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ance Notes on Codes and Abbreviations" appearing at the begin-
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(54) Title: 3-ALKYLATED-5,5',6,6',7,7',8,8'-OCTAHYDRO-2,2'-BINAPHTHOLS AND 3,3'-DIALKYLATED-
5,5',6,6',7,7',8,8'-OCTAHYDRO-2,2'-BINAPHTHOLS AND PROCESSES FOR MAKING THEM(57) Abstract: The compositions 3-alkylated-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol and 3,3'-dialkylated-5,5',6,6',7,7',8,8'-
octahydro-2,2'-binaphthol are disclosed, as well as various processes for making them, all involving the alkylation of
5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol.

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TITLE

3-ALKYLATED-5,5',6,6',7,7',8,8'-OCTAHYDRO-2,2'-
5 BINAPHTHOLS AND 3,3'-DIALKYLATED-5,5',6,6',7,7',8,8'-
OCTAHYDRO-2,2'-BINAPHTHOLS AND PROCESSES FOR MAKING THEM

FIELD OF THE INVENTION

This invention relates to the compositions 3-
10 alkylated-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthols
and certain 3,3'-dialkylated-5,5',6,6',7,7',8,8'-
octahydro-2,2'-binaphthols and to processes for making
3-alkylated-, and 3,3'-dialkylated-5,5',6,6',7,7',8,8'-
octahydro-2,2'-binaphthols, generally.

15

BACKGROUND OF THE INVENTION

Phosphorous-based ligands are useful as part of the
catalyst system in industrially important reactions such
as hydroformylation and hydrocyanation. The useful
20 ligands include phosphines, phosphinites, phosphonites,
and phosphites. See PCT patent applications WO 99/06146
and WO 99/62855. Both mono(phosphorous) ligands and
bis(phosphorous) ligands are utilized in the art.
Mono(phosphorous) ligands are compounds that contain a
25 single phosphorus atom which serves as a donor to a
transition metal, while bis(phosphorus) ligands, in
general, contain two phosphorus donor atoms and
typically form cyclic chelate structures with transition
metals.

30 Processes for the preparation of 3,3'-dialkyl-
5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthols, unlike
their 3-alkyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-
binaphthol analogs, appear in the literature. One such
process, disclosed in J. Chem. Soc., C 1971, 23, teaches

the preparation of 3,3'-di-t-butyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthols by the coupling of 3-t-butyl-5,6,7,8-tetrahydro-2-naphthol using potassium
5 ferricyanide and FeCl_3 -based methods with yields of only 25% and 6%, respectively. Also disclosed is the coupling of 3-t-butyl-5,6,7,8-tetrahydro-2-naphthol to give 3,3'-di-t-butyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol can be carried out with a large excess MnO_2
10 (20 times in weight).

Another process, disclosed in Acta Chem. Scand. 1970, 24, 580, teaches the coupling of 3,4-dimethyl-5,6,7,8-tetrahydro-2-naphthol to give 3,3',4,4'-tetramethyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-
15 binaphthol with 43% yield. J. Org. Chem. 1978, 43, 1930 discloses the preparation of 3,3'-dimethyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol by LiAlH_4 reduction of 3,3'-di(bromomethyl)-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol.

20 There has been no report in the prior art regarding acid catalyzed alkylation of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol to produce 3-alkyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthols or 3,3'-dialkyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthols.

25 Acid catalyzed alkylation of phenols is known. For example, U.S. Patent 4,912,264 discloses heteropoly acid catalyzed phenol and naphthol alkylation. U.S. Patent 2,733,274 discloses cresol sulfonic acid catalyzed phenol alkylation. J. Am. Chem. Soc., 1945, 67, 303
30 discloses aluminum chloride catalyzed phenol alkylation. Industrial and Engineering Chem., 1943, 35, 264 discloses sulfuric acid catalyzed phenol alkylation. Friedel-Crafts alkylation of aromatic compounds has also been reviewed. For example, see Olah, G. A. Friedel-

Crafts and Related Reactions, Wiley-Interscience: New York, 1964, Vol. II, part I, Roberts, R. *Friedel-Crafts Alkylation Chemistry*, Marcel Dekker, 1984, and March, J.

- 5 *Advanced Organic Chemistry*, 4th Edition, Wiley-Interscience: New York, 1992, pp 534-539.

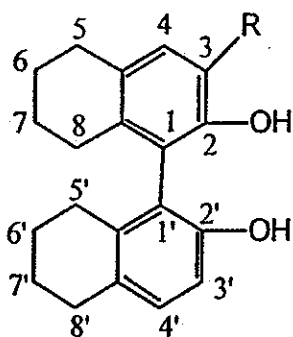
Recently, it was disclosed that rare earth metal trifluoromethanesulfonates as water-tolerant Lewis acid catalysts can be utilized in Friedel-Crafts alkylation
10 of benzene and phenol derivatives with secondary alkyl methanesulfonates. See SynLett, 1998, 255-256 and Synthesis, 1999, 603-606.

It is not practical to use LiAlH_4 , a large excess of MnO_2 , or even a stoichiometric amount of potassium
15 ferricyanide to carry out industrial scale preparations of alkylated, hydrogenated binaphthols. Such a process would be expected to generate a large amount of byproducts. Therefore, a need exists in the art for a practical and general method to prepare 3-alkylated-
20 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthols and 3,3'-dialkylated-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthols.

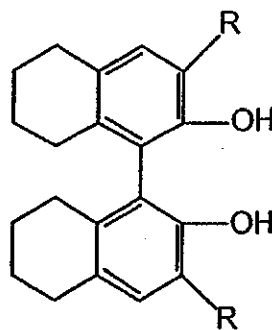
SUMMARY OF THE INVENTION

Disclosed herein, there may be provided 3-alkylated-5, 5', 6, 6', 7, 7', 8, 8'-

octahydro-2,2'-binaphthols of the formula (1) and 3,3'-dialkylated-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthols of the formula (2),

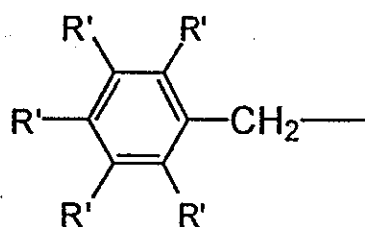


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wherein:

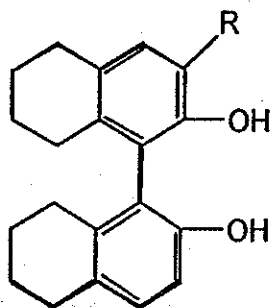


R is C₁ to C₂₀ alkyl, C₃ to C₂₀ cycloalkyl, or benzyl of the formula

wherein each R' is independently H, alkyl or cycloalkyl of up to 6 carbons; provided that in formula (2), when R is alkyl, the alkyl must be other than methyl or t-butyl.

In a first aspect, the present invention provides

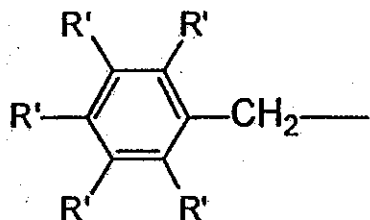
A compound of the formula



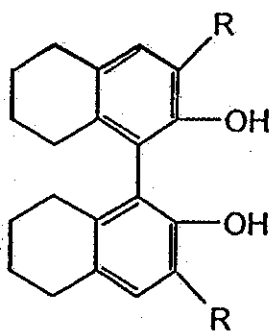
1

wherein:

R is C₁ to C₂₀ alkyl, C₃ to C₂₀ cycloalkyl, or benzyl of the formula

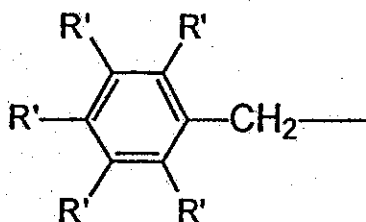


wherein each R' is independently H, alkyl or cycloalkyl of up to 6 carbons; and/or a compound of the formula



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wherein R is C₁ to C₂₀ alkyl other than methyl or t-butyl, C₃ to C₂₀ cycloalkyl, or benzyl of the formula



wherein each R' is independently H, alkyl or cycloalkyl of up to 6 carbons.

In a second aspect, the present invention provides a process for making 3-alkylated-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthols and 3,3'-dialkylated-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthols by contacting 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with at least one alkene or cycloalkene in the presence of an acid catalyst such as aluminum chloride, trifluoromethanesulfonic acid, tosylic acid, phosphotungstic acid, silicotungstic acid, phosphomolybdic acid, zirconium or aluminum triflate, polymeric perfluorinated sulfonic acid (such as the DuPont material sold as Nafion®) and polymeric sulfonic acid (such as the material sold by Aldrich as Amberlyst®)

15 ion-exchange resin or the material sold by Dow as Dowex 32®).

In a third aspect, the present invention provides a process for making 3-alkylated-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthols and 3,3'-dialkylated-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthols by contacting 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with benzyl halides or tertiary alkyl halides, wherein the halides are bromides or chlorides in the presence of a Lewis acid catalyst, such as aluminum chloride or zinc chloride.

In a 4th aspect, the present invention provides a process for making 3-alkylated-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthols and 3,3'-dialkylated-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthols by contacting 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with alkyl sulfonates,

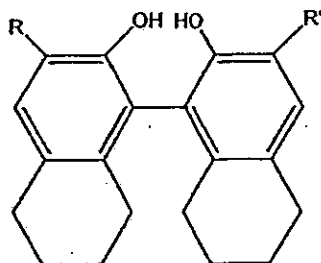
alkyl triflates, alkyl benzenesulfonates, or alkyl p-

toluenesulfonates in the presence of an acid catalyst

selected from the group consisting of aluminum chloride, tosylic acid, phosphotungstic acid, silicotungstic acid, phosphomolybdic acid, trifluoromethanesulfonic acid and a rare earth metal triflate selected from the group consisting of scandium trifluoromethanesulfonate, ytterbium trifluoromethanesulfonate, and lanthanum trifluoromethanesulfonate.

In a fifth aspect, the present invention provides a process for making 3-alkylated-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthols and 3,3'-dialkylated-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthols by contacting 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with benzyl alcohol, or secondary or tertiary alcohol containing from 3 to 20 carbon atoms, in the presence of an acid catalyst selected from the group consisting of aluminum chloride, trifluoromethanesulfonic acid, sulfuric acid, HF and phosphoric acid.

In a sixth aspect, the present invention provides a compound of the formula



5 wherein:

R is H; and

R' is ethyl, C₃ to C₆ secondary, tertiary, or cyclic alkyl;

or a compound of the above formula wherein

10 R and R' are the same and are selected from the group consisting of ethyl, C₃ to C₆ secondary or cyclic alkyl.

Preferred compounds are those wherein R and R' are the same are selected from the group consisting of
15 ethyl, isopropyl, cyclopentyl, and cyclohexyl.

DETAILED DESCRIPTION OF THE INVENTION

The alkylated 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthols of this invention may be prepared by
20 alkylation of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol in the presence of a catalyst, as shown below.

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disubstituted, tri-substituted, tetra-substituted or aryl-substituted alkenes are utilized as alkylating reagents. The alkylation reaction may be carried out
5 neat (without solvent) or in inert solvents such as nitromethane, methylene chloride, dichloroethane, chlorobenzene, dichlorobenzene, nitrobenzene or a combination of these solvents. Other solvents such as benzene, toluene, and xylene may also be used, but the
10 solvents may become alkylated. When the boiling point of the alkene is lower than the reaction temperature, the reaction may be carried out in an autoclave or by feeding the alkene at atmosphere pressure. The reaction may be carried out in an autoclave when the boiling
15 point of the solvent(s) is lower than the reaction temperature. A large excess of alkene over binaphthol gives double alkylated 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol, while about two equivalents or less of alkene (relative to 5,5',6,6',7,7',8,8'-octahydro-2,2'-
20 binaphthol) gives both mono and double alkylated 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthols.

The second process aspect of the present invention is a process for making alkylated 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol by the reaction of
25 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with benzyl halide or tertiary alkyl halide in the presence of a Lewis acid catalyst. Suitable catalysts include the following: aluminum chloride, zinc chloride, boron trichloride, SnCl_4 , SbCl_5 , and ZrCl_4 . Zinc chloride is
30 preferred. Suitable halides are bromides and chlorides. The reaction may be carried out at 0°C to 100°C , preferably at 20°C to 80°C . The alkylation reaction may be carried out in inert solvents such as nitromethane, methylene chloride, dichloroethane, chlorobenzene,

dichlorobenzene, nitrobenzene or a combination of these solvents. Other solvents such as benzene, toluene, and xylene may also be used, but the solvents may become alkylated. When tertiary alkyl halide is used as an alkylating reagent, the reaction is very selective towards mono-alkylated 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol even when several equivalents excess of tertiary alkyl halide are used. However, double alkylated 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol eventually is formed when a large excess of tertiary alkyl halide is used and the reaction is allowed to run at higher temperature and for longer time. When benzyl halide is used as an alkylating reagent, double benzylated 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol is formed when a large excess of benzyl halide relative to binaphthol is used, while one equivalent of the benzyl halide (relative to 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol) gives predominantly mono-benzylated 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthols.

The third process aspect of the present invention is a process for making alkylated 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol by the reaction of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with alkyl sulfonates such as alkyl methanesulfonates, alkyl triflates, alkyl p-toluenesulfonates, and alkyl benzenesulfonates in the presence of an acid catalyst. Suitable alkyl sulfonates are of the formula A-SO₃-B, wherein A is C₁ to C₈ alkyl, C₁ to C₈ fluorinated alkyl, C₆ to C₁₀ aryl, or C₆ to C₁₀ fluorinated aryl; and B is C₁ to C₂₀ alkyl. Suitable catalysts for alkylation of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with alkyl sulfonates include Lewis acids such as aluminum chloride

and boron trifluoride, as well as other acid catalysts such trifluoromethanesulfonic acid, tosylic acid, and rare earth metal triflates such as scandium

5 trifluoromethanesulfonate, ytterbium trifluoromethanesulfonate, or lanthanum trifluoromethanesulfonate. Trifluoromethanesulfonic acid and scandium trifluoromethanesulfonate are the preferred catalysts. Alkylation of 5,5',6,6',7,7',8,8'-octahydro-

10 2,2'-binaphthol may be carried out at 20°C to 220°C, preferably at 90°C to 180°C. The alkylation reaction may be carried out in inert solvents such as nitromethane, methylene chloride, carbon tetrachloride, dichloroethane, chlorobenzene, dichlorobenzene,

15 nitrobenzene or a combination of these solvents. Other solvents such as benzene, toluene, and xylene may also be used, but the solvents may become alkylated. The product of the reaction of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with alkyl sulfonates varies

20 depending on stoichiometry and alkylation reagent used. A large excess of alkyl sulfonate gives double alkylated 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol, while about 1.5 equivalents or less of alkyl sulfonate (relative to 5,5',6,6',7,7',8,8'-octahydro-2,2'-

25 binaphthol) gives predominately mono alkylated 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthols.

The fourth process aspect of the present invention is a process for making alkylated 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol by the reaction of

30 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with benzyl alcohol, secondary and tertiary alcohols containing 3 to 20 carbon atoms, in the presence of an acid catalyst. Suitable catalysts include the following: trifluoromethanesulfonic acid, tosylic acid,

aluminum chloride, phosphotungstic acid, silicotungstic acid, phosphomolybdic acid, polymeric perfluorinated sulfonic acid (such as Nafion®) and polymeric sulfonic acid (such as Amberlyst®15 ion-exchange resin and Dowex 32®). Trifluoromethanesulfonic acid is preferred. Alkylation of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with alcohols may be carried out at 20°C to 220°C, preferably at 90°C to 180°C. The alkylation reaction may be carried out in inert solvents such as nitromethane, methylene chloride, carbon tetrachloride, dichloroethane, chlorobenzene, dichlorobenzene, nitrobenzene or a combination of these solvents. Other solvents such as benzene, toluene, and xylene may also be used, but the solvents may become alkylated. The product of the reaction of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with alcohol varies depending on stoichiometry and alkylation reagent used. When tertiary alcohol is used as the alkylating agent, mono alkylated 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthols were obtained predominantly, even when several equivalents excess of tertiary alcohol was applied. A large excess of the secondary alcohol (relative to 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol) gave rise to both mono and double alkylated products.

Catalysts used in the processes of the present invention may be unsupported or supported. Suitable supports include silicon dioxide, zeolites, aluminosilicates, and polystyrene.

The compounds which are produced by the process of the present invention can be used as reactants to make phosphorous-containing ligands that are useful to make catalysts that, in turn, are useful in both

hydrocyanation and hydroformylation reactions.

Bidentate phosphite ligands are particularly useful.

Bidentate phosphite ligands can be prepared as
5 described in U.S. Patent 5,235,113 by contacting
phosphorochloridites with the compounds made by the
processes of the present invention. More recent U.S.
Patents 6,031,120 and 6,069,267, incorporated herein by
reference, describe selective synthesis of bidentate
10 phosphite ligands in which a phosphorochloridite is
prepared in-situ from phosphorus trichloride and a
phenol such as o-cresol and then treated in the same
reaction vessel with an aromatic diol to give the
bidentate phosphite ligand. The alkylated products of
15 the processes of the present invention can be
substituted for the aromatic diol in the above process.

The compounds made by the processes of the present
invention can be used to make polymeric ligands by a
process which comprises (1) reacting the compounds made
20 by the processes of the present invention with a benzyl
chloride containing polymer, in the presence of a Lewis
acid catalyst, and (2) reacting the product of step (1)
with at least one phosphorochloridite compound in the
presence of an organic base. Preferably the Lewis acid
25 catalyst is zinc chloride or aluminum chloride, and the
organic base is a trialkylamine.

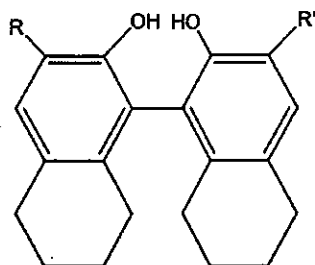
Two particularly important industrial catalytic
reactions using phosphorus-containing ligands are olefin
hydrocyanation and isomerization of branched nitriles to
30 linear nitriles. Phosphite ligands are particularly
useful for both reactions. The hydrocyanation of
unactivated and activated ethylenically unsaturated
compounds (olefins) using transition metal complexes
with monodentate and bidentate phosphite ligands is well

known. Bidentate phosphinite and phosphonite ligands are useful as part of a catalyst system for the hydrocyanation of ethylenically unsaturated compounds.

- 5 Bidentate phosphinite ligands are also useful as part of a catalyst system for the hydrocyanation of aromatic vinyl compounds.

Hydroformylation is another industrially useful process that utilizes catalysts made from phosphorus-containing ligands. The use of phosphine ligands, including diphosphines, is known for this purpose. The use of catalysts made from phosphite ligands is also known. Such catalysts usually contain a Group VIII metal. See for example, U.S. Patent 5,235,113, the disclosure of which is incorporated herein by reference.

The present invention also relates to compounds of the formula



wherein:

- 20 R is H; and

R' is ethyl, C₃ to C₆ secondary, tertiary, or cyclic alkyl;

or a compound of the above formula wherein

- R and R' are the same and are selected from the group consisting of ethyl, C₃ to C₆ secondary or cyclic alkyl.

Preferred compounds are those wherein R and R' are the same are selected from the group consisting of ethyl, isopropyl, cyclopentyl, and cyclohexyl.

EXAMPLES

The following non-limiting, representative examples
5 illustrate the processes and compositions of the present
invention.

Example 1

Synthesis of 3-isopropyl-5,5',6,6',7,7',8,8'-octahydro- 10 2,2'-binaphthol and 3,3'-diisopropyl- 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol

A mixture of 5,5',6,6',7,7',8,8'-octahydro-2,2'-
binaphthol (30.0 g), xylene (5 ml) and phosphotungstic
acid (1.5 g) was heated to 140°C. To the mixture was
15 added propylene (8.9 g) slowly via a dry-ice condenser.
GC analysis of the reaction mixture indicated that 98%
conversion of the 5,5',6,6',7,7',8,8'-octahydro-2,2'-
binaphthol. Small amounts of isopropylated xylene were
observed as well. The mixture was purified by flash
20 column to give 14.5 g of 3-isopropyl-
5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol, mp 110°C;
3.7 g of 3,3'-diisopropyl-5,5',6,6',7,7',8,8'-octahydro-
2,2'-binaphthol, mp 152-3°C; and a mixture (15 g)
containing 38% of 3-isopropyl-5,5',6,6',7,7',8,8'-
25 octahydro-2,2'-binaphthol and 33% of 3,3'-diisopropyl-
5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol.
3-isopropyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-
binaphthol:
¹³C NMR (CDCl₃): 22.57, 22.63, 22.96, 23.02, 23.2, 26.9,
30 27.09, 27.14, 29.3, 29.4, 112.9, 118.4, 119.2, 127.7,
129.5, 130.1, 131.0, 132.5, 133.9, 137.2, 148.7, 151.5
ppm. ¹H NMR (CDCl₃): 1.27 (d, J = 7 Hz, 6 H), 1.68 (m,
4H), 1.75 (m, 4H), 2.23 (m, 4H), 2.76 (m, 4H), 3.28

(septet, $J = 7$ Hz, 1H), 4.61 (s, 1H), 4.63 (s, 1H), 6.83 (s, 1H), 7.01 (s, 1H), 7.08 (s, 1H) ppm.

3,3'-diisopropyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-

5 binaphthol:

^1H NMR (CDCl_3): 1.27 (d, $J = 7$ Hz, 12 H), 1.68 (m, 4H), 1.73 (m, 4H), 2.17 (AB q & t, $J = 17, 6$ Hz, 4H), 2.78 (t, $J = 6$ Hz, 4H), 3.27 (septet, $J = 7$ Hz, 2H), 4.64 (s, 2H), 6.98 (s, 2H) ppm.

10

Example 2

15 Synthesis of 3,3'-diisopropyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol

A mixture of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (44.0 g), dichlorobenzene (10 ml) and phosphotungstic acid (2.3 g) was heated to 130°C. To the
20 mixture was added excess propylene via a dry-ice condenser. The reaction was monitored by GC analysis. The reaction mixture contained 6 % of monoisopropylated product and 83 % of diisopropylated product. The mixture was purified by flash column to give 20.0 g of
25 3,3'-diisopropyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol.

Example 3

30 Synthesis of 3,3'-dicyclopentyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol:

A mixture of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (48 g), phosphotungstic acid (2.4 g) and cyclopentene (58 g) was charged into a Hastelloy reactor. The reactor was heated to 180°C for 40 hours.

The mixture was purified by column chromatography (silica gel, eluting with 2% ethyl acetate/hexane) to yield 29.5 g (42 %) of 3,3'-dicyclopentyl-

5 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol, mp 143-152°C. ¹³C NMR (CDCl₃): 22.96, 25.31, 26.68, 29.19, 32.72, 32.75, 39.20, 118.58, 128.14, 129.20, 129.74, 133.91, 149.14 ppm. ¹H NMR (CDCl₃): 1.60 (m, 10 H), 2.0 (d, 4H), 2.65 (t, J = 4 Hz, 2H), 3.27 (quintet, J = 7 Hz, 10 1H), 4.55 (s, 1H), 6.92 (s, 1H) ppm.

Example 4

Alkylation of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with propylene and phosphotungstic acid catalyst

15

A solution of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol in o-dichlorobenzene and dodecane (24 weight % of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol, 63 weight% o-dichlorobenzene, 13 weight% dodecane) was 20 heated to 140°C for 3 hours under 60 to 70 psi of propylene in the presence of 17 weight% of phosphotungstic acid. GC analysis indicated 100% conversion of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol and formation of 3,3'-diisopropyl- 25 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (55%).

Example 5

Alkylation of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with propylene and Amberlyst®15 ion-exchange resin catalyst

30

A solution of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol in o-dichlorobenzene and dodecane (24 weight % of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol, 63 weight% o-dichlorobenzene, 13 weight% dodecane) was

heated to 140°C for 3 hours under 60 to 70 psi of propylene in the presence of 17 weight% of Amberlyst®15 ion-exchange resin purchased from Aldrich (PO Box 355, Milwaukee, WI 53201 USA). GC analysis indicated 100% conversion of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol and formation of 3,3'-diisopropyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (53%) and 3-isopropyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (18%).

Example 6

Alkylation of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with propylene and Nafion®/silica catalyst

A solution of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol in o-dichlorobenzene and dodecane (24 weight % of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol, 63 weight% o-dichlorobenzene, 13 weight% dodecane) was heated to 140°C for 3 hours under 60 to 70 psi of propylene in the presence of 17 weight% Nafion®/silica purchased from Engelhard Corp (Nafion® SAC 13, Engelhard Corp. Beachwood, Ohio). GC analysis indicated 100% conversion of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol and formation of 3-isopropyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (22%) and of 3,3'-diisopropyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (54%).

Example 7

Alkylation of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with propylene and trifluoromethanesulfonic acid on silica catalyst

A solution of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol in o-dichlorobenzene and dodecane (24 weight

% of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol, 63 weight% o-dichlorobenzene, 13 weight% dodecane) was heated to 140°C for 3 hours under 60 to 70 psi of propylene in the presence of 17 weight% trifluoromethanesulfonic acid on silica purchased from United Catalysts (Louisville, PO Box 32370, KY 40232). GC analysis indicated 81% conversion of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol and formation of 3-isopropyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (55%) and of 3,3'-diisopropyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (25%) based on consumed 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol.

15

Example 8

Alkylation of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with propylene and sulfated zirconia catalyst

A solution of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol in o-dichlorobenzene and dodecane (24 weight % of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol, 63 weight% o-dichlorobenzene, 13 weight% dodecane) was heated to 140°C for 3 hours under 60 to 70 psi of propylene in the presence of 17 weight% sulfated zirconia purchased from MEL Chemicals (XZO682/01, MEL Chemicals, Flemington, NJ). GC analysis indicated 100% conversion of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol and formation of 3-isopropyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (5%) and of 3,3'-diisopropyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (77%).

Example 9

Alkylation of 5,5',6,6',7,7',8,8'-octahydro-2,2'-
5 binaphthol with propylene and Dowex 32® (ion exchange
resin based on sulfonic acids) catalyst

A solution of 5,5',6,6',7,7',8,8'-octahydro-2,2'-
binaphthol in o-dichlorobenzene and dodecane (24 weight
% of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol, 63
10 weight% o-dichlorobenzene, 13 weight% dodecane) was
heated to 140°C for 3 hours under 60 to 70 psi of
propylene in the presence of 17 weight% Dowex 32®, Dow
No. 8435445, purchased from Dow Chemical (Midland,
Michigan, USA). GC analysis indicated 100% conversion
15 of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol and
formation of 3-isopropyl-5,5',6,6',7,7',8,8'-octahydro-
2,2'-binaphthol (25%) and of 3,3'-diisopropyl-
5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (55%).

Example 10

Alkylation of 5,5',6,6',7,7',8,8'-octahydro-2,2'-
20 binaphthol with propylene and Deloxin® ASP
(alkylsulfonic acid on silica) catalyst

A solution of 5,5',6,6',7,7',8,8'-octahydro-2,2'-
25 binaphthol in o-dichlorobenzene and dodecane (24 weight
% of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol, 63
weight% o-dichlorobenzene, 13 weight% dodecane) was
heated to 140°C for 3 hours under 60 to 70 psi of
propylene in the presence of 17 weight % of Deloxin®
30 ASP (alkylsulfonic acid on silica) produced by Degussa
(Hanau, Deutschland). GC analysis indicated 100%
conversion of 5,5',6,6',7,7',8,8'-octahydro-2,2'-
binaphthol and formation of 3-isopropyl-
5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (63%) and

of 3,3'-diisopropyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (<10%).

5

Example 11

Alkylation of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with tertiary-butyl chloride and zinc chloride catalyst

A mixture of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (5.0 g), zinc chloride (0.4 g), chloroform (5 ml), and tertiary-butyl chloride (10 g) was heated to 60°C for 4 hours. GC analysis indicated 90% conversion of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol and formation of 3-t-butyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (95%) and of 3,3'-di-t-butyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (~2.4%) based on consumed of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol. The mixture was purified by flash column chromatography to yield 4.36 g of solid. ¹H NMR (CDCl₃): 1.43 (s, 9H), 1.65-1.88 (m, 8H), 2.09-2.34 (m, 4H), 2.71-2.79 (m, 4H), 4.66 (s, 1H), 4.87 (s, 1H), 6.82 (d, 1H, J = 8 Hz), 7.04 (d, 1H, J = 8Hz), 7.10 (s, 1H) ppm. ¹³C NMR (CDCl₃): 22.9, 23.0, 23.1, 23.2, 26.8, 27.0, 29.2, 29.4, 29.6, 34.5, 113.0, 119.1, 119.3, 128.2, 128.9, 130.0, 131.0, 133.8, 134.2, 137.2, 149.9, 151.6 ppm.

20

25

Example 12

Alkylation of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with benzyl alcohol and trifluoromethanesulfonic acid

30

A mixture of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (1.5 g), trifluoromethanesulfonic (61 mg), o-carbon tetrachloride (2 ml), and benzyl alcohol (0.55 g)

was heated to 80°C for 2.5 hours. GC analysis indicated 73% conversion of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol and formation of 3-benzyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (90%) based on consumed of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol. To the cooled reaction mixture was added 10 mL 10% NaOH. The layers were separated, and the aqueous layer was extracted with ethyl acetate. The organic layers were combined, washed with brine, dried and concentrated. The crude material was purified by flash column chromatography (silica gel, eluting with 2% ethyl acetate/hexanes to 5% ethyl acetate/hexanes), to yield 1.13g white solid (58% yield). ¹H NMR (CDCl₃): 1.56-1.67 (m, 8H), 2.03-2.21 (m, 4H), 2.59-2.67 (m, 4H), 3.93 (s, 2H), 4.47 (s, 1H), 4.56 (s, 1H), 6.72 (d, 1H, J= 5Hz), 6.79 (s, 1H), 6.96 (d, 1H, J = 5Hz), 7.10 - 7.21 (m, 5H) ppm. ¹³C NMR (CDCl₃): 22.79, 22.87, 22.91, 26.79, 26.94, 29.00, 29.07, 35.72, 112.78, 118.52, 118.90, 125.02, 125.71, 128.18, 128.68, 129.62, 129.94, 130.83, 131.68, 134.76, 136.96, 140.85, 149.07, 151.23 ppm.

Example 13

Alkylation of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with benzyl chloride and zinc chloride catalyst

A mixture of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (0.59 g), zinc chloride (40 mg), chloroform (2 ml), and benzyl chloride (0.27g) was heated to 60°C for 4.5 hours. GC analysis indicated 70% conversion of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol and formation of 3-benzyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (95%)

based on consumed of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol.

5

Example 14

Synthesis of 3-isopropyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol

A mixture of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (2 g, 6.8 mmol), isopropyl methanesulfonate (5.5 mmol), scandium triflate (0.34 g, 5mol%), and carbon tetrachloride (10 ml) was brought to reflux under argon. After 18 hours, GC indicated 65% conversion to give 78% desired product. Additional isopropyl methanesulfonate (3.1mmol) was added, and the reaction mixture was refluxed for another 8 hours. GC showed 86% conversion, and 76% selectivity to 3-isopropyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol. The mixture was diluted with ether (20 ml) and 10% HCl (20 ml). The layers were separated, and the aqueous layer was extracted with ether (3 X 20 ml). The ether layers were combined, dried (MgSO₄), and concentrated. The crude product was purified by column chromatography (SiO₂, 2% ethyl acetate/hexanes) to yield 1.1 g white solid (48%). MP: 100-102°C.

25

Example 15

Synthesis of 3-cyclopentyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol

A mixture of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (2 g, 6.8 mmol), cyclopentyl methanesulfonate (6.34 mmol), scandium triflate (0.34 g, 5 mol%), and carbon tetrachloride (10 ml) was heated to reflux under argon for 10 hours. GC showed 93% conversion and 77% selectivity to 3-cyclopentyl-5,5',6,6',7,7',8,8'-

octahydro-2,2'-binaphthol. The mixture was diluted with ether (20 ml) and 10% HCl (20 ml). The layers were separated, and the aqueous layer was extracted with ether (3 X 20 ml). The ether layers were combined, dried (MgSO₄), and concentrated. The crude product was purified by column chromatography (SiO₂, 2% ethyl acetate/hexanes) to yield 1.4 g white solid (57%). ¹H NMR (CDCl₃): 1.58 (m, 14 H), 2.05 (m, 6H), 2.66 (m, J= 5 Hz, 4H), 3.18 (quintet, J = 8 Hz, 1H), 4.52 (s, 1H), 4.51 (s, 1H), 6.73 (d, J=8Hz, 1H), 6.92 (s, 1H), 6.97 (d, J=8Hz, 1H) ppm. ¹³C NMR (CDCl₃): 22.82, 22.87, 23.01, 25.36, 26.70, 26.94, 29.09, 29.20, 32.73, 32.75, 39.28, 112.73, 118.23, 119.13, 128.24, 129.19, 129.85, 130.72, 133.72, 137.03, 149.14, and 151.33 ppm.

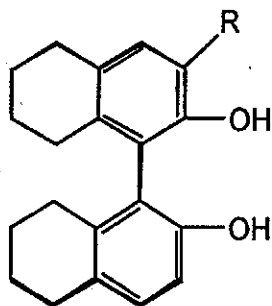
Example 16

Synthesis of 3-tert-butyl-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol

A mixture of 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol (1.0 g, 3.4 mmol), tert-butyl alcohol (1.4 g), trifluoromethanesulfonic acid (0.04 g) was dissolved in 2 ml 1,2-dichlorobenzene. The mixture was heated at 120°C for 2.5 hours. GC showed 97% conversion to 87% mono-butylated product, and 10% bis-butylated product. The mixture was cooled, and diluted with 10 ml water and 10 ml ether. The layers were separated, and the organic layer was washed with sodium bicarbonate solution, dried, and concentrated. The crude product was purified by flash column chromatography (silica gel, 2% ethyl acetate/hexanes) to yield 0.7g of white solid.

WHAT IS CLAIMED IS:

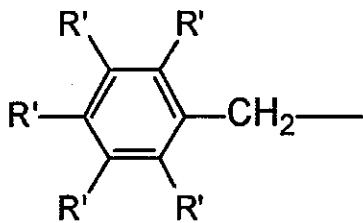
- 5 1. A compound of the formula



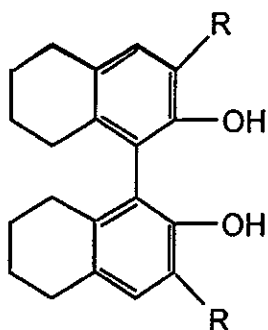
1

wherein:

- 10 R is C₁ to C₂₀ alkyl, C₃ to C₂₀ cycloalkyl, or benzyl of the formula

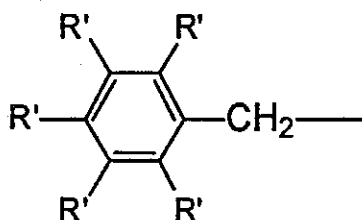


- 15 wherein each R' is independently H, alkyl or cycloalkyl of up to 6 carbons; and/or a compound of the formula



2

wherein R is C₁ to C₂₀ alkyl other than methyl or t-butyl, C₃ to C₂₀ cycloalkyl, or benzyl of the formula



wherein each R' is independently H, alkyl or cycloalkyl of up to 6 carbons.

2. A process for making 3-alkylated-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol and/or 3,3'-dialkylated-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol, comprising contacting 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with at least one alkene or cycloalkene in the presence of an acid catalyst.

3. The process of claim 2 wherein the at least one alkene or cycloalkene is monoethylenically unsaturated and contains from 3 to 20 carbon atoms.

4. The process of claim 3 wherein at least one alkene or cycloalkene is selected from the group consisting of

propylene, butene, pentene, hexene, cyclopentene, and cyclohexene.

5. The process of claim 2 wherein the acid catalyst is
5 selected from the group consisting of aluminum chloride, trifluoromethanesulfonic acid, tosylic acid, phosphotungstic acid, silicotungstic acid, phosphomolybdic acid, zirconium triflate, aluminum triflate, polymeric perfluorinated sulfonic acid and
10 polymeric sulfonic acid.

6. The process of claim 5 wherein the acid catalyst is aluminum chloride, phosphotungstic acid, or
15 phosphomolybdic acid.

7. The process of claim 6 wherein the acid catalyst is phosphotungstic acid.

8. The process of claim 2 wherein the contacting is
20 done in the presence of at least one solvent selected from the group consisting of nitromethane, methylene chloride, dichloroethane, chlorobenzene, dichlorobenzene, and nitrobenzene.

25 9. The process of claim 2 wherein the contacting is done at a temperature between 20°C and 220°C.

10. The process of claim 9 wherein the temperature is between 90°C and 180°C and wherein the
30 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol is contacted with a mono- or 1,2-disubstituted alkene.

11. The process of claim 9 wherein the temperature is between 40°C and 90°C and wherein the

5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol is contacted with at least one alkene selected from the group consisting of 1,1-disubstituted alkene, tri-substituted alkene, tetra-substituted alkene or aryl-substituted alkene.

12. A process for making 3-alkylated-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol and/or 3,3'-dialkylated-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol, comprising contacting 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with a benzyl halide or tertiary alkyl halide, wherein the halide is bromide or chloride, in the presence of a Lewis acid catalyst.

13. The process of claim 12 wherein the Lewis acid catalyst is selected from the group consisting of aluminum chloride, zinc chloride, boron trichloride, SnCl_4 , SbCl_5 , and ZrCl_4 .

14. The process of claim 13 wherein the Lewis acid catalyst is zinc chloride.

15. A process for making 3-alkylated-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol and/or 3,3'-dialkylated-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol, comprising contacting 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with an alkyl sulfonate, alkyl triflate, alkyl p-toluenesulfonate, or alkyl benzenesulfonate, in the presence of an acid catalyst selected from the group consisting of aluminum chloride, tosylic acid, phosphotungstic acid, silicotungstic acid, phosphomolybdic acid, trifluoromethanesulfonic acid and a rare earth metal triflate selected from the group

consisting of scandium trifluoromethanesulfonate, ytterbium trifluoromethanesulfonate, and lanthanum trifluoromethanesulfonate.

5

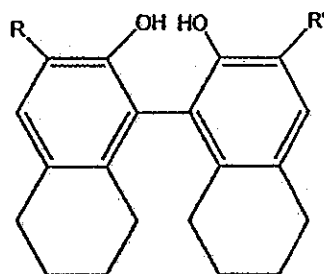
16. The process of Claim 15 in which the alkyl sulfonate is of the formula $A-SO_3-B$, wherein A is C_1 to C_8 alkyl, C_1 to C_8 fluorinated alkyl, C_6 to C_{10} aryl, or C_6 to C_{10} fluorinated aryl; and B is C_1 to C_{20} alkyl.

10

17. A process for making 3-alkylated-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol and/or 3,3'-dialkylated-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol, comprising contacting 5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthol with a benzyl, secondary or tertiary alcohol containing from 3 to 20 carbon atoms, in the presence of an acid catalyst selected from the group consisting of trifluoromethanesulfonic acid, sulfuric acid, HF , phosphoric acid, and aluminum chloride.

20

18. A compound of the formula



25 wherein:

R is H; and

R' is ethyl, C_3 to C_6 secondary, tertiary, or cyclic alkyl;

or a compound of the above formula wherein

R and R' are the same and are selected from the group consisting of ethyl, C₃ to C₆ secondary or cyclic alkyl.

5

19. A compound of claim 18 wherein R and R' are the same are selected from the group consisting of ethyl, isopropyl, cyclopentyl, and cyclohexyl.

10