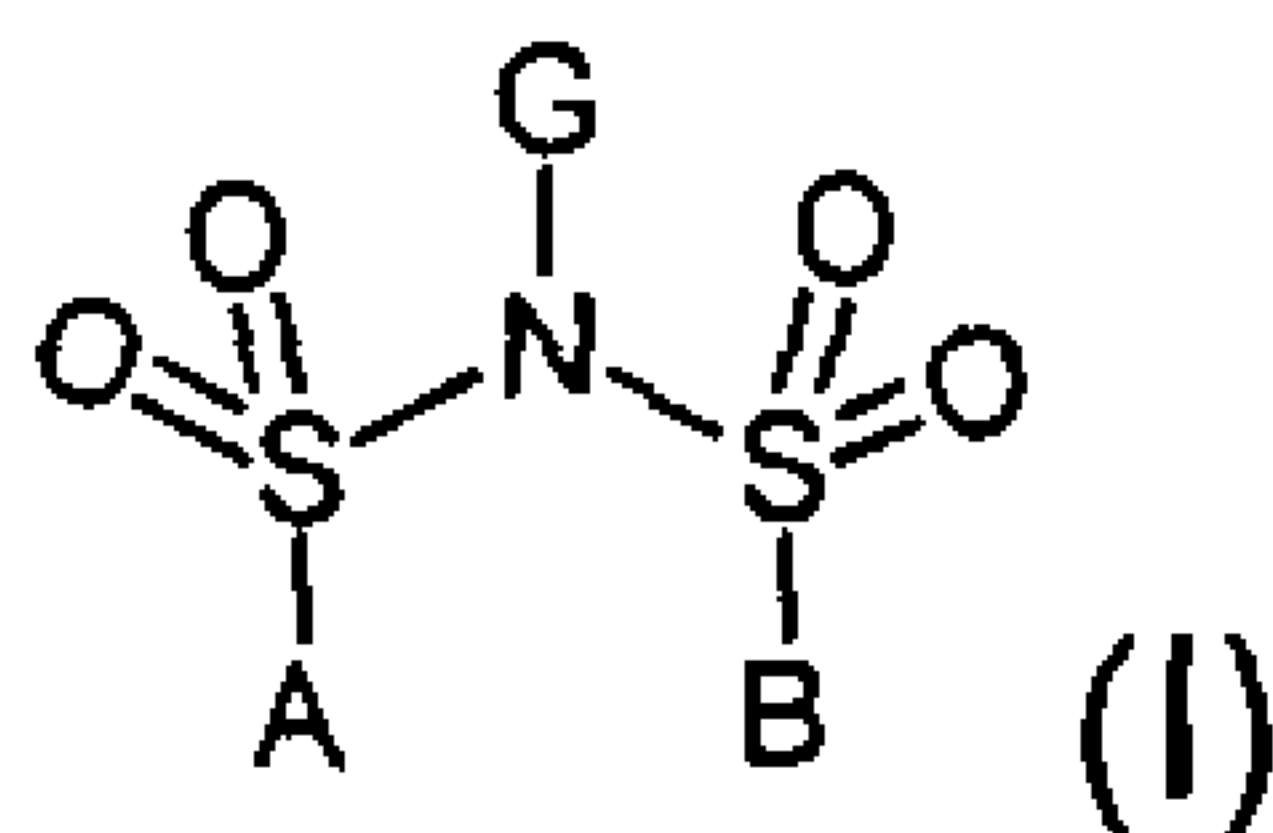
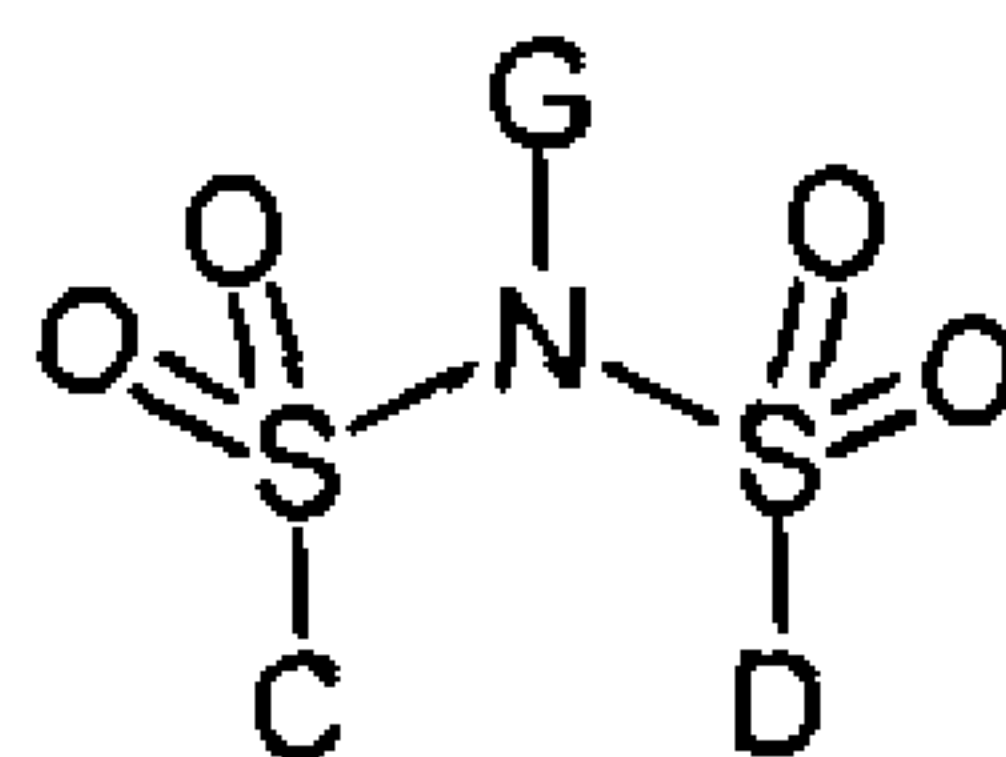
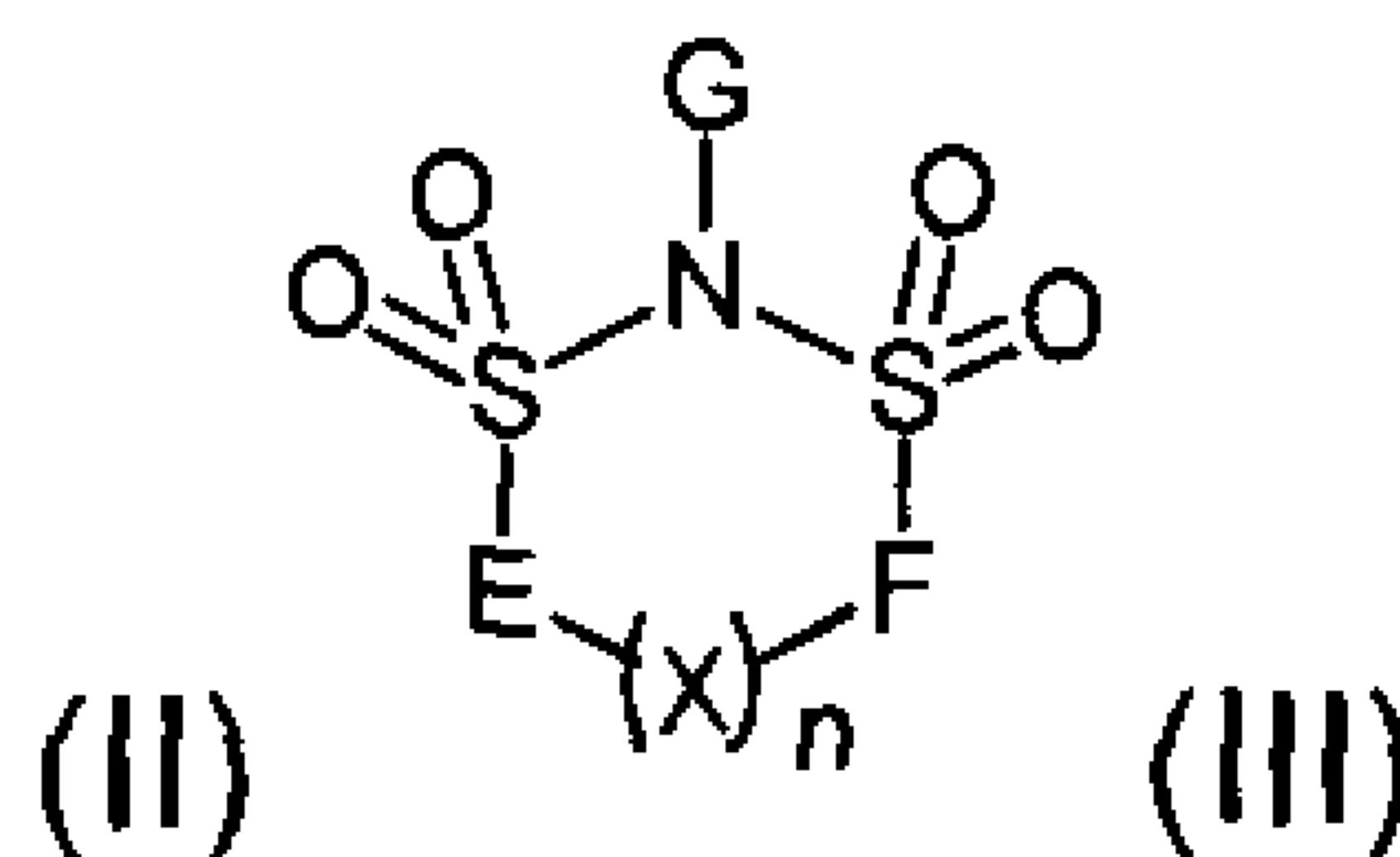




(86) **Date de dépôt PCT/PCT Filing Date:** 2010/03/02
(87) **Date publication PCT/PCT Publication Date:** 2010/09/10
(45) **Date de délivrance/Issue Date:** 2017/11/28
(85) **Entrée phase nationale/National Entry:** 2011/09/02
(86) **N° demande PCT/PCT Application No.:** DE 2010/000226
(87) **N° publication PCT/PCT Publication No.:** 2010/099786
(30) **Priorité/Priority:** 2009/03/02 (DE10 2009 011 055.0)

(51) **Cl.Int./Int.Cl.** **C07D 285/01** (2006.01)
(72) **Inventeurs/Inventors:**
LIST, BENJAMIN, DE;
LAY, FRANK, DE;
GARCIA-GARCIA, PILAR, ES
(73) **Propriétaire/Owner:**
STUDIENGESELLSCHAFT KOHLE MBH, DE
(74) **Agent:** BERESKIN & PARR LLP/S.E.N.C.R.L., S.R.L.

(54) **Titre : DISULFONIMIDES CHIRAUX**
(54) **Title: CHIRAL DISULFONIMIDES**



(57) **Abrégé/Abstract:**

The invention relates to chiral disulfonimides having the general formula I to III, wherein at least one of the groups A and B in the compound of formula I, C and D of the compound in formula II, and E and F of the compound in formula III is a chiral group, or E and F together form a chiral backbone, X is C, Si, O, N or S, and n is 0, 1, 2, 3, 4, 5 or 6, where n is > 1 only if X is C, G is H, C₁-C₆-alkyl, C₂-C₆-alkenyl or C₂-C₆-alkinyl, an aryl, aryl-(C₁-C₆)-alkyl, hetero(C₁-C₆)-alkyl, or heteroaryl group, or SiR¹⁴R¹⁵R¹⁶ is Br, Cl, I, F, where R¹⁴, R¹⁵, R¹⁶ is C₁-C₆-alkyl, C₂-C₆-alkenyl or C₂-C₆-alkinyl, aryl-, aryl-(C₁-C₆)-alkyl, hetero-(C₁-C₆)-alkyl, heteroaryl, which may optionally be substituted, and to the organic salts, metal salts and metal complexes thereof. The compounds are suited as NMR shift reagents and as reagents for racemate splitting, and also as chiral Bronsted acid catalysts or chiral Lewis acid catalysts for activating ketones, aldehydes and alkenes, and also as catalysts in the organic synthesis.



(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES
PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG(19) Weltorganisation für geistiges Eigentum
Internationales Büro(43) Internationales Veröffentlichungsdatum
10. September 2010 (10.09.2010)(10) Internationale Veröffentlichungsnummer
WO 2010/099786 A1(51) Internationale Patentklassifikation:
C07D 285/01 (2006.01)

(21) Internationales Aktenzeichen: PCT/DE2010/000226

(22) Internationales Anmeldedatum:
2. März 2010 (02.03.2010)

(25) Einreichungssprache: Deutsch

(26) Veröffentlichungssprache: Deutsch

(30) Angaben zur Priorität:
10 2009 011 055.0 2. März 2009 (02.03.2009) DE(71) Anmelder (für alle Bestimmungsstaaten mit Ausnahme von US): **STUDIENGESELLSCHAFT KOHLE MBH** [DE/DE]; Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr (DE).

(72) Erfinder; und

(75) Erfinder/Anmelder (nur für US): **LIST, Benjamin** [DE/DE]; Lembkestrasse 30, 45470 Mülheim an der Ruhr (DE). **LAY, Frank** [DE/DE]; Scharpenberg 7, 45468 Mülheim an der Ruhr (DE). **GARCIA-GARCIA, Pilar** [ES/ES]; C/Teide, 39 Valdelagua, Santa Marta de Tor-
mes, 37194 Salamanca (ES).

(81) Bestimmungsstaaten (soweit nicht anders angegeben, für jede verfügbare nationale Schutzrechtsart): AE, AG, AL,

AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

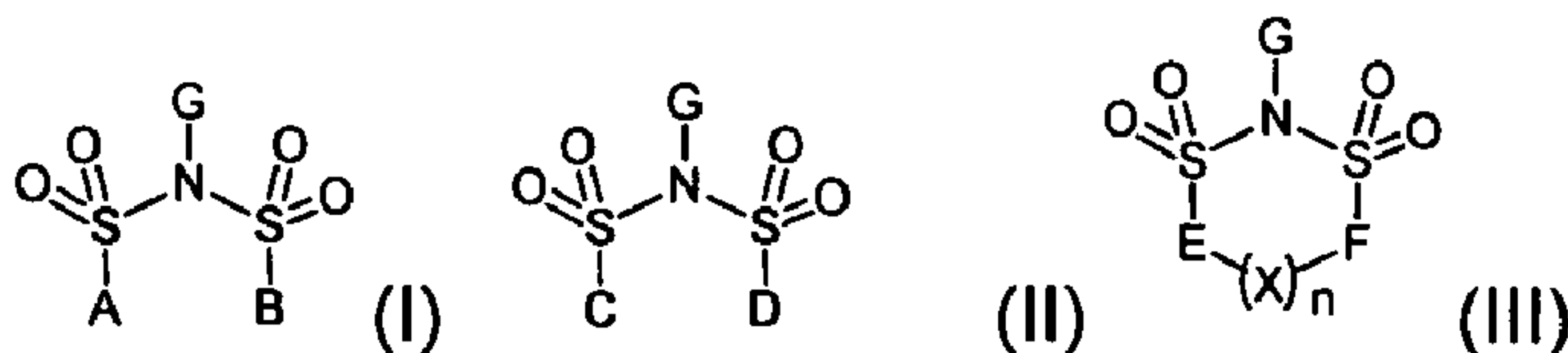
(84) Bestimmungsstaaten (soweit nicht anders angegeben, für jede verfügbare regionale Schutzrechtsart): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), eurasisches (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Veröffentlicht:

- mit internationalem Recherchenbericht (Artikel 21 Absatz 3)
- vor Ablauf der für Änderungen der Ansprüche geltenden Frist; Veröffentlichung wird wiederholt, falls Änderungen eingehen (Regel 48 Absatz 2 Buchstabe h)

(54) Title: CHIRAL DISULFONIMIDES

(54) Bezeichnung : CHIRALE DISULFONIMIDE



(57) **Abstract:** The invention relates to chiral disulfonimides having the general formula I to III, wherein at least one of the groups A and B in the compound of formula I, C and D of the compound in formula II, and E and F of the compound in formula III is a chiral group, or E and F together form a chiral backbone, X is C, Si, O, N or S, and n is 0, 1, 2, 3, 4, 5 or 6, where n is > 1 only if X is C, G is H, C₁-C₆-alkyl, C₂-C₆-alkenyl or C₂-C₆-alkinyl, an aryl, aryl-(C₁-C₆)-alkyl, hetero(C₁-C₆)-alkyl, or heteroaryl group, or SiR¹⁴R¹⁵R¹⁶ is Br, Cl, I, F, where R¹⁴, R¹⁵, R¹⁶ is C₁-C₆-alkyl, C₂-C₆-alkenyl or C₂-C₆-alkinyl, aryl-, aryl-(C₁-C₆)-alkyl, hetero-(C₁-C₆)-alkyl, heteroaryl, which may optionally be substituted, and to the organic salts, metal salts and metal complexes thereof. The compounds are suited as NMR shift reagents and as reagents for racemate splitting, and also as chiral Bronsted acid catalysts or chiral Lewis acid catalysts for activating ketones, aldehydes and alkenes, and also as catalysts in the organic synthesis.

(57) **Zusammenfassung:** Die Erfindung betrifft chirale Disulfonimide mit der allgemeinen Formeln I bis III in denen mindestens einer der Reste A und B in der Verbindung der Formel I, C und D der Verbindung der Formel II und E und F der Verbindung der Formel III ein chiraler Rest ist oder E und F gemeinsam ein chirales Rückgrat bilden, X für C, Si, O, N oder S und n für 0, 1, 2, 3, 4, 5 oder 6 steht, wobei n nur dann > 1 ist, wenn X für C steht, G steht für H, C₁-C₆-Alkyl-, C₂-C₆-Alkenyl- oder C₂-C₆-Alkinyl-, Gruppe Aryl-, Aryl-(C₁-C₆)-alkyl, Hetero(C₁-C₆)-alkyl-, Heteroaryl, oder SiR¹⁴R¹⁵R¹⁶ Br, Cl, I, F steht, wobei R¹⁴, R¹⁵, R¹⁶ für C₁-C₆-Alkyl-, C₂-C₆-Alkenyl- oder C₂-C₆-Alkinyl-, Aryl-, Aryl-(C₁-C₆)-alkyl, Hetero-(C₁-C₆)-alkyl-, Heteroaryl, die ggf. substituiert sein können, sowie deren organische Salze, Metallsalze und Metallkomplexe. Die Verbindungen

[Fortsetzung auf der nächsten Seite]

WO 2010/099786 A1



eignen sich als NMR-Shift Reagenzien und als Reagenzien zur Racematspaltung sowie als chirale Bronsted-Säure-Katalysatoren bzw. chirale Lewis-Säure-Katalysatoren zur Aktivierung von Ketonen, Aldehyden und Alkenen und auch als Katalysatoren in der organischen Synthese.

Chiral Disulfonimides

5 The present invention relates to chiral disulfonimides and also their salts and metal complexes and their use as catalysts.

Many chemical transformations are catalyzed by Brønsted acids. In enantioselective organocatalysis, this possibility of metal-free, and in the case of chiral Brønsted acids also enantioselective, catalysis is a rapidly growing field with increasing applications. In this field
10 of organocatalysis, a distinction is made between hydrogen bond catalysts such as thioureas and also TADDOL and BINOL derivatives and stronger Brønsted acids such as phosphoric diesters and derivatives thereof. However, the possibility of activation by means of these chiral, organic Brønsted acids is restricted to reactive electrophiles such as imines and nitroolefins and also in a few cases to ketones and activated aldehydes. The preparation of
15 very strong, chiral Brønsted acids for activating simple ketones, aldehydes and alkenes is therefore desirable.

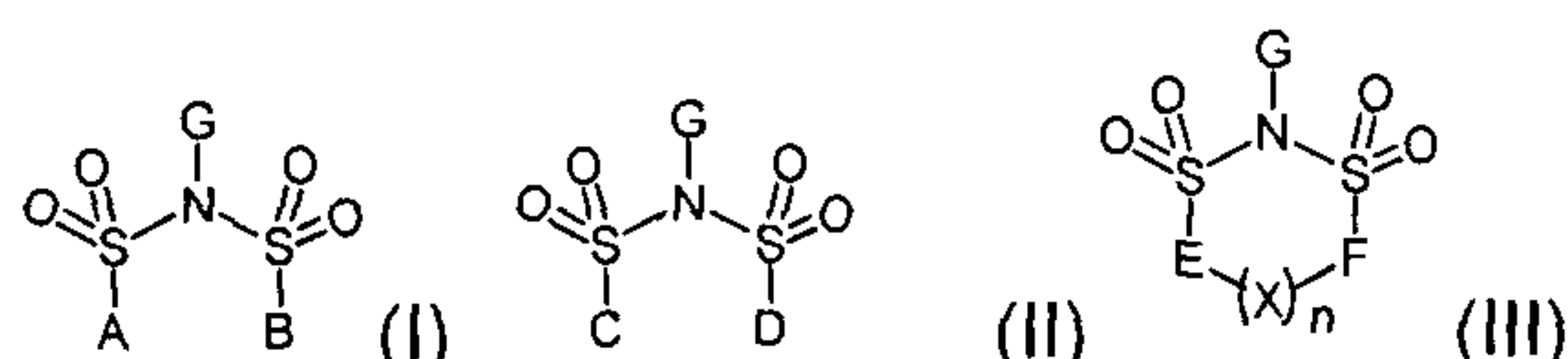
In *J. Am. Chem. Soc.* 2006, 128, 9626-9627, Yamamoto et al. introduce chiral, substituted *N*-triflylphosphoramides as strong Brønsted acids for the activation of ketones. The
20 preparation of a likewise strong, chiral Brønsted acid, viz. 1,1'-binaphthalene-2,2'-disulfonic acid, has been described by Barber and Smiles in *J. Chem. Soc.* 1928, 1141-1149. In *J. Chem. Soc.* 1957, 13-22, Armarego and Turner examined the optical activity and optical stability of this acid. The Japanese patents 2005-132815, 2005-132816 and 2005-134365 disclose the enantiomerically pure preparation of this acid, its use as reagent for resolution
25 of racemates and its use as NMR shift reagent. List et al used this acid as chiral Brønsted acid catalyst in *Adv. Synth. Catal.* 2008, 350, 962-966 and *Chem. Asian. J.* 2008, 3, 430-437, but without achieving enantioselectivity. Ishihara et al. used 1,1'-binaphthalene-2,2'-disulfonic acid in combination with substituted pyridines as chiral Brønsted acid-based organocatalysts in *J. Am. Chem. Soc.* 2008, 130, 16858-16860.

30 The unknown cyclic disulfonimide of 1,1'-binaphthalene-2,2'-disulfonic acid, its substituted derivatives and the substituted derivatives of 1,1'-binaphthalene-2,2'-disulfonic acid can similarly be classified as strong Brønsted acid. The conjugated bases of the disulfonic acids and disulfonimides are likewise suitable as chiral anions in enantioselective catalysis by
35 counterions and in Lewis acid catalysis.

- 2 -

It was accordingly an object of the present invention to provide chiral disulfonimides and a simple process for preparing chiral disulfonimides and also their use in catalysis.

The present invention accordingly provides chiral disulfonimides having the general formulae I to III

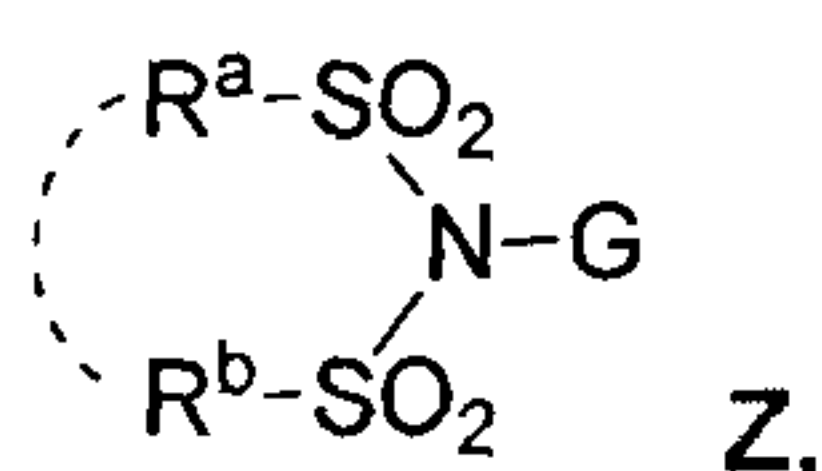


where at least one of the radicals A and B in the compound of the formula I, C and D of the compound of the formula II and E and F of the compound of the formula III is a chiral radical or E and F together form a chiral backbone,

G is H, C₁-C₆-alkyl, C₂-C₆-alkenyl or C₂-C₆-alkynyl, aryl, aryl-(C₁-C₆)-alkyl, hetero(C₁-C₆)-alkyl, heteroaryl, or SiR¹⁴R¹⁵R¹⁶, Br, Cl, I, F, where R¹⁴, R¹⁵, R¹⁶ are each C₁-C₆-alkyl, C₂-C₆-alkenyl or C₂-C₆-alkynyl, aryl, aryl-(C₁-C₆)-alkyl, hetero(C₁-C₆)-alkyl, heteroaryl, which may optionally be substituted,

X is C, Si, O, N or S and n is 0, 1, 2, 3, 4, 5 or 6, where n is > 1 only when X is C, and also their organic salts, metal salts and metal complexes.

The compounds having the formulae I, II and III can also be summarized by the general formula Z



One of R^a and R^b or both is/are chiral radicals as for the radicals A, B, C, D, E and F or they together form a chiral backbone and G is H, C₁-C₆-alkyl, C₂-C₆-alkenyl or C₂-C₆-alkynyl, aryl, aryl-(C₁-C₆)-alkyl, hetero(C₁-C₆)-alkyl, heteroaryl, or SiR¹⁴R¹⁵R¹⁶, Br, Cl, I, F, where R¹⁴, R¹⁵, R¹⁶ are each C₁-C₆-alkyl, C₂-C₆-alkenyl or C₂-C₆-alkynyl, aryl, aryl-(C₁-C₆)-alkyl, hetero(C₁-C₆)-alkyl, heteroaryl, which may optionally be substituted.

In the compounds which are derived from TADDOL (17 + 18 in the examples), BINOL (1-3, 21 + 22) and VAPOL (4) and in the case of the spiro compound (19), the radicals E and F together form a chiral backbone. The chirality in the compounds derived from BINOL and VAPOL and the spiro compounds results from axial chirality. In this type of chirality, the rotation about the axis of the aryl(E)-aryl(F) bond (X) is limited. The two aryls are not

- 3 -

5 themselves chiral, but by means of the connection via an axis about which free rotation is limited they together form a chiral axis. This results in a chiral backbone for the disulfonimides. The compound having the formula Z and the compounds having the formulae I, II and III can also have a helical, chiral or planar backbone, for example compound 24.

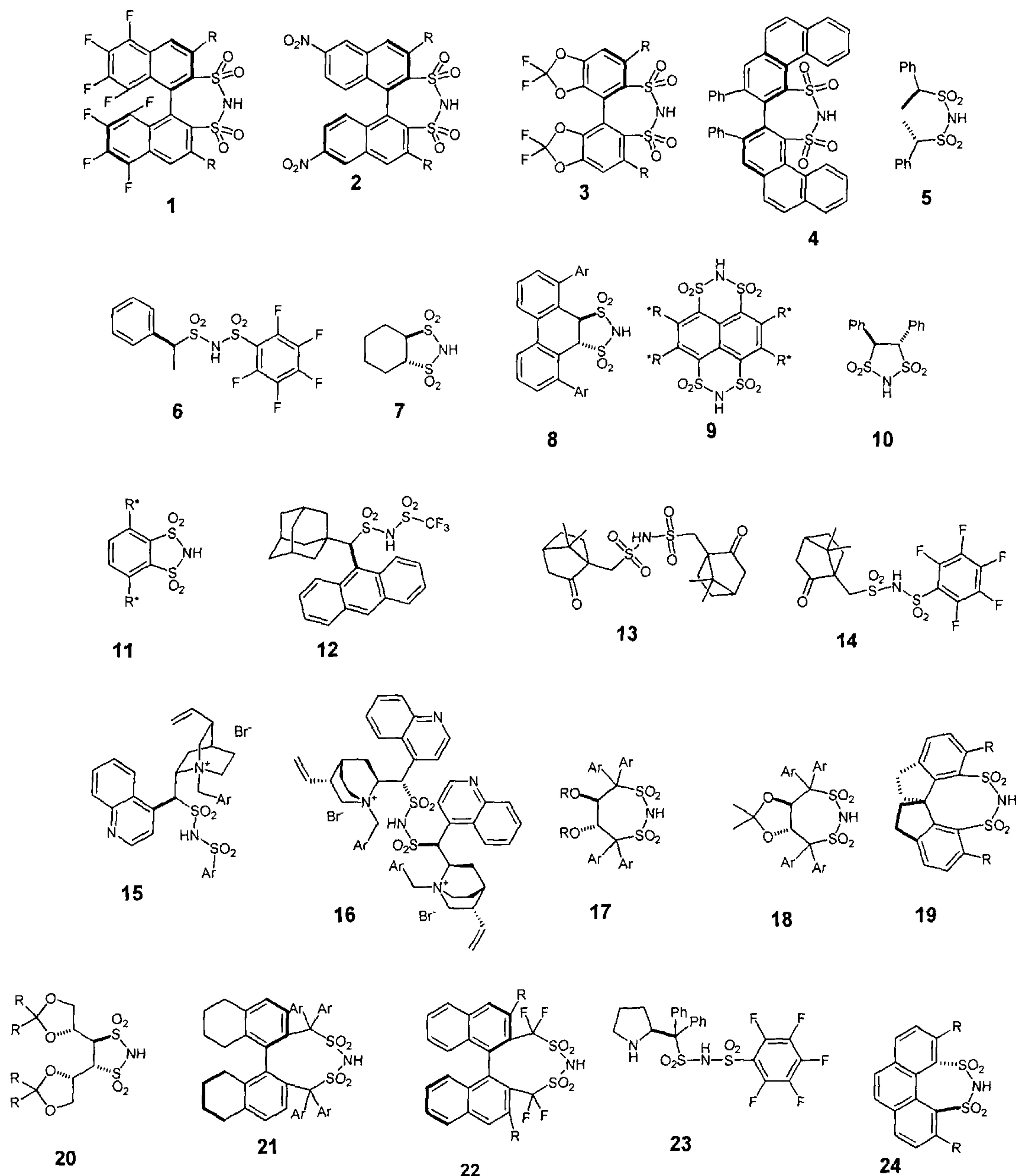
10 For the purposes of the present invention, "chiral sulfonimides" means that one of the enantiomers is present in excess, i.e. the compound is enriched in the one enantiomer, or the reaction product is present in enantiomerically pure form. If the compounds according to the invention are obtained as a racemic or scalemic mixture as reaction product, the enantiomers can be separated by means of methods which are well known from the prior art, for example by separation by means of chiral, preparative HPLC or by reaction of the compounds with chiral agents and subsequent separation of the diastereomers. The enantiomers can also be separated when the mixture is to be enriched further in the enantiomer present in excess, i.e. the ee is to be increased.

15

Any chiral radicals are possible as chiral radicals. If the other radical in each case is not chiral, the radicals A or B, C or D and E or F are any organic radical which may be saturated or unsaturated, linear, cyclic or heterocyclic, aromatic and/or heteroaromatic.

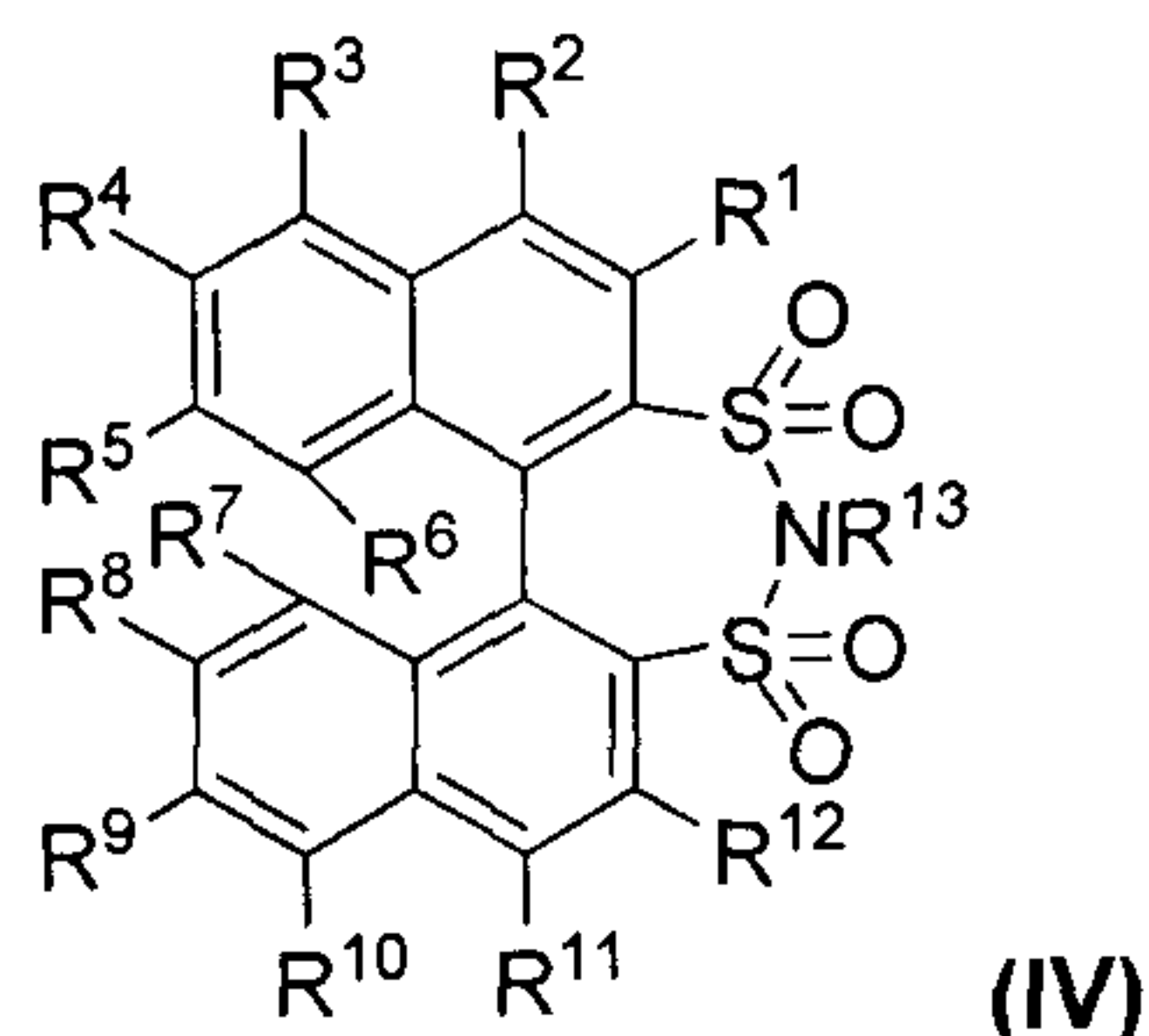
20 Examples of compounds having the formulae I, II and III are shown below:

- 4 -



5 In organic synthesis, particularly in the synthesis of pharmaceutical active compounds, chiral compounds are frequently used as catalysts in order to obtain the desired product in a high enantiomeric purity or diastereomeric purity. Compounds in which the radicals in the compounds of the formulae I to III are derived from BINOL have been found to be particularly suitable for use as catalysts in organic synthesis. These preferred compounds are represented by the general formula IV

- 5 -



where

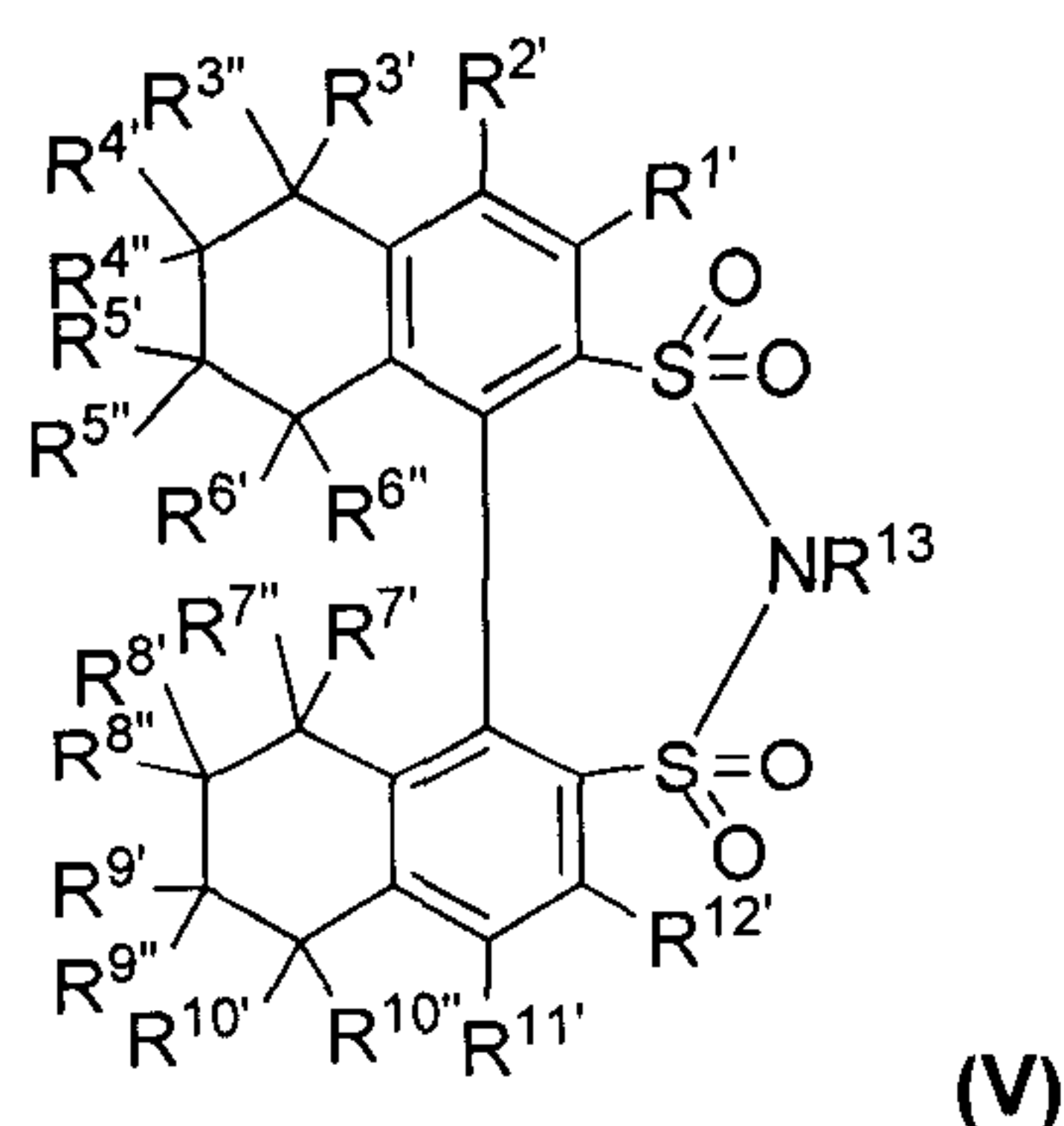
R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹ and R¹² can be identical or different and are each, independently of one another, H, OH, F, Cl, Br, I, CN, NO₂, NO, SO₂, SO₃H, NH₂, PH₃,

5 COOH, SO₃X, COOY, where X and Y are each Na or K, a C₁-C₂₀-alkyl, C₂-C₂₀-alkenyl or C₂-C₂₀-alkynyl, aryl, aryl-(C₁-C₆)-alkyl, hetero(C₁-C₆)-alkyl, heteroaryl group, which may optionally be substituted,

R¹³ is H, C₁-C₆-alkyl, C₂-C₆-alkenyl or C₂-C₆-alkynyl, aryl, aryl-(C₁-C₆)-alkyl, hetero(C₁-C₆)-alkyl, heteroaryl, or SiR¹⁴R¹⁵R¹⁶, Br, Cl, I, F, where R¹⁴, R¹⁵, R¹⁶ are each C₁-C₆-alkyl, C₂-C₆-alkenyl or C₂-C₆-alkynyl, aryl, aryl-(C₁-C₆)-alkyl, hetero(C₁-C₆)-alkyl, heteroaryl, which may optionally be substituted,

and also their organic salts, metal salts and metal complexes.

The present invention further provides chiral disulfonimides derived from H8-BINOL having the general formula V



where

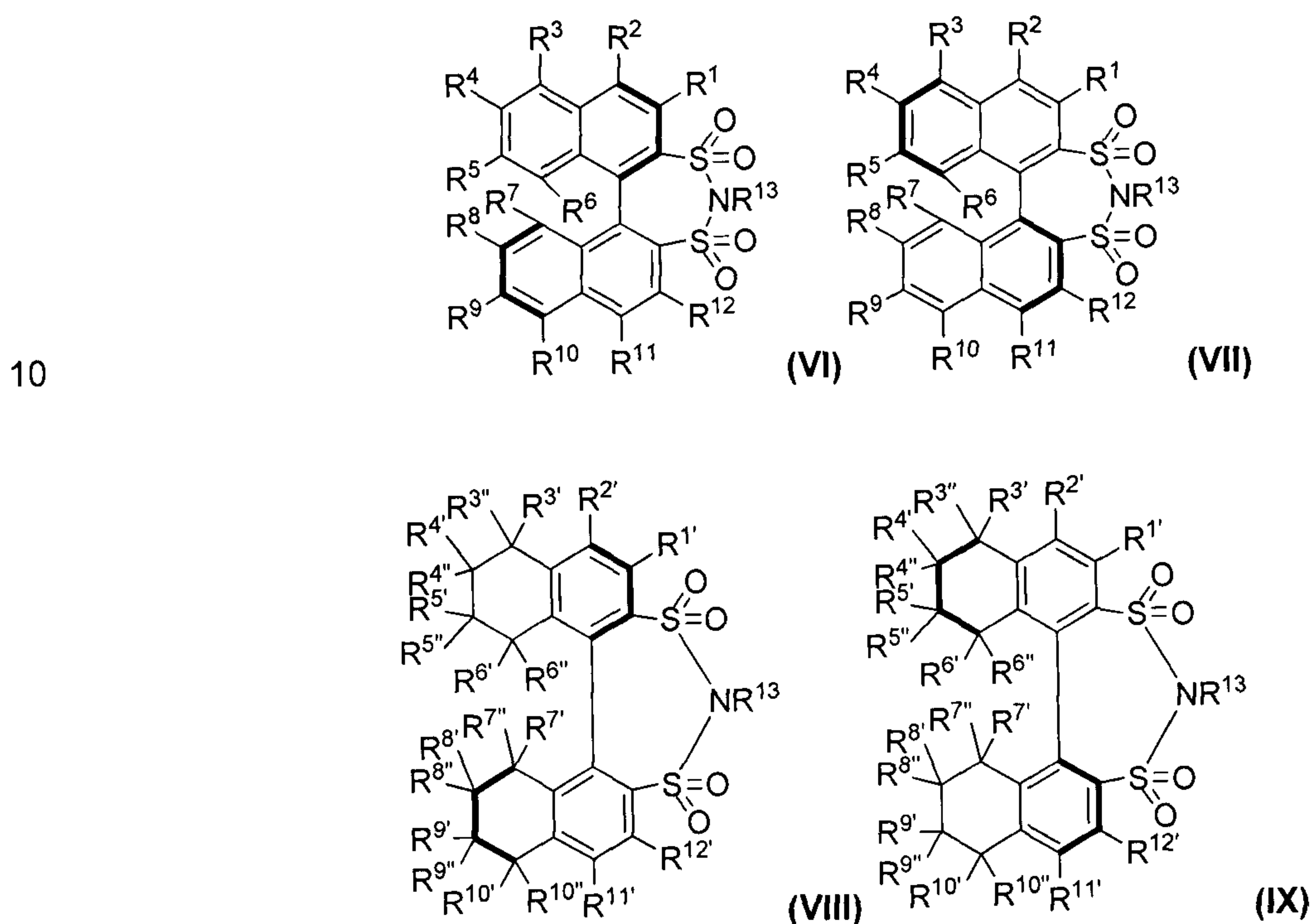
20 R¹, R², R³, R^{3'}, R⁴, R^{4'}, R⁵, R^{5''}, R⁶, R^{6''}, R⁷, R^{7''}, R⁸, R^{8''}, R⁹, R^{9''}, R¹⁰, R^{10''}, R¹¹ and R¹² can be identical or different and are each, independently of one another, H, OH, F, Cl, Br, I, CN, NO₂, NO, SO₂, SO₃H, NH₂, PH₃, COOH, SO₃X, COOY, where X and Y are each Na or K, a C₁-C₂₀-alkyl, C₂-C₂₀-alkenyl or C₂-C₂₀-alkynyl, group, aryl, aryl-(C₁-C₆)-alkyl, hetero(C₁-C₆)-alkyl, heteroaryl, which may optionally be substituted,

- 6 -

R^{13} is H, C_1 - C_6 -alkyl, C_2 - C_6 -alkenyl or C_2 - C_6 -alkynyl, aryl, aryl- (C_1-C_6) -alkyl, hetero(C_1-C_6)-alkyl, heteroaryl, or $SiR^{14}R^{15}R^{16}$, Br, Cl, I, F, where R^{14} , R^{15} , R^{16} are each C_1 - C_6 -alkyl, C_2 - C_6 -alkenyl or C_2 - C_6 -alkynyl, aryl, aryl- (C_1-C_6) -alkyl, hetero(C_1-C_6)-alkyl, heteroaryl, which may optionally be substituted,

5 and also their organic salts, metal salts and metal complexes.

A further preferred embodiment provides compounds having the following general formulae VI, VII, VIII and IX



15 where the radicals $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}$ and $R^{12}, R^{1'}, R^{2'}, R^{3'}, R^{3''}, R^{4'}, R^{4''}, R^{5'}, R^{5''}, R^{6'}, R^{6''}, R^{7'}, R^{7''}, R^{8'}, R^{8''}, R^{9'}, R^{9''}, R^{10'}, R^{10''}, R^{11'}$ and $R^{12'}$ and also R^{13} are as defined above, where the enantiomers are present in a ratio of from 98 : 2 to 100 : 0, i.e. in enantiomerically pure form.

20 It has been found that the compounds according to the invention are well suited as catalysts for enantioselective synthesis. Here, they function as chiral Brønsted acids or in the case of $R^{13} = SiR^{14}R^{15}R^{16}$ as Lewis acids or the conjugated base thereof as chiral anions in enantioselective catalyses by counterions.

- 7 -

The following definitions for the individual radicals R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} and R^{12} apply equally to the radicals $R^{1'}$, $R^{2'}$, $R^{3'}$, $R^{3''}$, $R^{4'}$, $R^{4''}$, $R^{5'}$, $R^{5''}$, $R^{6'}$, $R^{6''}$, $R^{7'}$, $R^{7''}$, $R^{8'}$, $R^{8''}$, $R^{9'}$, $R^{9''}$, $R^{10'}$, $R^{10''}$, $R^{11'}$ and $R^{12'}$ and the radical R^{13} .

- 5 C_1 - C_{20} -Alkyl can be unbranched (linear) or branched and has 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 carbon atoms. Alkyl is preferably C_1 - C_6 -alkyl, in particular methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl or tert-butyl, likewise pentyl, 1-, 2- or 3-methylpropyl, 1,1-, 1,2- or 2,2-dimethylpropyl, 1-ethylpropyl, hexyl, 1-, 2-, 3- or 4-methylpentyl, 1,1-, 1,2-, 1,3-, 2,2-, 2,3- or 3,3-dimethylbutyl, 1- or 2-ethylbutyl, 1-ethyl-1-
- 10 methylpropyl, 1-ethyl-2-methylpropyl, 1,1,2- or 1,2,2-trimethylpropyl. Preferred substituted alkyl radicals are trifluoromethyl, pentafluoroethyl and 1,1,1-trifluoroethyl.

Cycloalkyl is preferably cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl or cycloheptyl. Alkylene is preferably methylene, ethylene, propylene, butylene, pentylene or hexylene, but

15 also branched alkylene.

Alkenyl is preferably vinyl.

Alkynyl is preferably $C\equiv CH$.

20

Halogen is F, Cl, Br or I.

Alkoxy is preferably methoxy, ethoxy, propoxy or butoxy.

- 25 C_3 - C_8 -Heterocycloalkyl having one or more heteroatoms selected from among N, O and S is preferably 2,3-dihydro-2-, -3-, -4- or -5-furyl, 2,5-dihydro-2-, -3-, -4- or -5-furyl, tetrahydro-2- or -3-furyl, 1,3-dioxolan-4-yl, tetrahydro-2- or -3-thienyl, 2,3-dihydro-1-, -2-, -3-, -4- or -5-pyrrolyl, 2,5-dihydro-1-, -2-, -3-, -4- or -5-pyrrolyl, 1-, 2- or 3-pyrrolidinyl, tetrahydro-1-, -2- or -4-imidazolyl, 2,3-dihydro-1-, -2-, -3-, -4- or -5-pyrazolyl, tetrahydro-1-, -3- or -4-pyrazolyl,
- 30 1,4-dihydro-1-, -2-, -3- or -4-pyridyl, 1,2,3,4-tetrahydro-1-, -2-, -3-, -4-, -5- or -6-pyridyl, 1-, 2-, 3- or 4-piperidinyl, 2-, 3- or 4-morpholinyl, tetrahydro-2-, -3- or -4-pyranyl, 1,4-dioxanyl, 1,3-dioxan-2-, -4- or -5-yl, hexahydro-1-, -3- or -4-pyridazinyl, hexahydro-1-, -2-, -4- or -5-pyrimidinyl, 1-, 2- or 3-piperazinyl, 1,2,3,4-tetrahydro-1-, -2-, -3-, -4-, -5-, -6-, -7- or -8-quinolyl, 1,2,3,4-tetrahydro-1-, -2-, -3-, -4-, -5-, -6-, -7- or -8-isoquinolyl, 2-, 3-, 5-, 6-, 7- or 8-
- 35 3,4-dihydro-2H-benzo-1,4-oxazinyl.

Optionally substituted means unsubstituted or monosubstituted, disubstituted, trisubstituted, tetrasubstituted or pentasubstituted.

Aryl is preferably phenyl, naphthyl or biphenyl.

Arylalkyl is preferably benzyl.

5

Heteroaryl having one or more heteroatoms selected from among N, O and S is preferably 2- or 3-furyl, 2- or 3-thienyl, 1-, 2- or 3-pyrrolyl, 1-, 2-, 4- or 5-imidazolyl, 1-, 3-, 4- or 5-pyrazolyl, 2-, 4- or 5-oxazolyl, 3-, 4- or 5-isoxazolyl, 2-, 4- or 5-thiazolyl, 3-, 4- or 5-isothiazolyl, 2-, 3- or 4-pyridyl, 2-, 4-, 5- or 6-pyrimidinyl, also preferably 1,2,3-triazol-1-, -4- or -5-yl, 1,2,4-triazol-1-, -3- or -5-yl, 1- or 5-tetrazolyl, 1,2,3-oxadiazol-4- or -5-yl, 1,2,4-oxadiazol-3- or -5-yl, 1,3,4-thiadiazol-2- or -5-yl, 1,2,4-thiadiazol-3- or -5-yl, 1,2,3-thiadiazol-4- or -5-yl, 3- or 4-pyridazinyl, pyrazinyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-Indolyl, 4- or 5-isoindolyl, 1-, 2-, 4- or 5-benzimidazolyl, 1-, 3-, 4-, 5-, 6- or 7-benzopyrazolyl, 2-, 4-, 5-, 6- or 7-benzoxazolyl, 3-, 4-, 5-, 6- or 7-benzisoxazolyl, 2-, 4-, 5-, 6- or 7-benzothiazolyl, 2-, 4-, 5-, 6- or 7-benzisothiazolyl, 4-, 5-, 6- or 7-benz-2,1,3-oxadiazolyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-quinolyl, 1-, 3-, 4-, 5-, 6-, 7- or 8-isoquinolyl, 3-, 4-, 5-, 6-, 7- or 8-cinnolyl, 2-, 4-, 5-, 6-, 7- or 8-quinazolinyl, 5- or 6-quinoxalyl, 2-, 3-, 5-, 6-, 7- or 8-2H-benzo-1,4-oxazinyl, also preferably 1,3-benzodioxol-5-yl, 1,4-benzodioxan-6-yl, 2,1,3-benzothiadiazol-4- or -5-yl or 2,1,3-benzoxadiazol-5-yl.

10

15

In a preferred embodiment of the present invention, at least one of R^1 and R^{12} or $R^{1'}$ and $R^{12'}$ is not hydrogen and is selected from among phenyl-, 2,4,6-triisopropylphenyl, mesityl, 9-phenanthryl, 9-anthracenyl, ferrocenyl, N-(perfluorophenyl)acetamide, N-(4-chlorophenyl)acetamide, N-(naphthalen-1-yl)acetamide, N-benzhydrylacetamide, N-(2,6-diisopropylphenyl)acetamide, 1-anthracenyl, corannulene, porphyrin, 1-naphthyl, 2-naphthyl, 4-biphenyl, 3,5-(trifluoromethyl)phenyl, 2,6-dimethylphenyl, tert-butyl, tris-mesitylsilyl, tris-phenylsilyl, 4-nitrophenyl and 2,6-methyl-4-butylphenyl, trifluoromethyl, unbranched (linear) and branched (C_1 - C_{12})-perfluoroalkyls, 3,4,5-trifluorophenyl, 1,3-bis(perfluoropropan-2-yl)phenyl, 1,3-bis(perfluorobutyl)phenyl and/or pentafluorophenyl and also chloride, iodide, fluoride, $B(OH)_2$, $B(alkyl)_2$, $B(Oalkyl)_2$, $B(pinacol)$, BF_3X where $X=Na$ or K , OTf, MgCl, MgBr, ZnCl. The other radicals are preferably hydrogen.

20

25

30

In a further preferred embodiment of the present invention, at least one of the radicals R^4 and R^9 or $R^{4'}$, $R^{4''}$, $R^{9'}$ and $R^{9''}$ is selected from among NO_2 and I.

The compounds according to the invention can be converted in process steps which are well known per se to those skilled in the art into organic salts, metal salts or metal complexes. In

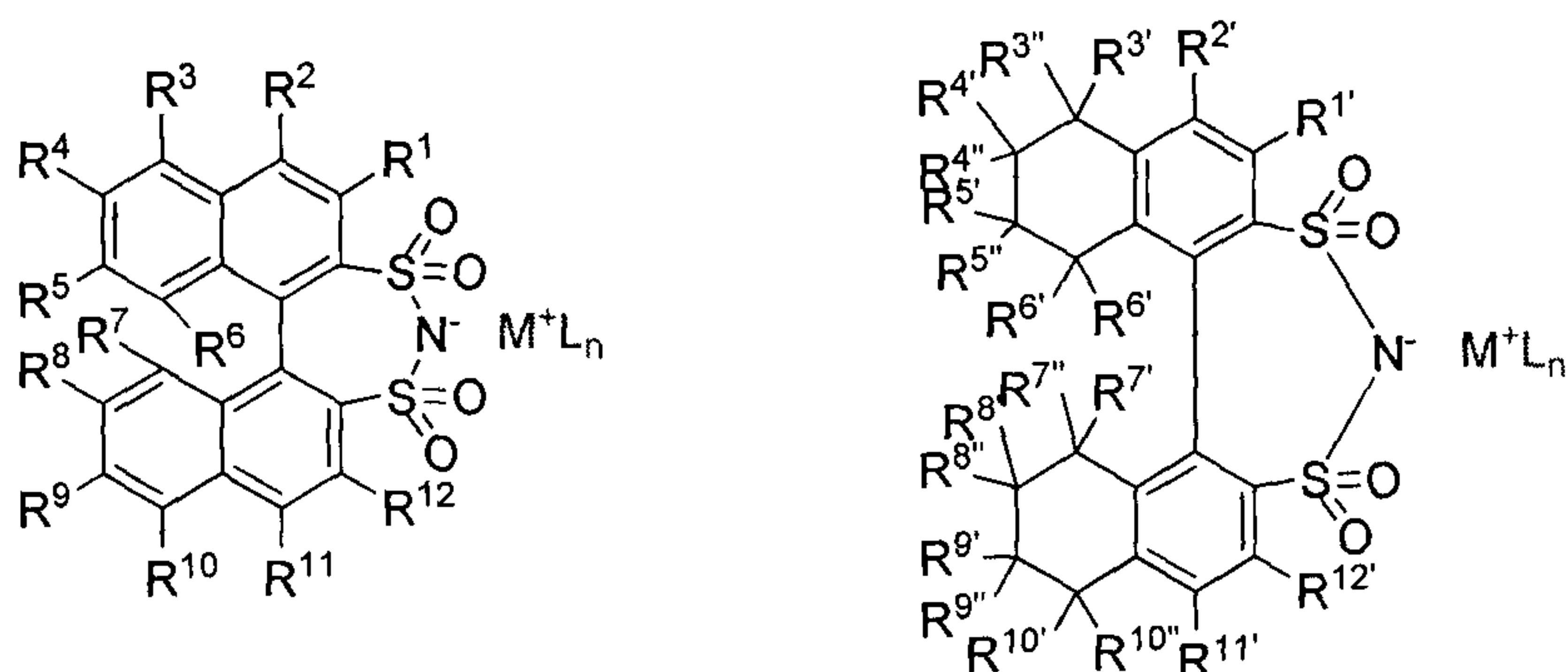
35

- 9 -

one possible embodiment, the disulfonimides are reacted with an appropriate metal salt, for example with the carbonate of the appropriate metal.

Examples of organic salts, metal salts and metal complexes are shown in the following scheme:

5



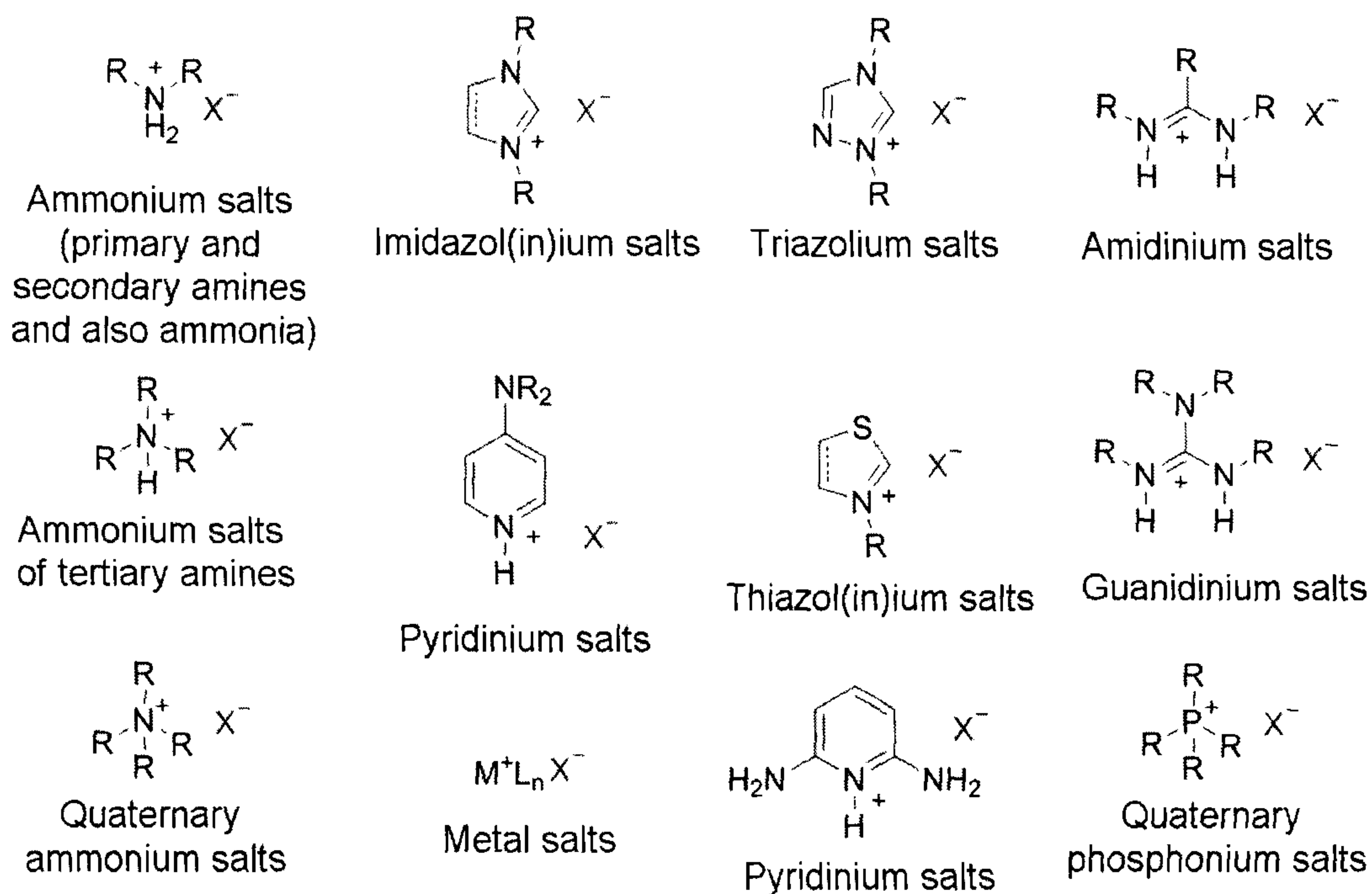
Scheme 1: General examples of metal salts and metal complexes of the disulfonimides IV and disulfonimides V.

10

In scheme 1, any metals or organic cations, e.g. tertiary ammonium ions, can be represented by M. L refers to any ligands present in the number $n = 0-10$. Even though the compounds are shown as salts in scheme 1, the precise structure with metals is not known; they can also have the structure of metal complexes. The formulation metal salts or metal complexes is therefore used for the purposes of the present invention. The metal compounds are not restricted to particular metal compounds or complexes. Suitable metal compounds are derived from Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Mo, Ru, Rh, Pd, Ag, W, Re, Os, Ir, Pt, Au, Al, Pb, La, Sm, Eu, Yb.

15

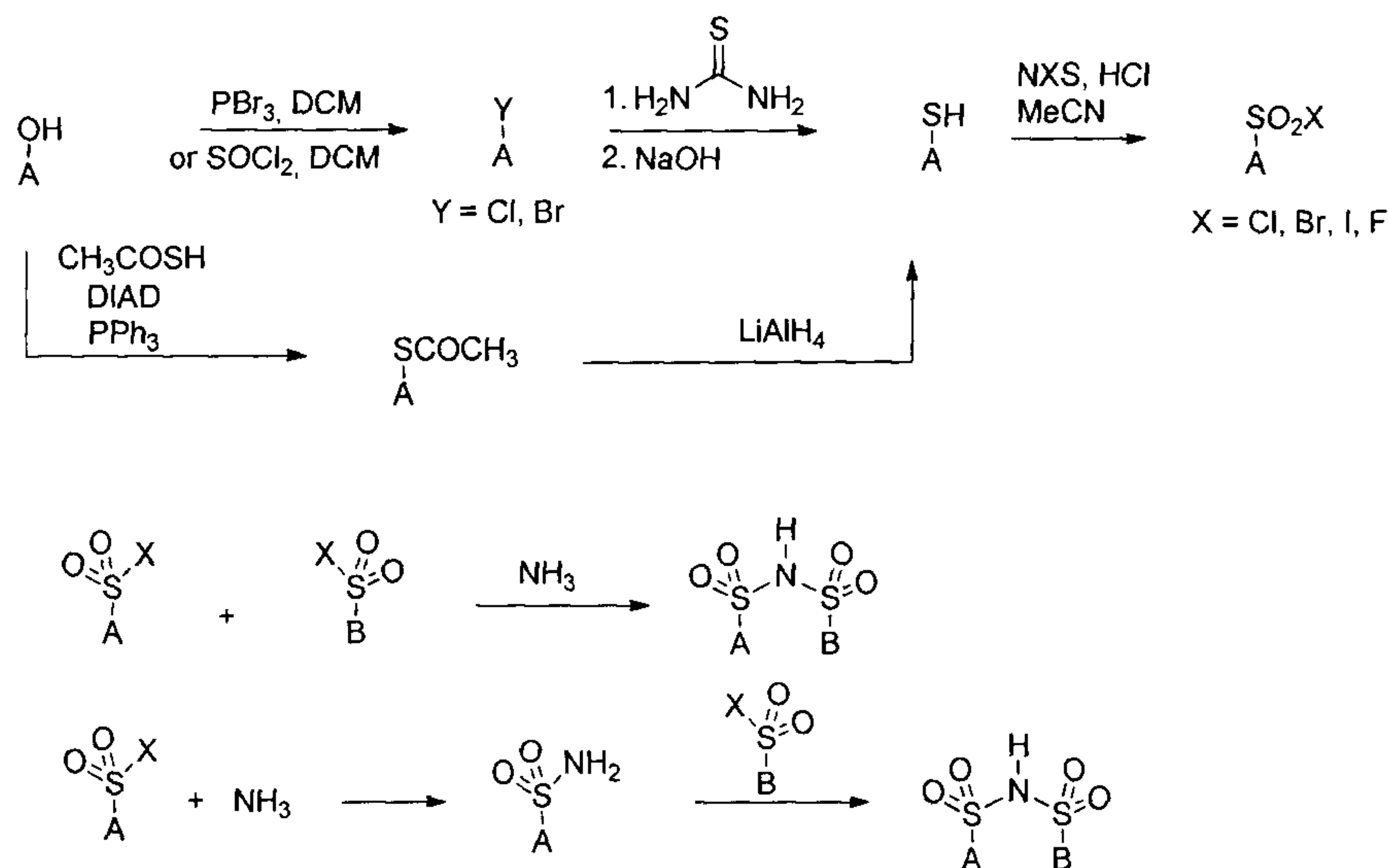
- 10 -



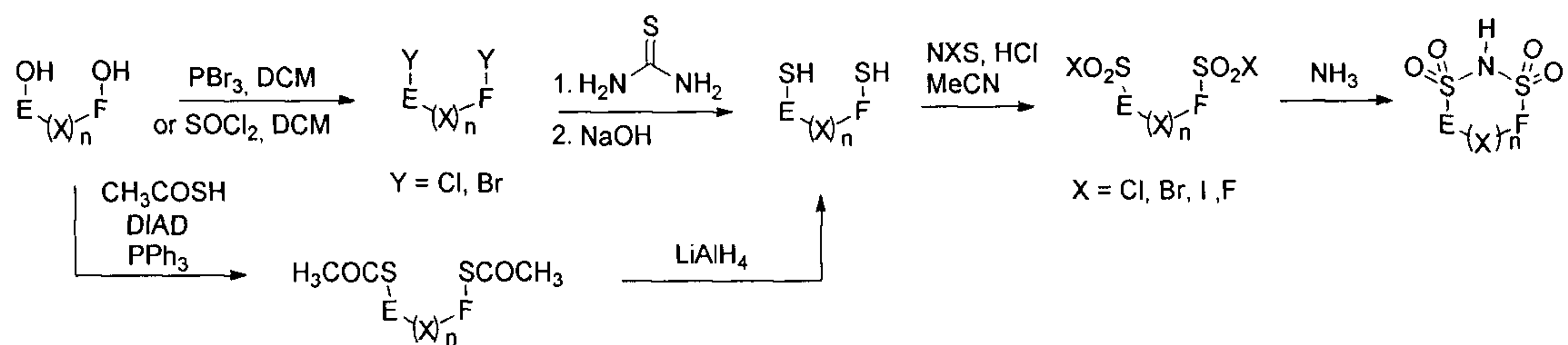
Scheme 2: Examples of possible cations.

5

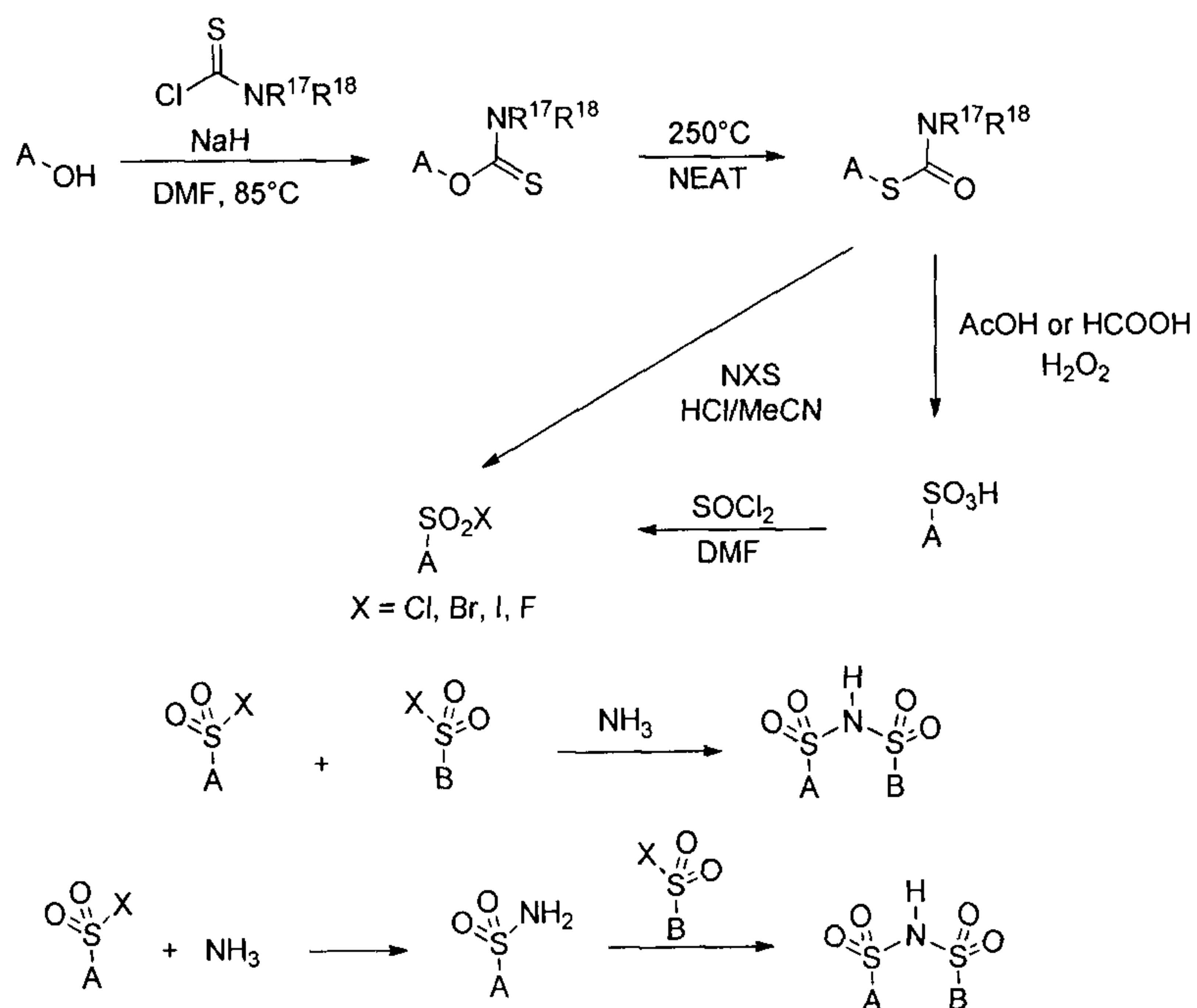
Examples of synthetic routes in which A and/or B, C and/or D and also E and/or F are chiral aliphatic radicals:



- 11 -

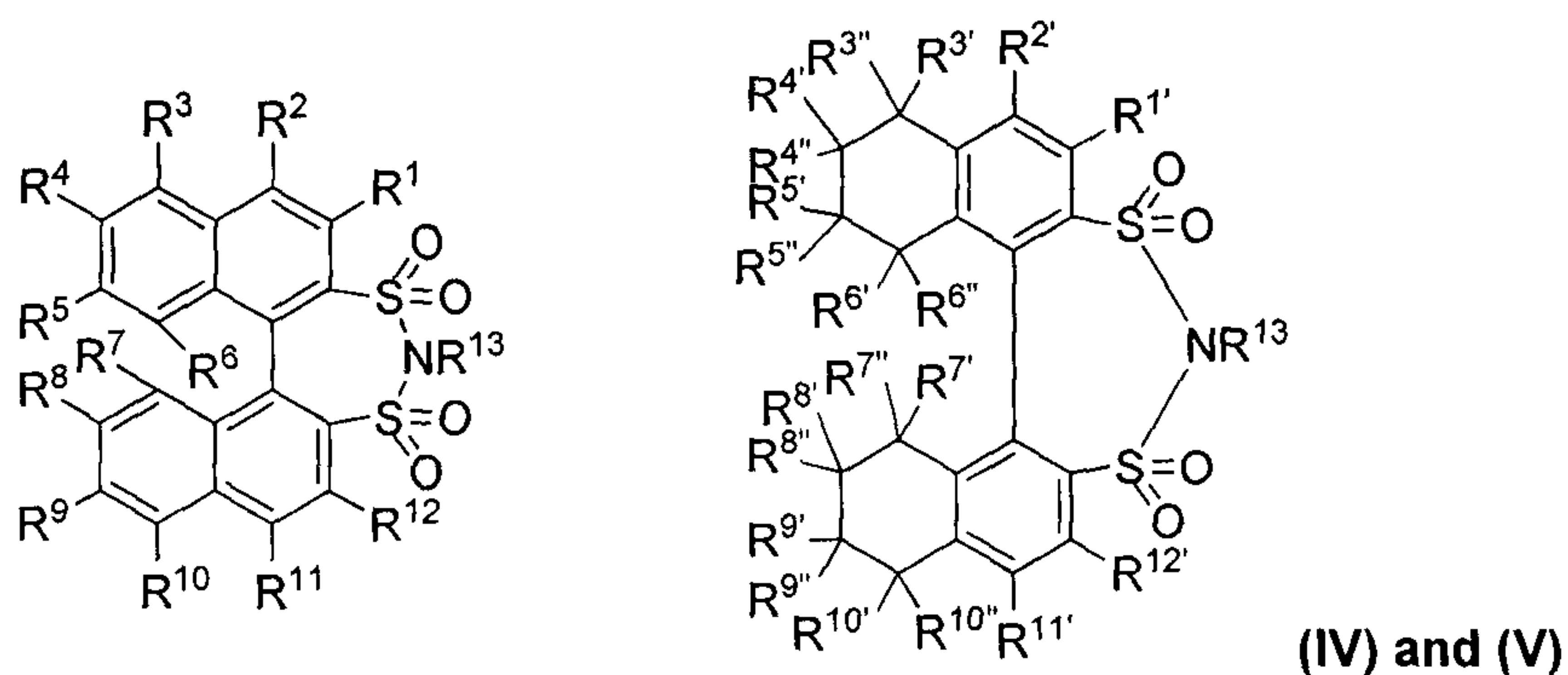


5 If A, B, C, D, E, F are aromatic radicals, the synthesis can be carried out via a Newman-Kwart rearrangement:



10 A preferred preparative process of the present invention is a process for preparing substituted disulfonimides having the general formula I or II, i.e. disulfonimides having a chiral BINOL and H8 BINOL backbone:

- 12 -

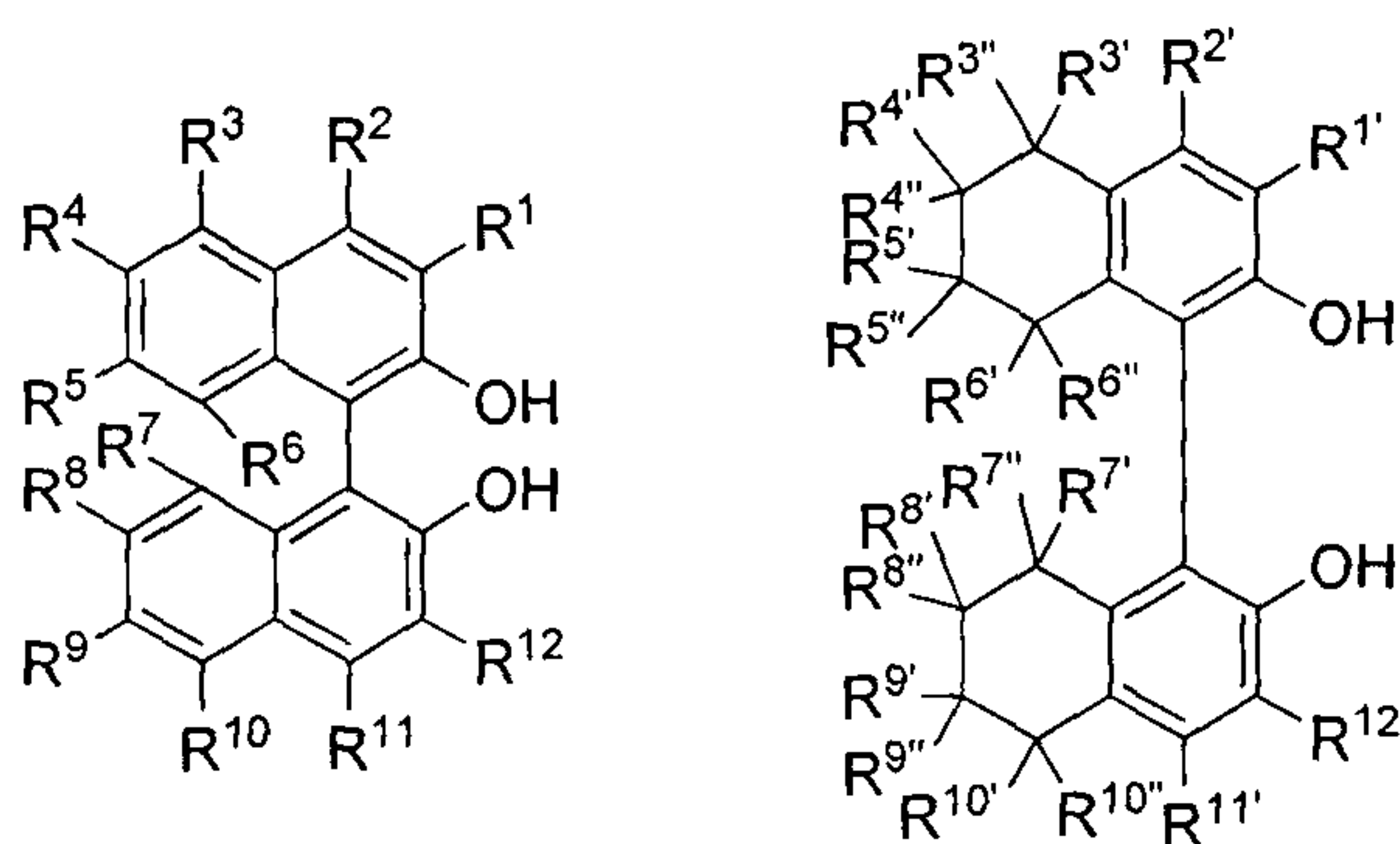


where

R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R^{1'}, R^{2'}, R^{3'}, R^{3''}, R^{4'}, R^{4''}, R^{5'}, R^{5''}, R^{6'}, R^{6''}, R^{7'}, R^{7''}, R^{8'}, R^{8''}, R^{9'}, R^{9''}, R^{10'}, R^{10''}, R^{11'} and R^{12'} and R¹³ are as defined above,

5 where

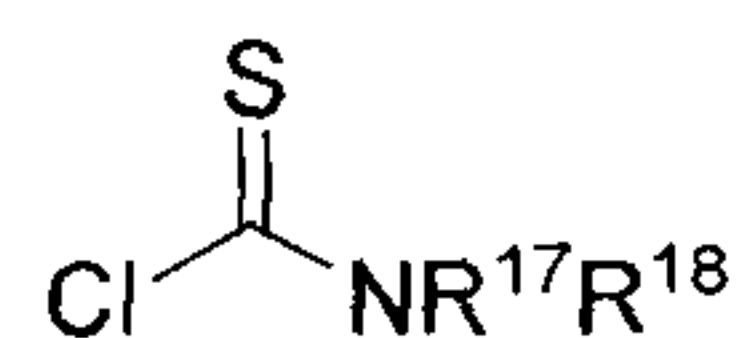
(A) is a Binol derivative having the general formula X or an H8-Binol derivative having the general formula XI



10

(X) and (XI)

is reacted with a thiocarbamoyl chloride of the general formula XII

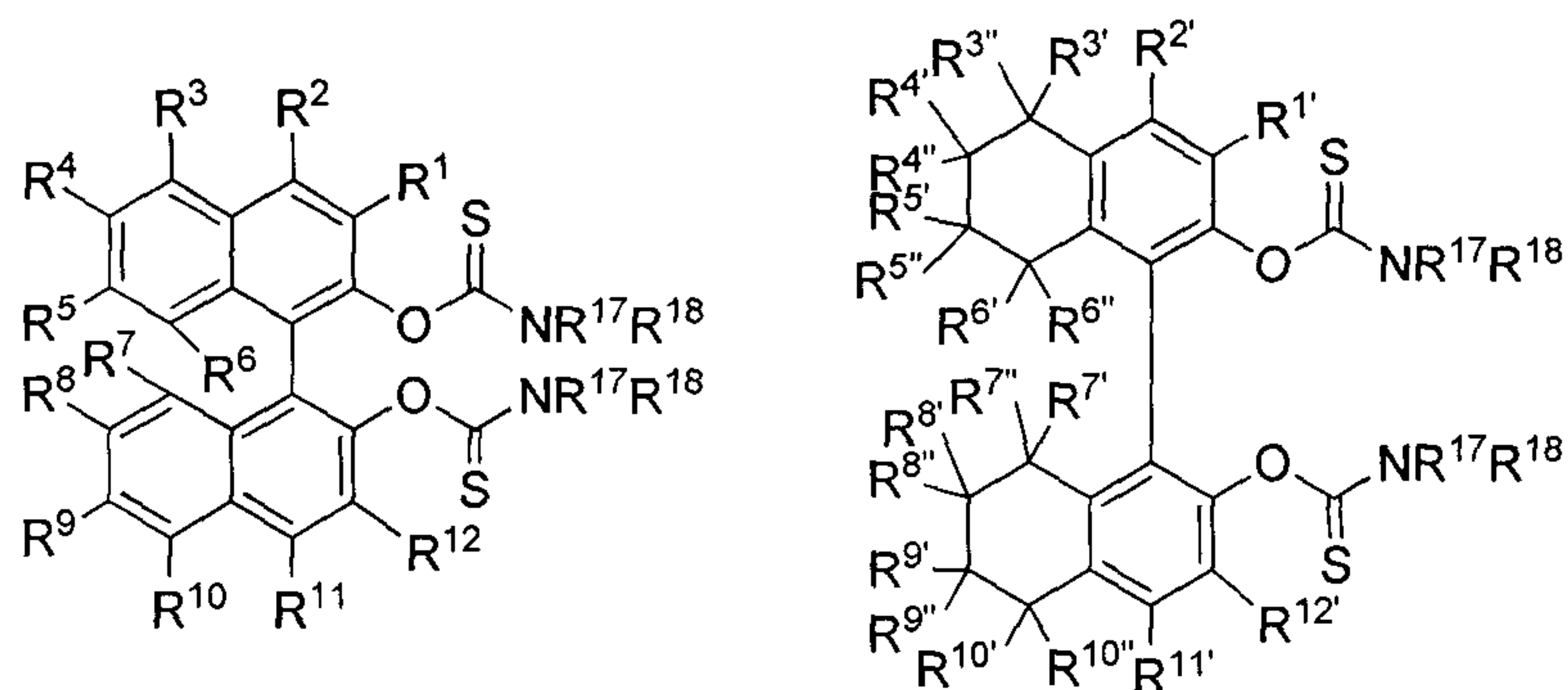


(XII)

15

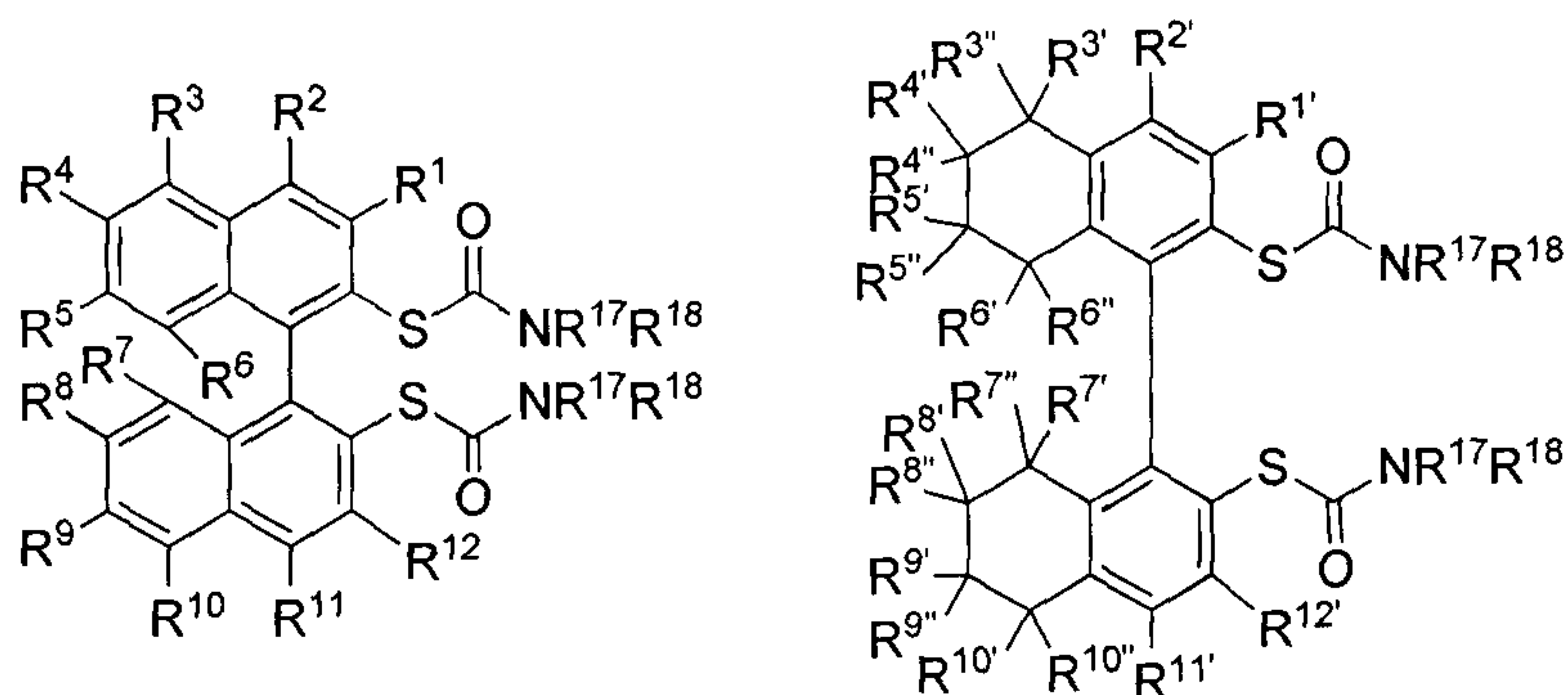
where R¹⁷ and R¹⁸ can be identical or different and are each a C₁-C₆-alkyl group, to form an O-arylthiocarbamate having the general formula XIII or XIV,

- 13 -



(XIII) and (XIV)

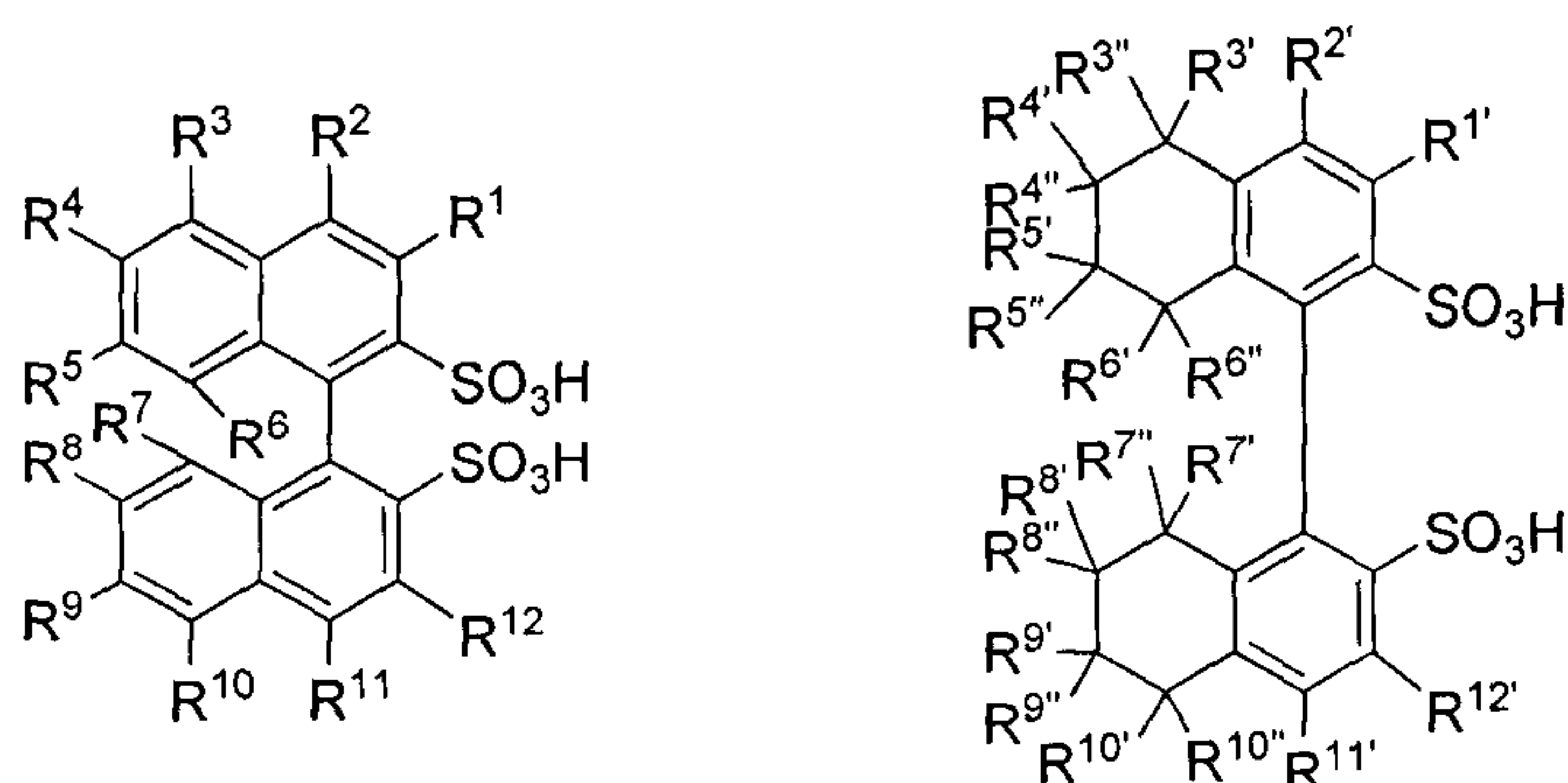
- 5 (B) the O-arythiocarbamate having the formula XII is converted into the corresponding S-arythiocarbamate having the formula XV or XVI,



(XV) and (XVI)

and

- (C) the S-arythiocarbamate is converted in the presence of an oxidant into the compounds having the formula XVII or XVIII.

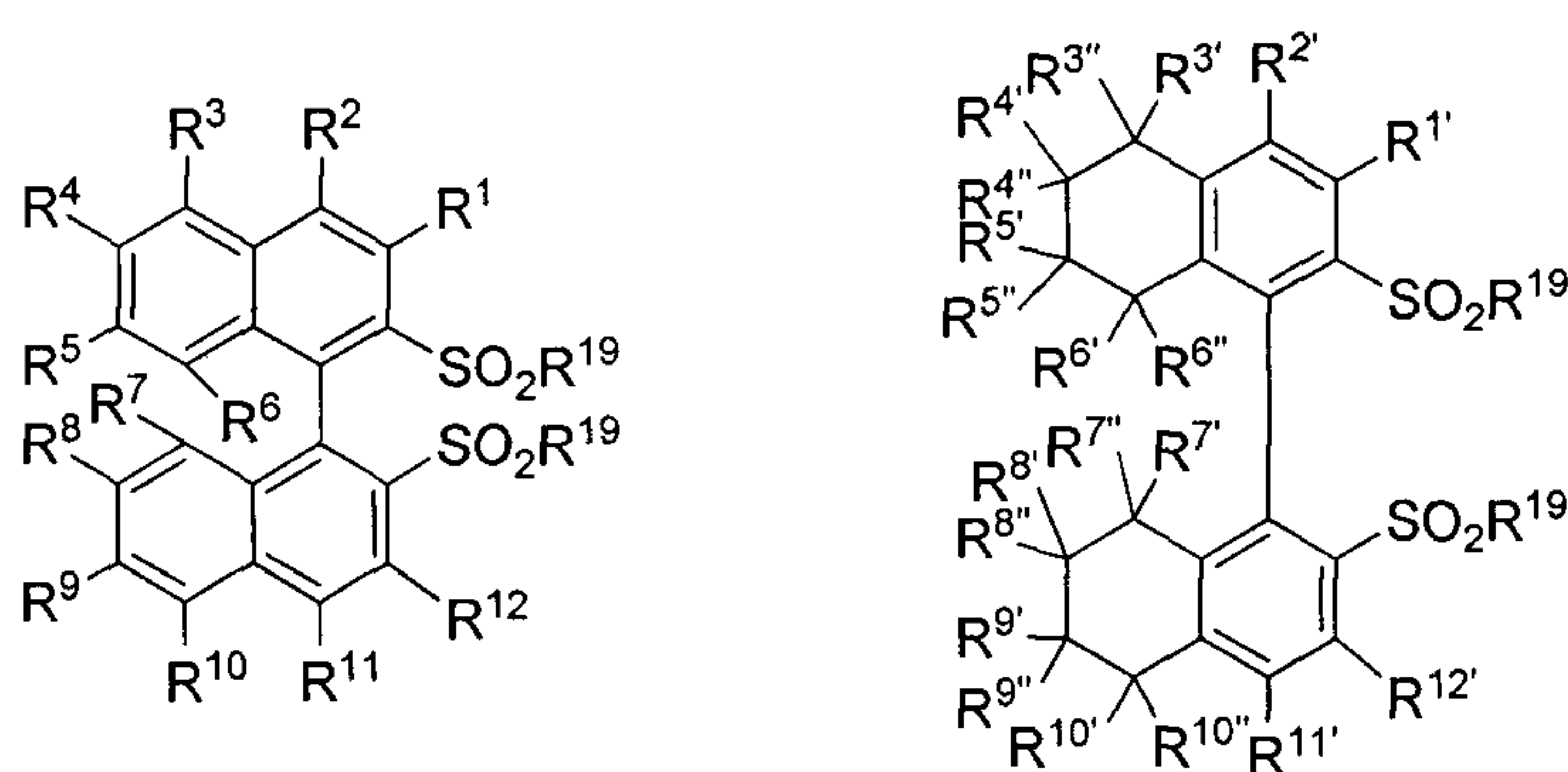


(XVII) and (XVIII)

10

In a process step (D), the sulfonic acids having the formula (VI) are converted in a manner known per se into the acid halides having the formula XIX or XX, where R¹⁹ = Cl, Br, I or F,

- 14 -



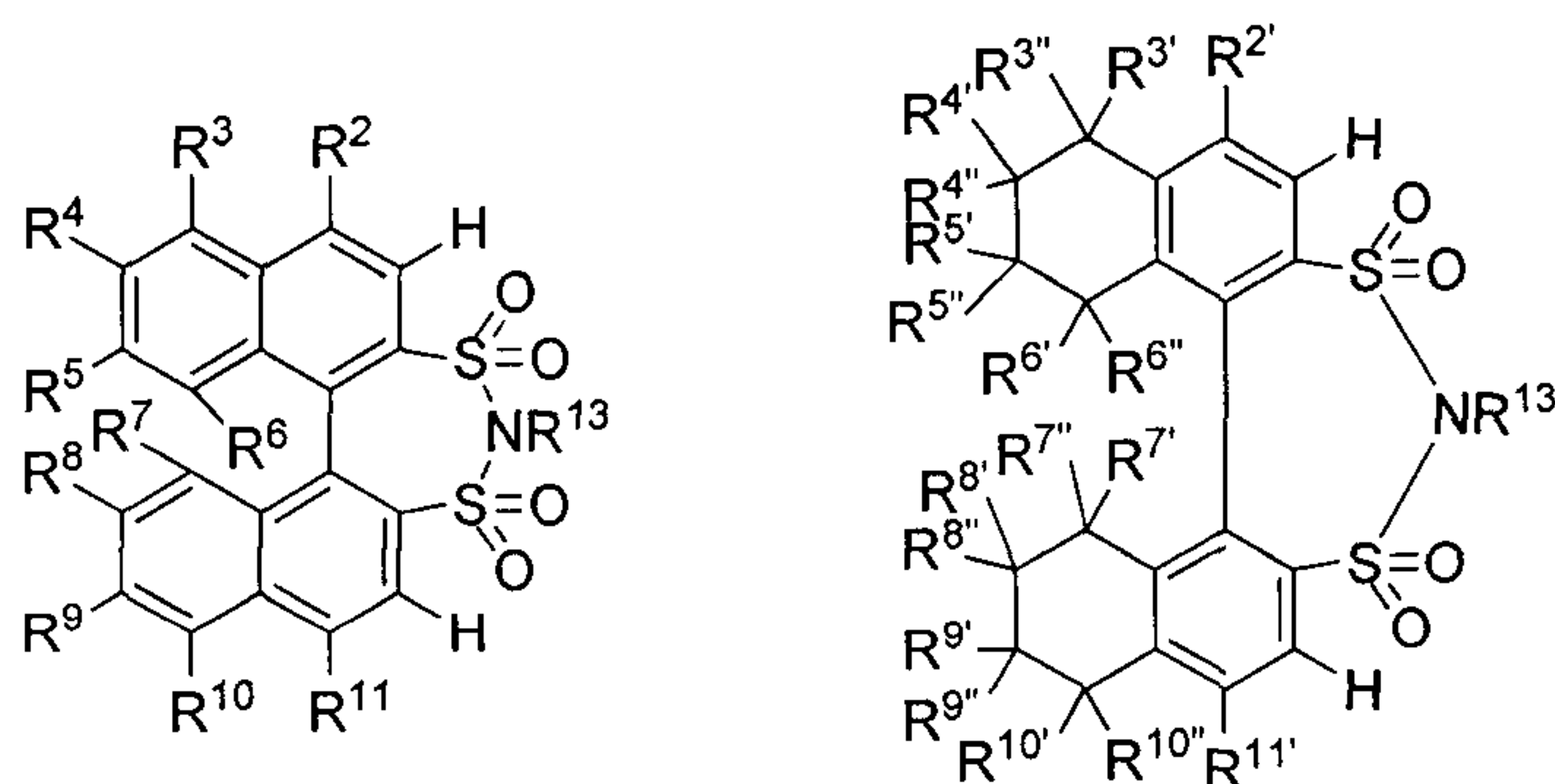
(XIX) and (XX)

and in a subsequent process step

- 5 (E) are subsequently converted by means of ammonia or a primary amine into the corresponding imide having the formula IV or V.

As an alternative, the S-arylthiocarbamate having the formula XV or XVI can in this synthetic route be converted directly into the acid halides having the formula XIX or XX, where R¹⁹ =
10 Cl, Br, I or F, in a process step (D1) known to those skilled in the art.

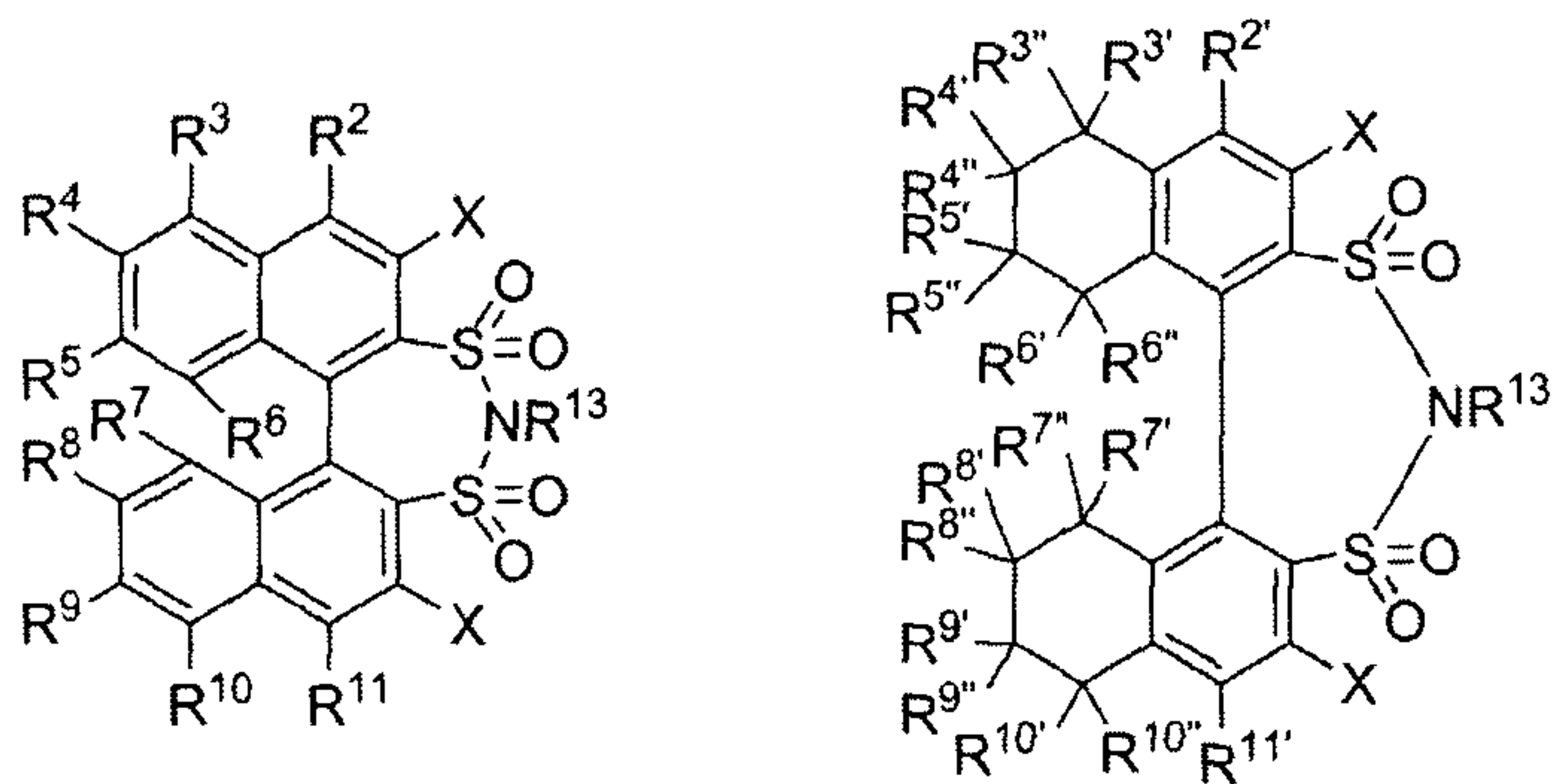
An alternative synthetic route starts out from a 3,3'-unsubstituted disulfonimide having the general formula IVa or Va (R¹, R¹² = H or R^{1'}, R^{12'} = H), which can be prepared by the above synthetic route.



(IVa) and (Va)

This is converted in a process step F) known to those skilled in the art into a 3,3'-dihalide (R¹, R¹² = Cl, Br, I or F or R^{1'}, R^{12'} = Cl, Br, I or F) or a 3,3'-ditriflate (R¹, R¹² = OTf or R^{1'}, R^{12'} = OTf) having the general formula XX or XXI.

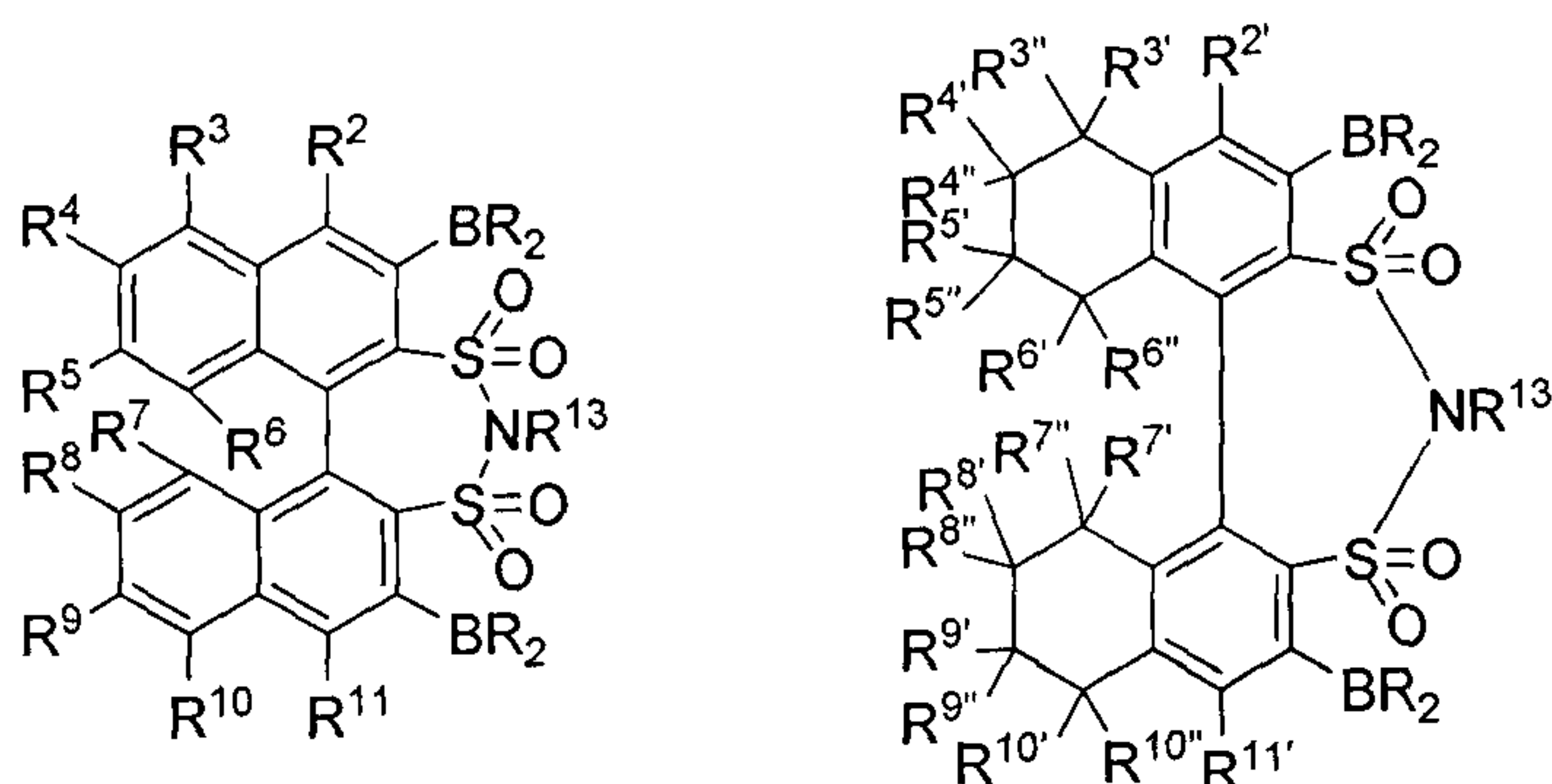
- 15 -



X = Cl, Br, I, F or OTf

(XX) and (XXI)

As an alternative, the disulfonimides IVa or Va can be converted in this synthetic route into a 3,3'-diboronate ($R^1, R^{12} = B(OH)_2, B(alkyl)_2, B(Oalkyl)_2, B(pinacol), BF_3X$ X=Na, K or $R^1, R^{12} = B(OH)_2, B(alkyl)_2, B(Oalkyl)_2, B(pinacol), BF_3X$ where X=Na, K) having the general formula XXiill or XXIII in a process step G) known to those skilled in the art.



(XXII) and (XXIII)

- 10 The halides and ditriflates having the general formula XX or XXI or the boronates having the general formula XXII or XXIII serve as starting substances for the coupling reactions well known to those skilled in the art as process step H) to give the imides having the formula IV or V.
- 15 The individual reaction steps of the process of the invention are processes known from the prior art. In process step SA, the dihydroxy compound having the formula IV or V is reacted with a thiocarbamoyl chloride of the formula XII in the presence of a hydride in a solvent at elevated temperatures. Possible solvents are all organic solvents which do not have an adverse effect on the reaction.

- 16 -

The reaction step B is preferably carried out in a suitable solvent or in the absence of solvent by heating the O-arylthiocarbamate obtained in step A. The S-arylthiocarbamate having the formula XV or XVI obtained is converted in the next process step C into a sulfonic acid having the formula XVII or XVIII. This process step is preferably carried out in the presence of an oxidant such as H₂O₂ and an acid and/or an organic peracid.

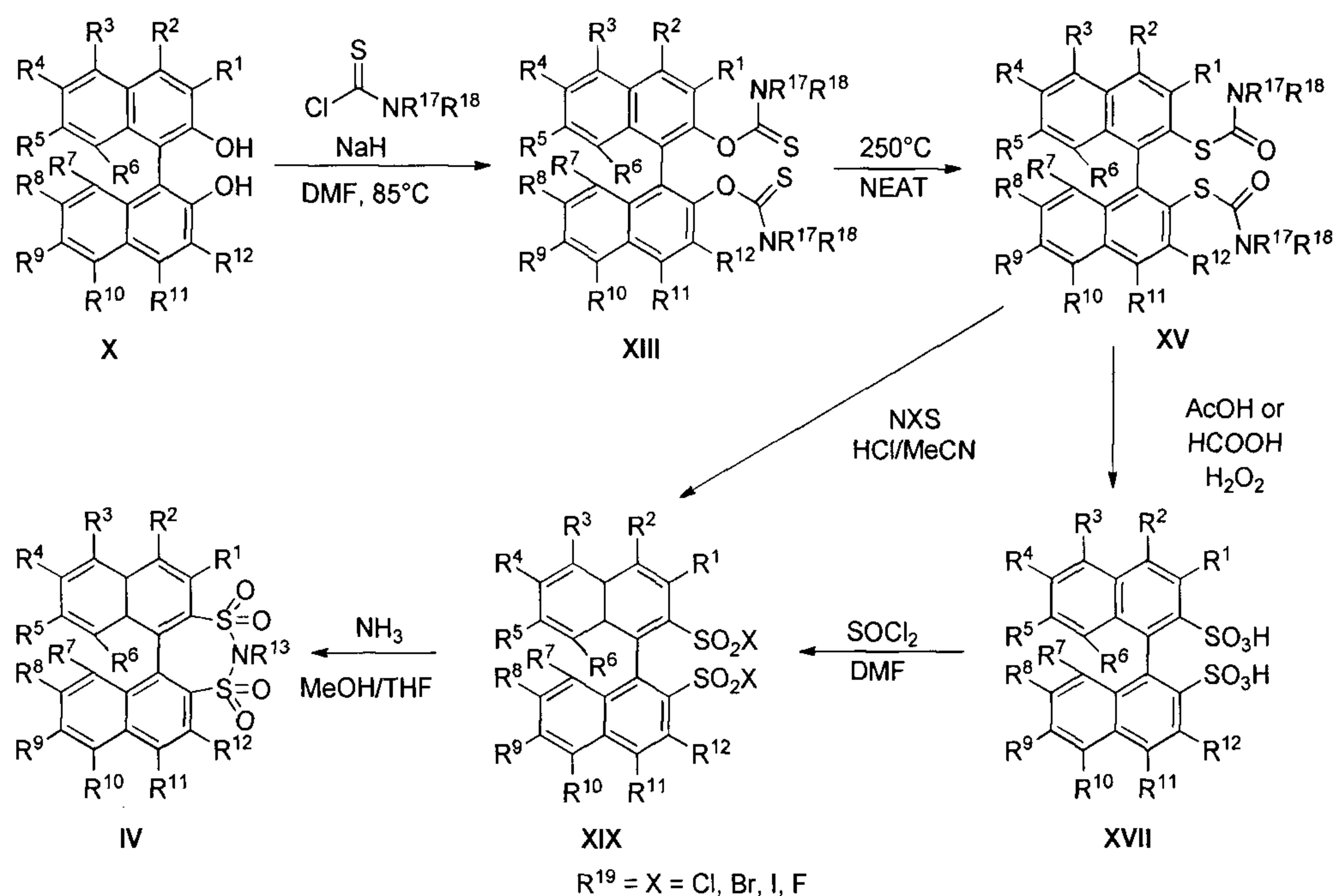
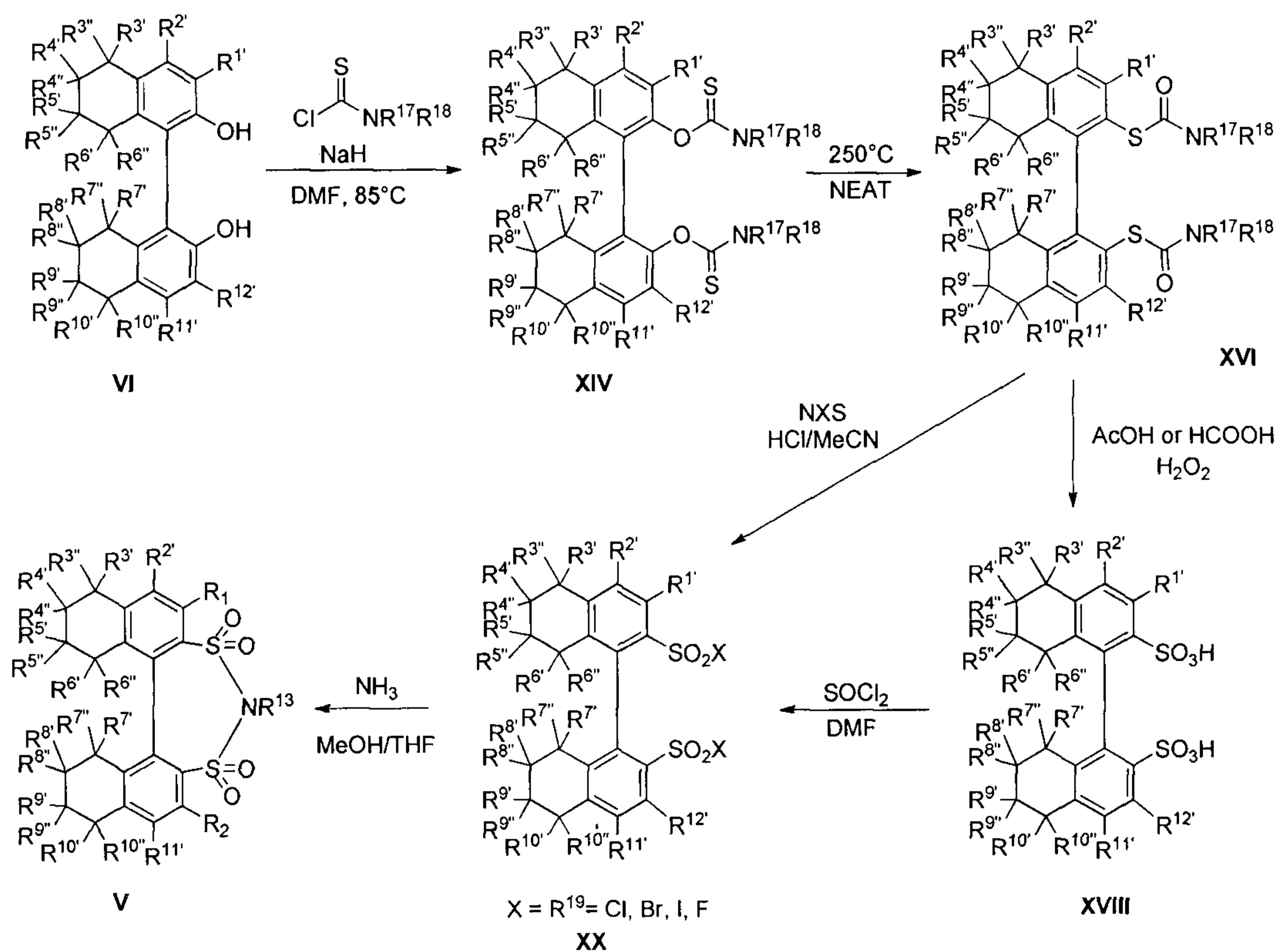
The conversion of the sulfonic acid having the formula XVII or XVIII into the acid imide having the formula IV or V can be carried out in a manner known per se using process steps which are well known to those skilled in the art.

As an alternative, the S-arylthiocarbamate having the formula XV or XVI can be converted directly in the synthetic route into the acid halides having the formula XVII or XVIII, where R¹⁹ = Cl, Br, I or F, in a process step (D1) known to those skilled in the art.

An example of a general synthetic route from BINOL X to disulfonimide IV is shown in scheme 3. The synthetic route for disulfonimide V is analogous and starts out from an H8-BINOL XI (scheme 4). Starting substances are corresponding substituted or unsubstituted BINOLs X or H8-BINOLs XI, and these are converted by means of dimethylthiocarbamoyl chloride into the corresponding O-arylthiocarbamate XIII or XIV. A Newman-Kwart rearrangement gives the S-arylthiocarbamate XV or XVI which is converted under oxidative conditions into the disulfonic acid XVII or XVIII. Conversion of this acid into the corresponding sulfonic acid halides XIX or XX and ring closure by means of ammonia give the disulfonimide IV or V.

As an alternative, the S-arylthiocarbamate having the formula XV or XVI can be converted directly in this synthetic route into the acid halides having the formula XIX or XX in a process step (D1) known to those skilled in the art. Ring closure by means of ammonia gives the disulfonimide IV or V. A general description of the preparation of the disulfonimides is given in the experimental part.

- 17 -

**Scheme 3.** Synthetic route according to the invention to disulfonimide IV.**Scheme 4.** Synthetic route according to the invention to disulfonimide V.

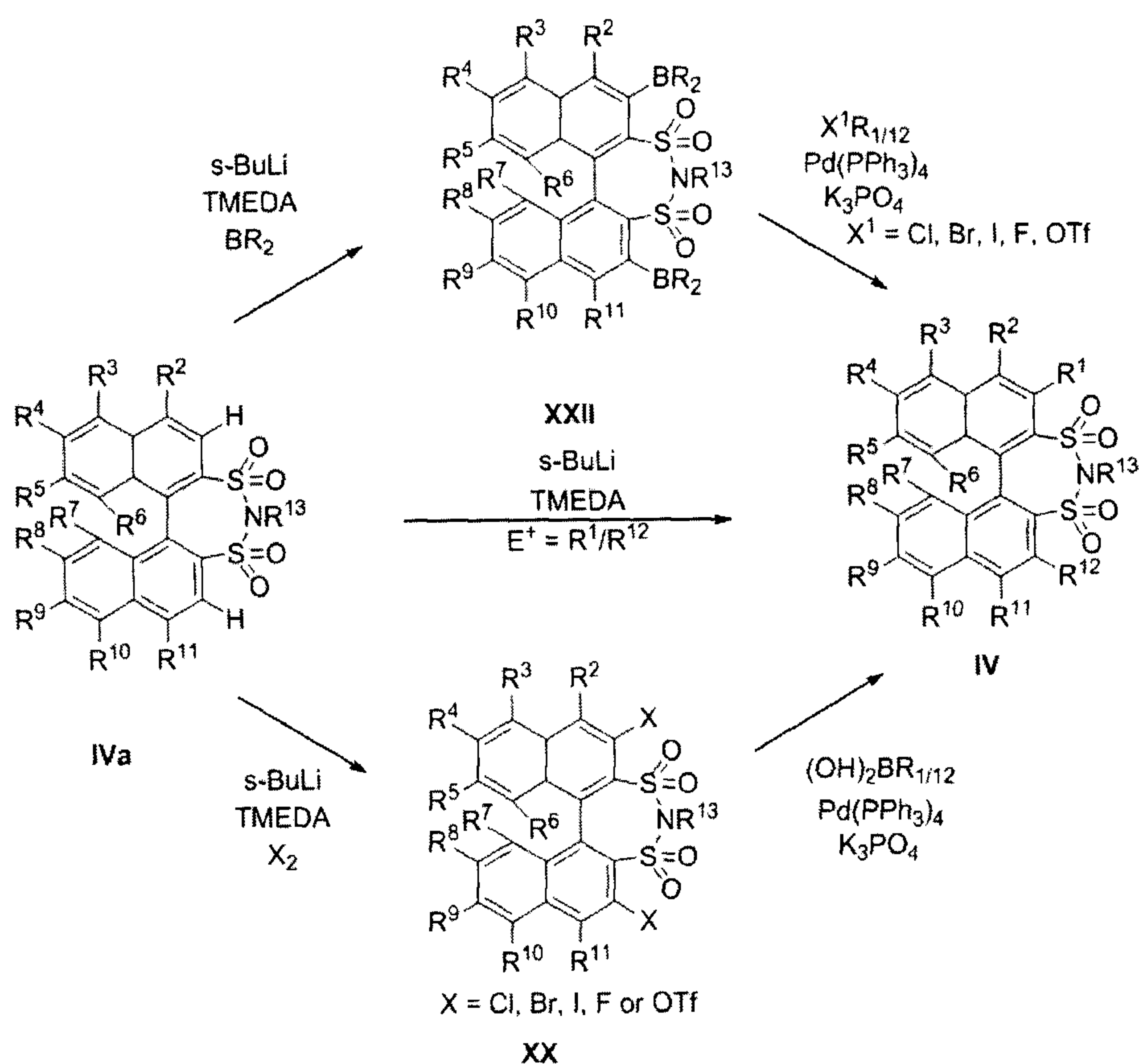
5

In an alternative synthetic route, the disulfonimides IVa or Va prepared by the above route ($R^1, R^{12} = \text{H}$ or $R^{1'}, R^{12'} = \text{H}$) serve as starting substances. The disulfonimides IVa or Va are

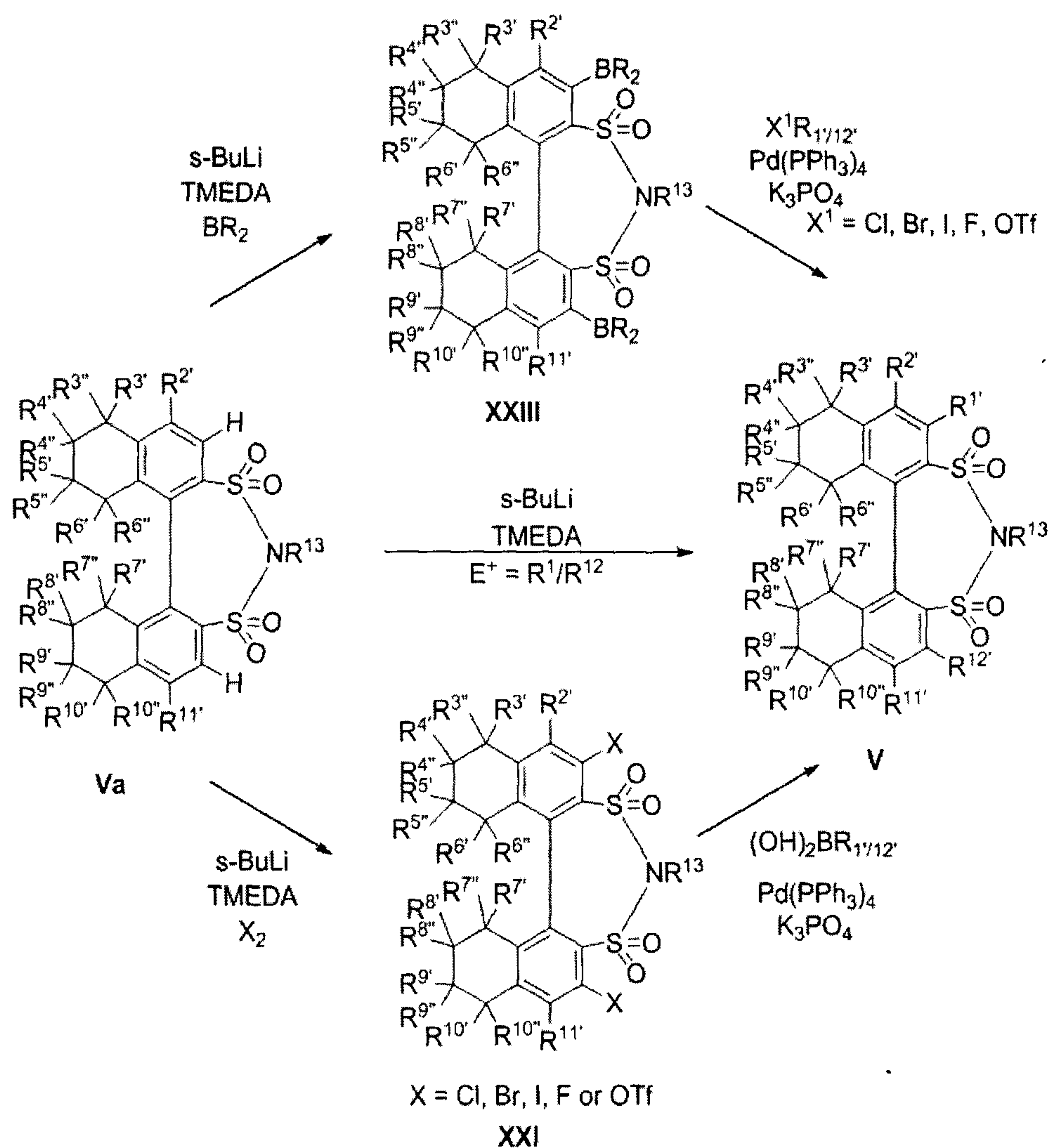
- 18 -

converted by means of a process step which is well known to those skilled in the art into the halides or ditriflates having the general formula XX or XXI or the boronates having the general formula XXII or XXIII. These serve as starting substances for coupling reactions to form the imides having the formula IV or V. Variation of R^1 , R^{12} or $R^{1'}$, $R^{12'}$ via the

5 disulfonimides IVa or Va is also possible by not quenching the metal species formed *in situ* by means of a directing ortho-metallization (R^1 , R^{12} = Li, Mg, Zn, Cu or $R^{1'}$, $R^{12'}$ = Li, Mg, Zn, Cu) with halogen sources but rather with other, suitable electrophiles such as CO_2 , perfluoroalkyl iodides or isocyanates, aldehydes or ketones.



10 **Scheme 5.** Synthetic routes according to the invention to disulfonimide IV via disulfonimide IVa



Scheme 6. Synthetic routes according to the invention to disulfonimide V via disulfonimide Va.

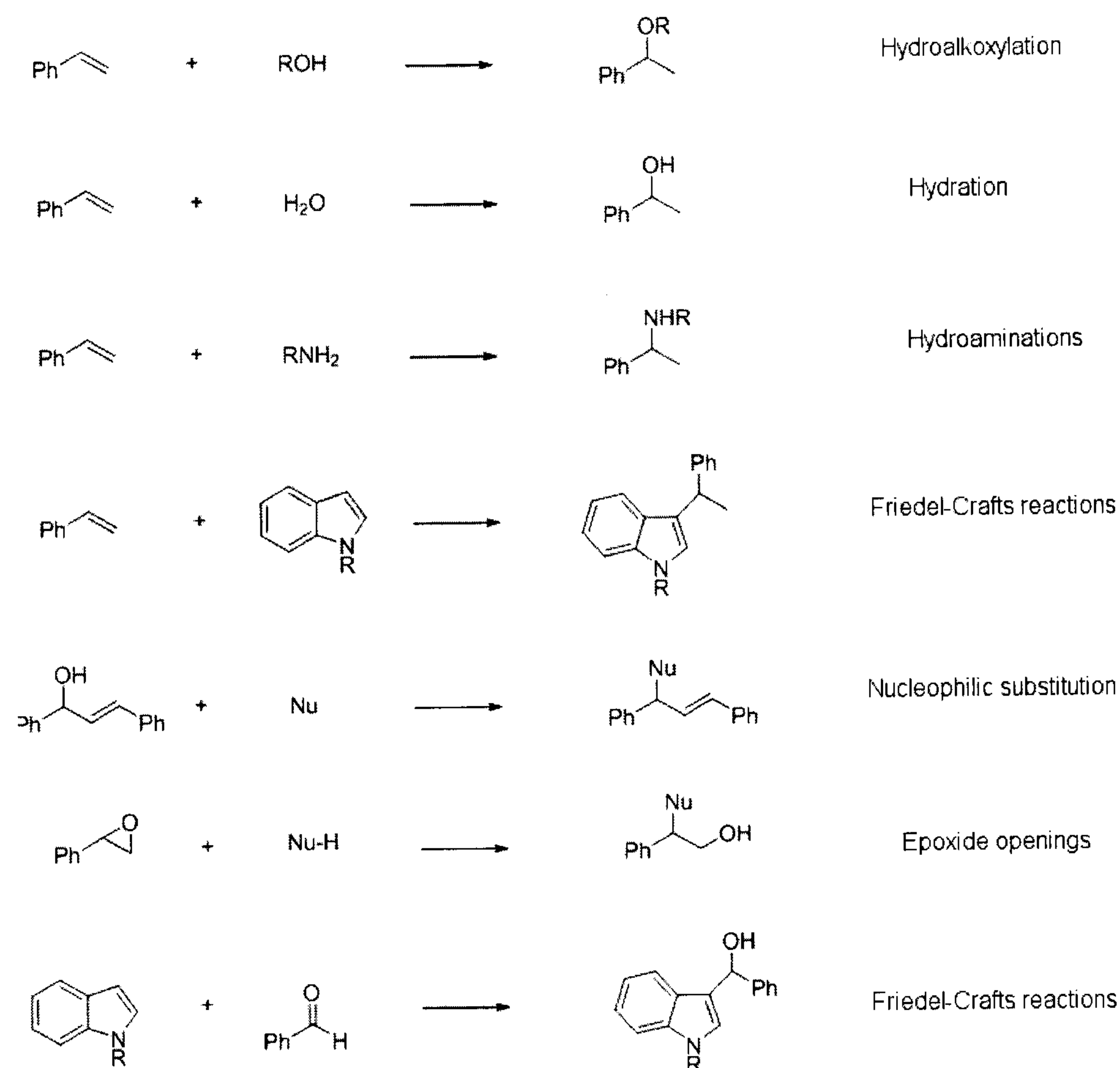
5 Use as catalysts

The disulfonimides I-III of the invention and their organic salts, metal salts and metal complexes are particularly suitable as strong, chiral Brønsted acid catalysts or chiral Lewis acid catalysts for many reactions, in particular for the activation of ketones, aldehydes and alkenes. A particularly good catalytic activity is displayed by compounds in which R^{13} is H, F, Cl, Br, I or $\text{SiR}^{14}\text{R}^{15}\text{R}^{16}$, where R^{14} , R^{15} , R^{16} are each C_1 - C_6 -alkyl, C_2 - C_6 -alkenyl or C_2 - C_6 -alkynyl. R^{13} is particularly preferably $\text{SiR}^{14}\text{R}^{15}\text{R}^{16}$ or I.

- 20 -

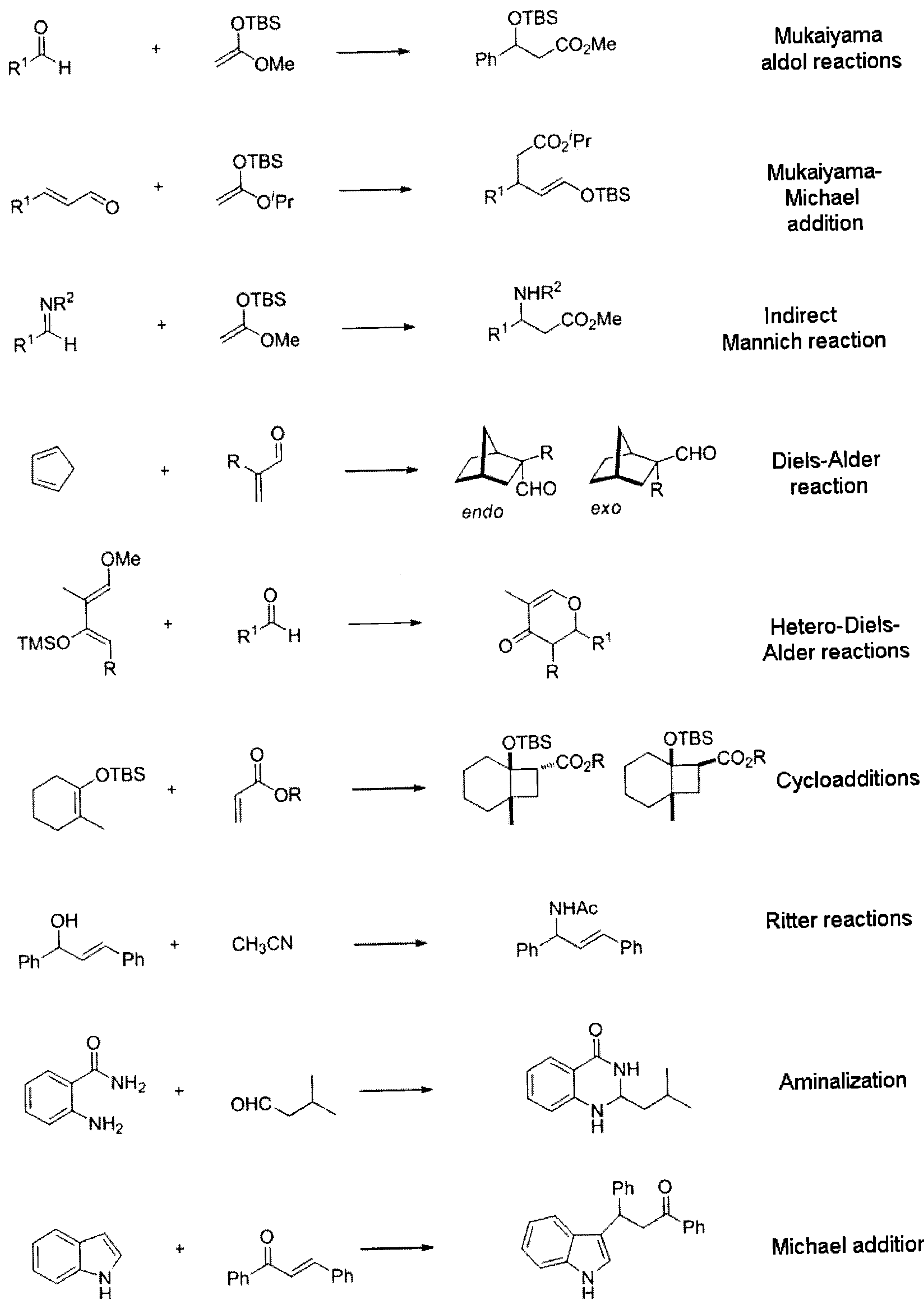
The reactions in which the compounds according to the invention can be used as catalysts include reactions such as aldol reactions, vinylic aldol reactions, Mukaiyama aldol reactions, vinylic Mukaiyama aldol reactions, Mukaiyama-Michael reactions, Michael additions, Mannich reactions, TMS-CN additions onto aldehydes and ketones, esterifications, etherifications, pinacol rearrangements, as acetalizations and related reactions, cycloadditions, hydroaminations, hydroalkoxylation, hydrations, olefin activations in general, Friedel-Crafts reactions, epoxide openings, Ritter reactions, nucleophilic substitutions of alcohols, asymmetric ring openings, asymmetric reductions, transfer hydrogenations, alkyne additions, allylations, epoxidations, olefin metathesis, isomerizations, iminium catalysis and enamine catalysis.

A selection of these reactions is shown in schemes 7 and 8.



- 21 -

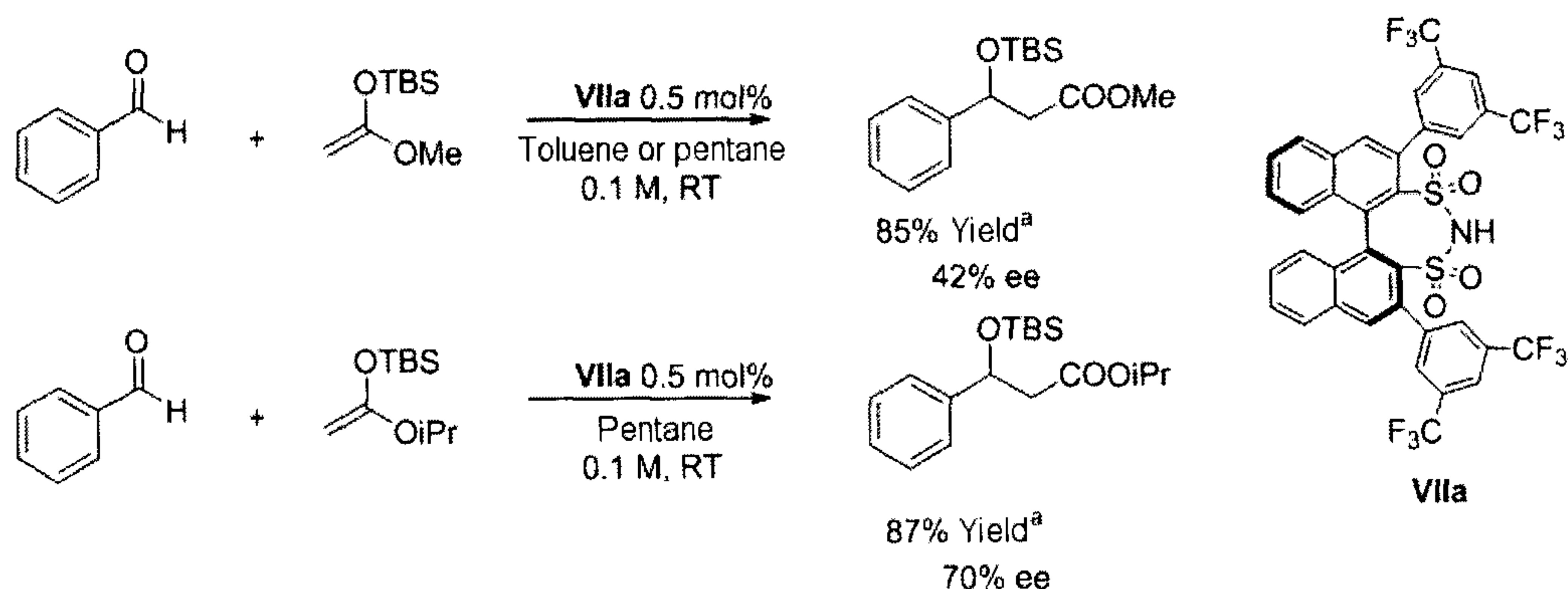
Scheme 7. Selection of possible reactions.



Scheme 8. Selection of possible reactions.

First results achieved in the Mukaiyama aldol reaction using disulfonimide VIIa are shown by way of example in scheme 9.

5



^aNMR yield based on 0.05 mmol of Ph₃PH as internal standard

Scheme 9. Selection of results achieved using disulfonimide VIIa.

- 10 Further fields of application of the compounds according to the invention are
- As ligands for metal complexes; the replacement of the two chloride ligands by the disulfonimides of the general formulae I to III in the known Grubbs catalysts and Hoveyda-Grubbs catalysts may be mentioned by way of example;
 - 15 In deprotonated form, the disulfonimides having the general formulae I to III are also suitable as chiral anion in asymmetric synthesis.

The present invention further provides for the use of the compounds having the formulae I to III as NMR shift reagents and as reagents for resolution of racemates.

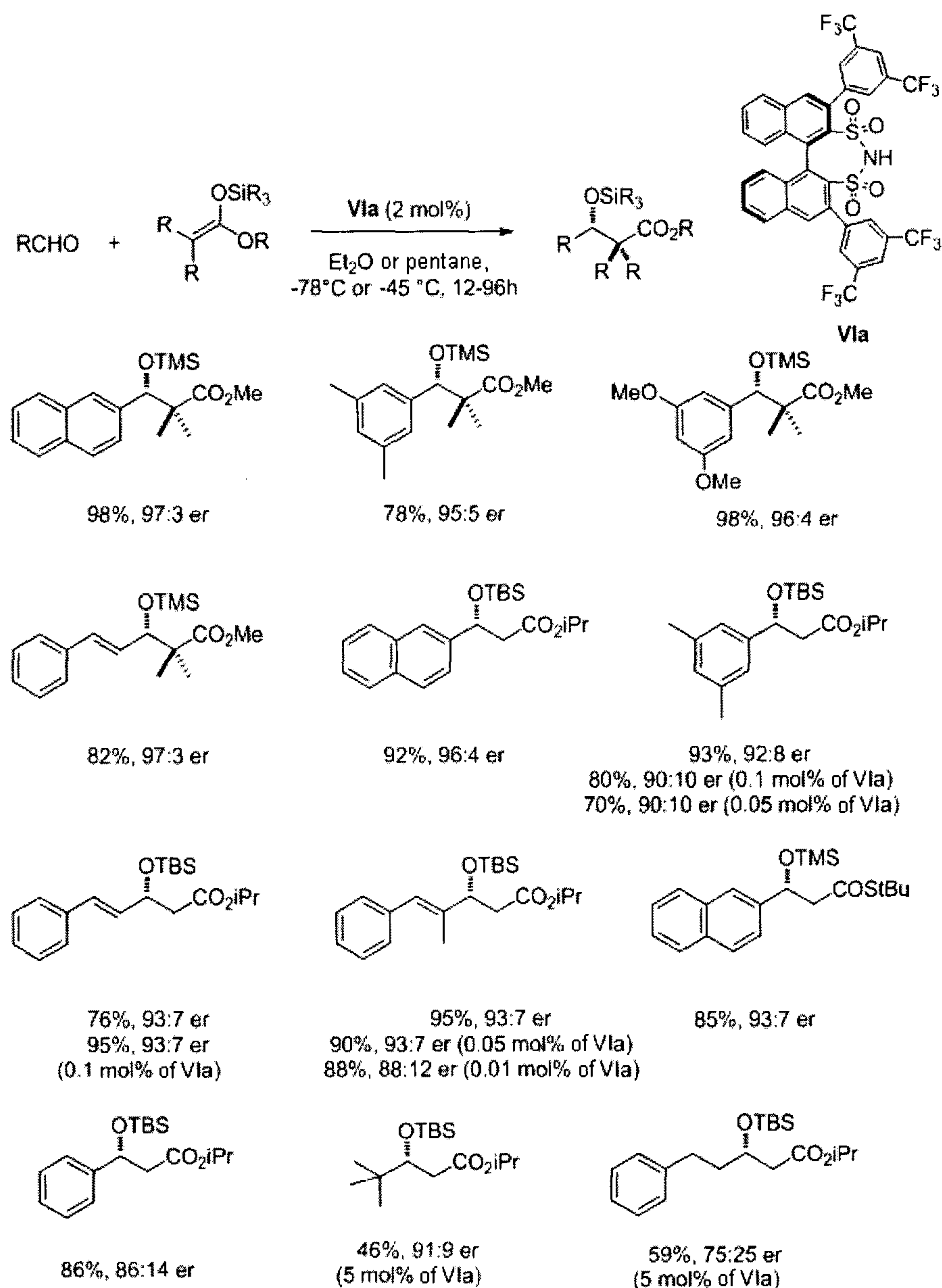
20 Experimental part**General method for the Mukaiyama aldol reaction at room temperature**

Disulfonimide VIIa (0.41 mg, 0.5 mol%) and benzaldehyde (10 μL , 0.1 mmol) together with 0.5 ml of toluene or pentane are placed in a reaction vessel at room temperature. tert-Butyl(1-methoxyvinyl)dimethylsilane or tert-butyl(1-isopropoxyvinyl)dimethylsilane (0.11 mmol) is added dropwise and the mixture is stirred at room temperature for 1-2 hours. The solvent is then removed under reduced pressure and 0.05 mmol of Ph₃CH is added as

25

- 23 -

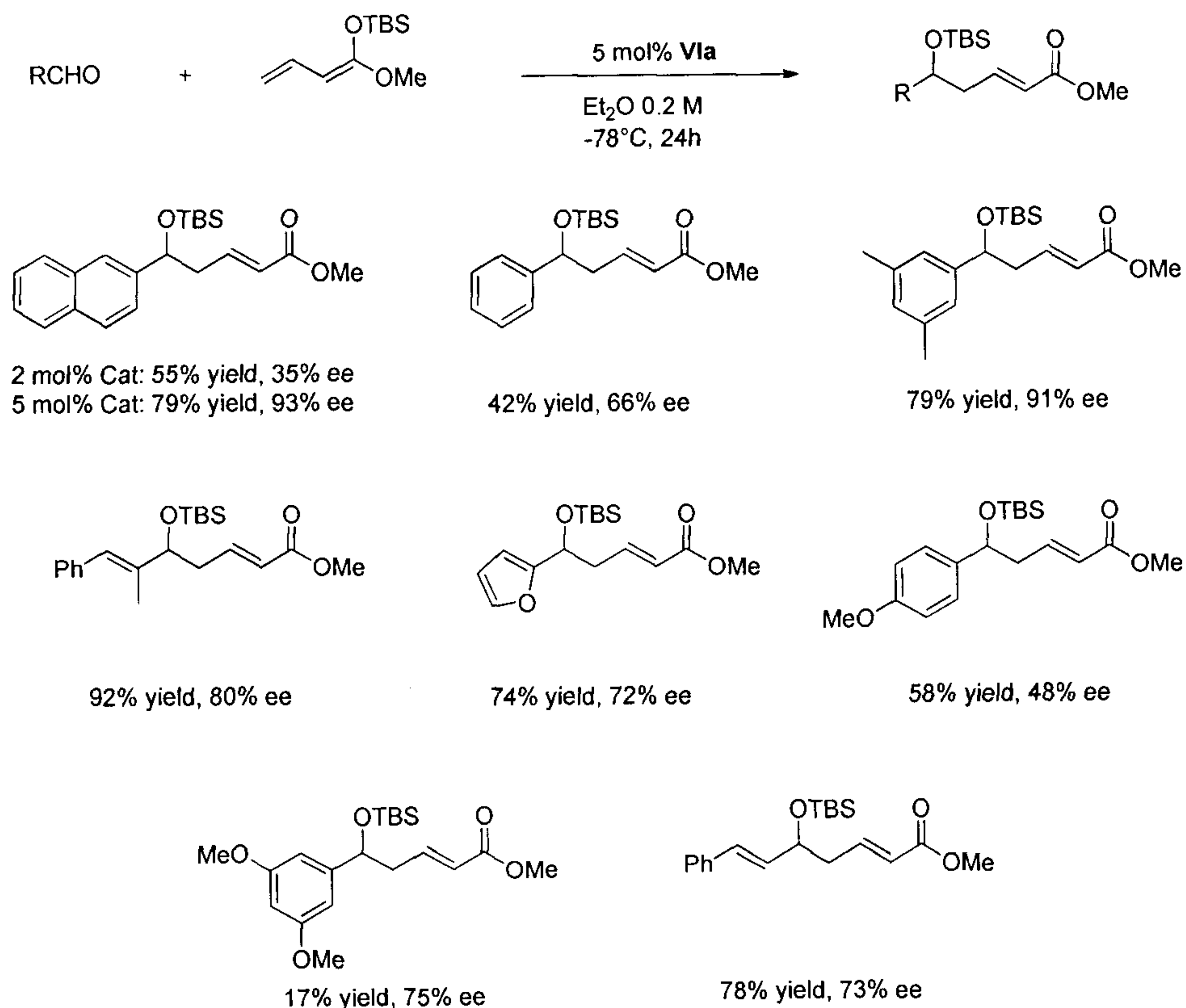
internal standard for an NMR measurement for determining the yield. The mixture is dissolved in about 1 ml of CDCl_3 , and 0.5-0.75 ml is taken for an NMR measurement. The remaining solution is used for preparative thin layer chromatography. The enantiomeric excess is determined by means of a chiral GC or chiral HPLC measurement on the product isolated from this thin layer chromatography.



Scheme 10: Selection of results achieved using disulfonimide **Vla** in the Mukaiyama aldol reaction at -78°C .

- 24 -

Disulfonimide **Vla** (2.05 mg, 5 mol%) and the appropriate aldehyde (0.05 mmol, 1 eq) together with 0.25 ml of Et₂O are placed in a reaction vessel at -78°C. (Z)-tert-Butyl((1-ethoxybuta-1,3-dien-1-yl)oxy)dimethylsilane (0.065 mmol, 1.3 eq) is added dropwise and the mixture is stirred at -78°C for 72 hours. The mixture is then quenched with saturated NaHCO₃ solution (0.25 ml) and diluted with dichloromethane (5 ml). The solution is dried over Na₂SO₄. The solvent is then removed under reduced pressure and 0.05 mmol of Ph₃PH is added as internal standard for an NMR measurement to determine the yield. The mixture is dissolved in about 1 ml of CDCl₃ and 0.5-0.75 ml is taken for an NMR measurement. The remaining solution is used for preparative thin layer chromatography. The enantiomeric excess is determined by means of a chiral GC or chiral HPLC measurement on the product isolated from this thin layer chromatography.

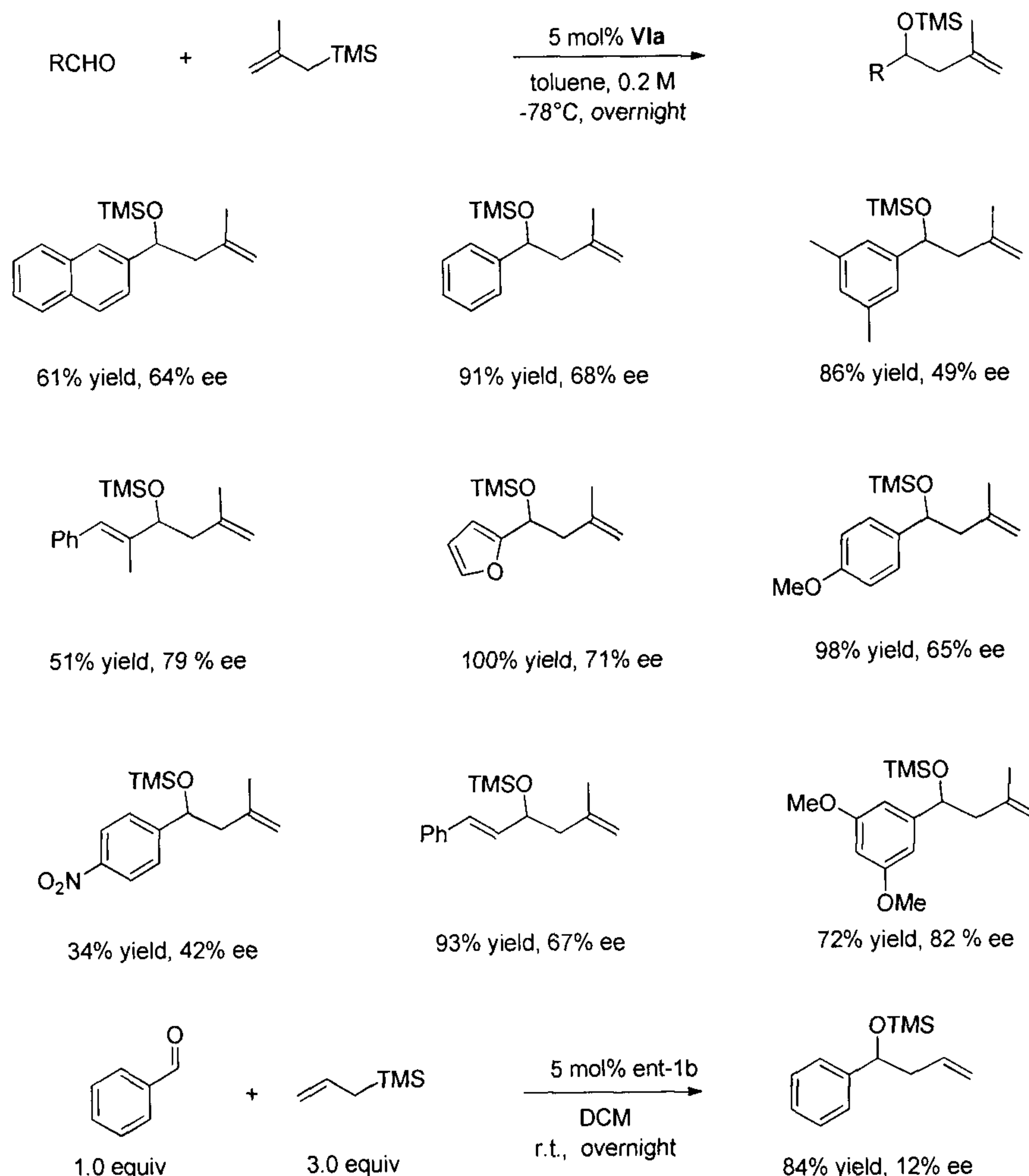


Scheme 11: Selection of results achieved using disulfonimide **Vla** in the vinylic Mukaiyama aldol reaction.

- 25 -

General synthetic method for the allylation of aldehydes

Disulfonimide VIa (2.05 mg, 5 mol%) and the appropriate aldehyde (0.05 mmol, 1 eq) together with 0.25 ml of Et₂O are placed in a reaction vessel at -78°C. Trimethyl(2-methylallyl)silane (0.065 mmol, 1.3 eq) is added dropwise and the mixture is stirred at -78°C for 12-16 hours. The mixture is then quenched with saturated NaHCO₃ solution (0.25 ml) and diluted with dichloromethane (5 ml). The solution is dried over Na₂SO₄. The solvent is then removed under reduced pressure and 0.05 mmol of Ph₃PH is added as internal standard for an NMR measurement for determining the yield. The mixture is dissolved in about 1 ml of CDCl₃ and 0.5-0.75 ml is taken for an NMR measurement. The remaining solution is used for preparative thin layer chromatography. The enantiomeric excess is determined by means of a chiral GC or chiral HPLC measurement on the product isolated from this thin layer chromatography.

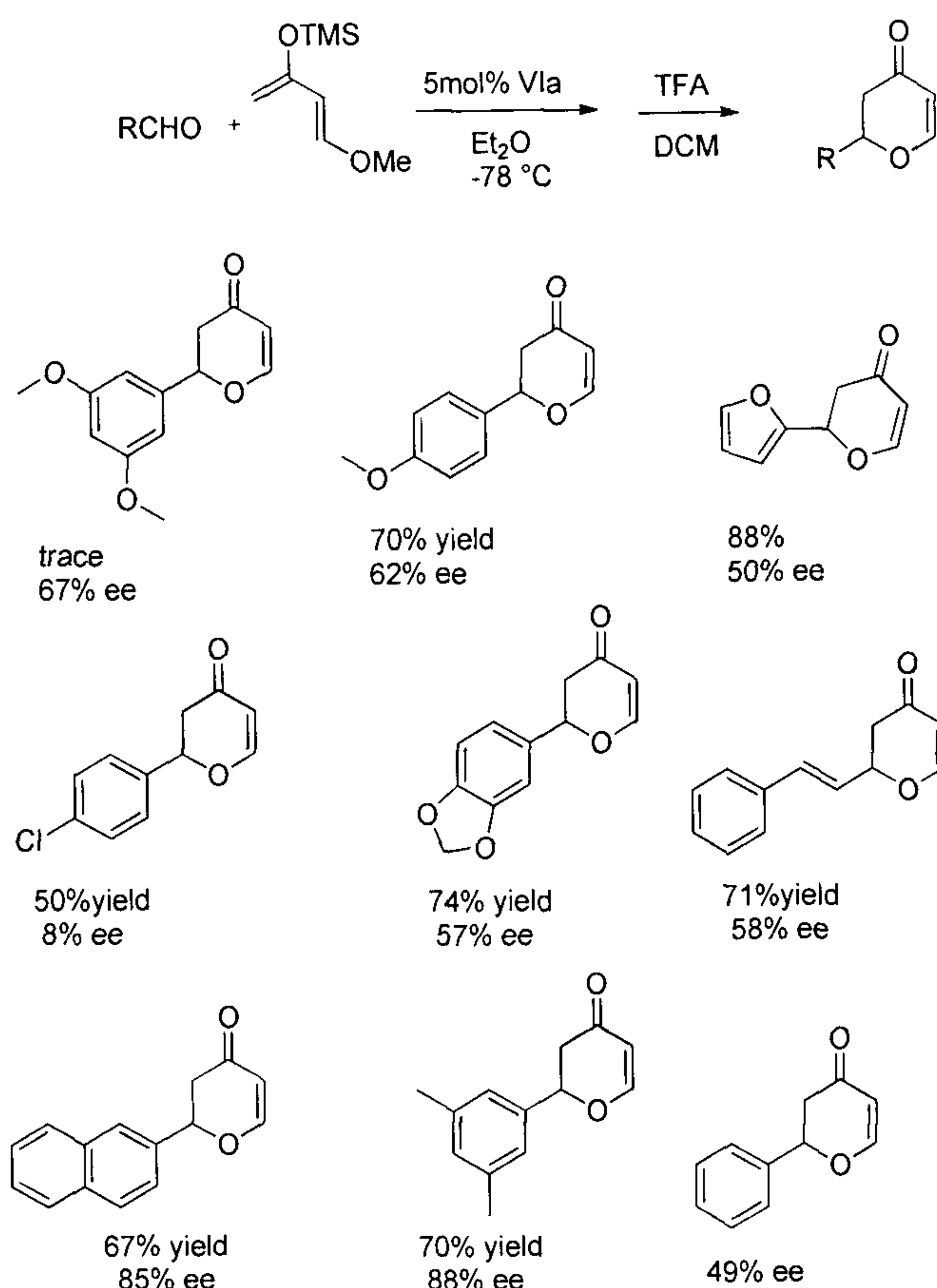


- 26 -

Scheme 12: Selection of results achieved using disulfonimide **Vla** in the allylation of aldehydes.

General synthetic method for the hetero-Diels-Alder reaction

Disulfonimide **Vla** (2.05 mg, 5 mol%) and the appropriate aldehyde (0.05 mmol, 1 eq) together with 0.25 ml of Et₂O are placed in a reaction vessel at -78°C. (E)-((4-methoxybuta-1,3-dien-2-yl)oxy)trimethylsilane (0.06 mmol, 1.2 eq) is added dropwise and the mixture is stirred at -78°C. The mixture is then quenched with a 10% strength TFA solution in dichloromethane at -78°C. The solvent is removed under reduced pressure and 0.05 mmol of Ph₃PH is added as internal standard for an NMR measurement to determine the yield. The mixture is dissolved in about 1 ml of CDCl₃ and 0.5-0.75 ml is taken for an NMR measurement. The remaining solution is used for preparative thin layer chromatography. The enantiomeric excess is determined by means of a chiral GC or chiral HPLC measurement on the product isolated from this thin layer chromatography.

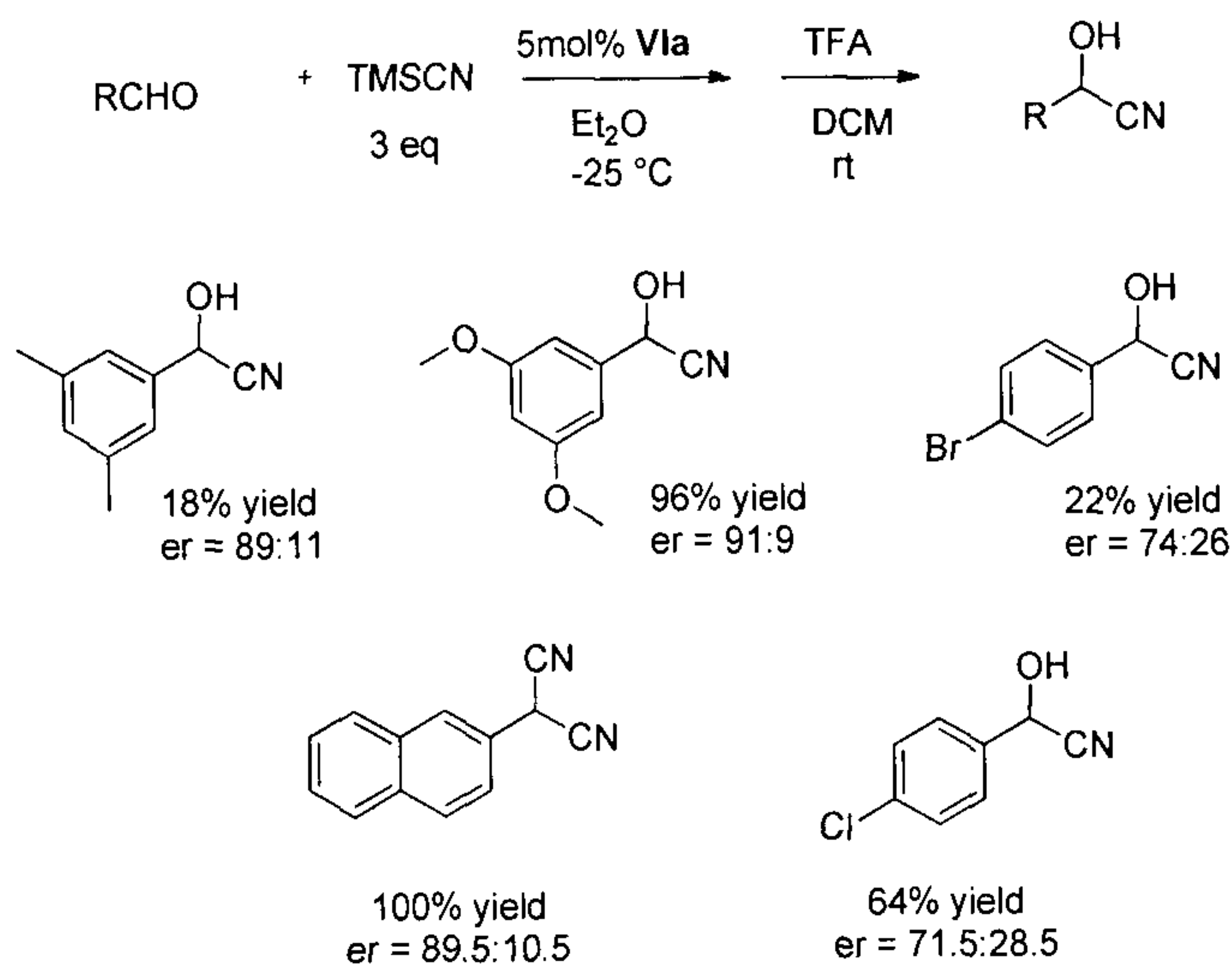


Scheme 13: Selection of results achieved using disulfonimide **Vla** in the hetero-Diels-Alder reaction.

- 28 -

General synthetic method for TMSCN addition onto aldehydes

Disulfonimide **Vla** (2.05 mg, 5 mol%) and the appropriate aldehyde (0.05 mmol, 1 eq) together with 0.25 ml of Et₂O are placed in a reaction vessel at -25°C. TMSCN (0.15 mmol, 3 eq) is added and the mixture is stirred at -78°C. The mixture is then quenched with 10% strength TFA solution in dichloromethane at -25°C. The solvent is removed under reduced pressure and 0.05 mmol of Ph₃PH is added as internal standard for an NMR measurement to determine the yield. The mixture is dissolved in about 1 ml of CDCl₃ and 0.5-0.75 ml is taken for an NMR measurement. The remaining solution is used for preparative thin layer chromatography. The enantiomeric excess is determined by means of a chiral GC or chiral HPLC measurement on the product isolated from this thin layer chromatography.



Scheme 14: Selection of results achieved using disulfonimide **Vla** in the TMSCN addition reaction.

General method for preparing the disulfonimidesa) Preparation of the O-arylthiocarbamates **XIII** and **XIV**.

The appropriate diol (1 eq) together with DMF (0.2 M) is placed in a reaction vessel at 0°C or room temperature. 60% strength NaH in oil (4 eq) is added quickly but a little at a time. After stirring at room temperature for 5 minutes, *N,N*-dimethylthiocarbamoyl chloride in DMF (6 mmol/ml) is added by means of a syringe. The mixture is subsequently heated at 80°C for 12-18 hours. After cooling, the solution is admixed with 2% strength KOH. The precipitate formed is filtered off with suction, washed with 2% strength KOH, dissolved in dichloromethane and washed with water. The organic phase is dried over Na₂SO₄ and evaporated. Column chromatography (SiO₂, ethyl acetate/hexane) gives the desired O-arylthiocarbamate.

b) Preparation of the S-arylthiocarbamates **XV** and **XVI**

The O-arylthiocarbamate is heated at 250°C under argon for 80-90 minutes. Purification by column chromatography (SiO₂, ethyl acetate/hexane) gives the desired S-arylthiocarbamate.

c) Preparation of the disulfonic acids **XVI** and **XVIII**

Acetic acid or formic acid (10 times the volume of 30% strength H₂O₂) is placed in a reaction vessel at 0°C or room temperature and 30% strength H₂O₂ (30 eq) is added dropwise. After stirring at RT for 1 hour, the S-arylthiocarbamate dissolved in acetic acid, THF or dichloromethane (5 times the volume of 30% strength H₂O₂) is added. After stirring at room temperature for 1-72 hours, the solution is evaporated or filtered through silica gel and then evaporated. Column chromatography (SiO₂, dichloromethane/methanol) gives the salt of the desired acid. This is converted into the desired acid by washing with 2-6M HCl or by means of ion exchange chromatography.

d) Preparation of the disulfonic acid chlorides **XIX** and **XX**

The appropriate disulfonic acid together with thionyl chloride is placed under argon in a reaction vessel. After addition of a catalytic amount of DMF, the mixture is refluxed for 1-4 hours. The thionyl chloride is removed under reduced pressure and the product is purified by digestion with diethyl ether or by column chromatography (SiO₂, hexane/ethyl acetate).

d1) Preparation of the disulfonic acid chlorides **XIX** and **XX**

The appropriate S-arylthiocarbamate is suspended in a mixture of 2M HCl/acetonitrile (1:5) at 0°C. *N*-Chlorosuccinimide (4-30 eq) is added a little at a time. After stirring at just under

- 30 -

20°C for 10-240 minutes, the suspension is extracted with diethyl ether, washed with saturated NaCl solution and evaporated. Purification is carried out by means of column chromatography (SiO₂, ethyl acetate/pentane).

5 e) Preparation of the disulfonimides **IV** and **V**

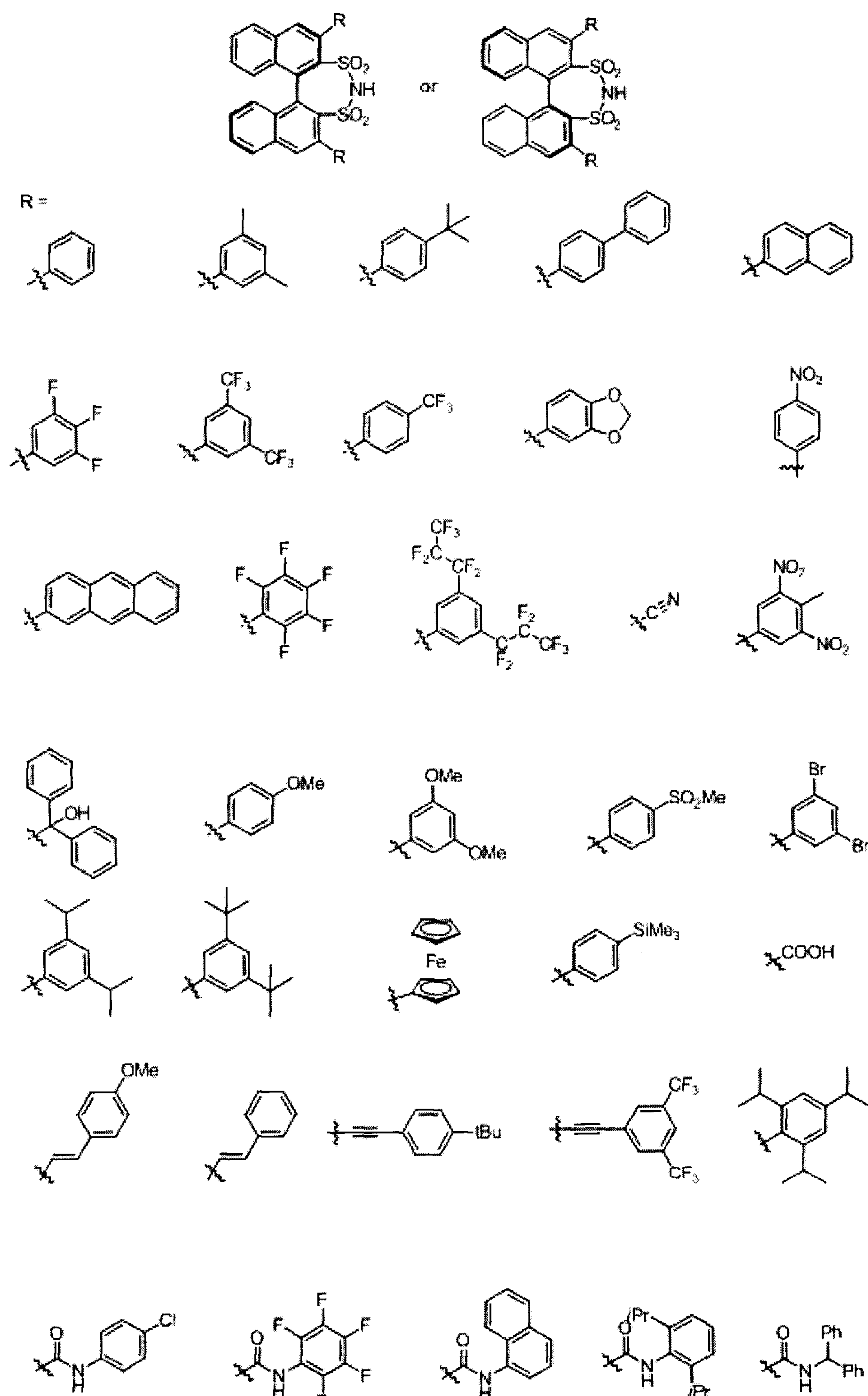
The appropriate disulfonic acid chloride is dissolved in THF. Ammonia (5-30eq) in methanol is added a little at a time or via a syringe pump at from -10°C to 60°C and the mixture is stirred at this temperature for 6-120 hours. After removal of the solvent, the salt of the disulfonimide is obtained by purification by means of column chromatography (SiO₂,
10 hexane/ethyl acetate). This is converted into the desired disulfonimide by washing with 2-6M HCl or by means of ion exchange chromatography.

e1) Preparation of the disulfonimides **IV** and **V** via the diboronates **XXII** and **XXIII** or the dihalides **XX** and **XXI**

15 The appropriate disulfonimide **IVa** or **Va** ($R^1, R^{12} = H$ or $R^{1'}, R^{12'} = H$) is deprotenated by means of n-BuLi, sec-BuLi or tert-BuLi at from -78°C to 0°C. Addition of a halide source or a boron source at from -78°C to 0°C gives the dihalides **XX** or **XXI** or diboronates **XXII** or **XXIII**. After stirring at room temperature for 1-120 hours, the solution is quenched with ammonium chloride. The aqueous phase is extracted with a suitable organic solvent. The
20 organic phase is dried over Na₂SO₄ and evaporated. Column chromatography (SiO₂, dichloromethane/methanol) gives the salt of the desired dihalide **XX** or **XXI** or diboronate **XXII** or **XXIII**. This salt is converted into the desired acid by washing with 2-6M HCl or by means of ion exchange chromatography.

25 The diiodide is heated with the appropriate boronic acid (2-20eq) and 1-40 mol% of Pd(PPh₃)₄ under argon in a degassed mixture of 2M Na₂CO_{3aq}. (2-30 eq) and DME at 50-150°C for 1-72 hours. After cooling the reaction mixture, the mixture is diluted with water. The mixture is extracted with ethyl acetate, the organic phases are dried over Na₂SO₄ and evaporated. Column chromatography (SiO₂, dichloromethane/methanol) gives the salt of the
30 desired disulfonimide **IV** or **V**. This salt is converted into the desired acid by washing with 2-6M HCl or by means of ion exchange chromatography.

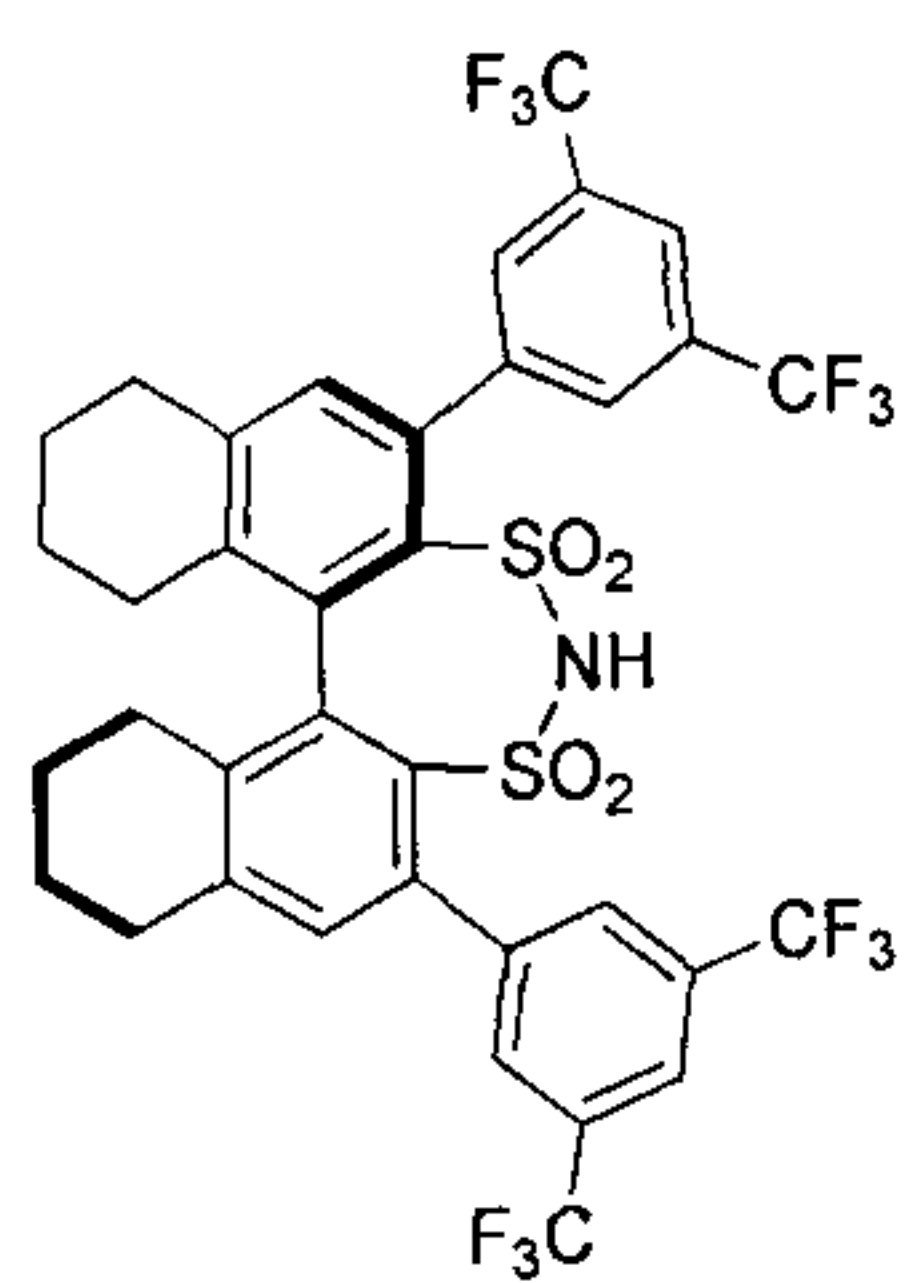
- 31 -



oder = or

Scheme 15: Disulfonimides having a chiral BINOL backbone prepared.

- 32 -

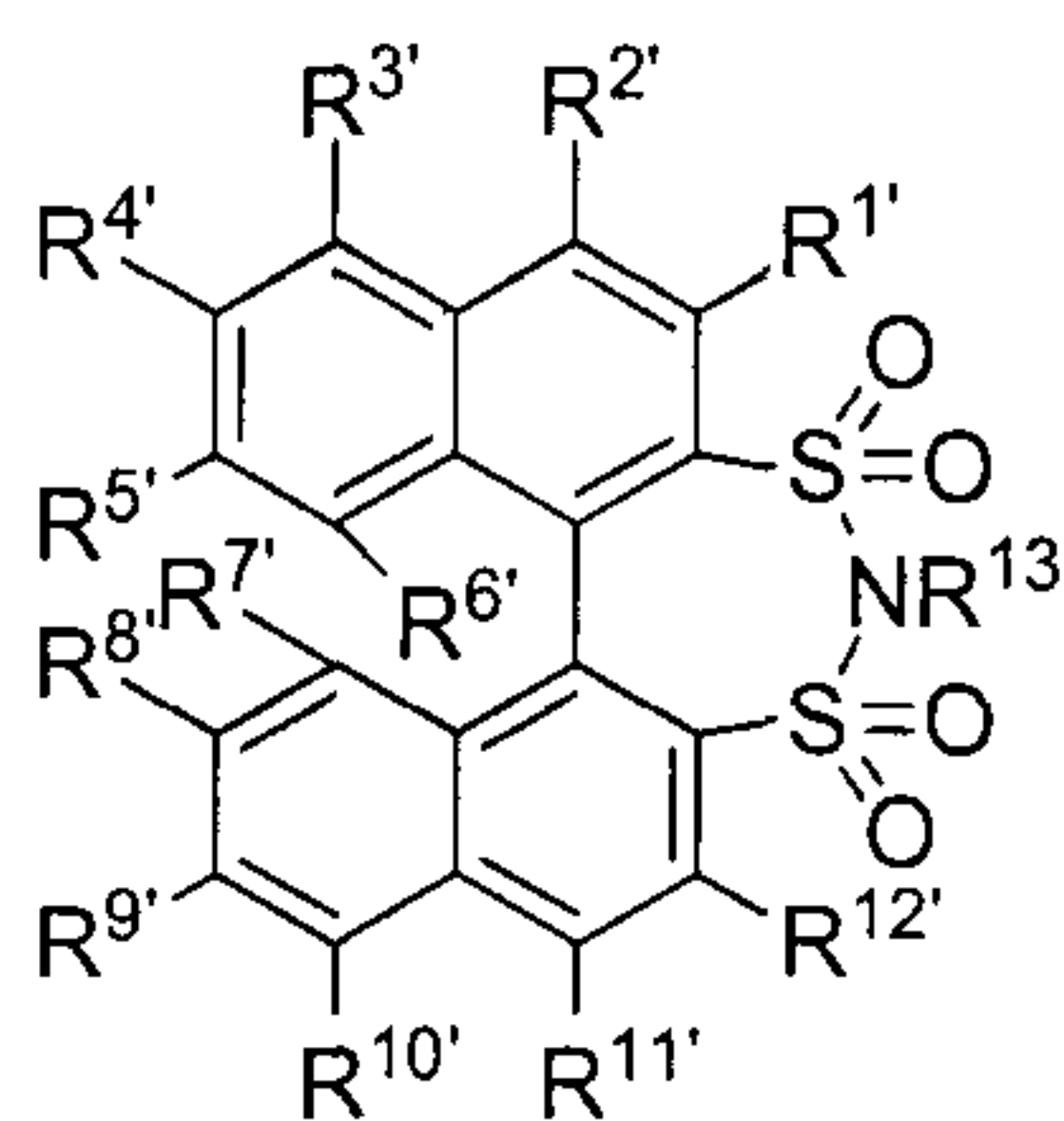


Scheme 16: Disulfonimide having a chiral H8-BINOL backbone prepared.

- 33 -

Claims

1. A chiral disulfonimide having the formula IV:



(IV)

wherein

$R^{1'}$ and $R^{12'}$ are identical or different and each, independently of one another, represents

H,

OH,

F,

Cl,

Br,

I,

CN,

NO_2 ,

NO,

SO_2 ,

SO_3H ,

NH_2 ,

PH_3 ,

COOH ,

SO_3X , wherein X is Na or K,

COOY , wherein Y is Na or K,

substituted or unsubstituted $\text{C}_1\text{-C}_{20}$ -alkyl,

substituted or unsubstituted $\text{C}_2\text{-C}_{20}$ -alkenyl,

substituted or unsubstituted $\text{C}_2\text{-C}_{20}$ -alkynyl,

substituted or unsubstituted aryl,

substituted or unsubstituted aryl-($\text{C}_1\text{-C}_6$)-alkyl,

substituted or unsubstituted hetero($\text{C}_1\text{-C}_6$)-alkyl,

substituted or unsubstituted heteroaryl,

- 34 -

tris-mesitylsilyl, or

tris-phenylsilyl;

R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} and R^{11} are identical or different and each, independently of one another, represents

- | | |
|----|--|
| 5 | H, |
| | OH, |
| | F, |
| | Cl, |
| | Br, |
| 10 | I, |
| | CN, |
| | NO ₂ , |
| | NO, |
| | SO ₂ , |
| 15 | SO ₃ H, |
| | NH ₂ , |
| | PH ₃ , |
| | COOH, |
| | SO ₃ X, wherein X is Na or K, |
| 20 | COOY, wherein Y is Na or K, |
| | substituted or unsubstituted C ₁ -C ₂₀ -alkyl, |
| | substituted or unsubstituted C ₂ -C ₂₀ -alkenyl, |
| | substituted or unsubstituted C ₂ -C ₂₀ -alkynyl, |
| | substituted or unsubstituted aryl, |
| 25 | substituted or unsubstituted aryl-(C ₁ -C ₆)-alkyl, |
| | substituted or unsubstituted hetero(C ₁ -C ₆)-alkyl, or |
| | substituted or unsubstituted heteroaryl; and |
| | R^{13} is |
| | H, |
| 30 | F, |
| | Cl, |
| | Br, |
| | I, |
| | substituted or unsubstituted C ₁ -C ₆ -alkyl, |
| 35 | substituted or unsubstituted C ₂ -C ₆ -alkenyl, |
| | substituted or unsubstituted C ₂ -C ₆ -alkynyl, |
| | substituted or unsubstituted aryl, |

- 35 -

substituted or unsubstituted aryl-(C₁-C₆)-alkyl,
 substituted or unsubstituted hetero(C₁-C₆)-alkyl,
 substituted or unsubstituted heteroaryl, or
 SiR¹⁴R¹⁵R¹⁶, wherein R¹⁴, R¹⁵ and R¹⁶ are each

- 5 substituted or unsubstituted C₁-C₆-alkyl,
 substituted or unsubstituted C₂-C₆-alkenyl,
 substituted or unsubstituted C₂-C₆-alkynyl,
 substituted or unsubstituted aryl,
 substituted or unsubstituted aryl-(C₁-C₆)-alkyl,
 10 substituted or unsubstituted hetero(C₁-C₆)-alkyl, or
 substituted or unsubstituted heteroaryl,
 or an organic salt, metal salt or metal complex thereof.

2. The chiral disulfonimide as claimed in claim 1, wherein at least one of R^{1'} and R^{12'} is not
 15 hydrogen and is selected from the group consisting of phenyl, 2,4,6-triisopropylphenyl, mesityl,
 9-phenanthryl, 9-anthracenyl, 1-naphthyl, 2-naphthyl, 4-biphenyl, 3,5-(trifluoromethyl)phenyl,
 2,6-dimethylphenyl, tert-butyl, tris-mesitylsilyl, tris-phenylsilyl, 4-nitrophenyl, 2,6-methyl-4-
 butylphenyl, trifluoromethyl, 3,4,5-trifluorophenyl, and pentafluorophenyl.

20 3. The chiral disulfonimide as claimed in claim 1, wherein at least one of the radicals R^{4'}
 and R^{9'} is selected from the group consisting of NO₂ and I.

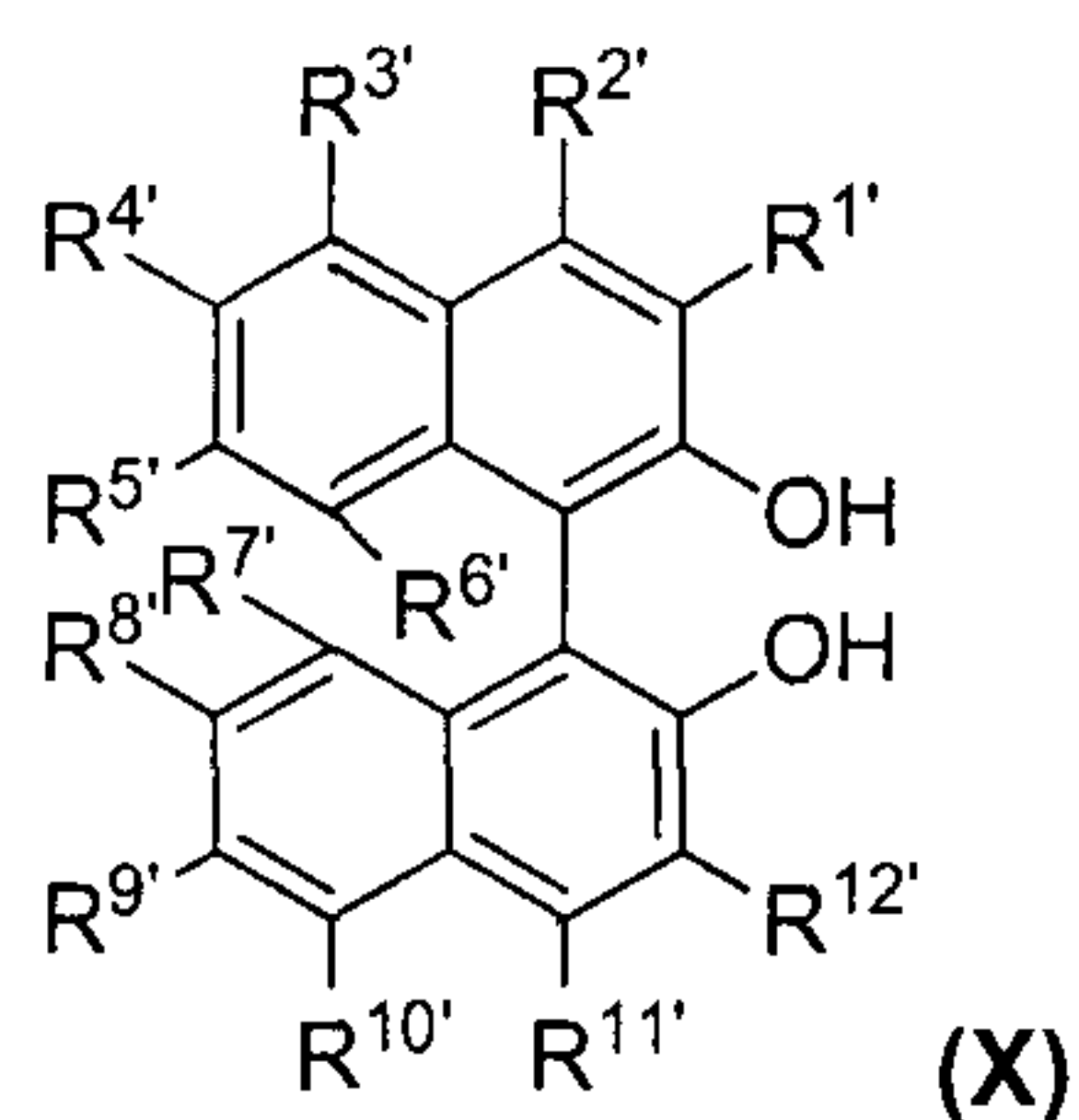
4. The chiral disulfonimide as claimed in claim 1, wherein R¹³ is H, F, Cl, Br, I or
 SiR¹⁴R¹⁵R¹⁶, wherein R¹⁴, R¹⁵ and R¹⁶ are each C₁-C₆-alkyl, C₂-C₆-alkenyl or C₂-C₆-alkynyl.

25 5. The chiral disulfonimide as claimed in claim 4, wherein R¹³ is SiR¹⁴R¹⁵R¹⁶ and R¹⁴,
 R¹⁵ and R¹⁶ are as defined in claim 4.

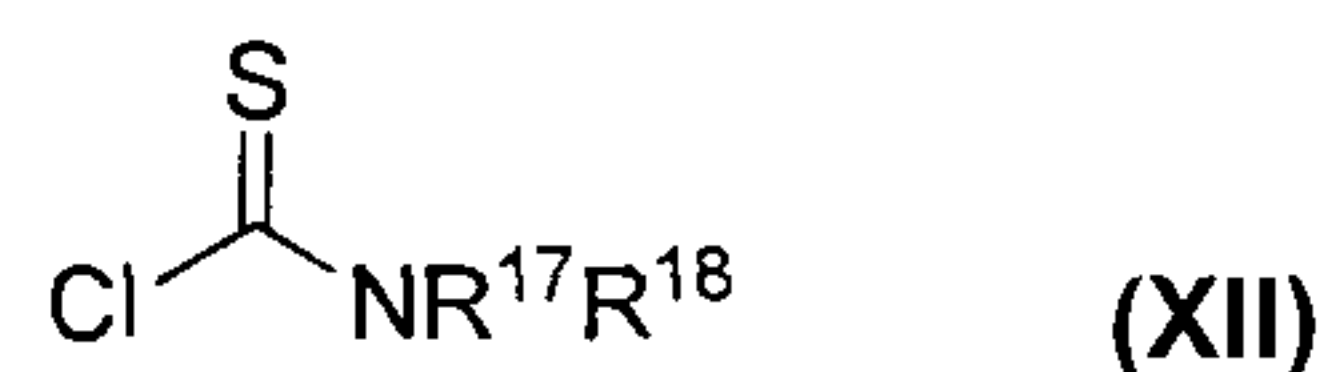
6. A process for preparing a chiral disulfonimide having the formula IV as defined in
 30 claim 1, said process comprising the following steps:

(A) reacting a Binol derivative having the formula X:

- 36 -

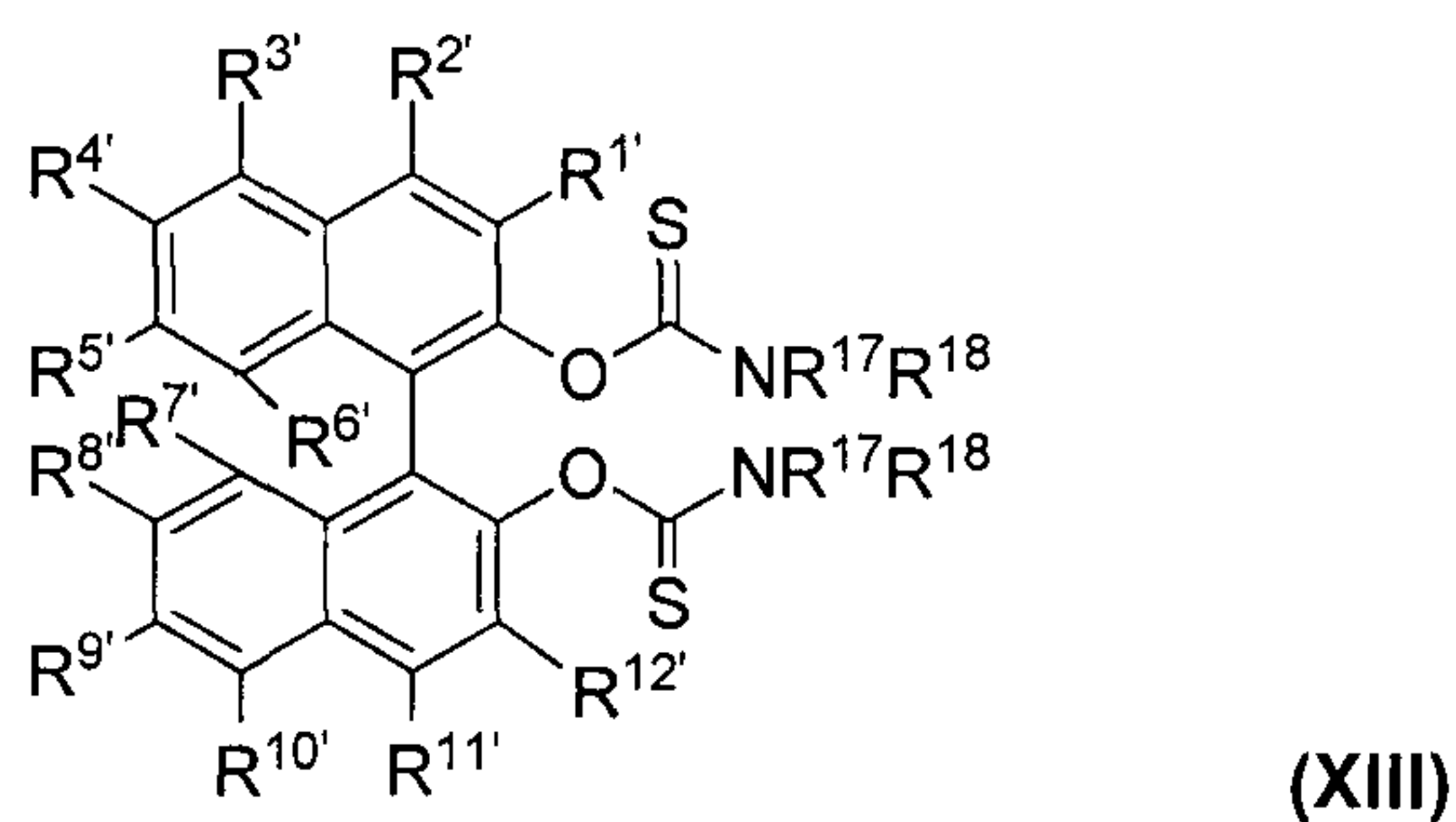


with a thiocarbamoyl chloride of the formula XII:

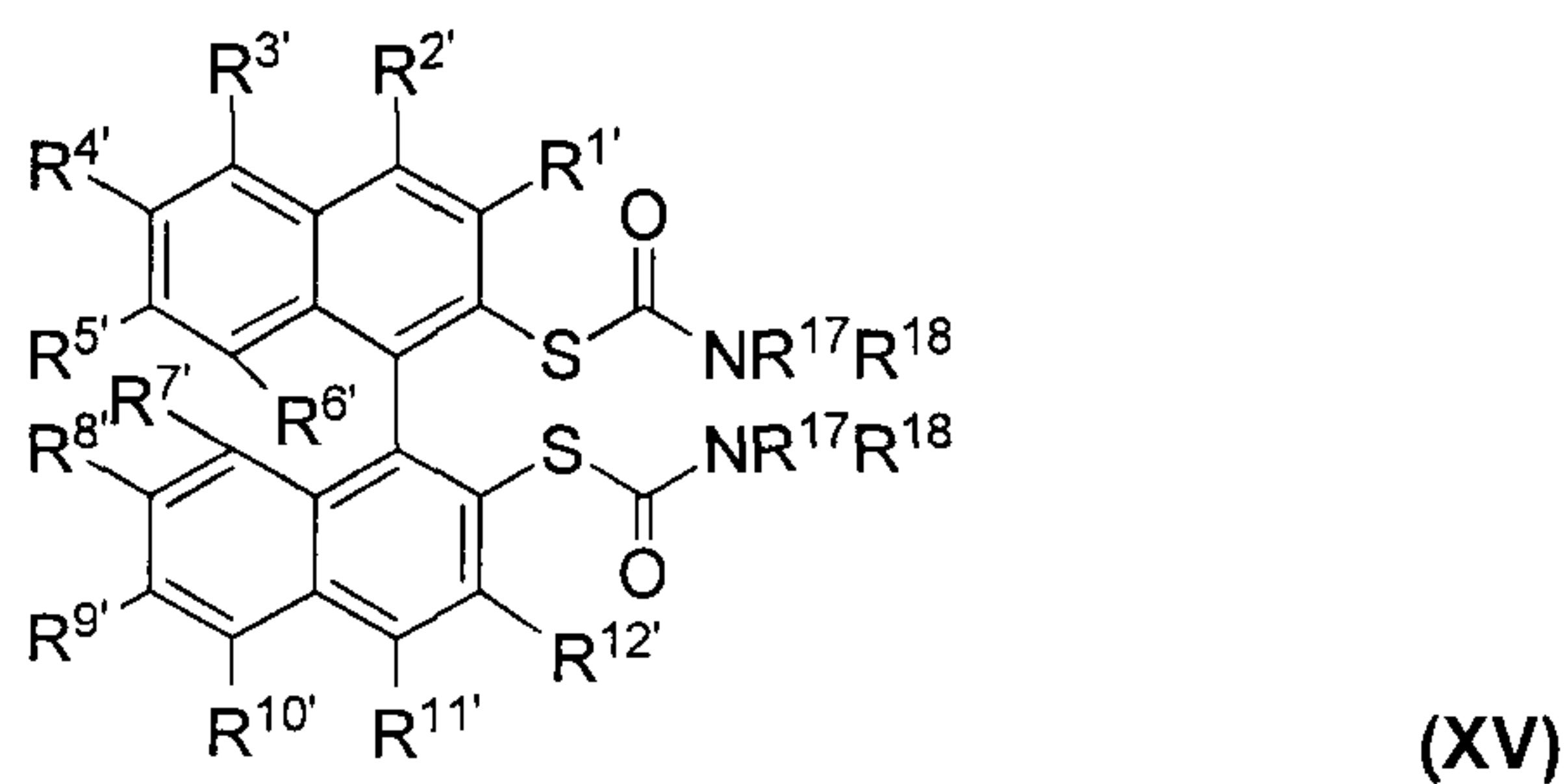


5 wherein the radicals $R^{1'}$, $R^{2'}$, $R^{3'}$, $R^{4'}$, $R^{5'}$, $R^{6'}$, $R^{7'}$, $R^{8'}$, $R^{9'}$, $R^{10'}$, $R^{11'}$ and $R^{12'}$ are as defined in claim 1; and

wherein R^{17} and R^{18} are identical or different and are each a C_1 - C_6 -alkyl group,
to form an O-arylthiocarbamate having the formula XIII:

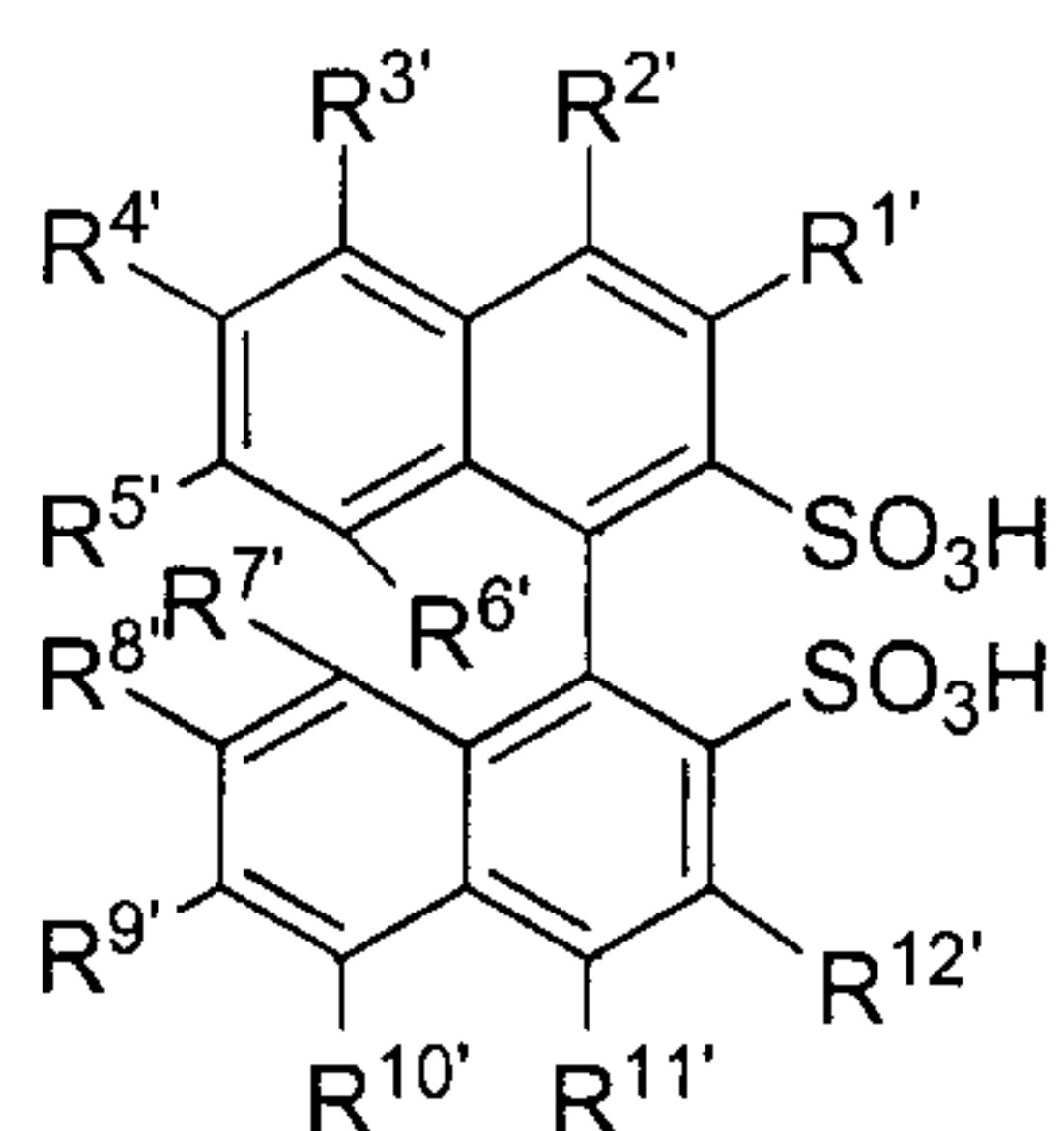


10 (B) converting the O-arylthiocarbamate having the formula XIII into the corresponding S-arylthiocarbamate having the formula XV:



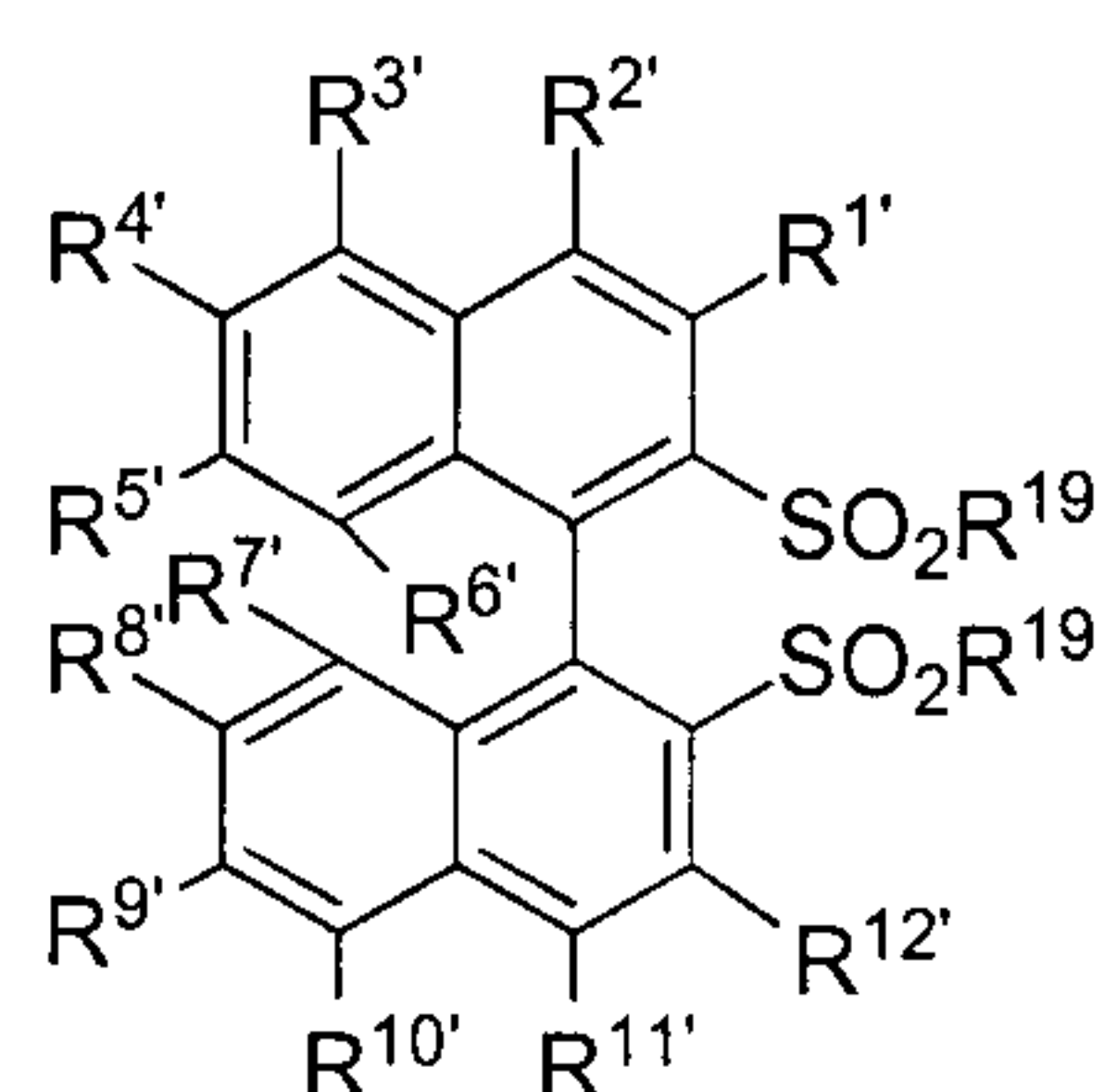
(C) converting the S-arylthiocarbamate in the presence of an oxidant into the compound having the formula XVII:

- 37 -



(XVII)

(D) converting the sulfonic acid obtained in step C into the acid halide having the formula XIX:



(XIX)

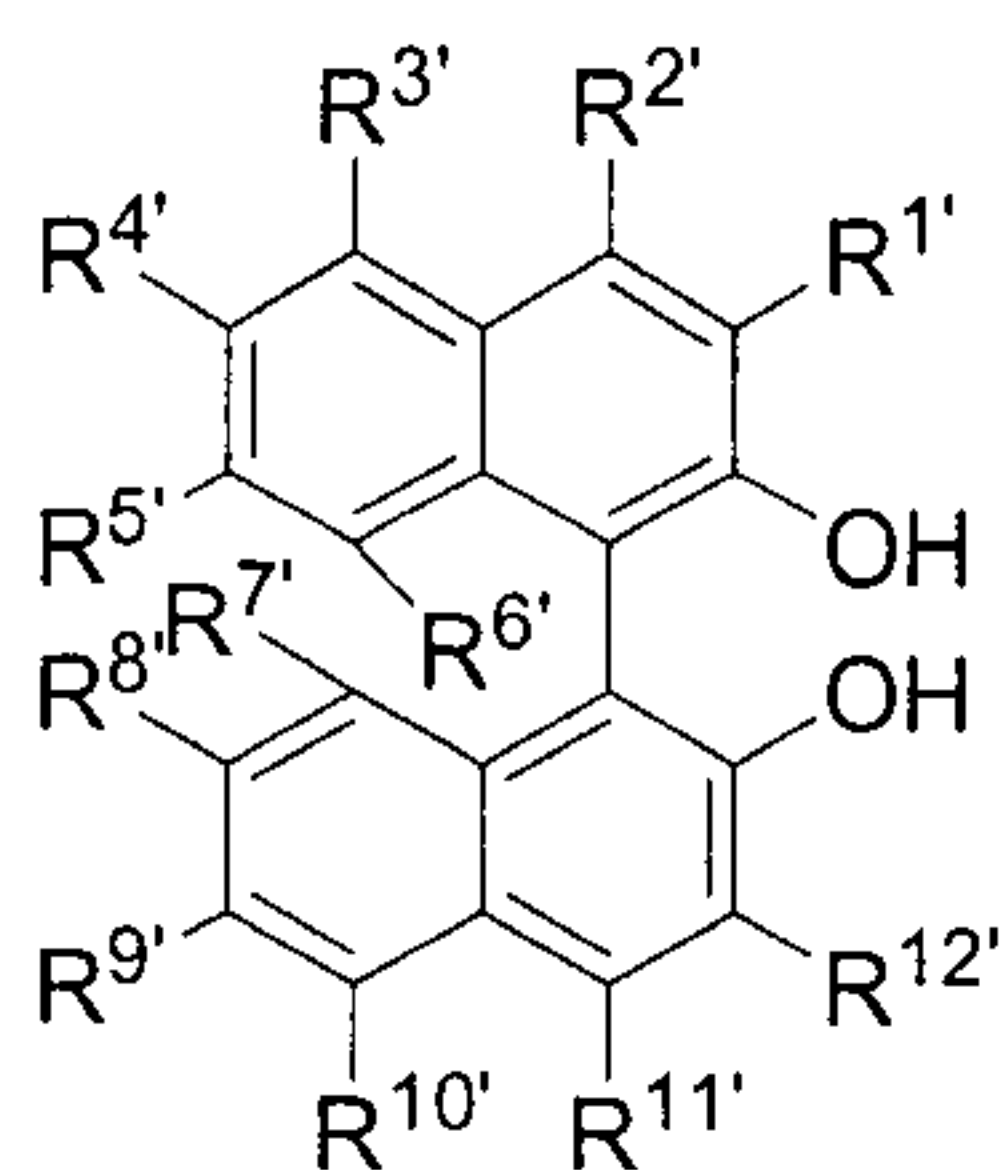
5 wherein R¹⁹ is Cl,

and in a subsequent process step

(E) converting the acid halide having the formula XIX by means of ammonia or a primary amine into the corresponding imide having the formula IV.

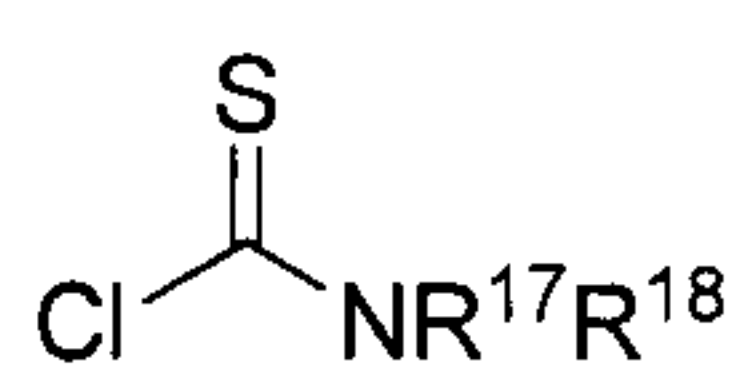
10 7. A process for preparing a chiral disulfonimide having the formula IV as defined in claim 1, said process comprising the following steps:

(A) reacting a Binol derivative having the formula X:



(X)

with a thiocarbamoyl chloride of the formula XII:

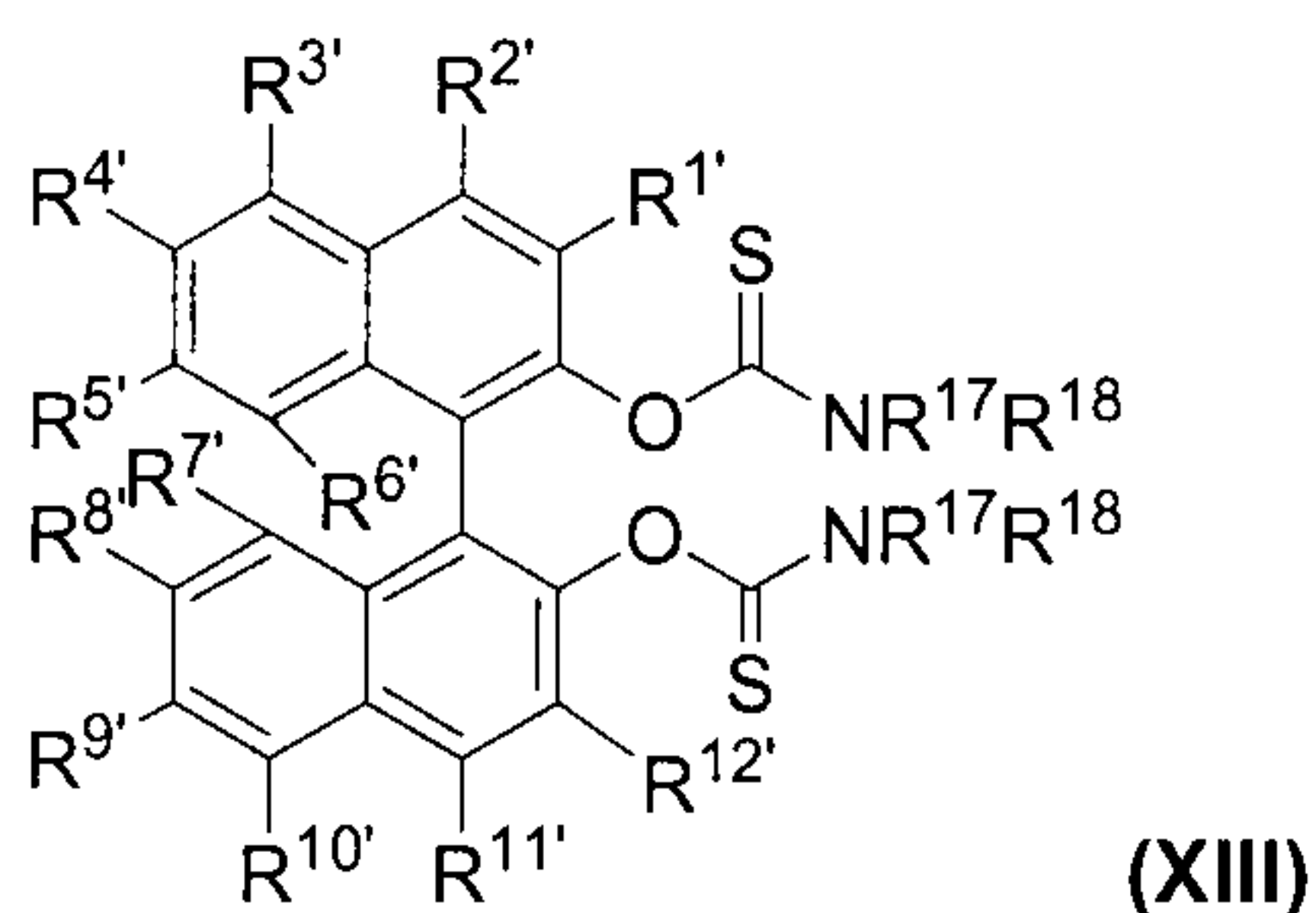


(XII)

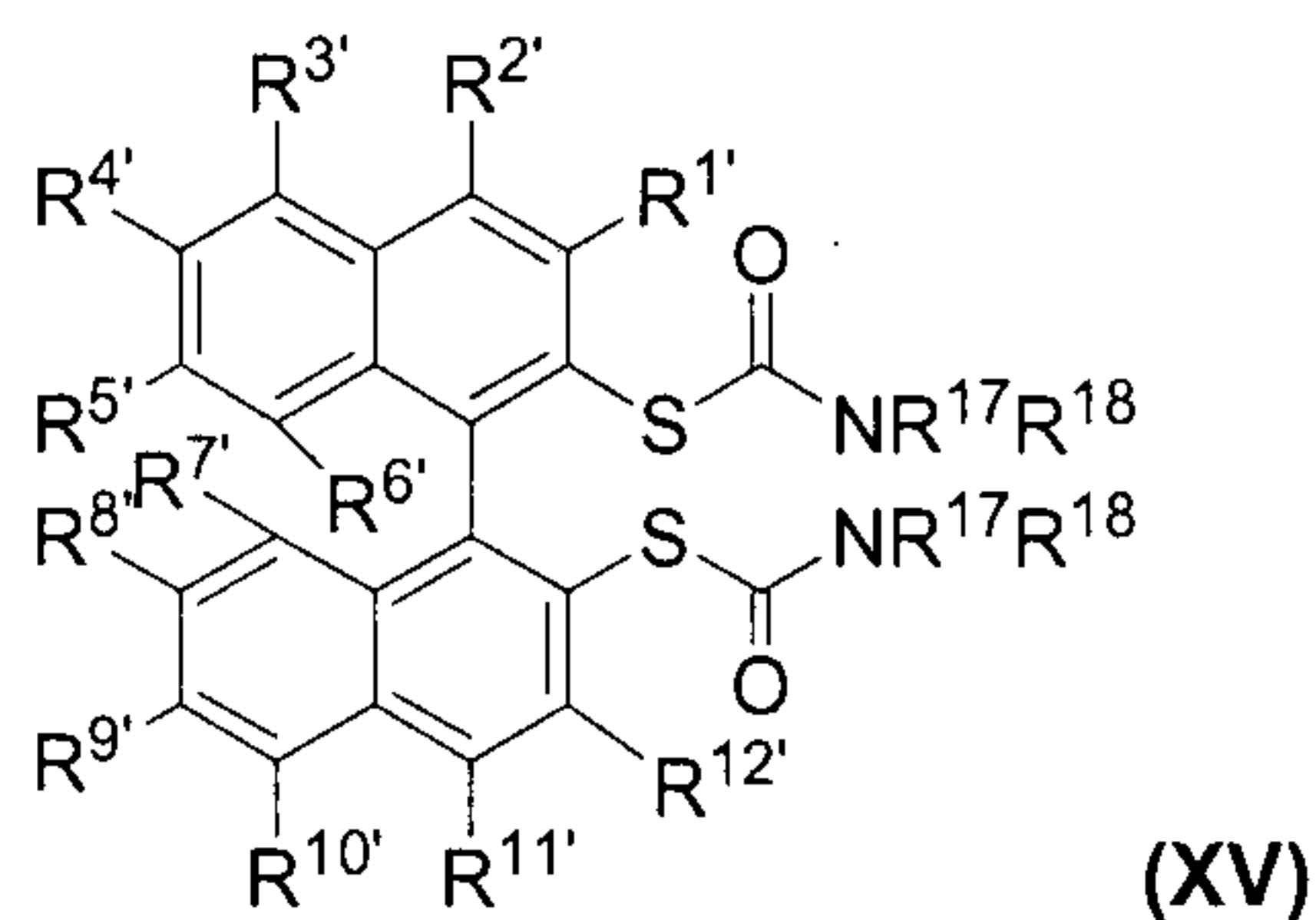
- 38 -

wherein the radicals R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} and R^{12} are as defined in claim 1; and

wherein R^{17} and R^{18} are identical or different and are each a C_1 - C_6 -alkyl group,
to form an O-arylthiocarbamate having the formula XIII:

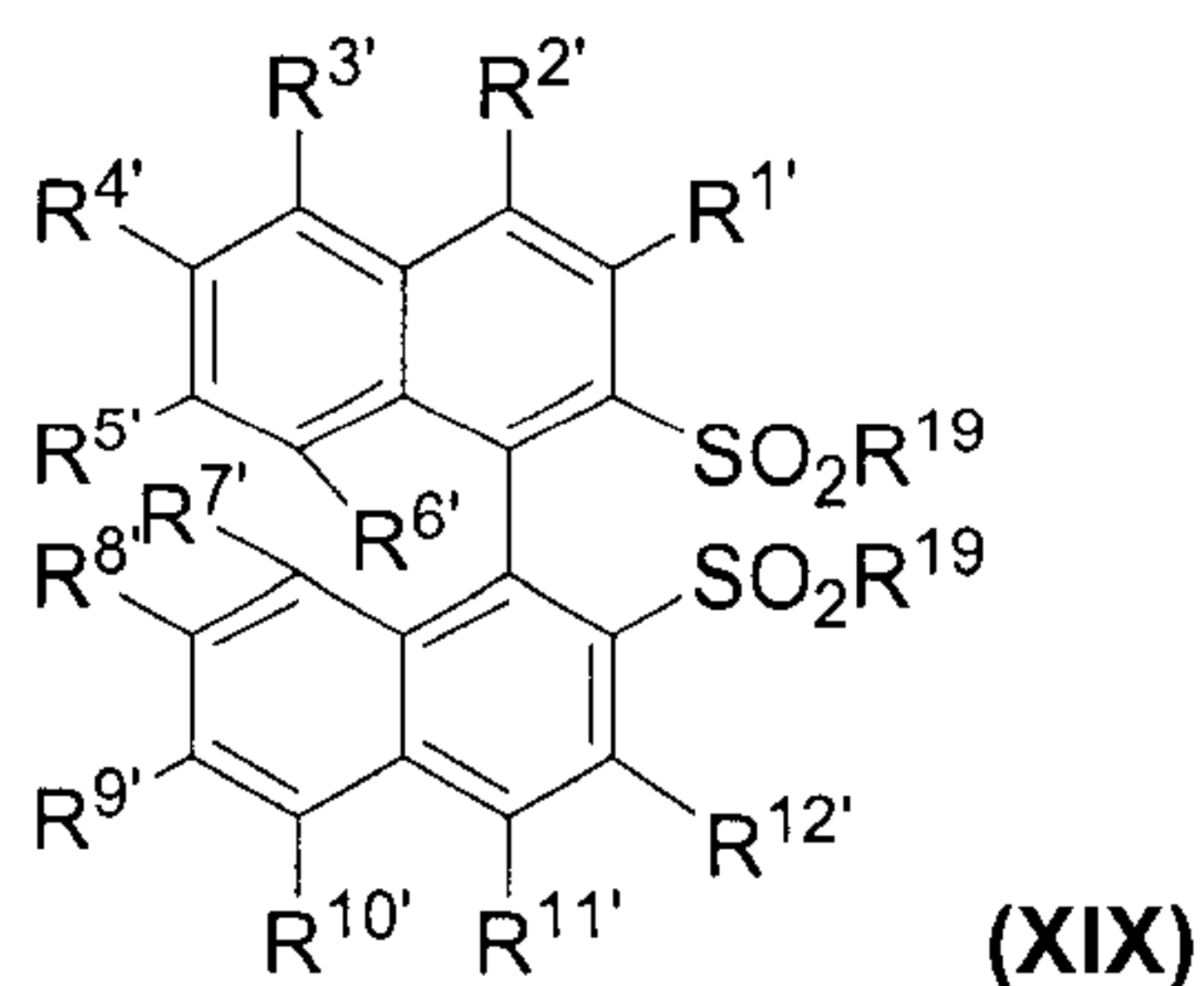


(B) converting the O-arylthiocarbamate having the formula XIII into the corresponding S-arylthiocarbamate having the formula XV:



and

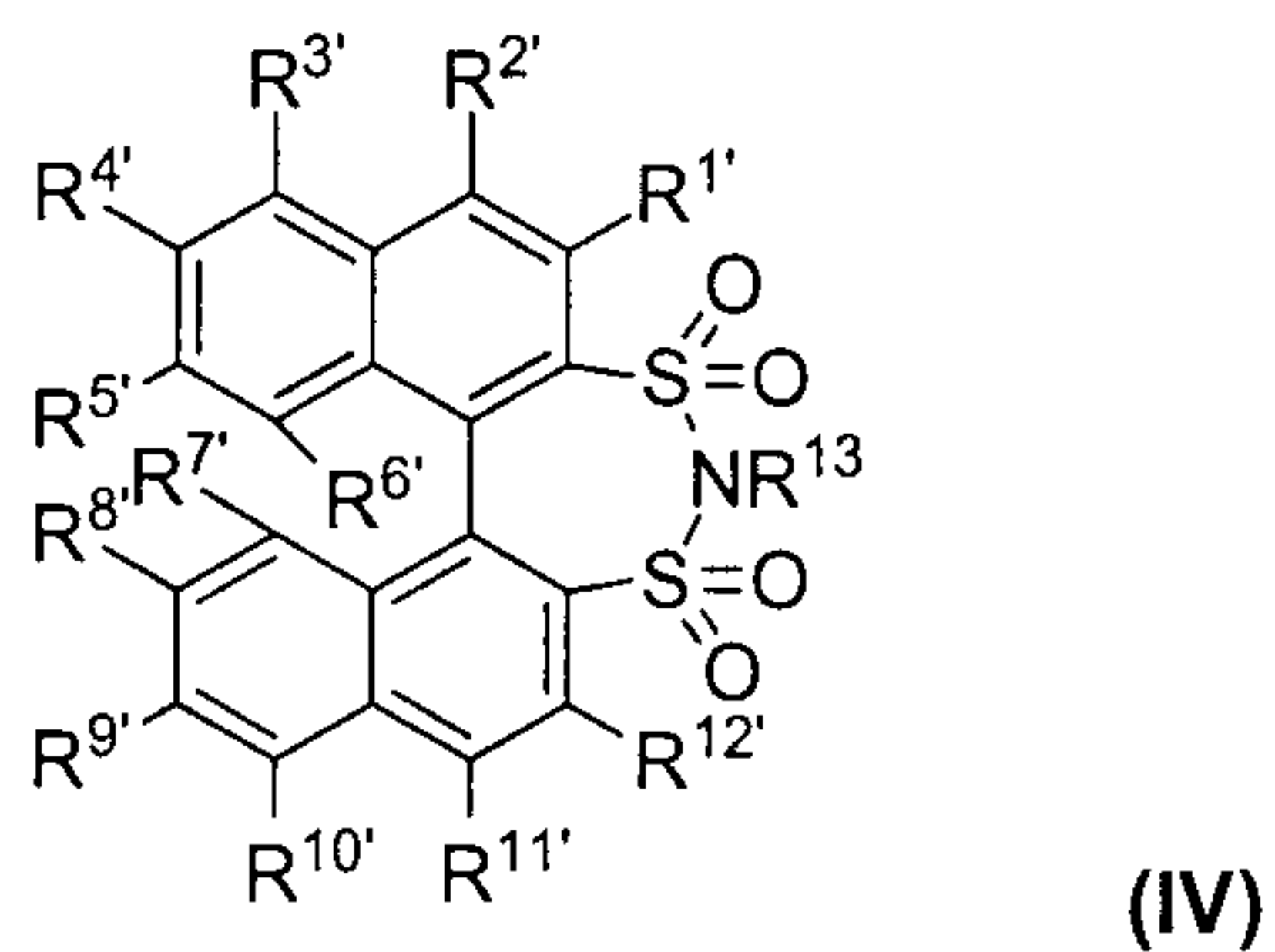
(C) converting the S-arylthiocarbamate having the formula XV directly into the compound having the formula XIX:



wherein R^{19} is Cl.

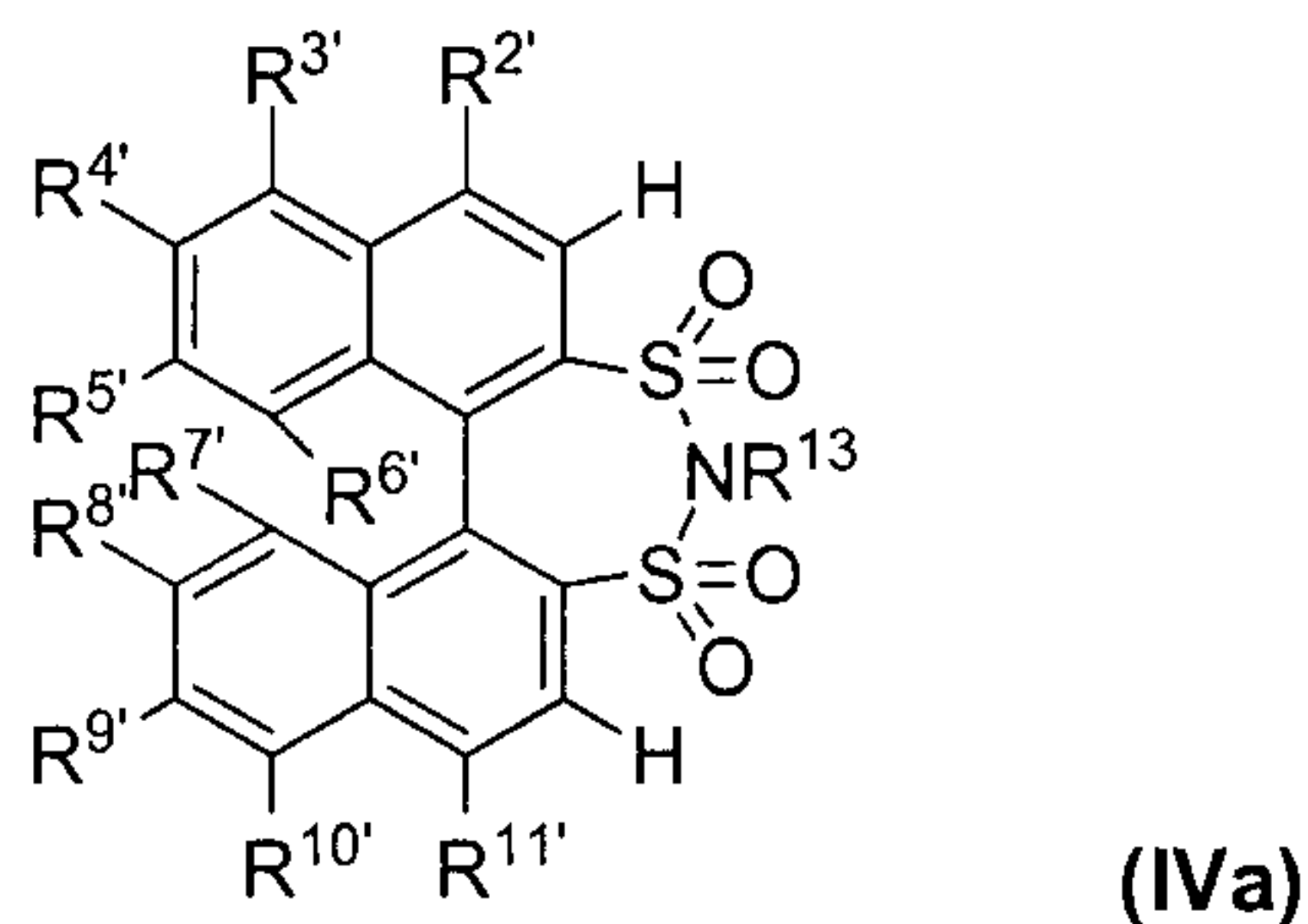
8. A process for preparing a compound having the formula IV as defined in claim 1 or an organic salt, metal salt or metal complex thereof:

- 39 -



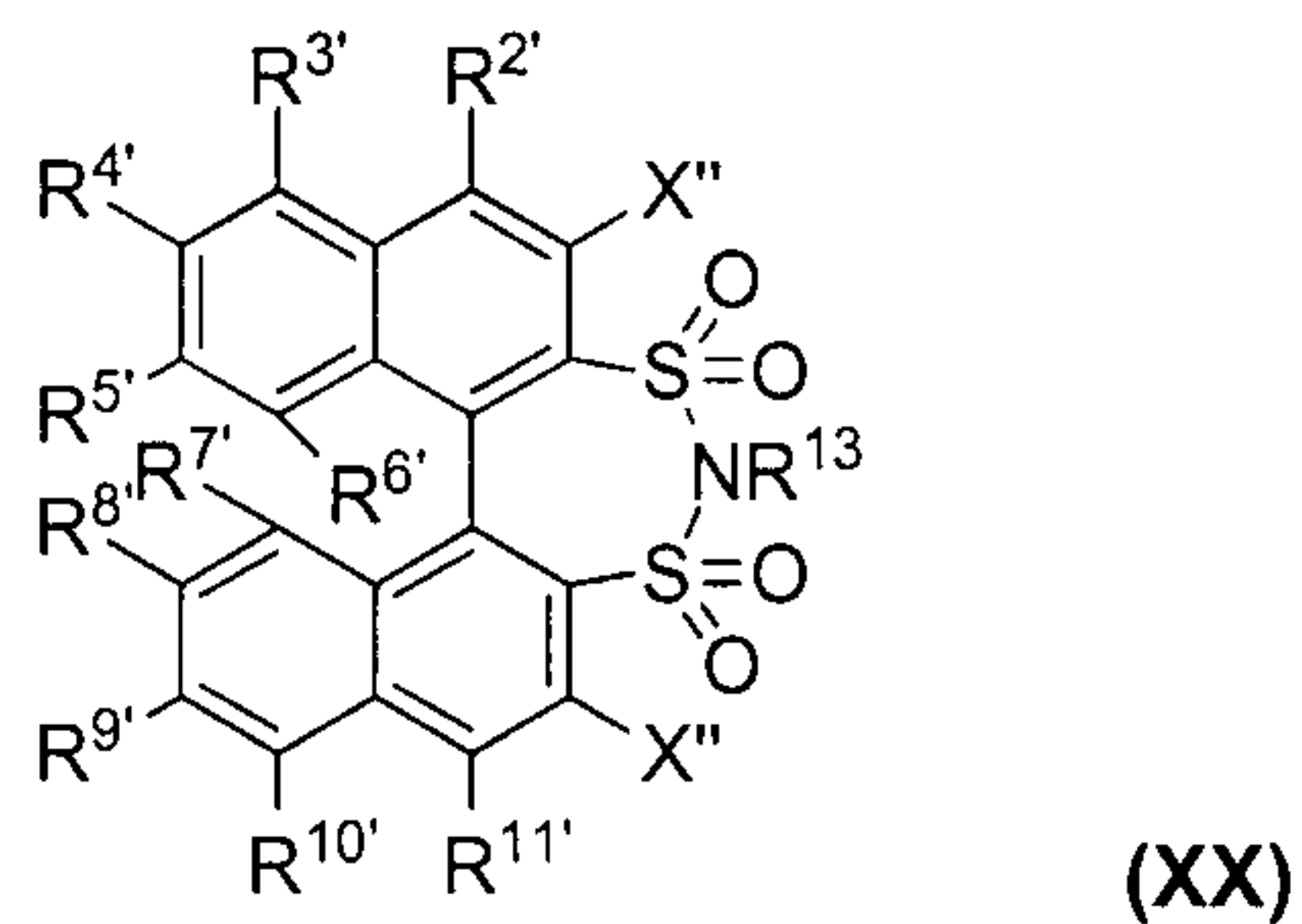
wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} and R^{13} are as defined in claim 1, said process comprising the following steps:

(F) converting a 3,3'-unsubstituted disulfonimide having the formula IVa:



5

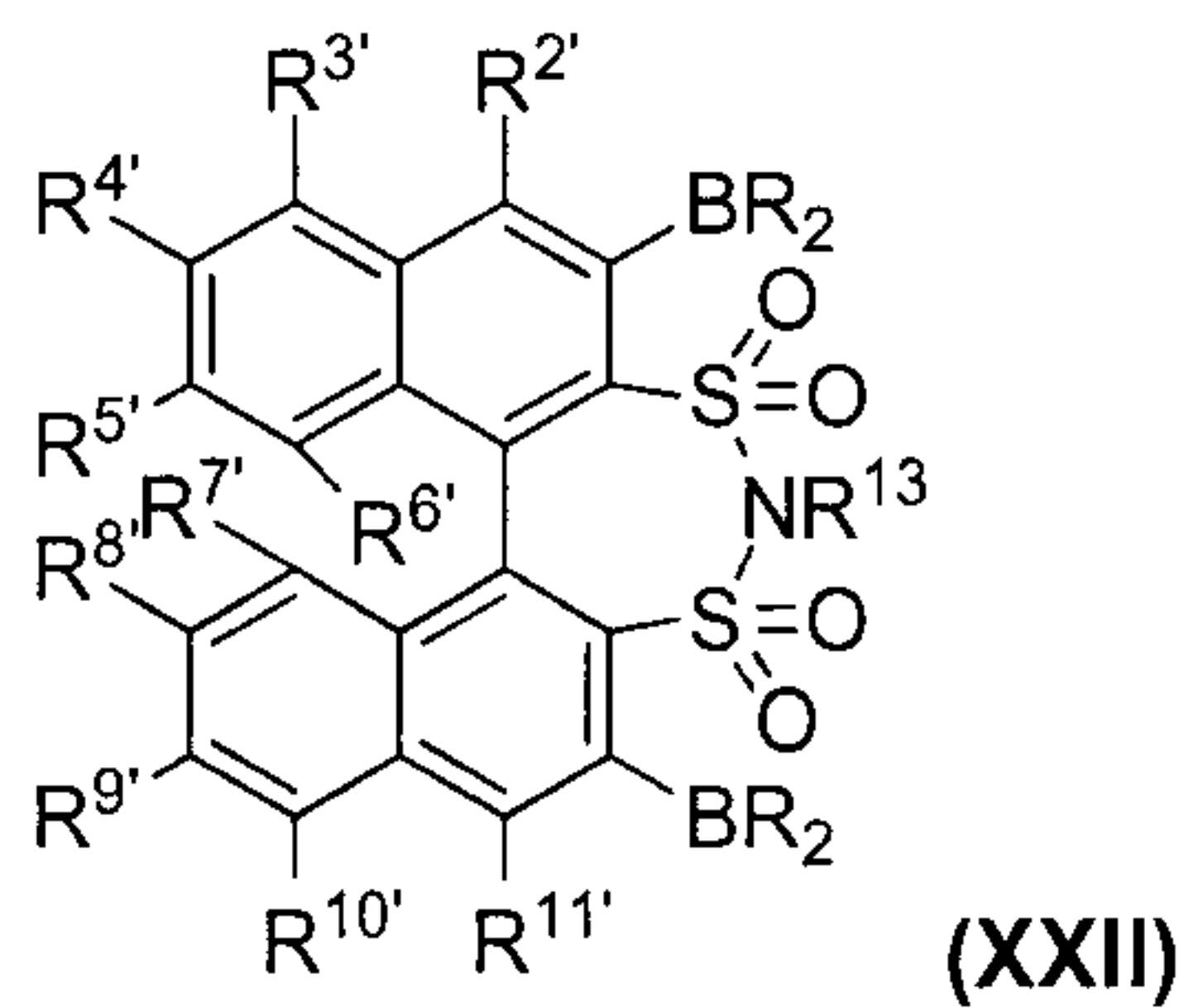
into a 3,3'-dihalide or a 3,3'-ditriflate having the formula XX



wherein $X'' = \text{Cl, Br, I, F or OTf}$;

or

10 (G) converting a disulfonimide IVa into a 3,3'-diboronate having the formula XXII:

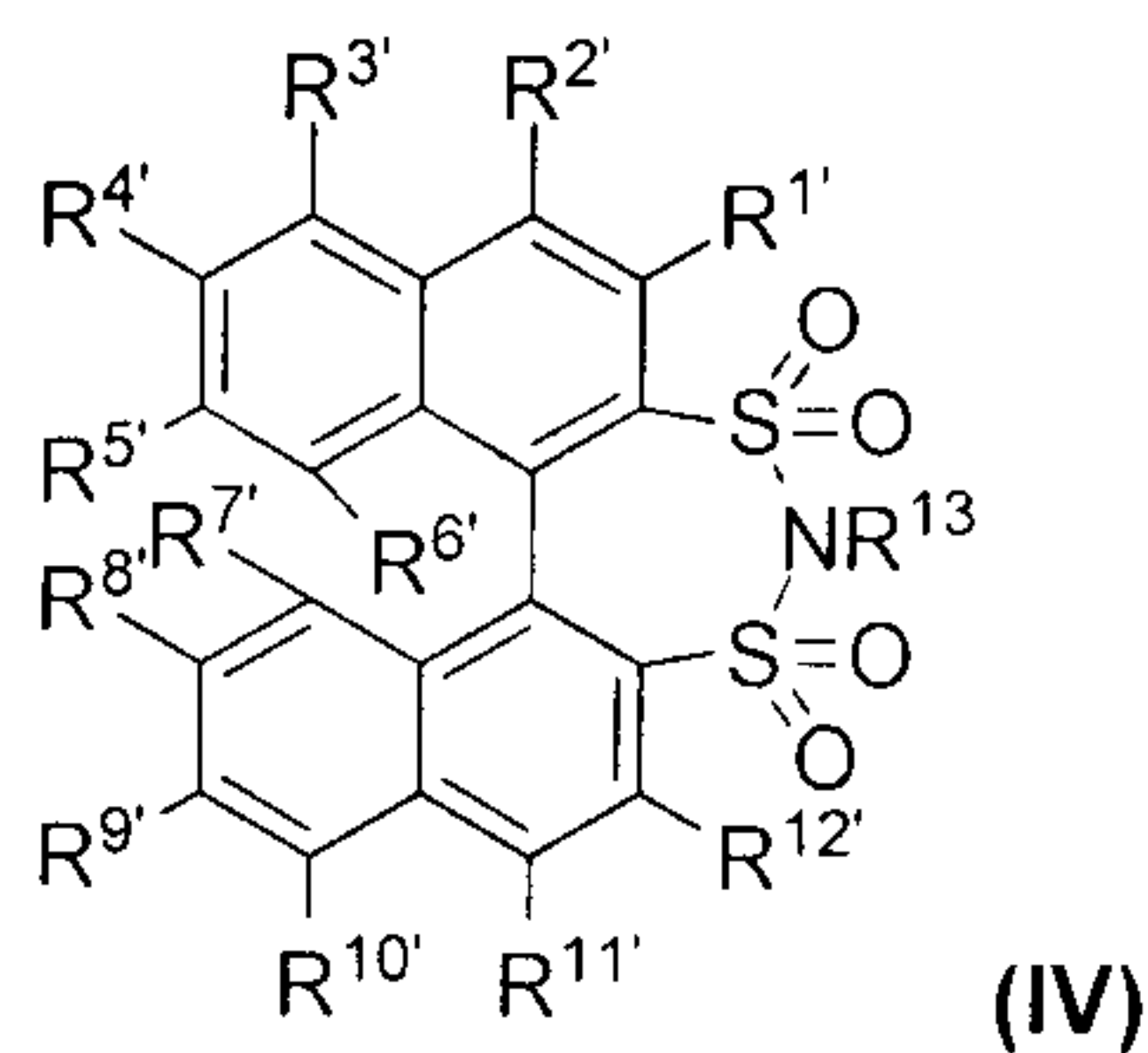


wherein the radicals BR^2 in XXII are identical or different and are each $B(OH)_2$, $B(alkyl)_2$, $B(Oalkyl)_2$, $B(pinacol)$ or BF_3X' , wherein X' is Na or K; and

(H) in a further process step, converting a compound having the formulae XX or XXII by means of a coupling reaction into the imide having the formula IV.

5

9. A use of a compound having the formula IV:



wherein

R^1' , R^2' , R^3' , R^4' , R^5' , R^6' , R^7' , R^8' , R^9' , R^{10}' , R^{11}' and R^{12}' are identical or different and each, independently of one another, represents

10

H,

OH,

F,

Cl,

15

Br,

I,

CN,

NO_2 ,

NO,

20

SO_2 ,

SO_3H ,

NH_2 ,

PH_3 ,

$COOH$,

25

SO_3X , wherein X is Na or K,

$COOY$, wherein Y is Na or K,

substituted or unsubstituted C_1 - C_{20} -alkyl,

substituted or unsubstituted C_2 - C_{20} -alkenyl,

substituted or unsubstituted C_2 - C_{20} -alkynyl,

30

substituted or unsubstituted aryl,

- 41 -

substituted or unsubstituted aryl-(C₁-C₆)-alkyl,
 substituted or unsubstituted hetero(C₁-C₆)-alkyl, or
 substituted or unsubstituted heteroaryl; and

R¹³ is

5

H,
 F,
 Cl,
 Br,
 I, or

10

SiR¹⁴R¹⁵R¹⁶, wherein R¹⁴, R¹⁵ and R¹⁶ are each

substituted or unsubstituted C₁-C₆-alkyl,
 substituted or unsubstituted C₂-C₆-alkenyl,
 substituted or unsubstituted C₂-C₆-alkynyl,
 substituted or unsubstituted aryl,

15

substituted or unsubstituted aryl-(C₁-C₆)-alkyl,
 substituted or unsubstituted hetero(C₁-C₆)-alkyl, or
 substituted or unsubstituted heteroaryl,

or a salt or metal complex thereof,

as a chiral Brønsted acid catalyst or a chiral Lewis acid catalyst.

20

10. The use as claimed in claim 9, wherein R¹³ is SiR¹⁴R¹⁵R¹⁶, and R¹⁴, R¹⁵ and R¹⁶ are as defined in claim 9.

25

11. A use of a compound having the formula IV as defined in claim 1 as an NMR shift reagent or as a reagent for the resolution of a racemic mixture.

30

12. A use of a compound having the formula IV as defined in claim 1 as a chiral Brønsted acid catalyst or a chiral Lewis acid catalyst for the activation of ketones, aldehydes and alkenes.

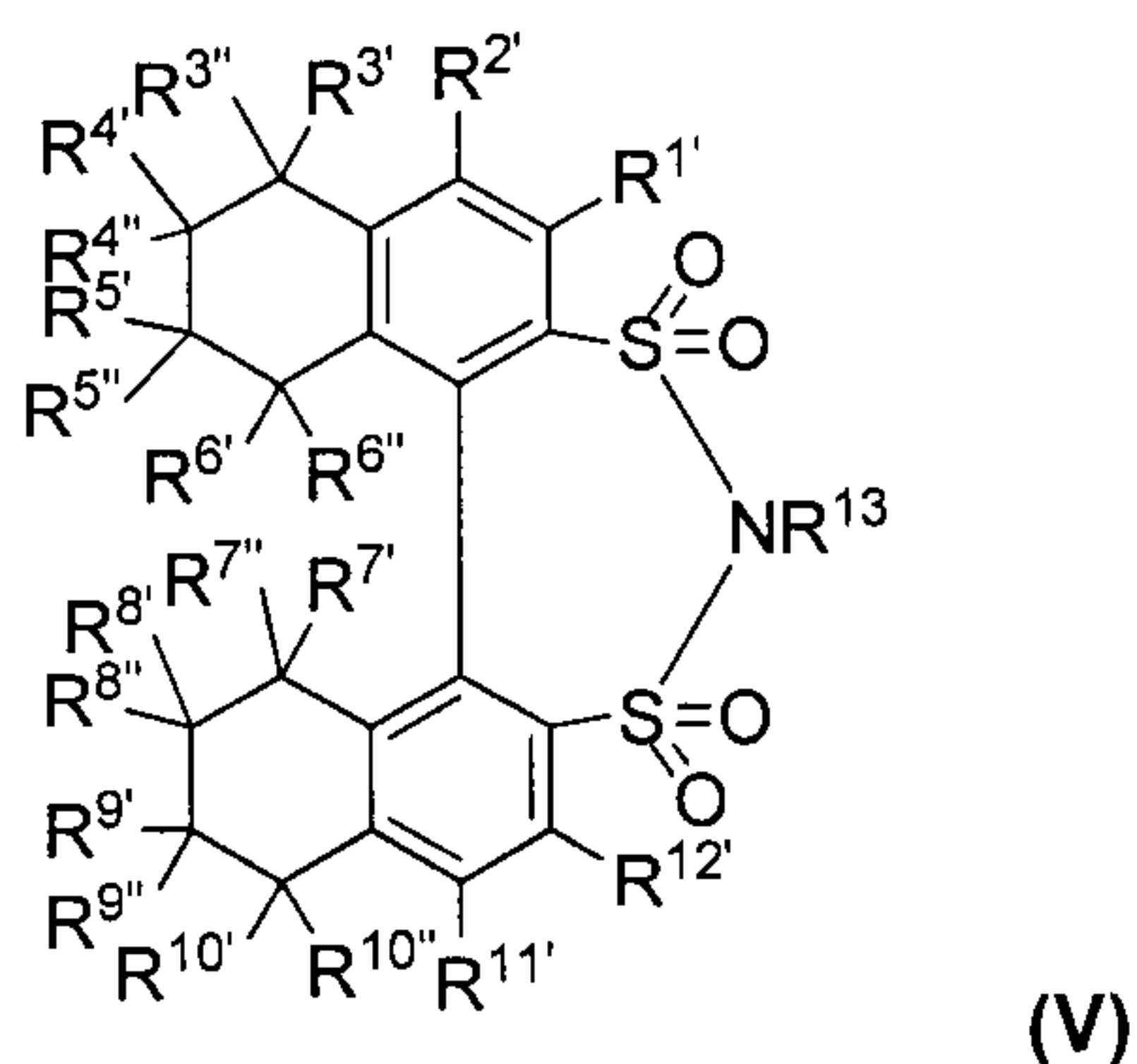
35

13. A use of a compound having the formula IV as defined in claim 1 as a catalyst in a chemical reaction, wherein the chemical reaction is selected from the group consisting of aldol reactions, Mukaiyama aldol reactions, Mukaiyama-Michael reactions, Michael additions, Mannich reactions, esterifications, etherifications, pinacol rearrangements, acetalizations and related reactions, cycloadditions, hydroaminations, hydroalkoxylation, hydrations, olefin activations, Friedel-Crafts reactions, epoxide openings, Ritter reactions, nucleophilic substitutions of alcohols, asymmetric ring openings, transfer hydrogenations,

- 42 -

alkyne additions, allylations, epoxidations, olefin metathesis, isomerizations, iminium catalysis and enamine catalysis.

14. A chiral disulfonimide having the formula V:



wherein

$R^{1'}$ and $R^{12'}$ are identical or different and each, independently of one another, represents

H,

OH,

F,

Cl,

Br,

I,

CN,

NO_2 ,

NO,

SO_2 ,

SO_3H ,

NH_2 ,

PH_3 ,

COOH ,

SO_3X , wherein X is Na or K,

COOY , wherein Y is Na or K,

substituted or unsubstituted $\text{C}_1\text{-C}_{20}$ -alkyl,

substituted or unsubstituted $\text{C}_2\text{-C}_{20}$ -alkenyl,

substituted or unsubstituted $\text{C}_2\text{-C}_{20}$ -alkynyl,

substituted or unsubstituted aryl,

substituted or unsubstituted aryl-($\text{C}_1\text{-C}_6$)-alkyl,

substituted or unsubstituted hetero($\text{C}_1\text{-C}_6$)-alkyl,

- 43 -

substituted or unsubstituted heteroaryl,

tris-mesitylsilyl, or

tris-phenylsilyl;

R^{2'}, R^{3'}, R^{4'}, R^{5'}, R^{6'}, R^{7'}, R^{8'}, R^{9'}, R^{10'}, R^{11'}, R^{3''}, R^{4''}, R^{5''}, R^{6''}, R^{7''}, R^{8''}, R^{9''} and R^{10''} are

5 identical or different and each, independently of one another, represents

H,

OH,

F,

Cl,

10 Br,

I,

CN,

NO₂,

NO,

15 SO₂,SO₃H,NH₂,PH₃,

COOH,

20 SO₃X, wherein X is Na or K,

COOY, wherein Y is Na or K,

substituted or unsubstituted C₁-C₂₀-alkyl,substituted or unsubstituted C₂-C₂₀-alkenyl,substituted or unsubstituted C₂-C₂₀-alkynyl,

25 substituted or unsubstituted aryl,

substituted or unsubstituted aryl-(C₁-C₆)-alkyl,substituted or unsubstituted hetero(C₁-C₆)-alkyl, or

substituted or unsubstituted heteroaryl; and

R¹³ is

30 H,

F,

Cl,

Br,

I,

35 substituted or unsubstituted C₁-C₆-alkyl,substituted or unsubstituted C₂-C₆-alkenyl,substituted or unsubstituted C₂-C₆-alkynyl,

- 44 -

substituted or unsubstituted aryl,
 substituted or unsubstituted aryl-(C₁-C₆)-alkyl,
 substituted or unsubstituted hetero(C₁-C₆)-alkyl,
 substituted or unsubstituted heteroaryl, or
 5 SiR¹⁴R¹⁵R¹⁶, wherein R¹⁴, R¹⁵ and R¹⁶ are each

substituted or unsubstituted C₁-C₆-alkyl,
 substituted or unsubstituted C₂-C₆-alkenyl,
 substituted or unsubstituted C₂-C₆-alkynyl,
 substituted or unsubstituted aryl,

10 substituted or unsubstituted aryl-(C₁-C₆)-alkyl,
 substituted or unsubstituted hetero(C₁-C₆)-alkyl, or
 substituted or unsubstituted heteroaryl,

or an organic salt, metal salt or metal complex thereof.

15 15. The chiral disulfonimide as claimed in claim 14, wherein at least one of R^{1'} and R^{12'} is not hydrogen and is selected from the group consisting of phenyl, 2,4,6-triisopropylphenyl, mesityl, 9-phenanthryl, 9-anthracenyl, 1-naphthyl, 2-naphthyl, 4-biphenyl, 3,5-(trifluoromethyl)phenyl, 2,6-dimethylphenyl, tert-butyl, tris-mesitylsilyl, tris-phenylsilyl, 4-nitrophenyl, 2,6-methyl-4-butylphenyl, trifluoromethyl, 3,4,5-trifluorophenyl, and pentafluorophenyl.

20

16. The chiral disulfonimide as claimed in claim 14, wherein at least one of the radicals R^{4'} and R^{9'} or R^{4''} and R^{9''} is selected from the group consisting of NO₂ and I.

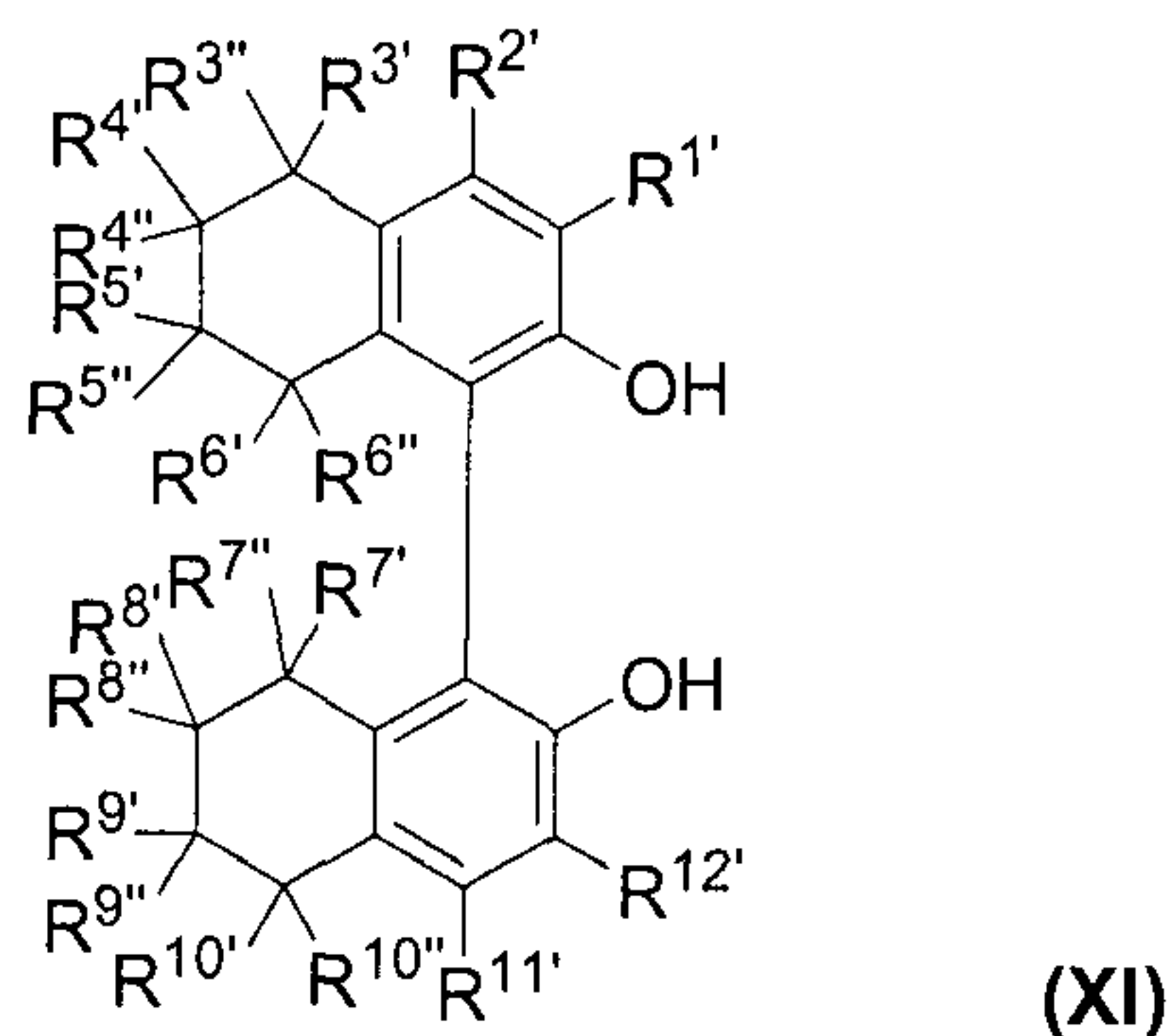
25 17. The chiral disulfonimide as claimed in claim 14, wherein R¹³ is H, F, Cl, Br, I or SiR¹⁴R¹⁵R¹⁶, wherein R¹⁴, R¹⁵ and R¹⁶ are each C₁-C₆-alkyl, C₂-C₆-alkenyl or C₂-C₆-alkynyl.

18. The chiral disulfonimide as claimed in claim 17, wherein R¹³ is SiR¹⁴R¹⁵R¹⁶ and R¹⁴, R¹⁵ and R¹⁶ are as defined in claim 17.

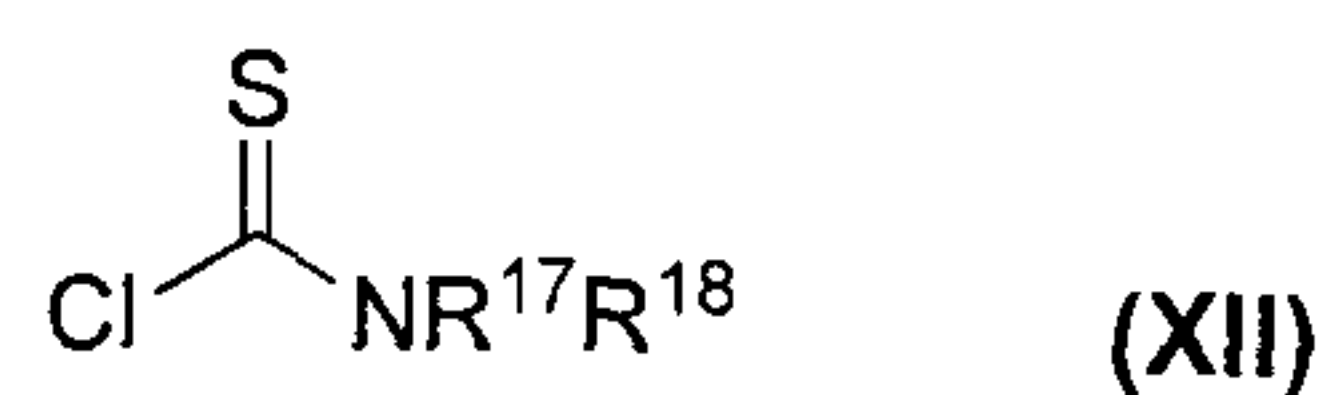
30 19. A process for preparing a chiral disulfonimide having the formula V as defined in claim 14, said process comprising the following steps:

(A) reacting an H8-Binol derivative having the formula XI:

- 45 -

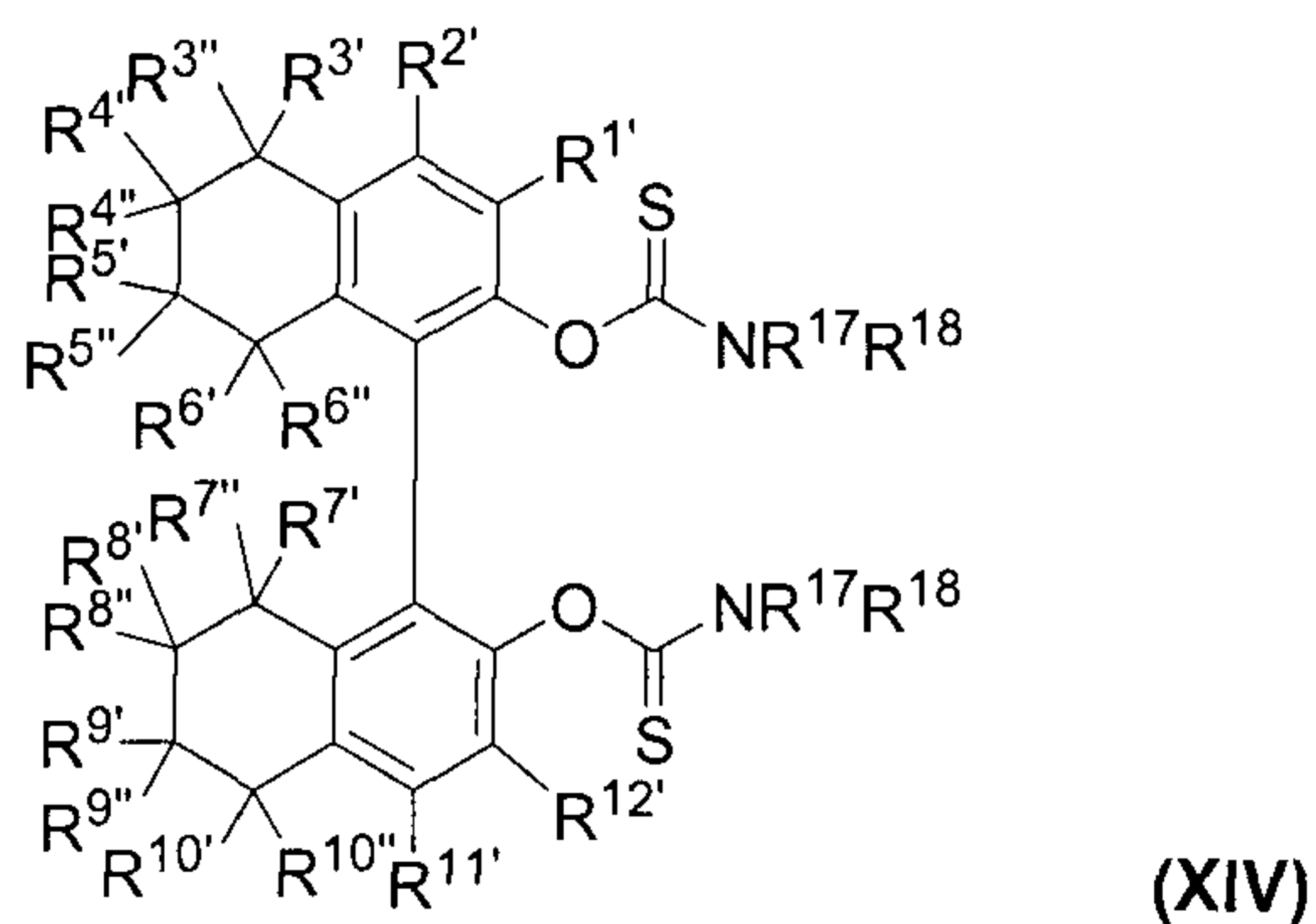


with a thiocarbamoyl chloride of the formula XII:

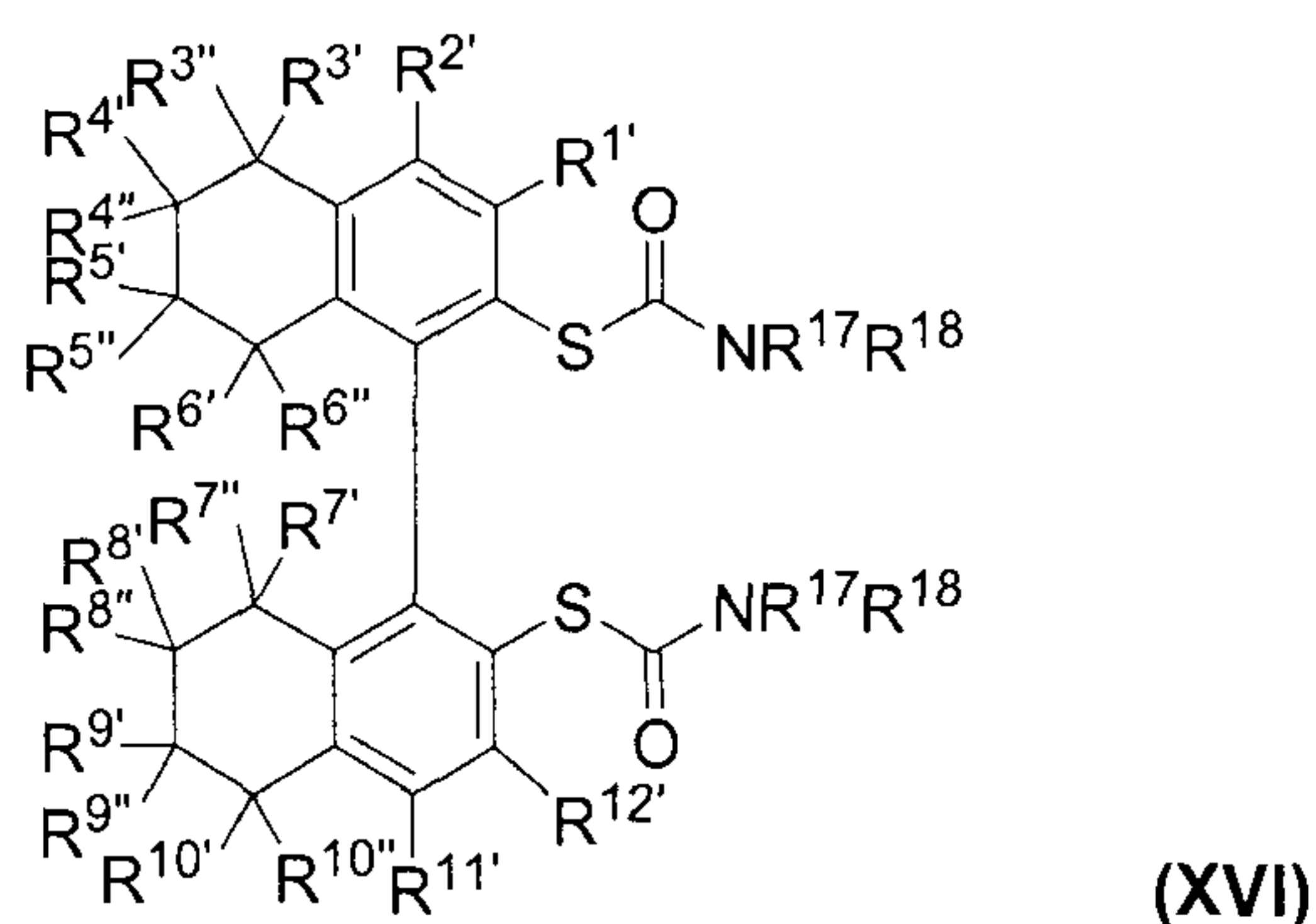


wherein the radicals $R^{1'}$, $R^{2'}$, $R^{3'}$, $R^{4'}$, $R^{5'}$, $R^{6'}$, $R^{7'}$, $R^{8'}$, $R^{9'}$, $R^{10'}$, $R^{11'}$, $R^{12'}$, $R^{3''}$, $R^{4''}$, $R^{5''}$, $R^{6''}$, $R^{7''}$, $R^{8''}$, $R^{9''}$ and $R^{10''}$ are defined as in claim 14; and

wherein R^{17} and R^{18} are identical or different and are each a C_1 - C_6 -alkyl group,
to form an *O*-arylthiocarbamate having the formula XIV:

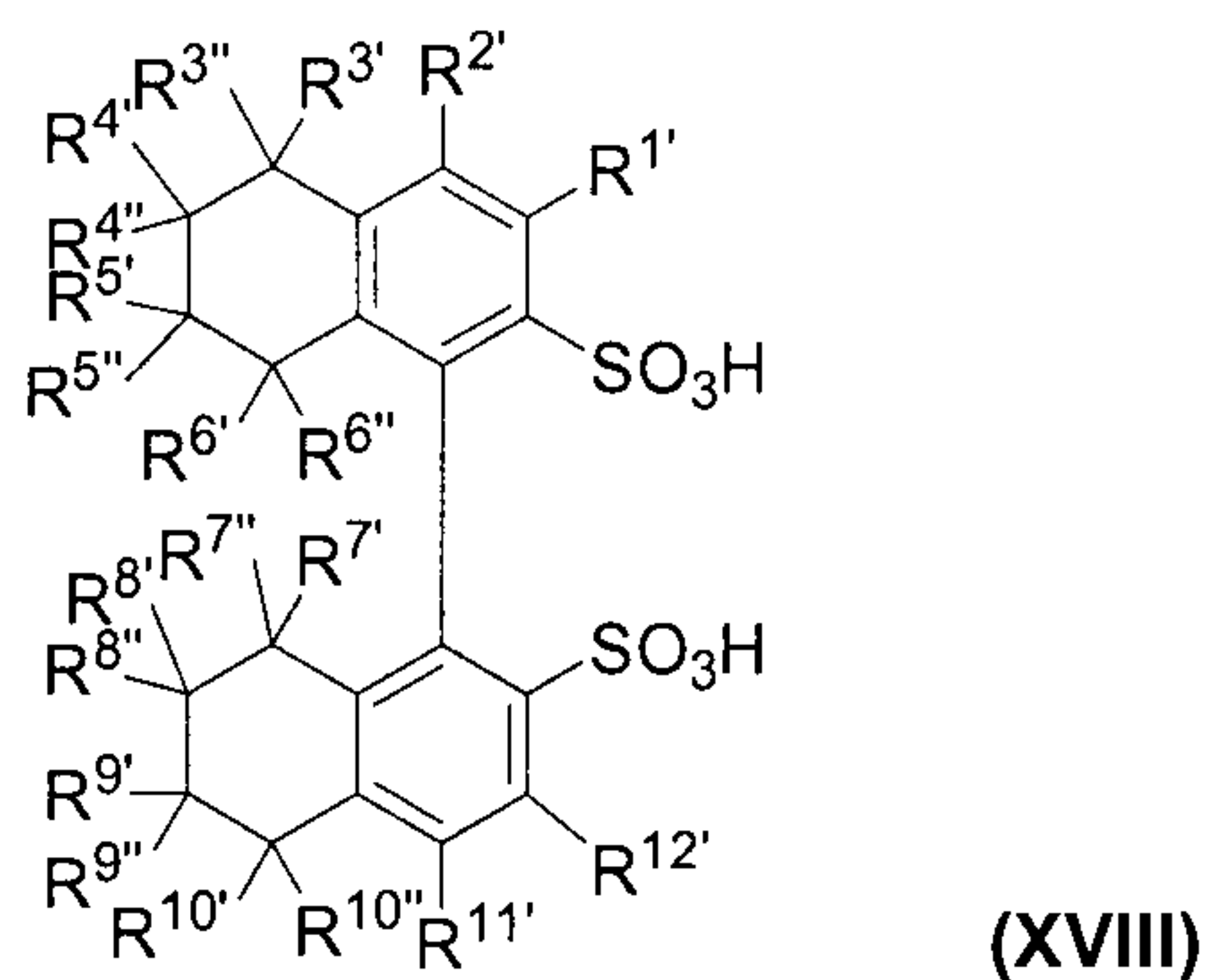


(B) converting the *O*-arylthiocarbamate having the formula XIV into the corresponding *S*-arylthiocarbamate having the formula XVI:

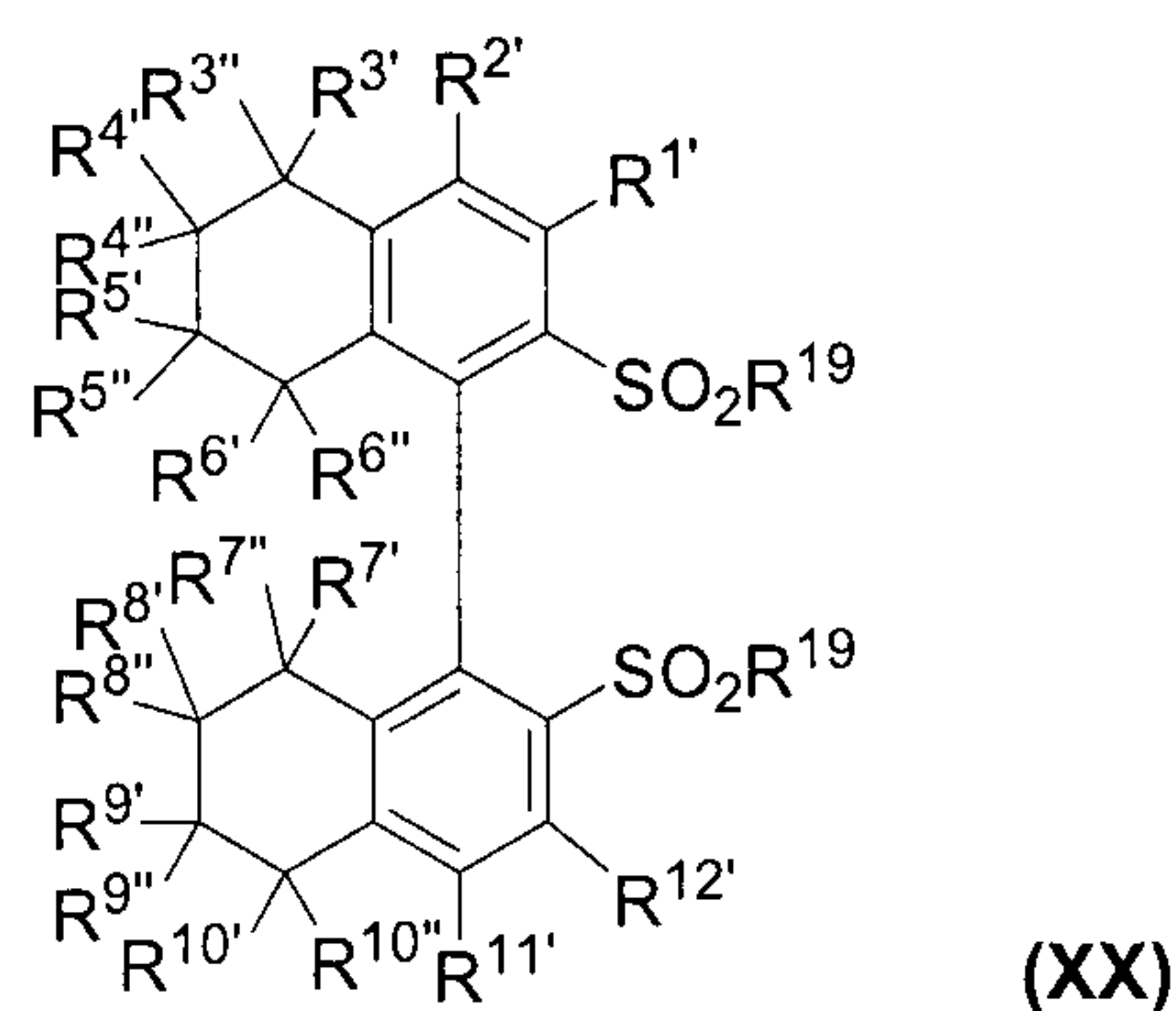


(C) converting the *S*-arylthiocarbamate in the presence of an oxidant into the compound having the formula XVIII:

- 46 -



(D) converting the sulfonic acid obtained in step C into the acid halide having the formula XX:

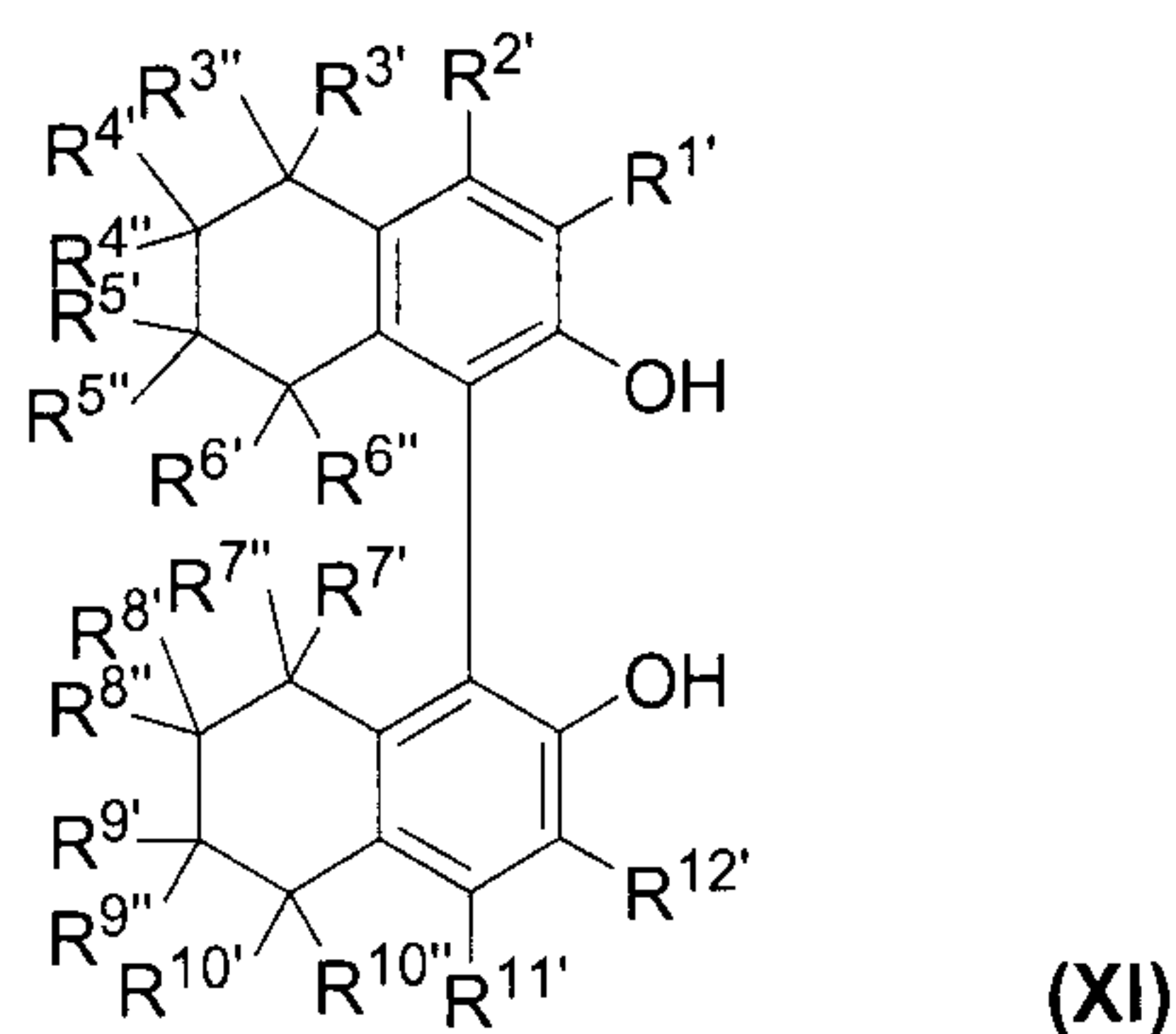


5 wherein R¹⁹ is Cl, Br, I or F,
and in a subsequent process step

(E) converting the acid halide having the formula XX by means of ammonia or a primary amine into the corresponding imide having the formula V.

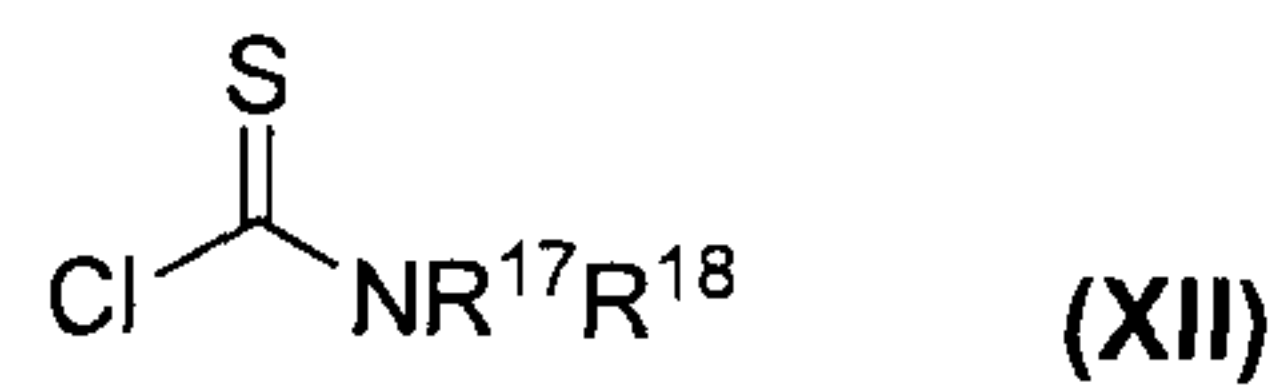
10 20. A process for preparing a chiral disulfonimide having the formula V as claimed in claim 14, said process comprising the following steps:

(A) reacting an H8-Binol derivative having the formula XI:



with a thiocarbamoyl chloride of the formula XII:

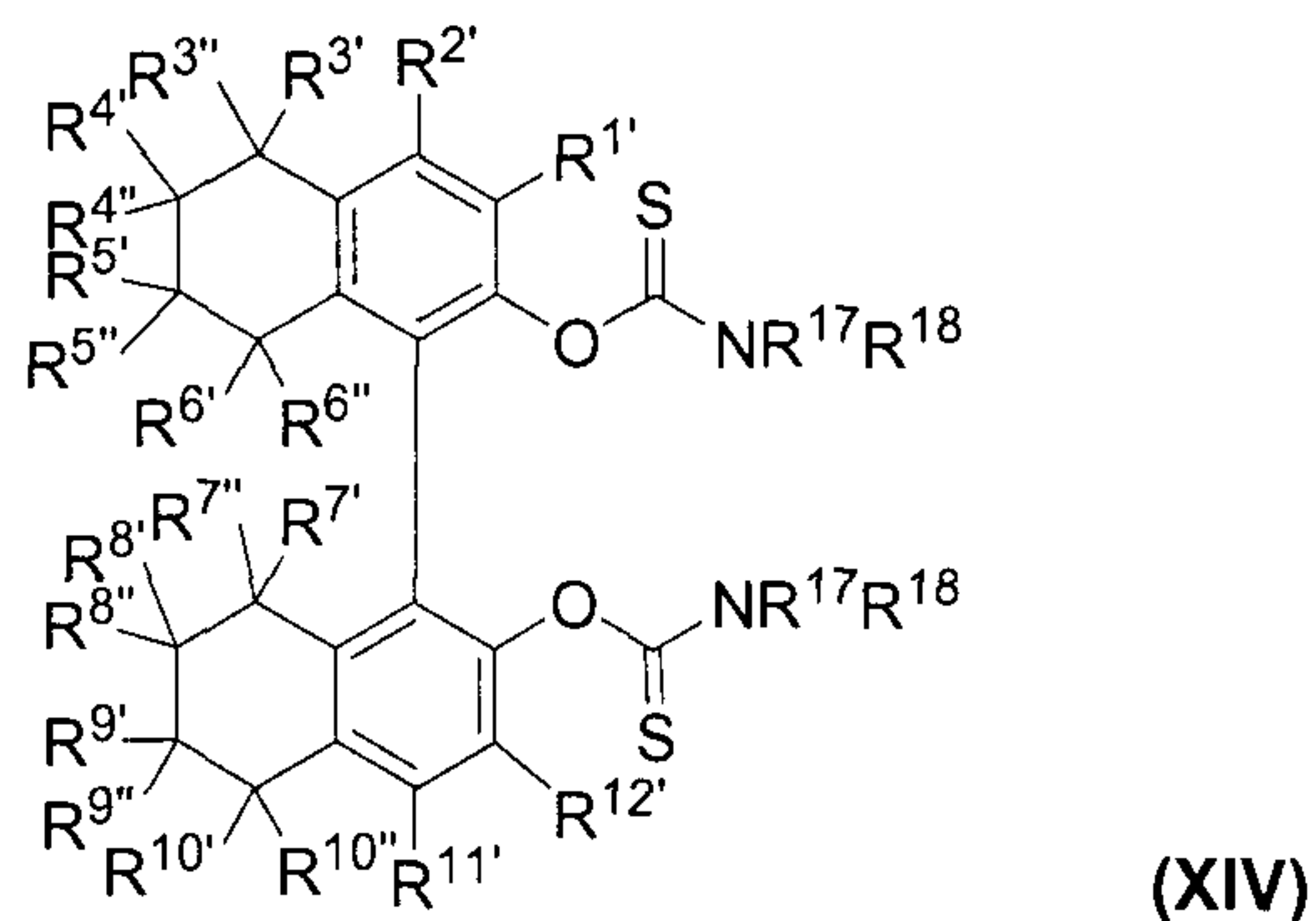
- 47 -



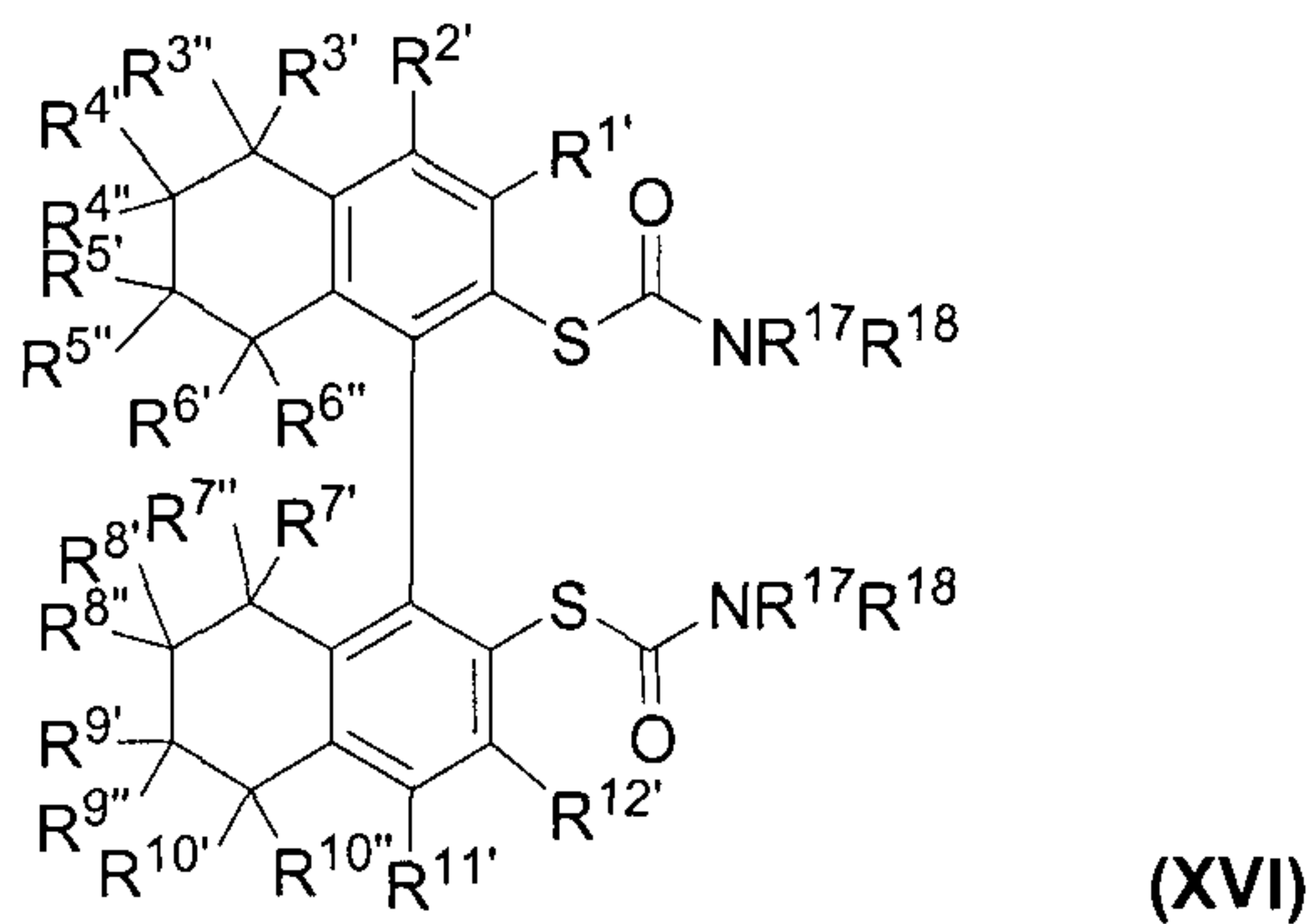
wherein the radicals $\text{R}^{1'}$, $\text{R}^{2'}$, $\text{R}^{3'}$, $\text{R}^{4'}$, $\text{R}^{5'}$, $\text{R}^{6'}$, $\text{R}^{7'}$, $\text{R}^{8'}$, $\text{R}^{9'}$, $\text{R}^{10'}$, $\text{R}^{11'}$, $\text{R}^{12'}$, $\text{R}^{3''}$, $\text{R}^{4''}$, $\text{R}^{5''}$, $\text{R}^{6''}$, $\text{R}^{7''}$, $\text{R}^{8''}$, $\text{R}^{9''}$ and $\text{R}^{10''}$ are defined as in claim 14; and

wherein R^{17} and R^{18} are identical or different and are each a C_1 - C_6 -alkyl group,

5 to form an O-arylthiocarbamate having the formula XIV,

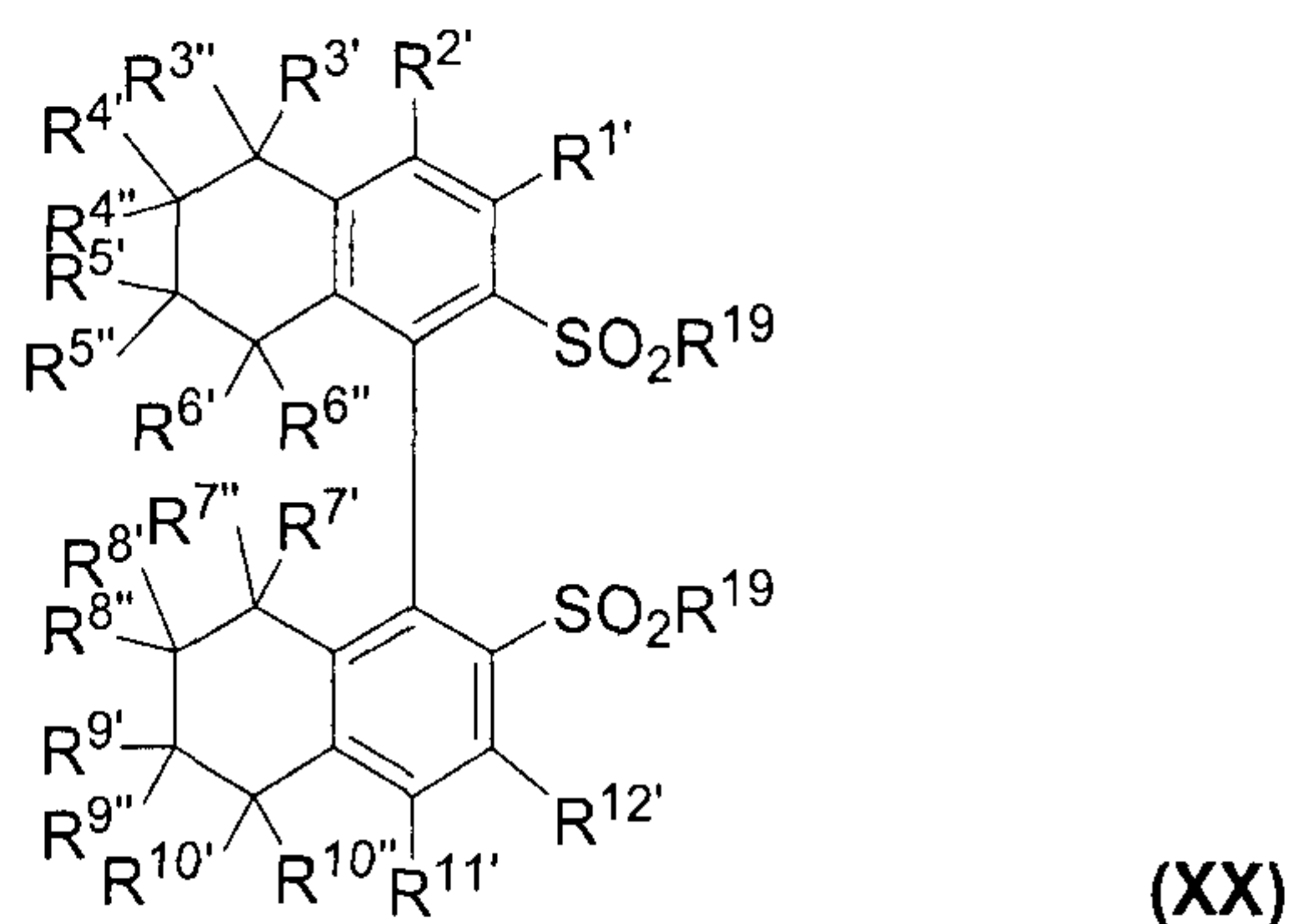


(B) converting the O-arylthiocarbamate having the formula XIV into the corresponding S-arylthiocarbamate having the formula XVI:



10 and

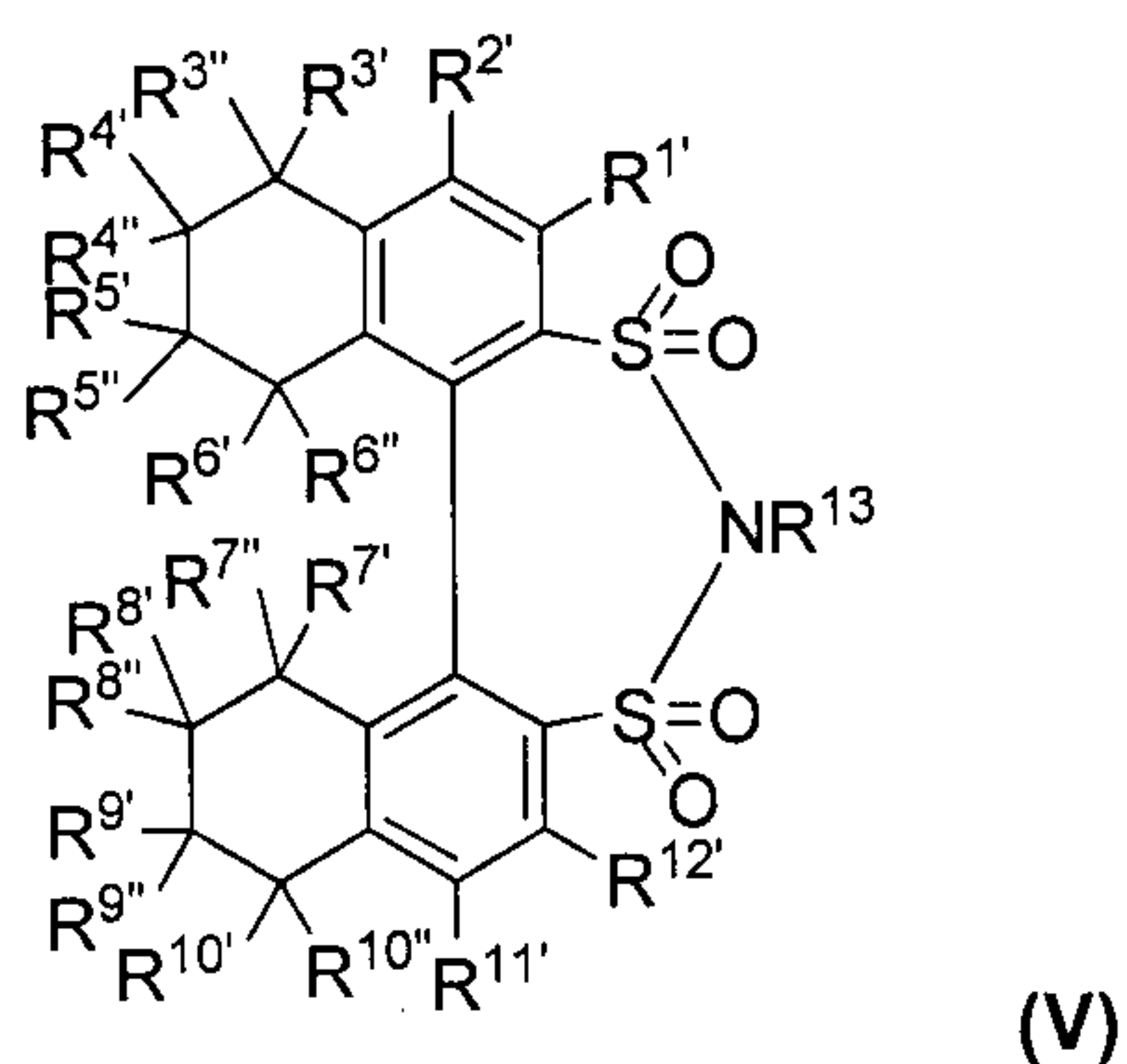
(C) converting the S-arylthiocarbamate having the formula XVI directly into the compound having the formula XX:



- 48 -

wherein R^{19} is Cl, Br, I or F.

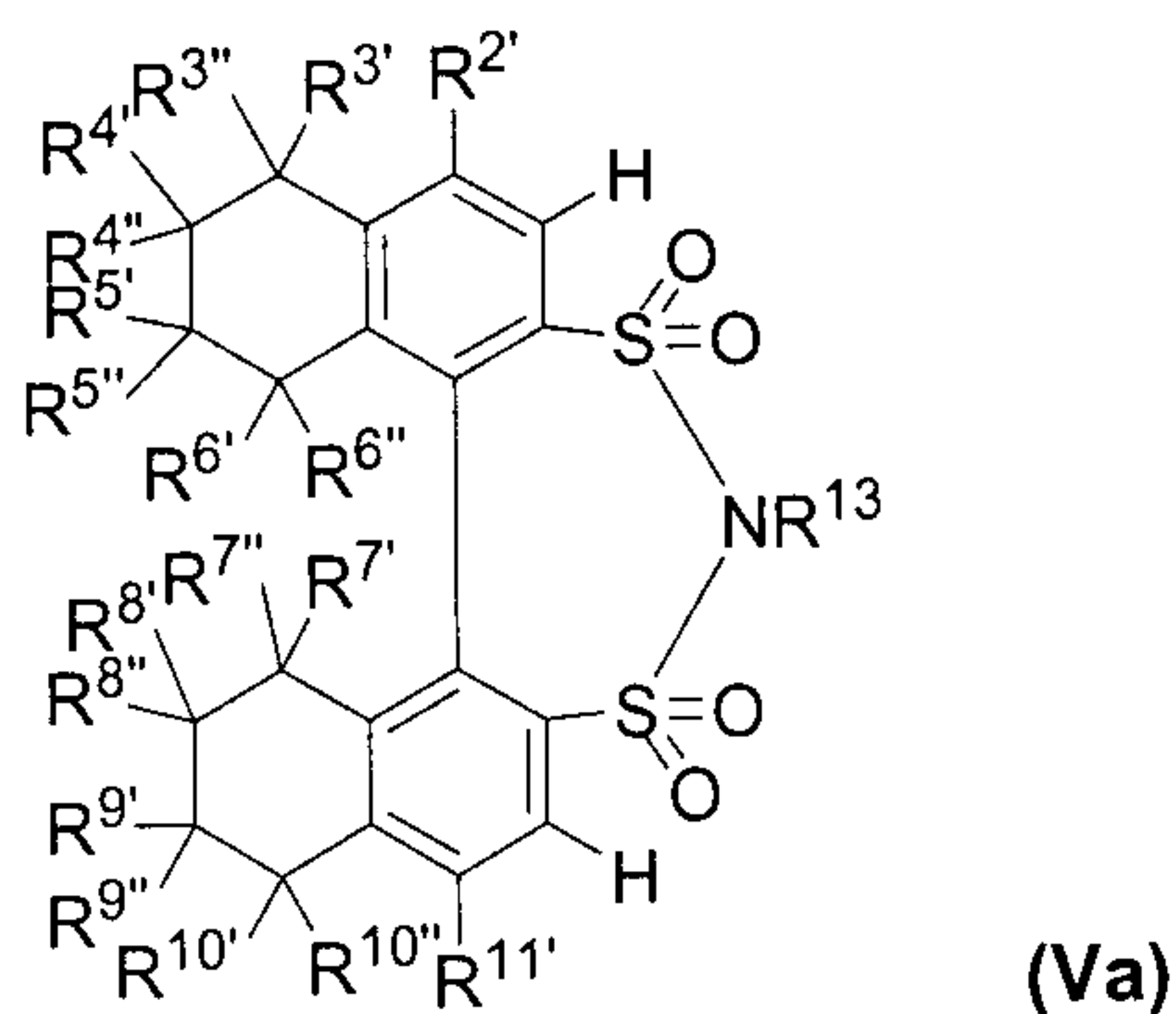
21. A process for preparing a compound having the formula V as defined in claim 16 or an organic salt, metal salt or metal complex thereof:



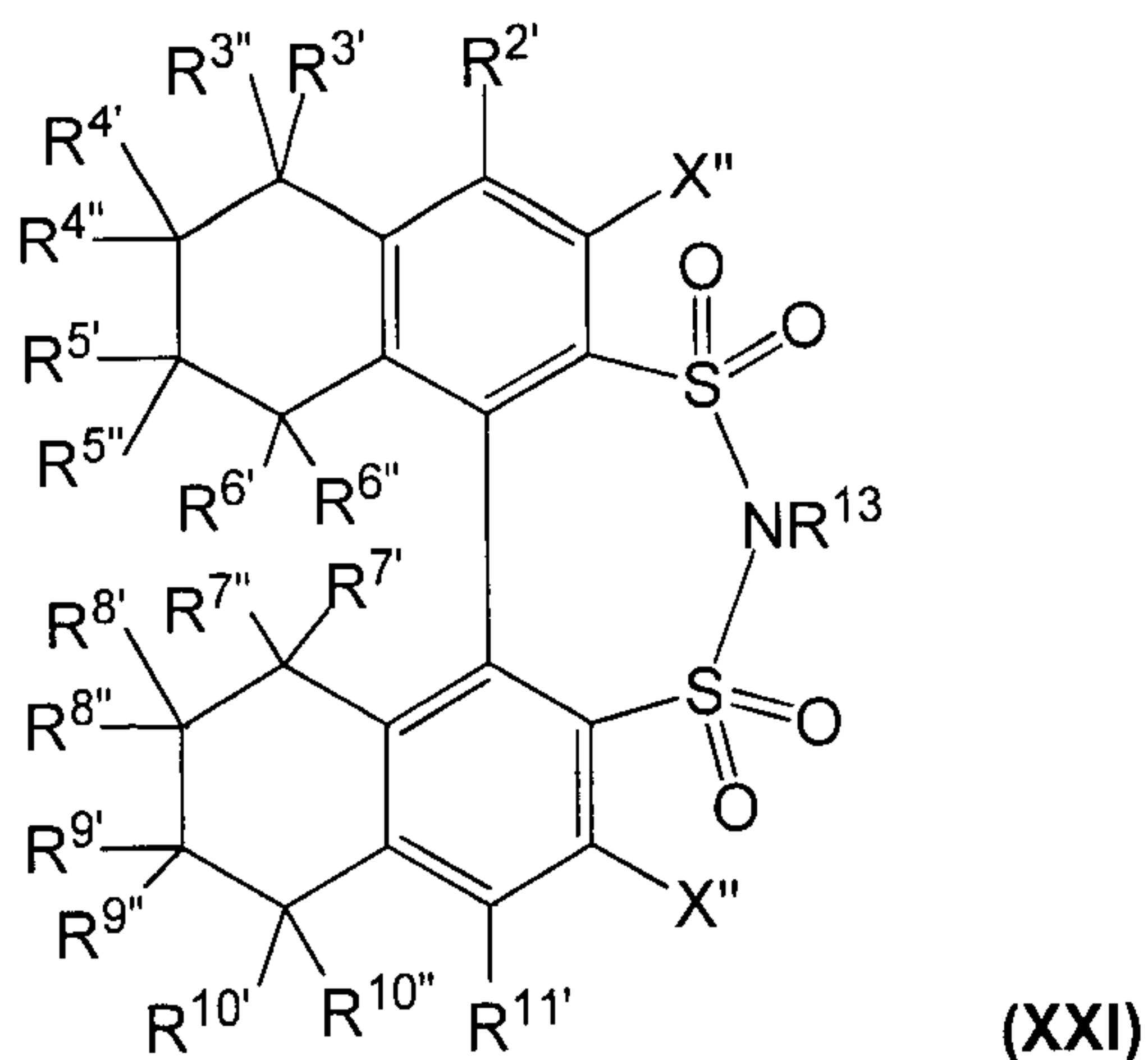
5

wherein $R^{1'}$, $R^{2'}$, $R^{3'}$, $R^{4'}$, $R^{5'}$, $R^{6'}$, $R^{7'}$, $R^{8'}$, $R^{9'}$, $R^{10'}$, $R^{11'}$, $R^{12'}$, $R^{3''}$, $R^{4''}$, $R^{5''}$, $R^{6''}$, $R^{7''}$, $R^{8''}$, $R^{9''}$, $R^{10''}$ and R^{13} are as defined in claim 14, said process comprising the following steps:

(F) converting a 3,3'-unsubstituted disulfonimide having the formula Va:



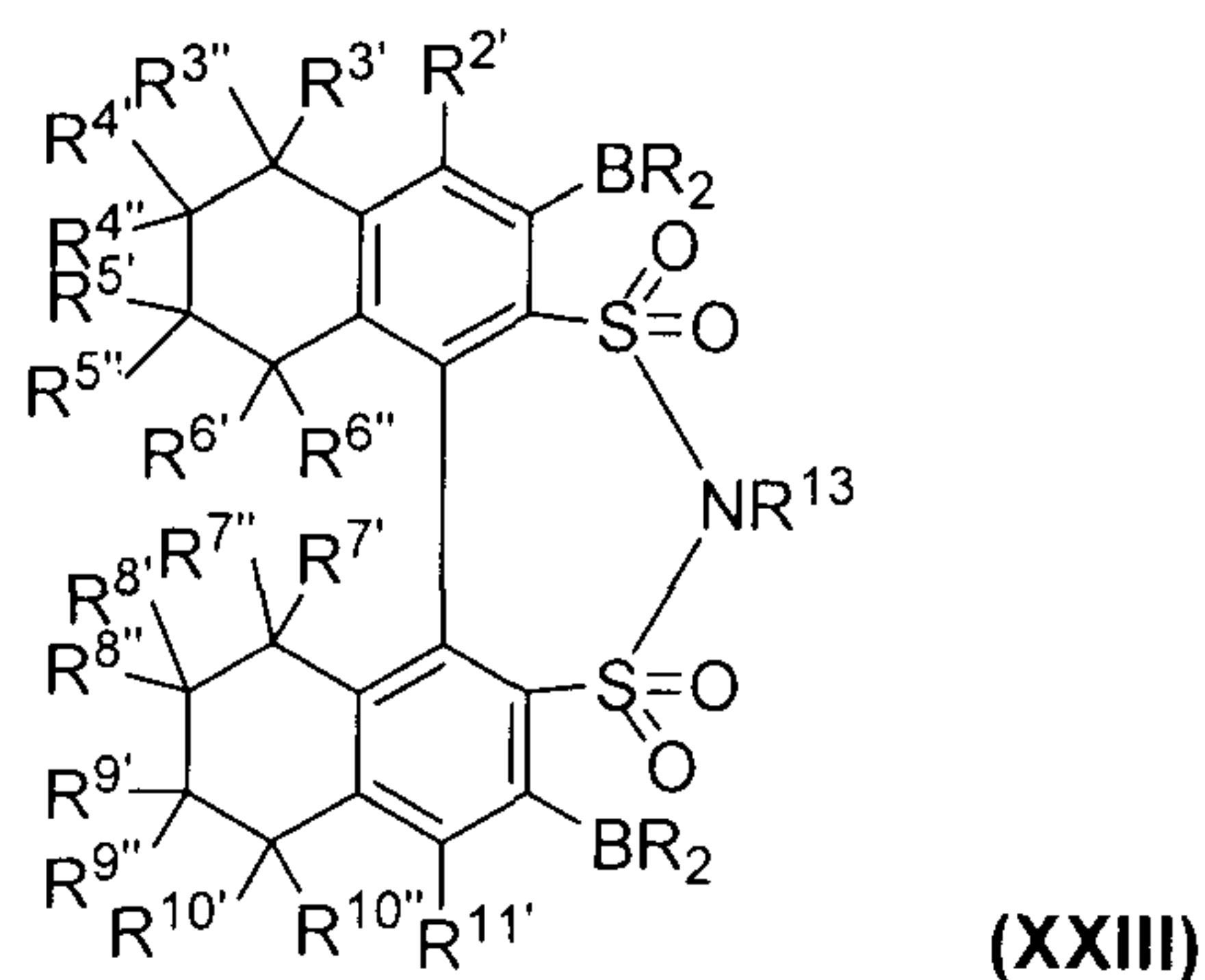
10 into a 3,3'-dihalide or a 3,3'-ditriflate having the formula XXI:



wherein $X'' = \text{Cl, Br, I, F or OTf}$;

or

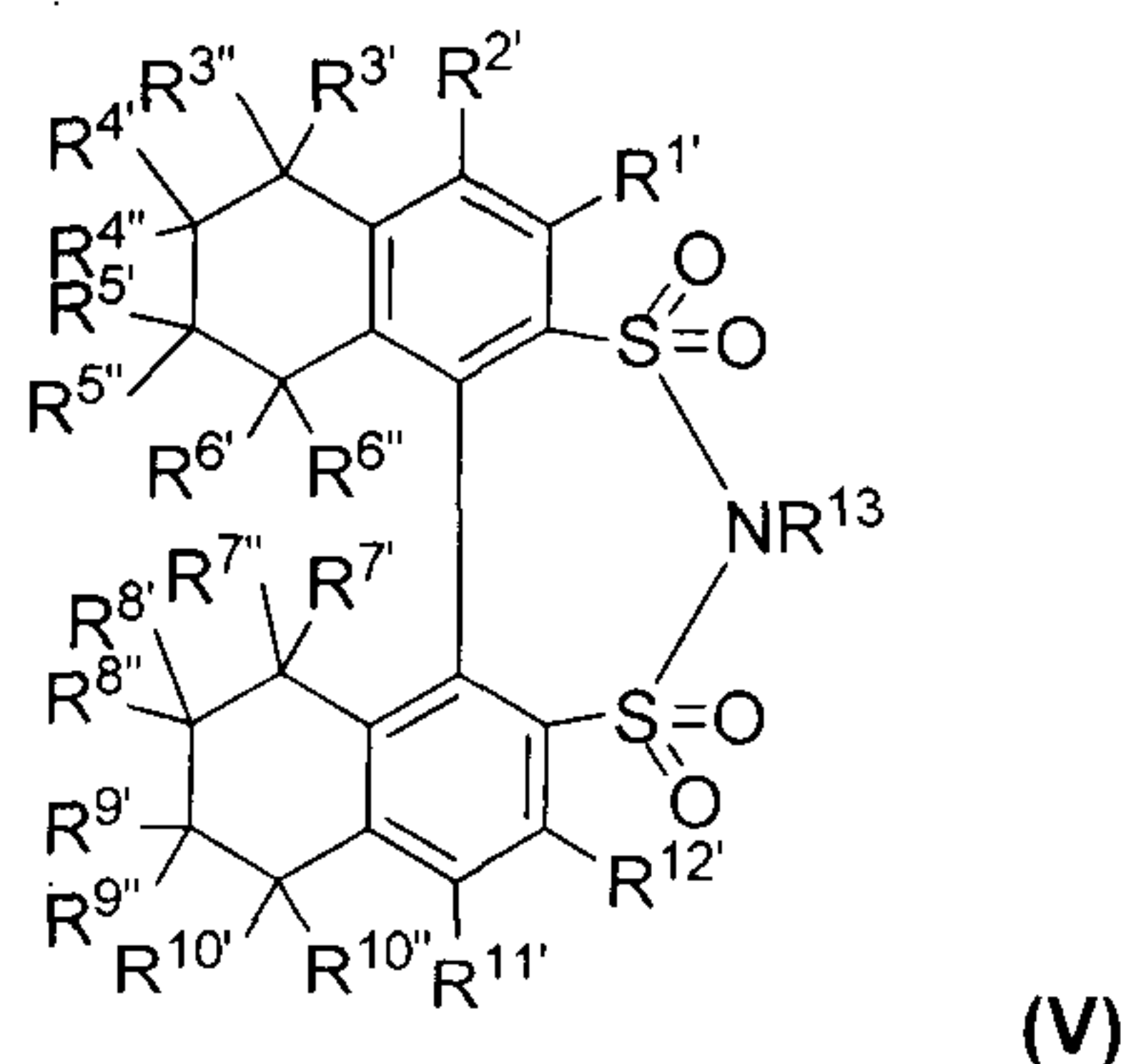
(G) converting a disulfonimide Va into a 3,3'-diboronate having the formula XXIII:



wherein the radicals BR^2 in XXIII are identical or different and are each $B(OH)_2$, $B(alkyl)_2$, $B(Oalkyl)_2$, $B(pinacol)$ or BF_3X , wherein X is Na or K; and

(H) in a further process step, converting a compound having the formulae XXII or XXIII by means of a coupling reaction into the imide having the formula V.

22. A process for preparing a compound having the formula V as defined in claim 14 or an organic salt, metal salt or metal complex thereof:

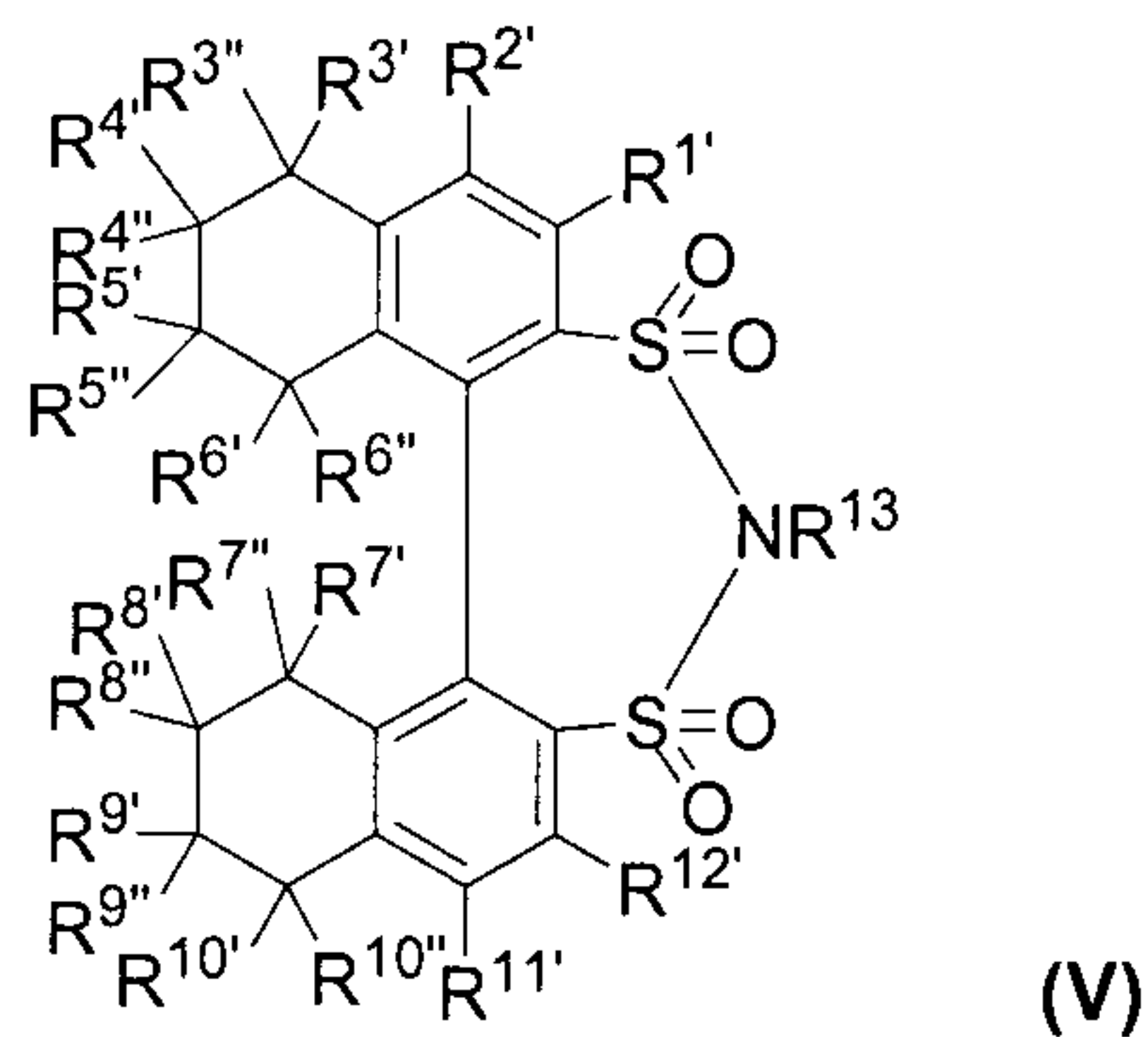


wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{20} and R^{21} are as defined in claim 14,

said process comprising carrying out a directing ortho-metallization to form metal species of the compound V *in situ*, in which R^1 and R^{12} are Li, Mg, Zn or Cu, and reacting said metal species with a suitable electrophile selected from the group consisting of CO_2 , perfluoroalkyl iodides, perfluoroalkyl isocyanates, aldehydes and ketones.

23. A use of a compound having the formula V:

- 50 -



wherein

$R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}$ and R^{19} are identical or different and are each, independently of one another,

- | | |
|----|--|
| 5 | H, |
| | OH, |
| | F, |
| | Cl, |
| | Br, |
| 10 | I, |
| | CN, |
| | NO ₂ , |
| | NO, |
| | SO ₂ , |
| 15 | SO ₃ H, |
| | NH ₂ , |
| | PH ₃ , |
| | COOH, |
| | SO ₃ X, wherein X is Na or K, |
| 20 | COOY, wherein Y is Na or K, |
| | unsubstituted or substituted C ₁ -C ₂₀ -alkyl, |
| | unsubstituted or substituted C ₂ -C ₂₀ -alkenyl, |
| | unsubstituted or substituted C ₂ -C ₂₀ -alkynyl, |
| | unsubstituted or substituted aryl, |
| 25 | unsubstituted or substituted aryl-(C ₁ -C ₆)-alkyl, |
| | unsubstituted or substituted hetero(C ₁ -C ₆)-alkyl, or |
| | unsubstituted or substituted heteroaryl; and |

R^{13} is

H,

- 51 -

F,
Cl,
Br,
I, or

5 SiR¹⁴R¹⁵R¹⁶, wherein R¹⁴, R¹⁵ and R¹⁶ are each
 unsubstituted or substituted C₁-C₆-alkyl,
 unsubstituted or substituted C₂-C₆-alkenyl,
 unsubstituted or substituted C₂-C₆-alkynyl,
 unsubstituted or substituted aryl,
10 unsubstituted or substituted aryl-(C₁-C₆)-alkyl,
 unsubstituted or substituted hetero(C₁-C₆)-alkyl, or
 unsubstituted or substituted heteroaryl,

or a salt or metal complex thereof,

as a chiral Brønsted acid catalyst or a chiral Lewis acid catalyst.

15

24. The use as claimed in claim 23, wherein R¹³ is SiR¹⁴R¹⁵R¹⁶ and R¹⁴, R¹⁵ and R¹⁶ are as defined in claim 23.

20

25. A use of a compound having the formula V as defined in claim 14 as an NMR shift reagent or as a reagent for the resolution of a racemic mixture.

25

26. A use of a compound having the formula V as defined in claim 14 as a chiral Brønsted acid catalyst or a chiral Lewis acid catalyst for the activation of ketones, aldehydes and alkenes.

30

27. A use of a compound having the formula V as defined in claim 14 as a catalyst in a chemical reaction, wherein the chemical reaction is selected from the group consisting of aldol reactions, vinylic aldol reactions, Mukaiyama aldol reactions, vinylic Mukaiyama aldol reactions, Mukaiyama-Michael reactions, Michael additions, Mannich reactions, TMSCN additions onto aldehydes and ketones, esterifications, etherifications, pinacol rearrangements, as acetalizations and related reactions, cycloadditions, hydroaminations, hydroalkoxylation, hydrations, olefin activations, Friedel-Crafts reactions, epoxide openings, Ritter reactions, nucleophilic substitutions of alcohols, asymmetric ring openings, asymmetric reductions, transfer hydrogenations, alkyne additions, allylations, epoxidations, olefin metathesis, isomerizations, iminium catalysis and enamine catalysis.

35

