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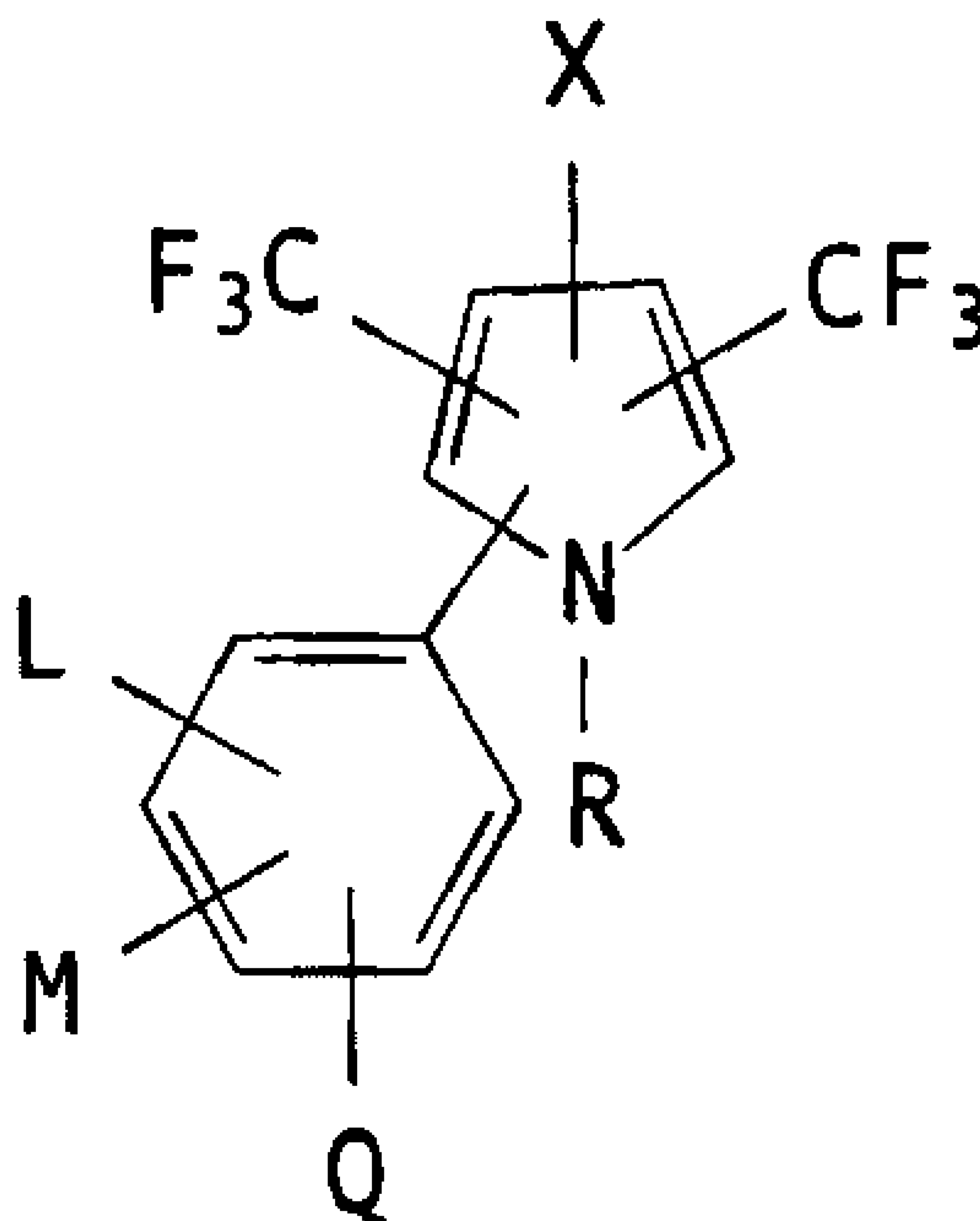
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(54) Titre : AGENTS ACARICIDES ET INSECTICIDES DE BI- ET DE TRI(TRIFLUOROMETHYL)ARYLPYRROLE

(54) Title: BIS- AND TRIS(TRIFLUOROMETHYL)ARYLPYRROLE INSECTICIDAL AND ACARICIDAL AGENTS



(57) Abrégé/Abstract:

Bis- and tris(trifluoromethyl)arylpyrrole compounds which are effective for the control of insects and acarids are described. A method for the insecticidal and acaricidal use of said compounds and methods for the preparation of said compounds are presented.



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BIS- AND TRIS(TRIFLUOROMETHYL)ARYLPYRROLE
INSECTICIDAL AND ACARICIDAL AGENTS

ABSTRACT

Bis- and tris(trifluoromethyl)arylpyrrole compounds which are effective for the control of insects and acarids are described. A method for the insecticidal and acaricidal use of said compounds and methods for the preparation of said compounds are presented.

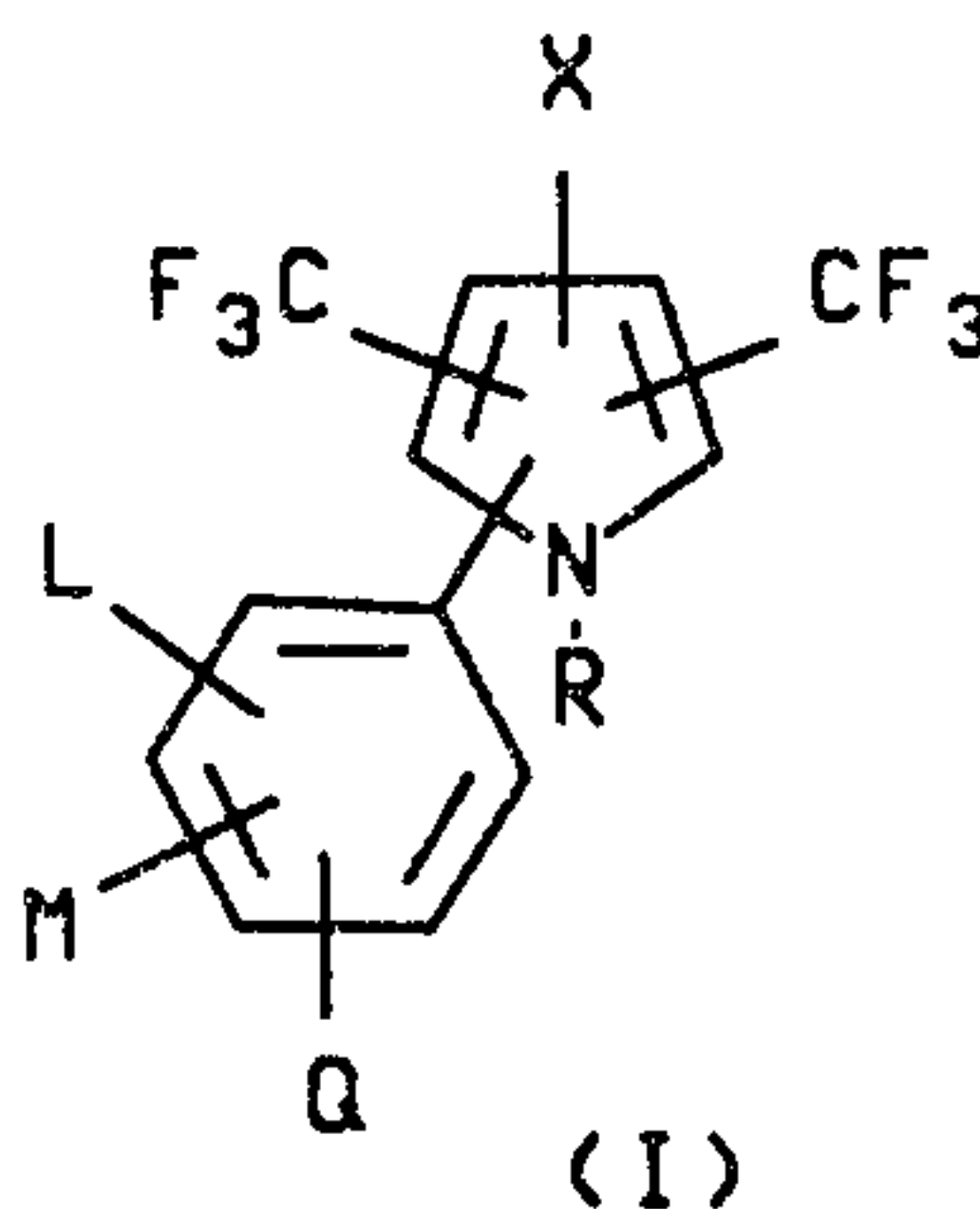
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BIS- AND TRIS(TRIFLUOROMETHYL)ARYLPYRROLE
INSECTICIDAL AND ACARICIDAL AGENTS

SUMMARY OF THE INVENTION

The present invention describes bis- and tris(trifluoromethyl)arylpyrrole compounds that are highly effective insecticidal and acaracidal agents useful for the control of insect and acarid pests and for protecting agronomic crops from the ravages of said pests.

The bis- and tris(trifluoromethyl)arylpyrrole compounds of the present invention have the structural formula I



wherein L is H, Cl, Br or F;

M and Q are each independently H, F, Cl, Br, CN, NO₂,
CF₃, C₁-C₄ alkyl or C₁-C₃ alkoxy;

X is Cl, Br, I or CF₃;

R is $\begin{array}{c} \text{O} \\ \parallel \\ \text{CR}_1 \end{array}$, hydrogen, cyano,

- 5 C₁-C₆ alkyl optionally substituted with one to
 three halogen atoms,
 one tri(C₁-C₄ alkyl)silyl,
 one hydroxy,
 one cyano,
10 one or two C₁-C₄ alkoxy groups optionally
 substituted with one to three halogen
 atoms,
 one C₁-C₄ alkylthio,
 one phenyl optionally substituted with one to
15 three halogen atoms, one to three C₁-C₄
 alkyl groups or one to three C₁-C₄
 alkoxy groups,
 one phenoxy group optionally substituted with
 one to three halogen atoms, one to three
20 C₁-C₄ alkyl groups or one to three C₁-C₄
 alkoxy groups,
 one benzyloxy group optionally substituted on
 the phenyl ring with one to three
 halogen atoms, one to three C₁-C₄ alkyl
25 groups or one to three C₁-C₄ alkoxy
 groups,
 one C₁-C₆ alkylcarbonyloxy group optionally
 substituted with one to three halogen
 atoms,
30 one C₂-C₆ alkenylcarbonyloxy group optionally
 substituted with one to three halogen
 atoms,
 one phenylcarbonyloxy group optionally
 substituted with one to three halogen
35 atoms, one to three C₁-C₄ alkyl groups

or one to three C_1-C_4 alkoxy groups,
one C_1-C_6 alkoxycarbonyl group optionally
substituted with one to three halogen
atoms or one to three C_1-C_4 alkoxy
groups, or
one benzyloxycarbonyl group optionally
substituted on the phenyl ring with one
to three halogen atoms, one to three
 C_1-C_4 alkyl groups or one to three C_1-C_4
alkoxy groups,
 C_3-C_6 alkenyl optionally substituted with one
to three halogen atoms or one phenyl group,
or
 C_3-C_6 alkynyl optionally substituted with one
to three halogen atoms or one phenyl group;
and
 R_1 is C_1-C_6 alkyl optionally substituted with one to
three halogen atoms,
one hydroxy,
one cyano,
one or two C_1-C_4 alkoxy groups optionally
substituted with one to three halogen
atoms,
one C_1-C_4 alkylthio,
one phenyl optionally substituted with one to
three halogen atoms, one to three C_1-C_4
alkyl groups or one to three C_1-C_4
alkoxy groups,
one phenoxy group optionally substituted with
one to three halogen atoms, one to three
 C_1-C_4 alkyl groups or one to three C_1-C_4
alkoxy groups,
one benzyloxy group optionally substituted on
the phenyl ring with one to three
halogen atoms, one to three C_1-C_4 alkyl

- groups or one to three C_1-C_4 alkoxy groups,
- 5 one C_1-C_6 alkylcarbonyloxy group optionally substituted with one to three halogen atoms,
- one C_2-C_6 alkenylcarbonyloxy group optionally substituted with one to three halogen atoms,
- 10 one phenylcarbonyloxy group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
- 15 one C_1-C_6 alkoxycarbonyl group optionally substituted with one to three halogen atoms or one to three C_1-C_4 alkoxy groups, or
- one benzyloxycarbonyl group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
- 20 C_3-C_6 alkenyl optionally substituted with one to three halogen atoms or one phenyl group,
- 25 C_3-C_6 alkynyl optionally substituted with one to three halogen atoms or one phenyl group,
- phenyl optionally substituted with one to three halogen atoms, one or two C_1-C_4 alkyl groups, one or two C_1-C_4 alkoxy groups, CF_3 , CN , NO_2 , di(C_1-C_4 alkyl)amino or C_1-C_4 alkanoylamino,
- 30 phenoxy optionally substituted with one to three halogen atoms, one or two C_1-C_4 alkyl groups, one or two C_1-C_4 alkoxy groups, CF_3 , CN , NO_2 , di(C_1-C_4 alkyl)amino or C_1-C_4 alkanoylamino,
- 35 C_1-C_6 alkoxy optionally substituted with one to three halogen atoms,

C_2-C_6 alkenyloxy optionally substituted with one to three halogen atoms,

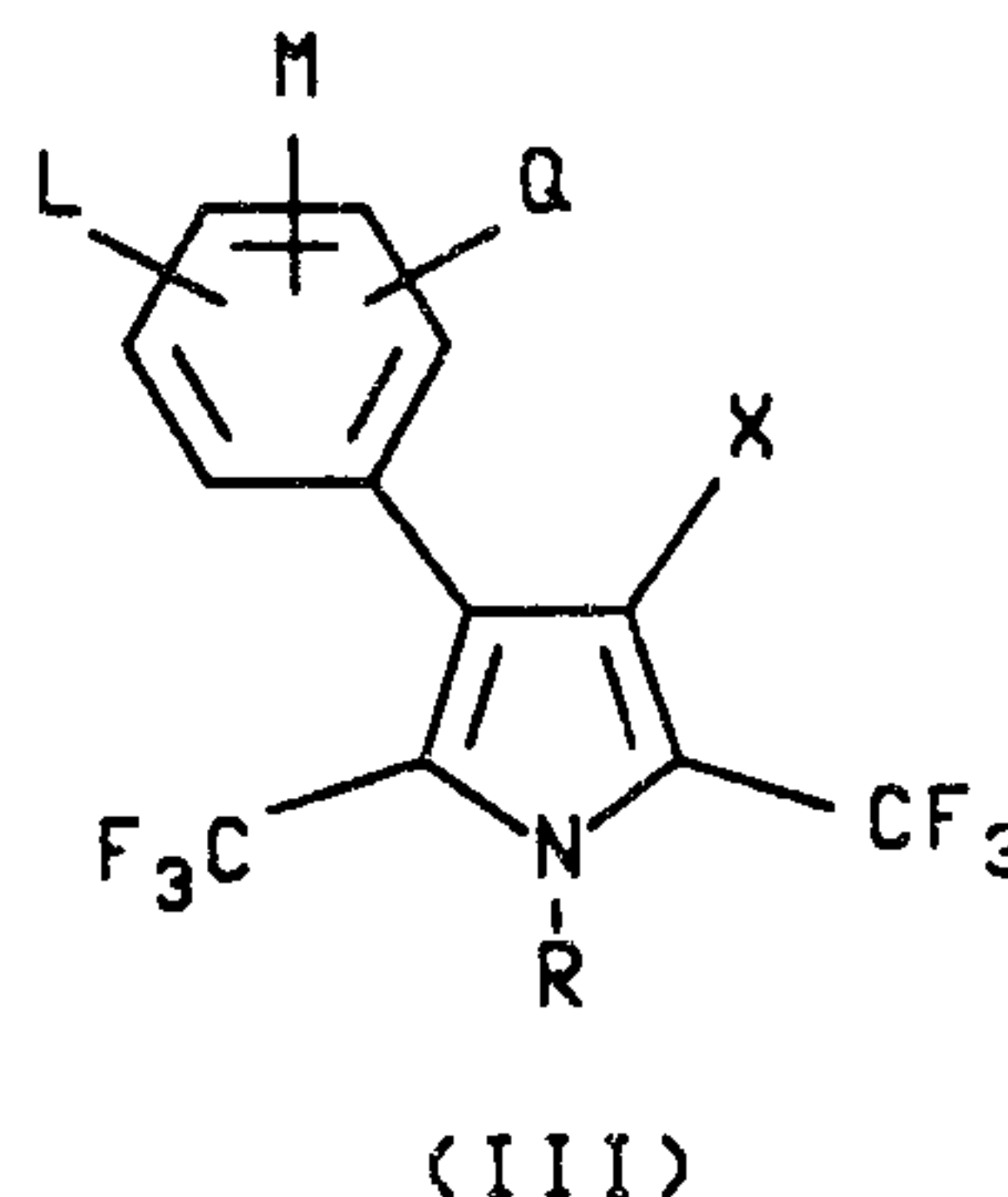
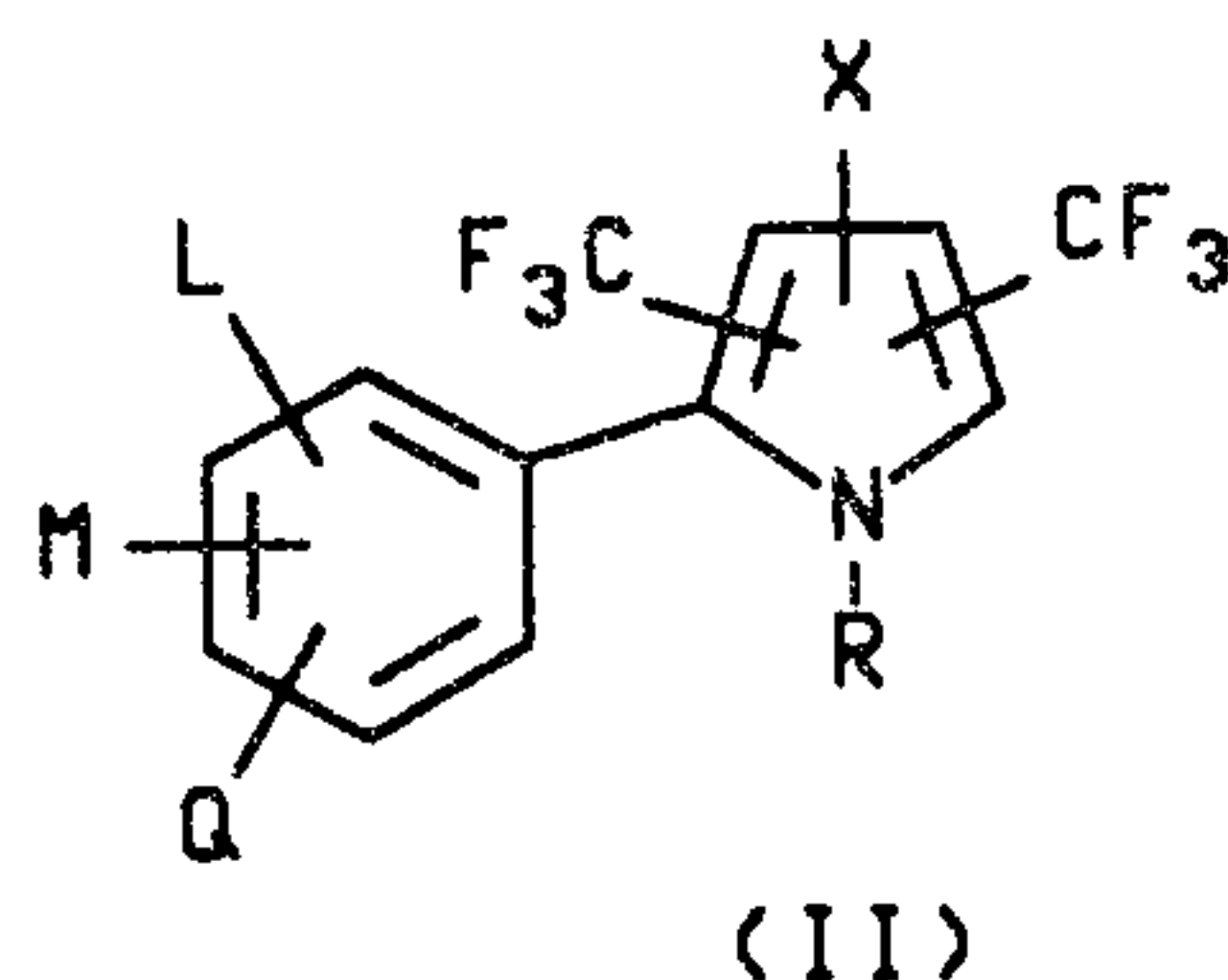
di(C_1-C_4 alkyl)amino,

N-(C_1-C_4 alkyl)-N-phenylamino or -N-halophenylamino, or

C_3-C_6 polymethyleneimino; provided that when the pyrrole ring is substituted with CF_3 at each of the pyrrole carbon atoms adjacent to the ring nitrogen atom and X is Cl, Br or I then R cannot be hydrogen.

DETAILED DESCRIPTION OF THE INVENTION

The compounds of the present invention are excellent insecticidal and acaricidal agents. The present invention provides a method for controlling undesirable pests by applying a pesticidally effective amount of a bis- or tris(trifluoromethyl)arylpyrrole compound to the breeding grounds, food supply or habitat of said pests. Preferred groups of bis- and tris(trifluoromethyl)arylpyrroles are illustrated by formula II and formula III



wherein L, M, Q, X R and R_1 , are as described above; provided that in Formula III when X is Cl, Br or I then

R cannot be hydrogen.

Preferred formula I bis- and tris(trifluoromethyl)-arylpyrroles of the invention are those in which

5

X is Br or CF₃;

L is H;

M is H, F, Cl or Br;

Q is H, F, Cl, Br or CF₃;

10

R is $\overset{\text{O}}{\parallel}\text{CR}_1$, hydrogen, cyano,
 C₁-C₆ alkyl optionally substituted with one to
 three halogen atoms,
 one tri(C₁-C₄ alkyl)silyl,
 one cyano,
 one or two C₁-C₄ alkoxy groups,
 one phenoxy group,
 one benzyloxy group,
 one C₁-C₆ alkylcarbonyloxy group,
 one C₂-C₆ alkenylcarbonyloxy group,
 one phenylcarbonyloxy group,
 one C₁-C₆ alkoxycarbonyl group, or
 one benzyloxycarbonyl group,

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C₃-C₆ alkenyl, or
 C₃-C₆ alkynyl; and
 R₁ is C₁-C₆ alkyl optionally substituted with one to
 three halogen atoms,
 one cyano,
 one or two C₁-C₄ alkoxy groups,
 one phenyl,
 one phenoxy group,
 one benzyloxy group,
 one C₁-C₆ alkylcarbonyloxy group,
 one C₂-C₆ alkenylcarbonyloxy group,
 one phenylcarbonyloxy group,
 one C₁-C₆ alkoxycarbonyl group, or

30

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one benzyloxycarbonyl group,
 C_3-C_6 alkenyl,
 C_3-C_6 alkynyl,
 phenyl,
 5 phenoxy,
 C_1-C_6 alkoxy,
 C_2-C_6 alkenyloxy; provided that when the pyrrole
 ring is substituted with CF_3 at each of the
 pyrrole carbon atoms adjacent to the ring
 10 nitrogen atom and X is Br then R cannot be
 hydrogen.

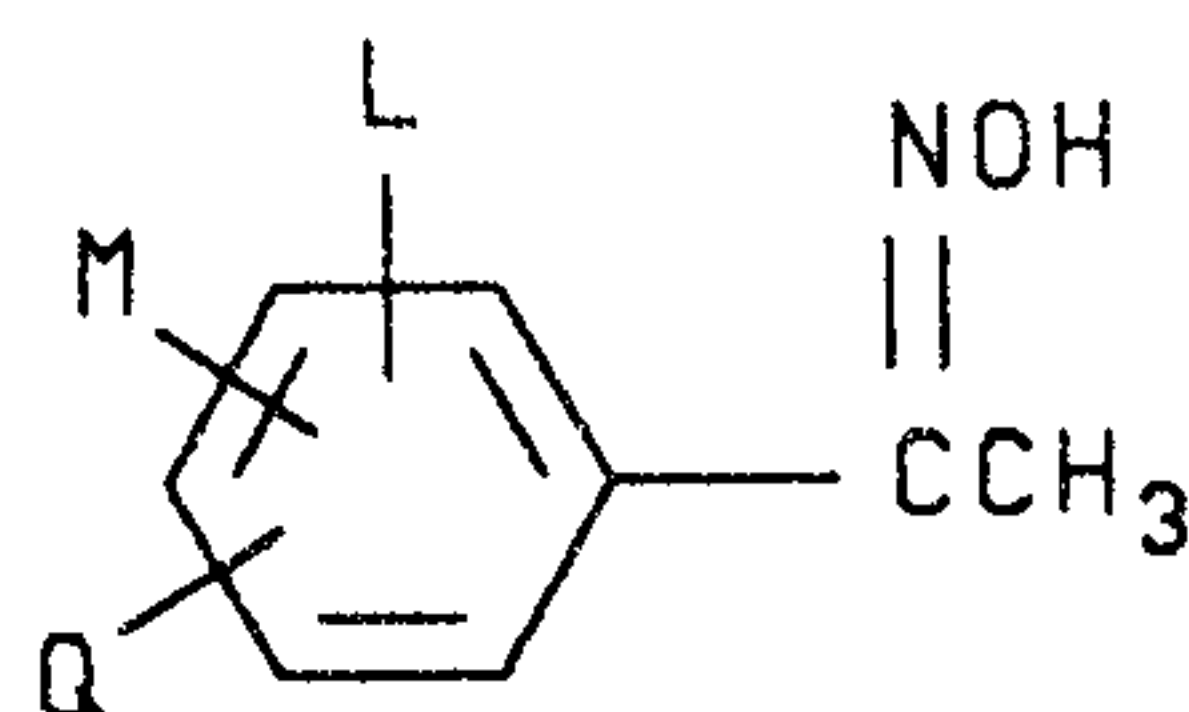
Preferred formula II compounds which are
 especially effective as insecticidal and/or acaricidal
 agents are those in which
 15 L is H, Cl, Br or F;
 M and Q are each independently H, F, Cl, Br, CN, NO_2 or
 CF_3 ;
 X is Cl, Br, I or CF_3 ;
 20 $\begin{array}{c} O \\ || \\ R \text{ is } CR_1 \end{array}$, hydrogen, cyano or C_1-C_6 alkyl optionally
 substituted with one to three halogen atoms, CN,
 C_1-C_4 alkoxy, C_1-C_6 alkylcarbonyloxy or benzyloxy-
 carbonyl; and
 25 R_1 is phenyl optionally substituted with one to three
 halogen atoms.

Bis(trifluoromethyl)arylpyrrole compounds of
 formula II may be prepared by reacting an acetophenone

30

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oxime or a substituted acetophenone oxime represented by the structural formula IV



(IV)

10 wherein

L is H, Cl, Br or F;

M and Q are each independently H, F, C₁, Br, CN, No₂, CF₃, C₁-C₄ alkyl or C₁-C₃ alkoxy; with at least an equivalent amount of commercially available hexafluoro-2-butyne and a base such as an alkali metal alkoxide in the presence of a solvent to give both the appropriately substituted O-[1,2-bis(trifluoromethyl)vinyl]-acetophenone oxime, vinyl-(Z) represented by formula V and the appropriately substituted 2-aryl-4,5-trans-bis-(trifluoromethyl)-1-pyrrolin-5-ol represented by formula VI. The O-[1,2-bis(trifluoromethyl)vinyl]-acetophenone oxime, vinyl-(Z) is then heated in the presence of a solvent at an elevated temperature range (e.g. 80° to 190°C) to form 2-aryl-4,5-bis(trifluoromethyl)-1-pyrrolin-4-ol, trans- and cis- represented by structural formula VII. The 2-aryl-4,5-trans-bis(trifluoromethyl)-1-pyrrolin-5-ol or 2-aryl-4,5-bis(trifluoromethyl)-1-pyrrolin-4-ol, trans- or cis- compounds are then reacted with at least an equivalent amount of hydrochloric acid in an alcohol to obtain a 5-aryl-2,3-bis(trifluoromethyl)pyrrole. The 5-aryl-2,3-bis(trifluoromethyl)pyrrole is then reacted with at least an equivalent amount of a halogenating agent in the presence of a solvent to obtain the

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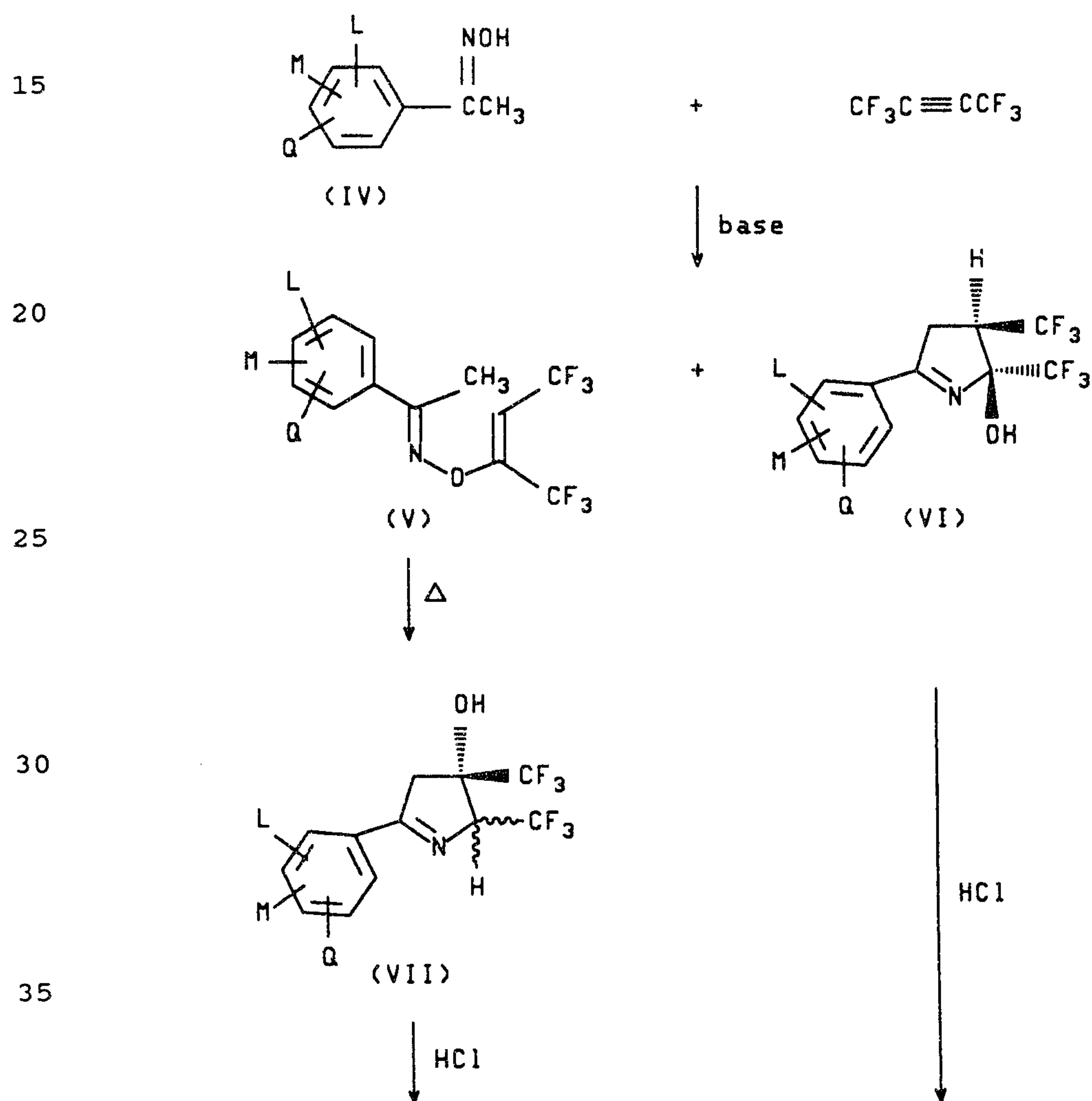
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formula II bis(trifluoromethyl)arylpyrrole wherein L, M and Q are as described above and X is Cl, Br or I. Halogenating agents that may be employed include sodium hypochlorite, bromine, N-bromosuccinimide, chlorine, N-chlorosuccinimide, sulfuryl chloride, sulfuryl bromide, tert-butylhypochlorite, iodine, N-iodosuccinimide and the like. Solvents suitable for use in the above reaction include dioxane, tetrahydrofuran, acetic acid or a chlorinated hydrocarbon solvent. The reactions are illustrated in Flow Diagram I.

FLOW DIAGRAM I



FLOW DIAGRAM I CONTINUED

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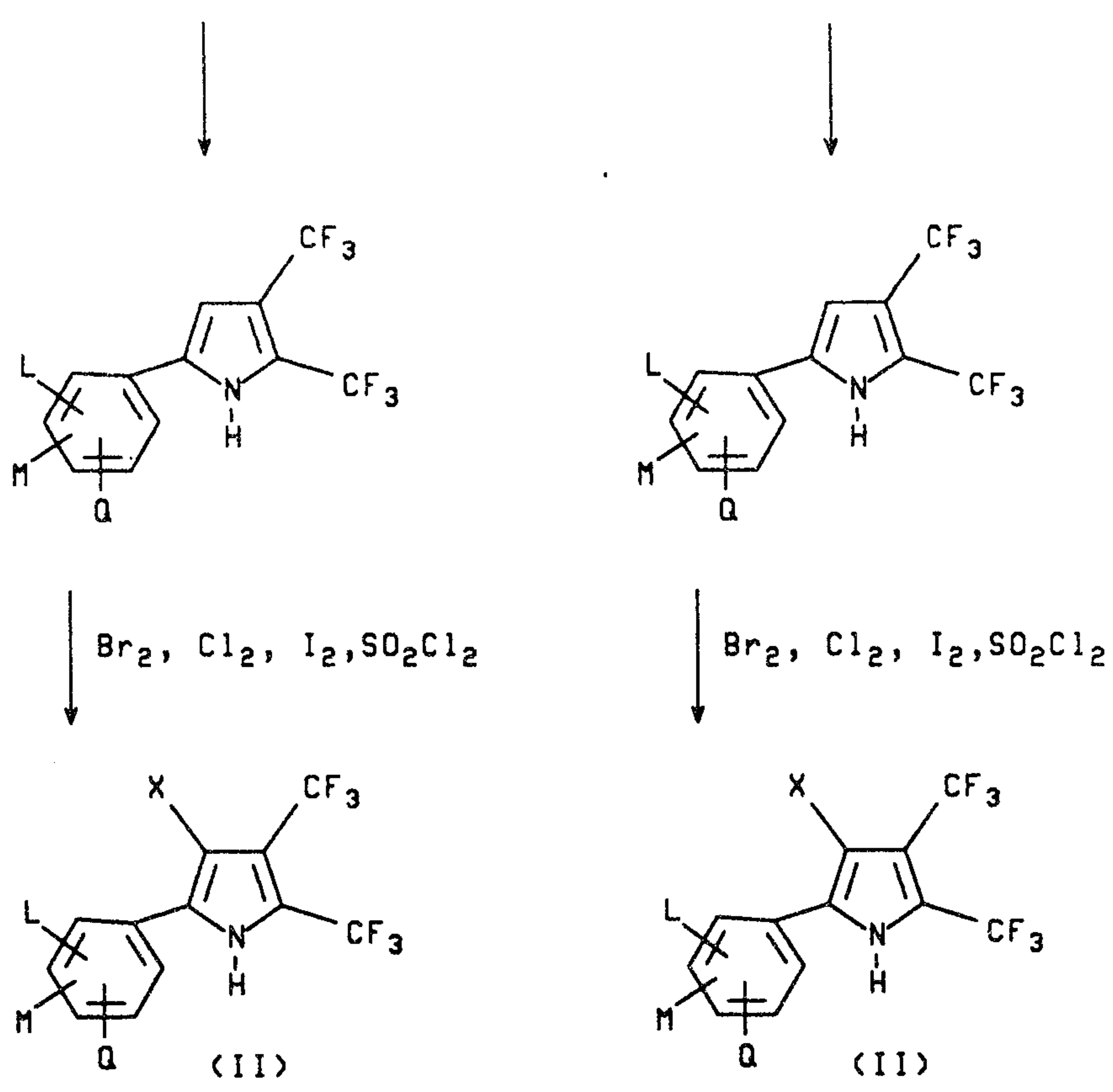
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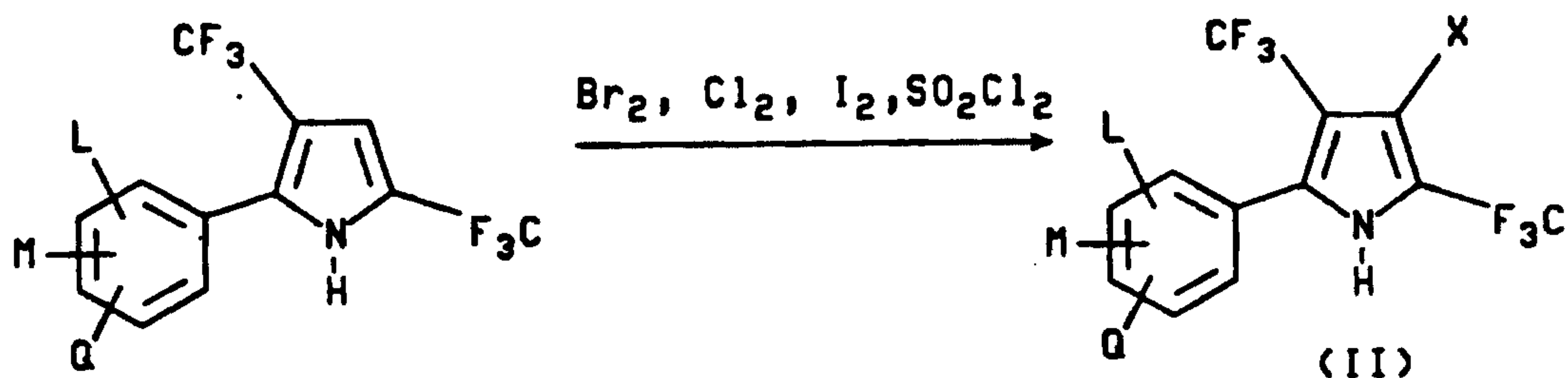
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Similarly, other formula II bis(trifluoromethyl)arylpyrroles may be prepared by the halogenation of 2-aryl-3,5-bis(trifluoromethyl)pyrroles, which are described elsewhere by using the above-mentioned halogenating techniques as illustrated below

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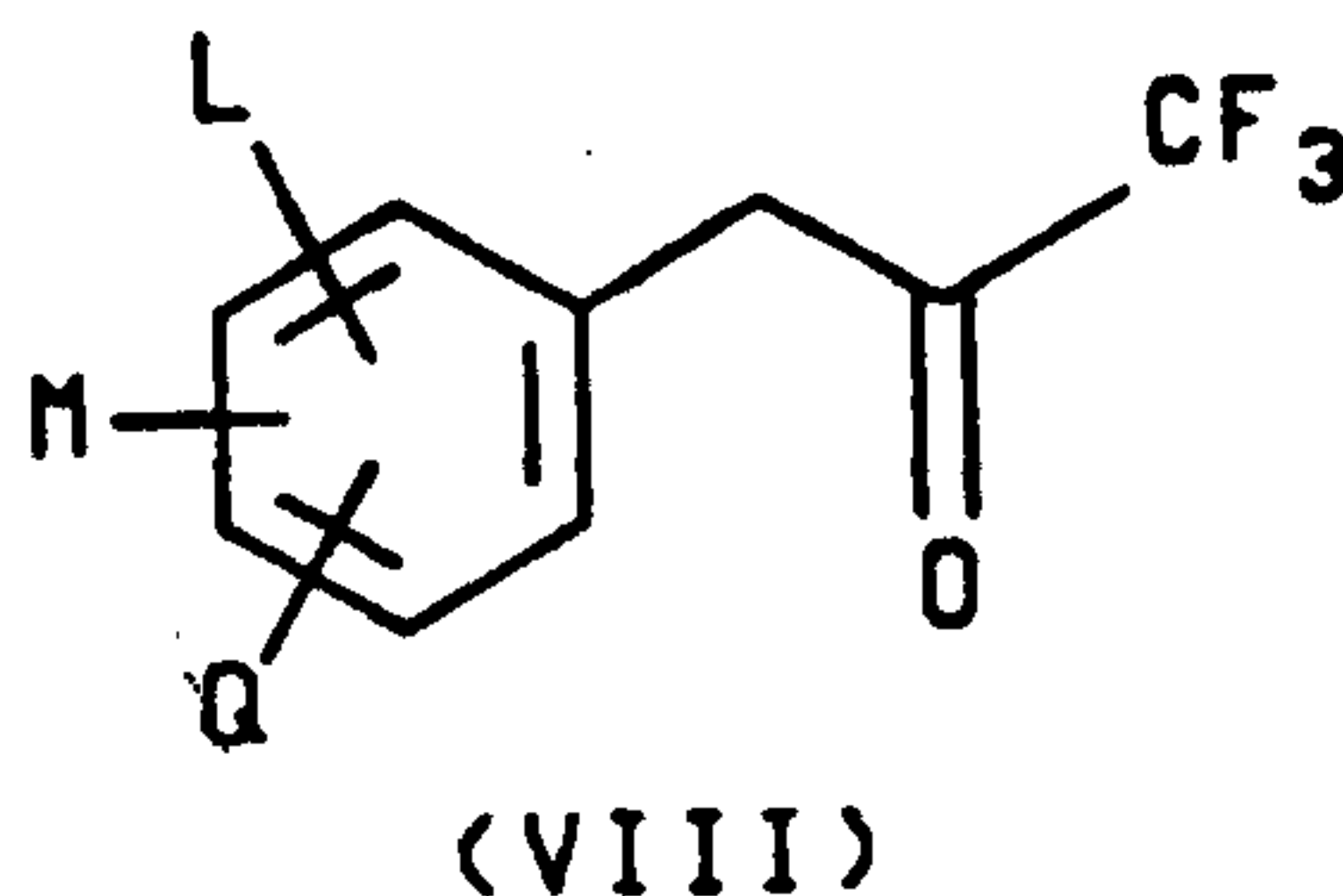


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Certain bis(trifluoromethyl)arylpyrrole compounds of formula III may be prepared by reacting 3-bromo-1,1,1-trifluoropropanone with at least an equivalent amount of hydroxylamine hydrochloride in the presence of an organic solvent to obtain 3-bromo-1,1,1-trifluoro-2-propanone, oxime. The 3-bromo-1,1,1-trifluoro-2-propanone, oxime is then reacted with at least an equivalent amount of a 3-aryl-1,1,1-trifluoro-2-propanone compound represented by formula VIII

30



wherein

35

L is H, Cl, Br or F;

M and Q are independently H, F, Cl, Br, CN, NO₂, CF₃, C₁-C₄ alkyl or C₁-C₃ alkoxy; in the presence of at least an equivalent amount of a base such as an alkali metal alkoxide in an organic solvent to give the appropriately substituted 3-aryl-1,1,1,6,6,6-hexafluoro-2,5-hexanedione, 5-oxime. The 3-aryl-1,1,1,6,6,6-hexafluoro-2,5-hexanedione, 5-oxime is then reacted with at least an equivalent amount of hydrochloric acid in an alcohol to obtain a 3-aryl-2,5-bis(trifluoromethyl)-1-hydroxypyrrole. The said hydroxypyrrole intermediate is then reacted with at least an equivalent amount of zinc in a solvent such as acetic acid to give 3-aryl-2,5-bis(trifluoromethyl)pyrrole. The resultant 3-aryl-2,5-bis(trifluoromethyl)pyrrole is then reacted with at least one molar equivalent of a halogenating agent in the presence of a solvent to give a bis(trifluoromethyl)arylpyrrole compound represented by formula IX wherein L, M, and Q are as described above and X is Cl, Br or I. The formula IX bis(trifluoromethyl)arylpyrrole is then reacted with an alkylating, acylating or cyanating agent such as, cyanogen bromide, p-chlorobenzoyl chloride, methyl iodide, chloromethyl ethyl ether and the like in the presence of a base such as an alkali metal alkoxide in an organic solvent to obtain the formula III bis(trifluoromethyl)arylpyrrole wherein L, M, Q and X are as described above and

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{R is CR}_1, \text{ cyano} \end{array}$$
 C₁-C₆ alkyl optionally substituted with one to three halogen atoms,
 one tri(C₁-C₄ alkyl)silyl,
 one hydroxy,
 one cyano,
 one or two C₁-C₄ alkoxy groups optionally

substituted with one to three halogen
atoms,
one C₁-C₄ alkylthio,
5 one phenyl optionally substituted with one to
three halogen atoms, one to three C₁-C₄
alkyl groups or one to three C₁-C₄
alkoxy groups,
one phenoxy group optionally substituted with
10 one to three halogen atoms, one to three
C₁-C₄ alkyl groups or one to three C₁-C₄
alkoxy groups,
one benzyloxy group optionally substituted on
the phenyl ring with one to three
15 halogen atoms, one to three C₁-C₄ alkyl
groups or one to three C₁-C₄ alkoxy
groups,
one C₁-C₆ alkylcarbonyloxy group optionally
substituted with one to three halogen
20 atoms,
one C₂-C₆ alkenylcarbonyloxy group optionally
substituted with one to three halogen
atoms,
one phenylcarbonyloxy group optionally
25 substituted with one to three halogen
atoms, one to three C₁-C₄ alkyl groups
or one to three C₁-C₄ alkoxy groups,
one C₁-C₆ alkoxycarbonyl group optionally
substituted with one to three halogen
30 atoms or one to three C₁-C₄ alkoxy
groups, or
one benzyloxycarbonyl group optionally
substituted on the phenyl ring with one
to three halogen atoms, one to three
35 C₁-C₄ alkyl groups or one to three C₁-C₄
alkoxy groups,

- C_3-C_6 alkenyl optionally substituted with one
to three halogen atoms or one phenyl group,
or
- 5 C_3-C_6 alkynyl optionally substituted with one
to three halogen atoms or one phenyl group;
and
- R_1 is C_1-C_6 alkyl optionally substituted with one to
three halogen atoms,
10 one hydroxy,
one cyano,
one or two C_1-C_4 alkoxy groups optionally
substituted with one to three halogen
atoms,
15 one C_1-C_4 alkylthio,
one phenyl optionally substituted with one to
three halogen atoms, one to three C_1-C_4
alkyl groups or one to three C_1-C_4
alkoxy groups,
20 one phenoxy group optionally substituted with
one to three halogen atoms, one to three
 C_1-C_4 alkyl groups or one to three C_1-C_4
alkoxy groups,
one benzyloxy group optionally substituted on
25 the phenyl ring with one to three
halogen atoms, one to three C_1-C_4 alkyl
groups or one to three C_1-C_4 alkoxy
groups,
one C_1-C_6 alkylcarbonyloxy group optionally
30 substituted with one to three halogen
atoms,
one C_2-C_6 alkenylcarbonyloxy group optionally
substituted with one to three halogen
atoms,
35 one phenylcarbonyloxy group optionally

5 substituted with one to three halogen
atoms, one to three C₁-C₄ alkyl groups
or one to three C₁-C₄ alkoxy groups,
one C₁-C₆ alkoxycarbonyl group optionally
substituted with one to three halogen
atoms or one to three C₁-C₄ alkoxy
groups, or
one benzyloxycarbonyl group optionally
10 substituted on the phenyl ring with one
to three halogen atoms, one to three
C₁-C₄ alkyl groups or one to three C₁-C₄
alkoxy groups,
C₃-C₆ alkenyl optionally substituted with one
15 to three halogen atoms or one phenyl group,
C₃-C₆ alkynyl optionally substituted with one
to three halogen atoms or one phenyl group,
phenyl optionally substituted with one to three
halogen atoms, one or two C₁-C₄ alkyl groups,
20 one or two C₁-C₄ alkoxy groups, CF₃, CN, NO₂,
di(C₁-C₄ alkyl)amino or C₁-C₄ alkanoylamino,
phenoxy optionally substituted with one to three
halogen atoms, one or two C₁-C₄ alkyl groups,
one or two C₁-C₄ alkoxy groups, CF₃, CN, NO₂,
25 di(C₁-C₄ alkyl)amino or C₁-C₄ alkanoylamino,
C₁-C₆ alkoxy optionally substituted with one to
three halogen atoms,
C₂-C₆ alkenyloxy optionally substituted with one
to three halogen atoms,
30 di(C₁-C₄ alkyl)amino,
N-(C₁-C₄ alkyl)-N-phenylamino or
-N-halophenylamino, or
C₃-C₆ polymethyleneimino.

The above reaction scheme is illustrated in Flow Diagram II.

FLOW DIAGRAM II

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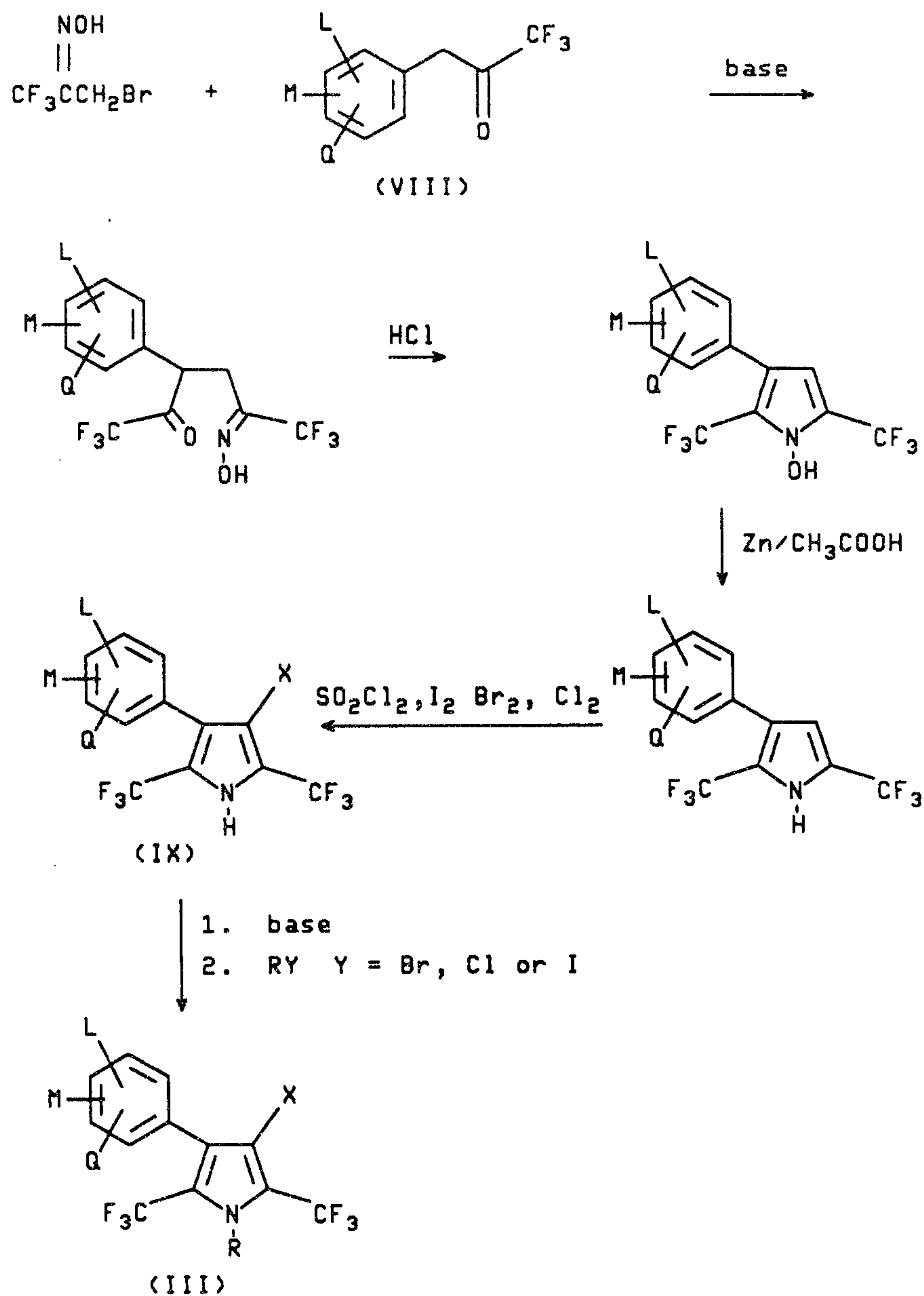
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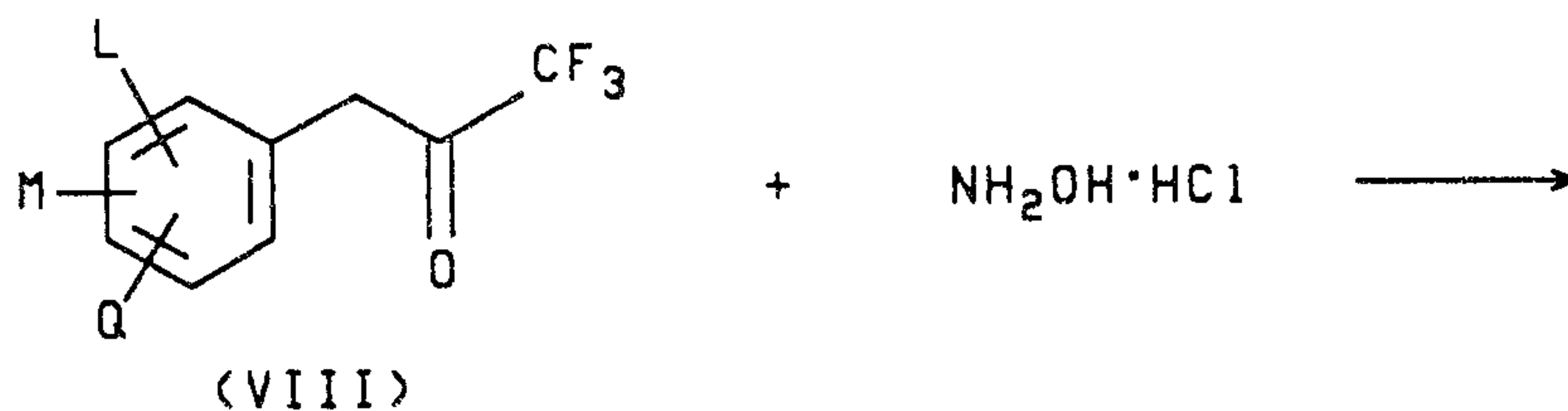


The formula I tris(trifluoromethyl)aryl-
pyrrole compounds of the present invention may be
prepared by reacting the formula VIII 3-aryl-1,1,1-tri-
fluoro-2-propanone with at least one molar equivalent
of hydroxylamine hydrochloride in a solvent to give
3-aryl-1,1,1-trifluoro-2-propanone, oxime. The result-
ing oxime is then reacted in a pressure bottle with at
least an equivalent amount of liquid hexafluoro-2-
butyne in the presence of at least a ten mole percent
amount of a base such as an alkali metal alkoxide in a
solvent at an elevated temperature range (e.g.
50°-80°C) to obtain 3-aryl-5a-hydroxy-2,4-a, 5
b-tris(trifluoromethyl)-1-pyrroline. The said
pyrroline is then reacted with at least one molar
equivalent of hydrochloric acid in an alcohol to give
the formula I tris(trifluoromethyl)arylpyrrole
compounds as illustrated below in Flow Diagram III.

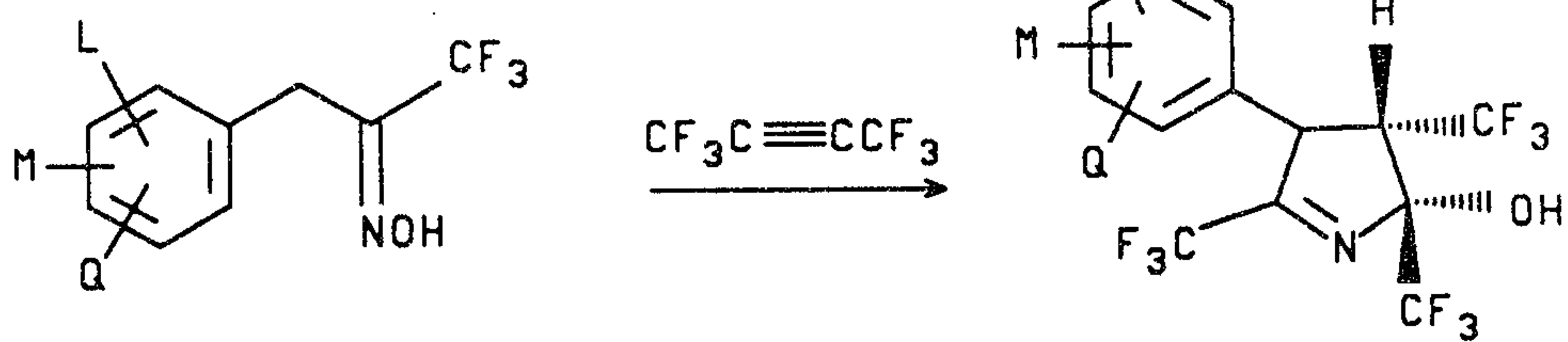
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FLOW DIAGRAM III

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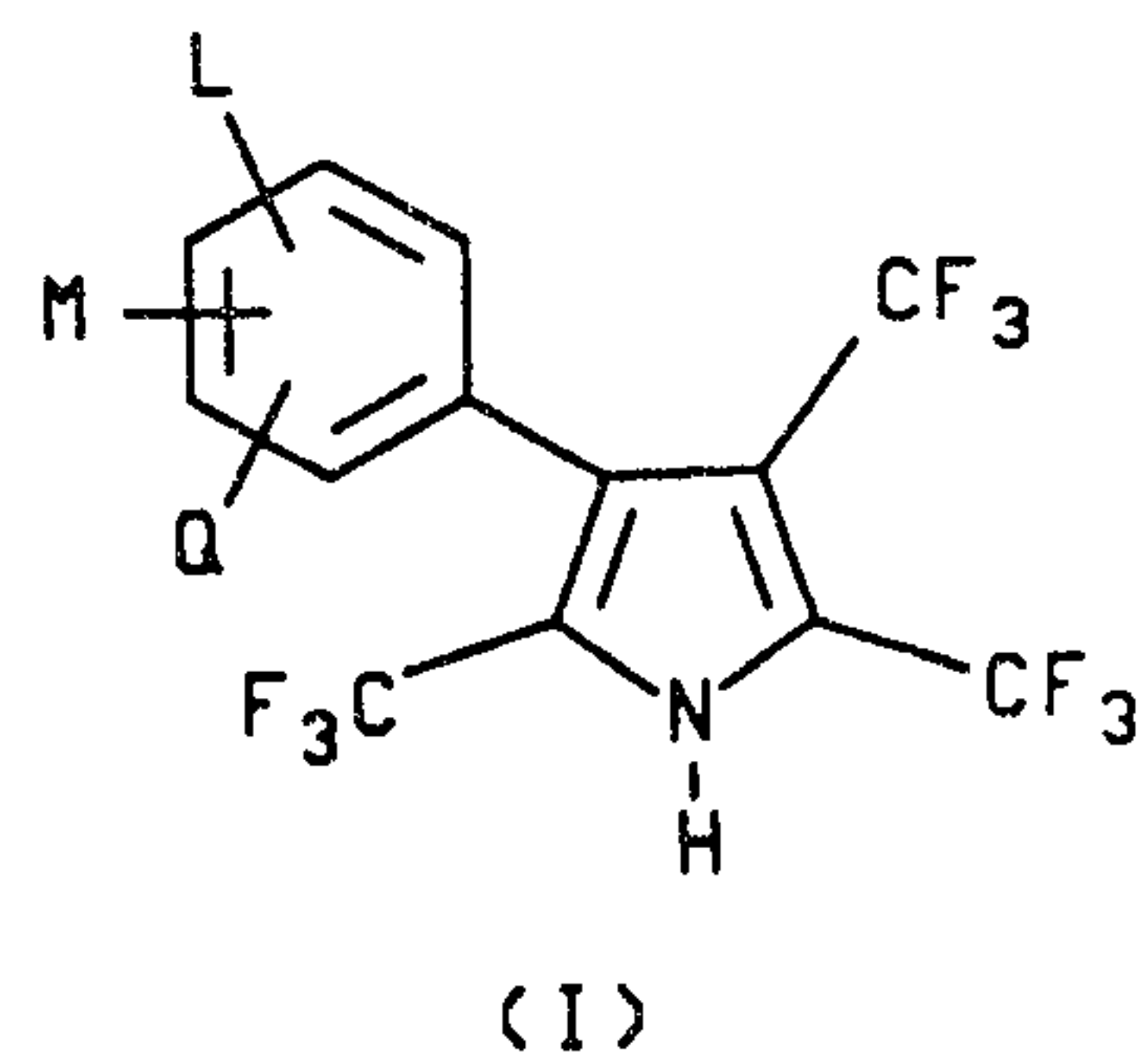
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Reaction with HCl leads to the final product (I).

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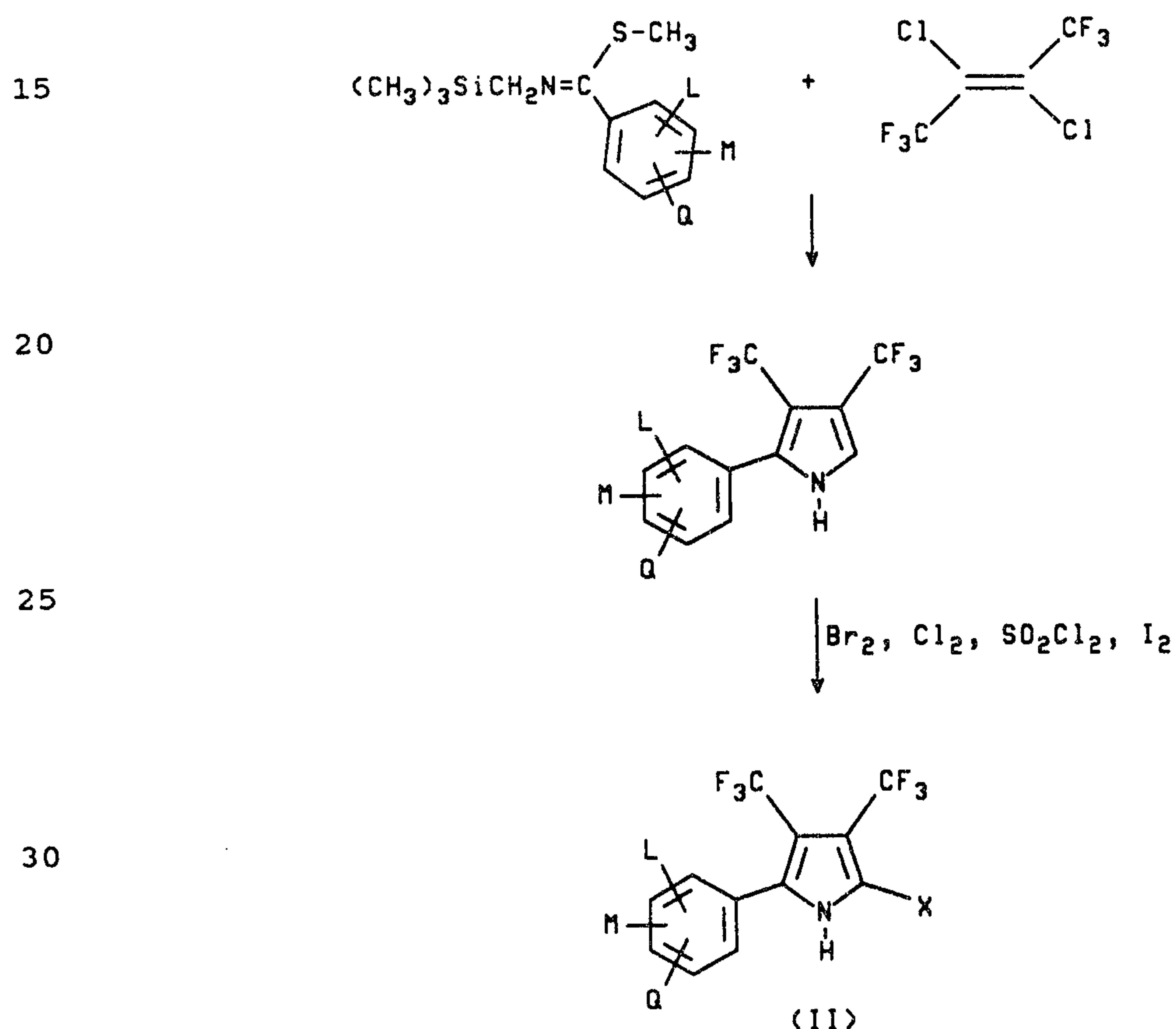


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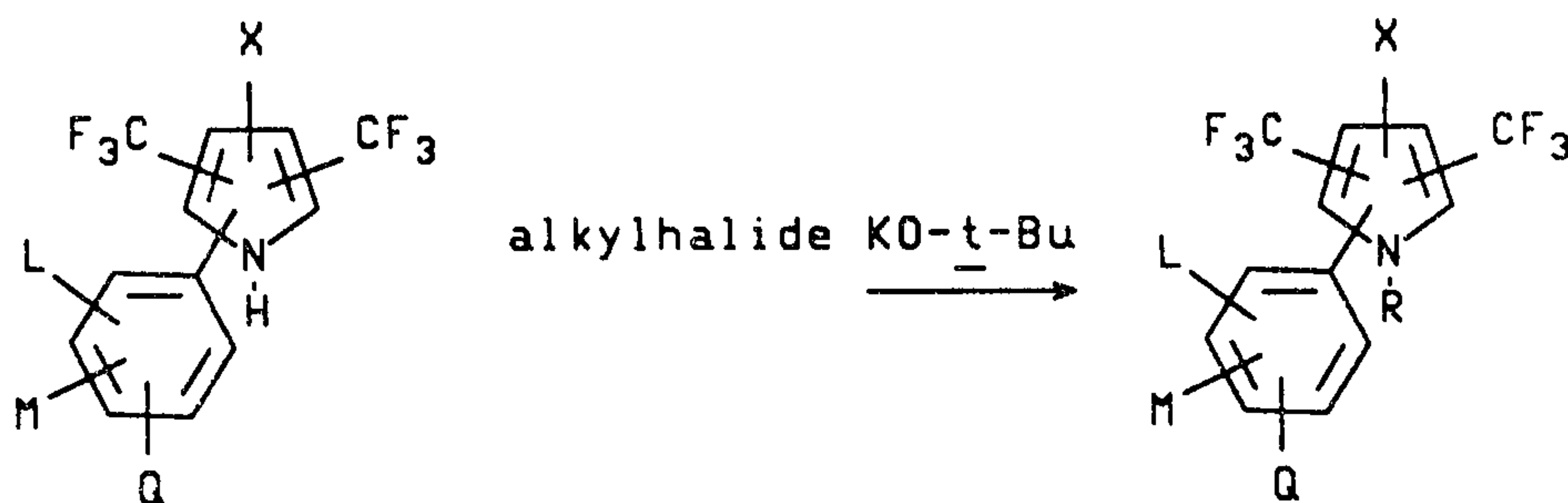
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Formula II compounds of the present invention may be prepared by reacting a methyl N-[(trimethylsilyl)methyl]thio benzimidate with at least a molar equivalent of commercially available 2,3-dichloro-
 5 hexafluorobutene in a solvent to obtain 2-aryl-3,4-bis-(trifluoromethyl)pyrrole. The resultant bis(trifluoromethyl)pyrrole is halogenated by conventional techniques to give formula II bis(tri-
 10 fluoromethyl)arylpyrroles. The above reactions are illustrated in Flow Diagram IV.

FLOW DIAGRAM IV



Preparation of R-substituted formula I bis- and tris(trifluoromethyl)arylpyrrole compounds can be achieved by reaction of the appropriately substituted formula I bis- or tris(trifluoromethyl)arylpyrrole having R as hydrogen with an alkylating or acylating agent in the presence of an alkali metal alkoxide or hydride. For example, a formula I bis- or tris(trifluoromethyl)arylpyrrole, wherein R is hydrogen and X, L, M, and Q are as described for formula I above, is reacted with an appropriate alkylating agent such as a C₁-C₆ alkylhalide in which the alkyl group is straight or branched and is optionally substituted with from one to three halogen atoms, one hydroxy, one cyano, one C₁-C₄ alkoxy, one C₁-C₄ alkylthio, one phenyl group, optionally substituted with from one to three halogen atoms, or one benzyloxy group, optionally substituted with from one to three halogen atoms, and an alkali metal alkoxide such as sodium or potassium *t*-butoxide. This reaction provides a bis- or tris(trifluoromethyl)-arylpyrrole having the same substituents as the starting material, but in addition is substituted on the nitrogen with a C₁-C₆ alkyl group optionally substituted as described above. This reaction may be illustrated as follows:

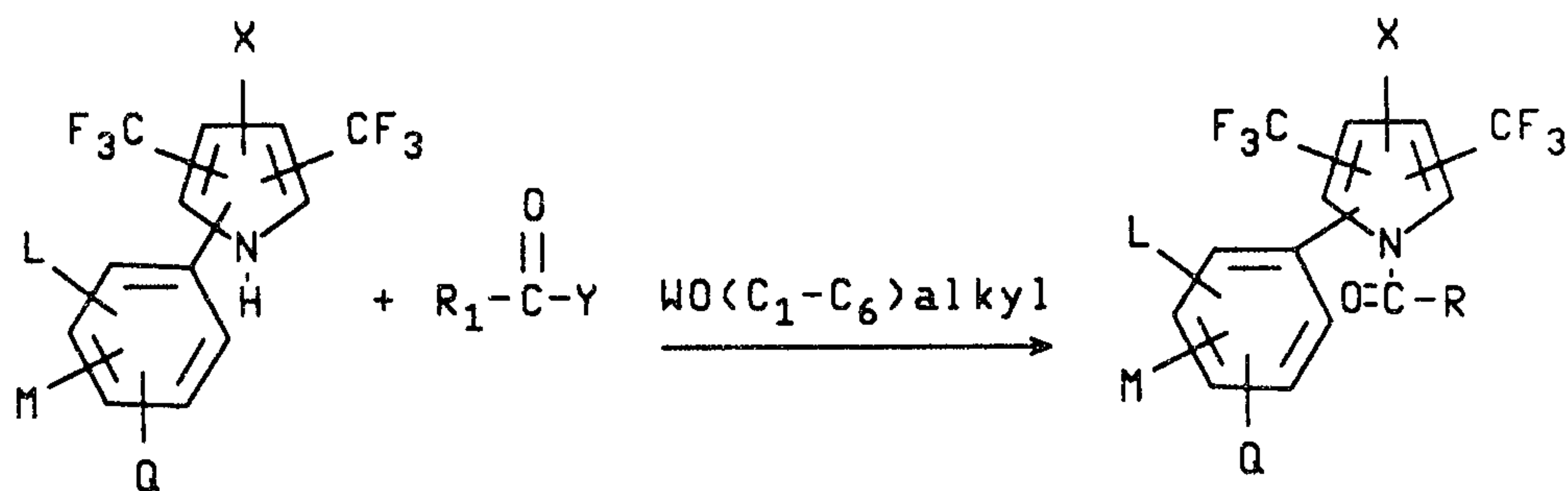


In a similar reaction cyanogen bromide is substituted for the alkylhalide and yields the formula I bis- or

tris(trifluoromethyl)arylpyrrole having a carbonitrile, rather than an alkyl group, on the nitrogen.

Advantageously, the above-described alkylation procedure of the formula I bis- or tris(trifluoromethyl)arylpyrrole compounds, in which R is hydrogen, may also be applied to the preparation of formula I bis- or tris(trifluoromethyl)arylpyrroles having an N-C₃-C₆ alkenyl or N-C₃-C₆ alkynyl substituent. This N-substitution is obtained by simply substituting a C₃-C₆ alkenyl halide or C₃-C₆ alkynyl halide for the C₁-C₆ alkyl halide in the above-described reaction.

In a similar manner, preparation of N-acylated bis- or tris(trifluoromethyl)arylpyrrole compounds may be achieved by the reaction of an appropriately substituted formula I bis- or tris(trifluoromethyl)arylpyrrole wherein R is hydrogen with an acylating agent in the presence of an alkali metal alkoxide. Acylating agents such as C₁-C₆ alkyl or C₂-C₆ alkenyl acid chloride, substituted C₁-C₆ alkyl or C₂-C₆ alkenyl acid chloride, benzoyl chloride, substituted benzoyl chloride, phenylchloroformate, substituted phenylchloroformate, C₁-C₆ alkyl or C₂-C₆ alkenylchloroformate, substituted C₁-C₆ alkyl or C₂-C₆ alkenylchloroformate, N-substituted carbamoyl chloride and the like may be employed. The reaction may be illustrated as follows:



wherein Y is halogen, W is an alkali metal and X, L, M, Q and R₁ are as described hereinabove for formula I.

5 The bis- and tris(trifluoromethyl)arylpyrroles of the present invention are effective for controlling insects and acarina. These compounds are also effective for protecting growing or harvested crops from attack by the above-said pests.

10 In practice generally about 10 ppm to 10,000 ppm and preferably 100 ppm to about 5,000 ppm of a formula I bis- or tris(trifluoromethyl)arylpyrrole, dispersed in water, or another inexpensive liquid carrier, is effective when applied to the plants, the crops or the soil in which said crops are growing to
15 protect said crops from attack by insects and/or acarina.

The formula I bis- and tris(trifluoromethyl)-
20 arylpyrroles of this invention are also effective for controlling insects and acarina when applied to the foliage of plants and/or to the soil or water in which said plants are growing in sufficient amount to provide a rate of from about 0.1 Kg/ha to 4.0 Kg/ha of active ingredient.

25 While the bis- and tris(trifluoromethyl)arylpyrroles of this invention are effective for controlling insects and acarina when employed alone, they may also be used in combination with other biological chemicals, including other insecticides and acaricides. For example, the bis- and tris(trifluoromethyl)arylpyrroles of this invention may be used effectively in
30 conjunction or combination with phosphates, carbamates, pyrethroids, formamidines, chlorinated hydrocarbons, halobenzoylureas and the like.

35 Advantageously, the above-said bis- and tris(trifluoromethyl)arylpyrroles may be formulated into dry compacted granules, suspension concentrates,

5 wettable powders, dusts, dust concentrates, emulsifiable concentrates, granular formulations, flowable compositions, micro-emulsions and the like, all of which lend themselves to soil, water and/or foliage application and provide the requisite plant protection. Such formulations include the compounds of the invention admixed with inert, pharmacologically-acceptable solid or liquid diluents.

10 A typical suspension concentrate formulation may be prepared by grinding together about 5% to 25% by weight of a formula I bis- or tris(trifluoromethyl)-arylpyrrole, about 3% to 20% by weight of an anionic surfactant such as dodecyl benzene sulfonic acid, about 1% to 5% by weight of a nonionic surfactant such as an
15 ethylene oxide block copolymer having about 8 to 11 mols of ethoxylation, about 1% to 5% by weight of an alkylphenol polyethylene oxide condensate with 9 to 10 mols of ethoxylation and q.s. to 100% with a petroleum aromatic solvent.

20 Wettable powders, dusts and dust concentrate formulations of the invention can be prepared by grinding together about 3% to 20%, by weight, of the formula I bis- or tris(trifluoromethyl)arylpyrrole compound, with about 3% to 20% by weight of a solid
25 anionic surfactant. One suitable anionic surfactant is a dioctyl ester of sodium sulfosuccinic acid, specifically Aerosol OTB® surfactant, marketed by the American Cyamamid Company. About 60% to 94%, by weight, of an inert solid diluent, such as montmorillonite, attapul-
30 gite, chalk, talc, kaolin, diatomaceous earth, limestone, silicates or the like also is used in such formulations.

35 Compacted granules especially useful for soil or water application can be prepared by grinding together in about equal parts, usually about 3 to 20

parts of the bis- or tris(trifluoromethyl)arylpyrrole and a solid surfactant, with about 60 to 94 parts of gypsum. Thereafter, the mixture is compacted into small granular particles, about 24/48 mesh or larger.

Other suitable solid surfactants useful in the present formulations include not only the anionic dioctyl ester of sodium sulfosuccinic acid but also nonionic block copolymers of ethylene oxide and propylene oxide. Such block copolymers are marketed by BASF Wyandotte Corporation as Pluronic 10R8,, 17R8, 25R8, F28, F68, F77, or F87, and are especially effective for the preparation of compacted granules.

In addition to the powders and concentrate formulations described hereinabove, wettable powders and flowables may be used because they may be dispersed in water. Preferably, such flowables will be applied at the locus with the aqueous compositions being sprayed on the foliage of plants to be protected. These sprays also may be applied to the breeding ground, food supply or habitat of the insects and acarina sought to be controlled.

Where solid formulations of the compounds of this invention are to be used in combination treatments with other pesticidal agents, the formulations can be applied as an admixture of the components or may be applied sequentially.

Similarly, liquid formulations of the bis- and tris(trifluoromethyl)arylpyrroles in combination with other pesticidal agents may be tank mixed or may be applied separately, sequentially, as liquid sprays. Liquid spray formulations of the compounds of the invention should contain about 0.001% to 0.1% by weight of the active bis- or tris(trifluoromethyl)arylpyrrole.

In order to facilitate a further understanding of the invention, the following examples are

presented primarily for the purpose of illustrating
more specific details thereof. The invention is not to
be deemed limited thereby except as defined in the
claims.

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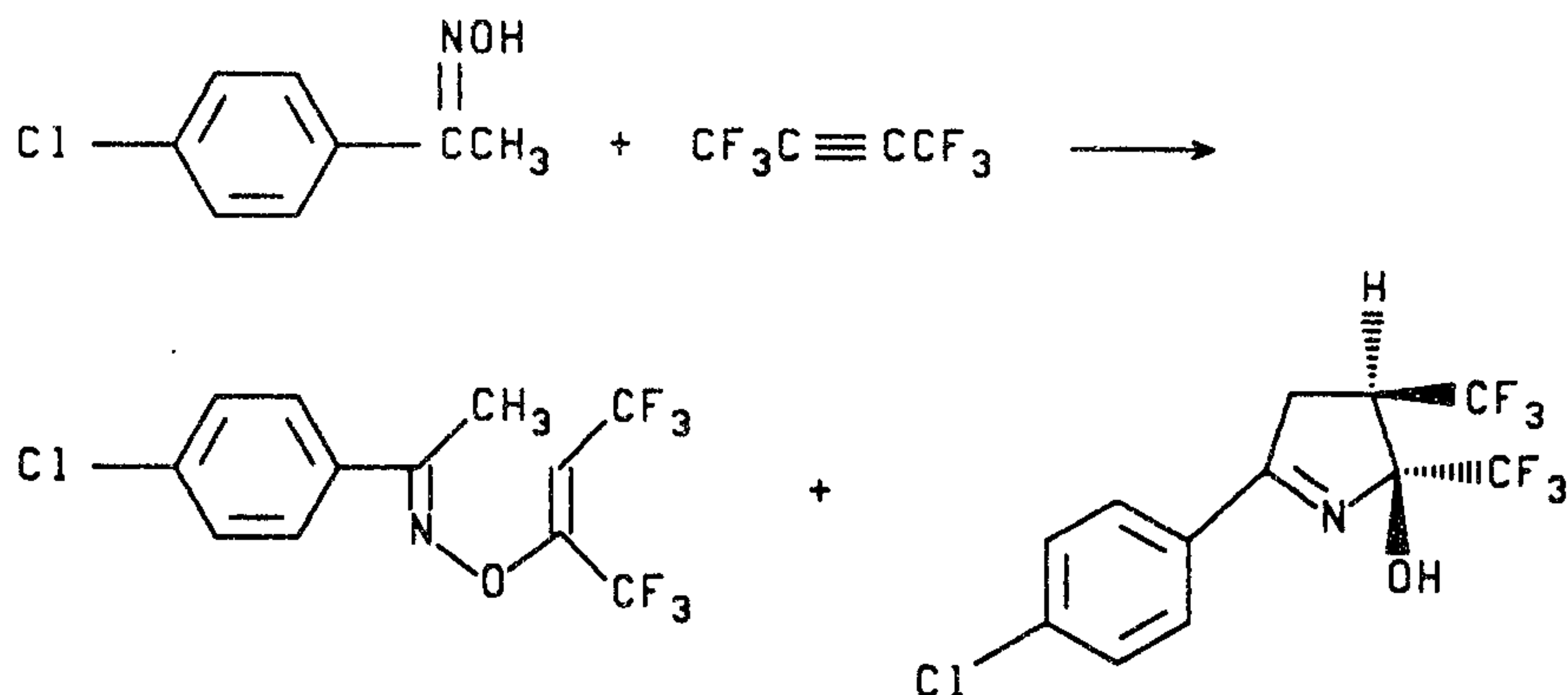
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EXAMPLE 1

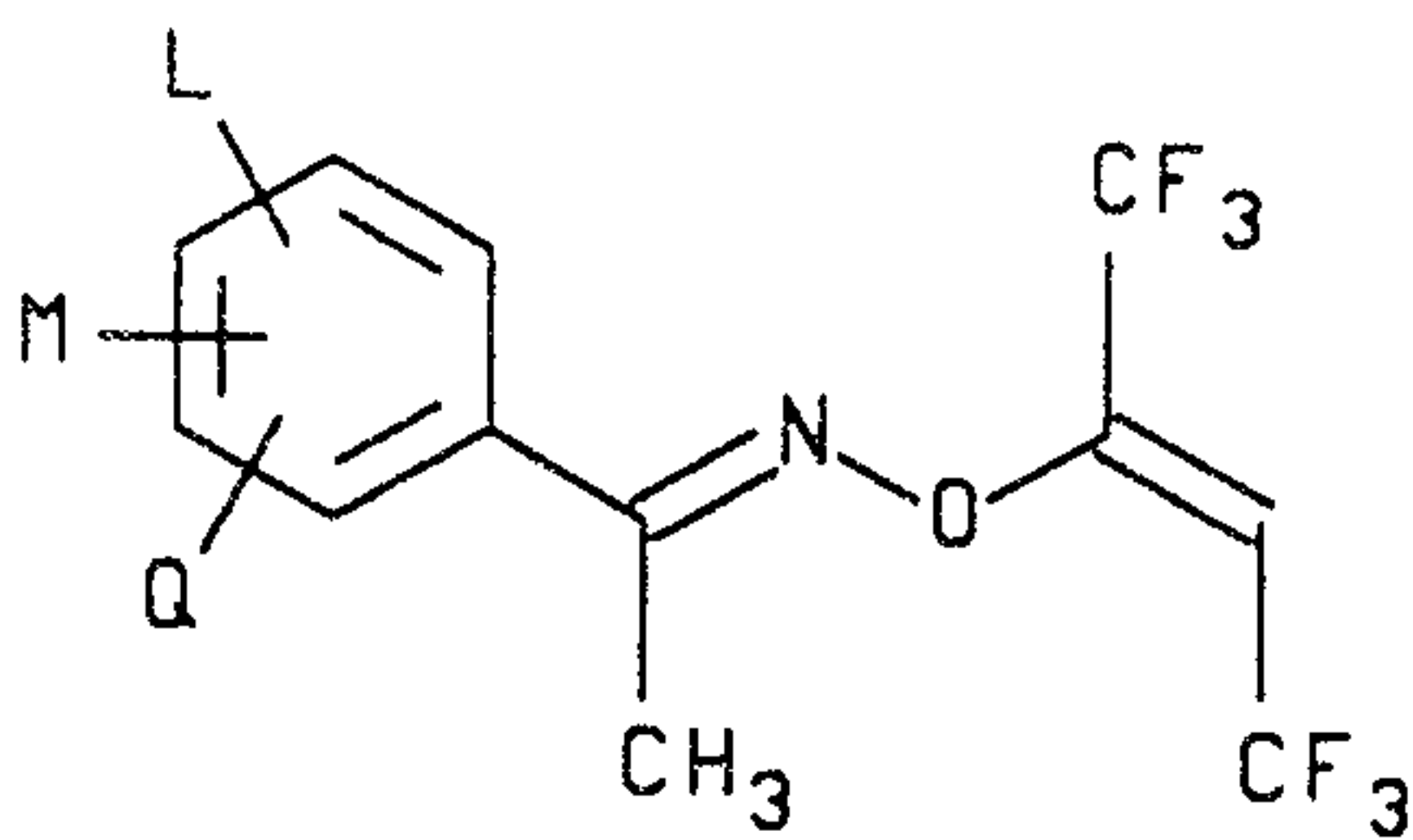
Preparation of p-Chloro-0-[1,2-bis(trifluoromethyl)-
vinyl]acetophenone oxime, vinyl-(Z) and 2-(p-chloro-
phenyl)-4,5-trans-bis(trifluoromethyl)-1-pyrrolin-5-ol



Hexafluoro-2-butyne is slowly bubbled through a $55^\circ\text{--}60^\circ\text{C}$ solution of p-chloroacetophenone oxime (17.0g, 0.10 mol), methanol (80 mL) and potassium tert-butoxide (1.12g, 0.01 mol) over a 5 hour period. The solvent is removed in vacuo to obtain a liquid which is poured into water and extracted with ether. The combined organic extracts are washed sequentially with water and brine, dried over anhydrous sodium sulfate and concentrated in vacuo to give an oil. The oil is chromatographed using silica gel and eluted with 1% ethylacetate in methylene chloride to 5% ethyl acetate in methylene chloride to give p-chloro-0-[1,2-bis(trifluoromethyl)vinyl]acetophenone oxime, vinyl-(Z) as a yellow liquid (21.5g, 65%) and 2-(p-chlorophenyl)-4,5-trans-bis(trifluoromethyl)-1-pyrrolin-5-ol as a white solid (2.35g, mp $152.5^\circ\text{--}153^\circ\text{C}$, 7%).

Following the procedure of example 1, but substituting the appropriately substituted acetophenone oxime yields the following compounds.

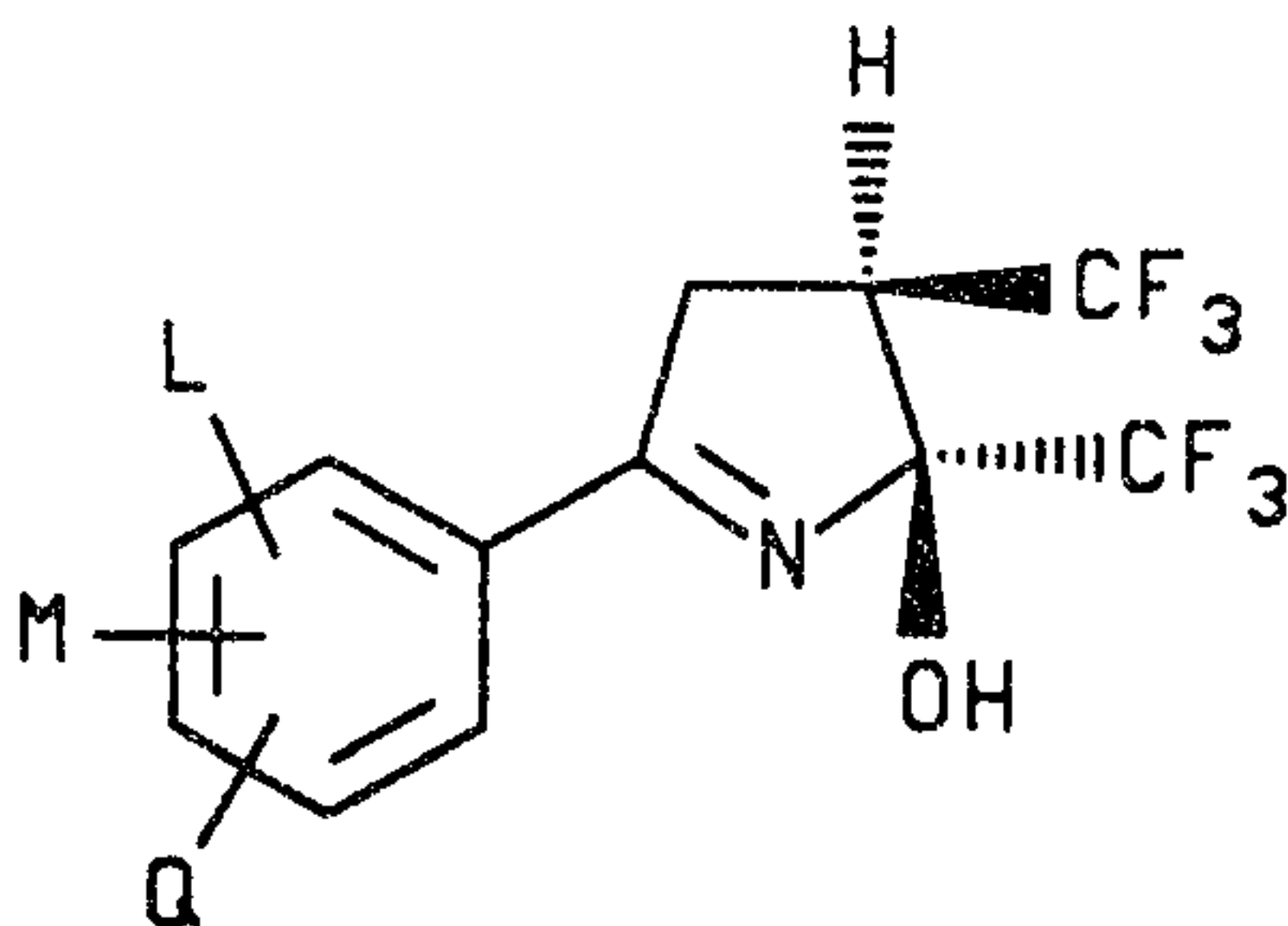
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10

<u>L</u>	<u>M</u>	<u>Q</u>
H	4-CF ₃	H
H	4-Cl	3-Cl
H	H	H

15



20

<u>L</u>	<u>M</u>	<u>Q</u>	<u>mp °C</u>
H	3-Cl	4-Cl	147-148

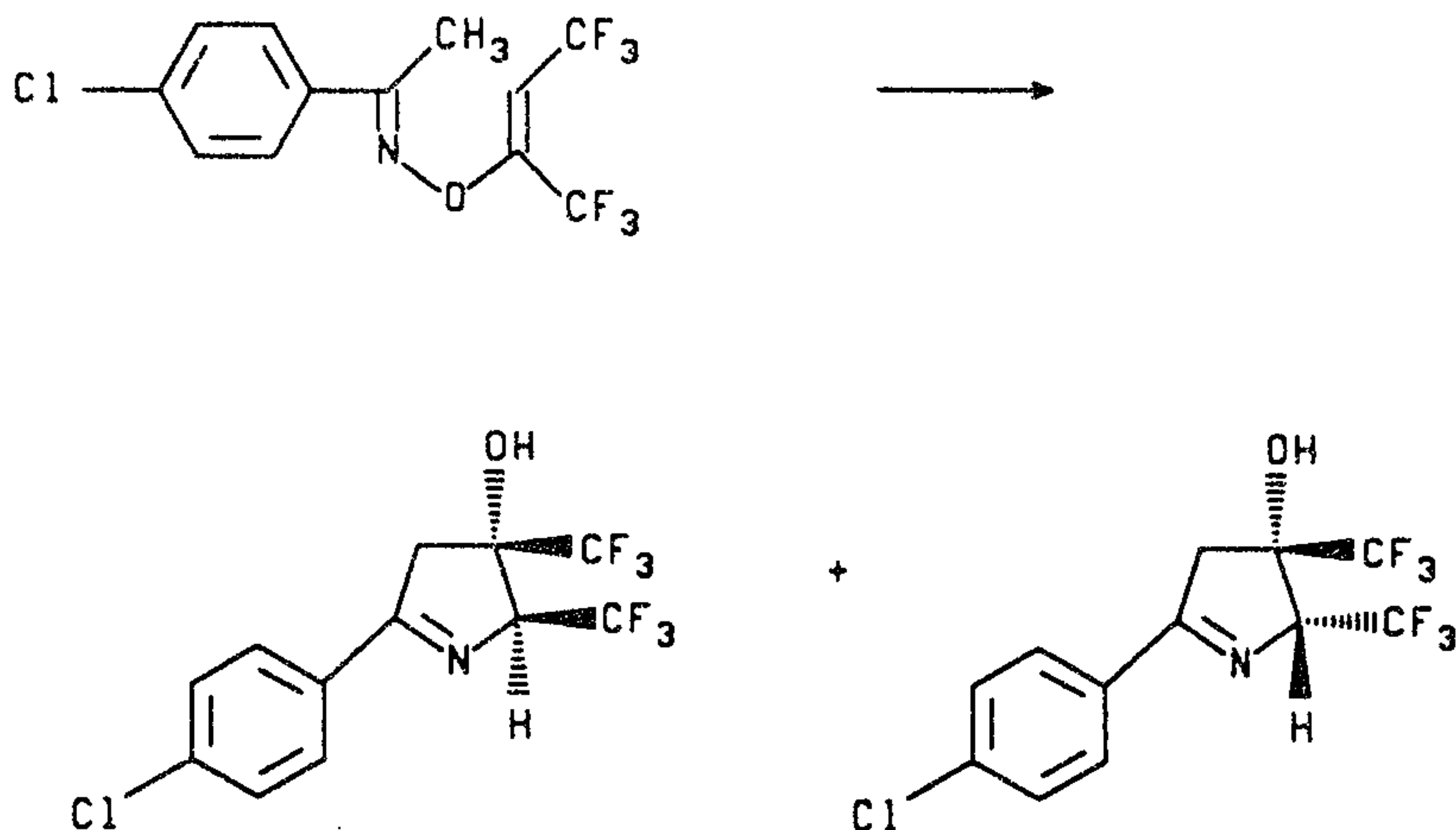
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EXAMPLE 2

Preparation of 2-(p-chlorophenyl)-4,5-bis-(trifluoromethyl)-1-pyrrolin-4-ol, trans- and cis-

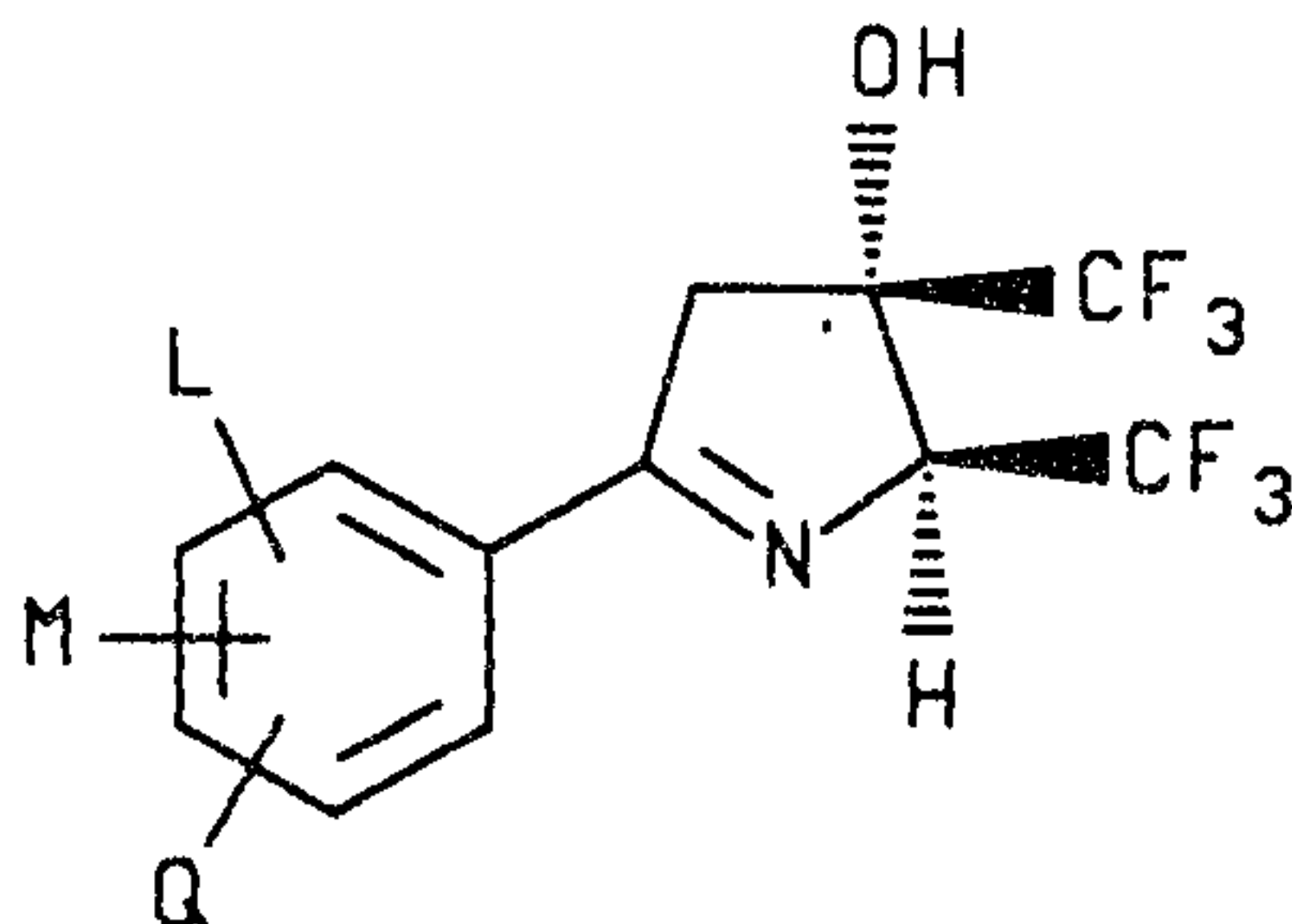


A solution of p-chloro-0-[1,2-bis(trifluoromethyl)vinyl]acetophenone oxime, vinyl-(Z) (10.0g, 0.03 mol) and xylene (50 mL) is heated at reflux temperature for 2 1/2 hours. The solvent is removed in vacuo to give a semi-solid. The semi-solid is crystallized from a chloroform/hexanes mixture to give 2-(chlorophenyl)-4,5-bis(trifluoromethyl)-1-pyrrolin-4-ol, trans- as a white solid (3.7g, mp 111.0°-111.5°C, 37%). The filtrate is concentrated in vacuo to give an oil which is chromatographed using silica gel and eluted with 1% and 3% ethyl acetate in methylene chloride to give additional 2-(p-chlorophenyl)-4,5-bis(trifluoromethyl)-1-pyrrolin-4-ol, trans- (0.20g) and 2-(p-chlorophenyl)-4,5-bis(trifluoromethyl)-1-pyrrolin-4-ol, cis- as a white solid (0.95g, mp 99°-101°C, 9.5%).

Following the procedure of example 2 but substituting the appropriately substituted 0-[1,2-bis-(trifluoromethyl)vinyl]acetophenone, oxime for p-chloro-

O-[1,2-bis(trifluoromethyl)vinyl]acetophenone, oxime
yields the following compounds.

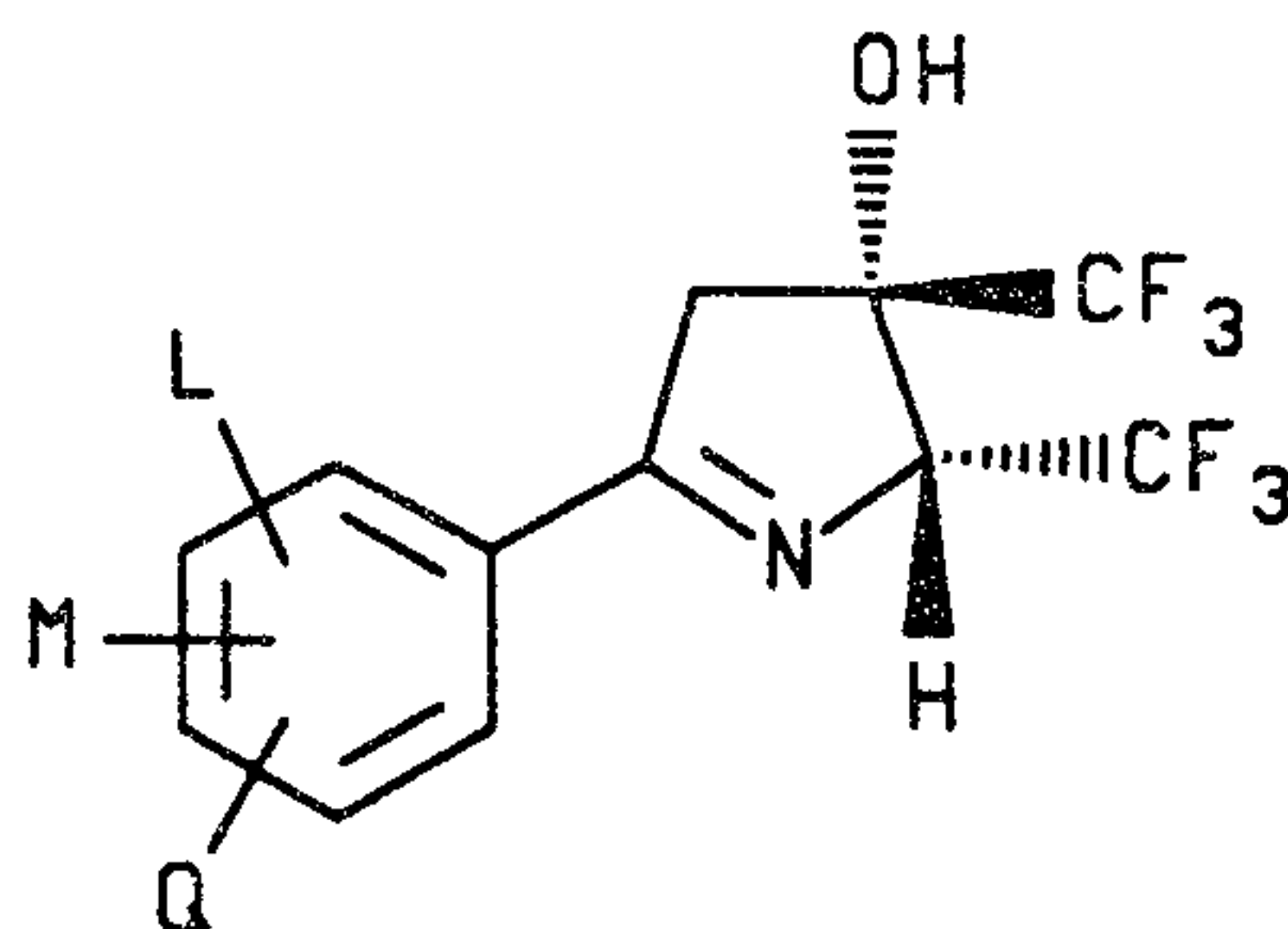
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<u>L</u>	<u>M</u>	<u>Q</u>	<u>mp</u> ^o C
H	4-CF ₃	H	115.5-116.5
H	3-Cl	4-Cl	oil

15



20

<u>L</u>	<u>M</u>	<u>Q</u>	<u>mp</u> ^o C
H	H	H	
H	4-CF ₃	H	
H	3-Cl	4-Cl	oil

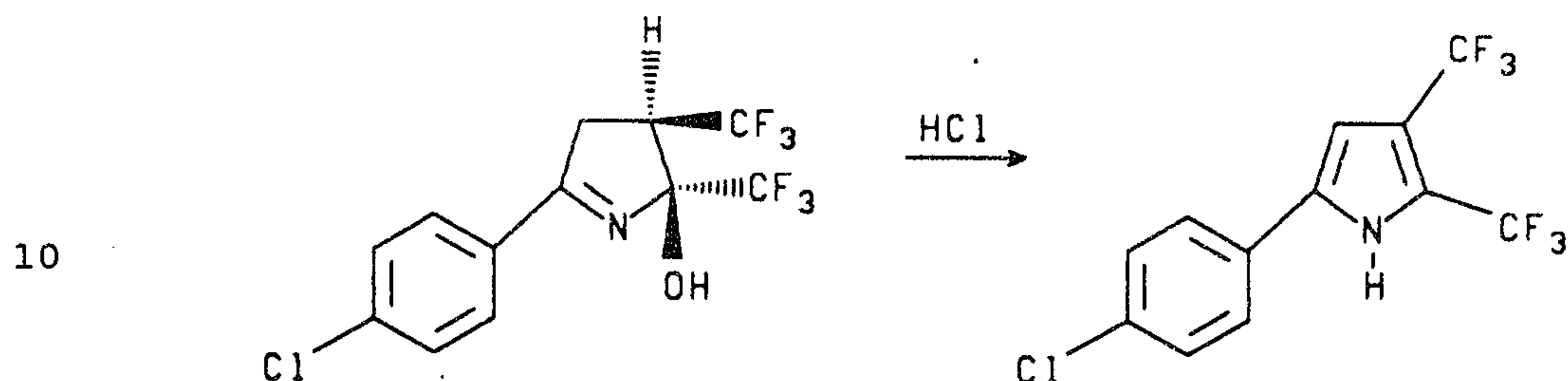
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EXAMPLE 3Preparation of 5-(p-Chlorophenyl)-2,3-bis(trifluoromethyl)pyrrole

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To ethanol (12mL) saturated with hydrochloric acid gas is added 2-(p-chlorophenyl)-4,5-trans-bis(trifluoromethyl)-1-pyrrolin-5-ol (1.2g, 3.6 mmol). The reaction mixture is refluxed for 15 minutes, diluted with water and extracted with ether. The combined organic extracts are washed sequentially with water and brine, dried over anhydrous sodium sulfate and concentrated in vacuo to give a solid. Crystallization of the solid from hexanes gives the title product as a white solid (0.94g, mp 72°-73°C, 83%).

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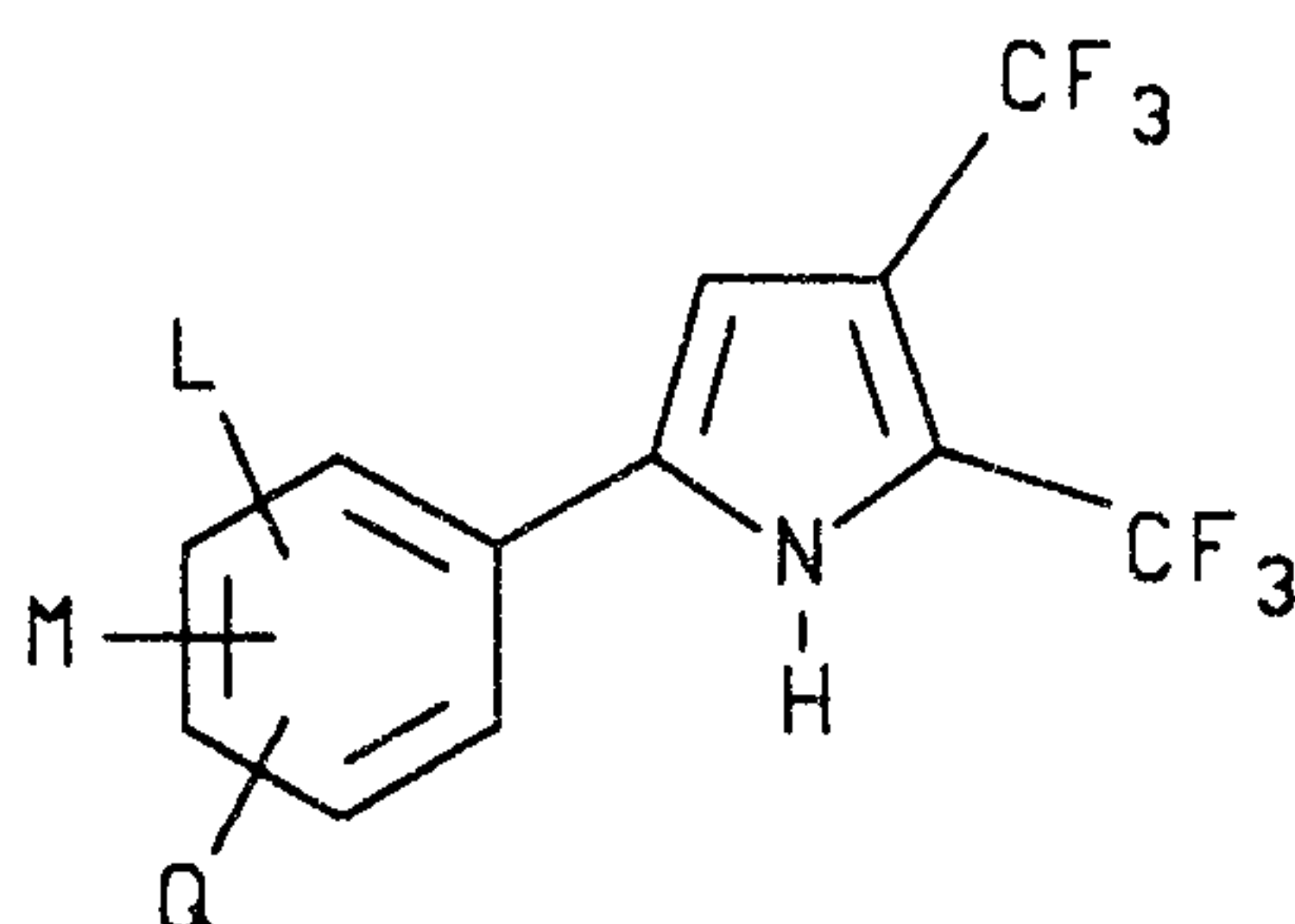
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Following the procedure of example 3, but substituting the appropriately substituted 2-aryl-4,5-bis(trifluoromethyl)-1-pyrrolin-5-ol or 2-aryl-4,5-bis(trifluoromethyl)-1-pyrrolin-4-ol for 2-(p-chlorophenyl)-4,5-trans-bis(trifluoromethyl)-1-pyrrolin-5-ol yields the following compounds.

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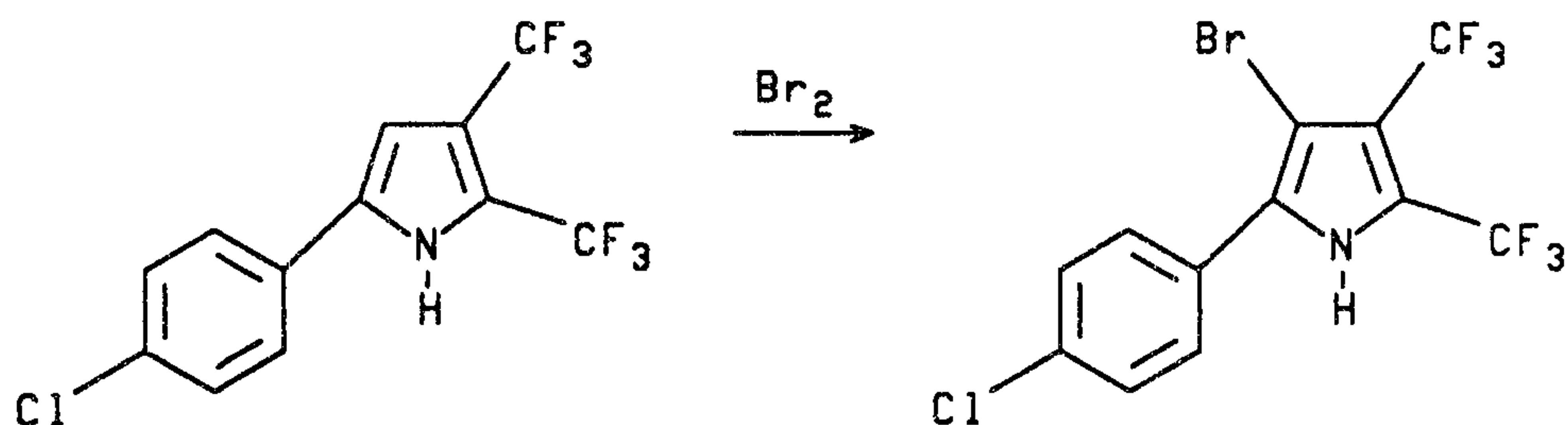


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<u>L</u>	<u>M</u>	<u>Q</u>	<u>mp</u> ^{°C}
H	H	H	61.0-61.5
H	3-Cl	4-Cl	51.5-53.0
H	4-CF ₃	H	43-44

15 EXAMPLE 4

Preparation of 3-Bromo-2-(p-chlorophenyl)-4,5-bis(tri-fluoromethyl)pyrrole

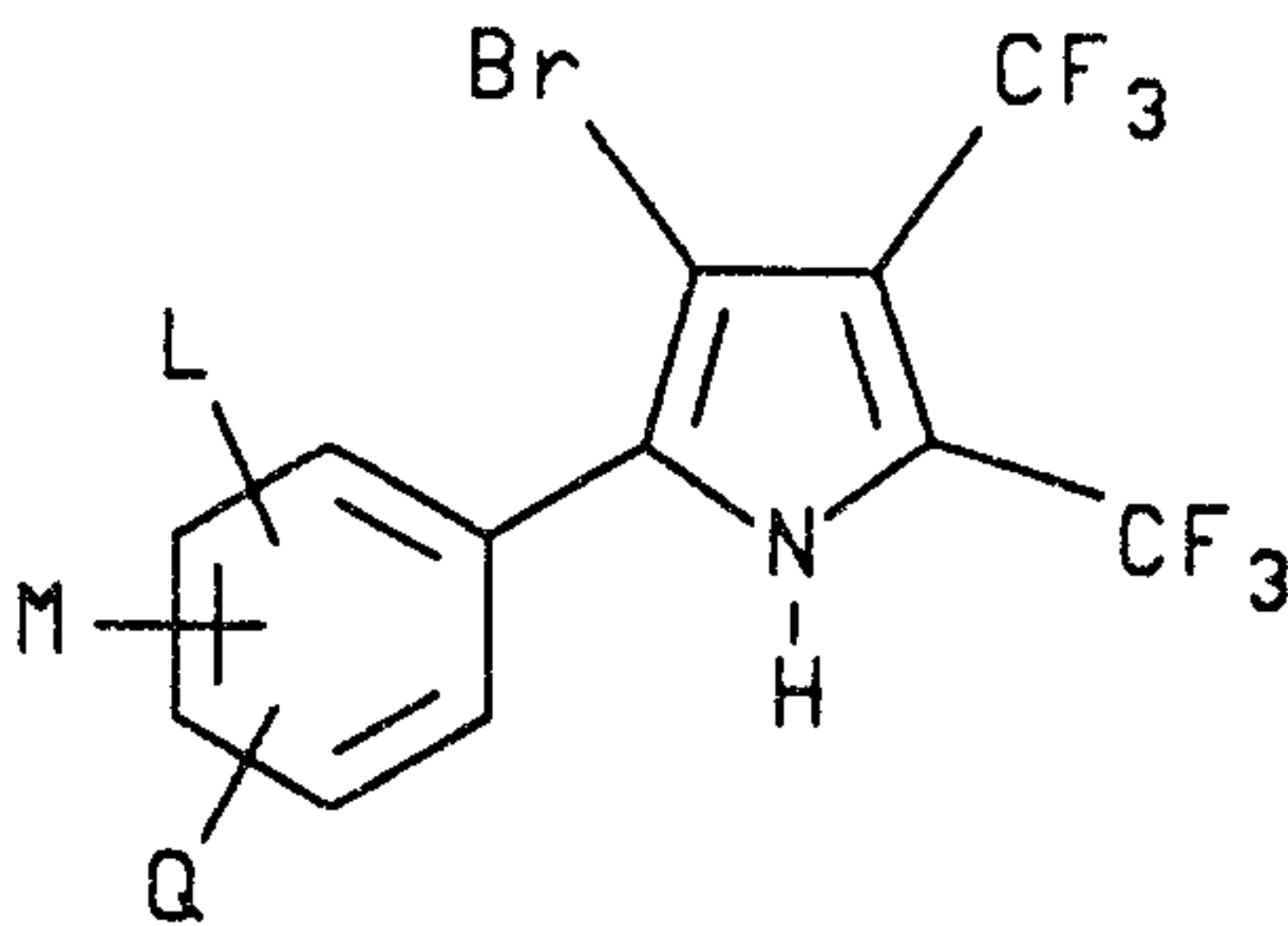


30 Bromine (0.527g, 3.3 mmol) is added to a room temperature solution of 5-(p-chlorophenyl)-2,3-bis(tri-fluoromethyl)pyrrole (0.94g, 3.0 mmol), acetic acid (5mL) and sodium acetate (0.492g, 6 mmol). After stirring for 2 hours the reaction mixture is diluted with water and extracted with ether. The combined organic extracts are washed sequentially with water, sodium metabisulfite solution, water and brine, dried over anhydrous magnesium sulfate and concentrated in vacuo to obtain a solid. Crystallization of the solid

35

from hexanes gives the title product as white crystals (0.77g, mp 64.5°-65.0°C, 65%).

Following the procedure of example 4, but substituting the appropriate 5-aryl-2,3-bis(trifluoromethyl)pyrrole for 5-(p-chlorophenyl)-2,3-bis(trifluoromethyl)pyrrole yields the following compounds.



<u>L</u>	<u>M</u>	<u>Q</u>	<u>mp</u> ^{°C}
H	3-Cl	4-Cl	84.5-86
H	4-CF ₃	H	76.5-79

EXAMPLE 5

Preparation of 3-Bromo-2-(3,4-dichlorophenyl)-1-(ethoxymethyl)-4,5-bis(trifluoromethyl)pyrrole

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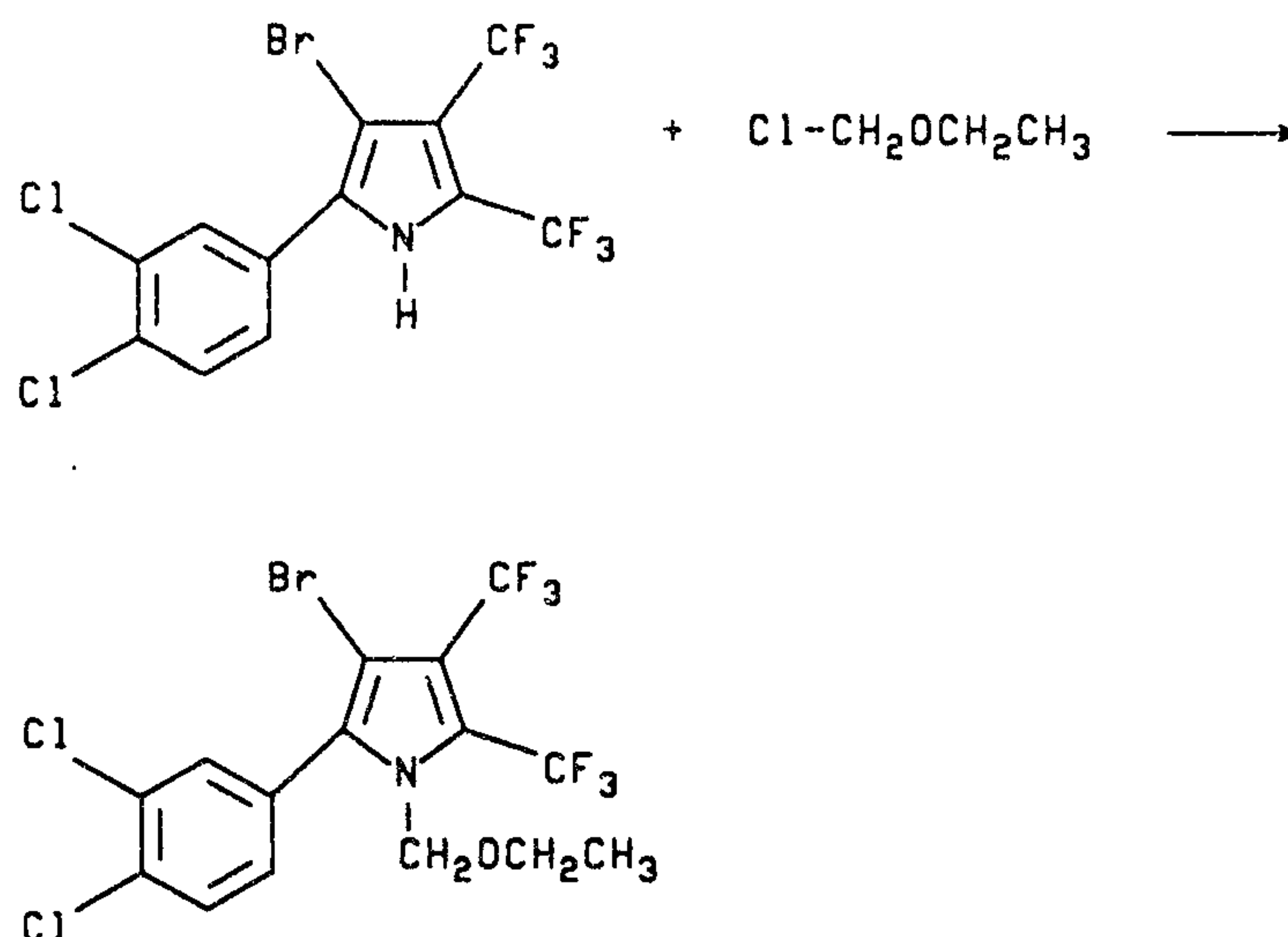
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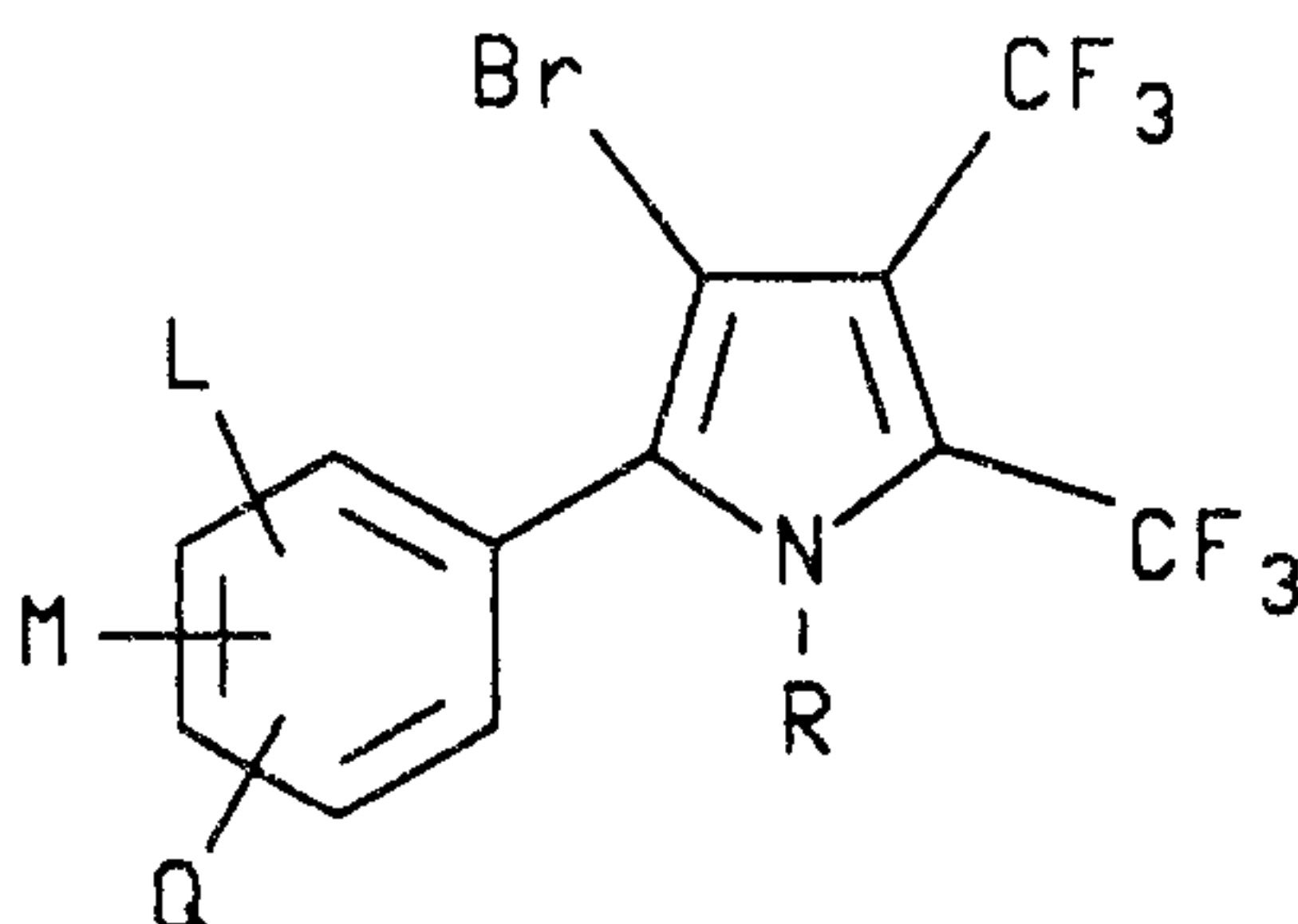
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To a chilled solution of 3-bromo-2-(3,4-dichlorophenyl)-4,5-bis(trifluoromethyl)pyrrole (0.854g, 2 mmol) and tetrahydrofuran is added potassium tert-butoxide (0.247g, 2.2 mmol). After stirring at ice bath temperature for 15 minutes chloromethyl ethyl ether (0.208g, 2.2 mmol) is added to the reaction mixture and the ice bath is removed. Stirring is continued for 1 1/2 hours then the reaction mixture is diluted with water and extracted with ether. The combined organic extracts are washed sequentially with water and brine, dried over anhydrous sodium sulfate and concentrated in vacuo to give the title compound as a yellow liquid (0.91g, 94%). Identified by IR and NMR spectral analyses.

Following the procedure described in example 5, but using the appropriately substituted 3-bromo-2-phenyl-4,5-bis(trifluoromethyl)pyrrole and the

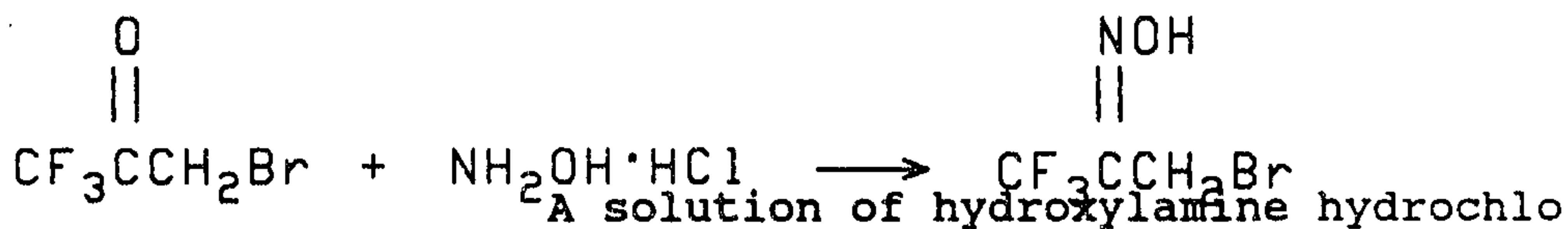
appropriate alkylating or cyanating agent, the compounds shown below are obtained.



	<u>R</u>	<u>L</u>	<u>M</u>	<u>Q</u>	<u>mp</u> ^{°C}
5	CH ₂ OCH ₂ CH ₃	H	4-CF ₃	H	oil
10	C≡N	H	4-Cl	H	113.5-114.5
15	CH ₃ W				
	CH-O-CH(CH ₃) ₂	H	4-Cl	3-Cl	oil
	CH ₃	H	3-Cl	4-Cl	101-103.5
	CH ₂ OCH ₂ CH ₃	H	4-Cl	H	48-49
20	C≡N	H	3-Cl	4-Cl	71.5-72.5

EXAMPLE 6

Preparation of 3-Bromo-1,1,1-trifluoro-2-propanone, oxime

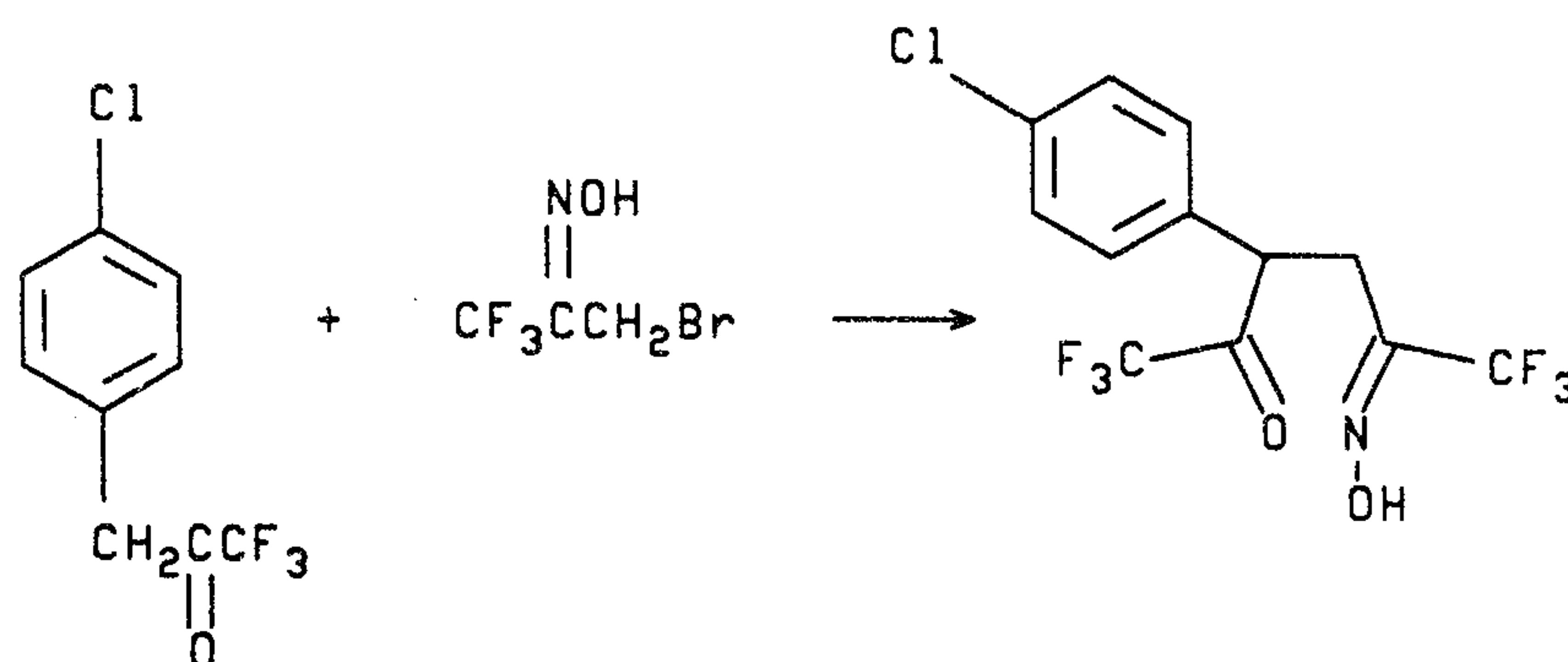


(13.9g, 0.2 mol) and methanol (100 mL) is added at room temperature over 30 minutes to 3-bromo-1,1,1-trifluoro-propanone (38.2g, 0.2 mol) and stirred for 2 days. The solvent is removed in vacuo to give a liquid. The liquid is diluted with water and extracted with methylene chloride. The combined organic extracts are washed sequentially with water and brine, dried over

anhydrous sodium sulfate and concentrated in vacuo to obtain a liquid. Vacuum distillation of the liquid gives the title product as a colorless liquid (20.0g, bp 50°-54°C, 7.5mm, 49%).

EXAMPLE 7

Preparation of 3-(p-Chlorophenyl)-1,1,1,6,6,6-hexafluoro-2,5-hexanedione, 5-oxime

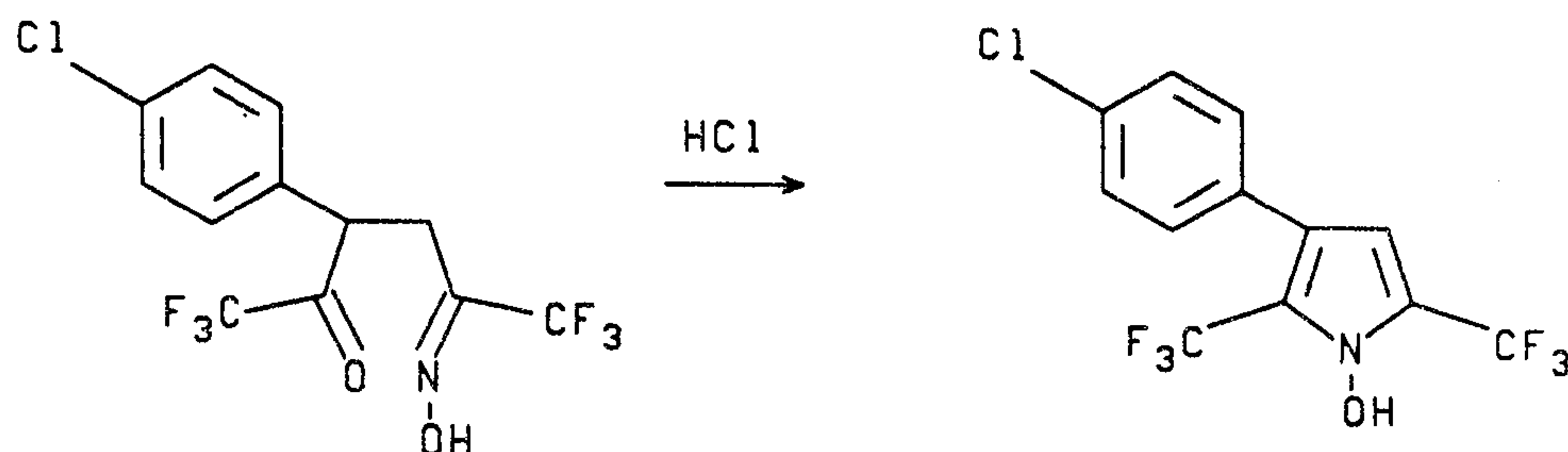


A solution of 3-(p-chlorophenyl)-1,1,1-trifluoro-2-propanone (8.9g, 0.04 mol) and tetrahydrofuran (25 mL) is added dropwise over fifteen minutes to a solution of potassium tert-butoxide (4.93g, 0.044 mol) and tetrahydrofuran (50 mL) under a nitrogen blanket. The reaction mixture heats up to 35°C during the addition. After stirring for 15 minutes a solution of 3-bromo-1,1,1-trifluoro-2-propanone, oxime (8.24g, 0.04 mol) and tetrahydrofuran (20 mL) is added dropwise to the reaction mixture and the temperature of the reaction mixture rises to 35°. After 1 1/2 hours the reaction mixture is diluted with water and extracted with ether. The combined organic extracts are washed

sequentially with water and brine, dried over anhydrous sodium sulfate and concentrated in vacuo to obtain an oil. Crystallization of the oil from hexanes gives the title product as a white solid (9.0g, mp 106.5°-107.5°C, 65%).

EXAMPLE 8

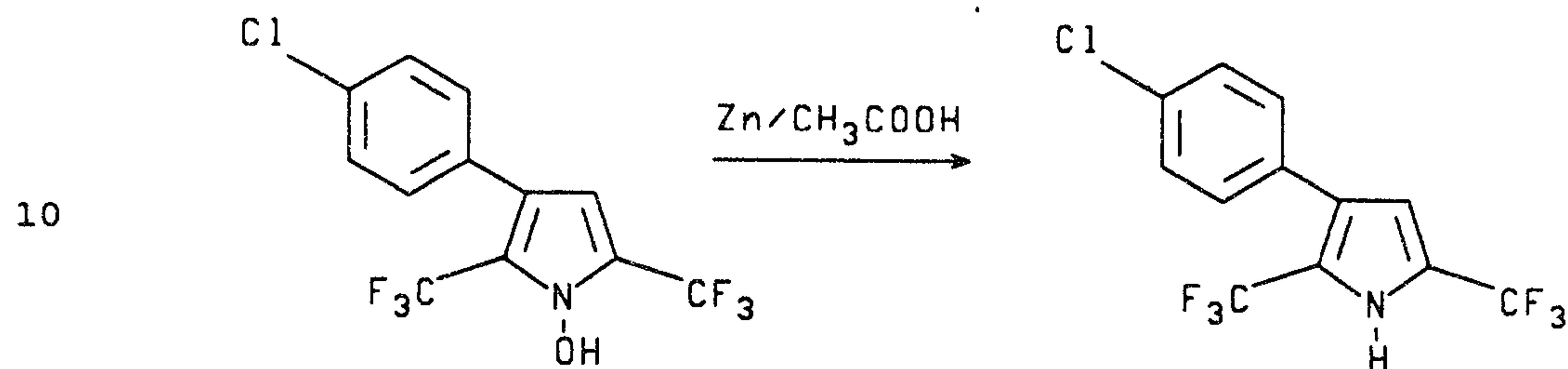
Preparation of 3-(p-Chlorophenyl)-2,5-bis(trifluoromethyl)-1-hydroxypyrrole



A solution of 3-(p-chlorophenyl)-1,1,1,6,6,6-hexafluoro-2,5-hexanedione, 5-oxime (17.1g, 0.049 mol) and ethanol saturated with hydrochloric acid gas is refluxed for forty minutes. The reaction mixture is diluted with water and extracted with ether. The combined organic extracts are washed sequentially with water and brine, dried over anhydrous sodium sulfate and concentrated in vacuo to obtain a liquid. Vacuum distillation of the liquid gives the title compound as a pale yellow viscous liquid (12.9g, bp 82°-95°C/0.2mm, 80%).

EXAMPLE 9Preparation of 3-(p-Chlorophenyl)-2,5-bis(trifluoromethyl)pyrrole

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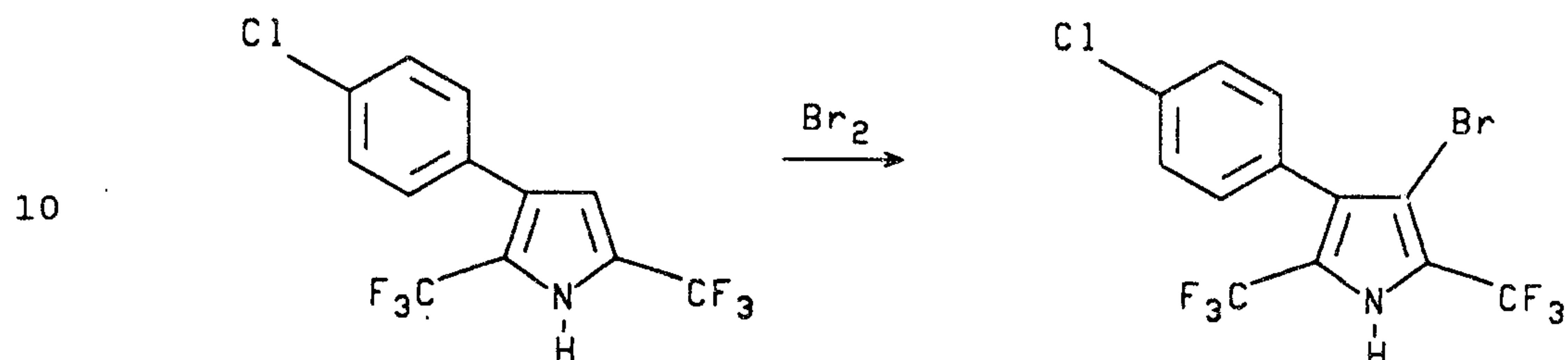
Zinc dust (20g, 0.3 mol) is added to a solution of 3-(p-chlorophenyl)-2,5-bis(trifluoromethyl)-1-hydroxypyrrole (7.5g, 0.023 mol) and acetic acid (50 mL). The reaction mixture is refluxed for 1/2 hour, cooled to room temperature, filtered to remove solids, diluted with water and extracted with ether. The combined organic extracts are washed sequentially with water, sodium carbonate solution and brine, dried over anhydrous magnesium sulfate and concentrated in vacuo to give a pale red liquid (6.8g). A portion of the red liquid (1.6g) is chromatographed using silica gel and eluted with methylene chloride to give the title product as a colorless liquid (1.1g). Identified by IR and NMR spectral analyses.

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EXAMPLE 10Preparation of 3-Bromo-4-(p-chlorophenyl)-2,5-bis(tri-fluoromethyl)pyrrole

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15 Bromine (0.527g, 0.17 mL, 0.0033 mol) is added to a solution of 3-(p-chlorophenyl)-2,5-bis(tri-fluoromethyl)pyrrole (0.94g, 0.003 mol), acetic acid (6 mL) and sodium acetate (0.984g, 0.012 mol). After 1 hour the reaction mixture is diluted with water and

20 extracted with ether. The combined organic extracts are washed sequentially with water, sodium metabisulfite solution, water and brine, dried over anhydrous sodium sulfate and concentrated in vacuo to give a colorless oil. The oil is chromatographed using silica

25 gel and eluted with methylene chloride to give the title compound as a colorless oil (0.4g, 34%). Identified by IR and NMR spectral analyses.

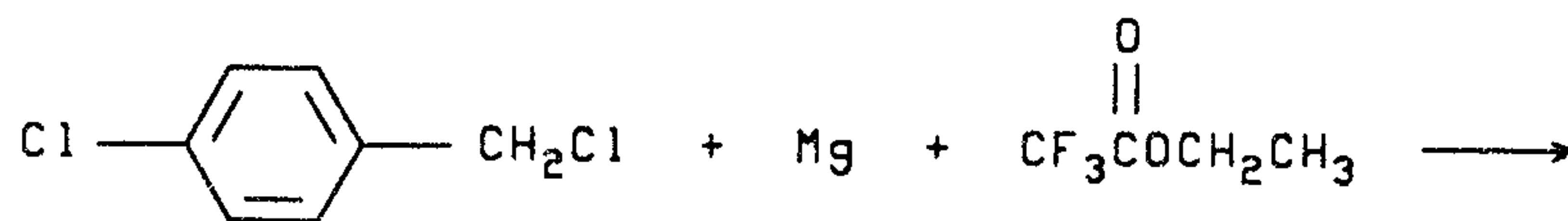
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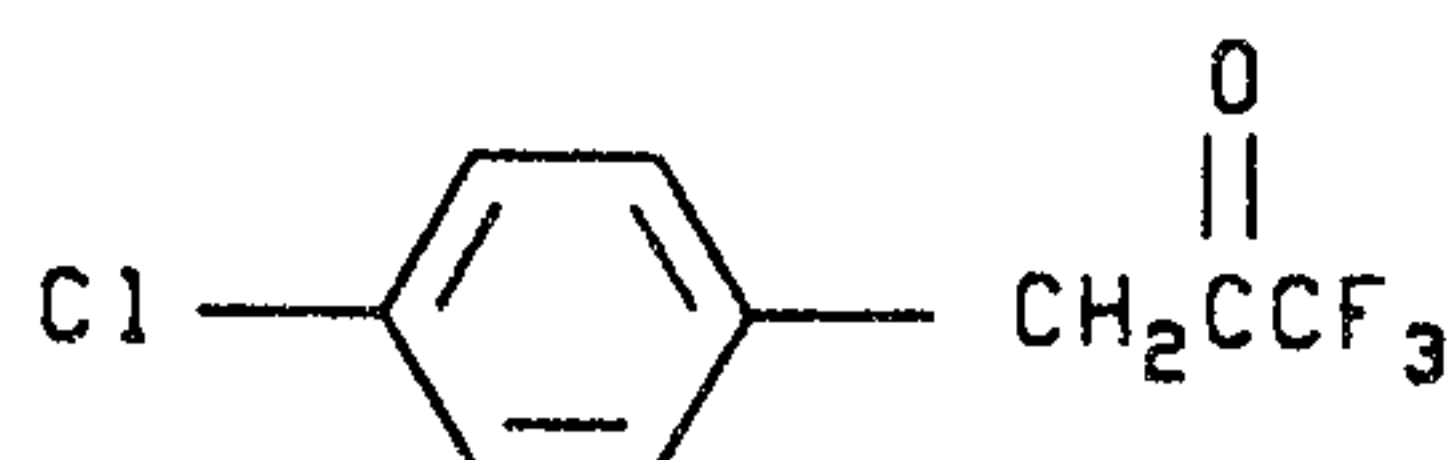
EXAMPLE 11

Preparation of 3-(p-Chlorophenyl)-1,1,1-trifluoro-2-propanone

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A solution of p-chlorobenzyl chloride (80.5g, 0.5 mol) and ether (150 mL) is slowly added to a vigorously stirred slurry of magnesium turnings (12.15g, 0.5 mol) and ether (50 mL) over a 45 minute period. After the addition is complete, the reaction mixture is refluxed for 1/2 hour then cooled in an ice bath. The Grignard reagent is then added to a solution of ethyl trifluoroacetate (71.04g, 0.5 mol) and ether (150 mL) at -60° to -70°C (acetone-dry ice bath) over a 45 minute period. The cooling bath is removed and the reaction mixture is allowed to warm to -10°C. The reaction mixture is then quenched with saturated ammonium chloride solution and then acidified with 10% hydrochloric acid solution. The organic layer is separated, washed sequentially with water and brine, dried over anhydrous magnesium sulfate and concentrated in vacuo to obtain a liquid. Vacuum distillation of the liquid gives the title product as a clear liquid (52.8g, bp 72°-74°C/34 mm, 47%).

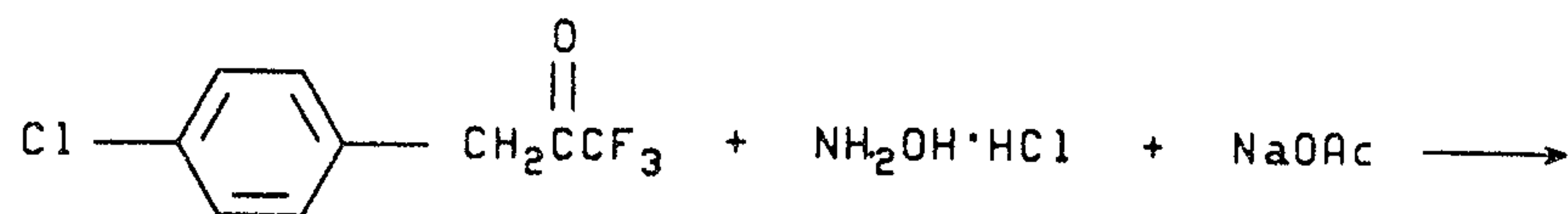
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EXAMPLE 12

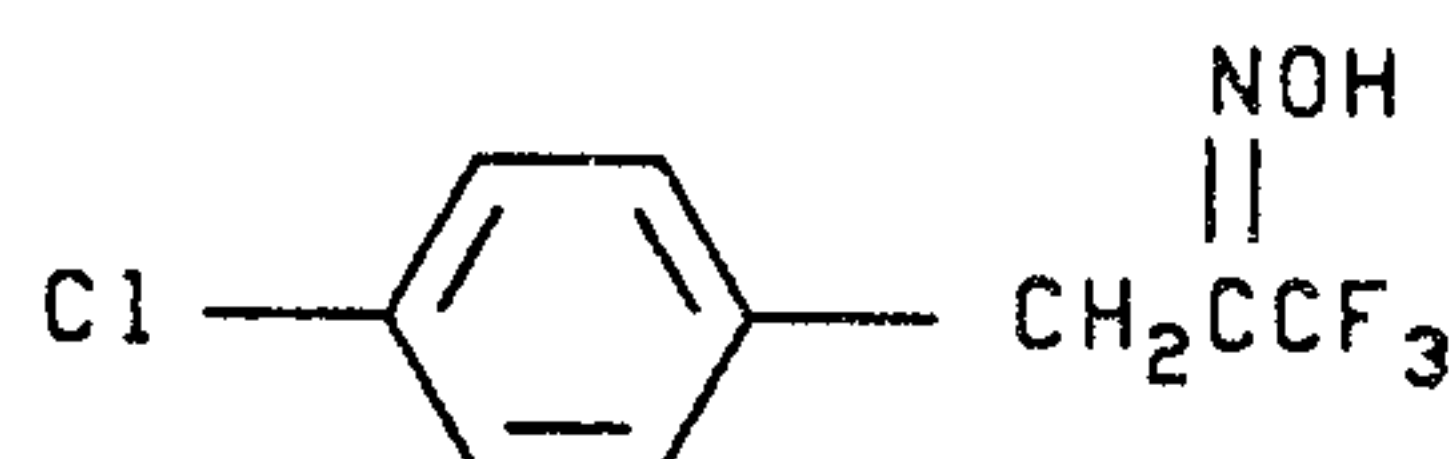
Preparation of

3-(p-Chlorophenyl)-1,1,1-trifluoro-2-propanone oxime

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A solution of 3-(p-Chlorophenyl)-1,1,1-tri-
fluoro-2-propanone (10.0g, 0.045 mol) and ethanol
(60 mL) is treated with a solution of hydroxylamine
hydrochloride (4.68g, 0.067 mol) and water (20 mL) and
then with a solution of sodium acetate (5.53g, 0.067
mol) and water (20 mL). The reaction mixture is then
refluxed for 2 hours, cooled to room temperature,
diluted with water and extracted with ether. The
combined organic extracts are washed sequentially with
water and brine, dried over anhydrous sodium sulfate
and concentrated in vacuo to give a liquid which
solidifies upon standing to give the title product as
white needles (11.84g). Identified by IR and NMR
spectral analyses.

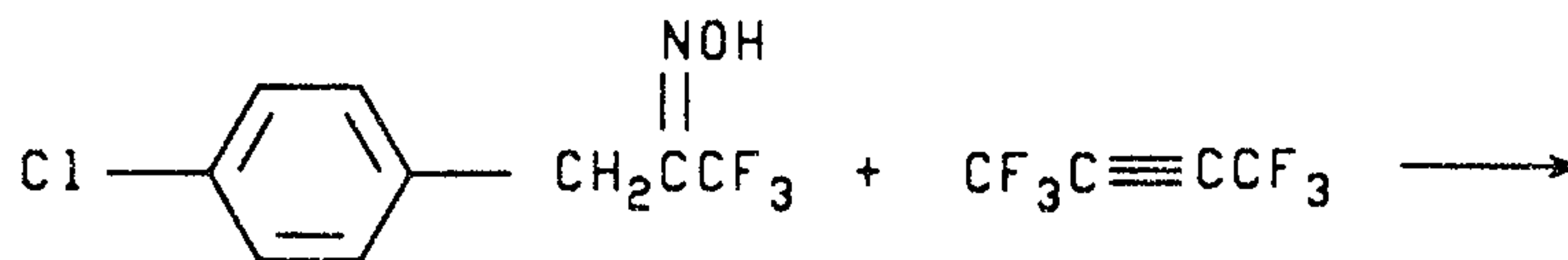
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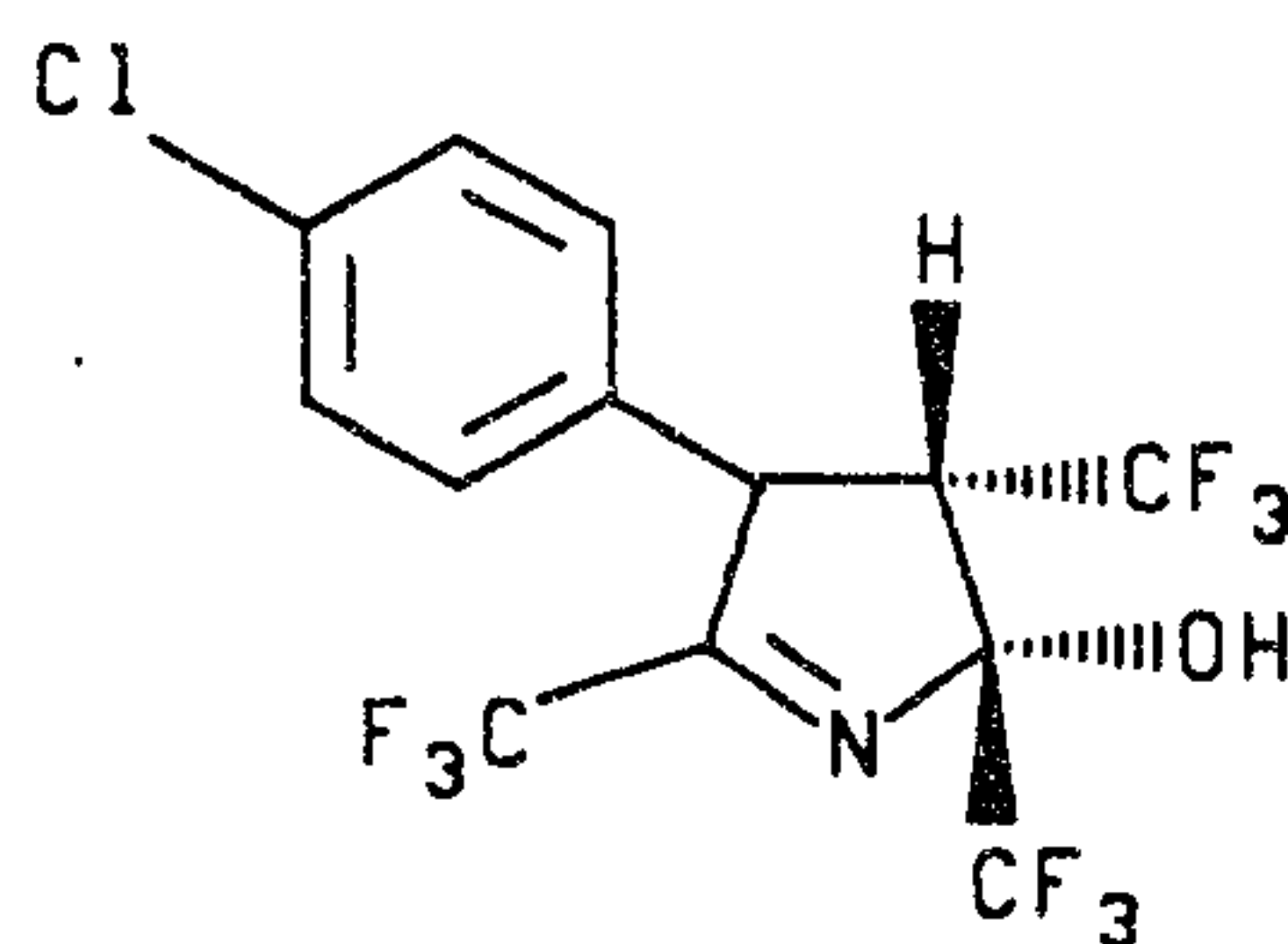
EXAMPLE 13

Preparation of 3-(p-Chlorophenyl)-5a-hydroxy-2,4-a,5b-tris(trifluoromethyl)-1-pyrroline

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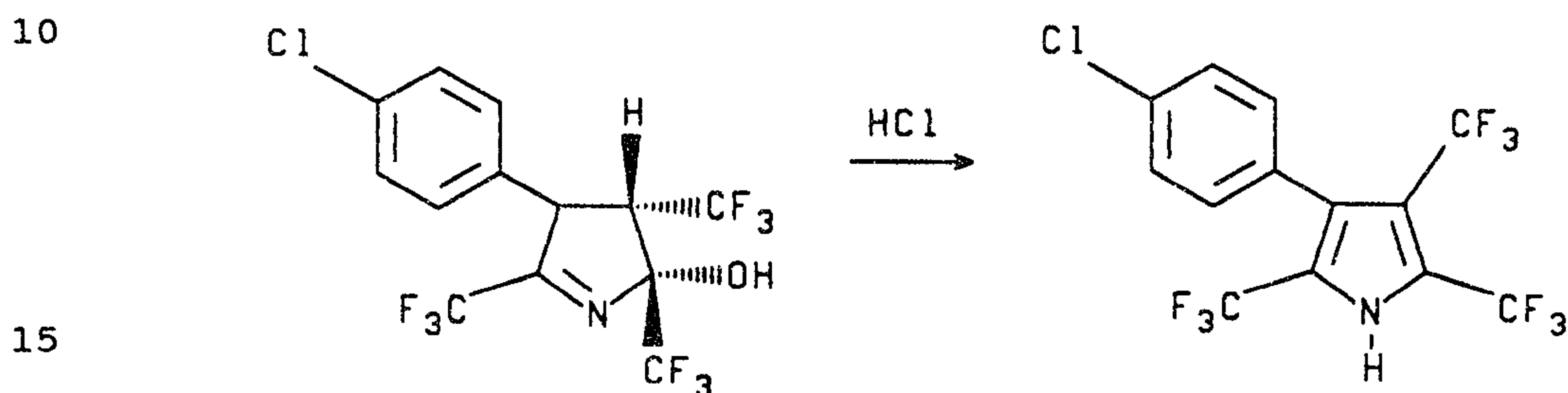
A solution of 3-(p-chlorophenyl)-1,1,1-trifluoro-2-propanone oxime (7.13g, 0.03 mol), potassium tert-butoxide (0.337g, 0.003 mol) and methanol (25 mL) in a pressure bottle is cooled in an acetone dry ice bath and treated with previously condensed liquid hexafluoro-2-butyne (30g). The pressure bottle is then sealed and the reaction mixture is heated to 60°-70°C over a 90 minute period. The pressure rises to 100 psi and after 1/2 hour drops slowly to about 15-20 psi. The reaction mixture is then allowed to stand at room temperature overnight, poured into water and extracted with ether. The combined organic extracts are washed sequentially with water and brine, dried over anhydrous sodium sulfate and concentrated in vacuo to give an oil. Chromatography of the oil using silica gel and 3% ethylacetate in methylene chloride as eluant gives 3-(p-chlorophenyl)-1,1,1-trifluoro-0-[3,3,3-trifluoro-1-(trifluoromethyl)propenyl]-2-propanone, oxime, vinyl-, (E)- as a yellow liquid (8.5g, 71%) and the

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title product as a yellow syrup (0.46g, 4%). Identified by IR and NMR spectral analyses.

EXAMPLE 14

Preparation of 3-(p-Chlorophenyl)-2,4,5-tris(trifluoromethyl)pyrrole



3-(p-Chlorophenyl)-5a-hydroxy-2,4-a,5b-tris(trifluoromethyl)-1-pyrroline (0.4g, 1 mmol) is dissolved into ethanol (8 mL) saturated with hydrochloric acid gas and the resulting solution is refluxed for 1 1/2 hours. The reaction mixture is diluted with water and extracted with ether. The combined organic extracts are washed sequentially with water and brine, dried over anhydrous magnesium sulfate and concentrated in vacuo to give an oil. Chromatography of the oil using silica gel and methylene chloride as eluant give the title product as a colorless liquid (0.13g, 34%). Identified by IR and NMR spectral analyses.

EXAMPLE 15

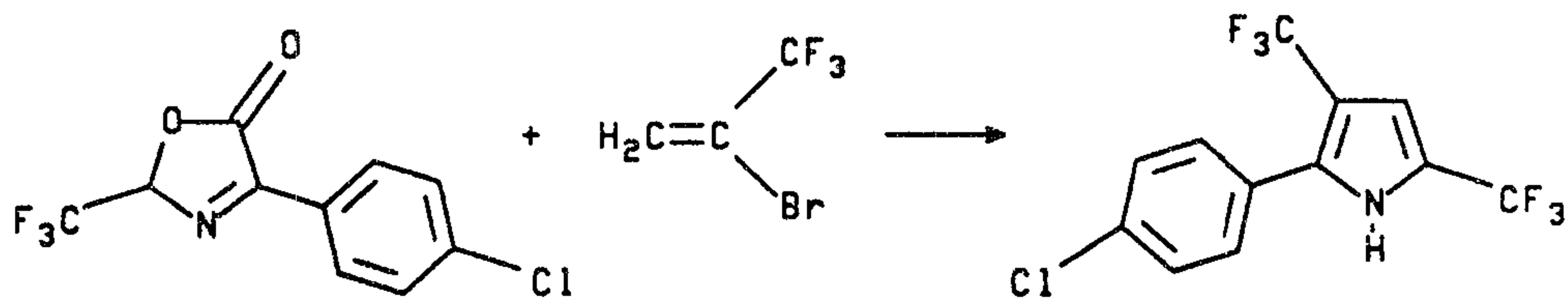
Preparation of 4-(p-Chlorophenyl)-2-trifluoromethyl-2-oxazolin-5-one

In a single portion, trifluoroacetic anhydride, (1.7 mL; 0.012 mol) is added to powdered 2-(p-chlorophenyl)glycine (11.4g; 0.06 mol), causing an

immediate exotherm to about 40°C, a yellow color forms on the surface of the solid. As the mixture is slowly heated to 70°C, more of the solid dissolves to an orange/amber oil. All the solid dissolves in approximately 2 hours, and heating is continued another hour. Solvent is removed under reduced pressure on a rotary evaporator. Toluene is twice added and removed under reduced pressure, but the odor of trifluoroacetic acid is still evident. This yellow semi-solid (yield theoretical; purity > 90% by HPLC) is the above-identified compound and is used in the next step without further purification.

EXAMPLE 16

Preparation of 2-(p-Chlorophenyl)-3,5-bis(trifluoromethyl)pyrrole



A solution of 3.0g of 4-(2-(trifluoromethyl)-5-oxo-1,2,4-oxazol-3-yl)phenyl chloride, 2.0g of 2-bromo-3,3,3-trifluoropropene and acetonitrile is treated with 1.2g of triethylamine, heated at reflux temperature for one hour, and concentrated in vacuo to give a residue. The residue is chromatographed on silica gel using a 4:1 mixture of hexane:ethyl acetate to give the title compound as a colorless solid, 1.6g mp 41°C-43°C.

EXAMPLE 17Preparation of 3-Bromo-5-(p-chlorophenyl)-2,4-bis(trifluoromethyl)pyrrole

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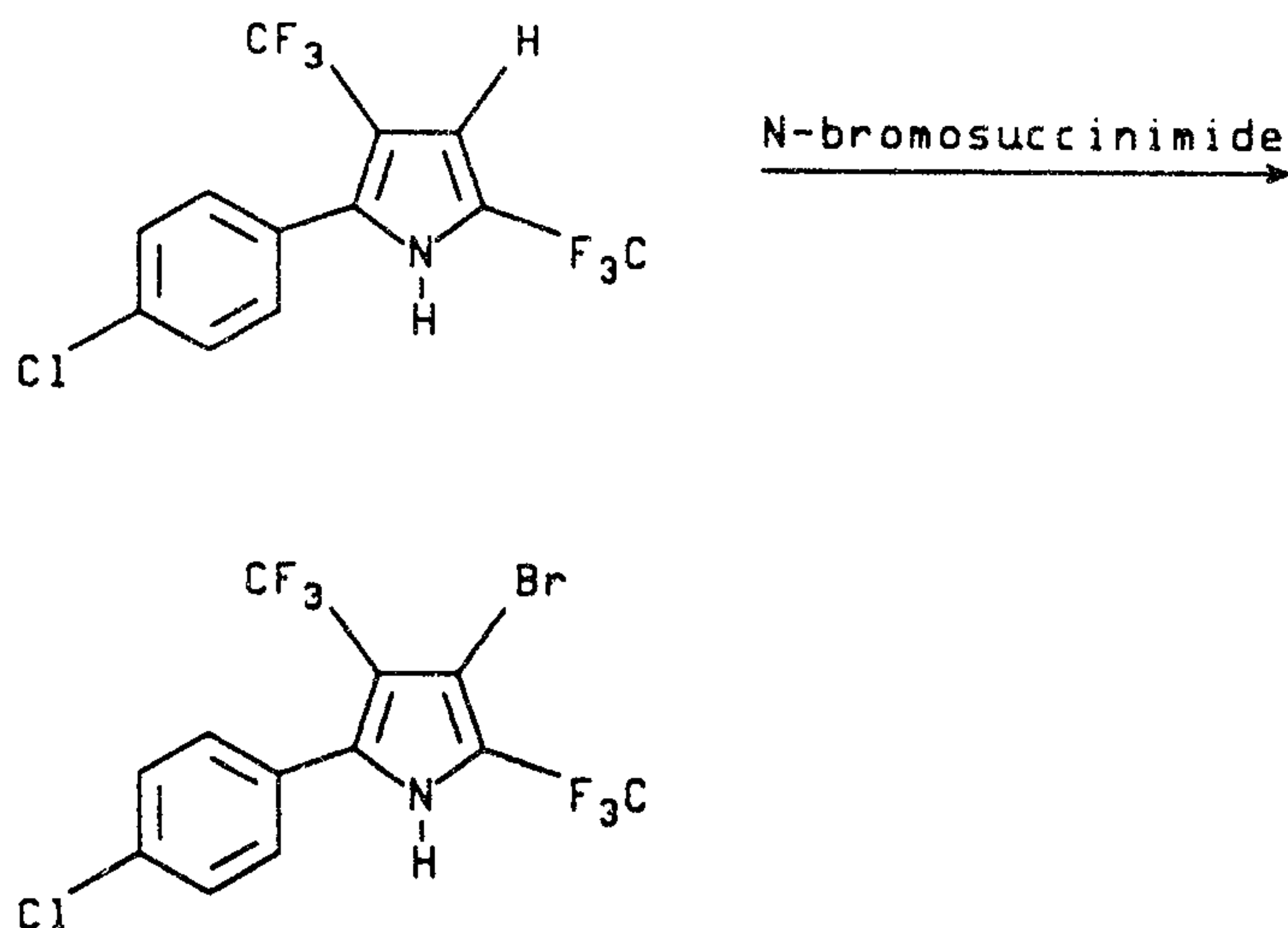
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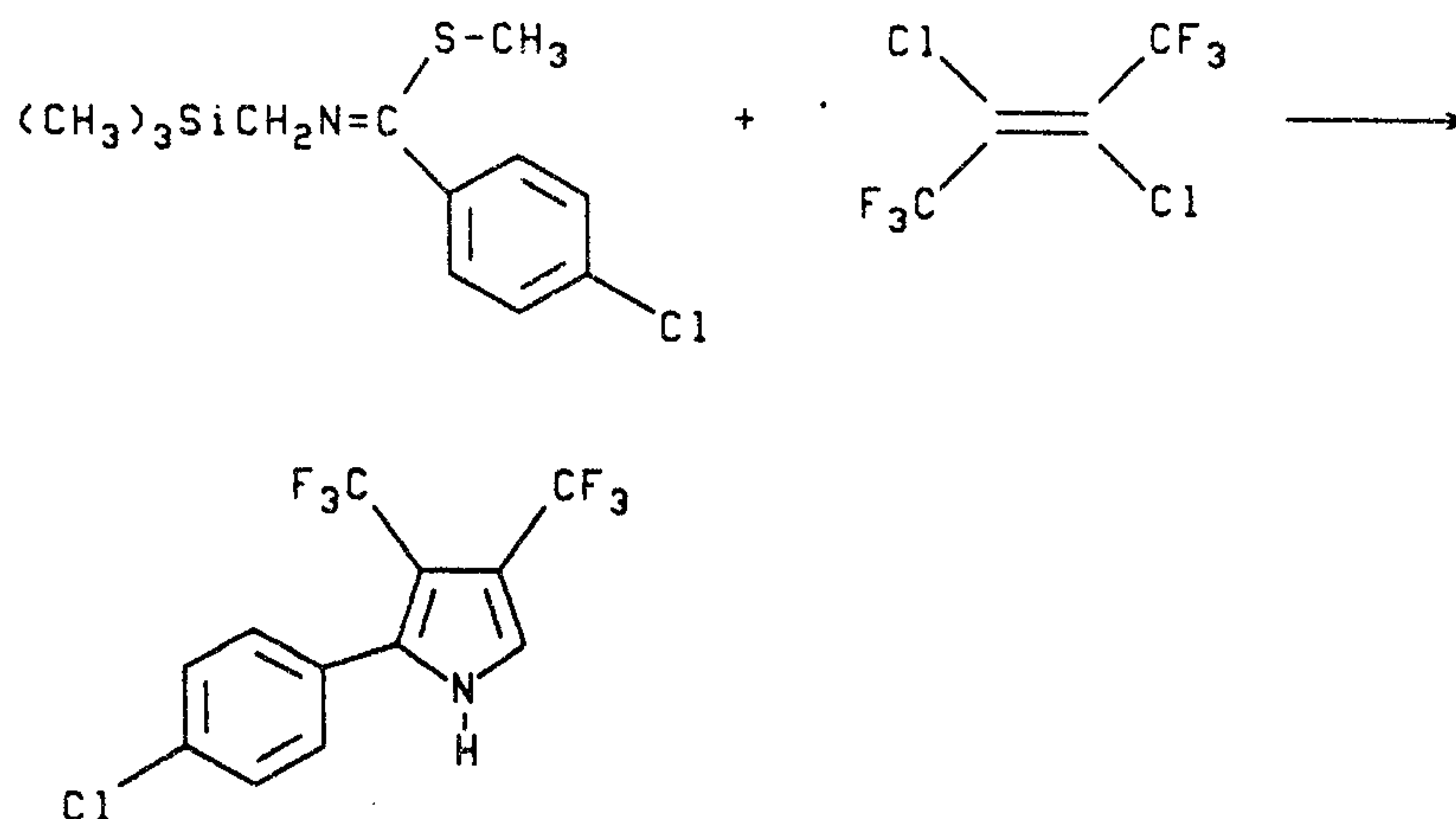
N-Bromosuccinimide (0.9g, 5 mmol) is added to a solution of 2-(p-chlorophenyl)-3,5-bis(trifluoromethyl)pyrrole (0.78g, 2.5 mmol) and tetrahydrofuran (50 mL). The reaction mixture is stirred at room temperature overnight then concentrated in vacuo to give a solid. The solid is chromatographed using silica gel and 20% ethyl acetate in hexanes as eluant to yield the title compound as a light green solid (0.376g, mp 71°-75°C, 38%).

EXAMPLE 18Preparation of 2-(p-Chlorophenyl)-3,4-bis(trifluoromethyl)pyrrole

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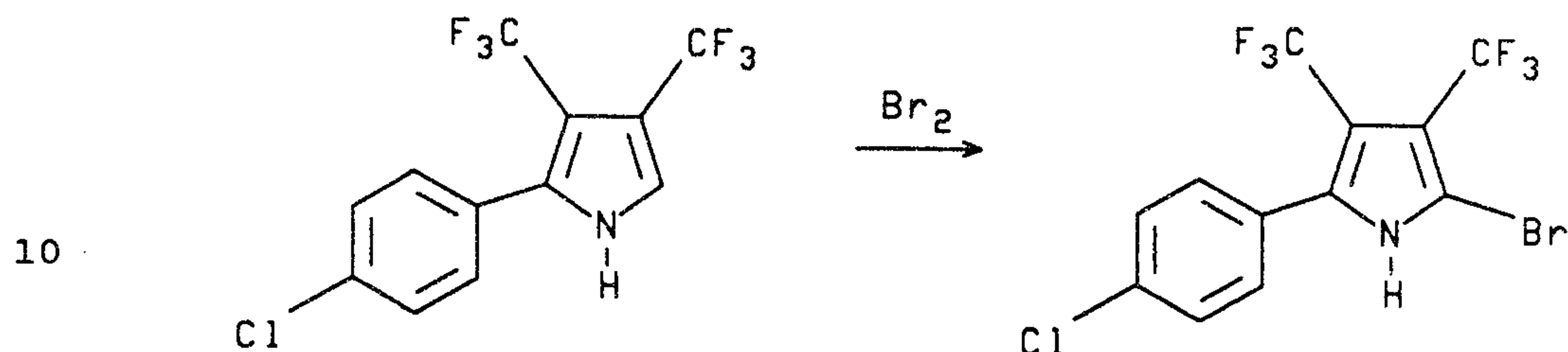
15



Under a nitrogen purge, methyl p-chlorothio-N-[(trimethylsilyl)methyl]benzimidate (2.7g, 0.01 mol) is dissolved in hexamethylphosphoramide (HMPA, 15 mL) to form a clear solution. In a single portion, 2,3-dichloro-hexafluorobutene (2.3g, 0.01 mol) is added, washed in with a 10 mL portion of HMPA. Water (0.55 mL, 0.03 mol) is then added, washed in with 5 mL of HMPA, causing a slight exotherm. When the exotherm subsides the clear solution is heated gently with a heat gun, first to 45°C, then to 60°C, whereupon a spontaneous exotherm occurs, bringing the reaction mixture temperature to 85°C. The resulting red solution is allowed to cool to room temperature and stirred for 16 hours. The reaction mixture is then poured onto ice/water, filtered, washed with cold water and dried on the filter. Recrystallization of the solid from hexanes gives the title product as white crystals as a solvate with 0.5 mole of HMPA (1.3g, mp 117°C-119°C, 33%). Identified by IR and spectral analyses.

EXAMPLE 19Preparation of 2-Bromo-5-(p-chlorophenyl)-3,4-bis(trifluoromethyl)pyrrole

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15 Under a nitrogen purge, a solution of bromine (0.05 mL, 0.001 mol) and chloroform (5 mL) is added dropwise to a solution of 2-(p-chlorophenyl)-3,4-bis-(trifluoromethyl)pyrrole (0.39g, 0.001 mol) and chloroform (10 mL). The orange reaction mixture is stirred for 16 hours at room temperature then concentrated in vacuo to give an oil. The oil is extracted with methyl

20 cyclohexane and the combined organic extracts are treated with carbon black and the solvent is removed in vacuo. The residue is dissolved in a small amount of hot hexane, decanted from insolubles and cooled in the freezer. Filtration of the cold solution gives the

25 title compound as white crystals containing a half mole of HMPA (0.32g mp $97^\circ\text{--}100^\circ\text{C}$, 68%). Identified by IR and NMR spectral analyses.

EXAMPLE 20

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Insecticide and acaricide evaluations

The following tests show the efficacy of the compounds as insecticides and acaricides. All tests are performed using technical materials and kept at 27°C . The test concentrations are in terms of active

35 ingredient.

Spodoptera eridania, 3rd instar larvae, southern
armyworm

5 A sieva lima bean leaf expanded to 7 to 8 cm
in length is dipped in the test suspension with agita-
tion for 3 seconds and placed in a hood to dry. The
leaf is then placed in a 100 x 10 mm petri dish con-
taining a damp filter paper on the bottom and 10 3rd
10 instar caterpillars. The dish is maintained for 5 days
before observations are made of mortality, reduced
feeding, or any interference with normal moulting.

Spodoptera eridania, 7-day residual

15 The plants treated in the above test are
maintained under high intensity lamps in the greenhouse
for 7 days. These lamps duplicate the effects of a
bright sunny day in June in New Jersey and are kept on
for 14 hour day length. After 7 days, the foliage is
sampled and assayed as in the above-said test.

20 Aphis fabae, mixed instar, bean aphid

Pots containing single nasturtium plants
(Tropaeolum sp.) about 5 cm tall are infested with
about 100 to 200 aphids one day before the test. Each
25 pot is sprayed with the test formulation for 2 revolu-
tions of a 4 rpm turntable in a hood, using a #154
DeVilbiss atomizer. The spray tip is held about 15 cm
from the plant and the spray directed so as to give
complete coverage of the plants and the aphids. The
30 sprayed pots are set on their sides on white enamel
trays and held for 2 days, following which mortality
estimates are made.

Tetranychus urticae (P-resistant strain), 2-spotted spider mite

5 Sieva lima bean plants with primary leaves expanded to 7 to 8 cm are selected and cut back to one plant per pot. A small piece is cut from a leaf taken from the main colony and placed on each leaf of the test plants. This is done about 2 hours before treatment to allow the mites to move over to the test plant and to lay eggs. The size of the cut piece is varied 10 to obtain about 100 mites per leaf. At the time of the treatment, the piece of leaf used to transfer the mites is removed and discarded. The mite-infested plants are dipped in the test formulation for 3 seconds with 15 agitation and set in the hood to dry. Plants are kept for 2 days before estimates of adult kill are made using the first leaf. The second leaf is kept on the plant for another 5 days before observations are made of the kill of eggs and/or newly emerged nymphs.

20 Diabrotica undecimpunctata howardi, 3rd instar southern corn rootworm

One cc of fine talc is placed in a 30 mL wide-mouth screw-top glass jar. One mL of the appropriate acetone suspension is pipetted onto the talc so 25 as to provide 1.25 and 0.25 mg of active ingredient per jar. The jars are set under a gentle air flow until the acetone is evaporated. The dried talc is loosened, 1 cc of millet seed is added to serve as food for the insects and 25 mL of moist soil is added to each jar. 30 The jar is capped and the contents thoroughly mixed on a Vortex Mixer. Following this, 10 3rd instar rootworms are added to each jar and the jars are loosely capped to allow air exchange for the larvae. The treatments are held for 6 days before mortality counts 35 are made. Missing larvae are presumed dead, since they

decompose rapidly and can not be found. The concentrations used in this test correspond approximately to 50 and 10 kg/ha, respectively.

5

Rating Scale:

	0 = no effect	5 = 56 to 65% kill
	1 = 10 to 25% kill	6 = 66 to 75% kill
	2 = 26 to 35% kill	7 = 76 to 85% kill
10	3 = 36 to 45% kill	8 = 86 to 99% kill
	4 = 46 to 55% kill	9 = 100% kill

The data obtained for the above-described evaluations are reported in Table I.

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TABLE I
Insecticide And Acaricide Evaluations

Compound	BEAN APHIDS		Southern Armyworm		P.RES MITES	SCRW ¹
	(ppm) 100	(ppm) 1000	(ppm) 100	Residual 7 days, 1000 ppm	(ppm) 300	
2-bromo-5-(p-chlorophenyl)-3,4-bis-(trifluoromethyl)pyrrole	9	9	9	9	9	0
3-bromo-2-(p-chlorophenyl)-4,5-bis-(trifluoromethyl)pyrrole-1-carbonitrile	9	9	9	9	9	8
3-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-4,5-bis(trifluoromethyl)pyrrole	0	9	9	9	0	9
3-bromo-2-(p-chlorophenyl)-4,5-bis-(trifluoromethyl)pyrrole	9	9	9	9	9	9
3-bromo-5-(p-chlorophenyl)-2,4-bis-(trifluoromethyl)pyrrole	0	9	9	9	9	0
3-(p-chlorophenyl)-2,4,5-tris(trifluoromethyl)pyrrole	0	9	9	0	9	9
3-bromo-2-(3,4-dichlorophenyl)-4,5-bis(trifluoromethyl)pyrrole	9	9	9	9	9	9
3-bromo-2-(3,4-dichlorophenyl)-4,5-bis(trifluoromethyl)pyrrole-1-carbonitrile	9	9	9	9	9	9

TABLE I CONT.

Insecticide And Acaricide Evaluations

Compound	BEAN			Southern Armyworm			P.RES	SCRW ¹
	APHIDS	(ppm) 100	(ppm) 1000	(ppm) 100	7 days	MITES	(ppm) 300	
3-bromo-2-(3,4-dichlorophenyl)-1-(ethoxymethyl)-4,5-bis(trifluoromethyl)pyrrole	9	9	9	9	9	0	0	9
3-bromo-4-(p-chorophenyl)-2,5-bis-(trifluoromethyl)pyrrole	0	9	9	0	-	9	9	9
3-bromo-2-(3,4-dichlorophenyl)-1-methyl-4,5-bis(trifluoromethyl)pyrrole	8	9	9	0	9	0	0	0
3-bromo-2-(3,4-dichlorophenyl)-1-(1-isopropoxyethyl)-4,5-bis(trifluoromethyl)pyrrole	8	9	9	9	9	9	9	9
3-bromo-4,5-bis(trifluoromethyl)-2-(alpha, alpha, alpha-trifluoro-p-tolyl)pyrrole	6	9	9	9	9	9	9	9
3-bromo-1-(ethoxymethyl)-4,5-bis(trifluoromethyl)-2-(alpha, alpha, alpha-trifluoro-p-tolyl)pyrrole	0	9	9	9	0	0	0	9

1 SCRW designates southern corn rootworm

The above test results show the efficacy of the compounds as insecticides and acaricides.

EXAMPLE 21

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The following tests show the efficacy of the compounds as insecticides. All tests are performed using technical materials and kept at 27°C. The test concentrations are in terms of active ingredient.

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Heliothis virescens, 3rd instar tobacco budworm

Cotton cotyledons are dipped in the test formulation and allowed to dry in a hood. When dry, each is cut into quarters and ten sections placed individually in 30 mL plastic medicine cups containing a 5 to 7 mm long piece of damp dental wick. One 3rd instar caterpillar is added to each cup and a cardboard lid placed on the cup. Treatments are maintained for 3 days before mortality counts and estimates of reduction in feeding damage are made.

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Empoasca abrupta, adults, western potato leafhopper

A Sieva lima bean leaf about 5 cm long is dipped in the test formulation for 3 seconds with agitation and placed in a hood to dry. The leaf is placed in a 100 x 10 mm petri dish containing a moist filter paper on the bottom. About 10 adult leafhoppers are added to each dish and the treatments are kept for 3 days before mortality counts are made.

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Blattella germanica, bait test, adult male German cockroach

A 0.1% bait is prepared by pipetting 1 mL of a 1000 ppm solution of the test compound in acetone onto 1 gram of cornmeal in a 30 mL wide-mouth bottle. The bait is dried by passing a gentle stream of air

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into the bottle. The bait is placed in a 1 pint wide-mouth Mason jar and 10 adult male cockroaches are added. A screen lid is placed on the jar and a small piece of cotton soaked in 10% honey is put on the top of the screen lid. Mortality counts are made after 3 days.

Blattella germanica, residue test, adult male German cockroach

One mL of a 1000 ppm acetone solution of the test material is pipetted slowly over the bottom of a 150 x 15 mm petri dish so as to give as uniform coverage as possible. After the deposit has dried, 10 adult male cockroaches are placed in each dish and the lid is added. Mortality counts are made after 3 days.

Spodoptera eridania, systemic uptake, 3rd instar larvae, southern armyworm

The compound is formulated as an emulsion containing 0.1 gm of the test material, 0.2 gm of Emulphor EL-620® emulsifier, 10 mL of acetone and 90 mL of water. This is diluted 10-fold with water to give a 100 ppm emulsion for the test. Subsequent 10-fold dilutions are made with water as needed. Sieva lima bean plants, with the primary leaves expanded to a length of 7 to 8 cm, are cut off at least 3 cm above the soil level to avoid contamination with soil bacteria that will cause decay of the stem during the test. The cut stems are placed in the test emulsions and each stem is wrapped with a bit of cotton to hold the stem off the bottom of the bottle and to limit evaporation and volatilization of the compound. The test is maintained for 3 days at 27°C to allow the compounds to be taken up into the plant. Following this, one leaf is removed from the plant and placed in

a 100 x 10 mm petri dish with 10 southern armyworms. Mortality counts and observations of feeding damage are made 3 and 5 days later.

5

Empoasca abrupta, adults, western potato leafhoppers, systemic uptake

10 The compound is formulated as an emulsion containing 0.1 gm of the test material, 0.2 gm of Emulphor EL-620® emulsifier, 10 mL of acetone and 90 mL of water. This is diluted 10 fold with water to give a 100 ppm emulsion for the test. Subsequent 10-fold dilutions are made with water as needed. Sieva lima bean plants, with the primary leaves expanded to a length of 7 to 8 cm, are cut off at least 3 cm above the soil level to avoid contamination with soil bacteria that will cause decay of the stem during the test. The cut stems are placed in the test emulsion and each stem is wrapped with a bit of cotton to hold the stem off the bottom of the bottle and to limit evaporation and volatilization of the compound. The test is maintained for 3 days at 27°C to allow the compounds to be taken up into the plant. Following this, one leaf is removed from the plant and placed in a 100 x 10 mm petri dish with 10 adult western potato leafhoppers. After 3 days, mortality counts are made.

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The rating scale for the above evaluations is the same as described in Example 20.

The data obtained are reported in Table II.

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TABLE II

Insecticide Evaluations

<u>Compound</u>	<u>LEAF HOPPER</u> (ppm) <u>100</u>	<u>Tobacco Budworm</u>		<u>G. COCKROACH</u>	
		(ppm) <u>1000</u>	(ppm) <u>100</u>	<u>Bait</u> (ppm) <u>1000</u>	<u>Res</u> (ppm) <u>1000</u>
2-bromo-5-(p-chlorophenyl)-3,4-bis(trifluoromethyl)pyrrole	9	9	4	9	9
3-bromo-2-(p-chlorophenyl)-4,5-bis(trifluoromethyl)pyrrole-1-carbonitrile	9	9	8	9	9
3-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-4,5-bis(trifluoromethyl)pyrrole	9	9	9	9	9
3-bromo-2-(p-chlorophenyl)-4,5-bis(trifluoromethyl)pyrrole	9	9	9	9	9
3-bromo-5-(p-chlorophenyl)-2,4-bis(trifluoromethyl)pyrrole	0	9	9	9	9
3-(p-chlorophenyl)-2,4,5-tris(trifluoromethyl)pyrrole	9	-	9	-	9
3-bromo-2-(3,4-dichlorophenyl)-4,5-bis(trifluoromethyl)pyrrole	9	9	9	0	9
3-bromo-2-(3,4-dichlorophenyl)-4,5-bis(trifluoromethyl)pyrrole-1-carbonitrile	9	9	9	0	9

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TABLE II CONT.

Insecticide Evaluations

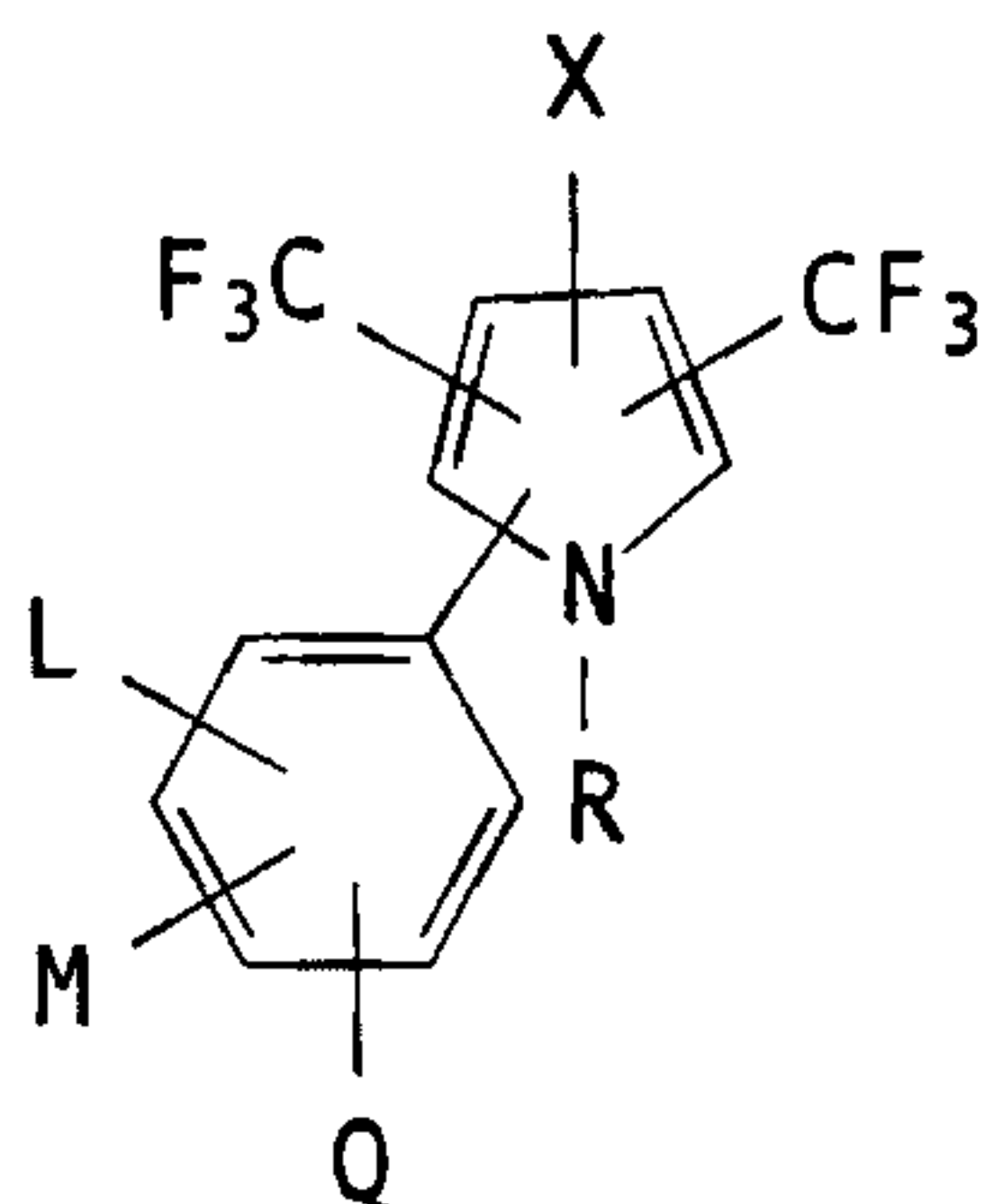
Compound	LEAF HOPPER	Tobacco Budworm		G. COCKROACH	
	(ppm) 100	(ppm) 1000	(ppm) 100	Bait (ppm) 1000	Res (ppm) 1000
3-bromo-2-(3,4-dichlorophenyl)-1-(ethoxy- methyl)-4,5-bis(trifluoromethyl)pyrrole	9	9	9	0	9
3-bromo-4-(p-chlorophenyl)-2,5- bis(trifluoromethyl)pyrrole	9	5	0	0	9
3-bromo-2-(3,4-dichlorophenyl)-1-methyl- 4,5-bis(trifluoromethyl)pyrrole	8	0	0	0	9
3-bromo-2-(3,4-dichlorophenyl)-1-(1-iso- propoxyethyl)-4,5-bis(trifluoromethyl)- pyrrole	9	9	9	4	9
3-bromo-4,5-bis(trifluoromethyl)-2- (alpha, alpha, alpha-trifluoro-p- tolyl)pyrrole	9	9	9	0	9
3-bromo-1-(ethoxymethyl)-4,5-bis(tri- fluoromethyl)-2-(alpha, alpha, alpha- trifluoro-p-tolyl)pyrrole	8	0	0	0	9

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CLAIMS:

1. A compound having the structure



wherein

L is H, F, Cl or Br;

M and Q are each independently H, F, Cl, Br, CN,
10 NO₂, CF₃, C₁-C₄ alkyl or C₁-C₃ alkoxy;

X is Cl, Br, I or CF₃;

R is $\begin{array}{c} \text{O} \\ || \\ \text{CR}_1 \end{array}$,

hydrogen, cyano, C₁-C₆ alkyl, one tri(C₁-C₄ alkyl)silyl, one
15 hydroxy, one cyano, one or two C₁-C₄ alkoxy groups, one C₁-C₄
alkylthio, one phenyl, one phenoxy group, one benzyloxy
group, one C₁-C₆ alkylcarbonyloxy group, one C₂-C₆
alkenylcarbonyloxy group, one phenylcarbonyloxy group, one
C₁-C₆ alkoxy carbonyl group, one benzyloxy carbonyl group, C₃-C₆
20 alkenyl, or C₃-C₆ alkynyl; and

R₁ is C₁-C₆ alkyl, one hydroxy, one cyano, one or
two C₁-C₄ alkoxy groups, one C₁-C₄ alkylthio, one phenyl, one
phenoxy group, one benzyloxy group, one C₁-C₆
alkylcarbonyloxy group, one C₂-C₆ alkenylcarbonyloxy group,
25 one phenylcarbonyloxy group, one C₁-C₆ alkoxy carbonyl group,
one benzyloxy carbonyl group, C₃-C₆ alkenyl, C₃-C₆ alkynyl, C₁-

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C₆ alkoxy, C₂-C₆ alkenyloxy, di(C₁-C₄ alkyl)amino, N-(C₁-C₄alkyl)-N-phenylamino or -N-halophenylamino, or C₃-C₆ polymethyleneimino; provided that when the pyrrole ring is substituted with CF₃ at each of the pyrrole carbon atoms adjacent to the ring nitrogen atom and X is Cl, Br, or I then R cannot be hydrogen.

2. The compound according to claim 1, wherein, when R or R₁ is any one of C₁-C₆ alkyl, C₁-C₄ alkoxy, phenyl, phenoxy, C₁-C₆ alkylcarbonyloxy, C₂-C₆ alkenylcarbonyloxy, phenylcarbonyloxy, and C₁-C₆ alkoxycarbonyl, said R or R₁ is substituted with one to three halogen atoms.

3. The compound according to claim 1, wherein, when R or R₁ is any one of phenyl, phenoxy, and phenylcarbonyloxy, said R or R₁ is substituted with one to three C₁-C₄ alkyl groups.

4. The compound according to claim 1, wherein, when R or R₁ is any one of phenyl, phenoxy, phenylcarbonyloxy, and C₁-C₆ alkoxycarbonyl, said R or R₁ is substituted with one to three C₁-C₄ alkoxy groups.

5. The compound according to claim 1, wherein, when R or R₁ is benzyloxy or benzyloxycarbonyl, said R or R₁ is substituted on its phenyl ring with one to three halogen atoms, one to three C₁-C₄ alkyl groups or one to three C₁-C₄ alkoxy groups.

6. The compound according to claim 1, wherein, when R or R₁ is C₃-C₆ alkenyl or C₃ to C₆ alkynyl, said R or R₁ is substituted with one to three halogen atoms or one phenyl group.

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7. The compound according to claim 1, wherein, when R₁ is phenyl or phenoxy, said R₁ is substituted with CF₃, CN, NO₂, di(C₁-C₄alkyl)amino or C₁-C₄ alkanoylamino.

8. The compound according to claim 1, wherein, when R₁ is C₁-C₆ alkoxy or C₂-C₆ alkenyloxy, said R₁ is substituted with one to three halogen atoms.

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9. The compound according to any one of claims 1 to 8, wherein:

X is Br or CF₃;

L is H;

M is H, F, Cl or Br;

Q is H, F, Cl, Br or CF₃;

R is $\overset{\text{O}}{\parallel}\text{CR}_1$, hydrogen, cyano,
 C₁-C₆ alkyl,
 one tri(C₁-C₄ alkyl)silyl,
 one cyano,
 one or two C₁-C₄ alkoxy groups,
 one phenoxy group,
 one benzyloxy group,
 one C₁-C₆ alkylcarbonyloxy group,
 one C₂-C₆ alkenylcarbonyloxy group,
 one C₁-C₆ alkoxycarbonyl group, or
 one benzyloxycarbonyl group,

C₃-C₆ alkenyl, or

C₃-C₆ alkynyl; and

R₁ is C₁-C₆ alkyl,
 one cyano,
 one or two C₁-C₄ alkoxy groups,
 one phenyl,
 one phenoxy group,
 one benzyloxy group,
 one C₁-C₆ alkylcarbonyloxy group,
 one C₂-C₆ alkenylcarbonyloxy group,
 one phenylcarbonyloxy group,
 one C₁-C₆ alkoxycarbonyl group, or
 one benzyloxycarbonyl group,

C₃-C₆ alkenyl,

C₃-C₆ alkynyl,

phenyl,

phenoxy,

C₁-C₆ alkoxy, or

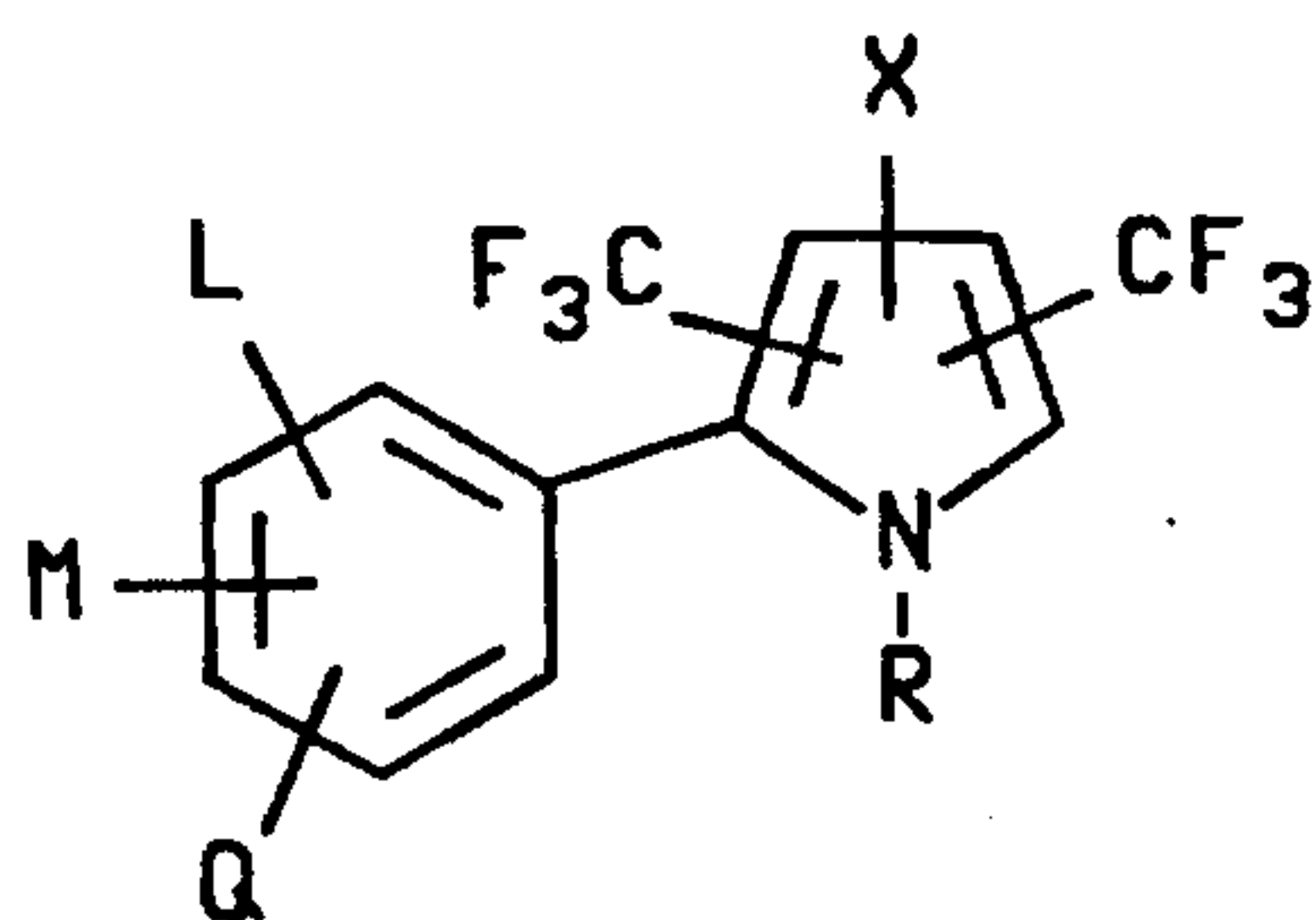
C₂-C₆ alkenyloxy.

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10. The compound according to claim 9, wherein, when R or R₁ is C₁ to C₆ alkyl, said R or R₁ is substituted with one to three halogen atoms.

11. The compound according to any one of claims 1 to 8, wherein said compound has the structure



and

L is H, Cl, Br or F;

M and Q are each independently H, F, Cl, Br, CN, NO₂ or CF₃;

X is Cl, Br, I or CF₃;

R is $\overset{\text{O}}{\parallel}\text{CR}_1$, hydrogen, cyano or C₁-C₆ alkyl optionally substituted with one to three halogen atoms, CN, C₁-C₄ alkoxy, C₁-C₆ alkylcarbonyloxy or benzyloxy-carbonyl; and

R₁ is phenyl optionally substituted with one to three halogen atoms.

12. The compound according to claim 11, wherein, when R is C₁-C₆ alkyl, said R is substituted with one to three halogen atoms.

13. The compound according to claim 11, wherein, when R₁ is phenyl, said R₁ is substituted with one to three halogen atoms.

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14. A method for controlling insects and acarina which comprises contacting said insects and acarina, their breeding grounds, food supply or habitat with an insecticidally or acaricidally effective amount of a bis- or tris(trifluoromethyl)arylpyrrole compound as described in any one of claims 1 to 13.

15. The method according to Claim 14, the compound is selected from the group consisting of 2-bromo-5-(p-chlorophenyl)-3,4-bis(trifluoromethyl)pyrrole; 3-bromo-2-(p-chlorophenyl)-4,5-bis(trifluoromethyl)pyrrole-1-carbonitrile; 3-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-4,5-bis(trifluoromethyl)pyrrole; 3-bromo-2-(p-chlorophenyl)-4,5-bis(trifluoromethyl)pyrrole; 3-bromo-5-(p-chlorophenyl)-2,4-bis(trifluoromethyl)pyrrole; 3-(p-chlorophenyl)2,4,5-tris(trifluoromethyl)pyrrole; 3-bromo-2-(3,4-dichlorophenyl)-4,5-bis(trifluoromethyl)pyrrole; 3-bromo-2-(3,4-dichlorophenyl)-4,5-bis(trifluoromethyl)pyrrole-1-carbonitrile; 3-bromo-2-(3,4-dichlorophenyl)-1-(ethoxymethyl)-4,5-bis(trifluoromethyl)pyrrole; 3-bromo-4-(p-chlorophenyl)-2,5-bis(trifluoromethyl)pyrrole; 3-bromo-2-(3,4-dichlorophenyl)-1-methyl-4,5-bis(trifluoromethyl)pyrrole; 3-bromo-2-(3,4-dichlorophenyl)-1-(1-isopropoxyethyl)-4,5-bis(trifluoromethyl)pyrrole; 3-bromo-4,5-bis(trifluoromethyl)-2-(α - α - α -trifluoro-p-tolyl)pyrrole; and 3-bromo-1-(ethoxymethyl)-4,5-bis(trifluoromethyl)-2-(α - α - α -trifluoro-p-tolyl)pyrrole.

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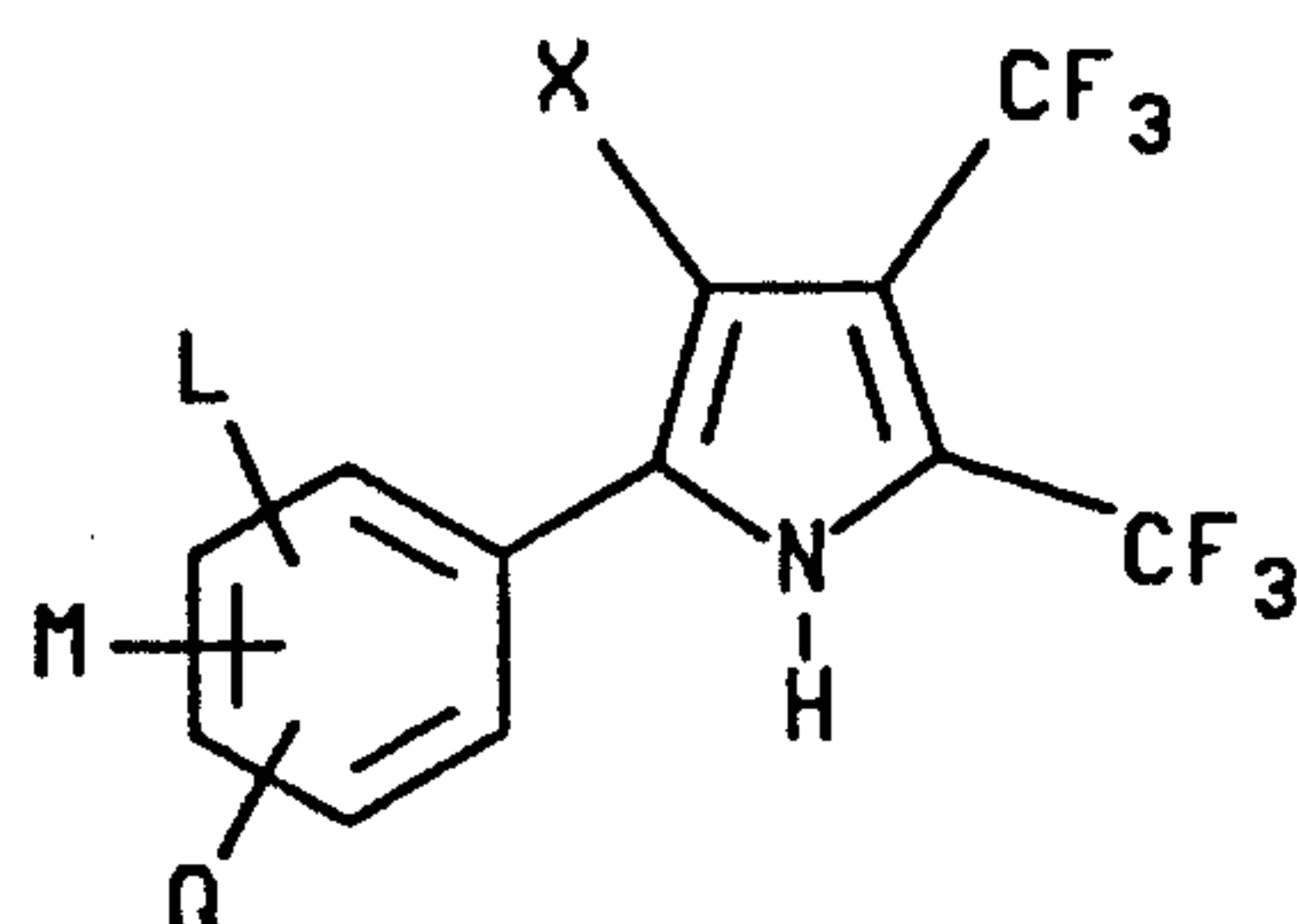
16. A composition for controlling insects and acarina comprising an agronomically acceptable carrier and an insecticidally or acaricidally effective amount of a bis- or tris(trifluoromethyl)arylpyrrole compound as described in any one of claims 1 to 13.

17. A method for protecting growing plants from attack by insects and acarina which comprises applying to the foliage of said plants or to the soil or water in which they are growing an insecticidally or acaricidally effective amount of a bis- or tris(trifluoromethyl)arylpyrrole compound as described in any one of claims 1 to 13.

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18. A method for the preparation of a first compound having the structure

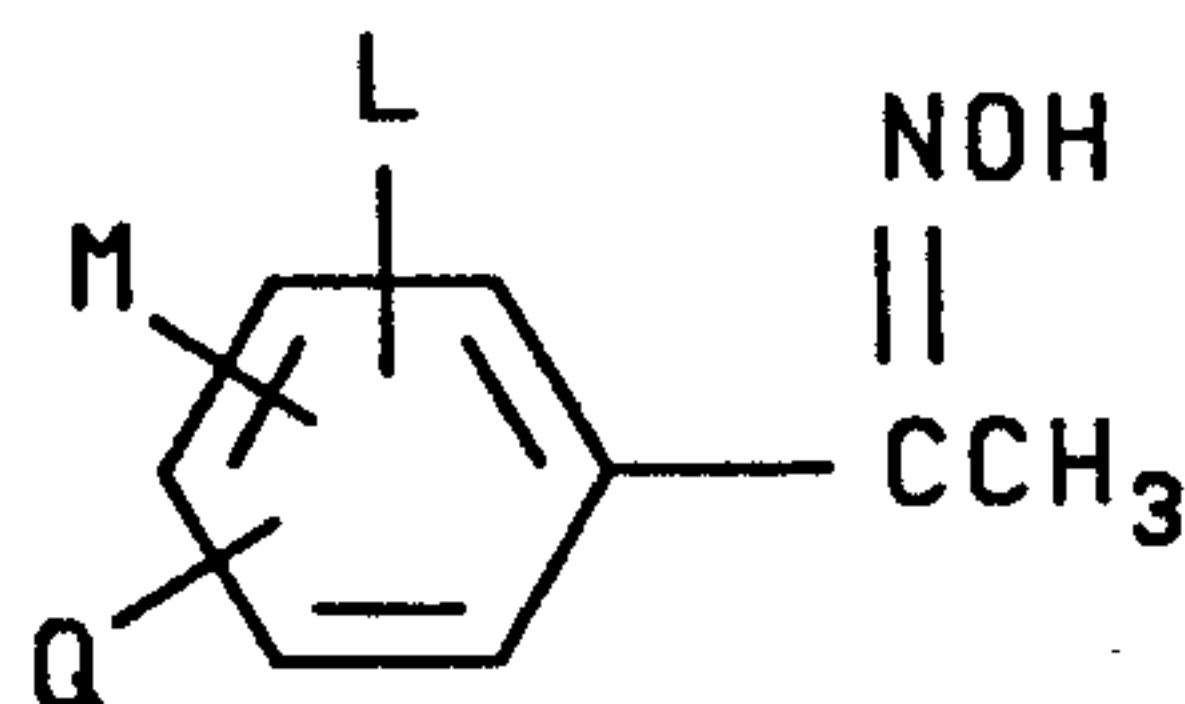


wherein

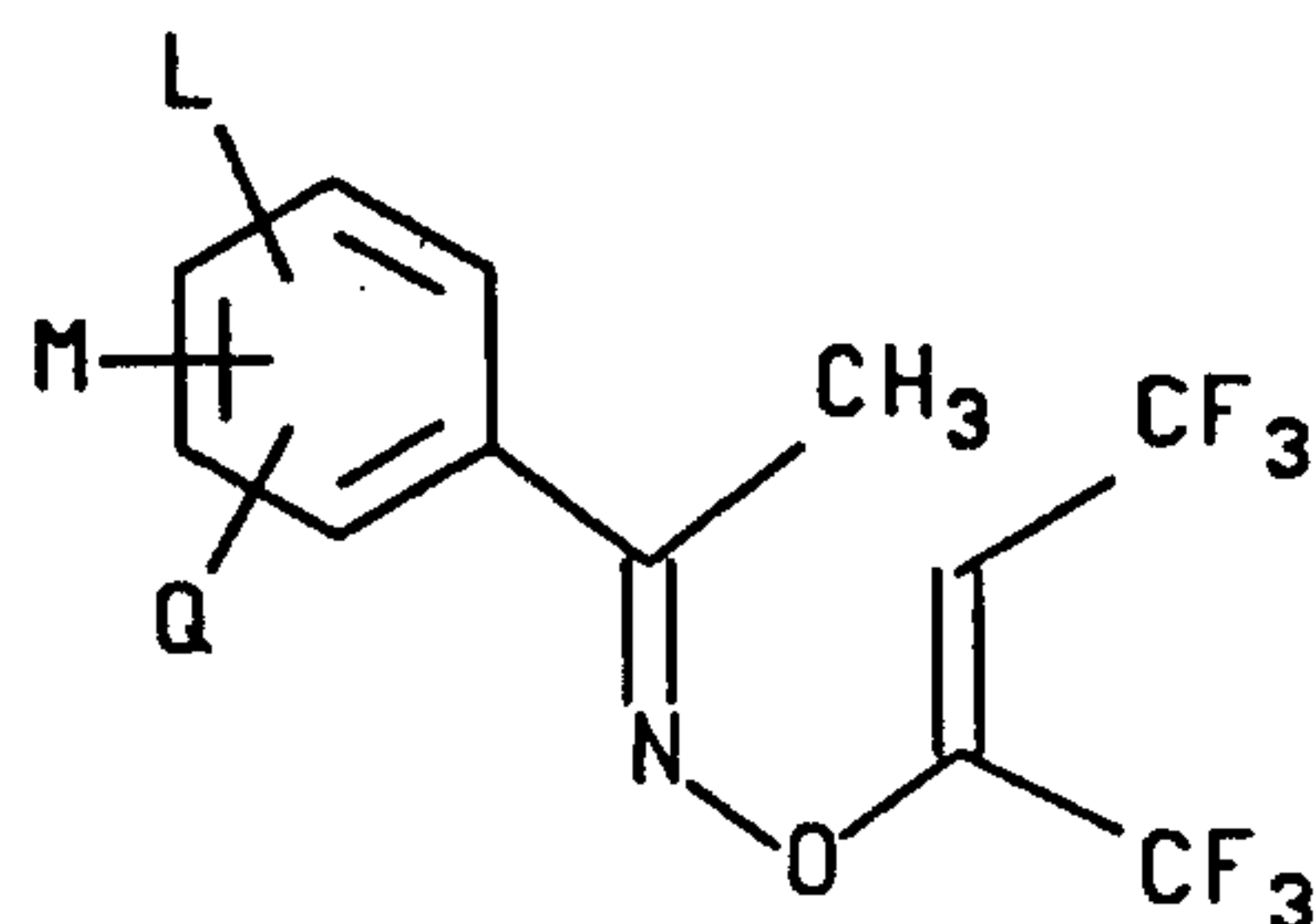
L is H, Cl, Br or F;

M and Q are each independently H, F, Cl, Br, CN, NO₂, CF₃, C₁-C₄ alkyl or C₁-C₃ alkoxy; and

X is Cl, Br or I; which comprises reacting an acetophenone oxime having the structure



wherein L, M, and Q are as described above with hexafluoro-2-butyne and a base in the presence of a solvent to obtain an O-[1,2-bis(trifluoromethyl)vinyl]acetophenone oxime, vinyl-(Z) having the structure

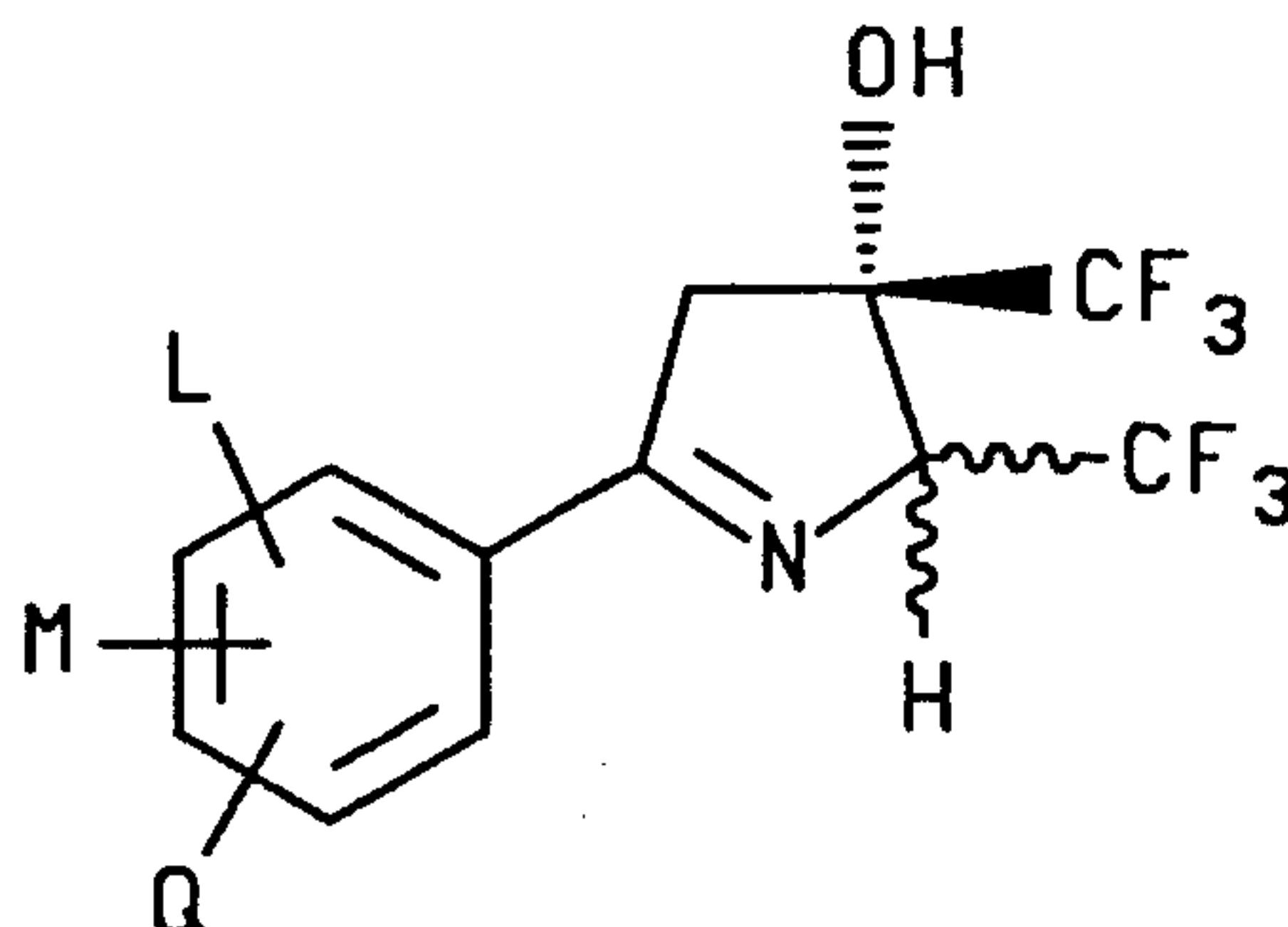


wherein L, M and Q are as described above and heating the thus formed O-[1,2-bis(trifluoromethyl)vinyl]acetophenone oxime, vinyl-(Z) in the presence of a solvent at an elevated temperature to yield a

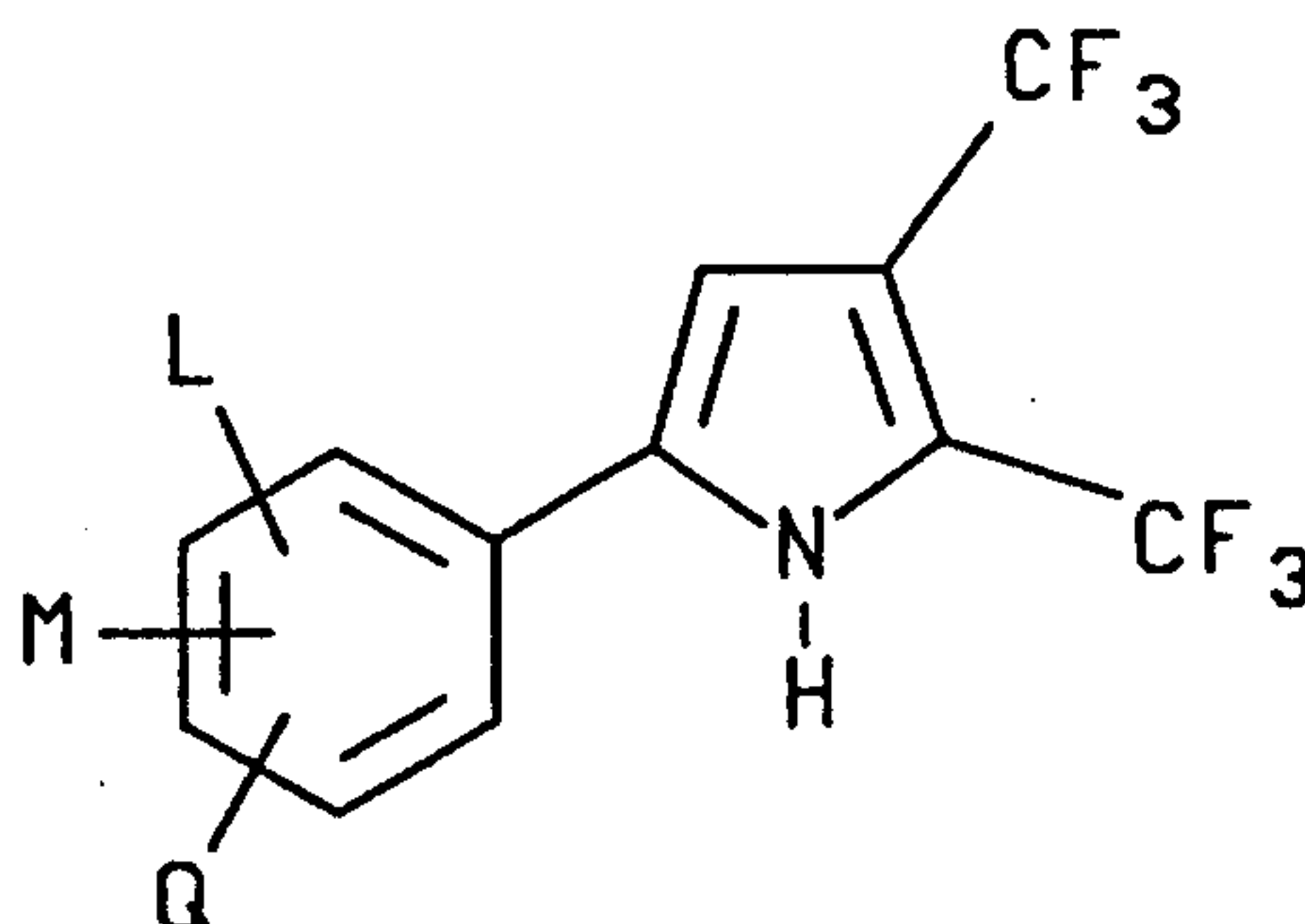
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2-aryl-4,5-bis(trifluoromethyl)-1- pyrrolin-4-ol,
trans- and cis- intermediate compound having the
structure



wherein L, M and Q are as described above and reacting
said intermediate compound with hydrochloric acid in an
alcohol to give a 5-aryl-2,3-bis(trifluoromethyl)-
pyrrole having the structure

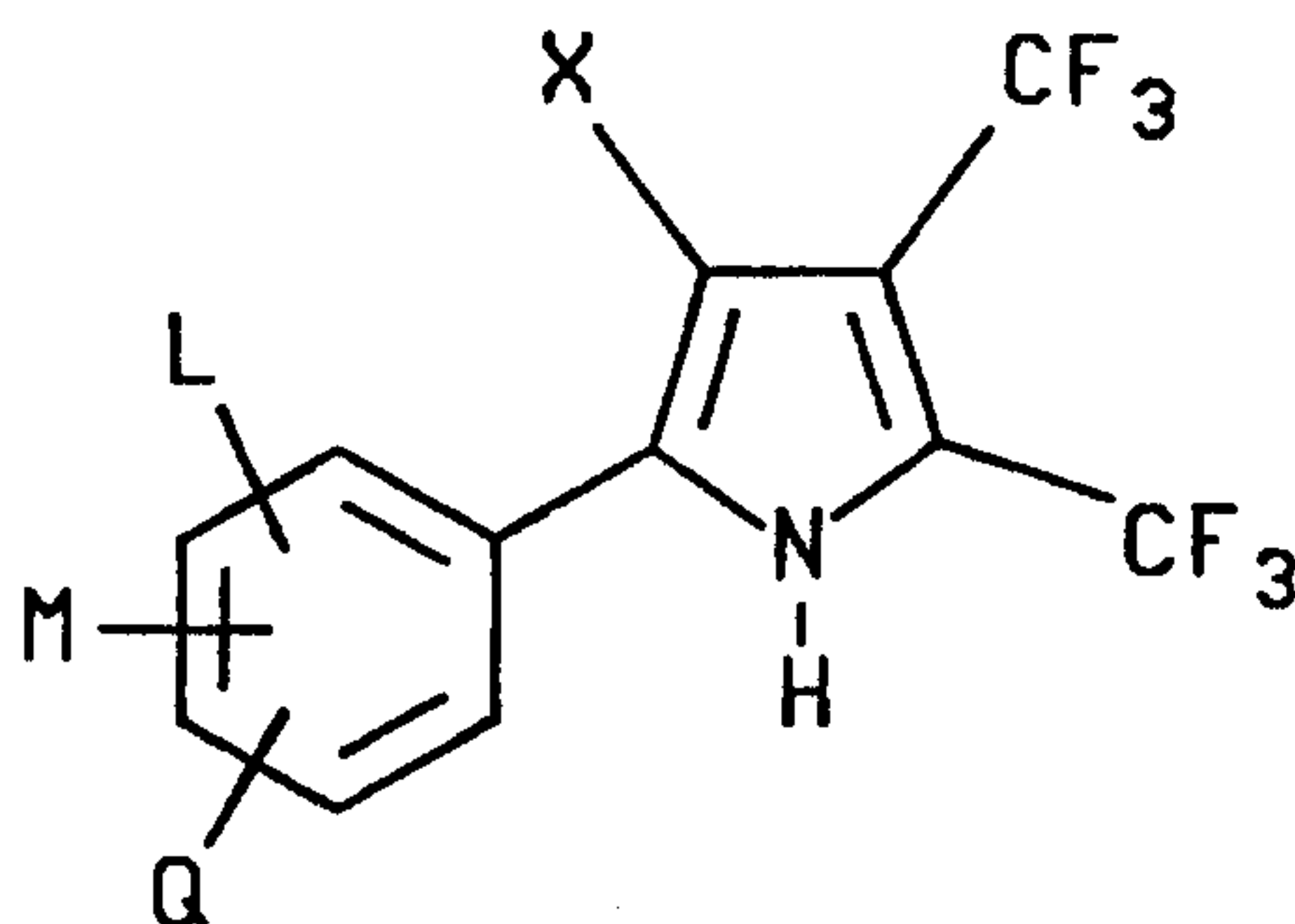


wherein L, M and Q are as described above and reacting
said 5-aryl-2,3-bis(trifluoromethyl)pyrrole with a
halogenating agent to yield said first compound.

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19. A method for the preparation of a first compound having the structure

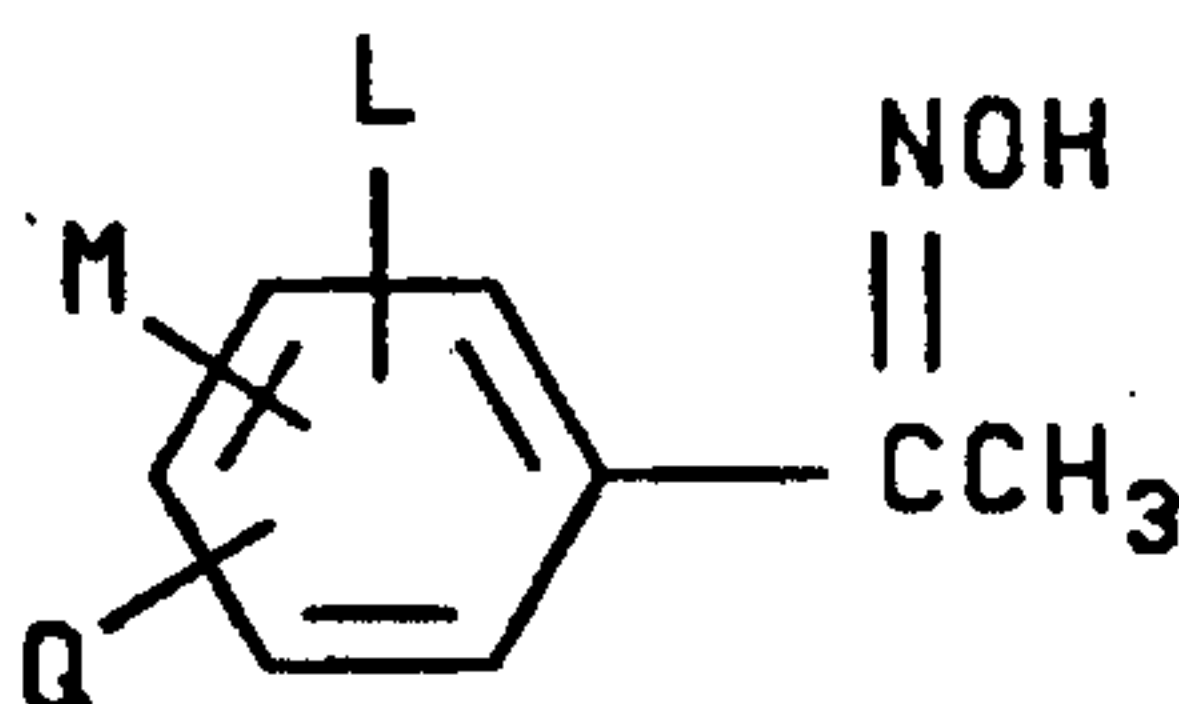


wherein

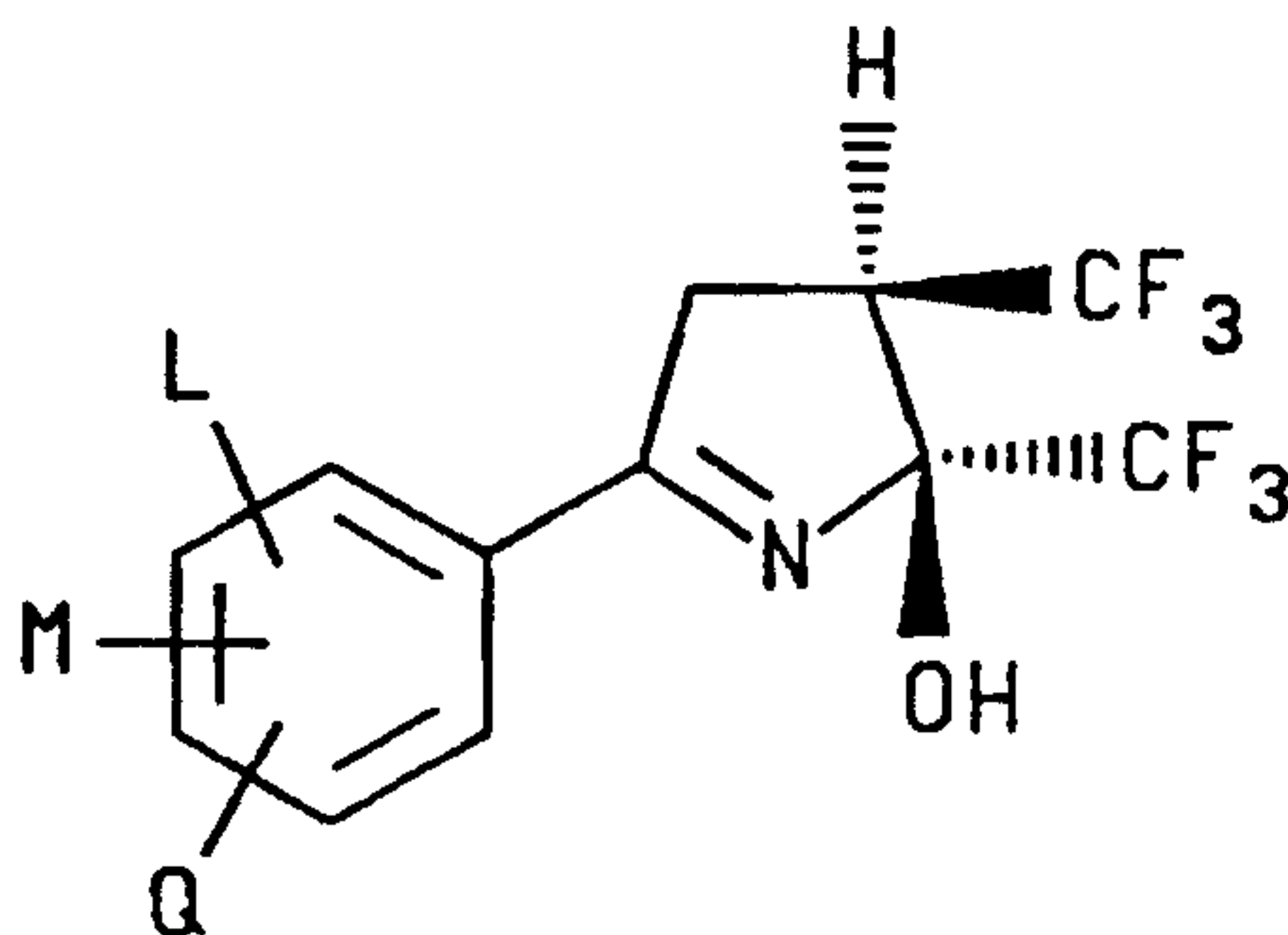
L is H, Cl, Br or F;

M and Q are each independently H, F, Cl, Br, CN, NO₂, CF₃, C₁-C₄ alkyl or C₁-C₃ alkoxy; and

X is Cl, Br or I; which comprises reacting an acetophenone oxime having the structure



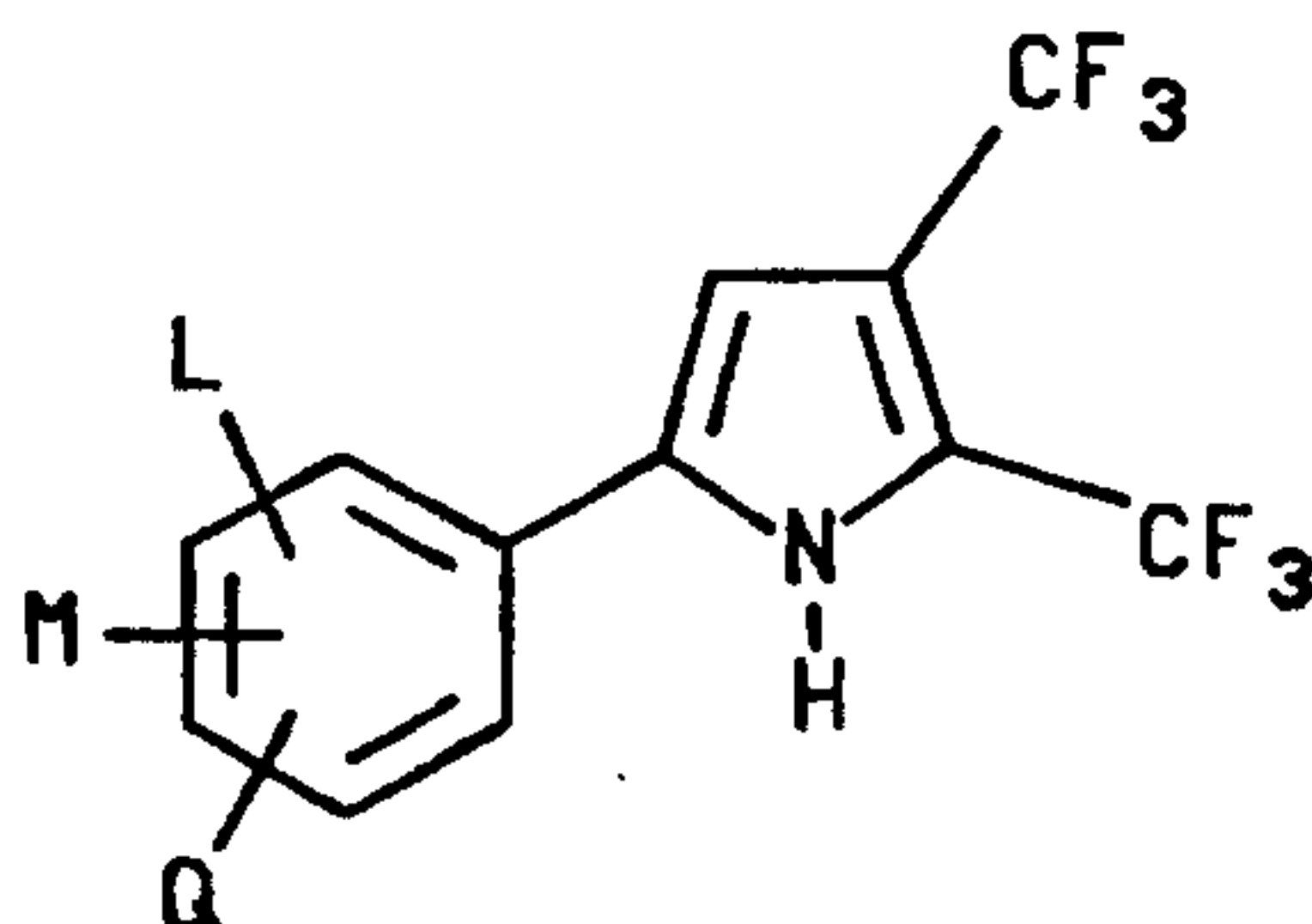
wherein L, M, and Q are as described above with hexafluoro-2-butyne and a base in the presence of a solvent to obtain a 2-aryl-4,5-trans-bis(trifluoromethyl)-1-pyrrolin-5-ol intermediate compound having the structure



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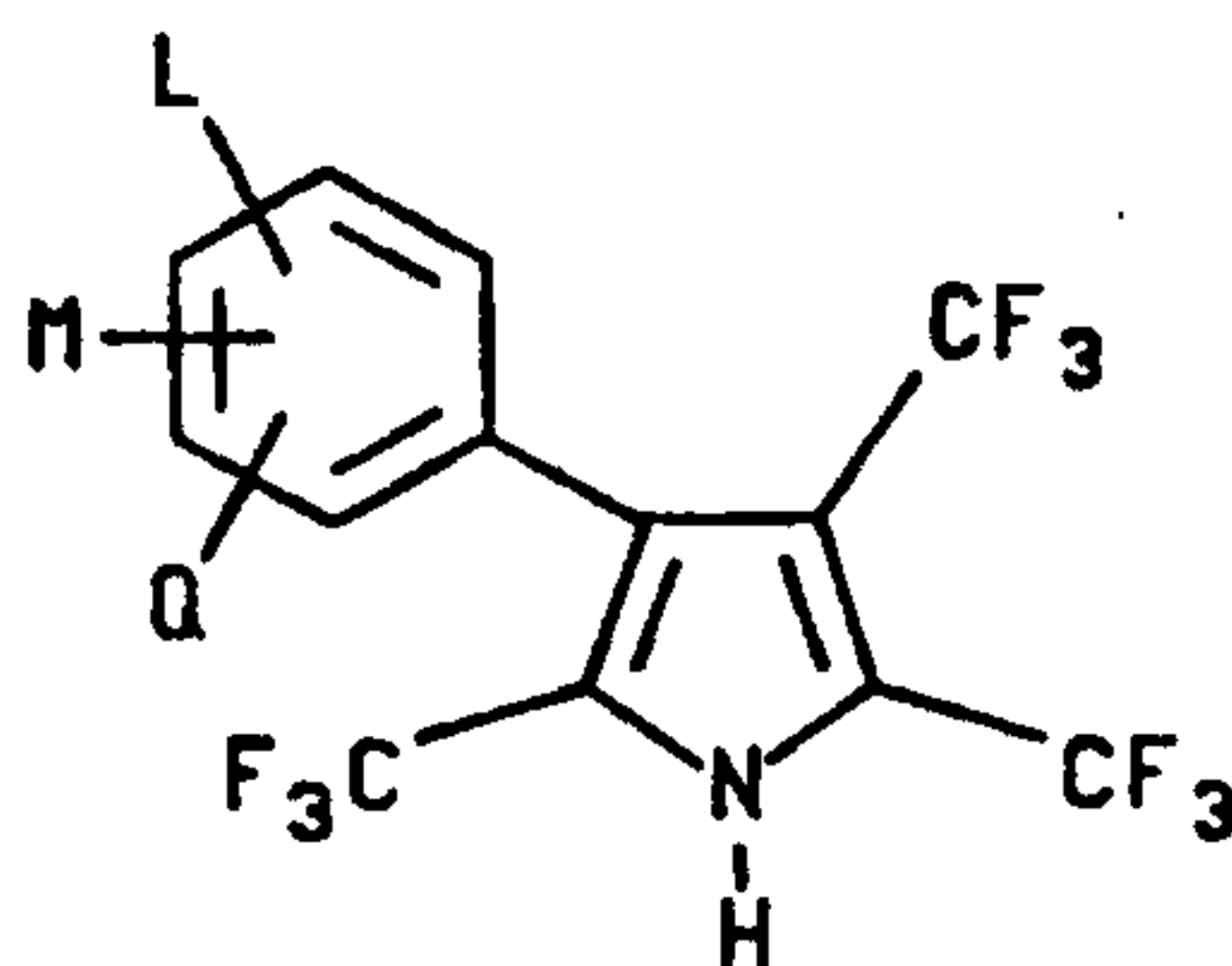
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wherein L, M and Q are as described above and reacting said intermediate compound with hydrochloric acid in an alcohol to give a 5-aryl-2,3-bis(trifluoromethyl)-pyrrole having the structure



wherein L, M and Q are as described above and reacting the resultant 5-aryl-2,3-bis(trifluoromethyl)pyrrole with a halogenating agent to form said first compound.

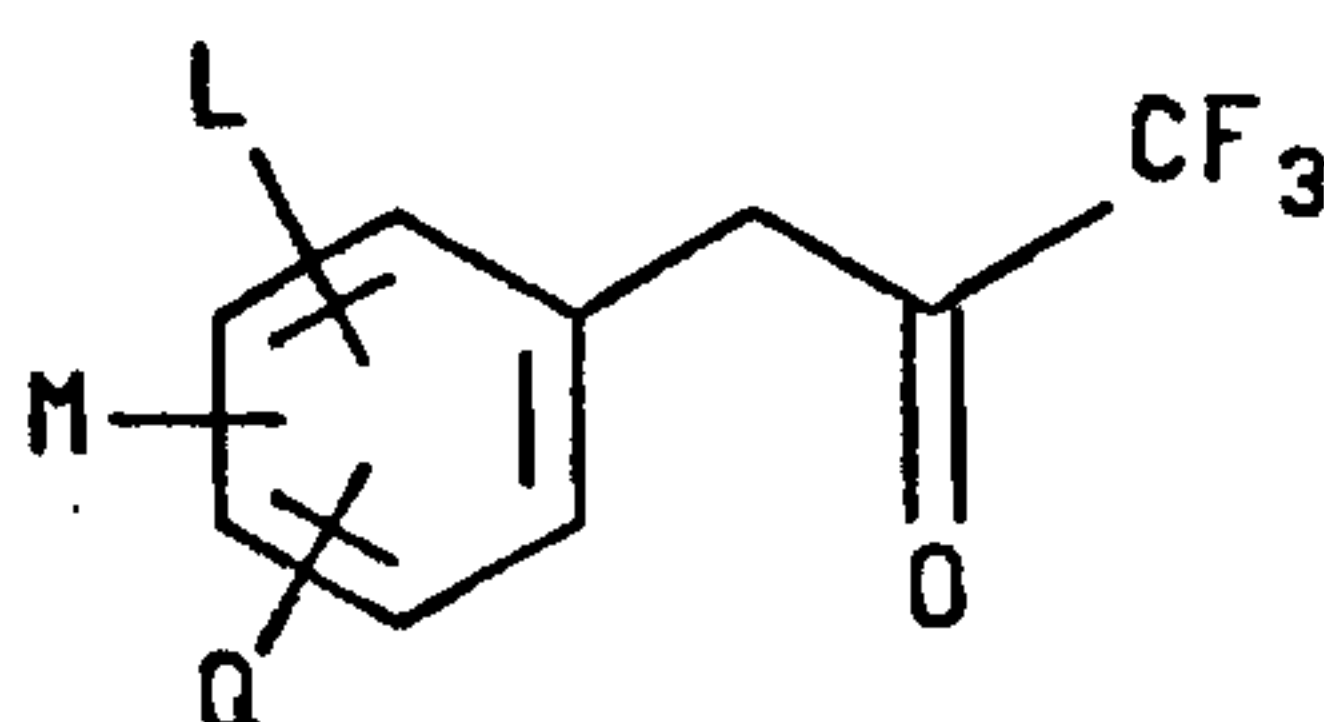
20. A method for the preparation of a first compound having the structure



wherein

L is H, Cl, Br or F; and

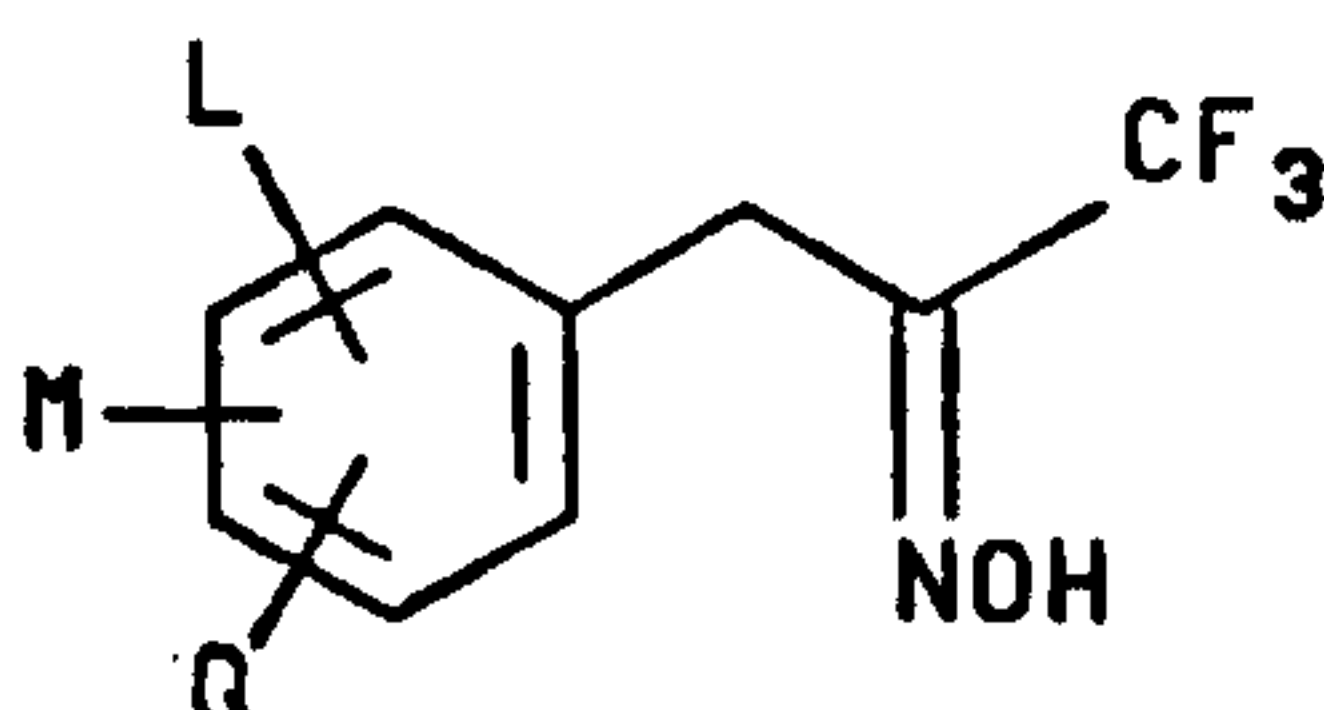
M and Q are each independently H, F, Cl, Br, CN, NO₂, CF₃, C₁-C₄ alkyl or C₁-C₃ alkoxy; which comprises reacting a 3-aryl-1,1,1-trifluoro-2-propanone having the structure



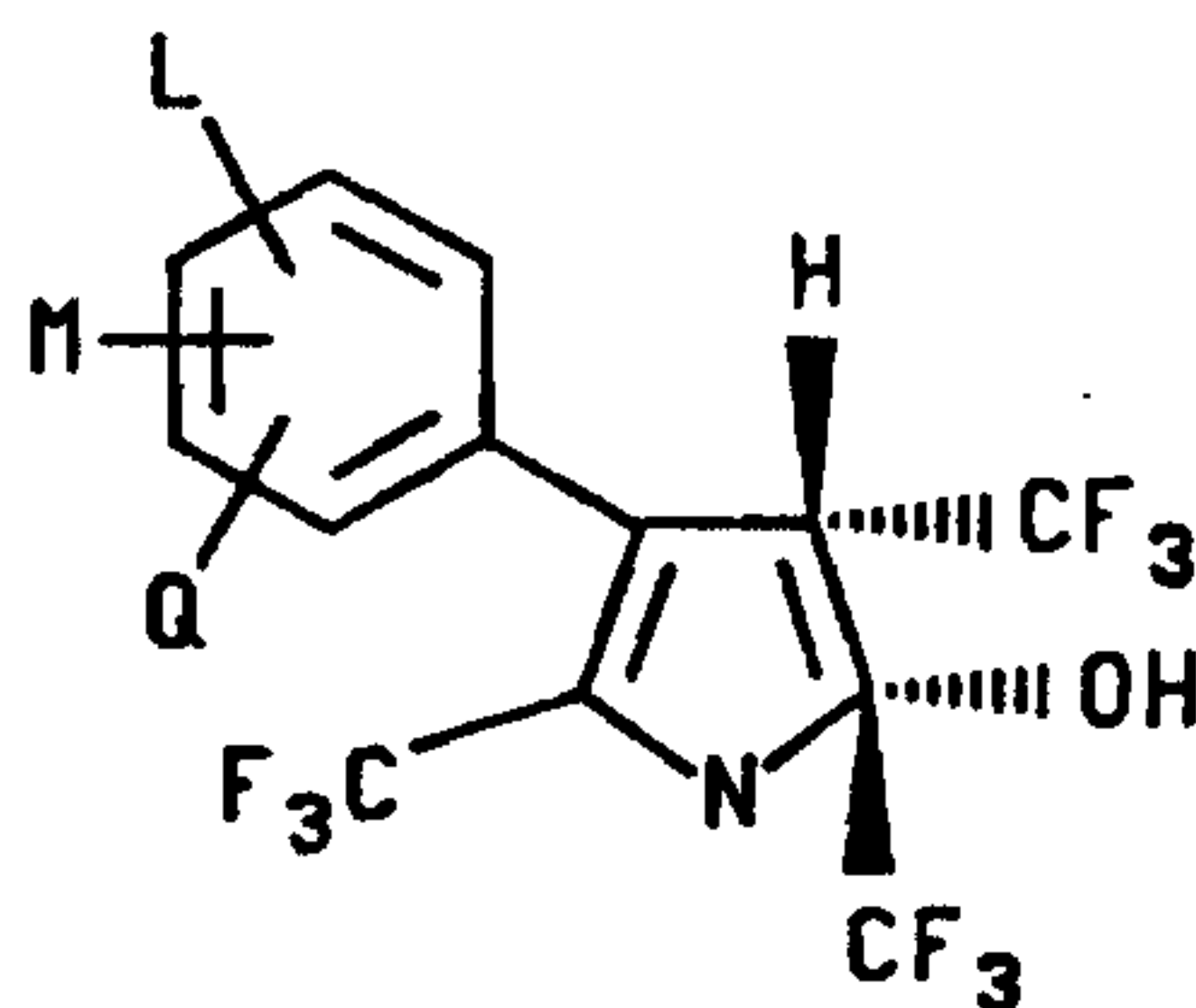
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wherein L, M, and Q are as described above with hydroxylamine hydrochloride in the presence of a solvent at an elevated temperature to obtain a 3-aryl-1,1,1-trifluoro-2-propanone, oxime having the structure



wherein L, M, and Q are as described above; reacting the thus obtained 3-aryl-1,1,1-trifluoro-2-propanone, oxime with hexafluoro-2-butyne and a base in the presence of a solvent of an elevated temperature to give a 3-aryl-5- α -hydroxy-2,4- α ,5 β -tris(trifluoromethyl)-1-pyrroline intermediate compound having the structure

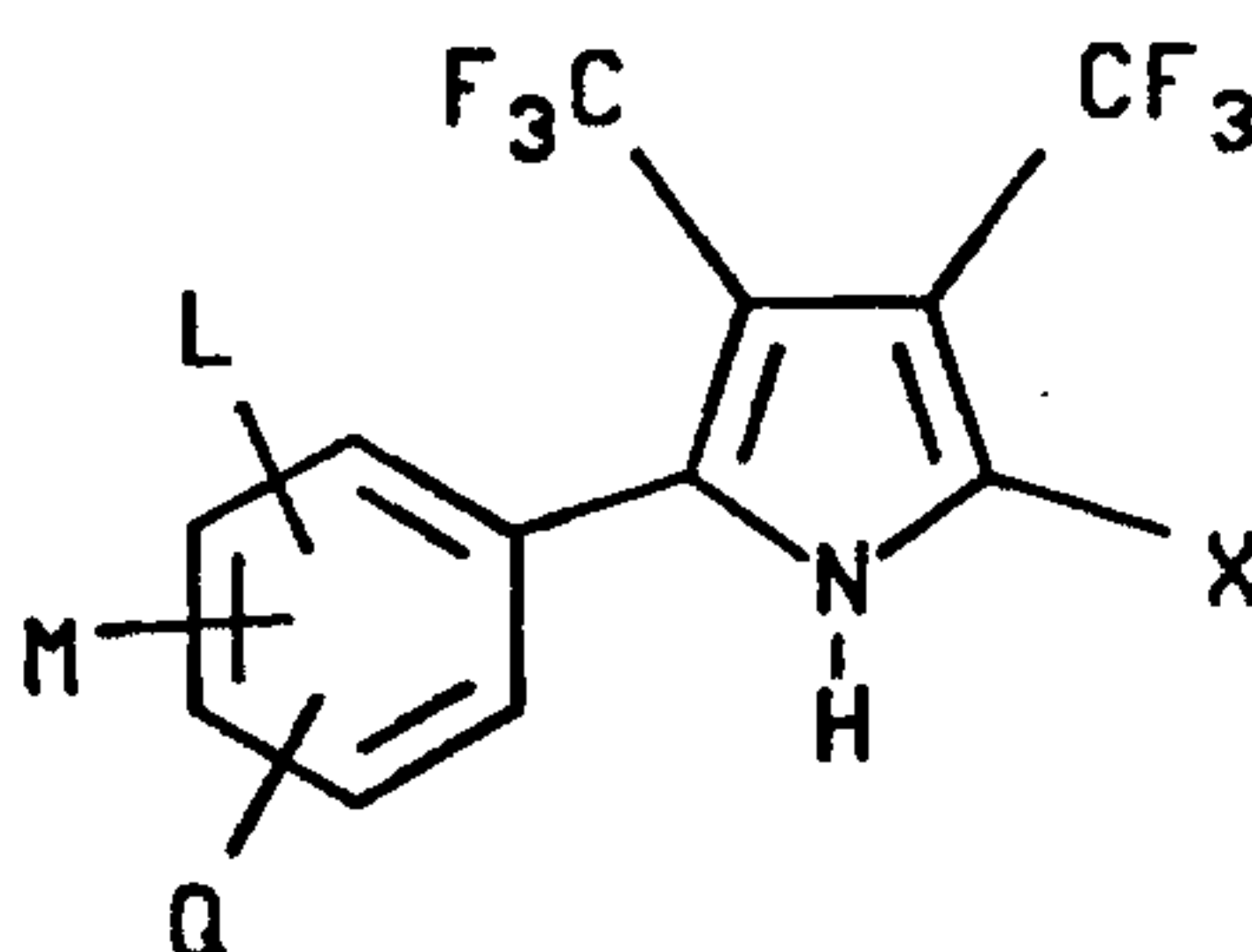


wherein L, M and Q are as described above; and reacting the intermediate compound with hydrochloric acid in the presence of an alcohol to yield said first compound.

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21. A method for the preparation of a first compound having the structure

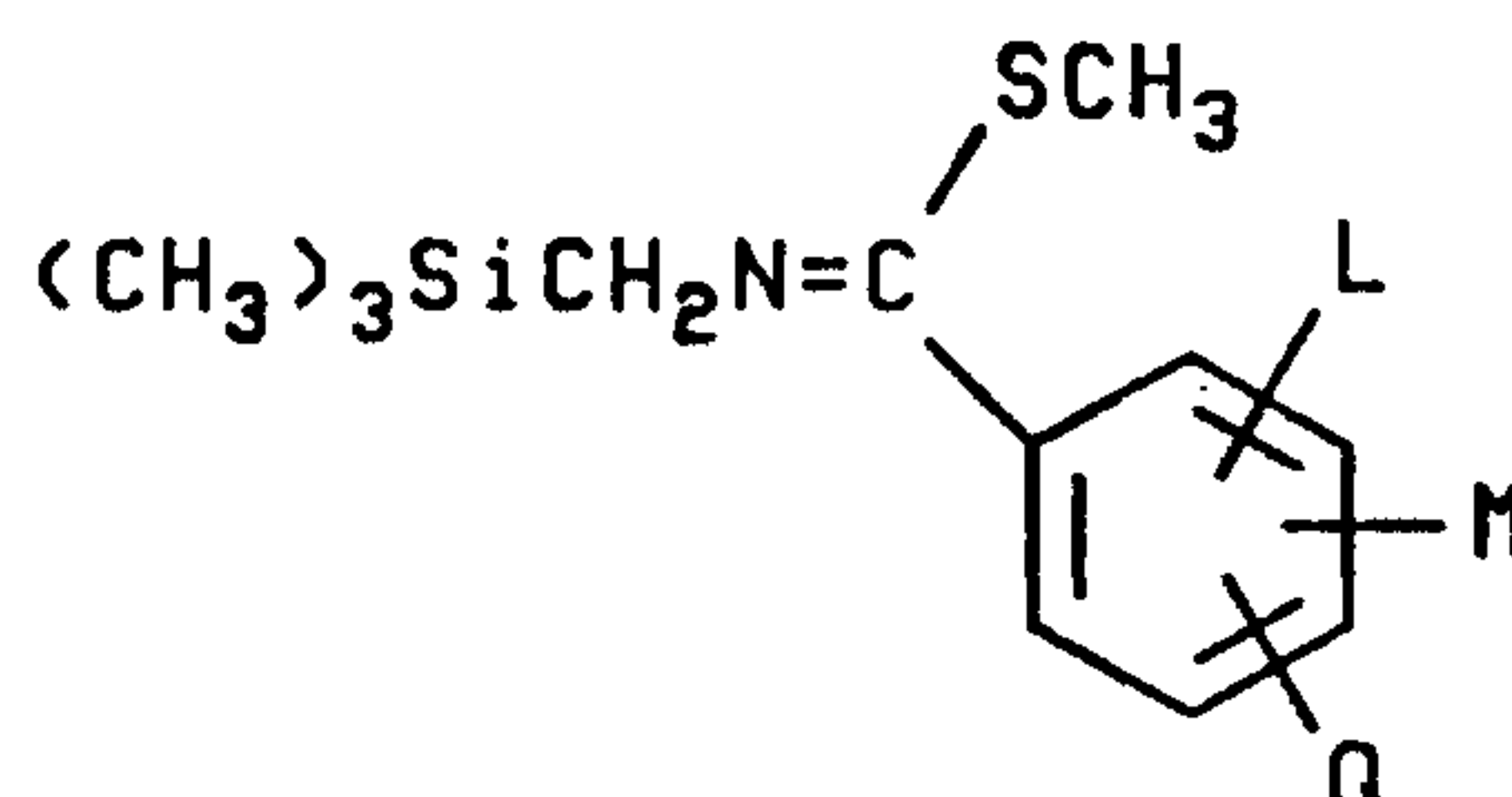


wherein

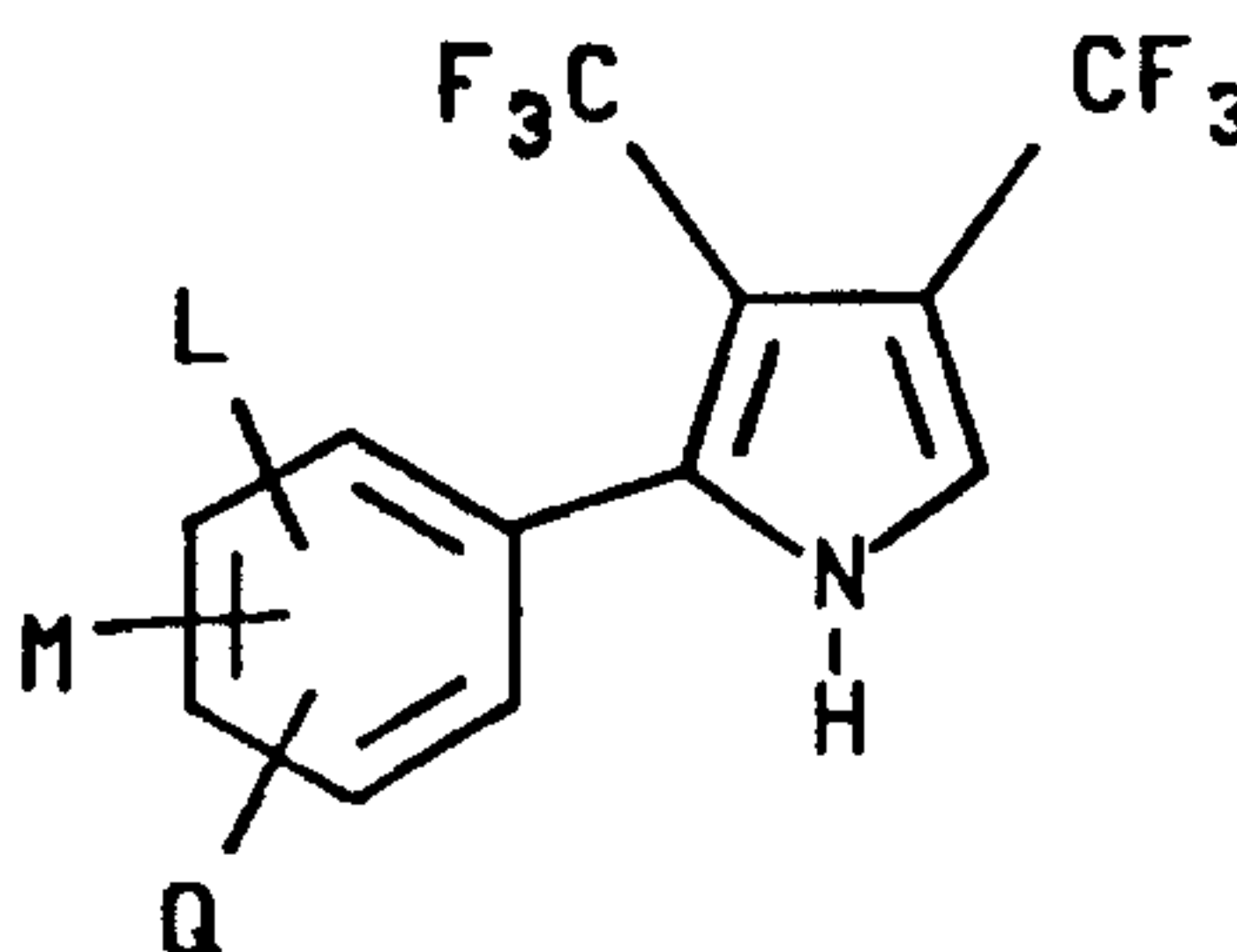
L is H, Cl, Br or F;

M and Q are each independently H, F, Cl, Br, CN, NO₂, CF₃, C₁-C₄ alkyl or C₁-C₃ alkoxy; and

X is Cl, Br or I; which comprises reacting a methyl N-[(trimethylsilyl)methyl]thiobenzimidate having the structure



wherein L, M and Q are as described above with 2,3-dichloro-hexafluorobutene in a solvent to give a 2-aryl-3,4-bis(trifluoromethyl)pyrrole intermediate compound having the structure

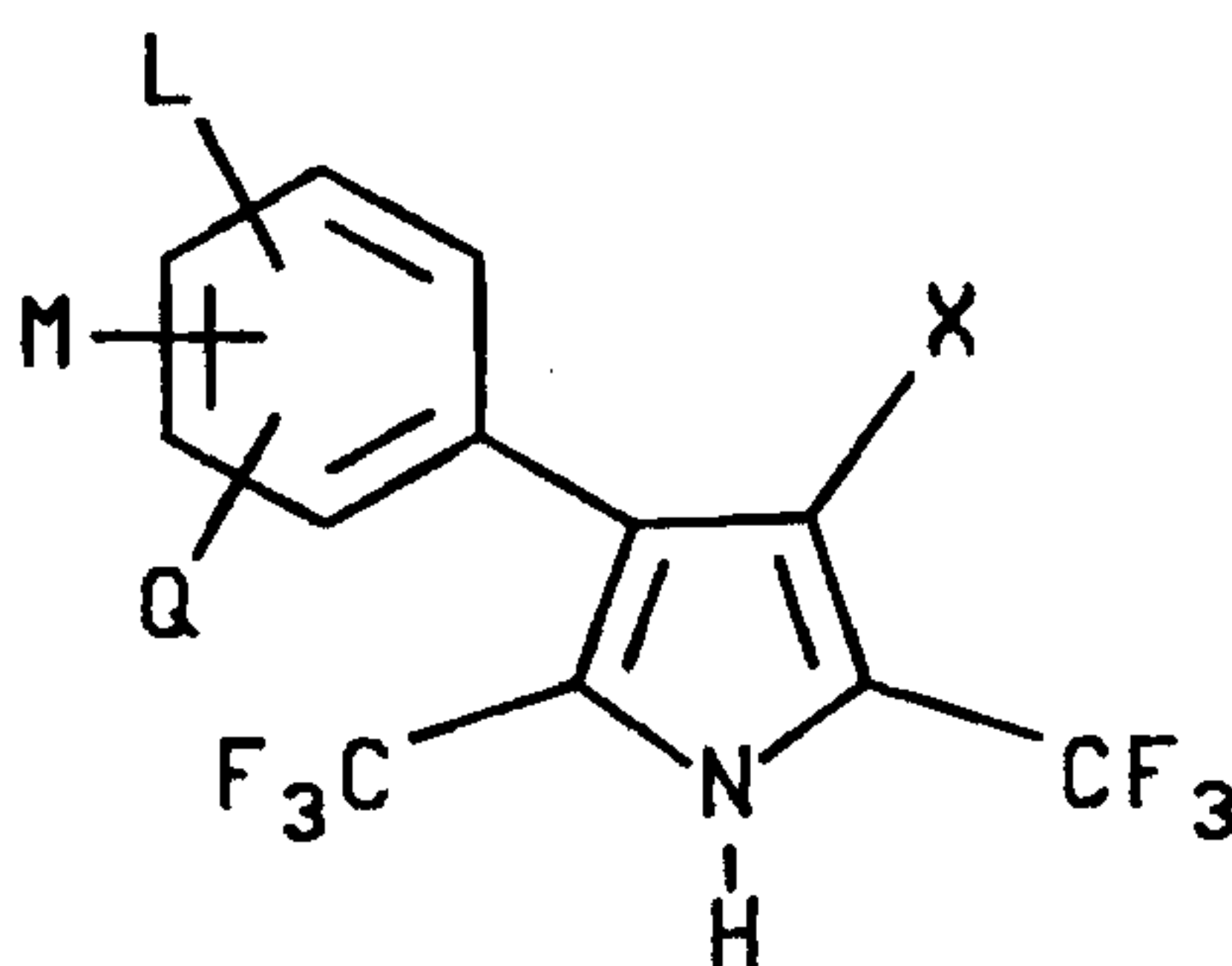


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wherein L, M and Q are as described above and reacting the resultant intermediate compound with a halogenating agent to give said first compound.

22. A method for the preparation of a first compound having the structure

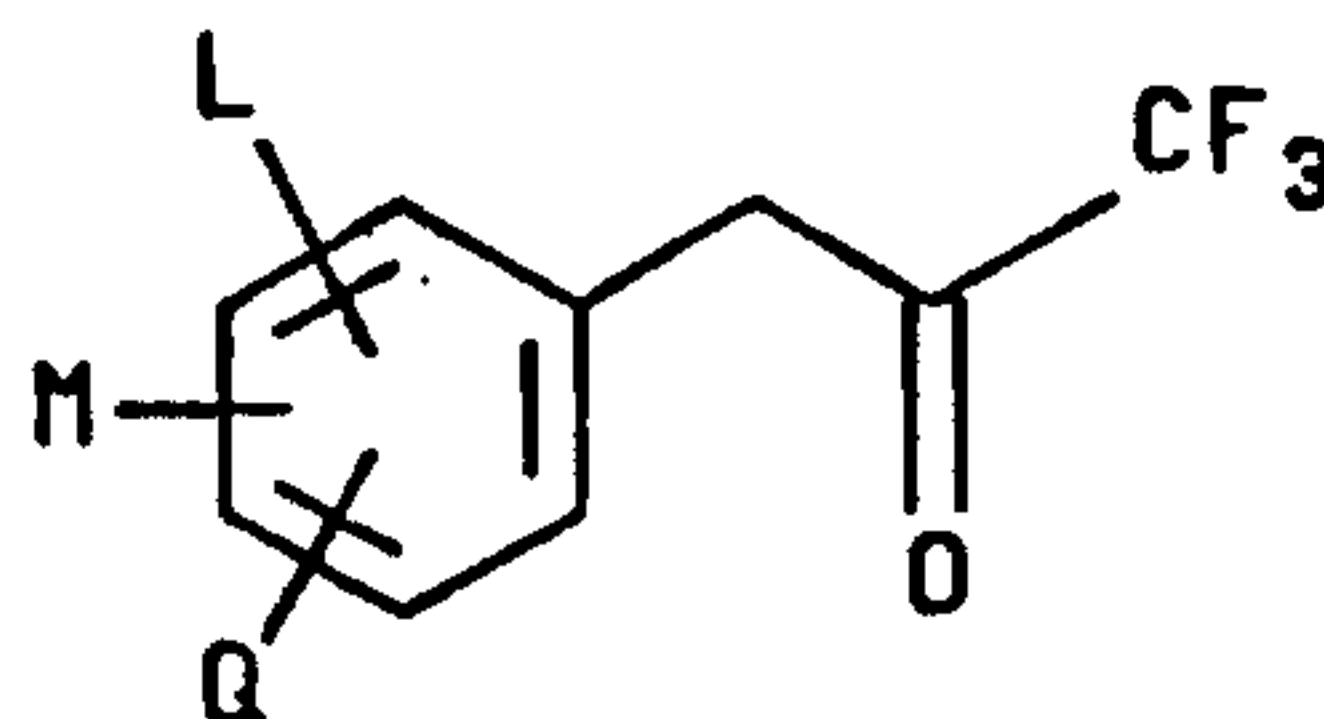


wherein

L is H, Cl, Br or F;

M and Q are each independently H, F, Cl, Br, CN, NO₂, CF₃, C₁-C₄ alkyl or C₁-C₃ alkoxy; and

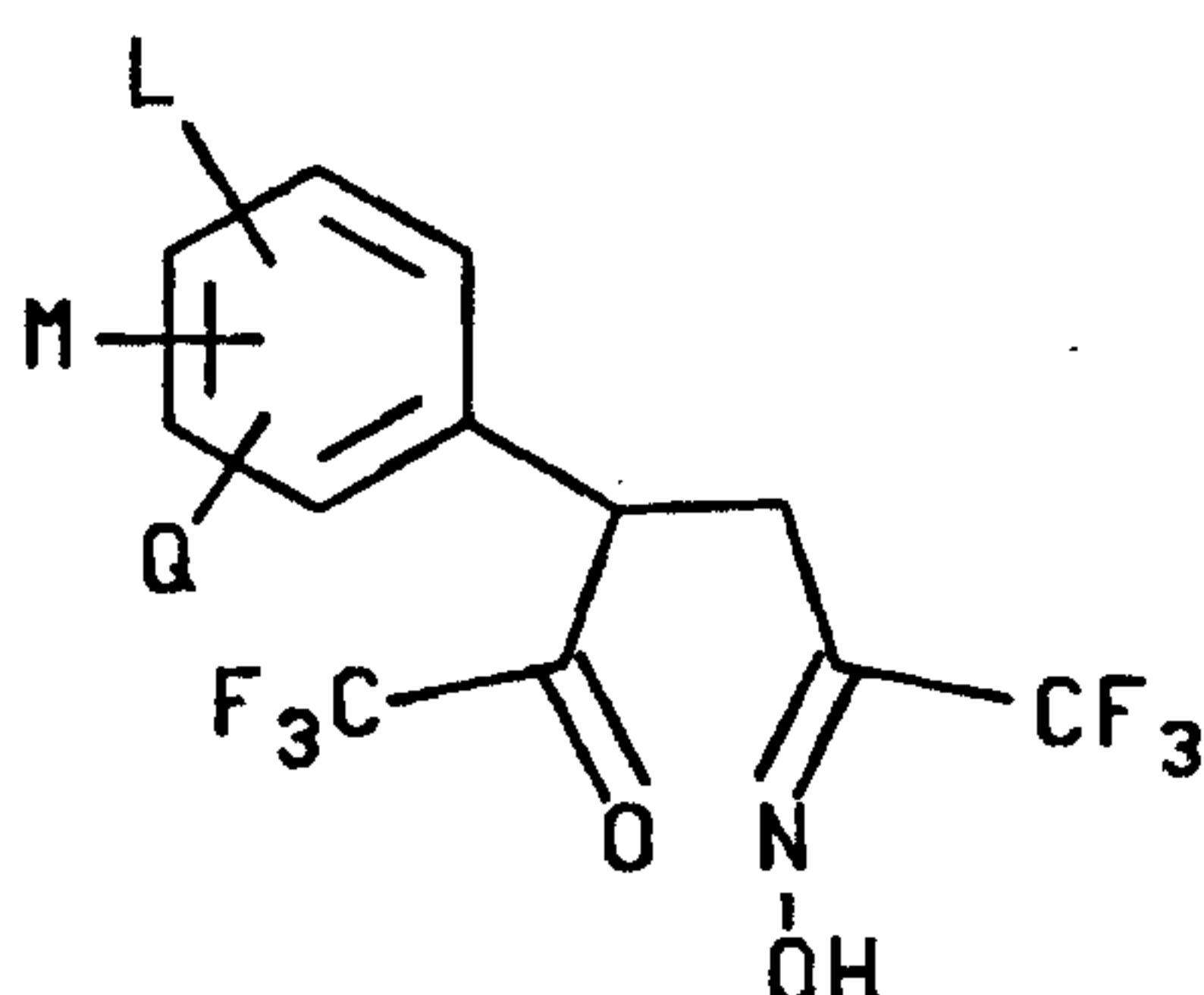
X is Cl, Br or I; which comprises reacting 3-bromo-1,1,1-trifluoropropanone with hydroxylamine hydrochloride in a solvent to obtain 3-bromo-1,1,1-trifluoro-2-propanone, oxime and reacting the 3-bromo-1,1,1-trifluoro-2-propanone, oxime with a 3-aryl-1,1,1-trifluoro-2-propanone having the structure



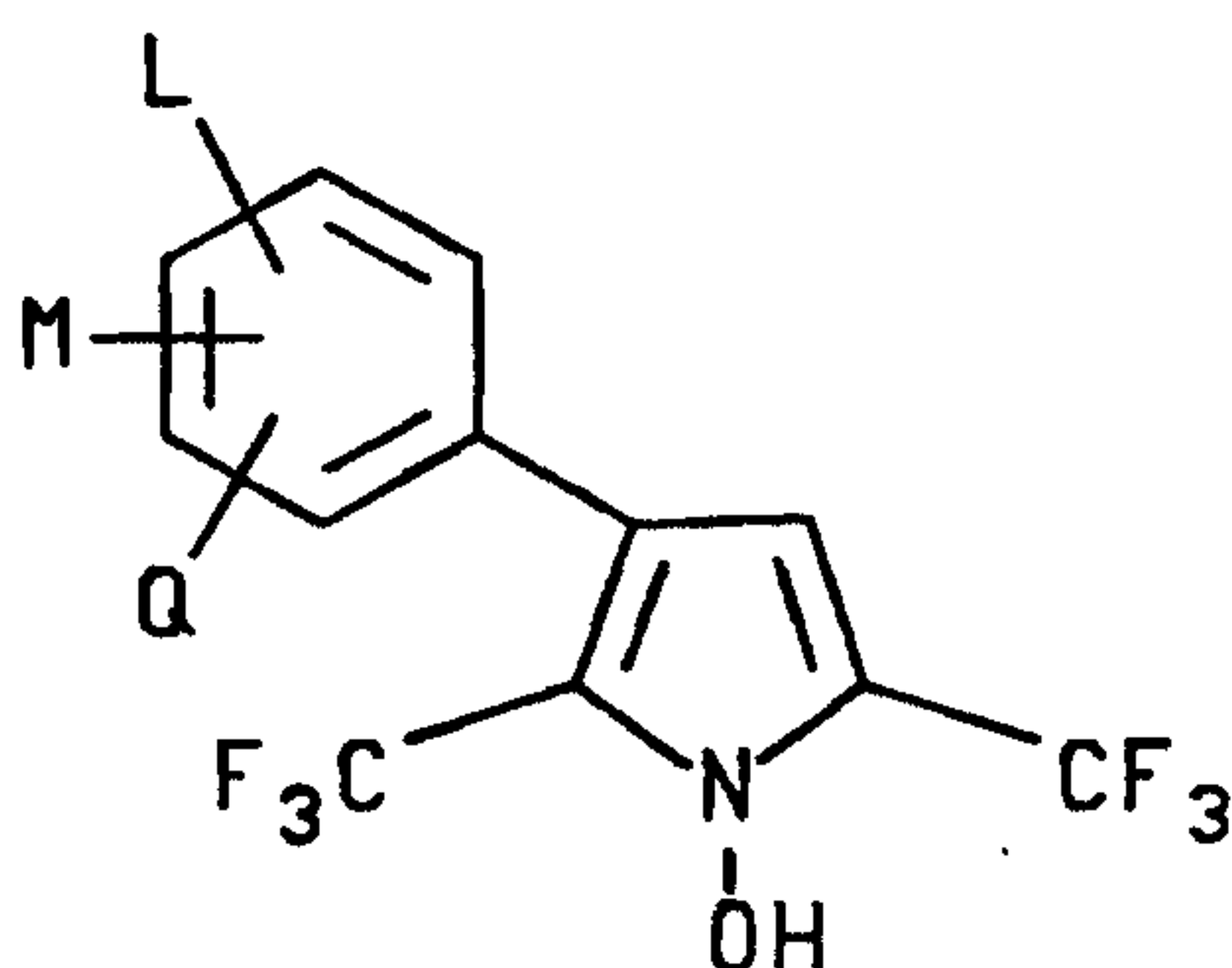
wherein L, M and Q are as described above in the presence of a base to give a 3-aryl-1,1,1,6,6,6-hexafluoro-2,5-hexanedione,5-oxime intermediate compound having the structure

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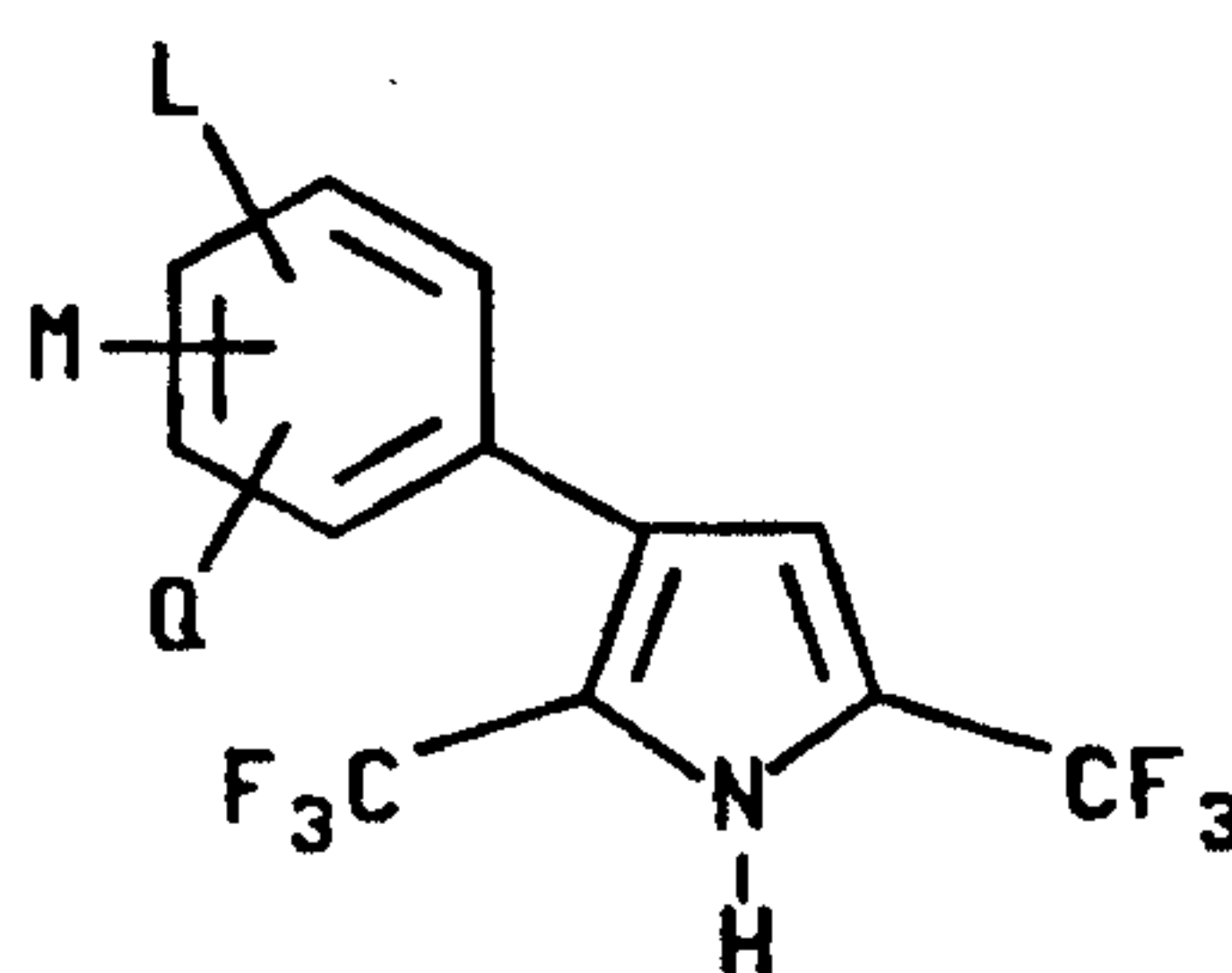
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wherein L, M and Q are as described above; reacting said 5-oxime intermediate compound with hydrochloric acid in an alcohol to yield a 3-aryl-2,5-bis(trifluoromethyl)-1-hydroxypyrrole having the structure



wherein L, M and Q are as described above; reacting said 3-aryl-2,5-bis(trifluoromethyl)-1-hydroxypyrrole with zinc in the presence of acetic acid at an elevated temperature to obtain a 3-aryl-2,5-bis(trifluoromethyl)pyrrole having the structure



wherein L, M and Q are as described above; and reacting said 3-aryl-2,5-bis(trifluoromethyl)pyrrole with a halogenating agent to form said first compound.

