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(54) **BIREFRINGENT POLYMER FILM WITH NEGATIVE OPTICAL DISPERSION**

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C09K 19/02	(2006.01)
C09K 19/06	(2006.01)
C09K 19/00	(2006.01)
C09K 19/38	(2006.01)
C09K 19/32	(2006.01)
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C09K 19/30	(2006.01)
C09K 19/04	(2006.01)
C09K 19/34	(2006.01)
G02B 5/30	(2006.01)

(52) **U.S. Cl.**

CPC ***C09K 19/38*** (2013.01); ***C09K 19/3059*** (2013.01); ***C09K 19/32*** (2013.01); ***C09K 19/406*** (2013.01); *C09K 2019/0429* (2013.01); *C09K 2019/0448* (2013.01); *C09K 2019/0496* (2013.01); *C09K 2019/3416* (2013.01); *C09K 2019/3422* (2013.01); *C09K 2219/03* (2013.01); *G02B 5/3016* (2013.01); *G02B 5/3083* (2013.01); *Y10T 428/10* (2015.01)

(58) **Field of Classification Search**

None

See application file for complete search history.

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(57) **ABSTRACT**

The invention relates to a polymer film having negative optical dispersion, novel polymerisable compounds and liquid crystal (LC) materials for its preparation, and the use of the polymer film and novel compounds and materials in optical, electrooptical, electronic, semiconducting or luminescent components or devices.

42 Claims, 5 Drawing Sheets

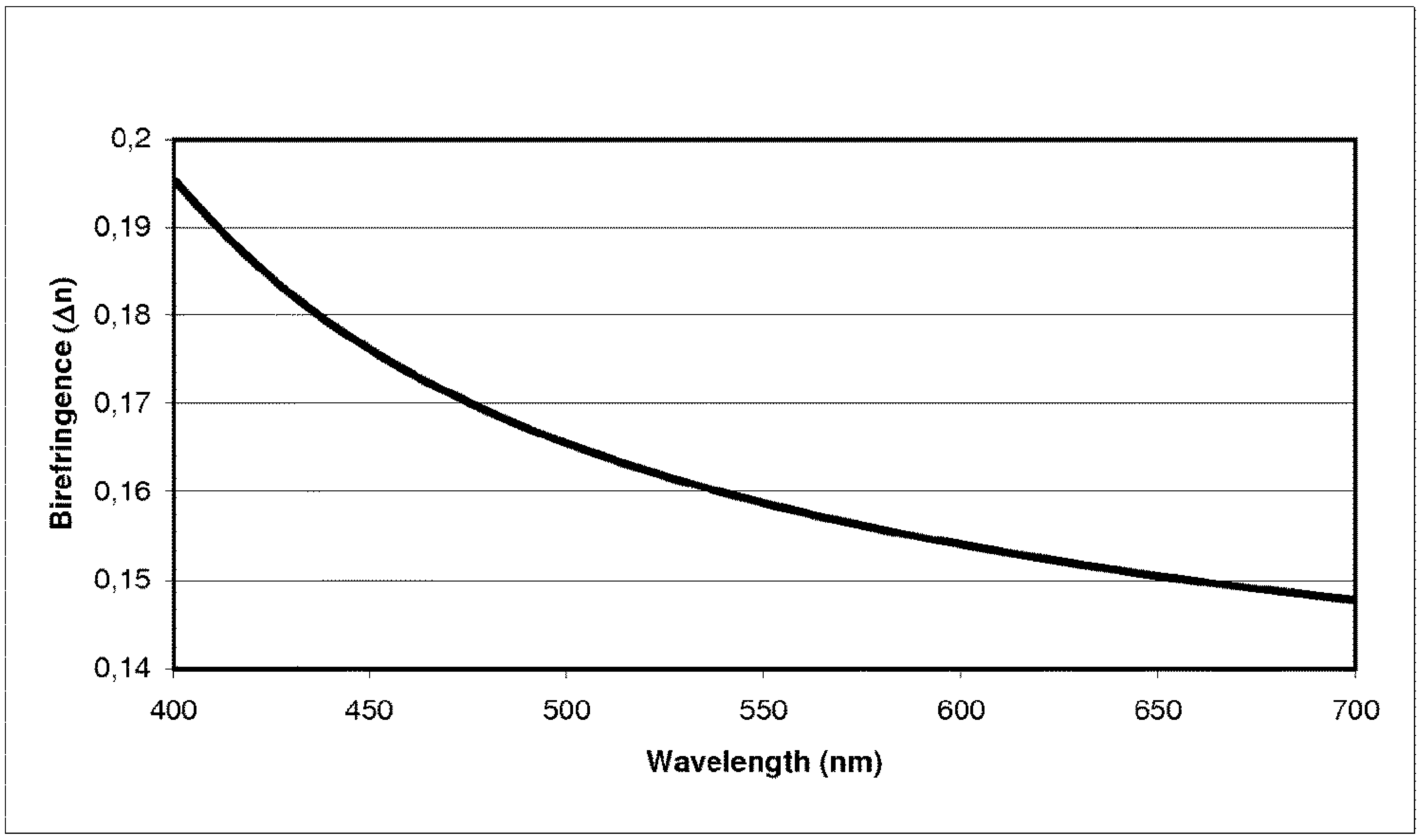


Figure 1

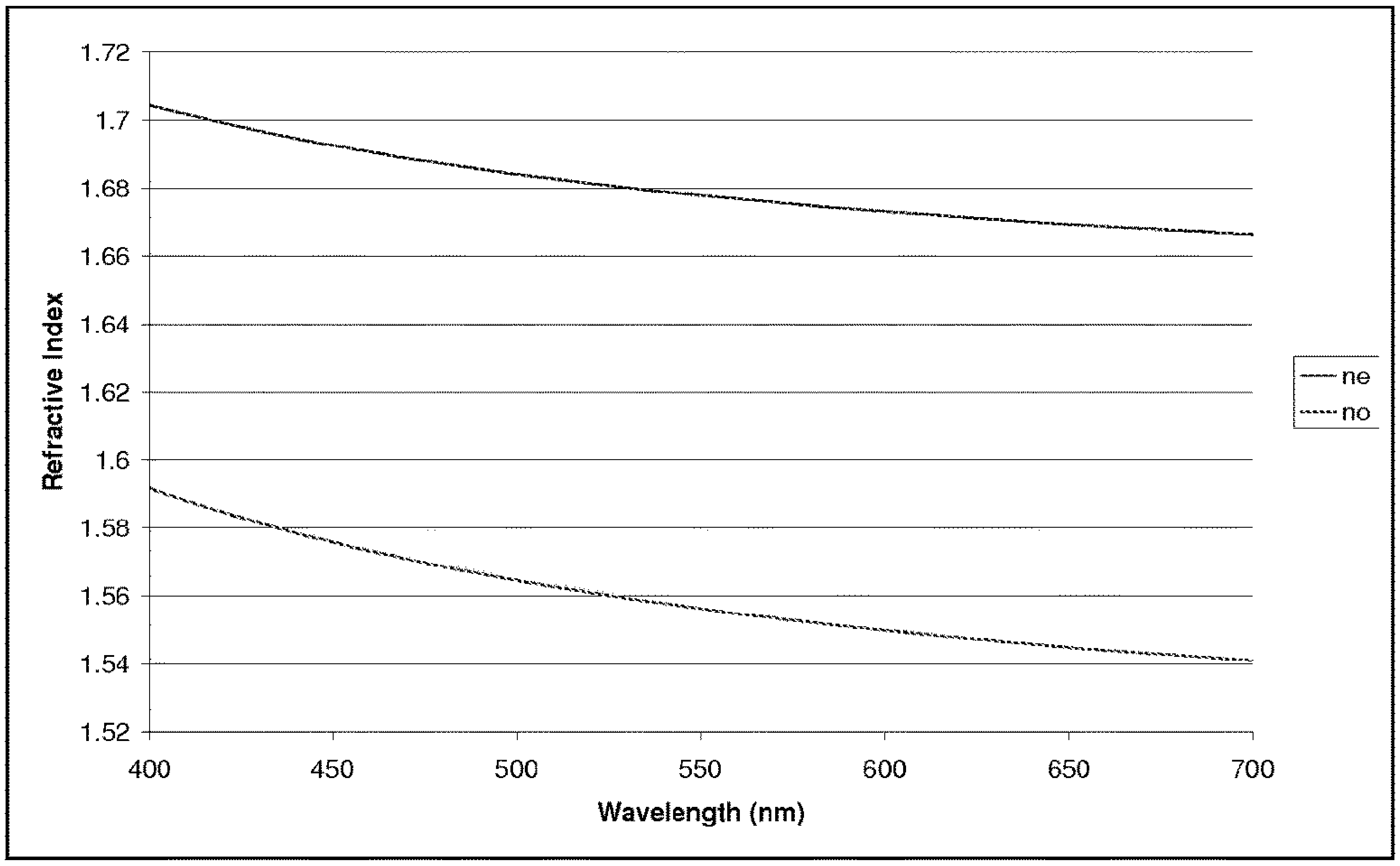


Figure 2

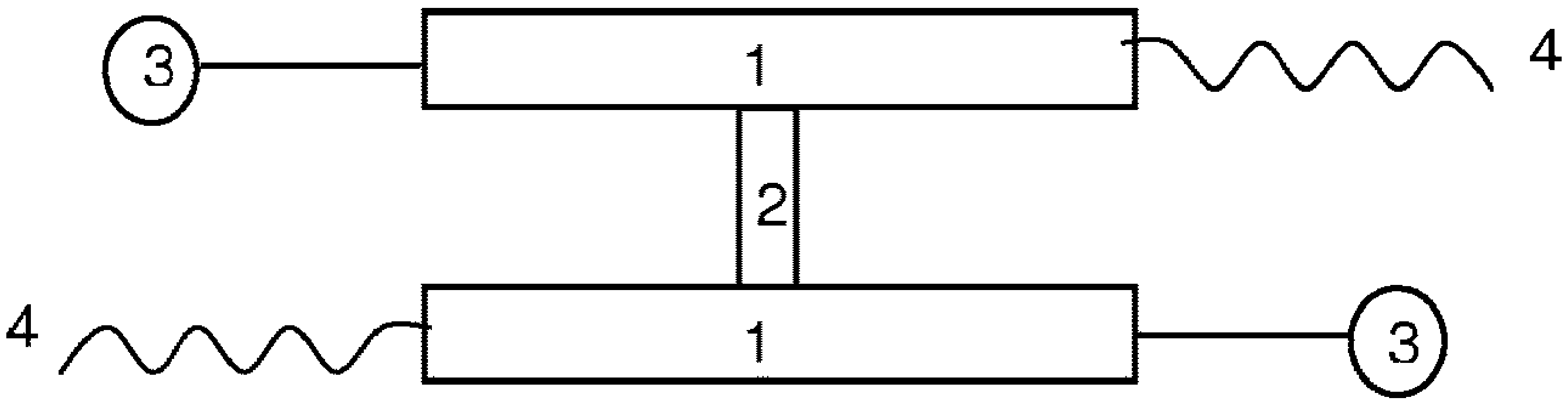


Figure 3a

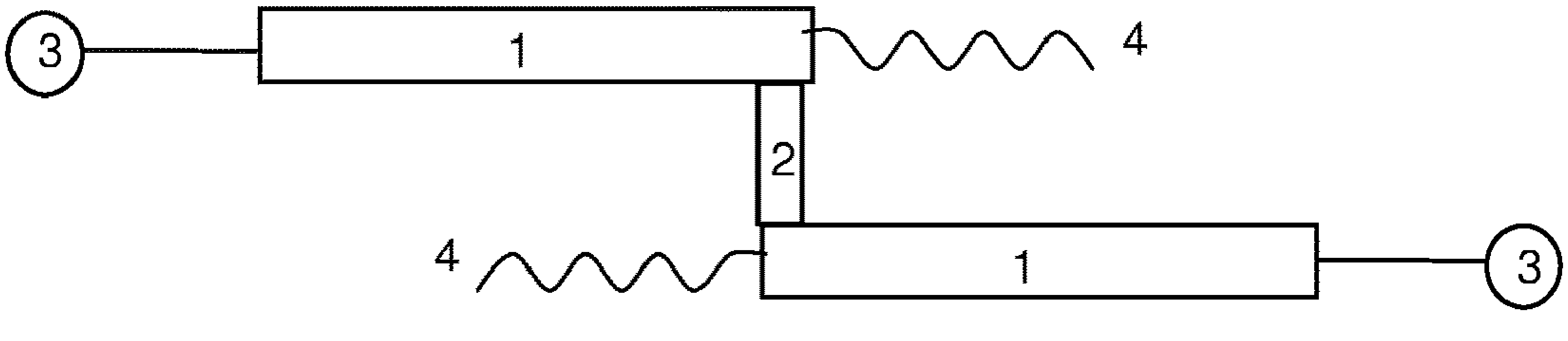


Figure 3b

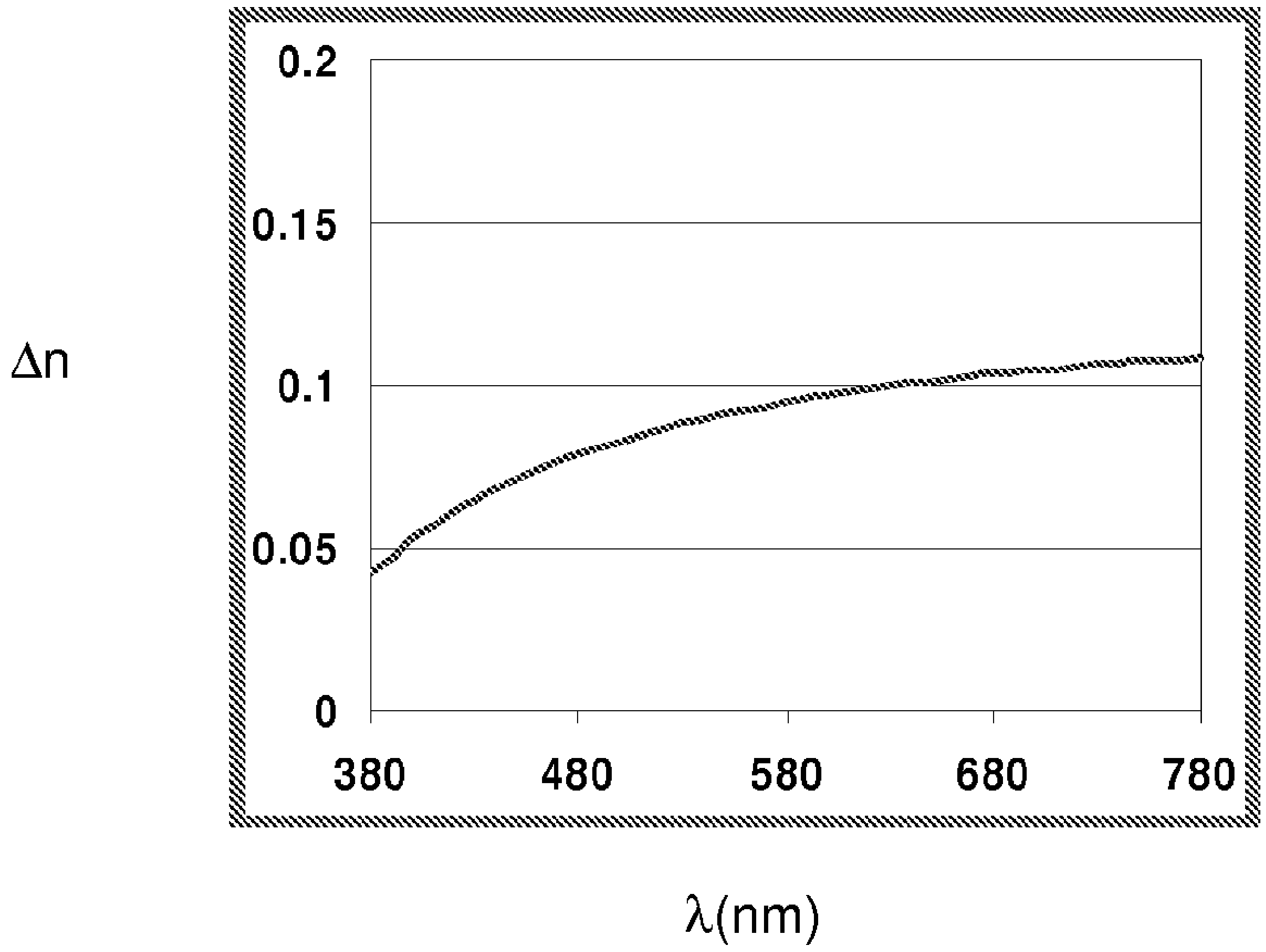


Figure 4a

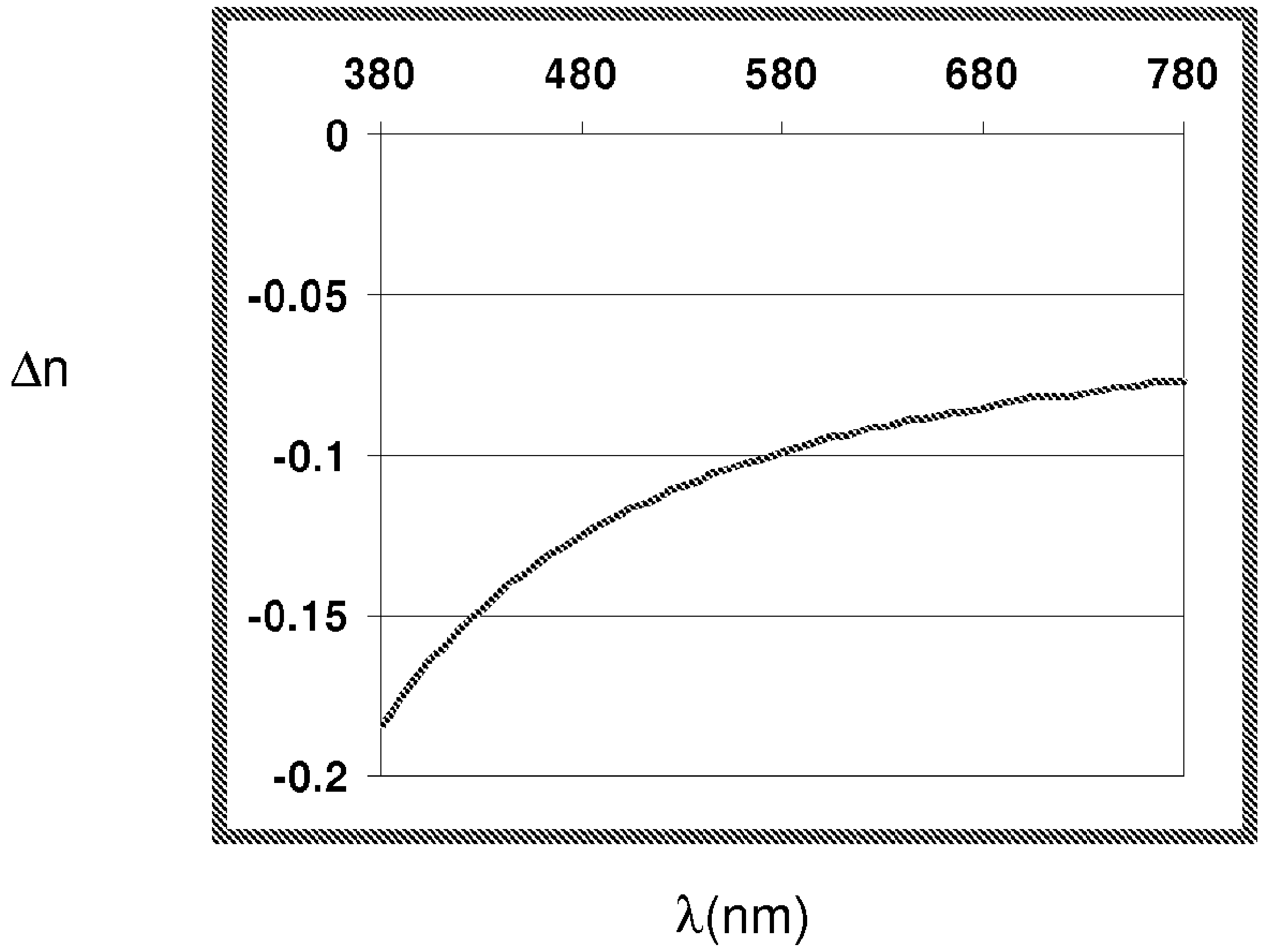


Figure 4b

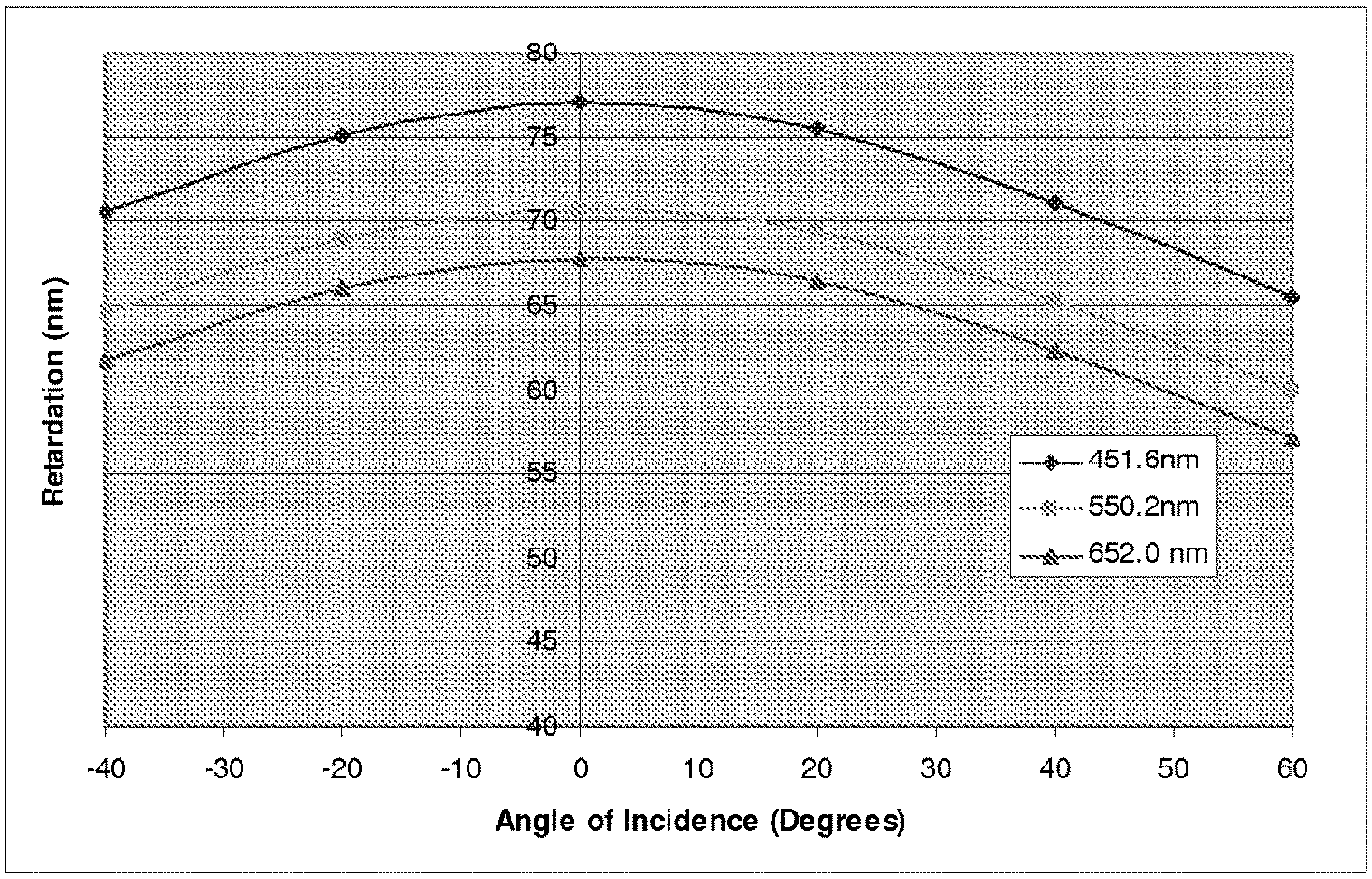


Figure 5

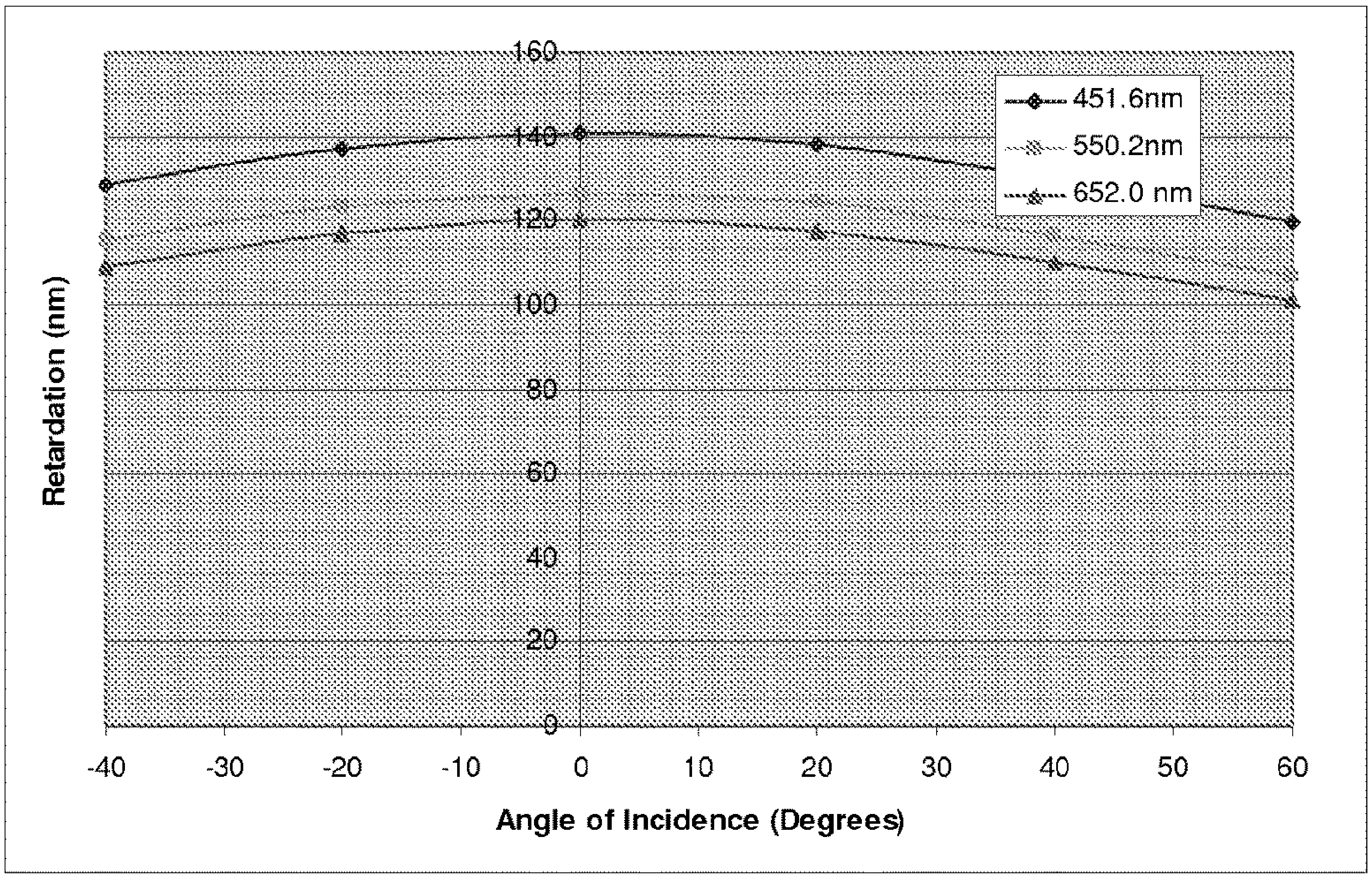


Figure 6

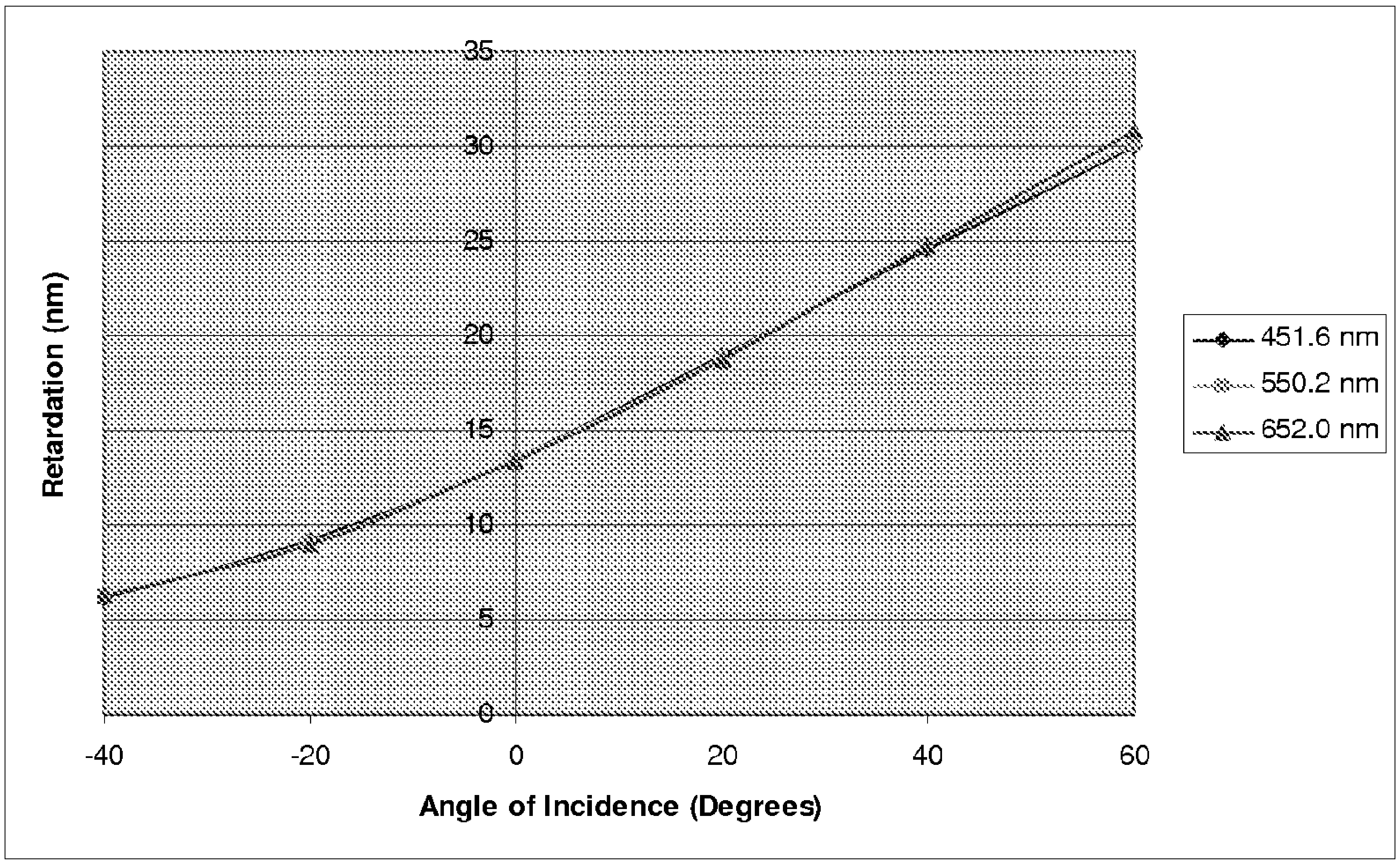


Figure 7

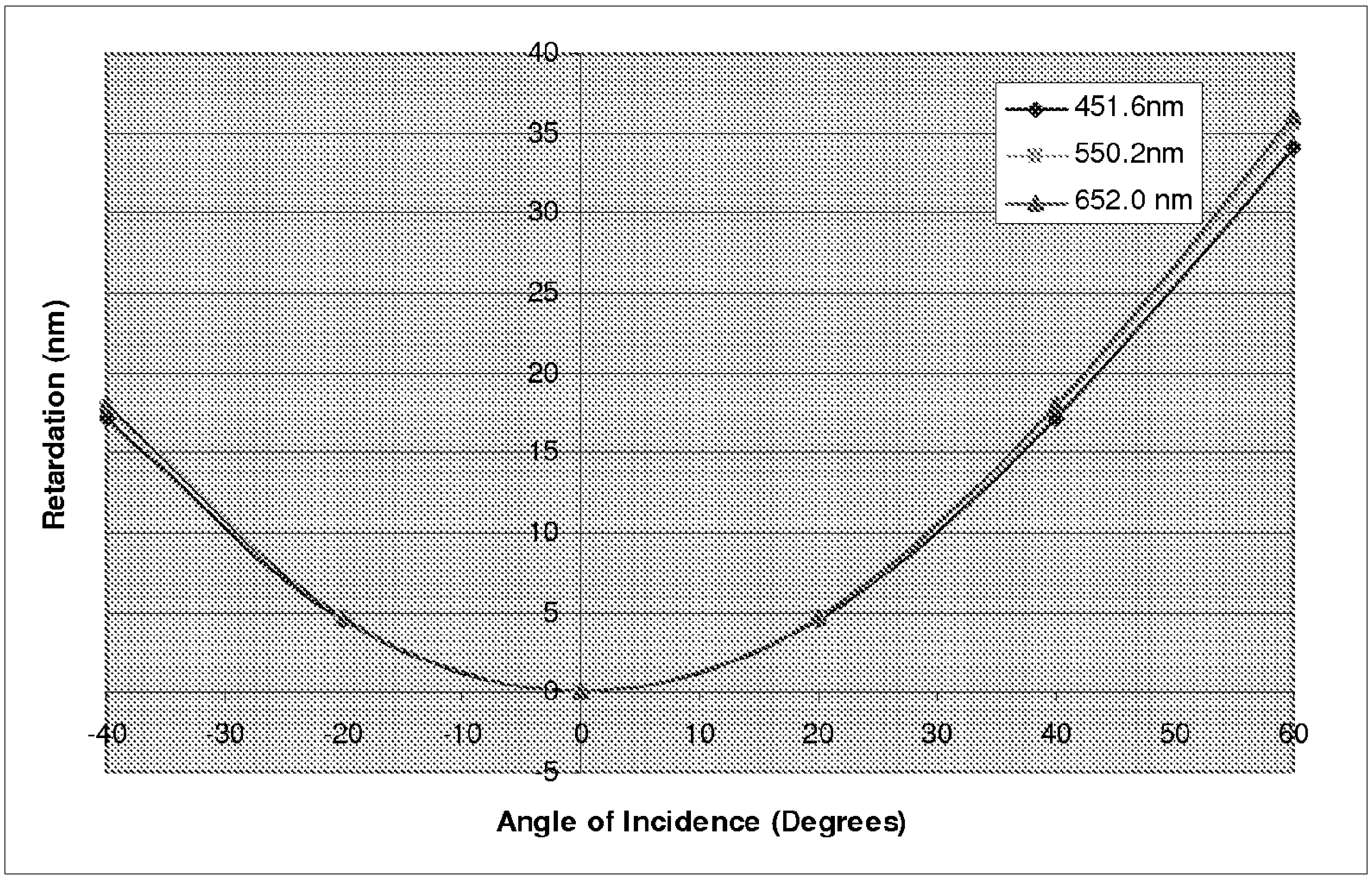


Figure 8

BIREFRINGENT POLYMER FILM WITH NEGATIVE OPTICAL DISPERSION

Matter enclosed in heavy brackets [ ] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue; a claim printed with strikethrough indicates that the claim was canceled, disclaimed, or held invalid by a prior post-patent action or proceeding.

FIELD OF THE INVENTION

The invention relates to a birefringent polymer film having negative optical dispersion, novel polymerisable compounds and liquid crystal (LC) materials for its preparation, and the use of the polymer film and novel compounds and materials in optical, electrooptical, electronic, semiconducting or luminescent components or devices.

BACKGROUND AND PRIOR ART

There is a need for anisotropic optical films that demonstrate negative optical retardation dispersion. For example, a quarter wave film made with negative dispersion birefringent materials will be largely achromatic. Devices such as a reflective LCD that utilises such a quarter wave film will have a dark state that is not coloured. Currently such devices have to use two retarder films to achieve this effect. The dispersive power of such a film can be defined in many ways, however one common way is to measure the optical retardation at 450 nm and divide this by the optical retardation measured at 550 nm (R_{450}/R_{550}). If the on-axis retardation of a negative retardation dispersion film at 550 nm is 137.5 nm and the R_{450}/R_{550} value is 0.82, then such a film will be a largely a quarter wave for all wavelengths of visible light and a liquid crystal display device (LCD) using this film as, for example, a circular polariser would have a substantially black appearance. On the other hand, a film made with an on axis of 137.5 nm which had normal positive dispersion (typically $R_{450}/R_{550}=1.13$) would only be a quarter wave for one wavelength (550 nm), and an LCD device using this film as, for example, a circular polariser would have a purple appearance. Another way of representing this information is to plot the change in birefringence as a function of wavelength. FIG. **1** shows a typical birefringence against wavelength plot for a polymerised film made from the commercially available reactive mesogen RM257 (Merck KgaA, Darmstadt, Germany). The R_{450}/R_{550} for this compound is around 1.115.

In an anisotropic optical film formed by rod-shaped, optically anisotropic molecules, the origin of the retardation dispersion is due to the fact that the two refractive indices n_e, n_o, of the anisotropic molecules (wherein n_e is the "extraordinary refractive index" in the direction parallel to the long molecular axis, and n_o is the "ordinary refractive index" in the directions perpendicular to the long molecular axis) are changing with wavelength at different rates, with n_e changing more rapidly than n_o towards the blue end of the visible wavelength spectrum. One way of preparing material with low or negative retardation dispersion is to design molecules with increased n_o dispersion and decreased n_e dispersion. This is schematically shown in FIG. **2**. Such an approach has been demonstrated in prior art to give LC's with negative birefringence and positive dispersion as well as compounds with positive birefringence and negative dispersion.

Thus, molecules that can be formed into anisotropic films that demonstrate the property of negative or reverse retardation dispersion have been disclosed in prior art. For example, JP2005-208416 A1 and WO 2006/052001 A1 disclose polymerisable materials based on a "cardo" core group. JP2005-208414 A1 discloses molecules that have covalently bonded discs and rods. JP2005-208415 A1 and JP2002-267838 A1 disclose materials that possess a cross-shape with short high refractive index parts of the molecule crossed with longer lower refractive index parts. WO 2005-085222 A1 discloses molecules that have two lower refractive index parts connected by a higher refractive index bridge part. The bridge is predominantly connected to the rods via a fused five-membered heterocyclic ring. All the above-mentioned documents disclose molecules that not only demonstrate negative dispersion, but also contain at least one polymerisable group and can therefore be polymerised when exposed to either heat or UV irradiation. These materials can be processed either as single materials, or as a mixture to give thin films which under the appropriate conditions can demonstrate uniform anisotropic properties. If photoinitiator is also included in the mixture, the anisotropic properties can be locked in by exposing the film to UV irradiation. This method of preparing optical films is well known. Another class of materials which is claimed to demonstrate negative birefringence is disclosed in U.S. Pat. No. 6,139,771, which describes compounds generally consisting of two rod-shaped LC parts connected by a acetylenic or bis-acetylenic bridging group. The bridging group is connected to the two rod-shaped parts using a benzene ring. However the document does neither disclose nor suggest polymerisable versions of these compounds.

U.S. Pat. No. 6,203,724 discloses molecules generally consisting of two rod-shaped LC parts connected by highly dispersive bridging groups. The bridging group is connected to the rod-shaped parts via the axial position of a cyclohexane ring. However the document does neither disclose nor suggest to use such compounds for the preparation of optical polymer films having negative optical dispersion.

U.S. Pat. No. 5,567,349 discloses dimers (or H-shaped RM's) wherein the bridging group is connected to the rod shaped part of the molecule via a phenyl ring, however, this document does not report that the molecules demonstrate negative dispersion or negative birefringence.

However, the materials already disclosed in the literature have thermal properties that are not suitable for processing under standard industrial processes, or are not soluble in the solvents commonly used in standard industrial processes or are not compatible with host RM materials commonly used in standard industrial processes, or are too expensive to manufacture.

This invention has the aim of providing improved polymer films and compounds and materials for their preparation not having the drawbacks of the prior art materials.

Another aim of the invention is to extend the pool of polymer films and materials having negative dispersion that are available to the expert. Other aims are immediately evident to the expert from the following description.

It has been found that these aims can be achieved by providing polymer films, compounds and materials as claimed in the present invention.

SUMMARY OF THE INVENTION

The invention relates to a birefringent polymer film with $R_{450}/R_{550}<1$, wherein R_{450} is the optical on-axis retardation at a wavelength of 450 nm and R_{550} is the optical on-axis retardation at a wavelength of 550 nm, said film being obtainable by polymerising one or more polymerisable compounds, wherein said polymerisable compounds contain

two mesogenic groups comprising one or more non-aromatic rings,

one or more polymerisable groups attached to at least one of the mesogenic groups either directly or via spacer groups, and

a bridging group connecting the mesogenic groups, comprising one or more subgroups selected from pi-conjugated linear carbyl or hydrocarbyl groups, aromatic and heteroaromatic groups, and being linked to a sp^3-hybridised C-atom or Si-atom in a non-aromatic ring of each mesogenic group.

The invention further relates to novel polymerisable compounds as described above and below.

The invention further relates to a polymerisable LC material comprising one or more polymerisable compounds as described above and below and one or more further compounds that are optionally polymerisable and/or mesogenic or liquid crystalline.

The invention further relates to an anisotropic polymer obtainable by polymerising a polymerisable compound or a polymerisable LC material as described above and below, preferably in its LC phase in an oriented state in form of a thin film.

The invention further relates to the use of compounds, materials and polymers as described above and below in optical, electronic and electrooptical components and devices, preferably in optical films, retarders or compensators having negative optical dispersion.

The invention further relates to an optical, electronic or electrooptical component or device, comprising a compound, material or polymer as described above and below.

Said devices and components include, without limitation, electrooptical displays, LCDs, optical films, retarders, compensators, polarisers, beam splitters, reflective films, alignment layers, colour filters, holographic elements, hot stamping foils, coloured images, decorative or security markings, LC pigments, adhesives, non-linear optic (NLO) devices, optical information storage devices, electronic devices, organic semiconductors, organic field effect transistors (OFET), integrated circuits (IC), thin film transistors (TFT), Radio Frequency Identification (RFID) tags, organic light emitting diodes (OLED), organic light emitting transistors (OLET), electroluminescent displays, organic photovoltaic (OPV) devices, organic solar cells (O-SC), organic laser diodes (O-laser), organic integrated circuits (O-IC), lighting devices, sensor devices, electrode materials, photoconductors, photodetectors, electrophotographic recording devices, capacitors, charge injection layers, Schottky diodes, planarising layers, antistatic films, conducting substrates, conducting patterns, photoconductors, electrophotographic applications, electrophotographic recording, organic memory devices, biosensors, biochips.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** shows the birefringence versus wavelength plot for a polymerised film made from a reactive mesogen of prior art.

FIG. **2** shows the refractive index versus wavelength plot of a modelled molecule with low or negative retardation dispersion, showing increased n_o dispersion and decreased n_e dispersion.

FIG. **3**a and FIG. **3**b do schematically depict a compound according to the present invention.

FIG. **4**a and FIG. **4**b show the birefringence versus wavelength plot for a compound with negative optical dispersion (4a) and positive optical dispersion (4b), respectively.

FIGS. **5**-**8** show the retardation profile of films of the invention.

TERMS AND DEFINITIONS

The term "liquid crystal or mesogenic compound" means a compound comprising one or more calamitic (rod- or board/lath-shaped) or discotic (disk-shaped) mesogenic groups. The term "mesogenic group" means a group with the ability to induce liquid crystal (LC) phase behaviour. The compounds comprising mesogenic groups do not necessarily have to exhibit an LC phase themselves. It is also possible that they show LC phase behaviour only in mixtures with other compounds, or when the mesogenic compounds or materials, or the mixtures thereof, are polymerised. For the sake of simplicity, the term "liquid crystal" is used hereinafter for both mesogenic and LC materials. For an overview of definitions see C. Tschierske, G. Pelzl and S. Diele, Angew. Chem. 2004, 116, 6340-6368.

A calamitic mesogenic group is usually comprising a mesogenic core consisting of one or more aromatic or non-aromatic cyclic groups connected to each other directly or via linkage groups, optionally comprising terminal groups attached to the ends of the mesogenic core, and optionally comprising one or more lateral groups attached to the long side of the mesogenic core, wherein these terminal and lateral groups are usually selected e.g. from carbyl or hydrocarbyl groups, polar groups like halogen, nitro, hydroxy, etc., or polymerisable groups.

The term "reactive mesogen" (RM) means a polymerisable mesogenic or liquid crystal compound.

Polymerisable compounds with one polymerisable group are also referred to as "monoreactive" compounds, compounds with two polymerisable groups as "direactive" compounds, and compounds with more than two polymerisable groups as "multireactive" compounds. Compounds without a polymerisable group are also referred to as "non-reactive" compounds.

The term "film" includes rigid or flexible, self-supporting or free-standing films with mechanical stability, as well as coatings or layers on a supporting substrate or between two substrates.

The term "pi-conjugated" means a group containing mainly C atoms with sp^2-hybridisation, or optionally also sp-hybridisation, which may also be replaced by hetero atoms. In the simplest case this is for example a group with alternating C—C single and double bonds, or triple bonds, but does also include groups like 1,3- or 1,4-phenylene. Also included in this meaning are groups like for example aryl amines, aryl phosphines and certain heterocycles (i.e. conjugation via N-, O-, P- or S-atoms).

The term "carbyl group" means any monovalent or multivalent organic radical moiety which comprises at least one carbon atom either without any non-carbon atoms (like for example $—C \equiv C—$), or optionally combined with at least one non-carbon atom such as N, O, S, P, Si, Se, As, Te or Ge (for example carbonyl etc.). The term "hydrocarbyl group" denotes a carbyl group that does additionally contain one or more H atoms and optionally contains one or more hetero atoms like for example N, O, S, P, Si, Se, As, Te or Ge. A carbyl or hydrocarbyl group comprising a chain of 3 or more C atoms may also be linear, branched and/or cyclic, including spiro and/or fused rings.

On the molecular level, the birefringence of a liquid crystal depends on the anisotropy of the polarizability ($\Delta\alpha=\alpha_{\|}-\alpha\perp$). "Polarizability" means the ease with which the electron distribution in the atom or molecule can be distorted. The polarizability increases with greater number of electrons and a more diffuse electron cloud. The polarizability can be calculated using a method described in eg Jap. J. Appl. Phys. 42, (2003) p 3463.

The "optical retardation" at a given wavelength $R(\lambda)$ (in nm) of a layer of liquid crystalline or birefringent material is defined as the product of birefringence at that wavelength $\Delta n(\lambda)$ and layer thickness d (in nm) according to the equation

$$R(\lambda)=\Delta n(\lambda)\cdot d$$

The optical retardation R represents the difference in the optical path lengths in nanometers traveled by S-polarised and P-polarised light whilst passing through the birefringent material. "On-axis" retardation means the retardation at normal incidence to the sample surface.

The term "negative (optical) dispersion" refers to a birefringent or liquid crystalline material or layer that displays reverse birefringence dispersion where the magnitude of the birefringence (Δn) increases with increasing wavelength (λ). i.e $|\Delta n(450)|<|\Delta n(550)|$, or $\Delta n(450)/\Delta n(550)<1$, where $\Delta n(450)$ and $\Delta n(550)$ are the birefringence of the material measured at wavelengths of 450 nm and 550 nm respectively. In contrast, positive (optical) dispersion" means a material or layer having $|\Delta n(450)|>|\Delta n(550)|$ or $\Delta n(450)/\Delta n(550)>1$. See also for example A. Uchiyama, T. Yatabe "Control of Wavelength Dispersion of Birefringence for Oriented Copolycarbonate Films Containing Positive and Negative Birefringent Units". J. Appl. Phys. Vol. 42 pp 6941-6945 (2003).

This is shown schematically in FIG. **4**a.

Since the optical retardation at a given wavelength is defined as the product of birefringence and layer thickness as described above [$R(\lambda)=\Delta n(\lambda)d$], the optical dispersion can be expressed either as the "birefringence dispersion" by the ratio $\Delta n(450)/\Delta n(550)$, or as "retardation dispersion" by the ratio $R(450)/R(550)$, wherein $R(450)$ and $R(550)$ are the retardation of the material measured at wavelengths of 450 nm and 550 nm respectively. Since the layer thickness d does not change with the wavelength, $R(450)/R(550)$ is equal to $\Delta n(450)/\Delta n(550)$. Thus, a material or layer with negative or reverse dispersion has $R(450)/R(550)<1$ or $|R(450)|<|R(550)|$, and a material or layer with positive or normal dispersion has $R(450)/R(550)>1$ or $|R(450)|>|R(550)|$.

In the present invention, unless stated otherwise "optical dispersion" means the retardation dispersion i.e. the ratio $(R(450)/R(550)$.

The retardation ($R(\lambda)$) of a material can be measured using a spectroscopic ellipsometer, for example the M2000 spectroscopic ellipsometer manufactured by J. A. Woollam Co., This instrument is capable of measuring the optical retardance in nanometers of a birefringent sample e.g. Quartz over a range of wavelengths typically, 370 nm to 2000 nm. From this data it is possible to calculate the dispersion ($R(450)/R(550)$ or $\Delta n(450)/\Delta n(550)$) of a material.

A method for carrying out these measurements was presented at the National Physics Laboratory (London, UK) by N Singh in October 2006 and entitled "Spectroscopic Ellipsometry, Part1—Theory and Fundamentals, Part 2—Practical Examples and Part 3—measurements". In accordance with the measurement procedures described Retardation Measurement (RetMeas) Manual (2002) and Guide to WVASE (2002) (Woollam Variable Angle Spectroscopic Ellipsometer) published by J. A. Woollam Co. Inc (Lincoln, Nebr., USA). Unless stated otherwise, this method is used to determine the retardation of the materials, films and devices described in this invention.

DETAILED DESCRIPTION OF THE INVENTION

Preferably the birefringent polymer film according to the present invention is prepared by polymerising a formulation comprising one or more polymerisable compounds having the structural features as described above and below, hereinafter referred to as "guest component" or "guest compound", and an LC material, hereinafter referred to as "host component" or "host mixture", preferably a polymerisable LC host mixture having a nematic phase. The terms "guest" and "host" do not exclude the possibility that the amount of the guest component in the final LC mixture is >50% by weight, and the amount of the host component in the final LC mixture is <50% by weight.

The birefringent polymer film preferably has positive birefringence and negative (or "reverse") dispersion.

The host component preferably has positive birefringence and positive (or "normal") dispersion.

The guest component preferably has

(1) Negative birefringence at 550 nm and normal (positive) birefringence dispersion (e.g. negative calamitic compound) or

(2) Positive birefringence at 550 nm and reverse (negative) birefringence dispersion. In this case $\Delta n(450)/\Delta n(550)$ can be negative if the guest component has a negative birefringence at 450 nm.

In the guest compounds, the mesogenic groups do preferably exhibit a low polarizability and are preferably calamitic groups, very preferably rod-shaped groups.

The mesogenic groups are preferably comprising mainly non-aromatic, most preferably fully saturated, carbocyclic or heterocyclic groups which are connected directly or via linkage groups, wherein "mainly" means that each mesogenic group comprises more saturated rings than unsaturated or aromatic rings, and very preferably does not comprise more than one unsaturated or aromatic ring.

In the guest compounds, the two mesogenic groups can be identical or different from each other.

The bridging group does preferably exhibit a high polarizability and is preferably consisting mainly, very preferably exclusively, of subgroups selected from pi-conjugated linear groups, aromatic and heteroaromatic groups.

Preferably the bridging group consists, very preferably exclusively, of one or more subgroups selected from groups having a bonding angle of 120° or more, preferably in the range of 180°. Suitable and preferred subgroups include, without limitation, groups comprising sp-hybridised C-atoms, like —C≡C—, or divalent aromatic groups connected to their neighboured groups in para-position, like e.g. 1,4-phenylene, naphthalene-2,6-diyl, indane-2,6-diyl or thieno[3,2-b]thiophene-2,5-diyl.

Preferably the bridging group is connected to an sp^3-hybridised C-atom or Si-atom located in a non-aromatic ring of the mesogenic group. Very preferably the bridging group is connected in axial position to a cyclohexylene or silanane ring comprised in the mesogenic group, which is optionally substituted and wherein one or more non-adjacent C-atoms are optionally replaced by Si and/or one or more non-adjacent CH_2 groups are optionally replaced by —O— and/or —S—.

FIG. **3**a and FIG. **3**b do schematically illustrate the structure of a guest compound according to the present invention, without limiting its scope. Therein 1 denotes mesogenic calamitic groups, 2 denotes a bridging group, 3 denotes polymerisable groups that are attached to the mesogenic groups 1 via spacer groups, and 4 denotes non-polymerisable terminal groups like carbyl or hydrocarbyl.

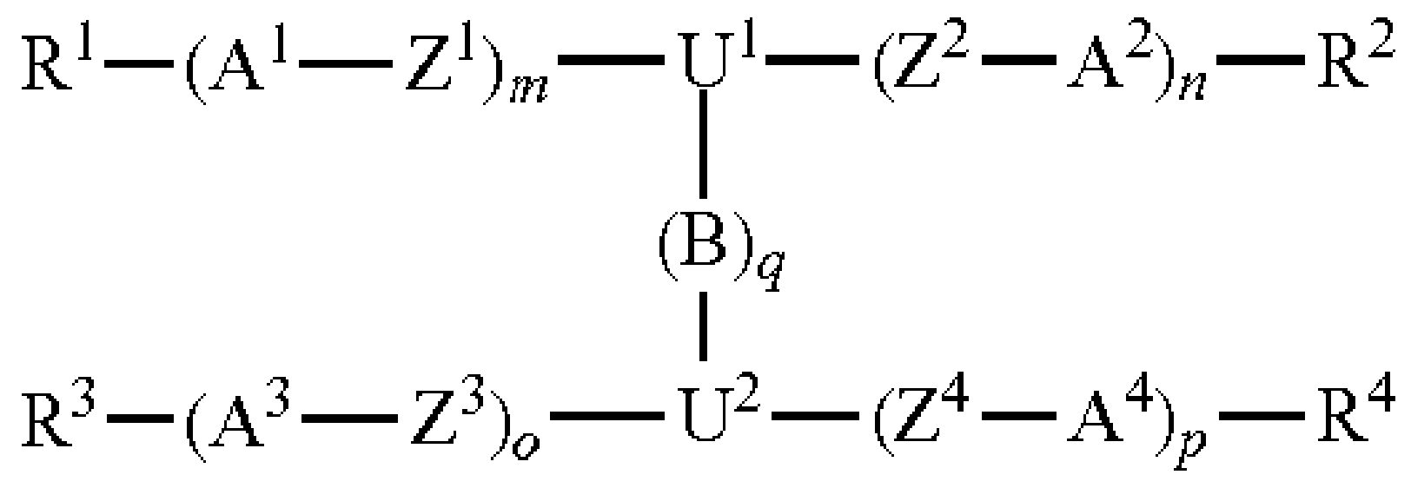
The guest compounds according to the present invention are not limited to the structures shown in FIGS. **3**a and **3**b. For example, the compounds may also comprise polymerisable groups in other positions than those shown in FIGS. **3**a and **3**b, or in addition to those shown in FIGS. **3**a and **3**b, e.g. at the end of the terminal groups 4. The polymerisable groups may also be attached directly to the mesogenic groups without spacer groups. The terminal groups 4 may also be omitted.

Since the bridging group is a linear group consisting of subgroups having bonding angles of approx. 180°, and is linked to the mesogenic groups via an sp^3-hybridised C-atom or Si-atom (i.e. with a bonding angle of approx. 109°), the compounds of the present invention have an H-shaped or L-shaped structure, wherein the mesogenic groups are substantially parallel to each other and substantially perpendicular to the bridging group, as illustrated in FIG. **3**a and FIG. **3**b.

In addition, the bridging group, which essentially consists of subgroups with pi-conjugation, has a high polarizability and a high refractive index, whereas the mesogenic groups, which essentially consist of non-aromatic rings, have a low polarizability and a low refractive index. As a result, the compounds show, depending on their exact structure, either positive birefringence and negative dispersion, as schematically depicted in FIG. **4**a, or negative birefringence with positive dispersion, as schematically depicted in FIG. **4**b.

As a reference normal calamitic materials have positive birefringence and polsitive dispersion. It is desirable to have materials where the magnitude of Δn decreases at shorter wavelength, and compounds with both positive dispersion and negative birefringence can be mixed with a host material to give a mixture which possesses a range of dispersion (depending on the concentration of the dopant and host) varying from positive birefringence with positive dispersion through to positive birefringence with negative dispersion.

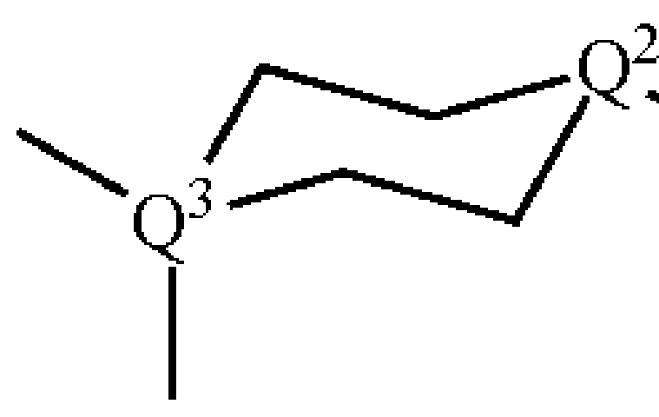
Preferably the guest compounds are selected of formula I



$$\begin{array}{c} R^1-(A^1-Z^1)_m-U^1-(Z^2-A^2)_n-R^2 \\ | \\ (B)_q \\ | \\ R^3-(A^3-Z^3)_o-U^2-(Z^4-A^4)_p-R^4 \end{array} \qquad \text{I}$$

wherein

$U^{1,2}$ are independently of each other selected from



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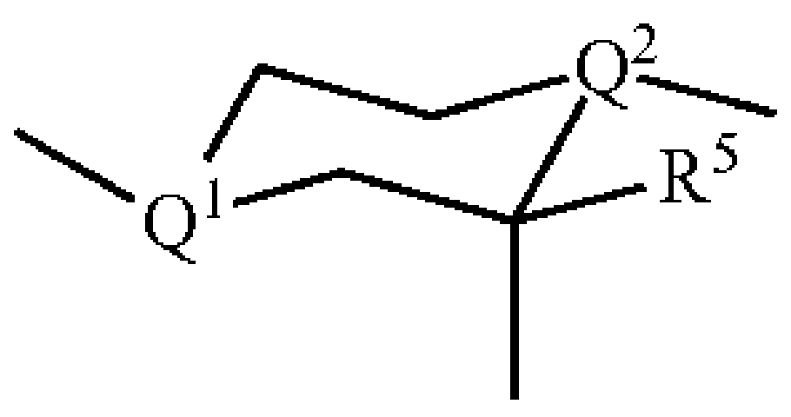

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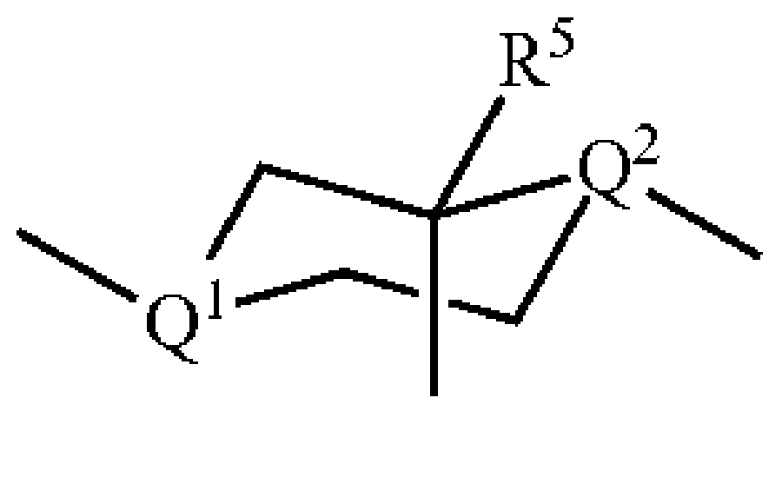


including their mirror images, wherein the rings U^1 and U^2 are each bonded to the group $-(B)_q-$ via the axial bond, and one or two non-adjacent CH_2 groups in these rings are optionally replaced by O and/or S, and the rings U^1 and U^2 are optionally substituted by one or more groups L,

$Q^{1,2}$ are independently of each other CH or SiH,

Q^3 is C or Si,

B is in each occurrence independently of one another —C≡C—, $-CY^1=CY^2-$ or an optionally substituted aromatic or heteroaromatic group,

$Y^{1,2}$ are independently of each other H, F, Cl, CN or R^0,

q is an integer from 1 to 10, preferably 1, 2, 3, 4, 5 or 6,

A^{1-4} are independently of each other selected from non-aromatic, aromatic or heteroaromatic carbocylic or heterocyclic groups, which are optionally substituted by one or more groups R^5, and wherein each of $-(A^1-Z^1)_m-U^1-(Z^2-A^2)_n-$ and $-(A^3-Z^3)_o-U^2-(Z^4-A^4)_p-$ does not contain more aromatic groups than non-aromatic groups and preferably does not contain more than one aromatic group,

Z^{1-4} are independently of each other —O—, —S—, —CO—, —COO—, —OCO—, —O—COO—, $-CO-NR^0-$, $-NR^0-CO-$, $-NR^0-CO-NR^0-$, $-OCH_2-$, $-CH_2O-$, $-SCH_2-$, $-CH_2S-$, $-CF_2O-$, $-OCF_2-$, $-CF_2S-$, $-SCF_2-$, $-CH_2CH_2-$, $-(CH_2)_3-$, $(CH_2)_4-$, $-CF_2CH_2-$, $-CH_2CF_2-$, $-CF_2CF_2-$, —CH═CH—, $-CY^1=CY^2-$, —CH═N—, —N═CH—, —N═N—, $-CH=CR^0-$, —C≡C—, —CH═CH—COO—, —OCO—CH═CH—, CR^0R^{00} or a single bond,

R^0 and R^{00} are independently of each other H or alkyl with 1 to 12 C-atoms,

m and n are independently of each other 0, 1, 2, 3 or 4,

o and p are independently of each other 0, 1, 2, 3 or 4,

R^{1-5} are independently of each other identical or different groups selected from H, halogen, —CN, —NC, —NCO, —NCS, —OCN, —SCN, $-C(=O)NR^0R^{00}$, $-C(=O)X^0$, $-C(=O)R^0$, $-NH_2$, $-NR^0R^{00}$, —SH, $-SR^0$, $-SO_3H$, $-SO_2R^0$, —OH, $-NO_2$, $-CF_3$, $-SF_5$, P-Sp-, optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 40 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, or denote P or P-Sp-, or are substituted by P or P-Sp-, wherein the compounds comprise at least one group R^{1-5} denoting or being substituted by P or P-Sp-,

P is a polymerizable group,

Sp is a spacer group or a single bond.

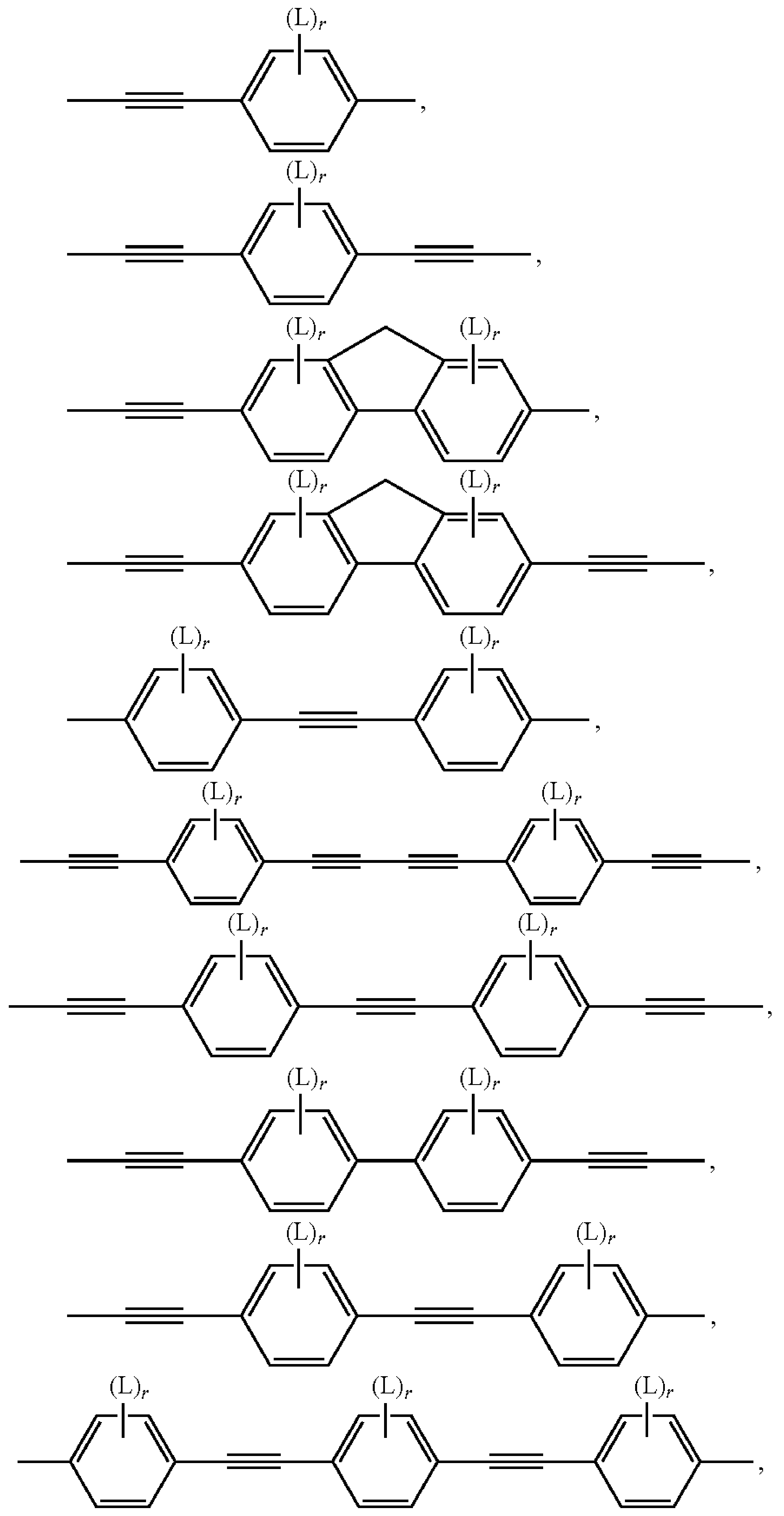
In the guest compounds of the present invention, the subgroups forming the bridging group, like B in formula I, are preferably selected from groups having a bonding angle of 120° or more, preferably in the range of 180°. Very preferred are —C≡C— groups or divalent aromatic groups connected to their adjacent groups in para-position, like e.g. 1,4-phenylene, naphthalene-2,6-diyl, indane-2,6-diyl or thieno[3,2-b]thiophene-2,5-diyl.

Further possible subgroups include —CH═CH—, $-CY^1=CY^2-$, —CH═N—, —N═CH—, —N═N— and $-CH=CR^0-$ wherein Y^1, Y^2, R^0 have the meanings given above.

Preferably the bridging group, like $-(B)_q-$ in formula I, comprises one or more groups selected from the group consisting of —C≡C—, optionally substituted 1,4-phenylene and optionally substituted 9H-fluorene-2,7-diyl. The subgroups, or B in formula I, are preferably selected from the group consisting of —C≡C—, optionally substituted 1,4-phenylene and optionally substituted 9H-fluorene-2,7-

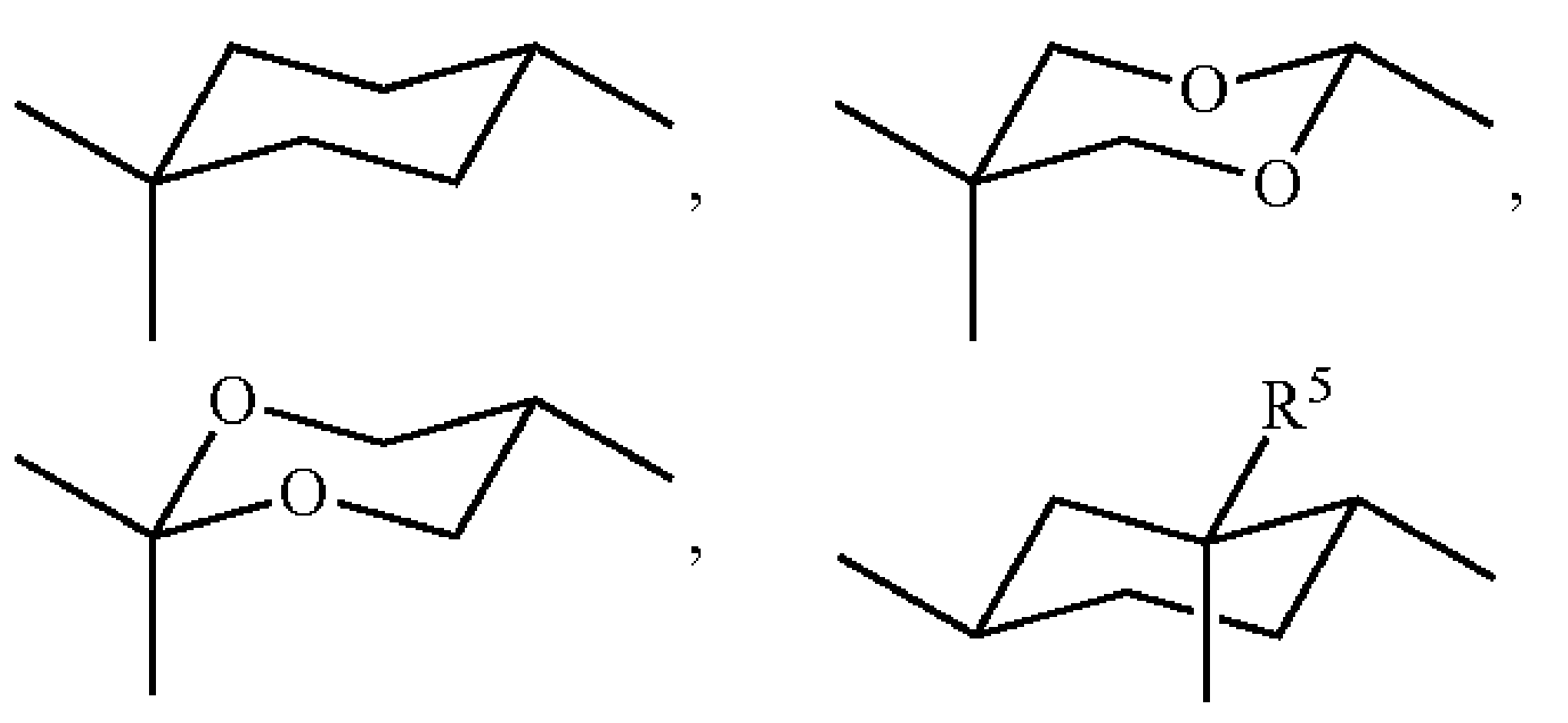
diyl, wherein in the fluorene group the H-atom in 9-position is optionally replaced by a carbyl or hydrocarbyl group.

Very preferably the bridging group, or —$(B)_q$— in formula I, are selected from —C≡C—, —C≡C—C≡C—, —C≡C—C≡C—C≡C—, —C≡C—C≡C—C≡C—C≡C—,



wherein r is 0, 1, 2, 3 or 4 and L has the meaning as described below.

In the guest compounds of the present invention, the non-aromatic rings of the mesogenic groups where the bridging group is attached, like U^1 and U^2 in formula I, are preferably selected from



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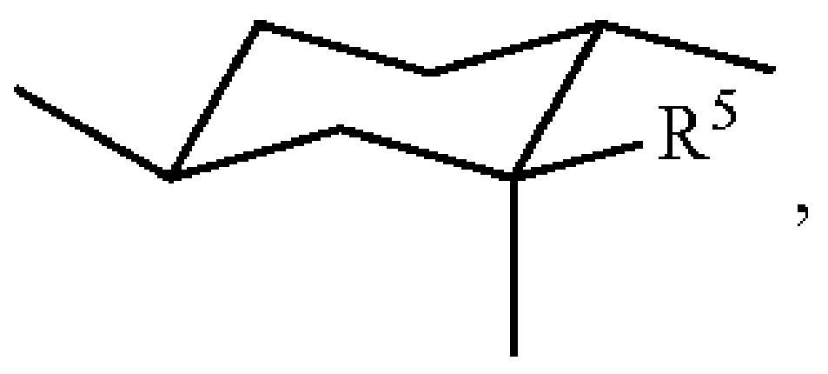


wherein R^5 is as defined in formula I.

In the guest compounds of the present invention, the aromatic groups, like A^{1-4} in formula I, may be mononuclear, i.e. having only one aromatic ring (like for example phenyl or phenylene), or polynuclear, i.e. having two or more fused rings (like for example napthyl or naphthylene). Especially preferred are mono-, bi- or tricyclic aromatic or heteroaromatic groups with up to 25 C atoms that may also comprise fused rings and are optionally substituted.

Preferred aromatic groups include, without limitation, benzene, biphenylene, triphenylene, [1,1':3'1"]terphenyl-2'-ylene, naphthalene, anthracene, binaphthylene, phenanthrene, pyrene, dihydropyrene, chrysene, perylene, tetracene, pentacene, benzpyrene, fluorene, indene, indenofluorene, spirobifluorene, etc.

Preferred heteroaromatic groups include, without limitation, 5-membered rings like pyrrole, pyrazole, imidazole, 1,2,3-triazole, 1,2,4-triazole, tetrazole, furan, thiophene, selenophene, oxazole, isoxazole, 1,2-thiazole, 1,3-thiazole, 1,2,3-oxadiazole, 1,2,4-oxadiazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, 1,3,4-thiadiazole, 6-membered rings like pyridine, pyridazine, pyrimidine, pyrazine, 1,3,5-triazine, 1,2,4-triazine, 1,2,3-triazine, 1,2,4,5-tetrazine, 1,2,3,4-tetrazine, 1,2,3,5-tetrazine, and fused systems like carbazole, indole, isoindole, indolizine, indazole, benzimidazole, benzotriazole, purine, naphthimidazole, phenanthrimidazole, pyridimidazole, pyrazinimidazole, quinoxalinimidazole, benzoxazole, naphthoxazole, anthroxazole, phenanthroxazole, isoxazole, benzothiazole, benzofuran, isobenzofuran, dibenzofuran, quinoline, isoquinoline, pteridine, benzo-5,6-quinoline, benzo-6,7-quinoline, benzo-7,8-quinoline, benzoisoquinoline, acridine, phenothiazine, phenoxazine, benzopyridazine, benzopyrimidine, quinoxaline, phenazine, naphthyridine, azacarbazole, benzocarboline, phenanthridine, phenanthroline, thieno[2,3b]thiophene, thieno[3,2b]thiophene, dithienothiophene, dithienopyridine, isobenzothiophene, dibenzothiophene, benzothiadiazothiophene, or combinations thereof.

In the compounds of the present invention, the non-aromatic carbocyclic and heterocyclic rings, like A^{1-4} in formula I, include those which are saturated (also referred to as "fully saturated"), i.e. they do only contain C-atoms or hetero atoms connected by single bonds, and those which are unsaturated (also referred to as "partially saturated"), i.e. they also comprise C-atoms or hetero atoms connected by double bonds. The non-aromatic rings may also comprise one or more hetero atoms, preferably selected from Si, O, N and S.

The non-aromatic carbocyclic and heterocyclic groups may be mononuclear, i.e. having only one ring (like for example cyclohexane), or polynuclear, i.e. having two or more fused rings (like for example decahydronaphthalene or bicyclooctane). Especially preferred are fully saturated groups. Further preferred are mono-, bi- or tricyclic non-aromatic groups with up to 25 C atoms that optionally comprise fused rings and are optionally substituted. Very preferred are 5-, 6-, 7- or 8-membered carbocyclic rings wherein one or more non-adjacent C-atoms are optionally replaced by Si and/or one or more non-adjacent CH groups are optionally replaced by N and/or one or more non-adjacent CH_2 groups are optionally replaced by —O— and/or —S—, all of which are optionally substituted.

Preferred non-aromatic groups include, without limitation, 5-membered rings like cyclopentane, tetrahydrofuran, tetrahydrothiofuran, pyrrolidine, 6-membered rings like cyclohexane, silinane, cyclohexene, tetrahydropyran, tetrahydrothiopyran, 1,3-dioxane, 1,3-dithiane, piperidine, 7-membered rings like cycloheptane, and fused systems like bicyclo[2.2.2]octane, tetrahydronaphthalene, decahydronaphthalene, indane, or combinations thereof.

Preferably the non-aromatic and aromatic rings, or A^{1-4} in formula I, are selected from trans-1,4-cyclohexylene and 1,4-phenylene that is optionally substituted with one or more groups L.

Preferably the mesogenic groups comprise not more than one, very preferably no aromatic ring, most preferably no aromatic or unsaturated ring.

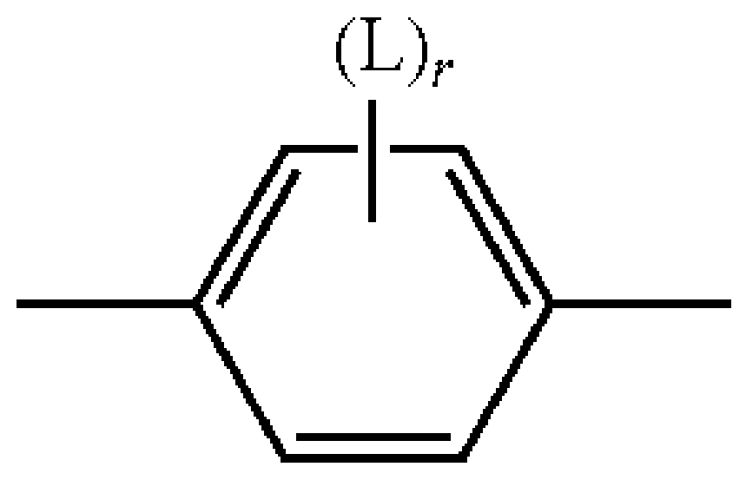
Very preferred are compounds of formula I wherein m and p are 1 and n and o are 1 or 2. Further preferred are compounds of formula I wherein m and p are 1 or 2 and n and o are 0. Further preferred are compounds wherein m, n, o and p are 2.

In the guest compounds of the present invention, the linkage groups connecting the aromatic and non-aromatic cyclic groups in the mesogenic groups, like Z^{1-4} in formula I, are preferably selected from —O—, —S—, —CO—, —COO—, —OCO—, —O—COO—, —CO—NR^0—, —NR^0—CO—, —NR^0—CO—NR^0—, —OCH_2—, —CH_2O—, —SCH_2—, —CH_2S—, —CF_2O—, —OCF_2—, —CF_2S—, —SCF_2—, —CH_2CH_2—, —$(CH_2)_3$, —$(CH_2)_4$—, —CF_2CH_2—, —CH_2CF_2—, —CF_2CF_2—, —CH=CH—, —CY^1=CY^2—, —CH=N—, —N=CH—, —N=N—, —CH=CR^0—, —C≡C—, —CH=CH—COO—, —OCO—CH=CH—, CR^0R^{00} or a single bond, very preferably from —COO—, —OCO— and a single bond.

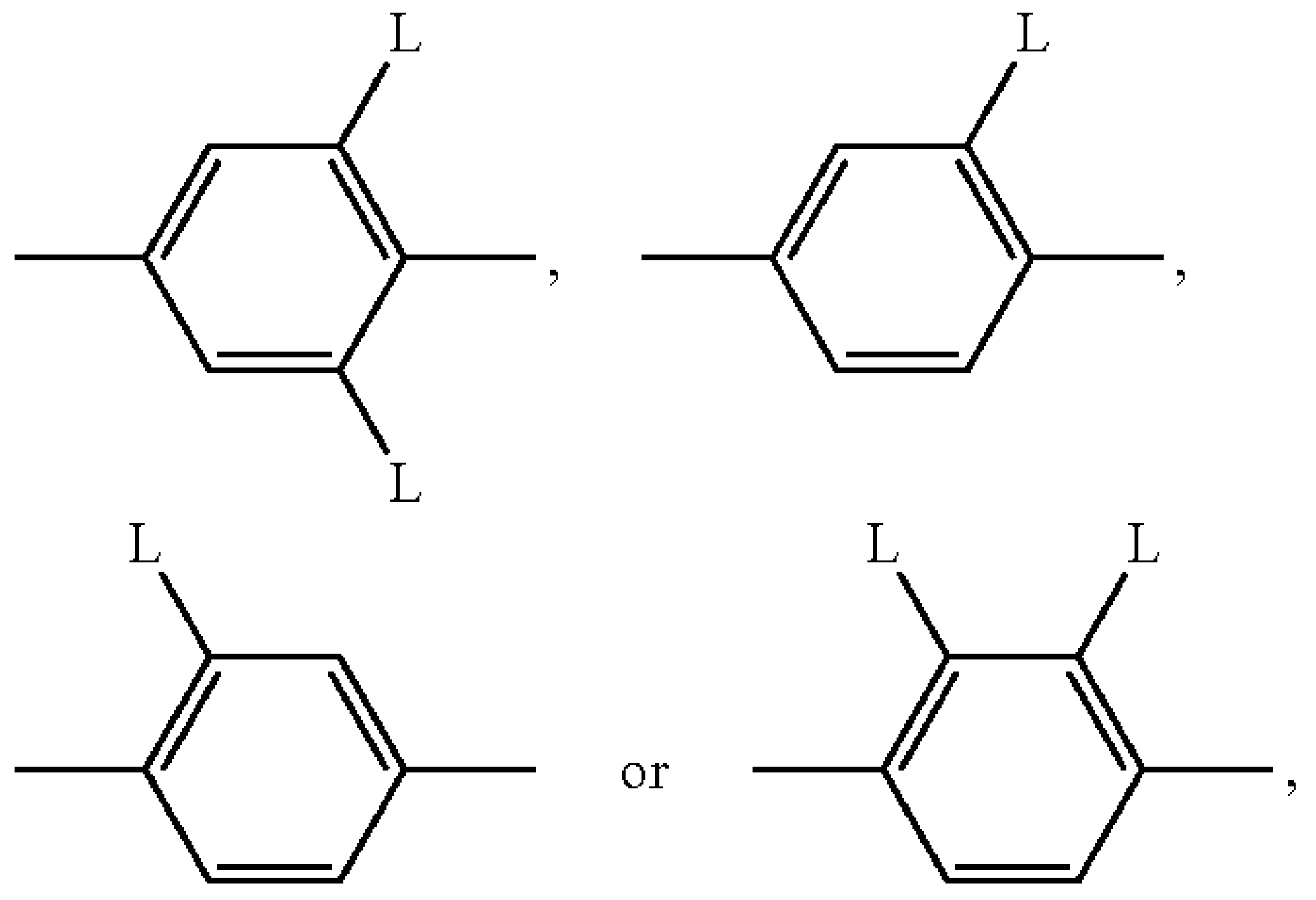
In the guest compounds of the present invention, the substituents on the rings, like L in formula I, are preferably selected from P-Sp-, F, Cl, Br, I, —CN, —NO_2, —NCO, —NCS, —OCN, —SCN, —C(=O)NR^0R^{00}, —C(=O)X, —C(=O)OR^0, —C(=O)R^0, —NR^0R^0, —OH, —SF_5, optionally substituted silyl, aryl or heteroaryl with 1 to 12, preferably 1 to 6 C atoms, and straight chain or branched alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy with 1 to 12, preferably 1 to 6 C atoms, wherein one or more H atoms are optionally replaced by F or Cl, wherein R^0 and R^{00} are as defined in formula I and X is halogen.

Preferred substituents are selected from F, Cl, CN, NO_2 or straight chain or branched alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl, alkylcarbonlyoxy or alkoxycarbonyloxy with 1 to 12 C atoms, wherein the alkyl groups are optionally perfluorinated, or P-Sp-.

Very preferred substituents are selected from F, Cl, CN, NO_2, CH_3, C_2H_5, $C(CH_3)_3$, $CH(CH_3)_2$, $CH_2CH(CH_3)C_2H_5$, OCH_3, OC_2H_5, $COCH_3$, COC_2H_5, $COOCH_3$, $COOC_2H_5$, CF_3, OCF_3, $OCHF_2$, OC_2F_5 or P-Sp-, in particular F, Cl, CN, CH_3, C_2H_5, $C(CH_3)_3$, $CH(CH_3)_2$, OCH_3, $COCH_3$ or OCF_3, most preferably F, Cl, CH_3, $C(CH_3)_3$, OCH_3 or $COCH_3$, or P-Sp-.



is preferably



with L having each independently one of the meanings given above.

In the guest compounds of the present invention, the carbyl and hydrocarbyl groups, like R^{1-5} in formula I, are preferably selected from straight-chain, branched or cyclic alkyl with 1 to 40, preferably 1 to 25 C-atoms, which is unsubstituted, mono- or polysubstituted by F, Cl, Br, I or CN, and wherein one or more non-adjacent CH_2 groups are optionally replaced, in each case independently from one another, by —O—, —S—, —NH—, —NR^0—, —SiR^0R^{00}—, —CO—, —COO—, —OCO—, —O—CO—O—, —S—CO—, —CO—S—, —SO_2—, —CO—NR^0—, —NR^0—CO—, —NR^0—CO—NR^{00}—, —CY^1=CY^2— or —C≡C— in such a manner that O and/or S atoms are not linked directly to one another, wherein Y^1 and Y^2 are independently of each other H, F, Cl or CN, and R^0 and R^{00} are independently of each other H or an optionally substituted aliphatic or aromatic hydrocarbon with 1 to 20 C atoms.

Very preferably the carbyl and hydrocarbyl groups, and R^{1-5} in formula I, are selected from, C_1-C_{20}-alkyl, C_1-C_{20}-oxaalkyl, C_1-C_{20}-alkoxy, C_2-C_{20}-alkenyl, C_2-C_{20}-alkynyl, C_1-C_{20}-thioalkyl, C_1-C_{20}-silyl, C_1-C_{20}-ester, C_1-C_{20}-amino, C_1-C_{20}-fluoroalkyl.

An alkyl or alkoxy radical, i.e. where the terminal CH_2 group is replaced by —O—, can be straight-chain or branched. It is preferably straight-chain, has 2, 3, 4, 5, 6, 7 or 8 carbon atoms and accordingly is preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, or octoxy, furthermore methyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, nonoxy, decoxy, undecoxy, dodecoxy, tridecoxy or tetradecoxy, for example.

Oxaalkyl, i.e. where one CH_2 group is replaced by —O—, is preferably straight-chain 2-oxapropyl(=methoxymethyl), 2-(=ethoxymethyl) or 3-oxabutyl(=2-methoxyethyl), 2-, 3-, or 4-oxapentyl, 2-, 3-, 4-, or 5-oxahexyl, 2-, 3-, 4-, 5-, or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl or 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl, for example.

An alkyl group wherein one or more CH_2 groups are replaced by —CH=CH— can be straight-chain or branched. It is preferably straight-chain, has 2 to 10 C atoms and accordingly is preferably vinyl, prop-1-, or prop-2-enyl, but-1-, 2- or but-3-enyl, pent-1-, 2-, 3- or pent-4-enyl, hex-1-, 2-, 3-, 4- or hex-5-enyl, hept-1-, 2-, 3-, 4-, 5- or hept-6-enyl, oct-1-, 2-, 3-, 4-, 5-, 6- or oct-7-enyl, non-1-, 2-, 3-, 4-, 5-, 6-, 7- or non-8-enyl, dec-1-, 2-, 3-, 4-, 5-, 6-, 7-, 8- or dec-9-enyl.

Especially preferred alkenyl groups are C_2-C_7-1E-alkenyl, C_4-C_7-3E-alkenyl, C_5-C_7-4-alkenyl, C_6-C_7-5-alkenyl and C_7-6-alkenyl, in particular C_2-C_7-1E-alkenyl, C_4-C_7-3E-alkenyl and C_5-C_7-4-alkenyl. Examples for particularly preferred alkenyl groups are vinyl, 1E-propenyl, 1E-butenyl, 1E-pentenyl, 1E-hexenyl, 1E-heptenyl, 3-butenyl, 3E-pentenyl, 3E-hexenyl, 3E-heptenyl, 4-pentenyl, 4Z-hexenyl, 4E-hexenyl, 4Z-heptenyl, 5-hexenyl, 6-heptenyl and the like. Groups having up to 5 C atoms are generally preferred.

In an alkyl group wherein one CH_2 group is replaced by —O— and one by —CO—, these radicals are preferably neighboured. Accordingly these radicals together form a carbonyloxy group —CO—O— or an oxycarbonyl group —O—CO—. Preferably this group is straight-chain and has 2 to 6 C atoms. It is accordingly preferably acetyloxy, propionyloxy, butyryloxy, pentanoyloxy, hexanoyloxy, acetyloxymethyl, propionyloxymethyl, butyryloxymethyl, pentanoyloxymethyl, 2-acetyloxyethyl, 2-propionyloxyethyl, 2-butyryloxyethyl, 3-acetyloxypropyl, 3-propionyloxypropyl, 4-acetyloxybutyl, methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, butoxycarbonyl, pentoxycarbonyl, methoxycarbonylmethyl, ethoxy-carbonylmethyl, propoxycarbonylmethyl, butoxycarbonylmethyl, 2-(methoxycarbonyl)ethyl, 2-(ethoxycarbonyl)ethyl, 2-(propoxy-carbonyl) ethyl, 3-(methoxycarbonyl)propyl, 3-(ethoxycarbonyl) propyl, 4-(methoxycarbonyl)-butyl.

An alkyl group wherein two or more CH_2 groups are replaced by —O— and/or —COO— can be straight-chain or branched. It is preferably straight-chain and has 3 to 12 C atoms. Accordingly it is preferably bis-carboxy-methyl, 2,2-bis-carboxy-ethyl, 3,3-bis-carboxy-propyl, 4,4-bis-carboxy-butyl, 5,5-bis-carboxy-pentyl, 6,6-bis-carboxy-hexyl, 7,7-bis-carboxy-heptyl, 8,8-bis-carboxy-octyl, 9,9-bis-carboxy-nonyl, 10,10-bis-carboxy-decyl, bis-(methoxycarbonyl)-methyl, 2,2-bis-(methoxycarbonyl)-ethyl, 3,3-bis-(methoxycarbonyl)-propyl, 4,4-bis-(methoxycarbonyl)-butyl, 5,5-bis-(methoxycarbonyl)-pentyl, 6,6-bis-(methoxycarbonyl)-hexyl, 7,7-bis-(methoxycarbonyl)-heptyl, 8,8-bis-(methoxycarbonyl)-octyl, bis-(ethoxycarbonyl)-methyl, 2,2-bis-(ethoxycarbonyl)-ethyl, 3,3-bis-(ethoxycarbonyl)-propyl, 4,4-bis-(ethoxycarbonyl)-butyl, 5,5-bis-(ethoxycarbonyl)-hexyl.

An alkyl or alkenyl group that is monosubstituted by CN or CF_3 is preferably straight-chain. The substitution by CN or CF_3 can be in any desired position.

An alkyl or alkenyl group that is at least monosubstituted by halogen is preferably straight-chain. Halogen is preferably F or Cl, in case of multiple substitution preferably F. The resulting groups include also perfluorinated groups. In case of monosubstitution the F or Cl substituent can be in any desired position, but is preferably in ω-position. Examples for especially preferred straight-chain groups with a terminal F substituent are fluoromethyl, 2-fluorethyl, 3-fluorpropyl, 4-fluorbutyl, 5-fluorpentyl, 6-fluorhexyl and 7-fluorheptyl. Other positions of F are, however, not excluded.

R^0 and R^{00} are preferably selected from H, straight-chain or branched alkyl with 1 to 12 C atoms.

—CY^1═CY^2— is preferably —CH═CH—, —CF═CF— or —CH═C(CN)—.

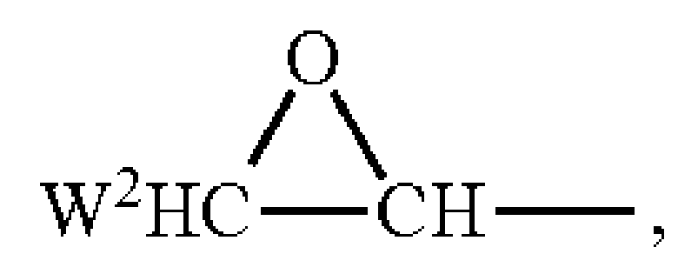
Halogen is F, Cl, Br or I, preferably F or Cl.

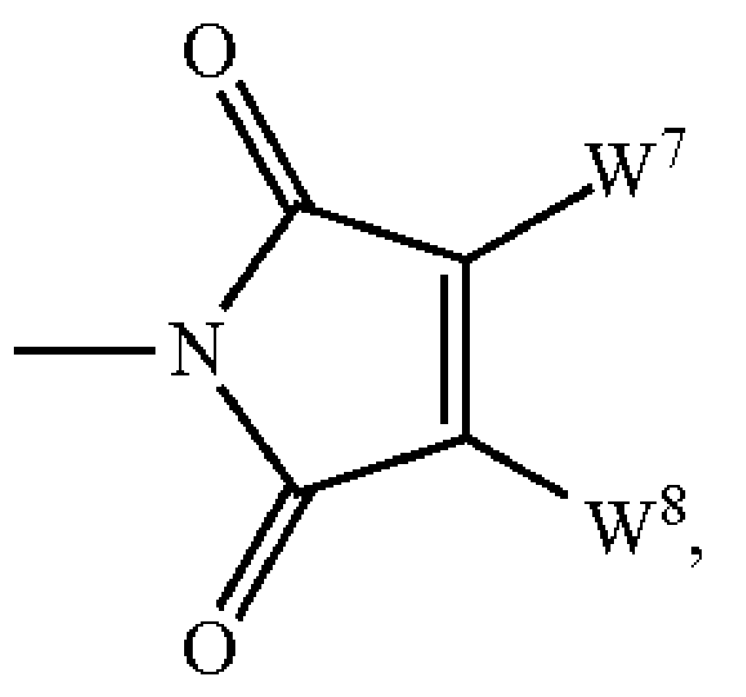
R^{1-5} can be an achiral or a chiral group. Particularly preferred chiral groups are 2-butyl(=1-methylpropyl), 2-methylbutyl, 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 2-propylpentyl, in particular 2-methylbutyl, 2-methylbutoxy, 2-methylpentoxy, 3-methylpentoxy, 2-ethylhexoxy, 1-methylhexoxy, 2-octyloxy, 2-oxa-3-methylbutyl, 3-oxa-4-methylpentyl, 4-methylhexyl, 2-hexyl, 2-octyl, 2-nonyl, 2-decyl, 2-dodecyl, 6-methoxyoctoxy, 6-methyloctoxy, 6-methyloctanoyloxy, 5-methylheptyloxycarbonyl, 2-methylbutyryloxy, 3-methylvaleroyloxy, 4-methylhexanoyloxy, 2-chlorpropionyloxy, 2-chloro-3-methylbutyryloxy, 2-chloro-4-methylvaleryloxy, 2-chloro-3-methylvaleryloxy, 2-methyl-3-oxapentyl, 2-methyl-3-oxahexyl, 1-methoxypropyl-2-oxy, 1-ethoxypropyl-2-oxy, 1-propoxypropyl-2-oxy, 1-butoxypropyl-2-oxy, 2-fluorooctyloxy, 2-fluorodecyloxy, 1,1,1-trifluoro-2-octyloxy, 1,1,1-trifluoro-2-octyl, 2-fluoromethyloctyloxy for example. Very preferred are 2-hexyl, 2-octyl, 2-octyloxy, 1,1,1-trifluoro-2-hexyl, 1,1,1 -trifluoro-2-octyl and 1,1,1-trifluoro-2-octyloxy.

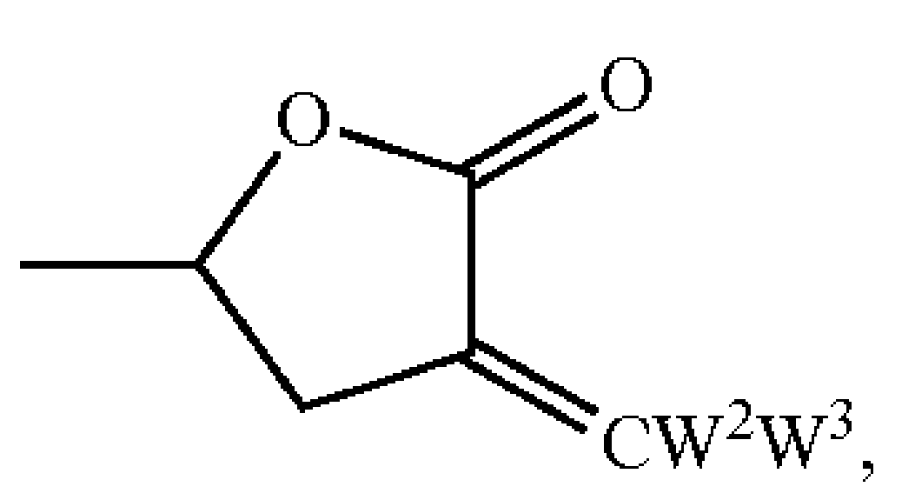
Preferred achiral branched groups are isopropyl, isobutyl (=methylpropyl), isopentyl(=3-methylbutyl), isopropoxy, 2-methyl-propoxy and 3-methylbutoxy.

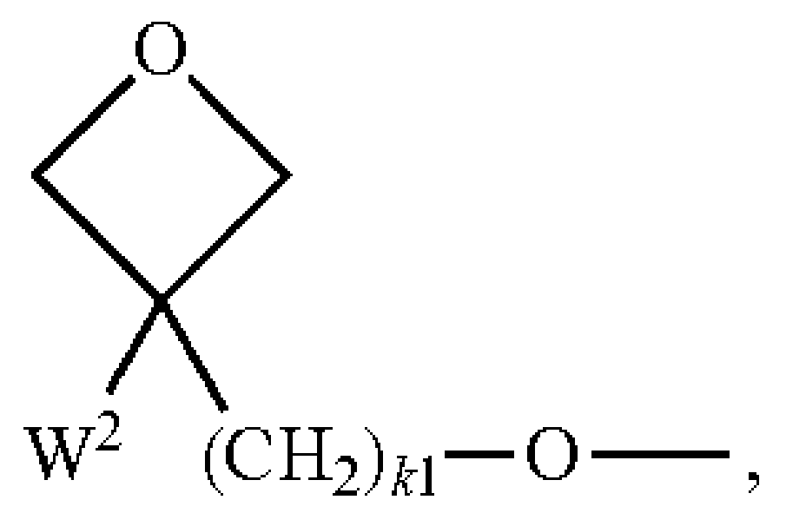
In the guest compounds of the present invention, the polymerisable group, like P in formula I, is a group that is capable of participating in a polymerisation reaction, like radical or ionic chain polymerisation, polyaddition or polycondensation, or capable of being grafted, for example by condensation or addition, to a polymer backbone in a polymer analogous reaction. Especially preferred are polymerisable groups for chain polymerisation reactions, like radical, cationic or anionic polymerisation. Very preferred are polymerisable groups comprising a C—C double or triple bond, and polymerisable groups capable of polymerisation by a ring-opening reaction, like oxetanes or epoxides.

Suitable and preferred polymerisable groups include, without limitation, CH_2═CW^1—COO—, CH_2═CW^1—CO—,



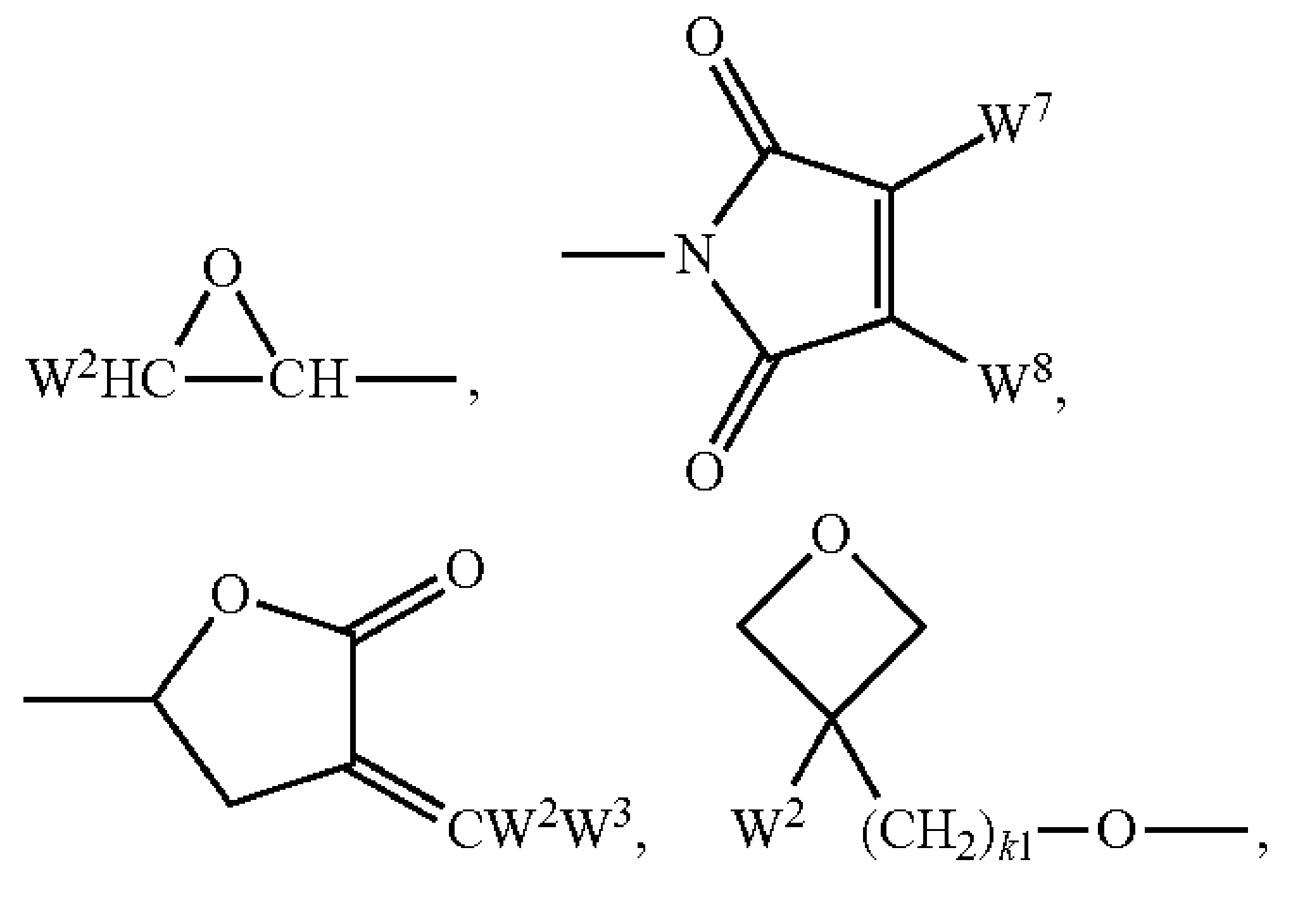






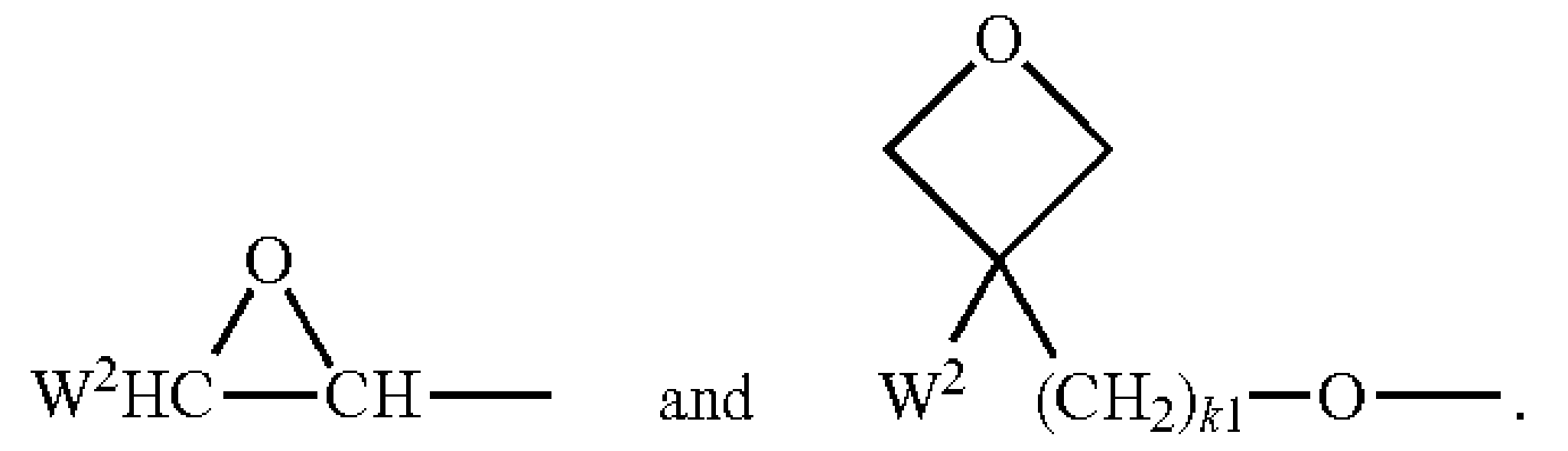
CH_2═CW^2—$(O)_{k1}$—, CH_3—CH═CH—O—, $(CH_2$═$CH)_2CH$—OCO—, $(CH_2$═CH—$CH_2)_2CH$—OCO—, $(CH_2$═$CH)_2CH$—O—, $(CH_2$═CH—$CH_2)_2N$—, $(CH_2$═CH—$CH_2)_2N$—CO—, HO—CW^2W^3—, HS—CW^2W^3—, HW^2N—, HO—CW^2W^3—NH—, CH_2═CW^1—CO—NH—, CH_2═CH—$(COO)_{k1}$-Phe-$(O)_{k2}$—, CH_2═CH—$(CO)_{k1}$-Phe-$(O)_{k2}$—, Phe-CH═CH—, HOOC—, OCN—, and $W^4W^5W^6Si$—, with W^1 being H, F, Cl, CN, CF_3, phenyl or alkyl with 1 to 5 C-atoms, in particular H, F, C_1 or CH_3, W^2 and W^3 being independently of each other H or alkyl with 1 to 5 C-atoms, in particular H, methyl, ethyl or n-propyl, W^4, W^5 and W^6 being independently of each other Cl, oxaalkyl or oxacarbonylalkyl with 1 to 5 C-atoms, W^7 and W^8 being independently of each other H, Cl or alkyl with 1 to 5 C-atoms, Phe being 1,4-phenylene that is optionally substituted, preferably by one or more groups L as defined above (except for the meaning P-Sp-), and k_1 and k_2 being independently of each other 0 or 1.

Very preferred polymerisable groups are selected from CH_2═CW^1—COO—, CH_2═CW^1—CO—,



(CH$_2$=CH)$_2$CH—OCO—, (CH$_2$=CH—CH$_2$)$_2$CH—OCO—, (CH$_2$=CH)$_2$CH—O—, (CH$_2$=CH—CH$_2$)$_2$N—, (CH$_2$=CH—CH$_2$)$_2$N—CO—, HO—CW^{2}W^3—, HS—CW^{2}W^3—, HW^{2}N—, HO—CW^{2}W^3—NH—, CH$_2$=CW^1—CO—NH—, CH$_2$=CH—(COO)$_{k1}$-Phe-(O)$_{k2}$—, CH$_2$=CH—(CO)$_{k1}$-Phe-(O)$_{k2}$—, Phe-CH=CH—, HOOC—, OCN—, and W^{4}W^{5}W^{6}Si—, with W^1 being H, F, Cl, CN, CF$_3$, phenyl or alkyl with 1 to 5 C-atoms, in particular H, F, C$_1$ or CH$_3$, W^2 and W^3 being independently of each other H or alkyl with 1 to 5 C-atoms, in particular H, methyl, ethyl or n-propyl, W^4, W^5 and W^6 being independently of each other Cl, oxaalkyl or oxacarbonylalkyl with 1 to 5 C-atoms, W^7 and W^8 being independently of each other H, Cl or alkyl with 1 to 5 C-atoms, Phe being 1,4-phenylene that is optionally substituted preferably by one or more groups L as defined above (except for the meaning P-Sp-), and k$_1$ and k$_2$ being independently of each other 0 or 1.

Most preferred polymerisable groups are selected from CH$_2$=CH—COO—, CH$_2$=C(CH$_3$)—COO—, CH$_2$=CF—COO—, (CH$_2$=CH)$_2$CH—OCO—, (CH$_2$=CH)$_2$CH—O—,



Polymerisation can be carried out according to methods that are known to the ordinary expert and described in the literature, for example in D. J. Broer; G. Challa; G. N. Mol, Macromol. Chem., 1991, 192, 59.

The term "spacer group" is known in prior art and suitable spacer groups, like Sp in formula I, are known to the skilled person (see e.g. Pure Appl. Chem. 73(5), 888 (2001). The spacer group is preferably selected of formula Sp'-X', such that P-Sp- is P-Sp'-X'—, wherein

Sp' is alkylene with 1 to 20 C atoms, preferably 1 to 12 C-atoms, which is optionally mono- or polysubstituted by F, Cl, Br, I or CN, and wherein one or more non-adjacent CH$_2$ groups are optionally replaced, in each case independently from one another, by —O—, —S—, —NH—, —NR^0—, —SiR^{0}R^{00}—, —CO—, —COO—, —OCO—, —OCO—O—, —S—CO—, —CO—S—, —NR^0—CO—O—, —O—CO—NR^0—, —NR^0—CO—NR^0—, —CH=CH— or —C≡C— in such a manner that O and/or S atoms are not linked directly to one another,

X' is —O—, —S—, —CO—, —COO—, —OCO—, —O—COO—, —CO—NR^0—, —NR^0—CO—, —NR^0—CO—NR^0—, —OCH$_2$—, —CH$_2$O—, —SCH$_2$—, —CH$_2$S—, —CF$_2$O—, —OCF$_2$—, —CF$_2$S—, —SCF$_2$—, —CF$_2$CH$_2$—, —CH$_2$CF$_2$—, —CF$_2$CF$_2$—, —CH=N—, —N=CH—, —N=N—, —CH=CR^0—, —CY^1=CY^2—, —C≡C—, —CH=CH—COO—, —OCO—CH=CH— or a single bond,

R^0 and R^{00} are independently of each other H or alkyl with 1 to 12 C-atoms, and

Y^1 and Y^2 are independently of each other H, F, Cl or CN.

X' is preferably —O—, —S—CO—, —COO—, —OCO—, —O—COO—, —CO—NR^0—, —NR^0—CO—, —NR^0—CO—NR^0— or a single bond.

Typical groups Sp' are, for example, —(CH$_2$)$_{p1}$—, —(CH$_2$CH$_2$O)$_{q1}$—CH$_2$CH$_2$—, —CH$_2$CH$_2$—S—CH$_2$CH$_2$— or —CH$_2$CH$_2$—NH—CH$_2$CH$_2$— or —(SiR^{0}R^{00}—O)$_{p1}$—, with p1 being an integer from 2 to 12, q1 being an integer from 1 to 3 and R^0 and R^{00} having the meanings given above.

Preferred groups Sp' are ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene, dodecylene, octadecylene, ethyleneoxyethylene, methyleneoxy-butylene, ethylene-thioethylene, ethylene-N-methyl-iminoethylene, 1-methylalkylene, ethenylene, propenylene and butenylene for example. Further preferred are chiral spacer groups.

Further preferred are compounds wherein the polymerisable group is directly attached to the mesogenic group without a spacer group Sp.

In case of compounds with two or more groups P-Sp-, the polymerisable groups P and the spacer groups Sp can be identical or different.

In another preferred embodiment the guest compounds comprise one or more terminal groups, like R$^{1-4}$, or substituents, like R^5, that are substituted by two or more polymerisable groups P or P-Sp- (multifunctional polymerisable groups). Suitable multifunctional polymerisable groups of this type are disclosed for example in U.S. Pat. No. 7,060,200 B1 oder US 2006/0172090 A1. Very preferred are compounds comprising one or more multifunctional polymerisable groups selected from the following formulae:

—X-alkyl-CHP^1—CH$_2$—CH$_2$P^2 P1

—X'-alkyl-C(CH$_2$P^1)(CH$_2$P^2)—CH$_2$P^3 P2

—X'-alkyl-CHP^{1}CHP^2—CH$_2$P^3 P3

—X^1-alkyl-C(CH$_2$P^1)(CH$_2$P^2)—C$_a$H$_{2a+1}$ P4

—X'-alkyl-CHP^1—CH$_2$P^2 P5

—X'-alkyl-CHP^{1}P^2 P5

—X'-alkyl-CP^{1}P^2—C$_a$H$_{2a+1}$ P6

—X'-alkyl-C(CH$_2$P^1)(CH$_2$P^2)—CH$_2$OCH$_2$—C
(CH$_2$P^3)(CH$_2$P^4)CH$_2$P^5 P7

—X'-alkyl-CH((CH$_2$)$_a$P^1)((CH$_2$)$_b$P^2) P8

—X'-alkyl-CHP^{1}CHP^2—C$_a$H$_{2a+1}$ P9

wherein

alkyl is straight-chain or branched alkylene having 1 to 12 C-atoms which is unsubstituted, mono- or polysubstituted by F, Cl, Br, I or CN, and wherein one or more non-adjacent CH$_2$ groups are optionally replaced, in each case independently from one another, by —O—, —S—, —NH—, —NR^0—, —SiR^{0}R^{00}—, —CO—, —COO—, —OCO—, —O—CO—O—, —S—CO—, —CO—S—, —SO$_2$—, —CO—NR^0—, —NR^0—CO—, —NR^0—CO—NR^{00}—, —CY^1=CY^2— or —C≡C— in such a manner that O and/or S atoms are not linked directly to one another, with R^0 and R^{00} having the meanings given above, or denotes a single bond,

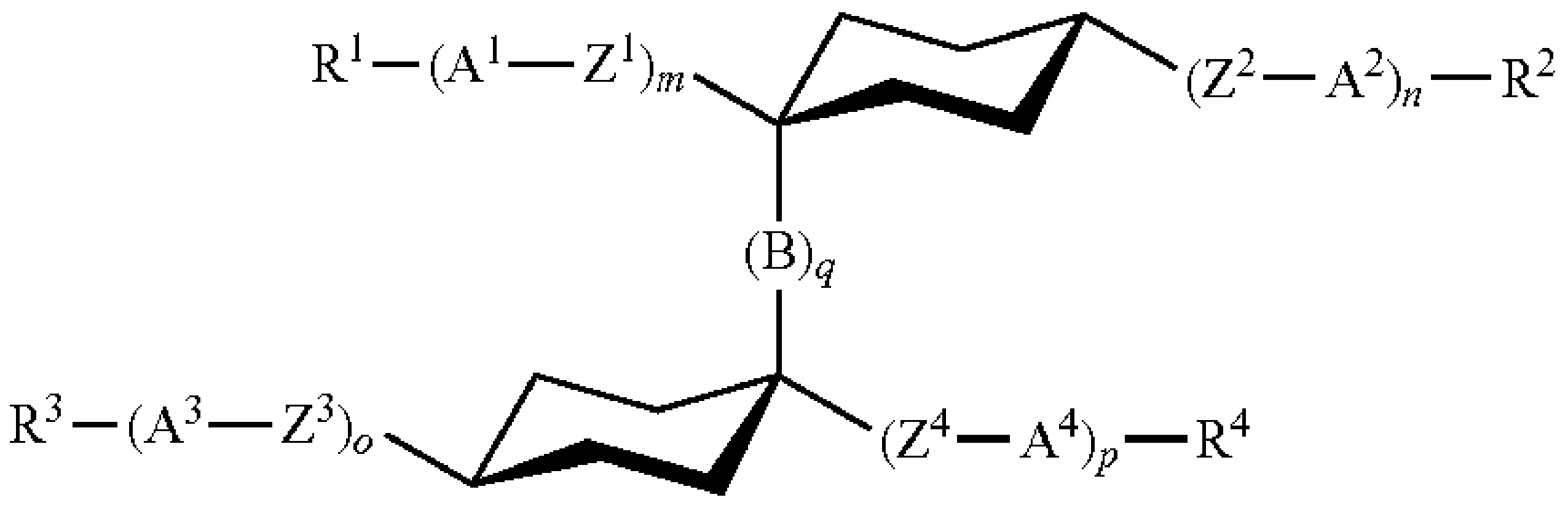
a and b are independently of each other 0, 1, 2, 3, 4, 5 or 6,

X' is as defined above, and

P^{1-5} independently of each other have one of the meanings given for P above.

Very preferred compounds of formula I are those of the following subformulae:

Ia



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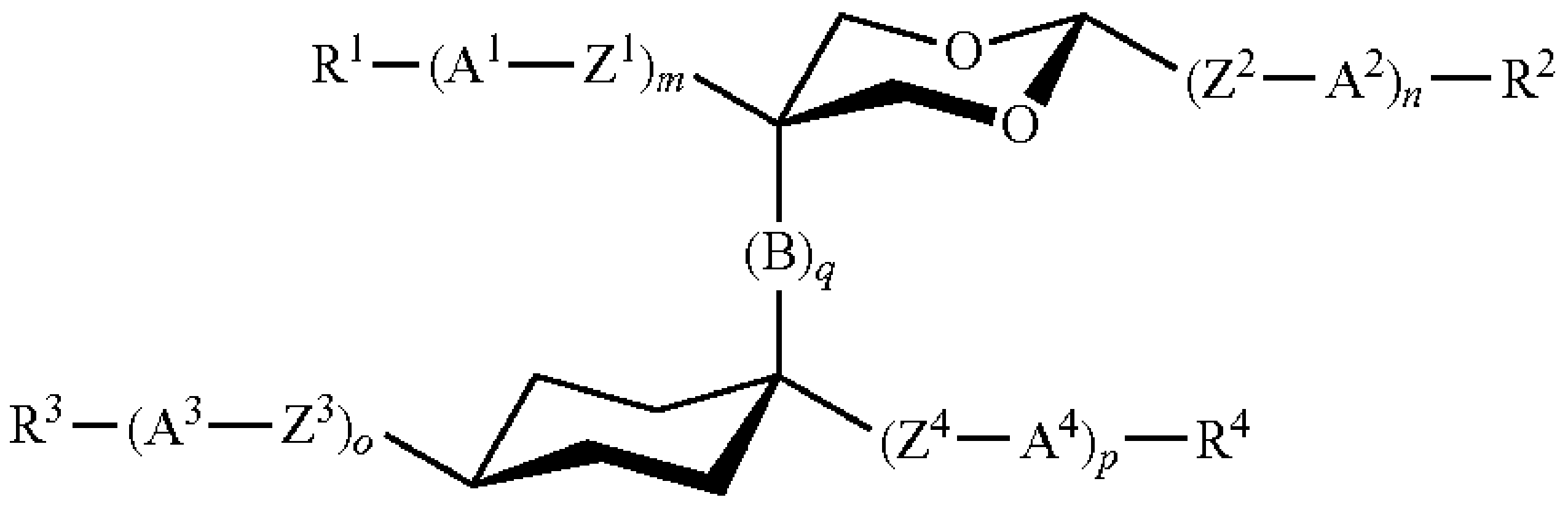
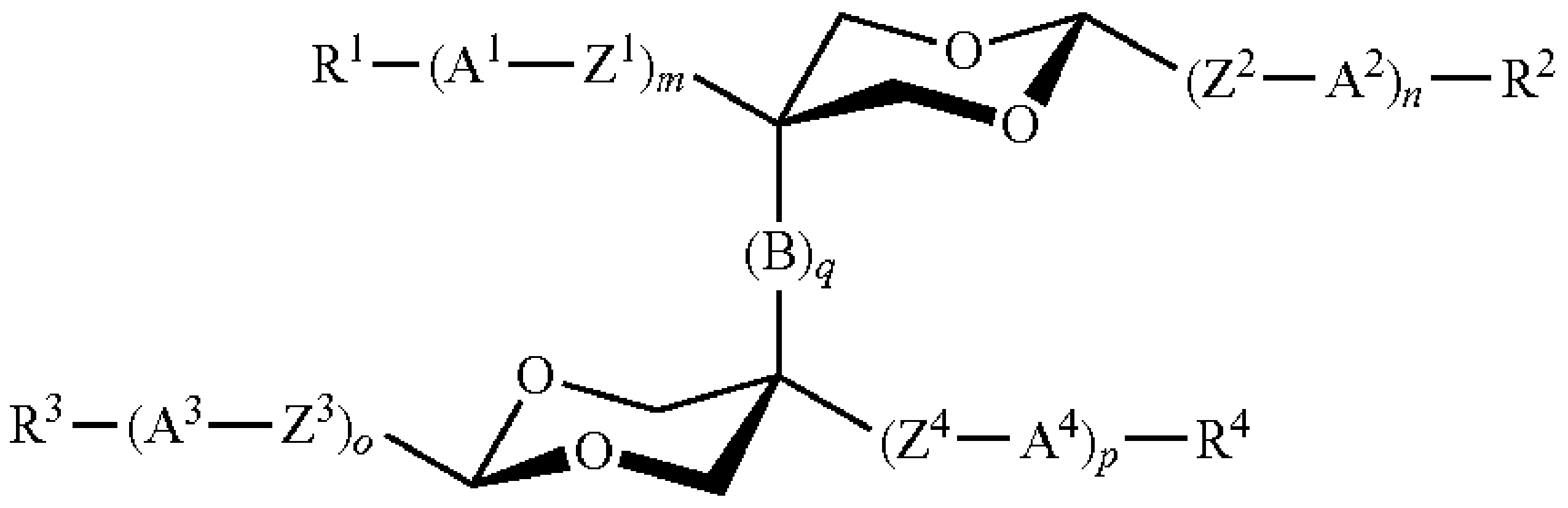
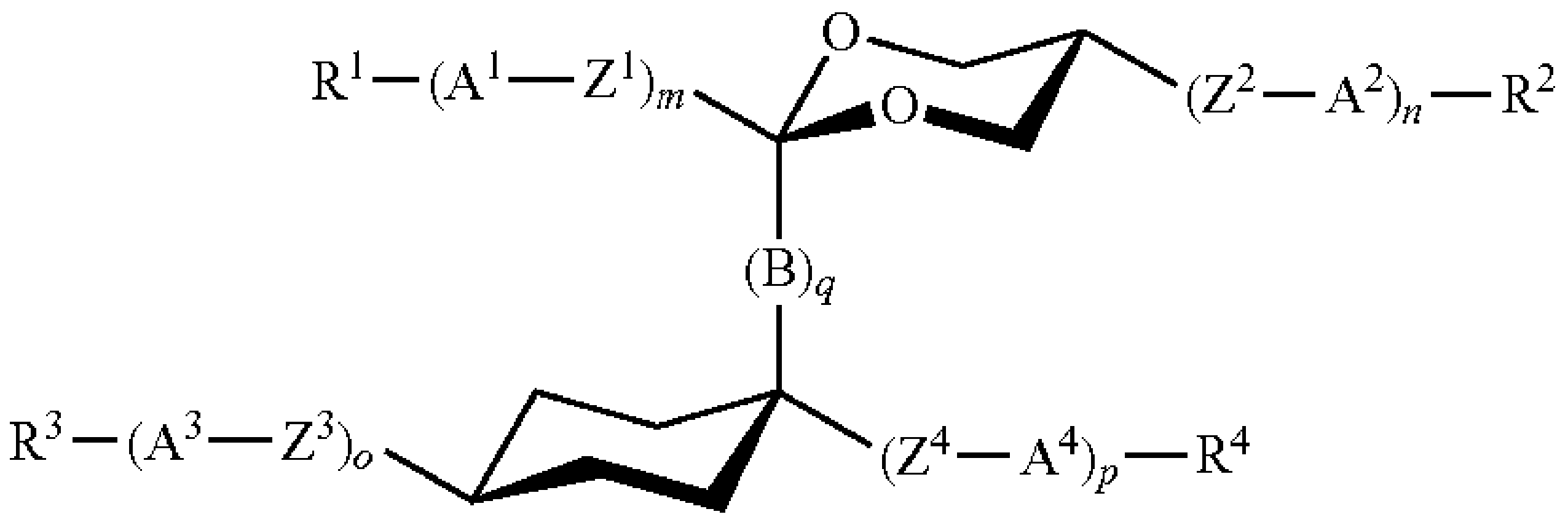


Ic



Id



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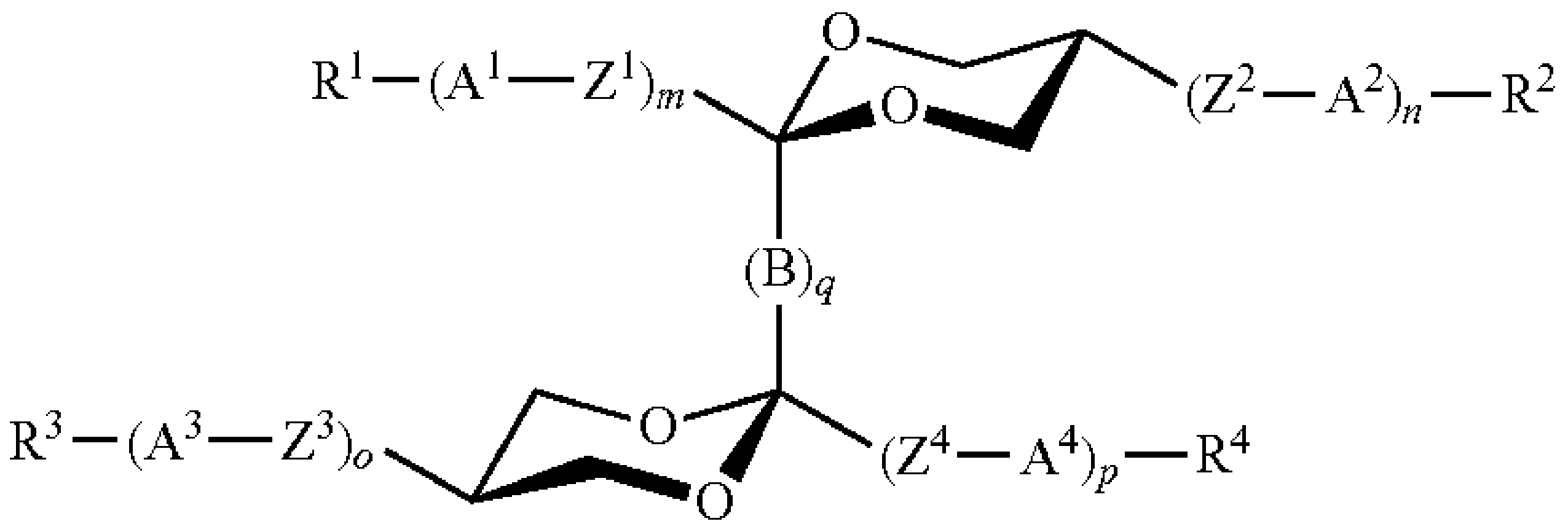

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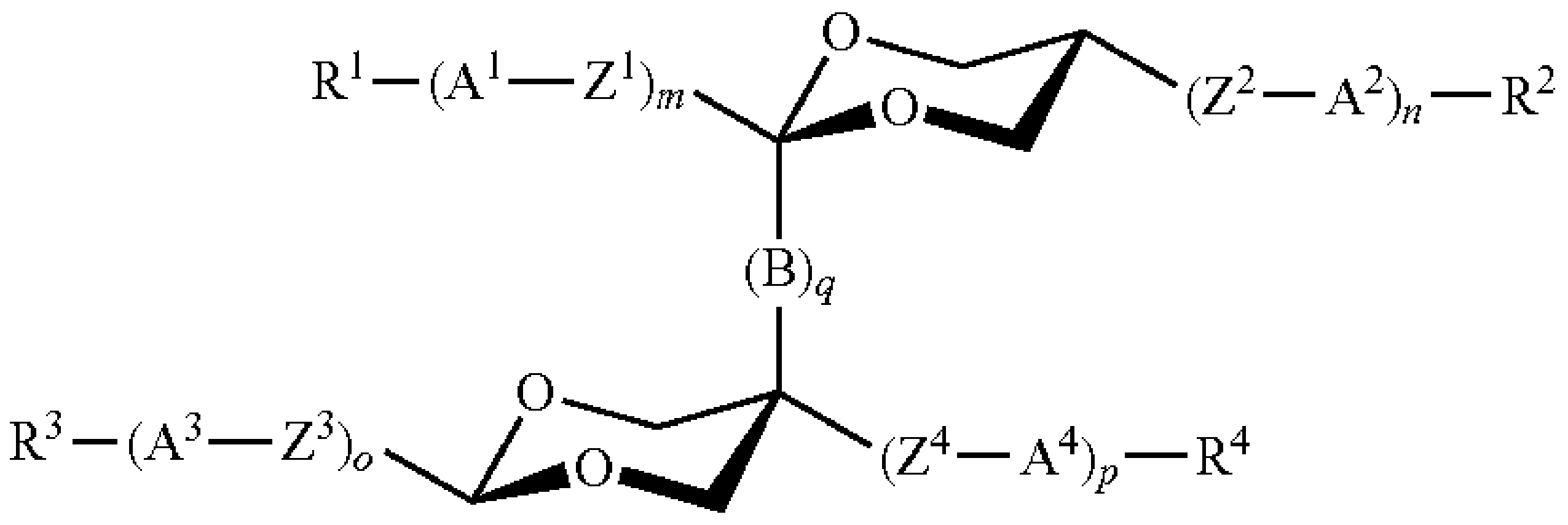

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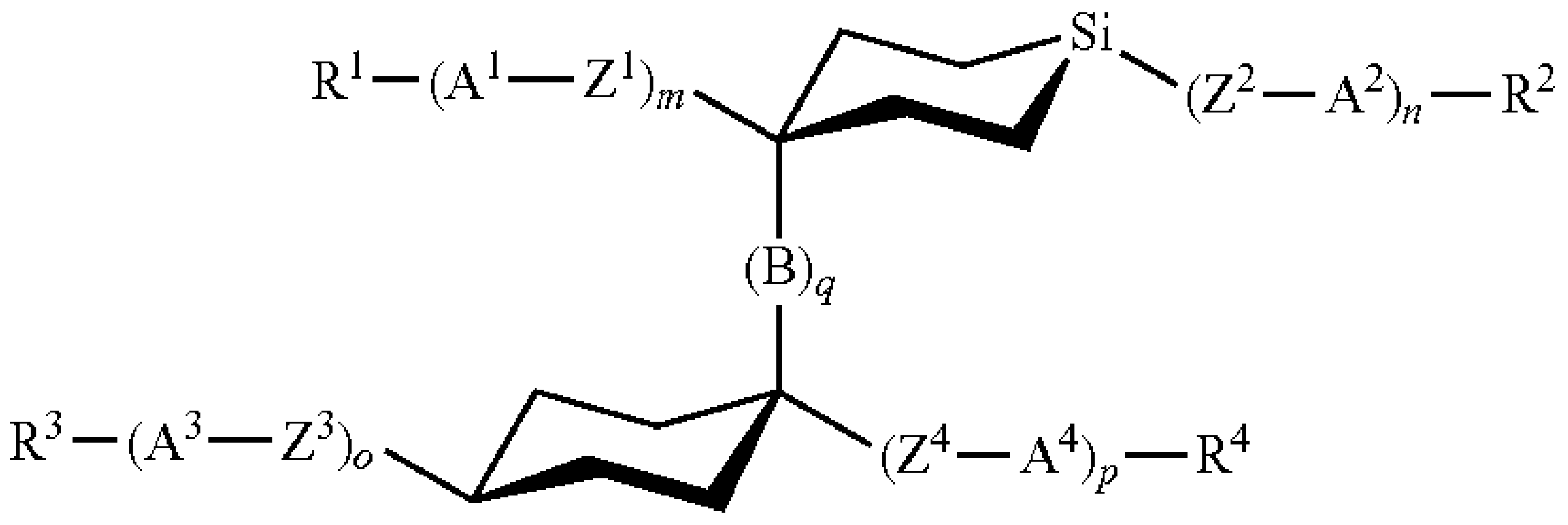

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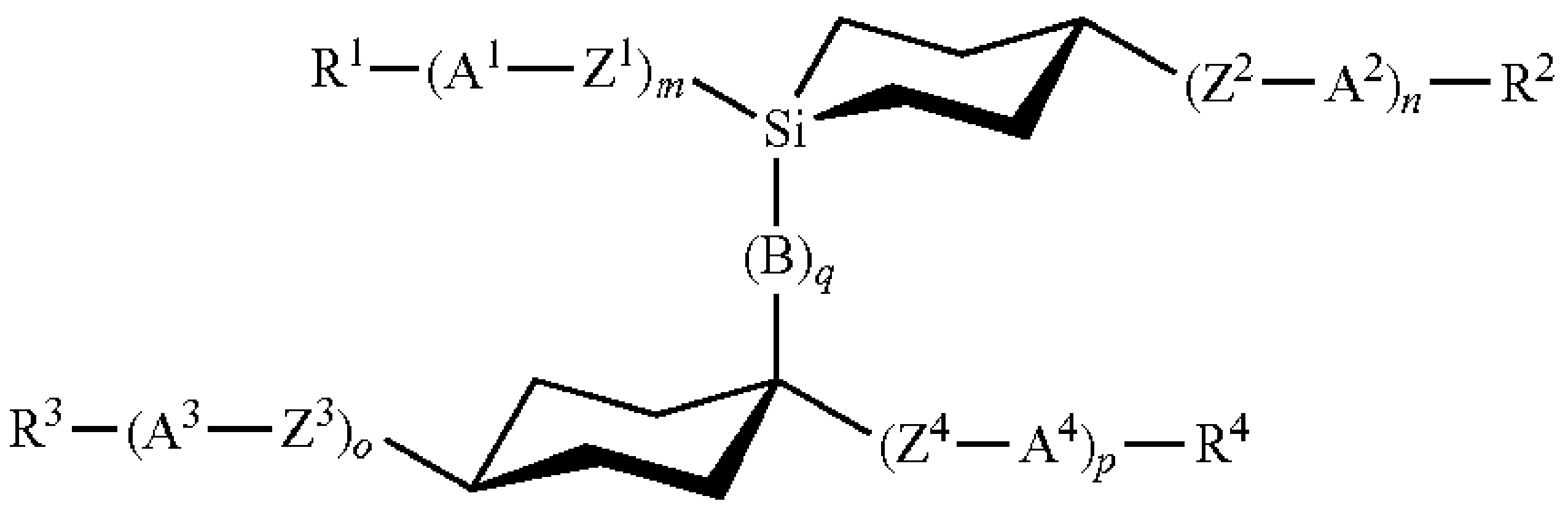
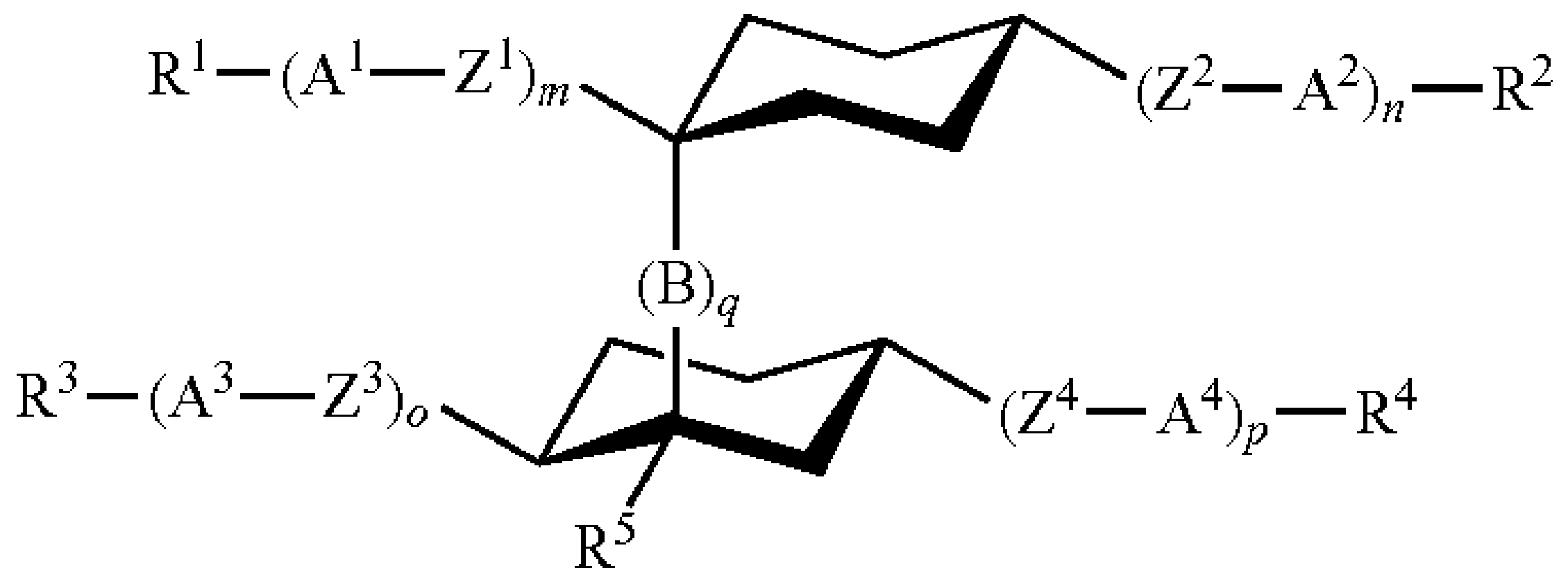
Ih



Ii



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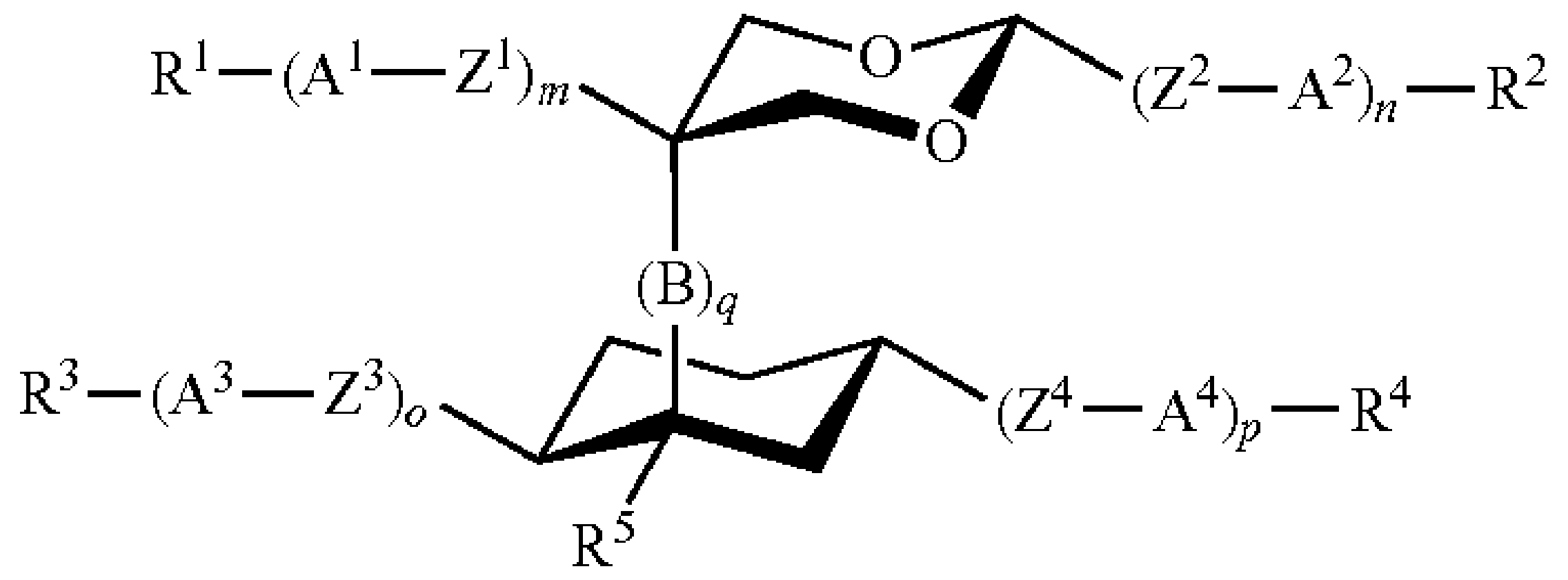

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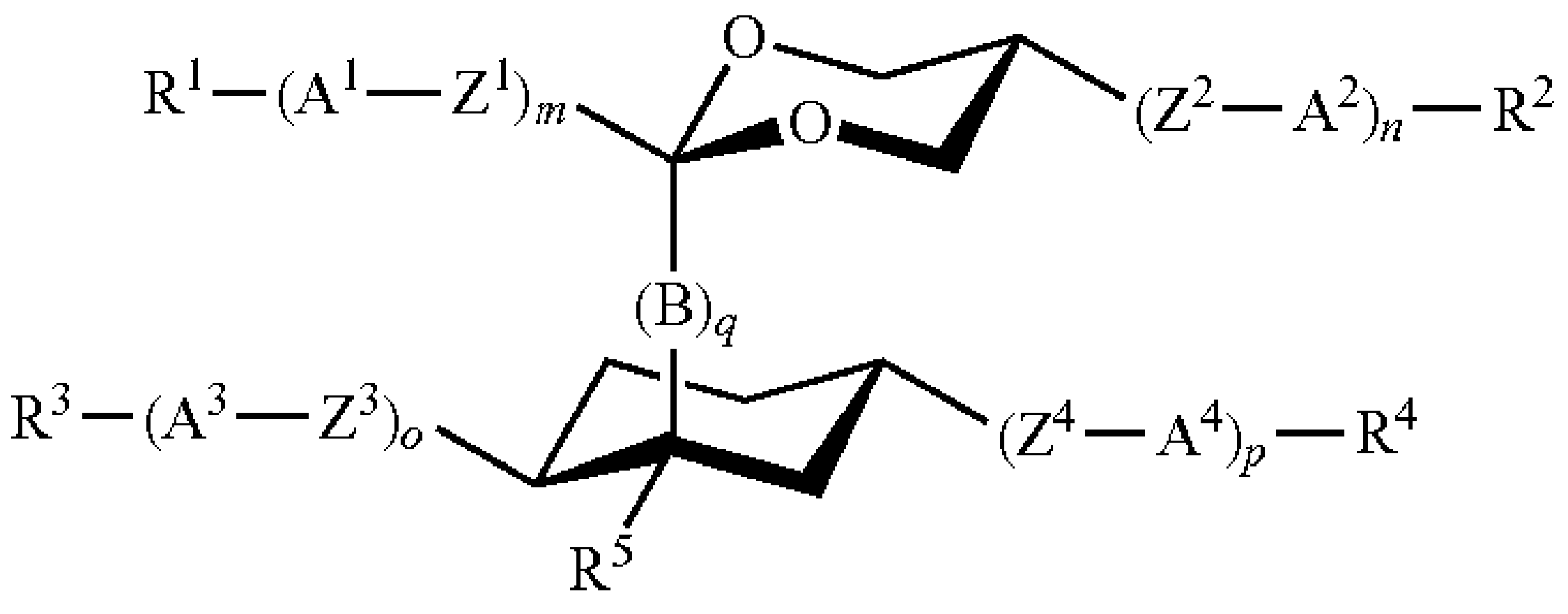

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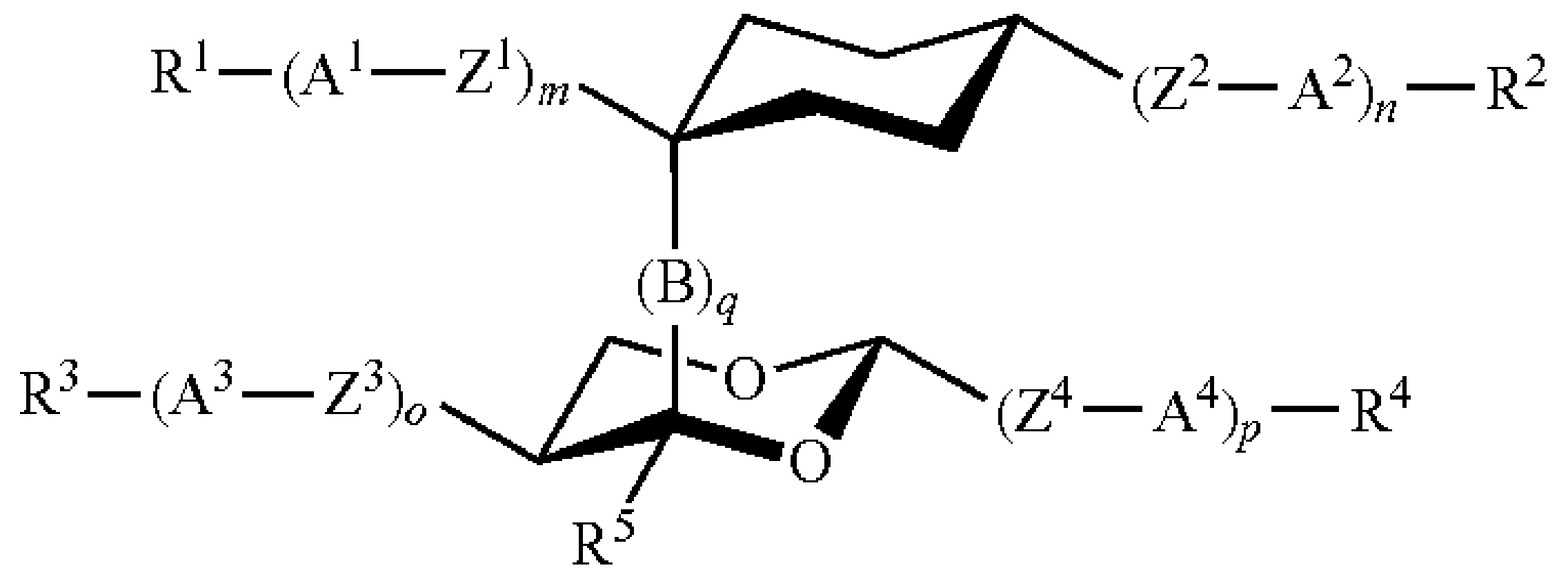

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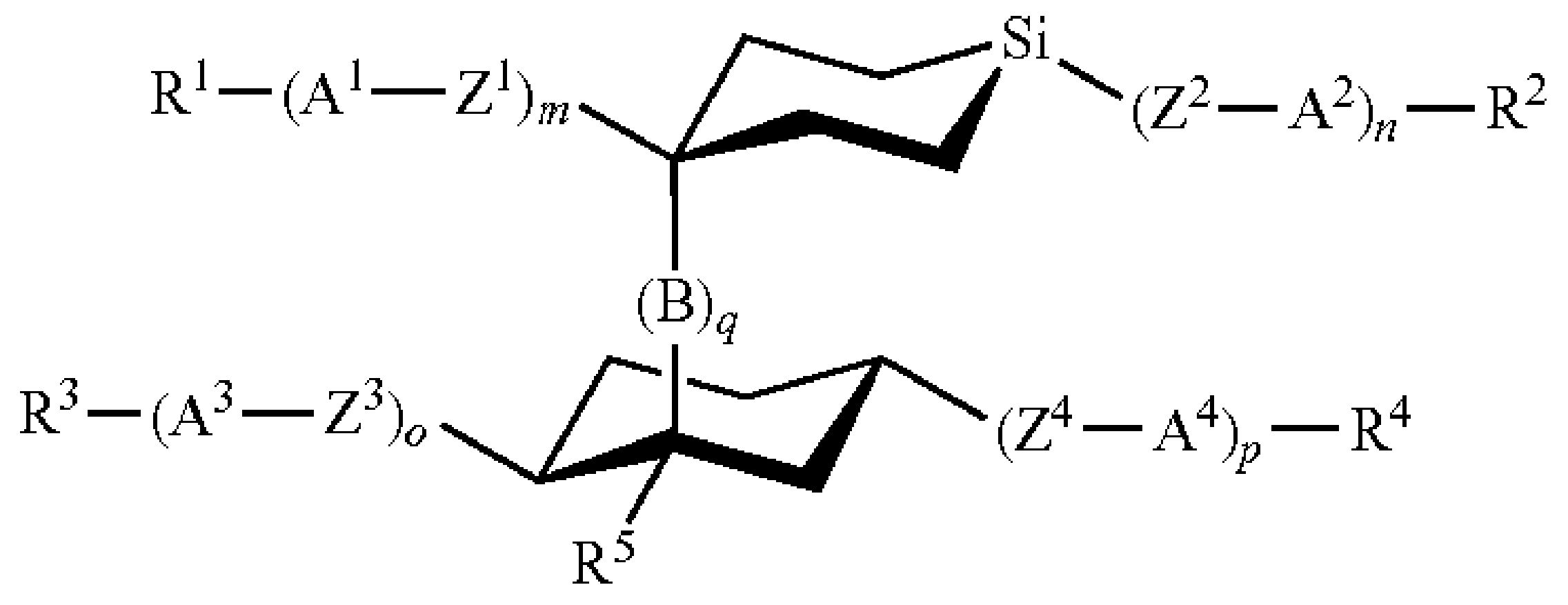

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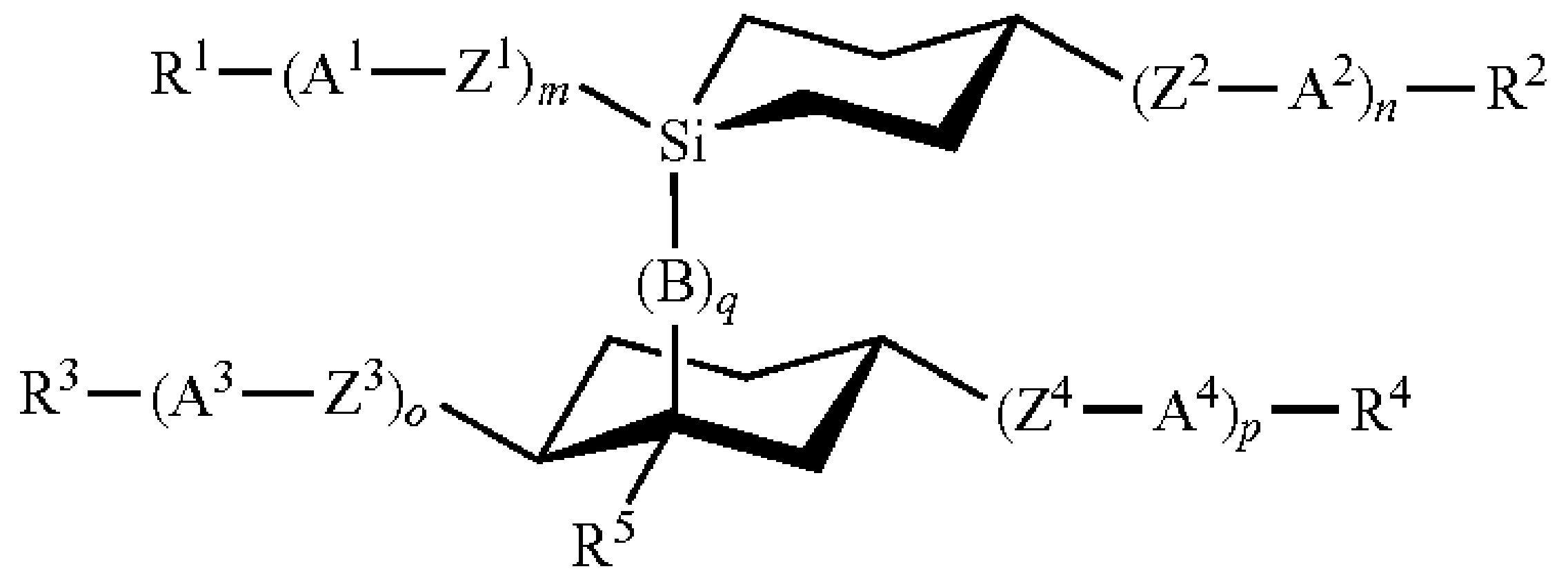

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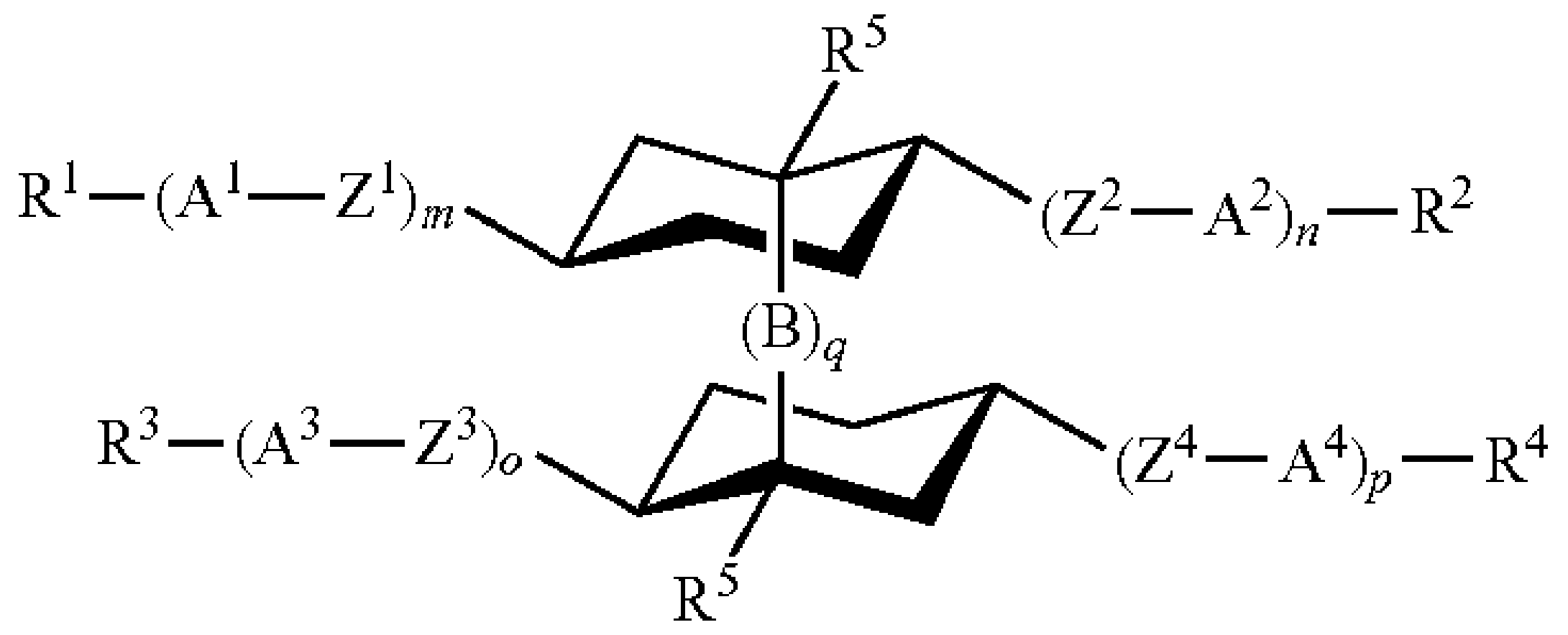

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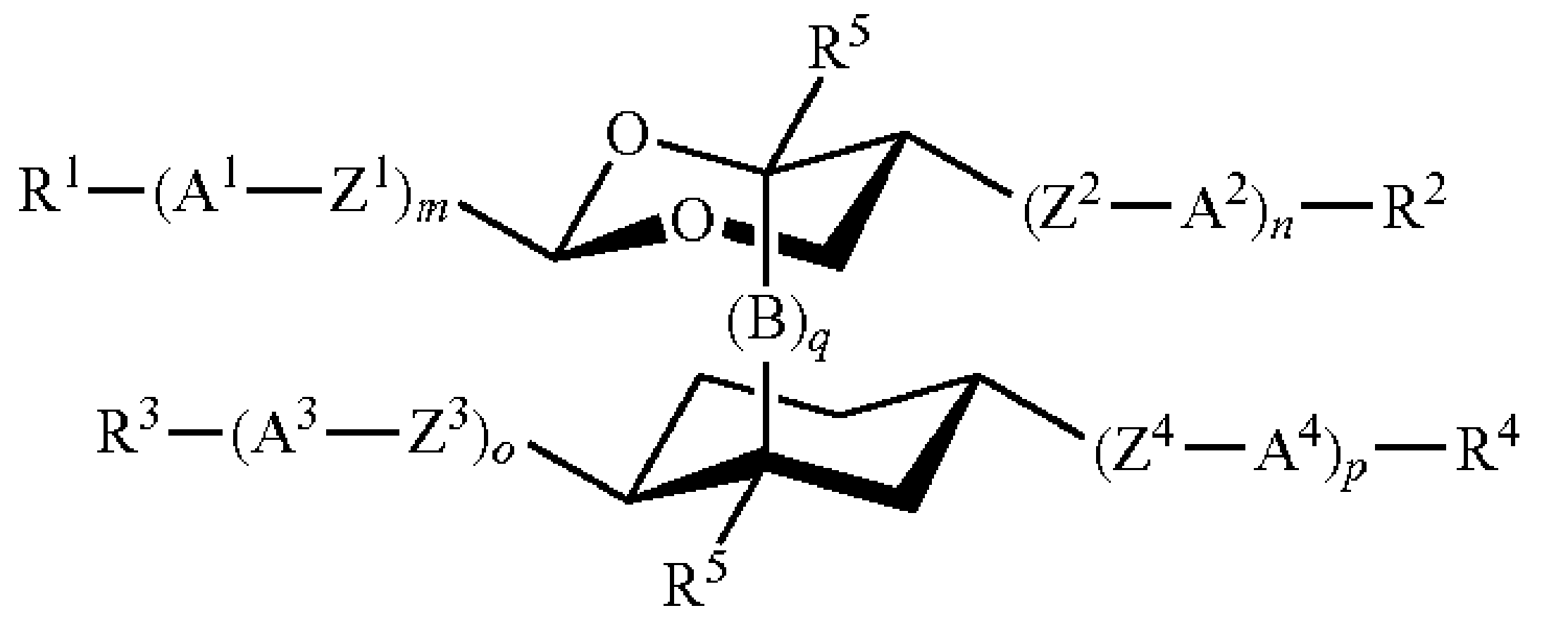

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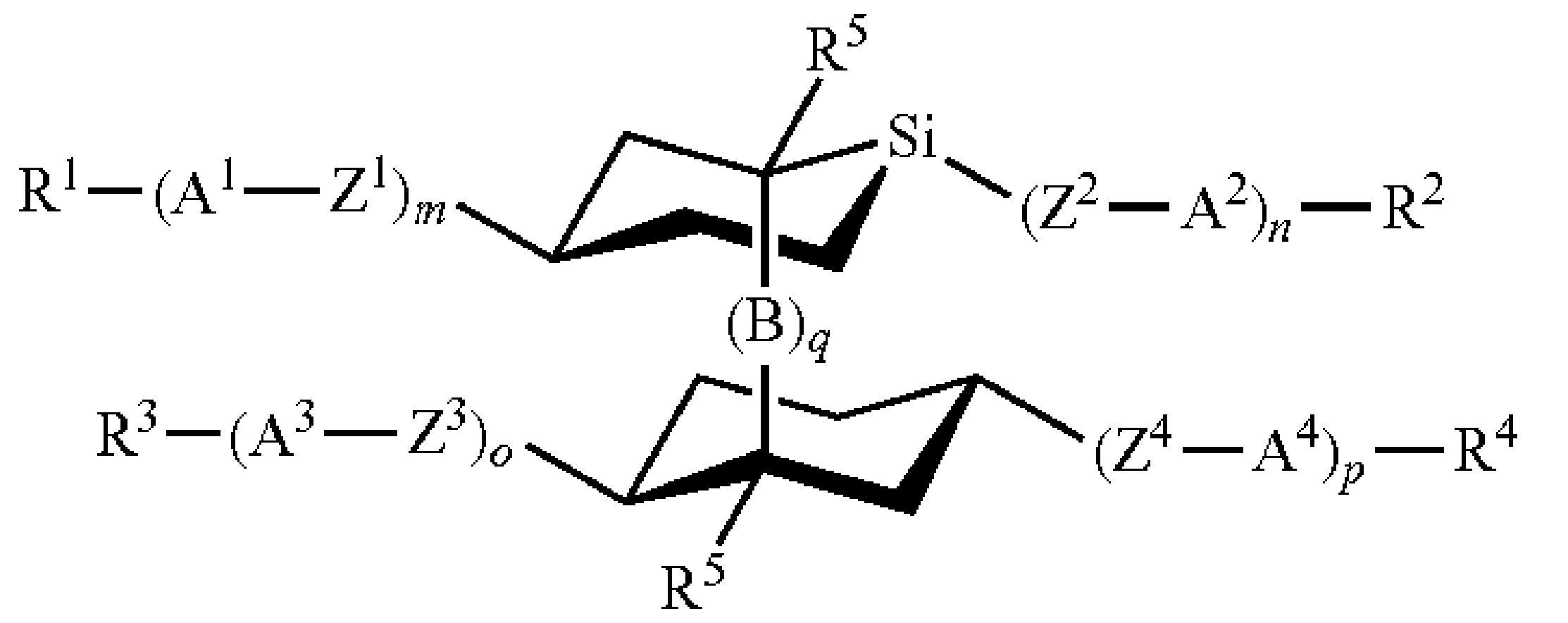

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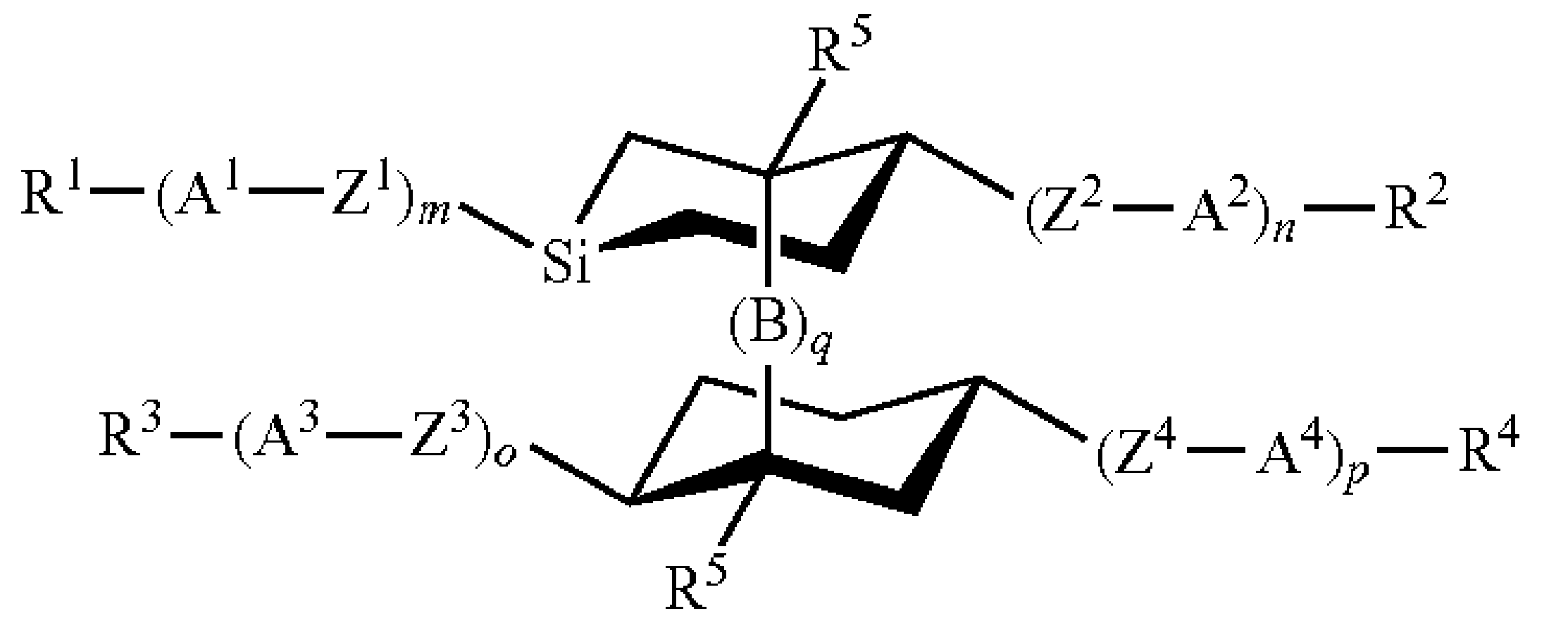

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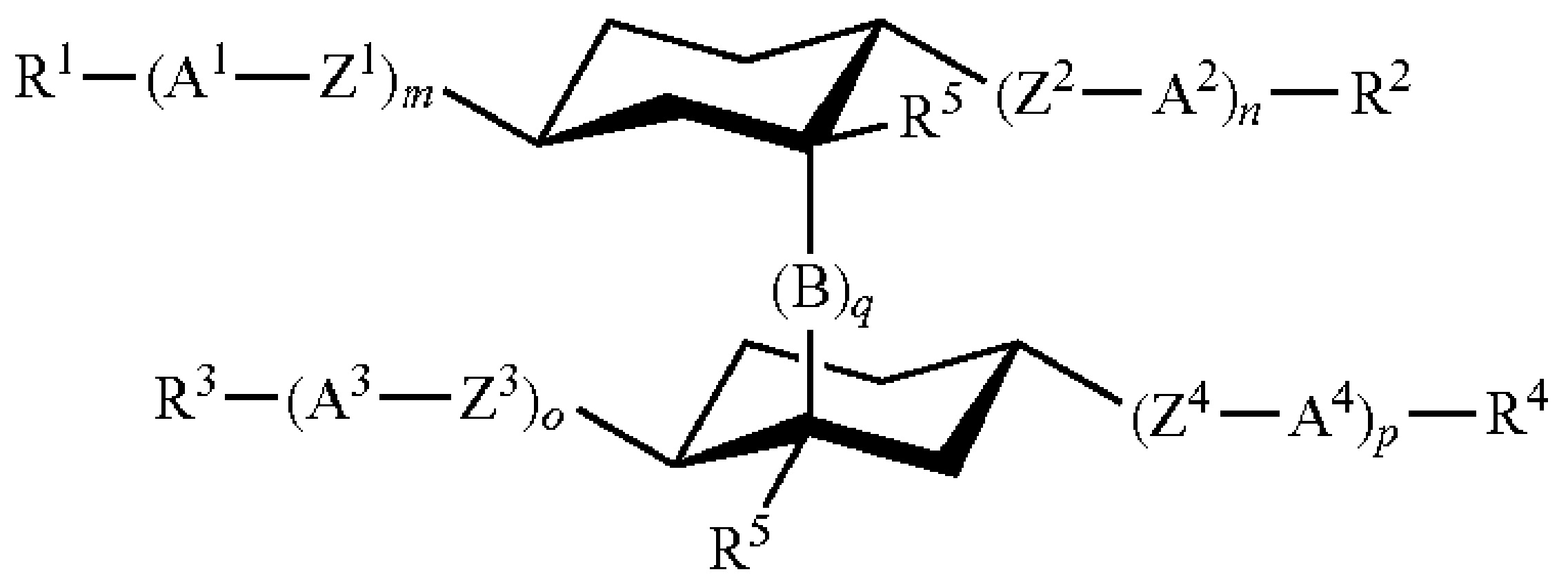

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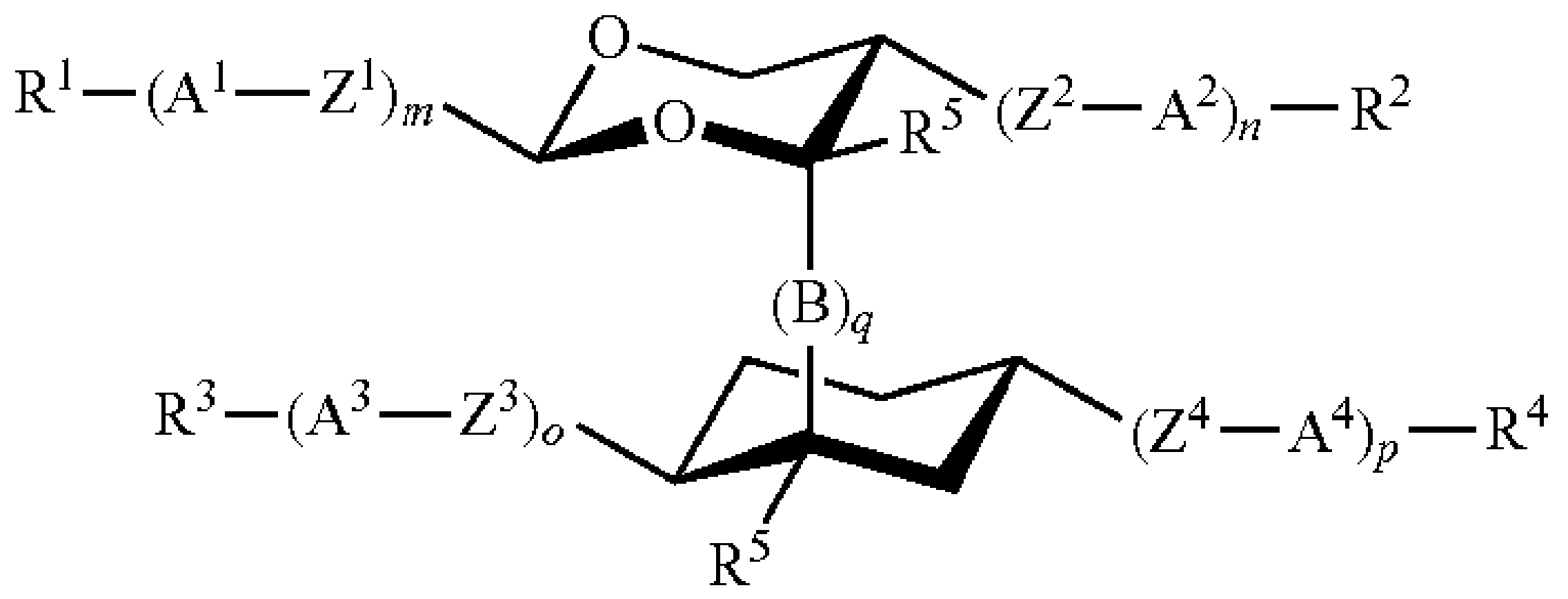

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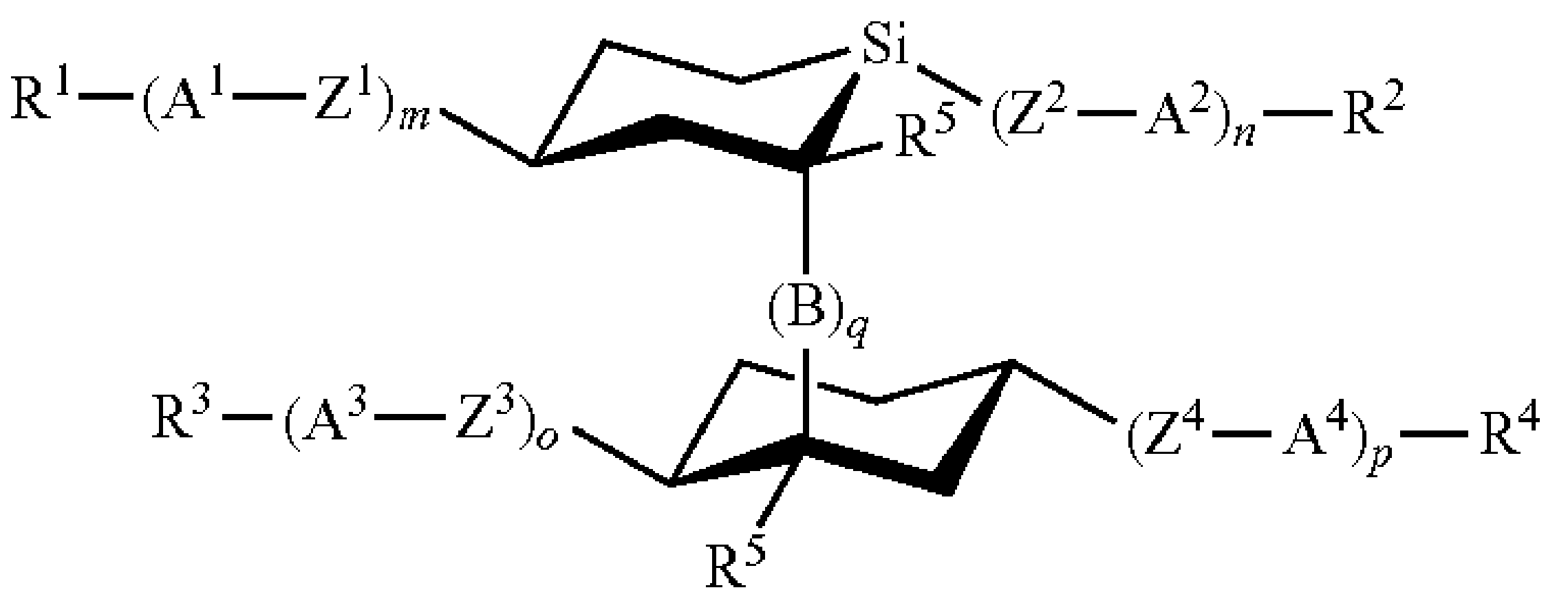
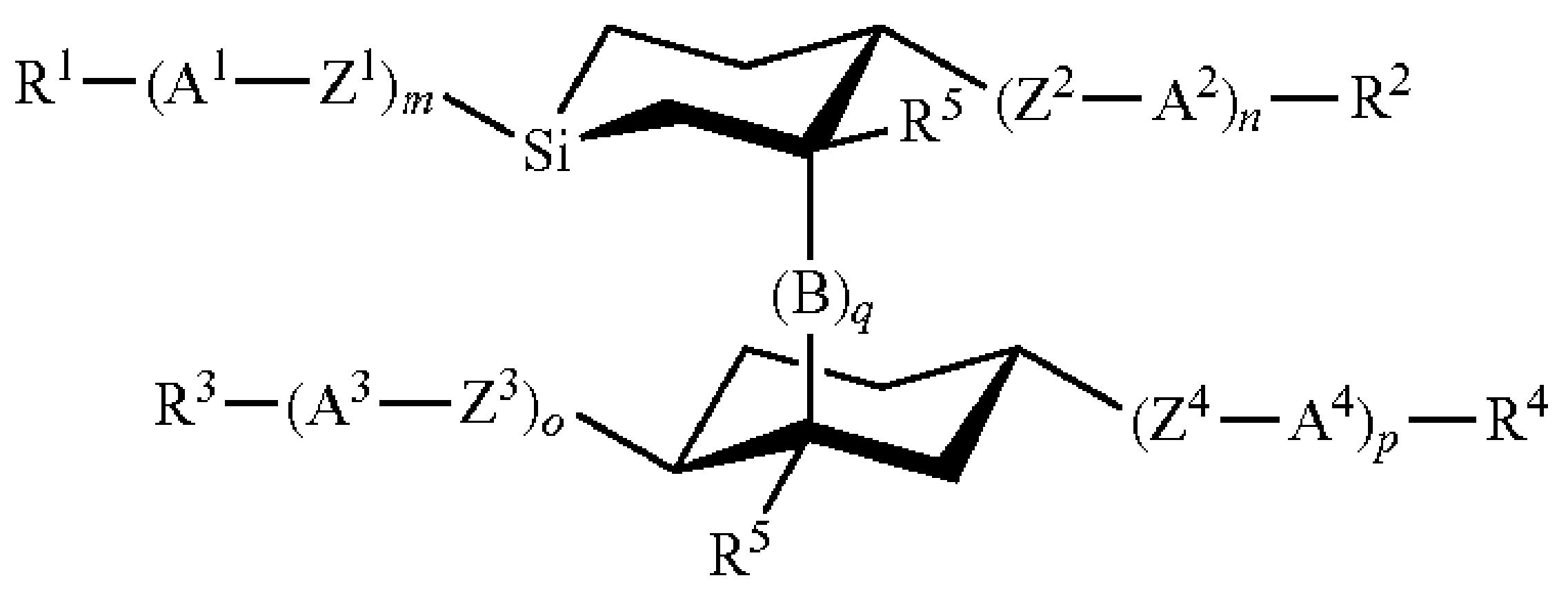


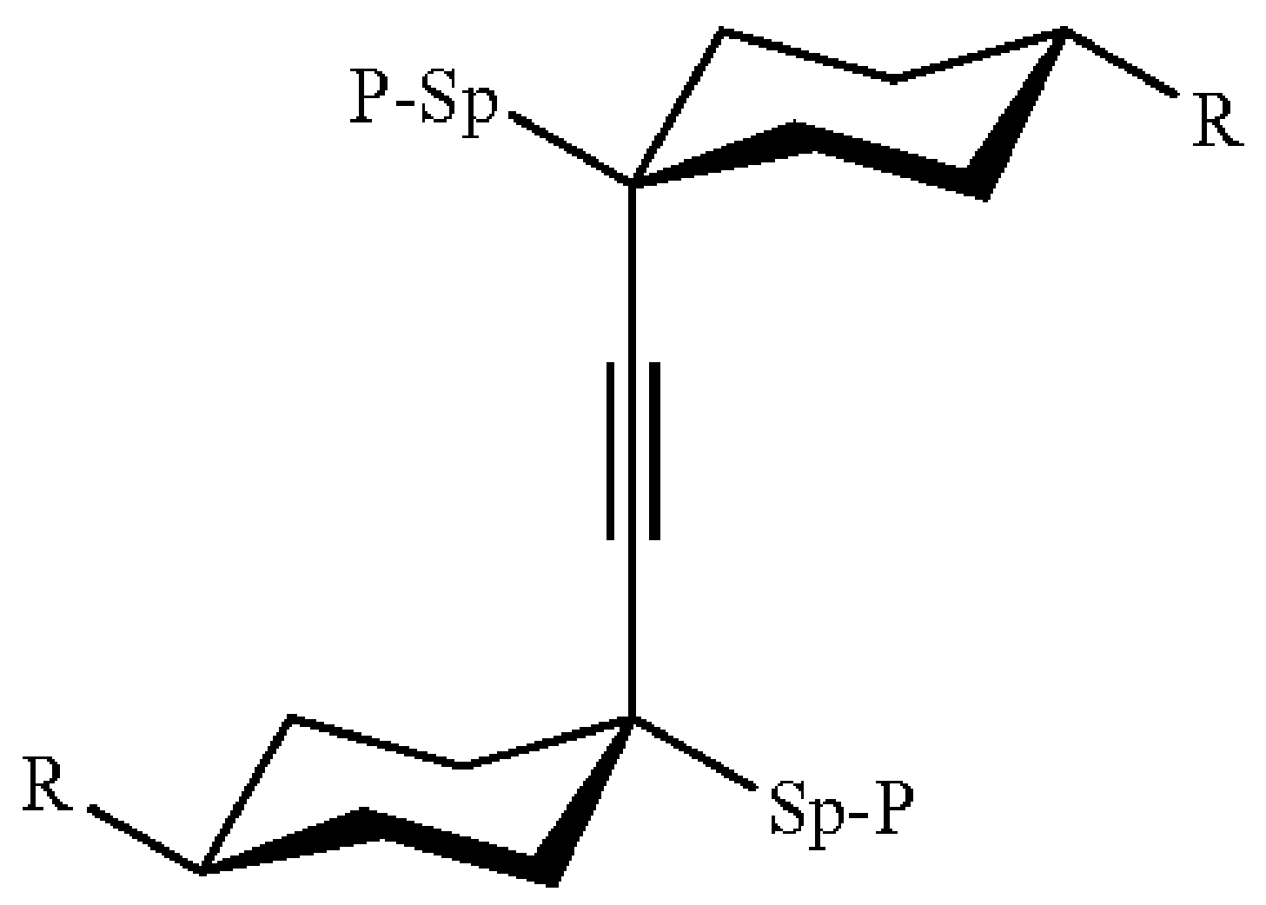
Iw



Ix

wherein R^{1-5}, A^{1-4}, Z^{1-4}, B, m, n, o, p and q have the meanings given above.

Especially preferred are compounds of the following subformulae:



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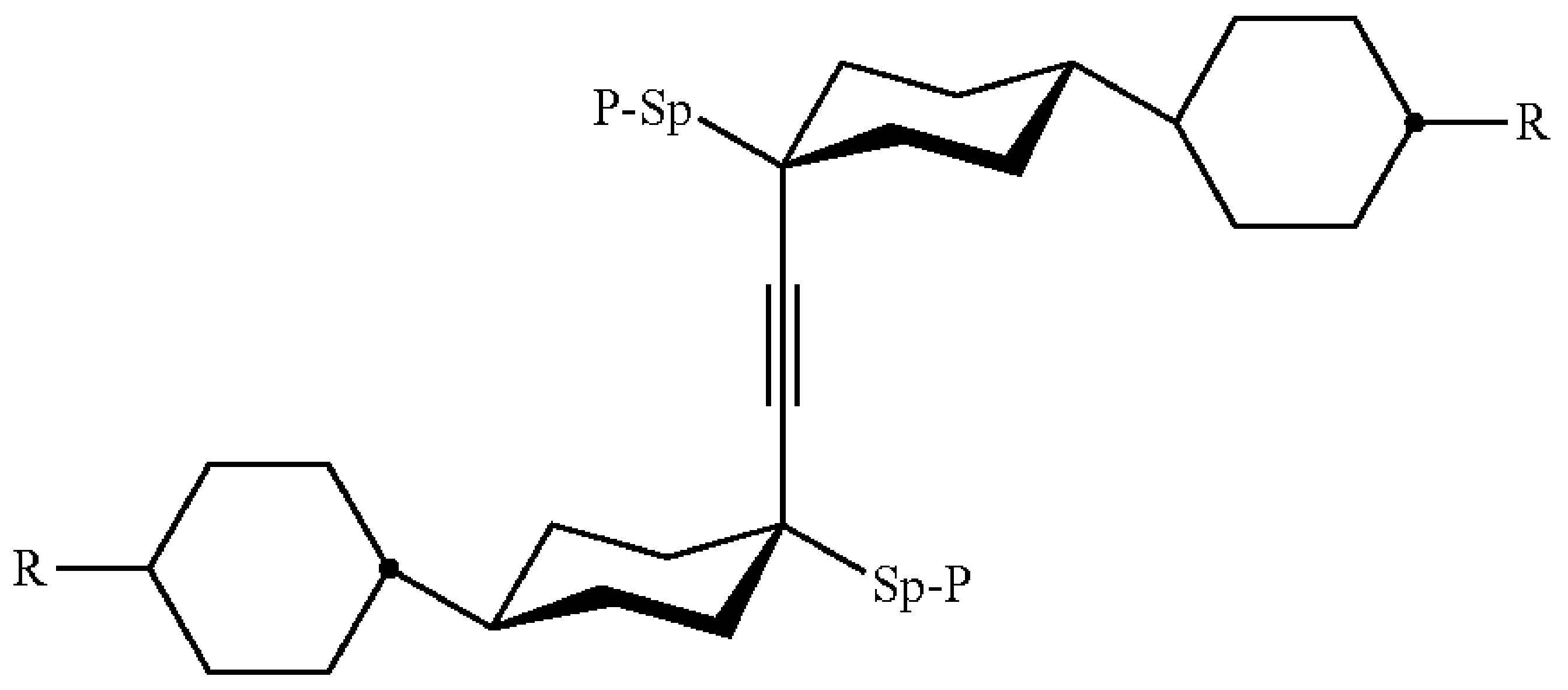
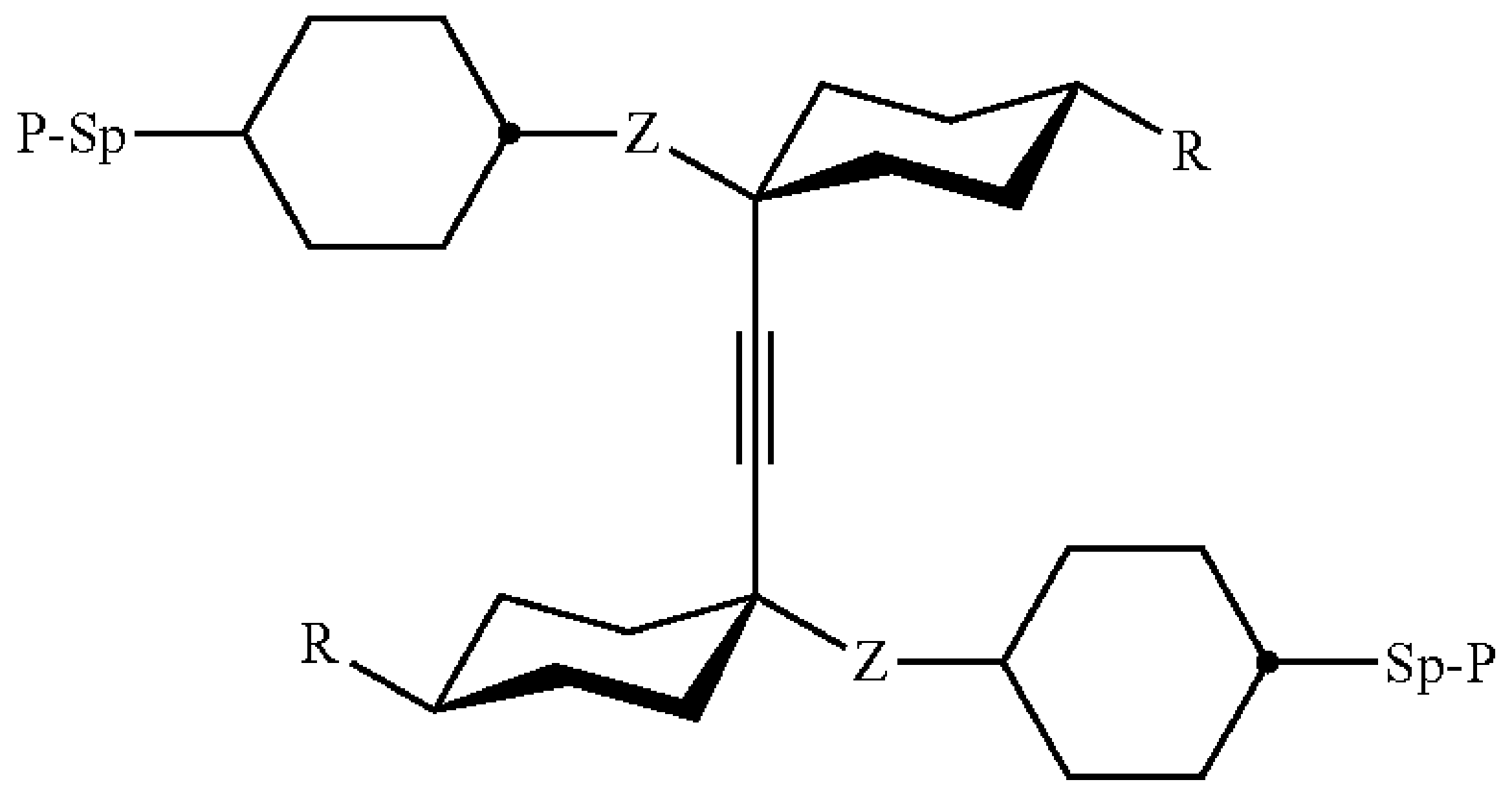


I2



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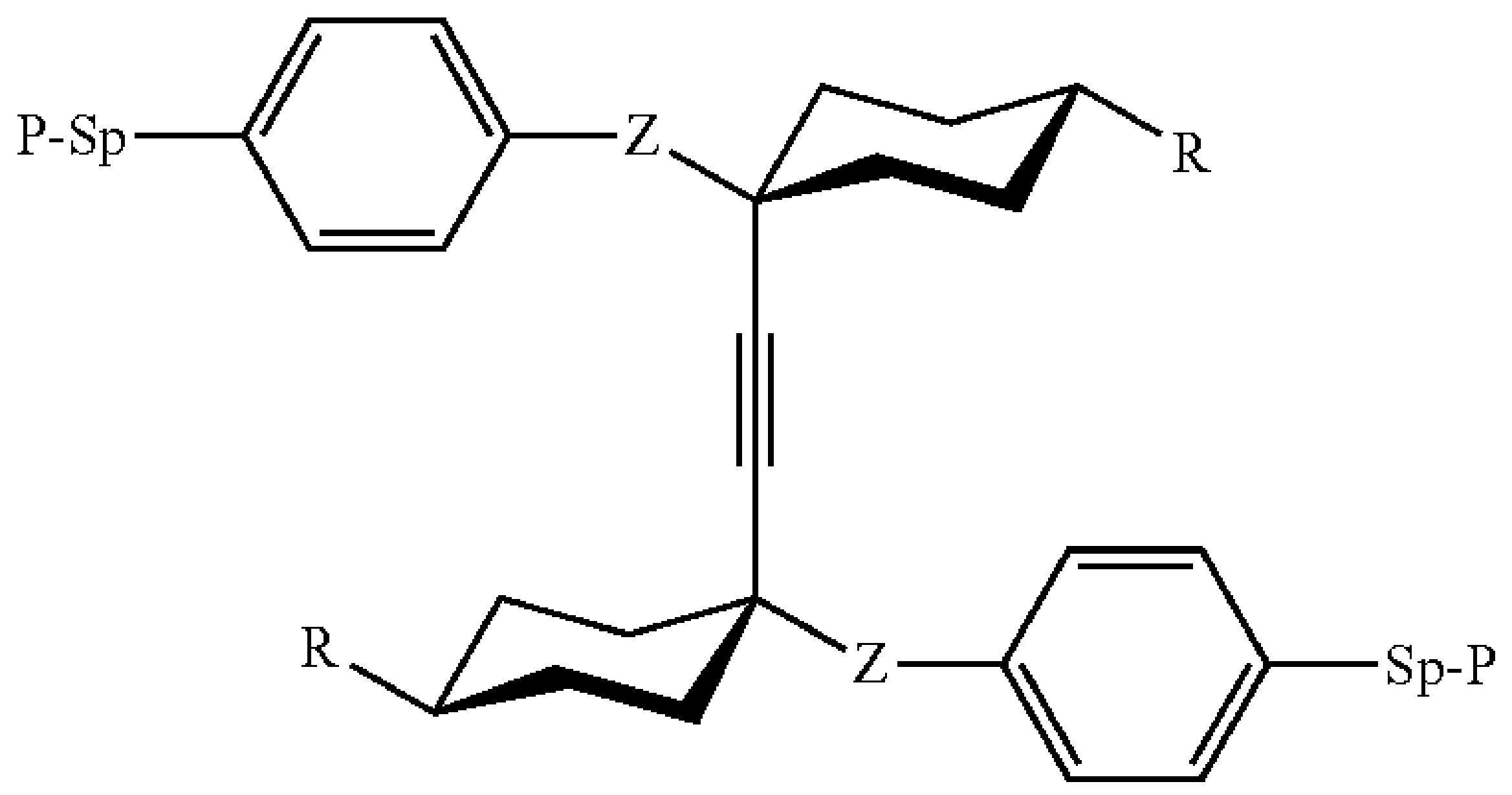

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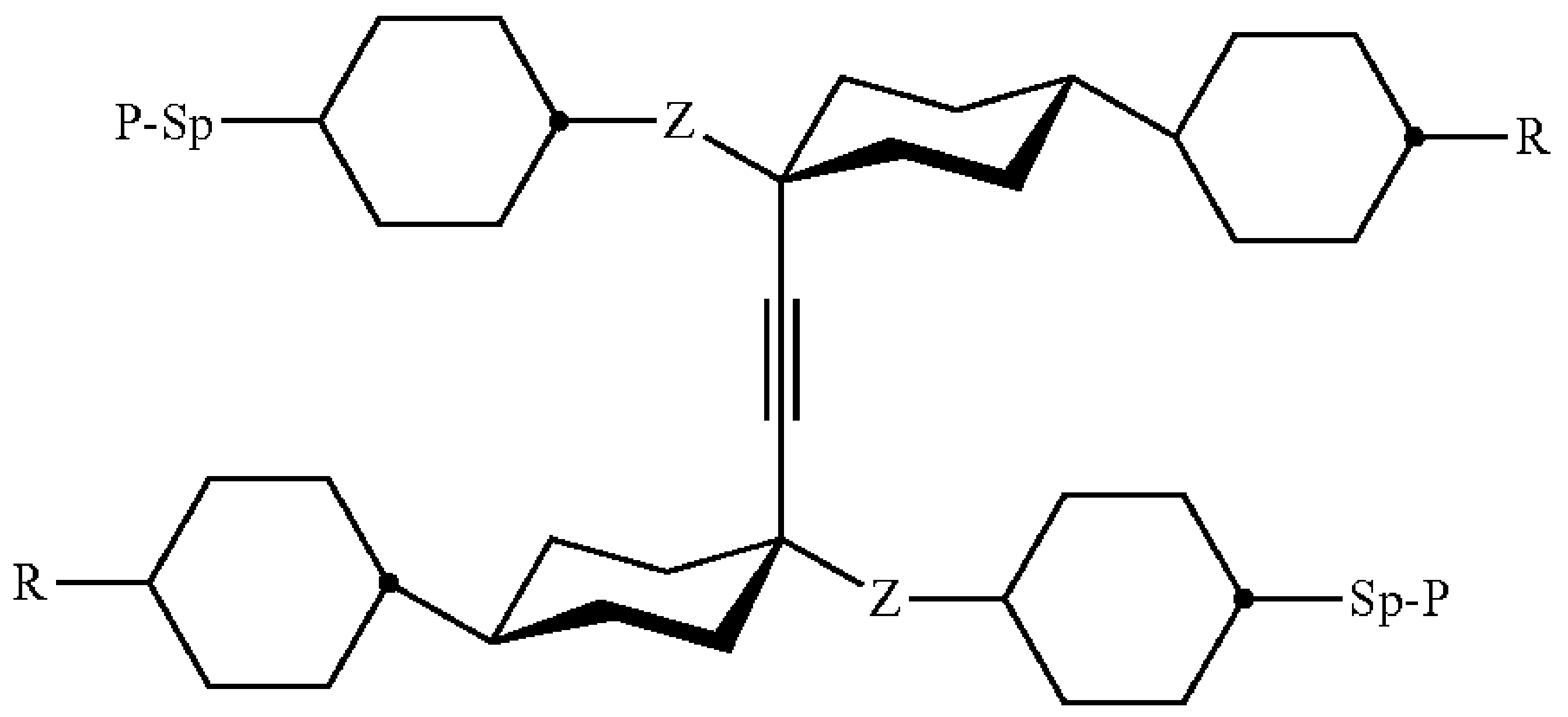

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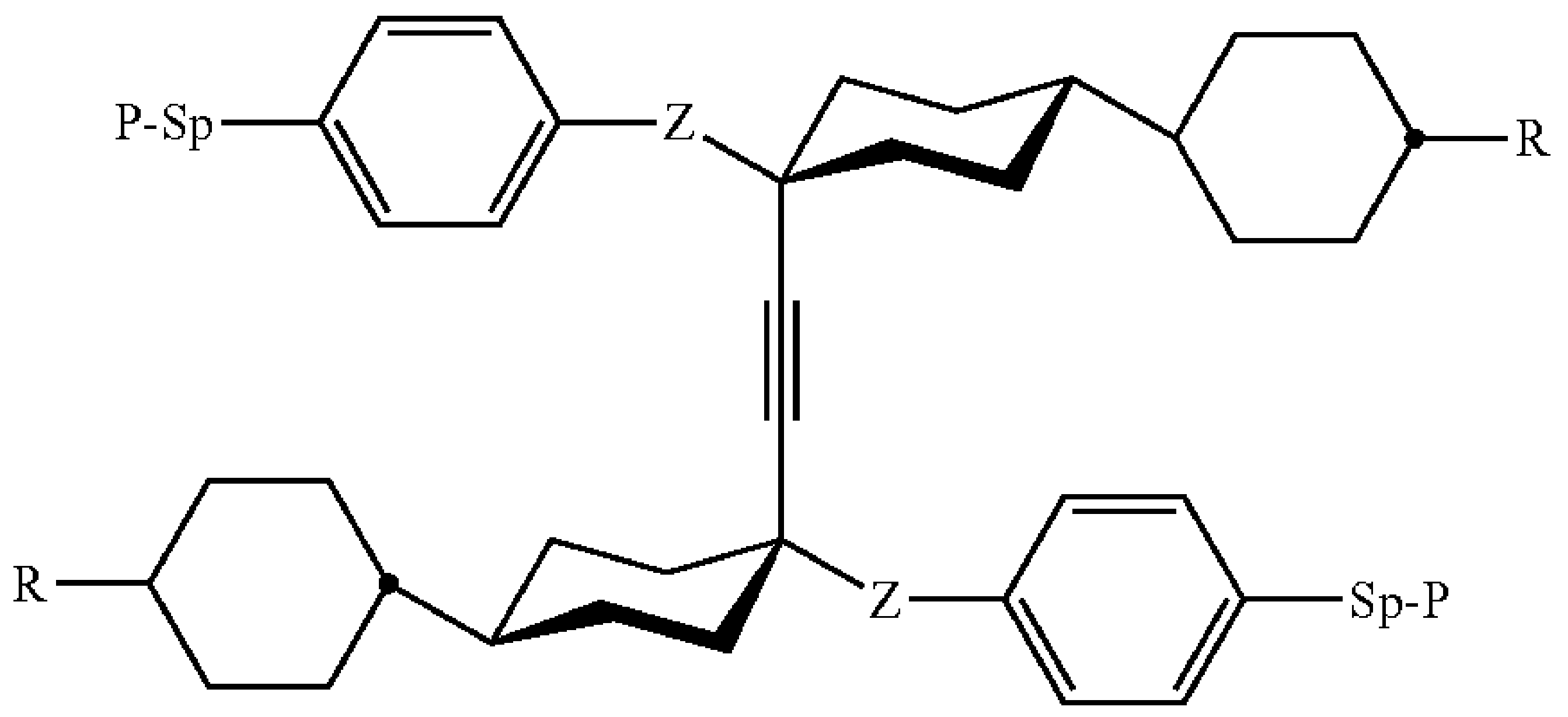

I6

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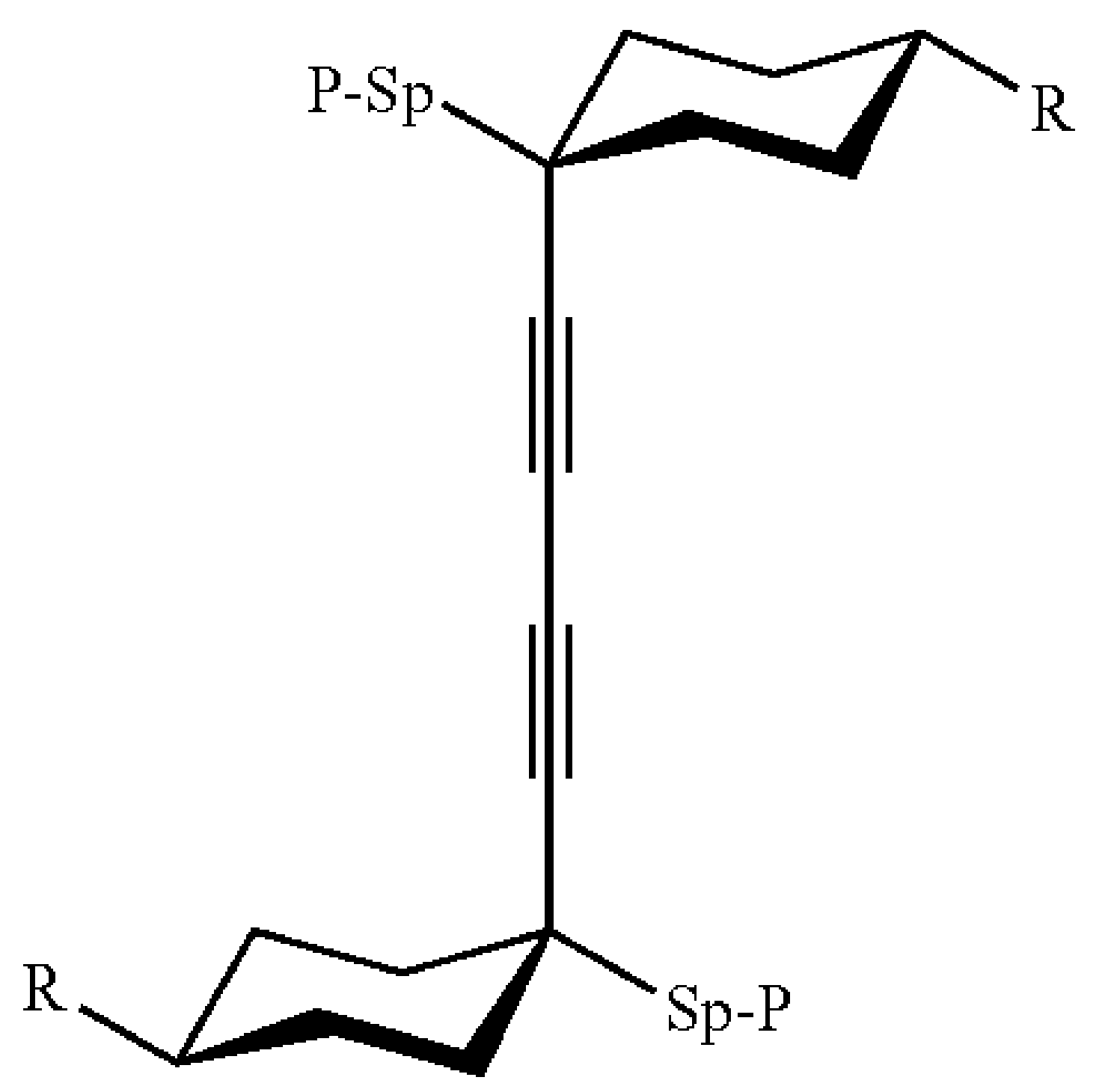
I7



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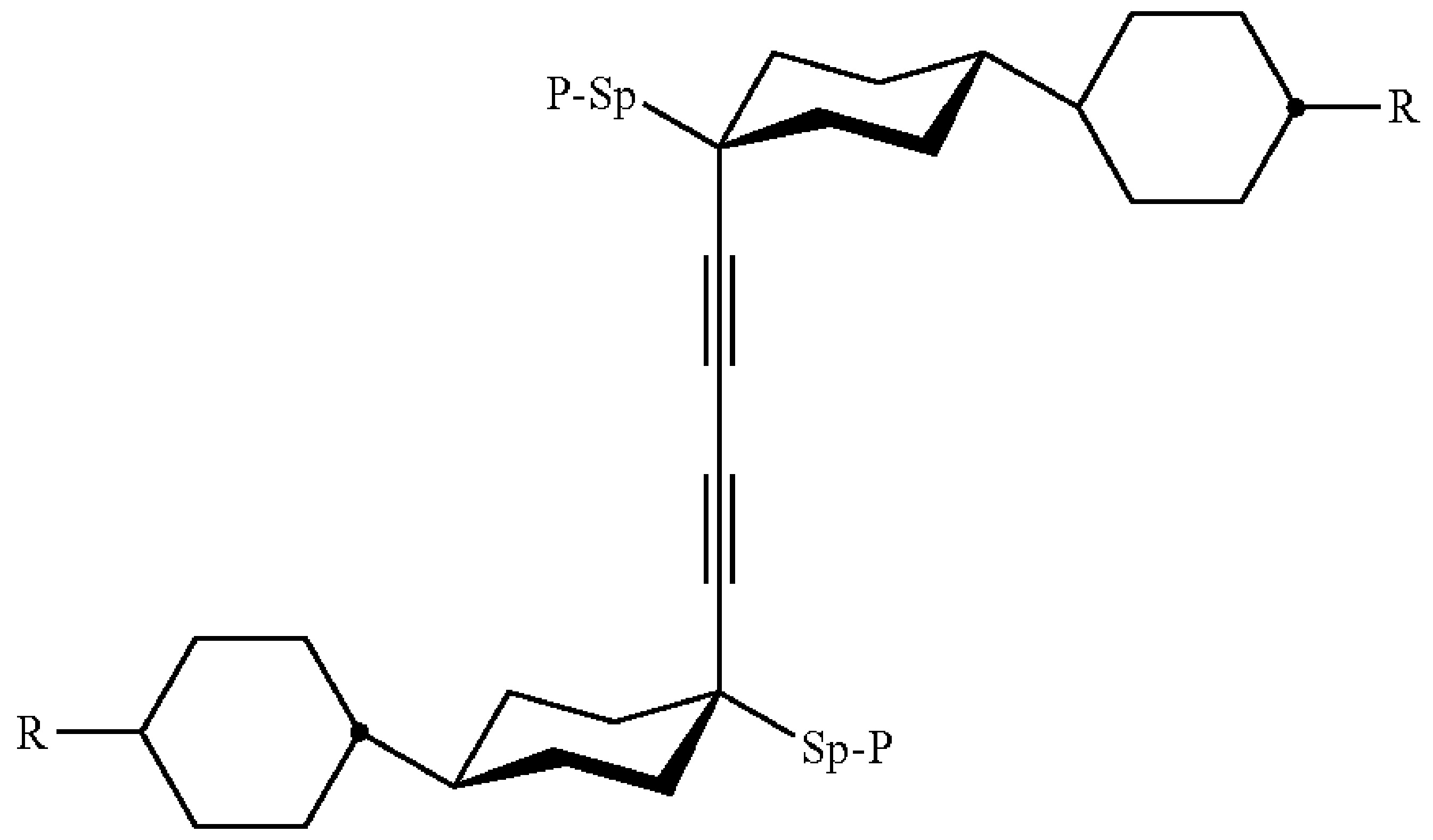

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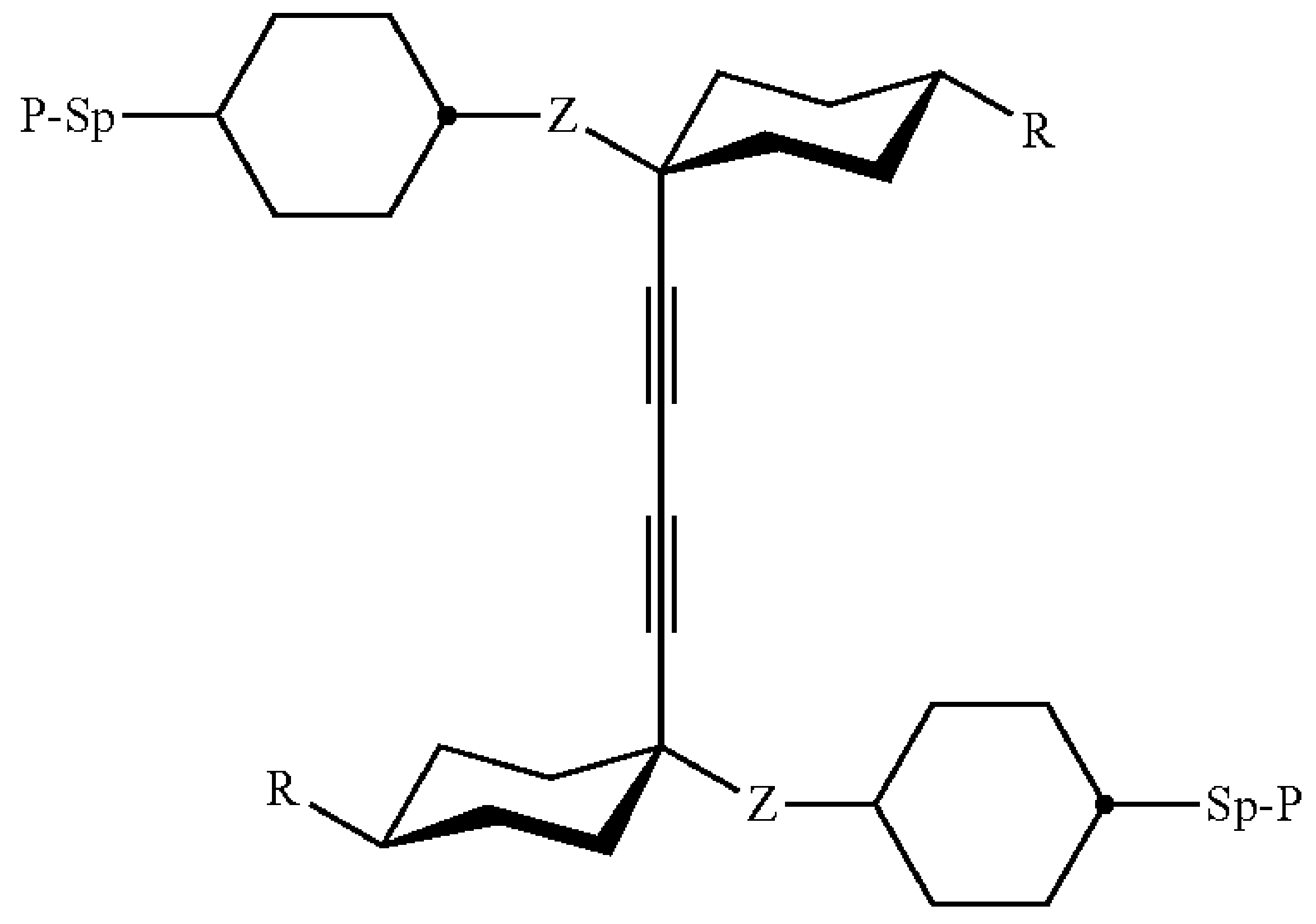

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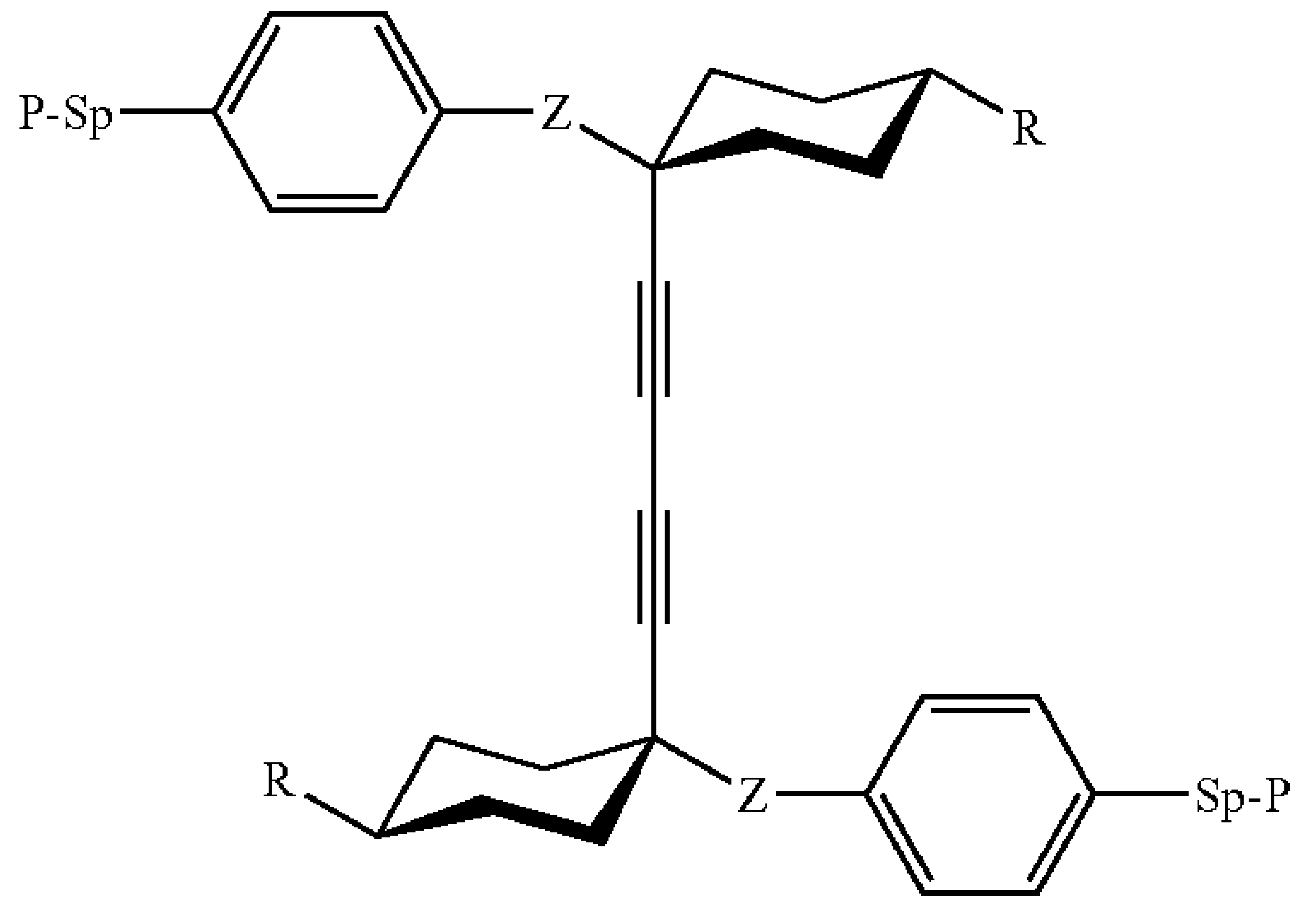

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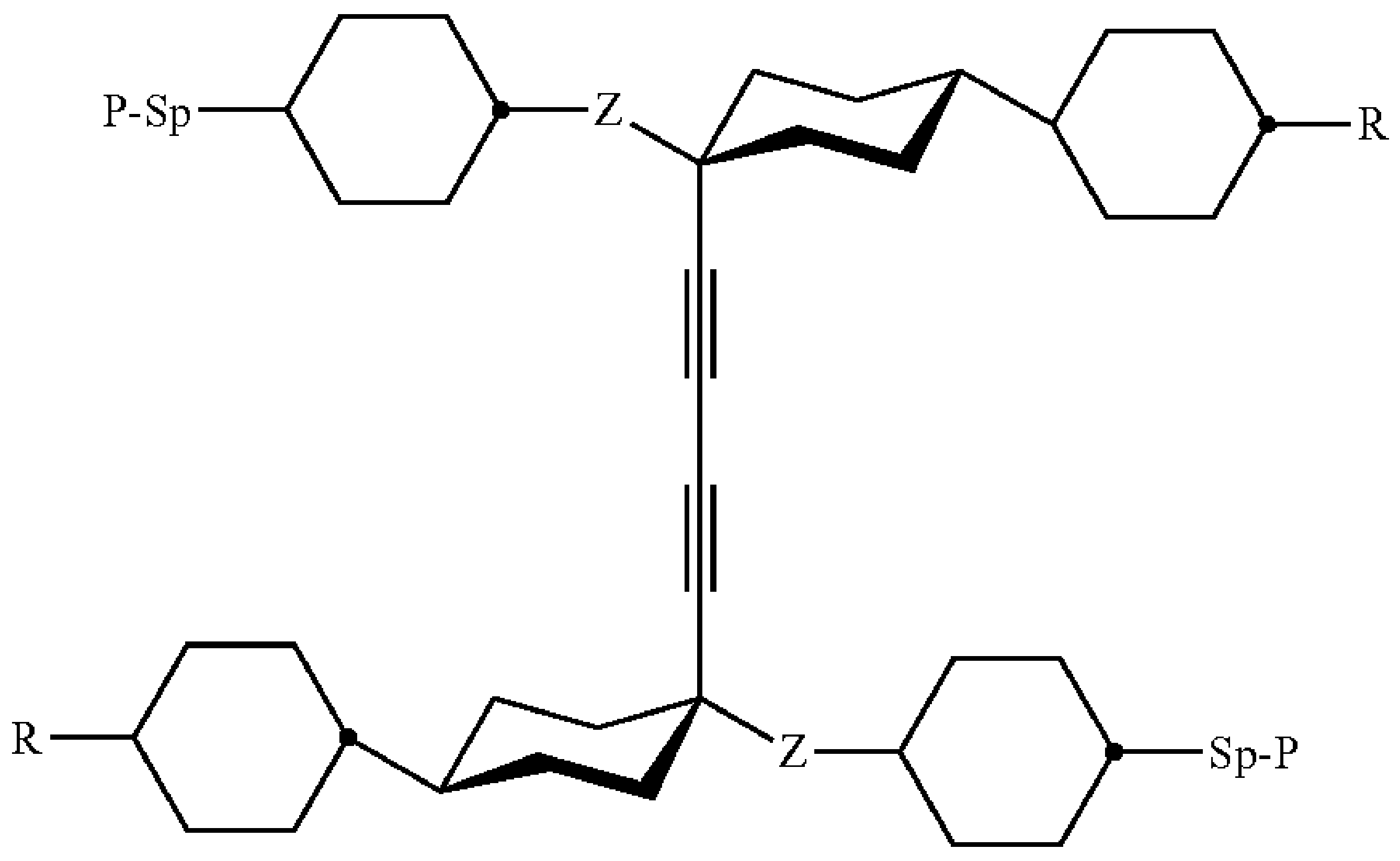

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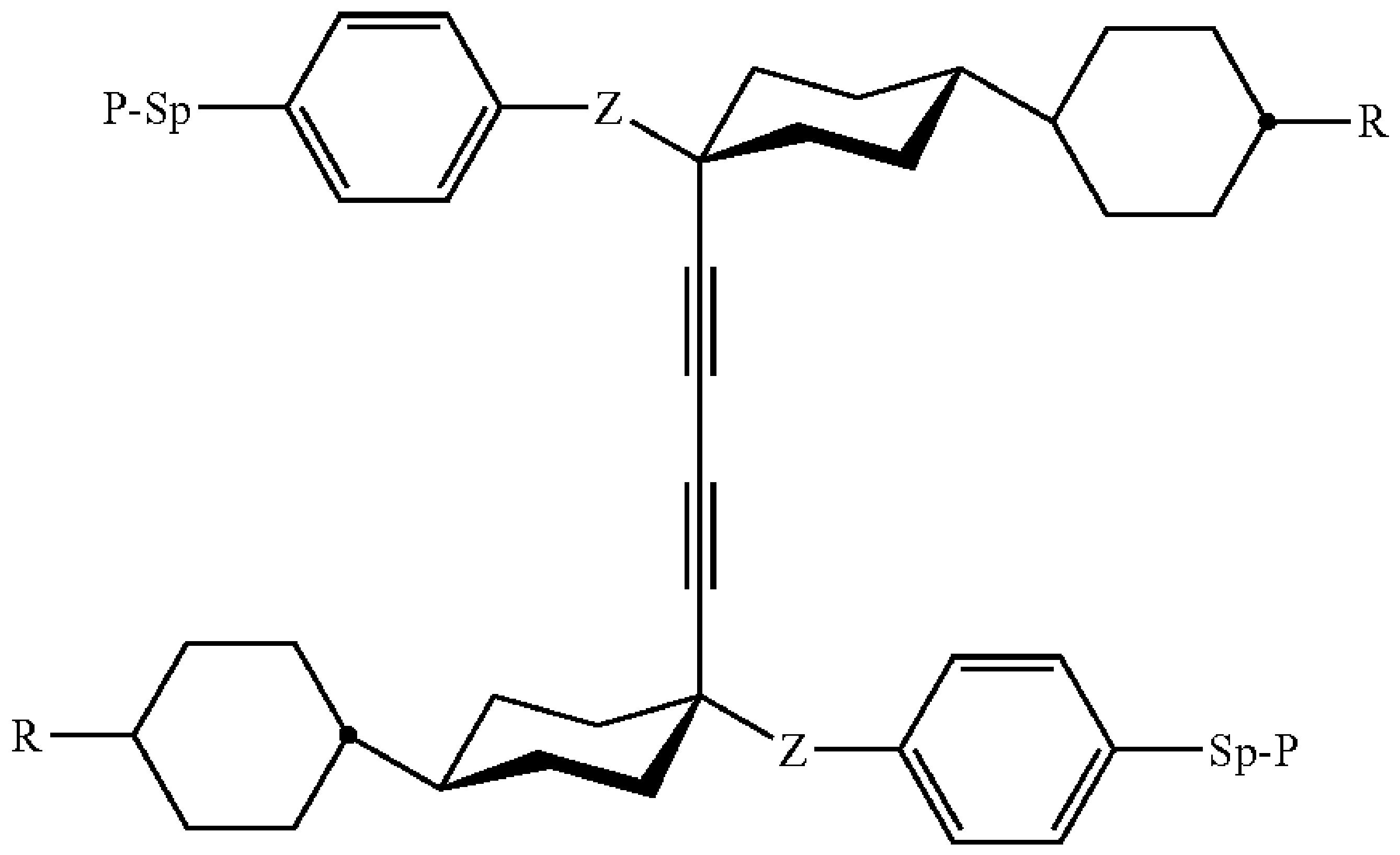

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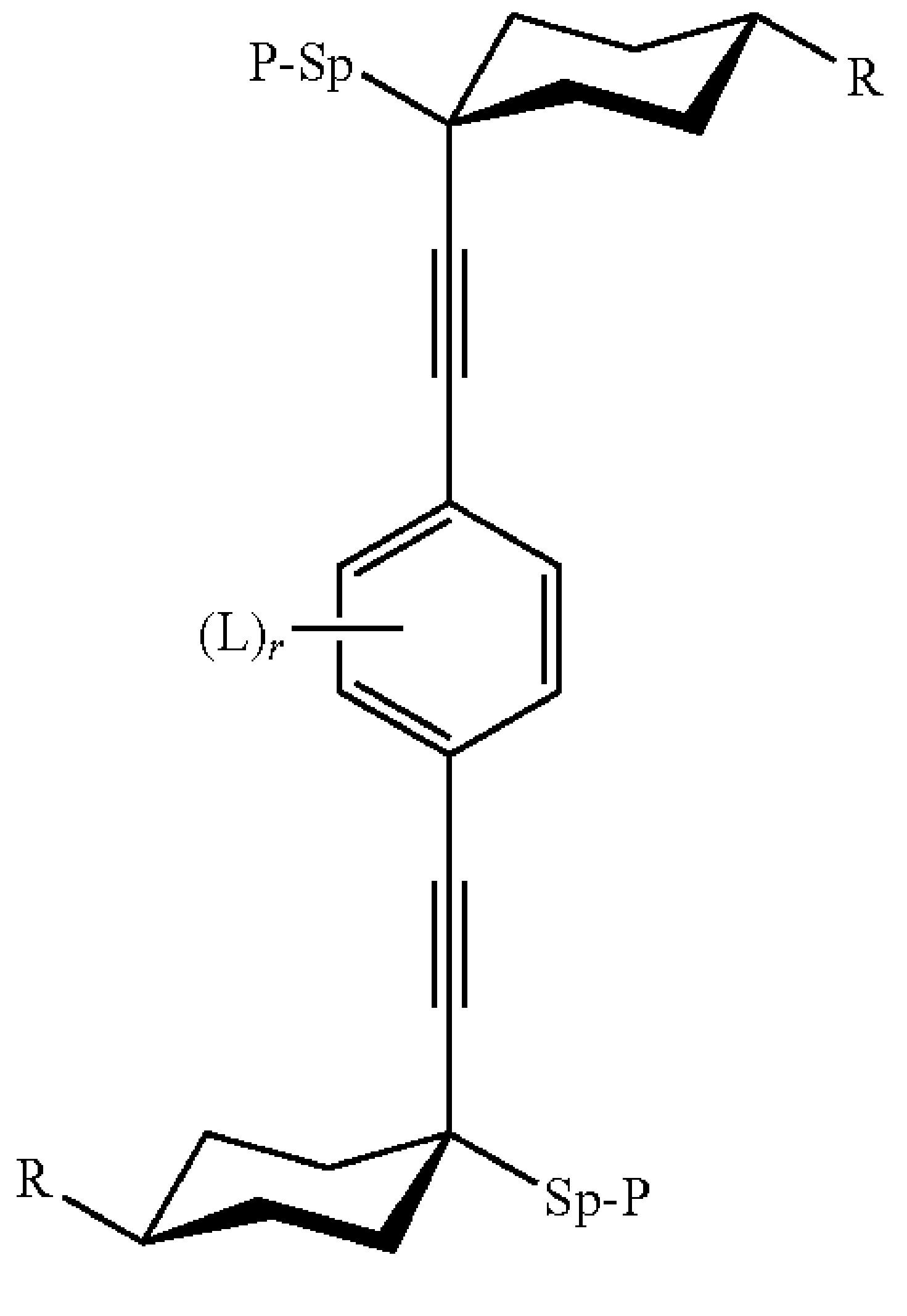

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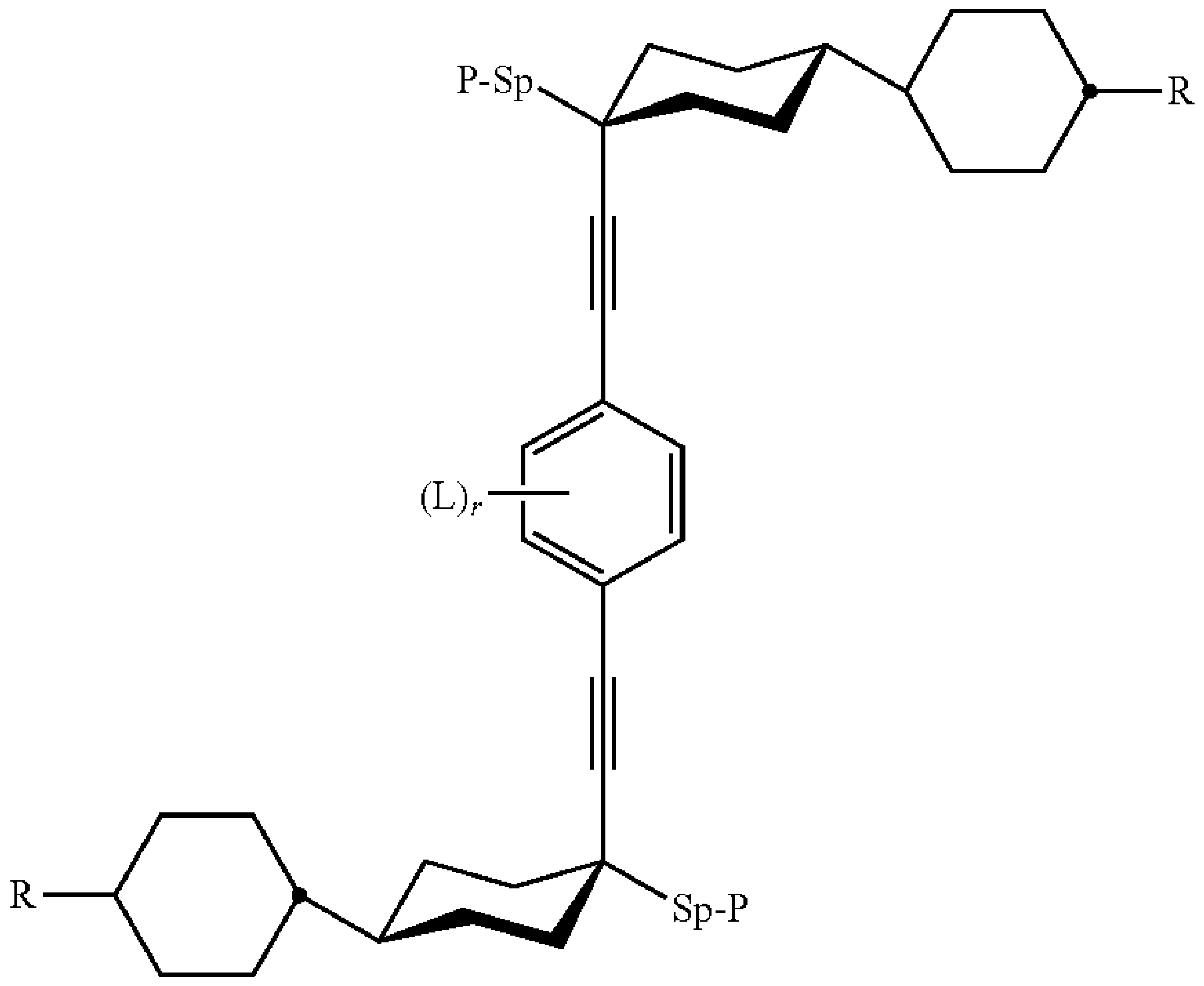

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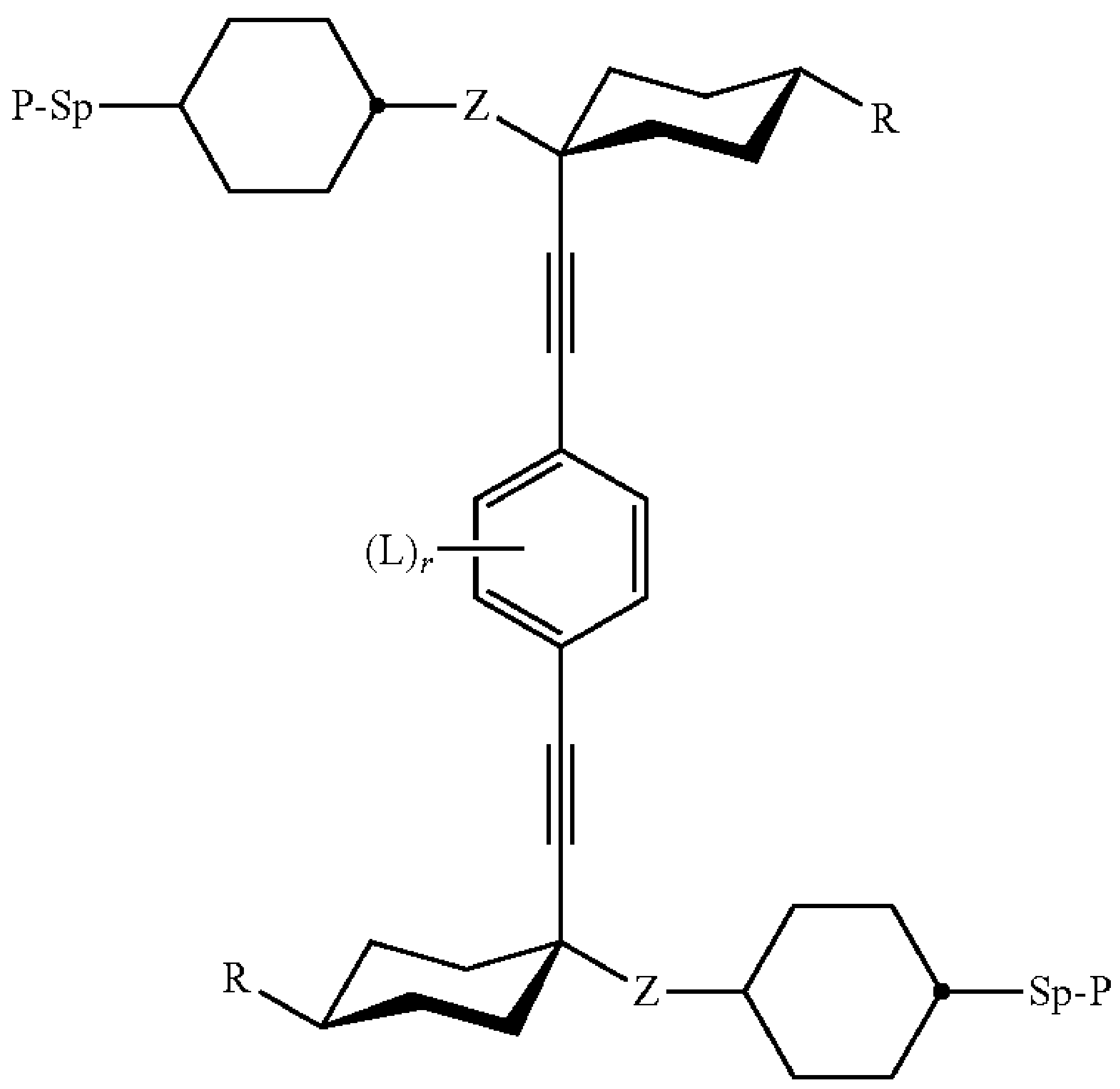

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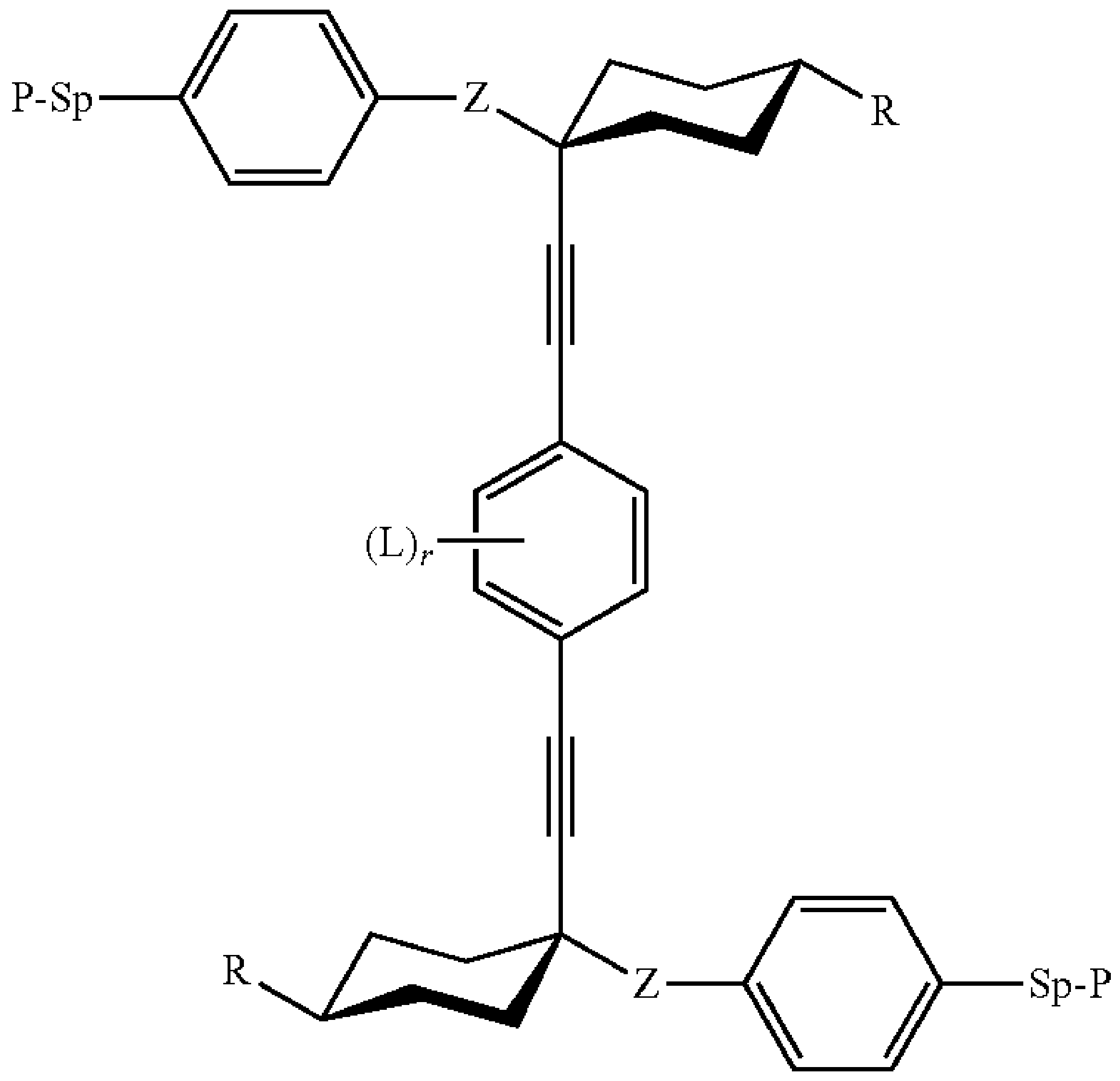

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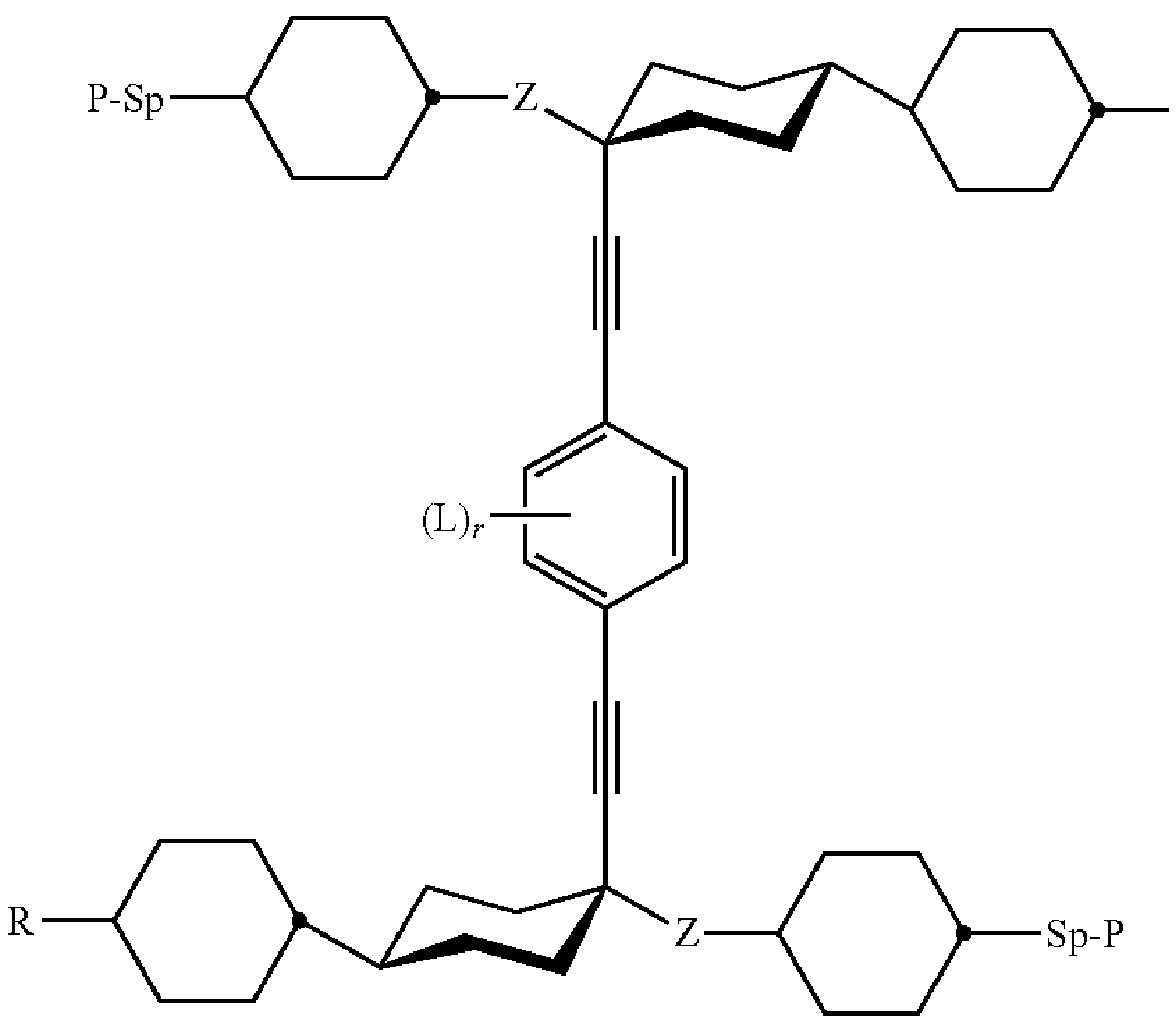

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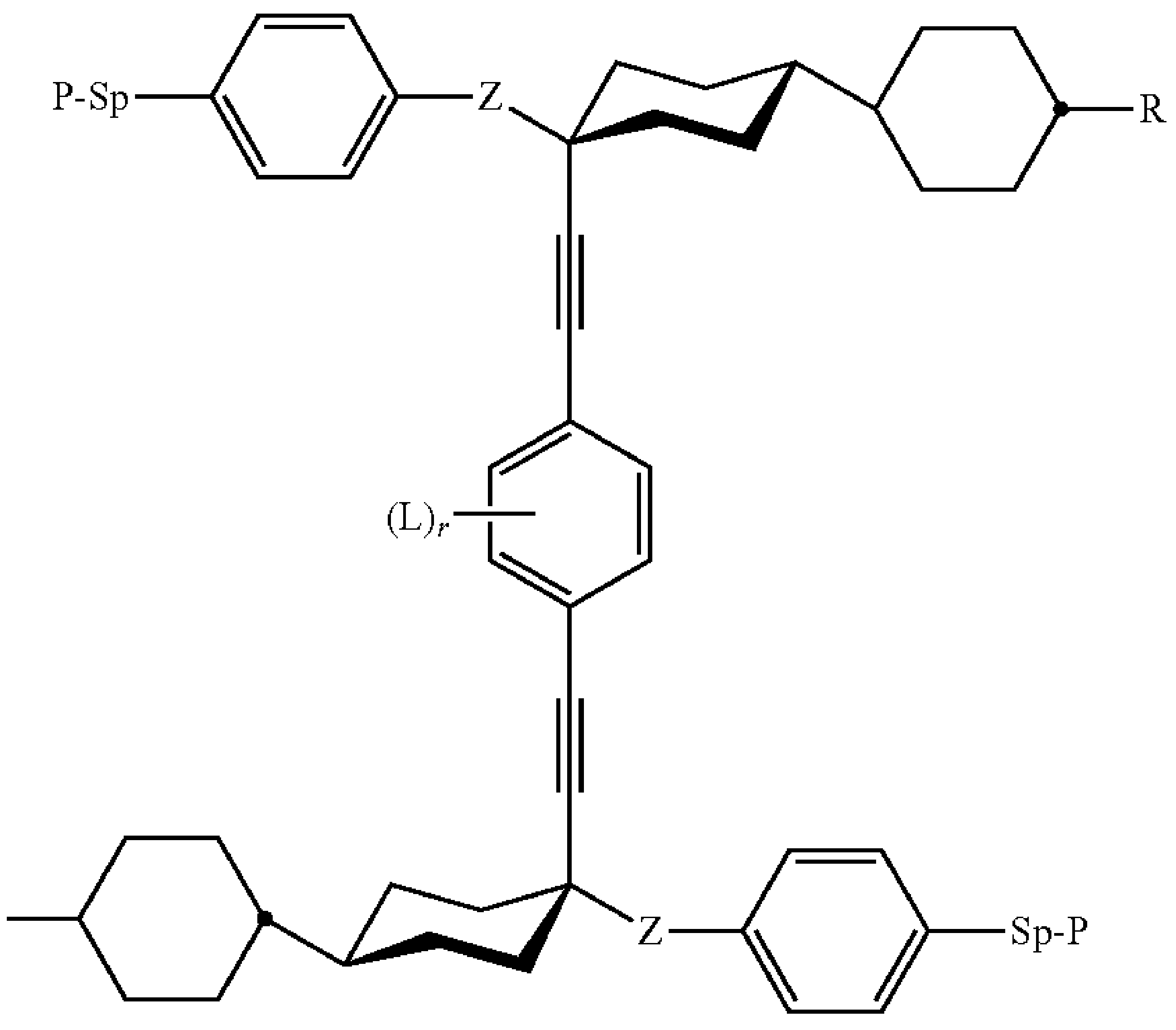

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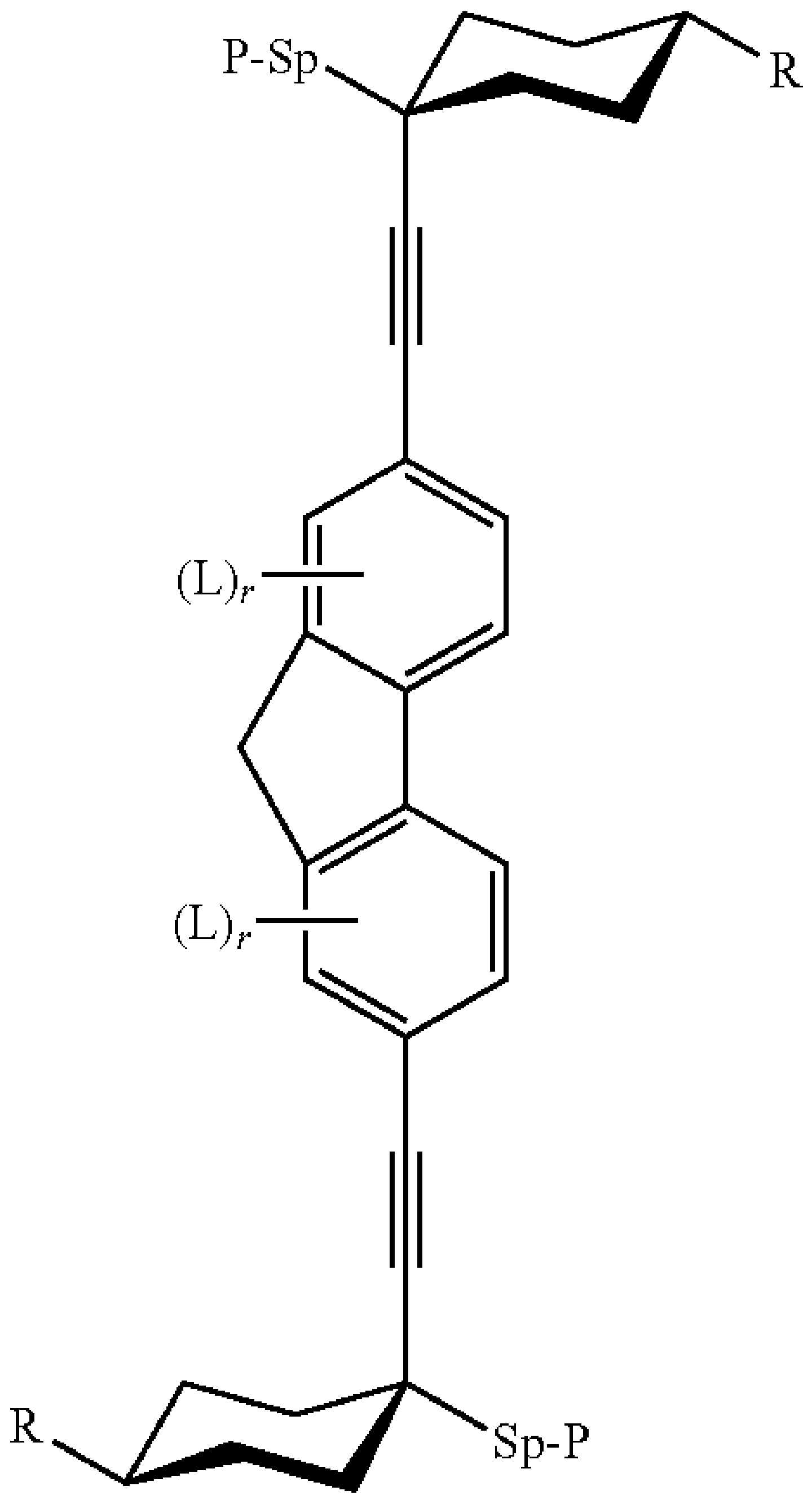

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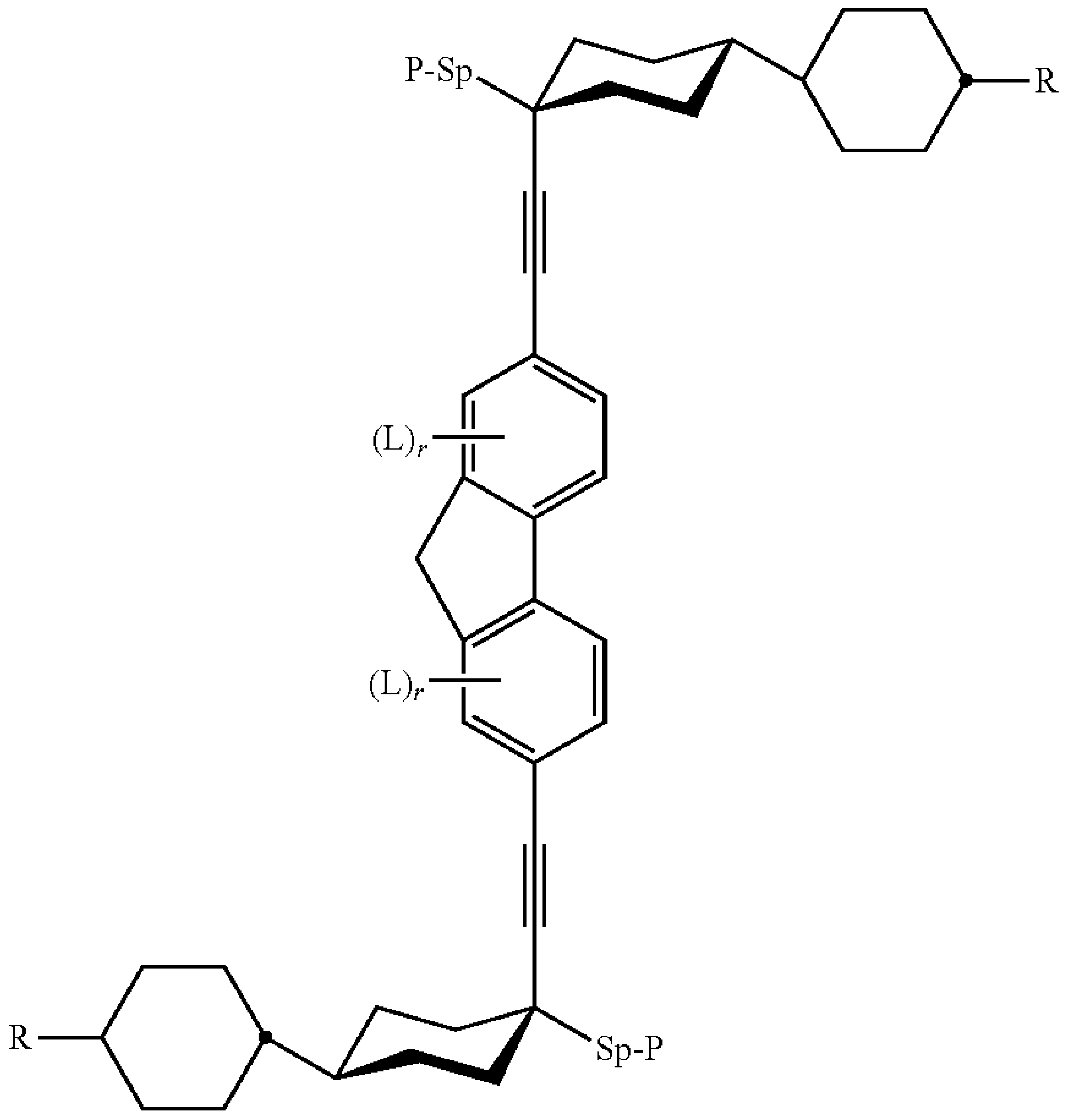

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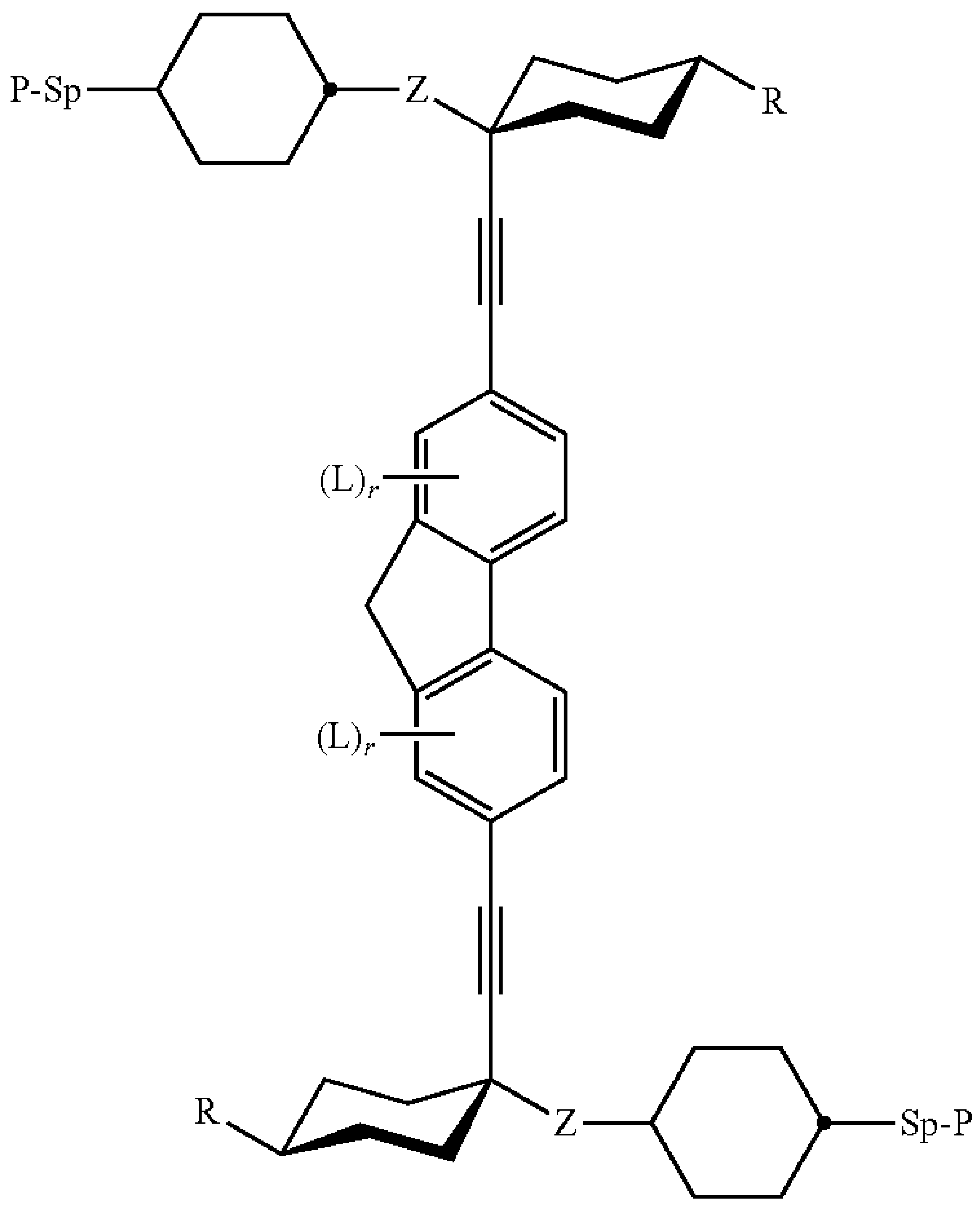

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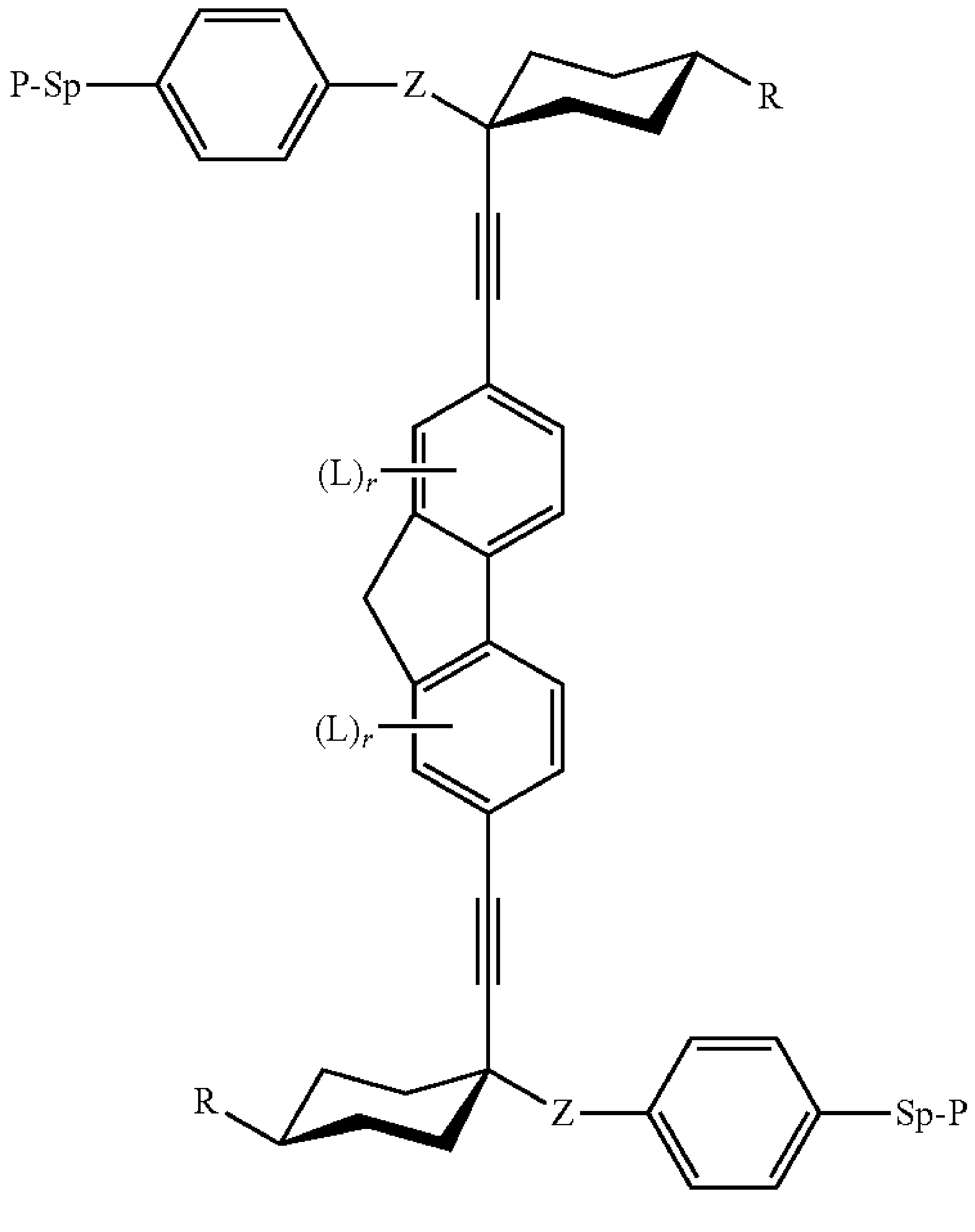

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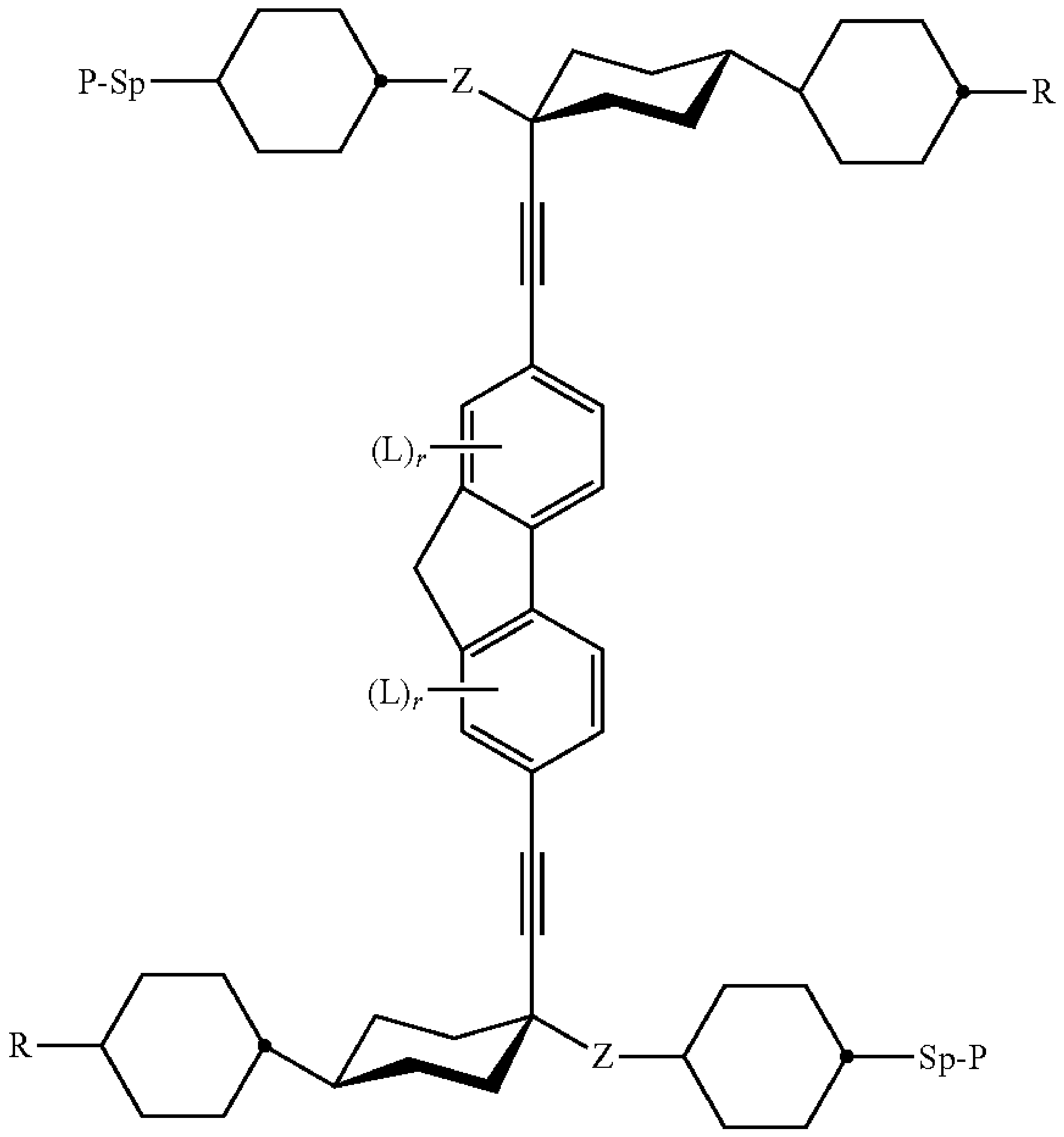

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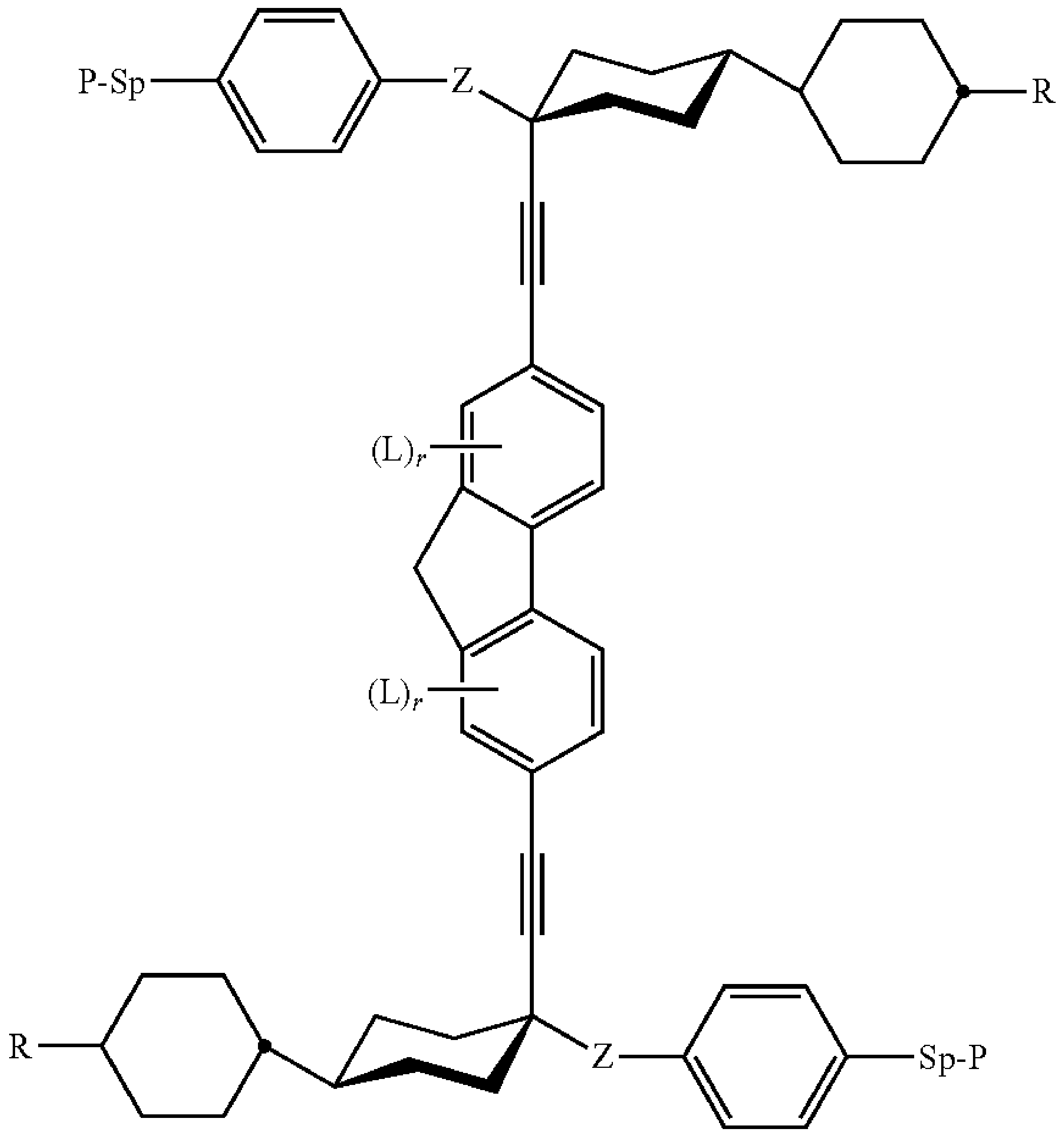

wherein Z has one of the meanings of Z^1 given above, R has one of the meanings of R^1 as given above that is different from P-Sp-, and P, Sp, L and r are as defined above, and the benzene rings in the mesogenic groups are optionally substituted by one or more groups L as defined above.

P-Sp- in these preferred compounds is preferably P-Sp'-X', with X' preferably being —O—, —COO— or —OCOO—. Z is preferably —COO— or —OCO—.

The compounds of formula I can be synthesized according to or in analogy to methods which are known per se and which are described in the literature and in standard works of organic chemistry such as, for example, Houben-Weyl, Methoden der organischen Chemie, Thieme-Verlag, Stuttgart. Especially suitable methods are disclosed in U.S. Pat. No. 6,203,724. Further suitable methods of synthesis are also described below and in the examples.

The compounds of formula I can be generally synthesized by initially reacting a suitably substituted acetylene, e.g. (trimethylsilyl)acetylene, with a suitable cyclohexanone in the presence of butyllithium, as described e.g. in ACS Symposium Series (2001), 798 (Anisotropic Organic Materials), 195-205. After separation of the isomers by chromatography, the axial acetylenic substituents can either be homocoupled to form a dimer, (i.e. intermediate 2 in example 1) or coupled to another ring, such as dihalodobenzene, by palladium catalyzed coupling reactions as described e.g. in either J. Org. Chem. 1997, 62, 7471, or Tetrahedron Lett. 1993, 6403. With suitable choice of halo substituted phenyl rings, this can either give the symmetrical dimer or the axial-phenylacetylenic substituted cyclohexanones, which can be further coupled to another axially substituted acetylenic cyclohexanone to give unsymmetrical examples. All the above examples generally give coupled products that are either mono or di-tertiary alcohols. Esterification of the dialcohols with a suitable carboxylic acid yields a diester product.

An alternative synthetic route involves the formation of the axial-substituted cyclohexanone by the methods described above, followed by esterification of the tertiary alcohols with a suitable carboxylic acid. The ester with an axial substituted acetylenic group can be homocoupled to give the diacetylenes, or coupled to a suitably substituted halo benzene via a palladium catalyzed coupling reaction.

The methods of preparing a guest compound as described above and below are another aspect of the invention. Especially preferred is a method comprising the following steps:

a) reacting a suitably substituted acetylene with an optionally substituted cyclohexanone in the presence of butyllithium,
b) separating the isomers thereby formed,
c) homocoupling an isomer prepared by steps a) and b) via its axial acetylenic substituents to give a dimer, or
d) coupling an isomer prepared by steps a) and b) via its axial acetylenic substituent to another optionally substituted cyclohexanone, or
e) coupling an isomer prepared by steps a) and b) via its axial acetylenic substituent to an aromatic ring, and coupling the resulting product to an identical or different isomer prepared by steps a+b).

Another aspect of the invention is a polymerisable material, preferably a polymerisable LC material, comprising one or more guest compounds as described above and below, and one or more additional compounds, which are preferably mesogenic or liquid crystalline and/or polymerisable. Very preferably the LC material comprises one or more additional compounds selected from reactive mesogens (RMs), most preferably selected from mono- and direactive RMs. These additional compounds constitute the polymerisable LC host material.

Preferably the polymer films according to the present invention are crosslinked, and the polymerisable guest compounds and/or the polymerisable host materials comprise at least one compound with two or more polymerisable groups (di- or multireactive).

The concentration of the guest compound(s) of the present invention in the polymerisable LC material (including both the guest and the host material) is preferably from 5 to 90 wt. %, very preferably from 30 to 70 wt. %.

The additional RMs of the polymerisable LC host material can be prepared by methods which are known per se and which are described in standard works of organic chemistry like for example Houben-Weyl, Methoden der organischen Chemie, Thieme-Verlag, Stuttgart. Suitable RMs are disclosed for example in WO 93/22397, EP 0 261 712, DE 195 04 224, WO 95/22586, WO 97/00600, U.S. Pat. No. 5,518,652, U.S. Pat. No. 5,750,051, U.S. Pat. No. 5,770,107 and U.S. Pat. No. 6,514,578. Examples of particularly suitable and preferred RMs are shown in the following list.

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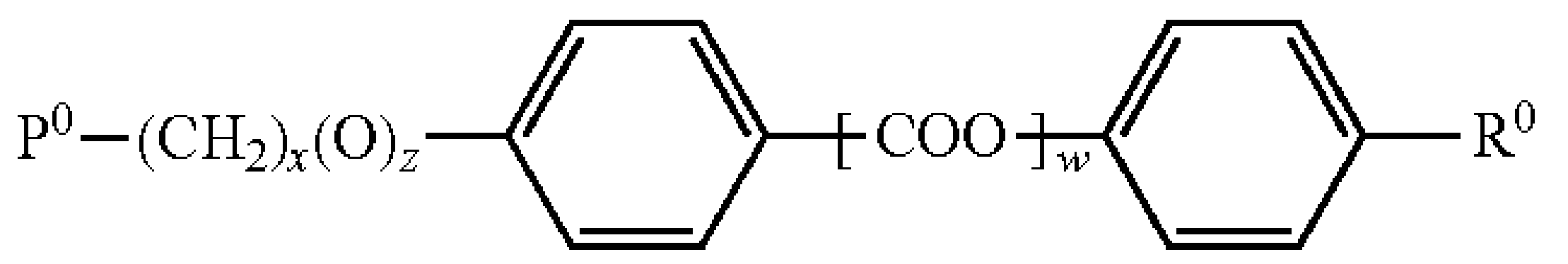

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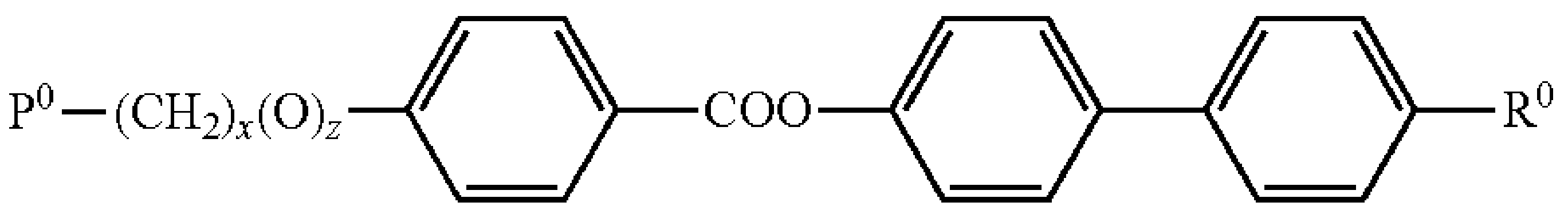

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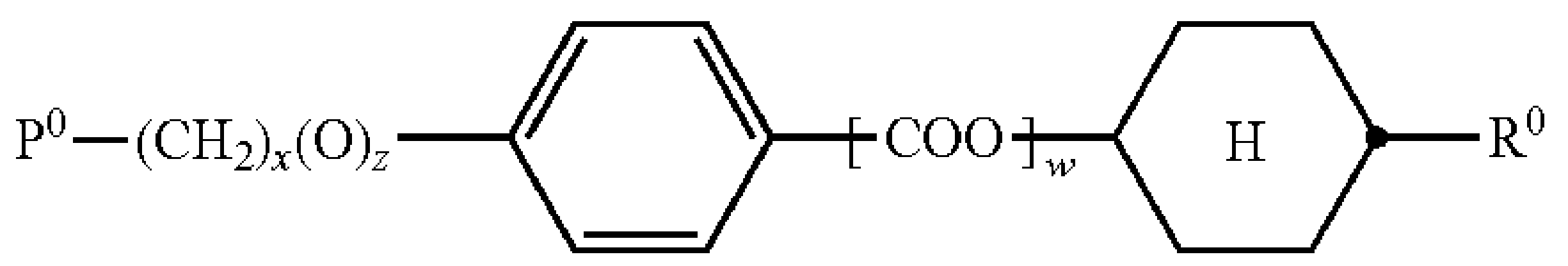

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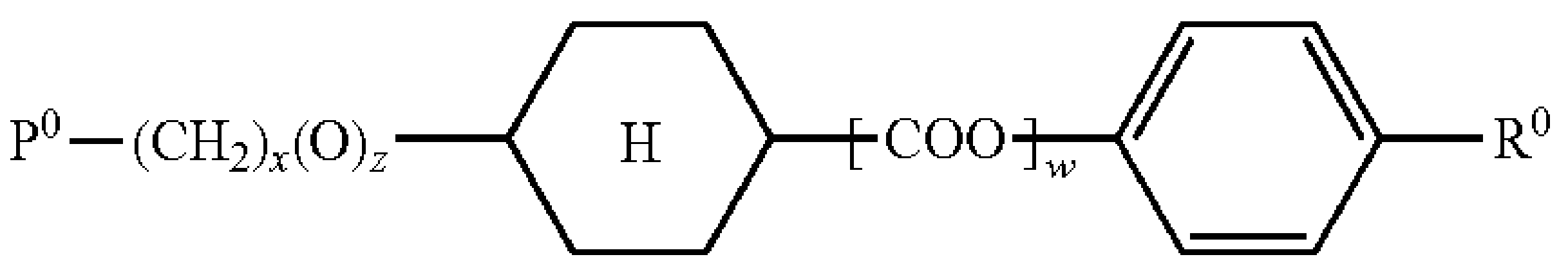

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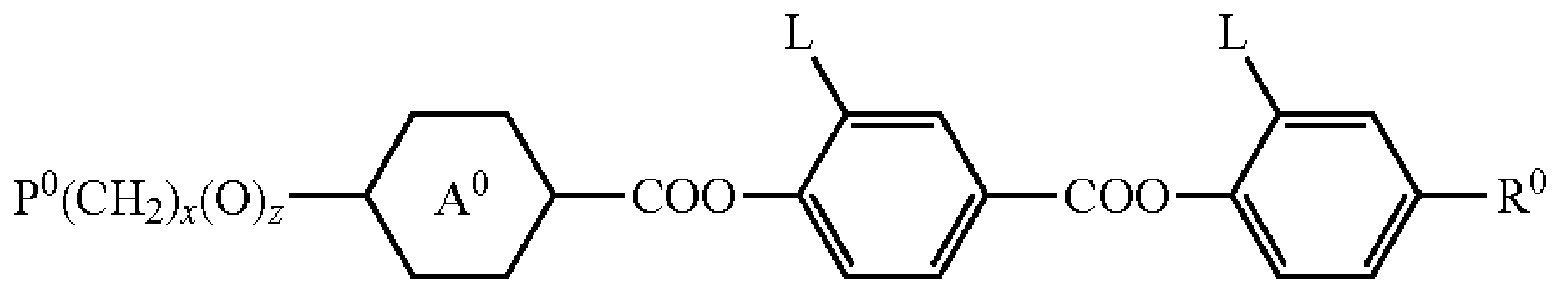

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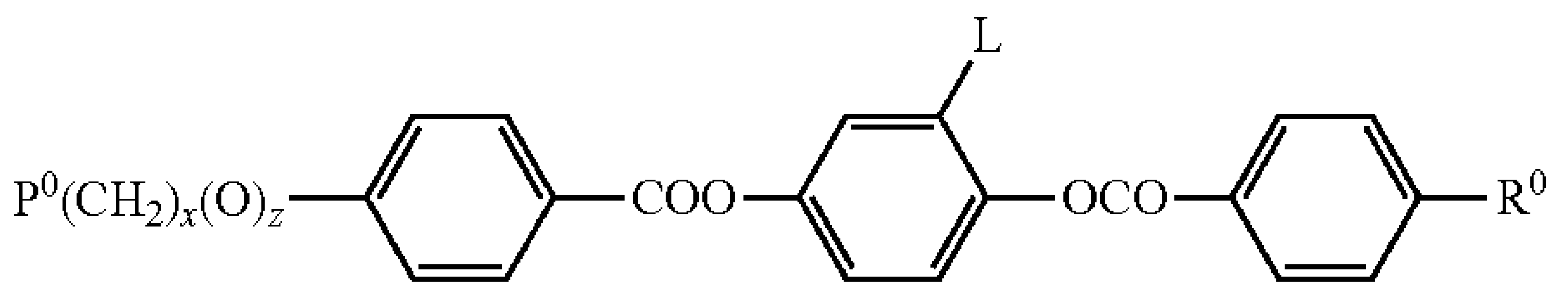

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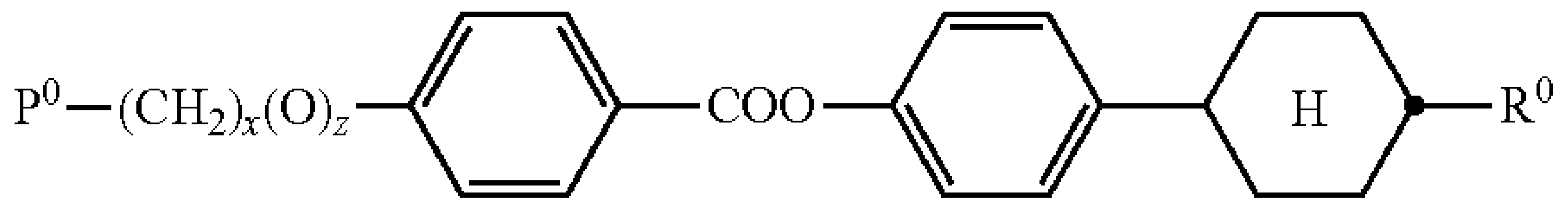

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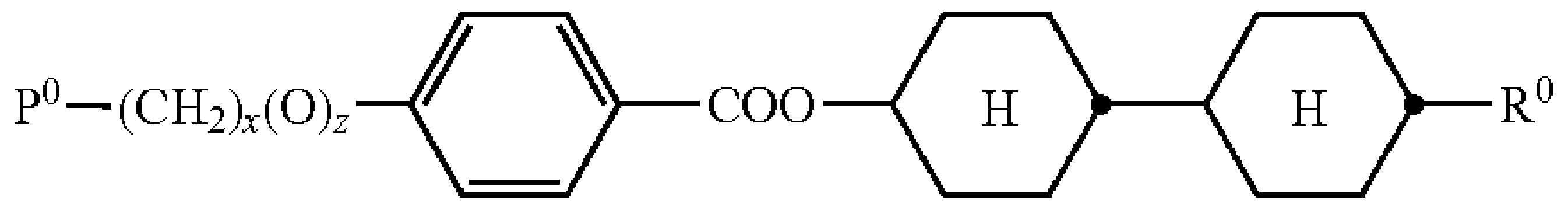

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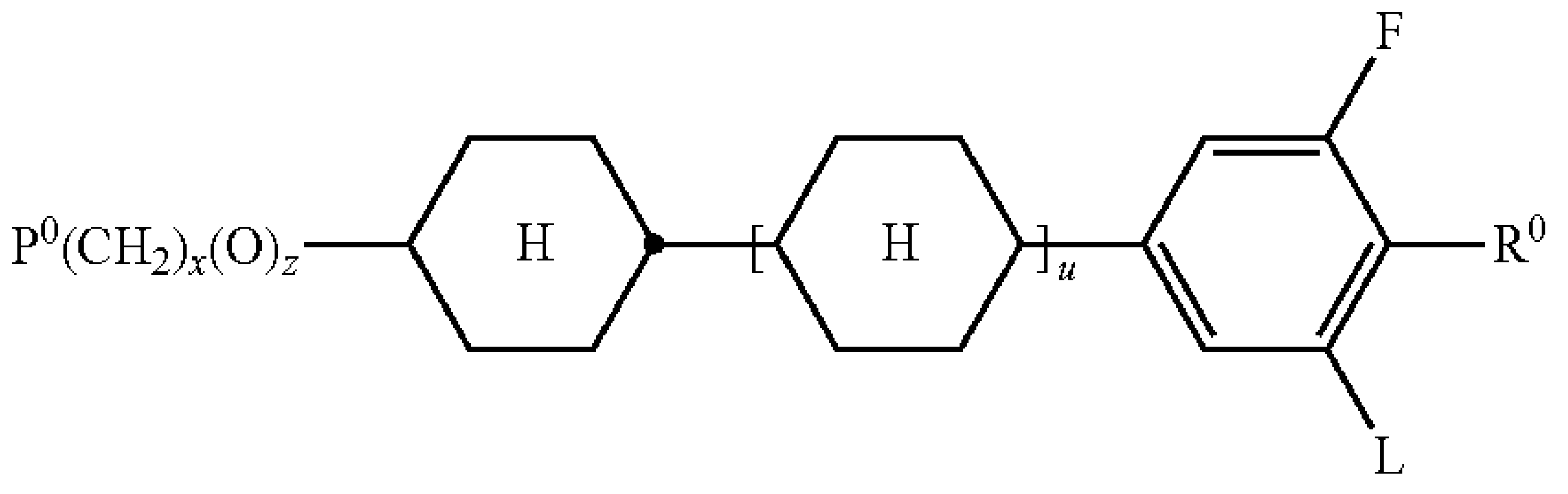

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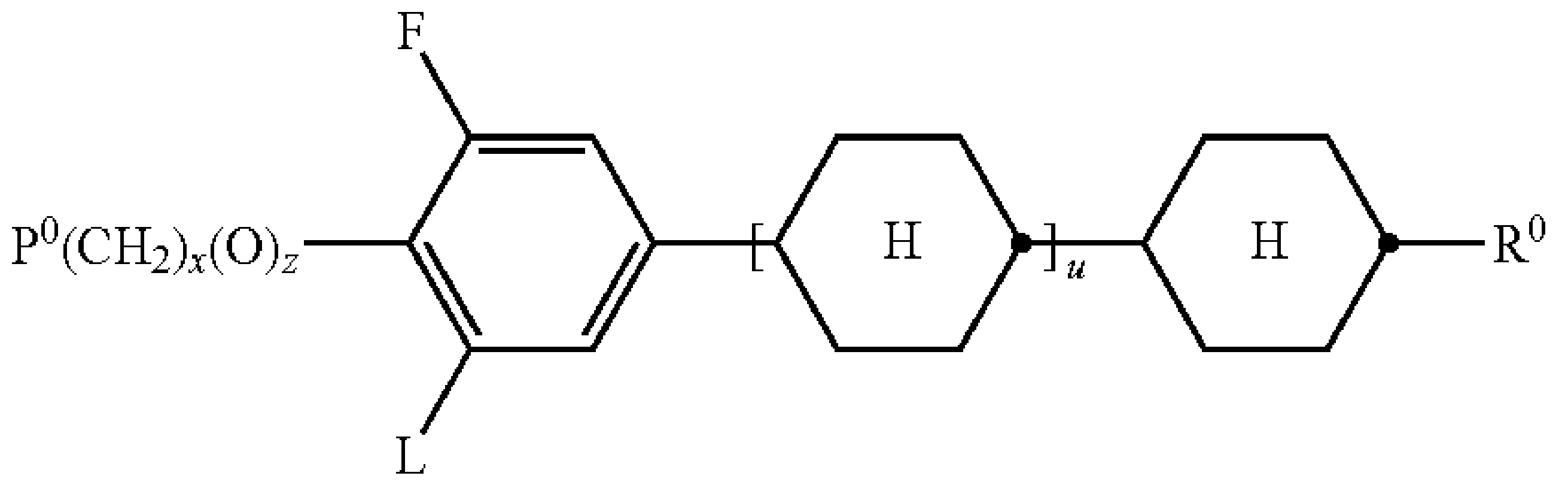

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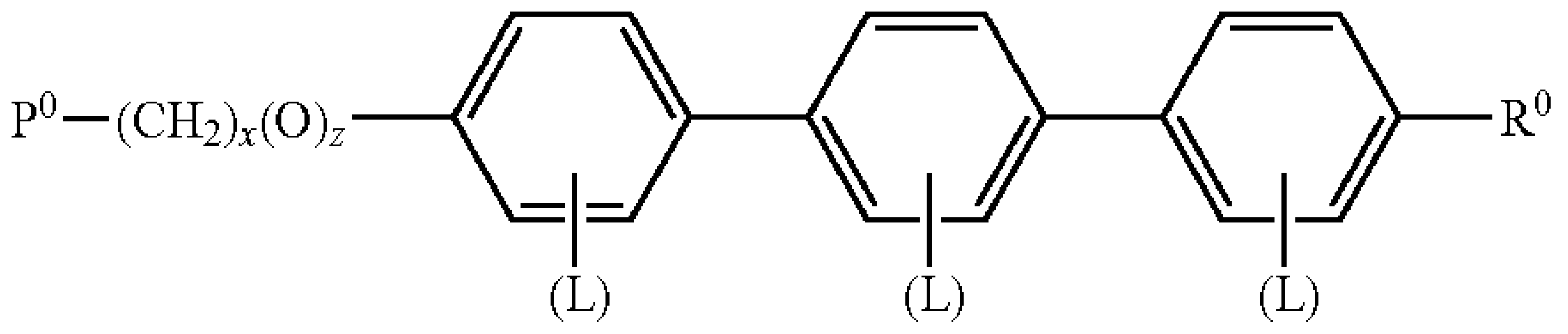

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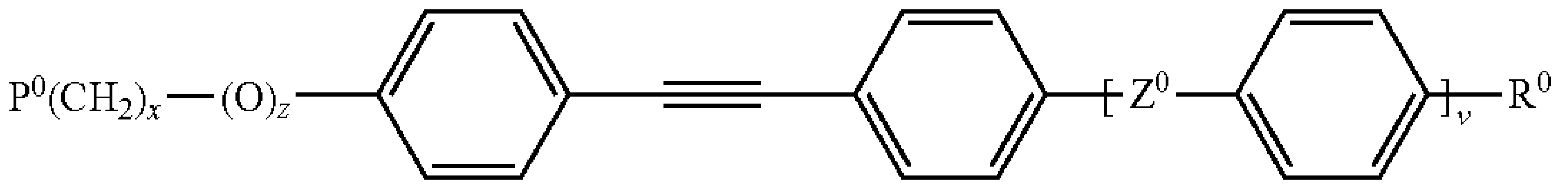

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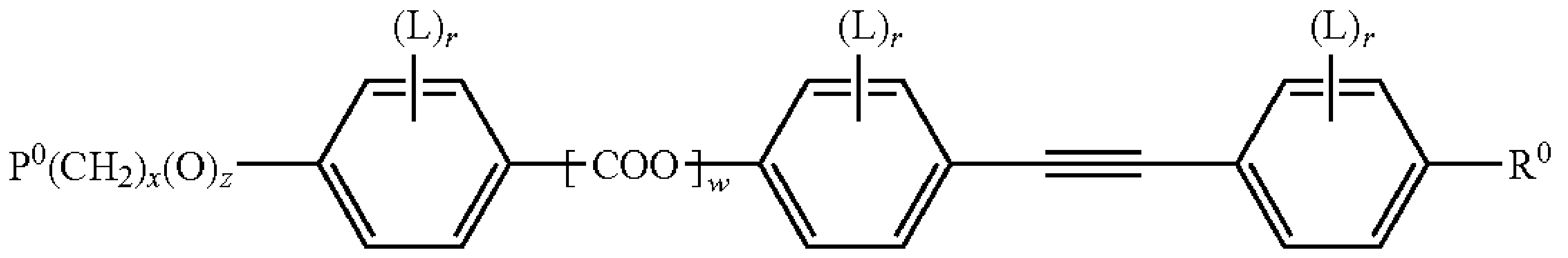

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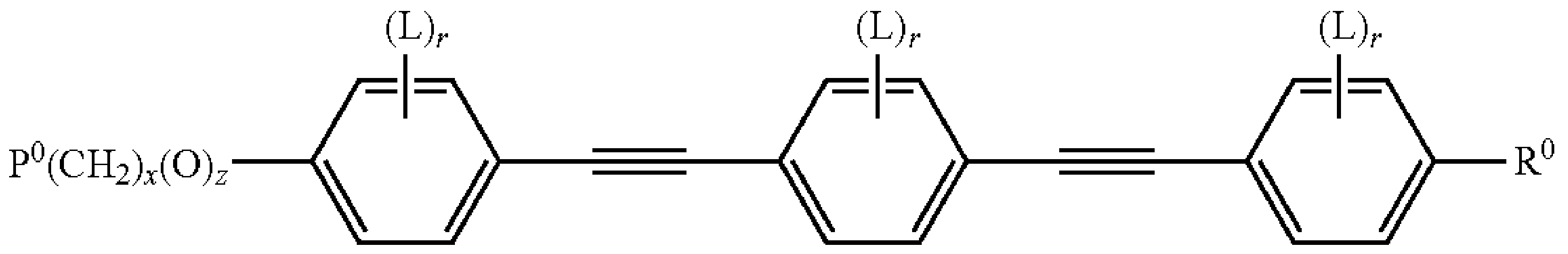

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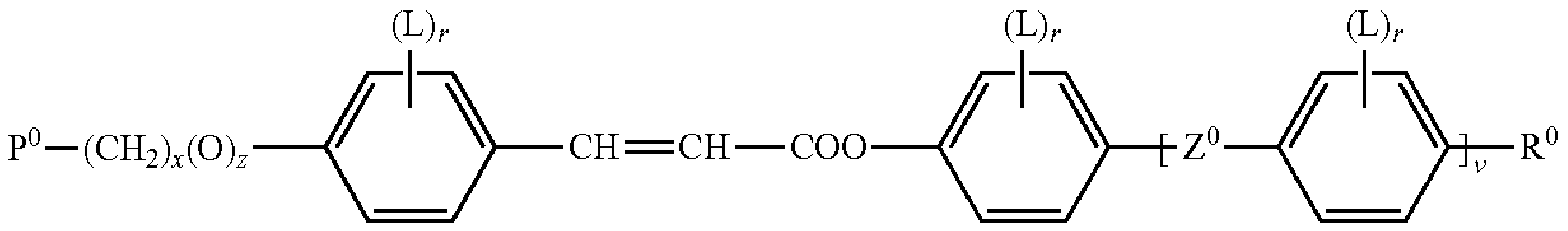

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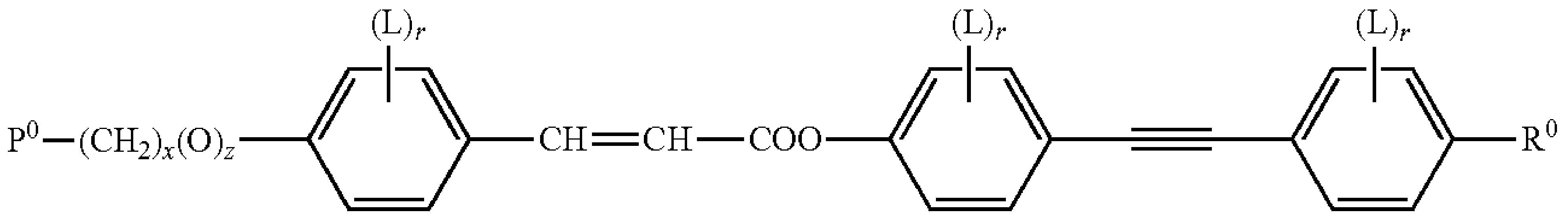

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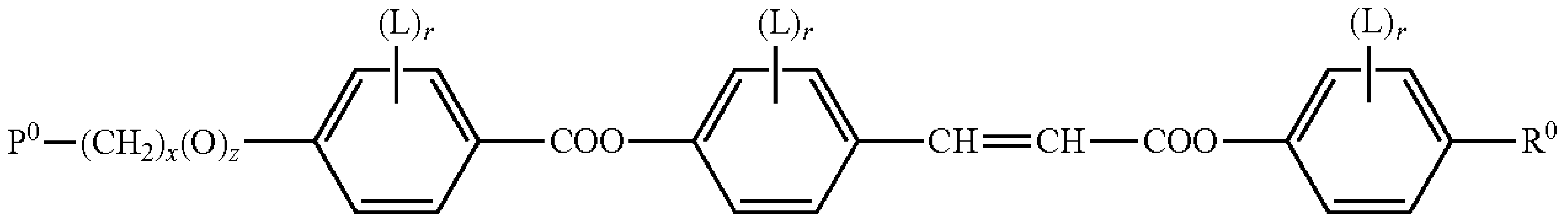

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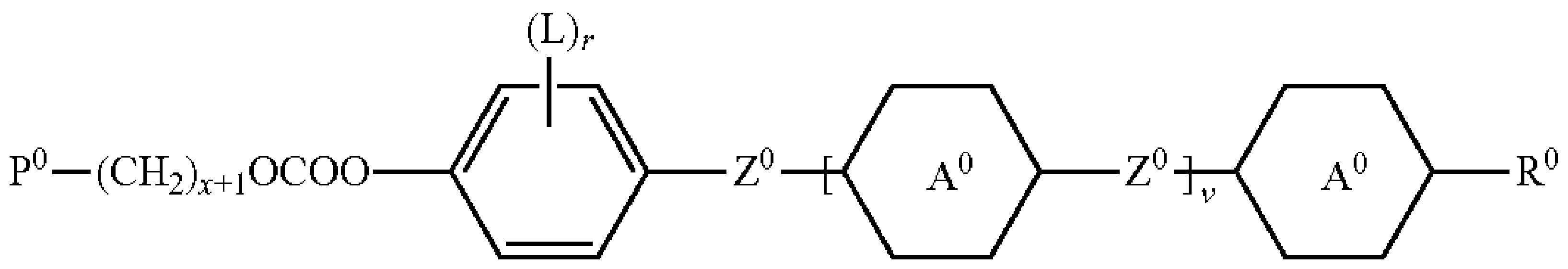

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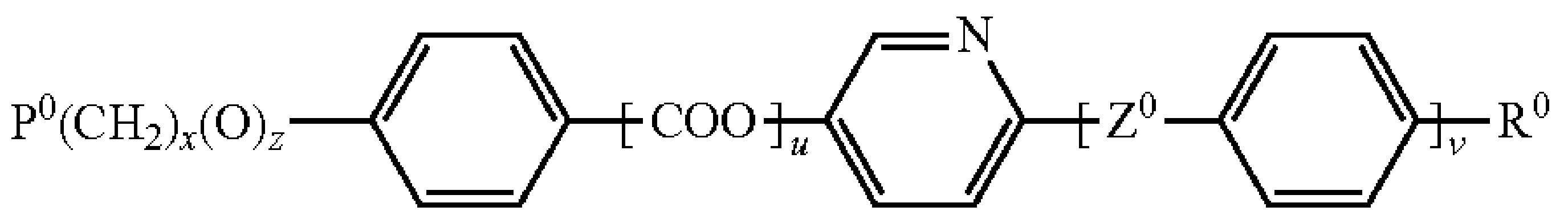

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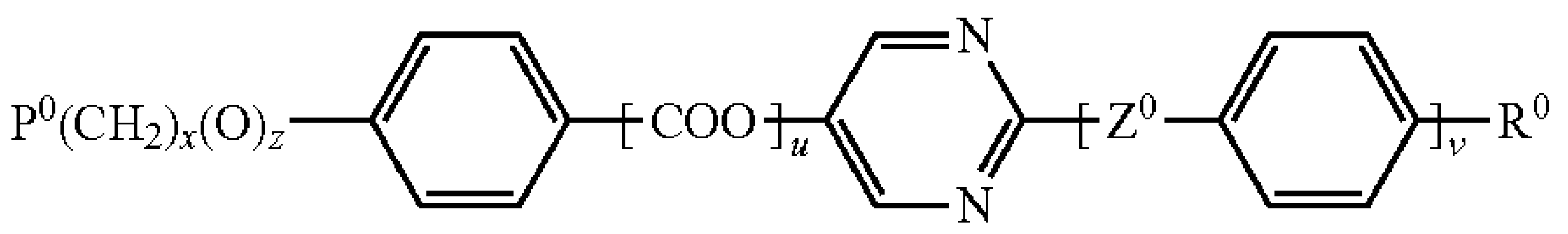

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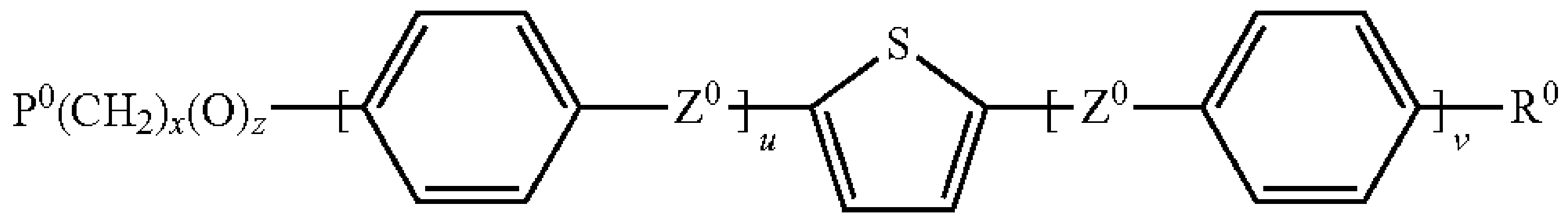

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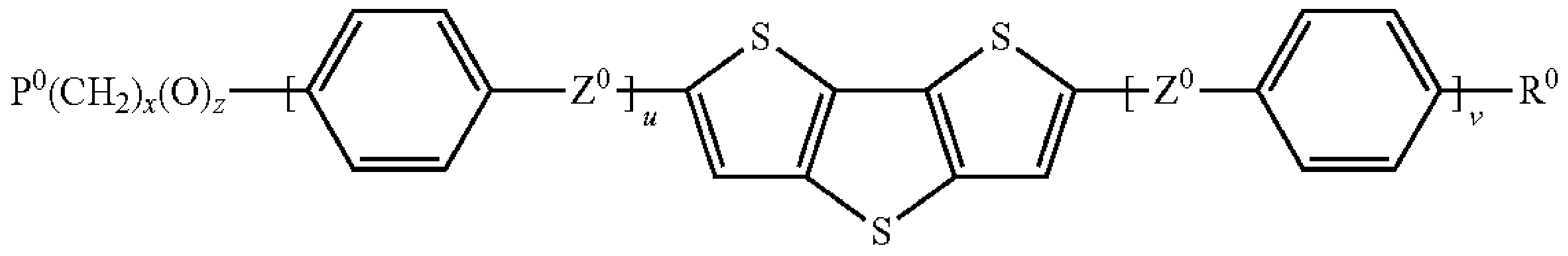

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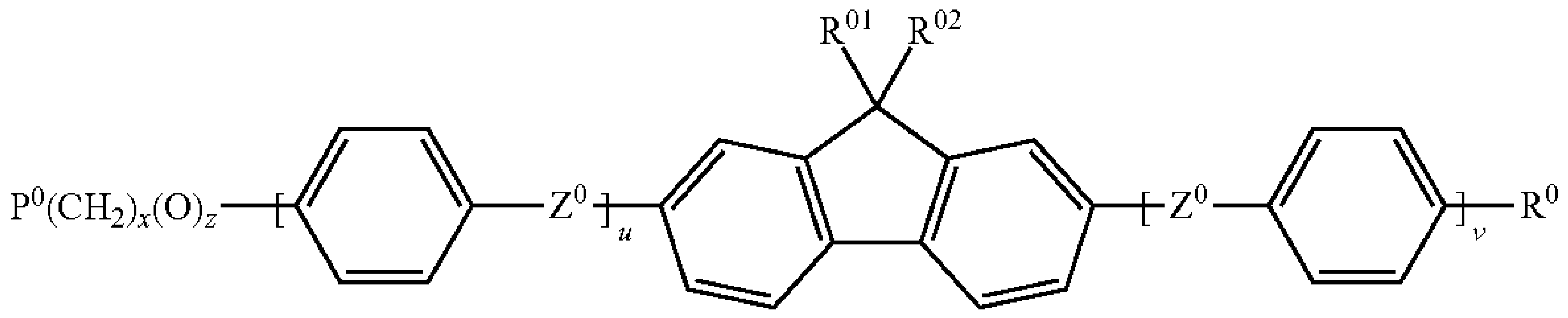

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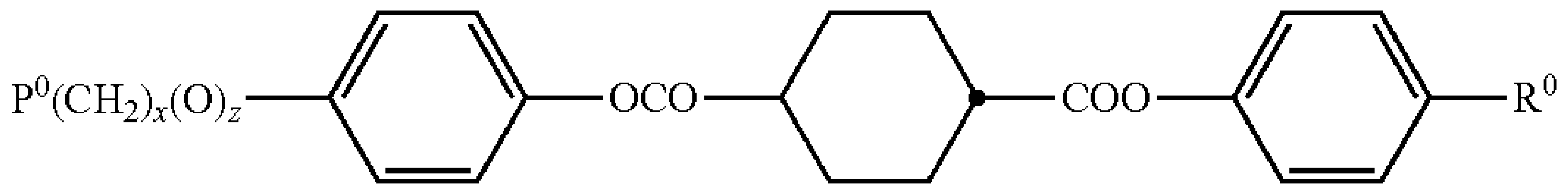

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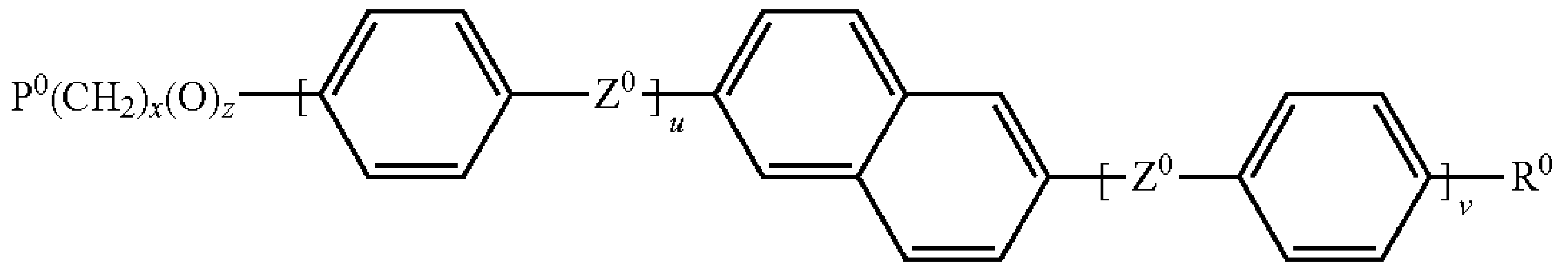

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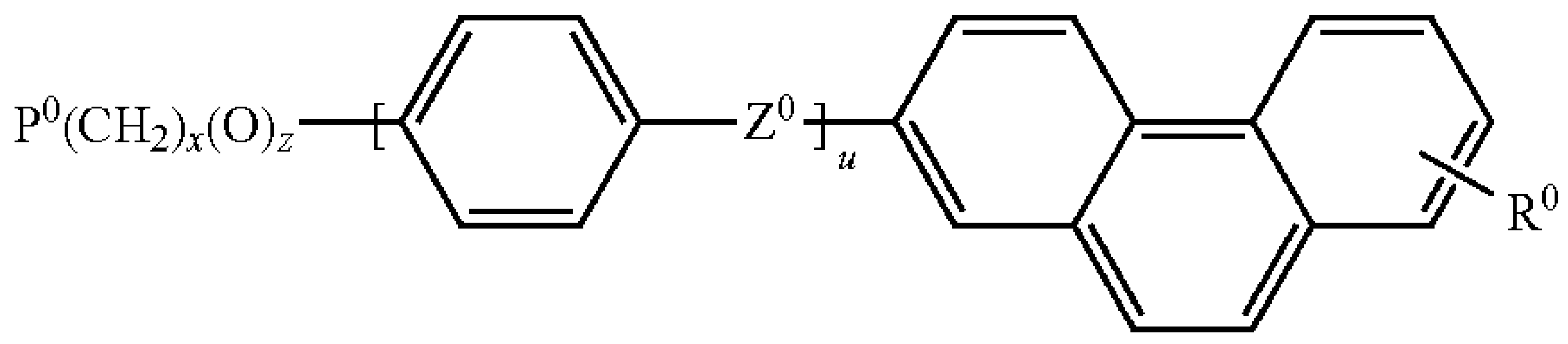
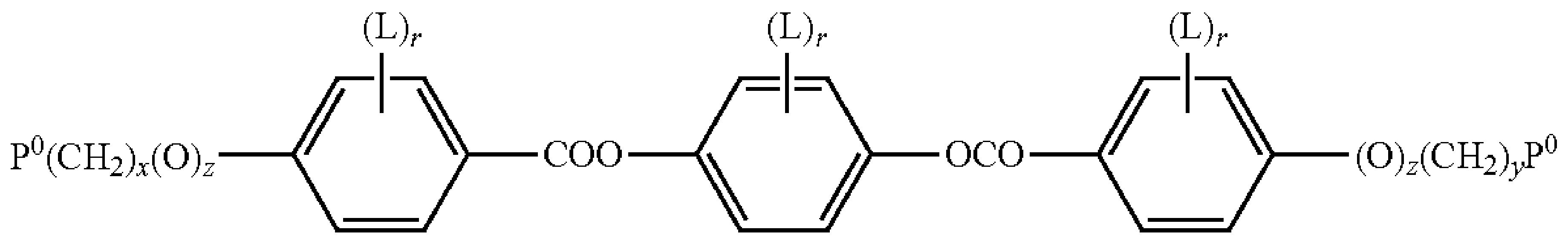


(DR1)



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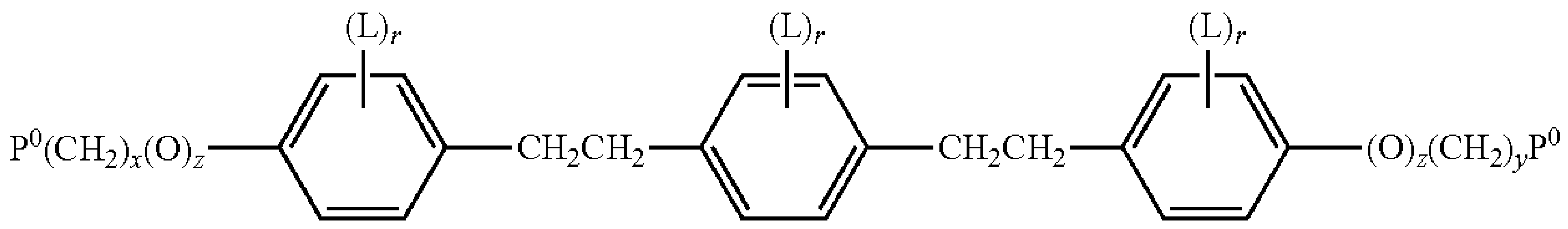

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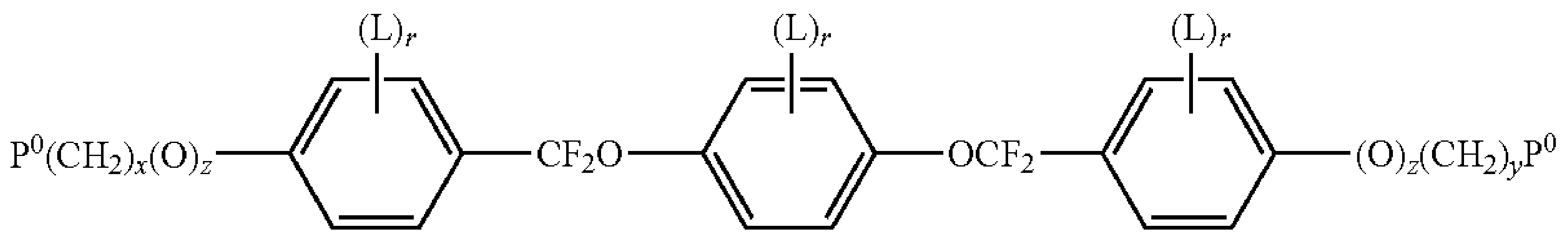

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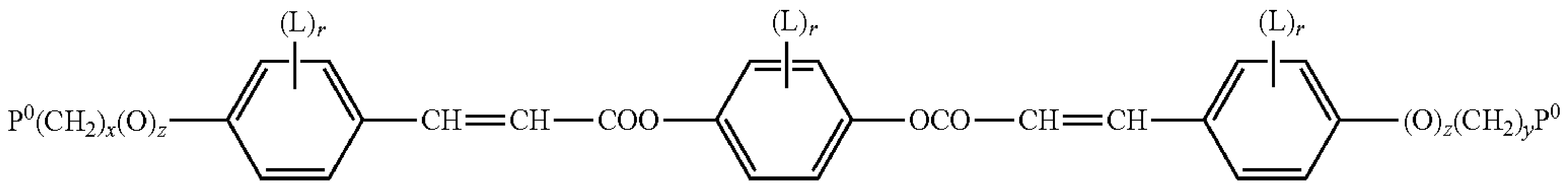

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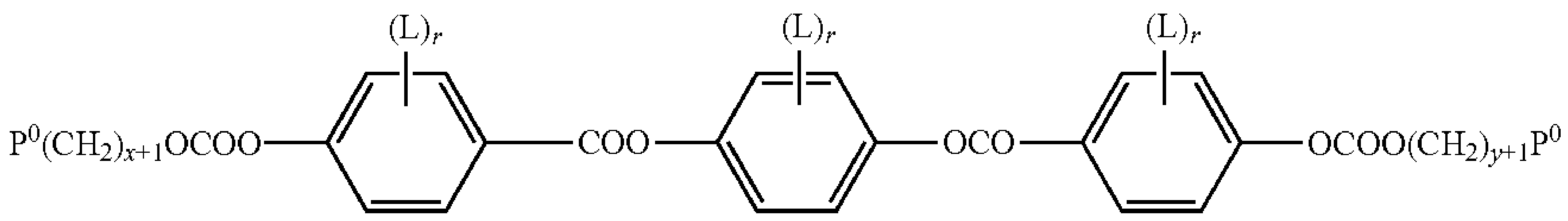

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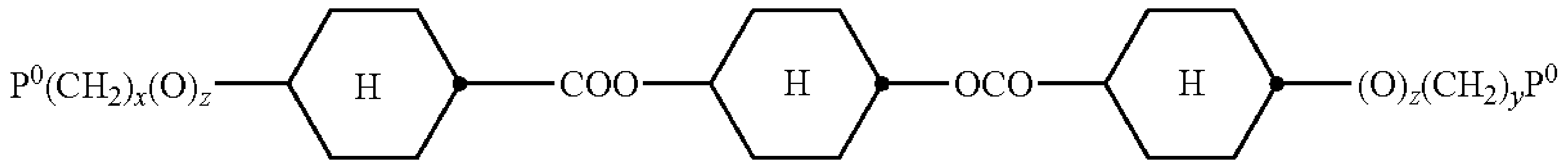

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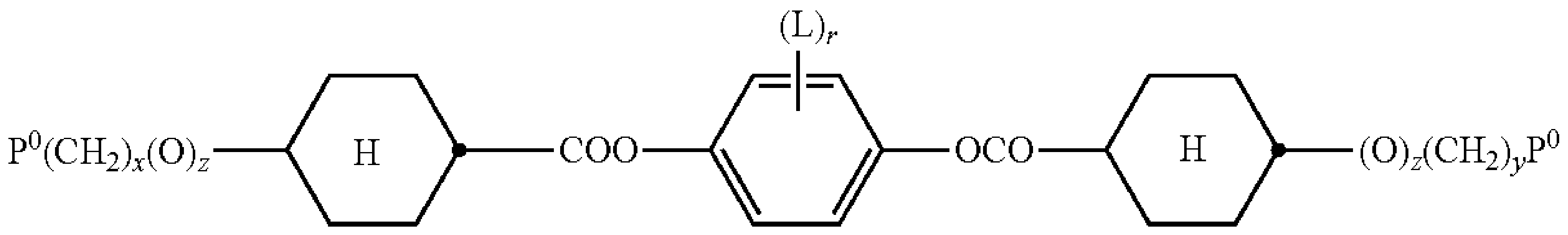

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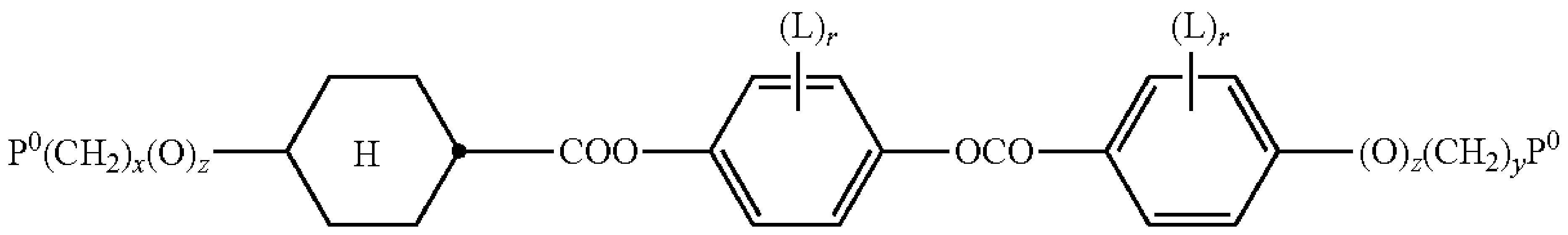

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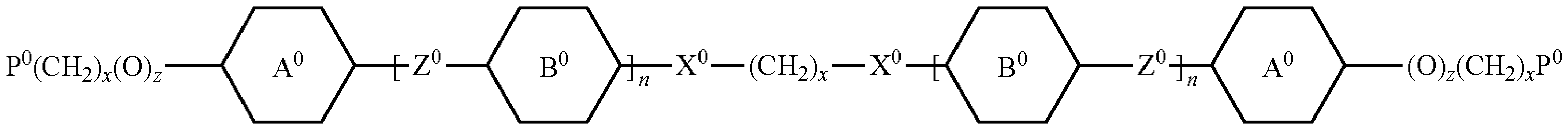

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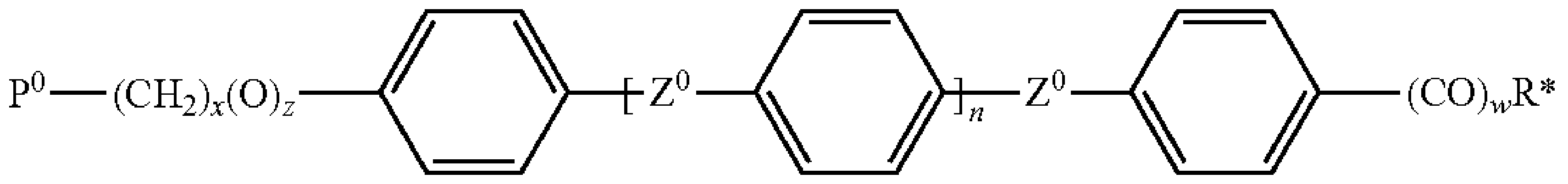

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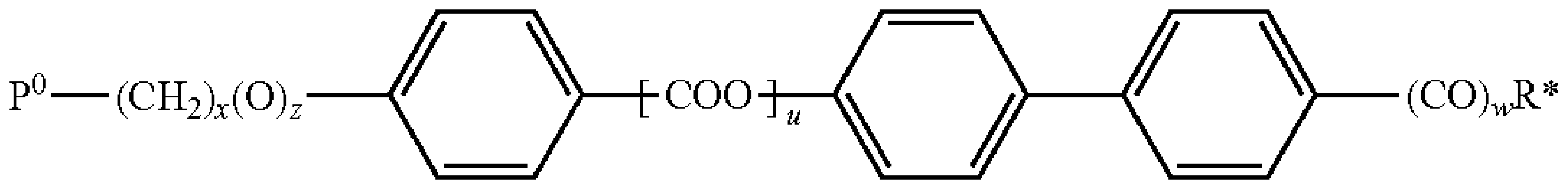

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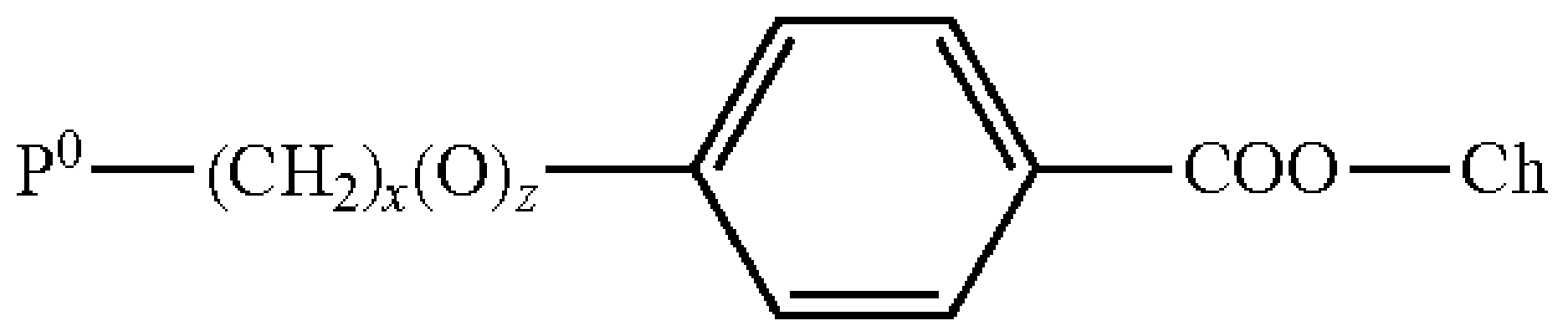

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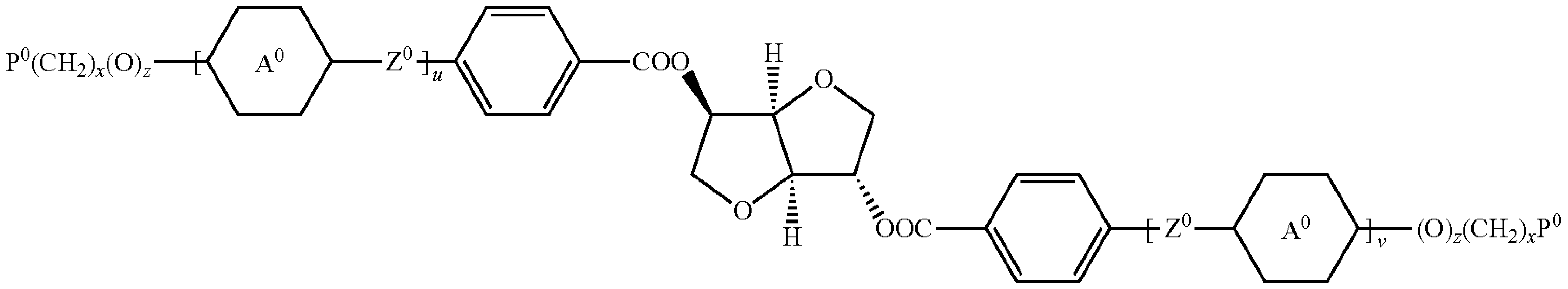

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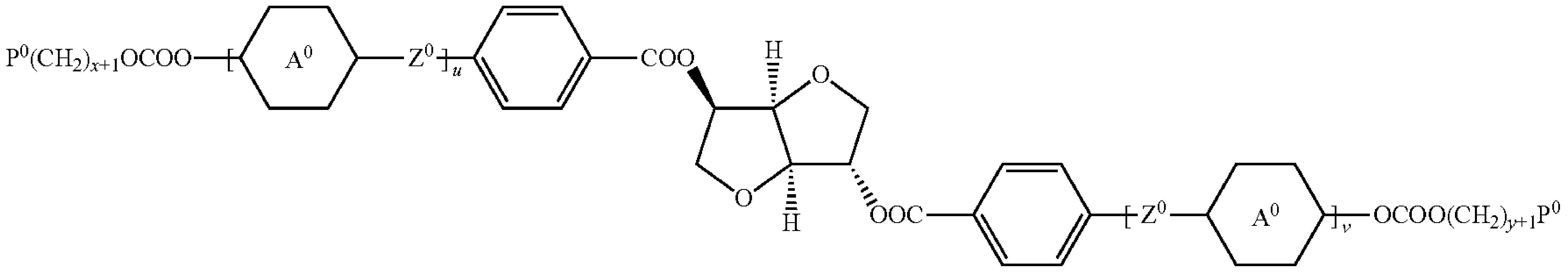

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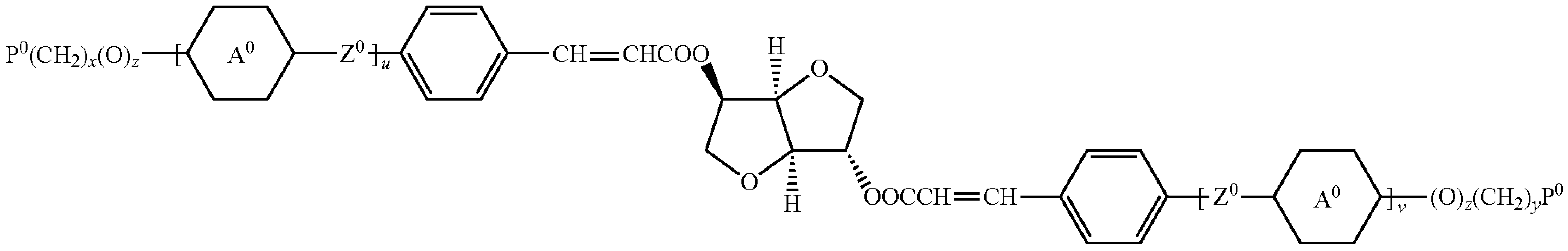

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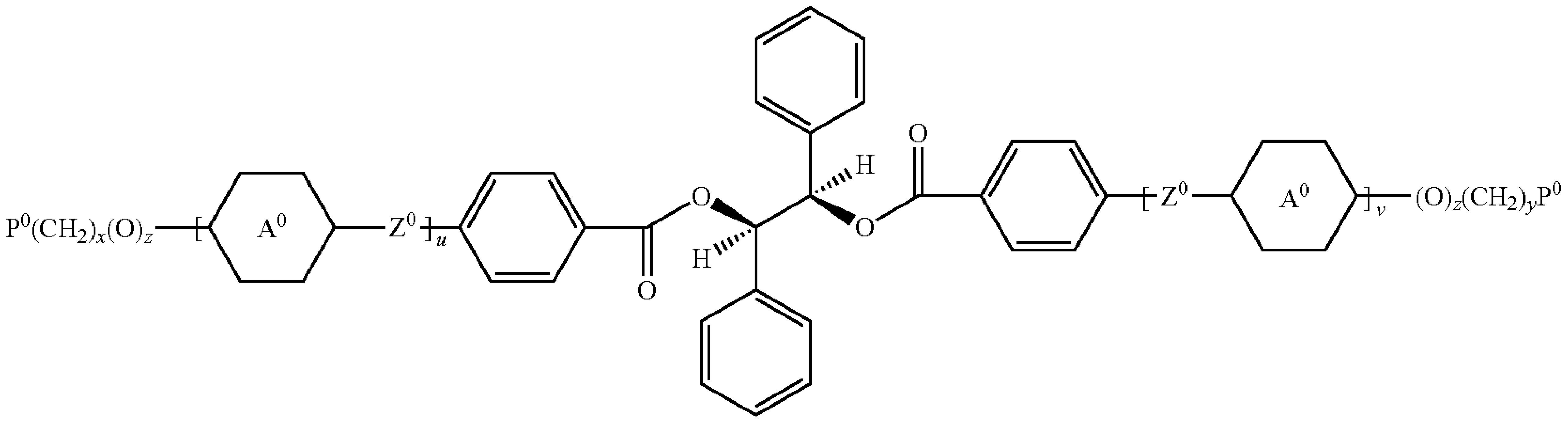

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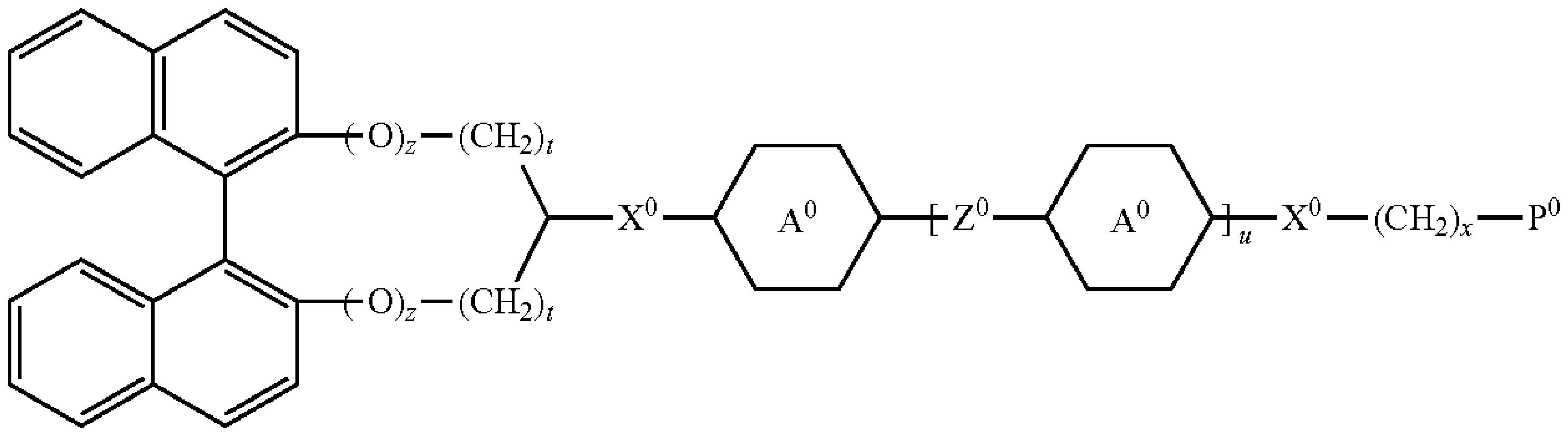


wherein

P^0 is, in case of multiple occurrence independently of one another, a polymerisable group, preferably an acryl, methacryl, oxetane, epoxy, vinyl, vinyloxy, propenyl ether or styrene group,

A^0 and B^0 are, in case of multiple occurrence independently of one another, 1,4-phenylene that is optionally substituted with 1, 2, 3 or 4 groups L, or trans-1,4-cyclohexylene,

Z^0 is, in case of multiple occurrence independently of one another, —COO—, —OCO—, —CH_2CH_2—, —C≡C—, —CH=CH—, —CH=CH—COO—, —OCO—CH=CH— or a single bond,

R^0 is alkyl, alkoxy, thioalkyl, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy with 1 or more, preferably 1 to 15 C atoms which is optionally fluorinated, or is Y^0 or $P—(CH_2)_y—(O)_z—$,

Y^0 is F, Cl, CN, NO_2, OCH_3, OCN, SCN, SF_5, optionally fluorinated alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy with 1 to 4 C atoms, or mono-oligo- or polyfluorinated alkyl or alkoxy with 1 to 4 C atoms,

$R^{01,02}$ are independently of each other H, R^0 or Y^0,

R* is a chiral alkyl or alkoxy group with 4 or more, preferably 4 to 12 C atoms, like 2-methylbutyl, 2-methyloctyl, 2-methylbutoxy or 2-methyloctoxy,

Ch is a chiral group selected from cholesteryl, estradiol, or terpenoid radicals like menthyl or citronellyl,

L is, in case of multiple occurrence independently of one another, H, F, Cl, CN or optionally halogenated alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy with 1 to 5 C atoms,

r is 0, 1, 2, 3 or 4,

t is, in case of multiple occurrence independently of one another, 0, 1, 2 or 3,

u and v are independently of each other 0, 1 or 2,

w is 0 or 1,

x and y are independently of each other 0 or identical or different integers from 1 to 12,

z is 0 or 1, with z being 0 if the adjacent x or y is 0,

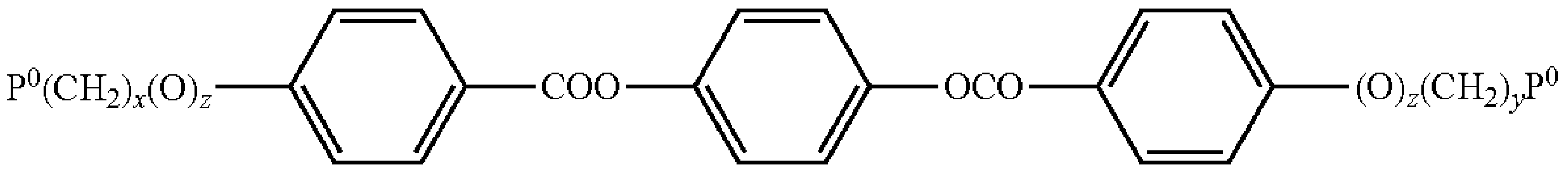
and wherein the benzene and napthalene rings can additionally be substituted with one or more identical or different groups L.

Especially preferably the polymerisable LC host material contains only achiral compounds and no chiral compounds.

Further preferably the polymerisable LC host material comprises one or more compounds selected from formula MR3, MR4, MR7, MR8, MR9, MR10, MR18, DR6, DR7 and DR8, furthermore DR1 and DR5.

Further preferably the polymerisable LC host material comprises one or more compounds selected from the following formulae:

(DR1a)



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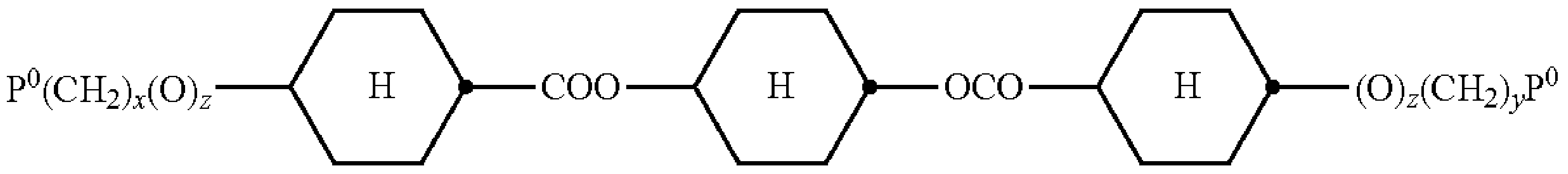
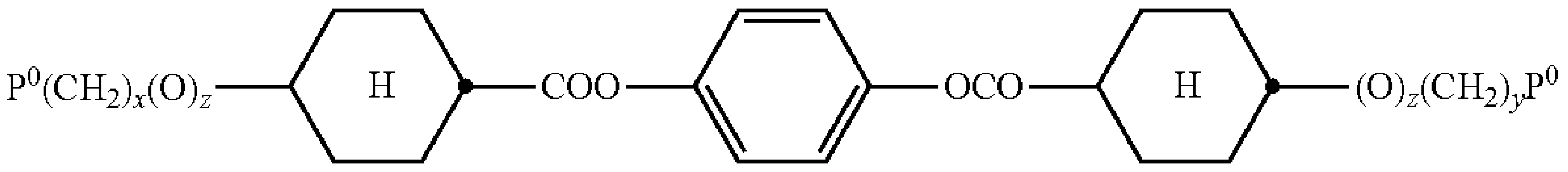
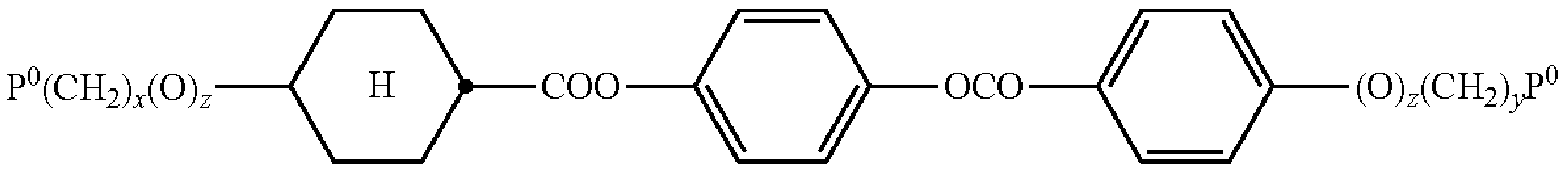


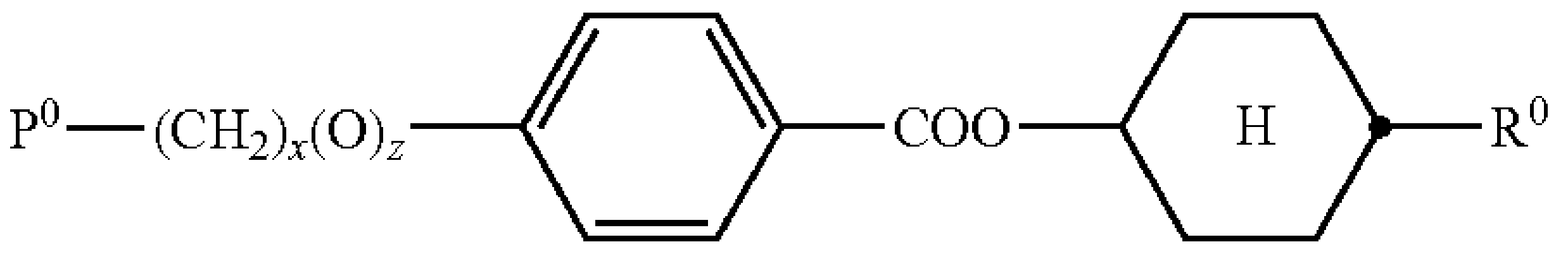
(DR7a)



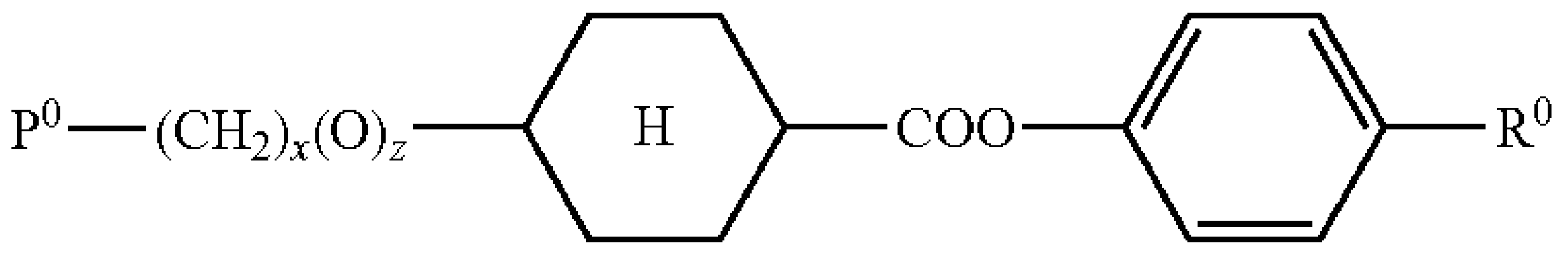
(DR8a)



(MR3a)



(MR4a)



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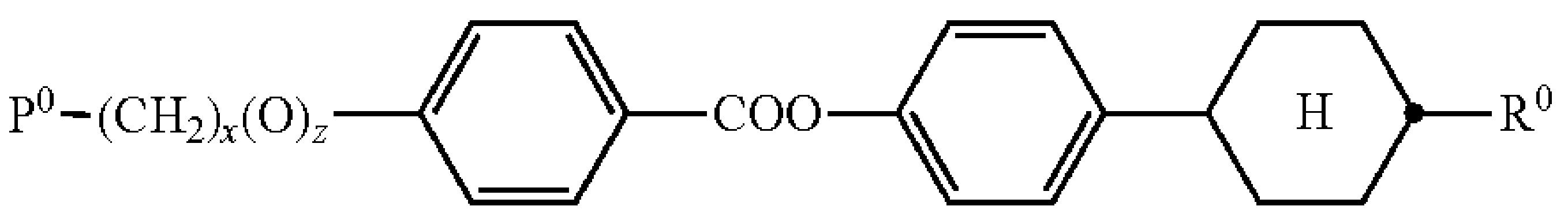

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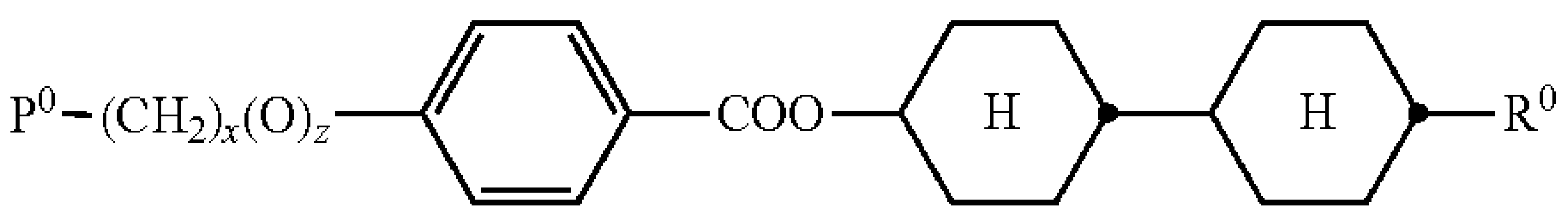

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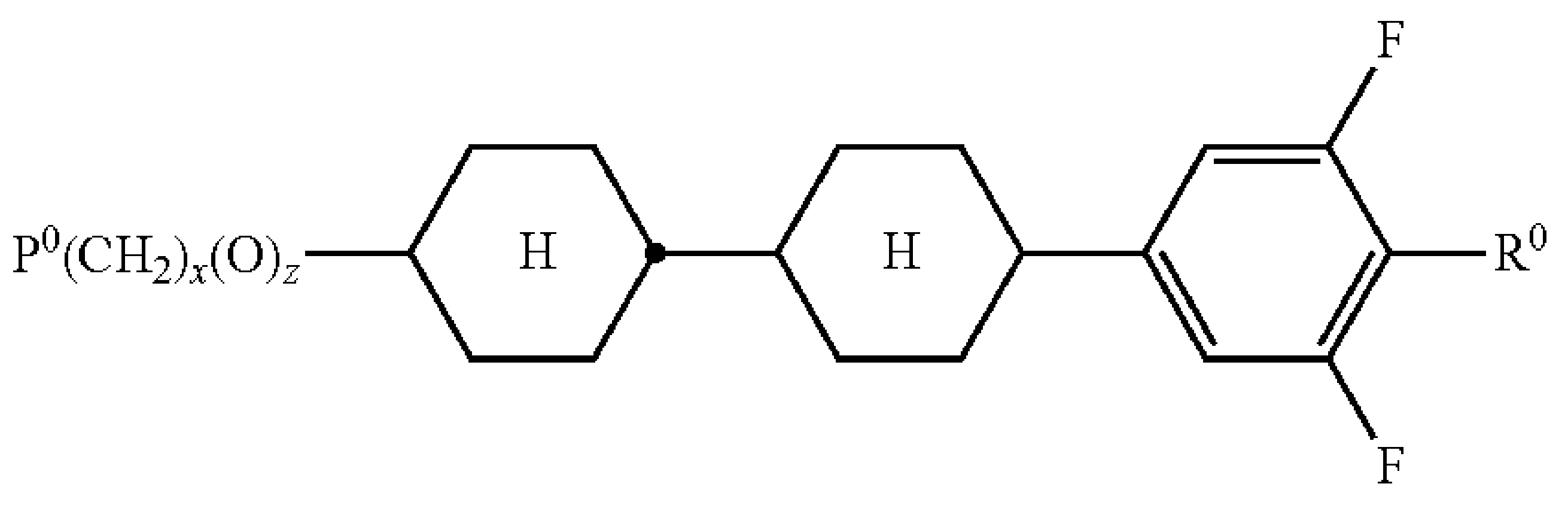
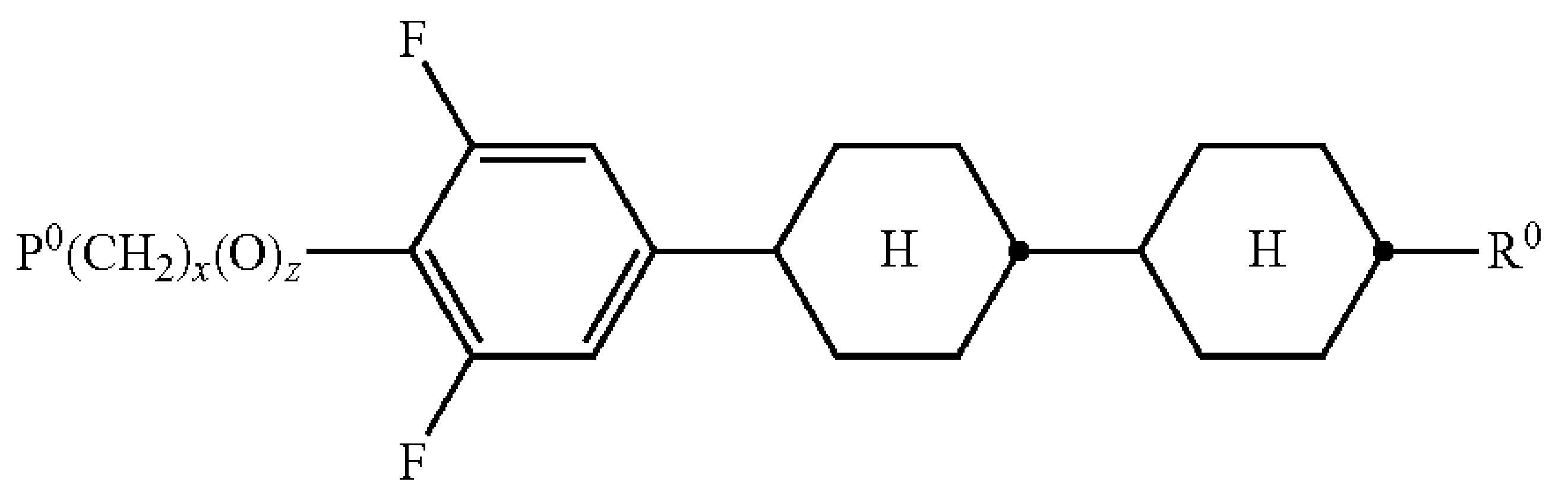
(MR9a)



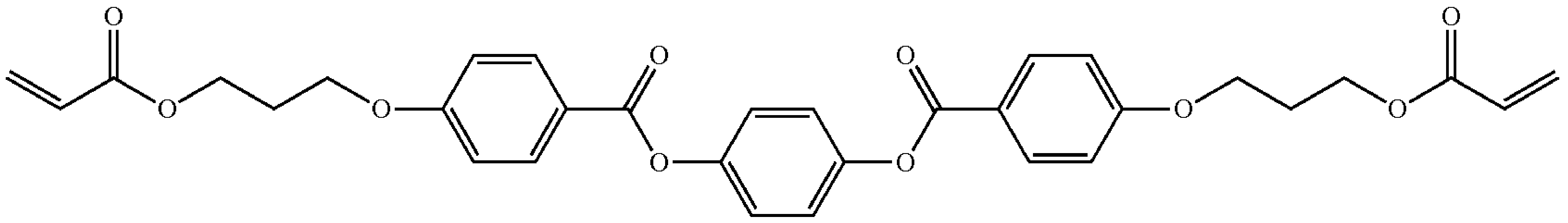
(MR10a)



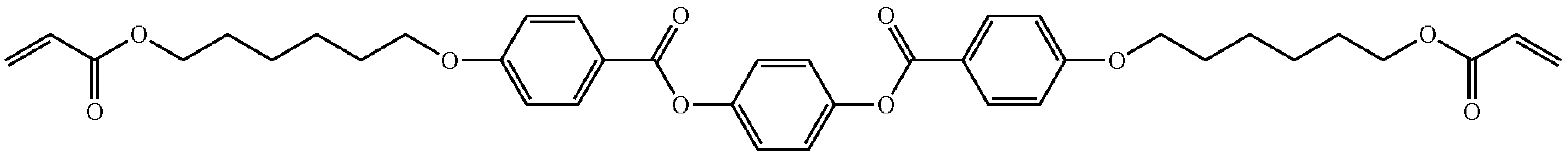
wherein P^0, R^0, x, y, and z are as defined above.

Further preferably the polymerisable LC host material comprises one or more compounds selected from the following formulae:

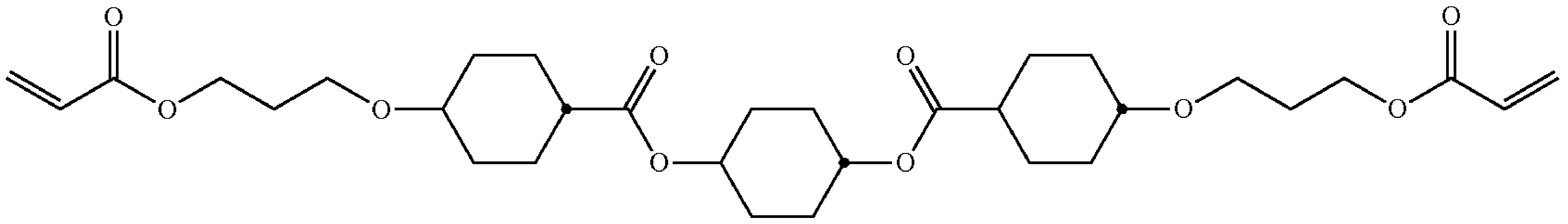
(DR1a1)



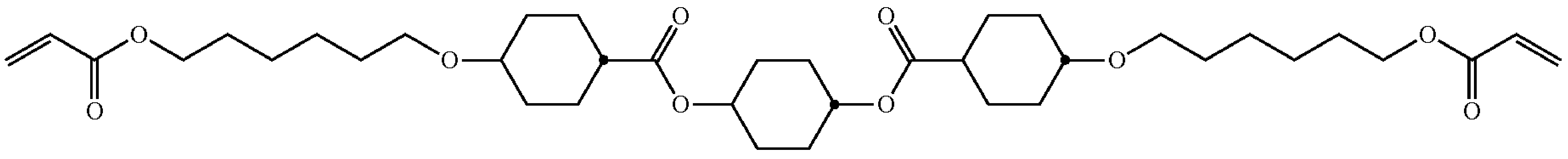
(DR1a2)



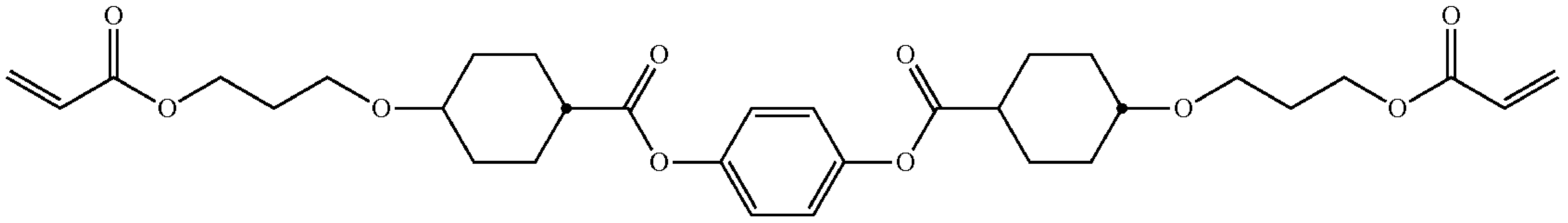
(DR6a)



(DR6b)



(DR7a1)



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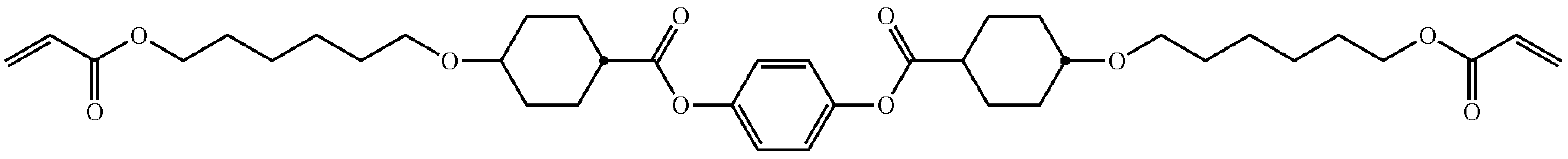

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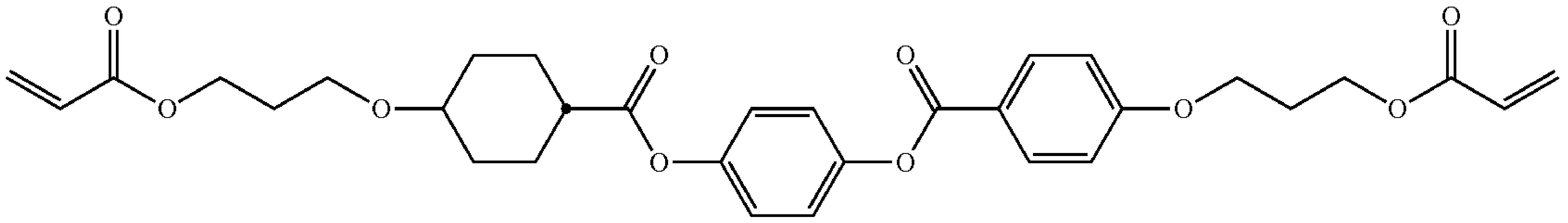

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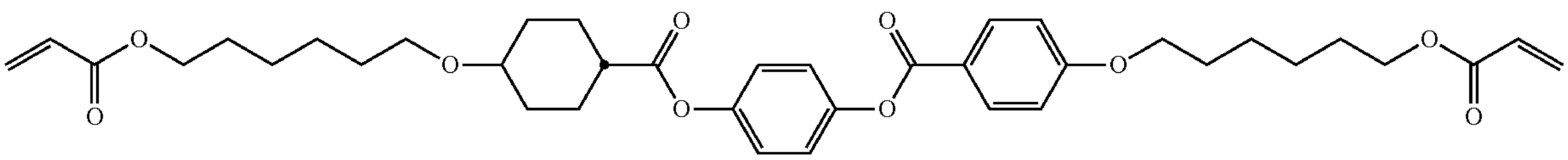

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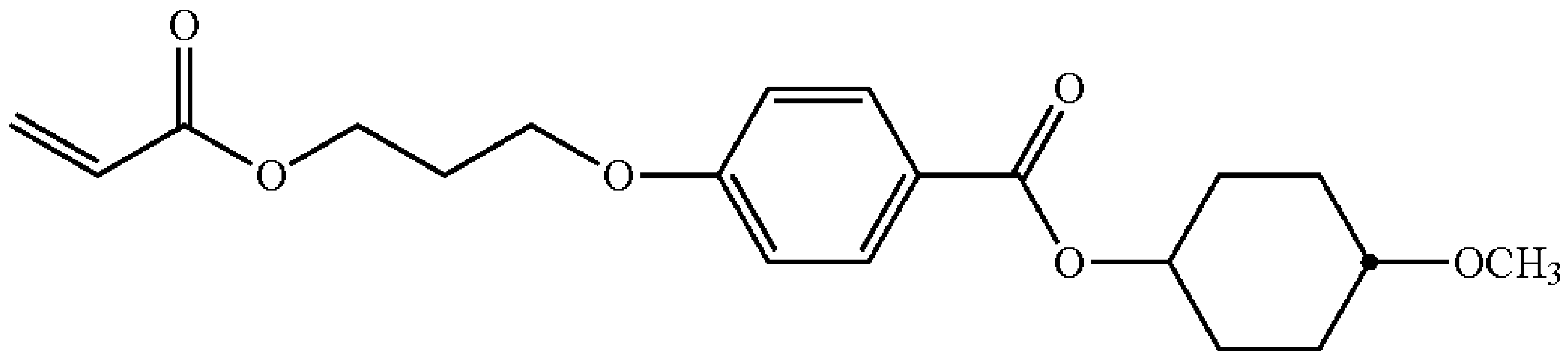

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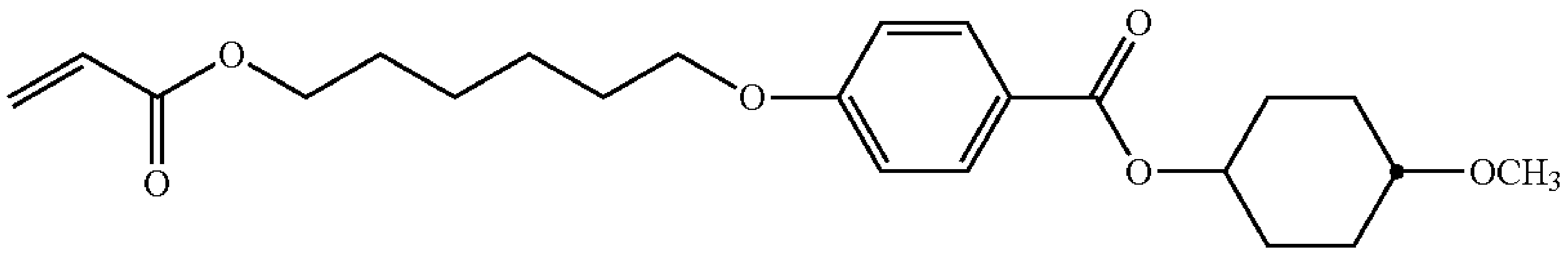

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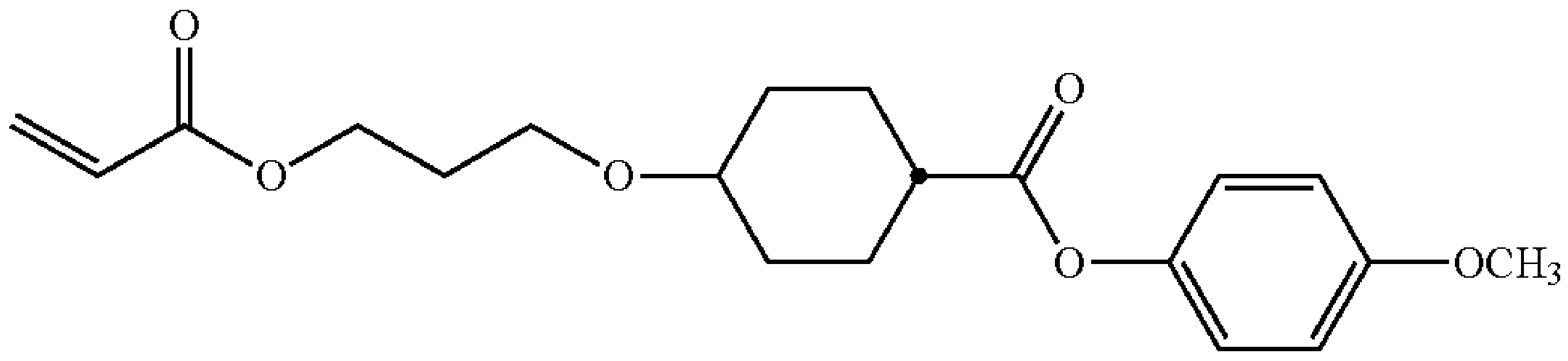

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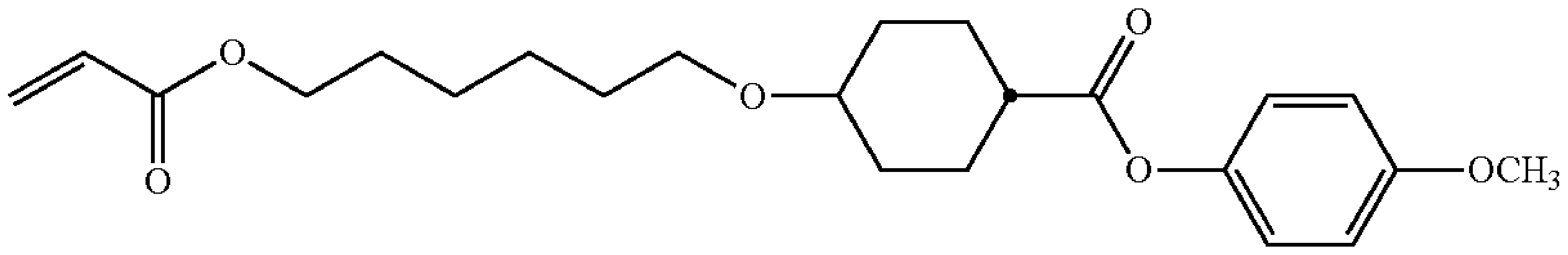

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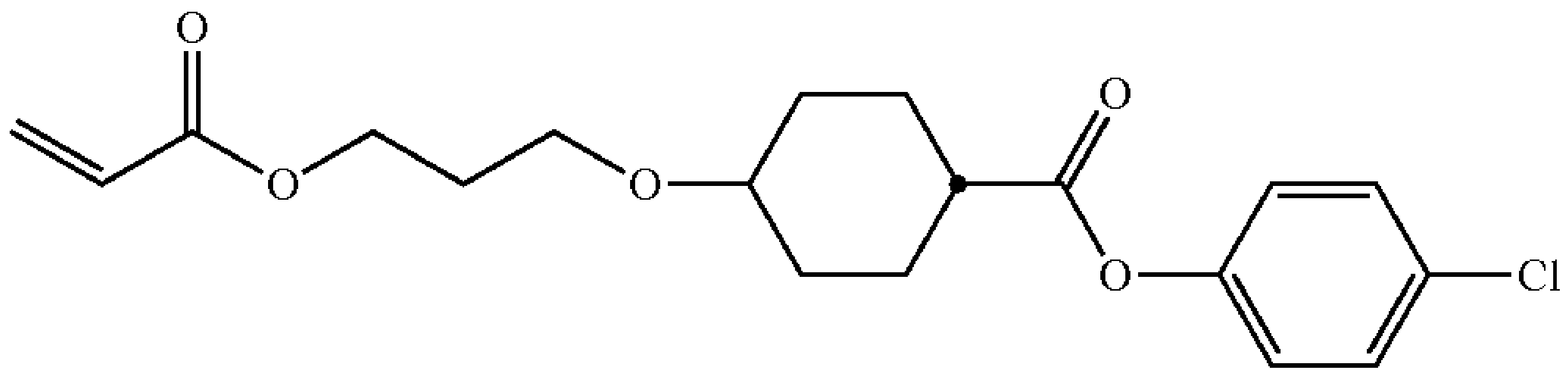

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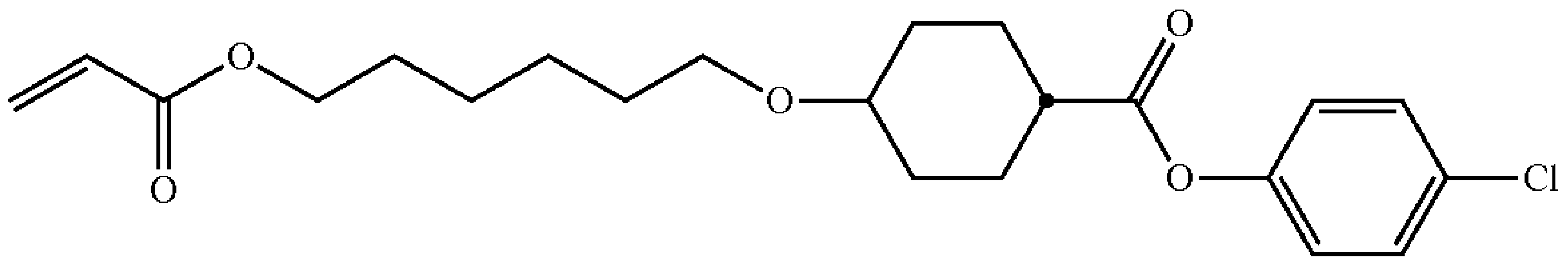

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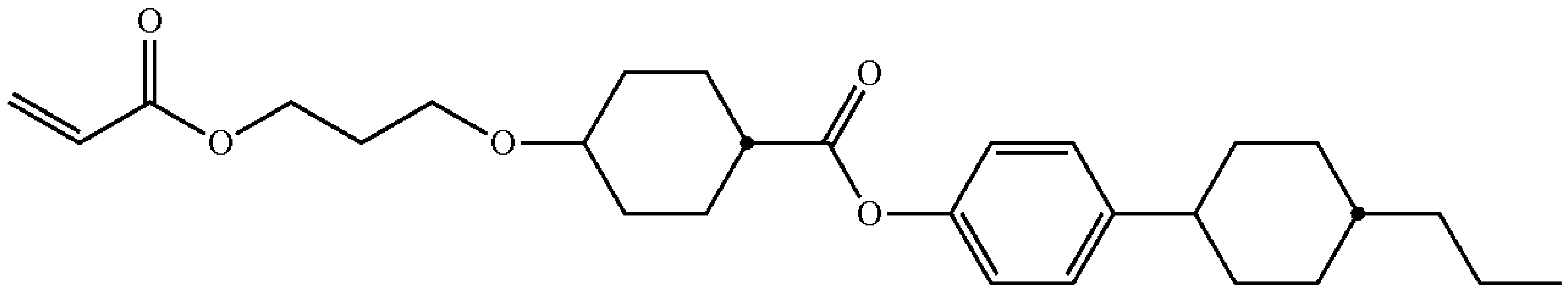

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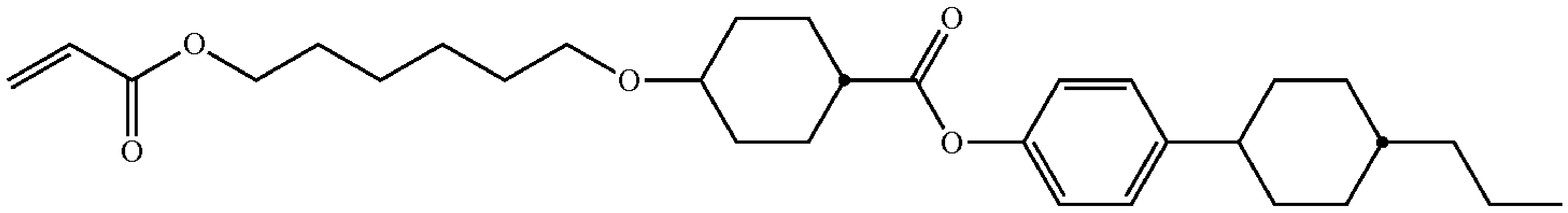
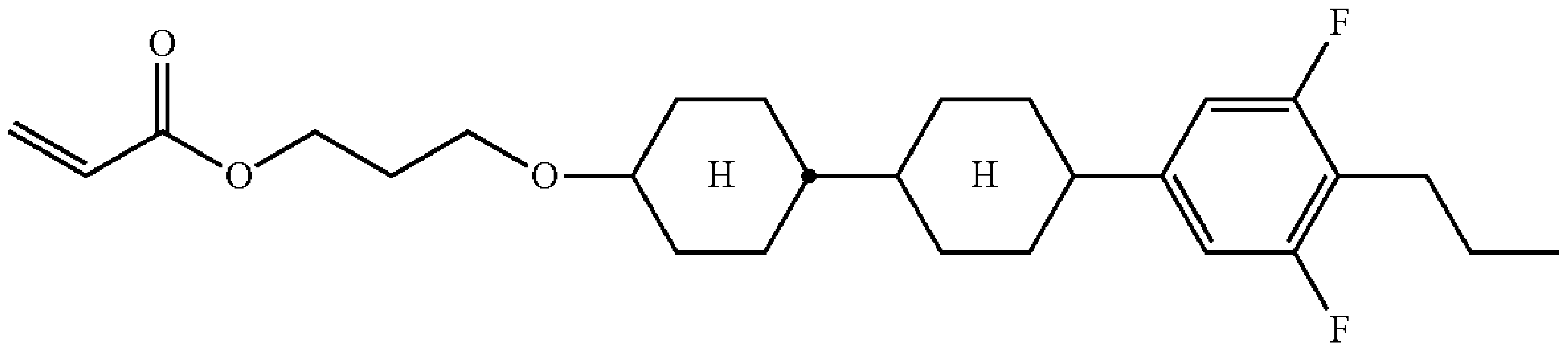


(MR9a1)



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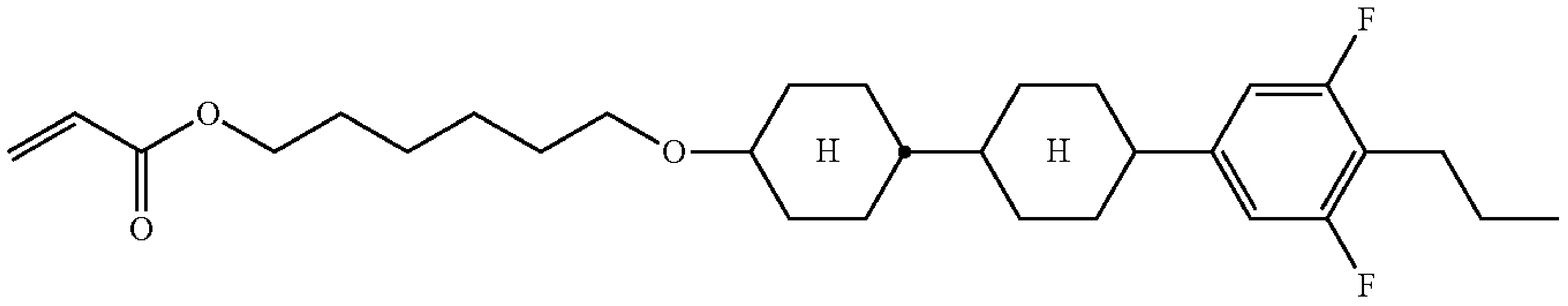
(MR9a2)



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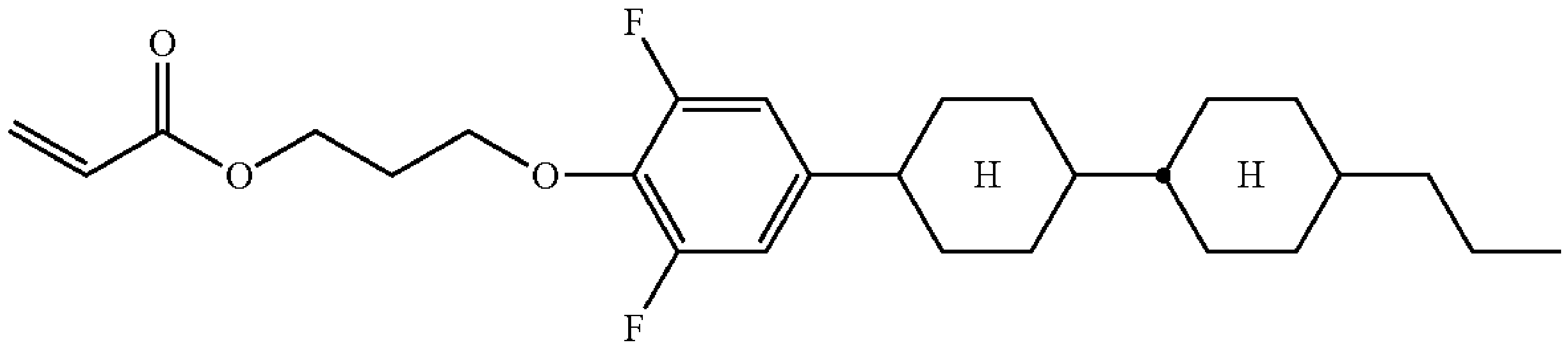

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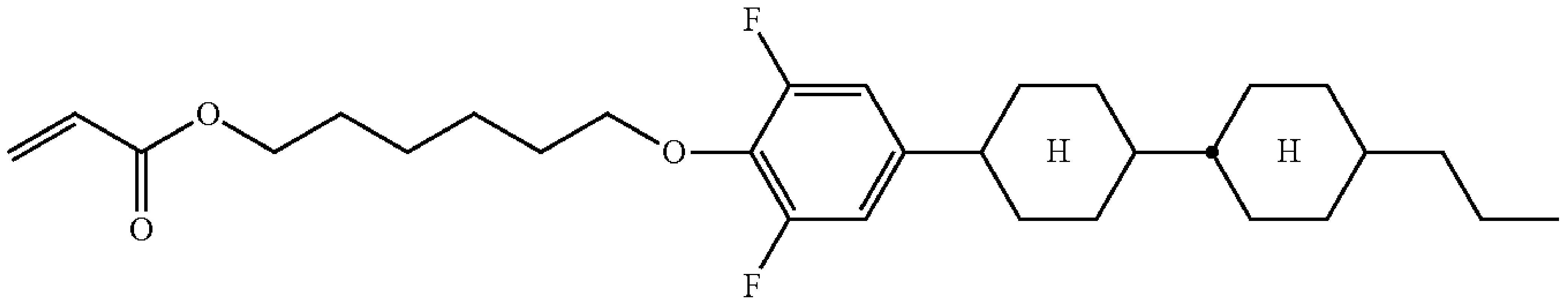


Preferably the polymerisable compounds of the polymerisable LC host material are selected from compounds, very preferably mono- or direactive RMs, having low birefringence.

Especially preferred is a polymerisable host material having an absolute value of the birefringence from 0.01 to 0.2, very preferably from 0.04 to 0.16.

The general preparation of polymer LC films according to this invention is known to the ordinary expert and described in the literature, for example in D. J. Broer; G. Challa; G. N. Mol, Macromol. Chem., 1991, 192, 59. Typically a polymerisable LC material is coated or otherwise applied onto a substrate where it aligns into uniform orientation, and polymerised in situ in its LC phase at a selected temperature for example by exposure to heat or actinic radiation, preferably by photo-polymerisation, very preferably by UV-photopolymerisation, to fix the alignment of the LC molecules. If necessary, uniform alignment can promoted by additional means like shearing or annealing the LC material, surface treatment of the substrate, or adding surfactants to the LC material.

As substrate for example glass or quartz sheets or plastic films can be used. It is also possible to put a second substrate on top of the coated material prior to and/or during and/or after polymerisation. The substrates can be removed after polymerisation or not. When using two substrates in case of curing by actinic radiation, at least one substrate has to be transmissive for the actinic radiation used for the polymerisation. Isotropic or birefringent substrates can be used. In case the substrate is not removed from the polymerised film after polymerisation, preferably isotropic substrates are used.

Suitable and preferred plastic substrates are for example films of polyester such as polyethyleneterephthalate (PET) or polyethylene-naphthalate (PEN), polyvinylalcohol (PVA), polycarbonate (PC) or triacetylcellulose (TAC), very preferably PET or TAC films. As birefringent substrates for example uniaxially stretched plastics film can be used. PET films are commercially available for example from DuPont Teijin Films under the trade name Melinex®.

The polymerisable material can be applied onto the substrate by conventional coating techniques like spin-coating or blade coating. It can also be applied to the substrate by conventional printing techniques which are known to the expert, like for example screen printing, offset printing, reel-to-reel printing, letter press printing, gravure printing, rotogravure printing, flexographic printing, intaglio printing, pad printing, heat-seal printing, ink-jet printing or printing by means of a stamp or printing plate.

It is also possible to dissolve the polymerisable material in a suitable solvent. This solution is then coated or printed onto the substrate, for example by spin-coating or printing or other known techniques, and the solvent is evaporated off before polymerisation. In many cases it is suitable to heat the mixture in order to facilitate the evaporation of the solvent. As solvents for example standard organic solvents can be used. The solvents can be selected for example from ketones such as acetone, methyl ethyl ketone, methyl propyl ketone or cyclohexanone; acetates such as methyl, ethyl or butyl acetate or methyl acetoacetate; alcohols such as methanol, ethanol or isopropyl alcohol; aromatic solvents such as toluene or xylene; halogenated hydrocarbons such as di- or trichloromethane; glycols or their esters such as PGMEA (propyl glycol monomethyl ether acetate), γ-butyrolactone, and the like. It is also possible to use binary, ternary or higher mixtures of the above solvents.

Initial alignment (e.g. planar alignment) of the polymerisable LC material can be achieved for example by rubbing treatment of the substrate, by shearing the material during or after coating, by annealing the material before polymerisation, by application of an alignment layer, by applying a magnetic or electric field to the coated material, or by the addition of surface-active compounds to the material. Reviews of alignment techniques are given for example by I. Sage in "Thermotropic Liquid Crystals", edited by G. W. Gray, John Wiley & Sons, 1987, pages 75-77; and by T. Uchida and H. Seki in "Liquid Crystals—Applications and Uses Vol. 3", edited by B. Bahadur, World Scientific Publishing, Singapore 1992, pages 1-63. A review of alignment materials and techniques is given by J. Cognard, Mol. Cryst. Liq. Cryst. 78, Supplement 1 (1981), pages 1-77.

Especially preferred is a polymerisable material comprising one or more surfactants that promote a specific surface alignment of the LC molecules.

Suitable surfactants are described for example in J. Cognard, Mol. Cryst. Liq. Cryst. 78, Supplement 1, 1-77 (1981). Preferred aligning agents for planar alignment are for example non-ionic surfactants, preferably fluorocarbon surfactants such as the commercially available Fluorad FC-171® (from 3M Co.) or Zonyl FSN® (from DuPont), multiblock surfactants as described in GB 2 383 040 or polymerisable surfactants as described in EP 1 256 617.

It is also possible to apply an alignment layer onto the substrate and provide the polymerisable material onto this alignment layer. Suitable alignment layers are known in the art, like for example rubbed polyimide or alignment layers prepared by photoalignment as described in U.S. Pat. No. 5,602,661, U.S. Pat. No. 5,389,698 or U.S. Pat. No. 6,717,644.

It is also possible to induce or improve alignment by annealing the polymerisable LC material at elevated temperature, preferably at its polymerisation temperature, prior to polymerisation.

Polymerisation is achieved for example by exposing the polymerisable material to heat or actinic radiation. Actinic radiation means irradiation with light, like UV light, IR light or visible light, irradiation with X-rays or gamma rays or irradiation with high energy particles, such as ions or electrons. Preferably polymerisation is carried out by UV irradiation. As a source for actinic radiation for example a single UV lamp or a set of UV lamps can be used. When using a high lamp power the curing time can be reduced. Another possible source for actinic radiation is a laser, like for example a UV, IR or visible laser.

Polymerisation is preferably carried out in the presence of an initiator absorbing at the wavelength of the actinic radiation. For this purpose the polymerisable LC material preferably comprises one or more initiators, preferably in a concentration from 0.01 to 10%, very preferably from 0.05 to 5%. For example, when polymerising by means of UV light, a photoinitiator can be used that decomposes under UV irradiation to produce free radicals or ions that start the polymerisation reaction. For polymerising acrylate or methacrylate groups preferably a radical photoinitiator is used. For polymerising vinyl, epoxide or oxetane groups preferably a cationic photoinitiator is used. It is also possible to use a thermal polymerisation initiator that decomposes when heated to produce free radicals or ions that start the polymerisation. Typical radical photoinitiators are for example the commercially available Irgacure® or Darocure® (Ciba Geigy AG, Basel, Switzerland). A typical cationic photoinitiator is for example UVI 6974 (Union Carbide).

The polymerisable material may also comprise one or more stabilizers or inhibitors to prevent undesired spontaneous polymerisation, like for example the commercially available Irganox® (Ciba Geigy AG, Basel, Switzerland).

The curing time depends, inter alia, on the reactivity of the polymerisable material, the thickness of the coated layer, the type of polymerisation initiator and the power of the UV lamp. The curing time is preferably ≤5 minutes, very preferably ≤3 minutes, most preferably ≤1 minute. For mass production short curing times of 30 seconds are preferred.

Preferably polymerisation is carried out in an inert gas atmosphere like nitrogen or argon.

The polymerisable material may also comprise one or more dyes having an absorption maximum adjusted to the wavelength of the radiation used for polymerisation, in particular UV dyes like e.g. 4,4"-azoxy anisole or Tinuvin® dyes (from Ciba AG, Basel, Switzerland).

In another preferred embodiment the polymerisable material comprises one or more monoreactive polymerisable non-mesogenic compounds, preferably in an amount of 0 to 50%, very preferably 0 to 20%. Typical examples are alkylacrylates or alkylmethacrylates.

In another preferred embodiment the polymerisable material comprises one or more di- or multireactive polymerisable non-mesogenic compounds, preferably in an amount of 0 to 50%, very preferably 0 to 20%, alternatively or in addition to the di- or multireactive polymerisable mesogenic compounds. Typical examples of direactive non-mesogenic compounds are alkyldiacrylates or alkyldimethacrylates with alkyl groups of 1 to 20 C atoms. Typical examples of multi-reactive non-mesogenic compounds are trimethylpropanetrimethacrylate or pentaerythritoltetraacrylate.

It is also possible to add one or more chain transfer agents to the polymerisable material in order to modify the physical properties of the polymer film. Especially preferred are thiol compounds, for example monofunctional thiols like dodecane thiol or multifunctional thiols like trimethylpropane tri(3-mercaptopropionate). Very preferred are mesogenic or LC thiols as disclosed for example in WO 96/12209, WO 96/25470 or U.S. Pat. No. 6,420,001. By using chain transfer agents the length of the free polymer chains and/or the length of the polymer chains between two crosslinks in the polymer film can be controlled. When the amount of the chain transfer agent is increased, the polymer chain length in the polymer film decreases.

The polymerisable material may also comprise a polymeric binder or one or more monomers capable of forming a polymeric binder, and/or one or more dispersion auxiliaries. Suitable binders and dispersion auxiliaries are disclosed for example in WO 96/02597. Preferably, however, the polymerisable material does not contain a binder or dispersion auxiliary.

The polymerisable material can additionally comprise one or more additives like for example catalysts, sensitizers, stabilizers, inhibitors, chain-transfer agents, co-reacting monomers, surface-active compounds, lubricating agents, wetting agents, dispersing agents, hydrophobing agents, adhesive agents, flow improvers, defoaming agents, deaerators, diluents, reactive diluents, auxiliaries, colourants, dyes, pigments or nanoparticles.

The thickness of a polymer film according to the present invention is preferably from 0.3 to 5 microns, very preferably from 0.5 to 3 microns, most preferably from 0.7 to 1.5 microns. For use as alignment layer, thin films with a thickness of 0.05 to 1, preferably 0.1 to 0.4 microns are preferred.

The polymer films and materials of the present invention can be used as retardation or compensation film for example in LCDs to improve the contrast and brightness at large viewing angles and reduce the chromaticity. It can be used outside the switchable LC cell of the LCD or between the substrates, usually glass substrates, forming the switchable LC cell and containing the switchable LC medium (incell application).

The polymer film and materials of the present invention can be used in conventional LC displays, for example displays with vertical alignment like the DAP (deformation of aligned phases), ECB (electrically controlled birefringence), CSH (colour super homeotropic), VA (vertically aligned), VAN or VAC (vertically aligned nematic or cholesteric), MVA (multi-domain vertically aligned), PVA (patterned vertically aligned) or PSVA (polymer stabilised vertically aligned) mode; displays with bend or hybrid alignment like the OCB (optically compensated bend cell or optically compensated birefringence), R—OCB (reflective OCB), HAN (hybrid aligned nematic) or pi-cell (π-cell) mode; displays with twisted alignment like the TN (twisted nematic), HTN (highly twisted nematic), STN (super twisted nematic), AMD-TN (active matrix driven TN) mode; displays of the IPS (in plane switching) mode, or displays with switching in an optically isotropic phase.

The layers, films and materials of the present invention can be used for various types of optical films, preferably selected from optically uniaxial films (A-plate, C-plate, negative C-plate, O-plate), twisted optical retarders, like for example twisted quarter wave foils (QWF), achromatic retarders, achromatic QWFs or half wave foils (HWF), and optically biaxial films. The LC phase structure in the layers and materials can be selected from cholesteric, smectic, nematic and blue phases. The alignment of the LC material in the layer can be selected from homeotropic, splayed, tilted, planar and blue-phase alignment. The layers can be uniformly oriented or exhibit a pattern of different orientations.

The films can be used as optical compensation film for viewing angle enhancement of LCD's or as a component in a brightness enhancement films, furthermore as an achromatic element in reflective or transflective LCD's. Further preferred applications and devices include

retarding components in optoelectronic devices requiring similar phase shift at multiple wavelengths, such as combined CD/DVD/HD-DVD/Blu-Ray, including reading, writing re-writing data storage systems

achromatic retarders for optical devices such as cameras

achromatic retarders for displays including OLED and LCD's.

The following examples are intended to explain the invention without restricting it. The methods, structures and properties described hereinafter can also be applied or transferred to materials that are claimed in this invention but not explicitly described in the foregoing specification or in the examples.

Above and below, percentages are percent by weight. All temperatures are given in degrees Celsius. m.p. denotes melting point, cl.p. denotes clearing point, T_g denotes glass transition temperature. Furthermore, C=crystalline state, N=nematic phase, S=smectic phase and I=isotropic phase. The data between or behind these symbols represent the transition temperatures. Δn denotes the optical anisotropy ($\Delta n=n_e-n_o$, where n_o denotes the refractive index parallel to the longitudinal molecular axes and n_e denotes the refractive index perpendicular thereto), measured at 589 nm and 20° C. The optical and electrooptical data are measured at 20° C., unless expressly stated otherwise.

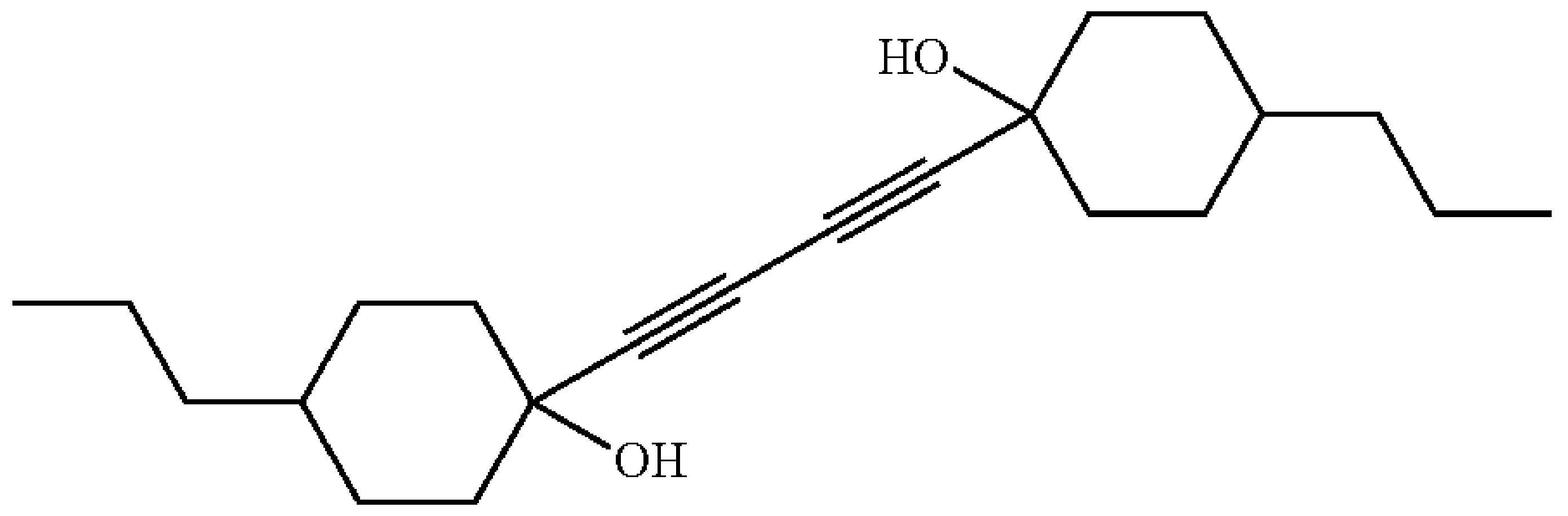
Method of measuring the refractive indices of the novel materials:

The refractive indices of a liquid crystal mixture commercially available from Merck KGaA under the product code ZL14792 are measured using an Abbe refractometer at 20° C. and using a light of wavelength 589 nm. This mixture is then doped with 10% w/w of the material under test and the refractive indices are remeasured. Extrapolation to 100% gives the refractive index of the material under test.

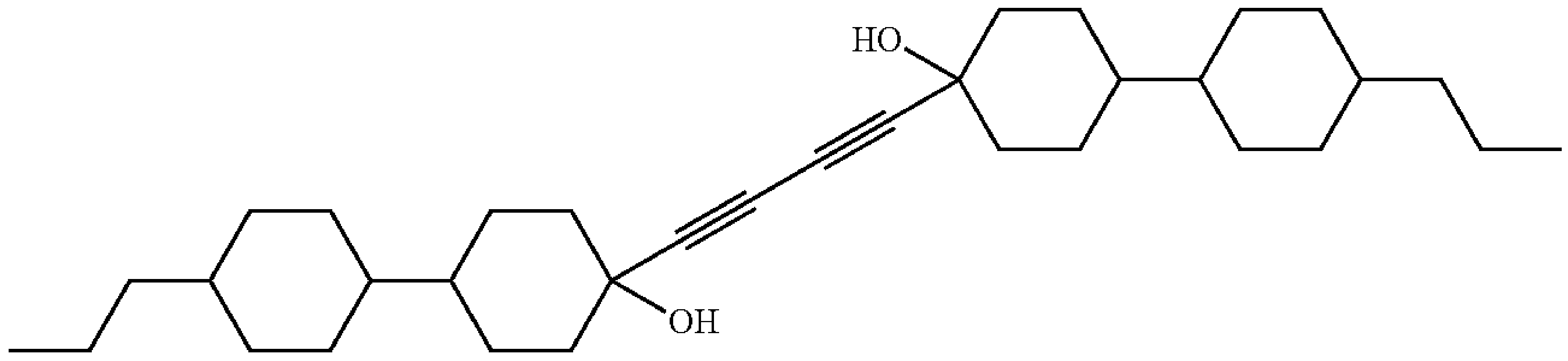
Unless stated otherwise, the percentages of components of a polymerisable mixture as given above and below refer to the total amount of solids in the mixture polymerisable mixture, i.e. not including solvents.

EXAMPLE 1

Key intermediates used in the synthesis of many examples are the two intermediates shown below:

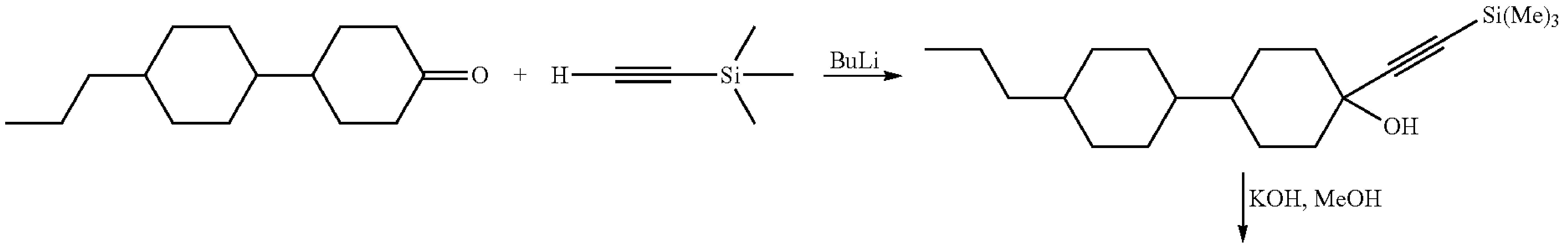


Intermediate 1



Intermediate 2

The synthetic route used to prepare intermediate 2 is shown below. Intermediate 1 is also prepared via a similar route (shown below)



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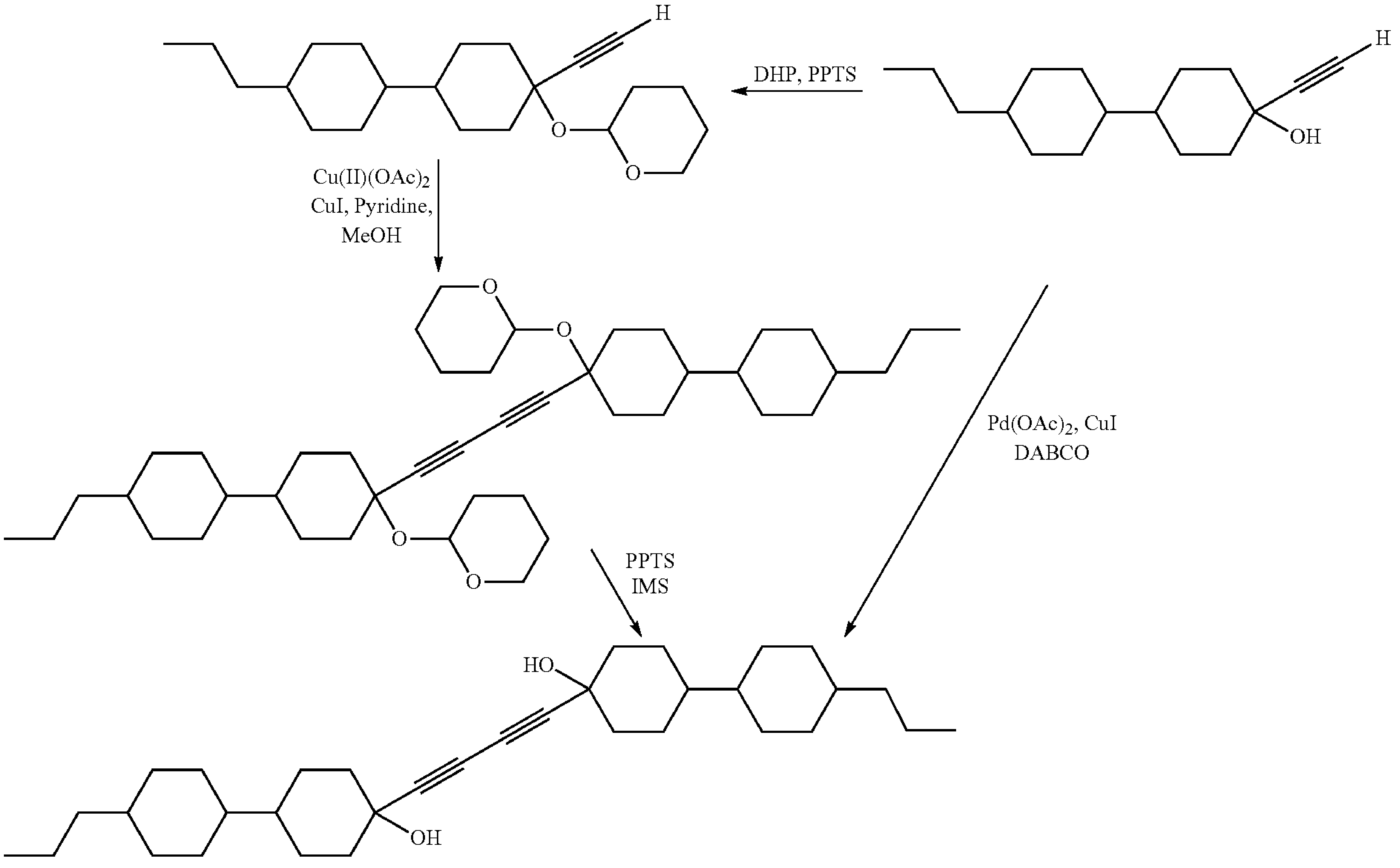


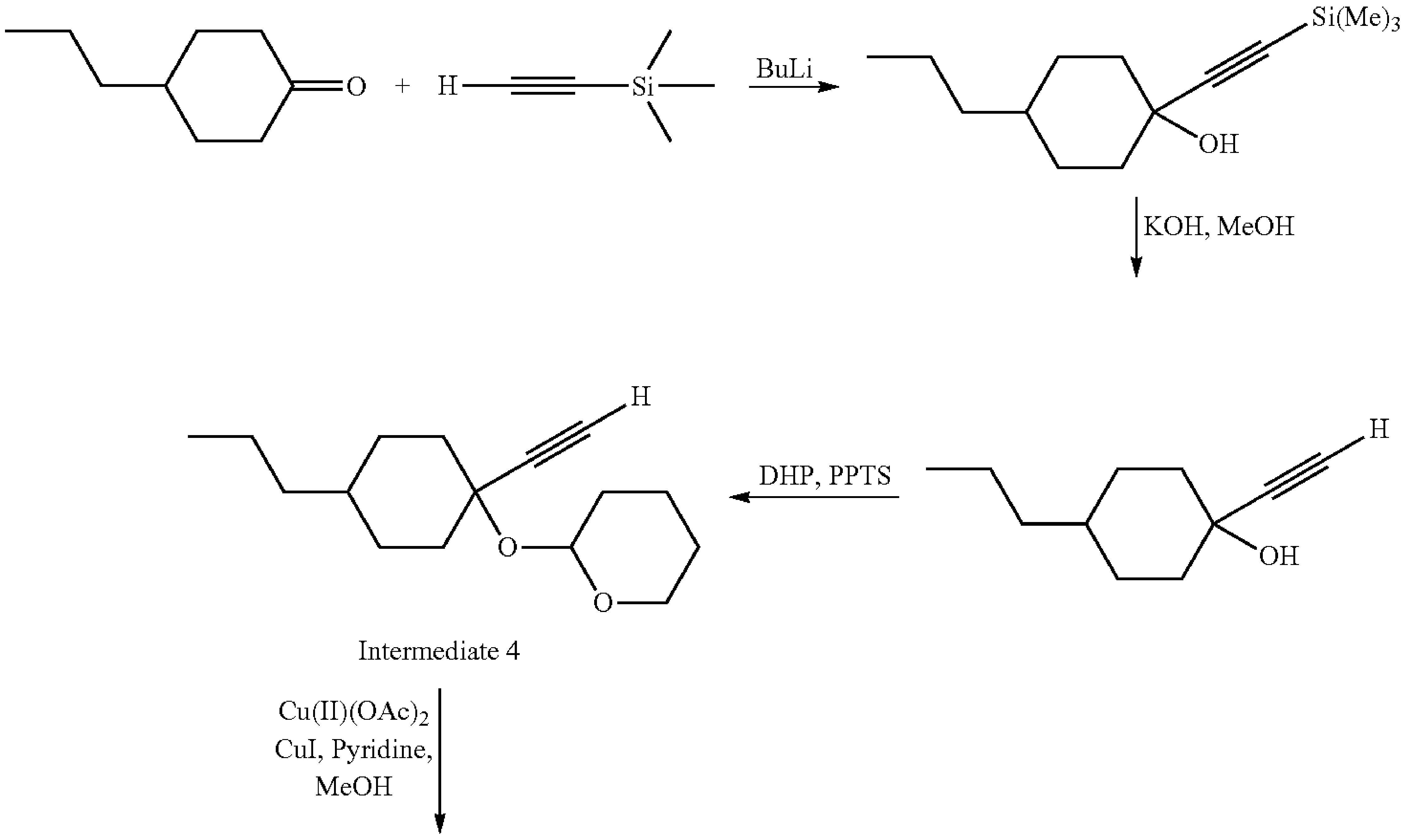
Intermediate 2

There are two possible methods of converting the product of stage 2 of the above reaction scheme. The first method uses a THP protecting group to protect the alcohol before the acetylene-containing product is coupled. The second method directly converts the product of stage 2 into intermediate 2 using a method disclosed by Lee et al in Journal of Organic Chemistry (2005) 70, 4393.

The synthetic routes that can be used to synthesise the above examples are shown below. Example 2 can also be prepared via an analogous route. Example 3 is prepared via a similar route to example 1, however in this case, intermediate 2 is used rather than intermediate 1

EXAMPLE 2

Compound (1) is prepared via the following route:



Intermediate 4

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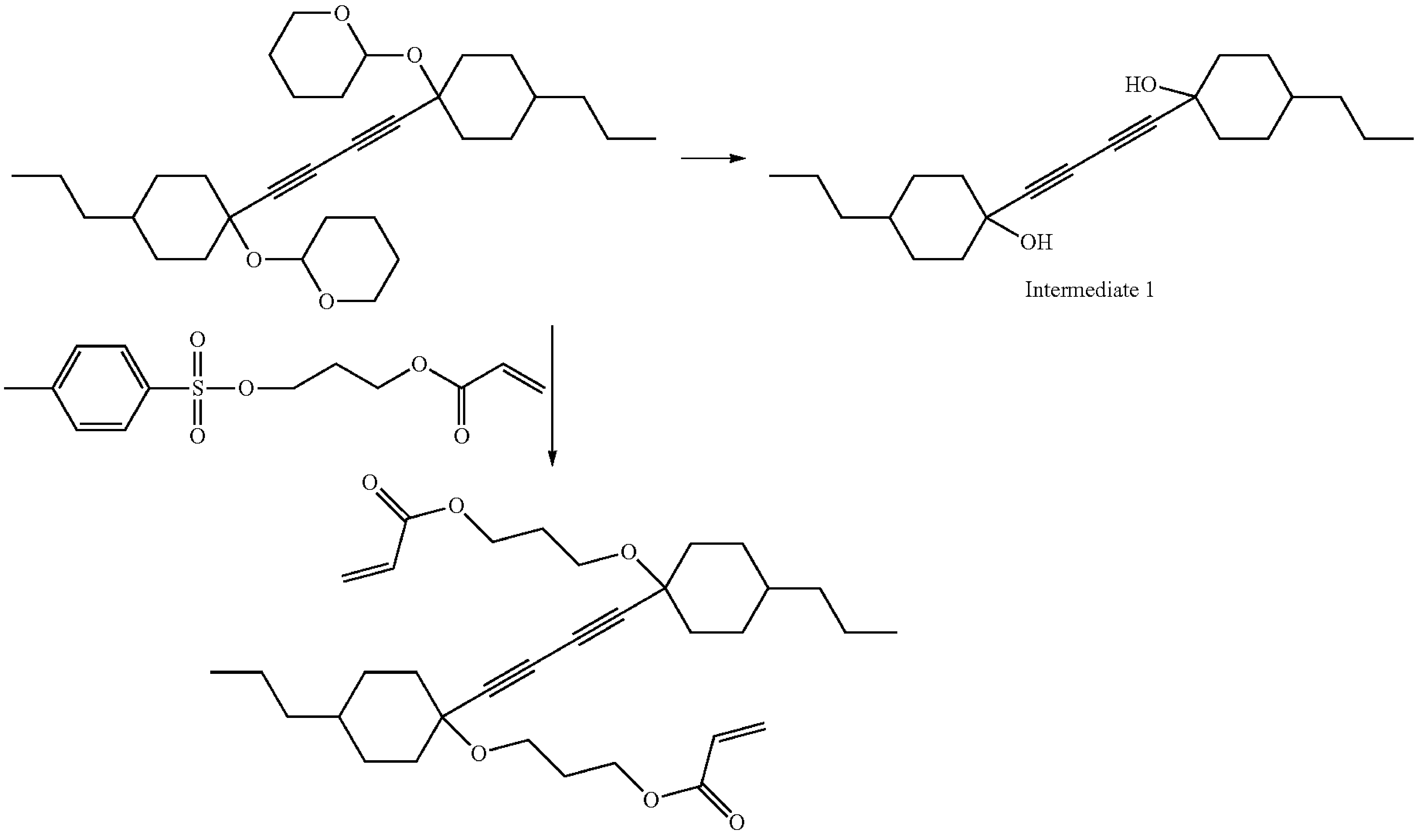

Intermediate 1

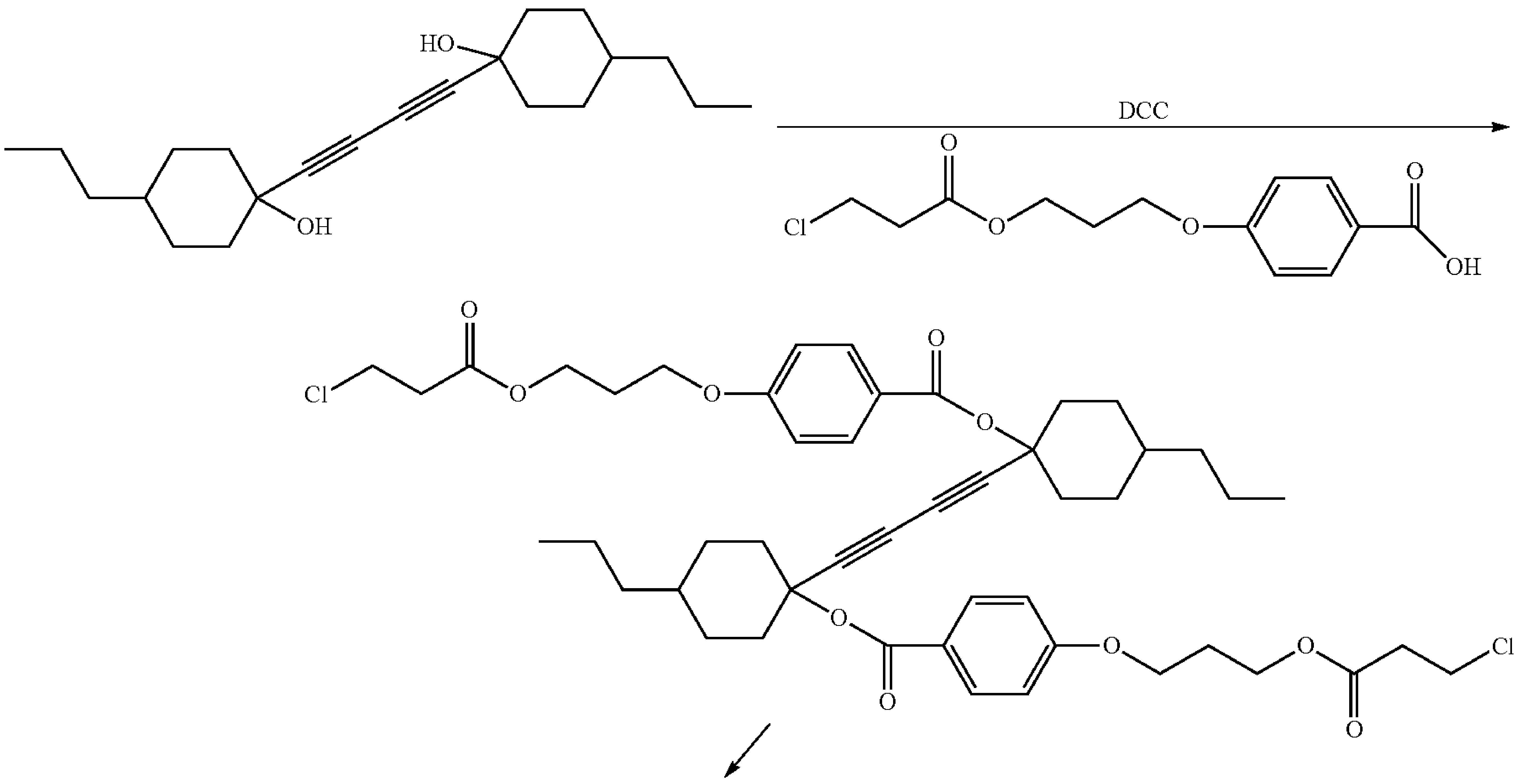
(1)

A method of preparing 2-[(1-ethynylcyclohexyl)oxy]tetrahydropyran—a compound similar to the key intermediate, the THP protected acetylene (intermediate 4)- has previously been reported in the literature:

1. Lithium hexafluorophosphate-catalyzed efficient tetrahydropyranylation of tertiary alcohols under mild reaction conditions. Syn. Lett. (2004), (10), 1802-1804.
2. Triphenylphosphine hydrobromide: A mild and efficient catalyst for tetrahydropyranylation of tertiary alcohols. Tetrahedron Letters (1988), 29, (36), 4583-6.
3. Bismuth triflate: An efficient catalyst for the formation and deprotection of tetrahydropyranyl ethers. European Journal of Organic Chemistry (2003), (19), 3827-3831.

EXAMPLE 3

Compound (2) is prepared via the following route:



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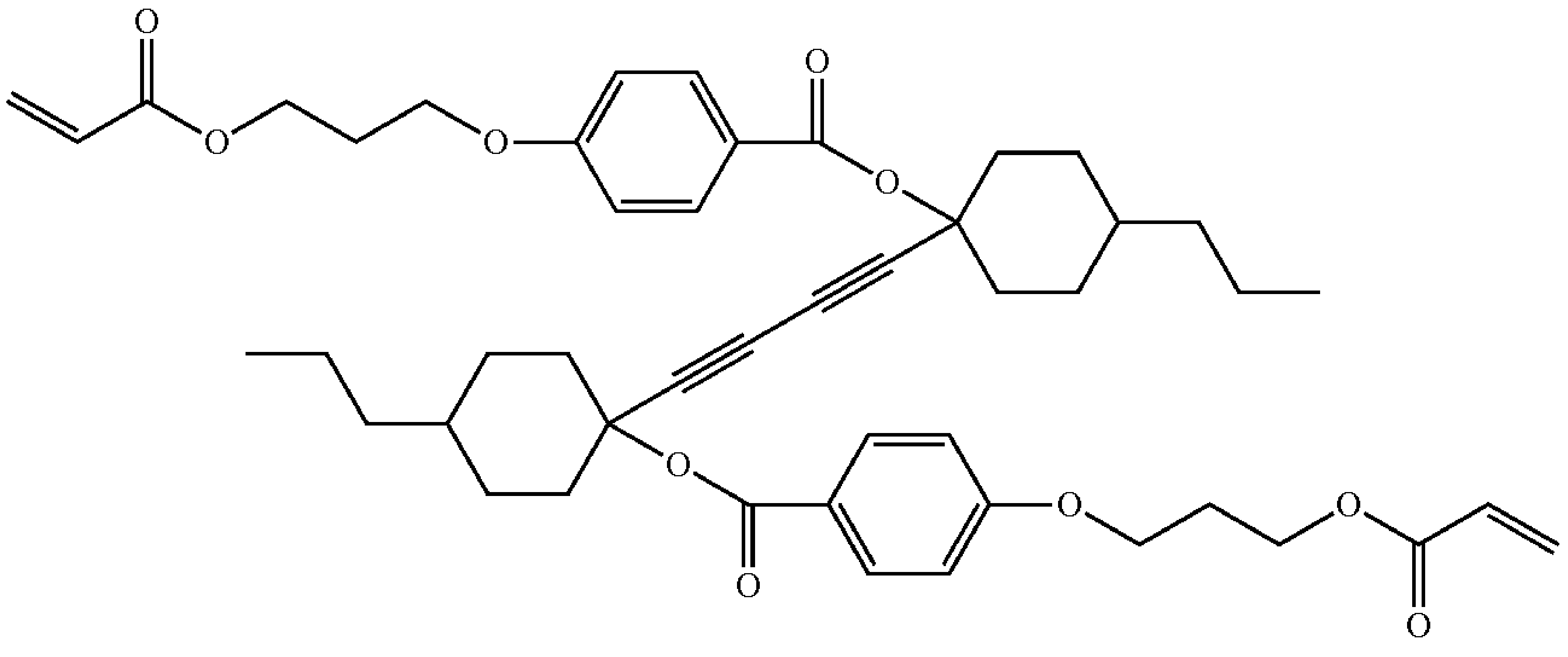


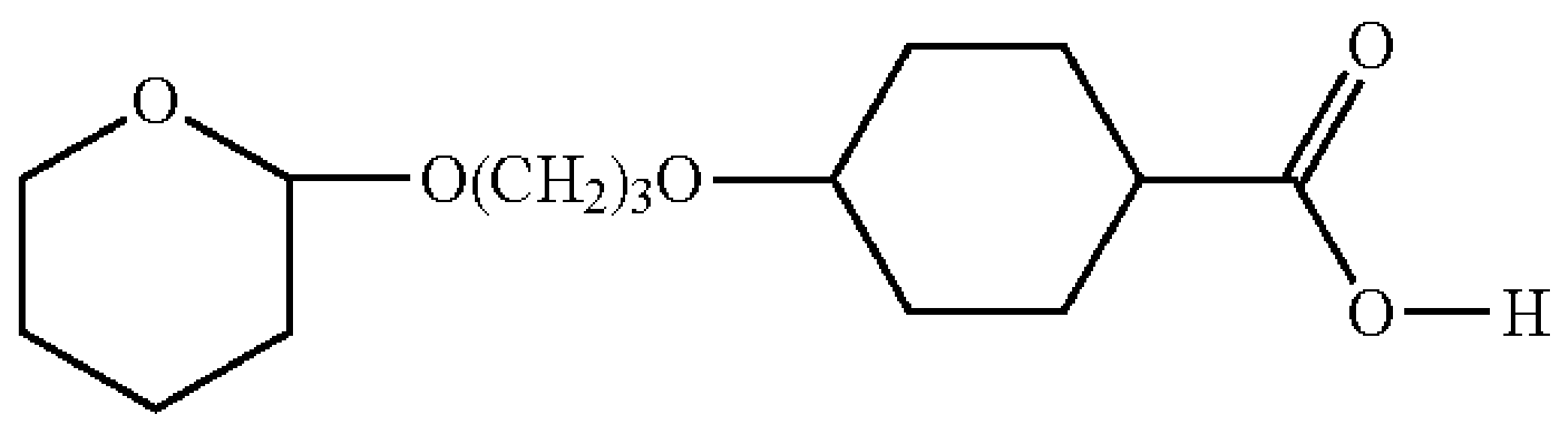
(2)

EXAMPLE 4

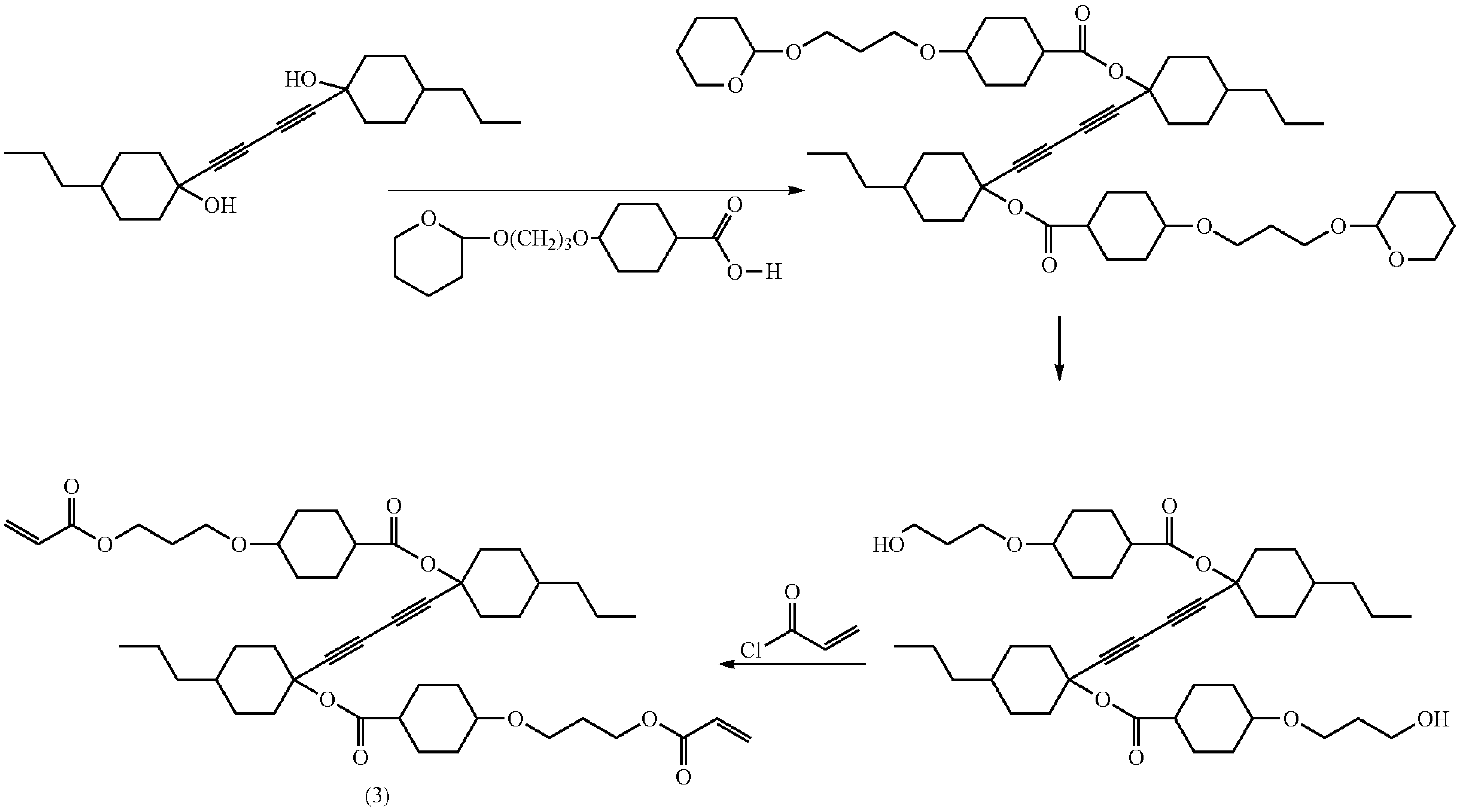
The synthetic route to compound (3) involves the synthesis of the saturated acid shown below: The synthetic route to this intermediate has been described in the literature (Lub et al in Recueil des Travaux Chimiques der Pays-Bas, (1996), 115, 321)

EXAMPLE 5

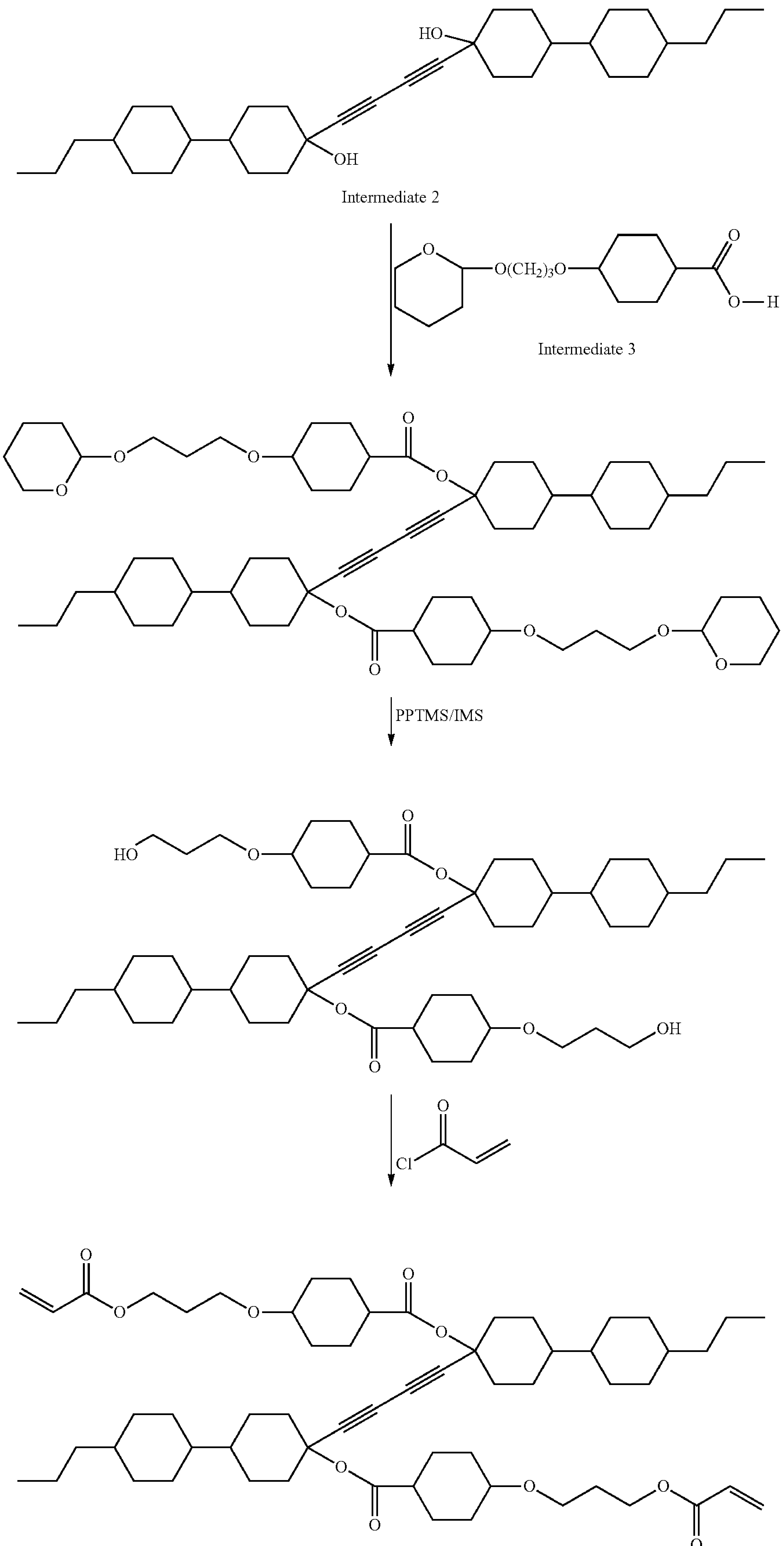
Compounds (4) and (5) are prepared by one of two possible routes. The first route uses intermediate 2 as a key intermediate whilst in the alternative route; the ester is prepared first before being dimerised to form the target diacetylene:



Intermediate 3

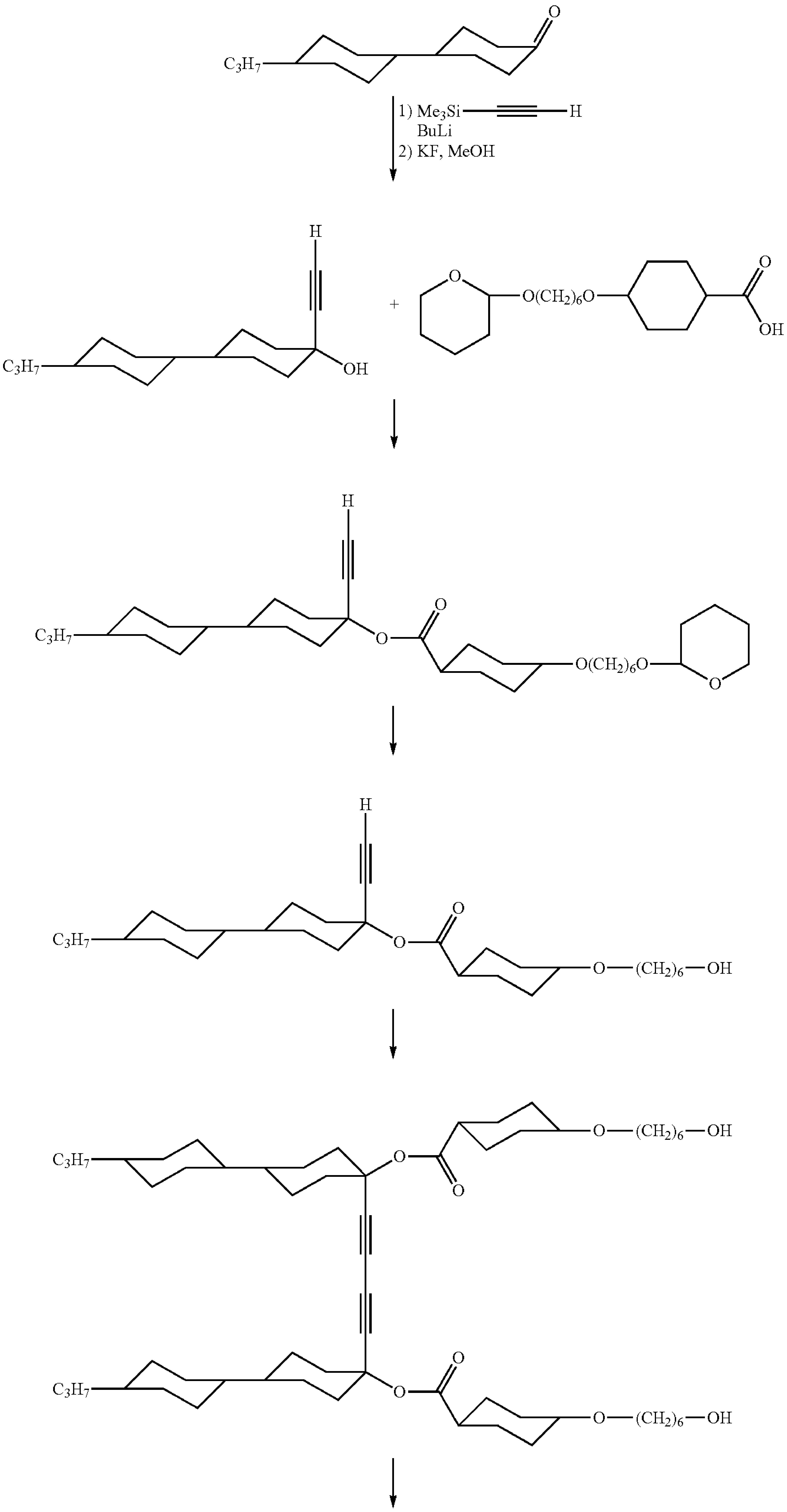


(3)



(4)

Alternative route (here shown for compound (5)):



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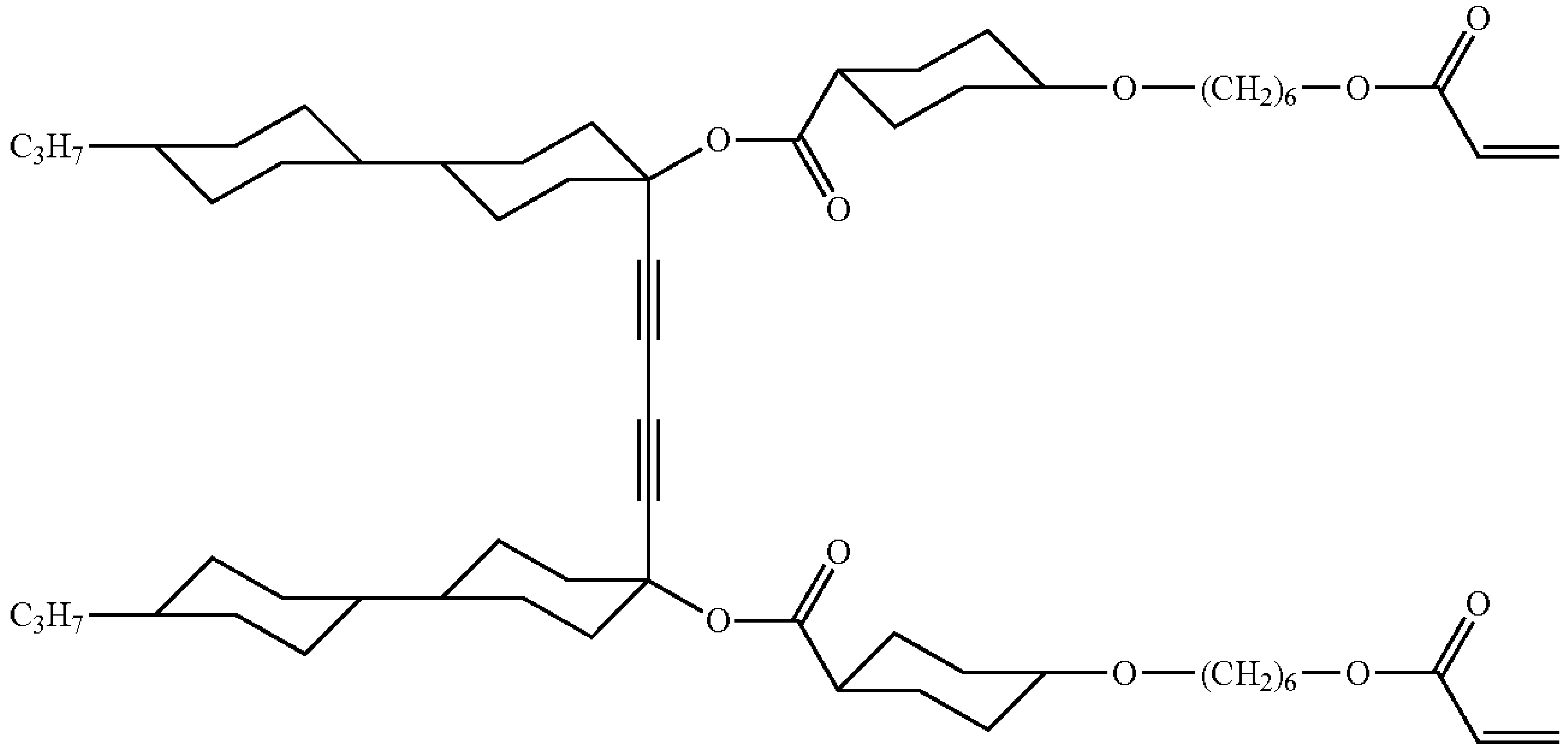
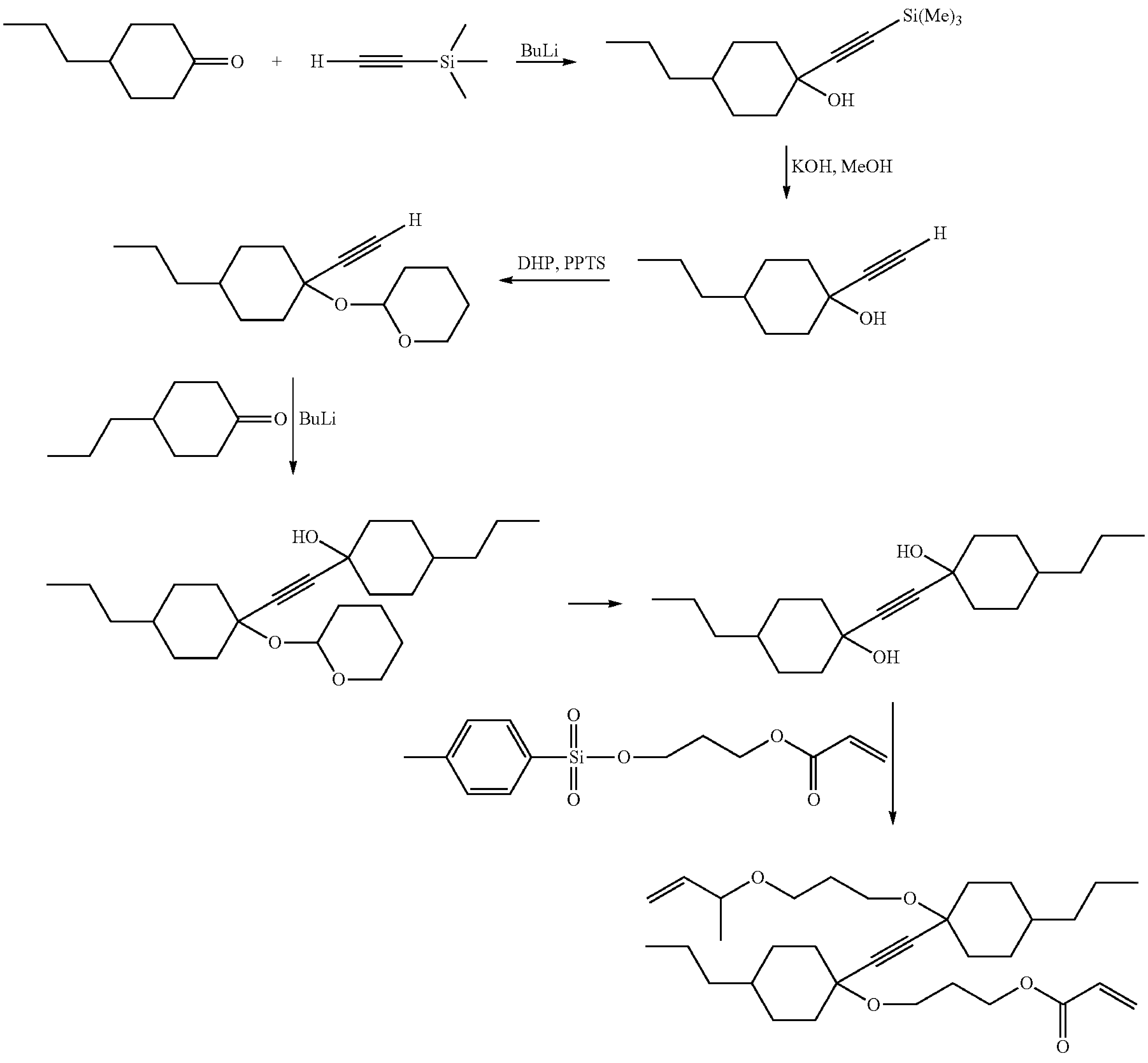


(5)

EXAMPLE 6

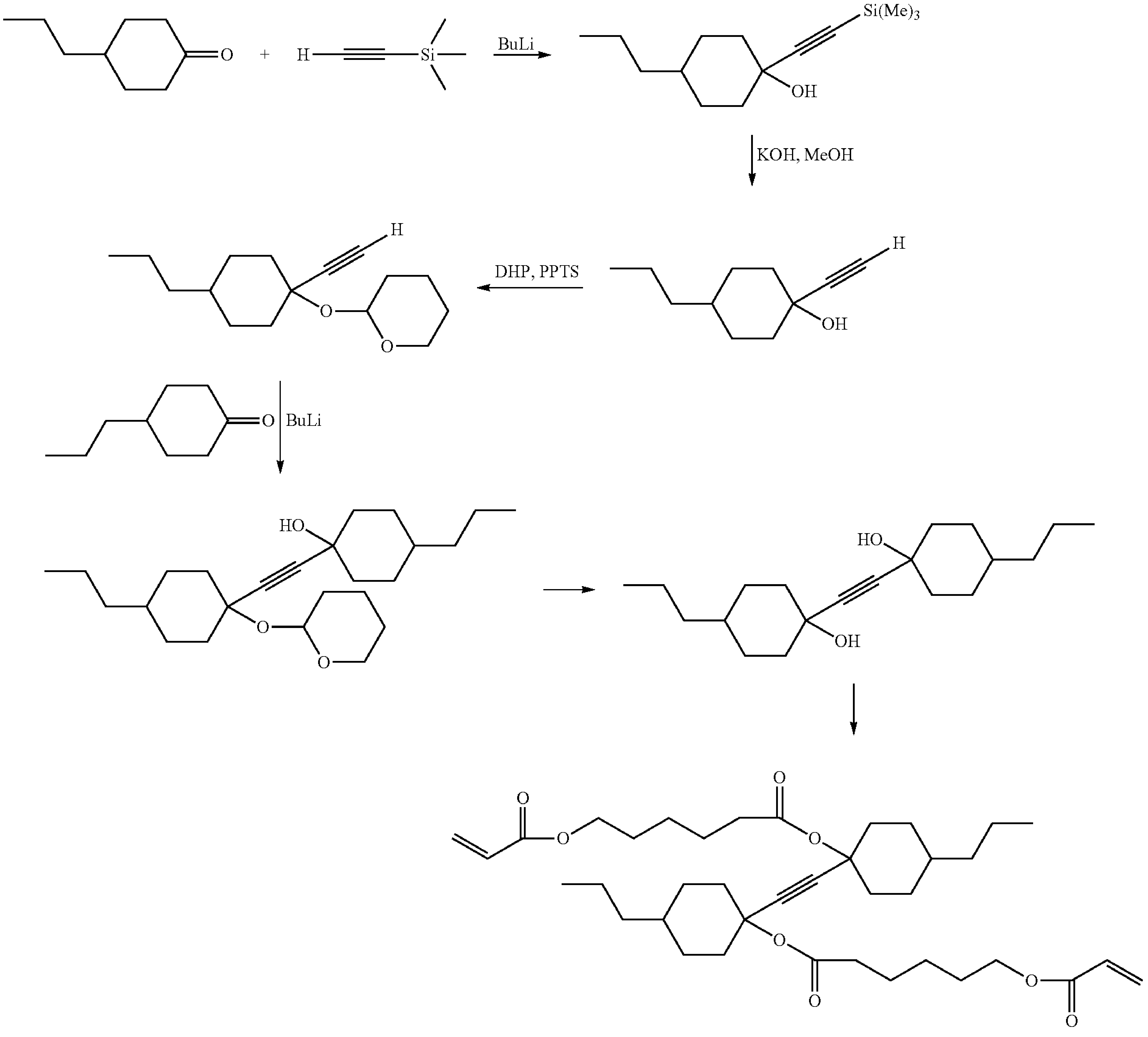
Compound (6) is prepared via the following route:



(6)

EXAMPLE 7

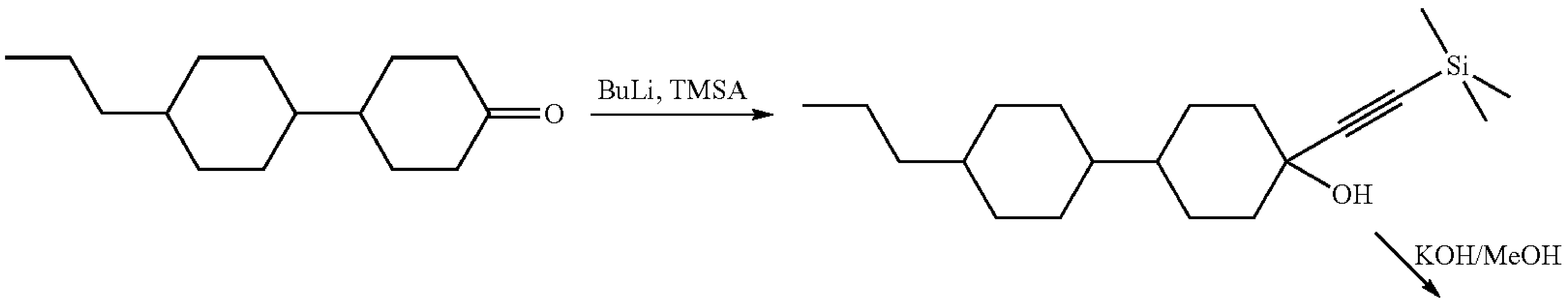
Compound (7) is prepared via the following route:



(7)

EXAMPLE 8

The 1,4-diethynylbenzene compound (8) is prepared via the route shown below:



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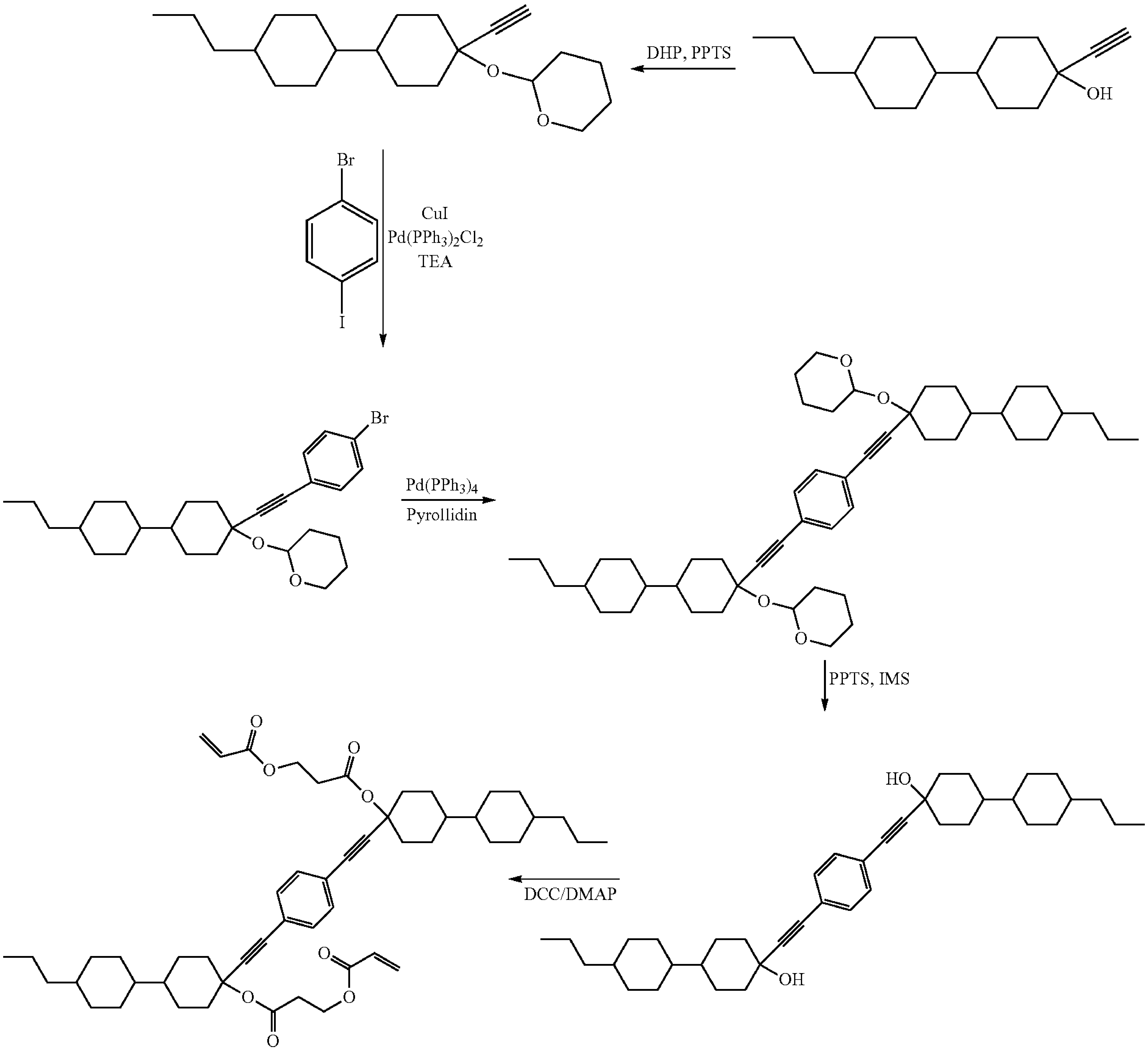
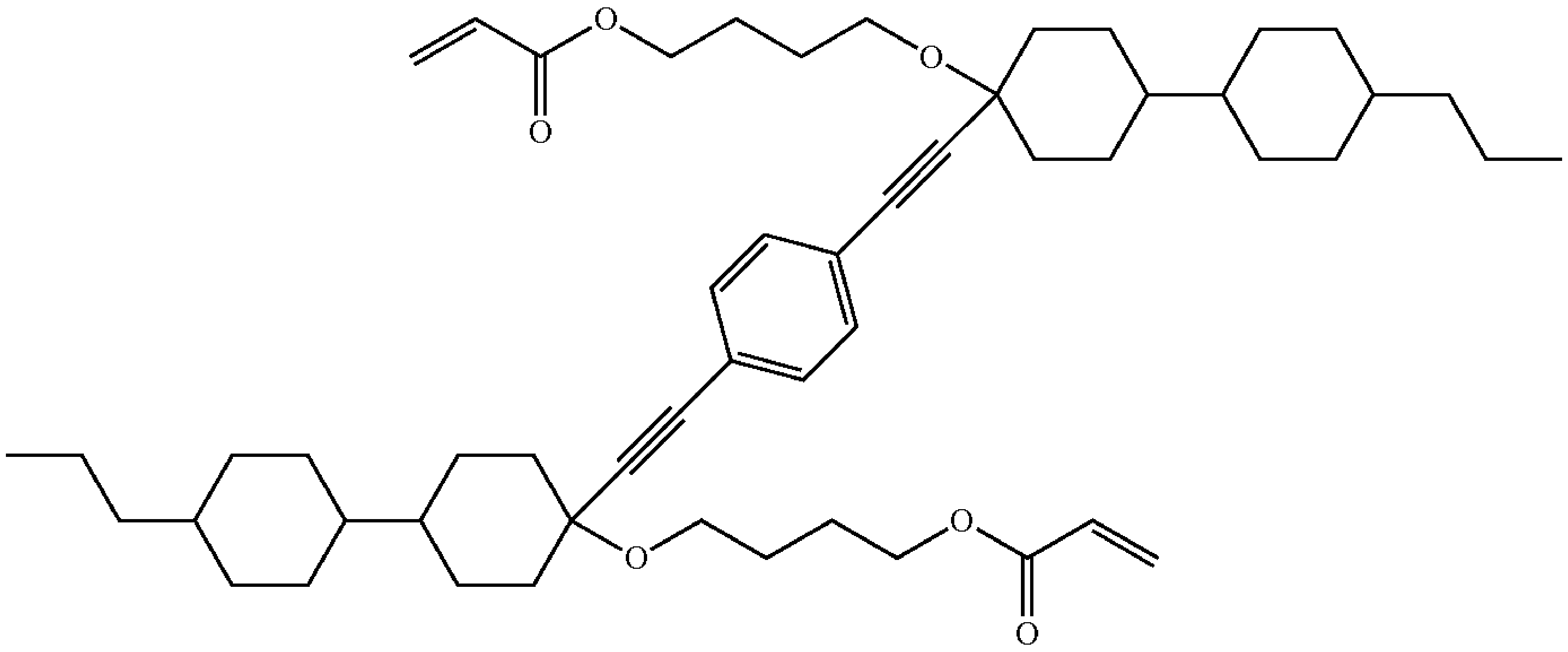


EXAMPLE 9

Compound (9) is prepared in analogy to Example 8.

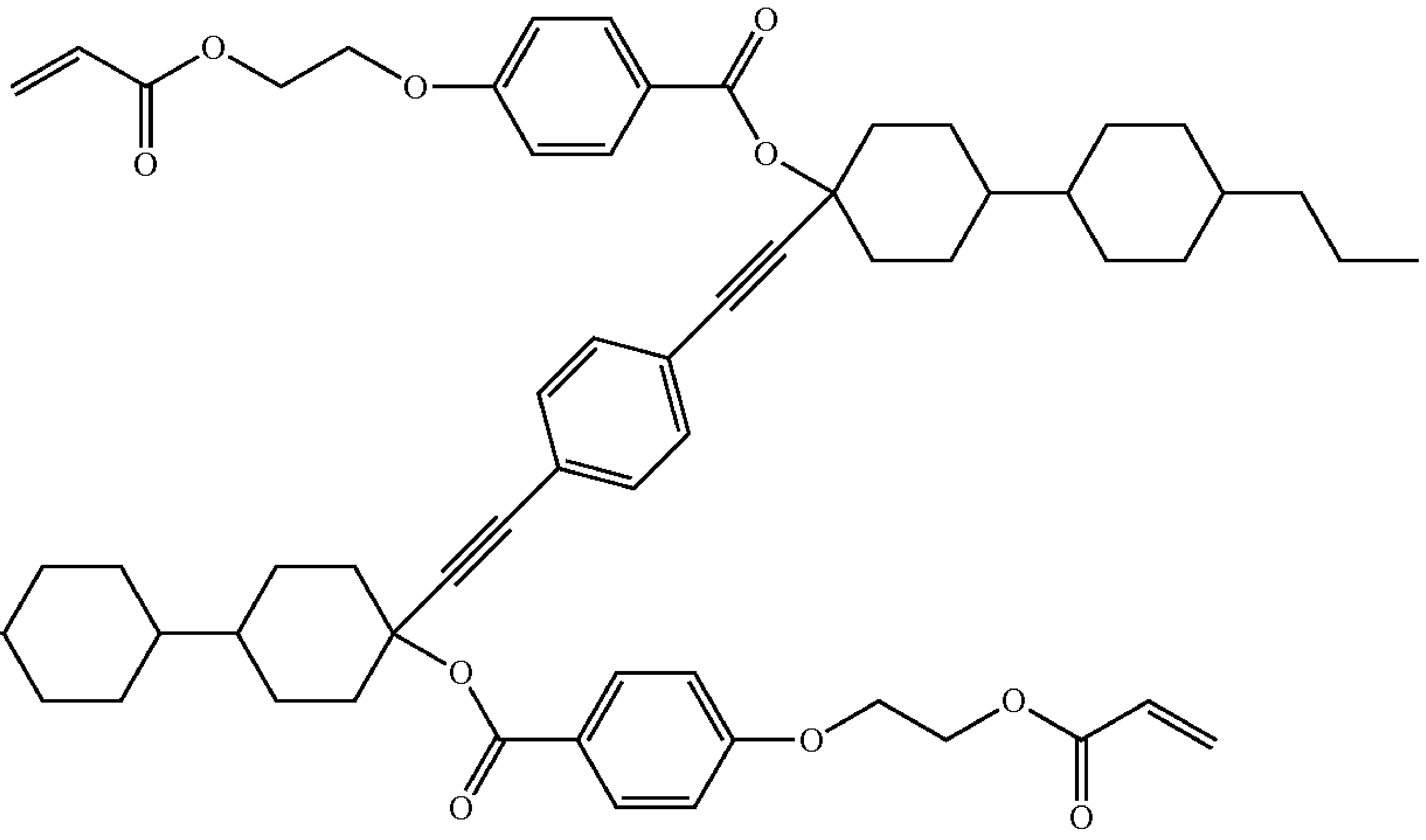


(9)

EXAMPLE 10

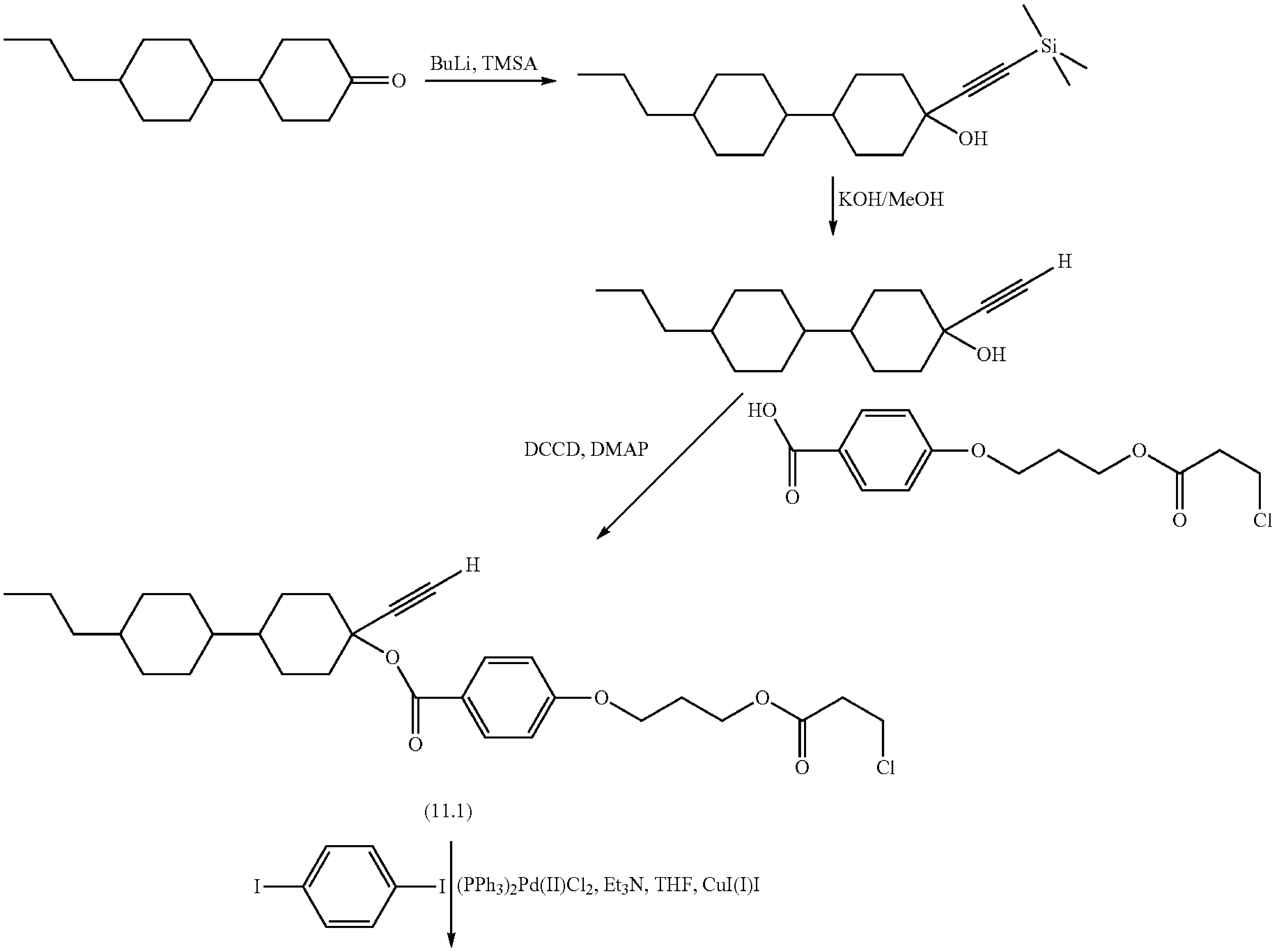
Compound (10) is prepared in analogy to Example 8.

(10)



EXAMPLE 11

Compound (11) is prepared as shown below



(11.1)

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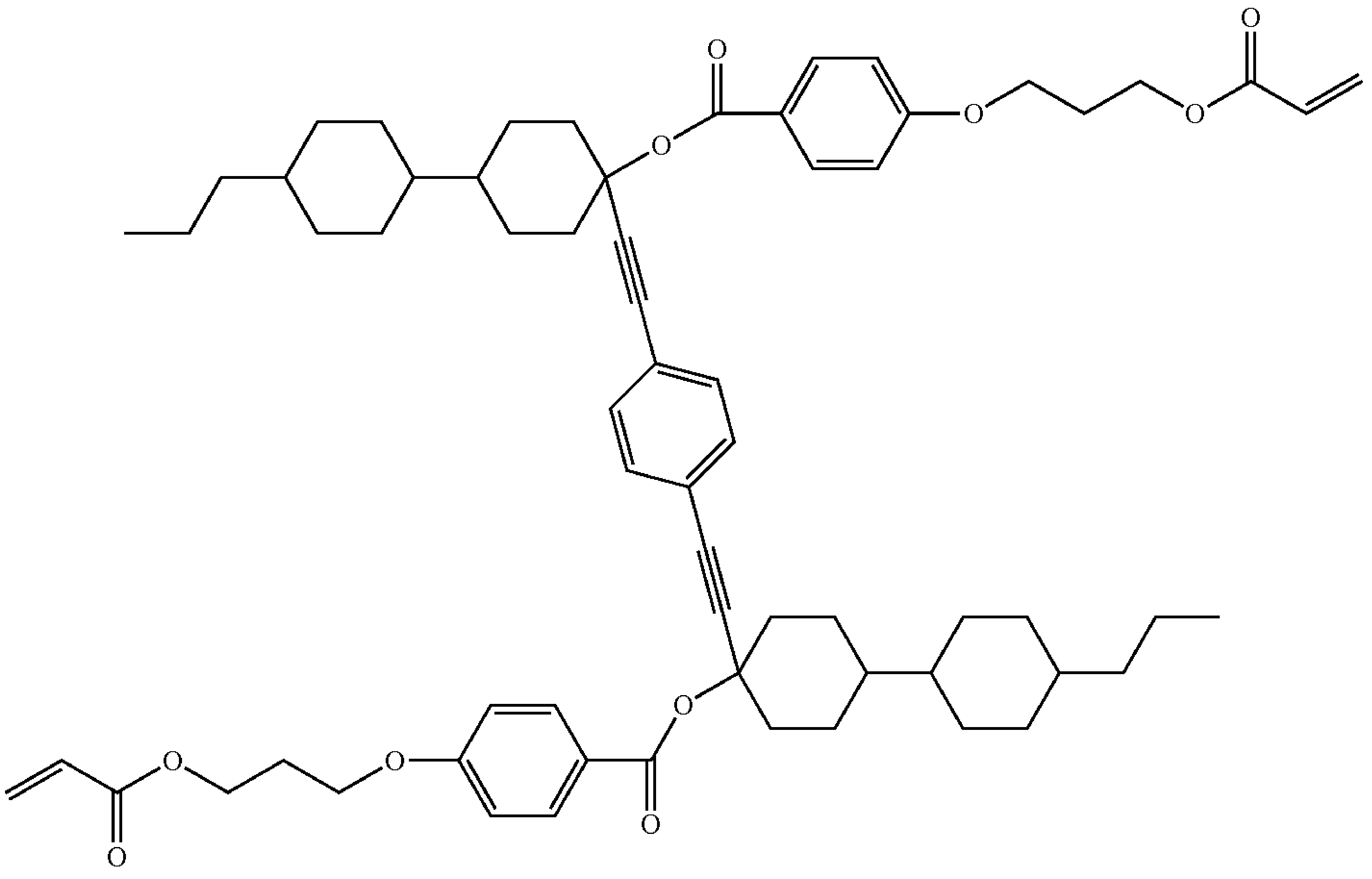


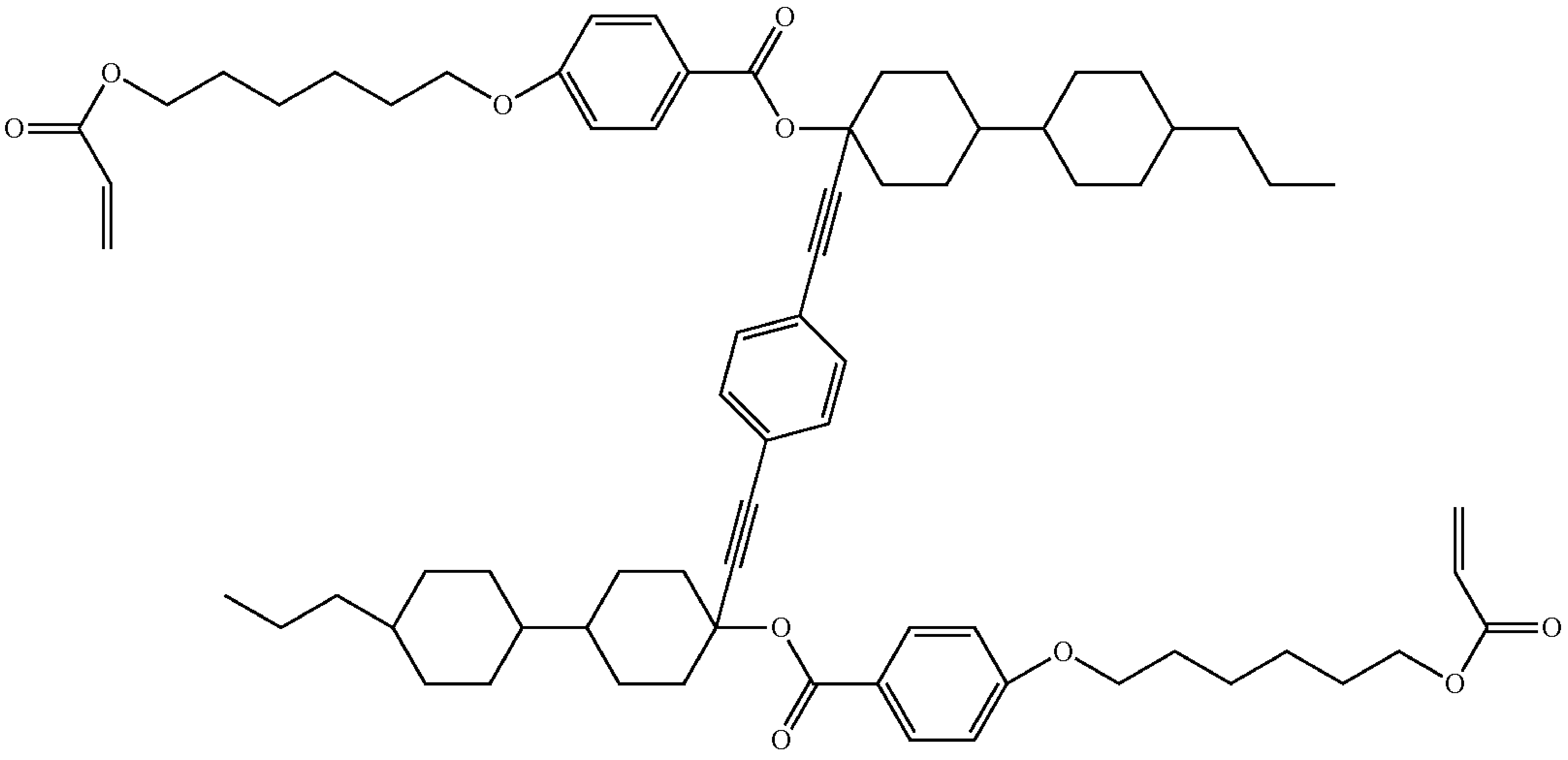
(11)

Compound (11.1) is prepared by reacting, 4-[3-(3-chloro-1-oxopropoxy)propoxy]benzoic acid with 4-ethynyl-4'-propyl-(trans,trans)-[1,1'-bicyclohexyl]-4-ol. Compound (11) is prepared by reacting compound (11.1) with 1,4-diiodobenzene under Sonogashira conditions.

Compound (11) has the following physical properties:
K-I 155.7° C.
n_e=1.5759
n_o=1.5271
Δn=0.0488

EXAMPLE 12 3

(12)



Compound 12 is prepared by a route similar to that shown for example 11 (compound 11). It has the following properties:

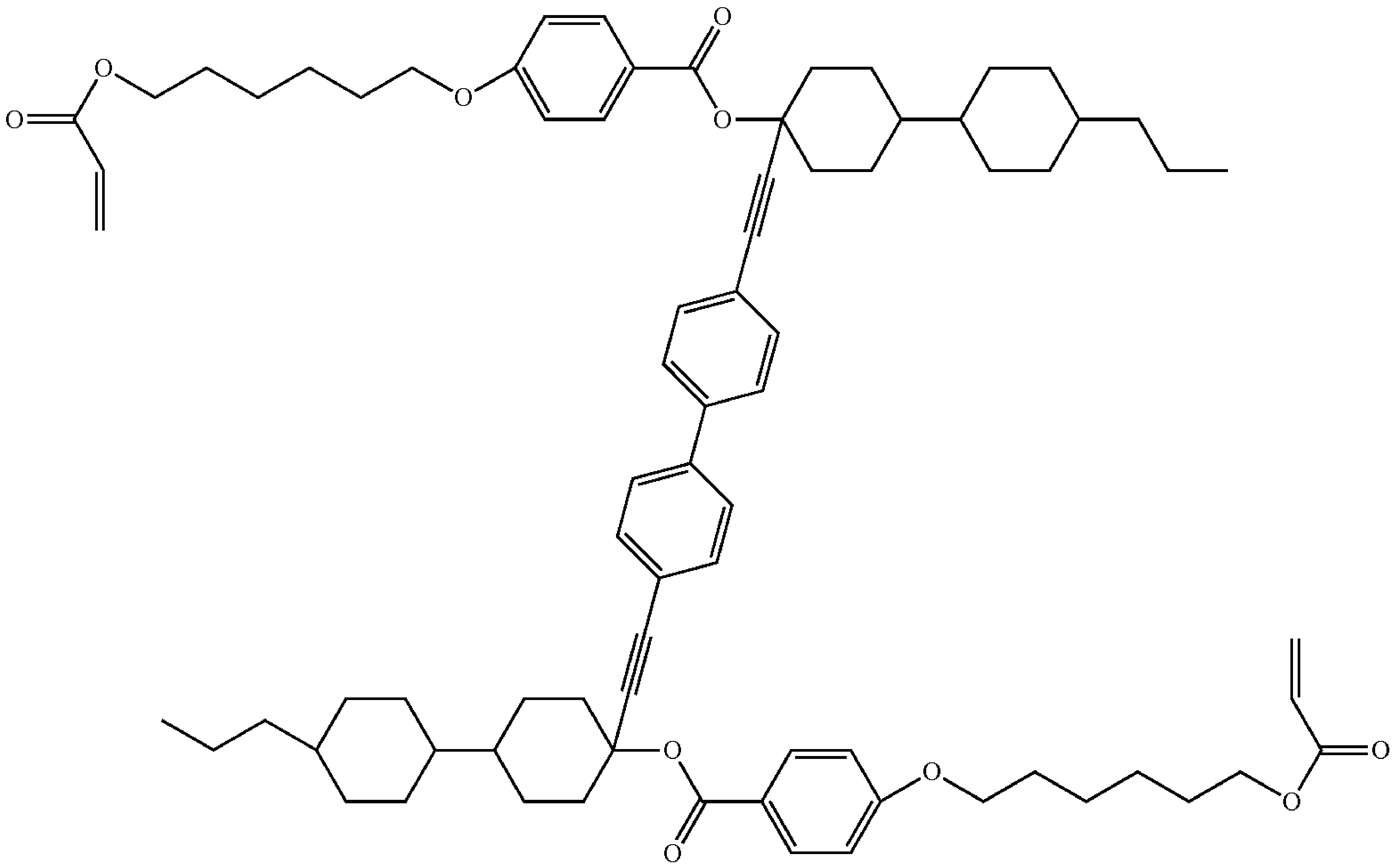
K-I 121.8° C.

n_e=1.5623

n_o=1.5218

Δn=0.0405

EXAMPLE 13



(13)

Compound 13 is prepared via a synthetic route similar to that described in example 11, but wherein 4,4'-diiodo-1,1'-biphenyl is used for the final Sonagashira reaction step. Compound 13 has the following properties:

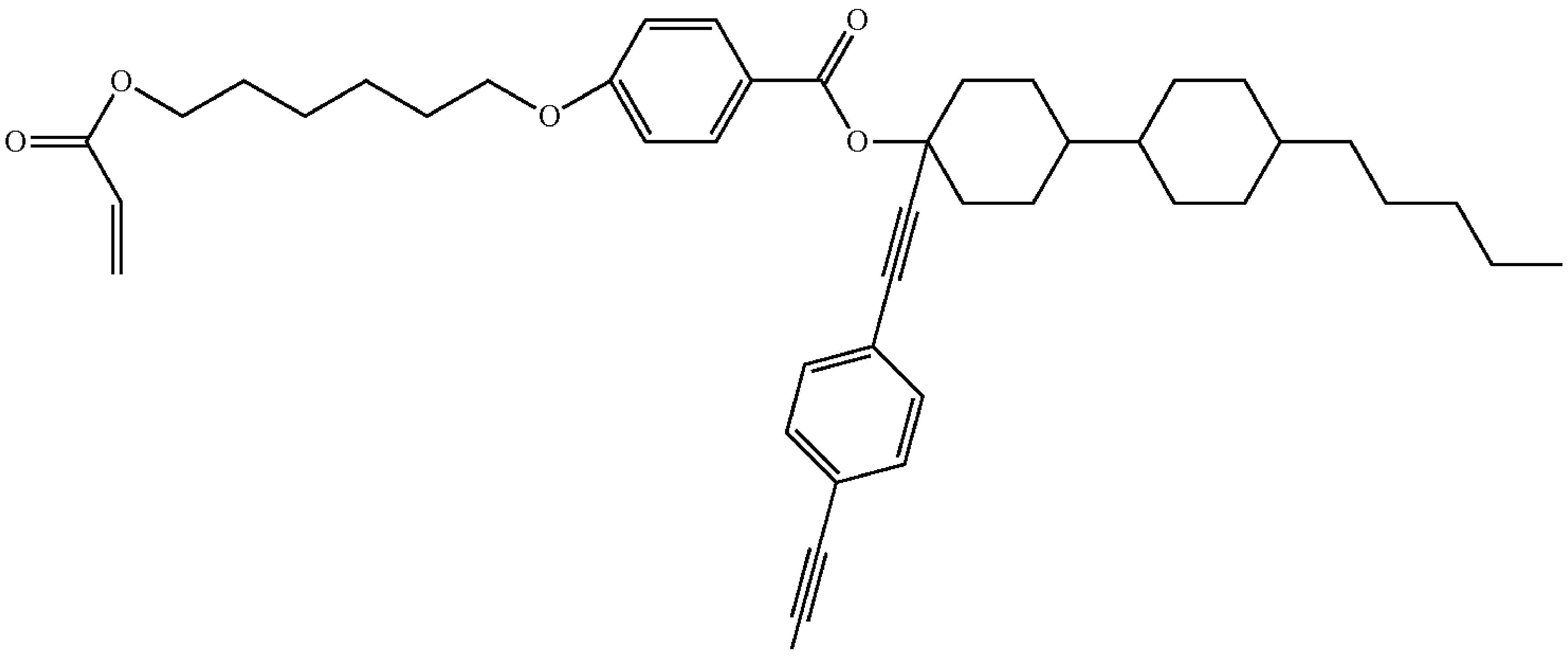
K-I 120.7° C.

n_e=1.5861

n_o=1.5508

Δn=0.0353

EXAMPLE 14



(14)

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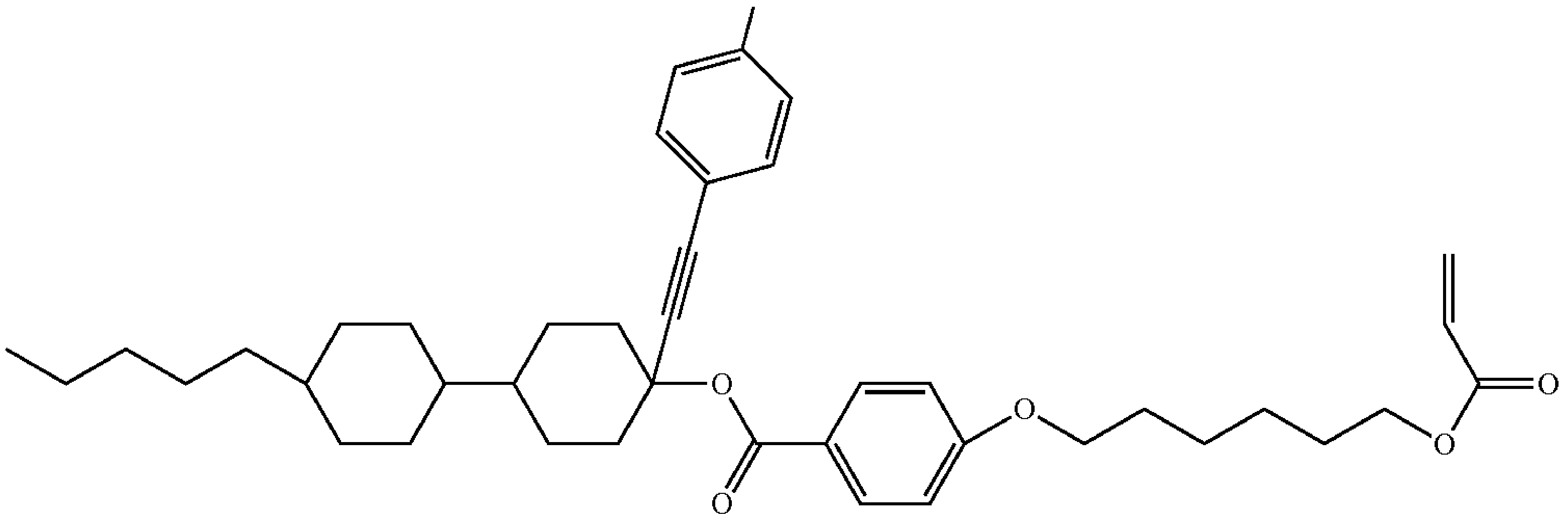
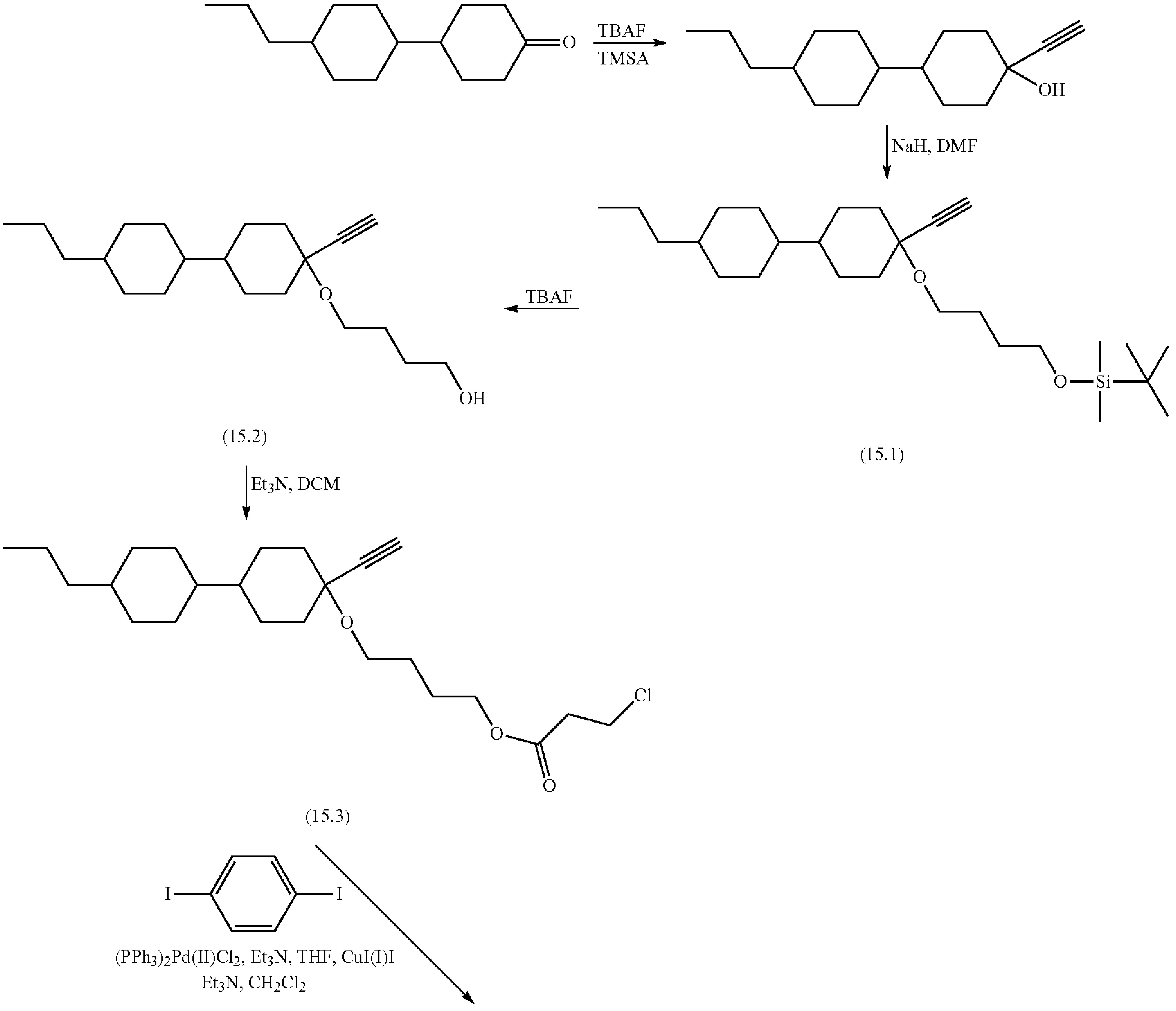


Compound 14 is prepared via a synthetic route similar to that described in example 11, but wherein 4'-Pentylbicyclohexyl-4-one is used as starting material, and 1,1'-(1,2-ethynediyl)bis[4-iodobenzene] is used for the final Sonagashira reaction step. Compound 14 has the following properties:

K-I=95.6° C.
ne=1.5840
no=1.5670
Δn=0.0140

EXAMPLE 15



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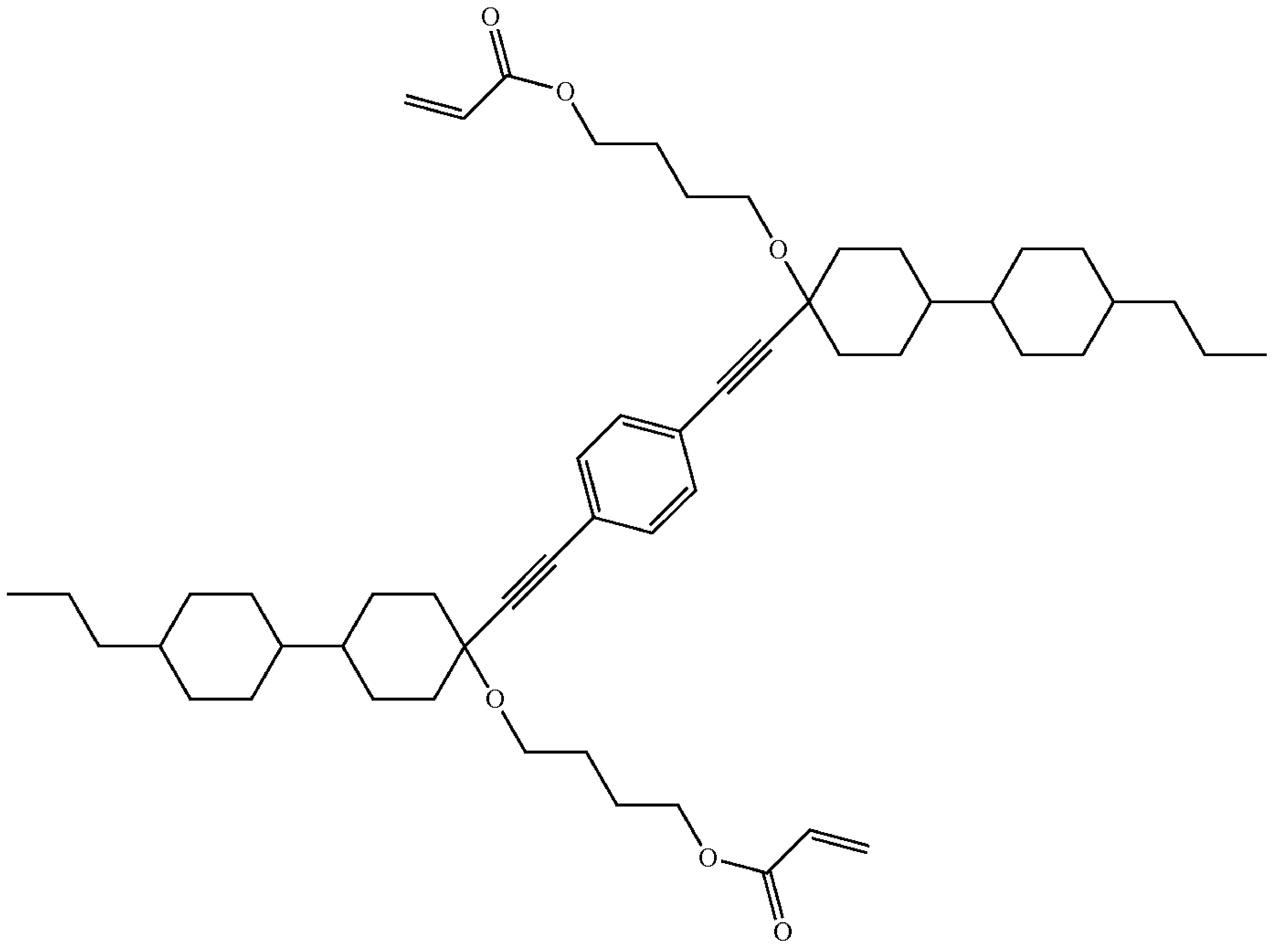


(15)

Compound 15 is prepared by the route shown above. 4-ethynyl-4'-propyl-(trans,trans)-[1,1'-bicyclohexyl]-4-ol is prepared via the method shown in Example 1. This tertiary alcohol is reacted with 4-(tert-butyl-(4-iodobutoxy)dimethylsilane and sodium hydride in DMF to give the ether tert-butyl-[4-(4-ethynyl-4'-propylbicyclohexyl-4-yloxy)-butoxy]-dimethyl-silane (compound 15.1). Deprotection of this ether gives the alcohol (15.2) which is subsequently esterified with chloropropionyl chloride to give the ester (compound 15.3). This compound is reacted with diiodobenzene under Sonagashira conditions to give the final product (compound 15). Compound 15 has the following physical properties:

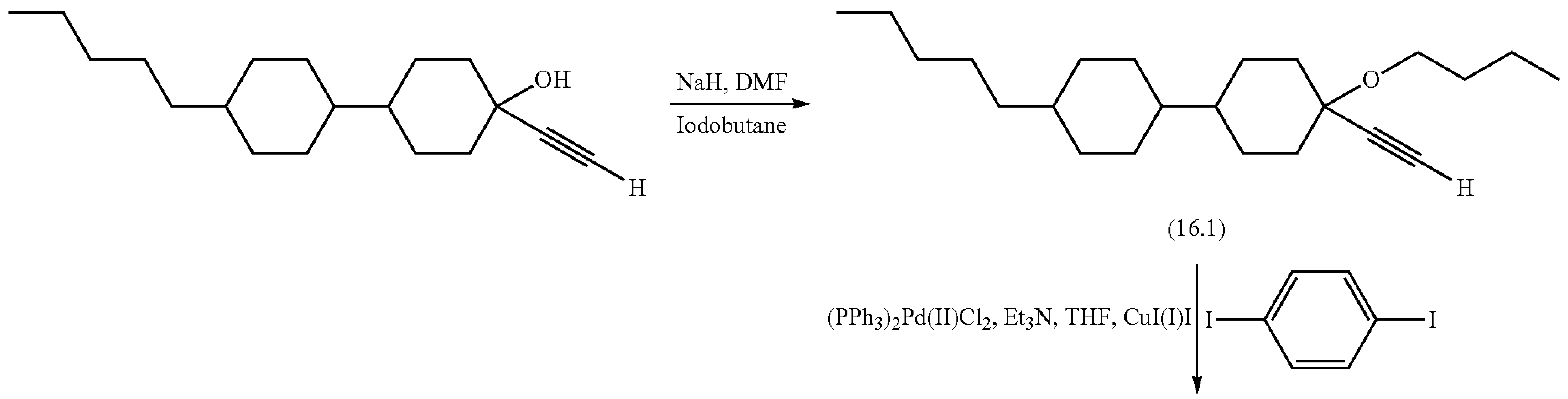
K-I 94.6° C.

ne=1.5230

no=1.5292

Δn=−0.0062

EXAMPLE 16



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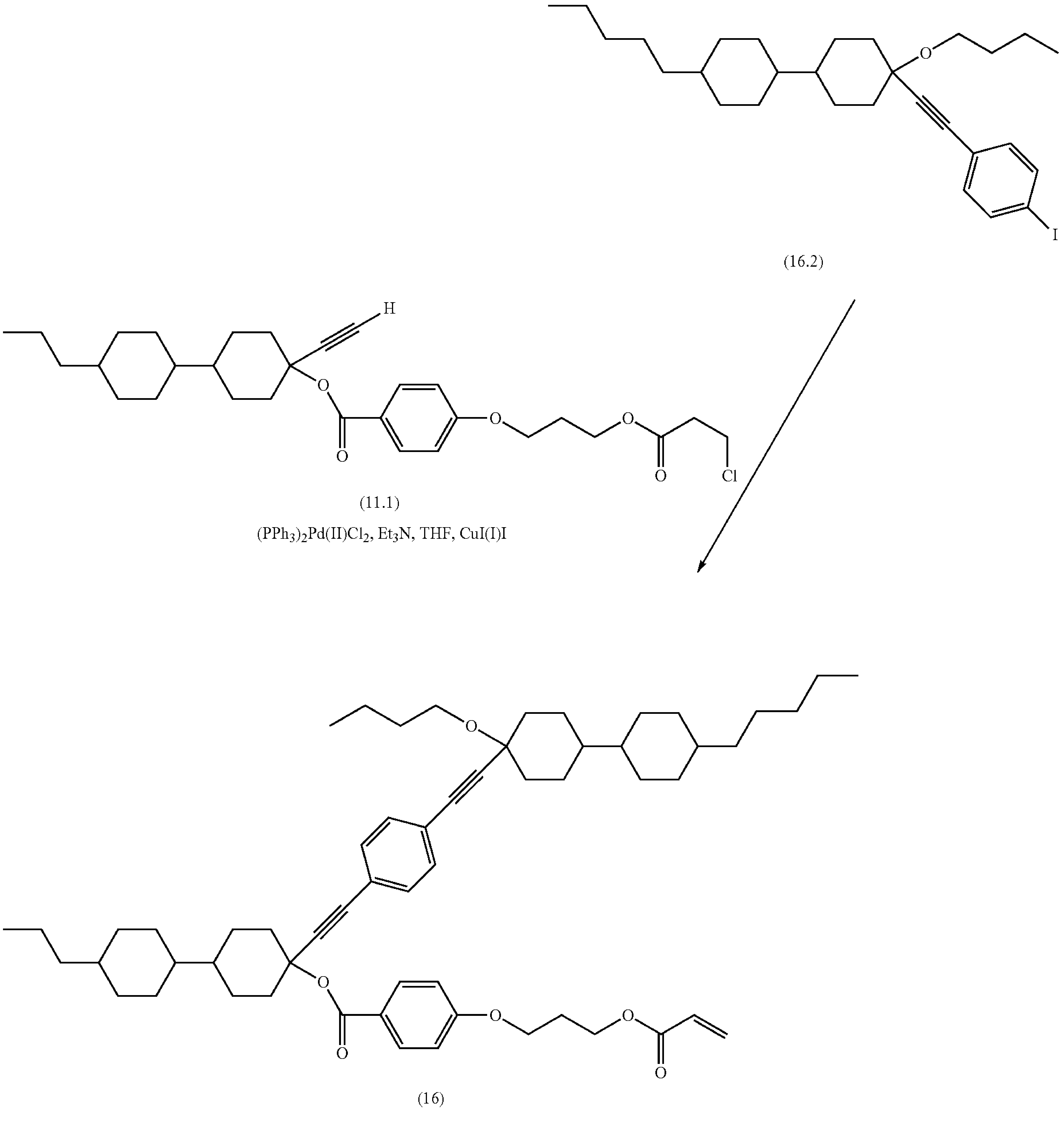


(16.2)

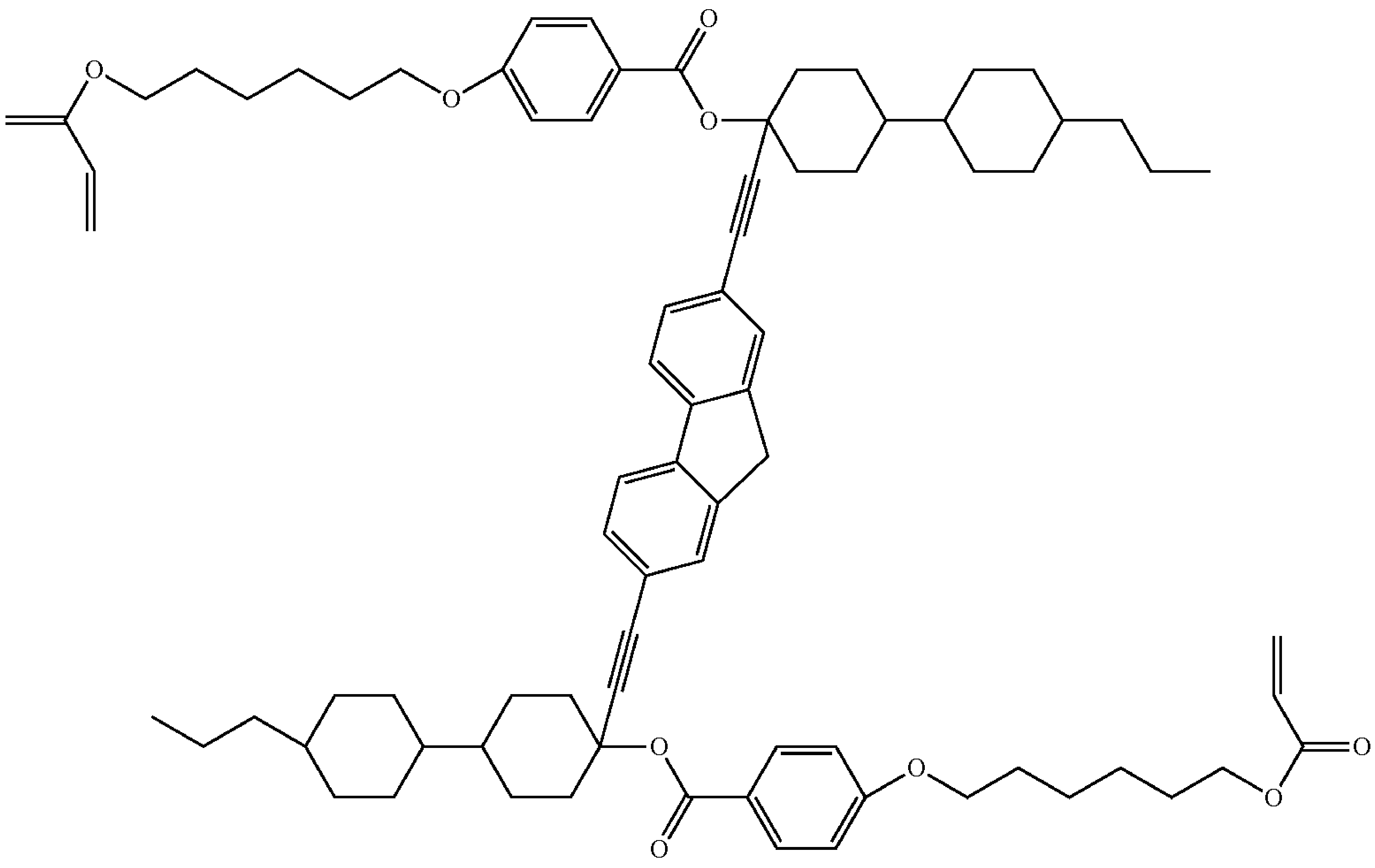
(11.1)

(PPh$_3$)$_2$Pd(II)Cl$_2$, Et$_3$N, THF, CuI(I)I

(16)

Compound 16 is prepared by the route shown above. 4-ethynyl-4'-propyl-(trans,trans)-[1,1'-bicyclohexyl]-4-ol is prepared via the method shown in Example 1. This tertiary alcohol is reacted with iodobenzene and sodium hydride in DMF to give the ether (compound 16.1). Reaction of this compound with an excess of 1,4-diiodobenzene under Sonagashira conditions gives predominantly the monoreacted product, compound 16.2. Subsequent reaction of this compound with compound (11.1) under Sonagashira conditions gives the final unsymmetrical product (compound 16). Compound 16 has the following properties: K-I 91.8° C.

EXAMPLE 17



(17)

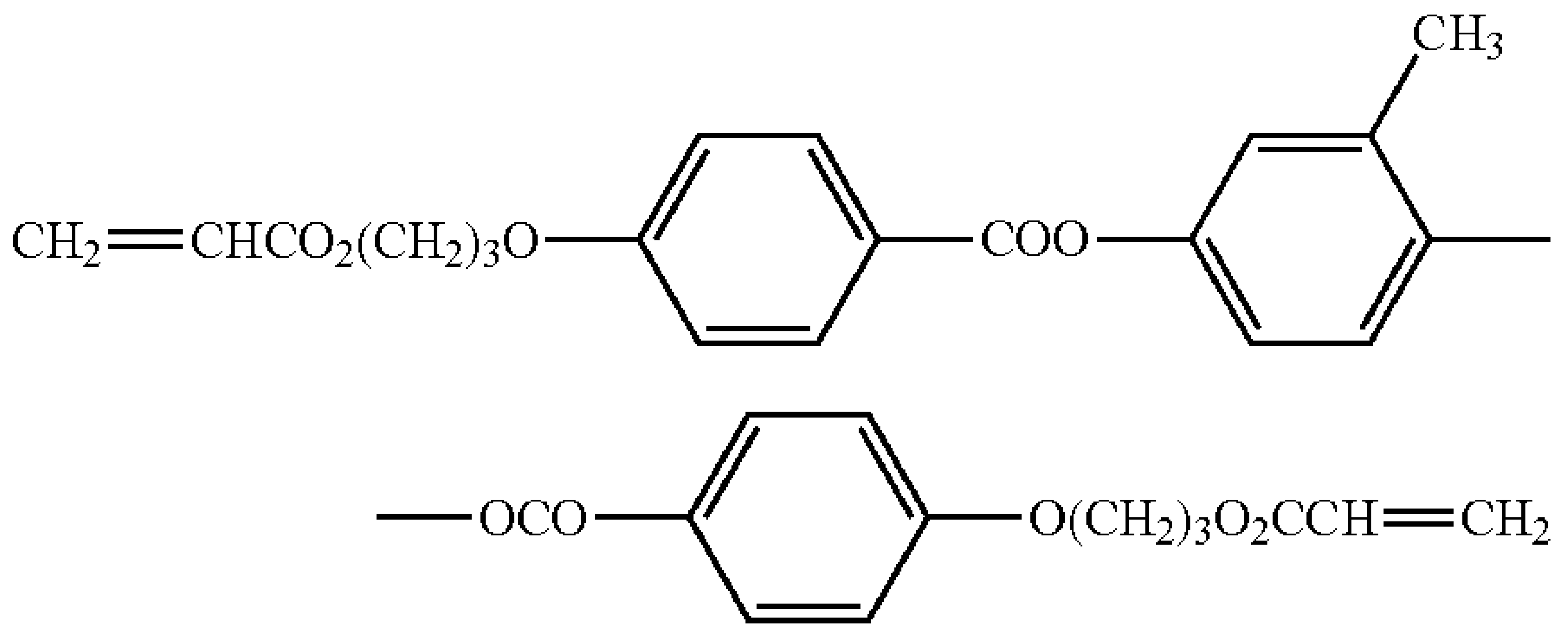
Compound 17 is prepared via a synthetic route similar to that described in example 11, but wherein 2,7-diiodo-9H-fluorene is used for the final Sonagashira reaction step. Compound 17 has the following optical properties:

ne=1.5820
no=1.5540
Δn=0.0280

EXAMPLE 18

The following mixture is prepared:

FC 171 ®	0.26%
Irg 651 ®	0.38%
Irg 1076 ®	0.03%
Compound (A)	15.32%
Compound 12	24.01%
Toluene	60.00



(A)

FC 171 is a fluorosurfactant commercially available from 3M, Irgacure 651 and 1076 are photoinitiators commercially available from Ciba AG. Compound A is described in the literature (see e.g. D. J. Broer; G. Challa; G. N. Mol, Macromol. Chem., 1991, 192, 59).

The formulation is spin coated at 3000 rpm on to a PI coated glass slide. The samples are annealed at 60° C. for 60 s. After annealing, each sample is polymerised using the EFOS lamp (200 mW/cm2) 365 nm filter, under nitrogen at 60° C. for 60 s. The retardation of each slide is measured using the Ellipsometer and the thickness of each slide is measured using the surface profilometer.

The retardation profile of the film is shown in FIG. **5**, and indicates that it has the optical property of an A-plate, and that the film has positive dispersion with $R_{450}/R_{550}=1.091$, but the dispersion is lower than the same mixture which does not contain Compound 12 (see Comparative Example 1).

COMPARATIVE EXAMPLE 1

The following mixture is prepared:

FC 171	0.26%
Irg 651 ®	0.38%
Irg 1076 ®	0.03%
(A)	39.33%
Toluene	60.00%

The formulation is spin coated at 3000 rpm on to a PI coated glass slide. The samples are annealed at 60° C. for 60 s. After annealing, each sample is polymerised using the EFOS lamp (200 mW/cm2) 365 nm filter, under nitrogen at 60° C. for 60 s. The retardation of each slide is measured using the Ellipsometer and the thickness of each slide is measured using the surface profilometer.

The retardation profile of the film is shown in FIG. **6**, and indicates that it has the optical property of an A-plate, and that the film has positive dispersion with $R_{450}/R_{550}=1.112$.

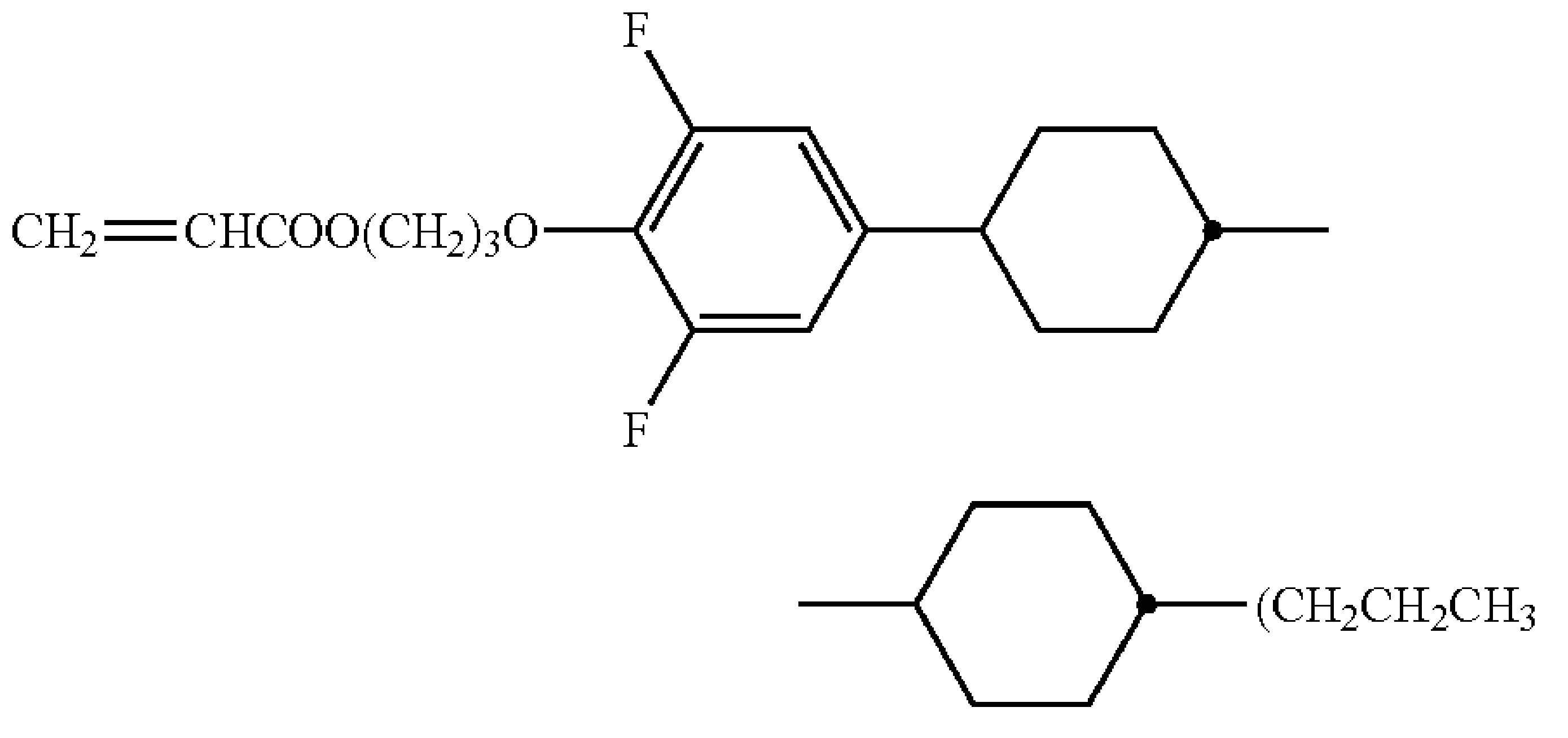
EXAMPLE 19

The following mixture is prepared:

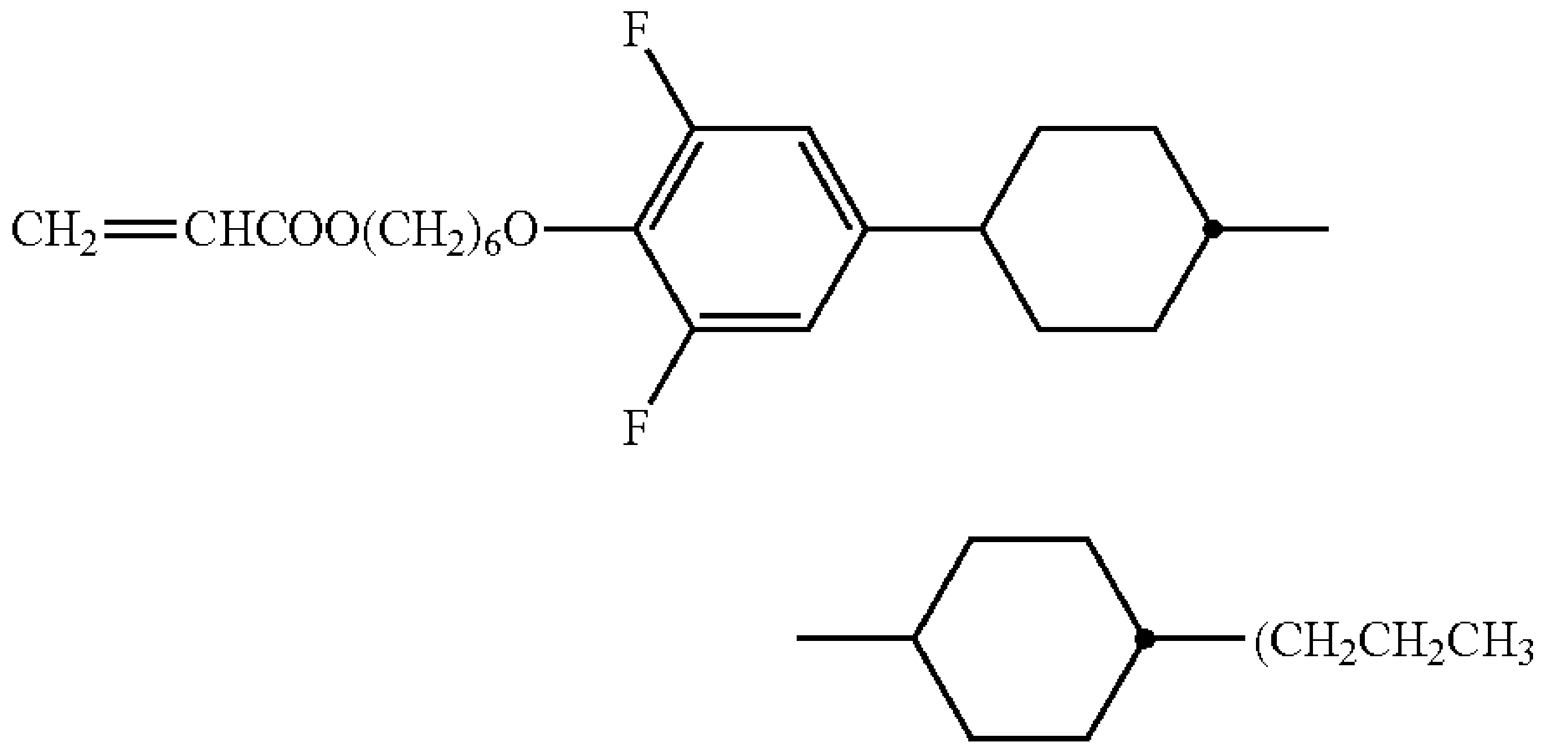
Irg 651 ®	0.42
Irg 1076 ®	0.02
(A)	2.82

-continued

(B)	7.12
(C)	9.63
Compound 15	19.99
Toluene	60.00



(B)



(C)

Compounds B and C are described in U.S. Pat. No. 6,183,822.

The formulation is spin coated at 3000 rpm on to a PI coated glass slide. The samples are annealed at 40° C. for 60 s. After annealing, each sample is polymerised using the EFOS lamp (200 mW/cm2) 365 nm filter, under nitrogen at 40° C. for 60 s. The retardation of each slide is measured using the Ellipsometer and the thickness of each slide is measured using the surface profilometer.

The retardation profile of the film is shown in FIG. **7**, and indicates that it has the optical property of an O-plate, and that the film has positive dispersion with $R_{450}/R_{550}=1.00$ when measured normal to the plane of the film.

EXAMPLE 20

The following mixture is prepared:

Irgacure 651 ®	0.40
Irganox 1076 ®	0.03
(A)	1.61
(C)	12.36
Compound 15	8.00
Compound 13	17.60
Toluene	60.00

The formulation is spin coated at 3000 rpm on to a PI coated glass slide. The samples are annealed at 50° C. for 30 s. After annealing, each sample is polymerised using the EFOS lamp (200 mW/cm2) 365 nm filter, under nitrogen at 40° C. for 60 s. The retardation of each slide is measured using the Ellipsometer and the thickness of each slide is measured using the surface profilometer.

The retardation profile of the film is shown in FIG. **8**, and indicates that it has the optical property of an +C-plate, and that the film has negative dispersion with $R_{450}/R_{550}=0.96$ when measured at an angle of between 20 and 60° out to the plane of the film.

The invention claimed is:

1. A polymer film with $R_{450}/R_{550}<1$, wherein R_{450} is the optical on-axis retardation at a wavelength of 450 nm and R_{550} is the optical on-axis retardation at a wavelength of 550 nm, said film being obtainable by polymerizing one or more polymerizable compounds, wherein said polymerizable compounds contain

two mesogenic groups comprising one or more non-aromatic rings,

one or more polymerizable groups attached to at least one of the mesogenic groups either directly or via spacer groups, and

a bridging group connecting the mesogenic groups, comprising one or more subgroups selected from pi-conjugated linear carbyl or hydrocarbyl groups, aromatic and heteroaromatic groups, and being linked to a sp^3-hybridized C-atom or Si-atom in a non-aromatic ring of each mesogenic group.

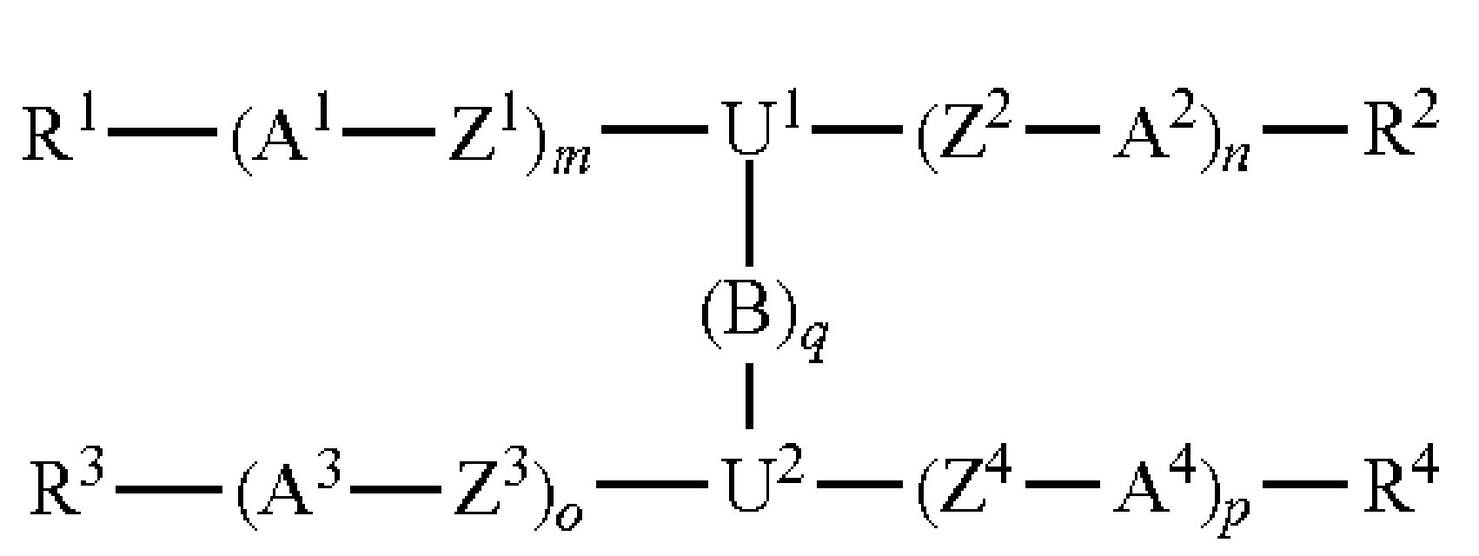
2. The polymer film according to claim **1**, wherein the mesogenic groups are calamitic groups.

3. The polymer film according to claim **1**, wherein the mesogenic groups comprise more saturated rings than unsaturated or aromatic rings.

4. The polymer film according to claim **1**, wherein the bridging group is a subgroup selected from the group consisting of pi-conjugated linear groups, aromatic and heteroaromatic groups.

5. The polymer film according to claim **1**, wherein the bridging group is connected in axial position to a cyclohexylene or silanane ring comprised in the mesogenic group, which is optionally substituted and wherein one or more non-adjacent C-atoms are optionally replaced by Si and/or one or more non-adjacent CH_2 groups are optionally replaced by —O— and/or —S—.

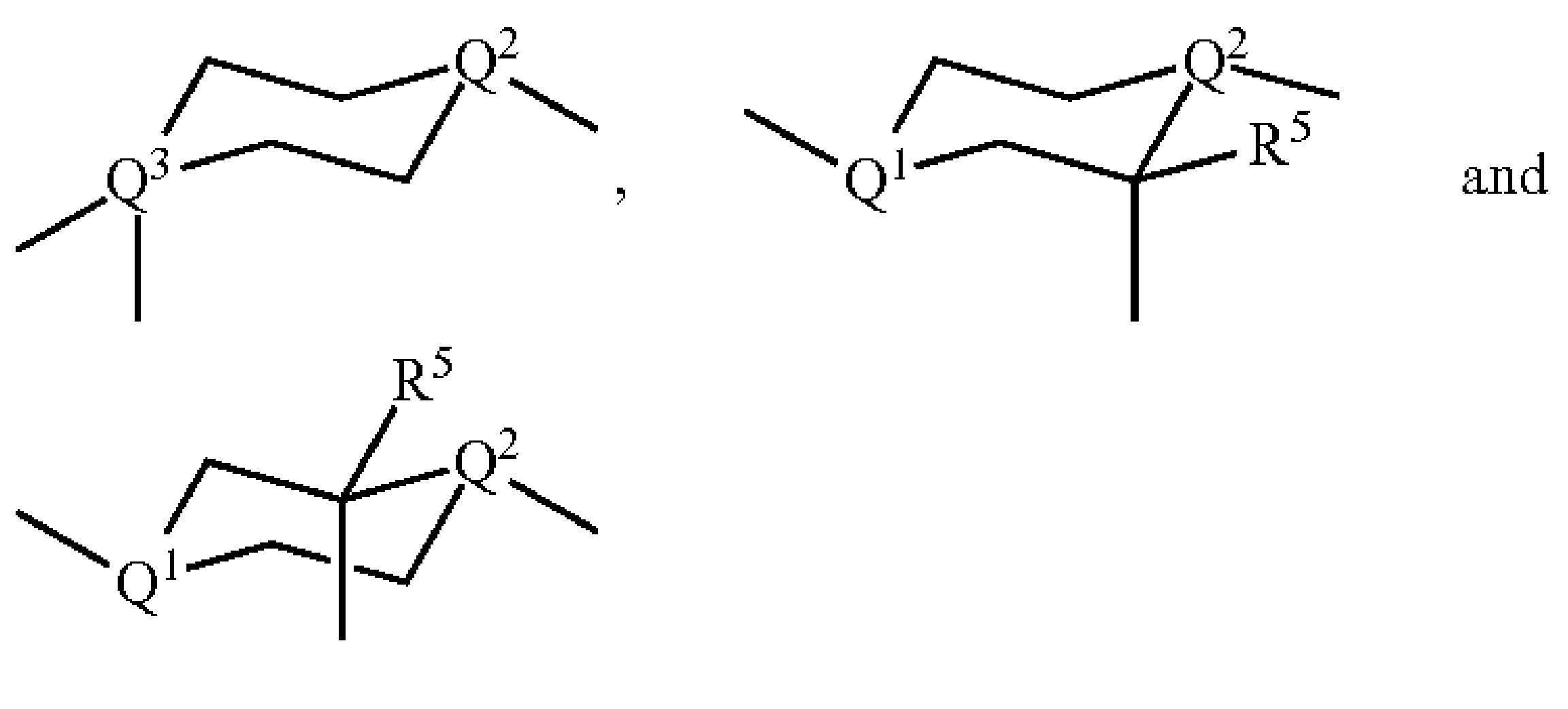
6. The polymer film according to claim **1**, wherein the polymerizerable compounds are of the following formula



$$\begin{array}{c} R^1—(A^1—Z^1)_m—U^1—(Z^2—A^2)_n—R^2 \\ | \\ (B)_q \\ | \\ R^3—(A^3—Z^3)_o—U^2—(Z^4—A^4)_p—R^4 \end{array} \qquad \text{I}$$

wherein

$U^{1,2}$ are independently of each other selected from



including their mirror images, wherein the rings U^1 and U^2 are each bonded to the group —$(B)_q$— via the axial bond, and one or two non-adjacent CH_2 groups in these rings are optionally replaced by O and/or S, and the rings U^1 and U^2 are optionally substituted by one or more groups L,

$Q^{1,2}$ are independently of each other CH or SiH,

Q^3 is C or Si,

B is in each occurrence independently of one another —C≡C—, $-CY^1{=}CY^2-$ or an optionally substituted aromatic or heteroaromatic group,

$Y^{1,2}$ are independently of each other H, F, Cl, CN or R^0,

q is an integer from 1 to 10, preferably 1, 2, 3, 4, 5 or 6,

A^{1-4} are independently of each other non-aromatic carbocylic or heterocyclic groups and aromatic and heteroaromatic groups, which are optionally substituted by one or more groups R^5, and wherein each of $-(A^1\text{-}Z^1)_m-U^1-(Z^2\text{-}A^2)_n-$ and $-(A^3\text{-}Z^3)_o-U^2-(Z^4\text{-}A^4)_p-$ does not contain more aromatic groups than non-aromatic groups,

Z^{1-4} are independently of each other —O—, —S—, —CO—, —COO—, —OCO—, —O—COO—, $-CO-NR^0-$, $-NR^0-CO-$, $-NR^0-CO-NR^0-$, $-OCH_2-$, $-CH_2O-$, $-SCH_2-$, $-CH_2S-$, $-CF_2O-$, $-OCF_2-$, $-CF_2S-$, $-SCF_2-$, $-CH_2CH_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, $-CF_2CH_2-$, $-CH_2CF_2-$, $-CF_2CF_2-$, —CH═CH—, $-CY^1{=}CY^2-$, —CH═N—, —N═CH—, —N═N—, $-CH{=}CR^0-$, —C≡C—, —CH═CH—COO—, —OCO—CH═CH—, CR^0R^{00} or a single bond,

R^0, R^{00} are independently of each other H or alkyl with 1 to 12 C-atoms,

m and n are independently of each other 0, 1, 2, 3 or 4,

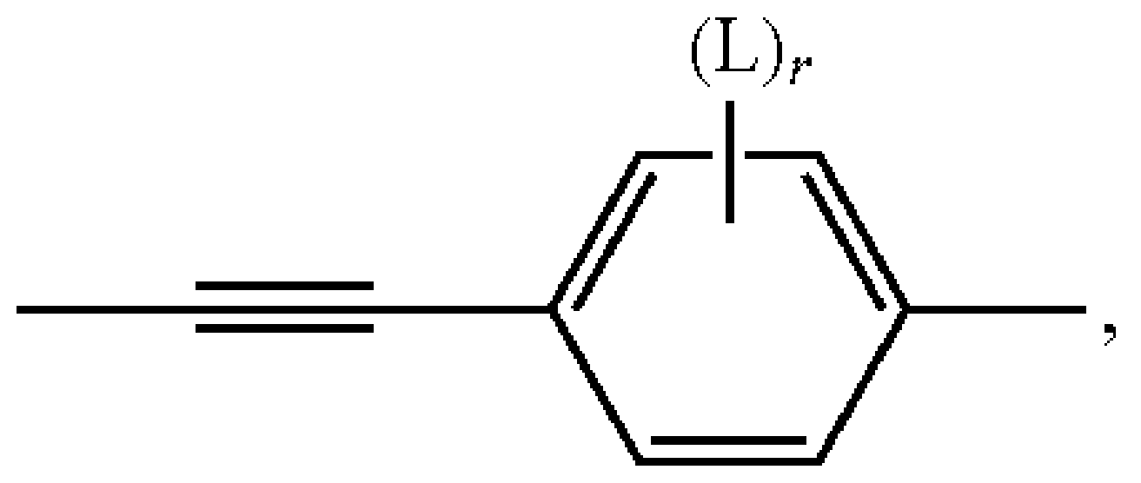
o and p are independently of each other 0, 1, 2, 3 or 4,

R^{1-5} are independently H, halogen, —CN, —NC, —NCO, —NCS, —OCN, —SCN, $-C({=}O)NR^0R^{00}$, $-C({=}O)X^0$, $-C({=}O)R^0$, $-NH_2$, $-NR^0R^{00}$, —SH, $-SR^0$, $-SO_3H$, $-SO_2R^0$, —OH, $-NO_2$, $-CF_3$, $-SF_5$, P-Sp-, optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 40 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, or denote P or P-Sp-, or are substituted by P or P-Sp-, wherein the compounds comprise at least one group R^{1-5} denoting or being substituted by P or P-Sp-,

P is a polymerizable group, and

Sp is a spacer group or a single bond.

7. The polymer film according to claim **1**, wherein the bridging group, is —C≡C—, —C≡C—C≡C—, —C≡C—C≡C—C≡C—, —C≡C—C≡C—C≡C—C≡C—,



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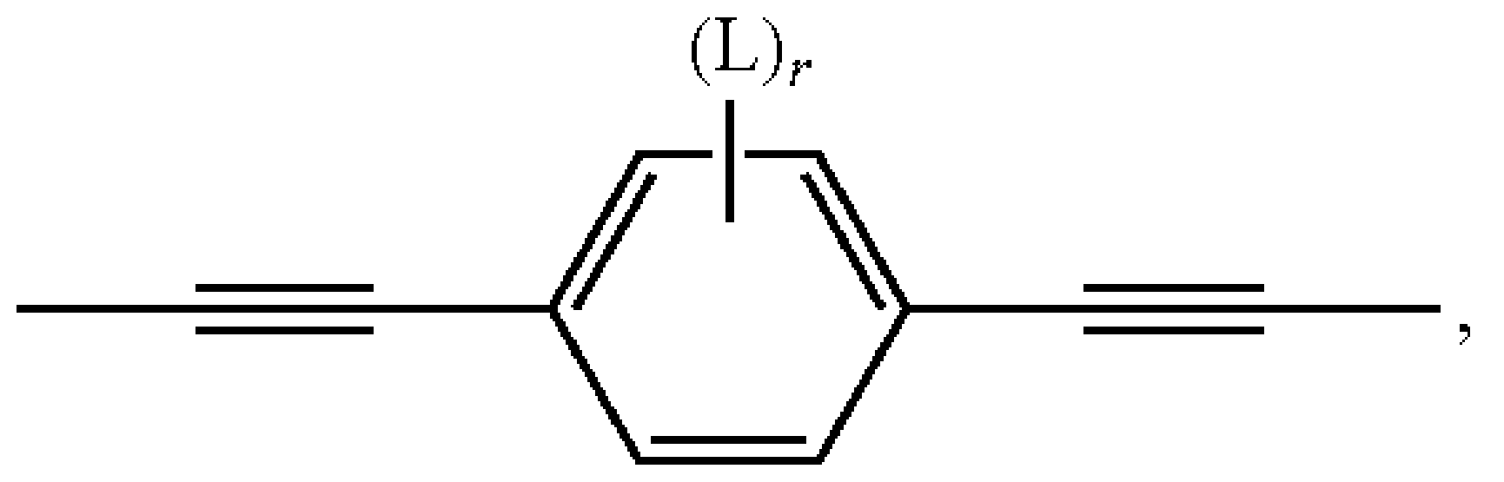

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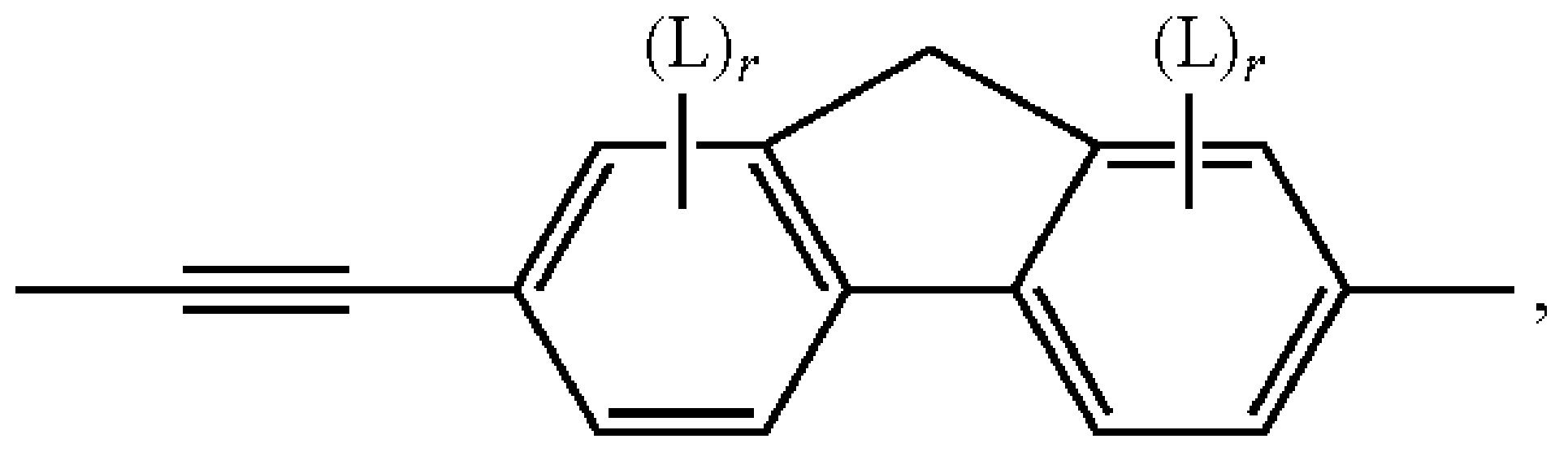

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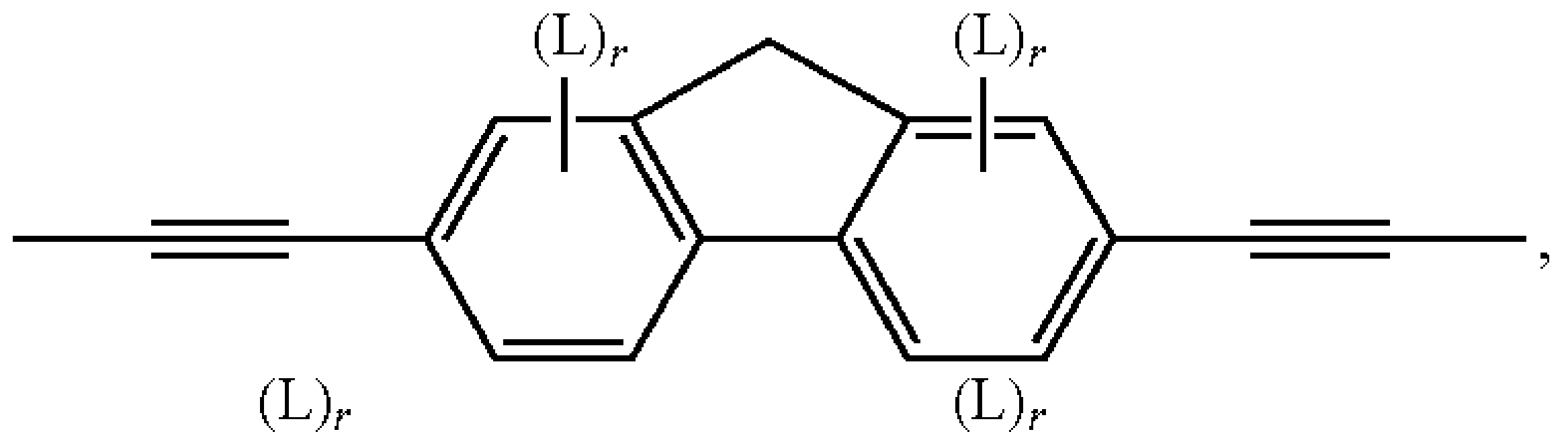

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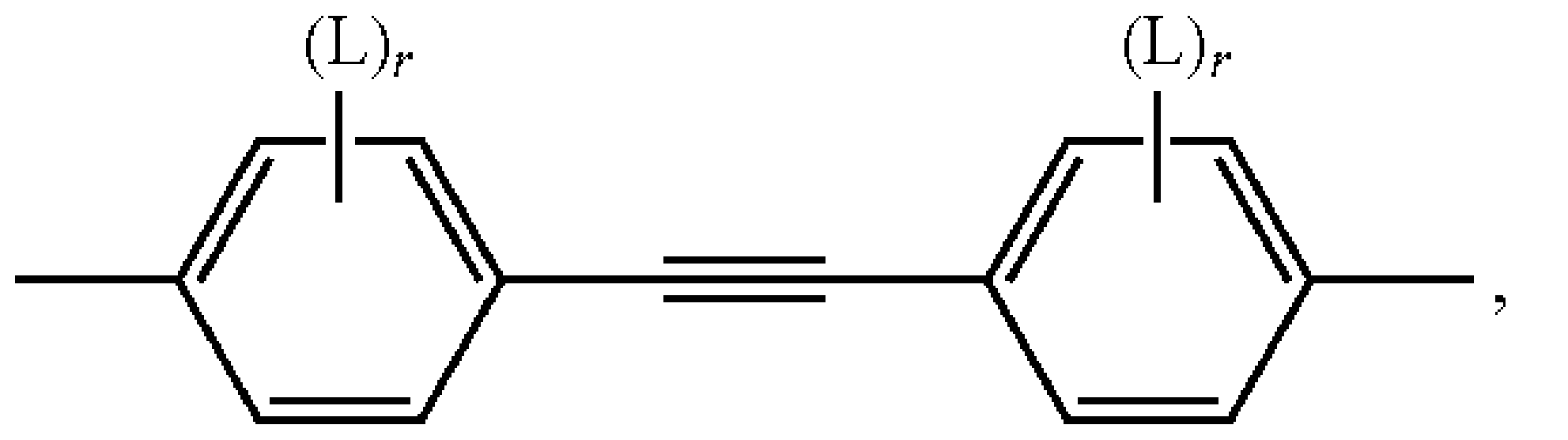

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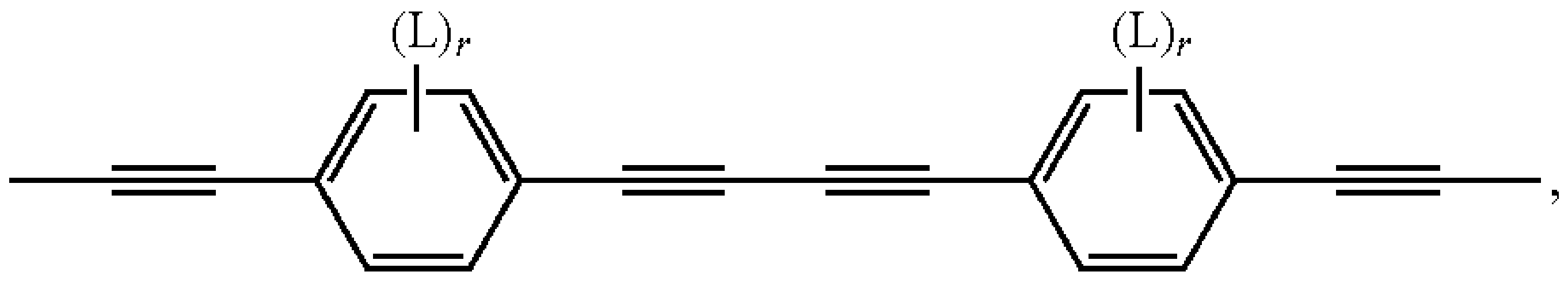

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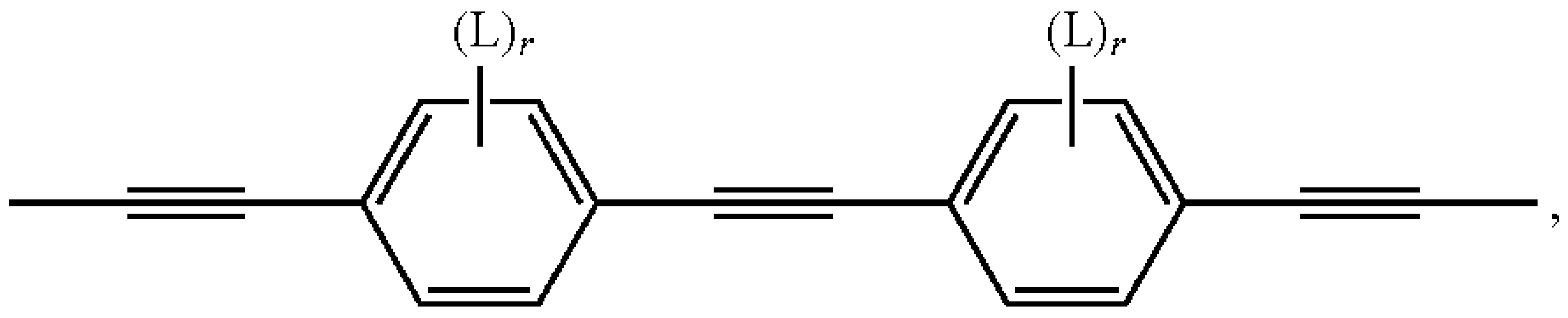

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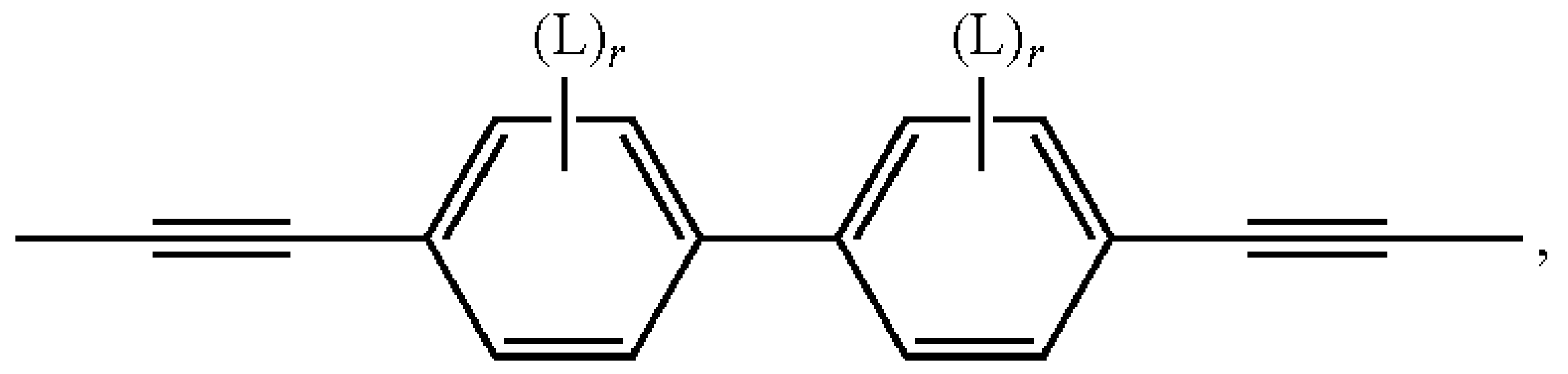

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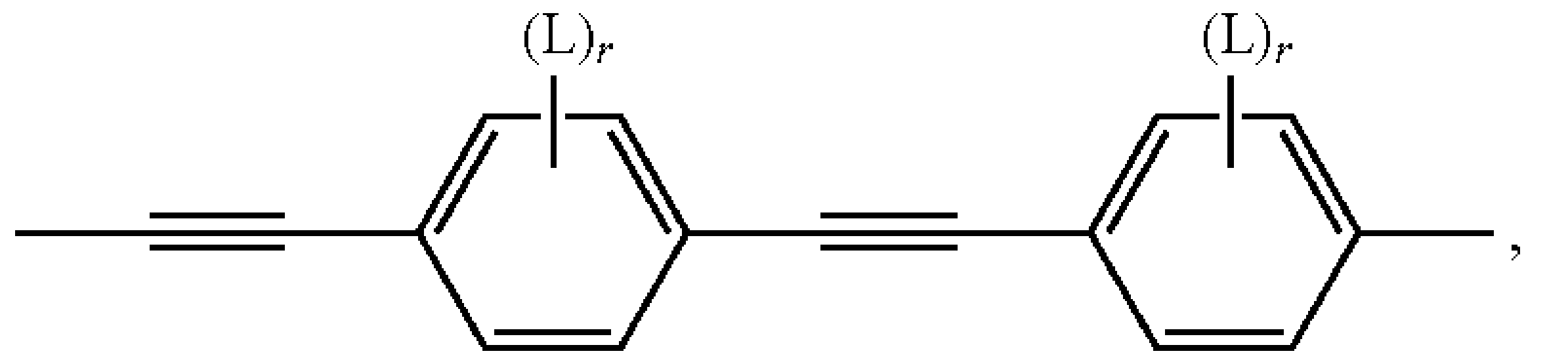

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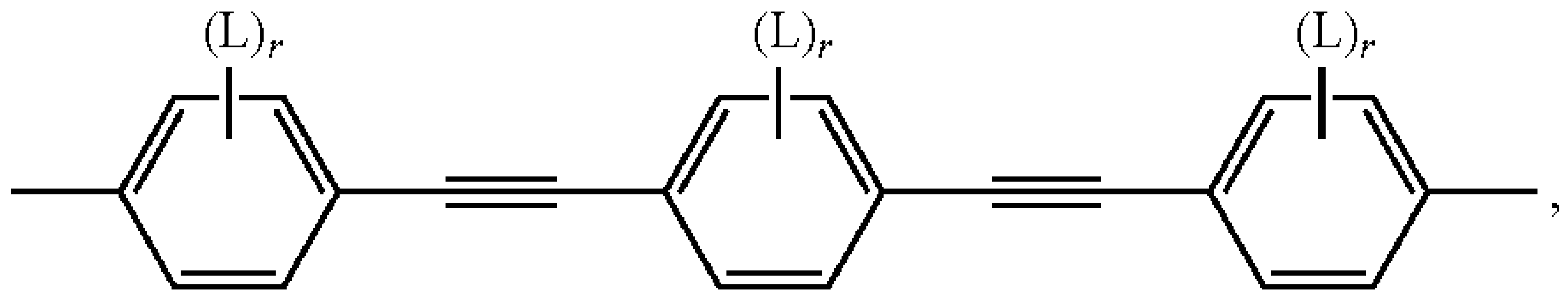

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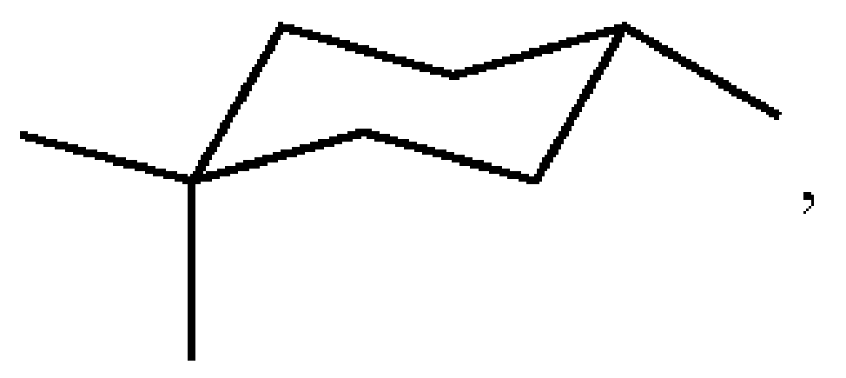
wherein r is 0, 1, 2, 3 or 4 and L is P Sp-, F, Cl, Br, I, —CN, $-NO_2$, —NCO, —NCS, —OCN, —SCN, $-C({=}O)NR^0R^{00}$, $-C({=}O)X$, $-C({=}O)OR^0$, $-C({=}O)R^0$, $-NR^0R^{00}$, —OH, $-SF_5$, optionally substituted silyl, aryl with 1 to 12 C atoms, or straight chain or branched alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy with 1 to 12 C atoms, wherein one or more H atoms are optionally replaced by F or Cl, wherein R^0 and R^{00} are independently H or alkyl with 1-12 C atoms and X is halogen.

8. The polymer film according to claim **1**, characterized in that the non-aromatic rings of the mesogenic groups where the bridging group is attached, or U^1 and U^2 in formula I, are selected from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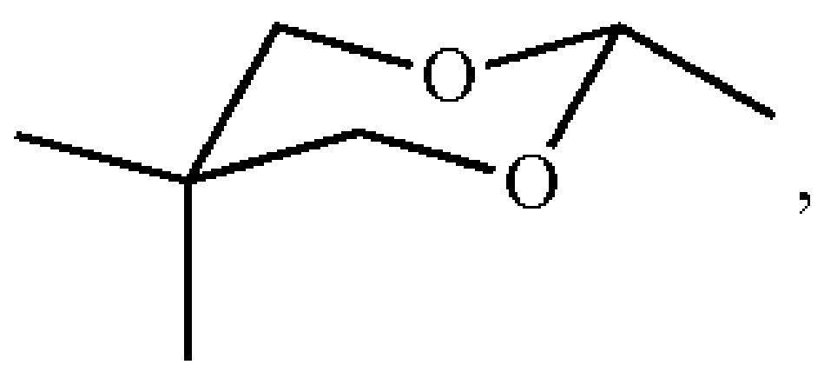

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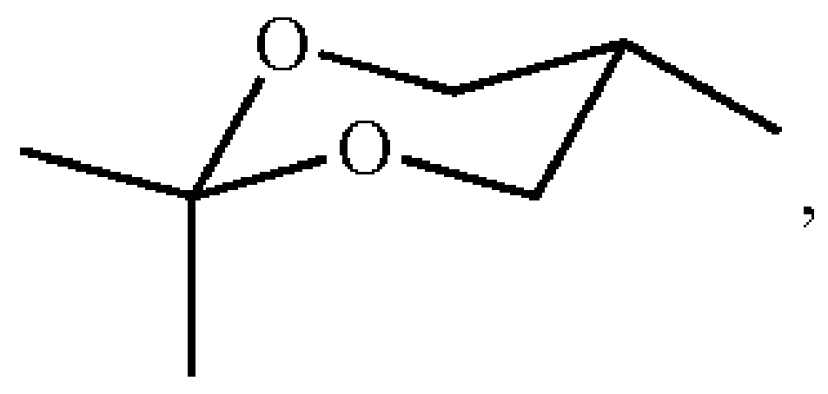

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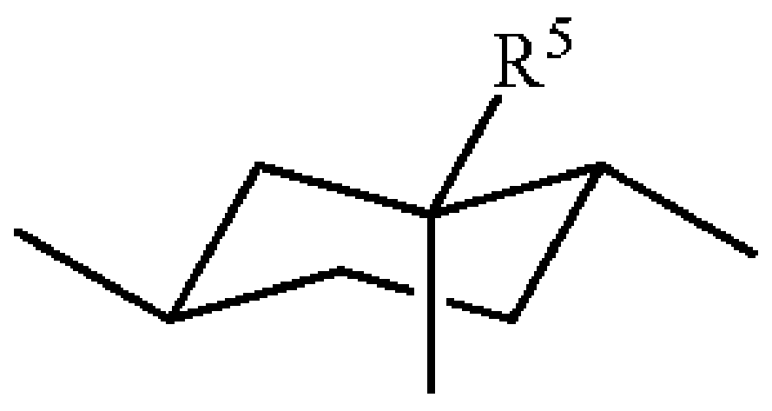

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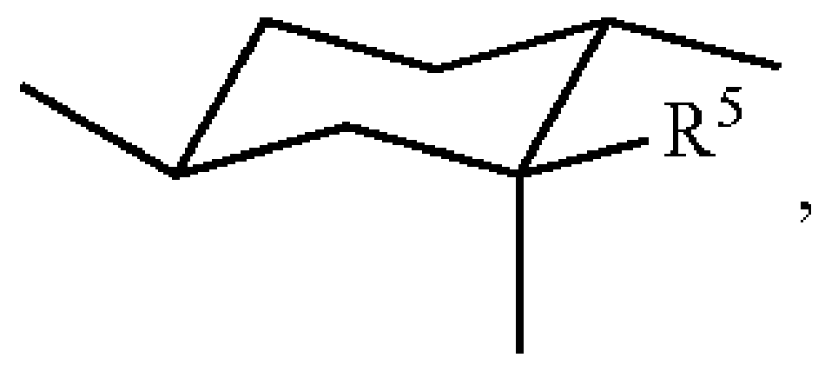

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wherein R^5 is H, halogen, —CN, —NC, —NCO, —NCS, —OCN, —SCN, $-C({=}O)NR^0R^{00}$, $-C({=}O)X^0$, $-C({=}O)R^0$, $-NH_2$, $-NR^0R^{00}$, —SH, $-SR^0$, $-SO_3H$, $-SO_2R^0$, —OH, $-NO_2$, $-CF_3$, $-SF_5$, P-Sp-, optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 40 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, or denote P or P-Sp-, or are substituted by P or P-Sp-, wherein the compounds comprise at least one group R^{1-5} denoting or being substituted by P or P-Sp-,

P is a polymerizable group, and

Sp is a spacer group or a single bond.

9. The polymer film according to claim **1**, wherein the aromatic and non-aromatic groups, are trans-1,4-cyclohexylene and 1,4-phenylene that is optionally substituted with one or more groups L, and L is P-Sp-, F, Cl, Br, I, —CN, —NO_2, —NCO, —NCS, —OCN, —SCN, —C(═O)NR^0R^{00}, —C(═O)X, —C(═O)OR^0, —C(═O)R^0, —NR^0R^{00}, —OH, —SF_5, optionally substituted silyl, aryl with 1 to 12 C atoms, or straight chain or branched alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy with 1 to 12 C atoms, wherein one or more H atoms are optionally replaced by F or Cl, wherein R^0 and R^{00} are independently H or alkyl with 1-12 C atoms and X is halogen.

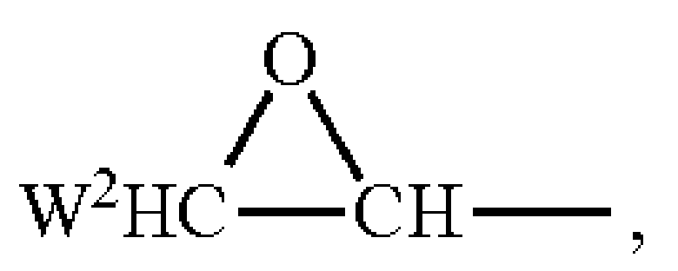
10. The polymer film according to claim **1**, wherein the mesogenic groups do not comprise more than one unsaturated or aromatic ring.

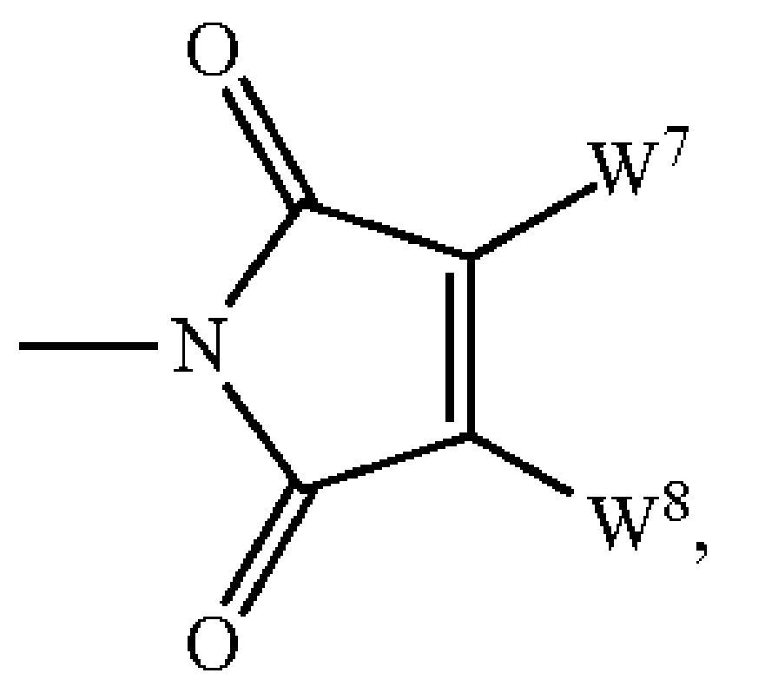
11. The polymer film according to claim **1**, wherein **[**linkage**]** *bridging* groups connecting the aromatic and non-aromatic cyclic groups in the mesogenic groups, are —O—, —S—, —CO—, —COO—, —OCO—, —O—COO—, —CO—NR^0—, —NR^0—CO—, —NR^0—CO—NR^0—, —OCH_2—, —CH_2O—, —SCH_2—, —CH_2S—, —CF_2O—, —OCF_2—, —CF_2S—, —SCF_2—, —CH_2CH_2—, —$(CH_2)_3$—, —$(CH_2)_4$—, —CF_2CH_2—, —CH_2CF_2—, —CF_2CF_2—, —CH═CH—, —CY^1═CY^2—, —CH═N—, —N═CH—, —N═N—, —CH═CR^0—, —C≡C—, —CH═CH—COO—, —OCO—CH═CH—, CR^0R^{00} or a single bond, are

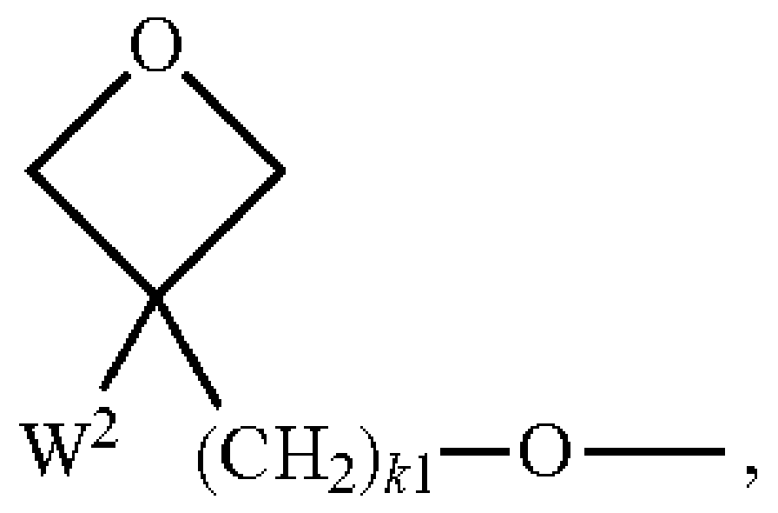
R^0, R^{00} are independently of each other H or alkyl with 1 to 12 C-atoms, and

Y^1 and Y^2 are $Y^{1,2}$ are independently of each other H, F, Cl, CN or R^0.

12. The polymer film according to claim **1**, wherein the polymerizable group, is CH_2═CW^1—COO—, CH_2═CW^1—CO—,







CH_2═CW^2—$(O)_{k1}$—, CH_3—CH═CH—O—, (CH_2═CH$)_2$CH—OCO—, (CH_2═CH—$CH_2)_2$CH—OCO—, (CH_2═CH$)_2$CH—O—, (CH_2═CH—$CH_2)_2$N—, (CH_2═CH—$CH_2)_2$N—CO—, HO—CW^2W^3—, HS—CW^2W^3—, HW^2N—, HO—CW^2W^3—NH—, CH_2═CW^1—CO—NH—, CH_2═CH—$(COO)_{k1}$-Phe-$(O)_{k2}$—, CH_2═CH—$(CO)_{k1}$-Phe-$(O)_{k2}$—, Phe-CH═CH—, HOOC—, OCN—, **[**and**]** *or* $W^4W^5W^6$Si—, with W^1 being H, F, Cl, CN, CF_3, phenyl or alkyl with 1 to 5 C-atoms, W^2 and W^3 being independently of each other H or alkyl with 1 to 5 C-atoms, W^4, W^5 and W^6 being independently of each other Cl, oxaalkyl or oxacarbonylalkyl with 1 to 5 C-atoms, W^7 and W^8 being independently of each other H, Cl or alkyl with 1 to 5 C-atoms, Phe being 1,4-phenylene that is optionally substituted, and k_1 and k_2 being independently of each other 0 or 1.

13. The polymer film according to claim **1**, wherein the spacer group is Sp'-X', such that P-Sp- is P-Sp'-X'—, wherein

Sp' is alkylene with 1 to 20 C atoms, preferably 1 to 12 C-atoms, which is optionally mono- or polysubstituted by F, Cl, Br, I or CN, and wherein one or more non-adjacent CH_2 groups are optionally replaced, in each case independently from one another, by —O—, —S—, —NH—, —NR^0—, —SiR^0R^{00}—, —CO—, —COO—, —OCO—, —OCO—O—, —S—CO—, —CO—S—, —NR^0—CO—O—, —O—CO—NR^0—, —NR^0—CO—NR^0—, —CH═CH—or —C≡C—in such a manner that O and/or S atoms are not linked directly to one another,

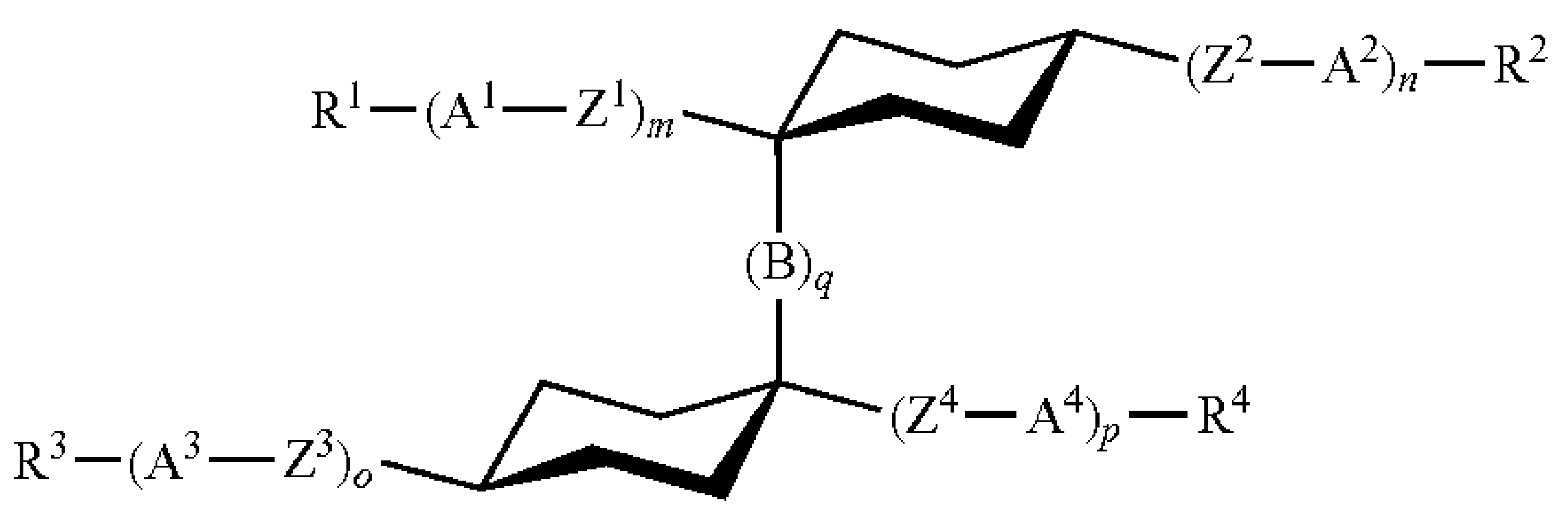
X' is —O—, —S—, —CO—, —COO—, —OCO—, —O—COO—, —CO—NR^0—, —NR^0—CO—, —NR^0—CO—NR^0—, —OCH_2—, —CH_2O—, —SCH_2—, —CH_2S—, —CF_2O—, —OCF_2—, —CF_2S—, —SCF_2—, —CF_2CH_2—, —CH_2CF_2—, —CF_2CF_2—, —CH═N—, —N═CH—, —N═N—, —CH═CR^0—, —CY^1═CY^2—, —C≡C—, —CH═CH—COO—, —OCO—CH═CH—or a single bond,

R^0, R^{00} are independently of each other H or alkyl with 1 to 12 C-atoms,

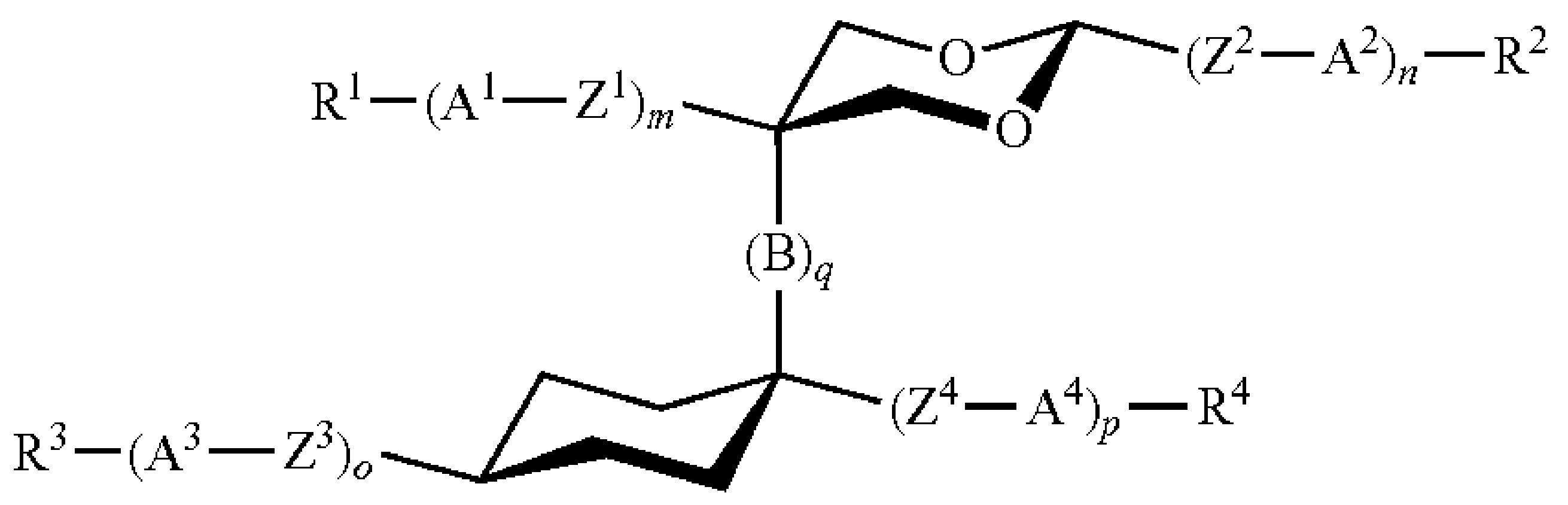
$Y^{1,2}$ are independently of each other H, F, Cl, CN or R^0.

14. The polymer film according to claim **1**, wherein the **[**polymerisable**]** *polymerizable* compounds are:

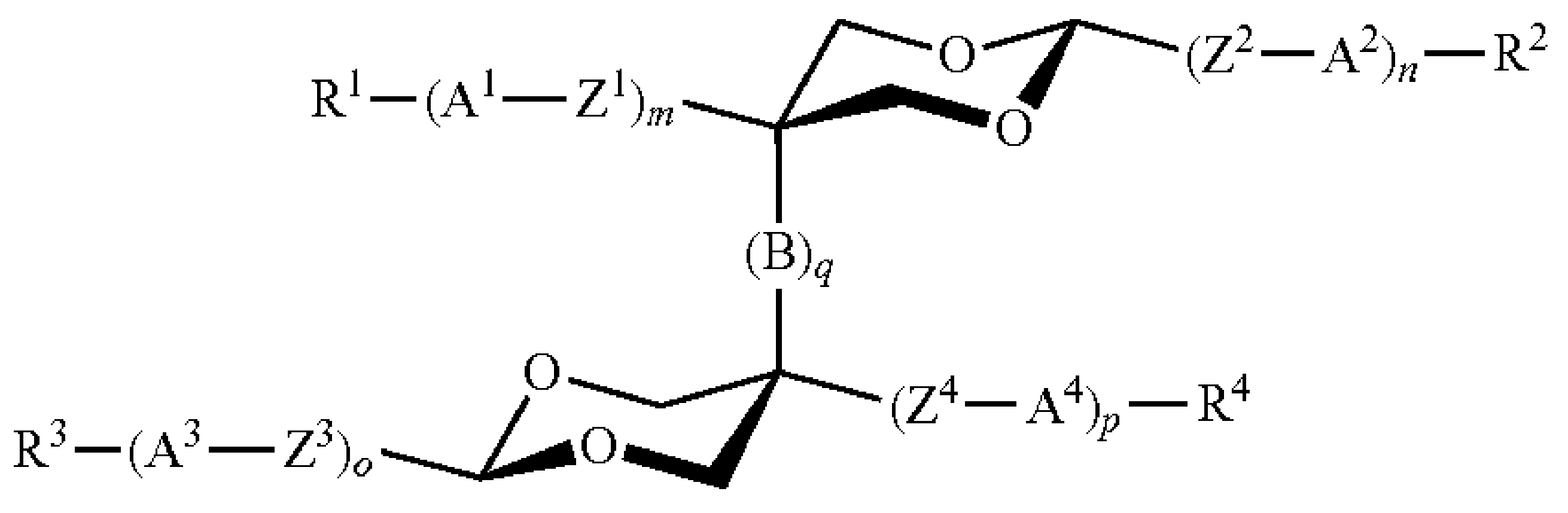
Ia



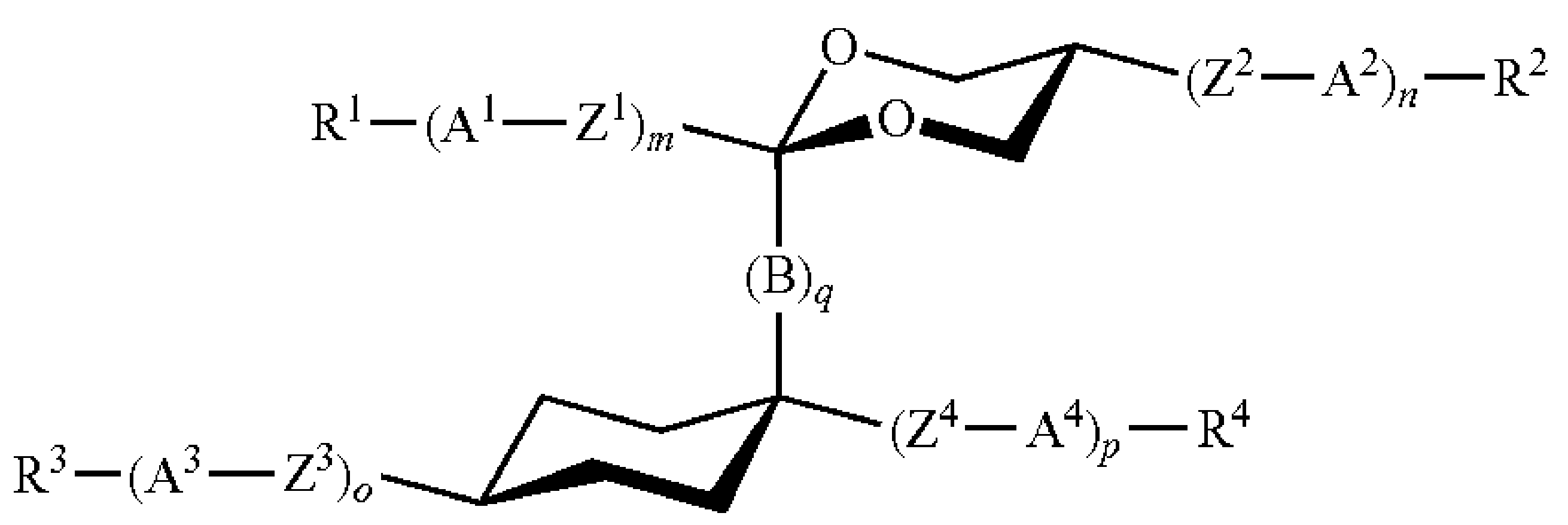
Ib



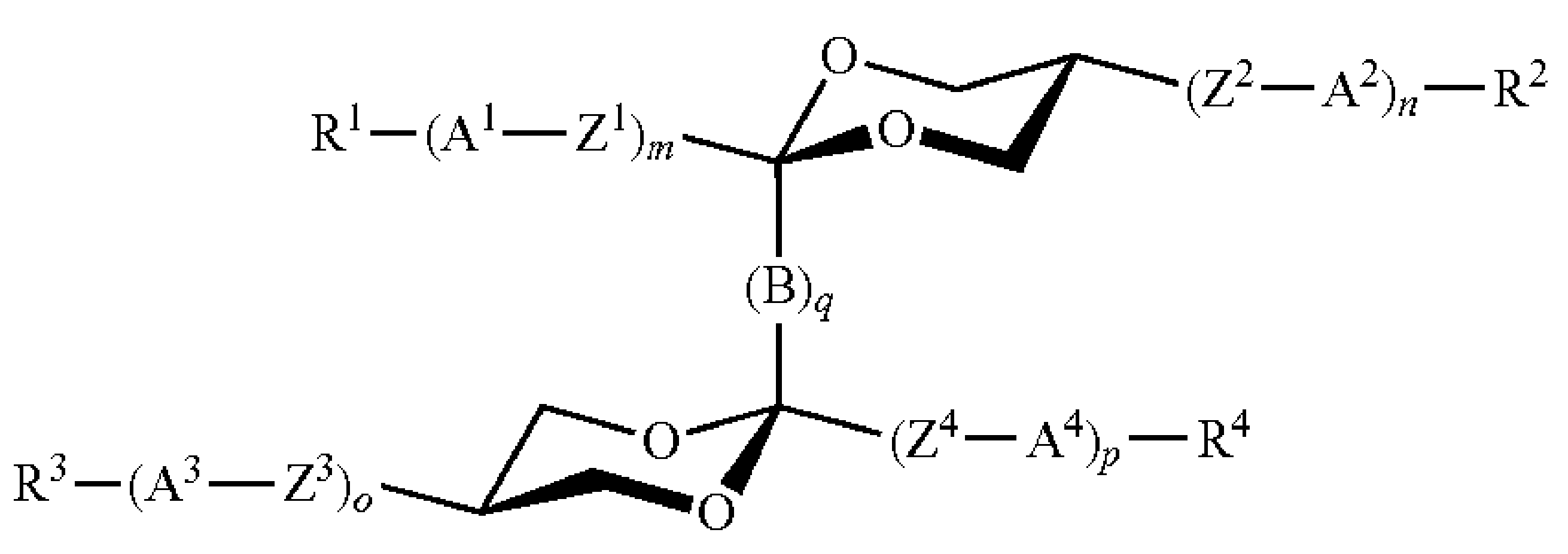
Ic



Id



Ie



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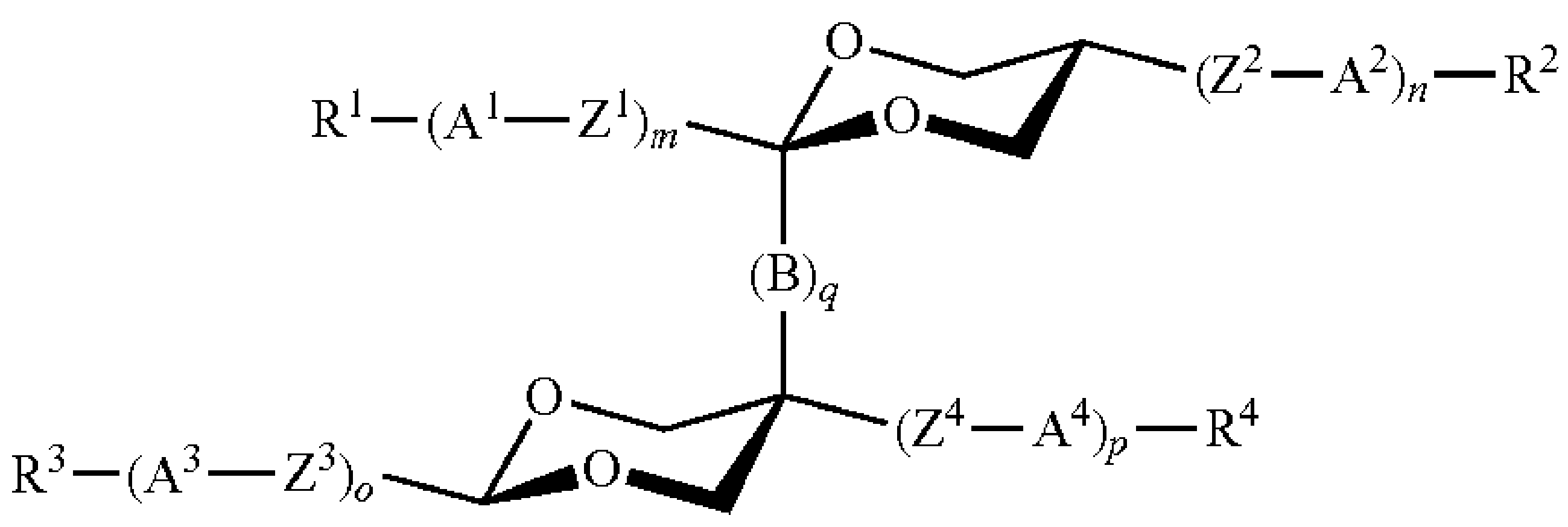
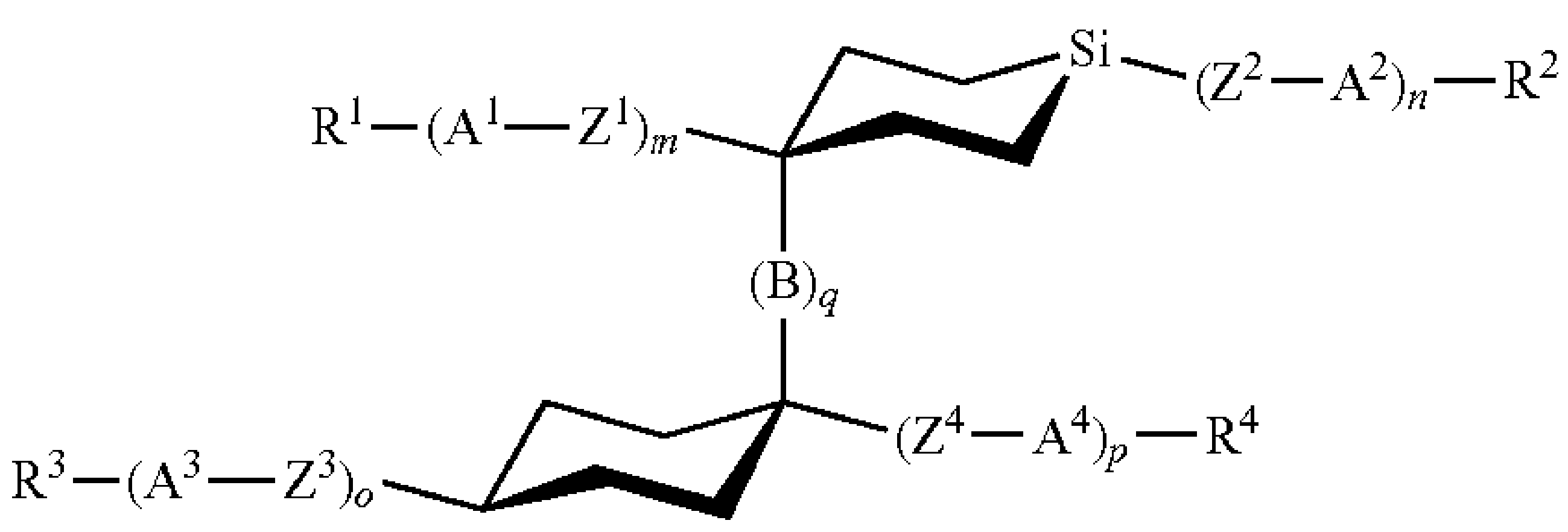
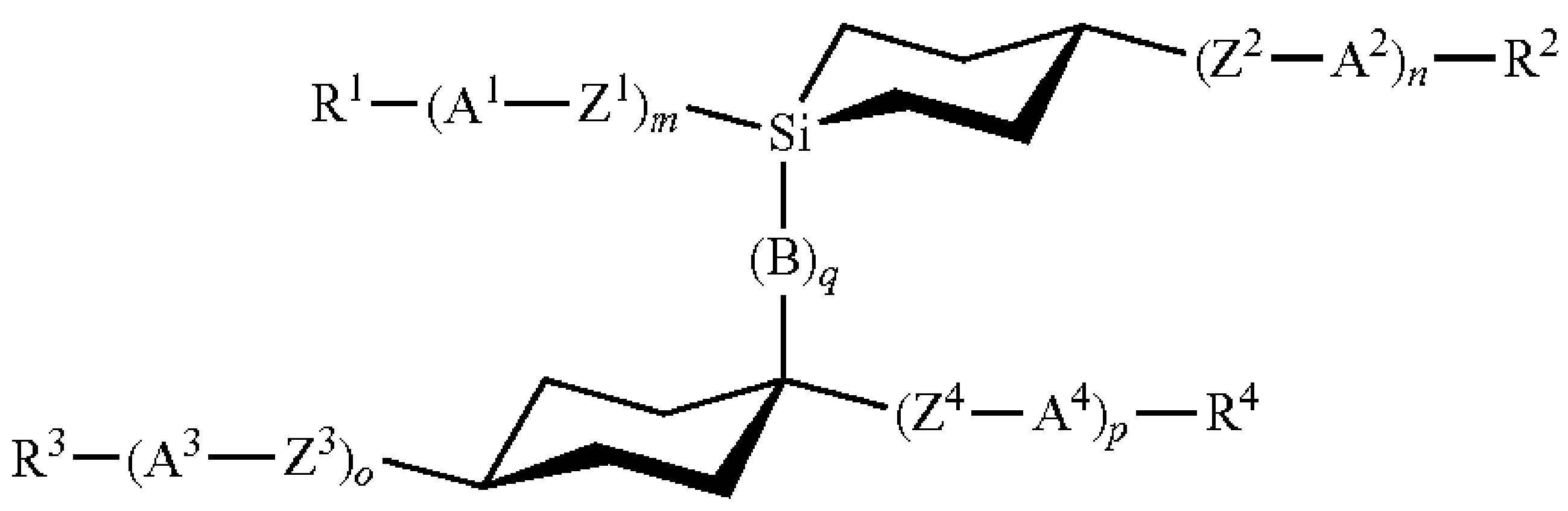


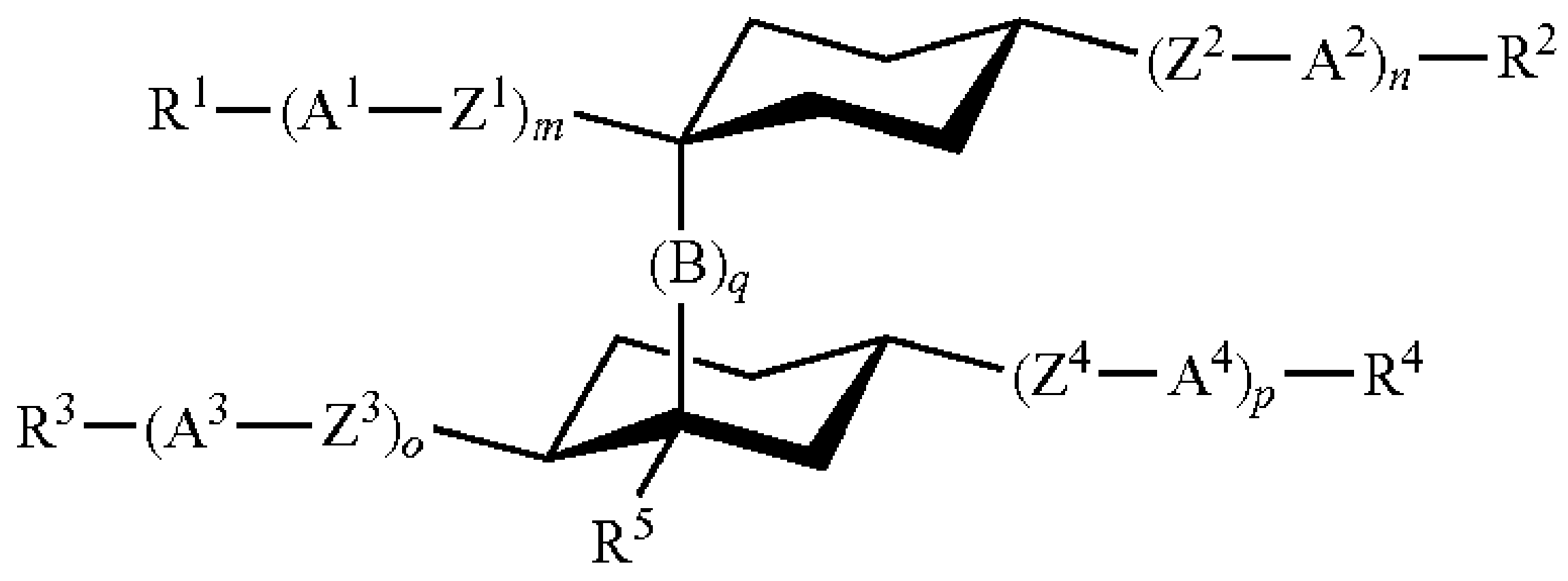
Ig



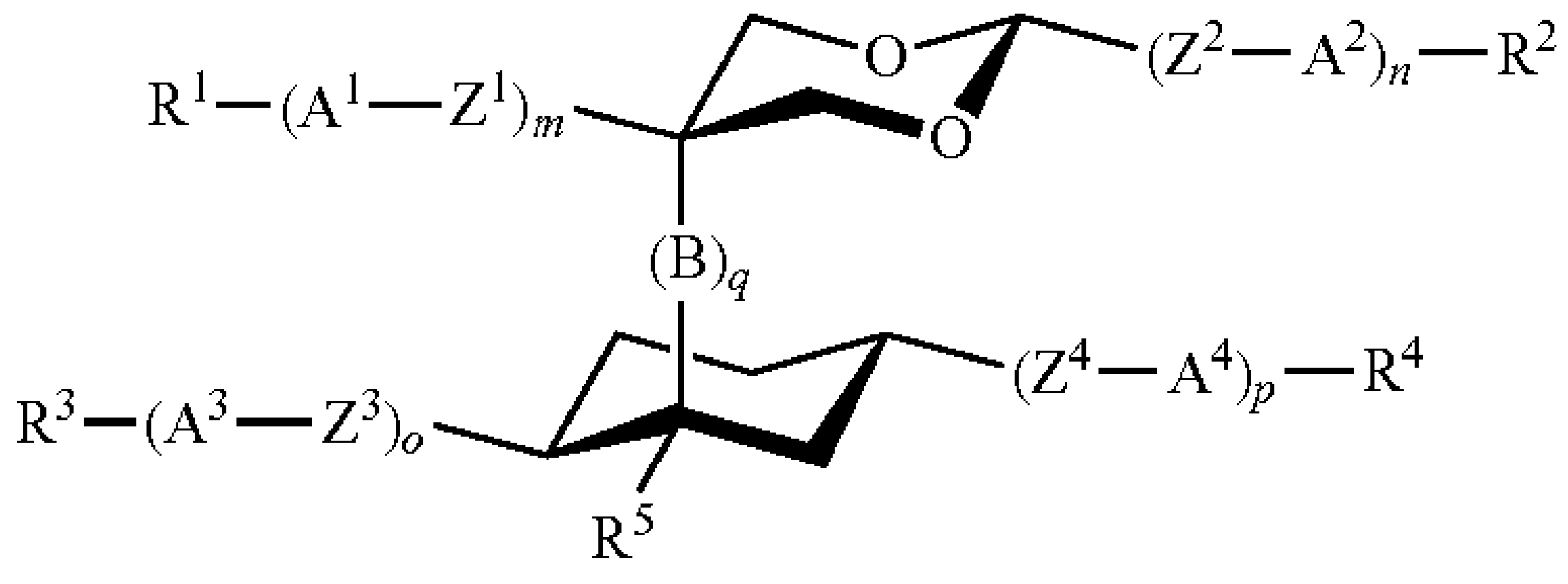
Ih



Ii



Ik



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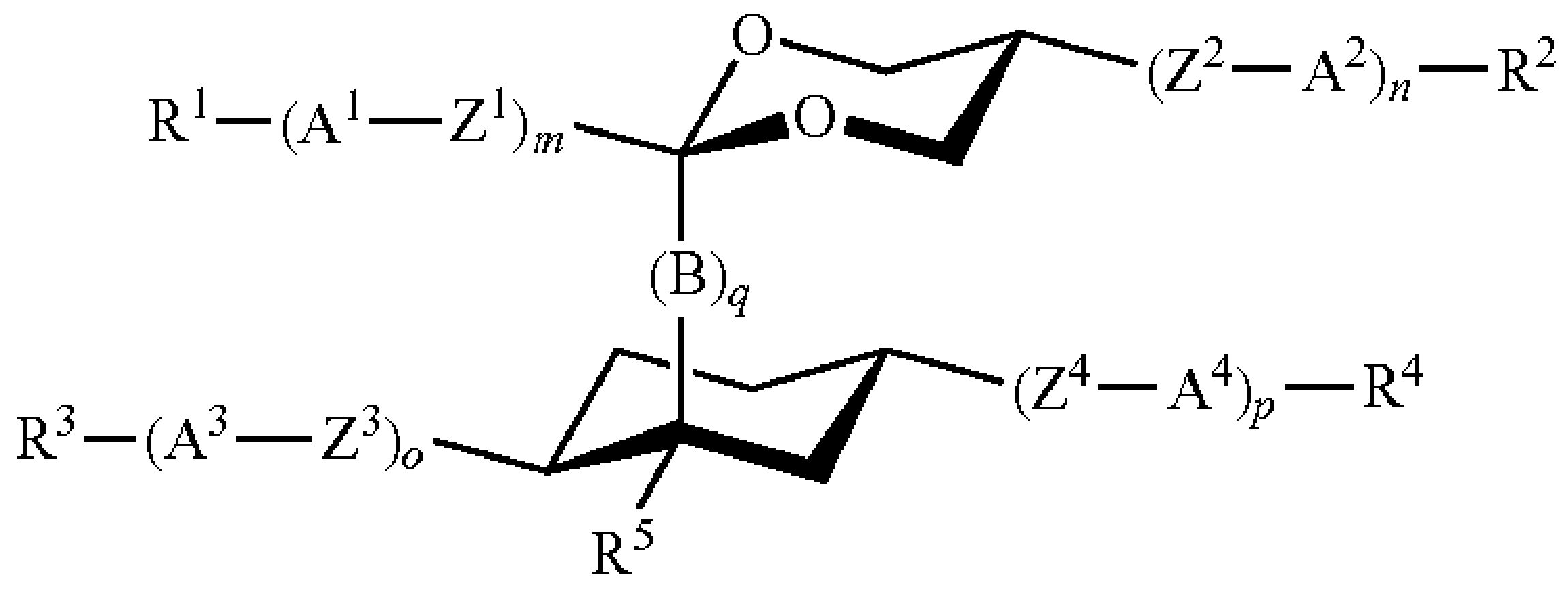

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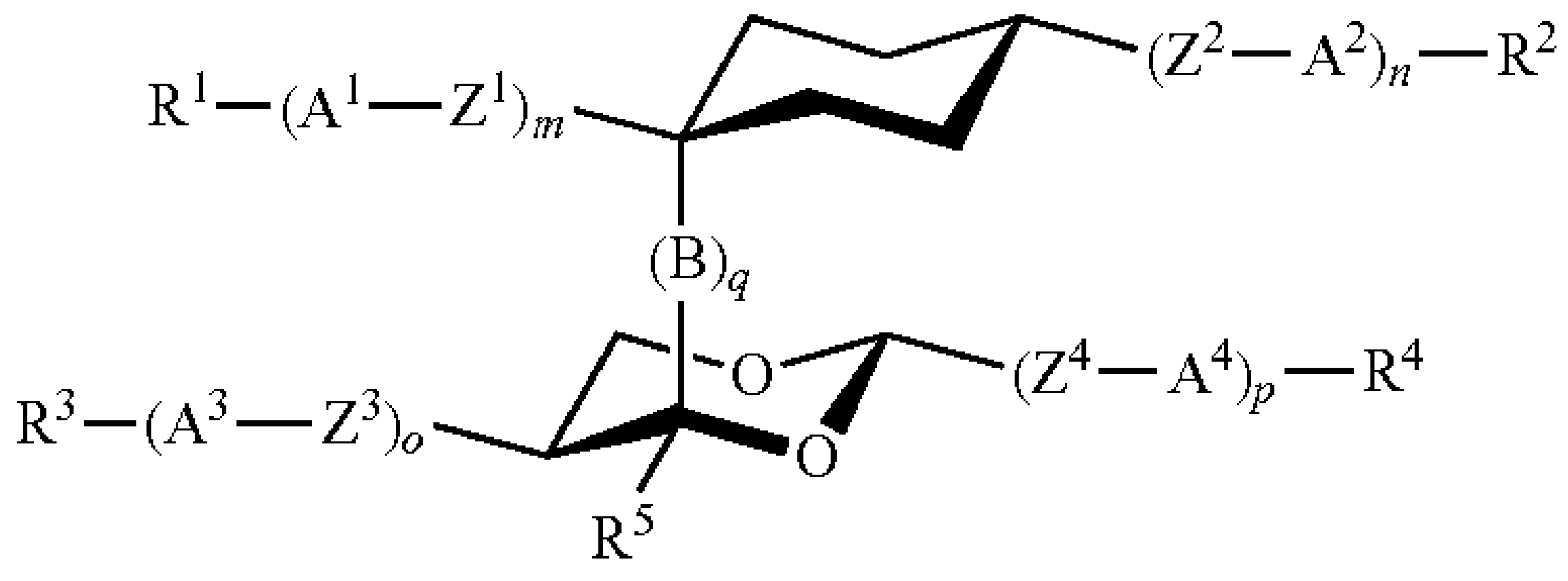

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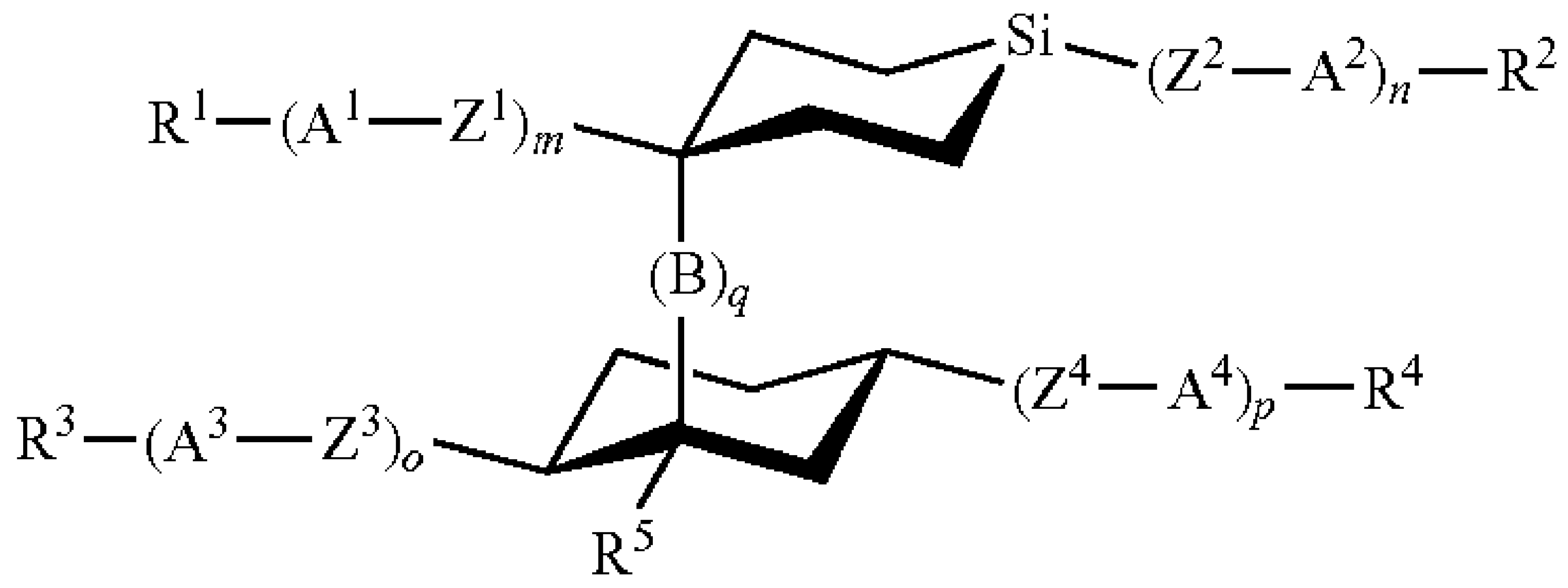

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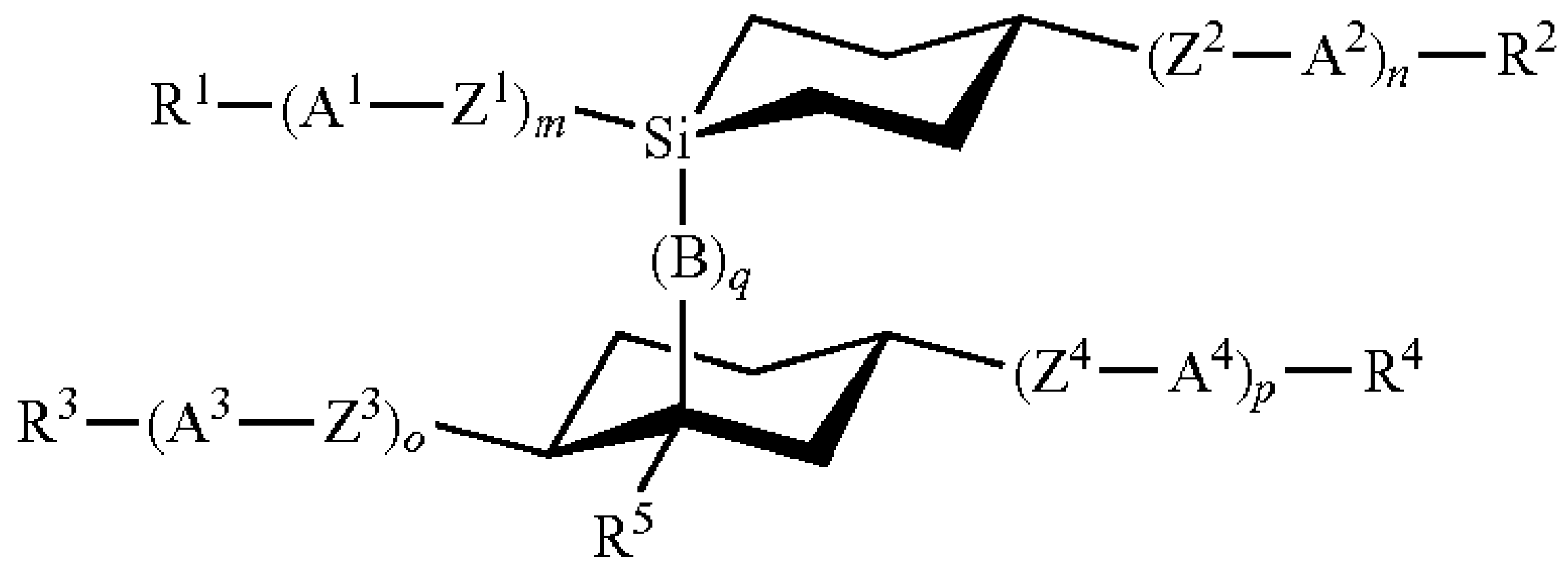
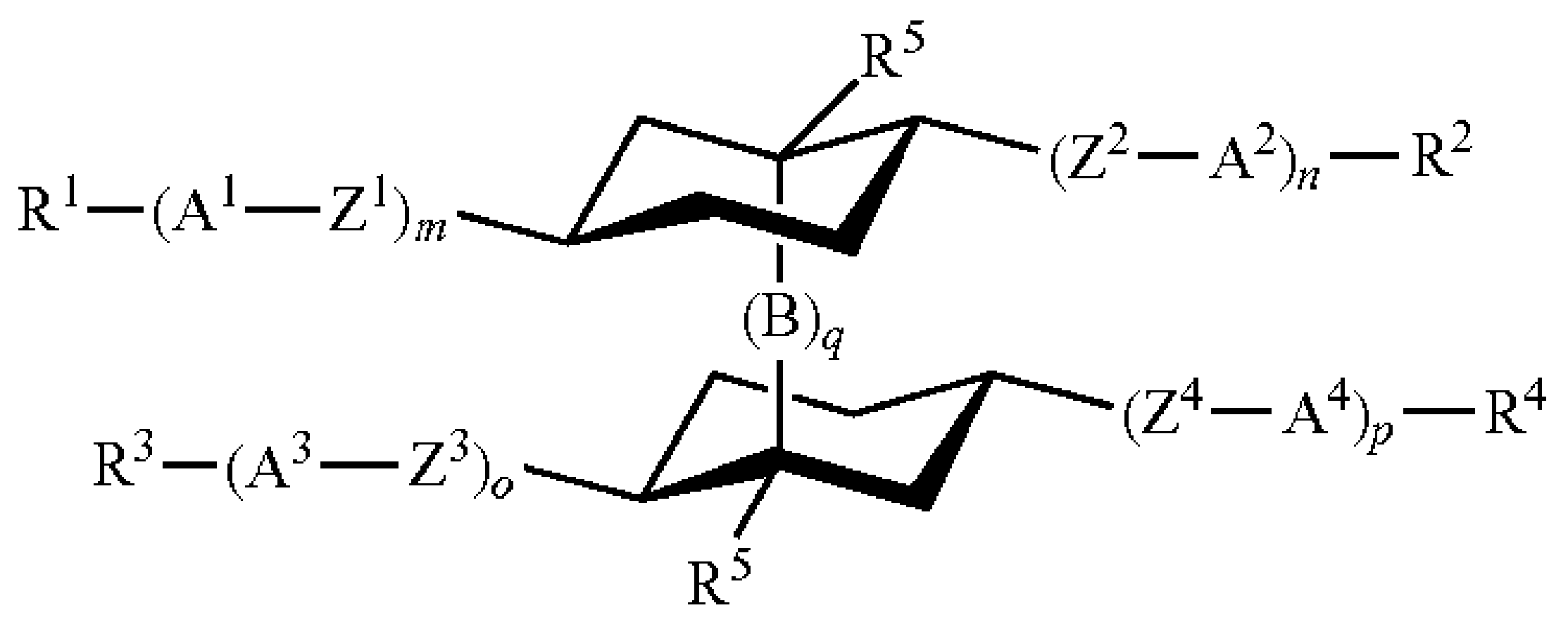
Ip



Iq



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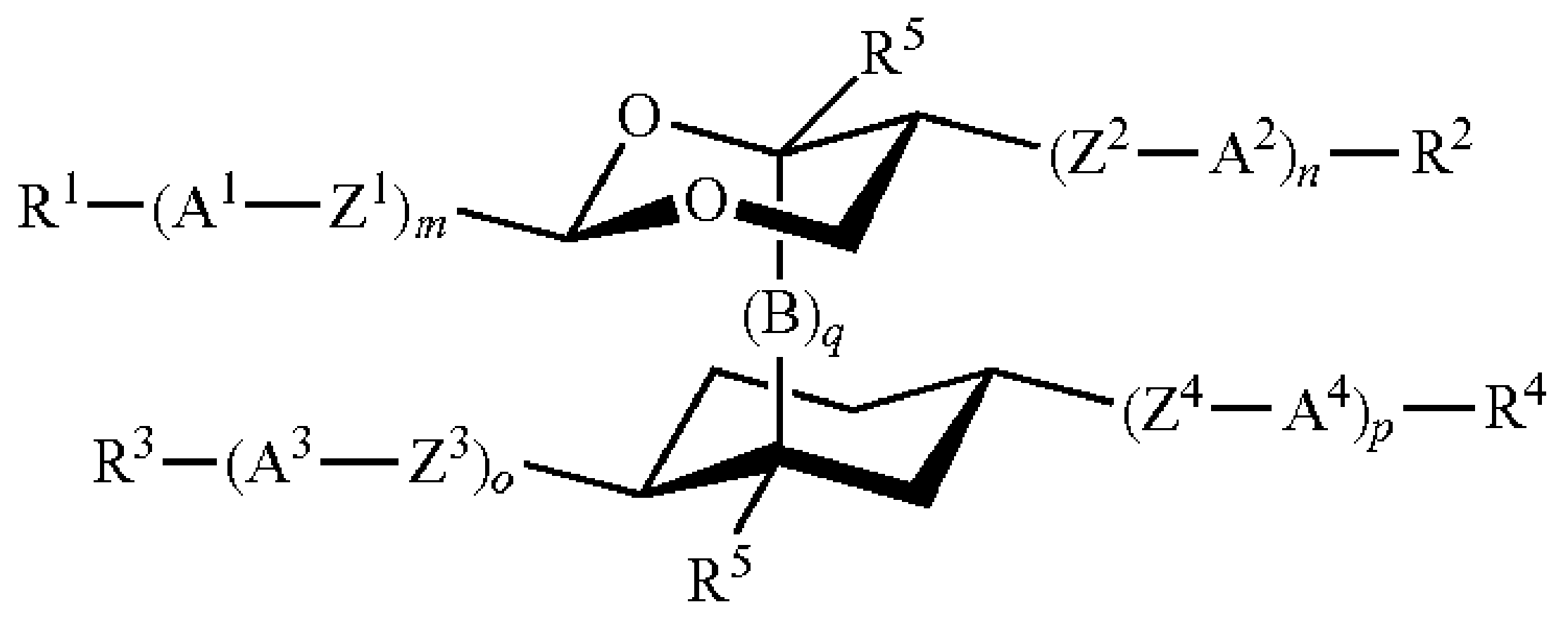

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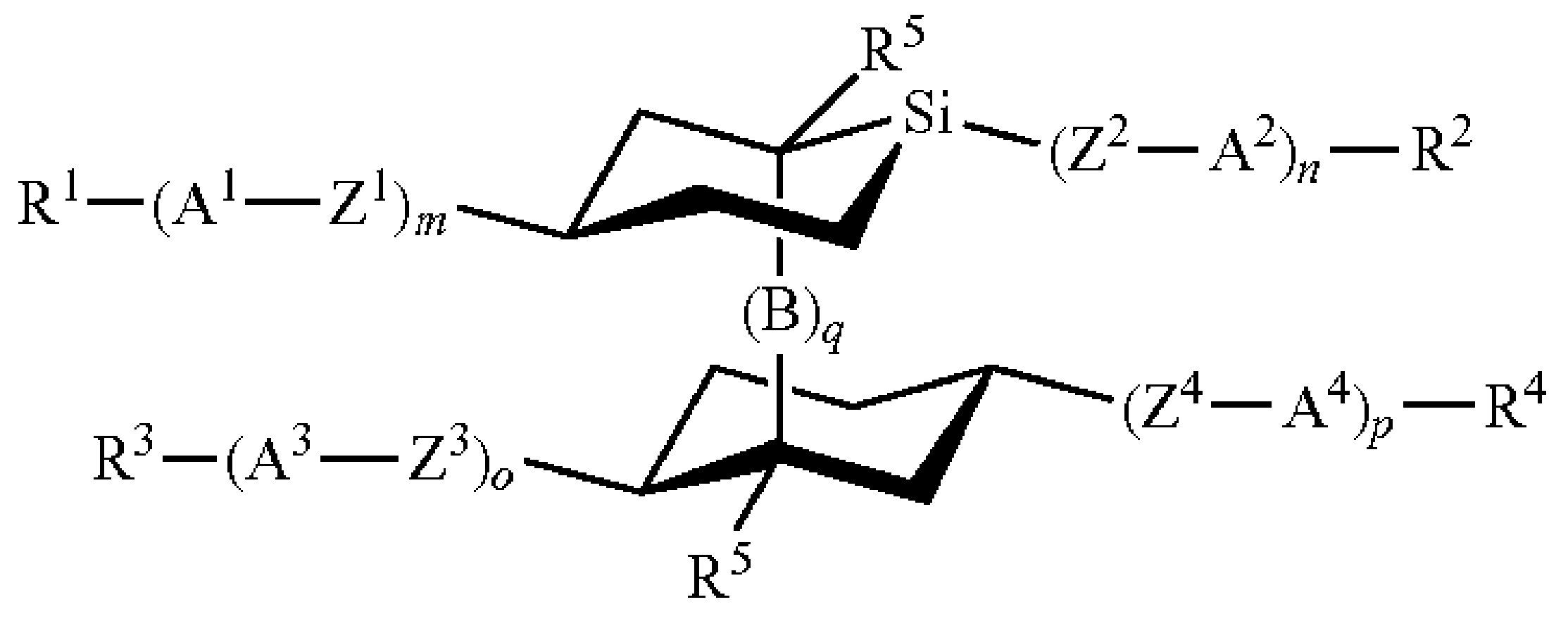

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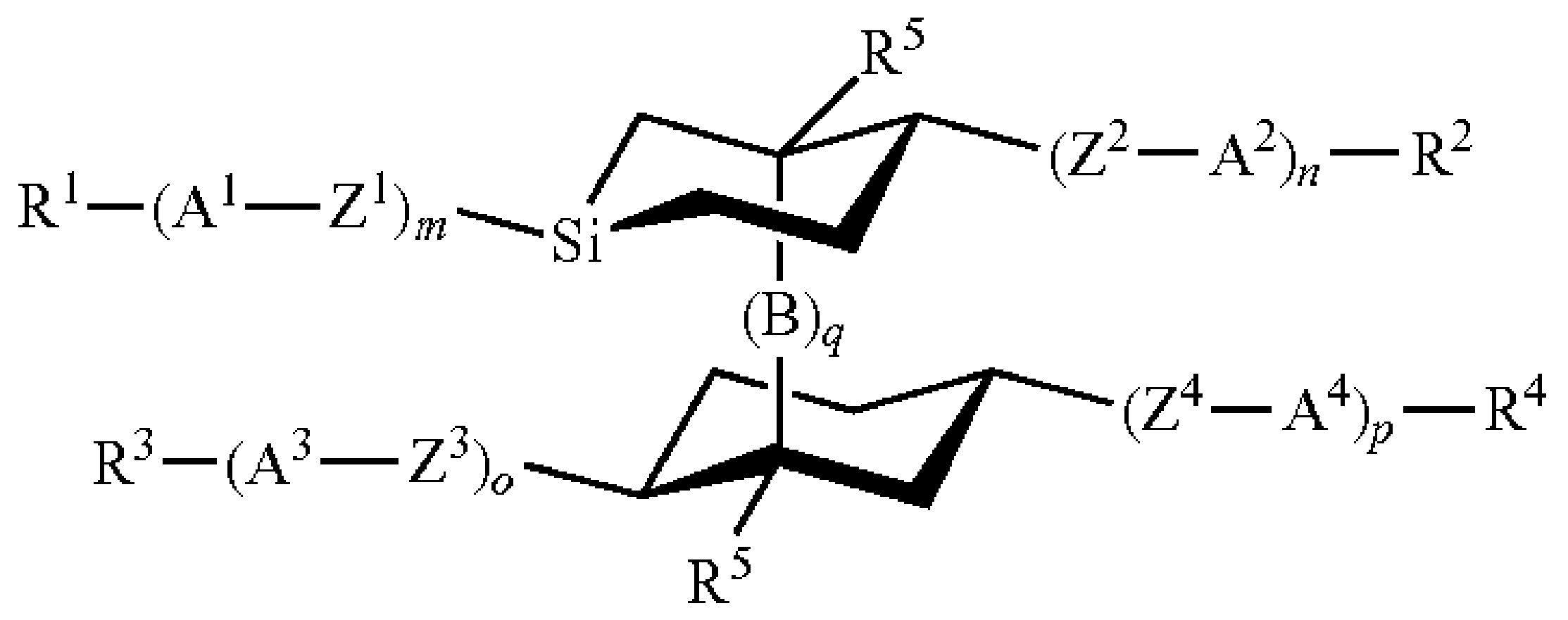
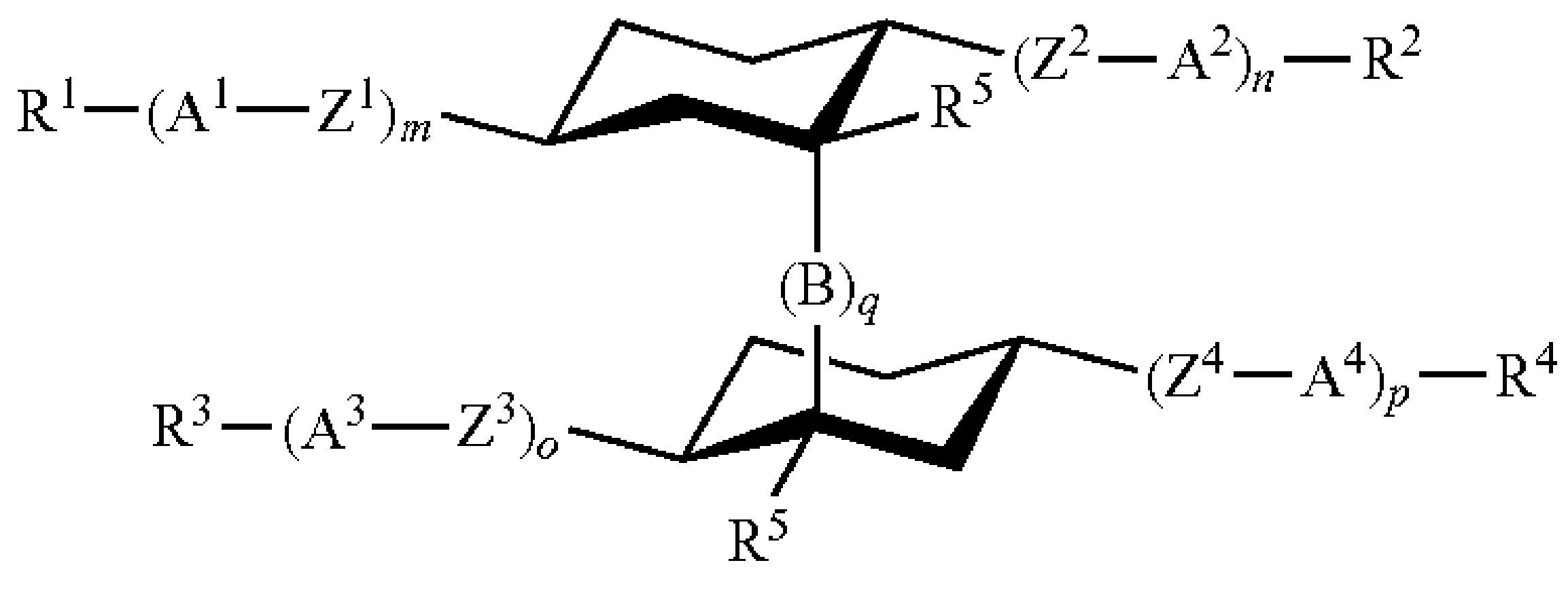
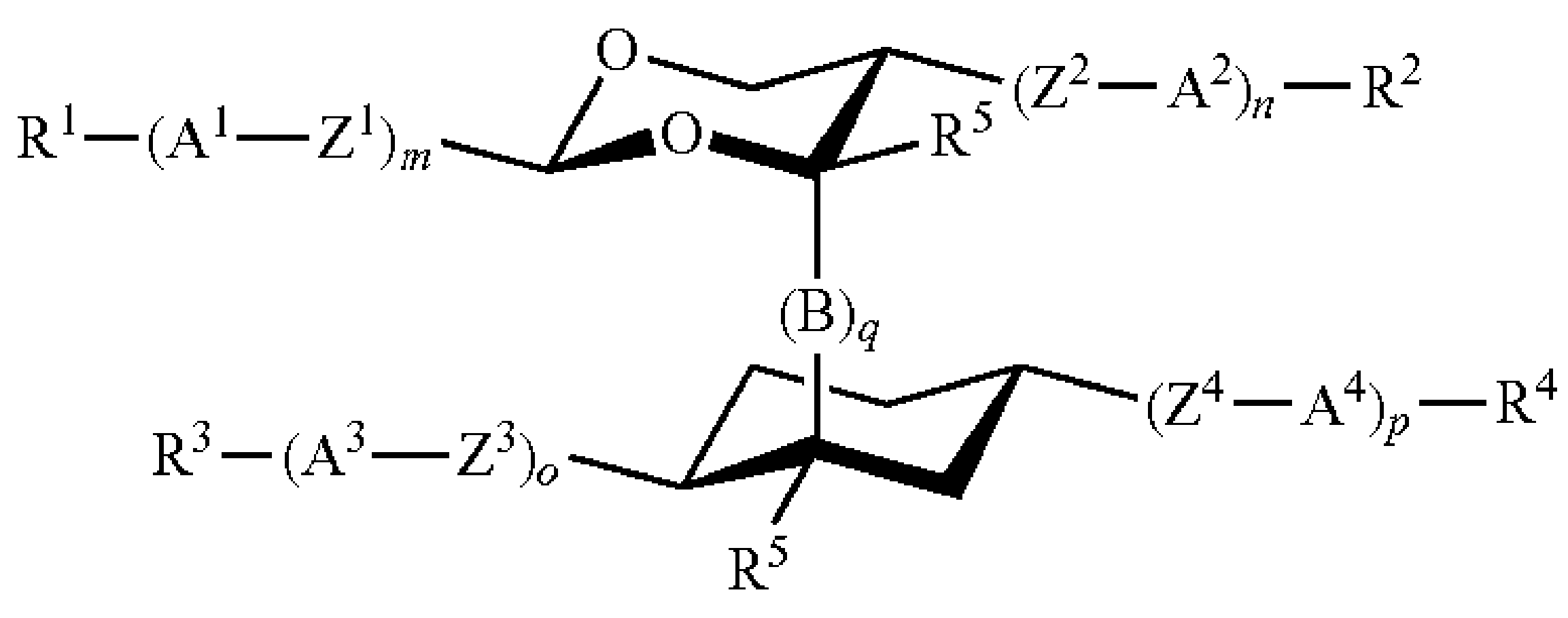


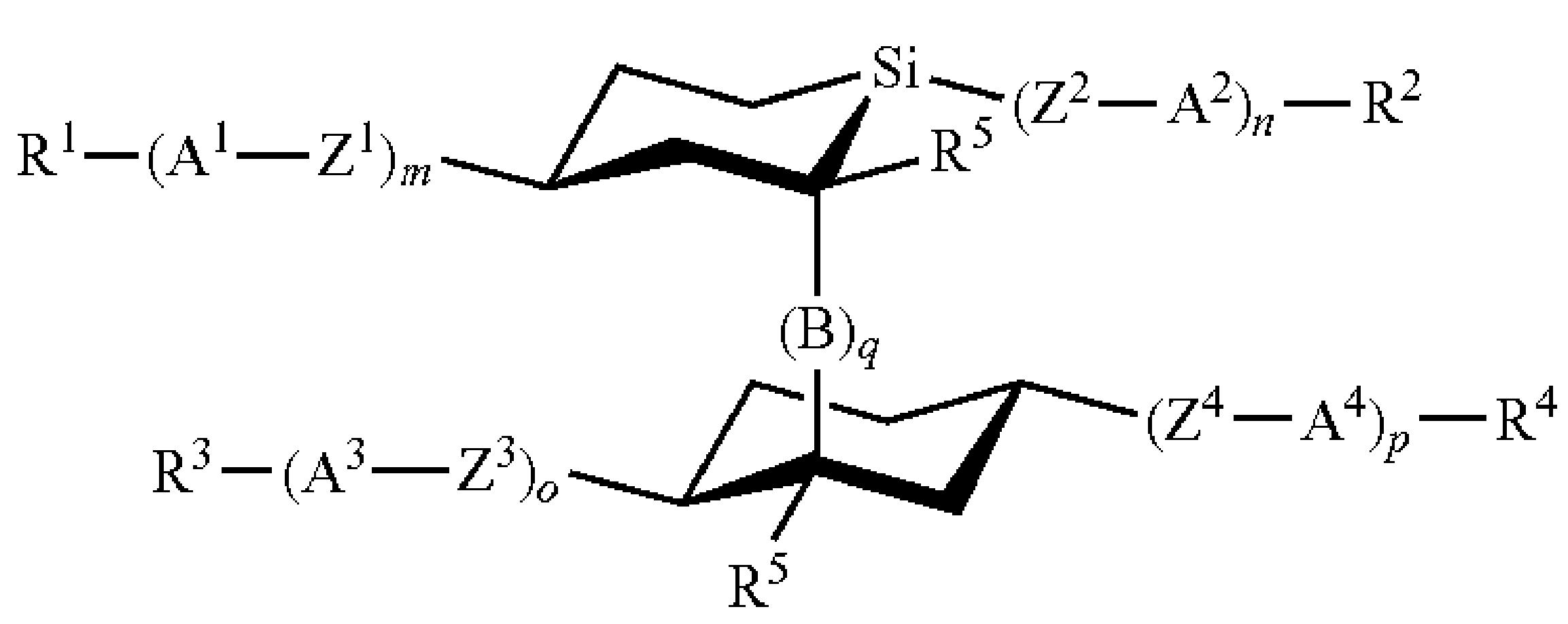
Iu



Iv



Iw



or

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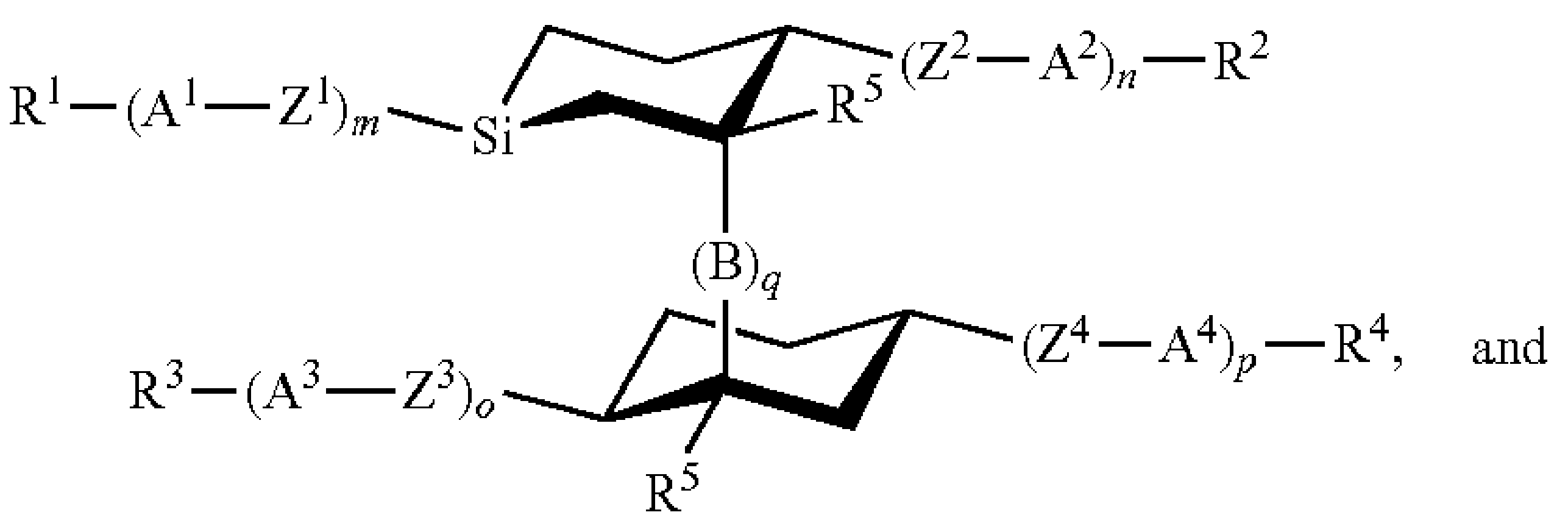
Ix



and

A^{1-4} are independently of each other non-aromatic carbocylic or heterocyclic groups and aromatic and heteroaromatic groups, which are optionally substituted by one or more groups R^5, and wherein each of $-(A^1Z^1)_m-U^1-(Z^2-A^2)_n-$ and $-(A^3Z^3)_o-U^2-(Z^4-A^4)_p-$ does not contain more aromatic groups than non-aromatic groups,

Z^{1-4} are independently of each other —O—, —S—, —CO—, —COO—, —OCO—, —O—COO—, —CO—NR^0—, —NR^0—CO—, —NR^0—CO—NR^0—, —OCH$_2$—, —CH$_2$O—, —SCH$_2$—, —CH$_2$S—, —CF$_2$O—, —OCF$_2$—, —CF$_2$S —, —SCF$_2$—, —CH$_2$CH$_2$—, —(CH$_2$)$_3$—, —(CH$_2$)$_4$—, —CF$_2$CH$_2$—, —CH$_2$CF$_2$—, —CF$_2$CF$_2$—, —CH═CH—, —CY^1═CY^2—, —CH═N—, —N═CH—, —N═N—, —CH═CR^0—, —C≡C—, —CH═CH—COO—, —OCO—CH═CH—, CR^{0}R^{00} or a single bond,

R^0, R^{00} are independently of each other H or alkyl with 1 to 12 C-atoms,

m and n are independently of each other 0, 1, 2, 3 or 4,

o and p are independently of each other 0, 1, 2, 3 or 4,

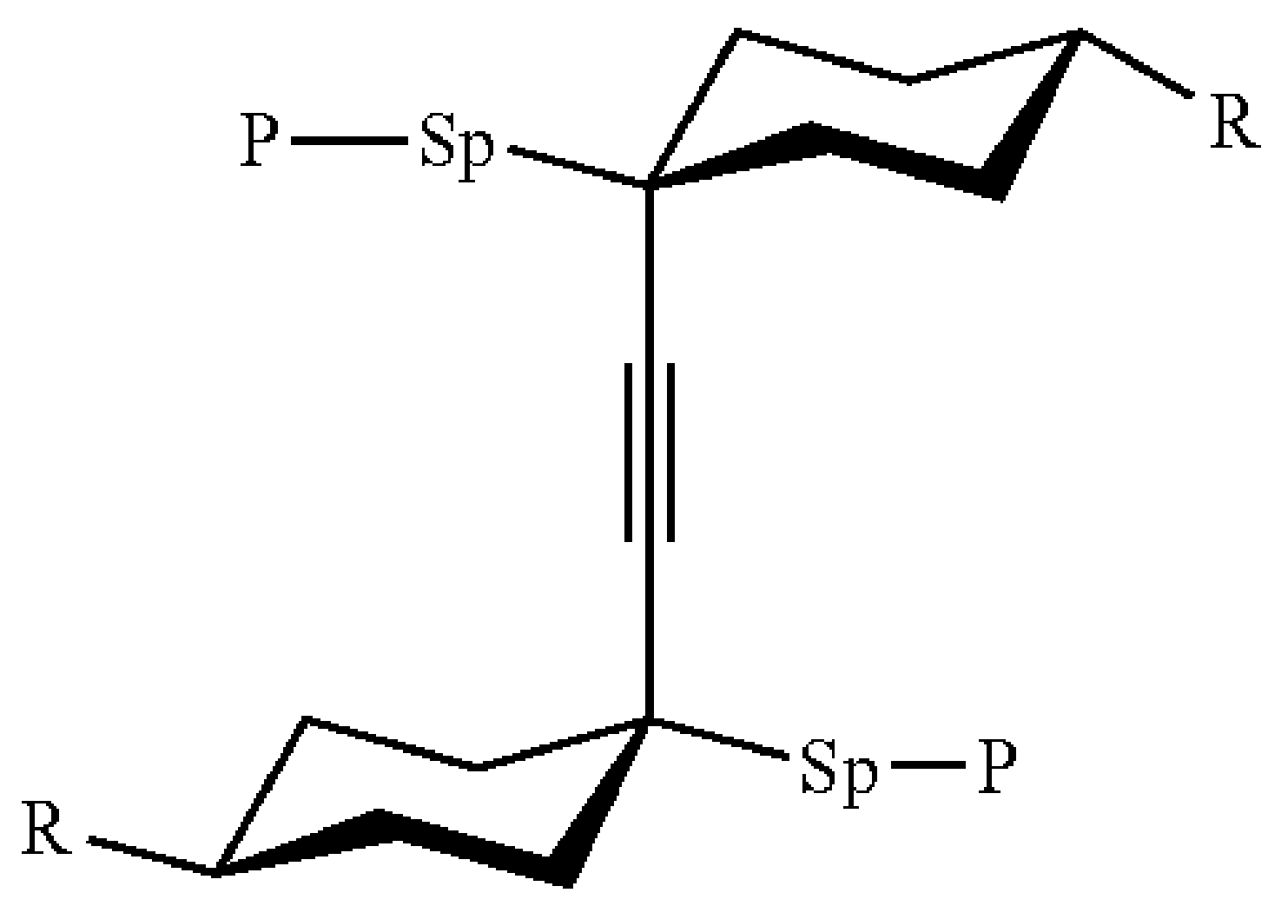
R^{1-5} are independently H, halogen, —CN, —NC, —NCO, —NCS, —OCN, —SCN, —C(═O)NR^{0}R^{00}, —C(═O)X^0, —C(═O)R^0, —NH$_2$, —NR^{0}R^{00}, —SH, —SR^0, —SO$_3$H, —SO$_2$R^0, —OH, —NO$_2$, —CF$_3$, —SF$_5$, P-Sp-, optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 40 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, or denote P or P-Sp-, or are substituted by P or P-Sp-, wherein the compounds comprise at least one group R^{1-5} denoting or being substituted by P or P-Sp-,

P is a polymerizable group, and

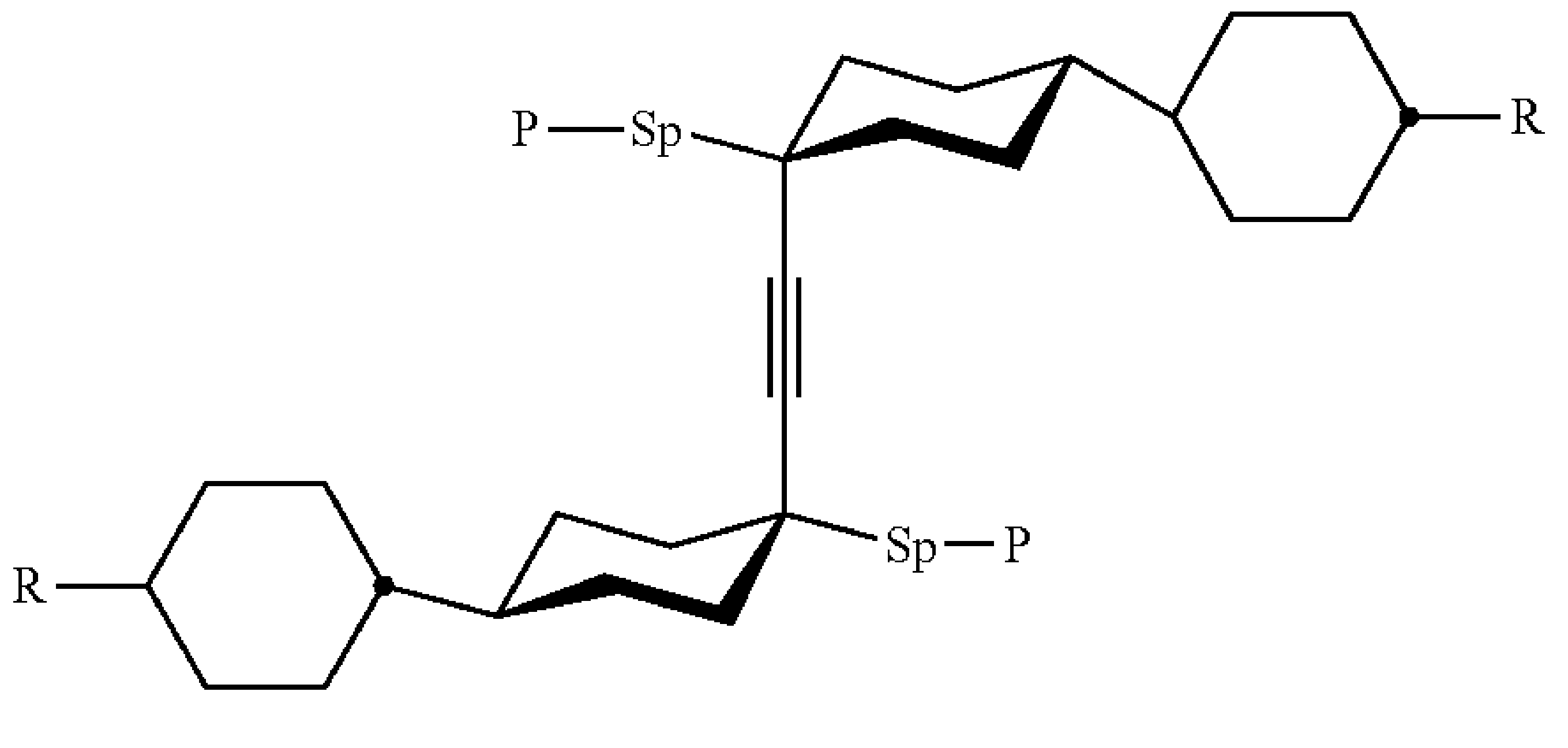
Sp is a spacer group or a single bond.

15. The polymer film according to claim **6**, wherein the polymerizable compounds are:

I1



I2



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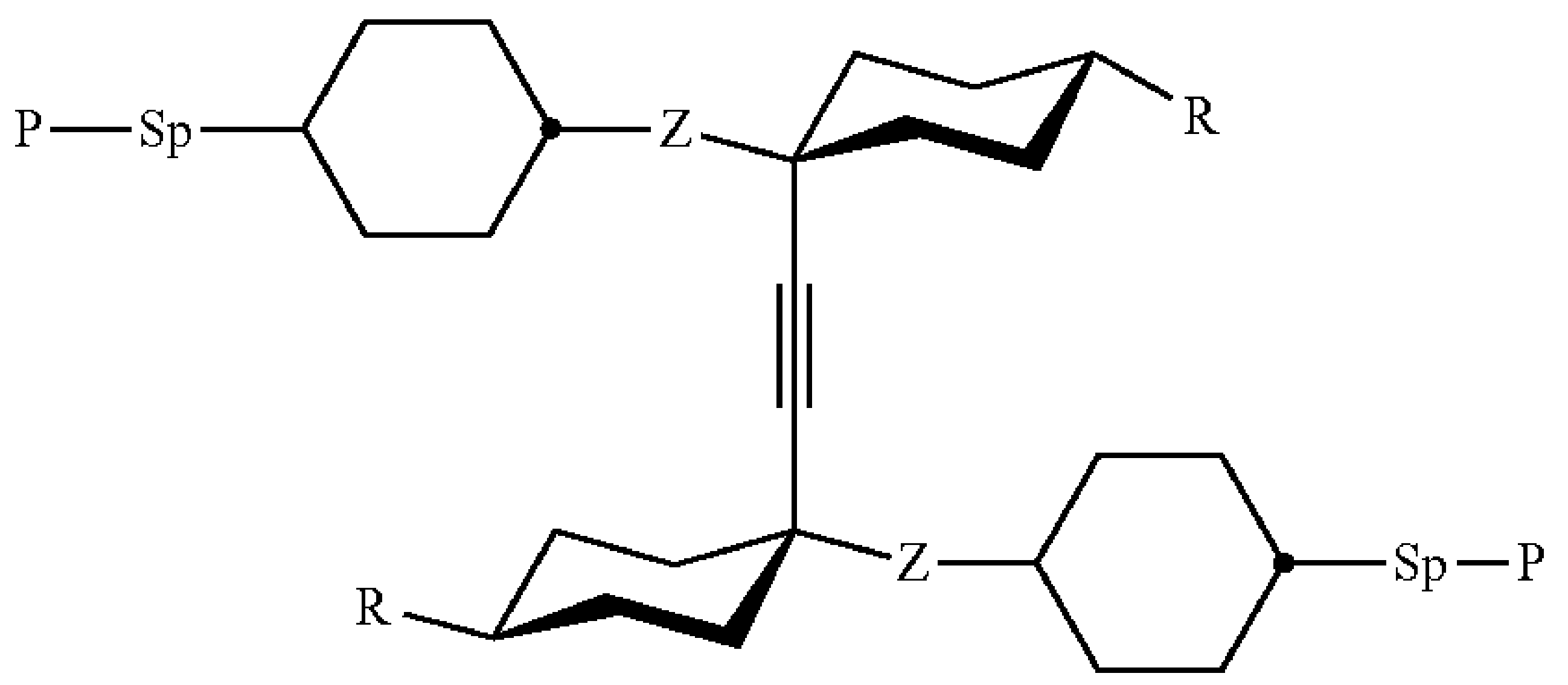
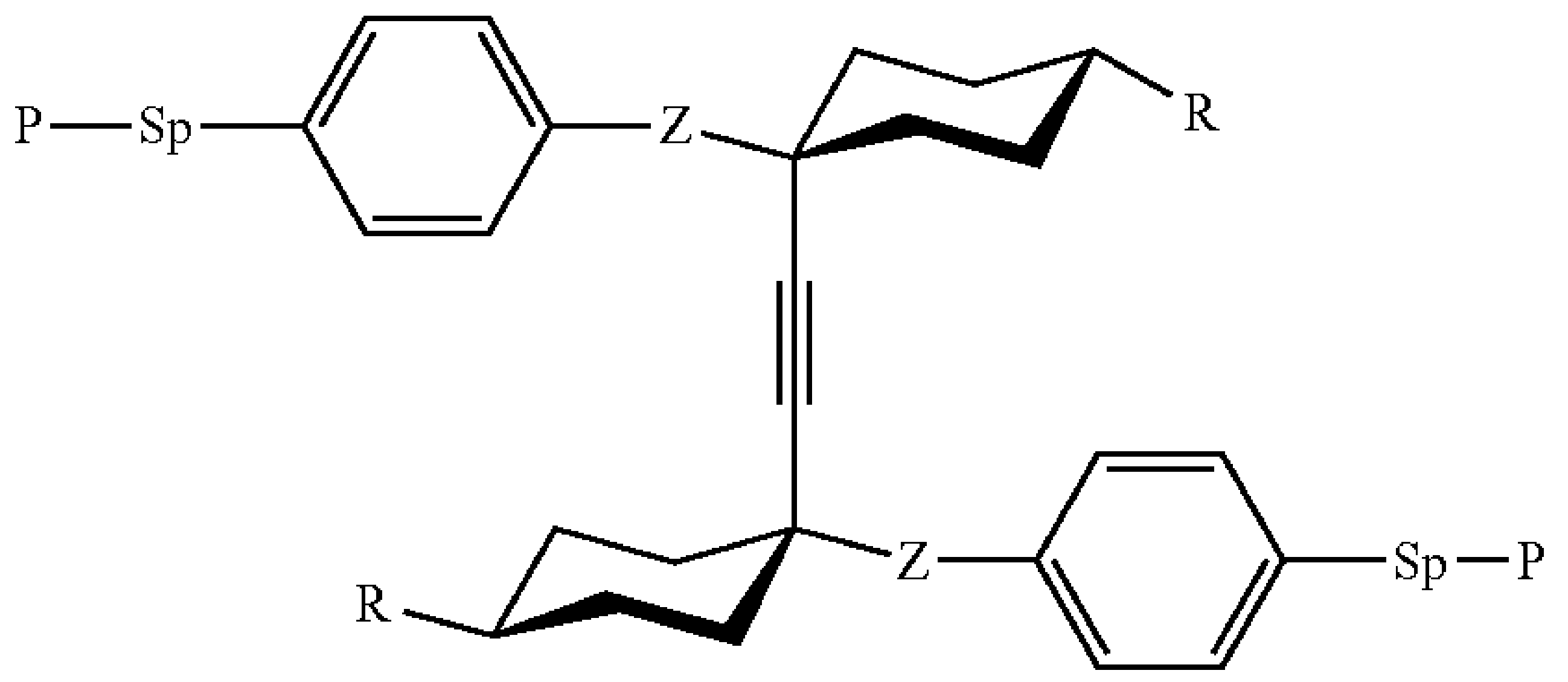
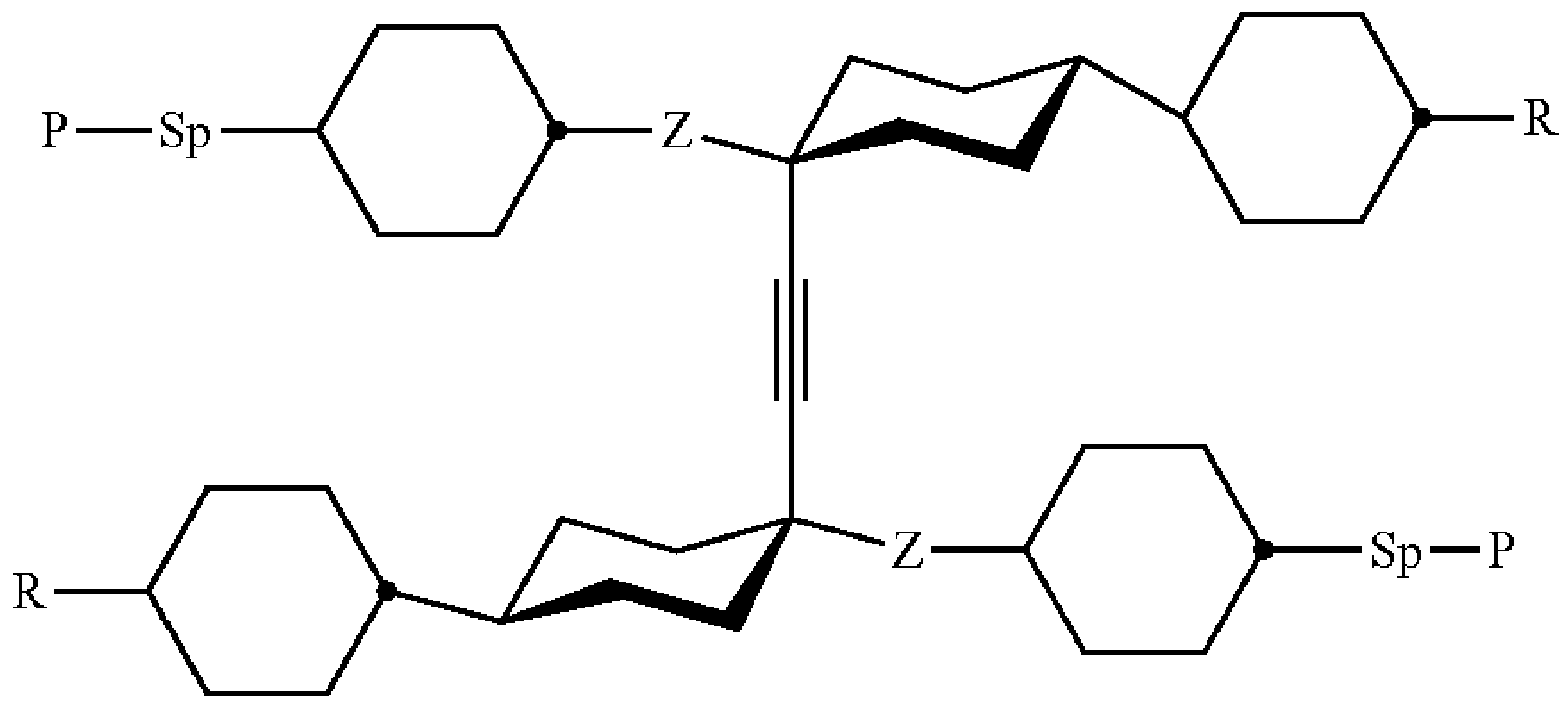
I3



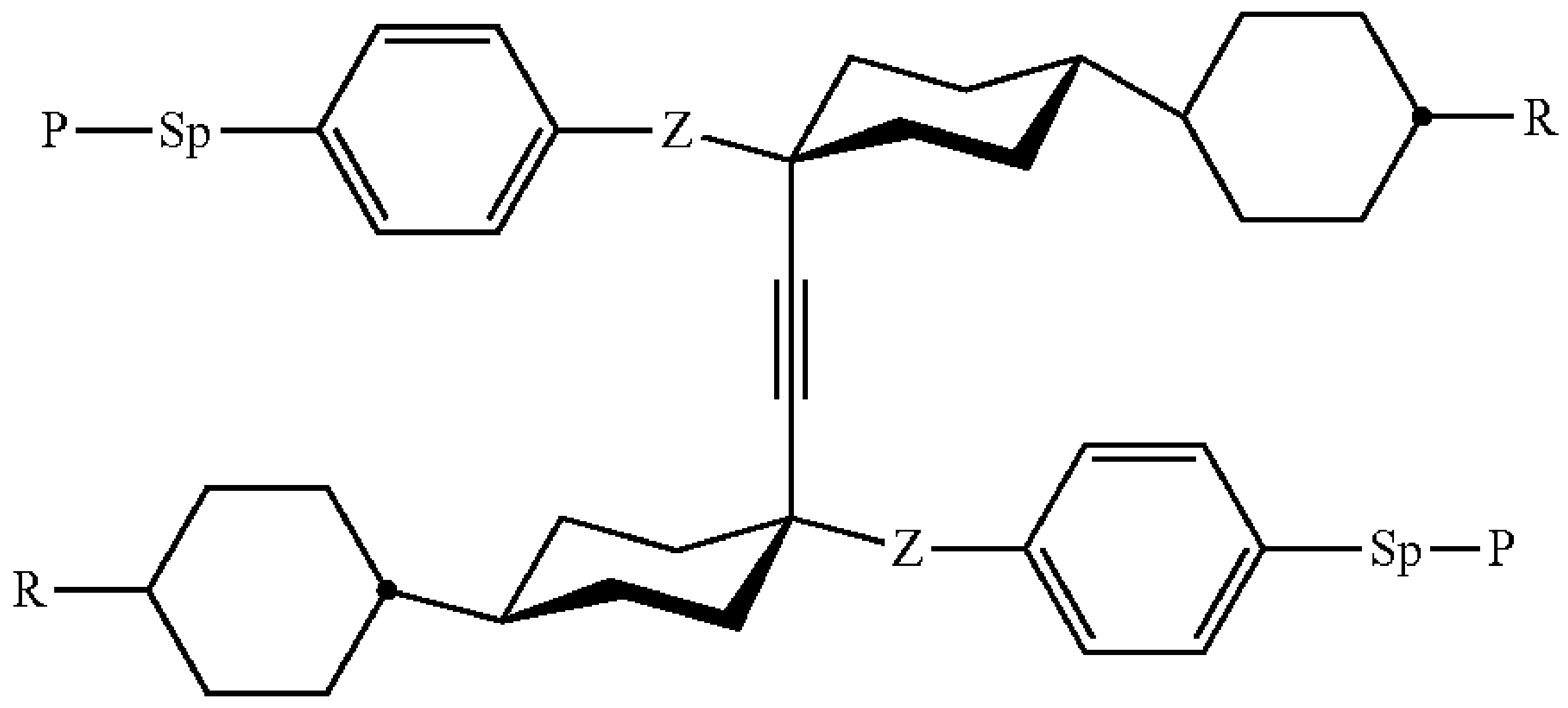
I4



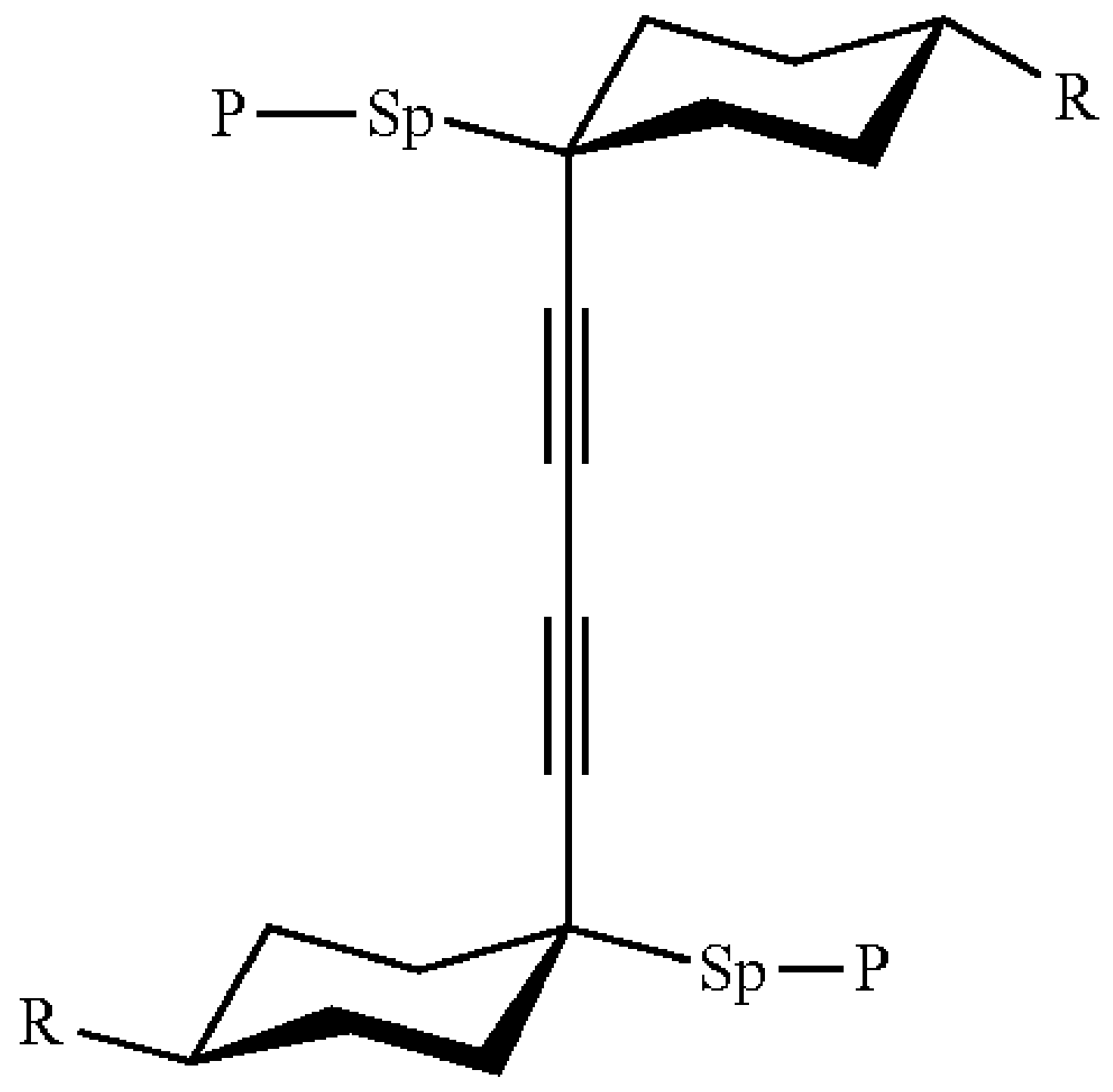
I5



I6



I7



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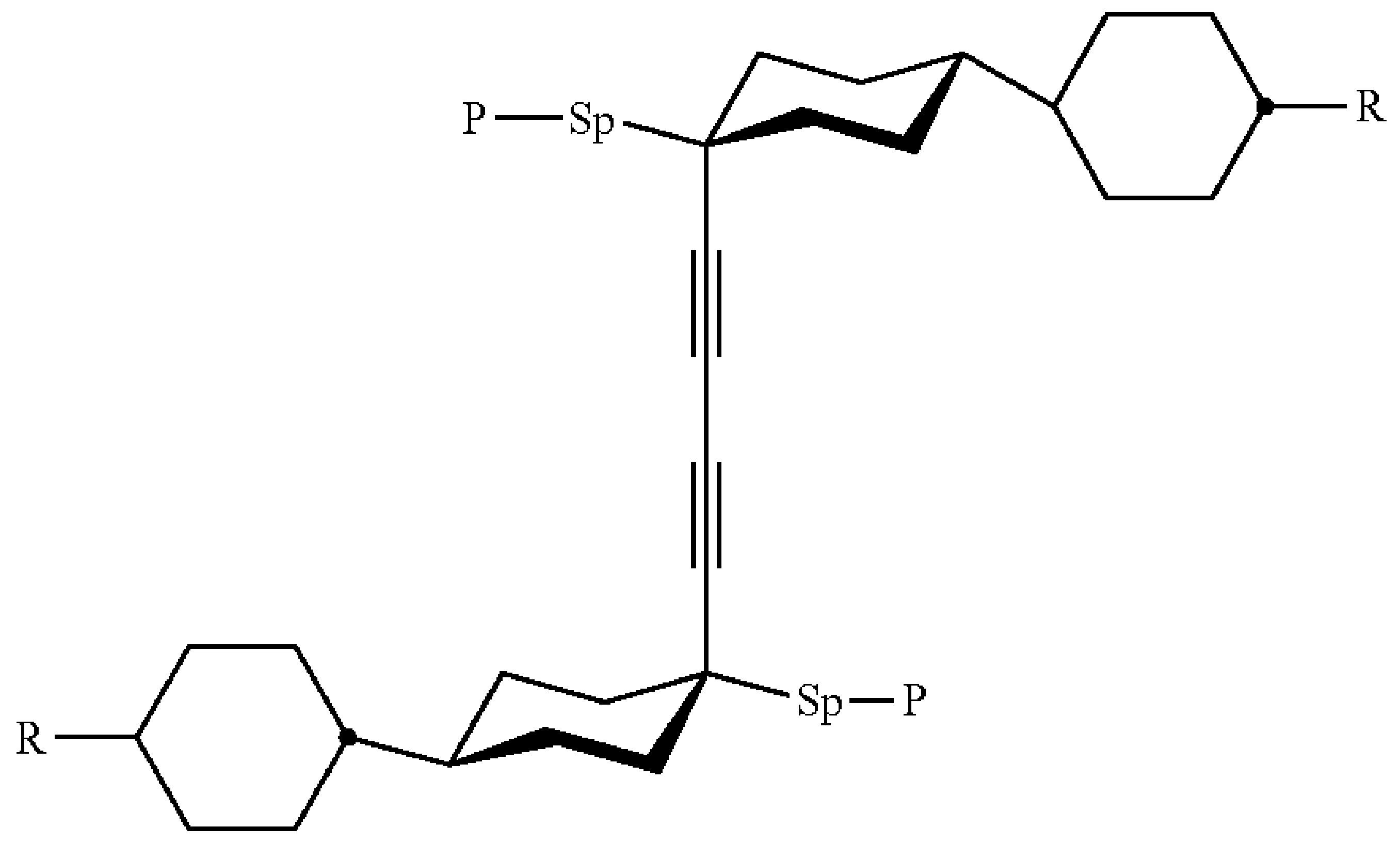
I8



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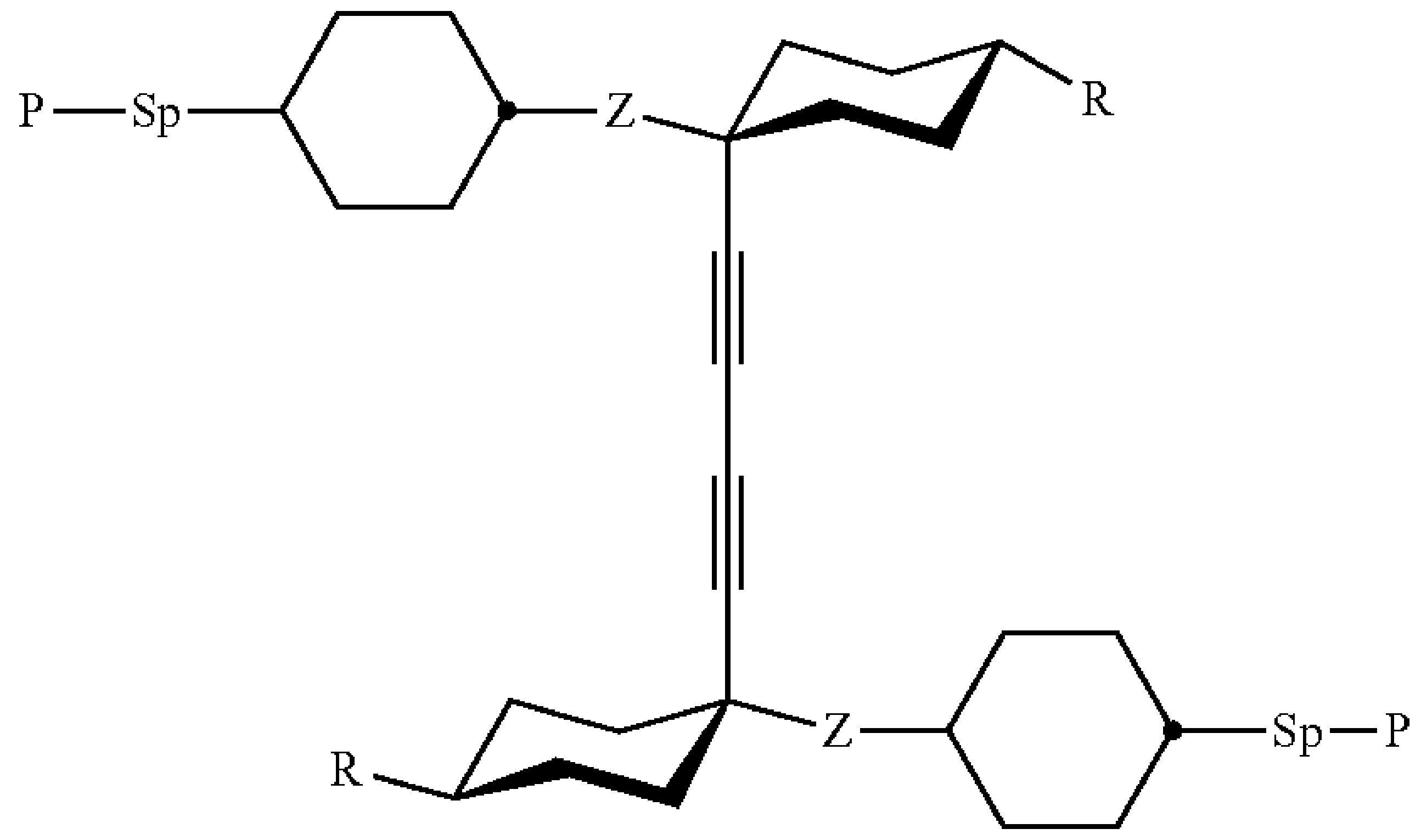

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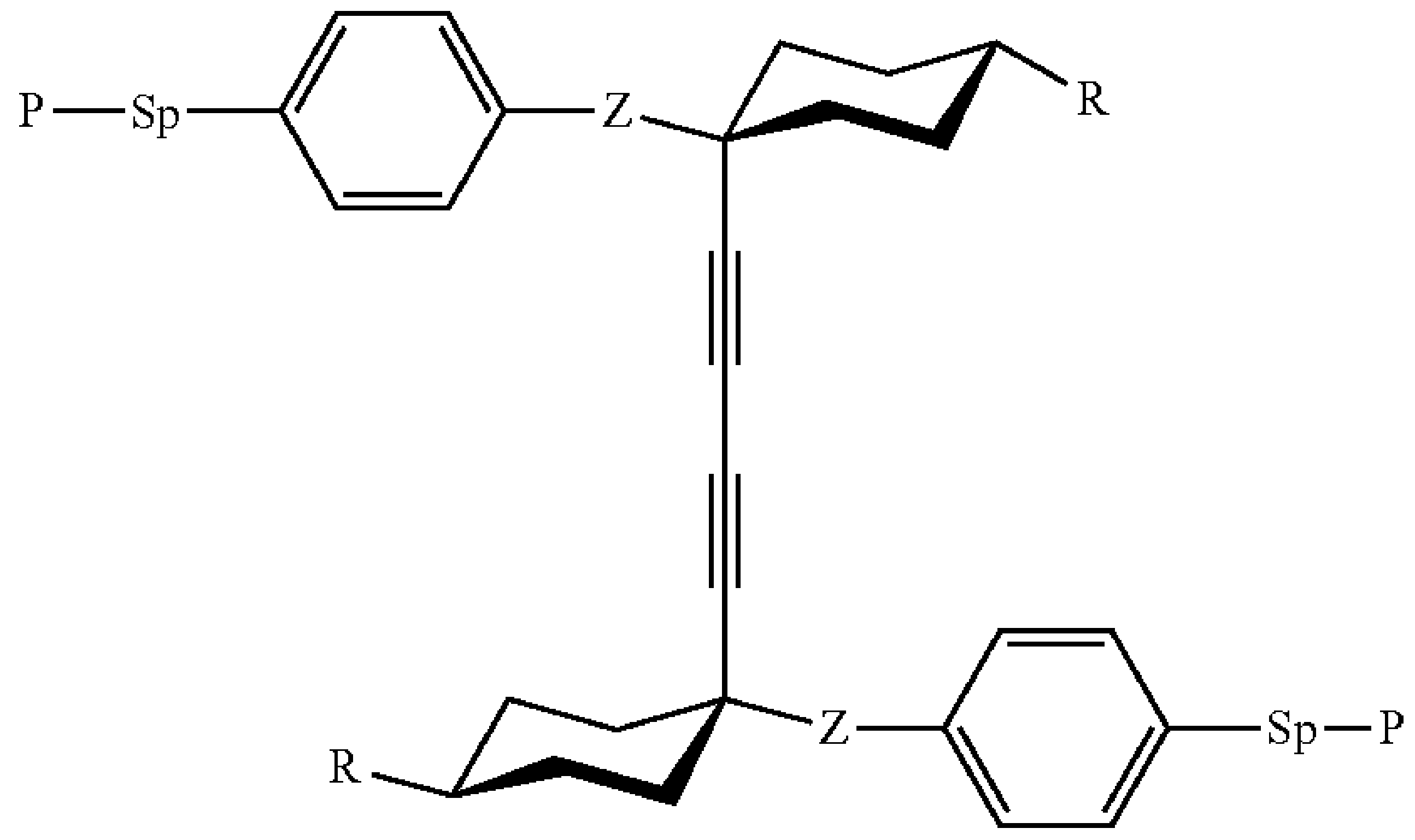

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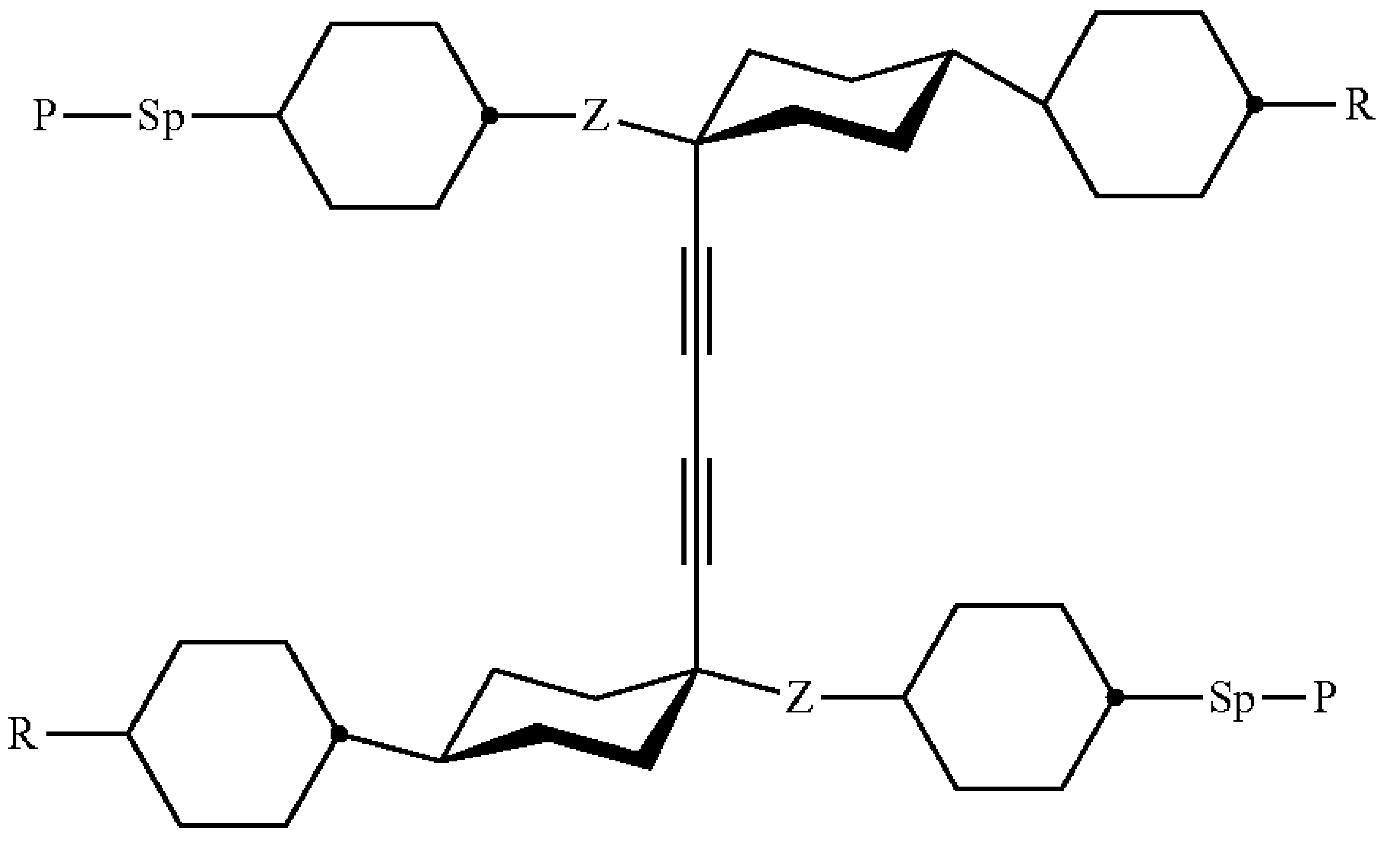

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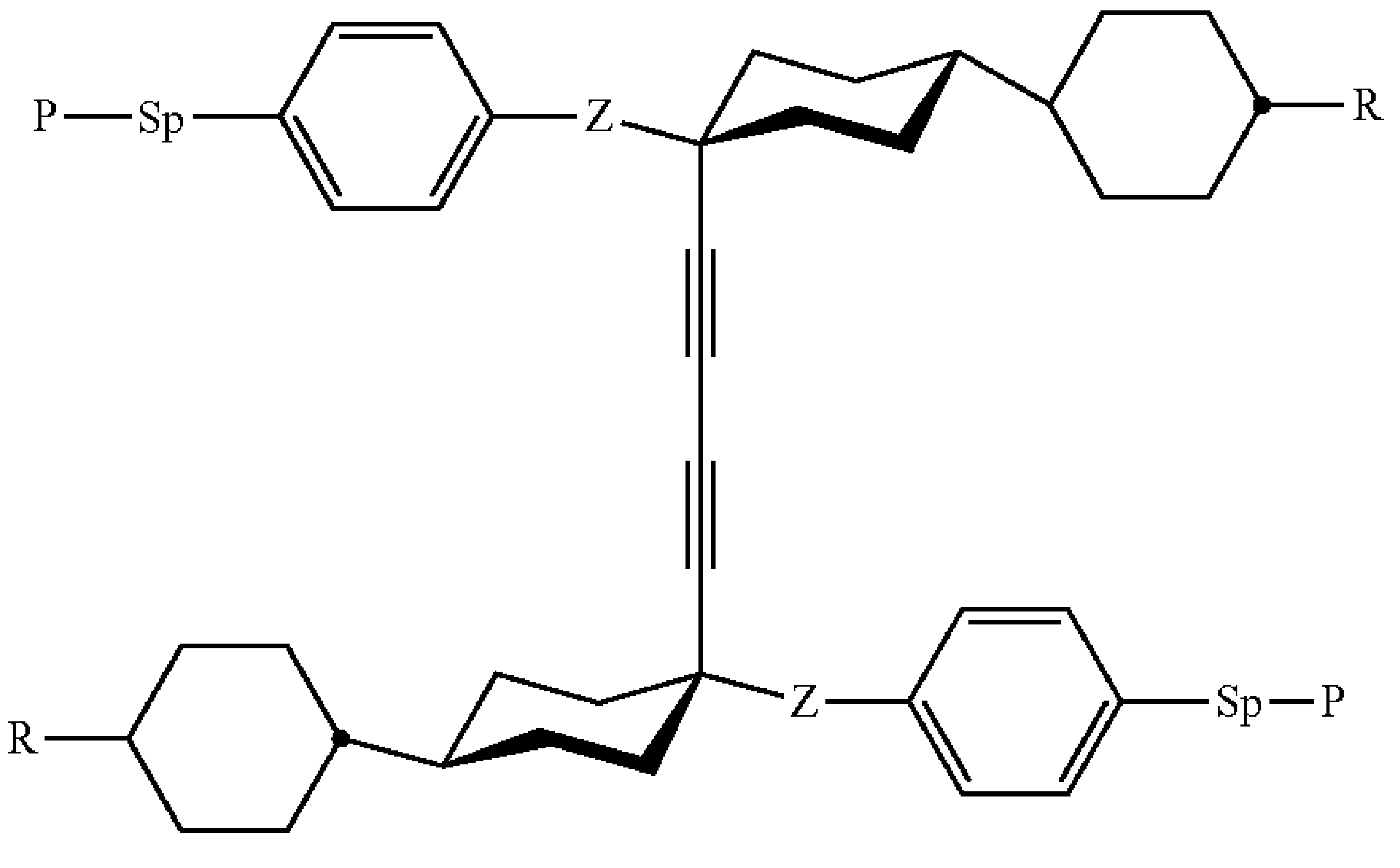

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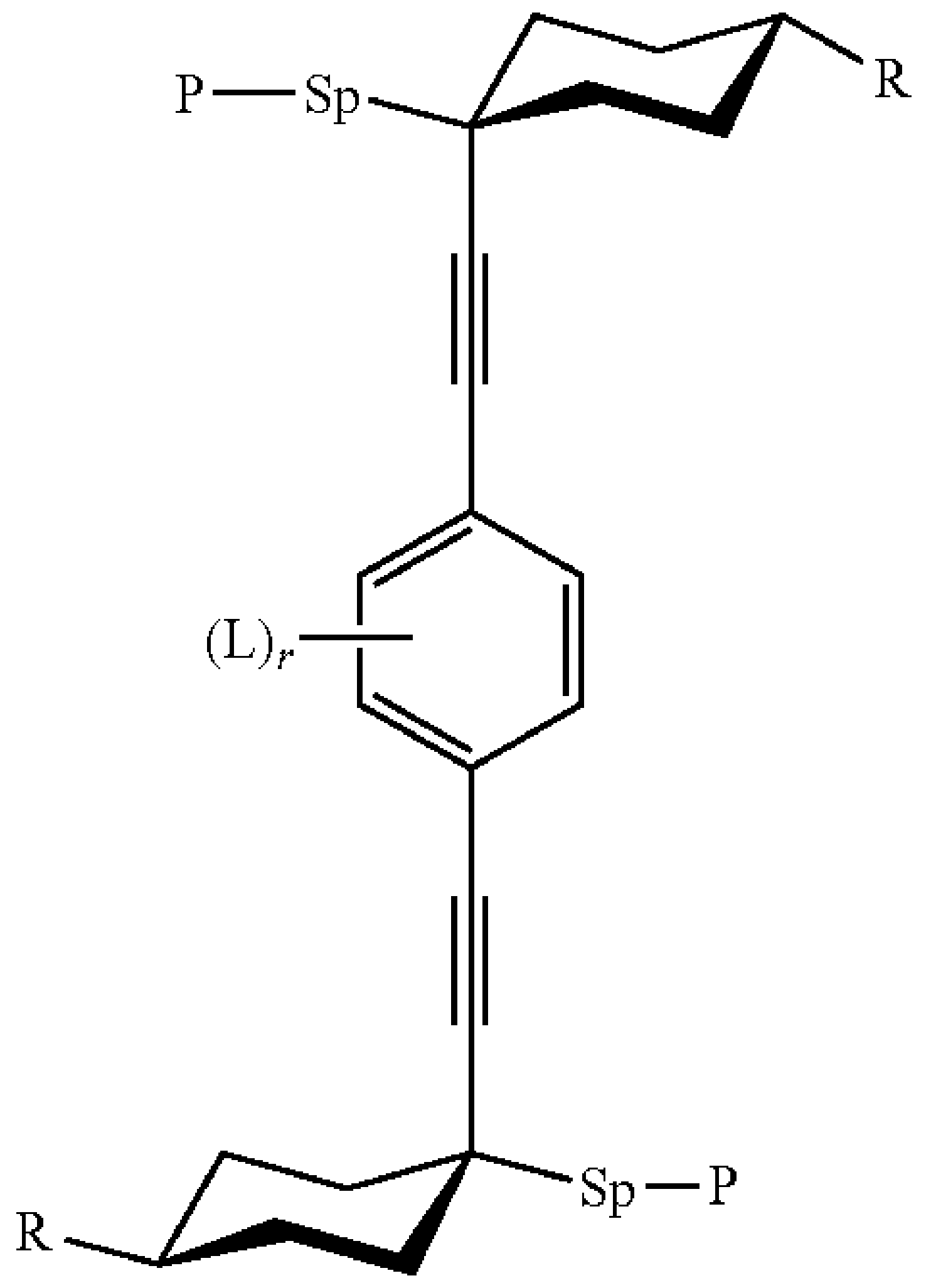

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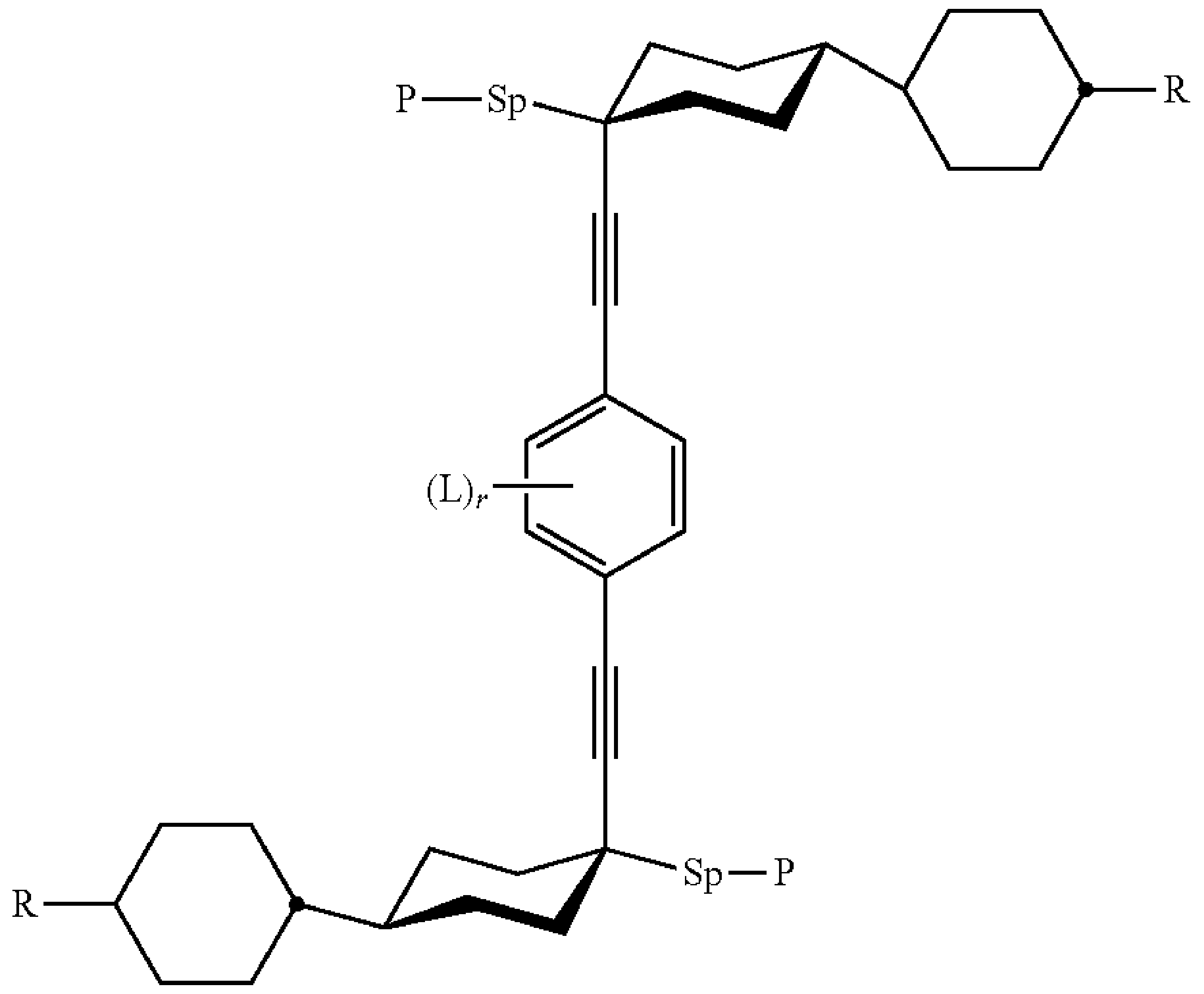

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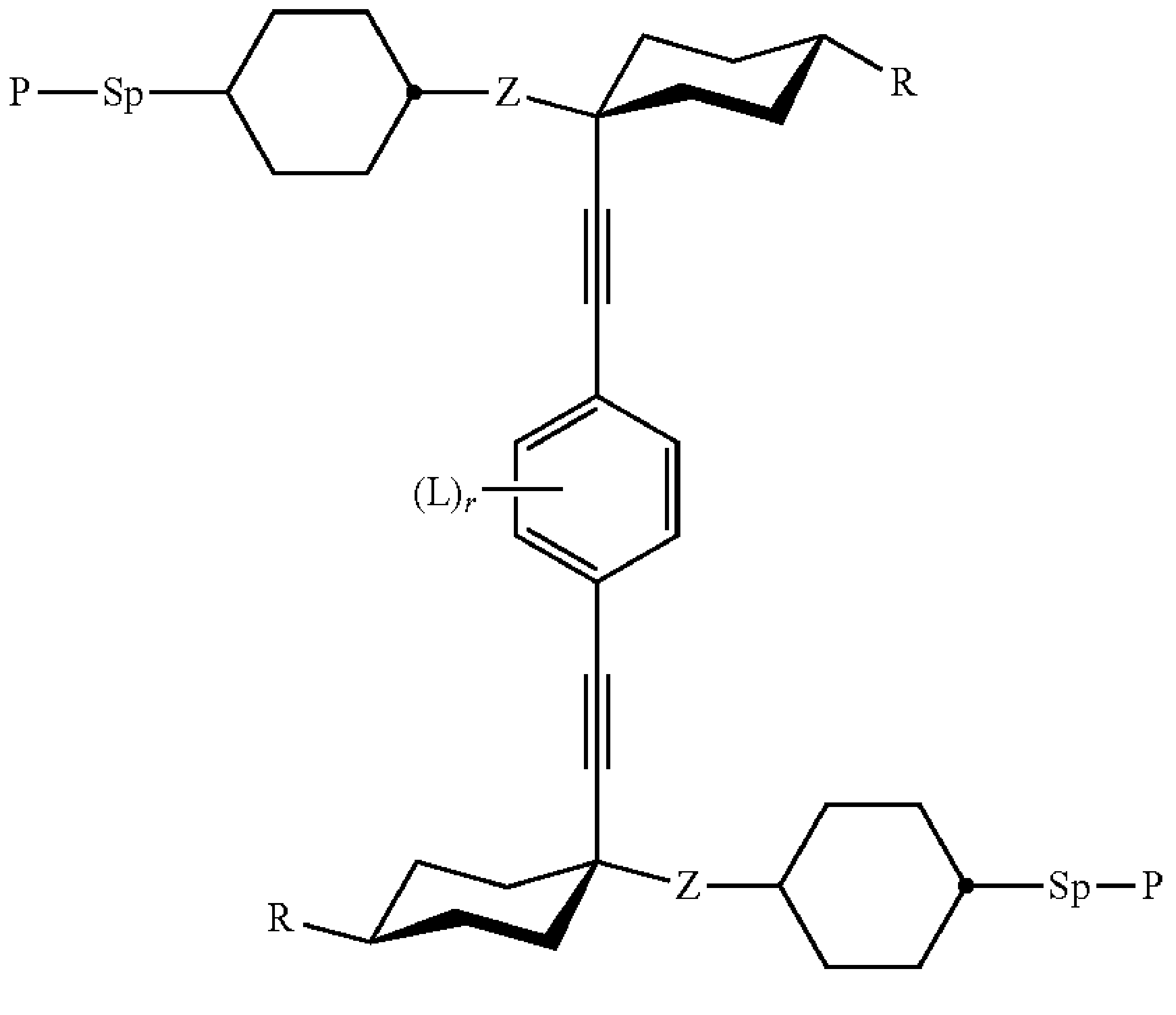

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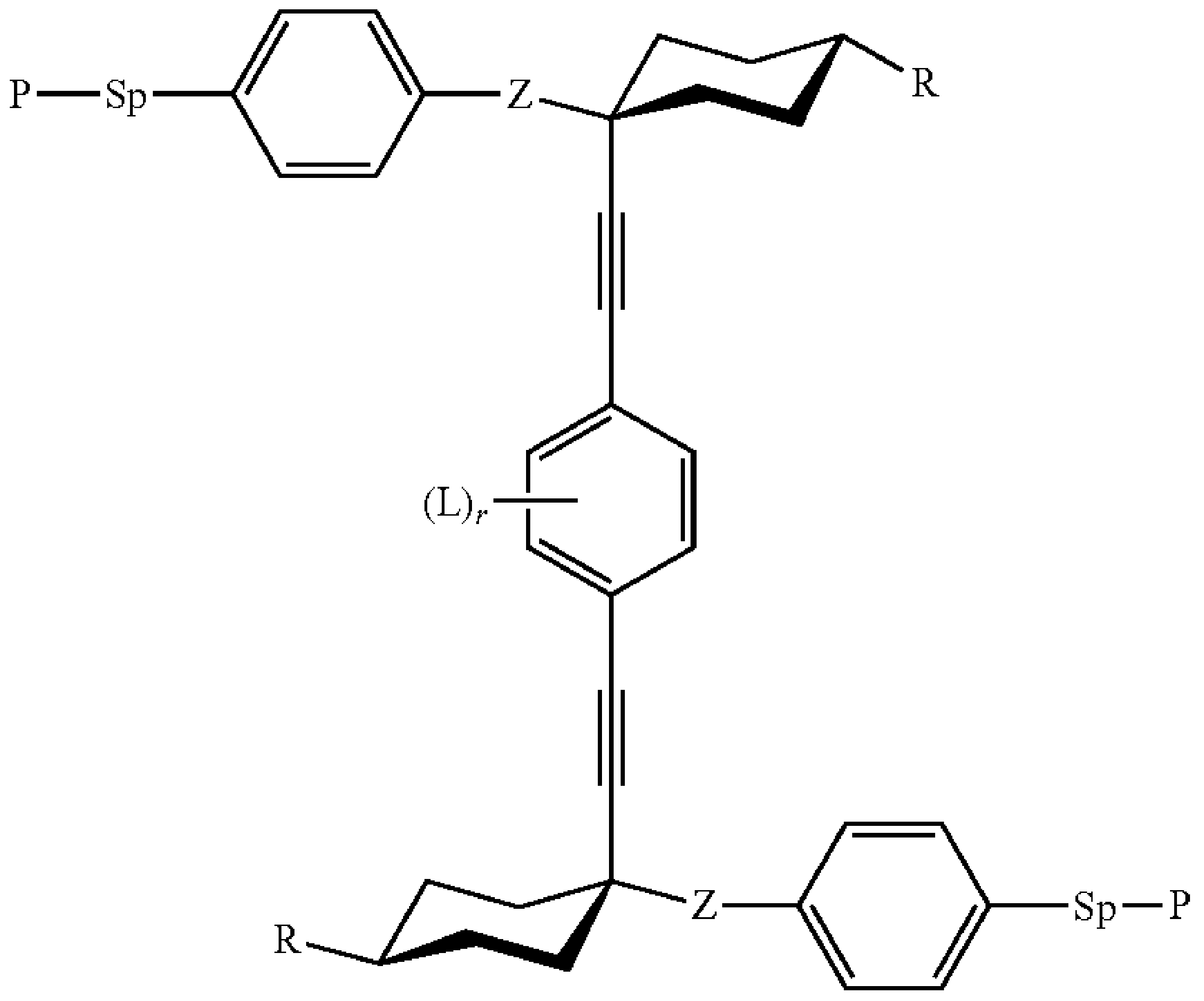

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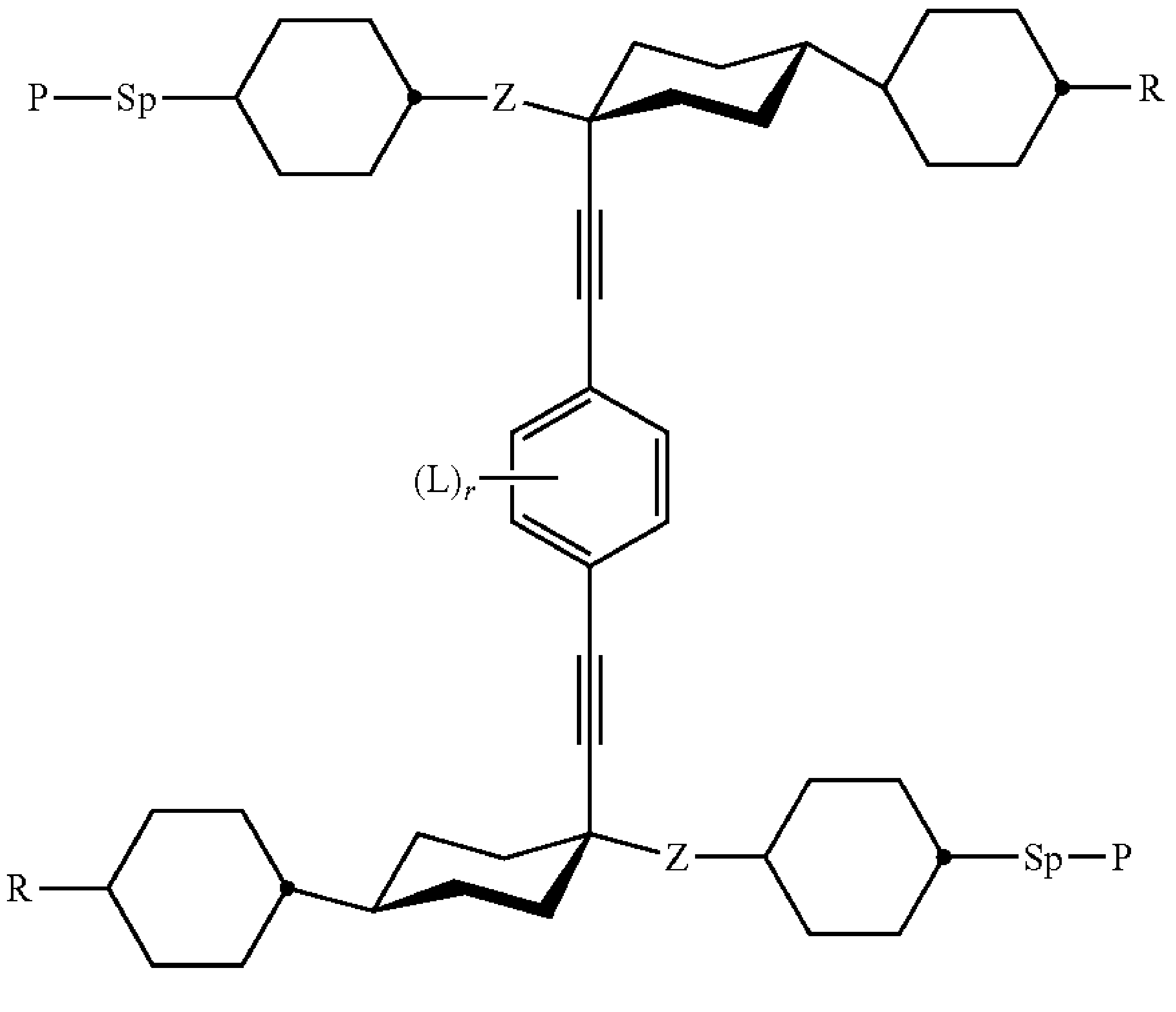

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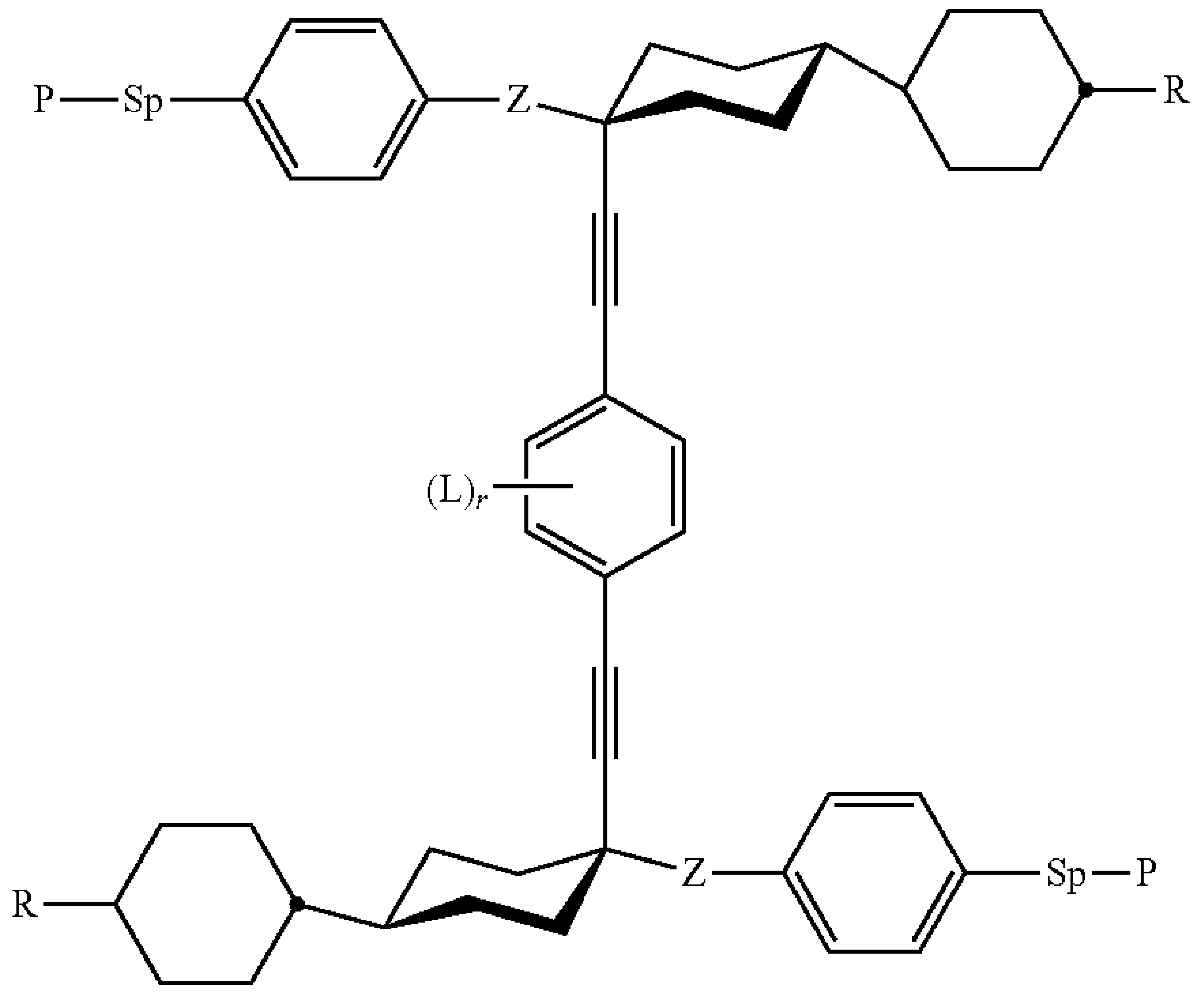

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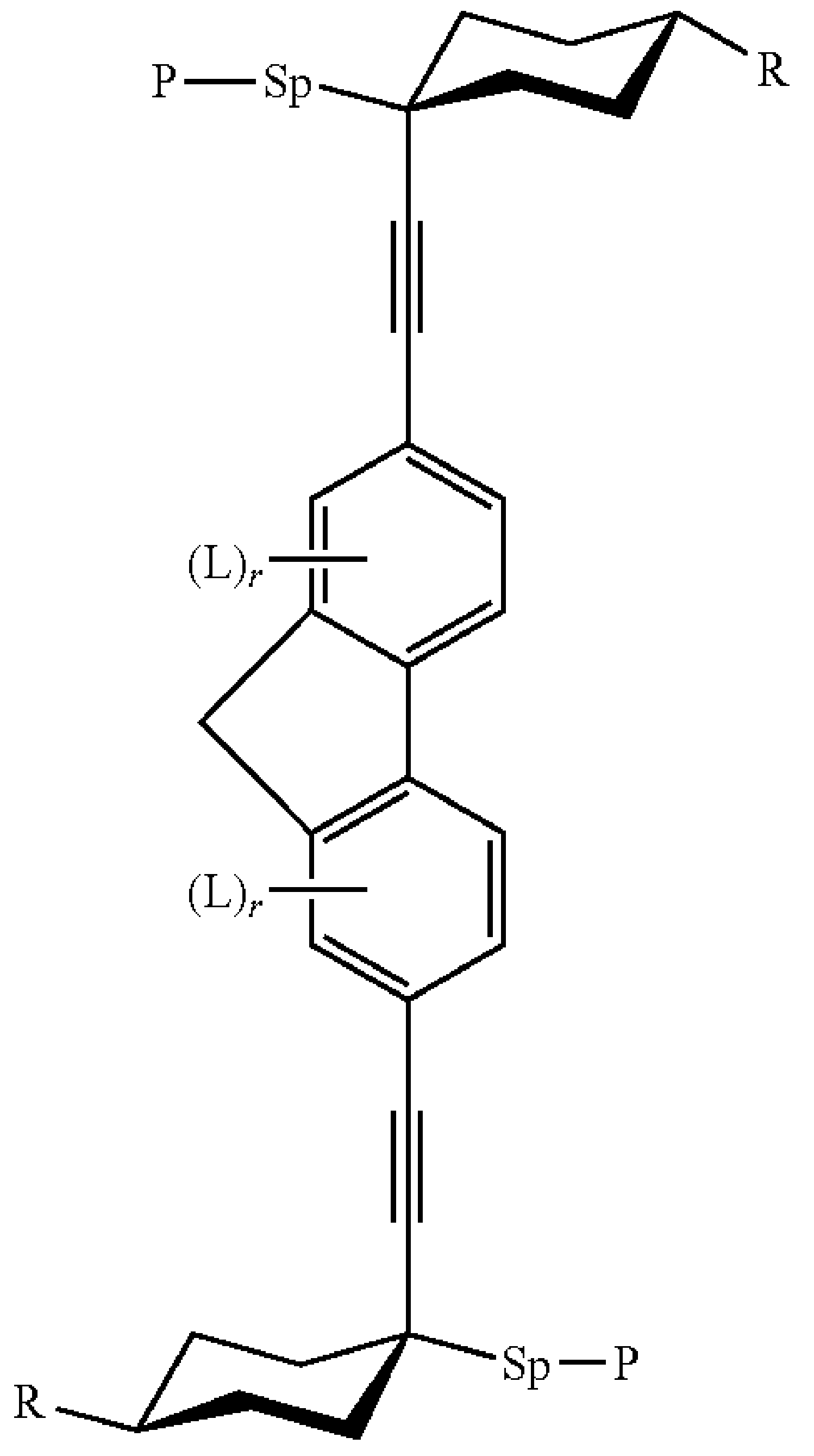

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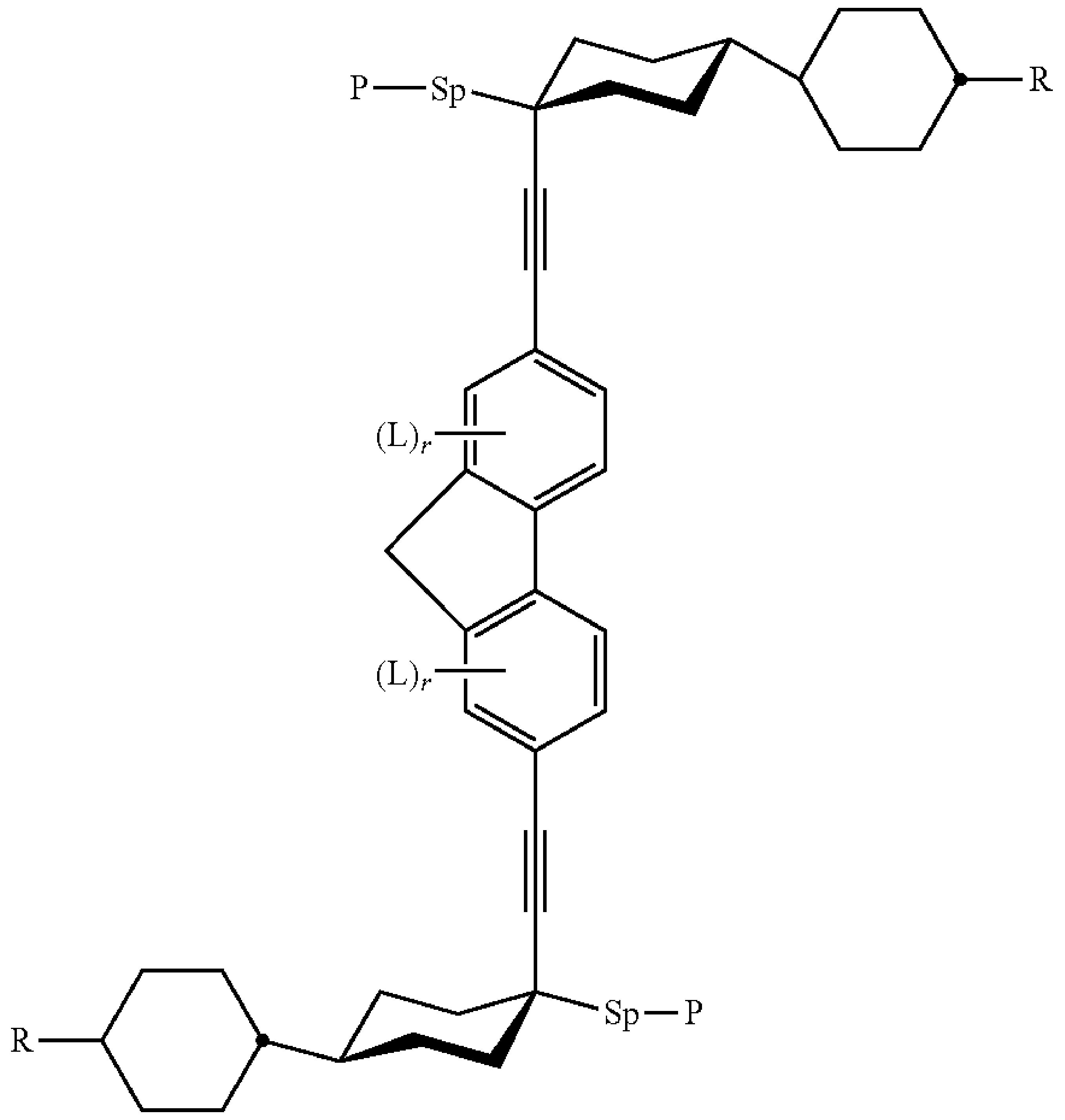

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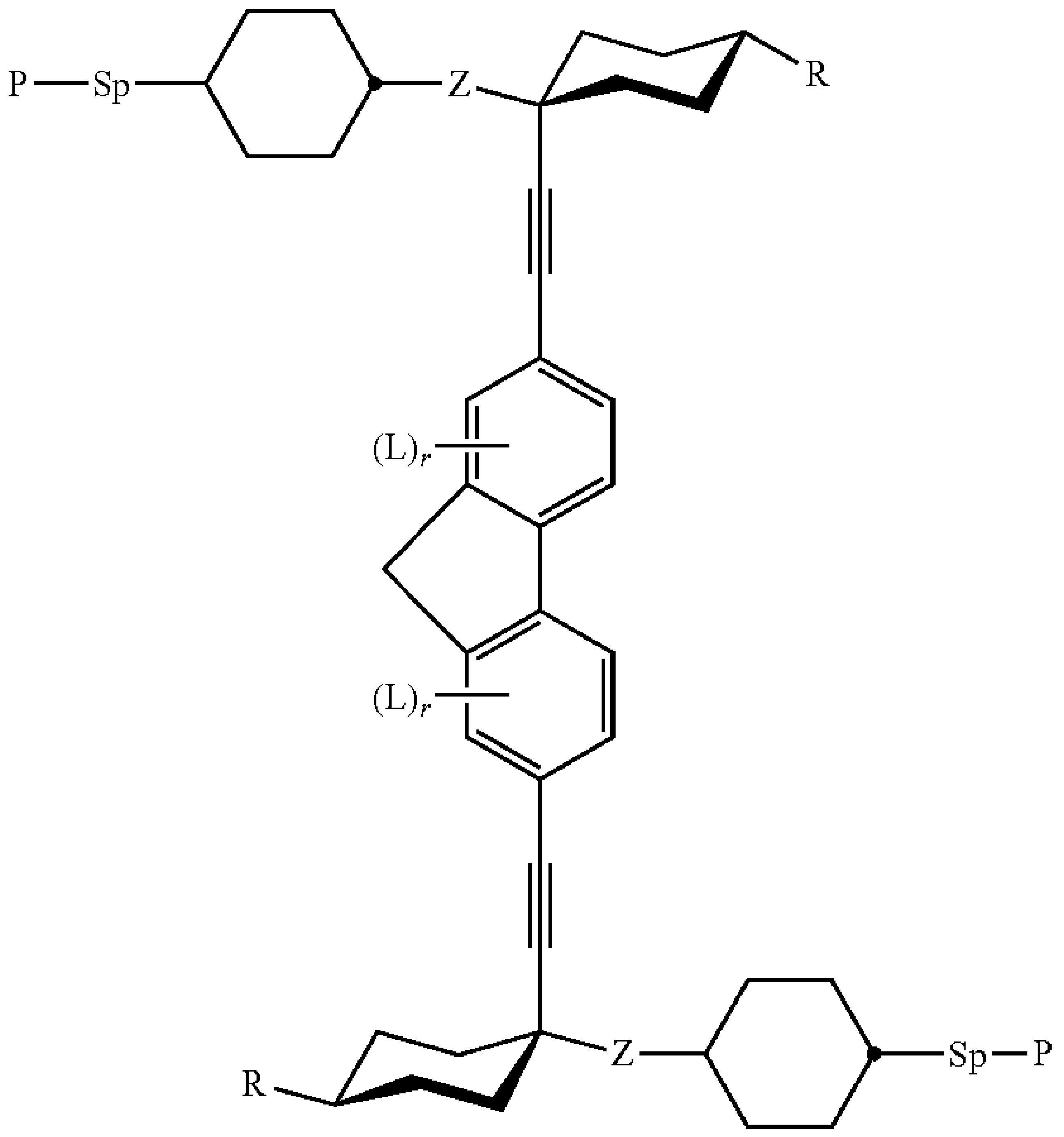

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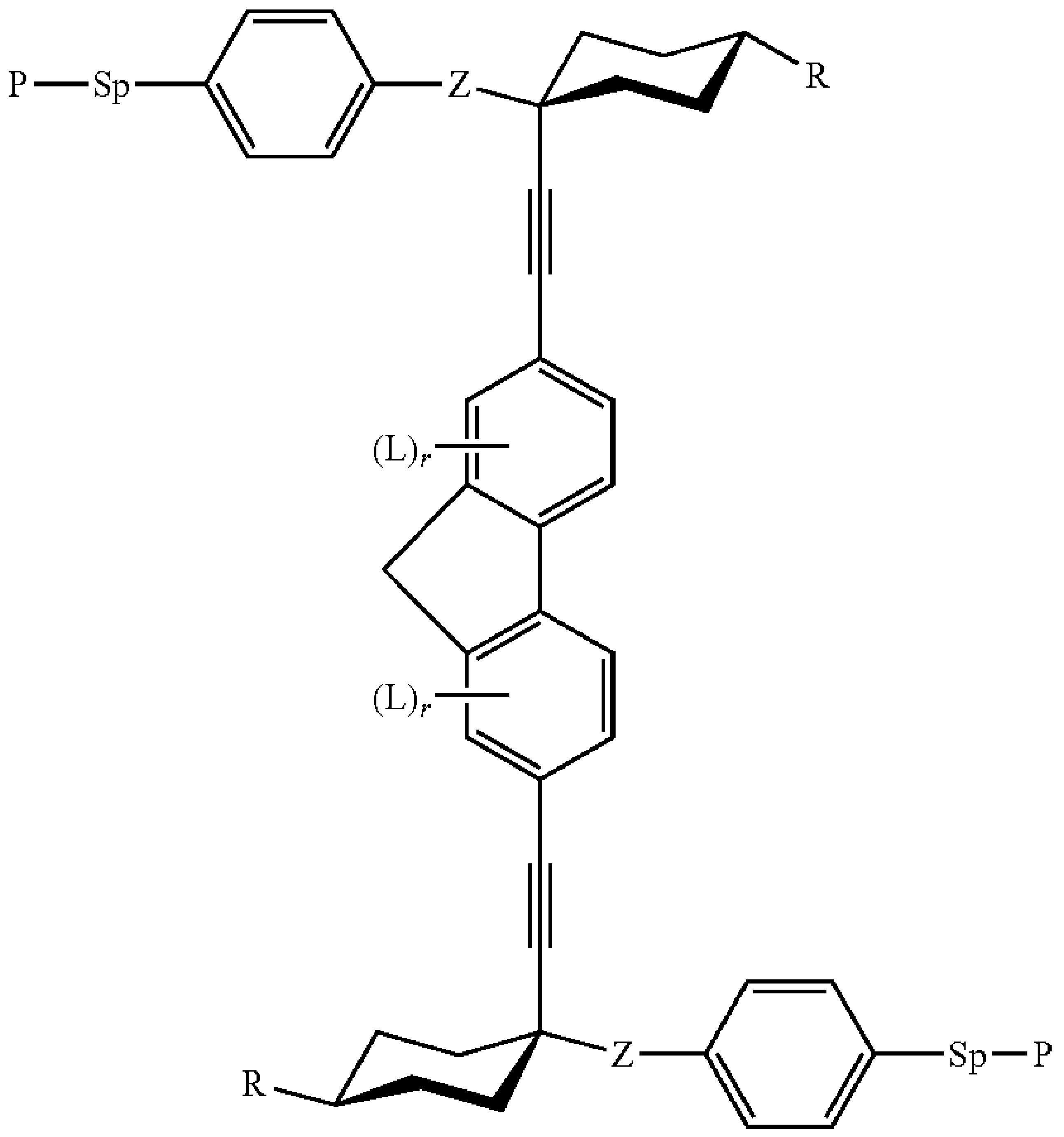

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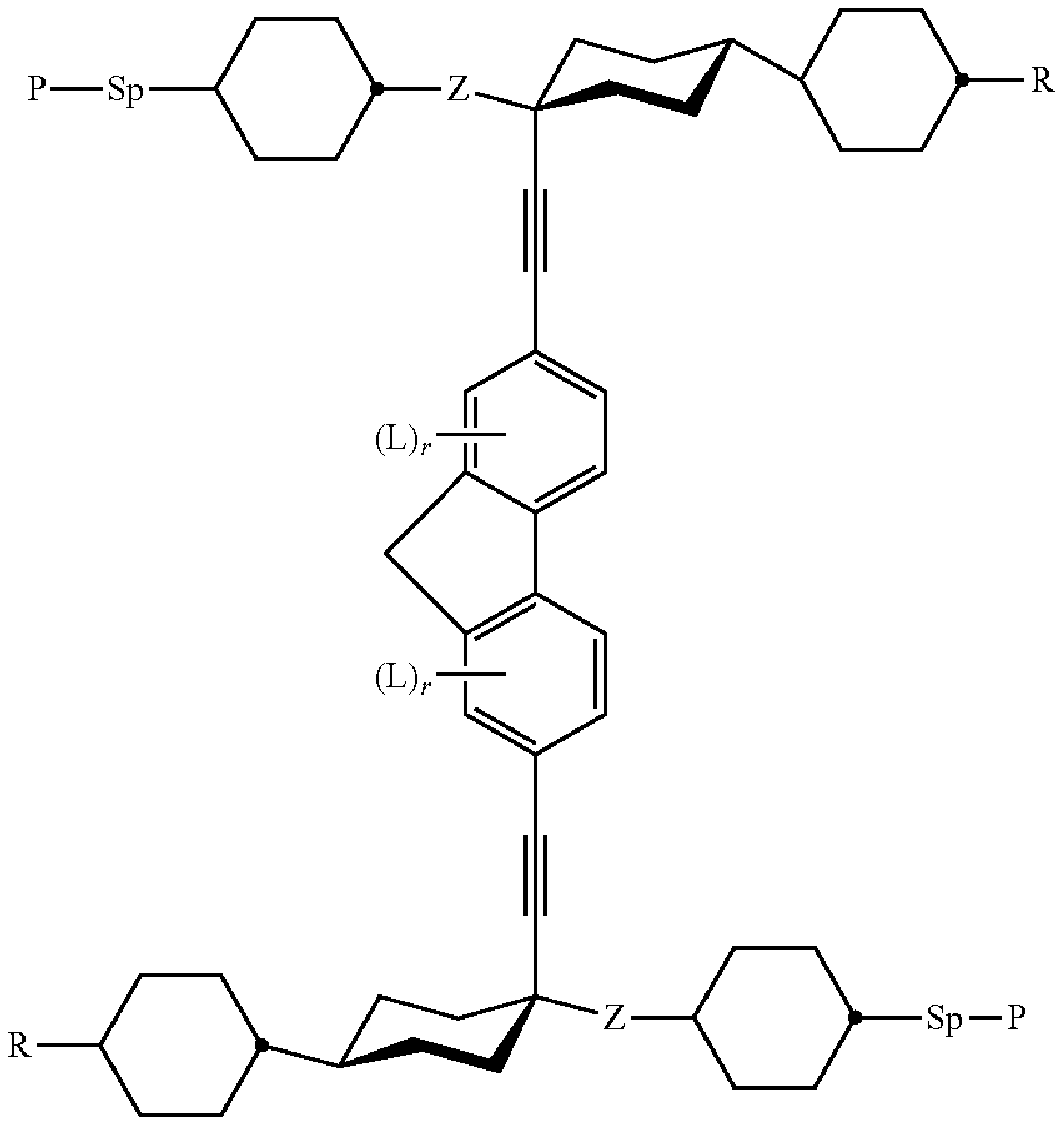
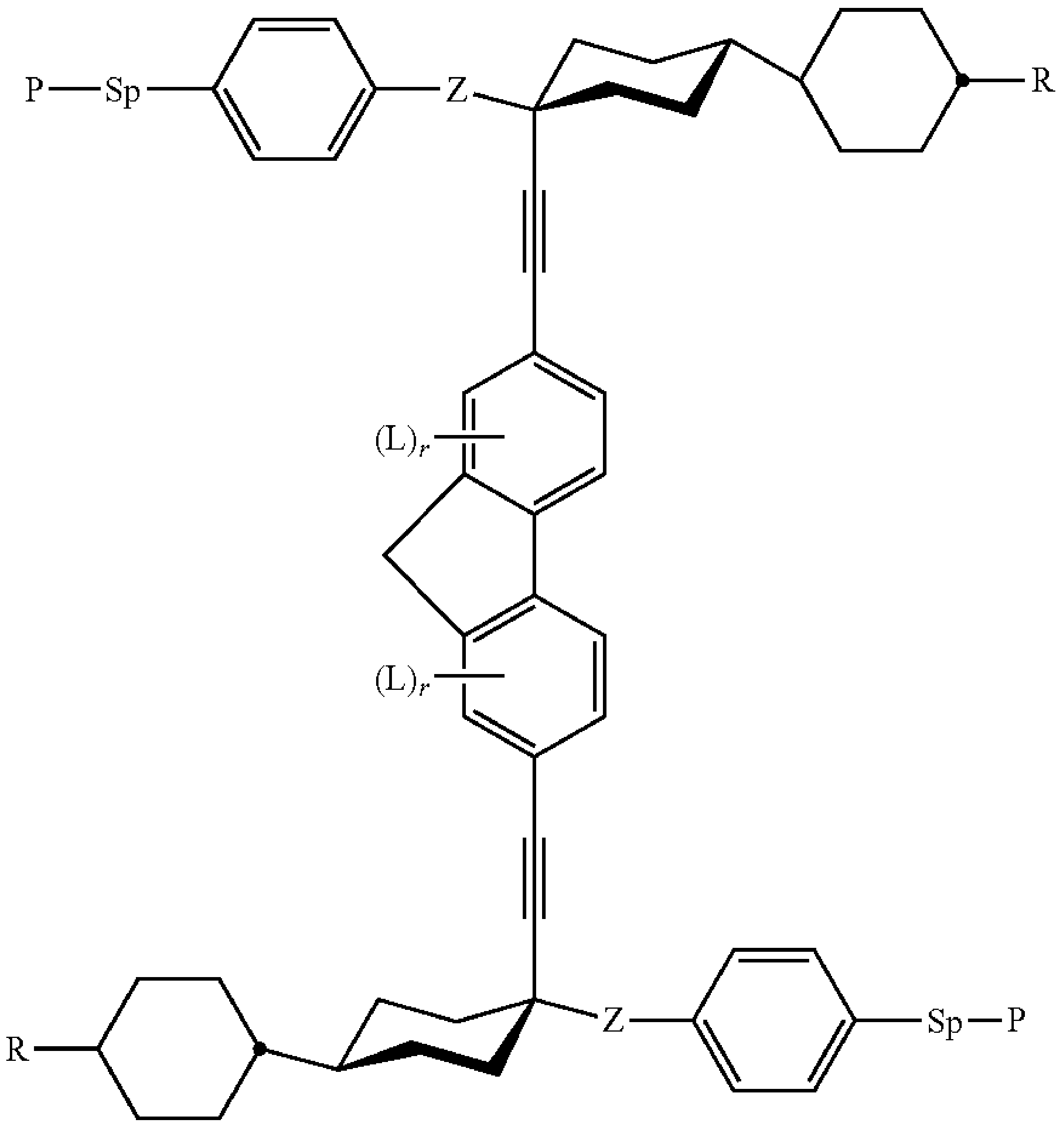


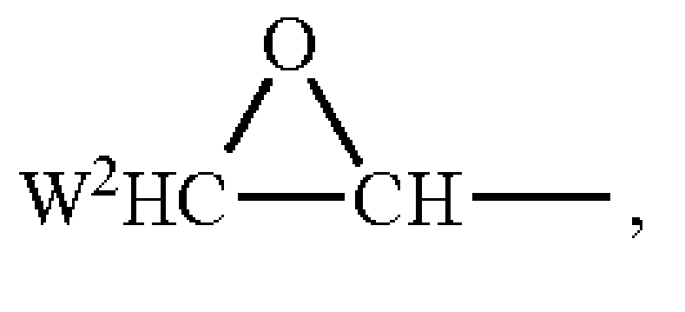
or

I24



wherein Z has one of the meanings of Z^1 given in claim **6**, R has one of the meanings of R^1 given in claim **6** that is different from P-Sp-, and P, Sp, L and r are as defined in claim **6**, and the benzene rings in the meosgenic groups are optionally substituted by one or more groups L.

16. The polymerizable film according to claim **1**, wherein the polymerizable groups are $CH_2{=}CW^1{-}COO{-}$, $CH_2{=}CW^1{-}CO{-}$,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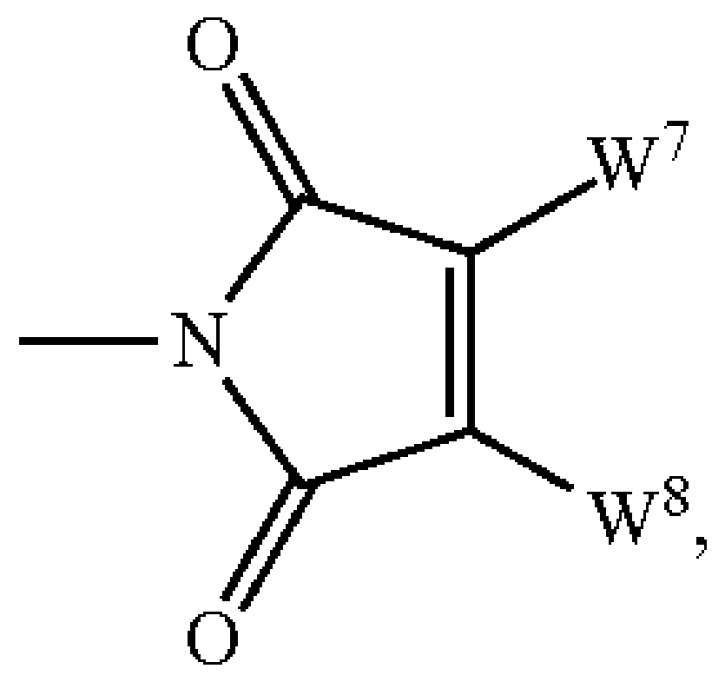
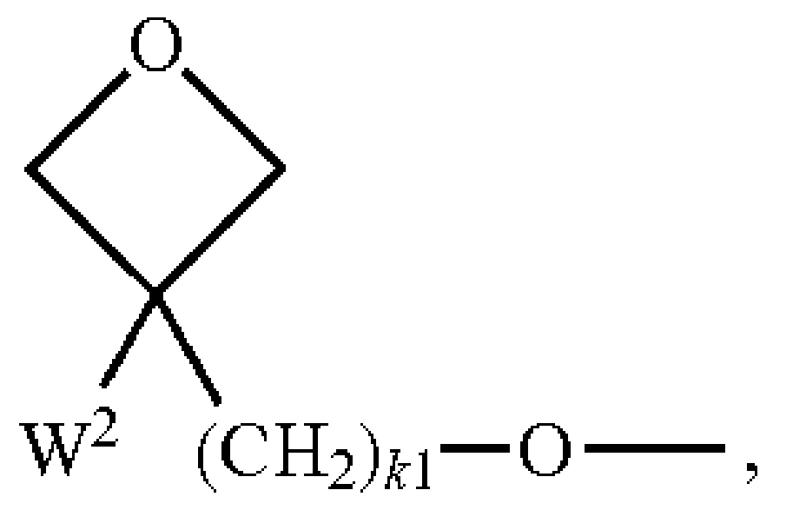



,

$(CH_2{=}CH)_2CH$—OCO—, $(CH_2{=}CH{-}CH_2)_2CH$—OCO—, $(CH_2{=}CH)_2CH$—O—, $(CH_2{=}CH{-}CH_2)_2N$—, $(CH_2{=}CH{-}CH_2)_2N$—CO—, HO—CW^2W^3—, HS—CW^2W^3—, HW^2N—, HO—CW^2W^3—NH—, $CH_2{=}CW^1$—CO—NH—, $CH_2{=}CH$—$(COO)_{k1}$-Phe-$(O)_{k2}$—, —$CH_2{=}CH$—$(CO)_{k1}$-Phe-$(O)_{k2}$—, Phe—CH═CH—, HOOC—, OCN—, or $W^4W^5W^6Si$—, with W^1 being H, F, Cl, CN, CF_3, phenyl or alkyl with 1 to 5 C-atoms, W^2 and W^3 being independently of each other H or alkyl with 1 to 5 C-atoms, W^4, W^5 and W^6 being independently of each other Cl, oxaalkyl or oxacarbonylalkyl with 1 to 5 C-atoms, W^7 and W^8 being independently of each other H, Cl or alkyl with 1 to 5 C-atoms, Phe being 1,4-phenylene that is optionally substituted, and k_1 and k_2 being independently of each other 0 or 1.

17. A polymerizable LC material comprising one or more films as defined in claim **1** and one or more further compounds that are optionally polymerizable and/or mesogenic or liquid crystalline.

18. An anisotropic polymer obtainable by polymerizing a LC material as defined in claim **1** in its LC phase in an oriented state in form of a thin film.

19. An optical, electronic or electrooptical device, or a component thereof, comprising a polymer film, according to claim **1**.

20. The optical component according to claim **19**, that is an optically uniaxial film selected from an A-plate, C-plate, negative C-plate or O-plate, a twisted optical retarder, a twisted quarter wave foil (QWF), an optically biaxial film, an achromatic retarder, an achromatic QWF or half wave foil (HWF), a film having a cholesteric, smectic, nematic or blue phase, a film having homeotropic, splayed, tilted, planar or blue-phase alignment, which is uniformly oriented or exhibits a pattern of different orientations.

21. The optical component according to claim **19**, that is an optical compensation film enhancing the viewing angle of LCD's, a component in a brightness enhancement films, or an achromatic element in reflective or transflective LCD's.

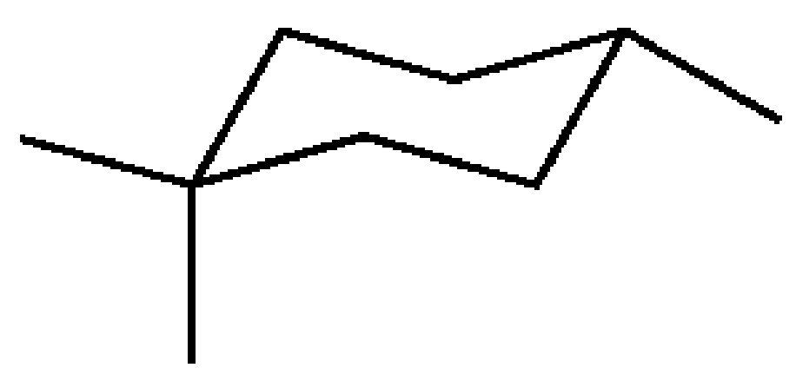
22. The device or component according to claim **19**, that is electrooptical displays, LCDs, optical films, polarizers, compensators, beam splitters, reflective films, alignment layers, color filters, holographic elements, hot stamping foils, colored images, decorative or security markings, LC pigments, adhesives, non-linear optic (NLO) devices, optical information storage devices, electronic devices, organic semiconductors, organic field effect transistors (OFET), integrated circuits (IC), thin film transistors (TFT), Radio Frequency Identification (RFID) tags, organic light emitting diodes (OLED), organic light emitting transistors (OLET), electroluminescent displays, organic photovoltaic (OPV) devices, organic solar cells (O-SC), organic laser diodes (O-laser), organic integrated circuits (O-IC), lighting devices, sensor devices, electrode materials, photoconductors, photodetectors, electrophotographic recording devices, capacitors, charge injection layers, Schottky diodes, **[**planarising**]** *planarizing* layers, antistatic films, conducting substrates, conducting patterns, photoconductors, electrophotographic applications, electrophotographic recording, organic memory devices, biosensors, biochips, optoelectronic devices requiring similar phase shift at multiple wavelengths, combined CD/DVD/HD-DVD/Blu-Rays, reading, writing re-writing data storage systems, or cameras.

23. The device or component according to claim **22**, that is electrooptical displays, LCDs, optical films, polarizers, compensators, beam splitters, reflective films, alignment layers, color filters, holographic elements, hot stamping foils, colored images, decorative or security markings, LC pigments, adhesives, non-linear optic (NLO) devices, optical information storage devices, electronic devices, organic semiconductors, organic field effect transistors (OFET), integrated circuits (IC), thin film transistors (TFT), Radio Frequency Identification (RFID) tags, organic light emitting diodes (OLED), organic light emitting transistors (OLET), electroluminescent displays, organic photovoltaic (OPV) devices, organic solar cells (O-SC), organic laser diodes (O-laser), organic integrated circuits (O-IC), lighting devices, sensor devices, electrode materials, photoconductors, photodetectors, electrophotographic recording devices, capacitors, charge injection layers, Schottky diodes, **[**planarising**]** *planarizing* layers, antistatic films, conducting substrates, conducting patterns, photoconductors, electrophotographic applications, electrophotographic recording, organic memory devices, biosensors , or biochips.

24. A method for preparing the polymer film according to claim **16**, in which the polymerizable compound is prepared by

a) reacting a suitably substituted acetylene with an optionally substituted cyclohexanone in the presence of butyllithium,
b) separating the isomers thereby formed,
c) homocoupling an isomer prepared by steps a) and b) via its axial acetylenic substituents to give a dimer, or
d) coupling an isomer prepared by steps a) and b) via its axial acetylenic substituent to another optionally substituted cyclohexanone, or
e) coupling an isomer prepared by steps a) and b) via its axial acetylenic substituent to an aromatic ring, and coupling the resulting product to an identical or different isomer prepared by steps a+b).

25. The polymer film according to claim **6**, wherein U^1 and U^2 are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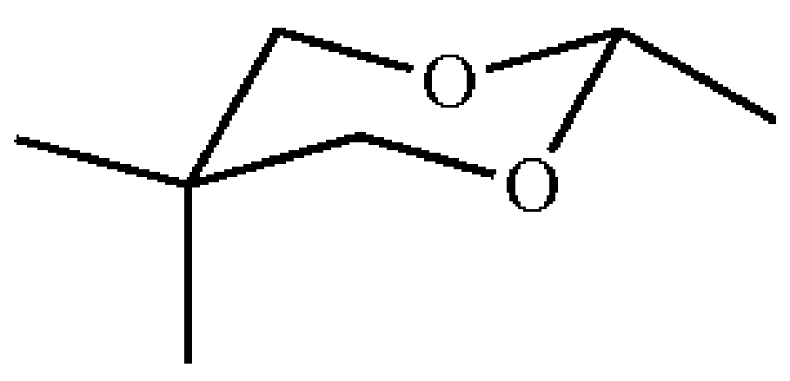
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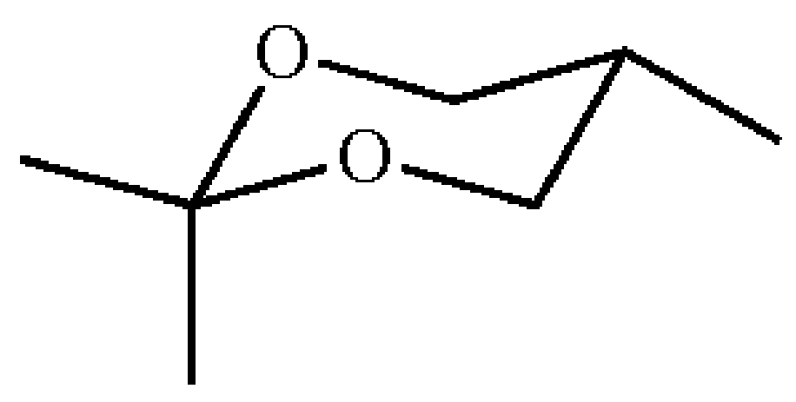
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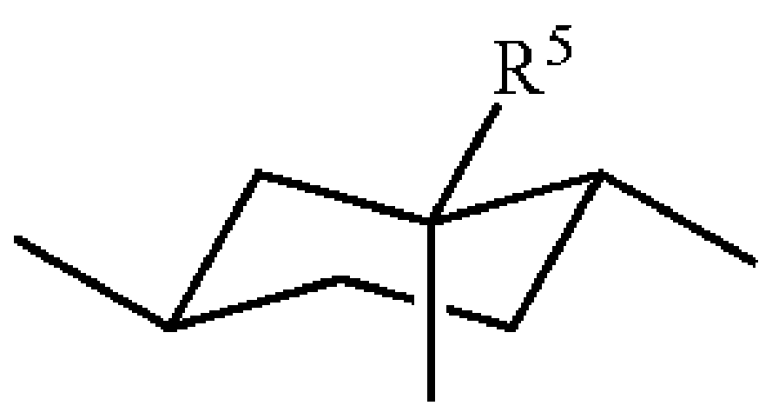
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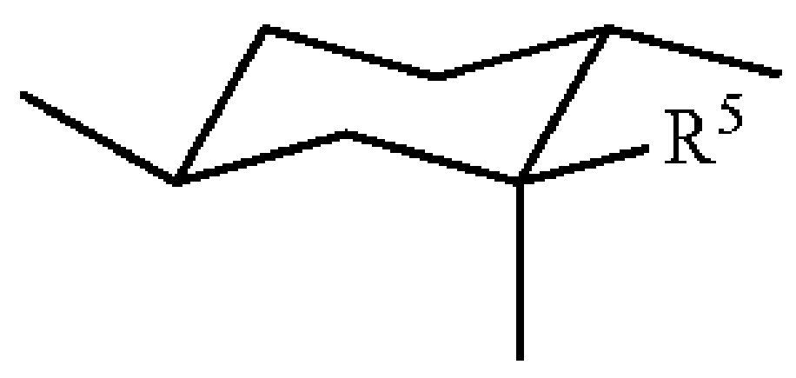

,

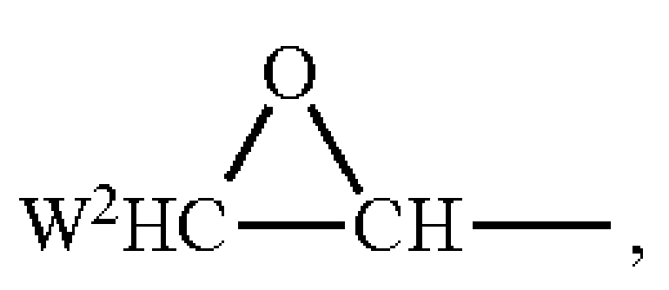
wherein R^5 is

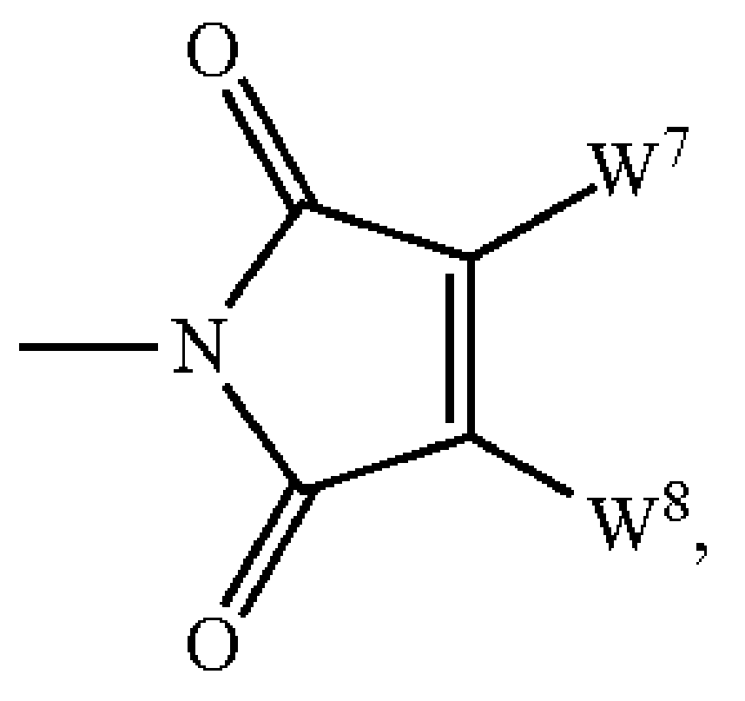
H, halogen, —CN, —NC, —NCO, —NCS, —OCN, —SCN, —C(═O)NR^0R^{00}, —C(═O)X^0, —C(═O)R^0, —NH_2, —NR^0R^{00}, —SH, —SR^0, —SO_3H, —SO_2R^0, —OH, —NO_2, —CF_3, —SF_5, P-Sp-, optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 40 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, or denote P or P-Sp-, or are substituted by P or P-Sp-, wherein the compounds comprise at least one group R^{1-5} denoting or being substituted by P or P-Sp-,

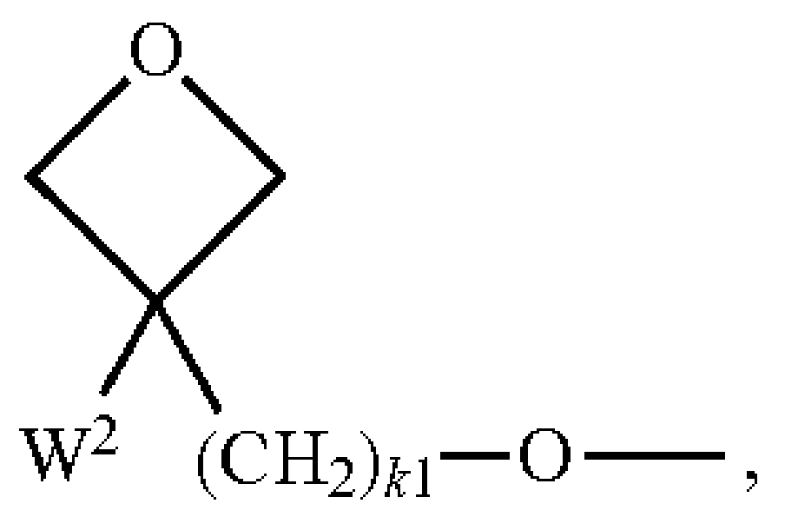
P is a polymerizable group, and

Sp is a spacer group or a single bond.

26. The polymer film according to claim **6**, wherein P is $CH_2{=}CW^1{-}COO{-}$, $CH_2{=}CW^1{-}CO{-}$,







$CH_2{=}CW^2{-}(O)_{k1}{-}$, $CH_3{-}CH{=}CH{-}O{-}$, $(CH_2{=}CH)_2CH{-}OCO{-}$, $(CH_2{=}CH{-}CH_2)_2CH{-}OCO{-}$, $(CH_2{=}CH)_2CH{-}O{-}$, $(CH_2{=}CH{-}CH_2)_2N{-}$, $(CH_2{=}CH{-}CH_2)_2N{-}CO{-}$, $HO{-}CW^2W^3{-}$, $HS{-}CW^2W^3{-}$, $HW^2N{-}$, $HO{-}CW^2W^3{-}NH{-}$, $CH_2{=}CW^1{-}CO{-}NH{-}$, $CH_2{=}CH{-}(COO)_{k1}$-Phe-$(O)_{k2}{-}$, $CH_2{=}CH{-}(CO)_{k1}$-Phe-$(O)_{k2}{-}$, Phe-$CH{=}CH{-}$, $HOOC{-}$, $OCN{-}$, and $W^4W^5W^6Si{-}$, with W^1 being H, F, Cl, CN, CF_3, phenyl or alkyl with 1 to 5 C-atoms, W^2 and W^3 being independently of each other H or alkyl with 1 to 5 C-atoms, W^4, W^5 and W^6 being independently of each other Cl, oxaalkyl or oxacarbonylalkyl with 1 to 5 C-atoms, W^7 and W^8 being independently of each other H, Cl or alkyl with 1 to 5 C-atoms, Phe being 1,4-phenylene that is optionally substituted, and k_1 and k_2 being independently of each other 0 or 1.

27. The polymer film according to claim **6**, wherein Sp is Sp'-X', such that P-Sp- is P-Sp'-X'—, wherein

Sp' is alkylene with 1 to 20 C atoms, preferably 1 to 12 C-atoms, which is optionally mono- or polysubstituted by F, Cl, Br, I or CN, and wherein one or more non-adjacent CH_2 groups are optionally replaced, in each case independently from one another, by —O—, —S—, —NH—, $—NR^0—$, $—SiR^0R^{00}—$, —CO—, —COO—, —OCO—, —OCO—O—, —S—CO—, —CO—S—, $—NR^0—CO—O—$, $—O—CO—NR^0—$, $—NR^0—CO—NR^0—$, —CH=CH— or $—C{\equiv}C—$ in such a manner that O and/or S atoms are not linked directly to one another,

X' is —O—, —S—, —CO—, —COO—, —OCO—, —O—COO—, $—CO—NR^0—$, $—NR^0—CO—$, $—NR^0—CO—NR^0—$, $—OCH_2—$, $—CH_2O—$, $—SCH_2—$, $—CH_2S—$, $—CF_2O—$, $—OCF_2—$, $—CF_2S—$, $—SCF_2—$, $—CF_2CH_2—$, $—CH_2CF_2—$, $—CF_2CF_2—$, —CH=N—, —N=CH—, —N=N—, $—CH{=}CR^0—$, $—CY^1{=}CY^2—$, $—C{\equiv}C—$, —CH=CH—COO—, —OCO—CH=CH— or a single bond,

R^0, R^{00} are independently of each other H or alkyl with 1 to 12 C-atoms,

$Y^{1,2}$ are independently of each other H, F, Cl, CN or R^0.

28. A polymerizable compound containing

two mesogenic groups comprising one or more non-aromatic rings,

one or more polymerizable groups attached to at least one of the mesogenic groups either directly or via spacer groups, and

a bridging group connecting the mesogenic groups, comprising one or more subgroups selected from pi-conjugated linear carbyl or hydrocarbyl groups, aromatic and heteroaromatic groups, and being linked to a sp^3-hybridized C-atom or Si-atom in a non-aromatic ring of each mesogenic group.

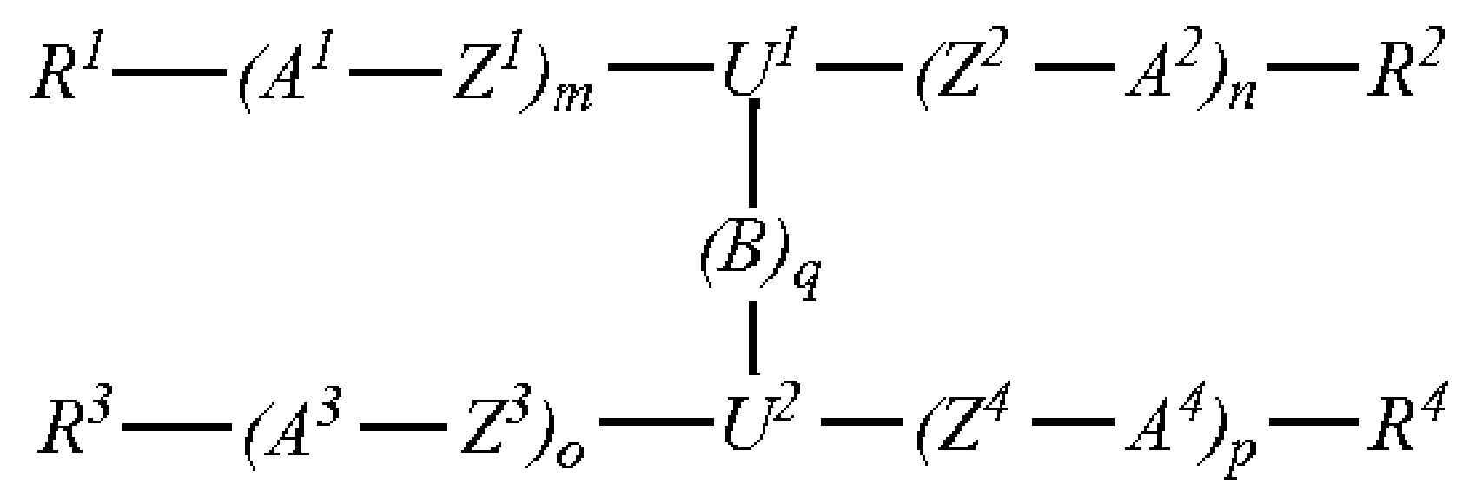
29. The polymerizable compound according to claim 28, wherein the mesogenic groups are calamitic groups.

30. The polymerizable compound according to claim 28, wherein the mesogenic groups comprise more saturated rings than unsaturated or aromatic rings.

31. The polymerizable compound according to claim 28, wherein the bridging group is a subgroup selected from the group consisting of pi-conjugated linear groups, aromatic and heteroaromatic groups.

32. The polymerizable compound according to claim 28, wherein the bridging group is connected in axial position to a cyclohexylene or silanane ring comprised in the mesogenic group, which is optionally substituted and wherein one or more non-adjacent C-atoms are optionally replaced by Si and/or one or more non-adjacent CH_2 groups are optionally replaced by —O— and/or —S—.

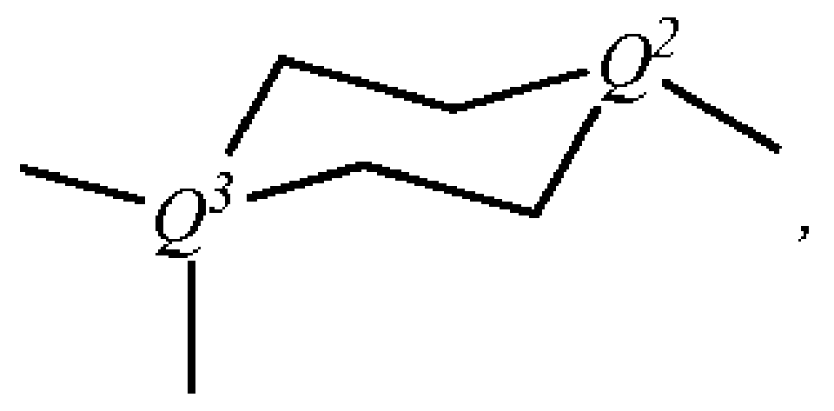
33. The polymerizable compound according to claim 28, wherein the polymerizerable compounds are of the following formula



$$\begin{array}{c} R^1{-}(A^1{-}Z^1)_m{-}U^1{-}(Z^2{-}A^2)_n{-}R^2 \\ | \\ (B)_q \\ | \\ R^3{-}(A^3{-}Z^3)_o{-}U^2{-}(Z^4{-}A^4)_p{-}R^4 \end{array} \qquad I$$

wherein

$U^{1,2}$ are independently of each other selected from



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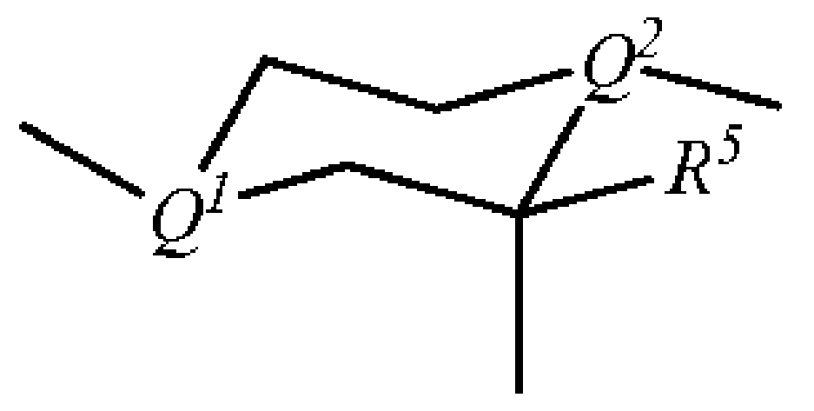
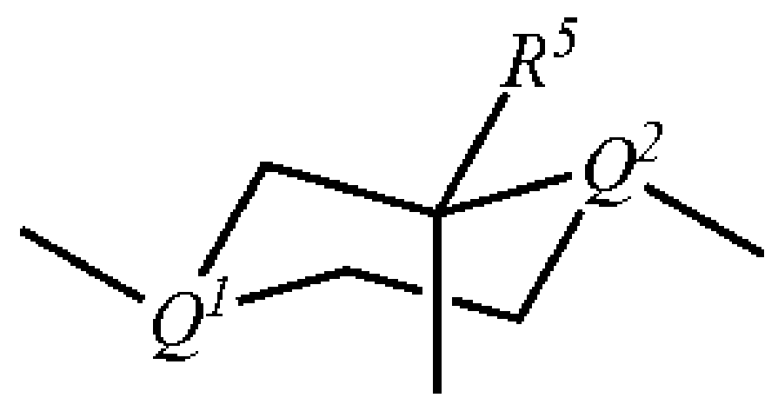


and



including their mirror images, wherein the rings U^1 and U^2 are each bonded to the group $—(B)_q—$ via the axial bond, and one or two non-adjacent CH_2 groups in these rings are optionally replaced by O and/or S, and the rings U^1 and U^2 are optionally substituted by one or more groups L,

$Q^{1,2}$ are independently of each other CH or SiH,

Q^3 is C or Si,

B is in each occurrence independently of one another $—C{\equiv}C—$, $—CY^1{=}CY^2—$ or an optionally substituted aromatic or heteroaromatic group,

$Y^{1,2}$ are independently of each other H, F, Cl, CN or R^0,

q is an integer from 1 to 10, preferably 1, 2, 3, 4, 5 or 6,

A^{1-4} are independently of each other non-aromatic carbocylic or heterocyclic groups and aromatic and heteroaromatic groups, which are optionally substituted by one or more groups R^5, and wherein each of -(A^1-Z^1)$_m$—U^1—(Z^2-A^2)$_n$— and —(A^3-Z^3)$_o$—U^2—(Z^4-A^4)$_p$— does not contain more aromatic groups than non-aromatic groups,

Z^{1-4} are independently of each other —O—, —S—, —CO—, —COO—, —OCO—, —O—COO—, —CO—NR^0—, —NR^0—CO—, —NR^0—CO—NR^0—, —OCH$_2$—, —CH$_2$O—, —SCH$_2$—, —CH$_2$S—, —CF$_2$O—, —OCF$_2$—, —CF$_2$S—, —SCF$_2$—, —CH$_2$CH$_2$—, —(CH$_2$)$_3$—, —(CH$_2$)$_4$—, —CF$_2$CH$_2$—, —CH$_2$CF$_2$—, —CF$_2$CF$_2$—, —CH═CH—, —CY^1═CY^2—, —CH═N—, —N═CH—, —N═N—, —CH═CR^0—, —C≡C—, —CH═CH—COO—, —OCO—CH═CH—, CR^{0}R^{00} or a single bond,

R^0, R^{00} are independently of each other H or alkyl with 1 to 12 C-atoms,

m and n are independently of each other 0, 1, 2, 3 or 4,

o and p are independently of each other 0, 1, 2, 3 or 4,

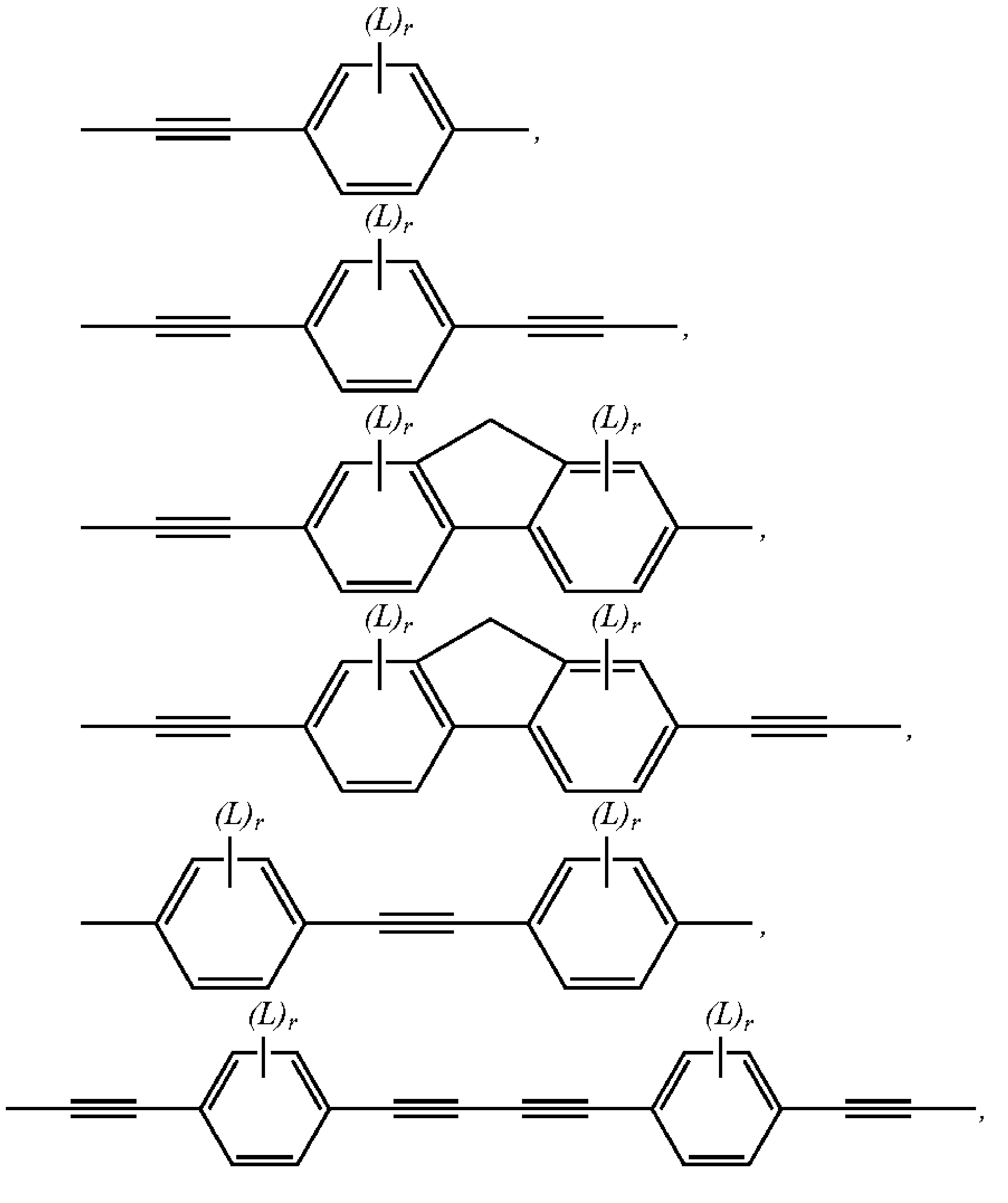
R^{1-5} are independently

H, halogen, —CN, —NC, —NCO, —NCS, —OCN, —SCN, —C(═O)NR^{0}R^{00}, —C(═O)X^0, —C(═O)R^0, —NH$_2$, —NR^{0}R^{00}, —SH, —SR^0, —SO$_3$H, —SO$_2$R^0, —OH, —NO$_2$—, —CF$_3$, —SF$_5$, P-Sp-, optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 40 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, or denote P or P-Sp-, or are substituted by P or P-Sp-, wherein the compounds comprise at least one group R^{1-5} denoting or being substituted by P or P-Sp-,

P is a polymerizable group, and

Sp is a spacer group or a single bond.

34. The polymerizable compound according to claim 28, wherein the bridging group, is —C≡C—, —C≡C—C≡C—, —C≡C—C≡C—C≡C—, —C≡C—C≡C—C≡C—C≡C—,



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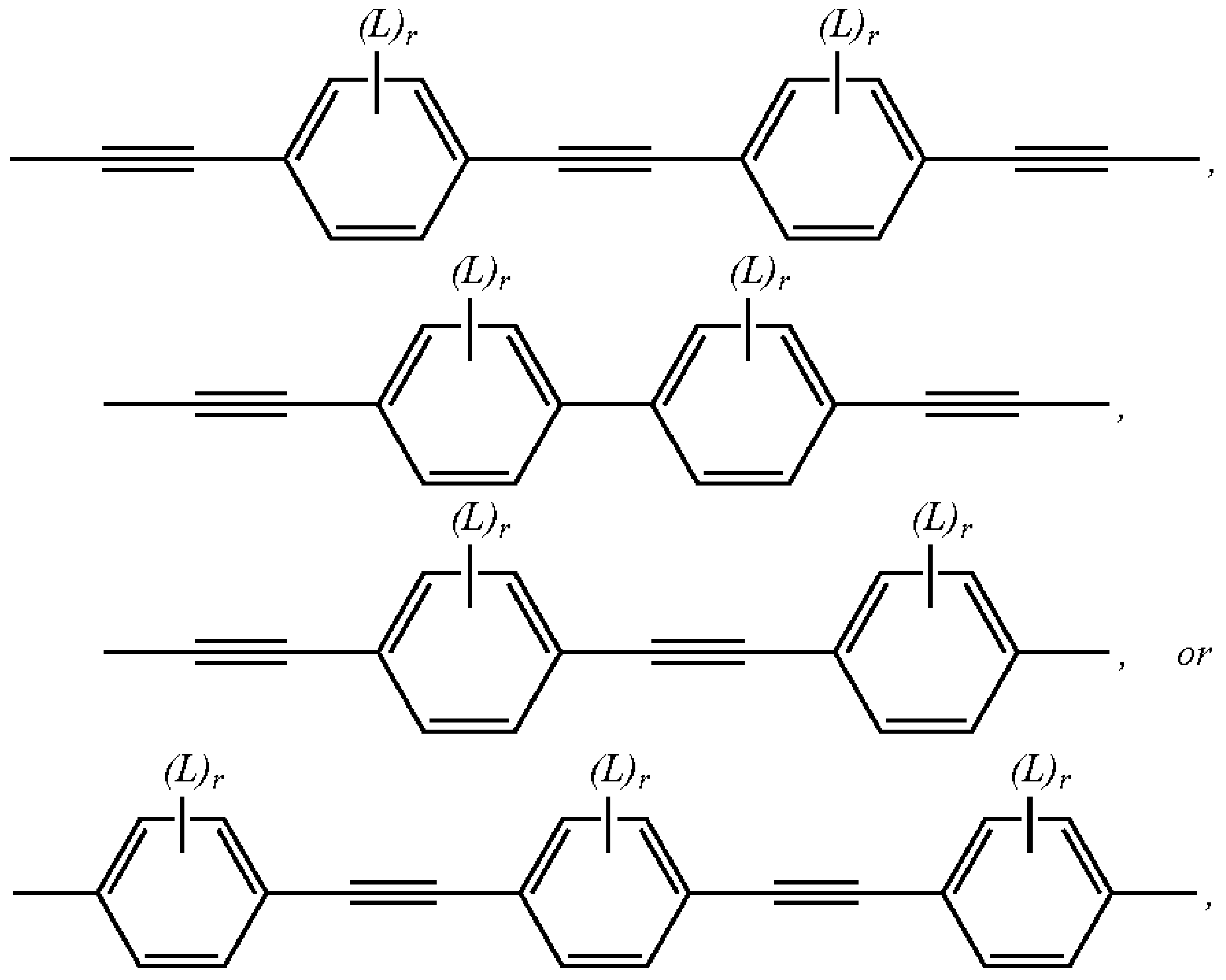
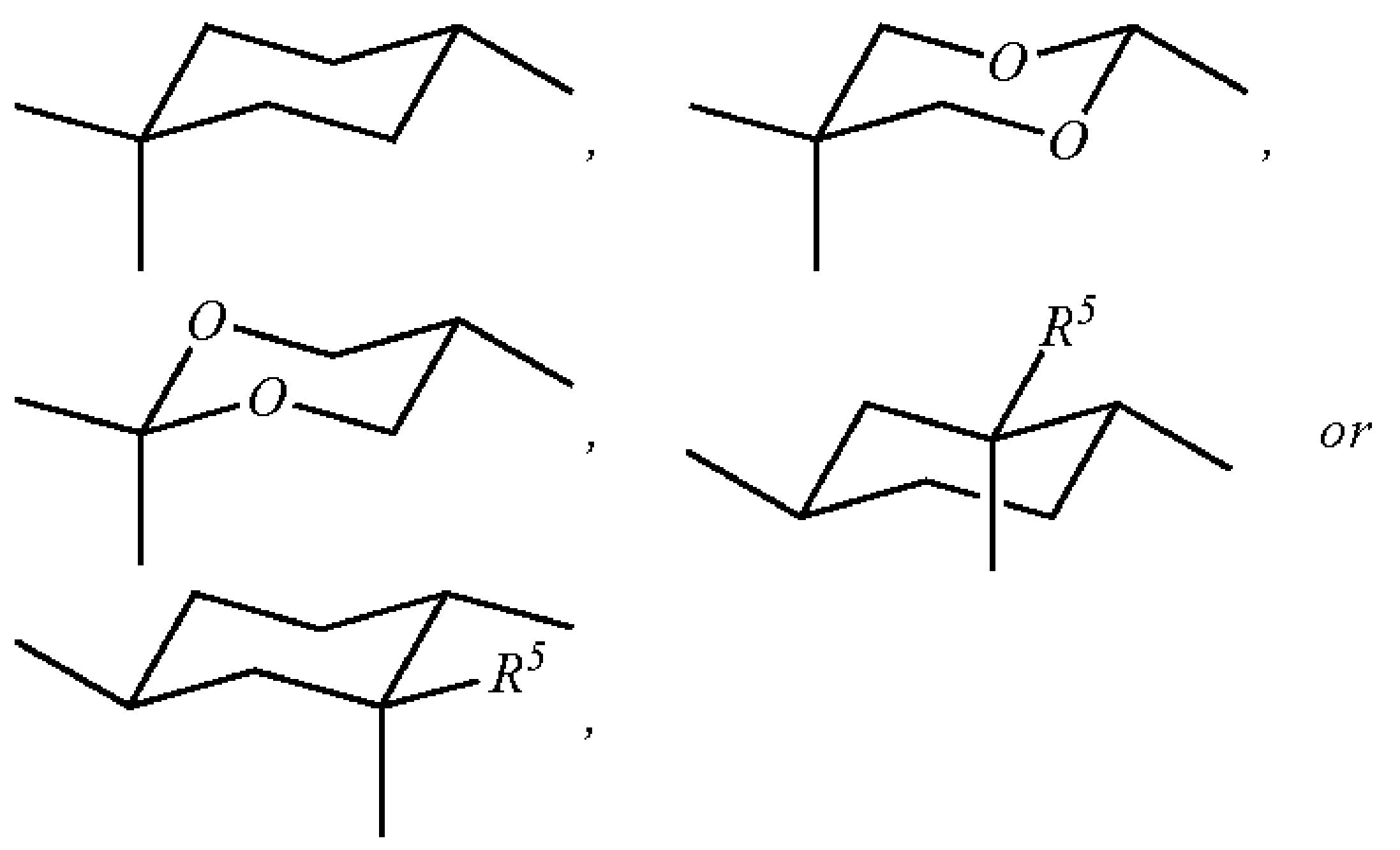


wherein r is 0, 1, 2, 3 or 4 and L is P-Sp-, F, Cl, Br, I, —CN, —NO$_2$, —NCO, —NCS, —OCN, —SCN, —C(═O)NR^{0}R^{00}, —C(═O)X, —C(═O)OR^0, —C(═O)R^0, —NR^{0}R^{00}, —OH, —SF$_5$, optionally substituted silyl, aryl with 1 to 12 C atoms, or straight chain or branched alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy with 1 to 12 C atoms, wherein one or more H atoms are optionally replaced by F or Cl, wherein R^0 and R^{00} are independently H or alkyl with 1-12 C atoms and X is halogen.

35. The polymerizable compound according to claim 28, wherein the non-aromatic rings of the mesogenic groups where the bridging group is attached are



wherein R^5 is H, halogen, —CN, —NC, —NCO, —NCS, —OCN, —SCN, —C(═O)NR^{0}R^{00}, —C(═O)X^0, —C(═O)R^0, —NH$_2$, —NR^{0}R^{00}, —SH, —SR^0, —SO$_3$H, —SO$_2$R^0, —OH, —NO$_2$, —CF$_3$, —SF$_5$, P-Sp-, optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 40 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, or denote P or P-Sp-, or are substituted by P or P-Sp-, wherein the compounds comprise at least one group R^{1-5} denoting or being substituted by P or P-Sp-,

P is a polymerizable group, and

Sp is a spacer group or a single bond.

36. The polymerizable compound according to claim 28, wherein the aromatic and non-aromatic groups, are trans-1,4-cyclohexylene and 1,4-phenylene that is optionally substituted with one or more groups L, and L is P-Sp-, F, Cl, Br, I, —CN, —NO$_2$, —NCO, —NCS, —OCN, —SCN, —C(═O)NR^{0}R^{00}, —C(═O)X, —C(═O)OR^0, —C(═O)R^0, —NR^{0}R^{00}, —OH, —SF$_5$, optionally substituted silyl, aryl *with 1 to 12 C atoms, or straight chain or branched alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy with 1 to 12 C atoms, wherein one or more H atoms are optionally replaced by F or Cl, wherein* R^0 *and* R^{00} *are independently H or alkyl with 1-12 C atoms and X is halogen.*

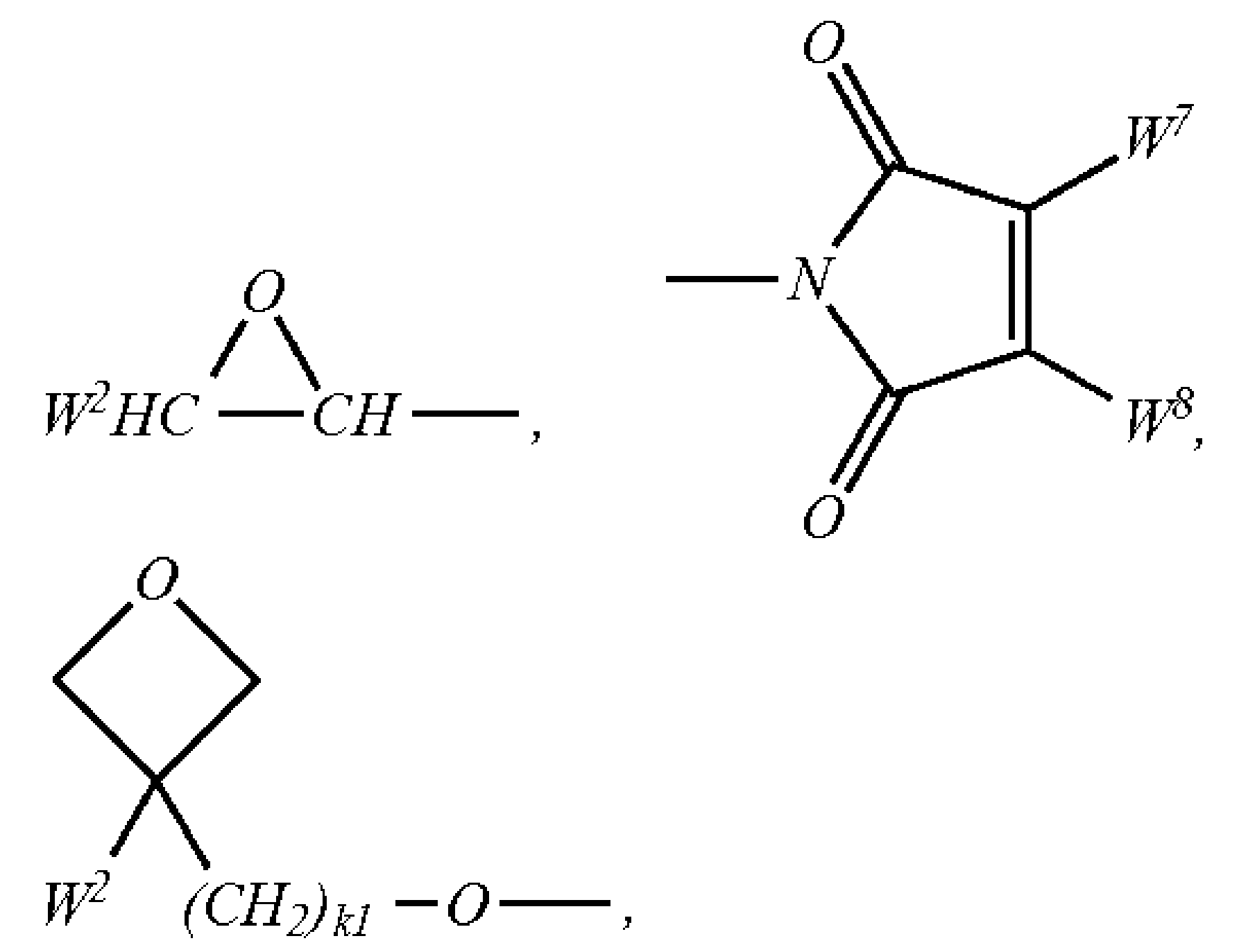
37. The polymerizable compound according to claim 28, wherein the mesogenic groups do not comprise more than one unsaturated or aromatic ring.

38. The polymerizable compound according to claim 28, wherein bridging groups connecting the aromatic and non-aromatic cyclic groups in the mesogenic groups, are —O—, —S—, —CO—, —COO—, —OCO—, —O—COO—, —CO—NR^0—, —NR^0—CO—, —NR^0—CO—NR^0—, —OCH_2—, —CH_2O—, —SCH_2—, —CH_2S—, —CF_2O—, —OCF_2—, —CF_2S—, —SCF_2—, —CH_2CH_2—, —$(CH_2)_3$—, —$(CH_2)_4$—, —CF_2CH_2—, —CH_2CF_2—, —CF_2CF_2—, —CH═CH—, —CY^1═CY^2—, —CH═N—, —N═CH—, —N═N—, —CH═CR^0—, —C≡C—, —CH═CH—COO—, —OCO—CH═CH—, CR^0R^{00} *or a single bond,*

R^0, R^{00} *are independently of each other H or alkyl with 1 to 12 C-atoms, and*

Y^1 *and* Y^2 *are* $Y^{1,2}$ *are independently of each other H, F, Cl, CN or* R^0.

39. The polymerizable compound according to claim 28, wherein the polymerizable group, is CH_2═CW^1—COO—, CH_2═CW^1—CO—,



CH_2═CW^2—$(O)_{k1}$—, CH_3—CH═CH—O—, $(CH_2$═$CH)_2$ CH—OCO—, $(CH_2$═CH—$CH_2)_2$CH—OCO—, $(CH_2$═$CH)_2$CH—O—, $(CH_2$═CH—$CH_2)_2$N—, $(CH_2$═CH—$CH_2)_2$N—CO—, HO—CW^2W^3—, HS—CW^2W^3—, HW^2N—, HO—CW^2W^3—NH—, CH_2═CW^1—CO—NH—, CH_2═CH—$(COO)_{k1}$—Phe—$(O)_{k2}$—, CH_2═CH—$(CO)_{k1}$—Phe—$(O)_{k2}$—, Phe—CH═CH—, HOOC—, OCN—, *or* $W^4W^5W^6$Si—, *with* W^1 *being H, F, Cl, CN,* CF_3, *phenyl or alkyl with 1 to 5 C-atoms,* W^2 *and* W^3 *being independently of each other H or alkyl with 1 to 5 C-atoms,* W^4, W^5 *and* W^6 *being independently of each other Cl, oxaalkyl or oxacarbonylalkyl with 1 to 5 C-atoms,* W^7 *and* W^8 *being independently of each other H, Cl or alkyl with 1 to 5 C-atoms, Phe being 1,4-phenylene that is optionally substituted, and* k_1 *and* k_2 *being independently of each other 0 or 1.*

40. The polymerizable compound according to claim 28, wherein the spacer group is Sp'-X', such that P-Sp- is P-Sp'-X'-, wherein

Sp' is alkylene with 1 to 20 C atoms, preferably 1 to 12 C-atoms, which is optionally mono- or polysubstituted by F, Cl, Br, I or CN, and wherein one or more non-adjacent CH_2 *groups are optionally replaced, in each case independently from one another, by* —O—, —S—, —NH—, —NR^0—, —SiR^0R^{00}—, —CO—, —COO—, —OCO—, —OCO—O—, —S—CO—, —CO—S—, —NR^0—CO—O—, —O—CO—NR^0—, —NR^0—CO—NR^0—, —CH═CH— *or* —C≡C— *in such a manner that O and/or S atoms are not linked directly to one another,*

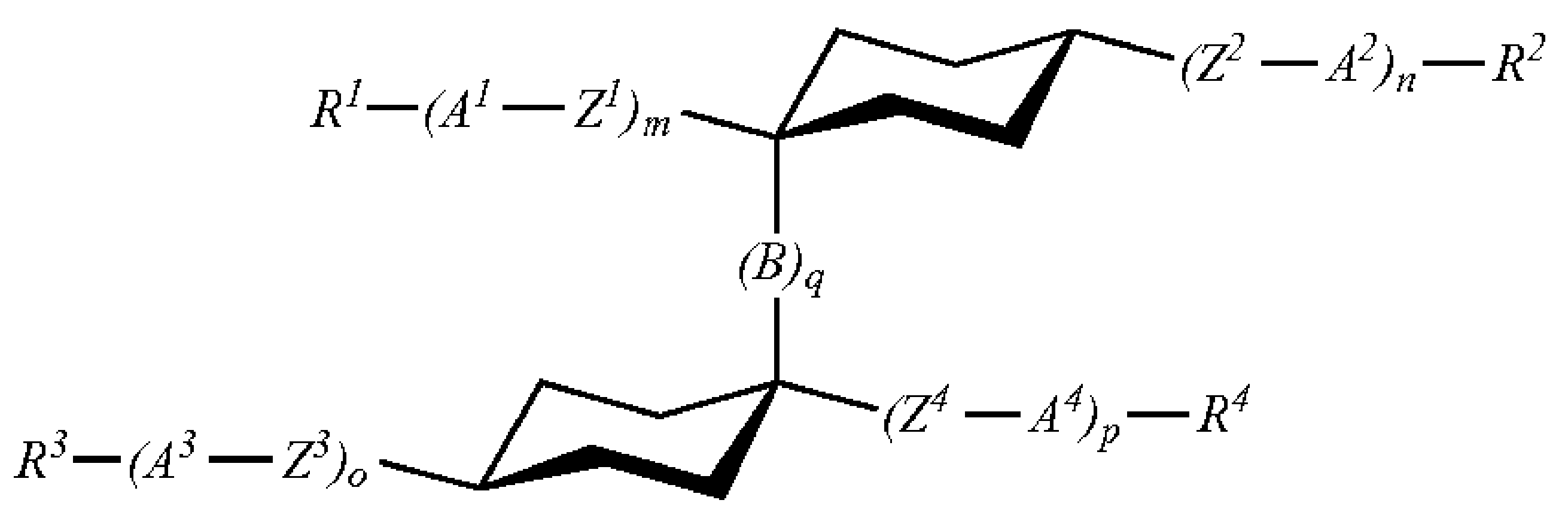
X' is —O—, —S—, —CO—, —COO—, —OCO—, —O—COO—, —CO—NR^0—, —NR^0—CO—, —NR^0—CO—NR^0—, —OCH_2—, —CH_2O—, —SCH_2—, —CH_2S—, —CF_2O—, —OCF_2—, —CF_2S—, —SCF_2—, —CF_2CH_2—, —CH_2CF_2—, —CF_2CF_2—, —CH═N—, —N═CH—, —N═N—, —CH═CR^0—, —CY^1═CY^2—, —C≡C—, —CH═CH—COO—, —OCO—CH═CH— *or a single bond,*

R^0, R^{00} *are independently of each other H or alkyl with 1 to 12 C-atoms,*

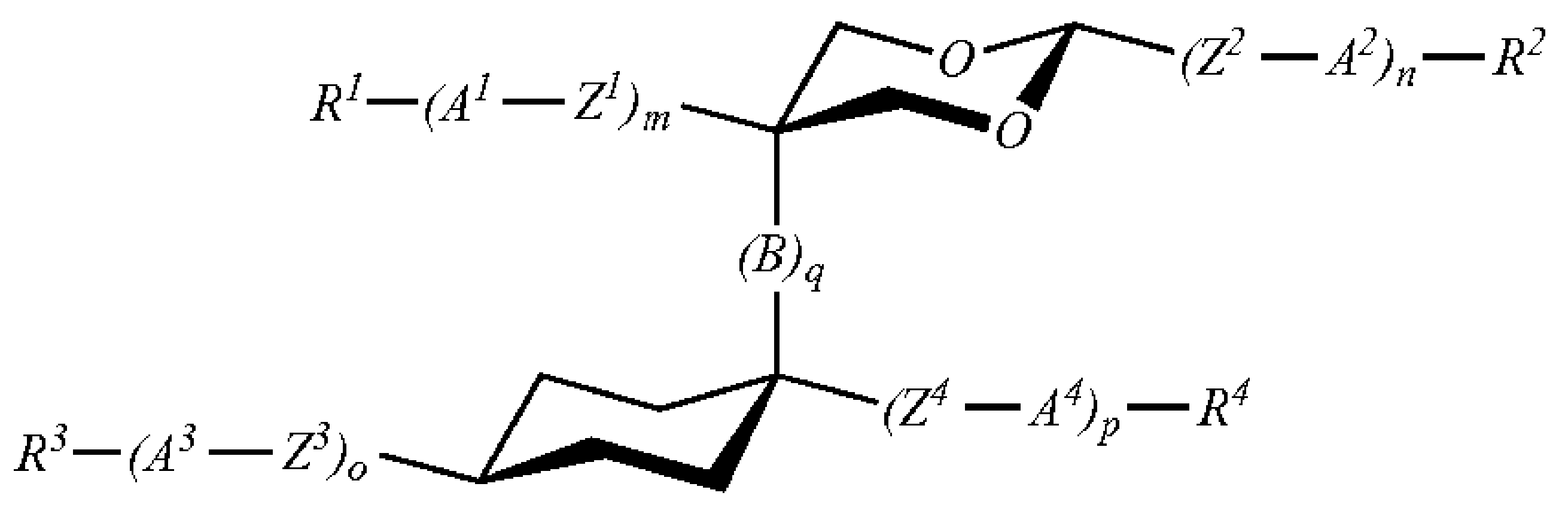
$Y^{1,2}$ *are independently of each other H, F, Cl, CN or* R^0.

41. The polymerizable compound according to claim 28, wherein the polymerizable compounds are:

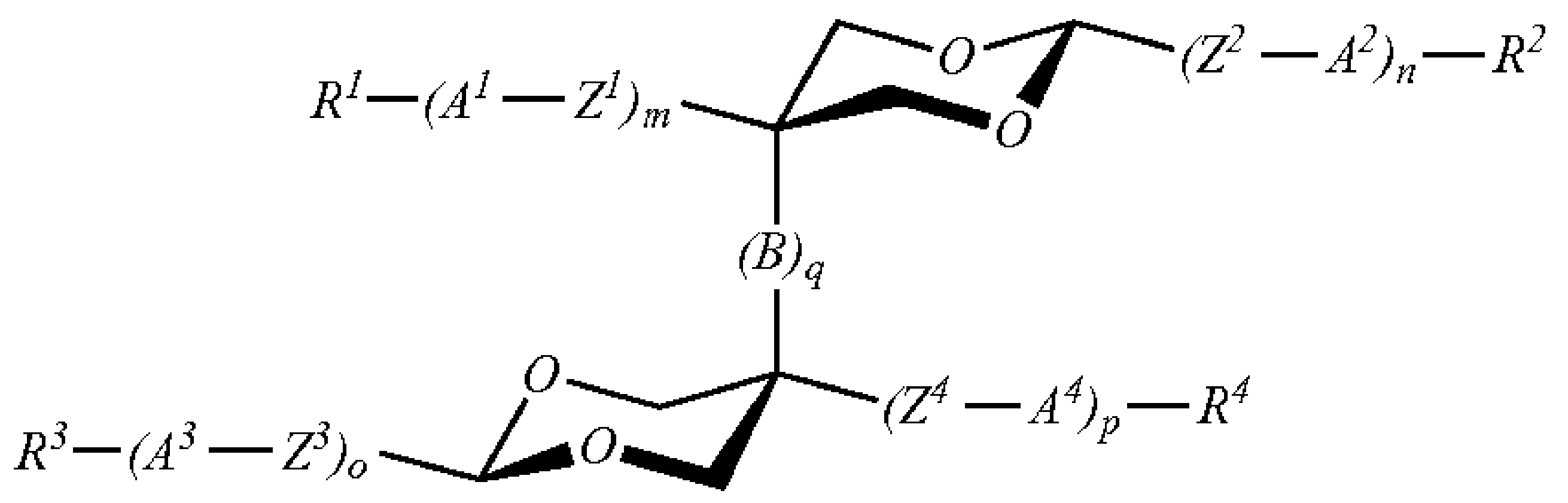
Ia



Ib



Ic



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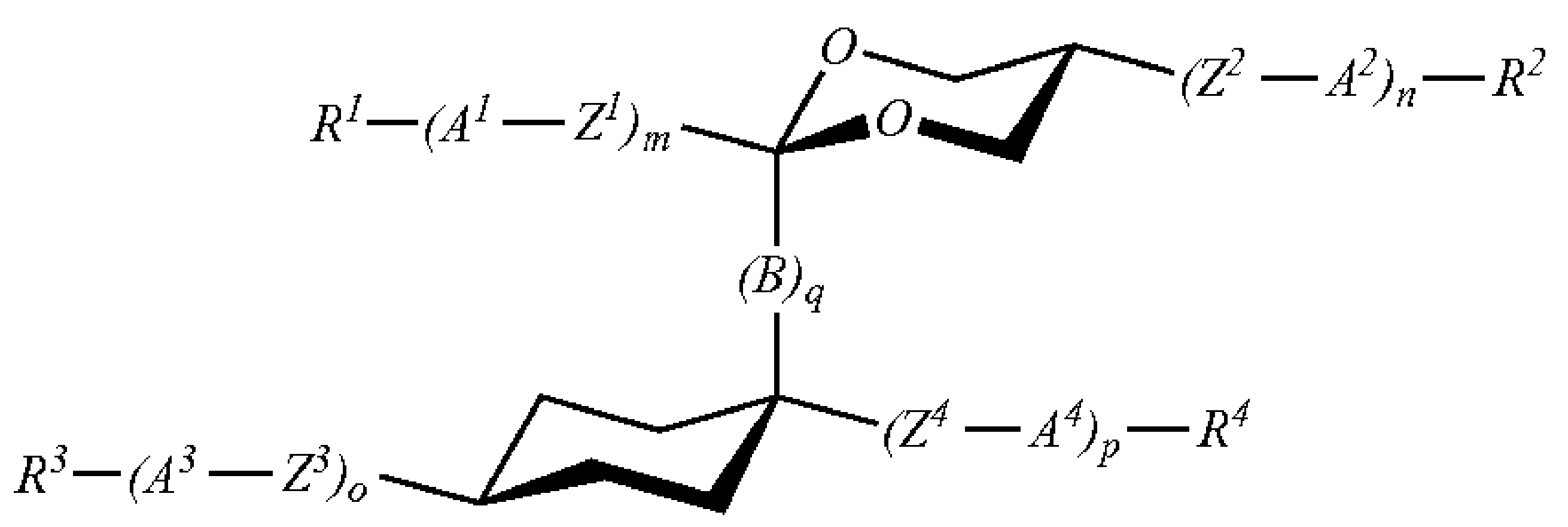
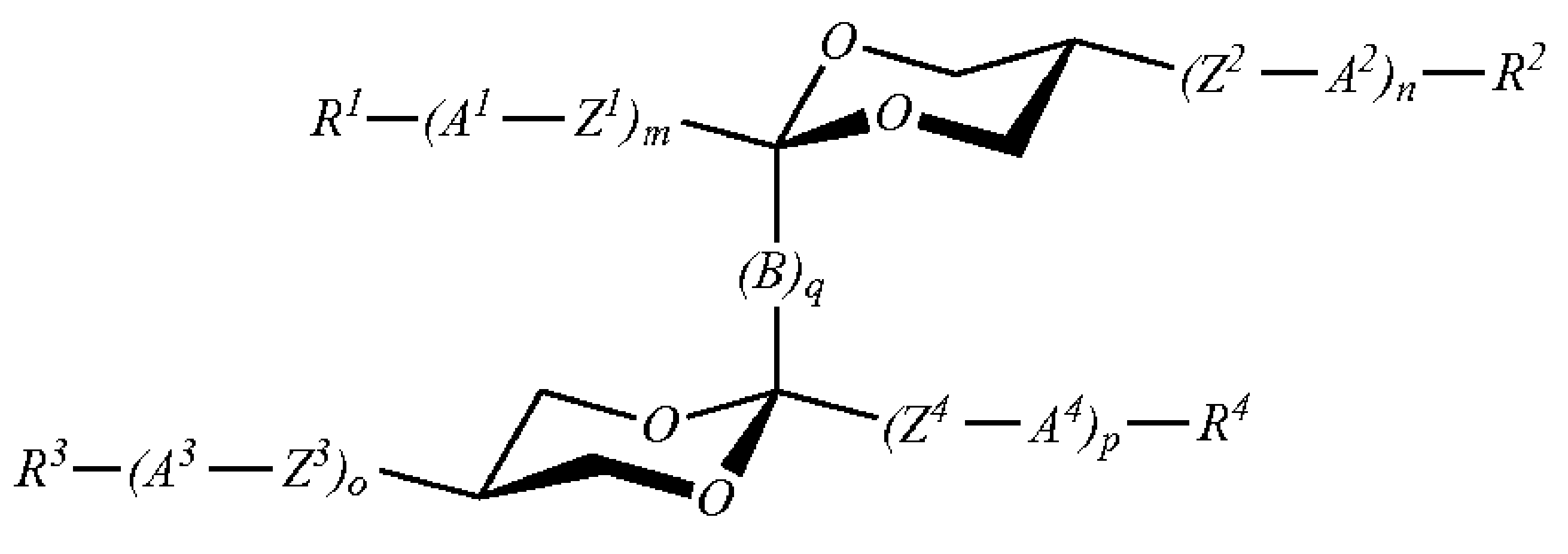


Ie



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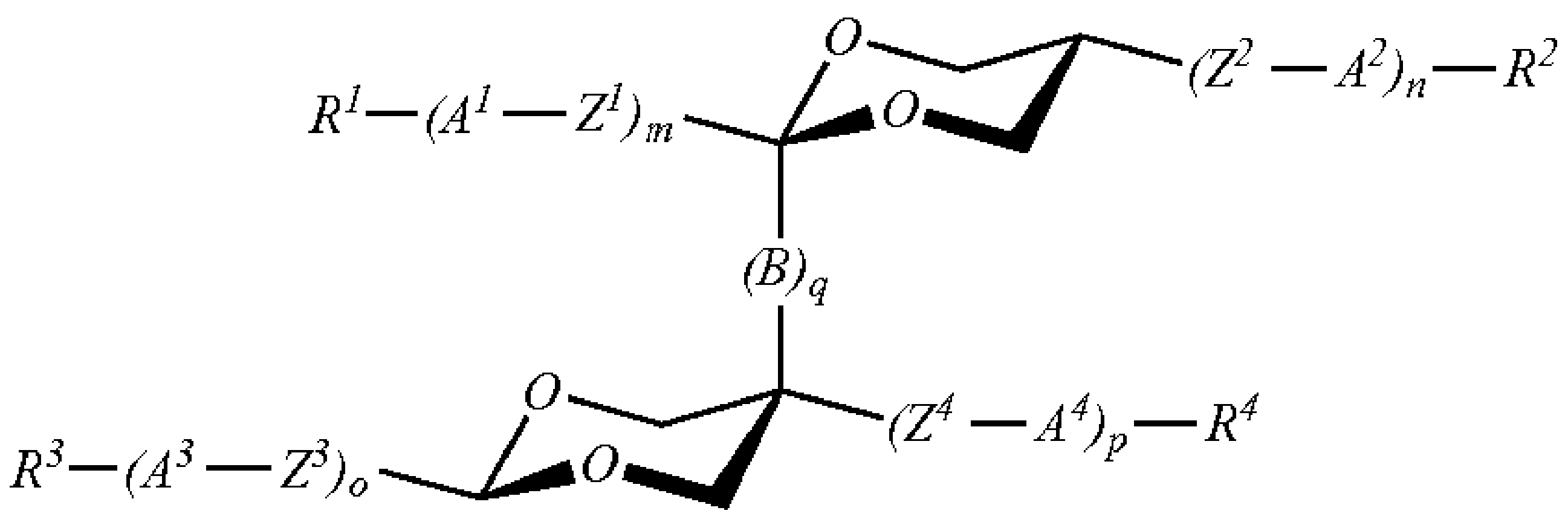
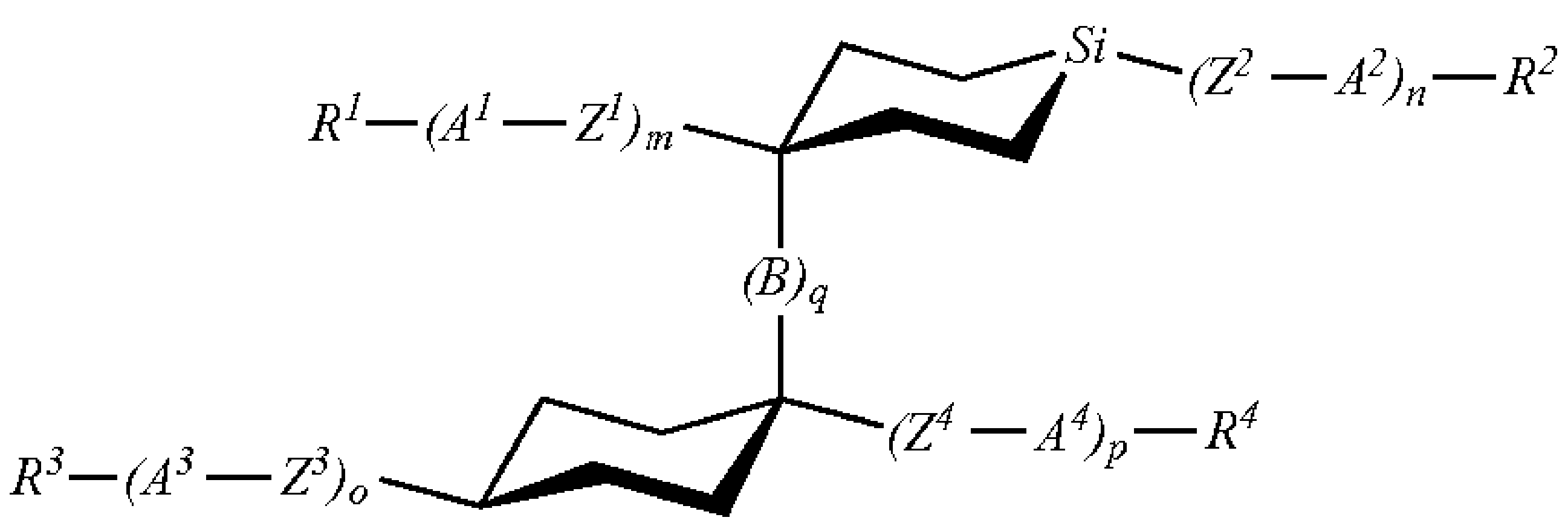


Ig



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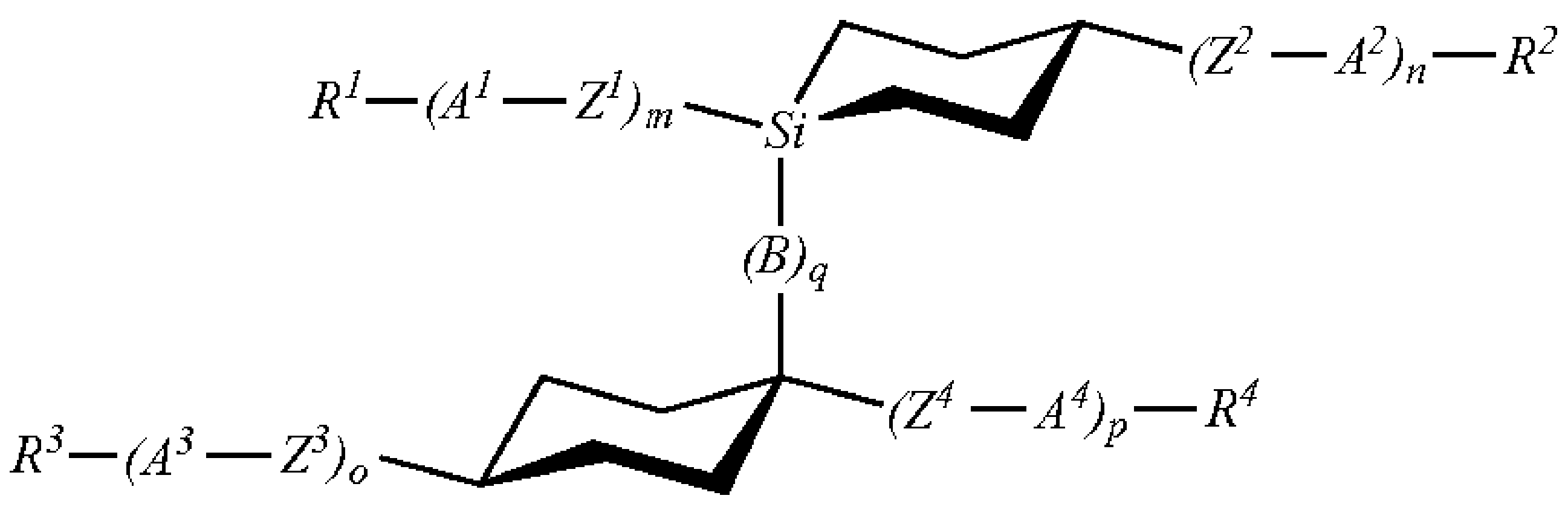

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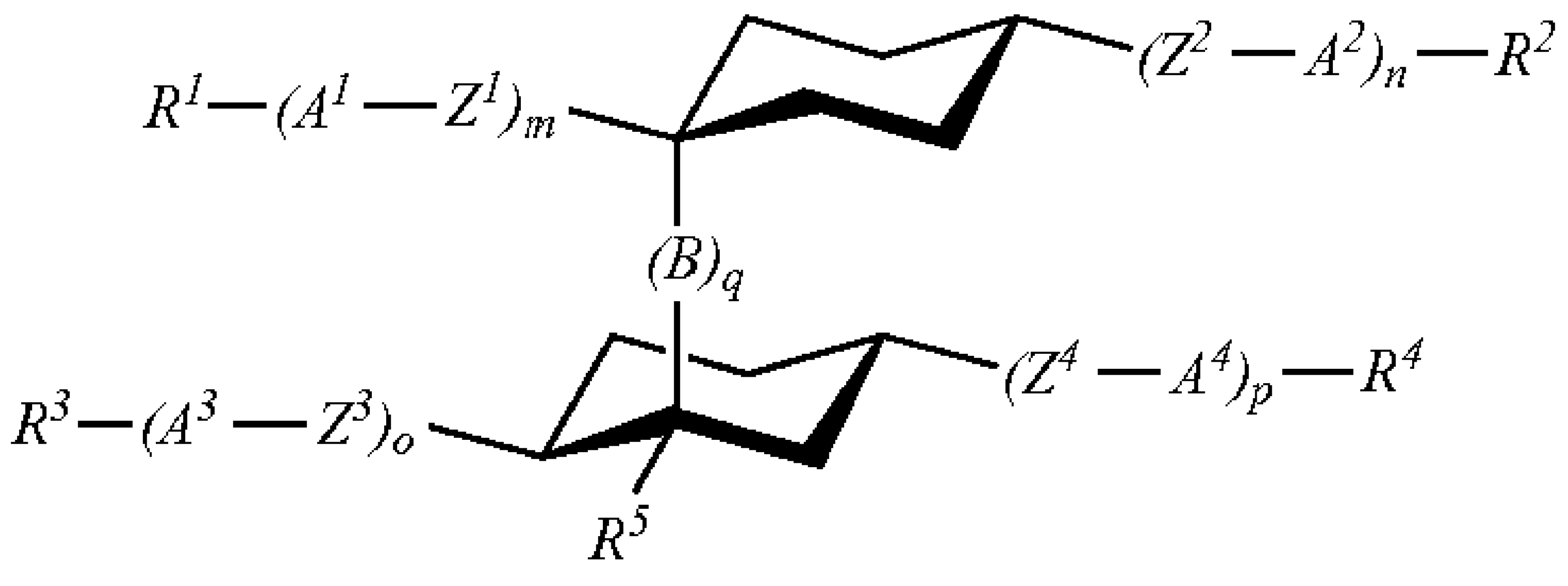

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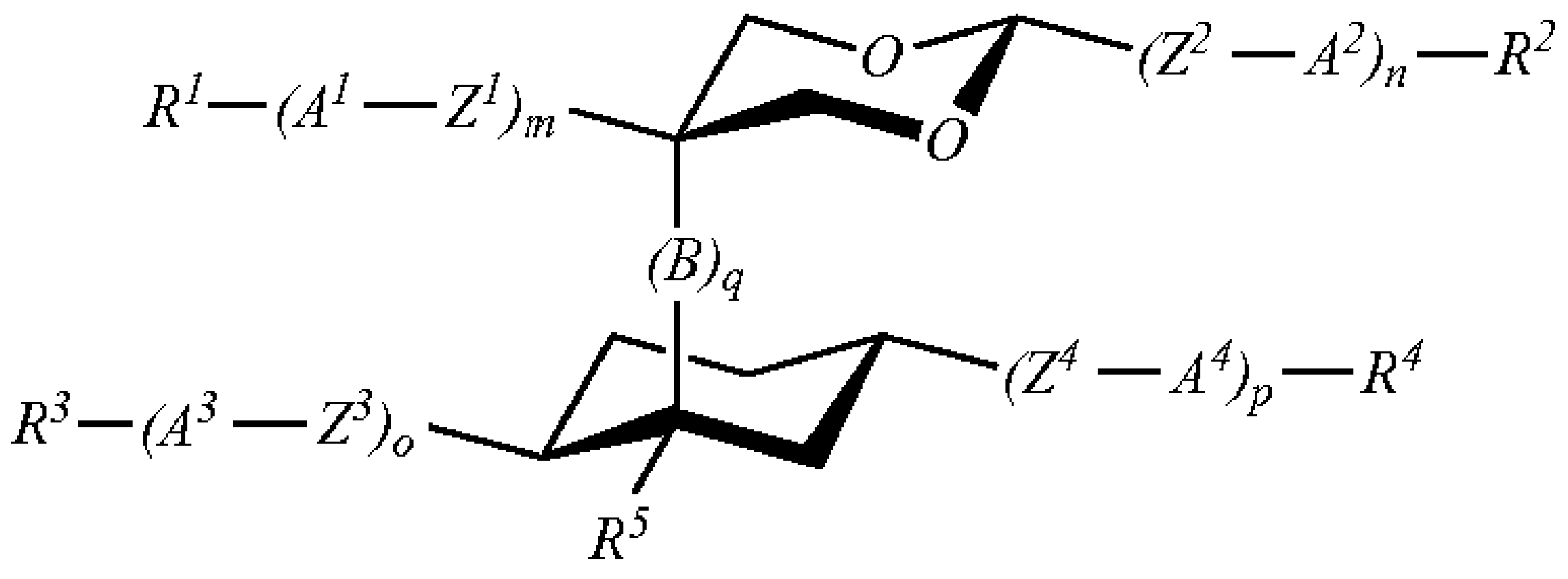

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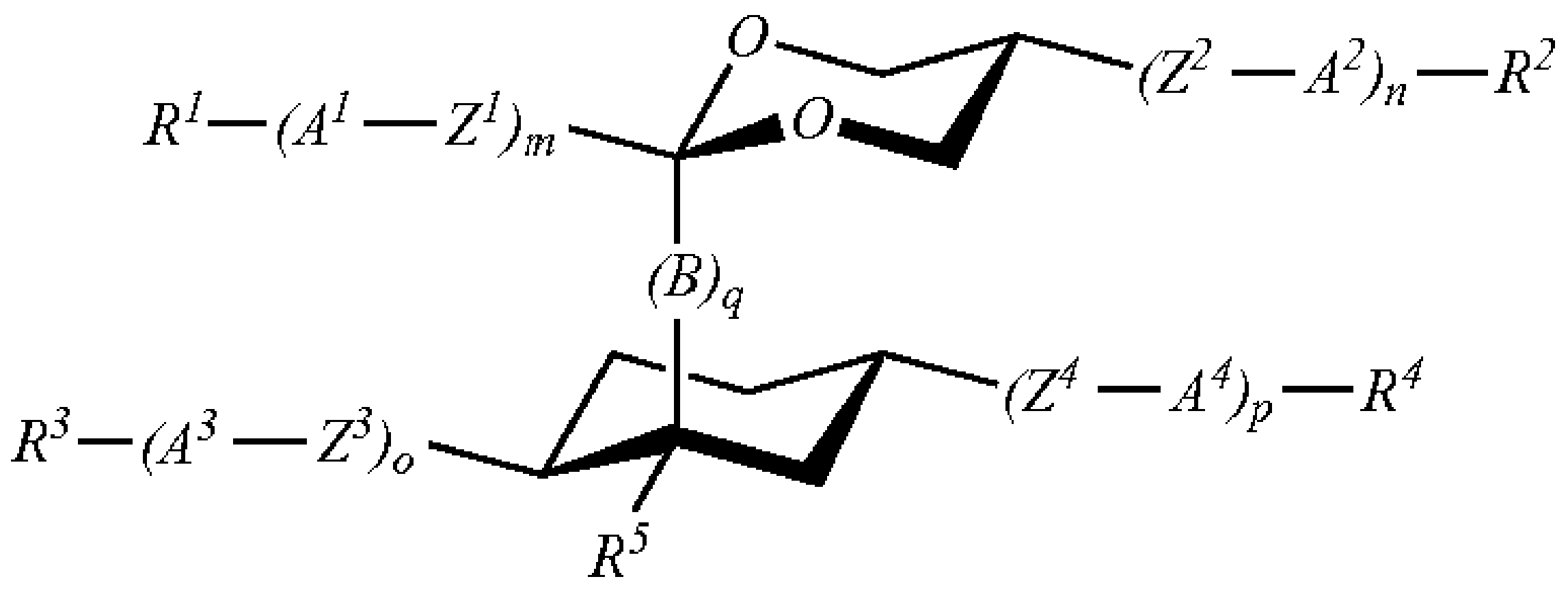

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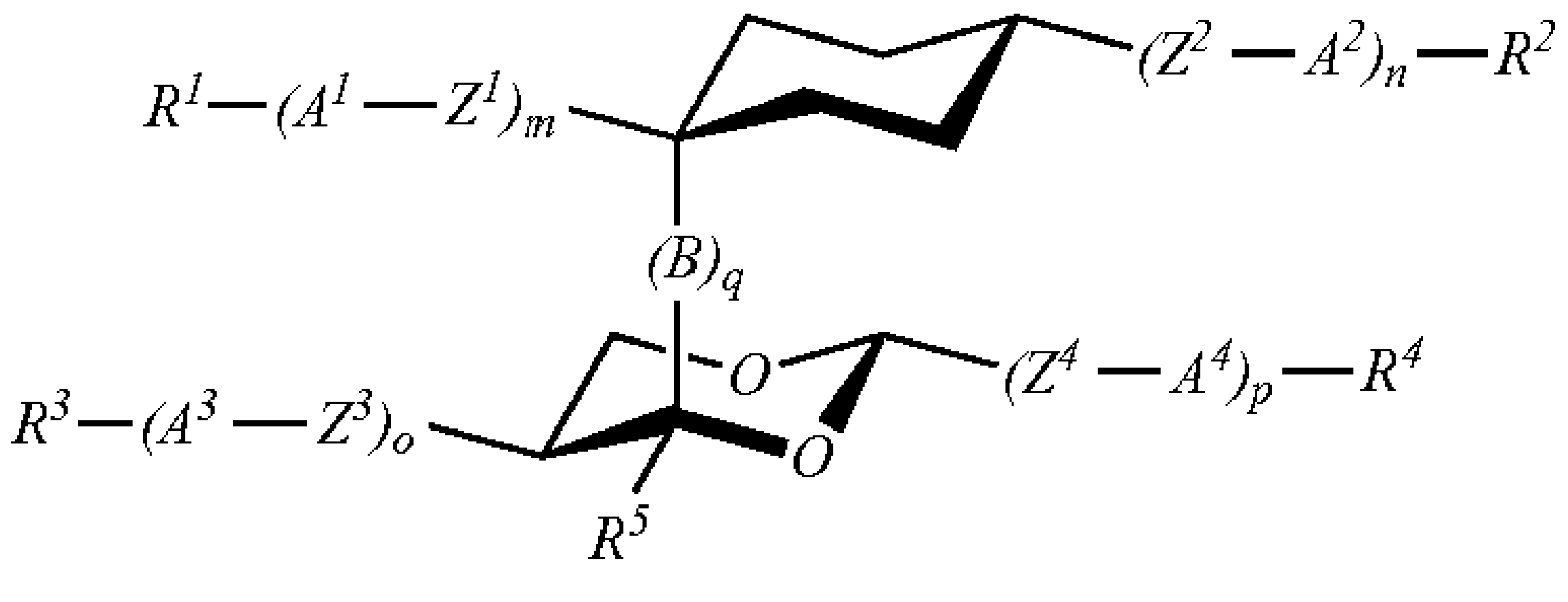

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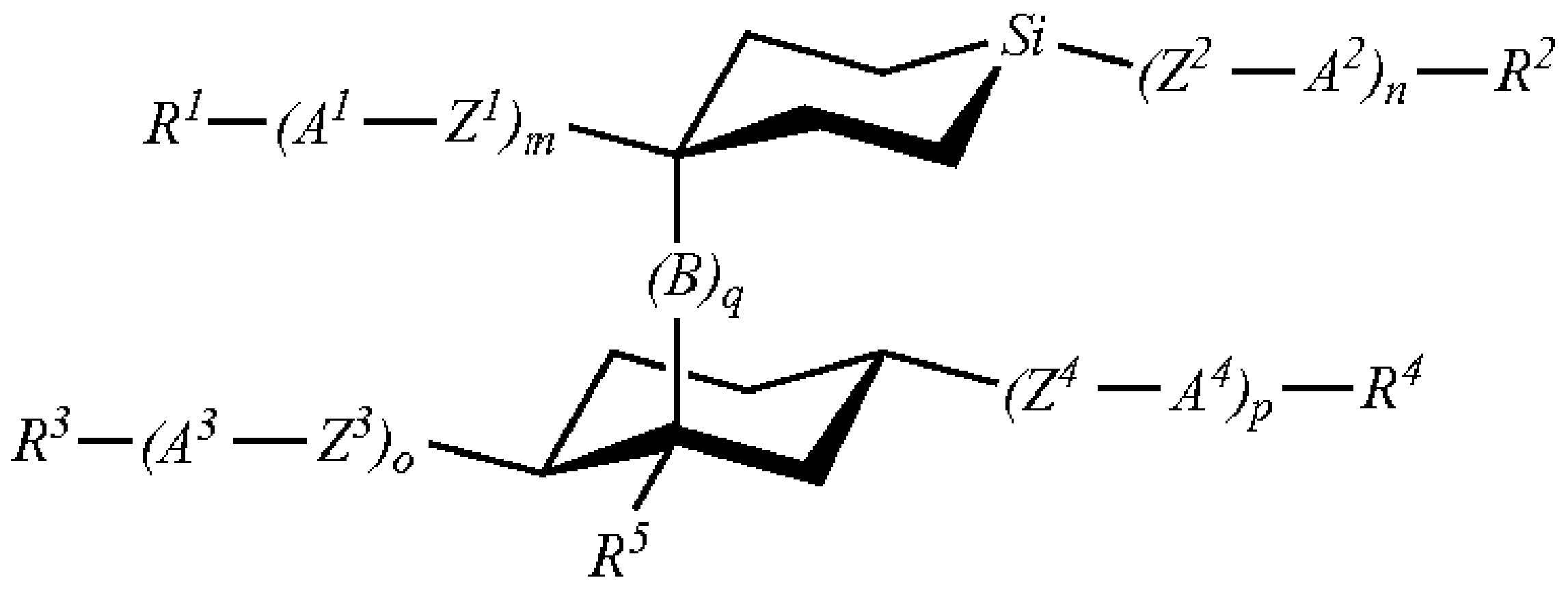

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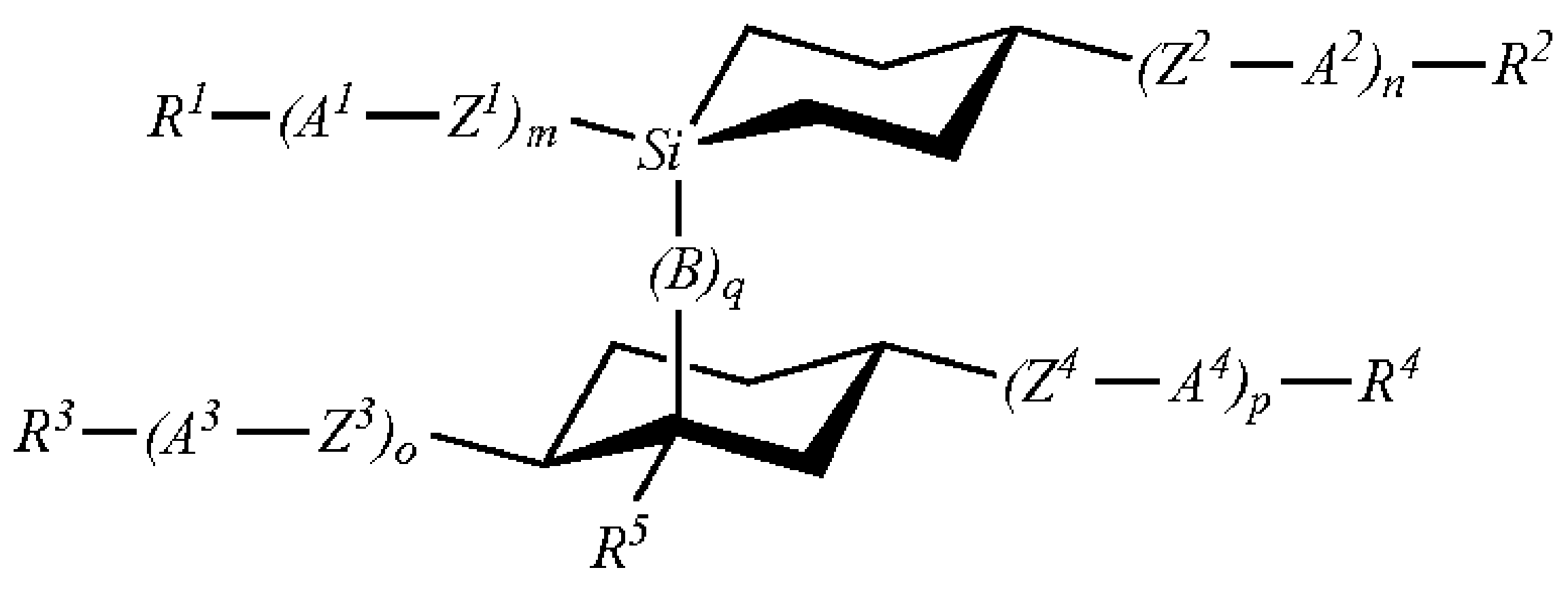

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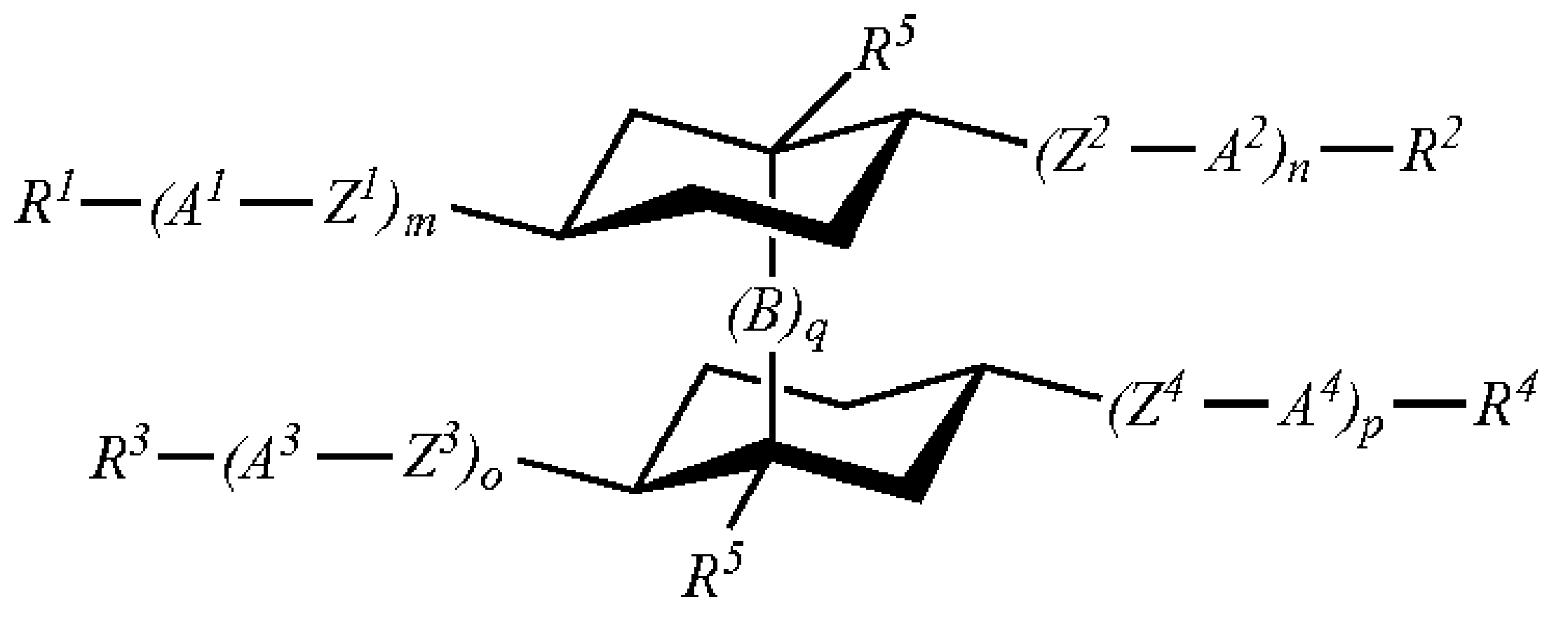

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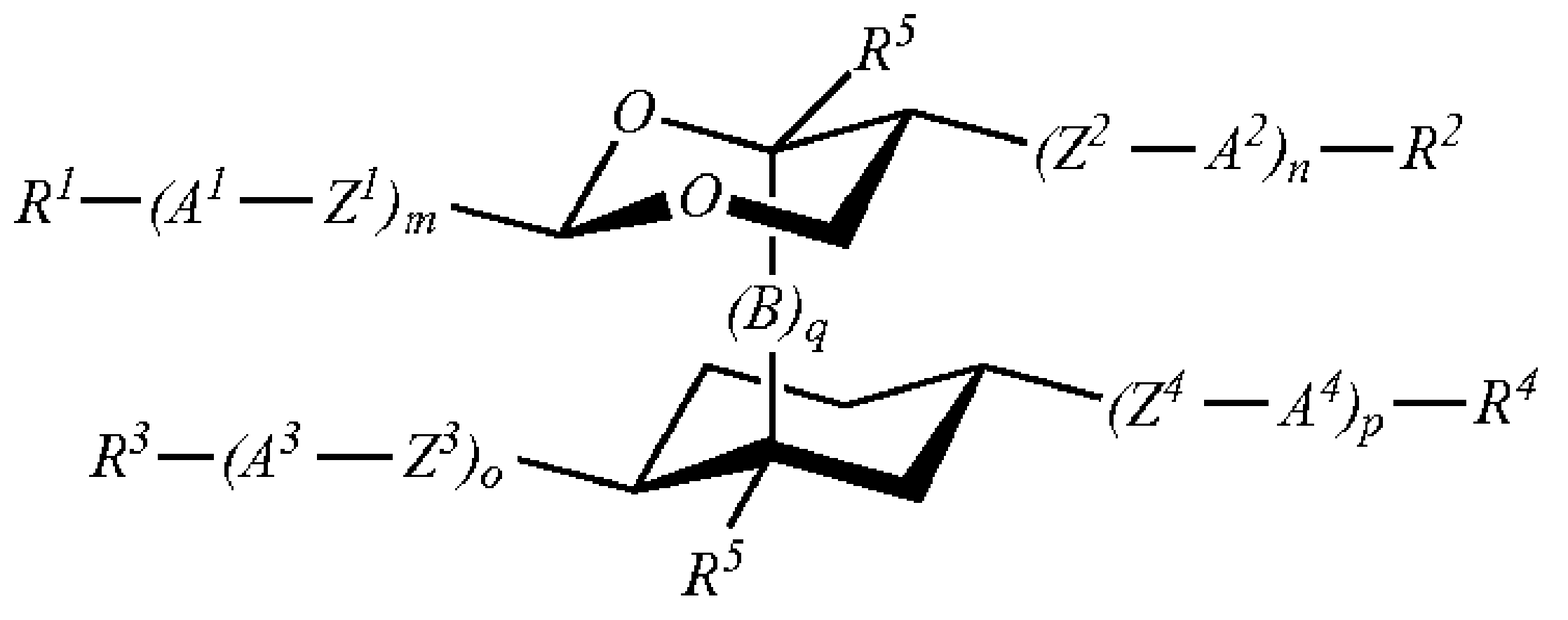

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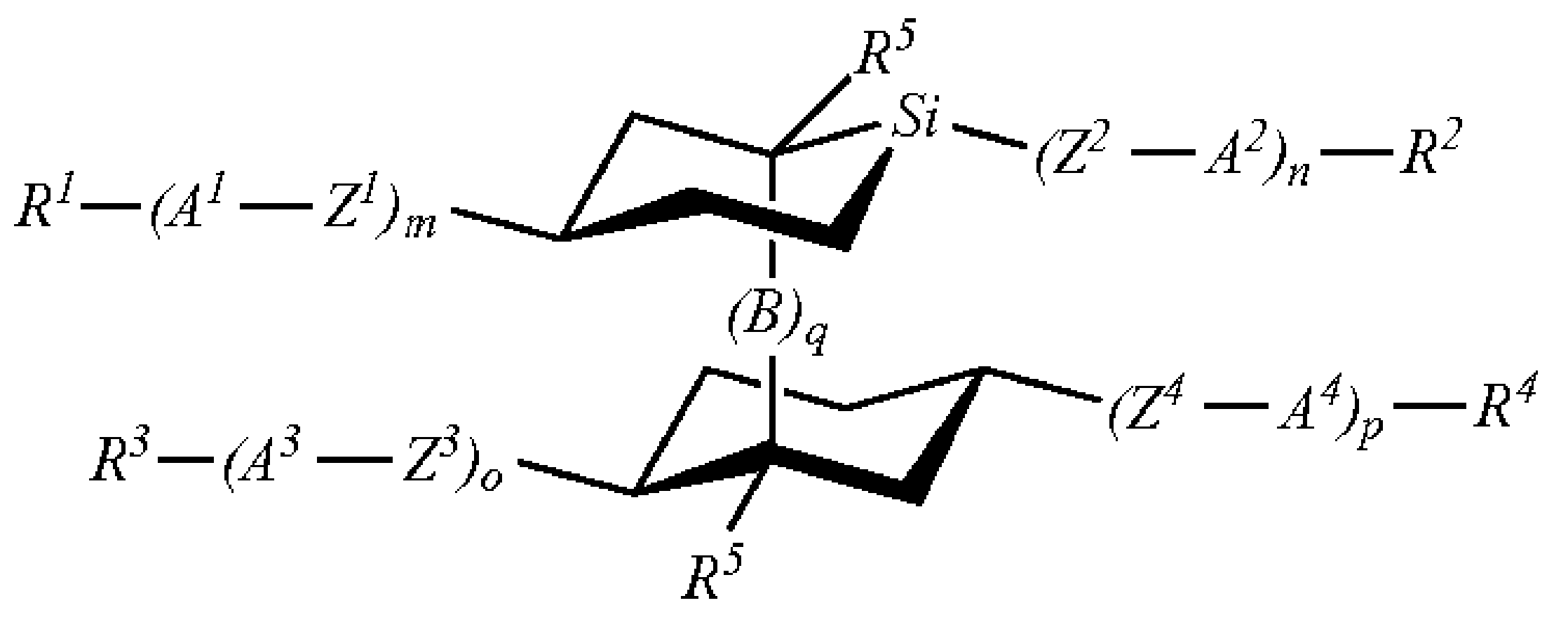

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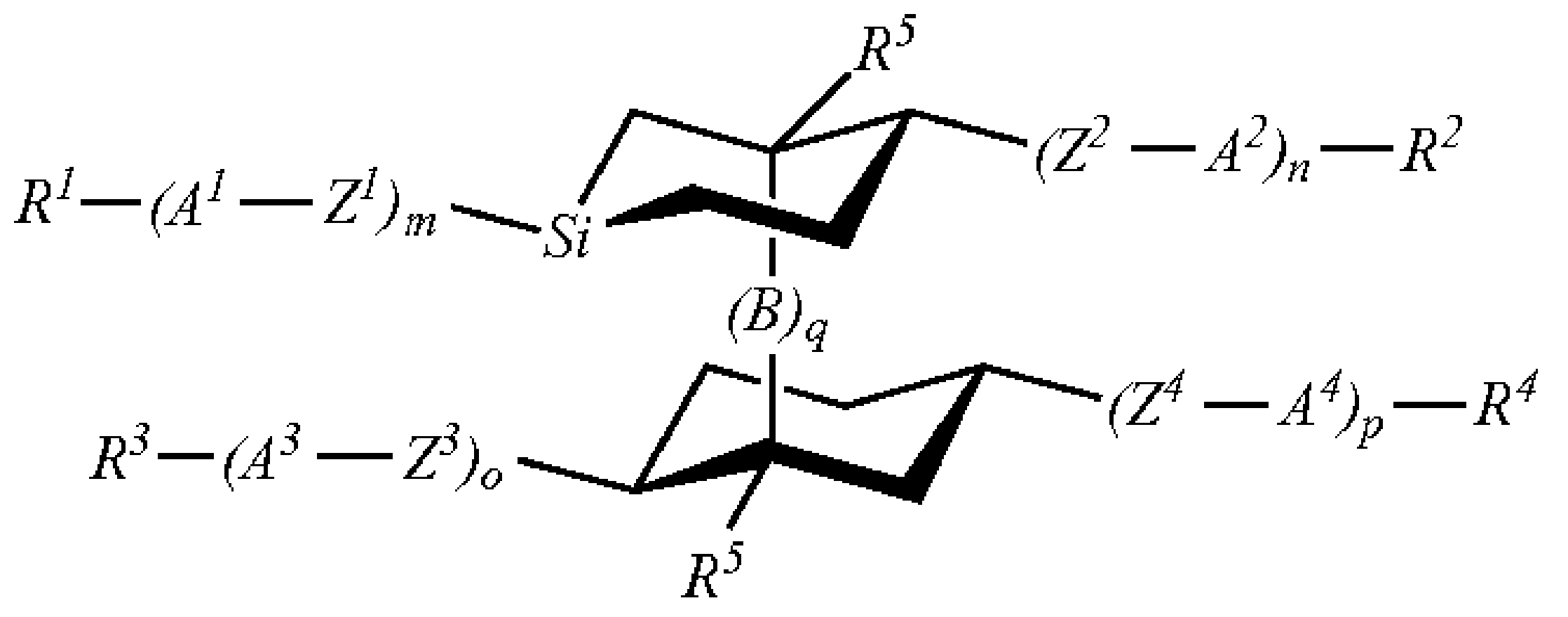

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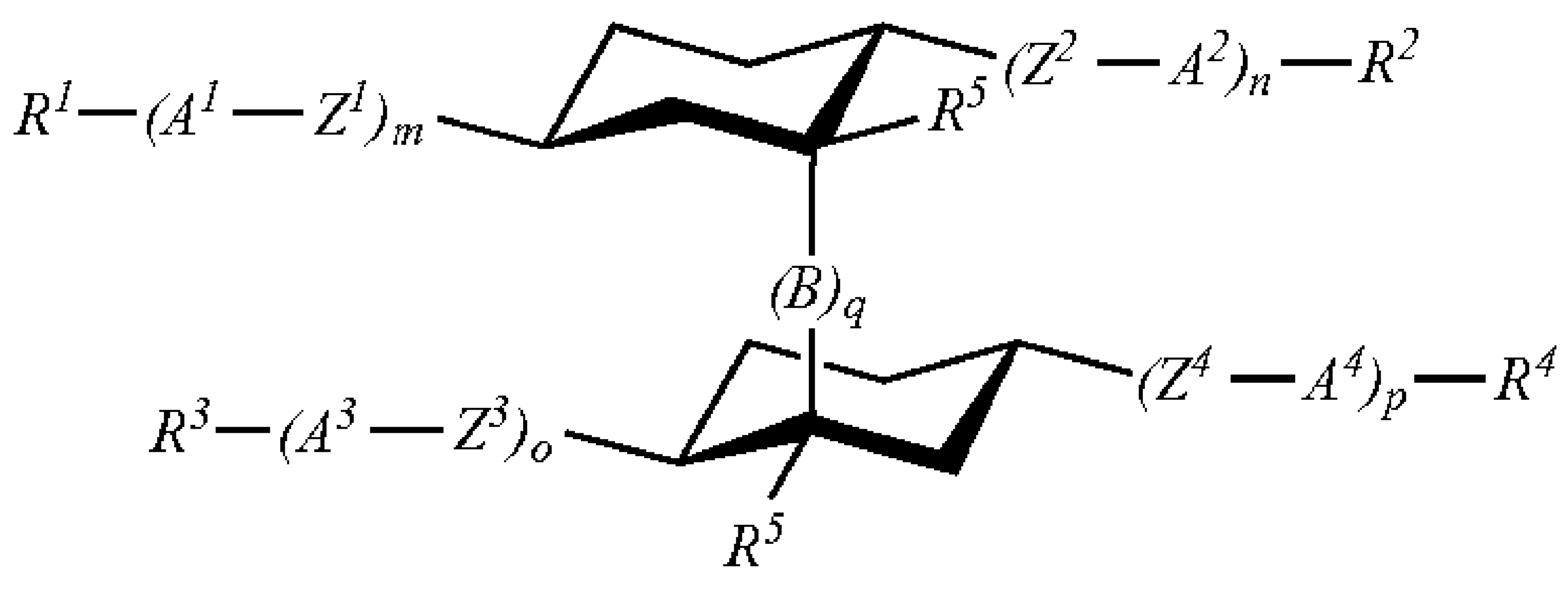

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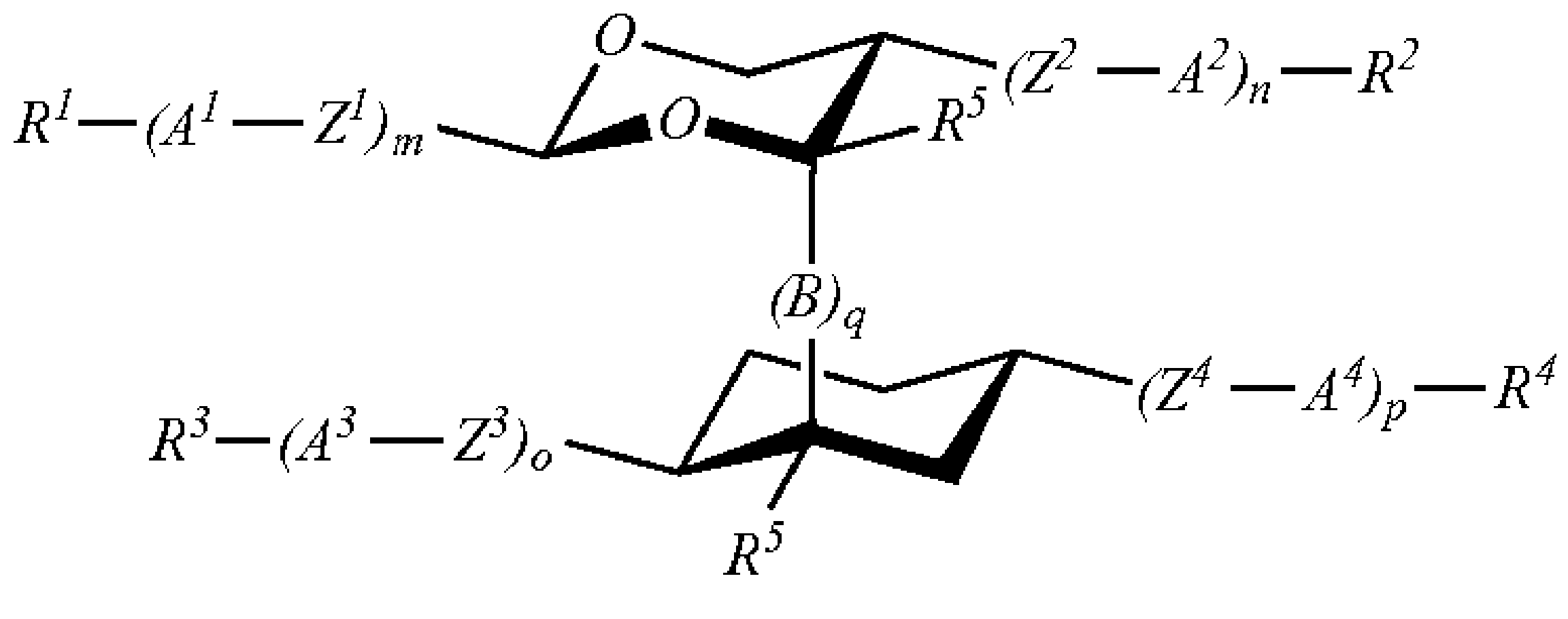

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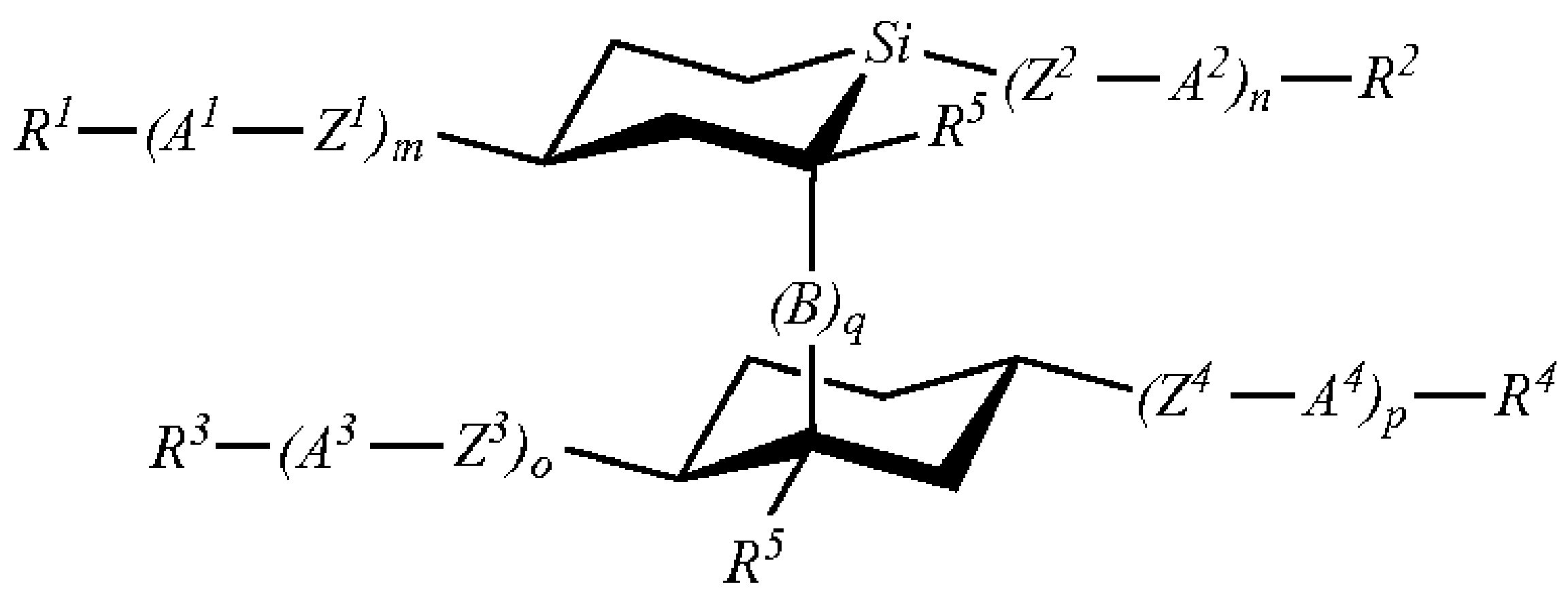

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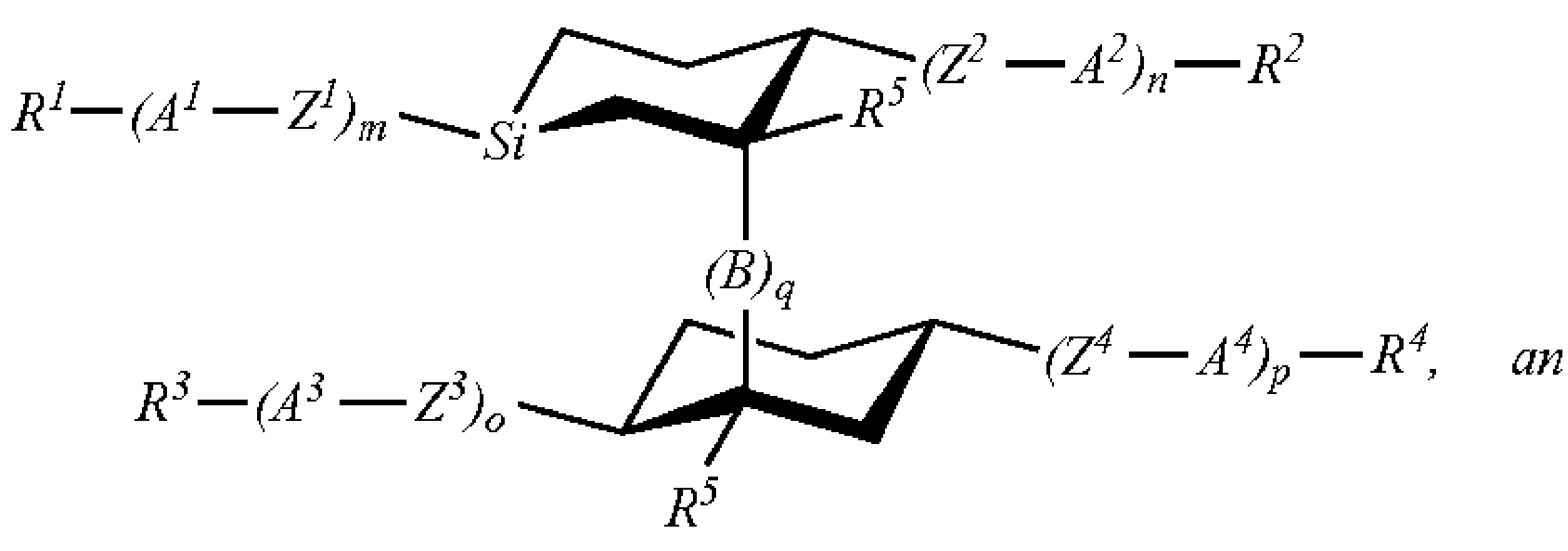


Ix

and

A^{1-4} are independently of each other non-aromatic carbocylic or heterocyclic groups and aromatic and heteroaromatic groups, which are optionally substituted by one or more groups R^5, and wherein each of $-(A^1\text{-}Z^1)_m—U^1—(Z^2\text{-}A^2)_n\text{-}$ and $-(A^3\text{-}Z^3)_o—U^2—(Z^4\text{-}A^4)_p\text{-}$ does not contain more aromatic groups than non-aromatic groups,

Z^{1-4} are independently of each other —O—, —S—, —CO—, —COO—, —OCO—, —O—COO—, —CO—NR^0—, —NR^0—CO—, —NR^0—CO—NR^0—, —OCH_2—, —CH_2O—, —SCH_2—, —CH_2S—, —CF_2O—, —OCF_2—, —CF_2S—, —SCF_2—, —CH_2CH_2—, —$(CH_2)_3$—, —$(CH_2)_4$—, —CF_2CH_2—, —CH_2CF_2—, —CF_2CF_2—, —CH═CH—, —CY^1═CY^2—, —CH═N—, —N═CH—, —N═N—, —CH═CR^0—, —C≡C—, —CH═CH—COO—, —OCO—CH═CH—, CR^0R^{00} or a single bond,

R^0, R^{00} are independently of each other H or alkyl with 1 to 12 C-atoms,

m and n are independently of each other 0, 1, 2, 3 or 4,

o and p are independently of each other 0, 1, 2, 3 or 4,

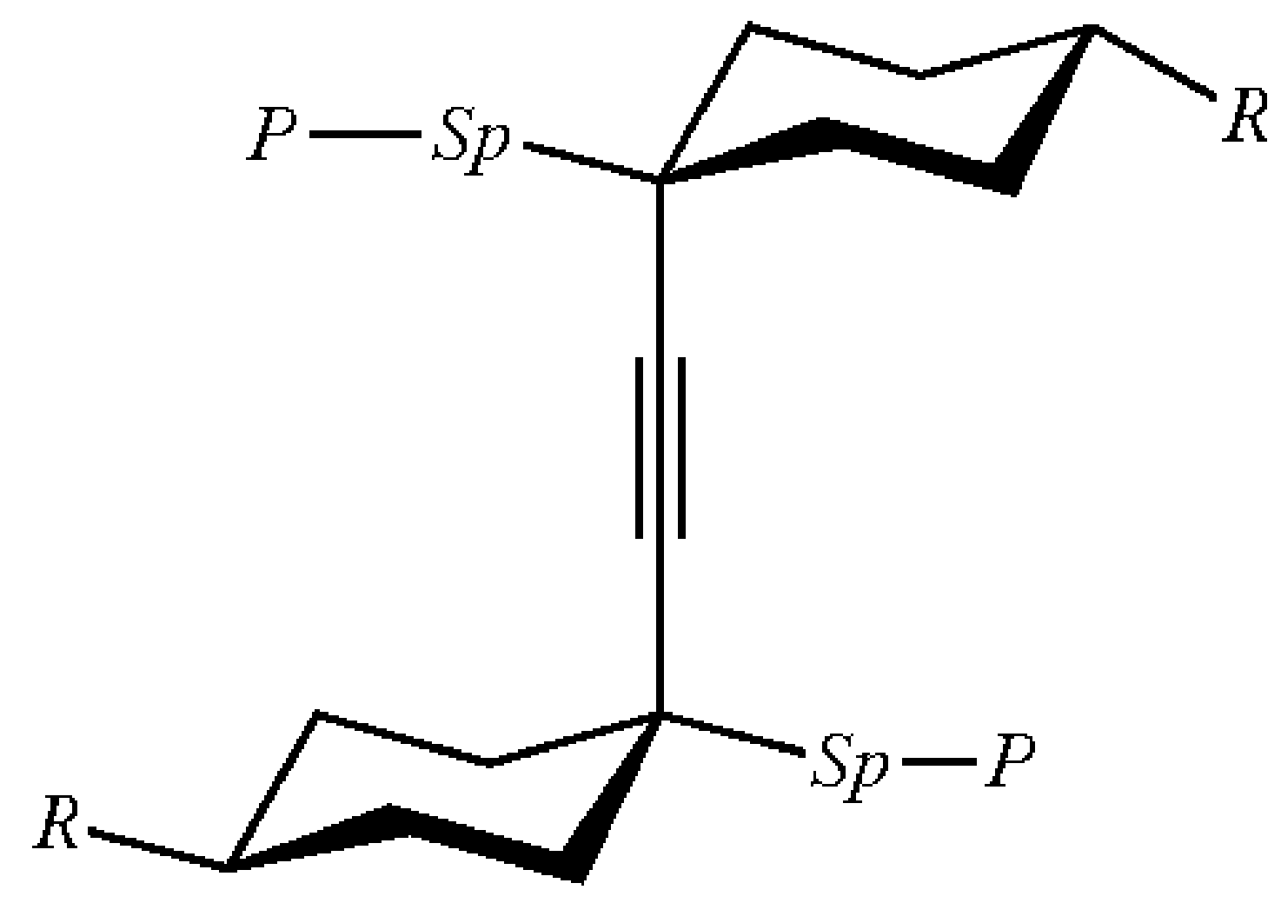
R^{1-5} are independently H, halogen, —CN, —NC, —NCO, —NCS, —OCN, —SCN, —C(═O)NR^0R^{00}, —C(═O)X^0, —C(═O)R^0, —NH_2, —NR^0R^{00}, —SH, —SR^0, —SO_3H, —SO_2R^0, —OH, —NO_2, —CF_3, —SF_5, P-Sp-, optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 40 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, or denote P or P-Sp-, or are substituted by P or P-Sp-, wherein the compounds comprise at least one group R^{1-5} denoting or being substituted by P or P-Sp-,

P is a polymerizable group, and

Sp is a spacer group or a single bond.

42. The polymerizable compound according to claim 33, wherein the polymerizable compounds are:

I1



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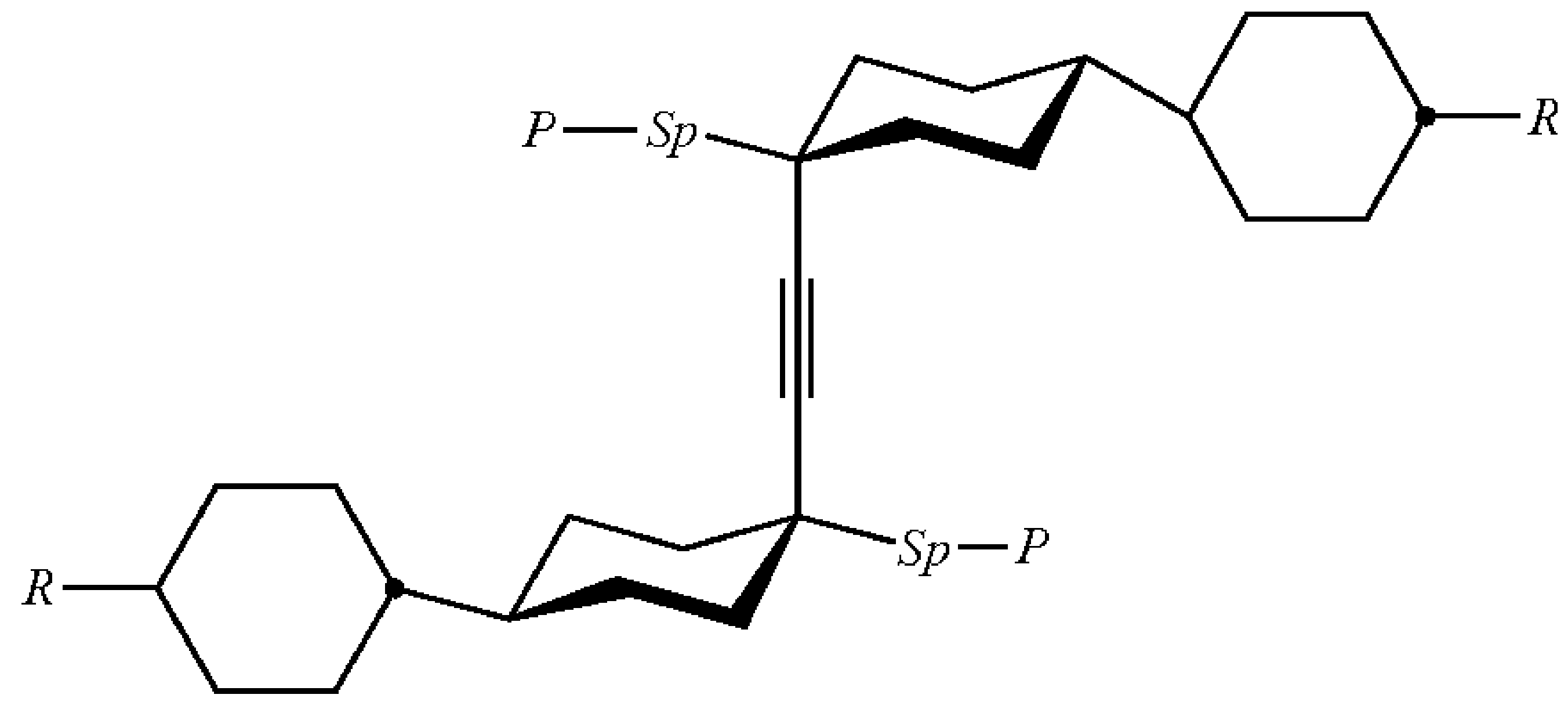

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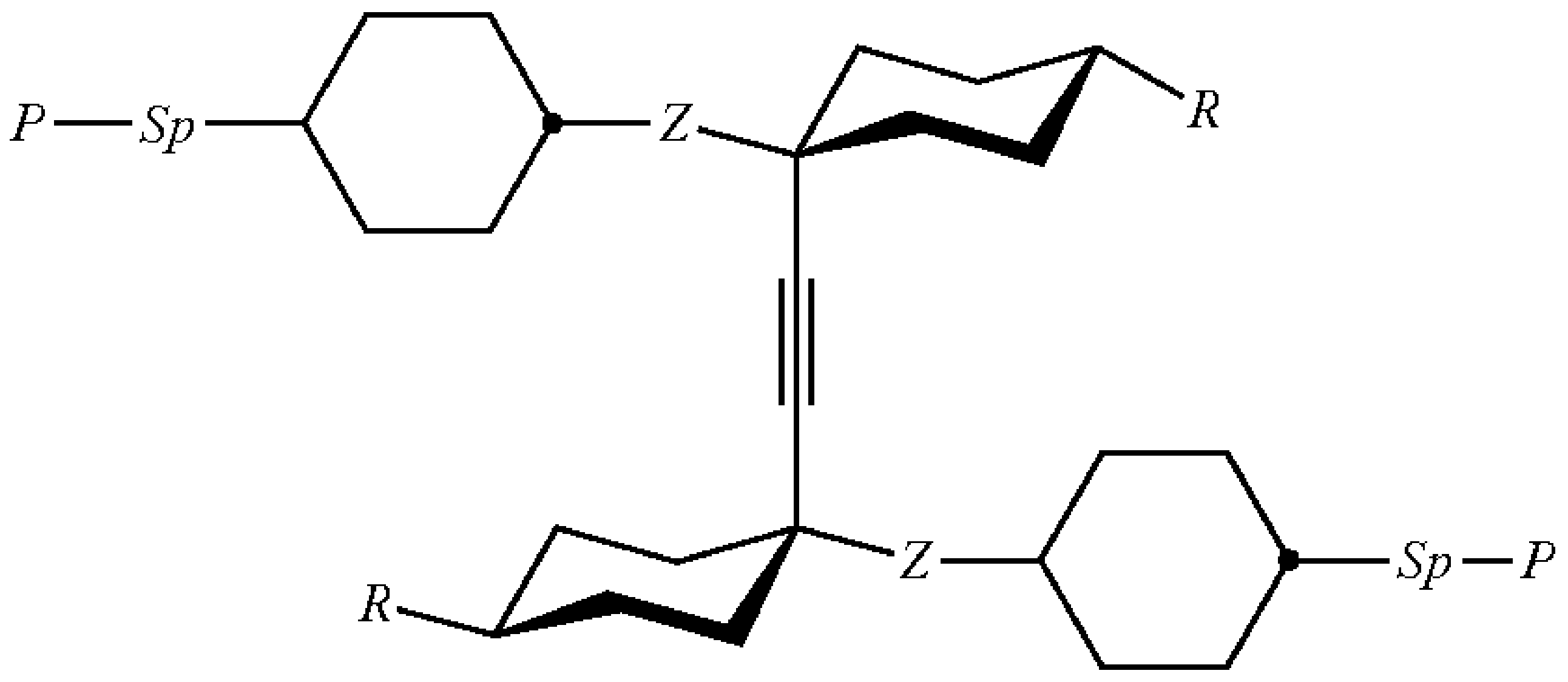

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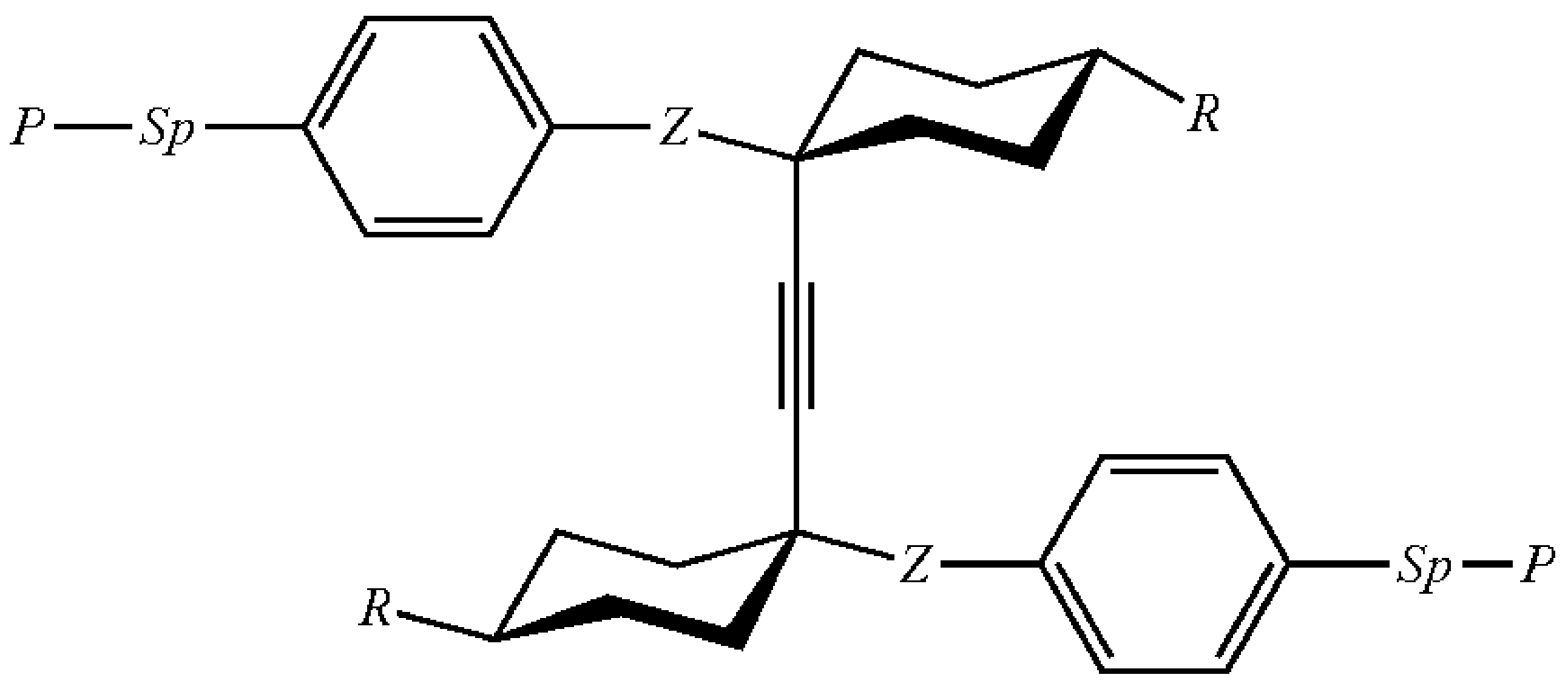

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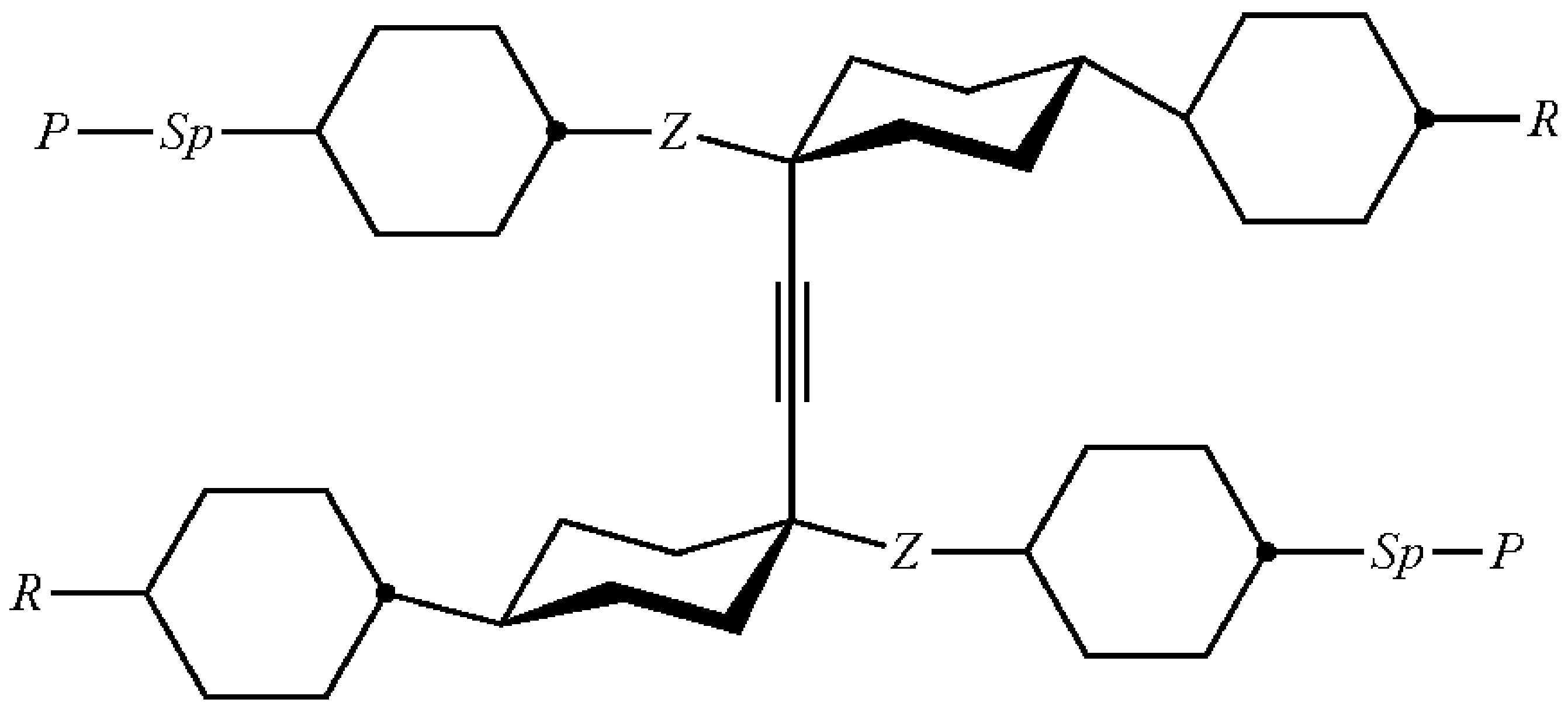

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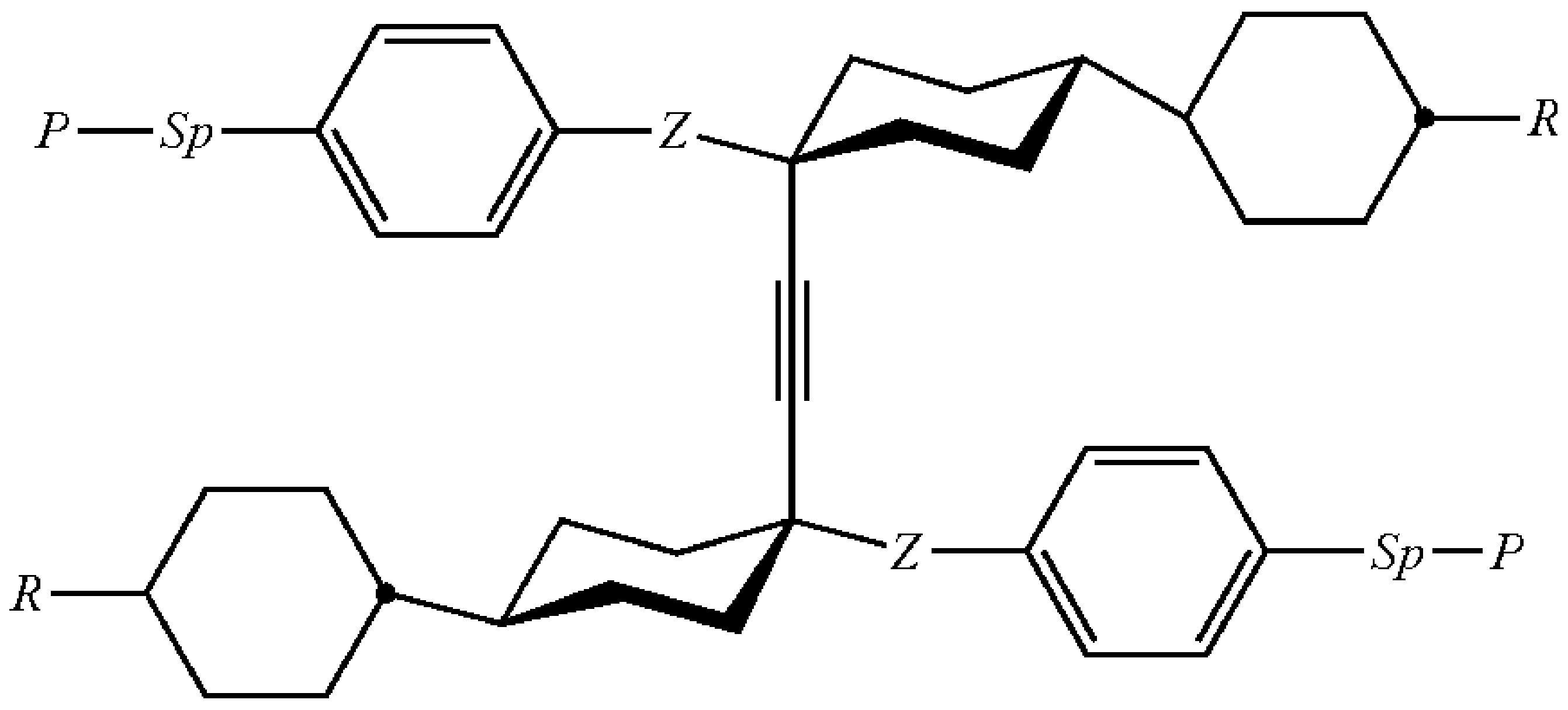

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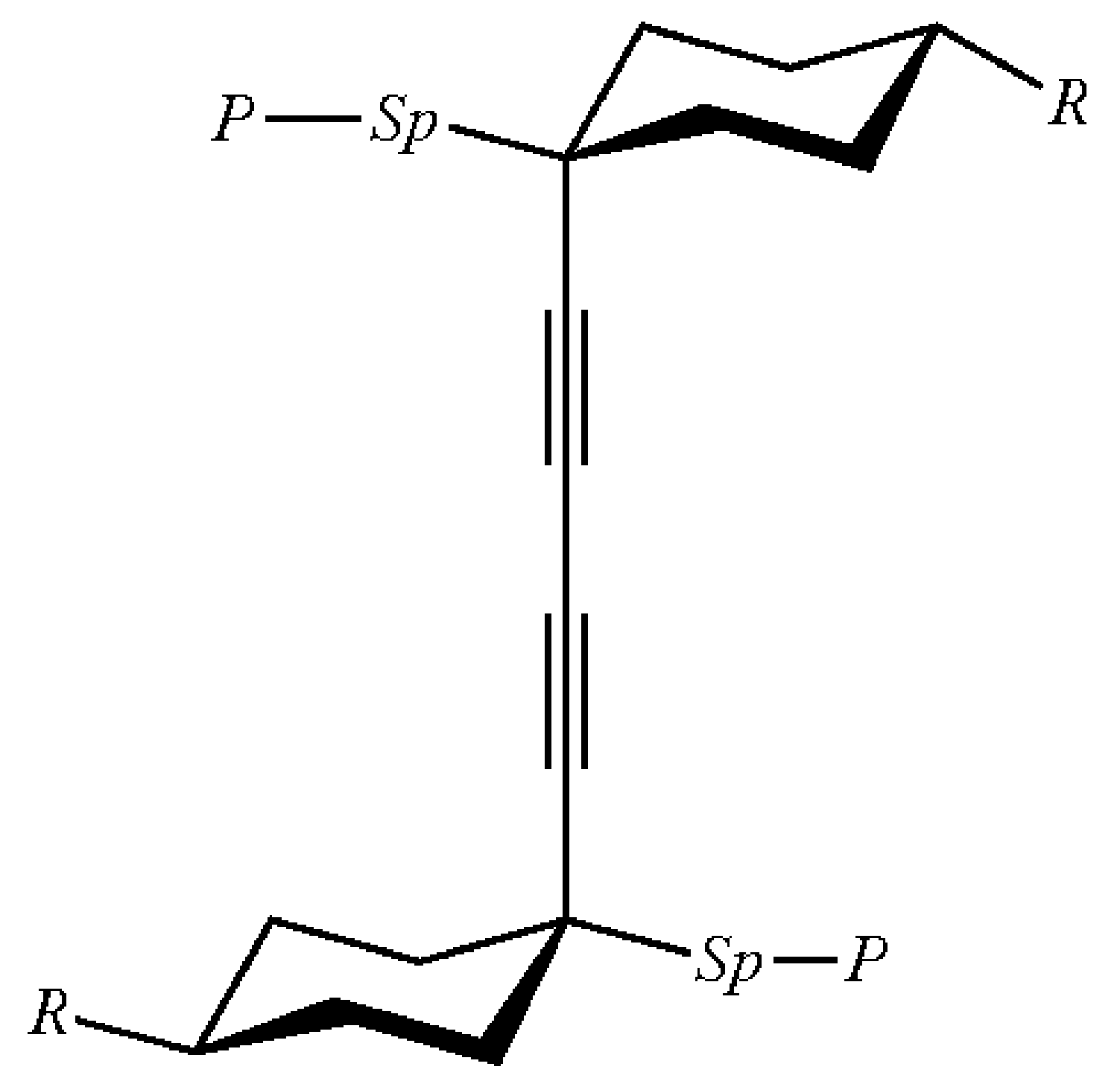

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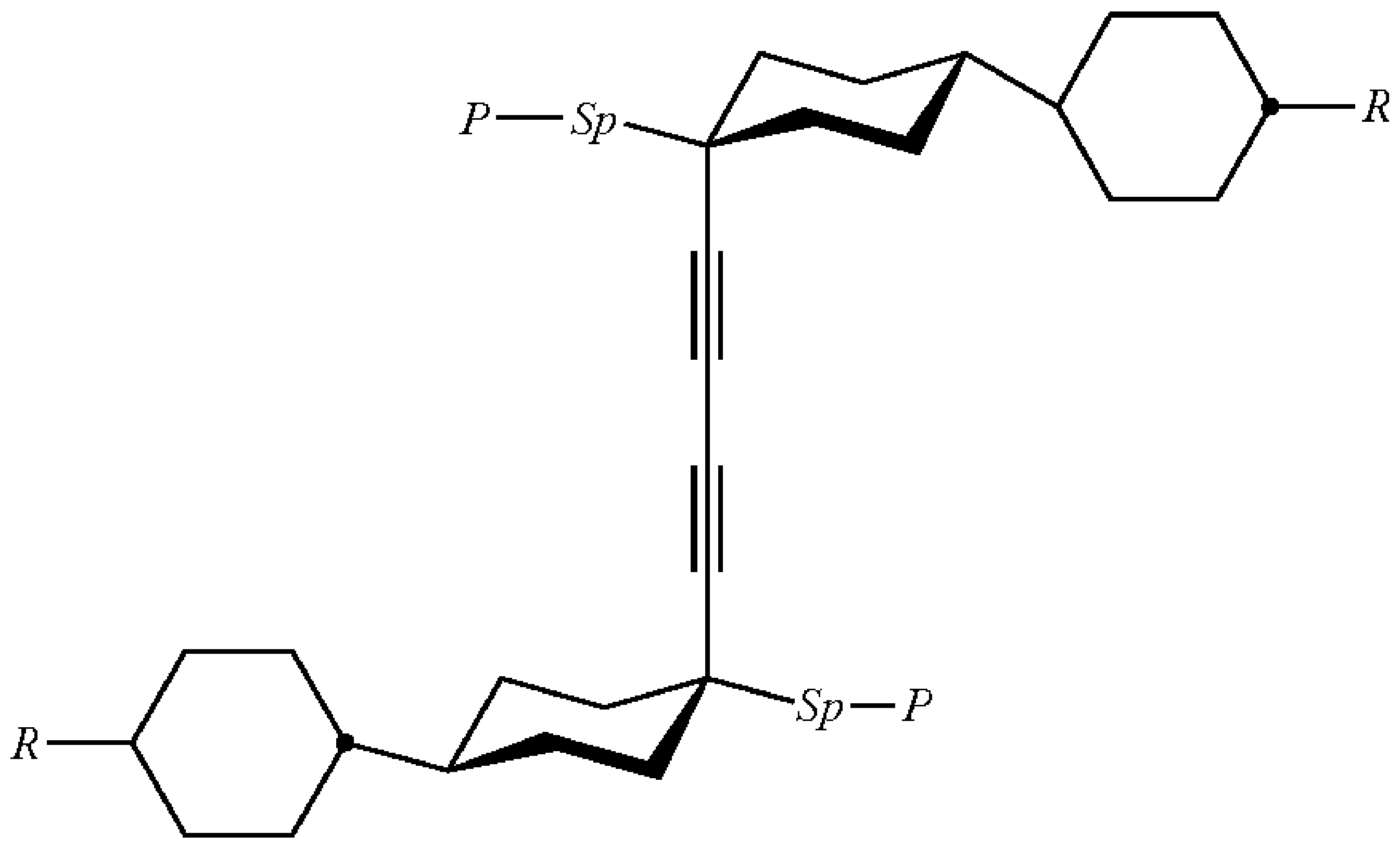

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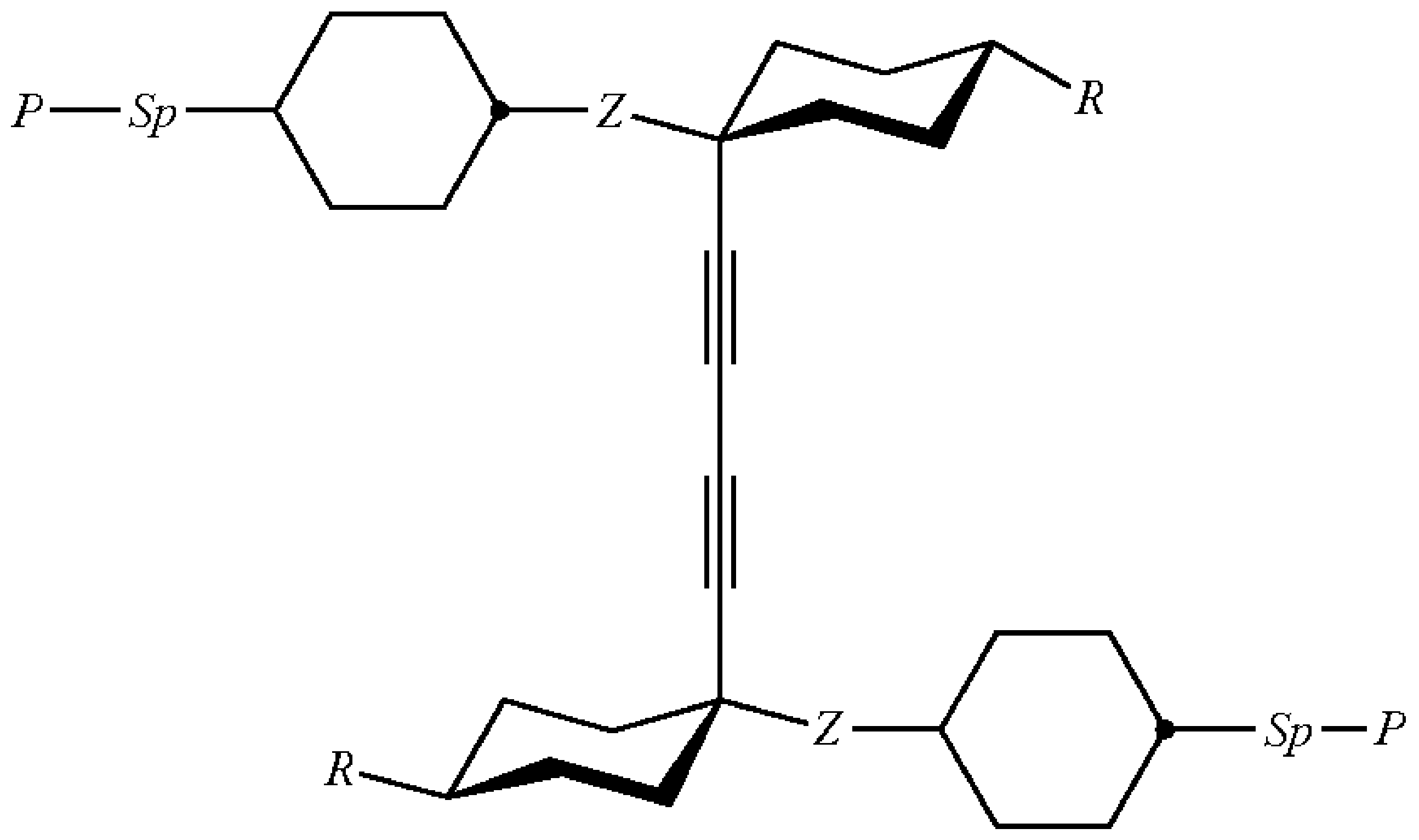

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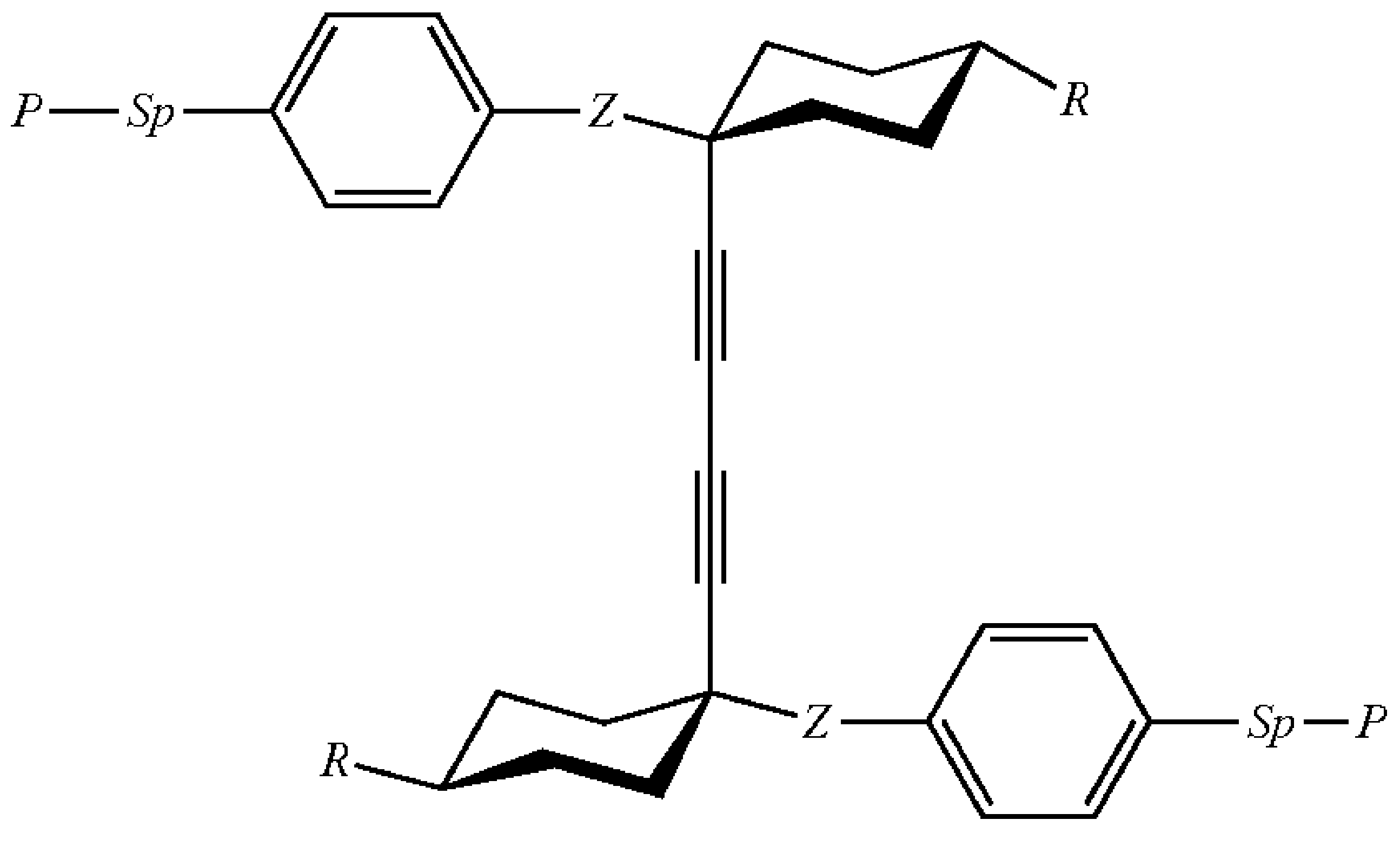

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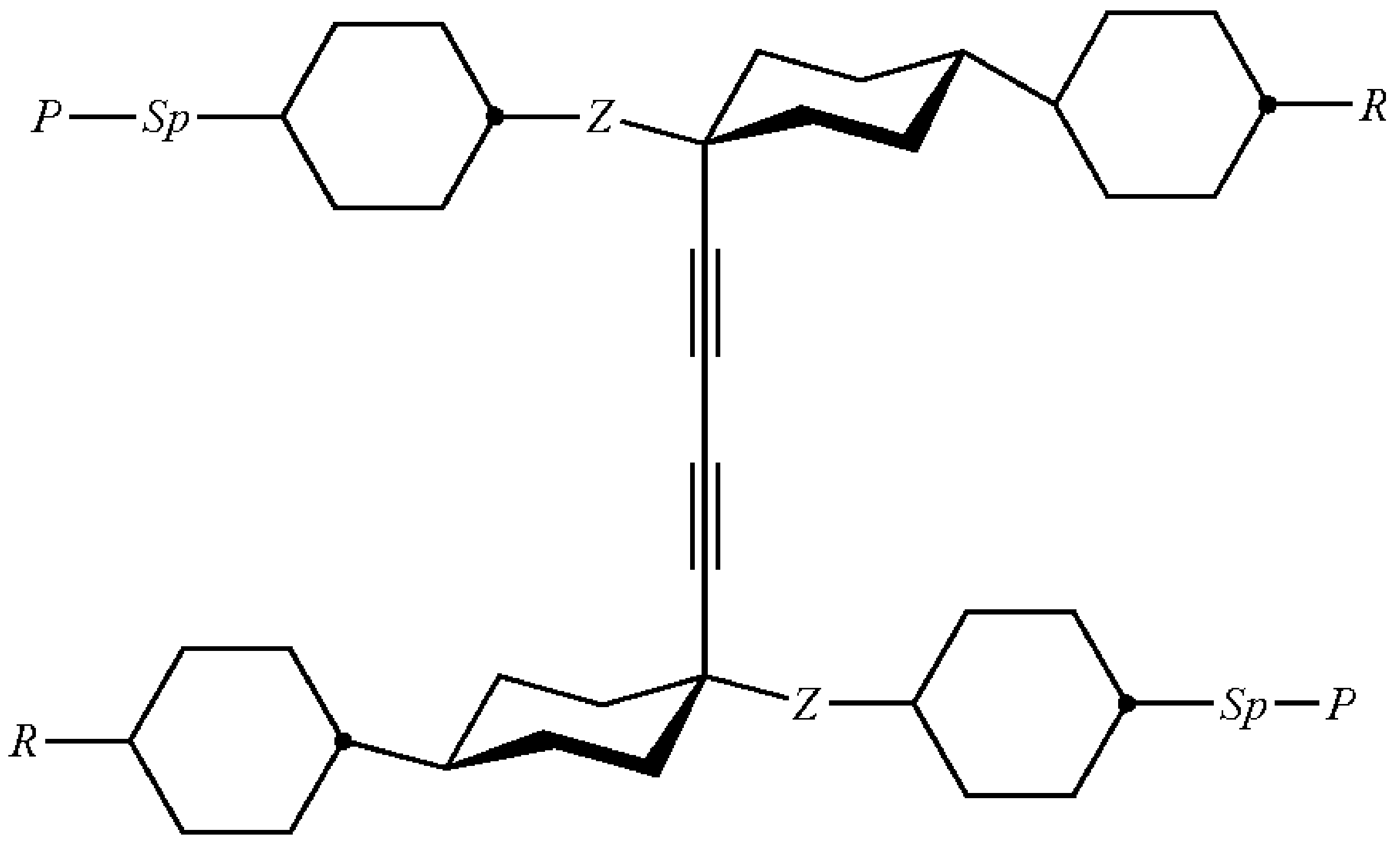

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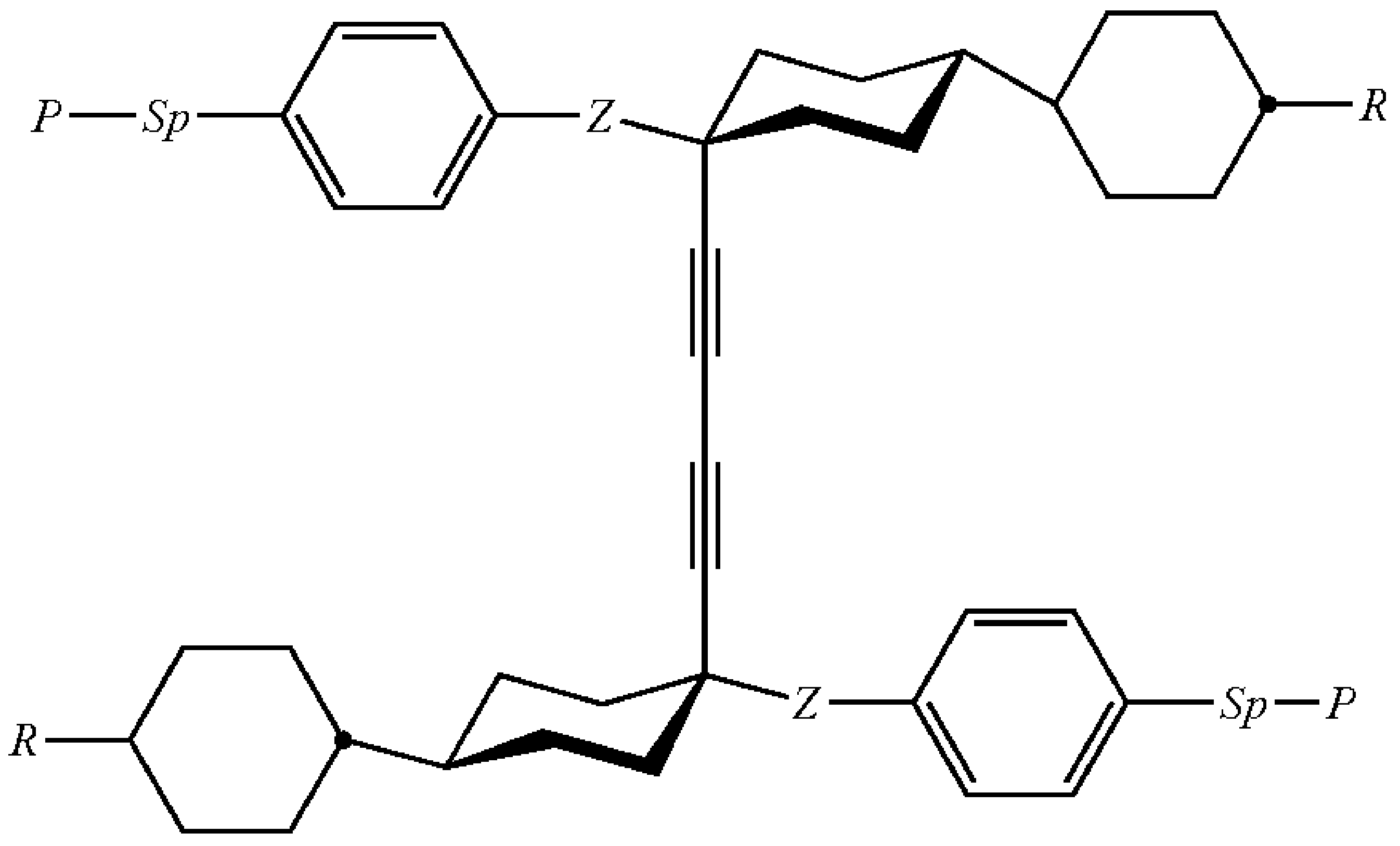

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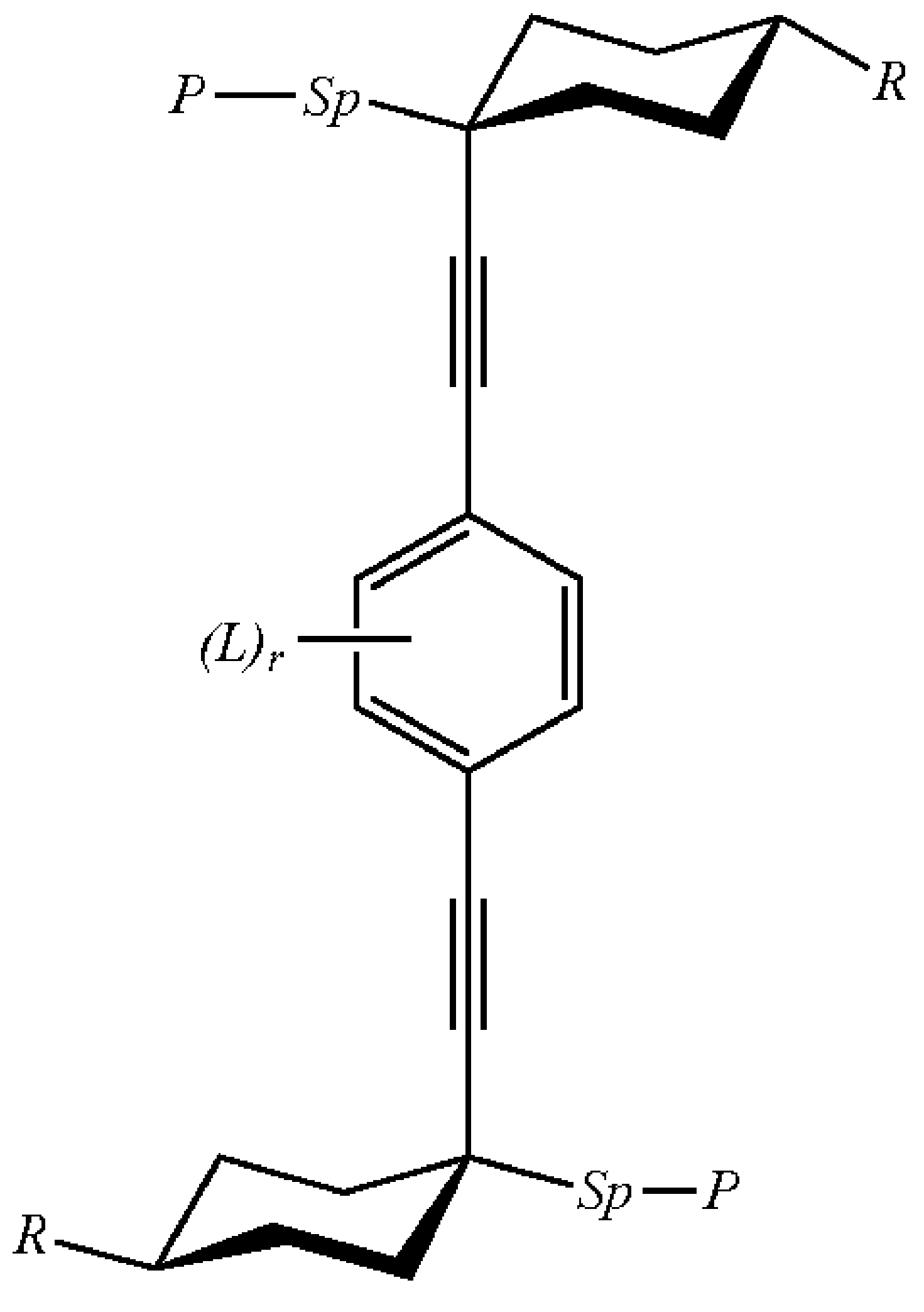

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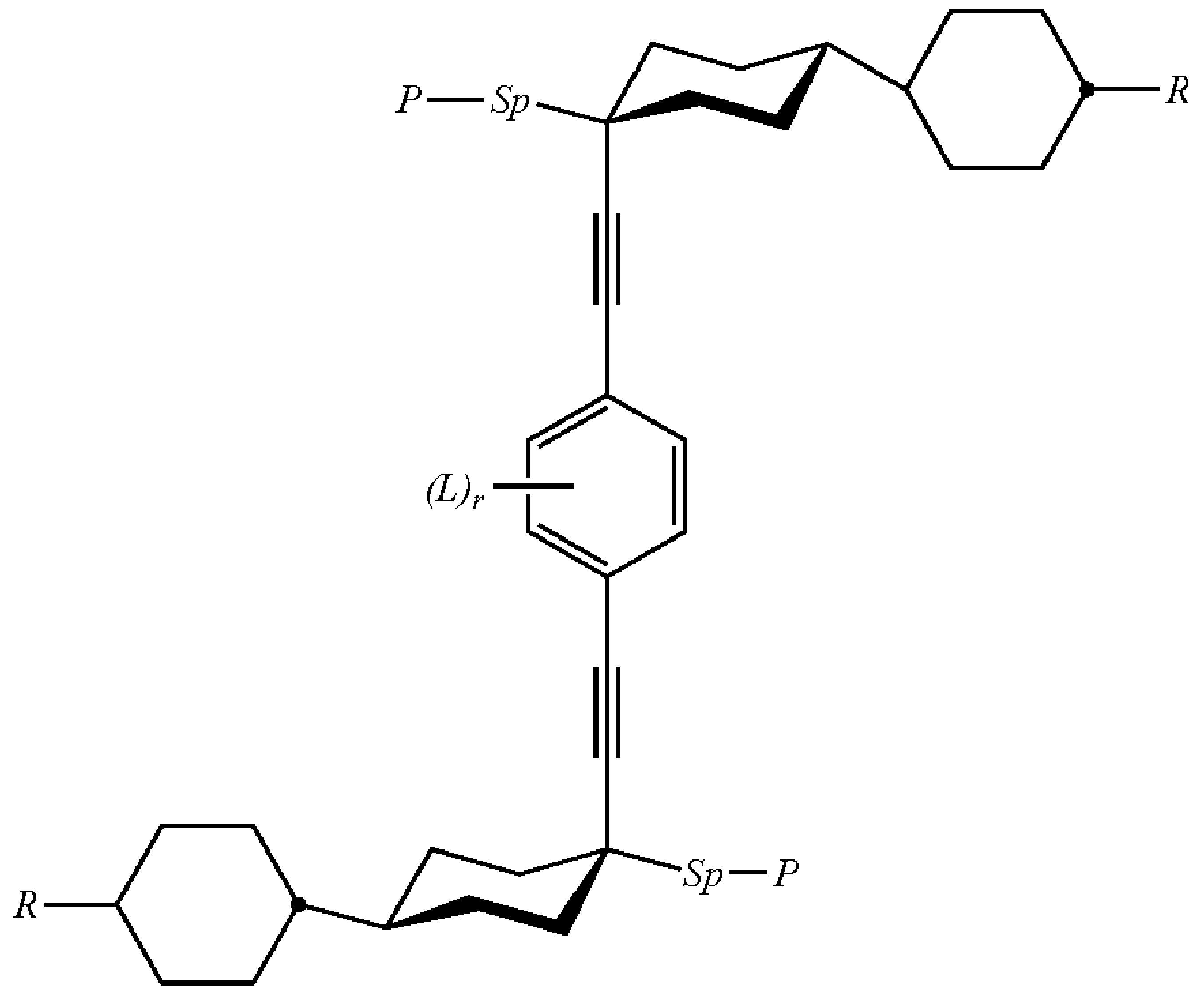

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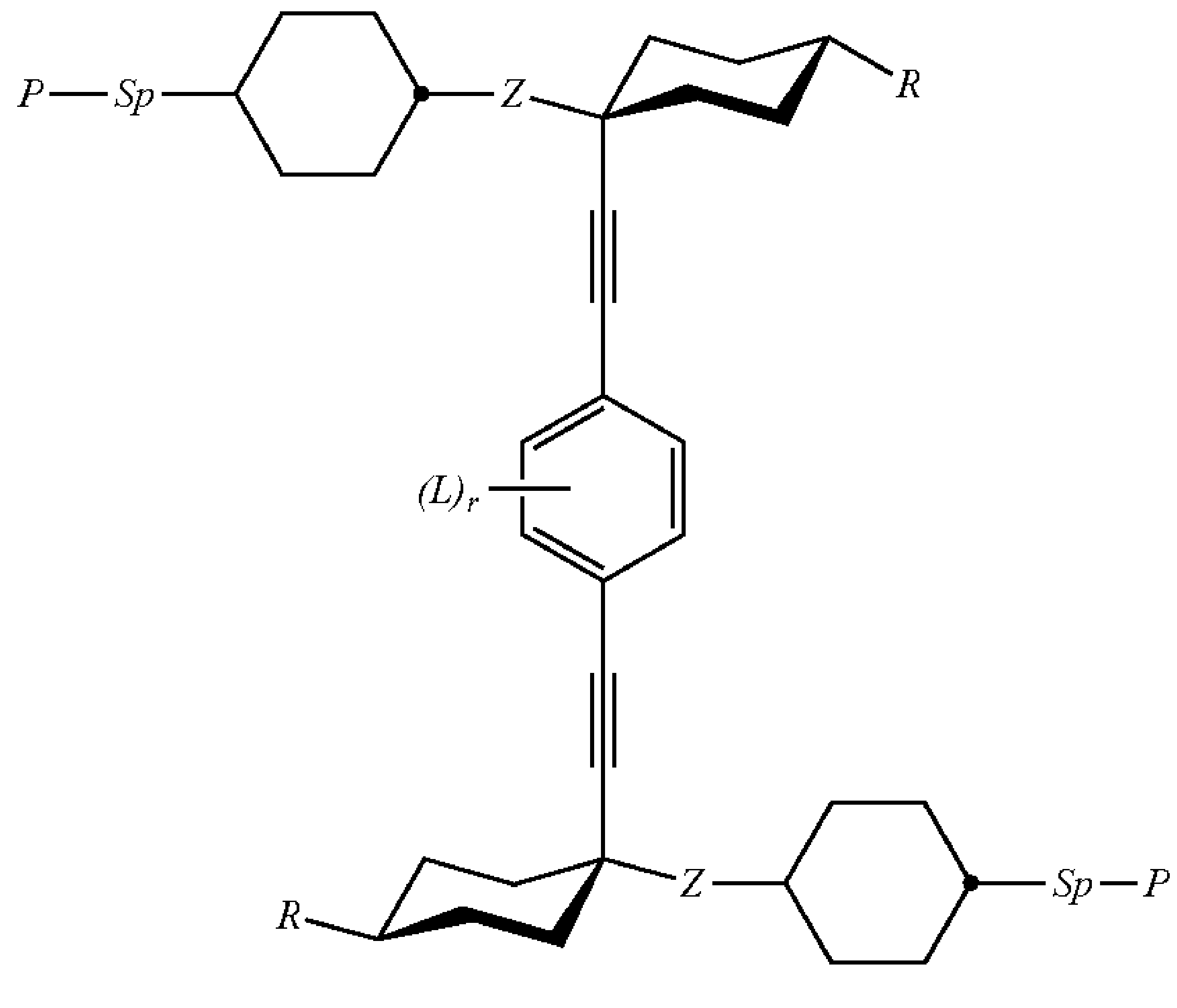

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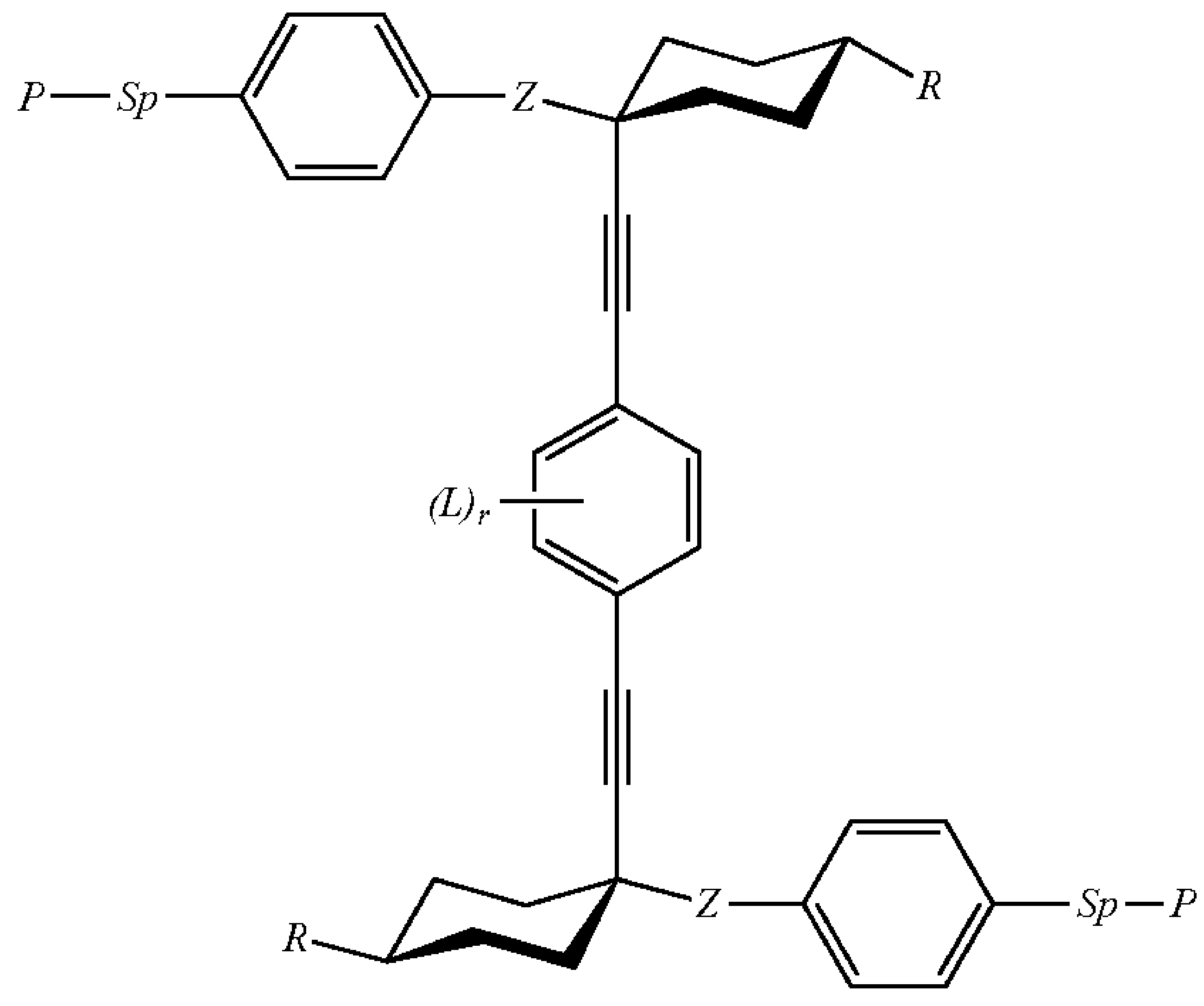

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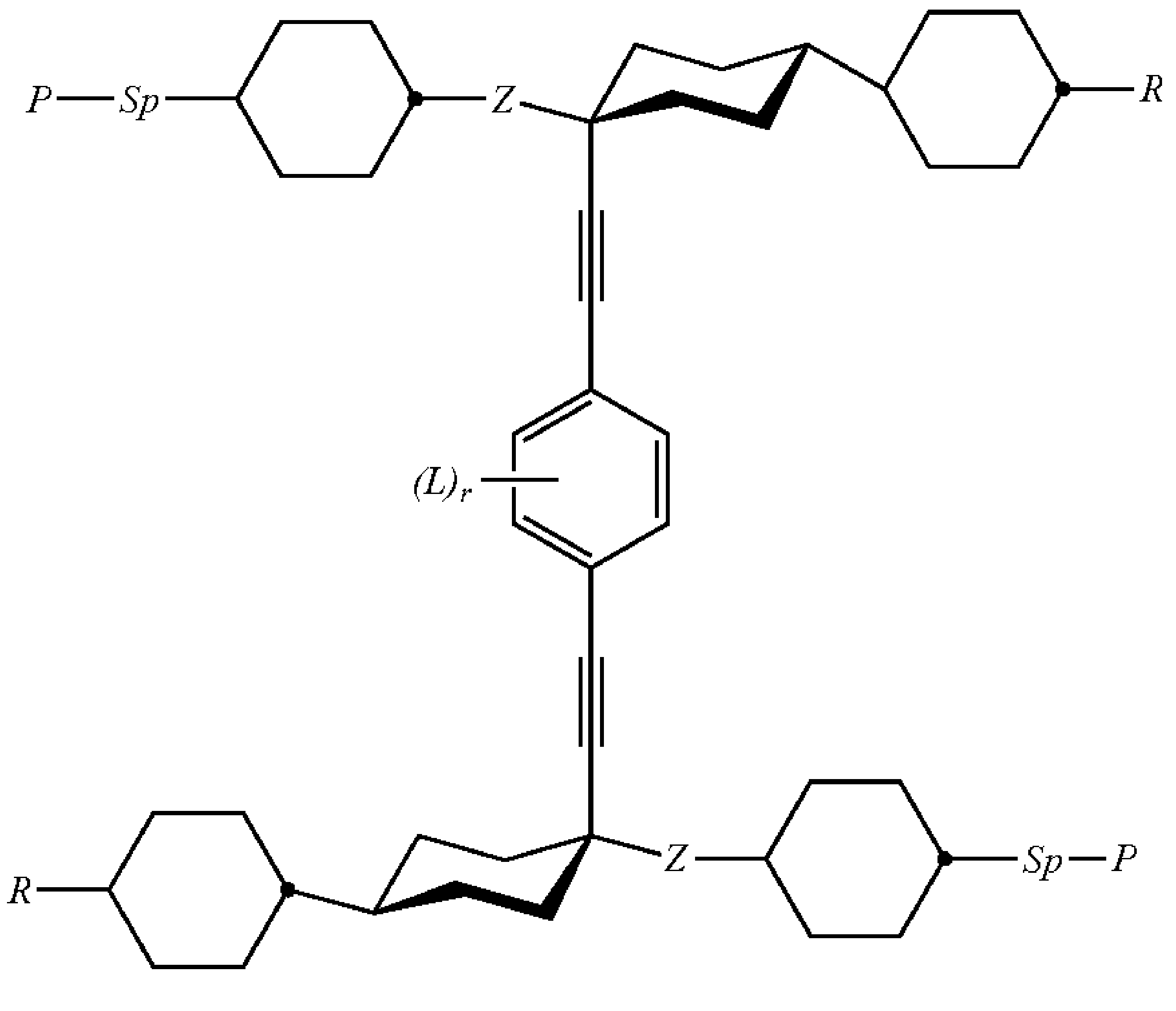

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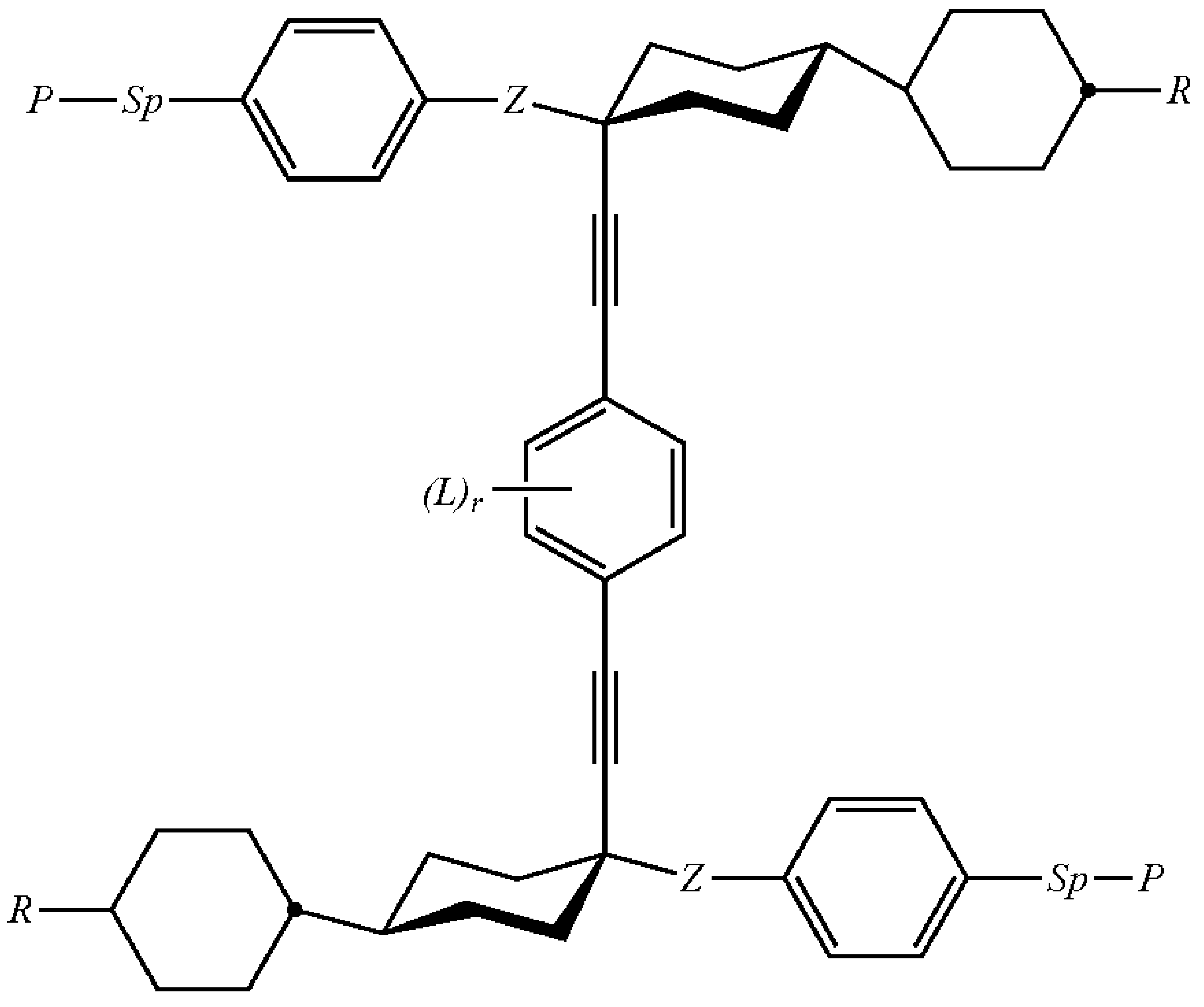

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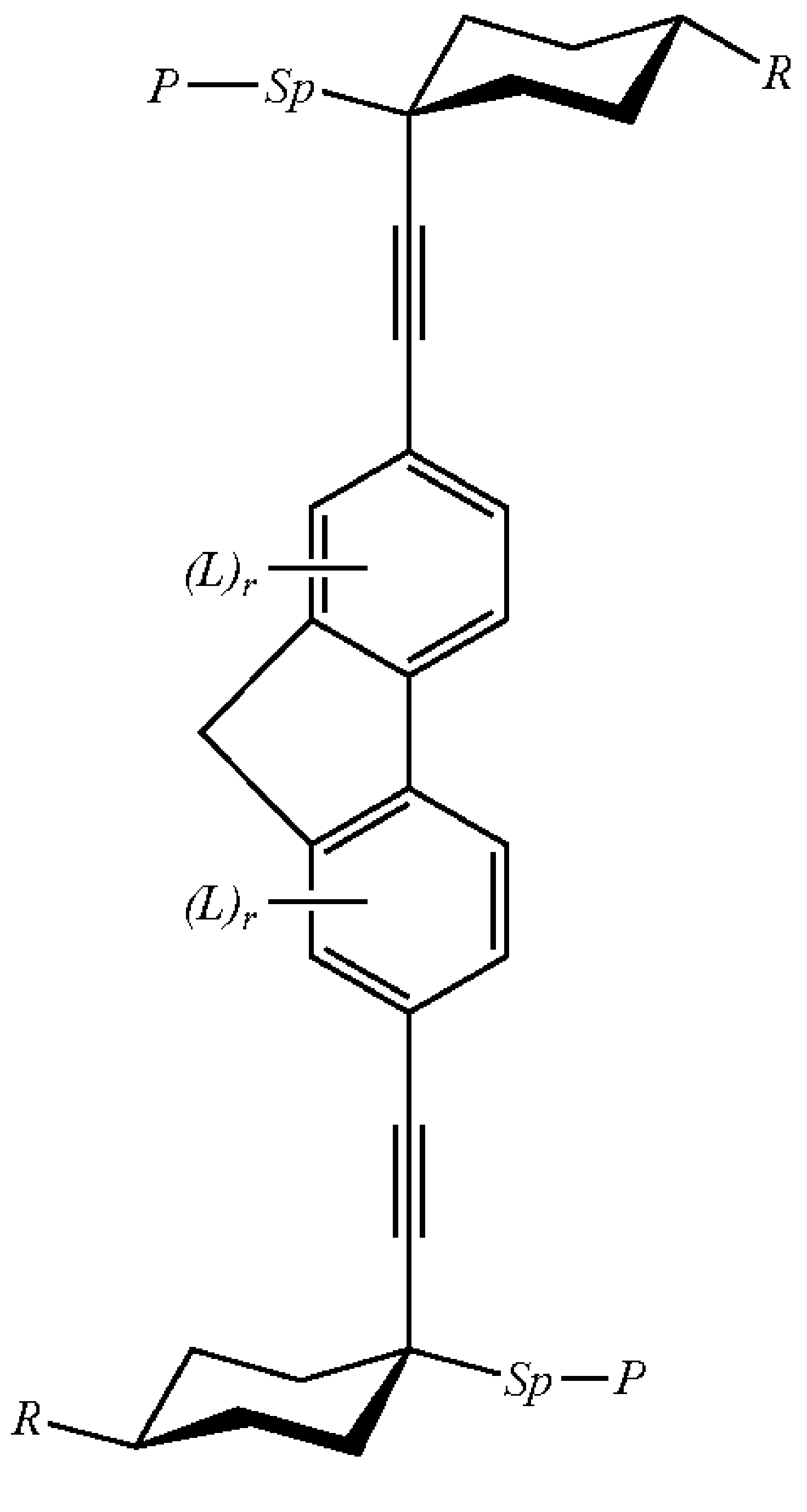

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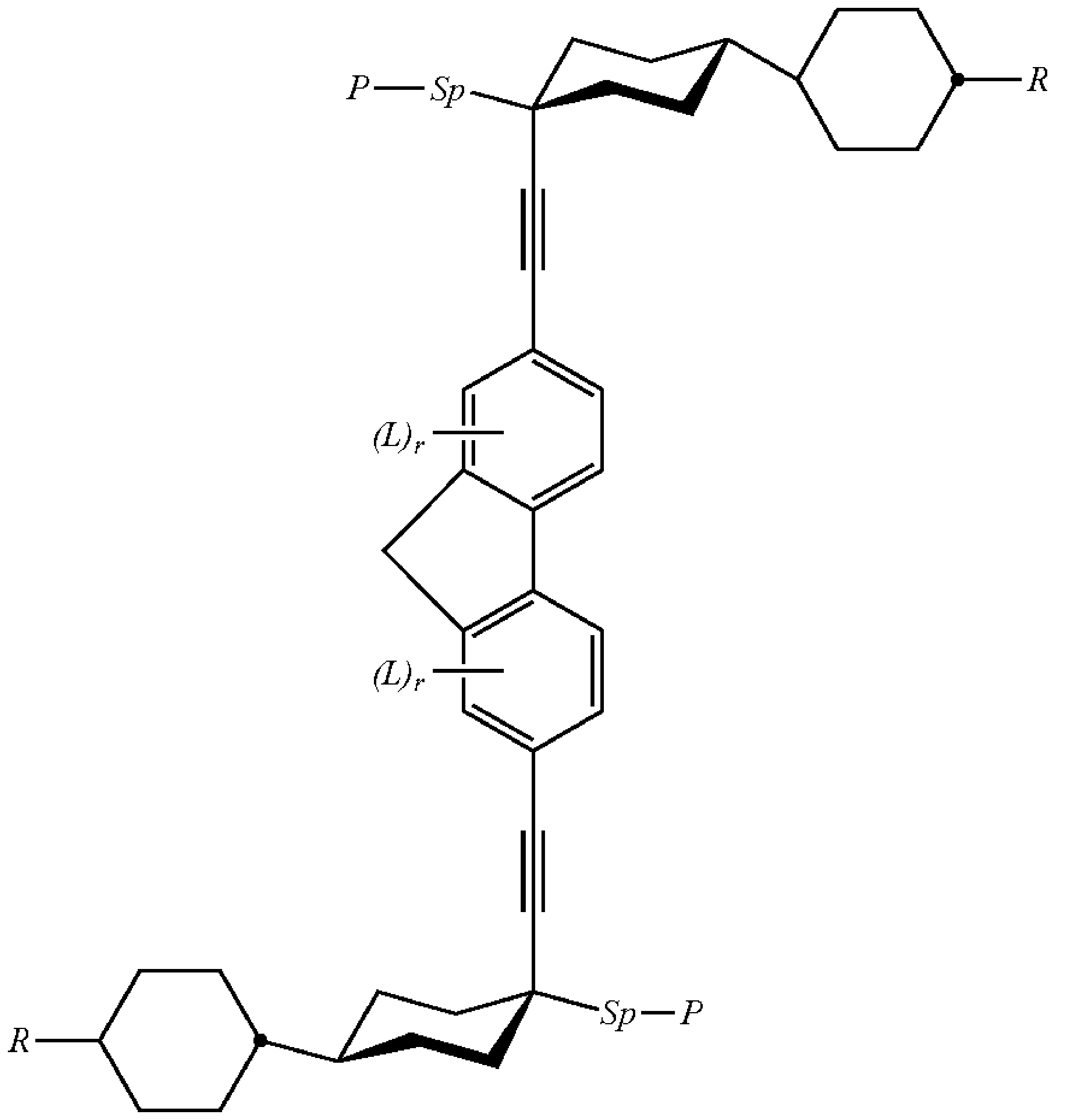

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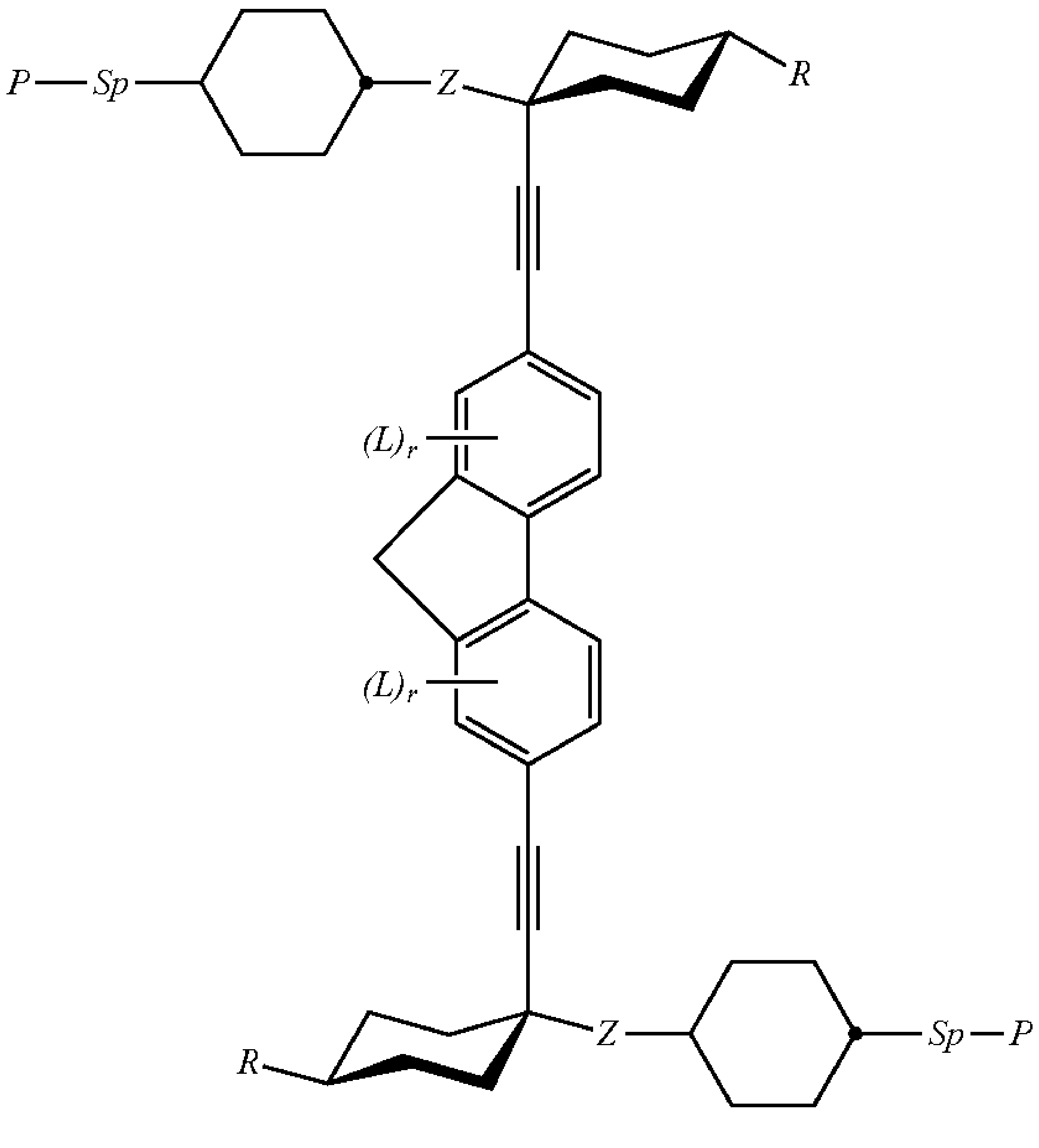

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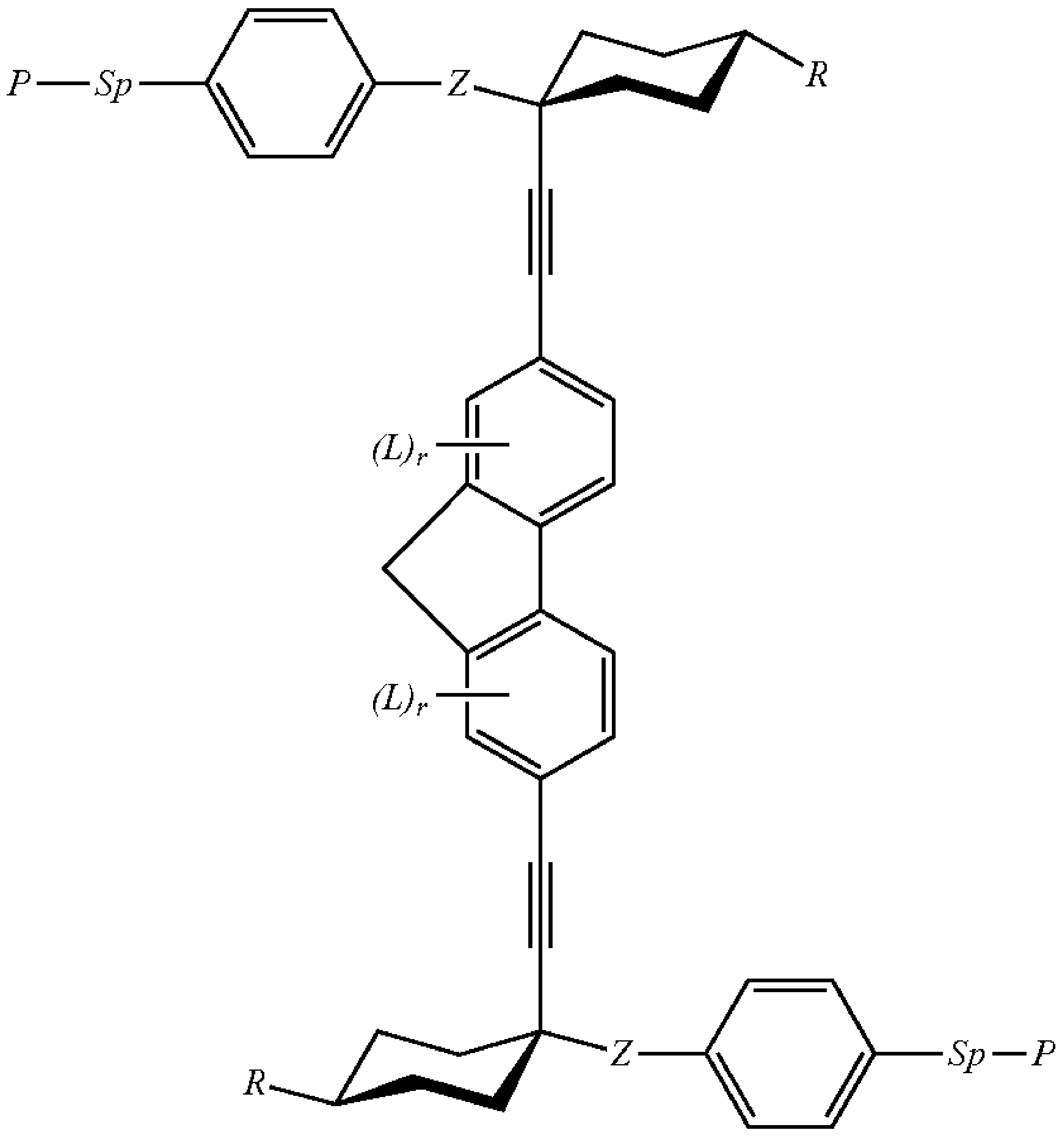

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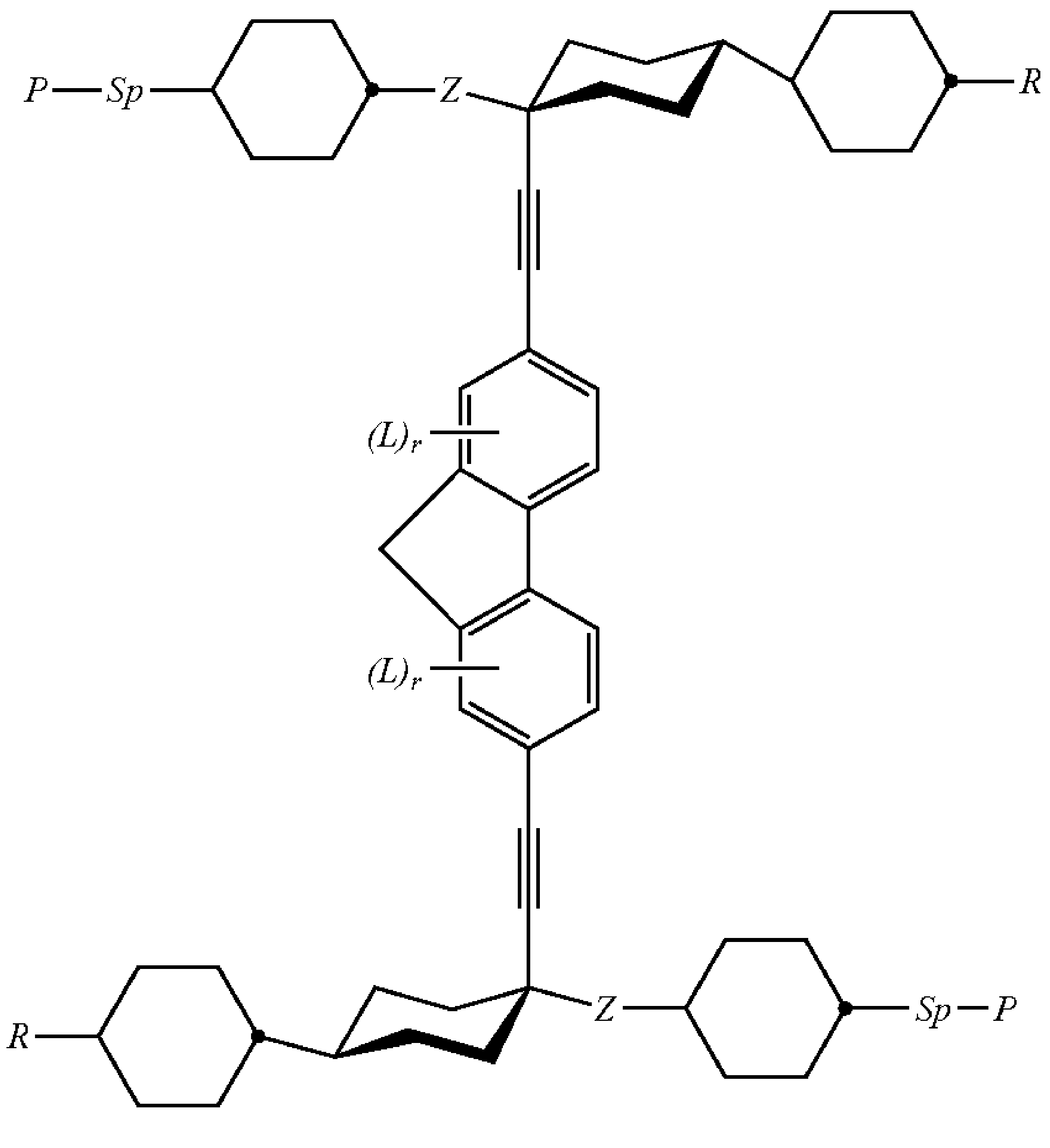

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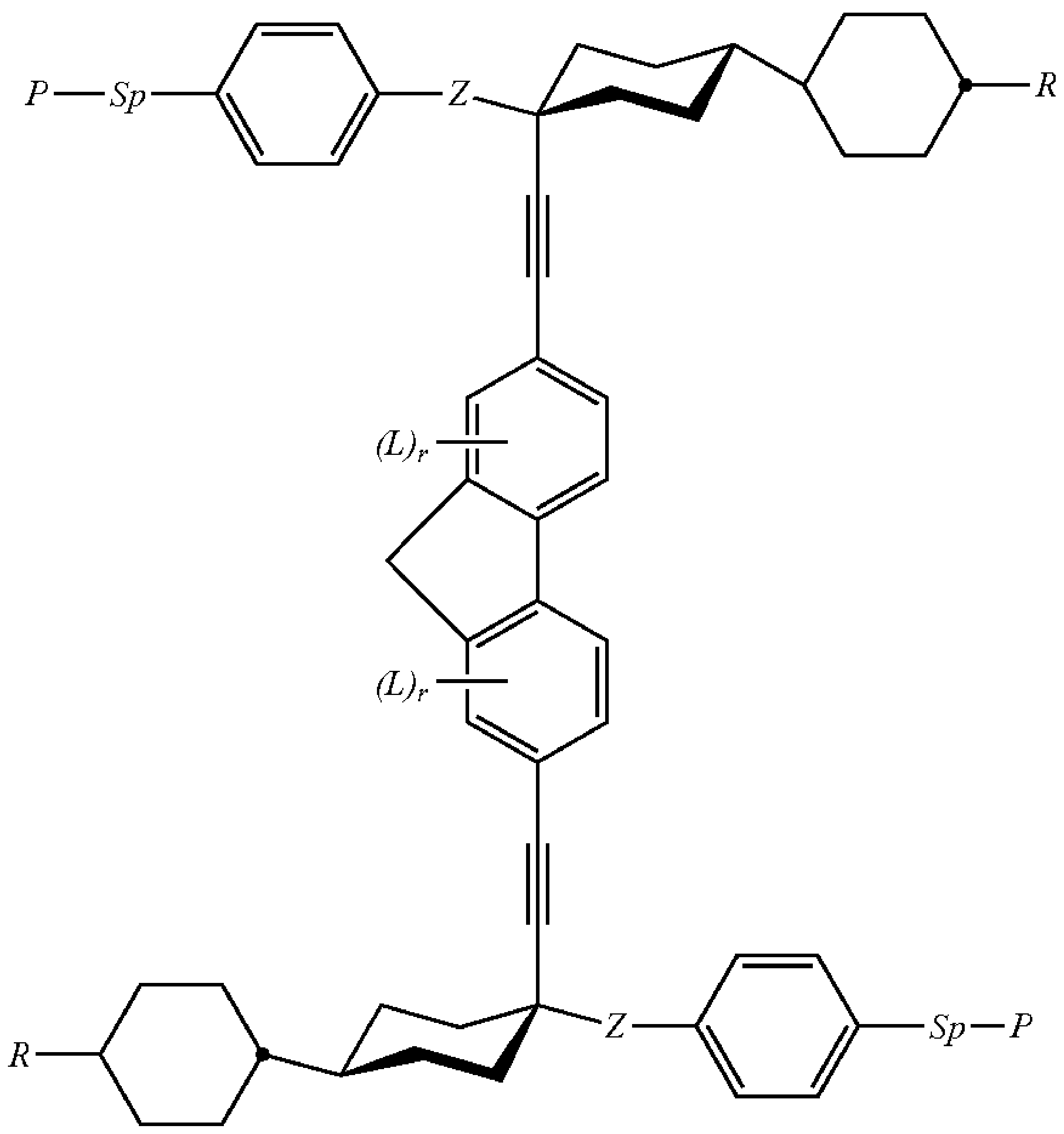
I24



wherein Z has one of the meanings of Z^1 in claim 33, R has one of the meanings of R^1 in claim 33 that is different from P-Sp- and the benzene rings in the meosgenic groups are optionally substituted by one or more groups L.

* * * * *