

**OLYVINYL SUBSTITUTED DI- AND TRI- PHENYL COMPOUNDS
FOR USE IN FORMING SPIN-ON LAYERS**

Field of the invention

5 The present invention relates to a reactive chemical compound, preferably being a photo-curable compound, use of the compound, method for forming a layer, and a cured layer.

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

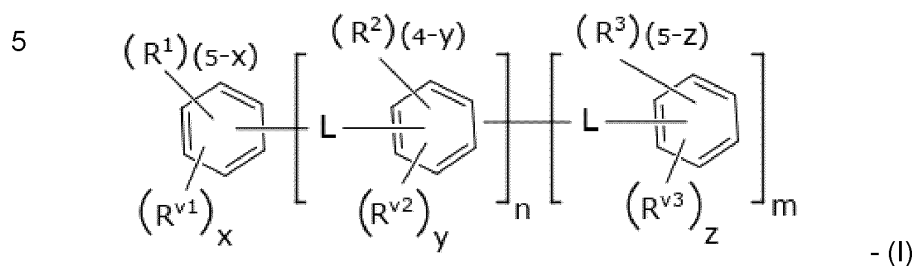
Summary of the invention

- 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 chemical compound which may realize a carbon-rich flat
 underlayer; providing a new compound having a low viscosity with relatively
 low vapor pressure, preferably suitable for ink-jet printing, providing a new
 chemical compound having improved crosslinking property, preferably
20 which may form highly crosslinked thermosets after UV-induced radical
 polymerization; and/or providing a new chemical compound may realize
 improved thermal stability after curing, preferably at about 350°C or more;
 lower shrinkage after curing; and/or improved etching resistance of a cured
 layer; improved planarization performance of a cured layer, namely over
25 different pattern topographies of a substrate.

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

- 30 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 chemical compound represented by chemical formula (I)



10 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
 15 $3 \leq x+z+y \leq 14$ when m and n are both 1;
 R^{v1} , R^{v2} and R^{v3} 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^1 , R^2 and R^3 are at each occurrence, independently or dependently of
 20 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
 25 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 by D, F, Cl, Br, I, CN or NO_2 , wherein the formula (I) does not include 1,1'-Biphenyl, 3,4',5-triethenyl.

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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.

- 5 In another aspect, the present invention also relates to use of the compound of the present invention, for Inkjet Adaptive Planarization composition.

- 10 In another aspect, the present invention also relates to a method for forming a layer, preferably for forming an underlayer Spin-on carbon comprises the following step:

(i) Applying the compound of the present invention for Inkjet Adaptive Planarization.

- 15 In another aspect, the present invention also relates to a cured layer, preferably it is a photo-cured layer formed from the compound of the present invention.

Technical effects of the invention

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

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.

5 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
10 term “about.”

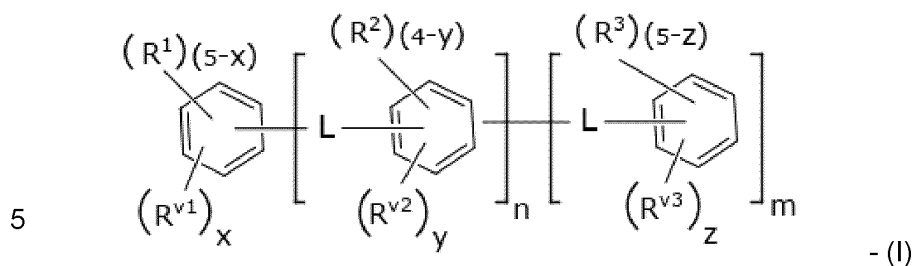
Where a numerical range is disclosed herein such range is continuous, inclusive of both the minimum and maximum values of the range as well as every value between such minimum and maximum values. Still
15 further, where a range refers to integers, every integer between the minimum and maximum values 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
20 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
25 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 chemical compound is represented by chemical formula (I)

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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^{v1} , R^{v2} and R^{v3} 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^1 , R^2 and R^3 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 , 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.

In a preferred embodiment of the present invention, R^{v1} , R^{v2} and R^{v3} 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

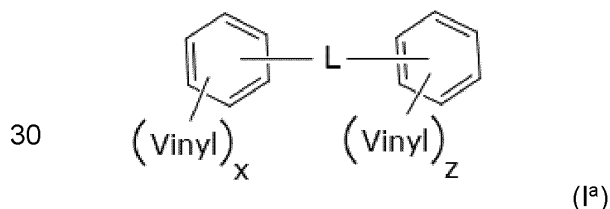
may further lead improved thermal stability of the cured film and chemical resistance.

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.

Preferably, L of the chemical formula (I) is a direct bond, straight alkylene group having carbon atoms 1 to 5, 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.

Preferably n is 0 and m is 1.

In a preferred embodiment of the present invention, the compound is represented by one of the following chemical formulae (I^a)



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,

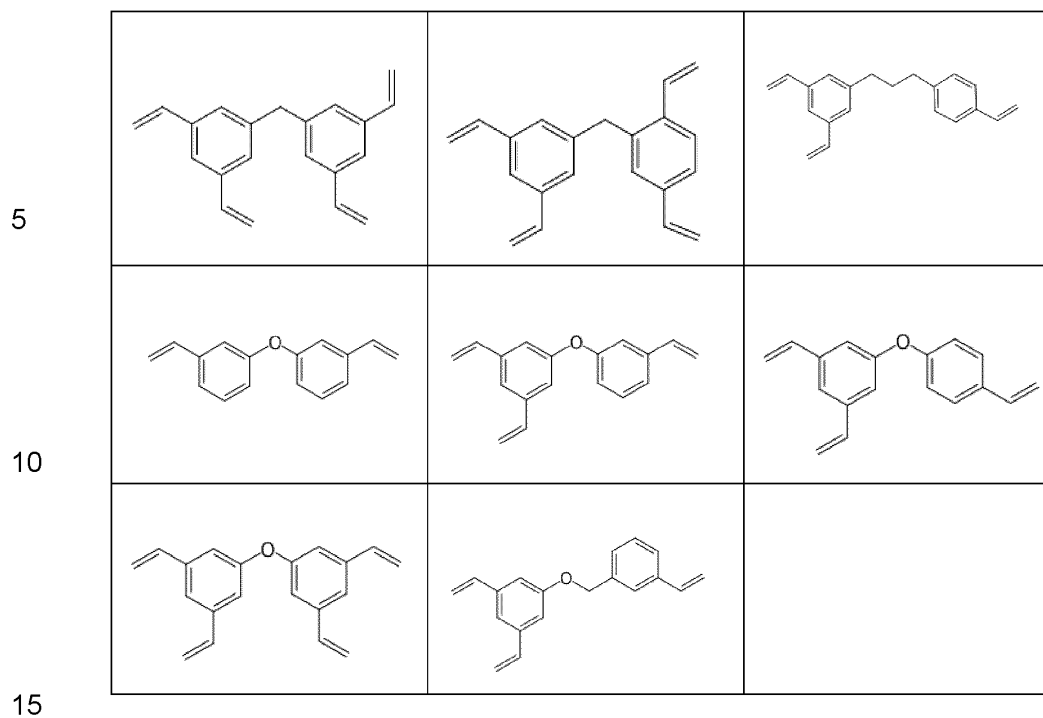
wherein one or more non-adjacent CH_2 groups of said alkylene or

5 alkenylene group may be replaced by oxygen atom, $\text{C}=\text{O}$, $\text{C}=\text{S}$, $\text{C}=\text{Se}$,
 $\text{C}=\text{NH}$, SiH_2 , 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 .

Below table A shows preferable examples of the compound.

10 Table A:

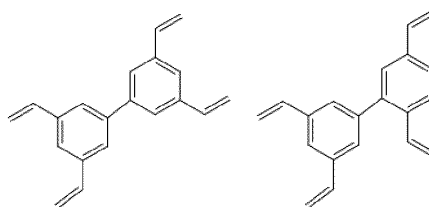
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In one preferred embodiment of the present invention, L is a direct bond,
 $2 \leq x \leq 5$, $2 \leq z \leq 5$, $4 \leq x+z \leq 10$.

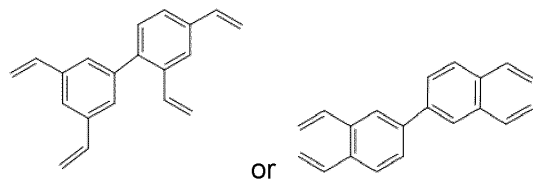
Below is the examples of the above mentioned preferred embodiment.

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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.

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

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Such chemical compounds can be synthesized by using a publicly known method or the method disclosed in the synthesis examples described below in the section of **“Examples.”**

5 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.

10 In another aspect, the present invention also relates to use of the compound of the present invention, for Inkjet Adaptive Planarization composition.

In another aspect, the present invention also relates to a method for forming a layer, preferably for forming an underlayer Spin-on carbon
15 comprises the following step:

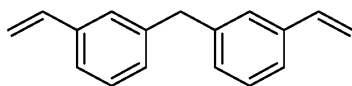
(ii) Applying the compound of the present invention for Inkjet Adaptive Planarization.

20 In another aspect, the present invention also relates to a cured layer, preferably it is a photo-cured layer formed from the compound of the present invention. In a preferable embodiment, said 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.

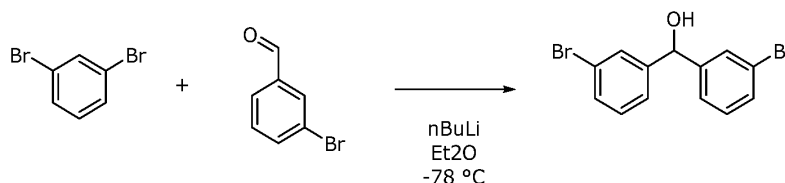
25 The present invention is further illustrated by the examples following herein- after which shall in no way be construed as limiting. The skilled person will acknowledge that various modifications, additions and alternations may be made to the invention without departing from the spirit and scope of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

Examples

Part A: Synthesis of chemical compounds

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

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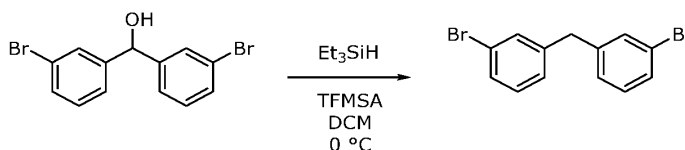
Step 1: Synthesis of bis(3-bromophenyl)methanol

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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.

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

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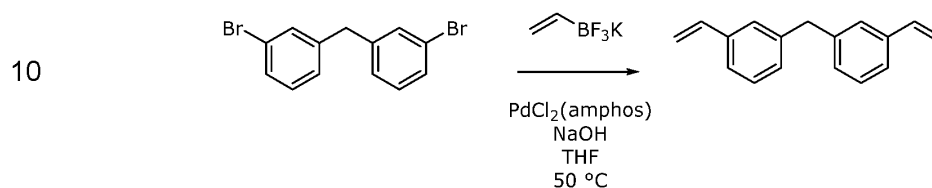
Bis(3-bromophenyl)methanol (51.6 g, 140 mmol) is dissolved in 400 mL DCM, treated with triethylsilane (Merck, CAS: 617-86-7, 88 mL, 550 mmol) and cooled to 0 °C. Trifluoromethanesulfonic acid (Merck, CAS: 1493-13-6, 48 mL, 550 mmol) is added dropwise and the mixtures stirred at room temperature for 3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

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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) ppm.

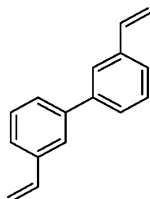
Step 3: Synthesis of bis(3-vinylphenyl)methane



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 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.

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.

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



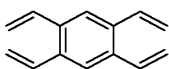
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Reference Example 2 is synthesized using 3,3'-dibromo-1,1'-biphenyl (CAS: 16400-51-4) with the same conditions as step 3 of Reference Example 1.

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.

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



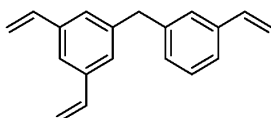
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Reference Example 3 is synthesized using 1,2,4,5-tetrabromobenzene (Merck, CAS: 636-28-2) with the same conditions as step 3 of Reference Example 1.

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.

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



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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.

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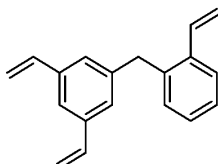
18.5 g (78%) of a colorless liquid is obtained in the Suzuki step.

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

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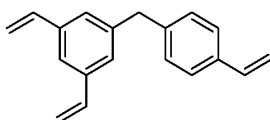
10 In general, the same synthesis conditions are used as for Reference Example 1. In step 1, 1,3,5-tribromobenzene (Merck, CAS: 626-39-1) is used instead of 1,3-dibromobenzene and 2-bromobenzaldehyde (Merck, CAS: 6630-33-7) instead of 3-bromobenzaldehyde.

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

15 ^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.

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



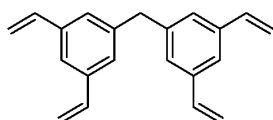
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In general, the same synthesis conditions are used as for Reference Example 1. In step 1, 1,3,5-tribromobenzene (Merck, CAS: 626-39-1) is used instead of 1,3-dibromobenzene and 4-bromobenzaldehyde (Merck, CAS: 1122-91-4) instead of 3-bromobenzaldehyde.

30 17.5 g (97%) of a colorless liquid is obtained in the Suzuki step.

^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.

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

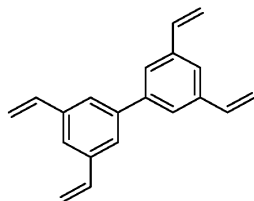


10 In general, the same synthesis conditions are used as for Reference Example 1. In step 1, 1,3,5-tribromobenzene (Merck, CAS: 626-39-1) is used instead of 1,3-dibromobenzene and 3,5-dibromobenzaldehyde (Merck, CAS: 56990-02-4) instead of 3-bromobenzaldehyde.

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

15 ^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.

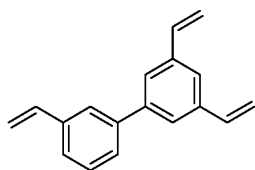
20 **Synthesis Example 5:** Preparation of 3,3',5,5'-tetravinyl-1,1'-biphenyl



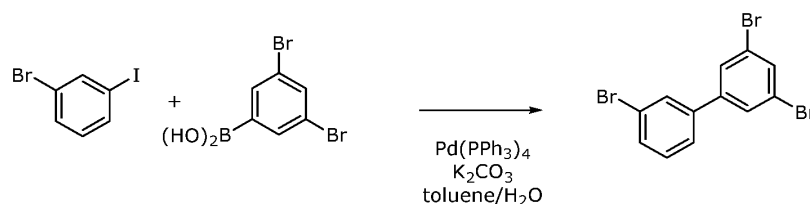
25 Example 5 is synthesized using 3,3',5,5'-tetrabromobiphenyl (CAS: 16400-50-3) with the same conditions as step3 of Reference Example 1.

^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.

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



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



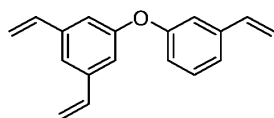
10 3-Bromo-1-iodobenzene (Merck, CAS: 591-18-4, 20 g, 70.7 mmol) is dissolved together with 3,5-dibromophenylboronic acid (Merck, CAS: 117695-55-3, 19.8 g, 70.7 mmol) in toluene (325 mL) and water (300 mL). K_2CO_3 (48.9 g, 353 mmol) and tetrakis(triphenylphosphine)palladium (Merck, 0.41 g, 0.35 mmol) are added and the mixture stirred overnight at
15 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 Na_2SO_4 , filtered and evaporated to dryness. The crude product is purified by silica chromatography using heptane as eluent, yielding 18.5 (67 %) of a colorless
20 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.

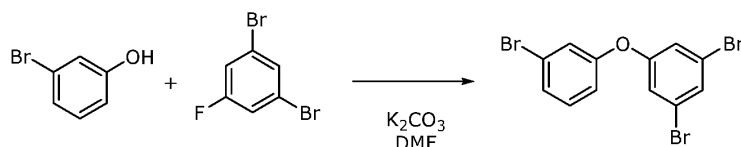
25 1H NMR (500 MHz, Chloroform- d) δ = 7.68 (d, J = 1.9 Hz, 1H), 7.60 – 7.50 (m, 3H), 7.52 – 7.43 (m, 3H), 6.85 (ddd, J = 17.6, 10.9, 4.3 Hz, 3H), 5.94 – 5.85 (m, 3H), 5.37 (dd, J = 11.0, 4.6 Hz, 3H) ppm.

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



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

5



10

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

15 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.

20

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

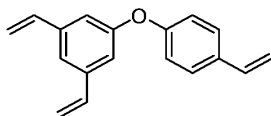
25

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.

30

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



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.

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.

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.

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

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

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) & 3 wt% Irgacure651.

5 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) & 3 wt% Irgacure651.

10 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) & 3 wt% Irgacure651.

Viscosities

15 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

20 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
25 measured via TGA (TA Discovery or TA TGA Q50).

- Preparation of photocurable compositions as reference examples 4 and 5

30 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.

- 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.

Table 2 summarizes examples in which different ratios of different polyvinyl compounds and 5.6 wt% 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.

Table 1:

Example	C-content	Viscosity (23 °C)	T _{d2%}	weight loss/min
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
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

^a 3wt% IrgacureOXE02 & 3 wt% Irgacure651

^b 3wt% IrgacureOXE02 & 3 wt% Irgacure819

^c 6 wt% IrgacureOXE02

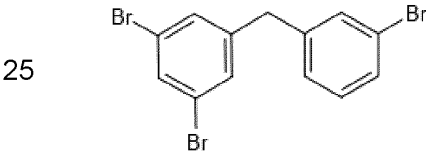
Table 2:

	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
10	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
	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
15	W.E.13	56.6 wt% Ref. Example 2	37.7 wt% Example 1	-	24.3 cP	450 °C
	W.E.14	47.2 wt% Example 8	47.2 wt% Example 9	-	24.9 cP	450 °C

20

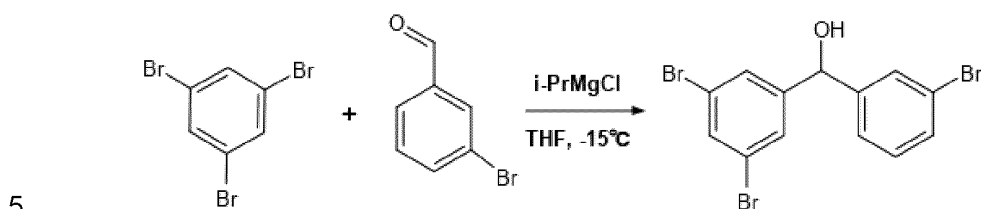
Part C: Synthesis of preferred specific polyhalogenated benzene examples:

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



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

30



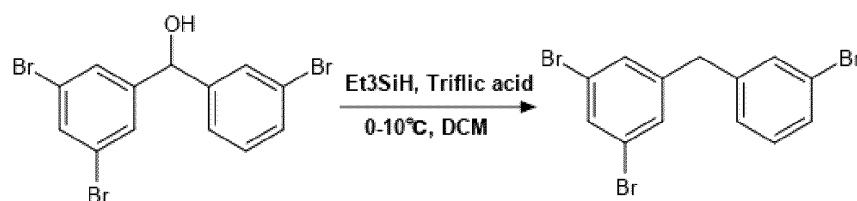
Synthesis option a)

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 2 h 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).

20 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).

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



5

(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%). 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%.

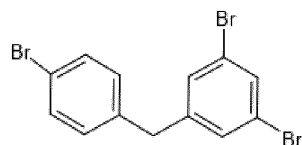
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15

Alternatives to trifluoromethanesulfonic acid are e.g. trifluoroacetic acid and trimethylsilyl trifluoromethanesulfonate.

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

20

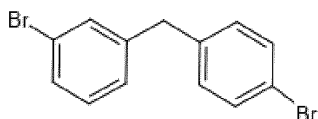


In general, the same synthesis conditions are used as for example C-1. In step 1, 4-bromobenzaldehyde (Merck, CAS: 1122-91-4) is used instead of 3-bromobenzaldehyde.

25

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

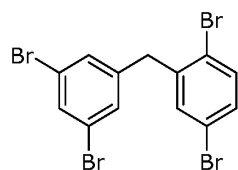
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In general, the same synthesis conditions are used as for example C-1. In step 1, 1,3-dibromobenzene (Merck, CAS: 108-36-1) is used instead of 1,3,5-tribromobenzene and 4-bromobenzaldehyde (Merck, CAS: 1122-91-4) instead of 3-bromobenzaldehyde.

5

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



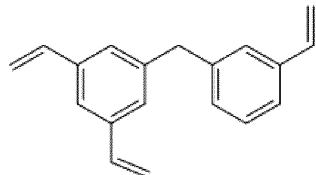
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In general, the same synthesis conditions are used as for example C-1. In step 1, 2,5-dibromobenzaldehyde (Merck, CAS: 74553-29-04) is used instead of 3-bromobenzaldehyde.

15

Part D: Synthesis of preferred specific polyvinyl benzene examples:

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

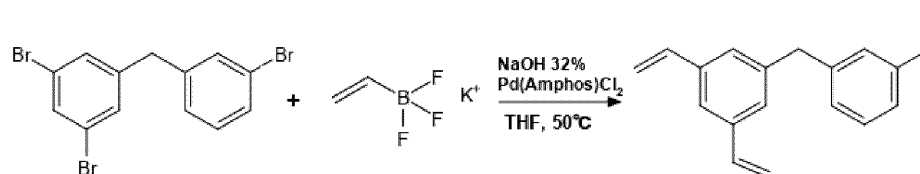


20

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

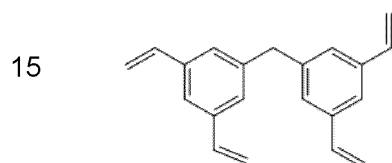


30

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)

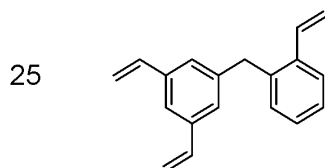
(1.3g, 0.0032 mol) are dissolved in tetrahydrofuran (4.3 L). The mixture is heated up to 50 °C. At this temperature, a sodium hydroxide solution (w-50%, 1.19 L, 14.6 mol) is added dropwise. The reaction mixture is stirred overnight at 50 °C. Then, 2.6 L n-heptane (17.9 mol) and 14.9 L water are added. 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. The mixture is heated up to 40 °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). GC-MS: 96.1% product.

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

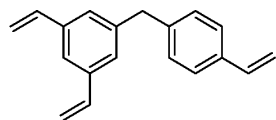


In general, the same synthesis conditions are used as for example D-1. In step 1, 3,5-dibromobenzaldehyde (Merck, CAS: 56990-02-4) is used instead of 3-bromobenzaldehyde. 4.5 g (63% yield) of a colorless solid is obtained in the Suzuki step.

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



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

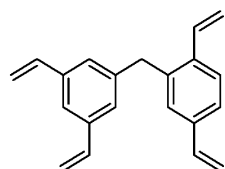
Example D-4: 1,3-divinyl-5-(4-vinylbenzyl)benzene

5

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.

10

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

15

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.

20

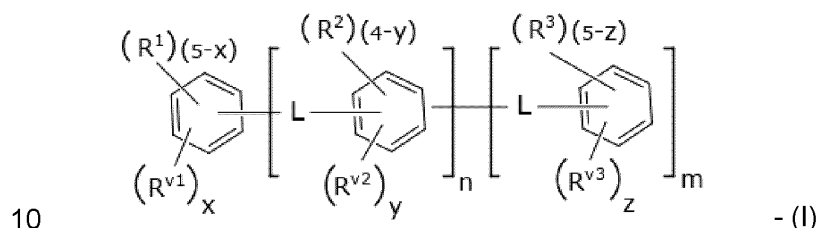
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30

Patent Claims

1. A chemical compound represented by chemical formula (I)

5



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 $n=0$, $m=1$;

15

$3 \leq x+z \leq 10$ 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^{v1} , R^{v2} and R^{v3} 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;

20

R^1 , R^2 and R^3 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,

25

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 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

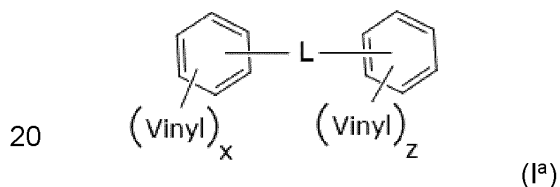
2. The compound of claim 1, wherein R^{v1} , R^{v2} and R^{v3} are vinyl group.

3. The compound of claim 1 or 2, wherein R^1 , R^2 and R^3 are hydrogen atom.

4. The compound of any one of preceding claims, 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 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 by D, F, Cl, Br, I, CN or NO_2 .

5. The compound of any one of preceding claims, wherein n is 0 and m is 1.

6. The compound of any one of preceding claims, is represented by one of the following chemical formulae (I^a)

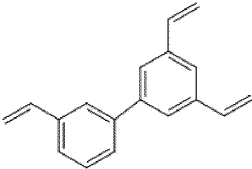
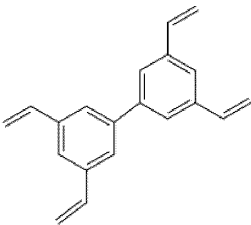
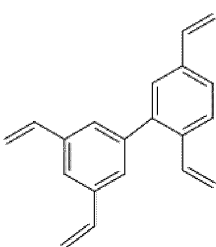
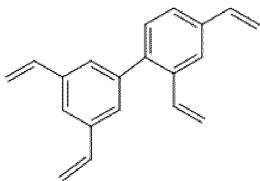
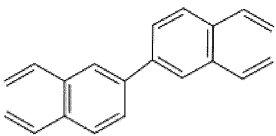
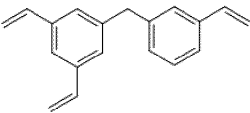
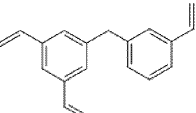
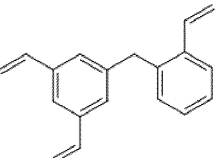
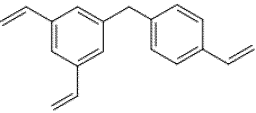
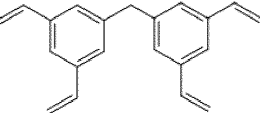
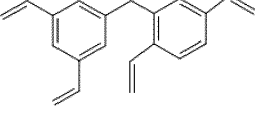
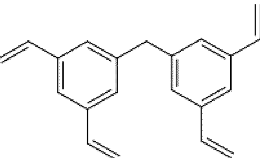
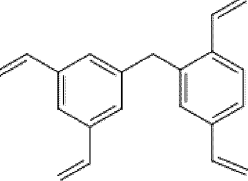
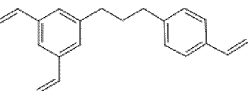
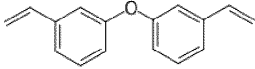
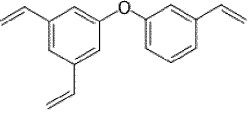
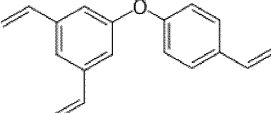


where $1 \leq x \leq 5$, $0 \leq z \leq 5$, $3 \leq x+z \leq 10$;

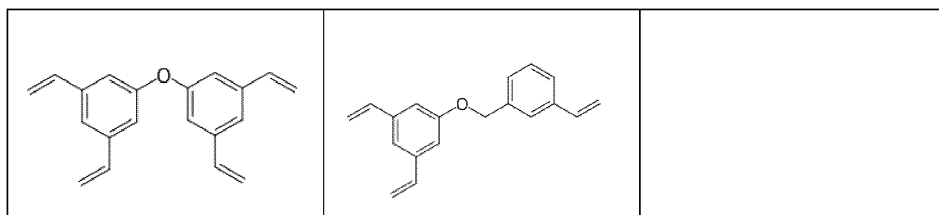
L is a direct bond, straight alkylene group having carbon atoms 1 to 5 or straight alkenylene group having carbon atoms 2 to 5,

25 wherein one or more non-adjacent CH_2 groups of said alkylene or alkenylene group may be replaced by oxygen atom, $C=O$, $C=S$, $C=Se$, $C=NH$, SiH_2 , 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 .

30 7. The compound of any one of claims 1 to 6 is selected from the group consisting of:

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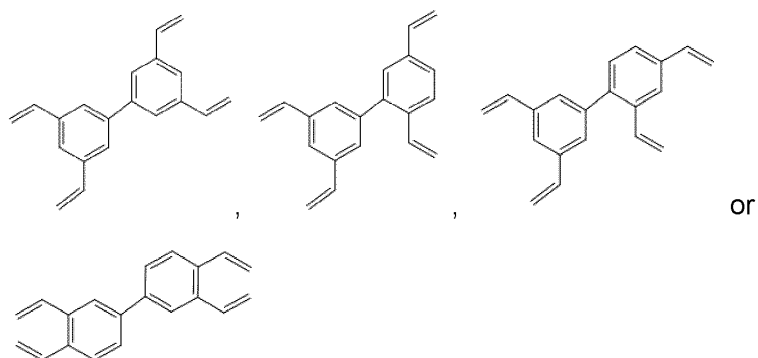


8. The compound of any one of preceding claims, where L is a direct bond, $2 \leq x \leq 5$, $2 \leq z \leq 5$, $4 \leq x+z \leq 10$.

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9. The compound of claim 8, is selected from

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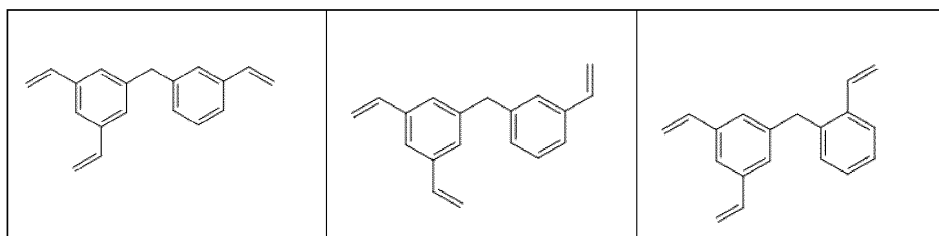
20

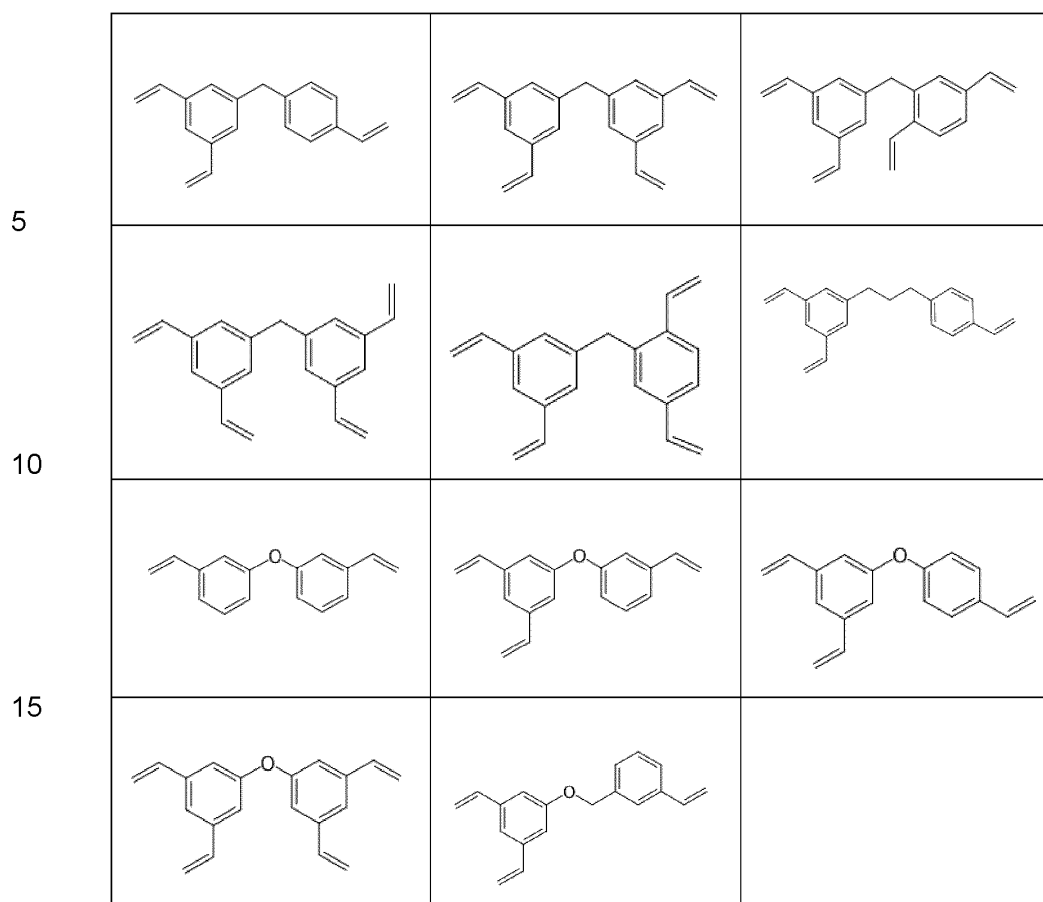
10. The compound of any one of claims 1 to 7, wherein L is a straight alkylene group having carbon atoms 1 to 5 or straight alkenylene group having carbon atoms 2 to 5, wherein one or more non-adjacent CH₂ groups of said alkylene or alkenylene group may be replaced by oxygen atom, C=O, C=S, C=Se, C=NH, 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.

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11. The compound of claim 10 is selected from the group consisting of:

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12. Use of the compound of any one of preceding claims 1 to 11, for forming a layer, preferably for forming an underlayer Spin-on carbon.

13. Use of the compound of any one of preceding claims 1 to 11, for Inkjet Adaptive Planarization composition.

14. Method for forming a layer, preferably for forming an underlayer Spin-on carbon comprises the following step:

(iii) Applying the compound of any one of claims 1 to 10 for Inkjet Adaptive Planarization.

15. A cured layer, preferably it is a photo-cured layer formed from the compound of any one of claims 1 to 10.