal of the State of Indiana,  
at Indianapolis, this Tenth day of  
February, 1998



Sue Anne Gilroy  
Secretary of State  
by: Mary Deever  
Deputy



CERTIFICADO NOTARIAL (INDIVIDUO)

A los 6 días del mes de FEBRERO de 19 98  
ante mí, Notario Público de ESTADO DE INDIANA  
compareció(eron) personalmente KENNETH L. LOERTSCHER

a quien(es) doy fe de conocer y me consta que es(son) la(s)  
persona(s) firmante(s) del documento que precede, y quien(es)  
tiene(n) capacidad legal para otorgarlo.

Notario Público Notary Public

NOTARIAL CERTIFICATE (INDIVIDUAL)

On this 6<sup>th</sup> day of February 19 98  
before me, a Notary Public of State of Indiana  
personally appeared Kenneth L. Loertscher

to me known, and known to me to be the person(s) who  
executed that foregoing document, and who has(have) legal  
capacity to execute it.

CERTIFICADO NOTARIAL (SOCIEDAD)

Hoy, 6 de FEBRERO de 19 98  
compareció(eron) ante mí  
KENNETH L. LOERTSCHER  
a quien(es) conozco personalmente y que firma(n) este documen  
to en representación de la Sociedad/compañía  
denominada Dow AgroSciences LLC

Certifico:

1. Que he visto los siguientes documentos:  
CERTIFICADO DE CONSTITUCION, FECHADO 1 JULIO 1997  
CERTIFICADO DE MODIFICACION, FECHADO 1 OCT. 1997  
RESOLUCION JUNTA DIRECTIVA, FECHADO 23 OCT. 1997  
CONSENTIMIENTO ESCRITO DE LA JUNTA, 1 JULIO 1997

2. Que dichos documentos prueban lo siguiente:

2.1. Que Dow AgroSciences LLC  
es una Sociedad/Compañía legalmente constituida y existente  
de acuerdo con las leyes de 1 Estado de Delaware,  
Estados Unidos de América

2.2. Que el domicilio de dicha Sociedad/Compañía es  
9330 Zionsville Road, Indianapolis, Indiana  
46268, Estados Unidos de America.

2.3. Que el objeto u objeto para los cuales se otorga el presente  
poder están comprendidos dentro del objeto social de la  
mencionada Sociedad/Compañía.

2.4. Que el(los) Sr.(Sres.) KENNETH L. LOERTSCHER  
SECRETARIO ASISTENTE y ASESOR LEGAL PATENTES

está(n) autorizado(s) para otorgar el presente Poder.

Ciudad INDIANAPOLIS

Estado INDIANA

Hoy 6 FEB. de 19 98

NOTARIAL CERTIFICATE (CORPORATION)

On this 6<sup>th</sup> day of February 19 98  
appeared before me  
Kenneth L. Loertscher  
who(m) I know personally and who(m) signed this document as  
representative(s) of the Dow AgroSciences LLC Limited  
named Dow AgroSciences LLC Liability  
Company.

I Certify:

1. That I have seen the following documents:

Certificate of formation, dated July 1, 1997  
Certificate of amendment, dated October 1, 1997  
Board resolution, dated October 23, 1997  
Board written consent, dated July 1, 1997

2. That the above documents duly prove the following:

2.1. That Dow AgroSciences LLC  
is a Limited Liability Company legally constituted and in existence  
in accordance with the laws of the State of Delaware,  
United States of America

2.2. That the domicile of said Limited Liability Company is  
9330 Zionsville Road, Indianapolis, Indiana  
46268, United States of America.

2.3. That the purpose of purposes for which the present Power  
of Attorney is granted are comprised within the corporation  
purposes set forth in the charter of the mentioned  
Company.

2.4. That Mr.(Messrs.) Kenneth L. Loertscher  
Assistant Secretary and General Patent Counsel  
is(are) authorized to grant the present Power of Attorney.

City Indianapolis

State Indiana

This 6<sup>th</sup> day of Feb. 19 98

Lydia S. Owens

Notario Publico / Notary Public, State of Indiana  
DE SANTAFE DE BOGOTA, HAGO CONSTAR QUE  
ESTA COPIA FOTOSTATICA COINCIDE CON EL ORIGINAL QUE HE TENIDO A LA VISTA  
Commission Expires 03/05/00  
4 ENE 2002

\* Los documentos deben identificarse con fecha y origen.

\* Documents must be identified with date and origin.

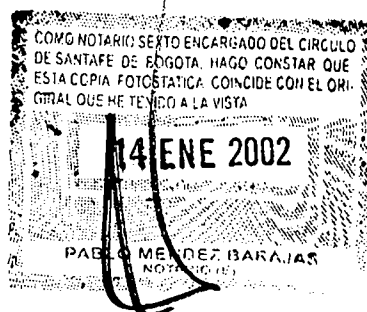
**CERTIFICACION NOTARIAL  
Y AUTENTICACION CONSULAR**

1. Es necesaria la legalización con certificado notarial. El Notario Público debe certificar:
  - 1.1. Que la compañía está legalmente constituida y actualmente existente.
  - 1.2. Su domicilio.
  - 1.3. Que el propósito del poder está incluido en el objeto social de la compañía.
  - 1.4. Que el poderdante está autorizado para dar el poder en nombre de la compañía.
2. Los documentos que hay que mostrarle al Notario Público para probar los puntos anteriores, deben estar expresados en el Certificado Notarial con fecha y origen:
  - 2.1. Respecto a los puntos 1.1, 1.2 y 1.3 sugerimos referirse a los artículos de constitución con fecha y lugar de otorgamiento; y
  - 2.2. Para el punto 1.4 sugerimos mencionar la resolución de la Junta Directiva o los estatutos, según los cuales la persona que otorga el poder está autorizada para ello.
3. Enseguida el Señor Cónsul de Colombia e autenticar la firma del Notario Público.

**NOTARIAL CERTIFICATION AND  
CONSULAR AUTENTIFICATION**

1. Notarial legalization is necessary. The Notary Public must certify:
  - 1.1. That the company is legally constituted and presently existent.
  - 1.2. Its place of business.
  - 1.3. That the purpose of the Power-of-Attorney is included in the activities of the company.
  - 1.4. That the grantor is empowered to give the Power of Attorney in the name of the company he represents.
2. The documents which the Notary Public had before him to prove the above points must be listed by him in the Notarial Certificate with dated and origin:
  - 2.1. In connection with points 1.1., 1.2. and 1.3 we suggest referring to the articles of incorporation with date and place of execution.
  - 2.2. For point 1.4 we suggest to mention the resolution of the Board of Directors and/or the by-laws whereby the person who grants the Power of Attorney has been authorized to give it.
3. Then the Colombian Consul must legalize the signature of the Notary Public.

NOTA PARA EL SEÑOR CONSUL COLOMBIANO: Según el artículo 259 del C. de P.C. el Señor Cónsul debe autenticar la última precedente autenticación.



TRADUCCION OFICIAL No.03.075.98 de un documento escrito en inglés el cual para su identificación se sella con el sello del Traductor al mismo tiempo que la presente. Esta traducción ha sido preparada por Bernarda R. de Martínez, Traductora Oficial debidamente reconocida por el Ministerio de Relaciones Exteriores y aprobada por el Ministerio de Justicia de Colombia mediante Resolución No. 683 de 1991.

(Se traducen sellos y legalizaciones que aparecen a continuación de un documento escrito en inglés y español por medio del cual Dow AgroSciences LLC, otorga Poder a favor de GERMAN CAVELIER, GONZALO PERDOMO, EMILIO FERRERO y LUZ CLEMENCIA DE PAEZ.)

Dado y firmado hoy 6 de febrero de 1998, en Indianápolis, Indiana, E.E.U.U., por Kenneth L. Loertscher, Subsecretario y Asesor General de Patentes.

(Sellos parciales en tinta del Consulado General de Colombia en Chicago.)

CERTIFICADO NOTARIAL (INDIVIDUO), en inglés y español referente a la capacidad legal que tenía KENNETH L. LOERTSCHER para otorgar el documento antes mencionado, expedido el 6 de febrero de 1998 en el Estado de Indiana.

COMO NOTARIO, SE TO ENCARGADO DEL CIRCULO  
EXPEDIDO EN LA CIUDAD DE INDIANAPOLIS, INDIANA, E.E.U.U., EL 6 DE FEBRERO DE 1998.  
ESTA COPIA FOTOSTATICA COINCIDE CON EL ORIGINAL QUE HE TENIDO A LA VISTA

14 ENE 2002

CERTIFICADO NOTARIAL (SOCIEDAD), en inglés y español, referente a la existencia legal de la sociedad Dow AgroSciences LLC, expedido en la Ciudad de Indianápolis, Indiana, E.E.U.U., el 6 de febrero de 1998.

(Firmado), Lydia S. Owens, Notario Público

(Sello notarial en tinta), LYDIA S. OWENS Notario Público,  
Estado de Indiana, Condado de Hendricks Mi comisión expira el  
03/05/00

(Sello notarial seco), LYDIA S. OWENS NOTARIO PUBLICO INDIANA

(Sello parcial en tinta del Consulado General de Colombia en  
Chicago.)

---

ESTADO UNIDOS DE AMERICA

CERTIFICADO DEL CARGO

ESTADO DE INDIANA

Yo, SUE ANN GILROY, Secretario de Estado de Indiana, POR EL  
PRESENTE CERTIFICO: que, de acuerdo con los archivos que obran  
en mi oficina, LYDIA S. OWENS fue debidamente elegido y  
nombrado para el cargo de NOTARIO PUBLICO en y para el Condado  
de Hendricks y que el término de dicho cargo incluía la fecha  
del 6 de febrero de 1998: que a todos sus actos oficiales se  
les debe dar completa fe y crédito dentro y fuera de todas las  
Corte de Justicia. EN TESTIMONIO DE LO CUAL, he firmado y  
estampado el Gran Sello del Estado de Indiana, en Indianápolis,  
hoy 10 de febrero de 1998.

(Firma facsimilar), Sue Ann Gilroy

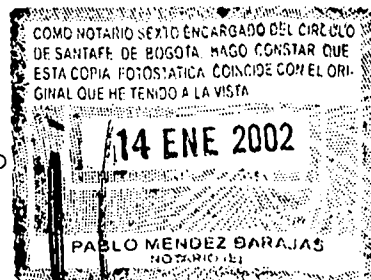
Secretario de Estado

(Firmado),

Por: Mary Reeve

Suplente

(Adherido se encuentra sello de oblea dorado con texto en  
relieve), SELLO DEL ESTADO DE INDIANA 1816



(Sello parcial en tinta del Consulado General de Colombia en Chicago.)

(En español), Certificación de la firma y cargo de MARY REEVER, de la existencia legal de la compañía DOW AGROSCIENCES LLC y de la autoridad que tenía su representante Legal, KENNETH L. LOERTSCHER, para otorgar el poder mencionado arriba. Esta certificación fue expedida por el CONSULADO GENERAL DE COLOMBIA EN CHICAGO, ILLINOIS, bajo el N° 254, de fecha 20 de febrero de 1998 y firmada por Carlos Alfonso Negret Mosquera, Cónsul General. Pagados Impuesto de Timbre y Derechos Consulares por valor de veintiún dólares.

(Sello parcial en tinta del Consulado General de Colombia en Chicago.)

(al dorso), Legalización de la firma que antecede expedida el MINISTERIO DE RELACIONES EXTERIORES bajo el No. 221220, de fecha 11 de marzo de 1998 y firmada por el Jefe de Legalizaciones.

Es traducción fiel y completa de la cual se deja copia en los archivos de esta oficina para su confrontación y a la cual me remito.

Bogotá, 17 de marzo de 1998

COLO 6641-801-001-3  
BRM.137

COMO NOTARIO SEXTO ENCARGADO DEL CIRCULO DE SANTAFE DE BOGOTA, HAGO CONSTAR QUE ESTA COPIA FOTOSTATICA COINCIDE CON EL ORIGINAL QUE HE TENIDO A LA VISTA

14 ENE 2002

PABLO MENDOZA BARRAJAS  
NOTARIO

*Bernarda R. de Martínez*

Bernarda R. de Martínez  
Traductora e Interprete Oficial  
Resolución 683 Minjusticia 1994

COMO NOTARIO SEXTO DEL CIRCULO DE SANTAFE DE BOGOTA, HAGO CONSTAR QUE LA(S) ANTERIOR(ES) FIRMA(S) PUESTA(S) POR

*[Signature]*

IDENTIFICADOS CON C.C. No.(s)

ES(SON) AUTENTICA(S)

SANTAFE DE BOGOTA, 17 MAR 1998



NO SE ASUME  
RESPONSABILIDAD DEL TEXTO

99 MAR 18 AM 11:56

JEFE DE LEGALIZACIONES  
SANTAFE DE BOGOTA D.C.

MINISTERIO DE RELACIONES  
EXTERIORES

022686

CUYA FIRMA APARECE EN  
DOCUMENTO DESEMPLEO  
LAS FUNCIONES INDICADAS

COMO NOTARIO SEXTO ENCARGADO DEL CIRCULO DE SANTAFE DE BOGOTA, HAGO CONSTAR QUE ESTA COPIA FOTOSTATICA COINCIDE CON EL ORIGINAL QUE HE TENIDO A LA VISTA

14 ENE 2002

PABLO MENDEZ BARAJAS  
NOTARIO (E)

# CAVELIER

ABOGADOS

TENET ®  
CABLES: CAVELEYES  
TELEX: 45479 CAVE-CO  
TELEX: (23) 7407375 CAVE-UC

EDIFICIO SISKI  
CARRERA 4 No. 72 - 35  
BOGOTA 8, COLOMBIA

TELEFONOS: (57) (1) 347-36 11  
(57) (1) 212-01 00  
TELEFAX: (57) (1) 217-92 11  
(57) (1) 235-88 50

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

Poderdante: DOW AGROSCIENCES LLC

Poder conferido el: 06-02-98

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

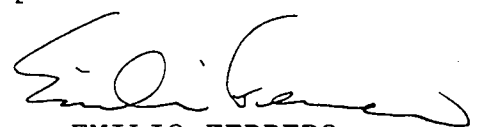
Hago la anterior sustitución conforme al artículo 66 del Código de Procedimiento Civil ya que los otros sustitutos faltan en este momento.

Señor Jefe,

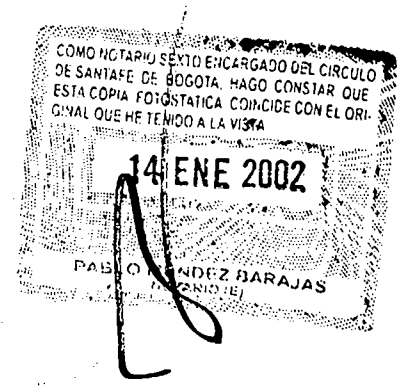
  
GERMAN CAVELIER

T.P.A. No. 832  
C.C. No. 2.877.924 de Bogotá

Acepto:

  
EMILIO FERRERO

T.P.A. No 31.929  
C.C. No. 438.019 de Usaquén



2e-780-2

NOTARIA SEXTA DE BOGOTA

RECONOCIMIENTO Y PRESENTACION PERSONAL

Santos, D. C.

25 FEB 1998

NOTARIO MI, PABLO MENDEZ BARAJAS S.

NOTARIO SEXTO ENCARGADO DEL CIRCULO DE BOGOTA.

Compareceron

*[Handwritten signatures]*

que son de la(s) persona(s) C. C.

478019

2877924

77832

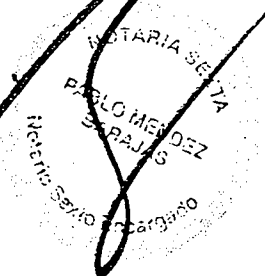
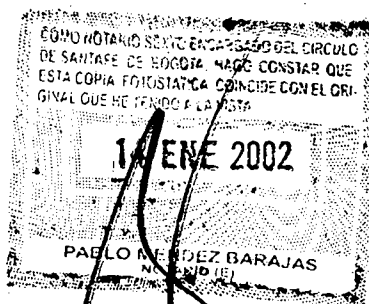
772/8229

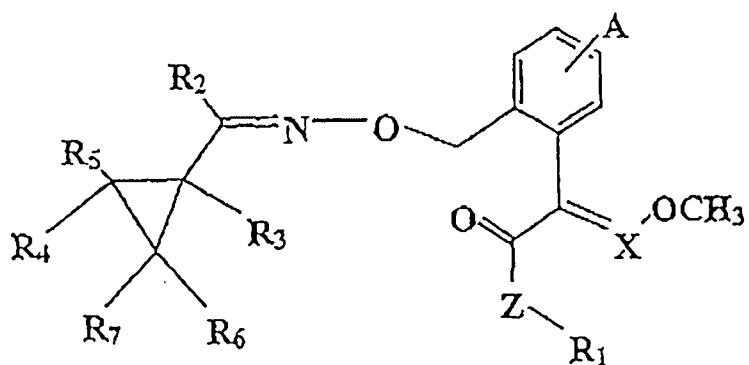
domiciliado(s) en Bogotá y declararon que la(s) firma(s) que aparecen(n) en el presente documento es(son) la(s) suya(s) y que el contenido del mismo es cierto.

En constancia se firma esta Diligencia.

*[Handwritten signature]*

*[Handwritten signature]*







# Industria y Comercio

## SUPERINTENDENCIA

SUPERINTENDENCIA Y COMERCIO  
 Radicacion : 02002621 00000000 Folios: 64  
 Fecha (AMB): 2002-01-15 16:20:37  
 Trámite : 333 TEMPORAL 411 PRESENTIA  
 Dependencia: 2028 DIVISION DE NUEVAS CREACIONES

NIT : 900176089-2

RECIBO SOCIAL DE CAJA : 01 - 77,144  
 FECHA : DICIEMBRE 10 DE 2001

### \*\*\*\*\* CONSIGNACION \*\*\*\*\*

| DEPOSITANTE       | TIPO PAGO    | BANCO         | CUENTA      | No. PAGO | FECHA PGO  | Vr. PAGO     |
|-------------------|--------------|---------------|-------------|----------|------------|--------------|
| CAVELIER ABOGADOS | CONSIGNACION | BANCO POPULAR | 050-00110-6 | 6482939  | 10/12/2001 | 8.429,480.00 |

### \*\*\*\*\* CONCEPTO \*\*\*\*\*

| CANT. | RENTISTICO           | CONCEPTO                            | TOTAL CONCEPTO |
|-------|----------------------|-------------------------------------|----------------|
| 1     | 05-01-01 SOLICITUDES | 1 TRAMITES DE SOL. DE PATENTE DE IN | 356,640.00     |
|       |                      | TOTAL :                             | \$ 356,640.00  |

SOM: TRESCIENTOS CINCUENTA Y SEIS MIL SEISCIENTOS CUARENTA PESOS

RESPONSABLE :

RECIBO DE CAJA APLICADO AL EXPEDIENTE No.

Colo 10975-801-007-7

Carrera 13 No. 27-00 Pisos 5, 7 y 10  
 Conmutador 382 0840  
 Fax 350 5220  
 E-mail: info@sic.gov.co  
 www.sic.gov.co  
 Bogotá, D.C., Colombia



# Industria y Comercio

## SUPERINTENDENCIA

NIT : 800176089-2

Radicacion : 02002821 00000000

Folios: 84

Fecha (AND): 2002-01-15 16:20:37

Tramite : 333 TEMPORAL

411 PRESENTA

Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

CERTIFICACION DE EXCEDENTE : 02 - 406  
FECHA : ENERO 8 DE 2002

### \*\*\*\*\* CONSIGNACION \*\*\*\*\*

| DEPOSITANTE       | TIPO PAGO    | BANCO         | CUENTA      | No. PAGO | FECHA PGO  | Vr. PAGO     |
|-------------------|--------------|---------------|-------------|----------|------------|--------------|
| CAVELIER ABOGADOS | CONSIGNACION | BANCO POPULAR | 050-00110-6 | 6482963  | 08/01/2002 | 1,219,502.00 |

### \*\*\*\*\* CONCEPTO \*\*\*\*\*

| CANT. | ANALITICO   | CONCEPTO                           | TOTAL CONCEPTO |
|-------|-------------|------------------------------------|----------------|
| 1     | 50005-01-09 | OTROS SERVICIOS DE PROPIEDAD I     |                |
|       |             | 99 OTROS SERVICIOS ADMINISTRATIVOS | 21,360.00      |
|       |             | TOTAL :                            | \$ 21,360.00   |

CON: VEINTIUNO MIL TRESCIENTOS SESENTA PESOS

RESPONSABLE :

RECIBO DE CAJA APLICADO AL EXPEDIENTE No.

ESTA CERTIFICACION DE EXCEDENTE DE PAGO SOLO PODRA SER UTILIZADA  
COMO PARTE DE LA CANCELACION DE UNA TARIFA VIGENTE Y NO PODRA SER  
SUSTITUIDA POR NINGUN RECIBO.

Colo

10975-801-007-7

Carrera 13 No. 27-00 Pisos 5, 7 y 10  
Conmutador 382 0840  
Fax 350 5220  
E-mail: info@sic.gov.co  
www.sic.gov.co  
Bogotá, D.C., Colombia

4/6  
200

**Industria y Comercio**  
SUPERINTENDENCIA

**REQUISITOS NECESARIOS PARA PRESENTACIÓN Y AGILIZACIÓN DEL TRAMITE**

|                                                                                     | USUARIO | RADICADOR |
|-------------------------------------------------------------------------------------|---------|-----------|
| <b>PATENTE DE INVENCION</b> [ ]                                                     |         |           |
| <b>MODELO DE UTILIDAD</b> [ ]                                                       | [ ]     | [ ]       |
| • Indicación de que se solicita la concesión de una patente                         | [ ]     | [ ]       |
| • Datos de identificación del solicitante o de la persona que presenta la solicitud | [ ]     | [ ]       |
| • Descripción de la invención                                                       | [ ]     | [ ]       |
| • Dibujos de ser estos pertinentes                                                  | [ ]     | [ ]       |
| • Comprobante de Pago de las tasas establecidas                                     | [ ]     | [ ]       |
| <b>COMPLETA</b> [ ]                                                                 |         |           |
| <b>INCOMPLETA</b>                                                                   | [ ]     | [ ]       |

**DISEÑO INDUSTRIAL** [ ]

|                                                                                                               |     |     |
|---------------------------------------------------------------------------------------------------------------|-----|-----|
| • Indicación de que se solicita el registro de Diseño Industrial.                                             | [ ] | [ ] |
| • Datos de identificación del solicitante o de la persona que presenta la solicitud.                          | [ ] | [ ] |
| • Representación gráfica y fotográfica del Diseño Industrial o muestra del material que incorpora el diseño . | [ ] | [ ] |
| • Comprobante de pago de las tasas establecidas.                                                              | [ ] | [ ] |
| <b>COMPLETA</b> [ ]                                                                                           |     |     |
| <b>INCOMPLETA</b>                                                                                             | [ ] | [ ] |

**ESQUEMA DE TRAZADO** [ ]

|                                                                                      |     |     |
|--------------------------------------------------------------------------------------|-----|-----|
| • Indicación de que se solicita el registro de un Esquema de trazado.                | [ ] | [ ] |
| • Datos de identificación del solicitante o de la persona que presenta la solicitud. | [ ] | [ ] |
| • Representación gráfica del esquema de trazado                                      | [ ] | [ ] |
| • Comprobante de pago de las tasas establecidas.                                     | [ ] | [ ] |
| <b>COMPLETA</b> [ ]                                                                  |     |     |
| <b>INCOMPLETA</b>                                                                    | [ ] | [ ] |

Firma Responsable

SUPERINDUSTRIA Y COMERCIO

Radicación : 02802621 00000000

Folios: 84

Fecha (AÑO): 2002-01-15 16:20:37

Tramite : 333 TEMPORAL

411 PRESENTA

Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

Carrera 13 No. 27-00 Piso 2 mezzanino  
Conmutador: 362 06 40

Fax: 350 52 20 e-mail: info@sic.gov.co  
Bogotá D.C. - Colombia