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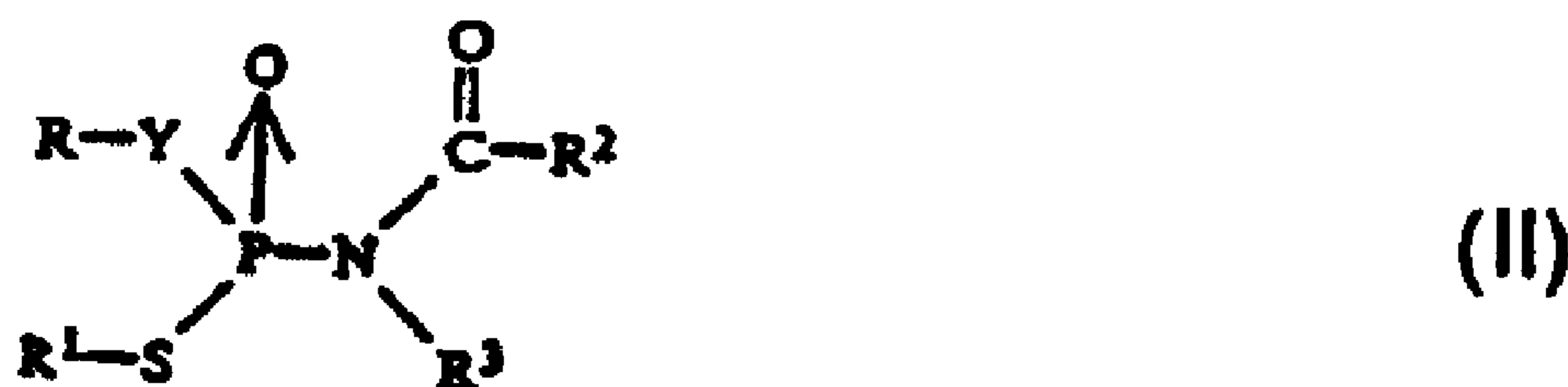
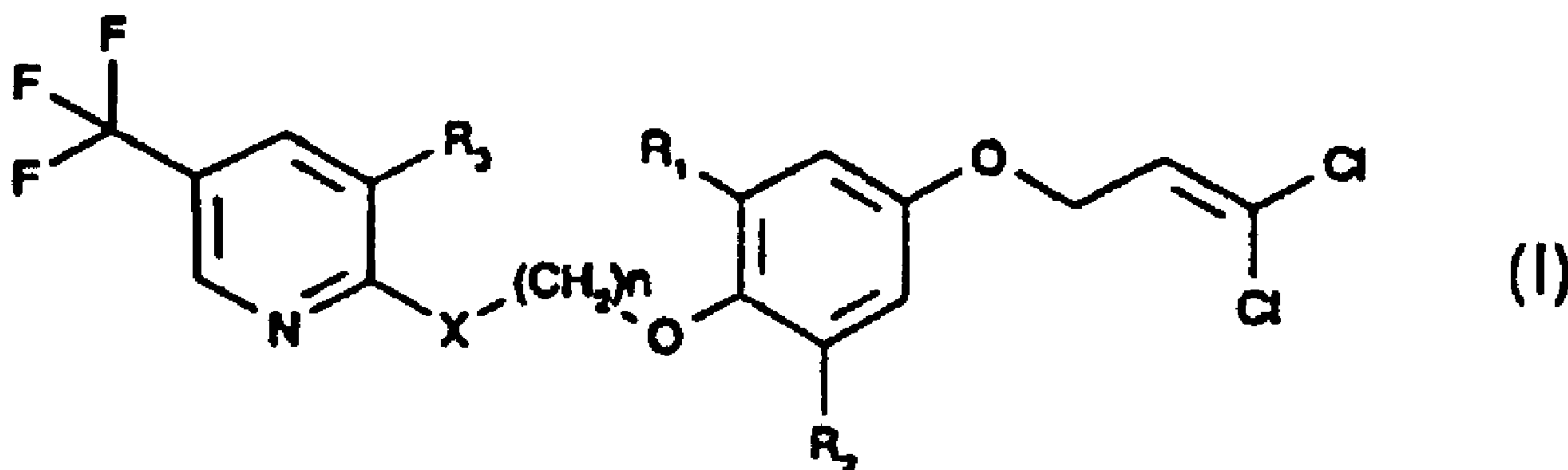
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(54) Titre : COMPOSITION INSECTICIDE ET PROCEDE D'UTILISATION

(54) Title: INSECTICIDAL COMPOSITION AND METHOD FOR THE USE THEREOF



(57) Abrégé/Abstract:

An insecticidal composition includes (1) at least one compound of formula (I) wherein R_1 is bromine, chlorine, methyl, or ethyl, R_2 is bromine, chlorine, or ethyl, R_3 is hydrogen, halogen, or trifluoromethyl, X is -O-, -S-, or -NH-, and n is 2, 3, or 4, and (2) at least one compound of formula (II) wherein R and R^1 independently are an alkyl, alkenyl, or alkynyl group containing up to 6 carbon atoms, R^2 is hydrogen, an alkyl group containing 1 to 18 carbon atoms, a cycloalkyl group containing 3 to 8 carbon atoms, an alkenyl

(57) **Abrégé(suite)/Abstract(continued):**

group containing 2 to 18 carbon atoms, or an alkynyl group containing 3 to 18 carbons atoms, R^3 is hydrogen or an alkyl group containing 1 to 6 carbon atoms, and Y is -O- or -S-. A method for killing insects such as the tobacco budworm and other Lepidopteran pests of cotton includes applying an insecticidally effective amount of such a composition to an area to be treated.

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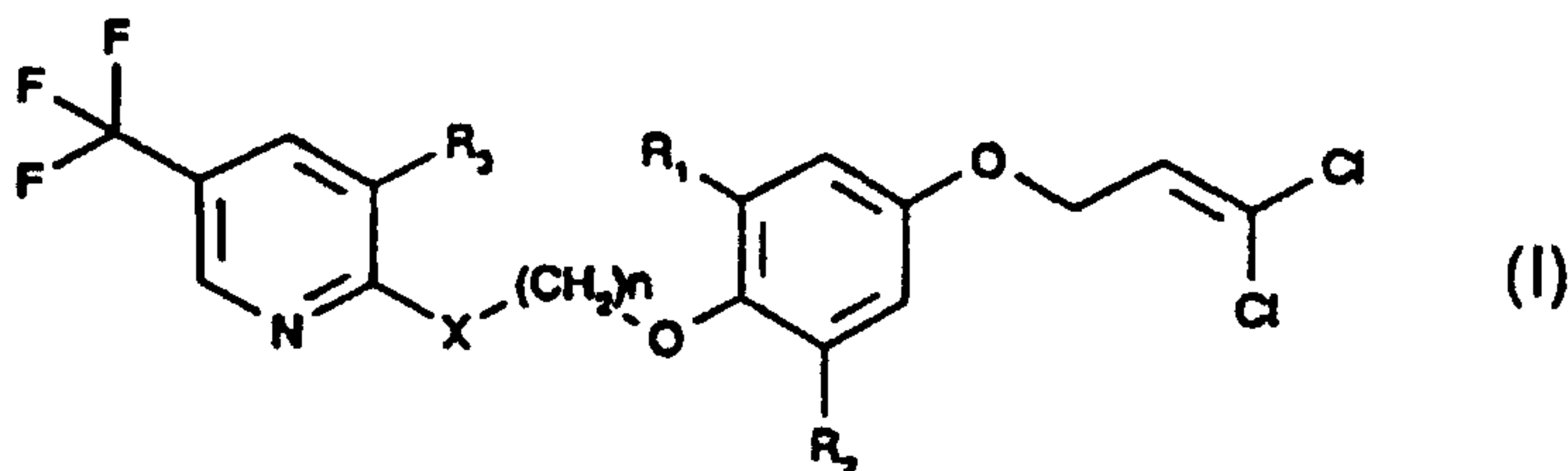
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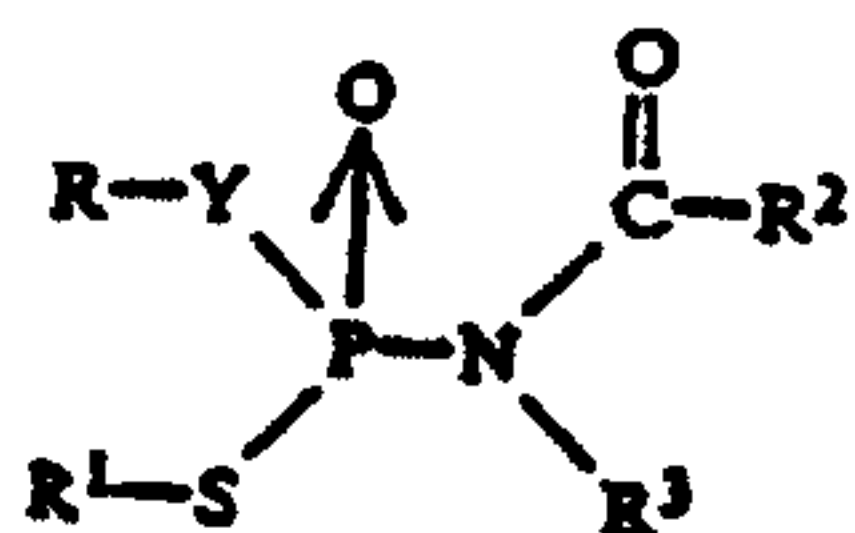
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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(54) Title: INSECTICIDAL COMPOSITION AND METHOD FOR THE USE THEREOF



(I)



(II)

(57) Abstract: An insecticidal composition includes (1) at least one compound of formula (I) wherein R₁ is bromine, chlorine, methyl, or ethyl, R₂ is bromine, chlorine, or ethyl, R₃ is hydrogen, halogen, or trifluoromethyl, X is -O-, -S-, or -NH-, and n is 2, 3, or 4, and (2) at least one compound of formula (II) wherein R and R¹ independently are an alkyl, alkenyl, or alkynyl group containing up to 6 carbon atoms, R² is hydrogen, an alkyl group containing 1 to 18 carbon atoms, a cycloalkyl group containing 3 to 8 carbon atoms, an alkenyl group containing 2 to 18 carbon atoms, or an alkynyl group containing 3 to 18 carbons atoms, R³ is hydrogen or an alkyl group containing 1 to 6 carbon

atoms, and Y is -O- or -S-. A method for killing insects such as the tobacco budworm and other Lepidopteran pests of cotton includes applying an insecticidally effective amount of such a composition to an area to be treated.

WO 00/72680 A1

WO 00/72680

PCT/US00/08229

INSECTICIDAL COMPOSITION AND METHOD FOR THE USE THEREOF

FIELD OF THE INVENTION

The present invention is directed to an insecticidal composition and to a method for the use thereof. In particular, the present invention is directed to an insecticidal composition which takes advantage of the synergistic action of two particular insecticides and to a method of
5 using the composition to kill insects such as the tobacco budworm and other Lepidopteran pests of cotton.

BACKGROUND OF THE INVENTION

The tobacco budworm and other Lepidopteran insects are
10 serious pests of cotton fruit (squares and bolls). Moderate or heavy infestations can dramatically reduce lint yields.

The tobacco budworm, Heliothis virescens, and cotton bollworm, Helicoverpa zea, have developed resistance to major classes of insecticides used to control them, as discussed in Martin et al., "Effects
15 of Selected Synergists on Insecticide Toxicity in Tobacco Budworm (Lepidoptera: Noctuidae) in Laboratory and Field Studies," J. Econ. Entomol. 90(3)723-731 (1997), Kanga et al., "Tolerance to Cypermethrin and Endosulfan in Field Populations of the Bollworm (Lepidoptera: Noctuidae) from Texas," J. Econ. Entomol. 89(3)583-589
20 (1996), Kanga et al., "Monitoring for Resistance to Organophosphorus, Carbamate, and Cyclodiene Insecticides in Tobacco Budworm Adults

(Lepidopteria: Noctuidae)," J. Econ. Entomol. 88(5)1144-1149 (1995),
and Elzen et al., "Resistance to Pyrethroids, Carbamate, and
Organophosphate Insecticides in Field Populations of Tobacco
Budworms (Lepidoptera: Noctuidae) in 1990," J. Econ. Entomol.
5 85(6):2064-2072 (1992).

New and better control alternatives are always needed to
maintain crop production and provide alternative chemistry for rotation
purposes, as discussed in Laws, Delta Agricultural Digest, Intertec
Publishing (1998).

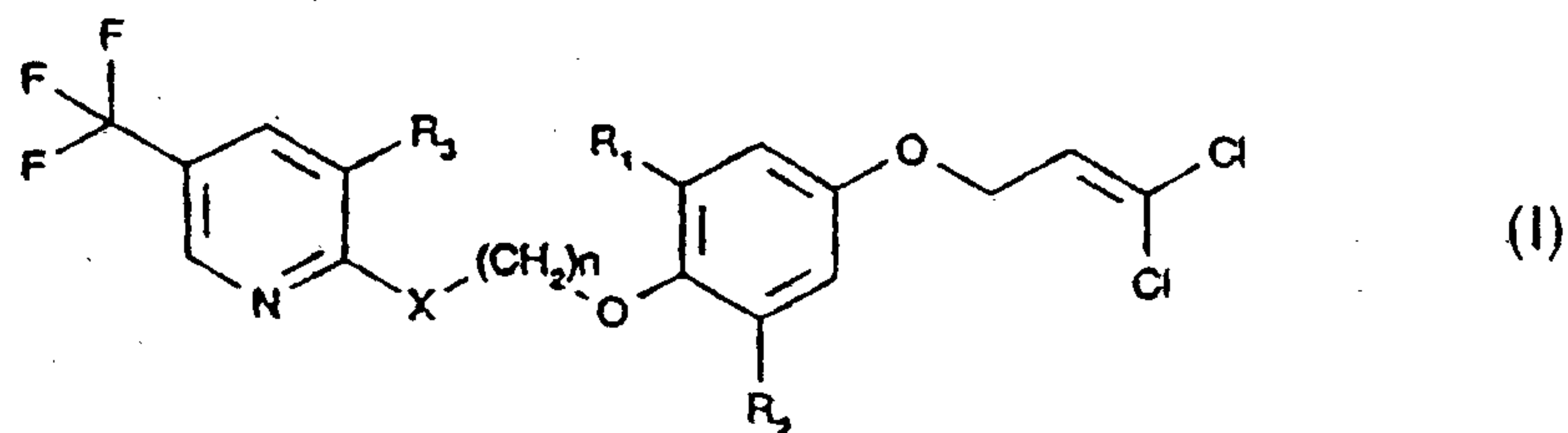
10 While the compositions in the art have provided some control of
Lepidopteran pests of cotton, there has been a need in the art for
significantly greater control.

SUMMARY OF THE INVENTION

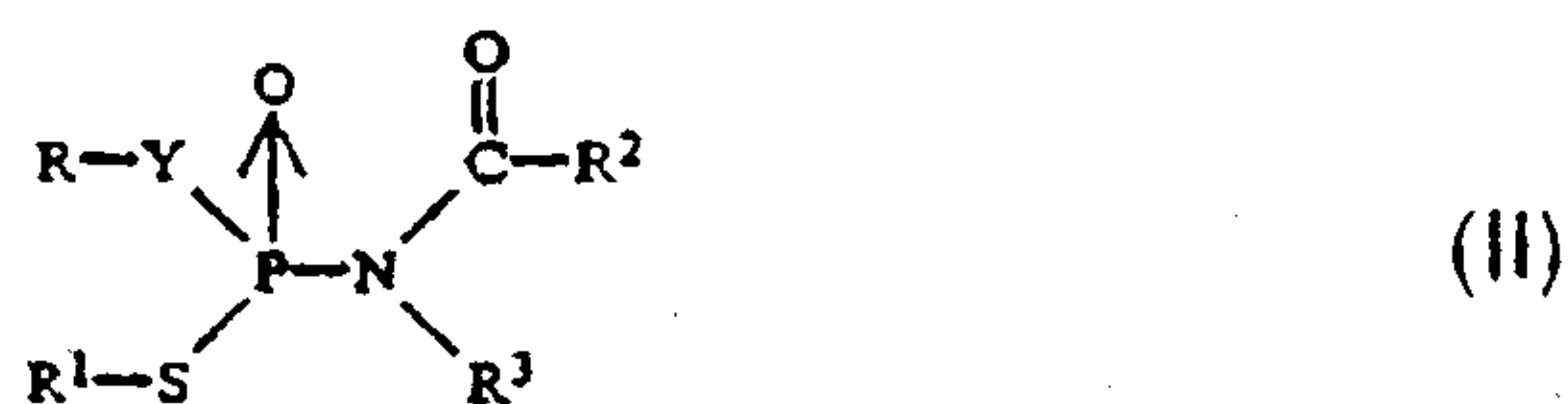
An object of the present invention is to provide significantly
15 greater control of tobacco budworm, cotton bollworm, and other
Lepidopteran pests of cotton than has been provided previously in the
art.

Accordingly, the present inventors conducted extensive
experimentation and, as a result, they achieved the present invention,
20 which provides a novel and highly effective, multi-chemistry alternative
that provides synergistic results for the control of Lepidopteran insects
on cotton and other crops on which they might be present.

In particular, the present invention is directed to an insecticidal composition comprising synergistically insecticidally effective amount of (1) at least one compound of formula (I):



wherein R_1 is bromine, chlorine, methyl, or ethyl, R_2 is bromine, chlorine, or ethyl, R_3 is hydrogen, halogen, or trifluoromethyl, X is $-O-$, $-S-$, or $-NH-$, and n is 2, 3, or 4, and (2) at least one compound of formula (II):

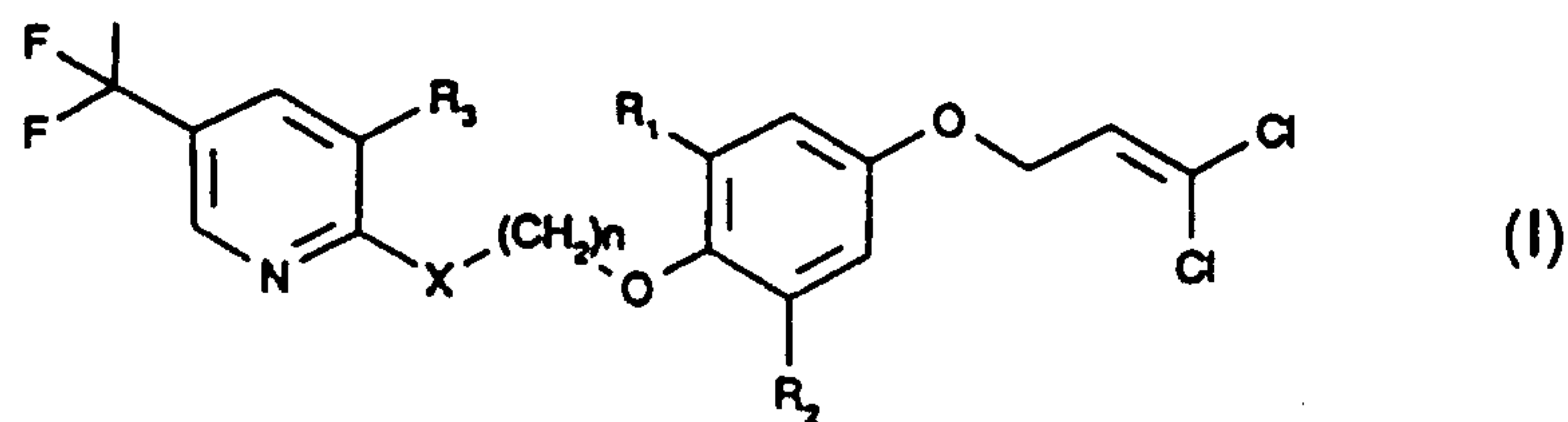


wherein R and R^1 independently are an alkyl, alkenyl, or alkynyl group containing up to 6 carbon atoms, R^2 is hydrogen, an alkyl group containing 1 to 18 carbon atoms, a cycloalkyl group containing 3 to 8 carbon atoms, an alkenyl group containing 2 to 18 carbon atoms, or an alkynyl group containing 3 to 18 carbon atoms, R^3 is hydrogen or an alkyl group containing 1 to 6 carbon atoms, and Y is $-O-$ or $-S-$.

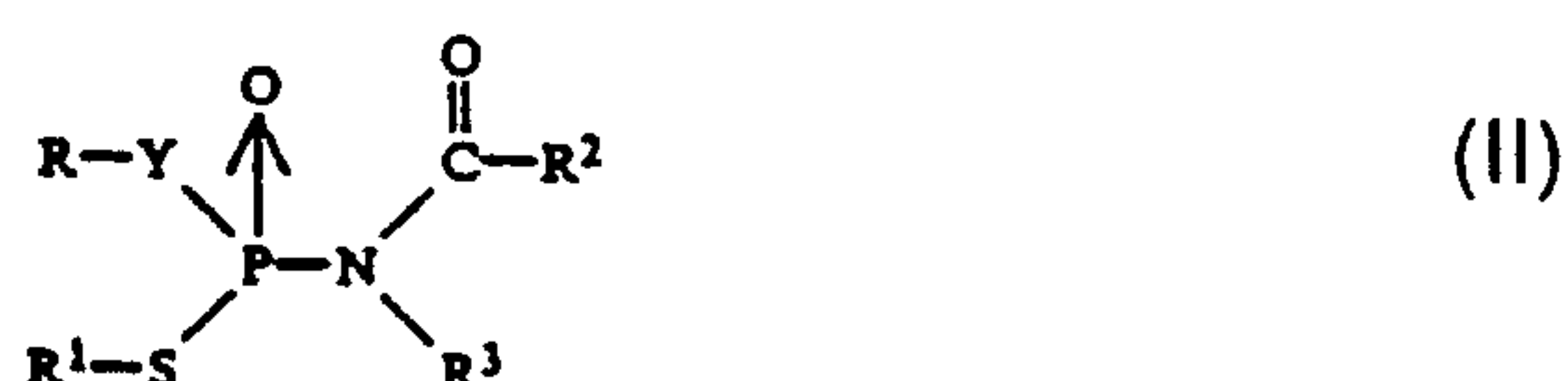
Also, the present invention is directed to a method of killing Lepidopteran insects comprising applying to an area to be treated synergistically insecticidally effective amounts of a composition comprising (1) at least one compound of formula (I):

WO 00/72680

PCT/US00/08229



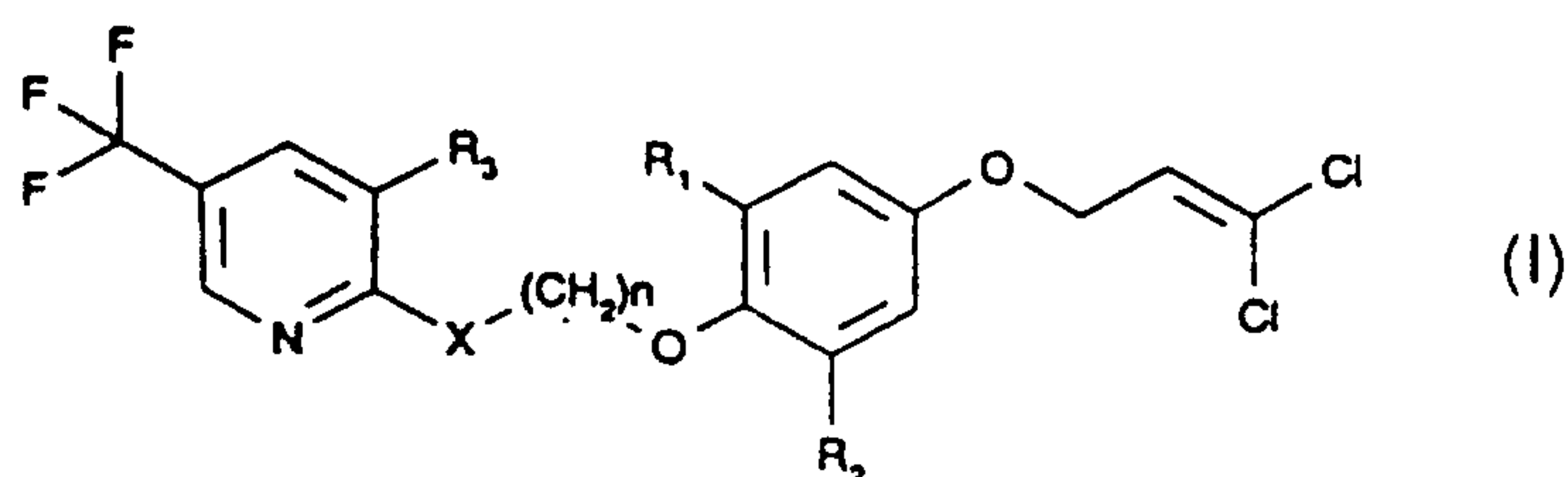
wherein R_1 is bromine, chlorine, methyl, or ethyl, R_2 is bromine, chlorine, or ethyl, R_3 is hydrogen, halogen, or trifluoromethyl, X is $-O-$, $-S-$, or $-NH-$, and n is 2, 3, or 4, and (2) at least one compound of formula (II):



- 5 wherein R and R^1 independently are an alkyl, alkenyl or alkynyl group containing up to 6 carbon atoms, R^2 is hydrogen, an alkyl group containing 1 to 18 carbon atoms, a cycloalkyl group containing 3 to 8 carbon atoms, an alkenyl group containing 2 to 18 carbon atoms, or an alkynyl group containing 3 to 18 carbon atoms, R^3 is hydrogen or an
- 10 alkyl group containing 1 to 6 carbon atoms, and Y is $-O-$ or $-S-$.

DETAILED DESCRIPTION OF THE INVENTION

One component of the composition of the present invention is a compound of formula (I):



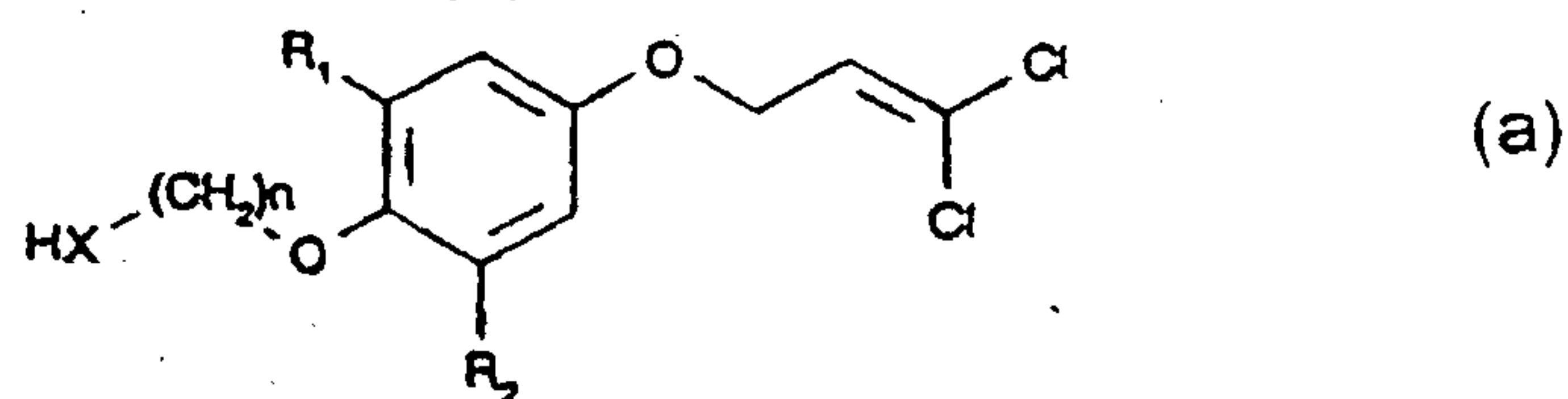
- where R_1 is bromine, chlorine, methyl, or ethyl, R_2 is bromine, chlorine, or ethyl, R_3 is hydrogen, halogen, or trifluoromethyl, X is $-O-$, $-S-$, or $-$
- 15

NH-, and n is 2, 3, or 4. This compound and methods for its preparation are described in detail in WO 96/11909.

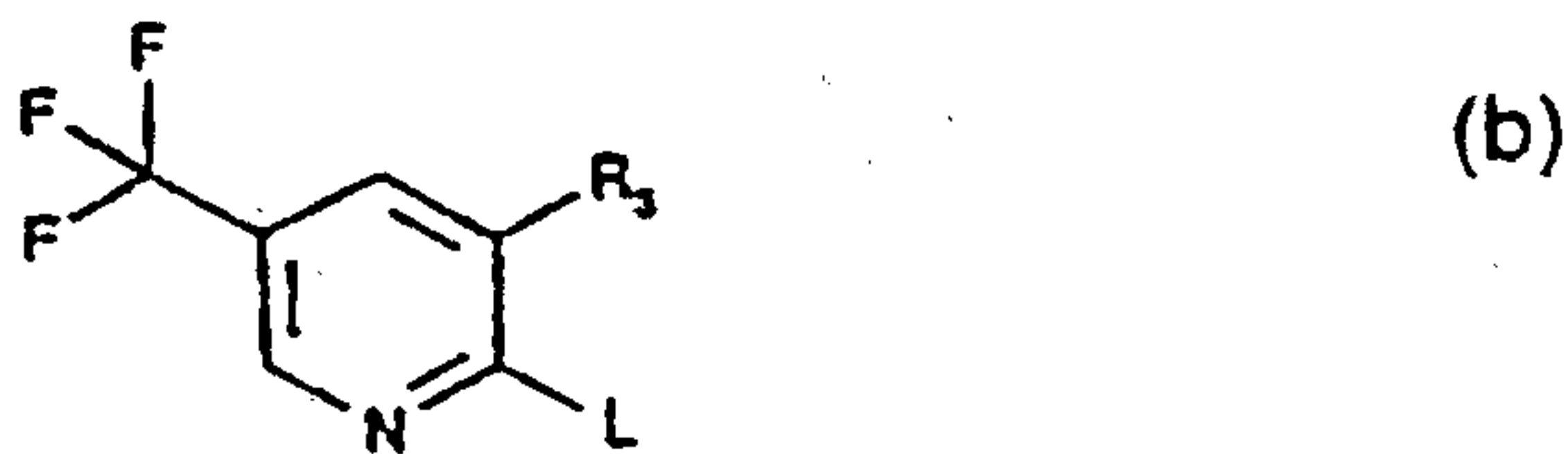
A particularly preferred compound within formula (I) is one in which R₁ is chlorine, R₂ is chlorine, R₃ is hydrogen, X is -O-, and n is 3, i.e., 2-[3-[2,6-dichloro-4-(3,3-dichloroprop-2-enyloxy)phenoxy]propoxy]-5-(trifluoromethyl)pyridine (which has been revised from 3,5-dichloro-4-(3-(5-trifluoromethyl-2-pyridyloxy)propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene).

A compound of formula (I) can be prepared by the following method.

A compound of formula (a)



wherein R₁ is bromine, chlorine, methyl, or ethyl, R₂ is bromine, chlorine, or ethyl, X is -O-, -S-, or -NH-, and n is 2, 3, or 4, is reacted with a compound of formula (b)



where R₃ is hydrogen, halogen, or trifluoromethyl and L is halogen (e.g., chlorine, bromine, or iodine), mesyloxy, or tosyloxy.

The reaction is preferably effected in an inert solvent in the presence of a suitable base.

Examples of the solvent which can be used are ketones such as acetone, methyl ethyl ketone and cyclohexanone; ethers such as 1,2-
5 dimethoxyethane, tetrahydrofuran, dioxane and dialkyl (e.g., C₁-C₄) ethers (e.g., diethyl ether, diisopropyl ether); N,N-dimethylformamide, dimethylsulfoxide, hexamethylphosphoric triamide, sulforane, acetonitrile, nitromethane; halogenated hydrocarbons such as dichloromethane, chloroform, 1,2-dichloroethane and chlorobenzene;
10 hydrocarbons such as toluene, benzene and xylene; and water. If necessary, a mixture of these solvents can be used.

Examples of the base which can be used are hydroxides of alkali metals or alkaline earth metals, such as lithium hydroxide, sodium hydroxide, potassium hydroxide and calcium hydroxide;
15 carbonates of alkali metals or alkaline earth metals, such as lithium carbonate, potassium carbonate, sodium carbonate and calcium carbonate; hydrides of alkali metals or alkaline earth metals, such as lithium hydride, sodium hydride, potassium hydride and calcium hydride; alkali metal alkoxides (e.g., C₁-C₄) such as sodium methoxide,
20 sodium ethoxide and potassium tert-butoxide; and organic bases such as triethylamine and pyridine. If necessary, catalysts such as ammonium salts (e.g., triethylbenzylammonium chloride) may be

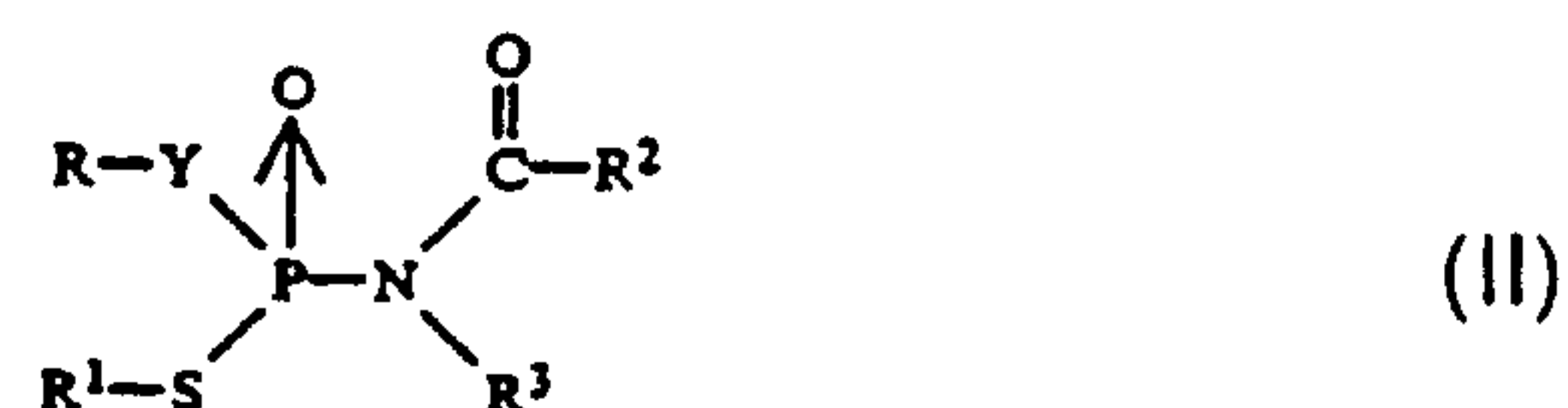
added to the reaction system at a ratio of 0.01 to 1 mole per mole of the compound of formula (a).

The reaction temperature is usually set within the range of -20°C to 150°C or the boiling point of a solvent used in the reaction, preferably -5°C to 100°C or the boiling point of a solvent used in the reaction.

The molar ratio of the starting materials and dehydrating agents to be used in the reaction can be freely determined, but it is favorable to effect the reaction at an equimolar ratio or a ratio closer thereto.

After completion of the reaction, the reaction mixture is subjected to ordinary post-treatments such as organic solvent extraction and concentration, and the desired compound of the present invention can be isolated. Further, purification can be carried out by an ordinary technique such as chromatography, distillation or recrystallation.

Another component of the composition of the present invention is a compound of formula (II):



wherein R and R¹ independently are an alkyl, alkenyl, or alkynyl group containing up to 6 carbon atoms, R² is hydrogen, an alkyl group

containing 1 to 18 carbon atoms, a cycloalkyl group containing 3 to 8 carbon atoms, an alkenyl group containing 2 to 18 carbon atoms, or an alkynyl group containing 3 to 18 carbon atoms, R^3 is hydrogen or an alkyl group containing 1 to 6 carbon atoms, and Y is -O- or -S-. This
5 compound and methods for its preparation are described in detail in U.S. Patents 3,176,600, 3,845,172, and 3,914,417.

A preferred compound within formula (II) is one in which R and R^1 independently are a methyl, ethyl, allyl or alkenyl group, R^2 is hydrogen or an alkyl group, R^3 is hydrogen, and Y is -O-.

10 A particularly preferred compound within formula (II) is one in which R, R^1 and R^2 are methyl groups, R^3 is hydrogen, and Y is -O-. This compound is known as acephate and is commercially available, e.g., from the Chevron Chemical Company under the trade name Orthene®.

15 The composition of the present invention comprises a mixture of at least one compound of formula (I) and at least one compound of formula (II). A particularly preferred composition of the present invention comprises a mixture of 2-[3-[2,6-dichloro-4-(3,3-dichloroprop-2-enyloxy)phenoxy]propoxy]-5-(trifluoromethyl)pyridine (hereinafter
20 referred to as "S-1812" for convenience) and acephate.

In the composition of the present invention, the ratio of the compound of formula (I): the compound of formula (II) can vary

preferably from 1:3.3 to 1:127.8, more preferably from 1:3.3 to 1:64, even more preferably from 1:3.3 to 1:15, on a parts by weight basis. For example, the ratio of S-1812:acephate can vary from 1 part S-1812:5 parts acephate to 1 part S-1812:127.8 parts acephate. As an
5 example within this range, the ratio of S-1812:acephate can vary from 1 part S-1812:16 parts acephate to 1 part S-1812:127.8 parts acephate. As another example within this range, the ratio of S-1812:acephate can vary from 1 part S-1812:5 parts acephate to 1 part S-1812:10 parts acephate.

10 Other components which can be present in the invention composition include emulsifiers and solvents. For example, an emulsifiable concentrate formulation of S-1812 can be prepared using anionic-nonionic emulsifier blends such as Atlox 3454 and Atlox 3455, manufactured by Uniqema (formerly ICI Surfactants), and an aromatic
15 hydrocarbon solvent such as SolvessoTM 150, manufactured by Exxon Chemical Company. When added to water, this formulation of S-1812 forms a solution containing S-1812 which can then be added to an acephate-containing solution to form a solution of the composition of the present invention.

20 Once formulated, the invention composition is useful in a method for controlling Lepidopteran insects by application of the composition onto the insecticidal habitat. In general, the invention

WO 00/72680

PCT/US00/08229

composition can be applied onto the habitat in an amount effective to be insecticidal to the insects.

In the solution application of the present invention, the invention composition can be dissolved in from about 3 gallons to about 10
5 gallons of water for application per acre, such that preferably at least about 0.063 lb and 0.5 lb of active ingredient (compounds of formula (I) and formula (II), respectively), more preferably from about 0.063 lb and 0.5 lb to about 0.1 lb and 0.75 lb of active ingredient is applied per acre.

10 The composition of the present invention has been demonstrated in the laboratory and in the field to be highly effective against Lepidopteran insects, bollworm, beet armyworm, soybean looper, and tarnished plant bug, providing synergistic results as compared with the performance of the individual active ingredients. As
15 a result, the present invention provides excellent control of Lepidopteran pests of cotton and other crops on which they might occur.

The following examples illustrate specific embodiments of the present invention, but should not be construed as limiting the scope of
20 the claims in any way. All parts, percents, ratios and the like are by weight unless otherwise indicated.

EXAMPLES

Example 1

An S-1812-containing formulation identified as "S-1812 0.83EC" was prepared by mixing the following components (w/v%):

5	S-1812 (active ingredient)	10.3%
	Atlox 3454F (emulsifier)	2.0%
	Atlox 3455F (emulsifier)	8.0%
	Solvesso 150 (solvent)	<u>79.7%</u>
	Total	100.0%

10 As set forth above, S-1812 0.83EC has 10.3% ai on a w/v% basis, i.e., 0.83 lb ai/gallon [(0.1 g ai/ml)(3785 ml/1gallon)(1 lb/454 g)].

0.2g of S-1812 0.83EC was added to 800 ml distilled H₂O and stirred to give a 25 ppm_{ai} (parts per million active ingredient) solution. This solution was serially diluted by 300 ml stock/300 ml distilled H₂O
15 to yield solution concentrations of 12.5, 6.25 and 3.13 ppm_{ai}.

0.02g of acephate (Orthene, technical grade, 98% pure) was added to 50 ml of S-1812 6.25 ppm_{ai} stock and 50 ml of S-1812 3.13 ppm_{ai} stock to give 400 ppm_{ai} acephate + 6.25 ppm_{ai} S-1812, and 400 ppm_{ai} acephate + 3.13 ppm_{ai} S-1812 mixtures.

20 The above procedure was repeated with 0.01g of acephate to yield 200 ppm_{ai} acephate + 6.25 or 3.13 ppm_{ai} S-1812 mixtures.

WO 00/72680

PCT/US00/08229

The procedure set forth in the preceding paragraph was repeated with 100 ml of S-1812 3.13 or 6.25 ppm stock to yield 100 ppm acephate + 6.25 or 3.13 ppm S-1812 mixtures.

Solutions of acephate alone of the various concentrations were
5 prepared in a similar manner using distilled H₂O.

The testing substrate was composed of 2.0 ml of prepared artificial tobacco budworm diet mix (Bio-Serv) dispensed into the bottom of a clear one ounce cup. The diet was dispensed in such a way that the surface when dry was level and smooth (no pits).

10 0.2 ml of the test mixture was pipetted onto the surface of the diet. The treated diet was placed under a fume hood to dry the test solution onto the diet surface (approximately one hour).

After drying, one second instar tobacco budworm larvae was placed into each cup, and the cup was sealed with a tight fitting, but
15 not airtight, lid. The cups were held at 25°C and 50% RH and evaluated after seven days. Larvae were rated as dead or alive at this point. There were 20 replicates per treatment with one cup = one replication.

The results of this testing are shown in Table 1 below.

WO 00/72680

PCT/US00/08229

**TABLE 1: SYNERGISM BETWEEN ORTHENE AND S-1812
IN A LABORATORY EXPERIMENT WITH SECOND
INSTAR TOBACCO BUDWORM LARVAE**

S-1812 Ppm ai	S-1812 % Mortality	Orthene Ppm ai	Orthene % Mortality	S-1812 & Orthene Additive % Mortality	S-1812 Ppm ai + Orthene Ppm ai (Mixture)	Mixture % Mortality	Increase In % Mortality of Mixture Over Additive
3.13	5	100	10	15	3.13+100	35	20
3.13	5	200	5	10	3.13+200	25	15
3.13	5	400	30	35	3.13+400	75	40
6.25	30	100	10	40	6.25+100	65	25
6.25	30	200	5	35	6.25+200	65	30
6.25	30	400	30	60	6.25+400	100	40

As can be seen from the results presented above in Table 1, the
5 compounds of formulas (I) and (II) act synergistically together to
increase the mortality rate beyond the sum of the rates for the
compounds individually and thereby provide unexpectedly superior
control of a Lepidopteran pest.

Example 2

10 Spray treatments were applied by a tractor mounted (highboy)
spray boom to cotton field plots in Greenville, Mississippi that
measured 40-50 ft by 13.2 ft by 13.2 ft with 3-4 replications per
treatment. Treatments were applied at 10 gallons of spray volume per
acre. Tank-mixes were made by measuring both compounds
15 independently and then adding them to the appropriate amount of

WO 00/72680**PCT/US00/08229**

water to produce the spray mixture. Treatments were applied in July/August at approximately one week intervals.

Plots were evaluated by sampling all damaged and undamaged bolls on 10 plants per plot. Cotton plots were evaluated for yield by
5 machine picking the center two rows of each plot. The results are shown in Table 2 below.

WO 00/72680

PCT/US00/08229

TABLE 2: FIELD EFFICACY OF S-1812 + ORTHENE AGAINST TOBACCO BUDWORM AND COTTON BOLLWORM IN COTTON

Trt	Application	No. of Applications	Product	Conc/FM	Lb ai/A Application Rate	Meth	% Damaged Bolls	Bolls/ Plant	Yield-Lbs Seed Cotton/A
1		0	UTC				55.30	3.87	843.55
2	ABCDE	5	Curacron	8EC	.500	FOSP	26.33	8.70	1578.26
	ABCDE		Larvin	3.2FL	.300	FOSP			
3	ABCDE	5	AsanaXL	.66EC	.050	FOSP	16.63	7.30	1823.16
4	ABCDE	5	Karate	1.0EC	.040	FOSP	23.27	8.00	1687.10
5	AC	2	AsanaXL	.66EC	.050	FOSP	38.90	5.63	1142.88
6	ABCDE	5	Orthene	90SP	1.0	FOSP	21.40	7.10	1537.45
7	ABCDE	5	S-1812	.83EC	.150	FOSP	14.37	7.93	1972.82
8	AC	2	S-1812	.83EC	.150	FOSP	23.53	7.07	1551.05
9	ABCDE	5	S-1812	.83EC	.075	FOSP	14.10	8.83	2204.12
	ABCDE		Orthene	90SP	.500	FOSP			
			CV				34.34	23.20	15.04
			LSD				16.78	2.69	388.02

Trt = treatment
Conc/FM = concentration and formulation
FOSP = foliar spray method
ABCDE (under Application) = five applications, coded A, B, C, D & E

WO 00/72680

PCT/US00/08229

UTC = untreated cotton
Curacron = profenofos
Larvin = thiodicarb
Asana XL = esfenvalerate
5 Karate = lambda cyhalothrin
Orthene = acephate

EC = emulsifiable concentrate
FL = flowable concentrate
10 SP = soluble powder

8EC has 8 lb ai/gallon
3.2FL has 3.2 lb ai/gallon
.66EC has 0.66 lb ai/gallon
15 1.0EC has 1.0 lb ai/gallon
90SP has 90% ai on a per weight basis
.83EC has 0.83 lb ai/gallon

CV = Coefficient of Variation (a statistic for comparison of like
20 experiments)
LSD = Fisher's Least Significant Difference (a statistical method of
comparing two means for significant difference by providing the
smallest valid difference)

WO 00/72680

PCT/US00/08229

As can be seen from the data presented above in Table 2, a mixture of compounds of formulas (I) and (II) provides unexpectedly superior results with respect to reducing the percentage of damaged bolls, providing a higher number of bolls per plant, and providing a
5 higher yield in pounds of seed cotton per acre as compared with the use of compounds of formulas (I) and (II) individually and as compared with the use of other insecticides.

Example 3

Additional testing was conducted against a variety of
10 Lepidopteran pests as shown in Table 3 below.

WO 00/72680

PCT/US00/08229

TABLE 3

Test Subjects				
Crop		GOSHI		GOSHI
Pest			SPOEI	
Test Subject No.		1	2	3
Reporting Standard		PDSQ	NOTF	NOTF
Comment				
Days After Trt		6 DA-A	6 DA-A	6 DA-A

Trt No	Product	Form Conc	Fm Tp	Appl Rate	Rate Unit	Appl Meth	Appl Code				
1	UTC							31.0 a	54.0 a	11.8 a	35.0 a
2	S1812	35	WP	.05	LBAI/A	FOSP	ABCDE	21.0 ab	7.8 c	6.8 a	7.0 de
2	ORTHENE	90	SP	.75	LBAI/A	FOSP	ABCDE				
3	S1812	35	WP	.063	LBAI/A	FOSP	ABCDE	14.0 b	17.8 bc	8.0 a	10.0 cde
3	ORTHENE	90	SP	.5	LBAI/A	FOSP	ABCDE				
4	S1812	35	WP	.063	LBAI/A	FOSP	ABCDE	16.0 b	9.5 bc	9.5 a	6.0 de
4	ORTHENE	90	SP	.75	LBAI/A	FOSP	ABCDE				
5	S1812	35	WP	.075	LBAI/A	FOSP	ABCDE	16.0 b	12.5 bc	11.3 a	6.0 de
5	ORTHENE	90	SP	.5	LBAI/A	FOSP	ABCDE				
6	S1812	35	WP	.1	LBAI/A	FOSP	ABCDE	13.0 b	13.3 bc	10.5 a	6.0 de
6	ORTHENE	90	SP	.33	LBAI/A	FOSP	ABCDE				
7	ORTHENE	90	SP	.33	LBAI/A	FOSP	ABCDE	19.0 ab	14.5 bc	13.0 a	17.0 bcd
8	ORTHENE	90	SP	.5	LBAI/A	FOSP	ABCDE	11.0 b	54.5 a	11.8 a	12.0 b-e
9	ORTHENE	90	SP	.75	LBAI/A	FOSP	ABCDE	20.0 ab	24.0 abc	9.5 a	21.0 bc
10	S1812	35	WP	.05	LBAI/A	FOSP	ABCDE	16.0 b	23.8 abc	7.0 a	7.0 de
11	S1812	35	WP	.063	LBAI/A	FOSP	ABCDE	14.0 b	20.3 bc	11.0 a	23.0 b
12	S1812	35	WP	.075	LBAI/A	FOSP	ABCDE	22.0 ab	43.0 ab	10.0 a	13.0 b-e
13	S1812	35	WP	.1	LBAI/A	FOSP	ABCDE	19.0 ab	14.8 bc	10.0 a	17.0 bcd
14	TRACER	4	SC	.09	LBAI/A	FOSP	ABCDE	10.0 b	9.8 bc	3.8 a	3.0 e
LSD (P=.05)								12.60	29.53	7.89	10.11
Standard Deviation								8.82	20.67	5.52	7.07
CV								51.02	90.07	57.79	54.12
Replicate F								0.064	0.821	1.924	1.574
Replicate Prob(F)								0.9787	0.4904	0.1417	0.2111
Treatment F								1.483	2.401	0.790	6.203
Treatment Prob(F)								0.1677	0.0174	0.6658	0.0001

Means followed by same letter do not significantly differ (P=.05, Duncan's New MRT)

WO 00/72680

PCT/US00/08229

TABLE 3 (CONTINUED)

Test Subjects							SPOEI	TRINI	LYLGI
Crop							2	3	4
Pest									
Test Subject No.									
Reporting Standard							NOTF	NOTF	NOSW
Comment									ADULT
Days After Trt							2 DA-C	2 DA-C	3 DA-C
Trt No	Product	Form Conc	Fm Tp	Appl Rate Rate	Rate Unit	Appl Meth	Appl Code		
1	UTC							16.5 a	6.8 a 0.120 a
2	S1812	35	WP	.05	LBAI/A	FOSP ABCDE		3.3 cd	2.5 de 0.030 ab
2	ORTHENE	90	SP	.75	LBAI/A	FOSP ABCDE			
3	S1812	35	WP	.063	LBAI/A	FOSP ABCDE		1.5 d	2.3 de 0.050 ab
3	ORTHENE	90	SP	.5	LBAI/A	FOSP ABCDE			
4	S1812	35	WP	.063	LBAI/A	FOSP ABCDE		4.3 cd	1.3 e 0.000 b
4	ORTHENE	90	SP	.75	LBAI/A	FOSP ABCDE			
5	S1812	35	WP	.075	LBAI/A	FOSP ABCDE		6.3 cd	2.8 de 0.030 ab
5	ORTHENE	90	SP	.5	LBAI/A	FOSP ABCDE			
6	S1812	35	WP	.1	LBAI/A	FOSP ABCDE		3.0 cd	2.3 de 0.030 ab
6	ORTHENE	90	SP	.33	LBAI/A	FOSP ABCDE			
7	ORTHENE	90	SP	.33	LBAI/A	FOSP ABCDE		14.8 ab	5.8 abc 0.110 a
8	ORTHENE	90	SP	.5	LBAI/A	FOSP ABCDE		10.5 abc	3.5 b-e 0.050 ab
9	ORTHENE	90	SP	.75	LBAI/A	FOSP ABCDE		8.5 bcd	3.8 b-e 0.060 ab
10	S1812	35	WP	.05	LBAI/A	FOSP ABCDE		6.0 cd	5.0 a-d 0.080 ab
11	S1812	35	WP	.063	LBAI/A	FOSP ABCDE		6.8 cd	6.3 ab 0.060 ab
12	S1812	35	WP	.075	LBAI/A	FOSP ABCDE		7.0 cd	3.3 cde 0.120 a
13	S1812	35	WP	.1	LBAI/A	FOSP ABCDE		3.5 cd	1.3 e 0.070 ab
14	TRACER	4	SC	.09	LBAI/A	FOSP ABCDE		2.8 cd	1.3 e 0.040 ab
LSD (P=.05)								7.13	2.63 0.0891
Standard Deviation								4.99	1.84 0.0624
CV								73.93	53.89 102.7
Replicate F								1.638	8.138 0.341
Replicate Prob(F)								0.1963	0.0002 0.7961
Treatment F								3.259	4.128 1.353
Treatment Prob(F)								0.0021	0.0003 0.2261

Means followed by same letter do not significantly differ (P=.05, Duncan's New MRT)

WO 00/72680

PCT/US00/08229

TABLE 3 (CONTINUED)

Test Subjects

Crop
Pest
Test Subject No.

COCCHI 5 GEOPU 6 CHERCA 7 ARACH 8

Reporting Standard

NOSW NOSW NOSW NOSW

Comment
Days After Trt

3 DA-C 3 DA-C 3 DA-C 3 DA-C

Trt No	Product	Form Conc	Fm Tp	Appl Rate	Rate Unit	Appl Meth	Appl Code						
1	UTC							0.230	abc	0.020	b	0.030	a 0.000 b
2	S1812	35	WP	.05	LBAI/A	FOSP	ABCDE	0.240	abc	0.000	b	0.010	a 0.000 b
2	ORTHENE	90	SP	.75	LBAI/A	FOSP	ABCDE						
3	S1812	35	WP	.063	LBAI/A	FOSP	ABCDE	0.240	abc	0.000	b	0.010	a 0.000 b
3	ORTHENE	90	SP	.5	LBAI/A	FOSP	ABCDE						
4	S1812	35	WP	.063	LBAI/A	FOSP	ABCDE	0.120	c	0.010	b	0.000	a 0.010 a
4	ORTHENE	90	SP	.75	LBAI/A	FOSP	ABCDE						
5	S1812	35	WP	.075	LBAI/A	FOSP	ABCDE	0.290	abc	0.000	b	0.010	a 0.000 b
5	ORTHENE	90	SP	.5	LBAI/A	FOSP	ABCDE						
6	S1812	35	WP	.1	LBAI/A	FOSP	ABCDE	0.170	bc	0.010	b	0.010	a 0.000 b
6	ORTHENE	90	SP	.33	LBAI/A	FOSP	ABCDE						
7	ORTHENE	90	SP	.33	LBAI/A	FOSP	ABCDE	0.220	abc	0.020	b	0.010	a 0.000 b
8	ORTHENE	90	SP	.5	LBAI/A	FOSP	ABCDE	0.330	ab	0.000	b	0.000	a 0.000 b
9	ORTHENE	90	SP	.75	LBAI/A	FOSP	ABCDE	0.260	abc	0.000	b	0.000	a 0.000 b
10	S1812	35	WP	.05	LBAI/A	FOSP	ABCDE	0.330	ab	0.000	b	0.020	a 0.000 b
11	S1812	35	WP	.063	LBAI/A	FOSP	ABCDE	0.300	abc	0.050	a	0.010	a 0.000 b
12	S1812	35	WP	.075	LBAI/A	FOSP	ABCDE	0.350	ab	0.000	b	0.020	a 0.000 b
13	S1812	35	WP	.1	LBAI/A	FOSP	ABCDE	0.290	abc	0.000	b	0.020	a 0.000 b
14	TRACER	4	SC	.09	LBAI/A	FOSP	ABCDE	0.390	a	0.010	b	0.010	a 0.000 b
LSD (P=.05)								0.1702		0.0272		0.0341	0.0077
Standard Deviation								0.1191		0.0191		0.0238	0.0054
CV								44.34		222.39		208.63	758.11
Replicate F								5.614		0.210		1.072	0.974
Replicate Prob(F)								0.0027		0.8891		0.3721	0.4149
Treatment F								1.479		2.177		0.526	0.974
Treatment Prob(F)								0.1693		0.0306		0.8943	0.4927

Means followed by same letter do not significantly differ (P=.05, Duncan's New MRT)

WO 00/72680

PCT/US00/08229

TABLE 3 (CONTINUED)

Test Subjects			
Crop			
Pest			
Test Subject No.	LYLGI 9	GOSBJ 1	SPOEI 2
Reporting Standard	NOSW	FDSQ	NOTF
Comment	NYPH		
Days After Trt	3 DA-C	2 DA-D	2 DA-D

Trt No	Product	Form Conc	Fm Tp	Appl Rate	Rate Unit	Appl Meth	Appl Code			
1	UTC							0.100	abc	49.0 a 25.3 bc
2	S1812	35	WP	.05	LBAI/A	FOSP	ABCDE	0.010	d	7.0 cd 13.3 bc
2	ORTHENE	90	SP	.75	LBAI/A	FOSP	ABCDE			
3	S1812	35	WP	.063	LBAI/A	FOSP	ABCDE	0.030	cd	14.0 cd 6.8 c
3	ORTHENE	90	SP	.5	LBAI/A	FOSP	ABCDE			
4	S1812	35	WP	.063	LBAI/A	FOSP	ABCDE	0.000	d	10.0 cd 15.3 bc
4	ORTHENE	90	SP	.75	LBAI/A	FOSP	ABCDE			
5	S1812	35	WP	.075	LBAI/A	FOSP	ABCDE	0.000	d	9.0 cd 25.8 bc
5	ORTHENE	90	SP	.5	LBAI/A	FOSP	ABCDE			
6	S1812	35	WP	.1	LBAI/A	FOSP	ABCDE	0.020	cd	12.0 cd 13.5 bc
6	ORTHENE	90	SP	.33	LBAI/A	FOSP	ABCDE			
7	ORTHENE	90	SP	.33	LBAI/A	FOSP	ABCDE	0.050	bcd	29.0 b 79.3 a
8	ORTHENE	90	SP	.5	LBAI/A	FOSP	ABCDE	0.020	cd	14.0 cd 68.8 a
9	ORTHENE	90	SP	.75	LBAI/A	FOSP	ABCDE	0.000	d	20.0 bc 45.5 ab
10	S1812	35	WP	.05	LBAI/A	FOSP	ABCDE	0.100	abc	9.0 cd 10.5 bc
11	S1812	35	WP	.063	LBAI/A	FOSP	ABCDE	0.040	cd	8.0 cd 14.0 bc
12	S1812	35	WP	.075	LBAI/A	FOSP	ABCDE	0.130	ab	17.0 bcd 8.8 bc
13	S1812	35	WP	.1	LBAI/A	FOSP	ABCDE	0.100	abc	14.0 cd 3.5 c
14	TRACER	4	SC	.09	LBAI/A	FOSP	ABCDE	0.140	a	2.0 d 3.5 c
LSD (P=.05)								0.0746		12.87 32.87
Standard Deviation								0.0522		9.00 23.00
CV								98.71		58.9 96.56
Replicate F								0.518		0.390 1.753
Replicate Prob(F)								0.6725		0.7608 0.1721
Treatment F								3.762		6.722 4.348
Treatment Prob(F)								0.0007		0.0001 0.0002

Means followed by same letter do not significantly differ (P=.05, Duncan's New MRT)

WO 00/72680

PCT/US00/08229

TABLE 3 (CONTINUED)

Test Subjects			
Crop	TRINI	GOSHJ	GOSHJ
Pest	3	10	11
Test Subject No.			
Reporting Standard	NOTF	NOBP	FDBO
Comment	2 DA-D		
Days After Trt			

Trt No	Product	Form Conc	Fm Tp	Appl Rate Rate	Unit	Appl Meth	Appl Code				
1	UTC							6.0 ab	29.8 d	37.65 a	
2	S1812	35	WP	.05	LBAI/A	FOSP	ABCDE	3.3 bc	61.0 bc	12.65 cd	
2	ORTHENE	90	SP	.75	LBAI/A	FOSP	ABCDE				
3	S1812	35	WP	.063	LBAI/A	FOSP	ABCDE	1.5 c	69.3 abc	11.82 cd	
3	ORTHENE	90	SP	.5	LBAI/A	FOSP	ABCDE				
4	S1812	35	WP	.063	LBAI/A	FOSP	ABCDE	2.8 bc	84.3 ab	11.45 cd	
4	ORTHENE	90	SP	.75	LBAI/A	FOSP	ABCDE				
5	S1812	35	WP	.075	LBAI/A	FOSP	ABCDE	2.3 bc	71.3 abc	14.73 cd	
5	ORTHENE	90	SP	.5	LBAI/A	FOSP	ABCDE				
6	S1812	35	WP	.1	LBAI/A	FOSP	ABCDE	3.5 bc	83.8 ab	14.48 cd	
6	ORTHENE	90	SP	.33	LBAI/A	FOSP	ABCDE				
7	ORTHENE	90	SP	.33	LBAI/A	FOSP	ABCDE	8.5 a	52.0 c	28.00 ab	
8	ORTHENE	90	SP	.5	LBAI/A	FOSP	ABCDE	6.0 ab	54.3 c	33.40 ab	
9	ORTHENE	90	SP	.75	LBAI/A	FOSP	ABCDE	5.3 abc	57.5 c	22.03 bc	
10	S1812	35	WP	.05	LBAI/A	FOSP	ABCDE	6.3 ab	75.3 abc	10.58 cd	
11	S1812	35	WP	.063	LBAI/A	FOSP	ABCDE	4.5 abc	60.5 bc	9.02 cd	
12	S1812	35	WP	.075	LBAI/A	FOSP	ABCDE	3.0 bc	56.5 c	13.83 cd	
13	S1812	35	WP	.1	LBAI/A	FOSP	ABCDE	3.5 bc	67.8 abc	7.30 d	
14	TRACER	4	SC	.09	LBAI/A	FOSP	ABCDE	2.8 bc	87.5 a	2.55 d	
LSD (P=.05)								3.65	21.58	11.261	
Standard Deviation								2.56	15.10	7.880	
CV								60.65	23.22	48.07	
Replicate F								5.853	6.190	0.961	
Replicate Prob(F)								0.0021	0.0015	0.4208	
Treatment F								2.307	4.171	6.652	
Treatment Prob(F)								0.0221	0.0003	0.0001	

Means followed by same letter do not significantly differ (P=.05, Duncan's New MRT)

WO 00/72680

PCT/US00/08229

Trt = treatment

UTC = untreated cotton

- 5 WP = wettable powder
 SP = soluble powder
 SC = soluble concentrate

- 10 35 WP has 35% ai on a per weight basis
 90 SP has 90% ai on a per weight basis
 4 SC has 4 lb ai/gallon

FOSP = foliar spray method

- 15 GOSHJ = cotton

- SPOEI = beet armyworm, *Spodoptera exigua*
 TRINI = cabbage looper, *Trichoplusia ni*
 LYGLI = Tarnished plant bug, *Lygus lineolaris*
 20 COCCI = ladybird beetles
 GEOPU = bigeyed bug
 CHRCA = lacewings
 ARACH = spider

- 25 PDSQ = percent damaged cotton squares
 NOTF = number per 10 row feet using beat cloth sampling method
 NOSW = number per swing of a sweep net
 NOBP = number of cotton bolls (fruits) per cotton plant
 PDBO = percent damaged cotton bolls

- 30 6 DA-A = 6 days after application A

Tracer = Spinosyn A+ Spinosyn D

- 35 CV = Coefficient of Variation
 LSD = Fisher's Least Significant Difference

- 40 A treatment is a particular insecticide or insecticide mixture being tested.

The number of replicates or replications is the number of times a treatment is identically repeated within the same test (for example, tested on 3-4 plots in a field test).

WO 00/72680

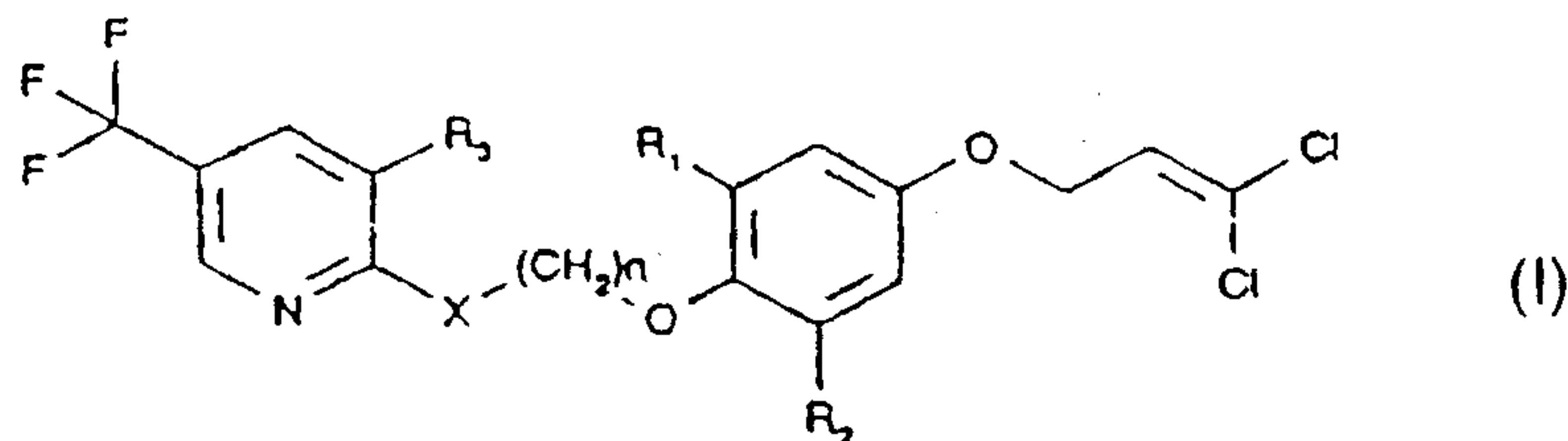
PCT/US00/08229

As can be seen from the results presented above in Table 3, the mixture of compounds as in the present invention again provided unexpectedly superior results as compared with the compounds individually and as compared with another insecticidal mixture.

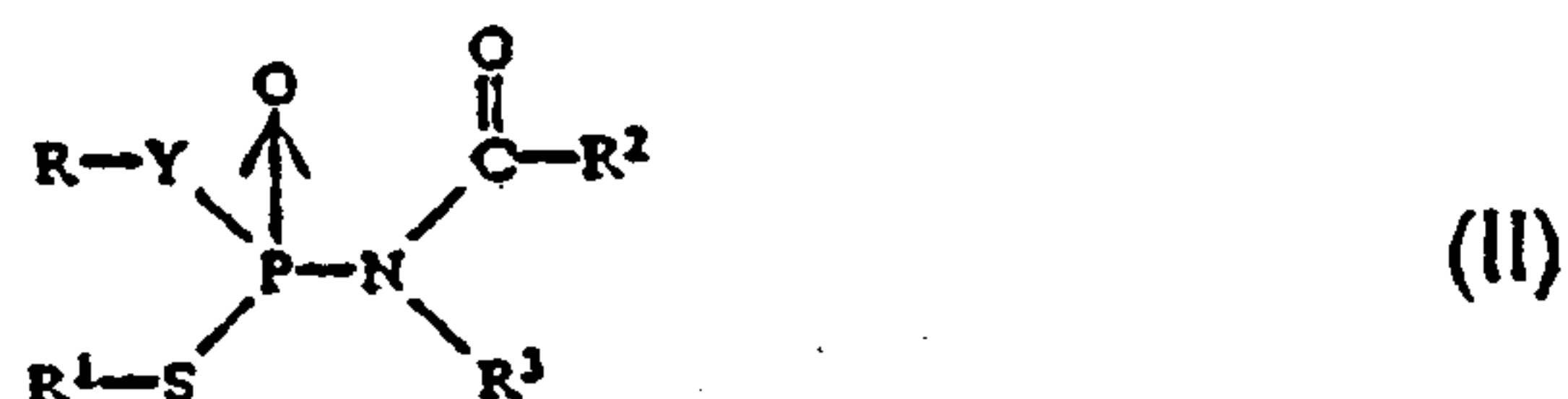
5 While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. An insecticidal composition comprising synergistically insecticidally effective amounts of (1) at least one compound of formula (I):



- 5 wherein R_1 is bromine, chlorine, methyl, or ethyl, R_2 is bromine, chlorine, or ethyl, R_3 is hydrogen, halogen or trifluoromethyl, X is -O-, -S-, or -NH-, and n is 2, 3, or 4, and (2) at least one compound of formula (II):



- 10 wherein R and R^1 independently are an alkyl, alkenyl, or alkynyl group containing up to 6 carbon atoms, R^2 is hydrogen, an alkyl group containing 1 to 18 carbon atoms, a cycloalkyl group containing 3 to 8 carbon atoms, an alkenyl group containing 2 to 18 carbon atoms, or an alkynyl group containing 3 to 18 carbon atoms, R^3 is hydrogen or an
- 15 alkyl group containing 1 to 6 carbon atoms, and Y is -O- or -S-.

2. An insecticidal composition as in claim 1, wherein the at least one compound of formula (I) is 2-[3-[2,6-dichloro-4-(3,3-dichloroprop-2-enyloxy)phenoxy]propoxy]-5-(trifluoromethyl)pyridine.

5 3. An insecticidal composition as in claim 1, wherein the at least one compound of formula (II) is a compound in which R and R¹ independently are a methyl, ethyl or, allyl group or an alkenyl group containing up to 6 carbon atoms, R² is hydrogen or an alkyl group containing 1 – 18 carbon atoms, R³ is hydrogen, and Y is -O-.

4. An insecticidal composition as in claim 3, wherein the at least one compound of formula (II) is acephate.

5. An insecticidal composition as in claim 2, wherein the at least one compound of formula (II) is a compound in which R and R¹ independently are a methyl, ethyl or allyl group or an alkenyl group containing up to 6 carbon atoms, R² is hydrogen or an alkyl group containing 1 – 18 carbon atoms, R³ is hydrogen, and Y is -O-.

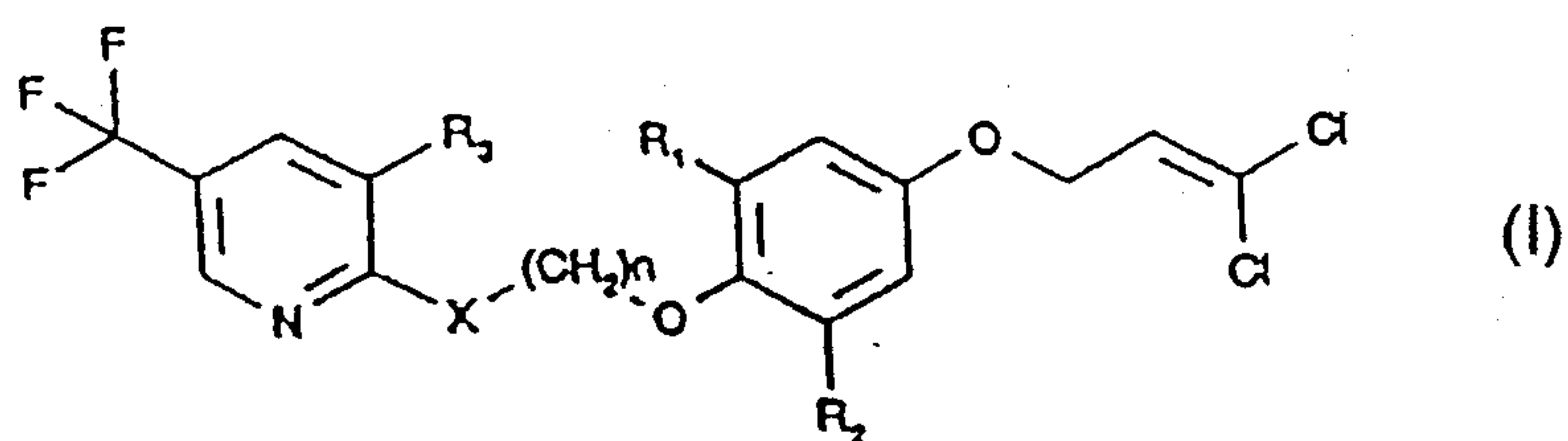
6. An insecticidal composition as in claim 5, wherein the at least one compound of formula (II) is acephate.

7. An insecticidal composition as in claim 6, wherein (1) the 2-[3-[2,6-dichloro-4-(3,3-dichloroprop-2-enyloxy)phenoxy]propoxy]-5-(trifluoromethyl)pyridine and (2) the acephate are present in a (1):(2) ratio of 1:5 to 1:127.8 on a parts by weight basis.

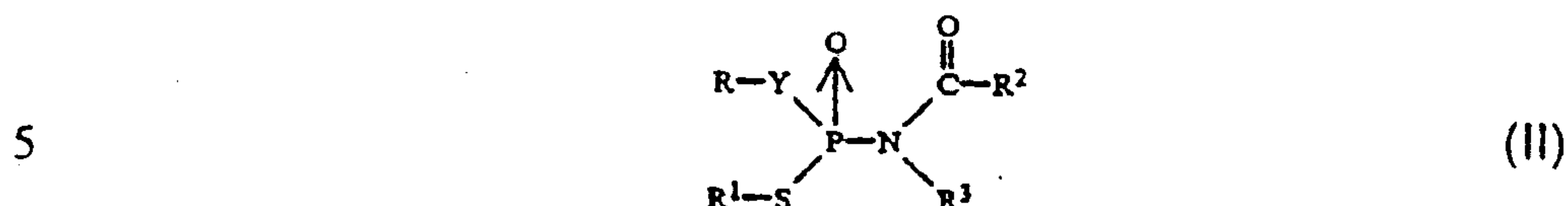
8. An insecticidal composition as in claim 7, wherein (1) the 2-[3-[2,6-dichloro-4-(3,3-dichloroprop-2-enyloxy)phenoxy]propoxy]-5-(trifluoromethyl)pyridine and (2) the acephate are present in a (1):(2) ratio of 1:16 to 1:127.8 on a parts by weight basis.

9. An insecticidal composition as in claim 7, wherein (1) the 2-[3-[2,6-dichloro-4-(3,3-dichloroprop-2-enyloxy)phenoxy]propoxy]-5-(trifluoromethyl)pyridine and (2) the acephate are present in a (1):(2) ratio of 1:5 to 1:10 on a parts by weight basis.

10. A method for killing Lepidopteran insects, comprising applying to an area to be treated synergistically insecticidally effective amounts of a composition comprising (1) at least one compound of formula (I):



wherein R_1 is bromine, chlorine, methyl, or ethyl, R_2 is bromine, chlorine, or ethyl, R_3 is hydrogen, halogen or trifluoromethyl, X is -O-, -S-, or -NH-, and n is 2, 3, or 4, and (2) at least one compound of formula (II):



wherein R and R^1 independently are an alkyl, alkenyl, or alkynyl group containing up to 6 carbon atoms, R^2 is hydrogen, an alkyl group containing 1 to 18 carbon atoms, a cycloalkyl group containing 3 to 8 carbon atoms, an alkenyl group containing 2 to 18 carbon atoms, or an alkynyl group containing 3 to 18 carbon atoms, R^3 is hydrogen or an alkyl group containing 1 to 6 carbon atoms, and Y is -O- or -S-.

10

11. A method as in claim 10, wherein the at least one compound of formula (I) is 2-[3-[2,6-dichloro-4-(3,3-dichloroprop-2-
 15 enyloxy)phenoxy]propoxy]-5-(trifluoromethyl)pyridine.

12. A method as in claim 10, wherein the at least one compound of formula (II) is a compound in which R and R^1

independently are a methyl, ethyl or allyl group or an alkenyl group containing up to 6 carbon atoms, R^2 is hydrogen or an alkyl group containing 1 to 18 carbon atoms, R^3 is hydrogen, and Y is -O-.

13. A method as in claim 12, wherein the at least one compound of formula (II) is acephate.

14. A method as in claim 11, wherein the at least one compound of formula (II) is a compound in which R and R^1 independently are a methyl, ethyl or allyl group or an alkenyl group containing up to 6 carbon atoms, R^2 is hydrogen or an alkyl group containing 1 to 18 carbon atoms, R^3 is hydrogen, and Y is -O-.

15. A method as in claim 14, wherein the at least one compound of formula (II) is acephate.

16. A method as in claim 15, wherein (1) the 2-[3-[2,6-dichloro-4-(3,3-dichloroprop-2-enyloxy)phenoxy]propoxy]-5-(trifluoromethyl)pyridine and (2) the acephate are present in a (1):(2) ratio of 1:5 to 1:127.8 on a parts by weight basis.

WO 00/72680

PCT/US00/08229

17. A method as in claim 16, wherein (1) the 2-[3-[2,6-dichloro-4-(3,3-dichloroprop-2-enyloxy)phenoxy]propoxy]-5-(trifluoromethyl)pyridine and (2) the acephate are present in a (1):(2) ratio of 1:16 to 1:127.8 on a parts by weight basis.

5

18. A method as in claim 16, wherein (1) the 2-[3-[2,6-dichloro-4-(3,3-dichloroprop-2-enyloxy)phenoxy]propoxy]-5-(trifluoromethyl)pyridine and (2) the acephate are present in a (1):(2) ratio of 1:5 to 1:10 on a parts by weight basis.

10

