



(86) Date de dépôt PCT/PCT Filing Date: 2003/01/21  
(87) Date publication PCT/PCT Publication Date: 2003/08/07  
(85) Entrée phase nationale/National Entry: 2004/07/29  
(86) N° demande PCT/PCT Application No.: EP 2003/000516  
(87) N° publication PCT/PCT Publication No.: 2003/064385  
(30) Priorité/Priority: 2002/02/01 (102 04 115.6) DE

(51) Cl.Int.<sup>7</sup>/Int.Cl.<sup>7</sup> C07D 207/20, A01N 43/36, C07D 401/12,  
C07D 417/10, C07D 413/10

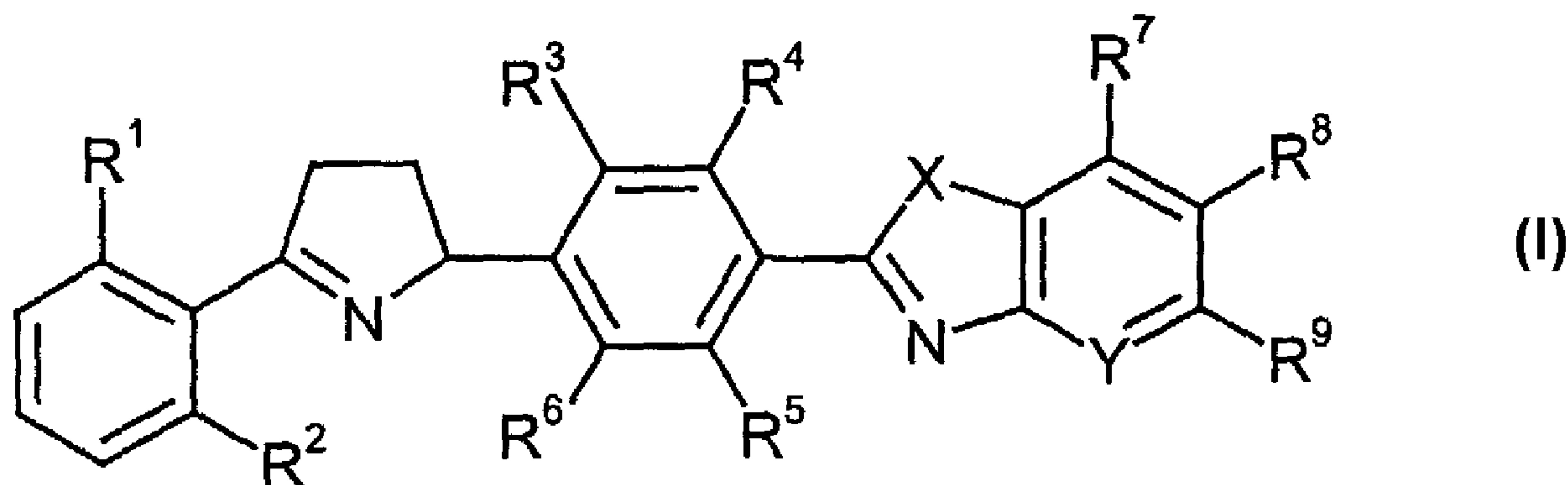
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(54) Titre : DELTA1-PYRROLINES

(54) Title: DELTA1-PYRROLINES



(57) Abrégé/Abstract:

The invention relates to novel  $\Delta^1$ -pyrrolines of formula (I), in which R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, X, Y, R<sup>7</sup>, R<sup>8</sup> and R<sup>9</sup> are defined as per the description. The invention also relates to several methods for producing said substances and to the use thereof for controlling pests, in addition to novel intermediate products and to methods for producing the latter.

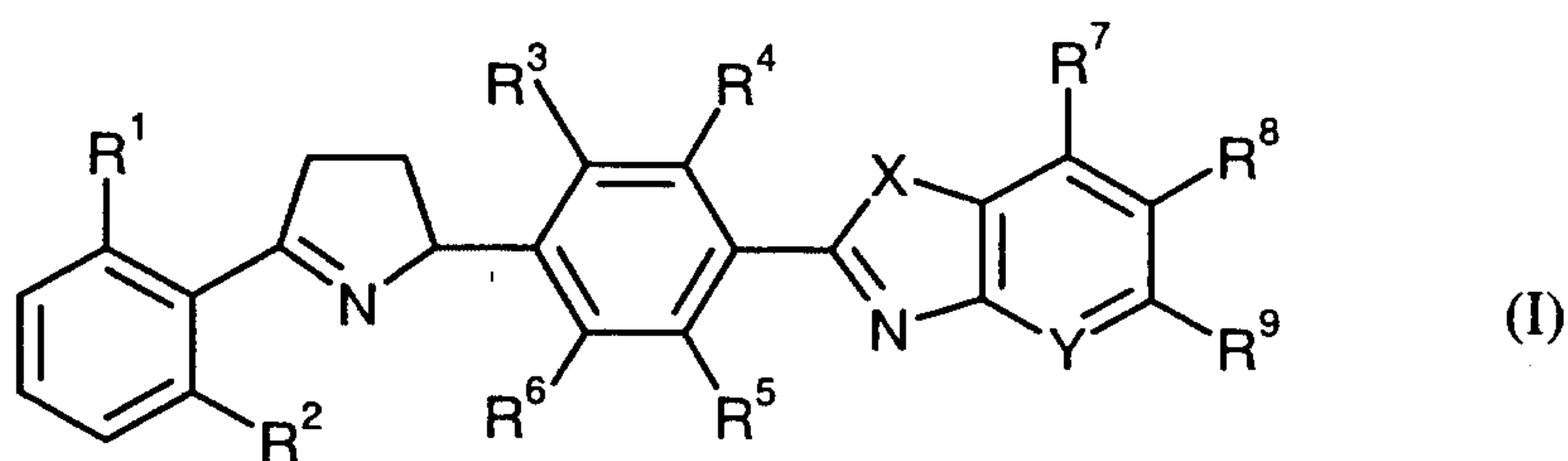


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 $\Delta^1$ -Pyrrolines

## Abstract

Novel  $\Delta^1$ -pyrrolines of the formula (I)



in which

$R^1, R^2, R^3, R^4, R^5, R^6, X, Y, R^7, R^8$  and  $R^9$  are as defined in the description,

a plurality of processes for preparing these substances and their use for controlling pests, and also novel intermediates and processes for their preparation.

$\Delta^1$ -Pyrrolines

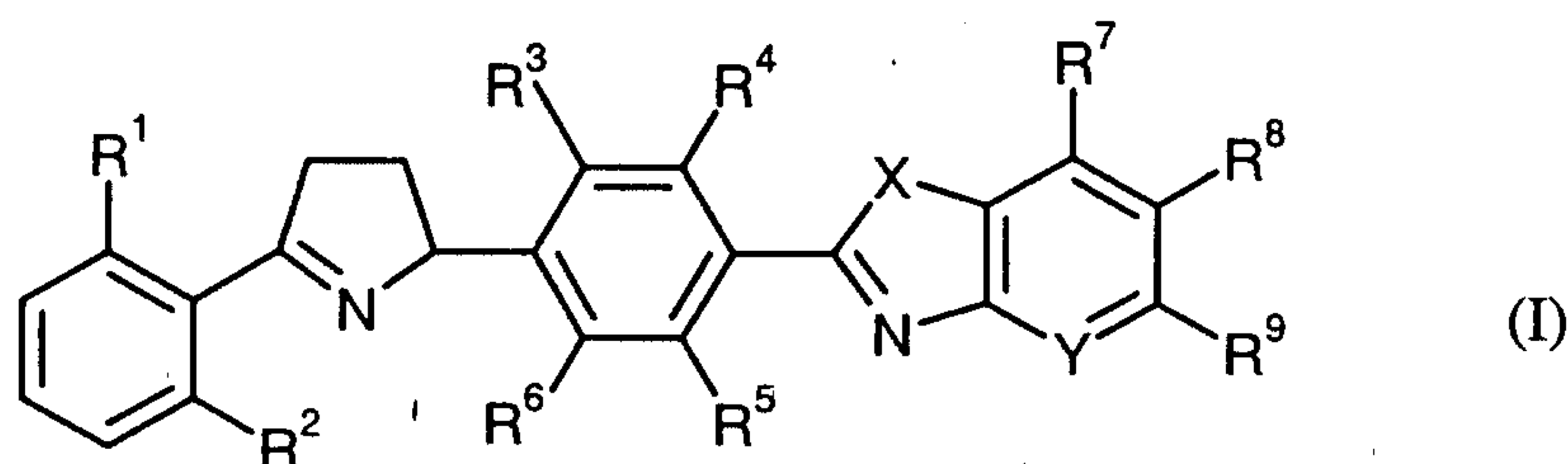
The present invention relates to novel  $\Delta^1$ -pyrrolines, to a plurality of processes for their preparation and to their use as pesticides.

5

It is already known that numerous  $\Delta^1$ -pyrrolines have insecticidal properties (cf. WO 00/21958, WO 99/59968, WO 99/59967 and WO 98/22438). The activity of these substances is good; however, in some cases it is unsatisfactory.

10

This invention now provides novel  $\Delta^1$ -pyrrolines of the formula (I)



in which

$R^1$  represents halogen or methyl,

15

$R^2$  represents hydrogen or halogen,

$R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  independently of one another represent hydrogen, halogen,  $C_1$ - $C_4$ -alkyl or  $C_1$ - $C_4$ -alkoxy,

20

X represents O (oxygen) or S (sulphur),

Y represents  $CR^{10}$  or N (nitrogen),

25

$R^7$ ,  $R^8$ ,  $R^9$  and  $R^{10}$  independently of one another represent hydrogen, halogen, nitro,  $C_1$ - $C_4$ -alkyl,  $C_1$ - $C_4$ -haloalkyl,  $C_1$ - $C_4$ -haloalkoxy,  $C_1$ - $C_4$ -haloalkylthio,  $C_1$ - $C_4$ -alkoxycarbonyl, phenyl,  $-(CH_2)_m-SO_2R^{11}$  or  $-SO_2NR^{12}R^{13}$ ,

or either  $R^7$  and  $R^8$  or  $R^8$  and  $R^9$  or  $R^9$  and  $R^{10}$  together form a further saturated or unsaturated 5- or 6-membered ring which again may contain one or two heteroatom groupings from the group consisting of N, O, S and  $SO_2$ ,

5 m represents 0 or 1,

$R^{11}$  represents  $C_1$ - $C_4$ -alkyl or morpholino,

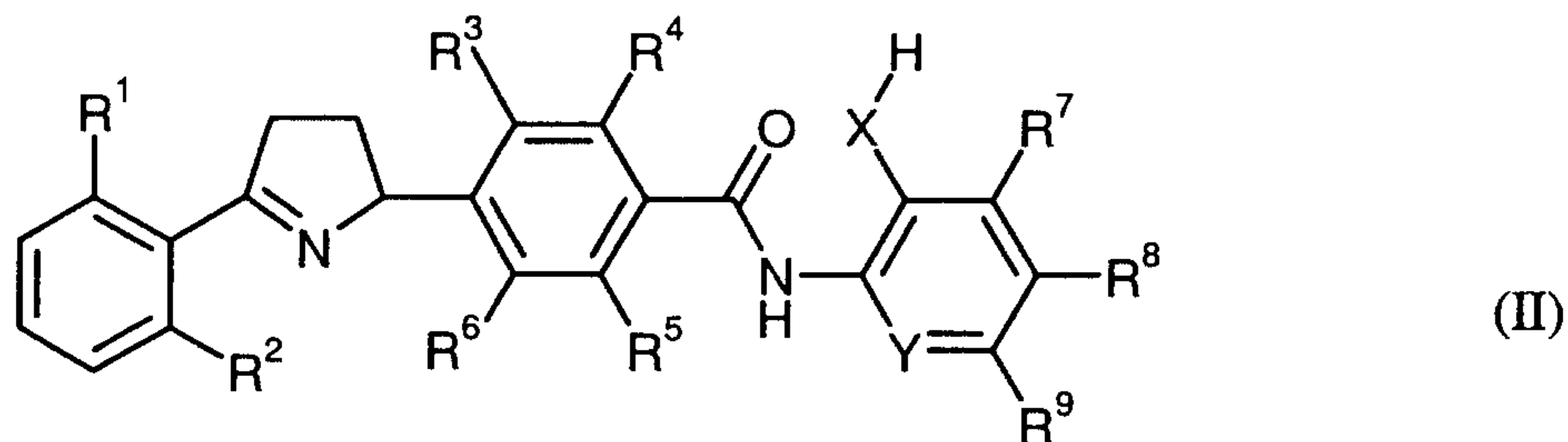
10  $R^{12}$  represents  $C_1$ - $C_4$ -alkyl or represents phenyl which is optionally mono- to tetrasubstituted by identical or different substituents from the group consisting of halogen,  $C_1$ - $C_4$ -alkyl and  $C_1$ - $C_4$ -alkoxy,

$R^{13}$  represents hydrogen or  $C_1$ - $C_4$ -alkyl.

15 Depending on the type and number of substituents, the compounds of the formula (I) may be present as geometrical and/or optical isomers or regioisomers or as mixtures of these isomers in varying composition. What is claimed by the invention are both the pure isomers and the isomer mixtures.

20 Furthermore, it has been found that the  $\Delta^1$ -pyrrolines of the formula (I) can be prepared by

A) reacting compounds of the formula (II)



25 in which

$R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $X$ ,  $Y$ ,  $R^7$ ,  $R^8$  and  $R^9$  are as defined above,

with p-toluenesulphonic acid, if appropriate in the presence of a diluent.

Finally, it has been found that the compounds of the formula (I) according to the invention have very good insecticidal properties and can be used both in crop protection and in the protection of materials for controlling unwanted pests, such as insects.

The formula (I) provides a general definition of the  $\Delta^1$ -pyrrolines according to the invention.

Preference is given to  $\Delta^1$ -pyrrolines of the formula (I) in which

$R^1$  represents fluorine, chlorine, bromine or methyl,

$R^2$  represents hydrogen, fluorine or chlorine,

$R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  independently of one another represent hydrogen, fluorine, chlorine, bromine,  $C_1$ - $C_4$ -alkyl or  $C_1$ - $C_4$ -alkoxy,

$X$  represents O (oxygen) or S (sulphur),

$Y$  represents  $CR^{10}$  or N (nitrogen),

$R^7$ ,  $R^8$ ,  $R^9$  and  $R^{10}$  independently of one another represent hydrogen, fluorine, chlorine, bromine, nitro,  $C_1$ - $C_4$ -alkyl;  $C_1$ - $C_4$ -haloalkyl,  $C_1$ - $C_4$ -haloalkoxy,  $C_1$ - $C_4$ -haloalkylthio having in each case 1 to 9 fluorine, chlorine and/or bromine atoms;  $C_1$ - $C_4$ -alkoxycarbonyl, phenyl,  $-(CH_2)_m-SO_2R^{11}$  or  $-SO_2NR^{12}R^{13}$ , or either  $R^7$  and  $R^8$  or  $R^8$  and  $R^9$  or  $R^9$  and  $R^{10}$  together form a further saturated or unsaturated 5- or 6-membered ring which again may contain one or two heteroatom groupings from the group consisting of N, O, S and  $SO_2$ ,

$m$  represents 0 or 1,

R<sup>11</sup> represents C<sub>1</sub>-C<sub>4</sub>-alkyl or morpholino,

R<sup>12</sup> represents C<sub>1</sub>-C<sub>4</sub>-alkyl or represents phenyl which is optionally mono- to tetrasubstituted by identical or different substituents from the group consisting of fluorine, chlorine, bromine, C<sub>1</sub>-C<sub>4</sub>-alkyl and C<sub>1</sub>-C<sub>4</sub>-alkoxy,

R<sup>13</sup> represents hydrogen or C<sub>1</sub>-C<sub>4</sub>-alkyl.

Particular preference is given to  $\Delta^1$ -pyrrolines of the formula (I) in which

R<sup>1</sup> represents fluorine, chlorine or methyl,

R<sup>2</sup> represents hydrogen, fluorine or chlorine,

R<sup>3</sup> and R<sup>6</sup> independently of one another represent hydrogen, fluorine, chlorine, methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl, methoxy or ethoxy,

R<sup>4</sup> and R<sup>5</sup> each represent hydrogen,

X represents O (oxygen) or S (sulphur),

Y represents CR<sup>10</sup> or N (nitrogen),

R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup> and R<sup>10</sup> independently of one another represent hydrogen, fluorine, chlorine, bromine, nitro, methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl; C<sub>1</sub>-C<sub>4</sub>-haloalkyl, C<sub>1</sub>-C<sub>4</sub>-haloalkoxy, C<sub>1</sub>-C<sub>4</sub>-haloalkylthio having in each case 1 to 9 fluorine, chlorine and/or bromine atoms; methoxycarbonyl, ethoxycarbonyl, phenyl, -(CH<sub>2</sub>)<sub>m</sub>-SO<sub>2</sub>R<sup>11</sup> or -SO<sub>2</sub>NR<sup>12</sup>R<sup>13</sup>,

or either R<sup>7</sup> and R<sup>8</sup> or R<sup>8</sup> and R<sup>9</sup> or R<sup>9</sup> and R<sup>10</sup> together form a further saturated or unsaturated 5- or 6-membered ring which again may contain one or two heteroatom groupings from the group consisting of N, O, S and SO<sub>2</sub>,

m represents 0 or 1,

R<sup>11</sup> represents methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl or morpholino,

5

R<sup>12</sup> represents methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl or represents phenyl which is optionally mono- to trisubstituted by identical or different substituents from the group consisting of fluorine, chlorine, bromine, methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl, methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, i-butoxy, s-butoxy, t-butoxy,

10

R<sup>13</sup> represents hydrogen or methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl.

15 Very particular preference is given to  $\Delta^1$ -pyrrolines of the formula (I) in which

R<sup>1</sup> represents fluorine, chlorine or methyl,

R<sup>2</sup> represents hydrogen, fluorine or chlorine,

20

R<sup>3</sup> represents hydrogen, fluorine, chlorine, methyl, methoxy or ethoxy,

R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each represent hydrogen,

25 X represents O (oxygen),

Y represents CR<sup>10</sup> or N (nitrogen),

30 R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup> and R<sup>10</sup> independently of one another represent hydrogen, fluorine, chlorine, bromine, nitro, methyl, i-propyl, t-butyl, trifluoromethyl, trifluoromethoxy, trifluoromethylthio, methoxycarbonyl, phenyl, -SO<sub>2</sub>-morpholino,

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-CH<sub>2</sub>SO<sub>2</sub>Me, -SO<sub>2</sub>NHMe, -SO<sub>2</sub>NMe<sub>2</sub>, -SO<sub>2</sub>NH-(3,4-dichlorophenyl) or -SO<sub>2</sub>NH-(2-methoxyphenyl).

5 Preference is furthermore given to  $\Delta^1$ -pyrrolines of the formula (I) in which R<sup>1</sup> and R<sup>2</sup> represent fluorine.

Preference is furthermore given to  $\Delta^1$ -pyrrolines of the formula (I) in which Y represents CR<sup>10</sup> and particularly preferably represents CH.

Preference is furthermore given to  $\Delta^1$ -pyrrolines of the formula (I) in which R<sup>3</sup> represents hydrogen or fluorine.

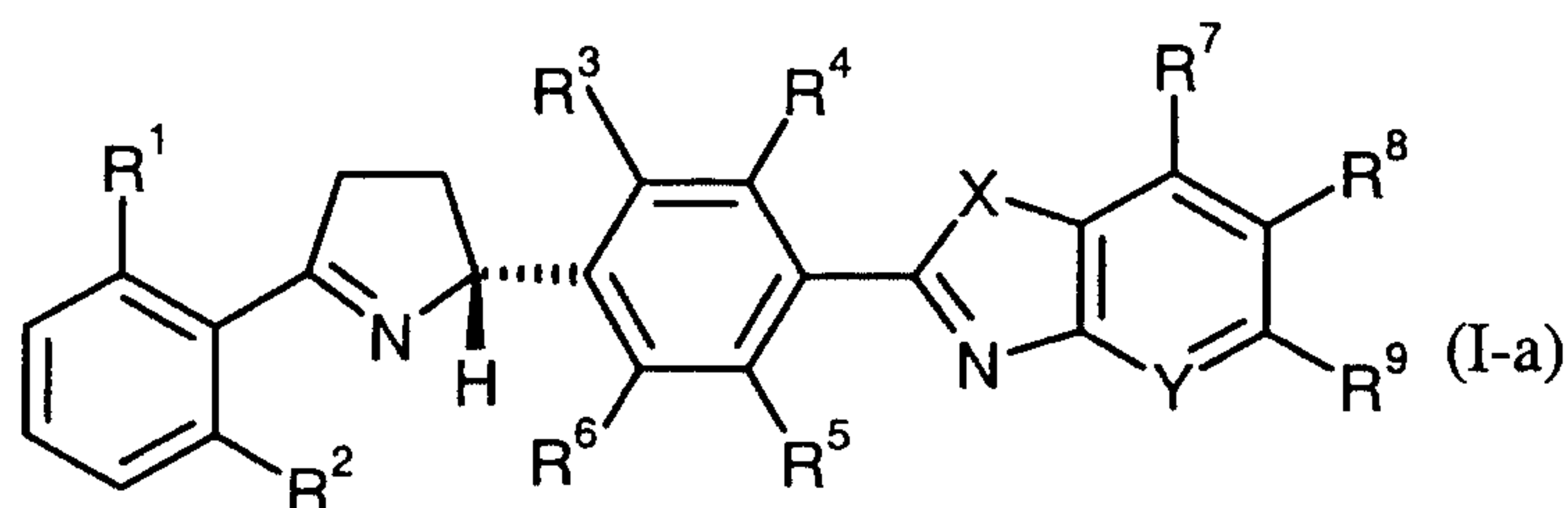
10 Preference is furthermore given to  $\Delta^1$ -pyrrolines of the formula (I) in which X represents O (oxygen).

Preference is furthermore given to  $\Delta^1$ -pyrrolines of the formula (I) in which X represents S (sulphur).

15 Preference is furthermore given to  $\Delta^1$ -pyrrolines of the formula (I) in which R<sup>4</sup> and R<sup>5</sup> represent hydrogen.

Preference is furthermore given to  $\Delta^1$ -pyrrolines of the formula (I) in which R<sup>1</sup> and R<sup>2</sup> represent fluorine, X represents O (oxygen) and Y represents CH.

Very particular preference is given to (R)-configured compounds of the formula (I-a)



20

in which

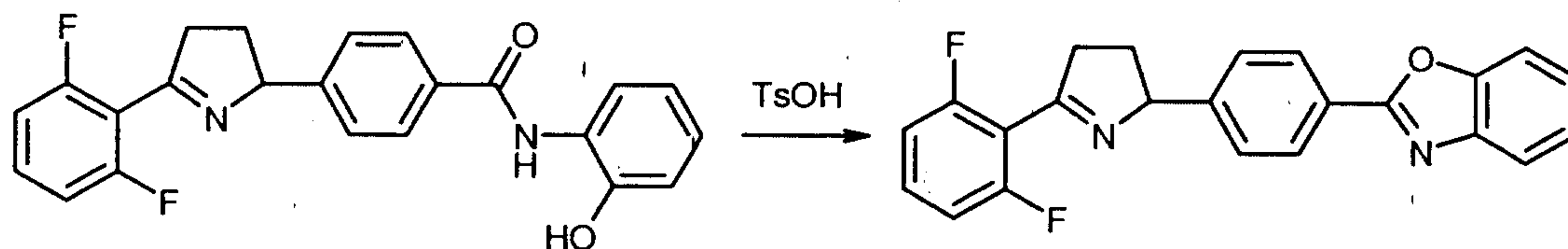
R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, X, Y, R<sup>7</sup>, R<sup>8</sup> and R<sup>9</sup> are as defined above.

25 Compounds of the formula (I-a) are obtained by customary processes for optical resolution, such as, for example, by chromatography of the corresponding racemates on a chiral stationary phase. In this manner, it is possible to resolve both racemic end products and racemic intermediates into the two enantiomers.

As far as this is possible, saturated hydrocarbon radicals, such as alkyl, can in each case be straight-chain or branched.

However, the general or preferred radical definitions or illustrations listed above can also be combined with one another, i.e. between the respective ranges and preferred ranges. The definitions apply both to the end products and, correspondingly to precursors and intermediates.

Using 4-[5-(2,6-difluorophenyl)-3,4-dihydro-2H-pyrrol-2-yl]-N-(2-hydroxy-phenyl)benzamide as starting material in the presence of p-toluenesulphonic acid (TsOH), the course of the process (A) according to the invention can be illustrated by the formula scheme below.



## 15 Explanation of the processes and intermediates

### Process (A)

The formula (II) provides a general definition of the starting materials required for carrying out the process (A) according to the invention. In this formula,  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ , X, Y,  $R^7$ ,  $R^8$  and  $R^9$  preferably, particularly preferably and very particularly preferably have those meanings which have already been mentioned in connection with the description of the compounds of the formula (I) according to the invention as being preferred, particularly preferred, etc., for these radicals.

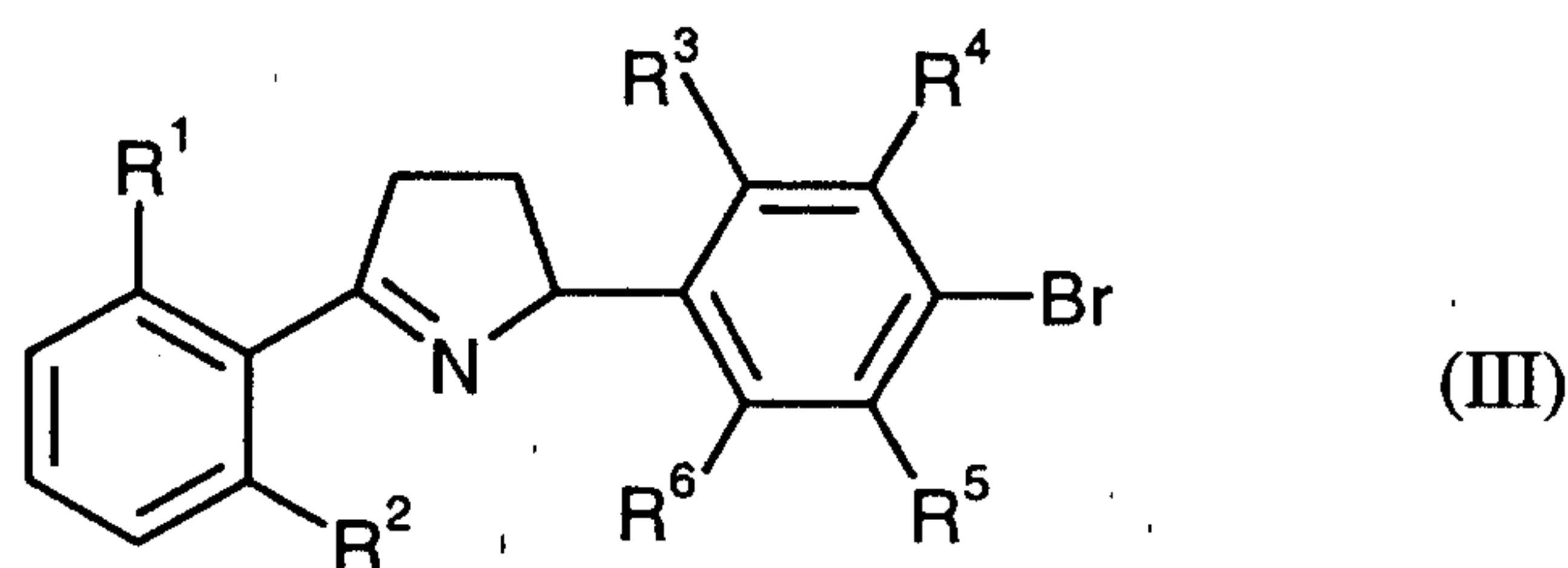
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The compounds of the formula (II) are novel. They also have insecticidal action (cf. the Use Examples).

Compounds of the formula (II) can be prepared by

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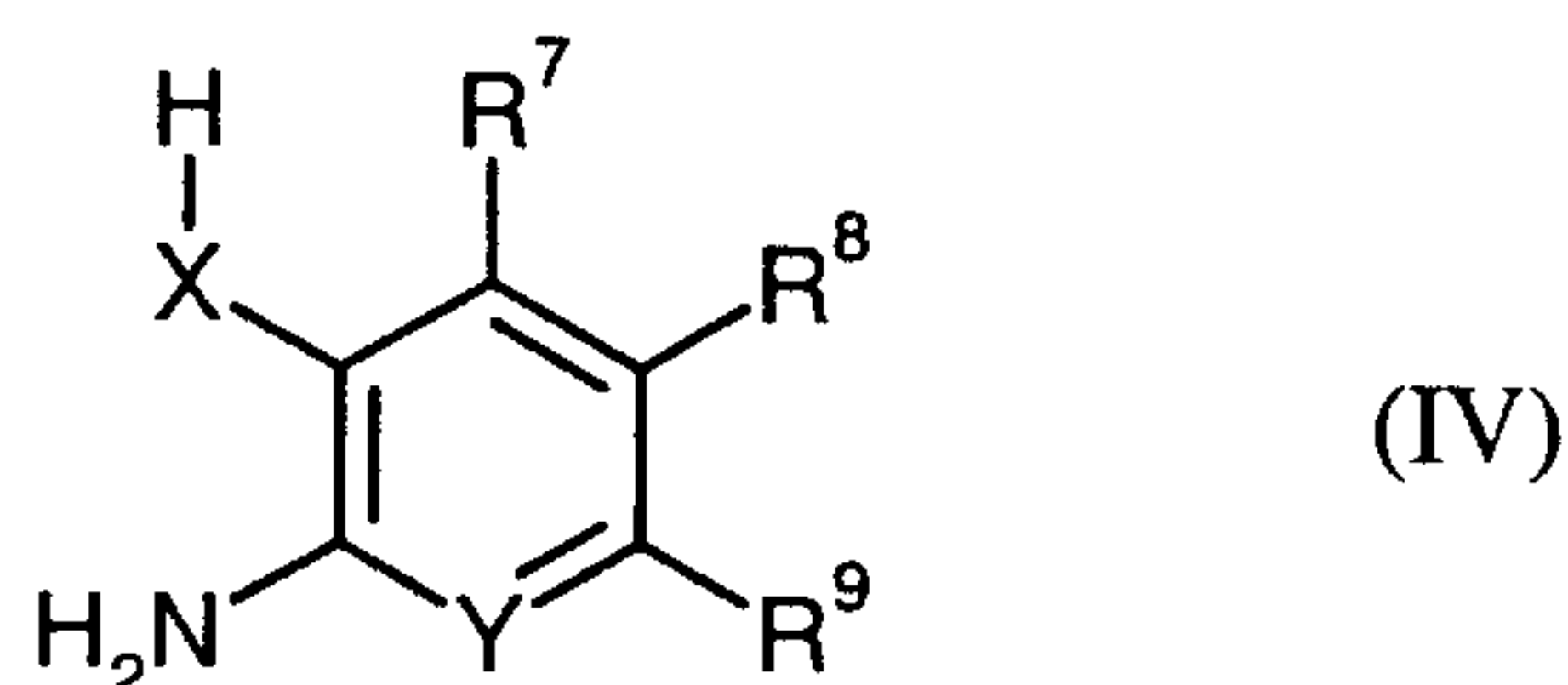
a) reacting  $\Delta^1$ -pyrrolines of the formula (III)



in which

5  $R^1, R^2, R^3, R^4, R^5$  and  $R^6$  are as defined above,

with an aniline derivative of the formula (IV)



in which

10

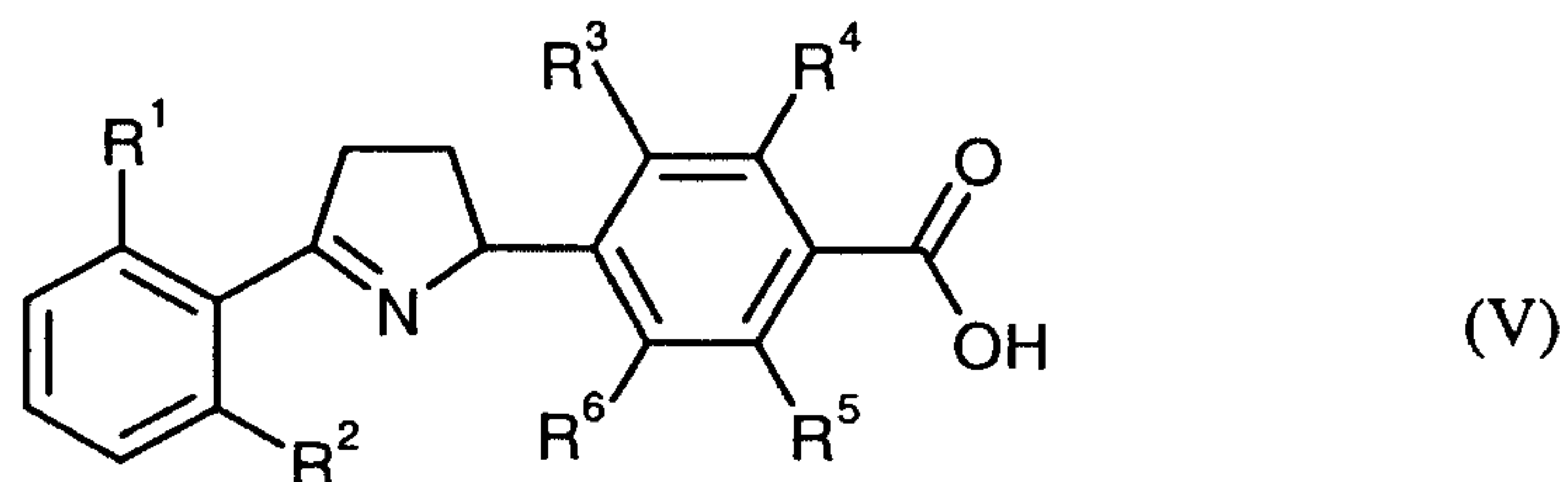
$X, Y, R^7, R^8$  and  $R^9$  are as defined above,

in the presence of carbon monoxide, if appropriate in the presence of a diluent (for example toluene or dimethylformamide), if appropriate in the presence of an acid binder (for example 1,8-diazabicyclo[5.4.0]undec-7-ene, DBU) and, if appropriate, in the presence of a catalyst (for example  $PdCl_2/PPh_3/dppp$  [ $dppp$  = 1,3-bis(diphenylphosphino)propane]),

15

or

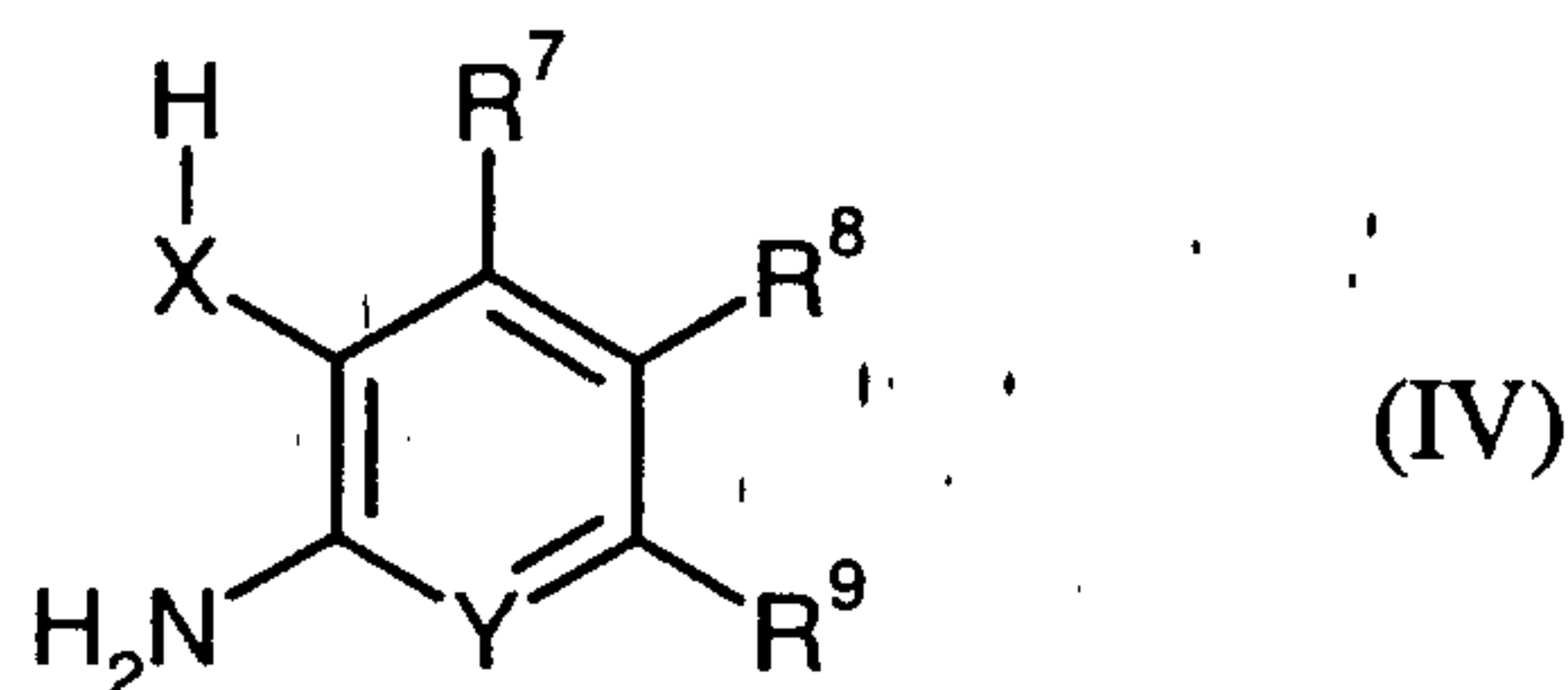
20 b) reacting  $\Delta^1$ -pyrrolines of the formula (V)



in which

$R^1, R^2, R^3, R^4, R^5$  and  $R^6$  are as defined above,

with an aniline derivative of the formula (IV)



5 in which

$X, Y, R^7, R^8$  and  $R^9$  are as defined above,

10 if appropriate in the presence of a base (for example diisopropylethylamine = Hünig's base) and, if appropriate, in the presence of a reaction auxiliary (for example bis-(2-oxo-oxazolidinyl)phosphoryl chloride = BOP-Cl) and, if appropriate, in the presence of a diluent.

15 The formula (III) provides a general definition of the  $\Delta^1$ -pyrrolines required as starting materials for carrying out the process (a) according to the invention. In this formula,  $R^1, R^2, R^3, R^4, R^5$  and  $R^6$  preferably, particularly preferably and very particularly preferably have those meanings which have already been mentioned in connection with the description of the compounds of the formula (I) according to the invention as being preferred, particularly preferred, etc., for these radicals.

20

$\Delta^1$ -Pyrrolines of the formula (III) are known and/or can be prepared by known processes (cf. WO 98/22438 and DE10047109.9).

25 The formula (V) provides a general definition of the  $\Delta^1$ -pyrrolines required as starting materials for carrying out the process (b) according to the invention. In this formula,  $R^1, R^2, R^3, R^4, R^5$  and  $R^6$  preferably, particularly preferably and very particularly preferably have those meanings which have already been mentioned in connection with the description of the compounds of the formula (I) according to the invention as being preferred, particularly preferred, etc., for these radicals.

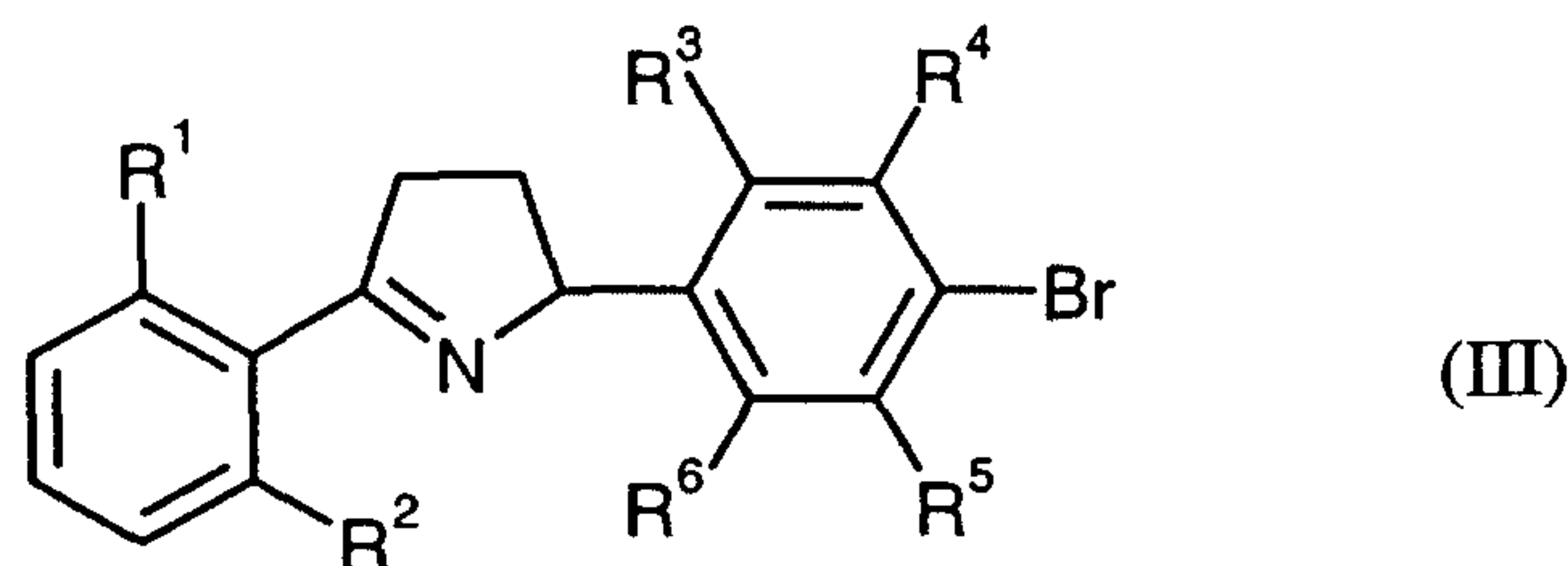
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$\Delta^1$ -Pyrrolines of the formula (V) are known and/or can be prepared by known processes (cf. WO 98/22438 and DE10047109.9).

$\Delta^1$ -Pyrrolines of the formula (V) can also be prepared by

5

c) reacting  $\Delta^1$ -pyrrolines of the formula (III)



in which

10

$R^1, R^2, R^3, R^4, R^5$  and  $R^6$  are as defined above,

in a first step with an alcohol of the formula (VI)



in which

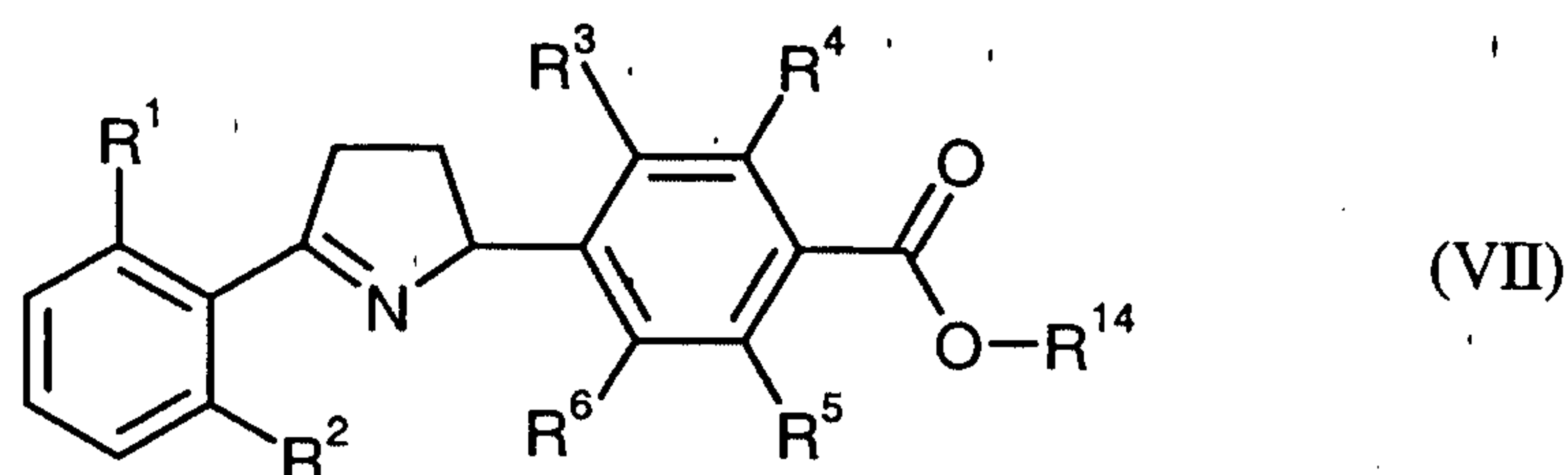
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$R^{14}$  represents  $C_2$ - $C_6$ -alkyl, preferably  $C_2$ - $C_4$ -alkyl, particularly preferably ethyl or n-butyl, very particularly preferably n-butyl,

20

in the presence of carbon monoxide, in the presence of a base (for example diisopropylethylamine) and in the presence of a catalyst (for example  $PdCl_2/PPh_3/dppp$ )

and, in a second step, hydrolyzing the resulting  $\Delta^1$ -pyrrolines of the formula (VII)



in which

R<sup>14</sup> is as defined above

5

in the presence of an acid (for example 20% strength HCl) and, if appropriate,  
in the presence of a diluent (for example ethylene glycol dimethyl ether).

10 The formula (IV) provides a general definition of the aniline derivatives required as  
starting materials for carrying out the processes (a) and (b) according to the  
invention. In this formula, X, Y', R<sup>7</sup>, R<sup>8</sup> and R<sup>9</sup> preferably, particularly preferably and  
very particularly preferably have those meanings which have already been mentioned  
in connection with the description of the compounds of the formula (I) according to  
the invention as being preferred, particularly preferred, etc., for these radicals.

15

Aniline derivatives of the formula (IV) are known and/or can be prepared by known  
processes.

20 Aniline derivatives of the formula (IV) can be prepared, for example, from the  
analogous nitroaryl compounds (cf. WO 99/32436). The reduction of the nitro group  
to the amine is carried out either by using a metal catalyst (for example Ni, Pd, Pt) in  
the presence of hydrogen or a hydride donor (for example formate, cyclohexadiene,  
borohydride) (cf. Rylander: Hydrogenation Methods; Academic Press, London 1985).  
Nitroaryls can also be reduced directly by employing a strong hydride source (for  
25 example LiAlH<sub>4</sub>, cf. Seyden-Penne: Reductions by the Alumino- and Borohydrides in  
Organic Synthesis; VCH Publishers, New York 1991) or by using a zerovalent metal  
(for example Fe, Sn, Ca), if appropriate in the presence of an acid. The nitroaryl

compounds are obtained by known processes (cf. March: Advanced Organic Chemistry, 3<sup>rd</sup> Ed., John Wiley, New York 1985).

5 The  $\Delta^1$ -pyrrolines of the formula (III) required as starting materials for carrying out the process (c) according to the invention have already been described above.

The alcohols of the formula (VI) required as starting materials for carrying out the process (c) according to the invention are known.

10 Suitable diluents for carrying out the process (A) according to the invention are all customary inert organic solvents. Preference is given to using optionally halogenated aliphatic, alicyclic or aromatic hydrocarbons, such as petroleum ether, hexane, heptane, cyclohexane, methylcyclohexane, benzene, toluene, xylene or decalin; chlorobenzene, dichlorobenzene, dichloromethane, chloroform, carbon tetrachloride, 15 dichloroethane or trichloroethane; ethers, such as diethyl ether, diisopropyl ether, methyl tert-butyl ether, methyl tert-amyl ether, dioxane, tetrahydrofuran, 1,2-dimethoxyethane, 1,2-diethoxyethane or anisole; nitriles, such as acetonitrile, propionitrile, n- or isobutyronitrile or benzonitrile; amides, such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methylformanilide, N-methylpyrrolidone or 20 hexamethylphosphoric triamide; esters, such as methyl acetate or ethyl acetate; sulfoxides, such as dimethyl sulphoxide; or sulphones, such as sulfolane. Particular preference is given to using acetone, dimethoxyethane, dioxane, tetrahydrofuran, dimethylformamide, dimethylacetamide, dimethyl sulphoxide, ethanol, toluene or, if appropriate, mixtures of the diluents mentioned with water. Particular 25 preference is given to using toluene or benzene.

When carrying out the process (A) according to the invention, the reaction temperatures can be varied within a relatively wide range. In general, the process is carried out at temperatures between 0°C and 140°C, preferably between 20°C and 30 120°C, particularly preferably between 80°C and 120°C.

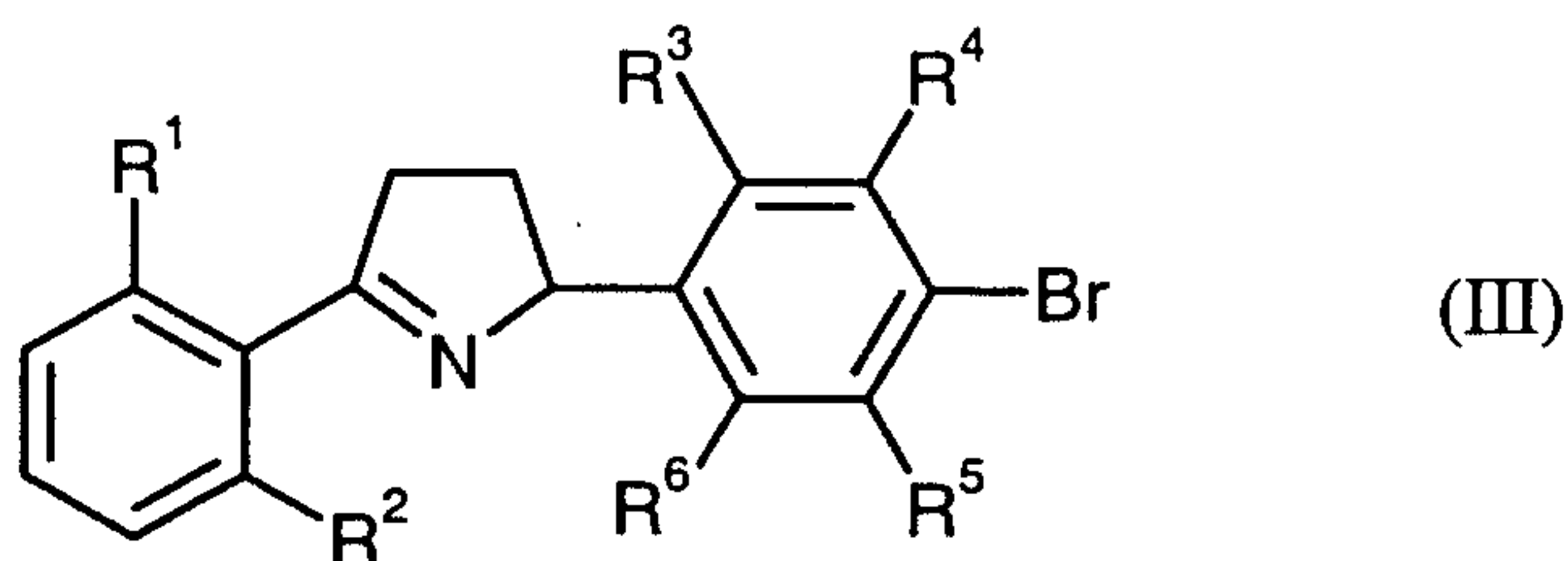
All of the processes according to the invention are generally carried out under atmospheric pressure. However, in each case it is also possible to operate under elevated or reduced pressure.

5 When carrying out the process (A) according to the invention, in general from 2 to 4 mol of p-toluenesulphonic acid are employed per mole of the compound of the formula (II). However, it is also possible to employ the reaction components in other ratios. Work-up is carried out by customary methods. In general, the reaction mixture is diluted and extracted with an organic solvent. The organic phase is washed, dried,  
 10 filtered and concentrated. If appropriate, the residue is freed of any impurities that may still be present using customary methods, such as chromatography or recrystallization.

Chiral compounds of the formula (I-a)

15

To produce chiral compounds of the formula (I-a), it is possible, for example, to subject the  $\Delta^1$ -pyrrolines, used as intermediates, of the formula (III)



20 in which

$R^1, R^2, R^3, R^4, R^5$  and  $R^6$  are as defined above,

25 to an optical resolution. This is effected, for example, using methods of preparative chromatography, preferably the High Performance Liquid Chromatography (HPLC) method. For this purpose, a chiral stationary silica gel phase is used. A tris-(3,5-dimethylphenylcarbamate) cellulose-modified silica gel has been found to be particularly suitable for separating the compounds of the formula (III) into the two

enantiomers. This separation material is commercially available. However, it is also possible to use other stationary phases. Suitable eluents are all customary inert organic solvents, and mixtures of these. Preference is given to using optionally halogenated aliphatic, alicyclic or aromatic hydrocarbons, such as petroleum ether, hexane, heptane, cyclohexane; dichloromethane, chloroform; alcohols, such as methanol, ethanol, propanol; nitriles, such as acetonitrile; esters, such as methyl acetate or ethyl acetate. Particular preference is given to using aliphatic hydrocarbons, such as hexane or heptane, and alcohols, such as methanol or propanol, very particularly preferably n-heptane and isopropanol, or mixtures of these. In general, this is effected at temperatures between 10°C and 60°C, preferably between 10°C and 40°C, particularly preferably at room temperature. The (R)-configured enantiomers obtained in this manner are then used as starting materials for process (a) or (c).

The active compounds, having good plant tolerance, favourable homeotherm toxicity and good environmental compatibility, are suitable for protecting plants and plant organs, for increasing harvest yields, for improving the quality of the harvested produce and for controlling animal pests, in particular insects, arachnids and nematodes, which are encountered in agriculture, in forests, in gardens and leisure facilities, in the protection of stored products and of materials, and in the hygiene sector. They are preferably used as crop protection agents. They are active against normally sensitive and resistant species and against all or some stages of development. The abovementioned pests include:

From the order of the Isopoda, for example, *Oniscus asellus*, *Armadillidium vulgare* and *Porcellio scaber*.

From the order of the Diplopoda, for example, *Blaniulus guttulatus*.

From the order of the Chilopoda, for example, *Geophilus carpophagus* and *Scutigera* spp.

From the order of the Symphyla, for example, *Scutigera immaculata*.

From the order of the Thysanura, for example, *Lepisma saccharina*.

From the order of the Collembola, for example, *Onychiurus armatus*.

- From the order of the Orthoptera, for example, *Acheta domesticus*, *Gryllotalpa* spp., *Locusta migratoria migratorioides*, *Melanoplus* spp. and *Schistocerca gregaria*.
- From the order of the Blattaria, for example, *Blatta orientalis*, *Periplaneta americana*, *Leucophaea maderae* and *Blattella germanica*.
- 5 From the order of the Dermaptera, for example, *Forficula auricularia*.
- From the order of the Isoptera, for example, *Reticulitermes* spp.
- From the order of the Phthiraptera, for example, *Pediculus humanus corporis*, *Haematopinus* spp., *Linognathus* spp., *Trichodectes* spp. and *Damalinia* spp.
- 10 From the order of the Thysanoptera, for example, *Hercinothrips femoralis*, *Thrips tabaci*, *Thrips palmi* and *Frankliniella accidentalis*.
- From the order of the Heteroptera, for example, *Eurygaster* spp., *Dysdercus intermedius*, *Piesma quadrata*, *Cimex lectularius*, *Rhodnius prolixus* and *Triatoma* spp.
- 15 From the order of the Homoptera, for example, *Aleurodes brassicae*, *Bemisia tabaci*, *Trialeurodes vaporariorum*, *Aphis gossypii*, *Brevicoryne brassicae*, *Cryptomyzus ribis*, *Aphis fabae*, *Aphis pomi*, *Eriosoma lanigerum*, *Hyalopterus arundinis*, *Phylloxera vastatrix*, *Pemphigus* spp., *Macrosiphum avenae*, *Myzus* spp., *Phorodon humuli*, *Rhopalosiphum padi*, *Empoasca* spp., *Euscelis bilobatus*, *Nephotettix cincticeps*, *Lecanium corni*, *Saissetia oleae*, *Laodelphax striatellus*, *Nilaparvata*
- 20 *lugens*, *Aonidiella aurantii*, *Aspidiotus hederae*, *Pseudococcus* spp. and *Psylla* spp.
- From the order of the Lepidoptera, for example, *Pectinophora gossypiella*, *Bupalus piniarius*, *Cheimatobia brumata*, *Lithocolletis blancardella*, *Hyponomeuta padella*, *Plutella xylostella*, *Malacosoma neustria*, *Euproctis chrysorrhoea*, *Lymantria* spp., *Bucculatrix thurberiella*, *Phyllocnistis citrella*, *Agrotis* spp., *Euxoa* spp., *Feltia* spp.,
- 25 *Earias insulana*, *Heliothis* spp., *Mamestra brassicae*, *Panolis flammea*, *Spodoptera* spp., *Trichoplusia ni*, *Carpocapsa pomonella*, *Pieris* spp., *Chilo* spp., *Pyrausta nubilalis*, *Ephestia kuehniella*, *Galleria mellonella*, *Tineola bisselliella*, *Tinea pellionella*, *Hofmannophila pseudospretella*, *Cacoecia podana*, *Capua reticulana*, *Choristoneura fumiferana*, *Clysia ambiguella*, *Homona magnanima*, *Tortrix viridana*,
- 30 *Cnaphalocerus* spp. and *Oulema oryzae*.
- From the order of the Coleoptera, for example, *Anobium punctatum*, *Rhizopertha dominica*, *Bruchidius obtectus*, *Acanthoscelides obtectus*, *Hylotrupes bajulus*,

Agelastica alni, Leptinotarsa decemlineata, Phaedon cochleariae, Diabrotica spp.,  
 Psylliodes chrysocephala, Epilachna varivestis, Atomaria spp., Oryzaephilus  
 surinamensis, Anthonomus spp., Sitophilus spp., Otiorrhynchus sulcatus,  
 5 Cosmopolites sordidus, Ceuthorrhynchus assimilis, Hypera postica, Dermestes spp.,  
 Trogoderma spp., Anthrenus spp., Attagenus spp., Lyctus spp., Meligethes aeneus,  
 Ptinus spp., Niptus hololeucus, Gibbium psylloides, Tribolium spp., Tenebrio  
 molitor, Agriotes spp., Conoderus spp., Melolontha melolontha, Amphimallon solsti-  
 tialis, Costelytra zealandica and Lissorhoptrus oryzophilus.

From the order of the Hymenoptera, for example, Diprion spp., Hoplocampa spp.,  
 10 Lasius spp., Monomorium pharaonis and Vespa spp.

From the order of the Diptera, for example, Aedes spp., Anopheles spp., Culex spp.,  
 Drosophila melanogaster, Musca spp., Fannia spp., Calliphora erythrocephala,  
 Lucilia spp., Chrysomyia spp., Cuterebra spp., Gastrophilus spp., Hyppobosca spp.,  
 Stomoxys spp., Oestrus spp., Hypoderma spp., Tabanus spp., Tannia spp., Bibio  
 15 hortulanus, Oscinella frit, Phorbia spp., Pegomyia hyoscyami, Ceratitis capitata,  
 Dacus oleae, Tipula paludosa, Hylemyia spp. and Liriomyza spp.

From the order of the Siphonaptera, for example, Xenopsylla cheopis and  
 Ceratophyllus spp.

From the class of the Arachnida, for example, Scorpio maurus, Latrodectus mactans,  
 20 Acarus siro, Argas spp., Ornithodoros spp., Dermanyssus gallinae, Eriophyes ribis,  
 Phyllocoptruta oleivora, Boophilus spp., Rhipicephalus spp., Amblyomma spp.,  
 Hyalomma spp., Ixodes spp., Psoroptes spp., Chorioptes spp., Sarcoptes spp.,  
 Tarsonemus spp., Bryobia praetiosa, Panonychus spp., Tetranychus spp.,  
 Hemitarsonemus spp. and Brevipalpus spp.

25 The plant-parasitic nematodes include, for example, Pratylenchus spp., Radopholus  
 similis, Ditylenchus dipsaci, Tylenchulus semipenetrans, Heterodera spp., Globodera  
 spp., Meloidogyne spp., Aphelenchoides spp., Longidorus spp., Xiphinema spp.,  
 Trichodorus spp. and Bursaphelenchus spp.

30 The compounds of the formula (I) according to the invention are particularly  
 effective against caterpillars, beetle larvae, spider mites, aphids and leaf-mining flies.

The compounds according to the invention additionally also have very good persistency, such as, for example, against the caterpillars of the cotton budworm (*Heliothis virescens*) or the caterpillars of the armyworm (*Spodoptera frugiperda*).

5 At certain concentrations or application rates, the compounds according to the invention may, if appropriate, also be used as herbicides and microbicides, for example as fungicides, antimycotics and bactericides. If appropriate, they may also be used as intermediates or precursors for the synthesis of further active compounds.

10 All plants and plant parts can be treated in accordance with the invention. Plants are to be understood as meaning in the present context all plants and plant populations such as desired and undesired wild plants or crop plants (inclusive of naturally occurring crop plants). Crop plants can be plants which can be obtained by conventional plant breeding and optimization methods or by biotechnological and  
15 recombinant methods or by combinations of these methods, inclusive of the transgenic plants and inclusive of the plant cultivars protectable or not protectable by plant breeders' rights. Plant parts are to be understood to mean all above-ground and underground parts and organs of plants, such as shoot, leaf, flower and root, examples which may be mentioned being leaves, needles, stalks, stems, flowers, fruit  
20 bodies, fruits, seeds, roots, tubers and rhizomes. The plant parts also include harvested material, and vegetative and generative propagation material, for example cuttings, tubers, rhizomes, offsets and seeds.

Treatment according to the invention of the plants and plant parts with the active  
25 compounds is carried out directly or by allowing the compounds to act on their surroundings, environment or storage space by the customary treatment methods, for example by immersion, spraying, evaporation, fogging, scattering, painting on and, in the case of propagation material, in particular in the case of seeds, also by applying one or more coats.

30

The active compounds can be converted into the customary formulations, such as solutions, emulsions, wettable powders, suspensions, powders, dusts, pastes, soluble

powders, granules, suspension-emulsion concentrates, natural and synthetic materials impregnated with active compound, and microencapsulations in polymeric substances.

5 These formulations are produced in a known manner, for example by mixing the active compounds with extenders, that is liquid solvents and/or solid carriers, optionally with the use of surfactants, that is emulsifiers and/or dispersants, and/or foam-formers.

10 If the extender used is water, it is also possible to employ for example organic solvents as auxiliary solvents. Essentially, suitable liquid solvents are: aromatics such as xylene, toluene or alkylnaphthalenes, chlorinated aromatics or chlorinated aliphatic hydrocarbons such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons such as cyclohexane or paraffins, for example petroleum fractions, mineral and vegetable oils, alcohols such as butanol or glycol and also their ethers and esters, ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone or  
15 cyclohexanone, strongly polar solvents such as dimethylformamide and dimethyl sulphoxide, and also water.

Suitable solid carriers are:

for example ammonium salts and ground natural minerals such as kaolins, clays, talc,  
20 chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as finely divided silica, alumina and silicates; suitable solid carriers for granules are: for example crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, and also synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize  
25 cobs and tobacco stalks; suitable emulsifiers and/or foam-formers are: for example nonionic and anionic emulsifiers, such as polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkylsulphonates, alkyl sulphates, arylsulphonates and also protein hydrolysates; suitable dispersants are: for example liginosulphite waste liquors and methylcellulose.

30

Tackifiers such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and

polyvinyl acetate, as well as natural phospholipids such as cephalins and lecithins, and synthetic phospholipids, can be used in the formulations. Other additives can be mineral and vegetable oils.

5 It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic dyes, such as alizarin dyes, azo dyes and metal phthalocyanine dyes, and trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

10 The formulations generally comprise between 0.1 and 95% by weight of active compound, preferably between 0.5 and 90%.

The active compounds according to the invention can be used as such or in their formulations as a mixture with known fungicides, bactericides, acaricides, nematocides  
15 or insecticides in order to extend the spectrum of activity or prevent resistances developing. In many cases, synergistic effects are thus obtained, ie. the efficacy of the mixture is greater than the efficacy of the individual components.

Examples of co-components in mixtures are the following compounds:

20

**Fungicides:**

aldimorph, ampropylfos, ampropylfos-potassium, andoprim, anilazine, azaconazole, azoxystrobin,  
benalaxyl, benodanil, benomyl, benzamacril, benzamacril-isobutyl, bialaphos,  
25 binapacryl, biphenyl, bitertanol, blasticidin-S, bromuconazole, bupirimate, buthiobate,  
calcium polysulphide, carpropamide, capsimycin, captafol, captan, carbendazim, carboxin, carvon, quinomethionate, chlobenthiazone, chlorfenazole, chloroneb, chloropicrin, chlorothalonil, chlozolate, clozylacon, cufraneb, cymoxanil,  
30 cyproconazole, cyprodinil, cyprofuram,  
debacarb, dichlorophen, diclobutrazole, diclofluanid, diclomezine, dicloran, diethofencarb, difenoconazole, dimethirimol, dimethomorph, diniconazole,

diniconazole-M, dinocap, diphenylamine, dipyrithione, ditalimfos, dithianon,  
 dodemorph, dodine, drazoxolon,  
 edifenphos, epoxiconazole, etaconazole, ethirimol, etridiazole,  
 famoxadon, fenapanil, fenarimol, fenbuconazole, fenfuram, fenitropan, fenciclonil,  
 5 fenpropidin, fenpropimorph, fentin acetate, fentin hydroxide, ferbam, ferimzone,  
 fluazinam, flumetover, fluoromide, fluquinconazole, flurprimidol, flusilazole,  
 flusulfamide, flutolanil, flutriafol, folpet, fosetyl-aluminium, fosetyl-sodium, fthalide,  
 fuberidazole, furalaxyl, furametpyr, furcarbonil, furconazole, furconazole-cis,  
 furnecyclox,  
 10 guazatine,  
 hexachlorobenzene, hexaconazole, hymexazole,  
 imazalil, imibenconazole, iminoctadine, iminoctadine albesilate, iminoctadine  
 triacetate, iodocarb, ipconazole, iprobenfos (IBP), iprodione, iprovalicarb,  
 irumamycin, isoprothiolane, isovaledione,  
 15 kasugamycin, kresoxim-methyl, copper preparations, such as: copper hydroxide,  
 copper naphthenate, copper oxychloride, copper sulphate, copper oxide, oxine-copper  
 and Bordeaux mixture,  
 mancopper, mancozeb, maneb, meferimzone, mepanipyrim, mepronil, metalaxyl,  
 metconazole, methasulfocarb, methfuroxam, metiram, metomeclam, metsulfovax,  
 20 mildiomyacin, myclobutanil, myclozolin,  
 nickel dimethyldithiocarbamate, nitrothal-isopropyl, nuarimol,  
 ofurace, oxadixyl, oxamocarb, oxolinic acid, oxycarboxim, oxyfenthiin,  
 paclobutrazole, pefurazoate, penconazole, pencycuron, phosdiphen, picoxystrobin,  
 pimaricin, piperalin, polyoxin, polyoxorim, probenazole, prochloraz, procymidone,  
 25 propamocarb, propanosine-sodium, propiconazole, propineb, pyraclostrobin,  
 pyrazophos, pyrifenoxy, pyrimethanil, pyroquilon, pyroxyfur,  
 quinconazole, quintozone (PCNB), quinoxifen,  
 sulphur and sulphur preparations, spiroxamines,  
 tebuconazole, tecloftalam, tecnazene, tetcyclacis, tetraconazole, thiabendazole,  
 30 thicyofen, thifluzamide, thiophanate-methyl, thiram, tioxyimid, tolclofos-methyl,  
 tolylfluanid, triadimefon, triadimenol, triazbutil, triazoxide, trichlamide, tricyclazole,  
 tridemorph, trifloxystrobin, triflumizole, triforine, triticonazole,

uniconazole,

validamycin A, vinclozolin, viniconazole,

zarilamide, zineb, ziram and also

Dagger G,

5 OK-8705, OK-8801,

$\alpha$ -(1,1-dimethylethyl)- $\beta$ -(2-phenoxyethyl)-1H-1,2,4-triazole-1-ethanol,

$\alpha$ -(2,4-dichlorophenyl)- $\beta$ -fluoro- $\beta$ -propyl-1H-1,2,4-triazole-1-ethanol,

$\alpha$ -(2,4-dichlorophenyl)- $\beta$ -methoxy- $\alpha$ -methyl-1H-1,2,4-triazole-1-ethanol,

10  $\alpha$ -(5-methyl-1,3-dioxan-5-yl)- $\beta$ -[[4-(trifluoromethyl)-phenyl]-methylene]-1H-1,2,4-triazole-1-ethanol,

(5RS,6RS)-6-hydroxy-2,2,7,7-tetramethyl-5-(1H-1,2,4-triazol-1-yl)-3-octanone,

(E)- $\alpha$ -(methoxyimino)-N-methyl-2-phenoxy-phenylacetamide,

1-(2,4-dichlorophenyl)-2-(1H-1,2,4-triazol-1-yl)-ethanone-O-(phenylmethyl)-oxime,

1-(2-methyl-1-naphthalenyl)-1H-pyrrole-2,5-dione,

15 1-(3,5-dichlorophenyl)-3-(2-propenyl)-2,5-pyrrolidinedione,

1-[(diiodomethyl)-sulphonyl]-4-methyl-benzene,

1-[[2-(2,4-dichlorophenyl)-1,3-dioxolan-2-yl]-methyl]-1H-imidazole,

1-[[2-(4-chlorophenyl)-3-phenyloxiranyl]-methyl]-1H-1,2,4-triazole,

1-[1-[2-[(2,4-dichlorophenyl)-methoxy]-phenyl]-ethenyl]-1H-imidazole,

20 1-methyl-5-nonyl-2-(phenylmethyl)-3-pyrrolidinol,

2',6'-dibromo-2-methyl-4'-trifluoromethoxy-4'-trifluoro-methyl-1,3-thiazole-5-carboxanilide,

2,6-dichloro-5-(methylthio)-4-pyrimidinyl-thiocyanate,

2,6-dichloro-N-(4-trifluoromethylbenzyl)-benzamide,

25 2,6-dichloro-N-[[4-(trifluoromethyl)-phenyl]-methyl]-benzamide,

2-(2,3,3-triiodo-2-propenyl)-2H-tetrazole,

2-[(1-methylethyl)-sulphonyl]-5-(trichloromethyl)-1,3,4-thiadiazole,

2-[[6-deoxy-4-O-(4-O-methyl- $\beta$ -D-glycopyranosyl)- $\alpha$ -D-glucopyranosyl]-amino]-4-methoxy-1H-pyrrolo[2,3-d]pyrimidine-5-carbonitrile,

30 2-aminobutane,

2-bromo-2-(bromomethyl)-pentanedinitrile,

2-chloro-N-(2,3-dihydro-1,1,3-trimethyl-1H-inden-4-yl)-3-pyridinecarboxamide,

- 2-chloro-N-(2,6-dimethylphenyl)-N-(isothiocyanatomethyl)-acetamide,  
 2-phenylphenol (OPP),  
 3,4-dichloro-1-[4-(difluoromethoxy)-phenyl]-1H-pyrrole-2,5-dione,  
 3,5-dichloro-N-[cyano-[(1-methyl-2-propynyl)-oxy]-methyl]-benzamide,  
 5 3-(1,1-dimethylpropyl)-1-oxo-1H-indene-2-carbonitrile,  
 3-[2-(4-chlorophenyl)-5-ethoxy-3-isoxazolidinyl]-pyridine,  
 4-chloro-2-cyano-N,N-dimethyl-5-(4-methylphenyl)-1H-imidazole-1-sulphonamide,  
 4-methyl-tetrazolo[1,5-a]quinazolin-5(4H)-one,  
 8-hydroxyquinoline sulphate,  
 10 9H-xanthene-2-[(phenylamino)-carbonyl]-9-carboxylic hydrazide,  
 bis-(1-methylethyl)-3-methyl-4-[(3-methylbenzoyl)-oxy]-2,5-thiophenedicarboxylate,  
 cis-1-(4-chlorophenyl)-2-(1H-1,2,4-triazol-1-yl)-cycloheptanol,  
 cis-4-[3-[4-(1,1-dimethylpropyl)-phenyl-2-methylpropyl]-2,6-dimethyl-  
 morpholinehydrochloride,  
 15 ethyl [(4-chlorophenyl)-azo]-cyanoacetate,  
 potassium hydrogen carbonate,  
 methanetetrahiol sodium salt,  
 methyl 1-(2,3-dihydro-2,2-dimethyl-1H-inden-1-yl)-1H-imidazole-5-carboxylate,  
 methyl N-(2,6-dimethylphenyl)-N-(5-isoxazolylcarbonyl)-DL-alaninate,  
 20 methyl N-(chloroacetyl)-N-(2,6-dimethylphenyl)-DL-alaninate,  
 N-(2,6-dimethylphenyl)-2-methoxy-N-(tetrahydro-2-oxo-3-furanyl)-acetamide,  
 N-(2,6-dimethylphenyl)-2-methoxy-N-(tetrahydro-2-oxo-3-thienyl)-acetamide,  
 N-(2-chloro-4-nitrophenyl)-4-methyl-3-nitro-benzenesulphonamide,  
 N-(4-cyclohexylphenyl)-1,4,5,6-tetrahydro-2-pyrimidinamine,  
 25 N-(4-hexylphenyl)-1,4,5,6-tetrahydro-2-pyrimidinamine,  
 N-(5-chloro-2-methylphenyl)-2-methoxy-N-(2-oxo-3-oxazolidinyl)-acetamide,  
 N-(6-methoxy)-3-pyridinyl)-cyclopropanecarboxamide,  
 N-[2,2,2-trichloro-1-[(chloroacetyl)-amino]-ethyl]-benzamide,  
 N-[3-chloro-4,5-bis-(2-propinyloxy)-phenyl]-N'-methoxy-methanimidamide,  
 30 N-formyl-N-hydroxy-DL-alanine sodium salt,  
 O,O-diethyl [2-(dipropylamino)-2-oxoethyl]-ethylphosphoramidothioate,  
 O-methyl S-phenyl phenylpropylphosphoramidothioate,

S-methyl 1,2,3-benzothiadiazole-7-carbothioate,  
 spiro[2H]-1-benzopyrane-2,1'(3'H)-isobenzofuran-3'-one,  
 4-[(3,4-dimethoxyphenyl)-3-(4-fluorophenyl)acryloyl]morpholine.

5 **Bactericides:**

bronopol, dichlorophen, nitrapyrin, nickel dimethyldithiocarbamate, kasugamycin, octhilinone, furancarboxylic acid, oxytetracyclin, probenazole, streptomycin, tecloftalam, copper sulphate and other copper preparations.

10 **Insecticides/acaricides/nematicides:**

abamectin, acephate, acetamiprid, acequinocyl, acrinathrin, alanycarb, aldicarb, aldoxycarb, alpha-cypermethrin, alphamethrin, amitraz, avermectin, AZ 60541, azadirachtin, azamethiphos, azinphos A, azinphos M, azocyclotin,

15 Bacillus popilliae, Bacillus sphaericus, Bacillus subtilis, Bacillus thuringiensis, Baculoviruses, Beauveria bassiana, Beauveria tenella, bendiocarb, benfuracarb, bensultap, benzoximate, betacyfluthrin, bifenazate, bifenthrin, bioethanomethrin, biopermethrin, bistrifluron, BPMC, bromophos A, bufencarb, buprofezin, butathiofos, butocarboxim, butylpyridaben,

20 cadusafos, carbaryl, carbofuran, carbophenothion, carbosulfan, cartap, chloethocarb, chlorethoxyfos, chlorfenapyr, chlorfenvinphos, chlorfluazuron, chlormephos, chlorpyrifos, chlorpyrifos M, chlovaporthrin, chromafenozide, cis-resmethrin, cispermethrin, clocythrin, cloethocarb, clofentezine, clothianidine, cyanophos, cycloprene, cycloprothrin, cyfluthrin, cyhalothrin, cyhexatin, cypermethrin, cyromazine,

25 deltamethrin, demeton M, demeton S, demeton-S-methyl, diafenthiuron, diazinon, dichlorvos, dicofol, diflubenzuron, dimethoate, dimethylvinphos, dimethylvinphos, dinetofuran, diofenolan, disulfoton, docusat-sodium, dofenapyn, eflusilanate, emamectin, empenthrin, endosulfan, Entomopftora spp., esfenvalerate, ethiofencarb, ethion, ethiprole, ethoprophos, etofenprox, etoxazole, etrimfos,

30 fenamiphos, fenazaquin, fenbutatin oxide, fenitrothion, fenothiocarb, fenoxacrim, fenoxycarb, fenpropathrin, fenpyrad, fenpyrithrin, fenpyroximate, fenthion, fenvalerate, fipronil, fluazuron, flubrocycythrinate, flucycloxuron, flucythrinate,

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- 24 -

flufenoxuron, flumethrin, flupyrazofos, flutenzine, fluvalinate, fonophos,  
 fosmethilan, fosthiazate, fubfenprox, furathiocarb,  
 granulosis viruses,  
 halofenozide, HCH, heptenophos, hexaflumuron, hexythiazox, hydroprene,  
 5 imidacloprid, indoxacarb, isazofos, isofenphos, isoxathion, ivermectin,  
 nuclear polyhedrosis viruses,  
 lambda-cyhalothrin, lufenuron,  
 malathion, mecarbam, metaldehyde, methamidophos, metharhizium anisopliae,  
 metharhizium flavoviride, methidathion, methiocarb, methoprene, methomyl,  
 10 methoxyfenozide, metolcarb, metoxadiazone, mevinphos, milbemectin, milbemycin,  
 monocrotophos,  
 naled, nitenpyram, nithiazine, novaluron,  
 omethoate, oxamyl, oxydemethon M,  
 Paecilomyces fumosoroseus, parathion A, parathion M, permethrin, phenthoate,  
 15 phorate, phosalone, phosmet, phosphamidon, phoxim, pirimicarb, pirimiphos A,  
 pirimiphos M, profenofos, promecarb, propargite, propoxur, prothiofos, prothoate,  
 pymetrozine, pyraclofos, pyresmethrin, pyrethrum, pyridaben, pyridathion,  
 pyrimidifen, pyriproxyfen,  
 quinalphos,  
 20 ribavirin,  
 salithion, sebufos, silafluofen, spinosad, spirodiclofen, sulfotep, sulprofos,  
 tau-fluvalinate, tebufenozide, tebufenpyrad, tebupirimiphos, teflubenzuron, teflu-  
 thrin, temephos, temivinphos, terbufos, tetrachlorvinphos, tetradifon,  
 thetacypermethrin, thiacloprid, thiamethoxam, thiapronil, thiatriphos, thiocyclam  
 25 hydrogen oxalate, thiodicarb, thiofanox, thuringiensin, tralocythrin, tralomethrin,  
 triarathene, triazamate, triazophos, triazurone, trichlophenidine, trichlorfon,  
 triflumuron, trimethacarb,  
 vamidothion, vaniliprole, Verticillium lecanii,  
 YI 5302,  
 30 zeta-cypermethrin, zolaprofos,  
 (1R-cis)-[5-(phenylmethyl)-3-furanyl]-methyl 3-[(dihydro-2-oxo-3(2H)-  
 furanylidene)-methyl]-2,2-dimethylcyclopropanecarboxylate,

- (3-phenoxyphenyl)-methyl 2,2,3,3-tetramethylcyclopropanecarboxylate,  
 1-[(2-chloro-5-thiazolyl)methyl]tetrahydro-3,5-dimethyl-N-nitro-1,3,5-triazine-  
 2(1H)-imine,  
 2-(2-chloro-6-fluorophenyl)-4-[4-(1,1-dimethylethyl)phenyl]-4,5-dihydro-oxazole,  
 5 2-(acetyloxy)-3-dodecyl-1,4-naphthalenedione,  
 2-chloro-N-[[[4-(1-phenylethoxy)-phenyl]-amino]-carbonyl]-benzamide,  
 2-chloro-N-[[[4-(2,2-dichloro-1,1-difluoroethoxy)-phenyl]-amino]-carbonyl]-  
 benzamide,  
 3-methylphenyl propylcarbamate,  
 10 4-[4-(4-ethoxyphenyl)-4-methylpentyl]-1-fluoro-2-phenoxy-benzene,  
 4-chloro-2-(1,1-dimethylethyl)-5-[[2-(2,6-dimethyl-4-phenoxyphenoxy)ethyl]thio]-  
 3(2H)-pyridazinone,  
 4-chloro-2-(2-chloro-2-methylpropyl)-5-[(6-iodo-3-pyridinyl)methoxy]-3(2H)-  
 pyridazinone,  
 15 4-chloro-5-[(6-chloro-3-pyridinyl)methoxy]-2-(3,4-dichlorophenyl)-3(2H)-  
 pyridazinone,  
 Bacillus thuringiensis strain EG-2348,  
 [2-benzoyl-1-(1,1-dimethylethyl)-hydrazinobenzoic acid,  
 2,2-dimethyl-3-(2,4-dichlorophenyl)-2-oxo-1-oxaspiro[4.5]dec-3-en-4-yl butanoate,  
 20 [3-[(6-chloro-3-pyridinyl)methyl]-2-thiazolidinylidene]-cyanamide,  
 dihydro-2-(nitromethylene)-2H-1,3-thiazine-3(4H)-carboxaldehyde,  
 ethyl [2-[[1,6-dihydro-6-oxo-1-(phenylmethyl)-4-pyridazinyl]oxy]ethyl]-carbamate,  
 N-(3,4,4-trifluoro-1-oxo-3-butenyl)-glycine,  
 N-(4-chlorophenyl)-3-[4-(difluoromethoxy)phenyl]-4,5-dihydro-4-phenyl-1H-  
 25 pyrazole-1-carboxamide,  
 N-[(2-chloro-5-thiazolyl)methyl]-N'-methyl-N''-nitro-guanidine,  
 N-methyl-N'-(1-methyl-2-propenyl)-1,2-hydrazinedicarbothioamide,  
 N-methyl-N'-2-propenyl-1,2-hydrazinedicarbothioamide,  
 O,O-diethyl [2-(dipropylamino)-2-oxoethyl]-ethylphosphoramidothioate.  
 30 N-cyanomethyl-4-trifluoromethylnicotinamide,  
 3,5-dichloro-1-(3,3-dichloro-2-propenyloxy)-4-[3-(5-trifluoromethylpyridin-2-  
 yloxy)propoxy]benzene.

A mixture with other known active compounds, such as herbicides, or with fertilizers and growth regulators, safeners or semiochemicals is also possible.

5 The active compounds according to the invention can furthermore be present when used as insecticides in their commercially available formulations and in the use forms, prepared from these formulations, as a mixture with synergistic agents. Synergistic agents are compounds which increase the effect of the active compounds, without the added synergistic agent itself having to be actively effective.

10 The active compounds according to the invention can furthermore be present when used as insecticides in their commercially available formulations and in the use forms, prepared from these formulations, as a mixture with inhibitors which reduce degradation of the active compound after use in the vicinity of the plant, on the  
15 surface of parts of plants or in plant tissues.

The active compound content of the use forms prepared from the commercially available formulations can vary within wide limits. The active compound concentration of the use forms can be from 0.0000001 to 95% by weight of active  
20 compound, preferably between 0.0001 and 1% by weight.

The compounds are employed in a customary manner appropriate for the use forms.

When used against hygiene pests and pests of stored products, the active compound  
25 is distinguished by an excellent residual action on wood and clay as well as a good stability to alkali on limed substrates.

As already mentioned above, it is possible to treat all plants and their parts according to the invention. In a preferred embodiment, wild plant species and plant cultivars, or  
30 those obtained by conventional biological breeding, such as crossing or protoplast fusion, and parts thereof, are treated. In a further preferred embodiment, transgenic plants and plant cultivars obtained by genetic engineering, if appropriate in

combination with conventional methods (Genetically Modified Organisms), and parts thereof are treated. The term "parts" or "parts of plants" or "plant parts" has been explained above.

5 Particularly preferably, plants of the plant cultivars which are in each case commercially available or in use are treated according to the invention. Plant cultivars are to be understood as meaning plants having novel properties ("traits") which have been obtained by conventional breeding, by mutagenesis or by recombinant DNA techniques. This can be varieties, bio- and genotypes.

10

Depending on the plant species or plant cultivars, their location and growth conditions (soils, climate, vegetation period, diet), the treatment according to the invention may also result in superadditive ("synergistic") effects. Thus, for example, reduced application rates and/or a widening of the activity spectrum and/or an  
15 increase in the activity of the substances and compositions to be used according to the invention, better plant growth, increased tolerance to high or low temperatures, increased tolerance to drought or to water or soil salt content, increased flowering performance, easier harvesting, accelerated maturation, higher harvest yields, better quality and/or a higher nutritional value of the harvested products, better storage  
20 stability and/or processability of the harvested products are possible which exceed the effects which were actually to be expected.

The transgenic plants or plant cultivars to be treated (i.e. those obtained by genetic engineering) which are preferred according to the invention include all plants which,  
25 in the genetic modification, received genetic material which imparted particularly advantageous useful traits to these plants. Examples of such traits are better plant growth, increased tolerance to high or low temperatures, increased tolerance to drought or to water or soil salt content, increased flowering performance, easier harvesting, accelerated maturation, higher harvest yields, better quality and/or a  
30 higher nutritional value of the harvested products, better storage stability and/or processability of the harvested products. Further and particularly emphasized examples of such traits are a better defence of the plants against animal and microbial

pests, such as against insects, mites, phytopathogenic fungi, bacteria and/or viruses, and also increased tolerance of the plants to certain herbicidally active compounds. Examples of transgenic plants which may be mentioned are the important crop plants, such as cereals (wheat, rice), maize, soya beans, potatoes, cotton, tobacco, oilseed rape and also fruit plants (with the fruits apples, pears, citrus fruits and grapevines), and particular emphasis is given to maize, soya beans, potatoes, cotton, tobacco and oilseed rape. Traits that are emphasized are in particular increased defence of the plants against insects, arachnids, nematodes and snails by toxins formed in the plants, in particular those formed by the genetic material from *Bacillus thuringiensis* (for example by the genes CryIA(a), CryIA(b), CryIA(c), CryIIA, CryIIIA, CryIIIB2, Cry9c, Cry2Ab, Cry3Bb and CryIF and also combinations thereof) in the plants (hereinbelow referred to as "Bt plants"). Traits that are also particularly emphasized are the increased defence of the plants to fungi, bacteria and viruses by systemic acquired resistance (SAR), systemin, phytoalexins, elicitors and resistance genes and correspondingly expressed proteins and toxins. Traits that are furthermore particularly emphasized are the increased tolerance of the plants to certain herbicidally active compounds, for example imidazolinones, sulphonylureas, glyphosate or phosphinotricin (for example the "PAT" gene). The genes which impart the desired traits in question can also be present in combination with one another in the transgenic plants. Examples of "Bt plants" which may be mentioned are maize varieties, cotton varieties, soya bean varieties and potato varieties which are sold under the trade names YIELD GARD® (for example maize, cotton, soya beans), KnockOut® (for example maize), StarLink® (for example maize), Bollgard® (cotton), Nucoat® (cotton) and NewLeaf® (potato). Examples of herbicide-tolerant plants which may be mentioned are maize varieties, cotton varieties and soya bean varieties which are sold under the trade names Roundup Ready® (tolerance to glyphosate, for example maize, cotton, soya bean), Liberty Link® (tolerance to phosphinotricin, for example oilseed rape), IMI® (tolerance to imidazolinones) and STS® (tolerance to sulphonylureas, for example maize). Herbicide-resistant plants (plants bred in a conventional manner for herbicide tolerance) which may be mentioned include the varieties sold under the name Clearfield® (for example maize). Of course, these statements also apply to plant cultivars having these or still-

to-be-developed genetic traits, which plants will be developed and/or marketed in the future.

5 The plants listed can be treated according to the invention in a particularly advantageous manner with the compounds of the general formula (I) or the active compound mixtures according to the invention. The preferred ranges stated above for the active compounds or mixtures also apply to the treatment of these plants. Particular emphasis is given to the treatment of plants with the compounds or the mixtures specifically mentioned in the present text.

10

The active compounds according to the invention act not only against plant, hygiene and stored product pests, but also in the veterinary medicine sector against animal parasites (ectoparasites), such as hard ticks, soft ticks, mange mites, leaf mites, flies (biting and licking), parasitic fly larvae, lice, hair lice, feather lice and fleas. These  
15 parasites include:

From the order of the Anoplurida, for example, *Haematopinus* spp., *Linognathus* spp., *Pediculus* spp., *Phtirus* spp. and *Solenopotes* spp.

20

From the order of the Mallophagida and the suborders Amblycerina and Ischnocerina, for example, *Trimenopon* spp., *Menopon* spp., *Trinoton* spp., *Bovicola* spp., *Werneckiella* spp., *Lepikentron* spp., *Damalina* spp., *Trichodectes* spp. and *Felicola* spp.

25

From the order Diptera and the suborders Nematocerina and Brachycerina, for example, *Aedes* spp., *Anopheles* spp., *Culex* spp., *Simulium* spp., *Eusimulium* spp., *Phlebotomus* spp., *Lutzomyia* spp., *Culicoides* spp., *Chrysops* spp., *Hybomitra* spp., *Atylotus* spp., *Tabanus* spp., *Haematopota* spp., *Philipomyia* spp., *Braula* spp., *Musca* spp., *Hydrotaea* spp., *Stomoxys* spp., *Haematobia* spp., *Morellia* spp., *Fannia* spp., *Glossina* spp., *Calliphora* spp., *Lucilia* spp., *Chrysomyia* spp., *Wohlfahrtia* spp., *Sarcophaga* spp., *Oestrus* spp., *Hypoderma* spp., *Gasterophilus* spp., *Hippobosca* spp., *Lipoptena* spp. and *Melophagus* spp.  
30

From the order of the Siphonapterida, for example, *Pulex* spp., *Ctenocephalides* spp., *Xenopsylla* spp. and *Ceratophyllus* spp.

From the order of the Heteropterida, for example, *Cimex* spp., *Triatoma* spp., *Rhodnius* spp. and *Panstrongylus* spp.

From the order of the Blattarida, for example, *Blatta orientalis*, *Periplaneta americana*, *Blattella germanica* and *Supella* spp.

5 From the subclass of the Acaria (Acarida) and the orders of the Meta- and Mesostigmata, for example, *Argas* spp., *Ornithodoros* spp., *Otobius* spp., *Ixodes* spp., *Amblyomma* spp., *Boophilus* spp., *Dermacentor* spp., *Haemophysalis* spp., *Hyalomma* spp., *Rhipicephalus* spp., *Dermanyssus* spp., *Railletia* spp., *Pneumonyssus* spp., *Sternostoma* spp. and *Varroa* spp.

10 From the order of the Actinedida (Prostigmata) and Acaridida (Astigmata), for example, *Acarapis* spp., *Cheyletiella* spp., *Ornithocheyletia* spp., *Myobia* spp., *Psorergates* spp., *Demodex* spp., *Trombicula* spp., *Listrophorus* spp., *Acarus* spp., *Tyrophagus* spp., *Caloglyphus* spp., *Hypodectes* spp., *Pterolichus* spp., *Psoroptes* spp., *Chorioptes* spp., *Otodectes* spp., *Sarcoptes* spp., *Notoedres* spp.,  
15 *Knemidocoptes* spp., *Cytodites* spp. and *Laminosioptes* spp.

The active compounds of the formula (I) according to the invention are also suitable for controlling arthropods which infest agricultural productive livestock, such as, for example, cattle, sheep, goats, horses, pigs, donkeys, camels, buffalo, rabbits,  
20 chickens, turkeys, ducks, geese and bees, other pets, such as, for example, dogs, cats, caged birds and aquarium fish, and also so-called test animals, such as, for example, hamsters, guinea pigs, rats and mice. By controlling these arthropods, cases of death and reduction in productivity (for meat, milk, wool, hides, eggs, honey etc.) should be diminished, so that more economic and easier animal husbandry is possible by use  
25 of the active compounds according to the invention.

The active compounds according to the invention are used in the veterinary sector in a known manner by enteral administration in the form of, for example, tablets, capsules, potions, drenches, granules, pastes, boluses, the feed-through process and  
30 suppositories, by parenteral administration, such as, for example, by injections (intramuscular, subcutaneous, intravenous, intraperitoneal and the like), implants, by nasal administration, by dermal use in the form, for example, of dipping or bathing,

spraying, pouring on and spotting on, washing and powdering, and also with the aid of moulded articles containing the active compound, such as collars, ear marks, tail marks, limb bands, halters, marking devices and the like.

5 When used for cattle, poultry, pets and the like, the active compounds of the formula (I) according to the invention can be used as formulations (for example powders, emulsions, free-flowing compositions), which comprise the active compounds according to the invention in an amount of 1 to 80% by weight, directly or after 100 to 10 000-fold dilution, or they can be used as a chemical bath.

10

It has furthermore been found that the compounds according to the invention also have a strong insecticidal action against insects which destroy industrial materials.

15

The following insects may be mentioned as examples and as being preferred - but without any limitation:

Beetles, such as

20

Hylotrupes bajulus, Chlorophorus pilosis, Anobium punctatum, Xestobium rufovillosum, Ptilinus pecticornis, Dendrobium pertinex, Ernobius mollis, Priobium carpini, Lyctus brunneus, Lyctus africanus, Lyctus planicollis, Lyctus linearis, Lyctus pubescens, Trogoxylon aequale, Minthes rugicollis, Xyleborus spec., Tryptodendron spec., Apate monachus, Bostrychus capucins, Heterobostrychus brunneus, Sinoxylon spec. and Dinoderus minutus.

25

Hymenopterons, such as

Sirex juvencus, Urocerus gigas, Urocerus gigas taignus and Urocerus augur.

Termites, such as

30

Kaloterme flavicollis, Cryptoterme brevis, Heteroterme indicola, Reticuliterme flavipes, Reticuliterme santonensis, Reticuliterme lucifugus, Mastoterme darwiniensis, Zootermopsis nevadensis and Coptoterme formosanus.

Bristletails, such as Lepisma saccharina.

Industrial materials in the present context are to be understood as meaning non-living materials, such as, preferably, plastics, adhesives, sizes, papers and cards, leather, wood and processed wood products and coating compositions.

5

Wood and processed wood products are materials to be protected, especially preferably, from insect infestation.

10

Wood and processed wood products which can be protected by the agent according to the invention or mixtures comprising this are to be understood as meaning, for example:

15

building timber, wooden beams, railway sleepers, bridge components, boat jetties, wooden vehicles, boxes, pallets, containers, telegraph poles, wood panelling, wooden windows and doors, plywood, chipboard, joinery or wooden products which are used quite generally in house-building or in building joinery.

The active compounds can be used as such, in the form of concentrates or in generally customary formulations, such as powders, granules, solutions, suspensions, emulsions or pastes.

20

The formulations mentioned can be prepared in a manner known per se, for example by mixing the active compounds with at least one solvent or diluent, emulsifier, dispersing agent and/or binder or fixing agent, a water repellent, if appropriate siccatives and UV stabilizers and if appropriate dyes and pigments, and also other processing auxiliaries.

25

The insecticidal compositions or concentrates used for the preservation of wood and wood-derived timber products comprise the active compound according to the invention in a concentration of 0.0001 to 95% by weight, in particular 0.001 to 60% by weight.

30

The amount of the compositions or concentrates employed depends on the nature and occurrence of the insects and on the medium. The optimum amount employed can be determined for the use in each case by a series of tests. In general, however, it is sufficient to employ 0.0001 to 20% by weight, preferably 0.001 to 10% by weight, of the active compound, based on the material to be preserved.

Solvents and/or diluents which are used are an organic chemical solvent or solvent mixture and/or an oily or oil-like organic chemical solvent or solvent mixture of low volatility and/or a polar organic chemical solvent or solvent mixture and/or water, and if appropriate an emulsifier and/or wetting agent.

Organic chemical solvents which are preferably used are oily or oil-like solvents having an evaporation number above 35 and a flashpoint above 30°C, preferably above 45°C. Substances which are used as such oily or oil-like water-insoluble solvents of low volatility are appropriate mineral oils or aromatic fractions thereof, or solvent mixtures containing mineral oils, preferably white spirit, petroleum and/or alkylbenzene.

Mineral oils having a boiling range from 170 to 220°C, white spirit having a boiling range from 170 to 220°C, spindle oil having a boiling range from 250 to 350°C, petroleum and aromatics having a boiling range from 160 to 280°C, turpentine oil and the like, are advantageously employed.

In a preferred embodiment, liquid aliphatic hydrocarbons having a boiling range from 180 to 210°C or high-boiling mixtures of aromatic and aliphatic hydrocarbons having a boiling range from 180 to 220°C and/or spindle oil and/or monochloronaphthalene, preferably  $\alpha$ -monochloronaphthalene, are used.

The organic oily or oil-like solvents of low volatility which have an evaporation number above 35 and a flashpoint above 30°C, preferably above 45°C, can be replaced in part by organic chemical solvents of high or medium volatility, providing that the solvent mixture likewise has an evaporation number above 35 and a

flashpoint above 30°C, preferably above 45°C, and that the insecticide/fungicide mixture is soluble or emulsifiable in this solvent mixture.

According to a preferred embodiment, some of the organic chemical solvent or solvent mixture is replaced by an aliphatic polar organic chemical solvent or solvent mixture. Aliphatic organic chemical solvents containing hydroxyl and/or ester and/or ether groups, such as, for example, glycol ethers, esters or the like, are preferably used.

Organic chemical binders which are used in the context of the present invention are the synthetic resins and/or binding drying oils which are known per se, are water-dilutable and/or are soluble or dispersible or emulsifiable in the organic chemical solvents employed, in particular binders consisting of or comprising an acrylate resin, a vinyl resin, for example polyvinyl acetate, polyester resin, polycondensation or polyaddition resin, polyurethane resin, alkyd resin or modified alkyd resin, phenolic resin, hydrocarbon resin, such as indene-cumarone resin, silicone resin, drying vegetable oils and/or drying oils and/or physically drying binders based on a natural and/or synthetic resin.

The synthetic resin used as the binder can be employed in the form of an emulsion, dispersion or solution. Bitumen or bituminous substances can also be used as binders in an amount of up to 10% by weight. Dyestuffs, pigments, water-repelling agents, odour correctants and inhibitors or anticorrosive agents and the like which are known per se can additionally be employed.

It is preferred according to the invention for the composition or concentrate to comprise, as the organic chemical binder, at least one alkyd resin or modified alkyd resin and/or one drying vegetable oil. Alkyd resins having an oil content of more than 45% by weight, preferably 50 to 68% by weight, are preferably used according to the invention.

All or some of the binder mentioned can be replaced by a fixing agent (mixture) or a plasticizer (mixture). These additives are intended to prevent evaporation of the active compounds and crystallization or precipitation. They preferably replace 0.01 to 30% of the binder (based on 100% of the binder employed).

5

The plasticizers originate from the chemical classes of phthalic acid esters, such as dibutyl, dioctyl or benzyl butyl phthalate, phosphoric acid esters, such as tributyl phosphate, adipic acid esters, such as di-(2-ethylhexyl) adipate, stearates, such as butyl stearate or amyl stearate, oleates, such as butyl oleate, glycerol ethers or higher molecular weight glycol ethers, glycerol esters and p-toluenesulphonic acid esters.

10

Fixing agents are based chemically on polyvinyl alkyl ethers, such as, for example, polyvinyl methyl ether or ketones, such as benzophenone or ethylenebenzophenone. Possible solvents or diluents are, in particular, also water, if appropriate as a mixture with one or more of the abovementioned organic chemical solvents or diluents, emulsifiers and dispersing agents.

15

Particularly effective preservation of wood is achieved by impregnation processes on a large industrial scale, for example vacuum, double vacuum or pressure processes.

20

The ready-to-use compositions can also comprise other insecticides, if appropriate, and also one or more fungicides, if appropriate.

Possible additional mixing partners are, preferably, the insecticides and fungicides mentioned in WO 94/29 268. The compounds mentioned in this document are an explicit constituent of the present application.

25

Especially preferred mixing partners which may be mentioned are insecticides, such as chlorpyrifos, phoxim, silafluofin, alphamethrin, cyfluthrin, cypermethrin, deltamethrin, permethrin, imidacloprid, NI-25, flufenoxuron, hexaflumuron, transfluthrin, thiacloprid, methoxyphenoxide, triflumuron, clothianidin, spinosad, tefluthrin and triflumuron,

30

and also fungicides, such as epoxyconazole, hexaconazole, azaconazole, propiconazole, tebuconazole, cyproconazole, metconazole, imazalil, dichlorfluanid, tolylfluanid, 3-iodo-2-propinyl-butyl carbamate, N-octyl-isothiazolin-3-one and 4,5-dichloro-N-octylisothiazolin-3-one.

5

The compounds according to the invention can at the same time be employed for protecting objects which come into contact with salt water or brackish water, such as hulls, screens, nets, buildings, moorings and signalling systems, against fouling.

10

Fouling by sessile Oligochaeta, such as Serpulidae, and by shells and species from the Ledamorpha group (goose barnacles), such as various Lepas and Scalpellum species, or by species from the Balanomorpha group (acorn barnacles), such as Balanus or Pollicipes species, increases the frictional drag of ships and, as a consequence, leads to a marked increase in operation costs owing to higher energy consumption and additionally frequent residence in the dry dock.

15

Apart from fouling by algae, for example Ectocarpus sp. and Ceramium sp., fouling by sessile Entomostraka groups, which come under the generic term Cirripedia (cirriped crustaceans), is of particular importance.

20

Surprisingly, it has now been found that the compounds according to the invention, alone or in combination with other active compounds, have an outstanding antifouling action.

25

Using the compounds according to the invention, alone or in combination with other active compounds, allows the use of heavy metals such as, for example, in bis-(trialkyltin) sulphides, tri-n-butyltin laurate, tri-n-butyltin chloride, copper(I) oxide, triethyltin chloride, tri-n-butyl-(2-phenyl-4-chlorophenoxy)tin, tributyltin oxide, molybdenum disulphide, antimony oxide, polymeric butyl titanate, phenyl-(bispyridine)-bismuth chloride, tri-n-butyltin fluoride, manganese ethylenebisthiocarbamate, zinc dimethyldithiocarbamate, zinc ethylenebisthiocarbamate, zinc salts and copper salts of 2-pyridinethiol 1-oxide, bisdimethyldithiocarbamoylzinc

30

ethylene-bisthiocarbamate, zinc oxide, copper(I) ethylene-bisdithiocarbamate, copper thiocyanate, copper naphthenate and tributyltin halides to be dispensed with, or the concentration of these compounds to be substantially reduced.

- 5 If appropriate, the ready-to-use antifouling paints can additionally comprise other active compounds, preferably algicides, fungicides, herbicides, molluscicides, or other antifouling active compounds.

10 Preferably suitable components in combinations with the antifouling compositions according to the invention are:

algicides such as

2-tert-butylamino-4-cyclopropylamino-6-methylthio-1,3,5-triazine, dichlorophen, diuron, endothal, fentin acetate, isoproturon, methabenzthiazuron, oxyfluorfen,  
15 quinoclamine and terbutryn;

fungicides such as

benzo[b]thiophenecarboxylic acid cyclohexylamide S,S-dioxide, dichlofluanid, fluorfolpet, 3-iodo-2-propinyl butylcarbamate, tolylfluanid and azoles such as  
20 azaconazole, cyproconazole, epoxyconazole, hexaconazole, metconazole, propiconazole and tebuconazole;

molluscicides such as

fentin acetate, metaldehyde, methiocarb, niclosamid, thiodicarb and trimethacarb and  
25 Fe-chelate;

or conventional antifouling active compounds such as

4,5-dichloro-2-octyl-4-isothiazolin-3-one, diiodomethylparatryl sulphone, 2-(N,N-dimethylthiocarbamoylthio)-5-nitrothiazyl, potassium, copper, sodium and zinc salts  
30 of 2-pyridinethiol 1-oxide, pyridine-triphenylborane, tetrabutyl-distannoxane, 2,3,5,6-tetrachloro-4-(methylsulphonyl)-pyridine, 2,4,5,6-tetrachloroisophthalonitrile, tetramethylthiuram disulphide and 2,4,6-trichlorophenylmaleimide.

The antifouling compositions used comprise the active compound according to the invention of the compounds according to the invention in a concentration of 0.001 to 50% by weight, in particular 0.01 to 20% by weight.

5

Moreover, the antifouling compositions according to the invention comprise the customary components such as, for example, those described in Ungerer, *Chem. Ind.* **1985**, 37, 730-732 and Williams, *Antifouling Marine Coatings*, Noyes, Park Ridge, **1973**.

10

Besides the algicidal, fungicidal, molluscicidal active compounds and insecticidal active compounds according to the invention, antifouling paints comprise, in particular, binders.

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Examples of recognized binders are polyvinyl chloride in a solvent system, chlorinated rubber in a solvent system, acrylic resins in a solvent system, in particular in an aqueous system, vinyl chloride/vinyl acetate copolymer systems in the form of aqueous dispersions or in the form of organic solvent systems, butadiene/styrene/acrylonitrile rubbers, drying oils such as linseed oil, resin esters or modified hardened resins in combination with tar or bitumens, asphalt and epoxy compounds, small amounts of chlorine rubber, chlorinated polypropylene and vinyl resins.

20

25

If appropriate, paints also comprise inorganic pigments, organic pigments or colorants which are preferably insoluble in salt water. Paints may furthermore comprise materials such as colophonium to allow controlled release of the active compounds. Furthermore, the paints may comprise plasticizers, modifiers which affect the rheological properties and other conventional constituents. The compounds according to the invention or the abovementioned mixtures may also be incorporated into self-polishing antifouling systems.

30

The active compounds are also suitable for controlling animal pests, in particular insects, arachnids and mites, which are found in enclosed spaces such as, for example, dwellings, factory halls, offices, vehicle cabins and the like. They can be employed in domestic insecticide products for controlling these pests alone or in  
5 combination with other active compounds and auxiliaries. They are active against sensitive and resistant species and against all development stages. These pests include:

From the order of the Scorpionidea, for example, *Buthus occitanus*.  
10 From the order of the Acarina, for example, *Argas persicus*, *Argas reflexus*, *Bryobia* spp., *Dermanyssus gallinae*, *Glyciphagus domesticus*, *Ornithodoros moubat*, *Rhipicephalus sanguineus*, *Trombicula alfreddugesi*, *Neutrombicula autumnalis*, *Dermatophagoides pteronissimus* and *Dermatophagoides forinae*.

From the order of the Araneae, for example, *Aviculariidae* and *Araneidae*.  
15 From the order of the Opiliones, for example, *Pseudoscorpiones chelifer*, *Pseudoscorpiones cheiridium* and *Opiliones phalangium*.

From the order of the Isopoda, for example, *Oniscus asellus* and *Porcellio scaber*.

From the order of the Diplopoda, for example, *Blaniulus guttulatus* and *Polydesmus* spp.

20 From the order of the Chilopoda, for example, *Geophilus* spp.

From the order of the Zygentoma, for example, *Ctenolepisma* spp., *Lepisma saccharina* and *Lepismodes inquilinus*.

From the order of the Blattaria, for example, *Blatta orientalis*, *Blattella germanica*, *Blattella asahinai*, *Leucophaea maderae*, *Panchlora* spp., *Parcoblatta* spp., *Periplaneta*  
25 *australasiae*, *Periplaneta americana*, *Periplaneta brunnea*, *Periplaneta fuliginosa* and *Supella longipalpa*.

From the order of the Saltatoria, for example, *Acheta domesticus*.

From the order of the Dermaptera, for example, *Forficula auricularia*.

From the order of the Isoptera, for example, *Kalotermes* spp. and *Reticulitermes* spp.

30 From the order of the Psocoptera, for example, *Lepinatus* spp. and *Liposcelis* spp.

From the order of the Coleptera, for example, *Anthrenus* spp., *Attagenus* spp., *Dermestes* spp., *Latheticus oryzae*, *Necrobia* spp., *Ptinus* spp., *Rhizopertha dominica*, *Sitophilus granarius*, *Sitophilus oryzae*, *Sitophilus zeamais* and *Stegobium paniceum*.

5 From the order of the Diptera, for example, *Aedes aegypti*, *Aedes albopictus*, *Aedes taeniorhynchus*, *Anopheles* spp., *Calliphora erythrocephala*, *Chrysosoma pluvialis*, *Culex quinquefasciatus*, *Culex pipiens*, *Culex tarsalis*, *Drosophila* spp., *Fannia canicularis*, *Musca domestica*, *Phlebotomus* spp., *Sarcophaga carnaria*, *Simulium* spp., *Stomoxys calcitrans* and *Tipula paludosa*.

10 From the order of the Lepidoptera, for example, *Achroia grisella*, *Galleria mellonella*, *Plodia interpunctella*, *Tinea cloacella*, *Tinea pellionella* and *Tineola bisselliella*.

From the order of the Siphonaptera, for example, *Ctenocephalides canis*, *Ctenocephalides felis*, *Pulex irritans*, *Tunga penetrans* and *Xenopsylla cheopis*.

15 From the order of the Hymenoptera, for example, *Camponotus herculeanus*, *Lasius fuliginosus*, *Lasius niger*, *Lasius umbratus*, *Monomorium pharaonis*, *Paravespula* spp. and *Tetramorium caespitum*.

From the order of the Anoplura, for example, *Pediculus humanus capitis*, *Pediculus humanus corporis* and *Phthirus pubis*.

From the order of the Heteroptera, for example, *Cimex hemipterus*, *Cimex lectularius*, *Rhodinus prolixus* and *Triatoma infestans*.

20

They are used in the household insecticides sector alone or in combination with other suitable active compounds such as phosphoric esters, carbamates, pyrethroids, neonicotinoids, growth regulators or active compounds from other known classes of insecticides.

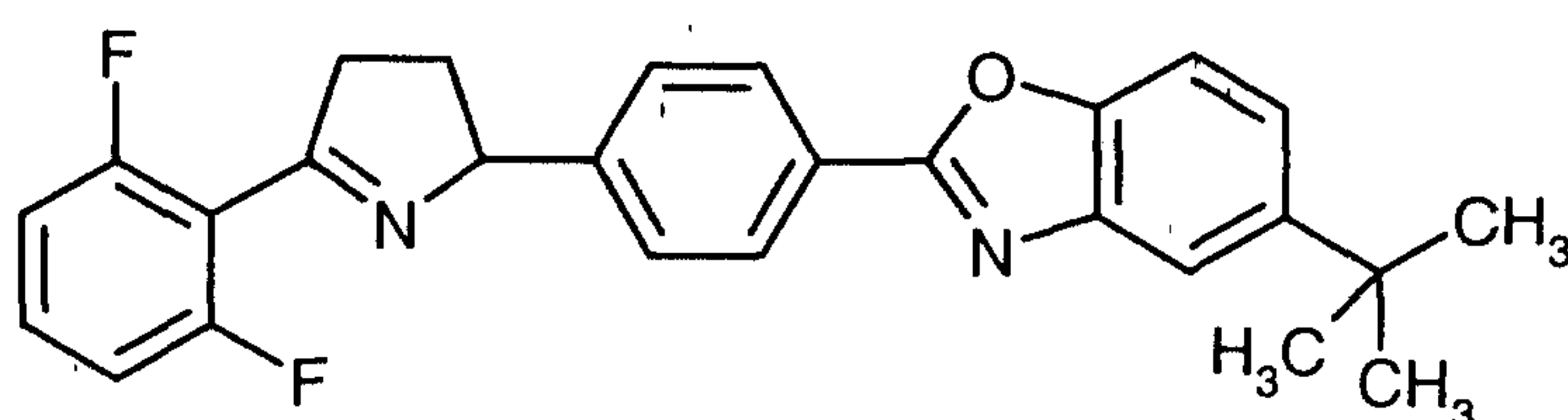
25

They are used in aerosols, pressure-free spray products, for example pump and atomizer sprays, automatic fogging systems, foggers, foams, gels, evaporator products with evaporator tablets made of cellulose or polymer, liquid evaporators, gel and membrane evaporators, propeller-driven evaporators, energy-free, or passive, evaporation systems, moth papers, moth bags and moth gels, as granules or dusts, in  
30 baits for spreading or in bait stations.

The preparation and the use of the compounds according to the invention is shown in the examples below.

## Preparation Examples

### Example 1



5

3.5 g of N-(5-tert-butyl-2-hydroxyphenyl)-4-[5-(2,6-difluorophenyl)-3,4-dihydro-2H-pyrrol-2-yl]benzamide (II-1) are dissolved in toluene, 4.13 g of p-toluenesulphonic acid are added and the mixture is, using a Soxleth with 3Å molecular sieves, heated under reflux for 16 h. After cooling, the mixture is diluted with ethyl acetate and extracted with water/sodium bicarbonate solution. The organic phase is dried, filtered and concentrated. The crude product is purified by silica gel chromatography (mobile phase: ethyl acetate/cyclohexane 1:1).

10

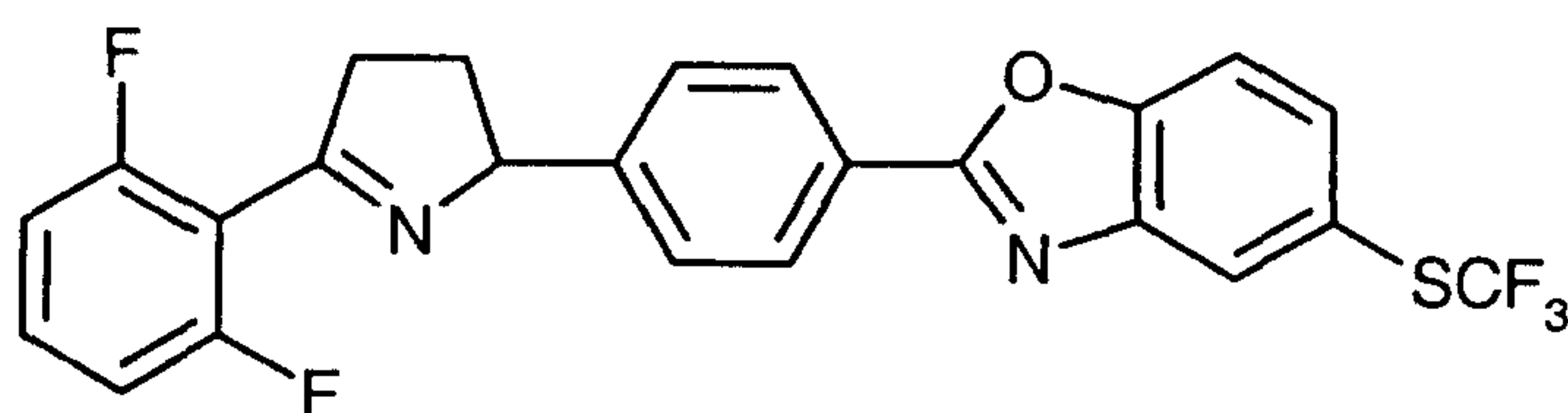
This gives 0.9 g (26% of theory) of 5-tert-butyl-2-{4-[5-(2,6-difluorophenyl)-3,4-dihydro-2H-pyrrol-2-yl]phenyl}-1,3-benzoxazole.

15

HPLC:  $\log P(2.3) = 5.11$

### Example 2

20



25

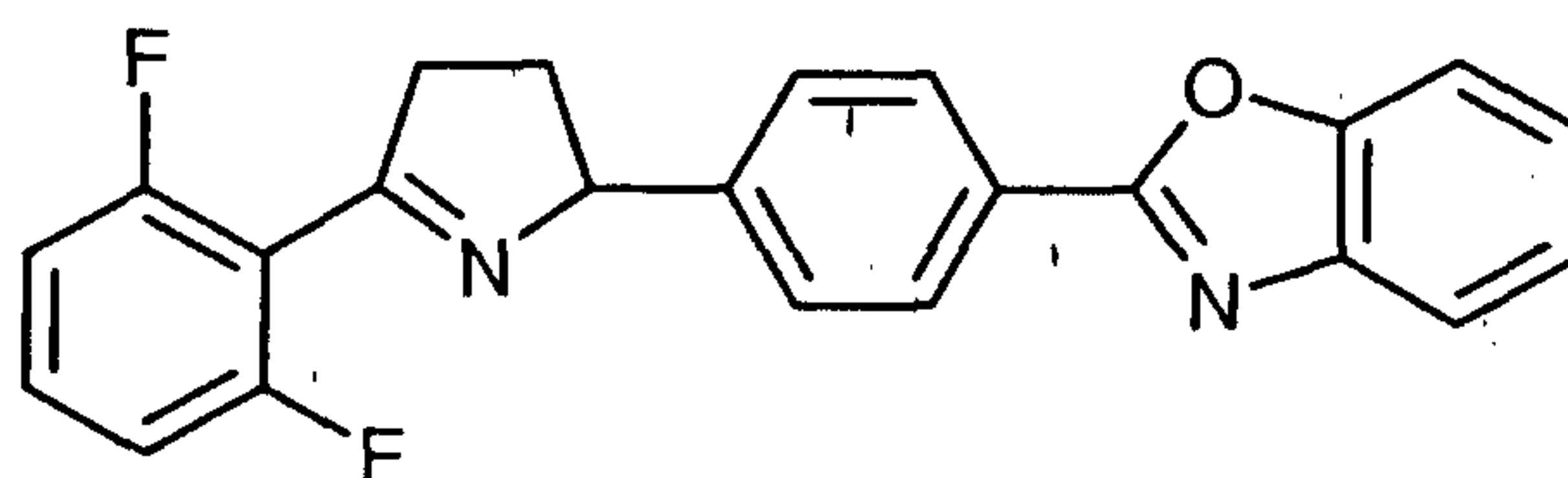
0.8 g of 4-[5-(2,6-difluorophenyl)-3,4-dihydro-2H-pyrrol-2-yl]-N-{2-hydroxy-5-[(trifluoromethyl)sulphonyl]phenyl}benzamide (II-2) is refluxed for 3 h with 0.8 g of p-toluenesulphonic acid in 120 ml of benzene using a Soxleth with 3Å molecular

sieves. After cooling, the mixture is concentrated, sodium bicarbonate is added to pH 8 and the mixture is stirred with aqueous sodium chloride solution and ethyl acetate. The mixture is extracted twice with ethyl acetate. The organic phase is dried, filtered and concentrated. The crude product is purified by silica gel chromatography (mobile phase: cyclohexane → cyclohexane/ethyl acetate 8:2).

This gives 0.37 g (48% of theory) of 2-{4-[5-(2,6-difluorophenyl)-3,4-dihydro-2H-pyrrol-2-yl]phenyl}-5-[(trifluoromethyl)sulphonyl]-1,3-benzoxazole.

HPLC:  $\log P(2.3) = 4.98$

### Example 3



2 g of 4-[5-(2,6-difluorophenyl)-3,4-dihydro-2H-pyrrol-2-yl]-N-(2-hydroxyphenyl)-benzamide (II-3) and 3.5 g of p-toluenesulphonic acid in 120 ml of benzene are refluxed for 16 h using a Soxhlet with 3 Å molecular sieves. After cooling, the mixture is concentrated, sodium bicarbonate is added to pH = 8 and the mixture is stirred with aqueous sodium chloride solution and ethyl acetate. The mixture is extracted twice with ethyl acetate. The organic phase is dried, filtered and concentrated. The crude product is purified by silica gel chromatography (mobile phase: cyclohexane → cyclohexane/ethyl acetate 8:2).

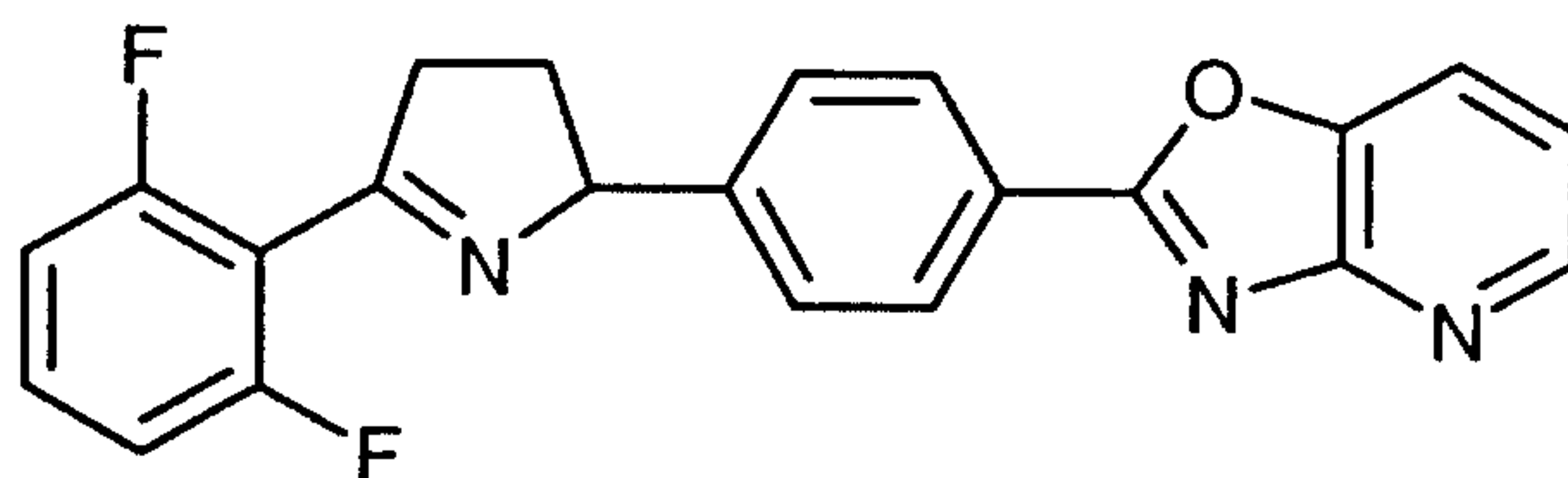
This gives 1.14 g (59% of theory) of 2-{4-[5-(2,6-difluorophenyl)-3,4-dihydro-2H-pyrrol-2-yl]phenyl}-1,3-benzoxazole.

HPLC:  $\log P(2.3) = 3.22$

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 8.25 (d, 2H), 7.75 (m, 1H), 7.55 (m, 1H), 7.5 (d, 2H), 7.35 (m, 3H), 7.0 (t, 2H), 5.55 (t, 1H), 3.1 (m, 2H), 2.75 (m, 1H), 1.9 (m, 1H) ppm.

5

#### Example 4



10 2 g of 4-[5-(2,6-difluorophenyl)-3,4-dihydro-2H-pyrrol-2-yl]-N-(3-hydroxy-2-pyridinyl)benzamide (II-4) and 2.93 g of p-toluenesulphonic acid in 100 ml of toluene are heated under reflux for 16 h using a Soxhlet with 3Å molecular sieves. The mixture is then neutralized by addition of sodium bicarbonate and the organic phase is dried over sodium sulphate, filtered and concentrated.

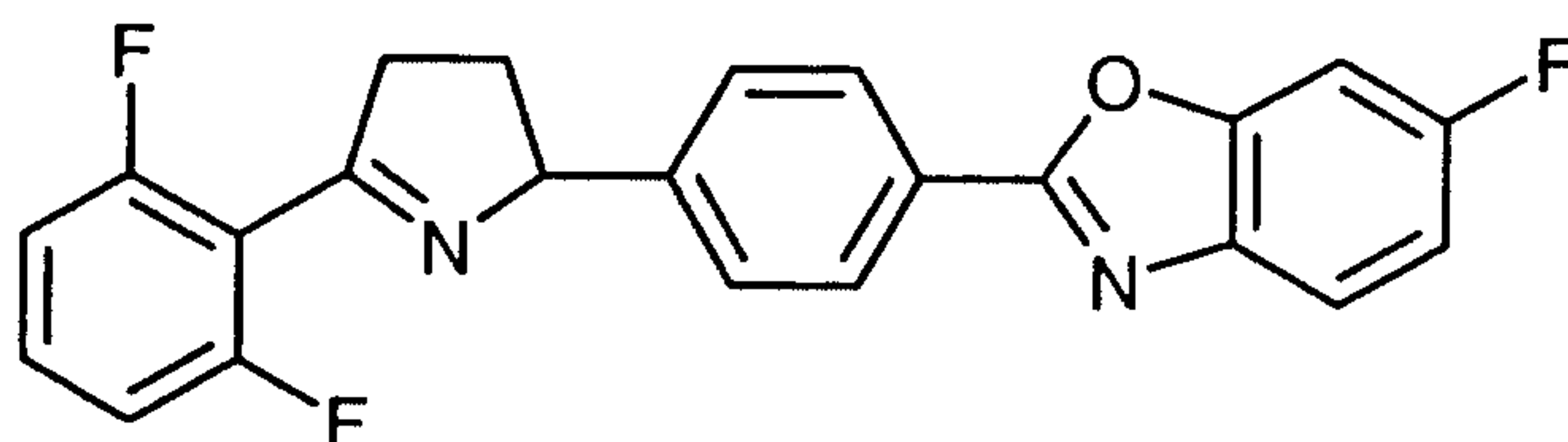
15

This gives 0.86g (44%) of 2-{4-[5-(2,6-difluorophenyl)-3,4-dihydro-2H-pyrrol-2-yl]-phenyl}[1,3]oxazole[4,5-b]pyridine.

HPLC: logP (2.3) = 2.06

20

#### Example 5



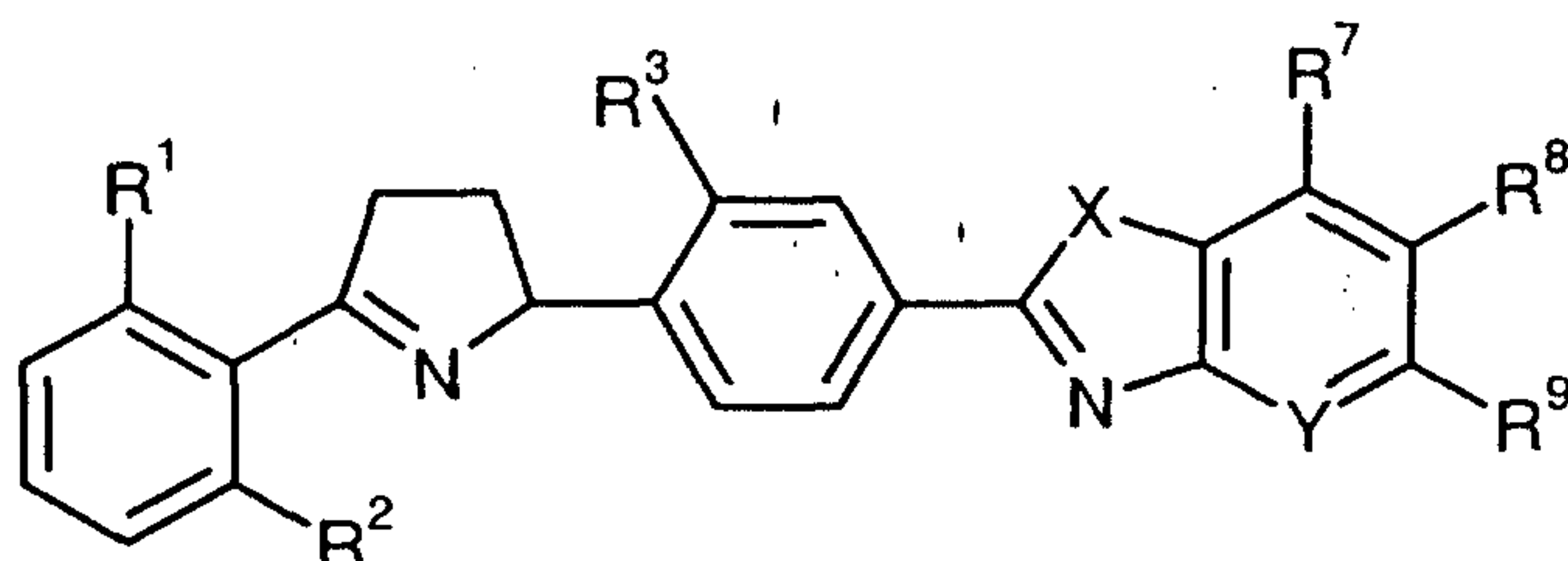
25 1.1 g of 4-[5-(2,6-difluorophenyl)-3,4-dihydro-2H-pyrrol-2-yl]-N-(5-fluor-2-hydroxyphenyl)benzamide are dissolved in 100 ml of benzene and, together with 1.2 g of p-

toluenesulphonic acid, heated under reflux using a Soxhlet with 3Å molecular sieves. After cooling, the mixture is diluted with ethyl acetate and neutralized with sodium bicarbonate. The organic phase is dried over sodium sulphate, filtered and concentrated. The crude product is purified by silica gel chromatography (mobile phase: ethyl acetate/cyclohexane 1:5).

This gives 0.24 g (30% of theory) of 2-{4-[5-(2,6-difluorophenyl)-3,4-dihydro-2H-pyrrol-2-yl]phenyl}-6-fluoro-1,3-benzoxazole.

HPLC:  $\log P(2.3) = 3.53$

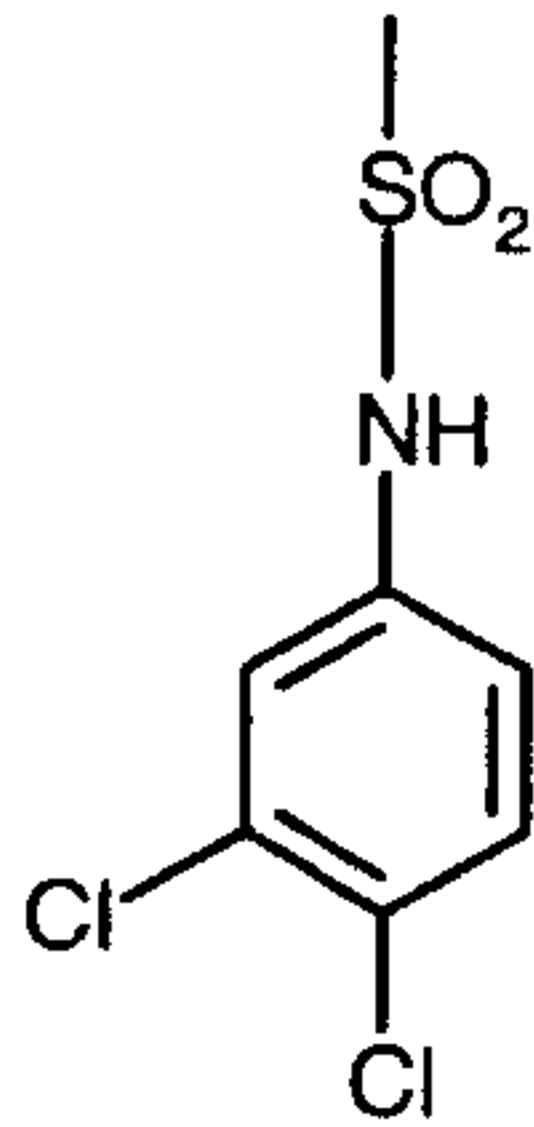
The following compounds of the formula (I) can be obtained analogously to Examples 1 to 5 and in accordance with the general description.

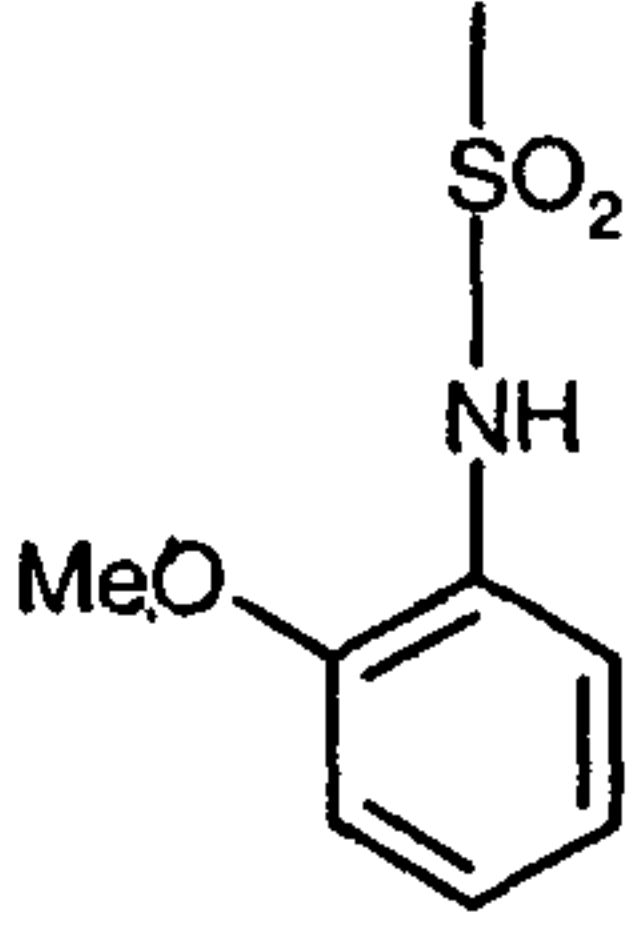


| No. | R <sup>1</sup> | R <sup>2</sup> | R <sup>3</sup> | X | Y                | R <sup>7</sup> | R <sup>8</sup>  | R <sup>9</sup> | R <sup>10</sup> | log P              |
|-----|----------------|----------------|----------------|---|------------------|----------------|-----------------|----------------|-----------------|--------------------|
| 6   | F              | F              | H              | O | CR <sup>10</sup> | H              | NO <sub>2</sub> | Cl             | H               | 4.12 <sup>a)</sup> |
| 7   | F              | F              | H              | O | CR <sup>10</sup> | H              | H               | Cl             | H               | 4.23 <sup>a)</sup> |
| 8   | F              | F              | H              | O | CR <sup>10</sup> | H              | Me              | H              | H               |                    |
| 9   | F              | F              | H              | O | CR <sup>10</sup> | H              | H               | Me             | H               |                    |
| 10  | F              | F              | H              | O | CR <sup>10</sup> | H              |                 | H              | H               |                    |
| 11  | Me             | H              | H              | O | CR <sup>10</sup> | H              | H               | H              | H               | 2.25 <sup>a)</sup> |
| 12  | F              | F              | H              | O | CR <sup>10</sup> | Cl             | H               | Cl             | H               | 5.44 <sup>a)</sup> |

## Le A 35 518-Foreign Countries

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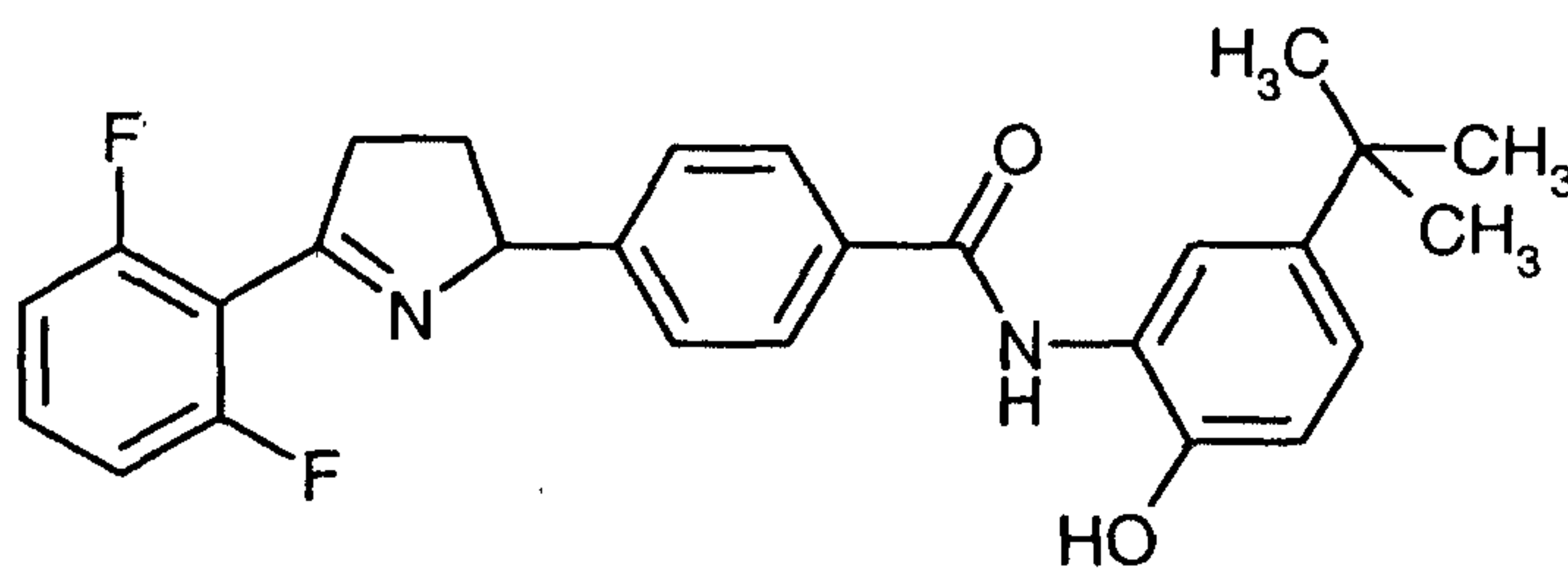
| No. | R <sup>1</sup> | R <sup>2</sup> | R <sup>3</sup> | X | Y                | R <sup>7</sup>  | R <sup>8</sup>                   | R <sup>9</sup>                                                                        | R <sup>10</sup> | log P              |
|-----|----------------|----------------|----------------|---|------------------|-----------------|----------------------------------|---------------------------------------------------------------------------------------|-----------------|--------------------|
| 13  | F              | F              | H              | O | CR <sup>10</sup> | H               | Cl                               | CF <sub>3</sub>                                                                       | H               |                    |
| 14  | F              | F              | F              | O | CR <sup>10</sup> | H               | H                                | H                                                                                     | H               | 4.25 <sup>a)</sup> |
| 15  | F              | F              | H              | O | CR <sup>10</sup> | H               | SO <sub>2</sub> NMe <sub>2</sub> | Cl                                                                                    | H               |                    |
| 16  | F              | F              | H              | O | CR <sup>10</sup> | H               | H                                | H                                                                                     | Me              | 3.90 <sup>a)</sup> |
| 17  | F              | F              | H              | O | CR <sup>10</sup> | H               | H                                | OCF <sub>3</sub>                                                                      | H               | 4.49 <sup>a)</sup> |
| 18  | F              | F              | H              | O | CR <sup>10</sup> | Cl              | H                                | Cl                                                                                    | Cl              |                    |
| 19  | F              | F              | H              | O | CR <sup>10</sup> | H               | H                                | -CH=CH-CH=CH-                                                                         |                 | 4.56 <sup>a)</sup> |
| 20  | F              | F              | H              | O | CR <sup>10</sup> | Cl              | H                                | CF <sub>3</sub>                                                                       | H               | 5.41 <sup>a)</sup> |
| 21  | F              | F              | H              | O | CR <sup>10</sup> | H               | Me                               | Cl                                                                                    | Me              | 5.81 <sup>a)</sup> |
| 22  | F              | F              | F              | O | CR <sup>10</sup> | H               | H                                | CF <sub>3</sub>                                                                       | H               | 5.31 <sup>a)</sup> |
| 23  | F              | F              | H              | O | CR <sup>10</sup> | H               | H                                | phenyl                                                                                | H               | 4.86 <sup>a)</sup> |
| 24  | F              | F              | H              | O | CR <sup>10</sup> | H               | SO <sub>2</sub> NHMe             | Cl                                                                                    | H               | 2.87 <sup>a)</sup> |
| 25  | F              | F              | F              | O | CR <sup>10</sup> | H               | H                                | Cl                                                                                    | H               | 5.22 <sup>a)</sup> |
| 26  | F              | F              | H              | O | CR <sup>10</sup> | H               | H                                | Br                                                                                    | H               | 4.38 <sup>a)</sup> |
| 27  | F              | F              | H              | S | CR <sup>10</sup> | H               | H                                | CF <sub>3</sub>                                                                       | H               | 4.77 <sup>a)</sup> |
| 28  | F              | F              | H              | O | CR <sup>10</sup> | CF <sub>3</sub> | H                                | CF <sub>3</sub>                                                                       | H               | 5.31 <sup>a)</sup> |
| 29  | F              | F              | H              | O | CR <sup>10</sup> | H               | H                                |  | H               |                    |
| 30  | F              | F              | H              | S | CR <sup>10</sup> | H               | H                                | H                                                                                     | H               |                    |
| 31  | F              | F              | H              | O | CR <sup>10</sup> | H               | CO <sub>2</sub> Me               | H                                                                                     | H               |                    |
| 32  | F              | F              | H              | O | CR <sup>10</sup> | H               | -CH=CH-CH=CH-                    |                                                                                       | H               | 4.46 <sup>a)</sup> |

| No. | R <sup>1</sup> | R <sup>2</sup> | R <sup>3</sup> | X | Y                | R <sup>7</sup> | R <sup>8</sup>                                                                      | R <sup>9</sup>                     | R <sup>10</sup> | log P              |
|-----|----------------|----------------|----------------|---|------------------|----------------|-------------------------------------------------------------------------------------|------------------------------------|-----------------|--------------------|
| 33  | F              | F              | H              | O | CR <sup>10</sup> | H              |  | Cl                                 | H               | 4.04 <sup>a)</sup> |
| 34  | F              | F              | H              | O | CR <sup>10</sup> | Cl             | -SO <sub>2</sub> -CH <sub>2</sub> -O-                                               |                                    | H               |                    |
| 35  | F              | F              | H              | O | CR <sup>10</sup> | H              | H                                                                                   | CH <sub>2</sub> SO <sub>2</sub> Me | H               |                    |
| 36  | F              | F              | F              | O | CR <sup>10</sup> | H              | H                                                                                   | phenyl                             | H               | 5.72 <sup>a)</sup> |

### Preparation of starting materials of the formula (II)

5

#### Example II-1



Under argon, a solution of 2.62 g of triphenylphosphine in toluene is added to 492  
 10 mg of palladium acetate in 50 ml of toluene. A solution of 3.03 g of 2-(4-  
 bromophenyl)-5-(2,6-difluorophenyl)-3,4-dihydro-2H-pyrrole, 2.97 g of 2-hydroxy-5-  
 tert-butylaniline and 2 g of Hünig base in toluene is then added, and the mixture is  
 allowed to react at a carbon monoxide pressure of 5 bar and at 100°C for 24 h. After  
 cooling, the mixture is diluted with ethyl acetate and extracted with water and the  
 15 organic phase is dried over sodium sulphate, filtered and concentrated. The crude  
 product is purified by silica gel chromatography (mobile phase: ethyl acetate/  
 cyclohexane 1:3 → 1:1).

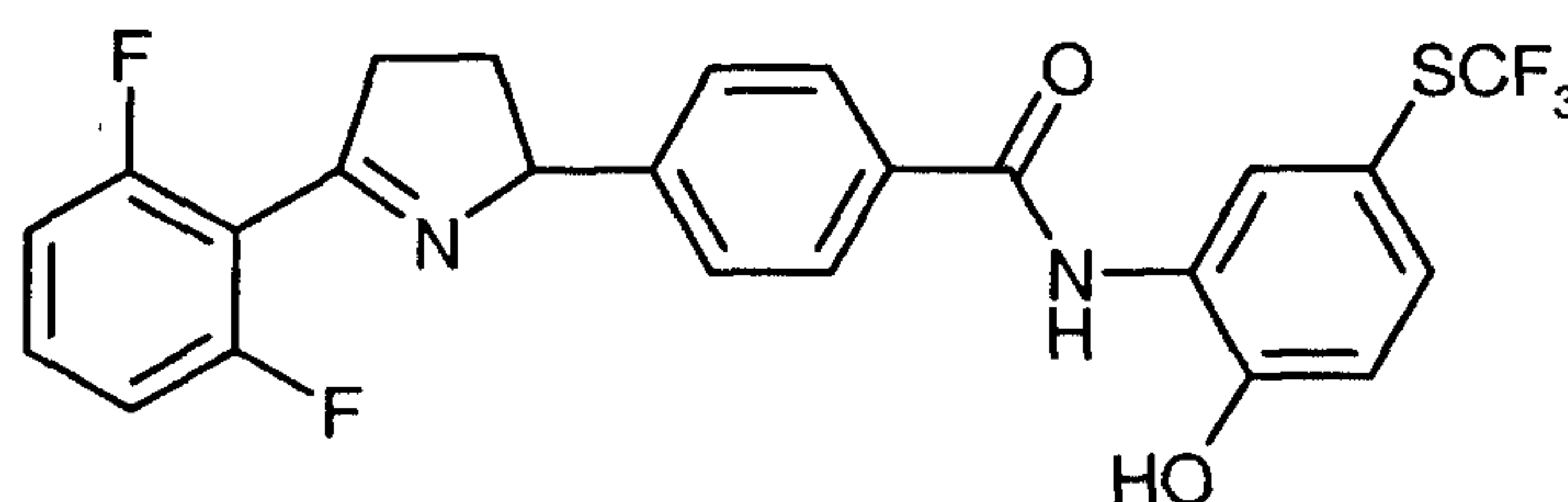
- 48 -

This gives 2.1 g (52% of theory) of N-(5-tert-butyl-2-hydroxyphenyl)-4-[5-(2,6-difluorophenyl)-3,4-dihydro-2H-pyrrol-2-yl]benzamide.

HPLC:  $\log P(2.3) = 3.22$

5

### Example II-2

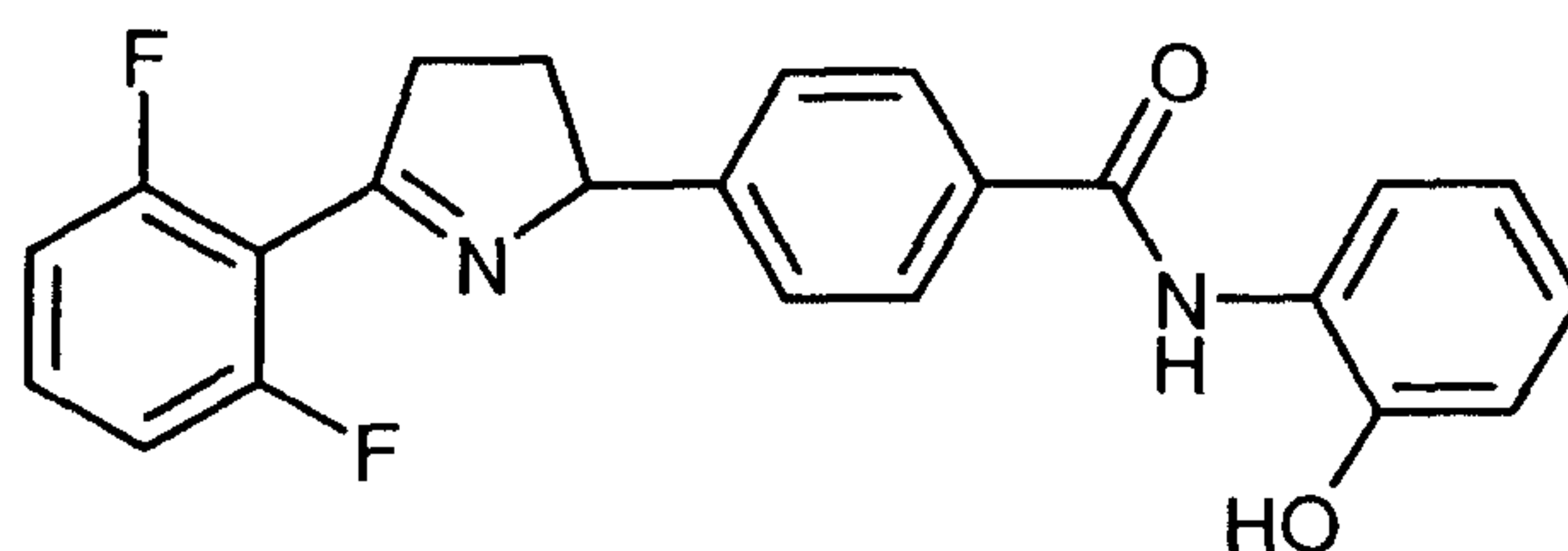


Under argon, 90 mg of palladium acetate are dissolved in 5 ml of toluene. 550 mg of triphenylphosphine in 10 ml of toluene, a solution of 900 mg of 2-amino-5-[(trifluoromethyl)sulphonyl]phenol and 1.38 g of 2-(4-bromophenyl)-5-(2,6-difluorophenyl)-3,4-dihydro-2H-pyrrole and 0.8 g of DBU in 5 ml of toluene are added successively. The mixture is stirred at 95°C under carbon monoxide for 16 h. After cooling, the reaction mixture is concentrated, citric acid, aqueous sodium chloride solution and 2N aqueous sodium hydroxide solution are added, and the reaction mixture is, at pH 3, extracted twice with ethyl acetate. The organic phase is dried, filtered and concentrated. The crude product is purified by silica gel chromatography (mobile phase: cyclohexane → cyclohexane/ethyl acetate 1:1).

This gives 0.5 g (24% of theory) of 4-[5-(2,6-difluorophenyl)-3,4-dihydro-2H-pyrrol-2-yl]-N-{2-hydroxy-5-[(trifluoromethyl)sulphonyl]phenyl}benzamide.

LC-MS: 493.0 [M+H]<sup>+</sup>

### Example II-3



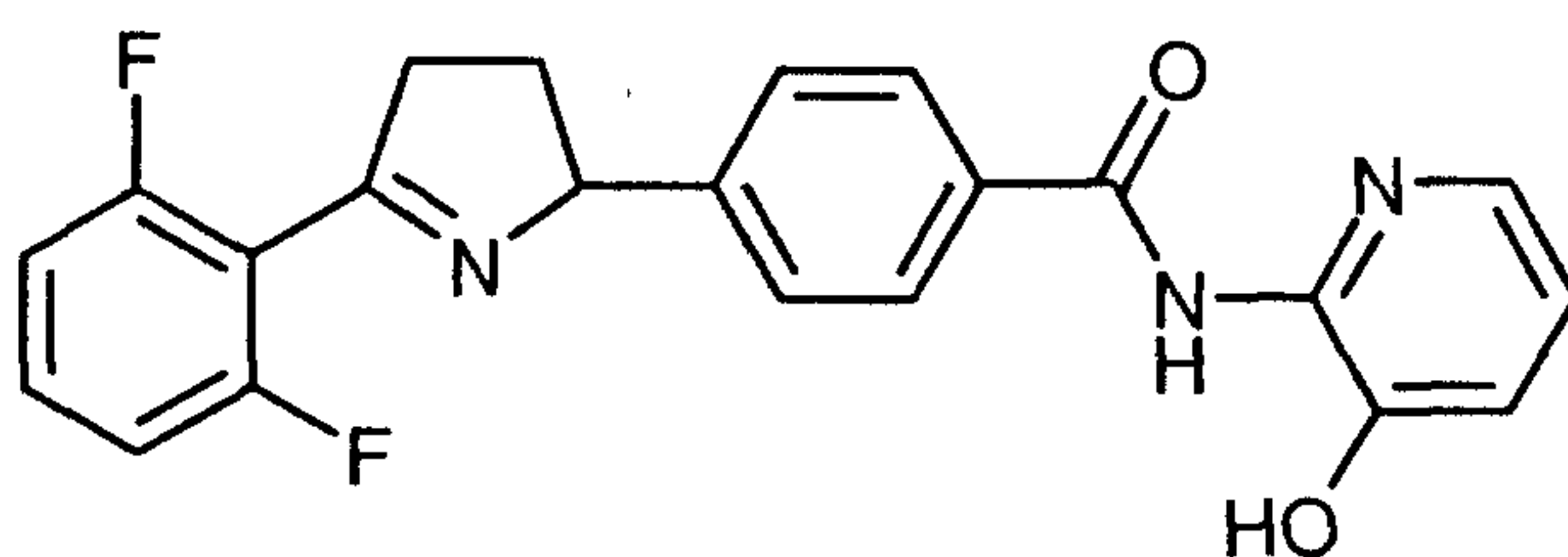
25

Under argon, 240 mg of palladium acetate are dissolved in 5 ml of toluene. 2.9 g of triphenylphosphine in 10 ml of toluene, a solution of 2 g of 2-aminophenol and 2.95 g of 2-(4-bromophenyl)-5-(2,6-difluorophenyl)-3,4-dihydro-2H-pyrrole and 2 g of Hünig base in 5 ml of toluene are added successively. The mixture is stirred at 95°C under carbon monoxide for 16 h. After cooling, the reaction mixture is concentrated, citric acid and aqueous sodium chloride solution and 2 N aqueous sodium hydroxide solution are added, and the reaction mixture is, at pH 3, extracted twice with ethyl acetate. The organic phase is dried, filtered and concentrated. The crude product is purified by silica gel chromatography (mobile phase: cyclohexane → cyclohexane/ethyl acetate 1:1).

This gives 3.1 g (90% of theory) of 4-[5-(2,6-difluorophenyl)-3,4-dihydro-2H-pyrrol-2-yl]-N-(2-hydroxyphenyl)benzamide.

<sup>1</sup>H-NMR (CD<sub>3</sub>CN): δ = 8.9 (br, 1H), 8.55 (br, 1H), 7.95 (br, 2H), 7.5 (m, 4H), 7.1 (m, 3H), 6.95 (m, 2H), 5.35 (t, 1H), 3.1 (m, 2H), 2.65 (m, 1H), 1.85 (m, 1H) ppm.

#### Example II-4



Under argon, a solution of 2.62 g of triphenylphosphine in toluene is added to 492 mg of palladium acetate in 50 ml of toluene. A solution of 3.02 g of 2-(4-bromophenyl)-5-(2,6-difluorophenyl)-3,4-dihydro-2H-pyrrole, 1.98 g of 2-amino-3-hydroxypyridine and 2 g of Hünig base in toluene is then added, a carbon monoxide pressure of 5 bar is applied and the mixture is allowed to react for 24 h. After cooling, the mixture is diluted with ethyl acetate and extracted with water and the organic phase is dried over sodium sulphate, filtered and concentrated. The crude

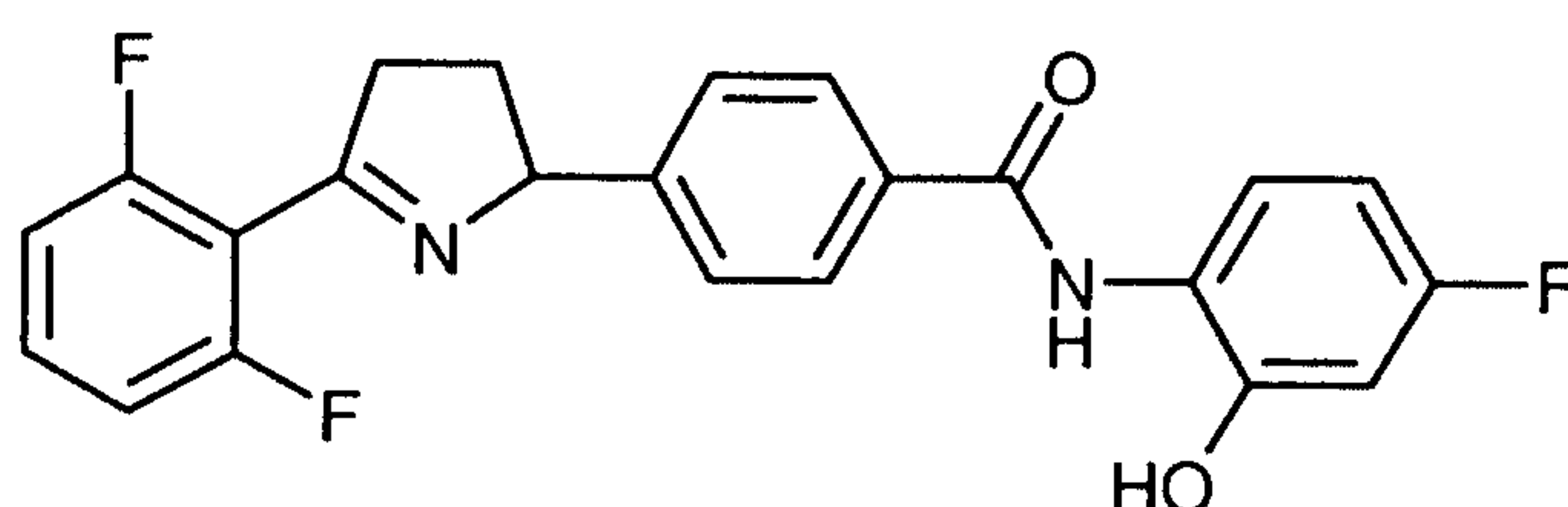
- 50 -

product is purified by silica gel chromatography (mobile phase: cyclohexane/ethyl acetate 1:1).

This gives 2 g (56% of theory) of 4-[5-(2,6-difluorophenyl)-3,4-dihydro-2H-pyrrol-2-yl]-N-(3-hydroxy-2-pyridinyl)benzamide.

HPLC:  $\log P(2.3) = 1.16$

### Example II-5



Under argon, 995 mg of triphenylphosphine are dissolved in 15 ml of toluene. A solution of 156 mg of palladium acetate in 5 ml of toluene is added. After 10 min, a solution of 0.89 g of 2-(4-bromophenyl)-5-(2,6-difluorophenyl)-3,4-dihydro-2H-pyrrole, 0.35 g of 2-hydroxy-4-fluoroaniline and 0.5 g of DBU in toluene is added, the atmosphere is changed to carbon monoxide and the mixture is heated at 95°C for about 20 h. Aqueous citric acid and sodium chloride are then added, and the mixture is extracted with ethyl acetate. The organic phase is dried over sodium sulphate, filtered and concentrated. The crude product is purified by silica gel chromatography (mobile phase: ethyl acetate/cyclohexane 1:1).

This gives 0.7 g (64% of theory) of 4-[5-(2,6-difluorophenyl)-3,4-dihydro-2H-pyrrol-2-yl]-N-(5-fluoro-2-hydroxyphenyl)benzamide.

LC-MS: 411.0 [M+H]<sup>+</sup>

The logP values given in the Tables and Preparation Examples above are determined in accordance with EEC Directive 79/831 Annex V.A8 by HPLC (High Performance Liquid Chromatography) using a reversed-phase column (C 18). Temperature: 43°C.

- 5 The determination in the acidic range is carried out at pH 2.3 using the mobile phases 0.1% aqueous phosphoric acid and acetonitrile; linear gradient from 10% acetonitrile to 90% acetonitrile. In the Tables, the values are marked a).

- 10 The determination in the neutral range is carried out at pH 7.5 using the mobile phases 0.01 molar aqueous phosphate buffer solution and acetonitrile; linear gradient 10% acetonitrile to 90% acetonitrile. In the Tables, the values are marked b).

- 15 Calibration is carried out using unbranched alkan-2-ones (of 3 to 16 carbon atoms) with known logP values (determination of the logP values by retention times using linear interpolation between two successive alkanones).

The lambda max values were determined in the maxima of the chromatographic signals using the UV spectra from 200 nm to 400 nm.

Use Examples

Example A

5      **Heliothis armigera test**

Solvent:                      7    parts by weight of dimethylformamide

Emulsifier:                 2    parts by weight of alkylaryl polyglycol ether

10      To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

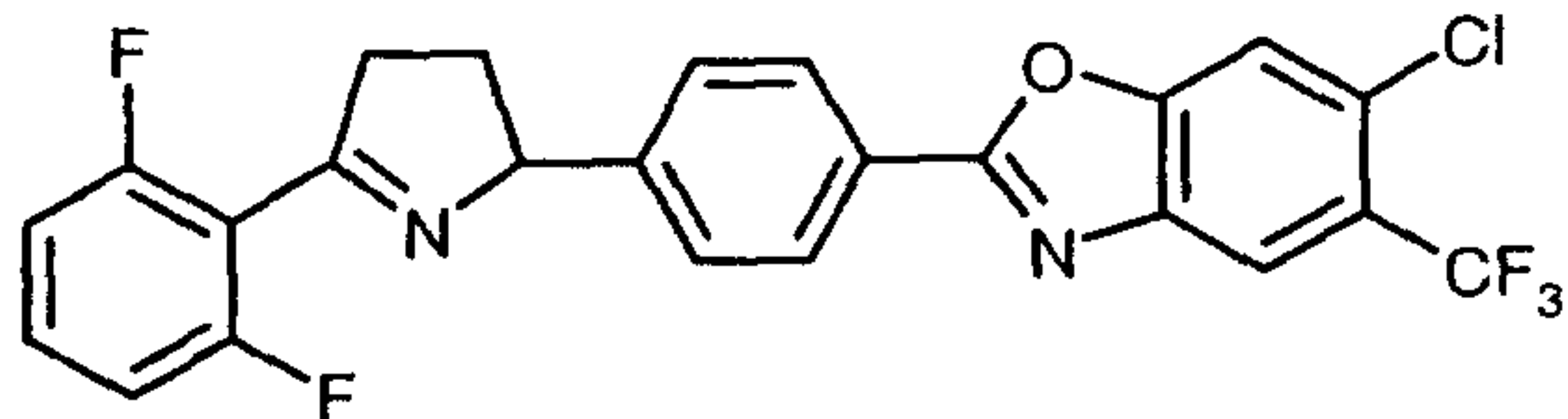
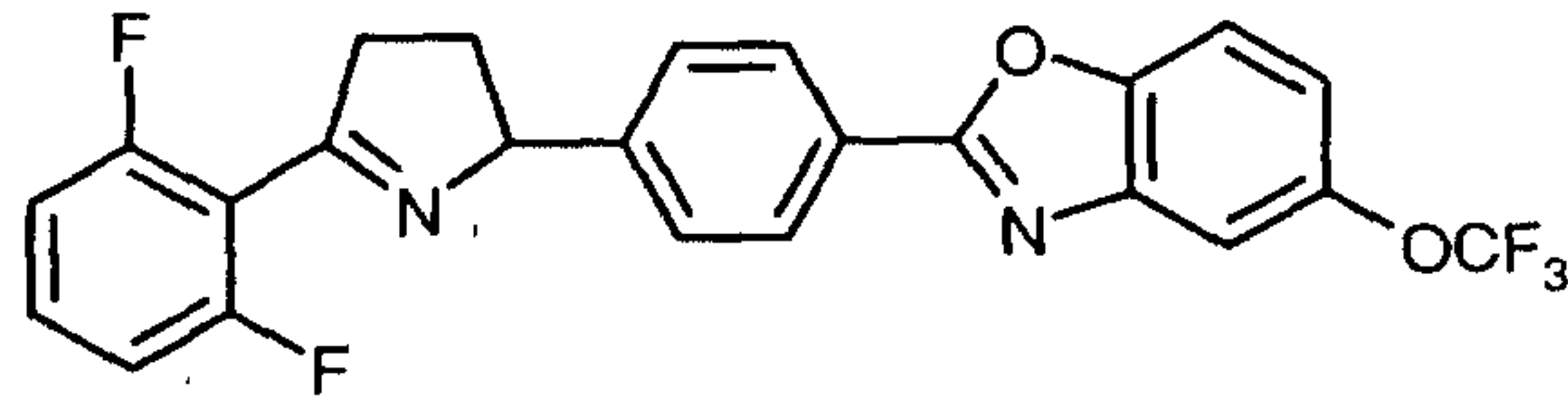
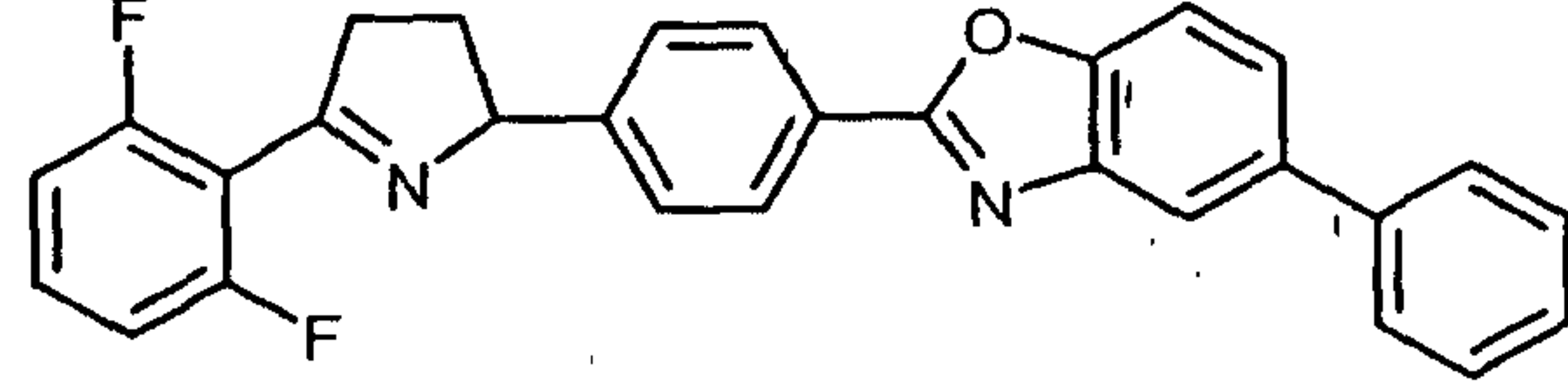
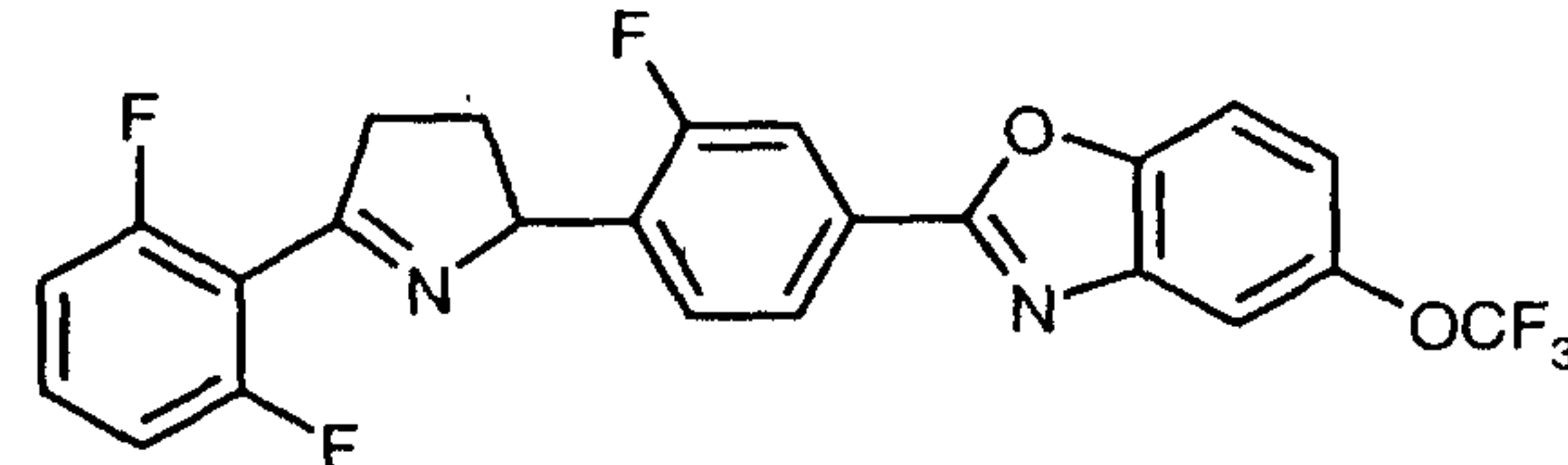
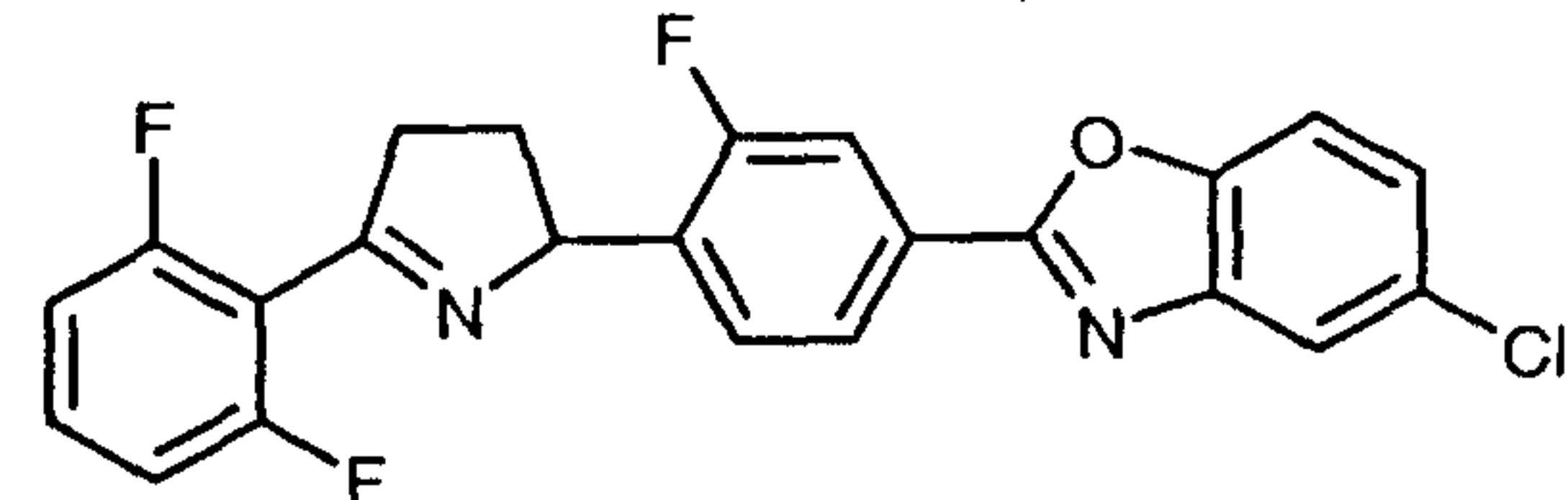
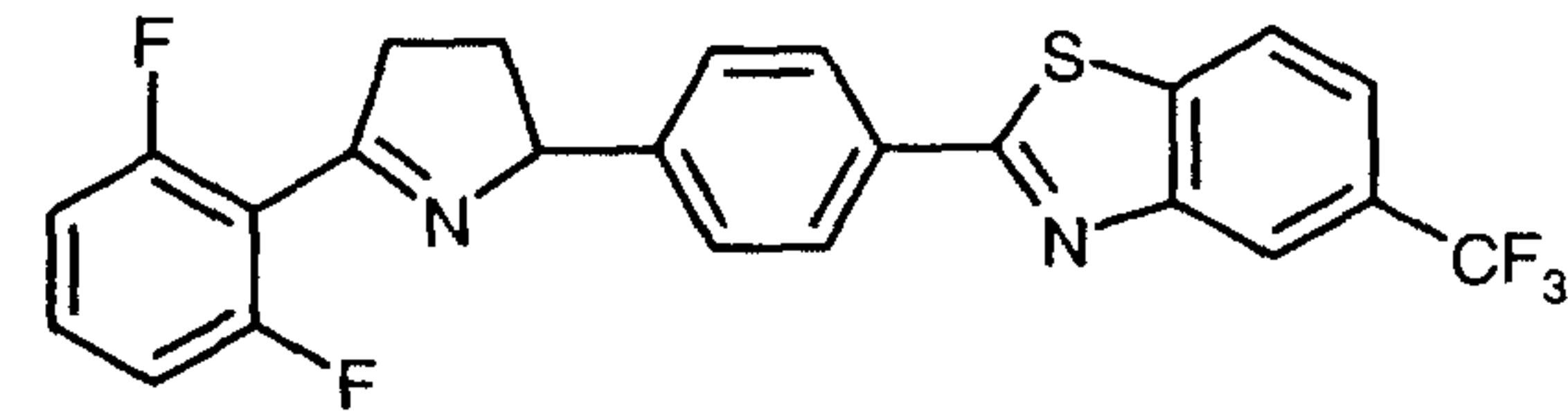
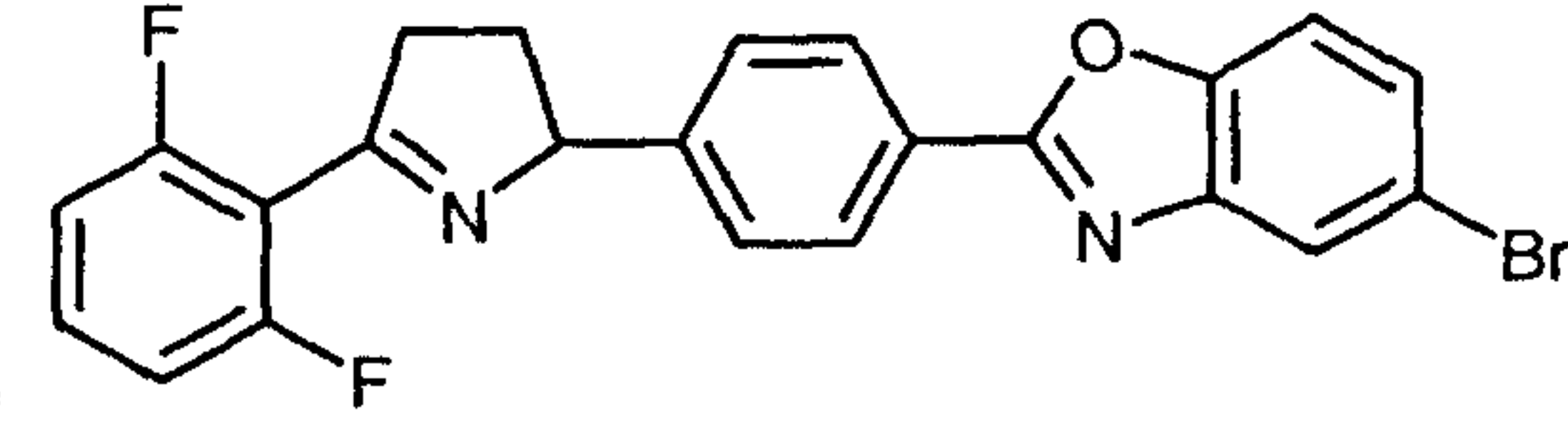
15      Soya bean shoots (Glycine max) are treated by being dipped into the preparation of active compound of the desired concentration and are populated with *Heliothis armigera* caterpillars while the leaves are still moist.

After the desired period of time, the kill in % is determined. 100% means that all caterpillars have been killed; 0% means that none of the caterpillars have been killed.

20

In this test, for example, the following compounds of the Preparation Examples show good activity:

Table A  
Plant-damaging insects  
***Heliothis armigera* test**

| Active compounds                                                                     | Concentration of active compound in ppm | Efficacy in % after 7 d |
|--------------------------------------------------------------------------------------|-----------------------------------------|-------------------------|
|   | 100                                     | 100                     |
|  | 100                                     | 100                     |
|  | 100                                     | 100                     |
|  | 100                                     | 100                     |
|  | 100                                     | 100                     |
|  | 100                                     | 100                     |
|  | 100                                     | 100                     |

Example B

**Meloidogyne test**

- 5      Solvent:                      7    parts by weight of dimethylformamide  
      Emulsifier:                2    parts by weight of alkylaryl polyglycol ether

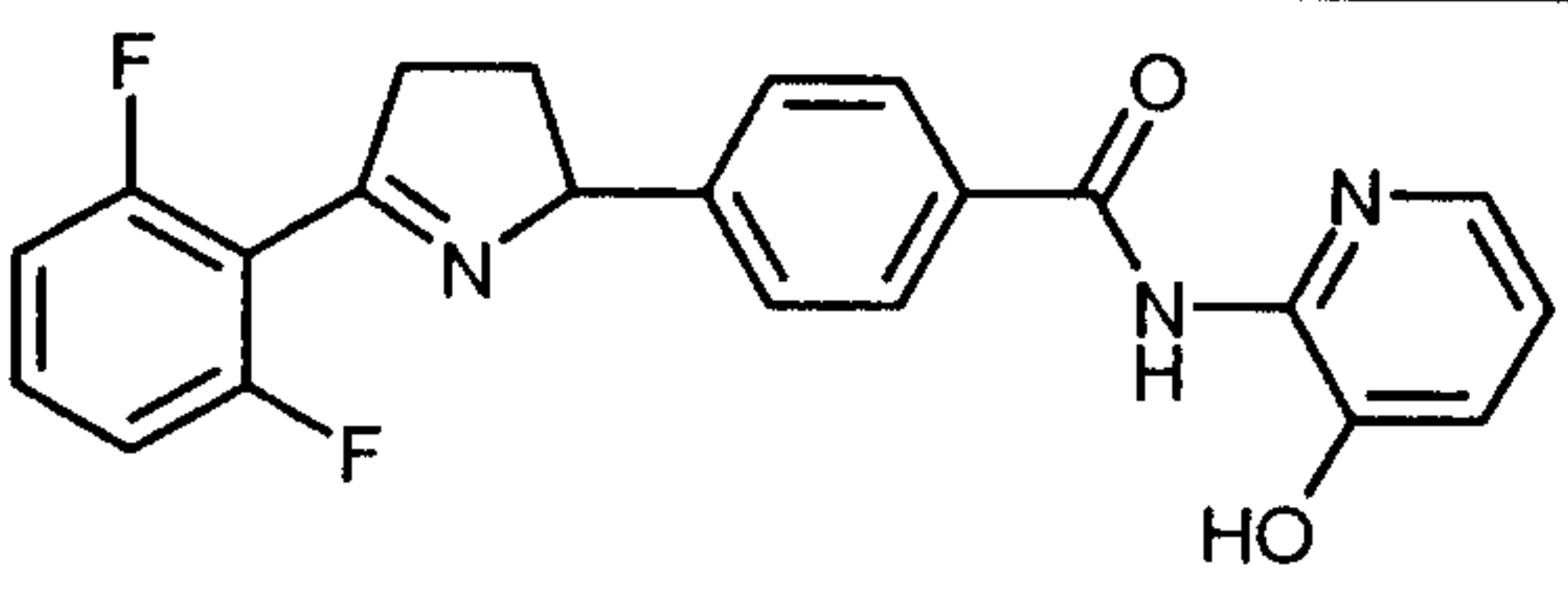
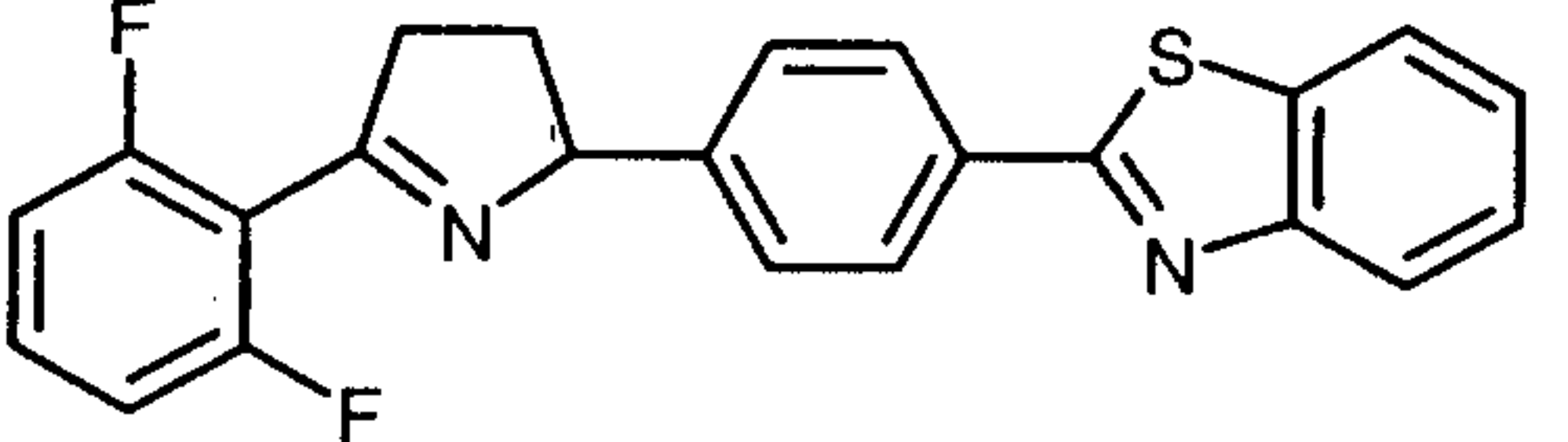
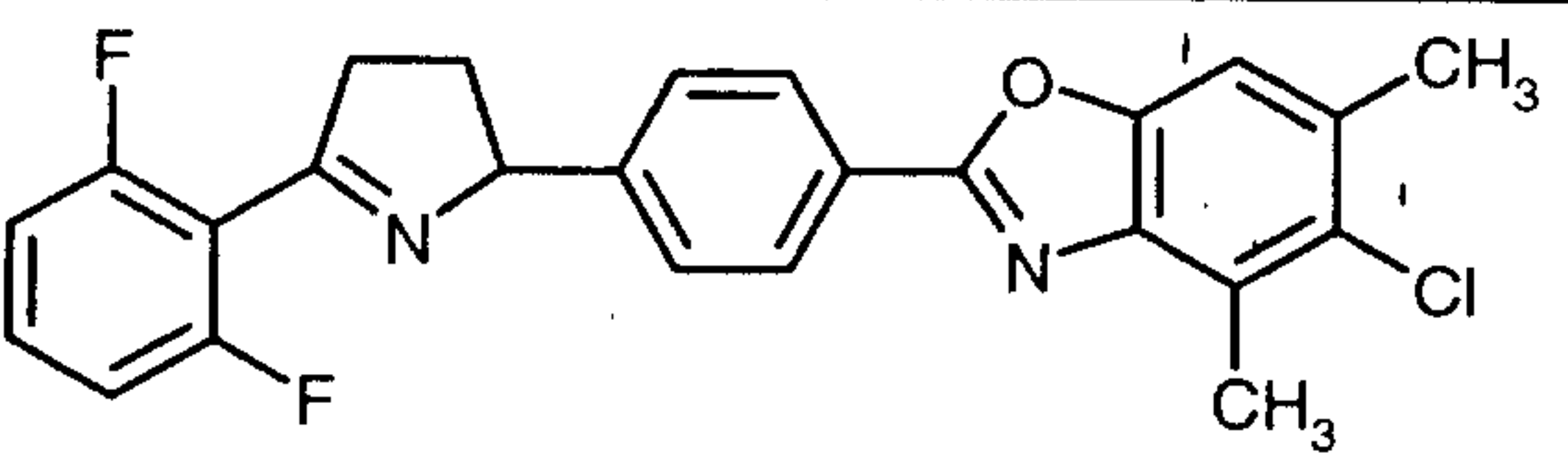
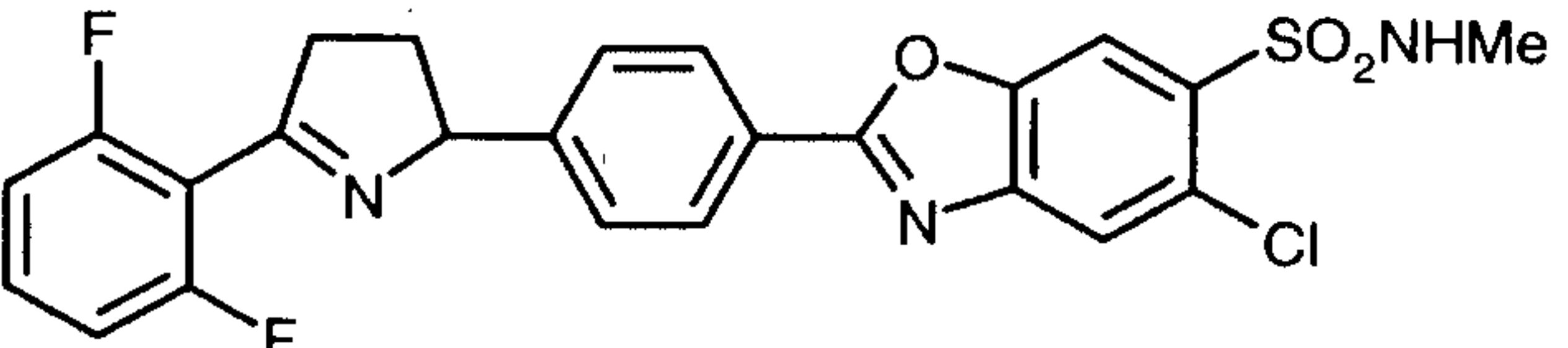
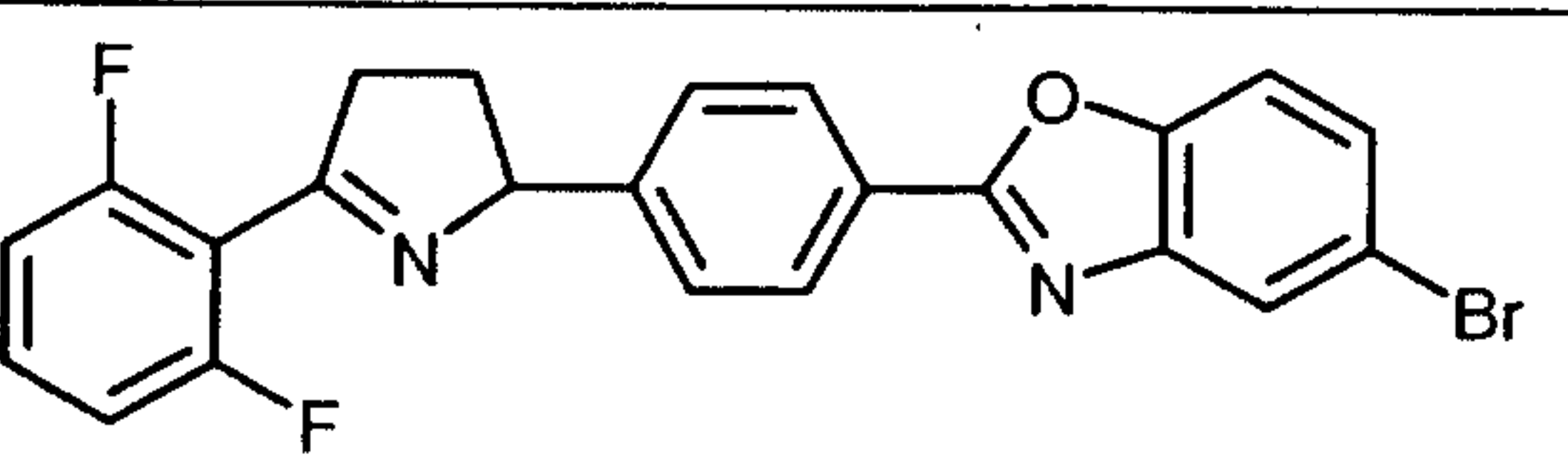
10      To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with water to the desired concentration.

15      Containers are filled with sand, solution of active compound, *Meloidogyne incognita* egg/larvae suspension and lettuce seeds. The lettuce seeds germinate and the plants develop. On the roots, galls are formed.

      After the desired period of time, the nematocidal action is determined in % by gall formation. 100% means that no galls were found; 0% means that the number of galls on the treated plants corresponds to that of the untreated control.

20      In this test, for example, the following compounds of the Preparation Examples show good activity:

Table B  
 Plant-damaging insects  
**Meloidogyne test**

| Active compound                                                                      | Concentration of active compound in ppm | Efficacy in % after 7 d |
|--------------------------------------------------------------------------------------|-----------------------------------------|-------------------------|
|   | 20                                      | 95                      |
|  | 20                                      | 80                      |
|  | 20                                      | 98                      |
|  | 20                                      | 80                      |
|  | 20                                      | 80                      |

Example C**Phaedon larvae test**

- 5      Solvent:                      7    parts by weight of dimethylformamide  
      Emulsifier:                2    parts by weight of alkylaryl polyglycol ether

10      To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

      Cabbage leaves (*Brassica oleracea*) are treated by being dipped into the preparation of active compound of the desired concentration and are populated with larvae of the mustard beetle (*Phaedon cochleariae*) while the leaves are still moist.

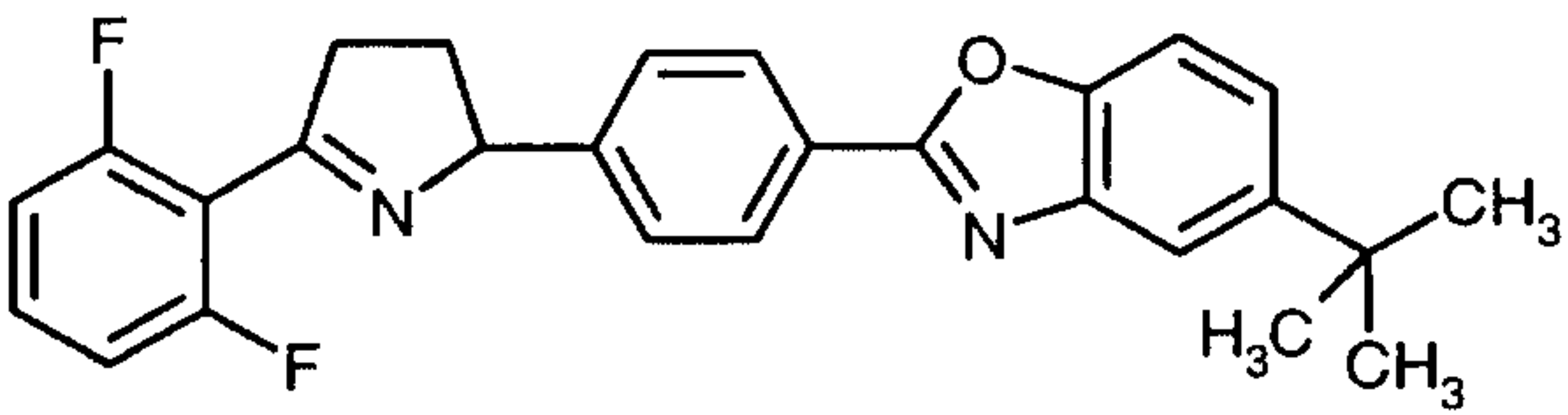
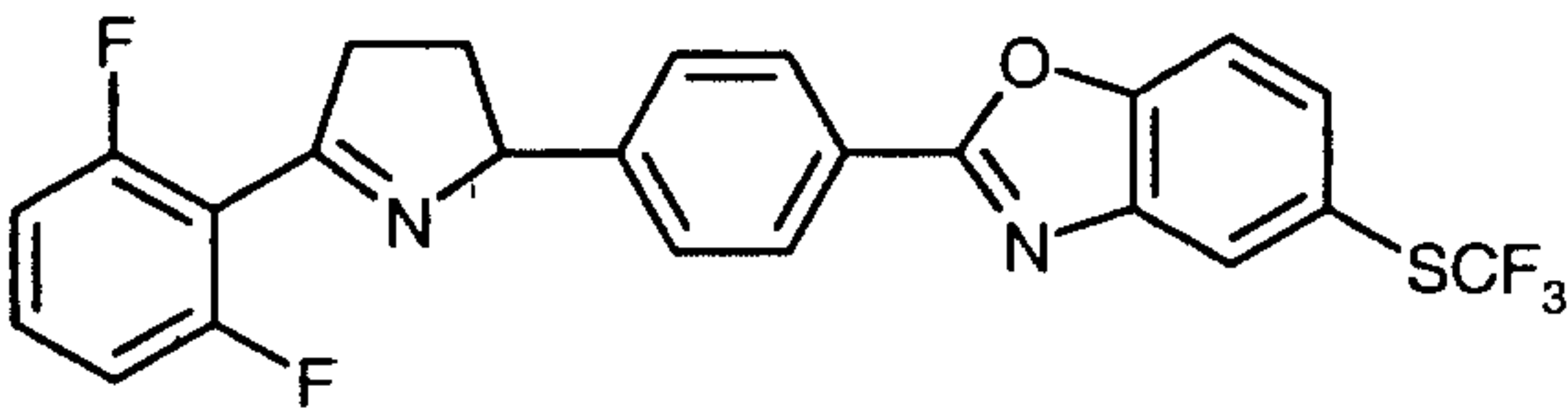
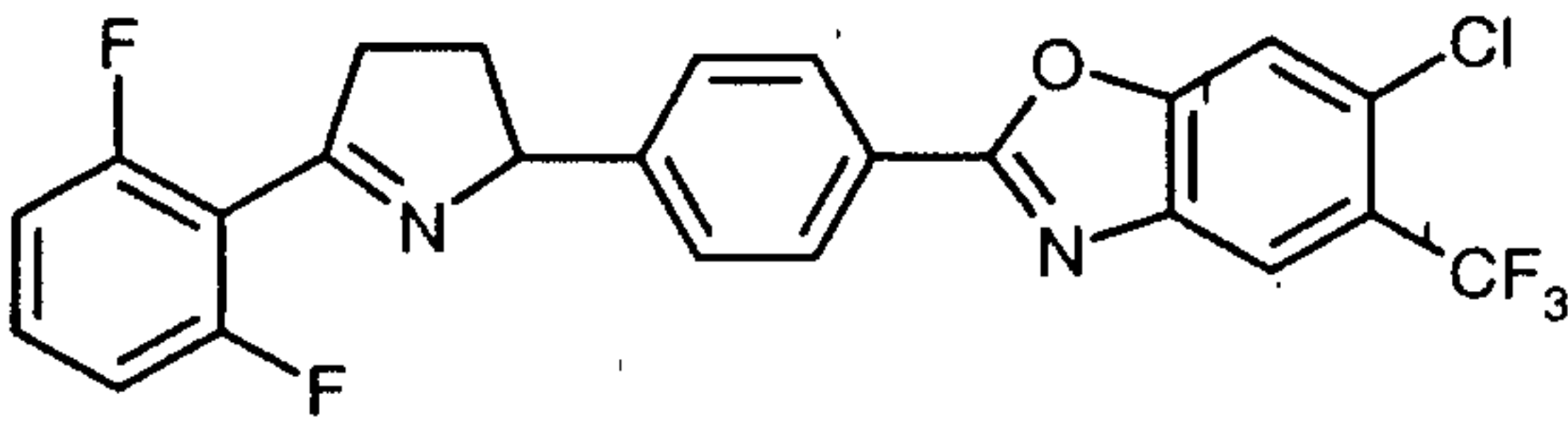
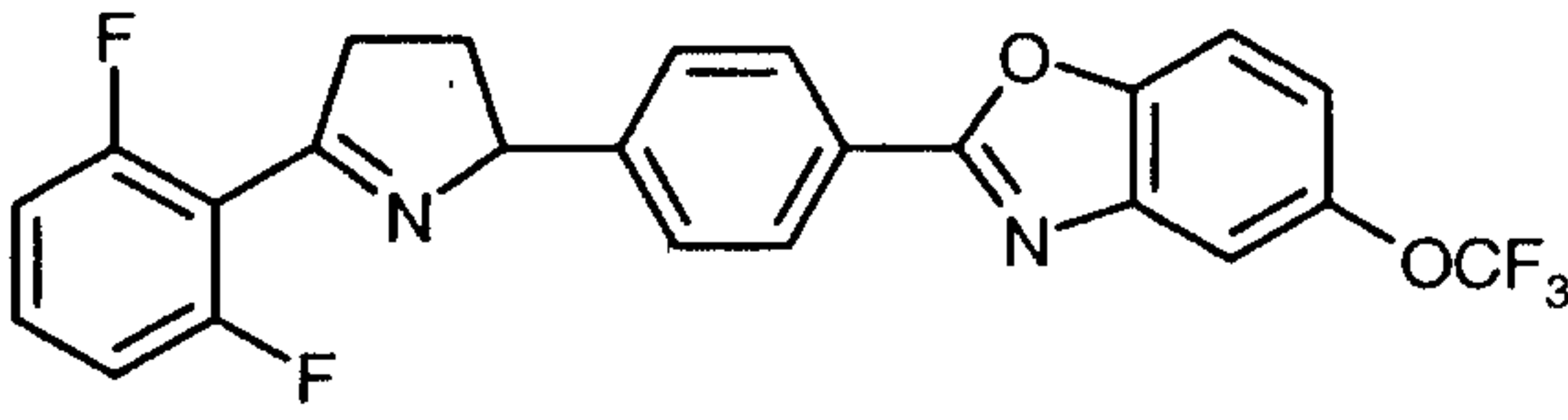
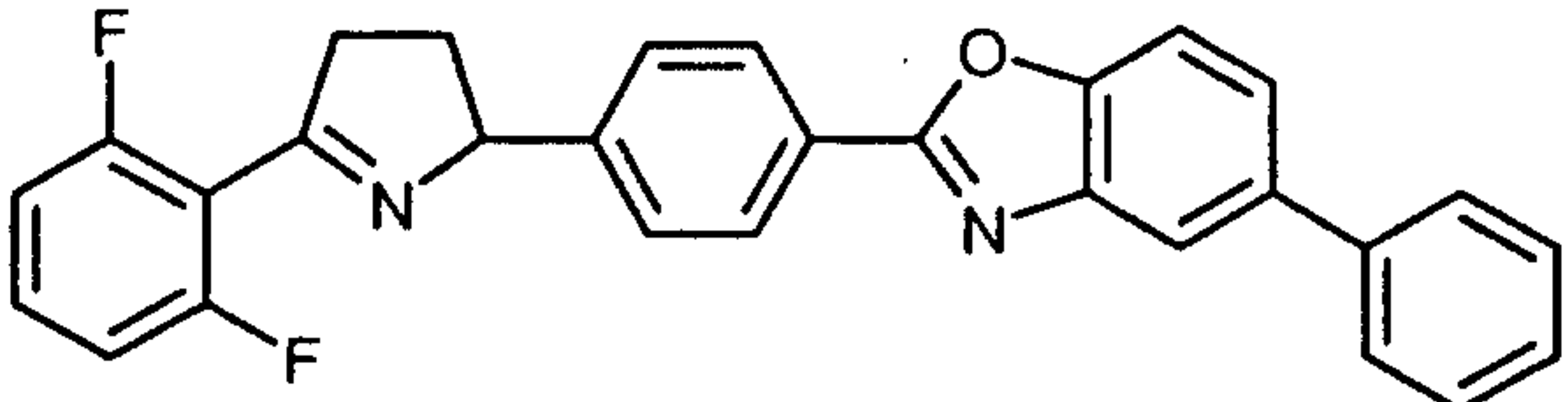
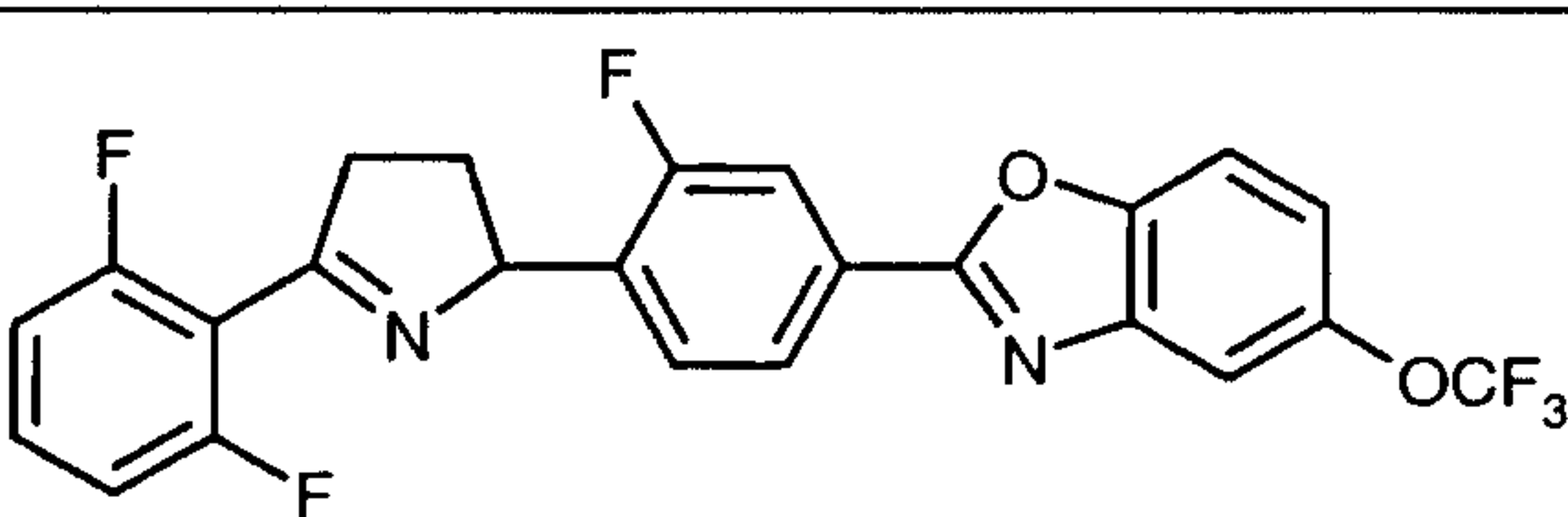
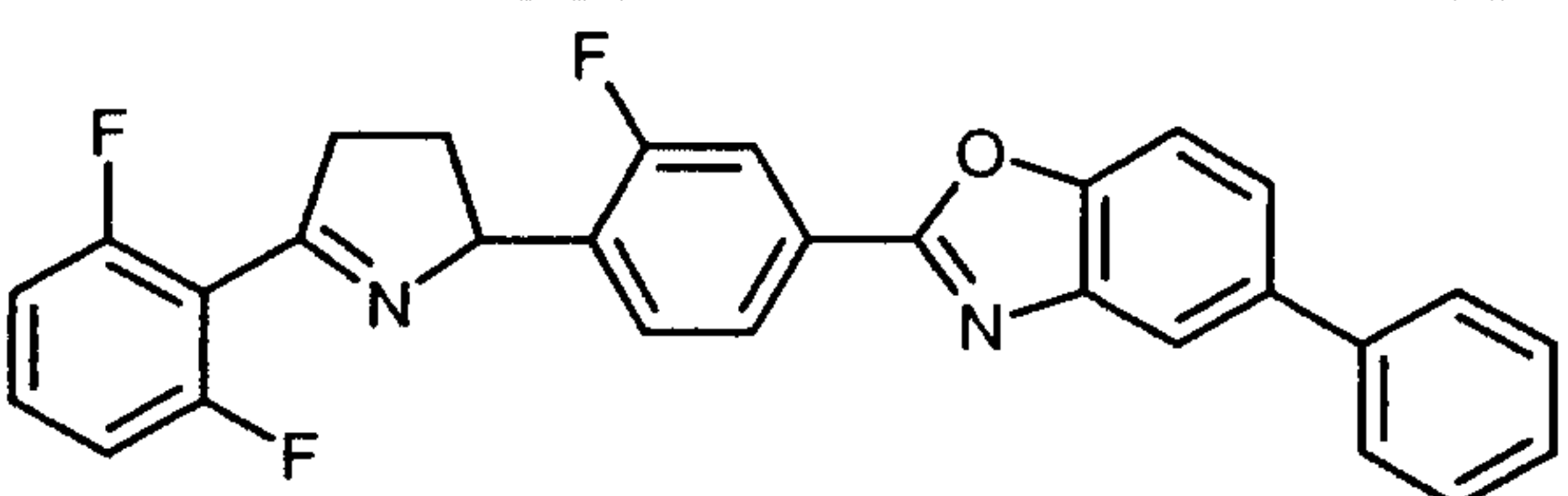
15

      After the desired period of time, the kill in % is determined. 100% means that all beetle larvae have been killed; 0% means that none of the beetle larvae have been killed.

20

      In this test, for example, the following compounds of the Preparation Examples show good activity:

Table C  
Plant-damaging insects  
Phaedon larvae test

| Active compounds                                                                     | Concentration of active compound in ppm | Efficacy in % after 7 d |
|--------------------------------------------------------------------------------------|-----------------------------------------|-------------------------|
|   | 500                                     | 100                     |
|  | 500                                     | 100                     |
|  | 100                                     | 100                     |
|  | 100                                     | 100                     |
|  | 100                                     | 100                     |
|  | 100                                     | 100                     |
|  | 100                                     | 100                     |

Example D

**Plutella test**

- 5      Solvent:                      7    parts by weight of dimethylformamide  
      Emulsifier:                2    parts by weight of alkylaryl polyglycol ether

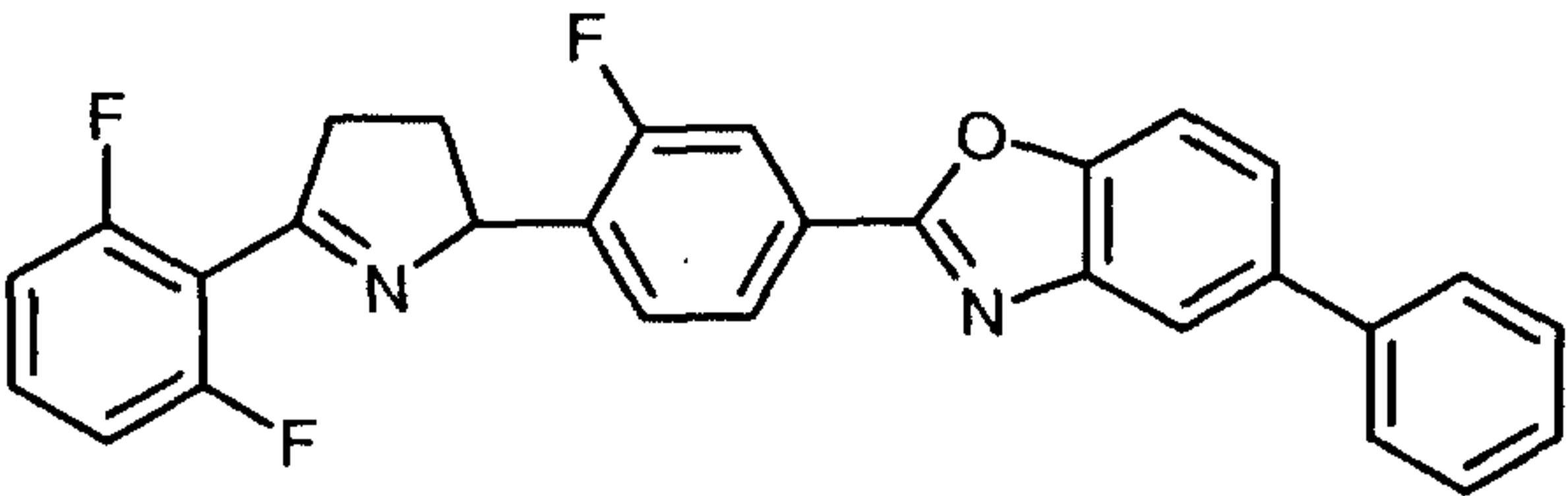
10      To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

15      Cabbage leaves (*Brassica oleracea*) are treated by being dipped into the preparation of active compound of the desired concentration and are populated with caterpillars of the diamondback moth (*Plutella xylostella*) while the leaves are still moist.

After the desired period of time, the kill in % is determined. 100% means that all caterpillars have been killed; 0% means that none of the caterpillars have been killed.

20      In this test, for example, the following compound of the Preparation Examples show good activity:

Table D  
Plant-damaging insects  
**Plutella test**

| Active compounds                                                                    | Concentration of<br>active compound in<br>ppm | Efficacy in %<br>after 7 d |
|-------------------------------------------------------------------------------------|-----------------------------------------------|----------------------------|
|  | 100                                           | 100                        |

Example E**Spodoptera exigua test**

- 5 Solvent: 7 parts by weight of dimethylformamide  
Emulsifier: 2 parts by weight of alkylaryl polyglycol ether

10 To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

Cabbage leaves (*Brassica oleracea*) are treated by being dipped into the preparation of active compound of the desired concentration and are populated with caterpillars of the armyworm (*Spodoptera exigua*) while the leaves are still moist.

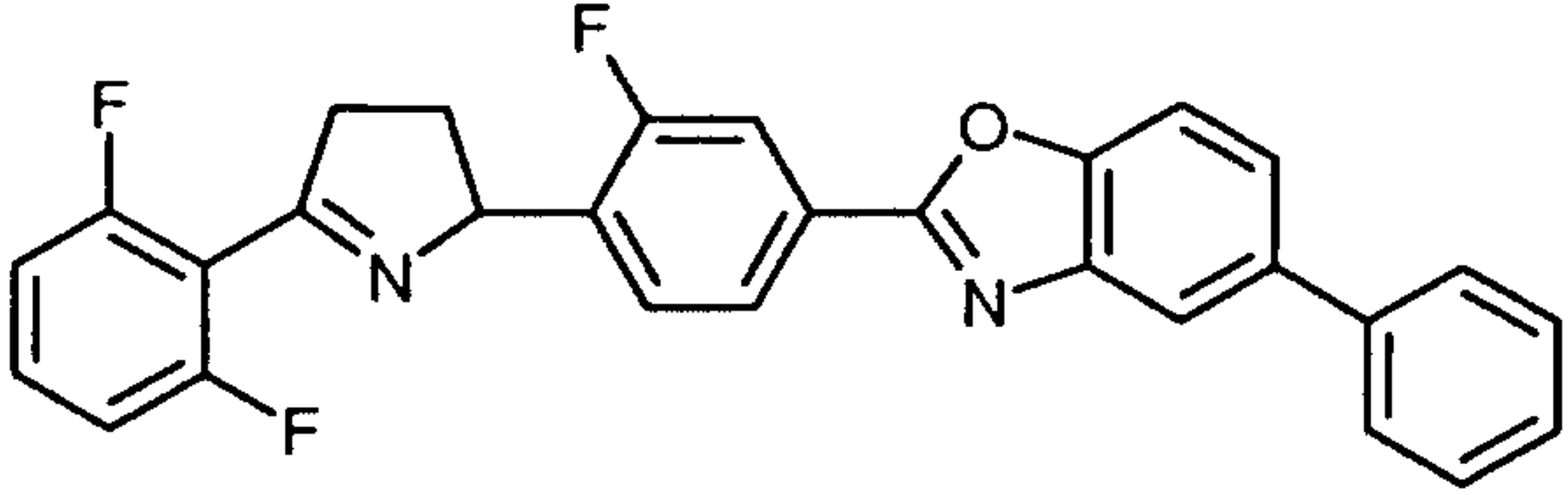
15

After the desired period of time, the kill in % is determined. 100% means that all caterpillars have been killed; 0% means that none of the caterpillars have been killed.

20

In this test, for example, the following compound of the Preparation Examples show good activity:

Table E  
Plant-damaging insects  
**Spodoptera exigua test**

| Active compounds                                                                    | Concentration of<br>active compound<br>in ppm | Efficacy in %<br>after 7 d |
|-------------------------------------------------------------------------------------|-----------------------------------------------|----------------------------|
|  | 100                                           | 100                        |

Example F**Spodoptera frugiperda test**

- 5 Solvent: 7 parts by weight of dimethylformamide  
Emulsifier: 2 parts by weight of alkylaryl polyglycol ether

10 To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

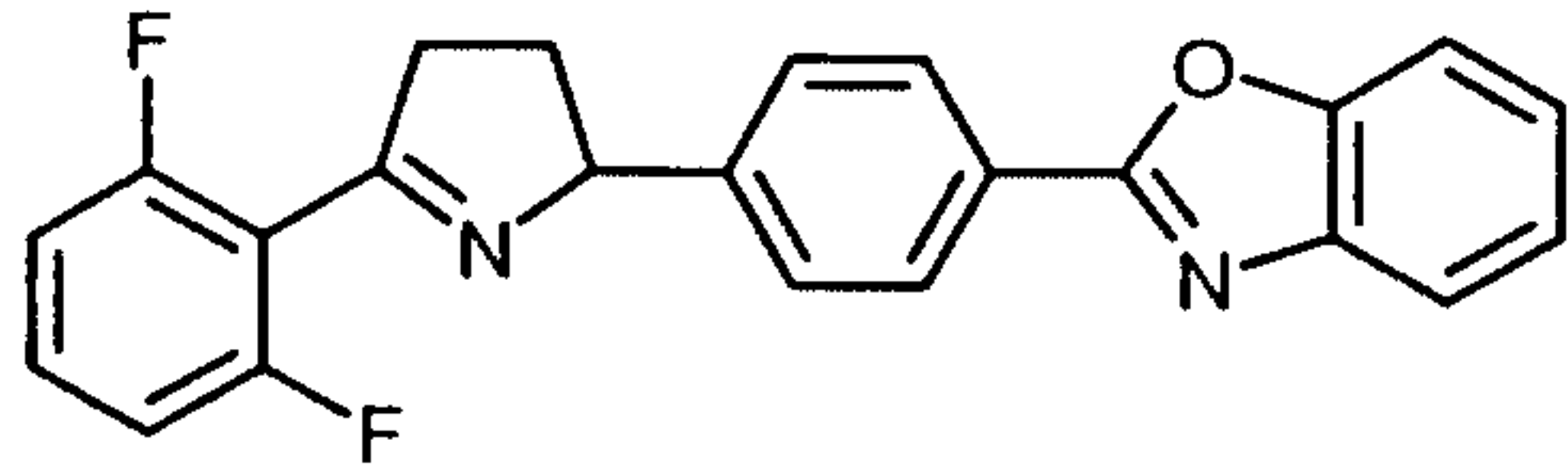
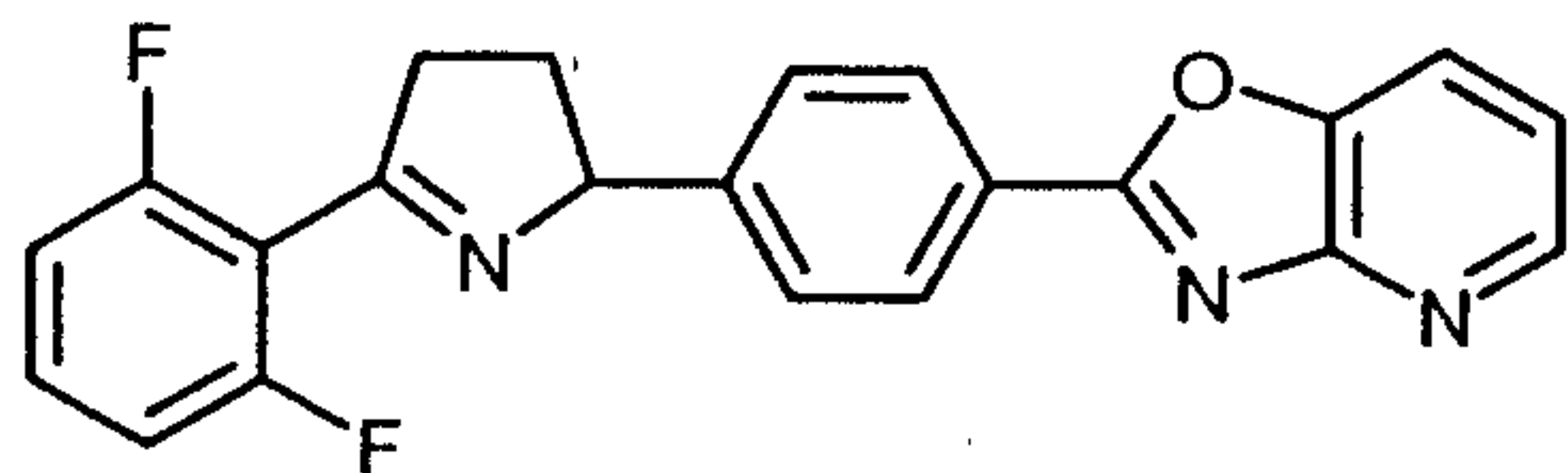
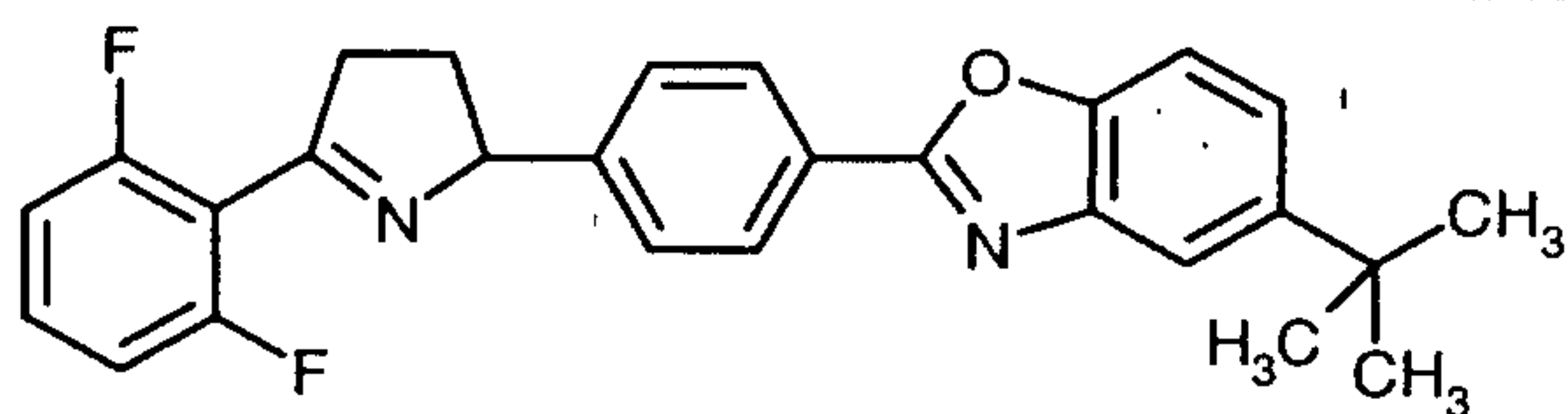
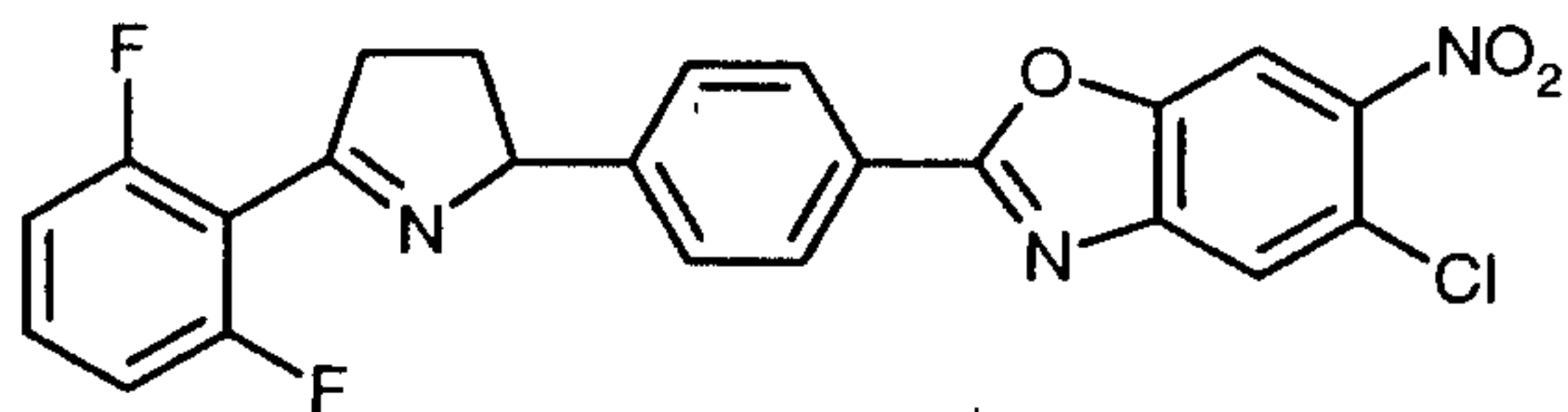
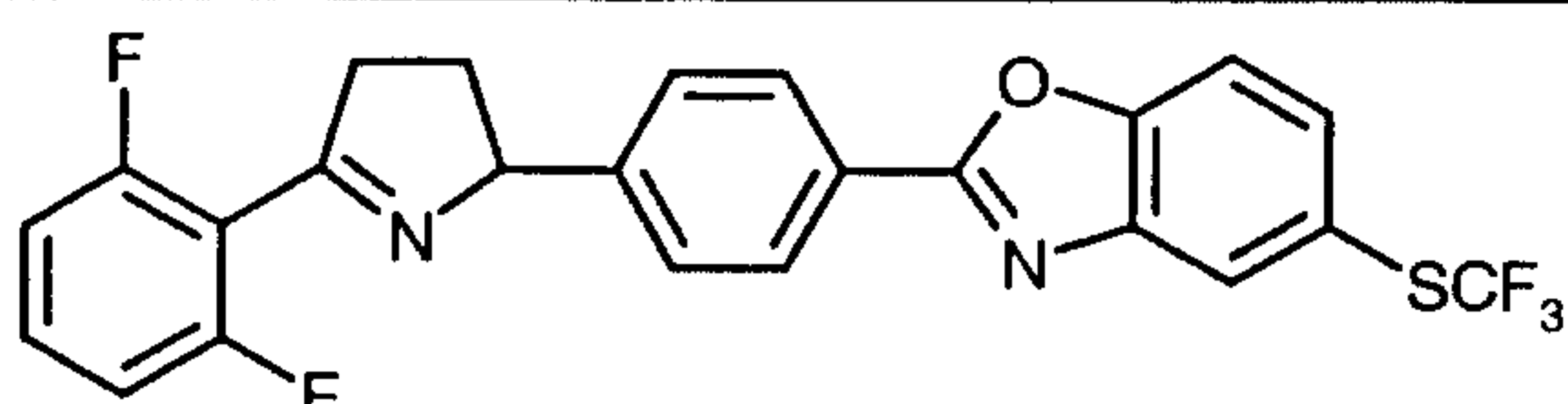
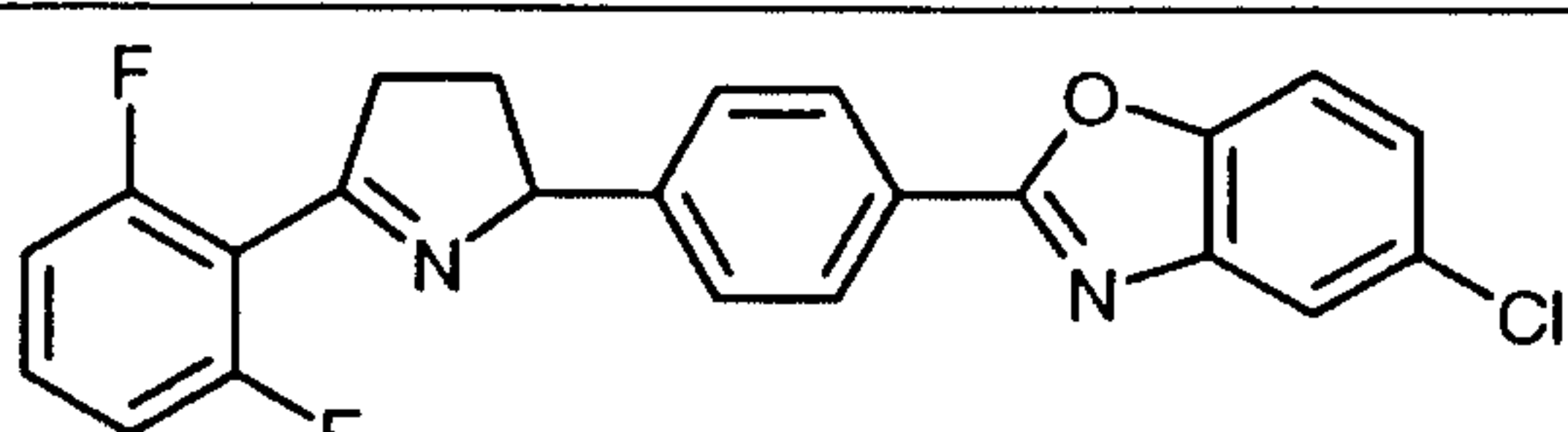
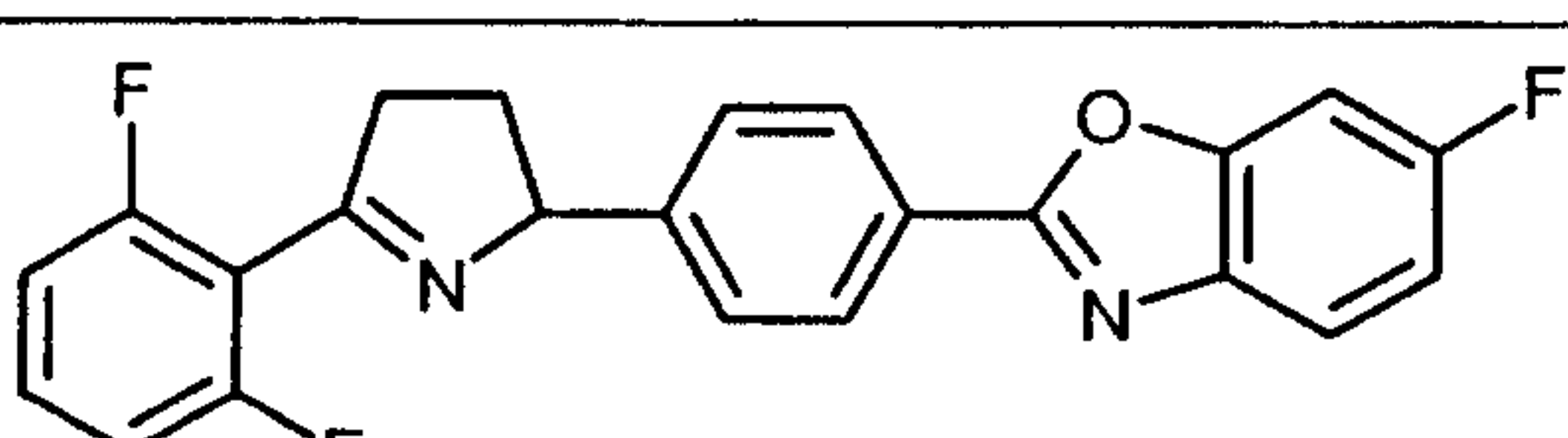
Cabbage leaves (*Brassica oleracea*) are treated by being dipped into the preparation of active compound of the desired concentration and are populated with caterpillars of the armyworm (*Spodoptera frugiperda*) while the leaves are still moist.

15

After the desired period of time, the kill in % is determined. 100% means that all caterpillars have been killed; 0% means that none of the caterpillars have been killed.

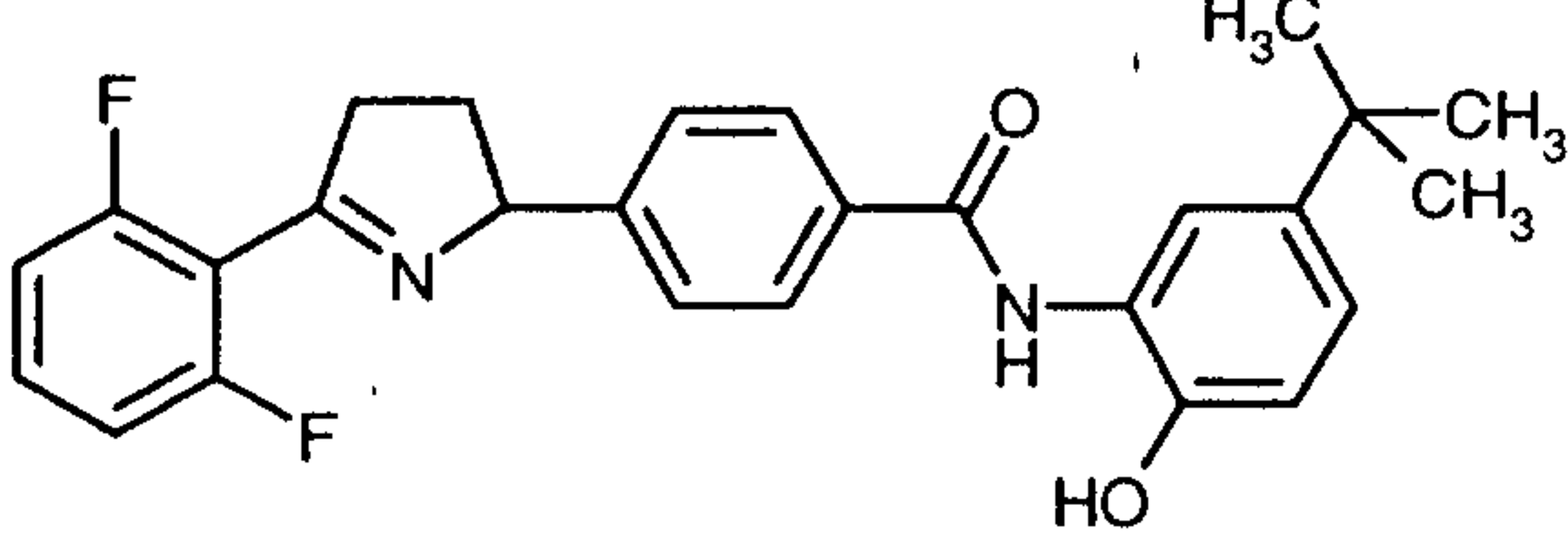
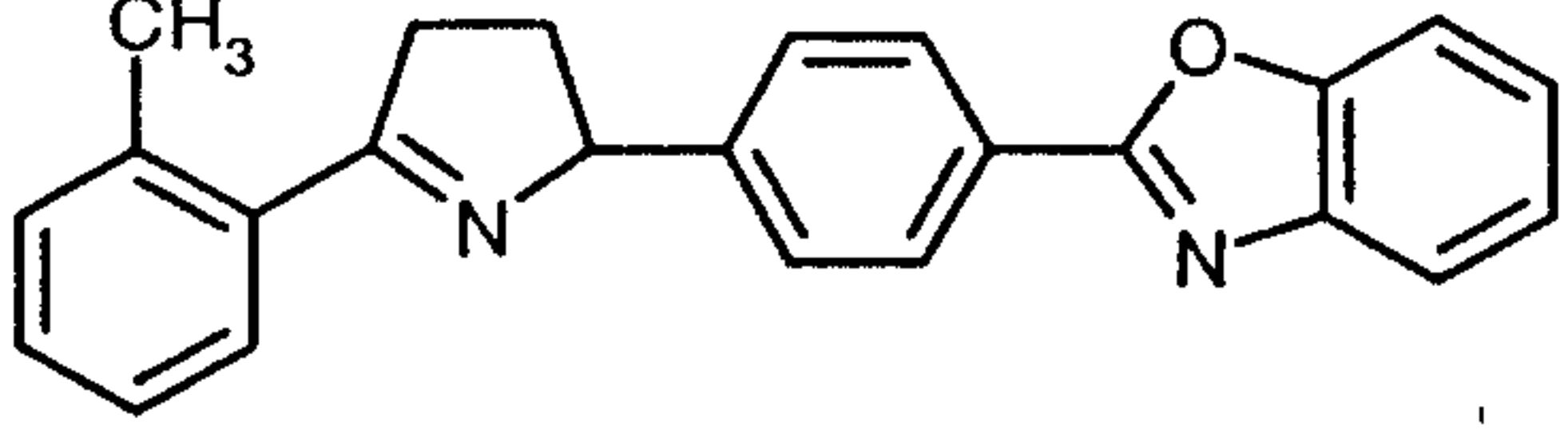
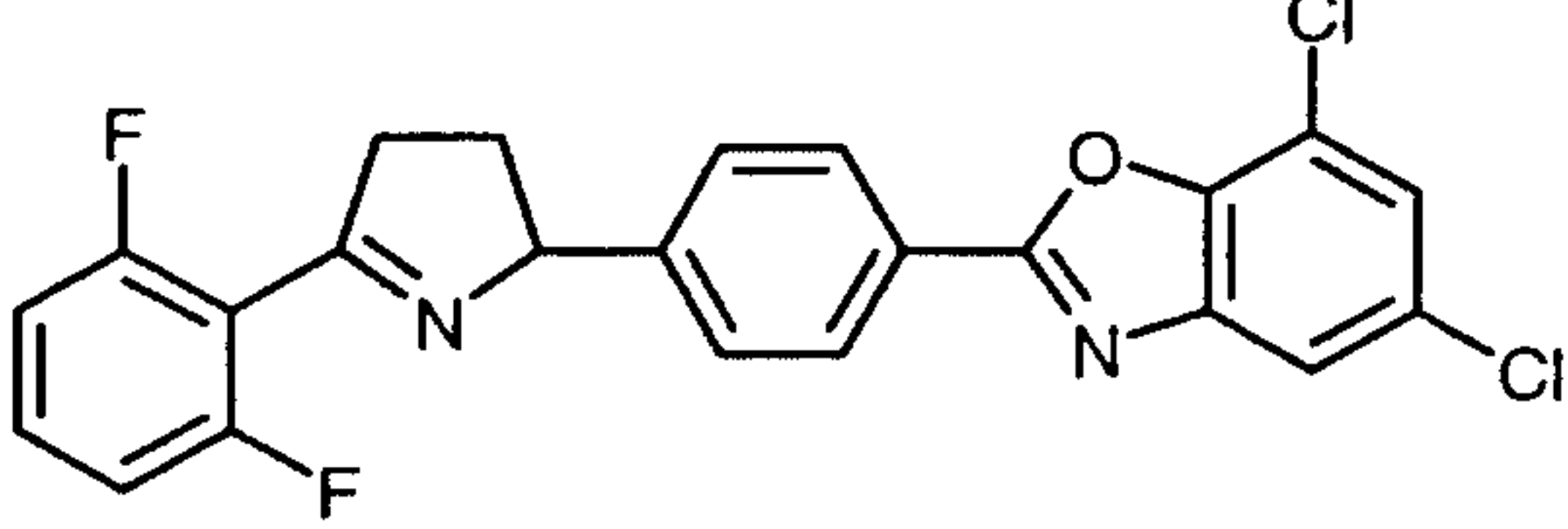
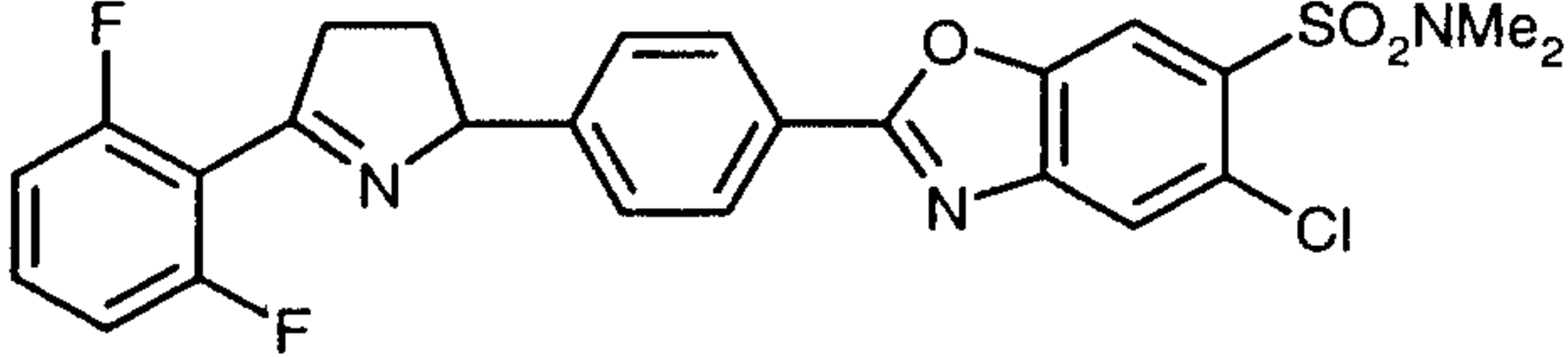
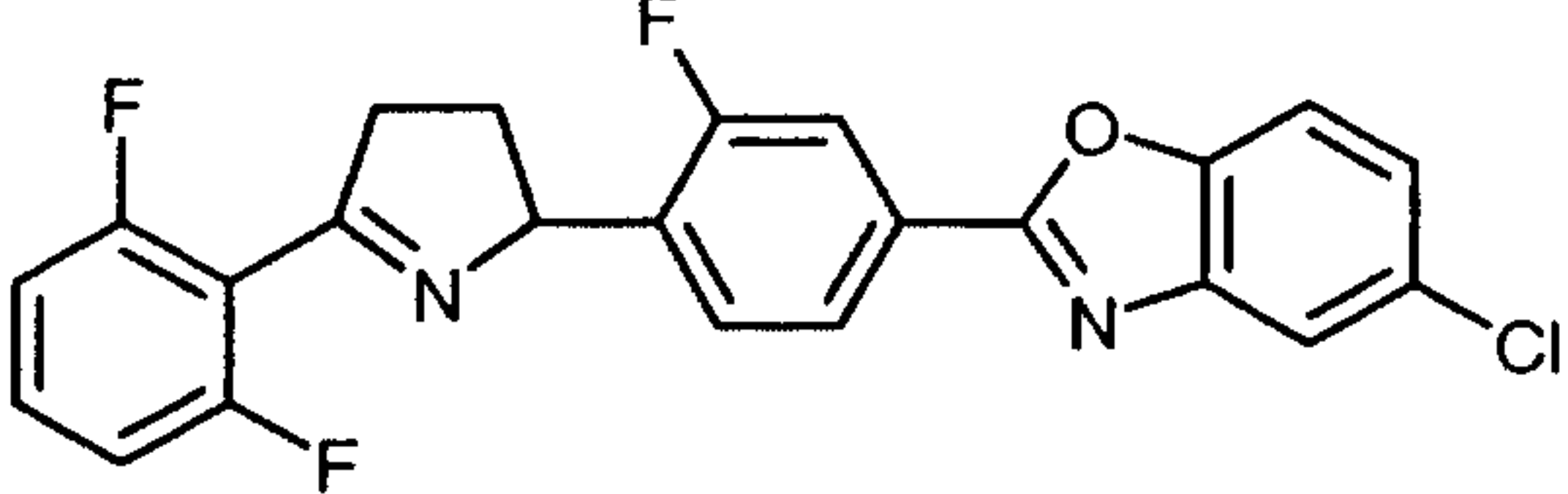
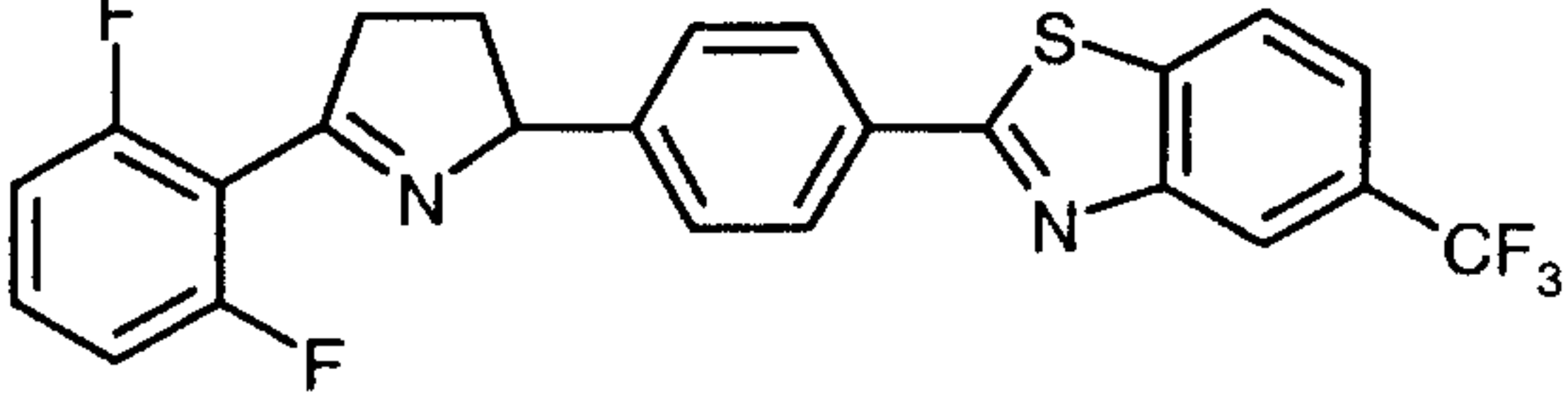
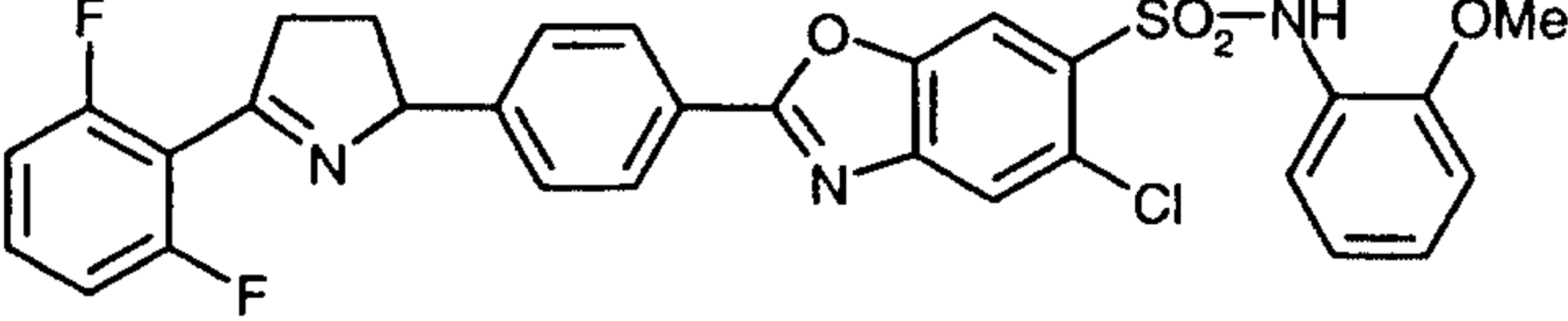
20 In this test, for example, the following compounds of the Preparation Examples show good activity:

Table F  
 Plant-damaging insects  
**Spodoptera frugiperda test**

| Active compounds                                                                     | Concentration<br>of active<br>compound in<br>ppm | Efficacy in %<br>after 7 d |
|--------------------------------------------------------------------------------------|--------------------------------------------------|----------------------------|
|   | 500                                              | 100                        |
|   | 500                                              | 100                        |
|  | 500                                              | 100                        |
|  | 500                                              | 100                        |
|  | 500                                              | 100                        |
|  | 100                                              | 100                        |
|  | 500                                              | 100                        |

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| Active compounds                                                                     | Concentration of active compound in ppm | Efficacy in % after 7 d |
|--------------------------------------------------------------------------------------|-----------------------------------------|-------------------------|
|    | 500                                     | 100                     |
|   | 100                                     | 100                     |
|  | 100                                     | 100                     |
|  | 100                                     | 100                     |
|  | 100                                     | 100                     |
|  | 100                                     | 100                     |
|  | 500                                     | 100                     |

Example G**Tetranychus test (OP-resistant/dip treatment)**

- 5 Solvent: 7 parts by weight of dimethylformamide  
Emulsifier: 2 parts by weight of alkylaryl polyglycol ether

10 To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

15 Bean plants (*Phaseolus vulgaris*) which are heavily infested by all stages of the greenhouse red spider mite (*Tetranychus urticae*) are treated by being dipped into a preparation of active compound of the desired concentration.

After the desired period of time, the effect in % is determined. 100% means that all spider mites have been killed; 0% means that none of the spider mites have been killed.

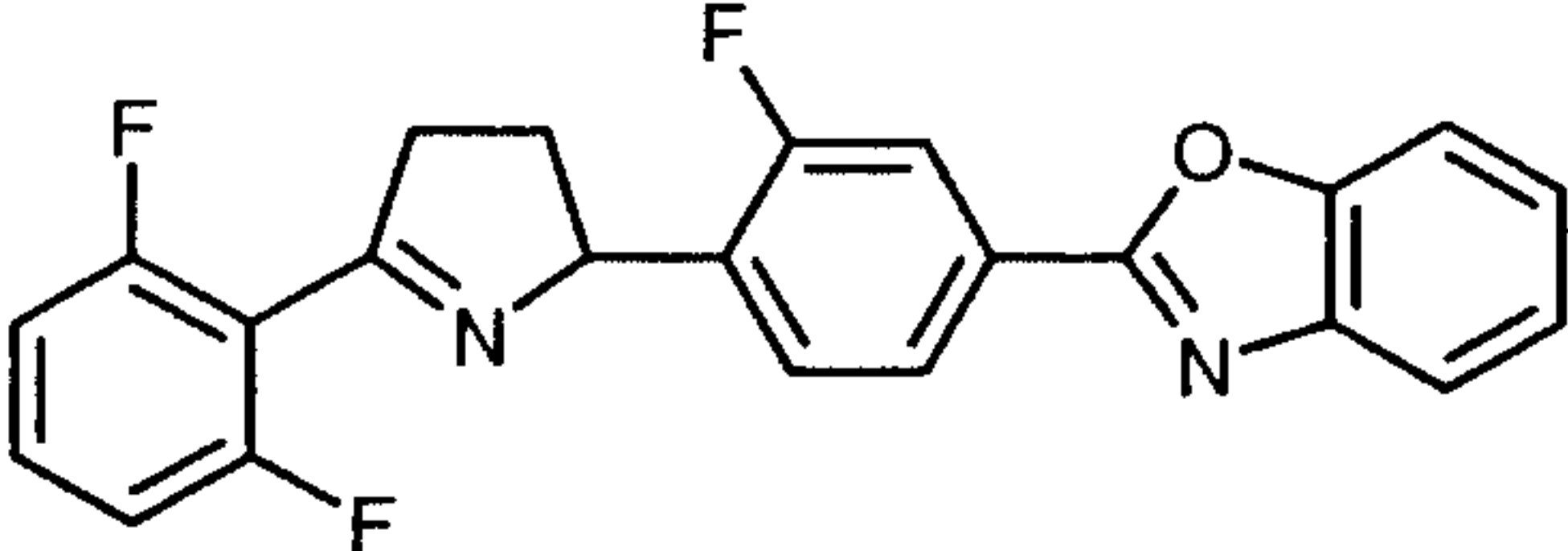
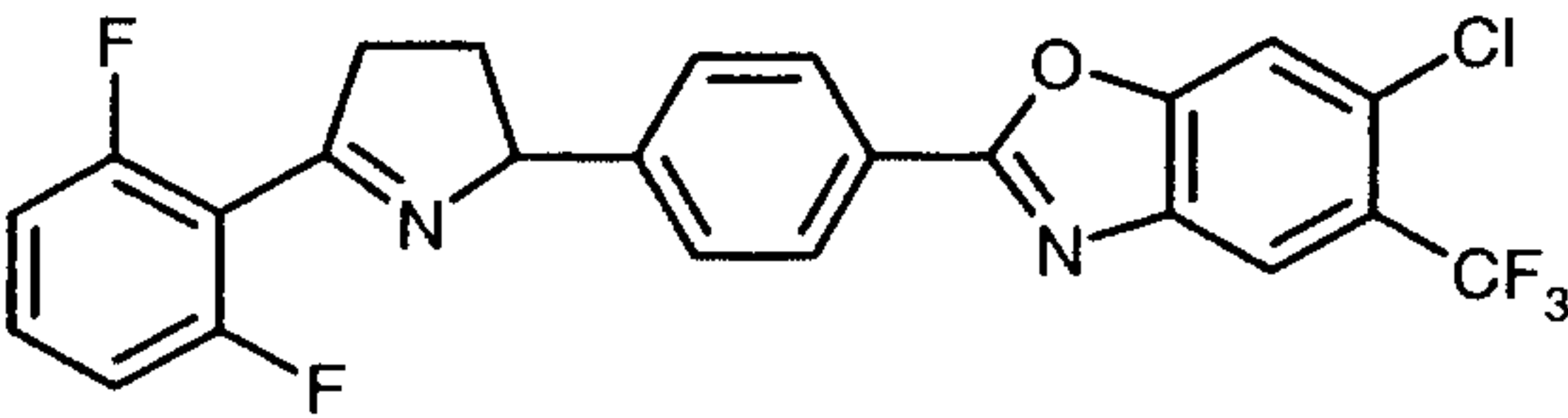
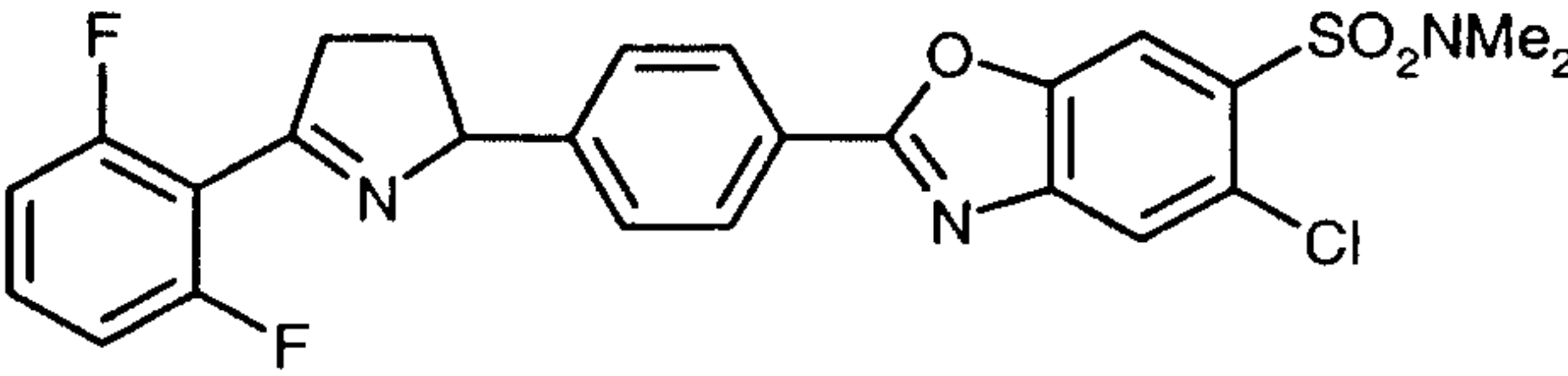
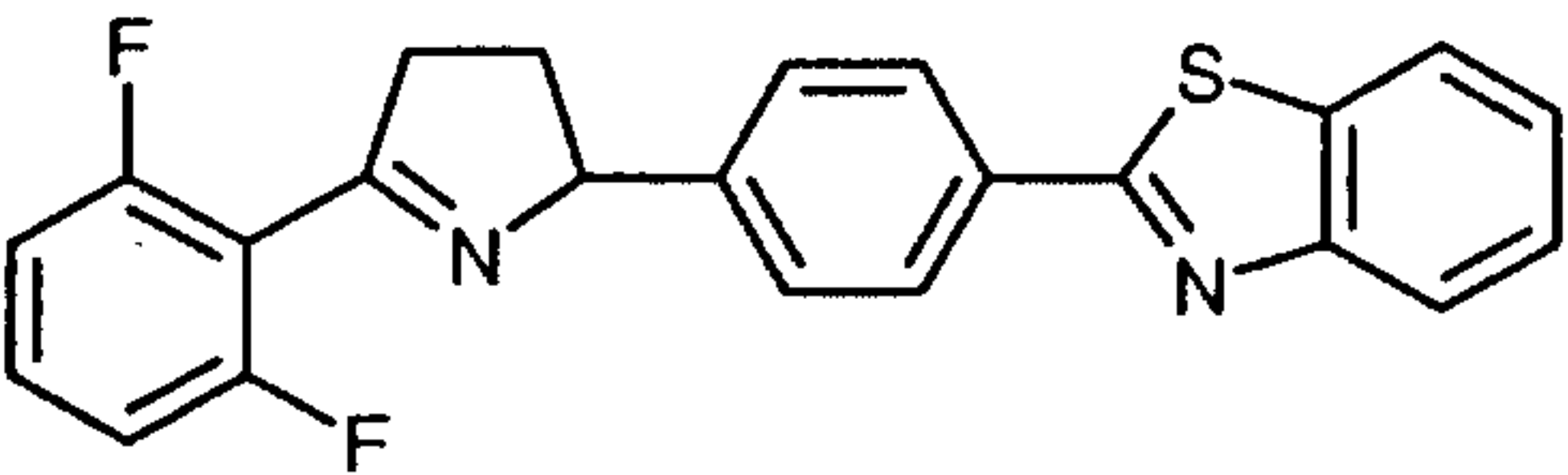
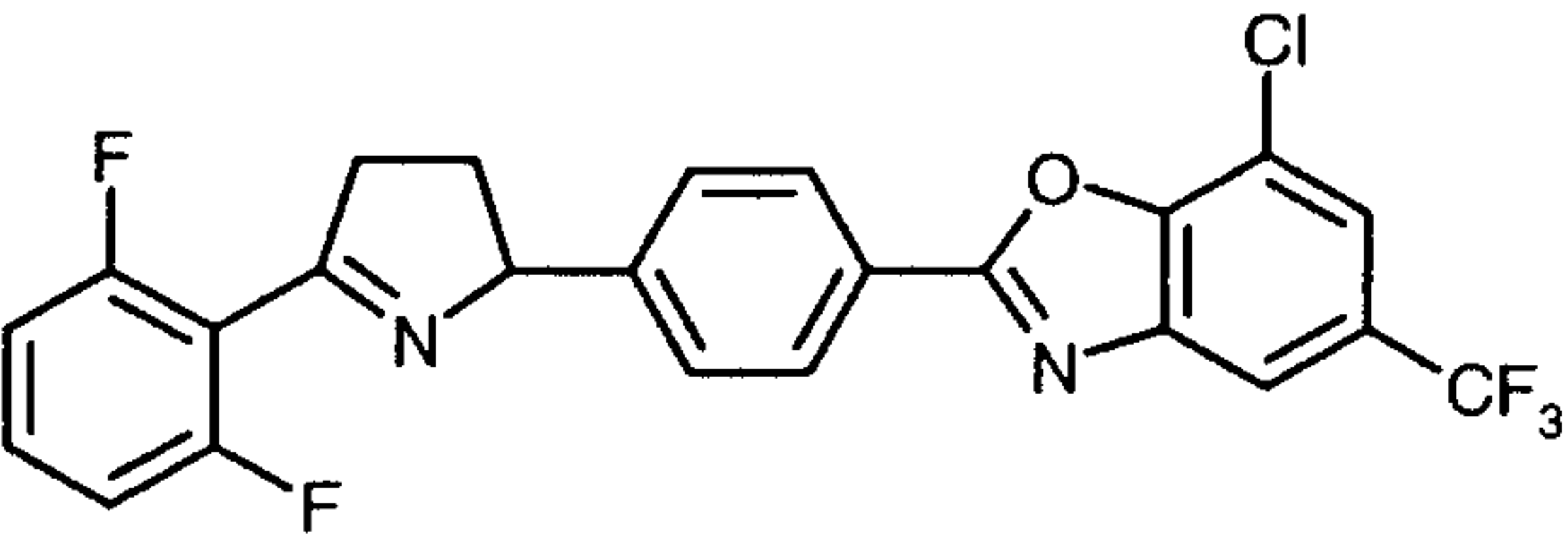
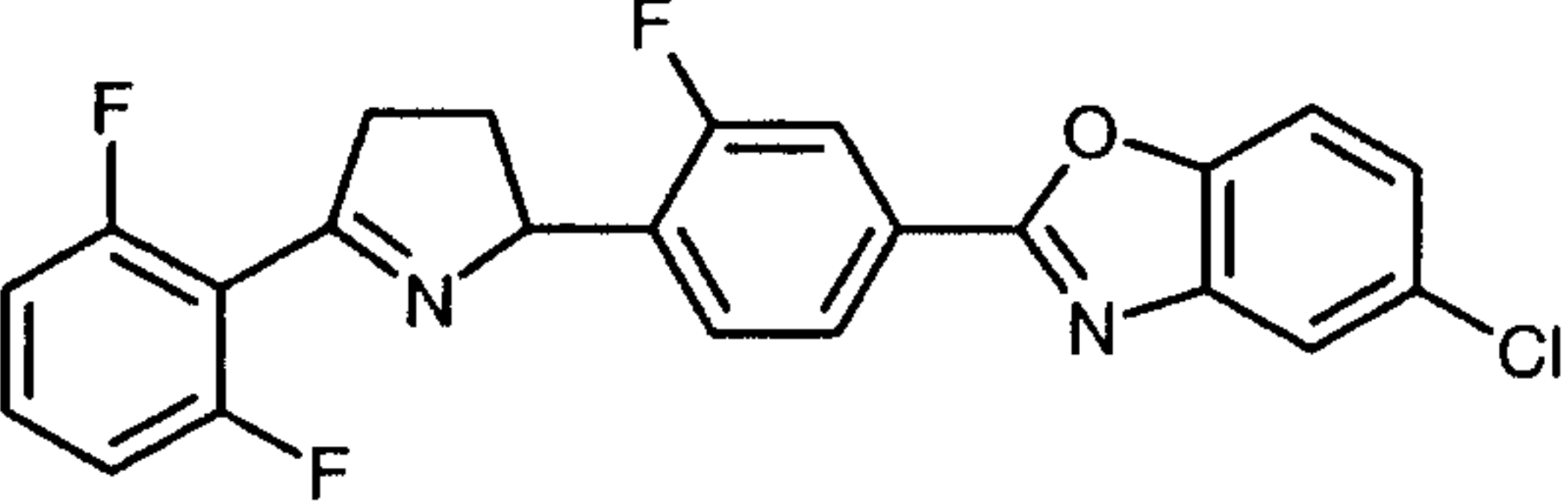
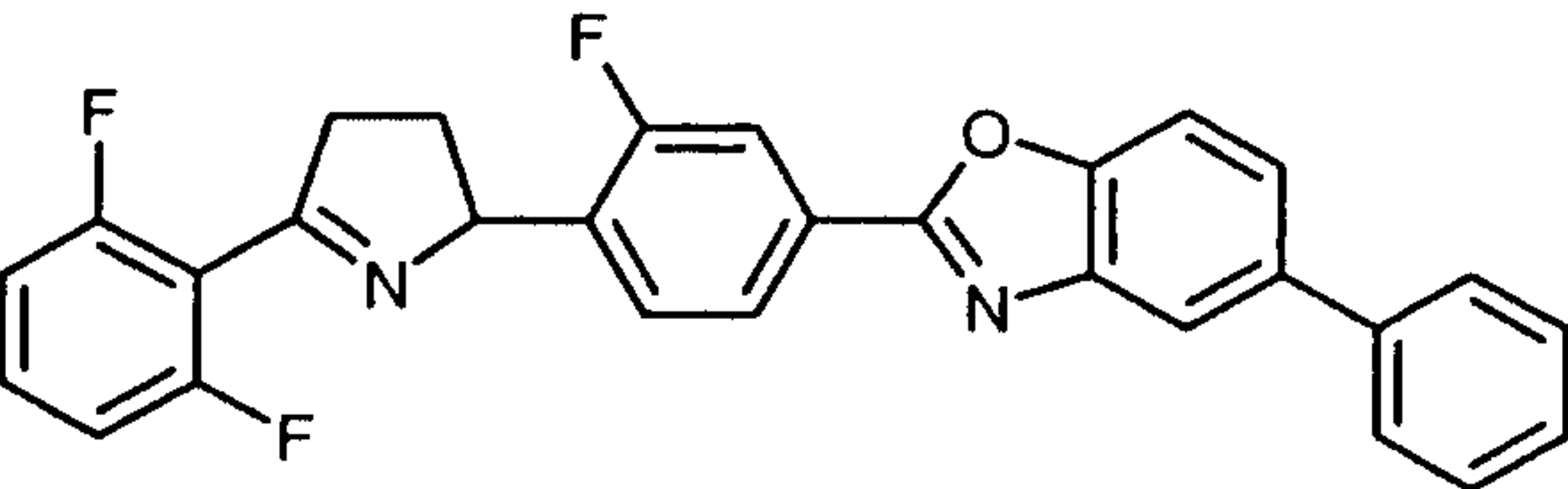
20 In this test, for example, the following compounds of the Preparation Examples show good activity:

- 66 -

Table G

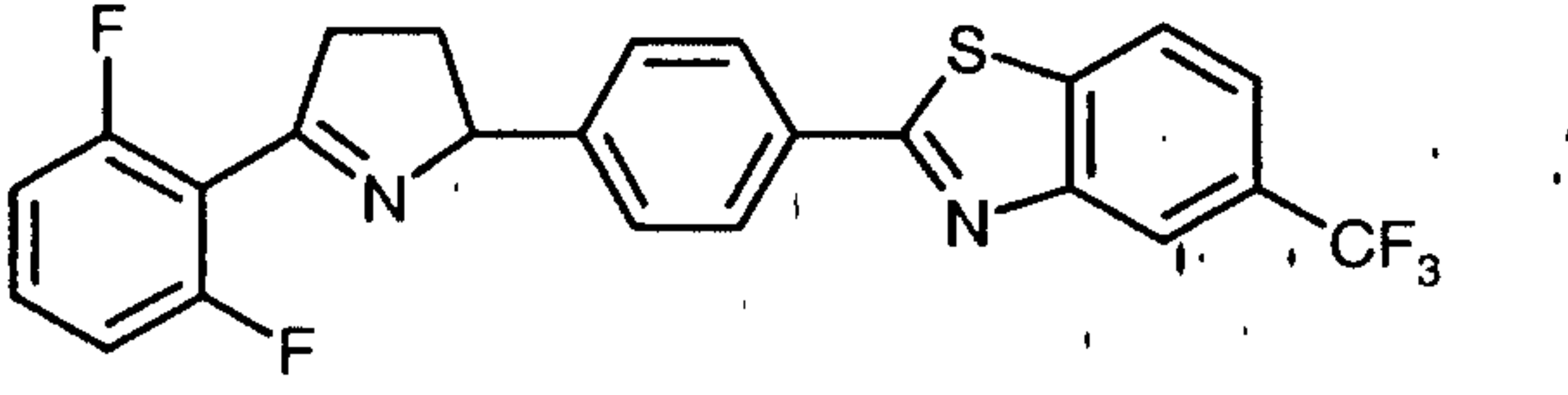
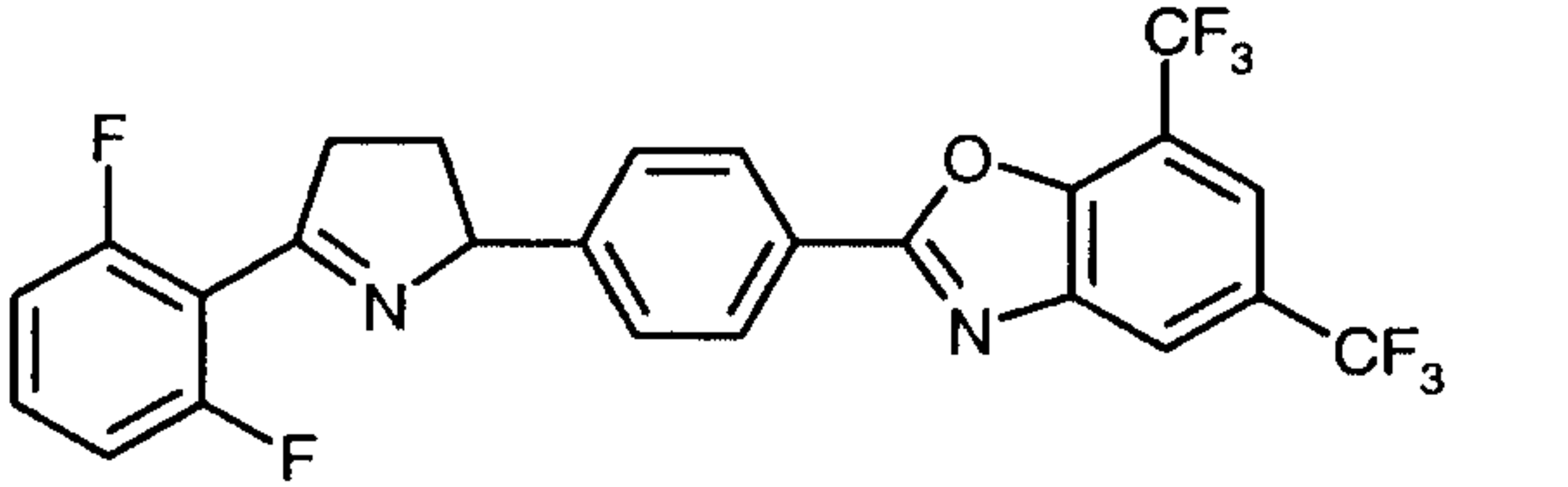
Plant-damaging insects

Tetranychus test (OP-resistant/dip treatment)

| Active compounds                                                                     | Concentration of active compound in ppm | Efficacy in % after 7 d |
|--------------------------------------------------------------------------------------|-----------------------------------------|-------------------------|
|   | 100                                     | 95                      |
|  | 100                                     | 98                      |
|  | 100                                     | 90                      |
|  | 100                                     | 99                      |
|  | 100                                     | 95                      |
|  | 100                                     | 95                      |
|  | 100                                     | 99                      |

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| Active compounds                                                                    | Concentration of active compound in ppm | Efficacy in % after 7 d |
|-------------------------------------------------------------------------------------|-----------------------------------------|-------------------------|
|   | 100                                     | 90                      |
|  | 100                                     | 100                     |

Example H

**Diabrotica balteata test (larvae in soil)**

Critical concentration test / soil insects – Treatment of transgenic plants

5

Solvent: 7 parts by weight of dimethylformamide

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

10

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent, the stated amount of emulsifier is added and the concentrate is diluted with water to the desired concentration.

15

The preparation of active compound is poured onto the soil. The concentration of active compound in the preparation is virtually immaterial, only the amount by weight of active compound per volume unit of soil, which is stated in ppm (mg/l) matters. The soil is filled into 0.25 l pots, and these are allowed to stand at 20°C.

20

Immediately after the preparation, 5 pregerminated maize corns of the cultivar YIELD GUARD (trademark of Monsanto Comp., USA) are placed into each pot. After 2 days, the corresponding test insects are placed into the treated soil. After a further 7 days, the efficacy of the active compound is determined by counting the number of maize plants that have emerged (1 plant = 20% activity).

Example I**Heliothis virescens test (treatment of transgenic plants)**

- 5 Solvent: 7 parts by weight of dimethylformamide  
Emulsifier: 1 part by weight of alkylaryl polyglycol ether

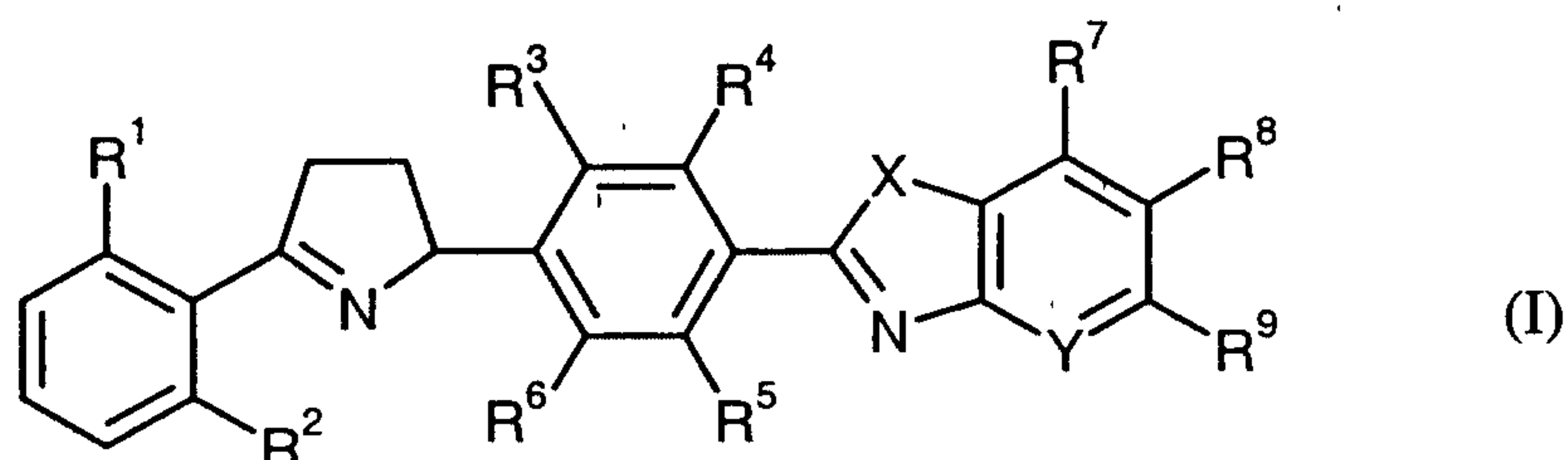
10 To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent and the stated amount of emulsifier, and the concentrate is diluted with water to the desired concentration.

15 Soya bean shoots (Glycine max) of the cultivar Roundup Ready (trademark of Monsanto Comp. USA) are treated by being dipped into the preparation of active compound of the desired concentration and are populated with the tobacco budworm caterpillar *Heliothis virescens* while the leaves are still moist.

After the desired period of time, the kill in % is determined. 100% means that all caterpillars have been killed; 0% means that none of the caterpillars have been killed.

**Patent Claims**

1.  $\Delta^1$ -Pyrrolines of the formula (I)



in which

$R^1$  represents halogen or methyl,

$R^2$  represents hydrogen or halogen,

$R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  independently of one another represent hydrogen, halogen,  $C_1$ - $C_4$ -alkyl or  $C_1$ - $C_4$ -alkoxy,

X represents O (oxygen) or S (sulphur),

Y represents  $CR^{10}$  or N (nitrogen),

$R^7$ ,  $R^8$ ,  $R^9$  and  $R^{10}$  independently of one another represent hydrogen, halogen, nitro,  $C_1$ - $C_4$ -alkyl,  $C_1$ - $C_4$ -haloalkyl,  $C_1$ - $C_4$ -haloalkoxy,  $C_1$ - $C_4$ -haloalkylthio,  $C_1$ - $C_4$ -alkoxycarbonyl, phenyl,  $-(CH_2)_m-SO_2R^{11}$  or  $-SO_2NR^{12}R^{13}$ ,

or either  $R^7$  and  $R^8$  or  $R^8$  and  $R^9$  or  $R^9$  and  $R^{10}$  together form a further saturated or unsaturated 5- or 6-membered ring which again may contain one or two heteroatom groupings from the group consisting of N, O, S and  $SO_2$ ,

m represents 0 or 1,

$R^{11}$  represents  $C_1$ - $C_4$ -alkyl or morpholino,

$R^{12}$  represents  $C_1$ - $C_4$ -alkyl or represents phenyl which is optionally mono-  
to tetrasubstituted by identical or different substituents from the group  
consisting of halogen,  $C_1$ - $C_4$ -alkyl and  $C_1$ - $C_4$ -alkoxy,

$R^{13}$  represents hydrogen or  $C_1$ - $C_4$ -alkyl.

2.  $\Delta^1$ -Pyrrolines of the formula (I) according to Claim 1 in which

$R^1$  represents fluorine, chlorine, bromine or methyl,

$R^2$  represents hydrogen, fluorine or chlorine,

$R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  independently of one another represent hydrogen, fluorine,  
chlorine, bromine,  $C_1$ - $C_4$ -alkyl or  $C_1$ - $C_4$ -alkoxy,

X represents O (oxygen) or S (sulphur),

Y represents  $CR^{10}$  or N (nitrogen),

$R^7$ ,  $R^8$ ,  $R^9$  and  $R^{10}$  independently of one another represent hydrogen, fluorine,  
chlorine, bromine, nitro,  $C_1$ - $C_4$ -alkyl;  $C_1$ - $C_4$ -haloalkyl,  $C_1$ - $C_4$ -halo-  
alkoxy,  $C_1$ - $C_4$ -haloalkylthio having in each case 1 to 9 fluorine,  
chlorine and/or bromine atoms;  $C_1$ - $C_4$ -alkoxycarbonyl, phenyl,  
- $(CH_2)_m$ - $SO_2R^{11}$  or - $SO_2NR^{12}R^{13}$ ,

or either  $R^7$  and  $R^8$  or  $R^8$  and  $R^9$  or  $R^9$  and  $R^{10}$  together form a further  
saturated or unsaturated 5- or 6-membered ring which again may  
contain one or two heteroatom groupings from the group consisting of  
N, O, S and  $SO_2$ ,

m represents 0 or 1,

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$R^{11}$  represents  $C_1$ - $C_4$ -alkyl or morpholino,

$R^{12}$  represents  $C_1$ - $C_4$ -alkyl or represents phenyl which is optionally mono- to tetrasubstituted by identical or different substituents from the group consisting of fluorine, chlorine, bromine,  $C_1$ - $C_4$ -alkyl and  $C_1$ - $C_4$ -alkoxy,

$R^{13}$  represents hydrogen or  $C_1$ - $C_4$ -alkyl.

10 3.  $\Delta^1$ -Pyrrolines of the formula (I) according to Claim 1 in which

$R^1$  represents fluorine, chlorine or methyl,

$R^2$  represents hydrogen, fluorine or chlorine,

$R^3$  and  $R^6$  independently of one another represent hydrogen, fluorine, chlorine, methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl, methoxy or ethoxy,

$R^4$  and  $R^5$  each represent hydrogen,

X represents O (oxygen) or S (sulphur),

Y represents  $CR^{10}$  or N (nitrogen),

$R^7$ ,  $R^8$ ,  $R^9$  and  $R^{10}$  independently of one another represent hydrogen, fluorine, chlorine, bromine, nitro, methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl;  $C_1$ - $C_4$ -haloalkyl,  $C_1$ - $C_4$ -haloalkoxy,  $C_1$ - $C_4$ -haloalkylthio having in each case 1 to 9 fluorine, chlorine and/or bromine atoms; methoxycarbonyl, ethoxycarbonyl, phenyl,  $-(CH_2)_m-SO_2R^{11}$  or  $-SO_2NR^{12}R^{13}$ ,

or either R<sup>7</sup> and R<sup>8</sup> or R<sup>8</sup> and R<sup>9</sup> or R<sup>9</sup> and R<sup>10</sup> together form a further saturated or unsaturated 5- or 6-membered ring which again may contain one or two heteroatom groupings from the group consisting of N, O, S and SO<sub>2</sub>,

5

m represents 0 or 1,

R<sup>11</sup> represents methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl or morpholino,

10

R<sup>12</sup> represents methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl or represents phenyl which is optionally mono- to trisubstituted by identical or different substituents from the group consisting of fluorine, chlorine, bromine, methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl, methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, i-butoxy, s-butoxy, t-butoxy,

15

R<sup>13</sup> represents hydrogen or methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl.

20

4.  $\Delta^1$ -Pyrrolines of the formula (I) according to Claim 1 in which

R<sup>1</sup> represents fluorine, chlorine or methyl,

25

R<sup>2</sup> represents hydrogen, fluorine or chlorine,

R<sup>3</sup> represents hydrogen, fluorine, chlorine, methyl, methoxy or ethoxy,

R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each represent hydrogen,

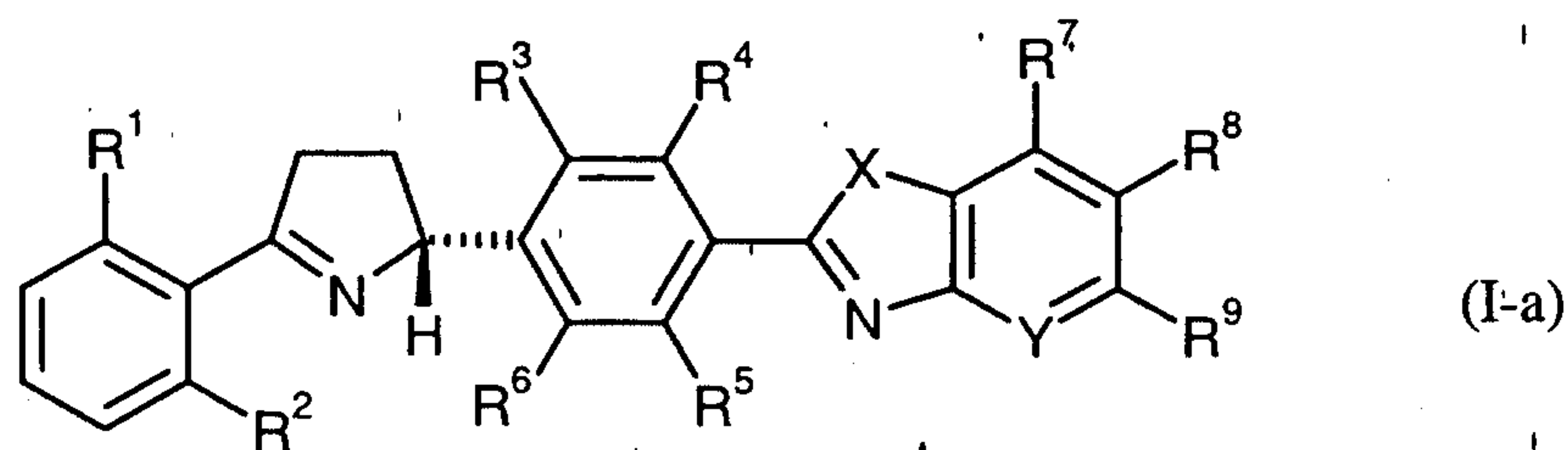
30

X represents O (oxygen),

Y represents CR<sup>10</sup> or N (nitrogen),

R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup> and R<sup>10</sup> independently of one another represent hydrogen, fluorine, chlorine, bromine, nitro, methyl, i-propyl, t-butyl, trifluoromethyl, tri-fluoromethoxy, trifluoromethylthio, methoxycarbonyl, phenyl, -SO<sub>2</sub>-morpholino, -CH<sub>2</sub>SO<sub>2</sub>Me, -SO<sub>2</sub>NHMe, -SO<sub>2</sub>NMe<sub>2</sub>, -SO<sub>2</sub>NH-(3,4-dichlorophenyl) or -SO<sub>2</sub>NH-(2-methoxyphenyl).

5.  $\Delta^1$ -Pyrrolines of the formula (I) according to Claim 1 in which R<sup>1</sup> and R<sup>2</sup> represent fluorine.
6.  $\Delta^1$ -Pyrrolines of the formula (I) according to Claim 1 in which Y represents CR<sup>10</sup> and preferably represents CH.
7.  $\Delta^1$ -Pyrrolines of the formula (I) according to Claim 1 in which R<sup>3</sup> represents hydrogen or fluorine.
8.  $\Delta^1$ -Pyrrolines of the formula (I) according to Claim 1 in which X represents O (oxygen).
9.  $\Delta^1$ -Pyrrolines of the formula (I) according to Claim 1 in which X represents S (sulphur).
10.  $\Delta^1$ -Pyrrolines of the formula (I) according to Claim 1 in which R<sup>4</sup> and R<sup>5</sup> represent hydrogen.
11.  $\Delta^1$ -Pyrrolines of the formula (I) according to Claim 1 in which R<sup>1</sup> and R<sup>2</sup> represent fluorine, X represents O (oxygen) and Y represents CH.
12. (R)-Configured compounds of the formula (I-a)



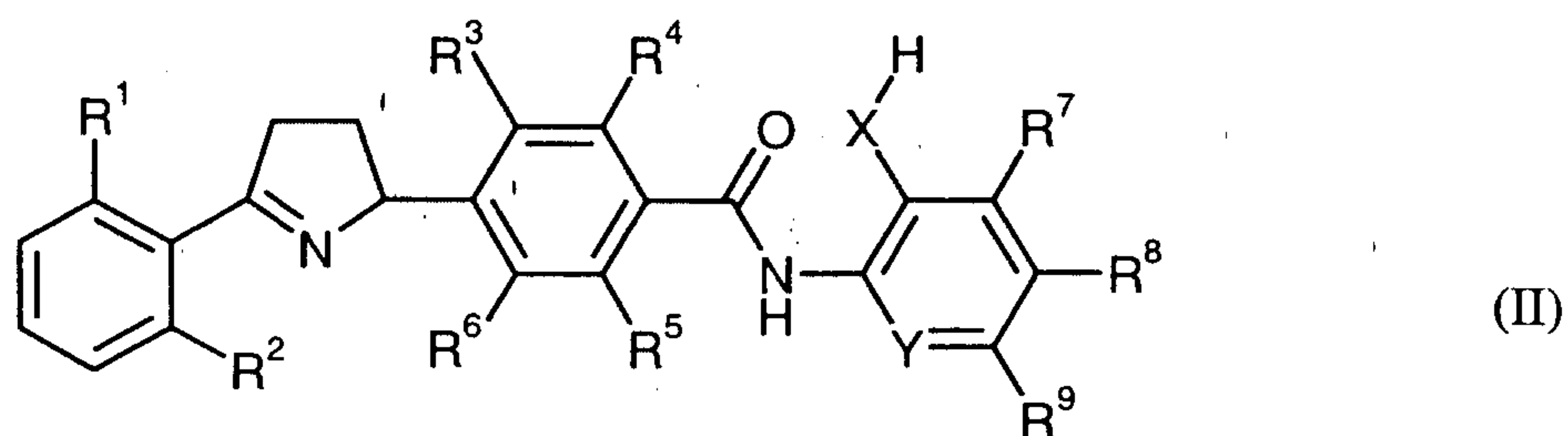
in which

$R^1, R^2, R^3, R^4, R^5, R^6, X, Y, R^7, R^8$  and  $R^9$  are as defined in Claim 1.

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13. Process for preparing compounds of the formula (I) according to Claim 1, characterized in that

A) compounds of the formula (II)



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in which

$R^1, R^2, R^3, R^4, R^5, R^6, X, Y, R^7, R^8$  and  $R^9$  are as defined in Claim 1,

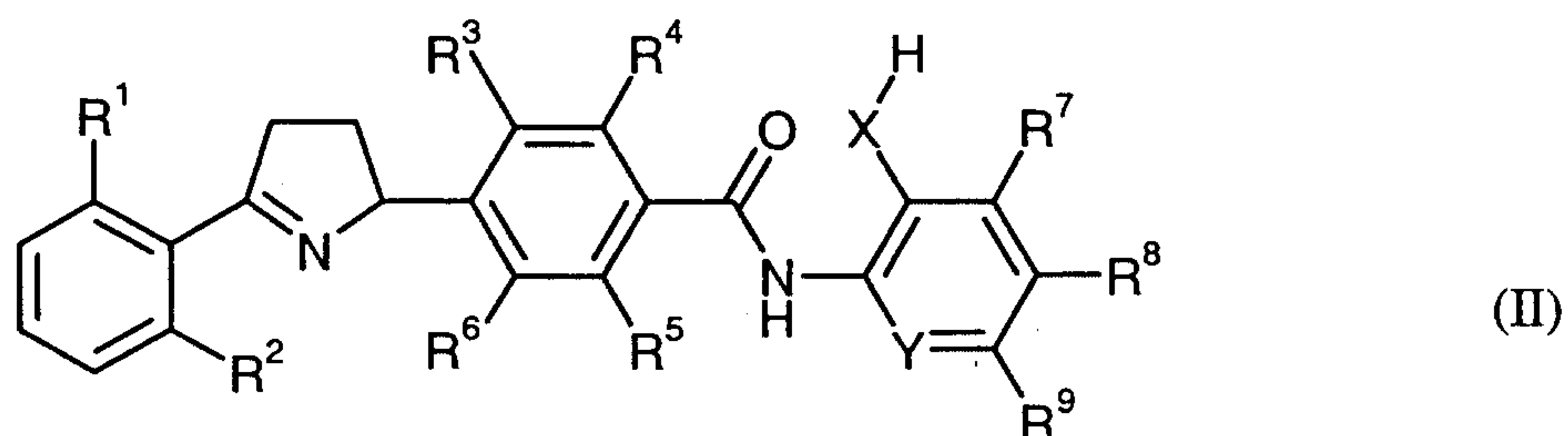
15

are reacted with p-toluenesulphonic acid, if appropriate in the presence of a diluent.

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14. Pesticides, characterized in that they comprise at least one compound of the formula (I) according to Claim 1, in addition to extenders and/or surfactants.
15. Use of compounds of the formula (I) according to Claim 1 for controlling pests.

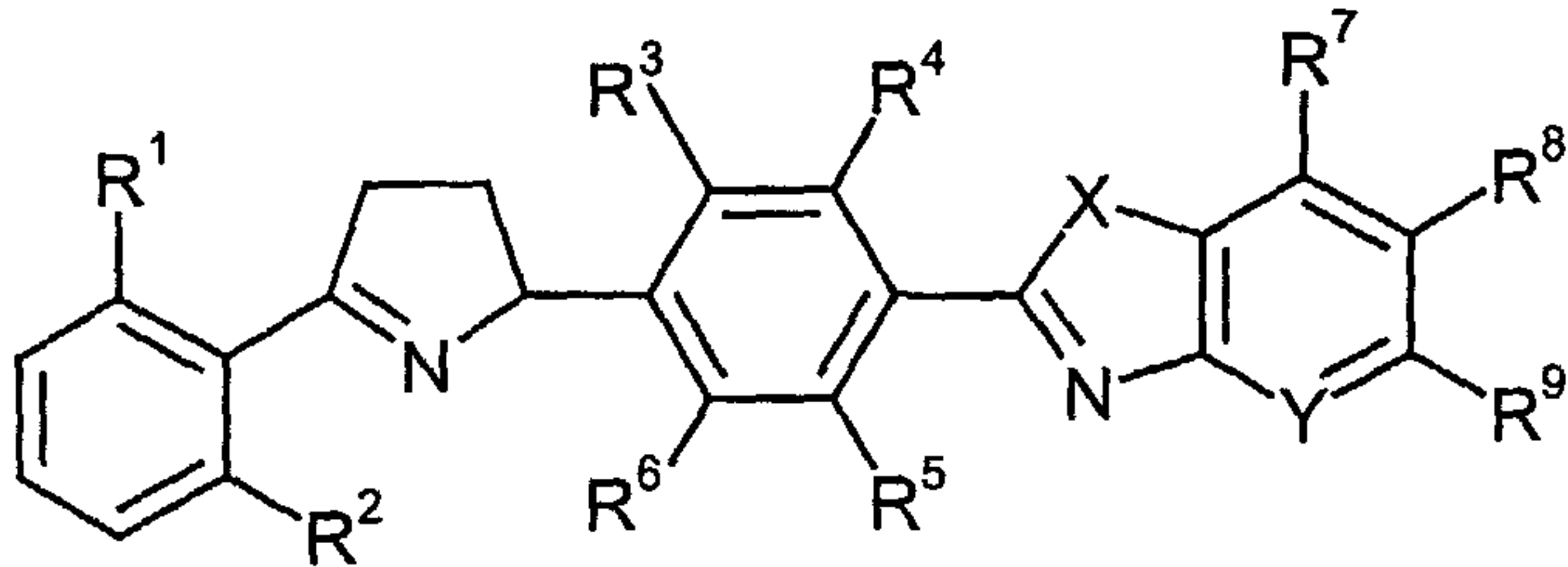
16. Method for controlling pests, characterized in that compounds of the formula (I) according to Claim 1 are allowed to act on pests and/or their habitat.
17. Process for preparing pesticides, characterized in that compounds of the formula (I) according to Claim 1 are mixed with extenders and/or surfactants.
18. Compounds of the formula (II)



in which

$R^1, R^2, R^3, R^4, R^5, R^6, X, Y, R^7, R^8$  and  $R^9$  are as defined in Claim 1.

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