



PROCESS FOR PREPARING NITRILE COMPOUNDS FROM
ETHYLENICALLY UNSATURATED COMPOUNDS

5 The present invention concerns a process for hydrocyanating ethylenically unsaturated organic compounds to compounds containing at least one nitrile function.

10 It relates more particularly to the hydrocyanation of diolefins such as butadiene or of substituted olefins such as alkenenitriles, for instance pentenenitriles. The hydrocyanation of butadiene to pentenenitriles is an important reaction which has been implemented industrially for a number of years, particularly in the
15 process for synthesizing adiponitrile, a major chemical intermediate which allows access in particular to the monomers of numerous polymers, foremost among which are the polyamides.

20 French patent 1 599 761 describes a process for preparing nitriles by addition of hydrocyanic acid with organic compounds having at least one ethylenic double bond, in the presence of a nickel catalyst and a triaryl phosphite. This reaction may be conducted in
25 the presence or absence of a solvent.

When a solvent is used in this prior art process it is preferably a hydrocarbon, such as benzene or xylenes, or a nitrile such as acetonitrile.

30 The catalyst employed is an organometallic complex of nickel, containing ligands such as phosphines, arsines, stibines, antimonites, arsenites, phosphites, phosphinites or phosphonites.

35 The processes for hydrocyanating dienes generally comprise two steps: a first hydrocyanation, leading to branched and linear unsaturated mononitriles, and a second step which allows the dinitriles to be obtained.



Often only the linear nitriles are of interest for the synthesis of new products such as, for example, adiponitrile. These processes therefore also include an intermediate step, which is referred to as the isomerization step and consists in treating the branched unsaturated mononitriles to convert them into linear unsaturated mononitriles.

The presence of a promoter to activate the catalyst, such as a boron compound or a metal salt, generally a Lewis acid, is also recommended for carrying out the second step.

Patent FR-A-2 338 253 proposed carrying out the hydrocyanation of compounds having at least one ethylenic unsaturation in the presence of an aqueous solution of a compound of a transition metal, particularly nickel, palladium or iron, and of a sulphonated phosphine.

The sulphonated phosphines described in said patent are sulphonated triarylphosphines and more particularly sulphonated triphenylphosphines.

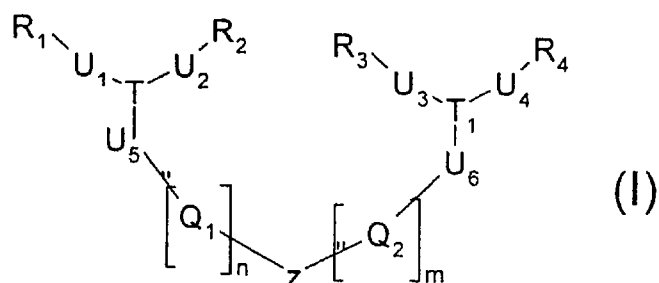
This process permits proper hydrocyanation, particularly of the butadiene and the pentenenitriles, easy separation of the catalytic solution, by simple decanting, and, consequently, goes as far as possible to avoid the discharge of effluent or of waste containing the metals used as catalyst.

Research has nevertheless been conducted in order to find new catalytic systems which give greater performance in terms of catalytic activity and of selectivity and stability.

One of the aims of the present invention is to propose a new class of ligands which with the transition metals make it possible to obtain catalytic systems exhibiting

in particular an improved selectivity to linear nitriles as compared with the known systems.

The present invention accordingly provides a process
 5 for hydrocyanating a hydrocarbon compound containing at least one ethylenic unsaturation by reacting it in a liquid medium with hydrogen cyanide in the presence of a catalyst comprising a metallic element selected from transition metals and an organic ligand, characterized
 10 in that the organic ligand corresponds to the general formula I below:



15 in which:

T and T₁, which are identical or different, represent a phosphorus, arsenic or antimony atom,

20 U₁, U₂, U₃, U₄, U₅ and U₆, which are identical or different, represent an oxygen atom or a radical NR, R representing an alkyl, aryl, sulphonyl or carbonyl radical,

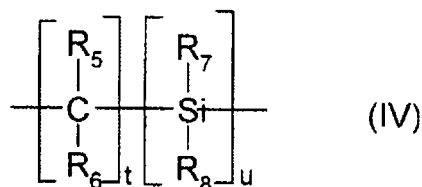
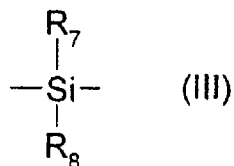
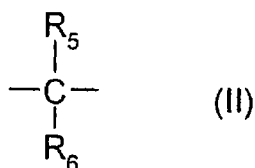
25 R₁, R₂, R₃ and R₄, which are identical or different, represent a substituted or unsubstituted, aromatic, aliphatic or cycloaliphatic radical comprising one or more rings, which are in fused form or not and which may contain one or more heteroatoms, where the radicals
 30 R₁ and R₂ on the one hand, R₃, R₄ and on the other hand may be interconnected by a covalent bond, a hydrocarbon chain or a heteroatom, and, when one of the radicals U₁, U₂, U₃ and U₄ includes an N atom, the associated radical

R₁, R₂, R₃ or R₄ may form a ring including the N element of the said radical,

m and n are identical or different integers between 0 and 6, where m + n must be greater than or equal to 1,

Q₁ and Q₂, which are identical or different, represent a group corresponding to the general formulae II, III or IV below:

10



in which R₅, R₆, R₇ and R₈, which are identical or different, represent aliphatic, cycloaliphatic or aromatic hydrocarbon radicals containing 1 to 12 carbon atoms, R₅ and R₆ also representing the hydrogen atom, and

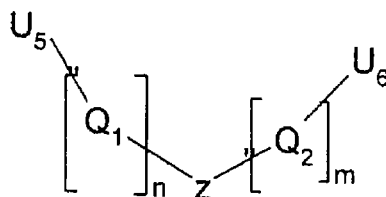
t and u represent integers between 0 and 6, with a sum u + t greater than or equal to 1,

Z representing a divalent radical selected from the group consisting of aromatic or cycloaliphatic radicals containing one or more rings, which are in fused form or not and which may be substituted and may contain

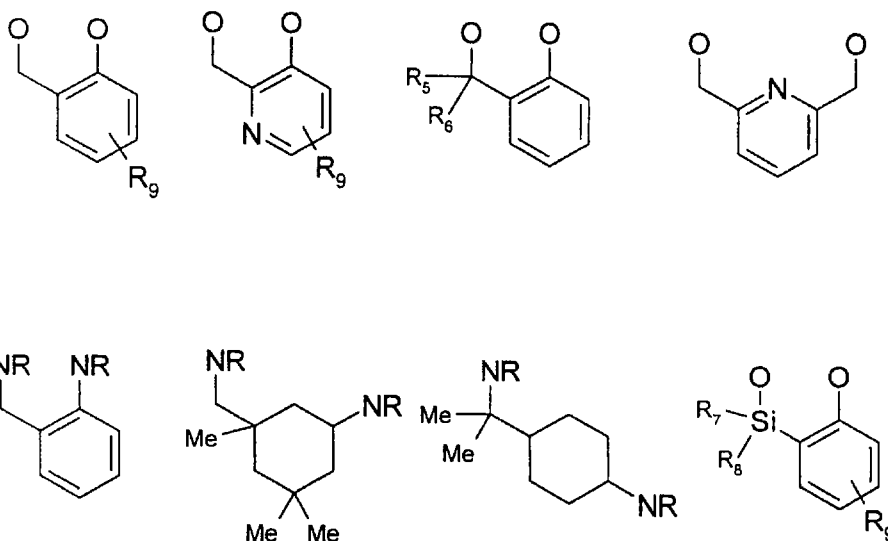
heteroatoms.

Suitable substituents for Z include alkyl, halogen, aryl, alkoxy, aryloxy, nitro, thioalkyl, secondary amine and nitrile groups.

Preferred ligands of the invention include those with the following structure of the formula (I):



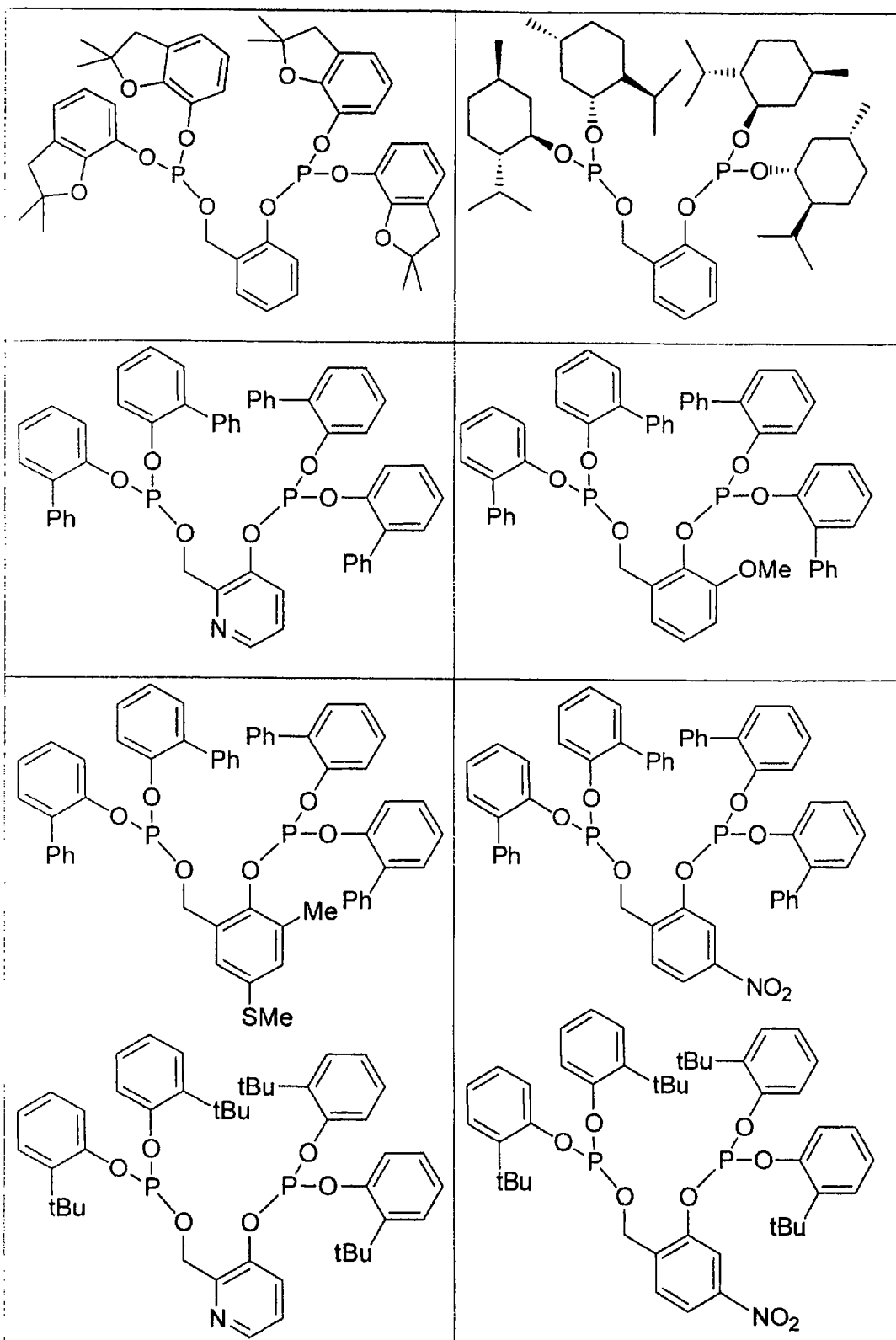
and selected from the group consisting of the following structures:

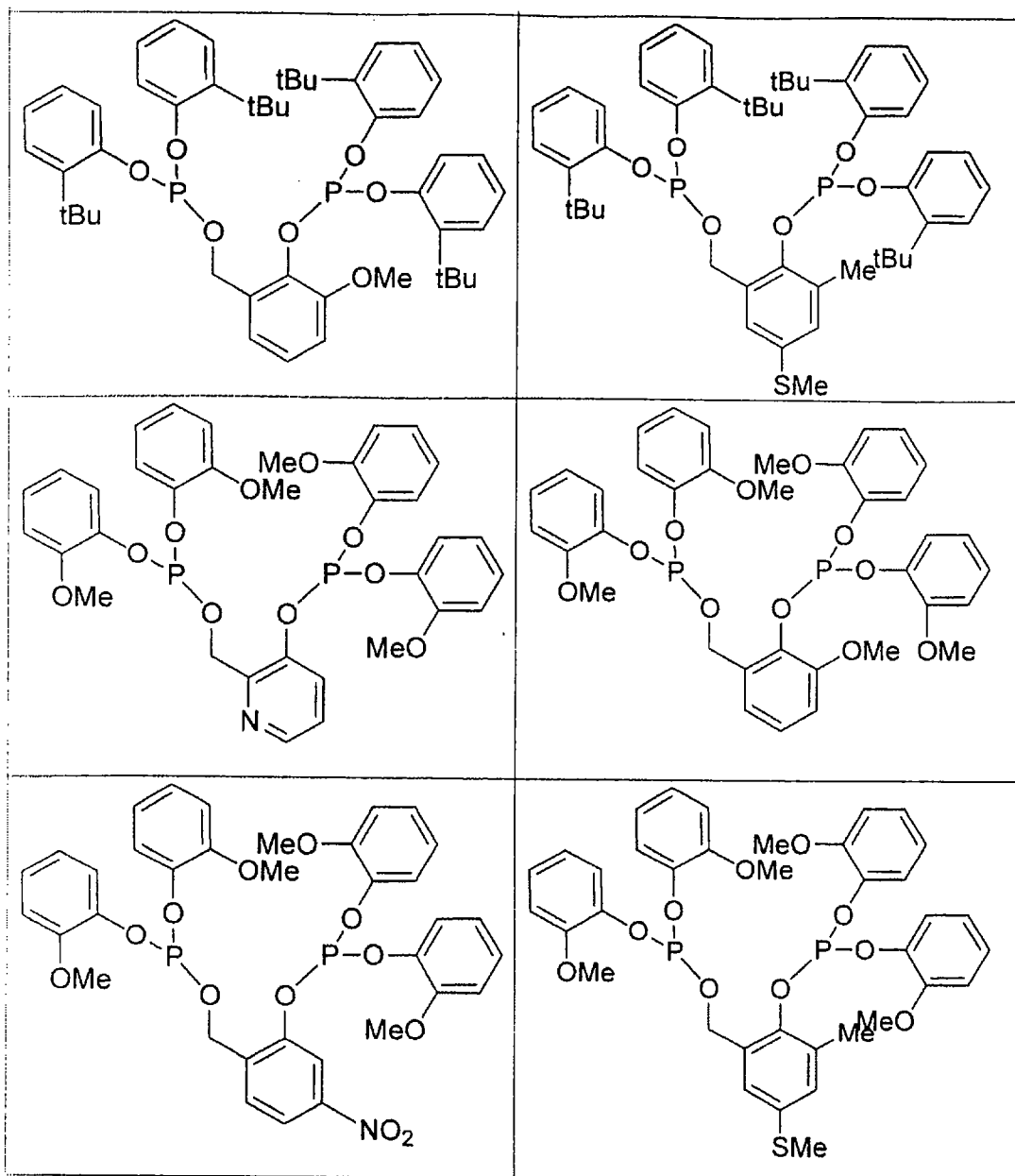


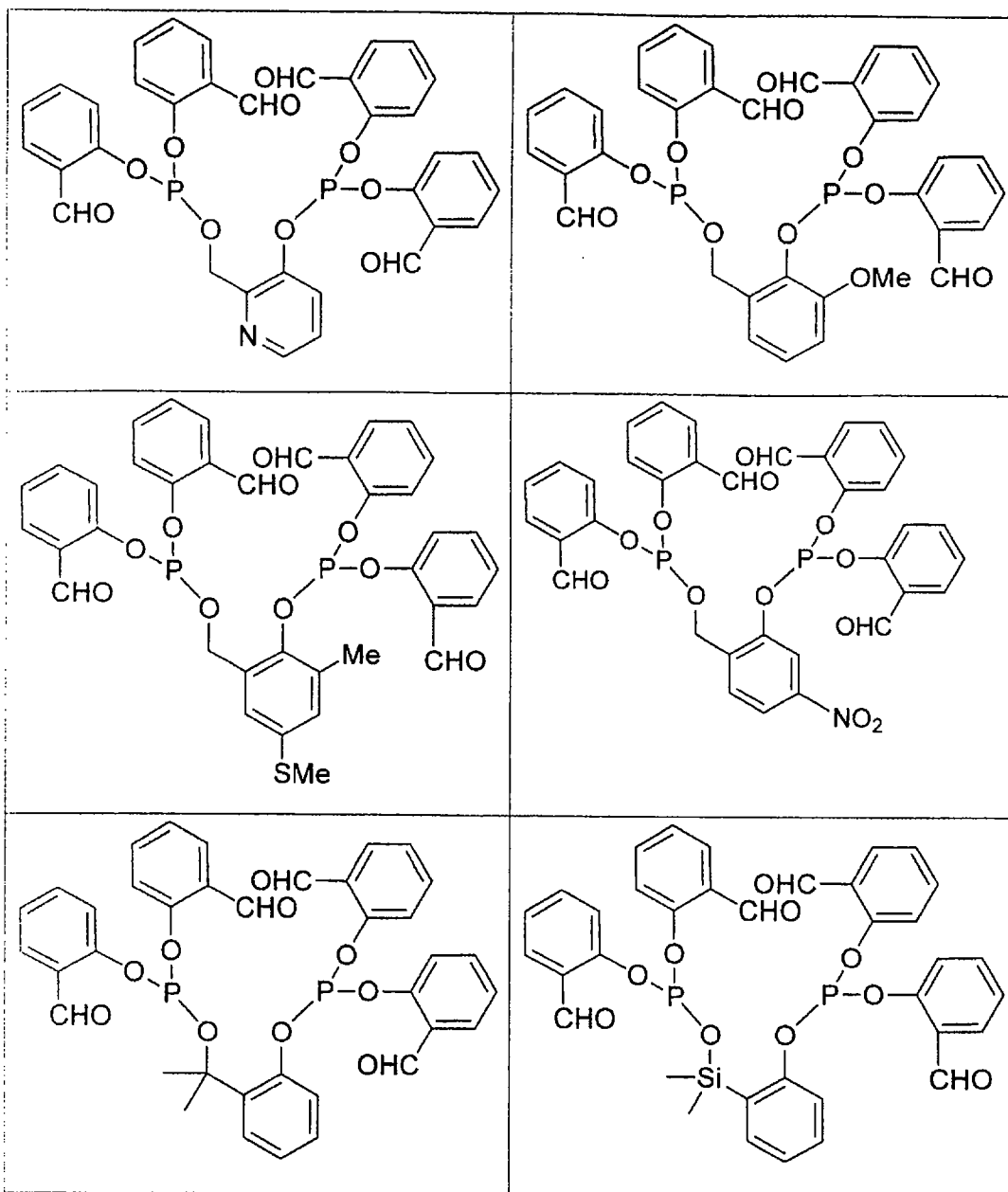
in which R₉ represent an alkyl, aryl, halogen, alkoxy, thiol, cyano, nitro, aryloxy, alkoxycarbonyl, acyl or formyl radical.

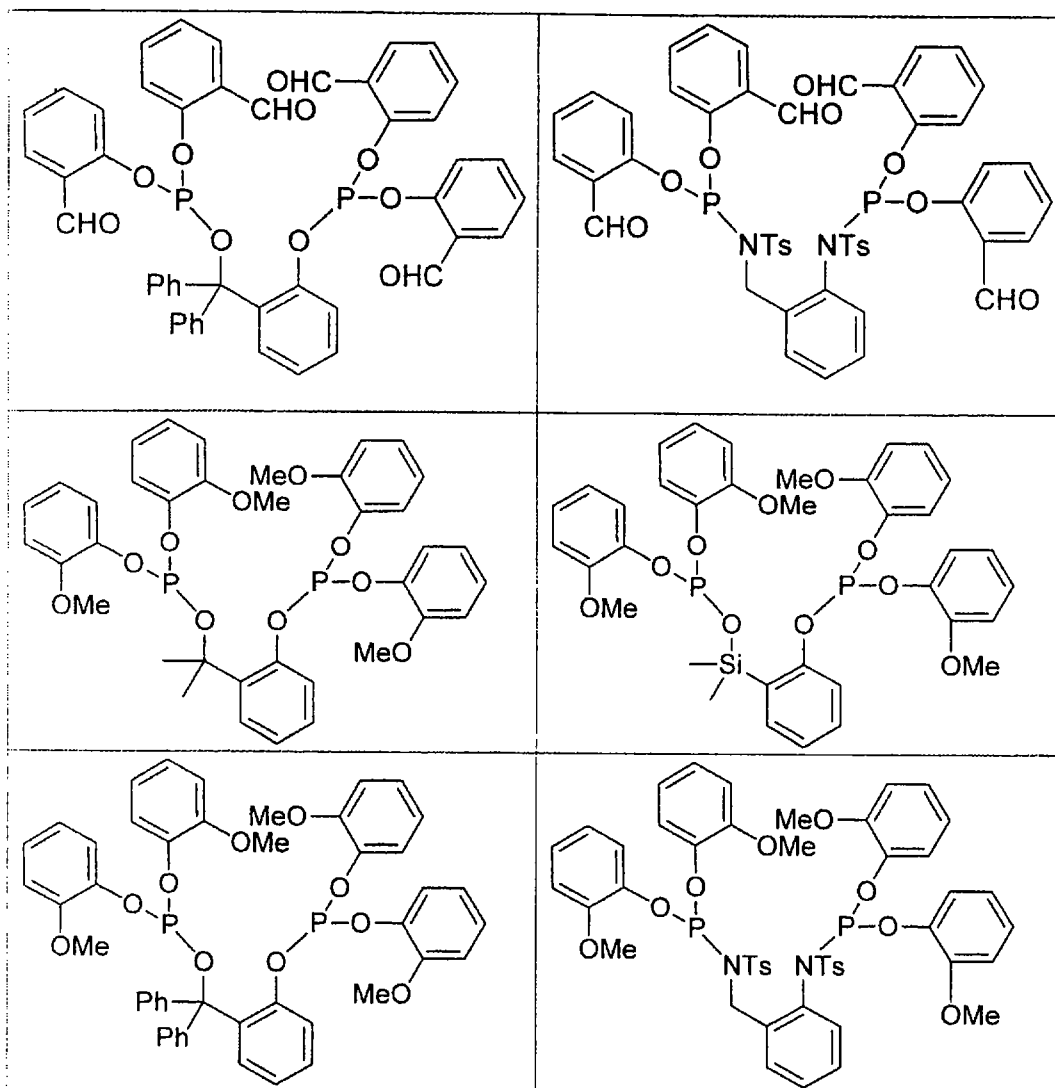
As examples of ligands which are suitable for the invention, mention may be made of the following compounds listed in table I below:

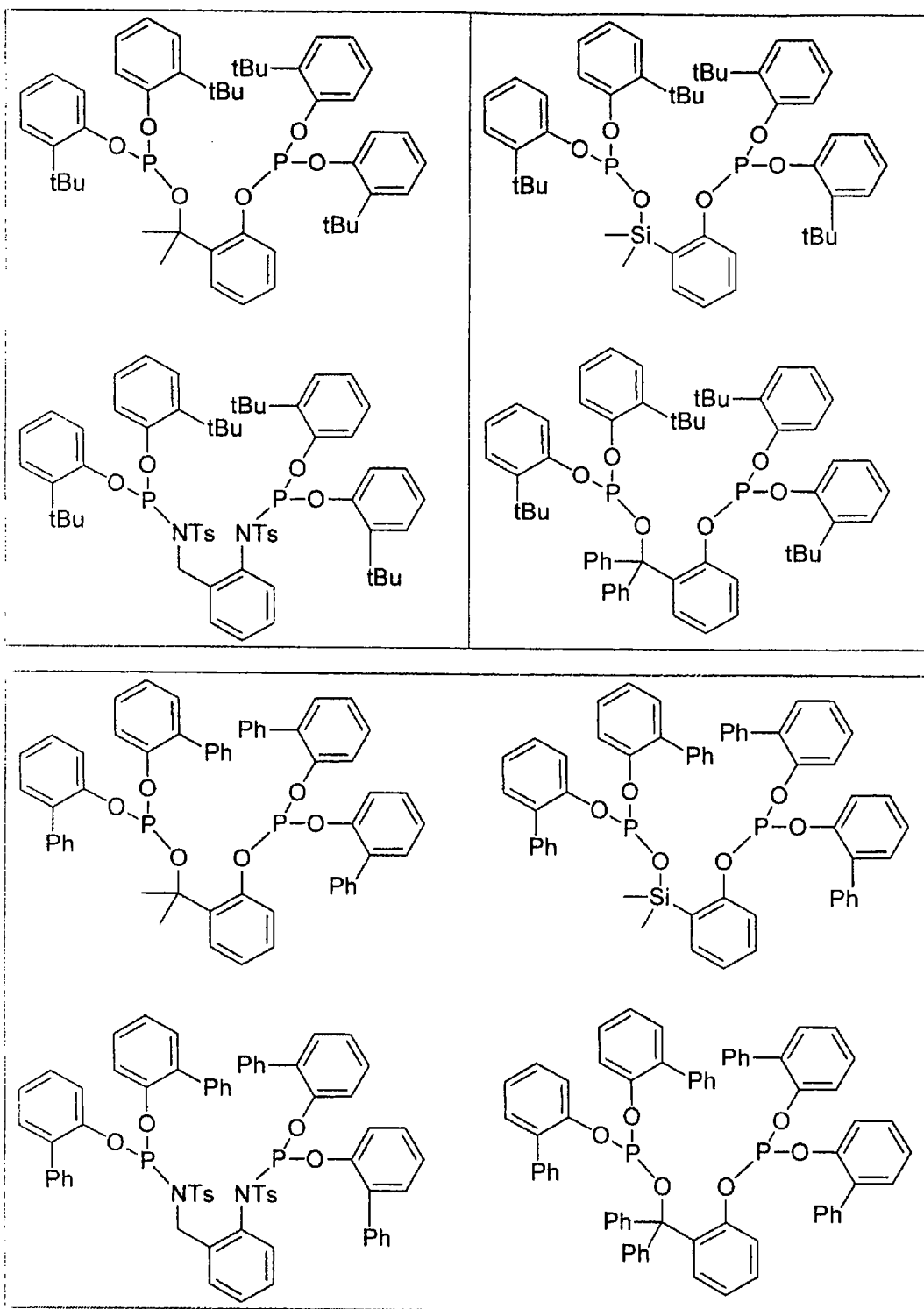
Table I:

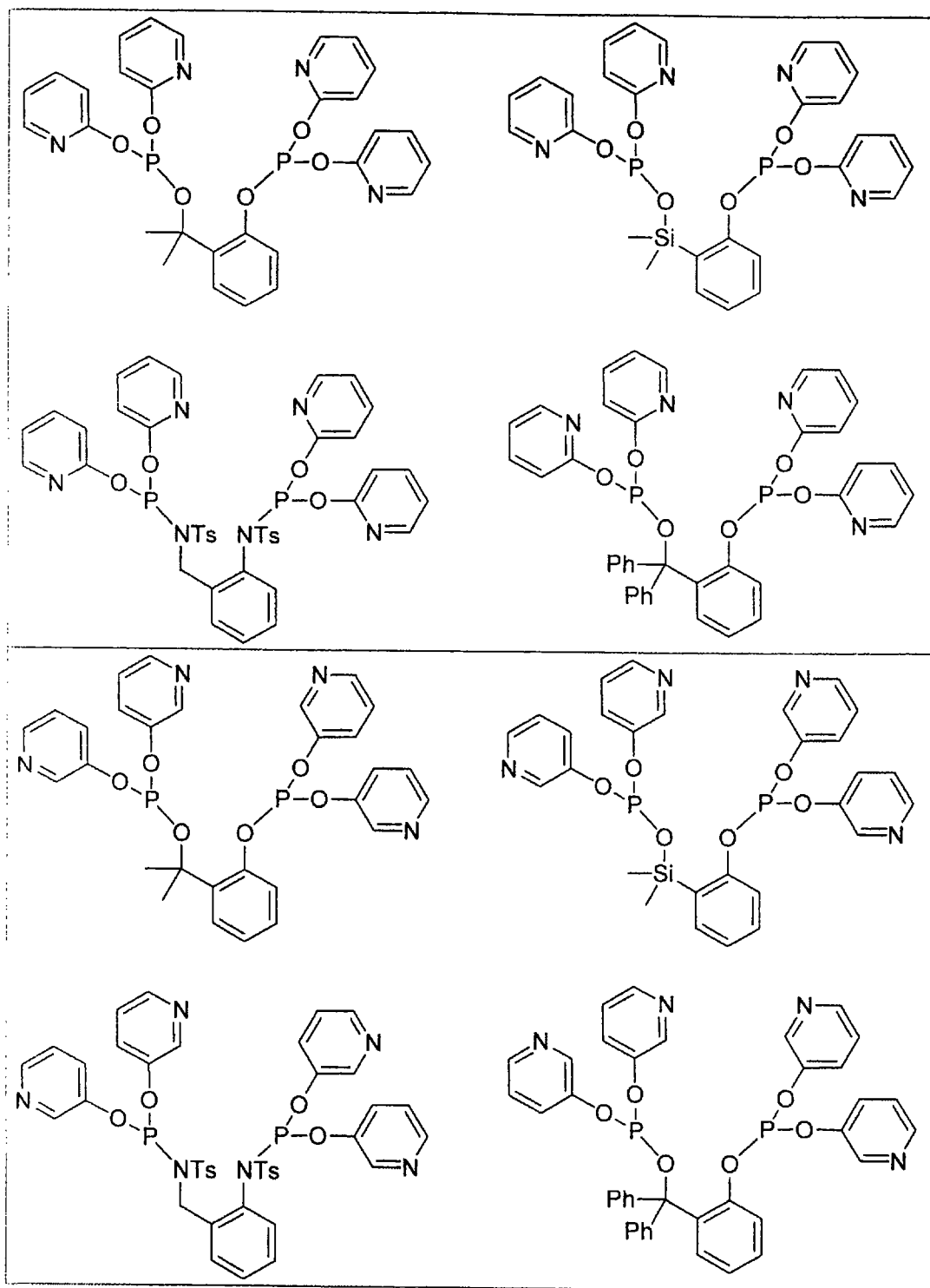


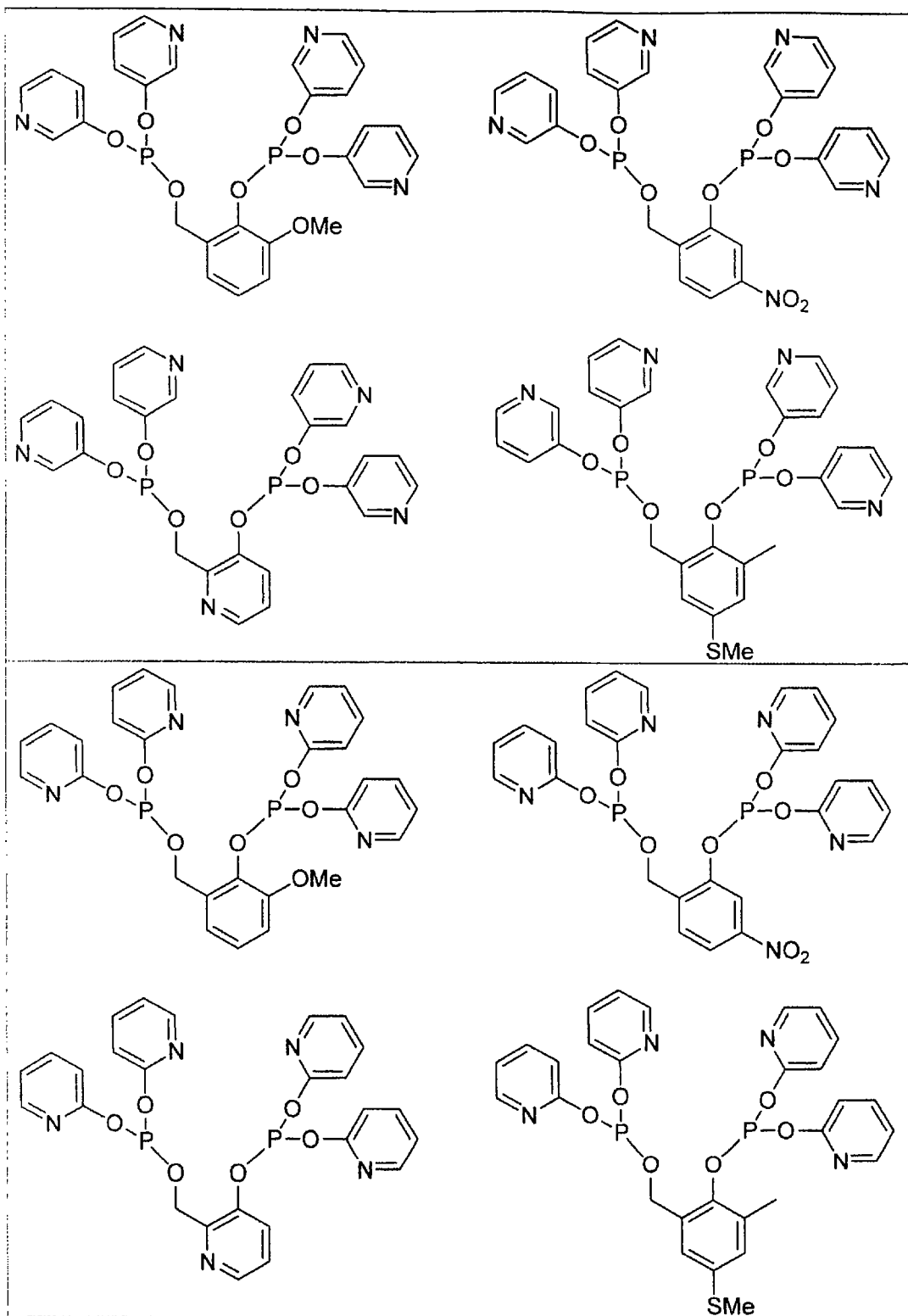


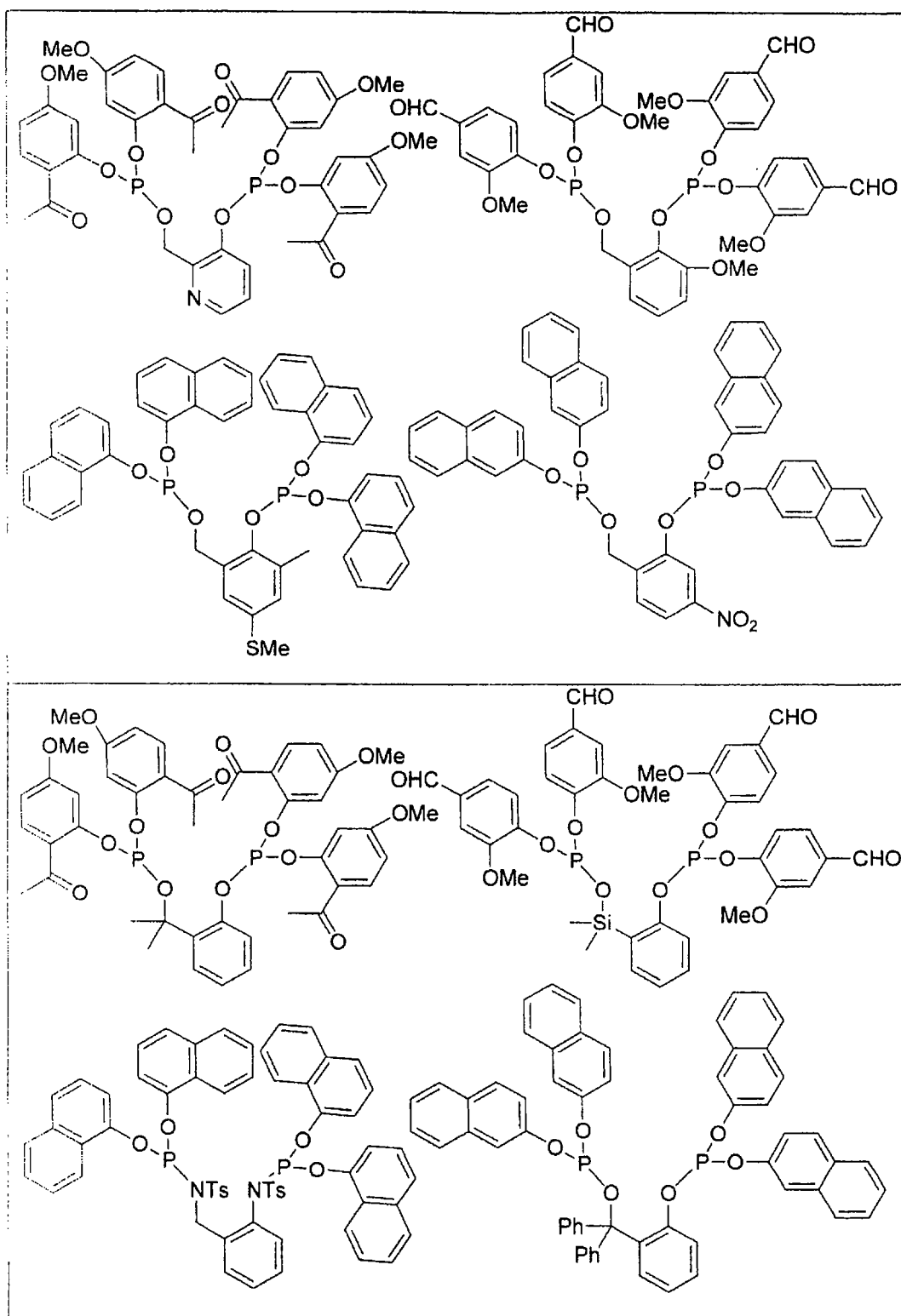


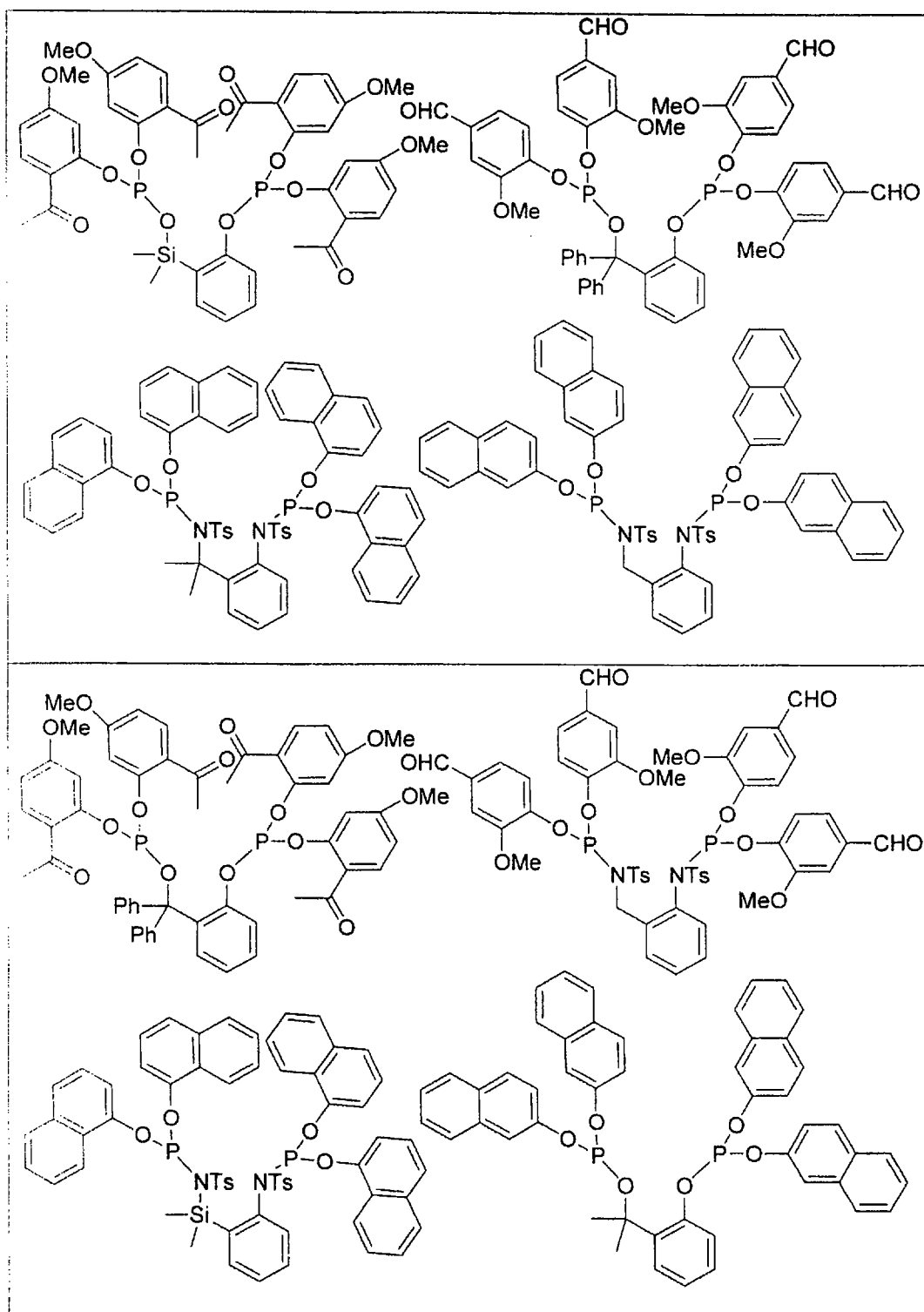


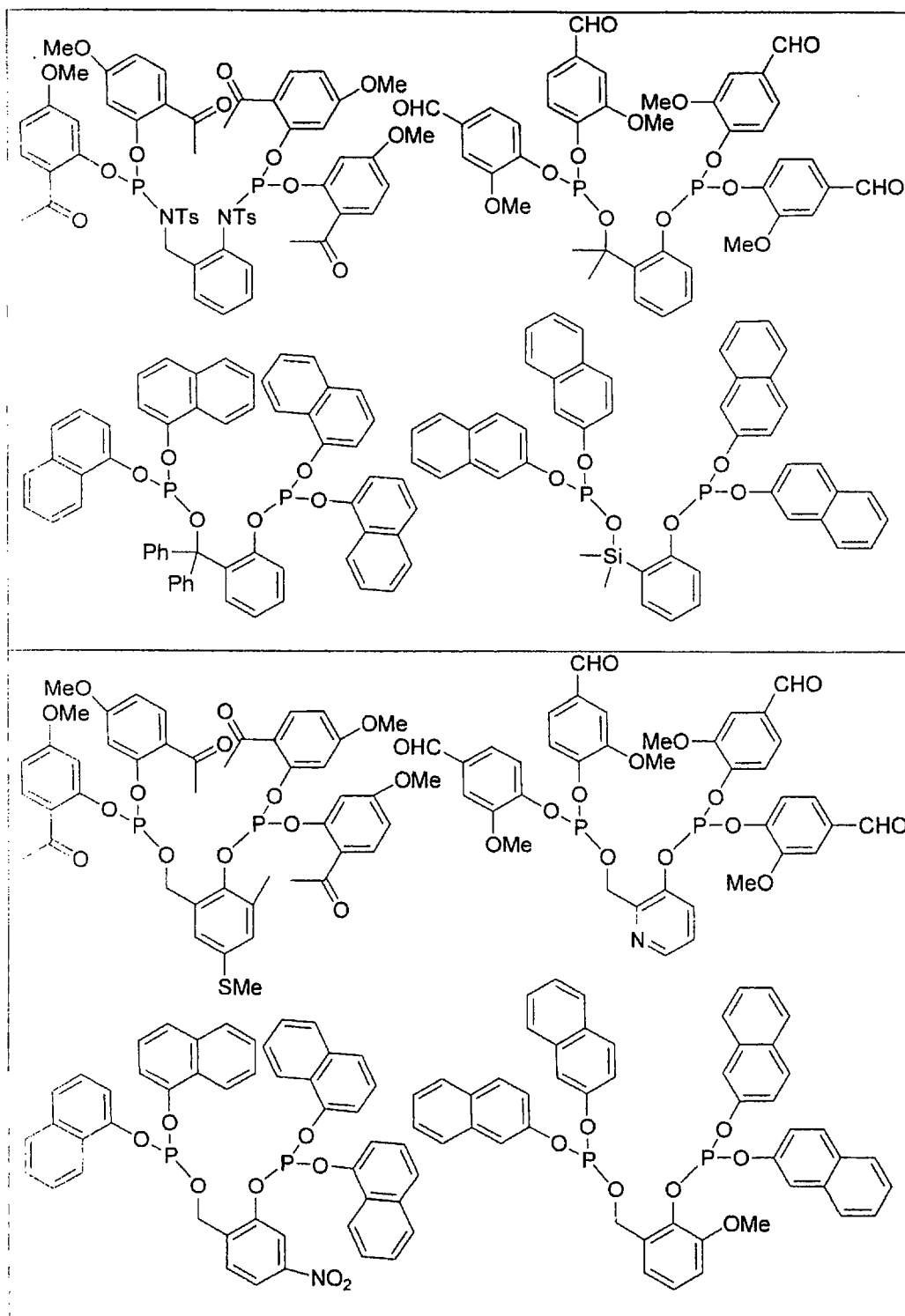


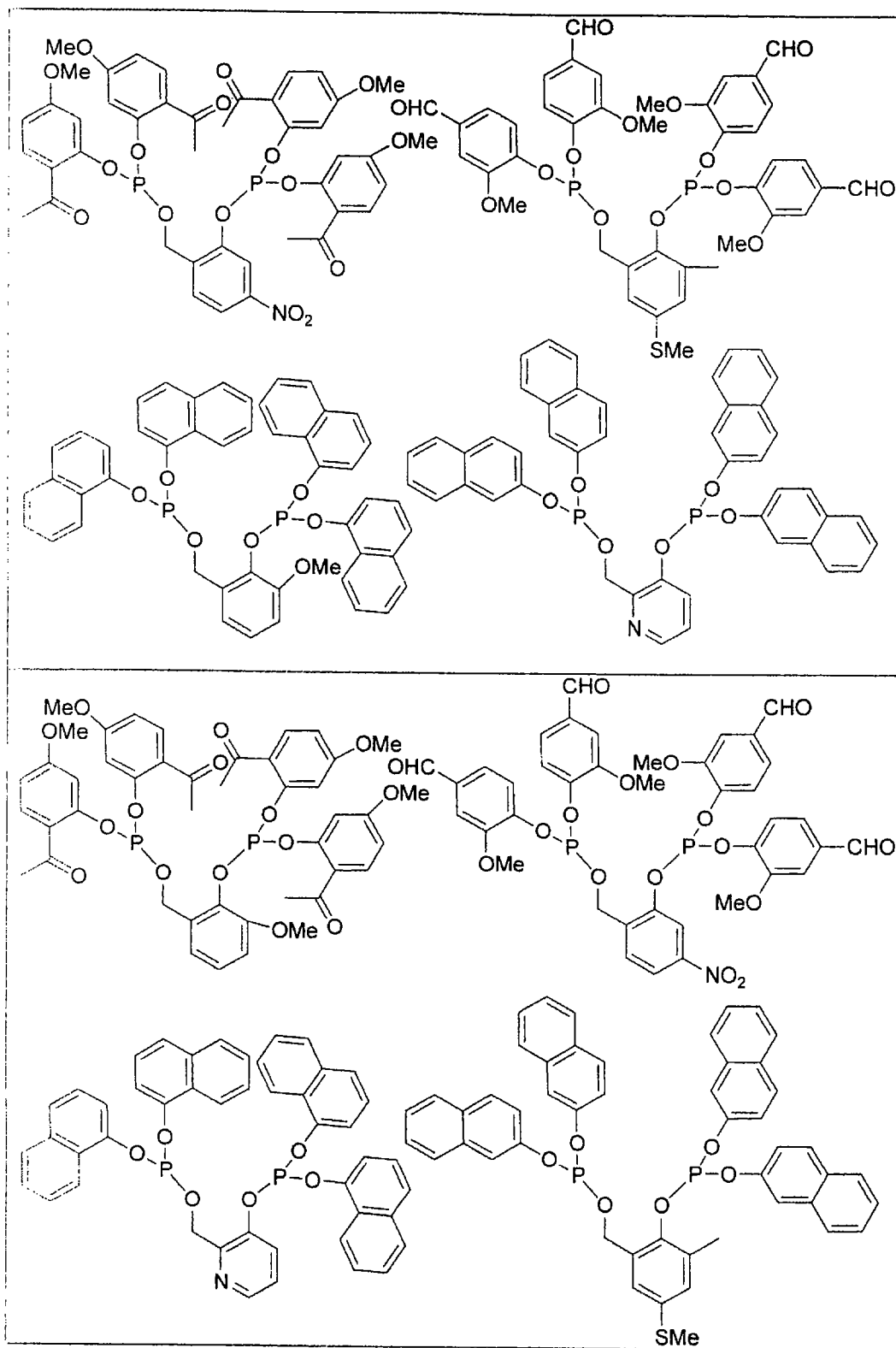


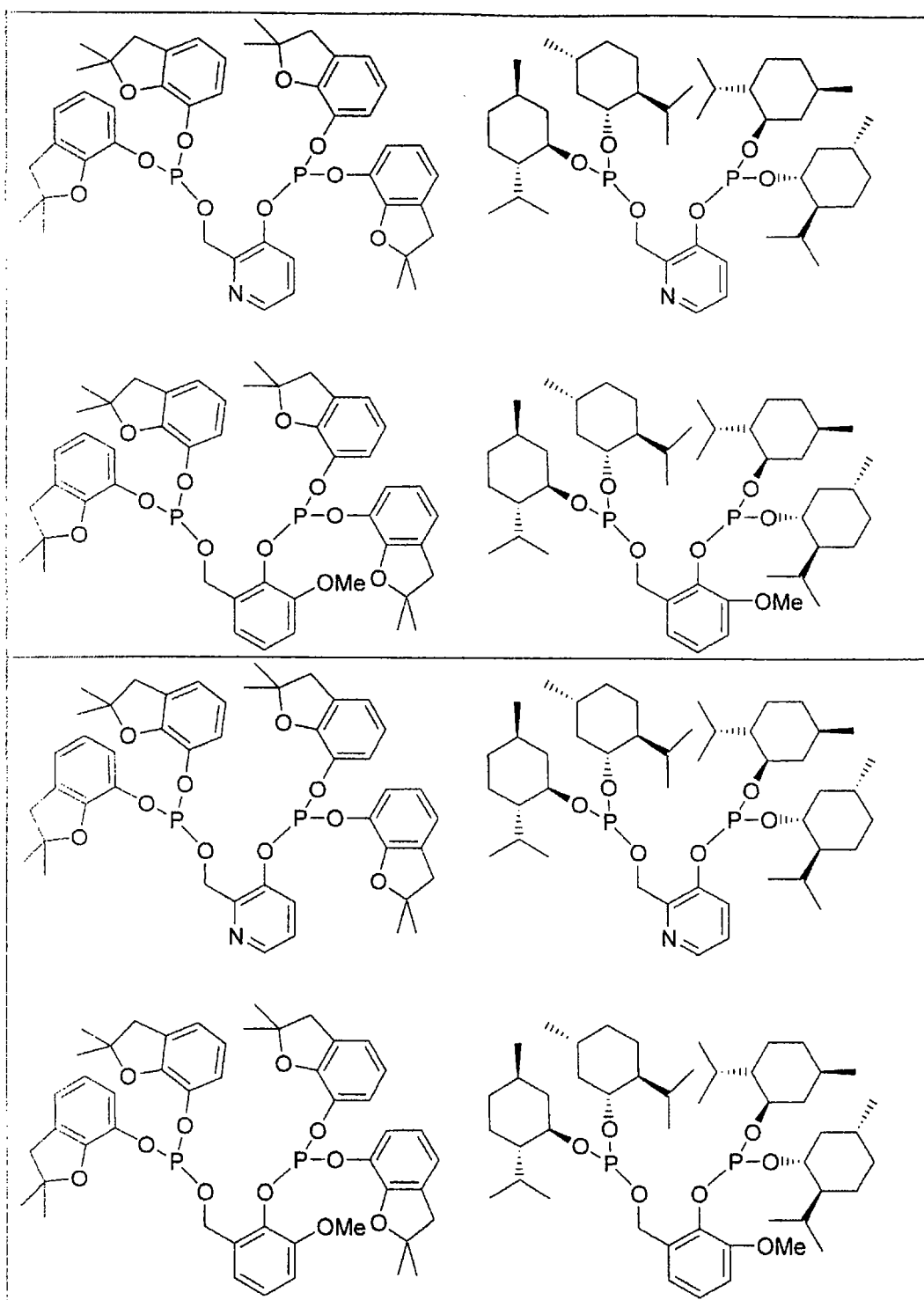


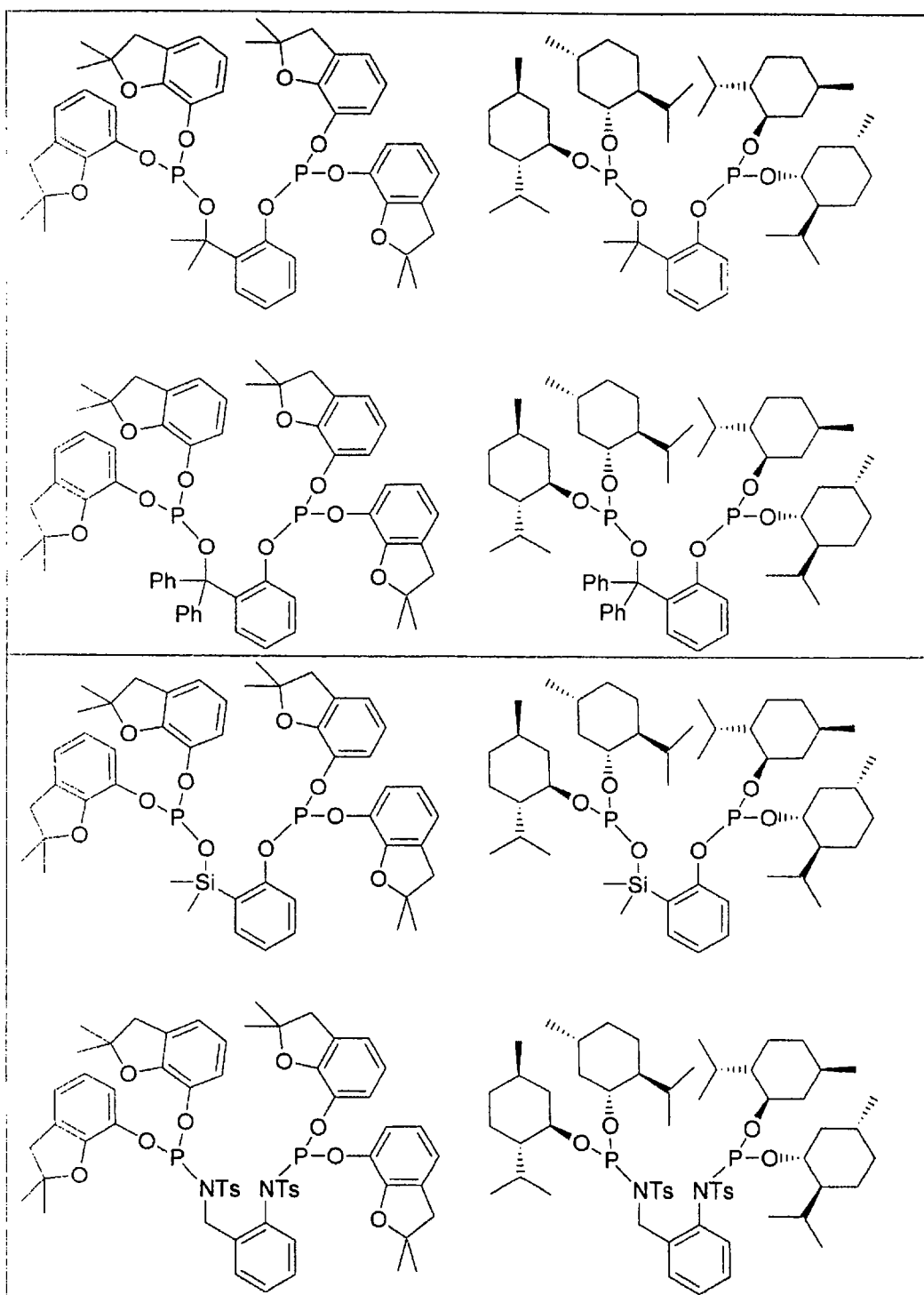


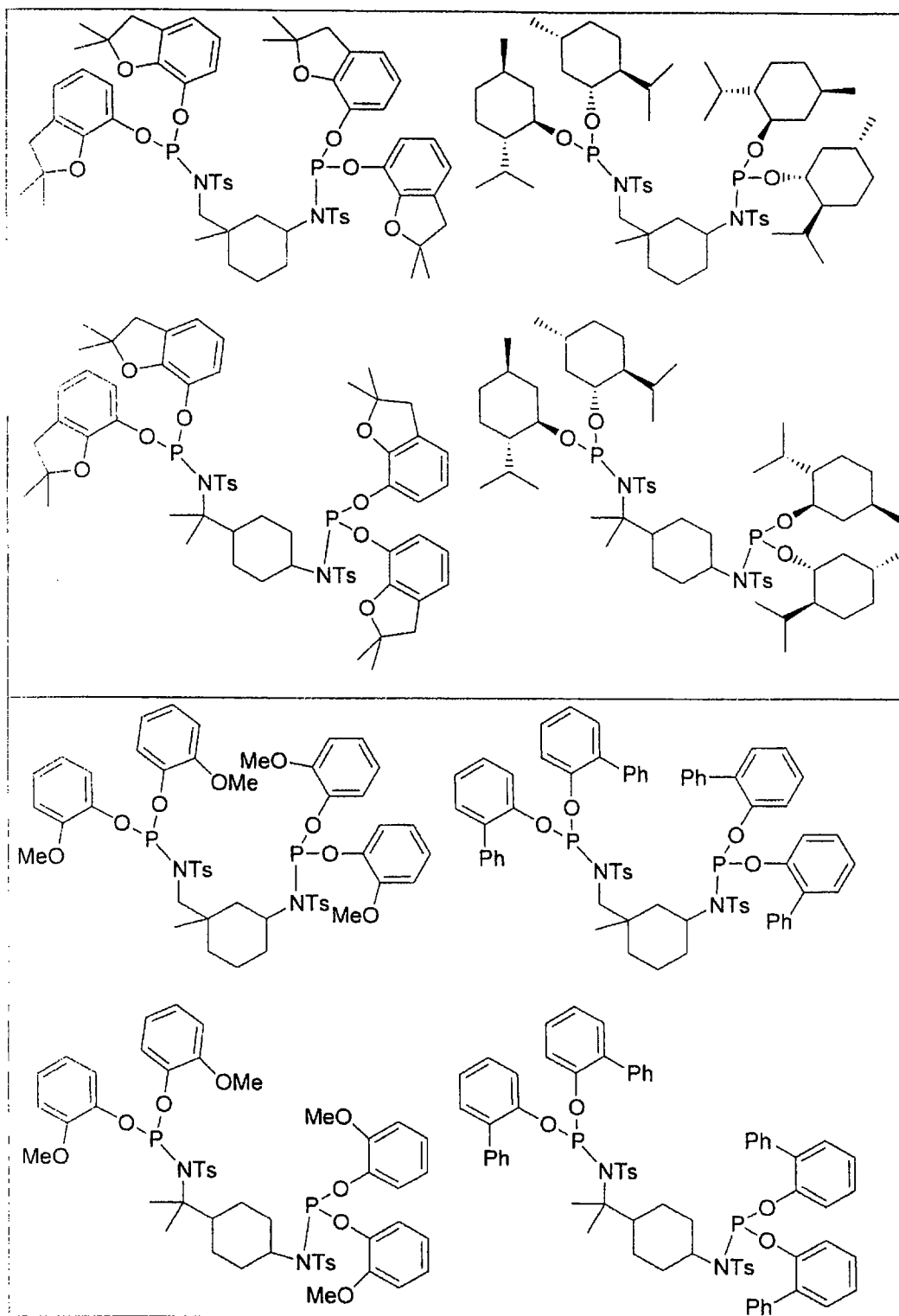


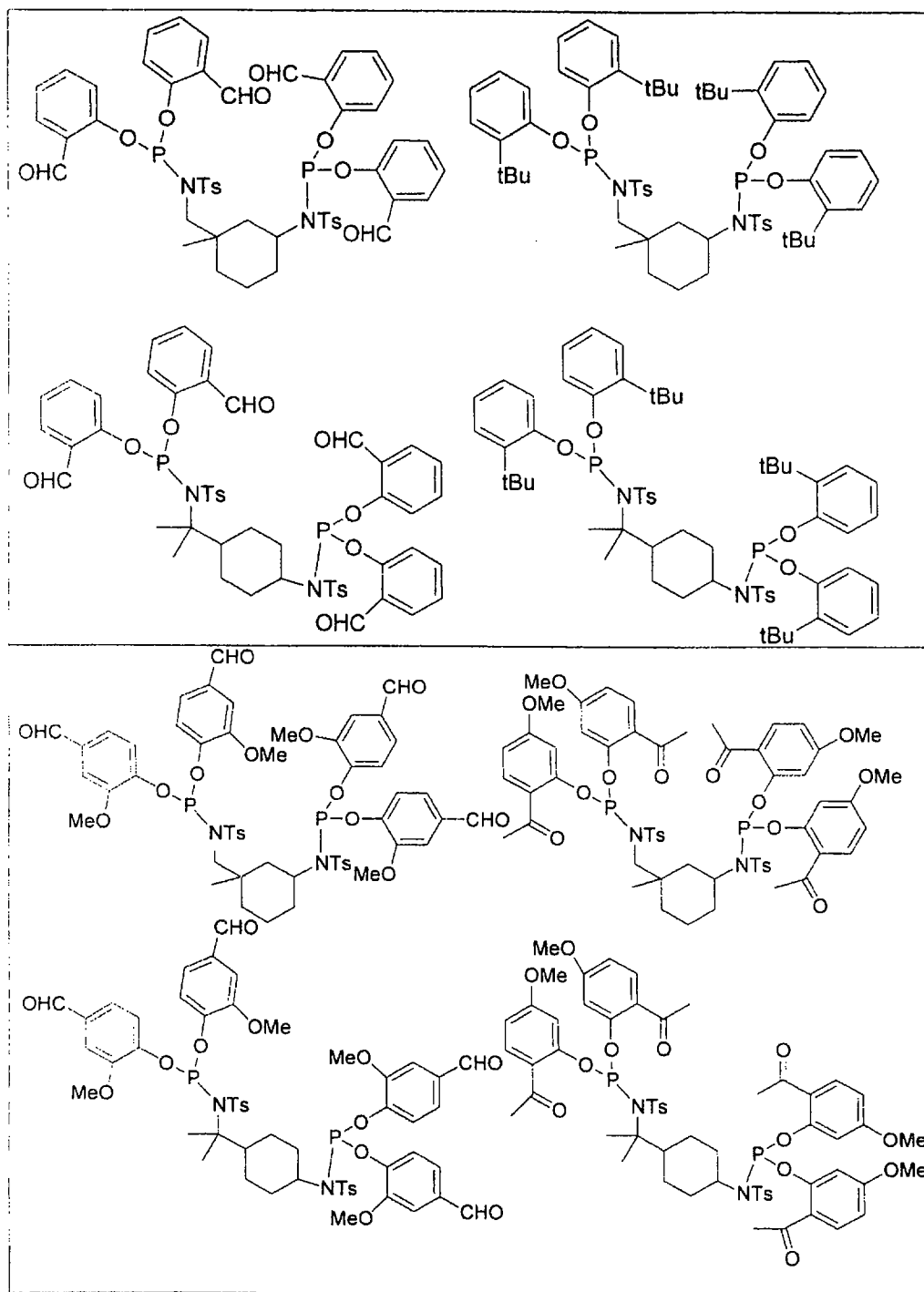


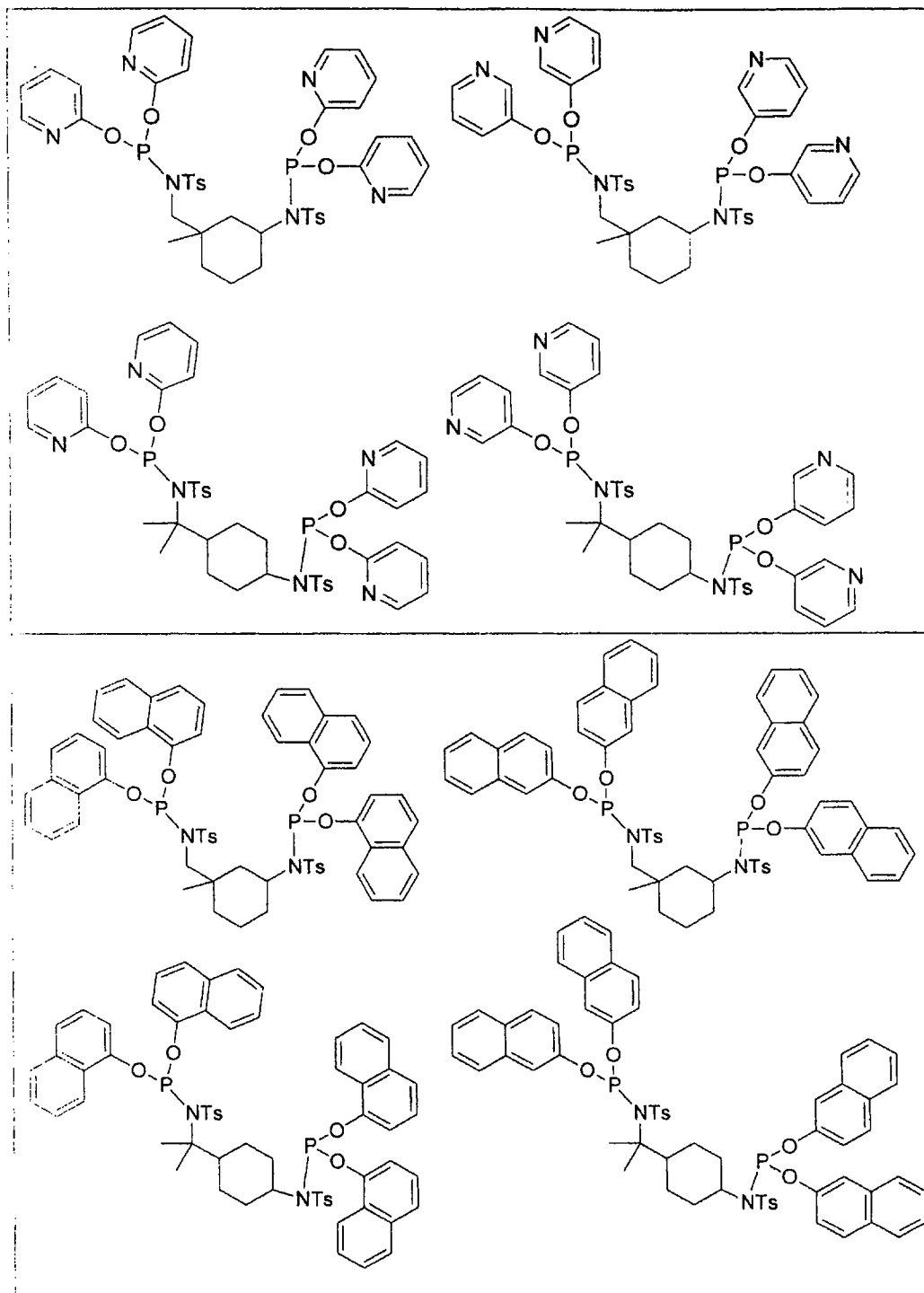


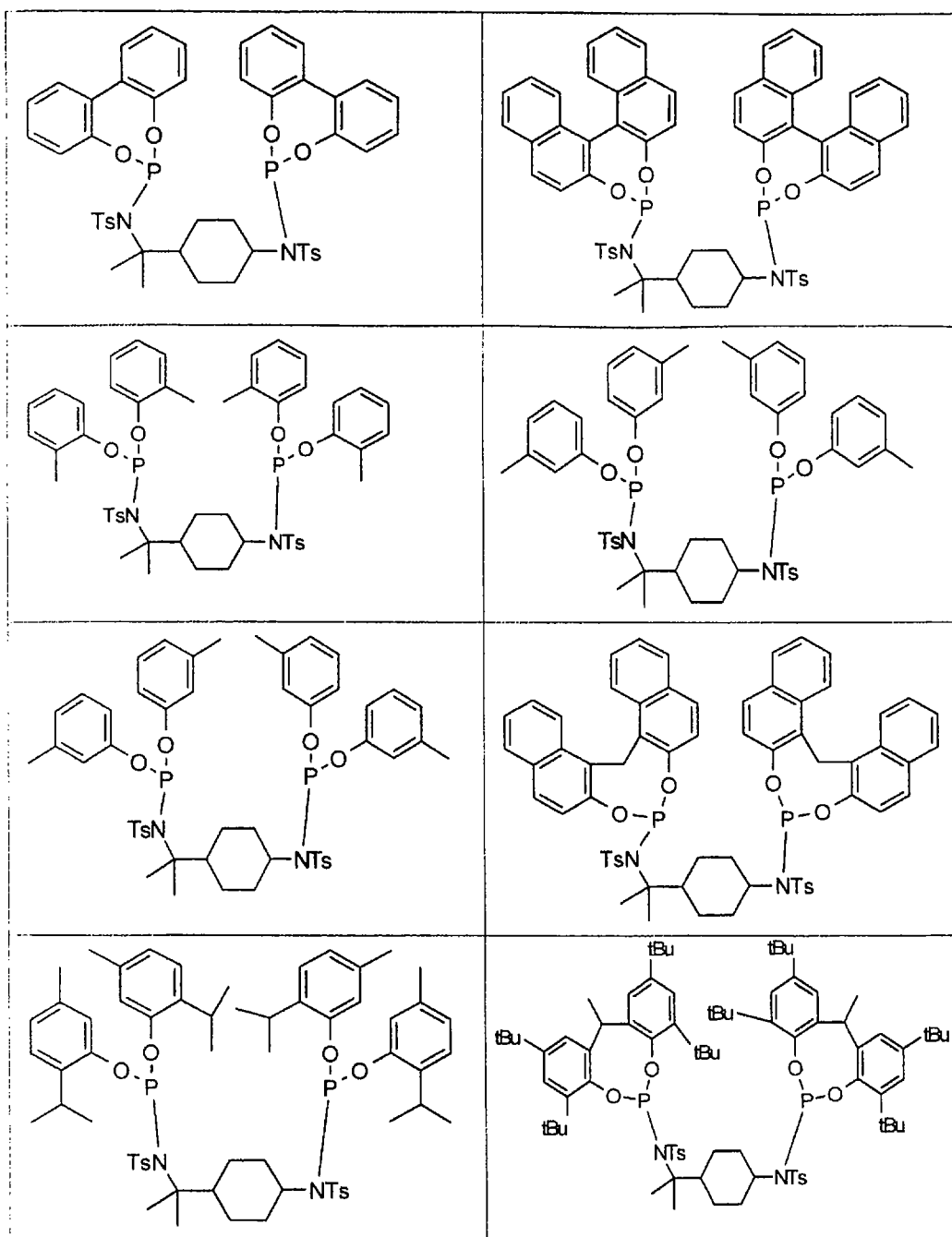


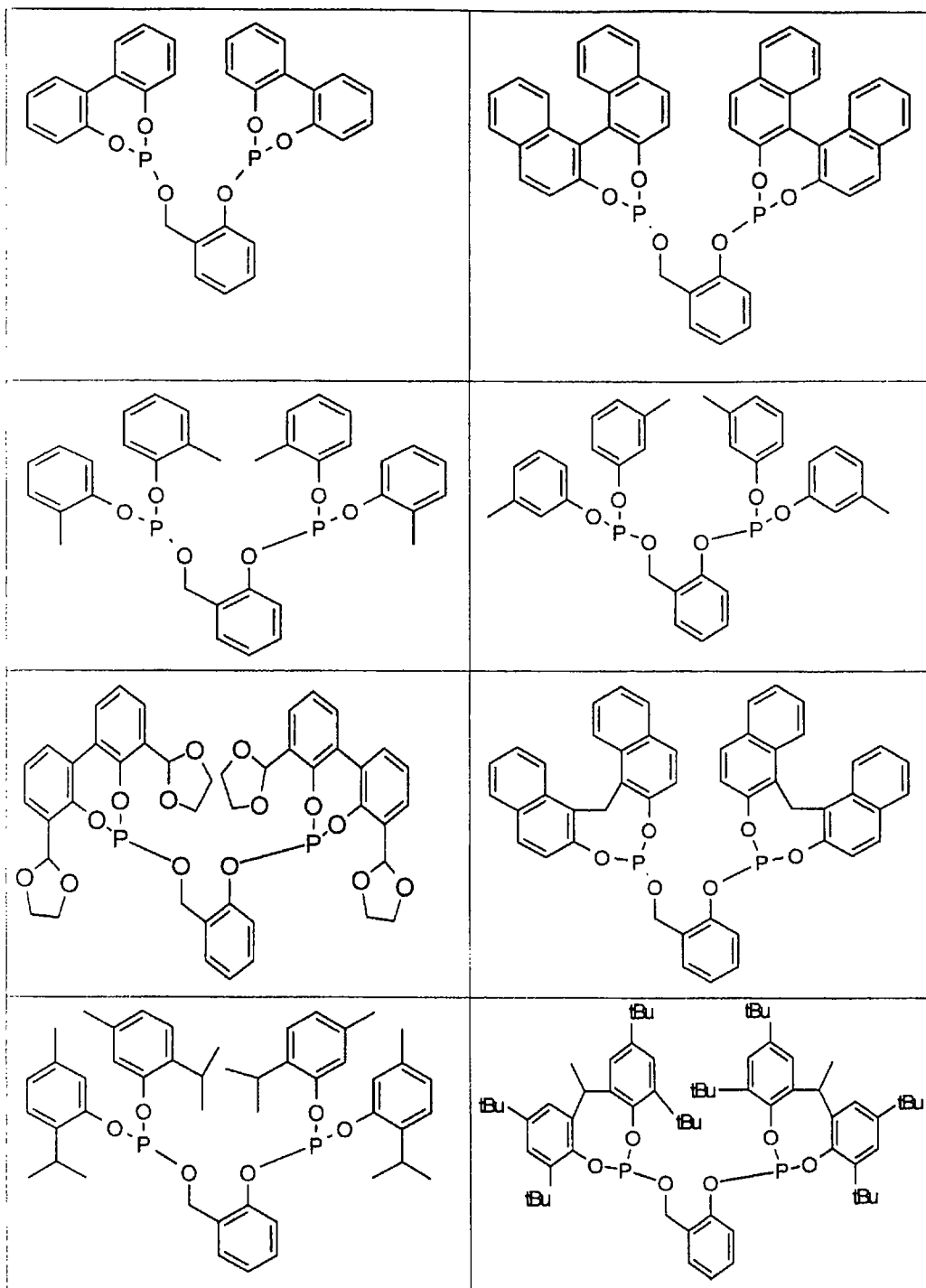


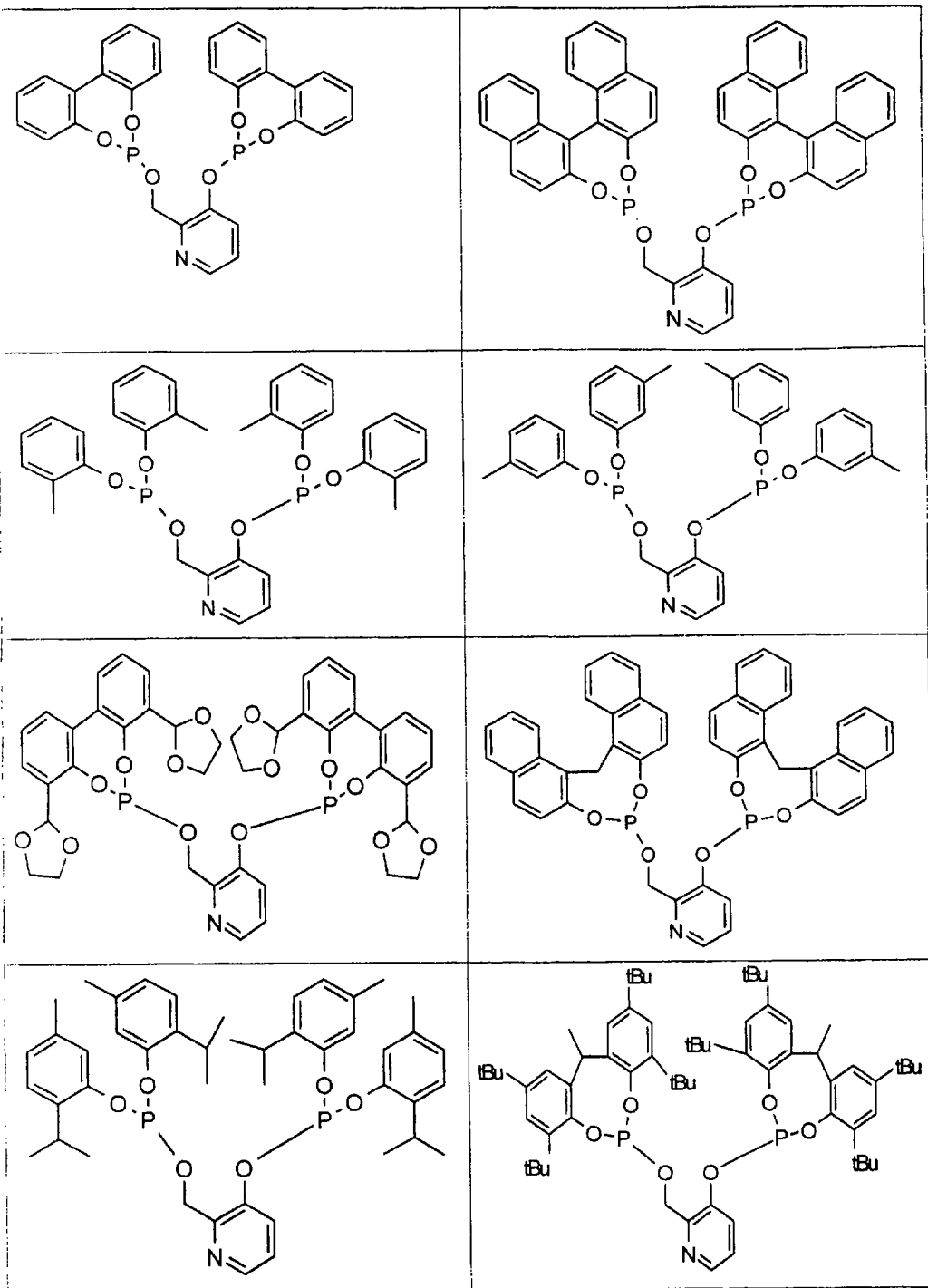


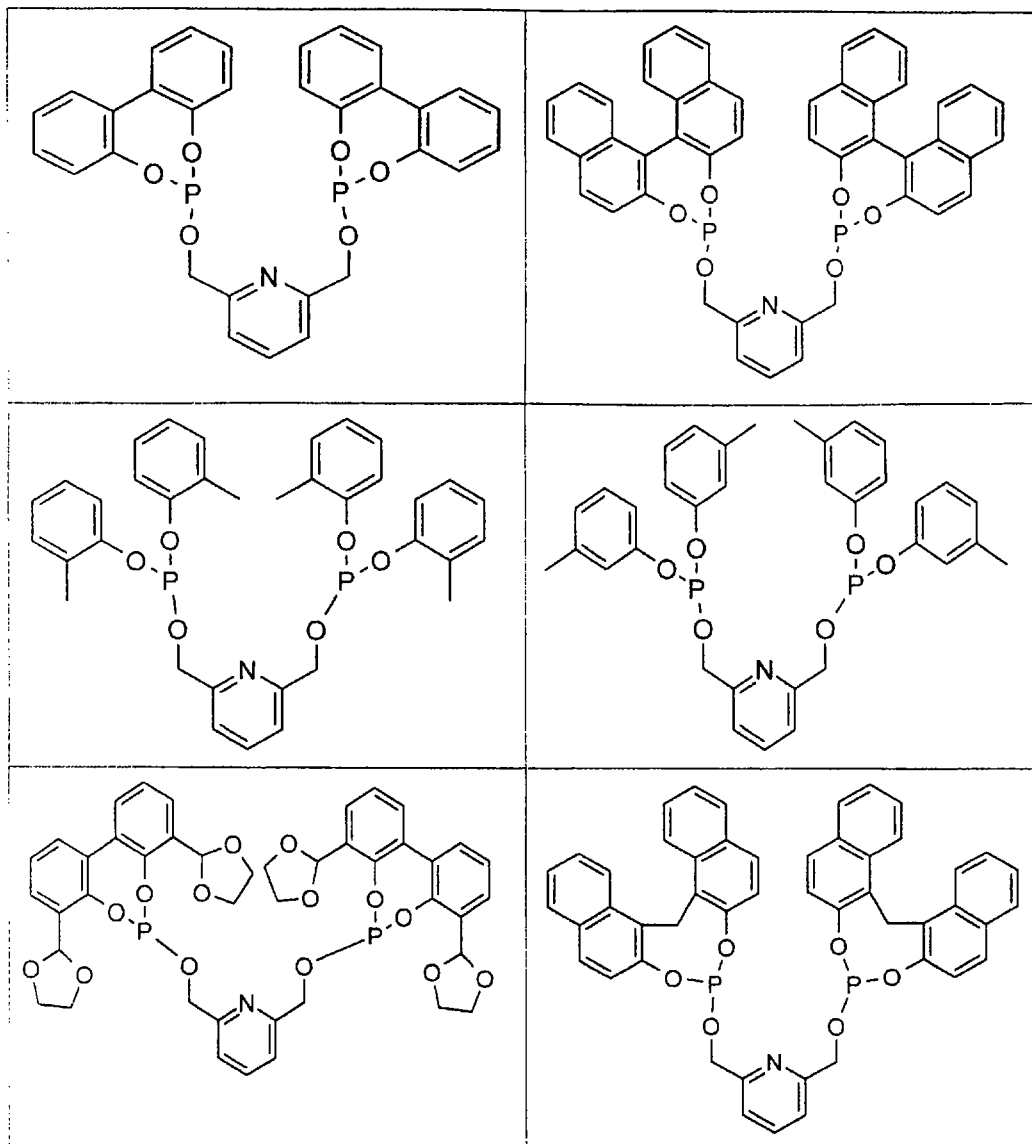


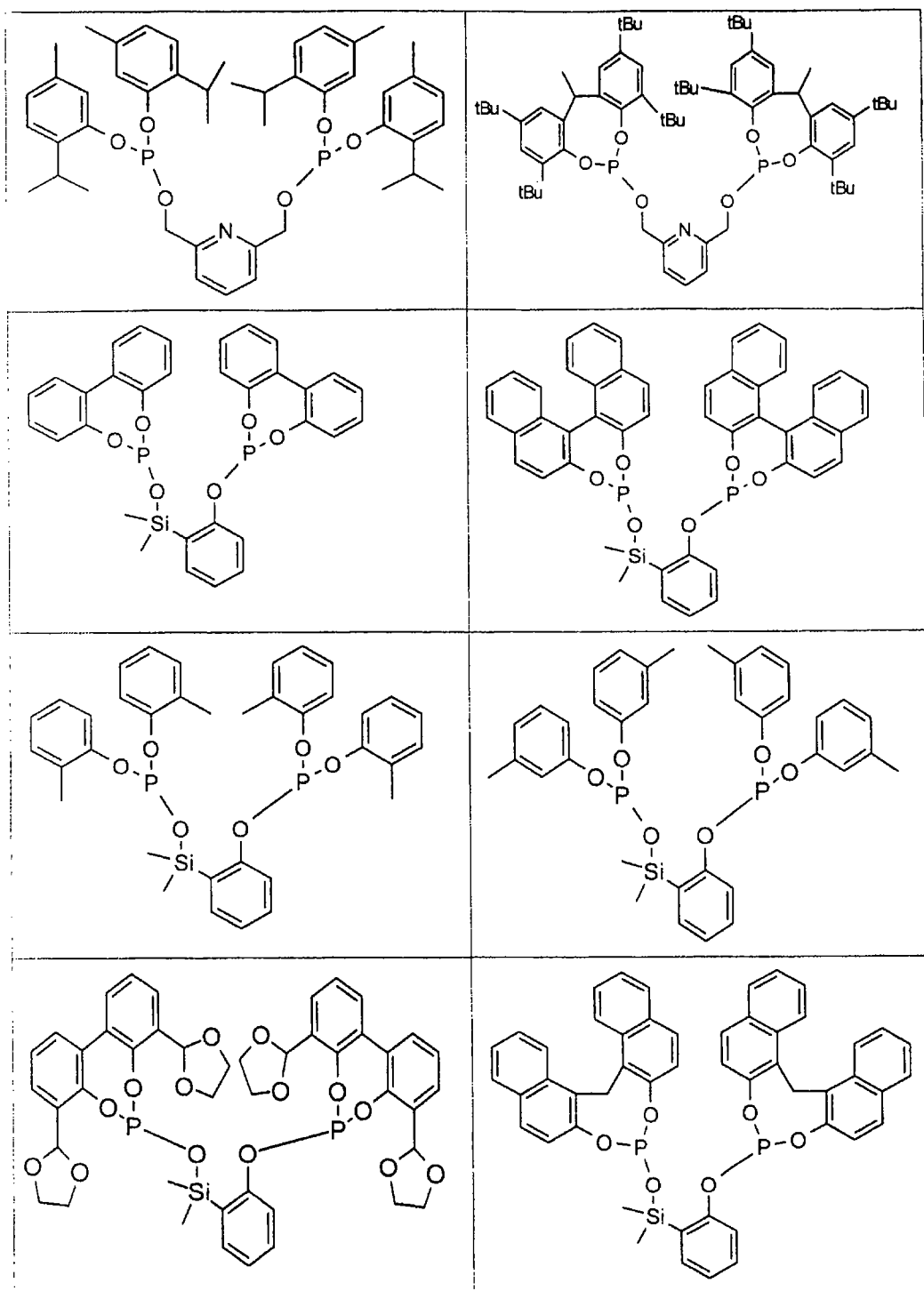


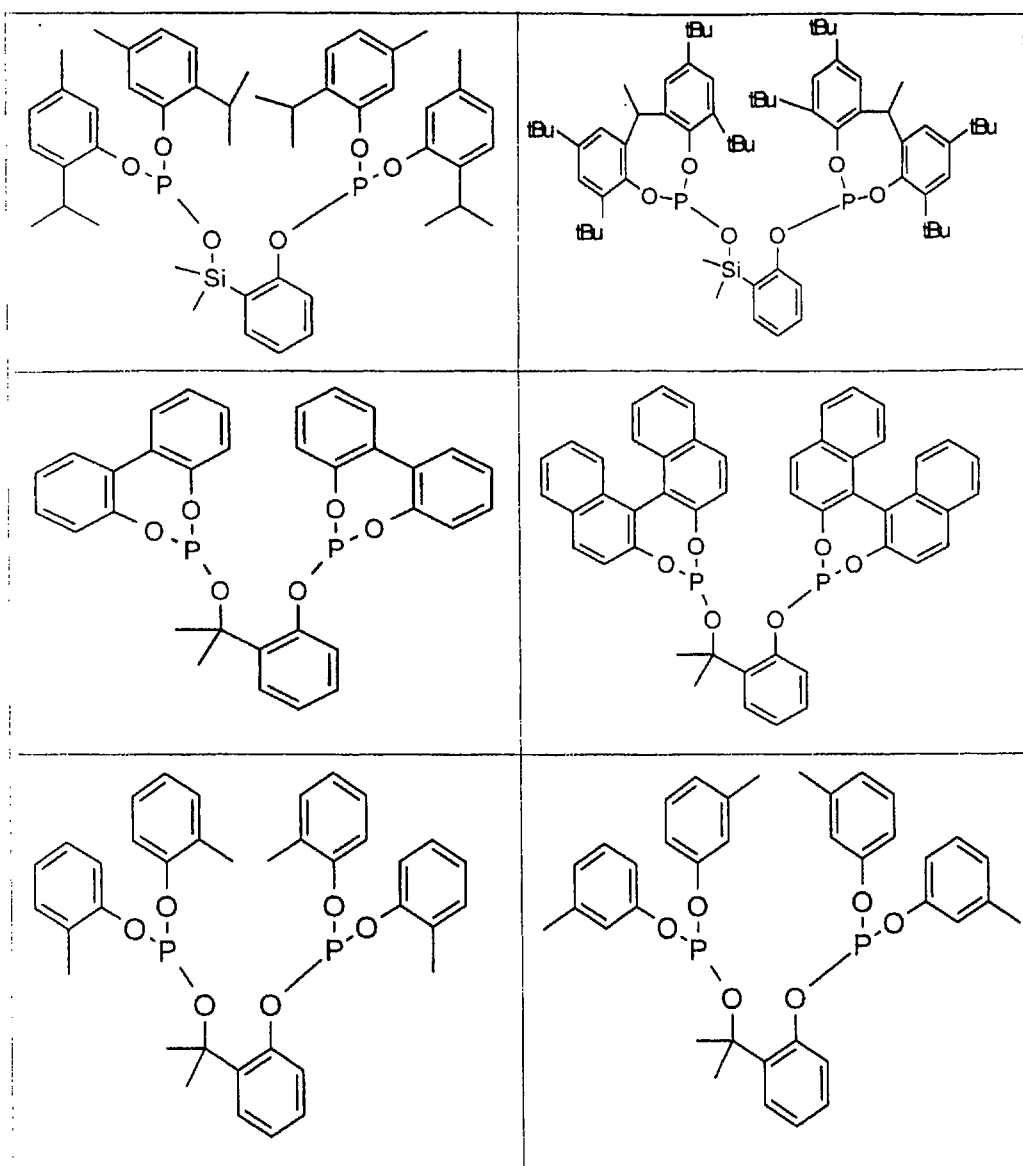


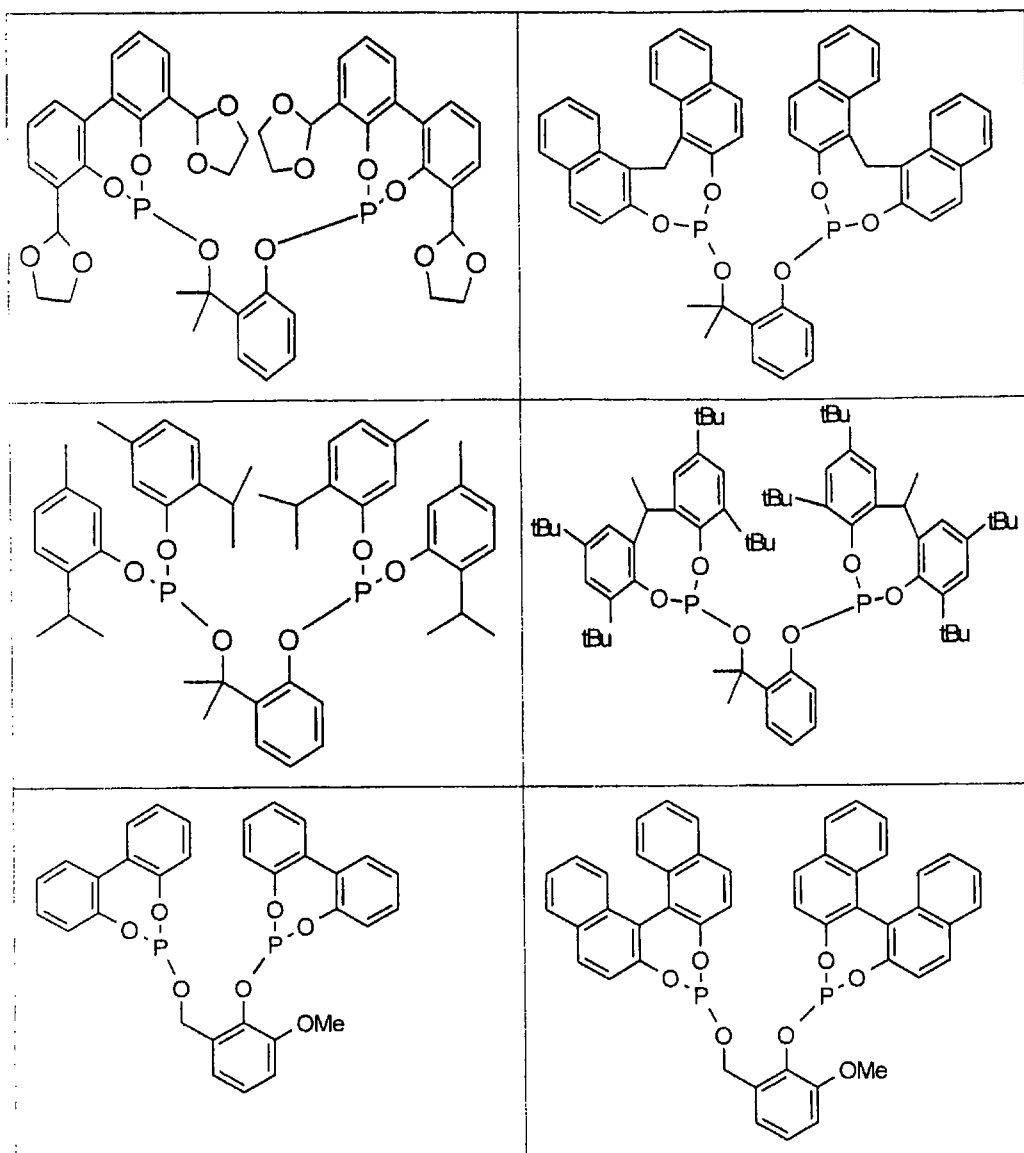


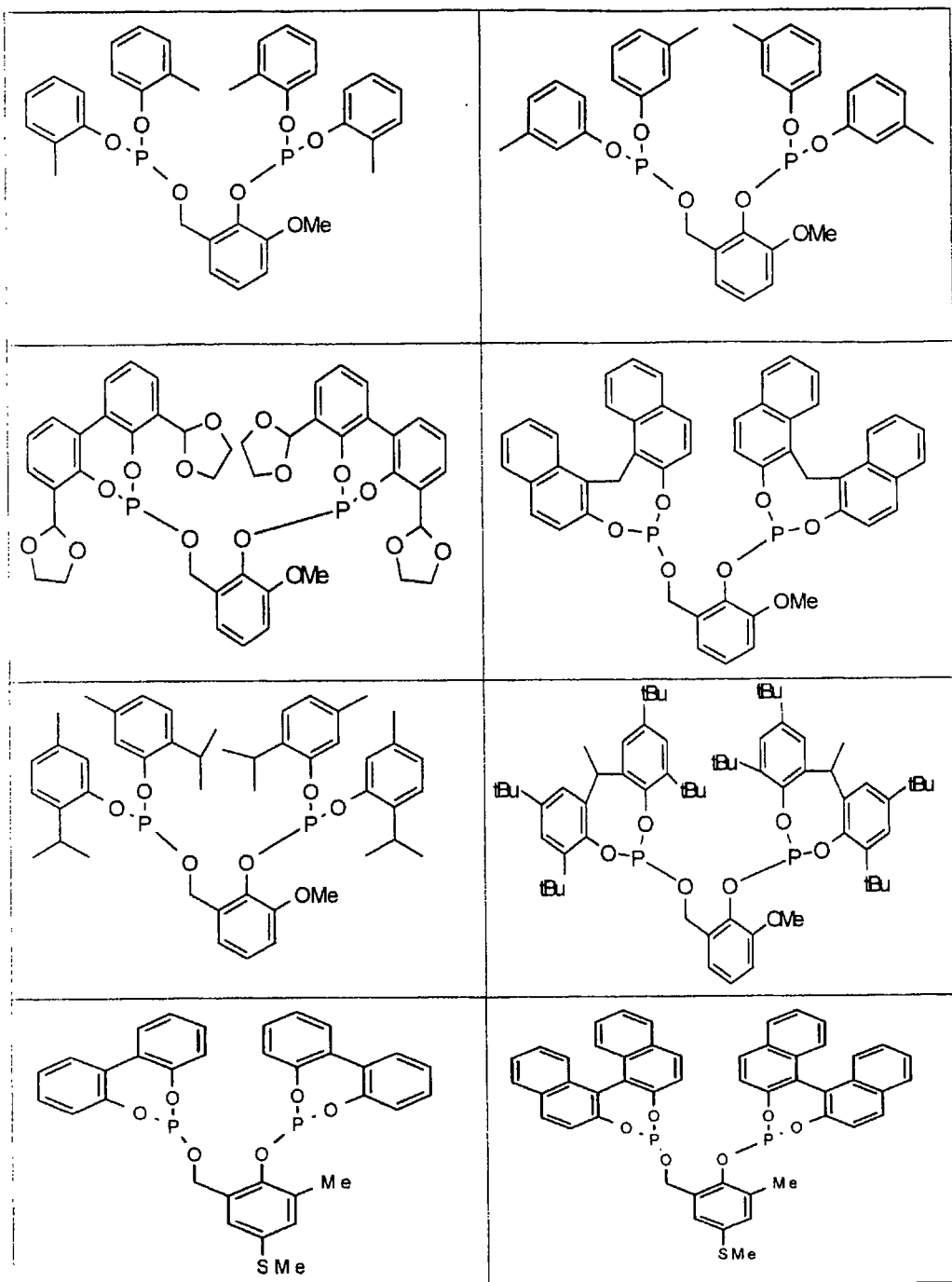


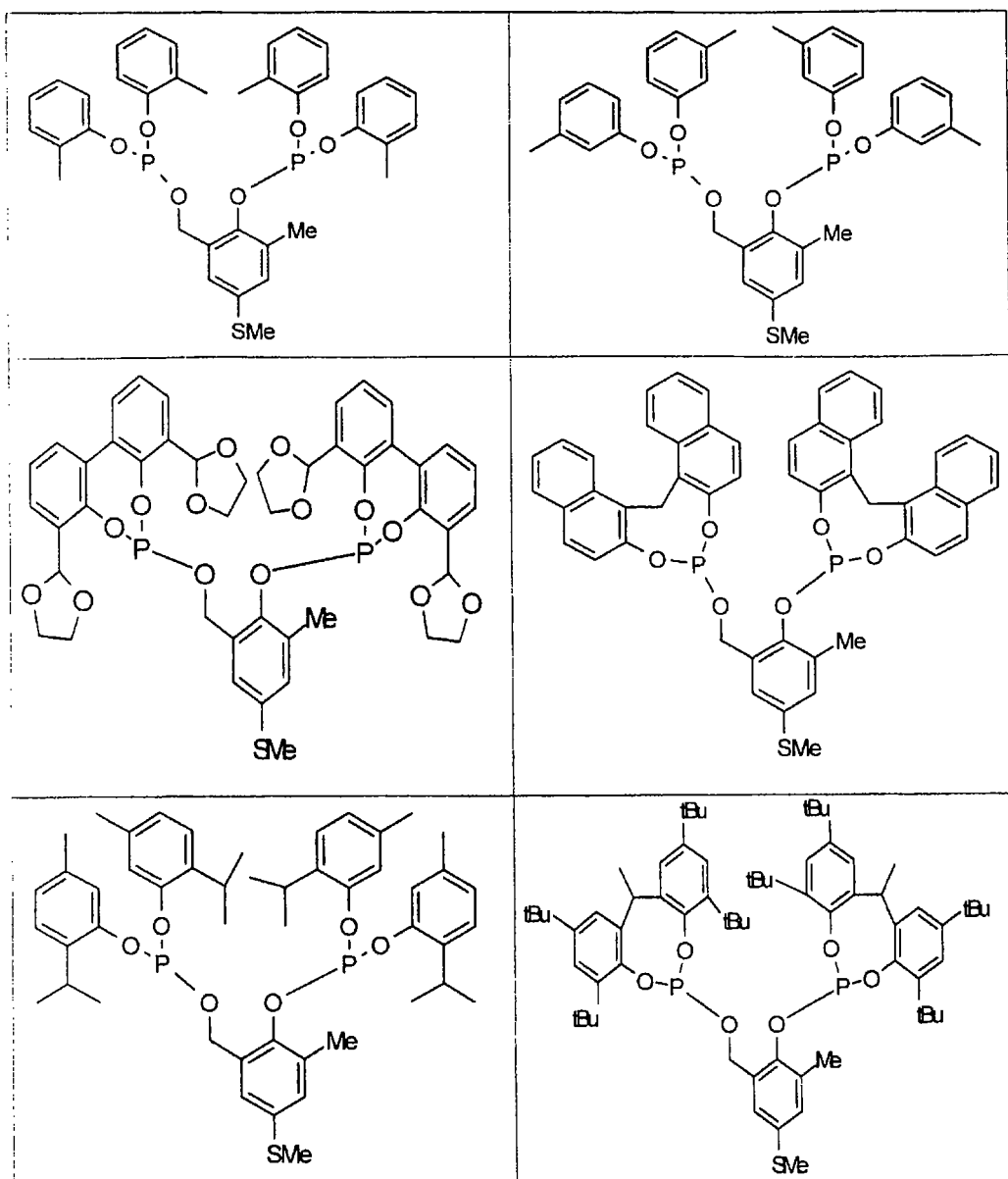


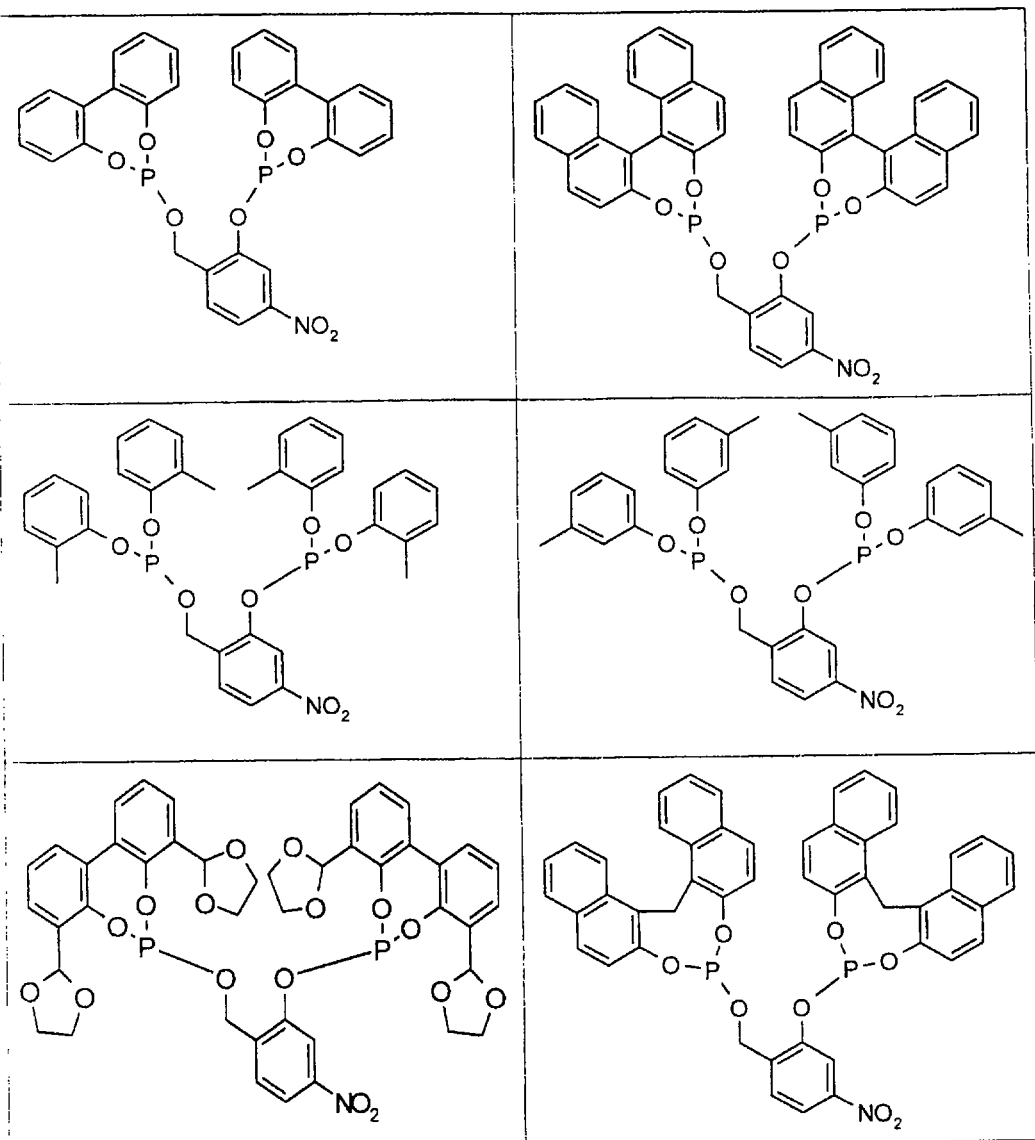


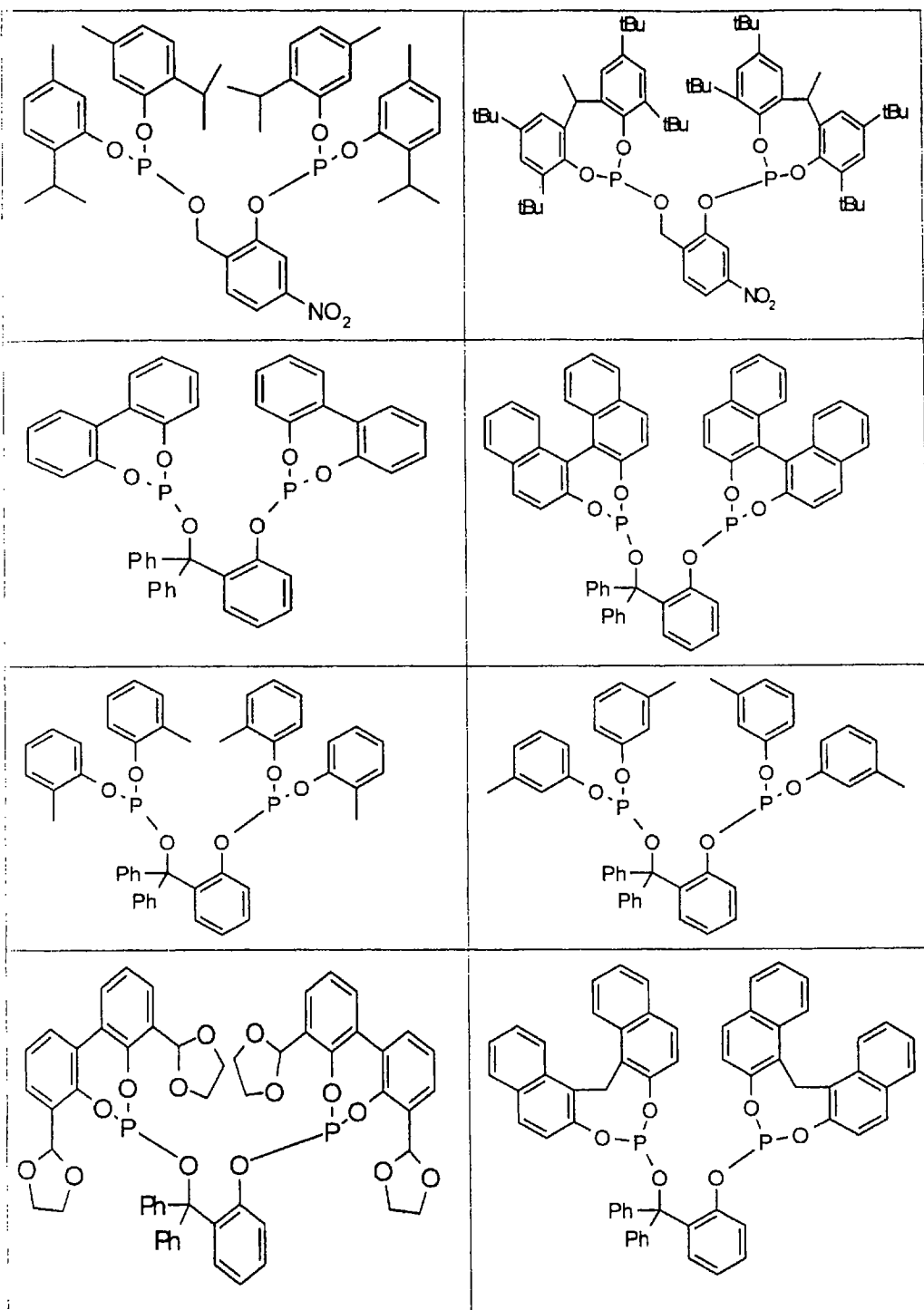


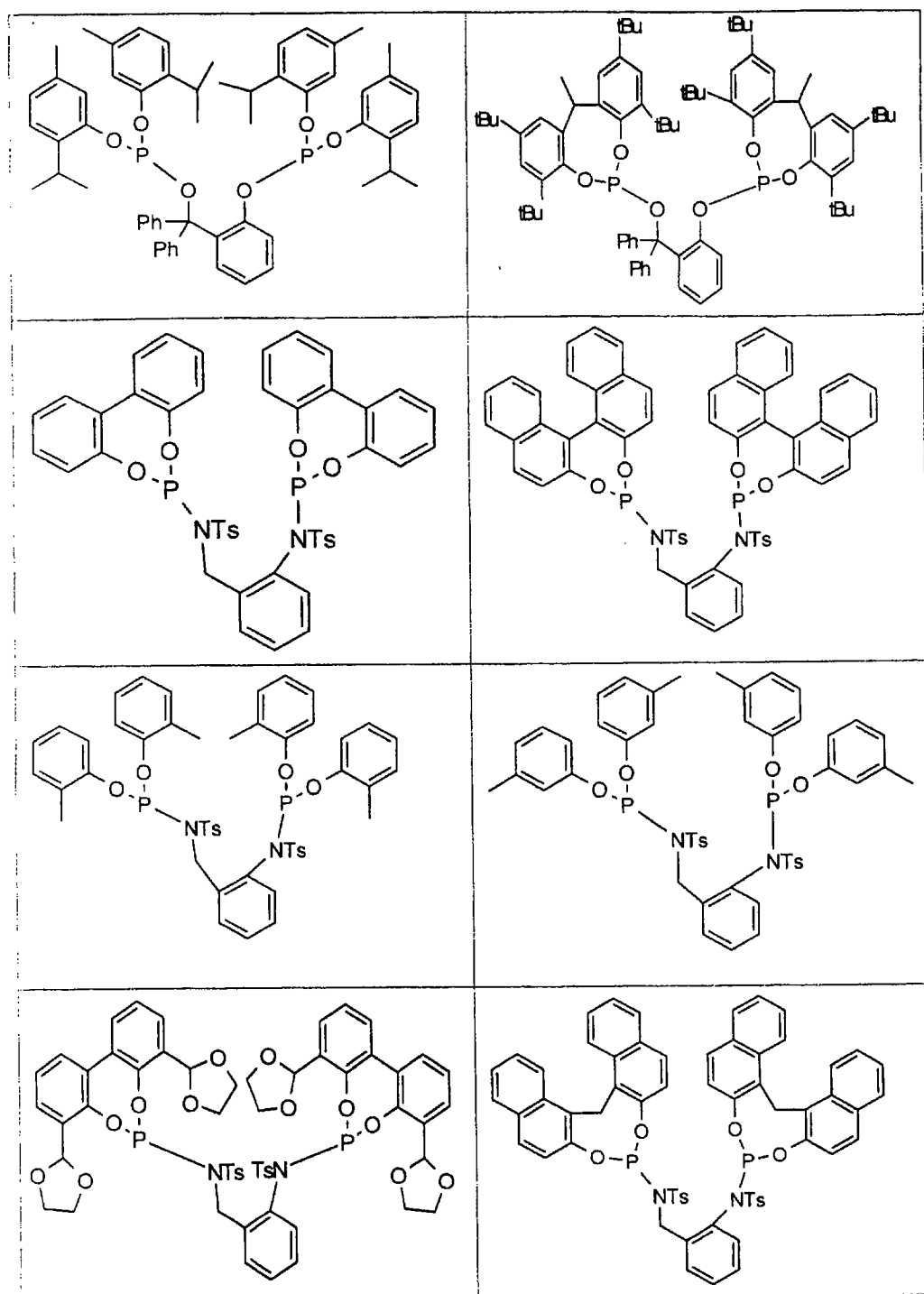


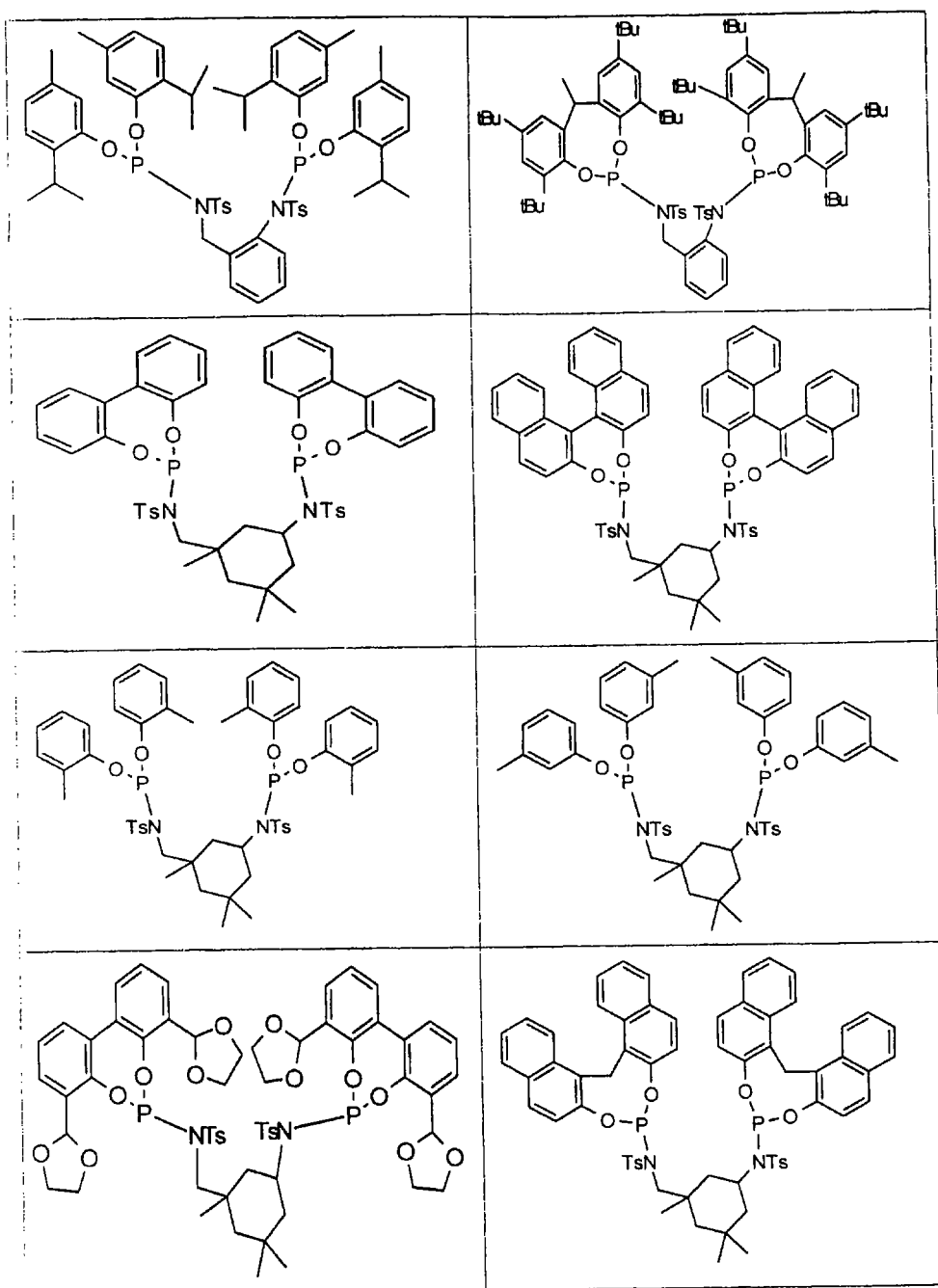


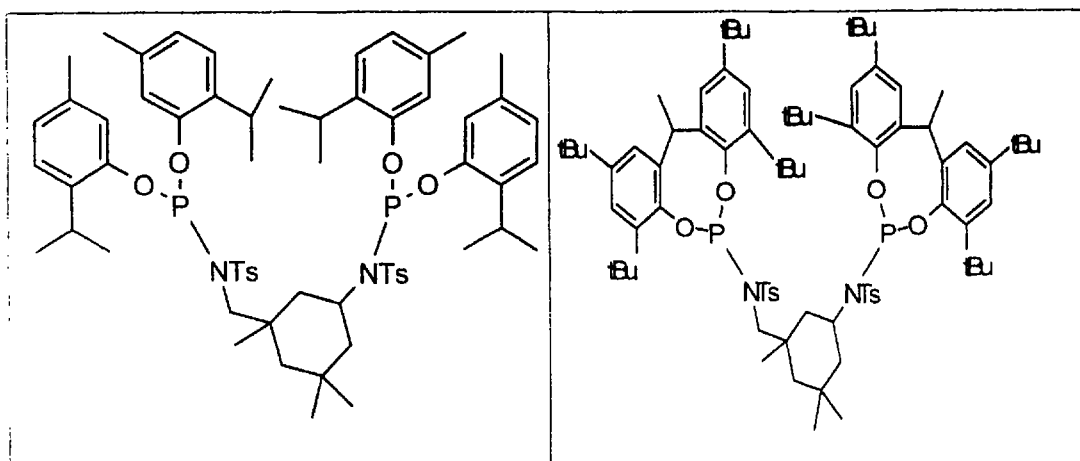












In which:

- 5 Ts represents the tolyl radical,
 tBu represents the tert-butyl group,
 Me represents the methyl group, and
 Ph represents the phenyl group.

10 According to the invention the catalyst corresponds
 advantageously to the general formula (V):



in which

- M is a transition metal,
 L_f represents the organic ligand of formula (I) and
 15 v represents a number between 1 and 4 (inclusive).

20 Metals which may be complexed by the organic ligands of
 the invention are generally all transition metals of
 groups 1b, 2b, 3b, 4b, 5b, 6b, 7b and 8 of the Periodic
 Table of the Elements, as published in the "Handbook of
 Chemistry and Physics", 51st Edition (1970-1971) from
 The Chemical Rubber Company.

25 Among these metals mention may be made more
 particularly of the metals mention may be made as non-
 limiting examples, of nickel, cobalt, iron, ruthenium,
 rhodium, palladium, osmium, iridium, platinum, copper,
 silver, gold, zinc, cadmium and mercury.

30 Organometallic complexes comprising the organic ligands

of the invention may be prepared by contacting a solution of a compound of the selected metal with a solution of the organic ligand of the invention.

5 The metal compound may be dissolved in a solvent.

The metal in the compound employed may be in the same oxidation state which it will have in the organometallic complex or in a higher oxidation state.

10

By way of example it is possible to indicate that in the organometallic complexes of the invention rhodium is in oxidation state (I), ruthenium in oxidation state (II), platinum in oxidation state (0), palladium in
15 oxidation state (0), osmium in oxidation state (II), iridium in oxidation state (I), cobalt in oxidation stage (I) and nickel in oxidation state (0).

If in the course of the preparation of the
20 organometallic complex the metal is employed in a higher oxidation state it will be possible for it to be reduced in situ.

The organometallic complexes comprising the organic
25 ligands of the invention may be used as catalysts in olefin hydrocyanation reactions.

As transition metal the transition metal compounds, more particularly the compounds of nickel, of
30 palladium, of cobalt, of iron or of copper, are preferably used.

Among the aforementioned compounds the most preferred compounds are those of nickel.

35

Non-limiting examples include:

- compounds in which nickel is in oxidation state zero, such as potassium tetracyanonickelate

$K_4[Ni(CN)_4]$, bis(acrylonitrile)nickel zero, bis(cycloocta-1,5-diene)nickel zero (also called $Ni(cod)_2$) and derivatives containing ligands, such as tetrakis(triphenylphosphine)nickel zero;

5

- compounds of nickel such as carboxylates (especially the acetate), carbonate, bicarbonate, borate, bromide, chloride, citrate, thiocyanate, cyanide, formate, hydroxide, hydrophosphite, phosphite, phosphate and derivatives, iodide, nitrate, sulphate, sulphite, aryl- and alkylsulphonates.

10

When the nickel compound used corresponds to a nickel oxidation state greater than zero a nickel reducing agent which reacts preferentially with the nickel under the reaction conditions is added to the reaction mixture. This reducing agent may be organic or inorganic. Non-limiting examples include borohydrides such as BH_4Na and BH_4K , Zn powder, magnesium or hydrogen.

15

20

When the nickel compound used corresponds to the zero oxidation state of nickel it is also possible to add a reducing agent of the aforementioned type, but such addition is not mandatory.

25

When an iron compound is used the same reducing agents are suitable.

30

In the case of palladium the reducing agents may be, furthermore, elements of the reaction mixture (phosphine, solvent, olefin).

The organic compounds containing at least one ethylenic double bond that are more particularly employed in the present process are diolefins such as butadiene, isoprene, hexa-1,5-diene, cycloocta-1,5-diene, ethylenically unsaturated aliphatic nitriles,

35

especially linear pentenenitriles such as pent-3-enenitrile and pent-4-enenitrile, monoolefins such as styrene, methylstyrene, vinyl naphthalene, cyclohexene, methylcyclohexene and mixtures of two or more of these
5 compounds.

The pentenenitriles in particular may contain amounts, generally minor amounts, of other compounds, such as 2-methylbut-3-enenitrile, 2-methylbut-2-enenitrile,
10 pent-2-enenitrile, valeronitrile, adiponitrile, 2-methylglutaronitrile, 2-ethylsuccinonitrile or butadiene, originating for example from the prior hydrocyanation reaction of the butadiene to unsaturated nitriles.

15 The reason for this is that the hydrocyanation of the butadiene is accompanied by the formation, along with the linear pentenenitriles, of not inconsiderable amounts of 2-methylbut-3-enenitrile and 2-methylbut-2-enenitrile.
20 enenitrile.

The catalyst system used for the hydrocyanation according to the process of the invention may be prepared before it is introduced into the reaction
25 zone; for example by adding the appropriate amount of selected transition metal compound and where appropriate of reducing agent to ligand in accordance with the invention, alone or in solution in a solvent. It is also possible to prepare the catalyst system "in
30 situ" by simply adding the ligand and the transition metal compound to the hydrocyanation reaction mixture before or after adding the compound to be hydrocyanated.

35 The amount of compound of nickel or of another transition metal used is selected so as to give a concentration, in moles of transition metal per mole of organic compounds to be hydrocyanated or isomerized, of between 10^{-4} and 1, and preferably between 0.005 and

0.5 mol of nickel or of the other transition metal employed.

5 The amount of organic ligands of the invention used to form the catalyst is selected such that the number of moles of this compound relative to 1 mol of transition metal is from 0.5 to 50 and preferably from 2 to 10.

10 Although the reaction is generally conducted without solvent it may be advantageous to add an inert organic solvent. The solvent may be a solvent for the catalyst which is miscible with the phase comprising the compound to be hydrocyanated at the hydrocyanation temperature. Examples of such solvents include
15 aromatic, aliphatic or cycloaliphatic hydrocarbons.

This solvent may also be partially miscible with the compounds to be hydrocyanated, particularly when the reaction mixture is at a temperature lower than the
20 reaction temperature. Hence at such temperatures a two-phase system may be obtained. Where the catalyst system is soluble in said solvent its extraction from the reaction mixture is thereby facilitated. Partially or immiscible solvents of this kind may be water or
25 organic salts in melt form with an ionic character. Such solvents are used particularly when the organic ligand contains anionic radicals which render it soluble in ionic media. These radicals are, for example, sulphonate, carbonate, carboxylate, phosphate, ammonium, guanidinium and imidazolium groups which are
30 substituents on the aromatic radicals of the ligand.

The hydrocyanation reaction is generally carried out at a temperature from 10°C to 200°C and preferably from
35 30°C to 120°C. Advantageously it is carried out in a single-phase medium at the reaction temperature.

The process of the invention may be implemented continuously or batchwise.

The hydrogen cyanide employed may be prepared from metal cyanides, especially sodium cyanide, or from cyanohydrins, such as acetone cyanohydrin, or by any
5 other known synthesis process.

The hydrogen cyanide is introduced into the reactor in gaseous form, as a gas mixture or in liquid form. It may also be dissolved beforehand in an organic solvent.

10

In the context of a batchwise implementation it is possible in practice to charge a reactor, purged beforehand by means of an inert gas (such as nitrogen or argon) either with a solution containing the
15 entirety or a part of the various constituents, such as the organic ligand of the invention, the transition metal compound, the reducing agents and solvents where appropriate, or with said constituents separately. Generally the reactor is then taken to the selected
20 temperature and then the compound to be hydrocyanated is introduced. The hydrogen cyanide is then itself introduced, preferably continuously and regularly.

When the reaction (whose development can be monitored
25 by assaying samples) is at an end the reaction mixture is withdrawn, after cooling, and the reaction products are isolated, by distillation for example.

An enhancement of the process for hydrocyanating
30 ethylenically unsaturated compounds according to the present invention relates in particular to the hydrocyanation of said ethylenically unsaturated nitrile compounds by reaction with hydrogen cyanide and consists in using a catalyst system in accordance with
35 the present invention with a cocatalyst composed of at least one Lewis acid.

The ethylenically unsaturated compounds which may be employed in this improvement are in general those which

were mentioned for the basic process. However, it is more particularly advantageous to apply it to the hydrocyanation reaction to dinitriles of the ethylenically unsaturated aliphatic mononitriles, particularly to apply it to linear pentenenitriles such as pent-3-enenitrile, pent-4-enenitrile and mixtures thereof.

These pentenenitriles may contain amounts, generally minor amounts, of other compounds, such as 2-methylbut-3-enenitrile, 2-methylbut-2-enenitrile, pent-2-enenitrile, valeronitrile, adiponitrile, 2-methylglutaronitrile, 2-ethylsuccinonitrile or butadiene, originating from the prior hydrocyanation reaction of the butadiene and/or from the isomerization of 2-methylbut-3-enenitrile to pentenenitriles.

The Lewis acid used as cocatalyst makes it possible in particular, in the case where ethylenically unsaturated aliphatic nitriles are hydrocyanated, to improve the linearity of the dinitriles obtained, in other words the percentage of linear dinitriles relative to the entirety of the dinitriles formed, and/or to enhance the activity and service life of the catalyst.

A Lewis acid in the present text, according to the usual definition, refers to compounds which accept electron pairs.

Use may be made in particular of the Lewis acids cited in the work edited by G.A. Olah, "Friedel-Crafts and related Reactions", volume I, pages 191 to 197 (1963).

The Lewis acids which may be employed as cocatalysts in the present process are selected from compounds of the elements of groups Ib, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the Periodic Table of the Elements. These compounds are most often salts, especially halides, such as chlorides or bromides,

sulphates, sulphonates, haloalkylsulphonates, perhalo-alkylsulphonates, especially fluoroalkylsulphonates or perfluoroalkylsulphonates, haloalkylacetates, perhaloalkylacetates, especially fluoroalkylacetates or
5 perfluoroalkylacetates, carboxylates and phosphates.

Non-limiting examples of such Lewis acids include zinc chloride, zinc bromide, zinc iodide, manganese chloride, manganese bromide, cadmium chloride, cadmium
10 bromide, stannous chloride, stannous bromide, stannous sulphate, stannous tartrate, indium trifluoromethylsulphonate, indium trifluoroacetate, zinc trifluoroacetate, the chlorides or bromides of rare earth elements such as lanthanum, cerium, praseodymium,
15 neodymium, samarium, europium, gadolinium, terbium, dysprosium, hafnium, erbium, thallium, ytterbium and lutetium, and cobalt chloride, ferrous chloride and yttrium chloride.

20 As a Lewis acid it is also possible to use organometallic compounds such as triphenylborane or titanium isopropoxide.

It will be appreciated that mixtures of two or more Lewis acids may be employed.

25

Among Lewis acids particular preference is given to zinc chloride, zinc bromide, stannous chloride, stannous bromide and triphenylborane and to zinc chloride/stannous chloride mixtures, indium tri-
30 fluoromethylsulphonate, indium trifluoroacetate and zinc trifluoroacetate.

The Lewis acid cocatalyst employed represents generally from 0.01 to 50 mol per mole of transition metal
35 compound, more particularly of nickel compound, and preferably from 0.5 to 10 mol per mole.

As for the implementation of the basic process of the invention, the catalyst solution used for the

- hydrocyanation in the presence of Lewis acid may be prepared prior to its introduction into the reaction zone; for example, by adding the ligand of formula (I), the appropriate amount of selected transition metal compound, Lewis acid and, where appropriate, reducing agent to the reaction mixture. It is also possible to prepare the catalyst solution "in situ" by simply mixing these various constituents.
- 10 It is also possible, under the conditions of the hydrocyanation process of the present invention, and especially when working in the presence of the above-described catalyst comprising at least one ligand of formula (I) and at least one transition metal compound,
- 15 to carry out the isomerization of 2-methylbut-3-enenitrile to pentenenitriles, and more generally of branched unsaturated nitriles to linear unsaturated nitriles, in the absence of hydrogen cyanide.
- 20 The 2-methylbut-3-enenitrile subjected to the isomerization according to the invention may be employed alone or in a mixture with other compounds.
- Thus 2-methylbut-3-enenitrile may be deployed as a mixture with 2-methylbut-2-enenitrile, pent-4-enenitrile, pent-3-enenitrile, pent-2-enenitrile, butadiene, adiponitrile, 2-methylglutaronitrile, 2-ethylsuccinonitrile or valeronitrile.
- 30 It is particularly advantageous to treat the reaction mixture originating from the hydrocyanation of butadiene by HCN in the presence of at least one ligand of formula (I) and at least one transition metal compound, more preferably a compound of nickel in
- 35 oxidation state 0, as defined above.

In the context of this preferred version the catalyst system is already present for the butadiene hydrocyanation reaction and it is therefore sufficient

to stop any introduction of hydrogen cyanide in order to allow the isomerization reaction to take place.

5 It is possible, where appropriate, in this version to effect a gentle purging of the reactor by means of an inert gas, such as nitrogen or argon for example, in order to expel the hydrocyanic acid which might still be present.

10 The isomerization reaction is generally carried out at a temperature from 10°C to 200°C and preferably from 60°C to 160°C.

15 In the preferred case of an isomerization immediately following the butadiene hydrocyanation reaction it will be advantageous to operate at the temperature at which the hydrocyanation was conducted.

20 As for the process of hydrocyanating ethylenically unsaturated compounds, the catalyst system used for the isomerization may be prepared prior to its introduction into the reaction zone; for example, by adding the ligand of formula (I), the appropriate amount of selected transition metal compound and, where
25 appropriate, reducing agent to a solvent. It is also possible to prepare the catalyst system "in situ" by simply adding these various constituents to the reaction mixture. The amount of transition metal compound, and more particularly of nickel compound,
30 that is used, and the amount of ligand of formula (I), are the same as for the hydrocyanation reaction.

Although the isomerization reaction is conducted generally without solvent it may be advantageous to add
35 an inert organic solvent, which may be that of the subsequent extraction. This is the case particularly when such a solvent has been employed in the butadiene hydrocyanation reaction that was used to prepare the mixture which is subjected to the isomerization

reaction. Such solvents may be selected from those which were identified above for the hydrocyanation.

5 The preparation of dinitrile compounds by hydrocyanation of an olefin such as butadiene may be carried out using a catalyst system in accordance with the invention for the above steps of formation of unsaturated mononitriles and the isomerization step; the hydrocyanation reaction of unsaturated mononitriles to dinitriles can be implemented with a catalyst system in accordance with the invention or any other catalyst system already known for this reaction.

15 Similarly the hydrocyanation reaction of the olefin to unsaturated mononitriles and the isomerization thereof may be carried out with a catalyst system other than that of the invention; the hydrocyanation step of the unsaturated mononitriles to dinitriles is employed with a catalyst system in accordance with the invention.

20 The invention likewise provides organophosphorus compounds corresponding to the general formula (I) above.

25 It likewise provides the organophosphorus compounds corresponding to the general formulae listed in Table I above.

The examples which follow illustrate the invention.

30 In the examples the abbreviations used have the meanings indicated below.

cod: 1,5-cyclooctadiene
35 eq: equivalent
3PN: 3-pentenitrile
4PN: 4-pentenitrile
3+4PN: 3PN + 4PN
DC(Y): degree of conversion of the product to be

hydrocyanated, Y, corresponding to the ratio of the number of moles of Y converted to the initial number of moles of Y

Linearity (L): ratio of the number of moles of adiponitrile (AdN) formed to the number of moles of dinitriles formed (sum of the moles of AdN, ethylsuccinonitrile (ESN) and methylglutaronitrile (MGN))

GC: gas chromatography
10 ml: millilitre
mol: mole(s)
mmol: millimole(s).

The various products in accordance with the invention
15 may be prepared by one of the two following procedures:

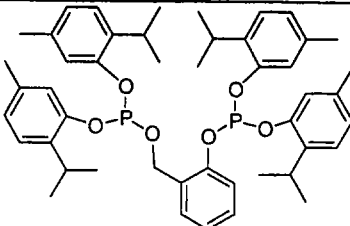
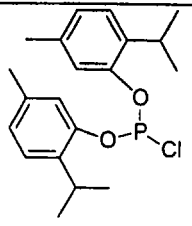
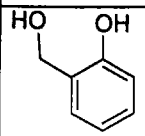
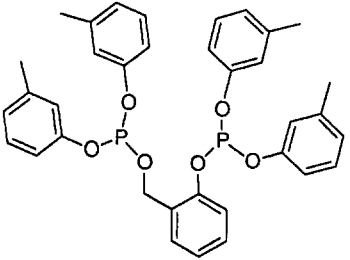
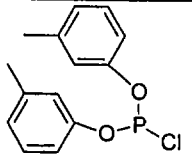
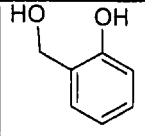
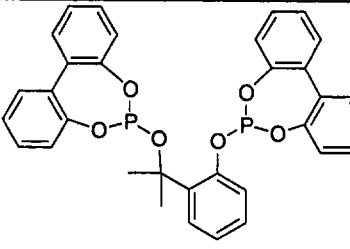
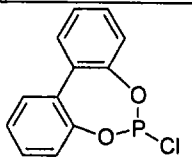
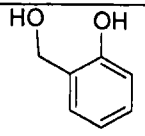
Procedure I:

A phosphochloridite is used which is prepared from a phenol or biphenol derivative and PCl_3 according to a
20 conventional procedure (see, for example, the method described by G. Buisman et al. in Tetrahedron, Asymmetry, vol. 4, (7), pp. 1625-34 (1993)), and a diol available commercially. The following general procedure
25 is representative:

In a 100 ml reactor under argon 6 mmol of phosphochloridite are dissolved in 20 ml of anhydrous toluene. The solution is stirred at -10°C . A solution of 3 mmol of diol and 10 mmol of triethylamine in 20 ml
30 of anhydrous toluene is introduced dropwise into the reaction mixture, which is held at -10°C : a white precipitate forms. The suspension is stirred vigorously at 25°C for 18 h and then filtered under argon over a bed of basic alumina. After rinsing with toluene, the
35 filtrate is concentrated under reduced pressure to give the desired product, which is used without further purification.

The following ligands were prepared according to the

procedure described above:

Example	Ligand	Structure	Phosphochloridite	Diol
1	A			
2	B			
3	C			

Procedure II:

5

A phosphoramidite is used which is prepared from Cl_2PNEt_2 (available commercially) and a substituted or unsubstituted phenol according to the following procedure:

10 A mixture of Cl_2PNEt_2 (0.20 mol) and triethylamine (0.44 mol) in toluene (800 ml) at 0°C is admixed slowly, with vigorous stirring, with a solution of phenol (0.40 mol) in toluene (100 ml). The formation of a white precipitate is observed. The mixture is allowed

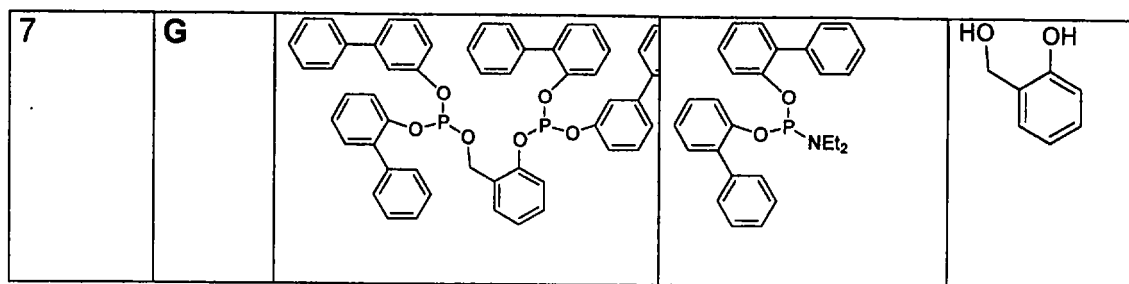
15 to climb to ambient temperature and is stirred, still vigorously, for 2 h. The mixture is subsequently filtered on a bed of silica and concentrated under vacuum to give the phosphoramidite $(\text{ArO})_2\text{PNEt}_2$ with a purity of more than 95%.

20 Additionally a commercially available diol is used. The following general procedure is representative:

In a 100 ml reactor under argon 6 mmol of phosphoramidite are introduced in 20 ml of anhydrous toluene. The solution is stirred at 0°C and 7.5 ml of a 2 M solution of hydrochloric acid in ether are added thereto over 30 minutes. The formation of a white precipitate is observed, and the mixture is stirred at ambient temperature for 1 hour. A solution of 3 mmol of diol and 10 mmol of triethylamine in 20 ml of anhydrous toluene is subsequently introduced dropwise into the reaction mixture, which is cooled at -10°C. The suspension is stirred vigorously at 25°C for 18 hours and then filtered under argon on a bed of basic alumina. After rinsing with toluene, the filtrate is concentrated under reduced pressure to give the desired product, which is used without further purification.

The following ligands were prepared according to the procedure described above:

Example	Ligand	Structure	Phosphoramidite	Diol
4	D			
5	E			
6	F			



Examples of hydrocyanation of 3-pentenenitrile (3PN) to adiponitrile (AdN)

- 5 The general procedure used is as follows:
Under an argon atmosphere a 60 ml Schott glass tube equipped with a septum stopper is charged in succession with
- 10 - the ligand (2.5 eq),
- 1.21 g (15 mmol; 30 eq) of anhydrous 3PN,
- 138 mg (0.5 mmol; 1 eq) of $\text{Ni}(\text{cod})_2$ and
- the Lewis acid (0.5 mmol; 1 eq).
- 15 The mixture is taken to 70°C with stirring. Acetone cyanohydrin is injected into the reaction mixture by means of a syringe driver at a rate of 0.45 ml per hour. After 3 hours of injection the syringe driver is stopped. The mixture is cooled to ambient temperature,
- 20 diluted with acetone and analysed by gas chromatography.

The results are compiled in the table below:

Example	Ligand	Lewis acid	DC (3PN)	Linearity
8	A	ZnCl_2	64%	70%
9	B	ZnCl_2	14%	71%
10	C	ZnCl_2	20%	73%
11	D	ZnCl_2	44%	76%
12	E	ZnCl_2	11%	72%
13	E	CoCl_2	32%	74%
14	F	ZnCl_2	16%	67%

15	G	ZnCl ₂	48%	80%
16	G	YCl ₃	64%	88%

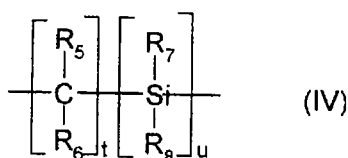
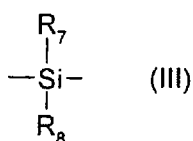
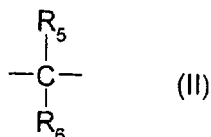
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m and n are identical or different integers between 0

and 6, where $m + n$ must be greater than or equal to 1,

Q_1 and Q_2 , which are identical or different, represent a group corresponding to the general formulae II, III or
5 IV below:

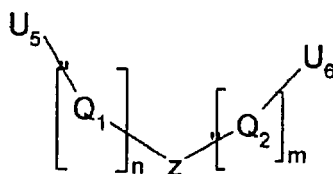


in which R_5 , R_6 , R_7 and R_8 , which are identical or
10 different, represent aliphatic, cycloaliphatic or aromatic hydrocarbon radicals containing 1 to 12 carbon atoms, R_5 and R_6 also representing the hydrogen atom, and

15 t and u represent integers between 0 and 6, with a sum $u + t$ greater than or equal to 1,

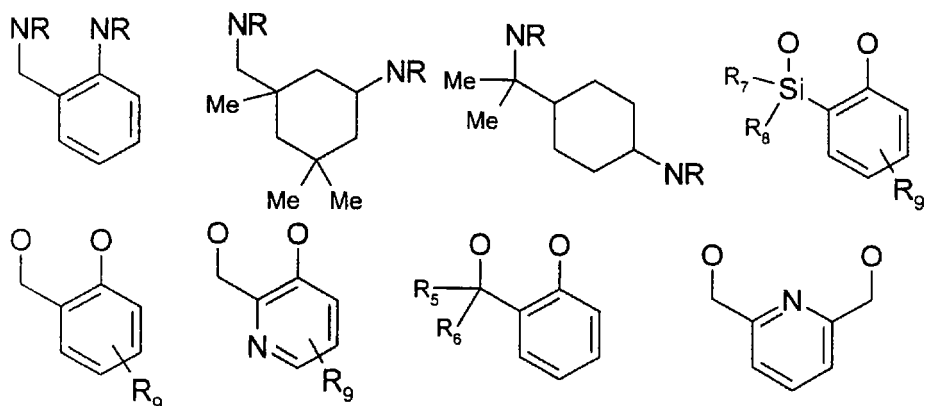
Z representing a divalent radical selected from the group consisting of aromatic or cycloaliphatic radicals
20 containing one or more rings, which are in fused form or not and which may be substituted and may contain heteroatoms.

2. Process according to Claim 1, characterized in
25 that the ligand of formula I comprises a structure of the formula below:



selected from the group consisting of the following structures:

5

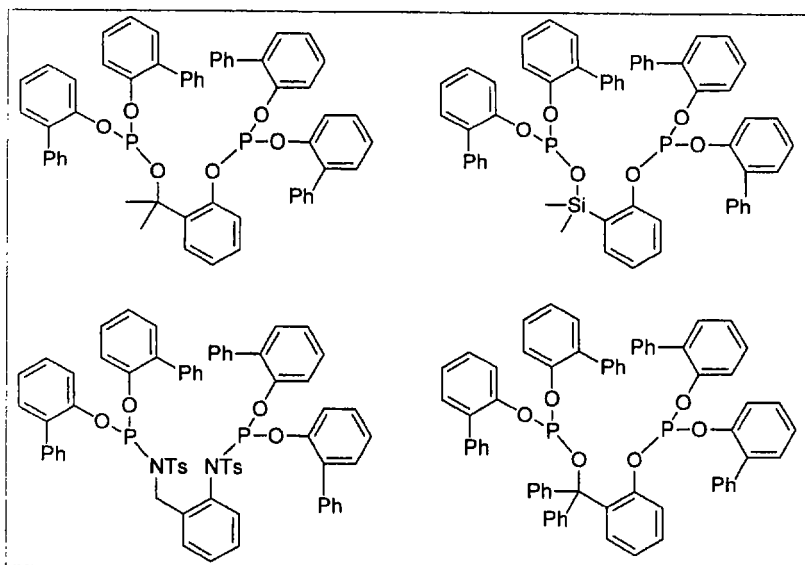


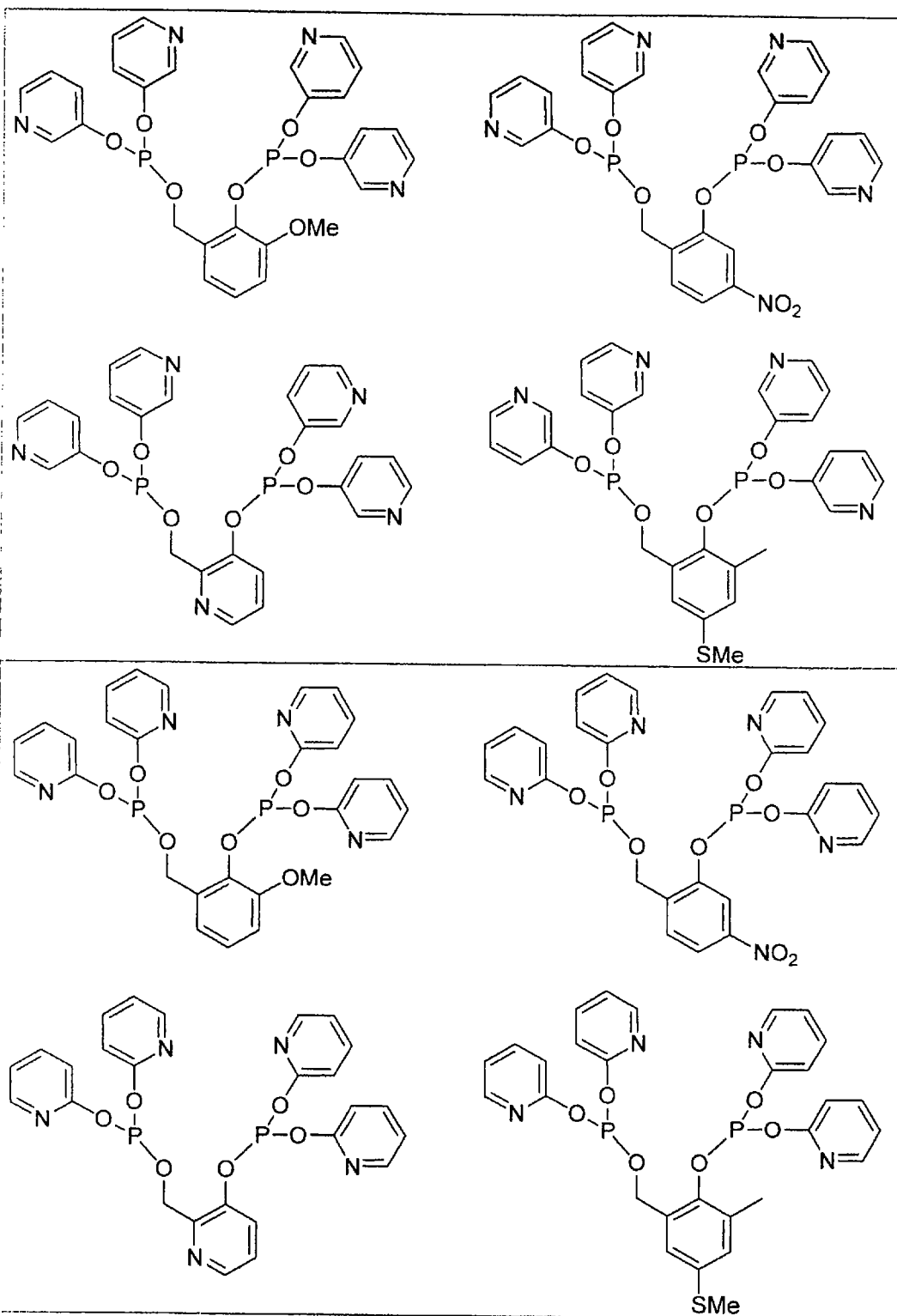
in which R₉ represents a halogen atom, the alkyl, halogen, aryl, alkoxy, aryloxy, nitro, thioalkyl, secondary amine and nitrile groups.

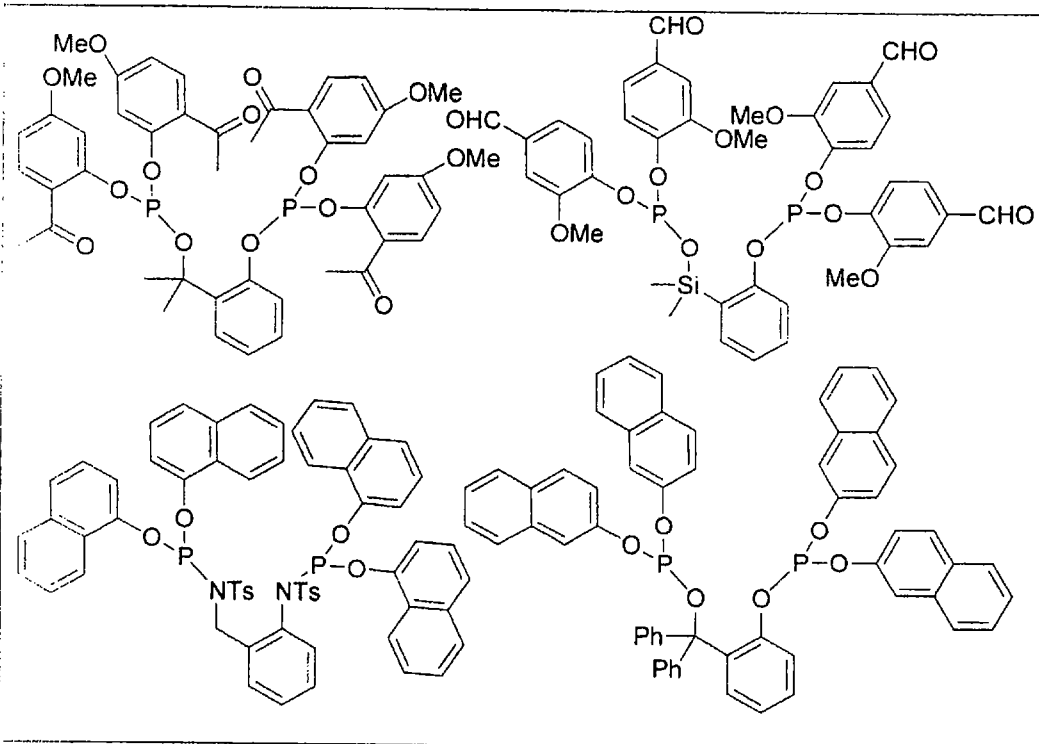
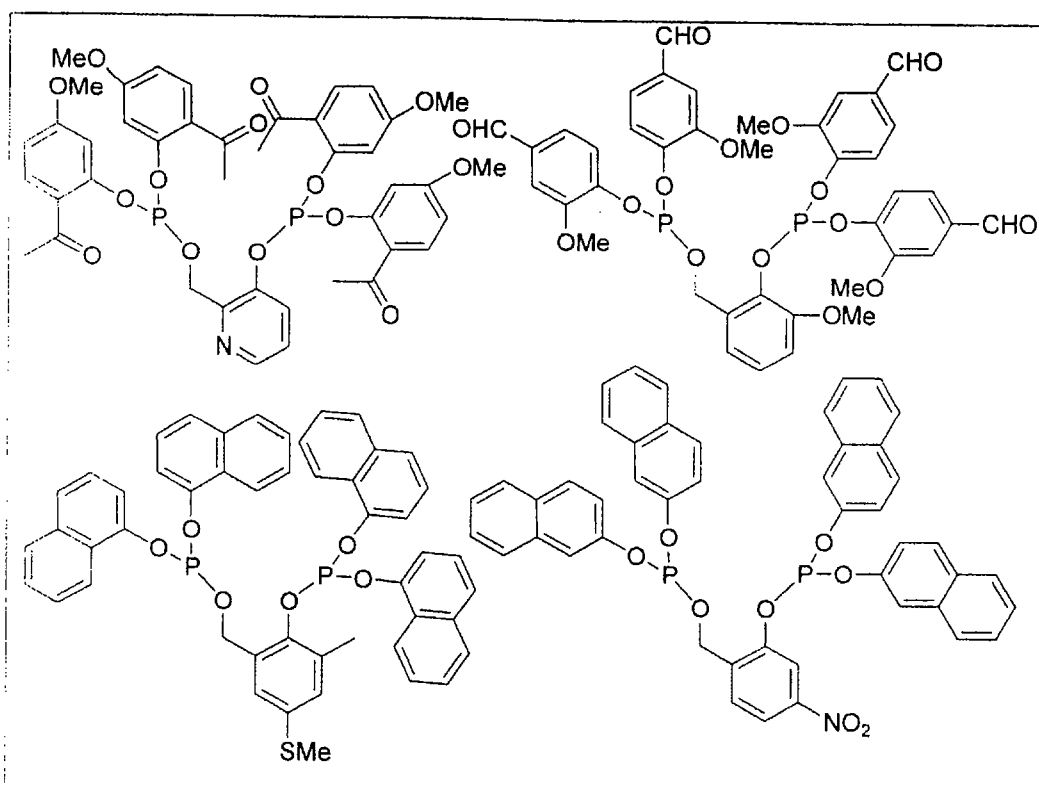
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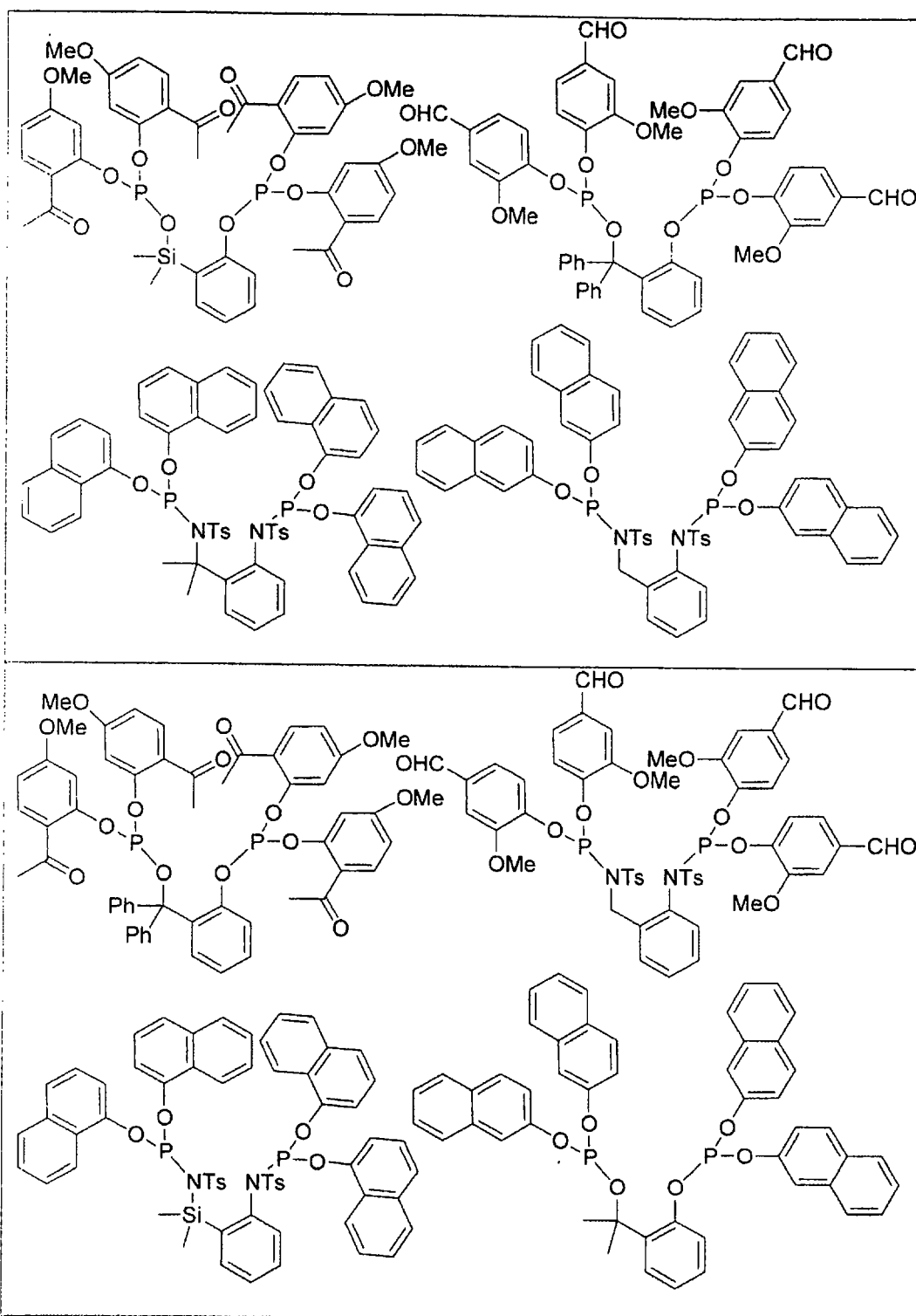
3. Process according to Claim 1 or 2, characterized in that the organic ligand is selected from the group consisting of the compounds of the formula below:

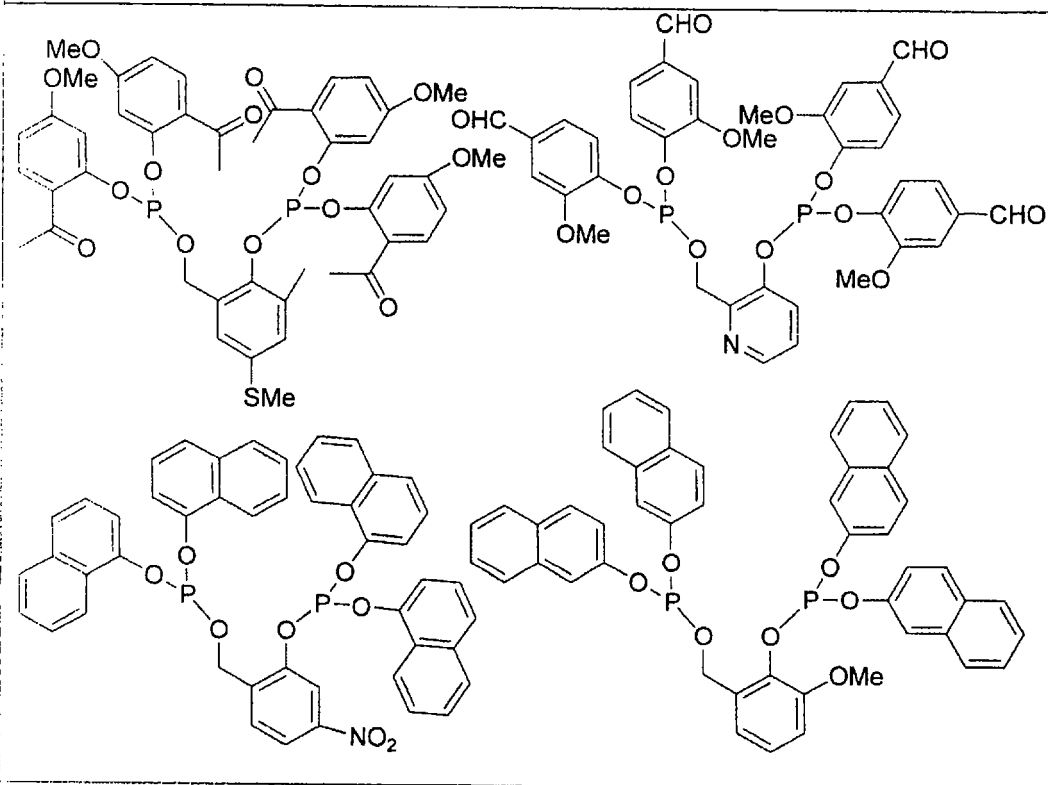
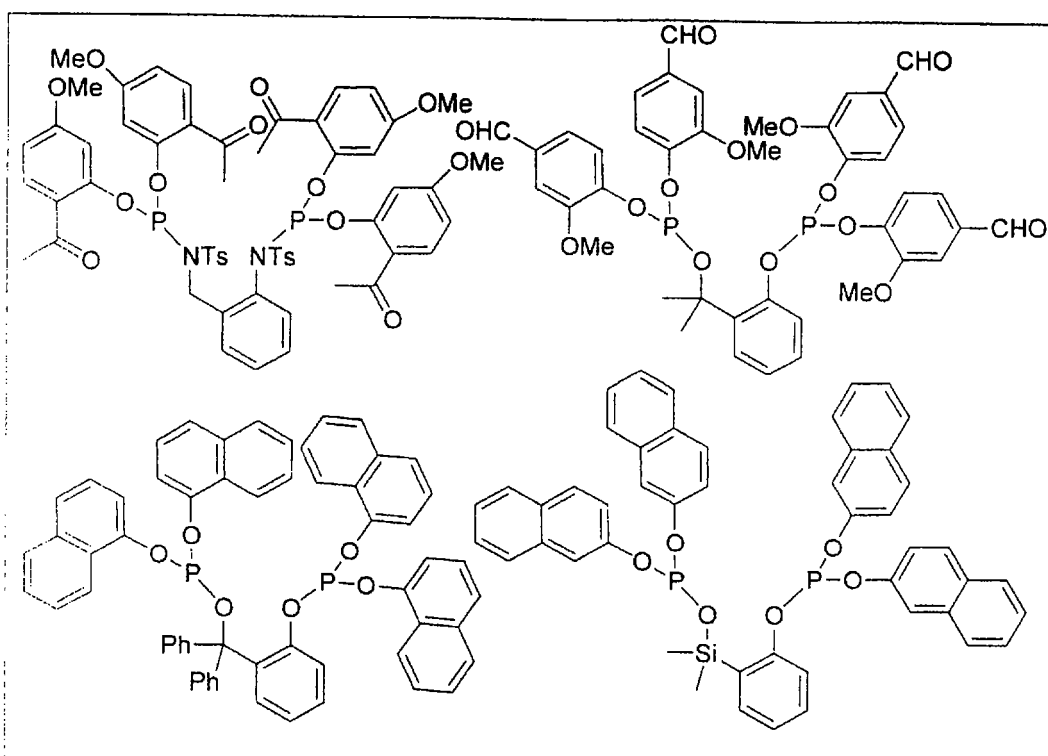
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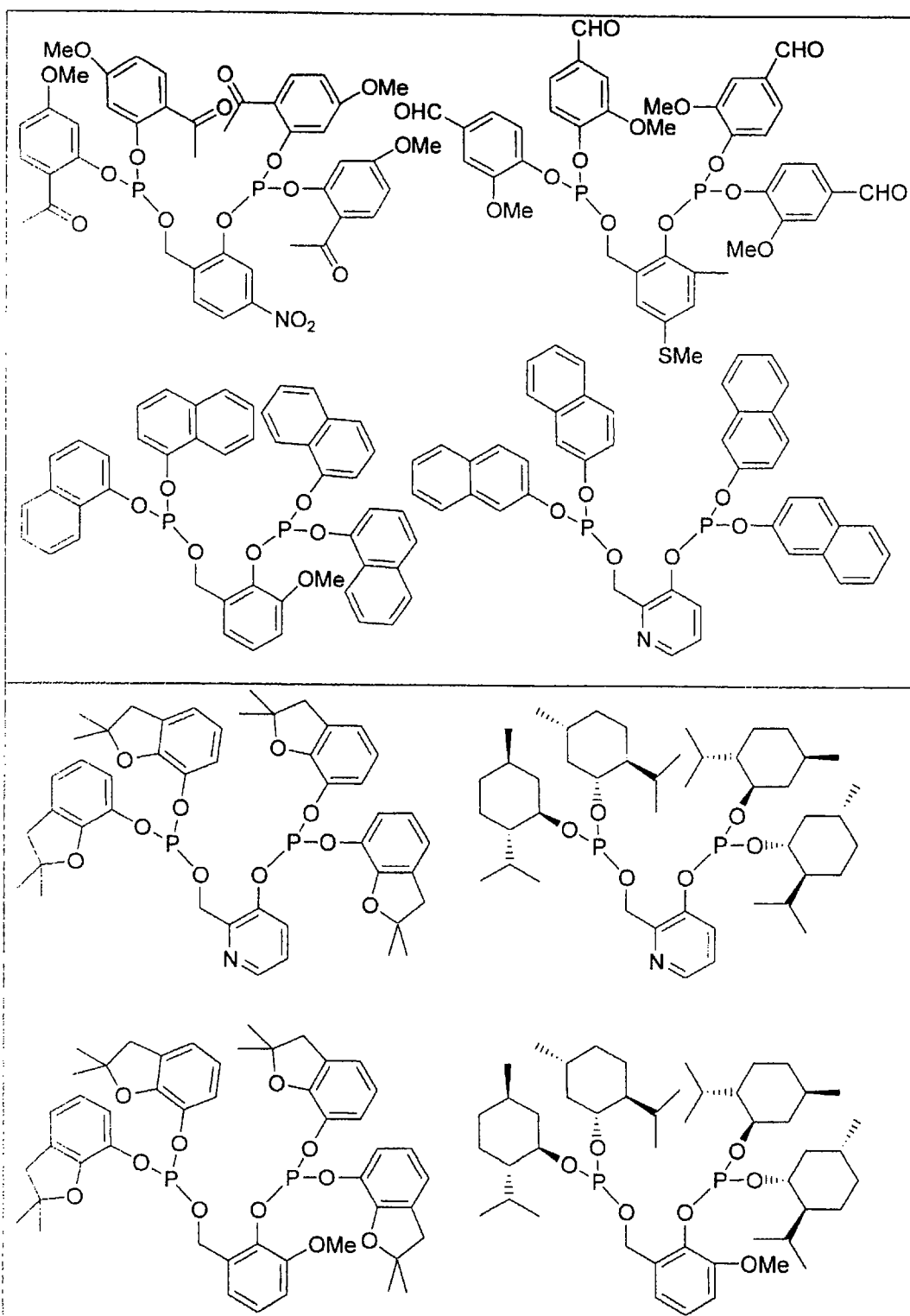


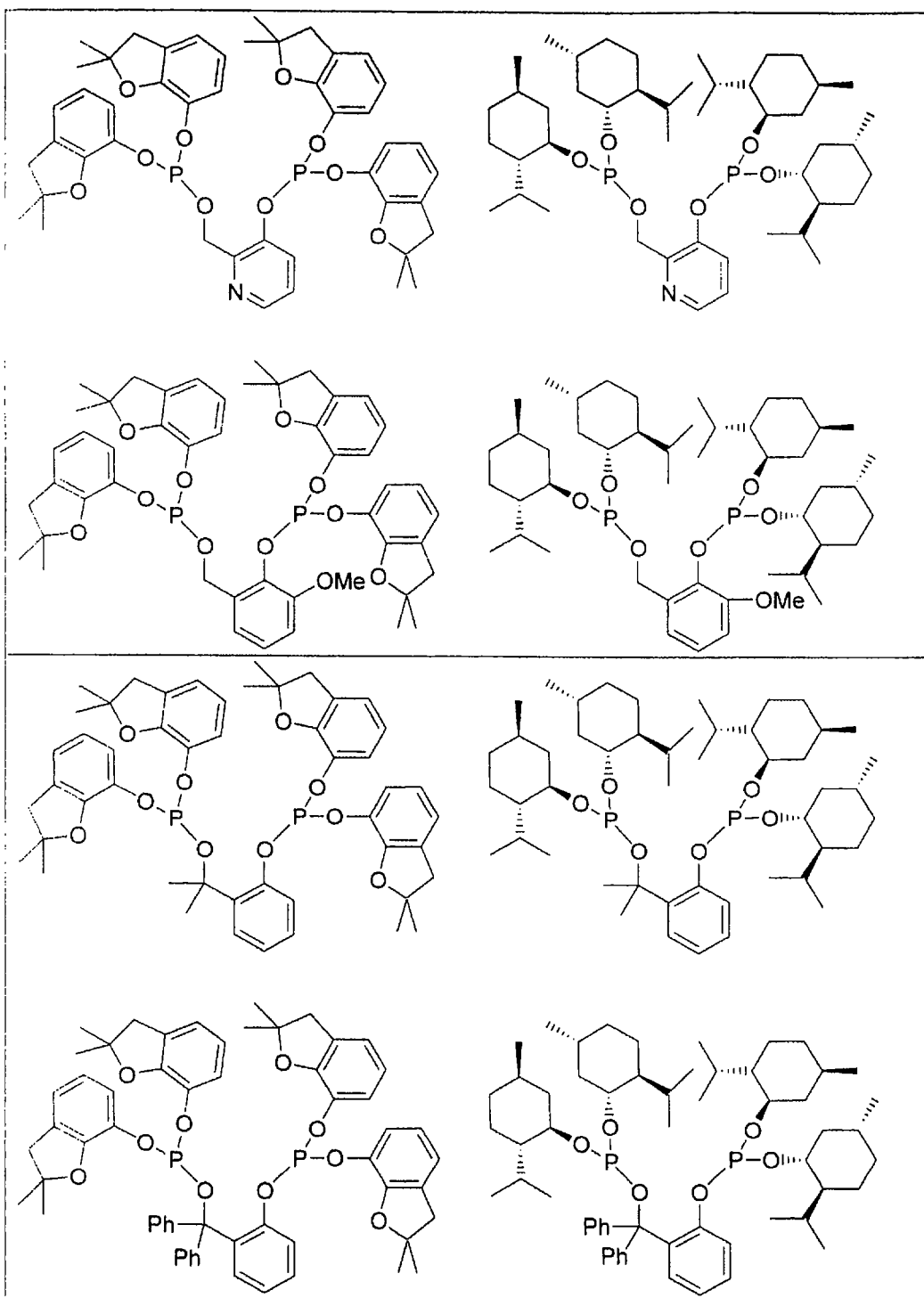


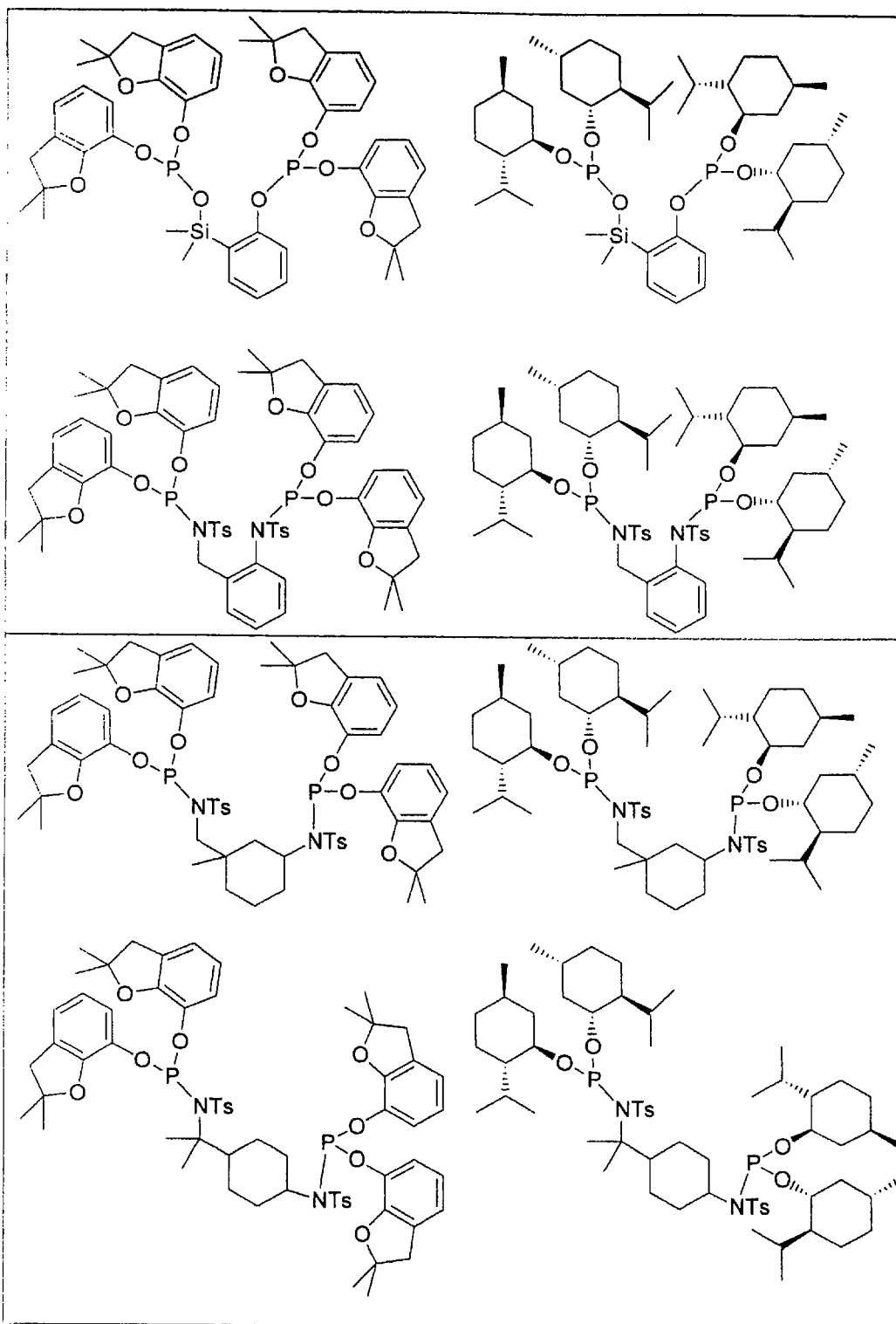


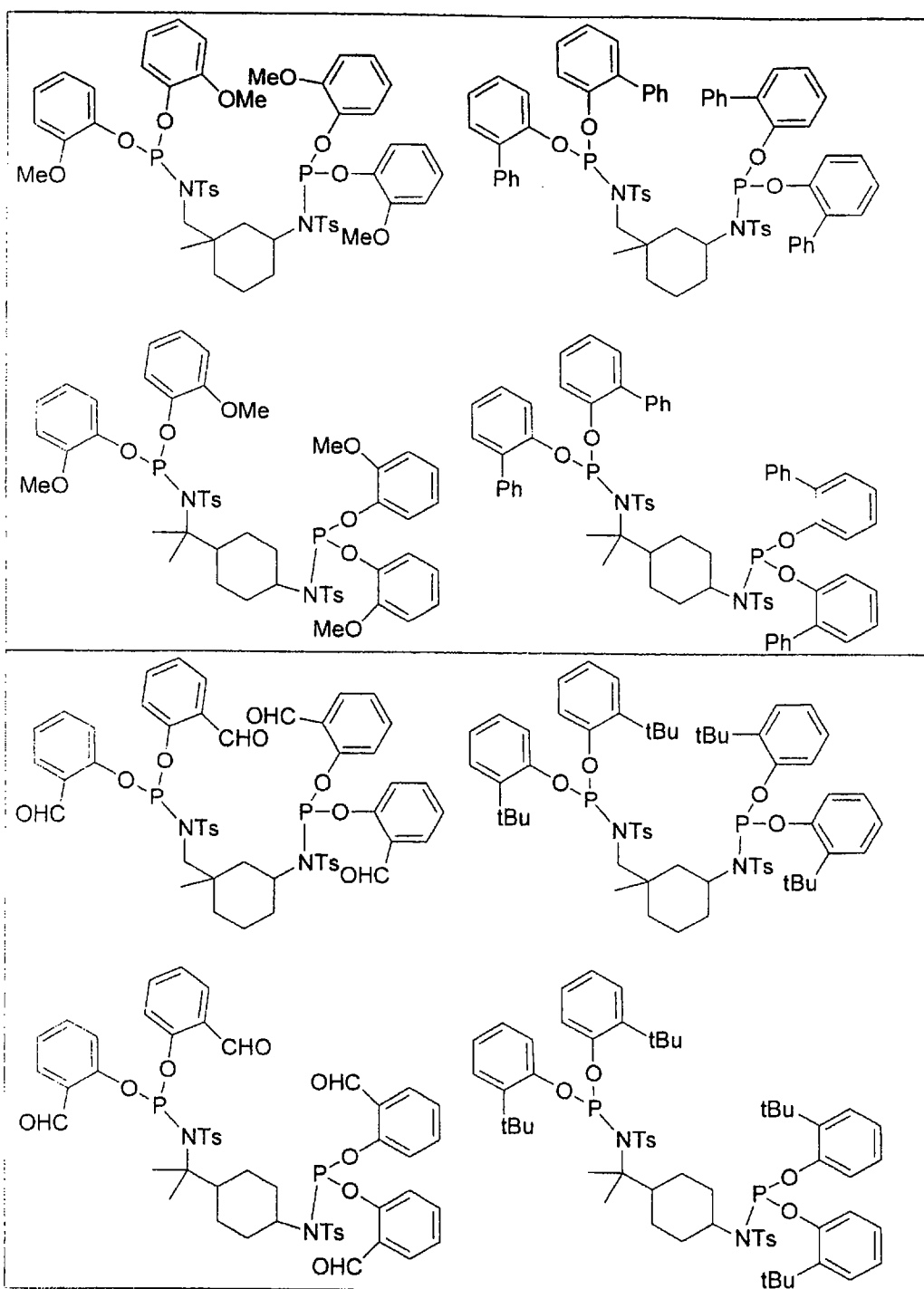


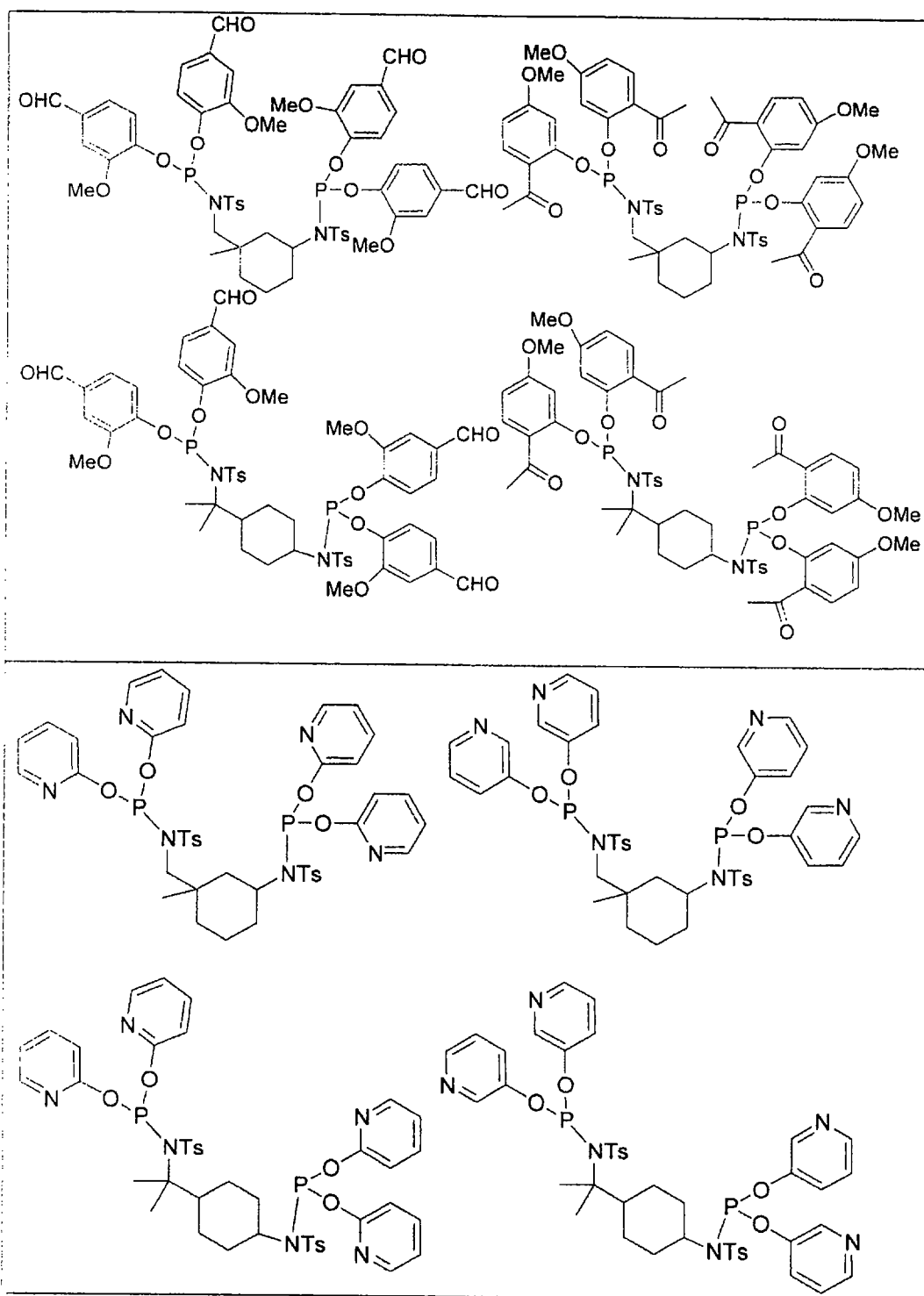


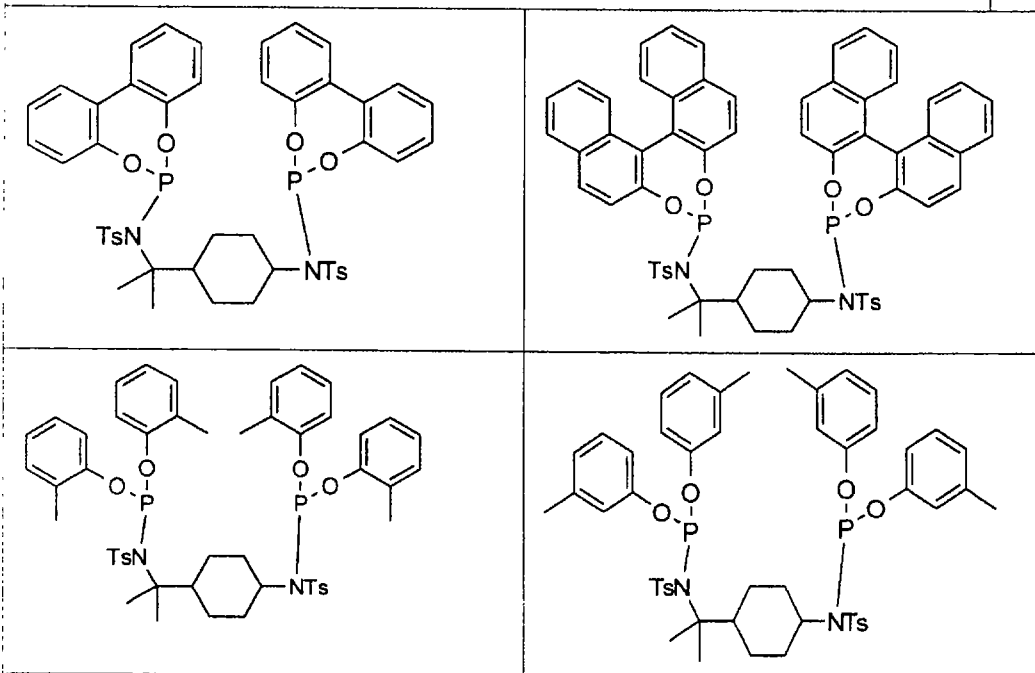
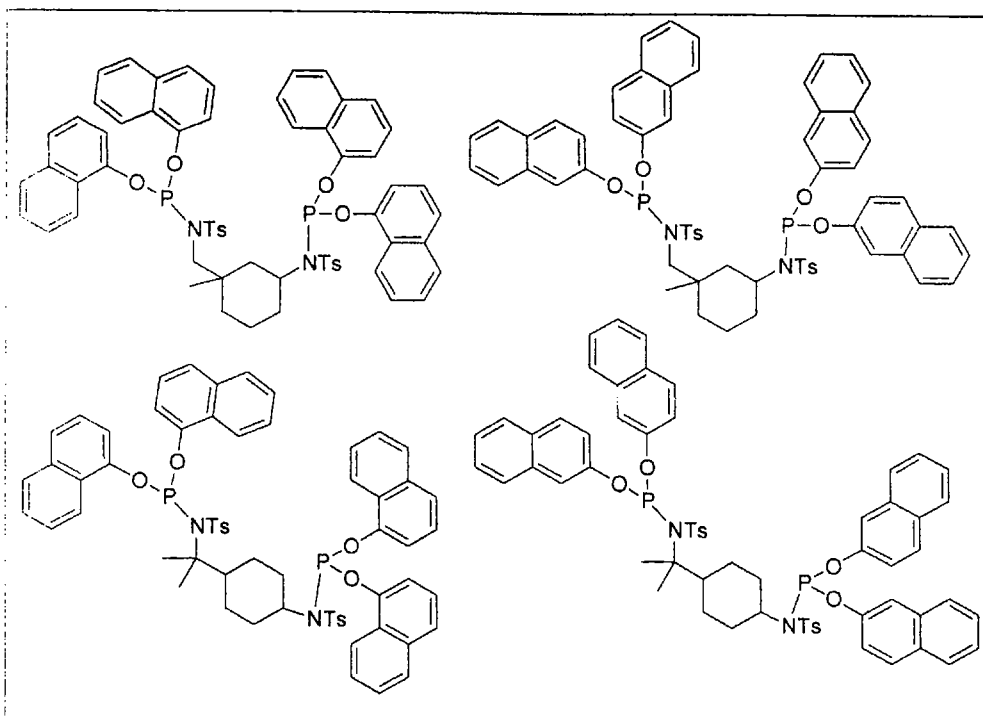


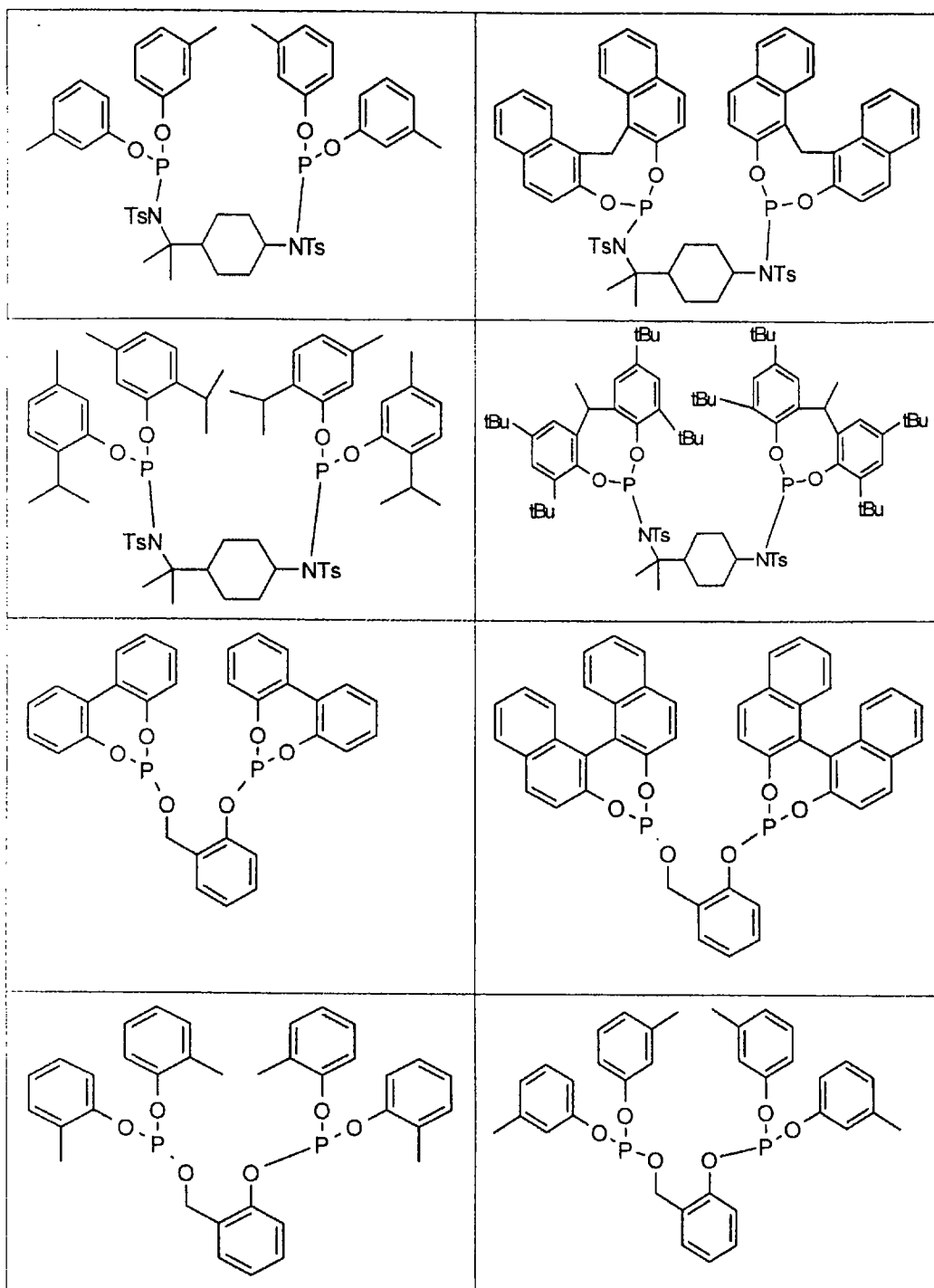


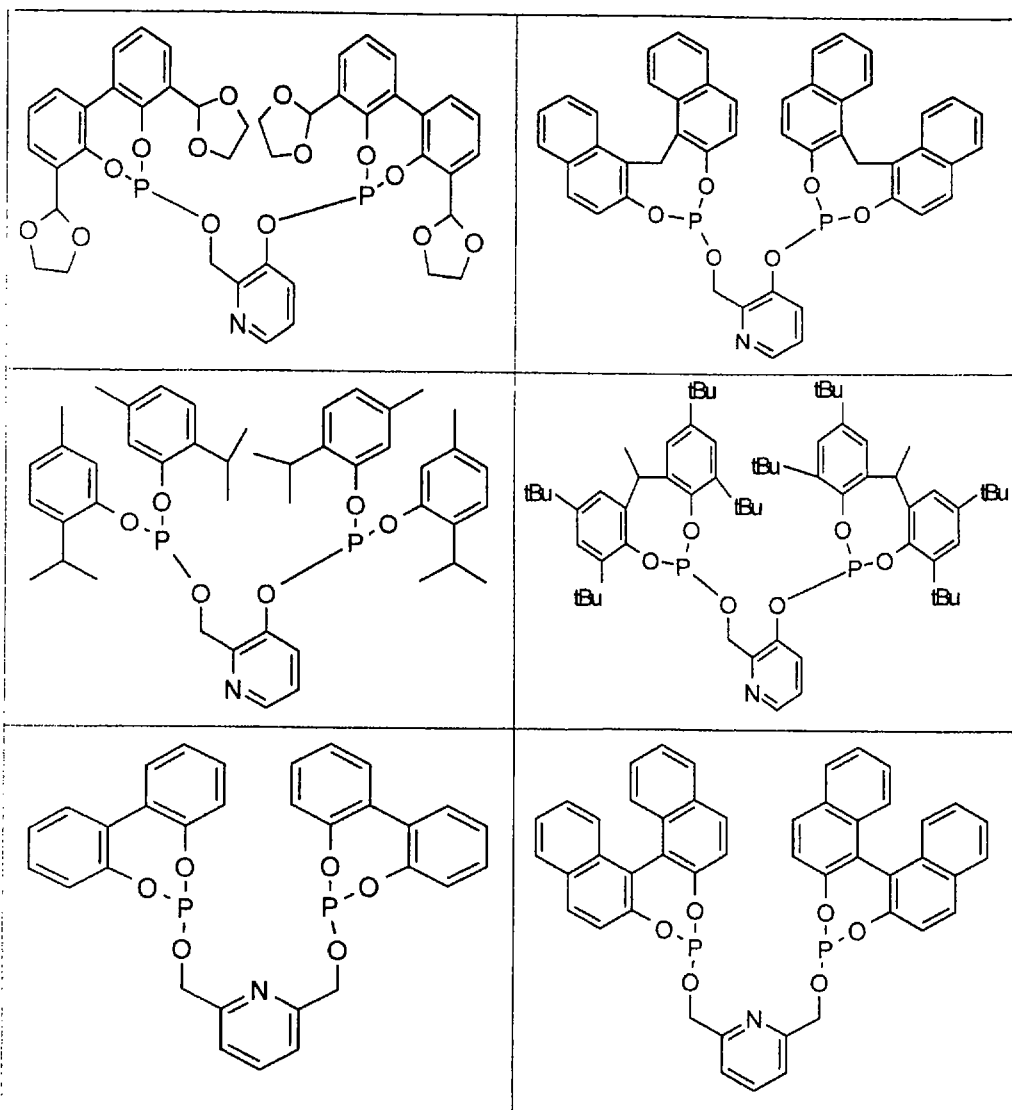


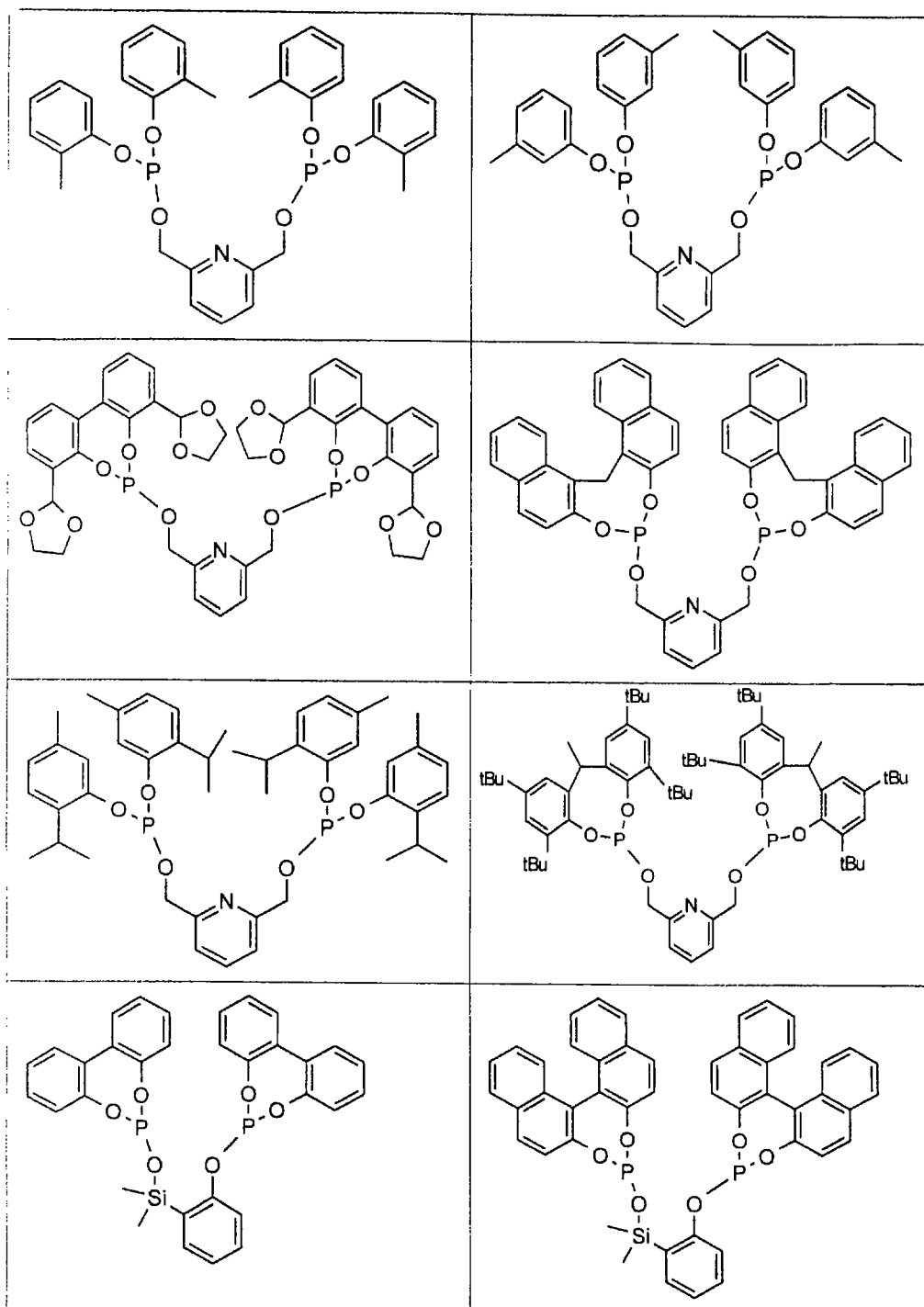


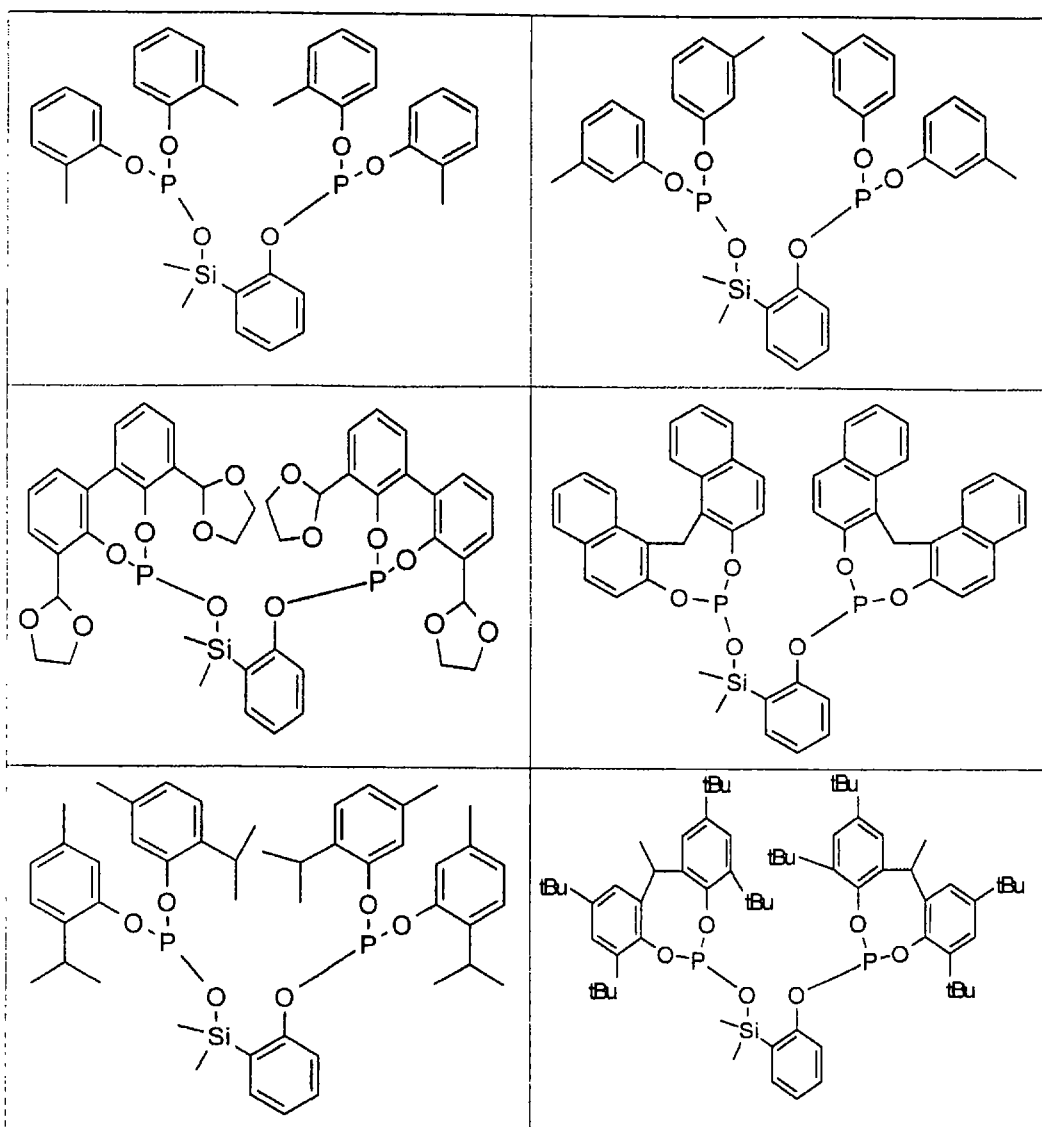


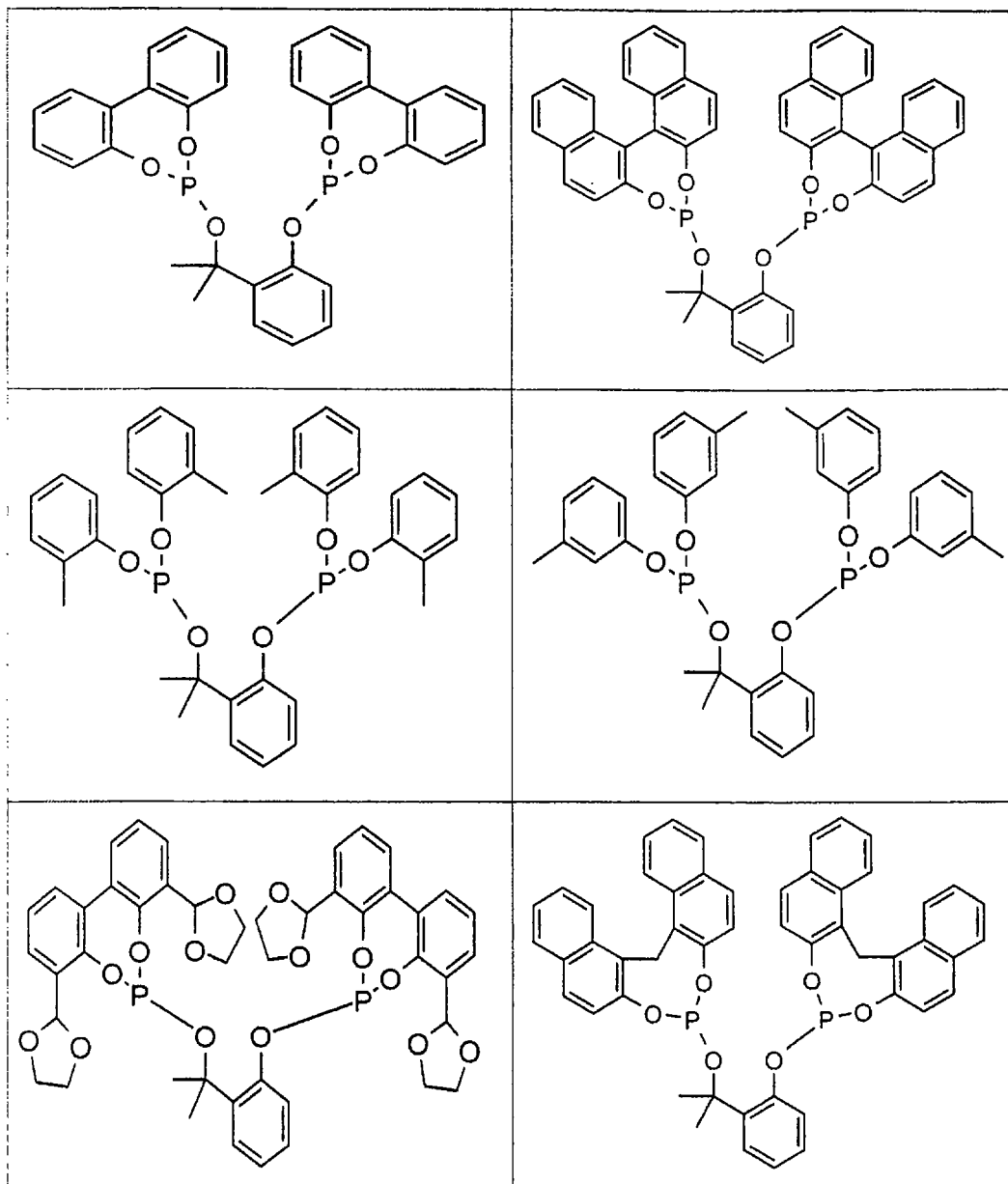


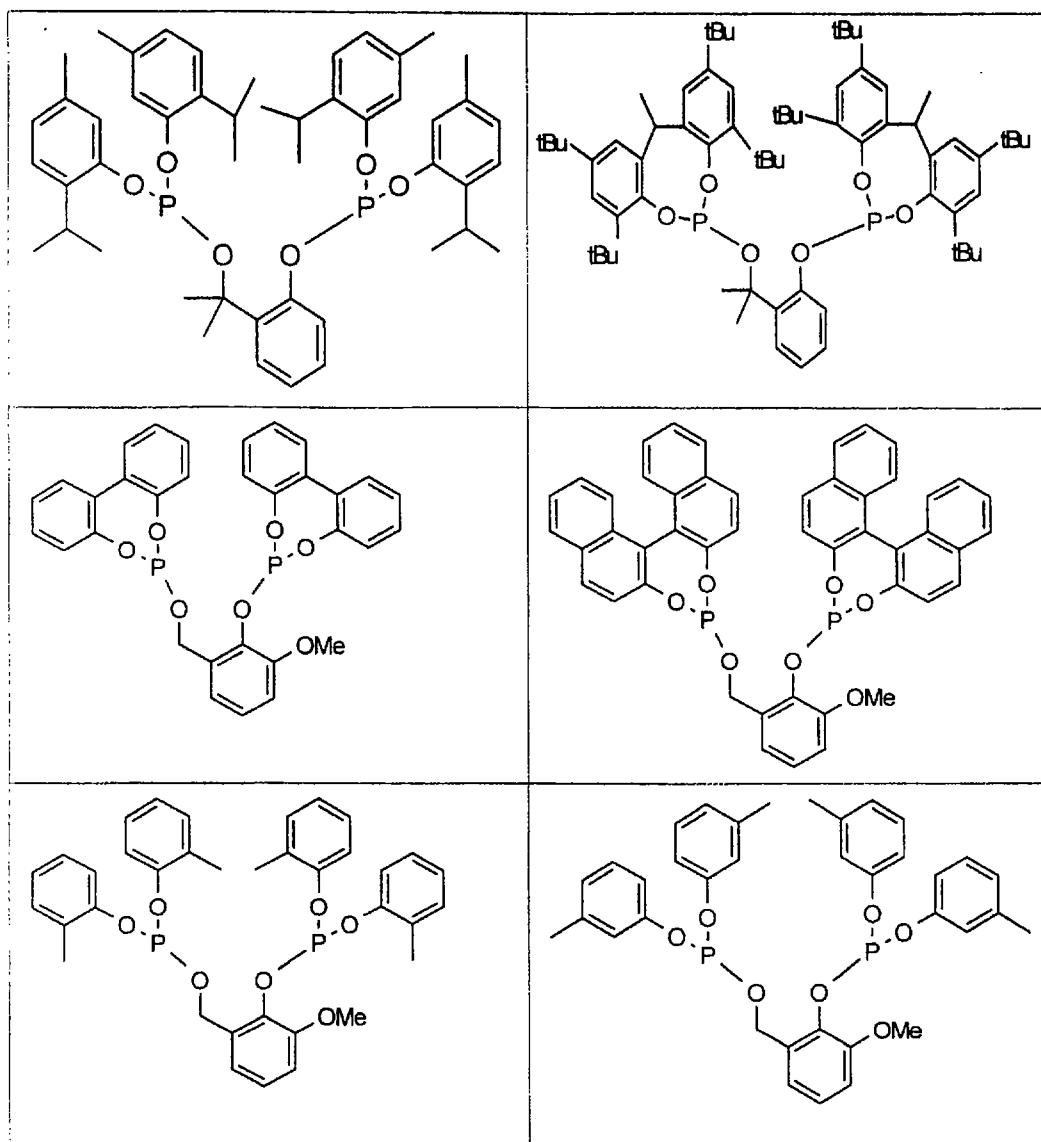


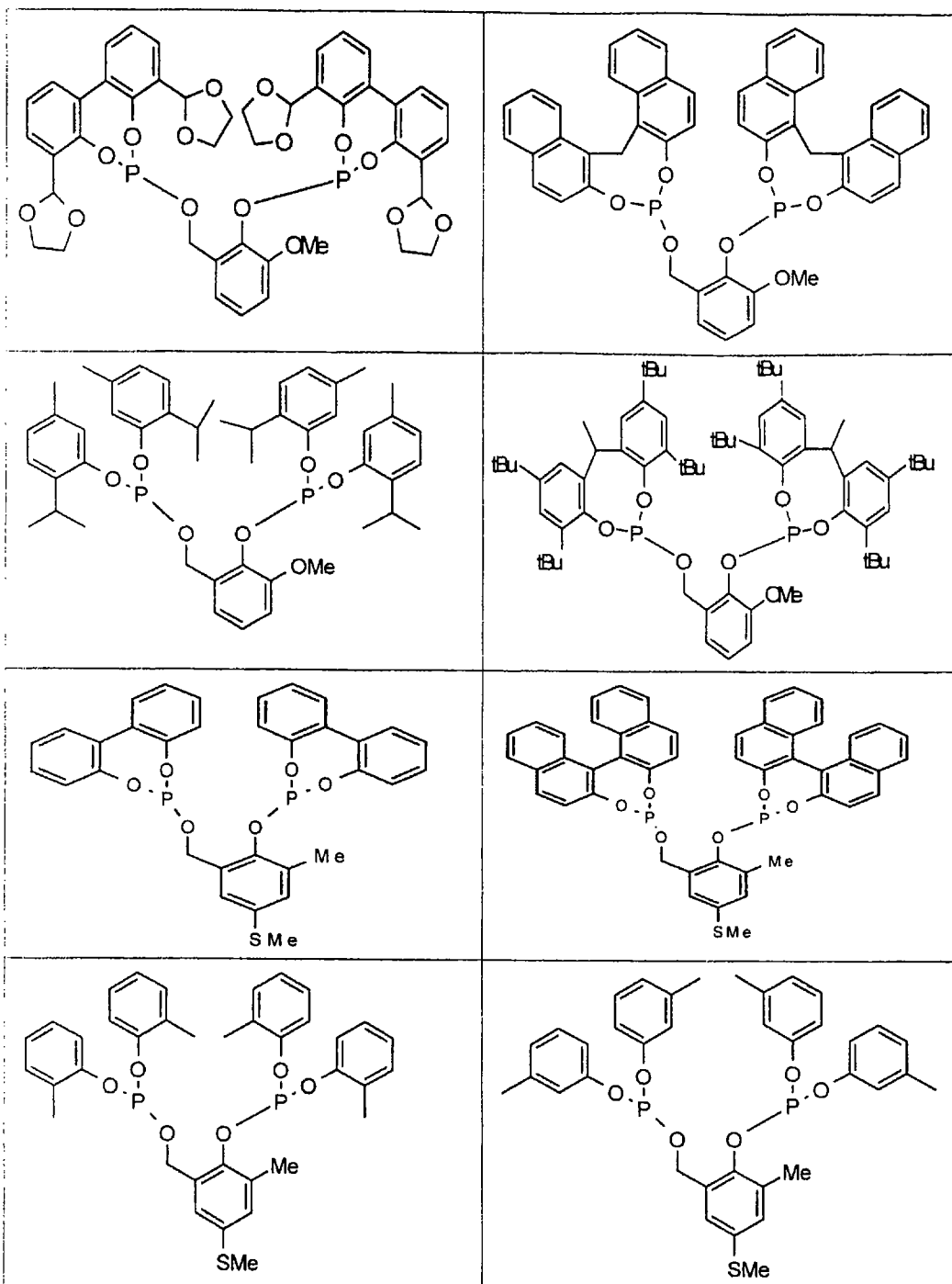


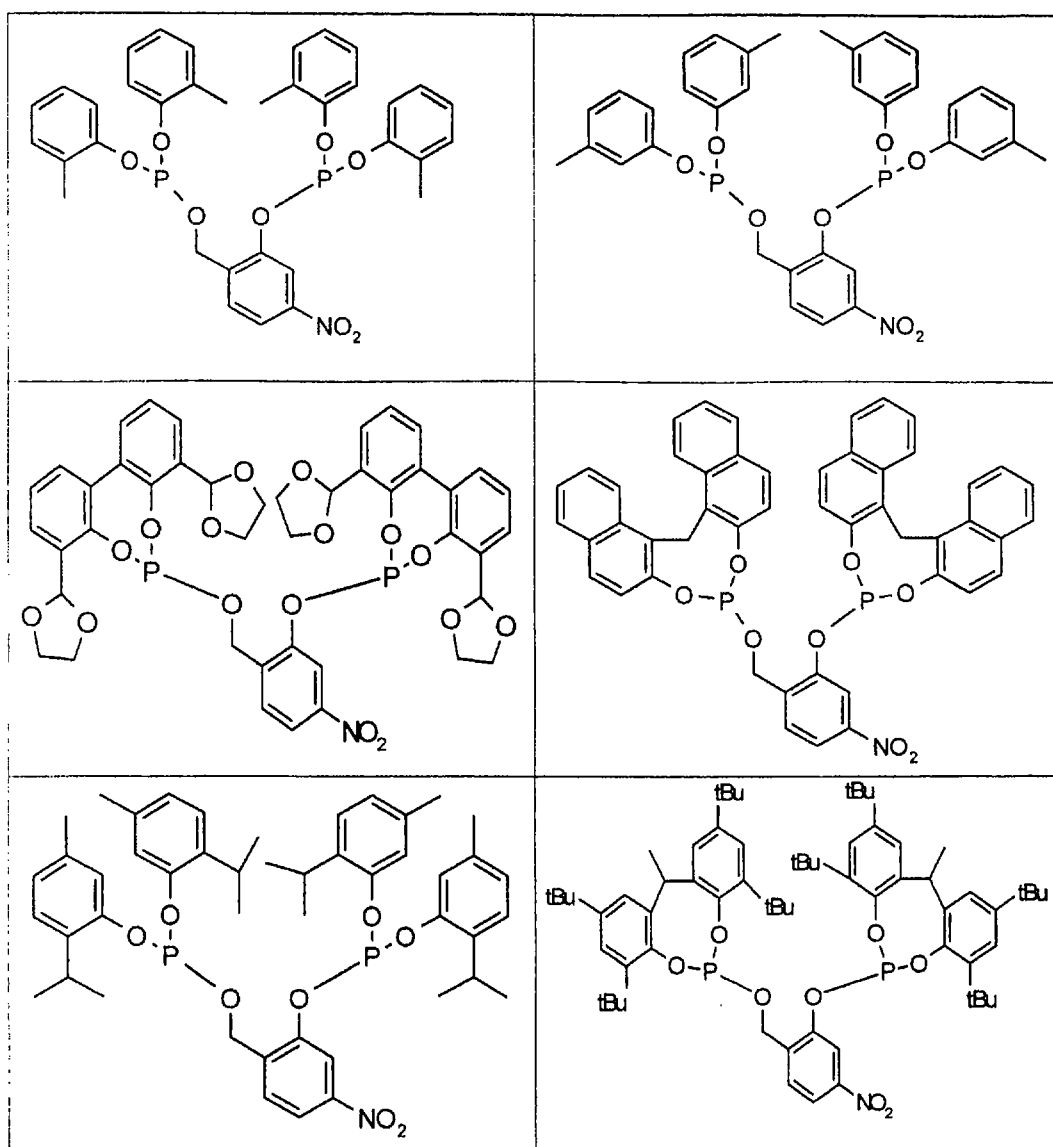


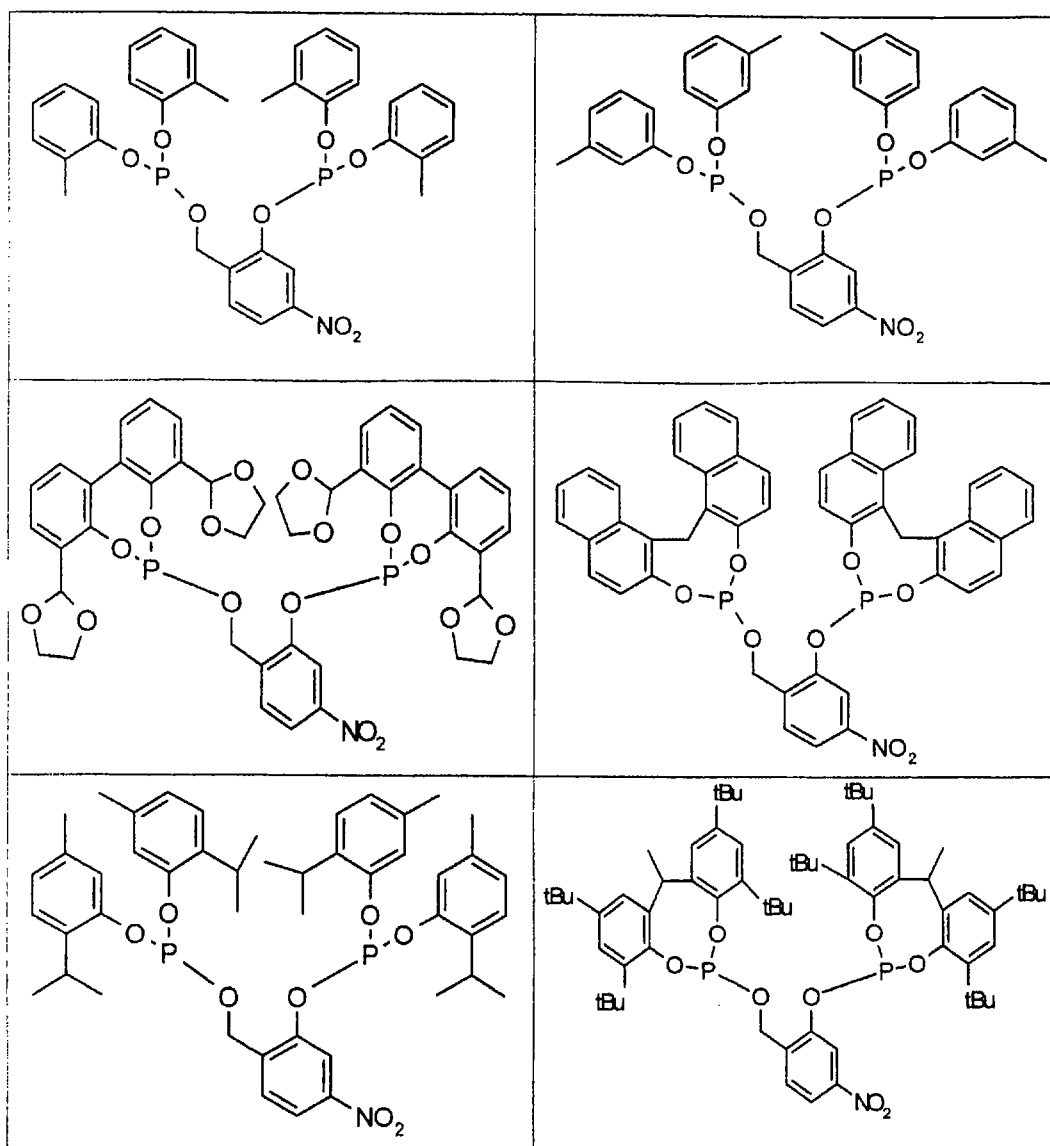


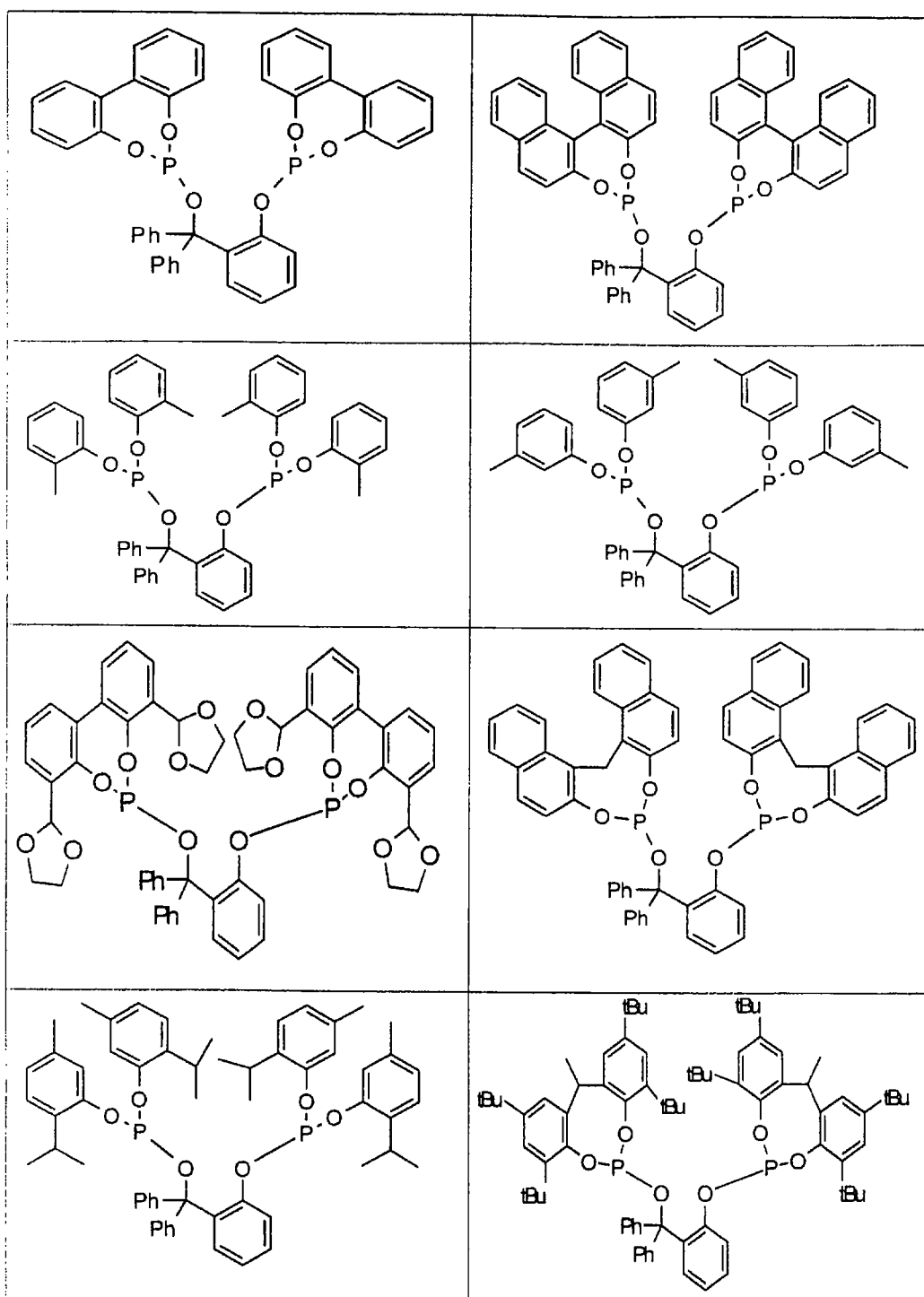


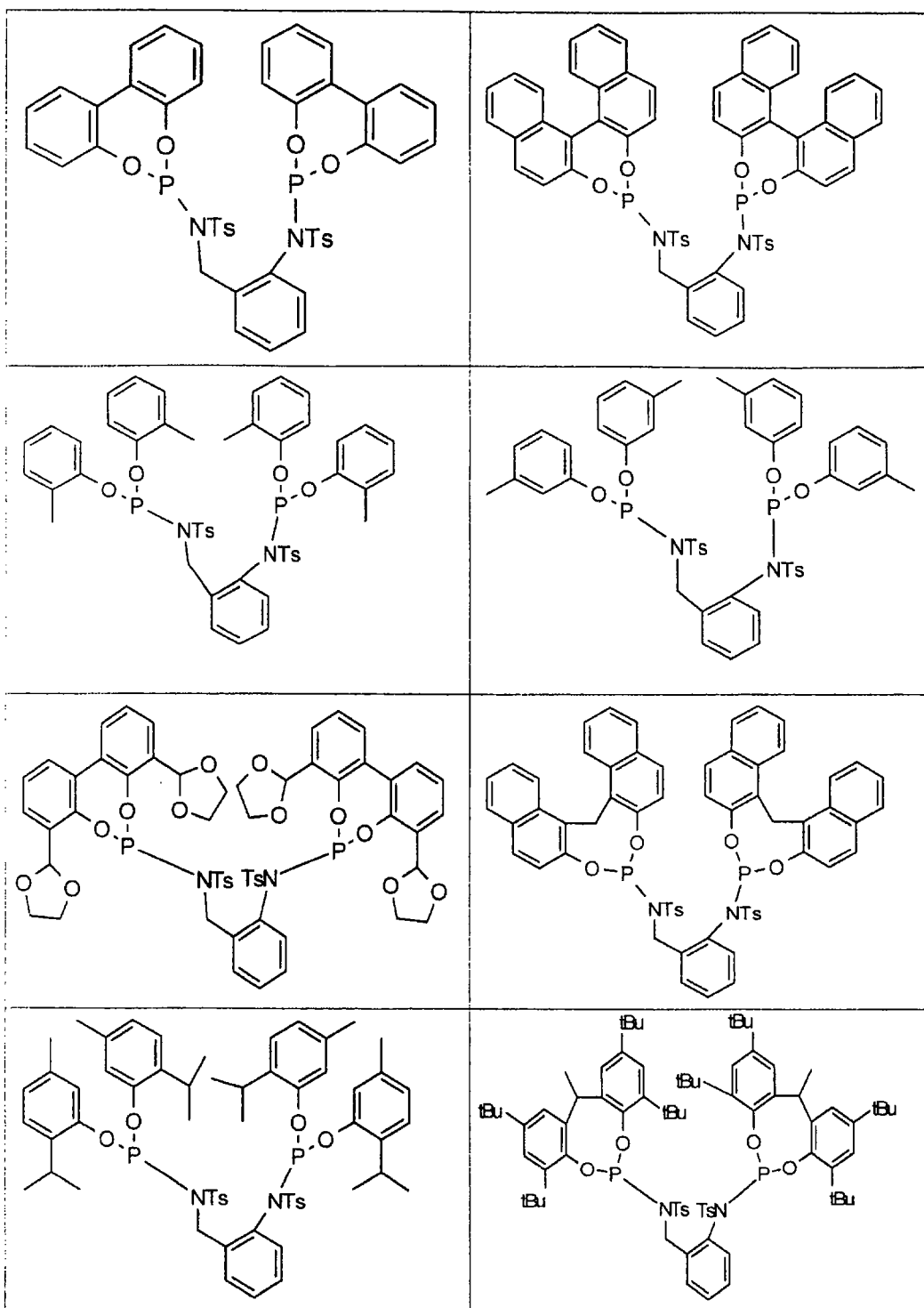


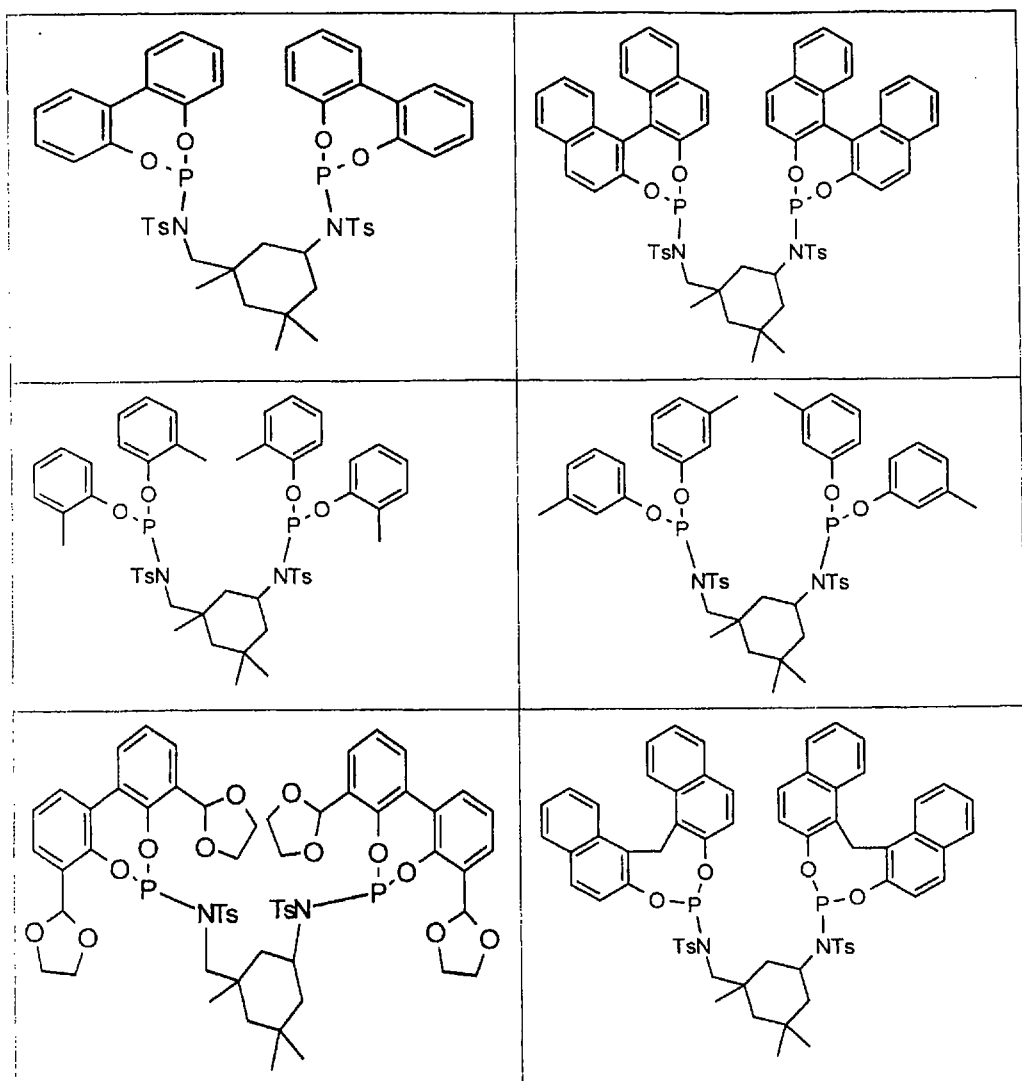


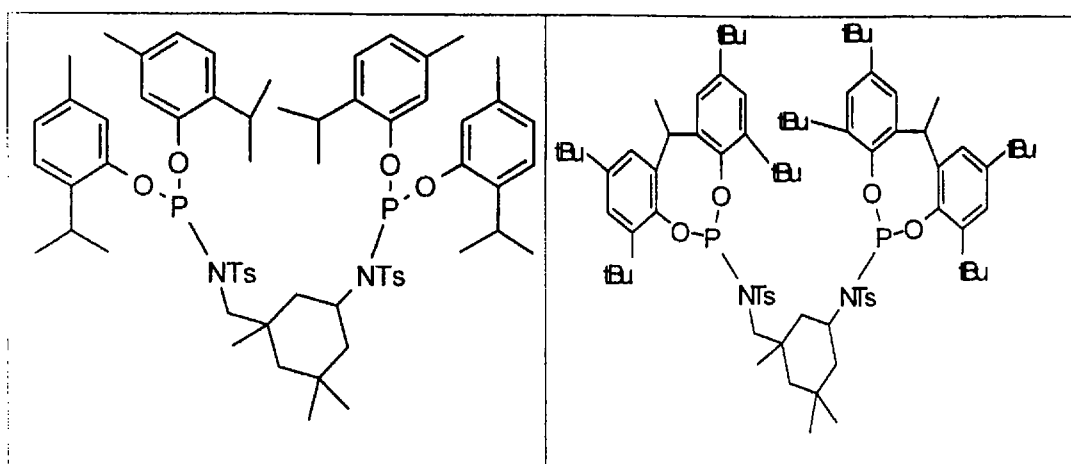












4. Process according to one of Claims 1 to 3,
5 characterized in that the metallic element is selected from the group consisting of nickel, cobalt, iron, ruthenium, rhodium, palladium, osmium, iridium, platinum, copper, silver, gold, zinc, cadmium and mercury.
- 10
5. Process according to one of the preceding claims, characterized in that the reaction is carried out in a single-phase medium.
- 15
6. Process according to one of the preceding claims, characterized in that the catalyst corresponds to the general formula (V):
$$M[L_f]_v \quad (V)$$

in which
20 M is a transition metal,
L_f represents the organic ligand of formula (I) and
v represents a number between 1 and 4 (inclusive).
- 25
7. Process according to one of the preceding claims, characterized in that the reaction mixture comprises a solvent for the catalyst which is miscible with the phase comprising the compound to be hydrocyanated at the hydrocyanation temperature.
- 30
8. Process according to one of the preceding claims,

characterized in that the transition metal compounds are nickel compounds selected from the group consisting of:

- 5 - compounds in which nickel is in oxidation state zero, such as potassium tetracyanonickelate $K_4[Ni(CN)_4]$, bis(acrylonitrile)nickel zero, bis-(cycloocta-1,5-diene)nickel zero and derivatives containing ligands, such as tetrakis(tri-
10 phenylphosphine)nickel zero;
- compounds of nickel such as carboxylates, carbonate, bicarbonate, borate, bromide, chloride, citrate, thiocyanate, cyanide, formate, hydroxide,
15 hydrophosphite, phosphite, phosphate and derivatives, iodide, nitrate, sulphate, sulphite, aryl- and alkylsulphonates.

9. Process according to one of the preceding claims,
20 characterized in that the organic compounds containing at least one ethylenic double bond are selected from diolefins such as butadiene, isoprene, hexa-1,5-diene, cycloocta-1,5-diene, ethylenically unsaturated aliphatic nitriles, especially linear pentenenitriles
25 such as pent-3-enenitrile and pent-4-enenitrile, monoolefins such as styrene, methylstyrene, vinyl-naphthalene, cyclohexene and methylcyclohexene and also mixtures of two or more of these compounds.

30 10. Process according to one of the preceding claims, characterized in that the amount of compound of nickel or of another transition metal used is selected such that per mole of organic compound to be hydrocyanated or isomerized between 10^{-4} and 1 mol of nickel or of the
35 other transition metal is employed and in that the amount of organic ligand of formula (V) used is selected such that the number of moles of this compound relative to 1 mol of transition metal is from 0.5 to 50.

11. Process according to one of the preceding claims, characterized in that the hydrocyanation reaction is carried out at a temperature from 10°C to 200°C.
- 5
12. Process according to one of the preceding claims for hydrocyanating ethylenically unsaturated nitrile compounds to dinitriles by reaction with hydrogen cyanide, characterized in that it is operated in the presence of a catalyst system comprising at least one transition metal compound, at least one organic compound of formula (I) or (V) and a cocatalyst composed of at least one Lewis acid.
- 10
13. Process according to Claim 12, characterized in that the ethylenically unsaturated nitrile compounds are selected from ethylenically unsaturated aliphatic nitriles comprising linear pentenenitriles such as pent-3-enenitrile and pent-4-enenitrile and mixtures thereof.
- 15
14. Process according to Claim 13, characterized in that the linear pentenenitriles contain amounts of other compounds selected from the group consisting of 2-methylbut-3-enenitrile, 2-methylbut-2-enenitrile, pent-2-enenitrile, valeronitrile, adiponitrile, 2-methylglutaronitrile, 2-ethylsuccinonitrile and butadiene.
- 20
15. Process according to one of Claims 12 to 14, characterized in that the Lewis acid employed as cocatalyst is selected from compounds of the elements of groups Ib, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the Periodic Table of the Elements.
- 25
16. Process according to one of Claims 12 to 15, characterized in that the Lewis acid is selected from salts selected from the group of halides, sulphates, sulphonates, haloalkylsulphonates, perhaloalkyl-
- 30
- 35

sulphonates, haloalkylacetates, perhaloalkylacetates, carboxylates and phosphates.

17. Process according to one of Claims 12 to 16,
5 characterized in that the Lewis acid is selected from zinc chloride, zinc bromide, zinc iodide, manganese chloride, manganese bromide, cadmium chloride, cadmium bromide, stannous chloride, stannous bromide, stannous sulphate, stannous tartrate, indium trifluoromethyl-
10 sulphonate, indium trifluoroacetate, zinc trifluoroacetate, the chlorides or bromides of rare earth elements such as lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, hafnium, erbium, thallium, ytterbium and
15 lutetium, and cobalt chloride, ferrous chloride, yttrium chloride and mixtures thereof.

18. Process according to one of Claims 12 to 17,
characterized in that the Lewis acid employed
20 represents from 0.01 to 50 mol per mole of transition metal compound.

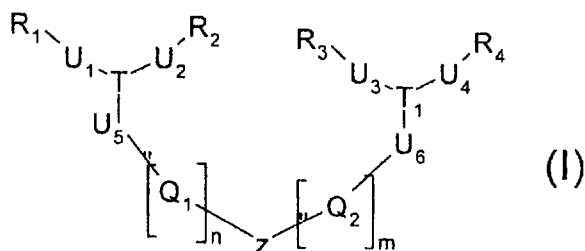
19. Process according to one of Claims 1 to 18,
characterized in that 2-methylbut-3-enenitrile, present
25 in the reaction mixture originating from butadiene hydrocyanation, is isomerized to pentenenitriles in the absence of hydrogen cyanide, in the presence of a catalyst comprising at least one organic ligand of general formula (I) or (V) and at least one transition
30 metal compound.

20. Process according to Claim 19, characterized in that the 2-methylbut-3-enenitrile subjected to isomerization is employed alone or in a mixture with
35 2-methylbut-2-enenitrile, pent-4-enenitrile, pent-3-enenitrile, pent-2-enenitrile, butadiene, adiponitrile, 2-methylglutaronitrile, 2-ethylsuccinonitrile or valeronitrile.

21. Process according to either of Claims 19 and 20, characterized in that the isomerization reaction is carried out at a temperature from 10°C to 200°C.

22. Process according to Claims 19 to 21, characterized in that the isomerization of 2-methylbut-3-enenitrile to pentenenitriles is carried out in the presence of at least one transition metal compound, at least one organic phosphorous ligand of the formula (I) and a cocatalyst composed of at least one Lewis acid.

23. Organophosphorus compounds corresponding to the general formula (I) below:



in which:

T and T₁, which are identical or different, represent a phosphorus, arsenic or antimony atom,

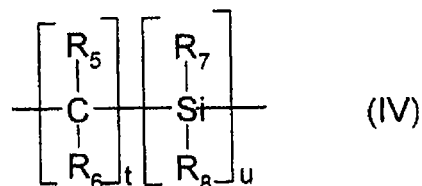
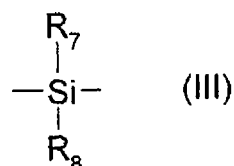
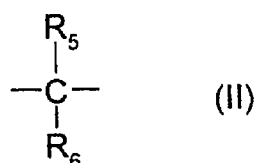
U₁, U₂, U₃, U₄, U₅ and U₆, which are identical or different, represent an oxygen atom or a radical NR, R representing an alkyl, aryl, sulphonyl or carbonyl radical,

R₁, R₂, R₃ and R₄, which are identical or different, represent a substituted or unsubstituted, aromatic, aliphatic or cycloaliphatic radical comprising one or more rings, which are in fused form or not and which may contain one or more heteroatoms, where the radicals R₁ and R₂ on the one hand, R₃, R₄ and on the other hand may be interconnected by a covalent bond, a hydrocarbon chain or a heteroatom, and, when one of the radicals U₁,

U₂, U₃ and U₄ includes an N atom, the associated radical R₁, R₂, R₃ or R₄ may form a ring including the N element of the said radical,

5 m and n are identical or different integers between 0 and 6, where m + n must be greater than or equal to 1,

Q₁ and Q₂, which are identical or different, represent a group corresponding to the general formulae II, III or
10 IV below:



15 in which R₅, R₆, R₇ and R₈, which are identical or different, represent aliphatic, cycloaliphatic or aromatic hydrocarbon radicals containing 1 to 12 carbon atoms, R₅ and R₆ also representing the hydrogen atom, and

20 t and u represent integers between 0 and 6, with a sum u + t greater than or equal to 1,

Z representing a divalent radical selected from the group consisting of aromatic or cycloaliphatic radicals
25 containing one or more rings, which are in fused form

or not and which may be substituted and may contain heteroatoms.

24. Organophosphorus compounds corresponding to the
5 formulae below:

