DESCRIPTION

Title of Invention:

NITROGEN ATOM-CONTAINING SUBSTRATE COATING AGENT COMPOSITION, RESIST UNDERLAYER FILM, LAMINATE, METHOD FOR FORMING RESIST PATTERN, AND METHOD FOR PRODUCING SEMICONDUCTOR DEVICE

Technical Field

[0001]

The present invention relates to a nitrogen atom-containing substrate coating agent composition, a resist underlayer film, a laminate, a method for forming a resist pattern, and a method for producing a semiconductor device.

Background Art

[0002]

The advancement of semiconductor manufacturing processes is in rapid progress, and accordingly, there is a strong demand for improving the quality or characteristics of resist underlayer films. For example, it has been found that in a case where a substrate that is used as a base of a resist underlayer film contains nitrogen atoms, the resolution of a resist is impaired by the diffusion of an amine component (Patent Documents 1 to 3). Usually, resist films are subjected to an exposure step and a development treatment in order immediately after being formed, but

there is a case where a resist film is subjected to a development treatment after a long period of time elapses from the formation of the resist film for the sake of convenience of the manufacturing process. In the case of such a process, it has been found that a problem of a change in the resolution of a resist is induced as compared with a case where a resist is exposed to light immediately after being applied. Furthermore, in the case of applying a resist underlayer film to the existing process to curb the diffusion of an amine component, when a process at the time of resist resolution or after resolution is taken into account, since formation of the resist underlayer film causes a change in reflectance and deterioration of the pattern shape or an increase in a process load at the time of pattern processing, there is a demand for extreme thinning of resist underlayer films.

Citation List

Patent Literature

[0003]

Patent Literature 1: JP 2008-39811 A

Patent Literature 2: JP 2008-39815 A

Patent Literature 3: JP 2010-134437 A

Summary of Invention

Technical Problem

[0004]

Therefore, a problem to be solved by the present invention is to provide a suitable coating agent composition that enables a resist film to maintain stable resolution even after being stored for a long period of time after the formation and does not affect reflectance or pattern processing in the case of using a nitrogen atom-containing substrate.

Solution to Problem

[0005]

As a result of intensive studies to solve the above-described problem, the present inventors found that the above-described problem can be solved and completed the present invention having the following gist.

[0006]

That is, the present invention includes the following aspects.

[1] A nitrogen atom-containing substrate coating agent composition containing: a resin (G) having a composite unit structure and a solvent,

wherein the composite unit structure has

a unit structure (A) having an aromatic ring and

a unit structure (B) having one or more carbon atoms,

the resin (G) is a resin obtained by a reaction of generating a covalent bond between a carbon atom constituting the aromatic ring of the unit structure (A) and the carbon atom in the unit structure (B),

the unit structure (A) includes a unit structure (A-I) containing at least a nitrogen atom,

a nitrogen atom-containing substrate is a substrate composed of a compound having a bond between a metal atom or a metalloid atom and a nitrogen atom or a substrate having a nitrogen atom-containing film composed of a compound having a bond between a metal atom or a metalloid atom and a nitrogen atom, and

the resin (G) is not a resin that is synthesized only from indole and 1-naphthaldehyde.

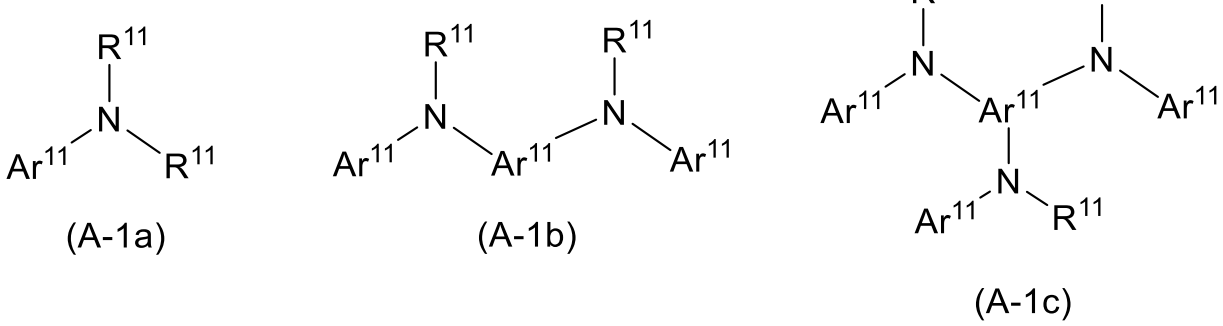
[2] The nitrogen atom-containing substrate coating agent composition according to [1], wherein the unit structure (A-I) has a skeleton having an aromatic ring, and the skeleton is at least any one of an aromatic amine skeleton and a nitrogen-containing aromatic heterocyclic skeleton.

[3] The nitrogen atom-containing substrate coating agent composition according to [1] or [2], wherein the unit structure (A-I) includes a unit structure not including a carbazole skeleton.

[4] The nitrogen atom-containing substrate coating agent composition according to any one of [1] to [3], wherein the

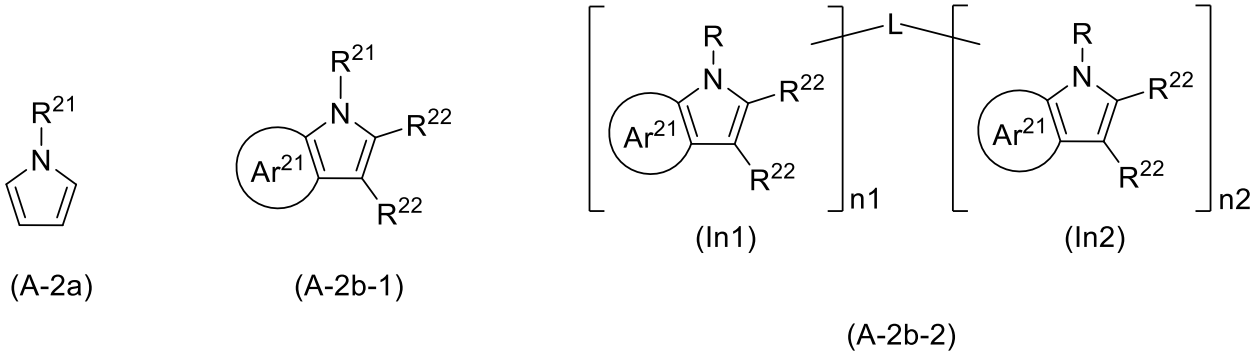
unit structure (A-I) has a skeleton having an aromatic ring, the skeleton is at least any one of skeletons represented by Formula (A-1a) below, Formula (A-1b) below, Formula (A-1c) below, Formula (A-2a) below, Formula (A-2b-1) below, and Formula (A-2b-2) below, and at least one hydrogen atom may be substituted with a substituent in the skeleton:

[Chem. 1]



(in Formula (A-1a) to Formula (A-1c), each Ar^{11} independently represents a residue of an aromatic ring, and each R^{11} independently represents a hydrogen atom or a residue of an aromatic ring)

[Chem. 2]



(in the formula, each Ar^{21} independently represents a residue of an aromatic ring,

each R^{21} independently represents a hydrogen atom or a residue of an aromatic ring,

each R^{22} independently represents a hydrogen atom, a hydrocarbon group having 1 to 5 carbon atoms, or a residue of an aromatic ring, two adjacent R^{22}'s may together form an unsaturated aliphatic ring, one unsaturated bond in the unsaturated aliphatic ring refers to an unsaturated bond constituting a pyrrole ring,

each R independently represents a hydrogen atom, a residue of an aromatic ring, or a bonding site to L, L represents a single bond or a linking group, n1 represents 1, n2 represents 1 or 2, in Formula (A-2b-2), in a case where L is a single bond, a partial structure (In1) and a partial structure (In2) bond to each other by two nitrogen atoms bonding to each other, two Ar^{21}'s bonding to each other, or a nitrogen atom and Ar^{21} bonding to each other, and in Formula (A-2b-2), in a case where L is a linking group, L bonds to N or Ar^{21}).

[5] The nitrogen atom-containing substrate coating agent composition according to [4], wherein in the skeleton, the substituent that may substitute at least one hydrogen atom is one or more groups selected from a halo group, an alkyl group, an alkenyl group, an alkynyl group, an alkoxy group,

an aryl group, an aryloxy group, an amino group, a hydroxy group, a hydroxyalkyl group, a carboxy group, a formyl group, a cyano group, a nitro group, an ester group, an amide group, a sulfonyl-containing group, a thiol group, a sulfide-containing group, and an ether bond-containing group.

[6] The nitrogen atom-containing substrate coating agent composition according to any one of [1] to [5], wherein the unit structure (B) includes a unit structure (B-I) derived from an aldehyde compound or an aldehyde equivalent.

[7] The nitrogen atom-containing substrate coating agent composition according to any one of [1] to [6], wherein the resin (G) is a resin that is synthesized from a reaction raw material containing an amine compound and an aldehyde compound or an aldehyde equivalent.

[8] The nitrogen atom-containing substrate coating agent composition according to [7], wherein the amine compound has a skeleton having an aromatic ring, and the skeleton is at least any one of an aromatic amine skeleton and a nitrogen-containing aromatic heterocyclic skeleton.

[9] The nitrogen atom-containing substrate coating agent composition according to any one of [1] to [8], wherein the solvent contains a solvent having a boiling point of 160°C or higher.

[10] The nitrogen atom-containing substrate coating agent

composition according to any one of [1] to [9], further containing: at least one selected from the group consisting of an acid, a salt thereof, and an acid generator.

[11] The nitrogen atom-containing substrate coating agent composition according to any one of [1] to [10], further containing: a crosslinking agent.

[12] The nitrogen atom-containing substrate coating agent composition according to [11], wherein the crosslinking agent is at least one selected from the group consisting of an aminoplast crosslinking agent and a phenoplast crosslinking agent.

[13] The nitrogen atom-containing substrate coating agent composition according to any one of [1] to [12], further containing: a surfactant.

[14] The nitrogen atom-containing substrate coating agent composition according to any one of [1] to [13] that is intended to form a resist underlayer film.

[15] A resist underlayer film on a nitrogen atom-containing substrate, the resist underlayer film being a cured product of the nitrogen atom-containing substrate coating agent composition according to any one of [1] to [14].

[16] The resist underlayer film according to [15], wherein a film thickness is less than 10 nm.

[17] A laminate including: a nitrogen atom-containing substrate; and the resist underlayer film according to [15]

or [16], wherein the nitrogen atom-containing substrate is a substrate composed of a compound having a bond between a metal atom or a metalloid atom and a nitrogen atom or a substrate having a nitrogen atom-containing film composed of a compound having a bond between a metal atom or a metalloid atom and a nitrogen atom.

[18] The laminate according to [17], wherein the resist underlayer film is a nitrogen atom-containing film, and the nitrogen atom-containing film constitutes an outermost layer of the nitrogen atom-containing substrate.

[19] The laminate according to [17] or [18], wherein the metal atom or metalloid atom is

(i) silicon,

(ii) titanium, or

(iii) tungsten, hafnium, zirconium, chromium, germanium, copper, silver, gold, aluminum, indium, gallium, arsenic, palladium, iron, tantalum, iridium, cobalt, manganese, molybdenum, or an alloy thereof.

[20] The laminate according to any one of [17] to [19], wherein the compound having a bond between a metal atom or a metalloid atom and a nitrogen atom is SiON, SiN, TiON, or TiN.

[21] A method for forming a resist pattern that is used to produce a semiconductor, the method including: a step of forming a resist underlayer film by applying the nitrogen

atom-containing substrate coating agent composition according to any one of [1] to [14] onto a nitrogen atom-containing semiconductor substrate and baking the composition.

[22] A method for producing a semiconductor device, the method including:

a step of forming a resist underlayer film on a nitrogen atom-containing semiconductor substrate using the nitrogen atom-containing substrate coating agent composition according to any one of [1] to [14];

a step of forming a resist film on the resist underlayer film;

a step of forming a resist pattern by irradiating the resist film with light or an electron beam and developing the resist film;

a step of forming a patterned resist underlayer film by etching the resist underlayer film through the resist pattern; and

a step of processing the nitrogen atom-containing semiconductor substrate through the patterned resist underlayer film.

[23] A method for producing a semiconductor device, the method including:

a step of forming a resist underlayer film on a nitrogen atom-containing semiconductor substrate using the

nitrogen atom-containing substrate coating agent composition according to any one of [1] to [14];

a step of forming a hard mask on the resist underlayer film;

a step of further forming a resist film on the hard mask;

a step of forming a resist pattern by irradiating the resist film with light or an electron beam and developing the resist film;

a step of forming a patterned hard mask by etching the hard mask through the resist pattern;

a step of forming a patterned resist underlayer film by etching the resist underlayer film through the patterned hard mask; and

a step of processing the nitrogen atom-containing semiconductor substrate through the patterned resist underlayer film.

[24] A method for producing a semiconductor device, the method including:

a step of forming a resist underlayer film on a nitrogen atom-containing semiconductor substrate using the nitrogen atom-containing substrate coating agent composition according to any one of [1] to [14];

a step of forming a hard mask on the resist underlayer film;

a step of further forming a resist film on the hard mask;

a step of forming a resist pattern by irradiating the resist film with light or an electron beam and developing the resist film;

a step of forming a patterned hard mask by etching the hard mask through the resist pattern;

a step of forming a patterned resist underlayer film by etching the resist underlayer film through the patterned hard mask;

a step of removing the hard mask; and

a step of processing the nitrogen atom-containing semiconductor substrate through the patterned resist underlayer film.

[25] A method for producing a semiconductor device, the method including:

a step of forming a resist underlayer film on a nitrogen atom-containing semiconductor substrate using the nitrogen atom-containing substrate coating agent composition according to any one of [1] to [14];

a step of forming a hard mask on the resist underlayer film;

a step of further forming a resist film on the hard mask;

a step of forming a resist pattern by irradiating the

resist film with light or an electron beam and developing the resist film;

a step of forming a patterned hard mask by etching the hard mask through the resist pattern;

a step of forming a patterned resist underlayer film by etching the resist underlayer film through the patterned hard mask;

a step of removing the hard mask;

a step of forming a deposited film on the resist underlayer film after removal of the hard mask;

a step of processing the deposited film by etching;

a step of removing the patterned resist underlayer film to leave a patterned deposited film; and

a step of processing the nitrogen atom-containing semiconductor substrate through the patterned deposited film.

[26] The method for producing a semiconductor device according to any one of [23] to [25], wherein the hard mask is formed by applying a composition containing an inorganic substance or depositing an inorganic substance.

[27] The method for producing a semiconductor device according to any one of [22] to [26], wherein a pattern is formed on the resist film by a nanoimprint method or with a self-assembled film.

[28] The method for producing a semiconductor device

according to [24] or [25], wherein the hard mask is removed by either etching or with an alkaline solution.

Advantageous Effects of Invention

[0007]

According to the present invention, it is possible to provide a suitable coating agent composition that enables a resist film to maintain stable resolution even after being stored for a long period of time after the formation and does not affect reflectance or pattern processing. This makes it possible to reduce the process load.

[0008]

In a case where a novolac resin of the present invention is applied onto a substrate containing a nitrogen atom, it is possible to curb the diffusion of an amine component that is contained in the substrate even when the novolac resin forms an ultrathin film of less than 10 nm, and in a case where a resist film is provided on a resist underlayer film containing the resin, it is possible to form a clean resist pattern having a vertical shape without impairing the resolution of the resist film.

In addition, the fact that a vertical resist pattern can be obtained leads to the diffusion of the amine component from a base film, that is, the substrate being curbed, and it can be thus said that the resist film

exhibits excellent resolution even in a case where the resist film is exposed after a long period of time elapses from the formation.

Furthermore, even when applied as an ultrathin film, the resin exhibits favorable coatability to various substrate types and stepped substrates and exhibits sufficient curability, and it is thus possible to curb a film thickness variation in the same wafer.

Description of Embodiments

[0009]

[Nitrogen atom-containing substrate coating agent composition]

A nitrogen atom-containing substrate coating agent composition (hereinafter also simply referred to as "coating agent composition") of the present invention contains a resin (G) having a composite unit structure and a solvent.

The composite unit structure has a unit structure (A) having an aromatic ring and a unit structure (B) having one or more carbon atoms.

The resin (G) is a resin obtained by a reaction of generating a covalent bond between a carbon atom constituting the aromatic ring of the unit structure (A) and the carbon atom in the unit structure (B).

The unit structure (A) includes a unit structure (A-I) containing at least a nitrogen atom.

A nitrogen atom-containing substrate is a substrate composed of a compound having a bond between a metal atom or a metalloid atom and a nitrogen atom or a substrate having a nitrogen atom-containing film composed of a compound having a bond between a metal atom or a metalloid atom and a nitrogen atom.

The resin (G) is not a resin that is synthesized only from indole and 1-naphthaldehyde.

In the present specification, the resin (G) may be referred to as “novolac resin”.

The resin (G) includes the unit structure (A) and the unit structure (B), whereby it is possible to provide a suitable coating agent composition that enables a resist film to maintain stable resolution even after being stored for a long period of time after the formation and does not affect reflectance or pattern processing.

[0010]

The coating agent composition is a coating agent used in an application for forming a coating film on a nitrogen atom-containing substrate. The coating agent composition is preferably used in an application for forming a resist underlayer film and is thereby capable of providing an advantage of enabling a clean resist pattern having a

vertical shape to be formed without impairing the resolution of a resist film even in a case where the resist film is exposed after a long period of time elapses from the formation. Usually, it is considered that the use of a thick film material as a resist underlayer film makes it possible to curb the diffusion of the amine component in the nitrogen atom-containing substrate, but an increase in process load or an increase in material cost in the subsequent processing, and deterioration of the resist shape due to the deterioration of a reflection-curbing capability are caused. Therefore, it is extremely important to achieve the diffusion of the amine component while avoiding such adverse effects as described above. The coating agent composition of the present invention is capable of sufficiently providing the above-described advantages even when used in an application for forming a resist underlayer thin film which is an ultrathin film having a film thickness of less than 10 nm.

[0011]

The reason for the novolac resin of the present invention curbing the diffusion of the amine component is not bound by theory, but is considered to be different from the diffusion of the amine component being inhibited by neutralizing the amine component with an acidic additive as described in the patent literature. Since the novolac

resin has many aromatic rings with a high carbon content in the skeleton and is highly rigid, it is considered that the gaps between molecules through which the amine component, which is a contaminant from the substrate, is capable of diffusing are significantly reduced, and accordingly, the diffusion of the amine component is inhibited.

[0012]

The unit structure (A) has, for example, at least any one of an oxygen atom constituting the aromatic ring, a sulfur atom constituting the aromatic ring, an oxygen atom bonding to the aromatic ring, a nitrogen atom constituting the aromatic ring, and a nitrogen atom bonding to the aromatic ring.

The unit structure (A) does not have, for example, any heteroatom as an atom constituting the aromatic ring and an atom bonding to the aromatic ring.

[0013]

The unit structure (B) preferably includes a unit structure (B-I) derived from an aldehyde compound or an aldehyde equivalent.

The aldehyde equivalent refers to an organic compound enabling a covalent bond with the aromatic ring and having a ketone group; an acetal group; a ketal group; a hydroxy group or alkoxy group bonding to a secondary or tertiary carbon atom; a hydroxy group, alkoxy group, or halo group

bonding to an α-position carbon atom of an alkylaryl group; or a carbon-carbon unsaturated bond.

[0014]

The nitrogen atom-containing substrate is a substrate composed of a compound having a bond between a metal atom or a metalloid atom and a nitrogen atom or a substrate having a nitrogen atom-containing film composed of a compound having a bond between a metal atom or a metalloid atom and a nitrogen atom.

As the metal atom or the metalloid atom,

(i) silicon,

(ii) titanium, or

(iii) tungsten, hafnium, zirconium, chromium, germanium, copper, silver, gold, aluminum, indium, gallium, arsenic, palladium, iron, tantalum, iridium, cobalt, manganese, molybdenum, or an alloy thereof

can be exemplified.

[0015]

In addition, typical examples of the compound having a bond between a metal atom or a metalloid atom and a nitrogen atom include SiON, SiN, TiON, or TiN.

[0016]

In addition, an aspect in which the effect of the coating agent composition according to an aspect of the present invention can be most effectively exhibited is an

aspect in which the coating agent composition is directly applied to a substrate composed of a compound having a bond between a metal atom or a metalloid atom and a nitrogen atom; or an aspect in which the coating agent composition is applied onto a substrate having a nitrogen atom-containing film composed of a compound having a bond between a metal atom or a metalloid atom and a nitrogen atom, in which the nitrogen atom-containing film constitutes the outermost layer of the substrate.

[0017]

[I. Definition of terms]

In the present specification, definitions of main terms related to a novolac resin which is an aspect of the present invention will be described below. Unless stated otherwise individually, the following definitions of terms apply to novolac resins.

[0018]

(I-1) "Novolac Resin"

The "novolac resin" is used in a broad sense to broadly include not only phenol-formaldehyde resins (so-called novolac type phenol resins) and aniline-formaldehyde resins (so-called novolac type aniline resins) in a narrow sense, but also resins formed by formation of a covalent bond (substitution reaction, addition reaction, condensation reaction, addition condensation reaction, and the like)

between an organic compound having a functional group that enables a covalent bond with an aromatic ring [for example, an aldehyde group, a ketone group, an acetal group, a ketal group, a hydroxy group or an alkoxy group bonding to secondary or tertiary carbon atom, a hydroxy group, an alkoxy group, or a halo group bonding to an α-position carbon atom (benzyl position carbon atom or the like) of the alkylaryl group; carbon-carbon unsaturated bonds such as divinylbenzene and dicyclopentadiene, and the like], and an aromatic ring in a compound having an aromatic ring (which preferably has a heteroatom such as an oxygen atom, a nitrogen atom, or a sulfur atom as an atom constituting the aromatic ring or an atom bonding to the aromatic ring), generally, in the presence of an acid catalyst or under reaction conditions equivalent thereto.

[0019]

Therefore, in the novolac resin described in the present specification, an organic compound containing a carbon atom derived from the functional group (sometimes referred to as a “linking carbon atom”) forms a covalent bond with an aromatic ring in a compound having an aromatic ring via the linking carbon atom, thereby linking a plurality of compounds having an aromatic ring to form a resin.

[0020]

In the present specification, terms “unit structure (A)” and “unit structure (B)” are used as the unit structures constituting the “novolac resin”. The unit structure (A) is a unit structure derived from a compound having an aromatic ring. The unit structure (B) is a unit structure derived from a compound having a functional group capable of covalent bonding with the aromatic ring of the unit structure (A).

[0021]

(I-2) “Residue”

The “residue” refers to an organic group in which a hydrogen atom bonding to a carbon atom or a heteroatom (nitrogen atoms, oxygen atoms, sulfur atoms, and the like) is substituted with a bonding site, and may be a monovalent group or a multivalent group. For example, when one hydrogen atom is substituted with one bonding site, a monovalent organic group is formed, and when two hydrogen atoms are substituted with bonding sites, a divalent organic group is formed.

[0022]

(I-3) “Aromatic ring” (Aromatic group, aryl group, arylene group)

The “aromatic ring” is a concept including an aromatic hydrocarbon ring, an aromatic heterocyclic ring, and residues thereof [which may also be referred to as an

“aromatic group”, an “aryl group” (in the case of a monovalent group), or an “arylene group” (in the case of a divalent group)], and includes not only a monocyclic ring (aromatic monocyclic ring) but also a polycyclic ring (aromatic polycyclic ring). In the case of polycyclic ring(s), at least one monocyclic ring is an aromatic monocyclic ring, but the remaining monocyclic ring forming a condensed ring with the aromatic monocyclic ring may be a monocyclic heterocyclic ring (heteromonocyclic ring) or a monocyclic alicyclic hydrocarbon (alicyclic monocyclic ring).

In the present specification, a heteroaryl group is included in an aryl group. A heteroarylene group is included in an arylene group.

[0023]

Examples of the aromatic rings include, but are not limited to, aromatic hydrocarbon rings such as benzene, indene, naphthalene, azulenes, styrene, toluene, xylene, mesitylene, cumene, anthracene, phenanthrene, triphenylene, benzoanthracene, pyrene, chrysene, fluorene, biphenyl, corannulene, perylene, fluoranthene, benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[ghi]perylene, coronene, dibenzo[g,p]chrysene, acenaphthylene, acenaphthene, naphthacene, pentacene, cyclooctatetraene, more typically, aromatic hydrocarbon rings such as benzene, naphthalene,

anthracene, pyrene, and aromatic heterocyclic rings such as furan, pyran, pyridine, pyrimidine, pyrazine, thiophene, pyrrole, N-alkylpyrrole, N-arylpyrrole, imidazole, pyridine, pyrimidine, pyrazine, triazine, thiazole, indole, phenylindole, bisindolefluorene, bisindolebenzofluorene, bisindoledibenzofluorene, purine, quinoline, isoquinoline, chromene, thianthrene, phenothiazine, phenoxazine, xanthene, acridine, phenazine, carbazole, indolocarbazole, and, more typically, furan, thiophene, pyrrole, indole, phenylindole, bisindolefluorene, phenothiazine, carbazole and indolocarbazole.

[0024]

The aromatic ring (e.g. benzene ring, naphthalene ring) may optionally have a substituent, and the substituent includes, for example, the following atoms and groups:

- Halogen atom,
- Saturated or unsaturated linear, branched or cyclic hydrocarbon group ($-R^a$) which may be interrupted one or more times by an oxygen atom in the middle of a hydrocarbon chain (alkyl, alkenyl, and alkynyl groups (for example, a propargyl group), aryl groups, and the like, which may be interrupted one or more times by an oxygen atom in the middle of the hydrocarbon chain),
- -OR (wherein R represents the hydrocarbon group-R^a),
- Aryloxy group,

- $-NH_2$, -NHR, or $-NR_2$ (the two Rs may be the same or different from each other), wherein R represents the hydrocarbon group-R^a,

- Hydroxy group,

- Hydroxyalkyl group,

- Carboxy group

- Formyl group,

- Cyano group,

- Nitro group,

- Ester group (for example, $-CO_2R$ or -OCOR, wherein R represents the hydrocarbon group $-R^a$),

- Amide group [for example, -NHCOR, -CONHR, -NRCOR (the two Rs may be the same or different from each other), or $-CONR_2$(the two Rs may be the same or different from each other), wherein R represents the hydrocarbon group-R^a],

- Sulfonyl-containing group (for example, $-SO_2R$, wherein R represents the hydrocarbon group $-R^a$ or hydroxy group -OH),

- Thiol group (-SH),

- Sulfide-containing group (-SR, wherein R represents the hydrocarbon group-R^a),

- Organic group containing ether bond [a residue of an ether compound represented by R^{11}-O-R^{11} (each R^{11} independently represents an alkyl group having 1 to 6 carbon atoms such as a methyl group or an ethyl group, or

an aryl group such as a phenyl group, a naphthyl group, an anthranil group, or a pyrenyl group), for example, an organic group containing an ether bond including a methoxy group, an ethoxy group, and a phenoxy group].

[0025]

The “aromatic ring” further includes an organic group having a condensed ring of one or more aromatic rings (benzene, naphthalene, anthracene, pyrene, and the like) and one or more aliphatic rings or heterocyclic rings. Examples of the aliphatic ring herein include cyclobutane, cyclobutene, cyclopentane, cyclopentene, cyclohexane, cyclohexene, methylcyclohexane, methylcyclohexene, cycloheptane, and cycloheptene, and examples of the heterocyclic ring include furan, thiophene, pyrrole, imidazole, pyran, pyridine, pyrimidine, pyrazine, pyrrolidine, piperidine, piperazine, and morpholine.

[0026]

The “aromatic ring” may be an organic group having a structure in which two or more aromatic rings are linked by a divalent linking group. Examples of the divalent linking group include an alkylene group, an arylene group, -NH-, -NHCO-, -O-, -COO-, -CO-, -S-, -SS-, and $-SO_2-$. The divalent linking group may be a divalent group obtained by removing one hydrogen atom from any substituent of the aromatic ring described above.

[0027]

(I-4) “Heterocyclic ring”

The “heterocyclic ring” is a concept that encompasses both an aliphatic heterocyclic ring and an aromatic heterocyclic ring, and encompasses not only a monocyclic (heteromonocyclic) ring but also a polycyclic (heteropolycyclic) ring. In the case of polycyclic rings, at least one monocyclic ring is a heteromonocyclic ring, but the remaining monocyclic rings may be aromatic hydrocarbon monocyclic rings or alicyclic monocyclic rings. As the aromatic heterocyclic ring, reference can be made to the example of (I-3) described above. As with the aromatic ring of (I-3), it may have a substituent.

[0028]

(I-5) “Non-aromatic ring” (aliphatic ring)

The “non-aromatic monocyclic ring” when the “non-aromatic ring” is a monocyclic ring refers to a monocyclic hydrocarbon not belonging to aromatics, and is typically a monocyclic ring of an alicyclic compound. It may also be referred to as an aliphatic monocyclic ring (an aliphatic heteromonocyclic ring may be included, or an unsaturated bond may be included as long as it does not belong to an aromatic compound). As with the aromatic ring of (I-3), it may have a substituent.

[0029]

Examples of the non-aromatic monocyclic ring (aliphatic ring, aliphatic monocyclic ring) include cyclopropane, cyclobutane, cyclobutene, cyclopentane, cyclopentene, cyclohexane, methylcyclohexane, cyclohexene, methylcyclohexene, cycloheptane, and cycloheptene.

[0030]

The "non-aromatic polycyclic ring" when the "non-aromatic ring" is a polycyclic ring refers to a polycyclic hydrocarbon not belonging to aromatics, and is typically a polycyclic ring of an alicyclic compound. It may also be referred to as an aliphatic polycyclic ring [an aliphatic heteropolycyclic ring (at least one of monocyclic rings constituting polycyclic rings is an aliphatic heterocyclic ring) may be included, or an unsaturated bond may be included as long as the unsaturated bond does not belong to an aromatic compound]. Non-aromatic bicyclic rings, non-aromatic tricyclic rings, and non-aromatic tetracyclic rings are included.

[0031]

The "non-aromatic bicyclic ring" when the "non-aromatic ring" is bicyclic, refers to a condensed ring composed of two monocyclic hydrocarbons that do not belong to aromatics, and is typically a condensed ring of two alicyclic compounds. In the present specification, it may be referred to as an aliphatic bicyclic ring (an aliphatic

heterobicyclic ring may be included, or an unsaturated bond may be included as long as it does not belong to an aromatic compound). Examples of the non-aromatic bicyclic ring include bicyclopentane, bicyclooctane, and bicycloheptene.

[0032]

When the "non-aromatic ring" is a tricyclic ring, the "non-aromatic tricyclic ring" refers to a condensed ring composed of three monocyclic hydrocarbons that do not belong to aromatics, and is typically a condensed ring of three alicyclic compounds (each may be a heterocyclic ring or may contain an unsaturated bond as long as it does not belong to an aromatic compound). Examples of the non-aromatic tricyclic ring include tricyclooctane, tricyclononane, and tricyclodecane.

[0033]

When the "non-aromatic ring" is a tetracyclic ring, the "non-aromatic tetracyclic ring" refers to a condensed ring composed of four monocyclic hydrocarbons that do not belong to aromatics, and is typically a condensed ring of four alicyclic compounds (each may be a heterocyclic ring or may contain an unsaturated bond as long as it does not belong to an aromatic compound). Examples of the non-aromatic tetracyclic ring include hexadecahydropyrene.

[0034]

(I-6)

The “carbon atom constituting the ring (moiety)” means a carbon atom constituting a hydrocarbon ring in a state without a substituent (may be any of an aromatic ring, an aliphatic ring, and a heterocyclic ring).

[0035]

(I-7)

The “hydrocarbon group” refers to a group obtained by removing one or two or more hydrogen atoms from a hydrocarbon, and examples of such a hydrocarbon include a saturated or unsaturated aliphatic hydrocarbon, a saturated or unsaturated alicyclic hydrocarbon, and an aromatic hydrocarbon.

[0036]

(I-8)

In the chemical structural formula indicating the unit structure of the novolac resin of the present specification, a bonding site (denoted by *) may be described for convenience, but such a bonding site can adopt any bonding position wherein bonding can be achieved in the unit structure, and does not limit the bonding position in the unit structure at all, unless otherwise specified.

[0037]

<Resin (G)>

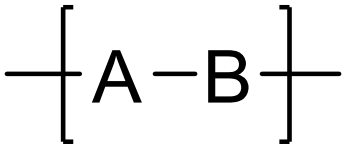
The resin (G) has a composite unit structure.

The composite unit structure has a unit structure (A) having an aromatic ring and a unit structure (B) having one or more carbon atoms.

[0038]

The composite unit structure of the resin (G) is represented by, for example, Formula (AB) below.

[Chem. 3]



(AB)

(In Formula (AB), A represents the unit structure (A), and B represents the unit structure (B).)

[0039]

<<A-1: Unit structure (A)>>

The unit structure (A) has an aromatic ring.

The unit structure (A) may have, for example, at least one of an oxygen atom constituting an aromatic ring, a sulfur atom constituting an aromatic ring, an oxygen atom bonding to an aromatic ring, a nitrogen atom constituting an aromatic ring, and a nitrogen atom directly bonding to an aromatic ring.

[0040]

The number of carbon atoms of the unit structure (A) is not particularly limited, and is, for example, 4 to 100,

preferably 4 to 50.

[0041]

Preferably, such an aromatic ring has a number of carbon atoms of 4 to 30, more preferably 4 to 24.

[0042]

Preferably, the aromatic ring is one or more benzene rings, naphthalene rings, anthracene rings, and pyrene rings, or a condensed ring (a fluorene ring, a benzofluorene ring, a dibenzofluorene ring, an indole ring, a carbazole ring, an indolocarbazole ring, and the like) of a benzene ring, a naphthalene ring, an anthracene ring, or a pyrene ring with a heterocyclic ring or an aliphatic ring.

[0043]

The aromatic ring may optionally have a substituent, but from the viewpoint of polymerization reactivity, the substituent may contain a minimum necessary amount of heteroatoms. In the aromatic ring, two or more aromatic rings may be linked by a linking group, and the linking group may contain the minimum necessary amount of heteroatoms. Examples of the heteroatom include an oxygen atom, a nitrogen atom, and a sulfur atom.

[0044]

An “aromatic ring” may include at least one heteroatom selected from N, S, and O on, within, or between rings.

[0045]

Examples of the heteroatom which may be contained on the ring include a nitrogen atom contained in an amino group (for example, a propargylamino group) or a cyano group; an oxygen atom contained in a formyl group, a hydroxy group, a carboxy group, an alkoxy group, an alkenyloxy group, an alkynyloxy group (for example, a propargyloxy group), or an aryloxy group, which are oxygen-containing substituents; and a nitrogen atom and an oxygen atom contained in a nitro group, which is an oxygen-containing substituent and a nitrogen-containing substituent.

Examples of the heteroatom which may be contained in the ring include an oxygen atom contained in furan or xanthene, a nitrogen atom contained in carbazole or pyrrole, and a sulfur atom contained in phenothiazine.

Examples of the heteroatom which may be contained in the linking group of two or more aromatic rings include a nitrogen atom, an oxygen atom, and a sulfur atom contained in -NH-, -NHCO-, -O-, -COO-, -CO-, -S-, -SS-, and $-SO_2-$.

In the present specification, "atoms constituting an aromatic ring" have the same meaning as "atoms contained in a ring". The "atom bonding to an aromatic ring" refers to, for example, "an atom directly bonding to a ring among atoms or groups contained on the ring" and "an atom

directly bonding to a ring among atoms contained between rings”.

For example, the atom constituting the benzene ring is a carbon atom.

For example, the atoms constituting the pyrrole ring are a carbon atom and a nitrogen atom.

For example, the oxygen atom of the hydroxy group of phenol is not an atom constituting an aromatic ring.

For example, the oxygen atom of the hydroxy group of phenol is an atom bonding to the benzene ring, and is an atom directly bonding to the benzene ring among the groups contained on the benzene ring.

[0046]

<<A-2: Example of skeleton constituting unit structure (A)>>

The unit structure (A) has, for example, a skeleton having an aromatic ring.

[0047]

As the skeleton having an aromatic ring, an aromatic amine skeleton, a nitrogen-containing aromatic heterocyclic skeleton, and a phenol skeleton are preferred.

[0048]

The unit structure (A) is, for example, a residue obtained by removing two hydrogen atoms from a skeleton having an aromatic ring.

The skeleton having an aromatic ring is derived from, for example, a compound having an aromatic ring when the resin (G) is synthesized. The skeleton having an aromatic ring is, for example, a residue derived from removing two hydrogen atoms from a compound having an aromatic ring when the resin (G) is synthesized.

[0049]

The skeleton having an aromatic ring may have a substituent.

Here, examples of the substituent include a halo group (halogen atom), an alkyl group, an alkenyl group, an alkynyl group, an alkoxy group, an aryl group, an aryloxy group, an amino group, a hydroxy group, a hydroxyalkyl group, a carboxy group, a formyl group, a cyano group, a nitro group, an ester group, an amide group, a sulfonyl-containing group, a thiol group, a sulfide-containing group, and an ether bond-containing group.

Examples of the alkyl group include a linear, branched, or cyclic alkyl group having 1 to 20 carbon atoms.

Examples of the alkenyl group include a linear, branched, or cyclic alkenyl group having 2 to 10 carbon atoms.

Examples of the alkynyl group include a linear, branched, or cyclic alkynyl group having 2 to 10 carbon atoms.

Examples of the alkoxy group include a group represented by -OR. Here, R represents a saturated or unsaturated linear, branched or cyclic hydrocarbon group (-R^a) which may be interrupted one or more times by an oxygen atom in the middle of the hydrocarbon chain. The number of carbon atoms of the alkoxy group is, for example, 1 to 20.

Examples of the aryl group include aryl groups having 6 to 30 carbon atoms.

Examples of the aryloxy group include aryloxy groups having 6 to 30 carbon atoms.

Examples of the amino group include a group represented by $-NH_2$, -NHR, or $-NR_2$. Here, R represents the hydrocarbon group $-R^a$, and in $-NR_2$, two Rs may be the same or different.

Examples of the hydroxyalkyl group include a linear, branched, or cyclic hydroxyalkyl group having 1 to 20 carbon atoms.

Examples of the ester group include a group represented by $-CO_2R$ or -OCOR. Here, R represents the hydrocarbon group $-R^a$.

Examples of the amide group include a group represented by -NHCOR, -CONHR, -NRCOR, or $-CONR_2$. Here, R represents the hydrocarbon group $-R^a$, and in a case where there are two Rs, the two Rs may be the same or different.

Examples of the sulfonyl-containing group include a

group represented by $-SO_2R$. Here, R represents the hydrocarbon group $-R^a$ or a hydroxy group -OH.

Examples of the sulfide-containing group include a group represented by -SR. Here, R represents the hydrocarbon group $-R^a$.

Examples of the ether bond-containing group include residues of an ether compound containing an ether bond represented by $R^{11}-O-R^{11}$. Here, each R^{11} independently represents an alkyl group having 1 to 6 carbon atoms such as a methyl group or an ethyl group, or an aryl group such as a phenyl group, a naphthyl group, an anthranil group, or a pyrenyl group. The ether bond-containing group may be, for example, an organic group containing an ether bond including a methoxy group, an ethoxy group, and a phenoxy group.

[0050]

<<A-3: Unit structure (A-I)>>

The unit structure (A) includes a unit structure (A-I) containing at least a nitrogen atom. The unit structure (A-I) has a skeleton having an aromatic ring. Here, the unit structure (A-I) is a subordinate concept of the unit structure (A) and does not refer to a partial structure of the unit structure (A).

Hereinafter, the skeleton having an aromatic ring in the unit structure (A-I) will be described.

[0051]

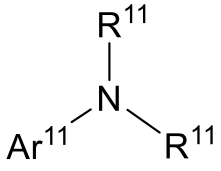
<<<A-3-1: Aromatic amine skeleton>>>

The aromatic amine skeleton refers to a skeleton having an aromatic ring and a nitrogen atom that bonds to the aromatic ring and does not constitute a ring.

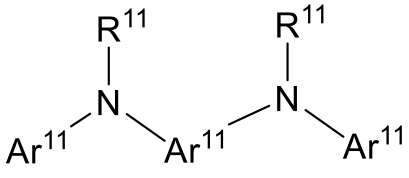
Examples of the aromatic amine skeleton include skeletons represented by Formulas (A-1a) to (A-1c) below.

As described later, in the unit structure (A-I), the hydrogen atom of the NH group may be substituted with a substituent. Examples of the substituent include the substituent described in (I-3) "Aromatic ring", the substituent described in (A-2) "Exemplary skeleton constituting unit structure (A)", and substituents (S) represented by Formulas (S1) to (S7) described later.

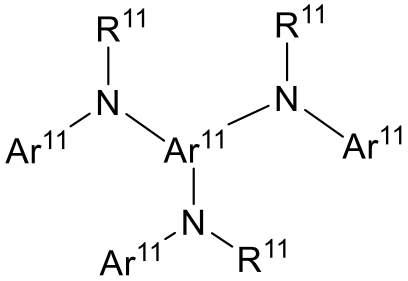
[Chem. 4]



(A-1a)



(A-1b)



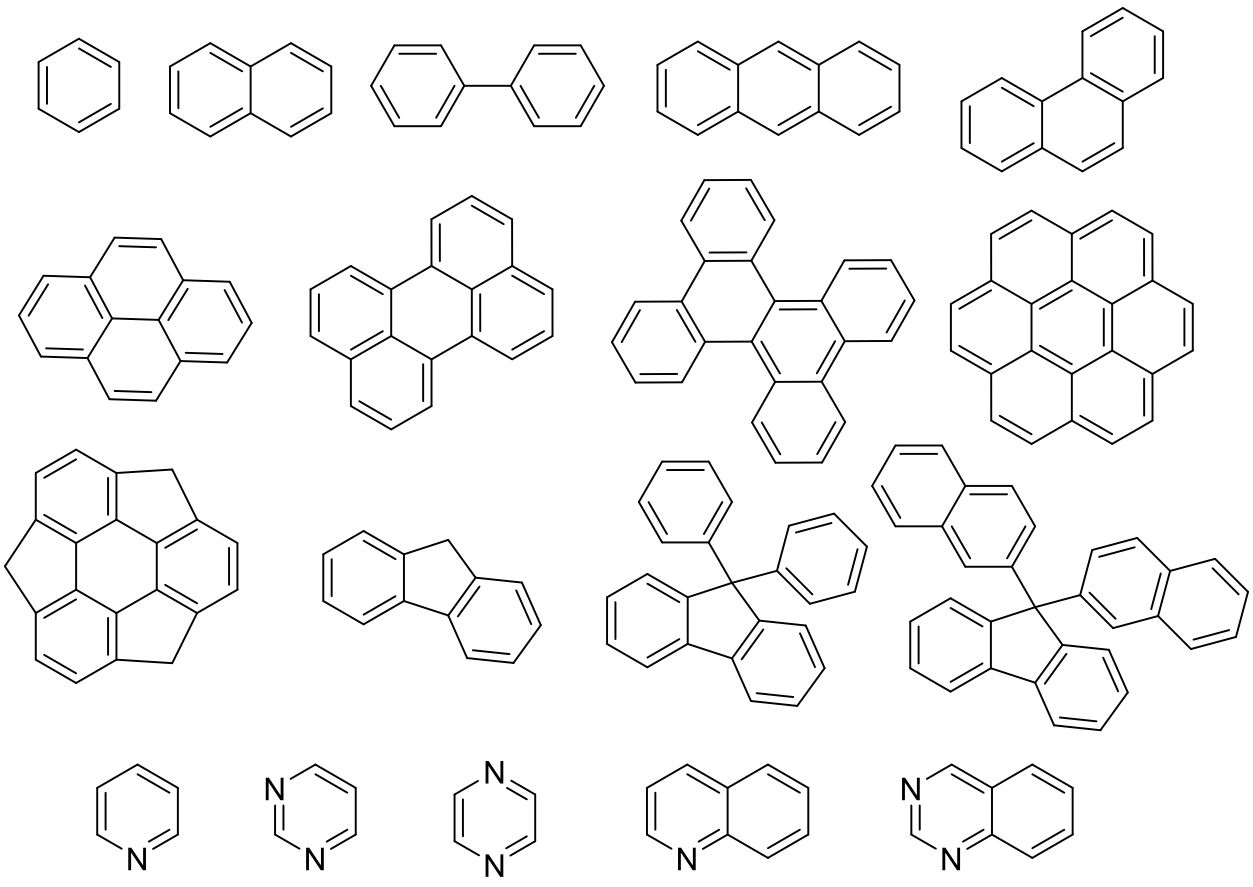
(A-1c)

(in Formula (A-1a) to Formula (A-1c), each Ar^{11} independently represents a residue of an aromatic ring, and each R^{11} independently represents a hydrogen atom or a residue of an aromatic ring)

[0052]

Examples of the aromatic ring in the residue of the aromatic ring of Ar^{11} and R^{11} include an aromatic ring represented by Formula (G1) below. These aromatic rings may have a substituent.

[Chem. 5]



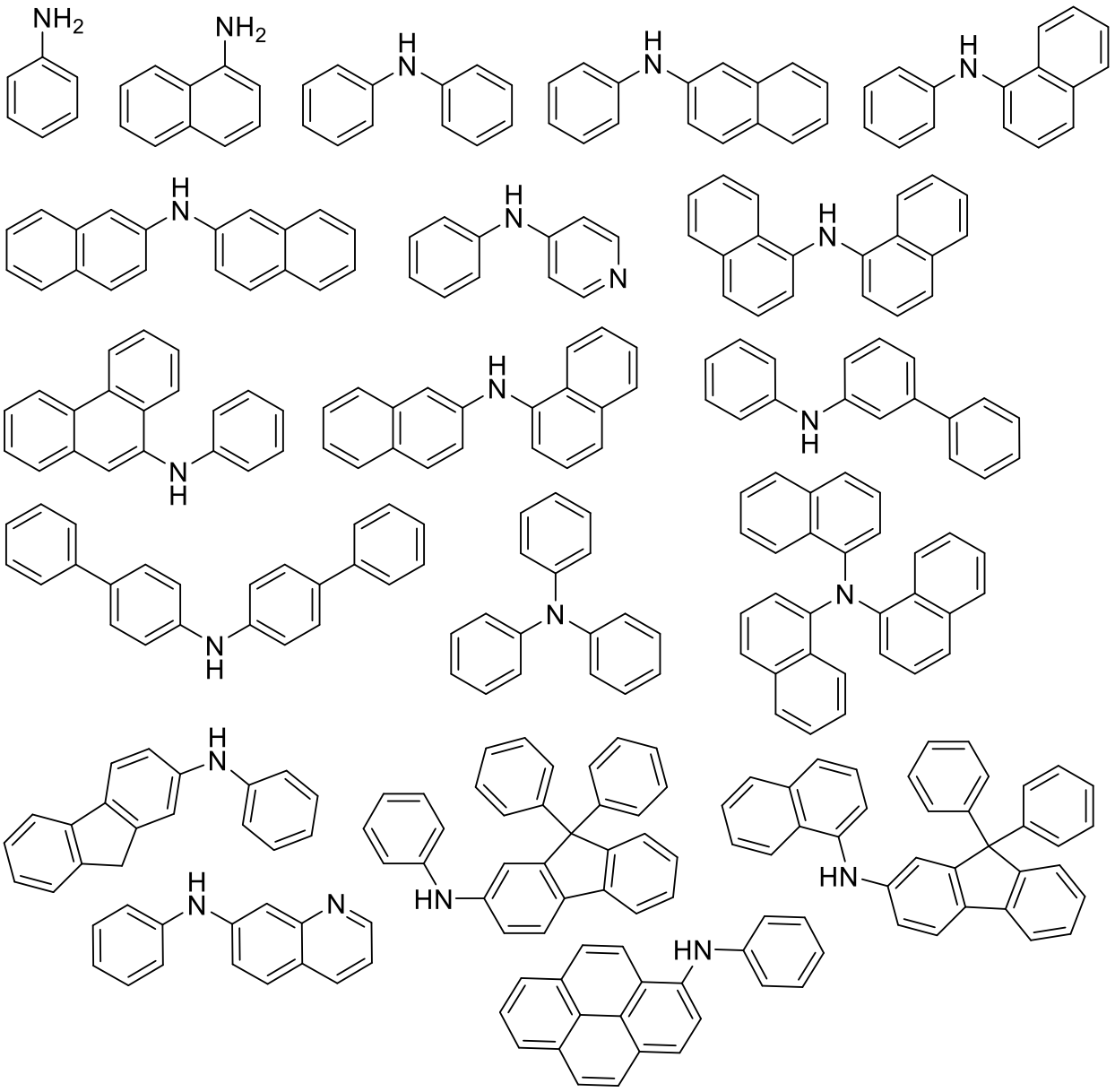
(G1)

[0053]

Examples of the skeleton represented by Formula (A-1a) include the following skeletons. The aromatic ring in these skeletons may have a substituent, and the hydrogen atom of the NH group may be substituted with a substituent.

The same applies to the following skeletons.

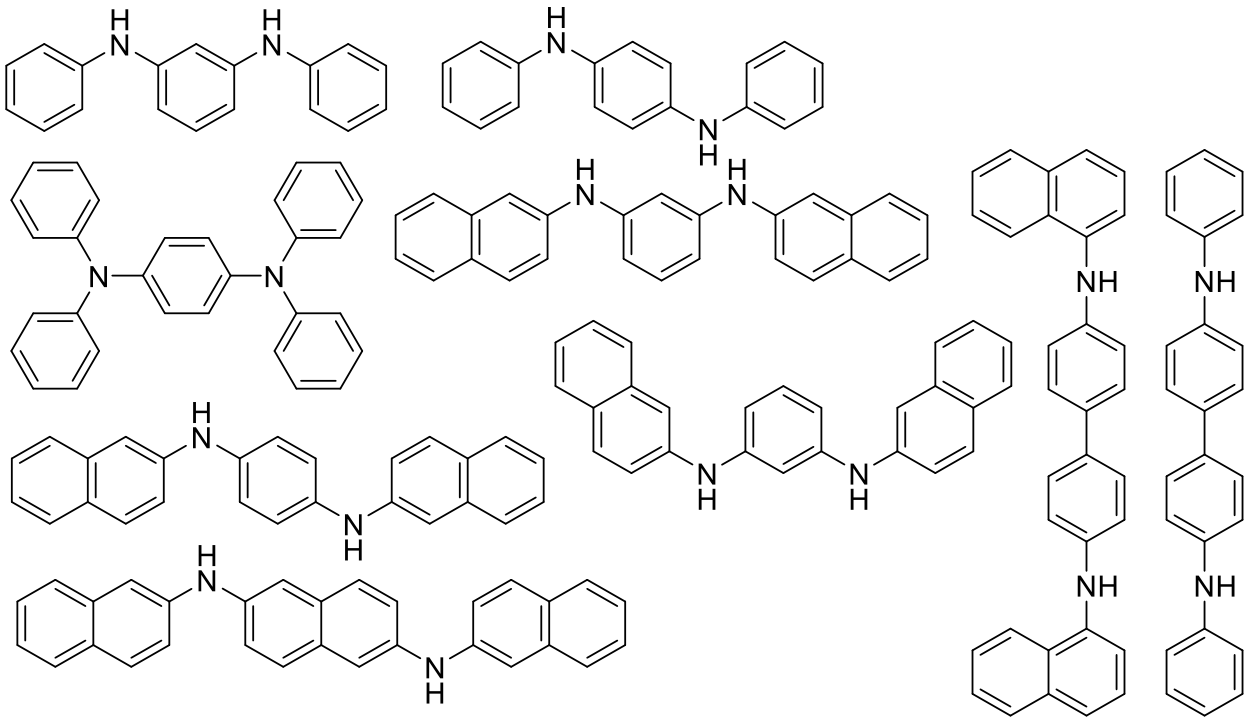
[Chem. 6]



[0054]

Examples of the skeleton represented by Formula (A-1b) include the following skeletons.

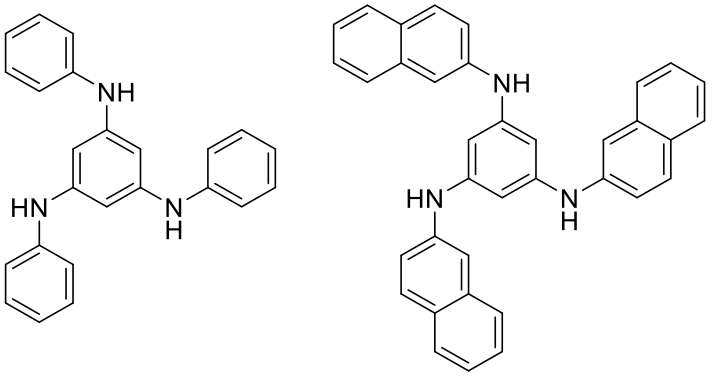
[Chem. 7]



[0055]

Examples of the skeleton represented by Formula (A-1c) include the following skeletons.

[Chem. 8]



[0056]

<<<A-3-2: Nitrogen-containing aromatic heterocyclic skeleton>>>

The nitrogen-containing aromatic heterocyclic skeleton

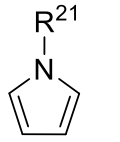
refers to a skeleton having an aromatic heterocyclic ring having a nitrogen atom among the atoms constituting the heterocyclic ring.

Examples of the nitrogen-containing aromatic heterocyclic ring include a pyrrole ring, an indole ring, a pyridine ring, an acridine ring, a phenoxazine ring, and a phenothiazine ring. These nitrogen-containing aromatic heterocyclic rings may have a substituent.

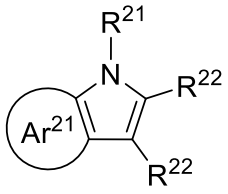
Examples of the nitrogen-containing aromatic heterocyclic skeleton include a skeleton represented by Formula (A-2a) below, Formula (A-2b-1) below, Formula (A-2b-2) below, Formula (A-2d) below, Formula (A-2e) below, Formula (A-3a) below, or Formula (A-3b) below.

As described later, in the unit structure (A-I), the hydrogen atom of the NH group may be substituted with a substituent. Examples of the substituent include the substituent described in (I-3) “Aromatic ring”, the substituent described in (A-2) “Exemplary skeleton constituting unit structure (A)”, and substituents (S) represented by Formulas (S1) to (S7) described later.

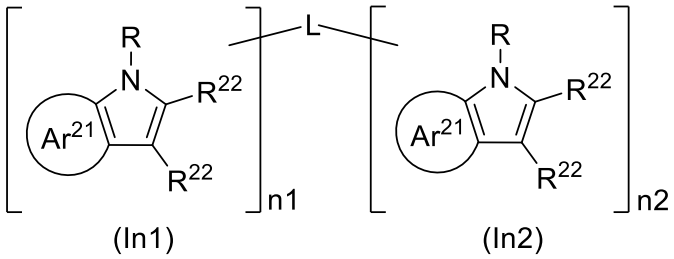
[Chem. 9]



(A-2a)



(A-2b-1)



(In1) (In2)

(A-2b-2)

(in the formula, each Ar^{21} independently represents a residue of an aromatic ring,

each R^{21} independently represents a hydrogen atom or a residue of an aromatic ring,

each R^{22} independently represents a hydrogen atom, a hydrocarbon group having 1 to 5 carbon atoms, or a residue of an aromatic ring, two adjacent R^{22}'s may together form an unsaturated aliphatic ring, one unsaturated bond in the unsaturated aliphatic ring refers to an unsaturated bond constituting a pyrrole ring,

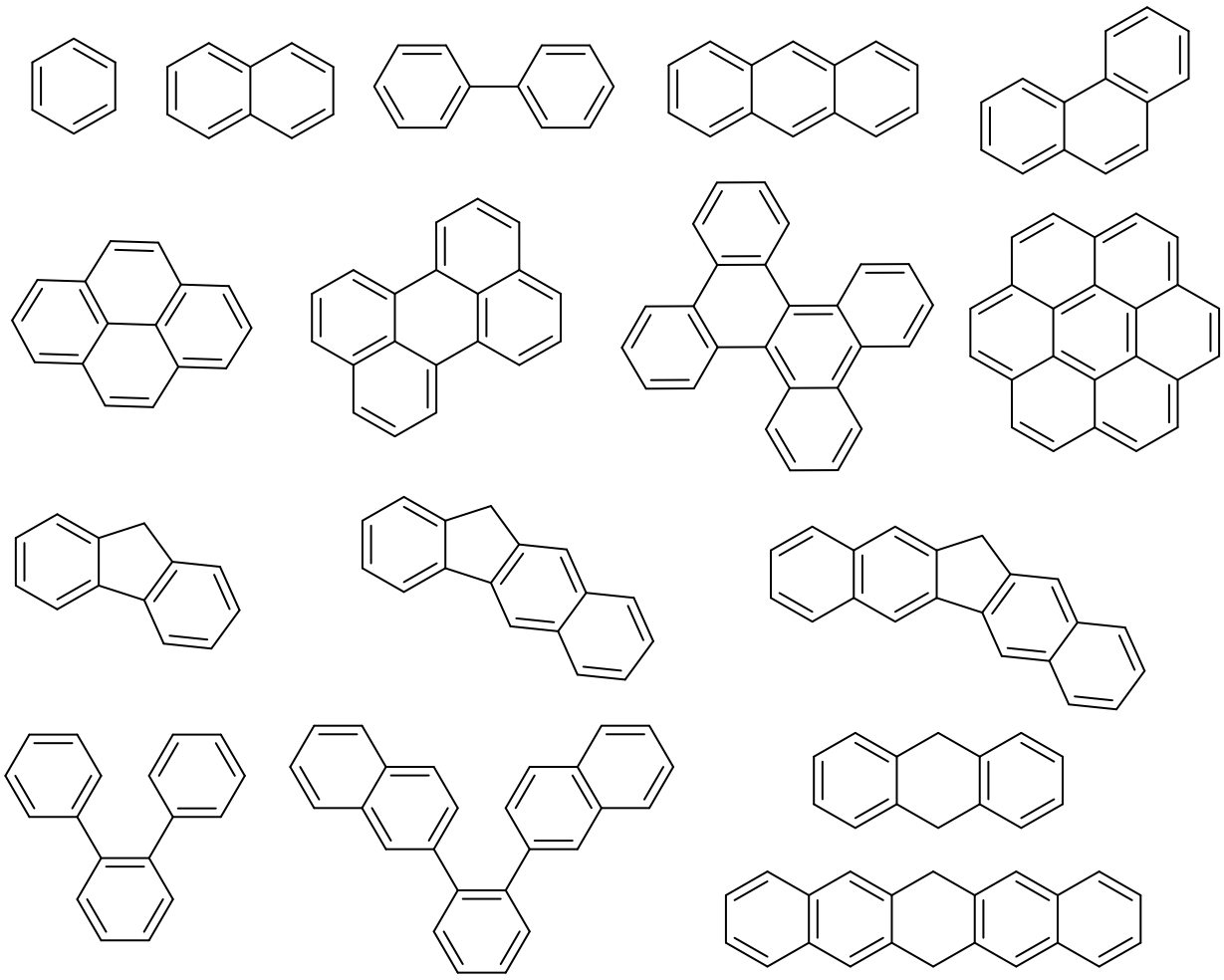
each R independently represents a hydrogen atom, a residue of an aromatic ring, or a bonding site to L, L represents a single bond or a linking group, n1 represents 1, n2 represents 1 or 2, in Formula (A-2b-2), in a case where L is a single bond, a partial structure (In1) and a partial structure (In2) bond to each other by two nitrogen atoms bonding to each other, two Ar^{21}'s bonding to each other, or a nitrogen atom and Ar^{21} bonding to each other, and in Formula (A-2b-2), in a case where L is a linking

group, L bonds to N or Ar^{21}).

[0057]

Examples of the aromatic ring in the residue of the aromatic rings of Ar^{21}, R^{21}, R^{22}, and R include an aromatic ring represented by Formula (G2) below. These aromatic rings may have a substituent.

[Chem. 10]



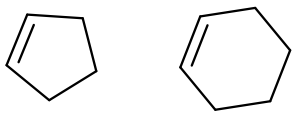
(G2)

[0058]

Examples of the unsaturated aliphatic ring formed by

two adjacent R^{22}s together include the following rings. These aliphatic rings may have a substituent.

[Chem. 11]



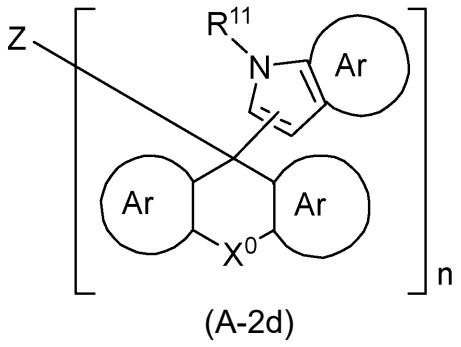
[0059]

Examples of the linking group in L include a (n1 + n2)-valent saturated hydrocarbon group having 1 to 5 carbon atoms and a residue obtained by removing (n1 + n2) hydrogen atoms from an aromatic ring.

[0060]

<Formula (A-2d)>

[Chem. 12]



(A-2d)

(In Formula (A-2d),

each R^{11} independently represents a hydrogen atom or an aromatic group,

Ar represents an aromatic ring moiety, and each independently represents a benzene ring, a condensed ring composed of 2 to 3 benzene rings, or a structure

represented by Formula (Ar01) below,

X^0 represents a single bond, -O-, -S-, -NR^{12}-, or -$CR^{13}R^{14}$-, R^{12} is the same as or different from R^{11} and has the same definition as R^{11}, and R^{13} and R^{14} each represent a hydrogen atom or a hydrocarbon group having 1 to 6 carbon atoms,

n is 1 or 2,

when n is 1, Z represents a monovalent organic group, and when n is 2, Z represents a divalent organic group.)

[0061]

Note that in the unit structure (A-I), R^{11} in Formula (A-2d) may be a substituent.

When R^{11} is a substituent or an aromatic group, R^{11} represents, for example:

(i) a methylol group;

(ii) an aryl group having 6 to 30 carbon atoms; or

(iii) a linear, branched, or cyclic alkoxymethyl group having 2 to 20 carbon atoms, a linear, branched, or cyclic alkyl group having 1 to 20 carbon atoms, an alkenyl group having 2 to 10 carbon atoms, or an alkynyl group having 2 to 10 carbon atoms;

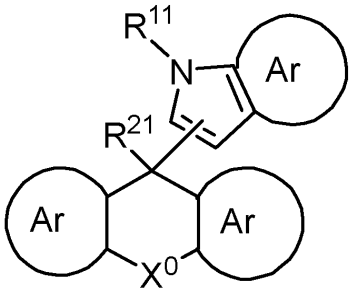
provided that, in the cases of (ii) and (iii), the group may be further substituted with an oxygen atom-containing substituent, a sulfur atom-containing substituent, a nitrogen atom-containing substituent, an

aryl group, or a halo group; or in the case of (iii), the hydrocarbon chain moiety may be further interrupted by an oxygen atom-containing substituent, a sulfur atom-containing substituent, a nitrogen atom-containing substituent, or an arylene group.

[0062]

Examples of the skeleton represented by Formula (A-2d) include a skeleton represented by Formula (A-2d-1) below.

[Chem. 13]



(A-2d-1)

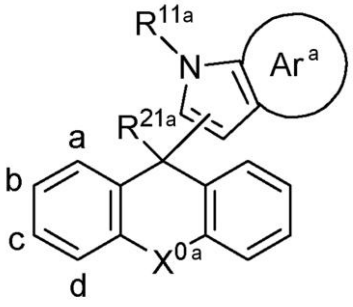
(In Formula (A-2d-1), R^{11}, Ar, and X^0 have the same meanings as R^{11}, Ar, and X^0 in Formula (A-2d), respectively. R^{21} is an aryl group having 6 to 30 carbon atoms, an alkenyl group having 2 to 10 carbon atoms, or an alkynyl group having 2 to 10 carbon atoms.)

[0063]

Ar in Formulas (A-2d) and (A-2d-1) is, for example, a benzene ring or a naphthalene ring.

Ar in Formulas (A-2d) and (A-2d-1) may have a structure represented by Formula (Ar01) below.

[Chem. 14]



(Ar01)

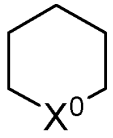
(where R^{11a} in Formula (Ar01) has the same meaning as R^{11} in Formula (A-2d-1), R^{21a} has the same meaning as R^{21} in Formula (A-2d-1), Ar^a has the same meaning as Ar in Formula (A-2d-1), and X^{0a} has the same meaning as X^0 in Formula (A-2d-1).

At the two carbon atoms a and b, b and c, or c and d in Formula (Ar01), a monocyclic moiety including X^0 in Formula (A-2d) or (A-2d-1) forms a condensed ring.)

[0064]

Here, the monocyclic moiety containing X^0 represents a monocyclic ring represented by Formula (AP011) below in Formula (A-2d).

[Chem. 15]

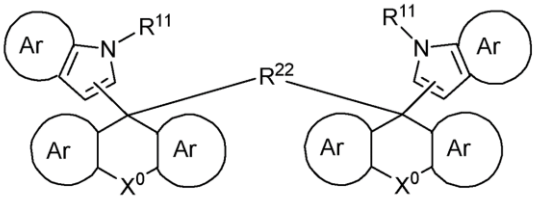


(AP011)

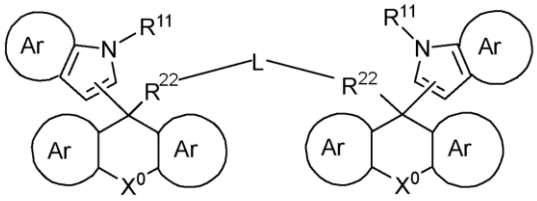
[0065]

Preferable examples of the skeleton represented by Formula (A-2d) include a skeleton represented by Formula (A-2d-1) above, a skeleton represented by Formula (A-2d-2) below, and a skeleton represented by Formula (A-2d-3) below.

[Chem. 16]



(A-2d-2)



(A-2d-3)

(In Formula (A-2d-2) and Formula (A-2d-3), R^{11}, Ar, and X^0 have the same meanings as R^{11}, Ar, and X^0 in Formula (A-2d), respectively.

L represents a single bond or a divalent linking group, and the divalent linking group represents, for example, -O-, -S-, $-SO_2-$, -CO-, -CONH-, -COO-, $-NR^{101}-$, $-(CR^{102}R^{103})m^1-$, $-(Ar^{101})m^2-$, $-CH_2-(Ar^{101})m^2-CH_2-$, or -(cyclo-R)-. R^{101}, R^{102}, and R^{103} each independently represent a hydrogen atom, a hydrocarbon group having 1 to 5 carbon atoms, or an aryl group having 6 to 30 carbon atoms; and m^1 represents an integer of 1 to 10. Ar^{101} each independently represents an

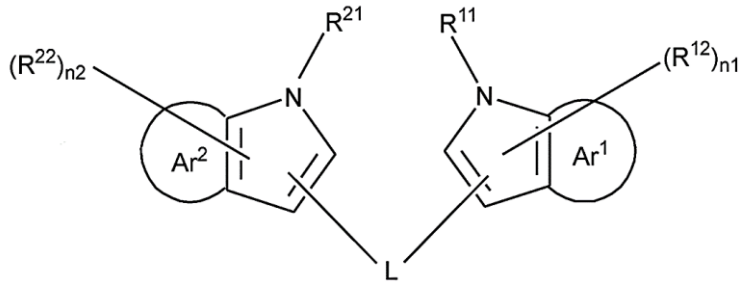
arylene group having 6 to 30 carbon atoms, and m^2 represents an integer of 1 to 3, which is the number of aromatic rings bonding to each other by a single bond. The term "cyclo-R" represents a divalent alicyclic hydrocarbon group having a 5 to 8 membered ring, preferably a 6 to 8 membered ring, which may form a condensed ring with one or two benzene rings or naphthalene rings.

R^{22} each independently represents an arylene group having 6 to 30 carbon atoms, alkenylene group having 2 to 10 carbon atoms, or alkynylene group having 2 to 10 carbon atoms that is optionally substituted.)

[0066]

<Formula (A-2e)>

[Chem. 17]



(A-2e)

(In Formula (A-2e), L represents a single bond or a divalent linking group between any two carbon atoms constituting each azaaryl condensed ring,

R^{11} and R^{21} each independently represent a hydrogen atom or a residue of an aromatic ring,

R^{12} and R^{22} each independently represent a substituent,

n1 and n2 each independently represent the number of substituents of R^{12} and R^{22}, and may be 0,

Ar^1 and Ar^2 are each independently a benzene ring or a condensed ring composed of 2 to 3 benzene rings forming a condensed ring with the pyrrole ring moiety in Formula (A-2e).)

[0067]

Note that in the unit structure (A-I), R^{11} and R^{21} in Formula (A-2e) may be substituents.

When R^{11} and R^{21} are each independently a substituent or a residue of an aromatic group, R^{11} and R^{21} are, for example:

(i) a methylol group;

(ii) an aryl group having 6 to 30 carbon atoms; or

(iii) a linear, branched, or cyclic alkoxymethyl group having 2 to 20 carbon atoms, a linear, branched, or cyclic alkyl group having 1 to 20 carbon atoms, an alkenyl group having 2 to 10 carbon atoms, or an alkynyl group having 2 to 10 carbon atoms;

provided that, in the cases of (ii) and (iii), the group may be further substituted with an oxygen atom-containing substituent, a sulfur atom-containing substituent, a nitrogen atom-containing substituent, an aryl group, or a halo group; or in the case of (iii), the

hydrocarbon chain moiety may be further interrupted by an oxygen atom-containing substituent, a sulfur atom-containing substituent, a nitrogen atom-containing substituent, or an arylene group.

[0068]

In Formula (A-2e), L represents a single bond or a divalent linking group. L may bond to any carbon atom constituting each azaaryl condensed ring, and may bond to Ar^1 or Ar^2, that is, an aromatic carbon atom constituting

[Chem. 18]



and

[Chem. 19]



in the azaaryl condensed ring, but preferably bonds to a carbon atom constituting the pyrrole ring moiety in the azaaryl condensed ring.

[0069]

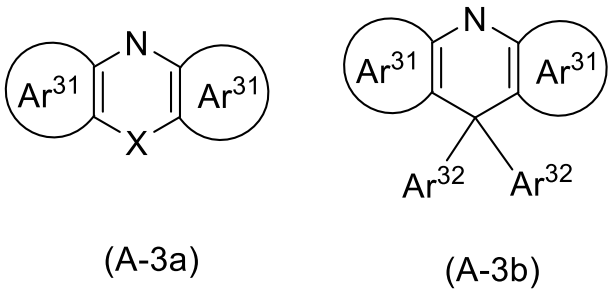
A preferable linking group (L) is selected from the group consisting of -O-, -S-, $-SO_2-$, -CO-, -CONH-, -COO-, -NH-, $-(CR^{102}R^{103})m^1-$, $-(Ar^{101})m^2-$, $-CH_2-(Ar^{101})m^2-CH_2-$, and -(cyclo-R)-. R^{102} and R^{103} each independently represent a hydrogen atom, a hydrocarbon group having 1 to 5 carbon

atoms, or an aryl group having 6 to 30 carbon atoms; and m^1 represents an integer of 1 to 10. Ar^{101} each represents an arylene group having 6 to 30 carbon atoms, m^2 represents an integer of 1 to 3, which is the number of aromatic rings bonding to each other by a single bond. The term "cyclo-R" represents a divalent alicyclic hydrocarbon group having a 5 to 8 membered ring, preferably a 6 to 8 membered ring, which may form a condensed ring with one or two benzene rings or naphthalene rings.

[0070]

<Formulas (A-3a) and (A-3b)>

[Chem. 20]



(A-3a) (A-3b)

(In the formula, Ar^{31} and Ar^{32} each independently represent a residue of an aromatic ring, or represent a residue of an aromatic ring together with a carbon atom bonded thereto. X represents -O, -S-, -NH-, $-CH_2-$, $-CH_2-CH_2-$, or -CH=CH-.)

[0071]

Examples of the aromatic ring in the residue of the aromatic ring of Ar^{31} and Ar^{32} include an aromatic ring

represented by Formula (G1) described above.

Examples of the aromatic ring formed by Ar^{31} and Ar^{32} together with the carbon atom bonded thereto include a fluorene ring, a benzofluorene ring, and a dibenzofluorene ring.

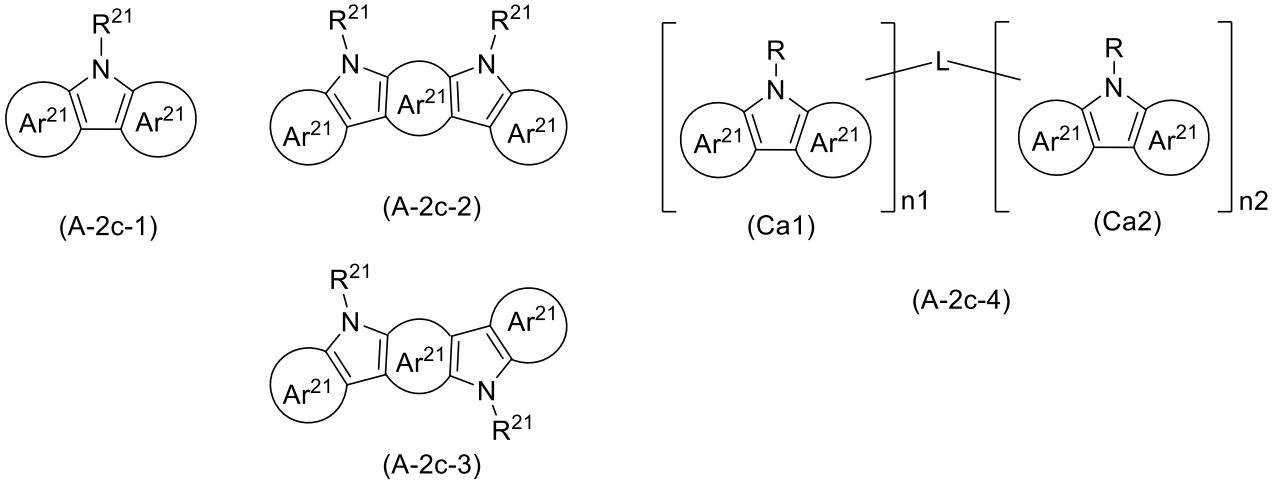
[0072]

The resin (G) preferably contains a unit structure not including a carbazole skeleton as the unit structure (A-I).

Here, "carbazole skeleton" refers to a skeleton including a carbazole ring.

Examples of the carbazole skeleton include a skeleton represented by Formula (A-2c-1) below, Formula (A-2c-2) below, Formula (A-2c-3) below, or Formula (A-2c-4) below.

[Chem. 21]



(in the formula, each Ar^{21} independently represents a residue of an aromatic ring,

each R^{21} independently represents a hydrogen atom or a

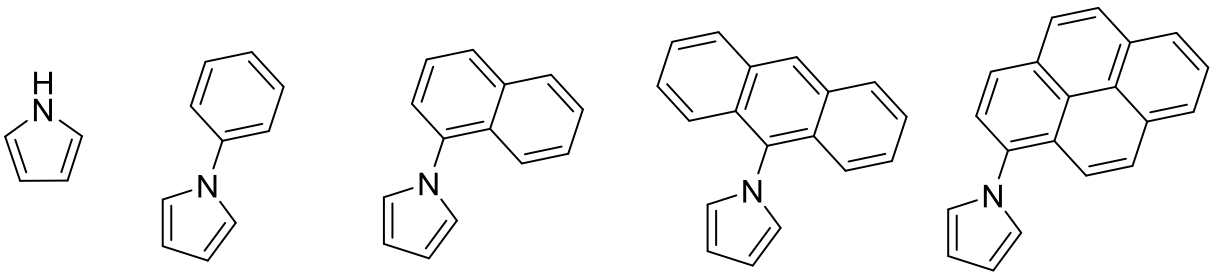
residue of an aromatic ring,

each R independently represents a hydrogen atom, a residue of an aromatic ring, or a bonding site to L, L represents a single bond or a linking group, n1 represents 1, n2 represents 1 or 2, In Formula (A-2c-4), in a case where L is a single bond, a partial structure (Ca1) and a partial structure (Ca2) bond to each other by two nitrogen atoms bonding to each other, two Ar^{21}'s bonding to each other, or a nitrogen atom and Ar^{21} bonding to each other. In Formula (A-2c-4), in a case where L is a linking group, L bonds to N or Ar^{21}.)

[0073]

Examples of the skeleton represented by Formula (A-2a) include the following skeletons. The aromatic ring in these skeletons may have a substituent, and the hydrogen atom of the NH group may be substituted with a substituent. The same applies to the following skeletons.

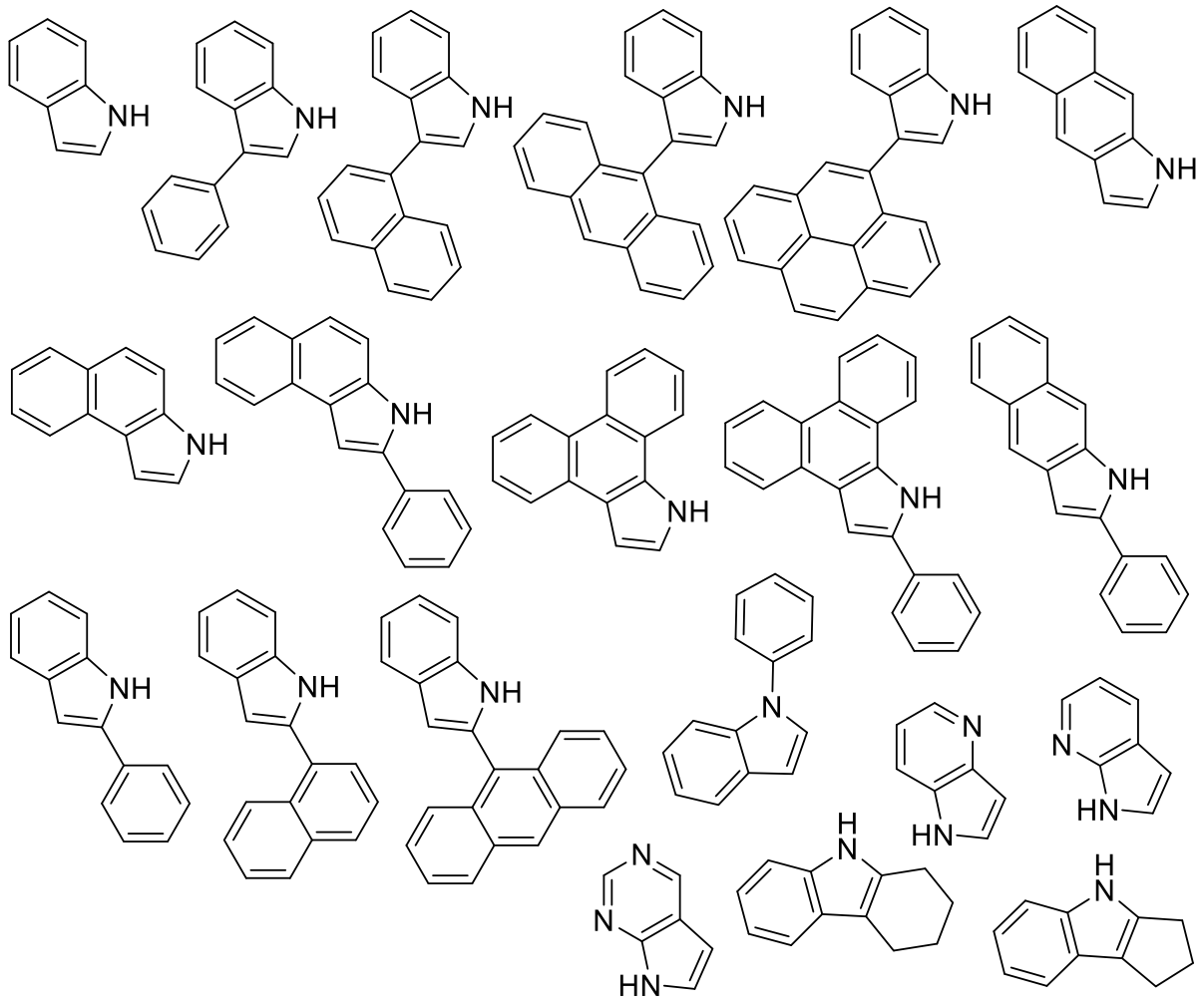
[Chem. 22]



[0074]

Examples of the skeleton represented by Formula (A-2b-1) include the following skeletons.

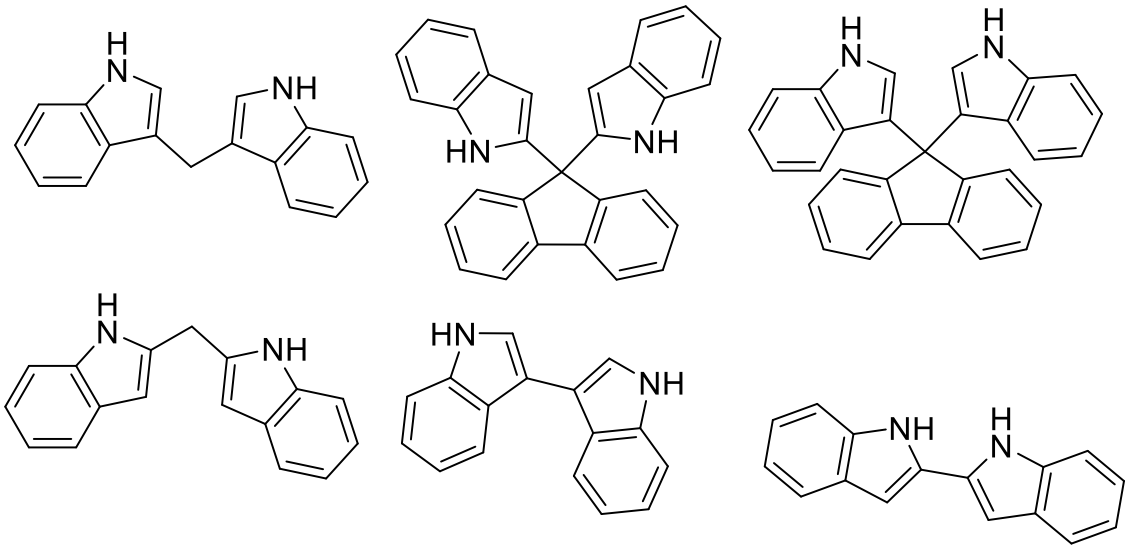
[Chem. 23]



[0075]

Examples of the skeleton represented by Formula (A-2b-2) include the following skeletons.

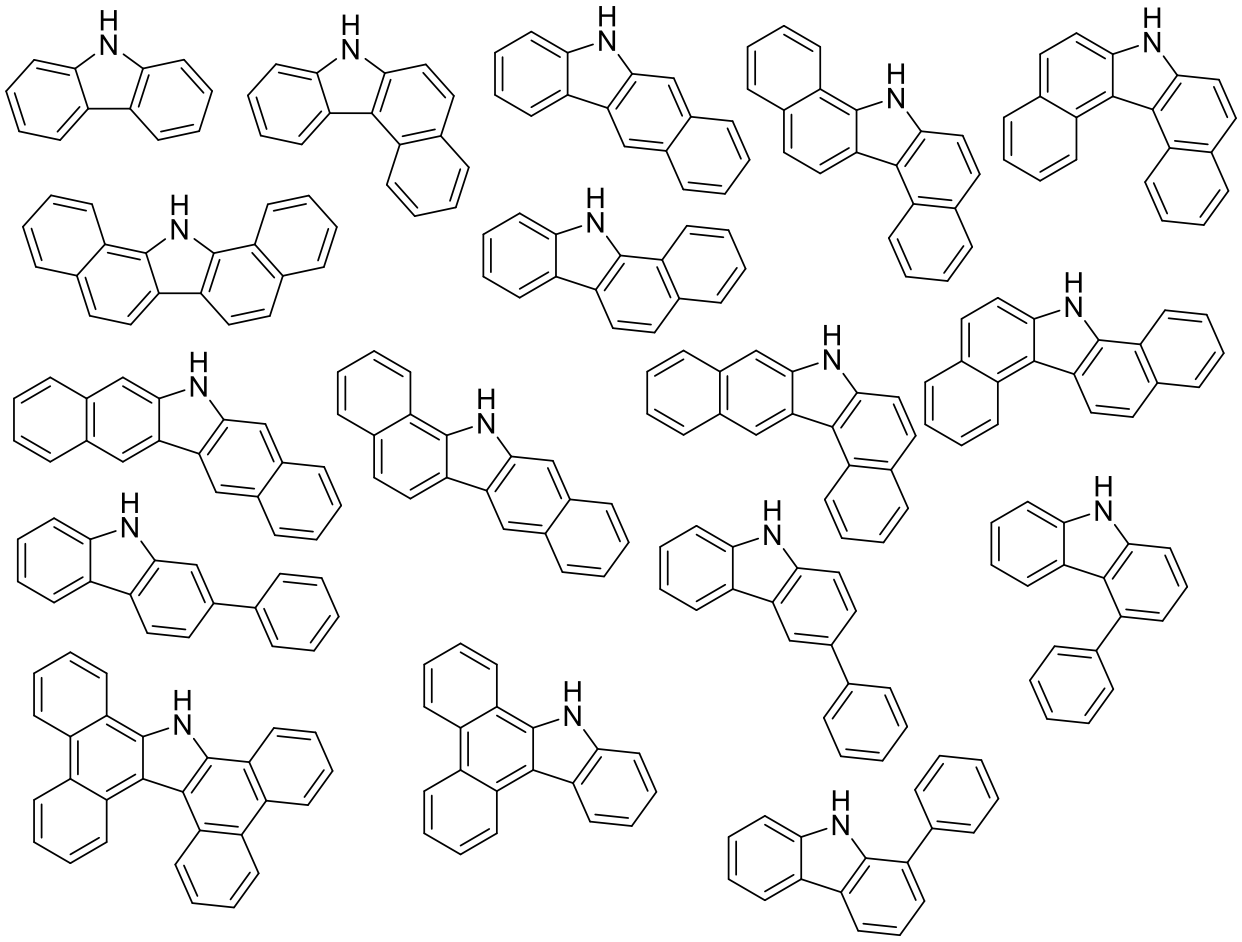
[Chem. 24]



[0076]

Examples of the skeleton represented by Formula (A-2c-1) include the following skeletons.

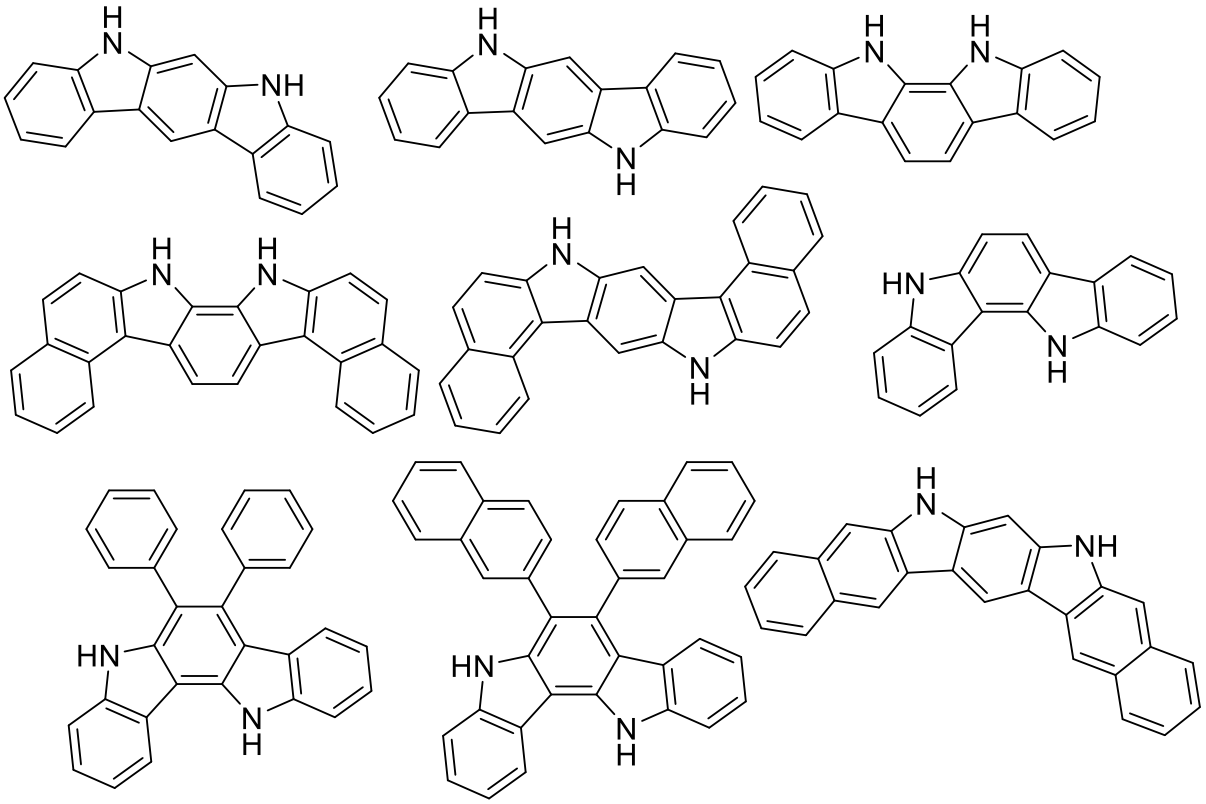
[Chem. 25]



[0077]

Examples of the skeleton represented by Formula (A-2c-2) or Formula (A-2c-3) include the following skeletons.

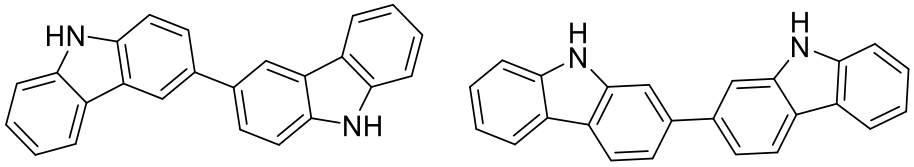
[Chem. 26]



[0078]

Examples of the skeleton represented by Formula (A-2c-4) include the following skeletons.

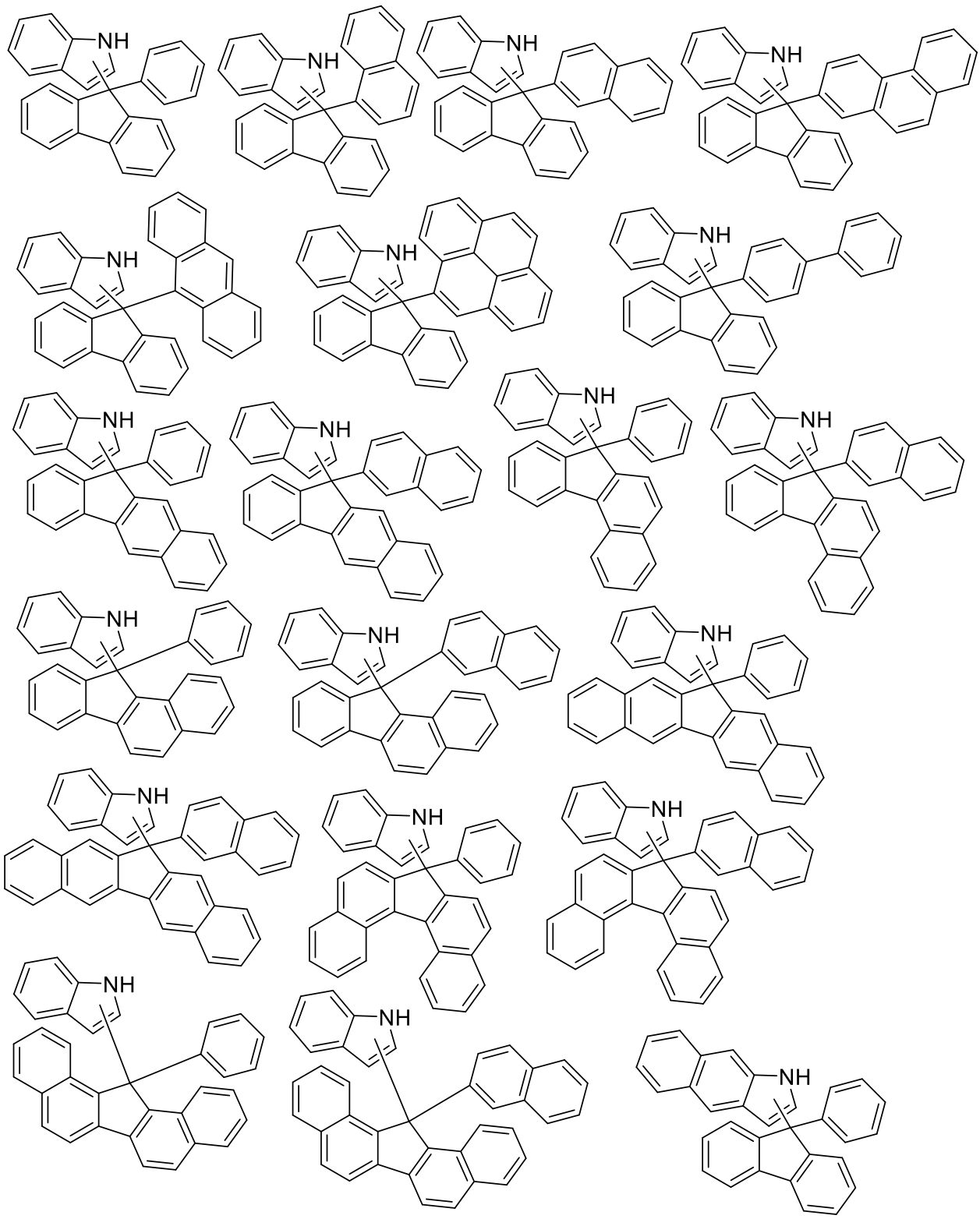
[Chem. 27]



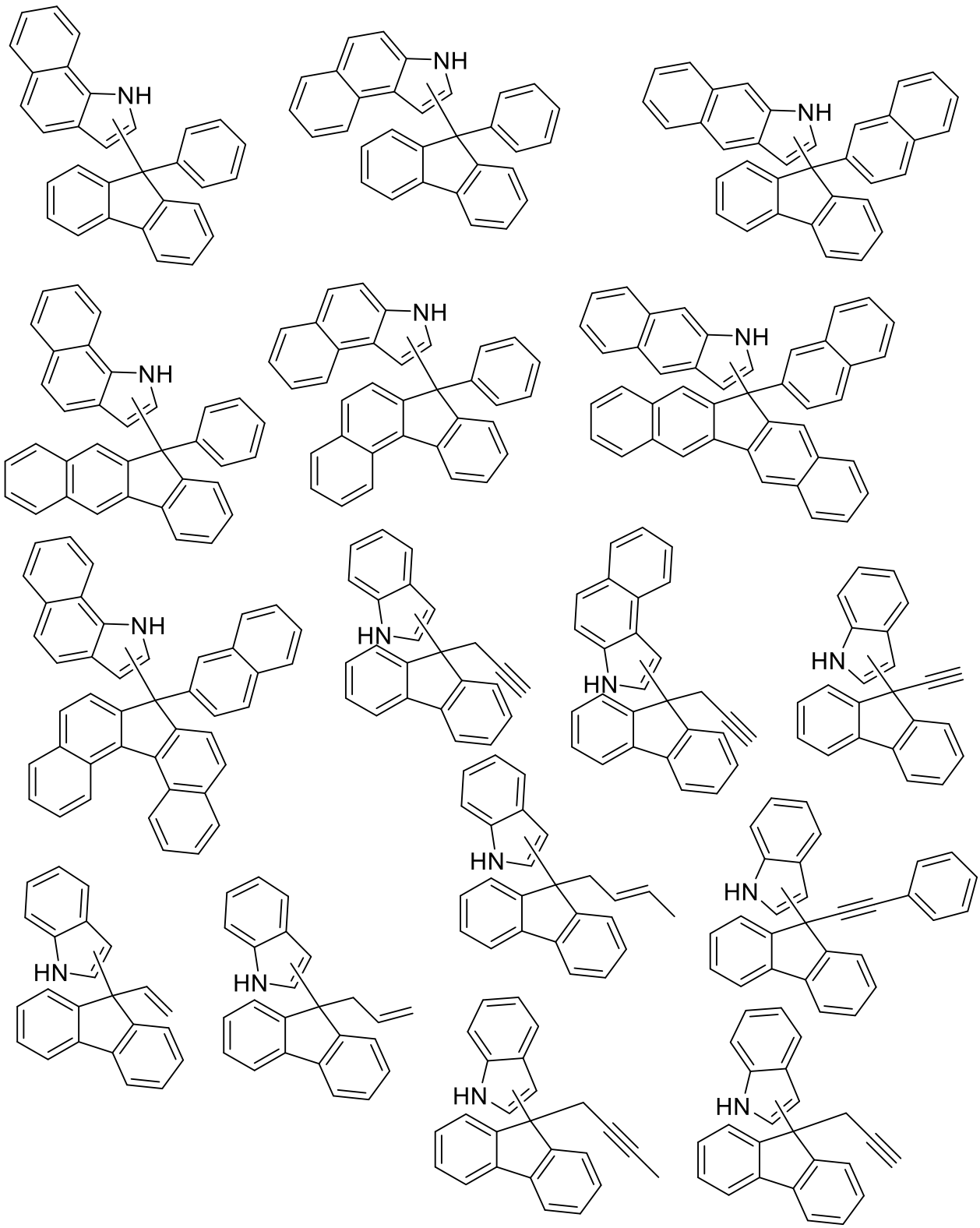
[0079]

Examples of the skeleton represented by Formula (A-2d) include the following skeleton:

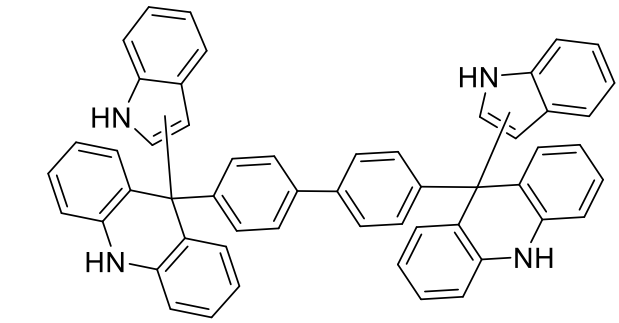
[Chem. 28]

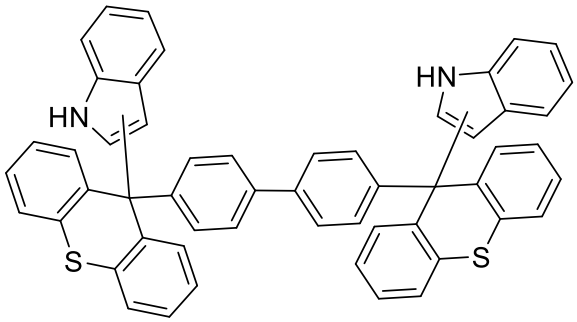


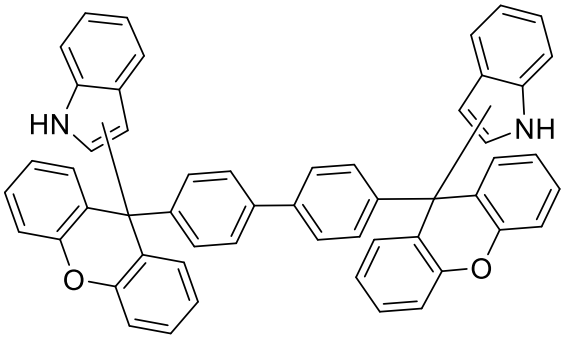
[Chem. 29]

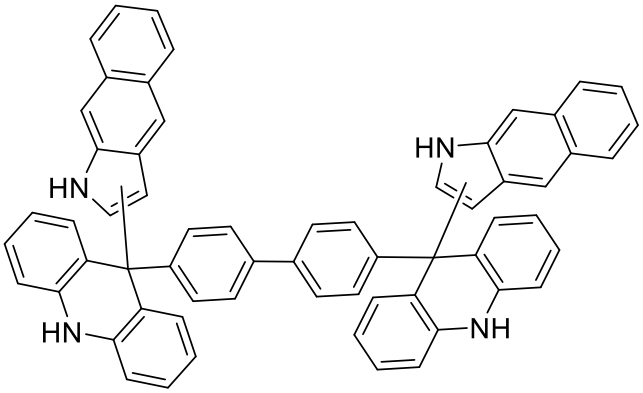


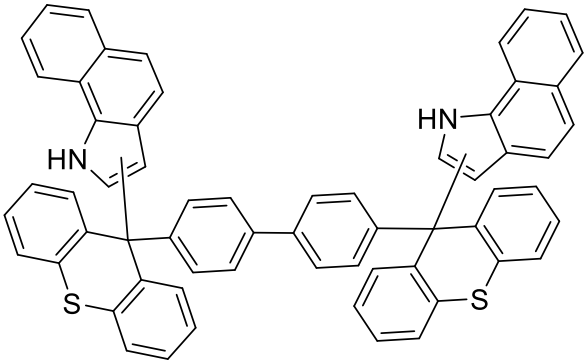
[Chem. 30]

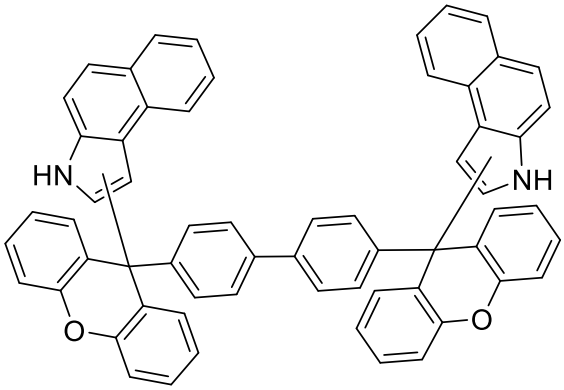

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HN
HN
NH

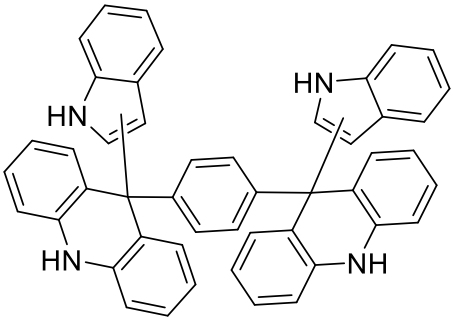

HN
HN
S
HN
S

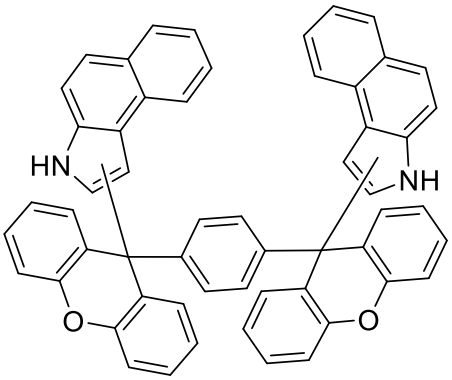

HN
NH
O
O


HN
HN
HN
NH

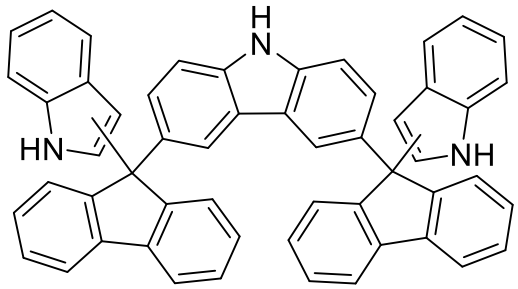
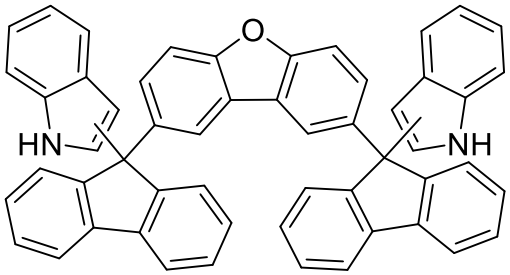
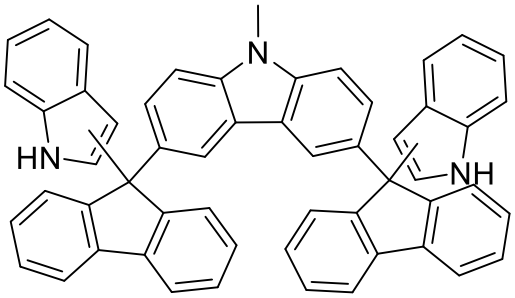
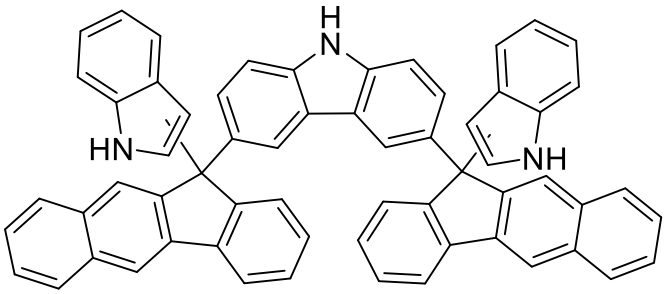
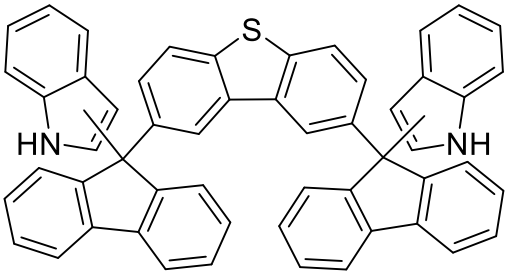
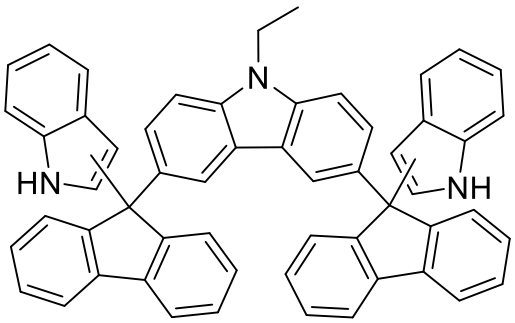
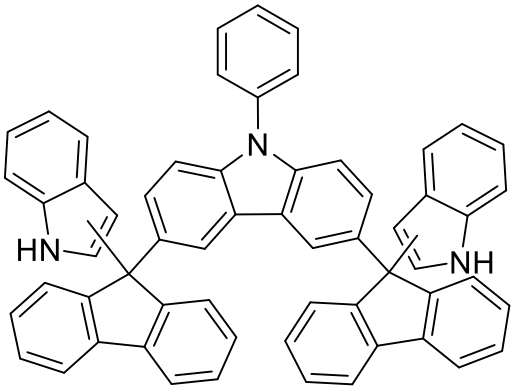
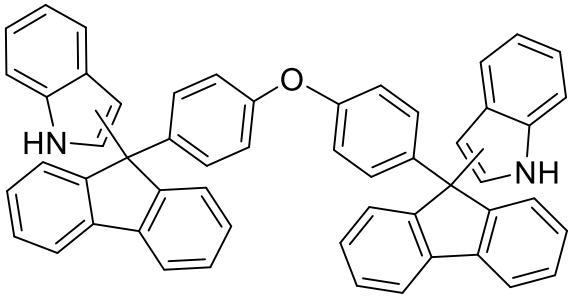
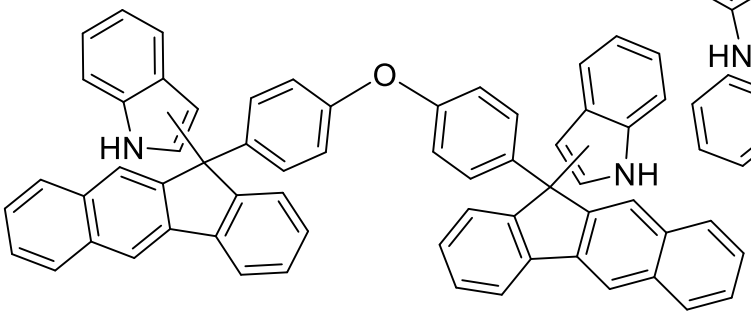
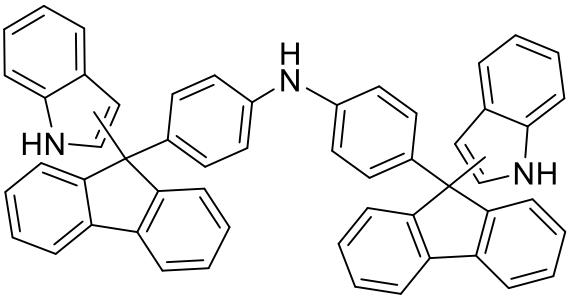

HN
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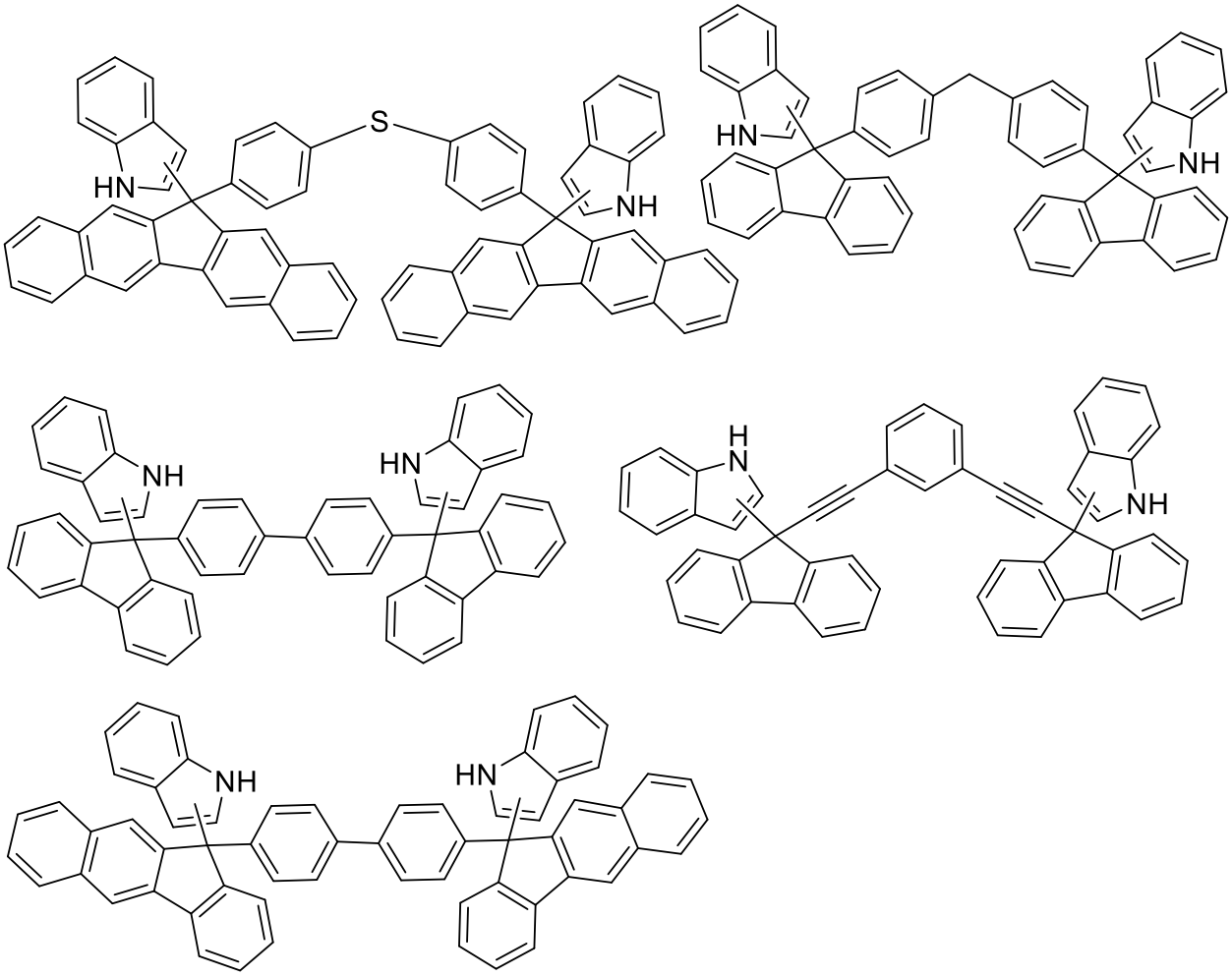

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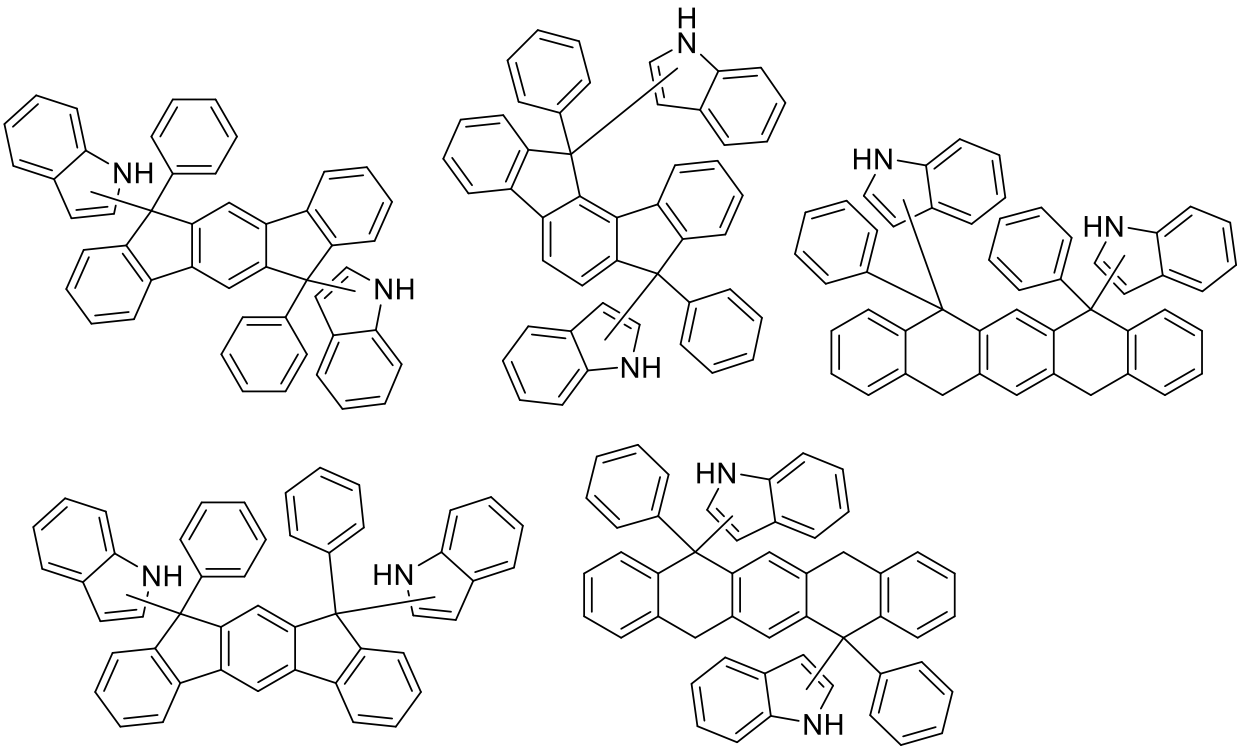
[Chem. 31]

[Chem. 32]



[Chem. 33]

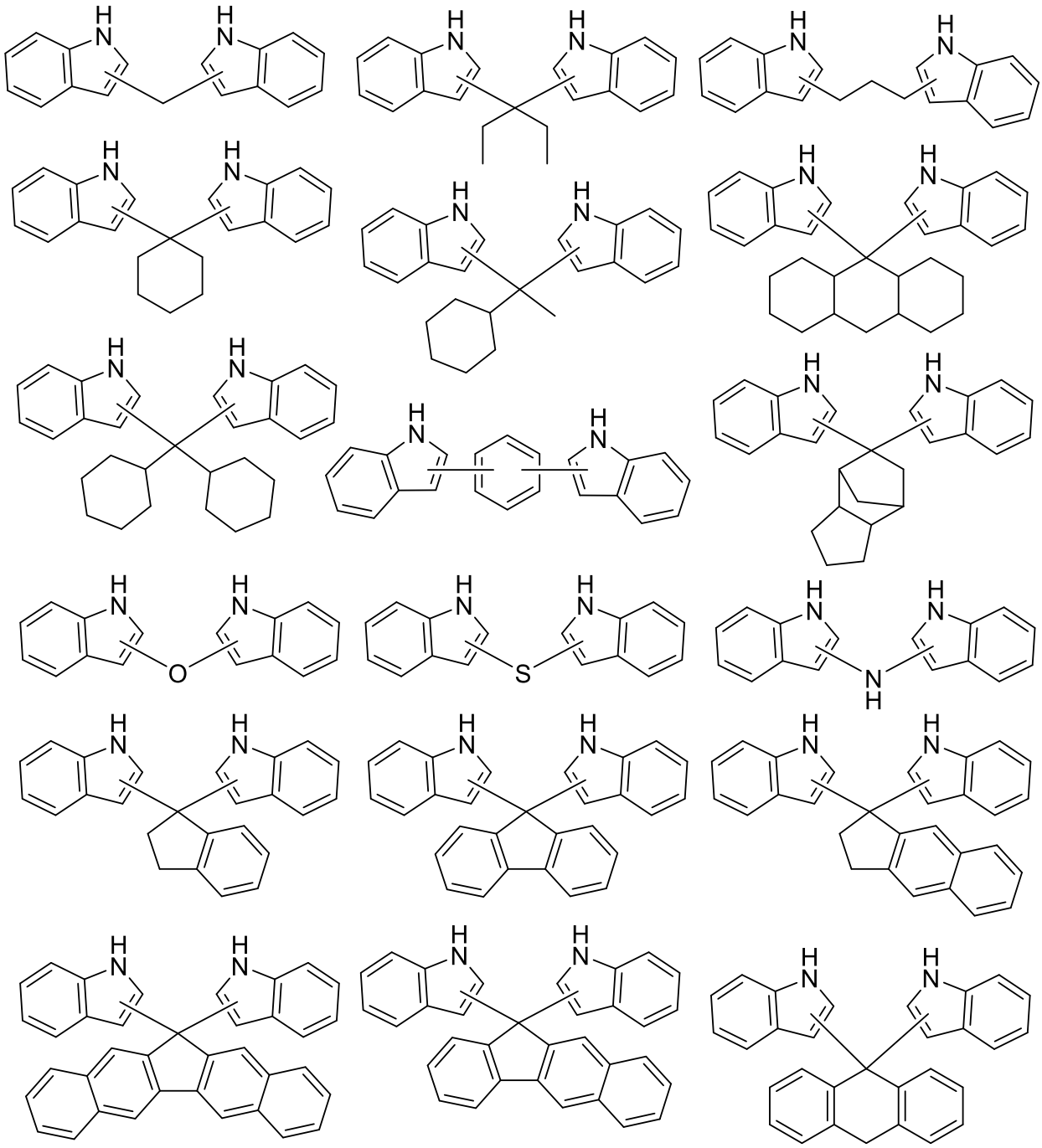


[0080]

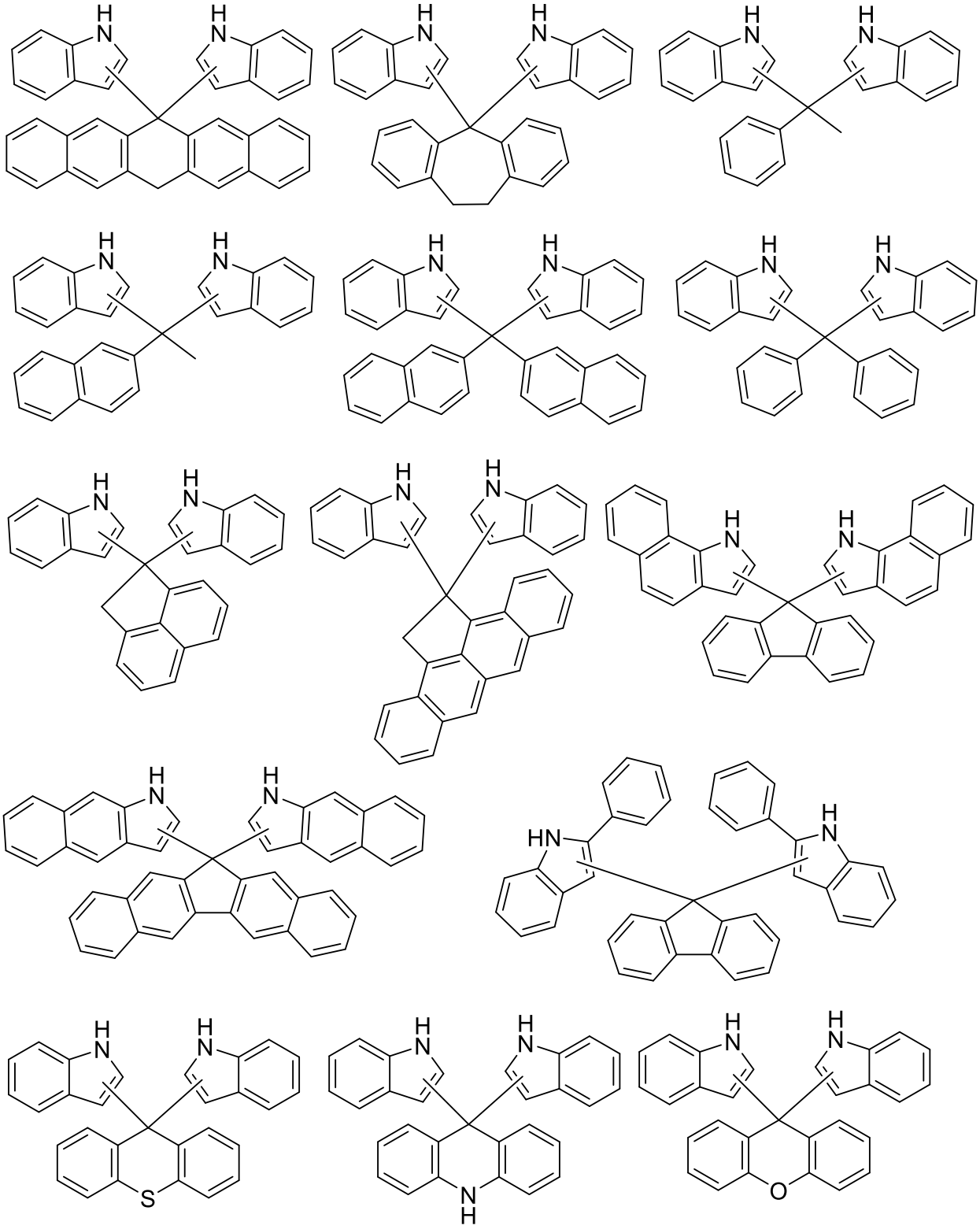
Examples of the skeleton represented by Formula (A-2e) include the following skeleton:

Note that specific examples of the skeleton represented by Formula (A-2d) and specific examples of the skeleton represented by Formula (A-2e) may overlap.

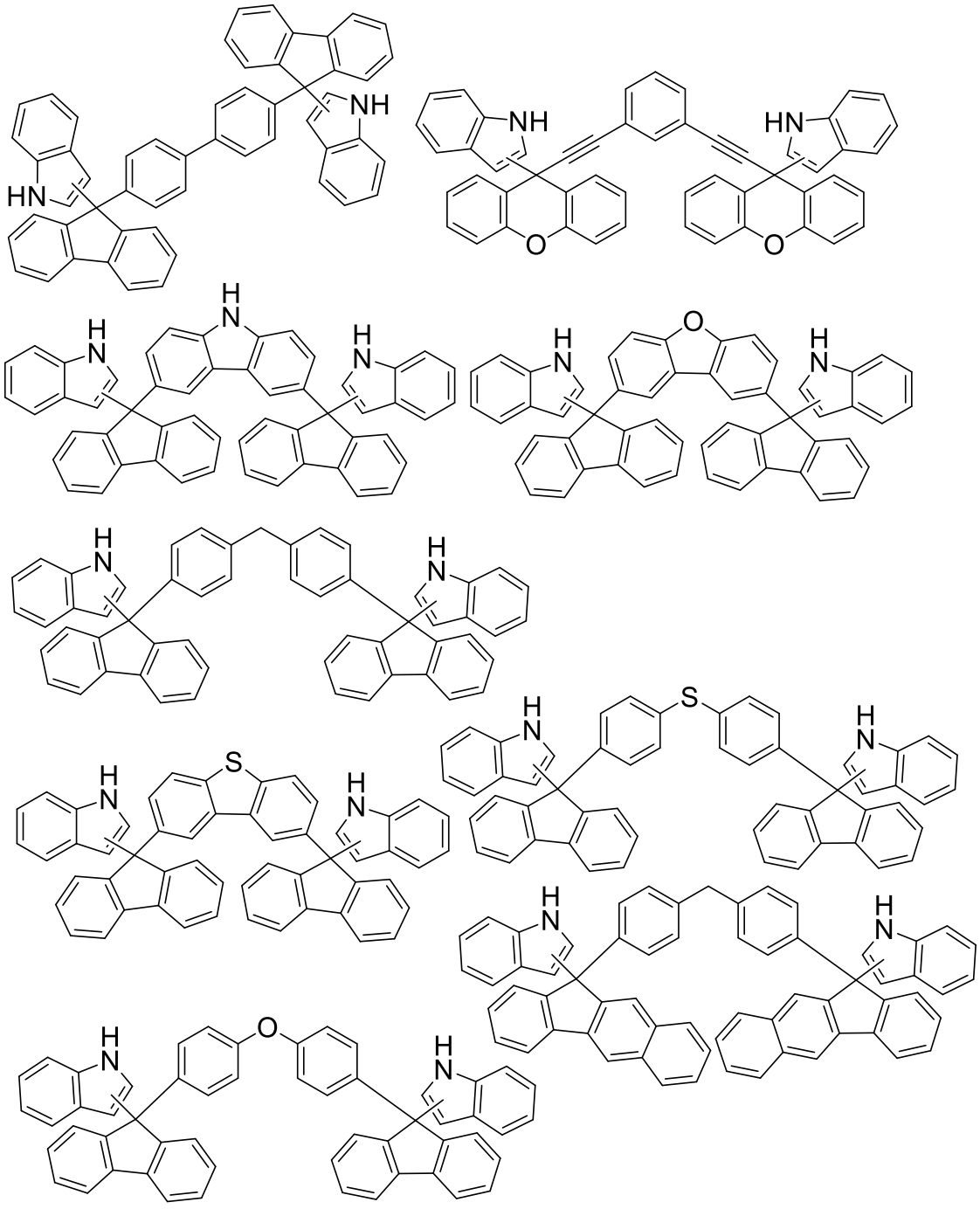
[Chem. 34]



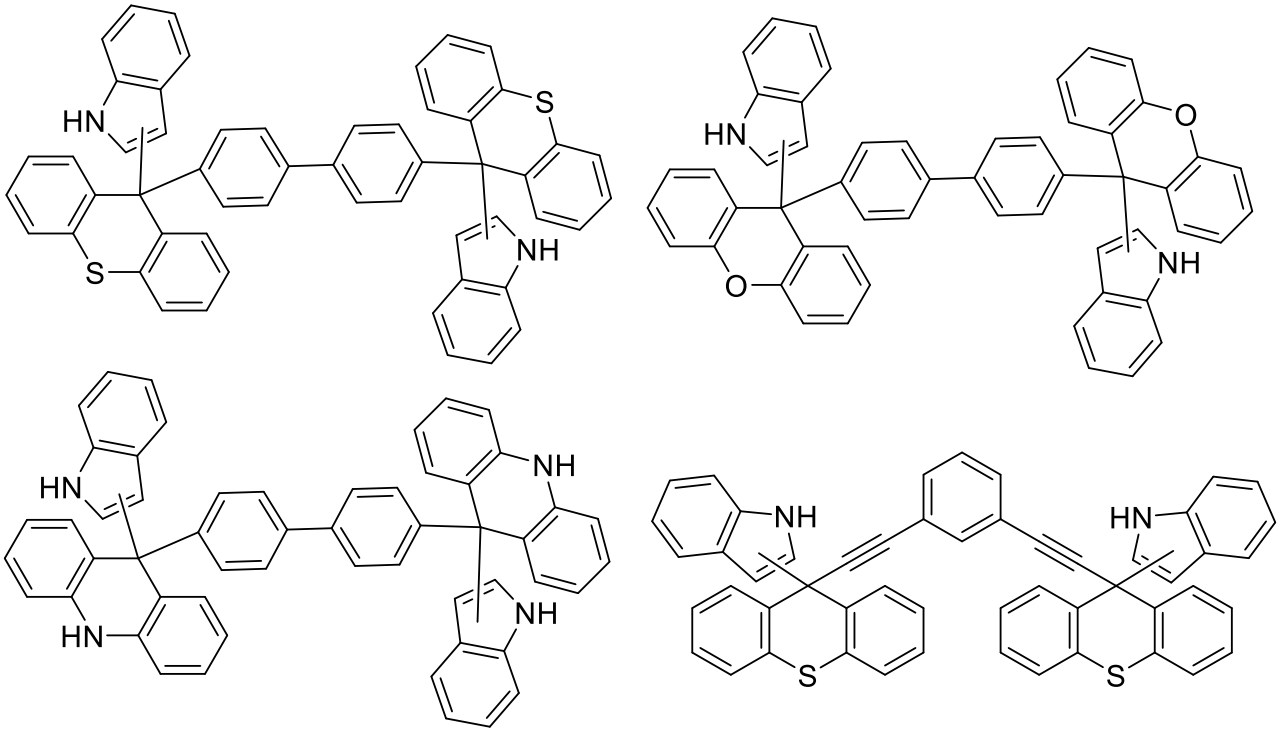
[Chem. 35]



[Chem. 36]



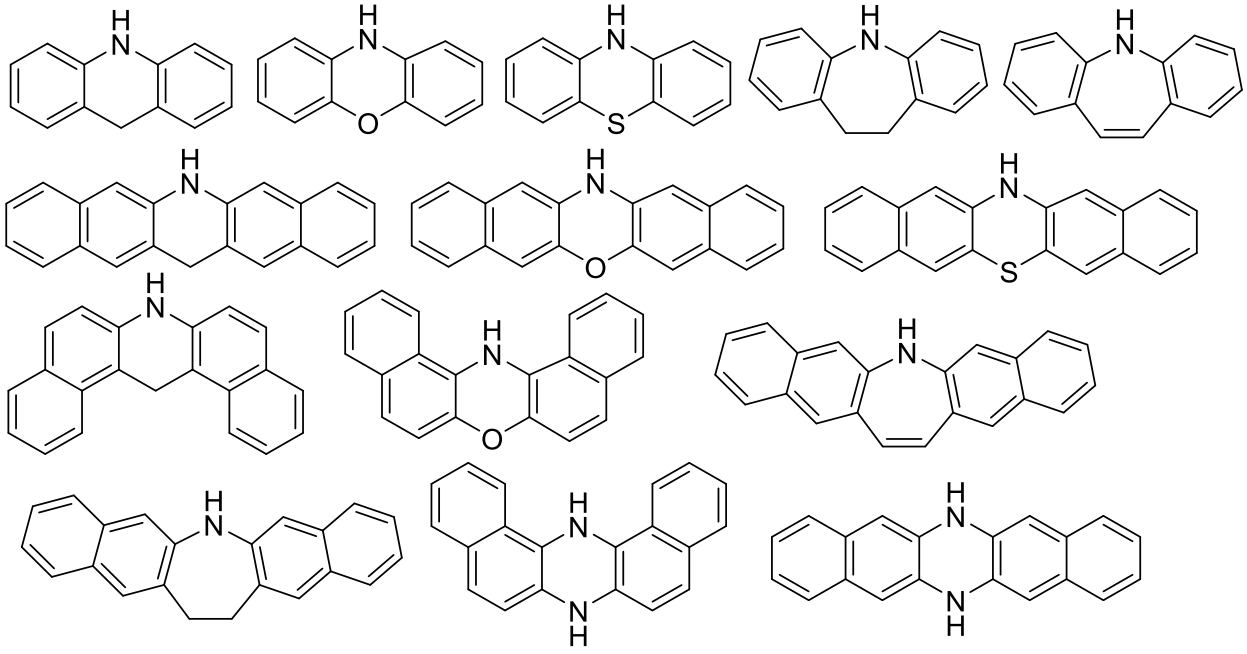
[Chem. 37]



[0081]

Examples of the skeleton represented by Formula (A-3a) include the following skeleton:

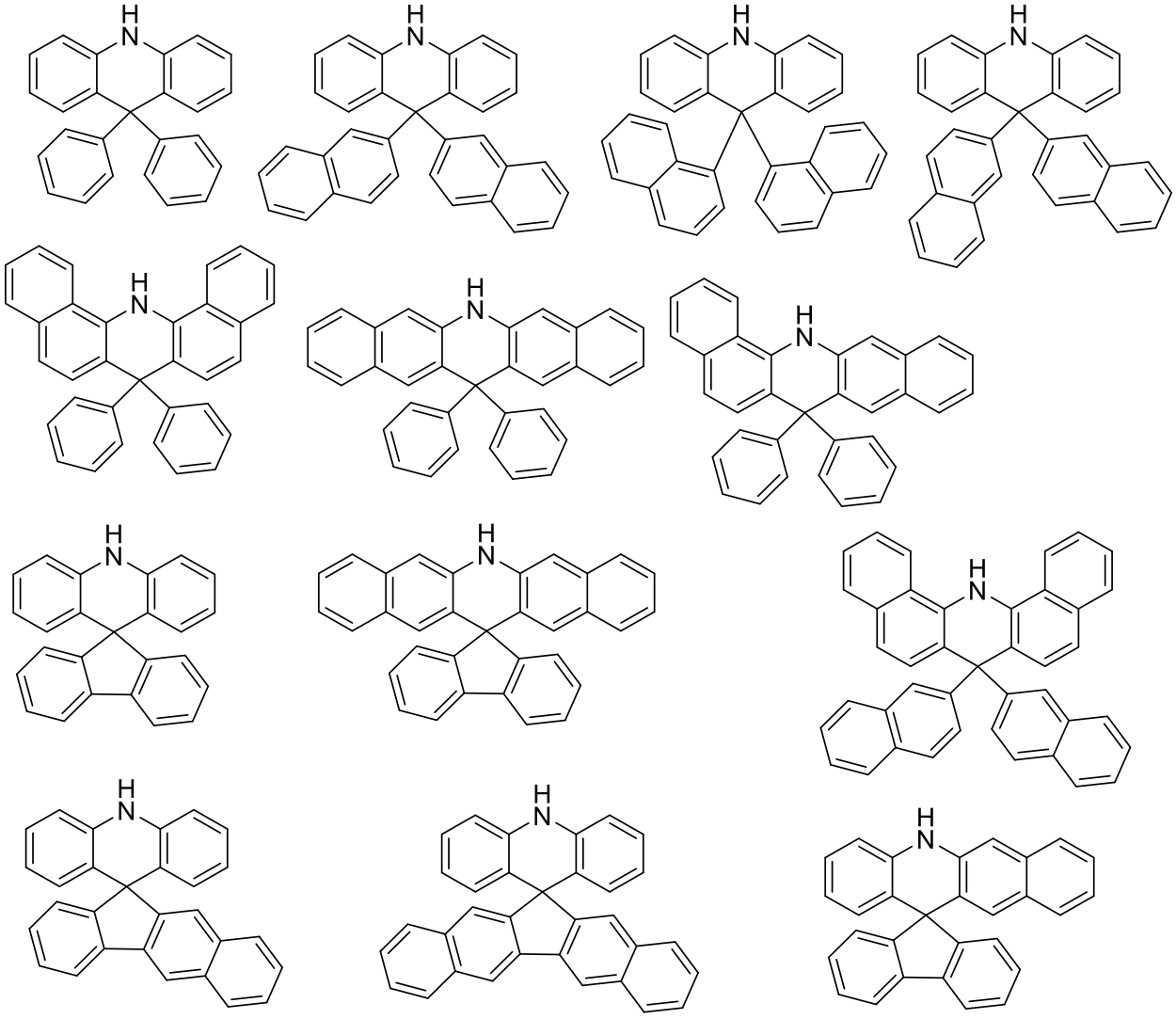
[Chem. 38]



[0082]

Examples of the skeleton represented by Formula (A-3b) include the following skeleton:

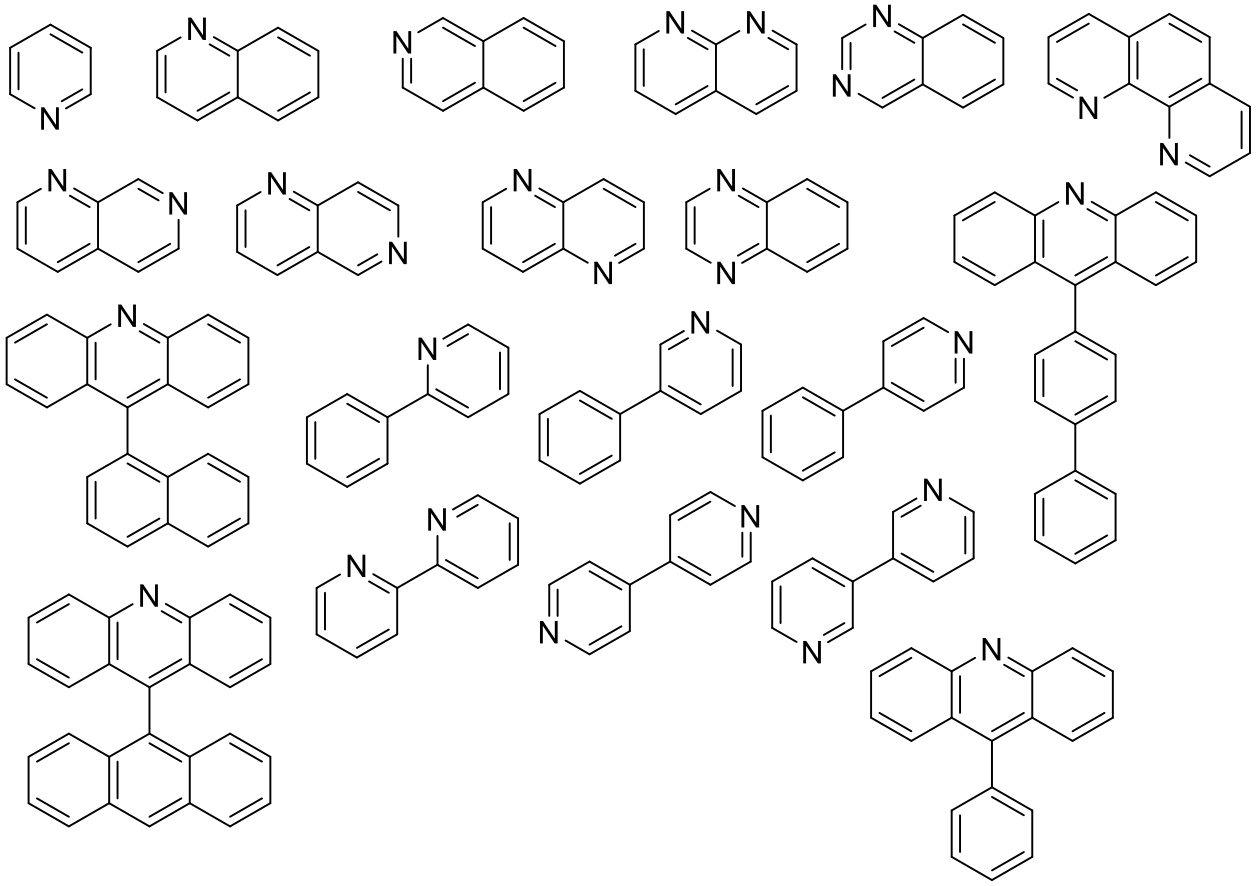
[Chem. 39]



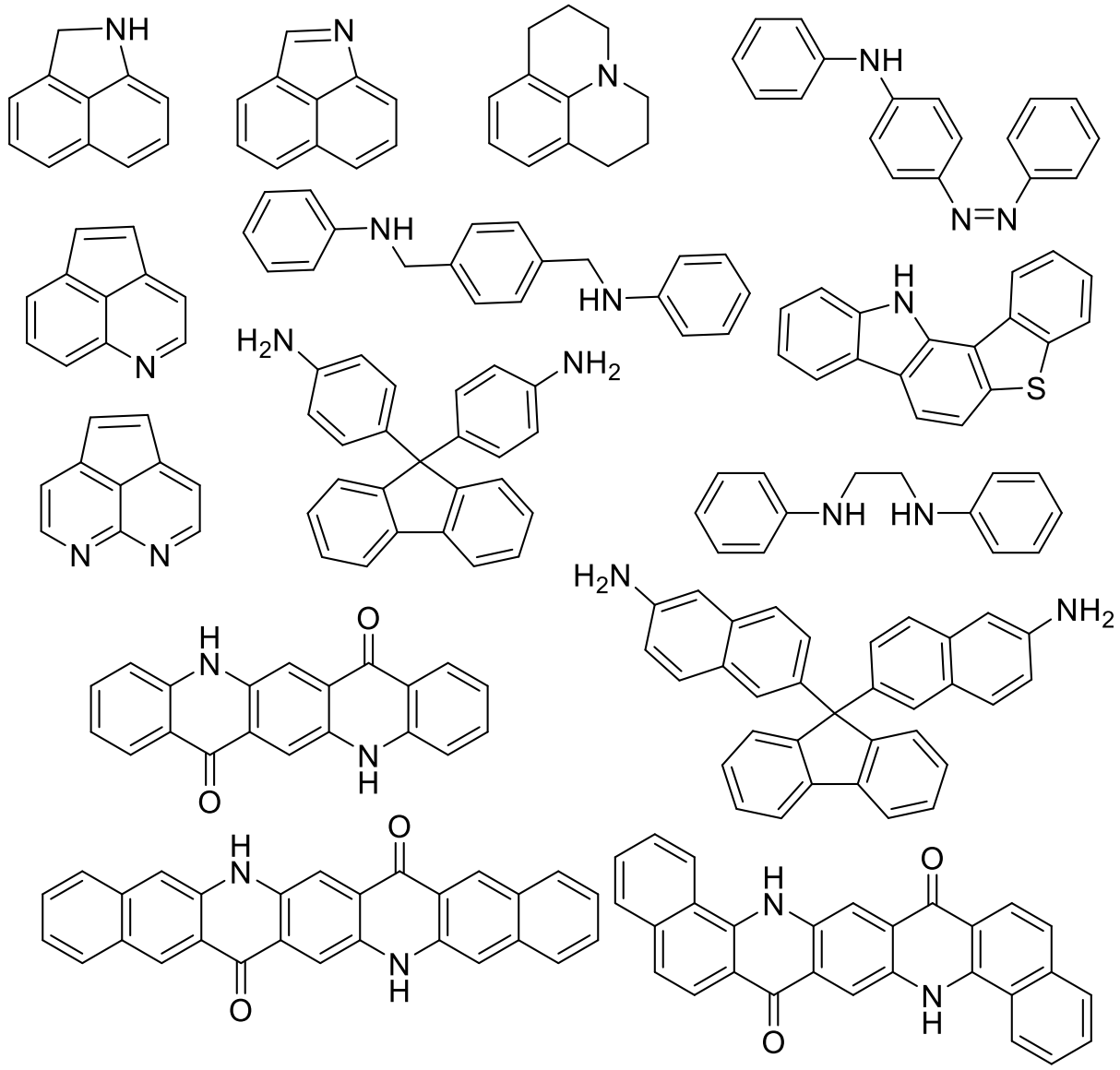
[0083]

Examples of other skeletons of the nitrogen-containing aromatic heterocyclic ring skeleton include the following skeleton:

[Chem. 40]



[Chem. 41]



[0084]

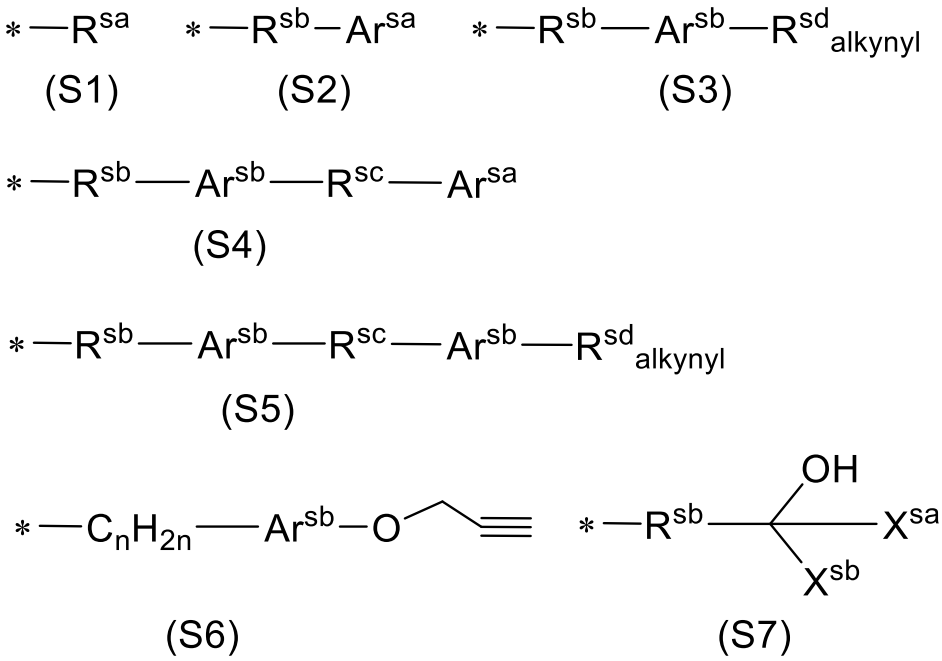
In addition, H of NH in the skeleton having the above aromatic ring, H of a hydroxy group bonding to an aromatic ring in the skeleton having an aromatic ring, and a hydrogen atom bonding to an aromatic ring in the skeleton having an aromatic ring may be substituted with a substituent.

Examples of the substituent include the substituent (S)

represented by Formulas (S1) to (S7) below.

[0085]

[Chem. 42]



(in Formulas (S1) to (S7),

R^{sa} represents a monovalent nonaromatic hydrocarbon group having 1 to 10 carbon atoms.

Each R^{sb} independently represents a single bond or a divalent nonaromatic hydrocarbon group having 1 to 10 carbon atoms.

Each R^{sc} independently represents a divalent nonaromatic hydrocarbon group having 1 to 10 carbon atoms.

Each $R^{sd}_{alkynyl}$ independently represents an alkynyl group having 2 to 4 carbon atoms.

Each Ar^{sa} independently represents a monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms.

Each Ar^{sb} independently represents a divalent aromatic hydrocarbon group having 6 to 20 carbon atoms.

X^{sa} and X^{sb} each independently represent a hydrogen atom or a monovalent hydrocarbon group having 1 to 20 carbon atoms, or X^{sa} and X^{sb} constitute a carbonyl group together with a carbon atom bonding to a hydroxy group.

n represents an integer of 0 to 5.

* represents a bonding site.)

[0086]

<R^{sa}>

Examples of the monovalent nonaromatic hydrocarbon group having 1 to 10 carbon atoms in R^{sa} include an alkyl group having 1 to 10 carbon atoms and a monovalent unsaturated hydrocarbon group having 2 to 10 carbon atoms.

The monovalent unsaturated hydrocarbon group having 2 to 10 carbon atoms has one or two or more carbon-carbon multiple bonds. When the monovalent unsaturated hydrocarbon group having 2 to 10 carbon atoms has two or more carbon-carbon multiple bonds, all of the two or more carbon-carbon multiple bonds may be carbon-carbon double bonds, all of the two or more carbon-carbon multiple bonds may be carbon-carbon triple bonds, or a mixture of a carbon-carbon double bond and a carbon-carbon triple bond may be used. Two or more carbon-carbon multiple bonds may or may not be conjugated.

[0087]

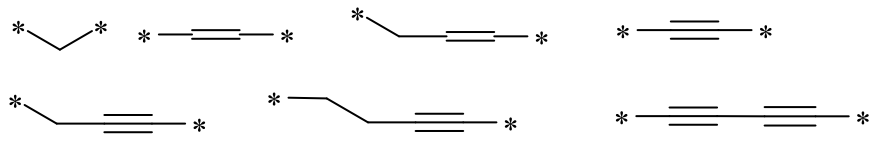
<R^{sb} and R^{sc}>

Examples of the divalent nonaromatic hydrocarbon group having 1 to 10 carbon atoms in R^{sb} and R^{sc} include an alkylene group having 1 to 10 carbon atoms and a divalent unsaturated hydrocarbon group having 2 to 10 carbon atoms.

The divalent unsaturated hydrocarbon group having 2 to 10 carbon atoms has one or two or more carbon-carbon multiple bonds. When the divalent unsaturated hydrocarbon group having 2 to 10 carbon atoms has two or more carbon-carbon multiple bonds, all of the two or more carbon-carbon multiple bonds may be carbon-carbon double bonds, all of the two or more carbon-carbon multiple bonds may be carbon-carbon triple bonds, or a mixture of a carbon-carbon double bond and a carbon-carbon triple bond may be used. Two or more carbon-carbon multiple bonds may or may not be conjugated.

Examples of R^{sb} and R^{sc} include the following groups:

[Chem. 43]



(* represents a bonding site.)

[0088]

<$R^{sd}_{alkynyl}$>

$R^{sd}_{alkynyl}$ represents an alkynyl group having 2 to 4 carbon atoms. Examples of the alkynyl group having 2 to 4 carbon atoms include an ethynyl group, a 1-propynyl group, a propargyl group (2-propynyl group).

[0089]

<Ar^{sa}>

The monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms in Ar^{sa} is a residue obtained by removing one hydrogen atom from an aromatic hydrocarbon having 6 to 20 carbon atoms. Examples of the aromatic hydrocarbon having 6 to 20 carbon atoms include benzene, naphthalene, anthracene, phenanthrene, perinaphthane, pyrene, fluorene and biphenyl.

[0090]

<Ar^{sb}>

The divalent aromatic hydrocarbon group having 6 to 20 carbon atoms in Ar^{sb} is a residue obtained by removing two hydrogen atoms from an aromatic hydrocarbon having 6 to 20 carbon atoms. Examples of the aromatic hydrocarbon having 6 to 20 carbon atoms include benzene, naphthalene, anthracene, phenanthrene, pyrene, fluorene and biphenyl.

[0091]

<X^{sa} and X^{sb}>

Examples of the monovalent hydrocarbon groups having 1 to 20 carbon atoms in X^{sa} and X^{sb} include a monovalent

nonaromatic hydrocarbon group having 1 to 10 carbon atoms and a monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms.

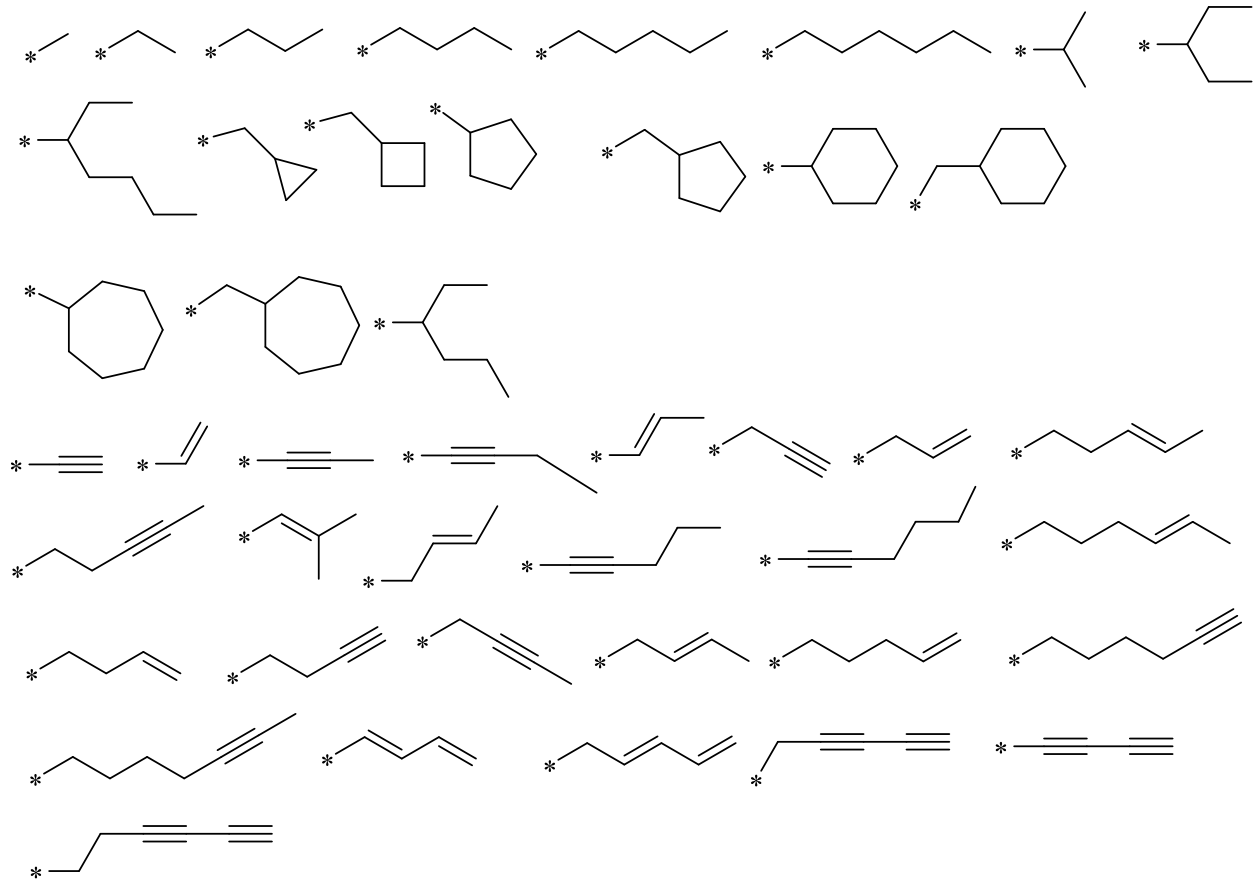
Examples of the monovalent nonaromatic hydrocarbon group having 1 to 10 carbon atoms include an alkyl group having 1 to 10 carbon atoms.

The monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms is a residue obtained by removing one hydrogen atom from an aromatic hydrocarbon having 6 to 20 carbon atoms. Examples of the aromatic hydrocarbon having 6 to 20 carbon atoms include benzene, naphthalene, anthracene, phenanthrene, perinaphthane, pyrene, fluorene and biphenyl.

[0092]

Examples of the substituent represented by Formula (S1) include the following groups:

[Chem. 44]

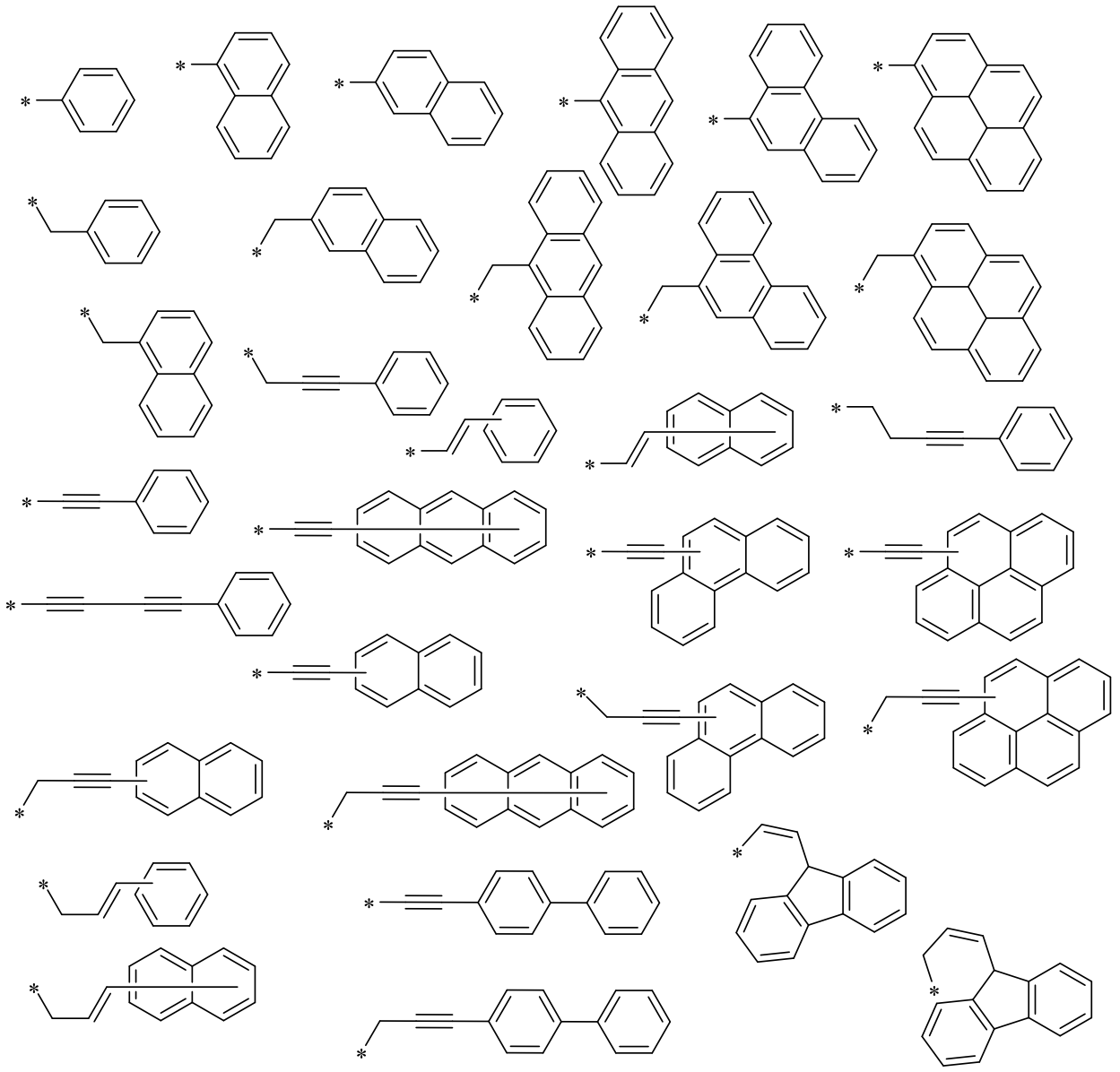


(* represents a bonding site.)

[0093]

Examples of the substituent represented by Formula (S2) include the following groups:

[Chem. 45]

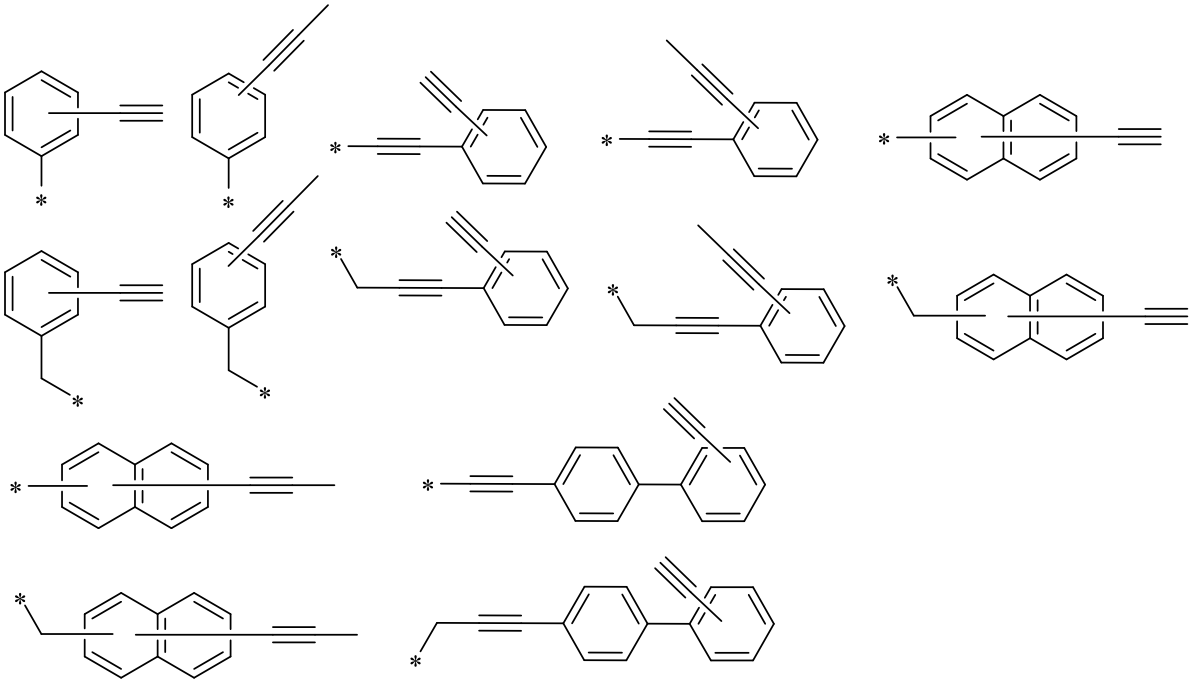


(* represents a bonding site.)

[0094]

Examples of the substituent represented by Formula (S3) include the following groups:

[Chem. 46]

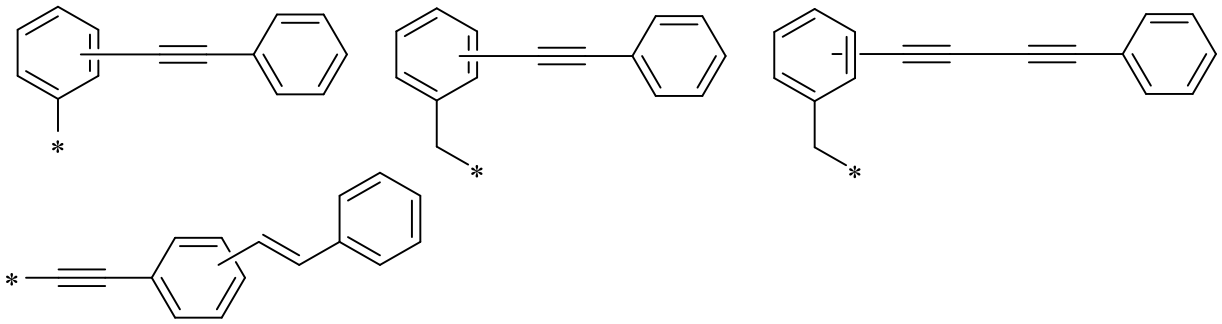


(* represents a bonding site.)

[0095]

Examples of the substituent represented by Formula (S4) include the following groups:

[Chem. 47]

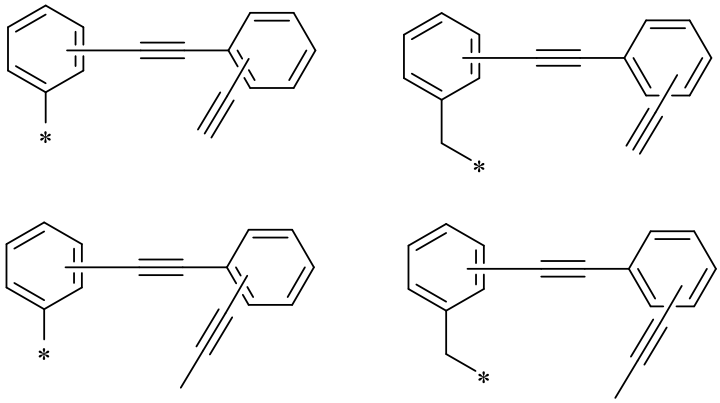


(* represents a bonding site.)

[0096]

Examples of the substituent represented by Formula (S5) include the following groups:

[Chem. 48]

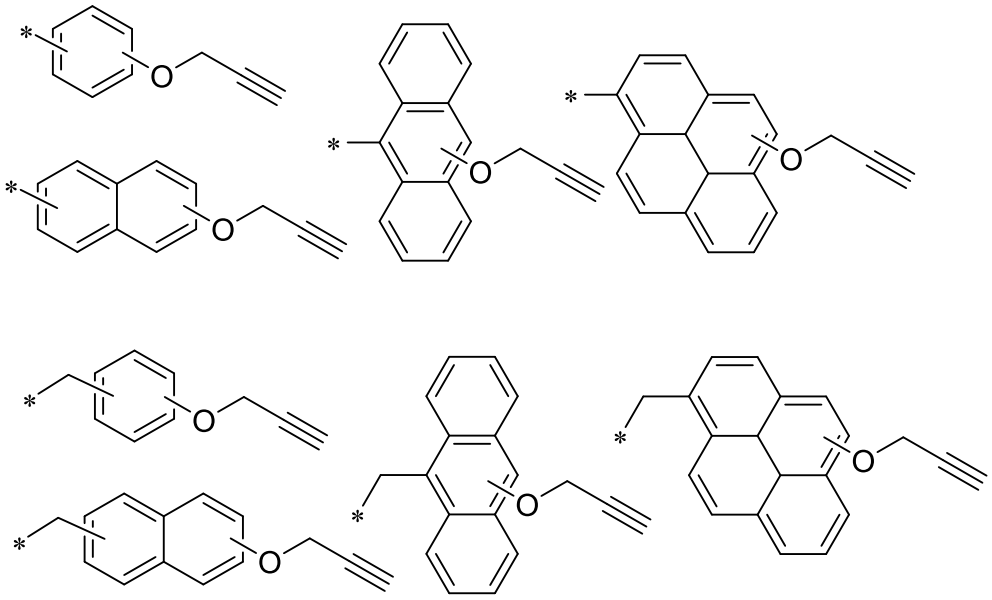


(* represents a bonding site.)

[0097]

Examples of the substituent represented by Formula (S6) include the following groups:

[Chem. 49]

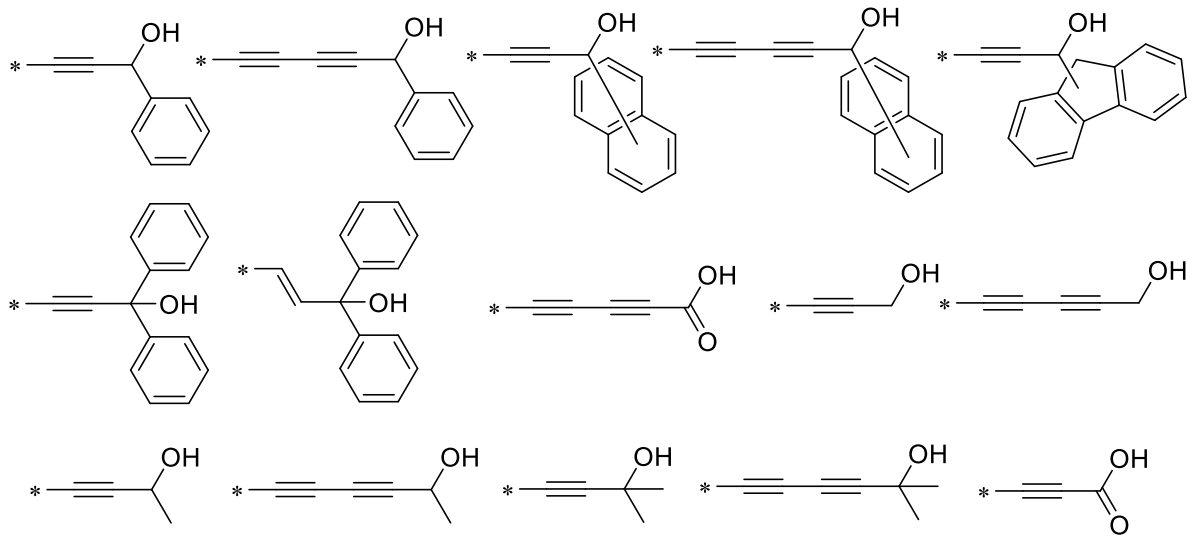


(* represents a bonding site.)

[0098]

Examples of the substituent represented by Formula (S7) include the following groups:

[Chem. 50]

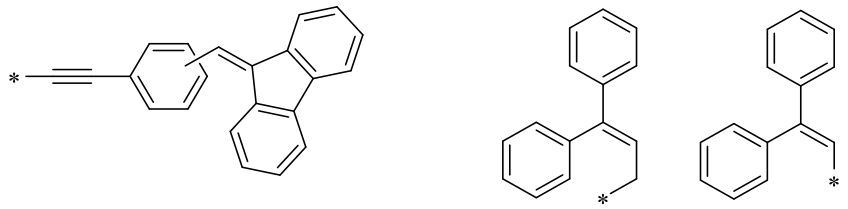


(* represents a bonding site.)

[0099]

Examples of other substituents include the following groups:

[Chem. 51]



(* represents a bonding site.)

[0100]

The unit structure (A-I) is preferably at least one selected from the following: Note that the positions of the two bonding sites indicated in each unit structure described below are merely indicated for convenience, and can extend from any possible carbon atom, respectively, and do not limit the positions.

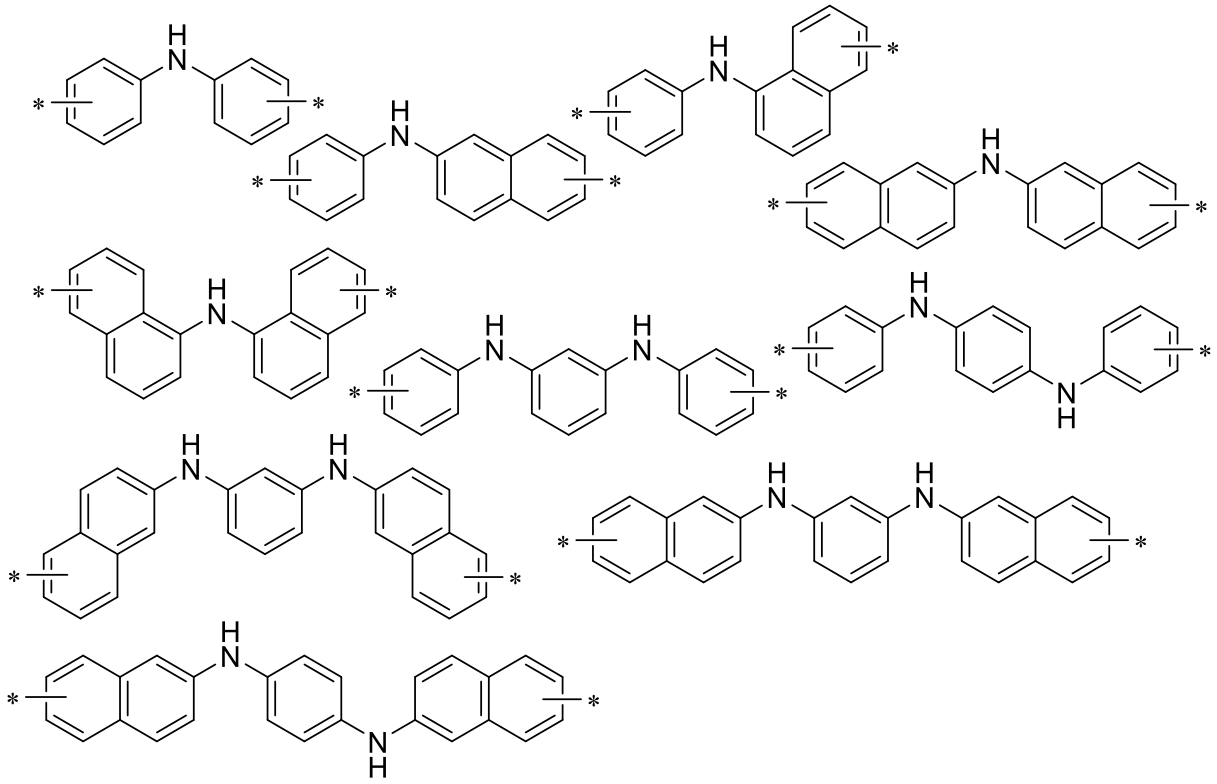
[0101]

(Example of unit structure composed of aromatic amine skeleton)

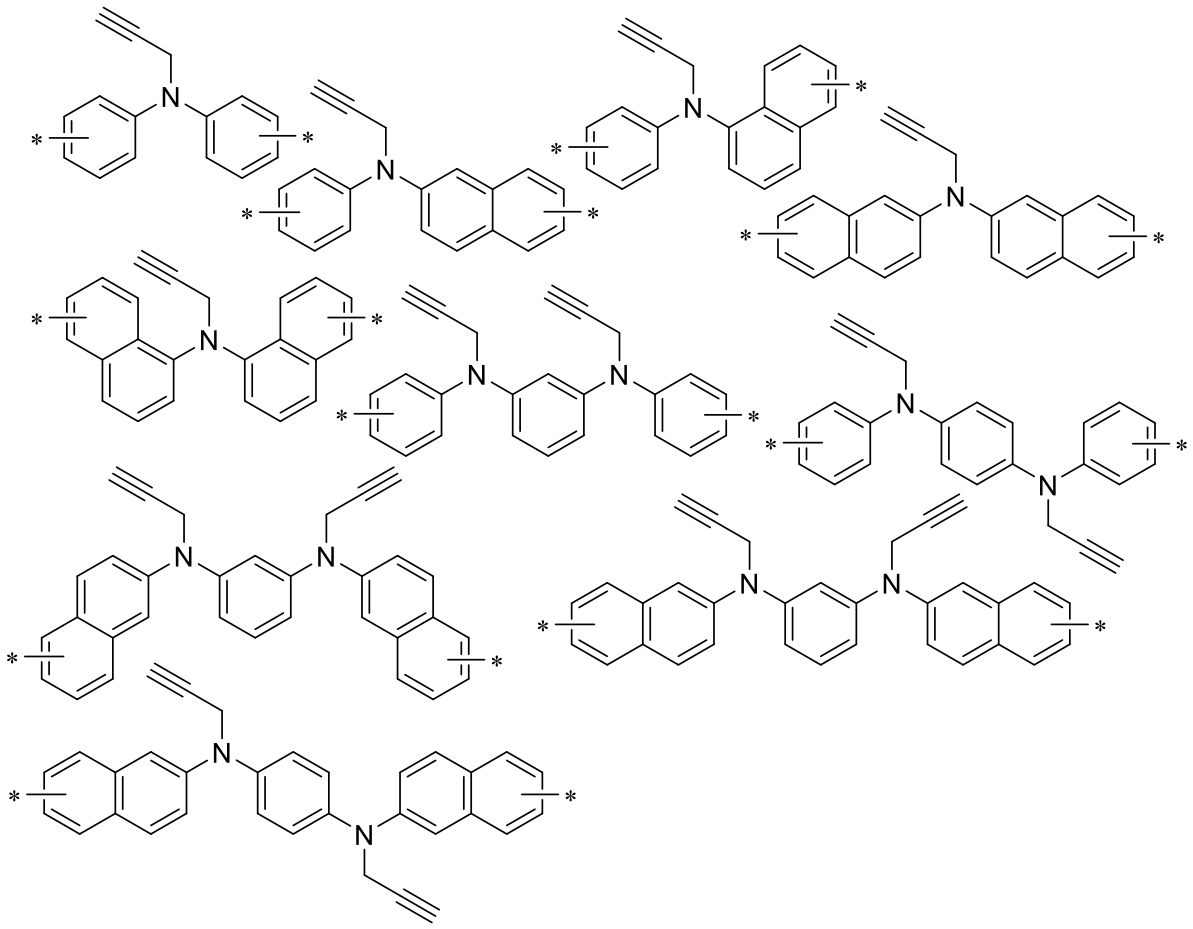
-NH- may have a structure in which a hydrogen atom on N is substituted.

[0102]

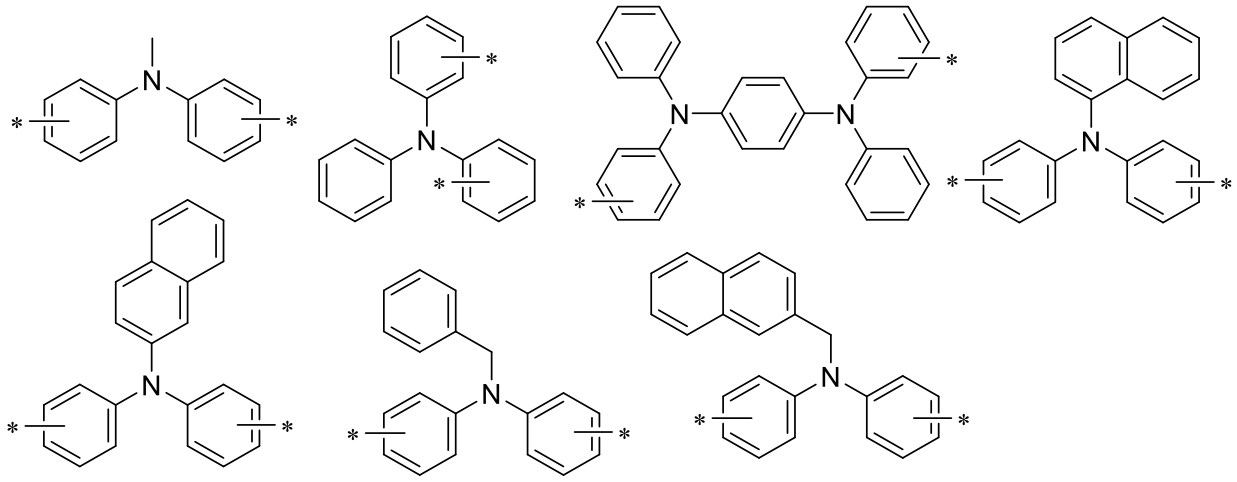
[Chem. 52]



[Chem. 53]



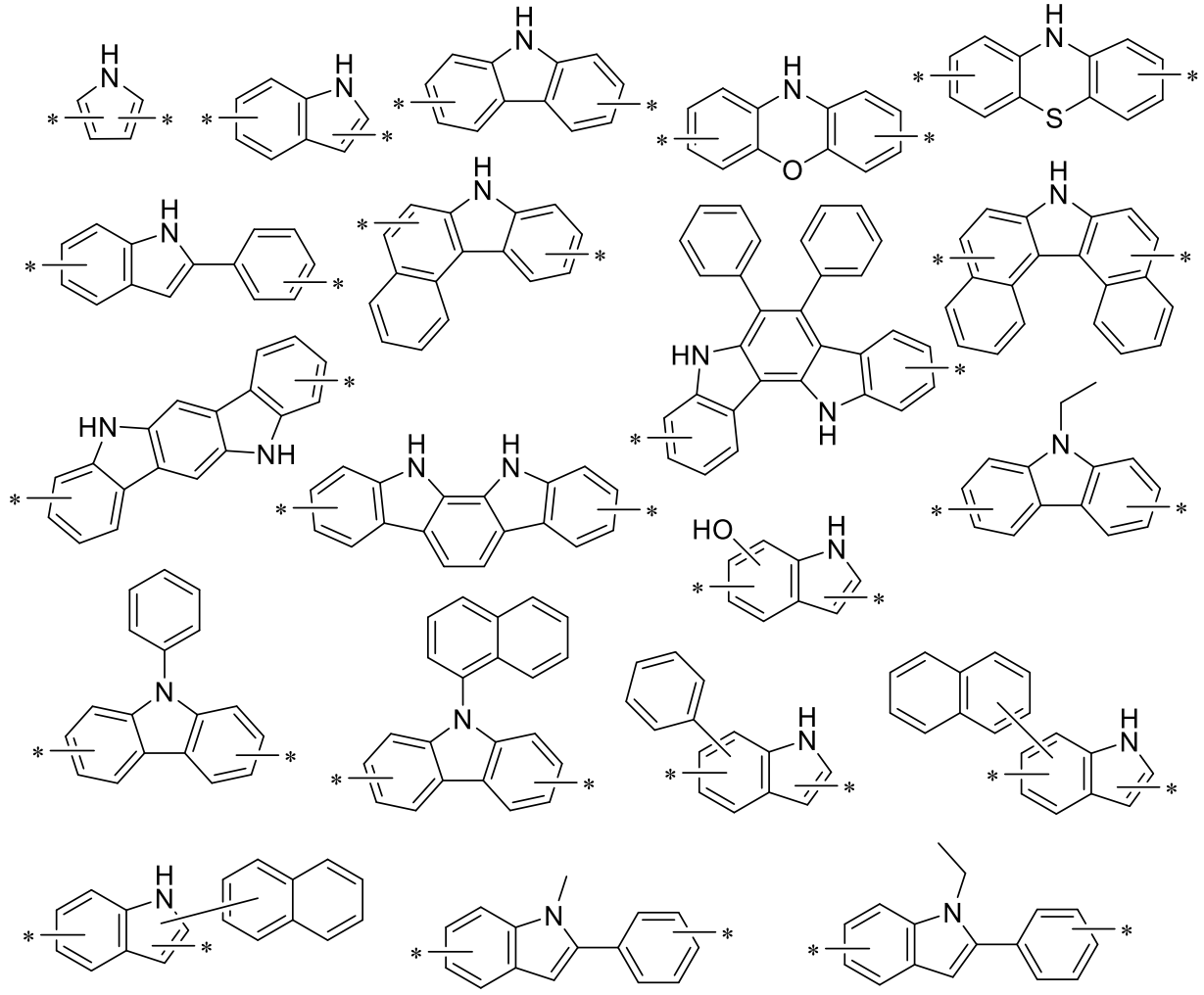
[Chem. 54]



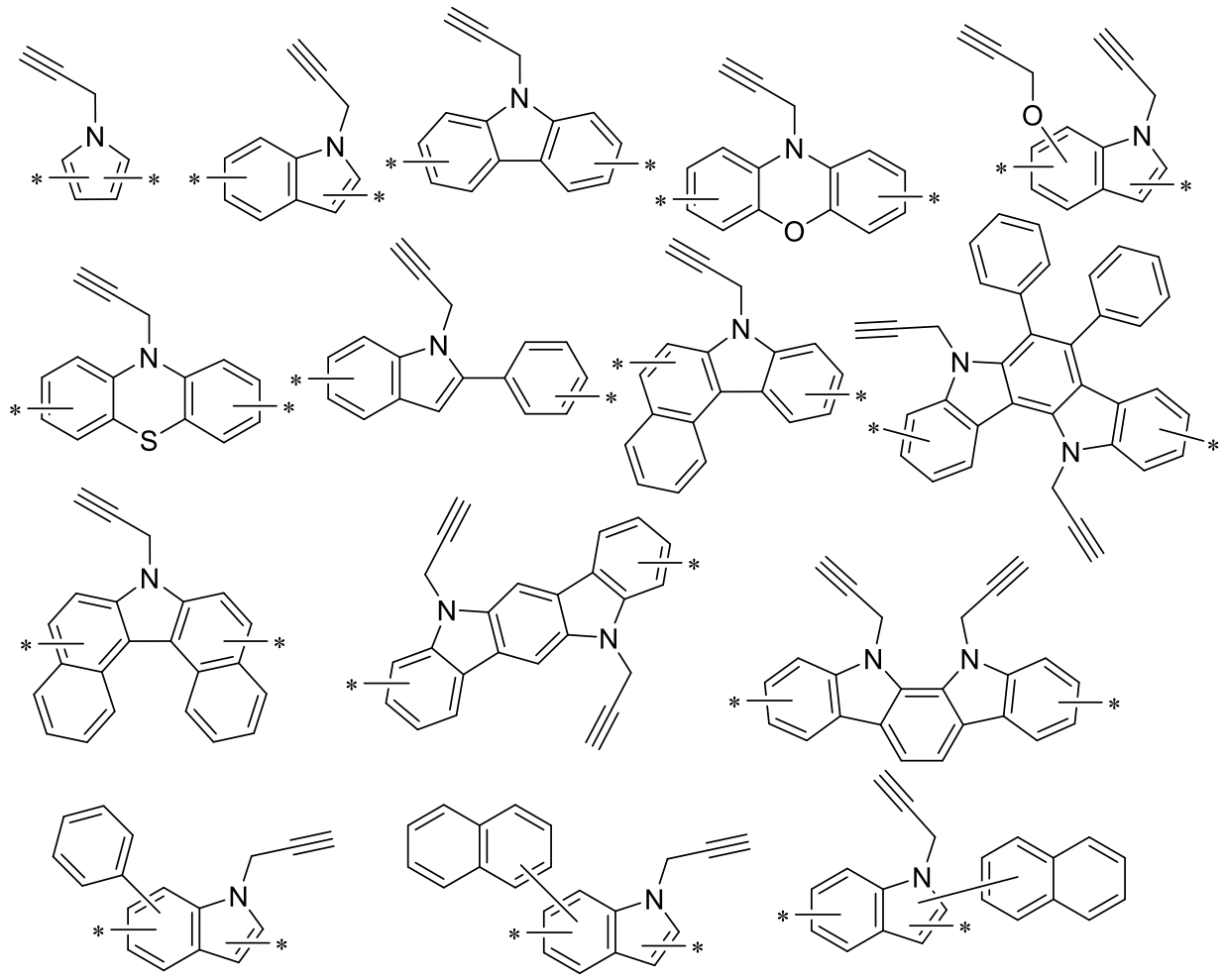
[0103]

(Example of unit structure composed of nitrogen-containing aromatic heterocyclic skeleton)

[Chem. 55]



[Chem. 56]



[0104]

The unit structure (A) in the resin (G) may include a unit structure other than the unit structure (A-I).

Examples of the unit structure other than the unit structure (A-I) include a unit structure having a phenol skeleton and the like.

[0105]

<<<A-4: Phenolic skeleton>>>

The phenolic skeleton refers to a skeleton having an aromatic ring and a hydroxy group bonding to the aromatic

ring.

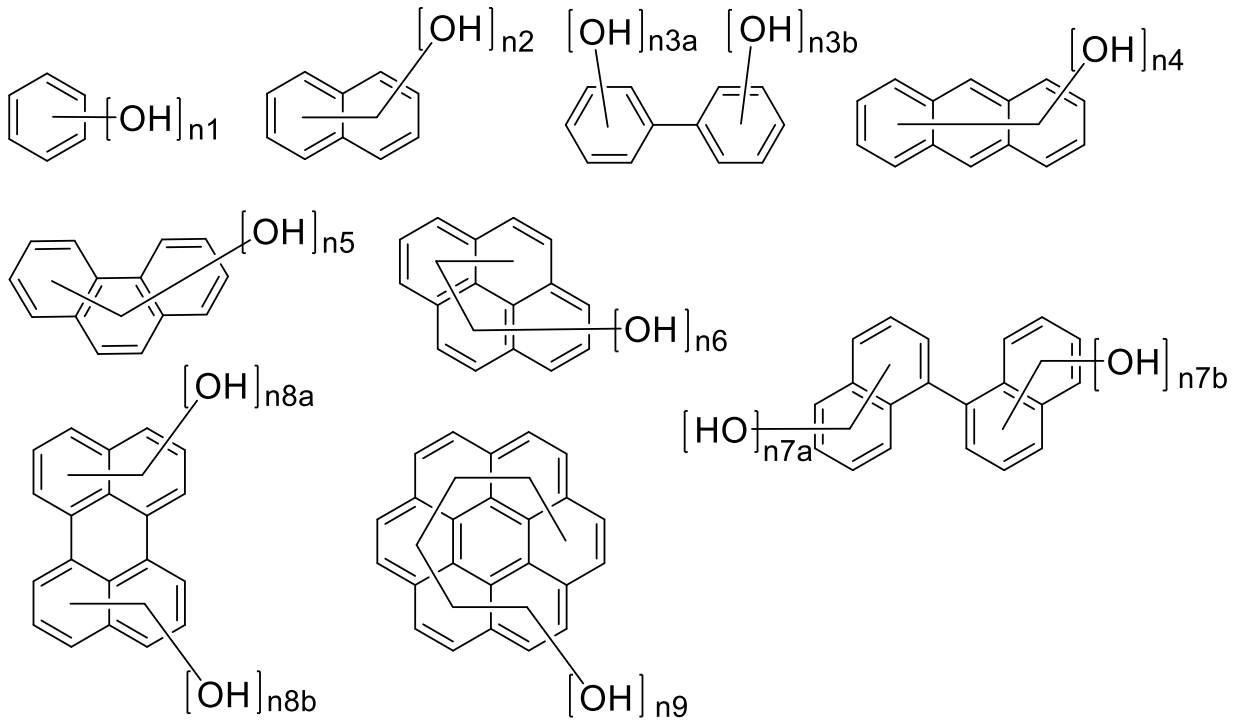
The number of hydroxy groups bonding to the aromatic ring of the phenolic skeleton is not particularly limited, and may be one or more. In a case of plurality, the number may be 2 to 10 or 2 to 8. In a case of plurality, the hydroxy group may bond to the same aromatic ring (for example, a benzene ring) or to different aromatic rings.

In the unit structure (A), the hydrogen atom of the hydroxy group bonding to the aromatic ring may be substituted with a substituent. Examples of the substituent include the substituent described in (I-3) “Aromatic ring”, the substituent described in (A-2) “Exemplary skeleton constituting unit structure (A)”, and substituents (S) represented by Formulas (S1) to (S7).

[0106]

Examples of the phenolic skeleton include each skeleton represented by Formula (A-4) shown below. The aromatic ring in these skeletons may have a substituent, and the hydrogen atom in the hydroxy group may be substituted with a substituent. The same applies to the following skeletons.

[Chem. 57]



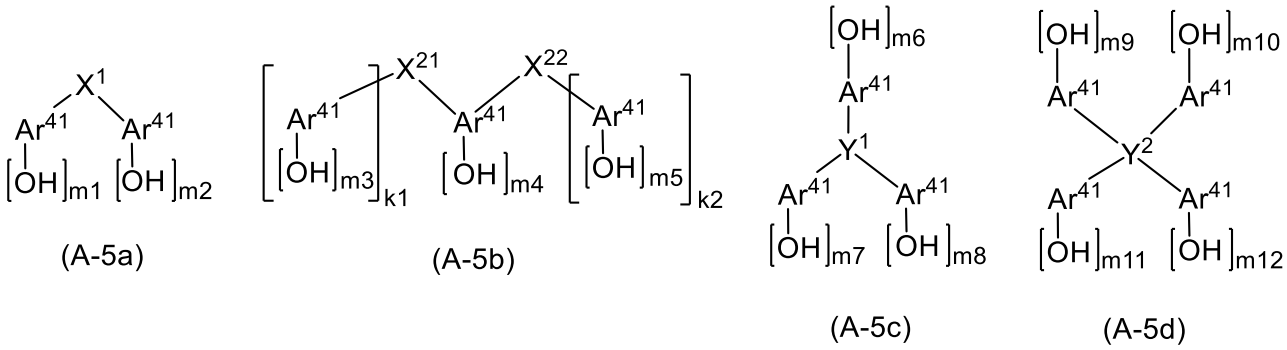
(A-4)

(wherein n1, n2, n4, n5, n6, and n9 each independently represent an integer of 1 to 4, n3a, n3b, n7a, n7b, n8a, and n8b, each independently represent an integer of 0 to 4, with the proviso that the sum of n3a and n3b is 1 or more, the sum of n7a and n7b is 1 or more, and the sum of n8a and n8b is 1 or more.)

[0107]

Examples of the phenolic skeleton include a skeleton represented by Formula (A-5a) below, Formula (A-5b) below, Formula (A-5c) below, or Formula (A-5d) below.

[Chem. 58]



(A-5a) (A-5b) (A-5c) (A-5d)

(wherein each Ar^{41} independently represents a residue of an aromatic ring,

k1 and k2 each independently represent an integer of 1 or 2.

X^1 represents -O-, -CO-, -S-, $-SO_2-$ or an alkylene group that may be substituted with a halogen atom.

When k1 is 1, X^{21} represents a single bond, -O-, -CO-, -S-, $-SO_2-$, or an alkylene group that may be substituted with a halogen atom.

When k2 is 1, X^{22} represents a single bond, -O-, -CO-, -S-, $-SO_2-$, or an alkylene group that may be substituted with a halogen atom.

When k1 is 2, X^{21} represents a trivalent saturated hydrocarbon group which may be substituted with a halogen atom.

When k2 is 2, X^{22} represents a trivalent saturated hydrocarbon group which may be substituted with a halogen atom.

Y^1 represents a trivalent saturated hydrocarbon group,

Y^2 represents a tetravalent saturated hydrocarbon

group,

m1 and m2 each independently represent an integer of 0 to 3, with the proviso that the sum of m1 and m2 is 1 or more,

m3 to m5 each independently represent an integer of 0 to 3, with the proviso that the sum of m3 to m5 is 1 or more,

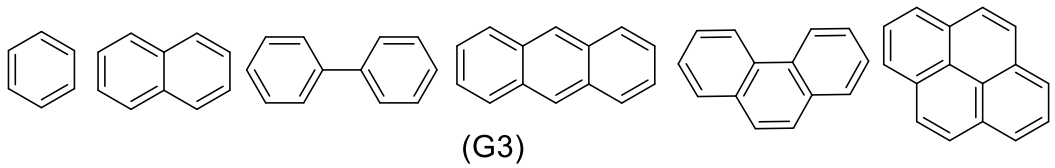
m6 to m8 each independently represent an integer of 0 to 3, with the proviso that the sum of m6 to m8 is 1 or more,

m9 to m12 each independently represent an integer of 0 to 3, with the proviso that the sum of m9 to m12 is 1 or more).

[0108]

Examples of the aromatic ring in the residue of the aromatic ring of Ar^{41} include an aromatic ring represented by Formula (G3) below. These aromatic rings may have a substituent.

[Chem. 59]



(G3)

[0109]

The number of carbon atoms of the alkylene group which may be substituted with a halogen atom in X^1 and X^2 is, for

example, 1 to 20. Examples of the structure of the alkylene group include linear, branched, and cyclic structures, and combinations of two or more thereof. Examples of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom.

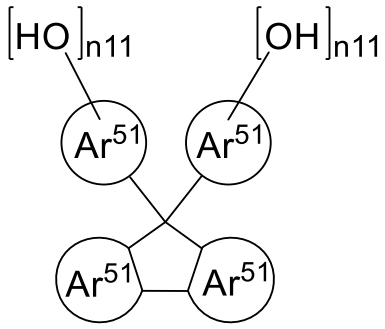
[0110]

The number of carbon atoms of the saturated hydrocarbon group in Y^1 and Y^2 is, for example, 1 to 20. Examples of the structure of the saturated hydrocarbon group include linear, branched, and cyclic structures, and combinations of two or more thereof.

[0111]

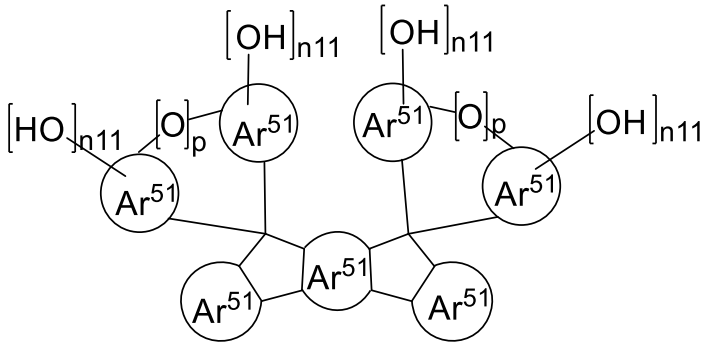
Examples of the phenolic skeleton include a skeleton represented by Formula (A-6a), Formula (A-6b-1), Formula (A-6b-2), Formula (A-6c) or Formula (A-6d) shown below.

[Chem. 60]

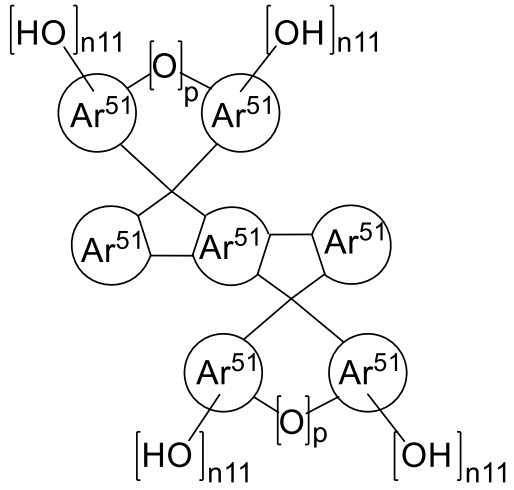


(A-6a)

[Chem. 61]

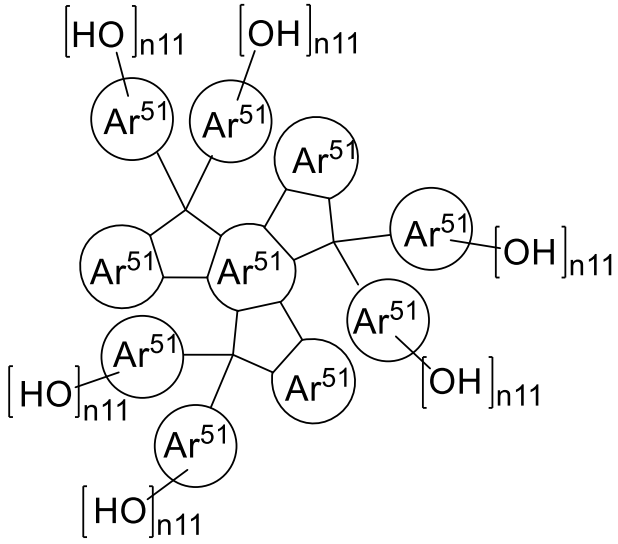


(A-6b-1)

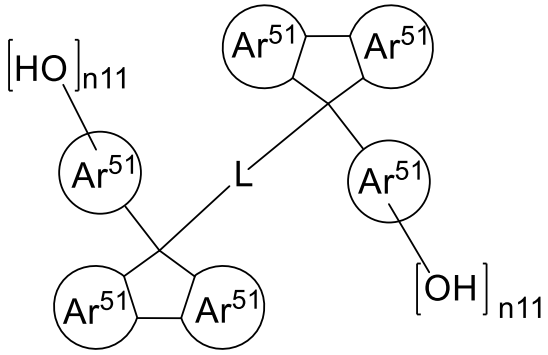


(A-6b-2)

[Chem. 62]



(A-6c)



(A-6d)

(In Formulas (A-6a), (A-6b-1), (A-6b-2), (A-6c), and (A-6d), each Ar^{51} independently represents a residue of an aromatic ring, each n11 independently represents an integer of 1 to 4, each p independently represents 0 or 1, When p is 1, an oxygen atom forms a cross-linked structure between

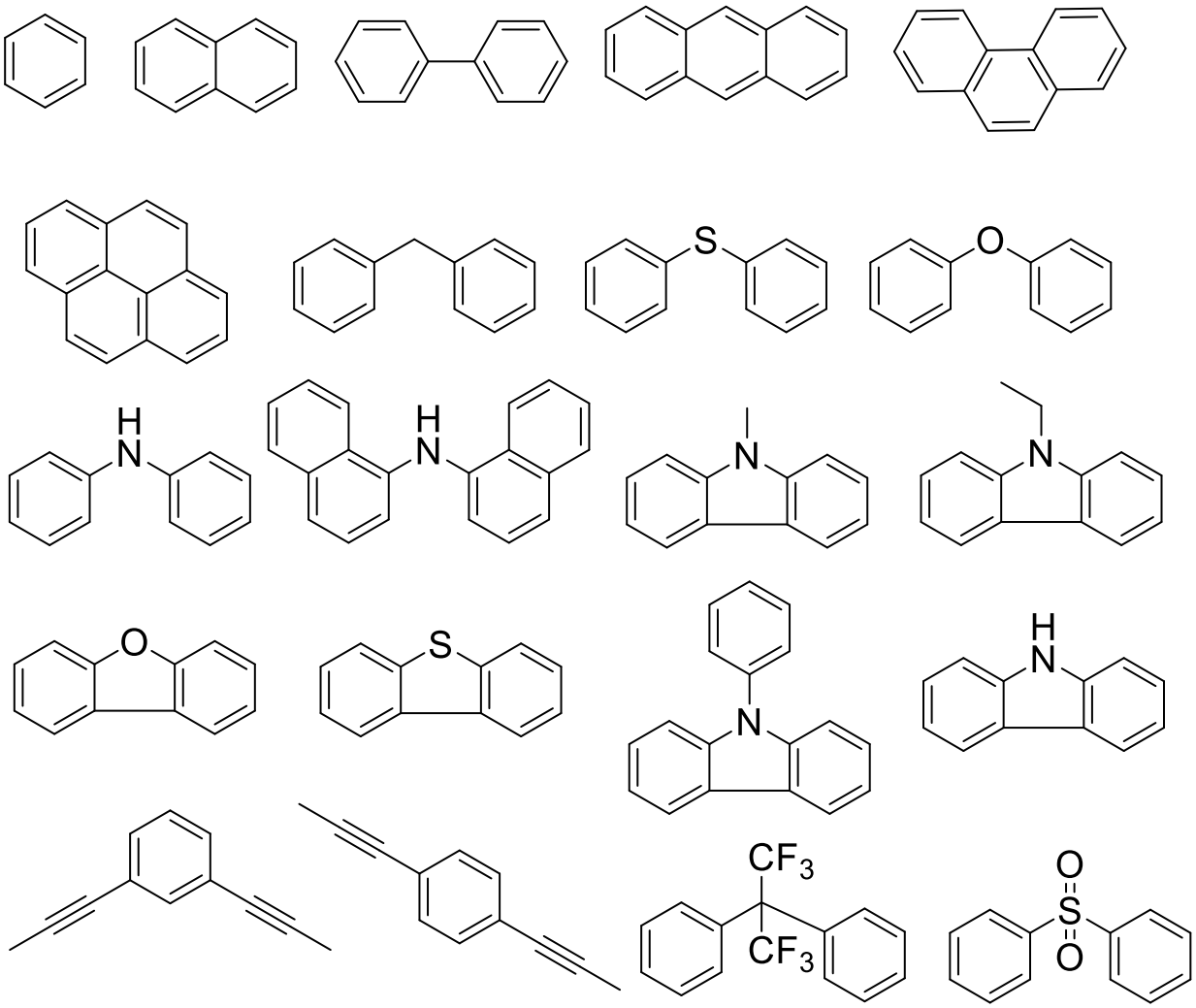
aromatic rings as an ether bond, and when p is 0, there is no ether bond that forms a cross-linked structure between aromatic rings. L represents a single bond or a divalent linking group).

[0112]

Examples of the aromatic ring in Ar^{51} include an aromatic ring represented by Formula (G1) above, preferably a benzene ring, a naphthalene ring.

Examples of L include a divalent group obtained by removing two hydrogen atoms from the following structure.

[Chem. 63]



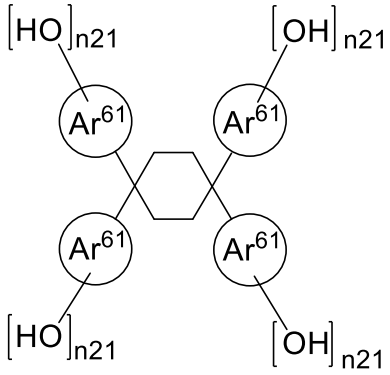
[0113]

Each n11 independently represents, for example, 1 or 2.

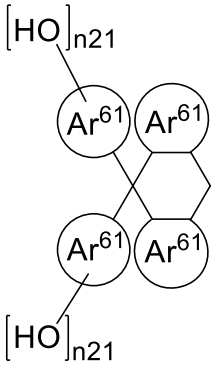
[0114]

Examples of the phenolic skeleton include a skeleton represented by Formula (A-7a), Formula (A-7b), or Formula (A-7c) shown below.

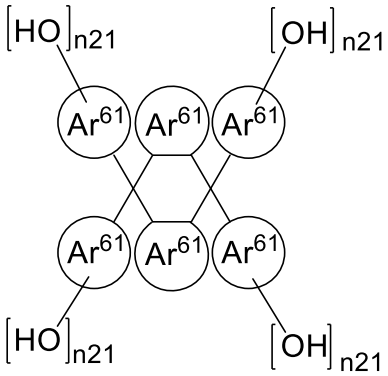
[Chem. 64]



(A-7a)



(A-7b)



(A-7c)

(In Formulas (A-7a), (A-7b), and (A-7c), each Ar^{61} independently represents a residue of an aromatic ring. Each n21 independently represents an integer of 1 to 4).

[0115]

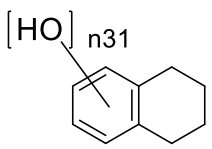
Examples of the aromatic ring in Ar^{61} include an aromatic ring represented by Formula (G1) above, and the aromatic ring in Ar^{61} is preferably a benzene ring or a naphthalene ring.

Each n21 independently represents, for example, 1 or 2.

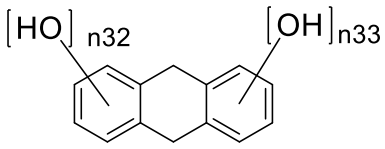
[0116]

Examples of the phenolic skeleton include a skeleton represented by Formula (A-8a-1), Formula (A-8a-2), Formula (A-8b), Formula (A-8c), Formula (A-8d), Formula (A-8e), Formula (A-8f), Formula (A-8g-1), or Formula (A-8g-2) shown below:

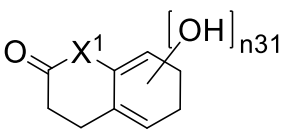
[Chem. 65]



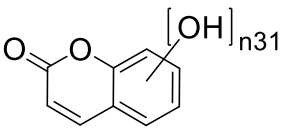
(A-8a-1)



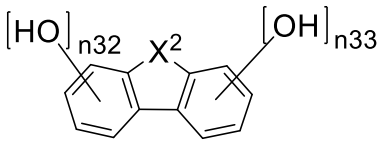
(A-8a-2)



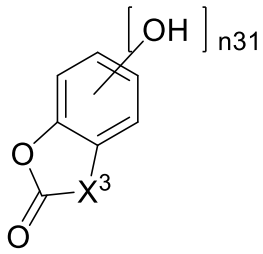
(A-8b)



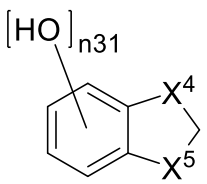
(A-8c)



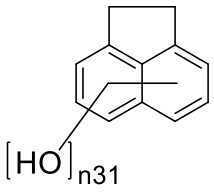
(A-8d)



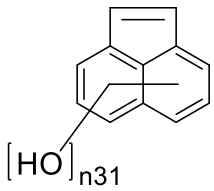
(A-8e)



(A-8f)



(A-8g-1)



(A-8g-2)

(In Formula (A-8a-1), Formula (A-8b), Formula (A-8c), Formula (A-8e), Formula (A-8f), Formula (A-8g-1), and Formula (A-8g-2), each n31 independently represents an integer of 1 to 4,

in Formula (A-8a-2), n32 and n33 each independently represent an integer of 0 to 4, with the proviso that the sum of n32 and n33 is 1 or more,

in Formula (A-8d), n32 and n33 each independently represent an integer of 0 to 4, with the proviso that the sum of n32 and n33 is 1 or more,

in Formula (A-8b), X^1 represents -O- or -NH-,

in Formula (A-8d), X^2 represents -O-, -S-, or $-CH_2-$,

in Formula (A-8e), X^3 represents -S-, $-CH_2-$ or -NH-,

in Formula (A-8f), X^4 represents -CO- or -O-, and X^5 represents $-CH_2-$ or -O-).

[0117]

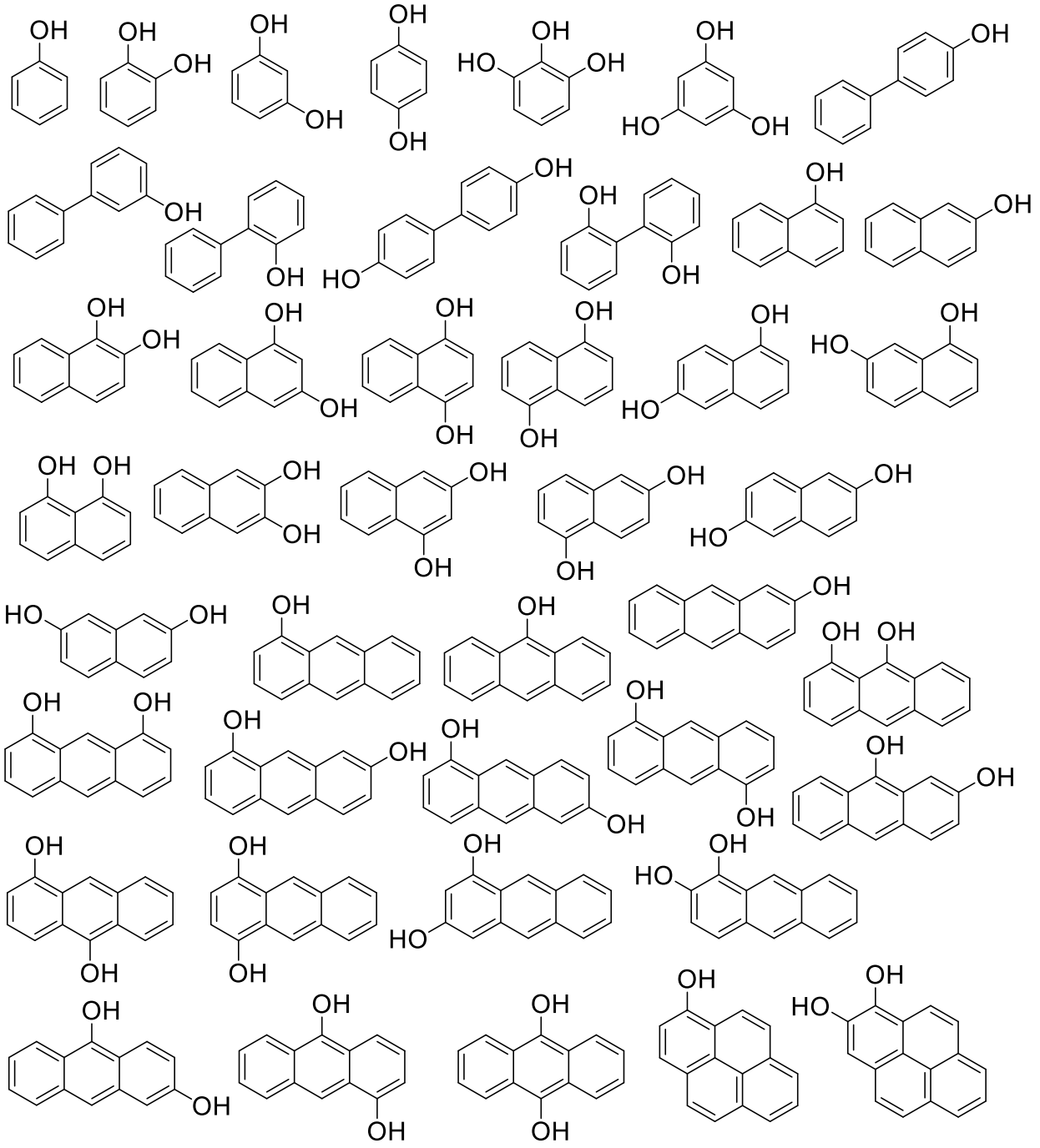
Each n31 independently represents, for example, 1 or 2.

n32 and n33, for example each independently represent 0, 1 or 2.

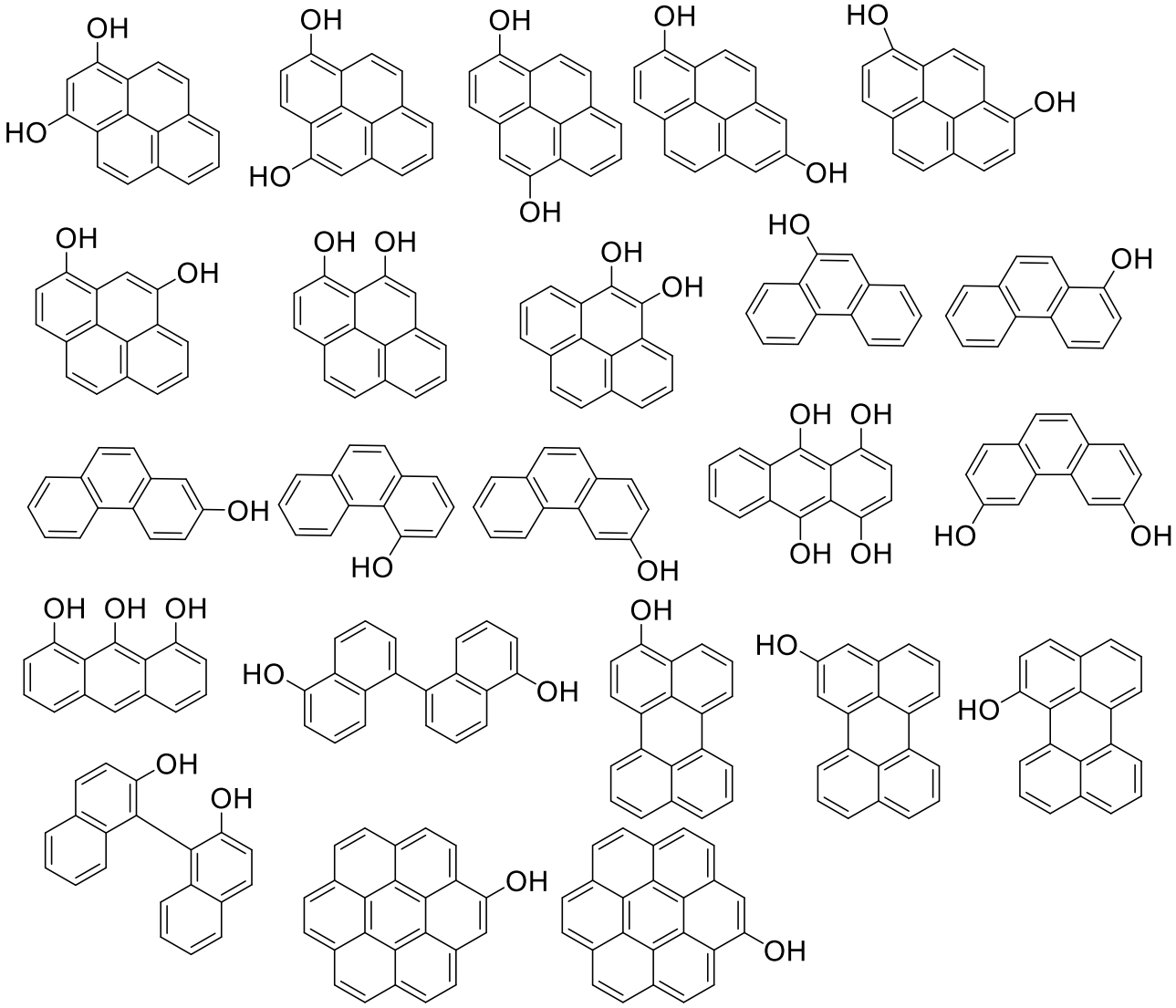
[0118]

Examples of the skeleton represented by Formula (A-4) include the following skeletons: The aromatic ring in these skeletons may have a substituent, and the hydrogen atom in the hydroxy group may be substituted with a substituent. The same applies to the following skeletons.

[Chem. 66]



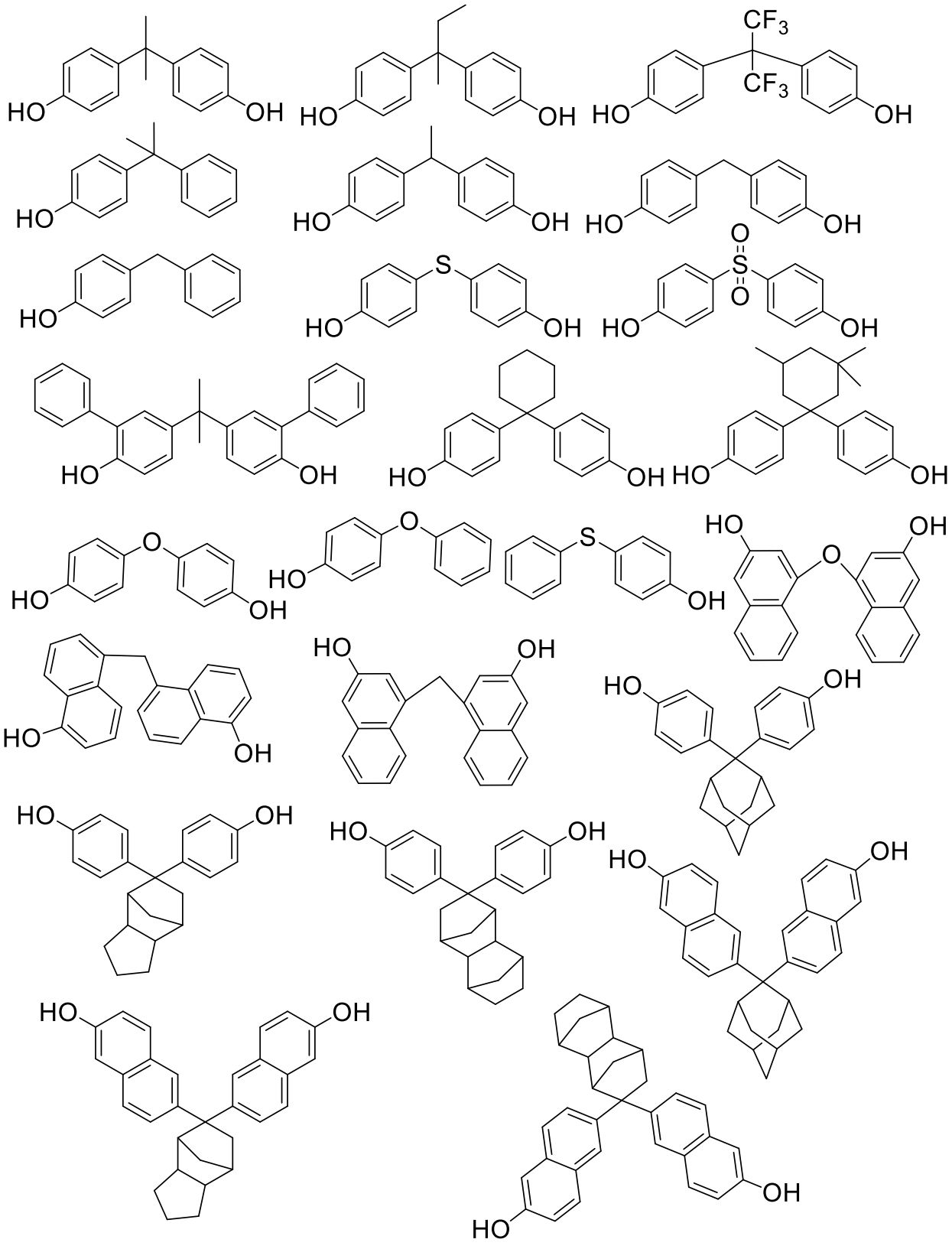
[Chem. 67]



[0119]

Examples of the skeleton represented by Formula (A-5a) include the following skeleton:

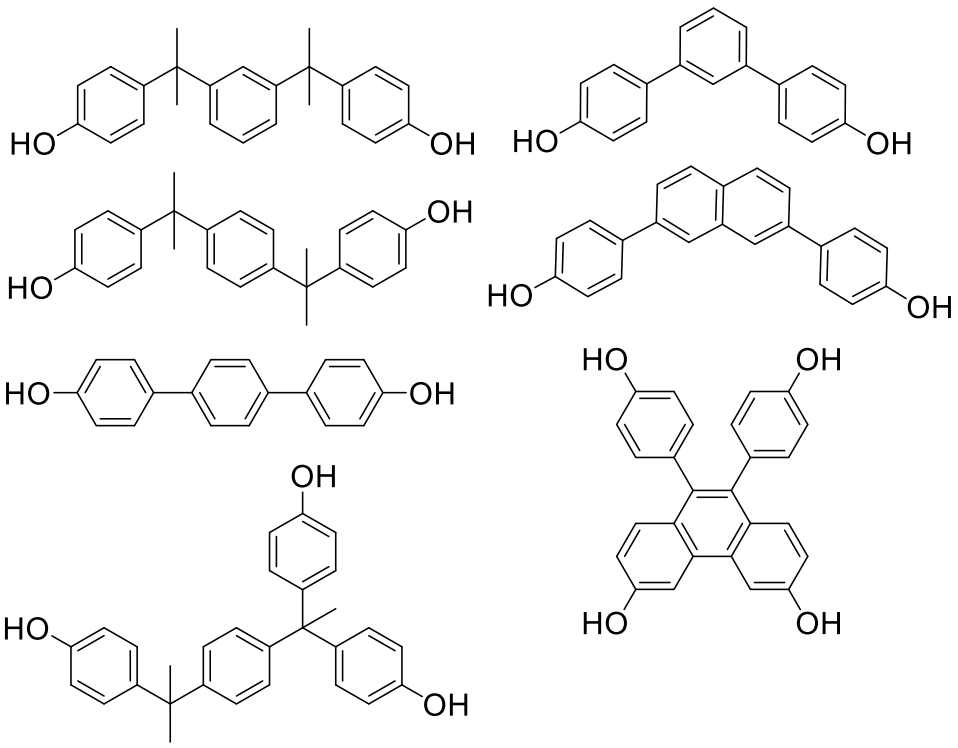
[Chem. 68]



[0120]

Examples of the skeleton represented by Formula (A-5b) include the following skeleton:

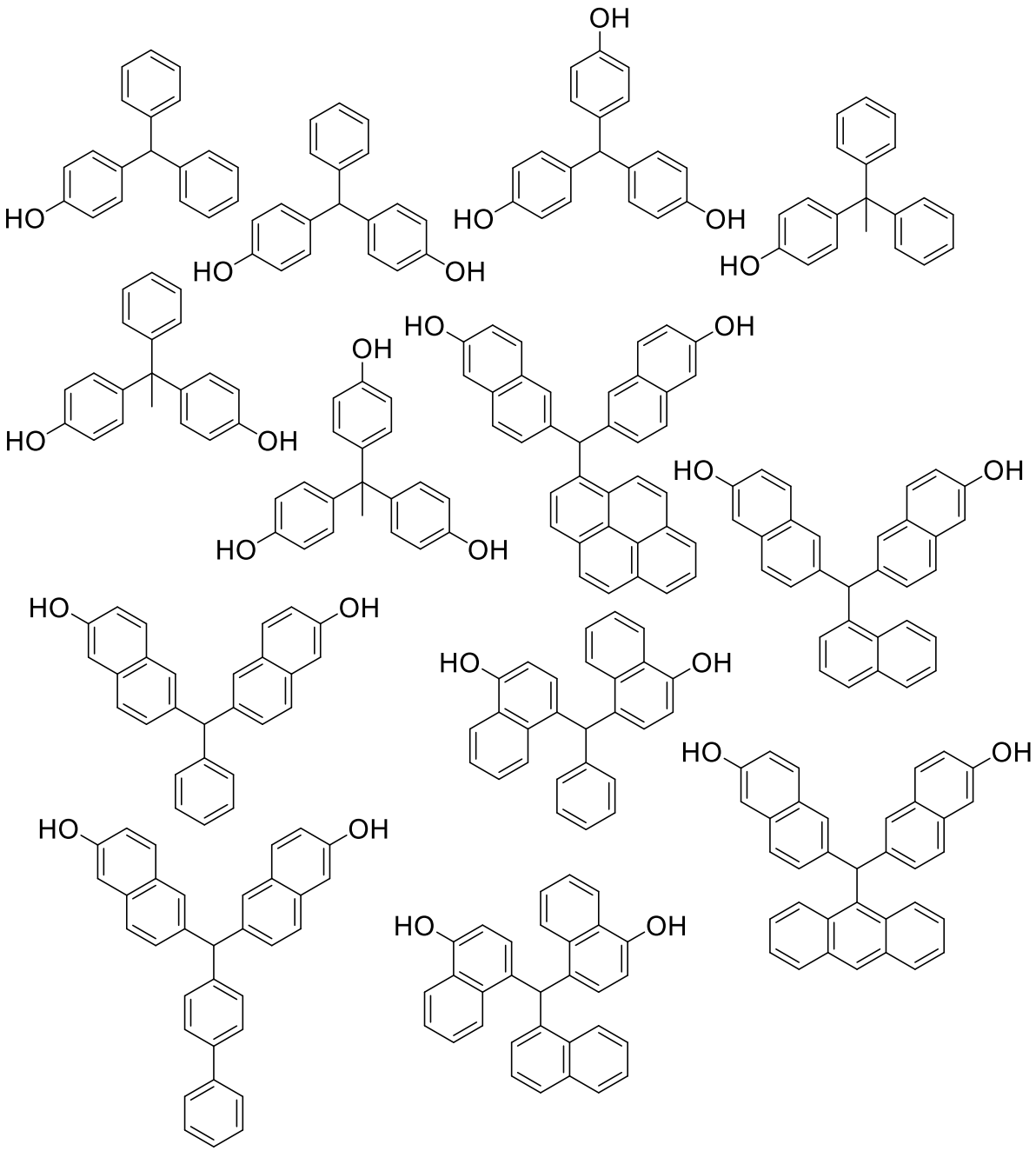
[Chem. 69]



[0121]

Examples of the skeleton represented by Formula (A-5c) include the following skeleton:

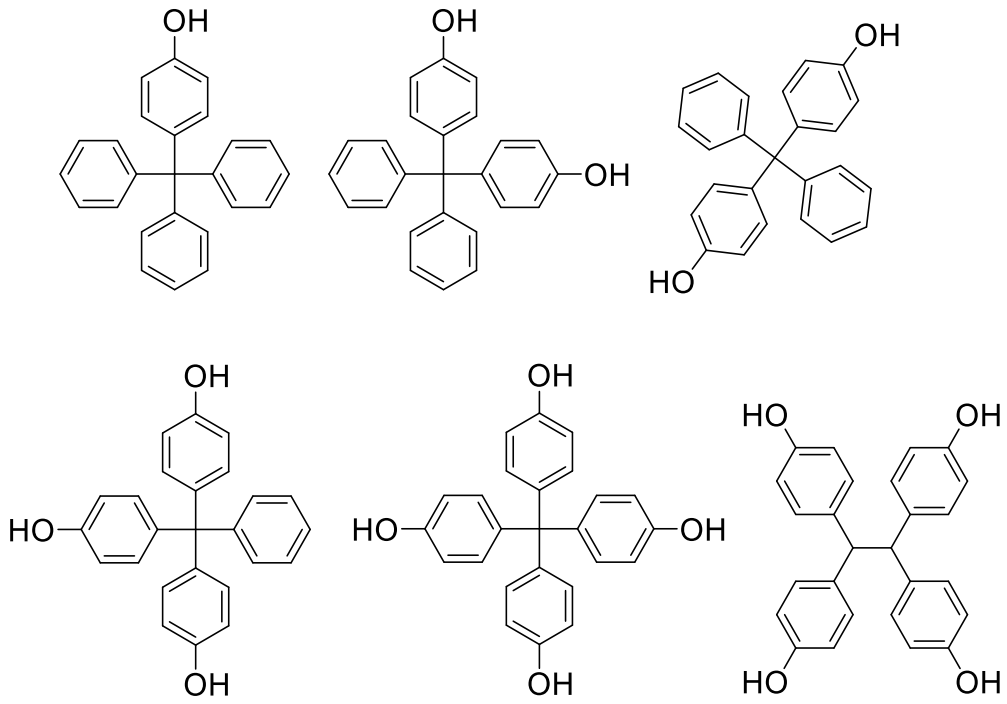
[Chem. 70]



[0122]

Examples of the skeleton represented by Formula (A-5d) include the following skeleton:

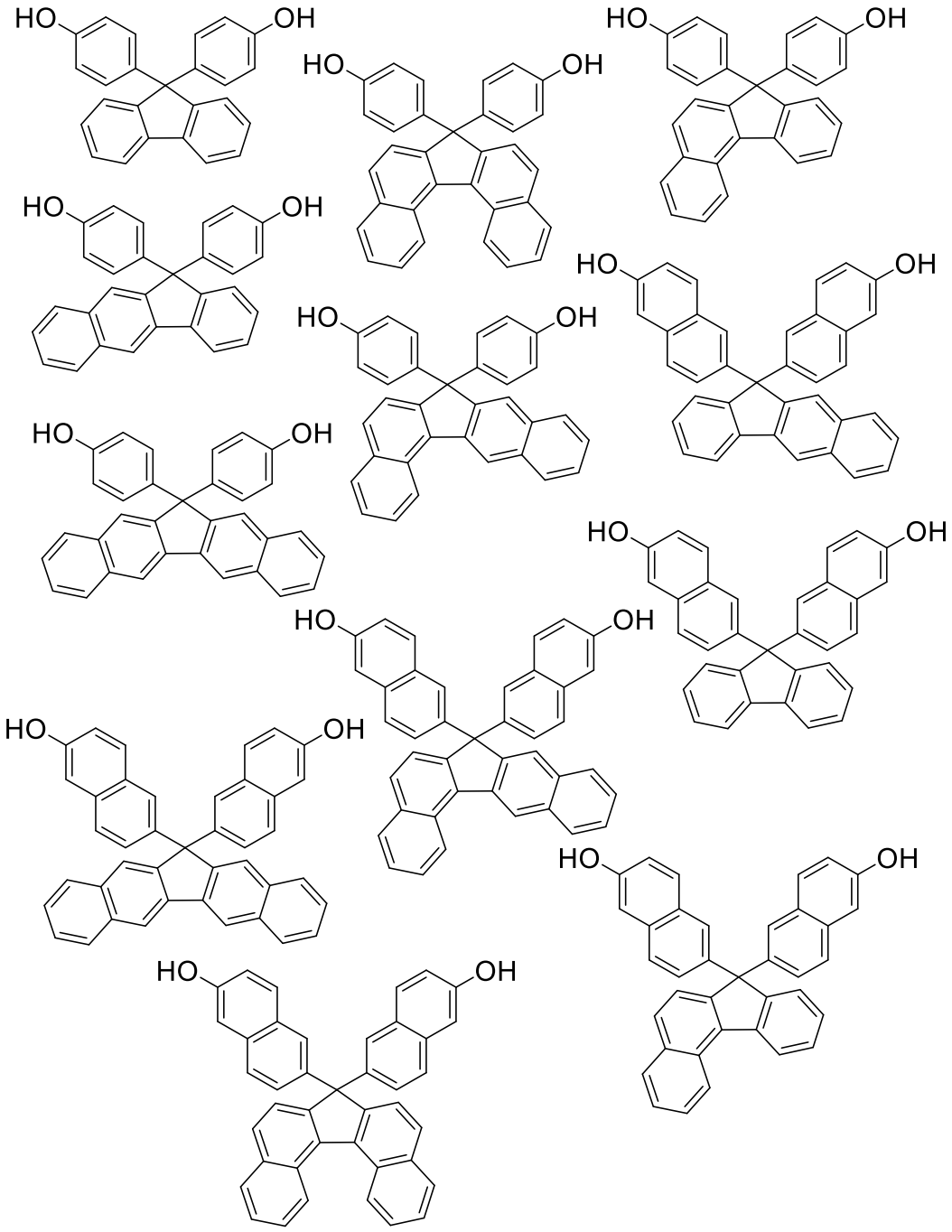
[Chem. 71]



[0123]

Examples of the skeleton represented by Formula (A-6a) include the following skeleton:

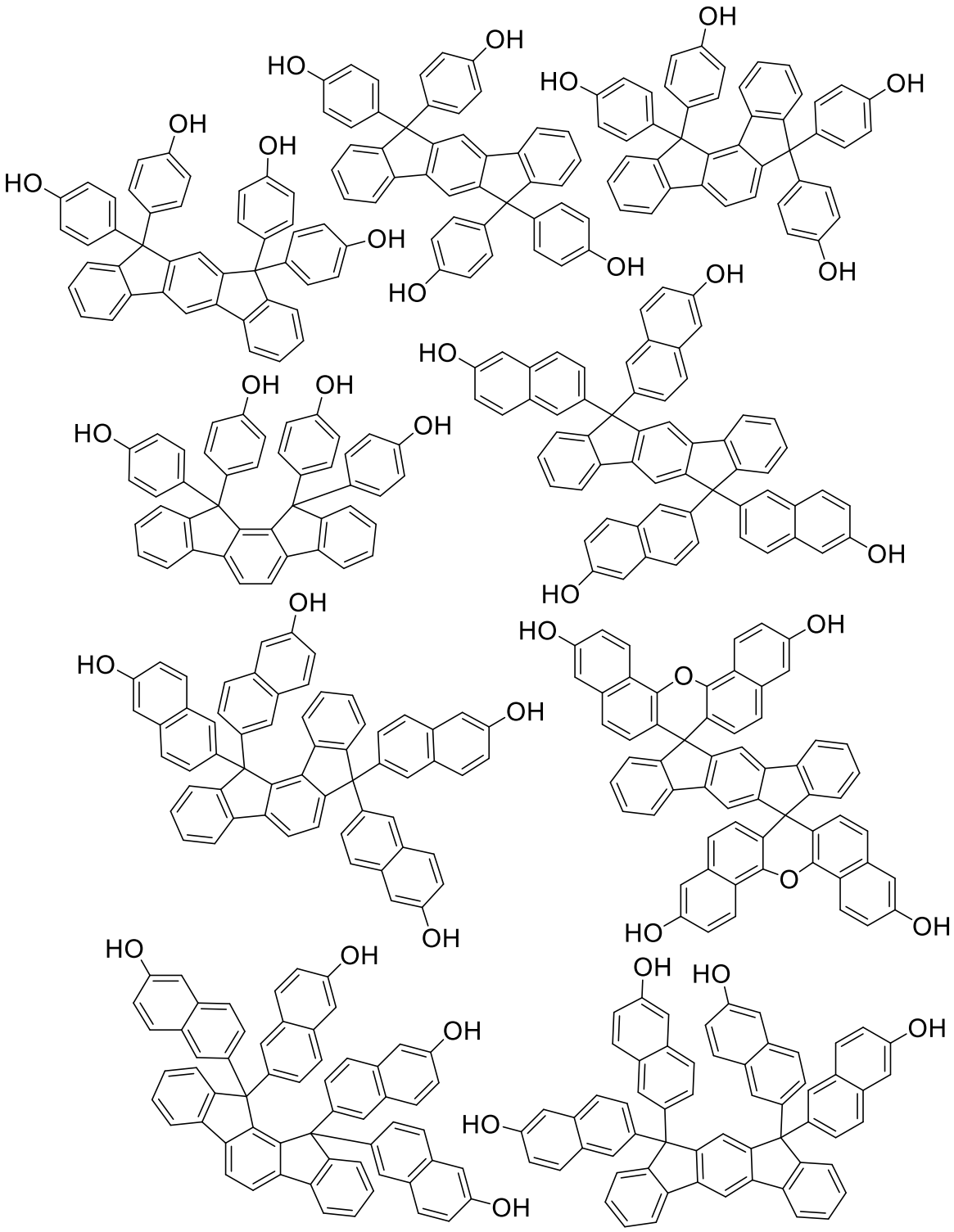
[Chem. 72]



[0124]

Examples of the skeleton represented by Formula (A-6b-1) or Formula (A-6b-2) include the following skeleton:

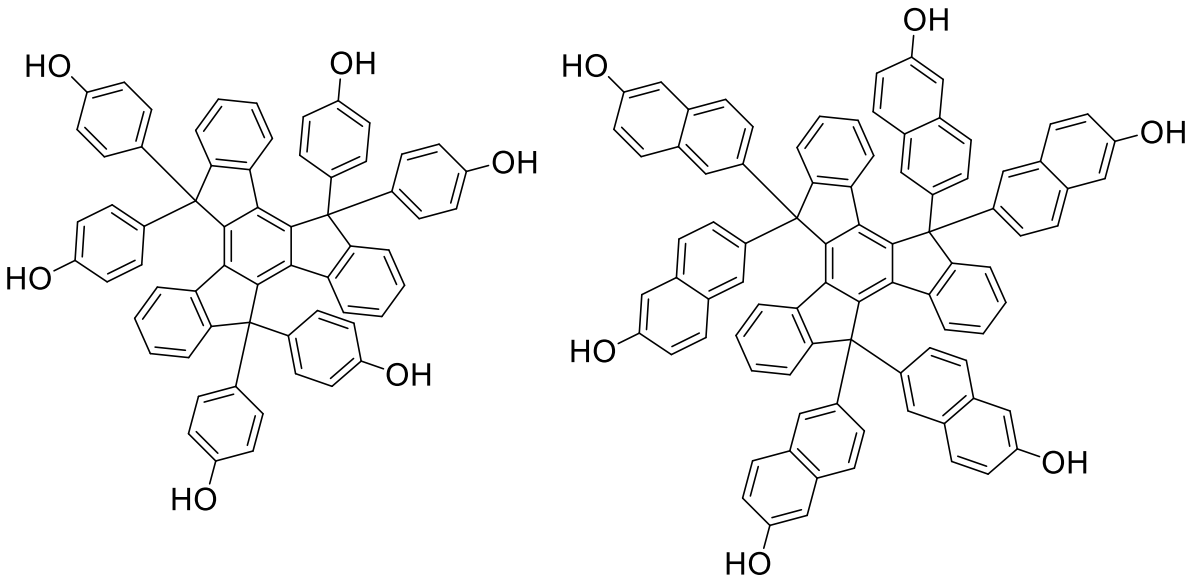
[Chem. 73]



[0125]

Examples of the skeleton represented by Formula (A-6c) include the following skeleton:

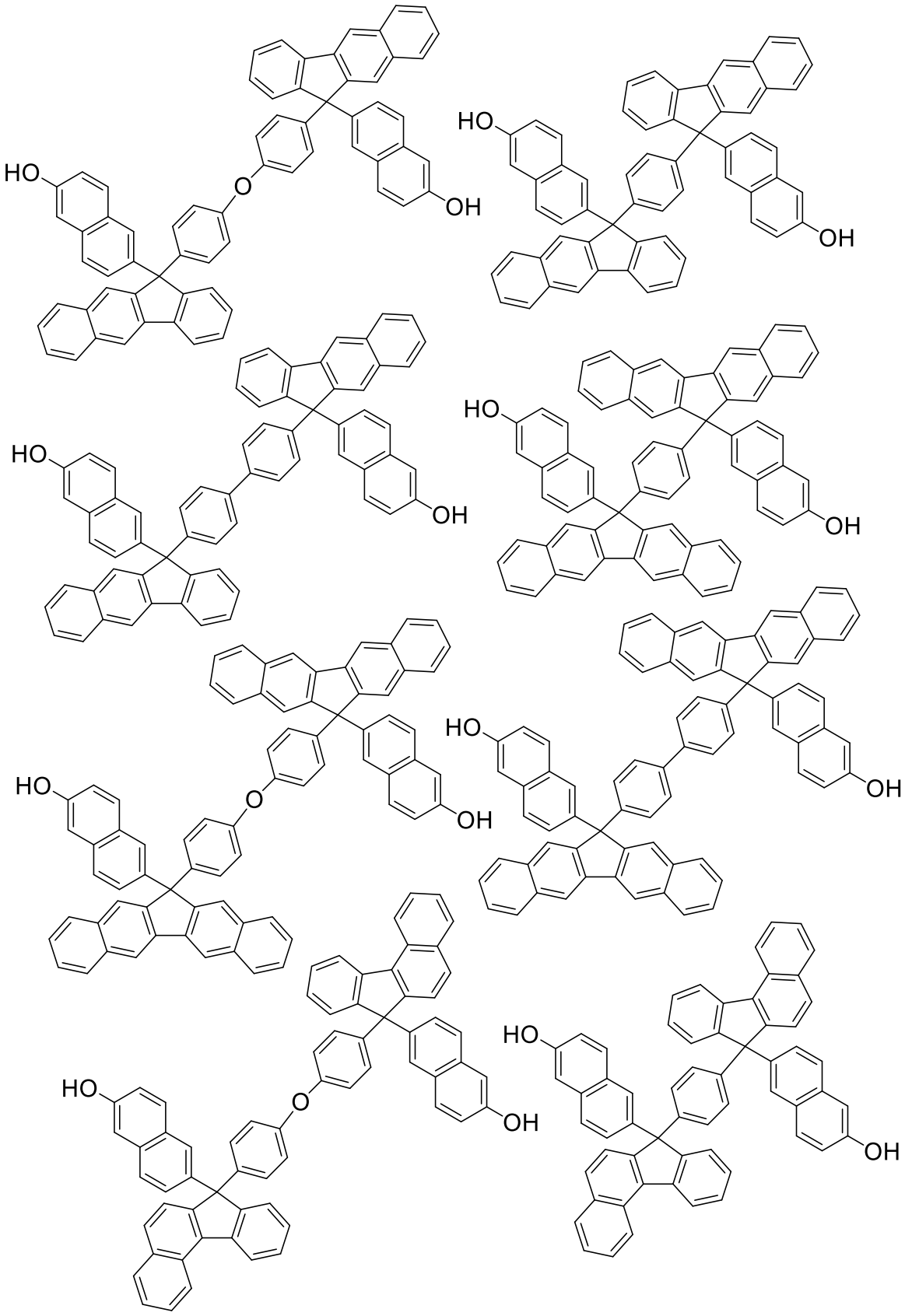
[Chem. 74]



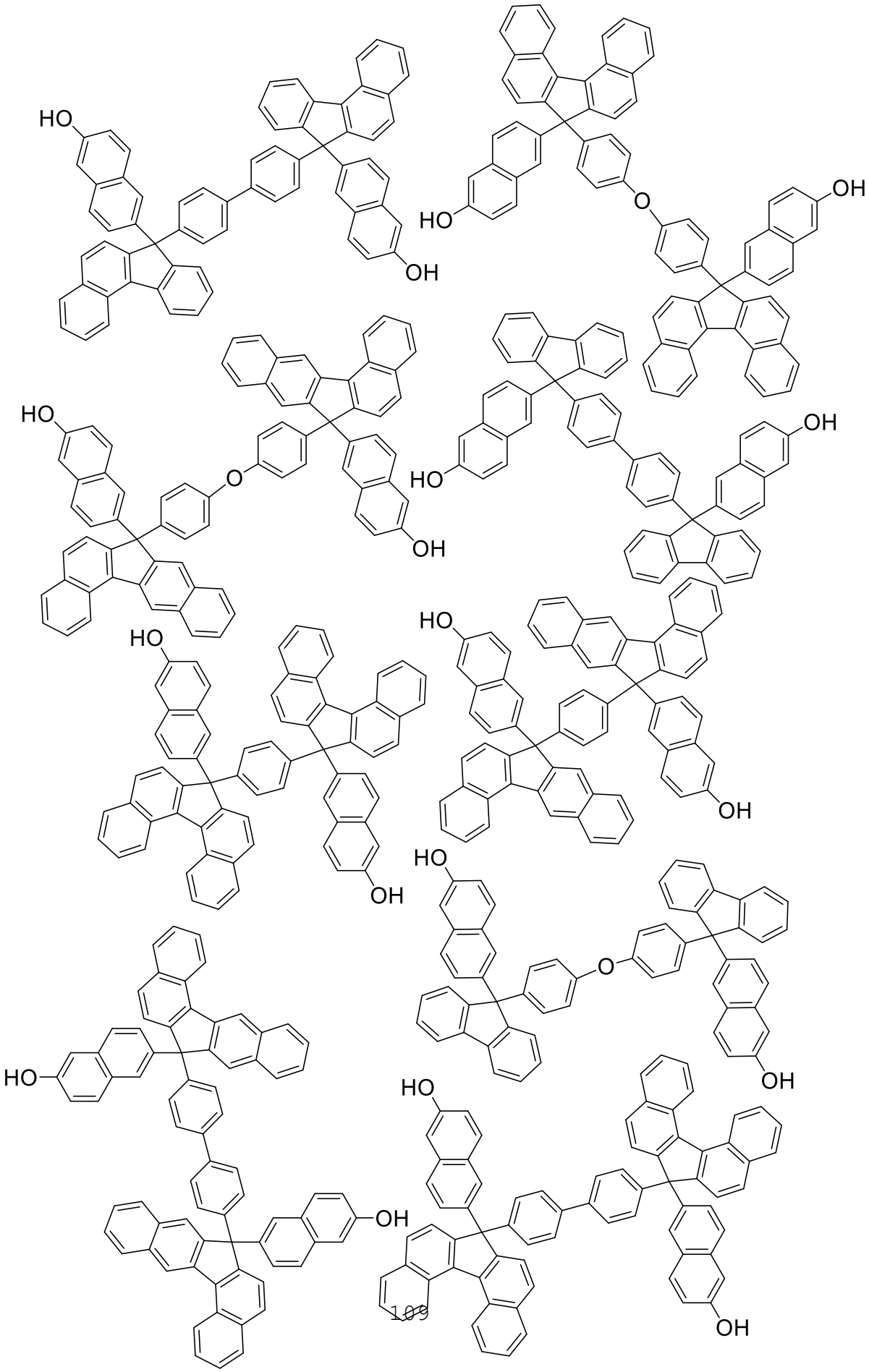
[0126]

Examples of the skeleton represented by Formula (A-6d) include the following skeletons:

[Chem. 75]


HO
O
OH
HO
OH
HO
OH
HO
OH
HO
O
OH
HO
OH
HO
O
OH
HO
OH

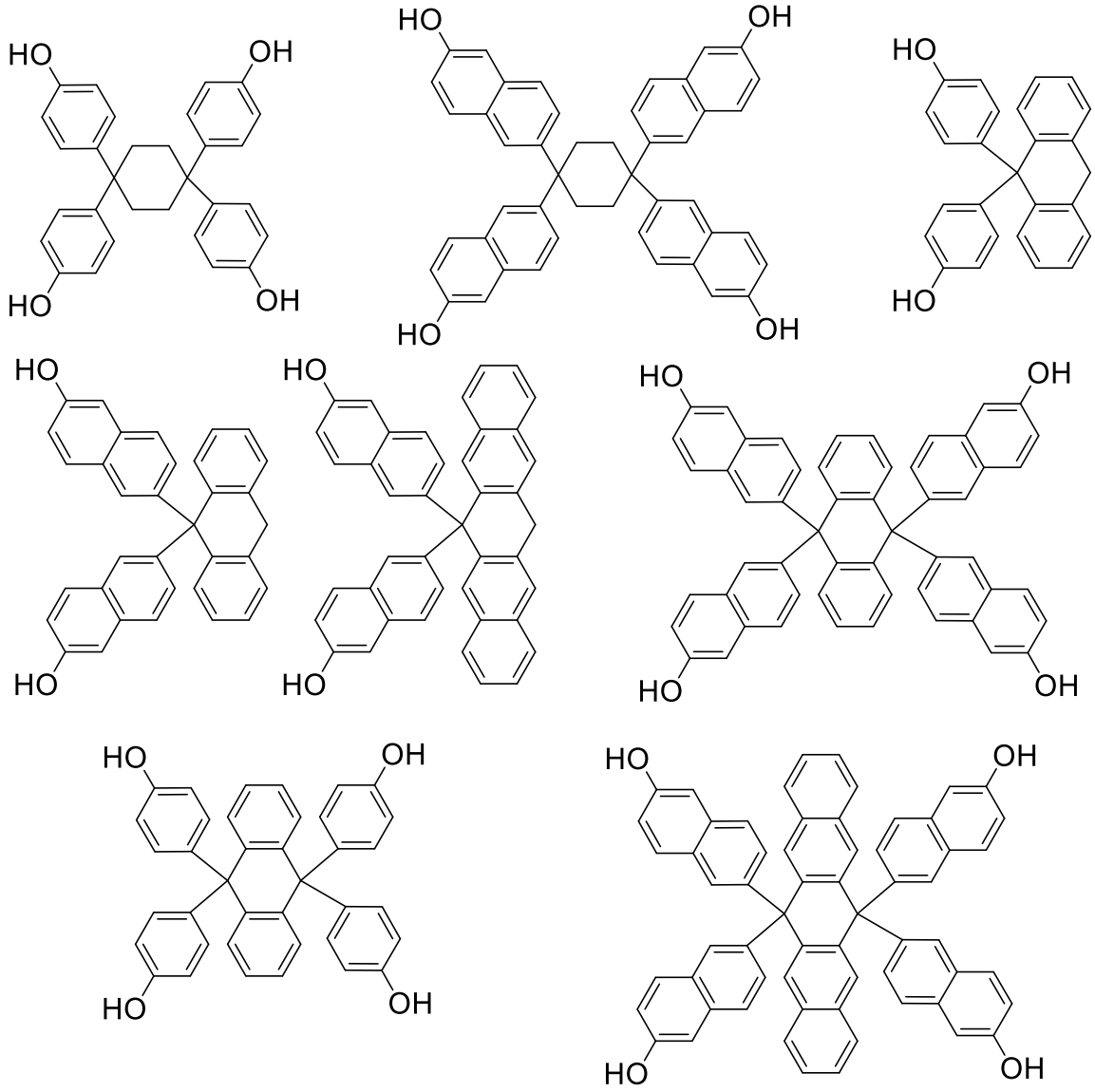
[Chem. 76]


HO
OH
HO
O
OH
HO
OH
HO
O
OH
HO
OH
HO
OH
HO
O
OH
HO
OH
HO
OH

[0127]

Examples of the skeleton represented by Formula (A-7a), Formula (A-7b), or Formula (A-7c) include the following skeleton:

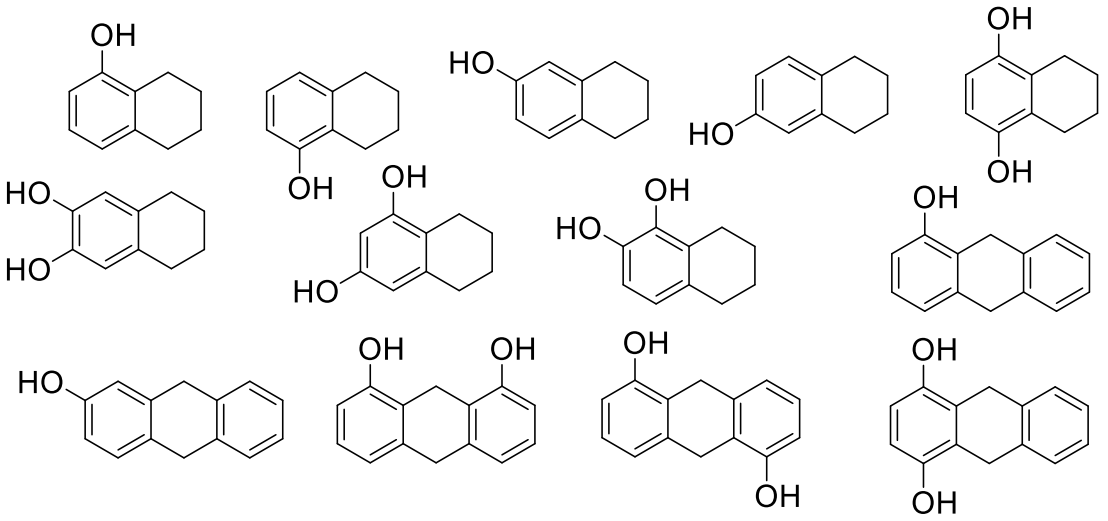
[Chem. 77]



[0128]

Examples of the skeleton represented by Formula (A-8a-1), or Formula (A-8a-2) include the following skeleton:

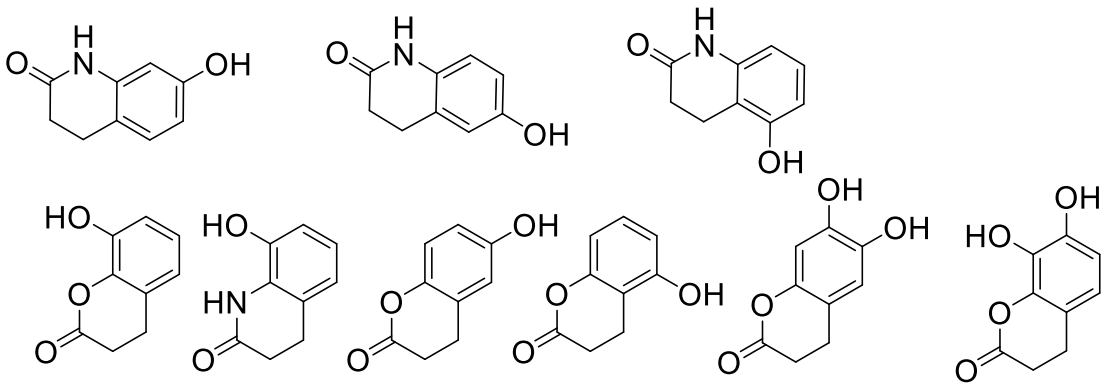
[Chem. 78]



[0129]

Examples of the skeleton represented by Formula (A-8b) include the following skeleton:

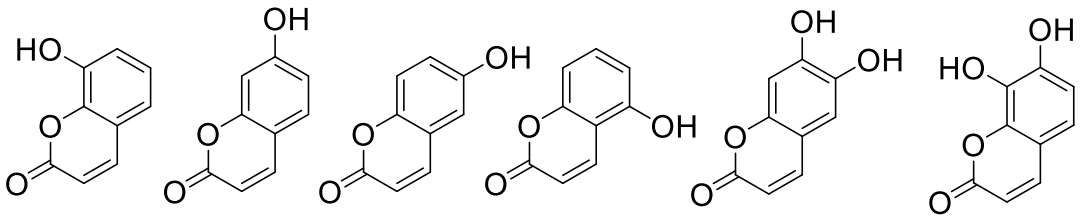
[Chem. 79]



[0130]

Examples of the skeleton represented by Formula (A-8c) include the following skeleton:

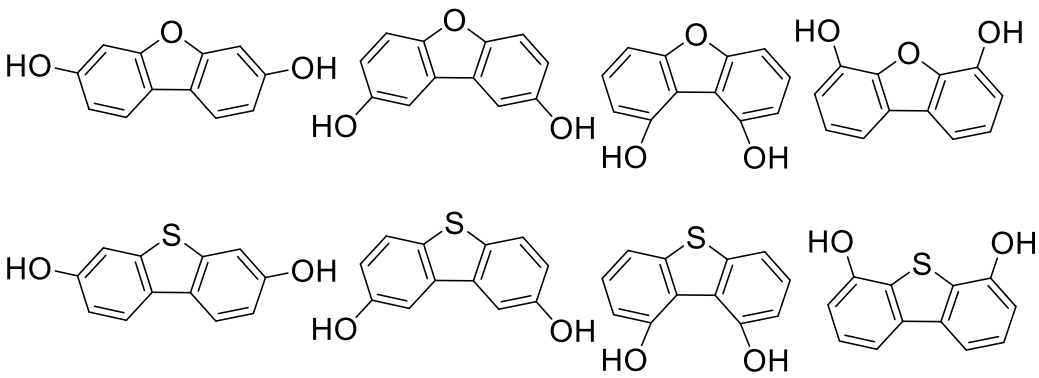
[Chem. 80]



[0131]

Examples of the skeleton represented by Formula (A-8d) include the following skeleton:

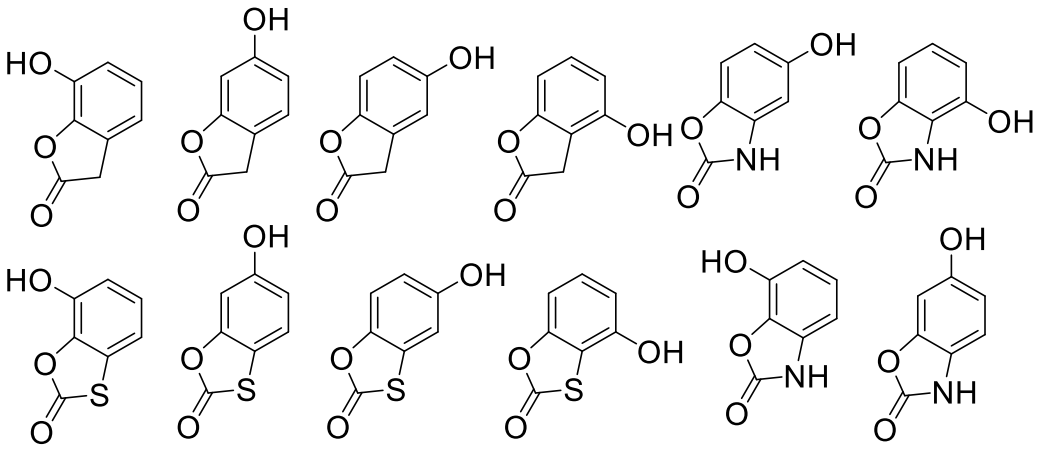
[Chem. 81]



[0132]

Examples of the skeleton represented by Formula (A-8e) include the following skeleton:

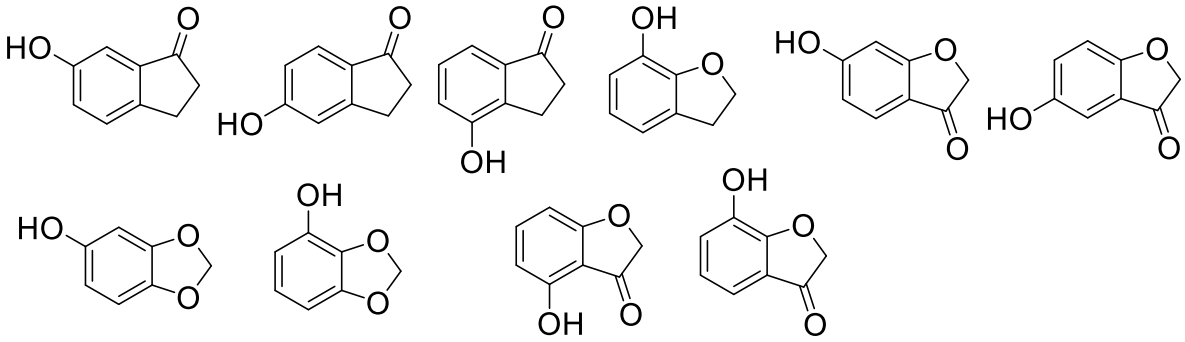
[Chem. 82]



[0133]

Examples of the skeleton represented by Formula (A-8f) include the following skeleton:

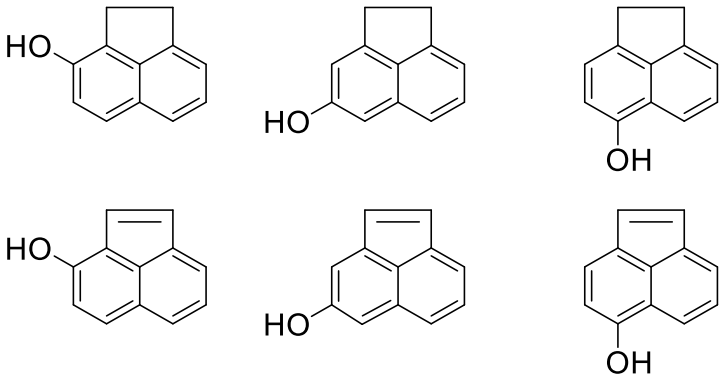
[Chem. 83]



[0134]

Examples of the skeleton represented by Formula (A-8g-1) or Formula (A-8g-2) include the following skeleton:

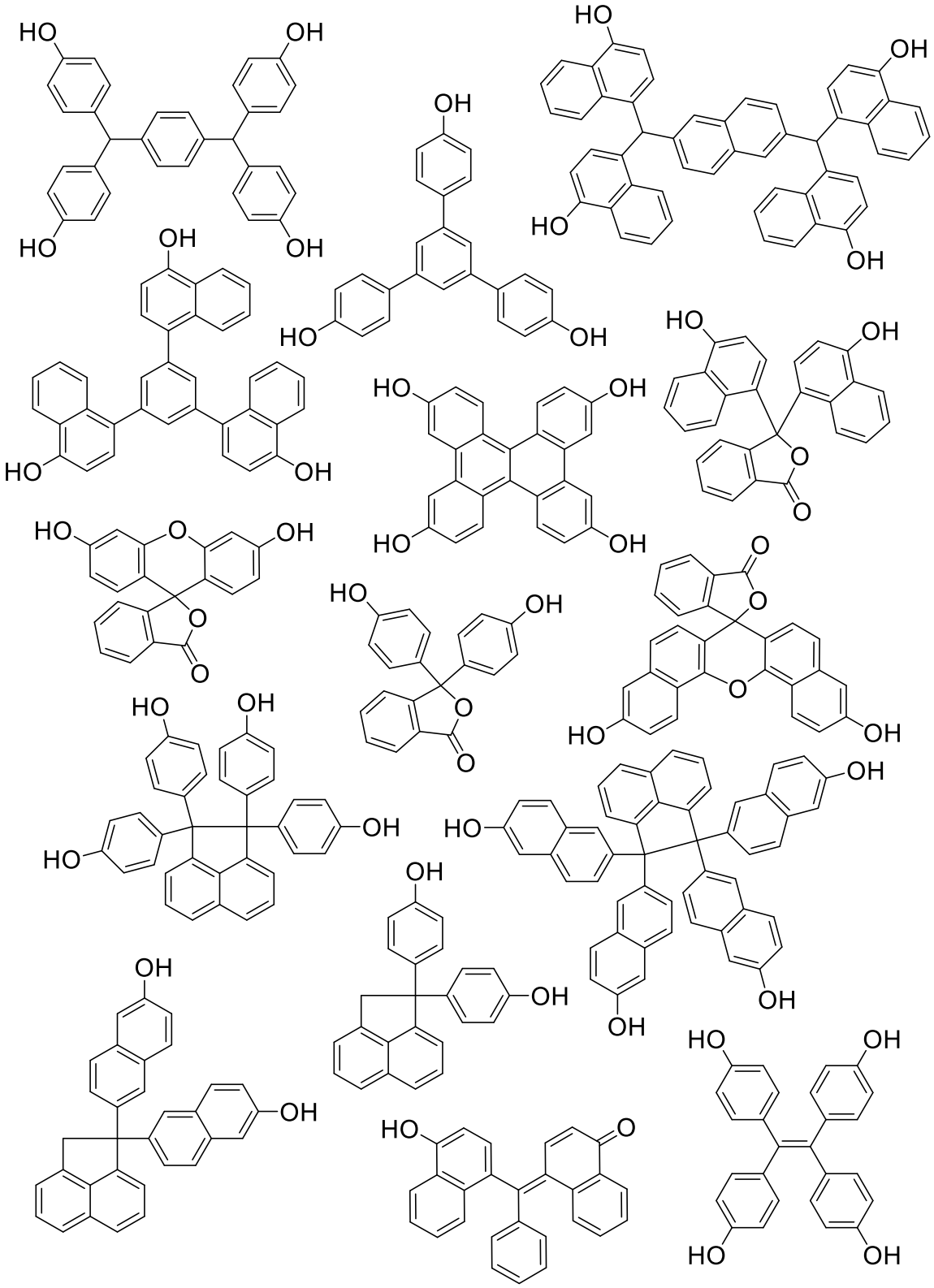
[Chem. 84]



[0135]

Examples of other skeletons of the phenolic skeleton include the following skeleton:

[Chem. 85]



[0136]

The H of the hydroxy group bonding to the aromatic ring

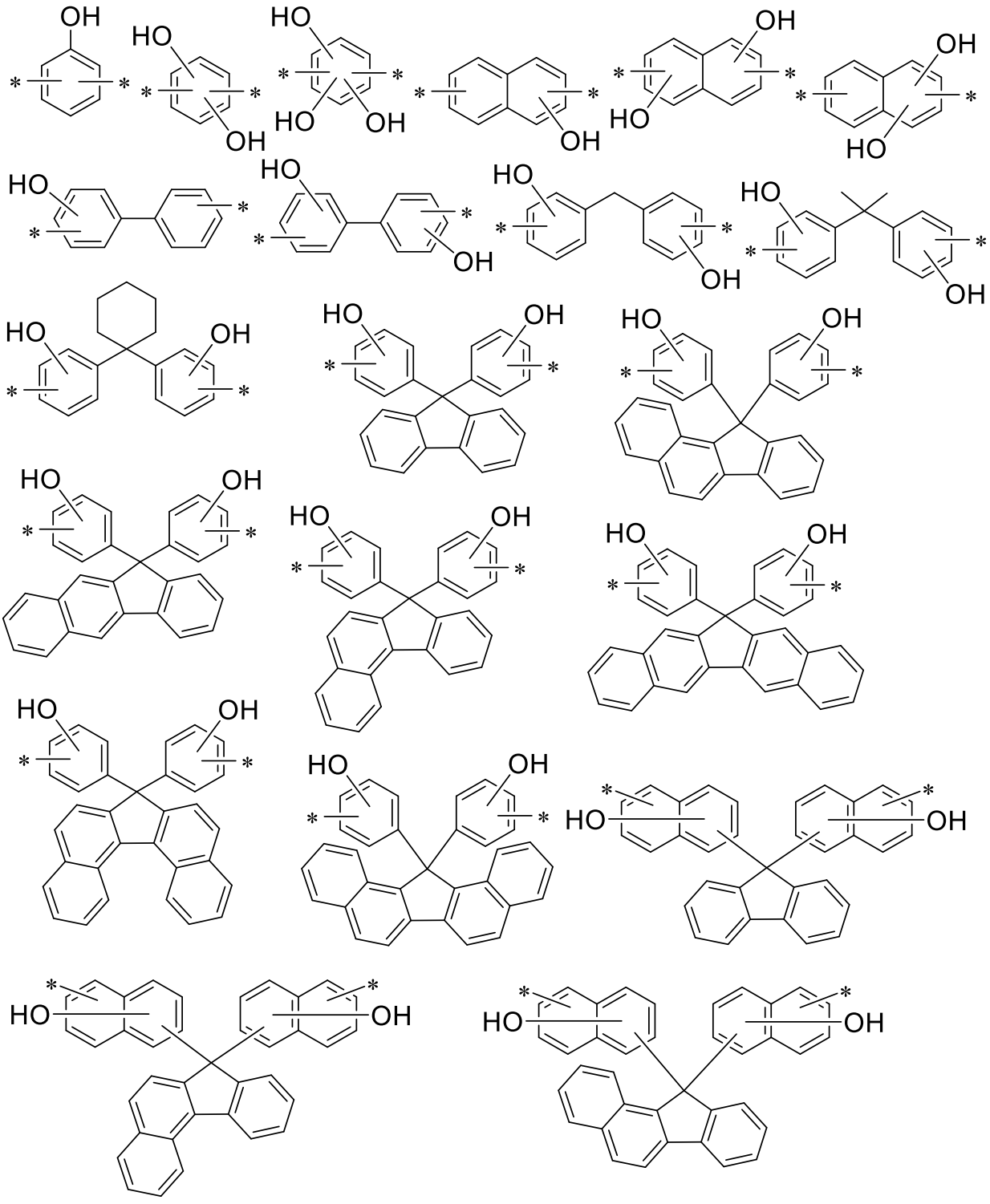
in the phenolic skeleton described above and the hydrogen atom bonding to the aromatic ring in the phenolic skeleton described above may be substituted with a substituent.

Examples of the substituent include the substituent (S) represented by Formulas (S1) to (S7) described above.

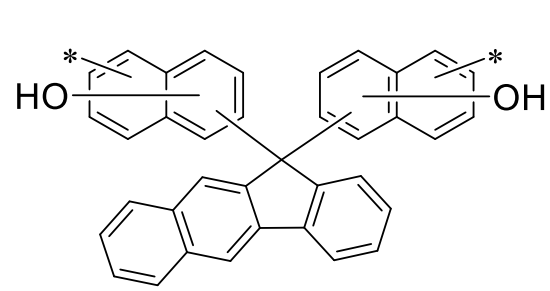
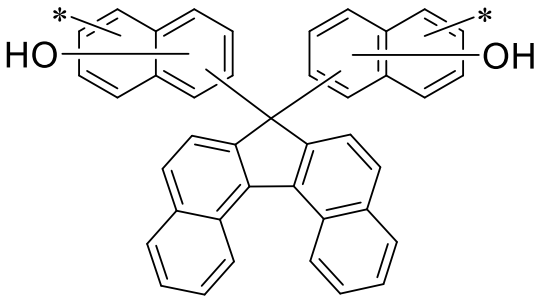
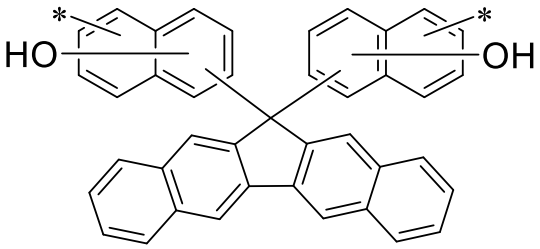
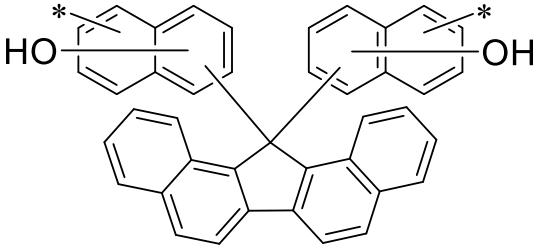
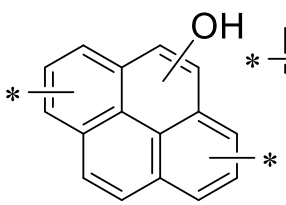
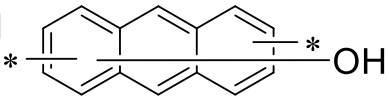
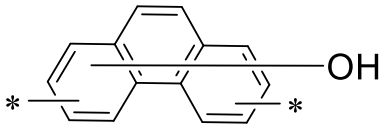
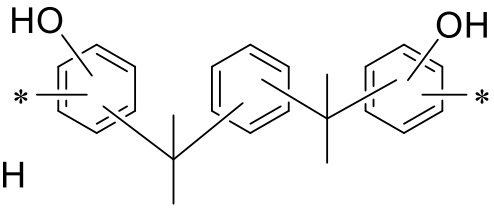
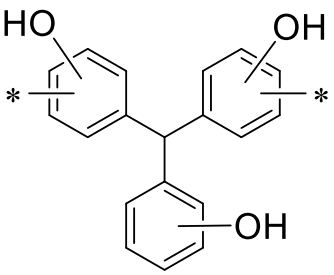
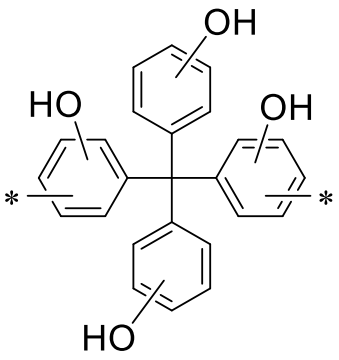
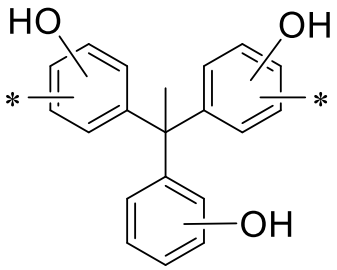
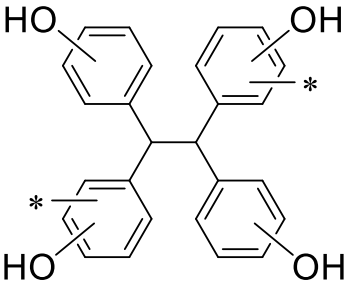
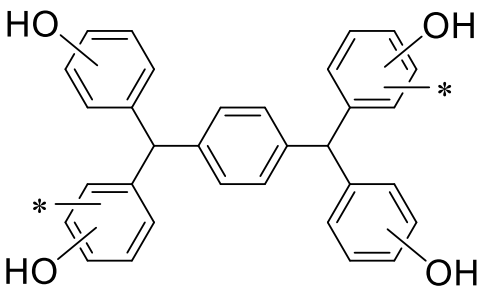
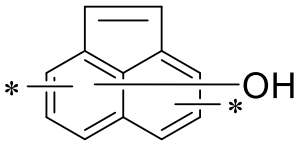
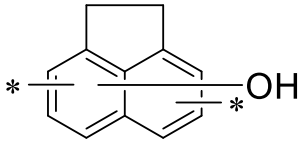
[0137]

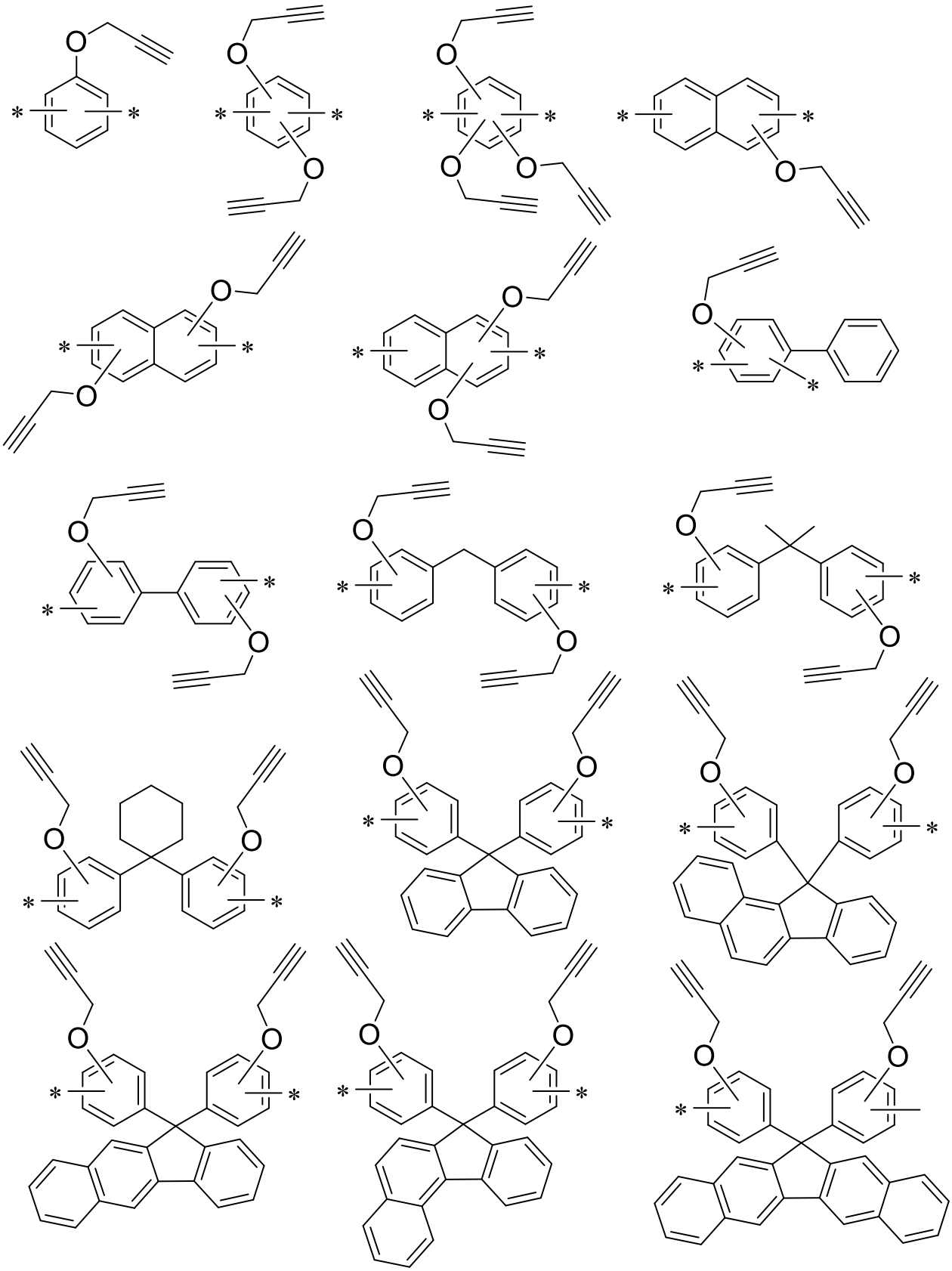
(Examples of unit structures composed of phenolic skeleton)

[Chem. 86]

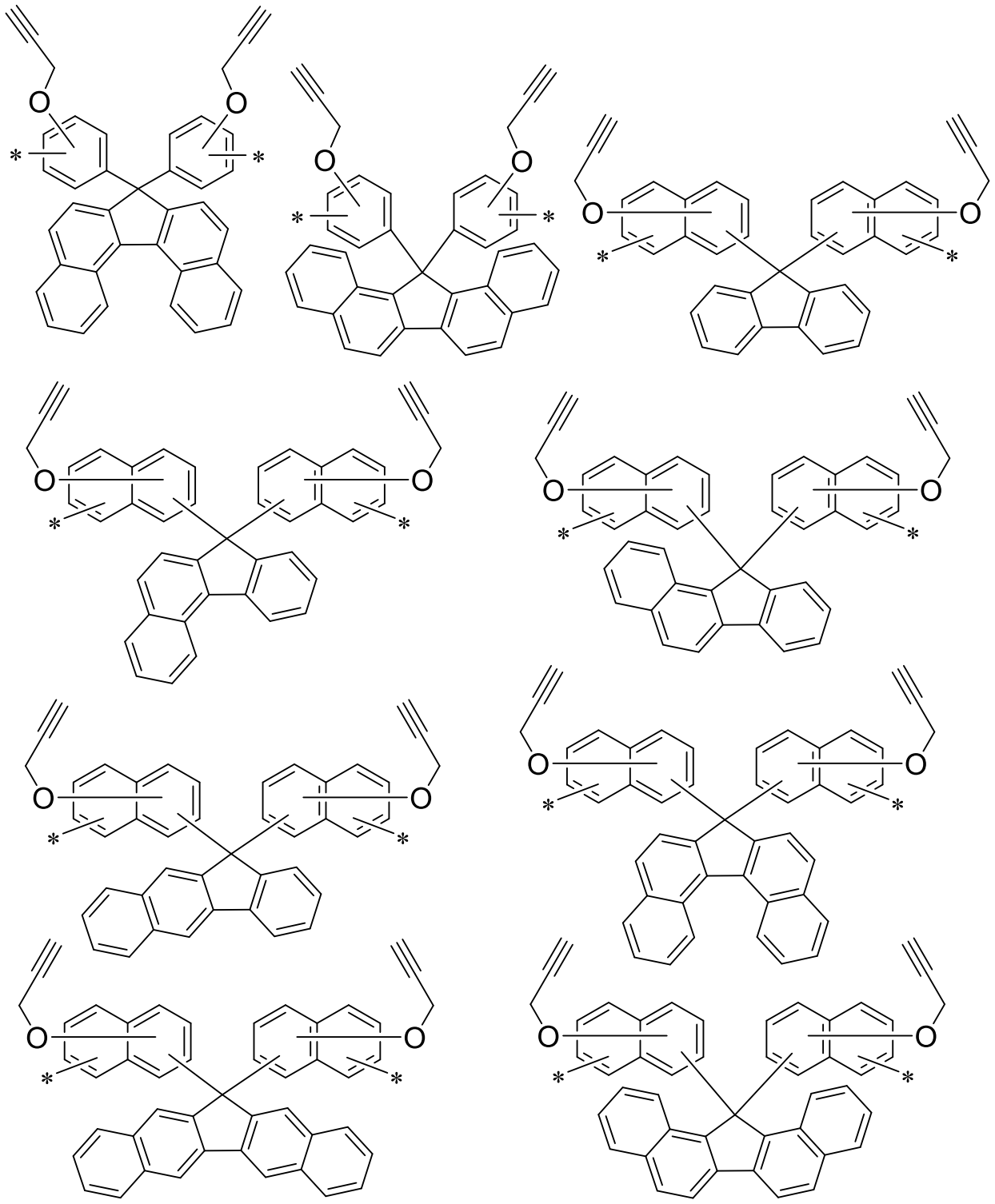


[Chem. 87]

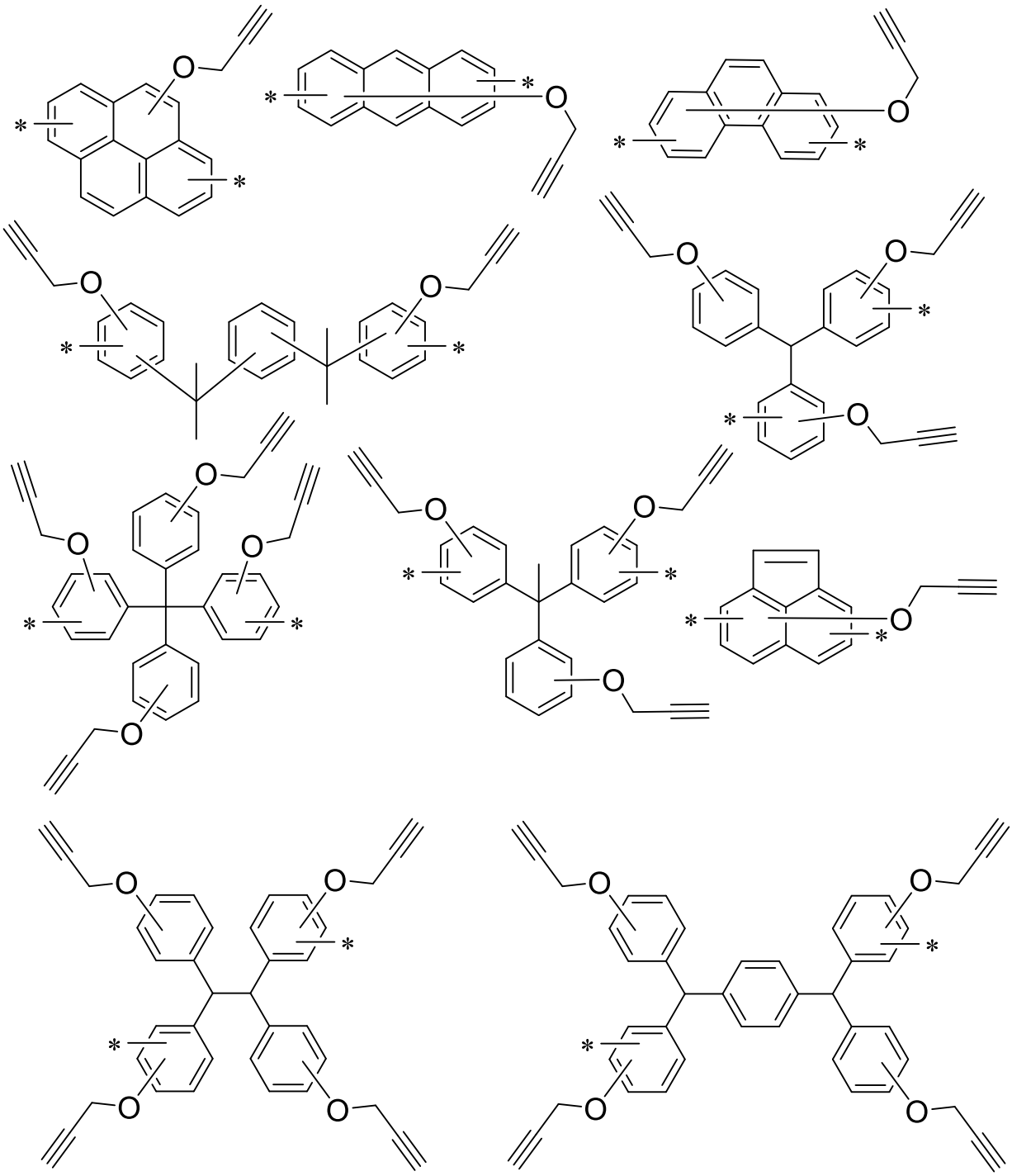


















[Chem. 89]



[Chem. 90]



[0138]

<<B-1: Unit structure (B)>>

The unit structure (B) has one or more carbon atoms.

The unit structure (B) is preferably, for example, a

unit structure (B-I) derived from an aldehyde compound or an aldehyde equivalent.

The unit structure (B) is one type or two or more types of unit structures containing a linking carbon atom [see (I-1) above] bonding to an aromatic ring in the unit structure (A), and includes, for example, a structure represented by Formulas (B1), (B2), or (B3) below. The unit structure (B) covalently bonds to the unit structure (A) and is thereby capable of connecting the two unit structures (A).

[0139]

<<B-2: Unit structure (B-I)>>

The unit structure (B) preferably includes the unit structure (B-I). The unit structure (B-I) is derived from an aldehyde compound or an aldehyde equivalent.

Here, the unit structure (B-I) is a subordinate concept of the unit structure (B) and does not refer to a partial structure of the unit structure (B).

Hereinafter, the unit structure (B-I) will be described.

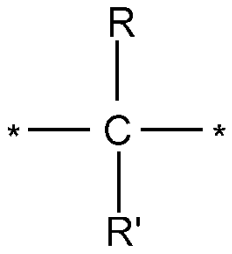
[0140]

<<<B-3: Formula (B1)>>>

The unit structure (B-I) includes, for example, a structure represented by Formula (B1) below. The unit structure (B-I) may be a structure represented by Formula

(B1) below.

[Chem. 91]



(B1)

In Formula (B1),

R and R' each independently represent a hydrogen atom, an aromatic ring optionally having a substituent and having 6 to 30 carbon atoms, a heterocyclic ring optionally having a substituent and having 3 to 30 carbon atoms, or a linear, branched or cyclic alkyl group optionally having a substituent and having 10 or less carbon atoms. R and R' may be taken together with the carbon atom to which they bond to form a structure having a ring structure. * represents a bonding site.

[0141]

Examples of the substituent include a hydroxy group, a carboxy group, a formyl group, a nitro group, an alkyl group, an alkoxy group, an aryl group, an aryloxy group, a cyano group, a group in which H of a hydroxy group is substituted with the substituent (S) above, and a halo group.

[0142]

In addition, each of the two bonding sites of Formula (B1) is capable of covalently bonding to each aromatic ring in the two unit structures (A).

[0143]

In the definitions of R and R' in Formula (B1), for "aromatic ring" and "heterocyclic ring", the above (I-3) and (I-4) can be referred to.

[0144]

In the definitions of R and R' in Formula (B1), examples of the "alkyl group" include a methyl group, an ethyl group, a n-propyl group, an i-propyl group, a cyclopropyl group, a n-butyl group, an i-butyl group, a s-butyl group, a t-butyl group, a cyclobutyl group, a 1-methyl-cyclopropyl group, a 2-methyl-cyclopropyl group, a n-pentyl group, a 1-methyl-n-butyl group, a 2-methyl-n-butyl group, a 3-methyl-n-butyl group, a 1,1-dimethyl-n-propyl group, a 1,2-dimethyl-n-propyl group, a 2,2-dimethyl-n-propyl group, a 1-ethyl-n-propyl group, a cyclopentyl group, a 1-methyl-cyclobutyl group, a 2-methyl-cyclobutyl group, a 3-methyl-cyclobutyl group, a 1,2-dimethyl-cyclopropyl group, a 2,3-dimethyl-cyclopropyl group, a 1-ethyl-cyclopropyl group, a 2-ethyl-cyclopropyl group, a n-hexyl group, a 1-methyl-n-pentyl group, a 2-methyl-n-pentyl group, a 3-methyl-n-pentyl group, a 4-methyl-n-pentyl group, a 1,1-dimethyl-n-butyl group, a 1,2-

dimethyl-n-butyl group, a 1,3-dimethyl-n-butyl group, a 2,2-dimethyl-n-butyl group, a 2,3-dimethyl-n-butyl group, a 3,3-dimethyl-n-butyl group, a 1-ethyl-n-butyl group, a 2-ethyl-n-butyl group, a 1,1,2-trimethyl-n-propyl group, a 1,2,2-trimethyl-n-propyl group, a 1-ethyl-1-methyl-n-propyl group, a 1-ethyl-2-methyl-n-propyl group, a cyclohexyl group, a 1-methyl-cyclopentyl group, a 2-methyl-cyclopentyl group, a 3-methyl-cyclopentyl group, a 1-ethyl-cyclobutyl group, a 2-ethyl-cyclobutyl group, a 3-ethyl-cyclobutyl group, a 1,2-dimethyl-cyclobutyl group, a 1,3-dimethyl-cyclobutyl group, a 2,2-dimethyl-cyclobutyl group, a 2,3-dimethyl-cyclobutyl group, a 2,4-dimethyl-cyclobutyl group, a 3,3-dimethyl-cyclobutyl group, a 1-n-propyl-cyclopropyl group, a 2-n-propyl-cyclopropyl group, a 1-i-propyl-cyclopropyl group, a 2-i-propyl-cyclopropyl group, a 1,2,2-trimethyl-cyclopropyl group, a 1,2,3-trimethyl-cyclopropyl group, a 2,2,3-trimethyl-cyclopropyl group, a 1-ethyl-2-methyl-cyclopropyl group, a 2-ethyl-1-methyl-cyclopropyl group, a 2-ethyl-2-methyl-cyclopropyl group, a 2-ethyl-3-methyl-cyclopropyl group, a n-heptyl group, a n-octyl group, a n-nonyl group, and a n-decyl group.

[0145]

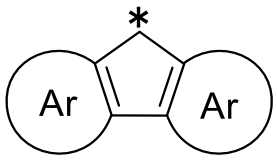
Preferably, R and R’ are each independently phenyl, naphthalenyl, anthracenyl, phenanthrenyl, naphthacenyl or pyrenyl.

More preferably, R is a hydrogen atom, and R′ is naphthalenyl.

[0146]

Examples of the structures having a ring structure formed by R and R′ together with a carbon atom bonded thereto include the structures represented by the following formula:

[Chem. 92]



(where each Ar independently represents a residue of an aromatic ring, the carbon atom represented by * is a carbon atom bonding to R and R′ in Formula (B1)).

[0147]

Examples of the aromatic ring of Ar include an aromatic ring represented by Formula (G1).

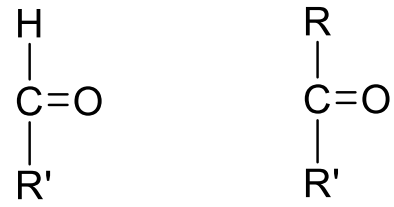
[0148]

The unit structure (B-I) including the structure represented by Formula (B1) is derived from, for example, an aldehyde compound or a ketone compound.

Examples of the aldehyde compounds include a compound represented by Formula (B-1a) below.

Examples of the ketone compounds include a compound represented by Formula (B-1b) below.

[Chem. 93]



(B-1a)

(B-1b)

(In Formulas (B-1a) and (B-1b), R and R’ have the same meanings as R and R’ in Formula (B1), respectively. However, R is other than a hydrogen atom.

In Formula (B-1b), R and R’ may be taken together with the carbon atom to which they bond to form a structure having a ring structure).

[0149]

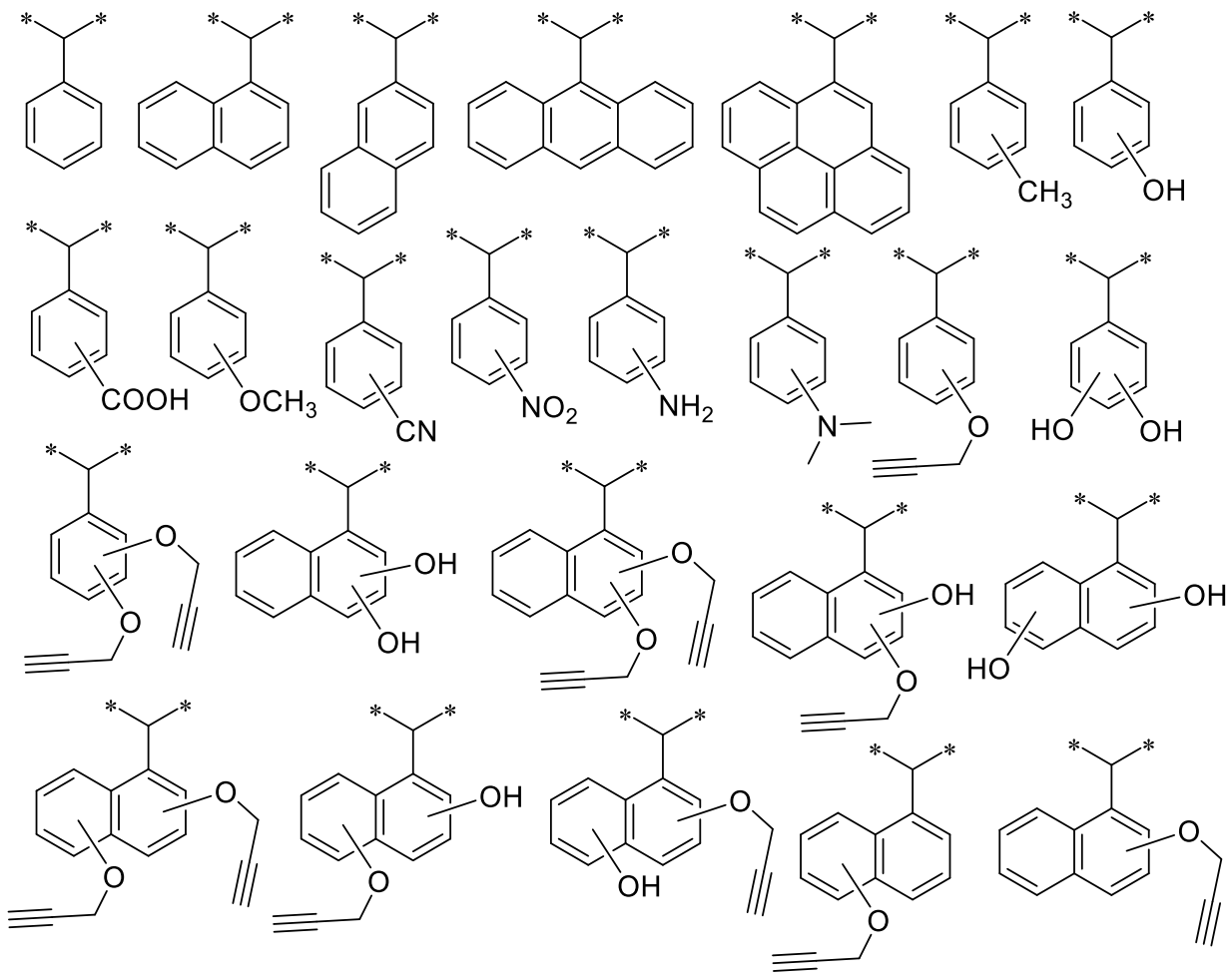
For example, in obtaining the resin (G), the carbonyl group in Formula (B-1a) and Formula(B-1b) is converted to *-C-* in Formula (B1).

[0150]

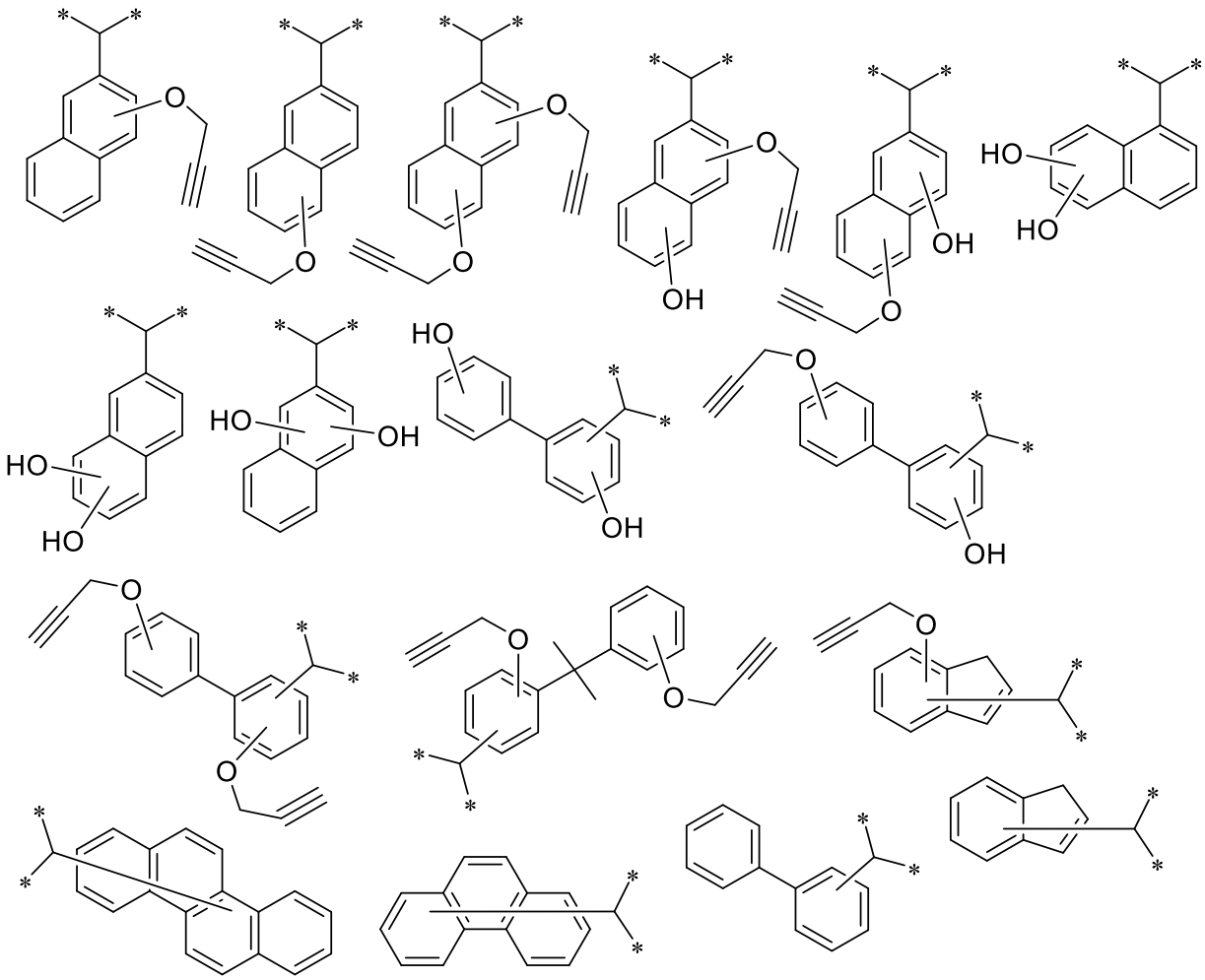
Some specific examples of the unit structure (B-I) including the structure represented by Formula (B1) are as follows. * basically indicates a binding site with the unit structure (A). Needless to say, the structure may include the exemplary structure as a part of the whole.

[0151]

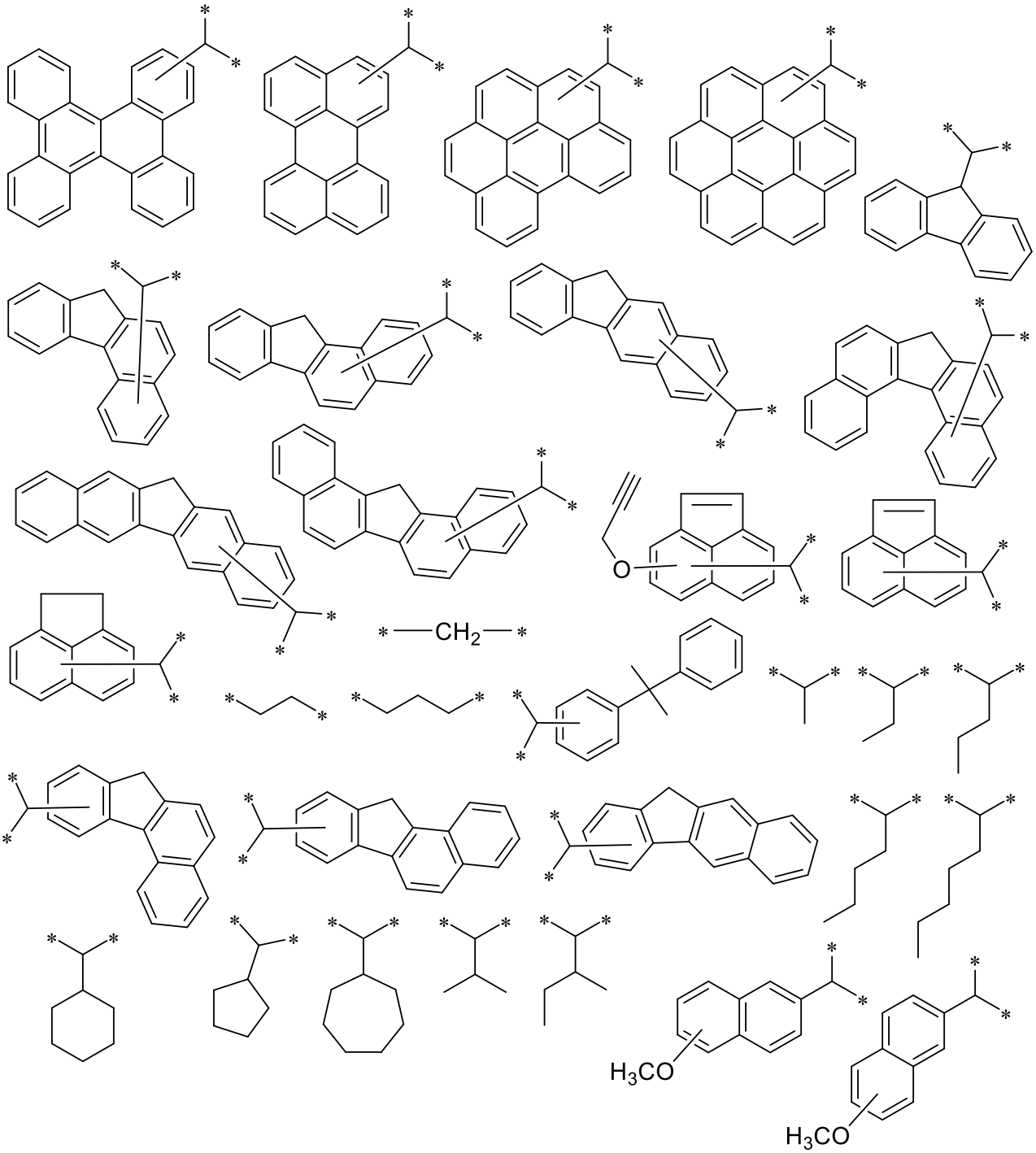
[Chem. 94]



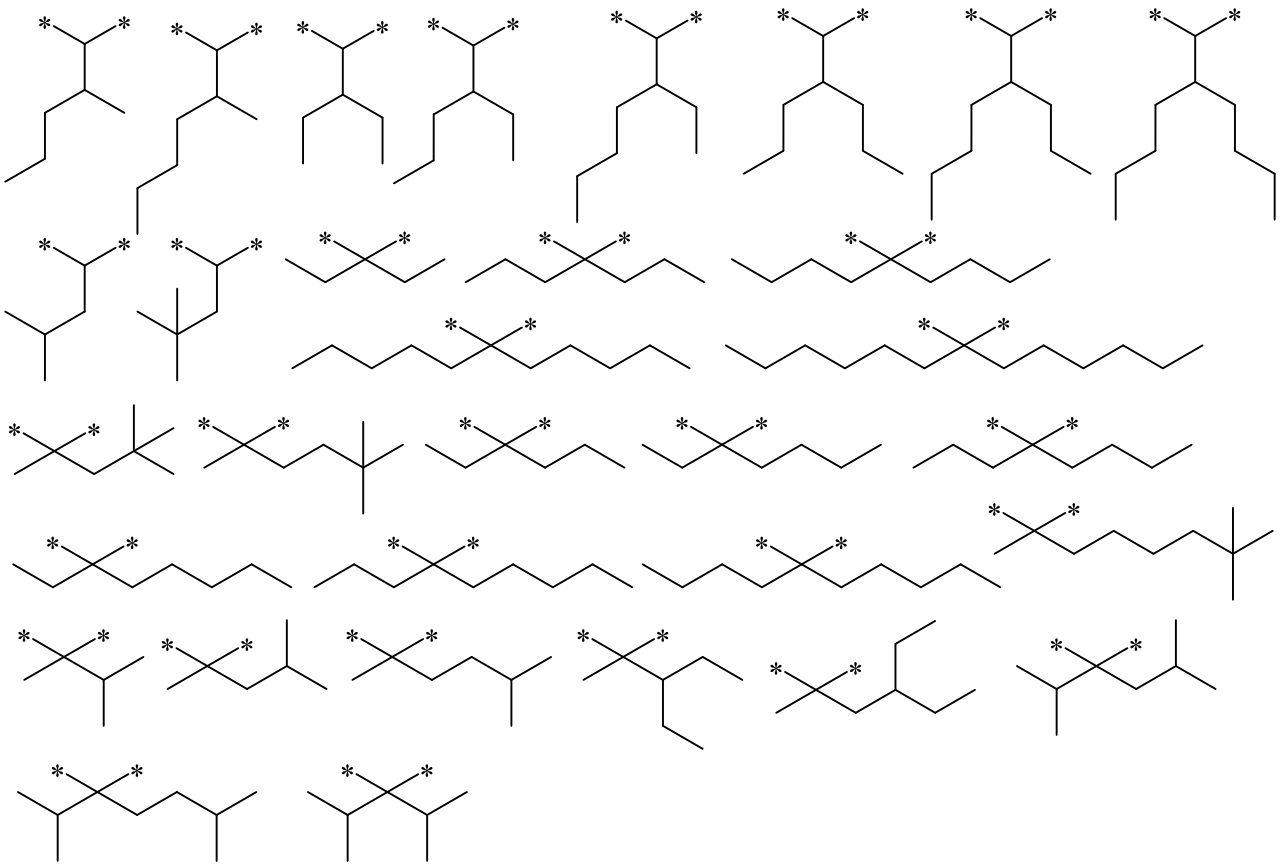
[Chem. 95]



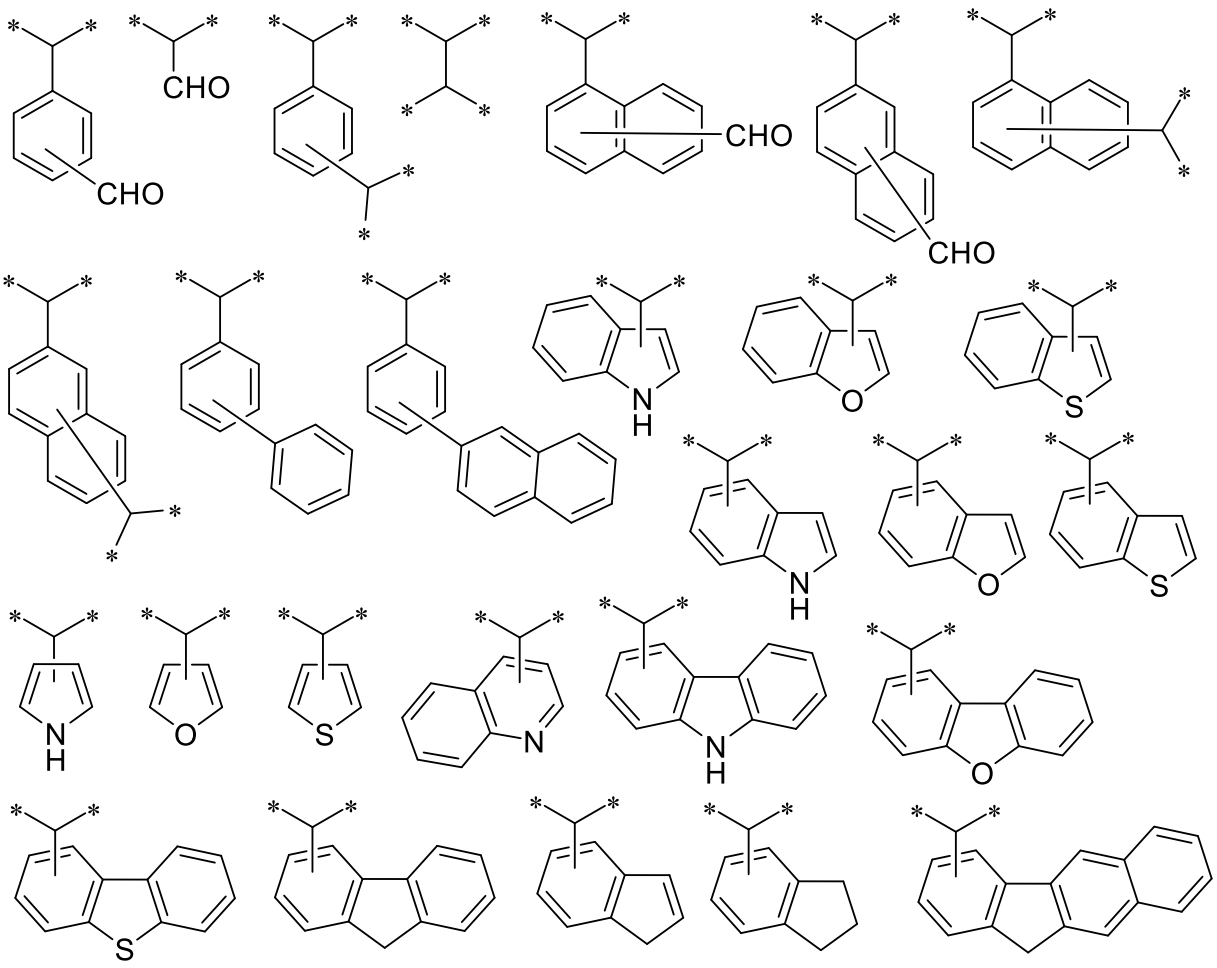
[Chem. 96]



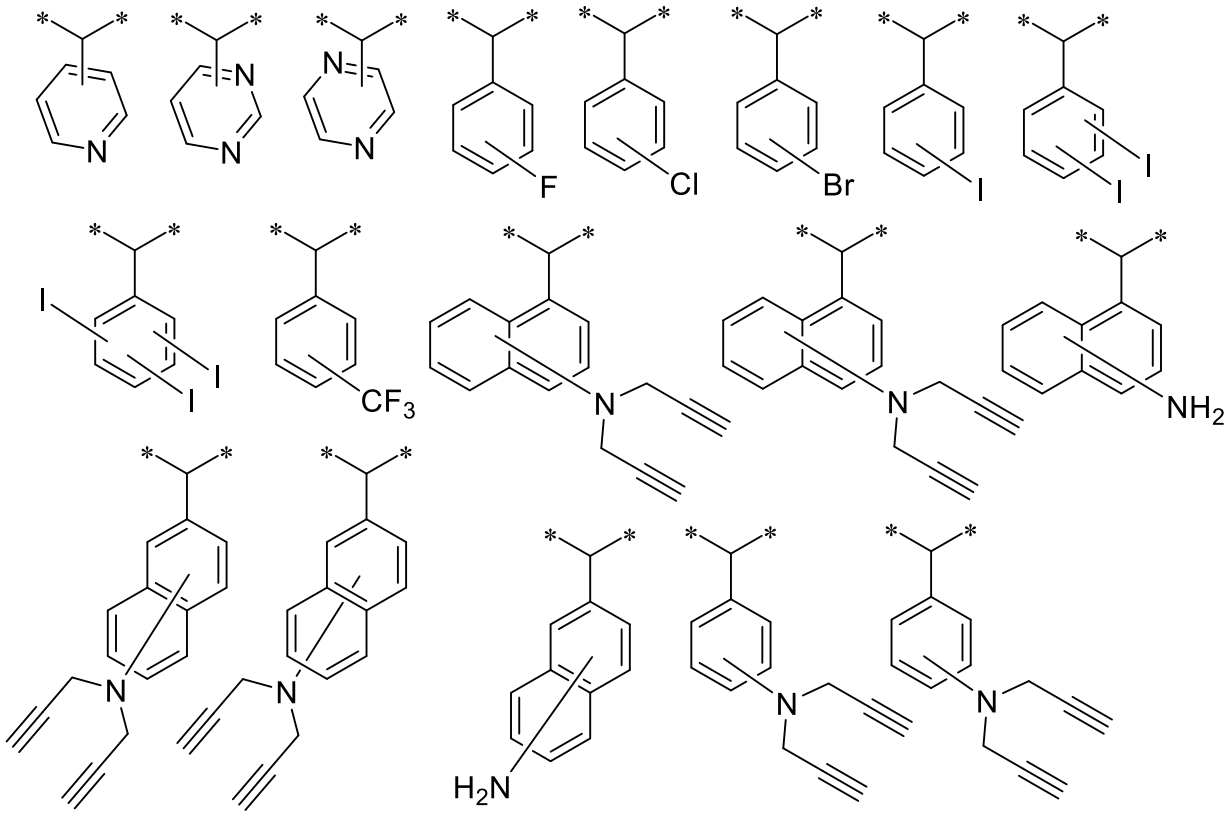
[Chem. 97]



[Chem. 98]



[Chem. 99]



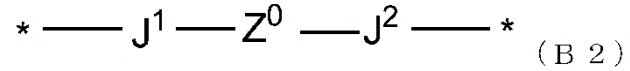
[0152]

<<<B-4: Formula (B2)>>>

The unit structure (B-I) includes, for example, a structure represented by Formula (B2) below. The unit structure (B-I) may be a structure represented by Formula (B2) below.

[0153]

[Chem. 100]



(B 2)

In Formula (B2),

Z^0 represents an aromatic ring residue or an aliphatic ring residue having 6 to 30 carbon atoms which may have a

substituent, or an organic group in which two or more aromatic or aliphatic rings are linked by a single bond. Examples of the organic groups in which two or more aromatic rings or aliphatic rings are linked by a single bond include divalent residues such as biphenyl, cyclohexylphenyl, and bicyclohexyl.

[0154]

Examples of the substituent include a hydroxy group, a carboxy group, a formyl group, a nitro group, an alkyl group, an alkoxy group, an aryl group, an aryloxy group, a cyano group, a group in which H of a hydroxy group is substituted with the substituent (S) above, and a halo group.

[0155]

J^1 and J^2 each independently represent a direct bond or a divalent organic group which may have a substituent. The divalent organic group is preferably a linear or branched alkylene group having 1 to 6 carbon atoms which may be substituted with a hydroxy group, an aryl group (such as phenyl group, substituted phenyl group), or a halo group (such as fluorine) as a substituent. Examples of the linear alkylene groups include a methylene group, an ethylene group, a propylene group, a butylene group, a pentylene group, and a hexylene group.

[0156]

The unit structure (B-I) including the structure represented by Formula (B2) is derived from, for example, a compound having a hydroxy group or an alkoxy group bonding to a secondary or tertiary carbon atom, a compound having a hydroxy group, an alkoxy group or a halo group bonding to an α-position carbon atom (such as a benzyl position carbon atom) of an alkylaryl group, or a compound having two carbon-carbon double bonds. These compounds are aldehyde equivalents.

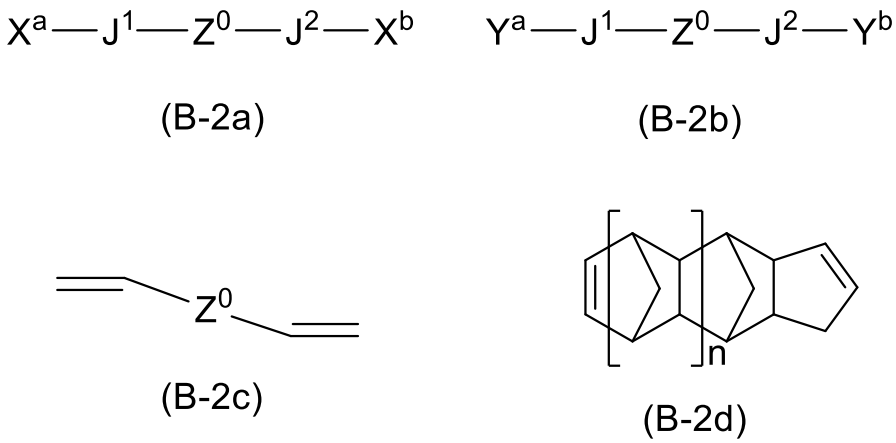
[0157]

Examples of the compound having a hydroxy group or an alkoxy group bonding to a secondary or tertiary carbon atom include a compound represented by Formula (B-2a) below.

Examples of the compound having a hydroxy group, an alkoxy group, or a halo group bonding to an α-position carbon atom (such as a benzyl position carbon atom) of the alkylaryl group include a compound represented by Formula (B-2b) below.

Examples of the compounds having two carbon-carbon double bonds include a compound represented by Formula (B-2c) below or Formula (B-2d) below.

[Chem. 101]



(B-2a) (B-2b)

(B-2c) (B-2d)

(In Formulas (B-2a), (B-2b), and (B-2b), J^1, J^2, and Z^0 have the same meanings as J^1, J^2, and Z^0 in Formula (B2), respectively.

In Formula (B-2a), X^a and X^b each independently represent a hydroxy group or an alkoxy group bonding to a secondary or tertiary carbon atom.

In Formula (B-2b), Y^a and Y^b each independently represent a hydroxy group, an alkoxy group or a halo group bonding to an α-position carbon atom (such as a benzyl position carbon atom) of an alkylaryl group.

In Formula (B-2d), n represents an integer of 0 to 4).

[0158]

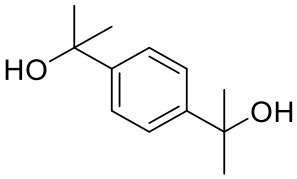
For example, in obtaining the resin (G), X^a-J^1 in Formula (B-2a) is converted to *-J^1 in Formula (B2). J^2-X^b is converted to J^2-* in Formula (B2).

For example, in obtaining the resin (G), Y^a-J^1 in Formula (B-2b) is converted to *-J^1 in Formula (B2). J^2-Y^b is converted to J^2-* in Formula (B2).

[0159]

An example of Formula (B-2a) is the following compound:

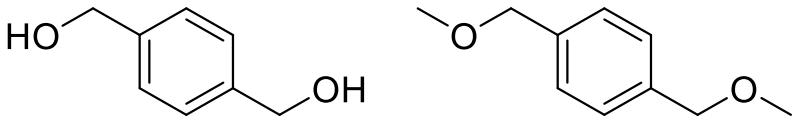
[Chem. 102]



[0160]

An example of Formula (B-2b) is the following compound:

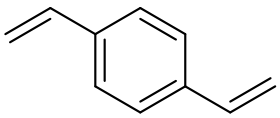
[Chem. 103]



[0161]

An example of Formula (B-2c) is the following compound:

[Chem. 104]

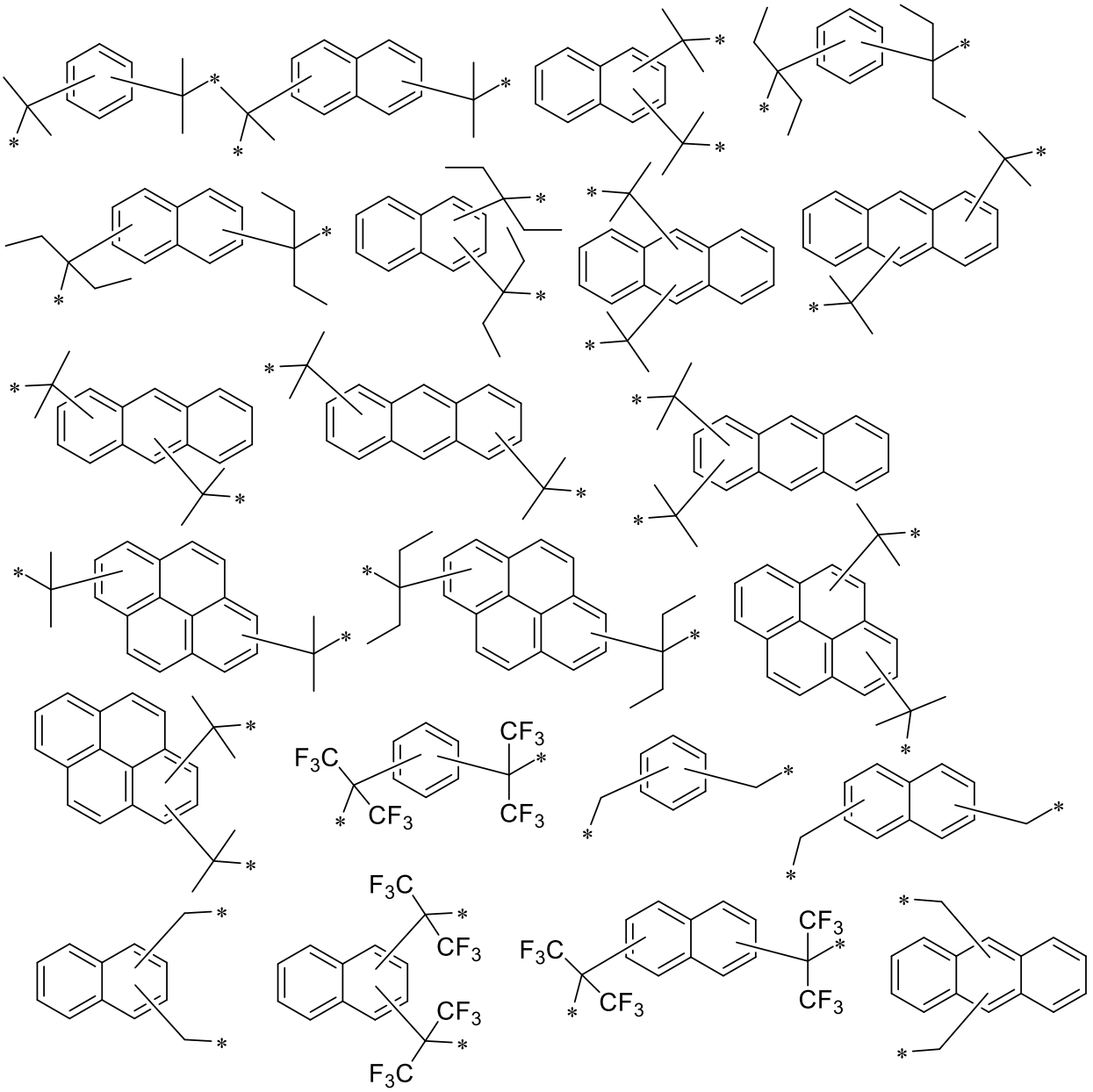


[0162]

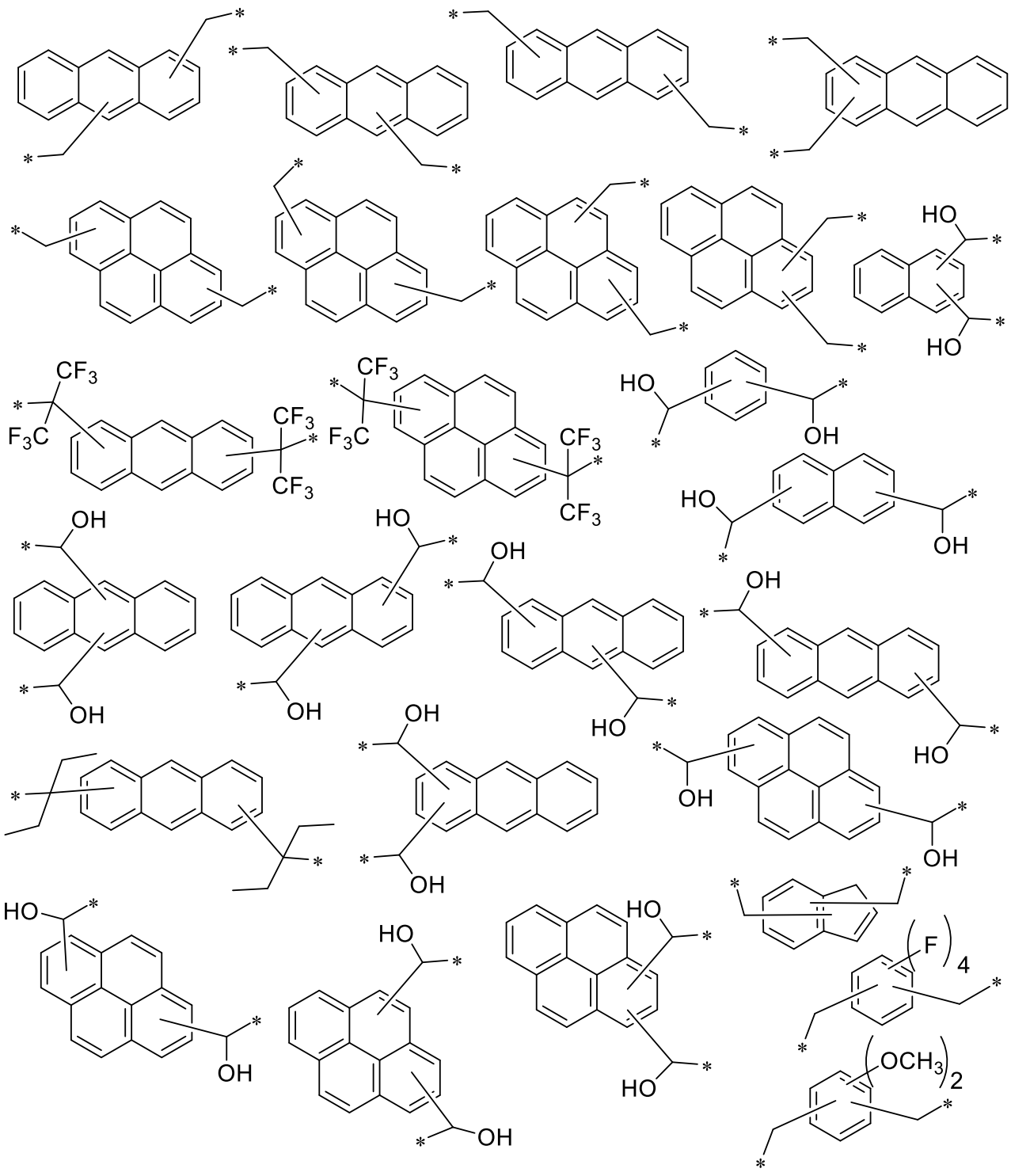
Some specific examples of the unit structures including the structure represented by Formula (B2) are as follows: * represents a binding site with the unit structure (A). Needless to say, the structure may be a unit structure including the exemplary structure as a part of the whole.

[0163]

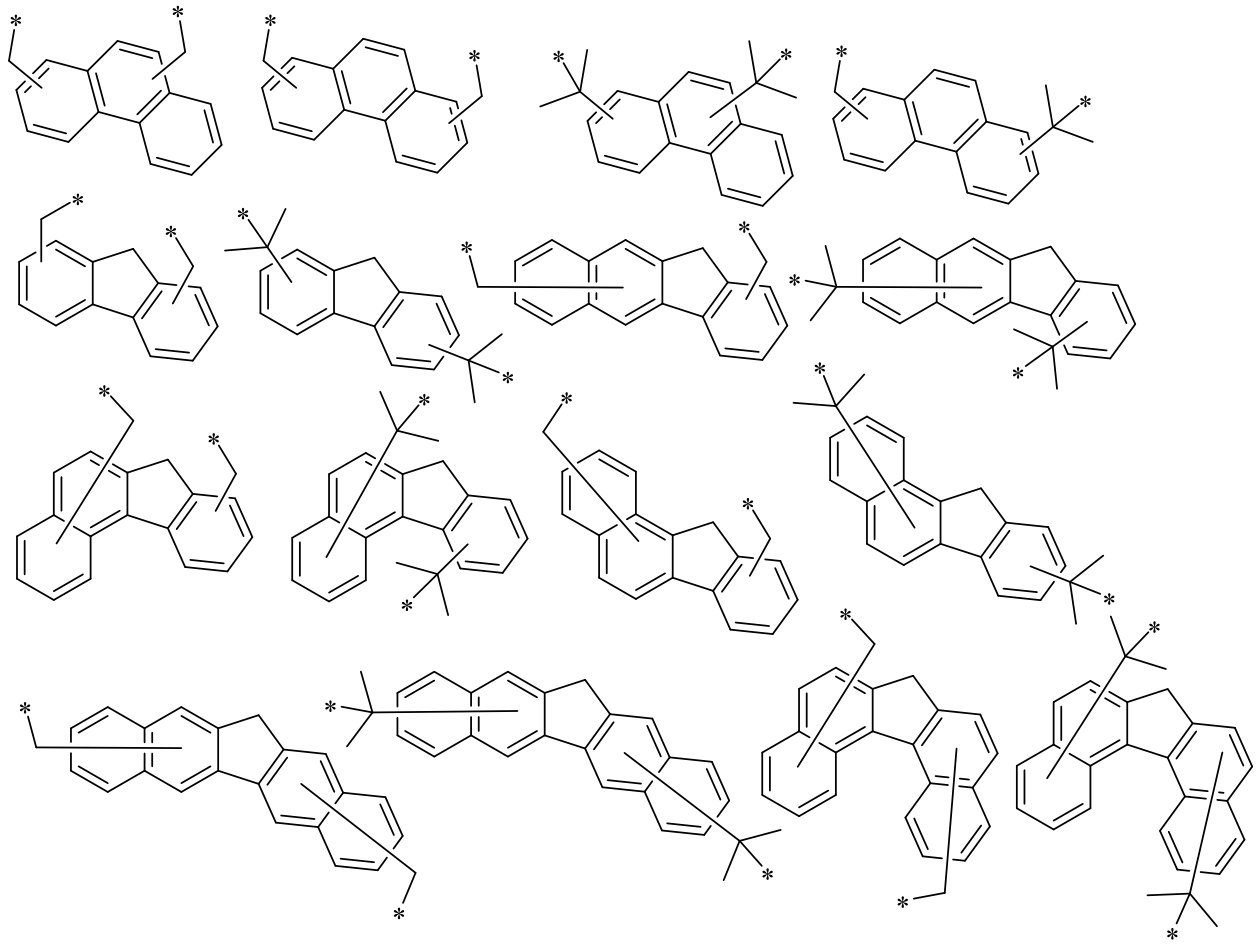
[Chem. 105]



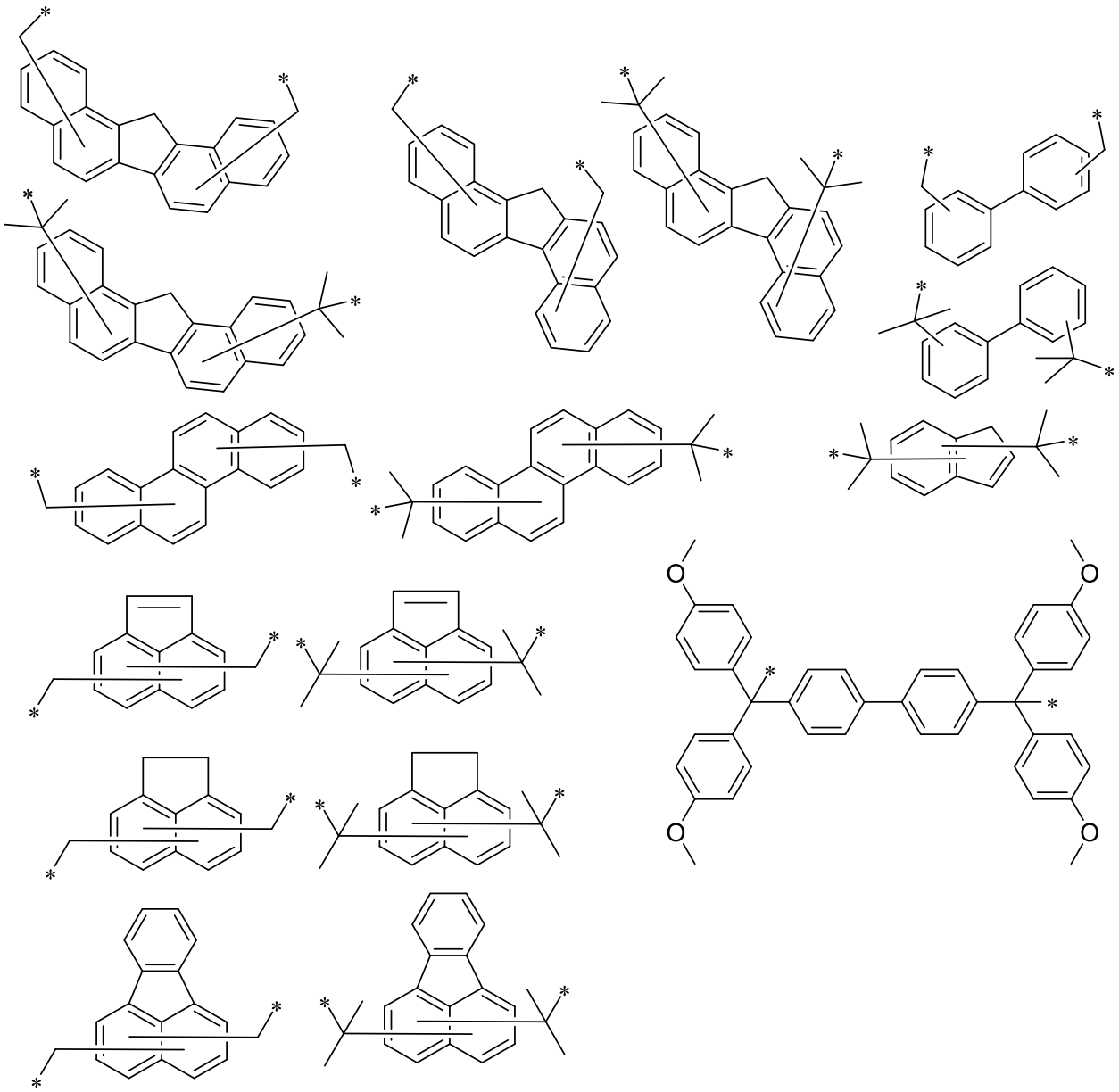
[Chem. 106]



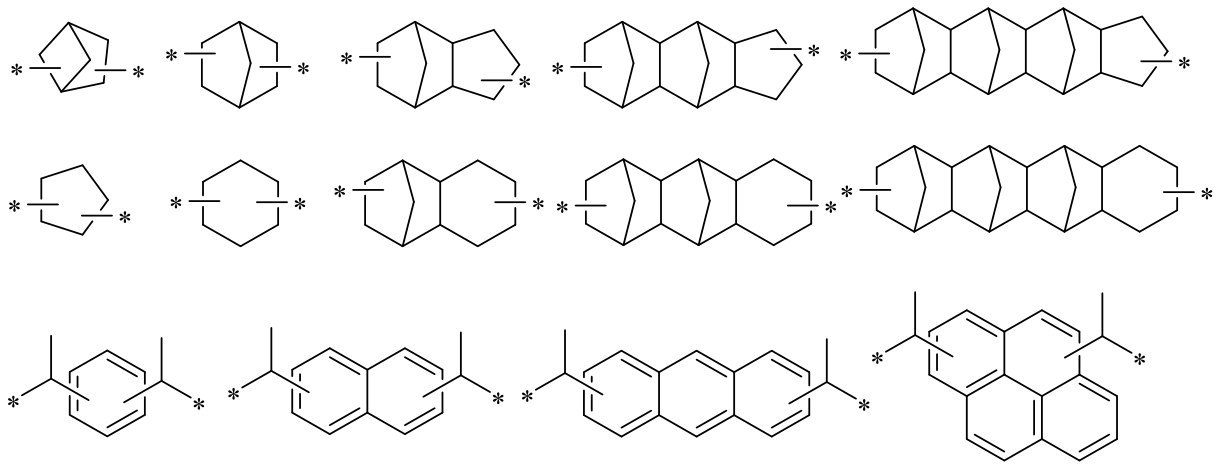
[Chem. 107]



[Chem. 108]



[Chem. 109]



[0164]

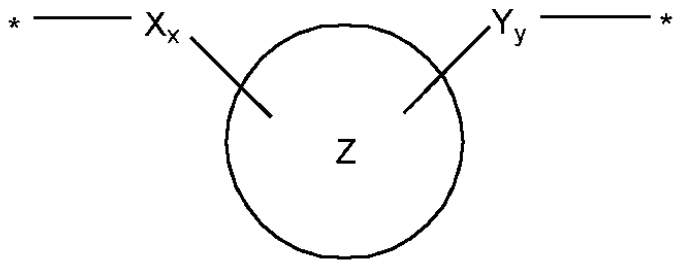
The unit structure (B-I) includes, for example, a structure represented by Formula (B3) below. The unit structure (B-I) may be a structure represented by Formula (B3) below.

The unit structure (B-I) including the structure represented by Formula (B3) is derived from, for example, a compound having a hydroxy group or an alkoxy group bonding to a secondary or tertiary carbon atom, a compound having a hydroxy group, an alkoxy group or a halo group bonding to an α-position carbon atom (such as a benzyl position carbon atom) of an alkylaryl group, or a compound having two carbon-carbon double bonds. These compounds are aldehyde equivalents.

[0165]

<<<B-5: Formula (B3)>>>

[Chem. 110]



(B3)

In Formula (B3), Z is a group having a monocyclic ring or a bicyclic, tricyclic, or tetracyclic condensed ring having 4 to 25 carbon atoms, which may have a substituent. The number of carbon atoms referred to herein means the number of carbon atoms constituting the ring skeleton of a monocyclic ring or a bicyclic, tricyclic, or tetracyclic condensed ring only, excluding a substituent, and does not include the number of heteroatoms constituting a heterocyclic ring when the monocyclic ring or the condensed ring is a heterocyclic ring.

[0166]

The monocyclic ring is a monocyclic ring (Hereinafter, it may be referred to as a “non-Huckel monocyclic ring”.) in which the number of π electrons does not satisfy 4n + 2 (n is an integer of 0 or more), and at least one of monocyclic rings constituting the bicyclic ring, the tricyclic ring, and the tetracyclic ring is a monocyclic ring in which the number of π electrons does not satisfy 4n + 2 (n is an integer of 0 or more), and the remaining monocyclic rings may be a monocyclic ring in which the

number of π electrons satisfies 4n + 2 (n is an integer of 0 or more) or a monocyclic ring in which the number of π electrons does not satisfy 4n + 2 (n is an integer of 0 or more).

[0167]

The monocyclic ring, or the bicyclic, tricyclic, or tetracyclic condensed ring may further form a condensed ring with one or more aromatic rings to form a pentacyclic or higher condensed ring; the number of carbon atoms of the pentacyclic or higher condensed ring is preferably 40 or less, and the number of carbon atoms referred to herein means the number of carbon atoms constituting the ring skeleton of the pentacyclic or higher condensed ring only, excluding substituents, and does not include the number of heteroatoms constituting a heterocyclic ring when the pentacyclic or higher condensed ring is a heterocyclic ring.

[0168]

X and Y are the same or different and each represent a $-CR^{31}R^{32}-$ group, and R^{31} and R^{32} are the same or different and each represent a hydrogen atom or a hydrocarbon group having 1 to 6 carbon atoms.

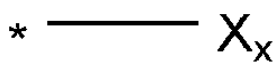
[0169]

x and y represent the number of X and the number of Y, respectively, and each independently represent 0 or 1.

[0170]

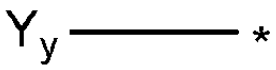
at least any one of

[Chem. 111]



in Formula (B3) and

[Chem. 112]

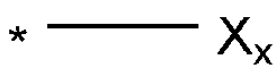


in Formula (B3) bonds to any carbon atom (referred to as "carbon atom Z") constituting the non-Hückel monocyclic ring of Z (when x = 1 and y = 1) or extends from the carbon atom Z (when x = 0 and y = 0).

[0171]

For example,

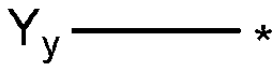
[Chem. 113]



in Formula (B3) bonds to any carbon atom (referred to as "carbon atom 1") constituting the non-Hückel monocyclic ring of Z (when x = 1) or extends from the carbon atom 1 (when x = 0), and

[0172]

[Chem. 114]



in Formula (B3) bonds to any carbon atom (referred to as "carbon atom 2") constituting the non-Hückel monocyclic ring of Z (when y = 1) or extends from the carbon atom 2 (when y = 0), the carbon atom 1 and the carbon atom 2 may be the same as or different from each other, and in the case of being different from each other, the carbon atom 1 and the carbon atom 2 may belong to the same non-Hückel monocyclic ring or to different non-Hückel monocyclic rings.

[0173]

In Formula (B3), optionally, a linked carbon atom other than carbon atom 1 and carbon atom 2 may be contained.

When Z is a tricyclic or more condensed ring, the permutation positional relationship in the condensed ring of one or two non-Hückel monocyclic rings to which carbon atoms 1 and 2 in Formula (B3) respectively belong and the remaining monocyclic rings is optional, and when carbon atoms 1 and carbon atoms 2 respectively belong to different non-Hückel monocyclic rings (referred to as "non-Hückel monocyclic ring 1" and "non-Hückel monocyclic ring 2", respectively), the permutation positional relationship in the condensed ring of the non-Hückel monocyclic ring 1 and the non-Hückel monocyclic ring 2 is also optional.

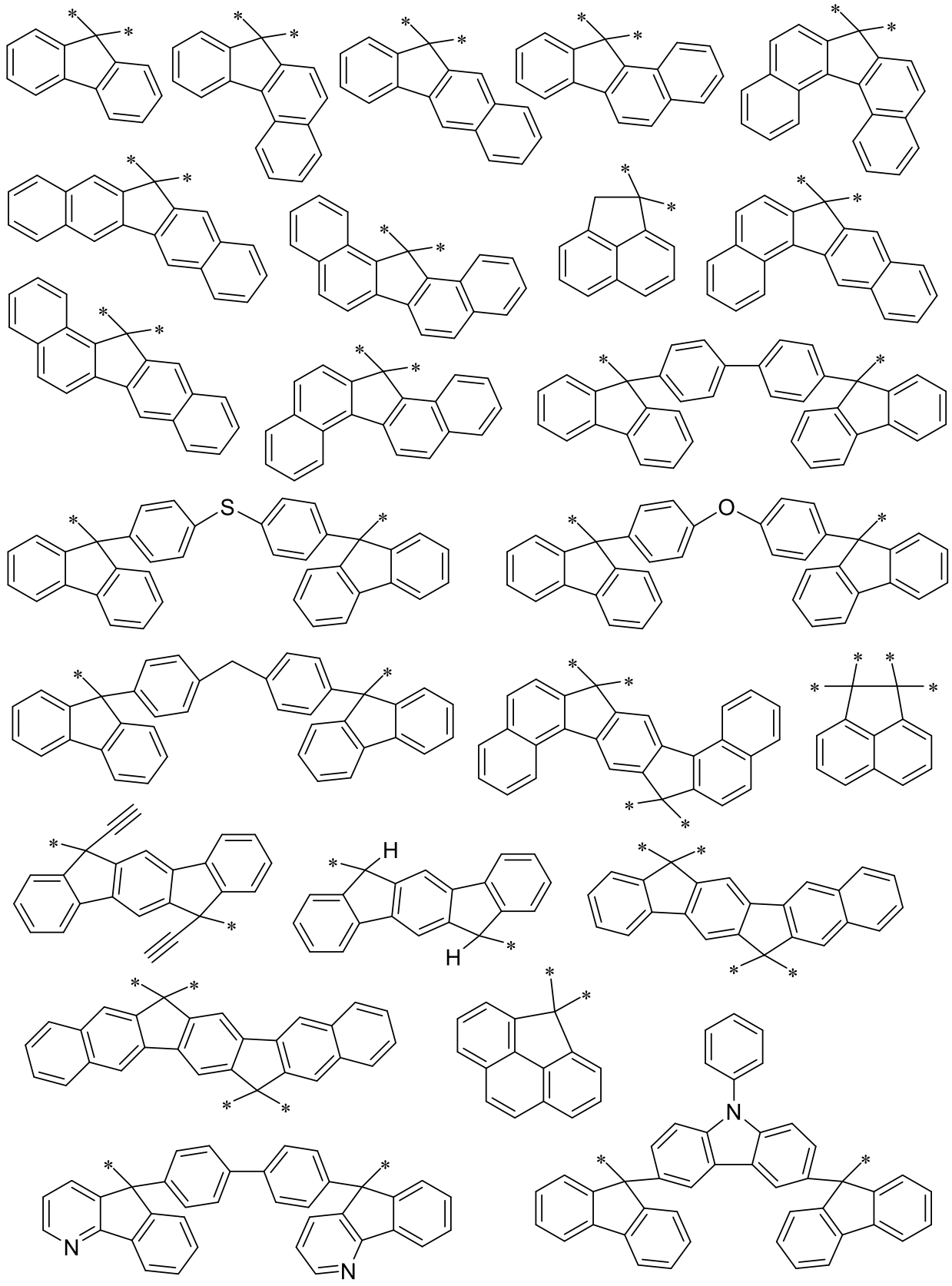
Specific examples of the organic group including the structure represented by Formula (B3) are as follows: The binding site with the unit structure (A) is not particularly limited. Needless to say, the structure may include the exemplary structure as a part of the whole.

[0174]

Although an example in which the number of bonding sites (*) exceeds 2 is also included, these surplus bonding sites can be used for bonding to an aromatic ring in another polymer chain, crosslinking, or the like, or may be bonding sites for hydrogen bonds.

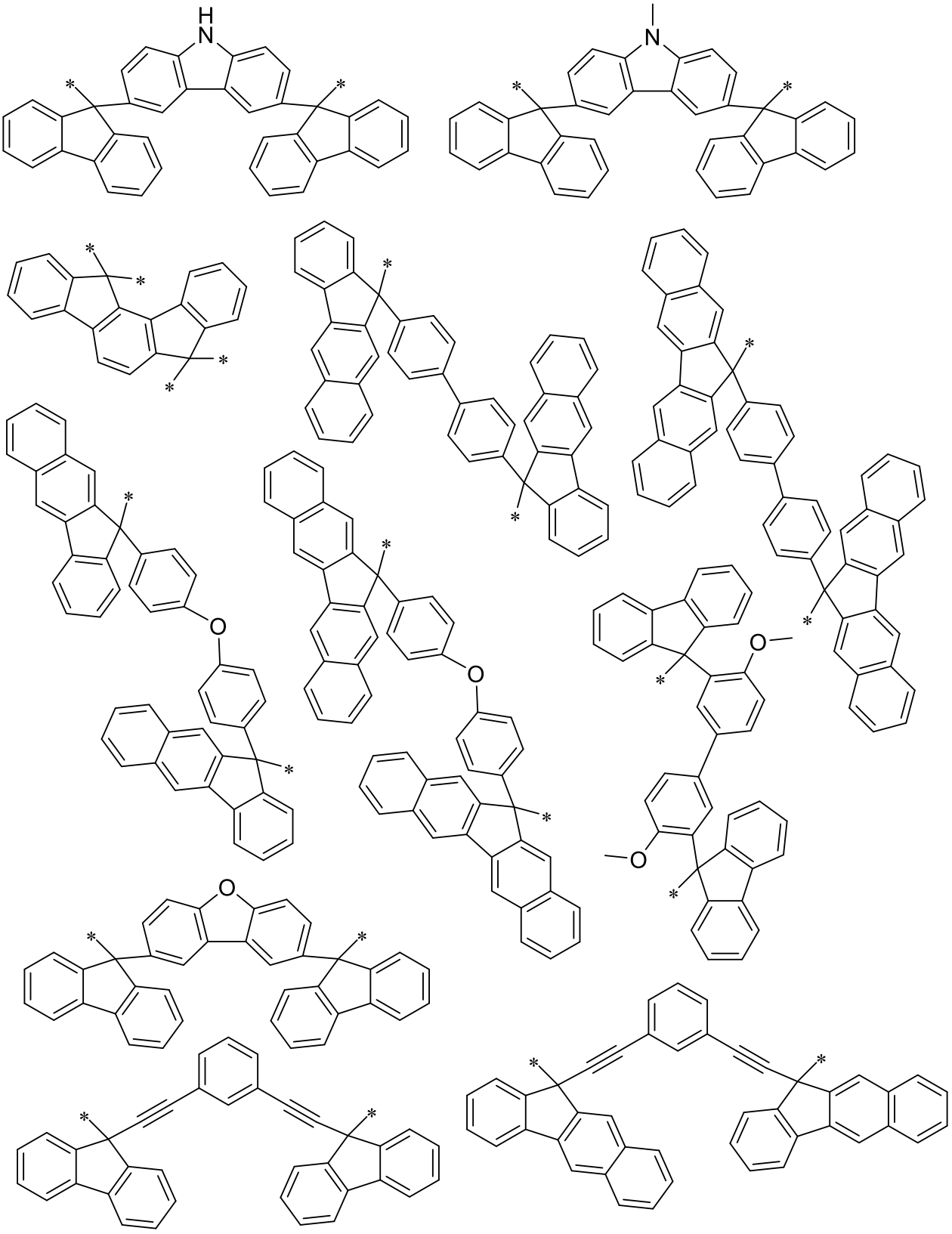
[0175]

[Chem. 115]



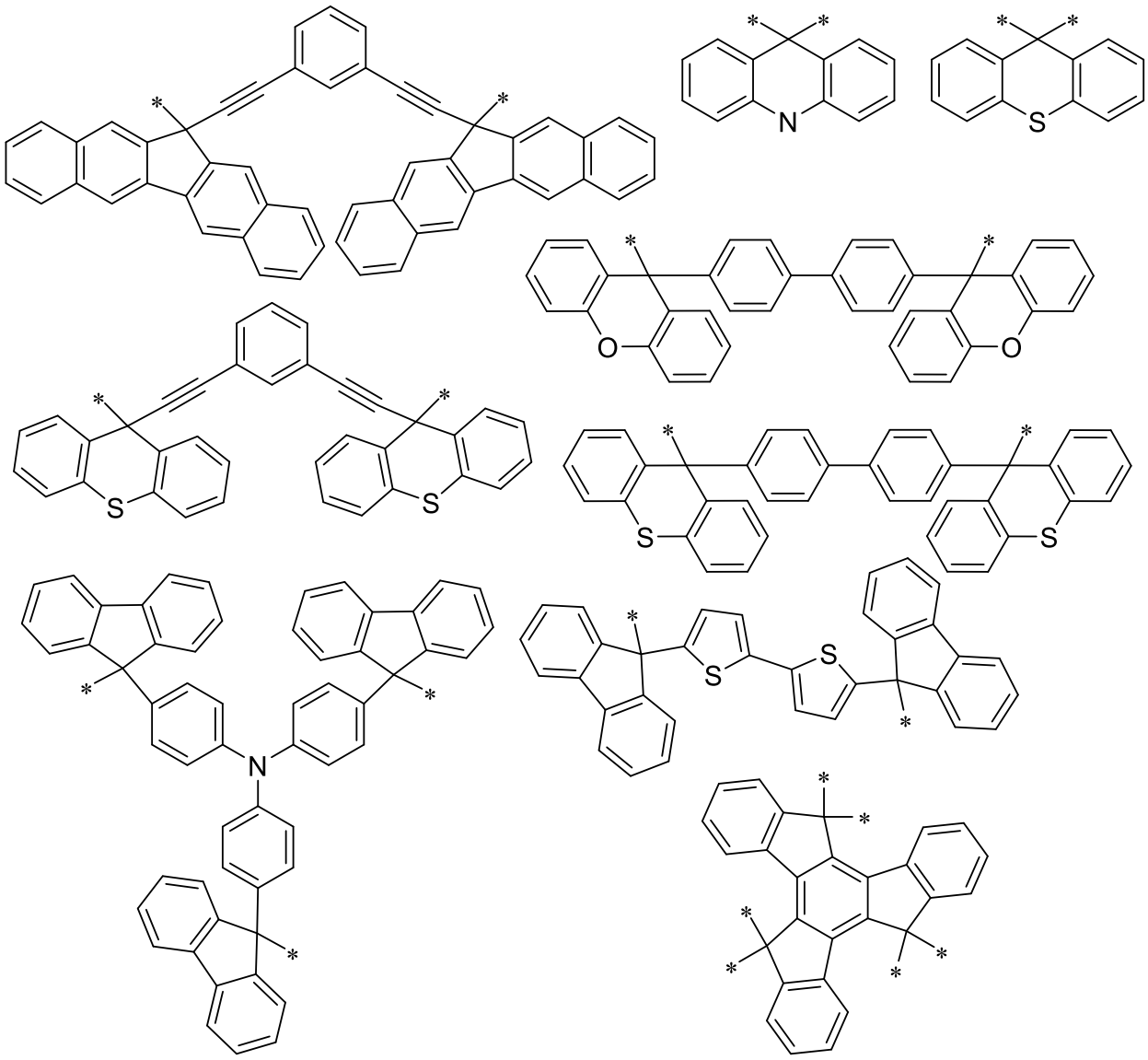
[0176]

[Chem. 116]



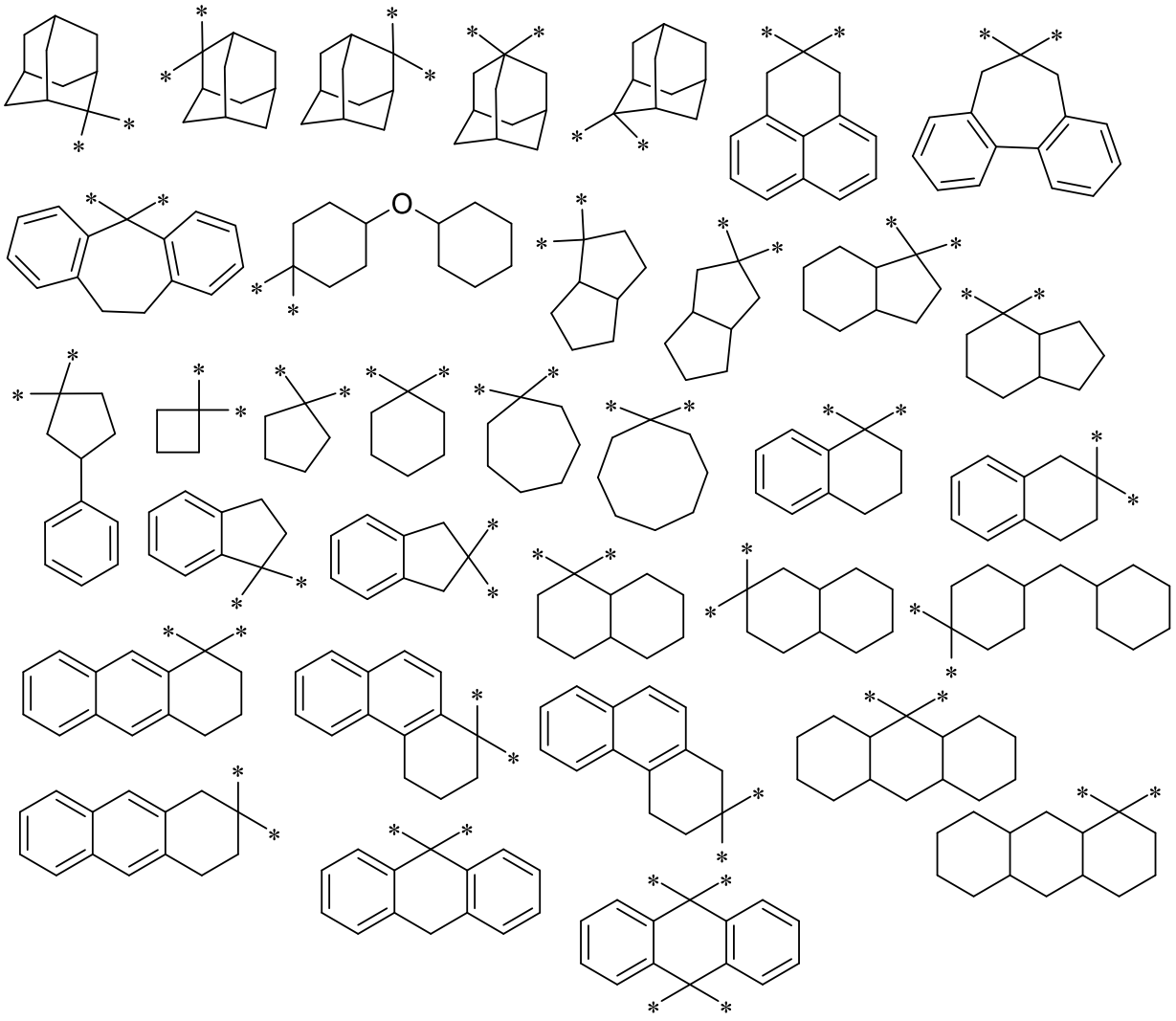
[0177]

[Chem. 117]



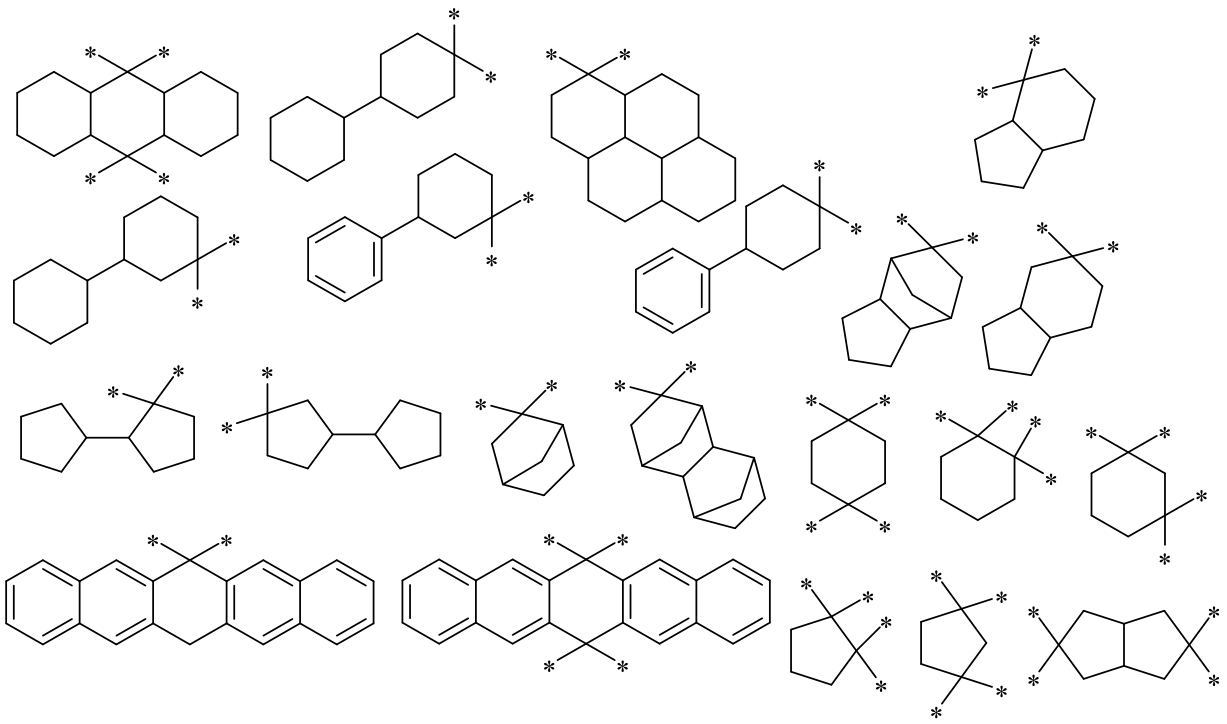
[0178]

[Chem. 118]



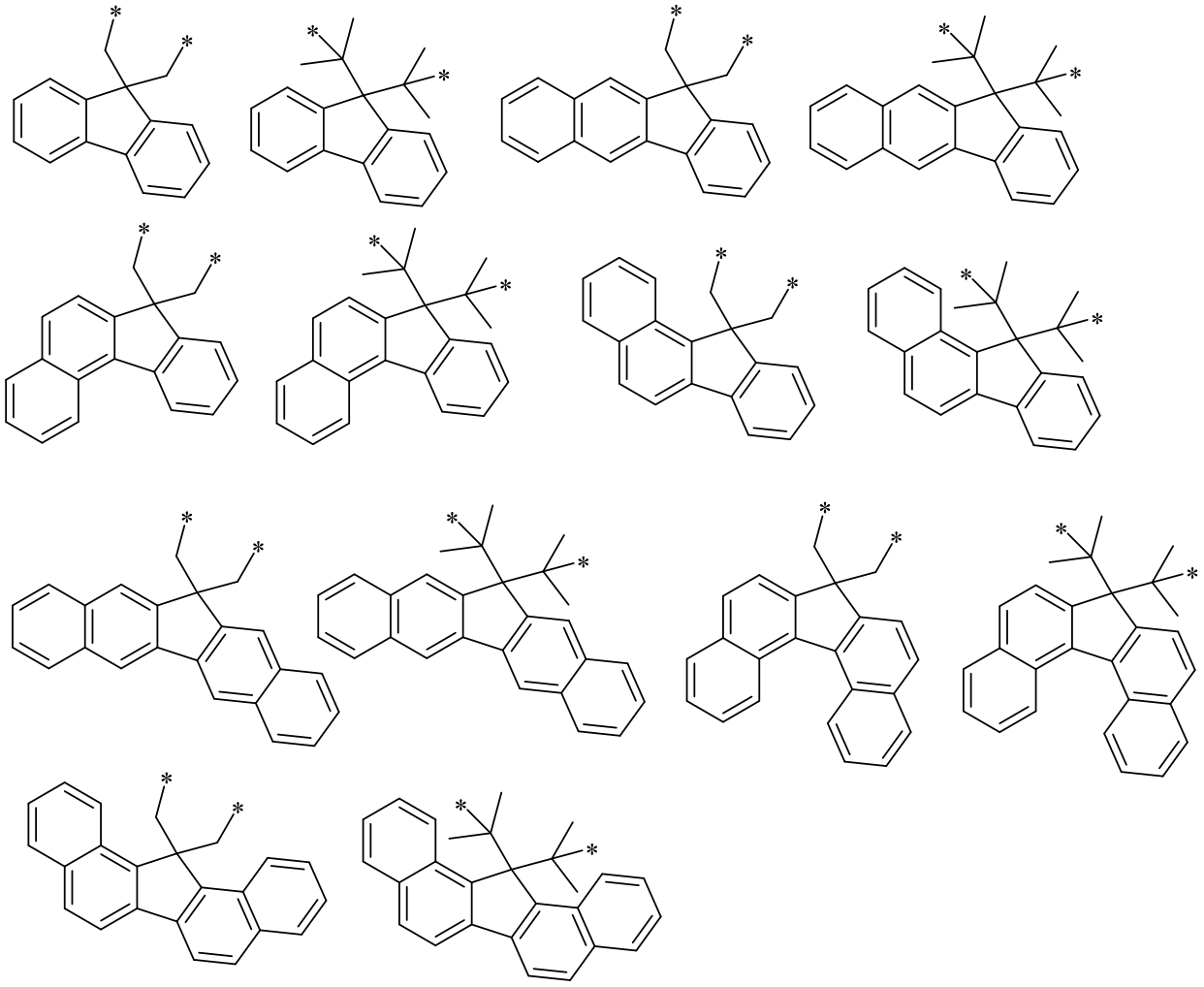
[0179]

[Chem. 119]



[0180]

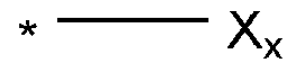
[Chem. 120]



[0181]

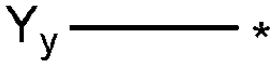
Hereinafter, a case where only one of

[Chem. 121]



in Formula (B3) and

[Chem. 122]



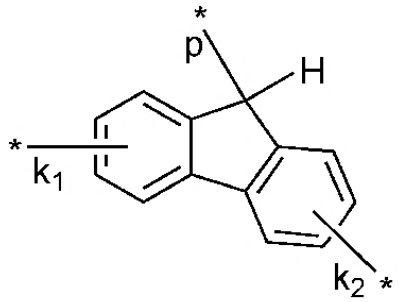
in Formula (B3) bonds to any carbon atom (referred to

as “carbon atom Z”) constituting the non-Hückel monocyclic ring of Z (when x = 1 and y = 1) or extends from the carbon atom Z (when x = 0 and y = 0) in Formula (B3) will be described.

As a more specific structure of Formula (B3) in this case, for example, in Formula (C31) below, among p, k_1, and k_2 that can form bonding sites, the unit structure (B-I) represented by Formula (B3) can be formed by p and k_1 or p and k_2. The remaining bonding sites bond to hydrogen atoms.

[0182]

[Chem. 123]

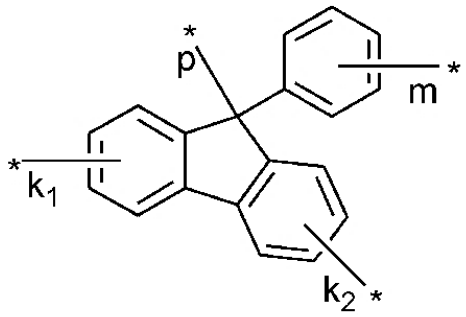


(C31)

In addition, in Formula (C32) below, among p, k_1, k_2, and m that can form bonding sites, the unit structure (B-I) represented by Formula (B3) can be formed by p and k_1, p and k_2, or p and m. The remaining bonding sites bond to hydrogen atoms.

[0183]

[Chem. 124]



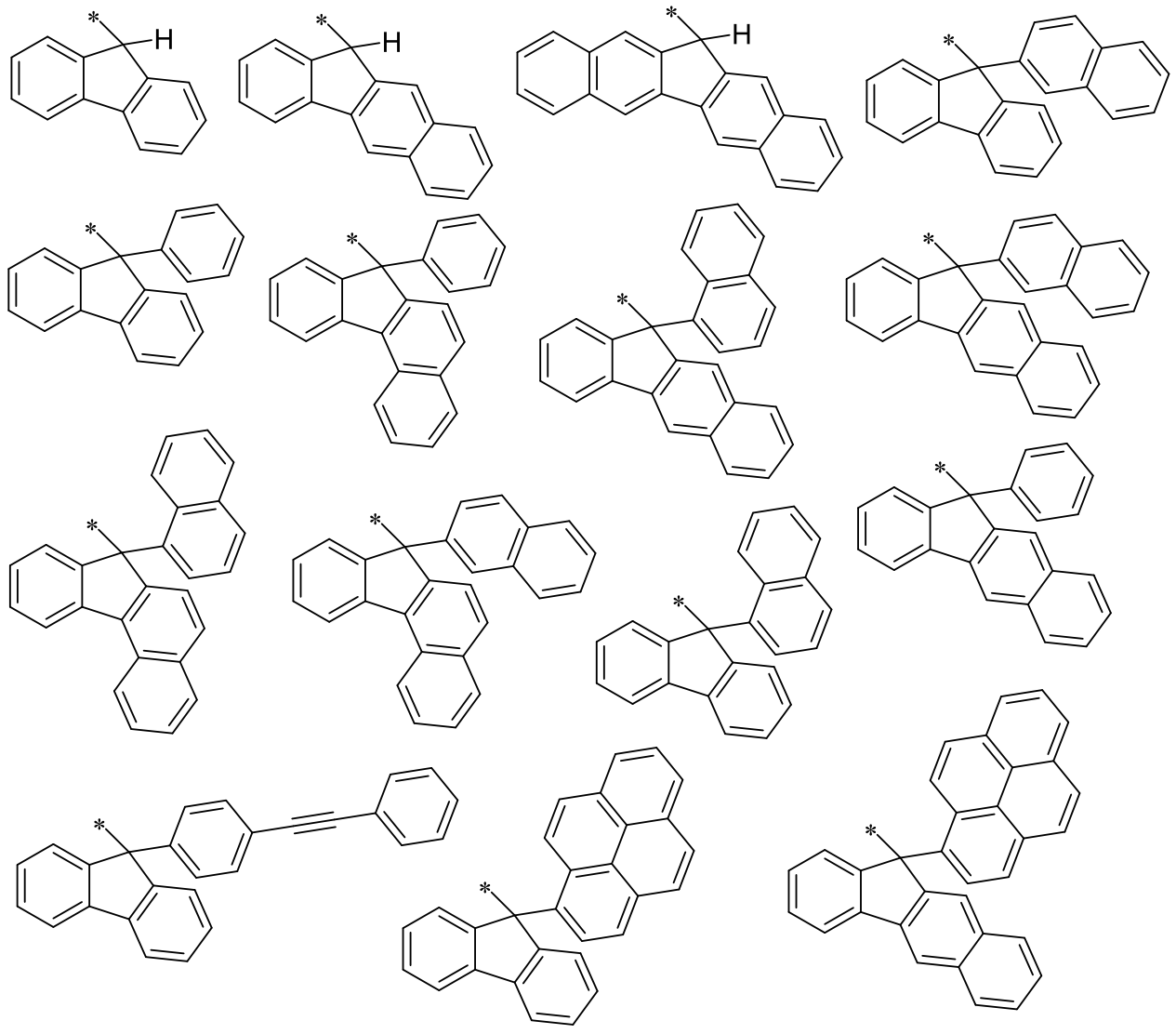
(C32)

More specific various examples of Formula (B3) corresponding to Formula (C31) or (C32) are as follows. * represents a binding site with the unit structure (A).

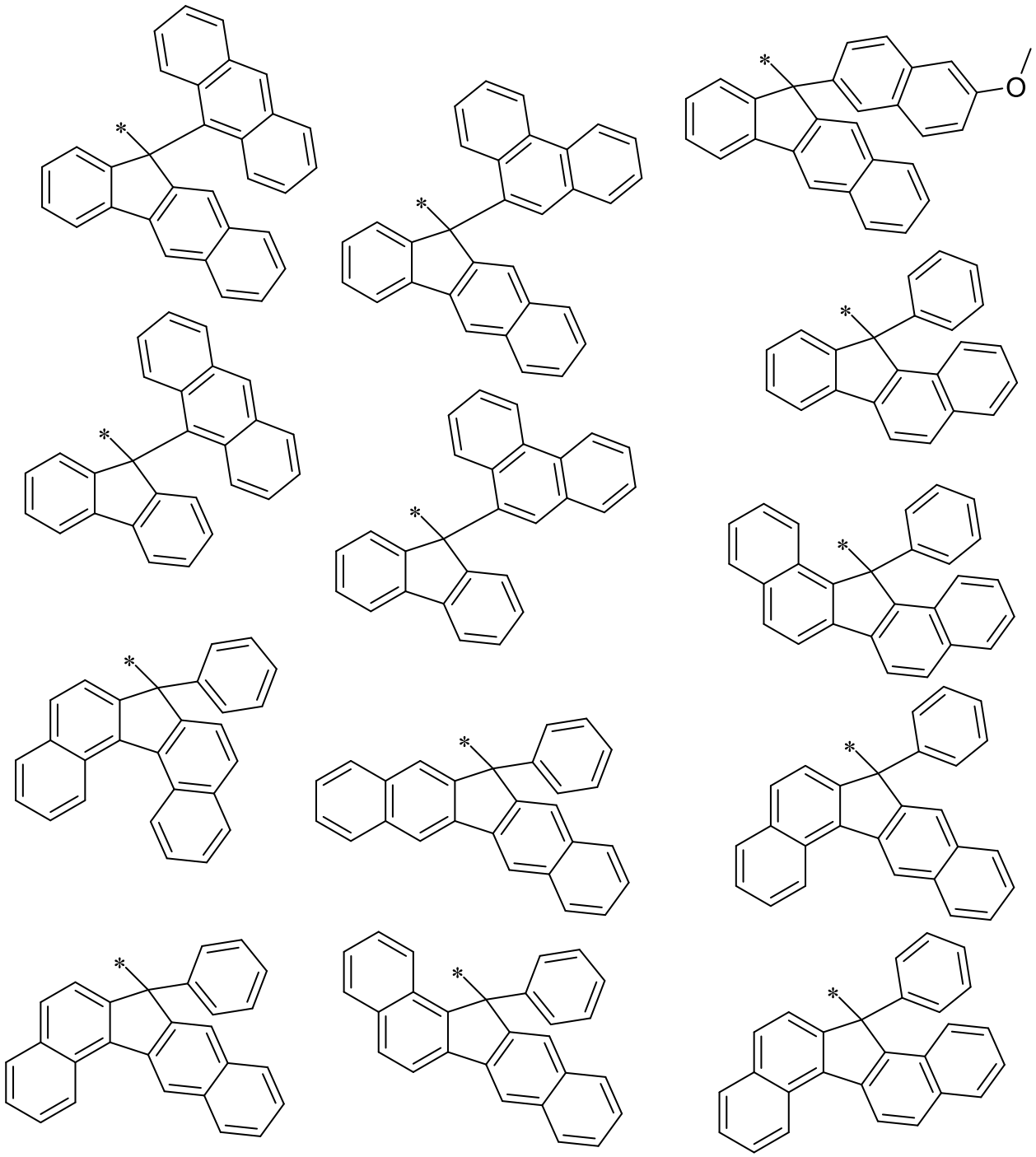
[0184]

In Formula (B3), a bond that bonds to another unit structure (for example, the unit structure (A)) separately extends from the aromatic ring in these structures, but such bonds are omitted in the following specific examples. Needless to say, the structure may be a unit structure including the exemplary structure as a part of the whole.

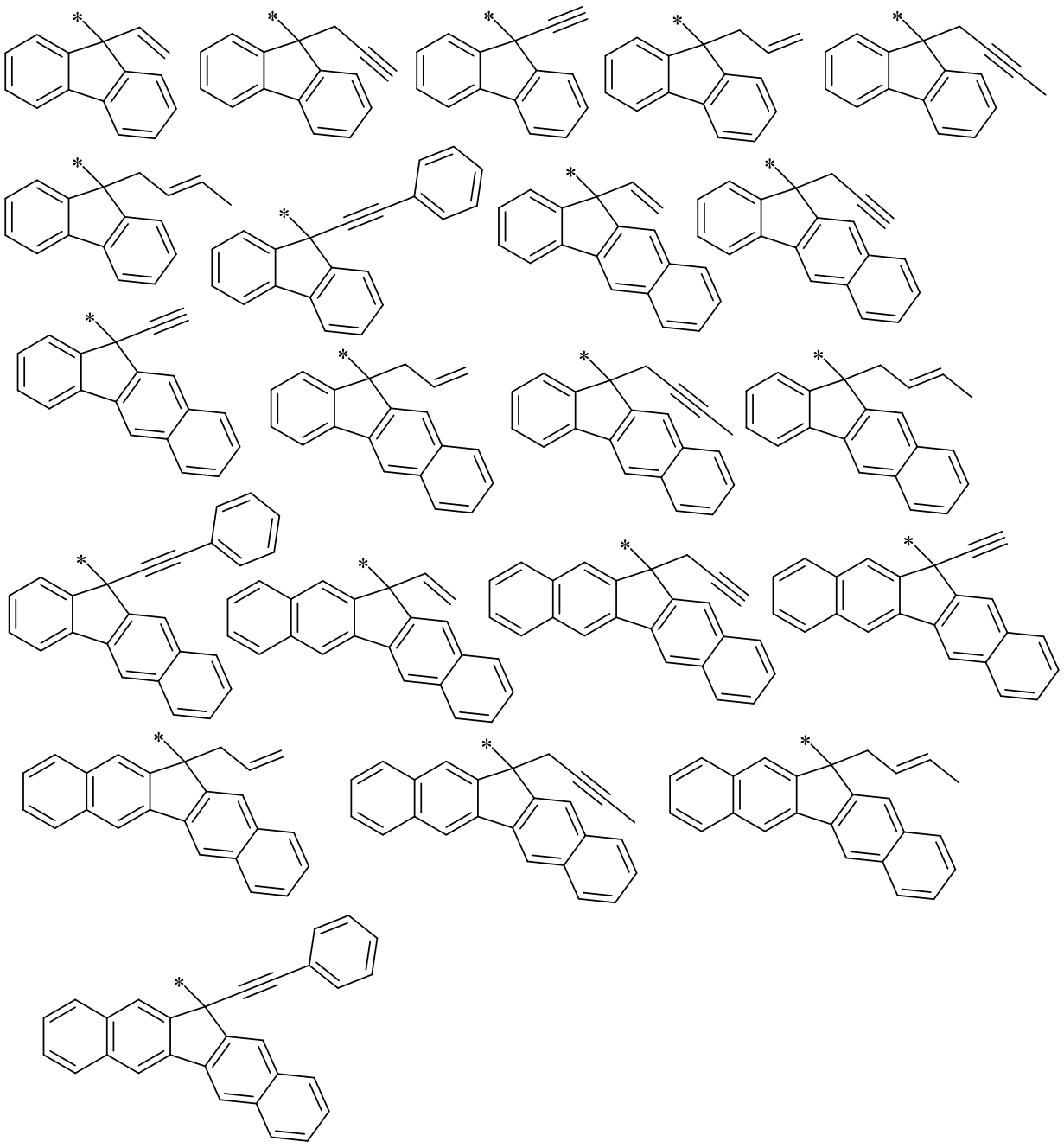
[Chem. 125]



[Chem. 126]



[Chem. 127]



In the above specific examples, when there is no bonding site from the aromatic ring, such a structure can be a specific example of a polymer terminal.

[0185]

The composite unit structure in the resin (G) may include a unit structure other than the unit structure (A)

and the unit structure (B).

However, the resin (G) does not contain a resin that is synthesized only from indole and 1-naphthaldehyde.

[0186]

The resin (G) is preferably a resin that is synthesized from a reaction raw material containing an amine compound and an aldehyde compound or an aldehyde equivalent.

Examples of the amine compound include compounds having a skeleton having an aromatic ring, and the skeleton is at least any one of an aromatic amine skeleton and a nitrogen-containing aromatic heterocyclic skeleton.

Examples of the aldehyde compound include a compound represented by Formula (B-1a) above.

Examples of the aldehyde equivalent include compounds represented by Formula (B-1b), Formula (B-2a), Formula (B-2b), Formula (B-2c), or Formula (B-2d) above.

[0187]

The novolac resin having the structure represented by Formula (AB) can be prepared by a known method. For example, it can be prepared by condensing a ring-containing compound represented by H-A-H with an oxygen-containing compound represented by OHC-B, O=C-B, RO-B-OR, RO-CH_2-B-CH_2-OR, or the like. Here, in the Formula, A and B have the same meaning as described above. R represents a hydrogen atom, halogen, or an alkyl group having about 1 to

3 carbon atoms.

[0188]

For both the ring-containing compound and the oxygen-containing compound, one type may be used alone, or two or more types may be used in combination. In this condensation reaction, the oxygen-containing compound can be used in a proportion of 0.1 to 10 mol, preferably 0.1 to 2 mol in 1 mol of the ring-containing compound.

[0189]

As the catalyst used in the condensation reaction, for example, mineral acids such as sulfuric acid, phosphoric acid, and perchloric acid, organic sulfonic acids such as p-toluenesulfonic acid, p-toluenesulfonic acid monohydrate, methanesulfonic acid, and trifluoromethanesulfonic acid, and carboxylic acids such as formic acid and oxalic acid can be used. The use amount of the catalyst varies depending on the type of the catalyst to be used, but is usually 0.001 to 10,000 parts by mass, preferably 0.01 to 1,000 parts by mass, and more preferably 0.05 to 100 parts by mass with respect to 100 parts by mass of the ring-containing compound (in the case of two or more types, the total thereof).

[0190]

The condensation reaction is also performed without a solvent, but is usually performed using a solvent. The

solvent is not particularly limited as long as it can dissolve the reactive substrate and does not inhibit the reaction. Examples thereof include 1,2-dimethoxyethane, diethylene glycol dimethyl ether, propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, tetrahydrofuran, tetrahydropyran, dioxane, 1,2-dichloromethane, 1,2-dichloroethane, toluene, N-methylpyrrolidone, and dimethylformamide. The condensation reaction temperature is usually 40°C to 200°C, and preferably 100°C to 180°C. The reaction time varies depending on the reaction temperature, but is usually 5 minutes to 50 hours, and preferably 5 minutes to 24 hours.

[0191]

The weight average molecular weight of the novolac resin according to an aspect of the present invention is usually 500 to 100,000, and preferably 600 to 50,000, 700 to 10,000, or 800 to 8,000.

[0192]

The content of the resin (G) in the coating agent composition is, for example, preferably 25 to 100 mass%, more preferably 50 to 100 mass%, and still more preferably 70 to 100 mass% with respect to the mass of the film-forming component.

Here, the film-forming component refers to a component obtained by removing a solvent component from the coating

agent composition.

[0193]

The molar ratio between the unit structure (A) and the unit structure (B) in the resin (G) is, for example, preferably 30:70 to 70:30, more preferably 30:70 to 50:50, still more preferably 40:60 to 50:50, and particularly preferably 50:55 to 50:50.

In addition, the molar ratio between the unit structure (A) and the unit structure (B) in the resin (G) can also be represented by the molar ratio between a compound (A) serving as a raw material of the unit structure (A) and a compound (B) serving as a raw material of the unit structure (B).

The molar ratio between the compound (A) and the compound (B) is, for example, preferably 30:70 to 70:30, more preferably 30:70 to 50:50, still more preferably 40:60 to 50:50, and particularly preferably 50:55 to 50:50. Here, the number of the types of the compounds (A) may be one or more. Similarly, the number of the types of the compounds (B) may be one or more.

[0194]

The content proportion (molar ratio) of the unit structure (A-I) in the unit structure (A) is preferably 10 mol% or more, more preferably 20 mol% or more, still more preferably 30 mol% or more, still more preferably 40 mol%

or more, still more preferably 50 mol% or more, still more preferably 60 mol% or more, still more preferably 70 mol% or more, still more preferably 80 mol% or more, and still more preferably 90 mol% or more, and may be 100 mol%.

In addition, the content proportion (molar ratio) of the unit structure (A-I) in the unit structure (A) can also be represented by the molar ratio of the compound (A-I) serving as a raw material of the unit structure (A-I) in the compound (A).

The molar ratio of the compound (A-I) in the compound (A) is preferably 10 mol% or more, more preferably 20 mol% or more, still more preferably 30 mol% or more, still more preferably 40 mol% or more, still more preferably 50 mol% or more, still more preferably 60 mol% or more, still more preferably 70 mol% or more, still more preferably 80 mol% or more, and still more preferably 90 mol% or more, and may be 100 mol%.

[0195]

The content proportion (molar ratio) of the unit structure (B-I) in the unit structure (B) is preferably 10 mol% or more, more preferably 20 mol% or more, still more preferably 30 mol% or more, still more preferably 40 mol% or more, still more preferably 50 mol% or more, still more preferably 60 mol% or more, still more preferably 70 mol% or more, still more preferably 80 mol% or more, and still

more preferably 90 mol% or more, and may be 100 mol%.

In addition, the content proportion (molar ratio) of the unit structure (B-I) in the unit structure (B) can also be represented by the molar ratio of the compound (B-I) serving as a raw material of the unit structure (B-I) in the compound (B).

The molar ratio of the compound (B-I) in the compound (B) is preferably 10 mol% or more, more preferably 20 mol% or more, still more preferably 30 mol% or more, still more preferably 40 mol% or more, still more preferably 50 mol% or more, still more preferably 60 mol% or more, still more preferably 70 mol% or more, still more preferably 80 mol% or more, and still more preferably 90 mol% or more, and may be 100 mol%.

[0196]

<Solvent>

The coating agent composition, which is an aspect of the present invention, contains a solvent.

[0197]

The solvent is not particularly limited as long as the solvent is capable of dissolving a specific novolac resin and other optional components added as necessary.

[0198]

Examples of the solvent include methyl cellosolve acetate, ethyl cellosolve acetate, propylene glycol,

propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol monopropyl ether, methyl isobutyl carbinol, propylene glycol monobutyl ether, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol monopropyl ether acetate, propylene glycol monobutyl ether acetate, toluene, xylene, methyl ethyl ketone, cyclopentanone, cyclohexanone, ethyl 2-hydroxypropionate, ethyl 2-hydroxy-2-methylpropionate, ethyl ethoxyacetate, ethyl hydroxyacetate, methyl 2-hydroxy-3-methylbutanoate, methyl 3-methoxypropionate, ethyl 3-methoxypropionate, ethyl 3-ethoxypropionate, methyl 3-ethoxypropionate, methyl pyruvate, ethyl pyruvate, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, ethylene glycol monopropyl ether acetate, ethylene glycol monobutyl ether acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol dipropyl ether, diethylene glycol dibutyl ether, propylene glycol monomethyl ether, propylene glycol dimethyl ether, propylene glycol diethyl ether, propylene glycol dipropyl ether, propylene glycol dibutyl ether, ethyl lactate, propyl lactate, isopropyl lactate,

butyl lactate, isobutyl lactate, methyl formate, ethyl formate, propyl formate, isopropyl formate, butyl formate, isobutyl formate, amyl formate, isoamyl formate, methyl acetate, ethyl acetate, amyl acetate, isoamyl acetate, hexyl acetate, methyl propionate, ethyl propionate, propyl propionate, isopropyl propionate, butyl propionate, isobutyl propionate, methyl butyrate, ethyl butyrate, propyl butyrate, isopropyl butyrate, butyl butyrate, isobutyl butyrate, ethyl hydroxyacetate, methyl 2-hydroxy-2-methylpropionate, ethyl 2-hydroxy-2-methylpropionate, methyl 3-methoxy-2-methylpropionate, methyl 2-hydroxy-3-methylbutyrate, ethyl methoxyacetate, ethyl ethoxyacetate, methyl 3-methoxypropionate, ethyl 3-ethoxypropionate, ethyl 3-methoxypropionate, 3-methoxybutyl acetate, 3-methoxypropyl acetate, 3-methyl-3-methoxybutyl acetate, 3-methyl-3-methoxybutyl propionate, 3-methyl-3-methoxybutyl butyrate, methyl acetoacetate, toluene, xylene, methyl ethyl ketone, methyl propyl ketone, methyl butyl ketone, 2-heptanone, 3-heptanone, 4-heptanone, cyclohexanone, N,N-dimethylformamide, N-methylacetamide, N,N-dimethylacetamide, N-methylpyrrolidone, 4-methyl-2-pentanol, and γ-butyrolactone. These solvents can be used alone or two or more types thereof can be used in combination.

[0199]

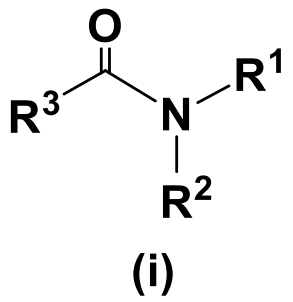
In addition, a solvent having a boiling point of 160°C or higher can be included in combination with a solvent having a boiling point of less than 160°C.

[0200]

As such a high boiling point solvent, for example, the following compounds described in WO 2018/131562 A1 can be preferably used.

[0201]

[Chem. 128]



(i)

[R^1, R^2 and R^3 in Formula (i) each represent an alkyl group having 1 to 20 carbon atoms which may be interrupted by a hydrogen atom, an oxygen atom, a sulfur atom, or an amide bond, may be the same or different, and may bond to each other to form a ring structure.]

Alternatively, 1,6-diacetoxyhexane (boiling point: 260°C), tripropylene glycol monomethyl ether (boiling point: 242°C) described in JP 2021-84974 A, and various other high boiling point solvents described in paragraph 0082 of the above-mentioned publication can be preferably used.

[0202]

Alternatively, dipropylene glycol monomethyl ether acetate (boiling point: 213°C), diethylene glycol monoethyl ether acetate (boiling point: 217°C), diethylene glycol monobutyl ether acetate (boiling point: 247°C), dipropylene glycol dimethyl ether (boiling point: 171°C), dipropylene glycol monomethyl ether (boiling point: 187°C), dipropylene glycol monobutyl ether (boiling point: 231°C), tripropylene glycol monomethyl ether (boiling point: 242°C), γ-butyrolactone (boiling point: 204°C), benzyl alcohol (boiling point: 205°C), propylene carbonate (boiling point: 242°C), tetraethylene glycol dimethyl ether (boiling point: 275°C), 1,6-diacetoxyhexane (boiling point: 260°C), dipropylene glycol (boiling point: 230°C), and 1,3-butylene glycol diacetate (boiling point: 232°C) described in JP 2019-20701 A, and various other high boiling point solvents described in paragraphs 0023 to 0031 of the publication can be preferably used.

[0203]

The coating agent composition, which is an aspect of the present invention, may contain an acid and/or a salt thereof and/or an acid generator.

[0204]

Examples of the acid include p-toluenesulfonic acid, trifluoromethanesulfonic acid, salicylic acid, 5-

sulfosalicylic acid, 4-phenolsulfonic acid, camphorsulfonic acid, 4-chlorobenzenesulfonic acid, benzenedisulfonic acid, 1-naphthalenesulfonic acid, citric acid, benzoic acid, hydroxybenzoic acid, and naphthalenecarboxylic acid.

[0205]

As the salt, a salt of the above-described acid can also be used. The salt is not limited, but an ammonia derivative salt such as a trimethylamine salt or a triethylamine salt, a pyridine derivative salt, a morpholine derivative salt, or the like can be suitably used.

[0206]

Only one type of the acid and/or the salt thereof can be used, or two or more types thereof can be used in combination. The blending amount is usually 0.0001 to 20 mass%, preferably 0.0005 to 10 mass%, and more preferably 0.01 to 5 mass% with respect to the total solid content.

[0207]

Examples of the acid generator include a thermal acid generator and a photoacid generator.

[0208]

Examples of the thermal acid generator include 2,4,4,6-tetrabromocyclohexadienone, benzoin tosylate, 2-nitrobenzyl tosylate, K-PURE [registered trademark] CXC-1612, CXC-1614, TAG-2172, TAG-2179, TAG-2678, TAG2689, and TAG2700

(manufactured by King Industries), and SI-45, SI-60, SI-80, SI-100, SI-110, and SI-150 (manufactured by Sanshin Chemical Industry Co., Ltd.), and other organic sulfonic acid alkyl esters.

[0209]

The photoacid generator generates an acid during exposure of the resist. Therefore, the acidity of the underlayer film can be adjusted. This is one method for matching the acidity of the underlayer film to the acidity of the upper layer resist. In addition, the pattern shape of the resist formed on the upper layer can be adjusted by adjusting the acidity of the underlayer film.

[0210]

Examples of the photoacid generator contained in the coating agent composition of the present invention include an onium salt compound, a sulfonimide compound, and a disulfonyl diazomethane compound.

[0211]

Examples of the onium salt compounds include iodonium salt compounds such as diphenyliodonium hexafluorophosphate, diphenyliodonium trifluoromethanesulfonate, diphenyliodonium nonafluoronormalbutanesulfonate, diphenyliodonium perfluoronormaloctanesulfonate, diphenyliodonium camphorsulfonate, bis(4-tert-butylphenyl)iodonium

camphorsulfonate, and bis(4-tert-butylphenyl)iodonium trifluoromethanesulfonate, sulfonium salt compounds such as triphenylsulfonium hexafluoroantimonate, triphenylsulfonium nonafluoronormalbutanesulfonate, triphenylsulfonium camphorsulfonate, and triphenylsulfonium trifluoromethanesulfonate, and the like.

[0212]

Examples of the sulfonimide compound include N-(trifluoromethanesulfonyloxy)succinimide, N-(nonafluoro-normal-butanesulfonyloxy)succinimide, N-(camphorsulfonyloxy)succinimide, and N-(trifluoromethanesulfonyloxy)naphthalimide.

[0213]

Examples of the disulfonyldiazomethane compounds include bis(trifluoromethylsulfonyl)diazomethane, bis(cyclohexylsulfonyl)diazomethane, bis(phenylsulfonyl)diazomethane, bis(p-toluenesulfonyl)diazomethane, bis(2,4-dimethylbenzenesulfonyl)diazomethane, and methylsulfonyl-p-toluenesulfonyl diazomethane.

[0214]

As the acid generator, only one type can be used, or two or more types can be used in combination.

[0215]

When the acid generator is used, the proportion thereof

is 0.01 to 10 parts by mass, 0.1 to 8 parts by mass, or 0.5 to 5 parts by mass with respect to 100 parts by mass of the solid content of the coating agent composition.

[0216]

The coating agent composition, which is an aspect of the present invention, may contain a crosslinking agent, a surfactant, a light absorbing agent, a rheology modifier, an adhesion aid, and the like, if necessary, in addition to the above-described components.

[0217]

Examples of the representative crosslinking agent include an aminoplast crosslinking agent and a phenoplast crosslinking agent.

[0218]

As the crosslinking agent, a crosslinking agent having high heat resistance can be used. As the crosslinking agent having high heat resistance, a compound containing a crosslink-forming substituent having an aromatic ring (e.g. a benzene ring or a naphthalene ring) in the molecule can be preferably used.

[0219]

Examples of the aminoplast crosslinking agent include highly alkylated, alkoxylated, or alkoxyalkylated melamine, benzoguanamine, glycoluril, urea, polymers thereof, and the like. Preferably, the crosslinking agent is a crosslinking

agent having at least two crosslink-forming substituents, and is a compound such as methoxymethylated glycoluril, butoxymethylated glycoluril, methoxymethylated melamine, butoxymethylated melamine, methoxymethylated benzoguanamine, butoxymethylated benzoguanamine, methoxymethylated urea, butoxymethylated urea, methoxymethylated thiourea, or methoxymethylated thiourea. In addition, condensates of these compounds can also be used.

[0220]

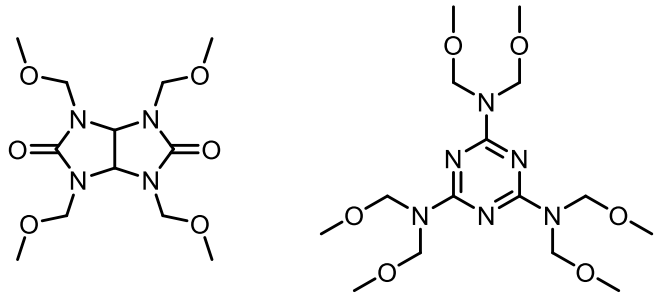
It is preferably at least one selected from the group consisting of tetramethoxymethylglycoluril and hexamethoxymethylmelamine.

[0221]

Specific examples are as follows.

[0222]

[Chem. 129]



[0223]

Examples of the phenoplast crosslinking agent include highly alkylated, alkoxylated, or alkoxyalkylated

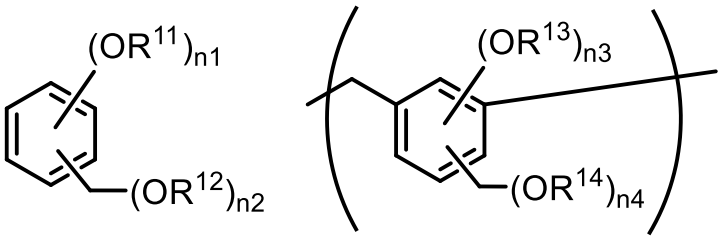
aromatics, polymers thereof, and the like. Preferably, the crosslinking agent is a compound having at least two crosslink-forming substituents in one molecule, such as 2,6-dihydroxymethyl-4-methylphenol, 2,4-dihydroxymethyl-6-methylphenol, bis(2-hydroxy-3-hydroxymethyl-5-methylphenyl)methane, bis(4-hydroxy-3-hydroxymethyl-5-methylphenyl)methane, 2,2-bis(4-hydroxy-3,5-dihydroxymethylphenyl)propane, bis(3-formyl-4-hydroxyphenyl)methane, bis(4-hydroxy-2,5-dimethylphenyl)formylmethane, or α,α-bis(4-hydroxy-2,5-dimethylphenyl)-4-formyltoluene. In addition, condensates of these compounds can also be used.

[0224]

In addition to the above-mentioned compounds, examples of such a compound include a compound having a partial structure of the following Formula (4), and a polymer or oligomer having a repeating unit of the following Formula (5).

[0225]

[Chem. 130]



(4) (5)

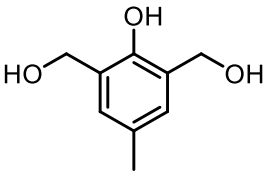
The R^{11}, R^{12}, R^{13}, and R^{14} each represent a hydrogen atom or an alkyl group having 1 to 10 carbon atoms, and the above-described examples can be used for these alkyl groups. n1 represents an integer of 1 to 4, n2 represents an integer of 1 to (5 - n1), and (n1 + n2) represents an integer of 2 to 5. n3 represents an integer of 1 to 4, n4 represents an integer of 0 to (4 - n3), and (n3 + n4) represents an integer of 1 to 4. The oligomer and polymer can be used when the number of repeating unit structures is 2 to 100 or 2 to 50.

[0226]

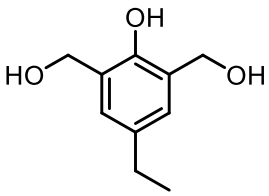
Specific examples are as follows.

[0227]

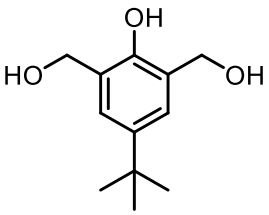
[Chem. 131]



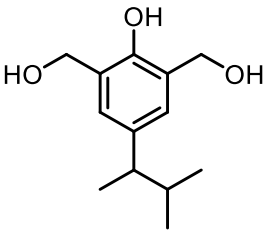
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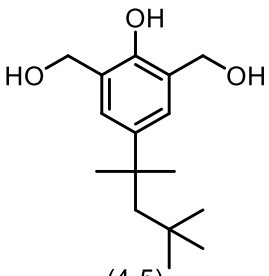
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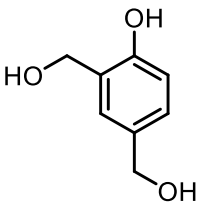
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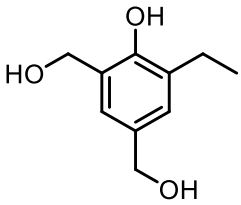
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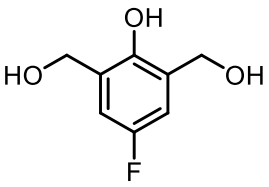
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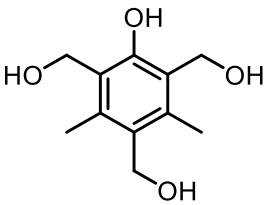
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(4-7)



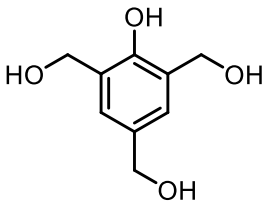
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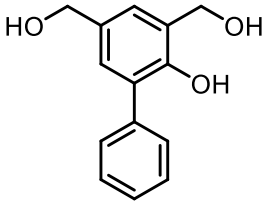
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[0228]

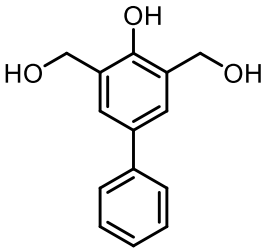
[Chem. 132]



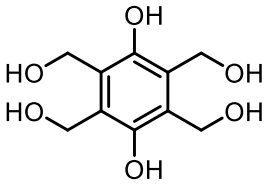
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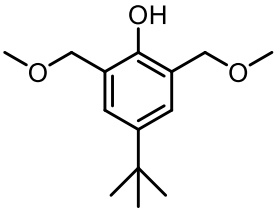
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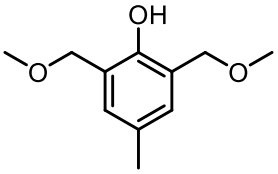
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(4-13)



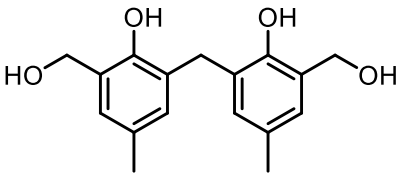
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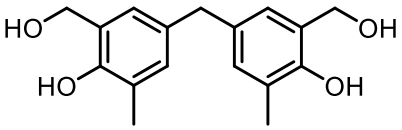
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[0229]

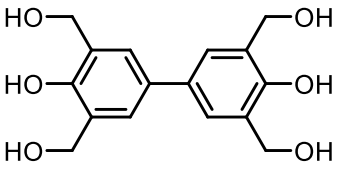
[Chem. 133]



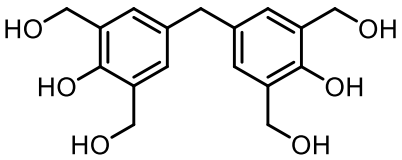
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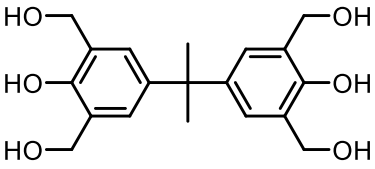
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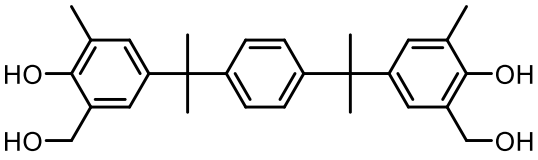
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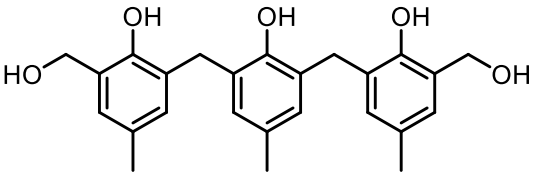
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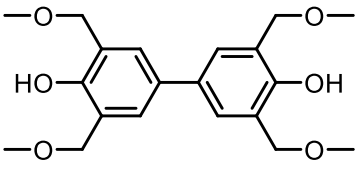
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(4-21)



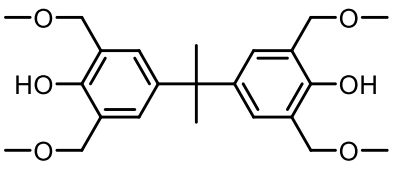
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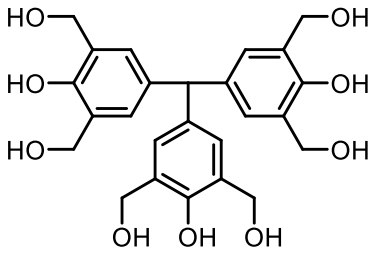
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[0230]

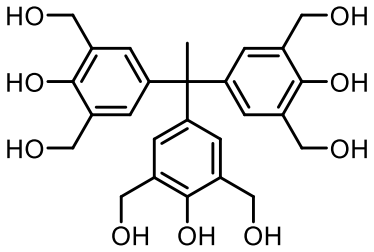
[Chem. 134]



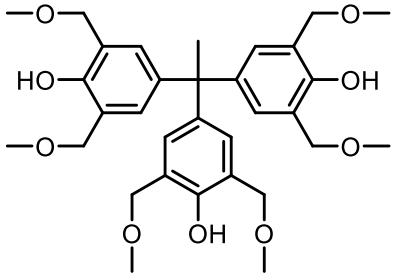
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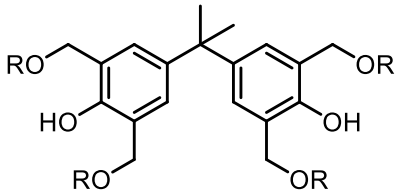
(4-25)



(4-26)



(4-27)



R : -H or -CH(CH$_3$)CH$_2$OCH$_3$

(4-28)

[0231]

Any one of the crosslinking agents such as an aminoplast crosslinking agent and a phenoplast crosslinking agent may be used alone, or two or more thereof may be used in combination. The aminoplast crosslinking agent can be produced by a method known per se or a method similar thereto, and a commercially available product may be used.

[0232]

In addition, the amount of the crosslinking agent such as an aminoplast crosslinking agent or a phenoplast

crosslinking agent to be used varies depending on the coating solvent to be used, the base substrate to be used, the required solution viscosity, the required film shape, and the like, but is 0.001 mass% or more, 0.01 mass% or more, 0.05 mass% or more, 0.5 mass% or more, or 1.0 mass% or more, and 80 mass% or less, 50 mass% or less, 40 mass% or less, 20 mass% or less, or 10 mass% or less with respect to the total solid content of the coating agent composition according to the present invention.

[0233]

In the coating agent composition according to the present invention, a surfactant can be blended in order to further improve the coatability for surface unevenness without generating pinholes, striations, and the like.

[0234]

Examples of the surfactant include nonionic surfactants such as polyoxyethylene alkyl ethers (for example, polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, polyoxyethylene cetyl ether, and polyoxyethylene oleyl ether), polyoxyethylene alkyl aryl ethers (for example, polyoxyethylene octylphenol ether and polyoxyethylene nonylphenol ether), polyoxyethylene/polyoxypropylene block copolymers, sorbitan fatty acid esters (for example, sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, sorbitan

monooleate, sorbitan trioleate, and sorbitan tristearate), and polyoxyethylene sorbitan fatty acid esters such as polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, polyoxyethylene sorbitan monostearate, polyoxyethylene sorbitan trioleate, and polyoxyethylene sorbitan tristearate;

fluorine surfactants such as EFTOP EF301, EF303, and EF352 (manufactured by Tokem Products Co., Ltd., trade name), MEGAFACE F171, F173, R-30, and R-40 (manufactured by DIC Corporation, trade name), FLUORAD FC430 and FC431 (manufactured by Sumitomo 3M Ltd., trade name), ASAHIGUARD AG710, SURFLON S-382, SC101, SC102, SC103, SC104, SC105, and SC106 (manufactured by AGC Inc., trade name); and

organosiloxane polymer KP341 (manufactured by Shin-Etsu Chemical Co., Ltd.).

[0235]

The blending amount of such a surfactant is usually 2.0 mass% or less, and preferably 1.0 mass% or less with respect to the total solid content of the coating agent composition according to the present invention. These surfactants may be added alone, or two or more types thereof can also be added in combination.

[0236]

As the light absorbing agent, commercially available light absorbing agents described in "Technique and Market

of Industrial Pigments" (CMC Publishing Co., Ltd.) or "Dye Handbook" (edited by The Society of Synthetic Organic Chemistry, Japan), such as C.I. Disperse Yellow 1, 3, 4, 5, 7, 8, 13, 23, 31, 49, 50, 51, 54, 60, 64, 66, 68, 79, 82, 88, 90, 93, 102, 114, and 124; C.I. Disperse Orange 1, 5, 13, 25, 29, 30, 31, 44, 57, 72, and 73; C.I. Disperse Red 1, 5, 7, 13, 17, 19, 43, 50, 54, 58, 65, 72, 73, 88, 117, 137, 143, 199, and 210; C.I. Disperse Violet 43; C.I. Disperse Blue 96; C.I. Fluorescent Brightening Agent 112, 135, and 163; C.I. Solvent Orange 2 and 45; C.I. Solvent Red 1, 3, 8, 23, 24, 25, 27, and 49; C.I. Pigment Green 10; and C.I. Pigment Brown 2, can be suitably used. The light absorbing agent is usually blended in a proportion of 10 mass% or less, and preferably 5 mass% or less, with respect to the total solid content of the coating agent composition according to the present invention.

[0237]

The rheology modifier is added mainly for the purpose of improving the fluidity of the coating agent composition, and particularly in the baking step, for the purpose of improving the film thickness uniformity of a resist underlayer film and improving the filling property of the coating agent composition into holes. Specific examples thereof include phthalic acid derivatives such as dimethyl phthalate, diethyl phthalate, diisobutyl phthalate, dihexyl

phthalate, and butyl isodecyl phthalate; adipic acid derivatives such as dinormal butyl adipate, diisobutyl adipate, diisooctyl adipate, and octyl decyl adipate; maleic acid derivatives such as di(n-butyl) maleate, diethyl maleate, and dinonyl maleate; oleic acid derivatives such as methyl oleate, butyl oleate, and tetrahydrofurfuryl oleate; and stearic acid derivatives such as n-butyl stearate and glyceryl stearate. These rheology modifiers are usually blended in a proportion of less than 30 mass% with respect to the total solid content of the coating agent composition according to the present invention.

[0238]

The adhesion aid is mainly added to improve adhesion of the coating agent composition to a nitrogen atom-containing substrate or a resist, and in particular, to prevent peeling of the resist in development. Specific examples include chlorosilanes such as trimethylchlorosilane, dimethylvinylchlorosilane, methyldiphenylchlorosilane, and chloromethyldimethylchlorosilane; alkoxysilanes such as trimethylmethoxysilane, dimethyldiethoxysilane, methyldimethoxysilane, dimethylvinylethoxysilane, diphenyldimethoxysilane, and phenyltriethoxysilane; silazanes such as hexamethyldisilazane, N,N'-bis(trimethylsilyl)urea, dimethyltrimethylsilylamine, and

trimethylsilylimidazole; silanes such as vinyltrichlorosilane, γ-chloropropyltrimethoxysilane, γ-aminopropyltriethoxysilane, and γ-glycidoxypropyltrimethoxysilane; heterocyclic compounds such as benzotriazole, benzimidazole, indazole, imidazole, 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, urazole, thiouracil, mercaptoimidazole, and mercaptopyrimidine; ureas such as 1,1-dimethylurea and 1,3-dimethylurea; and thiourea compounds. These adhesion aids are usually blended in a proportion of less than 5 mass%, and preferably less than 2 mass%, with respect to the total solid content of the coating agent composition according to the present invention.

[0239]

The solid content of the coating agent composition according to the present invention is preferably 0.1 to 70 mass% or 0.1 to 60 mass%. The solid content is the content proportion of all components excluding the solvent from the coating agent composition. The solid content may contain a crosslinkable resin in a proportion of 1 to 99.9 mass%, 50 to 99.9 mass%, 50 to 95 mass%, or 50 to 90 mass%.

[0240]

[Resist underlayer film]

A resist underlayer film can be formed on the nitrogen

atom-containing substrate using the nitrogen atom-containing substrate coating agent composition, which is an aspect of the present invention. That is, a resist underlayer film can be formed on the nitrogen atom-containing substrate as a baked product (cured product) of a coating film composed of the nitrogen atom-containing substrate coating agent composition. Another aspect of the present invention is a method for producing a laminate of two or more layers including the nitrogen atom-containing substrate and the resist underlayer film, the method including a step of applying the nitrogen atom-containing substrate coating agent composition to at least one surface of the nitrogen atom-containing substrate and a step of baking the obtained coating film to form a resist underlayer film. In the laminate, a resist film may be laminated (laminated in the order of the substrate/the resist underlayer film/the resist film) on the surface of the resist underlayer film opposite to the nitrogen atom-containing substrate. In addition, another aspect of the present invention is the use of the nitrogen atom-containing substrate coating agent composition for forming the resist underlayer film on the nitrogen atom-containing substrate.

Another aspect of the present invention is a laminate of two or more layers including the nitrogen atom-

containing substrate and the resist underlayer film. Still another aspect of the present invention is a laminate in which the resist underlayer film and the resist film are laminated in order on at least one surface of the nitrogen atom-containing substrate. Still another aspect of the present invention is the use of the nitrogen atom-containing substrate coating agent composition in the production of the laminate or semiconductor device.

[0241]

More specifically, the nitrogen atom-containing substrate coating agent composition, which is an aspect of the present invention, is applied onto, among substrates that are used to produce semiconductor devices, a nitrogen atom-containing substrate (for example, a silicon nitride substrate (SiN substrate), a silicon oxynitride substrate (SiON substrate), a titanium nitride substrate (TiN substrate), a titanium oxynitride substrate (TiON), or the like) by an appropriate coating method such as a spinner or a coater and then baked using heating means such as a hot plate, whereby a resist underlayer film is formed on the nitrogen atom-containing substrate. The baking conditions are appropriately selected from a baking temperature of 80°C to 800°C, and a baking time of 0.3 to 60 minutes. Preferably, the baking temperature is 150°C to 500°C (more preferably 150°C to 400°C), and the baking time is 0.5 to 2

minutes. As the atmospheric gas during baking, air may be used, and an inert gas such as nitrogen or argon can also be used. In an aspect, the oxygen concentration is particularly preferably 1% or less.

[0242]

Here, the film thickness of the resist underlayer film to be formed can be set to, for example, 10 to 1000 nm, 20 to 500 nm, 30 to 400 nm, or 50 to 300 nm, but the resist underlayer film is preferably an ultrathin film having a film thickness of less than 10 nm from the viewpoint of the cost or production. The film thickness is preferably 1 to less than 10 nm and more preferably 3 to less than 10 nm. Even on such an ultrathin film, the nitrogen atom-containing substrate coating agent composition, which is an aspect of the present invention, has favorable coatability by means of blending with a specific novolac resin and enables the resist film to maintain the resolution of a resist comparable to that immediately after the formation of the resist film even in the case of being exposed after a long period of time elapses from the formation.

[0243]

In addition, it is also possible to form an adhesion layer and/or a silicon-containing layer containing 99 mass% or less or 50 mass% or less of Si on the resist underlayer film, which is an aspect of the present invention, by

coating or vapor deposition. For example, a Si-based inorganic material film can be formed by a CVD method or the like, in addition to methods of forming, by spin coating, an adhesion layer described in JP 2013-202982 A or JP 5827180 B, and a silicon-containing resist underlayer film (inorganic resist underlayer film) using the composition described in WO 2009/104552 (A1).

[0244]

In addition, the coating agent composition, which is an aspect of the present invention, is applied onto a semiconductor substrate having a portion with a step and a portion with no steps (so-called a step substrate) and baked, whereby a step between the portion with a step and the portion with no steps can be reduced.

[0245]

[Laminate]

A laminate of the present invention includes a nitrogen atom-containing substrate and the resist underlayer film of the present invention.

A nitrogen atom-containing substrate is a substrate composed of a compound having a bond between a metal atom or a metalloid atom and a nitrogen atom or a substrate having a nitrogen atom-containing film composed of a compound having a bond between a metal atom or a metalloid atom and a nitrogen atom.

The resist underlayer film of the present invention is a cured product of the nitrogen atom-containing substrate coating agent composition of the present invention.

The resist underlayer film of the present invention is disposed on, for example, the nitrogen atom-containing substrate.

[0246]

In the laminate, which is an aspect of the present invention, it is preferable that the cured product of the nitrogen atom-containing substrate coating agent composition is a nitrogen atom-containing film and the nitrogen atom-containing film constitutes the outermost layer of the nitrogen atom-containing substrate.

[0247]

In the laminate, which is an aspect of the present invention, the metal atom or metalloid atom that is contained in the nitrogen atom-containing substrate is preferably

(i) silicon,

(ii) titanium, or

(iii) tungsten, hafnium, zirconium, chromium, germanium, copper, silver, gold, aluminum, indium, gallium, arsenic, palladium, iron, tantalum, iridium, cobalt, manganese, molybdenum, or an alloy thereof.

[0248]

In the laminate, which is an aspect of the present invention, the compound having a bond between a metal atom or a metalloid atom that is contained in the nitrogen atom-containing substrate and a nitrogen atom is preferably SiON, SiN, TiON, or TiN.

[0249]

[Pattern forming method]

A pattern forming method of the present invention includes at least a step of forming a resist underlayer film by applying the nitrogen atom-containing substrate coating agent composition on the nitrogen atom-containing semiconductor substrate and baking the composition.

The pattern forming method of the present invention may include the following steps:

· a step of forming a resist film on the resist underlayer film,

· a step of irradiating the resist film with light or an electron beam and then developing the resist film to obtain a resist pattern, and · a step of etching the resist underlayer film using the resist pattern as a mask.

[0250]

[Method for producing semiconductor device]

(i)

A method for producing a semiconductor device, which is an aspect of the present invention, includes

a step of forming a resist underlayer film on a nitrogen atom-containing semiconductor substrate using the coating agent composition, which is an aspect of the present invention,

a step of forming a resist film on the resist underlayer film,

a step of forming a resist pattern by irradiating the resist film with light or an electron beam and developing the resist film,

a step of forming a patterned resist underlayer film by etching the resist underlayer film through the resist pattern, and

a step of processing the nitrogen atom-containing semiconductor substrate through the patterned resist underlayer film.

[0251]

(ii)

In addition, a method for producing a semiconductor device, which is an aspect of the present invention, includes

a step of forming a resist underlayer film on a nitrogen atom-containing semiconductor substrate using the coating agent composition, which is an aspect of the present invention,

a step of forming a hard mask on the resist underlayer

film,

a step of further forming a resist film on the hard mask,

a step of forming a resist pattern by irradiating the resist film with light or an electron beam and developing the resist film,

a step of forming a patterned hard mask by etching the hard mask through the resist pattern,

a step of forming a patterned resist underlayer film by etching the resist underlayer film through the patterned hard mask, and

a step of processing the nitrogen atom-containing semiconductor substrate through the patterned resist underlayer film.

[0252]

(iii)

In addition, a method for producing a semiconductor device, which is an aspect of the present invention, includes

a step of forming a resist underlayer film on a nitrogen atom-containing semiconductor substrate using the coating agent composition, which is an aspect of the present invention,

a step of forming a hard mask on the resist underlayer film,

a step of further forming a resist film on the hard mask,

a step of forming a resist pattern by irradiating the resist film with light or an electron beam and developing the resist film,

a step of forming a patterned hard mask by etching the hard mask through the resist pattern,

a step of forming a patterned resist underlayer film by etching the resist underlayer film through the patterned hard mask,

a step of removing the hard mask, and

a step of processing the nitrogen atom-containing semiconductor substrate through the patterned resist underlayer film.

[0253]

(iv)

In addition, a method for producing a semiconductor device, which is an aspect of the present invention, includes

a step of forming a resist underlayer film on a nitrogen atom-containing semiconductor substrate using the coating agent composition, which is an aspect of the present invention,

a step of forming a hard mask on the resist underlayer film,

a step of further forming a resist film on the hard mask,

a step of forming a resist pattern by irradiating the resist film with light or an electron beam and developing the resist film,

a step of forming a patterned hard mask by etching the hard mask through the resist pattern,

a step of forming a patterned resist underlayer film by etching the resist underlayer film through the patterned hard mask,

a step of removing the hard mask,

a step of forming a deposited film (spacer) on the resist underlayer film after removal of the hard mask,

a step of processing the deposited film (spacer) by etching,

a step of removing the patterned resist underlayer film to leave a patterned deposited film (spacer), and

a step of processing the nitrogen atom-containing semiconductor substrate through the patterned deposited film (spacer).

[0254]

The nitrogen atom-containing semiconductor substrate can be processed using the production methods (i) to (iv).

[0255]

In the present specification, "nitrogen atom-containing

semiconductor substrate" refers to a semiconductor substrate having the above-described nitrogen atom-containing film on the substrate.

Examples of the nitrogen atom-containing semiconductor substrate include a semiconductor substrate having a SiON film, a SiN film, a TiON film, or a TiN film, which is a nitrogen atom-containing film, thereon, a silicon substrate (Si substrate) having a nitrogen atom-containing film thereon, and the like.

[0256]

The step of forming a resist underlayer film using the coating agent composition, which is an aspect of the present invention, is as described above in the [resist underlayer film] section.

[0257]

A hard mask such as a silicon-containing film may be formed as a second resist underlayer film on the resist underlayer film formed in the above step, and a resist pattern may be formed thereon [the above (ii) to (iv)].

[0258]

The hard mask may be a coating film of an inorganic substance or the like, or a deposited film of an inorganic substance or the like formed by a vapor deposition method such as CVD or PVD, and examples thereof include a SiON film, a SiN film, and a SiO_2 film.

[0259]

Furthermore, an antireflective film (BARC) may be formed on the hard mask, or a resist shape correction film having no antireflection performance may be formed.

[0260]

In the step of forming the resist pattern, exposure is performed through a mask (reticle) for forming a predetermined pattern or by direct drawing. As an exposure source, for example, a g-line, an i-line, a KrF excimer laser, an ArF excimer laser, an EUV, or an electron beam can be used. After the exposure, Post Exposure Bake is performed as necessary. Thereafter, development is performed with a developer (for example, 2.38 mass% aqueous tetramethylammonium hydroxide solution, butyl acetate), and rinsing is further performed with a rinse liquid or pure water to remove the used developer. Thereafter, post-baking is performed to dry the resist pattern and enhance adhesion to the base.

[0261]

The etching step performed after the resist pattern is formed is performed by dry etching.

[0262]

Note that the following gases, that is, CF_4, CHF_3, CH_2F_2, CH_3F, C_4F_6, C_4F_8, O_2, N_2O, NO_2, H_2, and He can be used for processing the hard mask (silicon-containing layer),

the resist underlayer film, and the substrate. These gases may be used alone or as a mixture of two or more types of gases. Furthermore, argon, nitrogen, carbon dioxide, carbonyl sulfide, sulfur dioxide, neon, or nitrogen trifluoride can be mixed with these gases and used.

[0263]

The resist film may be patterned by a nanoimprint method or a self-assembled film method.

[0264]

In the nanoimprint method, a resist composition is shaped using a patterned mold that is transparent to irradiation light. In addition, in the self-assembled film method, a pattern is shaped using a self-assembled film that naturally forms a regular structure on the order of nanometers, such as a diblock polymer (polystyrene-polymethyl methacrylate or the like).

[0265]

In the nanoimprint method, before a curable composition to be a resist film is applied, a silicon-containing layer (hard mask layer) may be optionally formed on the resist underlayer film by coating or vapor deposition, an adhesion layer may be formed on the resist underlayer film or the silicon-containing layer (hard mask layer) by coating or vapor deposition, and the curable composition to be a resist film may be applied on the adhesion layer.

[0266]

Note that a wet etching treatment may be performed for the purpose of simplifying the process steps and reducing damage to the processed substrate. This leads to suppression of variations in processing dimensions and reduction in pattern roughness, and enables processing of the substrate with high yield. Therefore, in the above (iii) to (iv), the removal of the hard mask can be performed by either etching or an alkaline chemical solution. In particular, when an alkaline chemical solution is used, the components are not limited, but as the alkaline component, those including the following are preferable.

[0267]

Examples of the alkali component include tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, methyltripropylammonium hydroxide, methyltributylammonium hydroxide, ethyltrimethylammonium hydroxide, dimethyldiethylammonium hydroxide, benzyltrimethylammonium hydroxide, hexadecyltrimethylammonium hydroxide, (2-hydroxyethyl)trimethylammonium hydroxide, monoethanolamine, diethanolamine, triethanolamine, 2-(2-aminoethoxy)ethanol, N,N-dimethylethanolamine, N,N-diethylethanolamine, N,N-

dibutylethanolamine, N-methylethanolamine, N-ethylethanolamine, N-butylethanolamine, N-methyldiethanolamine, monoisopropanolamine, diisopropanolamine, triisopropanolamine, tetrahydrofurfurylamine, N-(2-aminoethyl)piperazine, 1,8-diazabicyclo[5.4.0]undecene-7, 1,4-diazabicyclo[2.2.2]octane, hydroxyethylpiperazine, piperazine, 2-methylpiperazine, trans-2,5-dimethylpiperazine, cis-2,6-dimethylpiperazine, 2-piperidinemethanol, cyclohexylamine, 1,5-diazabicyclo[4,3,0]nonene-5, and the like. In particular, from the viewpoint of handling, tetramethylammonium hydroxide and tetraethylammonium hydroxide are particularly preferable, and an inorganic base may be used in combination with a quaternary ammonium hydroxide. As the inorganic base, hydroxides of alkali metals such as potassium hydroxide, sodium hydroxide, and rubidium hydroxide are preferable, and potassium hydroxide is more preferable.

[Examples]

[0268]

Next, the contents of the present invention will be specifically described with reference to Examples, but the present invention is not limited thereto.

[0269]

The weight average molecular weight Mw and Mw/Mn (polydispersity) of each of resins shown in Synthesis Examples 1 to 16 and Comparative Synthesis Examples 1 to 4 below are measurement results obtained by gel permeation chromatography (hereinafter abbreviated as GPC). In the measurement, a GPC apparatus manufactured by Tosoh Corporation was used, and measurement conditions and the like are as follows:

GPC column: TSKgel Super-MultiporeHZ-N (two columns)

Column temperature: 40°C

Solvent: Tetrahydrofuran (THF)

Flow rate: 0.35 ml/min

Standard sample: Polystyrene (manufactured by Tosoh Corporation)

[0270]

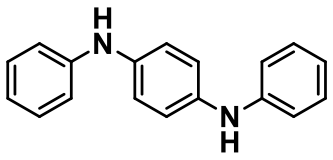
○ Synthesis of resin

In the synthesis of resins (S1) to (S9) used for resist underlayer films and the synthesis of a resin (SS1) as a comparative example, compound groups A to C, a catalyst group D, a solvent group E, a reprecipitation solvent group F, and a separation solvent group G, which will be described below, were used.

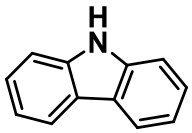
[0271]

○ Compound groups A to C

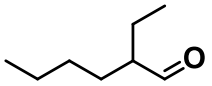
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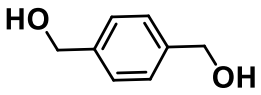
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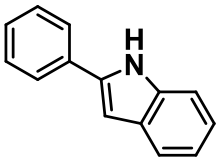
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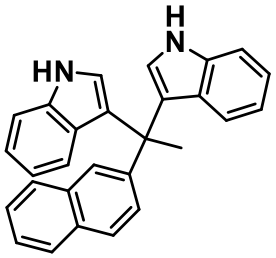
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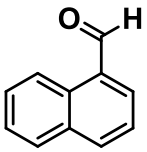
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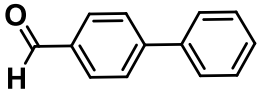
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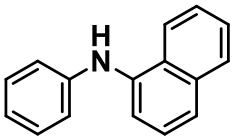
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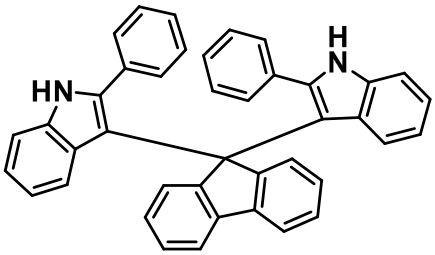
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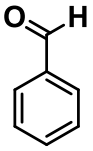
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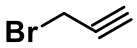
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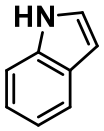
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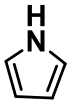
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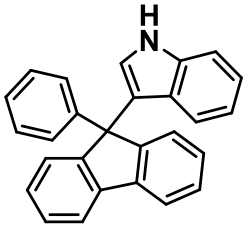
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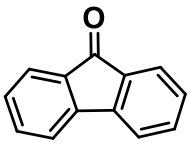
(A4)



(A5)



(A9)



(B4)

[0272]

○ Catalyst group D, solvent group E, reprecipitation solvent group F, and separation solvent group G

Methanesulfonic acid: D1

Tetrabutylammonium iodide: D2

Mercaptopropionic acid: D3

[0273]

Propylene glycol monomethyl ether acetate (= PGMEA): E1

Propylene glycol monomethyl ether (= PGME): E2

N-methyl-2-pyrrolidone: E3

Cyclohexanone: E4

25% aqueous sodium hydroxide solution: E5

Tetrahydrofuran (= THF): E6

[0274]

Methanol: F1

Methanol/water: F2

Butyl acetate/water: G1

[0275]

[Synthesis Example 1]

A flask was charged with 5.0 g of A1, 2.46 g of B1, 0.37 g of D1, and 18.3 g of PGMEA. Thereafter, the components were heated up to 150°C under nitrogen and reacted for about 20 hours. After the reaction was stopped, the components were reprecipitated with a mixed solvent (F2) of methanol and water and dried to obtain the resin (S1). The weight average molecular weight Mw measured in terms of polystyrene by GPC was about 1,300. The obtained resin was dissolved in PGMEA, and ion exchange was performed using a cation exchange resin and an anion exchange resin for 4 hours to obtain a target compound solution. The resin that did not dissolve in PGMEA was

dissolved in PGME or cyclohexanone (CYH), and ion exchange was performed in the same manner. The addition amounts of the compounds that served as raw materials of the resin, synthesis conditions, and the like are shown in Table 1.

[0276]

[Synthesis Examples 2 to 12]

Resins (S2) to (S11) and (SS1) were synthesized by the same operation as in Synthesis Example 1. A polymer that did not dissolve in PGMEA was dissolved in PGME or CYH, and ion exchange was performed in the same manner. The addition amounts of the compounds that served as raw materials of each resin, synthesis conditions, and the like are shown in Table 1.

[0277]

[Table 1]

Synthesis Example	Resin	Compound	Catalyst	Solvent	Temperature/hours	Reprecipitation
1	S1	A1/B1 5.0 g/2.46 g	D1 0.37 g	E1 18.3 g	150°C/20 hours	F2
2	S2	A2/B2 30.0 g/24.3 g	D1 2.98 g	E1 133.5 g	120°C/7 hours	F2
3	S3	A3/B2 5.0 g/3.60 g	D1 0.22 g	E1 35.1 g	120°C/3 hours	F2
4	S4	A3/B3 30.0 g/14.5 g	D1 1.31 g	E1 183.3 g	120°C/3 hours	F2
5	S5	A2/B1 10.0 g/6.63 g	D1 1.14 g	E1 158.4 g	120°C/20 hours	F2
6	S6	A7/B2 8.0 g/3.24 g	D1 0.60 g	E2/E3 19.3 g/8.3 g	100°C/20 hours	F2
7	S7	A7/B4	D1/D2	E1/E2	150°C/21 hours	F2

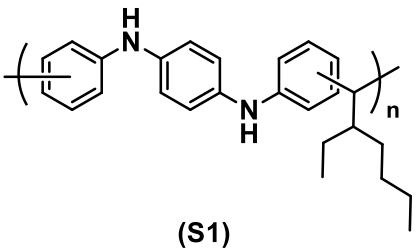
		20.0 g/9.33 g	7.47 g/1.10 g	38.6 g/16.6 g		
8	S8	A8/B4 25.0 g/8.21 g	D1/D2 8.76 g/2.42 g	E1 63.0 g	100°C/24 hours	F2
9	S9	A5/B2/B5 10.0 g/8.24 g/13.97 g	D1 0.14 g	E4 77.6 g	23°C/24 hours	F2
10	S10	A2/B6 18.0 g/17.0 g	D1 17.9 g	E1 123.4 g	100°C/24 hours	F2
11	S11	A9/A3/A6/B4 10.0 g/1.53 g/1.95 g/8.41 g	D1/D2 4.48 g/2.48 g	E1 61.6 g	100°C/24 hours	F2
12	SS1	A4/B2 15.0 g/23.1 g	D1 4.20 g	E1 62.7 g	120°C/5 hours	F1

[0278]

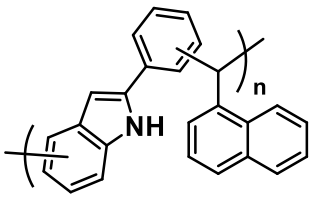
Structural formulas of the obtained resins (S1) to (S11) and resin (SS1) are shown below.

[0279]

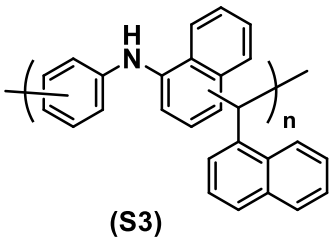
[Chem. 136]



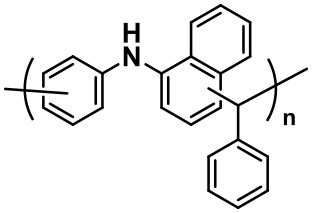
(S1)



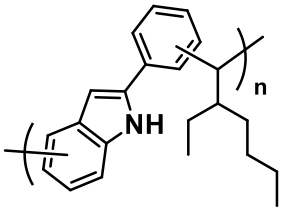
(S2)



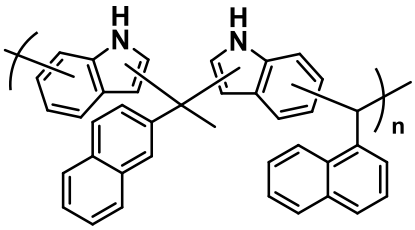
(S3)



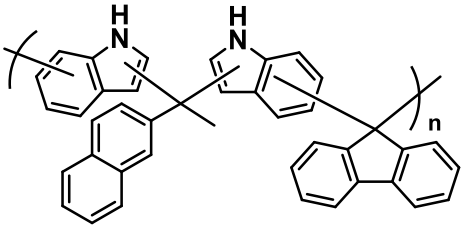
(S4)



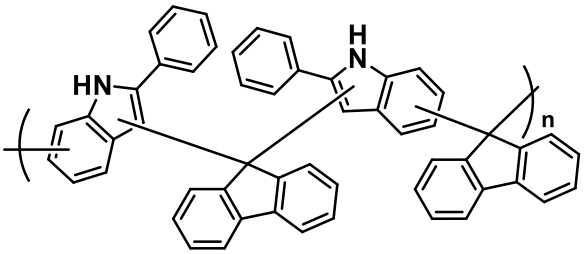
(S5)



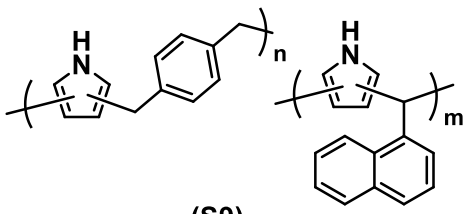
(S6)



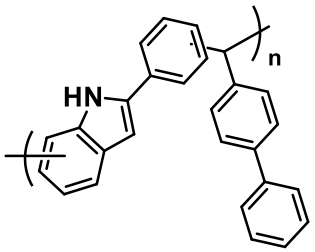
(S7)



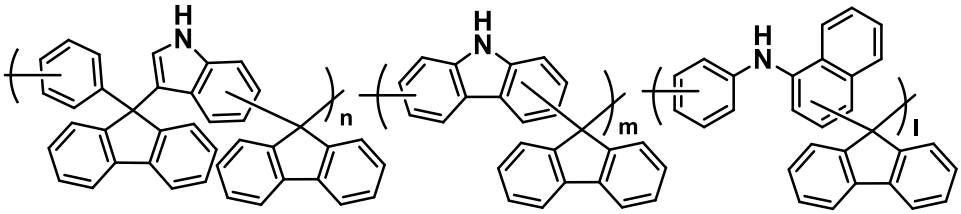
(S8)



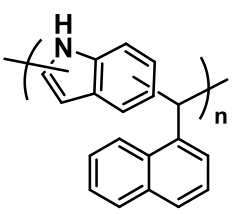
(S9)



(S10)



(S11)



(SS1)

[0280]

[Synthesis Example 6’]

A flask was charged with 6.50 g of S6, 4.42 g of C1, 0.23 g of D2, 7.53 g of E5, and 16.7 g of E6. The components were heated up to 55°C under nitrogen and reacted for about 23 hours. After the reaction was stopped, a liquid separation operation was repeated with a mixed solvent (G1) of butyl acetate and water, an organic phase was concentrated, reprecipitated using F2, and dried to obtain a resin (S6’). The weight average molecular weight Mw measured in terms of polystyrene by GPC was about 1,150. The obtained resin was dissolved in PGMEA, and ion exchange was performed using a cation exchange resin and an anion exchange resin for 4 hours to obtain a target compound solution. The addition amounts of the compounds that served as raw materials of the resin, synthesis conditions, and the like are shown in Table 2.

[0281]

[Synthesis Examples 7’ to 11’]

Resins (S7’) to (S11’) were synthesized by the same operation as in Synthesis Example 1’. A polymer that did not dissolve in PGMEA was dissolved in PGME or CYH, and ion exchange was performed in the same manner. The addition amounts of the compounds that served as raw materials of each resin, synthesis conditions, and the like are shown in Table 2.

[0282]

[Table 2]

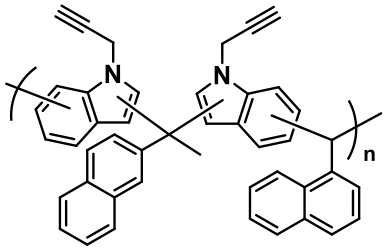
Synthesis Example	Resin	Compound	Catalyst	Solvent	Temperature/hours	Reprecipitation
6’	S6’	S6/C1 6.50 g/4.42 g	D2 0.23 g	E5/E6 7.53 g/16.7 g	55°C/23 hours	F2
7’	S7’	S7/C1 10.0 g/6.50 g	D2 0.34 g	E5/E6 11.4 g/25.3 g	55°C/24 hours	F2
8’	S8’	S8/C1 10.0 g/5.02 g	D2 0.26 g	E5/E6 10.3 g/22.9 g	55°C/21 hours	F2
9’	S9’	S9/C1 10.0 g/21.1 g	D2 1.09 g	E5/E6 21.7 g/48.3 g	55°C/21 hours	F2
10’	S10’	S10/C1 10.0 g/9.98 g	D2 0.52 g	E5/E6 13.8 g/30.8 g	55°C/21 hours	F2
11’	S11’	S11/C1 10.0 g/10.3 g	D2 0.53 g	E5/E6 14.1 g/31.3 g	55°C/18 hours	F2

[0283]

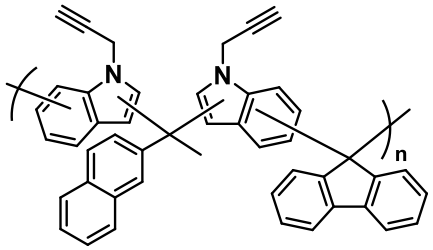
Structural formulas of the obtained resins (S6’) to (S11’) are shown below.

[0284]

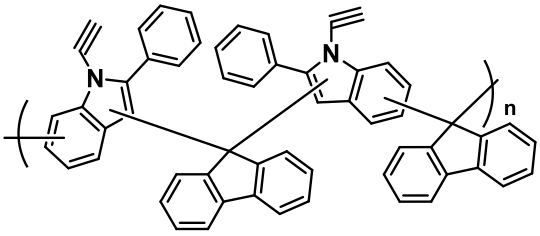
[Chem. 137]



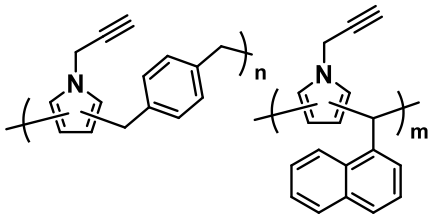
(S6')



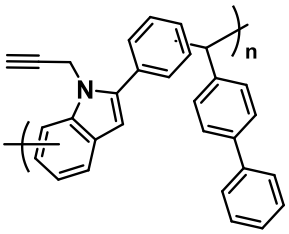
(S7')



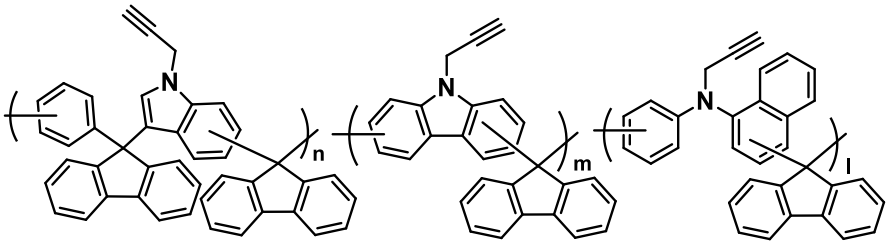
(S8')



(S9')



(S10')



(S11')

[0285]

○ Preparation of resist underlayer film

The resins (S1) to (S5), resins (S6') to (S11'), and resin (SS1), a crosslinking agent (CL1), an acid generator (Ad1), a solvent (propylene glycol monomethyl ether acetate (PGMEA), propylene glycol monomethyl ether (PGME), or cyclohexanone (CYH)), and MEGAFACE R-30 (manufactured by DIC Corporation, H1) as a surfactant were mixed together in proportions in Table 3 below (parts by weight relative to

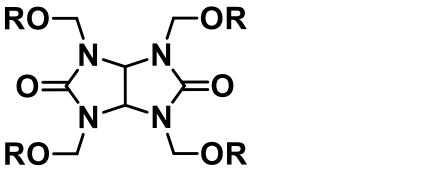
100 parts by weight of the resin for the crosslinking agent, the acid generator, and the surfactant; weight% relative to 100% of the total weight of the solvent for the solvent, independently of the weight of the resin), and mixtures were filtered through a 0.1 μm polytetrafluoroethylene microfilter to prepare resist underlayer film materials (M1 to M11, Comparative M1), which were nitrogen atom-containing substrate coating agent compositions.

[0286]

Structural formulas of crosslinking agents (CL1) and (CL2) and acid generators (Ad1) and (Ad2) are shown below. In the formulas, R represents a methyl group or a methoxyisopropyl group ($-CH(CH_3)CH_2OCH_3$). The plurality of R's may be the same as or different from each other.

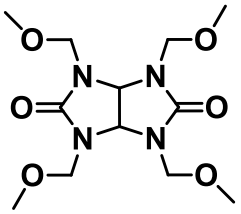
[0287]

[Chem. 138]

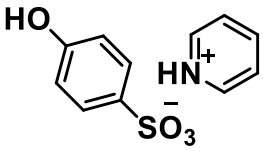


R= —CH_3 / —$CH(CH_3)CH_2OCH_3$

(CL1)



(CL2)



(Ad1)



(Ad2)

[0288]

[Table 3]

Composition	Resin		Crosslinking agent		Acid generator		Surfactant		Solvent (wt%)	
	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	PGMEA	PGME
M1	S1	100	CL1	56	Ad1	3.8	H1	0.1	70	30
M2	S2	100	CL1	56	Ad1	3.8	H1	0.1	70	30
M3	S3	100	CL1	56	Ad1	3.8	H1	0.1	70	30
M4	S4	100	CL1	56	Ad1	3.8	H1	0.1	70	30
M5	S5	100	CL1	56	Ad1	3.8	H1	0.1	70	30
M6	S6’	100	CL1	56	Ad1	3.8	H1	0.1	70	30
M7	S7’	100	CL1	56	Ad1	3.8	H1	0.1	70	30
M8	S8’	100	CL1	56	Ad1	3.8	H1	0.1	70	30
M9	S9’	100	CL1	56	Ad1	3.8	H1	0.1	70	30
M10	S10’	100	CL1	56	Ad1	3.8	H1	0.1	70	30
M11	S11’	100	CL1	56	Ad1	3.8	H1	0.1	70	30
Comparative M1	SS1	100	CL2	56	Ad2	3.8	H1	0.1	70	30

[0289]

[Examples 1 to 11 and Comparative Example 1]

[Coatability evaluation 1]

The resist underlayer film materials M1 to M11 and Comparative M1 were applied onto various substrates (SiON substrates or Si substrates) with no steps using a spin coater, respectively, and baked under an ambient atmosphere at predetermined temperatures for predetermined times shown in Table 4 to form resist underlayer films so that the film thicknesses of the films to be obtained reached 5 nm. The surfaces of the formed resist underlayer films were visually confirmed, and coatability was evaluated. In a case where the resist underlayer film material could be applied without pinholes, unevenness, or cissing, the coatability was judged as "o", and otherwise, the coatability was judged as "×". The results are shown in Table 4. Incidentally, in order to show that the resist underlayer film materials also had coatability comparable to that of the conventional materials with respect to Si substrates containing no nitrogen atoms, the results are shown for reference.

[0290]

[Table 4]

Example/ Comparative Example	Composition	Baking temperature /time	Coatability evaluation 1 (visual evaluation)	
			Substrate type	
			SiON substrate	Si substrate

Example 1	M1	400°C/60 sec	○	○
Example 2	M2	400°C/60 sec	○	○
Example 3	M3	350°C/60 sec	○	○
Example 4	M4	400°C/60 sec	○	○
Example 5	M5	400°C/60 sec	○	○
Example 6	M6	400°C/60 sec	○	○
Example 7	M7	400°C/60 sec	○	○
Example 8	M8	400°C/60 sec	○	○
Example 9	M9	400°C/60 sec	○	○
Example 10	M10	400°C/60 sec	○	○
Example 11	M11	400°C/60 sec	○	○
Comparative Example 1	Comparative M1	240°C/60 sec	○	○

[0291]

[Coatability evaluation 2]

The resist underlayer film materials M1 to M11 and Comparative M1 were applied onto various substrates using a coater/developer (ACT (registered trademark)-8 or Lithius (registered trademark) Pro) manufactured by Tokyo Electron Limited, respectively, and baked under an ambient atmosphere at predetermined temperatures for predetermined times shown in Table 5 to form resist underlayer films having a film thickness of 5 nm. The resist underlayer film materials were applied onto nitrogen atom-containing substrates (SiON substrates) having a SiON film (silicon oxynitride film) deposited thereon with ACT (registered trademark)-8 and onto silicon wafers (Si substrates) with Lithius (registered trademark) Pro. In the formed resist underlayer film, the film thicknesses of the entire wafer

were radially and concentrically measured at a total of 49 points, thereby evaluating the uniformity of the film thickness (film thickness uniformity) in the wafer surface. When the proportion of the film thickness variation width ((maximum film thickness) - (minimum film thickness)) in the average film thickness of 49 points was smaller than that in Comparative Example 1, the coatability was judged as "o", and Comparative Example 1 was judged as "×". The proportion of the film thickness variation width being small means higher uniformity of the film thickness in the wafer surface. The results are shown in Table 5. Incidentally, in order to show that the resist underlayer film materials also had coatability comparable to that of the conventional materials with respect to Si substrates containing no nitrogen atoms, the results are shown for reference.

[0292]

[Coatability evaluation 3]

The resist underlayer film materials M1 to M11 and Comparative M1 were applied onto nitrogen atom-containing substrates (SiON substrates) having SiON deposited thereon using a coater/developer (ACT (registered trademark)-8) manufactured by Tokyo Electron Limited, respectively, and baked under an ambient atmosphere at predetermined temperatures for predetermined times shown in Table 5 to

form resist underlayer films having a film thickness of 5 nm. Thereafter, the surface roughness was evaluated using AFM (atomic force microscope), and the coatability was evaluated. As a result of the AFM observation, in a case where there was no problem with coatability, the coatability was evaluated as "○", and in a case where film roughness such as pinholes or cissing was confirmed, the coatability was evaluated as "×". The results are shown in Table 5. Incidentally, in order to show that the resist underlayer film materials also had coatability comparable to that of the conventional materials with respect to Si substrates containing no nitrogen atoms, the results are shown for reference. In the table, "-" indicates that evaluation was not performed.

[0293]

[Table 5]

Example/ Comparative Example	Composition	Baking temperature /time	Coatability evaluation 2 (film thickness uniformity)		Coatability evaluation 3 (AFM)	
			Substrate type		Substrate type	
			SiON substrate	Si substrate	SiON substrate	Si substrate
Example 1	M1	400°C/60 sec	○	○	○	○
Example 2	M2	400°C/60 sec	○	○	○	○
Example 3	M3	400°C/60 sec	○	○	○	○
Example 4	M4	400°C/60 sec	○	○	○	○
Example 5	M5	400°C/60 sec	○	○	○	○
Example 6	M6	400°C/60 sec	○	○	○	○
Example 7	M7	400°C/60 sec	○	×	○	○
Example 8	M8	400°C/60 sec	○	○	○	○
Example 9	M9	400°C/60 sec	○	×	○	○

Example 10	M10	400°C/60 sec	○	○	○	○
Example 11	M11	400°C/60 sec	○	○	○	-
Comparative Example 1	Comparative M1	240°C/60 sec	○	○	○	-

[0294]

Based on Table 4 and Table 5, the nitrogen atom-containing substrate coating agent composition of the present invention exhibited excellent coatability with respect to the nitrogen atom-containing substrate, similarly to the silicon wafer, like conventional material compositions.

[0295]

[Lithography evaluation]

The resist underlayer film materials M1 to M11 and Comparative M1 were applied onto nitrogen atom-containing substrates (SiON substrates) having a SiON film formed thereon using a coater/developer (ACT (registered trademark)-8) manufactured by Tokyo Electron Limited, respectively, and baked under an ambient atmosphere at predetermined temperatures for predetermined times shown in Table 6 so that the film thicknesses of the films to be obtained reached 5 nm to form resist underlayer films. In addition, as comparative examples, in addition to Comparative Example 1, various substrates having no resist underlayer film formed thereon were prepared, and the test was also performed on Comparative Examples 2 to 4. A

commercially available resist solution for ArF (argon fluoride) (manufactured by Shin-Etsu Chemical Co., Ltd., trade name: SAIL X-206) was applied onto these resist underlayer films and baked at 85°C for 60 seconds to form photoresist films having a film thickness of 100 nm. After the above-described treatment, the resist films were left to stand for 48 hours without being developed. Each of the films was exposed using an ArF scanner (NSR-S307E, wavelength 193 nm, NA = 0.85, σ = 0.93/0.85) manufactured by Nikon Corporation through a mask set such that the line width and the width between the lines of the photoresist reached 0.1 μm, that is, 0.1 μm dense lines with a line and space (L/S) = 1/1 were formed after development. Thereafter, the film was baked on a hot plate at 95°C for 60 seconds, cooled, and then developed using butyl acetate for 60 seconds to form a positive-negative pattern on the resist underlayer film.

[0296]

The pattern size immediately after the formation of the resist pattern was observed using a CD-SEM (critical dimension SEM, manufactured by Hitachi High-Technologies Corporation). The dimensions of the resist pattern developed immediately after the formation of the resist film and the resist pattern developed after 48 hours elapsed were compared with each other, and the pattern

sizes were confirmed again using the same wafers after 48 hours elapsed. A case where a variation in pattern size was less than 4 nm of Comparative Example 1 was judged as "o", and a case where the variation was equal to or more than 4 nm of Comparative Example 1 was judged as "×".

Subsequently, a chip on which a target pattern size had been formed was cut and observed using a scanning electron microscope (S-4800) manufactured by Hitachi High-Technologies Corporation. A case where the resist shape was not affected by poisoning considered to arise from the nitrogen atom-containing substrate and the resist shape was a vertical shape was judged as "o", and a case where the resist shape was affected by the poisoning and the shape was not vertical was judged as "×". The results are shown in Table 6. In Table 6, "-" means that the composition (nitrogen atom-containing substrate coating agent composition) was not applied to the substrate.

[0297]

[Table 6]

Example/ Comparative Example	Composition	Baking temperature /time	Substrate type	Lithography evaluation	
				Shape	Pattern size variation
Example 1	M1	400°C/60 sec	SiON substrate	○	○
Example 2	M2	400°C/60 sec	SiON substrate	○	○
Example 3	M3	400°C/60 sec	SiON substrate	○	○
Example 4	M4	400°C/60 sec	SiON substrate	○	○
Example 5	M5	400°C/60 sec	SiON substrate	○	○
Example 6	M6	400°C/60 sec	SiON substrate	○	○

Example 7	M7	400°C/60 sec	SiON substrate	○	○
Example 8	M8	400°C/60 sec	SiON substrate	○	○
Example 9	M9	400°C/60 sec	SiON substrate	○	○
Example 10	M10	400°C/60 sec	SiON substrate	○	○
Example 11	M11	400°C/60 sec	SiON substrate	○	○
Comparative Example 1	Comparative M1	240°C/60 sec	SiON substrate	×	×
Comparative Example 2	-	Not baked	SiON substrate	×	×
Comparative Example 3	-	Not baked	SiN substrate	×	×
Comparative Example 4	-	Not baked	TiN substrate	×	×

[0298]

As described above, the novolac resins of Examples 1 to 11 exhibit extremely favorable curability under an ambient atmosphere even in a film thickness of less than 10 nm and can be used as a resist underlayer film in an ultrathin film state. In addition, these effects are not impaired even in a case where a triple bond is introduced into the NH group. Furthermore, the novolac resins exhibit favorable coatability with respect to various deposited film types even in a film thickness of less than 10 nm and have high in-plane uniformity of film thickness. In addition, the structure of the resin of the present example is capable of blocking an amine component that diffuses from a base substrate containing a nitrogen atom such as SiON, SiN, or TiN and is thus capable of maintaining the dimension and shape of a resist in a vertical shape even in a case where a development treatment is performed after a long period of time elapses from the formation of the

resist film as for a pattern developed immediately after the formation of the resist film. In addition, in the formed resist pattern, a variation in pattern size does not occur even after time elapses, and excellent pattern retention is exhibited. Therefore, the nitrogen atom-containing substrate coating agent composition is expected to be a material that can be widely applied in the coating application of nitrogen atom-containing substrates in the diversifying semiconductor production processes.

CLAIMS

[claim 1] A nitrogen atom-containing substrate coating agent composition comprising: a resin (G) having a composite unit structure; and a solvent,

wherein the composite unit structure has

a unit structure (A) having an aromatic ring and

a unit structure (B) having one or more carbon atoms,

the resin (G) is a resin obtained by a reaction of generating a covalent bond between a carbon atom constituting the aromatic ring of the unit structure (A) and the carbon atom in the unit structure (B),

the unit structure (A) includes a unit structure (A-I) containing at least a nitrogen atom,

a nitrogen atom-containing substrate is a substrate composed of a compound having a bond between a metal atom or a metalloid atom and a nitrogen atom or a substrate having a nitrogen atom-containing film composed of a compound having a bond between a metal atom or a metalloid atom and a nitrogen atom, and

the resin (G) is not a resin that is synthesized only from indole and 1-naphthaldehyde.

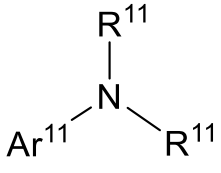
[claim 2] The nitrogen atom-containing substrate coating agent composition according to claim 1, wherein the unit structure (A-I) has a skeleton having an aromatic ring, and the skeleton is at least any one of an aromatic amine

skeleton and a nitrogen-containing aromatic heterocyclic skeleton.

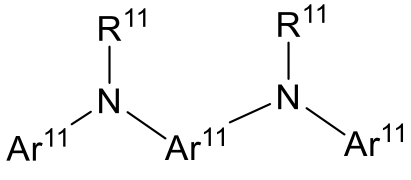
[claim 3] The nitrogen atom-containing substrate coating agent composition according to claim 1, wherein the unit structure (A-I) includes a unit structure not including a carbazole skeleton.

[claim 4] The nitrogen atom-containing substrate coating agent composition according to claim 1, wherein the unit structure (A-I) has a skeleton having an aromatic ring, the skeleton is at least any one of skeletons represented by Formula (A-1a) below, Formula (A-1b) below, Formula (A-1c) below, Formula (A-2a) below, Formula (A-2b-1) below, and Formula (A-2b-2) below, and at least one hydrogen atom may be substituted with a substituent in the skeleton:

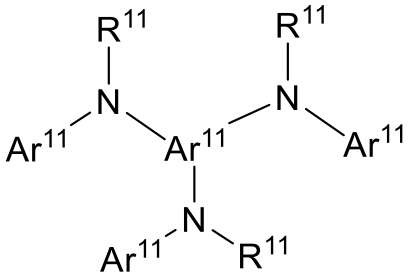
[Chem. 1]



(A-1a)



(A-1b)

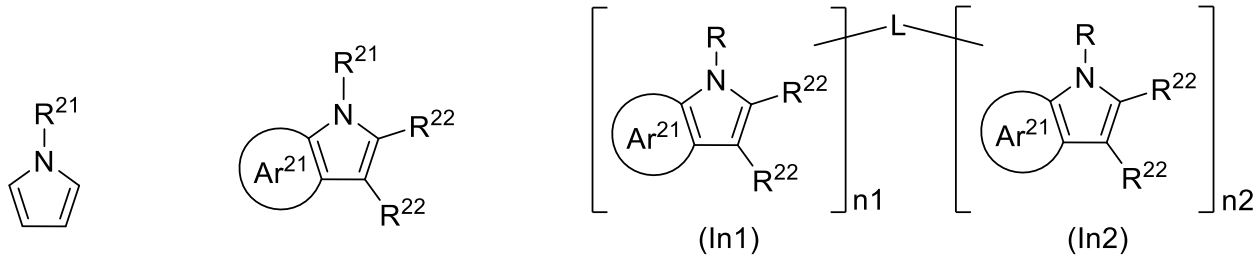


(A-1c)

(in Formula (A-1a) to Formula (A-1c), each Ar^{11} independently represents a residue of an aromatic ring, and

each R^{11} independently represents a hydrogen atom or a residue of an aromatic ring)

[Chem. 2]



(in the formula, each Ar^{21} independently represents a residue of an aromatic ring,

each R^{21} independently represents a hydrogen atom or a residue of an aromatic ring,

each R^{22} independently represents a hydrogen atom, a hydrocarbon group having 1 to 5 carbon atoms, or a residue of an aromatic ring,

two adjacent R^{22}'s may together form an unsaturated aliphatic ring,

one unsaturated bond in the unsaturated aliphatic ring refers to an unsaturated bond constituting a pyrrole ring,

each R independently represents a hydrogen atom, a residue of an aromatic ring, or a bonding site to L,

L represents a single bond or a linking group,

n1 represents 1, n2 represents 1 or 2,

in Formula (A-2b-2), in a case where L is a single bond, a partial structure (In1) and a partial structure (In2) bond to each other by two nitrogen atoms bonding to

each other, two Ar^{21}'s bonding to each other, or a nitrogen atom and Ar^{21} bonding to each other, and

in Formula (A-2b-2), in a case where L is a linking group, L bonds to N or Ar^{21}).

[claim 5] The nitrogen atom-containing substrate coating agent composition according to claim 4, wherein in the skeleton, the substituent that may substitute at least one hydrogen atom is one or more groups selected from a halo group, an alkyl group, an alkenyl group, an alkynyl group, an alkoxy group, an aryl group, an aryloxy group, an amino group, a hydroxy group, a hydroxyalkyl group, a carboxy group, a formyl group, a cyano group, a nitro group, an ester group, an amide group, a sulfonyl-containing group, a thiol group, a sulfide-containing group, and an ether bond-containing group.

[claim 6] The nitrogen atom-containing substrate coating agent composition according to claim 1, wherein the unit structure (B) includes a unit structure (B-I) derived from an aldehyde compound or an aldehyde equivalent.

[claim 7] The nitrogen atom-containing substrate coating agent composition according to claim 1, wherein the resin (G) is a resin that is synthesized from a reaction raw material containing an amine compound and an aldehyde compound or an aldehyde equivalent.

[claim 8] The nitrogen atom-containing substrate coating

agent composition according to claim 7, wherein the amine compound has a skeleton having an aromatic ring, and the skeleton is at least any one of an aromatic amine skeleton and a nitrogen-containing aromatic heterocyclic skeleton.

[claim 9] The nitrogen atom-containing substrate coating agent composition according to claim 1, wherein the solvent contains a solvent having a boiling point of 160°C or higher.

[claim 10] The nitrogen atom-containing substrate coating agent composition according to claim 1, further comprising: at least one selected from the group consisting of an acid, a salt thereof, and an acid generator.

[claim 11] The nitrogen atom-containing substrate coating agent composition according to claim 1, further comprising: a crosslinking agent.

[claim 12] The nitrogen atom-containing substrate coating agent composition according to claim 11, wherein the crosslinking agent is at least one selected from the group consisting of an aminoplast crosslinking agent and a phenoplast crosslinking agent.

[claim 13] The nitrogen atom-containing substrate coating agent composition according to claim 1, further comprising: a surfactant.

[claim 14] The nitrogen atom-containing substrate coating agent composition according to claim 1 that is intended to

form a resist underlayer film.

[claim 15] A resist underlayer film on a nitrogen atom-containing substrate, the resist underlayer film being a cured product of the nitrogen atom-containing substrate coating agent composition according to any one of claims 1 to 14.

[claim 16] The resist underlayer film according to claim 15, wherein a film thickness is less than 10 nm.

[claim 17] A laminate comprising: a nitrogen atom-containing substrate; and the resist underlayer film according to claim 15, wherein the nitrogen atom-containing substrate is a substrate composed of a compound having a bond between a metal atom or a metalloid atom and a nitrogen atom or a substrate having a nitrogen atom-containing film composed of a compound having a bond between a metal atom or a metalloid atom and a nitrogen atom.

[claim 18] The laminate according to claim 17, wherein the resist underlayer film is a nitrogen atom-containing film, and the nitrogen atom-containing film constitutes an outermost layer of the nitrogen atom-containing substrate.

[claim 19] The laminate according to claim 17, wherein the metal atom or metalloid atom is

(i) silicon,

(ii) titanium, or

(iii) tungsten, hafnium, zirconium, chromium, germanium, copper, silver, gold, aluminum, indium, gallium, arsenic, palladium, iron, tantalum, iridium, cobalt, manganese, molybdenum, or an alloy thereof.

[claim 20] The laminate according to claim 17, wherein the compound having a bond between a metal atom or a metalloid atom and a nitrogen atom is SiON, SiN, TiON, or TiN.

[claim 21] A method for forming a resist pattern that is used to manufacture a semiconductor, the method comprising: a step of forming a resist underlayer film by applying the nitrogen atom-containing substrate coating agent composition according to any one of claims 1 to 14 on a nitrogen atom-containing semiconductor substrate and baking the composition.

[claim 22] A method for producing a semiconductor device, the method comprising:

a step of forming a resist underlayer film on a nitrogen atom-containing semiconductor substrate using the nitrogen atom-containing substrate coating agent composition according to any one of claims 1 to 14;

a step of forming a resist film on the resist underlayer film;

a step of forming a resist pattern by irradiating the resist film with light or an electron beam and developing the resist film;

a step of forming a patterned resist underlayer film by etching the resist underlayer film through the resist pattern; and

a step of processing the nitrogen atom-containing semiconductor substrate through the patterned resist underlayer film.

[claim 23] A method for producing a semiconductor device, the method comprising:

a step of forming a resist underlayer film on a nitrogen atom-containing semiconductor substrate using the nitrogen atom-containing substrate coating agent composition according to any one of claims 1 to 14;

a step of forming a hard mask on the resist underlayer film;

a step of further forming a resist film on the hard mask;

a step of forming a resist pattern by irradiating the resist film with light or an electron beam and developing the resist film;

a step of forming a patterned hard mask by etching the hard mask through the resist pattern;

a step of forming a patterned resist underlayer film by etching the resist underlayer film through the patterned hard mask; and

a step of processing the nitrogen atom-containing

semiconductor substrate through the patterned resist underlayer film.

[claim 24] A method for producing a semiconductor device, the method comprising:

a step of forming a resist underlayer film on a nitrogen atom-containing semiconductor substrate using the nitrogen atom-containing substrate coating agent composition according to any one of claims 1 to 14;

a step of forming a hard mask on the resist underlayer film;

a step of further forming a resist film on the hard mask;

a step of forming a resist pattern by irradiating the resist film with light or an electron beam and developing the resist film;

a step of forming a patterned hard mask by etching the hard mask through the resist pattern;

a step of forming a patterned resist underlayer film by etching the resist underlayer film through the patterned hard mask;

a step of removing the hard mask; and

a step of processing the nitrogen atom-containing semiconductor substrate through the patterned resist underlayer film.

[claim 25] A method for producing a semiconductor device,

the method comprising:

a step of forming a resist underlayer film on a nitrogen atom-containing semiconductor substrate using the nitrogen atom-containing substrate coating agent composition according to any one of claims 1 to 14;

a step of forming a hard mask on the resist underlayer film;

a step of further forming a resist film on the hard mask;

a step of forming a resist pattern by irradiating the resist film with light or an electron beam and developing the resist film;

a step of forming a patterned hard mask by etching the hard mask through the resist pattern;

a step of forming a patterned resist underlayer film by etching the resist underlayer film through the patterned hard mask;

a step of removing the hard mask;

a step of forming a deposited film on the resist underlayer film after removal of the hard mask;

a step of processing the deposited film by etching;

a step of removing the patterned resist underlayer film to leave a patterned deposited film; and

a step of processing the nitrogen atom-containing semiconductor substrate through the patterned deposited

film.

[claim 26] The method for producing a semiconductor device according to claim 23, wherein the hard mask is formed by applying a composition containing an inorganic substance or depositing an inorganic substance.

[claim 27] The method for producing a semiconductor device according to claim 22, wherein a pattern is formed on the resist film by a nanoimprint method or with a self-assembled film.

[claim 28] The method for producing a semiconductor device according to claim 24, wherein the hard mask is removed by either etching or with an alkaline solution.