



- (72) STRYKER, JEFFREY MARK, CA
(72) VERKERK, UDO HENDRICK, CA
(72) FUJITA, MEGUMI, CA
(72) YASUDA, MAKOTO, CA
(71) THE GOVERNORS OF THE UNIVERSITY OF ALBERTA, CA
(51) Int.Cl.⁷ C07C 39/215, C07C 69/76, C07C 63/66, C07C 309/65,
C07F 9/50, C07F 7/08, C07C 69/017, C07C 39/373, C07C 69/24,
C07C 43/23, C07C 43/215
(30) 1999/06/18 (09/336,388) US
(54) **COMPOSES SUBSTITUES DE TETRAARYLETHYLENE**
(54) **SUBSTITUTED TETRAARYLETHYLENE COMPOUNDS**

(57) The present invention seeks to provide novel tetraarylethylene compounds which are substituted on the aryl rings ortho to the ethylenic carbon atoms and processes for the preparation for such compounds. The compounds have potential use as molecular templates.

10

20

30

SUBSTITUTED TETRAARYLETHYLENE COMPOUNDS**ABSTRACT OF THE INVENTION**

The present invention seeks to provide novel tetraarylethylene compounds which are substituted on the aryl rings ortho to the ethylenic carbon atoms and processes for the preparation for such compounds. The compounds have potential use as molecular templates.

FIELD OF THE INVENTION

The present invention relates to tetraarylethylene compounds. More particularly the present invention relates to substituted tetraaryl compounds, preferably which contain functional groups, most preferably terminal functional groups. Such compounds have the potential to act as molecular "templates" for metal complexation. That is, for example, a
10 tetraarylethylene compound having at least one, preferably at least two functional substituents on either side of the plane defined by the sigma bonds attached to the ethylenic carbon atoms could form a "supramolecular assembly" comprising alternating layers of a metal atom and the tetraaryl compound.

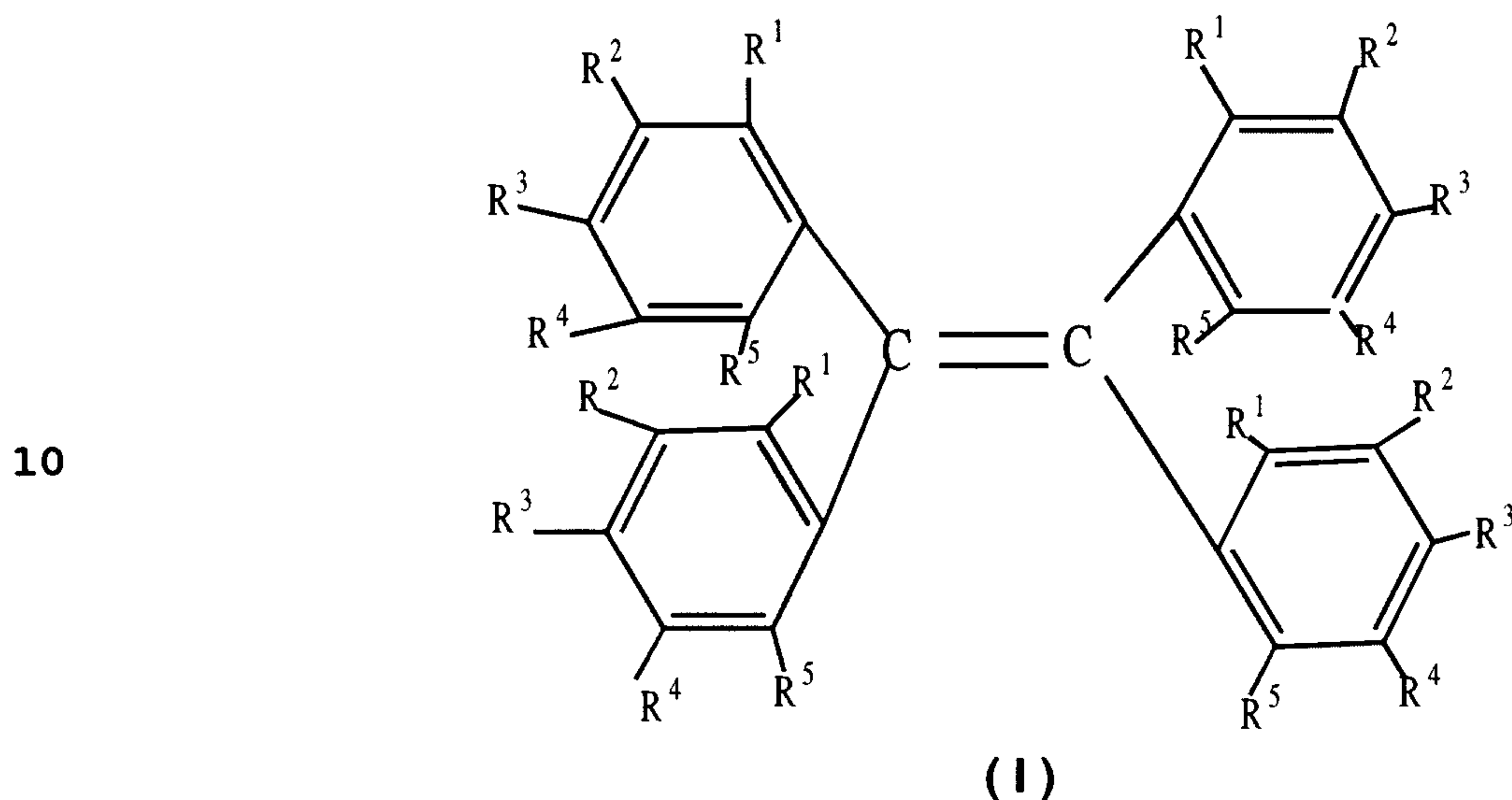
BACKGROUND OF THE INVENTION

20 Chemische Berichte, 1872, 5, 278 reports work by A. Behr to make a substituted tetraphenylethylene. The compound was manufactured from benzophenone and the resulting compounds are hydroxyl substituted in the aromatic (aryl) ring para to the ethylenic carbon atoms. There are a number of subsequent references to this paper, including Kogyo Kagaku Zasshi, 61, 481-2 (1958) by Yoshiro Nakamura, which clearly establishes that the oxidation and subsequent alkylation is para to the ethylenic carbon
30 atoms. The reference fails to clearly teach ortho substituted tetraarylethylenes. Further, the references also fail to teach tetraarylethylene which is substituted both above and below the plane defined by the sigma bonds attached to the ethylenic carbon atoms.

Accordingly, the present invention seeks to provide novel tetraarylethylene compounds.

SUMMARY OF THE INVENTION

The present invention provides a compound of formula I:



wherein at least two R^1 are the same and not a hydrogen atom; and R^1 , R^2 , R^3 , R^4 and R^5 are independently selected from the group consisting of a hydrogen atom; a halogen atom; a hydroxyl radical; a C_{1-20} alkyl radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; a C_{3-20} allyl radical; a C_{1-20} alkoxy radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; a C_{3-20} allyloxy radical; a carbalkoxy radical of the formula $-\text{COOR}^{20}$ wherein R^{20} is a hydrogen atom or a C_{1-20} alkyl radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; a carboxylate radical of the formula $-\text{OCOR}^{30}$ wherein R^{30} is a C_{1-20} alkyl radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a

hydroxyl radical or a carboxyl radical; a C₆₋₁₀ aryl radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; a C₆₋₁₀ aryloxy radical or a C₇₋₁₁ benzyloxy radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; an acyl R⁶CO– radical wherein R⁶ is a C₁₋₂₀ alkyl radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; an amido radical which is unsubstituted or substituted by up to two C₁₋₂₀ alkyl radicals; a (–O–)_n–P(R⁷)₂ radical wherein each R⁷ is independently selected from the group consisting of a C₁₋₂₀ alkyl radical, a C₁₋₂₀ alkoxy radical, a C₆₋₁₀ aryl radical and n is 0 or 1; a (–O–)_n–PO(R⁸)₂ radical wherein each R⁸ is independently selected from the group consisting of a C₁₋₂₀ alkyl radical, a C₁₋₂₀ alkoxy radical, a C₆₋₁₀ aryl radical and n is 0 or 1; a –Si(R⁹)₃ radical wherein each R⁹ is independently selected from the group consisting of a C₁₋₂₀ alkyl radical, a C₆₋₁₀ aryl radical, a hydrogen radical and an alkoxy radical; a trifluoromethanesulfonyloxy radical; or two or more of adjacent substituents R², R³, R⁴ and R⁵ may be taken together to form a fused ring.

The present invention also provides a process for the preparation of a 2,2',2'',2'''-(tetra C₁₋₆ alkoxy) tetraphenylethylene comprising acid catalyzed decomposition of the diazo derivative of 2,2'-di C₁₋₆ alkoxybenzophenone hydrazone at a temperature of less than 25°C in the absence of light.

The present invention also seeks to provide a process for the preparation of 2,2',2'',2''',6,6',6'',6'''-octa C₁₋₄ alkoxy tetraphenylethylene comprising the controlled oxidation of 1,1,2,2-tetrakis(2',6'-di C₁₋₆ alkoxyphenyl)ethane. Typically the oxidation takes place in the presence of triphenylmethyl hexafluorophosphate in an inert solvent at low temperatures typically from about 0°C to about 25°C. It is believed that the resulting 2,2',2'',2''',6,6',6'',6'''-octa C₁₋₆ alkoxy tetraphenylethylene compound may be dealkylated to 2,2',2'',2''',6,6',6'',6'''-octahydroxy tetraphenylethylene.

In a further embodiment the present invention provides a process for the preparation of 1,1,2,2-tetrakis(2',6'-di C₁₋₆ alkoxyphenyl)ethane comprising the radical coupling of bis(2,6-di C₁₋₆ alkoxyphenyl)methanol and bis(2,6-di C₁₋₄ alkoxyphenyl)methane in equimolar amounts in an inert solvent in the presence of p-toluene sulphonic acid.

A second method of preparation of 1,1,2,2-tetrakis(2',6'-di C₁₋₆ alkoxyphenyl)ethane is provided by the reductive radical coupling of bis(2,6-di C₁₋₆ alkoxyphenyl)methanol using chromous ion (CrCl₂) in an acidic medium (HCl).

A further aspect of the present invention provides a process for the synthesis of unsymmetrically substituted tetraphenylethylene compounds of formula 1 wherein two R¹ substituents on opposite ends of the central ethylene moiety are C₁₋₂₀ alkoxy radicals (as defined above) and two R¹ substituents on opposite ends of the central ethylene moiety are benzyloxy radicals (as defined above) comprising acid catalyzed decomposition of the diazo derivative of 2-C₇₋₁₁ benzyloxy, 2'-C₁₋₂₀ alkoxy benzophenone.

In the diazo-coupling reaction of 2-benzyloxy-2'-methoxybenzophenone hydrazone to give the dibenzyloxy-dimethoxytetraphenylethylene, both double bond isomers are produced, giving a mixture of E and Z - 1,2-di(2'-benzyloxyphenyl)-1,2-di(2'-methoxyphenyl)ethane. The subsequent hydrogenolysis of the mixture resulted in the separable E and Z - 1,2-di(2'-hydroxyphenyl)-1,2-di(2'-methoxyphenyl)ethylene.

10

In a further aspect of the present invention the resulting unsymmetrically substituted tetraphenylethylene compounds of formula I wherein two R¹ substituents on opposite ends of the central ethylene moiety are C₁₋₂₀ alkoxy radicals (as defined above) and two R¹ substituents on opposite ends of the central ethylene moiety are C₇₋₁₁ benzyloxy radicals (as defined above) may be subjected to catalytic hydrogenolysis (hydrogenation) to convert the benzyloxy radicals to hydroxyl radicals. Preferably the catalyst is palladium on carbon. Both E and Z isomers can be produced in this way and either separated and used individually or used as a mixture.

20

In a further embodiment the present invention provides a process for producing compounds of formula I above wherein all R¹ substituents are C₃₋₂₀ allyloxy radicals comprising reacting the compounds of formula I above wherein all R¹ substituents are hydroxyl radicals with excess 1-halo C₃₋₂₀ allyl compound. Preferably the halo substituent is a bromine atom. The resulting compound may be subject to a high temperature Claisen rearrangement to yield the compounds of formula I wherein all R¹ substituents are hydroxy radicals and all R² substituents are C₃₋₂₀ allyl

30

radicals. The resulting compounds may then be catalytically hydrogenated so that the allyl substituents (R^2) are hydrogenated to the corresponding alkane substituents.

DETAILED DESCRIPTION

In the compounds of the present invention preferably R^1 , R^2 , R^3 , R^4 and R^5 are independently selected from the group consisting of a

10 hydrogen atom; a halogen atom; a hydroxyl radical; a C_{1-6} alkyl radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; a C_{3-6} allyl radical; a C_{1-6} alkoxy radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl

20 radical; a C_{3-6} allyloxy radical; a carbalkoxy radical of the formula $-\text{COOR}^{20}$ wherein R^{20} is a hydrogen atom or a C_{1-6} alkyl radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; a carboxylate radical of the formula $-\text{OC}-\text{OR}^{30}$ wherein R^{30} is a C_{1-6} alkyl radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a

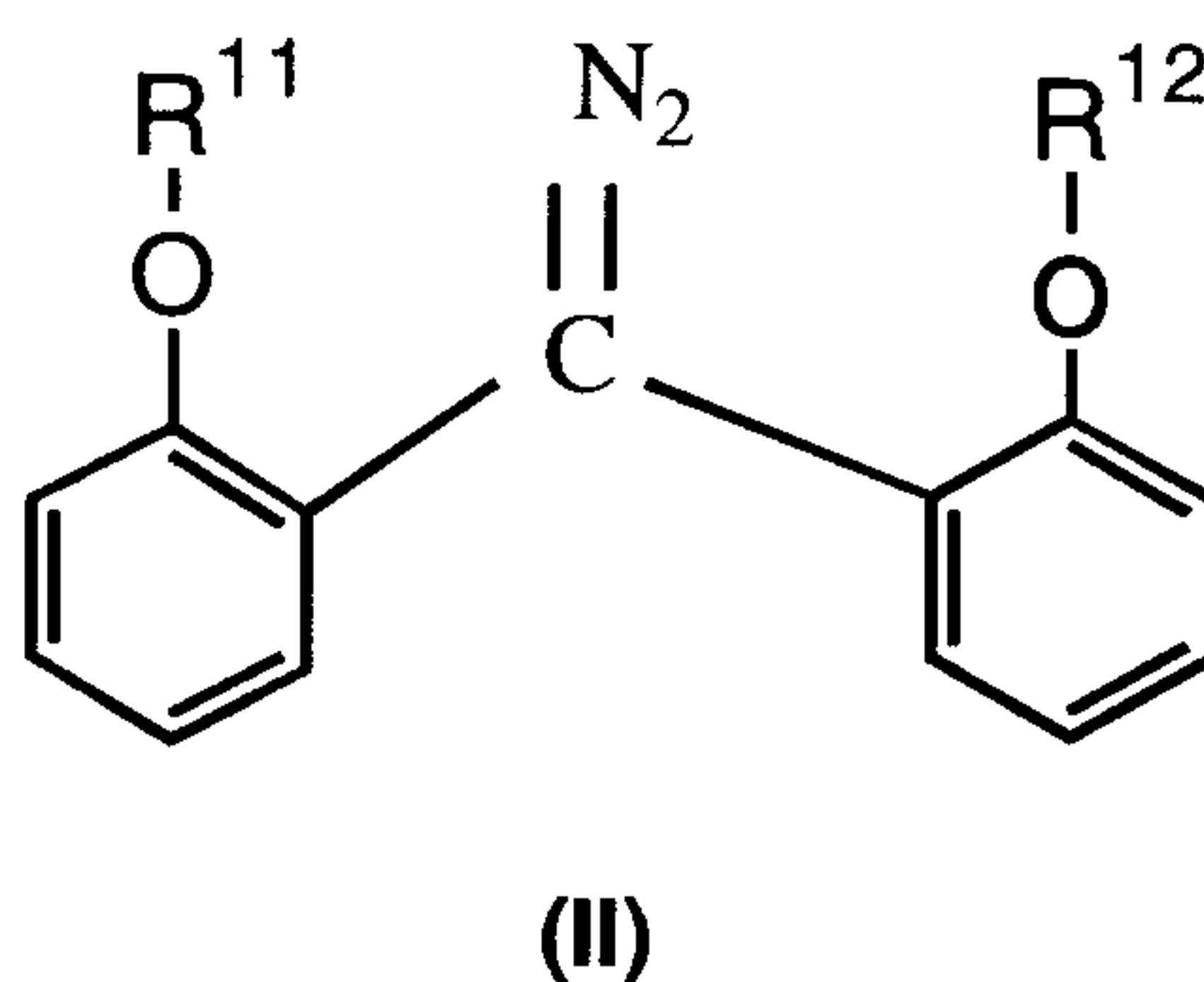
30 hydroxyl atom or a carboxyl atom; a C_{6-10} aryl radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; a C_{6-10} aryloxy radical or a C_{7-11} benzyloxy radical which may be unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl

radical; an acyl R^6CO- radical wherein R^6 is a C_{1-6} alkyl radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; an amido radical which is unsubstituted or substituted by up to two C_{1-6} alkyl radicals; a $(-O-)_n-P(R^7)_2$ radical wherein each R^7 is independently selected from the group consisting of a C_{1-6} alkyl radical, a C_{1-6} alkoxy radical, a C_{6-10} aryl radical and n is 0 or 1; a $(-O-)_n-PO(R^8)_2$ radical wherein each R^8 is independently selected from the group consisting of a C_{1-6} alkyl radical, a C_{1-6} alkoxy radical, a C_{6-10} aryl radical and n is 0 or 1; a $-Si(R^9)_3$ radical wherein each R^9 is independently selected from the group consisting of a C_{1-6} alkyl radical and a C_{6-10} aryl radical; and a trifluorosulfonyloxy radical. Preferably R^2 , R^3 and R^4 are selected from the group consisting of a hydrogen atom or a lower C_{1-4} alkyl radical, most preferably a hydrogen atom.

In a particularly preferred embodiment of the present invention, preferably at least two, more preferably up to four of the R^1 substituents are independently selected from the group consisting of hydroxyl radicals; alkoxy radicals; aryloxy radicals; carboxyl radical; a $(-O-)_n-P(R^7)_2$ radical wherein each R^7 is independently selected from the group consisting of a C_{1-6} alkyl radical, a C_{1-6} alkoxy radical, a C_{6-10} aryl radical and n is 0 or 1; and a trifluorosulfonyloxy radical. In a further preferred embodiment of the present invention at least two, most preferably up to four of the R^1 and at least two, most preferably up to four, of the R^5 radicals are independently selected from the group consisting of hydroxyl radicals; alkoxy, preferably C_{1-6} radicals; a $(-O-)_n-P(R^7)_2$ radical wherein each R^7 is independently

selected from the group consisting of a C₁₋₆ alkyl radical, a C₁₋₆ alkoxy radical, a C₆₋₁₀ aryl radical and n is 0 or 1; and aryloxy, preferably C₆₋₁₀ radicals; and a trifluoromethanesulfonyloxy radical. Preferably at least two and most preferably all four R¹ substituents are the same. Preferably at least two and most preferably all four R⁵ substituents are the same. In a further aspect of the present invention all the R¹ substituents are the same and all the R⁵ substituents are the same. In the above embodiments R¹ and R⁵ are as described above.

Some of the compounds of the present invention may be prepared by the acid catalyzed decomposition of a diazo compound of formula II:



wherein R¹¹ and R¹² are independently selected from the group consisting of a C₁₋₆ alkyl radical and a C₆₋₁₀ aryl radical, preferably a C₁₋₄ alkyl radical or a benzyl radical.

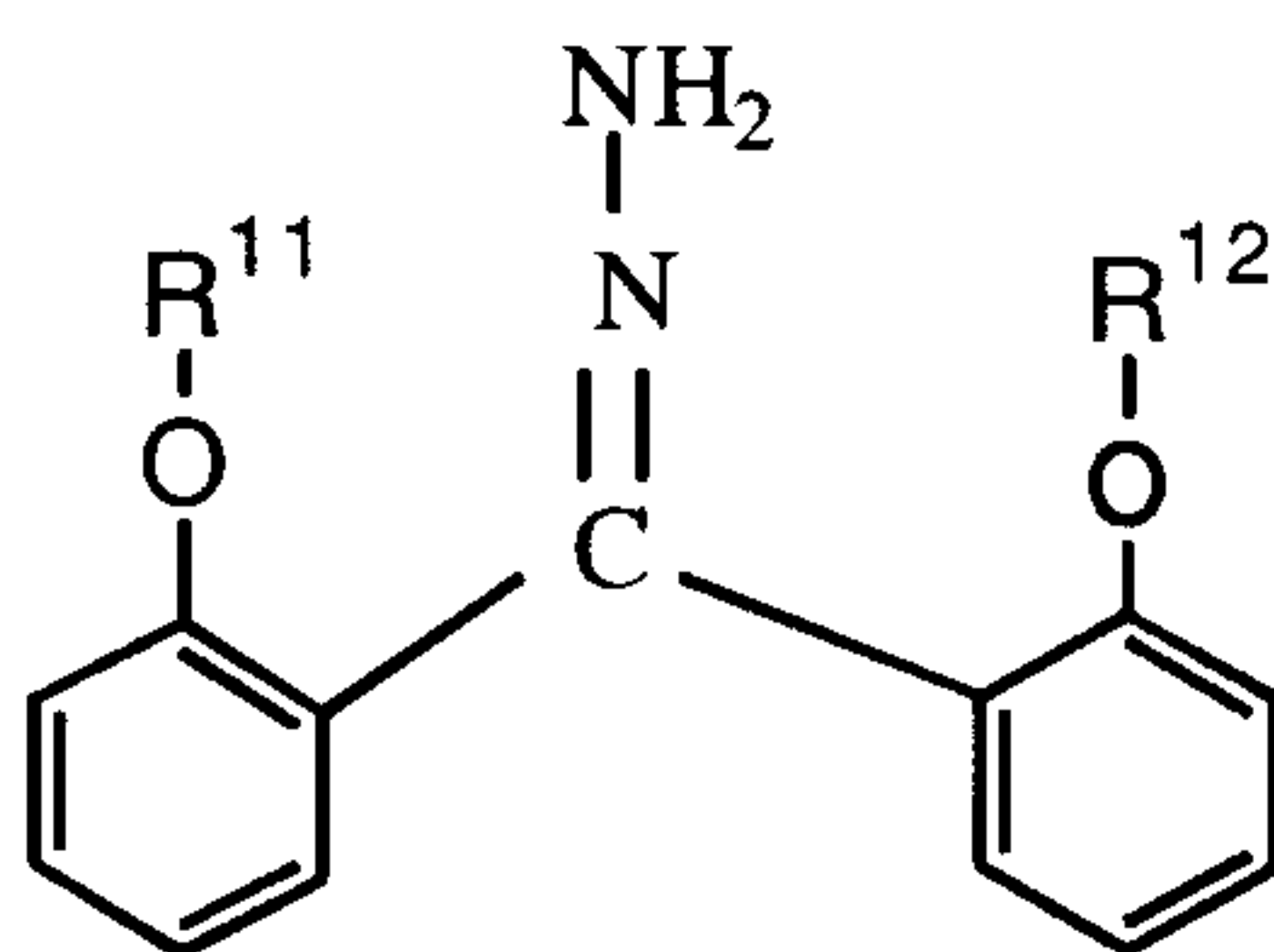
In one embodiment of the present invention, R¹¹ and R¹² are the same and are C₁₋₆, most preferably C₁₋₄ alkyl radicals, preferably methyl radicals (a symmetrically substituted compound). In another embodiment of the invention, R¹¹ is a C₁₋₆, most preferably a C₁₋₄ alkyl radical, preferably a methyl radical; and R¹² is a C₆₋₁₀ benzylic radical, preferably benzyl (i.e. an unsymmetrically substituted compound).

A suitable acid is anhydrous p-toluene sulphonic acid. The reaction is carried out at low temperatures, typically less than 25°C, in the absence of light or heat. In the case where R^{11} and R^{12} are the same and an alkyl radical, the resulting product is 2,2',2'',2'''-(tetraalkoxy)tetraphenylethylene. Preferably, the alkyl substituent is a C_{1-4} alkyl radical, most preferably methyl. In the case where R^{11} is an alkyl radical and R^{12} is a benzyl radical, the resulting product is a mixture of E and Z - 1,2-di(2'-benzyloxyphenyl)-1,2-di(2'-methoxyphenyl)ethylene.

In a further embodiment of the invention the mixture of unsymmetrically substituted E and Z - 1,2-di(2'-benzyloxyphenyl)-1,2-di(2'-methoxyphenyl)ethylene compounds may further be catalytically hydrogenolyzed at the benzyloxy substituents to produce separable E and Z - 1,2-di(2'-hydroxyphenyl)-1,2-di(2'-methoxyphenyl)ethylene compounds (i.e. the compounds of formula I wherein two R^1 substituents at opposite ends of the central ethylene moiety are hydroxyl radicals and two R^1 substituents at opposite ends of the central ethylene moiety are methoxy radicals).

The hydrogenolysis may be carried out in the presence of hydrogen under moderate pressure, from about 100 to 1000, preferably from about 300 to 600 psi (689.5×10^3 kPa to 6.895×10^3 kPa, preferably from about 2.068×10^3 kPa to 20.685×10^3 kPa).

The diazo starting material may be prepared by the oxidation of a compound of formula III:

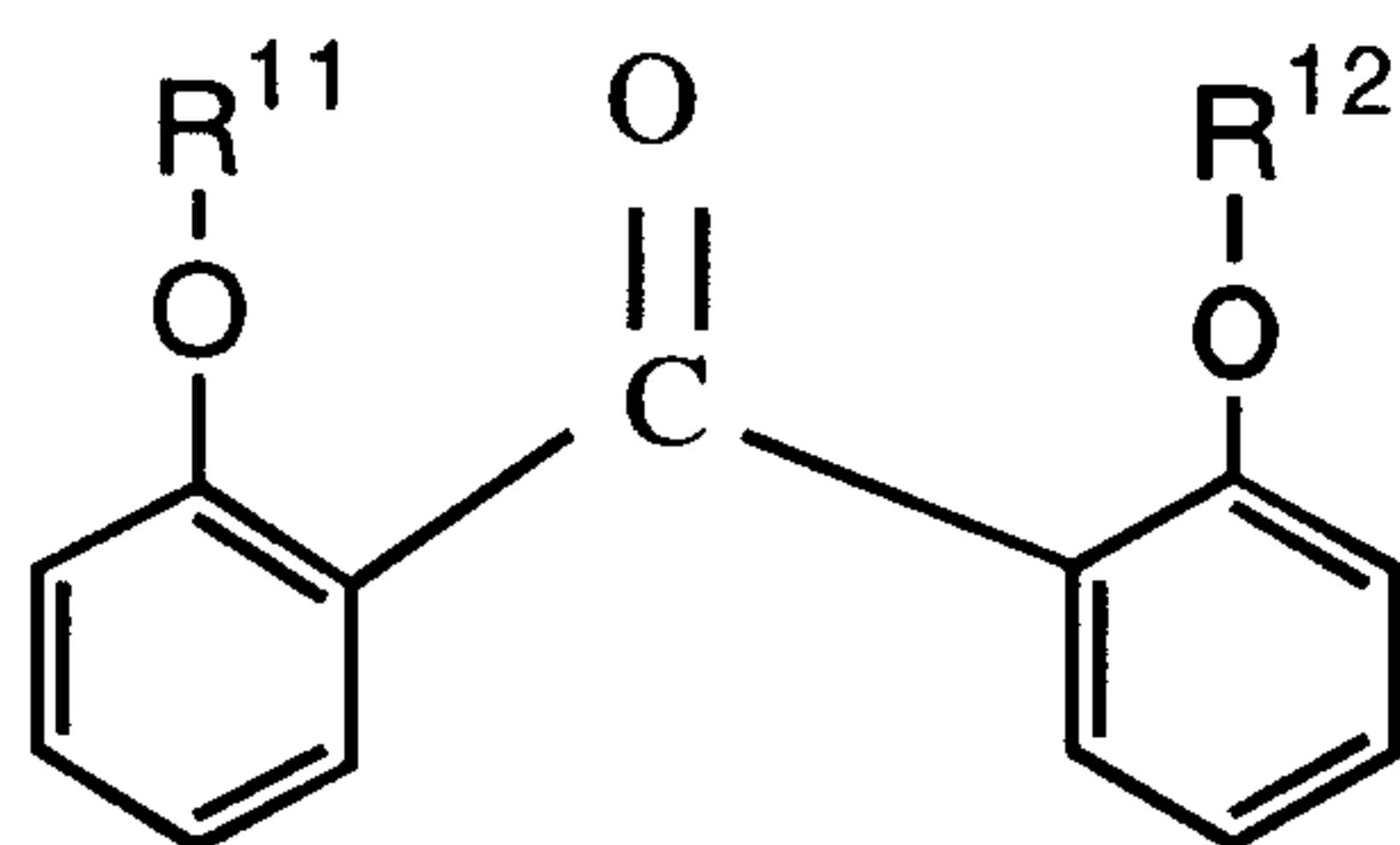


(III)

wherein R^{11} and R^{12} are as defined in formula II. If R^{11} and R^{12} are the same and a C_{1-6} alkyl radical, the compound (formula III), is a 2,2'- C_{1-6} alkoxybenzophenone hydrazone or a 2,2'- C_{1-6} alkoxy benzhydrylidene-hydrazine. If R^{11} is a C_{1-6} alkoxy radical and R^{12} is a benzyl radical the compound is a 2-benzyloxy-2'-alkoxybenzophenone hydrazone or a 2-benzyloxy-2'-alkoxybenzhydrylidene-hydrazine. As noted above, preferably the alkyl radical is a methyl radical and if present the benzyl radical is unsubstituted. Preferred starting materials are 2,2'-dimethoxybenzophenone hydrazone or 2,2'-dimethoxybenzhydrylidene-hydrazine, and 2-benzyloxy-2-methoxybenzophenone hydrazone or 2-benzyloxy-2-methoxybenzhydrylidene-hydrazine.

The oxidation may be carried out in the presence of nickel peroxide. Care must be taken with this oxidation. The reaction should be carried out at low temperatures, preferably 0°C or less (e.g. an ice-salt bath) and the reaction should be protected from light which will decompose the diazo product.

The compound of formula III may be prepared by the reaction of a compound of formula IV:



(IV)

wherein R^{11} and R^{12} are as defined above with hydrazine monohydrate (at
 10 high temperature).

For the symmetrically substituted compounds the starting 2,2'-
 dialkoxy benzophenone may be prepared by metallation of anisole with
 n-butyllithium in a suitable solvent such as
 diethylether/tetramethylethylenediamine and subsequent quenching with
 N,N-dimethylcarbonyl chloride or by methylation of commercially
 available 2,2'-dihydroxybenzophenone using excess methyl iodide and
 20 sodium hydroxide in a highly polar organic solvent (e.g. dimethyl sulfoxide
 (DMSO)).

For the unsymmetrically substituted compounds, the symmetrically
 substituted alkoxy compound is prepared and one of the alkoxy groups is
 converted to an unsymmetrically substituted 2-hydroxy-2'-
 methoxybenzophenone in the presence of boron trichloride at a
 30 temperature from -65°C to 25°C . The resulting 2-hydroxy-2'-
 methoxybenzophenone is then benzylated using benzyl bromide in the
 presence of potassium carbonate to yield 2-benzyloxy-2'-
 methoxybenzophenone. Alternative reaction routes would be known or
 derivable to those skilled in the art.

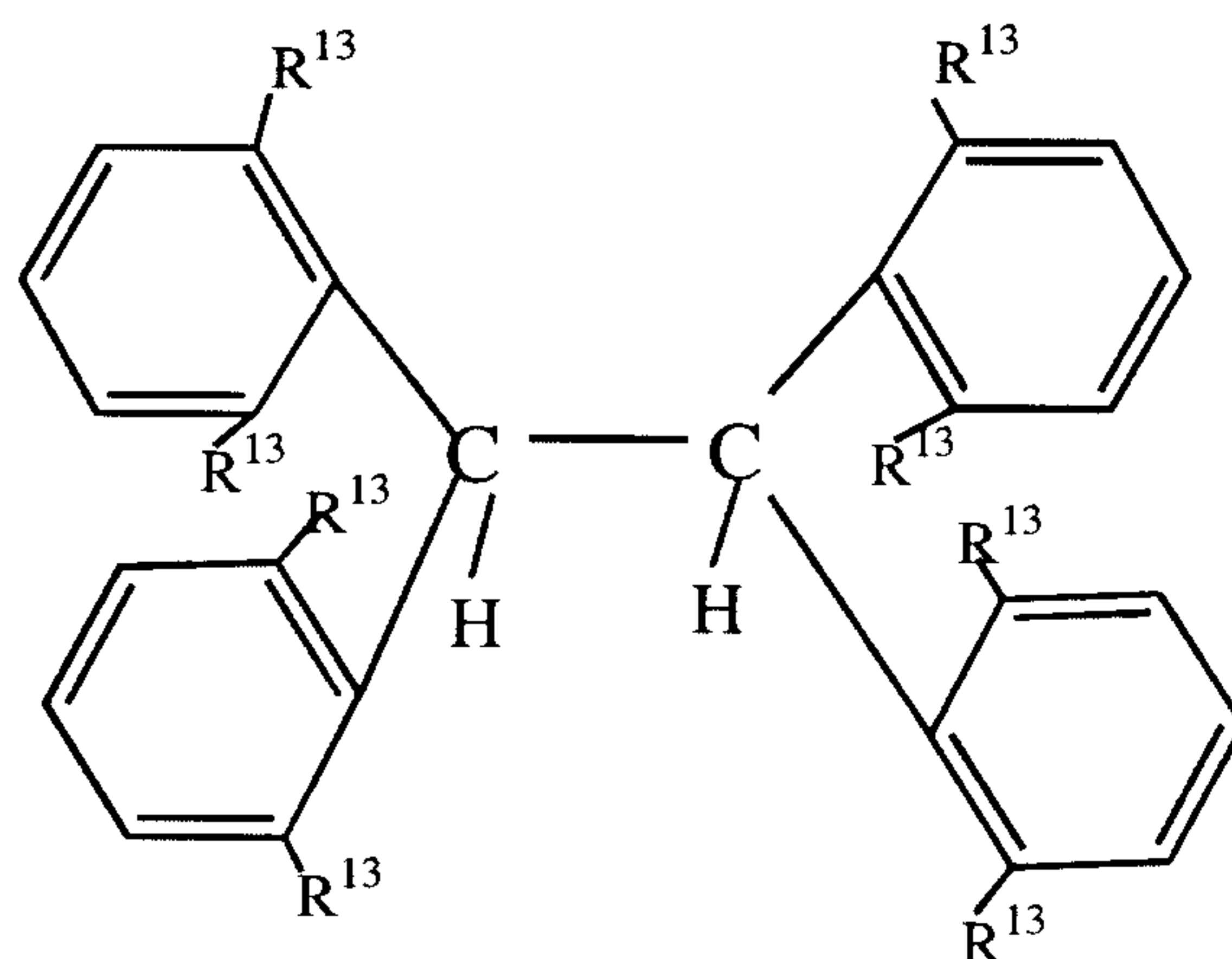
Once the 2,2',2'',2'''-(tetraalkoxy)tetraphenylethylene is prepared, the alkoxy groups may be de-alkylated to the tetra hydroxyl derivative. For example, 2,2',2'',2'''-(tetramethoxy)tetraphenylethylene may be demethylated using boron tribromide at low temperatures to produce the tetra hydroxyl derivative. Additionally, the 2,2',2'',2'''-(tetrahydroxy)tetraphenylethylene may be further treated, for example, with compounds such as anhydrides of C₁₋₆ carboxylic acids such as acetic anhydride in pyridine to produce 2,2',2'',2'''-(tetraacetoxyl)tetraphenylethylene and with trifluoromethanesulfonic anhydride to produce 2,2',2'',2'''-tetrakis(trifluorosulfonyloxy)tetraphenylethylene.

The 2,2',2'',2'''-(tetrahydroxy)tetraphenylethylene may also be reacted with a C₃₋₂₀, preferably a C₃₋₆ allylating agent such as a 1-halo C₃₋₂₀, preferably a C₃₋₆ allyl compound. The resulting 2,2',2'',2'''-tetra C₃₋₂₀, preferably C₃₋₆ allyloxy tetraphenylethylene may then be heated to cause a Claisen rearrangement resulting in a 2,2',2'',2'''-tetrahydroxy-3,3',3'',3'''-tetra C₃₋₂₀, preferably C₃₋₆, allyl tetraphenylethylene which may then be hydrogenated as described above to yield a 2,2',2'',2'''-tetrahydroxy-3,3',3'',3'''-tetra C₃₋₃₀, preferably C₃₋₆ alkyl tetraphenylethylene. The simplest allylating agent is allylbromide (1-bromo-2-propene) yielding sequentially as described above 2,2',2'',2'''-tetra(allyloxy)tetraphenylethylene (or 2,2',2'',2'''-tetra(2-propenyloxy)tetraphenylethylene); 2,2',2'',2'''-tetrahydroxy-3,3',3'',3'''-tetra(allyl)tetraphenylethylene (or 2,2',2'',2'''-tetrahydroxy-3,3',3'',3'''-tetra(2-

propenyl)tetraphenylethylene); and 2,2',2'',2'''-tetrahydroxy-3,3',3'',3'''-tetra(n-propyl)tetraphenylethylene, respectively.

Other reaction schemes and methods of altering the substituents are well known to those skilled in the art. For example, the hydroxy derivative could be esterified using common acid chlorides and anhydrides or phosphorylated using common chlorophosphines (ClPR^n_2) or chlorophosphates ($\text{ClP}(\text{O})\text{R}^n_2$). Further, the trifluorosulphenylate derivative may be transformed using palladium catalyzed substitution using appropriate carbon, nitrogen, phosphorus and oxygen nucleophiles.

In a further embodiment of the present invention the 2,2',2'',2''',6,6',6'',6'''-octa C_{1-6} alkoxy tetraphenylethylene (also tetrakis(2,6-di C_{1-6} alkoxyphenyl)ethylene) compound may be prepared by the controlled oxidation of a compound of formula V:



(V)

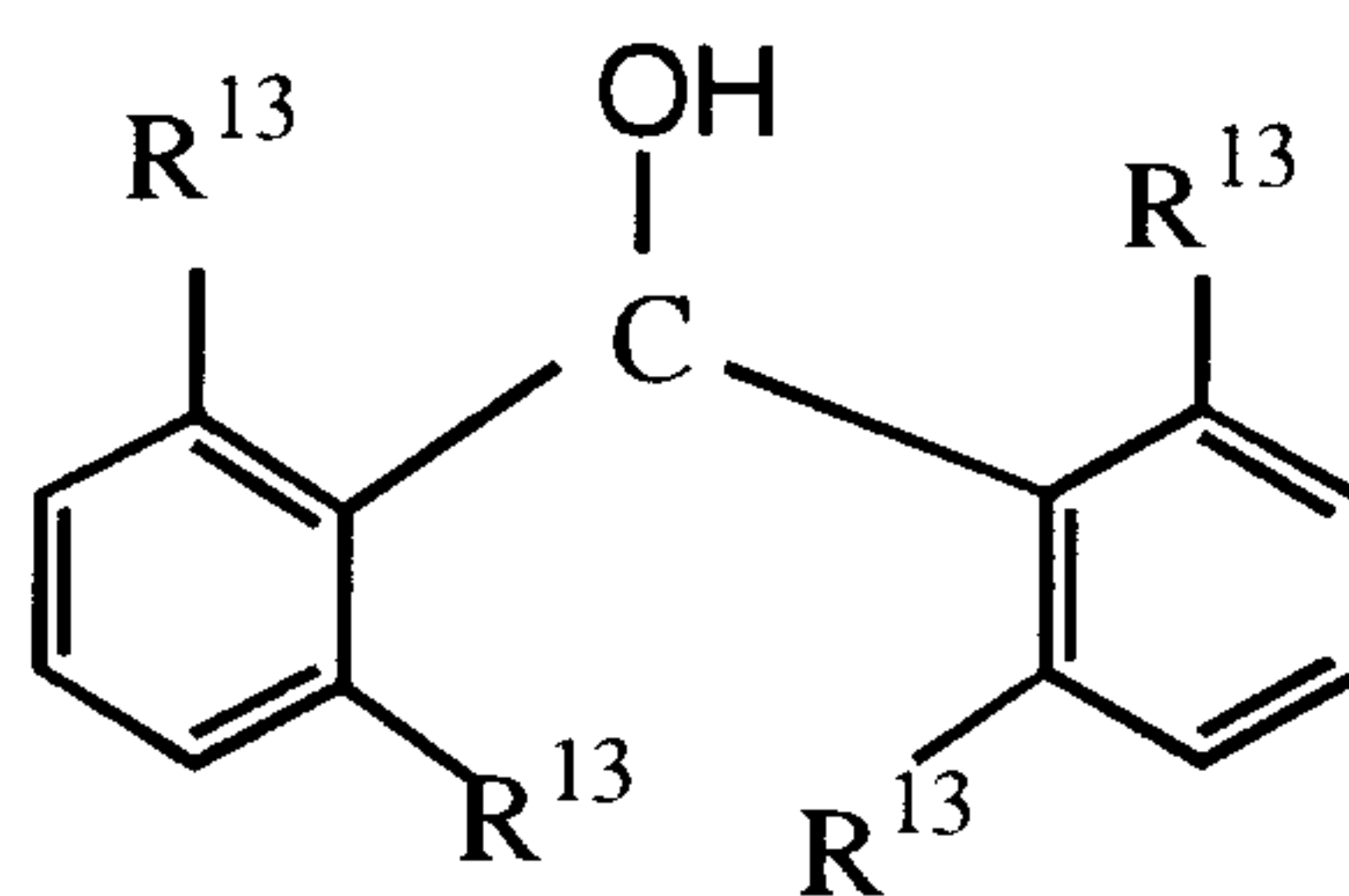
(2,2',2'',2''',6,6',6'',6'''-octa C_{1-6} alkoxy tetraphenylethane (also tetrakis(2,6-di C_{1-6} alkoxyphenyl)ethane) wherein R^{13} is a C_{1-6} , preferably a C_{1-4} alkoxy radical, most preferably methoxy or ethoxy. Most preferably all R^{13} radicals are the same. One method for the controlled oxidation of the compound is by reaction with triphenylmethylhexafluorophosphate in an

inert solvent such as dichloromethane. The reaction may be carried out at temperatures from 0°C to 25°C.

The resulting 2,2',2'',2''',6,6',6'',6'''-octa C₁₋₆ alkoxy tetraphenylethylene (also tetrakis(2,6-di C₁₋₆ alkoxyphenyl)ethylene) compounds may then be subjected to dealkylation to yield 2,2',2'',2''',6,6',6'',6'''-octahydroxyphenylethylene. The dealkylation has been described above. One method for dealkylation is to treat the 2,2',2'',2''',6,6',6'',6'''-octa C₁₋₆ alkoxy tetraphenylethylene (also tetrakis(2,6-di C₁₋₆ alkoxyphenyl)ethylene) compound with boron tribromide at temperatures from 0°C to 25°C.

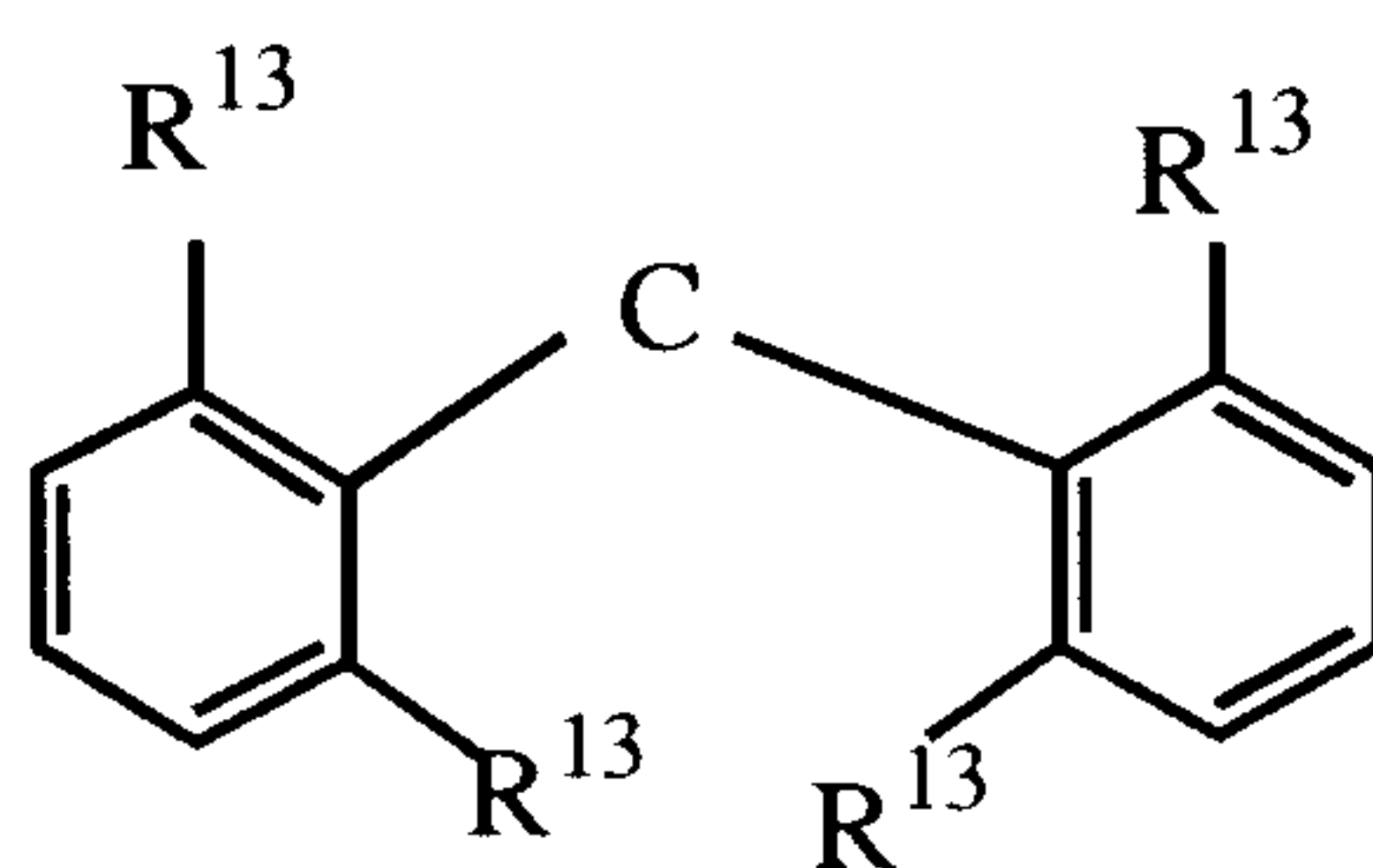
The resulting 2,2',2'',2''',6,6',6'',6'''-octahydroxyphenylethylene compound may be treated as described above (for example acetoxylation or allylated and subsequently subjected to a rearrangement reaction) to yield further derivatives as described above.

The compounds of formula V (2,2',2'',2''',6,6',6'',6'''-octa C₁₋₆ alkoxy tetraphenylethane (also tetrakis(2,6-di C₁₋₆ alkoxyphenyl)ethane) may be prepared by the radical coupling of a compound of formula VI:



(VI)

(bis(2,6-di C₁₋₆ alkoxyphenyl)methanol) wherein R¹³ is as defined above with a compound of formula VII:

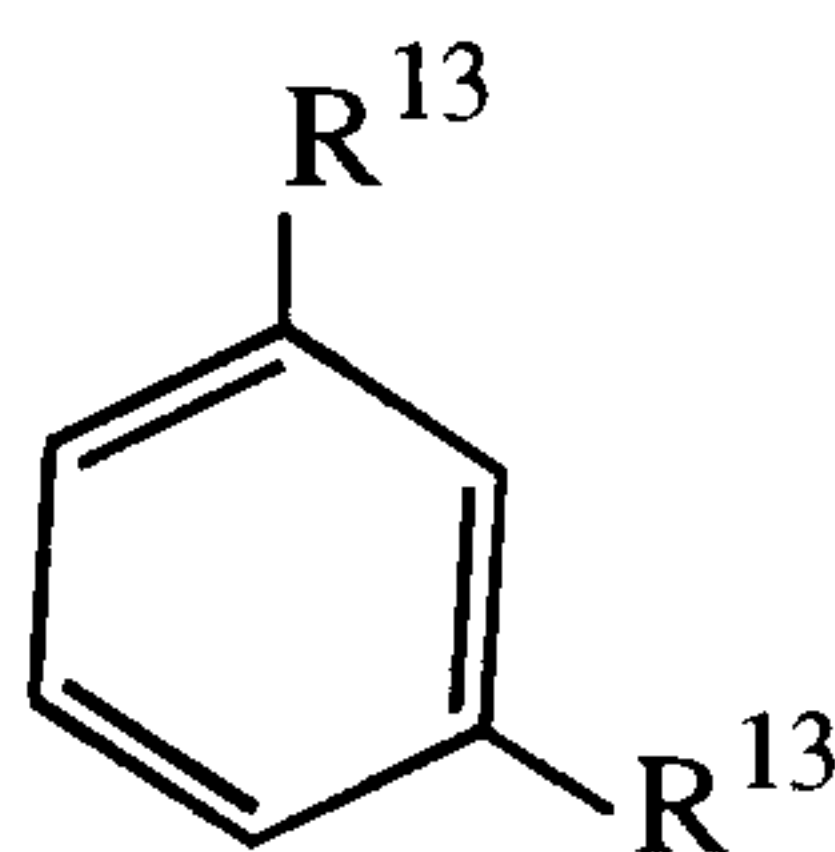


(VII)

10 (bis(2,6-di C₁₋₄ alkoxyphenyl)methane) wherein R¹³ is as defined above, in an inert solvent in the presence of p-toluene sulphonic acid.

A second method for generation of 1,1,2,2-tetrakis(2',6'-di C₁₋₆ alkoxyphenyl)ethane is by the reductive radical dimerization of compound (VI) using chromous chloride and hydrochloric acid in acetone solution. The products of these two coupling methods are rotational isomers, each with distinct chemical reactivity.

20 The compounds of formula VI may be prepared by metallation of a compound of formula VIII:



(VIII)

30 wherein R¹³ is as defined above with n-butyllithium in an inert solvent, preferably diethyl ether/tetramethylenediamine solution, followed by quenching with ethyl formate.

The compounds of formula VII above may be prepared by reducing the compounds of formula VI above for example by treatment with

stoichiometric amounts of p-toluenesulfonic acid in a mixture of acetonitrile and tetrahydrofuran.

The present invention will now be illustrated by the following non-limiting examples in which unless otherwise indicated parts means parts by weight (e.g. grams) and per cent means weight per cent.

Starting Hydrazone

10 A stirred suspension of 2,2'-dimethoxybenzophenone (20.72 g, 0.0855 mol) and 20 mL (0.412 mol) of hydrazine monohydrate in 25 mL of 1-butanol was heated to reflux overnight. After cooling to room temperature the two phase reaction mixture was poured into water and cooled to induce crystallization. The white precipitate was filtered, washed with water and petroleum ether and dried *in vacuo* to yield 2,2'-dimethoxybenzophenone hydrazone (**1**).

20

Example 1 - 2,2',2'',2'''-(tetramethoxy)tetraphenylethylene

To a solution of **1** (5.12 g, 0.020 mol) in 200 mL of anhydrous acetonitrile cooled to 0°C and protected from light was added in one portion and excess of nickel peroxide (12.7 g). The nickel peroxide was prepared as described in J. Org. Chem., 1962, 27, 1597. The mixture was stirred for one hour at 0°C and then filtered through basic alumina (Activity 30 I) to remove the nickel residues. After rinsing the alumina with acetonitrile the intense pink-red filtrate was cooled to 0°C and treated with one drop of a benzene solution of p-toluene sulfonic acid (3.6 g of p-toluene sulfonic acid in 39 mL of anhydrous benzene). Over about one hour a white precipitate slowly separates from the light yellow reaction mixture. The

precipitate was filtered and washed to yield 2,2',2'',2'''-(tetramethoxy)tetraphenylethylene (**2**).

Example 2 Demethylation of **2**

10 A suspension of **2** (0.466 g, 1.03 mmol) in 30 mL of anhydrous dichloromethane cooled to -65°C was treated with boron tribromide (0.7 mL, 7.04 mmol). The solids dissolved immediately and the purple solution warmed to room temperature and was stirred overnight. The reaction mixture was pored into cold saturated aqueous sodium bicarbonate and diluted with diethyl ether. The organic phase was washed with water and a saturated salt solution, dried over sodium sulfate, concentrated *in vacuo* and purified by recrystallization from diethyl ether to yield 2,2',2'',2'''-(tetrahydroxy)tetraphenylethylene (**3**).

20 Example 3 - Treatment of **3** with Acetic Anhydride

A suspension of **3** (0.50 g, 0.126 mmol) was treated with 1 mL of acetic anhydride and anhydrous pyridine at room temperature. The solids dissolved within a few minutes and after about 20 minutes the reaction mixture was diluted with 10 mL of dichloromethane and washed successively with water, 1N hydrochloric acid, saturated aqueous bicarbonate and saturated salt. The organic phase was dried over sodium sulfate and the volatiles removed *in vacuo* to yield the crude product, 30 which was subsequently purified by recrystallization from acetone to yield 2,2',2'',2'''-(tetraacetoxy)tetraphenylethylene (**4**) quantitatively.

Example 4 - Treatment of **3** with Trifluoromethanesulfonic Anhydride

To a mixture of **3** (4.30 g, 0.018 mmol) and 24 mL of anhydrous pyridine at 0°C under a nitrogen atmosphere was added dropwise via

syringe trifluoromethanesulphonic anhydride (15.5 g, 0.055 mol). The dark brown reaction mixture was warmed to room temperature and was stirred for 24 hours. The reaction was quenched by the addition of 60 mL of water. The crude mixture was repeatedly extracted with diethyl ether and the combined extracts washed sequentially with water, 10% aqueous HCl and saturated salt. The combined aqueous phases were back extracted with several portions of diethyl ether and the combined organic phases were dried over magnesium sulphate, filtered and evaporated to dryness. The yellow residue was purified by recrystallization from acetone or from acetone and acetonitrile to yield 2,2',2'',2'''-tetrakis(trifluoromethylsulfonyloxy)tetraphenylethylene (**5**) quantitatively.

Example 5 - Preparation of 2,2',2'',2''',6,6',6'',6'''-

octahydroxytetraphenylethylene (6**)**

A. Bis(2,6-dimethoxyphenyl)methanol (2**)**

To a solution of 1,3-dimethoxybenzene (19.5 mL, 0.150 mol) in diethyl ether at -78°C was added n-butyllithium (94 mL of a 1.6 M solution in hexanes) and dried N,N,N',N'-tetramethylethylenediamine (2.25 mL, 0.015 mol). The mixture was warmed gradually to room temperature over 2 hours and then re-cooled to -78°C . Ethyl formate (6.2 mL, 0.075 mol) was added slowly via syringe, after which the solution was warmed to room temperature and stirred for 15 hours. The reaction was quenched by the addition of water (40 mL) and 10% aqueous hydrochloric acid, giving a white solid which was collected by filtration and washed with water and ether to give pure bis(2,6-dimethoxyphenyl)methanol.

B. Bis(2,6-dimethoxyphenyl)methane (3)

To a solution of bis(2,6-dimethoxyphenyl)methanol (4.37 g, 0.014 mol) in acetonitrile (50 mL) and tetrahydrofuran (65 mL) was added p-toluenesulfonic acid monohydrate (2.73 g, 0.014 mol) at 0°C. The resulting solution was warmed to room temperature and stirred for 17 hours, after which water (60 mL) was added and the solvent removed under reduced pressure. The residue was extracted with diethyl ether and the combined extracts dried over anhydrous magnesium sulfate. Removal of the solvent *in vacuo* gave bis(2,6-dimethoxyphenyl)methane.

C(a). 1,1,2,2-tetrakis(2',6'-dimethoxyphenyl)ethane (4)

To a solution of bis(2,6-dimethoxyphenyl)methanol (1.52 g, 0.005 mol) in acetonitrile (50 mL) at room temperature was added p-toluenesulfonic acid monohydrate (0.95 g, 0.005 mol). To the resulting deep red solution was added bis(2,6-dimethoxyphenyl)methane (1.44 g, 0.005 mol). The reaction mixture decolorized within about one hour and was stirred for an additional 17 hours. The reaction was quenched by the addition of water (10 mL), extracted with dichloromethane and dried over anhydrous magnesium sulfate. Evaporation of the solvent and hot filtration using hexane/benzene gave 1,1,2,2-tetrakis(2',6'-dimethoxyphenyl)ethane as a mixture of rotational isomers after evaporation of the solvents and washing with diethyl ether.

C(b). 1,1,2,2-tetrakis(2',6'-dimethoxyphenyl)ethane (4)

To a suspension of commercial CrCl_2 (1.69 g, 13.75 mmol) in acetone (25.0 mL) and aqueous HCl (36%, 12.5 mL) was added bis(2,6-dimethoxyphenyl)methanol (1.52 g, 5 mol) at 0°C. The resulting mixture

was stirred and warmed to room temperature. After 3 hours, water (20 mL) was added and the mixture was extracted with dichloromethane. The combined organic phases were dried over MgSO_4 and concentrated to deposit 1,1,2,2-tetrakis(2',6'-dimethoxyphenyl)ethane as a white solid single rotational isomer.

D. Tetrakis(2,6-dimethoxyphenyl)ethylene (5)

10 To a solution of commercial triphenylmethylhexafluorophosphate (0.69 g, 1.8 mmol) in dichloromethane at room temperature was added a rotational isomer of 1,1,2,2-tetrakis(2',6'-dimethoxyphenyl)ethane (0.90 g, 1.5 mmol). After stirring for 18 hours, water (10 mL) was added and the resulting mixture was extracted with dichloromethane and dried over anhydrous magnesium sulfate. Filtration and removal of the solvent gave tetrakis(2,6-dimethoxyphenyl)ethylene after washing with diethyl ether.

20 {Note: Only one of the rotational isomers gives (5) upon treatment with trityl cation.}

E. 2,2',2'',2''',6,6',6'',6'''-octahydroxytetraphenylethylene [tetrakis(2,6-dihydroxyphenyl)ethylene] (6)

A solution of tetrakis(2,6-dimethoxyphenyl)ethylene (0.45 g, 0.8 mmol) in dichloromethane cooled to -78°C was treated with boron tribromide (1.0 mL, 10 mmol). The resulting solution was warmed to room temperature and stirred for 16 hours, after which the reaction mixture was poured into ice-cold saturated aqueous sodium bicarbonate. This mixture was extracted with ethyl acetate and the combined extracts dried over anhydrous magnesium sulfate. Removal of the solvent and washing with diethyl ether gave 2,2',2'',2''',6,6',6'',6'''-octahydroxytetraphenylethylene.

30

Example 6 - New Derivatives of the 2,2',2'',2'''-tetrahydroxytetraphenylethylene

A. 2,2',2'',2'''-tetra(allyloxy)tetraphenylethylene (8)

10 A solution of 2,2',2'',2'''-tetrahydroxytetraphenylethylene (**7**) (0.110 g, 0.277 mmol) and potassium carbonate (0.762 g, 5.51 mmol) in 8.5 mL of acetone was heated to reflux for 16 hours under a nitrogen atmosphere. After removal of the volatiles *in vacuo*, the residue was redissolved in 50 mL of water and extracted with 50 mL of dichloromethane. The organic layer was washed with water and brine and then dried over sodium sulfate, filtered, and the solvent was evaporated. The residue was recrystallized from dichloromethane-diethyl ether to give 2,2',2'',2'''-tetra(allyloxy)tetraphenylethylene.

20 B. 2,2',2'',2'''-tetrahydroxy-3,3',3'',3'''-tetra(allyl)tetraphenylethylene (9)

A solution of 2,2',2'',2'''-tetra(allyloxy)tetraphenylethylene (**8**) (0.085 g, 0.153 mmol) in 2 mL of mesitylene was degassed in a thick-walled glass vessel fitted with a teflon high vacuum stopcock. After backfilling with nitrogen, the vessel was sealed and heated to 200°C for 14 hours. After removing the solvent under vacuum, a white solid was obtained from the oily residue by addition of hexanes and ultrasonification. After removal of
30 volatiles, the nearly pure 2,2',2'',2'''-tetrahydroxy-3,3',3'',3'''-tetra(allyl)tetraphenylethylene (**9**) was obtained in quantitative yield and was used without further purification.

C. 2,2',2'',2'''-tetrahydroxy-3,3',3'',3'''-tetra(n-propyl)tetraphenylethylene (10)

A solution of 2,2',2'',2'''-tetrahydroxy-3,3',3'',3'''-tetra(allyl)tetraphenylethylene (**9**) (0.020 g, 0.0359 mmol) in 2 mL of methanol was maintained under 300 psig of hydrogen in the presence of 10% Pd-C catalyst (0.003 g, 0.0028 mmol) for 4 hours at room temperature. After filtration through celite and removal of the volatiles, 2,2',2'',2'''-tetrahydroxy-3,3',3'',3'''-tetra(n-propyl)tetraphenylethylene (**10**) was isolated as a white solid in quantitative yield.

D. 2-hydroxy-2'-methoxybenzophenone (12)

This procedure is based on that reported in Tetrahedron Lett., 1966, 4153. To a solution of 2,2'-dimethoxybenzophenone (**11**) (6.7 g, 0.0277 mol) in anhydrous dichloromethane (95 mL) cooled to -65°C under nitrogen was added 52 mL of a 1.0 M solution of boron trichloride in heptane (0.052 mol). The mixture was allowed to warm to room temperature and stirred for 75 minutes. The reaction mixture was slowly poured into a cold (0°C) solution of saturated aqueous sodium bicarbonate, which was then extracted with dichloromethane. The organic extracts were washed with water and saturated with NaCl, followed by drying over anhydrous sodium sulfate. Analytically pure product was obtained after removal of the solvent in quantitative yield.

E. 2-benzyloxy-2'-methoxybenzophenone (13)

A mixture of 2-hydroxy-2'-methoxybenzophenone (**12**) (8.08 g, 0.0354 mol), potassium carbonate (24.5 g, 0.177 mol) and benzyl bromide (4.4 mL, 0.037 mol) in 90 mL of dimethylsulfoxide was stirred overnight at

room temperature. The resulting reaction mixture was diluted with diethyl ether and water and the aqueous layer was extracted with fresh diethyl ether. The combined organic layers were washed with water, followed by saturated NaCl and dried over sodium sulfate. After purification by flash column chromatography (silica gel, dichloromethane/hexanes eluent), 2-benzyloxy-2'-methoxybenzophenone (13) was obtained as a colorless oil.

10 F. 2-benzyloxy-2'-methoxybenzophenone hydrazone (14)

A stirred suspension 2-benzyloxy-2'-methoxybenzophenone (13) (7.98 g, 0.025 mol) in hydrazine monohydrate (16 mL, 0.328 mol) and 1-butanol (25 mL) was heated to reflux overnight. After cooling to room temperature, the reaction mixture was poured into water saturated with salt and diluted with tetrahydrofuran. The organic phase which forms was separated, washed with water, saturated salt, and evaporated to dryness
20 by rotary evaporation followed by application of high vacuum and mild heating. The resulting oil, 2-benzyloxy-2'-methoxybenzophenone hydrazone (14), which sometimes solidifies, still contains n-butanol and was used without further purification.

G. E and Z – 1,2-di(2'-benzyloxyphenyl)-1,2-di(2'-methoxyphenyl)ethane (15)

30 To a solution of 2-benzyloxy-2'-methoxybenzophenone hydrazone (14) (2.246 g, 6.76 mmol) in anhydrous acetonitrile (80 mL) cooled to 0°C in an ice-salt bath and protected from ambient light using aluminum foil, was added nickel peroxide (5.5 g, excess, prepared as described in J. Org. Chem., 1962, 27, 1597) in one portion. The mixture was stirred for 1 hour at 0°C and then filtered through basic alumina (Activity I) to remove

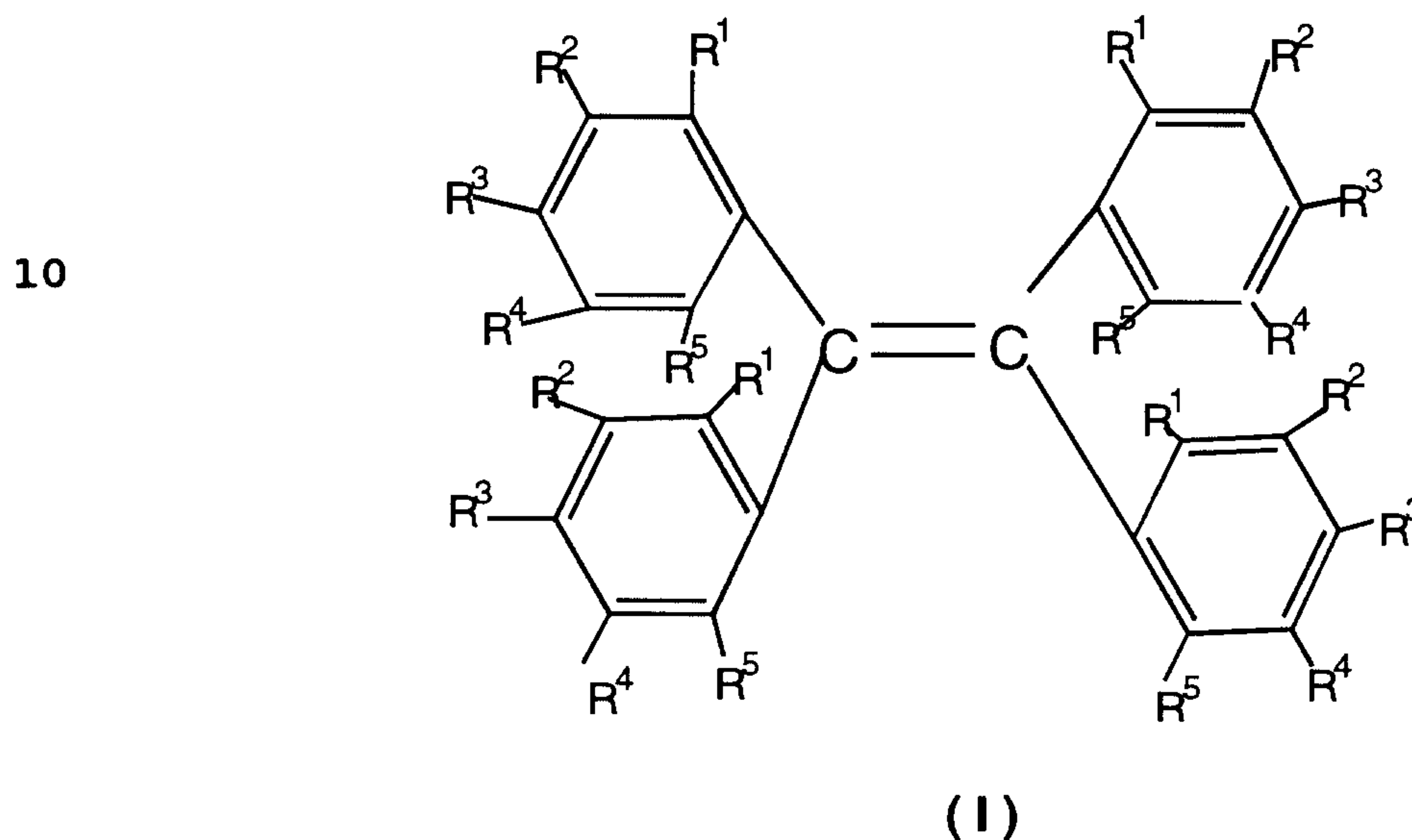
the nickel residues. After rinsing the alumina with additional acetonitrile (80 mL), the intense pink-red filtrate was cooled to 0°C and treated with a few drops of a benzene solution of anhydrous p-toluenesulfonic acid (prepared from 3.6 g anhydrous p-toluenesulfonic acid in 39 mL anhydrous benzene). The color immediately changed to yellow-brown. The acid was neutralized by the addition of a few drops of concentrated aqueous potassium hydroxide and the volatiles removed under reduced pressure. The residue was purified by flash chromatography on silica gel (dichloromethane/hexanes eluent) to give a mixture of E and Z - 1,2-di(2'-benzyloxyphenyl)-1,2-di(2'-methoxyphenyl)ethane (**15**) as a white solid.

H. E and Z - 1,2-di(2'-hydroxyphenyl)-1,2-di(2'-methoxyphenyl)ethylene (**16**)

A solution of E and Z - 1,2-di(2'-benzyloxyphenyl)-1,2-di(2'-methoxyphenyl)ethane (**15**) (0.020 g, 0.033 mmol) and 10% palladium on carbon (0.002 g, 0.002 mmol) in ethyl acetate (0.4 mL) and methanol (1.5 mL) was pressurized under hydrogen (610 psig) at room temperature for 18 hours. The resulting mixture was filtered through celite and the volatiles removed under reduced pressure. The oily solid that results solidifies to a white solid mixture of separable E and Z - 1,2-di(2'-hydroxyphenyl)-1,2-di(2'-methoxyphenyl)ethylene (**16**) after ultrasonification in hexanes and is isolated in quantitative yield.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A compound of formula I:



20 wherein at least two R^1 are the same and not a hydrogen atom; and R^1 , R^2 , R^3 , R^4 and R^5 are independently selected from the group consisting of a hydrogen atom; a halogen atom; a hydroxyl radical; a C_{1-20} alkyl radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; a C_{3-20} allyl radical; a C_{1-20} alkoxy radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; a C_{3-20} allyloxy radical; a carbalkoxy radical of the formula $-\text{COOR}^{20}$ wherein R^{20} is a hydrogen atom or a C_{1-20} alkyl radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; a carboxylate radical of the formula $-\text{OCOR}^{30}$ wherein R^{30} is a

30

C_{1-20} alkyl radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; a C_{6-10} aryl radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; a C_{6-10} aryloxy radical or a C_{7-11} benzyloxy radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; an acyl R^6CO- radical wherein R^6 is a C_{1-20} alkyl radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; and an amido radical which is unsubstituted or substituted by up to two C_{1-20} alkyl radicals; a $(-O-)_n-P(R^7)_2$ radical wherein each R^7 is independently selected from the group consisting of a C_{1-20} alkyl radical, a C_{1-20} alkoxy radical, a C_{6-10} aryl radical and n is 0 or 1; a $(-O-)_n-PO(R^8)_2$ radical wherein each R^8 is independently selected from the group consisting of a C_{1-20} alkyl radical, a C_{1-20} alkoxy radical, a C_{6-10} aryl radical and n is 0 or 1; a $-Si(R^9)_3$ radical wherein each R^9 is independently selected from the group consisting of a C_{1-20} alkyl radical, a C_{6-10} aryl radical, a hydrogen radical and an alkoxy radical; a trifluoromethanesulfonyloxy radical; or two or more of adjacent substituents R^2 , R^3 , R^4 and R^5 may be taken together to form a fused ring.

2. The compound according to claim 1, wherein R^1 is selected from the group consisting of a hydroxyl radical; a C_{1-6} alkoxy radical; a C_{6-10}

aryloxy radical; a C₃₋₆ allyloxy radical; a C₇₋₁₁ benzyloxy radical; a
 carboxylate radical of the formula –OCOR³⁰ wherein R³⁰ is a hydrogen
 atom or a C₁₋₆ alkyl radical; a carbalkoxy radical of the formula –COOR²⁰
 wherein R²⁰ is a hydrogen atom or a C₁₋₆ alkyl radical; a (–O–)_n–P(R⁷)₂
 radical wherein each R⁷ is independently selected from the group
 consisting of a C₁₋₆ alkyl radical, a C₁₋₆ alkoxy radical, a C₆₋₁₀ aryl radical
 10 and n is 0 or 1; and a trifluoromethanesulfonyloxy radical.

3. The compound according to claim 2, wherein two or more R¹
 substituents are hydroxyl radicals.

4. The compound according to claim 3, wherein two or more R²
 substituents are allyl radicals.

20

5. The compound according to claim 3, wherein two or more R²
 substituents are propyl radicals.

6. The compound according to claim 2, wherein two or more R¹
 substituents are C₁₋₆ alkoxy radicals.

30

7. The compound according to claim 2, wherein two or more R¹
 substituents are C₆₋₁₀ aryloxy radicals.

8. The compound according to claim 2, wherein two or more R¹
 substituents are C₃₋₆ allyloxy radicals.

9. The compound according to claim 2, wherein two or more R^1 substituents are benzyloxy radicals.

10. The compound according to claim 2, wherein two or more R^1 substituents are carboxylate radicals of the formula $-OCOR^{30}$ wherein R^{30} is a hydrogen atom or a C_{1-6} alkyl radical.

10

11. The compound according to claim 2, wherein two or more R^1 substituents are carbalkoxy radicals of the formula $-COOR^{20}$ wherein R^{20} is a hydrogen atom or a C_{1-6} alkyl radical.

12. The compound according to claim 2, wherein two or more R^1 substituents are $(-O-)_n-P(R^7)_2$ radicals wherein each R^7 is independently selected from the group consisting of a C_{1-6} alkyl radical, a C_{1-6} alkoxy radical, a C_{6-10} aryl radical and n is 0 or 1.

20

13. The compound according to claim 2, wherein two or more R^1 substituents are trifluoromethanesulfonyloxy radicals.

14. The compound according to claim 2, wherein R^2 , R^3 , R^4 and R^5 are independently selected from the group consisting of a hydrogen atom; a halogen atom; a hydroxyl radical; a C_{1-6} alkyl radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom; a hydroxyl radical or a carboxyl radical; a

30

C_{3-6} allyl radical; a C_{1-6} alkoxy radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; a C_{3-6} allyloxy radical; a carbalkoxy radical of the formula $-COOR^{20}$ wherein R^{20} is a hydrogen atom or a C_{1-6} alkyl radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; a carboxylate radical of the formula $-OCOR^{30}$ wherein R^{30} is a C_{1-6} alkyl radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; a C_{6-10} aryl radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; a C_{6-10} aryloxy radical or a C_{7-11} benzyloxy radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; an acyl R^6CO- radical wherein R^6 is a C_{1-6} alkyl radical which is unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, a hydroxyl radical or a carboxyl radical; an amido radical which is unsubstituted or substituted by up to two C_{1-6} alkyl radicals; a $(-O-)_n-P(R^7)_2$ radical wherein each R^7 is independently selected from the group consisting of a C_{1-6} alkyl radical, a C_{1-6} alkoxy radical, a C_{6-10} aryl radical or n is 0 or 1; a $(-O-)_n-PO(R^8)_2$ radical wherein each R^8 is selected from the group consisting of a C_{1-6} alkyl radical, a C_{1-6} alkoxy radical, a C_{6-10} aryl radical, and n is 0 or 1; a $-Si(R^9)_3$ radical wherein each R^9 is

independently selected from the group consisting of a C₁₋₆ alkyl radical and a C₆₋₁₀ aryl radical and a trifluoromethanesulfonyloxy radical.

15. The compound according to claim 14, wherein R⁵ is selected from the group consisting of a hydrogen atom; a hydroxyl radical; a C₁₋₆ alkoxy radical; a C₃₋₆ allyloxy radical; a C₆₋₁₀ aryloxy or C₇₋₁₁ benzyloxy radical; a
 10 carboxylate radical of the formula –OCOR³⁰ wherein R³⁰ is a hydrogen atom or a C₁₋₆ alkyl radical; a (–O–)_n–P(R⁷)₂ radical wherein each R⁷ is independently selected from the group consisting of a C₁₋₆ alkyl radical, a C₁₋₆ alkoxy radical, a C₆₋₁₀ aryl radical and n is 0 or 1; and a trifluoromethanesulfonyloxy radical.

16. The compound according to claim 15, wherein two or more R⁵
 20 substituents are the same.

17. The compound according to claim 16, wherein all R⁵ substituents are a hydrogen atom.

18. The compound according to claim 17, wherein two or more R¹
 30 substituents are hydroxyl radicals.

19. The compound according to claim 18, wherein two or more R² substituents are 2-propenyl radicals.

20. The compound according to claim 18, wherein two or more R^2 substituents are propyl radicals.

21. The compound according to claim 19, wherein all four R^1 substituents are hydroxyl radicals and all four R^2 substituents are 2-propenyl radicals.

10

22. The compound according to claim 20, wherein all four R^1 substituents are hydroxyl radicals and all four R^2 radicals are propyl radicals.

23. The compound according to claim 17, wherein two or more R^1 substituents are C_{1-6} alkoxy radicals.

20

24. The compound according to claim 17, wherein two or more R^1 substituents are C_{6-10} aryloxy radicals.

25. The compound according to claim 17, wherein two or more R^1 substituents are benzyloxy radicals.

30

26. The compound according to claim 17, wherein 2 or more R^1 substituents are carboxylate radicals of the formula $-OCOR^{30}$ wherein R^{30} is a hydrogen atom or a C_{1-6} alkyl radical.

27. The compound according to claim 17, wherein two or more R^1 substituents are $(-O-)_n-P(R^7)_2$ radicals wherein each R^7 is independently selected from the group consisting of C_{1-6} alkyl radicals.

28. The compound according to claim 17, wherein two or more R^1 substituents are trifluoromethanesulfonyloxy radicals.

10

29. The compound according to claim 15, wherein two or more R^5 substituents are hydroxyl radicals.

30. The compound according to claim 29, wherein two or more R^1 substituents are hydroxyl radicals.

20

31. The compound according to claim 30, wherein all four R^1 substituents and all four R^5 substituents are hydroxyl radicals.

32. The compound according to claim 29, wherein two or more R^1 substituents are C_{1-6} alkoxy radicals.

30

33. The compound according to claim 29, wherein two or more R^1 substituents are C_{6-10} aryloxy radicals.

34. The compound according to claim 29, wherein two or more R^1 substituents are benzyloxy radicals.

35. The compound according to claim 29, wherein two or more R^1 substituents are $(-O-)_n-P(R^7)_2$ radicals wherein each R^7 is independently selected from the group consisting of C_{1-6} alkyl radicals.

36. The compound according to claim 29, wherein two or more R^1 substituents are trifluoromethanesulfonyloxy radicals.

10

37. The compound according to claim 15, wherein two or more R^5 substituents are C_{1-6} alkoxy radicals.

38. The compound according to claim 37, wherein two or more R^1 substituents are hydroxyl radicals.

20

39. The compound according to claim 37, wherein two or more R^1 substituents are C_{1-6} alkoxy radicals.

40. The compound according to claim 37, wherein two or more R^1 substituents are C_{6-10} aryloxy radicals.

30

41. The compound according to claim 37, wherein two or more R^1 substituents are benzyloxy radicals.

42. The compound according to claim 37, wherein two or more R^1 substituents are $(-O-)_n-P(R^7)_2$ radicals wherein each R^7 is independently selected from the group consisting of C_{1-6} alkyl radicals.

43. The compound according to claim 37, wherein two or more R^1 substituents are trifluoromethanesulfonyloxy radicals.
44. The compound according to claim 15, wherein two or more R^5 substituents are C_{1-6} alkoxy radicals.
- 10 45. The compound according to claim 44, wherein two or more R^1 substituents are hydroxyl radicals.
46. The compound according to claim 44, wherein two or more R^1 substituents are C_{1-6} alkoxy radicals.
- 20 47. The compound according to claim 44, wherein two or more R^1 substituents are C_{6-10} aryloxy radicals.
48. The compound according to claim 44, wherein two or more R^1 substituents are benzyloxy radicals.
49. The compound according to claim 44, wherein two or more R^1 substituents are $(-O-)_n-P(R^7)_2$ radicals wherein each R^7 is independently selected from the group consisting of C_{1-6} alkyl radicals.
- 30 50. The compound according to claim 44, wherein two or more R^1 substituents are trifluoromethanesulfonyloxy radicals.

51. The compound according to claim 15, wherein two or more R^5 substituents are C_{6-10} aryloxy radicals.
52. The compound according to claim 51, wherein two or more R^1 substituents are hydroxyl radicals.
- 10 53. The compound according to claim 51, wherein two or more R^1 substituents are C_{1-6} alkoxy radicals.
54. The compound according to claim 51, wherein two or more R^1 substituents are C_{6-10} aryloxy radicals.
- 20 55. The compound according to claim 51, wherein two or more R^1 substituents are benzyloxy radicals.
56. The compound according to claim 51, wherein two or more R^1 substituents are $(-O-)_n-P(R^7)_2$ radicals wherein each R^7 is independently selected from the group consisting of C_{1-6} alkyl radicals.
- 30 57. The compound according to claim 51, wherein two or more R^1 substituents are trifluoromethanesulfonyloxy radicals.
58. The compound according to claim 15, wherein two or more R^5 substituents are $(-O-)_n-P(R^7)_2$ radicals wherein R^7 is a C_{1-6} alkyl radical.

59. The compound according to claim 57, wherein two or more R^1 substituents are hydroxyl radicals.

60. The compound according to claim 57, wherein two or more R^1 substituents are C_{1-6} alkoxy radicals.

10 61. The compound according to claim 57, wherein two or more R^1 substituents are C_{6-10} aryloxy radicals.

62. The compound according to claim 57, wherein two or more R^1 substituents are benzyloxy radicals.

20 63. The compound according to claim 57, wherein two or more R^1 substituents are $(-O-)_n-P(R^7)_2$ radicals wherein each R^7 is independently selected from the group consisting of a C_{1-6} alkyl radicals.

64. The compound according to claim 57, wherein two or more R^1 substituents are trifluoromethanesulfonyloxy radicals.

30 65. The compound according to claim 15, wherein two or more R^5 substituents are trifluoromethanesulfonyloxy radicals.

66. The compound according to claim 65, wherein two or more R^1 substituents are hydroxyl radicals.

67. The compound according to claim 65, wherein two or more R^1 substituents are C_{1-6} alkoxy radicals.
68. The compound according to claim 65, wherein two or more R^1 substituents are C_{6-10} aryloxy radicals.
- 10 69. The compound according to claim 65, wherein two or more R^1 substituents are benzyloxy radicals.
70. The compound according to claim 65, wherein two or more R^1 substituents are $(-O-)_n-P(R^7)_2$ radicals wherein each R^7 is independently selected from the group consisting of C_{1-6} alkyl radicals.
- 20 71. The compound according to claim 65, wherein two or more R^1 substituents are trifluoromethanesulfonyloxy radicals.
72. The compound according to claim 18, which is 2,2',2'',2'''-(tetrahydroxy)tetraphenylethylene.
- 30 73. The compound according to claim 21, which is 2,2',2'',2'''-tetrahydroxy-3,3',3'',3'''-(2-propenyl)tetraphenylethylene.
74. The compound according to claim 22, which is 2,2',2'',2'''-tetrahydroxy-3,3',3'',3'''-(n-propyl)tetraphenylethylene.

75. The compound according to claim 15, which is 2,2',2'',2'''-(tetraacetoxy)tetraphenylethylene.

76. The compound according to claim 28, which is 2,2',2'',2'''-tetrakis(trifluoromethylsulfonyloxy)tetraphenylethylene.

10 77. A compound according to claim 23, which is 2,2',2'',2'''-(tetramethoxy)tetraphenylethylene.

78. A compound according to claim 31, which is 2,2',2'',2''',6,6',6'',6'''-octahydroxytetraphenylethylene.

20 79. The compound according to claim 39, which is tetrakis(2,6-dimethoxyphenyl)ethylene.

80. The compound according to claim 23, wherein two R¹ substituents are methoxy radicals and two R¹ radicals are benzyloxy radicals.

30 81. The compound according to claim 80 which is selected from the group consisting of E and Z – 1,2-di(2'-benzyloxyphenyl)-1,2-di(2'-methoxyphenyl)ethane and mixtures thereof.

82. The compound according to claim 18, wherein two R¹ substituents are hydroxyl radicals and two R¹ substituents are C₁₋₆ alkoxy radicals.

83. The compound according to claim 82 which is selected from the group consisting of E and Z – 1,2-di(2'-hydroxyphenyl)-1,2-di(2'-methoxyphenyl)ethylene.

84. A process for preparing a 2,2',2'',2'''-tetra C₁₋₆ alkoxy tetraphenylethylene comprising acid catalyzed decomposition of the diazo compound derived from 2,2'-di C₁₋₆ alkoxybenzophenone hydrazone at a temperature of less than 25°C in the absence of light.

85. The process according to claim 84, wherein said acid is anhydrous p-toluene sulphonic acid.

86. The process according to claim 85, wherein said diazo compound derived from 2,2'-di C₁₋₆ alkoxybenzophenone hydrazone is prepared by the oxidization of 2,2'-di C₁₋₆ alkoxybenzophenone hydrazone at a temperature of not more than 0°C.

87. The process according to claim 86, wherein the oxidation is conducted in the presence of nickel peroxide.

88. The process according to claim 87, wherein the 2,2'-di C₁₋₆ alkoxybenzophenone hydrazone is prepared by the reaction of 2,2'-di C₁₋₆ alkoxybenzophenone with hydrazine monohydrate.

89. The process according to claim 84, further comprising dealkylating the 2,2',2'',2'''-tetra C₁₋₆ alkoxy tetraphenylethylene.

90. The process according to claim 89, wherein the dealkylation is by reaction with boron tribromide.

10 91. A process according to claim 90, for preparing 2,2',2'',2'''-(tetrahydroxy)tetraphenylethylene comprising dealkylating 2,2',2'',2'''-(tetramethoxy)tetraphenylethylene with boron tribromide.

92. The process according to claim 89, further comprising reacting the resulting 2,2',2'',2'''-(tetrahydroxy)tetraphenylethylene with an anhydride of a C₁₋₆ carboxylic acid.

20

93. The process according to claim 92, for preparing 2,2',2'',2'''-(tetraacetoxo)tetraphenylethylene comprising reacting 2,2',2'',2'''-(tetrahydroxy)tetraphenylethylene with anhydrous acetic anhydride.

94. The process according to claim 89, further comprising reacting the resulting 2,2',2'',2'''-(tetrahydroxy)tetraphenylethylene with trifluoromethanesulphonic anhydride.

30

95. A process according to claim 94, for preparing 2,2',2'',2'''-tetrakis(trifluoromethylsulfonyloxy)tetraphenylethylene comprising reacting

2,2',2'',2'''-(tetramethoxy)tetraphenylethylene with trifluoromethanesulphonic anhydride.

96. The process according to claim 90, further comprising reacting 2,2',2'',2'''-tetrahydroxyphenylethylene with a C₃₋₆ allylating agent.

10 97. The process according to claim 90, wherein the C₃₋₆ allylating agent is a 1-bromo C₃₋₆ allyl compound.

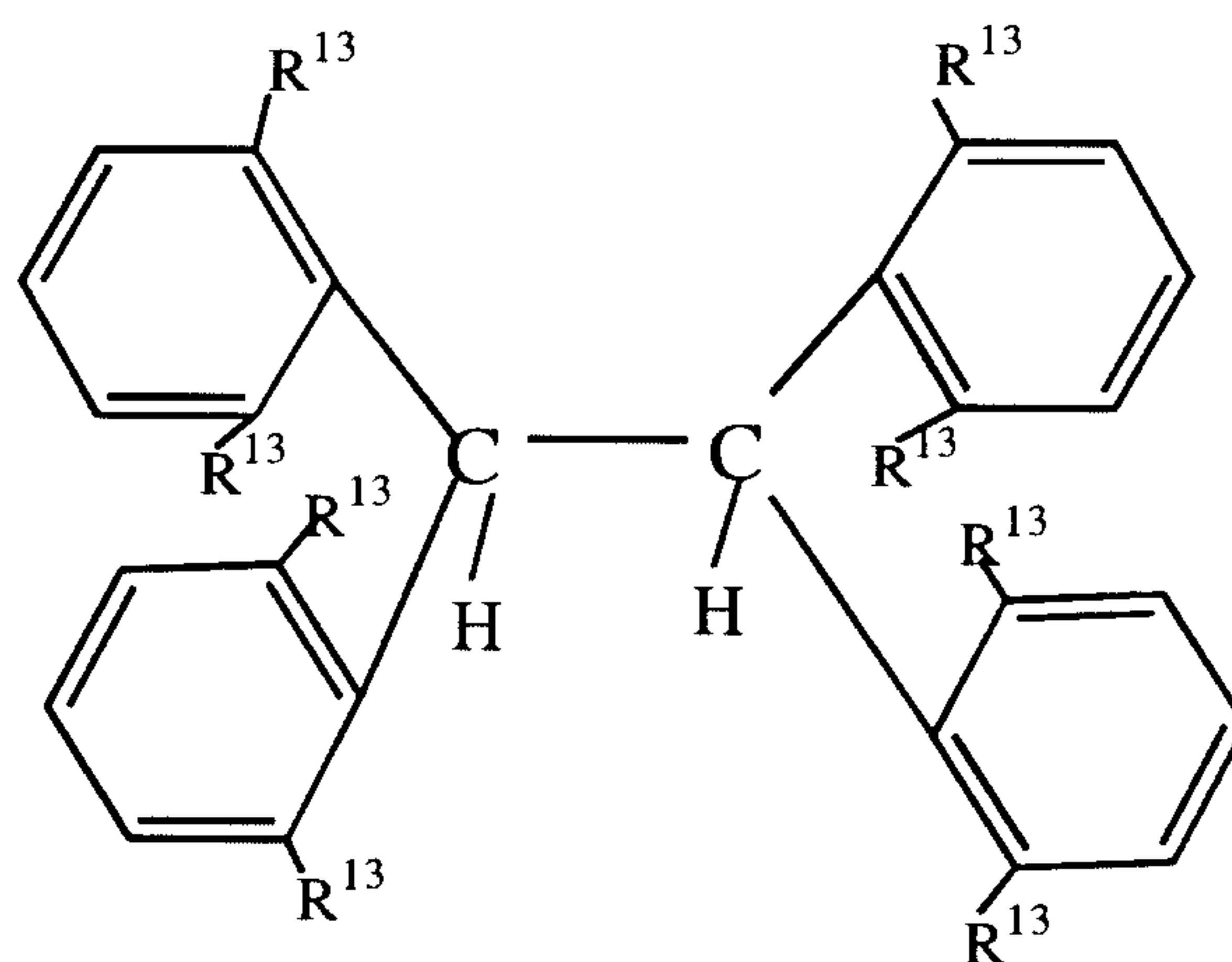
98. The process according to claim 97, further comprising subjecting the resulting 2,2',2'',2'''-tetra C₃₋₆ allyloxy tetraphenylethylene to a Claisen rearrangement resulting in a 2,2',2'',2'''-tetrahydroxy-3,3',3'',3'''-tetra C₃₋₆ allyl tetraphenylethylene.

20

99. The process according to claim 98, further comprising hydrogenating the 2,2',2'',2'''-tetrahydroxy-3,3',3'',3'''-tetra C₃₋₆ allyl tetraphenylethylene to yield a 2,2',2'',2'''-tetrahydroxy-3,3',3'',3'''-tetra C₃₋₆ alkyl tetraphenylethylene.

30 100. The process according to claim 97, wherein the allylating agent is allylbromide.

101. A process for preparation of 2,2',2'',2''',6,6',6'',6'''-octa C₁₋₄ alkoxy tetraphenylethylene by the controlled oxidation of one rotational isomer of a compound of formula V:



(V)

10

wherein R^{13} is a C_{1-4} alkoxy radical.

102. The process according to claim 101, the oxidation is carried out by reaction with triphenylmethyl hexafluorophosphate in an inert solvent at temperatures from 0°C to 25°C .

20

103. The process according to claim 101, further comprising dealkylating the resulting 2,2',2'',2''',6,6',6'',6'''-octa C_{1-4} alkoxy tetraphenylethylene compounds with boron tribromide at temperatures from 0°C to 25°C to yield 2,2',2'',2''',6,6',6'',6'''-octahydroxyphenylethylene.

30

104. The process according to claim 103, further comprising reacting the resulting 2,2',2'',2''',6,6',6'',6'''-octahydroxyphenylethylene with an anhydride of a C_{1-6} carboxylic acid.

105. The process according to claim 103, further comprising reacting the resulting 2,2',2'',2''',6,6',6'',6'''-octahydroxyphenylethylene with trifluoromethanesulphonic anhydride.

106. The process according to claim 103, further comprising reacting the resulting 2,2',2'',2''',6,6',6'',6'''-octahydroxyphenylethylene with a C₃₋₆ allylating agent.

107. The process according to claim 106, wherein the C₃₋₆ allylating agent is a 1-bromo C₃₋₆ allyl compound.

10

108. The process according to claim 106, further comprising subjecting the resulting 2,2',2'',2''',6,6',6'',6'''-octa C₃₋₆ allyloxy tetraphenylethylene to a Claisen rearrangement resulting in a 2,2',2'',2''',6,6',6'',6'''-octahydroxy-3,3',3'',3''',5,5',5'',5'''-octa C₃₋₆ allyl tetraphenylethylene.

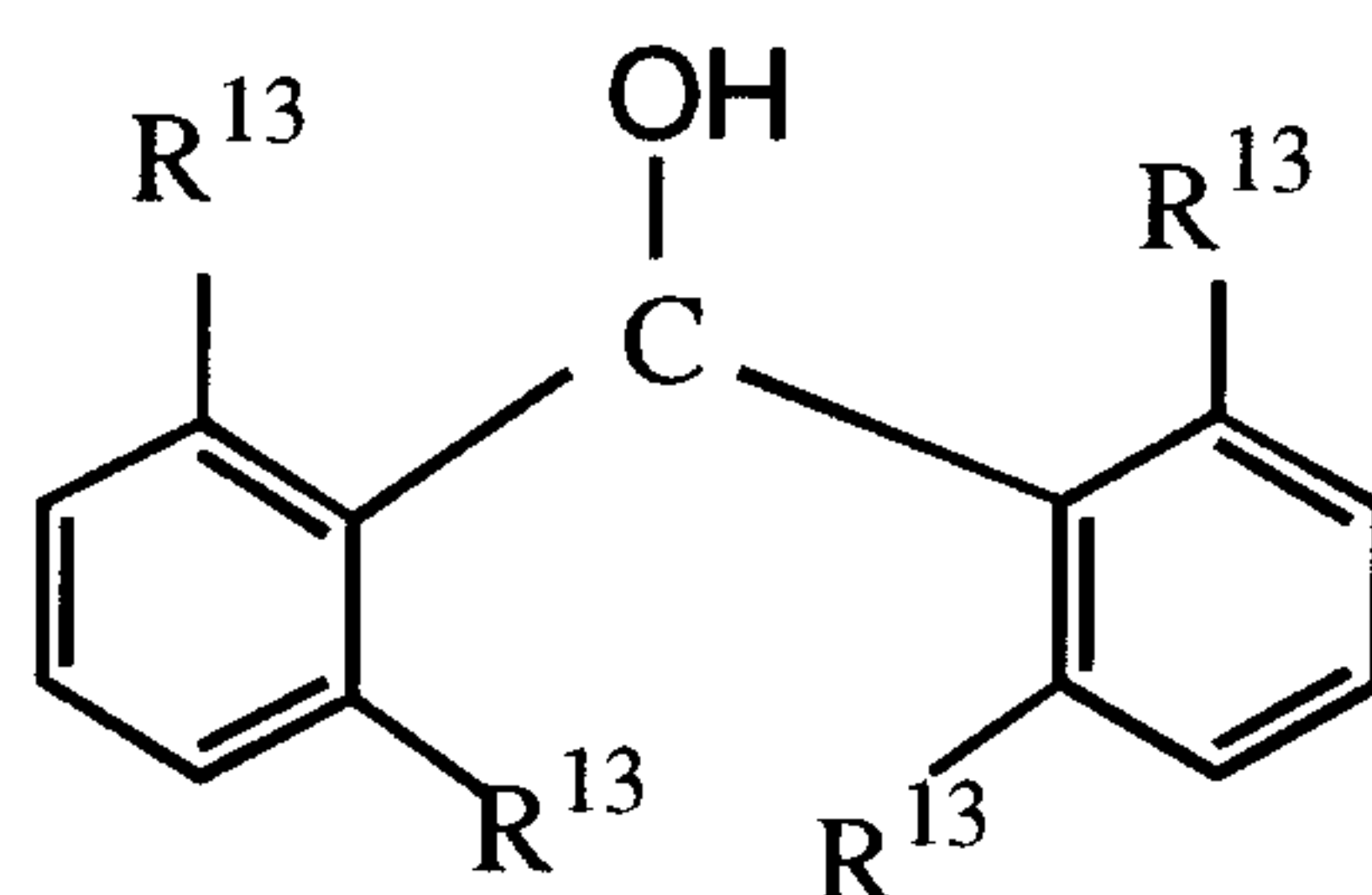
20

109. The process according to claim 108, further comprising hydrogenating the 2,2',2'',2''',6,6',6'',6'''-octahydroxy-3,3',3'',3''',5,5',5'',5'''-octa C₃₋₆ allyl tetraphenylethylene to yield a 2,2',2'',2''',6,6',6'',6'''-octahydroxy-3,3',3'',3''',5,5',5'',5'''-octa C₃₋₆ alkyl tetraphenylethylene.

110. The process according to claim 108, wherein the allylating agent is allylbromide.

30

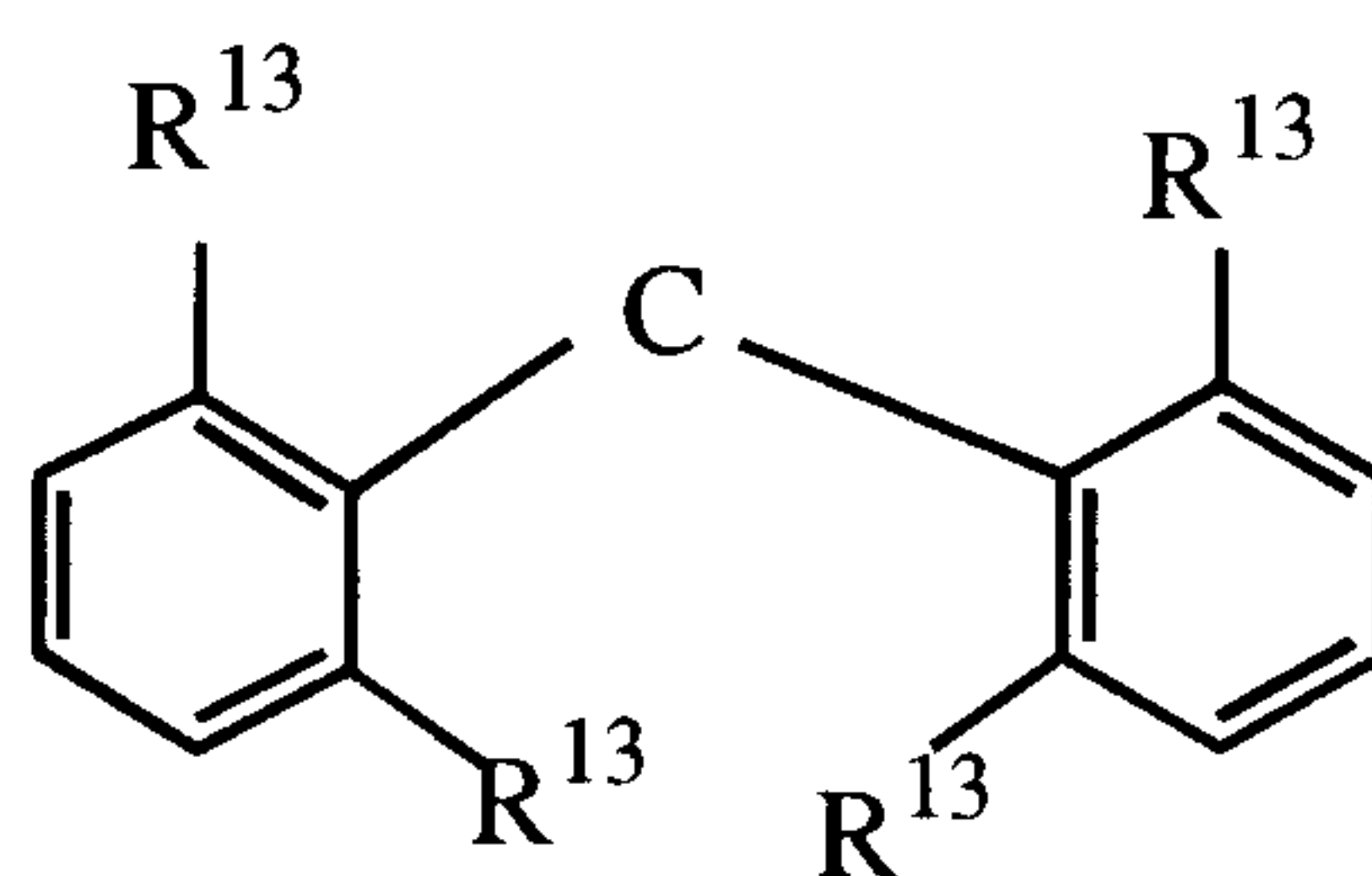
111. The process according to claim 101, wherein the compound of formula V as a mixture of rotational isomers is prepared by the radical coupling of a compound of formula VI:



(VI)

wherein R^{13} is a C_{1-4} alkoxy radical with a compound of formula VII:

10



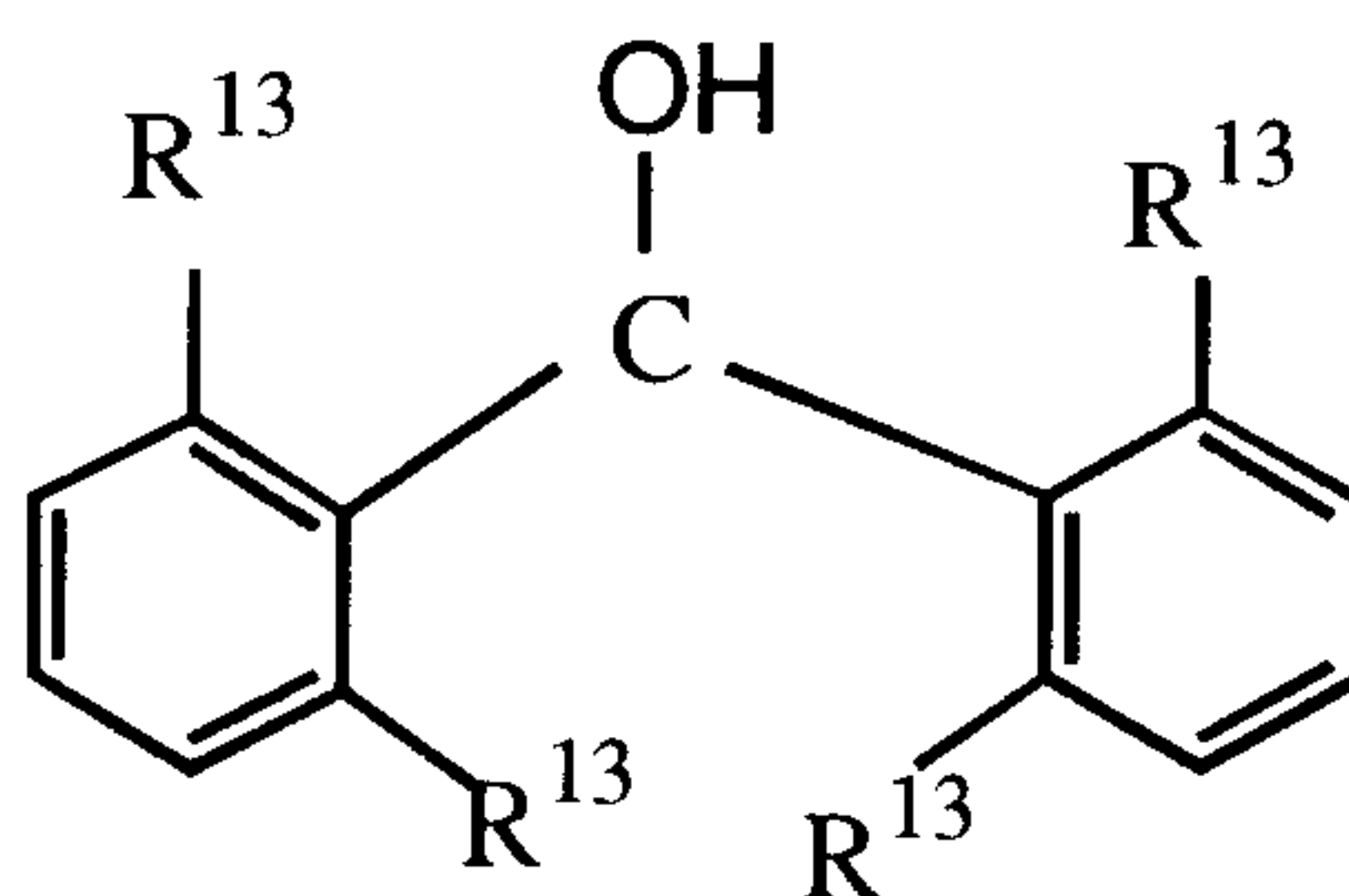
(VII)

wherein R^{13} is as defined above, in an inert solvent in the presence of p-toluene sulphonic acid.

20

112. The process according to claim 111, wherein the compound of formula V as a single rotational isomer is prepared by the homo-coupling of the radical derived from formula VI:

30



(VI)

wherein R^{13} is a C_{1-4} alkoxy radical by treatment with chromous ion in acidic medium.

113. The compound according to claim 15, wherein two or more R⁵ substituents are C₇₋₁₁ benzyloxy radicals.

10

20

30