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(72) Inventeurs/Inventors:
IKARIYA, TAKAO, JP;
HASHIGUCHI, SHOHEI, JP;
TAKEHARA, JUN, JP;
...

(73) Propriétaires/Owners:
...

(54) Titre : PROCÉDE DE PRÉPARATION DE COMPOSÉS OPTIQUEMENT ACTIFS
(54) Title: PROCESS FOR PREPARING OPTICALLY ACTIVE COMPOUNDS

(57) **Abrégé/Abstract:**

A novel and practically excellent process for preparing optically active compounds, such as optically active alcohols or amines, useful for various applications of, for example, synthetic intermediates of pharmaceuticals liquid crystalline materials, and reagents for optical resolution, wherein a hydrogen transfer type asymmetric reduction is carried out in the presence of both a transition metal complex and an optically active nitrogen compound or a transition metal complex having an optically active nitrogen compound as an asymmetric ligand, and a hydrogen-donating organic or inorganic compound. Further, optically active secondary alcohols are prepared from racemic secondary alcohols or meso-diols by a hydrogen transfer oxidation.

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- (72) Inventeurs(suite)/Inventors(continued): UEMATSU, NOBUYUKI, JP; MATSUMURA, KAZUHIKO, JP; NOYORI, RYOJI, JP; FUJII, AKIO, JP
- (73) Propriétaires(suite)/Owners(continued): NKK CORPORATION, JP; TAKASAGO INTERNATIONAL CORPORATION, JP; JAPAN SCIENCE AND TECHNOLOGY CORPORATION, JP; ASAHI KASEI PHARMA CORPORATION, JP; TAKEDA PHARMACEUTICAL COMPANY LIMITED, JP
- (74) Agent: OGILVY RENAULT LLP/S.E.N.C.R.L., S.R.L.



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(54)Title: PROCESS FOR PREPARATING OPTICALLY ACTIVE COMPOUNDS (54)発明の名称 光学活性化合物の製造方法 (57) Abstract A novel and practically excellent process for preparing optically active compounds, such as optically active alcohols or amines, useful for various applications of, for example, synthetic intermediates of pharmaceuticals, liquid crystalline materials, and reagents for optical resolution, wherein a hydrogen transfer type asymmetric reduction is carried out in the presence of both a transition metal complex and an optically active nitrogen compound or a transition metal complex having an optically active nitrogen compound as an asymmetric ligand, and a hydrogen-donating organic or inorganic compound. Further, optically active secondary alcohols are prepared from racemic secondary alcohols or meso-diols by a hydrogen transfer oxidation.													

(57) 要約

この発明では、医薬品の合成中間体や、液晶材料、光学分割剤等の各種用途において有用な光学活性アルコールや光学活性アミン等の光学活性化合物の実用性にすぐれた新しい製造法に関するものであって、遷移金属錯体と光学活性含窒素化合物または光学活性含窒素化合物を不斉配位子とする遷移金属錯体、並びに水素供与性の有機または無機化合物の存在下に水素移動型不斉還元して光学活性化合物を製造することを特徴としている。

また、水素移動型酸化反応によってラセミ体の２級アルコールまたはメソ型のジオールから光学活性２級アルコールを得ることも特徴としている。

情報としての用途のみ

PCTに基づいて公開される国際出願をパンフレット第一頁にPCT加盟国を同定するために使用されるコード

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DESCRIPTION

PROCESS FOR PREPARING OPTICALLY ACTIVE COMPOUNDS

Technical Field

The present invention relates to a method for producing optically active compounds such as optically active alcohols and optically active amines. More specifically, the present invention relates to a novel, highly practical method for producing optically active compounds useful for various utilities such as intermediates for synthesizing pharmaceutical chemicals, liquid crystal materials and agents for optical resolution.

Background Art

Various methods for producing optically active compounds have been known conventionally. As the method for asymmetric synthesis of optically active alcohol compounds, for example, the following methods have been known;

(1) a method by using enzymes such as baker's yeast; and
(2) a method for asymmetric hydrogenation of carbonyl compounds by using metal complex catalysts. For the method (2), in particular, a great number of examples of asymmetric catalytic reactions have been reported for example as follows; (1) an asymmetric hydrogenation of carbonyl compounds with functional groups, by means of optically active ruthenium catalysts, as described in detail in

Asymmetric Catalysis in Organic Synthesis, Ed. R. Noyori., pp..56-82 (1994); (2) a method through hydrogen transfer-type reduction by means of chiral complex catalysts of ruthenium, rhodium or iridium, as described in Chem. Rev., Vol.92, pp.1051-1069 (1992); (3) a process of asymmetric hydrogenation of tartaric acid by means of a modified nickel catalyst with tartaric acid as described in Oil Chemistry, pp.882-831 (1980) and Advances in Catalysis, Vol.32, pp.215 (1983), Ed. Y. Izumi; (4) an asymmetric hydrosilylation method, as described in Asymmetric Synthesis, Vol.5, Chap.4 (1985), Ed. J. D. Morrison and J. Organomet. Chem. Vol.346, pp.413-424 (1988); and (5) a borane reduction process in the presence of chiral ligands, as described J. Chem. Soc., Perkin Trans.1, pp.2039-2044 (1985) and J. Am. Chem. Soc., Vol.109, pp. 5551-5553 (1987).

By the conventional method by means of enzymes, however, alcohols can be recovered at a relatively high optical purity, but the reaction substrate therefor is limited and the absolute configuration in the resulting alcohols is limited to a specific one. By the asymmetric hydrogenation method by means of transition metal complex catalysts, optically active alcohols can be produced at a high selectivity, but a pressure-resistant reactor is required therefor because hydrogen gas is used as the hydrogen source, which is disadvantageous in terms of operational difficulty and safety. Furthermore, the method

through such asymmetric hydrogen transfer-type reduction by using conventional metal complex catalysts is limited in that the method requires reaction conditions under heating and the reaction selectivity is insufficient, disadvantageously in a practical sense.

Accordingly, it has been desired conventionally that a new, very general method for synthesizing optically active alcohols by using a highly active and highly selective catalyst with no use of hydrogen gas be achieved.

However, no highly efficient and highly selective method for producing such secondary alcohols through asymmetric synthetic reaction by using catalysts similar to those described above has not as yet been established.

As to the optically active secondary alcohols, a method for synthesizing optically active secondary alcohols via optical resolution of racemic secondary alcohols has been known for some reaction substrate which can hardly be reduced, although an excellent optical purity is hardly attained (Asymmetric Catalysis in Organic Synthesis, Ed. R. Noyori). Because hydrogen transfer-type reduction is a reversible reaction according to the method, dehydrogenation-type oxidation as its adverse reaction is used according to the method. Therefore, the method is called as kinetic optical resolution method. According to the method, however, no process of producing optically

active secondary alcohols with catalysts at a high efficiency has been reported yet.

As the method for synthetically producing optically active amine compounds, furthermore, a process of optically resolving once produced racemic compounds by using optically active acids and a process through asymmetric synthetic reaction have been known. By the optical resolution process, however, optically active acids should be used at an equal amount or more to amine compounds disadvantageously and complex procedures such as crystallization, separation and purification are required so as to recover optically active amine compounds. As the method through asymmetric synthesis, alternatively, the following processes have been known; (1) an enzymatic process; (2) a process by using metal hydride compounds; and (3) a process of asymmetric hydrogenation by using metal complex catalysts. As to the process for using metal hydride compounds as described above in (2), a great number of reports have been issued about a process of asymmetrically reducing carbon-nitrogen multiple bonds by using metal hydrides with chiral modifiers. As a general process thereof, for example, it has been known a stoichiometric reduction process of imine compounds and oxime compounds by using metal hydrides with an optically active ligand, as described in Comprehensive Organic Synthesis, EdS. B.M. Trost and I. Fleming, Vol.8, pp.25 (1991), Organic Preparation and Procedures Inc. O. Zhu, R.

O. Hutchins, and M. K. Huchins, Vol.26(2), pp.193-235 (1994) and Japanese Patent Laid-open No. 2-311446. The process includes a number of processes with excellent reaction selectivity, but these processes are disadvantageous because these processes require laborious purification procedures to recover optically active substances. As the process of asymmetric hydrogenation of carbon-nitrogen multiple bonds by using metal complex catalysts as the method (3), it has been known an asymmetric hydrogenation process of imine compounds with functional groups, by means of optically active metal complex catalysts, as described in Asymmetric Catalysis in Organic Synthesis, pp.82-85 (1994), Ed. R. Noyori. But the process has a drawback in terms of reaction velocity and selectivity.

By the method by using enzymes as the method (1), furthermore, amines at a relatively high optical purity can be recovered, but the reaction substrates are limited and the resulting amines have only specific absolute configurations. Furthermore, at a process of asymmetric hydrogenation by means of complex catalysts of transition metals using hydrogen gas, optically active amines have not yet been recovered at a high selectivity or pressure-resistant reactors are essentially required because hydrogen gas is used as the hydrogen source. Hence, such a process is disadvantageous because of technically difficult operation and safety problems.

Accordingly, it has been demanded that a novel method for synthesizing an optically active amine by using a very common, highly active and highly selective catalyst be realized.

Alternatively, a great number of transition metal complexes have been used conventionally as catalysts for organic metal reactions; particularly because rare metal complexes are highly active and stable with the resultant ready handleability despite of high cost, synthetic reactions using the complexes have been developed. The progress of such asymmetric synthetic reactions using chiral complex catalysts is innovative, and a great number of reports have been issued, reporting that highly efficient organic synthetic reactions have been realized.

Among them, a great number of asymmetric reactions using chiral complex catalysts with optically active phosphine ligands as the catalysts therefor have already been developed, and some of them have been applied industrially (Asymmetric Catalysis in Organic Synthesis, Ed. R. Noyori).

As complexes of optically active nitrogen compounds

coordinated with transition metals such as ruthenium, rhodium and iridium, a great number of such complexes additionally having excellent properties as catalysts for asymmetric synthetic action have been known. So as to enhance the properties of these catalysts, a great number of propositions concerning the use of optically active nitrogen compounds of specific structures have been done (Chem. Rev. , Vol.92, pp.1051-1069 (1992)).

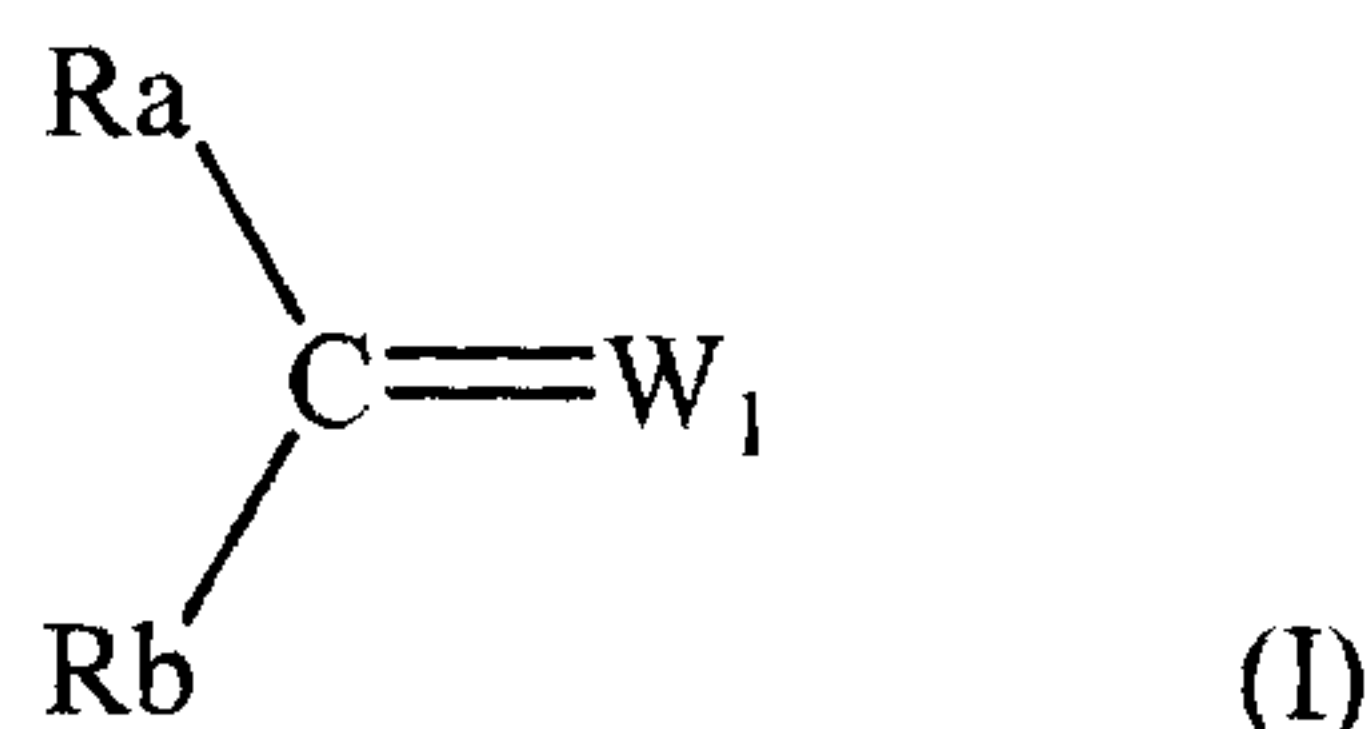
For example, reports have been issued about (1) optically active 1,2-diphenylethylenediamines and rhodium-diamine complexes with ligands of cyclohexanediamines, as described in Tetrahedron Asymmetry, Vol.6, pp.705-718 (1995); (2) ruthenium-imide complex with ligands of optically active bisaryliminocyclohexanes, as described in Tetrahedron, Vol.50, pp.4347-4354 (1994); (3) iridium-pyridine complex with ligands of pyridines, as described in Japanese Patent Laid-open Nos. 62-281861 and 63-119465; (4) optically active 1,2-diphenylethylenediamines or iridium-diamine complex with ligands of cyclohexanediamines, as described in Japanese Patent Laid-open No.62-273990; (5) ruthenium-diamine complex of $\text{RuCl}[\text{p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2]$ (arene) (chloro-(N-p-toluenesulfonyl-1,2-diphenylethylenediamine)(arene)ruthenium) (arene represents benzene which may or may not have a substituent), which is produced by coordinating ruthenium with optically active N-

p-toluenesulfonyl-1,2-diphenylethylenediamine [referred to as "p-TsNHCH(C₆H₅)CH(C₆H₅)NH₂ " hereinabove and below], as described in J. Am. Chem. Soc., Vol. 117, pp. 7562-7563(1995); J. Am. Chem. soc., Vol. 118, pp. 2521-2522 (1996) and J. Am. Chem. Soc., Vol. 118, pp. 4916-4917 (1996).

Even if these complexes are used, however, problems currently remain to be overcome for practical use, including insufficient catalyst activities, sustainability and optical purities, depending on the subjective reactions and reaction substrates.

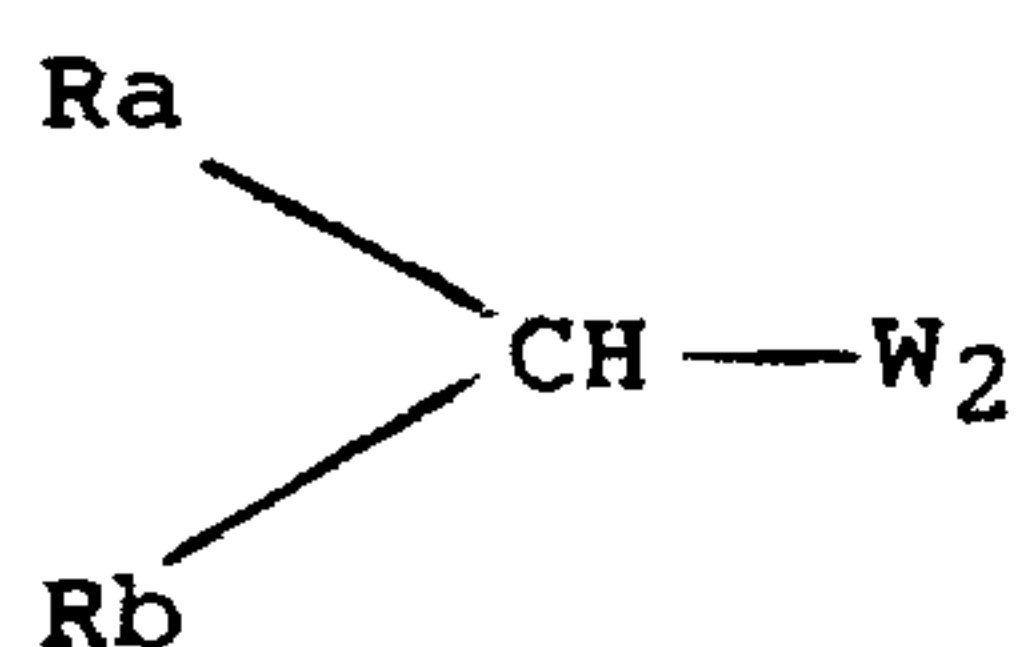
DISCLOSURE OF INVENTION

So as to overcome the aforementioned problems, the present invention is to provide a method for producing optically active compounds, comprising subjecting a compound represented by the following formula (I);



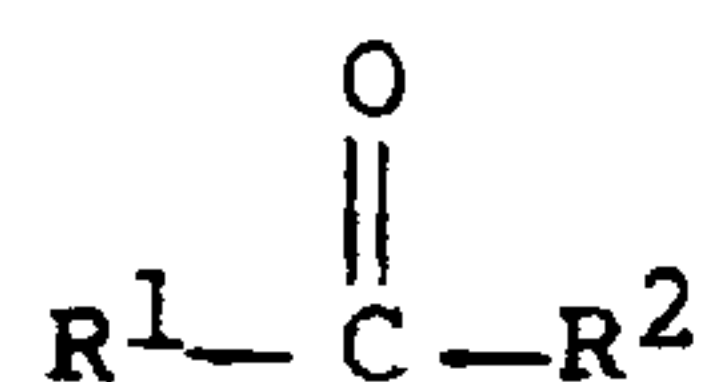
(wherein Ra represent a linear hydrocarbon group containing 1 to 10 carbon atoms, a mono-, bi- or tri-cyclic hydrocarbon group containing 3 to 14 carbon atoms, an aryl group, a heterocyclic group containing 2 to 13 carbon atoms and 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur atoms, or a ferrocenyl group; Rb represents a hydrogen atom, a linear hydrocarbon group containing 1 to 10 carbon atoms, a mono-, bi- or tri-cyclic hydrocarbon group containing 3 to 14 carbon atoms, an aryl group, a heterocyclic group containing 2 to 13 carbon atoms and 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur atoms, or a ferrocenyl group, or Ra and Rb are bonded together to form a ring containing 5 to 10 carbon atoms; W₁ represents oxygen atom, N--H, N--Rc, N--OH or N--O--Rd; and Rc and Rd represent the same hydrocarbon group or heterocyclic group as described above)

to transfer-type asymmetric reduction in the presence of a transition metal complex and an optically active nitrogen-containing compound or a transition metal complex with an optically active nitrogen-containing compound as an asymmetric ligand, along with a hydrogen-donating organic or inorganic compound, to produce an optically active compound represented by the following formula (II);



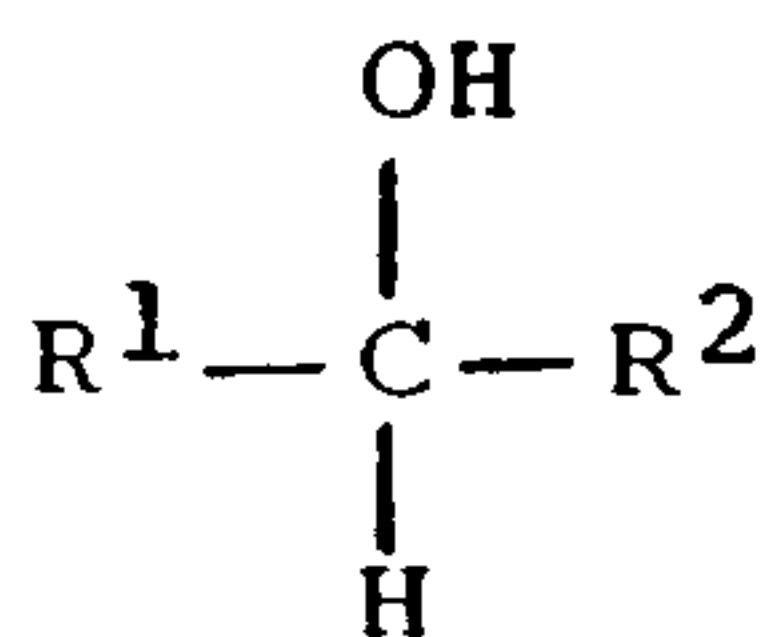
(wherein W₂ represents OH, NH₂, NH-Rc, NH-OH or NH-O-Rd; and Ra, Rb, Rc and Rd independently represent the same as those described above).

Additionally, the present invention is to provide a method for producing an optically active alcohol according to the aforementioned method, comprising asymmetrically reducing a carbonyl compound represented by the following formula (III);



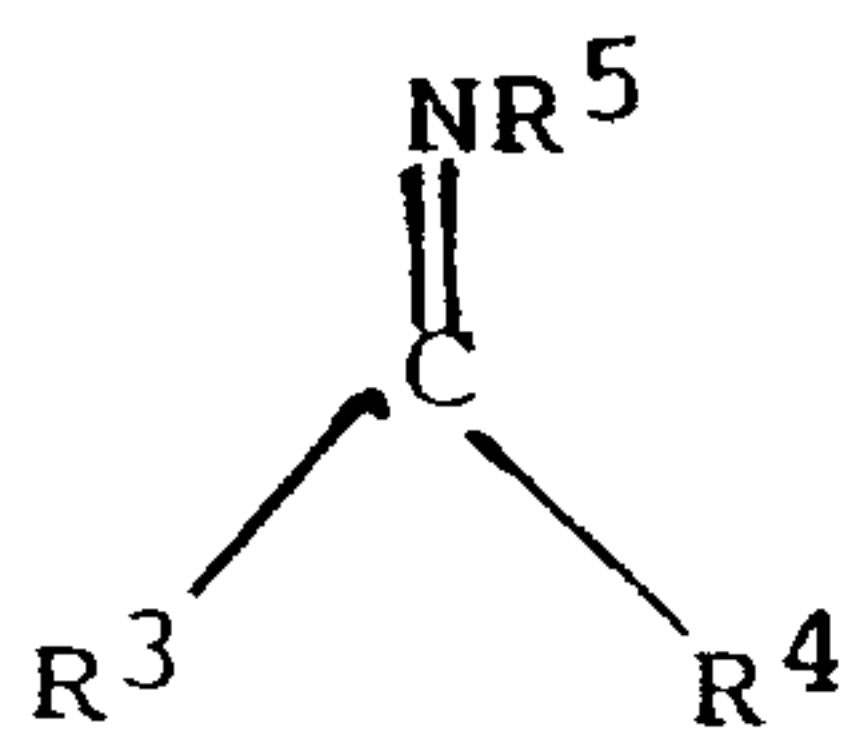
(wherein R¹ represents an aromatic hydrocarbon group, a saturated or unsaturated aliphatic hydrocarbon group or cyclic aliphatic hydrocarbon group, which may or may not have a substituent, or a heterocyclic group which may or may not have a substituent and contains hetero atoms such as nitrogen, oxygen, sulfur atoms and the like as atoms

composing the ring; R^2 represents hydrogen atom, a saturated or unsaturated aliphatic hydrocarbon group or cyclic aliphatic hydrocarbon group which may or may not have a substituent, or an aromatic hydrocarbon group, or the same heterocyclic group as described above; and R^1 and R^2 may satisfactorily be bonded together to form a ring preferably containing 5 to 10 carbon atoms),
to produce an optically active alcohol represented by the following formula (IV);



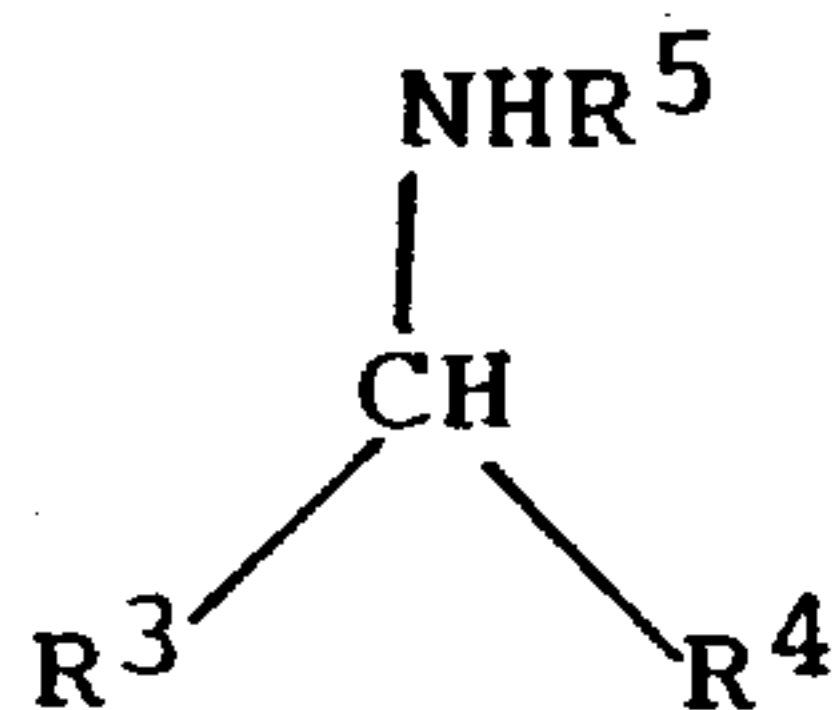
(wherein R^1 and R^2 are the same as described above).

Furthermore, the present invention is to provide a method for producing an optically active amine, comprising asymmetrically reducing an imine compound represented by the following formula (V);



(wherein R^3 represents an aromatic hydrocarbon group, a saturated or unsaturated aliphatic hydrocarbon group or cyclic aliphatic hydrocarbon group, which may or may not have a substituent, or a heterocyclic group which may or may not have a substituent and contains hetero atoms such as nitrogen, oxygen, sulfur atoms and the like as atoms composing the ring; R^4 represents hydrogen atom, a saturated

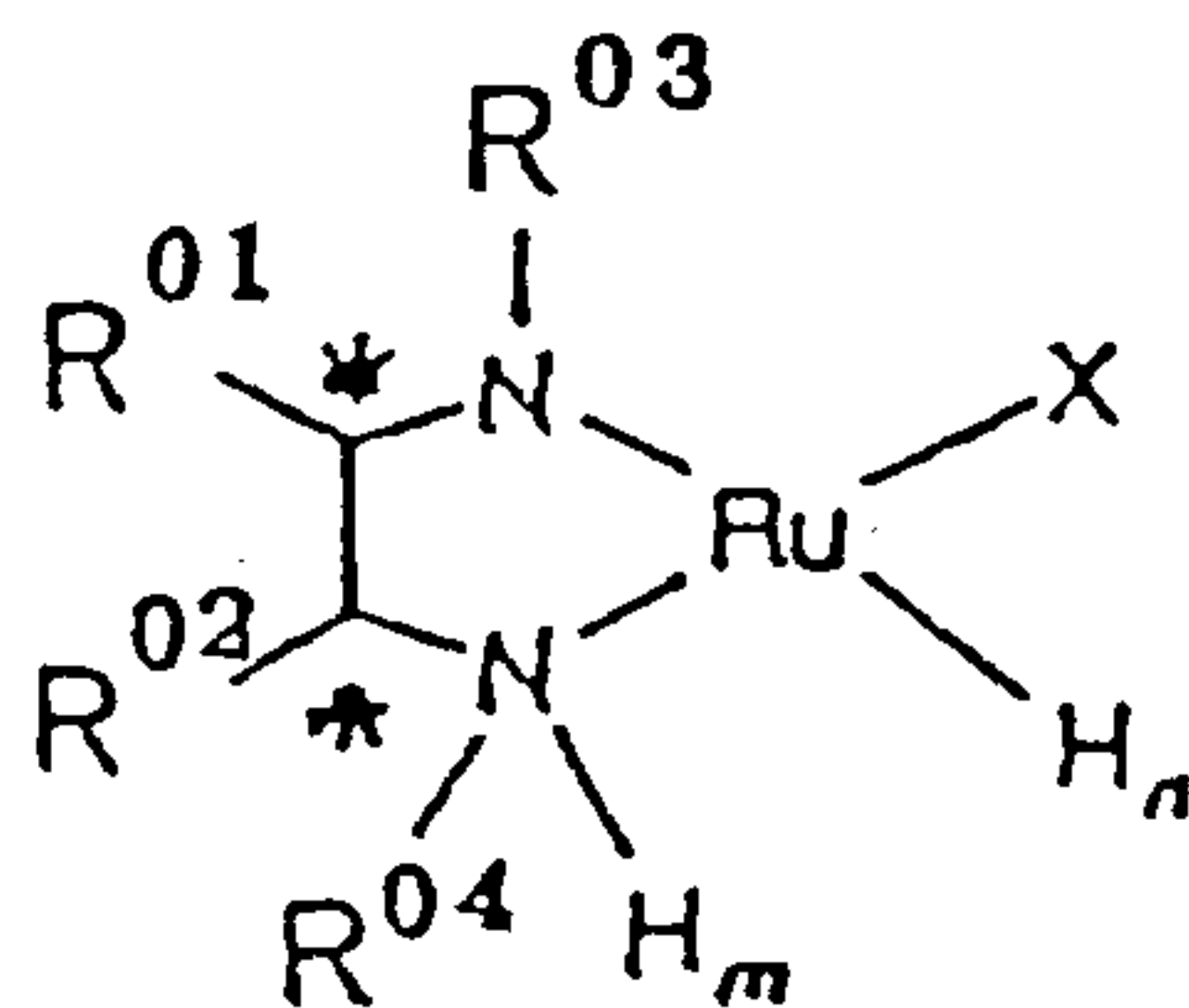
or unsaturated aliphatic hydrocarbon group or cyclic aliphatic hydrocarbon group which may or may not have a substituent, or an aromatic hydrocarbon group, or the same heterocyclic group as described above; R^5 represents hydrogen atom, or a saturated or unsaturated aliphatic hydrocarbon group or cyclic aliphatic hydrocarbon group, which may or may not have a substituent, or an aromatic hydrocarbon group, or the same heterocyclic group as described above, or the hydrocarbon group or heterocyclic group bonded together via hydroxyl group or oxygen atom; and R^3 and R^4 , R^3 and R^5 or R^4 and R^5 , are bonded together to form a ring containing preferably 5 to 10 carbon atoms), to produce optically active amines represented by the following formula (VI);



(wherein R^3 , R^4 and R^5 are the same as described above).

Still furthermore, the present invention is to provide a method for producing optically active secondary alcohols, comprising subjecting racemic secondary alcohols or meso-type

diols to hydrogen transfer reaction by using a catalyst of an optically active ruthenium-diamine complex represented by the following general formula (VII);



(wherein * represents an asymmetric carbon atom; R^{01} and R^{02} are the same or different, independently representing alkyl group, or phenyl group or cycloalkyl group which may or may not have an alkyl group; or R^{01} and R^{02} together form an alicyclic ring unsubstituted or substituted with an alkyl group; R^{03} represents methanesulfonyl group, trifluoromethanesulfonyl group, naphthylsulfonyl group, camphor sulfonyl group, or benzenesulfonyl group which may or may not be substituted with an alkyl group, an alkoxyl group or halogen atom, alkoxycarbonyl group, or benzoyl group which may or may not be substituted with an alkyl group; R^{04} represents hydrogen atom or alkyl group; X represents an aromatic compound which may or may not be substituted with an alkyl group; and m and n together represent 0 or 1).

The expression "linear hydrocarbon group" as used herein refers to a linear hydrocarbon group containing 1 to 10 carbon atoms.

The expression "cyclic hydrocarbon group" as used herein refers to a mono-, bi- or tri-cyclic hydrocarbon group containing 3 to 14 carbon atoms.

The expression "heterocyclic group" as used herein refers to a heterocyclic group containing 2 to 13 carbon atoms and 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur atoms.

The expression "aromatic hydrocarbon group" as used herein refers to an aryl group.

The expression "saturated or unsaturated hydrocarbon group" as used herein refers to a saturated or unsaturated hydrocarbon group containing 1 to 10 carbon atoms.

The expression "saturated or unsaturated cyclic hydrocarbon group" as used herein refers to a mono-, bi- or tri-cyclic hydrocarbon group containing 3 to 10 carbon atoms.

The expression "saturated or unsaturated aliphatic hydrocarbon group" as used herein refers to a saturated or unsaturated aliphatic hydrocarbon group containing 1 to 10 carbon atoms.

The expression "saturated or unsaturated cyclic aliphatic hydrocarbon group" as used herein refers to a mono-, bi- or tri-cyclic aliphatic hydrocarbon group containing 3 to 10 carbon atoms.

The expression "alkoxy group" as used herein refers to an alkoxy group containing 1 to 6 carbon atoms.

The expression "alcohol compounds" compounds when referring to hydrogen donating organic or inorganic compounds is intended to mean alcohol compounds containing 1 to 10 carbon atoms.

The expression "unsaturated hydrocarbon compounds" when referring to hydrogen donating organic or inorganic compounds is intended to mean unsaturated hydrocarbon compounds containing 5 to 10 carbon atoms.

The expression "aromatic monocyclic or polycyclic hydrocarbon group" refers to an aromatic mono-, bi- or tri-cyclic hydrocarbon group containing 6 to 14 carbon atoms.

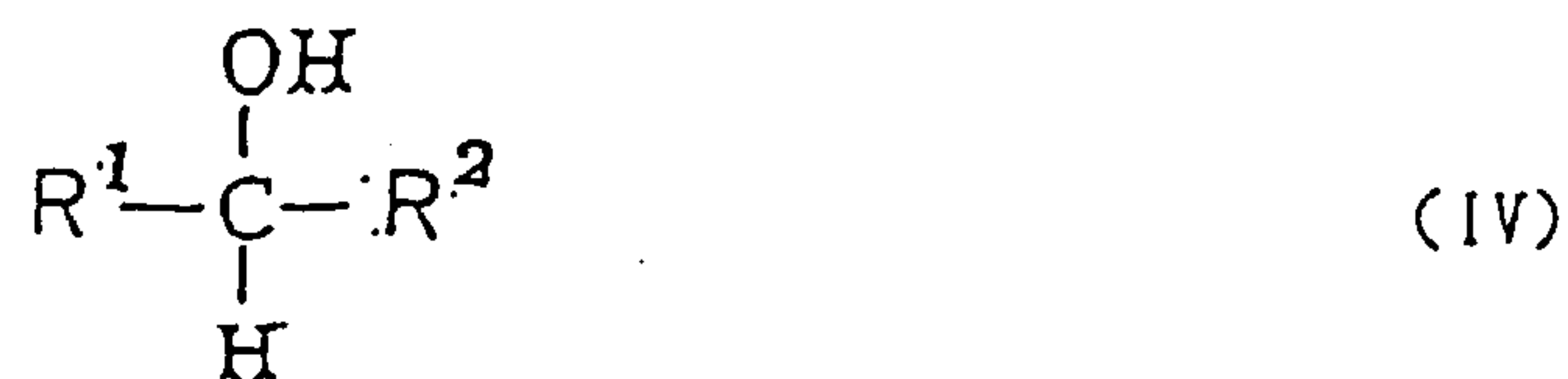
The expression "hetero monocyclic or polycyclic hydrocarbon group" refers to a hetero mono-, bi- or tri-cyclic group containing 2 to 13 carbon atoms and 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur atoms.

Best Mode for Carrying the Invention

In accordance with the present invention, the characteristic methods for producing optically active

compounds and catalysts therefor as described above are provided. The detail is described below.

Firstly, the method for producing an optically active alcohol of the general formula (I) wherein W_1 is oxygen atom and of the general formula (II) wherein R^2 is OH (hydroxyl group) is described. In the formulas (I) and (II), R_a and R_b independently represent a linear or cyclic hydrocarbon or heterocyclic group which may or may not have a substituent, and the carbonyl compound represented by R_a , R_b and W_1 (oxygen atom) are represented by the following formula (III) as described above, and the optically active alcohol compound produced by the hydrogen transfer-type asymmetric reduction of the carbonyl compound represented by the formula (III) may satisfactorily be represented by the formula (IV).



Herein, R^1 represents a monocyclic or polycyclic aromatic hydrocarbon group, a saturated or unsaturated aliphatic hydrocarbon group or cyclic aliphatic hydrocarbon group, which

may or may not have a substituent, or a heterocyclic group which may or may not have a substituent and contains hetero atoms such as nitrogen, oxygen, sulfur atoms and the like as atoms composing the ring. The cyclic aliphatic hydrocarbon group and heterocyclic group may satisfactorily be monocyclic or polycyclic like the aromatic hydrocarbon group. The cyclic hydrocarbon (aromatic or alicyclic) and the heterocyclic groups are of condensed series or non-condensed series if they are polycyclic.

For example, R¹ specifically includes aromatic monocyclic or polycyclic groups such as phenyl group, 2-methylphenyl, 2-ethylphenyl, 2-isopropylphenyl, 2-tert-butylphenyl, 2-methoxyphenyl, 2-chlorophenyl, 2-vinylphenyl, 3-methylphenyl, 3-ethylphenyl, 3-isopropylphenyl, 3-methoxyphenyl, 3-chlorophenyl, 3-vinylphenyl, 4-methylphenyl, 4-ethylphenyl, 4-isopropylphenyl, 4-tert-butylphenyl, 4-vinylphenyl, cumenyl (cumyl), mesityl, xylyl, 1-naphthyl, 2-naphthyl, anthryl, phenanthryl, and indenyl; hetero monocyclic or polycyclic groups such as thienyl, furyl, pyranyl, xanthenyl, pyridyl, pyrrolyl, imidazolynyl, indolyl, carbazoyl, and phenanthronyl; and ferrocenyl group.

Like these examples, the compound may satisfactorily have various substituents as the substituent, which may be hydrocarbon groups such as alkyl, alkenyl, cycloalkyl and cycloalkenyl; halogen atoms; oxygen-containing groups such as

alkoxy group, carboxyl group and ester group; nitro group; amino group and the like.

Alternatively, R^2 represents hydrogen atom, a saturated or unsaturated aliphatic hydrocarbon group or cyclic aliphatic hydrocarbon group which may or may not have a substituent or an aromatic hydrocarbon group, or the same heterocyclic group containing hetero atoms, as described above. These are for example alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl and heptyl; cycloalkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl; unsaturated hydrocarbon such as vinyl and allyl; and the same as those for R^1 . Furthermore, R^2 may satisfactorily include derivatives of β -keto acid with a functional group at position β . When R^1 and R^2 are bonded together to form a ring, R^2 is for example a saturated or unsaturated alicyclic group to form cyclic ketones, such as cyclopentanone, cyclohexanone, cycloheptanone, cyclopentenone, cyclohexenone, and cycloheptenone; and saturated and unsaturated alicyclic groups with a linear or cyclic hydrocarbon substituent group containing alkyl group, aryl group, unsaturated alkyl group and hetero atom on individual carbons.

According to the method for producing optically active alcohol compounds through asymmetric reduction of carbonyl compounds, an asymmetric reduction catalyst system of a transition metal complex and an optically active nitrogen-

containing compound is used for the asymmetric reduction.

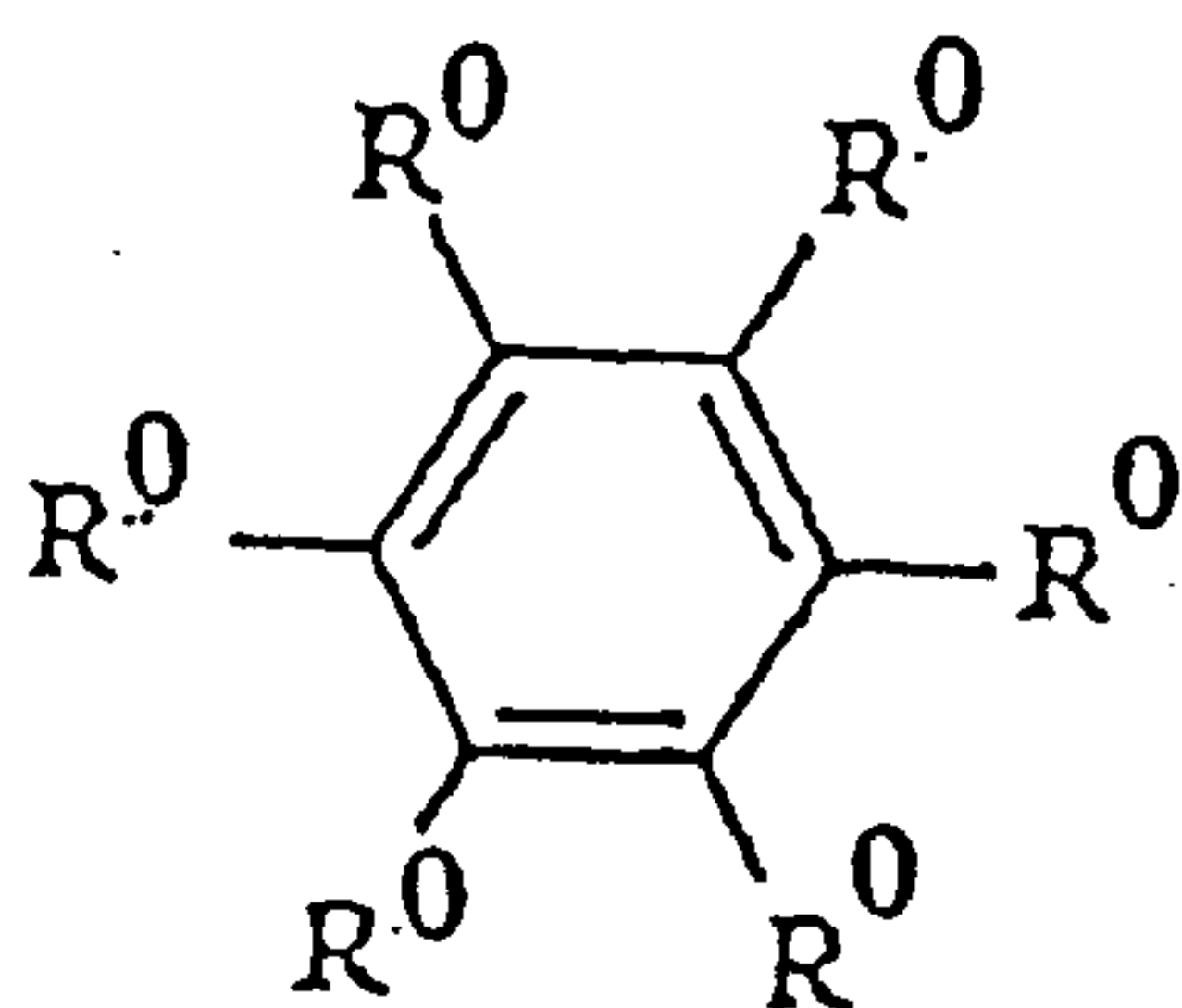
As the metal catalyst, then, use is made of various transition metals because they have ligands; particularly preferably, use is made of a transition metal complex represented by the following general formula (a);



(wherein M represents transition metals of group VIII, such as iron, cobalt, nickel, ruthenium, rhodium, iridium, osmium, palladium and platinum; X represents hydrogen, halogen atom, carboxyl group, hydroxy group and alkoxy group and the like; L represents neutral ligands such as aromatic compounds and olefin compounds; and m and n represent an integer ranging from 1 to 4). As the transition metals in these transition metal catalysts, ruthenium is one of preferable examples.

When the neutral ligands are aromatic compounds, a monocyclic aromatic compound represented by the following general formula (b) can be illustrated. Herein, R⁰'s are all the same or different substituent groups, including hydrogen atom, a saturated or unsaturated hydrocarbon group, allyl group or a functional group containing hetero atoms. For example, R⁰ includes alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, t-butyl, pentyl, hexyl, and heptyl; cycloalkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl; groups of unsaturated hydrocarbons such as

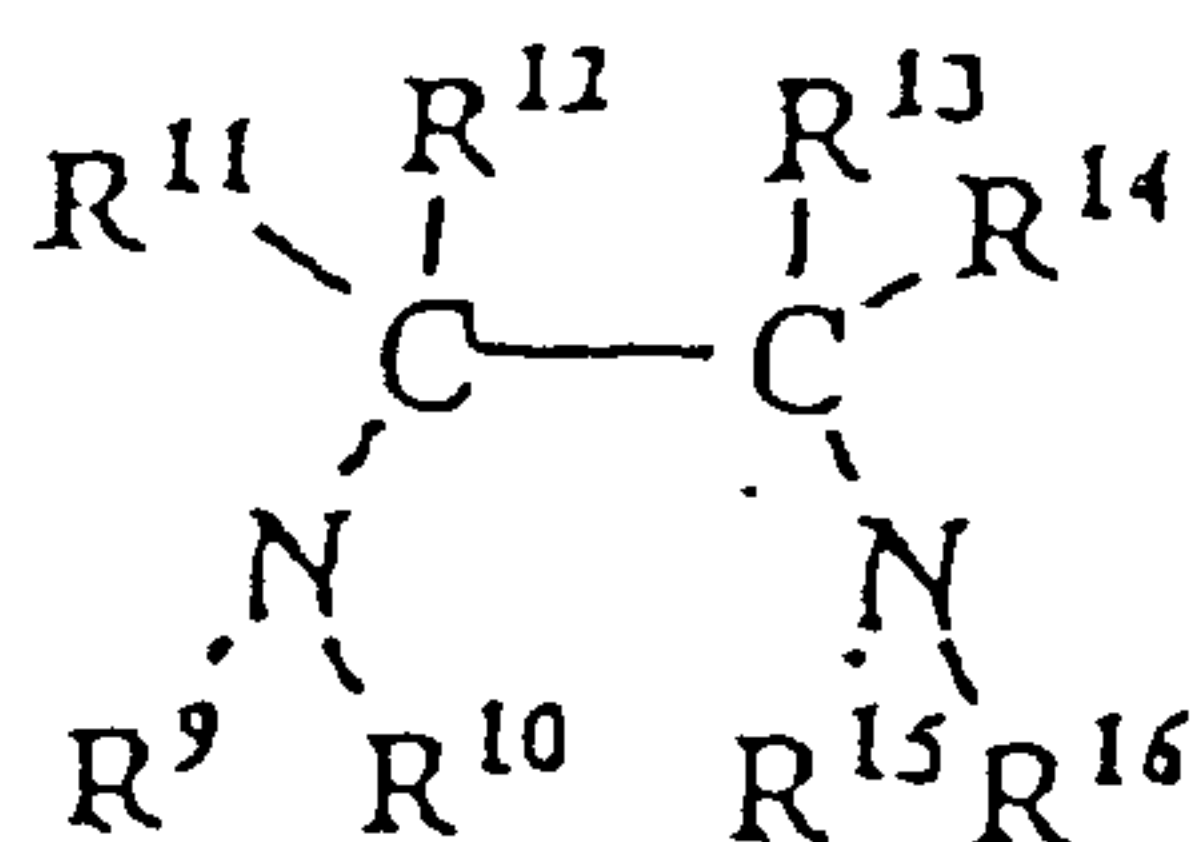
benzyl, vinyl, and allyl; functional groups containing hetero atoms, such as hydroxyl group, alkoxy group, and alkoxycarbonyl group. The number of the substituents R^0 's is an appropriate number of 1 to 6, and the substituents can occupy any position.



(b)

The transition metal catalysts of the group VIII and the like are used to an amount variable, depending on the size, mode and economy of the reactor, but the catalysts may satisfactorily be used within a molar ratio range of approximately 1/100 to 1/100,000, preferably 1/500 to 1/5,000 to the reaction substrate carbonyl compound.

In accordance with the present invention, use is made of optically active nitrogen-containing compounds in the asymmetric catalyst system, and it is possibly assumed that the compounds are present as asymmetric ligands to the transition metal complexes or serve as such. For more easily understandable expression, such optically active nitrogen-containing compounds may also be illustrated as "optically active amine compounds". The optically active amine compounds are optically active diamine compounds represented by the following general formula (c);



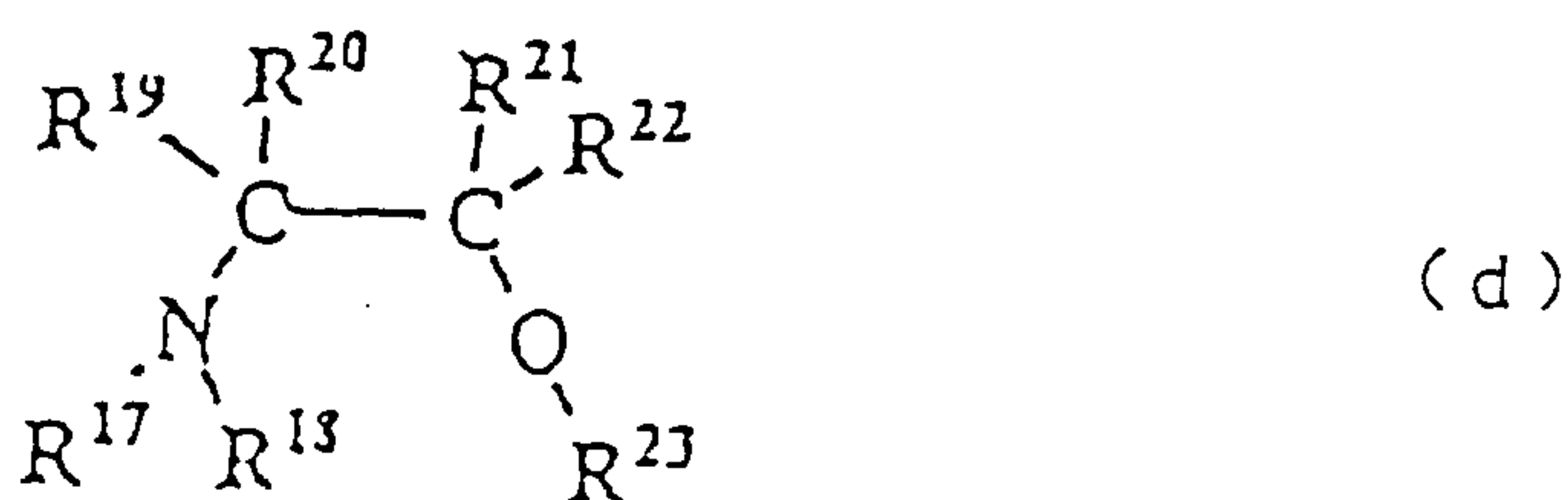
(c)

(wherein R^9 , R^{10} , R^{15} and R^{16} are independently hydrogen, a saturated or unsaturated hydrocarbon group, urethane group or sulfonyl group; R^{11} , R^{12} , R^{13} and R^{14} are the same or different so that the carbon bonded with these substituent groups might occupy the asymmetric center, including hydrogen atom, an aromatic group, a saturated or unsaturated aliphatic hydrocarbon group or cyclic aliphatic hydrocarbon group; even in this case, the aromatic or cyclic aliphatic group may be monocyclic or polycyclic; the polycyclic aromatic group is any of condensed series or non-condensed series; and furthermore, any one of R^{11} and R^{12} and any one of R^{13} and R^{14} are bonded together to form a ring containing 5 to 10 carbon atoms. For example, such compounds include optically active diamine compounds such as optically active 1,2-

diphenylethylenediamine, 1,2-cyclohexanediamine, 1,2-cycloheptanediamine, 2,3-dimethylbutanediamine, 1-methyl-2,2-diphenylethylenediamine, 1-isobutyl-2,2-diphenylethylenediamine, 1-isopropyl-2,2-diphenylethylenediamine, 1-methyl-2,2-di(p-methoxyphenyl)ethylenediamine, 1-isobutyl-2,2-di(p-methoxyphenyl)ethylenediamine, 1-isopropyl-2,2-di(p-methoxyphenyl)ethylenediamine, 1-benzyl-2,2-di(p-methoxyphenyl)ethylenediamine,

1-methyl-2,2-dinaphthyldiamine, 1-isobutyl-2,2-dinaphthylethylenediamine, 1-isopropyl-2,2-dinaphthylethylenediamine and the like. Additionally, optically active diamine compounds wherein any one or two of substituents R^9 through R^{15} are sulfonyl group, acyl group or urethane group are illustrated. Preferably, furthermore, use may be made of optically active diamine compounds with one sulfonyl group. Furthermore, the optically active diamine (compounds) for potential use are not limited to the illustrated optically active ethylenediamine derivatives, and use may be made of optically active propanediamine, butanediamine, and phenylenediamine derivatives.

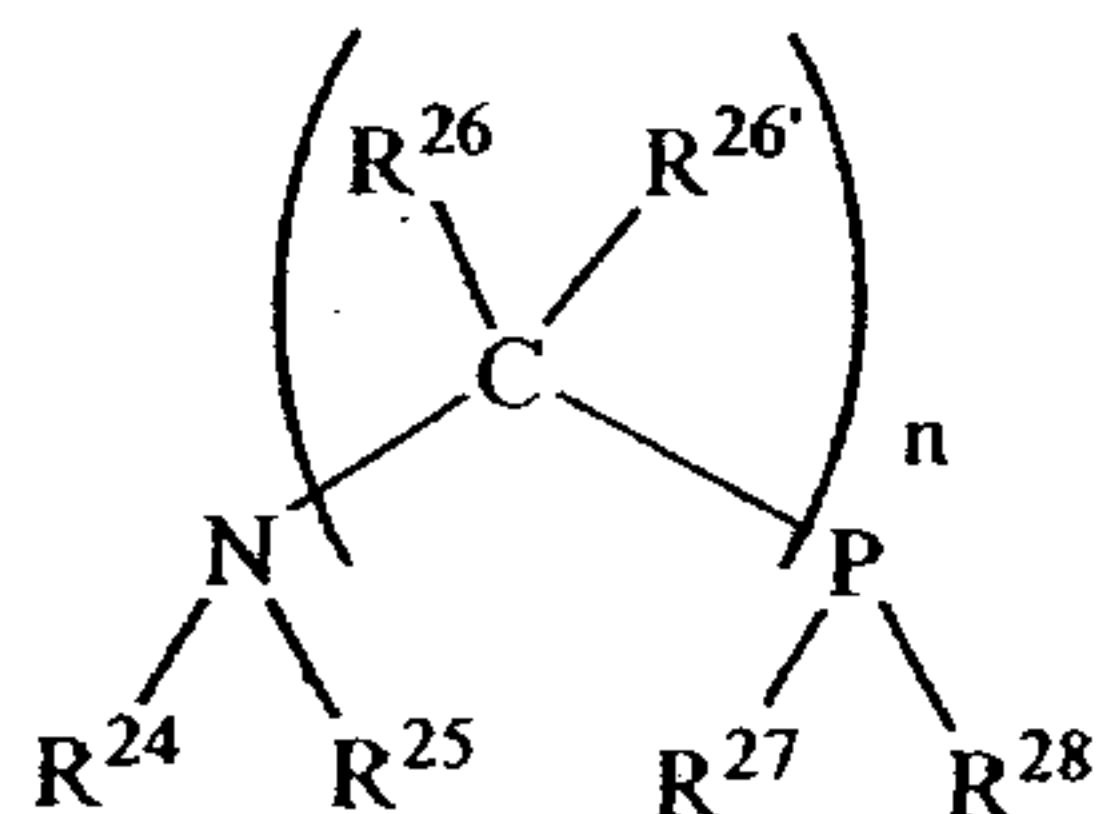
As the optically active amine compounds, use is made of optically active amino alcohol compounds represented by the following general formula (d).



Herein, at least one of R^{17} and R^{18} is hydrogen atom, and the remaining one is hydrogen atom, a saturated or unsaturated hydrocarbon group, urethane group or sulfonyl group; R^{19} , R^{20} , R^{21} and R^{22} are the same or different so that the carbon bonded with these substituent groups might occupy the asymmetric center, including hydrogen atom, a monocyclic or polycyclic

aromatic group, a saturated or unsaturated aliphatic hydrocarbon group, and a cyclic aliphatic hydrocarbon group; R^{23} represents hydrogen atom, a monocyclic or polycyclic aromatic group, a saturated or unsaturated aliphatic hydrocarbon group and cyclic aliphatic hydrocarbon group. Furthermore, any one of R^{19} and R^{20} and any one of R^{21} and R^{22} may satisfactorily be bonded together to form a ring containing 5 to 10 carbon atoms. Additionally, any one of R^{17} and R^{18} and any one of R^{20} and R^{21} may satisfactorily be bonded together to form a ring containing 5 to 10 carbon atoms. More specifically, use may satisfactorily be made of optically active amino-alcohols shown in the examples described below.

As the optically active amine compounds, furthermore, use may be made of aminophosphine compounds represented by the following general formula (e);



Herein, R^{24} and R^{25} are hydrogen atom, a saturated or unsaturated hydrocarbon group, urethane group, sulfonyl group and acyl group; R^{26} and $R^{26'}$ are the same or different so that the carbon bonded with these substituent groups might occupy the asymmetric center, including hydrogen atom, a monocyclic or polycyclic aromatic group, a saturated or unsaturated hydrocarbon group, and a cyclic hydrocarbon group; R^{27} and R^{28} represent hydrogen atom, and a saturated or unsaturated

hydrocarbon group, n is an integer ranging from 1 to 4. More specifically, use may be made of the optically active aminophosphines shown in the examples.

The optically active amine compounds as illustrated above are generally used for example at an amount at approximately 0.5 to 20 equivalents, and preferably used for example within a range of 1 to 4 equivalents, to the transition metal complex.

In the aforementioned catalyst system to be used for the method for producing optically active alcohols through asymmetric reduction of carbonyl compounds, advantageously, an additional basic substance is advantageously present currently.

Such basic substance includes for example metal salts or quaternary ammonium compounds represented by the following formula (f);



(wherein M^1 represents an alkali metal or alkali earth metal; and Y represents hydroxy group, alkoxy group, mercapto group and naphthyl group). More specifically, M^1 includes KOH, KOCH₃, KOCH(CH₃)₂, KOC(CH₃)₃, KC₁₀H₈, LiOH, LiOCH₃, LiOCH(CH₃)₂, LiOC(CH₃)₃, NaOH, NaOCH₃, NaOCH(CH₃)₂, NaC₁₀H₈, NaOC(CH₃)₃, and the like. Furthermore, quaternary ammonium salts may be used satisfactorily.

The amount of the base to be used is generally about 0.5 to 50 equivalents, preferably 2 to 10 equivalents to the transition metal complex.

As has been described above, the basic substance is used for smoothly progressing the asymmetric reduction. Therefore, the base is an important component so as to give optically active alcohol compounds with a high optical purity.

For the method for producing optically active alcohol compounds through hydrogen transfer-type asymmetric reduction in accordance with the present invention, it is inevitable to use hydrogen-donating organic or inorganic compounds. By these are meant compounds capable of donating hydrogen via thermal action or catalytic action, and the types of such hydrogen-donating compounds are not specifically limited, but preferably include alcohol compounds such as methanol, ethanol, 1-propanol, 2-propanol, butanol, and benzyl alcohol; formic acid and salts thereof, for example those in combination with amines; an unsaturated hydrocarbon and heterocyclic compounds having in part a saturated carbon bond, such as tetralin and decalin; hydroquinone or phosphorous acid or the like. Among them, alcohol compounds are preferable, and 2-propanol and formic acid are more preferable. The amount of an organic compound to be used and function as a hydrogen source is determined on the basis of the solubility and economy of the reaction substrate. Generally, the substrate concentration may be about 0.1 to 30 % by weight for some type of substrates, but preferably, the concentration is 0.1 to 10 % by weight.

When using formic acid and a combination of formic acid with amine as a hydrogen source, no solvent is necessarily used. If any solvent is intentionally used, use is made of aromatic compounds such as toluene and xylene; halogen compounds such as dichloromethane, organic compounds such as DMSO, DMF or acetonitrile.

According to the method for producing optically active alcohol compounds in accordance with the present invention, hydrogen pressure is essentially not required, but depending on the reaction conditions, hydrogen pressure may satisfactorily be loaded. Even if hydrogen pressure is loaded, the pressure may satisfactorily be about 1 atm. to several atm. because the catalyst system is extremely highly active.

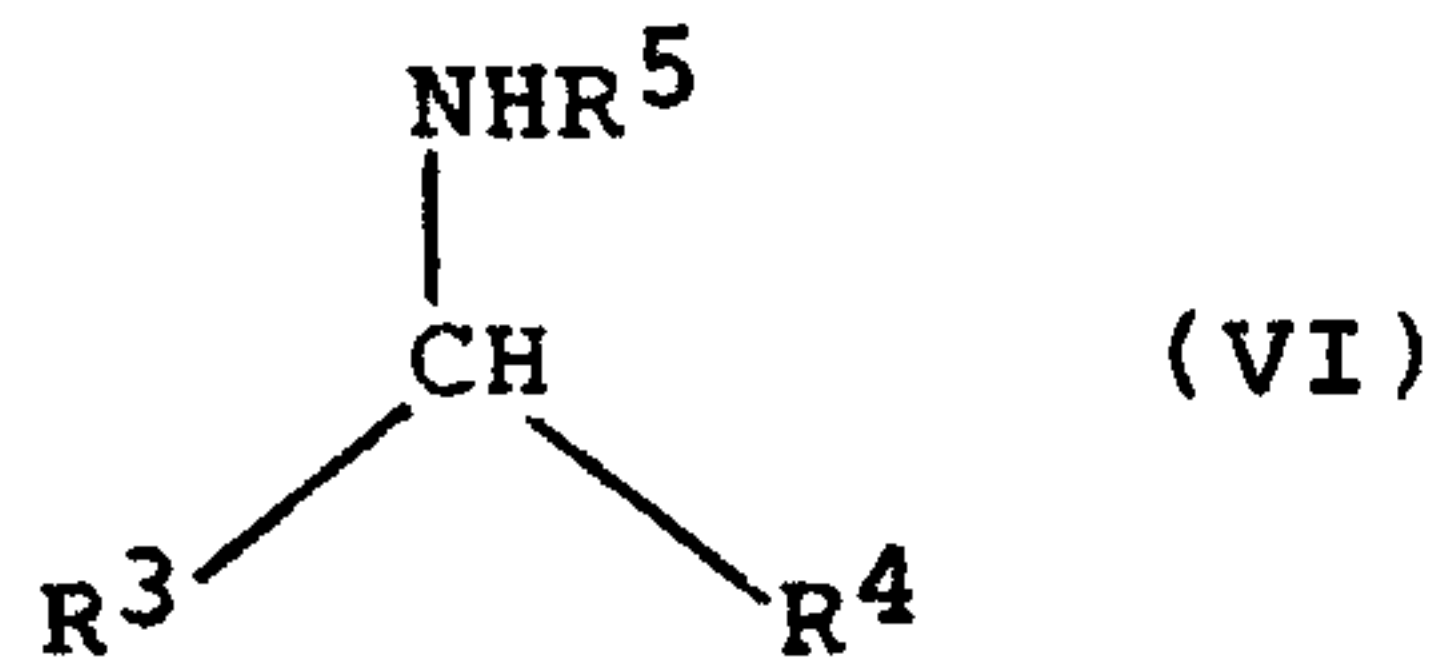
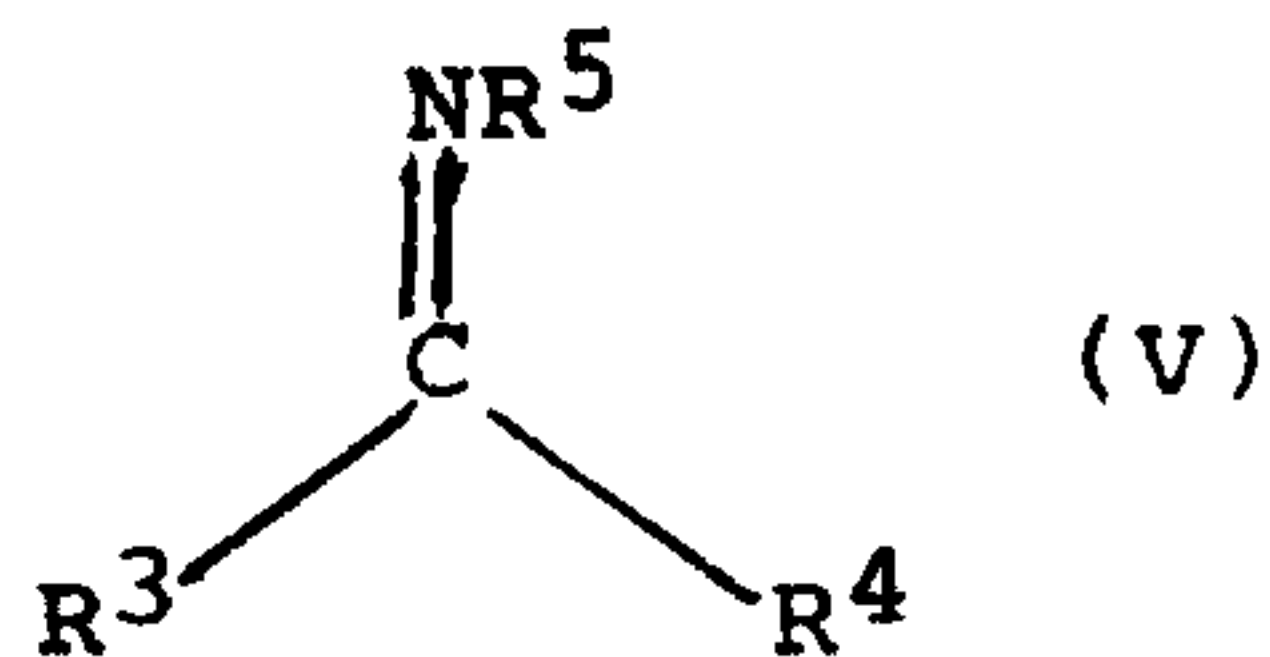
The reaction temperature is about -20 to 100 from the economical standpoint. More practically, the reaction can be carried out around room temperature of 25 to 40 . The reaction time varies, depending on the reaction conditions such as the concentration of a reaction substrate, temperature and pressure, but the reaction is on completion from several minutes to 100 hours.

For use, the metal complex is preliminarily mixed with an optically active amine compound as an optically active nitrogen-containing compound, but a chiral metal complex may be synthesized preliminarily by the following method, and the resulting complex may be used.

More specifically, the method comprises adding an optically active amine compound, a transition metal complex and a complex into for example alcohol, and subsequently heating the resulting mixture in an inactive gas under agitation. Then, the resulting solution is cooled and treated under reduced pressure, prior to recrystallization, to prepare an asymmetric complex catalyst.

Together with the method for producing optically active alcohol compounds as described above, the present invention is to provide a method for producing optically active amine compounds represented by the general formula (II) as described above, wherein W_1 is OH, NH_2 , $NH-R_c$, $NH-OH$ or $NH-O-R_d$, comprising asymmetric reduction by using an imine compound represented by the general formula (I) wherein W_1 is NH , $N-R_c$, $N-OH$ or $N-O-R_d$ (R_c and R_d independently represent a linear or cyclic hydrocarbon group which may or may not have a substituent, or a heterocyclic group).

More specifically, for example, the present invention is to provide a method for producing an optically active amine compound of the following formula (VI), comprising asymmetric reduction of an imine compound of the following formula (V).



Herein, R^3 and R^4 are almost the same as those in the case of the carbonyl compounds and the optically active alcohol compounds of the formulas (III) and (IV), respectively.

For example, R^3 is an aromatic monocyclic or polycyclic hydrocarbon group, unsubstituted or substituted, a saturated or unsaturated aliphatic hydrocarbon group or cyclic hydrocarbon group, unsubstituted or substituted, or a hetero monocyclic or polycyclic group containing hetero atoms such as nitrogen, oxygen, sulfur atoms and the like; more specifically, R^3 includes aromatic monocyclic or polycyclic hydrocarbon groups such as phenyl group, 2-methylphenyl, 2-ethylphenyl, 2-isopropylphenyl, 2-tert-butylphenyl, 2-methoxyphenyl, 2-chlorophenyl, 2-vinylphenyl, 3-methylphenyl, 3-ethylphenyl, 3-isopropylphenyl, 3-methoxyphenyl, 3-chlorophenyl, 3-vinylphenyl, 4-methylphenyl, 4-ethylphenyl, 4-isopropylphenyl, 4-tert-butylphenyl, 4-vinylphenyl, cumenyl, mesityl, xylyl, 1-naphthyl, 2-naphthyl, anthryl, phenanthryl, and indenyl groups; hetero monocyclic or polycyclic groups such as thienyl, furyl, pyranyl, xanthenyl, pyridyl, pyrrolyl, imidazolyl, indolyl, carbazoyl, and phenanthronyl; and ferrocenyl group. Like these examples, R^3 may contain any of various substituents, which may satisfactorily be hydrocarbon groups such as alkyl, alkenyl, cycloalkyl, and cycloalkenyl; halogen atom; oxygen-containing groups such as alkoxy group, carboxyl group

and ester group; nitro group; cyano group and the like.

Furthermore, R^4 represents hydrogen atom, a saturated or unsaturated hydrocarbon group, aryl group, hetero atom-containing functional groups, including for example alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl, and heptyl; cycloalkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl; unsaturated hydrocarbons such as vinyl and allyl; and the same as those for R^1 . Additionally, R^5 represents hydrogen atom, a saturated and unsaturated hydrocarbon group, aryl group, a hetero atom-containing heterocyclic group, or the hydrocarbon group or heterocyclic group bonded together via hydroxyl group or oxygen atom, including for example alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl and heptyl; cycloalkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl; unsaturated hydrocarbon groups such as benzyl, vinyl and allyl; hydroxyl group; alkyl ether groups; aryl ether groups; and the like. Furthermore, a saturated or unsaturated cyclic imine compound formed by bonding together R^3 and R^4 , R^3 and R^5 or R^4 and R^5 , is illustrated.

Non-cyclic imine compounds can be synthesized readily from the corresponding ketones and amines. In this case, the syn-form and anti-form or a mixture enriched with either one of these syn- and anti-forms may be used satisfactorily, but a purified product of the mixture may be used singly or a mixture thereof

with another imine compound may also be used.

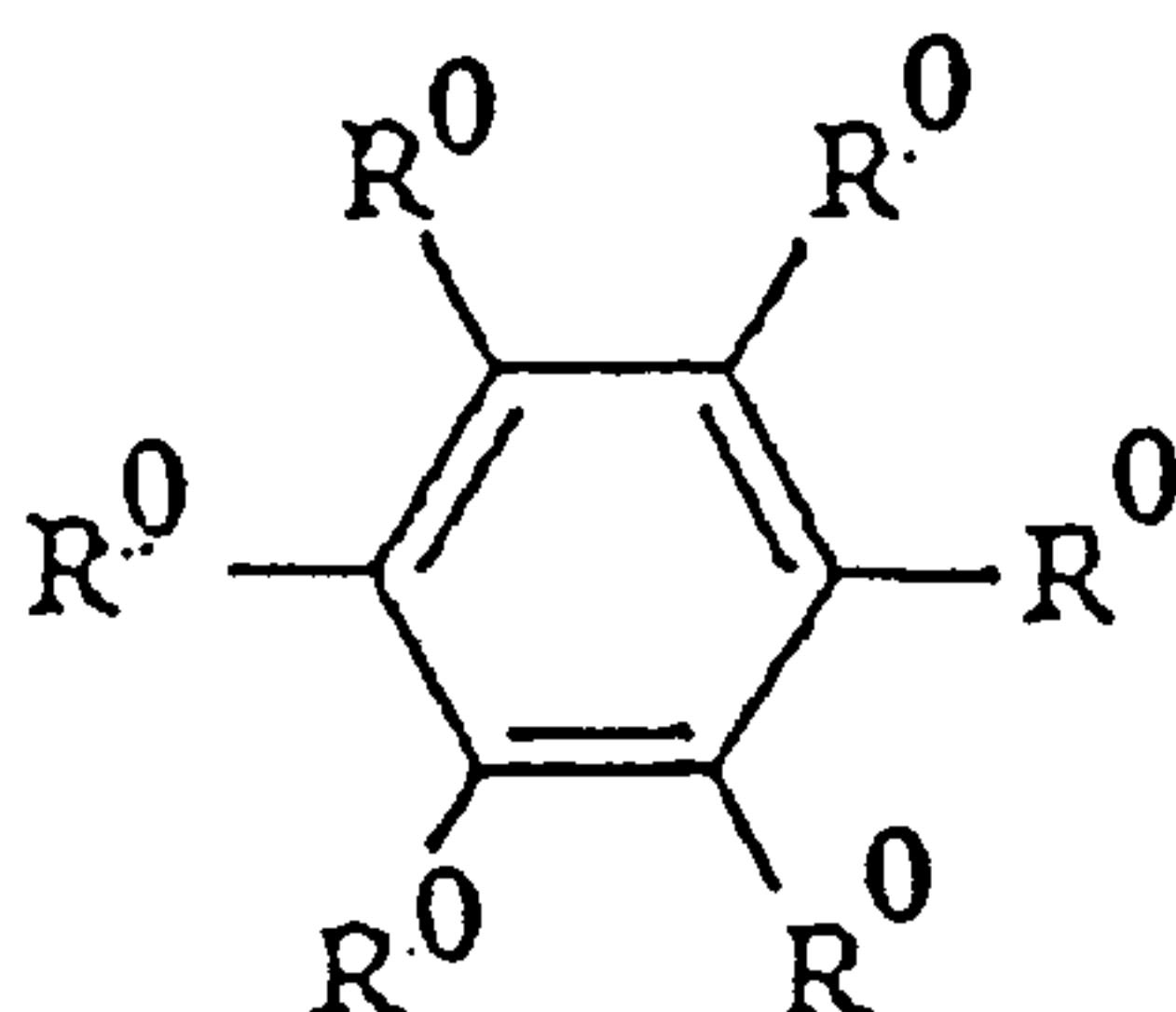
Even by the method for producing optically active amine compounds, like the method for producing optically active alcohol compounds, use is made of an asymmetric reduction catalyst composed of a transition metal complex and an optically active nitrogen-containing compound. In the transition metal complex among them, various transition metals with ligands are used, and particularly preferably, use is made of those similar to a transition metal complex represented by the general formula (a);



(wherein M is a transition metal of group VIII, such as iron, cobalt, nickel, ruthenium, rhodium, iridium, osmium, palladium and platinum; X represents hydrogen, halogen atom, carboxyl group, hydroxy group and alkoxy group and the like; L represents neutral ligands such as aromatic compounds and olefin compounds; m and n represent an integer). The transition metal in the transition metal complex is preferably rare metal, and specifically, ruthenium is one of preferable examples.

Like the method for producing optically active alcohols, a monocyclic aromatic compound represented by the general formula (b) is illustrated for the aromatic compound as the neutral ligand. Herein, R⁰'s are the same or different substituent groups, representing hydrogen atom, a saturated or

unsaturated hydrocarbon group, aryl group, and functional groups containing hetero atoms, for example alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, t-butyl, pentyl, hexyl, and heptyl; cycloalkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl; unsaturated hydrocarbon groups such as benzyl, vinyl, and allyl; hetero atom-containing functional groups such as hydroxyl group, alkoxy group and alkoxycarbonyl group. The number of the substituents R^0 's is an optional number of 1 to 6, and the substituents each can occupy any position.

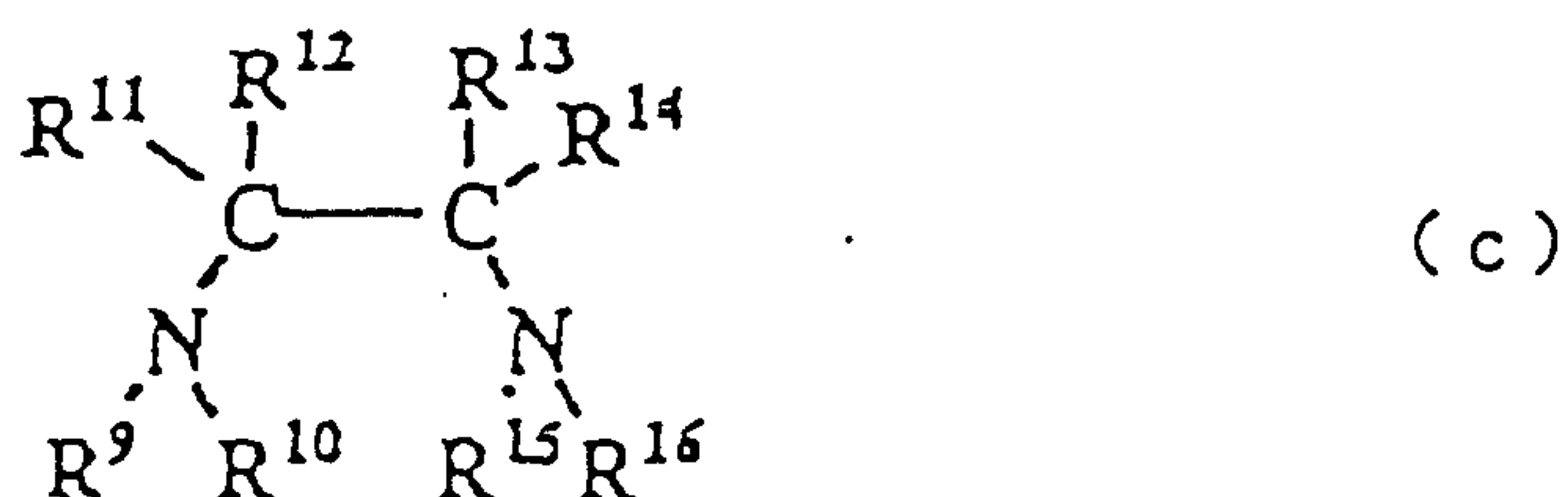


(b)

The transition metal catalysts are used at an amount variable, depending on the size, mode and economy of the reactor, but the catalysts may satisfactorily be used within a molar ratio range of approximately 1/100 to 1/100,000, preferably 1/200 to 1/5,000 to the reaction substrate imine compound.

According to the method for producing optically active amine compounds in accordance with the present invention, additionally, use is made of optically active nitrogen-containing compounds in the asymmetric catalyst system, and it is possibly assumed that the compounds may be present as

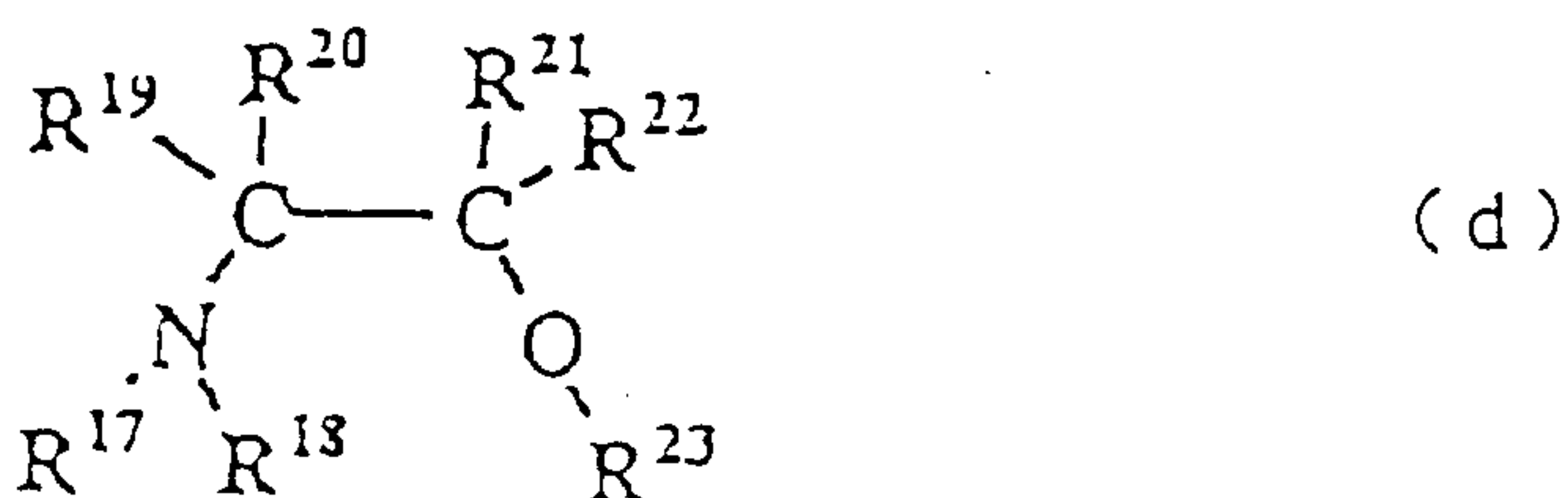
asymmetric ligands in the transition metal complexes or may serve as such. For more easily understandable expression, such optically active nitrogen-containing compounds are illustrated as "optically active amine compounds". As described above, the optically active amine compounds are optically active diamine compounds represented for example by the following general formula (c);



(wherein R^9 , R^{10} , R^{15} , and R^{16} are independently hydrogen, a saturated or unsaturated hydrocarbon group, urethane group or sulfonyl group; R^{11} , R^{12} , R^{13} and R^{14} are the same or different so that the carbon bonded with these substituent groups might occupy the asymmetric center, including hydrogen atom, aromatic monocyclic and polycyclic groups, a saturated or unsaturated hydrocarbon group or cyclic hydrocarbon group; even in this case, the aromatic, or cyclic, or cyclic aliphatic group may be monocyclic or polycyclic; the polycyclic aromatic group is any of condensed series or non-condensed series; and furthermore, any one of R^{11} and R^{12} may satisfactorily form a ring. For example, such compounds include optically active diamine compounds such as optically active 1,2-diphenylethylenediamine, 1,2-cyclohexanediamine, 1,2-cycloheptanediamine, 2,3-

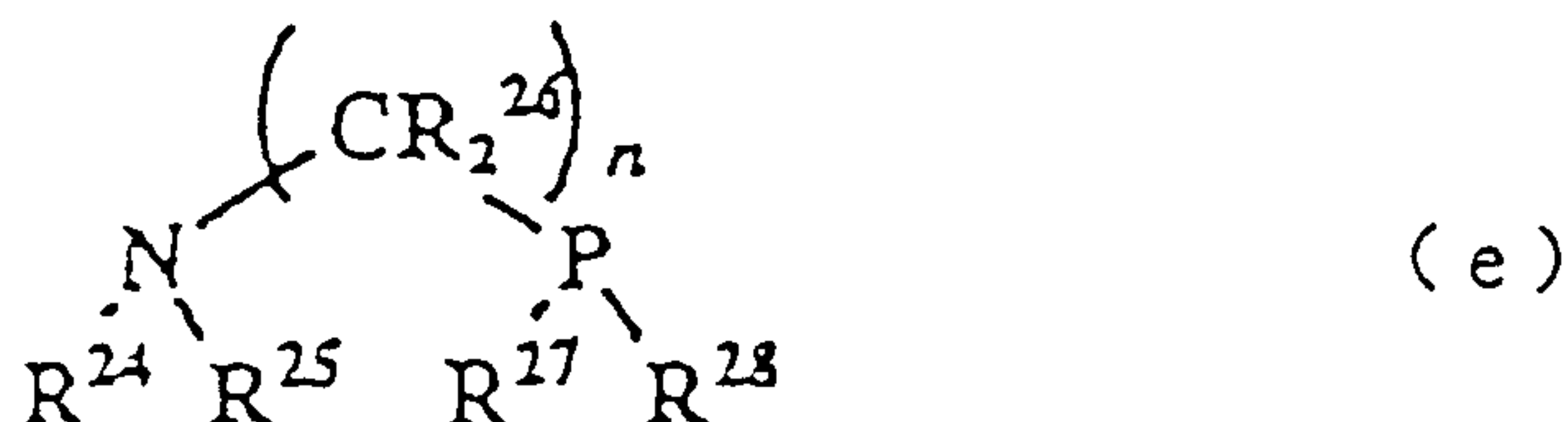
dimethylbutanediamine, 1-methyl-2,2-diphenylethylenediamine, 1-isobutyl-2,2-diphenylethylenediamine, 1-isopropyl-2,2-diphenylethylenediamine, 1-methyl-2,2-di(p-methoxyphenyl)ethylenediamine, 1-isobutyl-2,2-di(p-methoxyphenyl)ethylenediamine, 1-isopropyl-2,2-di(p-methoxyphenyl)ethylenediamine, 1-benzyl-2,2-di(p-methoxyphenyl)ethylenediamine, 1-methyl-2,2-dinaphthylethylenediamine, 1-isobutyl-2,2-dinaphthylethylenediamine, 1-isopropyl-2,2-dinaphthylethylenediamine and the like. Additionally, optically active diamine compounds wherein any one or two of substituents R^9 through R^{15} are sulfonyl group, acyl group or urethane group may also be used. Preferably, furthermore, use may be made of optically active diamine compounds with one sulfonyl group. Furthermore, optically active diamine (compounds) to be possibly used are not limited to the illustrated optically active ethylenediamine derivatives, and use may be made of optically active propanediamine, butanediamine, and phenylenediamine derivatives.

As the optically active amine compound, use is made of an optically active amino alcohol compound represented by the following general formula (d);



Herein, at least one of R^{17} and R^{19} is hydrogen atom, and the remaining one is hydrogen atom, a saturated or unsaturated hydrocarbon group, urethane group or sulfonyl group; R^{19} , R^{20} , R^{21} and R^{22} are the same or different so that the carbon bonded with these substituent groups might occupy the asymmetric center, including hydrogen atom, an aromatic monocyclic or polycyclic group, a saturated or unsaturated hydrocarbon group, or a cyclic hydrocarbon group; R^{23} represents hydrogen atom, an aromatic monocyclic or polycyclic group, a saturated or unsaturated hydrocarbon group and a cyclic hydrocarbon group. Furthermore, any one of R^{19} and R^{20} and any one of R^{21} and R^{22} may satisfactorily be bonded together to form a ring, or any one of R^{17} and R^{18} and any one of R^{20} and R^{21} may satisfactorily be bonded together to form a ring. More specifically, use is made of optically active amino alcohols shown in the examples described below.

As the optically active amine compound, furthermore, use is made of aminophosphine compound represented by the following general formula (e).



Herein, R^{24} and R^{25} are hydrogen atom, a saturated or unsaturated hydrocarbon group, urethane group, sulfonyl group and acyl group; $(CR_2^{26})_n$ are the same or different so that the

carbon bonded with these substituent groups might occupy the asymmetric center, including hydrogen atom, an aromatic monocyclic or polycyclic group, a saturated or unsaturated hydrocarbon group, and a cyclic hydrocarbon group; R^{27} and R^{28} represent hydrogen atom, a saturated or unsaturated hydrocarbon group, and allyl group. More specifically, use is made of the optically active aminophosphines shown in the examples.

The optically active amine compounds as illustrated above are used at an amount for example of approximately 0.5 to 20 equivalents, and preferably within a range of 1 to 2 equivalents, to the transition metal complex.

The transition metal catalyst to be used as the catalyst as described above and the optically active amine compound are essential components to progress the asymmetric reduction in a smooth manner thereby attaining a higher asymmetric yield, and amine compounds at a higher optical purity cannot be recovered at a sufficiently high reaction activity, if either one of the two is eliminated.

For the method for producing optically active amines through hydrogen transfer-type asymmetric reduction in accordance with the present invention, the presence of a hydrogen-donating organic or inorganic compound is indispensable. These compounds mean compounds capable of donating hydrogen through thermal action or catalytic action, and the types of these hydrogen-donating compounds are not

limited, but preferably include alcohol compounds such as methanol, ethanol, 1-propanol, 2-propanol, butanol, and benzyl alcohol; formic acid and salts thereof, such as those in combination with amines; unsaturated hydrocarbons and heterocyclic compounds having saturated carbon bonds in part, such as tetralin and decalin; hydroquinone or phosphorous acid or the like. Among them, alcohol compounds are preferable, and 2-propanol is more preferable. The amount of an organic acid to be used as a hydrogen source is determined, depending on the solubility and economy of the reaction substrate. Generally, the substrate is used at a concentration of approximately 0.1 to 30 % by weight, depending on the type of the substrate to be used, and is preferably at a concentration of 0.1 to 10 % by weight. When using formic acid and a combination of formic acid with amine as a hydrogen source, no solvent is necessarily used, but use may satisfactorily be made of aromatic compounds such as toluene and xylene; halogen compounds such as dichloromethane, or organic compounds such as DMSO, DMF or acetonitrile, if it intended to use any solvent.

Hydrogen pressure is essentially not required, but depending on the reaction conditions, hydrogen pressure may satisfactorily be loaded. Even if hydrogen pressure is loaded, the pressure may satisfactorily be about 1 atm. to 50 atm.

The reaction temperature is about -20°C to 100°C from the

economical standpoint. More practically, the reaction can be carried out around room temperature of 25 to 40 . The reaction time varies, depending on the reaction conditions such as the concentration of a reaction substrate, temperature and pressure, but the reaction is on completion from several minutes to 100 hours.

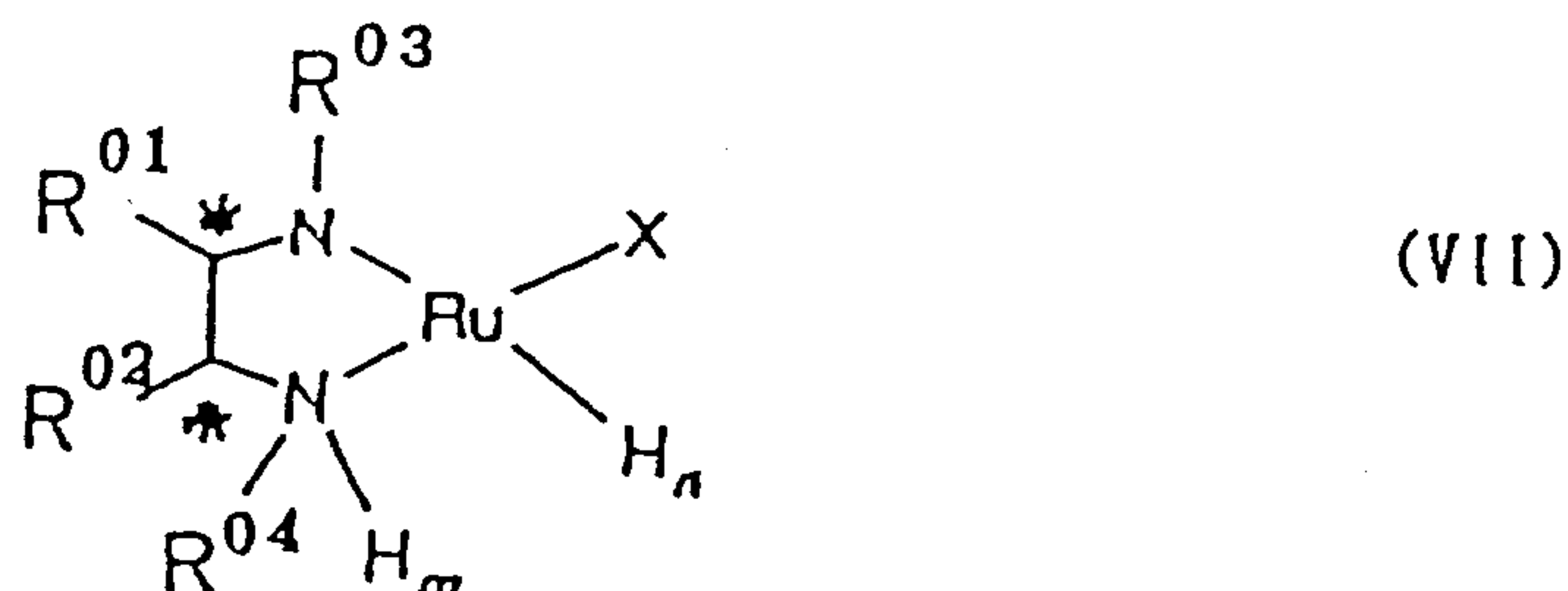
The metal complex to be used in accordance with the present invention is preliminarily mixed with an optically active amine compound, but an asymmetric metal complex may be preliminarily synthesized by the following method, and the resulting complex may be used.

More specifically, for example, a method is illustrated, comprising suspending a ruthenium-arene complex, an optically active amine compound and triethylamine in 2-propanol, heating the resulting mixture in argon or nitrogen gas stream under agitation, and cooling then the resulting reaction mixture, from which the solvent is then removed, and re-crystallizing the resulting mixture in an alcohol solvent to prepare an asymmetric complex.

The catalyst system to be used for the hydrogen transfer-type asymmetric reduction in accordance with the present invention is very characteristic and has never been known up to now.

The optically active ruthenium-diamine complex represented by the following formula (VII) as described above as one metal complex composed of a transition metal and an

optically active nitrogen-containing compound ligand is useful as a catalyst for producing optically active secondary alcohol compounds, comprising subjecting racemic secondary alcohol or meso-type diols to hydrogen transfer reaction, and therefore, the complex draws higher attention.



In the formula, * represents an asymmetric carbon atom; R^{01} and R^{02} are the same or different, independently representing alkyl group, or phenyl group or cycloalkyl group which may or may not have an alkyl group; or R^{01} and R^{02} together form an alicyclic ring unsubstituted or substituted with an alkyl group; R^{03} represents methanesulfonyl group, trifluoromethanesulfonyl group, naphthylsulfonyl group, camphor sulfonyl group, or benzenesulfonyl group which may or may not be substituted with an alkyl group, an alkoxyl group or halogen atom, alkoxycarbonyl group, or benzoyl group which may or may not be substituted with an alkyl group; R^{04} represents hydrogen atom or alkyl group; X represents an aromatic compound which may or may not be substituted with an alkyl group; and m and n together represent 0 or 1.

For more description of the optically active ruthenium-diamine complex of the formula (VII), the aromatic compound

which may or may not have an alkyl group represented by X, for example alkyl groups with C1 to C4, means for example benzene, toluene, xylene, mesitylene, hexamethylbenzene, ethylbenzene, tert-butylbenzene, p-cymene, and cumene and preferably includes benzene, mesitylene and p-cymene.

R^{01} and R^{02} represent a linear or branched alkyl group, if they represent an alkyl group, for example alkyl groups with C1 to C4. More specifically, the alkyl group includes methyl, ethyl, n-propyl, isopropyl, n-, iso-, sec- and tert-butyl. More preferably, the group includes methyl, ethyl, n-propyl or iso-propyl.

If R^{01} and R^{02} are bonded together to form an alicyclic group, the group may satisfactorily be a C5 to C7-membered ring. The alkyl group which may or may not be a substituent therefor, for example alkyl substituent group with C1 to C4, includes methyl group, ethyl group, n-propyl group, isopropyl group, and n-, iso-, sec- and tert-butyl groups. Preferably, the alkyl group is methyl.

R^1 and R^2 as phenyl group wherein R^{01} and R^{02} may have an alkyl group, for example methyl group, specifically include phenyl, o-, m- and p-tolyl groups.

R^{01} and R^{02} representing cycloalkyl group contain carbon atoms in 5 to 6-membered rings, preferably including cyclopentyl or cyclohexyl.

In more preferable examples, R^{01} and R^{02} are independently

phenyl or R^{01} and R^{02} together mean tetramethylene $-(CH_2)_4-$.

R^{03} represents methanesulfonyl group, trifluoromethanesulfonyl group, naphthylsulfonyl group, camphor sulfonyl group, or benzenesulfonyl group which may or may not be substituted with alkyl group, for example alkyl group with C1 to C3, alkoxy group for example alkoxy group with C1 to C3, or halogen atom, or benzoyl group which may or may not be substituted with alkyl group, for example C1 to C4 alkoxycarbonyl groups, or alkyl group, for example C1 to C4 alkyl group.

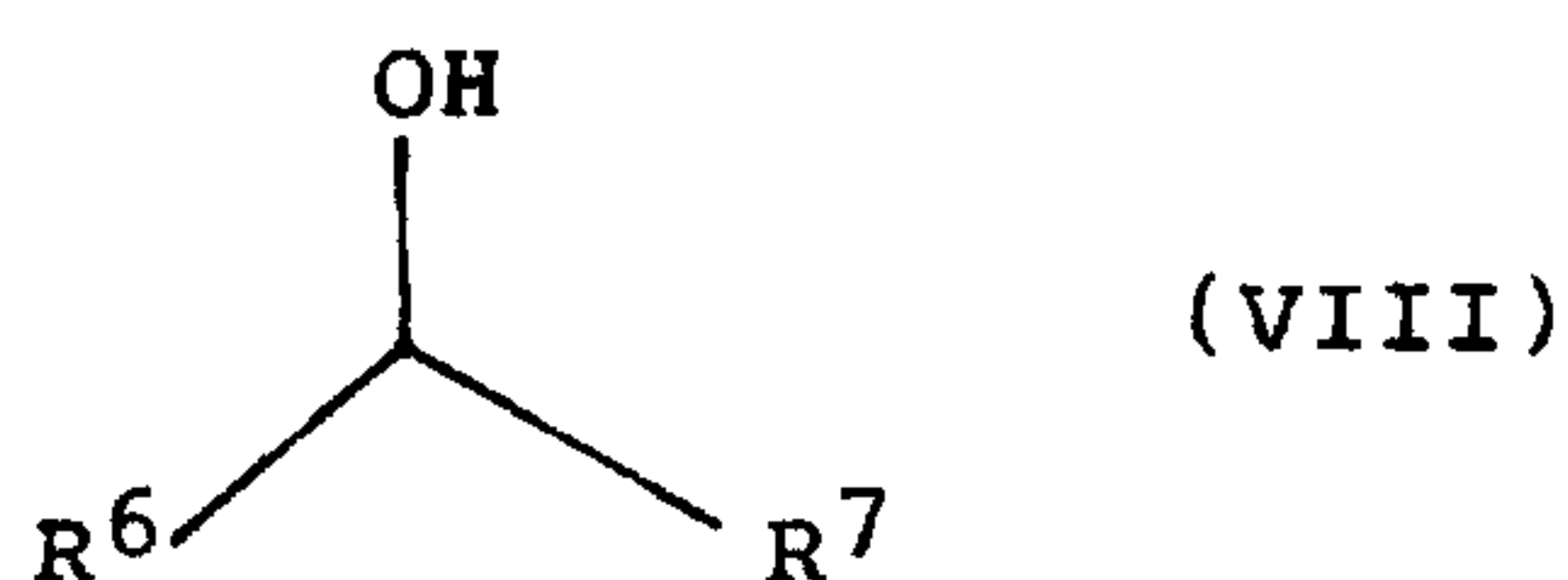
More specifically, R^{03} representing benzenesulfonyl group which may or may not be substituted with C1 to C3 alkyl group, C1 to C3 alkoxy group or halogen atom, includes benzenesulfonyl, o-, m- and p-toluenesulfonyl, o-, m-, and p-ethylbenzenesulfonyl, o-, m-, and p-methoxybenzenesulfonyl, o-, m-, and p-ethoxybenzenesulfonyl, o-, m-, and p-chlorobenzenesulfonyl, 2, 4, 6-trimethylbenzenesulfonyl, 2,4,6-triisopropylbenzenesulfonyl, p-fluorobenzenesulfonyl, and pentafluorobenzenesulfonyl, and more preferably includes benzenesulfonyl or p-toluenesulfonyl. Specifically, R^{03} representing C1 to C4 alkoxycarbonyl groups includes methoxycarbonyl, ethoxycarbonyl, isopropylloxycarbonyl, and tert-butoxycarbonyl, preferably including methoxycarbonyl or tert-butoxycarbonyl. R^{03} representing benzoyl group which may or may not be substituted with C1 to C4 alkyl groups specifically

includes benzoyl, o-, m-, and p-methylbenzoyl, o-, m-, and p-ethylbenzoyl, o-, m-, and p-isopropylbenzoyl, and o-, m-, and p-tert-butylbenzoyl, preferably including benzoyl or p-methylbenzoyl.

In the most preferable example, R^{03} is methanesulfonyl, trifluoromethanesulfonyl, benzenesulfonyl or p-toluenesulfonyl.

R^{04} representing hydrogen atom or alkyl group, for example C1 to C4 alkyl groups, specifically includes for example hydrogen, methyl, ethyl, n-propyl, isopropyl, n-, iso-, sec- and tert-butyl, and more preferably includes hydrogen atom or methyl group.

The optically active ruthenium-diamine complex is used for the method for producing optically active secondary alcohols from ketones as described above in accordance with the present invention, and in this case, the racemic secondary alcohols as the raw material compounds in accordance with the present invention are illustrated by the following formula (VIII). It is needless to say that the racemic alcohols are not limited to those represented by the formula.

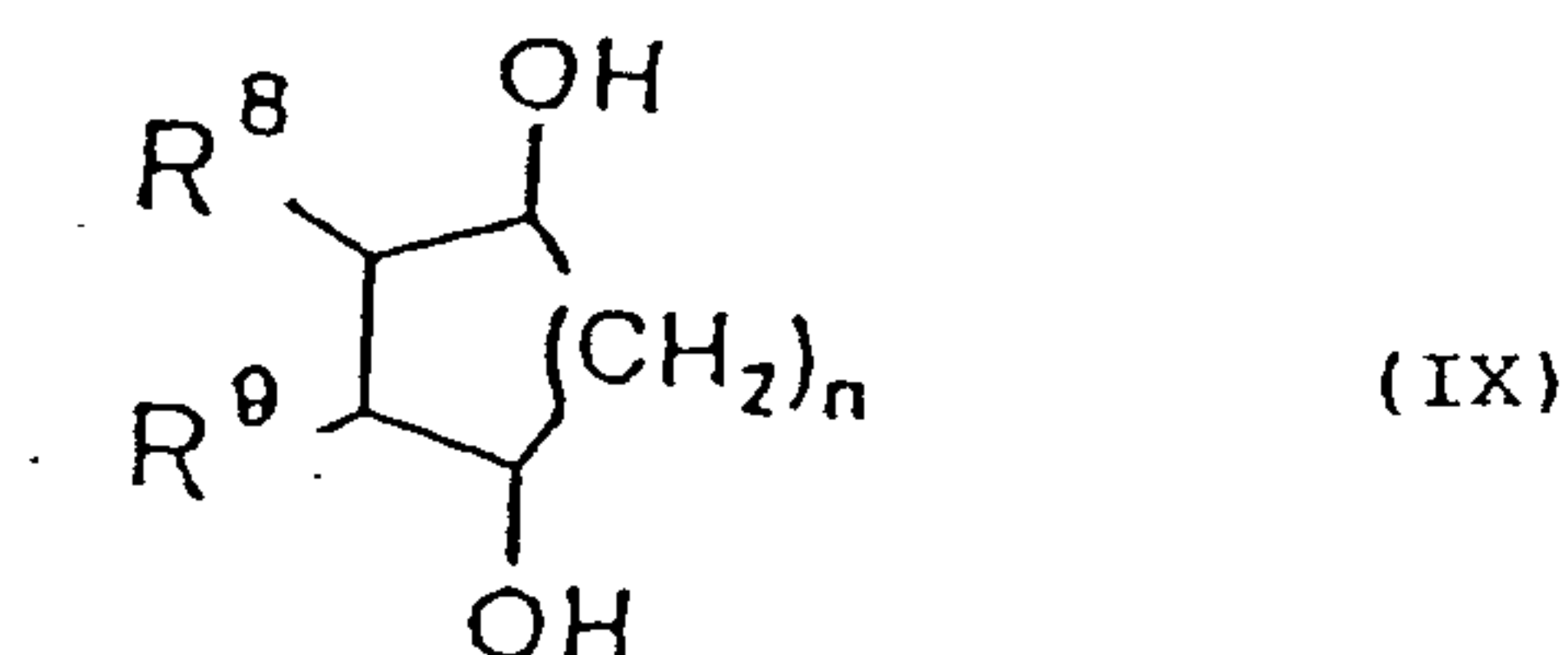


R^6 represents an aromatic monocyclic or polycyclic hydrocarbon group, unsubstituted or substituted or a hetero

monocyclic or polycyclic group containing hetero atoms including nitrogen, oxygen, sulfur atoms and the like, specifically representing aromatic monocyclic or polycyclic groups such as phenyl group, 2-methylphenyl, 2-ethylphenyl, 2-isopropylphenyl, 2-tert-butylphenyl, 2-methoxyphenyl, 2-chlorophenyl, 2-vinylphenyl, 3-methylphenyl, 3-ethylphenyl, 3-isopropylphenyl, 3-methoxyphenyl, 3-chlorophenyl, 3-vinylphenyl, 4-methylphenyl, 4-ethylphenyl, 4-isopropylphenyl, 4-tert-butylphenyl, 4-vinylphenyl, cumenyl, mesityl, xylyl, 1-naphthyl, 2-naphthyl, anthryl, phenanthryl, and indenyl; hetero monocyclic or polycyclic groups such as thienyl, furyl, pyranyl, xanthenyl, pyridyl, pyrrolyl, imidazolyl, indolyl, carbazoyl, and phenthronyl; and ferrocenyl group. Furthermore, R' represents hydrogen atom, a saturated or unsaturated hydrocarbon group, or a functional group containing hetero atoms, including for example alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, pentyl, hexyl, and heptyl; cycloalkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl; and unsaturated hydrocarbons such as benzyl, vinyl, and allyl. R⁶ and R⁷ may be bonded together to form a ring, and in this case, R⁷ includes for example a saturated or unsaturated alicyclic group giving a C₅-C₇ cyclic ketone such as cyclopentanone, cyclohexanone, cycloheptanone, cyclopentenone, cyclohexenone, and cycloheptenone; or a saturated and unsaturated alicyclic group

with a substituent group having an alkyl group, an aryl group, a unsaturated alkyl group or a linear or cyclic hydrocarbon group on each of the individual carbons.

Additionally, the meso-type diols are represented for example by the following formula (IX).



It is needless to say that the meso-diols are not limited to them.

In this case, R^8 and R^9 are the same and represent a saturated or unsaturated hydrocarbon group which may or may not have a substituent group, or R^8 and R^9 may be bonded together to form a saturated or unsaturated alicyclic group, having preferably 5 to 7 carbon atoms, which may or may not have a substituent group, and n is 1 or 2.

More specifically, the ruthenium-diamine complex of the present invention is for example such that m and n are simultaneously zero in the formula (VII). Herein, η^6 is used to represent the number of carbon atoms bonded to a metal in unsaturated ligands, and therefore, hexahapto (six carbon atoms bonded to metal) is represented by η^6 ; $p\text{-Ts}$ represents p -toluenesulfonyl group; Ms represents methanesulfonyl group; and Tf represents trifluoromethanesulfonyl group.

$Ru[(S, S)\text{-}p\text{-TsNCH}(C_6H_5)CH(C_6H_5)NH](\eta^6\text{-benzene})(((S, S)\text{-}N\text{-}p\text{-}$

toluenesulfonyl-1,2-diphenylethylenediamine)(η^6 -benzene)ruthenium)

$\text{Ru}[(R, R)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-benzene})((R, R)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-benzene})\text{ruthenium})$

$\text{Ru}[(S, S)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-p-cymene})((S, S)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

$\text{Ru}[(R, R)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-p-cymene})((R, R)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

$\text{Ru}[(S, S)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-mesitylene})((S, S)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

$\text{Ru}[(R, R)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-mesitylene})((R, R)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

$\text{Ru}[(S, S)\text{-MsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-benzene})((S, S)\text{-N-methanesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-benzene})\text{ruthenium})$

$\text{Ru}[(R, R)\text{-MsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-benzene})((R, R)\text{-N-methanesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-benzene})\text{ruthenium})$

$\text{Ru}[(S, S)\text{-MsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-p-cymene})((S, S)\text{-N-methanesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

cymene)ruthenium)

$\text{Ru}[(R, R)\text{-MsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-p-cymene})((R, R)\text{-N-methanesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

$\text{Ru}[(S, S)\text{-MsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-mesitylene})((S, S)\text{-N-methanesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

$\text{Ru}[(R, R)\text{-MsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-mesitylene})((R, R)\text{-N-methanesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

$\text{Ru}[(S, S)\text{-TfNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-benzene})((S, S)\text{-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-benzene})\text{ruthenium})$

$\text{Ru}[(R, R)\text{-TfNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-benzene})((R, R)\text{-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-benzene})\text{ruthenium})$

$\text{Ru}[(S, S)\text{-TfNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-p-cymene})((S, S)\text{-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

$\text{Ru}[(R, R)\text{-TfNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-p-cymene})((R, R)\text{-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

$\text{Ru}[(S, S)\text{-TfNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-mesitylene})((S, S)\text{-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

$\text{Ru}[(R, R)\text{-TfNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-mesitylene})(((R, R)\text{-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

$\text{Ru}[(S, S)\text{-C}_6\text{H}_5\text{SO}_2\text{NCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-benzene})(((S, S)\text{-N-benzenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-benzene})\text{ruthenium})$

$\text{Ru}[(R, R)\text{-C}_6\text{H}_5\text{SO}_2\text{NCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-benzene})(((R, R)\text{-N-benzenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-benzene})\text{ruthenium})$

$\text{Ru}[(S, S)\text{-C}_6\text{H}_5\text{SO}_2\text{NCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-p-cymene})(((S, S)\text{-N-benzenssulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

$\text{Ru}[(R, R)\text{-C}_6\text{H}_5\text{SO}_2\text{NCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-p-cymene})(((R, R)\text{-N-benzenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

$\text{Ru}[(S, S)\text{-C}_6\text{H}_5\text{SO}_2\text{NCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-mesitylene})(((S, S)\text{-N-benzenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

$\text{Ru}[(R, R)\text{-C}_6\text{H}_5\text{SO}_2\text{NCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-mesitylene})(((R, R)\text{-N-benzenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

$\text{Ru}[(S, S)\text{-N-p-Ts-1,2-cyclohexanediamine}](\eta^6\text{-benzene})(((S, S)\text{-N-p-toluenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-benzene})\text{ruthenium})$

$\text{Ru}[(R, R)\text{-N-p-Ts-1,2-cyclohexanediamine}](\eta^6\text{-benzene})(((R, R)\text{-N-p-toluenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-benzene})\text{ruthenium})$

R)-N-p-toluenesulfonyl-1,2-cyclohexanediamine)(η^6 -benzene)ruthenium)

Ru[(S, S)-N-p-Ts-1,2-cyclohexanediamine](η^6 -p-cymene)((S, S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine)(η^6 -p-cymene)ruthenium)

Ru[(R, R)-N-p-Ts-1,2-cyclohexanediamine](η^6 -p-cymene)((R, R)-N-p-toluenesulfonyl-1,2-cyclohexanediamine)(η^6 -p-cymene)ruthenium)

Ru[(S, S)-N-p-Ts-1,2-cyclohexanediamine](η^6 -mesitylene)((S, S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine)(η^6 -mesitylene)ruthenium)

Ru[(R, R)-N-p-Ts-1,2-cyclohexanediamine](η^6 -mesitylene)((R, R)-N-p-toluenesulfonyl-1,2-cyclohexanediamine)(η^6 -mesitylene)ruthenium)

Ru[(S, S)-N-Ms-1,2-cyclohexanediamine](η^6 -benzene)((S, S)-N-methanesulfonyl-1,2-cyclohexanediamine)(η^6 -benzene)ruthenium)

Ru[(R, R)-N-Ms-1,2-cyclohexanediamine](η^6 -benzene)((R, R)-N-methanesulfonyl-1,2-cyclohexanediamine)(η^6 -benzene)ruthenium)

Ru[(S, S)-N-Ms-1,2-cyclohexanediamine](η^6 -p-cymene)((S, S)-N-methanesulfonyl-1,2-cyclohexanediamine)(η^6 -p-cymene)ruthenium)

Ru[(R, R)-N-Ms-1,2-cyclohexanediamine](η^6 -p-cymene)((R, R)-N-methanesulfonyl-1,2-cyclohexanediamine)(η^6 -p-

cymene)ruthenium)

Ru[(S, S)-N-Ms-1,2-cyclohexanediamine](η^6 -mesitylene)((S, S)-N-methanesulfonyl-1,2-cyclohexanediamine)(η^6 -mesitylene)ruthenium)

Ru[(R, R)-N-Ms-1,2-cyclohexanediamine](η^6 -mesitylene)((R, R)-N-methanesulfonyl-1,2-cyclohexanediamine)(η^6 -mesitylene)ruthenium)

Ru[(S, S)-N-Tf-1,2-cyclohexanediamine](η^6 -benzene)((S, S)-N-trifluoromethanesulfonyl-1,2-cyclohexanediamine)(η^6 -benzene)ruthenium)

Ru[(R, R)-N-Tf-1,2-cyclohexanediamine](η^6 -benzene)((R, R)-N-trifluoromethanesulfonyl-1,2-cyclohexanediamine)(η^6 -benzene)ruthenium)

Ru[(S, S)-N-Tf-1,2-cyclohexanediamine](η^6 -p-cymene)((S, S)-N-trifluoromethanesulfonyl-1,2-cyclohexanediamine)(η^6 -p-cymene)ruthenium)

Ru[(R, R)-N-Tf-1,2-cyclohexanediamine](η^6 -p-cymene)((R, R)-N-trifluoromethanesulfonyl-1,2-cyclohexanediamine)(η^6 -p-cymene)ruthenium)

Ru[(S, S)-N-Tf-1,2-cyclohexanediamine](η^6 -mesitylene)((S, S)-N-trifluoromethanesulfonyl-1,2-cyclohexanediamine)(η^6 -mesitylene)ruthenium)

Ru[(R, R)-N-Tf-1,2-cyclohexanediamine](η^6 -mesitylene)((R, R)-N-trifluoromethanesulfonyl-1,2-cyclohexanediamine)(η^6 -mesitylene)ruthenium)

$\text{Ru}[(S, S)\text{-N-C}_6\text{H}_5\text{SO}_2\text{-1,2-cyclohexanediamine}](\eta^6\text{-benzene})(((S, S)\text{-N-benzenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-benzene})\text{ruthenium})$

$\text{Ru}[(R, R)\text{-N-C}_6\text{H}_5\text{SO}_2\text{-1,2-cyclohexanediamine}](\eta^6\text{-benzene})(((R, R)\text{-N-benzenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-benzene})\text{ruthenium})$

$\text{Ru}[(S, S)\text{-N-C}_6\text{H}_5\text{SO}_2\text{-1,2-cyclohexanediamine}](\eta^6\text{-p-cymene})(((S, S)\text{-N-benzenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

$\text{Ru}[(R, R)\text{-N-C}_6\text{H}_5\text{SO}_2\text{-1,2-cyclohexanediamine}](\eta^6\text{-p-cymene})(((R, R)\text{-N-benzenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

$\text{Ru}[(S, S)\text{-N-C}_6\text{H}_5\text{SO}_2\text{-1,2-cyclohexanediamine}](\eta^6\text{-mesitylene})(((S, S)\text{-N-benzenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

$\text{Ru}[(R, R)\text{-N-C}_6\text{H}_5\text{SO}_2\text{-1,2-cyclohexanediamine}](\eta^6\text{-mesitylene})(((R, R)\text{-N-benzenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

Those of the formula (VII) wherein m and n are simultaneously 1 are illustrated as follows. Herein, η is used to represent the number of carbon atoms bonded to a metal in unsaturated ligands, and therefore, hexahapto (six carbon atoms bonded to metal) is represented by η^6 ; p-Ts represents p-toluenesulfonyl group; Ms represents methanesulfonyl group;

and Tf represents trifluoromethanesulfonyl group.

$\text{RuH}[(S, S)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-benzene})(\text{hydride-}((S, S)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-benzene})\text{ruthenium})$

$\text{RuH}[(R, R)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-benzene})(\text{hydride-}((R, R)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-benzene})\text{ruthenium})$

$\text{RuH}[(S, S)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-p-cymene})(\text{hydride-}((S, S)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

$\text{RuH}[(R, R)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-p-cymene})(\text{hydride-}((R, R)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

$\text{RuH}[(S, S)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-mesitylene})(\text{hydride-}((S, S)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

$\text{RuH}[(R, R)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-mesitylene})(\text{hydride-}((R, R)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

$\text{RuH}[(S, S)\text{-MsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-benzene})(\text{hydride-}((S, S)\text{-N-methanesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-benzene})\text{ruthenium})$

$\text{RuH}[(R, R)\text{-MsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-benzene})(\text{hydride-}((R, R)\text{-N-methanesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-benzene})\text{ruthenium})$

benzene)ruthenium)

$\text{RuH}[(S, S)\text{-MsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-p-cymene})(\text{hydride-}((S, S)\text{-N-methanesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

$\text{RuH}[(R, R)\text{-MsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-p-cymene})(\text{hydride-}((R, R)\text{-N-methanesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

$\text{RuH}[(S, S)\text{-MsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-mesitylene})(\text{hydride-}((S, S)\text{-N-methanesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

$\text{RuH}[(R, R)\text{-MsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-mesitylene})(\text{hydride-}((R, R)\text{-N-methanesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

$\text{RuH}[(S, S)\text{-TfNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-benzene})(\text{hydride-}((S, S)\text{-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-benzene})\text{ruthenium})$

$\text{RuH}[(R, R)\text{-TfNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-benzene})(\text{hydride-}((R, R)\text{-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-benzene})\text{ruthenium})$

$\text{RuH}[(S, S)\text{-TfNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-p-cymene})(\text{hydride-}((S, S)\text{-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

$\text{RuH}[(R, R)\text{-TfNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-p-cymene})(\text{hydride-}((R, R)\text{-N-trifluoromethanesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

$\text{RuH}[(S, S)\text{-TfNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-mesitylene})(\text{hydride-}((S, S)\text{-N-trifluoromethanesulfonyl-1,2-}$

$\text{diphenylethylenediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

$\text{RuH}[(R, R)\text{-TfNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-mesitylene})(\text{hydride-}((R, R)\text{-N-trifluoromethanesulfonyl-1,2-}$

$\text{diphenylethylenediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

$\text{RuH}[(S, S)\text{-C}_6\text{H}_5\text{SO}_2\text{NCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-benzene})(\text{hydride-}((S, S)\text{-N-benzenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-}$

$\text{benzene})\text{ruthenium})$

$\text{RuH}[(R, R)\text{-C}_6\text{H}_5\text{SO}_2\text{NCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-benzene})(\text{hydride-}((R, R)\text{-N-benzenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-}$

$\text{benzene})\text{ruthenium})$

$\text{RuH}[(S, S)\text{-C}_6\text{H}_5\text{SO}_2\text{NCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-p-cymene})(\text{hydride-}((S, S)\text{-N-trifluoromethanesulfonyl-1,2-}$

$\text{diphenylethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

$\text{RuH}[(R, R)\text{-C}_6\text{H}_5\text{SO}_2\text{NCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-p-cymene})(\text{hydride-}((R, R)\text{-N-trifluoromethanesulfonyl-1,2-}$

$\text{diphenylethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

$\text{RuH}[(S, S)\text{-C}_6\text{H}_5\text{SO}_2\text{NCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-mesitylene})(\text{hydride-}((S, S)\text{-N-benzenesulfonyl-1,2-}$

$\text{diphenylethylenediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

$\text{RuH}[(R, R)\text{-C}_6\text{H}_5\text{SO}_2\text{NCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-mesitylene})(\text{hydride-}((R, R)\text{-N-benzenesulfonyl-1,2-}$

$\text{diphenylethylenediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

$\text{RuH}[(S, S)\text{-N-p-Ts-1,2-cyclohexanediamine}](\eta^6\text{-}$

benzene)(hydride-((S, S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine)(η^6 -benzene)ruthenium)

RuH[(R, R)-N-p-Ts-1,2-cyclohexanediamine](η^6 -benzene)(hydride-((R, R)-N-p-toluenesulfonyl-1,2-cyclohexanediamine)(η^6 -benzene)ruthenium)

RuH[(S, S)-N-p-Ts-1,2-cyclohexanediamine](η^6 -p-cymene)(hydride-((S, S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine)(η^6 -p-cymene)ruthenium)

RuH[(R, R)-N-p-Ts-1,2-cyclohexanediamine](η^6 -p-cymene)(hydride-((R, R)-N-p-toluenesulfonyl-1,2-cyclohexanediamine)(η^6 -p-cymene)ruthenium)

RuH[(S, S)-N-p-Ts-1,2-cyclohexanediamine](η^6 -mesitylene)(hydride-((S, S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine)(η^6 -mesitylene)ruthenium)

RuH[(R, R)-N-p-Ts-1,2-cyclohexanediamine](η^6 -mesitylene)(hydride-((R, R)-N-p-toluenesulfonyl-1,2-cyclohexanediamine)(η^6 -mesitylene)ruthenium)

RuH[(S, S)-N-Ms-1,2-cyclohexanediamine](η^6 -benzene)(hydride-((S, S)-N-methanesulfonyl-1,2-cyclohexanediamine)(η^6 -benzene)ruthenium)

RuH[(R, R)-N-Ms-1,2-cyclohexanediamine](η^6 -benzene)(hydride-((R, R)-N-methanesulfonyl-1,2-cyclohexanediamine)(η^6 -benzene)ruthenium)

RuH[(S, S)-N-Ms-1,2-cyclohexanediamine](η^6 -p-cymene)(hydride-((S, S)-N-methanesulfonyl-1,2-

cyclohexanediamine)(η^6 -p-cymene)ruthenium)

RuH[(R, R)-N-Ms-1,2-cyclohexanediamine](η^6 -p-cymene)(hydride-((R, R)-N-methanesulfonyl-1,2-cyclohexanediamine)(η^6 -p-cymene)ruthenium)

RuH[(S, S)-N-Ms-1,2-cyclohexanediamine](η^6 -mesitylene)(hydride-((S, S)-N-methanesulfonyl-1,2-cyclohexanediamine)(η^6 -mesitylene)ruthenium)

RuH[(R, R)-N-Ms-1,2-cyclohexanediamine](η^6 -mesitylene)(hydride-((R, R)-N-methanesulfonyl-1,2-cyclohexanediamine)(η^6 -mesitylene)ruthenium)

RuH[(S, S)-N-Tf-1,2-cyclohexanediamine](η^6 -benzene)(hydride-((S, S)-N-trifluoromethanesulfonyl-1,2-cyclohexanediamine)(η^6 -benzene)ruthenium)

RuH[(R, R)-N-Tf-1,2-cyclohexanediamine](η^6 -benzene)(hydride-((R, R)-N-trifluoromethanesulfonyl-1,2-cyclohexanediamine)(η^6 -benzene)ruthenium)

RuH[(S, S)-N-Tf-1,2-cyclohexanediamine](η^6 -p-cymene)(hydride-((S, S)-N-trifluoromethanesulfonyl-1,2-cyclohexanediamine)(η^6 -p-cymene)ruthenium)

RuH[(R, R)-N-Tf-1,2-cyclohexanediamine](η^6 -p-cymene)(hydride-((R, R)-N-trifluoromethanesulfonyl-1,2-cyclohexanediamine)(η^6 -p-cymene)ruthenium)

RuH[(S, S)-N-Tf-1,2-cyclohexanediamine](η^6 -mesitylene)(hydride-((S, S)-N-trifluoromethanesulfonyl-1,2-cyclohexanediamine)(η^6 -mesitylene)ruthenium)

$\text{RuH}[(R, R)\text{-N-Tf-1,2-cyclohexanediamine}](\eta^6\text{-mesitylene})(\text{hydride-}((R, R)\text{-N-trifluoromethanesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

$\text{RuH}[(S, S)\text{-N- C}_6\text{H}_5\text{SO}_2\text{-1,2-cyclohexanediamine}](\eta^6\text{-benzene})(\text{hydride-}((S, S)\text{-N-benzenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-benzene})\text{ruthenium})$

$\text{RuH}[(R, R)\text{-N- C}_6\text{H}_5\text{SO}_2\text{-1,2-cyclohexanediamine}](\eta^6\text{-benzene})(\text{hydride-}((R, R)\text{-N-benzenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-benzene})\text{ruthenium})$

$\text{RuH}[(S, S)\text{-N- C}_6\text{H}_5\text{SO}_2\text{-1,2-cyclohexanediamine}](\eta^6\text{-p-cymene})(\text{hydride-}((S, S)\text{-N-benzenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

$\text{RuH}[(R, R)\text{-N- C}_6\text{H}_5\text{SO}_2\text{-1,2-cyclohexanediamine}](\eta^6\text{-p-cymene})(\text{hydride-}((R, R)\text{-N-benzenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

$\text{RuH}[(S, S)\text{-N- C}_6\text{H}_5\text{SO}_2\text{-1,2-cyclohexanediamine}](\eta^6\text{-mesitylene})(\text{hydride-}((S, S)\text{-N-benzenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

$\text{RuH}[(R, R)\text{-N- C}_6\text{H}_5\text{SO}_2\text{-1,2-cyclohexanediamine}](\eta^6\text{-mesitylene})(\text{hydride-}((R, R)\text{-N-benzenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

Among the compounds represented by the general formula (VII) in accordance with the present invention, the complex of the formula (VII) wherein m and n are simultaneously 0 can be

produced as follows. More specifically,
 $\text{Ru}[(\text{S}, \text{S})-, (\text{R}, \text{R})-\text{TsNCH}(\text{R}^{01})\text{CH}(\text{R}^{02})\text{NH}](\eta^6\text{-p-cymene})-$
 $(((\text{S}, \text{S}) \text{ and } (\text{R}, \text{R})\text{-N-toluenesulfonyl-1,2-disubstituted}$
 $\text{ethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium (wherein } \text{R}^{01} \text{ and } \text{R}^{02}$
 $\text{are the same as described above and Ts is p-toluenesulfonyl}$
 $\text{group), is readily synthesized by reacting a raw}$
 $\text{material } [\text{RuCl}_2(\eta^6\text{-p-cymene})]_2(\text{tetrachlorobis}(\eta^6\text{-p-}$
 $\text{cymene})\text{diruthenium) prepared by the method described in a}$
 $\text{reference J. Chem. Soc., Dalton Trans., pp.233 - 241(1974)}$
 $\text{with } (\text{S}, \text{S})-, (\text{R}, \text{R})\text{-TsNHCH}(\text{R}^{01})\text{CH}(\text{R}^{02})\text{NH}_2((\text{S}, \text{S}) \text{ and}$
 $(\text{R}, \text{R})\text{-N-p-toluenesulfonyl-1,2-disubstituted ethylenedia-}$
 $\text{mine) in the presence of alkali metal hydroxide or alkali}$
 $\text{metal alcolate in a solvent.}$

The reaction is generally carried out quantitatively,
 by reacting a raw material $[\text{RuCl}_2(\eta^6\text{-p-cymene})]_2$
 $(\text{tetrachlorobis}(\eta^6\text{-p-cymene})\text{diruthenium (1 mole) and } (\text{S},$
 $\text{S})-, (\text{R}, \text{R})\text{-TsNHCH}(\text{R}^{01})\text{CH}(\text{R}^{02})\text{NH}_2((\text{S}, \text{S}) \text{ and } (\text{R}, \text{R})\text{-N-p-}$
 $\text{toluenesulfonyl-1,2-disubstituted ethylenediamine})(2 \text{ moles})$
 with alkali metal hydroxide or alkali metal alcolate in the
 stream of inactive gases such nitrogen, helium or argon in
 an inactive solvent at a temperature of -10 to 50°C for 30
 minutes to 3 hours, and leaving the reaction product to
 stand alone, prior to liquid separation procedure to remove
 the aqueous phase, and subsequently removing the solvent
 under reduced pressure.

The alkali metal hydroxide or alkali metal alcolate specifically includes NaOH, NaOCH₃, NaOC₂H₅, KOH, KOCH₃, KOC₂H₅, LiOH, LiOCH₃, and LiOC₂H₅, preferably including NaOH or KOH. The amount of the alkali metal hydroxide or alkali metal alcolate is 5 to 10 fold the amount of ruthenium. The inactive solvent appropriately includes for example hydrocarbons such as benzene, toluene, xylene, cyclohexane, and methylcyclohexane; ethers such as dimethyl ether, diethyl ether, diisopropyl ether, methyl tert-butyl ether, tetrahydrofuran, 1,3-dioxolane, and 1,4-dioxane; halogenated hydrocarbons such as chloroform, methylene chloride and chlorobenzene.

The complex can be produced by another method. Specifically,

$$\text{Ru}[(S, S)-, (R, R)\text{-TsNCH(R}^{01}\text{)CH(R}^{02}\text{)NH}](\eta^6\text{-p-cymene})(((S, S) \text{ and } (R, R)\text{-N-toluenesulfonyl-1,2-disubstituted ethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium (wherein R}^{01}\text{ and R}^{02}\text{ are the same as described above and Ts is p-toluenesulfonyl group),}$$

 is readily synthesized by reacting a raw material

$$\text{RuCl}[(S, S)-, (R, R)\text{-TsNCH(R}^{01}\text{)CH(R}^{02}\text{)NH}_2](\eta^6\text{-p-cymene})(\text{chloro-}((S, S) \text{ and } (R, R)\text{-N-p-toluenesulfonyl-1,2-disubstituted ethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium prepared through the reaction of } [\text{RuCl}_2(\eta^6\text{-p-cymene})_2(\text{tetrachlorobis}(\eta^6\text{-p-cymene})\text{diruthenium, } (S, S)-, (R, R)\text{-TsNHCH(R}^{01}\text{)CH(R}^{02}\text{)NH}_2((S, S) \text{ and } (R, R)\text{-N-p-toluenesulfonyl-1,2-disubstituted ethylenediamine) with a tertiary}$$

amine (for example, triethylamine) for example by the method described in J. Am. Chem. Soc., Vol.117, pp.7562-7563 (1995), J. Am. Chem. Soc., Vol.118, pp.2521-2522 (1996) and J. Am. Chem. Soc., Vol.118, pp.4916-4917 (1996), in the presence of alkali metal hydroxide or alkali metal alcolate in a solvent.

The reaction is generally carried out quantitatively, by reacting a raw material $\text{RuCl}[(\text{S}, \text{S})-, (\text{R}, \text{R})-\text{TsNCH}(\text{R}^{01})\text{CH}(\text{R}^{02})\text{NH}_2](\eta^6\text{-p-cymene})(\text{chloro-}((\text{S}, \text{S}) \text{ and } (\text{R}, \text{R})\text{-N-p-toluenesulfonyl-1,2-disubstituted ethylenedi-amine})(\eta^6\text{-p-cymene})\text{ruthenium})$ (1 mole) with alkali metal hydroxide or alkali metal alcolate in the stream of inactive gases such nitrogen, helium or argon in an inactive solvent at a temperature of -10 to 50°C for 30 minutes to 3 hours, and leaving the reaction product to stand alone, prior to liquid separation procedure to remove the aqueous phase, and subsequently removing the solvent under reduced pressure.

The alkali metal hydroxide or alkali metal alcolate specifically includes NaOH, NaOCH₃, NaOC₂H₅, KOH, KOCH₃, KOC₂H₅, LiOH, LiOCH₃, and LiOC₂H₅, preferably including NaOH or KOH. The amount of the alkali metal hydroxide or alkali metal alcolate is 1 to 2-fold in mole the amount of ruthenium. The inactive solvent appropriately includes for example hydrocarbons such as benzene, toluene, xylene, cyclohexane, and methylcyclohexane; ethers such as dimethyl ether, diethyl ether, diisopropyl ether, methyl tert-butyl

ether, tetrahydrofuran, 1,3-dioxolane, and 1,4-dioxane; and halogenated hydrocarbons such as chloroform, methylene chloride and chlorobenzene.

In accordance with the present invention, the complex represented by the general formula (V) wherein m and n are simultaneously 1 can be produced as follows. More specifically,

$\text{RuH}[(\text{S}, \text{S})-, (\text{R}, \text{R})-\text{TsNCH}(\text{R}^{01})\text{CH}(\text{R}^{02})\text{NH}_2](\eta^6\text{-p-cymene})$ -
(hydride-((S, S) and (R, R)-N-toluenesulfonyl-1,2-disubstituted ethylenediamine)(η^6 -p-cymene)ruthenium) (wherein R^{01} and R^{02} are the same as described above and Ts is p-toluenesulfonyl group), is readily synthesized, by reacting a raw material $\text{Ru}[(\text{S}, \text{S})-, (\text{R}, \text{R})-\text{TsNCH}(\text{R}^{01})\text{CH}(\text{R}^{02})\text{NH}](\eta^6\text{-p-cymene})$ (((S, S) and (R, R)-N-toluenesulfonyl-1,2-disubstituted ethylenediamine) (η^6 -p-cymene) ruthenium) (wherein R^{01} and R^{02} are the same as defined above; and Ts represents p-toluenesulfonyl group) in an alcohol solvent.

The reaction is generally carried out quantitatively, by reacting a raw material $\text{Ru}[(\text{S}, \text{S})-, (\text{R}, \text{R})-\text{TsNCH}(\text{R}^{01})\text{CH}(\text{R}^{02})\text{NH}](\eta^6\text{-p-cymene})$ (((S, S) and (R, R)-N-toluenesulfonyl-1,2-disubstituted ethylenediamine) (η^6 -p-cymene)ruthenium)(wherein R^{01} and R^{02} are the same as defined above; and Ts represents p-toluenesulfonyl group) in an inactive gas stream in an alcohol solvent at a temperature of 0 to 100°C for 3 minutes to 1 hour for hydrogen transfer reaction, and subsequently removing the

solvent under reduced pressure. Appropriate alcohol solvents include for example methanol, ethanol, n-propanol, isopropanol, n-butanol, iso-butanol, and sec-butanol.

The complex can be produced by another method. Specifically,

$\text{RuH}[(\text{S}, \text{S})-, (\text{R}, \text{R})-\text{TsNCH}(\text{R}^{01})\text{CH}(\text{R}^{02})\text{NH}_2](\eta^6\text{-p-cymene})-(\text{hydride}-((\text{S}, \text{S}) \text{ and } (\text{R}, \text{R})-\text{N-p-toluenesulfonyl-1,2-disubstituted ethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$ (wherein R^{01} and R^{02} are the same as described above and Ts is p-toluenesulfonyl group), is readily synthesized, by reacting for example a raw material $\text{Ru}[(\text{S}, \text{S})-, (\text{R}, \text{R})-\text{TsNCH}(\text{R}^{01})\text{CH}(\text{R}^{02})\text{NH}](\eta^6\text{-p-cymene})(((\text{S}, \text{S}) \text{ and } (\text{R}, \text{R})-\text{N-toluenesulfonyl-1,2-disubstituted ethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$ (wherein R^{01} and R^{02} are the same as defined above; and Ts represents p-toluenesulfonyl group), in a solvent in pressurized hydrogen.

The reaction is generally carried out quantitatively, by hydrogenating a raw material $\text{RuH}[(\text{S}, \text{S})-, (\text{R}, \text{R})-\text{TsNCH}(\text{R}^{01})\text{CH}(\text{R}^{02})\text{NH}_2](\eta^6\text{-p-cymene})(\text{hydride}-((\text{S}, \text{S}) \text{ and } (\text{R}, \text{R})-\text{N-toluenesulfonyl-1,2-disubstituted ethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$ (wherein R^{01} and R^{02} are the same as defined above; and Ts represents p-toluenesulfonyl group), in an inactive solvent at a temperature of 0 to 50°C for 30 minutes to 24 hours (preferably 1 to 10 hours) in pressurized hydrogen and subsequently removing the solvent

under reduced pressure. The hydrogen pressure is within a range of 1 to 150 atm, preferably 20 to 100 atm.

Appropriate inactive solvents include for example hydrocarbons such as benzene, toluene, xylene, hexane, heptane, cyclohexane, and methylcyclohexane; and ethers such as dimethyl ether, diethyl ether, diisopropyl ether, methyl-tert-butyl ether, tetrahydrofuran, 1,3-dioxolane and 1,4-dioxane.

An optically active diamine of the formula (S, S)-, (R, R)- $R^{03}NHCH(R^{01})CH(R^{02})NH_2$ ((S, S) and (R, R)-N-substituted-1,2-disubstituted ethylenediamines) (wherein R^{01} , R^{02} and R^{03} are the same as described above) is synthesized, by using raw materials (S, S)-, (R, R)- $NH_2CH(R^{01})CH(R^{02})NH_2$ ((S, S) and (R, R)-1,2-disubstituted ethylenediamines in a conventional manner [Protective Groups in Organic Synthesis, Vol.2, pp.309-405(1991)]. More specifically, (S, S)-, (R, R)-TsNHCH(R^{01})CH(R^{02})NH₂((S, S) and (R, R)-N-P-toluenesulfonyl-1,2-disubstituted ethylenediamines) (wherein R^{01} and R^{02} are the same as defined above; and Ts represents p-toluenesulfonyl group) are readily synthesized, by reacting for example (S, S)-, (R, R)- $NH_2CH(R^{01})CH(R^{02})NH_2$ ((S, S) and (R, R)-1,2-disubstituted ethylenediamines) as raw materials with TsCl (p-toluenesulfonyl chloride) in the presence of an alkali (for example, tertiary amine, alkali metal salts and the like) in a solvent.

The reaction is generally carried out quantitatively, by reacting together

(S, S)-, (R, R)-NH₂CH(R⁰¹)CH(R⁰²)NH₂((S, S) and (R, R)-1,2-disubstituted ethylenediamines) (1 mole) and TsCl (p-toluenesulfonyl chloride) (1 mole) with an alkali (for example, triethylamine) in an inactive solvent (for example, toluene, tetrahydrofuran, and methylene chloride) in an inactive gas stream such as nitrogen, helium or argon or the like at a temperature of 0 to 50 for 30 minutes to 3 hours, subsequently adding water to the resulting mixture to gently leave the reaction product to stand, prior to liquid separation procedure, to remove the aqueous phase, and evaporating the solvent under reduced pressure.

The optically active diamine (S, S)-, (R, R)-NH₂CH(R⁰¹)CH(R⁰²)NH₂((S, S) and (R, R)-1,2-disubstituted ethylenediamines)(wherein R⁰¹ and R⁰² are the same as defined above), is known and is sometimes commercially available or can be produced in a conventional manner or by conventional resolution process of racemates [Tetrahedron Lett., Vol.32, pp.999-1002) (1991), Tetrahedron Lett., Vol.34, pp.1905-1908 (1993)].

(S, S) and (R, R)- 1,2-diphenylethylenediamines and (S, S) and (R, R)- 1,2-cyclohexanediamines are commercially available.

For example, the optically active diamine of the general formula (e) can be produced by the following method [Tetrahedron

Lett., Vol.32, pp.999-1002 (1991)].

The optically active diamine of the general formula (e) ((S, S) and (R, R)-1,2-disubstituted ethylenediamines) can be produced readily at a high yield, by preparing cyclophosphate from raw materials optically active 1,2-disubstituted ethylene diols, which is then reacted with amidine to recover imidazoline, and ring opening the imidazoline by using an acid catalyst.

The ruthenium-diamine complex of the present invention may be isolated and used, but while generating the complex in a reaction solution, the resulting complex is used as a catalyst for asymmetric synthesis and the like.

The method for producing optically active secondary alcohols by utilizing the complex of the present invention as a hydrogen transfer-type oxidation catalyst will now be described below.

The racemic secondary alcohols or meso-type diols to be used as the reaction substrates for producing optically active secondary alcohols are represented by the aforementioned formulas (VIII) and (IXI). In the formula (VIII), the racemic secondary alcohols in this case specifically include 1-phenylethanol, 1-(2-methylphenyl)ethanol, 1-(2-ethylphenyl)ethanol, 1-(2-isopropylphenyl)ethanol, 1-(2-tert-butylphenyl)ethanol, 1-(2-methoxyphenyl)ethanol, 1-(2-ethoxyphenyl)ethanol, 1-(2-isopropoxyphenyl)ethanol, 1-(2-tert-butoxyphenyl)ethanol, 1-(2-dimethylaminophenyl)ethanol,

1-(3-methylphenyl)ethanol, 1-(3-ethylphenyl)-ethanol, 1-(3-isopropylphenyl)ethanol, 1-(3-tert-butylphenyl)ethanol, 1-(3-methoxyphenyl)ethanol, 1-(3-ethoxyphenyl)ethanol, 1-(3-isopropoxyphenyl)ethanol, 1-(3-tert-butoxyphenyl)ethanol, 1-(3-dimethylaminophenyl)-ethanol, 1-(4-methylphenyl)ethanol, 1-(4-ethylphenyl)-ethanol, 1-(4-isopropylphenyl)ethanol, 1-(4-tert-butyl-phenyl)ethanol, 1-(4-methoxyphenyl)ethanol, 1-(4-ethoxy-phenyl)ethanol, 1-(4-isopropoxyphenyl)ethanol, 1-(4-tert-butoxyphenyl)ethanol, 1-(4-dimethylaminophenyl)-ethanol, 1-cumenylethanol, 1-mesitylethanol, 1-xylylethanol, 1-(1-naphthyl)ethanol, 1-(2-naphthyl)ethanol, 1-phenanthrylethanol, 1-indenylethanol, 1-(3,4-dimethoxyphenyl)ethanol, 1-(3,4-diethoxyphenyl)ethanol, 1-(3,4-methylenedioxy-phenyl)ethanol, 1-ferrocenylethanol, 1-phenylpropanol, 1-(2-methylphenyl)propanol, 1-(2-ethylphenyl)propanol, 1-(2-isopropylphenyl)propanol, 1-(2-tert-butylphenyl)propanol, 1-(2-methoxyphenyl)propanol, 1-(2-ethoxyphenyl)propanol, 1-(2-isopropoxyphenyl)propanol, 1-(2-tert-butoxyphenyl)-propanol, 1-(2-dimethylaminophenyl)propanol, 1-(3-methylphenyl)-propanol, 1-(3-ethylphenyl)propanol, 1-(3-isopropyl-phenyl)propanol, 1-(3-tert-butylphenyl)propanol, 1-(3-methoxyphenyl)propanol, 1-(3-ethoxyphenyl)propanol, 1-(3-isopropoxyphenyl)propanol, 1-(3-tert-butoxyphenyl)-propanol, 1-(3-dimethylaminophenyl)propanol, 1-(4-methylphenyl)propanol, 1-(4-ethylphenyl)propanol, 1-(4-isopropylphenyl)propanol, 1-(4-tert-butylphenyl)propanol, 1-

(4-methoxyphenyl)propanol, 1-(4-ethoxyphenyl)propanol, 1-(4-isopropoxyphenyl)propanol, 1-(4-tert-butoxyphenyl)-propanol, 1-(4-dimethylaminophenyl)propanol, 1-cumenyl-propanol, 1-mesitylpropanol, 1-xylylpropanol, 1-(1-naphthyl) propanol, 1-(2-naphthyl)propanol, 1-phenanthryl-propanol, 1-indenylpropanol, 1-(3,4-dimethoxyphenyl) propanol, 1-(3,4-diethoxyphenyl) propanol, 1-(3,4-methyl-enedioxyphenyl) propanol, 1-ferrocenylpropanol, 1-phenyl-butanol, 1-(2-methylphenyl)butanol, 1-(2-ethylphenyl)-butanol, 1-(2-isopropylphenyl)butanol, 1-(2-tert-butyl-phenyl)butanol, 1-(2-methoxyphenyl)butanol, 1-(2-ethoxy-phenyl)butanol, 1-(2-isopropoxyphenyl)butanol, 1-(2-tert-butoxyphenyl)butanol, 1-(2-dimethylaminophenyl)butanol, 1-(3-methylphenyl)butanol, 1-(3-ethylphenyl)butanol, 1-(3-isopropylphenyl)butanol, 1-(3-tert-butylphenyl)butanol, 1-(3-methoxyphenyl)butanol, 1-(3-ethoxyphenyl)butanol, 1-(3-isopropoxyphenyl)butanol, 1-(3-tert-butoxyphenyl)butanol, 1-(3-dimethylamino-phenyl)butanol, 1-(4-methylphenyl)-butanol, 1-(4-ethylphenyl)butanol, 1-(4-isopropylphenyl)-butanol, 1-(4-tert-butylphenyl)butanol, 1-(4-methoxy-phenyl)butanol, 1-(4-ethoxyphenyl)butanol, 1-(4-isopropoxy-phenyl)butanol, 1-(4-tert-butoxyphenyl)butanol, 1-(4-dimethylaminophenyl)butanol, 1-cumenylbutanol, 1-mesityl-butanol, 1-xylylbutanol, 1-(1-naphthyl)butanol, 1-(2-naphthyl)butanol, 1-phenanthrylbutanol, 1-indenylbutanol, 1-(3,4-dimethoxyphenyl)butanol, 1-(3,4-diethoxyphenyl)-butanol, 1-

(3,4-methylenedioxyphenyl)butanol, 1-ferrocenyl-butanol, 1-phenylisobutanol, 1-(2-methylphenyl)isobutanol, 1-(2-ethylphenyl)isobutanol, 1-(2-isopropylphenyl)-isobutanol, 1-(2-tert-butylphenyl)isobutanol, 1-(2-methoxyphenyl)isobutanol, 1-(2-ethoxyphenyl)isobutanol, 1-(2-isopropoxyphenyl)isobutanol, 1-(2-tert-butoxyphenyl)-isobutanol, 1-(2-dimethylaminophenyl)isobutanol, 1-(3-methylphenyl)isobutanol, 1-(3-ethylphenyl)isobutanol, 1-(3-isopropylphenyl)isobutanol, 1-(3-tert-butylphenyl)-isobutanol, 1-(3-methoxyphenyl)isobutanol, 1-(3-ethoxyphenyl)isobutanol, 1-(3-isopropoxyphenyl)isobutanol, 1-(3-tert-butoxyphenyl)isobutanol, 1-(3-dimethylaminophenyl)-isobutanol, 1-(4-methylphenyl)isobutanol, 1-(4-ethylphenyl)isobutanol, 1-(4-isopropylphenyl)isobutanol, 1-(4-tert-butylphenyl)isobutanol, 1-(4-methoxyphenyl)isobutanol, 1-(4-ethoxyphenyl)isobutanol, 1-(4-isopropoxyphenyl)-isobutanol, 1-(4-tert-butoxyphenyl)isobutanol, 1-(4-dimethylaminophenyl)isobutanol, 1-cumenylisobutanol, 1-mesitylisobutanol, 1-xylylisobutanol, 1-(1-naphthyl)isobutanol, 1-(2-naphthyl)isobutanol, 1-phenanthrylisobutanol, 1-indenylisobutanol, 1-(3,4-dimethoxyphenyl)isobutanol, 1-(3,4-diethoxyphenyl)isobutanol, 1-(3,4-methylenedioxyphenyl)isobutanol, 1-ferrocenylisobutanol, 1-phenylpentanol, 1-(2-methylphenyl)pentanol, 1-(2-ethylphenyl)-pentanol, 1-(2-isopropylphenyl)pentanol, 1-(2-tert-butylphenyl)pentanol, 1-(2-methoxyphenyl)pentanol, 1-(2-ethoxy-

phenyl)pentanol, 1-(2-isopropoxyphenyl)pentanol, 1-(2-tert-butoxyphenyl)pentanol, 1-(2-dimethylaminophenyl)pentanol, 1-(3-methylphenyl)pentanol, 1-(3-ethylphenyl)pentanol, 1-(3-isopropylphenyl)pentanol, 1-(3-tert-butylphenyl)-pentanol, 1-(3-methoxyphenyl)pentanol, 1-(3-ethoxyphenyl)-pentanol, 1-(3-isopropoxyphenyl)pentanol, 1-(3-tert-butoxyphenyl)pentanol, 1-(3-dimethylaminophenyl)pentanol, 1-(4-methylphenyl)pentanol, 1-(4-ethylphenyl)pentanol, 1-(4-isopropylphenyl)pentanol, 1-(4-tert-butylphenyl)pentanol, 1-(4-methoxyphenyl)pentanol, 1-(4-ethoxyphenyl)pentanol, 1-(4-isopropoxyphenyl)pentanol, 1-(4-tert-butoxyphenyl)-pentanol, 1-(4-dimethylaminophenyl)pentanol, 1-cumenyl-pentanol, 1-mesitylpentanol, 1-xylylpentanol, 1-(1-naphthyl)pentanol, 1-(2-naphthyl)pentanol, 1-phenanthrylpentanol, 1-

indenylpentanol, 1-(3,4-dimethoxyphenyl)pentanol, 1-(3,4-diethoxyphenyl)pentanol, 1-(3,4-methylenedioxyphenyl)pentanol, 1-ferrocenylpentanol, 1-indanol, 1, 2, 3,4-tetrahydro-1-naphthol, 2-cyclopenten-1-ol, 3-methyl-2-cyclopenten-1-ol, 2-cyclohexen-1-ol, 3-methyl-2-cyclohexen-1-ol, 2-cycloheptan-1-ol, 3-methyl-2-cycloheptan-1-ol, 2-cyclooctan-1-ol, 3-methyl-2-cyclooctan-1-ol, and 4-hydroxy-2-cyclopenten-1-one. Additionally, the meso-type diol represented by the formula (IX) specifically represents meso-2-cyclopenten-1,4-diol, meso-2-cyclohexane-1,4-diol, meso-2-cycloheptane-1,4-diol, meso-2-cyclooctan-1,4-diol, 5,8-dihydroxy-1,4,4a, 5, 8, 8a-hexahydro-endo-1,4-methanonaphtharene and the like.

As the ruthenium-diamine complex to be used for the hydrogen transfer-type oxidation of the present invention, the optically active ligand diamine of the general formula (VII), namely (R, R) form or (S, S) form, may satisfactorily be used. Depending on the selection, an objective compound of the desired absolute configuration can be produced. Such ruthenium-diamine complex can be used at 1/10,000 to 1/10 fold in mole, preferably 1/2,000 to 1/200 fold in mole to the substrate compound.

For carrying out the reaction, the substrate compound and the ruthenium-diamine complex are added to ketone alone or an appropriate mixture of ketone with an inactive solvent, to prepare a homogenous solution, for reaction at a reaction

temperature of 0 to 100°C , preferably 10 to 50°C for 1 to 100 hours, preferably 3 to 50 hours.

Ketones including for example acetone, methyl ethyl ketone, diethyl ketone, diisopropyl ketone, methyl tert-butyl ketone, cyclopentanone, and cyclohexanone are used. More preferably, acetone is better. These ketones may satisfactorily be used singly or in a mixture with an inactive solvent. Ketones can be used at an amount of 0.1 to 30 fold (volume/weight), depending on the type of the substrate, but preferably at an amount of 2 to 5 fold (volume/weight).

Appropriate inactive solvents include for example hydrocarbons such as benzene, toluene, xylene, hexane, heptane, cyclohexane, and methylcyclohexane; and ethers such as dimethyl ether, diethyl ether, diisopropyl ether, methyl tert-butyl ether, tetrahydrofuran, 1,3-dioxolane, and 1,4-dioxane.

In accordance with the present invention, the reaction may be carried out in a batchwise manner or a continuous manner.

The resulting product can be purified by known processes such as silica gel column chromatography.

EXAMPLES

Example A

<Production of optically active alcohols>

Production examples of optically active alcohols are shown below, and the inventive method will further be described in detail. Tables 1, 2 and 3 collectively show reaction substrates, transition metal complexes and optically active amine compounds as chiral ligands, which are to be used as typical examples.

The instrumental analysis was done by using the following individual systems.

NMR: JEOL GSX-400/Varian Gemini-200 (¹H-NMR sample: TMS, ³¹P-NMR standard sample: phosphoric acid)

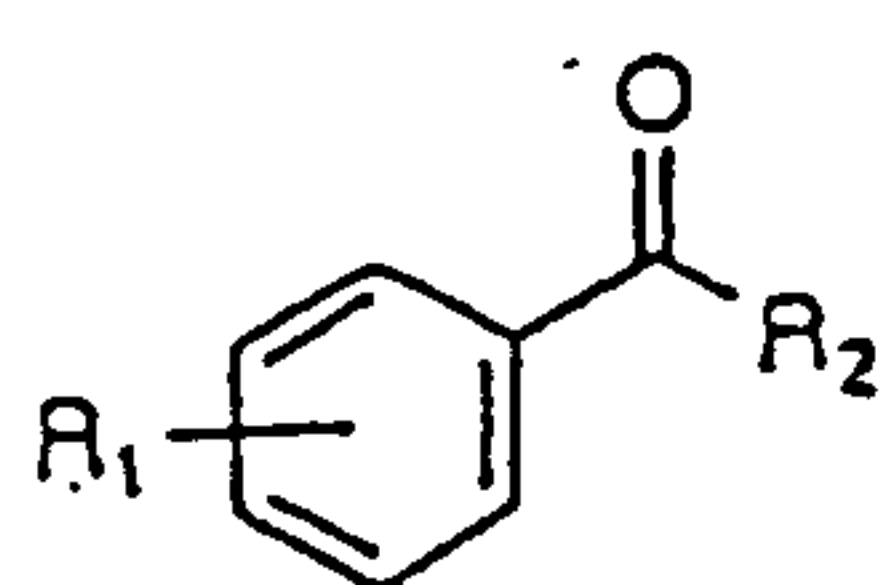
GLC: SHIMADZU GC-17A(column: chiral CP-Cyclodextrin-b-236-M19)

HPLC: JASCO GULLIVER (column: CHIRALCEL* OJ, OB-H, OB, OD)

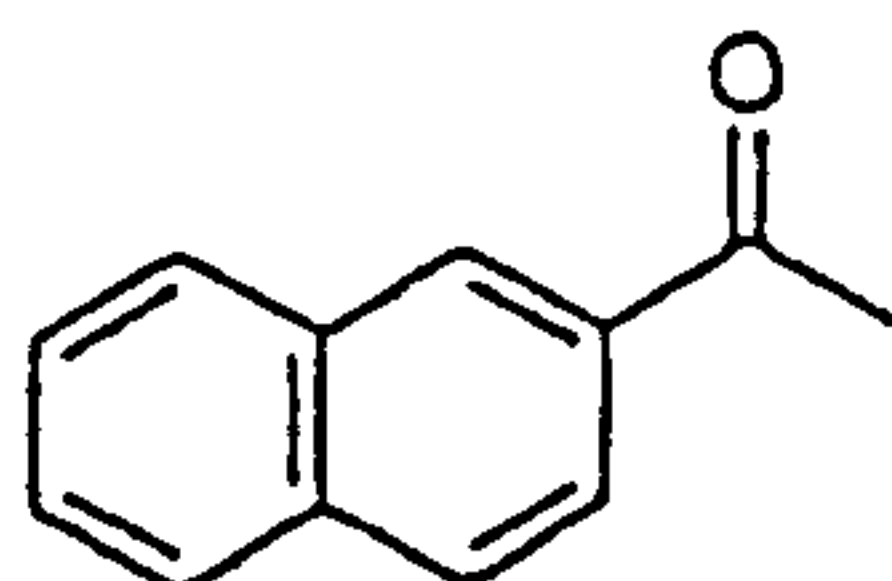
* Trade-mark

Table 1

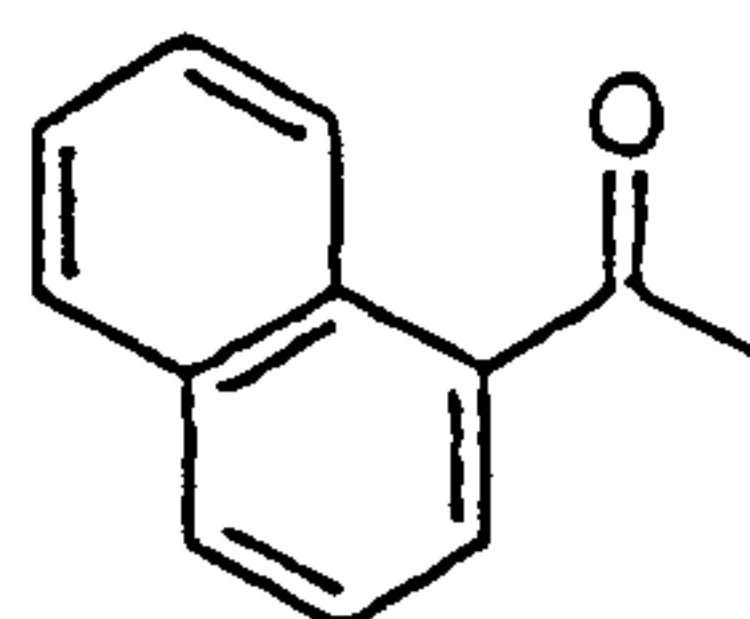
Carbonyl compounds



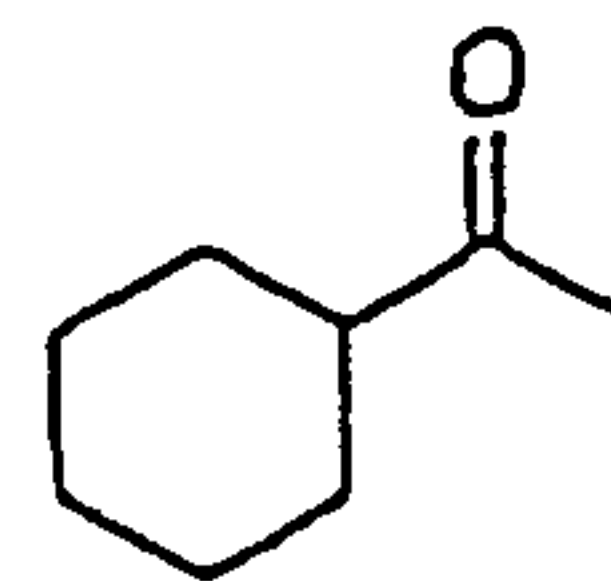
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2

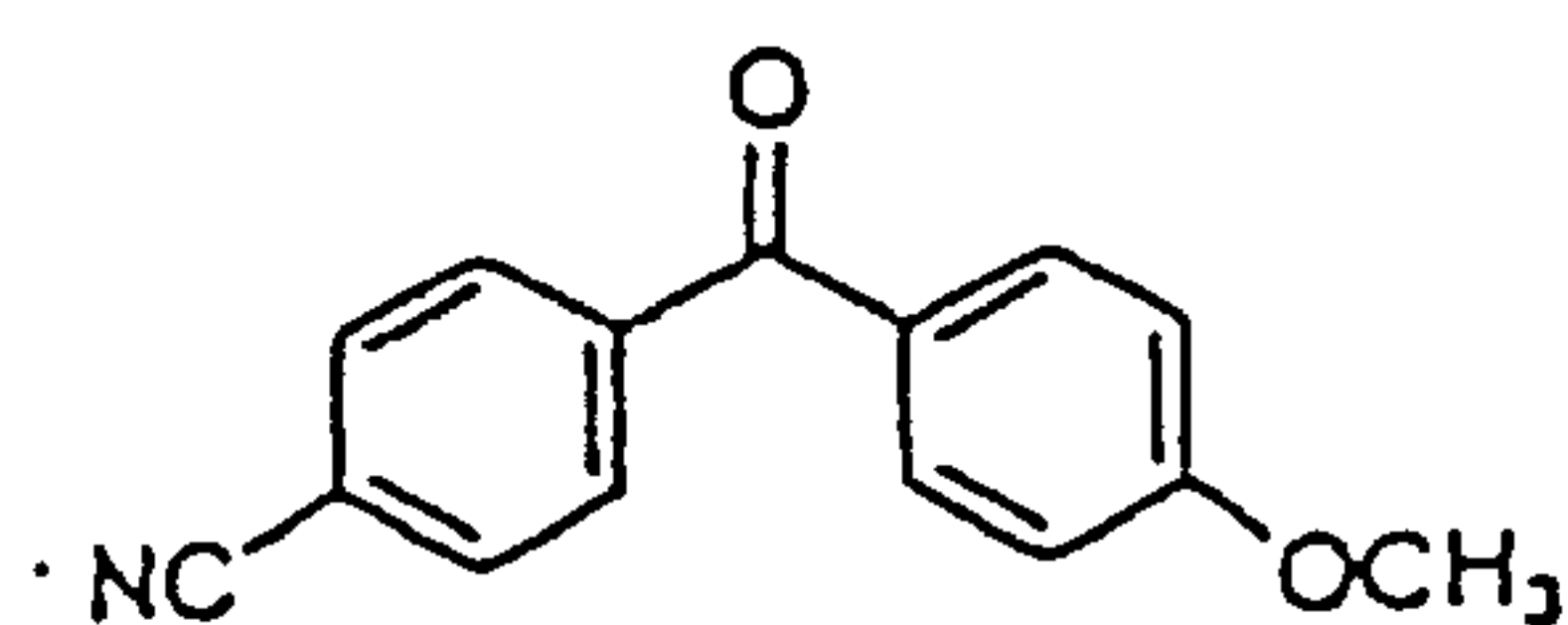


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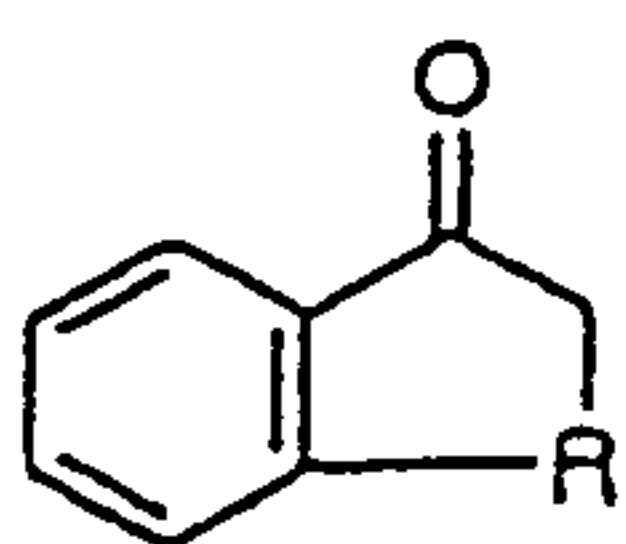


4

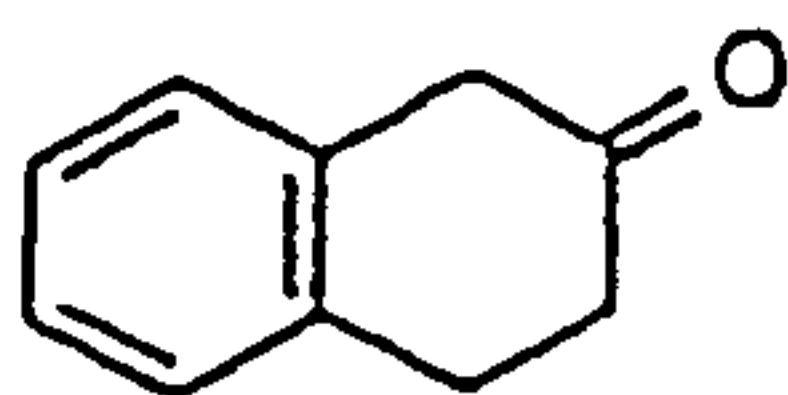
- a $R_1 = H, R_2 = CH_3$
 b $R_1 = H, R_2 = C_2H_5$
 c $R_1 = H, R_2 = CH(CH_3)_2$
 d $R_1 = H, R_2 = C(CH_3)_3$
 e $R_1 = CH_3, R_2 = CH_3$
 f $R_1 = Cl, R_2 = CH_3$
 g $R_1 = OCH_3, R_2 = CH_3$
 h $R_1 = CN, R_2 = CH_3$
 i $R_1 = H, R_2 = (CH_2)_3CO_2C_2H_5$



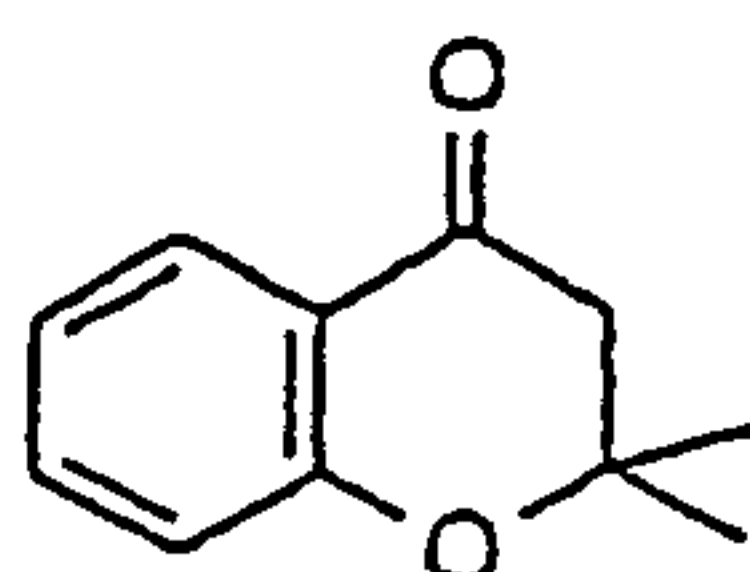
5



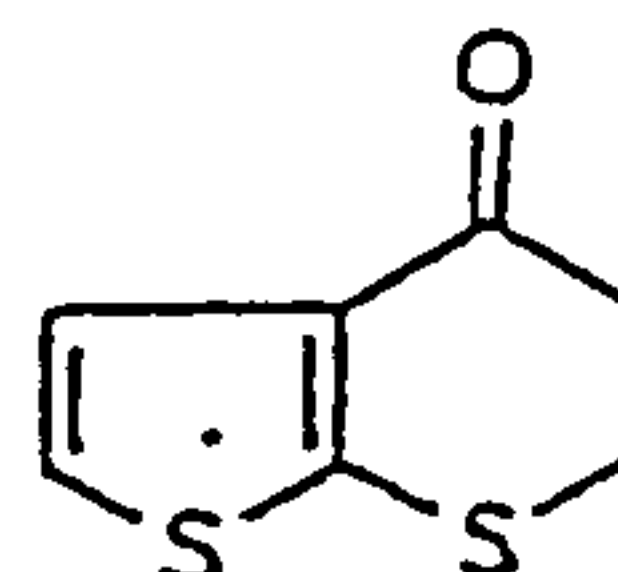
- 6 $R = CH_2$
 7 $R = (CH_2)_2$



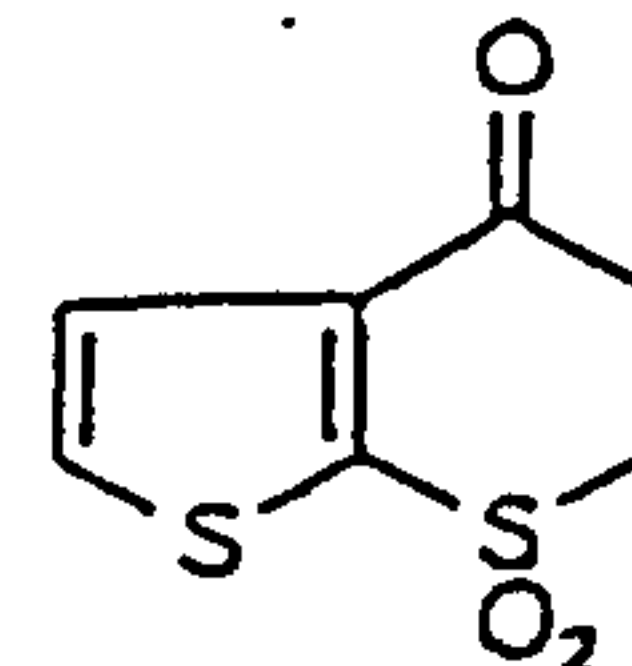
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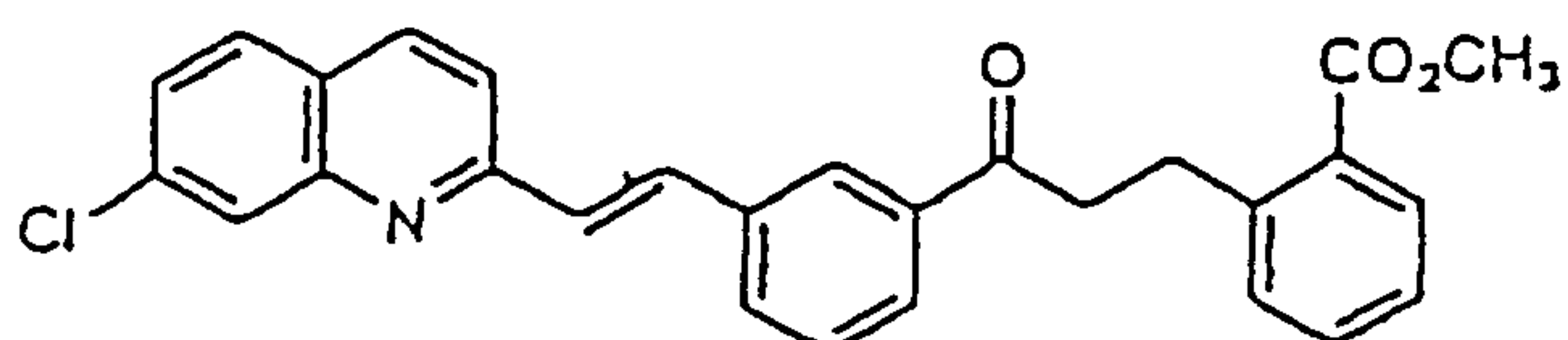
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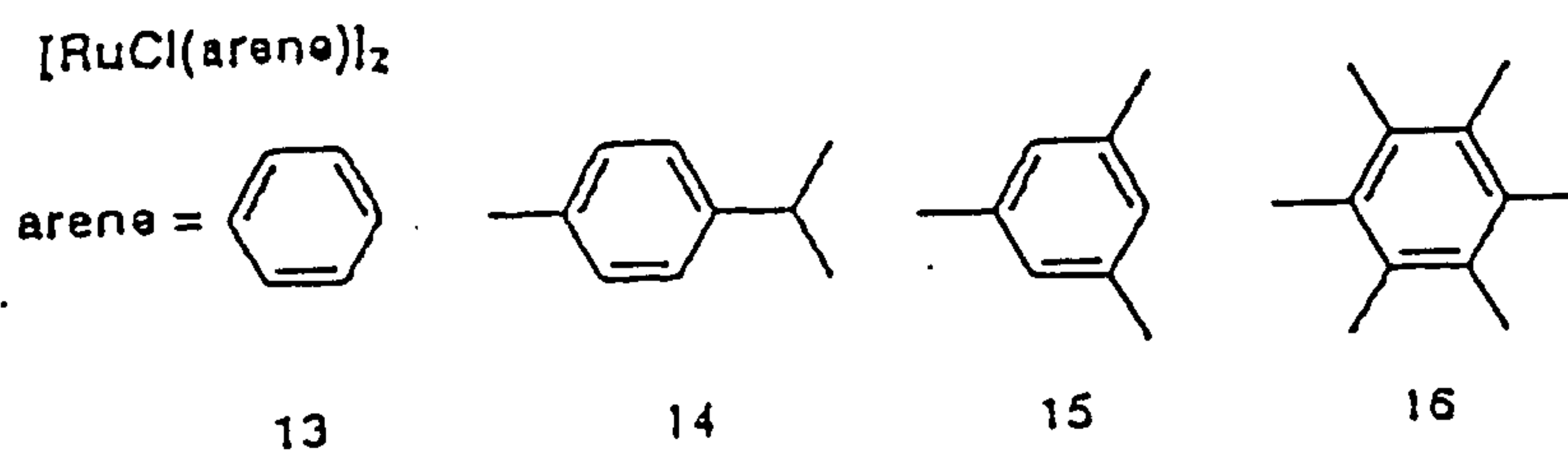
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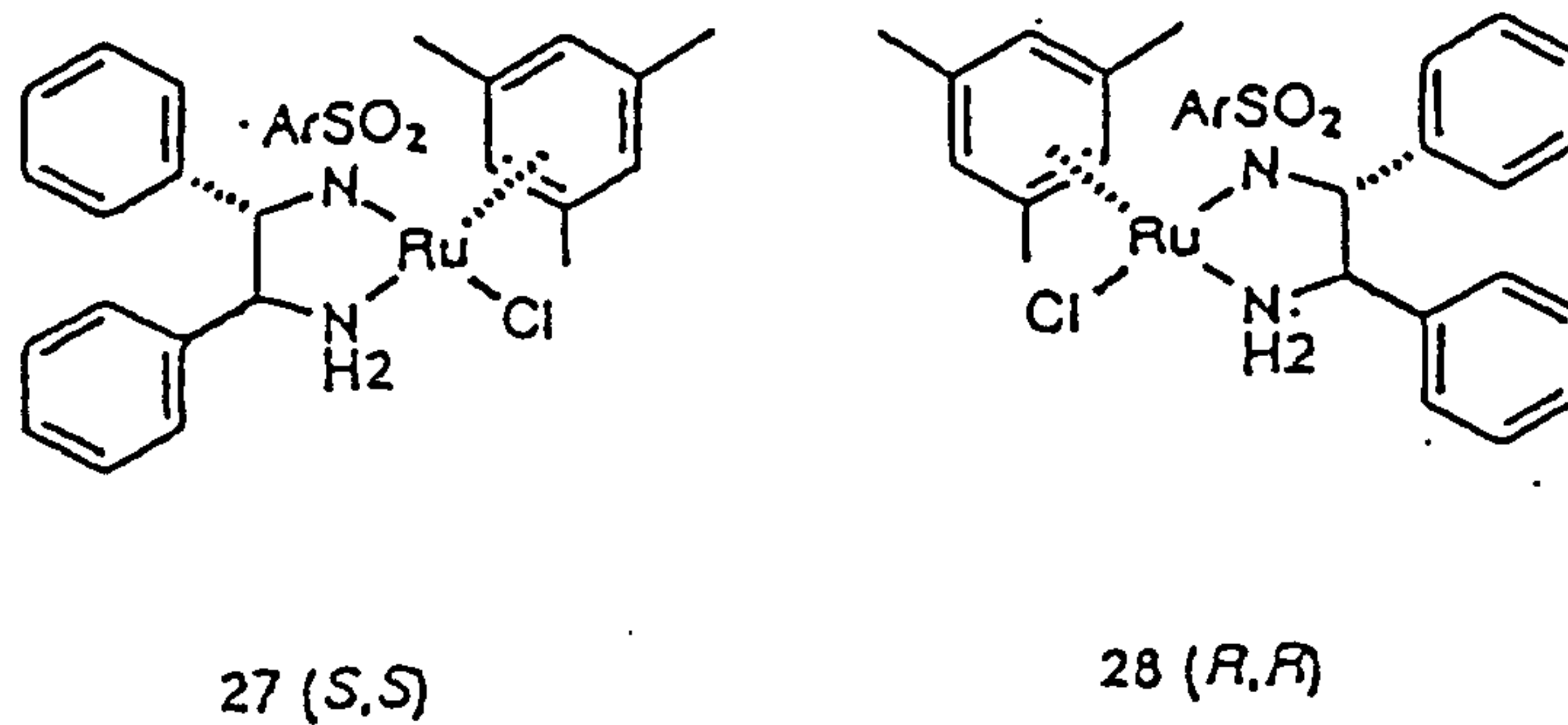
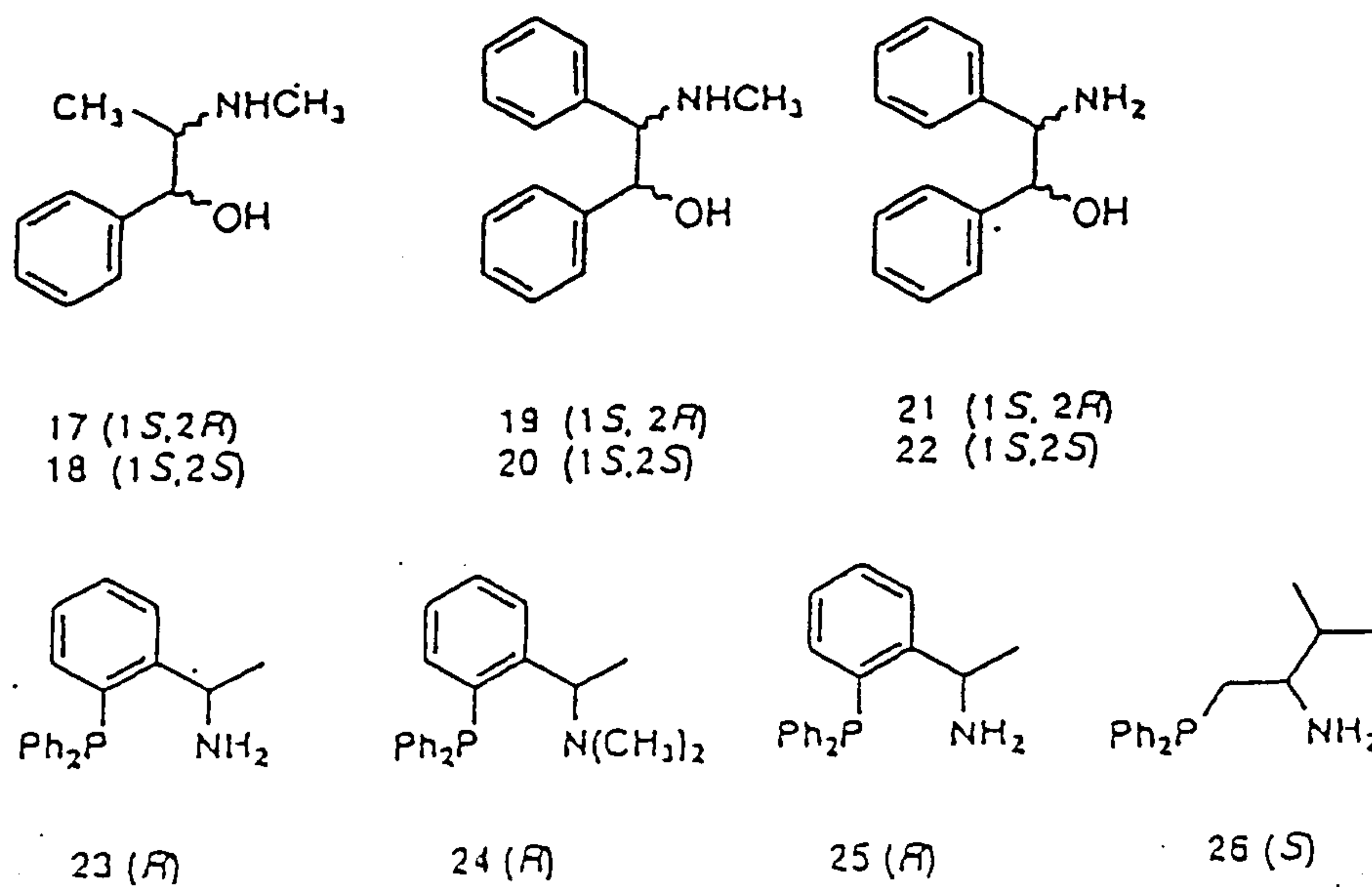
11



12

Table 2

Asymmetric metal complexes

Table 3

Examples 1 through 19

To dry 2-propanol (5.0 ml) were added various amino alcohol compounds (0.05 mmol) as chiral ligands of optically active amine compounds as shown in Table 3 and the ruthenium arene complex (0.0125 mmol) shown in Table 2, for agitation in argon or nitrogen gas atmosphere at 80°C for 20 minutes, and the resulting mixture was cooled to room temperature, to which were then added frozen and degassed dry 2-propanol (45.0 ml), various carbonyl compounds (5 mmol) deaerated and distilled as shown in Table 1, and a solution of 0.05M KOH in 2-propanol (2.5 ml; 0.125 mmol) in this order, for subsequent agitation at room temperature. After completion of the reaction, dilute hydrochloric acid was added to adjust the resulting mixture to acidity, from which most of 2-propanol was evaporated off under reduced pressure, followed by addition of saturated sodium chloride solution. The resulting product was extracted into ethyl acetate, rinsed with saturated sodium chloride solution several times and dried over anhydrous sodium sulfate. The solvent was distilled off from the product. The final product was analyzed by ^1H -NMR (CDCl_3), to calculate the conversion. Then, the product was purified by thin-layer silica gel chromatography, and the isolated alcohol fraction was used to determine the optical purity and absolute configuration by HPLC or GLC. The results are collectively shown in Table 4. Furthermore, the conversion and optical

purity of the sampled reaction solution can be calculated simultaneously by GLC.

Examples 20 to 23

Using the same method as in Example 1, aminophosphine compound was used as an optically active amine compound for the reaction. The results are collectively shown in Table 4.

Table 4

Examples	[RuCl ₂ (arene)] ₂	Ligands	Carbonyl compounds	Time	% conv	% ee	config.
1	13	19	1a	1	64	52	S
2	13	20	1a	1	91	17	S
3	14	20	1a	1	97	59	S
4	14	21	1a	1	97	56	S
5	15	20	1a	1	97	56	S
6	15	21	1a	1	62	52	S
7	16	17	1a	1	95	91	S
8	16	20	1a	1	94	92	S
9	16	21	1a	1	59	55	S
10	16	22	1a	1	96	75	S
11	16	20	1b	2	95	82	S
12	16	20	1c	15	93	5	S
13	16	20	1d	20	22	40	R
14	16	20	o-1e	6	96	83	S
15	16	18	o-1f	1	99	89	S
16	16	20	p-1g	4	73	79	S
17	16	20	3	2	99	93	S
18	16	18	4	3	93	75	S
19	16	16	7	4	62	94	S
20	13	23	1a	1	65	0.4	S
21	13	24	1a	1	61	61	R
22	13	25	1a	1	70		
23	13	26	1a	1	73	4	S

Examples 24 to 41

By using the same method as described in Example 1 and using optically active amine compounds, the chiral Ru complexes shown in Table 2 were synthesized. The complex catalysts and carbonyl compounds were added to a mixture of formic acid and triethylamine (5:2), for reaction at room temperature for a given period. After completion of the reaction, the reaction mixture was diluted with water, to extract the product in ethyl acetate. After drying the organic phase over anhydrous sodium sulfate and evaporating the solvent off, $^1\text{H-NMR}$ (CDCl_3) was analyzed to calculate the conversion. The optical purity and absolute configuration were determined by HPLC or GLC. The results are collectively shown in Table 5. The conversion and optical purity of each sampled reaction solution can be calculated simultaneously by GLC.

In accordance with the present invention, optically active alcohols can be produced at a high optical purity and a high synthetic yield.

Table 5

Examples	Ru complex	Carbonyl compounds	Time	% conv	% ee	config.
24	27(S, S)	1a	24	>99	98	S
25	27(S, S)	1b	60	>99	97	S
26	27(S, S)	m-1f	21	>99	97	S
27	27(S, S)	p-1f	24	>99	95	S
28	27(S, S)	m-1g	20	>99	98	S
29	27(S, S)	p-1g	50	>99	97	S
30	27(S, S)	p-1h	14	>99	90	S
31	27(S, S)	1i	60	>99	95	S
32	27(S, S)	2	60	93	83	S
33	27(S, S)	3	22	>99	96	S
34	27(S, S)	5	60	>54	66	S
35	27(S, S)	6	48	>99	99	S
36	27(S, S)	7	48	>99	99	S
37	27(S, S)	8	60	70	82	S
38	27(S, S)	9	40	47	97	S
39	28(R, R)	10	40	95	99	R
40	28(R, R)	11	65	95	98	R
41	28(R, R)	12	72	68	92	R

Example B

<Production of optically active amines>

Production examples of optically active amines are shown below and the present inventive method will be described in detail. Tables 6 and 7 show reaction substrates and asymmetric metal catalysts to be possibly used as typical examples.

The instrumental analysis was done by using the following individual systems.

NMR: JEOL GSX-400/Varian Gemini-200 (^1H -NMR sample: TMS, ^{31}P -NMR standard sample: phosphoric acid)

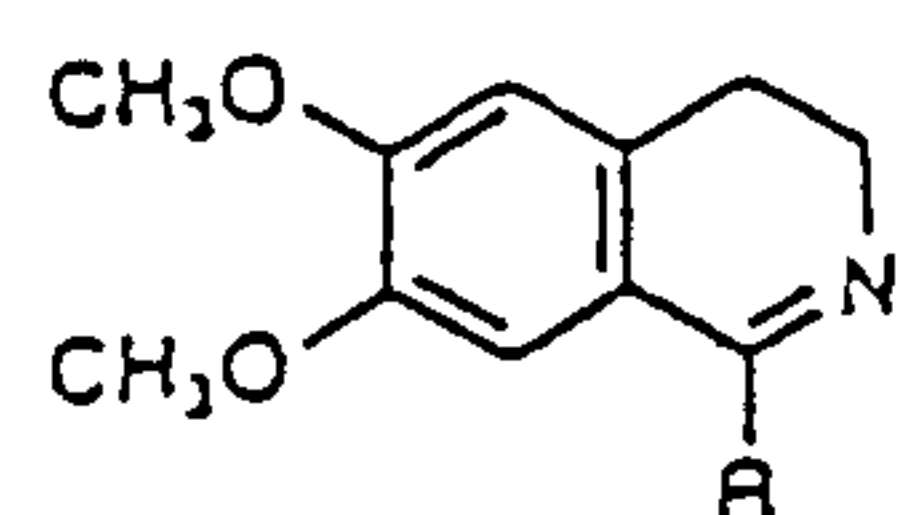
GLC: SHIMADZU GC-17A(column: chiral CP-Cyclodextrin-b-236-M19)

HPLC: JASCO GULLIVER (column: CHIRALCEL OJ, OB-H, OB, OD)

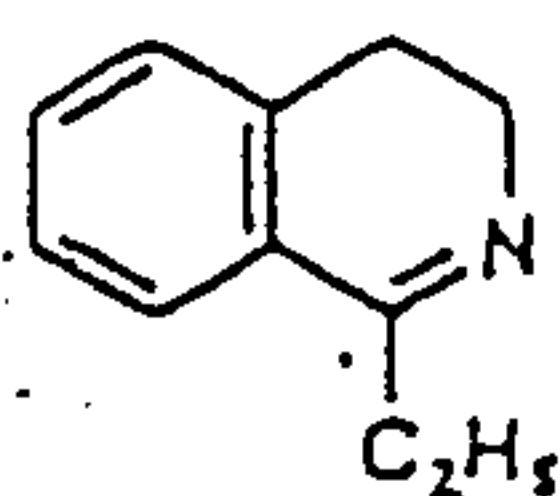
The absolute configurations of the resulting optically active amine compounds were determined on the basis of optical rotation and by HPLC and X-ray structural analysis. Blanks are not definitely shown.

Table 6

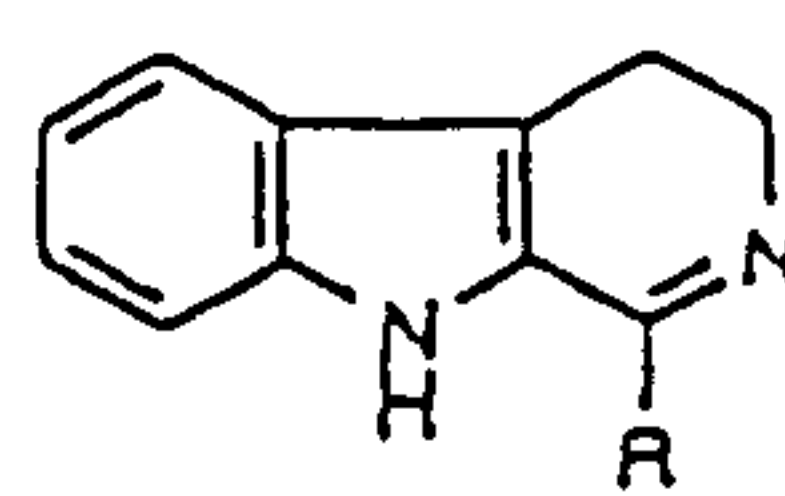
Imine compounds



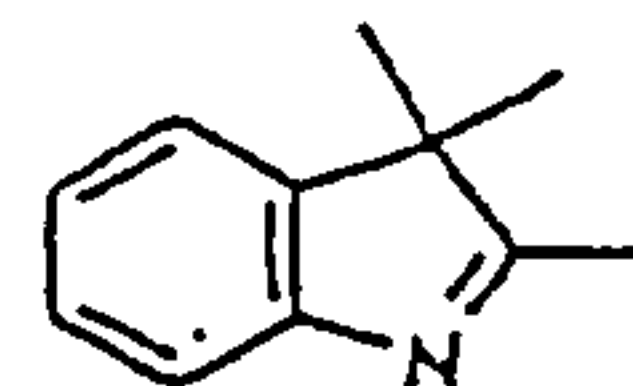
- 2a: R = CH₃
 2b: R = 3,4-(CH₃O)₂C₆H₃CH₂
 2c: R = 3,4-(CH₃O)₂C₆H₃(CH₂)₂
 2d: R = C₆H₅
 2e: R = 3,4-(CH₃O)₂C₆H₃
 2f: R = C₆H₅CH₂
 2g: R = 1-CH₃C₆H₄



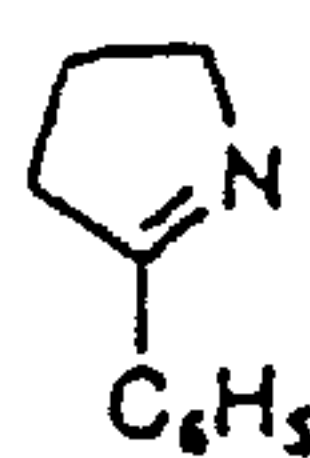
3



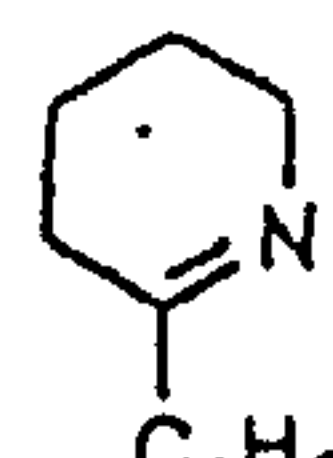
- 4a: R = CH₃
 4b: R = C₆H₅



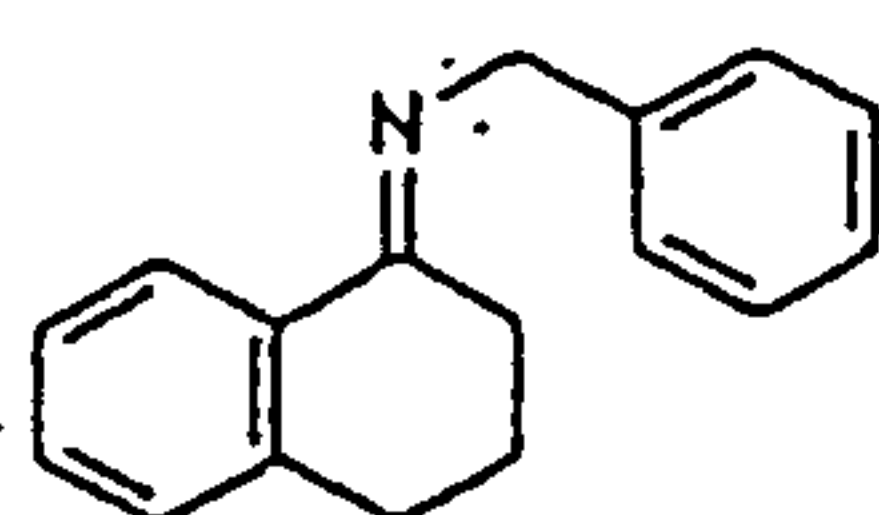
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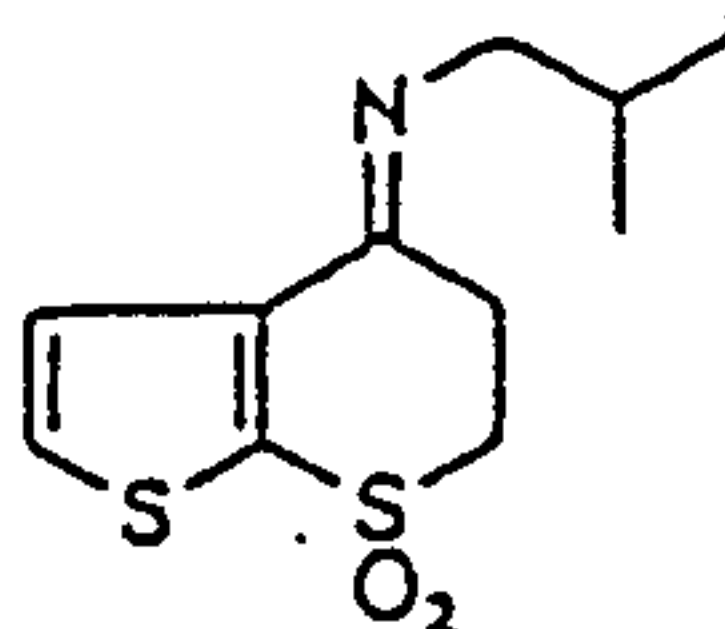
6



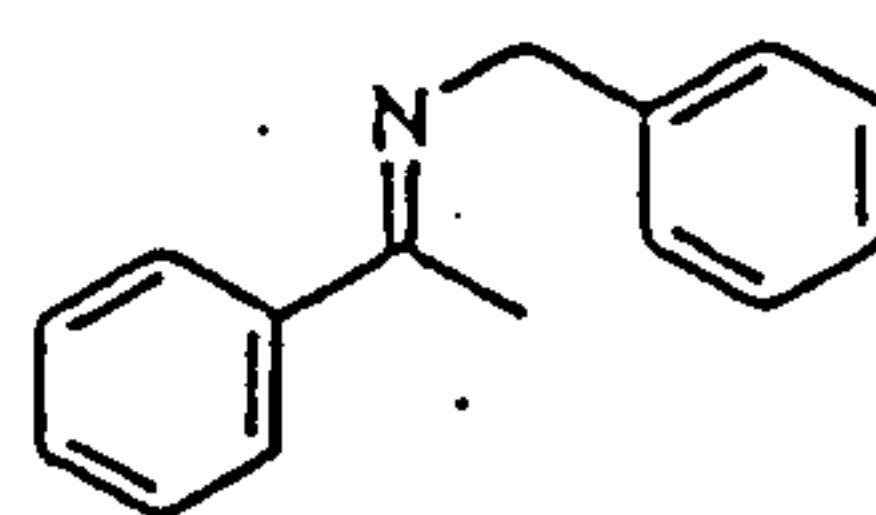
7



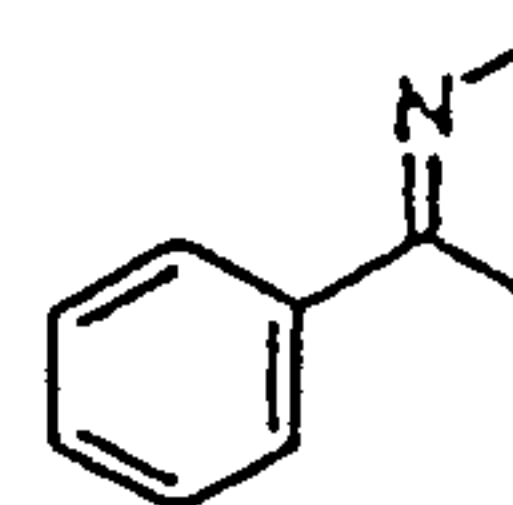
8



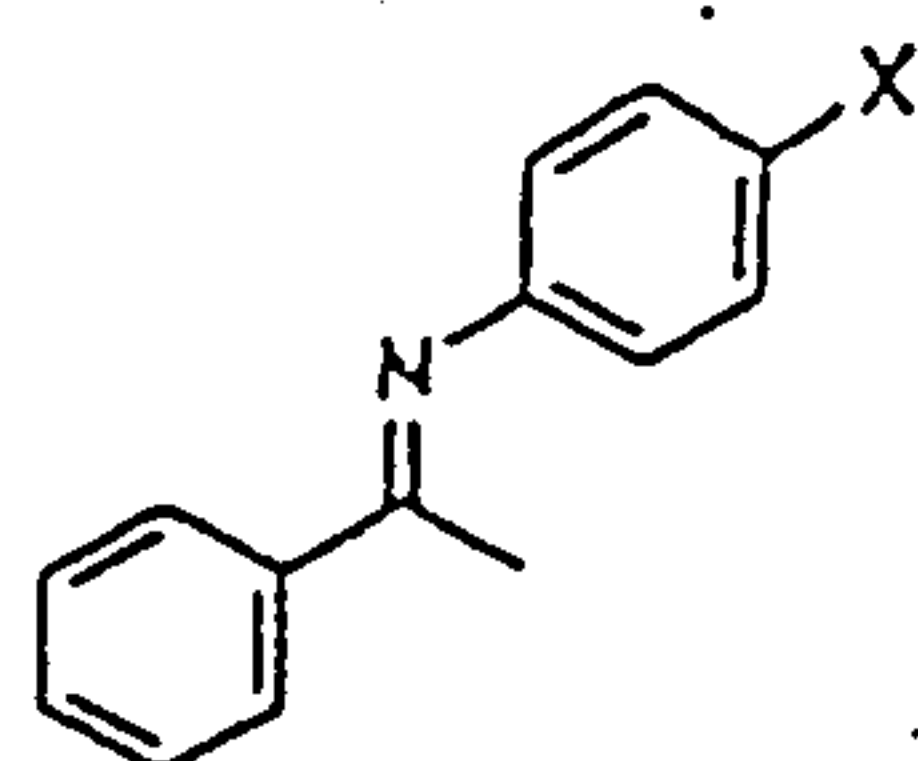
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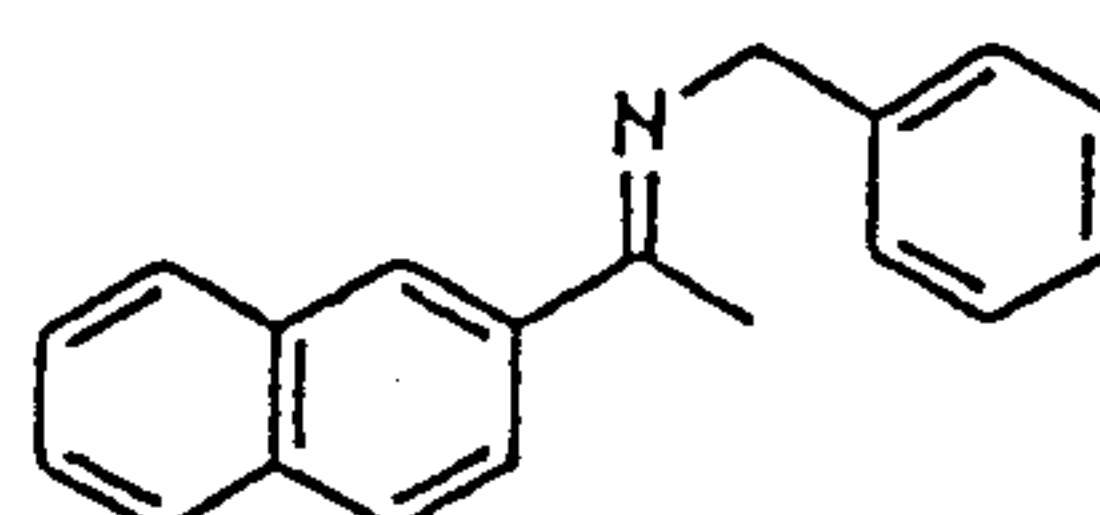
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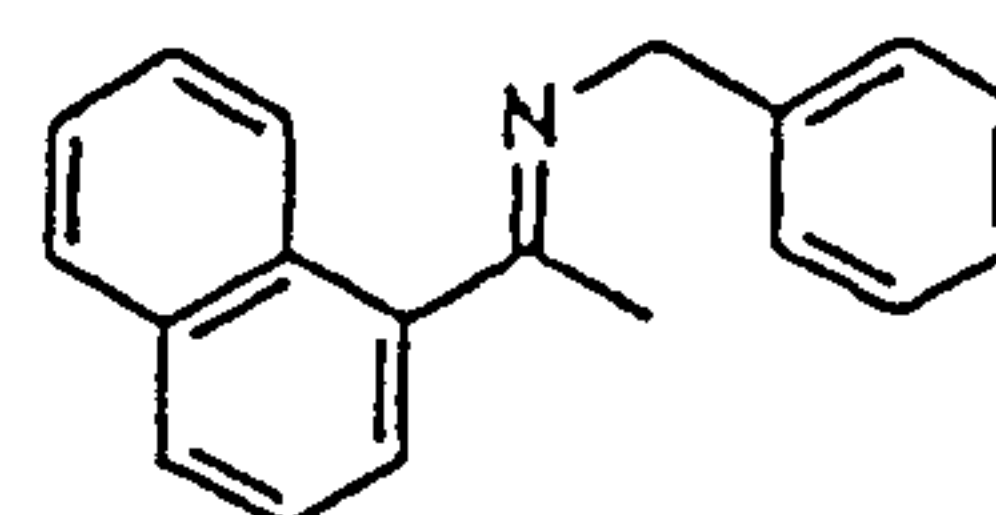
11



- 12a: X = H
 12b: X = Cl
 12c: X = CH₃O

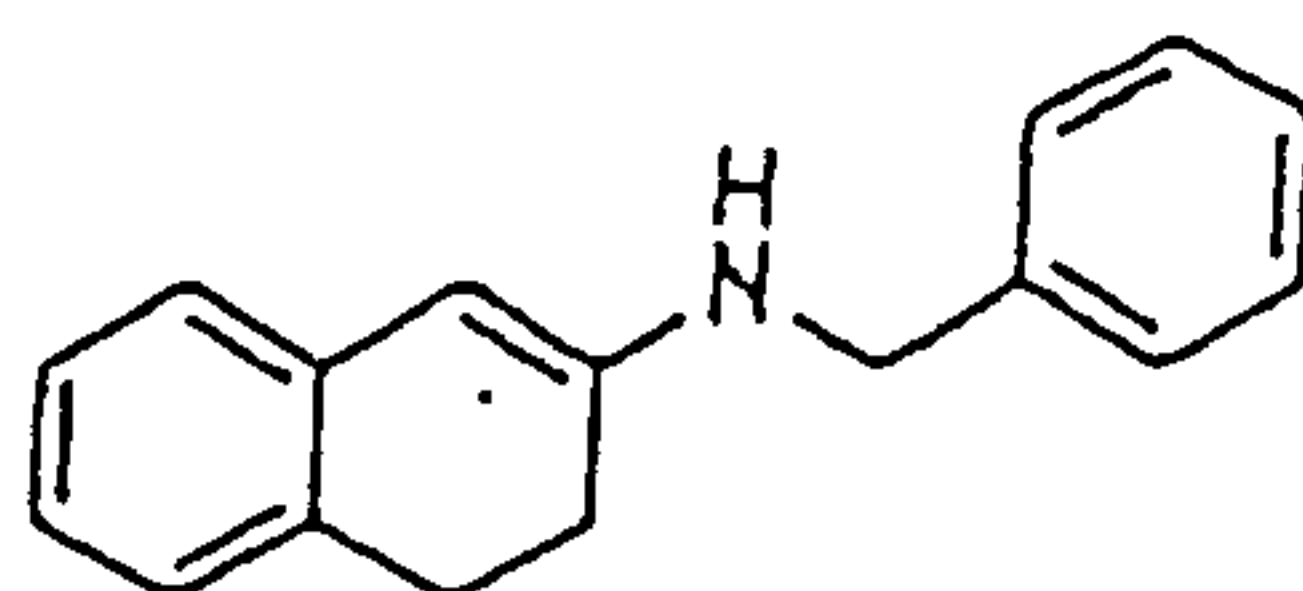


13



14

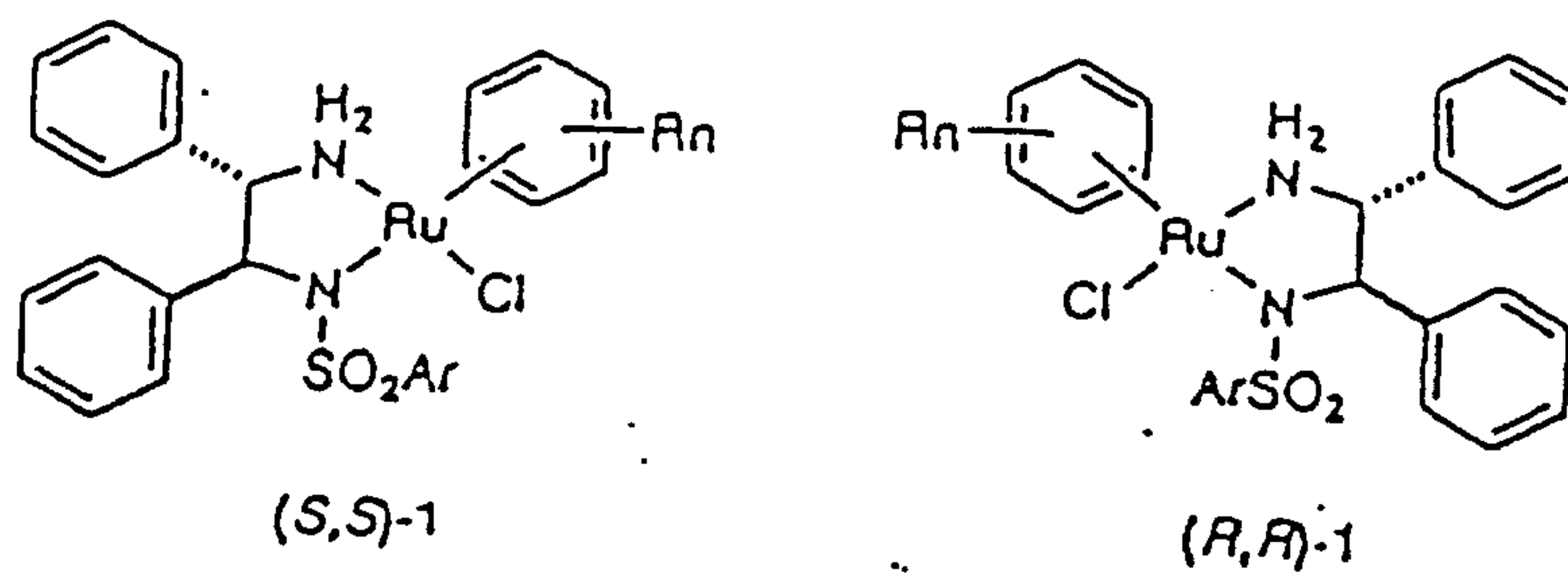
Enamine compounds



15

Table 7

Asymmetric metal complexes



- a: η^6 -arene = *p*-cymene ; Ar = *p*-CH₃C₆H₄
 b: η^6 -arene = *p*-cymene ; Ar = 2,4,6-(CH₃)₃C₆H₂
 c: η^6 -arene = benzene ; Ar = 1-naphthyl
 d: η^6 -arene = benzene ; Ar = 2,4,6-(CH₃)₃C₆H₂
 e: η^6 -arene = benzene ; Ar = *p*-CH₃C₆H₄

Example 42

6,7-Dimethoxy-1-methyl-3,4-dihydroxyisoquinoline (Table 6-2a) (1.03 g, 5 mmol) and a ruthenium catalyst (Table 7) (R, R)-1a (16 mg, 0.025 mmol) were dissolved in acetonitrile (10 ml), followed by addition of a mixture of formic acid-triethylamine (5 : 2), for agitation at 28°C for 3 hours. To the reaction mixture was added an aqueous sodium carbonate solution to extract the product in ethyl acetate. After evaporation of the solvent, $^1\text{H-NMR}(\text{CDCl}_3)$ of the resulting product was measured to calculate the conversion. Then, the product was purified by silica gel chromatography, to determine the optical purity and absolute configuration of the resulting optically active amine by HPLC or GLC. As collectively shown in Table 8, (S)-6,7-dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline (1.02 g, yield of 99 %, 96 % ee) was obtained.

Examples 43 to 69

By using the same reactor as in Example 42 but using different reaction substrates, catalysts, reaction solvents and ratios of reaction substrates/catalysts, the same experimental procedures as in Example 42 were carried out. The results are collectively shown in Table 8.

Example 70

Using the same reactor as in Example 42, the enamine compound was used for the same experimental procedures as in Example 42, so that the reaction progressed in a smooth manner, to recover the corresponding optically active amine compound. The results are collectively shown in Table 8.

Comparative Example 1

Under the same conditions as in Example 42, ruthenium-arene catalysts with no optically active amine ligands were used as catalysts, so that the reaction was facilitated, to recover a racemic amine compound quantitatively.

Comparative Example 2

Under the same conditions as in Example 51, ruthenium-arene catalysts with no optically active amine ligands were used as catalysts, so that no reaction was never facilitated.

As has been described above in detail, in accordance with the present invention, optically active amines can be produced at a high yield and an excellent optical purity.

Table 8

Examples	Imines	Catalysts	S/C	Solvents	Time . h	Amines		
						yield %	ee. %	absolute configuration
42	2a	(R, R)-1a	200	CH ₃ CN	3	99	96	S
43	2a	(R, R)-1a	200	CH ₂ Cl ₂	3	99	94	S
44	2a	(S, S)-1a	200	CH ₂ Cl ₂	3	99	93	R
45	2a	(R, R)-1a	200	acetone	3	99	95	S
46	2a	(R, R)-1a	200	DMF	3	99	95	S
47	2a	(R, R)-1a	200	DMSO	3	99	95	S
48	2a	(R, R)-1a	1000	CH ₂ Cl ₂	98	99	90	S
49	2b	(S, S)-1a	200	CH ₂ Cl ₂	8	81	87	R
50	2c	(S, S)-1b	200	CH ₂ Cl ₂	16	99	92	R
51	2d	(S, S)-1c	200	CH ₂ Cl ₂	8	99	84	R
52	2e	(S, S)-1c	100	CH ₂ Cl ₂	12	96	84	R
53	2f	(R, R)-1e	200	CH ₂ Cl ₂	18	68	82	
54	2g	(R, R)-1e	200	CH ₂ Cl ₂	14	94	98	
55	3	(S, S)-1a	200	CH ₂ Cl ₂	16	99	84	
56	4a	(S, S)-1a	200	DMF	5	86	97	R
57	4b	(S, S)-1a	200	DMF	5	83	96	R
58	5	(R, R)-1e	200	CH ₂ Cl ₂	48	59	78	
59	6	(S, S)-1c	200	CH ₂ Cl ₂	39	22	47	S
60	7	(S, S)-1c	200	CH ₂ Cl ₂	40	100	34	
61	8	(S, S)-1c	100	CH ₂ Cl ₂	6	90	89	S
62	9	(S, S)-1c	100	CH ₂ Cl ₂	12	64	88	S
63	10	(S, S)-1d	200	CH ₂ Cl ₂	36	72	77	S
64	11	(R, R)-1e	200	CH ₂ Cl ₂	15	13	36	
65	12a	(R, R)-1e	200	CH ₂ Cl ₂	37	43	46	
66	12b	(R, R)-1e	200	CH ₂ Cl ₂	109	35	36	
67	12c	(R, R)-1e	200	CH ₂ Cl ₂	65	67	25	
68	13	(S, S)-1c	200	CH ₂ Cl ₂	16	82	64	
69	14	(S, S)-1e	200	CH ₂ Cl ₂	67	71	12	R
70	15	(S, S)-1e	200	CH ₂ Cl ₂	12	69	43	

[In the table, s/c means the molar ratio of substrate/ruthenium-optically active diamine complex.]

Example C

<Production of optically active secondary alcohols by kinetic resolution method of alcohols>

Production examples of optically active secondary alcohols are shown below, and the inventive method will further be described in detail. However, the invention is not limited to these examples. Collectively, Table 9 shows racemic secondary alcohols or meso-type diols to be used as typical examples and Table 10 shows ruthenium-diamine complexes.

Abbreviations used in the present Example are as follows.
 η : representing the number of carbon atoms bonded to the metal of unsaturated ligand; and hexahapto (6 carbon atoms bonded to metal) is expressed as η^6 .

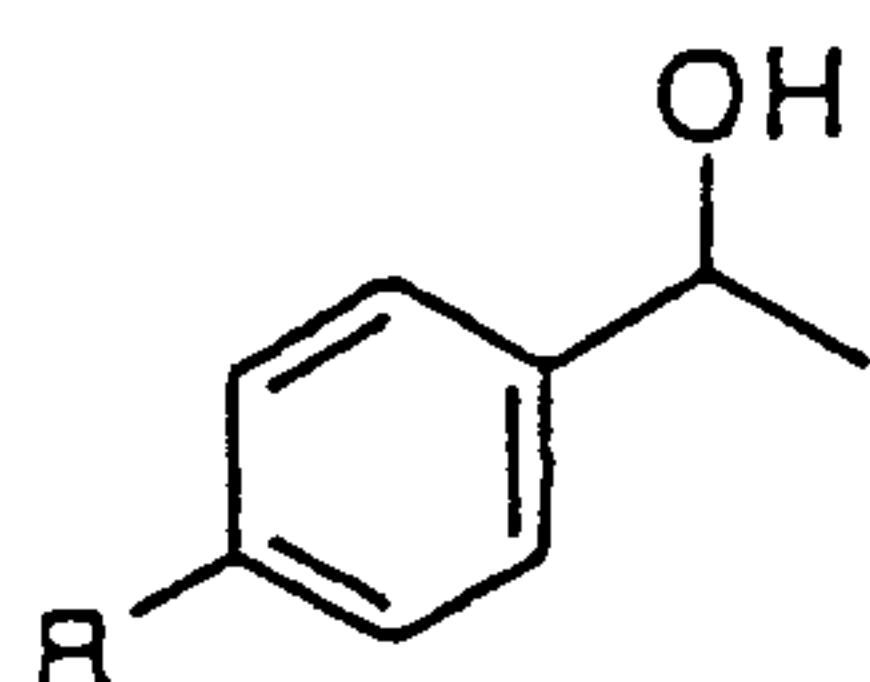
The instrumental analysis was done by using the following individual systems.

NMR: JEOL GSX-400/Varian Gemini-200 (^1H -NMR internal standard: TMS)

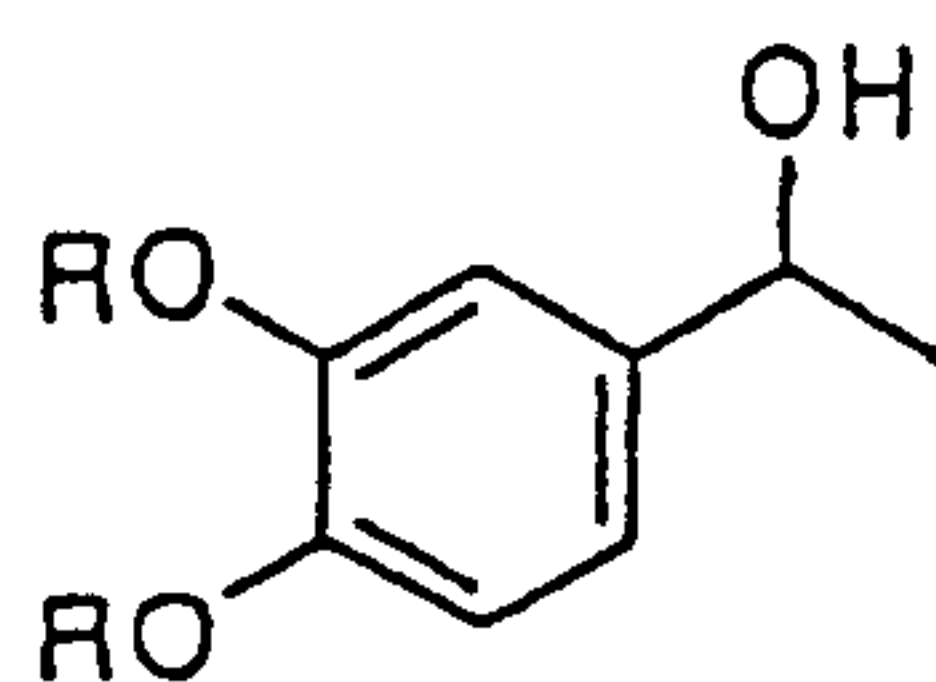
GLC: SHIMADZU GC-17A(column: chiral CP-Cyclodextrin-b-236-M19)

HPLC: JASCO GULLIVER (column: CHIRALCEL^{*} OJ, OB-H, OB, OD-H, OD)

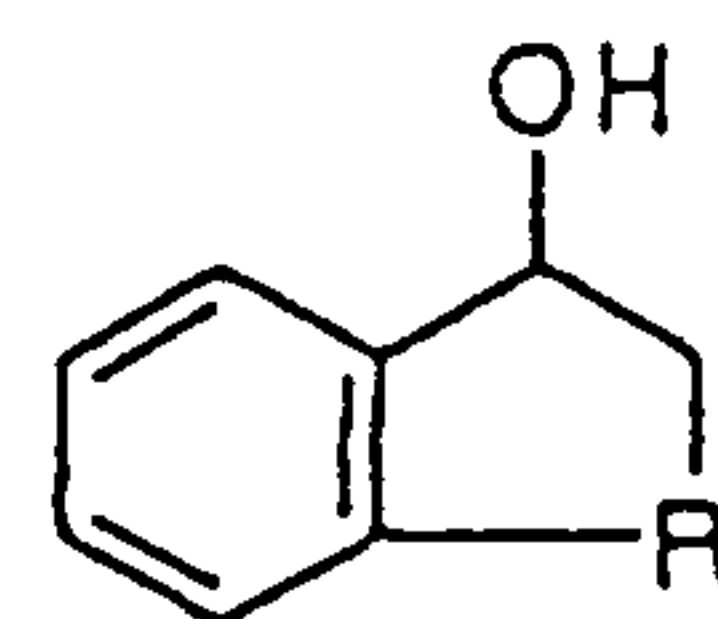
* Trade-mark

Table 9

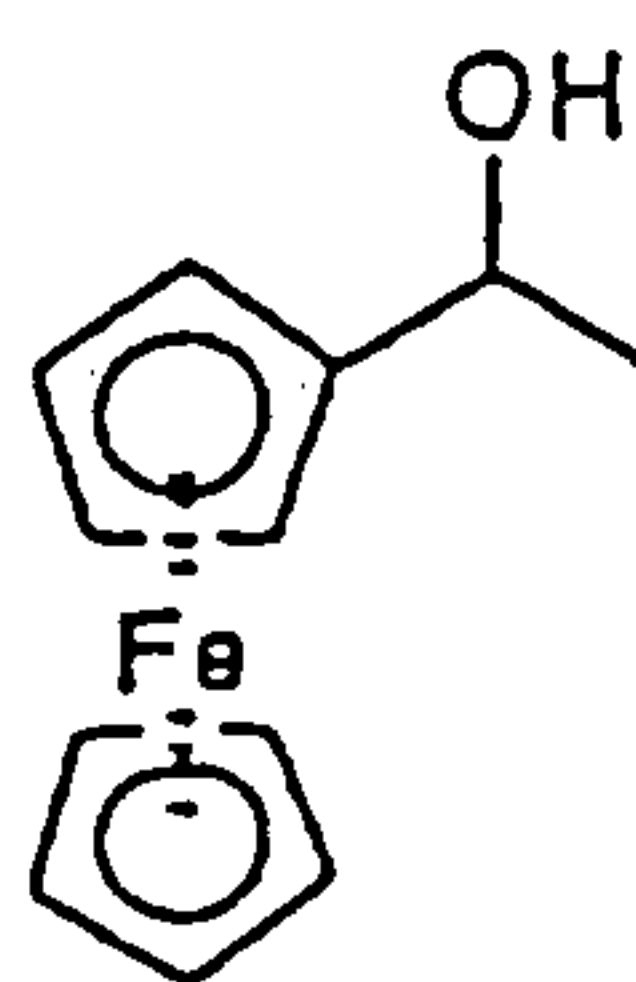
1a : R-H
 1b : R-CH₃O
 1c : R-(CH₃)₂N



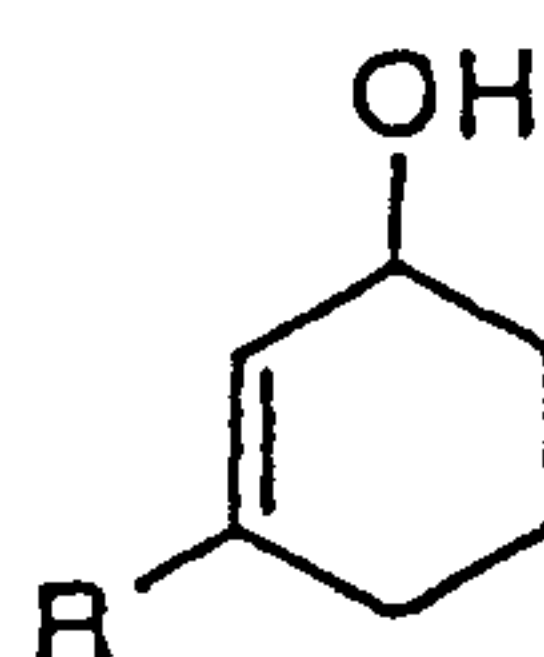
2a : R-CH₃
 2b : R-R=CH₂



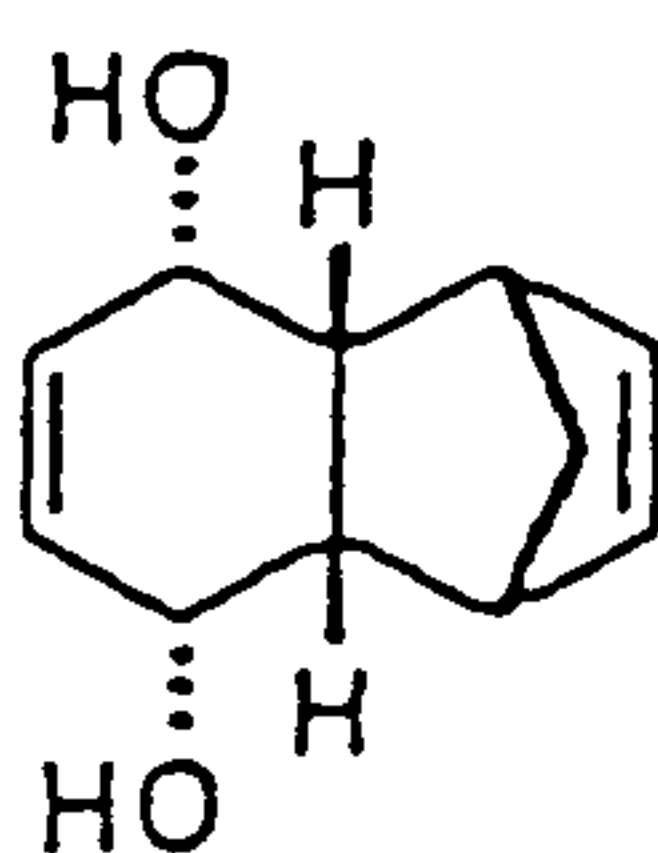
3a : R-CH₂
 3b : R-(CH₂)₂



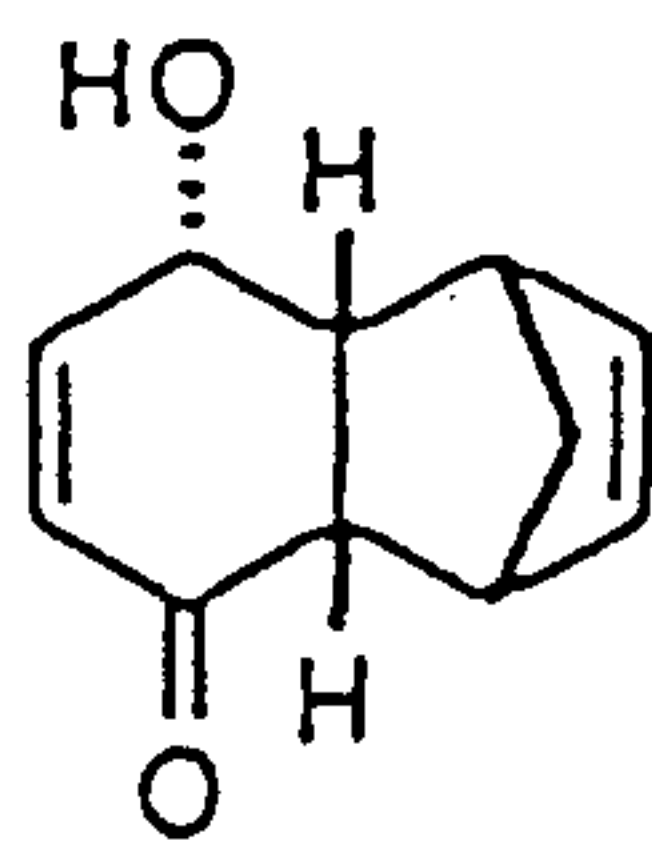
4



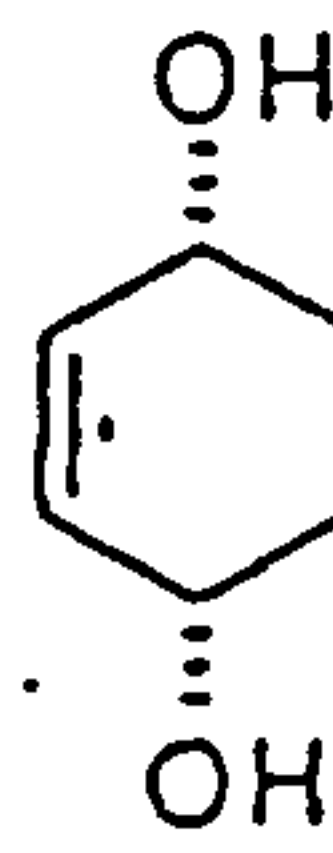
5a : R-H
 5b : R-CH₃



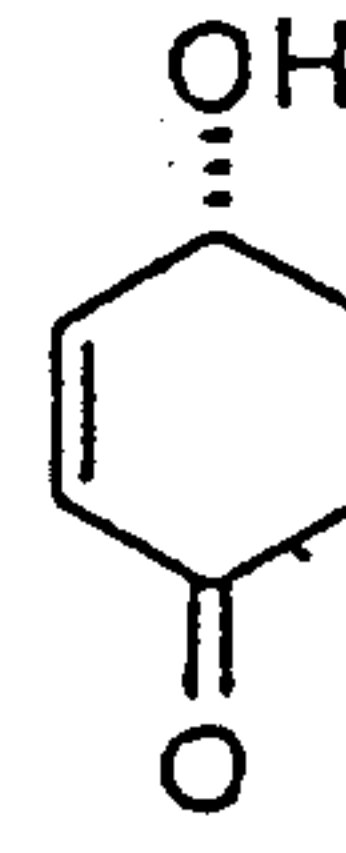
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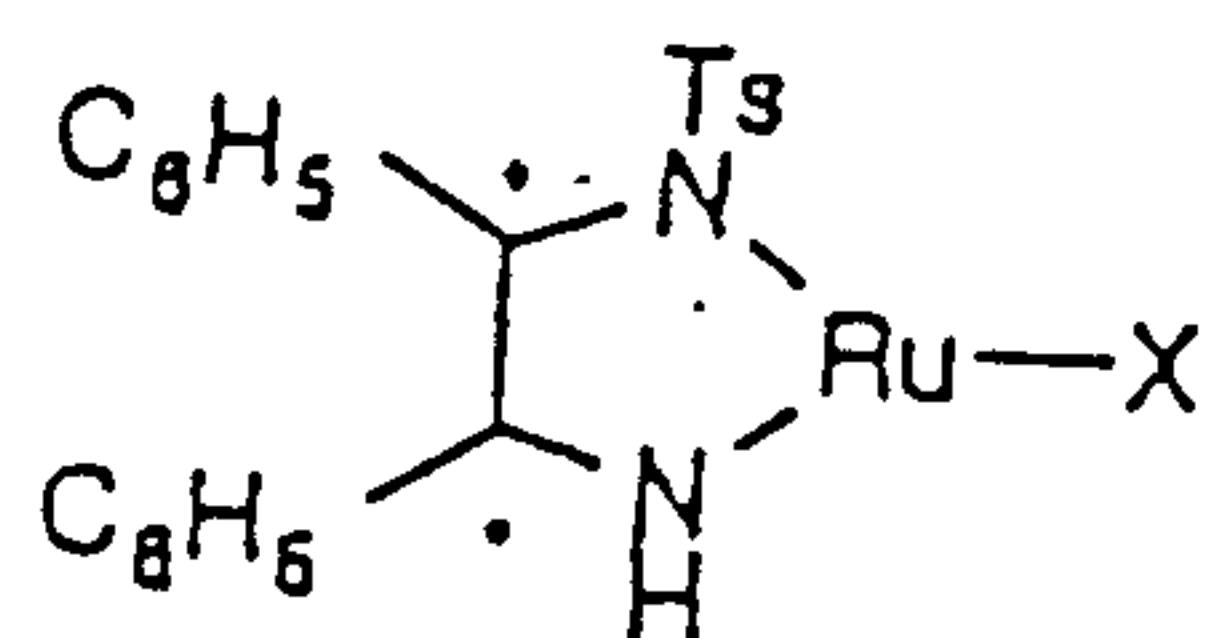
7



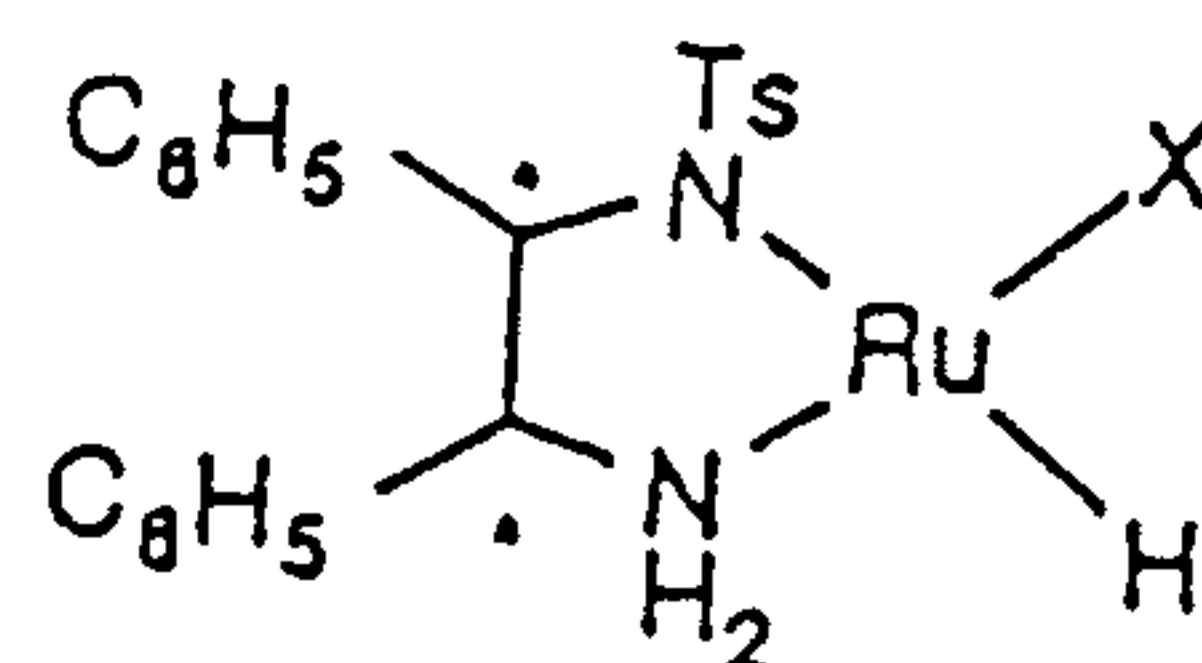
8



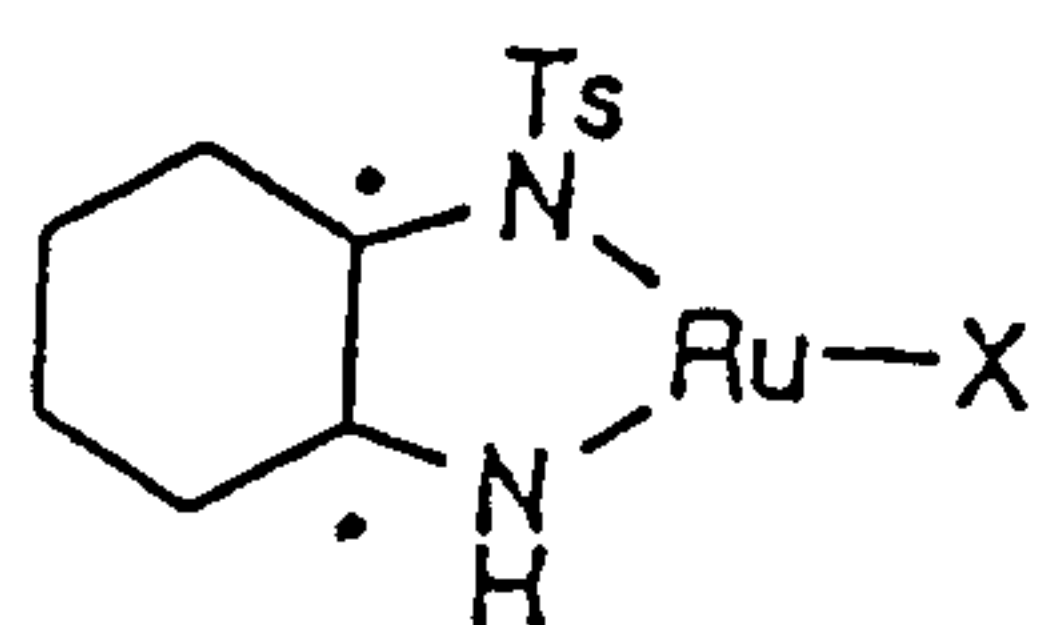
9

Table 10

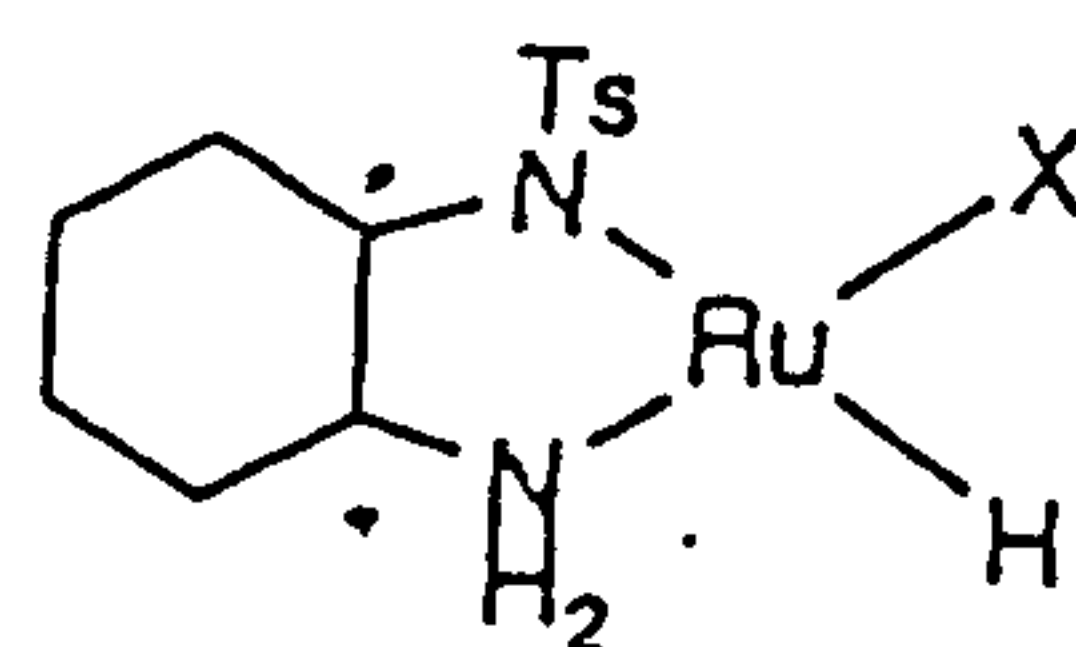
10 : X = *p*-cymene
 11 : X = mesitylene



12 : X = *p*-cymene
 13 : X = mesitylene



14 : X = *p*-cymene
 15 : X = mesitylene



16 : X = *p*-cymene
 17 : X = mesitylene.

Reference Example 1

Synthesis of $\text{RuCl}[(S, S)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-p-cymene})(\text{chloro}((S, S)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium}$
 $[\text{RuCl}_2(\eta^6\text{-p-cymene})]_2(\text{tetrachlorobis}(\eta^6\text{-p-cymene})\text{diruthenium})$ (1.53 g; 2.5 mmol) and $(S, S)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2((S, S)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})$ (1.83 g; 5.0 mmol) and triethylamine (1.4 ml; 10 mmol) are dissolved in 2-propanol (50 ml) in a Schlenk's reactor which is preliminarily dried in vacuum and of which the inside is then substituted with argon. The reaction solution was agitated at 80 for 1 hour and is then condensed, to recover crystal, which was then filtered and rinsed with a small amount of water, followed by drying under reduced pressure to recover orange crystal (2.99 g). The yield is 94 %.

m.p. > 100°C (decomposed)

IR(KBr)[cm^{-1}] : 3272, 3219, 3142, 3063
 3030, 2963, 2874

$^1\text{H-NMR}$ (400 MHz, ^2H -chloroform, δ): ppm

1.32 (d. 3H) 1.34 (d. 3H) 2.19 (s. 3H) 2.28 (s. 3H)
 3.07 (m. 1H) 3.26 (m. 1H) 3.54 (m. 1H) 3.54 (m. 1H) 3.66 (d. 1H),
 5.68 (d. 1H) 5.70 (d. 1H) 5.72 (d. 1H) 5.86 (d. 1H)
 6.61 (m. 1Hh) 6.29-7.20 (m. 14H)

Elemental analysis

(C₃₁H₃₅ClN₂O₂Ru)

	C	H	N	Cl	Ru
Theoretical values (%)	58.53	5.54	4.40	5.57	15.89
Elemental values (%)	58.37	5.44	4.36	5.75	18.83

The present catalyst was tested by X-ray crystallography. It was indicated that the complex was of a structure satisfying the analysis results.

Reference Example 2

Synthesis of RuCl[(S, S)-p-TsNCH(C₆H₅)CH(C₆H₅)NH₂](η^6 -mesitylene)(chloro((S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine)(η^6 -mesitylene)ruthenium

Instead of [RuCl₂(η^6 -p-cymene)]₂(tetrachlorobis(η^6 -p-cymene)diruthenium), [RuCl₂(η^6 -mesitylene)]₂(tetrachlorobis(η^6 -mesitylene)diruthenium) was used, and by the same procedures as in the Reference Example 1, the aforementioned catalyst was recovered as orange crystal. The yield was 64 %.

m.p. 218.6-222.5 (decomposed)

¹H-NMR (400 MHz, ²H-chloroform, δ): ppm

2. 2 4 (3 H) , 2. 3 8 (s, 9 H) , 3. 6 9 (d d, 1 H) , 3. 7 9 (d, 1 H) , 3. 9 9 (d d, 1 H) , 4. 1 9 (b r d, 1 H) , 5. 3 0 (s, 3 H) , 6. 6 5 - 6. 9 3 (m, 9 H) , 7. 0 6 - 7. 1 5 (m, 3 H) , 7. 3 5 (d, 2 H)

Reference Example 3

Synthesis of $\text{RuCl}[(S, S)\text{-N-p-Ts-cyclohexane-1,2-diamine}](\eta^6\text{-p-cymene})(\text{chloro-}((S, S)\text{-N-p-toluenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

Instead of $(S, S)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2((S, S)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})$, $(S, S)\text{-N-p-Ts-cyclohexane-1,2-diamine}((S, S)\text{-N-p-toluenesulfonyl-1,2-cyclohexanediamine})$ was used, and by the same procedures as in the Reference Example 1, the aforementioned catalyst was recovered as orange crystal. The yield is 60 %.

Reference Example 4

Synthesis of $\text{RuCl}[(S, S)\text{-N-p-Ts-cyclohexane-1,2-diamine}](\eta^6\text{-mesitylene})(\text{chloro-}((S, S)\text{-N-p-toluenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

Instead of $(S, S)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2((S, S)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})$, $(S, S)\text{-N-p-Ts-cyclohexane-1,2-diamine}((1S, 2S)\text{-N-p-toluenesulfonyl-1,2-cyclohexanediamine})$ was used, and by the same procedures as in the Reference Example 2, the aforementioned catalyst was recovered as orange crystal. The yield is 58 %.

Example 71-a

Synthesis of $\text{Ru}[(S, S)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-p-cymene})((S, S)\text{-N-p-toluenesulfonyl-1,2-diamine})(\eta^6\text{-p-cymene})$

cymene)ruthenium)

$[\text{RuCl}_2(\eta^6\text{-p-cymene})]_2$ (tetrachlorobis($\eta^6\text{-p-cymene}$)diruthenium) (306.2 mg; 0.5 mmol) and (S, S)-p-TsNCH(C₆H₅)CH(C₆H₅)NH₂ ((S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (366.4 mg; 1.0 mmol) and potassium hydroxide (400 mg; 7.1 mmol) are dissolved in methylene chloride (7 ml) in a Schlenk's reactor which is preliminarily dried in vacuum and of which the inside is then substituted with argon. The reaction solution was agitated at room temperature for 5 minutes, and by adding water (7 ml) to the reaction solution, the color of the reaction solution turned from orange to deep purple. The organic phase was separated and rinsed in water (7 ml). The organic phase was dried over calcium hydroxide, from which the solvent was distilled off. Then, the resulting product was dried under reduced pressure, to recover catalyst No.10 of deep purple crystal (522 mg) in Table 10. The yield is 87 %.

m.p. > 80 °C (decomposed)

IR(KBr)[cm⁻¹] : 3289, 3070, 3017, 2968
2920, 2859

¹H-NMR (400 MHz, ²H-toluene, δ): ppm

1. 20 (d. 3 H), 1. 25 (d. 3 H), 2. 05 (s. 3 H), 2. 22 (s. 3 H), 2. 53 (m. 1 H), 4. 08 (d. 1 H), 4. 89 (s. 1 H), 5. 11 (d. 1 H), 5. 27 (d. 1 H), 5. 28 (d. 1 H), 5. 39 (d. 1 H), 6. 64 (b r d. 1 H), 6. 87 (d. 2 H), 7. 67 (d. 2 H), 7. 2 - 7. 7 (m. 10 H)

Elemental analysis

(C₃₁H₃₄N₂O₂RuS)

	C	H	N	Ru
Theoretical values (%)	62.09	5.71	4.67	16.85
Elemental values (%)	62.06	5.77	4.66	16.47

The present catalyst was tested by X-ray crystallography. It was indicated that the complex was of a structure satisfying the analysis results.

Example 71-b

Alternative synthesis of Ru[(S, S)-p-TsNCH(C₆H₅)CH(C₆H₅)NH](η ⁶-p-cymene)((S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine)(η ⁶-p-cymene)ruthenium)

RuCl[(1S, 2S)-p-TsNCH(C₆H₅)CH(C₆H₅)NH₂](η ⁶-p-cymene)(chloro-(1S, 2S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine)(η ⁶-p-cymene)ruthenium) (318.6 mg; 0.5 mmol) and potassium hydroxide (200 mg; 3.5 mmol) are dissolved in methylene chloride (7 ml) in a Shlenk's reactor which is preliminarily vacuum dried and of which the inside is substituted with argon. The reaction solution was agitated at room temperature for 5 minutes, and by adding water (7 ml) to the reaction solution, the color of the reaction solution turned from orange to deep purple. The organic phase was separated and rinsed in water (7 ml). The organic phase was dried over calcium hydroxide, from which the solvent was distilled off.

Then, the resulting product was dried under reduced pressure, to recover crystal in deep purple crystal (522 mg). The yield is 87 %.

Example 72-a

Synthesis of $\text{Ru}[(S, S)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-mesitylene})(((S, S)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

Instead of $[\text{RuCl}_2(\eta^6\text{-p-cymene})]_2(\text{tetrachlorobis}(\eta^6\text{-p-cymene})\text{diruthenium})$,

$[\text{RuCl}_2(\eta^6\text{-mesitylene})]_2(\text{tetrachlorobis}(\eta^6\text{-mesitylene})\text{diruthenium})$ was used, and by the same procedures as in the Example 71-a, the catalyst in purple crystal as No.11 in Table 10 was recovered. The yield is 80 %.

$^1\text{H-NMR}$ (400 MHz, ^2H -chloroform, δ): ppm

1. 91 (s, 9 H), 1. 99 (s, 3 H), 3. 83 (d, 1 H), 4. 51 (s, 1 H), 4. 95 (s, 3 H), 5. 92 (b r d, 1 H), 6. 38 ~ 7. 71 (m, 14 H)

Example 72-b

Alternative synthesis of $\text{Ru}[(S, S)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-mesitylene})(((S, S)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

Instead of $\text{RuCl}[(S, S)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-p-cymene})(\text{chloro-}((S, S)\text{-N-p-toluenesulfonyl-1,2-}$

diphenylethylenediamine)(η^6 -p-cymene)ruthenium),
 RuCl[(S, S)-p-TsNCH(C₆H₅)CH(C₆H₅)NH₂](η^6 -
 mesitylene)(chloro-((S, S)-N-p-toluenesulfonyl-1,2-
 diphenylethylenediamine)(η^6 -mesitylene)ruthenium)
 synthesized as in the Reference Example 2 was used, and by the
 same procedures as in the Example 71-b, the catalyst in purple
 crystal was recovered. The yield is 90 %.

Example 73-a

Synthesis of Ru[(S, S)-N-p-Ts-1,2-cyclohexanediamine](η^6 -
 p-cymene)((S, S)-N-p-toluenesulfonyl-1,2-
 cyclohexanediamine)(η^6 -p-cymene)ruthenium)

Instead of (S, S)-p-TsNCH(C₆H₅)CH(C₆H₅)NH₂]((S, S)-N-p-
 toluenesulfonyl-1,2-diphenylethylenediamine), (S, S)-N-p-
 Ts-1,2-cyclohexanediamine((1S, 2S)-N-p-toluenesulfonyl-1,2-
 cyclohexanediamine) was used, and by the same procedures as in
 the Example 71-a, the catalyst in purple crystal as No.14 in
 Table 10 was recovered. The yield is 58 %.

Example 73-b

Alternative synthesis of Ru[(S, S)-N-p-Ts-1,2-
 cyclohexanediamine](η^6 -p-cymene)((S, S)-N-p-
 toluenesulfonyl-1,2-cyclohexanediamine)(η^6 -p-
 cymene)ruthenium)

Instead of RuCl[(S, S)-p-TsNCH(C₆H₅)CH(C₆H₅)NH₂]) (η^6 -

p-cymene)(chloro-((S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6 -p-cymene)ruthenium), RuCl[(S, S)-N-p-Ts-cyclohexane-1,2-diamine synthesized in the Reference Example 3 was used, and by the same procedures as in the Example 71-b, the catalyst in purple crystal was recovered. The yield is 62 %.

Example 74-a

Synthesis of Ru[(S, S)-N-p-Ts-1,2-cyclohexanediamine](η^6 -mesitylene)((S, S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine)(η^6 -mesitylene)ruthenium)

Instead of (S, S)-p-TsNCH(C₆H₅)CH(C₆H₅)NH₂((S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine), (S, S)-N-p-Ts-cyclohexane-1,2-diamine ((S, S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine) was used, and by the same procedures as in the Example 71-a, the catalyst as No.15 shown in Table 10 was recovered as purple crystal. The yield is 60 %.

Example 74-b

Alternative synthesis of Ru[(S, S)-N-p-Ts-1,2-cyclohexanediamine](η^6 -mesitylene)((S, S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine)(η^6 -mesitylene)ruthenium)

Instead of RuCl[(S, S)-p-TsNCH(C₆H₅)CH(C₆H₅)NH₂] (η^6 -p-cymene)(chloro-(S, S)-N-p-toluenesulfonyl-1,2-

diphenylethylenediamine)(η^6 -p-cymene)ruthenium),
 RuCl[(S, S)-N-p-Ts-1,2-cyclohexanediamine] (η^6 -
 mesitylene)(chloro-(1S, 2S)-N-p-toluenesulfonyl-1,2-
 cyclohexanediamine)(η^6 -mesitylene)ruthenium) synthesized in
 the Reference Example 4 was used, and by the same procedures
 as in the Example 71-b, the aforementioned catalyst was
 recovered as purple crystal. The yield is 62 %.

Example 75-a

Synthesis of RuH[(S, S)-p-TsNCH(C₆H₅)CH(C₆H₅)NH₂](η^6 -p-
 cymene)(hydride-(S, S)-N-p-toluenesulfonyl-1,2-
 diphenylethylenediamine)(η^6 -p-cymene)ruthenium)

Ru[(S, S)-p-TsNCH(C₆H₅)CH(C₆H₅)NH] (η^6 -p-cymene)((S,
 S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine)(η^6 -p-
 cymene)ruthenium) (600 mg; 1.0 mmol) is dissolved in 2-propanol
 (10 ml) in a Shlenk's reactor which is preliminarily vacuum dried
 and of which the inside is substituted with argon. The reaction
 solution was agitated at room temperature for 15 minutes. The
 solvent was recovered under reduced pressure at room
 temperature, to recover a compound in brown yellow. After
 rinsing the compound in cool pentane and recrystallizing the
 compound in methanol, the catalyst No.12 in Table 10 was
 recovered as orange crystal. The yield is 85 %.

m.p. > 60 °C (decomposed)

IR(KBr)[cm⁻¹] : 3335, 3317, 3228, 3153,

3060, 3025, 2960, 2917,
2867

^1H -NMR (400 MHz, ^2H -chloroform, δ): ppm

- 5.47 (s, 1H), 1.53 (d, 3H), 1.59 (d, 3H), 2.29 (d, 3H), 2.45 (s, 3H), 2.79 (m, 1H), 2.93 (m, 1H), 3.80 (d, 1H), 4.02 (m, 1H), 5.15 (d, 1H), 5.19 (d, 1H), 5.29 (m, 1H), 5.43 (d, 1H), 5.58 (d, 1H), 6.49 (d, 2H), 6.9-7.3 (m, 10H), 7.59 (d, 2H)

Elemental analysis

($\text{C}_{31}\text{H}_{36}\text{N}_2\text{O}_2\text{RuS}$)

	C	H	N	Ru
Theoretical values (%)	61.88	6.02	4.66	16.80
Experimental values (%)	61.79	5.94	4.70	16.56

The X-ray crystallography shows that the complex was of a structure satisfying the analytical results.

Example 75-b

Alternative synthesis of $\text{RuH}[(\text{S}, \text{S})\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-p-cymene})(\text{hydride-}((\text{S}, \text{S})\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

Toluene (7 ml) was added into the Ru[(S, S)-p-TsNCH(C₆H₅)CH(C₆H₅)NH] (η^6 -p-cymene)((S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6 -p-cymene)ruthenium) (306.2 mg; 0.5 mmol) synthesized in the Example 72 in an autoclave which was preliminarily vacuum dried and of which the inside was substituted with argon, for reaction at room temperature and a hydrogen pressure of 80 atm. After elimination of the solvent and rinsing in cool pentane and subsequent recrystallization in methanol, crystal in orange (420 mg) was recovered. The yield is 70 %.

Example 76-a

Synthesis of RuH[(S, S)-p-TsNCH(C₆H₅)CH(C₆H₅)NH₂] (η^6 -mesitylene)(hydride-((S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6 -mesitylene)ruthenium)

Instead of Ru[(S, S)-p-TsNCH(C₆H₅)CH(C₆H₅)NH] (η^6 -p-cymene)((S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6 -p-cymene)ruthenium), Ru[(S, S)-p-TsNCH(C₆H₅)CH(C₆H₅)NH] (η^6 -mesitylene)((S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine) (η^6 -mesitylene)ruthenium) synthesized in the Example 72 was used, and by the same procedures as in the Example 75-a, the aforementioned catalyst No.13 in Table 10 was recovered. The yield was 60 %.

Example 76-b

Alternative synthesis of $\text{RuH}[(S, S)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2](\eta^6\text{-mesitylene})(\text{hydride-}((S, S)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$

Instead of $\text{Ru}[(S, S)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-p-cymene})(((S, S)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$, $\text{Ru}[(S, S)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-mesitylene})(((S, S)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-mesitylene})\text{ruthenium})$ synthesized in the Example 72 was used, and by the same procedures as in the Example 75-b, the aforementioned catalyst was recovered. The yield is 60 %.

Example 77-a

Synthesis of $\text{RuH}[(S, S)\text{-N-p-Ts-1,2-cyclohexanediamine}](\eta^6\text{-p-cymene})(\text{hydride-}(S, S)\text{-N-p-toluenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$

Instead of $\text{Ru}[(S, S)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-p-cymene})((S, S)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$, $\text{Ru}[(S, S)\text{-N-p-Ts-1,2-cyclohexanediamine}](\eta^6\text{-p-cymene})((S, S)\text{-N-p-toluenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-p-cymene})\text{ruthenium})$ synthesized in the Example 73 was used, and by the same procedures as in the Example 75-a, the catalyst No.16

in Table 10 was recovered. The yield is 54 %.

Example 77-b

Alternative synthesis of $\text{RuH}[(S, S)\text{-N-p-Ts-1,2-cyclohexanediamine}](\eta^6\text{-p-cymene})(\text{hydride-(S, S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-p-cymene)ruthenium})$

Instead of $\text{Ru}[(S, S)\text{-p-TsNCH(C}_6\text{H}_5\text{)CH(C}_6\text{H}_5\text{)NH}](\eta^6\text{-p-cymene})(\text{chloro-(S, S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-p-cymene)ruthenium})$, $\text{Ru}[(S, S)\text{-N-p-Ts-1,2-cyclohexanediamine}](\eta^6\text{-p-cymene})((S, S)\text{-N-p-toluenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-p-cymene)ruthenium})$ synthesized in the Example 73 was used, and by the same procedures as in the Example 75-b, the catalyst was recovered. The yield is 55 %.

Example 78-a

Synthesis of $\text{RuH}[(S, S)\text{-N-p-Ts-1,2-cyclohexanediamine}](\eta^6\text{-mesitylene})(\text{hydride-(S, S)-N-p-toluenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-mesitylene)ruthenium})$

Instead of $\text{Ru}[(S, S)\text{-p-TsNCH(C}_6\text{H}_5\text{)CH(C}_6\text{H}_5\text{)NH}](\eta^6\text{-p-cymene})((S, S)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-p-cymene)ruthenium})$, $\text{Ru}[(S, S)\text{-N-p-Ts-1,2-cyclohexanediamine}](\eta^6\text{-mesitylene})((S, S)\text{-N-p-toluenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-$

mesitylene)ruthenium) synthesized in the Example 74 was used, and by the same procedures as in the Example 75-a, the catalyst No.17 in Table 10 was recovered. The yield is 52 %.

Example 78-b

Alternative synthesis of $\text{RuH}[(S, S)\text{-N-p-Ts-1,2-cyclohexanediamine}](\eta^6\text{-mesitylene})(\text{hydride}((S, S)\text{-N-p-toluenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-mesitylene)ruthenium})$

Instead of $\text{Ru}[(S, S)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-p-cymene})((S, S)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\eta^6\text{-p-cymene)ruthenium})$, $\text{Ru}[(S, S)\text{-N-p-Ts-1,2-cyclohexanediamine}](\eta^6\text{-mesitylene})((S, S)\text{-N-p-toluenesulfonyl-1,2-cyclohexanediamine})(\eta^6\text{-mesitylene)ruthenium})$ synthesized in the Example 74 was used, and by the same procedures as in the Example 75-b, the aforementioned catalyst was recovered. The yield is 48 %.

Example 79

Synthesis of (R)-1-indanol

$\text{Ru}[(S, S)\text{-p-TsNCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{NH}](\eta^6\text{-p-cymene})((S, S)\text{-N-p-toluenesulfonyl-1,2-diphenylethylenediamine})(\text{ruthenium-}\eta^6\text{-p-cymene mesitylene (6.0 mg; } 10 \mu\text{ mmol)})$ synthesized in the Example 71 and 1-indanol (671 mg; 5 mmol) were weighed in a Shlenk's reactor which was

preliminarily vacuum dried and of which the inside was substituted with argon, and acetone (2.5 ml) was then added to the resulting mixture for agitation at 28 °C for 6 hours. The solvent was distilled off under reduced pressure, prior to separation by silica gel chromatography (eluent; ethyl acetate : hexane = 1 : 3), to recover (R)-indanol (286 mg) in colorless crystal. The yield is 84 %.

m.p. 71 - 72 °C

$[\alpha]^{25}_D = -30.1^\circ$ (c = 1.96, chloroform)

The resulting (R)-1-indanol was analyzed by HPLC (high-performance liquid chromatography), and the objective (R)-1-indanol was at an optical purity of 97 % ee.

<HPLC analytical conditions>

Column: CHIRALCEL* OB (manufactured by Daicell Chemical Industry, Co.)

Developing solution: isopropanol : hexane = 10 : 90

Flow rate: 0.5 ml/min

Retention time: (S)-1-indanol 18.6 minutes

(R)-1-indanol 12.9 minutes.

Examples 80 to 93

According to the method described in Example 79, the optically active ruthenium-diamine complexes for racemic secondary alcohols and meso-type diols as reaction substrates as shown in Table 9 were used for reaction under reaction

* Trade-mark

conditions of reaction time, to recover the individually corresponding optically active secondary alcohols at high yields. The results are collectively shown in Table 11.

Table 11

Examples	Substrates	Catalysts	s/c	Reaction time (hr)	%(yield)	%ee	Products
80	1 a	(S, S)-10	500	36	50	92	1a(R)
81	1 a	(S, S)-11	500	30	51	94	1a(R)
82	1 a	(S, S)-10	500	22	47	92	1b(R)
83	1 b	(S, S)-11	500	30	44	98	1c(R)
84	1 c	(S, S)-11	500	36	47	97	2a(R)
85	2 a	(S, S)-11	500	24	47	97	2b(R)
79	2 b	(S, S)-10	500	6	46	97	3a(R)
86	3 a	(S, S)-10	500	6	49	99	3b(R)
87	3 b	(S, S)-11	500	36	51	98	4(R)
88	4	(S, S)-10	500	4.5	43	93	5a(R)
89	5 a	(S, S)-10	500	5	46	95	5b(R)
90	5 b	(S, S)-11	200	3	70	96	7
91	5	(S, S)-10	200	3	56	87	9
92	1 a	(S, S)-14	500	36	48	82	1a(R)
93	1 a	(S, S)-15	500	36	48	86	1a(R)

(In the table, s/c means the molar ratio of substrate/ruthenium-optically active diamine complex.)

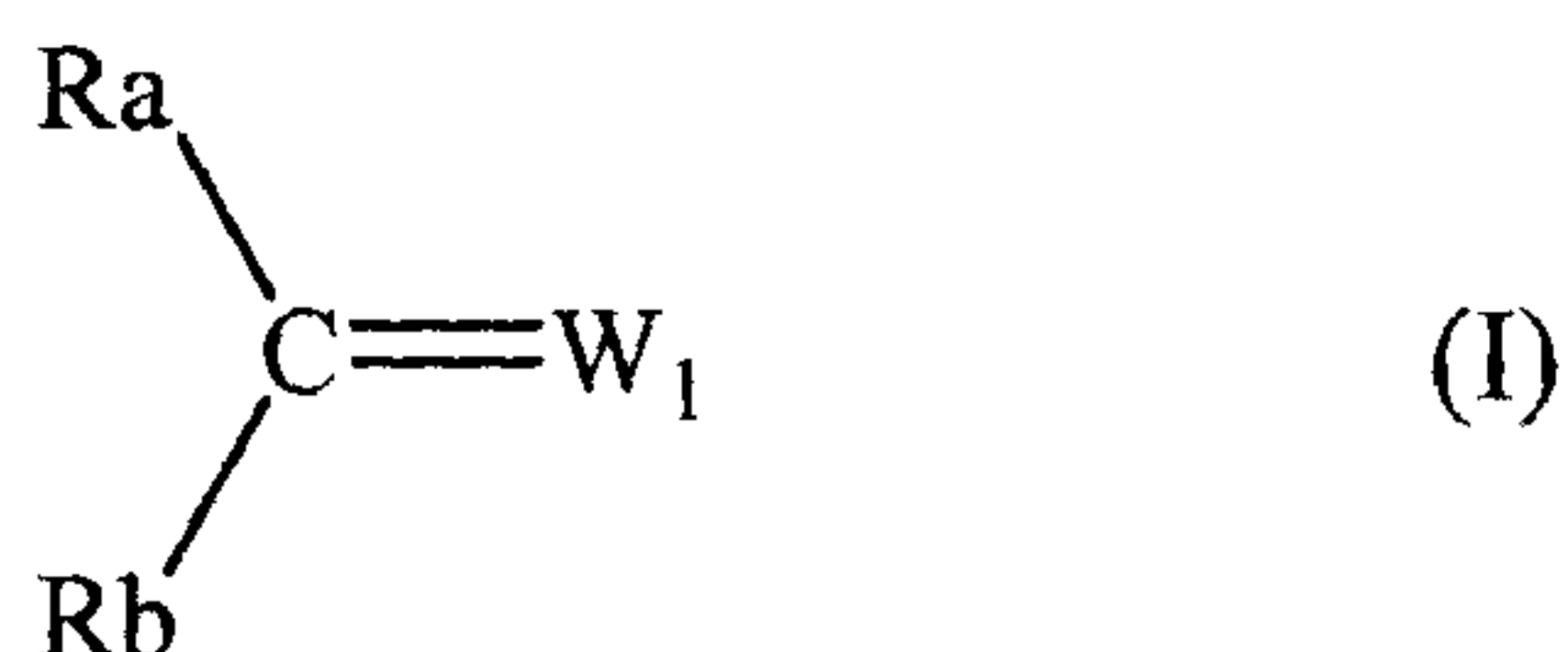
Industrial Applicability

In accordance with the present invention, optically active alcohols and optically active amines are provided, which are useful in various fields of pharmaceutical products, synthetic intermediates thereof, food, flavor, cosmetics, liquid crystal materials and the like.

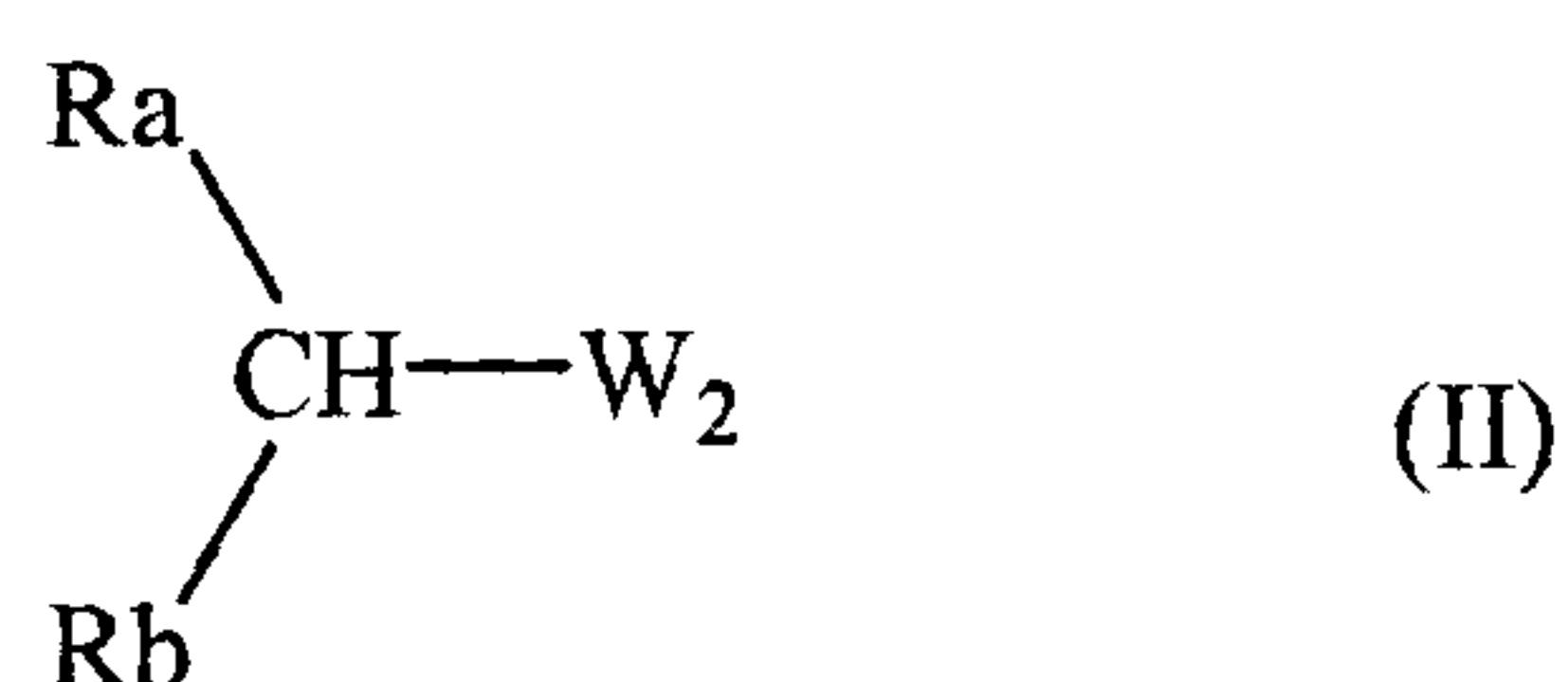
The ruthenium-diamine complex of the present invention is industrially useful as a chiral catalyst providing higher selectivity and activity in that the complex can be used for organic synthesis such as asymmetric synthetic reactions. If the complex is used as a hydrogen transfer-type asymmetric reduction catalyst of racemic secondary alcohols or meso-type diols, optically active secondary alcohols useful as production intermediates of drugs can be produced highly efficiently.

CLAIMS:

1. A method for producing optically active compounds, comprising subjecting a compound having formula (I):



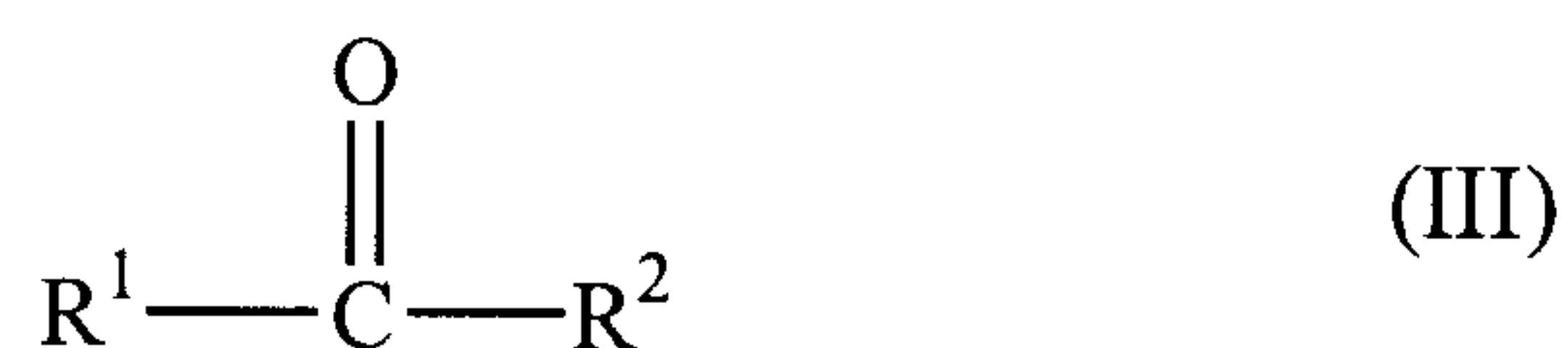
wherein Ra represent a linear hydrocarbon group containing 1 to 10 carbon atoms, a mono-, bi- or tri-cyclic hydrocarbon group containing 3 to 14 carbon atoms, an aryl group, a heterocyclic group containing 2 to 13 carbon atoms and 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur atoms, or a ferrocenyl group, Rb represents a hydrogen atom, a linear hydrocarbon group containing 1 to 10 carbon atoms, a mono-, bi- or tri-cyclic hydrocarbon group containing 3 to 14 carbon atoms, an aryl group, a heterocyclic group containing 2 to 13 carbon atoms and 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur atoms, or a ferrocenyl group, or Ra and Rb are bonded together to form a ring containing 5 to 10 carbon atoms, W₁ represents oxygen atom, N--H, N--Rc, N--OH or N--O--Rd; and Rc and Rd represent the same hydrocarbon group or heterocyclic group as described above, W₁ represents an oxygen atom, N-H, N-Rc, N-OH or N-O-Rd, and Rc and Rd independently represent a linear hydrocarbon group containing 1 to 10 carbon atoms, a mono-, bi- or tri-cyclic hydrocarbon group containing 3 to 14 carbon atoms, or a heterocyclic group containing 2 to 13 carbon atoms and 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur atoms, to a transfer-type asymmetric reduction in the presence of a transition metal complex and an optically active nitrogen-containing compound or a transition metal complex with an optically active nitrogen-containing compound as an asymmetric ligand, along with a hydrogen-donating organic or inorganic compound, to produce an optically active compound having formula (II):



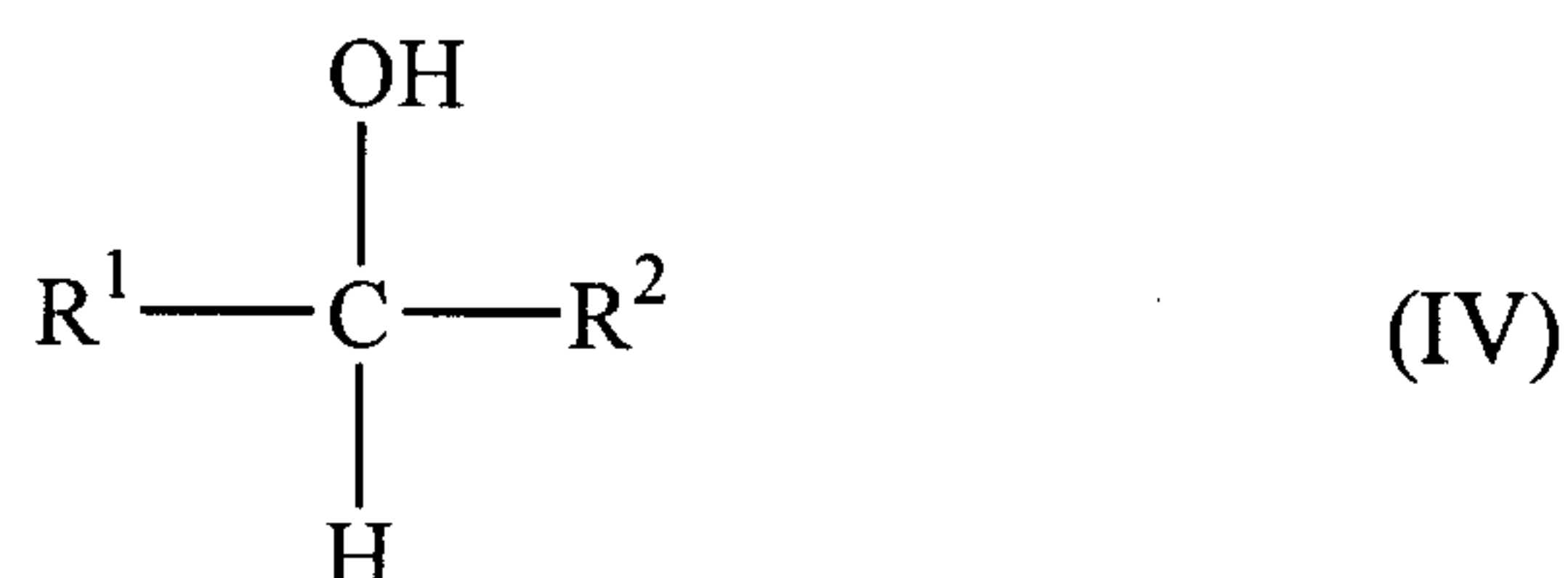
wherein Ra and Rb are as defined above, W₂ represents OH, NH₂, NH-Rc, NH-OH or NH-O-Rd, and Rc and Rd are as defined above.

2. A method according to claim 1, wherein the hydrogen transfer-type reduction is carried out in the presence of a base.

3. A method according to claim 1, for producing optically active alcohols, comprising asymmetrically reducing a carbonyl having formula (III):



wherein R¹ represents an aryl group, a saturated or unsaturated aliphatic hydrocarbon group containing 1 to 10 carbon atoms, a saturated or unsaturated mono-, bi- or tri-cyclic aliphatic hydrocarbon group containing 3 to 10 carbon atoms, a heterocyclic group containing 2 to 13 carbon atoms and 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur atoms, or a ferrocenyl group, R² represents a hydrogen atom, a saturated or unsaturated aliphatic hydrocarbon group containing 1 to 10 carbon atoms, a saturated or unsaturated mono-, bi- or tri-cyclic aliphatic hydrocarbon group containing 3 to 10 carbon atoms, an aryl group, or a heterocyclic group as defined above; or R¹ and R² are bonded together to form a ring containing 5 to 10 carbon atoms, to produce an optically active alcohol having formula (IV):



wherein R^1 and R^2 are as defined above.

4. A method according to claim 1 for producing optically active amines, comprising asymmetrically reducing an imine compound having formula (V):



wherein R^3 represents an aryl group, a saturated or unsaturated aliphatic hydrocarbon group containing 1 to 10 carbon atoms, a saturated or unsaturated mono-, bi- or tri-cyclic aliphatic hydrocarbon group containing 3 to 10 carbon atoms, a heterocyclic group containing 2 to 13 carbon atoms and 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur atoms, or a ferrocenyl group, R^4 represents a hydrogen atom, a saturated or unsaturated aliphatic hydrocarbon group containing 1 to 10 carbon atoms, a saturated or unsaturated mono-, bi- or tri-cyclic aliphatic hydrocarbon group containing 3 to 10 carbon atoms, an aryl group, or a heterocyclic group as defined above; R^5 represents a hydrogen atom, a saturated or unsaturated hydrocarbon group containing 1 to 10 carbon atoms, a saturated or unsaturated mono-, bi- or tri-cyclic aliphatic hydrocarbon group containing 3 to 10 carbon atoms, an aryl group, or a heterocyclic group as defined above, the hydrocarbon group or heterocyclic group being optionally bonded together via a hydroxyl group or an oxygen atom, or R^3 and R^4 , R^3 and R^5 or R^4 and R^5 are bonded together to form a ring containing 5 to 10 carbon atoms, to produce an optically active amine having formula (VI):



wherein R^3 , R^4 and R^5 are as defined above.

5. A method according to claim 1, wherein the transition metal catalyst is a complex of a transition metal of Group VIII.

6. A method according to claim 5, wherein the metal complex has formula:

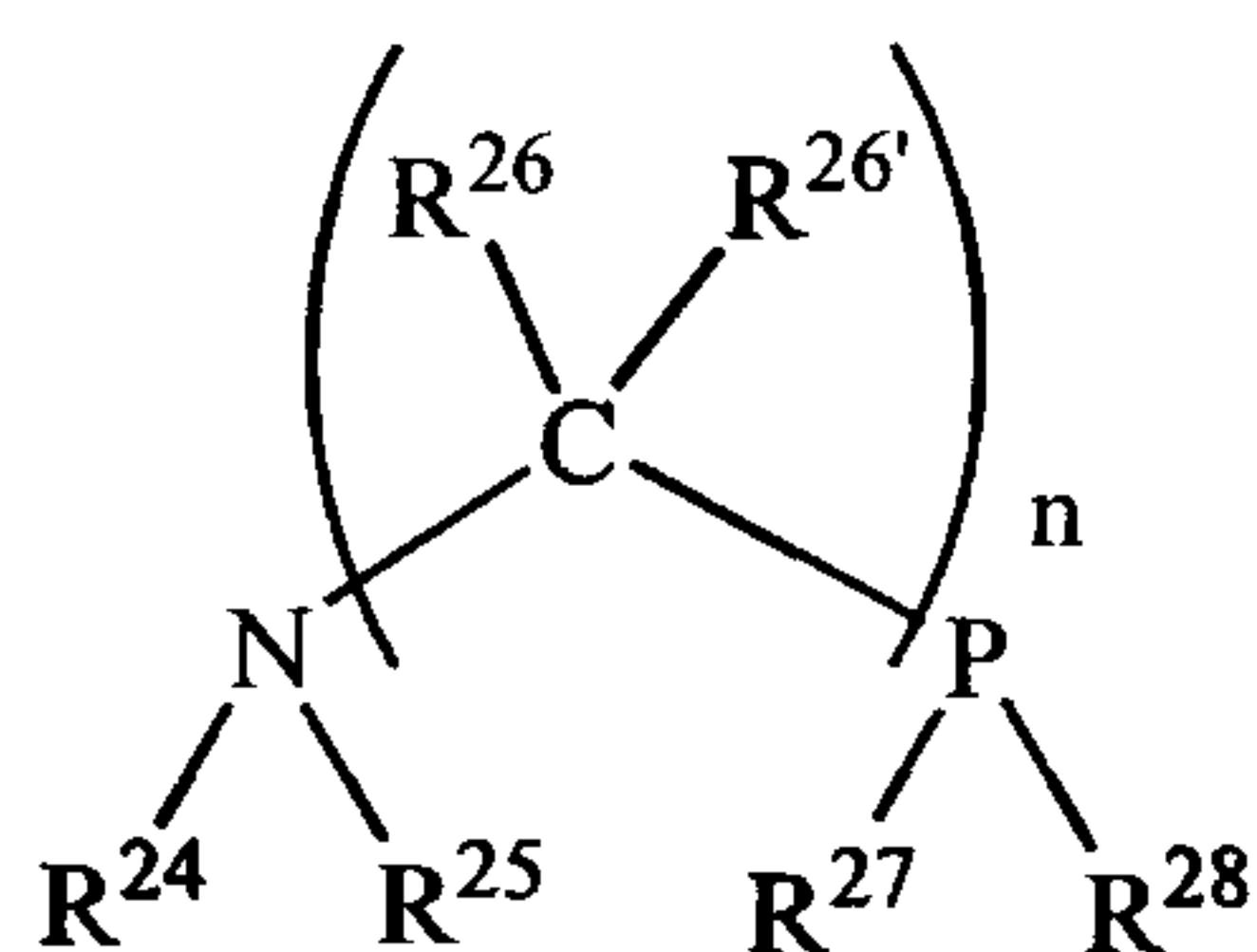
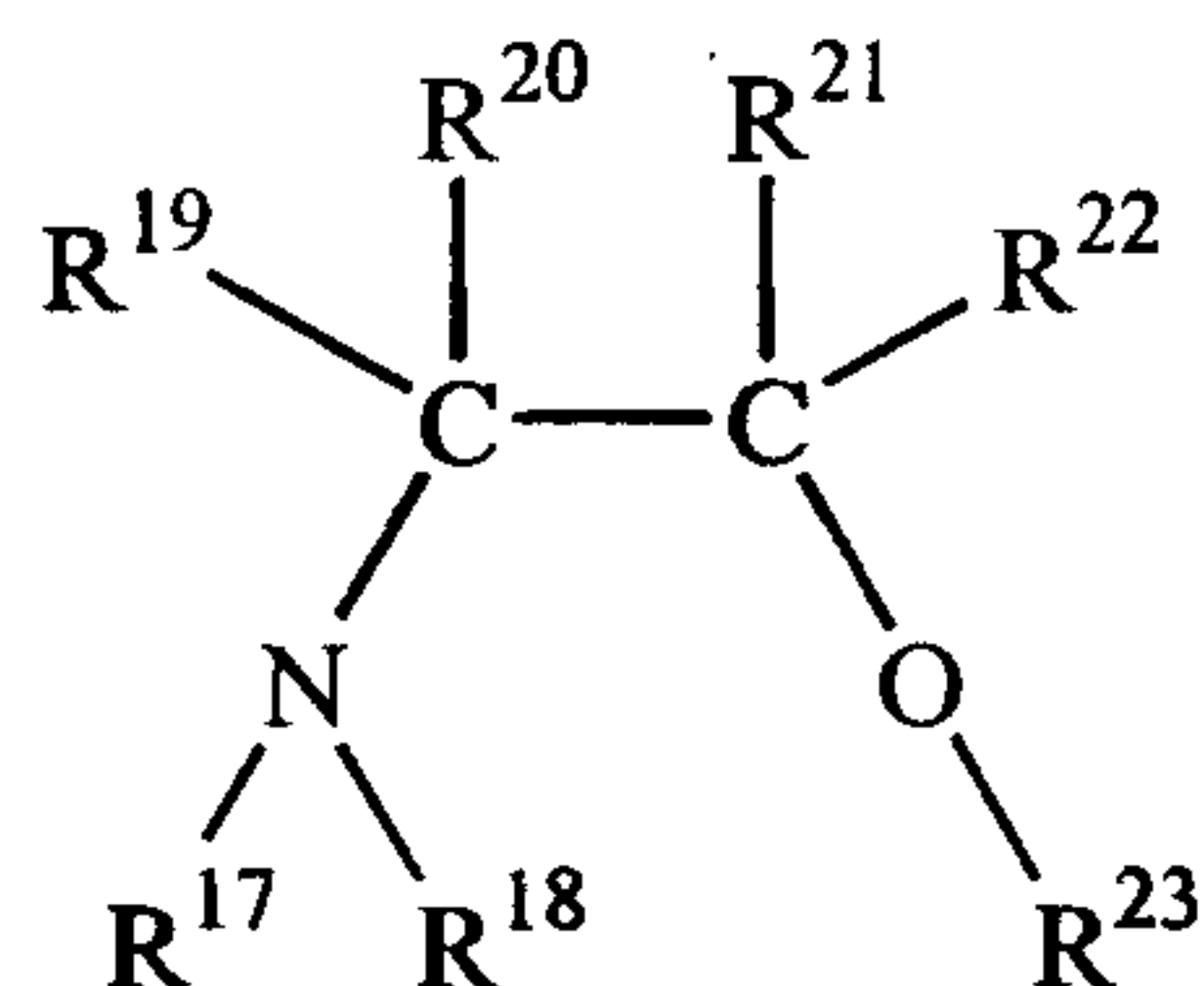
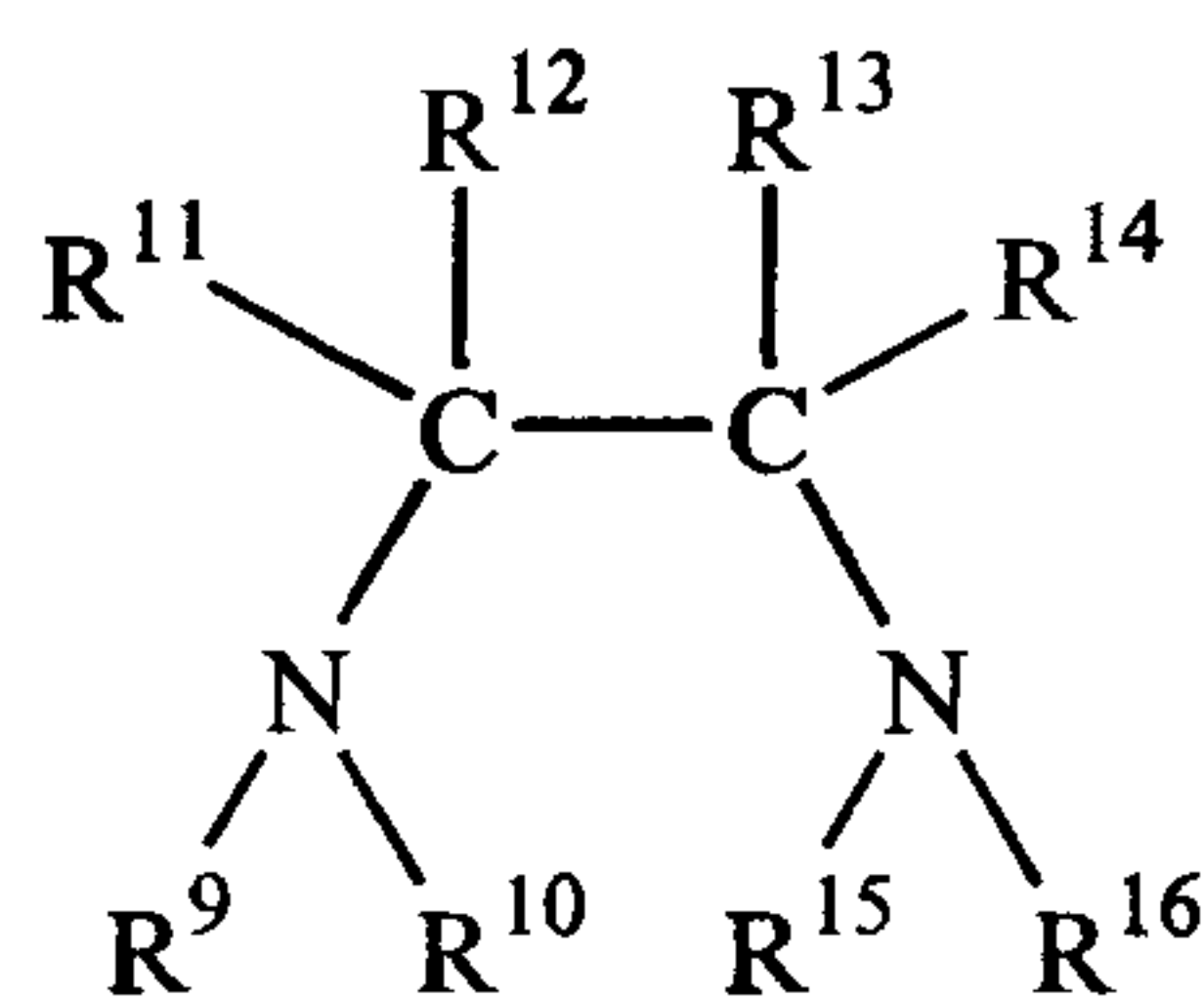


wherein M represents a transition metal of Group VIII, X represents a hydrogen atom, a halogen atom, a carboxyl group, a hydroxy group or an alkoxy group containing 1 to 6 carbon atoms, L represents a neutral ligand and m and n represent an integer ranging from 1 to 4.

7. A method according to claim 6, wherein M represents iron, cobalt, nickel, ruthenium, rhodium, iridium, osmium, palladium or platinum.

8. A method according to claim 7, wherein M represents ruthenium.

9. A method according to claim 1, wherein the optically active nitrogen-containing compound is an optically active amine derivative having any one of the following formulas:

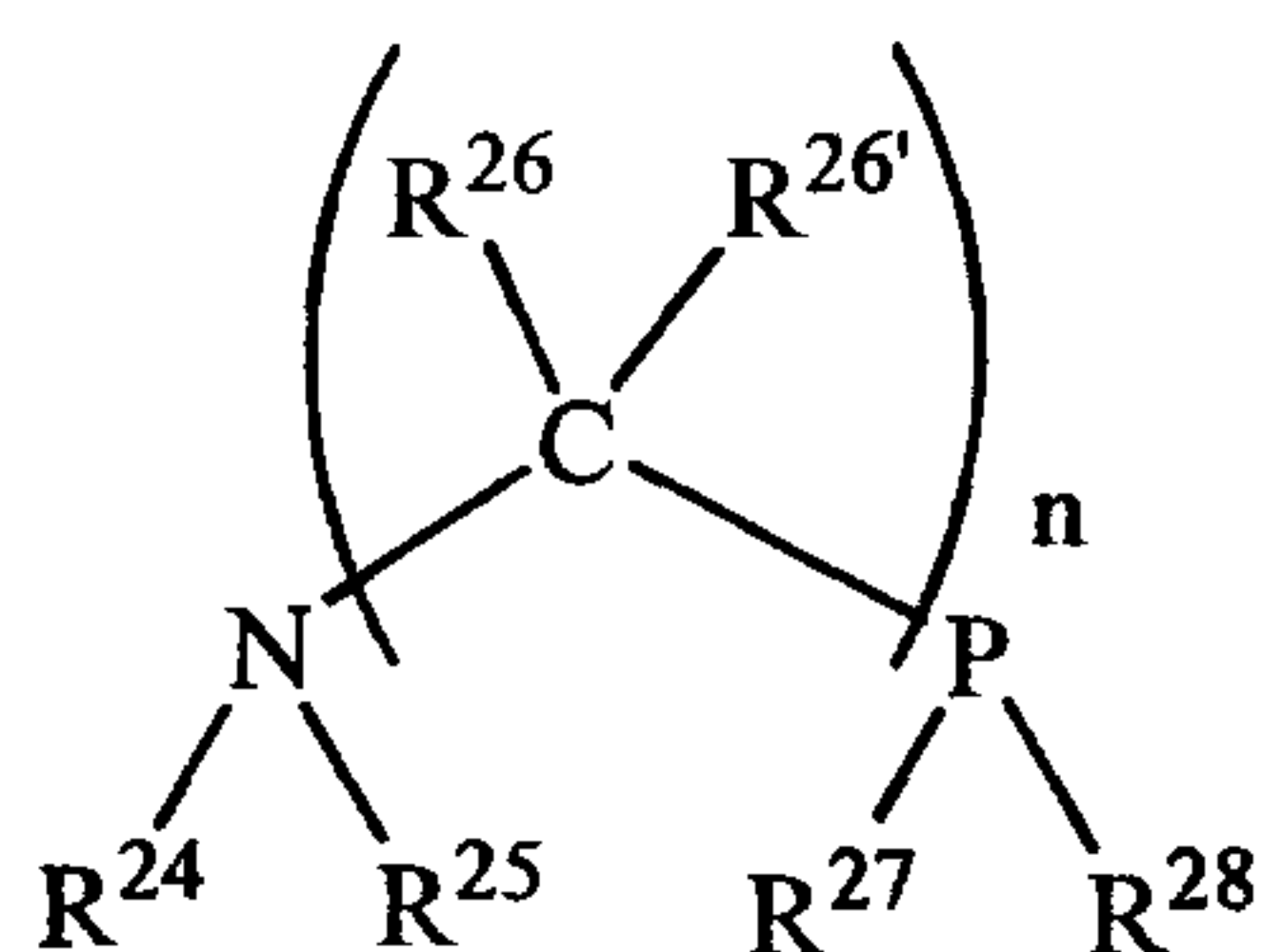
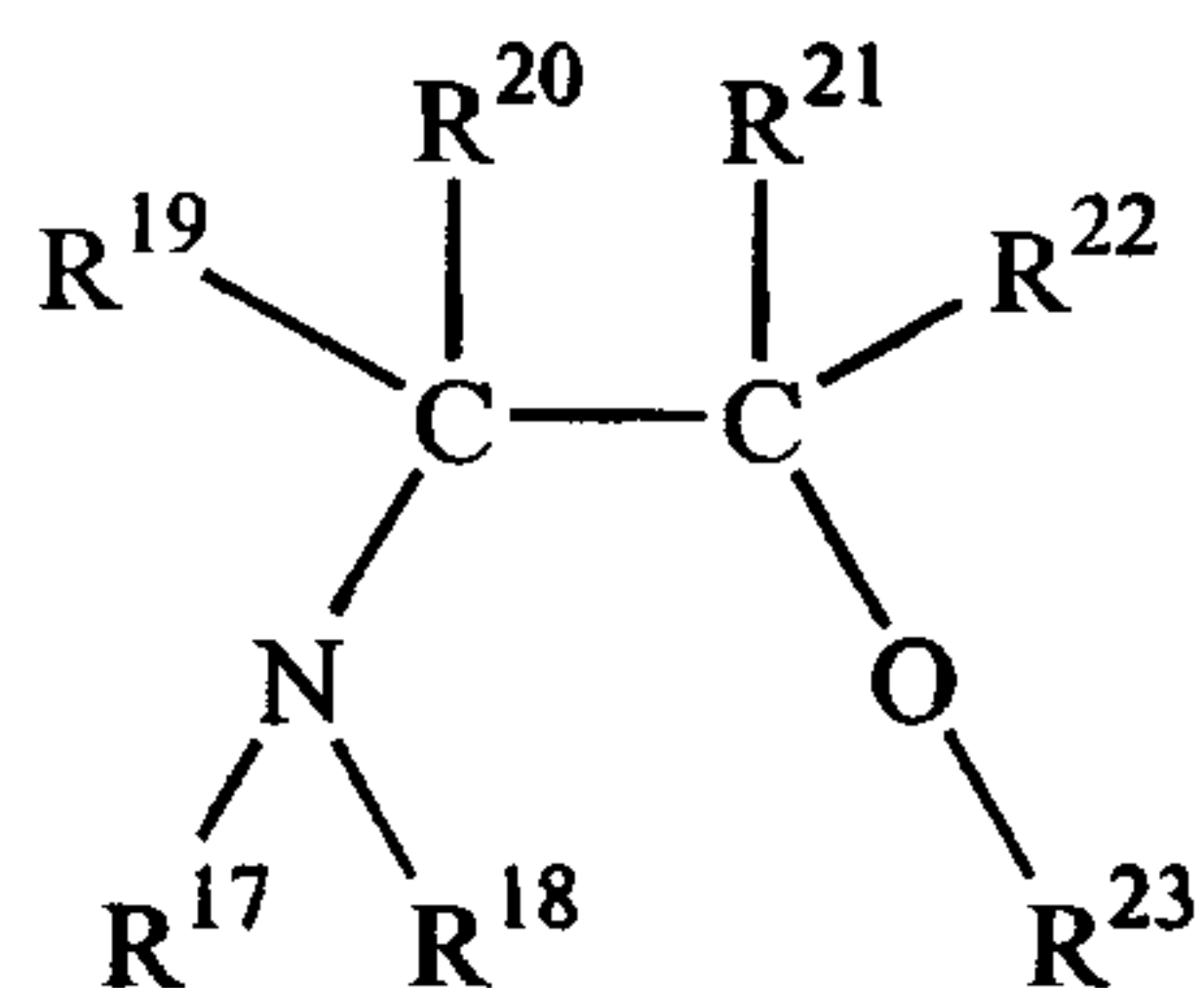
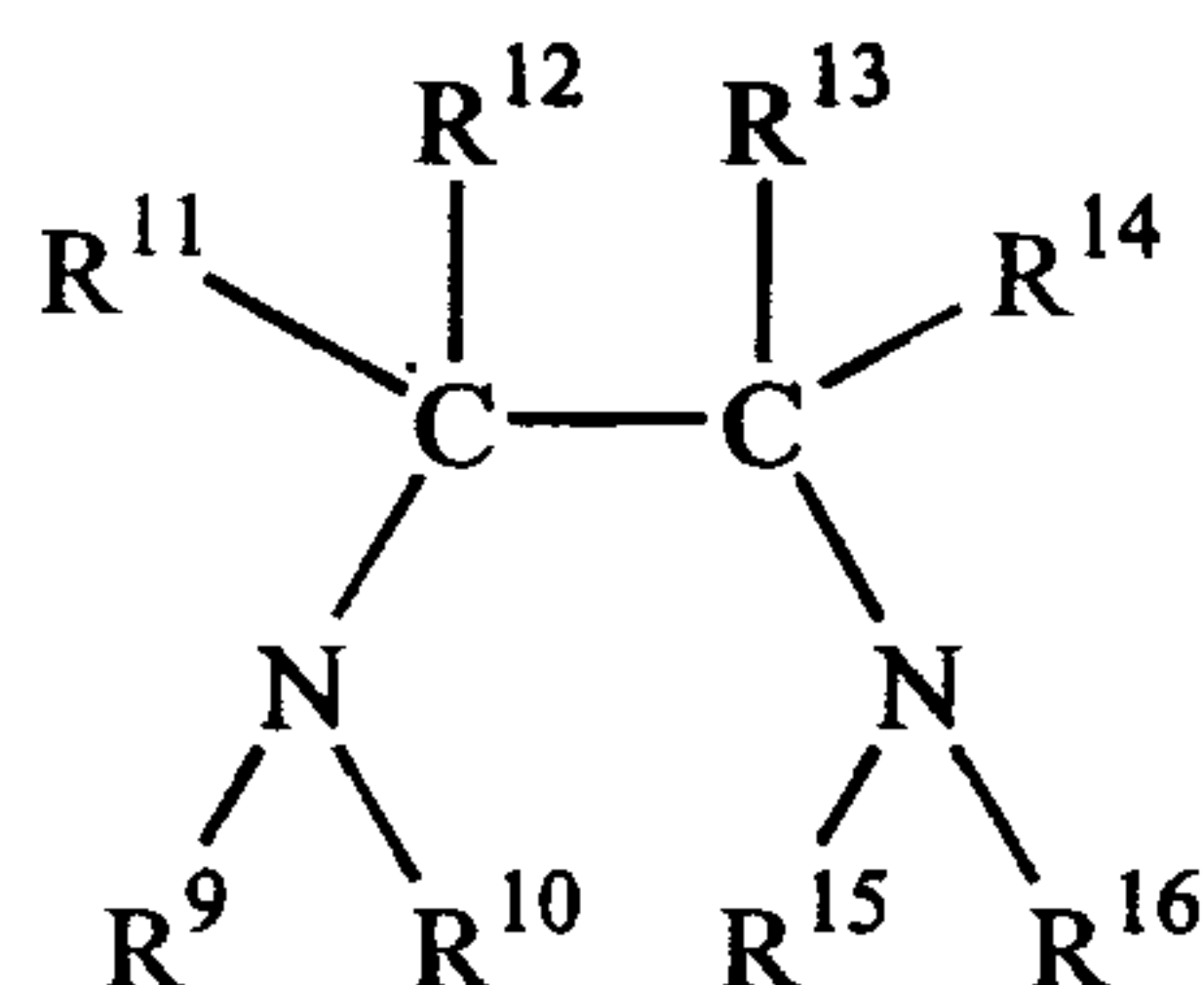


wherein R^9 , R^{10} , R^{15} and R^{16} independently represent a hydrogen atom, a saturated or unsaturated hydrocarbon group containing 1 to 10 carbon atoms, a urethane group or a sulfonyl group; R^{11} , R^{12} , R^{13} and R^{14} independently represent a hydrogen atom, an aryl group, a saturated or unsaturated aliphatic hydrocarbon group containing 1 to 10 carbon atoms, a saturated or unsaturated mono-, bi- or tri-cyclic aliphatic hydrocarbon group containing 3 to 10 carbon atoms; any one of R^{11} and R^{12} or any one of R^{13} and R^{14} being optionally bonded together to form a ring containing 5 to 10 carbon atoms; at least one of R^{17} and R^{18} is a hydrogen atom, and the other of R^{17} and R^{18} is a hydrogen atom, a saturated or unsaturated hydrocarbon group containing 1 to 10 carbon atoms, a urethane group or a sulfonyl group; R^{19} , R^{20} , R^{21} and R^{22}

independently represent a hydrogen atom, an aryl group, a saturated or unsaturated aliphatic hydrocarbon group containing 1 to 10 carbon atoms, a saturated or unsaturated mono-, bi- or tri-cyclic aliphatic hydrocarbon group containing 3 to 10 carbon atoms; R^{23} represents a hydrogen atom, an aryl group, a saturated or unsaturated aliphatic hydrocarbon group containing 1 to 10 carbon atoms, a saturated or unsaturated mono-, bi- or tri-cyclic aliphatic hydrocarbon group containing 3 to 10 carbon atoms; any one of R^{19} and R^{20} and any one of R^{21} and R^{22} being optionally bonded together to form a ring containing 5 to 10 carbon atoms or any one of R^{17} and R^{18} and any one of R^{20} and R^{21} being optionally bonded together to form a ring containing 5 to 10 carbon atoms; R^{24} and R^{25} are independently a hydrogen atom, a saturated or unsaturated hydrocarbon group containing 1 to 10 carbon atoms, a urethane group, a sulfonyl group or an acyl group; R^{26} and $R^{26'}$ independently represent a hydrogen atom, an aryl group, a saturated or unsaturated hydrocarbon group containing 1 to 10 carbon atoms, a saturated or unsaturated mono-, bi- or tri-cyclic hydrocarbon group containing 3 to 10 carbon atoms; R^{27} and R^{28} independently represent a hydrogen atom, or a saturated or unsaturated hydrocarbon group containing 1 to 10 carbon atoms, and n is an integer ranging from 1 to 4; and

wherein the carbon atom bearing R^{11}, R^{12} or R^{13}, R^{14} or R^{19}, R^{20} or R^{21}, R^{22} or $R^{26}, R^{26'}$ optionally occupies an asymmetric center.

10. A method according to claim 1, wherein the transition metal catalyst with an optically active nitrogen-containing compound as an asymmetric ligand is a metal complex of a transition metal of Group VIII and wherein the asymmetric ligand is an optically active amine derivative having any one of the following formulas:



wherein R^9 , R^{10} , R^{15} and R^{16} independently represent a hydrogen atom, a saturated or unsaturated hydrocarbon group containing 1 to 10 carbon atoms, a urethane group or a sulfonyl group; R^{11} , R^{12} , R^{13} and R^{14} independently represent a hydrogen atom, an aryl group, a saturated or unsaturated aliphatic hydrocarbon group containing 1 to 10 carbon atoms, a saturated or unsaturated mono-, bi- or tri-cyclic aliphatic hydrocarbon group containing 3 to 10 carbon atoms; any one of R^{11} and R^{12} or any one of R^{13} and R^{14} being optionally bonded together to form a ring containing 5 to 10 carbon atoms; at least one of R^{17} and R^{18} is a hydrogen atom, and the other of R^{17} and R^{18} is a hydrogen atom, a saturated or unsaturated hydrocarbon group containing 1 to 10 carbon atoms, a urethane group or a sulfonyl group; R^{19} , R^{20} , R^{21} and R^{22} independently represent a hydrogen atom, an aryl group, a saturated or unsaturated aliphatic hydrocarbon group containing 1 to 10 carbon atoms, a

saturated or unsaturated mono-, bi- or tri-cyclic aliphatic hydrocarbon group containing 3 to 10 carbon atoms; R^{23} represents a hydrogen atom, an aryl group, a saturated or unsaturated aliphatic hydrocarbon group containing 1 to 10 carbon atoms, a saturated or unsaturated mono-, bi- or tri-cyclic aliphatic hydrocarbon group containing 3 to 10 carbon atoms; any one of R^{19} and R^{20} and any one of R^{21} and R^{22} being optionally bonded together to form a ring containing 5 to 10 carbon atoms or any one of R^{17} and R^{18} and any one of R^{20} and R^{21} being optionally bonded together to form a ring containing 5 to 10 carbon atoms; R^{24} and R^{25} are independently a hydrogen atom, a saturated or unsaturated hydrocarbon group containing 1 to 10 carbon atoms, a urethane group, a sulfonyl group or an acyl group; R^{26} and $R^{26'}$ independently represent a hydrogen atom, an aryl group, a saturated or unsaturated hydrocarbon group containing 1 to 10 carbon atoms, a saturated or unsaturated mono-, bi- or tri-cyclic hydrocarbon group containing 3 to 10 carbon atoms; R^{27} and R^{28} independently represent a hydrogen atom, or a saturated or unsaturated hydrocarbon group containing 1 to 10 carbon atoms, and n is an integer ranging from 1 to 4; and

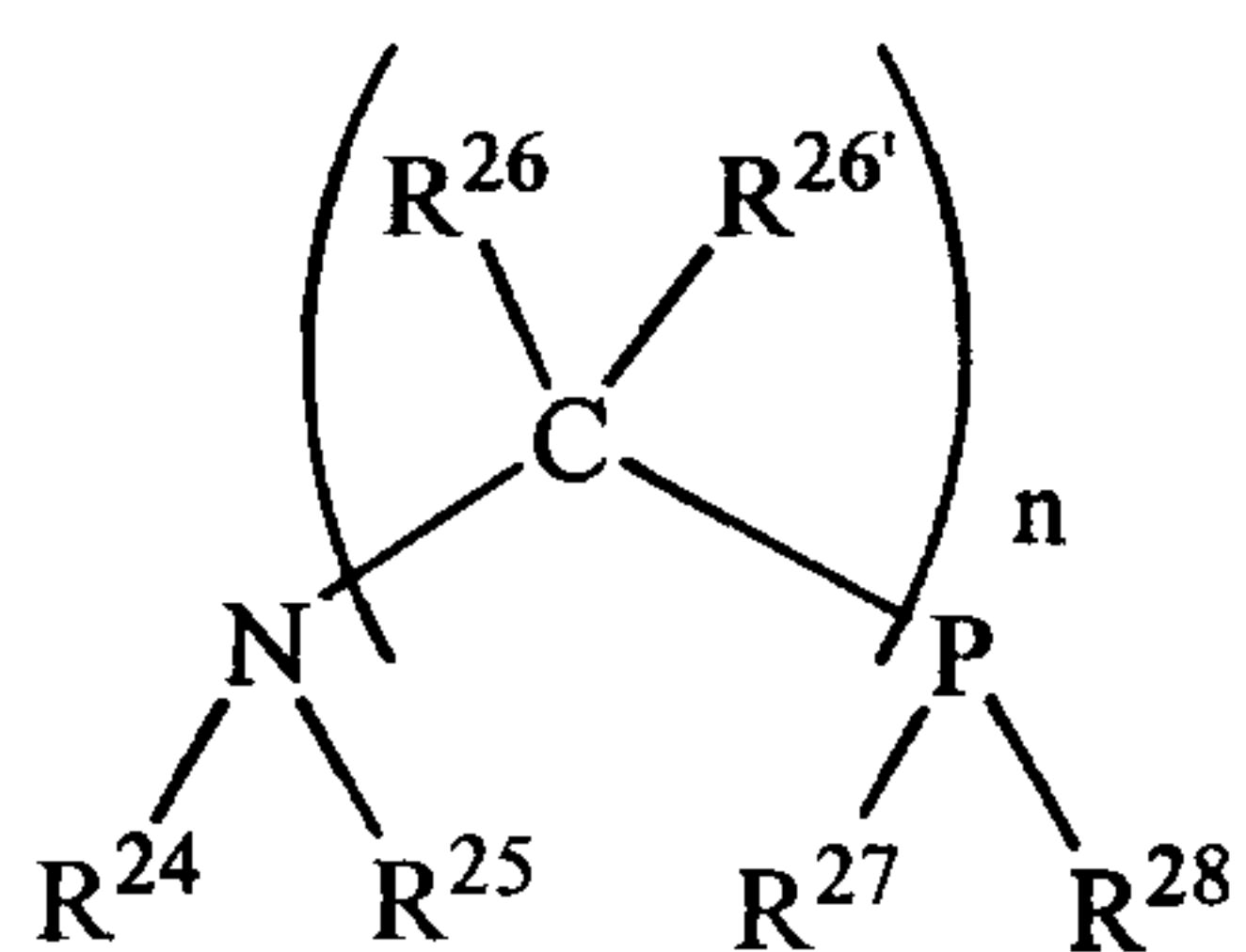
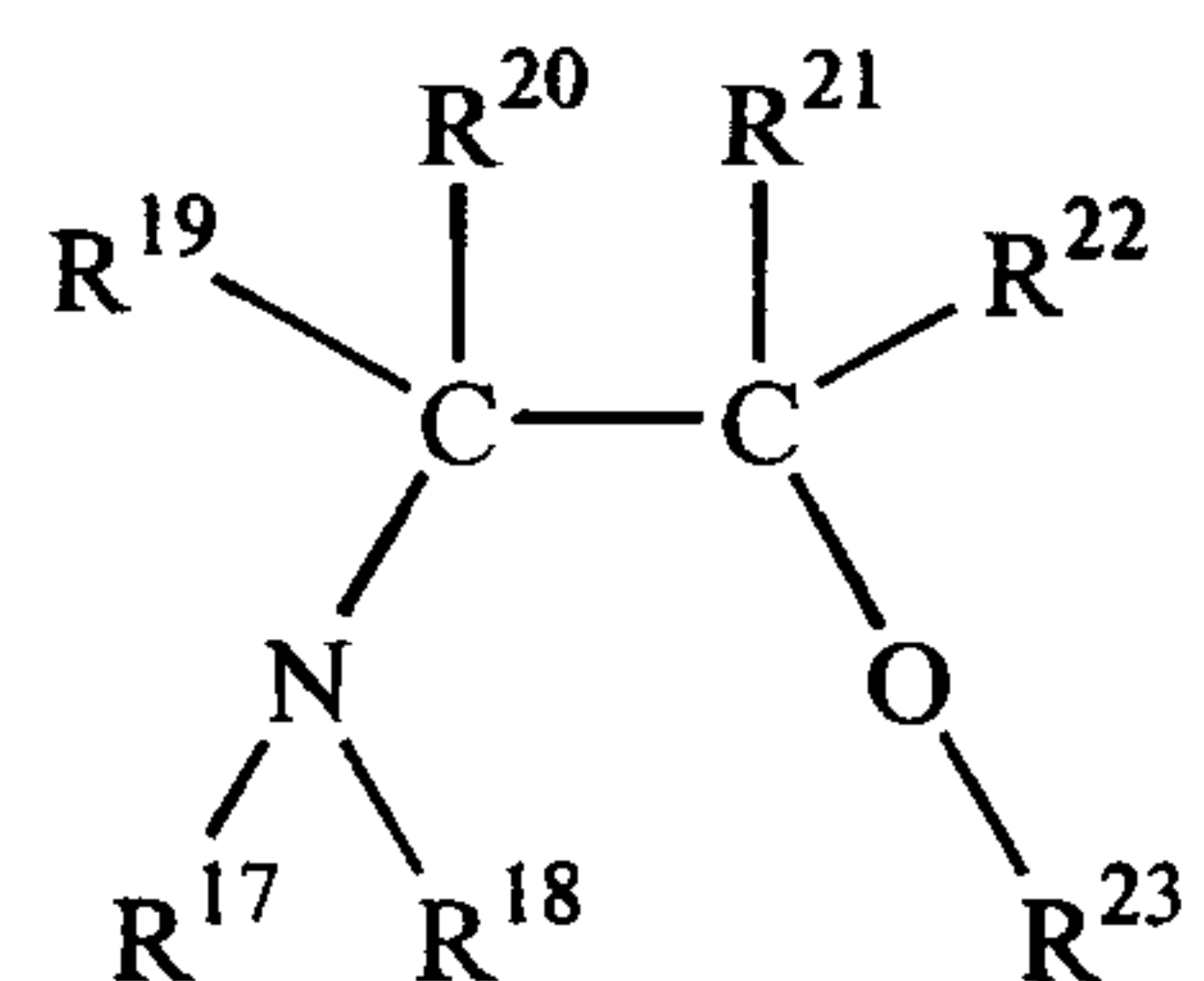
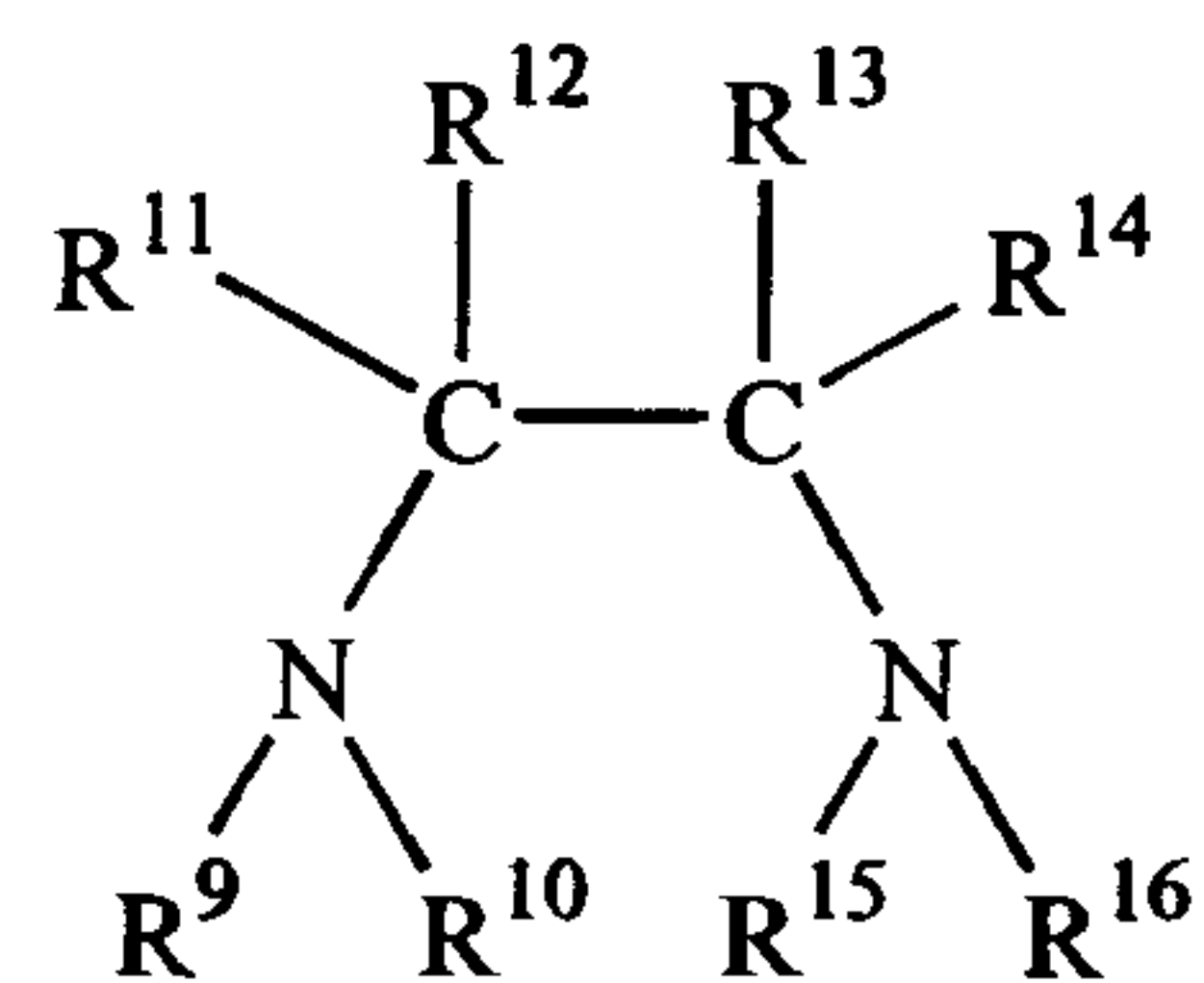
wherein the carbon atom bearing R^{11}, R^{12} or R^{13}, R^{14} or R^{19}, R^{20} or R^{21}, R^{22} or $R^{26}, R^{26'}$ optionally occupies an asymmetric center.

11. A method according to claim 10, wherein the transition metal is ruthenium.

12. A method according to claim 1, wherein the hydrogen-donating organic or inorganic compound is selected from the group consisting of alcohols containing 1 to 10 carbon atoms, formic acid, formate salts, unsaturated hydrocarbon compounds containing 5 to 10 carbon atoms, heterocyclic compounds containing 2 to 13 carbon atoms and 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur atoms, hydroquinone and phosphorous acid.

13. A method according to claim 2, wherein the base is an alkali metal or alkali earth metal hydroxide, an alkali metal or alkali earth metal salt or a quaternary ammonium salt.

14. An optically active catalyst composed of a transition metal catalyst and an optically active amine derivative having any one of the following formulas:



wherein R^9 , R^{10} , R^{15} and R^{16} independently represent a hydrogen atom, a saturated or unsaturated hydrocarbon group containing 1 to 10 carbon atoms, a urethane group or a sulfonyl group; R^{11} , R^{12} , R^{13} and R^{14} independently represent a hydrogen atom, an aryl group, a saturated or unsaturated aliphatic hydrocarbon group containing 1 to 10 carbon atoms, a saturated or unsaturated

mono-, bi- or tri-cyclic aliphatic hydrocarbon group containing 3 to 10 carbon atoms; any one of R^{11} and R^{12} or any one of R^{13} and R^{14} being optionally bonded together to form a ring containing 5 to 10 carbon atoms; at least one of R^{17} and R^{18} is a hydrogen atom, and the other of R^{17} and R^{18} is a hydrogen atom, a saturated or unsaturated hydrocarbon group containing 1 to 10 carbon atoms, a urethane group or a sulfonyl group; R^{19} , R^{20} , R^{21} and R^{22} independently represent a hydrogen atom, an aryl group, a saturated or unsaturated aliphatic hydrocarbon group containing 1 to 10 carbon atoms, a saturated or unsaturated mono-, bi- or tri-cyclic aliphatic hydrocarbon group containing 3 to 10 carbon atoms; R^{23} represents a hydrogen atom, an aryl group, a saturated or unsaturated aliphatic hydrocarbon group containing 1 to 10 carbon atoms, a saturated or unsaturated mono-, bi- or tri-cyclic aliphatic hydrocarbon group containing 3 to 10 carbon atoms; any one of R^{19} and R^{20} and any one of R^{21} and R^{22} being optionally bonded together to form a ring containing 5 to 10 carbon atoms or any one of R^{17} and R^{18} and any one of R^{20} and R^{21} being optionally bonded together to form a ring containing 5 to 10 carbon atoms; R^{24} and R^{25} are independently a hydrogen atom, a saturated or unsaturated hydrocarbon group containing 1 to 10 carbon atoms, a urethane group, a sulfonyl group or an acyl group; R^{26} and $R^{26'}$ independently represent a hydrogen atom, an aryl group, a saturated or unsaturated hydrocarbon group containing 1 to 10 carbon atoms, a saturated or unsaturated mono-, bi- or tri-cyclic hydrocarbon group containing 3 to 10 carbon atoms; R^{27} and R^{28} independently represent a hydrogen atom, or a saturated or unsaturated hydrocarbon group containing 1 to 10 carbon atoms, and n is an integer ranging from 1 to 4; and

wherein the carbon atom bearing R^{11}, R^{12} or R^{13}, R^{14} or R^{19}, R^{20} or R^{21}, R^{22} or $R^{26}, R^{26'}$ optionally occupies an asymmetric center.

15. A catalyst according to claim 14, wherein the transition metal complex is a metal complex having formula:

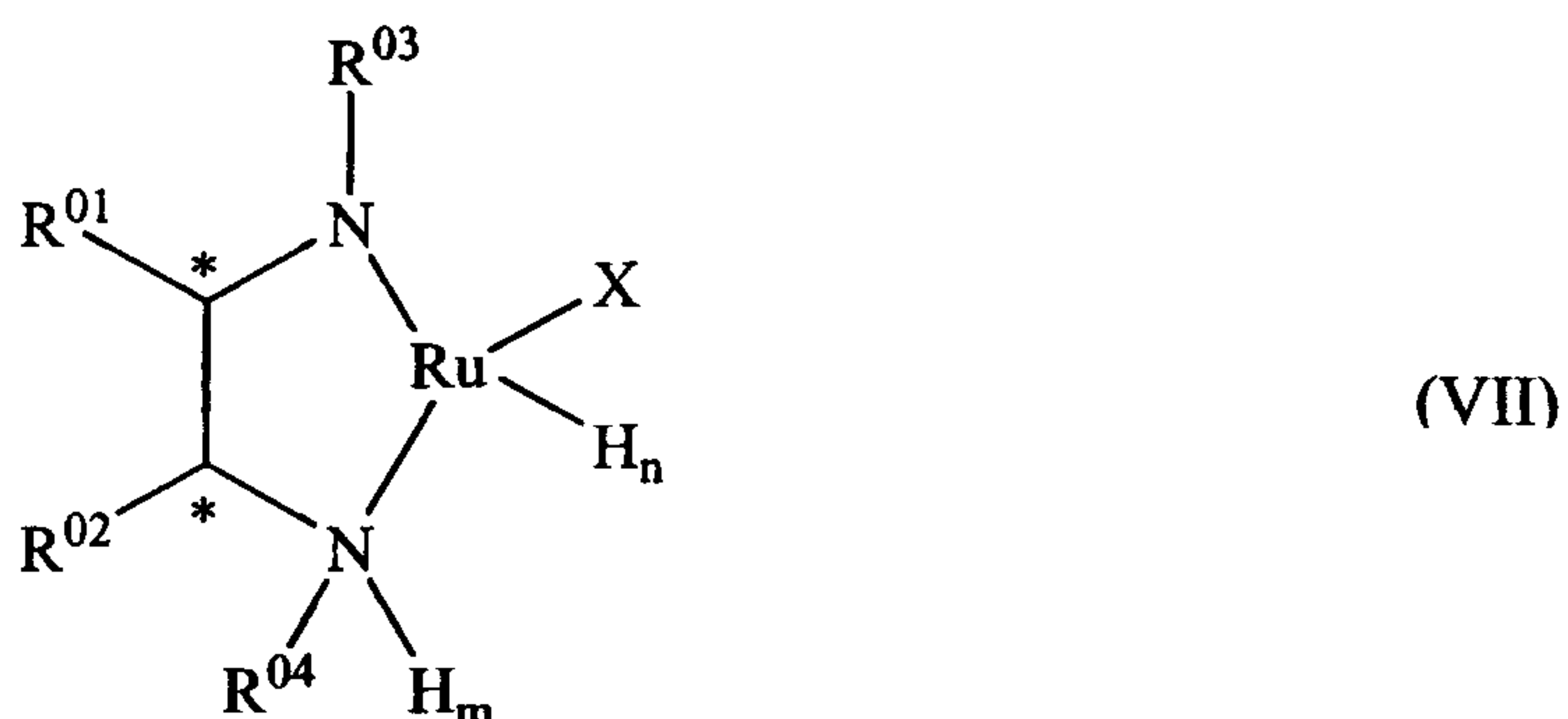


wherein M represents a transition metal of Group VIII, X represents a hydrogen atom, a halogen atom, a carboxyl group, a hydroxy group or an alkoxy group containing 1 to 6 carbon atoms, L represents a neutral ligand and m and n represent an integer ranging from 1 to 4.

16. A catalyst according to claim 15, wherein M represents iron, cobalt, nickel, ruthenium, rhodium, iridium, osmium, palladium or platinum.

17. A catalyst according to claim 16, wherein the transition metal complex is a complex of a transition metal of Group VIII.

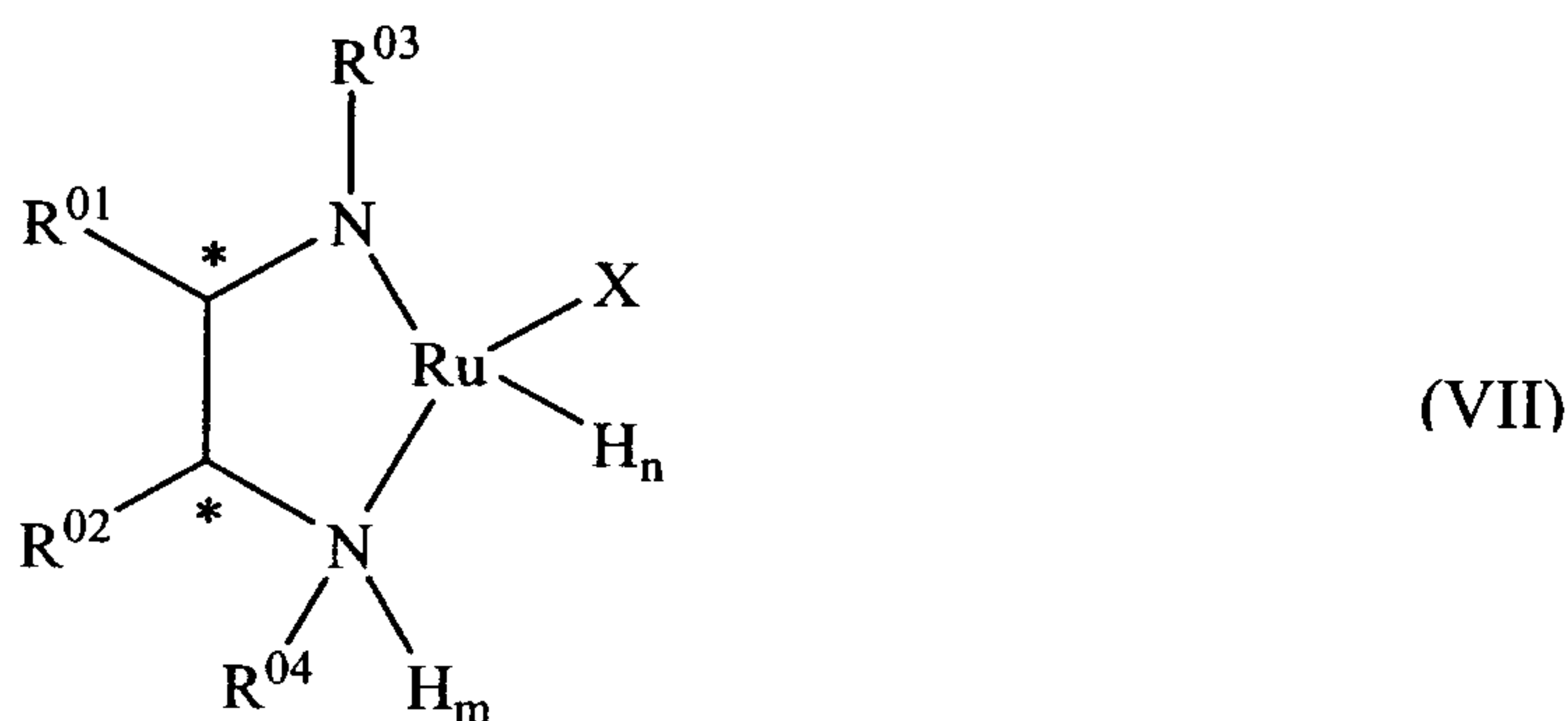
18. A catalyst according to claim 17, wherein the transition metal catalyst is an optically active ruthenium-diamine complex having formula (VII):



wherein * represents an asymmetric carbon atom; R^{01} and R^{02} independently represent an alkyl group containing 1 to 4 carbon atoms, a cycloalkyl group containing 5 or 6 carbon atoms or a phenyl group, or R^{01} and R^{02} together form an alicyclic ring containing 5 to 7 carbon atoms, the cycloalkyl, the phenyl group or the alicyclic ring being unsubstituted or substituted with an alkyl group containing 1 to 4 carbon atoms; R^{03} represents a methanesulfonyl group, a trifluoromethanesulfonyl group, a naphthylsulfonyl group, a camphor

sulfonyl group, a benzenesulfonyl group which is unsubstituted or substituted with a halogen atom or an alkyl or alkoxy group containing 1 to 3 carbon atoms, or a benzoyl group which is unsubstituted or substituted with an alkyl or alkoxycarbonyl group containing 1 to 4 carbon atoms; R^{04} represents a hydrogen atom or an alkyl group containing 1 to 4 carbon atoms; X represents an aryl group which is unsubstituted or substituted with an alkyl group containing 1 to 4 carbon atoms; and m and n together represent 0 or 1.

19. An optically active ruthenium-diamine complex having formula (VII):



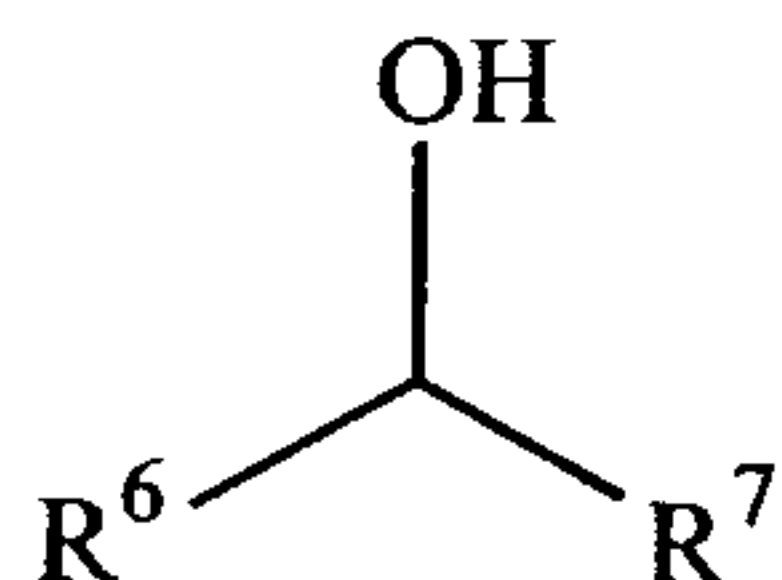
wherein * represents an asymmetric carbon atom; R^{01} and R^{02} independently represent an alkyl group containing 1 to 4 carbon atoms, a cycloalkyl group containing 5 or 6 carbon atoms or a phenyl group, or R^{01} and R^{02} together form an alicyclic ring containing 5 to 7 carbon atoms, the cycloalkyl, the phenyl group or the alicyclic ring being unsubstituted or substituted with an alkyl group containing 1 to 4 carbon atoms; R^{03} represents a methanesulfonyl group, a trifluoromethanesulfonyl group, a naphthylsulfonyl group, a camphor sulfonyl group, a benzenesulfonyl group which is unsubstituted or substituted with a halogen atom or an alkyl or alkoxy group containing 1 to 3 carbon atoms, or a benzoyl group which is unsubstituted or substituted with an alkyl or alkoxycarbonyl group containing 1 to 4 carbon atoms; R^{04} represents a hydrogen atom or an alkyl group containing 1 to 4 carbon atoms; X represents

an aryl group which is unsubstituted or substituted with an alkyl group containing 1 to 4 carbon atoms; and m and n together represent 0 or 1.

20. An optically active ruthenium-diamine complex according to claim 19, wherein R^{01} and R^{02} independently represent a phenyl group or together form an alicyclic ring containing 5 to 7 carbon atoms, the phenyl group or alicyclic ring being unsubstituted or substituted with an alkyl group containing 1 to 4 carbon atoms.

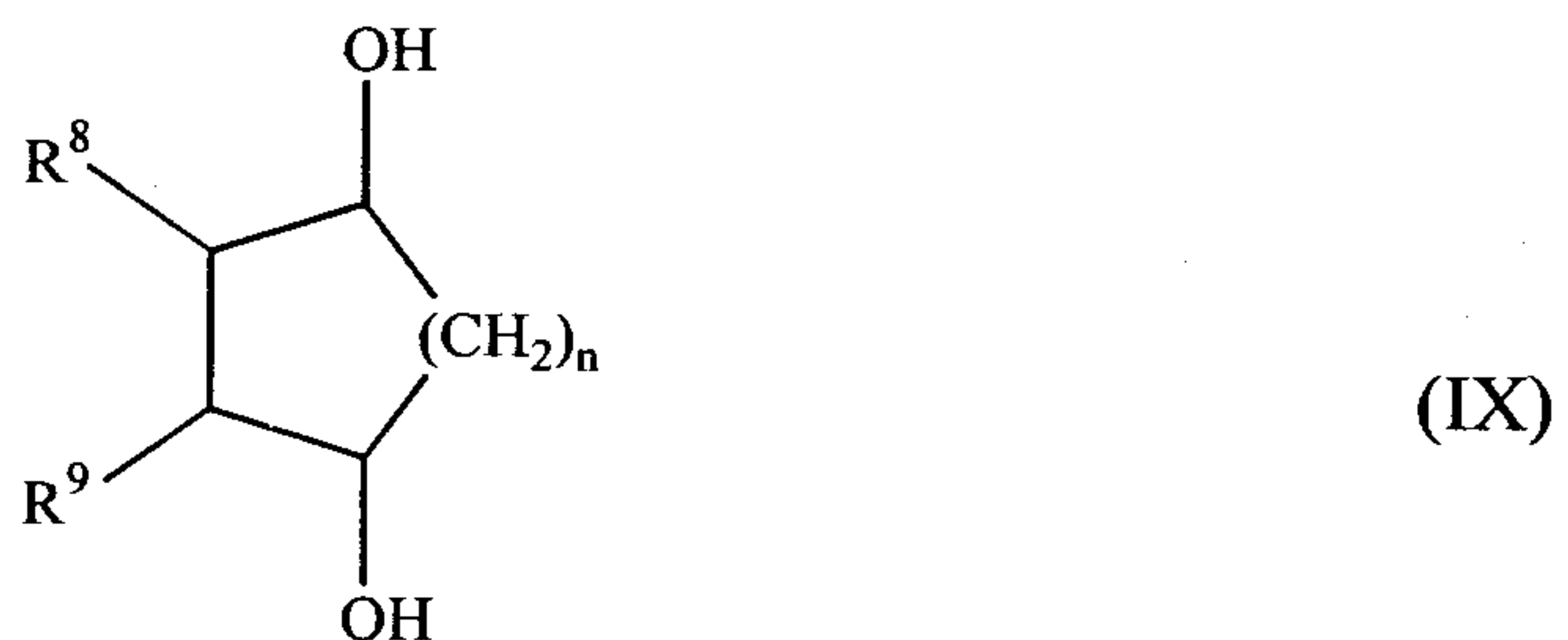
21. A method for producing an optically active secondary alcohol, comprising subjecting a racemic secondary alcohol or a meso-type diol to a hydrogen transfer reaction in the presence of an optically active ruthenium-diamine complex catalyst as defined in claim 18.

22. A method according to claim 21, wherein the racemic secondary alcohol has formula (VIII):



wherein R^6 represents an aromatic mono-, bi- or tri-cyclic hydrocarbon group containing 6 to 14 carbon atoms, a hetero mono-, bi- or tri-cyclic group containing 2 to 13 carbon atoms and 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur atoms, or a ferrocenyl group, and R^7 represents a hydrogen atom, a saturated or unsaturated hydrocarbon group containing 1 to 10 carbon atoms, or a functional group containing 1 to 3 hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur atoms, or R^6 and R^7 are bonded together to form a cyclic ketone containing 5 to 7 carbon atoms.

23. A method according to claim 21, wherein the meso-type diol has formula (IX):



wherein R^8 and R^9 independently represent a saturated or unsaturated hydrocarbon group containing 1 to 10 carbon atoms, or R^8 and R^9 are bonded together to form a saturated or unsaturated alicyclic group containing 5 to 7 carbon atoms, and n is 1 or 2.