

SUZUKI COUPLING ON BI- AND TRIPHENYL COMPOUNDSField of the invention

5 The present invention relates to a method for synthesizing a chemical compound and a chemical compound obtained or obtainable by a method for synthesizing a chemical compound.

Background Art

10 Downscaling is an unbroken trend in the semiconductor industry to increase performance of microchips. However, achieving 7nm node technology and beyond significantly increases complexity and requires some new process and material solutions.

15 Multilayer patterning processes play a prominent role in the transfer of fine lithography patterns to substrates and the importance will increase even more and more as the industry reaches the next stages of development of advanced nodes.

20 An underlayer Spin-on carbon (SOC) material with high etch resistance and good gap fill properties is a key material in these multilayer processes. As critical dimensions reach a few tens of nanometers, the existing topography becomes a major performance challenge. Reliable methods for planarizing such layers with classical chemical mechanical polishing (CMP) processes have not been established yet. New strategies to meet high levels of
25 planarization are therefore of great interest to the industry.

30 Inkjet Adaptive Planarization (IAP) is a method adapted from nanoimprint lithography (NIL) processes that can be used to planarize surfaces of substrates. For this purpose, liquid drops of a photocurable composition are printed on the surface of substrates. The drop pattern can be tailored to existing topographies. A flat superstrate is brought into direct contact with the printed liquid to form a flat layer of liquid. The flat liquid layer is typically cured

under the influence of UV-light, and after removal of the superstrate, a planar surface is obtained, which can be subjected to subsequent processing steps.

5 These cured layers can combine high etch resistance with high mechanical strength and good thermal stability that meet the requirements of hardmask materials for multilayer processes for the development of the next generation of microchips.

10 State-of-the-art photocurable compositions usually contain a high content of acrylate monomers as classic nanoimprint lithography (NIL) resist materials.

15 US 2020/0339828 A1 (Canon) claims, for example, the use of a photocurable composition comprising a polymerizable material and a photoinitiator, wherein at least 90 wt% of the polymerizable material comprise acrylate monomers including an aromatic group; and a total carbon content of the photocurable composition after curing is at least 70%.

20 US 2021/0070906 A1 (Canon) covers the use of curable compositions that comprise a polymerizable material and an initiator, wherein the polymerizable material comprises a first monomer and a second monomer, the second monomer including a ring structure selected from a maleimide-ring, a pyrone ring, or a 2-furanone ring and where the second monomer is soluble in the first monomer, and the curable composition has a viscosity of lower 10 cP. In addition, the formulation can contain one further monomer
25 that includes a substituted or unsubstituted divinyl benzene.

US 2021/0198400 A1 (Canon) deals with photocurable composition including 1,3-benzoxazine and acrylate monomers.

30 US 2022/0185914 A1 (Canon) describes a photocurable composition including the polymerizable material (divinylbenzene; in Examples) from about 15wt% to 85wt% and at least one multi-functional acrylate monomer

from 15wt% to 85wt% based on the total weight of the photocurable composition (Examples, claims).

Patent Literature

- 5 1. US 2020/0339828 A1
 2. US 2021/0070906 A1
 3. US 2021/0198400 A1
 4. US 2022/0185914 A1

10 Non- Patent Literature

No literature

Summary of the invention

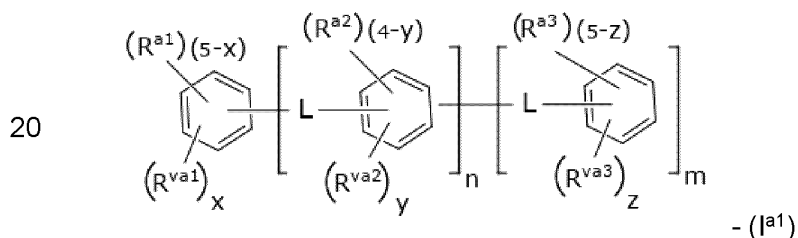
15 However, the inventors newly have found that there is still one or more of
 considerable problems for which improvement is desired, as listed below;
 providing a new synthesis method for synthesizing a chemical compound,
 preferably to provide a new chemical compound which may realize a
 carbon-rich flat underlayer, to provide a new compound having a low
 viscosity with relatively low vapor pressure, preferably suitable for ink-jet
20 printing, to provide a new chemical compound having improved crosslinking
 property, preferably which may form highly crosslinked thermosets after
 UV-induced radical polymerization; and/or to provide a new chemical
 compound may realize improved thermal stability after curing, preferably at
 about 350°C or more; realizing lower shrinkage after curing by providing a
25 new chemical compound synthesized by a new synthesis method; and/or
 realizing an improved etching resistance of a cured layer by providing a
 new chemical compound synthesized by a new synthesis method; realizing
 an improved planarization performance of a cured layer by providing a new
 chemical compound synthesized by a new synthesis method, namely over
30 different pattern topographies of a substrate; realizing a cost efficient,
 and/or environmentally friendly new synthesis method; providing a new
 synthesis method with reduced process steps.

The inventors aimed to solve one or more of the above-mentioned problems.

- 5 Then, the present inventors have surprisingly found that one or more of the above described technical problems can be solved by the features as defined in the claims.

Namely, it is found a novel method for synthesizing a chemical compound, comprising at least a following step;

- 10 (I^x) Applying Suzuki-Coupling to a precursor compound represented by the following chemical formula (I^{a1}) in the presence of an organoboron compound containing a group selected from one or members of the group selected from a vinyl group, alkyl vinyl group having carbon atoms 3 to 5 and a vinyl alcohol group;
- 15 to form a chemical compound derived from said precursor compound of (I^{a1}).



wherein

$1 \leq x \leq 5$, $0 \leq y \leq 4$, $0 \leq z \leq 5$;

- 25 n is 1 or 0, m is 1 or 0, $1 \leq n+m \leq 2$, preferably $n+m=1$, more preferably $n=0$, $m=1$;

$3 \leq x+z \leq 10$ when m is 1 and n is 0, $3 \leq x+y \leq 9$ when m is 0 and n is 1, and

$3 \leq x+z+y \leq 14$ when m and n are both 1;

R^{va1} , R^{va2} and R^{va3} are hydrogen atom, preferably it is selected from F, Cl,

- 30 Br, I, more preferably it is Br;

R^{a1} , R^{a2} and R^{a3} are at each occurrence, independently or dependently of each other, selected from H, D or alkyl group having carbon atoms 1 to 5;

L is at each occurrence, same or differently selected from the group consisting of a direct bond, alkylene group having carbon atoms 1 to 15, and alkenylene group having carbon atoms 2 to 15, where one or more non-adjacent CH₂ groups of said alkylene or alkenylene group may be replaced by oxygen atom, C=O, C=S, C=Se, C=NH, SiH₂, SO, SO₂, OS, or CONH and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂.

In another aspect, the present invention also relates to use of the compound of the present invention for forming a layer, preferably for forming an underlayer Spin-on carbon.

In another aspect, the present invention also relates to a chemical compound obtained or obtainable by the method of the present invention.

Technical effects of the invention

The present invention provides one or more of the following technical effects: providing a new synthesis method for synthesizing a chemical compound, preferably to provide a new chemical compound which may realize a carbon-rich flat underlayer, to provide a new compound having a low viscosity with relatively low vapor pressure, preferably suitable for ink-jet printing, to provide a new chemical compound having improved crosslinking property, preferably which may form highly crosslinked thermosets after UV-induced radical polymerization; and/or to provide a new chemical compound may realize improved thermal stability after curing, preferably at about 350°C or more; realizing lower shrinkage after curing by providing a new chemical compound synthesized by a new synthesis method; and/or realizing an improved etching resistance of a cured layer by providing a new chemical compound synthesized by a new synthesis method; realizing an improved planarization performance of a cured layer by providing a new chemical compound synthesized by a new synthesis method, namely over different pattern topographies of a

substrate; realizing a cost efficient, and/or environmentally friendly new synthesis method; providing a new synthesis method with reduced process steps.

5 Definition of the terms

The terms as used herein have the following meanings:

The articles “a,” “an,” and “the” include plural referents unless otherwise expressly and unequivocally limited to one referent.

10 Since all numbers, values and/or expressions referring to quantities of ingredients, reaction conditions, etc., used herein and in the claims appended hereto, are subject to the various uncertainties of measurement encountered in obtaining such values, unless otherwise indicated, all are to be understood as modified in all instances by the
15 term “about.”

Where a numerical range is disclosed herein such range is continuous, inclusive of both the minimum and maximum values of the range as well as every value between such minimum and maximum values. Still
20 further, where a range refers to integers, every integer between the minimum and maximum values of such range is included. In addition, where multiple ranges are provided to describe a feature or characteristic, such ranges can be combined. That is to say that, unless otherwise indicated, all ranges disclosed herein are to be
25 understood to encompass any and all sub-ranges subsumed therein.

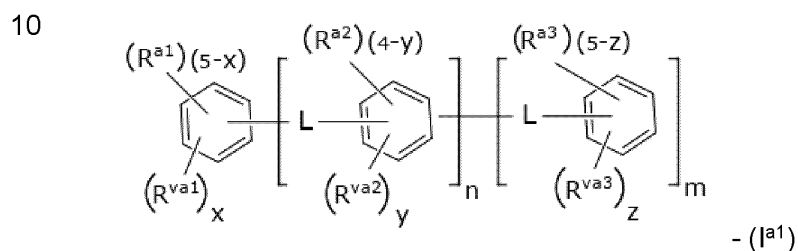
For example, a stated range of from “1 to 10” should be considered to include any and all sub-ranges between the minimum value of 1 and the maximum value of 10. Exemplary sub-ranges of the range 1 to 10
30 include, but are not limited to, 1 to 6.1, 3.5 to 7.8, and 5.5 to 10, etc.

Detailed description of the invention

According to the present invention, said method for synthesizing a chemical compound, comprising at least a following step;

(I*) Applying Suzuki-Coupling to a precursor compound represented by the following chemical formula (I^{a1}) in the presence of an organoboron

5 compound containing a group selected from one or members of the group selected from a vinyl group, alkyl vinyl group having carbon atoms 3 to 5 and a vinyl alcohol group; to form a chemical compound derived from said precursor compound of (I^{a1}).



15 wherein

$1 \leq x \leq 5$, $0 \leq y \leq 4$, $0 \leq z \leq 5$;

n is 1 or 0, m is 1 or 0, $1 \leq n+m \leq 2$, preferably $n+m=1$, more preferably $n=0$, $m=1$;

20 $3 \leq x+z \leq 10$ when m is 1 and n is 0, $3 \leq x+y \leq 9$ when m is 0 and n is 1, and $3 \leq x+z+y \leq 14$ when m and n are both 1;

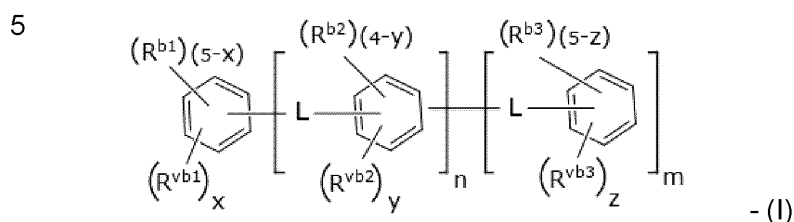
R^{va1} , R^{va2} and R^{va3} are hydrogen atom, preferably it is selected from F, Cl, Br, I, more preferably it is Br;

R^{a1} , R^{a2} and R^{a3} are at each occurrence, independently or dependently of each other, selected from H, D or alkyl group having carbon atoms 1 to 5;

25 L is at each occurrence, same or differently selected from the group consisting of a direct bond, alkylene group having carbon atoms 1 to 15, and alkenylene group having carbon atoms 2 to 15,

where one or more non-adjacent CH_2 groups of said alkylene or alkenylene group may be replaced by oxygen atom, C=O, C=S, C=Se, C=NH, SiH_2 , SO, SO_2 , OS, or CONH and where one or more H atoms may be replaced
30 by D, F, Cl, Br, I, CN or NO_2 .

According to the present invention, said chemical compound derived from the precursor compound of (I^{a1}) is represented by chemical formula (I).



- 10 wherein
 $1 \leq x \leq 5$, $0 \leq y \leq 4$, $0 \leq z \leq 5$;
 n is 1 or 0, m is 1 or 0, $1 \leq n+m \leq 2$, preferably $n+m=1$, more preferably $n=0$, $m=1$;
 $3 \leq x+z \leq 10$ when m is 1 and n is 0, $3 \leq x+y \leq 9$ when m is 0 and n is 1, and
 $3 \leq x+z+y \leq 14$ when m and n are both 1;
 R^{vb1} , R^{vb2} and R^{vb3} are at each occurrence, independently or dependently of
each other, selected from vinyl group, alkyl vinyl group having carbon
atoms 3 to 5 or vinyl alcohol group, preferably it is vinyl group;
 R^{b1} , R^{b2} and R^{b3} are at each occurrence, independently or dependently of
each other, selected from H, D or alkyl group having carbon atoms 1 to 5;
 L is at each occurrence, same or differently selected from the group
consisting of a direct bond, alkylene group having carbon atoms 1 to 15,
and alkenylene group having carbon atoms 2 to 15,
where one or more non-adjacent CH_2 groups of said alkylene or alkenylene
group may be replaced by oxygen atom, $C=O$, $C=S$, $C=Se$, $C=NH$, SiH_2 ,
25 SO , SO_2 , OS , or $CONH$ and where one or more H atoms may be replaced
by D, F, Cl, Br, I, CN or NO_2 , wherein the formula (I) does not include 1,1'-
Biphenyl, 3,4',5-triethenyl.
30 In a preferred embodiment of the present invention, R^{vb1} , R^{vb2} and R^{vb3} are
vinyl group.

It is believed that when the monomer compound has one or more carbon rings and at least 3 vinyl groups, crosslinking density can be improved. It may further lead improved thermal stability of the cured film and chemical resistance.

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It is believed that compounds containing high carbon content, preferably 80% or more in said compound, are useful for realizing carbon-rich flat underlayer, and low viscosity with relatively low vapor pressure can be ideally used in inkjet printing process, namely in the Inkjet Adaptive Planarization (IAP) process according to the present invention. It is further believed that the 1st monomer compound of the present invention can form highly crosslinked thermosets after UV-induced radical polymerization. A high crosslinking density contributes to increasing chemical and thermal stability and is the key to its function as hardmask.

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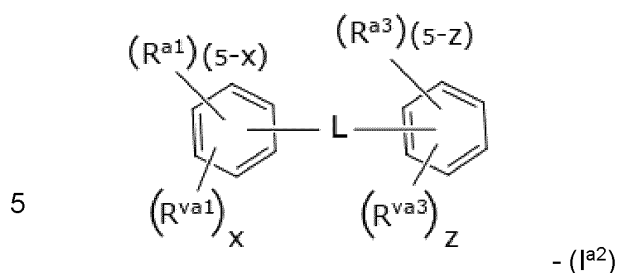
Preferably, L of the chemical formula (I) and/or (I^{a1}) is a direct bond, straight alkylene group having carbon atoms 1 to 5 or straight alkenylene group having carbon atoms 2 to 5, preferably L is a straight alkylene group having carbon atoms 1 to 5 or straight alkenylene group having carbon atoms 2 to 5, wherein one or more non-adjacent CH₂ groups of said alkylene or alkenylene group may be replaced by oxygen atom, C=O, C=S, C=Se, C=NH, SiH₂, SO, SO₂, OS, or CONH and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂, more preferably L is a straight alkylene group having carbon atoms 1 to 5.

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Preferably n of the chemical formula (I) and (I^{a1}) is 0 and m is 1.

In a preferred embodiment of the present invention, the precursor compound of chemical formula (I^{a1}) is represented by chemical formula (I^{a2}).

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R^{va1} , R^{va2} and R^{va3} are hydrogen atom, preferably it is selected from F, Cl, Br, I, more preferably it is Br;

10 R^{a1} , R^{a2} and R^{a3} are at each occurrence, independently or dependently of each other, selected from H, D or alkyl group having carbon atoms 1 to 5, preferably R^{a1} , R^{a2} and R^{a3} are all H;

L is a direct bond, straight alkylene group having carbon atoms 1 to 5 or straight alkenylene group having carbon atoms 2 to 5,

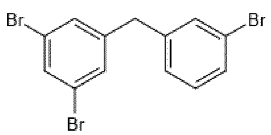
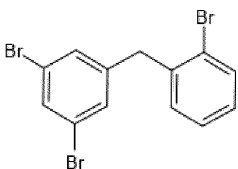
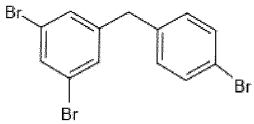
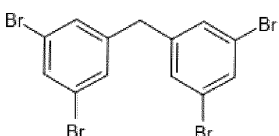
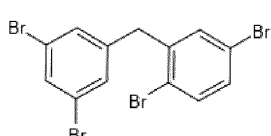
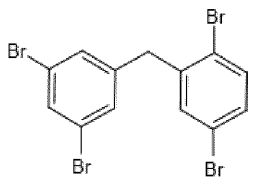
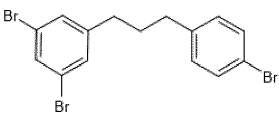
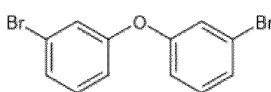
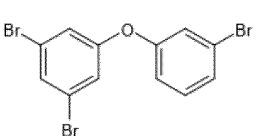
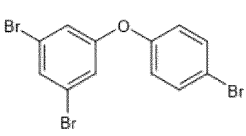
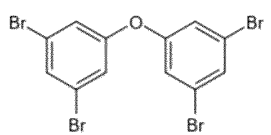
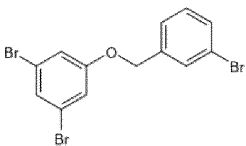
15 wherein one or more non-adjacent CH_2 groups of said alkylene or alkenylene group may be replaced by oxygen atom, C=O, C=S, C=Se, C=NH, SiH₂, SO, SO₂, OS, or CONH and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂.

Below table A shows preferable examples of the compound.

Table A:

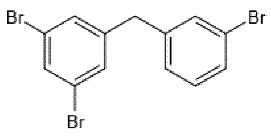
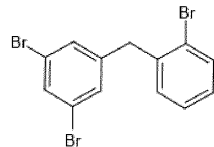
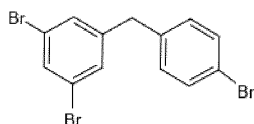
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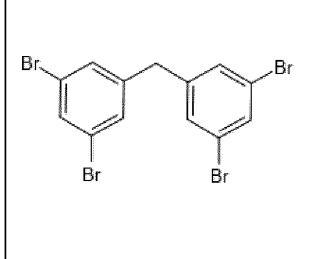
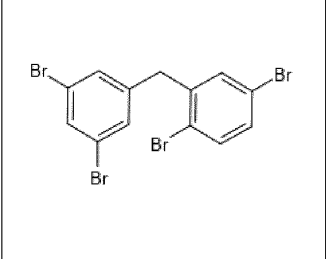
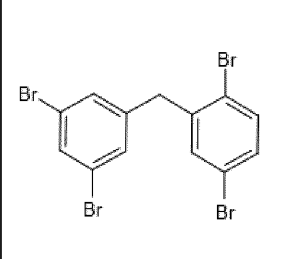
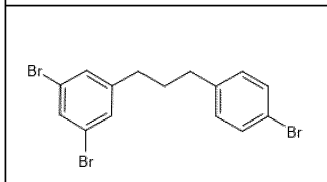
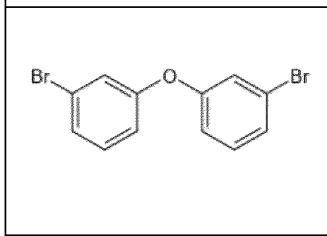
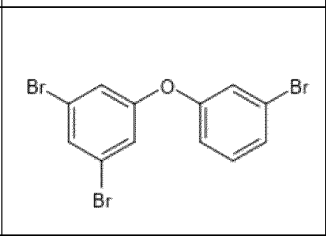
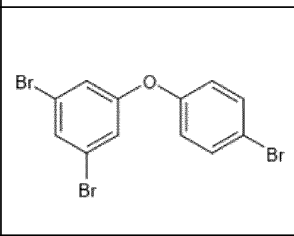
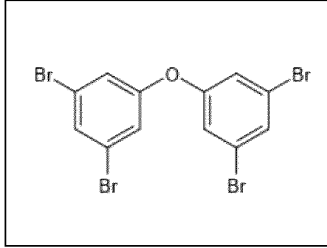
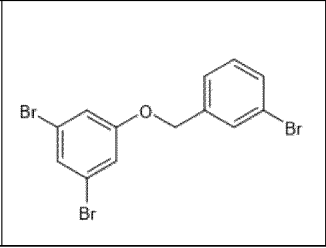
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More preferably, the precursor compound mentioned below in Table A' can be used.

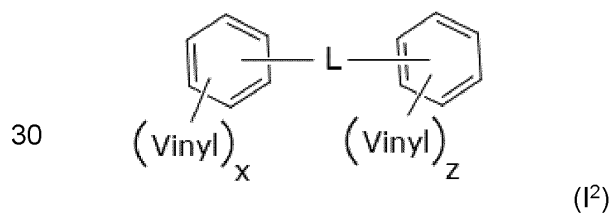
Table A':

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Such precursor compounds of the present invention can be synthesized by known method or the method described in working examples.

In a preferred embodiment of the present invention, the compound of formula (I) is represented by one of the following chemical formulae (I²), where $1 \leq x \leq 5$, $0 \leq z \leq 5$, $3 \leq x+z \leq 10$;



where $1 \leq x \leq 5$, $0 \leq z \leq 5$, $3 \leq x+z \leq 10$;

L is a direct bond, straight alkylene group having carbon atoms 1 to 5 or

straight alkenylene group having carbon atoms 2 to 5,

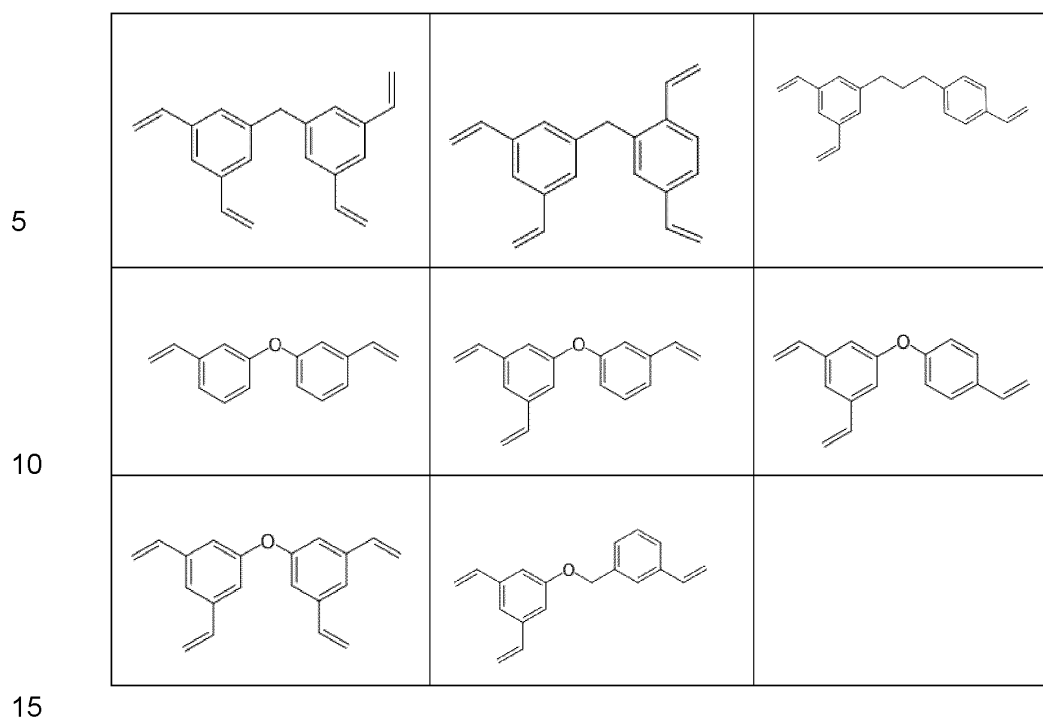
wherein one or more non-adjacent CH₂ groups of said alkylene or

5 alkenylene group may be replaced by oxygen atom, C=O, C=S, C=Se, C=NH, SiH₂, SO, SO₂, OS, or CONH and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂.

Below table B shows preferable examples of the compound.

10 Table B:

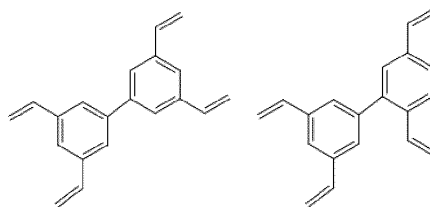
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In one preferred embodiment of the present invention, L is a direct bond,
 $2 \leq x \leq 5$, $2 \leq z \leq 5$, $4 \leq x+z \leq 10$.

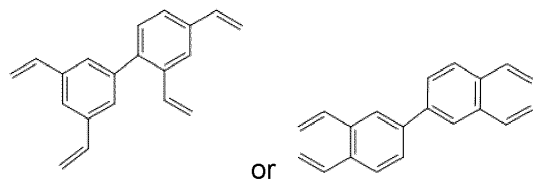
Below is the examples of the above mentioned preferred embodiment.

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The compound is selected from

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In another preferred embodiment of the present invention, L is a straight
 alkylene group having carbon atoms 1 to 5 or straight alkenylene group
 having carbon atoms 2 to 5, wherein one or more non-adjacent CH₂ groups

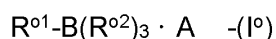
of said alkylene or alkenylene group may be replaced by oxygen atom, C=O, C=S, C=Se, C=NH, SiH₂, SO, SO₂, OS, or CONH and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂.

- 5 More preferably, said compound of the above mentioned another preferred embodiment is selected from the below table.

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According to the present invention, the chemical compound obtained or obtainable by the method of the present invention can be used for fabricating a cured layer, preferably it is a photo-cured layer formed from the compound of the present invention. In a preferable embodiment, said
 5 photo-cured layer is a to be used as an interlayer insulating film of a semiconductor device or as an underlayer Spin-on carbon (SOC) for fabricating semiconductors. Such as LSI, system LSI, DRAM, SDRAM, RDRAM or D-RDRAM.

10 In a preferred embodiment of the present invention, said organoboron compound of step (I^x) contains at least one vinyl group, preferably said organoboron compound is represented by chemical formula (I^o);



15 where

R^{o1} is vinyl group, alkyl vinyl group having carbon atoms 3 to 5 or vinyl alcohol group, preferably it is vinyl group;

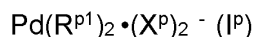
R^{o2} is a hydrogen atom, preferably it is each independently of each other, at each occurrence, selected from F, Cl, Br, I, more preferably it is F;

20 A is a monovalent cation, preferably it is selected from H⁺, Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Fr⁺, more preferably it is Li⁺, Na⁺, K⁺, Rb⁺, even more preferably it is K⁺.

25 A publicly known chemical compound falls within chemical formula (I^o) like potassium vinyltrifluoroborate, can be used preferably.

In a preferred embodiment of the present invention, Suzuki-Coupling of step (I^x) is performed in the presence of a palladium catalyst, preferably said palladium catalyst is selected from one or more members of the group
 30 consisting of a palladium catalyst represented by the following formula (I^p), Pd₂(dba)₃-n(dba), Pd₂(dba)₃, Pd(OAc)₂, Pd(PPh₃)₄ and [1,3-Bis(2,6-

Diisopropylphenyl)imidazole-2-ylidene](3-chloropyridyl)palladium(II)
dichloride (PEPPSI™-IPr: CAS 905459-27-0);



5 wherein

R^{P1} is a hydrogen atom, preferably it is each independently of each other, at each occurrence, selected from F, Cl, Br, I, more preferably it is Cl;

X^{P} is Amphos (di-tert-butyl (4-dimethylaminophenyl)phosphine) or dtbpf (di-tert-butylphosphino)ferrocene). Preferably, said palladium catalyst is

10 selected from $\text{Pd}(\text{R}^{\text{P1}})_2 \cdot (\text{X}^{\text{P}})_2 \cdot (\text{I}^{\text{P}})$ where X^{P} is Amphos (di-tert-butyl (4-dimethylaminophenyl)phosphine), $\text{Pd}_2(\text{dba})_3 \cdot \text{n}(\text{dba})$ or $\text{Pd}_2(\text{dba})_3$.

Preferably, said step (I^{x}) is carried out at the temperature in the range from 10°C to 90°C, preferably it is in the range from 20 to 80°C, more preferably
15 from 35 to 65°C.

In a preferred embodiment of the present invention, Suzuki-Coupling of step (I^{x}) is carried out in the presence of a solvent or a solvent mixture.

20 Preferably said solvent or solvents of the solvent mixture is/are selected from one or more of polar aprotic solvents, preferably it is selected from one or more members of the group consisting of dichloromethane (BP: 39.6°C), acetone (BP: 56.05°C), tetrahydrofuran (BP: 66°C), ethyl acetate (BP: 77.11°C), acetonitrile (BP: 81.3-82.1°C), pyridine (BP: 115°C), dimethylformamide (BP: 153°C), dimethyl sulfoxide (BP: 189°C),
25 hexamethylphosphoramide (BP: 235.5°C), dimethylpropyleneurea (BP: 246.5°C) and sulfolane (BP: 286°C).

In a preferred embodiment of the present invention, Suzuki-Coupling of step (I^{x}) is performed in the presence of base material. More preferably said
30 base material is selected from NaOH, TIOH, Ti_2Co_3 , TIOEt, NaOMe or a combination of any of them. These perform optimally in THF or H_2O solvent systems. Or base material can be selected from K_2CO_3 , K_3PO_4 or a

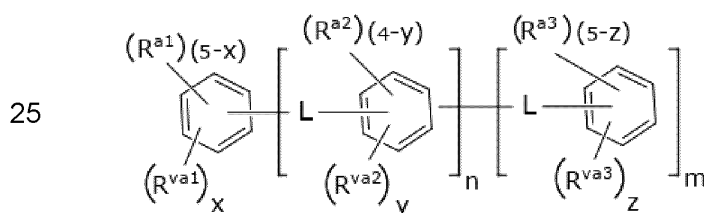
combination of them. These perform optimally in DMF. Even more preferably, said base material is selected from NaOH, TIOH, Ti₂Co₃, TIOEt, NaOMe or a combination of any of them. Furthermore preferably, said base material is selected from NaOH, TIOH, Ti₂Co₃, TIOEt, NaOMe or a combination of any of them and solvent contains at least THF, H₂O or THF and H₂O both. Particularly preferably, said base material selected from NaOH, TIOH, Ti₂Co₃, TIOEt, NaOMe or a combination of any of them is used in THF or H₂O solvent.

For more details of Suzuki-Coupling can be found for examples in Ishiyama, T.; Miyaura, N.; Suzuki, A. *Synlett*, 1991, 687; Miyaura, N.; Suzuki, A. *Chem. Rev.*, 1995, 95, 2457, Beller, M; Fischer, H.; Herrmann, W. A.; Ofele, K.; Brossmer, C. *Angew. Chem. Int. Ed.* 1995, 34, 1848; Suzuki, A. *Proc. Jpn. Acad., Ser. B.* 2004, 80, 8, 359.

- Step (I^w): Deoxygenation

In a preferred embodiment of the present invention, said method further contains following step (I^w), preferably the method contains said step (I^w) before step (I^x);

(I^w) performing deoxygenation of an alcohol group of a precursor compound represented by chemical formula (I^{c1}) by applying an acid catalyst and a reducing agent to synthesize the precursor compound of (I^{a1})



(I^{c1}) it is tentative one.

Shall be replaced with the optimized one later)

wherein

1 ≤ x ≤ 5, 0 ≤ y ≤ 4, 0 ≤ z ≤ 5;

n is 1 or 0, m is 1 or 0, $1 \leq n+m \leq 2$, preferably $n+m=1$, more preferably $n=0$, $m=1$;

$3 \leq x+z \leq 10$ when m is 1 and n is 0, $3 \leq x+y \leq 9$ when m is 0 and n is 1, and

$3 \leq x+z+y \leq 14$ when m and n are both 1;

5 R^{va1} , R^{va2} and R^{va3} are hydrogen atom, preferably it is selected from F, Cl, Br, I, more preferably it is Br;

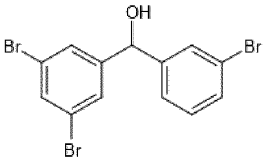
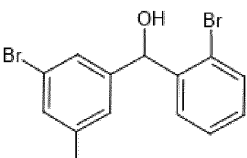
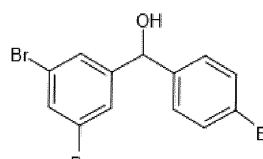
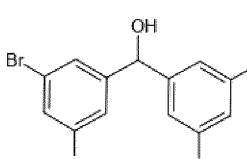
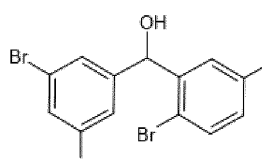
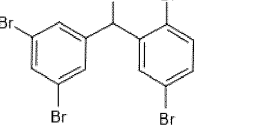
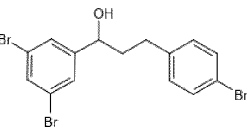
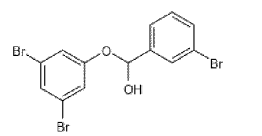
R^{a1} , R^{a2} and R^{a3} are at each occurrence, independently or dependently of each other, selected from H, D or alkyl group having carbon atoms 1 to 5;

10 L is at each occurrence, same or differently selected from an alkylene group having carbon atoms 1 to 15, and alkenylene group having carbon atoms 2 to 15,

where at least one non-adjacent CH_2 group of said alkylene or alkenylene group is replaced by COH.

15 Preferably, said precursor compound of formula (I^{c1}) can be selected from following table C.

Table C:

20			
25			
30			

In a preferred embodiment, said acid catalyst is triflic acid (TFMSA), trifluoroacetic acid (TFA), Boron Trifluoride – Diethyl Ether Complex (BF_3OEt_2), Indium(III) chloride (InCl_3); and said reducing agent is Triethylsilane (Et_3SiH), Dimethylchlorosilane (Me_2SiHCl), sodium borohydride (NaBH_4). Preferably, a combination of triflic acid (TFMSA) as the acid catalyst and Triethylsilane (Et_3SiH) as the reducing agent, a combination of trifluoroacetic acid (TFA) and Triethylsilane (Et_3SiH), a combination of Dimethylchlorosilane (Me_2SiHCl) and Indium(III) chloride (InCl_3), a combination of trifluoroacetic acid (TFA) and sodium borohydride (NaBH_4) are used in step (I^w).

In a preferred embodiment, the step (I^w) is carried out at the temperature in the range from -20°C to 20°C , preferably from -10°C to 10°C .

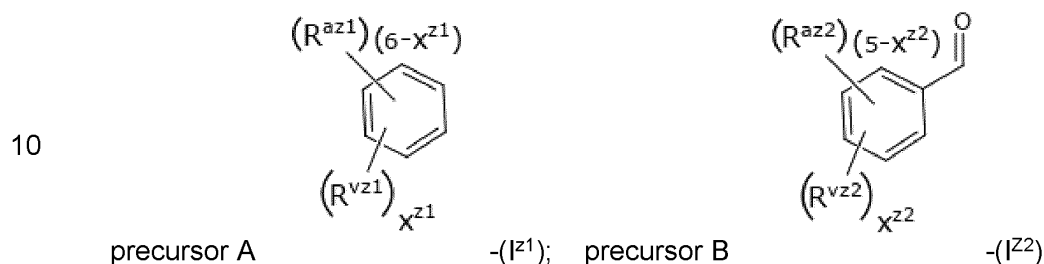
In a preferred embodiment, the step (I^w) is carried out in the presence of a solvent or a solvent mixture. Preferably said solvent or solvents of the solvent mixture is/are selected from alkyl halides, preferably it is selected from one or more members of the group consisting of alkyl fluorides, alkyl chlorides, alkyl bromides, and alkyl iodides, more preferably selected from chloromethane, dichloromethane (DCM), trichloromethane(chloroform), chloroethane, dichloroethane, trichloroethane, bromomethane, dibromomethane, bromoethane, dibromoethane and any combination of thereof; preferably selected from dichloromethane (DCM), trichloromethane(chloroform) or a mixture of them. More details of deoxygenation can be found for examples in Journal of Medicinal Chemistry. 2003, 46, 453-456, Chemistry – A European Journal, Supporting Information, “Methylene Bridging Effect on the Structures, Lewis Acidities and Optical Properties of Semi-planar Triarylboranes”

Even more preferably, the combination of $\text{Et}_3\text{SiH}/\text{BF}_3\text{OEt}_2$ in DCM, $\text{Et}_3\text{SiH}/\text{TFA}$ in DCM, $\text{InCl}_3/\text{Me}_2\text{SiHCl}$ in DCM, and/or NaBH_4/TFA in DCM can be used.

- Step (I²)

In a preferred embodiment of the present invention, said method further contains following step (I²), preferably after step (I^w);

- 5 (I²) reacting precursor A represented by formula (I²¹) and precursor B represented by formula (I²²) in the presence of nBuLi.



wherein

X^{z1} is 1 to 6; X^{z2} is 0 to 5;

- 15 R^{vz1} and R^{vz2} are hydrogen atom, preferably it is selected from F, Cl, Br, I, more preferably it is Br;

R^{az1} and R^{az2} are at each occurrence, independently or dependently of each other, selected from H, D or alkyl group having carbon atoms 1 to 5.

- 20 A publicly available chemical compound falls within chemical formulae (I²¹) and (I²²), like 1,3-Dibromobenzene (Merck, CAS: 108-36-1) and 3-bromobenzaldehyde (Merck, CAS: 3132-99-8), can be used preferably.

- 25 In a preferred embodiment of the present invention, said reaction step (I²) is performed in the presence of a solvent or a solvent mixture, preferably it is selected from diethyl ether, tetrahydrofuran (THF), tetramethylethylenediamine (TMEDA) or a combination of any of them.

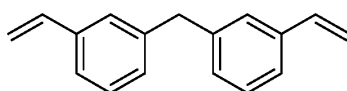
- 30 Reaction quenching and solvent removal, drying can be done by a known method, e.g. quenching by isopropanol, then washed by DI water, solvent removed under vacuum at 40°C; quenching by brine (salt water), then aqueous phase extracted with DCM, dried over Na₂SO₄.

The present invention is further illustrated by the examples following herein-
after which shall in no way be construed as limiting. The skilled person will
acknowledge that various modifications, additions and alternations may be
made to the invention without departing from the spirit and scope of the
invention as defined in the appended claims.

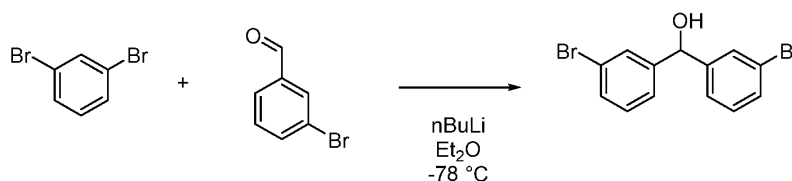
Examples

Part A: Synthesis of chemical compounds

Reference Example 1: Preparation of bis(3-vinylphenyl)methane



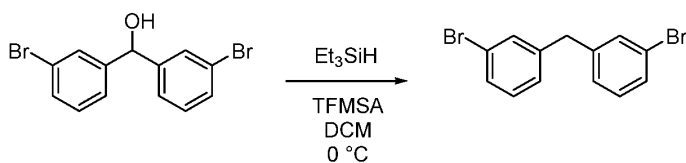
Step 1: Synthesis of bis(3-bromophenyl)methanol



1,3-Dibromobenzene (Merck, CAS: 108-36-1, 33.7 g, 143 mmol) is dissolved
in anhydrous diethyl ether (Merck, 585 mL). The solution is cooled to -78 °C
and n-butyllithium solution (1.6 M in hexane, 98 mL, 156 mmol) is added
dropwise. Then, 3-bromobenzaldehyde (Merck, CAS: 3132-99-8, 24 g, 130
mmol) is added and the reaction mixture stirred while it is brought to room
temperature. The mixture is carefully quenched with 100 mL brine, separated
and the aqueous phase extracted 3 times with DCM. The combined organic
phases are dried over Na₂SO₄, filtered and the solvent removed under
vacuum, resulting 51.6 g (116 %) of a brown oil that is used without further
purification.

Step 2: Synthesis of bis(3-bromophenyl)methanol

- 23 -



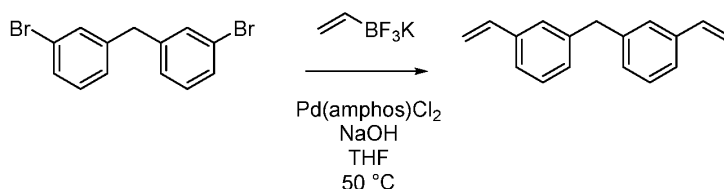
5 Bis(3-bromophenyl)methanol (51.6 g, 140 mmol) is dissolved in 400 mL DCM, treated with triethylsilane (Merck, CAS: 617-86-7, 88 mL, 550 mmol) and cooled to 0 °C. Trifluoromethanesulfonic acid (Merck, CAS: 1493-13-6, 48 mL, 550 mmol) is added dropwise and the mixtures stirred at room temperature for 3 h. Ice is carefully added and the aqueous phase is

10 separated 3 times with DCM. The combined organic phases are dried over Na₂SO₄, filtered and the solvent removed under vacuum, resulting 110 g of a yellow oil. The product (35 g, 78%) is obtained by crystallization in ethanol.

¹H NMR (500 MHz, Chloroform-*d*): δ = 7.38 (dt, *J* = 7.9, 1.4 Hz, 2H), 7.35 (d, *J* = 1.9 Hz, 2H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 2H), 3.93 (s, 2H)

15 ppm.

Step 3: Synthesis of bis(3-vinylphenyl)methane



20 Bis(3-bromophenyl)methanol (29 g, 90 mmol) is dissolved in anhydrous THF (1.4 L), treated with potassium vinyltrifluoroborate (Merck, CAS:13682-77-4, 196 mmol, 26 g) and stirred under nitrogen at room temperature for 1 h. A NaOH solution (250 mL, 10wt%) and Pd(amphos)Cl₂ (Merck, CAS: 887919-35-9, 2.5 g, 3.6 mmol) is added and the reaction mixture stirred at 50 °C for 12 h. The mixture is cooled to room temperature, treated with water and extracted 3 times with ethyl acetate. The combined organic phases are dried

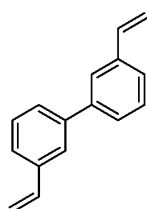
25 over Na₂SO₄, filtered and the solvent removed under vacuum. The crude product is purified with silica column chromatography using heptane as solvent, which eventually yielded 12.3 g (62.5 %) of a colorless liquid.

30

¹H NMR (500 MHz, Chloroform-*d*): δ = 7.35 – 7.26 (m, 6H), 7.13 (dt, *J* = 6.7, 2.0 Hz, 2H), 6.74 (dd, *J* = 17.6, 10.9 Hz, 2H), 5.77 (d, *J* = 17.5 Hz, 2H), 5.27 (d, *J* = 10.9 Hz, 2H), 4.02 (s, 2H) ppm.

5

Reference Example 2: Preparation of 3,3'-divinyl-1,1'-biphenyl



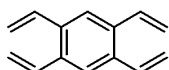
10

Reference Example 2 is synthesized using 3,3'-dibromo-1,1'-biphenyl (CAS: 16400-51-4) with the same conditions as step 3 of Reference Example 1.

¹H NMR (500 MHz, Chloroform-*d*) δ = 7.68 (q, *J* = 1.5 Hz, 2H), 7.55 (dt, *J* = 6.2, 2.2 Hz, 2H), 7.51 – 7.44 (m, 4H), 6.85 (dd, *J* = 17.6, 10.9 Hz, 2H), 5.89 (dd, *J* = 17.6, 0.9 Hz, 2H), 5.36 (dd, *J* = 10.9, 0.9 Hz, 2H) ppm.

15

Reference Example 3: Preparation of 1,2,4,5-tetravinylbenzene



20

Reference Example 3 is synthesized using 1,2,4,5-tetrabromobenzene (Merck, CAS: 636-28-2) with the same conditions as step 3 of Reference Example 1.

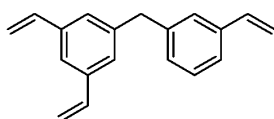
¹H NMR (500 MHz, Methylene Chloride-*d*₂) δ = 7.54 (s, 2H), 6.98 (dd, *J* = 17.4, 11.0 Hz, 4H), 5.66 (dd, *J* = 17.4, 1.3 Hz, 4H), 5.32 (dd, *J* = 11.0, 1.3 Hz, 4H) ppm.

25

Synthesis Example 1: Preparation of 1,3-divinyl-5-(3-vinylbenzyl)benzene

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- 25 -



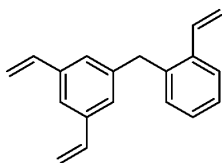
5 In general, the same synthesis conditions are used as for Reference Example 1. In step 1, 1,3,5-tribromobenzene (Merck, CAS: 626-39-1) is used instead of 1,3-dibromobenzene.

18.5 g (78%) of a colorless liquid is obtained in the Suzuki step.

¹H NMR (500 MHz, Chloroform-*d*) δ = 7.35 (d, *J* = 1.8 Hz, 1H), 7.34 – 7.26 (m, 3H), 7.18 (d, *J* = 1.5 Hz, 2H), 7.13 (dt, *J* = 6.9, 1.9 Hz, 1H), 6.73 (ddd, *J* = 17.6, 10.8, 3.7 Hz, 3H), 5.78 (ddd, *J* = 17.6, 4.4, 0.9 Hz, 3H), 5.28 (ddd, *J* = 10.9, 5.6, 1.0 Hz, 3H), 4.01 (s, 2H) ppm.

Synthesis Example 2: Preparation of 1,3-divinyl-5-(2-vinylbenzyl)benzene

15



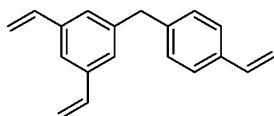
20 In general, the same synthesis conditions are used as for Reference Example 1. In step 1, 1,3,5-tribromobenzene (Merck, CAS: 626-39-1) is used instead of 1,3-dibromobenzene and 2-bromobenzaldehyde (Merck, CAS: 6630-33-7) instead of 3-bromobenzaldehyde.

4.4 g (90%) of a colorless liquid is obtained in the Suzuki step.

¹H NMR (500 MHz, Chloroform-*d*) δ = 7.57 (dd, *J* = 7.1, 2.1 Hz, 1H), 7.35 – 7.19 (m, 3H), 7.16 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.10 (d, *J* = 1.5 Hz, 2H), 6.99 (dd, *J* = 17.3, 11.0 Hz, 1H), 6.70 (dd, *J* = 17.6, 10.8 Hz, 2H), 5.76 (d, *J* = 1.0 Hz, 1H), 5.72 (d, *J* = 1.0 Hz, 1H), 5.68 (dd, *J* = 17.3, 1.4 Hz, 1H), 5.30 (dd, *J* = 11.0, 1.4 Hz, 1H), 5.26 (dd, *J* = 10.8, 0.9 Hz, 2H), 4.09 (s, 2H) ppm.

Synthesis Example 3: Preparation of 1,3-divinyl-5-(4-vinylbenzyl)benzene

30



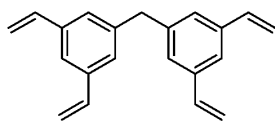
5 In general, the same synthesis conditions are used as for Reference Example 1. In step 1, 1,3,5-tribromobenzene (Merck, CAS: 626-39-1) is used instead of 1,3-dibromobenzene and 4-bromobenzaldehyde (Merck, CAS: 1122-91-4) instead of 3-bromobenzaldehyde.

17.5 g (97%) of a colorless liquid is obtained in the Suzuki step.

10 ^1H NMR (500 MHz, Chloroform- d) δ = 7.42 – 7.38 (m, 2H), 7.36 (s, 1H), 7.24 – 7.17 (m, 4H), 6.75 (d, J = 17.6, 10.9, 8.1 Hz, 3H), 5.81 (s, 1H), 5.82 – 5.73 (m, 2H), 5.31 (s, 1H), 5.30 – 5.24 (m, 2H), 4.01 (s, 2H) ppm.

Synthesis Example 4: Preparation of bis(3,5-divinylphenyl)methane

15



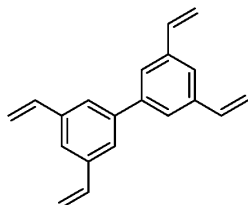
20 In general, the same synthesis conditions are used as for Reference Example 1. In step 1, 1,3,5-tribromobenzene (Merck, CAS: 626-39-1) is used instead of 1,3-dibromobenzene and 3,5-dibromobenzaldehyde (Merck, CAS: 56990-02-4) instead of 3-bromobenzaldehyde.

4.5 g (63%) of a colorless solid is obtained in the Suzuki step.

25 ^1H NMR (500 MHz, Chloroform- d) δ = 7.34 (d, J = 1.7 Hz, 2H), 7.17 (d, J = 1.6 Hz, 4H), 6.71 (dd, J = 17.6, 10.8 Hz, 4H), 5.77 (dd, J = 17.7, 0.9 Hz, 4H), 5.27 (dd, J = 10.8, 0.9 Hz, 4H), 3.99 (s, 2H) ppm.

Synthesis Example 5: Preparation of 3,3',5,5'-tetravinyl-1,1'-biphenyl

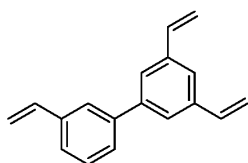
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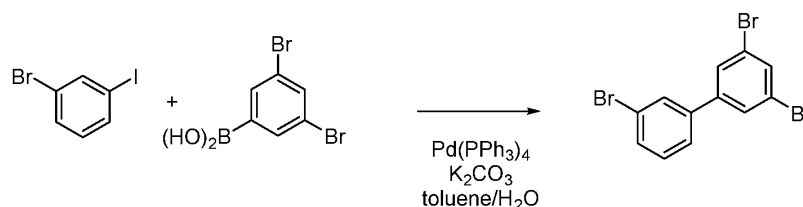
Example 5 is synthesized using 3,3',5,5'-tetrabromobiphenyl (CAS: 16400-50-3) with the same conditions as step3 of Reference Example 1.

¹H NMR (500 MHz, THF-*d*₈) δ = 7.65 (d, *J* = 1.5 Hz, 4H), 7.55 (t, *J* = 1.7 Hz, 2H), 6.85 (dd, *J* = 17.6, 10.9 Hz, 4H), 5.93 (dd, *J* = 17.6, 0.9 Hz, 4H), 5.31 (dd, *J* = 10.8, 0.9 Hz, 4H) ppm.

Synthesis Example 7: Preparation of 3,3',5-trivinyl-1,1'-biphenyl



Step 1: Synthesis of 3,3',5-tribromo-1,1'-biphenyl



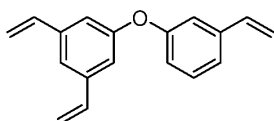
3-Bromo-1-iodobenzene (Merck, CAS: 591-18-4, 20 g, 70.7 mmol) is dissolved together with 3,5-dibromophenylboronic acid (Merck, CAS: 117695-55-3, 19.8 g, 70.7 mmol) in toluene (325 mL) and water (300 mL). K₂CO₃ (48.9 g, 353 mmol) and tetrakis(triphenylphosphine)palladium (Merck, 0.41 g, 0.35 mmol) are added and the mixture stirred overnight at reflux under nitrogen. The mixture is cooled to room temperature and the phases separated. The aqueous phase is extracted 3 times with ethyl acetate, the organic phases are combined and dried over Na₂SO₄, filtered and evaporated to dryness. The crude product is purified by silica chromatography using heptane as eluent, yielding 18.5 (67 %) of a colorless solid.

Step 2: Synthesis of 3,3',5-trivinyl-1,1'-biphenyl

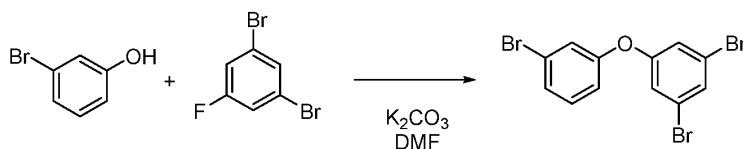
Example 7 is synthesized using 3,3',5-tribromo-1,1'-biphenyl (step 1) with the same conditions as step 3 of Example 1.

^1H NMR (500 MHz, Chloroform- d) δ = 7.68 (d, J = 1.9 Hz, 1H), 7.60 – 7.50 (m, 3H), 7.52 – 7.43 (m, 3H), 6.85 (ddd, J = 17.6, 10.9, 4.3 Hz, 3H), 5.94 – 5.85 (m, 3H), 5.37 (dd, J = 11.0, 4.6 Hz, 3H) ppm.

Synthesis Example 8: Preparation of 1,3-divinyl-5-(3-vinylphenoxy)benzene



Step 1: Synthesis of 1,3-dibromo-5-(3-bromophenoxy)benzene



15

3-Bromophenol (Merck, CAS: 591-20-8, 6.8 g, 39.4 mmol) is dissolved together with 1,3-dibromo-5-fluorobenzene (Merck, CAS: 1435-51-4, 10 g, 39.4 mmol) and K_2CO_3 (5.4 g, 39.4 mmol) in DMF (91.5 mL) and treated overnight at 160 °C under nitrogen. The reaction mixture is cooled to room temperature and treated with water, forming an oil. The aqueous phase is extracted twice with MTBE and the combined organic phases are dried with Na_2SO_4 , filtered and evaporated to dryness. Finally, the crude product is purified by silica chromatography (heptane/ethyl acetate, 9 : 1), wherein 13 g (81 %) of a colorless solid are obtained.

25

^1H NMR (500 MHz, Chloroform- d) δ = 7.45 (t, J = 1.6 Hz, 1H), 7.35 (ddd, J = 7.9, 1.8, 1.0 Hz, 1H), 7.27 (t, J = 8.1 Hz, 1H), 7.21 (t, J = 2.1 Hz, 1H), 7.10 (d, J = 1.6 Hz, 2H), 6.98 (ddd, J = 8.2, 2.4, 1.0 Hz, 1H) ppm.

Step 2: Synthesis of 1,3-divinyl-5-(3-vinylphenoxy)benzene

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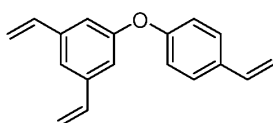
Example 8 is synthesized using 1,3-dibromo-5-(3-bromophenoxy)benzene (step 1) with the same conditions as step 3 of Example 1.

^1H NMR (500 MHz, Chloroform- d) δ = 7.33 (t, J = 7.9 Hz, 1H), 7.25 – 7.17 (m, 2H), 7.13 (t, J = 2.1 Hz, 1H), 7.02 (d, J = 1.4 Hz, 2H), 6.95 (dd, J = 8.1, 2.4 Hz, 1H), 6.71 (ddd, J = 17.6, 10.8, 6.7 Hz, 3H), 5.77 (d, J = 17.6 Hz, 3H), 5.31 (dd, J = 10.8, 3.1 Hz, 3H) ppm.

5

Synthesis Example 9: Preparation of 1,3-divinyl-5-(4-vinylphenoxy)benzene

benzene



10

Step 1: Synthesis of 1,3-dibromo-5-(4-bromophenoxy)benzene

The synthesis is carried out according to step 1 of Example 8, wherein 3-bromophenol is replaced by 4-bromophenol (Merck, CAS: 106-41-2). 11 g (69 %) of a colorless solid is obtained.

15

^1H NMR (500 MHz, THF- d_8) δ = 7.55 – 7.50 (m, 2H), 7.48 (t, J = 1.7 Hz, 1H), 7.16 (d, J = 1.7 Hz, 2H), 7.03 – 6.95 (m, 2H) ppm.

Step 2: Synthesis of 1,3-divinyl-5-(4-vinylphenoxy)benzene

Example 9 is synthesized using 1,3-dibromo-5-(4-bromophenoxy)benzene (step 1) with the same conditions as step 3 of Example 1.

20

^1H NMR (500 MHz, THF- d_8) δ = 7.42 – 7.36 (m, 2H), 7.25 (t, J = 1.6 Hz, 1H), 7.02 (d, J = 1.6 Hz, 2H), 6.99 – 6.93 (m, 2H), 6.68 (ddd, J = 17.6, 10.9, 3.0 Hz, 3H), 5.76 (dd, J = 17.6, 1.0 Hz, 2H), 5.67 (dd, J = 17.6, 1.0 Hz, 1H), 5.22 (dd, J = 11.0, 1.0 Hz, 2H), 5.14 (dd, J = 11.0, 1.0 Hz, 1H) ppm.

25

Part B: Preparing of photocurable compositions for evaluation of synthesized chemical compounds

- **Preparation of photocurable compositions as Ref. Example 1^a, 2^b, and as Example 1^a, 2^a, 3^a, 8^c and 9^c**

30

Table 1 shows an overview of a non-limiting number of different compositions based on just one vinylbenzene component together with either a) 3wt%

Irgacure OXE02 (BocSciences, CAS: 478556-66-0) & 3wt% Irgacure651 (Merck, CAS: 24650-42-8) or b) 3wt% Irgacure OXE02 & 3wt% Irgacure819 (Merck, CAS: 162881-26-7) or c) 6wt% Irgacure OXE02. Curing energy is 5.5 J/cm² at 365 nm.

5

For examples, Ref. Example 1^a in Table 1 means that the chemical compound from reference example 1 is used together with a) 3wt% Irgacure OXE02 (BocSciences, CAS: 478556-66-0) & 3wt% Irgacure651.

10 And Example 1^a means that the chemical compound from synthesis example 1 is used together with a) 3wt% Irgacure OXE02 (BocSciences, CAS: 478556-66-0) & 3wt% Irgacure651.

15 Similarly, example 2^a means that the chemical compound from synthesis example 2 is used together with a) 3wt% Irgacure OXE02 (BocSciences, CAS: 478556-66-0) & 3wt% Irgacure651.

Viscosities

20 The viscosities of the photocurable compositions are measured using an Anton Paar MCR 92 rheometer (Anton Paar, Graz, Austria) using a cone-plate geometry. Viscosities are determined at a shear rate of 500 s⁻¹ using a rotational cone-plate geometry (d = 25 mm) at 23 °C.

Thermal Stability of Photo-Cured Layers

25 Photo-cured films are prepared by applying a 60 µm thick layer of the photocurable composition in a sandwich set-up consisting of two glass slides and curing the film at room temperature with UV light with a wavelength of 365 nm in varying curing energies (5.5 J/cm² or 10 J/cm²). The films may have been baked after UV-curing at 250 °C for 2 min on a hotplate and then
30 measured via TGA (TA Discovery or TA TGA Q50).

- **Preparation of photocurable compositions as reference examples 4 and 5**

5 Reference photocurable compositions 4 and 5 including at least one of the polyvinylbenzene compounds are prepared as mentioned in Table 2. The compositions varied in the ratios of the polyvinyl compounds used. Reference example 4 contains a small amount of a poly-functional acrylate monomer (SR295, CAS: 4986-89-4). All compositions further contained 5.6 to 5.7wt% Irgacure OXE02.

10 - **Preparation of photocurable compositions as Working Examples (W.E.)10 to 14**

Photocurable compositions as W.E.10 to 14 are prepared as mentioned in Table 2. All compositions further contained 5.6 to 5.7wt% Irgacure OXE02.

15 Table 2 summarizes examples in which different ratios of different polyvinyl compounds and 5.6wt% Irgacure OXE02 are used. The photocurable compositions are cured with 10 J/cm² using a post-exposure bake at 250 °C for 2 min on a hotplate.

20 Table 1:

25

30

	Example	C- content	Viscosity (23 °C)	T _{d2%}	weight loss/min
5	Ref.example 1 ^a	91.70%	8.8 cP	-	0.79%/min
	Example 1 ^a	91.70%	22.0 cP	435 °C	0.09 %/min
	Example 2 ^a	91.70%	23.9 cP	-	0.75%/min
	Example 3 ^a	91.70%	22.4 cP	-	0.06%/min
10	Ref.example 2 ^b	92.10%	23.0 cP	446 °C	0.87%/min
	Example 8 ^c	86.40%	16.0 cP	426 °C	-
	Example 9 ^c	86.40%	37.0 cP	478 °C	0.03%/min

15 ^a 3wt% IrgacureOXE02 & 3 wt% Irgacure651
 ^b 3wt% IrgacureOXE02 & 3 wt% Irgacure819
 ^c 6wt% IrgacureOXE02

Table 2:

20

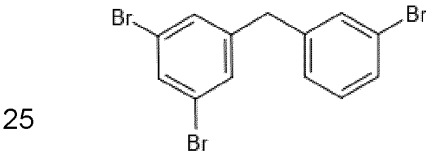
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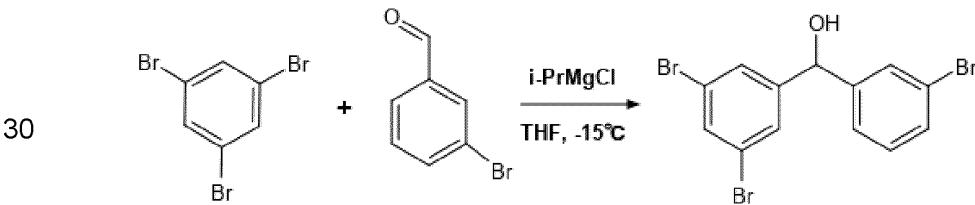
	Working Example	Compound d 1	Compound d 2	Compound d 3	Viscosity (23 °C)	T _{d2%}
5	Ref. example 4	47.2 wt% Ref. Example 2	47.2 wt% Ref. Example 3	-	9.7 cP	432 °C
	Ref. Example 5	47.2 wt% Ref. Example 2	37.7 wt% Ref. Example 3	9.4 wt% SR295	11.0 cP	395 °C
	W.E.10	47.2 wt% Ref. Example 2	18.9 wt% Ref. Example 3	28.3 wt% Example 5	28.0 cP	460 °C
10	W.E.11	56.6 wt% Ref. Example 2	37.7 wt% Example 7	-	47.0 cP	461 °C
	W.E.12	56.6 wt% Ref. Example 2	37.7 wt% Example 8	-	18.4 cP	435 °C
	W.E.13	56.6 wt% Ref. Example 2	37.7 wt% Example 1	-	24.3 cP	450 °C
15	W.E.14	47.2 wt% Example 8	47.2 wt% Example 9	-	24.9 cP	450 °C

20 **Part C: Synthesis of preferred specific polyhalogenated benzene examples:**

Example C-1: 1,3-dibromo-5-(3-bromobenzyl)benzene:



Step 1: Synthesis of (3-bromophenyl)(3,5-dibromophenyl)methanol



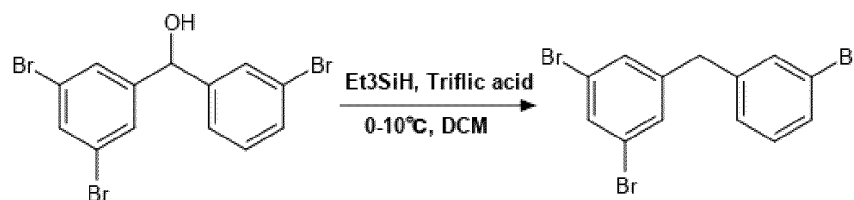
Synthesis option a)

1,3,5-Tribromobenzene (5 g, 0.02 mol) is dissolved in tetrahydrofuran (0.617 mol). The solution is cooled to -15 °C and Isopropyl magnesium chloride solution (2 M in THF, 8.3 mL, 0.02 mol) is added dropwise. The reaction mixture is stirred for 2h at this temperature. Then, the reaction temperature is increased to 0 °C and 3-bromobenzaldehyde (3.8 g, 0.017 mol) dissolved in THF (16.8 mL, 0.208 mol) is added. The reaction mixture is stirred for 1 h at 0 °C and afterwards it is brought to room temperature. The mixture is carefully quenched with hydrochloric acid (40 mL, 0.04 mol). Dichloromethane is added and the aqueous phase is separated. The organic phase is washed twice with DI water and the solvent is removed under vacuum at 40 °C. A beige brown residue is obtained (6.6 g, 98.7% yield).

Synthesis option b)

1,3,5-Tribromobenzene (56.2 g, 0.178 mol) is dissolved in diethyl ether (4.86 mol). The suspension is cooled to -70 °C and n-butyllithium solution (2.5 M in hexane, 46.2 mL 0.195 mol) is added dropwise. The reaction mixture is stirred for 1 h at this temperature. Then, 3-bromobenzaldehyde (30 g, 0.16 mol) is added dropwise. The reaction mixture is brought to room temperature. The solution is carefully quenched with isopropanol (2.9 g, 0.049 mol). The organic layer is washed 3 times with DI water. Afterwards, the solvent is removed under vacuum at 40 °C. A beige brown residue is obtained (74.4 g, 93.7% yield).

Step 2: Synthesis of 1,3-dibromo-5-(3-bromobenzyl)benzene

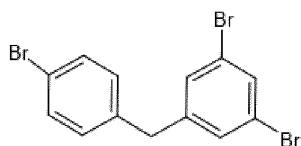


(3-Bromophenyl)(3,5-dibromophenyl)methanol (2.84 g, 0.0067 mol) is dissolved in 20 mL DCM. Triethyl silane (3.16 g, 0.027 mol) is added and

the mixture is cooled to 0 °C. Trifluoromethanesulfonic acid (4.0 g, 0.027 mol) is added dropwise and the mixture stirred at room temperature for 3 h. Afterwards, the reaction is quenched with DI water (20 g, 1.1 mol). The organic layer is washed several times with water and NaHCO₃-sol. (5%).
5 Afterwards, the solvent is removed under vacuum (40 °C), resulting in a brownish solid (5.5 g). The crude product (91.7% purity, HPLC) is purified via crystallization in n-heptane. The product (1.8 g, 97% purity) is obtained with a yield of 63.9%.

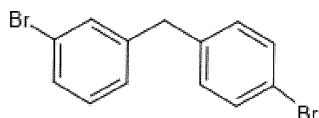
Alternatives to trifluoromethanesulfonic acid are e.g. trifluoroacetic acid and
10 trimethylsilyl trifluoromethansulfonate.

Example 2 (C-2): 1,3-dibromo-5-[(4-bromophenyl)methyl]benzene:



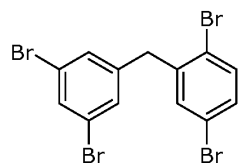
In general, the same synthesis conditions are used as for example C-1. In step 1, 4-bromobenzaldehyde (Merck, CAS: 1122-91-4) is used instead of 3-bromobenzaldehyde.

Example 3 (C-4): 1-bromo-3-[(4-bromophenyl)methyl]benzene:



In general, the same synthesis conditions are used as for example C-1. In step 1, 1,3-dibromobenzene (Merck, CAS: 108-36-1) is used instead of 1,3,5-tribromobenzene and 4-bromobenzaldehyde (Merck, CAS: 1122-91-4) instead of 3-bromobenzaldehyde.

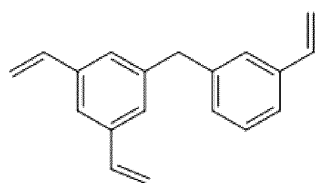
Example 4 (C-4): 1,4-dibromo-2-(3,5-dibromobenzyl)benzene



5 In general, the same synthesis conditions are used as for example C-1. In step 1, 2,5-dibromobenzaldehyde (Merck, CAS: 74553-29-04) is used instead of 3-bromobenzaldehyde.

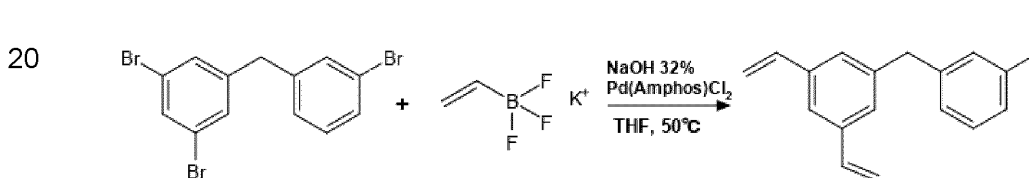
Part D: Synthesis of preferred specific polyvinyl benzene examples:

10 **Example D-1: 1,3-diethenyl-5-[(3-ethenylphenyl)methyl]benzene:**



15 Step 1 & step 2 follow the same procedure as described in part C for the synthesis of preferred specific polyhalogenated benzene examples.

Step 3: Synthesis of 1,3-diethenyl-5-[(3-ethenylphenyl)methyl]benzene



25 1,3-dibromo-5-[(3-bromophenyl)methyl]benzene (500 g, 1.2 mol, from Exaple C-1), potassium vinyltrifluoroborate (95%, 565 g, 4.0 mol) and bis-(di-*tert*-butyl-(4-dimethylaminophenyl)-phosphin)-dichloro-palladium(II) (1.3g, 0.0032 mol) are dissolved in tetrahydrofuran (4.3 L). The mixture is heated up to 50 °C. At this temperature, a sodium hydroxide solution (w-50%, 1.19 L, 14.6 mol) is added dropwise. The reaction mixture is stirred overnight at 50 °C. Then, 2.6 L n-heptane (17.9 mol) and 14.9 L water are added. The aqueous phase is separated. A solution of N-acetylcysteine (99.2 g, 0.61 mol) in water (3.3L, 183.3 mol) is added to the organic layer.

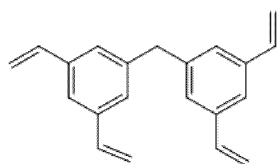
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The mixture is heated up to 60 °C and stirred for 1 h. Afterwards, the aqueous phase is separated. The organic phase is fritted over aluminum oxide. The solvent of the obtained filtrate is removed under vacuum (40 °C), resulting in the liquid product (282.4g, 94.2% yield).

5 GC-MS: 96.1% product.

Example D-2: 1-[(3,5-diethenylphenyl)methyl]-3,5-diethenylbenzene:

10

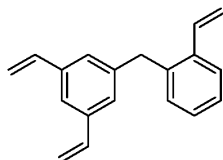


In general, the same synthesis conditions are used as for example D-1. In step 1, 3,5-dibromobenzaldehyde (Merck, CAS: 56990-02-4) is used instead of 3-bromobenzaldehyde.

15 4.5 g (63% yield) of a colorless solid is obtained in the Suzuki step.

Example D-3: 1,3-divinyl-5-(2-vinylbenzyl)benzene

20

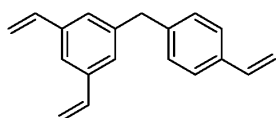


In general, the same synthesis conditions are used as for example D-1. In step 1, 2-bromobenzaldehyde (Merck, CAS: 6630-33-7) is used instead of 3-bromobenzaldehyde.

25 4.4 g (90% yield) of a colorless liquid is obtained in the Suzuki step.

Example D-4: 1,3-divinyl-5-(4-vinylbenzyl)benzene

30

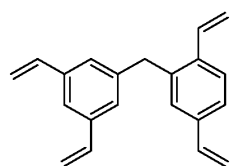


In general, the same synthesis conditions are used as for example D-1. In step 1, 4-bromobenzaldehyde (Merck, CAS: 1122-91-4) is used instead of 3-bromobenzaldehyde.

17.5 g (97% yield) of a colorless liquid is obtained in the Suzuki step.

5

Example D-5: 1,4-divinyl-2-(3,5-divinyl)benzene



10

In general, the same synthesis conditions are used as for example D-1. In step 1, 2,5-dibromobenzaldehyde (Merck, CAS: 74553-29-04) instead of 3-bromobenzaldehyde.

15

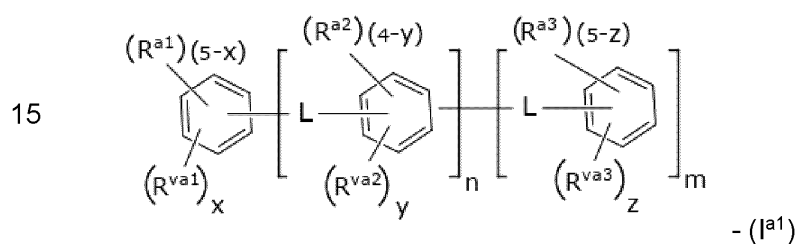
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Claims

1. Method for synthesizing a chemical compound, comprising at least a
 5 following step;
 (I^x) Applying Suzuki-Coupling to a precursor compound represented by the
 following chemical formula (I^{a1}) in the presence of an organoboron
 compound containing a group selected from one or members of the group
 selected from a vinyl group, alkyl vinyl group having carbon atoms 3 to 5
 10 and a vinyl alcohol group; to form a chemical compound derived from said
 precursor compound of (I^{a1}).



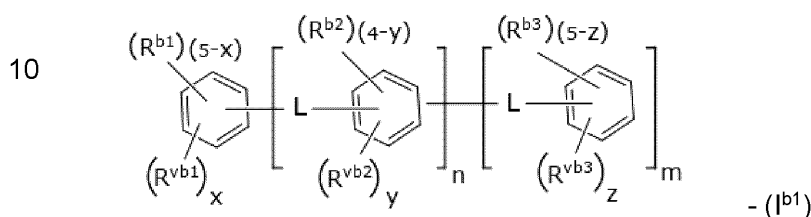
where

- 20 $1 \leq x \leq 5$, $0 \leq y \leq 4$, $0 \leq z \leq 5$;
 n is 1 or 0, m is 1 or 0, $1 \leq n+m \leq 2$, preferably $n+m=1$, more preferably $n=0$,
 $m=1$;
 $3 \leq x+z \leq 10$ when m is 1 and n is 0, $3 \leq x+y \leq 9$ when m is 0 and n is 1, and
 $3 \leq x+z+y \leq 14$ when m and n are both 1;
 R^{va1} , R^{va2} and R^{va3} are hydrogen atom, preferably it is selected from F, Cl,
 25 Br, I, more preferably it is Br;
 R^{a1} , R^{a2} and R^{a3} are at each occurrence, independently or dependently of
 each other, selected from H, D or alkyl group having carbon atoms 1 to 5;
 L is at each occurrence, same or differently selected from the group
 consisting of a direct bond, alkylene group having carbon atoms 1 to 15,
 30 and alkenylene group having carbon atoms 2 to 15,

where one or more non-adjacent CH₂ groups of said alkylene or alkenylene group may be replaced by oxygen atom, C=O, C=S, C=Se, C=NH, SiH₂, SO, SO₂, OS, or CONH and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂.

5

2. The method of claim 1, wherein the chemical compound derived from the precursor compound of (I^{a1}) is represented by chemical formula (I^{b1})



where

15

$1 \leq x \leq 5$, $0 \leq y \leq 4$, $0 \leq z \leq 5$;

n is 1 or 0, m is 1 or 0, $1 \leq n+m \leq 2$, preferably $n+m=1$, more preferably $n=0$, $m=1$;

$3 \leq x+z \leq 10$ when m is 1 and n is 0, $3 \leq x+y \leq 9$ when m is 0 and n is 1, and

$3 \leq x+z+y \leq 14$ when m and n are both 1;

20

R^{vb1} , R^{vb2} and R^{vb3} are at each occurrence, independently or dependently of each other, selected from vinyl group, alkyl vinyl group having carbon atoms 3 to 5 or vinyl alcohol group, preferably it is vinyl group;

R^{b1} , R^{b2} and R^{b3} are at each occurrence, independently or dependently of each other, selected from H, D or alkyl group having carbon atoms 1 to 5;

25

L is at each occurrence, same or differently selected from the group consisting of a direct bond, alkylene group having carbon atoms 1 to 15, and alkenylene group having carbon atoms 2 to 15,

where one or more non-adjacent CH₂ groups of said alkylene or alkenylene group may be replaced by oxygen atom, C=O, C=S, C=Se, C=NH, SiH₂,

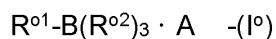
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SO, SO₂, OS, or CONH and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂, wherein the formula (I) does not include 1,1'-Biphenyl, 3,4',5-triethenyl.

3. The method of claim 1 or 2, wherein L is a direct bond, straight alkylene group having carbon atoms 1 to 5 or straight alkenylene group having carbon atoms 2 to 5, preferably L is a straight alkylene group having carbon atoms 1 to 5 or straight alkenylene group having carbon atoms 2 to 5, wherein one or more non-adjacent CH₂ groups of said alkylene or alkenylene group may be replaced by oxygen atom, C=O, C=S, C=Se, C=NH, SiH₂, SO, SO₂, OS, or CONH and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂, more preferably L is a straight alkylene group having carbon atoms 1 to 5.

4. The method of any one of claims 1 to 3, wherein n is 0 and m is 1.

5. The method of any one of preceding claims, wherein said organoboron compound contains at least one vinyl group, preferably said organoboron compound is represented by chemical formula (I^o);



where

R^{o1} is vinyl group, alkyl vinyl group having carbon atoms 3 to 5 or vinyl alcohol group, preferably it is vinyl group;

R^{o2} is a hydrogen atom, preferably it is each independently of each other, at each occurrence, selected from F, Cl, Br, I, more preferably it is F;

A is a monovalent cation, preferably it is selected from H⁺, Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Fr⁺, more preferably it is Li⁺, Na⁺, K⁺, Rb⁺, even more preferably it is K⁺.

6. The method of any one of preceding claims, wherein Suzuki-Coupling of step (I^x) is performed in the presence of a palladium catalyst, preferably said palladium catalyst is selected from one or more members of the group consisting of a palladium catalyst represented by the following formula (I^p),

$\text{Pd}_2(\text{dba})_3\text{-n}(\text{dba})$, $\text{Pd}_2(\text{dba})_3$, $\text{Pd}(\text{OAc})_2$, $\text{Pd}(\text{PPh}_3)_4$ and [1,3-Bis(2,6-Diisopropylphenyl)imidazole-2-ylidene](3-chloropyridyl)palladium(II) dichloride;

5 $\text{Pd}(\text{R}^{\text{P1}})_2 \cdot (\text{X}^{\text{P}})_2 \cdot (\text{I}^{\text{P}})$

where

R^{P1} is a hydrogen atom, preferably it is each independently of each other, at each occurrence, selected from F, Cl, Br, I, more preferably it is Cl;

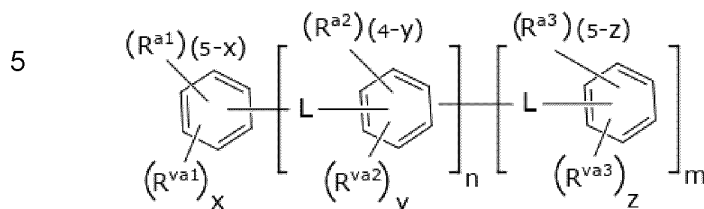
10 X^{P} is Amphos (di-tert-butyl (4-dimethylaminophenyl)phosphine) or dtbpf (di-tert-butylphosphino)ferrocene). Preferably, said palladium catalyst is selected from $\text{Pd}(\text{R}^{\text{P1}})_2 \cdot (\text{X}^{\text{P}})_2 \cdot (\text{I}^{\text{P}})$ where X^{P} is Amphos (di-tert-butyl (4-dimethylaminophenyl)phosphine), $\text{Pd}_2(\text{dba})_3\text{-n}(\text{dba})$ or $\text{Pd}_2(\text{dba})_3$.

15 7. The method of any one of preceding claims, wherein the step (I^{x}) is carried out at the temperature in the range from 10°C to 90°C, preferably it is in the range from 20 to 80°C, more preferably from 35 to 65°C.

20 8. The method of any one of preceding claims, wherein the step (I^{x}) is carried out in the presence of a solvent or a solvent mixture. Preferably said solvent or solvents of the solvent mixture is/are selected from one or more of polar aprotic solvents, preferably it is selected from one or more members of the group consisting of dichloromethane (BP: 39.6°C), acetone (BP: 56.05°C), tetrahydrofuran (BP: 66°C), ethyl acetate (BP: 77°C), acetonitrile (BP: 81.3-82.1°C), pyridine (BP: 115°C), dimethylformamide (BP: 153°C), dimethyl sulfoxide (BP: 189°C), hexamethylphosphoramide (BP: 235.5°C), dimethylpropyleneurea (BP: 246.5°C) and sulfolane (BP: 286°C).

30 9. The method of any one of preceding claims further contains following step (I^{w});

(I^w) performing deoxygenation of an alcohol group of a precursor compound represented by chemical formula (I^{c1}) by applying an acid catalyst and a reducing agent to synthesize the precursor compound of (I^{a1}).



(I^{c1}) it is tentative one.

Shall be replaced with the optimized one later)

where

$1 \leq x \leq 5$, $0 \leq y \leq 4$, $0 \leq z \leq 5$;

n is 1 or 0, m is 1 or 0, $1 \leq n+m \leq 2$, preferably $n+m=1$, more preferably $n=0$, $m=1$;

$3 \leq x+z \leq 10$ when m is 1 and n is 0, $3 \leq x+y \leq 9$ when m is 0 and n is 1, and

$3 \leq x+z+y \leq 14$ when m and n are both 1;

R^{va1} , R^{va2} and R^{va3} are hydrogen atom, preferably it is selected from F, Cl, Br, I, more preferably it is Br;

R^{a1} , R^{a2} and R^{a3} are at each occurrence, independently or dependently of each other, selected from H, D or alkyl group having carbon atoms 1 to 5;

L is at each occurrence, same or differently selected from an alkylene group having carbon atoms 1 to 15, and alkenylene group having carbon atoms 2 to 15,

where at least one non-adjacent CH_2 group of said alkylene or alkenylene group is replaced by COH.

10. The method of claim 9, wherein said acid catalyst is trifilic acid (TFMSA), trifluoroacetic acid (TFA), Boron Trifluoride – Diethyl Ether Complex (BF_3OEt_2), Indium(III) chloride ($InCl_3$); and said reducing agent is Triethylsilane (Et_3SiH), Dimethylchlorosilane (Me_2SiHCl), sodium borohydride ($NaBH_4$). Preferably, a combination of trifilic acid (TFMSA) as the acid catalyst and Triethylsilane (Et_3SiH) as the reducing agent, a

combination of trifluoroacetic acid (TFA) and Triethylsilane (Et_3SiH), a combination of Dimethylchlorosilane (Me_2SiHCl) and Indium(III) chloride (InCl_3), a combination of trifluoroacetic acid (TFA) and sodium borohydride (NaBH_4) are used in step (I^w) of claim 9.

5

11. The method of claim 9 or 10, wherein the step (I^w) is carried out at the temperature in the range from -20°C to 20°C , preferably from -10°C to 10°C .

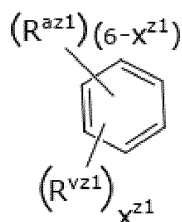
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12. The method of any one of claims 9 to 11, wherein the step (I^w) is carried out in the presence of a solvent or a solvent mixture. Preferably said solvent or solvents of the solvent mixture is/are selected from alkyl halides, preferably it is selected from one or more members of the group consisting of alkyl fluorides, alkyl chlorides, alkyl bromides, and alkyl iodides, more preferably selected from chloromethane, dichloromethane (DCM), trichloromethane(chloroform), chloroethane, dichloroethane, trichloroethane, bromomethane, dibromomethane, bromoethane, dibromoethane and any combination of thereof; preferably selected from dichloromethane (DCM), trichloromethane(chloroform) or a mixture of them.

15

13. The method of any one of preceding claims, further contains following step (I^z), preferably after step (I^w); (I^z) reacting precursor A represented by formula (I^{z1}) and precursor B represented by formula (I^{z2}) in the presence of $n\text{BuLi}$.

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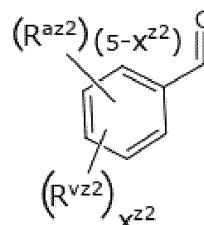


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precursor A

- (I^{z1});

precursor B

- (I^{z2})

wherein

X^{z1} is 1 to 6; X^{z2} is 0 to 5;

R^{vz1} and R^{vz2} are hydrogen atom, preferably it is selected from F, Cl, Br, I, more preferably it is Br;

R^{az1} and R^{az2} are at each occurrence, independently or dependently of each other, selected from H, D or alkyl group having carbon atoms 1 to 5.

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14. The method of claim 13, wherein said reaction step (I^2) is performed in the presence of a solvent or a solvent mixture, preferably it is selected from diethyl ether, tetrahydrofuran (THF), tetramethylethylenediamine (TMEDA) or a combination of any of them.

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15. A chemical compound obtained or obtainable by the process of any one of claims 1 to 14.

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